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ABSTRACTS

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Invited Talk

Structural complexity of iron oxides at high pressures and temperatures

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The Fe-O binary system is widely studied both in solid state and mineral physics. Oxides of iron are present in nature in the form of FeO (known at normal conditions as wüstite, rock-salt structure), Fe_2O_3 (hematite, corundum structure), and Fe_3O_4 (magnetite, inverse spinel structure). High-pressure behaviour of natural iron oxides was a subject of studies since early 60s but still many controversies, in particular, regarding crystal structures of high-pressure high-temperature (HPHT) polymorphs, remained. For instance, many structures have been proposed for a high-pressure polymorph of Fe_3O_4, among them monoclinic one with octahedrally coordinated iron atoms [1], $CaMn_2O_4$-type [2], and $CaTi_2O_4$-type (space group *Bbmm*, No. 63) structures [3,4]. Orthorhombic $GdFeO_3$ perovskite [5] and Rh_2O_3-II [6] structural types have been proposed as candidates for a high-pressure polymorph of Fe_2O_3 which exists above 45 GPa.

We report here the crystal structures of novel iron oxides, synthesized at HPHT conditions. HPHT polymorphs of Fe_2O_3 and Fe_3O_4, and iron oxides with completely new stoichiometry, as e.g. Fe_5O_7 and $Fe_{25}O_{32}$, were observed in our experiments in laser-heated diamond anvil cells. They were characterized using single-crystal X-ray diffraction and synchrotron Mössbauer source spectroscopy. Our crystallographic data allowed to explain electronic and magnetic changes in Fe_2O_3 and Fe_3O_4 induced by HPHT.

We found similarities in the crystal structures of Fe_5O_7, some high-pressure polymorphs of Fe_2O_3 and Fe_3O_4, and the recently discovered Fe_4O_5 [7] and Fe_5O_6 [8]. Based on the study of Guignard *et al.* [9] we suggest a homological series of iron oxides with a common formula $m\mathrm{FeO}\cdot n\mathrm{Fe_2O_3}$ ($m \geq 1$, $n \geq 0$). The crystal structures of the iron oxides belonging to the homological series are composed of FeO6 trigonal prisms and octahedra. So far we experimentally observed six representatives of the series. Our results suggest that unusual trigonal prismatic oxygen coordination of iron may be common for iron-oxygen compounds at conditions of the Earth's lower mantle.

References

[1] H.-K. Mao, T. Takahashi, W. A. Bassett, G. L. Kinsland, L. Merrill, *J. Geophys. Res.* **79**, 1165 (1974).
[2] Y. Fei, D. J. Frost, H.-K. Mao, C. T. Prewitt, D. Haeusermann, *Am. Mineral.* **84**, 203 (1999).
[3] C. Haavik, S. Stølen, H. Fjellvåg, *Am. Mineral.* **85**, 514 (2000).
[4] L. S. Dubrovinsky, N. A. Dubrovinskaia, C. McCammon, G. K. Rozenberg, R. Ahuja, J. M. Osorio-Guillen, V. Dmitriev, H.-P. Weber, T. Le Bihan, B. Johansson, *J. Phys. Condens. Matter* **15**, 7697 (2003).
[5] J. S. Olsen, C. S. G. Cousins, L. Gerward, H. Jhans, B. J. Sheldon, *Phys. Scr.* **43**, 327 (1991).
[6] G. Rozenberg, L. Dubrovinsky, M. Pasternak, O. Naaman, T. Le Bihan, R. Ahuja, *Phys. Rev. B* **65**, 064112 (2002).
[7] B. Lavina, Y. Meng, R. T. Downs, P. F. Weck, S. R. Sutton, Y. Zhao, *Proc. Natl. Acad. Sci. USA* **108**, 17281 (2011).
[8] B. Lavina, Y. Meng, *Sci. Adv.* **1**, e1400260 (2015).
[9] J. Guignard, W. A. Crichton, *Mineral. Mag.* **78**, 361 (2014).

Keywords: X-ray diffraction, iron oxides, high pressure, high temperature

O 1.1

Reliability of multigrain indexing for orthorhombic polycrystals above 1 MBar: application to $MgSiO_3$ post-perovskite

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Recently, multigrain crystallography emerged as a novel method in the literature (Sørensen *et al,* 2012). This method combined with third generation synchrotrons allows characterizing hundreds of crystals in a polycrystalline material. This technique has also been adapted for Diamond Anvil Cell (DAC) high pressure experiments (Ice *et al,* 2005; Nisr *et al,* 2012,2014*;* Barton *et al, 2012; Zhang et al, 2013, R*osa *et al, 2015)*. DAC multigrain crystallography is usefulforthe determination ofthe orientation, strain tensor, and position of individual grains. It is also useful forstudying microstructures in deformed materials, following phase transformations, or solving new crystal structures under high pressure. However, the method remains difficult to apply because of limitations due to the DAC itself (smallsample size and small opening angle), tedious data processing, and questions regarding reliability of the results.

Here, we use multigrain crystallography to characterize orthorhombic polycrystalline materials at high pressure. The applicability and resolution of the method is validated using simulations and tested on an experimental dataset collected on $MgSiO_3$ post-perovskite at 135 GPa. In simulations, ≈95% of the grains can be indexed successfully with ≈80 % of the peaks assigned. The theoretical resolution in grain orientation and position are 0.2° and 4µm, respectively. In the experiment, we index 159 grains of post-perovskite, corresponding to 30 % of the diffraction peaks. The resolution in grain location is not sufficient for in-situ microstructural analysis at high pressure. Grain orientations, on the other hand, are well resolved and sufficient for following processes such as plastic deformation or phase transformation. We also explore the effect of indexing parameters and experimental constraints such as rotation range and step on the validity of the results allowing for more efficient experiments.

Articles

Barton & Bernier (2012). J. Appl. Crystallogr. 45 1145-1155.

C. & Poulsen, H. F. (2012). Z Kristallogr 227 63-78.

Ice *et al* (2005). 12 608-617.

Nisr *et al* (2012). J. Geophys.Res. Sol. Earth, 117.

Nisr *et al* (2014). High Pressure Res.34, 158-166.

Rosa *et al* (2015).J. Appl. Crystallogr.48, 1346-1354.

Sørensen *et al*(2012). Z Kristallogr, 227, 63-78.

Zhang *et al* (2013). vol. 110, 6292-6295.

O 1.2

Variant selection in the bcc-hcp transition in Fe

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The pressure-induced bcc to hcp phase transformation in Fe is observed at around 13 GPa at ambient temperature. Several experimental evidences point towards a transformation mechanism similar to that proposed by Burgers for the α-β transformation in Zr [1], including a recent study in which the 12 hcp orientation variants predicted for the Burgers path were effectively observed in an experiment starting from a bcc-Fe single crystals [2]. Indeed, upon increasing pressure, transformation from a single bcc orientation along the Burgers path allows for 12 potential orientations of the hcp daughter phase. Conversely, during pressure decrease, each orientation of hcp-Fe can give rise to 6 potential orientations for bcc-Fe. As such, multiple cycles of bcc-hcp transformations in Fe could multiply the number of crystal orientations and, hence, randomize the sample texture. It is also known, however, than materials often show variant selection and texture memory while undergoing phase transformations [3]. This process is well known in materials science and is used in the design of shape memory alloys [4].

In this study, we investigate the effect of the bcc-hcp transformation in Fe polycrystals. Fe-foils are compressed in diamond anvil cell under hydrostatic conditions (He pressure medium). The starting texture of the Fe foil is used as a reference and we follow the evolution of texture through multiple cycles of bcc-hcp transformations. Our measurements show that variant selection plays an important role in the nucleation of the hcp-Fe phase, with an appearance of hcp-Fe in specific orientations relative to the original bcc sample and the geometry of the diamond anvil cell. Upon reverse transformation, from hcp to bcc, we do not observe variant selection related to the experimental geometry, but some amount of texture memory with some proportions of the bcc grains returning to their original orientation.

[1] Burgers, Physica, 1, 561-586, 1934

[2] Dewaele, Denoual, Anzellini, Occelli, Mezouar, Cordier, Merkel, Véron & Rausch, Phys. Rev. B, 91, 174105, 2015

[3] Daymond, Holt, Cai, Mosbrucker & Vogel, Acta Mater., 58, 4053-4066, 2010

[4] Hodgson, Wu & Biermann ASM Handbook Volume 2: Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, ASM International, 897-902, 1990

O 1.3

A new high pressure phase transition in clinoferrosilite: *in situ* single crystal X-ray diffraction study

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Pyroxenes, $M1M2Si_2O_6$, are one of the major constituent minerals of the Earth's upper mantle and therefore they have an important influence on its mineralogy, thermodynamics and geological structure. A well-constrained correlation between chemical compositions, crystal structures and elastic properties of pyroxenes is hence necessary for the modeling of their behavior in the Earth's interior. We report high-pressure single-crystal X-ray diffraction (SC XRD) data of the pyroxene Fe end-member: clinoferrosilite (CFs). CFs transforms from $P2_1/c$ to $C2/c$ structure between 1.48 and 1.75 GPa at room temperature (Hugh-Jones *et al.*, 1996), however little is known about its structural behavior at Earth's mantle pressures.

Single crystals of CFs synthesized at 9.5 GPa and 1100 °C were loaded together with a ruby sphere or an Au foil for pressure estimation into diamond anvil cells. Neon was used as pressure-transmitting medium. *In situ* high-pressure SC XRD experiments were performed at the synchrotron stations P02.2 at Petra III and ID09 at the European Synchrotron Radiation Facility.

A phase transition from $P2_1/c$ to $C2/c$ space group has been detected between 1.3 and 3 GPa, in agreement with the study reported by Hugh-Jones *et al*. (1996). The $C2/c$ crystal structure is based on chains of vertice-sharing SiO_4 tetrahedra and of edge-sharing FeO_6 octahedra. Up to 30 GPa, the $C2/c$ phase undergoes an anisotropic compression according to the scheme $\beta_b>\beta_c\approx\beta_a>\beta_{a\sin\beta}$ usually observed for pyroxenes. With increasing pressure, the crystal structure accommodates the compression by kinking of the tetrahedral chains. The bulk modulus of the $C2/c$ phase and its pressure derivative are determined to be 113(3) and 6.3(3) GPa by fitting a third-order Birch-Murnaghan equation of state. Between 30 and 35.8 GPa a $C2/c$ to HP-$P2_1/c$ transformation occurs due to the rearrangement of half of the layers of corner-sharing SiO_4 tetrahedra into layers of edge-sharing SiO_6 octahedra. The compression scheme of the HP-$P2_1/c$ is determined to be $\beta_b>\beta_a\approx\beta_{a\sin\beta}>\beta_c$ indicating a change in the compression mechanism. The $C2/c \rightarrow$HP-$P2_1/c$ transformation supports the hypothesis of a direct transition from pyroxene to akimotoite in cold subducting slubs where the expected dissociation to spinel and stishovite is kinetically hindered (Argusta *et al.*, 2014).

O 1.4

Occupancy transitions in hexagonal clathrate hydrates

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The discovery that the hexagonal clathrate structure (SH) was observed in simple-gas water systems like methane-water at high pressure [1] was unexpected. The hexagonal clathrate structure had previously been only known in mixtures of water and large organic molecules where the organic molecule filled the large cages that are a distinguishing feature of the structure. The issue of how small-guest molecules and atoms like methane, argon, nitrogen, krypton and xenon - which are all found form SH clathrates - fill these large cages remained unclear. In argon hydrate-II, neutron diffraction suggested a five-fold filling with two atoms at the ends of the cage and three disordered over six sites in the waist [2]. However, this configuration appeared incompatible with the size of the other guest species, with molecular dynamics modelling studies [3], and with diffraction measurements [4]. Furthermore, Raman and visual observation experiments reported ''transitions'' within the stability field of the SH hydrates of methane and krypton which produced free water indicating that the occupancy of the hydrate had increased at the transition [5].

The nature of these transitions and of the occupancies of the simple-gas SH hydrates is of importance. Methane hydrate has been implicated in the process by which methane is transported and stored in the interiors of icy moons [1], and the calculations of occupancies provide benchmarks for the interatomic potentials which underlie them [3]. Based on a reanalysis of methane hydrate data and of the geometric factors involved we have developed a comprehensive model of the behaviour of the simple-gas SH hydrates. This model accounts for the observed behaviour in all five systems with full occupancy of the large cages at all pressures in argon and nitrogen SH hydrates, transitions from occupancies of three to five in the methane and krypton systems and an occupancy of only two in xenon SH hydrate.

[1] J.S. Loveday et al, Nature, **410**, 661-3 (2001).

[2] A.Y. Manakov et al, J. Incl. Phen., **48**, 11-18 (2004).

[3] S. Alavi et al, J. Chem. Phys., **125**, 124708 (2007). S. Alavi et al, J. Chem. Phys, **125**, 104501 (2006).

[4] C.A. Tulk et al, J. Chem. Phys., **136**, 054502 (2012). C.A. Tulk et al, Phys. Rev. B, **80**, 052101 (2009).

[5] T. Kumazaki et al, Chem. Phys. Lett., **388**, 18-22 (2004). S. Sasaki et al, J. Phys. Chem., **110**, 9838-9842 (2006).

O 1.5

Phase-diagrams of the elements - What do we learn?

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The phase-diagrams of the elements are related to changes in the electronic structure under pressure to illustrate some general rules useful for the understanding of the behavior of condensed matter under strong compression. Additional rules for the understanding of the effects of temperature are discussed and a general view of the phase-diagrams of all the elements is presented.

O 1.6

High-pressure X-ray diffraction, Raman, and computational studies of $MgCl_2$ up to 1 Mbar: Extensive pressure stability of the β-$MgCl_2$ layered structure

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Magnesium chloride with the rhombohedral layered $CdCl_2$-type structure (α-$MgCl_2$) has been studied using x-ray diffraction and Raman spectroscopy up to 1 Mbar. The results reveal a pressure-induced second-order phase transition to a hexagonal layered CdI_2-type structure (β-$MgCl_2$) at 0.7 GPa, in-line with previous studies on $FeCl_2$ [1]. This phase transition mainly affects the stacking sequence of the Cl anions, resulting to a shorter *c*-axis. An anisotropic compression along the *c*-axis was observed during initial compression. Above 10 GPa, the anisotropy is altered due to the repulsion of Cl anions between adjacent Cl-layers.

According to previous theoretical studies [2], a series of phase transitions towards, initially, the 3D rutile structure (with 6-fold Mg cations) at ~17 GPa and to fluorite structure (with 8-fold Mg cations) at ~70 GPa are proposed. However, according to our experimental results $MgCl_2$ remains in a 2D layered structure up to 1Mbar keeping the 6-fold coordination of Mg cations. To elucidate the mechanisms that extend the remarkable structural stability of $MgCl_2$ we performed first principle enthalpy calculations as a function of pressure for the β-$MgCl_2$ phase and the hypothetical rutile, fluorite and cottunite phases of $MgCl_2$. From the enthalpy vs pressure plot, β-$MgCl_2$ remains the more stable phase up to 100 GPa. Moreover, the enthalpy difference between the β-$MgCl_2$ and the candidate phases increases with pressure. Thus, it is not expected that these structures will become energetically favorable even above 100 GPa. This observation contradicts with the general structural behavior of highly compressed AB_2 compounds.

Figure 1. (a) Pressure dependence of the lattice parameters and (b) Volume-pressure data for $CdCl_2$ and CdI2-type phases of $MgCl_2$. The inset in (a) shows the normalized lattice parameters of the CdI_2-type phase.

[1] G. Rozenberg, et al., Phys. Rev. B 79, 214105 (2009).

[2] G. D. Barrera, N. L. Allan and M. R. Soriano, Chem. Phys. Lett. 278, 267{271 (1997).

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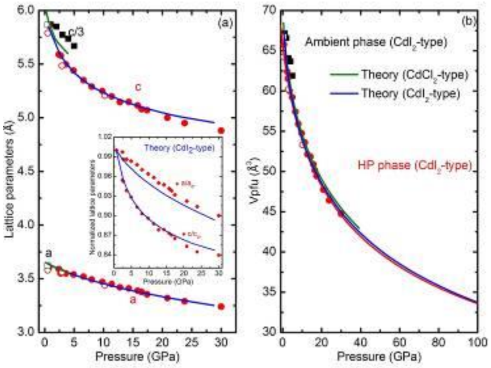
Figure 1


(a)
Lattice parameters (Å)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Pressure (GPa)
0
5
10
15
20
25
30
c/3
c
a
a
Theory (CdI$_2$-type)
Normalized lattice parameters
1.02
0.99
0.96
0.93
0.90
0.87
0.84
a/a_0
c/c_0
(b)
Vpfu (Å^3)
70
65
60
55
50
45
40
35
30
0
20
40
60
80
100
Ambient phase (CdI$_2$-type)
Theory (CdCl$_2$-type)
Theory (CdI$_2$-type)
HP phase (CdI$_2$-type)

O 1.7

Revised phase diagram of the FeSe superconductor

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Although the superconductive *β*-FeSe phase crystallizes in a relatively simple tetragonal PbO-type structure (*P*4/*nmm*), its behavior as a function of temperature and pressure is still not well understood. The crystal structure of its HP orthorhombic modification is not well studied mainly because of the limitation of powder diffraction, including synchrotron, in resolving an 1D diffraction signal of likely disordered FeSe phase[1-4]. High quality *T*-*P*-dependent single crystal diffraction data is needed to unveil structural details of the HP FeSe polymorph.

For these studies pure single crystals of FeSe were synthesized using chemical vapour transport method. *P*-dependent single crystal XRD experiments were performed on the ID27 HP beamline at ESRF. The pressure range of up to 14 GPa was studied at 20, 50 and 300 K.

We clearly show that the HP modification of FeSe belongs to the MnP-type structure (*Pnma*). It features double chains of face sharing FeSe6 octahedra and is not direct structural derivative of the parent LP tetragonal FeSe phase. No intermediate hexagonal NiAs-type phase ($P6_3/mmc$) was observed.

At 20 K the HP FeSe phase appears between 6.2 and 6.9 GPa. It coexists with the LP *P*4/*nmm* FeSe phase up to at least 10 GPa where HP FeSe is the dominant one. At 50 K the HP FeSe modification appears between 9.1 and 10.2 GPa and, similarly, coexists with the LT FeSe phase up to at least 14 GPa. The coexistence of the LP and HP modifications of FeSe in a wide pressure region of at least 4 GPa indicates a first order structural transformation with a relatively slow kinetics of transformation at these temperatures. Indeed, no coexistence of the LP and HP phases is observed at 300 K and the transformation takes place between 6.6 and 8.1 GPa.

This work clearly shows that the superconductivity in the FeSe system correspond solely to the 2D layered tetragonal structural arrangement. The superconductivity is being suppressed when the structure is changed to a 3D orthorhombic arrangement thus confirming a 2D character of the superconductive mechanism in this system.

[1] Garbarino, G. et. al. *Europhys. Lett.* 2009, *86*, 27001.

[2] Margadonna, S. et. al. *Phys. Rev. B* 2009, *80*, 064506.

[3] Braithwaite, D. et. al. *J. Phys.: Cond. Matt.* 2009, *21*, 232202.

[4] Kumar, R. S. et. al. *J. Phys. Chem. B* 2010, *114*, 12597.

O 1.9

"Pressure - composition" phase diagram of hydrogen sulfide

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The search for high-temperature superconductors and explanation of this phenomenon are one of the key problems in modern physics. Recently, it has been found that hydrogen sulfide becomes superconductive at a temperature of 203K and pressures above 100 GPa. Clearly, the crystal structure of this compound is still under discussion. In a number of theoretical and experimental studies it has been shown that H3S is a potential candidate for superconductive compound. Other works predicted the existence of H2S3, H3S2, H4S3, HS2, H5S2 and other stoichiometries in a wide pressure range. Obviously, the phase diagram of hydrogen sulfide is complex and requires a comprehensive study.

Variable-composition structure searches using the USPEX code with up to 32 atoms in the unit cell in the pressure range from 0 to 200 GPa have been carried out for H-S system. At a pressures with 10 GPa step convex hull diagrams were built, so the most stable compounds were chosen. Considering all earlier predicted structures pressure-composition phase diagram was constructed. Our calculation showed that two new H5S8 and H3S5 (Fig. 1) stoichiometries are stable in a fairly wide pressure range. We also propose I4mm H3S structure which is more stable than previously predicted Cccm and R3m H3S structures at pressures from 100 to 160 GPa. It was shown that because of the existence of stable HS2, H3S5 and H5S8 compounds at a pressures from 42 to 100 GPa the transition to previously predicted H4S3 is less favourable, so its stability range reduces significantly. Experimental data confirm the existence of H5S8, H3S5 and HS2 phases. Within the harmonic approximation Tc values for all new predicted phases were calculated.

Figure 1. Crystal structures of H5S8 (a) and H3S5 (b) obtained by USPEX.

Figure 1

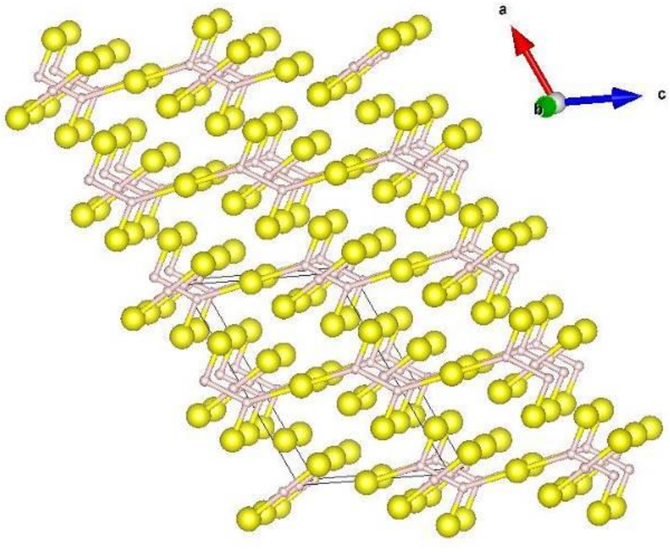
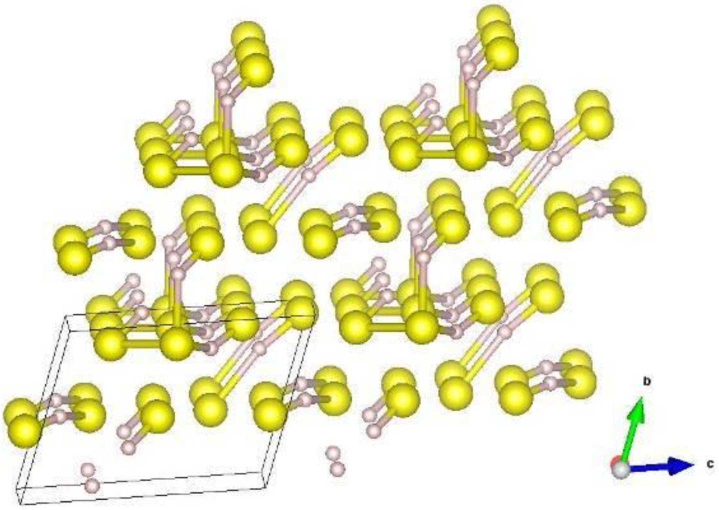


Figure 2



O 1.10

New high-pressure phase with Ni_2In-type structure in lithium disulfide (Li_2S)

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We intended to accomplish the systematic studies of pressure-induced phase transitions in alkaline metal sulfides A_2S to elucidate their origins, pathways and testing the theoretical approaches proposed these compounds and related families of oxides and water ices.

Li_2S, Na_2S, K_2S, and Rb_2S crystalize at ambient conditions in the antifluorite structure (*Fm*-3*m* space group). Under high pressure they undergo a phase transition to anticotunnite (*Pnma* sp. gr.). Applying of increasing pressure caused a second phase transition from anticotunnite to a Ni_2In-type structure ($P6_3/mmc$ sp. gr.). However, for Li_2S the later transition was only predicted by *ab initio* calculations at 28.8 - 40.6 GPa. The antifluorite to anticotunnite transition was observed at ~ 50 GPa for Li_2O the only studied alkali oxide A_2O.

Recently the mechanism of the hole superconductivity [1], alternative to the conventional electron-phonon one, was proposed to explain the recording critical transition temperatures observed in H_2S under ultra-high pressures [2]. According to this approach the insulating light alkali metals sulfides were proposed as high temperature superconductors at high pressures [1]. These materials were not studied experimentally above 20 GPa, thus, motivating us to shift this limit towards the 1 Mbar (100 GPa) pressure range.

Raman spectroscopy and synchrotron angle-dispersive x-ray diffraction were applied for investigation of pressure-induced phase transitions in lithium disulfide (Li_2S) up to 60 GPa. We observed two reversible first order transitions from the cubic antifluorite to orthorhombic anticotunnite phase at about 13 GPa and then transition to the hexagonal Ni_2In-type structure above 30 GPa accompanied by the volume effects of 6.0 % and 4.9 % respectively. The sample remained transparent up to the highest pressures attained in our experiments. Thus, we proved experimentally that Li_2S as all other alkali sulfides undergo the same sequence (antifuorite-anticotunnite-Ni_2In type) of pressure induced phase transitions.

[1] J. E. Hirsch and F. Marsiglio, Physica C: Superconductivity and its Applications **511**, 45 (2015).

[2] A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov, and S. I. Shylin, Nature **525**, 73 (2015).

O 1.11

Deformation peculiarities and phase transformations in boron carbide and silicon after the treatment in planetary mill. HRTEM studies

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Boron carbide and silicon after the planetary mill treatment were studied by HRTEM methods. Three types of defects were found in boron carbide: cracks, twins and distorted stacking faults. High pressure phases SiIII и SiIV were found in silicon. It is shown that SiIV was formed by two ways: a) as a result of stacking faults formation and b) by the transformation through the SiIII-phase.

Nanostructured materials have attracted great interest because of unusual properties. Nanopowders can be produced in particular by a mechanical handling of materials in a planetary mill. The goal of the present work is to study processes, occurred in the planetary mill during the boron carbide and silicon milling.

Precursor components were treated in a Fritsch Planetary Micro Mill PULVERISETTE 7 premium line with Si_3N_4 milling balls. The obtained samples were studied by JEM-2010 transmission electron microscope.

We observed three types of defects in B_4C: narrow cracks along {20-21}, twins along {10-11} and distorted stacking faults along {10-14}. The cracks orientation is associated with the structural features of the B_4C crystal cell. Distorted stacking faults can be caused by the destruction by the deformation of the icosahedra composed of boron atoms.

{111}-twins were found in SiI. It was shown that fragments of SiIV phase are formed as a result of twinning. Mutual orientation of SiI and SiIV phases is traditional:

$(001)_{SiIV} || (111)_{SiI}$

Another orientation relationship (OR) between SiIV and SiI was found for SiIV-fragments inside SiI-grain:

$(001)_{SiIV} || (110)_{SiI}$ and $[100]_{SiIV} || [1\text{-}10]_{SiI}$.

This OR can be realized as a result of SiI→SiIII→SiIV transformation. It is known that mechanical milling can induce the structural transformations in solids. Local temperature and pressure rise can be estimated to be more than 8 GPa and 425°C. Such appreciations can be made on the basis of the Hertzian impact theory. The formation of SiIII and SiIV phases indicate that significant values of temperature, deformation and pressure were achieved inside planetary mill.

Three types of defects in the boron carbide and high pressure phases SiIII и SiIV of silicon were found by TEM studies of these materials after the milling.

O 1.12

Pressure dependence of multiphonon resonant Raman scattering on *2Hc*-MoS_2 microcrystalline samples

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Two-dimensional atomic crystals, such as graphene, hexagonal boron nitride, and transition metal dichalcogenides (TMDCs), have attracted considerable attention because of their unique electrical, optical, and mechanical properties. TMDCs are especially interesting for the next generation of electronic and optoelectronic devices because, in contrast to graphene, they are semiconductors with a nonzero bandgap. Among them, molybdenum disulphide, MoS_2, has been the most intensively studied. $2H_c$-MoS2 has P_{63}/mmc space group symmetry and consists of a hexagonal plane of Mo atoms sandwiched by two hexagonal planes of S atoms. The unit cell contains two alternating layers with an AB stacking along the c axis. In the bulk, it is a semiconductor with a direct (indirect) band gap of 1.96 eV (1.2 eV) at 300K. In this work Raman-scattering spectra of $2H_c$-MoS_2 were measured at room temperature under hydrostatic pressures up to 30 GPa, in diamond anvil cells. In order to get a deeper insight into the lattice dynamics of $2H_c$-MoS2, we performed measurements in a backscattering geometry with a resonant (E_L= 1.92 eV) and a non-resonant excitation (E_L= 2.54 eV). From the results we have estimated the pressure dependence of the multiphonon resonant Raman scattering process involving the LA(M) and the TA(M) and/or ZA(M) phonon replicas of vibrational modes from M points of the Brillouin zone. At 22 GPa, we have observed a splitting in the frequencies of the E_{1g} and E^1_{2g} first-order modes and also a small discontinuity in the 2*LA(M)* mode. In this pressure range, simulations predict a structural phase transition, where the original $2H_c$ stacking changing to $2H_a$ stacking typical of 2*H*-$NbSe_2$, through layer sliding [1]. This first-order transition has also been observed by X-ray diffraction and electrical measurements under pressure [2].

[1] Liliana Hromadová, Roman Martonák, and Erio Tosatti., Phys, Rev. B, **87**, 144105 (2013).

[2] Zhen-Hua Chi, Xiao-Miao Zhao, Haidong Zhang, Alexander F. Goncharov, Sergey S. Lobanov, Tomoko Kagayama, Masafumi Sakata, and Xiao-Jia Chen, Phys. Rev. Lett, **113**, 036802 (2014).

O 1.13

On the high-pressure phase stability and elastic properties of β-titanium alloys

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The desirable mechanical properties of titanium and our ability to precisely vary these properties through alloying with different elements are responsible for the wide range of industrial applications of titanium alloys. What is particularly important is our ability to stabilise different phases of titanium at ambient conditions by alloying with different elements. However, surprisingly little data is available that directly observes the stabilising effect of alloying with different elements by observing their effects on high pressure phase transitions in titanium. In this work we have studied the phase stability of β-titanium alloys Ti-7Mo and Ti-7Mo-1O as well as commercially available Ti-24Nb-4Zr-8Sn (Ti2448) and Ti-36Nb-2Ta-0.3O (gum metal). We find good phase stability of these alloys in the β phase up to 40 GPa, well into the ω phase region on the pure titanium phase diagram. Gum metal was pressurised to much higher pressure (72.4 GPa) and a transformation into a mixture of high pressure phases was observed commencing above 70 GPa.

O 1.14

Structural stability of gallium garnets in the Mbar pressure range

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The combination of the luminescence properties of RE^{3+} and the hardness, high optical transparency, and mechanical and chemical stabilities of the nano-garnets makes them extremely useful in laser, phosphor, scintillator, NIR bio-imaging, and pressure and temperature sensor nano-devices **[1]**. The Nd^{3+}-doped $Y_3Al_5O_{12}$ (YAG) garnet has been traditionally considered as the standard laser material despite of their limited doping concentration. This disadvantage can be overcome by replacing aluminium with gallium, since the latter garnet has a larger unit cell, higher refractive index and RE^{3+} solubility. The study of the properties of these new nano-garnets trigger their structural characterization at extreme conditions. For this purpose, the yttrium ($Y_3Ga_5O_{12}$) and lutetium ($Lu_3Ga_5O_{12}$) gallium nano-garnets have been studied by x-ray diffraction in the Mbar pressure range at ID27 beamline of the European Synchrotron Radiation Facility (ESRF). Both samples crystallize in a cubic structure with space group Ia-3d. This crystalline phase consists in a network of corner-sharing GaO_4 tetrahedra and GaO_6 octahedra. These polyhedral units are arranged in chains along the three crystallographic directions and form dodecahedral cavities which are occupied by Y (or Lu) atoms. The two garnets, $Y_3Ga_5O_{12}$ and $Lu_3Ga_5O_{12}$, are stables up to 74 GPa and 82 GPa, respectively, showing a pressure-induced amorphization above these pressures. This phenomenon is an intrinsic property of the nano-material since it is independent of the used pressure transmitting medium. The outcomes experimentally obtained agree with *ab initio* theoretical calculations **[2, 3]** resulting in a complete picture of the structural behavior of these materials at extreme conditions.

[1] S. F. León-Luis et al. RSC Adv., 4, 57691 (2014).

[2] V. Monteseguro et al. Phys.Chem.Chem.Phys. 17, 9454 (2015).

[3] V. Monteseguro et al. J. Phys. Chem. C, 118, 13177−13185 (2014).

O 1.15

Pressure-induced phase transitions in the MO_2 systems, M=Re, Mo, Tc

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The transition metal oxides are commonly used in catalytic activity or as semiconductors. The rutile structure type is prevalent in transition metal dioxides. A nonclassical rutile-type structure in the monoclinic crystal system is formed by MoO_2, ReO_2, WO_2 and TcO_2. The rutile structure is characterized by chains of edge sharing octahedral along the [001] crystallographic direction. Differentiation of octahedral is possible in the MoO_2 structure type where there are alternating shorter and longer metal-metal distances at ambient pressure.

Using powder and single crystal diffraction in a diamond-anvil cell the high pressure phase diagram of MoO_2, ReO_2, and TcO_2 has been investigated. Significant anisotropic compression behavior is observed in each compound with the application of modest pressure. For MoO_2 multiple metastable phases have been observed between 25 - 70 GPa with the final transition to the $CaCl_2$ structure type being recoverable. In the recovered sample, the metal atoms no longer have higher order bonding as is evident from a metal-metal distance of 2.8151 Å. The phase diagram of each transition metal dioxide will be discussed in light of new experimental and genetic algorithm structure prediction results.

O 1.16

Re-evaluation of the compressibility of Re_3B and Re_7B_3

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Numerous transition metal borides are high-performance materials. In this context, the system Re-B is of special interest. While ReB_2 has been studied extensively [1], Re_7B_3 and Re_3B have attracted less interest. In addition, a new monoclinic modification of Re_3B has recently been synthesized, but only the ambient pressure structure has been reported [2].

The object of this study is to re-evaluate the compressibility of Re_7B_3 and orthorhombic Re_3B on phase pure samples and to establish the compressibility of the new modification. In an earlier study [3], Re_7B_3 was found to be very incompressible with a bulk modulus of 435(16) GPa, while the compressibility of Re_3B with a B_0 of 320(15) GPa was much lower than expected from DFT calculations.

In the earlier study [3], the Re-borides had been synthesized in a laser-heated DAC and were present as parts of complex phase mixtures. Here, samples were synthesized phase pure in a HF furnace and via arc-melting. X-ray diffraction experiments were performed at the beamline P02.2 at PETRA III. In order to better understand the structure-property relations of the synthesized samples we complemented the experiments with DFT calculations.

For monoclinic Re_3B, which was synthesized in a HF furnace at ambient *p,* the experimentally determined B_0 = 379(4) GPa. This is in reasonable agreement with a calculated value of 362 GPa (figure 1). The bulk modulus of Re_7B_3 was experimentally found to be B_0 = 390(11) GPa, which is considerably lower than the value found earlier and much closer to the theoretically derived value of 394 GPa (figure 2). Data for orthorhombic Re_3B have been collected recently and will also be presented.

Financial support by the DFG and the FWF in the framework of an ERA-chemistry project (WI 1232 and I 1636-N19) and by the BMBF (project 05K13RF1) is gratefully acknowledged.

[1] M. Frotscher, M. Hölzel, and B. Albert. *Z. Anorg. Allg. Chem.* **636** (2010),1783-1786.

[2] E. A. Juarez-Arellano, B. Winkler, A. Friedrich, L. Bayarjargal, W. Morgenroth, M. Kunz, and V. Milman. *Solid State Sci.* **25** (2013), 85 - 92.

[3] A.P. Tyutyunnik, T.V. Dyachkova, Y.G. Zaynulin, and S.A. Gromilov, *J. Struct. Chem.* **55** (2014), 84-88.

Figure 1: Compressibility of Re_3B

Figure 2: Compressibility of Re_7B_3

Figure 1

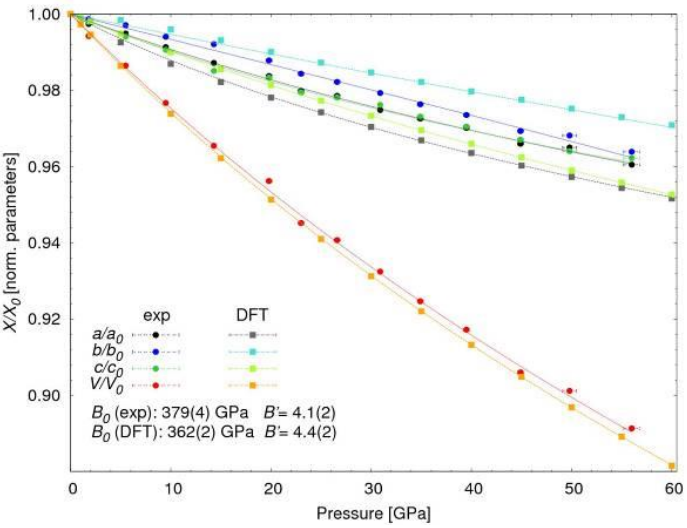
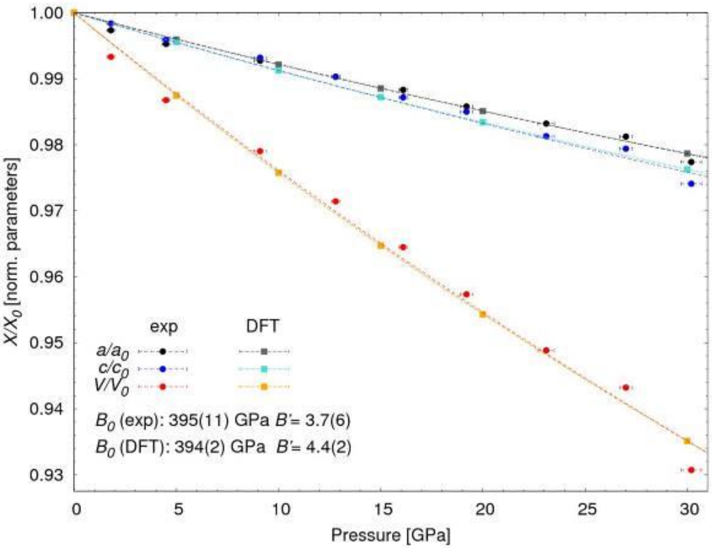


Figure 2



O 1.17

High-pressure investigation of single crystals of α-boron

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Knowledge about high-pressure, high-temperature behavior of elemental materials is important for fundamental understanding of bonding evolution, phase transformations, and establishing of PT phase diagrams, which are of high significance for materials' synthesis and applications. Boron has five currently established allotropes (α-B, β-B, γ-B, δ-B (T-50), and ε-B), and all of them have a common structural feature, B_{12} icosahedra as major building blocks. Each allotrope possesses a unique Raman spectrum. Rhombohedral α-B (space group *Rm*) has the simplest structure among all of boron phases: it consists of B_{12} icosahedra located at the corners of its rhombohedral unit cell. Although its structure was established long ago, the bonding situation in *α*-B at ambient pressure was experimentally clarified only recently due to the analysis of the electron-density in *α*-B based on single-crystal X-ray diffraction data.

In the present work we have undertaken investigation of the behavior of *α*-B under pressure using high-purity single crystals synthesized by the high-pressure high-temperature large volume press technique. The structure of α-B was studied at pressures at up to 60 GPa by single-crystal X-ray diffraction in a diamond anvil cell. The bulk modulus of α-B was found to be K = 224(7) GPa, while the bulk modulus of individual B12 icosahedra appeared to be K_{ico} = 303(12) GPa. Thus, the compressibility of icosahedra is considerably lower than that of the bulk material. Measurements of interatomic distances as a function of pressure revealed that the intericosahedral B1-B1 2e2c bonds are almost as stiff as intraicosahedral ones. This is in accordance with the previous experimental data [1], which showed that the B1-B1 bond is the strongest one among all bonds in *α*-B, since it has the highest magnitudes of electron density and Laplacian at its bond critical point, as revealed the topological analysis of the electron density [1]. The B2-B2 2e3c intericosahedral bond shows much higher compliance compared to other bonds inα-B. The vibrational properties ofα-B under pressure were investigated by Raman spectroscopy, which gave evidence of the structural stability of this boron allotrope at pressures up to 160 GPa. An attempt was undertaken to study evolution of IR spectra ofα-B at pressures up to 53 GPa. It has shown that the IR spectroscopy technique in a diamond anvil cell requires further development.

[1] S. Mondal et al., PRB, 88 (2013) 8.

O 1.18

The best of both worlds: Combined X-ray and neutron studies at high-pressure using lab source X-ray diffractometers and Laue Neutron Diffraction

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Neutron diffraction is an important tool in the study of light atomed systems containing elements such as H, Li, Be and C. Such studies are often used to complement simultaneous X-ray studies on the same material. Due to the weakly interacting nature of neutrons and the weak sources of neutron radiation available, however, often much larger sample volumes are required, typically, orders of magnitude larger than equivalent X-ray experiments. The requirement of large sample volume has limited the use of high-pressure neutron diffraction in terms of maximum achievable pressures and data of sufficient quality for quantitative solution and refinement of structural data.[1,2]

Previously the Paris-Edinburgh press has been the work horse of high-pressure neutron diffraction work while developments elsewhere has seen diamond anvil cell techniques developed and adapted in order to achieve pressures of up to 90 GPa with sample volumes equivalent to those used in high-pressure X-ray diffraction experiments albeit with limits to the observable reciprocal space.[3] Recently Binns *et al* have suggested an alternative approach, adapting a standard Merrill-Bassett design, typically associated with high-pressure X-ray work for a combined X-ray and neutron diffraction study at high-pressure. Through the use of a polychromatic beam and the Laue technique it is possible to perform both single crystal neutron diffraction and X-ray diffraction on the same sample loaded in the same cell ensuring consistency in the sample and the pressure it is subjected to.

We report the first combined high-pressure X-ray and neutron diffraction study of l-arginine at high-pressure. The data collected is from a single high-pressure loading of a single crystal (~ 0.3 x 0.2 x 0.2 mm^3) at pressures up to 1.5 GPa and suggests that such an approach should be investigated further in order to achieve higher pressures while maintaining relatively small sample volumes.

Figure 1. Laue diffraction image taken from the KOALA beamline at ANSTO. The insert demonstrates the relative clarity of the diffraction and the easy with which it may be distinguished from parasitic diamond diffraction.

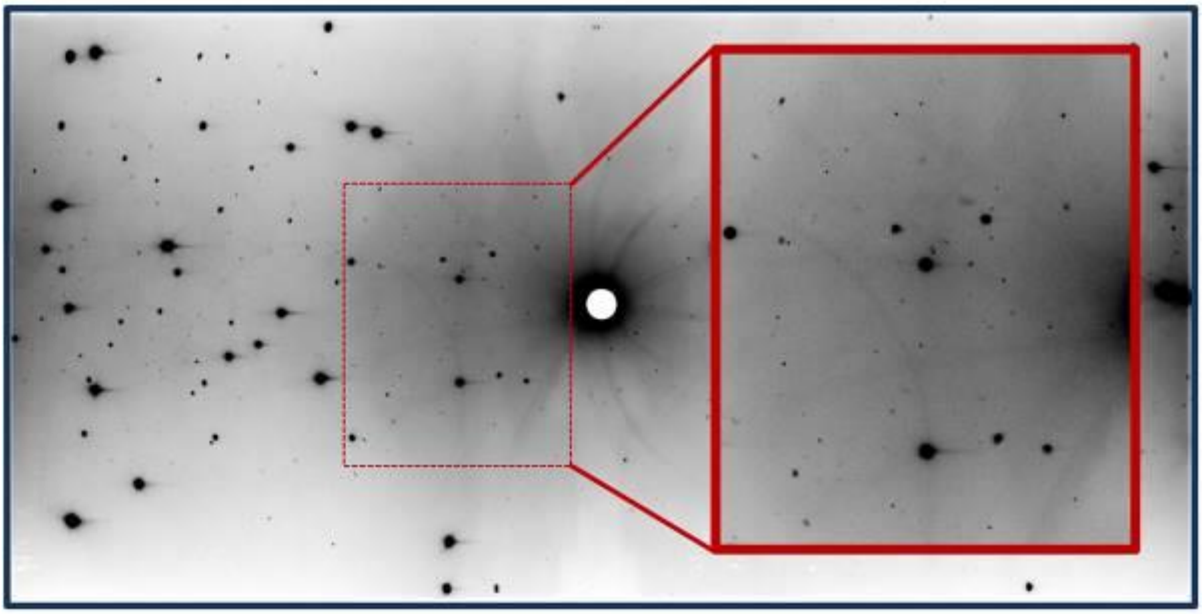
References

[1] Guthrie, M. *J. Phys.: Condens. Matter* 2015, *27*, 153201.

[2] Binns, J. *et al IUCrJ* 2016, *3*.

[3] Boehler, R. *el al High Pressure Research* 2013, *33*, 546.

Figure 1



P 1.1

High-pressure behavior of Y/Sm oxalates showing thermomechanical effects on dehydration

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Solid state chemical reactions give solid products with new crystal structures and volume different from that of the initial reactant. Structural and volume changes cause deformations and stresses at the reaction sites where the reaction is localized, and this can influence the reaction in two ways. First of all, stress can influence the elementary stages. Second, as stress relaxes, via plastic deformation or fracture, a variety of defects can be produced. These defects, in turn, can influence the chemical reaction rate and morphology of reaction products. Thus, feedback between reaction and deformation arises. The influence of strain on chemical reaction is most significant during thermal decomposition reaction due to very large volume changes, which, in turn, result in large stresses and crystal fragmentation during the reaction. Oxalates of lanthanides are convenient objects to study this phenomenon. One of the main advantages of these compounds is that dehydration can proceed preserving a single crystal. This allows one to study the changes of crystal morphology and strain in the course of the chemical reaction. In this contribution we examined the reaction-related strain and tried to identify the main factors that control the morphology of fracture during the solid-state chemical reaction. To do that, we studied the mechanism of structural transformation, structural strain and mechanical phenomena during decomposition of samarium and yttrium oxalates decahydrates. The phenomenon was followed by single-crystal X-ray diffraction and optical microscopy. To follow robustness of structure forming motifs and directions of structure compression we have also investigated behavior of initial compounds up to 5 GPa that allowed us to correlate strain during chemical reaction with structure forming units and strain on compression.

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Keywords: high pressures, solid-state reactions, crystal morphology

P 1.2

High pressure infiltration sintering and performance of cBN-Si composites

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Cubic boron nitride (cBN) is a well known superharder materials, with high hardness second only to diamond. It is widely used in high speed cutting of hardened steel, iron and iron alloys where diamond completely disabled. Generally, the cBN and the catalyst are mixed and then sintered at high pressure and high temperature(HTHP). However, it is difficult to control the homogeneity of the mixed power. Here, polycrystalline cubic boron nitride (PcBN) compacts have been prepared through high pressure infiltration method. The results show that the cBN-Si composites have a great homogeneous microstructures and high hardness, high thermal stability and high cutting performance. The performance of our sintered samples is also superior to the commercial PcBN.

P 1.3

Effect of high pressures on the crystal structure and on negative magnetoresistance of multicomponent tetragonal chalcogenides

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The multicomponent chalcogenide semiconductors such as CuInCh2, (ACh)1-x(CuBCh2)x, Ch - chalcogen, A - Ge, In; B - As, Sb, exhibit a combination of interesting physical properties, demonstrate negative magnetoresistance (NMR) under high pressure at room temperatures [1, 2], and undergo the baric and temperature phase transitions. The causes of manifestation of NMR in semiconductors at high pressures have not been studied in detail. To identify these causes it is important to reveal the relationship between the crystal structure of materials and their properties. We present the results of investigation on influence of pressure up to 60 GPa on the crystal structure of (InSe)0.5(CuAsSe2)0.5 exhibiting NMR at high pressure. The crystal structure at high pressures was studied by synchrotron X-ray diffraction technologies. To measure magnetoresistance under pressure up to 50 GPa in transverse magnetic field (up to B=1 T) high pressures have been generated in the cell with synthetic carbonado-type diamond anvils [3]. The compound (InSe)0.5(CuAsSe2)0.5 (just as well as (InS)0.5(CuAsS2)0.5 and (InS)0.5(CuSbS2)0.5), crystallizes in the tetragonal crystal system with chalcopyrite structure at atmospheric pressure. According to X-ray studies with a gradual increase in pressure two structural transitions were observed: from chalcopyrite structure to a cubic NaCl-type in the range (8-10) GPa and from NaCl-type to the orthorhombic structure in the range (32-38) GPa. In the pressure range 36 GPa -38 GPa the noticeable changes in a behavior of NMR were observed. In the same pressure range the noticeable changes of the impedance and the admittance, the tangent of loss angle, the relaxation time have been established earlier [2,4]. The changes in a behavior of NMR and other electrical characteristics are caused by structural transitions and due to a change of electron structure.

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[1] N. V. Melnikova et al. BRAS: Phys. 2014. 78(4). P. 299.

[2] N. V. Melnikova et al. J. Phys.: Conf. Ser. 2015. 653. 012098.

[3] A.N. Babushkin. High Press. Res. 6 (1992), pp. 349.

[4] N. V. Melnikova et al. SEMST. 2010. 1(4). P. 52.

P 1.4

Bond distances and effective pair potentials in CuBr under high pressure and high temperature

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Local structure in the CuBr investigated by in-situ XAFS observation under high pressure and high temperature. XAFS experiments for the Br K-edge spectra were performed under pressure and temperature up to 8.5 GPa and 1500 K using a multi-anvil high-pressure device and synchrotron radiation from Spring-8, Hyogo. X-ray absorption near-edge structure (XANES) spectra are useful for phase study under high pressure and high temperature. The modifications in XANES spectra with increasing pressure provide evidence for changes in the local structure of liquid CuBr. Rapid increases in bond distances are observed along with the changes from tetrahedral coordination to the octahedral coordination. Gradual changesin bond distances are observed in the liquid phases. The anharmonic effective pair potentials $V(u)=\alpha u^2/2+\beta u^3/3!$ for Br-Cu bond in various phases have been investigated by the pressure and temperature dependence of EXAFS Debye-Waller factors. The potential parameter α for sphalerite-type phase at 0.1 MPa was 2.38(5) eV/A^2. The potential parameters do not change appreciably through the transition of the sphalerite- to α-AgI-type phases with same coordination numbers at 0.1 MPa. The potential coefficients, α, for the sphalerite phase at 4.0 GPa was 2.68(5) eV/A^2. The potential parameter at 0.1 MPa increases by about 12% at the pressure of 4.0 GPa. The energies of the third-order anharmonic potential coefficient, β, maintain nearly constant values with pressure in the phase (-10.6(10) eV/A^3 at 4.0 GPa). The anharmonic effective pair potential for each phase is influenced by pressure and become steeper with increasing pressure. The Grüneisen parameter $\boldsymbol{\gamma}_G$ for the sphalerite phase was estimated from the potential parameters as 1.6. The octahedrally coordinated ion in the rock-salt type phase has a broader effective pair potential and a larger mean square relative displacement of thermal vibration than the tetrahedally coordinated ion.

P 1.5

Structural, vibrational, and electronic study of α-As_2Te_3 under compression

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Group-15 sesquichalcogenides with generic formula A_2X_3 (A=As, Sb, Bi; X= S, Se, Te), and in particular arsenic telluride (As_2Te_3), have been widely studied because of their outstanding thermoelectric properties **[1-3]**. Here, we present a study of α-As_2Te_3 phase at high pressure (HP) in order to better understand its properties and to explore if it can show pressure-induced topological changes. We report a HP structural, vibrational, and electronic characterization of α-As_2Te_3 at room temperature by means of powder X-ray diffraction and Raman scattering measurements up to 17 GPa, which are complemented with *ab initio* total energy and lattice dynamics calculations. Our results show that α-As_2Te_3 remains in its initial monoclinic structure up to 14 GPa and exhibits a reversible phase transition near 17 GPa. However, some structural and vibrational changes have been noted between 2 and 4 GPa, which have been interpreted on the basis of electronic band structure calculations. They suggest that there is a progressive closing of the bandgap with increasing pressure leading from a semiconducting to a metallic behavior above 4 GPa. We have found no clear evidence for any topological change on increasing pressure.

References

[1] Nolas, G.S.; Sharp, J.; Goldsmid, J. *Thermoelectrics.* Eds.; Springer: Berlin, 2001.

[2] Scherrer H.; Scherrer S. Thermoelectric Properties of Bismuth Antimony Telluride Solid Solutions. *Thermoelectrics Handbook: Macro to Nano.* Ed. D.M. Rowe, CRC Press: Boca Raton, FL, 2005.

[3] Stordeur, M. Valence Band Structure and the Thermoelectric Figure-of-Merit of $(Bi_{1-x}Sb_x)Te_3$ Crystals. CRC Handbook of Thermoelectrics, Ed. D.M. Rowe, CRC Press: Boca Raton, FL, 1995.

P 1.6

Stability of the fergusonite phase in $GdNbO_4$ investigated by high pressure XRD and Raman experiments

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Fergusonite (F) is the name given to a mineral whose main component is $YNbO_4$. The fergusonite structure appears in the high pressure (HP) phase diagram of ABO_4 tungstates (B=W) or molibdates (B=Mo) [1,2] where it is observed between the low pressure tetragonal scheelite (SCH) type phase and HP polymorphs with higher coordination numbers. The transition to the F-phase is associated to the existence of a ferroelastic instability. The monoclinic distortion is enhanced by HP. In $BiVO_4$, however, the thermodynamically stable polymorph of $BiVO_4$ in ambient conditions is F-$BiVO_4$. High temperatures and/or HP decrease the monoclinic distortion inducing the formation of SCH-$BiVO_4$ at moderate temperatures (237ºC) or high pressure (1.4 GPa). The destabilization is related to the existence of an optical soft mode.

$GdNbO_4$ crystallizes in the fergusonite structure [3]. In temperature, F-$GdNbO_4$ is stable up to 1003 K, where the ferroelastic instability causes the transformation to the SCH phase [4]. Although moderate pressures (110 MPa) have been employed as a tool to reduce temperature in the synthesis of $GdNbO_4$ by the hydrothermal method [5], there is no previous knowledge about the high pressure properties and stability of F-$GdNbO_4$.

We have performed HP XRD and Raman experiments in order to characterize the stability of $GdNbO_4$ and relate its HP behavior to that of related compounds, in particular $BiVO_4$.

HP was generated using a diamond-anvil cell (DAC), using Ne as pressure transmitting medium. Pressure was determined using the ruby luminescence. Powder XRD patterns were acquired at the MPSD beamline at the ALBA synchrotron. A monochromatic beam of wavelength 0.4246 Å was used. Diffraction images were collected using a Rayonix CCD detector and integrated with the FIT2D software. Raman spectra were collected in the backscattering geometry using the 632.8 nm line of an He-Ne laser and a Jobin−Yvon spectrometer in combination with a thermoelectric-cooled multichannel CCD detector with spectral resolution below 2 cm^{-1}.

Preliminary analysis of the spectra does not show any sign of phase transition up to the maximum pressure achieved, around 25 GPa.

[1] D. Errandonea, Europhys. Lett. 77, 56001 (2007)

[2] D. Errandonea and F. J. Manjón, Materials Research Bulletin 44, 807-811 (2009)

[3] V. K. Trunov and L. N., Kinzhibalo, Doklady Akademii Nauk SSSR 263, 348-351 (1982)

[4] L. L. Kukueva, L. A. Ivanova, Yu. W. Venevtsev, Ferroelectrics. 55, 129-133 (1984).

[5] M. Yang, X. Zhao, Y. Ji, F. Liu, W. Liu, J. Sun and X. Liu, New J. Chem. 38, 4249-4257 (2014).

P 1.7

Crystal structure of new high-pressure strontium germanate $SrGe_2O_5$

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Germanates have extensively been investigated for various industrial applications as represented in germanate glasses. Meanwhile, germanates have frequently been employed as model substances for the corresponding silicates because they exhibit similar phase-transformations to silicates at lower pressures. Phase and structural studies of germinates have thus provided important insights into phase transformations of silicate minerals in the Earth's interior. However, some germanate systems have not yet been fully examined. The system Sr-Ge-O is one of such examples, although it is a potentially good low-pressure analog of the system Ca-Si-O, one of the major components in the constituent minerals of Earth's crust and mantle. To our knowledge, the four forms of $SrGeO_3$, $SrGe_4O_9$, Sr_2GeO_4 and Sr_3GeO_5 have only been known in the system Sr-Ge-O. However, we recently discovered a new high-pressure strontium germanate $SrGe_2O_5$. We here report the crystal structure of this new phase and its structural features.

Single crystals of $SrGe_2O_5$ crystallized as a coexistent phase with $SrGeO_3$ perovskite single-crystals, in the sample recovered in the high-pressure experiment of $SrGeO_3$ pseudowollastonite conducted at 6 GPa and 1223 K. Single-crystal X-ray diffraction technique was used for the determination and refinement of the crystal structure.

The resulting crystallographic data are as follows: orthorhombic; space group *Cmca*; a = 5.4653(6) Å, b = 9.7379(9) Å, c = 13.7710(12) Å and V = 732.90(13) Å^3; Z = 8; D_x = 5.670 g/cm^3. The crystal structure consists of germanium-oxygen framework layers stacked along [001] with Sr atoms located at 12-fold coordinated cuboctahedral site; the layers are formed by the corner-linkages between GeO_6 octahedra and between GeO_6 octahedra and GeO_4 tetrahedra. This is isostructural with the high-pressure phases of $SrSi_2O_5$ and $BaGe_2O_5$. From comparison of the present $SrGe_2O_5$ structure with the reported $SrSi_2O_5$ and $BaGe_2O_5$ structures, the effect of cation size on the crystal structure will be discussed in terms of chemical bonding nature.

P 1.8

The photochemical reaction in crystals at high pressure: crystallographic studies

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High pressure influences photochemical reactivity of molecules in crystals. We have observed the decrease in the reaction rate in the case of the Norrish-Yang reaction (Scheme 1) of 4-(2,4,6-triisopropylbenzoyl) benzoate benzylammonium [1] and the salt of 6,6-diethyl-5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid with (1S)-1-(4-methylphenyl) ethylamine [2, 3].

Scheme 1. The equation of the Norrish-Yang reaction.

In the poster, we will present the comparison of the crystal structure of the latter compound at 1.8 GPa and 0.1 MPa, namely concerning:

- intermolecular interactions (Fig. 1a)
- free space in crystals (Fig. 1b)
- changes in the values of the geometrical parameters describing the compound susceptibility to the reaction.

Figure 1. (a) The Hirshfeld surfaces of the photoactive anion and (b) the free space in the crystals at 0.1 MPa and 1.8 GPa.

Moreover, we will analyze the changes in the unit cell parameters brought about by the photochemical reaction at 1.0 GPa and 1.8 GPa.

The studies let us identify geometrical factors as having a strong impact on the photochemical reation rate at high pressure.

References

[1] Konieczny, K.; Bąkowicz, J.; Turowska-Tyrk, I. *CrystEngComm* **17** (2015) 7693-7701.

[2] Konieczny, K.; Bąkowicz, J.; Turowska-Tyrk, I., *J. Photochem. Photobiol. A: Chem.*, accepted.

[3] Turowska-Tyrk, I.; Bąkowicz, J.; Scheffer, J.R. *Acta Crystallogr., Sect. B: Struct. Sci.* **63** (2007) 933-940.

Scheme 1

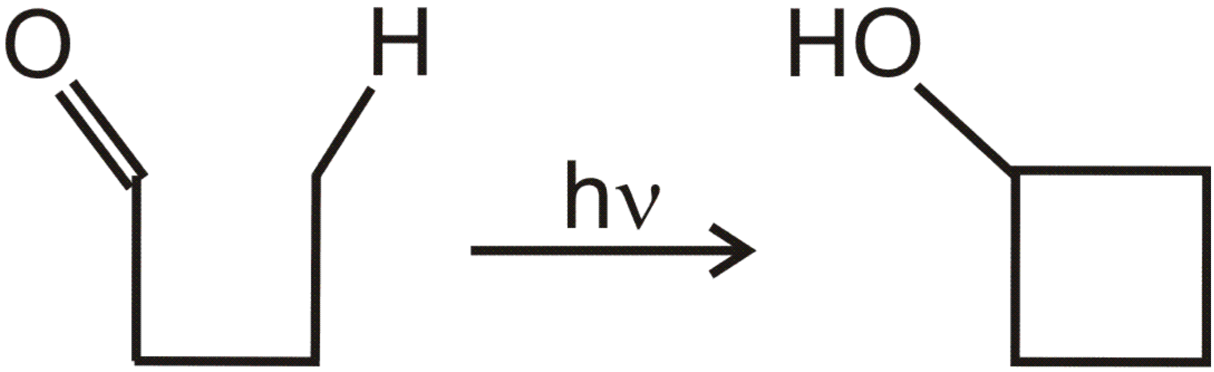
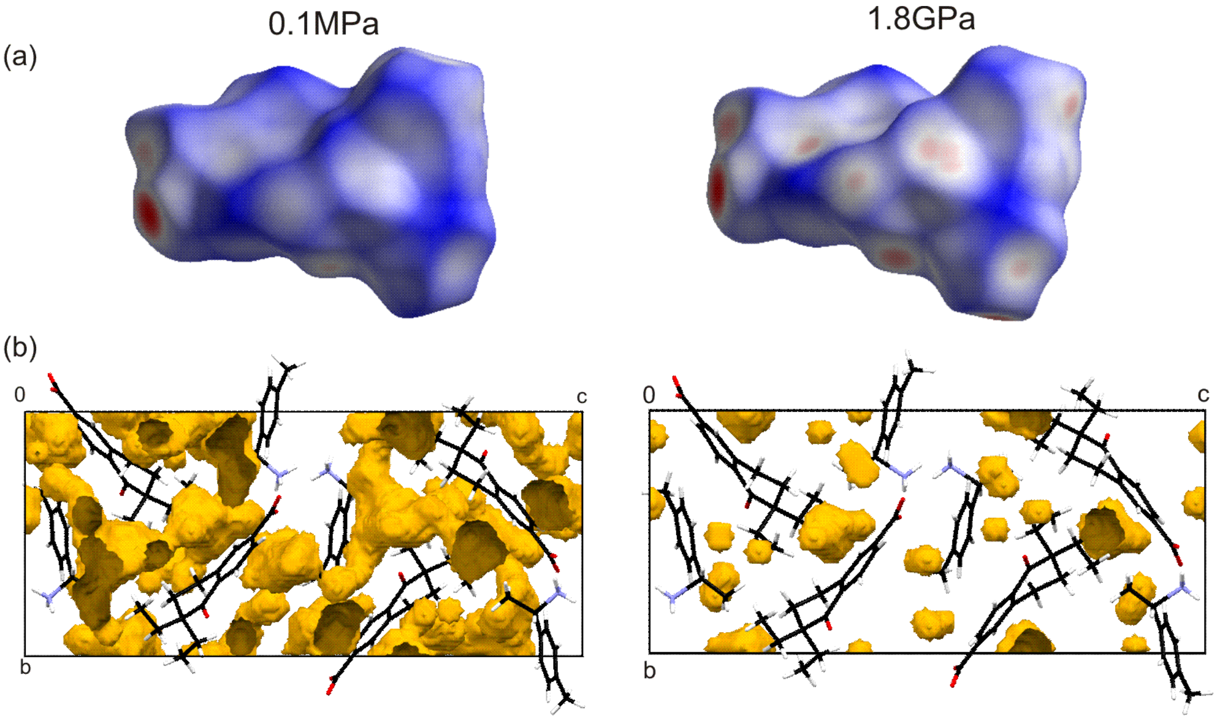


Figure 2



P 1.9

The monitoring of structural transformations brought about by a photochemical reaction in crystals at high pressure

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2,6-difluorocinnamic acid undergoes the [2+2] photodimerization in crystals under the influence of UV radiation at ambient and high pressures (Scheme 1).

Scheme 1. The equation of the [2+2] photodimerization.

The crystal structures were determined for the pure reactant crystal and for the partly reacted crystals, *i.e.* containing both reactant and product molecules, at 0.1 MPa, 0.5 GPa and 1.0 GPa (Fig. 1).

The course of the photochemical reaction was monitored at ambient and high pressures by means of diffraction images, cell parameters, intermolecular geometry, free space in the crystal and the content of product molecules.

The variations in these cell parameters brought about by the photochemical reaction were smaller at 1.0 GPa than at 0.5 GPa. However, the direction of the variations did not change.

The volume of free space in the pure reactant crystal decreased by 31 Å^3 and the intermolecular distance between the photoactive double bonds decreased from 3.886 Å to 3.790 Å *en route* from 0.1 MPa to 1.0 GPa. The amount of influence of these opposingly acting factors on the reaction rate will be discussed.

Figure 1. The crystal in the Boehler-Almax diamond anvil cell at 1.0 GPa.

Figure 2. The molecules in the pure reactant crystal (left) and in the partly reacted crystal containing 18% of the product (right) at 1.0 GPa. Only the cyclobutane ring of the product was shown.

Scheme 1

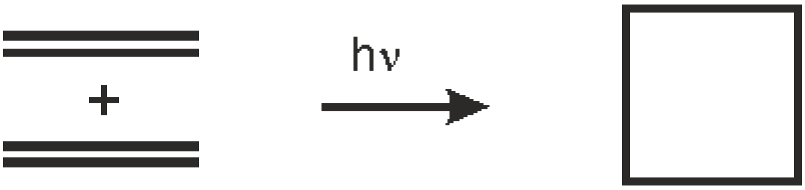


Figure 1

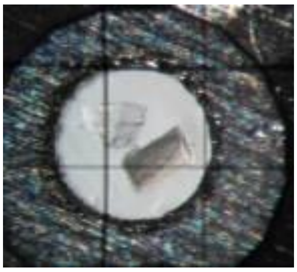
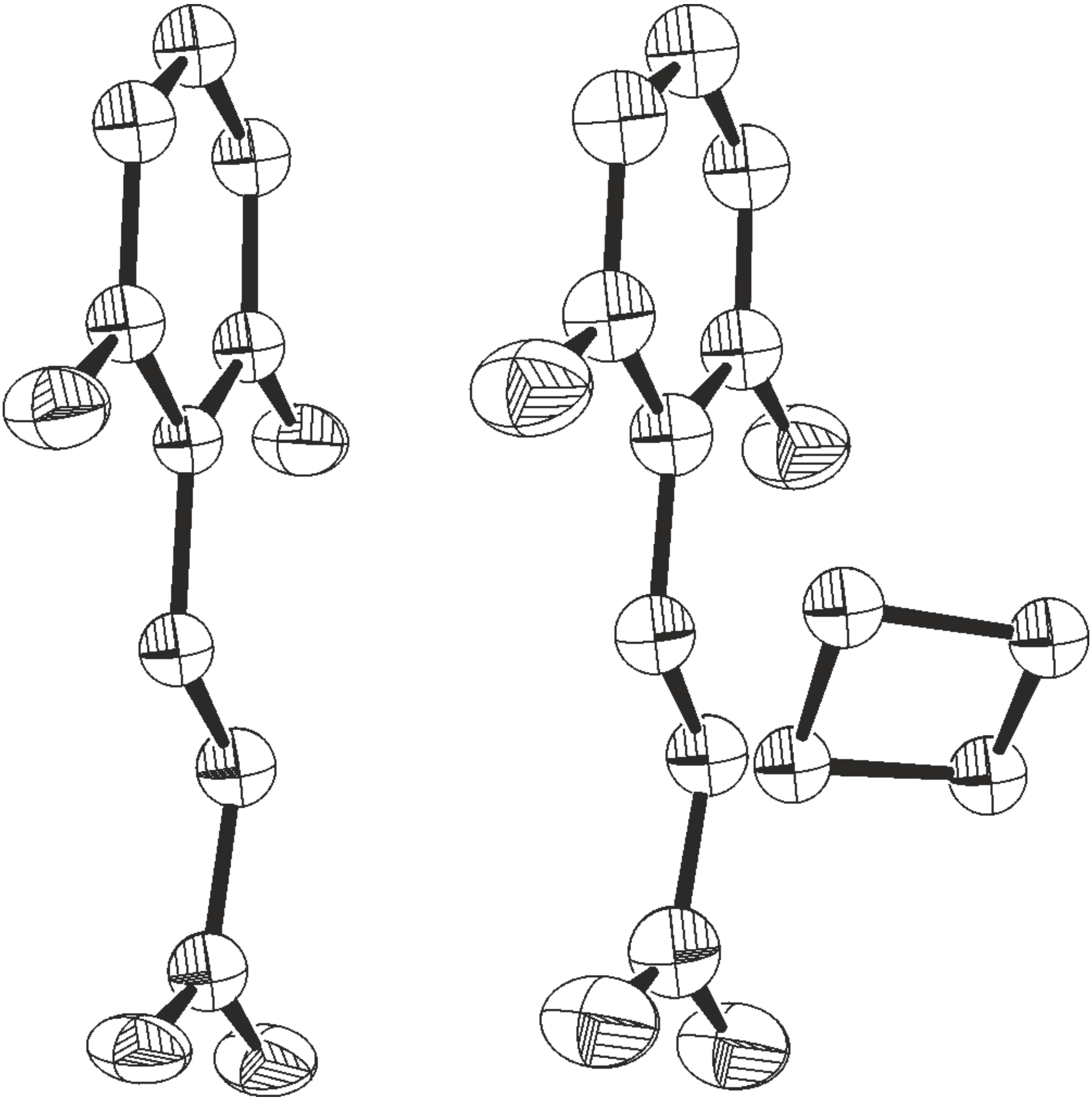


Figure 2



P 1.10

Phase transitions in Silicon from 16 GPa up to 50 GPa

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Silicon has been studied under high pressure for a long time, his phase diagram is built up to 230 GPA and there are about 12 high pressure phases. But still remains question about lattice structure under range of compression from 30 Gpa to 40 Gpa. Which afterwards were identified as Si—VI. Currently, work is underway to determine the existence of Si—IV and determine phase structure of Si—VI.

In this Letter we investigated Silicon electrical resistance under pressures from 16 GPa to 50 Gpa to examine boundaries of possible transition in range from 32 GPa to 35 Gpa.

During the experiment were received dependence of electrical resistance under fixed pressure to time. As a result of approximation time relaxations were determined for each pressure measurement. According to changes we can find out about possible phase transition [1]. If time dependence can not be described as exponent and represents random beats, or relaxation time increases sharply, we can conclude that applied pressure causes structural changes in the sample.

Based on the obtained relation we assume that between 36 Gpa and 40 Gpa endures an area with small relaxation time, that indicates the existence of stable crystalline structure. Peaks indicate boundaries of the presence of the crystal structure at 34 and 44 Gpa. Moreover, the completion of a phase transition at 16 Gpa to simple hexagonal lattice in initial range of the figure. Received data coincide with phase diagrams, which are described in contemporary researchers [1,3].

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References

[1] Ichiro Hatta, Masato Shibuya Experimental study on the critical dynamics of the order-disorder transition in binary alloys // Journal of the physical society of Japan. (1978). V. 45. No 2. P. 487 - 494.

[2] Qingyang Fan, Changchun Chai, Qun Wei Prediction of novel phase of silicon and Si-Ge alloys // Journal of Solid State Chemistry. (2015). V. 233. P. 471 - 483.

[3] H. Olijnyk, S.K. Sikka, W.B. Holzapfel Structural phase transitions in Si and Ge under pressures up to 50 Gpa // J. Physics Letters. (1983). V. 103A. No 3. P.137 - 140.

P 1.11

High-pressure studies of energetic co-crystals

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The performance of an energetic material (explosives, propellants and pyrotechnics) is governed by many factors: primarily their sensitivity to stimuli, chemical reactivity, and stability. Conventionally, these are controlled either through physical processes such as particle size reduction; or chemically through synthesis of novel molecules [1]. However, these routes tend to be complex and time-consuming.

Co-crystallisation is a process which has gained traction within the pharmaceutical industry in recent years. By co-crystallising two APIs together, it has shown the ability to tune parameters such solubility and bioavailability [2]. More recently, the same process has been adapted to energetic materials, showing that performance and sensitivity can be tuned by co-crystallising energetic materials with other energetic or non-energetic components [3].

However, to date **no** high-pressure studies of energetic *co-crystal* materials have been published. Looking at an energetic material under pressure offers valuable insights into processes that can take place during the detonation process where extremes of pressure are routinely observed. In addition, the application of pressure can yield recoverable higher-density polymorphs of an energetic material with greater performance than the original material [4].

Here we aim to show preliminary work we have pursued in this field - high-pressure structural studies of co-crystals based around CL-20, a secondary explosive; and nitroguanidine, a propellant. Studies have been made using a combination of x-ray diffraction with diamond-anvil cells, and neutron diffraction with Paris-Edinburgh cells, with equations of state derived where possible.

[1] - J. Akhavan, *"The Chemistry of Explosives"*, 3rd ed., RSC, Cambridge, (2011).

[2] - P. Vishweshwar *et al.*, *J. Pharm. Sci.*, (2006), **95**, p499-516.

[3] - K.B. Landenberger *et al.*, *Cryst. Growth Des.*, (2012), **12**, p4311-4314.

[4] - D.I.A. Millar *et al.*, *Crystallog. Rev.*, (2010), **16**, p115-132.

P 1.12

Phase transition systematics in $BiVO_4$ by means of high pressure-high temperature Raman experiments

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The photocatalytic activity of $BiVO_4$ strongly depends on the crystalline phase and sample form, being nanoparticles of particular interest. The thermodynamically stable polymorph of $BiVO_4$ at ambient conditions is a monoclinic distortion of a scheelite-type phase (SCH), named fergusonite (F). The relationship between both phases is dictated by a ferroelastic instability. $BiVO_4$ can also be prepared with a zircon (Z) structure.

The high pressure (HP)-high temperature (HT) F-SCH phase boundary has been studied by XRD [1]. The pressure and temperature coefficients of the optical A_g soft mode (63 cm^{-1}) have been also determined [2-3].

We report here HP-HT Raman experiments performed on F-$BiVO_4$ powder and single crystal samples. We also present results from nano powders of Z-$BiVO_4$. We complement previous Raman experiments discussing the behavior of the whole set of Raman active modes as well as extending the pressure range and introducing simultaneously HP-HT conditions. The HP behavior of Z-$BiVO_4$will be discussed for the first time.

HP was generated using a diamond-anvil cell (DAC). HT was achieved by external heating of the DAC. The pressure transmitting medium was either Ne or a 16:3:1 methanol−ethanol−water mixture. Pressure was determined using the ruby or $SrB_4O_7:Sm^{2+}$ luminescence. Temperature was measured with a K-type thermocouple. The 632.8 nm line of a He-Ne laser was used to excite Raman spectra, which were collected in the backscattering geometry.

The temperature and pressure behavior of the F lattice modes reflect the distortions associated to the ferroelastic instability. The linear coefficients of the Z phase are in sharp contrast with the behavior observed in the F phase.

The F to SCH second order phase transition occurs at 1.4 GPa (ambient temperature) and 237ºC (ambient pressure). The Z to SCH, irreversible, first order phase transition is observed from 386 to 490 ºC (ambient pressure) and from 3.3 to 4.3 GPa (ambient temperature).

We found evidences of additional structural changes around 18 GPa, which in the downstroke were found to be not completely reversible.

[1] R. M. Hazen and J. W. E. Mariathasan, Science 216, 992-993 (1982).

[2] A. Pinczuk, B. Welver and F. H. Dacol, Sol. State Comm. 29, 515-518 (1979).

[3] A. Pinczuk, G. Burns and F. H. Dacol, Sol. State Comm. 24, 163-165 (1977).

P 1.13

Pressure-induced structural changes of Europium hydride under high-pressure H_2 condition

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Introduction

Europium dihydride (EuH_2) is stable (*Pnma*, phase I) at ambient pressure. When EuH_2 is compressed in hydrogen, three phase transitions to *P*6₃/*mmc* (phase II), *I*4/*m* (phase III), and *I*4/*mmm* (phase IV) take place at 7.2 GPa, 8.4 GPa, and 8.7 GPa.[1] Phase III and IV are the products resulting from chemical reaction of EuH_2 with H_2, and they are considered to be represented EuH_x ($x > 2$).[1] EuH_2 is ferromagnetic with magnetic moment of divalent Eu^{2+}, on the other hand Eu in phase IV is estimated to be in non-magnetic trivalent state Eu^{3+} by Mössbauer spectroscopy measurement.[1] If phase III is in mixed valence state, novel magnetic states may be expected.

Objectives

The detailed reaction process of EuH_2 with H_2 under high pressure, such as the stoichiometry changes associated with crystal structure transformations, has not been clarified. Raman scattering measurement can be superior to XRD with respect to the obtaining information about H atom position.

Materials & Methods

We performed Raman scattering measurements (JASCO-NRS2100G) of EuH_2/H_2 mixture at high pressures and room temperature using diamond anvil cells.

Results

Several Raman peaks that were not assigned to phase II appeared at 7.2 GPa. With increasing pressure, we found further four transitions at 9.9 GPa, 12.7 GPa, 14.8 GPa, and 15.6 GPa, in contrast to the previous XRD results that report three transitions above 7.2 GPa. The present results suggest that phase II is unstable. We renamed the previous phases as phase α (EuH_2, *Pnma*, 0 ~ 7.2 GPa), phase β (EuH_2, *P*6₃/*mmc*, 7.2 GPa ~, without H_2), phase γ (7.5 ~ 9.9 GPa), phase δ (9.9 ~ 12.7 GPa), phase ε (12.7 ~ 14.8 GPa), phase ζ (14.8 ~ 15.6 GPa), and phase η (*I*4/*mmm*, 15.6 GPa ~), respectively. As EuH_x at 14.3 GPa has been found to be in trivalent state, the reaction of EuH_x with H_2 is considered to complete below 14 GPa. Thus, intermediate phases may be expected to have mixed valence states.

Conclusion

Raman scattering measurements of EuH_x under high-pressure H_2 condition revealed the existence of five phases not recognized in previous XRD. The results indicate that phase β starts chemical reaction with H_2 immediately after the transition from phase α. This study revealed that EuH_x ($x > 2$) is synthesized through the reaction of H_2 with phase β (EuH_2) as a gateway.

References

[1] T. Matsuoka., *Phys. Rev. Lett.* **107**, 025501 (2011).

P 1.14

High pressure diffraction study of K_2AgF_4

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Among compounds containing divalent silver and fluoride, one can find a plethora of valuable properties: magnetic (antiferromagnets [1], ferromagnets [2], canted antiferromagnets [3]), structural (perovskites, post-perovskites [4], Ruddlesden-Popper phases [5]) and electronic ones (narrow gap semiconductors, ionic conductors [6]). Due to the similarities in electronic configuration between fluoroargentates(II) and oxocuprates(II), it has been postulated that the former might serves as precursors of high-T_C superconductors [7].

Objectives of the work were to investigate the phase diagram of K_2AgF_4 in the high pressure region. Preliminary calculations predicted, that up to 2.2 GPa there should occur at least two different phase transitions (α: perovskite --> β: post-perovskite [8] --> γ: another post-perovskite phase). In this study we have performed HP diffraction measurements and DFT calculations to estimate a possibility of obtaining 2D AFM ordering in K_2AgF_4.

α-K_2AgF_4 powder synthesized from AgF_2 and KF 1:2 molar mixture, was studied. Neon or fluorinated polymer (FEP, PTFE) was used as pressure-transmitting medium. X-ray powder diffraction data were collected using synchrotron radiation in the pressure range from 7.9 to 41.0 GPa. An AgF impurity was present in the sample, although its amount did not increase substantially during the compression (pressure-induced decomposition has not been observed). Additionally, DFT methods were used to calculate the possible high pressure structures of K_2AgF_4.

Significant changes in the diffraction patterns were observed during compression between 7.9 and 13.3 GPa, suggesting the presence of a structural phase transition.

[1]: P. Malinowski et al., *Angew. Chem. Int. Ed. Engl.* **49,** 1683 (2010)

[2]: S.E. McLain et al., *Nat. Mater*. **5**, 561 (2006)

[3]: W. Grochala, P. P. Edwards, *Phys. Status Solidi B* **240**, R11 (2003)

[4]: Dominik Kurzydłowski, PhD thesis, Univ. Warsaw (2012)

[5]: Z. Mazej et al., *CrystEngComm* **11**, 1702 (2009)

[6]: Adamczyk W, et al., *J. Fluor. Chem.,* **174**: 22 (2015)

[7]: W. Grochala, R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **40**, 2742 (2001)

[8]: D. Kurzydłowski et al., *Eur. J. Inorg. Chem.* **2010**, 2919 (2010)

P 1.15

Structural and vibrational properties of single crystals of Scandia, Sc_2O_3 under high pressure

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We investigated structural and vibrational properties of single crystals of Scandia, Sc_2O_3 at ambient temperature under high pressure up to 55 and 28 GPa, respectively. Both X-ray diffraction and Raman studies indicated a phase transition from the cubic bixbyite phase (so-called 'C-Res' phase) to a monoclinic *C2/m* phase (so-called 'B-Res' phase) at pressures around 25-28 GPa. The transition was accompanied by a significant volumetric drop by ~ 6.7%. In addition, the Raman spectroscopy detected a minor crossover around 10-12 GPa, which manifested in the appearance of new and disappearance of some Raman modes, as well as in softening of one Raman mode. We found the bulk modulus values of the both C-Res and B-Res phases as B_0 = 198.2(3) and 171.2(1) GPa (for fixed B'= 4), respectively. Thus, the denser high-pressure lattice of Sc2O3 is much softer than the original lattice. In this presentation we will display the above dataset for Sc_2O_3 and compare this case with the other sesquioxides adopting the same cubic bixbyite lattice at ambient conditions.

P 1.16

High-pressure phase transition of AgO, a prototypical mixed-valent system: Raman, XRD, and DFT study

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We report the methods and results of the joint theoretical and experimental high-pressure studies of AgO. Silver (I,III) oxide is a prototypical mixed-valence semiconductor.[1] It crystallizes in a monoclinic-type structure ($P2_1/c$)[2,3]; tetragonal form ($I4_1/a$) is also known.[4] It has been recently predicted by means of hybrid DFT calculations that the electronic band gap at the Fermi level for $P2_1$/c type narrows with increasing pressure and should close at 50-60 GPa.[5] Preceding this, $P2_1/c$ structure should undergo a phase transition to $C2/c$ structure ($Ag^IAg^{III}O_2$ à $Ag^{II}Ag^{II}O_2$).[5] Initial spin-polarized calculations considering minimal possible antiferromagnetic model equivalent to the crystallographic $C2/c$ unit cell (Z=4) predicted that the resulting high-pressure $C2/c$ phase is an antiferromagnetic metal at 55-85 GPa.[5] It was simultaneously predicted that comproportionation is preceded by phonon-induced phase transition to a disproportionated *P-1* polytype at 45 GPa (low-DOS metal).[5]

Our most recent hybrid DFT calculations[6], for an antiferromagnetic $P2_1/c$ model with a larger unit cell Z=8 (CuO type), predict the comproportionated structure to be favoured over the phonon-induced mixed valence *P-1* one at all pressures below 80 GPa. The new antiferromagnetic model (with band gap at Fermi level of approximately 1 eV at ambient pressure) is predicted to be energetically favoured over the ambient-pressure mixed valence $P2_1/c$ structure already at 20 GPa.

Raman spectra collected from AgO samples in diamond-anvil cells in the pressure range of 10-80 GPa reveal a sharp increase of frequencies of Ag-O stretching modes between 20 GPa and 30 GPa, which likely correspond to the first order phase transition. Moreover, X-ray diffraction data for AgO under pressures up to 60 GPa show a qualitative change in the diffraction pattern at about 20 GPa, which further confirms the appearance of a new crystalline phase.

References

[1] J. P. Allen, D. O. Scanlon, G. W. Watson, *Phys. Rev. B* **81**, 161103(R) (2010).

[2] J. A. McMillan, *J. Inorg. Nucl. Chem.* **13**, 28-31 (1960).

[3] M. Jansen, P. Fischer, *J. Less-Common Met.* **137**, 123 (1988).

[4] K. Yvon, A. Bezinge, P. Tissot, P. Fischer, *J. Solid State Chem.* **65**, 225-230 (1986).

[5] I. Włodarska, M. Derzsi, W. Grochala, *Phys. Status Solidi RRL* **9**, 401-404 (2015).

[6] M. Derzsi, P. Piekarz, in preparation (2016).

P 1.17

Inspecting high pressure 'self-insertion' in $CoSb_3$ by means of single crystal X-ray diffraction

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$CoSb_3$ belongs to the broad class of unfilled skutterudites including $IrSb_3$, $RhSb_3$ and the most recent $FeSb_3$ (I m-3 structure). Doping and filling the structure with guests leads to significantly enhanced of thermoelectric which makes skutterudites interesting for both material synthesis and studies of origin of transport properties [1]. At ambient conditions skutterudites have cubic lattice with space group Im-3 and large octahedral voids at the 2a positions, a position that is occupied upon filling.

A recent high pressure study proposed that the structure of $CoSb_3$ and similar compounds undergoes a ‘self-insertion’ process, [2] with compression inducing filling of the 2a position by atoms originally at the 24g position and with no volume discontinuity [2]. This new phenomenon could be typical for a broad range of compositions [3]. The new state is quenchable to ambient pressure [2,3] and thus the `self-insertion` mechanism opens a new way for preparation of filled skutterudite materials with enhanced thermal properties.

Here we investigate the $CoSb_3$ crystal structure as a function of pressure (<50GPa, He, Ne pressure medium) and temperature (<2000K). We provide new high pressure single crystal X-ray diffraction data with a refined material equation of state at ambient conditions and focus on the pressure region of the 'self-insertion' crossover. By means of resistive heating technique we re-investigate the high pressure high temperature stability region of 'self-insertion' (Kramer et al. [2]) and use laser heating as a final test for stability of $CoSb_3$ at high temperatures and pressures below and above the critical point of the crossover.

References

[1] B.C. Sales, D. Mandrus, R.K. Williams, Science 272, 1325 (1996)

[2] A.C. Kraemer et al. Phys. Rev. B 75, 024105 (2007) doi: 10.1103/PhysRevB.75.024105

[3] K. Matsui et al. Journal of the Physical Society of Japan 81, 104604, (2012) doi: 10.1143/JPSJ.81.104604

P 1.18

Influence of plastic deformation under pressure upon synthesis of Al-Fe and Zr-Fe alloys from elemental powders

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Nowadays the methods of intensive plastic deformation under pressure are extensively applied to receive body materials with new functional properties. One of such technologies is the synthesis of alloys from elemental powders using intensive plastic deformation by torsion in Bridgman anvils. To carry out the research there were prepared elemental powder mixes of zirconium and iron with the content of iron from 5 to 90 at. % and elemental powder mixes of aluminum and iron with the content of iron from 5 to 60 at. %. The received mixes were subjected to mechanical alloying in Bridgman anvils under pressure of 8 GPa at room temperature.

Research revealed that in all synthesized alloys the nanocrystalline state is formed. The minimum size of grain in synthesized alloys under the applied conditions of deformation is ~ 10 nm. It was determined that solubility of iron in zirconium reaches 10 at. %, and in aluminum it is significantly less - ~ 1 at. %. In alloys of system Zr-Fe there is formation of ω-phase -a high pressure phase of zirconium, and in alloy Al-50 at. % Fe an unordered solid solution FeAl is formed.

Measurement of density of alloys Al-Fe synthesized under pressure of 5 GPA and at 5 turns of anvils showed that it monotonously grows with increase in content of iron. The systematic deviation of experimental values from the values calculated according to Vegard's law demonstrates that with increase in content of iron the degree of structure imperfection of alloys increases.

Study of change of electrical resistance showed that concentration dependence of specific resistance is characterized by nonlinear growth. After achieving the maximum value in alloy Al-40 at. % Fe (370-414 µΩcm), the resistance of alloy Al-55 at % Fe decreases to values of 39-41 µΩcm that is about 4 times more than specific resistance of pure iron. The growth of electrical resistance is caused by different reasons: the reduction of grain size, the emergence of amorphous areas, and the increase in degree of structure imperfection. The reason of reduction of resistance in Al-55 at % Fe can be connected with the formation of the unordered alloy AlFe. However, interpretation of this effect demands further study.

All synthesized alloys are ferromagnetic. Obtained data show that with increase in content of iron the magnetization of alloys Al-Fe grows, and the coercive force decreases. The reduction of coercive force is caused by the reduction of grain size in alloys with high content of iron.

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P 1.19

Nonmetallization and band inversion in beryllium dicarbide at high pressure

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Carbides have attracted much attention owing to their interesting physical and chemical properties. Here, we systematically investigated global energetically stable structures of BeC_2 in the pressure range of 0-100 GPa using a first-principles structural search. A transition from the ambient-pressure α-phase to the high-pressure β-phase was theoretically predicted. Chemical bonding analysis revealed that the predicted phase transition is associated with the transformation from sp^2 to sp^3 C-C hybridization. The electrical conductivity of the high-pressure phase changed from a metal (α-phase) to a narrow bandgap semiconductor (β-phase), and the β-phase had an inverted band structure with positive pressure dependence. Interestingly, the β-phase was a topological insulator with the metallic surface states protected by the time-reversal symmetry of the crystal. The results indicate that pressure modulates the electronic band structure of BeC_2, which is an important finding for fundamental physics and for a wide range of potential applications in electronic devices.

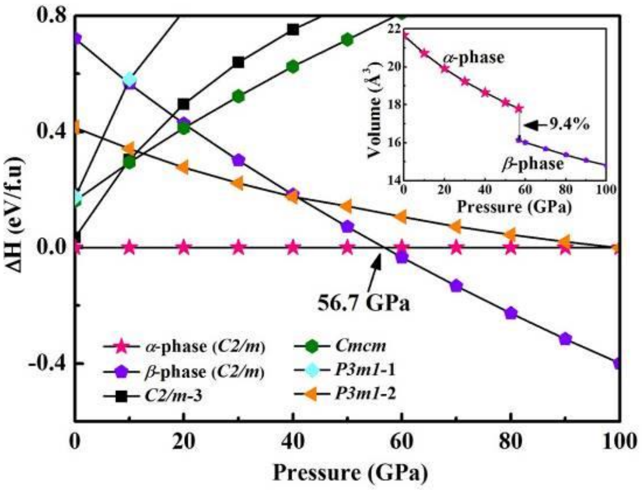
Figure 1. Enthalpies per formula unit of various structures as a function of pressure with respect to ambient pressure of the α-phase. Insert: The calculated equations of states for the predicted structures.

References

[1] Li, Y. L. et al. Pressure-induced Superconductivity in CaC_2. Proc. Natl. Acad. Sci. U. S. A. 110, 9289 - 9294 (2013).

[2] Zhang, M. et al. Superhard BC_3 in Cubic Diamond Structure. Phys. Rev. Lett. 114, 015502 - 015507 (2015).

Figure 1



P 1.20

Pressure confinement effect in monolayer and few layer MoS_2s

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Two-dimensional (2D) materials with similar layered hexagonal structure like graphene have attracted considerable attention, monolayer molybdenum disulfide (MoS_2), as one of the important transition metal dichalcogenides, is a kind of semiconductor with strong light absorption and emission ability and has received extensive attention.

In this study, we investigate the pressure confinement effect on monolayer MoS_2 by *in situ* high pressure Raman and photoluminescence (PL) measurements. Our results reveal a structural deformation of monolayer MoS_2 starting from 0.84GPa, which is evidenced by the splitting of E^1_{2g} and A_{1g} modes. At higher pressure of 5.8GPa, the appearance of two new peaks located at 200 and 240 cm^{-1} suggest a structural transformation might take place. This is a distinct feature of monolayer MoS_2 compared with bulk MoS_2. The new structure is supposed to have a distorted unit with the S atoms sided within a single layer like that of metastable 1T'-MoS_2. However, unlike the non-photoluminescent 1T'-MoS_2 structure, our monolayer shows a remarkable PL peak and a pressure induced blue shift up to 13.1GPa. We also investigated the Raman spectra of trilayer and quadlayer MoS_2 flakes under high pressures, we found that a pressure induced structure transformation from 2H to AB' stacker in trilayer MoS_2 at 8GPa, while quadlayer MoS_2 persists 2H structure with some extent distortion due to the layer number dependent interlayer coupling effect. This pressure tuned behavior might enable the development of novel devices with multiple phenomena involving the strong coupling of the mechanical, electrical and optical properties of layered nanomaterials.

Acknowledgements

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P 1.21

High pressure spectroscopic study of $In_xAl_{1-x}N$ (x~0.7)

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Introduction

$In_xAl_{1-x}N$ nanostructures find application in optoelectronics due to their remarkable electronic properties, while their *x*-dependent bandgaps cover the spectral range from ultraviolet to near-infrared. Raman and photoluminescence (PL) spectroscopy are well-established, non-destructive techniques for assessing the crystalline structure, quality, stress distribution and free carrier concentration of these systems.

Objectives

Raman and PL spectroscopy at high pressure are used to probe the structural stability and the pressure response of the vibrational and electronic properties of a ternary $In_xAl_{1-x}N$ (x~0.7) thin film.

Materials and methods

The studied $In_xAl_{1-x}N$ (x= 0.72) sample with ~100 nm thickness was grown by Molecular Beam Epitaxy on a 4 µm GaN/Al_2O_3 template. After thinning the substrate to ~70 mm, the sample was pressurized by means of a diamond anvil cell, using the 4:1 methanol-ethanol mixture as pressure transmitting medium. Raman measurements were conducted using a LabRam HR or a T64000 spectrometer. A laser beam at 515 nm was used for excitation, focused on the sample by means of a 50x objective at a power of ~1 mW.

Results

In the Raman spectrum of the InAlN film, five broad Raman bands can be resolved at ambient conditions at 212 (E_2^1, AlN-like), 334 (B_1), 528 (E_2^2, InN-like), 611 (E_2^2, AlN-like), and 699 cm^{-1} (LO, asymmetric peak). Pressure application up to 7 GPa causes the reversible hardening of all the Raman bands with slopes 1.0-6.5 $cm^{-1}GPa^{-1}$. While the pressure slopes for the two E_2^2 peaks {5.4 (InN-like) and 4.5 $cm^{-1}GPa^{-1}$ (AlN-like)} are similar to those for the corresponding end members of the $In_xAl_{1-x}N$ series, the pressure slope for the LO peak (6.5 $cm^{-1}GPa^{-1}$) is higher, possibly due to pressure induced changes of the electron-phonon coupling and the resonance conditions. The PL peak of the film is located at ~1.61 eV, very close to the absorption edge energy and in agreement with the literature. However, its pressure slope (16 $meVGPa^{-1}$) is rather small compared to earlier theoretical explorations, suggesting a possible clustered arrangement of the In atoms.

Conclusion

The pressure slopes of the phonon frequencies and the energy gap of a ternary InAlN film have been experimentally obtained, providing important information for its structural and electronic properties.

P 1.22

A new ethane polymorph

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Ethane (C_2H_6) is structurally the simplest hydrocarbon that contains a single carbon-carbon bond. Along with methane, ethane constitutes the largest natural organic deposit on Earth and is one of the most common fuels. Ethane has three solid phases at ambient pressure.[1] An orientationally disordered phase I exists between the freezing point at 90.32 K and 89.78 K.[1,2] This plastic phase crystallize in cubic space group $Im3m$.[3] The orientationally ordered phase II exists in the extremely narrow range from 89.78 K to 89.68 K.[1,2] Below 89.68 K the ordered phase III crystallizes in monoclinic space group $P2_1/n$.[3] The phase diagram of ethane has been determined by DSC[1] and NMR[2] measurements up to 1.3 GPa in the temperature range from 210 K to 89 K. It has been concluded, that plastic phase I disappears at about 1.3 GPa and 217 K. High pressure Raman scattering of liquid and solid ethane in the diamond-anvil cell (DAC) up to 8 GPa at 300 K has been performed by Shimizu *et al.*, 1989.[4] The pressure-induced liquid-solid II phase transition of ethane at 300 K has been determined at 2.5 GPa and the solid II-solid III transition at 3.3 GPa.[4] In our present study we have determined the structure of new ethane phase IV at high pressure by single crystal X-ray diffraction. We have measured the compression of its intermolecular contacts up to 5.90(2) GPa. We have also actualized the P/T phase diagram of ethane.

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References

[1] van der Putten, L., Schouten, J. A. & Trappeniers, N. J. (1986). *Physica B+C* **139-140**, 215-217.

[2] Schutte, M. H. M., Prins, K. O. & Trappeniers, N. J. (1987). *Physica B+C* **144**, 357-367.

[3] van Nes, G. J. H. & Vos, A. (1978). *Acta Cryst.* **B34**, 1947-1956.

[4] Shimizu, H., Shimazaki, I. & Sasaki, S. (1989). *Japanese Journal of Applied Physics* **28**, 1632-1635.

P 1.23

Neutron diffraction studies of shockwave-synthesized γ - Si_3N_4 material

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The high pressure spinel-type γ-Si_3N_4 was prepared by using shock wave synthesis at the peak shock pressures around 34 GPa. It was found previously that the synthesized material contains a fraction of a secondary amorphous phase which is oxygen rich [1]. Among others, this amorphous phase produces a diffuse scattering during the neutron diffraction measurements which impedes the data interpretation for the crystalline phase, especially the determination of its oxygen content. To remove the amorphous phase, the samples were etched by hydrofluoric acid. Afterwards they were measured by neutron diffraction again. The results of the neutron diffraction measurements will be presented in the present paper.

[1] A. Köhler, T. Schlothauer, C. Schimpf, V. Klemm, M. Schwarz, G. Heide, D. Rafaja, E. Kroke: The role of oxygen in shockwave-synthesized γ - Si_3N_4 material, J. Eur. Ceram. Soc. 35 (2015) 3283

P 1.24

Pressure-induced structural transformations in $AFeX_4$ (A: $[C_nH_{2n+1}]_4N$; n=1-4; X: Cl, Br) compounds

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Alkylammonium tetrahalometallates are inorganic-organic hybrid systems showing interesting ferroic properties (ferromagnetism, ferroelectricity, and ferroelasticity) associated with a very rich but complicated phase diagram, which includes incommensurate structures and subtle structural changes induced by temperature [1]. Although general phase diagrams of A_2MX_4 (A: $[C_nH_{2n+1}]_4N$, M: divalent transition-metal (TM) ion, X: Cl, Br, I) compounds were early established [2], structural studies in related AMX_4 (M: trivalent TM ion) systems are less common. In any case, structures representing thermal response are linked to the ordering of the involved polyhedral species, which are fixed through weak H bonding interactions. Nevertheless, structural characterization is still challenging in some cases due to the delicate phase equilibrium close to ambient conditions, sometimes yielding controversial results [3,4]. In addition, high pressure studies on these systems are very scarce although very advisable [5], since they can clarify the role of the polyhedral interaction in the structural arrangements, tuned by subtle changes under continuous compression.

This work is focused on the behaviour of $AFeX_4$ (A: $[C_nH_{2n+1}]_4N$; X: Cl, Br) compounds under high pressure. The structural evolution of several members of this family has been explored by ADXRD. Especial attention has been paid to the end members, TMN and TBN (see Fig.1), exploring the hydrostatic regime: 0-15 GPa. Differences regarding compressional behaviour (crystal and polyhedra), pressure-induced phase transitions and amorphization have been studied in both Chlorides and Bromides, trying to establish general rules for the high pressure response of hybrid systems. Raman spectroscopy has also been employed as supplementary characterization technique of high pressure phases, and particularly of the local structure variations undergone by both organic and inorganic tetrahedral under pressure.

Fig.1 Unit cells of $[CH_3]_4NFeCl_4$ ($TMNFeCl_4$): S.G. *Pma2*, *a*= 14.2753 Å, *b*= 6.4471 Å, c= 6.4526 Å (left) and $[C_4H_9]_4NFeCl_4$ ($TMNFeCl_4$): S.G. *Pnna*, *a*= 18.4370 Å *b*= 11.5539 Å, *c*= 11.4345 Å (right). Depicted polyhedra correspond to $FeCl_4$ units in both cases.

References

[1] S. Shimomura, N. Hamaya, Y. Fujii, *Phys. Rev. B* 53, 8975 (1996).

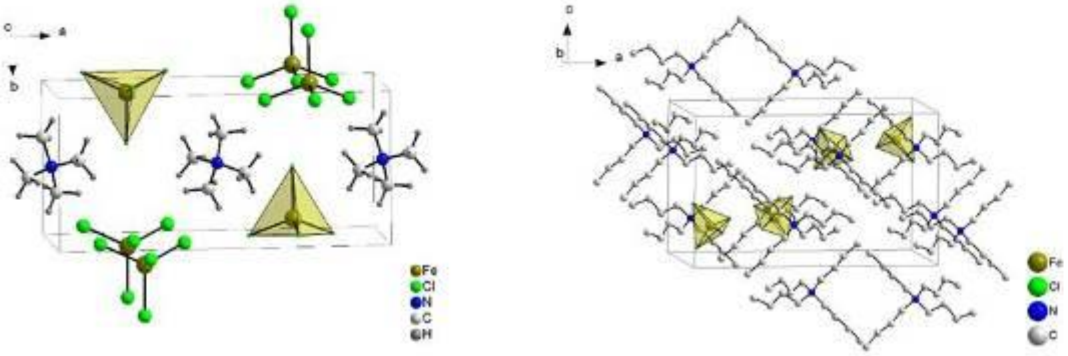
[2] K. Gesi, *J. Phys. Soc. Jpn.* 52, 2931 (1983).

[3] Z. Czapla, O. Czupiflski, Z. Galewski, L. Sobczyk, *Solid State Comm.* 56, 741 (1985).

[4] D. Wyrzykowski, *et al.*, *Inorg. Chim. Acta* 361, 262 (2008).

[5] J.A. Barreda-Argüeso, *et al.*, *Inorg. Chem.* **53**, 10708 (2014).

Figure 1



P 1.25

The high pressure behavior of Mo_2GaC and Mo_2Ga_2C

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$M_{n+1}AX_n$ (MAX) phases with n=1-3 are a class of hexagonal nanolaminated materials, where M is an early transition metal, A is a main group element, and X is C or N.[1] They are characterized by slabs of carbide or nitride ($M_{n+1}X_n$) separated by monolayers of pure A element. Having this layered structure, the MAX phases exhibit a combination of the beneficial properties of both ceramic and metallic compounds, making them attractive for many technological applications.

Mo_2GaC is the only MAX phase with Mo fully occupying the M site synthesized so far. Its counterpart Mo_2Ga_2C, was recently reported.[2] Both are of great interest because of their structural similarity; Mo_2Ga_2C is also laminated, but it contains a Ga double-layer interleaving between the Mo_2C blocks, instead of a Ga monolayer in the MAX phase Mo_2GaC.

Mo_2GaC was first synthesized in 1967. It was found to be superconducting below 7 K.[3] Many theoretical works were published in the recent years regarding its physical properties at ambient pressure. The mechanical properties and structural evolution under pressure of both Mo_2GaC and Mo_2Ga_2C were calculated by first-principles.[4,5] For both compounds a substantial difference in the compressibilities along the different axes was found - the *a* axis is much softer than the *c* axis. For Mo_2GaC the compressibility anomaly of *c* axis is closely reflected by the internal coordinate shift of Mo atom that shows three different slopes within 0-15 GPa, 20-60 GPa, and 70-100 GPa, respectively.[4] For Mo_2Ga_2C, a phase transition is predicted at 48 GPa with an abrupt increase of *c* and a rapid decrease in *a*.[5]

The current work focuses on experimental investigation of the high pressure behavior of Mo_2GaC and Mo_2Ga_2C. XRD measurements of samples loaded in diamond anvil cells were used to retrieve the structure of the compounds under pressure. The experimental results will be compared to the theoretical predictions.

[1] M.W. Barsoum, *MAX Phases: Properties of Machinable Carbides and Nitrides*, Wiley VCH GmbH & Co., Weinheim, 2013.

[2] C. Hu *et al*., *Chem. Commun.* **51**, 6560 (2015).

GmbH & Co., Weinheim, 2013.

[3] L. E. Toth and J. Less *Common Met.* **13**, 129 (1967).

[4] Q.-H. Gao *et al*., *J. Appl. Phys.* **119**, 015901 (2016).

[5] Z.-J. Yang *et al*., *Mod. Phys. Lett. B* **30**, 1650105 (2016).

P 1.26

A New Approach for in-situ Determination of Pressure and Temperature in Multi-Anvil High Pressure Apparatus

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In this study, we developed a new method for in-situ pressure determination in multi-anvil, high- pressure apparatus using an acoustic travel time approach within the framework of acoustoelastic- ity. The ultrasonic travel times of polycrystalline Al_2O_3 were calibrated against NaCl pressure scale up to 15GPa and 900ºC in a Kawai-type double-stage multi-anvil apparatus in conjunction with synchrotron X-radiation, thereby providing a convenient and reliable gauge for pressure determination at ambient and high temperatures. The pressures derived from this new travel time method are in excellent agreement with those from the fixed-point methods. Application of this new pressure gauge in an offline experiment revealed a remarkable agreement of the densities of coesite with those from the previous single crystal compression studies under hydrostatic conditions, thus pro- viding strong validation for the current travel time pressure scale. The travel time approach not only can be used for continuous in-situ pressure determination at room temperature, high temperatures, during compression and decompression, but also bears a unique capability that none of the previous scales can deliver, i.e., simultaneous pressure and temperature determination with a high accuracy (+0.16GPa in pressure and+17ºC in temperature). Therefore, the new in-situ Al_2O_3 pressure gauge is expected to enable new and expanded opportunities for offline laboratory studies of solid and liquid materials under high pressure and high temperature in multi-anvil apparatus.

P 3.2

A monitoring of pressure-induced phase transitions in Si beneath diamond indenters; in-situ and ex-situ approaches

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Extreme environments such as high pressure and high temperature are of interest because these conditions make possible to cause phase transitions and materials syntheses. Especially, different from the diamond anvil cell technique which causes hydrostatic pressures an indentation technique with pyramidal or conical diamond penetrator can promote phase transitions due to high contact pressure as well as shear stress beneath the indenter.

In this study, we try to observe pressure-induced phase transitions in Si through in-situ and ex-situ approaches. Contact pressure and deformation strain formed in an impression rely on the apex angle of the used indenter. Thus we use few pyramidal indenters with different apex angles to form impressions and then structural changes from the crystalline Si (diamond cubic structure at ambient pressure) are observed with a micro-Raman spectroscopy. Impressions corresponding to relatively sharp cube-corner indenter always accompany microcracks ahead of their corners and amorphous signals measured from the ex-situ spectroscopy are weaker than those from blunt impressions.

With a series of ex-situ measurements, a novel spectroscopy-combined indenter is developed and used for an in-situ observation beneath a contacting indenter. A diamond anvil with a narrow culet radius of 2.5 µm is used for the in-situ deformation observation; the diamond anvil contacts the Si wafer by applying mechanical load formed by a screw bolt joining and a laser beam focused narrower than 3.0 µm is exposed into the transparent diamond anvil. Reflected scattering beam through the diamond anvil is detected with the micro-Raman spectroscopy; a broadening of Raman signal near the frequency of 525 cm^{-1} can be clearly identified through the loading cycle.

Invited Talk

Incommensurate crystal structures of transition metal oxychlorides at high pressure

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Transition metal oxychlorides MOCl (M = Ti, V, Cr, Fe) have been recently intensively studied due to their magnetic and catalytic properties. At low temperatures the behavior of these low-dimensional magnets strongly depends on the transition metal atom. For instance, Ti^{3+} has only one *d* electron and TiOCl behaves as a quasi-one-dimensional antiferromagnet and is susceptible to a spin-Peierls distortion [1,2]. V, Cr and Fe oxychlorides are quasi-two-dimensional antiferromagnets and form different complex magnetic and nuclear superstructures below corresponding Neel temperatures. For highly anisotropic systems, like MOCl, the application of hydrostatic pressure provides a way of modifying magnetic intrachain and interchain exchange parameters, and allows to get a broader understanding of the interplay between different degrees of freedom in these systems.

We have studied MOCl using synchrotron-based single-crystal X-ray diffraction in diamond anvil cells. We have found out that independently of the transition metal atom MOCl undergo pressure-induced normal-incommensurate phase transitions in the vicinity of 15 GPa [3,4]. The mechanism of the transitions is related to an optimization of the packing of Cl atoms in the interlayer space and is not of electronic or magnetic origin. The metal atom only slightly influences the pressure of the transition and the modulation wave vector. In case of TiOCl, the enhancement of its quasi-one-dimensional behavior with pressure leads to a substantial increase of a spin-Peierls transition temperature. An interplay between the spin-Peierls distortion and the 15 GPa transition leads to very complex high-pressure structures of TiOCl, in which two kinds of independent incommensurate distortions present at the same time.

In this contribution we will present the analysis of complex high-pressure crystal structures of MOCl and discuss mechanisms of pressure-induced phase transitions.

[1] Seidel A, et al. Phys. Rev. B. **67**:020405(R) (2003).

[2] Shaz M et al. Phys. Rev. B. **71**:100405(R) (2005).

[3] Bykov M et al. Sci. Rep. **5**:9647 (2015).

[4] Bykov M et al. Phys. Rev. B. **88**:014110 (2013).

O 2.1

Complex crystal structures in bismuth tellurides at high pressure

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Bismuth tellurides, Bi_mTe_n, are a class of intermetallic compounds with intriguing physical properties. Bi_2Te_3 is one of the best bulk thermoelectric materials for operation near room temperature, and it has recently attracted much interest in the context of topological insulators. Several members of the series are superconductors at high pressure. We have studied a series of bismuth tellurides — Bi_2Te_3, Bi_4Te_5, BiTe, Bi_4Te_3, Bi_2Te and Bi_7Te_3 — at high pressure using x-ray diffraction and electronic structure calculations. Some of the phases were found to adopt complex incommensurate crystal structures. We will present the observed crystal structures and variations across the series of compounds and report on unusual pressure-induced order-disorder transitions. The thermal and electronic properties of these phases will be discussed in the context of thermoelectric properties.

O 2.2

Structure-property relationships in multiferroic metal-organic frameworks at high pressure

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Dense metal-organic frameworks (MOFs) show promise for a new class of multiferroic materials, [1-5] which have technological importance in sophisticated multistate memory devices. MOFs offer attractive perspectives as intrinsic multiferroic systems due to the large chemical and structural diversity that can be varied through the metal ion, ligand, and organic counterion. In particular, the MOF families of $AM(HCOO)_3$, where M^{2+} = Mn-Cu, and A^+ = alkylammonium cation, have shown multiferroic properties at certain compositions upon cooling, and rely on hydrogen bonding interactions for the coupling of ferroic parameters. [4,5] The chemical and structural diversity of MOFs would allow the ferroic parameters and their coupling to be readily tuned. However, a much greater understanding of the structure-property relationships is needed before the design of functional multiferroic MOFs can be achieved.

In order to investigate the effect of significant structural modifications on the magnetic and electric properties in MOFs, we study two MOF families as a function of pressure: $[NH_4][M(HCOO)_3]$ and $[(CH_3)_2NH_2][M(HCOO)_3]$ where M^{2+} = Fe, Ni. High-pressure single-crystal X-ray diffraction measurements were performed to follow the structural transformations upon compression, and thus estimate the evolution of structural polarity. [6] Structural studies are complemented with high-pressure Mössbauer spectroscopy to investigate the magnetic properties of the MOFs. These data allow us to derive structure-property relationships for a wide range of $AM(HCOO)_3$ atomic configurations. Moreover, investigating the structural evolution under pressure is important for determining the way chemical pressure should be used to modify the temperatures at which ferroelectric and ferromagnetic properties are observed.

References

[1] G. Rogez, N. Viart and M. Drillon, *Angew. Chem. Int. Ed.*, 2010, **49**, 1921-1923.

[2] A. Stroppa, P. Jain, P. Barone *et al.*, *Angew. Chem. Int. Ed.*, 2011, **50**, 5847-5850.

[3] P. Jain, V. Ramachandran, R. J. Clark *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 13625-13627.

[4] Y. Tian, A. Stroppa, Y. Chai *et al.*, *Sci. Rep.*, 2014, **4**, 6062.

[5] L. C. Gómez-Aguirre, B. Pato-Doldán, J. Mira *et al.*, *J. Am. Chem. Soc.*, 2015.

[6] I. E. Collings, E. Bykova, M. Bykov *et al.*, *In review*, 2016.

Invited Talk

High pressures studies of electronic reconstructions

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Quantum phase transitions feature a plethora of unconventional behavior and pose a continuing challenge to experiment and theory alike. The reconstruction of the electronic structure at a quantum phase transition is a particularly outstanding question relevant to a multitude of materials including the cuprate high-temperature superconductors. Reconstructions of the electronic structure can arise from gaping of the Fermi surface due to density wave formation. The arguably most drastic reconstruction, however, arises at the approach of a Mott transition where the entire Fermi surface vanishes. Understanding the mechanisms for these two scenarios will provide fundamental insight for correlated systems. In particular, this will allow scrutinizing the boundaries of the quasiparticle concept of Fermi-liquid theory.

Here, we present high pressure studies of selected materials from two classes of charge order quantum phase transitions, the Mott insulator NiS_2 and the charge density wave (CDW) metal $LaAgSb_2$. We report on novel techniques used for the investigation of the unconventional behavior in both materials and the evolution of the electronic structure as deduced from quantum oscillation measurements.

In $LaAgSb_2$ we can track the suppression of the CDW via resistivity and Hall effect measurements. We use a simplified method to produce patterned anvils for these transport studies. These allow us to detect quantum oscillations. We find no indications for a mass renormalization on the approach of the CDW quantum critical point. This is interpreted as a small coupling of quantum fluctuations to electrons on the Fermi surface. We discuss this in relation to unconventional superconductivity.

We succeeded to grow highest purity NiS_2 single crystals. These allow investigating the pressure-induced Mott transition finding unprecedented low disorder in the metallic phase. We employ novel pressure techniques to study this material in a clean way. The usage of patterned anvil cells with fluid pressure media promotes best hydrostaticity. In addition, we use a tunnel diode oscillator for contactless measurements of the resistivity and quantum oscillations.

We characterize our NiS_2 single crystals and discuss the phase diagram. Measurements of the Fermi surface in the high-pressure metallic phase are presented in comparison with band structure calculations of the non-correlated case. Our results show a strong enhancement of the quasiparticle mass in the vicinity of the Mott insulating state corresponding to a reduced quasiparticle weight and thus providing evidence for the correlation driven Mott transition. Furthermore, we can rule out alternative scenarios assuming a reduction of charge carrier concentration.

O 3.1

The equation of state of 5-nitro-2,4-dihydro-1,2,4,-triazol-3-one (α-NTO) determined via *in-situ* optical microscopy and interferometry measurements

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High-pressure equations of state (EOS) are typically determined, for crystalline solids, by measuring unit-cell volumes using x-ray diffraction (XRD) techniques. However, when characterizing low-symmetry materials with large unit cells, conventional XRD approaches may become problematic. To overcome this issue, we examined the utility of a “direct” approach toward determining high-pressure EOS by measuring surface area and sample thickness using optical microscopy and interferometry (OMI) respectively. We present OMI direct measurements of relative volumes from two statically compressed anisotropic crystalline materials: triamino-trinitrobenzene (TATB) and α-NTO (5-nitro-2,4-dihydro-1,2,4,-triazol-3-one). α-NTO crystallizes with four-component twins and a triclinic symmetry (Space Group: P-1) [1]. Hence α-NTO represents the most difficult type of a crystalline system to characterize under pressure.

We present an extended EOS for TATB and compare it with published XRD results [2]. This benchmark study serves to verify the validity of direct high-pressure volume measurements. We also report the first high-pressure EOS of α-NTO up to 28 GPa, a record pressure for energetic materials. According to our experimental results, the α -NTO phase remain stable up to 28 GPa however, a significant anisotropic compressibility is observed in agreement with a very recent theoretical study [3]. Additionally, we demonstrate how this approach can be extended to simultaneously determine pressure dependent anisotropic refractive indices. Lastly, we discuss general technical limitations of this direct 3D methodology to measure the EOS of compressed and also propose additional applications of this technique to composite materials.

Figure 1. EOS data of TATB as measured in this study using OMI. The black line is 3rd-order BM fit to XRD data from Ref.2

Figure 2. EOS of α- NTO as measured in this study using OMI.

[1] N. Bolotina, K. Kirschbaum, and A. A. Pinkerton, Acta Crystallogr. B 61, 577 (2005).

[2] L. L. Stevens, N. Velisavljevic, D. E. Hooks, and D. M. Dattelbaum, Propellants Explos.

Pyrotech. 33, 286 (2008).

[3] A. A. Rykounov, CrystEngComm 17, 7653 (2015).

This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Security, LLC under Contract DE-AC52-07NA27344.

Figure 1

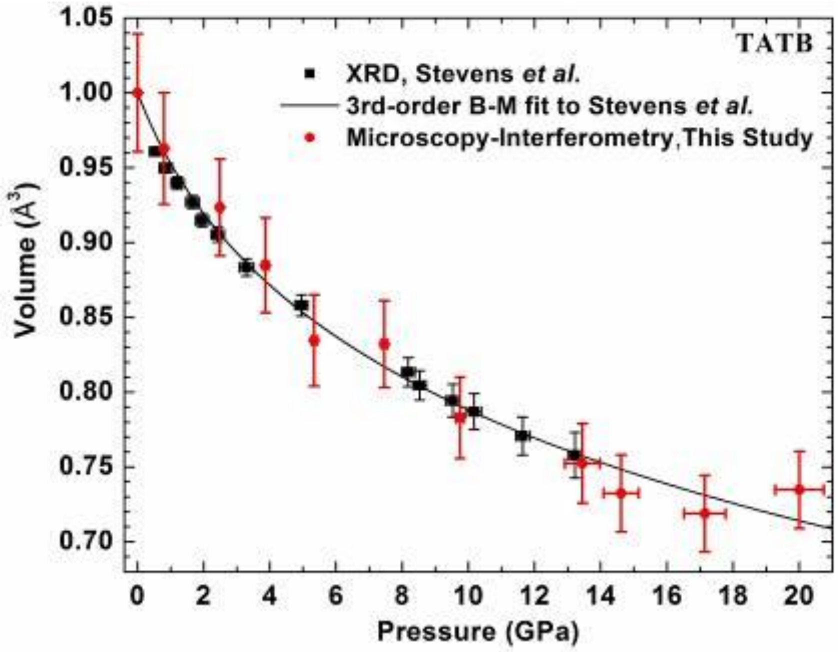
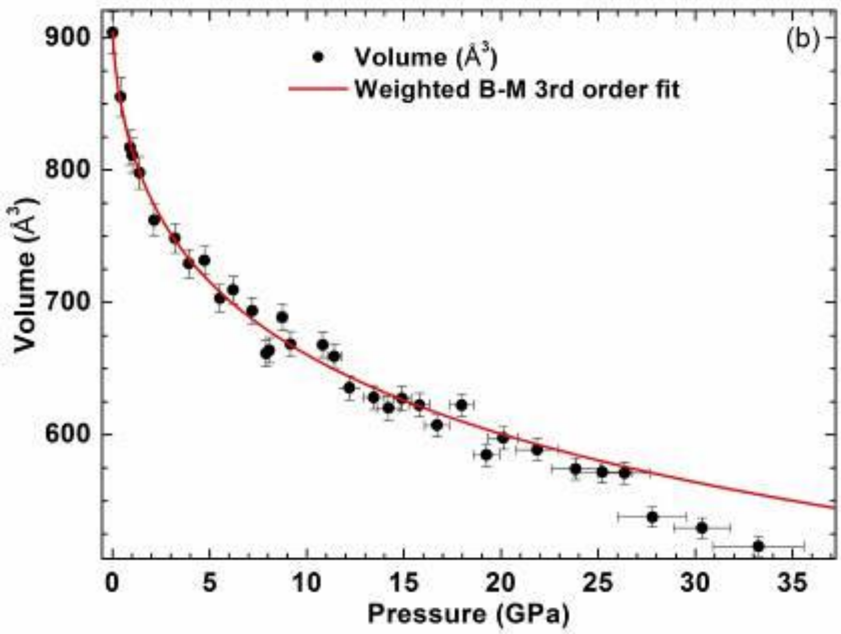


Figure 2



O 3.2

The equation of state of a polymer blended composite measured directly via *in-situ* tabletop optical microscopy and interferometry measurements (OMI)

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Quasi-static isothermal high-pressure equations of state (EOS) are routinely determined, for crystalline solids, by determining unit-cell volumes from model-refined x-ray diffraction (XRD) Bragg peaks. Large-volume presses or diamond-anvil cells (DACs) are used to encapsulate high-pressure materials for such EOS studies. Recently we reported using a more direct measurement approach using DACs to determine the EOS of a triclinic symmetry material (α-NTO, 5-nitro-2,4-dihydro-1,2,4,-triazol-3-one) consisting of fourling component twins [1]. This structurally complex molecule is not amenable to XRD-based approach because conventional model-based refinements simply can't yield unique solutions for such extraordinarily dense Bragg peak patterns. Using commonly available in-house tabletop diagnostics we directly measured pressure dependent crystalline surface area by making Optical Microscopy measurements and sample height by optical Interferometry (OMI) measurements. We first tested this approach on crystalline triaminotrinitrobenzene (TATB). The synchrotron-XRD [2] and tabletop OMI EOS results match remarkably well. For optically transparent materials, we also conduct interferometry measurements to determine high-pressure anisotropic indices of refraction. The technical advantages and disadvantages of OMI vs. XRD methods are discussed in our report [1].

Here we present tabletop OMI-based V(P) measurements conducted on a composite material, LX-17, which is a polymer blended energetic formulation consisting of 92.5 % TATB and 7.5% of Kel-F 800 plastic binder. We modified 400 µm diameter diamond-culets to encapsulate samples that are 125 µm tall and with a maximum diameter of 120 µm. This modification is important to characterize composites and alloys, up to 10s of GPa, that consist of < ~50 µm dimensional grain size constituents. These are the first-reported quasi-static high-pressure EOS results measured from a composite material.

Figure 1. OMI-based EOS data of TATB. The black line is a 3rd-order Birch-Murnaghan fit of the XRD data from Ref. 2.

Figure 2. Pressure dependent OMI-based TATB index of refraction, n_β, along the *β*-optical axis.

[1] E. Stavrou*, J.M. Zaug*, S. Bastea, and J.C. Crowhurst, *JAP* 119(14), (2016).

[2] L.L. Stevens, N. Velisavljevic, D.E. Hooks, and D.M. Dattelbaum, *PEP* 33, 286 (2008).

This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Security, LLC under Contract DE-AC52-07NA27344.

Figure 1

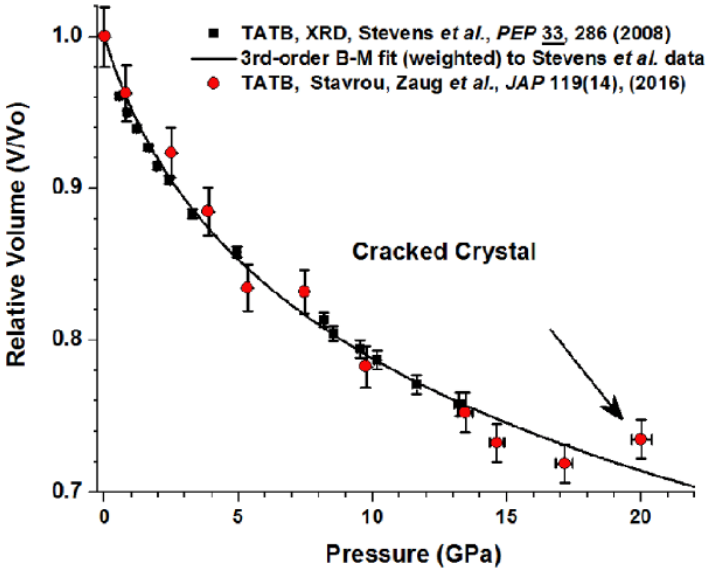
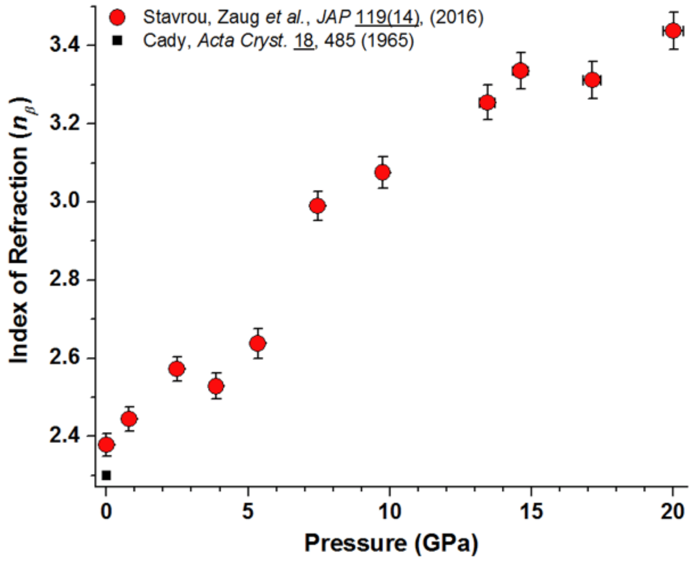


Figure 2



O 3.3

Development of spherical pressure cell for rotation in high magnetic field

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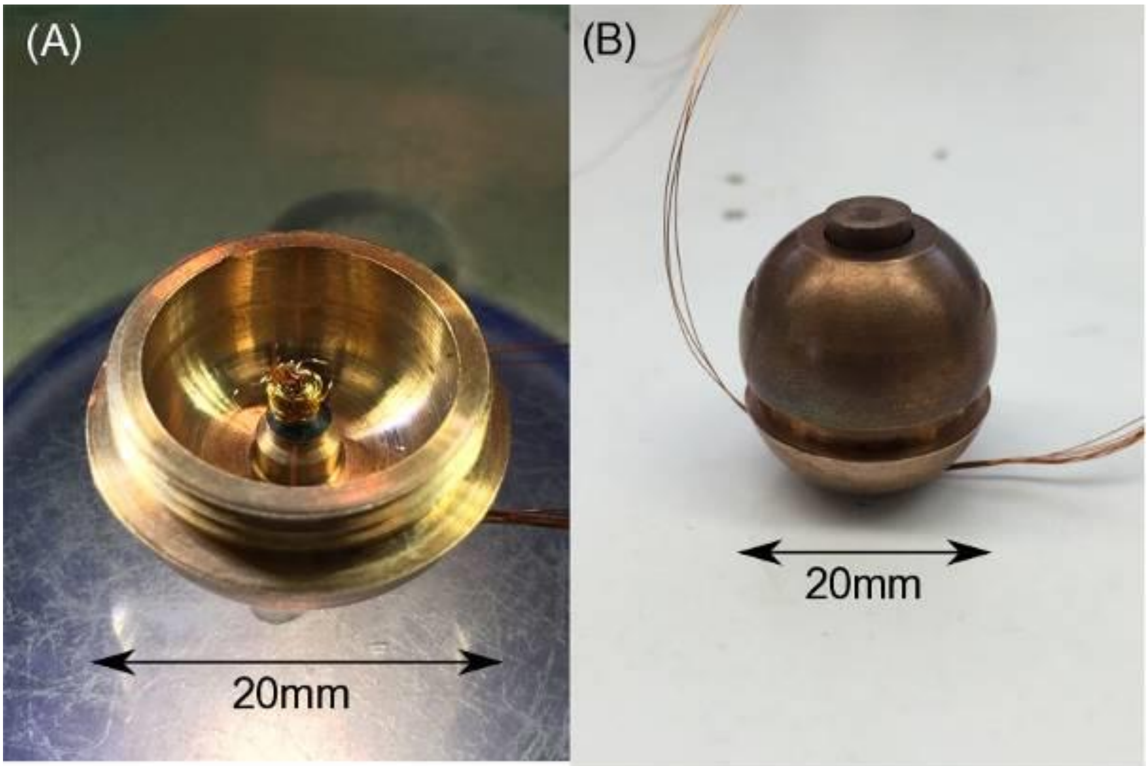
Applied magnetic fields can be used to modify a number of complex material properties, though are particularly useful for the study of strongly correlated electronic materials, such as superconductors. At low temperatures and high fields, quantum oscillations in resistivity relate directly to the Fermi surface, characterising the electronic properties of the material. High pressure can be used as a thermodynamic parameter to tune the strength of interactions within the material; coupling this with electronic measurements in a magnetic field can lead to an understanding of its effects on the topology of the Fermi surface.

Performing high pressure electronic measurements is not uncommon, though measuring multiple field orientations can be time consuming, and technically challenging, requiring that the sample be aligned within the pressure cell prior to pressurisation, whilst assuming that it remains aligned throughout the measurement. Here we present the design of a compact (20 mm diameter) non-magnetic spherical piston cylinder cell for high field electronic measurements, designed for measurements with multiple field orientations. The cell can be cooled to 1.8K in a standard cryostat and rotated in-situ using a two axis rotation stage. The spherical form of the cell, and the central sample position, result in highly isotropic field conditions on the sample, independent of orientation, such that geometric corrections are not required. Furthermore, the electrical contacts within the pressure region allow for sample pressure to be determined over the full temperature range of the cell. There are a number of other novel features implemented in the design of the pressure cell, and the methodology of its loading, which will be presented. Figure (A) plug/piston of disassembled cell, (B) fully assembled spherical cell before pressurisation.

Figure 1



O 3.4

Novel experimental design for high pressure - high temperature measurements of the electrical resistance in a 'Paris-Edinburgh' large volume press

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We present a novel experimental design for high sensitivity measurements of the electrical resistance of samples at high pressures (0-6GPa) and high temperatures (0-1000K) in a ’Paris-Edinburgh’ type large volume press. Uniquely, the electrical measurements are carried out directly on a small sample, thus greatly increasing the sensitivity of the measurement. The sensitivity to even minor changes in electrical resistance can be used to clearly identify phase transitions in material samples. Electrical resistance measurements are relatively simple, rapid to execute and the efficacy of the present experimental design is demonstrated by measuring the electrical resistance of Pb, Sn and Bi across a wide domain of temperature-pressure phase space and employing it to identify the loci of phase transitions.

Based on these results, the phase diagrams of these elements are reconstructed to high accuracy and found to be in excellent agreement with previous studies. In particular, by mapping the locations of several well-studied reference points in the phase diagram of Sn and Bi, it is demonstrated that a standard calibration exists for the temperature and pressure, thus eliminating the need for direct or indirect temperature and pressure measurements. The present technique allows simple and accurate mapping of phase diagrams under extreme conditions and may be of particular importance in advancing studies of liquid state anomalies.

O 3.5

High-sensitivity nuclear magnetic resonance up to 30 GPa

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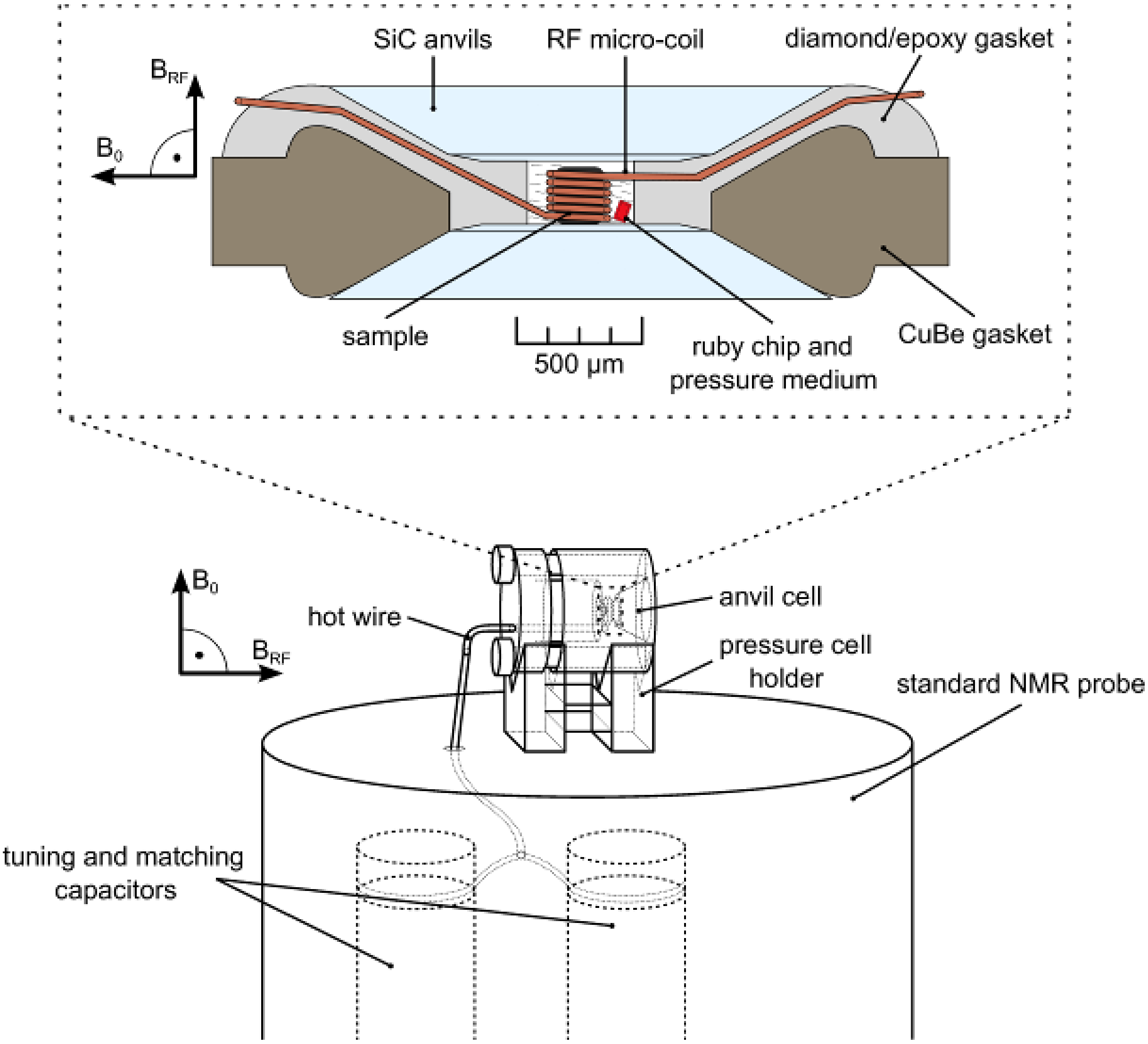
Nuclear Magnetic Resonance as one of the most versatile but also challenging spectroscopic techniques was widely considered impossible to implement in DACs for the last decades, due to severe limitations in sensitivity and signal-to-noise ratios (SNR). Here, I present a novel technique which was introduced in 2009, using a resonating radio-frequency multi-turn micro-coil placed directly into the high-pressure sample chamber of a DAC. It will be shown that the approach allows for a significant increase in sensitivity, as well as high-resolution NMR measurements at unprecedented pressures of up to 30.5 GPa. Finally, with an observed electronic delocalisation in the ternary chalcogenide $AgInTe_2$ I will demonstrate the capabilities of NMR at extreme conditions.

Figure 1



O 3.6

Towards smarter high pressure cells: Integrated pressure calibration for individual heated multianvil experiments

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Despite the impressive developments in the application of large volume presses at synchrotron facilities, catching up with the long-established diamond anvil cell technique (DAC), still the vast majority of multianvil high pressure experiments is and will be performed at in-house facilities without possibility for in-situ characterization using X-ray or neutron beams. For these traditional/conventional experiments the correllation between sample pressure and applied load needs to be determined by 'calibration runs', therafter only allowing for minor deviations from a 'standard assembly' without compromising the established pressure scale. The objective of our development was to find a way of performing heated multianvil experiments with built-in pressure calibration for every single run, independent from synchrotron sources. Based on previous results [1], we managed to accommodate one or more fixed-point calibrants together with a piezoresistive manganine gauge within octahedral pressure cells of various sizes, without interfering with the furnace assembly. The method gives the whole compression curve and the final pressure within the octahedron before heating. It moreover yields important information on the unloading path of the experiment and proved to be a useful tool to speed-up testing of new multianvil assemblies and configurations. Three commonly used octahedron sizes, 10, 14 and 18 mm (edge length) were tested in different configurations. The accuracy of the room-temperature pressure calibration was cross-checked by simultaneous synchroton measurements and showed good agreement. Moreover, we present equation-of-state measurements of the piezoresistive alloys manganin and noventin^{TM} that play an important role in our method up to 17 GPa. The new method might become a useful tool for high pressure science and materials synthesis using large volume presses, equivalent to the long-established ruby pressure scale for DACs.

[1] M.R. Schwarz, J.Phys.: Conf. Series **215**, 012193 (2010).

O 3.8

In-situ measurement of the high temperature distribution inside diamond anvil cell by acousto-optical spectral imaging system

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[2]*Institute of Cristallography of Russian Academy of Sciences, Moscow, Russian Federation*
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The laser-heated diamond-anvil cell (LH-DAC) is the only experimental tool able to create extreme static pressures (P > 100 GPa) and temperatures (T > 3000 K) and therefore it is widely used role in high-pressure research and geophysics. A significant drawback to the laser heating method is the unavoidable, strong temperature gradient. Further progress in the development of the laser heating techniques requires the knowledge of the two dimensional (2-*D*) temperature field in a material induced by laser beam radiation. Recently it was shown that imaging tandem acousto-optical tunable filter (TAOTF) synchronized with a video camera allows in-situ measurement the 2-*D* temperature distribution over the surface of microscopic specimens [1]. The objective of this research is to demonstrate that TAOTF spectroscopic system can be used for the measurement of the real 2-*D* temperature distribution in LH-DAC.

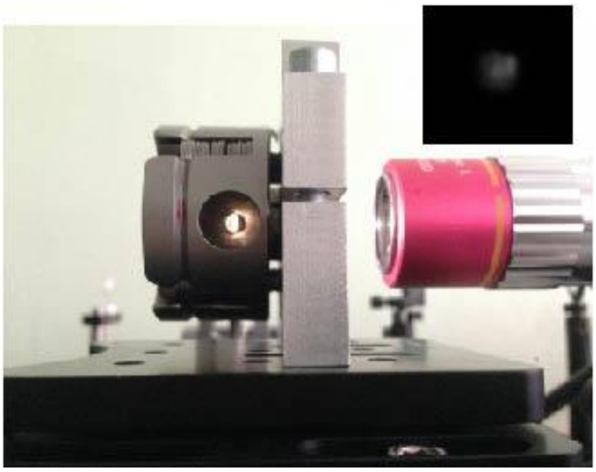
A graphitic C_3N_4 (g-C_3N_4) phase was loaded in a symmetrical DAC where the NaCl was used as a pressure medium. At pressure of 32 GPa the g-C_3N_4 was heated by a laser to a high temperature (Fig. 1). The 2-*D* temperature distribution of the heated g-C_3N_4 was obtained from ten spectroscopic images taken at different wavelengths. The distributions of the temperature $T(x,y)$ were determined then by fitting the actual signal to Planck's equation at each point of the specimen’s surface. In this study, we assume the variation of the specimen’s emissivity to be small over the spectral tuning range and the measured temperature range.

Figure 1. Laser heating of the g-C3N4 specimen. Insert is the spectroscopic image taken at 1020 nm.

References

[1] Machikhin, A.S., P.V. Zinin, A.V. Shurygin, D.D. Khokhlov, *Opt. Lett.*, 2016. **41** 901.

Figure 1



P 3.1

Polymer-precursor-derived SiC/TiC composites for resistive heaters in multianvil high pressure/high-temperature experiments

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The employment of tube-shaped electric resistance heaters in large-volume high pressure sample assemblies is commonplace since many decades. Due to a variety of constraints, the number of appropriate heater materials for these HP/HT techniques is quite limited. Graphite, being easily machinable and cheap, is certainly the most used material but starts to convert to diamond above 10 GPa and 1500°C. Refractory metals such as Re, Mo or V and the like are in use as thin foils, but generate relatively high thermal gradients along the furnace axis, Re is very expensive and other metals are less stable at very high temperatures. Lanthanum chromite can generate temperatures up to 2700°C and is a good thermal insulator, but its electrical characteristics are highly dependent on the level and type of doping and the commercial availability of the respective qualities is not always given. Recently, boron-doped graphite with in-situ conversion to conductive diamond, capable to produce temperatures in excess of 3000°C, has been presented as a new heater material [1,2]. However, the graphite-to-diamond conversion leads to a ten- to hundred-fold increase in resistivity and is therefore not suitable for many power supplies. Also, in general, machining of thin walled tubes from a bulk does generally lead to a large waste of material.

Here we present a new concept [3] based on ceramic precursor technology. A slurry consisting of a commercial SiC-precursor polymer and TiC powder as conductive filler was applied to the inner walls of zirconia insulation tubes, using a centrifugation-casting method. Resistive coatings with homogeneous thickness of 200 µm were obtained. The heaters were tested in octahedral multi-anvil assemblies at ~10 GPa with simultaneous recording of heating voltage and current. Up to a maximum temperature of ~1800°C they showed temperature vs. power characteristics reproducible from batch to batch. Further improvement of coating procedure and materials combination (precursor/filler/insulator substrate) may result in advanced coatings, operational well beyond 2000°C.

[1] A. Shatskiy, Rev. Sci. Instrum., 2009, 80, 023907

[2] A. Yoneda, et al. High Pressure Res. 2014, 34, 392-403

[3] L. Guan, M. Schwarz, R. Zhang, E. Kroke, High Pressure Res. 2016, **DOI:** 10.1080/08957959.2016.1164857.

P 3.3

Generation of pressures over 40 GPa using Kawai-type multi-anvil apparatus with tungsten carbide anvils

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[2]*Japan Synchrotron Radiation Research Institute, Kouto, Japan*
[3]*Okayama University, Misasa, Japan*

We present a technique to generate pressure over 40 GPa at ambient temperature and a temperature of 2000 K using Kawai-type multi-anvil press (KMAP) with tungsten carbide anvils. We established the high-pressure generation technique with KMAP by combining conventional good points for high-pressure generation: (1) high hardness of tungsten carbide, (2) tapering of second-stage anvil faces, (3) materials with high bulk modulus in a high-pressure cell, and (4) high heating efficiency. Pressures of 43 and 44 GPa were obtained at ambient temperature and 2000 K, respectively, by using these techniques. This work provides the relatively simple method than before to generate higher pressure.

P 3.4

A system for low temperature experiments in a 3000-ton multi-anvil press

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Introduction

Most large volume high pressure devices are capable of experiments at elevated temperatures typically by using localized resistive heating of a metal foil or graphite or ceramic sleeve inside a thermally insulated sample volume in a high pressure cell. Temperatures below 295K are more difficult to achieve mainly because the steel components of the press, which are in good thermal contact with each other under high load, act as large heat reservoirs and pathways that oppose the removal of heat from the pressure cell.

Objectives

We describe a new custom-designed system developed for a 3000-ton multi-anvil press to reach temperatures below 295K at high pressures.

Materials & Methods

The system was designed to selectively and conductively remove heat from the sample volume through six of the eight WC cubes in direct contact with the octahedral pressure cell. Cooling fins made of Cu are sandwiched between, and in thermal contact with, neighboring anvil faces and are each connected to a dedicated Cu heat exchanger chamber through which liquid nitrogen flows. The chamber internal geometry consists of square pillars that double the internal surface area of the rectangular parallelepiped enclosed volume. Gas from each chamber is vented to the lab through an exhaust pipe.

Results

Results will be presented of several temperature monitoring points in the center of the pressure cell and on the surfaces of the WC cubes and steel wedges which recorded the time-dependent cooling progress.

Conclusion

The system is essentially functioning but several aspects of the thermal pathways to the sample, including thermal conductivity of materials used at interfaces and flow rates of liquid nitrogen, still need to be addressed.

Invited Talk

The High Energy Density science instrument at European XFEL: a new user facility for high-pressure research

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[1]European XFEL GmbH, Hamburg, Germany
[2]Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany

The European X-ray Free Electron Laser Facility (XFEL) is a 4th generation light source user facility coming online in 2017. The High Energy Density science instrument (HED), one of the six baseline instrument stations, is dedicated for research at extreme conditions. The Helmholtz International Beamline of Extreme Fields (HIBEF) will contribute key-instrumentation to reach extreme conditions. The extreme conditions can either be created within Diamond Anvil Cells or using high-intense, resp. high-energy lasers (either 200 kHz/3 mJ/15 fs, 10 Hz/multi 100 TW/25 fs or 10 Hz/100J/ns) or pulsed magnetic fields (up to 60 T) or the pump-probe highly intense XFEL beam (delays of up to 2 -23 ps for 5 -20 keV using a split-and-delay unit). The short-lived extreme states can be probed with a FEL beam with pulse lengths of 2 -100 fs and 10^{12} photons per pulse. A very high instrument time resolution of 10 fs is planned for HED, which is based on laser-X-ray cross correlation. European XFEL will operate at a burst repetition rate of up to 4.5 MHz, but 10 Hz and shot-on-demand experiments will also be feasible.

Probing at HED can be achieved with X-rays in the energy range of 5 - 25 keV. Different energy bandwidths of the photon beam will be available: seeding is foreseen, as well as natural and wide SASE radiation. In addition, energy bandwidthsof 10^{-4} and 10^{-6} will be made available through monochromators. Focussing at HED is based on CRL optics, which will allow providing beam sizes of 2µm, 10-20µm and 150- 260µm at the sample position. Multiple X-ray techniques are planned, such as X-ray diffraction, X-ray spectroscopy and X-ray imaging.

The short-pulsed nature of the FEL beam opens new applications such as ultra-short laser heating experiments in double stage DACs or dynamic driven DACs as well as time-resolved shock and ramp compression experiments.

HED is in its final design phase and first user experiments are foreseen for early 2018. In this contribution, we will present the current design for high-pressure experiments at HED and discuss the emerging facilities for high-pressure research.

Invited Talk

Spectroscopy of Rubidium under extreme conditions

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Transformations of alkali metals at high pressures is one of the hot topics of modern condensed matter physics. Exotic crystalline structures with very large and complex unit cells, unusual melting lines showing maxima and minima, pressure induced metal to non-metal transitions are some examples of this fascinating scenario emerging recently. I will describe recent spectroscopy studies (Raman and X ray absorption experiments) on solid Rubidium at extreme pressures. Furthermore, preliminary XRD data show a transformation in the liquid state at high pressures and temperatures. Ab initio simulations have also been performed to help the data analysis and to show the evolution of the electronic, structural and dynamic properties in Rubidium extending to conditions still difficult to reach experimentally.

O 4.1

The new high pressure diffraction beamline ID15B of the ESRF

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ID09A was a state of the art high pressure diffraction beamline at the ESRF, carrying out monochromatic diffraction experiments with large area detectors. Powder and single crystal diffraction experiments could be performed at high pressures in diamond anvil cells, permitting accurate determination of crystallographic properties of the investigated samples. After more than 20 years of successful operation, ID09A has been closed in November 2015. It will be replaced by a new and improved beamline, ID15B.

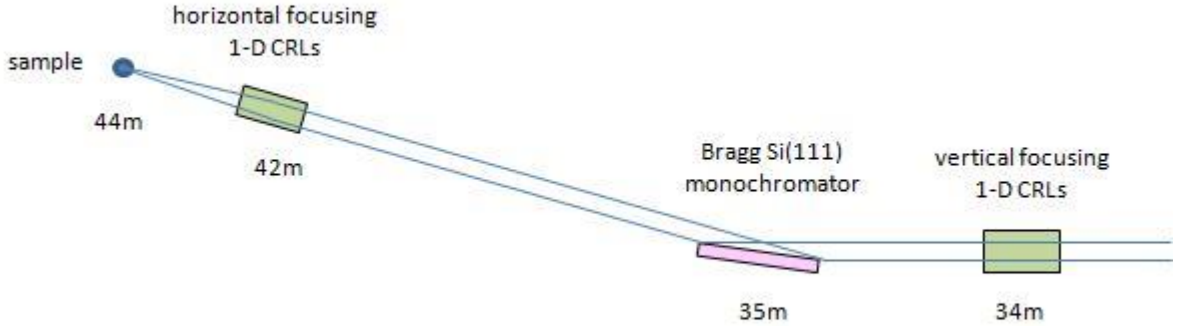
On ID15 two beamlines with a canted straight section are presently under construction. The first one (ID15A) will be for materials chemistry and engineering applications, the second one (ID15B) for monochromatic high pressure diffraction with large area detectors, replacing ID09A. Due to canting the two beamlines can be operated independently.

X-ray source for ID15B will be the U20 in vacuum undulator from ID09A. The monochromator will be a horizontally diffracting nitrogen cooled Si (111) single bounce Bragg monochromator. ID15B will operate at a fixed angle with an energy of 30 keV. Experience with ID09A has shown, that 30 keV is well matched for high pressure diffraction experiments in DACs. Two transfocators with 200 mm diameter linear (1-D) beryllium compound refractive lenses for vertical and horizontal focussing, respectively, will provide a highly variable and very clean beam with an expected minimum spot size on the sample of less than 5 x 5 mm^2. The expected flux will be comparable to ID09A. The experimental setup, build mostly from components already in use on ID09A, will be located on an extremely stable granite table. Data will be collected with the MAR555 flat panel detector. The ID09A sample preparation and Laser laboratory will be relocated to accommodations close to the beamline.

When finished ID15 B will offer similar possibilities for data collection as ID09A, powder and single crystal diffraction with high resolution well into the megabar pressure range with if requested variable temperatures from a few to several hundred Kelvin. Commissioning will start during the summer, first users are expected end of October.

Figure 1: Optical layout of ID15B.

Figure 1



O 4.2

Cutting-edge synchrotron facilities for advanced sample characterization at extreme conditions

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Understanding the complex nature of the deep interiors of the Earth and giant planets requires knowledge of physical and chemical properties of their constituting elements and compounds at relevant extreme P-T conditions. To provide new constrains on models for planetary evolution and origin, essential properties (melting, structure, phase relation, chemical reactions, and kinetics, transport, elastic, electronic properties, etc) of a wide range of minerals must be studied *in-situ* at ultra-extreme conditions of pressure, temperature up to 1TPa and 10,000K. These formidable experiments can only be conducted at dedicated synchrotron beamlines, like GSECARS (Sector 13, Advanced Photon Source), where state-of-the-art high-pressure on- and off-line techniques have been implemented and are currently being developed. Recent progress in continues and pulse laser heating technique, including application of fiber lasers and flat top laser beam shaping optics, result in significant improvement of the quality of x-ray data collected *in-situ* at high pressures and high temperatures in the diamond anvil cell [1]. Combining the double stage anvils technique [2] with pulse laser heating [3] coupled with the gating options of the new, large area CdTe 1M Pilatus detector, we will be able to study materials *in-situ* in the TPa pressure range and temperatures up to 10,000K for both static and dynamic experiments. Such unique capabilities at ultra-high P-T conditions approaching the warm dense state of matter will open an entire new research area creating a bridge between shockwave and DAC experiments that provides fundamental structural, thermodynamic, and transport property information for understanding the composition, origin and evolution of planetary systems.

Details and future developments of cutting-edge techniques at GSECARS for comprehensive characterization of materials *in-situ* at extreme conditions in view of planned APS diffraction limited storage ring upgrade will be discussed.

[1] V. Prakapenka, A. Kubo, A. Kuznetsov at al. High Pressure Research. **28** (3), 225-235 (2008)

[2] L. Dubrovinsky, N. Dubrovinskaia, V. Prakapenka et al. Nature Communications **3**, 1163-1-1163-7 (2012)

[3] A. Goncharov, V. Prakapenka, V. Struzhkin et al. Review of Scientific Instruments, **81** (11), 113902-1-113902-5 (2010)

O 4.3

Status of the dedicated high pressure diffraction beamline “Xpress” at Elettra Sychrotron Trieste

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Recently with the opening of the Xpress beamline [1], the high pressure diffraction user community of the Elettra synchrotron facility have a dedicated experimental set up at their disposal. This new beamline is part of a scientific partnership between India and Italy under a project administered through the IISc Bangalore, for the development of a macromolecular and a high pressure x-ray diffraction facilities, respectively XRD2 [2] and Xpress. A multipole superconducting wiggler (SCW) is the source of these two beamlines. A liquid nitrogen cooled silicon single crystal (cut along the (111) direction) hosted in the splitter chamber in the Front-End section intercepts the beam from the source (SCW) and directs it to the focusing mirror of the Xpress at a fixed energy of 25 keV. At this energy, the SCW provides a factor of 14 higher photon flux compared to the permanent magnet wiggler of XRD1, the existing diffraction beamline. The beam is focused using a toroidal mirror of 1.4 m long and 2.9 mrad grazing angle with a Pt coating to achieve 80% reflectivity at 25 keV. Focused beam from the mirror is further optimized by collimators (presently 80 micron diameter) to have intense and well defined monochromatic beam required for the high pressure x-ray diffraction experiments. On-line pressure monitoring is achieved through a ruby fluorescence microscope connected side-by-side to the final beam collimator stage. The present experimental stage is equipped to host room temperature - high pressure powder diffraction measurements using various kinds of Diamond Anvil Cells (DAC) in the pressure range 0-50 GPa. An image plate MAR345, with a controllable linear movement along the beam direction at two fixed vertical positions is available for recording the diffraction pattern. An upgrade to perform single crystal diffraction will be taken up very soon.

[1] http://www.elettra.eu/elettra-beamlines/xpress.html

[2] http://www.elettra.eu/elettra-beamlines/xrd2.html

O 4.4

Structure of low Z liquids under extreme conditions: from dream to reality

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The discovery of polymorphism in disordered (glassy, amorphous) solids and fluids have largely questioned our understanding of these states of matter. So far, however, the number of systems for which this phenomena has been evidenced by experiments remains limited, and the existence of a first-order transition in a homogenous isotropic melt has been only clearly established in the case of phosphorus [1]. First-order transitions between a molecular and a polymeric liquid have been recently predicted by first-principles calculations in liquid nitrogen at 88 GPa and 2000 K [2] and in liquid CO_2 at 45 GPa and 1850 K [3]. The only device presently capable of reaching these extreme conditions is the diamond anvil cell (DAC). However, the sample in the DAC is sandwiched between two diamond anvils of thickness 100 times larger. Consequently, the diffracted signal from the sample is very weak compared to the Compton signal of the anvils, and hardly measurable for pressures above 20 GPa. We will present here a newly developed experimental setup, installed at ESRF ID27 beamline, which drastically reduces the background signal and enables the measurement of the structure factor of low-Z simple fluids to higher pressures [4]. It is based on the adaptation of a multichannel collimator originally designed for angular-dispersive x-ray diffraction with large-volume presses [5]. Experimental results on fluid hydrogen [6], carbon dioxide [7] and light alkali metals [8] will serve as examples to show the large signal-to-noise improvement achieved with this setup, from which quantitative structure factors could be extracted.

[1] Katayama Y. et al. (2000). *Nature*, 403, 170.

[2] Boates B. & Bonev S. A. (2009). *Phys. Rev. Lett.,* 102, 015701.

[3] Boates B. el al. (2010). *Proc. Natl. Acad. Sci*., 107, 12799.

[4] Weck G. et al., (2013). *Rev. Sci. Ins.*, 84, 063901.

[5] Yaoita K. et al. (1997). *Rev. Sci. Ins*. 68, 2106; Mezouar M. et al. (2002) *Rev. Sci. Ins.*, 73, 3570

[6] Weck G. et al. (2015). *Phys. Rev. B*, 91, 180204.

[7] Datchi F. et al., *submitted*

[8] G. Garbarino et al, *in prep.*

O 4.5

X-ray diffraction experiments on the materials in extreme conditions (MEC) LCLS x-ray FEL beamline to study phase transformation kinetics in NaCl

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The experiments described here were conducted on the Materials in Extreme Conditions (MEC) beamline hutch at the Linac Coherent Light Source (LCLS) located at the Stanford Linear Accelerator Center (SLAC). A 10 ns 527 nm laser pulse with up to 30 J in two beams was used to shock compress 60-100 µm thick NaCl [100] samples. LCLS x-rays (50 fs, 8 keV), scattered off the sample at different times during shock transit and subsequent isentropic pressure release. The diffracted x-ray pattern, as recorded on several CSPAD's (Cornell-SLAC Pixel Array Detectors) positioned downstream, were used to determine changes in crystal structure at Mbar pressures and over nanosecond timescales.

In this talk we detail the experimental setup, the current capabilities of the MEC laser and the considerations for optimizing the target design. We will describe the wave interactions within the shock-compressed target and the use of a 1D hydrocode to describe the pressure and density conditions within the target assembly as a function of time and Lagrangian position. We present observations of strong time-dependence of the NaCl B2->B1 phase transformation under conditions of rapid isentropic pressure release. These data are compared to longer timescale release experiments conducted on the Los Alamos gas gun facility.

O 4.6

Large-volume high pressure research at the advanced photon source

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The large volume press (LVP) is an indispensable technique in high pressure research that complements capabilities of the diamond anvil cell (DAC). While the maximum attainable temperature (T) and pressure (P) conditions are somewhat limited compared to the DAC, LVP offers more uniform and better controlled P-T conditions with much larger sample volumes. This makes LVP an ideal tool for accurate measurements of bulk properties and systematic studies on complex systems. Recent advents in pressure generation, synchrotron radiation technology, and methodologies of multiple probes of in-situ physical property measurements have revolutionized LVP research. This presentation is intended to review the recent scientific achievements in high pressure research using LVP at the Advanced Photon Source (APS). The employment of sintered diamond anvils has dramatically expanded the LVP pressure range (currently about 40 GPa) at high temperatures. New diffraction techniques have made it possible to determine atomic structures of both crystalline and non-crystalline materials under extreme P and T conditions. New imaging techniques have been developed to examine microstructures in 3D under high P and T. Efforts in incorporating other in-situ probing techniques (ultrasonic interferometry, acoustic emission detection, imaging, electrical resistivity sensors, etc.) with synchrotron radiation have made it possible to measure many physical properties (elasticity, brittle failure, melt viscosity, electrical resistivity, etc.) simultaneously with X-ray diffraction an dimaging. Selected scientific achievements will be highlighted along with important technical breakthroughs. Prospects of LVP developments for future multi-bend achromat (MBA) synchrotron storage rings will be discussed.

O 4.7

Millisecond time resolved diffraction study of $SrCO_3$ at high pressures and temperatures

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Strontium carbonate, $SrCO_3$, is isostructural to aragonite. At ambient pressure, $SrCO_3$ transforms at 1185 K to a disordered rhombohedral phase [1, 2] (calcite-V structure). Upon further heating, $SrCO_3$ transforms into a cubic phase [3] (NaCl structure) at 1690 K. At ambient temperature, $SrCO_3$ undergoes a pressure induced phase transition. In earlier studies, transition pressure between 10-35 GPa have been reported [4-6]. In a more recent study [7], the transition pressure was found to be 25 (2) GPa. Rapoport & Pistorius [8] studied the aragonite-type to calcite-V type transition from ambient pressure up to 4 GPa, and found that the transition temperature increases with pressure up to 1500 K at 4 GPa.

In this study a previously unexplored p-T range of the $SrCO_3$ phase diagram was investigated. Synthetic $SrCO_3$ powder sample was synthesized by the hydrothermal method, and single crystals were grown from powder in a multi-anvil press. Diffraction experiments were performed at the Extreme Conditions Beamline P02.2 at PETRA III, Hamburg, in the double-sided laser-heated diamond anvil cell (DAC).

The sample was heated up to the melting point at 8-9 GPa. Heating and cooling processes were observed by time resolved diffraction using the LAMBDA detector [9]. For experiments at static p-T conditions we employed a flat panel PerkinElmer detector.

At high temperature (T ~1600 K) and at 8 GPa, the rhombohedral phase of $SrCO_3$ was observed, along with other new phases. Time resolved data show that the cooling process lasts a few milliseconds only. We have also observed the melting and recrystallisation on a ms time scale. A detailed data analysis will be presented.

The study is supported by projects DFG-ANR WI1232/41-1 and BMBF 05K13RF1.

[1] J. J. Lander, *J. Chem. Phys.,* vol. 17, pp. 892-901, 1949.

[2] K. Strømme, *Acta Chem. Scand. A,* vol. 29, p. 105, 1975.

[3] E. H. Baker, *J. Chem. Soc.,* pp. 2525-2526, 1962.

[4] S. Ono, et al., *Phys. Chem. Miner.,* vol. 32, pp. 8-12, 2005.

[5] M. Wanget al., *Phys. Chem. Minerals,* vol. 42, pp. 517-527, 2015.

[6] C.-C. Lin and C.-g. Liu, *Eur. J. Mineral.*, vol. 9, pp. 785-792, 1997.

[7] N. Biedermann et al., this conference.

[8] E. Rapoport and C. Pistorius, *J. Geophys. Res.,* vol. 72, pp. 6353-6357, 1967.

[9] T. Hatsui and H. Graafsma, *IUCrJ,* vol. 2, pp. 371-383, 2015.

O 4.8

Neutron depolarization imaging on the pressure dependence of the chromium spinel $HgCr_2Se_4$

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The isostructural family of the Chromium spinels (ACr_2X_4) show diverse magnetic ground states due to an interesting variety of competing magnetic interactions between the chromium ions [1,2,3]. We report the magnetization of ferromagnetic mercury chromium spinel $HgCr_2Se_4$ up to 1.7 GPa. To extend these data we used high pressure neutron depolarization measurements inside a miniturized moissanite anvil cell (Fig. 1), allowing us to quantify the evolution of ferromagnetic domains up to 4 GPa and down to very low temperatures. Surprisingly, the critical temperature displays a complex phase diagram, pointing to a loss of ferromagnetism above 2.7 GPa (Fig. 2). Our results demonstrate, on a proof of principle level, the feasibility of combining miniaturized moissanite anvil cells, with neutron depolarization imaging. This paves the way for studies of ferromagnetic and superconducting phases up to very high pressures in a rather simple manner.

[1] P. K. Baltzer, Phys. Rev. **151**, 367-77 (1966)

[2] A. N. Yaresko, Phys. Rev. B, **77**, 115106 (2008)

[3] T. Rudolf, New J. Phys. **9**, 76 (2007)

Figure 1: The left panel shows the pressure cell (1) attached to the sample stick of the cryostat (2). We use a cadmium foil (3) with 0.8 mm pinhole to shield the pressure cell from the neutrons. The right panel shows a neutron radiography of the cell taken in the axial direction, where the region of interest (ROI) selects the neutrons that go through the optical aperture of the cell.

Figure 2: Pressure dependent magnetic phase diagram of the chromium spinel $HgCr_2Se_4$.

Figure 1

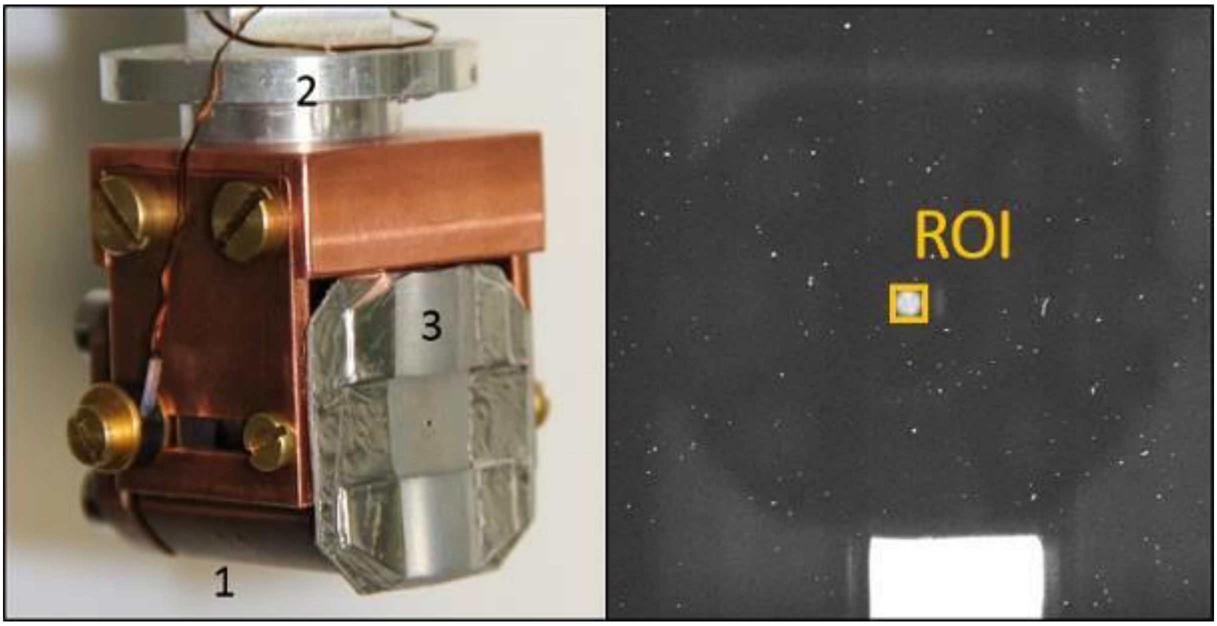
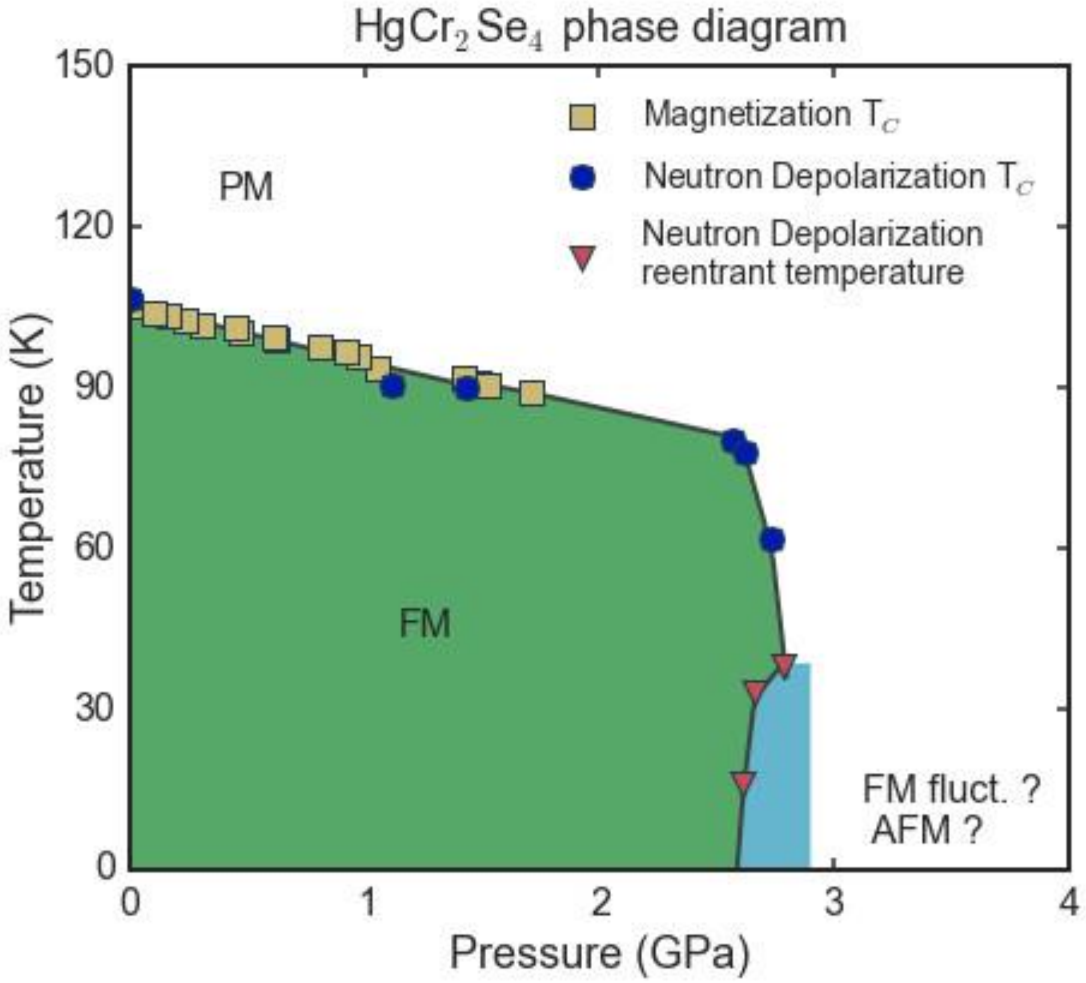


Figure 2



$HgCr_2Se_4$ phase diagram
Magnetization T_C
Neutron Depolarization T_C
Neutron Depolarization reentrant temperature
PM
FM
FM fluct. ?
AFM ?
Temperature (K)
Pressure (GPa)
0
30
60
90
120
150
0
1
2
3
4

P 4.1

A fast LAMBDA detector and pink beam at the extreme conditions beamline P02.2 at PETRA III

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The Extreme Conditions Beamline (ECB) P02.2 at PETRA III [1] is a beamline for micro X-ray diffraction studies of matter at simultaneous high pressure and high/low temperature in the diamond anvil cell. One fast LAMBDA detector (Large Area Medipix-Based Detector Array, *X-Spectrum GmbH*) will be operated at the ECB during the first half of 2016 at the ECB in various users' projects requiring an acquisition rate of up to 2 kHz. Pink beam at the ECB will offer the full central undulator cone transported by mirrors and focused by Kirkpatrick-Baez mirrors. A second pink beam option will use off-axis beam from the undulator which is red-shifted and with a broader energy band compared to on-axis beam.

Within this presentation we will describe the capabilities of the Extreme Conditions Beamline to conduct time-resolved X-ray diffraction experiments with pink beam and the LAMBDA detector.

An example of time resolved laser heating experiments using the LAMBDA detector are shown in the contribution of Stekiel et al. which is presented elsewhere at this conference.

The authors gratefully acknowledge financial support from the BMBF (project 05K13RF1).

[1] H.-P. Liermann et al., "The Extreme Conditions Beamline P02.2 and The Extreme Conditions Science Infrastructure at PETRA III", JSR 22, 908-924, (2015)

P 4.2

Development of multi-axis DAC oscillation system for powder XRD experiments

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Introduction

Recent advanced experimental techniques for a diamond anvil cell (DAC) provide wide pressure and temperature range for surveying physical properties of materials. Particularly, low emittance and high brilliance x-ray from a synchrotron radiation source contributes high pressure x-ray diffraction (XRD) experiments within a small part of the sample in the DAC. However, there is a significant statistical problem in collecting the powder XRD image described below.

Objectives

The spotty patterns diffracted by coarse grains, which are likely formed during laser heating experiments, influence on the quality of the x-ray diffraction image. Then, Debye rings including such spotty diffractions yield an unreliable peak profile, which is highly deviated from an ideal powder diffraction pattern. As a result, we hardly reach a correct structure in Rietveld analysis. To improve this kind of statistical problem in the diffraction image, we constructed a multi-axis DAC oscillation system for XRD experiments.

Methods

The goniometer of this oscillation system has three oscillation axes, which are horizontal (θ), vertical swivel (ω), and rotating axes (φ) perpendicular to θ. The DAC with a large angular aperture (90°), which is also newly developed for the oscillation system, is inserted into the holder on φ axis. The diffracted x-rays are detected with an imaging plate. This system has been installed in a SR x-ray beam line (BL04B2) at SPring-8 (JASRI).

Results

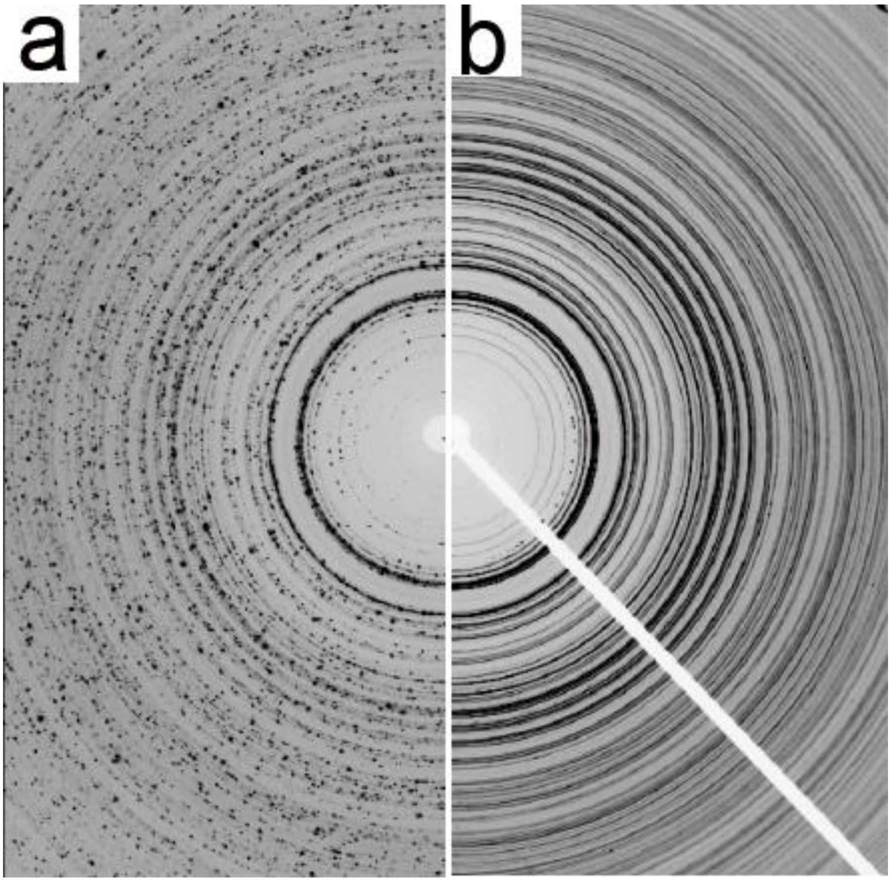
We tested the oscillation system for coarse grained (c.a. ~ 5 microns) bismuth oxide with a monochromatic x-ray collimated to 50 microns in size. The multi axis oscillation (θ ~±5°, and ω~±5° with φ turning 360°) drastically improved the statistics of the diffraction image. Statistical simulation based on the motion of the oscillation axes exhibits more than 100 times improvement in the diffraction image.

Conclusion

The multi axis DAC oscillation system is an effective method for improving XRD patterns under high pressure. This technique would be particularly useful for high pressure XRD experiments using an ultra-low emittance x-ray at a next generation SR facility.

Figure 1. Comparison between (a) non-oscillation and (b) oscillation images.

Figure 1



P 4.3

Laser-heating capabilities on I15 at diamond light source

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A double sided laser heating system combining diamond anvil cells and synchrotron X-ray Diffraction (XRD) has been recently built on the I15 beamline at Diamond. The system has been implemented on the beamline's micro-focus station, where X-rays beam sizes of about 9 µm x 6 µm can be achieved for energies between 20-40 keV.

Two 100 W YAG lasers (l= 1093 nm) are focused onto both sides of the sample with an on-axis configuration through a pair of apochromatic lenses. In order to align the X-rays with the laser hot spots and the temperature reading, a mirror with two vertically separated pinholes is placed at the entrance of the spectrometer. The thermal radiation emitted from the sample surfaces is optically collected through a long path refractive-optic system and imaged on the pinholes at the entrance of a spectrometer for temperature measurement. The optical components are mounted and pre-aligned on an optical breadboard attached to the micro-focus station. Motors attached to the breadboard provide horizontal and vertical translations of the pre-aligned optical system. Thus, it can be easily moved to the X-ray focal spot without any further alignment. A flat panel detector for recording the 2D-XRD pattern can be positioned at variable distances from the sample. Further details of the online laser-heating system on the extreme condition beamline at Diamond Light Source will be reported.

P 4.4

Fast compression using dynamic DAC and LAMBDA detector at ECB, PETRAIII, DESY

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Time resolved diffraction at simultaneous fast compression/heating is now an emerging field that will enable us studying matter in intermediate state between static and dynamic high-pressure physics. The technique utilizing the dynamic Diamond Anvil Cell (dDAC, Evans et al., 2007) is used to determine Equation of State (EOS) and/or investigate phase stability and phase kinetics at very high pressures, temperatures *and* high strain rates which is not achievable with conventional static high-pressure techniques. While dynamic compression diffraction experiments are possible at 3rd generation sources in the kHz (ms) regime, it will require new 4th generation sources, such as the European XFEL, to be able to conduct time resolved experiments in the MHz (ns) regime.

We have explored the effects of changing compression rates on the location and kinetics of solid-solid as well as solid-liquid phase transitions using the dDAC and X-ray diffraction probe (Chen et al., 2014). Limitation in achievable compression rates is imposed by the x-ray flux and speed/efficiency of the x-ray detector. Within, we present a new experimental setup at the Extreme Conditions Beamline, P02.2, PETRAIII in Hamburg featuring a new design of the dDAC achieving pressure jumps of above a TPa/s and a new GaAs LAMBDA detector capable of 2 kHz frame rate. An experiment on a bismuth example will be presented.

References

[1] Evans, W. J., Yoo, C.-S., Lee, G. W., Cynn, H., Lipp, M. J., & Visbeck, K. (2007). Dynamic diamond anvil cell (dDAC): a novel device for studying the dynamic-pressure properties of materials. The Review of Scientific Instruments, 78(7), 073904. http://doi.org/10.1063/1.2751409

[2] Chen, J.-Y., Yoo, C.-S., Evans, W. J., Liermann, H.-P., Cynn, H., Kim, M., & Jenei, Z. (2014). Solidification and fcc to metastable hcp phase transition in krypton under variable compression rates. Physical Review B, 90(14), 144104. http://doi.org/10.1103/PhysRevB.90.144104

P 4.5

Development of the falling-sphere technique for measuring the viscosity of liquid under high pressure

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The falling-sphere method is the only way to measure the viscosity of liquid under high pressure[1]. Combining synchrotron X-rays with the multi-anvil press, the X-ray radiography falling-sphere method enables the determination of the viscosity of a liquid sample at high pressure based on Stokes' flow law. X-ray radiographic images are captured using a high-speed CCD camera, with sufficient contrast between a metal marker sphere and the liquid sample to determine the terminal sinking velocity. However, in the viscosity measurement of liquid metal alloy, a chemical reaction between the metal marker sphere and the liquid sample is a serious problem. Rutter et al. (2002)[2] used a composite sphere consisting of Pt core in a ruby mantle and successfully measured the viscosity of pure liquid Fe up to 5.5 GPa. However, because the size of the composite sphere is quite large (500 µm in a diameter), it is difficult to use this for the viscosity measurement at higher pressure than 6 GPa. In this study, we developed a newly alumina coated metal sphere (Pt and W), whose diameter is 100 µm with a very thin alumina layer (2 µm in a thickness). Use of the alumina coated metal sphere can prevent such a chemical reaction, and the viscosity of liquid metal alloy can be successfully obtained at higher pressures. Also, we have developed a diamond/SiC composite anvil which has superior hardness compare to a conventional tungsten carbide (WC) anvil and has good X-ray transparency[3]. Combining the diamond/SiC composite anvil with the X-ray radiography falling-sphere method, the metal marker sphere can be observed through the diamond/SiC composite anvil. Therefore, the measurable pressure range can be expanded, when observable visible range becomes very limited by narrowing the anvil gap of the multi-anvil press. Here we present theX-ray radiography falling-sphere technique and the results of the viscosities, such as Fe-S alloy and sulfur, at pressures up to 14 GPa.

References

[1] I. Kushiro, *Earth Planet. Sci. Lett*., 41, 87 (1978).

[2] M. Shimono and S. Kume, *J. Am. Ceram. Soc.*, 87, 752 (2004).

[3] M.D. Rutter et al., *Phys. Rev.* B 66, 060102(R) (2002).

P 4.6

A new large volume press with six hydraulic rams installed at P61.2 in PETRAIII extension project

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A new large volume press with six hydraulic rams (6-rams LVP) has been installed at P61.2 in PETRAIII extension project. This is the first 6-rams LVP installed in a synchrotron facility. Each hydraulic ram has 500-tonf capacity with oil pressure of 600 bar. Displacements of all the pistons and oil pressures of all the hydraulic rams can be monitored. The edge length of the first stage anvil is 60 mm. All the six rams can be operated independently, which enables us to perform uniform compression and deformation experiments under high pressure and temperature.

Cupper block compression tests were performed between 50 and 600 bar at every 50 bar. Deformation of the cubic space compressed by the first stage anvils is evaluated by measuring face-to-face distances (one vertical and two horizontals) of the recovered cupper blocks. Deviation from the cubic geometry is less than ten micrometers at every oil pressure. This result indicates that the anvil assembly that consists of sintered diamond anvils can be compressed using this instrument.

We have started commissioning of this instrument since December, 2015. Two types of anvil-assembly are compressed using the first stage anvils with edge length of 60 mm: (1), 6-8 anvil assembly with tungsten carbide (WC) anvils with edge length of 32 mm; (2) 6-6 anvil assembly with WC anvils with truncated edge length of 15 mm (20 mm cube for pressure medium). For the 6-8 setup, pressure and temperature generation up to 22 GPa and 1700°C was confirmed using the 10/4 assembly. MgSiO3 akimotoite and bridgmanite polycrystals were successfully synthesized. For the 6-6 setup, pressure up to 7 GPa was generated at room temperature and SiO_2 coesite was synthsied at 5.5 GPa and 1500°C with the sample diameter of 6 mm.

P 4.7

Multi-Staging in LVPs

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For measurements under experimentally simulated Earth's mantle conditions LVPs and DACs are the suitable tools. DACs can reach Earth's core pressures and more. Classical LVPs are limited to a depth equivalent of about 1000 km, but the sample volume is 10^3 to 10^7 bigger and could be even further increased in principle. Latest since ultradeep subduction was verified by global seismic tomography we have to realize the existence of deep mantle complex rocks. In principle the physical properties of a complex system cannot be determined if the volume under investigation is much smaller than the smallest component of the system. We also have to take into account that the properties of a complex system do not correspond the sum of the properties of its constituents. First Utsumi *et al.*, 1986 published a technique to reach 60 GPa pressure by using sintered diamond anvils as second stage in a single-stage DIA-type multi-anvil apparatus. Li, 2001 published a peak pressure of more than 26 GPa for a single-stage DIA even though the diamond anvils had been broken. Irifune et al., 2011 published a multiple diamond apparatus (MCA) apparatus using nano-polycrystalline diamond (NPD). This way Mbar pressures could be reached. The paper describes several approaches towards a multi-staging multi anvil apparatus including the measurement of physical properties under this conditions.

P 4.8

Advanced high-resolution integrated optical system

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Raman and optical spectroscopy *in-situ* at extreme high pressure and temperature conditions relevant to the planets' deep interior is as a versatile tool for characterization of wide range of properties of minerals essential for understanding the structure, composition, and evolution of terrestrial and giant planets. Optical methods, greatly complementing X-ray diffraction and spectroscopy techniques, become crucial when dealing with light elements. Study of vibrational and optical properties of minerals and volatiles, which are relevant for the Earth's and planetary interiors, was a topic of many research efforts in past decades. A great deal of information on the materials properties under extreme pressure and temperature has been acquired including that related to structural phase changes, electronic transitions, and chemical transformations. These provide an important insight into physical and chemical states of planetary interiors (e.g. nature of deep reservoirs) and their dynamics including heat and mass transport (e.g. deep carbon cycle). Optical and vibrational spectroscopy can be also very instrumental for elucidating the nature of the materials molten states such as those related to the Earth's volatiles (CO_2, CH_4, H_2O), aqueous fluids and silicate melts, planetary ices (H_2O, CH_4, NH_3), noble gases, and H2. The optical spectroscopy study performed concomitantly with X-ray diffraction and spectroscopy measurements at the GSECARS beamlines (sector 13, APS) on the same sample and at the same P-T conditions would greatly enhance the quality of this research and, moreover, will provide unique new information on chemical state of matter.

The advanced high-resolution user-friendly integrated optical system is currently under construction and expected to be completed by 2016. In our conceptual design we have implemented Raman spectroscopy with five excitation wavelengths (266, 473, 532, 660, 946 nm), confocal imaging, double sided IR laser heating combined with high temperature Raman (including coherent anti-Stokes Raman scattering) and transient (based on a bright supercontinuum light source) spectroscopies in a wide spectral range (200-1600 nm).

Details and future combination of this innovative system with high-resolution synchrotron micro-diffraction at GSECARS for full characterization of materials *in-situ* at extreme conditions will be discussed.

Invited Talk

High pressure neutron scattering at Oak Ridge National Laboratory

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Over the past few years neutron scattering from samples held under high pressure has made significant advances, including the adaptation of diamond anvil cell techniques to neutron powder diffraction. Due to the compact size of the devices the implementation of diamond cell techniques opens a wide range of science to the benefits of neutron scattering. Gas loading, facilitated using well understood techniques, provides access to 'normally' gaseous samples such as hydrogen and a hydrostatic pressure environment, heating, both resistively and with lasers, is now a possibility, and diamonds provide optical access to the sample allowing ruby pressure markers and simultaneous Raman Spectroscopy. This is made possible by the new generation of very high flux neutron sources that have recently been constructed, or are being constructed, in the US, Japan and Europe. At Oak Ridge National Laboratory at the SNAP beamline we have a wide range of pressure devices ranging from low pressure precise gas cells, to toroidal anvil Paris-Edinburgh presses, and, by now, several generations of large volume neutron diamond anvil cells. We have conducted experiments in the megabar range at room temperature, up to 40 GPa at low temperature (13 K), up to 35 GPa with resistive heating up to 600 K. Here I will give an overview of how neutron scattering complements x-ray scattering, the neutron high pressure techniques we have developed, and provide scientific examples using each of our pressure devices. Finally, I will give a hint of future directions taking shape in Oak Ridge over the next five years and how we are moving toward a bigger high pressure effort across the facility.

O 5.1

High pressure science at the european spallation source

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The European Spallation Source (ESS), currently under construction in Lund, Sweden, will be the most powerful neutron source ever built. Dramatic improvements in flux, coupled with new guide and detector technologies offer the possibility of a complete revision of what is possible in high-pressure neutron science. To take maximum advantage of these new capabilities, the ESS is taking a holistic approach with the goal of enabling high pressure on as many instruments as possible. This will include traditional techniques such as diffraction and spectroscopy, which will be made available under new regimes of pressure (exceeding 50 GPa for the latter and 10 GPa for the former). In addition, capabilities that have not yet been exploited for extreme-conditions research - such as small-angle scattering and imaging - may also be possible. Here, an overall view of the strategy for pressure at the ESS will be presented.

Complementing the broad, platform-based, approach to high pressure is a proposal for a dedicated DAC-based diffraction beamline, targeting neutron science in excess of 120 GPa. Provisionally called ESPRESSO (the Extreme Sample PRESsure Spallation Observatory), this instrument is competing for one of the final 6 beam ports available at the ESS from ~ 2020. The proposal is underpinned by a worldwide effort to develop DACs for neutrons. Early successes at the SNS have shown the feasibility of neutron diffraction in the megabar regime and this work continues. Now, a new initiative is underway to enable DACs on PEARL, the UK-based neutron diffractometer. Lastly, we are investigating the possibility of a preliminary DAC station on DREAM, which is likely to be one of the first diffractometers that will be constructed at the ESS.

O 5.2

High-pressure neutron diffraction under extreme conditions at the IBR-2 reactor: recent developments

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The dramatic progress in extreme condition research is caused by a discovery of great number of novel interesting phenomena in condensed matter physics and material science, chemistry, geophysics and planetary research. In comparison to other experimental methods, the application of high pressure is a direct method of controlled variation of physical properties by modification of interatomic interactions by tuning of bond distances and angles. However, the evolution of high-pressure neutron diffraction methods is seriously restricted by drastically low intensity of neutron sources (in many orders of magnitude) in comparison with synchrotron radiation ones. Nevertheless, the neutron diffraction has many advantages for studies of the crystal structure of materials containing light atoms like hydrogen and oxygen and, especially, for studies of the magnetic structure of materials.

A new DN-6 diffractometer at the IBR-2 high flux reactor with a long pulse was specially constructed for studies of atomic and magnetic structure of materials under extreme conditions using diamond anvil cells (DAC). High neutron flux on the sample and the wide solid angle of the detector system allow studies of the samples with a volume of about 0.01-0.02 mm^3 and even less. The use of closed-cycle refrigerator allows to conduct the experiments with DAC in a wide range of temperatures 4-300 K. Some examples of recent studies at pressures up to 35 GPa are presented. The prospects for further development of high pressure neutron diffraction at the IBR-2 reactor are discussed.

O 5.3

High-pressure neutron beamline PLANET at pulsed neutron source at J-PARC

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PLANET [1] is a high-pressure neutron beamline recently constructed at Materials and Life Science Facility (MLF) in J-PARC. Most characteristic feature of the beamline is to possess the large six-axis multi-anvil high-pressure ATSUHIME press [2], which enables *in-situ* neutron diffraction under high pressure and high temperature condition up to 10 GPa and 2000 K. Smaller presses, a Paris-Edinburgh press [3] and Mito cell [4], are also available at PLANET and the accessible PT conditions with each device are 20 GPa at room temperature and 5 GPa at 77 K, respectively. The beamline is equipped with incident slits and receiving collimators that eliminates parasitic scattering from the high-pressure cell assembly to obtain clean data. The high performance of the diffractometer (the resolution: Δd/d ~ 0.6%, the accessible d-spacing range: 0.2-8.4 Å) and low-parasitic scattering characteristics enables precise structure determination of crystals and *liquids* under high pressure and temperature conditions [1]. The beamline had been constructed until 2013 and is opened for general users. In this presentation, the specification of the PLANET and recent results obtained at PLANET are introduced.

References

[1] T. Hattori *et al*., Nucl. Instrum. Methods Phys. Res. A **780**, 55 (2015).

[2] A. Sano-Furukawa *et al*., Rev. Sci. Instrum. **85**, 113905 (2014).

[3] J. M. Besson *et al.*, Phyica B **180-181**, 907 (1992).

[4] K. Komatsu *et. al.*, High Press. Research **33**, 208 (2013).

Figure 1

O 5.4

The new extreme conditions neutron diffractometer at ILL: XtremeD

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The behaviour of condensed matter under extreme conditions is of the highest importance to large areas of knowledge and has become one of the priority research lines worldwide. Neutron diffraction can have a significant contribution in this field, mainly in two large areas: crystallography/geosciences and magnetism/solid-state physics. Attending to the interests of the user community and the capabilities of neutron diffraction in a reactor source, the XtremeD project has been conceived. XtremeD will be a new extreme-conditions neutron diffractometer for both powders and single crystals. It concentrates on two of the possible extreme parameters: high pressures and magnetic fields. With a particular accent on the performance for large d spacing problems, it will match the current growing interest for the study of matter under extreme conditions, particularly in the fields where the capabilities of neutron diffraction are unique. The project is entering the execution phase and it is expected that the instrument will be operational by 2019.

The main characteristics of the proposed instrument are:

- Energy and Q-range: wavelength: 1 - 3.5Å (optimized at around 2Å); Q: 0.15 - 11 $Å^{-1}$

- Extreme conditions: Intense continuous magnetic fields and very high pressures (and combinations of both)

- Experimental fields: The instrument will be suited both for powder and single crystal samples, with a 2D detector with good resolution in both directions (horizontal and vertical).

- Beam requirements: The use of pressure cells implies that the instrument will have to operate with very small sample sizes such as 1 mm^3, with a very intense and well collimated beam at the sample in order keep the background low. (flux ca. $5x10^7$ $n \cdot cm^{-2} \cdot s^{-1}$ at 2.5 Å in a sample area of 1 x 1 mm^2).

O 5.5

High pressure neutron diffraction to beyond 20 GPa and below 1.8 K using Paris-Edinburgh load frames

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A large part of neutron diffraction deals with physical phenomena which appear only at very low temperatures close to 0 K, such as many magnetic ordering and quantum critical phenomena. There is a growing interest to investigate these phenomena with high pressure since the interatomic distances, and thus the interaction parameters controlling these phenomena, can be tuned in a continuous and controlled fashion. The simultaneous generation of high pressure and very low temperatures is a well-known problem in neutron scattering [1], in particular for pressures in the multi-GPa range where the pressure cells are rather massive and therefore need a more complex cryogenic solution. Here we describe a method for collecting neutron diffraction patterns simultaneously at high pressure (> 22 GPa) and low temperature (< 1.8 K) [2]. The system uses ~ 5-10 mm^3 samples compressed by double-toroidal sintered diamond anvils, with the required forces generated by a Paris-Edinburgh press of 30 kg mass. The pressure cell is cooled by a two-stage closed-cycle refrigerator (CCR) with a base temperature of 3.6 K, and further cooling is achieved by pumping on a liquid helium bath in contact with the cell. Technical details are given and diffraction data of epsilon-iron at 22.6 GPa and 1.79 K are presented.

[1] S. Klotz, *Techniques in High Pressure Neutron Scattering*, CRC-Press, 2013.

[2] S. Klotz, Th. Strässle, B. Lebert, M. d'Astuto, Th. Hansen, High Pressure Res. 36, 73 (2016)

O 5.6

Neutron inelastic scattering with large volume diamond cells

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We show first results of inelastic neutron scattering at high pressure in a diamond cell. The measurements were performed at the Oak Ridge National Laboratory at the VISION beamline. A hydrogen-rich material (hexamethylbenzene) with a volume of 1.5 mm^3 produced excellent spectra with relatively short exposures (1 hr). We used both large single crystal CVD diamonds with 10 mm diameter and height (about 10 ct) and polycrystalline diamond (PCD) anvils. The diamond cell is of novel design: very compact, spring loaded (max. > 10 tons), allowing a very large area detector coverage (120 degrees double sided). This cell has also been tested for large angle neutron diffraction.

O 5.7

Neutron total scattering of crystalline materials in the gigapascal regime

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Neutron total scattering of disordered crystalline materials provides direct experimental access to the local (short-range) structure, the ways in which it agrees (or disagrees) with the average (long-range) crystal structure, and the important structure-property relationships encoded within. High-pressure neutron diffraction using the Paris-Edinburgh (P-E) pressure cell allows experimenters to explore the ways in which materials are affected by extreme pressures, can reveal new synthetic routes to novel functional materials and has important applications in many areas, including geology, engineering and planetary science.

The combination of these two experimental techniques poses unique challenges for both data collection and analysis. In this paper it is shown that high-quality total scattering data can be obtained from crystalline materials in the gigapascal pressure regime on the PEARL diffractometer at ISIS through the use of minor modifications to the standard P-E press setup and a simple data-processing pathway. The quality of the data is assessed through the calculation of coordination numbers and the use of reverse Monte Carlo (RMC) refinements. The time required to collect data of sufficient quality for detailed analysis is assessed and is found to be of the order of 8 hours.

Finally, data from the perovskite $LaCo_{0.35}Mn_{0.65}O_3$ is presented and reveals that PEARL total scattering data offers the potential for the extraction of local structural information from complex materials at high pressure.

O 5.8

Diamond-silicon carbide and polycrystalline cubic boron nitride (PcBN) anvils for high pressure neutron diffraction

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Introduction

Diamond-silicon carbide and PcBN materials have a combination of exceptional strength, superior hardness, and high modulus, they may improve pressure transmitting efficiency and extend the pressure limit of neutron diffraction.

Objectives

Find new functional materials replacing current tungsten carbide and Moissanite anvils of high pressure neutron instruments.

Materials & Methods

Synthesis diamond-silicon carbide and PcBN anvil materials under 6 GPa/1400 Celsius in a large volume cubic pressure, and test them on high pressure neutron diffraction instruments.

Results

We have experiments scheduled in new few months, and hoping we can present the results in the conference.

Conclusion

We are hoping diamond-SiC and PcBN anvils may extend the pressure limit of current neutron diffraction facilities.

O 5.9

Investigation of the magnetism of UGe_2 under high pressure with XMCD

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The discovery that ferromagnetism and superconductivity could coexist sparked a wave of scientific interest at the beginning of the millennium [1], yet there are still few materials that display this unique behaviour. The most commonly studied, is the compound UGe2, which has pressure-temperature and magnetic field-temperature phase diagrams, rich with unusual physical phenomena [2].

At ambient pressure, UGe2 is a ferromagnet with a Curie temperature of ~53 K. Below 12kbar (at 2.3K), it is in a so-called ferromagnetic phase 2 (FM2). A very interesting feature of this material is that a second ferromagnetic phase transition FM1 appears as a jump in the magnetization above ~12kbar. This magnetic moment versus pressure change has been interpreted by Sandeman, Lonzarich, and Schofield [3] as a first-order Stonerlike phase transition in spin-only magnetization due to a sharp double-peak density of states (DOS) very near the Fermi level. Above this ~12kbar pressure, the transition FM1→FM2 can be induced by a magnetic field.

We have carried out X-ray magnetic circular dichroism (XMCD) measurements under high pressure on UGe_2 single crystal at the ESRF beamline ID12. It is well established that XMCD at the U M4,5-edges provides accurate quantitatively measurements of the U 5*f* orbital magnetic moment providing the number of 5*f* holes is known. To perform this challenging experiment, we have used a specific diamond anvil cell which combines a fully perforated anvil and a 30µm thin plate of diamond through which the total fluorescence yield signal from the sample is collected. The incident X-ray beam was focused on the sample using parabolic Be refractive lenses with typical beam size of few microns vertically and few tens of microns horizontally. We have measured the XMCD spectra at the U M4,5-edges in both FM1 and FM2 phase of UGe_2 by tuning the pressure at around ~14kbar at 2.7K. By just varying the magnetic field, we were able record good quality XMCD at the U M4,5-edges in the FM1 phase (1T) and in the FM2 phase (4T). We found that the orbital-to-spin ratio of the U 5*f* magnetic moments is different for both FM1 and FM2 phases.

References

[1] S. S. Saxena *et al.* Nature **406**, 587 (2000)

[2] C. Pfleiderer and A. D. Huxley, Phys. Rev. Lett. **89**, 147005 (2002)

[3] K. Sandeman et al., Phys. Rev. Lett. **90**, 167005 (2003).

O 5.10

3D laser sintered collimation for neutron diffraction from micro powder samples

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Collimation is essential to reduce levels of parasitic scattering from neutron instruments and large pieces of sample environment (such as aluminium shielding on cryostats). The increasing demand for variety of sample environment at neutron facilities means that the sample space be kept relatively large to incorporate a range of auxiliary equipment (magnets, fridges, furnaces), which places a limit on the efficiency of the collimator. For cylinder pressure cells a typical ratio of cell to sample diameter is 4:1 depending on the design, so the volume of cell material visible to the instrument compared with sample volume is significant. This is worse for opposed anvil measurements using gasketing, where the ratio is closer to 10:1.

Here we present a novel technique to incorporate significantly improved collimation into the sample environment, through 3D laser sintering custom made collimators. 3D laser sintering allows for the extremely precise construction of otherwise unmachineable geometries. This has particular applicability for high pressure instrumentation, where levels of background are significantly higher. The customisability of the design technique means that numerous collimators can be printed relatively cheaply, and quickly, improving the quality of a wide range of different measurements for a particular neutron instrument, for a number of different pressure cells. Details of simulations characterising the effect of near sample collimation, current printed designs, and neutron test comparisons will be presented, alongside future development projects. Recent results collected from sample volumes of 0.01 mm^3 within an opposed anvil pressure cell will also be presented. Figure 1, collimation for piston cylinder cells. Figure 2, collimation for opposed anvil cell [1].

[1] Jacobsen et el. Rev Sci Instrum 85 043904 (2014)

Figure 1

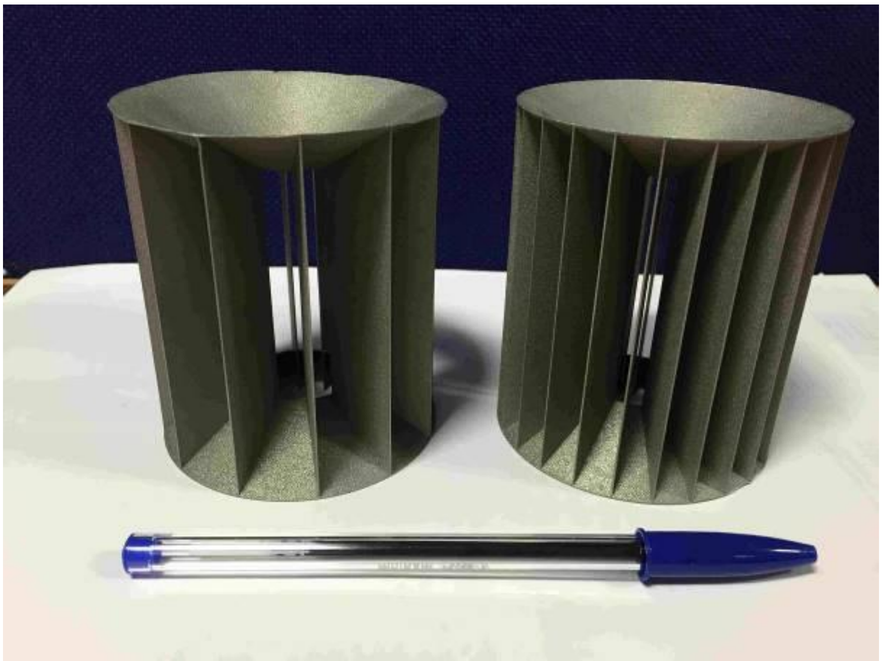

Figure 2

P 5.1

Octahedral tilting and structural changes in the perovskite LaCo0:9Mn0:1O3 at high pressure

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Perovskites are a class of materials which have attracted a considerable attention for the huge variety of structural and physical properties1-3.

Among the broad selection of available elements which can be accommodated in the perovskite structure, the $LaCo_xMn_{1-x}O_3$ cobaltite-manganite exhibits remarkable changes in its electrical and magnetic properties in response to a variation of the composition x or volume of the material.

Significant volume changes can be induced by the application of high pressure. In particular, interatomic distances are extremely sensitive to the applied pressure, which can be used to explore structure-property relationships in this material. In this frame, high-pressure neutron diffraction is essential as it is strongly sensitive to O positions that would be masked in x-ray diffraction by the much stronger scattering of signal of Mn, La and Co. Besides, unlike x-rays, neutrons can distinguish between the Co and Mn which differ by only two electrons.

In this study, we report the structural properties of the high cobalt content $LaCo_{0.9}Mn_{0.1}O_3$ perovskites investigated by high-pressure powder neutron diffraction.

We show and found that the rhombohedral structure R3c is confirmed[4] at pressures up to 3GPa and report its equation of state. We have also determined the evolution of the octahedral tilt (from the idealised cubic symmetry) and octahedral strain as a function of the applied pressure.

[1] Mitchell R H, 2002, Perovskites: Modern and Ancient, Ontario: Almaz Press;

[2] Borowski M, 2010, Perovskites: Structures, Properties and Uses, New York: Nova Science;

[3] Muller K A and Kool T W, 2010, Properties of Perovskites and Other Oxides, Singapore: World Scientific;

[4] Autret C, Hejtmanek J, Knizek K, Marysko M, Jirak Z, Dlouha M and Vratislav S, 2005, Electric transport and magnetic properties of perovskites $LaCo_xMn_{1-x}O_3$ up to 900k, J. Phys.: Condens. Matter 17 1601

Invited Talk

High critical temperature in conventional superconductors

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Superconductivity with Tc>200 K has been found in hydrogen sulfide at high pressures (Drozdov, Eremets et al. 2015) The superconductivity has been proved by observation of zero resistance, Meissner effect, and isotope effect. X-ray diffraction studies (Einaga, Sakata et al. 2016) confirm predicted cubic structure of the superconductive phases. Fig. 1 summarizes the pressure dependence of superconducting temperature for hydrogen sulfide and its isotope deuterium sulfide. Apparently this pressure dependence reflects two phases with different pressure dependences. The determined cubic structure of these high Tc phases is in a good agreement with the R3m and Im3m structure predicted for H3S (Duan, Liu et al. 2014).

We will present recent results on further study of the superconductivity in hydrogen sulfide and other hydrides by different methods and compare the experimental results with available theoretical calculations.

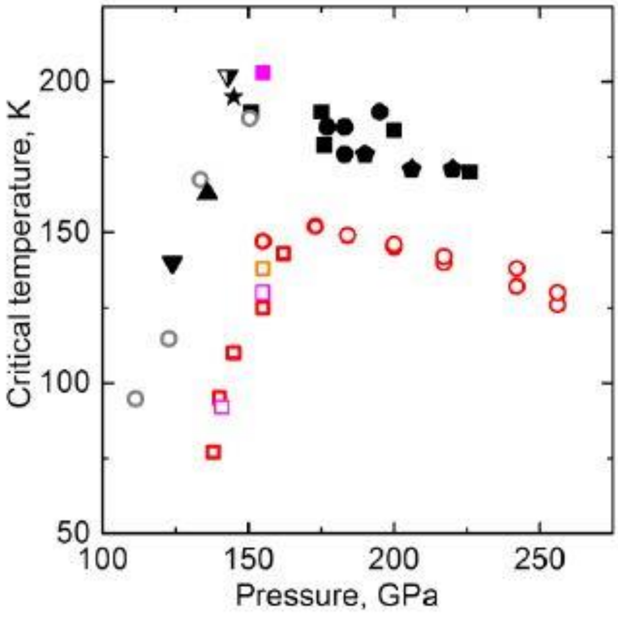
Figure 1: The pressure dependence of the critical temperature of superconductive transition for hydrogen sulfide (black points) and deuterium sulfide (red points) derived from electrical measurements. Magenta points are obtained from the magnetic susceptibility measurements in SQUID.

Drozdov, A. P., M. I. Eremets, I. A. Troyan, V. Ksenofontov and S. I. Shylin (2015). "Conventional superconductivity at 203 K at high pressures." Nature 525: 73-77.

Duan, D., Y. Liu, F. Tian, D. Li, X. Huang, Z. Zhao, H. Yu, B. Liu, W. Tian and T. Cui (2014). "Pressure-induced metallization of dense (H2S)2H2 with high-Tc superconductivity." Sci. Reports 4: 6968.

Einaga, M., M. Sakata, T. Ishikawa, K. Shimizu, M. I. Eremets, A. P. Drozdov, I. A. Troyan, S. Imada, N. Hirao and Y. Ohishi (2016). "Crystal structure of the 200 K-superconducting phase of sulfur hydride." Nature Physics 12.

Figure 1



O 6.1

Pressure effects on the transport and crystallographic properties of the iron based superconductors

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The study of the pressure effects on the crystal and electronic structure is a powerful tool that helps to find clues to analyze the superconducting state. The new iron based superconductors is an excellent example, where there are still plenty of opened questions to be answered.

In this presentation, we will discuss the effect of structural parameters under pressure on the superconducting properties on compounds belonging to 1111, 111, 11 and 42622 Fe based family. In particular, we have observed a strong correlation of the crystal structure parameters on the T_C in (La,Sm)FeAs$O_{1-x}F_x$, LiFeAs and FeSe compounds [1,2,3,4]. We have analyzed in detail the pressure dependence of the inter(intra)layer distance, the angle Fe-As-Fe and its effect on the T_C. These results are of great importance for band structure calculations based on realistic atomic positions that permit to obtain a detailed microscopic interpretation of the subtle effects on the electronic properties, explaining the effects on the superconducting transition.

This is the approach that we used to explain the pressure evolution of superconducting transition in SmFeAs$O_{1-x}F_x$ and Sr_2VO_3FeAs [2,5]. We also studied the pressure evolution of the structural and spin density wave transition in the SmFeAsO compound and we will correlate it with the superconducting properties.

[1] G. Garbarino et al, Phys Rev B (R), 2008, **78**, 100507

[2] G. Garbarino et al, Phys Rev B, 2011, **84**, 024510

[3] M. Mito, M. Pitcher, W. Crichton, G. Garbarino et al, J. Am. Chem. Soc, 2009, **131**, 2986

[4] G. Garbarino et al, EPL, 2009, **131**, 2986

[5] G. Garbarino, et al, EPL, 2011, **96**, 57002

O 6.2

Transport properties of $GeSb_2Te_4$ at elevated pressure

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GeSbTe (GST) is a high chalcogenide phase change material that has attracted considerable attention for the last decade due to its tunable Metal to Insulator Transition, (MIT) [[i], [ii]] and many potential applications in the electronics industry [[iii], [iv], [v]].

From the point of view of basic science, it is a very interesting material system, since it was conjectured [1] that the MIT in GST should be only driven by disorder-induced Anderson localization, whereas the alternative Mott transition is very unlikely to take place. This conjecture is based on the fact that the Mott parameter $(n_c)^{1/3}a_H{}^*$ in the vicinity of the MIT is by a few orders of magnitude larger than the critical value of 0.26 as expected for a Mott transition.

It has been previously demonstrated that the ambient temperature resistance of as-prepared amorphous $GeSb_2Te_4$ (a-GST) can be varied dramatically by over 4 orders of magnitude not only by the annealing process, converting the material into crystalline phase c-GST at elevated temperature [1,2], but also by elevated pressure at ambient temperature [[vi]]. The observed resistance changes, as well as reversible c-GST to a-GST phase transition, have been explained using DFT(?) simulations [ix, [vii], [viii]].

Here, we report on the results of the detailed studies of transport properties in both a-GST, and c-GST at elevated pressures up to about 50 GPa and at low temperatures down to 2.5 K. Special features of the electrical transport behavior of different GST phases (amorphous or when it forms a hexagonal, *bcc* or orthorhombic lattice) obtained at different cycles: compression, decompression and recompression, will be discussed.

[i] T. Siegrist, P. Jost, H. Volker, M. Woda, P. Merkelbach, C. Schlockermann, M. Wuttig, *Nat. Mater*, *10,* 202 **2011**

[ii] K. S. Siegert, F. R. L. Lange, E. R. Sittner, H. Volker, C. Schlockermann, T. Siegrist, M. Wuttig, *Rep. Prog. Phys.*, *78*, 013001 **2015**

[iii] D. Loke, T. H. Lee, W. J. Wang, L. P. Shi, R. Zhao, Y. C. Yeo, T. C. Chong, S. R. Elliott, *Science*, *336,* 1566 **2012**.

[iv] D. Lencer, M. Salinga, B. Grabowski, T. Hickel, J. Neugebauer, M. Wuttig, *Nat. Mater.*, *7*, 972 **2008**.

[v] J. Hegedus, S. R. Elliott, *Nat. Mater.*, *7*, 399 **2008**

[vi] M. Xu, Y. Q. Cheng, L. Wang, H. W. Sheng, Y. Meng, W. G. Yang, X. D. Han, and E. Ma, PNAS E1055 **2012**

[vii] Zhimei Sun, Jian Zhou, Yuanchun Pan, Zhitang Song, Ho-Kwang Mao, and Rajeev Ahuja, PNAS 108, 10410 **2011**

[viii] Ming Xu, Wei Zhang , Riccardo Mazzarello , and Matthias Wuttig, Adv. Sci, 2, 1500117 **2015**.

O 6.3

Pressure induced superconductivity in Weyl-semimetal $MoTe_2$

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Transition metal chalcogenides have attracted the research interest over the last few decades due to their interesting structural chemistry, unusual electronic properties, rich intercalation chemistry and wide spectrum of potential applications. One of the very interesting properties observed in TMC's is the superconductivity appearing on the borderline with charge-density wave formation. Thus, TMC's provide a platform for one of the most exciting and important areas of condensed matter research involving elucidation the competition between diverse and exotic phases in strongly correlated matter. The family of layered TX_2 materials is structurally well-defined: the structure is formed by stacks of the hexagonally packed planes in the sequence providing either the trigonal prismatic or octahedral coordination of metallic atoms.

Molybdenum ditelluride ($MoTe_2$) is unique among the transition-metal dichalcogenides since it is the only material that can be grown in two forms. Thermodynamically stable at ambient conditions is α-$MoTe_2$ (2H) with trigonal prismatic coordination of Mo-atoms. The β-$MoTe_2$ is metastable at room temperature, and has monoclinic 1T' structure in which the Mo atoms are octahedrally coordinated, and at temperatures below 260 K Td-$MoTe_2$ is completely isostructural with WTe_2. Electronic band structure calculations have shown that the Td-$MoTe_2$ is a type-II Weyl semimetal and recently this prediction is confirmed experimentally.

Here, we report on the electrical and structural properties of the both polytypes of $MoTe_2$ under high external pressures. We find that T_d-$MoTe_2$ exhibits superconductivity with T_c = 0.10 K. Application of pressure below 1 GPa dramatically enhances the T_c, and a dome-shaped T_c-P phase diagram is observed with maximum T_c = 8.2 K at 11.7 GPa (app. 80 times larger than the ambient pressure value). In contrast, we do not observe any traces of superconductivity in the 2H phase, even when it becomes metallic under pressure. We assume that the extreme sensitivity of the superconductivity to pressure is a consequence of the unique electronic structure. Thus, $MoTe_2$ presents the opportunity to study the interaction of topological physics and superconductivity in a bulk material.

O 6.4

High-pressure-high-temperature synthesis of new superconducting metastable phases of topological insulators Sb_2Te_3, Bi_2Te_3 and Bi_2Se_3

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We synthesized for the first time superconducting bulk polycrystalline samples of new metastable phases of Sb_2Te_3, Bi_2Te_3 and Bi_2Se_3 topological insulators by a rapid quenching after high-pressure-high-temperature treatment at pressures of 4 *GPa* and 7.7 *GPa* in the temperature range of 873 - 1573 *K* and investigated their structure, electrical and magnetic properties in the temperature range of 0.5-300 *K*. The crystal structure of metastable phases was investigated by X-ray powder diffraction and electron microscopy diffraction analysis. Atomic coordinates of m-Sb_2Te_3 phase were calculated using full profile X-ray diffraction pattern analysis and *ab initio* calculations. We calculated DOS and band structure for m-Sb_2Te_3 nanocluster. The crystal structure of m-Sb_2Te_3 phase is monoclinic (C2/m) with the cell dimensions: a=15.644(80) Å, b=4.282(8) Å, c=9.382(20) Å, β=89.70(5)°. The structure of m-Bi_2Te_3 phase quenched after treatment at P =7.7 GPa; T = 973 *K* is rhombohedral (*R3m,* sp.g. No 160), the lattice parameters are: a=4.42 Å, b=29.84 Å. The m-Bi_2Se_3 phase quenched after treatment at 7.7 *GPa* and 1473 *K* has monoclinic primitive structure with about 10% fraction of a tetragonal (or cubic) phase.

Unlike pristine materials, the quenched metastable phases of Sb_2Te_3 and Bi_2Se_3 possess superconductivity transition with T_C^{onset} = 2.5 *K* at normal pressure and T_C^{onset} = 7 *K* in Bi_2Te_3. The low critical current value of about 2 *mA* in the metastable Sb_2Te_3 phase and an absence of the detectable heat capacity effect at the superconducting transition indicate a low-dimensional character of the superconductivity which may refer to the surface of the crystal grains. The zero-field magnetic susceptibility cusp and linear positive magnetoresistance indicate the topological insulator state. Thus metastable phases of Sb_2Te_3 and Bi_2Se_3 topological insulators obtained by high-pressure-high-temperature treatment possesses weak superconductivity at normal pressure and may be interesting for Majorana fermions search. The semimetal-like temperature dependencies of electrical conductivity in the range of 2.5-300 *K* may confirm the topological semimetal state recently described theoretically [1].

[1] A. Soluyanov, D. Gresch, Z. Wanget al., Nature 527, 495 (2015).

O 6.5

Metal-insulator transition in 2D antiferromagnet $FePS_3$ upon applied pressure

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$FePS_3$ belongs to a rich family of structurally and magnetically quasi two-dimensional compounds, with a magnetic ground state in which spins are ordered as ferromagnetic chains coupled antiferromagnetically. At ambient pressure, it is an insulator with a direct gap of approximately 0.5 eV and a room temperature resistivity of approximately 104 Ωcm.

We present the results of resistivity measurements under pressures up to 110 kbar for this material. The insulating phase is suppressed at a pressure in the range 40-70 kbar giving way to a new metallic phase. Interesting intermediate behaviour is seen at pressures around the transition as the gap closes. At high pressure, the resistivity develops linear temperature dependence with an upturn in resistivity which may indicate a low temperature phase transition or impurity scattering.

O 6.6

Direct measurements of thermal conductivity at planetary core conditions

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The transport properties of minerals and fluids control the flow of thermal energy inside the Earth and other planets, ruling over their internal dynamics and evolution. In the Earth's core, the thermal conductivity of iron alloys defines the adiabatic heat flux and thus, the energy available to support geodynamo (Nimmo, 2015). Recently, a 'core paradox' (Olson, 2013) emerged as a consequence of high thermal conductivity of the core material as proposed from recent theoretical studies at high temperatures (de Koker et al., 2012 and Pozzo et al., 2012) and experimental electrical resistivity measurements at ambient temperatures (Gomi et al., 2013).

In this study, we used a modified flash heating measurement of thermal conductivity, applied to a pre-heated compressed iron foil in the diamond anvil cell, and directly determined the thermal conductivity of iron up to planetary core temperatures and pressures. The evolution of thermal disturbance was characterized by nanosecond-resolved radiative temperature measurements using a streak camera coupled to a grating spectrograph that records the thermal incandescent history from both sides of the foil. The temperature evolution was fit to time-dependent finite element models of the laser heated diamond cell to determine thermal conductivity of iron samples.

Our measurements place the thermal conductivity of Earth core material near the lower end of previous estimates, at 18-44 W/m/K. The results are in agreement with core thermal conductivity estimates based on the electrical resistivity behavior of iron at high pressure and temperature by Stacey and Loper (2007) and Seagle et al. (2013) and mitigate the thermal transport problem in Earth's core.

Nimmo, F. in *Treatise on Geophysics (Second Edition)* (ed Gerald Schubert)

150 27-55, 201-219 (Elsevier, 2015).

Olson, P. The New Core Paradox. *Science* **342**, 431-432 (2013).

de Koker, N., et al. *Proc. Natl. Acad. Sci. U. S. A.* **109**, 4070-4073 (2012).

Pozzo, M., et al. *Nature* **485**, 355-U399 (2012).

Gomi, H. *et al. Phys. Earth Planet. Inter.* **224**, 88-103 (2013).

Stacey, F. D., & Loper, D. E. (2007). *Physics of The Earth and Planetary Interiors*, *161*(1-2), 13-18.

Seagle, C. T., Cottrell, E., Fei, Y., Hummer, D. R., & Prakapenka, V. B. (2013). Geophys. Res. Lett., 40, 5377-5381.

O 6.7

High-pressure thermopower in MnSi

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The present study reports thermopower in non-centrosymmetric, itinerant ferromanget MnSi in the pressure range 1 - 11GPa. MnSi is a well-established strongly correlated material, with unconventional magnetic and electrical properties at low temperatures. Magnetic field induced skyrmion phase [1] and Non-Fermi Liquid behaviour at low pressure [2] are some examples. The ferromagnetic transition in this material is suppressed at a critical pressure P_C~1.46GPa. [2]

The temperature dependence of the thermopower in this system is investigated against a two-band Koterlyn model, which has been successfully implemented in many heavy fermion compounds. [3] Our results show tentatively a characteristic pressure scale P_{C2}~4GPa where the inherent behaviour of the thermopower changes. A possible explanation for these findings may lie in subtle changes of the Fermi surface topology. Comparisons to electrical resitivity in MnSi under pressure will be discussed. [4]

[1] R.Ritz, M. Halder, M. Wagner, C. Franz, A. Bauer and C. Pfleiderer, Nature, 497, 231,2013

[2] C. Pfleiderer, D. Reznik, L. Pintschovius, H. v.Lohneysen, M. Garst and A. Rosch, Nature, 427, 227, 2004

[3] M.D. Koterlyn, O.I. Babych, G.M. Koterlyn, Journal of Alloys and Compounds, 325, 6-11, 2001

[4] P. Pedrazzini, D. Jaccard, G. Lapertot, J. Flouquet, Y. Inada, H. Kohara, Y. Onuki, Physica B, 378-380, 165-166, 2006

O 6.8

Emergent phases near quantum critical transitions

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This talk will focus on experimental search and discovery of novel forms of quantum order in metallic and insulating magnets, and ferroelectric systems. Particularly discussed will be the pressure-induced critical phenomena in the vicinity of quantum phase transitions.

Materials tuned to the neighbourhood of a zero temperature phase transition often show the emergence of novel quantum phenomena. Much of the effort to study these new emergent effects, like the breakdown of the conventional Fermi-liquid theory in metals has been focused in narrow band electronic systems. But Spin or Charge ordered phases in insulating systems can also be tuned to absolute zero using hydrostatic pressure. Close to such a zero temperature phase transition, physical quantities like resistivity, magnetisation and dielectric constant change into radically unconventional forms due to the fluctuations experienced in this region giving rise to new kinds ordered states including superconductivity in the metallic systems.

O 6.9

Anharmonic effects in atomic hydrogen: superconductivity and lattice dynamical stability

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Introduction

The recent measurement of a superconducting critical temperature (Tc) of 203 K in the sulfur hydrogen system is a major breakthrough in the field of superconductivity. It ultimately validates Ashcroft's idea that hydrogen and hydrogen-dominant metallic compounds can be high-temperature superconductors. This measurement offers new hopes to find sooner than later room-temperature superconductivity in other hydrogen-rich compounds or hydrogen itself.

Objectives

We present first-principles calculations of metallic atomic hydrogen in the 400-600 GPa pressure range in a tetragonal structure with space group I41/amd, which is predicted to be its first atomic phase, an characterize anharmonic phonon frequencies and the modification on its predicted superconducting transition temperature.

Computational Methods

We performed our DFT calculations within the Perdew-Burke-Ernzerhof parametrization of the generalized-gradient approximation as implemented in Quantum ESPRESSO. We use the SSCHA to calculate the anharmonic renormalization of the phonon spectrum.

Results

Our calculations show a band structure close to the free-electron-like limit due to the high electronic kinetic energy induced by pressure. Bands are properly described even in the independent electron approximation fully neglecting the electron-electron interaction. Anharmonic effects harden high-energy optical modes and soften transverse acoustic modes up to a 20% in energy.

Conclusions

Despite anharmonicity modifies phonon frequencies up to approximately a 20% it has a minor effect on superconductivity, only suppressing Tc by a 6%. This is in stark contrast to other hydrides where anharmonicity has a huge impact on the superconducting properties. This raises the interesting question whether anharmoncicity impacts superconductivity in hydrides simply because hydrogen is light and vibrates far from equilibrium or for another particular reason. Our results suggest that determining whether anharmonicity has a strong impact on Tc cannot be related exclusively to the lightness of the ions present in the system, but to the presence of softened optical modes.

O 6.10

Observation of superconductivity in highly compressed H_2S with the help of Mössbauer spectroscopy

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High temperature superconductivity remains in focus of experimental and theoretical research.

Recent resistivity and magnetic susceptibility measurements indicated that a superconducting transition occurs in H_2S compressed to 150-190 GPa with a high onset temperature of 203 K [1]. For an unambiguous identification of the superconducting state a direct observation of the Meissner effect in an external magnetic field is desirable.

We report on the direct observation of the expulsion of the magnetic field in H_2S compressed to 153 GPa [2]. A thin ^{119}Sn film placed into the H_2S sample volume was used as a sensor of the magnetic field inside the superconductor.

The idea to use the Mössbauer isotope ^{119}Sn of nonmagnetic tin as a highly sensitive nuclear probe of the magnetic states in crystals was first suggested and developed in numerous works of the Moscow research group of Institute Crystallography RAS (see as an example Ref. 3). In the present experiment, the magnetic field at the ^{119}Sn sensor was monitored using nuclear resonance scattering of synchrotron radiation (NRS) from the Mössbauer ^{119}Sn nuclei. Our results demonstrate that an external static magnetic field of about 0.7 Tesla is expelled from the volume of ^{119}Sn foil due to the shielding by the H_2S sample at temperatures between 4.7 and approximately 145 K, revealing a superconducting state of H_2S.

Acknowledgements

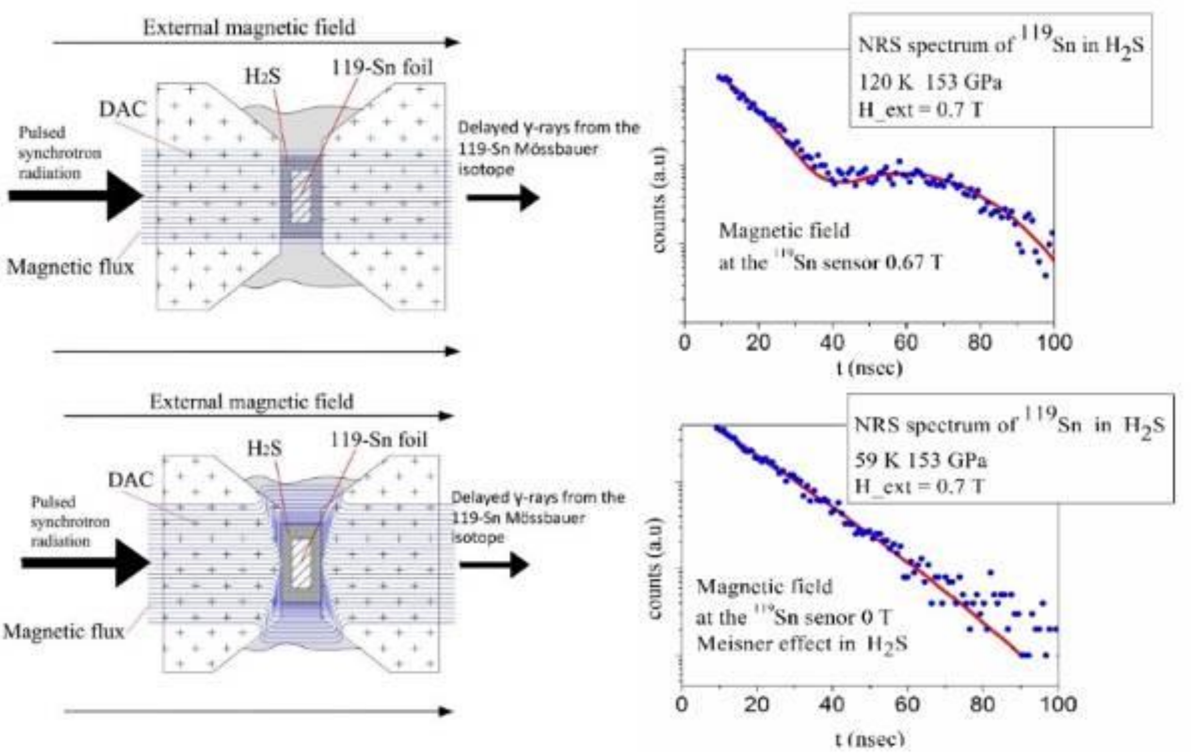
Supports by RFBR # 14-02-00483 and RScF # 14-02-00848 are acknowledged.

[1] A.P. Drozdov, M.I. Eremets, I.A. Troyan, V. Ksenofontov, S.I. Shylin, Nature **525**, 73 (2015).

[2] I.A. Troyan, A.G. Gavriliuk, R. Rüffer, A. Chumakov, A.A. Mironovich, I.S. Lyubutin, D. Perekalin, A. Drozdov, M. Eremets, Science **351**, 1303 (2016).

[3] I.S. Lyubutin, T.V. Dmitrieva, JETP Lett. **21**, 59 *(*1975).

Figure 1


External magnetic field
H2S
119-Sn foil
DAC
Pulsed synchrotron radiation
Delayed γ-rays from the 119-Sn Mössbauer isotope
Magnetic flux
NRS spectrum of ^{119}Sn in H_2S
120 K 153 GPa
H_ext = 0.7 T
Magnetic field at the ^{119}Sn sensor 0.67 T
counts (a.u)
t (nsec)
0
20
40
60
80
100
External magnetic field
H2S
119-Sn foil
DAC
Pulsed synchrotron radiation
Delayed γ-rays from the 119-Sn Mössbauer isotope
Magnetic flux
NRS spectrum of ^{119}Sn in H_2S
59 K 153 GPa
H_ext = 0.7 T
Magnetic field at the ^{119}Sn senor 0 T
Meisner effect in H_2S
counts (a.u)
t (nsec)
0
20
40
60
80
100

P 6.1

Electrical transport properties of the unconventional superconductor YFe_2Ge_2 under high pressure

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YFe_2Ge_2 is a paramagnetic d-electron system which stands out due to the high Sommerfeld ratio of its specific heat capacity of 100 mJ/ (mol K^2) and non Fermi-liquid $T^{3/2}$ power law temperature dependence of the electrical resistivity. The compound was found to be superconducting below about 1.8 K [1]. Recent measurements of resistivity, magnetisation and heat capacity performed on a new generation of high quality samples with residual resistivity ratio of the order of 200 provide strong evidence for the unconventional superconductivity [2]. Furthermore, YFe_2Ge_2 is expected to be located close to a quantum critical point, since its sibling compound $LuFe_2Ge_2$ orders antiferromagnetically at 9 K [3].

We present the results of our measurements of the electrical resistivity of YFe_2Ge_2 as a function of temperature under high hydrostatic pressure. We investigate its effect on the superconductivity as well as normal state properties and assess the applicability of the technique as a tool for tuning the material towards the quantum critical point.

[1] Y. Zou et al, Physica Status Solidi (RRL) **8,** 928 (2014)

[2] J. Chen et al. Phys. Rev. Lett. **116**, 127001 (2016)

[3] M. A. Avila, S. L. Bud’ko, and P. C. Canfield: J. Magn. Magn. Mater. **270** (2004) 51

P 6.2

Measurement of thermal conductivity using Laser Heated Diamond Anvil Cell

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Estimation of heat flux through Core Mantle Boundary (CMB) depend on properties of existing material under the extreme pressure and temperature conditions in the core, most critically on the thermal and electrical conductivities. In our laboratory we have measured thermal conductivity and emissivity of Iron upto 60 (± 2) GPa in the temperature range 1700-1900 K using single sided LHDAC facility.

We have carried thermal conductivity measurements using LHDAC on pure iron foil of thickness 10-12 µm and 80 µm in diameter. The sample is sandwitched between two NaCl pellets of thickness ~ 15-20 µm inside the sample chamber. An IR laser is focused down to 12-15 µm in diameter at one the edge of the sample and thermal radiation is collected from other edge from about 3 µm diameter of the sample surface for temperature estimation which is magnified 13-times at the pinhole entrance.

We have neglected radiative and convecting heat loss in the diamond anvil cell [1]. In our case radial conduction dominates as Q_{radial} / Q_{axial} is ~ 80 >>1 [2]. The absorbed energy by the sample surface will be, $Q_{abs.} = \beta(P) * Q_{inc.}$. Q_{abs} is the power absorbed by sample surface, β(P) is the pressure dependence absorption of the sample and $Q_{inc.}$ is the incident power on the sample. The absorptivity of the sample is estimated by applying Kirchoff's thermal radiation law. Emissivity is determined with a two-parameter fit (ε,T) to the Planck function and considering the radial heat flow we have measured thermal conductivity of Iron. The measured pressure dependence emissivity and thermal conductivity is shown in the figures.

The emissivity of Iron is found to be slightly higher than given by Seagle et al [3]. and thermal conductivity is found to be 20% higher than those estimated by Kiefer et al [4]. The sudden fall of emissivity value shown in Fig. 1 indicate fcc to bcc transition of Iron.

References

[1] Manga M. and R. Jeanloz, Geophys. Monogr., Vol. **101**, pp. 17-25,1998.

[2] Manga M. and R. Jeanloz, J. Geophys. Res. Lett., Vol. **102**, 1997.

[3] Seagle C. T., Heinz D. L., Liu Z. and Hemley R. J., App. Optics, Vol. **48,** 2009.

[4] Kiefer B. and Duffy S. T., J. Appl. Phys., Vol **99,** 2005.

Figure Captions

Figure 1: Emissivity of Iron with pressure.

Figure 2: Thermal Conductivity of Iron with pressure.

Figure 1

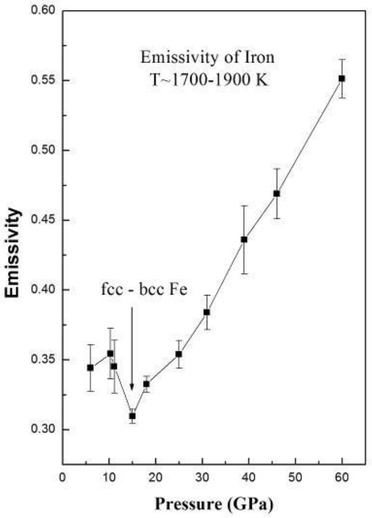
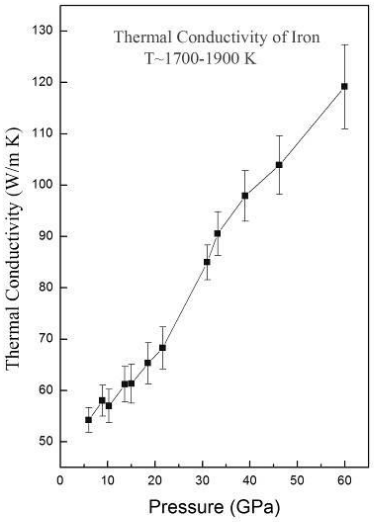


Figure 2



P 6.3

Superconductivity in high-pressure states of bismuth

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For pressures exceeding 27 kbar, elemental bismuth undergoes a structural transition into an incommensurate host-guest structure, termed Bi-III. This structure consists of two distinct lattices that coexist and interpenetrate; in the case of bismuth the two c-axis parameters are incommensurate, meaning there is no true unit cell. Although the high-pressure phase Bi-III has long been known to superconduct below about 7 K, the nature of the superconducting state has not yet been explored in detail.

We report resistivity and magnetisation measurements in the Bi-III phase, investigating the superconducting and normal states, in fields up to 9 T and temperatures down to 250 mK. Resistivity measurements were conducted in a piston cylinder cell; magnetisation was measured using a DC SQUID technique in an anvil pressure cell. We find evidence for a strikingly high critical field above 1 T, and an unusual temperature dependence of the resistivity above the superconducting transition. Magnetisation measurements suggest Bi-III is a Type II superconductor.

P 6.4

Resistivity kinetics and phase transformations in graphite and graphene at high pressures

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The electric properties of various types of graphite and graphene have been studied at pressures up to 50 GPa at room temperature. The kinetics of resistivity at changing pressure was also studied. Transport phenomena were used as a tool for finding and interpretation of phase transitions arisen under high pressure. Samples of graphene consisted of flakes with the number of layers from 5 to 20. High pressures have been generated in the high pressure cell with synthetic carbonado-type diamond anvils. The anvils are good conductors and can be used as electric contacts. The method used allows us to study the same sample at successive increasing and decreasing pressure and also to keep it loaded during a long time. After pressure treatment, the samples were examined by means of the workstation AURIGA CrossBeam, which is a scanning electron microscope (SEM) with the possibility of X-ray microanalysis.

The features of the phenomena studied found in graphite at the pressures of 15 to 20 GPa and at 30 GPa were ascribed to known phase transitions [1]. A new carbon phase was found to arise from graphite after long exposure under pressures up to 50 GPa at room temperature. The exposure time at each fixed value of pressure was twenty four hours. The SEM image of the sample subjected to the pressure of 45 GPa showed the inclusion of the new phase, which did not disappear after removal of the load. However, the new phase was poorly seen in the pressure dependence of resistivity because of shunting by a large amount of non-transformed graphite. Two different relaxation times were found. The first one was less than 40 s. The second relaxation time appeared only after continuous exposure under pressure in the range of 27 to 35 GPa and was several hours.

The baric dependence of resistance of graphene was of the same character as that for graphite, but with larger values of resistance (by almost one order of magnitude) and its relaxation times after changing pressure. The relaxation times increased in the vicinity of phase transitions (15-20 GPa) up to ~10 min. No new phase was found in the SEM image of graphene.

This work was supported by RFBR grants 16-02-01137 and 16-02-00857.

[1] S.E. Boulfelfel, A.R. Oganov, S. Leoni, *Scientific Reports* **2**, art. 471 (2012).

P 6.5

Thermoelectric properties of $Bi_{2-x}Sb_xTe_{3-y}Se_y$ crystals at high pressure up to 20 GPa

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Applied pressure strongly influences on thermoelectric (TE) properties of materials because of changing their electronic band structure under compression. The enhancement of TE properties of well known thermoelectric p-Bi_2Te_3 has been found recently under high pressure [1]. In recent times, bismuth chalcogenides were rediscovered within the novel context of topological insulators [2].

In the present work the behavior of TE and electrical conductivity of $Bi_{2-x}Sb_xTe_{3-y}Se_y$ compounds with different conductivity types was investigated under high pressure application up to 20 GPa at room temperature using an automated high-pressure set-up (mini-press) operating miniature anvil-type high-pressure cell with anvils made of synthetic diamonds and hard-alloys [3]. A different prototype models of thermo-element with p-, n-pellets that are being compressed between miniature boron-nitride anvils has been experimentally created and examined. The examination of the performance of this TE element showed the improvement of the power factor under high-pressure impact. We discuss possible applications of applied high pressure for thermoelectric devices.

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[1] S. V. Ovsyannikov, V. V. Shchennikov, G. V. Vorontsov, A. Y. Manakov, A. Y. Likhacheva, V. A. Kulbachinskii, J. Appl. Phys. 104, 53713 (2008).

[2] H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nature Phys. 5, 438 (2009)

[3] V. V. Shchennikov, S. V. Ovsyannikov, A. Y. Manakov. J. Phys. Chem. Solids 71, 1168 (2010).

P 6.6

Hall effect and electrical resistivity of Cd_3As_2 + MnAs (30%) composite at high pressure

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The composite Cd_3As_2 + 30% MnAs measured resistivity and the Hall coefficient at hydrostatic pressures up to 9 GPa at room temperatures.

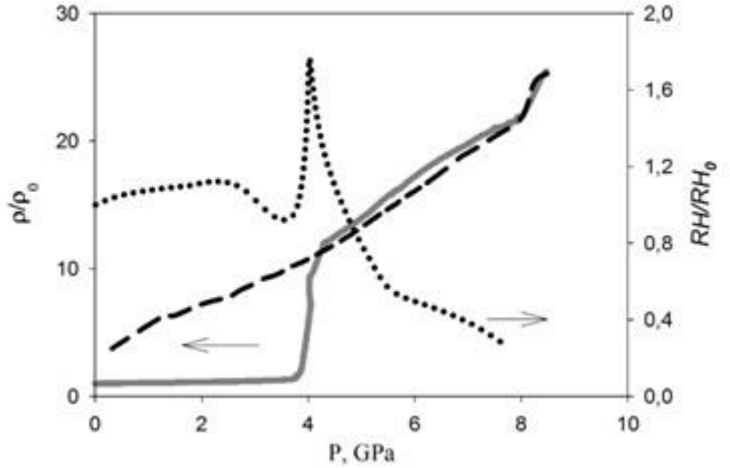
Cd_3As_2 + MnAs composites is ferromagnetic with Curie temperature about 320K and have metallic type of conductivity. Magnetization increases for these samples as the percentage of MnAs rise.

Baric dependence of specific resistivity $\rho(P)/\rho_0(P)$ and Hall coefficient $R_H(P)/R_{H0}(P)$ for Cd_3As_2 + 30% MnAs sample are presented on the figure. Specific resistivity does not change practically up to P»3.7 GPa, then one increases sharply by ~12 times, and the irreversible phase transition has been observed at P»4.3 GPa.

At pressure up to P»2.3 GPa baric dependence of Hall coefficient passes through maximum, then curve decreases to its minimum at P»3.6 GPa and increases by 2 times achieving a clear peak at P»4 GPa which was interpreted as phase transition. The baric dependence of Hall coefficient has good correlation with baric dependence ρ(P) which is characterized by peak at P»4.3 GPa too.

The concentration and mobility’s values measured before and after of pressure application let us suggest that irreversible structural phase transition semiconductor - semiconductor takes place in Cd_3As_2 + 30% MnAs at high hydrostatic pressure P≈4 ÷ 4.3 GPa.

Figure 1



P 6.7

Pressure-induced superconductivity above 55 K in disilane

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Recent discovery of the very high superconducting transition temperature (T_C) of 203 K in sulfur hydride at high pressures[1] initiated search of other materials with possibly higher T_C. It was found that phosphine is another higher temperature superconductor with T_C >100 K at pressures above 200 GPa[2]. For silane, maximum T_C =17 K was found at pressures above 100 GPa[3]. Disilane is a hydrogen-rich compound from the silane family. A very high T_C of ~139 K at 275 GPa has been predicted[4], but another work found different stable phase with very different Tc~20 K at 100 GPa[5]. We checked a possible superconductivity in Si_2H_6 experimentally. We conducted electrical measurements with four electrodes in the van der Pauw geometry. Si_2H_6 was liquefied in DAC below 240 K. Raman spectra showed characteristic peaks of Si_2H_6: around 433 cm^{-1}, 930 cm^{-1}, and 2146 cm^{-1}. To prevent the sample from a possible decomposition, we compressed it at low temperatures of < 200 K. Pressurization shifts peaks to higher frequencies, and decreases their intensities. At pressures of >40 GPa, Raman peaks disappear while the sample became opaque and metallic. At 46 GPa, we observed an indication of a possible superconductivity: sharp drop in resistance around 15.3 K appeared. Pressurization dropped resistance to zero evidencing a transition to superconductive state. The T_C increases with pressure reaching maximum value of 55 K at 323 GPa. To confirm the superconductivity, magnetic susceptibility should be measured too. Determination of the structure also is very important as our values of T_C do not agree with T_Cs calculated for the *P-1, Pm-3m, C2/c* structure[4] or the *Cmcm* structure[5]. We should note that likely we measured a low temperature phase which might be metastable. After warming the sample to room temperature at 118 GPa, T_C dropped from 20.2 K to 15.4 K.

[1] A. P. Drozdov *et al.*, Nature **525**, 73 (2015)

[2] A. P. Drozdov *et al*., arXiv:1508.06224

[3] M. I. Eremets *et al*., Science **319**, 1506 (2008)

[4] X. L. Jin *et al*., Proc. Natl. Acad. Sci. **107**, 9969 (2010)

[5] J. A. Flores-Livas *et al*., Phys. Rev. Lett. **108**, 117004 (2012)

P 6.8

Impedance and structure investigations of C70 at pressure up to 30 GPa

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The electrical properties of polycrystalline C70 (99.5%) are studied at direct and alternating current in a wide range of frequencies at high pressure and room temperature. Graphic analysis of the experimental data [1-3] in the view of equivalent circuits allowed us to get the pressure dependencies of resistance and capacity. We observed the features of impedance above 15 GPa. At ambient pressure C70 crystallized in the fcc structure. With a pressure's increasing the phase transition takes place, and at pressure up to 15 GPa the diffraction pattern corresponds to amorphous phase.

This work was supported by RFBR grants 16-02-01137 and 16-02-00857

Authors are grateful to Professor Leonid Dubrovinsky for the possibility of high pressure X-ray diffraction measurements.

[1] Macdonald, J.R., Impedance Spectroscopy, New York: Pergamon Press, 1987.

[2] Ivanov-Shits, A.K. and Murin, I.V., Ionika tverdogo tela (Solid State Ionics), St. Petersburg: St. Peterbsurg State Univ., 2000, vol. 1, p. 126.

[3] Armsrong, R.D., Dickinson, T., and Wills, M., Electroanal. Chem. Enterfacial Electrochem., 1974, N 53, p. 389.

P 6.9

Magnetic measurements on rare earth and actinide compounds with a miniature ceramic anvil high pressure cell

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Magnetic measurement at high pressure is an important experimental method for the study of magnetic properties of materials. Recently, we have developed a miniature ceramic-anvil high-pressure cell mCAC for magnetic measurements at pressures above 10 GPa in a commercial superconducting quantum interference (SQUID) magnetometer [1-3]. The anvils are made of inexpensive composite ceramic (FCY20A, Fuji Die Co.). The simplified mCAC without anvil alignment mechanism is easy-to-use for researchers who are not familiar with high-pressure technology. In this conference, we will present basic performance of the mCAC and show interesting physical phenomena in some rare earth and actinide compounds: pressure-induced ferromagnetism in YbCu2Si2 and pressure-induced ferromagnetic to nonmagnetic transition in uranium ferromagnetic superconductor UGe2. We reveal that the strong uniaxial ferromagnetic state is induced above 8 GPa YbCu2Si2. The particular 4f magnetism in the phase will be discussed. In UGe2, strong longitudinal spin fluctuation preserves in the high pressure non-magnetic phase. The mode-mode mode coupling plays an important role for the anomalous magnetic properties around the pressure-induced ferromagnetic critical point.

P 6.10

Diacell® ChicagoDAC, the ultimate tool for high pressure low temperature transport measurements

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We present the new Diacell® ChicagoDAC (see figure), a compact bellows-driven diamond anvil cell (DAC) for high pressure, low temperature transport measurements[1,2]. This DAC, compatible with Quantum Design's PPMS®, is made of silicon aluminium bronze, a non magnetic material. The ChicagoDAC provides in-situ pressure tuning and measurement via the helium-filled bellows and fiber-coupled ruby fluorescence spectroscopy, respectively.

Here we demonstrate our preliminary results at pressures up to 10 GPa and temperatures down to 8 K. These results are in good agreement with the results from literature[1]. The ChicagoDAC ultimately represents the convenient tool for transport measurements at low temperature, especially when it is equipped with our novel patterned diamond anvils. Being non magnetic itself, it also allows the users to probe magnetism and superconductivity over a wide pressure and temperature range.

References

[1] Yejun Feng, D. M. Silevitch, and T. F. Rosenbaum, Rev. of Sci. Inst. 2014, **85**, 033901.

[2] http://www.almax-easylab.com/ProductDetails.aspx?id=119&IID=10027

Keywords: Diamond anvil cell, Transport measurements, Magnetism, Superconductivity, Low temperature.

Figure 1

Invited Talk

New opportunities for studies of magnetism with Synchrotron Mössbauer Source at ESRF

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The Nuclear Resonance beamline [1] ID18 at ESRF offers users a Synchrotron Mössbauer Source (SMS) [2, 3] with a beam size suited for high-pressure studies using diamond anvil cells.

The device is based on a pure-nuclear reflection of a $^{57}FeBO_3$ crystal which selects only a single-line radiation component with the bandwidth of the nuclear transition [4]. In terms of x-ray optics, SMS is an in-line monochromator with the band-pass of ~10 neV (Fig.1). For users, its operation does not differ much from that of a radioactive source.

Figure 1. The optical scheme of the Synchrotron Mössbauer Source.

Within the ~15×15 μm^2 spot size, SMS provides ~10^4 photons/s, which is a factor of ~100 larger than a radioactive source with a similar aperture. In addition, the radiation contains less than 1% of background compared to ~90% for high-pressure studies with a radioactive source. This allows users to obtain data ~1000 times faster and with remarkably higher quality (Fig.2).

In this talk we review recent applications of SMS for studies of magnetism at high pressure.

Figure 2. The Mössbauer spectra of perovskite Mg0.6 57Fe0.4Si0.63Al0.37O3 at 95 GPa measured with a radioactive source (left) and with SMS (right) [5]. Courtesy of C. McCammon and L. Dubrovinsky.

[1] R. Rüffer and A. I. Chumakov, Hyperfine Interaction, 97/98 (1996) 589.

[2] G. V. Smirnov, U. van Bürck, A. I. Chumakov, A. Q. R. Baron, and R. Rüffer, Phys. Rev. B, **55** (1997) 5811.

[3] V. Potapkin, A. I. Chumakov, G. V. Smirnov, J.-P. Celse, R. Rüffer, C. McCammon, and L. Dubrovinsky, J. Synchrotron Rad. (2012). **19**, 559.

[4] G. V. Smirnov, M. V. Zelepukhin, and U. van Bürck, Pis'ma Zh. Eksp. Teor. Fiz. **43** (1986) 274.

[5] ESRF Spotlight, http://www.esrf.fr/home/news/spotlight/content-news/spotlight/spotlight195.html

Figure 1. The optical scheme of the Synchrotron Mössbauer Source.

Figure 2. The Mössbauer spectra of perovskite $Mg_{0.6}{}^{57}Fe_{0.4}Si_{0.63}Al_{0.37}O_3$ at 95 GPa measured with a radioactive source (left) and with SMS (right) [5]. Courtesy of C. McCammon and L. Dubrovinsky.

Figure 1

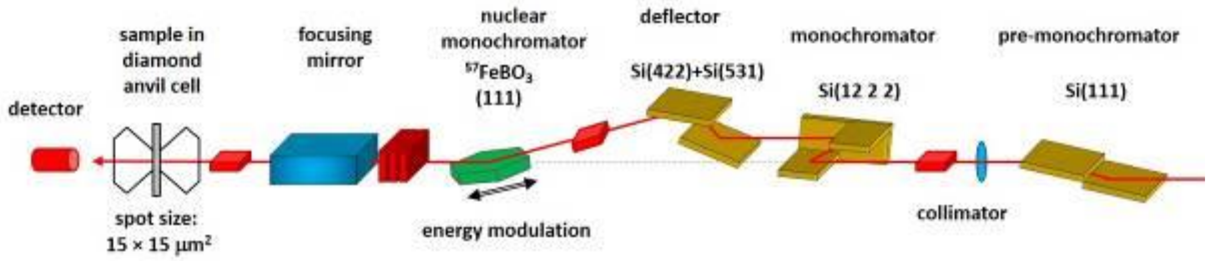
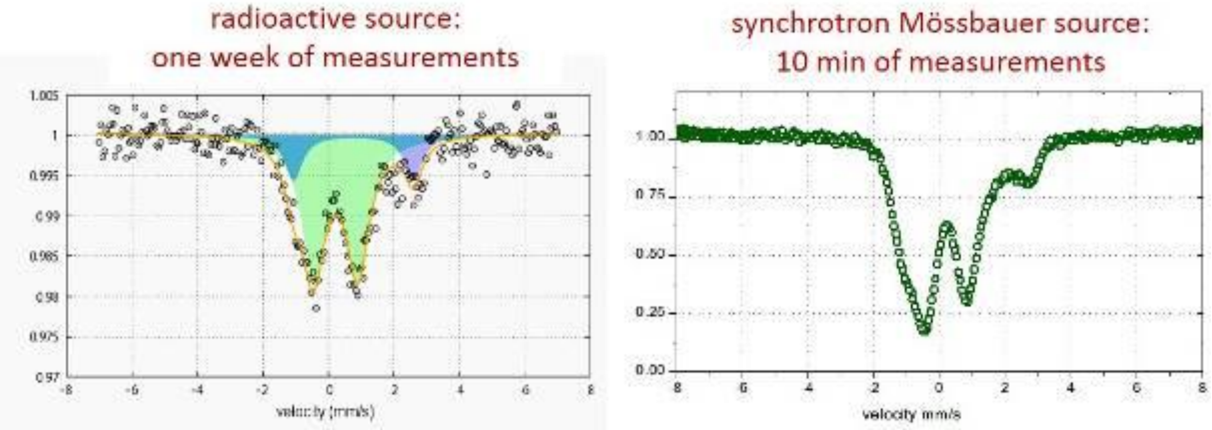


Figure 2


radioactive source: one week of measurements

synchrotron Mössbauer source: 10 min of measurements

O 7.1

Critical temperatures of iron oxides at high pressures

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Iron oxides are important magnetic carrier minerals and, thus, investigation of their properties is crucial for better understanding the planet's interiors. As a result, numerous studies have been dedicated to explore in details their high pressure behavior. For instance, their structure and elastic properties have been extensively investigated at pressures and temperatures relevant to the deep Earth's interior in order to identify their geophysical signatures.

Complementary to geophysical signatures, some iron oxides may carry important paleomagnetic records. For example, the information on the history of the remnant magnetization of magnetite might be a key for understanding the origin of life on our planet (Tarduno et al., 2015) and for revealing the evolution of magnetism on other planets (Carporzen et al., 2005).

Although, numerous studies were focused on the investigation of the electronic and magnetic properties of common iron oxides at high pressures and moderate temperatures, the information on their properties at relevant high temperatures is very limited. While it was generally assumed that magnetism is suppressed by pressure, recent studies have shown that magnetic carrier minerals may experience a complex sequence of magnetic ordering changes upon structural transitions at high pressures and high temperatures (Bykova et al., 2016; Shim et al., 2009).

One of the fundamental characteristics of magnetic materials is their critical temperature (i.e. the temperature above which a magnetic material becomes paramagnetic) and its pressure dependence. Here we will present our investigation on pressure dependence of critical temperatures of major iron oxides by means of Synchrotron Mössbauer Source spectroscopy in laser heated diamond anvil cells.

References

Bykova et al., 2016. Structural complexity of simple Fe_2O_3 at high pressures and temperatures. Nat. Commun. 7, 10661

Carporzen et al., 2005. Palaeomagnetism of the Vredefort meteorite crater and implications for craters on Mars. Nature 435, 198-201

Shim et al., 2009. Electronic and magnetic structures of the postperovskite-type Fe_2O_3 and implications for planetary magnetic records and deep interiors. PNAS 106, 5508-12

Tarduno et al., 2015. A Hadean to Paleoarchean geodynamo recorded by single zircon crystals. Science 349, 521-524

O 7.2

Pressure experiments on spin-orbit coupled hyper-honeycomb β-Li_2IrO_3

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Hexagonal iridates A_2IrO_3 (A = Na, Li) display novel electronic and magnetic properties due to the strong spin-orbit coupling and electronic correlations. They are proposed candidate materials for the realization of the frustrated bonding-dependent anisotropic Kitaev interaction. While the structure of Na_2IrO_3 and α-Li_2IrO_3 consists of a two-dimensional (2D) honeycomb planes, a 3D, so-called hyper-honeycomb, structure is realized in β-Li_2IrO_3. This material displays a complex antiferromagnetic ordering which is stabilized by the Kitaev interaction [1]. We performed thermal expansion and specific heat, found that the magnetic order temperature T_N = 38 K is coupled to the lattice. From the thermodynamic analysis, viz., by employing the Ehrenfest relation, the initial pressure dependence has been calculated dT_N/dp = +0.7 K/ GPa. Moreover, isothermal magnetostriction measurements predicts that the initial increase of magnetization with hydrostatic pressure. We investigated the bulk magnetization under hydrostatic pressure in a commercial SQUID magnetometer up to 2 GPa using Daphne oil as pressure medium and a small piece of lead as pressure sensor. While the T_N shifts to the higher temperature as pressure increases, $dT_N/dp \approx +1$ K/ GPa, consistent with thermodynamic analysis, the absolute value of the magnetic susceptibility for $T<T_N$ starts to increase up to 1.3 GPa. After that the value suddenly decrease and becomes significantly suppressed at p = 2 GPa, consistent with recent XMCD measurements [2]. This sudden depression could be related to a structural transition.

[1] A. Biffin *et al.*, PRB **90**, 205116 (14).

[2] T. Takayama *et al.*, PRL **114**, 077202 (2015).

Work in collaboration with F. Freund, R. Küchler, A. A. Tsirlin, A. Jesche, and P. Gegenwart.

O 7.3

High pressure structural study through magnetic quantum critical point

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In some strongly interacting electron systems if the conditions are correct, new ordered states are formed which can not be explained by the traditional low temperature theories of matter (e.g. Fermi-liquid theory). A rich discovery arena for such new ordered states has been in systems which are on the border of long range magnetic order. It is possible to see the evolution in to these new states in suitable high purity samples by the precise tuning of the lattice density by the application of hydrostatic pressure. The aim of this study is to investigate the inter-relationship between structure, magnetic and electronic properties when the magnetic ordering temperature is supressed to a quantum critical point by the application of pressure. We have performed low temperature, high pressure, powder synchrotron x-ray diffraction experiments to investigate the subtle changes in structure that occur in the ferromagnet $ZrZn_2$ around the magnetic quantum critical point. Measurements down to low temperatures of 14K and high pressures up to 20 GPa in a diamond anvil cell are presented. The results are discussed in relation to the properties of the material.

O 7.4

Exploring the structural, optical, and magnetic properties of Cu_2OSeO_3

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Among the cubic helical magnets crystallizing in the non-centrosymmetric space group $P2_13$ (No. 198), Cu_2OSeO_3 has characteristic properties which are not found in the mono-silicides and -germanides (*B*20 structure type) although the overall magnetic phase diagram close to the magnetic ordering temperature (T_c) appears to be very similar. The main differences with respect to the *B*20 compounds are, apart from its insulating properties [1], that the magnetic ion (Cu^{2+}) occupies two different crystallographic sites [2] and the increase of T_c under an applied external pressure [3]. These differences and the report of a segmented A-phase region [4] - apparently in common with FeGe [5] - deserve further investigations. Therefore, we performed structural, optical and magnetic (ac-susceptibility and small-angle neutron scattering) measurements.

The influence of external pressure on the structural and optical properties on Cu_2OSeO_3 has been explored by X-ray diffraction, Raman, and synchrotron-based micro-FT-IR measurements. All measurements revealed a pressure-induced structural phase transition at about 10 GPa. Here the initially green color of the crystal changes to black. However, the IR measurements show that the insulating properties are preserved at high pressure.

The magnetic phase diagram of Cu_2OSeO_3 has been examined in detail by ac-susceptibility (χ_{ac}) measurements. Here particular emphasis was placed on the details of the various phases (helical, conical and A-phase). It was observed that the A-phase boundaries are not sharp. This is interpreted as a softening of the underlying magnetic texture on macroscopic time scales, i.e., slower than 15 ms, over a relatively large field and temperature range. This and the details of pressure-induced structural and optical changes will be presented.

[1] G. Meunier, M. Bertram, and J. Galy, *J. Appl. Cryst.*, **9**, 364 (1976).

[2] K. Kohn, *J. Phys. Soc. Japan* **42**, 2065 (1977).

[3] C. L. Huang et al., Phys. Rev. B, **83**, 052402 (2011).

[4] S. Seki et al., Phys. Rev. B, **85**, 220406(R) (2012).

[5] H. Wilhelm et al., Phys. Rev. Lett., **107**, 127203 (2011).

O 7.5

Search for magnetism in epsilon iron with neutron diffraction and x-ray emission spectroscopy

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From Bridgman's first cells to modern laser shock experiments, iron and high pressure science have always been inextricably linked due to its geophysical significance. Despite this intense study, the pressure region of iron's superconductivity (15 GPa - 30 GPa) still remains a mystery[1]. Ambient α-iron undergoes a structural transition at ≈13 GPa to ε-iron due to a loss of ferromagnetism, however the magnetic state of ε-iron is disputed. Mössbauer[2] rules out a local magnetic moment >0.05 μ_B but theory, Raman, and x-ray emission spectroscopy (XES)[3] hint at a larger local moment. Theory[4] predicts an afmII phase that is compatible with Mössbauer due to a low hyperfine field. The debate over the magnetism is intimately linked to superconductivity since it could be involved in the Cooper pairing. Our objectives are to map the P-T region where magnetism in ε-iron is seen with Kβ XES and to search for the afmII phase using neutron diffraction (NPD)[5].

Kβ XES was performed in a DAC from 3 GPa to 50 GPa and 4 K to 583 K. NPD was performed using a VX5 Paris-Edinburgh cell with double-toroidal anvils. Diffraction patterns were taken from 0 to 21.3 GPa at 300 K and then cooling to 1.79 K with a final pressure of 22.6 GPa.

In XES, the satellite has a discontinuous decrease in intensity, increase in width, and shift in energy at the α-ε transition. The satellite disappears between 30 GPa and 50 GPa and shows no change in temperature between 4 K and 583 K. NPD shows a complete transition to ε-iron at 19.5 GPa. Preliminary analysis finds no afmII peaks with a magnetic moment >0.1 μ_B compared to the predicted 0.7 μ_B. XES shows qualitatively that the magnetism is intrinsic to ε-iron and not a remnant from the α phase. The existence region fits well with x-ray diffraction results showing the c/a ratio decreasing until around 50 GPa. NPD does not rule out the afmII phase completely, but it does considerably reduce the region where it can exist. Together these two experiments support an interpretation that magnetic fluctuations faster than Mössbauer's timescale exist in ε-iron and could be behind its superconductivity.

[1] K. Shimizu et al, *Nature* **412**, 316 (2001)

[2] S. Nasu et al, *J. Phys. Condens. Matter* **14**, 11167 (2002)

[3] A. Monza et al, *Phys. Rev. Lett.* **106**, 247201 (2011)

[4] G. Steinle-Neumann, *Proc. Natl. Acad. Sci. U. S. A.* **101**, 33 (2004)

[5] S. Klotz et al, *High Pressure Res.* **36**, 73 (2016)

P 7.1

Relevance between Li^+-ion diffusion and elastomagnetic softness in solids, high pressure muon-spin rotation and relaxation on $Li[Li_xMn_{2-x}]$ O_4 with $0 \leq x \leq 1/3$

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Recent global warming and environmental pollution require more high-power and high-energy density lithium-ion batteries (LIBs) for electric vehicles. It has been empirically known in the LIB field that a hard and brittle electrode material shows a low rate-capability, whereas a soft and flexible electrode material shows a high rate-capability. We herein report the relevance between Li^+-ion diffusion (D_{Li}) and elastomagnetic softness in electrode materials with high pressure (HP-) muon-spin rotation and relaxation (μSR) measurements on $Li[Li_xMn_{2-x}]O_4$ (LMO) with $0 \leq x \leq 1/3$.1)

LMO samples were prepared by a conventional solid-state reaction technique, and characterized by X-ray diffraction (XRD) and electrochemical measurements. Weak-transverse-field (wTF-) μSR measurements were performed at the GPD beam line at Paul Scherrer Institut to know the change in magnetic transition temperature (T_m) under pressure (P) as a function of x. The piston-cylinder-cell made of Cu-Be25 alloy was used apply P up to 2.8 GPa at room temperature (T).

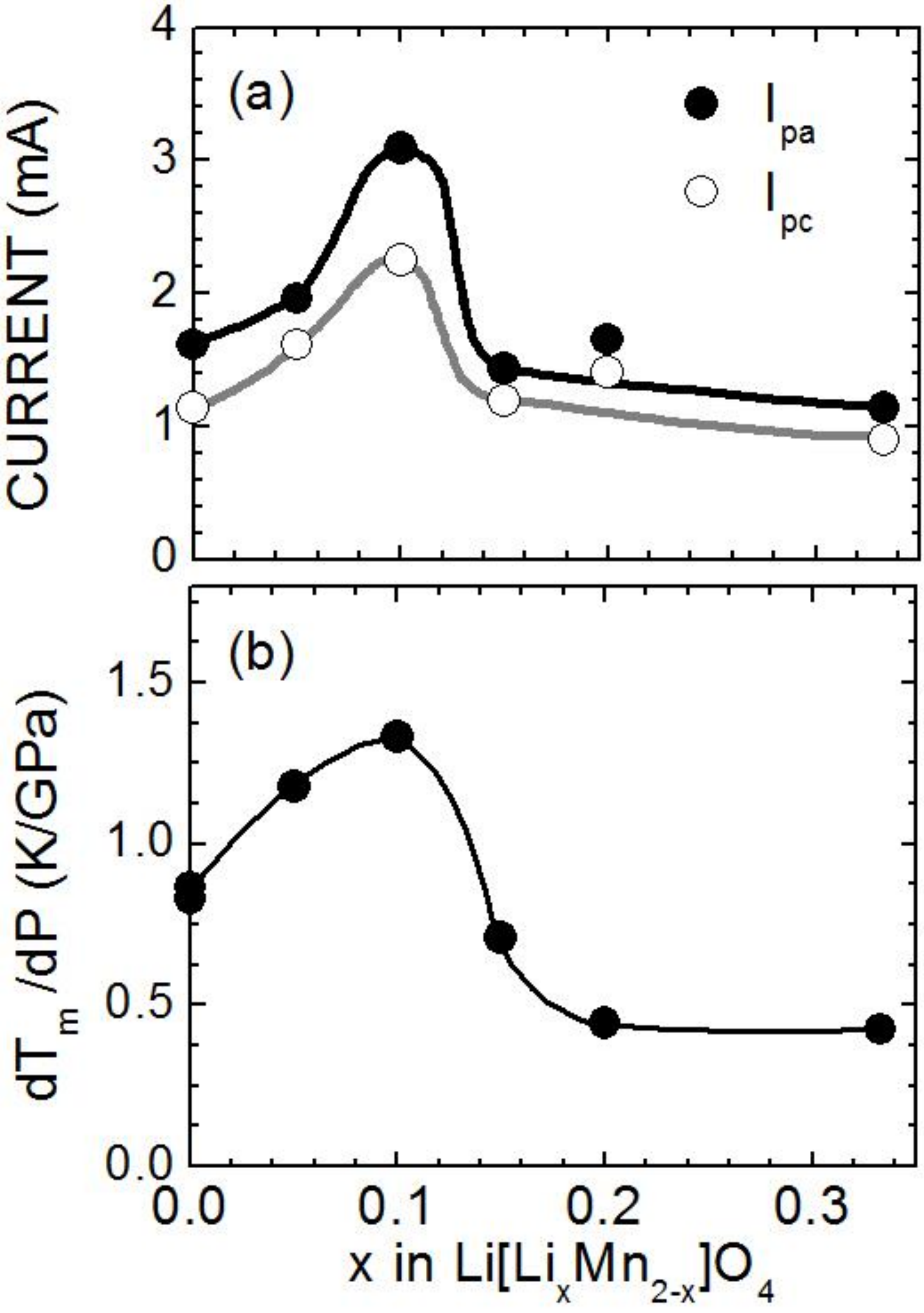
According to the XRD measurements, LMO has a spinel-framework structure, in which Li^+ ions occupy both tetrahedral 8*a* and octahedral 16*d* sites and Mn^{3+}/Mn^{4+} ions occupy only the octahedral 16*d* site in the *Fd*-3*m* space group.2) Figure 1(a) shows the x dependence of the peak current of at anodic direction (I_{pa}) and cathodic direction (I_{pc}) obtained by cyclic voltammomery. Both $I_{pa}(x)$ and $I_{pc}(x)$ curves exhibit a maximum at x = 0.1, indicating that D_{Li} has a maximum at x = 0.1 On the other hand, as seen in Figure 1(b), HP wTF-μSR measurements clarified that the P dependence of T_m (dT_m/dP) reaches a maximum at x = 0.1. Here, T_m means the Neel temperature for x = 0 sample and the freezing temperature of a spin-glass-like for $x \geq 0.05$, respectively. The x dependence of dT_m/dP implies that the x = 0.1 sample is softest in the whole x range. Since it has been reported that local compositional inhomogeneties during Li^+-ion diffusion generate a "diffusion-induced stress" (DIS),3) the elastomagnetic softness in the x = 0.1 sample is considered to relate with maximum D_{Li} in the LMO samples.

[1] K. Mukai et al., J. Appl. Phys. 113 (2013) 053904.

[2] G. Amatucci and J.-M. Tarascon, J. Electrochem. Soc. 149 (2002) K31.

[3] J. Christensen and J. Newman, J. Electrochem. Soc. 153 (2006) A1019.

Figure 1


(a)
● I_pa
○ I_pc
CURRENT (mA)
0
1
2
3
4
(b)
dT_m/dP (K/GPa)
0.0
0.5
1.0
1.5
0.0
0.1
0.2
0.3
x in Li[Li_xMn_2-x]O_4

P 7.2

Effect of low magnetic field and high pressure on the magnetic response of MnP clusters embedded in the chalcopyrite matrix

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The successful approach to integrate ferromagnetism with semiconductors involves ferromagnetic-semiconductor hybrid structures consisting of metallic clusters embedded into a semiconductoring host. An observation of very large magnetoresistance, the tunneling MR, and large magneto-optical effects in such hybrid composites making them a promising material for new magnetoelectronic devices [1]. The transport, structural and magnetic characteristics of hybrids may be tuned through the clusters size, shape, and the mean distance between clusters in the surrounding matrix. Here we present the hydrostatic pressure studies of the isothermal magnetization and volume changes up to 7 GPa of magnetic composite containing MnP clusters in the insulating CdGeP2 matrix. Instead of alleged superparamagnetic behavior, a pressure-induced magnetization process has found yet at zero magnetic field, showing enhancement at low field regime up to H≥5 kOe. We reveal that the maximum of zero-field magnetization at P=3.5 GPa is associated with the pressure-induced antiferromagnetic state of MnP clusters, followed by field-induced metamagnetism. In agreement with our observation [2], an unusual magnetization hysteresis at the pressure cycling also observed, showing gradual enhancement at magnetic field increasing. We discuss that the volume collapse by ~1.8% at *P*»5.5 GPa in the composite is the primary reason for this hysteresis which leads to different relaxation rates of both clusters and host matrix.

This work was supported by RFBR, (research projects: No 16-02-00210-a, No 16-32- 00661-mol_a) and partially supported by the RAS Presidium Program I.11 П.

[1] M. Tanaka, Semicond. Sci. Technol. 17, 327 (2002).

[2] T. R. Arslanov, L. Kilanski, S. López-Moreno, A. Yu. Mollaev, R. K. Arslanov, I. V. Fedorchenko, T. Chatterji, S. F. Marenkin, and R. M. Emirov, J. Phys. D: Appl. Phys. 49, 125007 (2016).

P 7.3

High-pressure synthesis and magnetic properties of A-site columnar ordered double perovskites, $\mathit{Ln}\mathrm{Mn}(\mathit{B}_{0.5}\mathrm{Ti}_{0.5})_2\mathrm{O}_6$

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There are many perovskites which can be synthesized by high-pressure method. However, there are only two reports for A-site columnar ordered double perovskites (general formula: $AA'B_2O_6$, Figure 1) *i.e.*, $CaFeTi_2O_6$ and $CaMnTi_2O_6$ [1,2]. These perovskites contain Ca^{2+} and Ti^{4+} ions in *A*- and *B*-site and no reports about the other cations in these sites of A-site columnar ordered double perovskite. In this study, A-site columnar ordered double perovskites $Ln\mathrm{Mn}(B_{0.5}\mathrm{Ti}_{0.5})_2\mathrm{O}_6$ (*Ln* = Sm, Gd, and *B* = Fe, Ga) have been successfully synthesized by high-pressure method. We refined the crystal structure and measured with the magnetic properties of these A-site columnar ordered double perovskites.

The A-site columnar ordered perovskites $Ln\mathrm{Mn}(B_{0.5}\mathrm{Ti}_{0.5})_2\mathrm{O}_6$ were all synthesized by high-pressure and high-temperature method using the stoichiometric mixtures of metal oxides. The recovered samples were subjected to synchrotron powder X-ray diffraction measurement with the wavelength of approximately 1 Å. Refinement of crystal structure was performed by Rietveld method. The magnetization of these compounds were measured by using SQUID magnetometer.

From the synchrotron powder X-ray diffraction patterns, almost all diffraction peaks can be indexed by space group $P4_2/nmc$ or $P4_2mc$ with lattice parameter a, $c \approx 7.5$ Å which indicates that the A-site ordered double perovskites $Ln\mathrm{Mn}(B_{0.5}\mathrm{Ti}_{0.5})_2\mathrm{O}_6$ (*Ln* = Sm, Gd, and *B* = Fe, Ga) were successfully synthesized. We will discuss about magnetic properties of these A-site columnar ordered double perovskites.

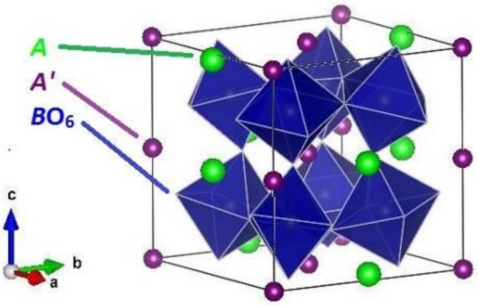
Figure 1. Crystal structure of A-site columnar ordered double perovskite $AA'B_2O_6$.

References

[1] K. Leinemweber, and J.B. Parise, J. Sol. Stat. Chem. 114, 277 (1995).

[2] A. Aimi, D. Mori, K. Hiraki, T. Takahashi, Y.J. Shan, Y. Shirako, J.-S. Zhou, and Y. Inaguma, Chem. Mater. 26, 2601 (2014).

Figure 1



P 7.4

Structural complexity at high pressure in supramolecular analogues of frustrated magnets

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The study of frustrated magnets has led to an understanding of some of the most beautiful and complex disordered structural states known [1]. In such materials, magnetic interactions compete with each other or with the underlying lattice geometry such that ordering cannot occur; for example, Ising spins arranged on a two-dimensional triangular lattice may never fully order antiferromagnetically [2]. Many of the most exotic frustrated magnets are not, however, physically realisable. We have recently shown how chemically 'simple' metal cyanides can act as supramolecular analogues of two-dimensional triangular XY magnets [3]. Here the key structural degrees of freedom—the relative shifts of neighbouring gold(I)/silver(I) cyanide chains in AgCN, AuCN and $Ag_{1/2}Au_{1/2}(CN)$ [4]—are mathematically equivalent of the phase angle of rotating planar spins [Fig.1]. Complex magnetic states predicted for this family of magnets, including collective spin-vortices of relevance to data storage applications [5], are realised in the structural chemistry of these cyanide polymers for the first time.

Undoubtedly the most exciting avenue of research is the exploration of excitations and/or response of these materials to external stimuli [6]. Are the screw dislocations observed in $Ag_{1/2}Au_{1/2}(CN)$ fixed or mobile? Do we observe pinning/unpinning phenomena known for spin vortices? Are high-pressure structures dominated by volume or interaction effects (or a combination of both)? Here we present studies on the high-pressure behaviour of AgCN and $Ag_{1/2}Au_{1/2}(CN)$ using a combination of synchrotron powder X-ray diffraction and quantum mechanical calculations. A series of phase transitions for each is interpreted primarily in the context of our theoretical understanding of frustrated magnets, but may also give insight into the behaviour of complex magnetic states under extreme conditions.

Figure 1. Crystal structures of (a) AuCN and (b) AgCN and their relationship to the ground states of triangular XY (anti)ferromagnets.

[1] J. A. M. Paddison *et al.*, *Science,* **2015,** *350,* 179-181.

[2] R. Moessner and A. P. Ramirez, *Phys. Today*, **2006,** *59,* 24-29.

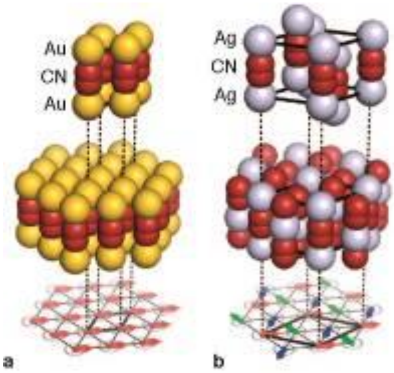
[3] A. B. Cairns *et al.*, *Nature Chem.*, **2016** (doi: 10.1038/nchem.2462).

[4] A. M. Chippindale *et al*., *J. Am. Chem. Soc.*, **2012,** *134,* 16387-16400.

[5] M. Žukovič and T. Idogaki, *Physica B*, **2003,** *329-333,* 1055-1056.

[6] F.-X. Coudert, *Chem. Mater.,* **2015,** *27,* 1905-1916.

Figure 1



Invited Talk

Pressure-induced multi-stage electronic transitions in Fe^{3+} oxides

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Iron oxides have been in the focus of research not only due to their applications as semiconductors, and features such as multiferroicity, and more recently superconductivity, but also due to their abundance in various layers of Earth's interiors. High-pressure has been known to change electronic/magnetic and structural properties of such compounds.

Our primary goal was to study the evolution of the pressure-induced structural and electronic/magnetic properties of a few iron oxides including a few ferrite spinels MFe$_2$O$_4$ (M=Mg, Co, Zn, Fe) and LiFe$_5$O$_8$, and Fe$_2$O$_3$ hematite.

Diamond anvil cells were used to induce pressure, in combination with synchrotron x-ray diffraction for determining the structure, Mössbauer spectroscopy measurements for probing the local environment of the Fe^{3+} cations, and electrical resistance measurements for observing any changes in transport properties.

Our studies reveal a new scenario of the Mott transition in ferric compounds - a *multi-stage site-selective correlation breakdown*. We demonstrate that in a material with a complex crystal structure, even if it contains only one cation, closure of the gap, collapse of magnetic moments, and the insulator-metal transition do not necessarily occur simultaneously and may propagate through different crystallographic sites at different degrees of compression. Each stage of the transition could be associated or unassociated with a structural re-arrangement. Moreover, for the particular case of Fe$_2$O$_3$, our work resolves the long-standing controversy regarding the nature and mechanism of a series of intricate structural/electronic-magnetic pressure-induced transitions. Our results suggest that the multi-stage correlation breakdown may occur in many different 3*d* TM compounds whose structure, similarly to the studied compounds, contains cation(s) in different environments. Furthermore, such an effect(s) may be common for crystalline materials and minerals constituent of Earth and planetary mantles. Indeed, major components of Earth's lower mantle contain iron (both ferrous and ferric), and changes in material state, induced by a correlation breakdown, may affect the properties of mantles. In all cases of studies of transition-metal bearing oxides the studied materials could serve as a model compound of the high-pressure behavior.

We have shown, for the first time, a few cases where the electronic transitions (Mott and high-spin to low-spin) can occur at different pressures for Fe located in different crystallographic sites, depending on the local environment (coordination number, average Fe-O distances).

O 8.1

Local structure and spin transition in Fe_2O_3 hematite at high-pressure

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The structural and electronic properties of Fe_2O_3 hematite as a function of pressure has been investigated for the first time by extended x-ray absorption fine structure up to about 79 GPa. Below the phase-transition, occurring at about 50 GPa, no increasing in the FeO_6 octahedra distortion is observed as pressure is applied, in contrast to Rozenberg et al. [1]. At the phase-transition, an abrupt decrease in the nearest-neighbor Fe-O distance is observed. Concurrently, we observe a decrease of the nearest-neighbor Fe-O static disorder, indicating a reduction in the FeO_6 distortion. These EXAFS results represent an excellent test-bench for proposed or new high-pressure forms of Fe_2O_3. Comparison to the different HP phases proposed in the literature rules out the $GdFeO_3$-type orthorhombic perovskite form as well as the most accepted distorted Rh_2O_3-II structure [1-3], and rather suggests that the orthorhombic structure with space group Aba2 [4] is the most appropriate among those reported in literature. Finally, the pressure-induced Fe^{3+} high-spin to low-spin transition has been monitored from the pre-edge peak of the Fe K-edge absorption spectra. The simultaneous comparison with the pressure evolution of the local structural transition determined by EXAFS, extracted from exactly the same spectrum and from exactly the same portion of sample, allows us to conclude that it is the electronic transition that drives the structural transition and not vice versa, thus definitively solving the longstanding controversy on the nature of the phase-transition. The details of the dynamics of this phase transition, and in particular, the nature of the observed metastable phase, call for further theoretical and experimental investigations.

[1] G. Kh. Rozenberg et al., Phys. Rev. B 65, 064112 (2002).

[2] Y. Syono et al., Solid State Commun. 50, 97 (1984).

[3] M. P. Pasternak et al., Phys. Rev. Lett. 82, 4663 (1999).

[4] E. Bykova et al., Nature Comm. 7, 10661 (2016).

O 8.2

Pressure-induced electronic change of iron in complicated silicate glasses

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Introduction

Deep magmas may explain seismic anomalies observed at various depths in the deep Earth. Since the stability and properties of deep magmas are still unknown, the existence of deep magmas is a controversial problem. In particular, the iron in magmas may affect several properties of magmas because iron is a heavy and abundant element in the Earth.

Silicate glasses are often used as an analog for deep magmas in high-pressure experiments. The studies about spin states of iron in silicate glasses suggested that a spin transition of iron from high-spin (HS) to low-spin (LS) state might change an iron distribution or optical properties of magmas.

Objective

We have focused on the effect of iron in deep magmas and measured the spin state of iron in basaltic glasses at high pressures (0-130 GPa). Basaltic melt is a typical complicated system on the Earth and thus is often used as analog for complicated deep magma.

Materials & Methods

Two glasses having different oxidizing conditions ($Fe^{2+}/\Sigma Fe \sim 0.33$ and $Fe^{2+} /\Sigma Fe \sim 0.93$) were prepared by quenching molten mixtures of oxides and carbonates in an atmospheric furnace. We have used a diamond anvil cell combined with synchrotron ^{57}Fe Mössbauer spectroscopy at BL10XU and BL11XU of SPring-8. The acquired spectra were analyzed using extended Voigt-based fitting method in MossA software. The Fe^{3+}-rich glass was recovered from 130 GPa and observed using a transmitted electron microscope.

Results

The Mössbauer spectra were fitted based on two-doublets models composed of HS Fe^{2+} and HS Fe^{3+} in two basaltic glasses at 0-130 GPa. A ratio of HS Fe^{2+} and Fe^{3+} in the Fe^{3+}-rich glass shows an unusual behavior: the $Fe^{2+}/\Sigma Fe$ decreases at pressures from 70 to 100 GPa. The recovered sample from 130 GPa recorded no structural changes. The Mössbauer spectrum of the recovered sample had a poor statistics. The measurements for Fe^{2+}-rich glass is now going on.

Conclusion

We studied the spin states of the basaltic glass containing both Fe^{2+} and Fe^{3+}. Both Fe^{2+} and Fe^{3+} in the glasses show high spin state, and no evidence for the spin transition to 130 GPa. However, the acquired spectra show the unusual decrease of the $Fe^{2+}/\Sigma Fe$ at 70-100 GPa in the Fe^{3+}-rich basaltic glass and the cause of the decrease was not able to be revealed. The more detailed studies are essential in future.

O 8.3

Pressure-induced spin pairing transition in trivalent iron octahedrally coordinated by oxygen

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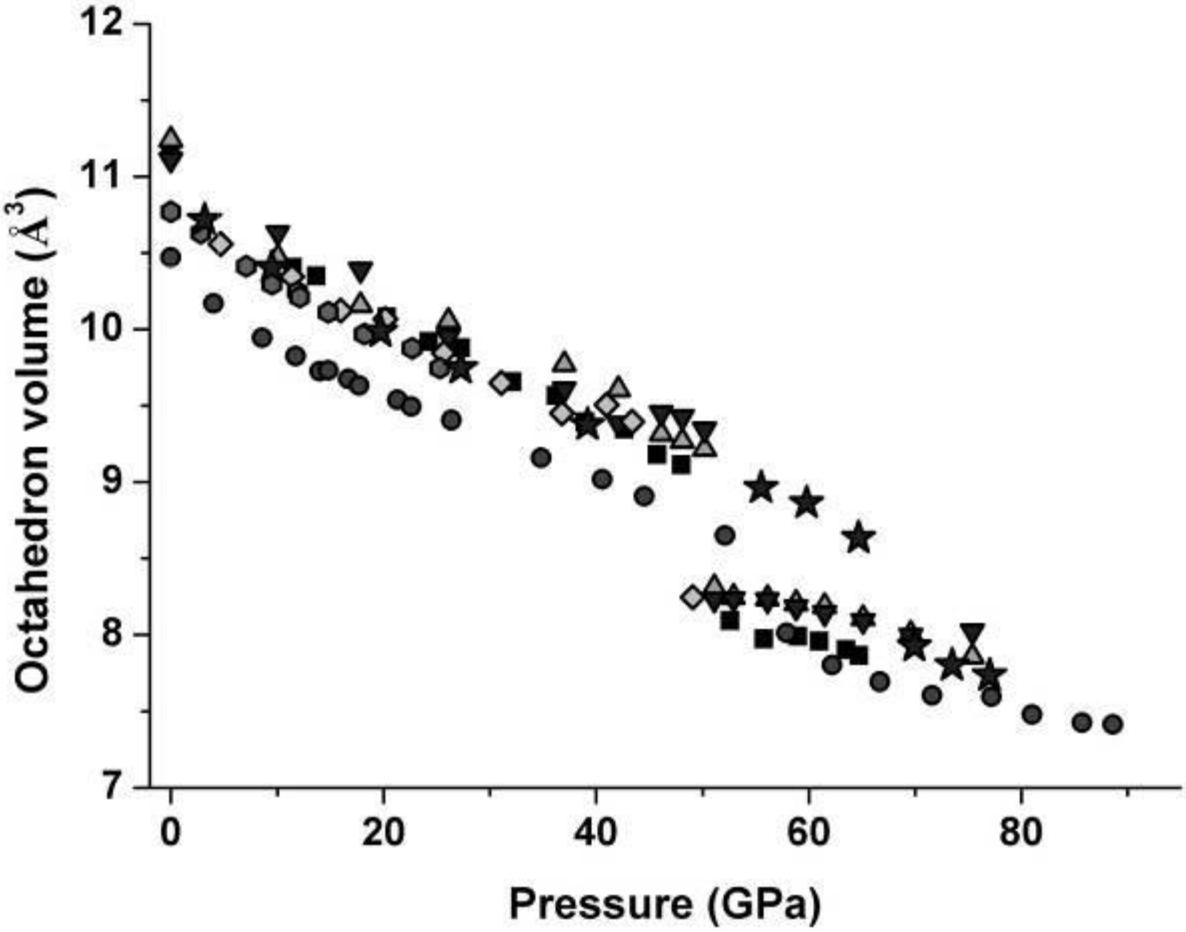
The spin pairing transition in transition metals (also known as spin crossover) is an important phenomenon that can cause drastic changes in the physical properties of materials, including volume, compressibility, electrical conductivity, magnetism and element partitioning. High pressure can provoke pressure-induced spin crossover in transition metal-bearing compounds that has important consequences for geochemistry and also attracts interest of fundamental science.

The Mössbauer spectroscopy (MS) coupled with single crystal X-ray diffraction are extremely powerful combination for investigation of spin crossover. Recent advances in high-pressure crystallography enable careful investigation of the geometry of the FeO_6 octahedron before and after the pressure-induced spin transition through single-crystal X-ray diffraction. We conducted a comparative study of compounds containing ferric iron octahedrally coordinated by oxygen (iron borate ($FeBO_3$), hematite (α-Fe_2O_3), skiagite - iron majorite solid solution ($Fe_3Fe_2(SiO_4)_3$- $Fe_3(FeSi)(SiO_4)_3$)) to reveal the regularities in the behaviors of hyperfine parameters and the correlation between them and crystal chemistry.

The analysis of our new data combined with results from the literature showed the following: (*i*) despite the different values of the crystal field splitting parameter and the Racah parameter B shown by the different compounds at ambient conditions, all undergo spin transition within a narrow range of pressures (45-60 GPa); (*ii*) in all compounds studied the transition starts at octahedron volumes between 9.0 and 9.4 Å^3; (*iii*) the significant spread of quadrupole splitting values for low spin Fe^{3+} may be related to the presence of a cooperative Jahn-Teller effect in some compounds.

Figure 1. Volume of $Fe^{3+}O_6$ octahedra as a function of pressure for different compounds. Squares correspond to iron borate, circles to skiagite - iron majorite, triangles to two different structural positions in calcium ferrite, diamonds to goethite, hexagons to hematite and stars to andradite.

Figure 1



O 8.4

Pressure-induced spin transition of Fe^{2+} in magnesio-siderite solid solution and siderite studied by x-ray Raman scattering

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Iron is the most abundant transition metal in the bulk Earth and has in contrast to other major Earth elements partially filled 3d electronic orbitals. The 3d electrons show a pressure induced high-spin (HS) to low-spin (LS) transition at conditions of the lower Earth's mantle [1]. This transition results in a volume collapse of the unit cell and an associated change of the magnetic properties. The transition influences macroscopic properties such as sound velocity, conductivity, compressibility as well as the geochemical behavior. Owing to the low solubility of carbon in Earth mantle silicate phases, carbonate minerals may form as evidenced by inclusions found in diamonds originating from the Earth’s mantle. Due to subduction at convergent boundaries carbonates are transported into the interior of the Earth from the Earth’s surface. Therefore, carbonates are candidates for carbon storage in the deep Earth and may play an important role for the Earth’s carbon cycle [2]. At conditions present in the lower mantle, magnesite ($MgCO_3$) and siderite ($FeCO_3$) form a solid solution. Previous investigations on the transition pressures and transition width of the end-member siderite and magnesio-siderite solid solution by x-ray emission (XES), x-ray diffraction and optical Raman spectroscopy delivered different results and led to controversial discussions with regard to the compositional effect on the spin transition [3,4,5].

We investigated the iron M- and L-edges of siderite and also the iron M-edge of [$(Mg_{0.6}Fe_{0.4})CO_3$] solid solution single crystal for pressures up to 50 GPa using diamond anvil cell by means of x-ray Raman scattering. The pressure induced spectral changes indicate, that the pressure range of the transition in the case of siderite is very sharp and starts at approximately 41 GPa. In addition, data measured on the solid solution, so far, suggest a considerable shift of the spin transition pressure to lower values. These results will be discussed and confronted with optical Raman, XES and Mössbauer studies.

[1] J. Badro., Annu. Rev. Earth Planet. Sci. 42, 231 (2014); [2] E. Boulard et al., J. Geophys. Res. 117, B02208 (2012); [3] J. Liu et al., Am. Mineral. 99, 84 (2014); [4] A. Spivak et al., Phys. Chem. Minerals. 41, 633 (2014); [5] V. Cerantola et al., Am. Mineral. 100, 2670 (2015);

O 8.5

Theoretical description of pressure induced electronic transitions: IMT, ETT, CLC

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Structural and magnetic transitions upon compression are well known. However, the extreme pressure affects the electronic structure as well. Insulator-to-metal transitions (IMT) [1] and the topological changes of the Fermi surface for valence electrons, the so-called electronic topological transition (ETT) [2], represent well-known examples of the electronic transitions. They have attracted substantial interest due to controversial claims on their observations, e.g. in NiO, Zn and Os. We discuss the IMT in NiO [3], ETT in hcp Fe [4] and Os [5], and emphasize the importance of correlation effects in the theoretical treatment of the electronic transitions. Moreover, considering Os compressed to over 770 GPa, we discuss the anomaly observed experimentally in the behavior of the unit cells parameters ratio *c/a* at ~440 GPa. We argue that the anomaly might be related to a new type of electronic transition, the core level crossing (CLC) transition, associated with interactions between the core electrons induced by pressure [5]. The generality of the CLC transitions is demonstrated in studies of other transition metals of the 6-th period [6].

[1] I. G. Austin and N. F. Mott, Science 168, 71 (1970).

[2] Lifshitz, I. M. Zh. Eksp. Teor. Fiz. 38, 1569 (1960); Sov. Phys. JETP 11, 1130 (1960).

[3] V. Potapkin, L. Dubrovinsky, I. Sergueev, M. Ekholm, I. Kantor, D. Bessas, E. Bykova, V. Prakapenka, R. Hermann, R. Rüffer, V. Cerantola, J. Jönsson, W. Olovsson, S. Mankovsky, H. Ebert, and I. A. Abrikosov (submitted to Phys. Rev. B).

[4] K. Glazyrin, L.V. Pourovskii, L. Dubrovinsky, O. Narygina, C. McCammon, B. Hewener, V. Schünemann, J. Wolny, K. Muffler, A. I. Chumakov, W. Crichton, M. Hanfland, V. Prakapenka, F. Tasnádi, M. Ekholm, M. Aichhorn, V. Vildosola, A. V. Ruban, M. I. Katsnelson, I. A. Abrikosov, Phys. Rev. Lett. **110**, 117206 (2013).

[5] L. Dubrovinsky, N. Dubrovinskaia, E. Bykova, M. Bykov, V. Prakapenka, C. Prescher, K. Glazyrin, H.-P. Liermann, M. Hanfland, M. Ekholm, Q. Feng, L. V. Pourovskii, M. I. Katsnelson, J. M. Wills, and I. A. Abrikosov, Nature **525**, 226-229 (2015).

[6] A. A. Tal, M. I. Katsnelson, M. Ekholm, J. Jönsson, L. Dubrovinsky, N. Dubrovinskaia, and I. A. Abrikosov, arXiv:1509.07433

O 8.6

Pressure-induced spin transitions in garnets at 45-70 GPa

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The importance of garnets within the Earth's mantle, the high symmetry of the garnet structure (space group *Ia*-3*d*), and the manifold cation and anion substitution mechanisms make garnets an ideal model system to study pressure-induced spin-pairing transitions of 3*d*-transition-metal cations. Specifically, the spin-pairing behavior in andradite may serve as a benchmark for that of Fe^{3+} located on the octahedral B-site of bridgmanite [1]. We have already reported on pressure-induced spin-pairing transitions in cubic andradite, $Ca_3Fe_2[SiO_4]_3$ (for Fe^{3+}) and tetragonal henritermierite, $Ca_3Mn_2[SiO_4]_2[O_4H_4]$ (for Mn^{3+}) [2,3], which occur in the pressure range of 55-70 GPa. In this study we will present our new results on the high-pressure structural compression and spin transitions of OH-free manganese garnets $Ca_3Mn_2[SiO_4]_3$ and blythite, $Mn_3Mn_2[SiO_4]_3$ up to 73 GPa.

$Ca_3Mn_2[SiO_4]_3$ and $Mn_3Mn_2[SiO_4]_3$ single crystals were synthesized at 6 GPa / 1100 °C and 5 GPa / 1100 °C, respectively, in a multi-anvil press and analyzed for their chemical compositions using the electron microprobe. Crystals were then pressurized in diamond anvil cells using neon as pressure-transmitting medium. High-pressure intensity data for single-crystal structure analyses were collected at the PETRA III synchrotron facility (beamline P02.2, DESY, Hamburg, Germany).

While the unit-cell compression does not show a distinct discontinuity at high pressure, the compression of the MnO_6-octahedra clearly shows a pronounced compression at about 45-65 GPa in both compounds, which can be related to the occurrence of a spin-pairing transition in Mn^{3+}. Results will be discussed with respect to our recent data on andradite and henritermierite [2,3].

Acknowledgements
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References

[1] J.-F. Lin, S. Speziale, Z. Mao, H. Marquardt, Rev. Geophys. 51, 244 (2013).

[2] A. Friedrich, B. Winkler, W. Morgenroth, J. Ruiz-Fuertes, M. Koch-Müller, D. Rhede, V. Milman, Phys. Rev. B 90, 094105 (2014).

[3] A. Friedrich, B. Winkler, W. Morgenroth, A. Perlov, V. Milman, Phys. Rev. B 92, 014117 (2015).

O 8.7

Interplay between H-bonding and charge ordering in $Fe_3(PO_4)_2(OH)_2$ barbosalite at high pressure

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Charge Ordering (CO) in transition metal oxides is an important parameter for obtaining original magnetic and/or electric properties. That was largely shown within the framework of the studies on colossal magneto-resistance in manganese perovskites and it again seems to be at the origin of the ferroelectricity in $CaMn_7O_{12}$ [1, 2] or $LuFe_2O_4$ [3, 4]. The mixed valence of iron in the system is a particular motivation in view of the long lasting research on the understanding of the effects of pressure on charge order/magnetic order in iron compounds such as the $LuFe_2O_4$ new charge ordered state [5, 6] and the pressure dependence of its magnetic order[7]. Here we focus on $Fe^{2+}Fe^{3+}_2(PO_4)_2(OH)_2$ barbosalite single crystal, an hydroxyphosphate of iron which exhibits a mixed valence state [8]. High pressure behaviour of barbosalite was succesfully characterized based on single crystal X-ray diffraction, Raman and infrared spectroscopies. $Fe^{2+}Fe^{3+}_2(PO_4)_2(OH)_2$ presents two phase transition at close to 3 and 8 GPa respectively which are clearly governed by an interplay between H-bonding and electron delocalization.

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References

[1] R. D. Johnson, L. C. Chapon, D. D. Khalyavin, P. Manuel, P. G. Radaelli, and C. Martin, Phys. Rev. Lett. ***108*** (2012).

[2] N. J. Perks, R. D. Johnson, C. Martin, L. C. Chapon, and P. G. Radaelli, Nat. Commun. ***3*** (2012).

[3] N. Ikeda, et al., Nature ***436***, 1136 (2005).

[4] M. Hervieu, A. Guesdon, J. Bourgeois, E. Elkaim, M. Poienar, F. Damay, J. Rouquette, A. Maignan, and C. Martin, Nat. Mater. ***13***, 74 (2014).

[5] J. Rouquette, et al., Phys. Rev. Lett. ***105*** (2010).

[6] F. Damay, et al., Phys. Rev. B ***91*** (2015).

[7] O. L. Makarova, et al., Applied Physics Letters ***103***, 082907 (2013).

[8] G. J. Redhammer, G. Tippelt, G. Roth, W. Lottermoser, and G. Amthauer, Physics and Chemistry of Minerals ***27***, 419 (2000).

O 8.8

Signatures for the pressure-induced phase transition in the iridates A_2IrO_3 (A = Na, Li) investigated by infrared spectroscopy

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The family of honeycomb iridates A_2IrO_3 (A = Na, Li) has recently attracted great interest due to its novel behavior and phases arising from the interplay of strong spin-orbit coupling, electron correlations, and lattice topology [1-3]. These materials show a magnetic order below » 15 K: Na_2IrO_3 has an antiferromagnetic insulating ground state with a zig-zag order, while Li_2IrO_3 has an incommensurate spiral order close to the spin liquid regime [4,5]. At ambient conditions, both compounds show an insulating behavior with a sizable gap of about 0.34 eV for Na_2IrO_3 and about 0.3 eV for α-Li_2IrO_3 [6-8].

Here, we report the results of a study on the electronic and vibrational properties of single-crystalline A_2IrO_3 (A = Na, Li) by reflectance and transmission measurements in the infrared frequency range under high pressure up to 15 GPa. With increasing pressure a reduction of the optical gap was observed. At around 5 GPa, the data show a lowering of the crystal symmetry via the splitting and the screening of the phonon modes, suggesting the occurrence of a pressure-induced structural phase transition.

[1] Ch. H. Kim et al., Phys. Rev. Lett. **108,** 106401 (2012).

[2] D. Pesin and L. Balents, Nature Phys. **6**, 376 (2010).

[3] B. J. Kim et al., Science **323**, 1329 (2009).

[4] Y. Singh and P. Gegenwart, Phys. Rev. B **82**, 064412 (2010).

[5] Y. Singh et al., Phys. Rev. Lett. **108**, 127203 (2012).

[6] C. H. Sohn et al., Phys. Rev. B **88**, 085125 (2013).

[7] R. Comin et al., Phys. Rev. Lett. **109**, 266406 (2012).

[8] Y. Li et al., Phys. Rev. B **91**, 161101(R) (2015).

O 8.9

Pressure-induced superconductivity in iron pnictide superconductor $BaFe_2(As_{1-x}P_x)_2$

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Iron pnictide superconductors are multiband high temperature superconductors that show a magnetically ordered (SDW) state in their parent compound. The superconducting (SC) state emerges from the SDW state with either doping or external pressure. In this study, temperature-dependent reflectivity measurements under pressure have been performed on $BaFe_2(As_{1-x}P_x)_2$ single crystals with x = 0 and 0.2 down to 6 K in a wide energy range. SDW and SC states have been investigated. The coexisting region has been observed for both samples, while it shifts to the lower pressure region with increasing P-content. The optimum pressure (maximum superconducting transition temperature under pressure) range has been observed in the coexisting region for the parent compound (x = 0). In contrast, for the slightly P-doped sample (x = 0.20), the optimum pressure region has been observed out of the coexisting region and shifts to the lower pressure range. The investigated pressure-induced superconducting state put forward resemblances between samples with x = 0 and x = 0.20, as well. In both cases nodeless superconductivity has been observed for the optimum pressure range. Previously, nodal superconductivity has been discussed for the P-substituted $BaFe_2As_2$ system, even though there was no consensus about the position of the nodes [1, 2]. Our observation of the nodeless superconductivity for x = 0.20 may indicate the crossover from nodal to nodeless superconductivity under pressure. However, we cannot rule out that the infrared spectroscopy measured in the current configuration is not sensitive to the portion of the Fermi surface, where the nodes exist.

[1] K. Hashimoto et al., Phys. Rev. B 81, 220501 (2010)

[2] P. J. Hirschfeld et al., Rep. Prog. Phys. 74, 124508 (2011)

Invited Talk

Phase transformations and relaxation in glassy chalcogenides under high pressure

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High precision measurements were taken of the specific volume of glassy germanium chalcogenides ($GeSe_2$, GeS_2, $Ge_{17}Se_{83}$, and Ge_8Se_{92}) and glassy As_2Te_3 under hydrostatic pressure to 9 GPa. For $GeSe_2$ and GeS_2 glasses in the pressure range to 3 GPa the behavior is elastic one with bulk modulus softening at pressures above 2 GPa. At higher pressures the relaxation processes begin that have logarithmic kinetics. The relaxation rate for $GeSe_2$ glasses has a clearly pronounced maximum at 3.5-4.5 GPa, which is indicative of the existence of several mechanisms of structural transformations. For As_2Te_3 glass the pressure range of elastic behavior is up to 1 GPa. At higher pressures there is unusual 2-stages transformation with logarithmic kinetics. For nonstoichiometric germanium-based glasses inelastic behavior is observed at pressures above 1-1.5 GPa, the relaxation rate being much less than that for stoichiometric ones. One can conclude that chalcogenide glasses under compression demonstrate both the features universal for disordered matter (elastic softening before conversion, transformation smearing, logarithmic relaxation, “loss of memory” about prehistory after isobaric aging, residual densification after depressurization) and specific features associated with details of chalcogenide glass structure. Such specific features are a coexistence of several mechanisms of structural modification and nonmonotonic concentration dependence of effective bulk modulus and its pressure derivative. The results obtained demonstrate high capacity of the volumetric measurements to reveal the nature of the transformations in glassy chalcogenides under compression.

O 9.1

Permanent structural changes of glassy carbon after compression in a diamond-anvil-cell

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Pressure-induced phase transformations in carbon continue to be a topic of much interest due to its significance in earth and other planetary sciences and its common usage in many technological applications requiring superhard, chemically inert materials. Despite a series of recent studies on the transformation from sp^2 bonded graphitic precursor materials to sp^3 bonded structures, a complete understanding of the phase transformation process on an atomic scale remains elusive.

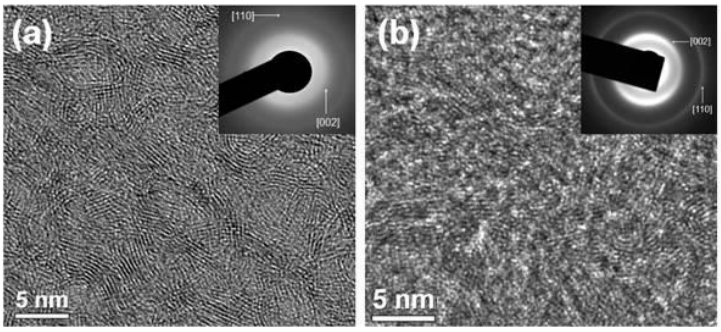
The focus of this work is to investigate the high-pressure phase transformation between sp^2 and sp^3 bonded carbon materials using glassy carbon as the precursor material. This is subjected to a high-pressure, high-temperature environment in a diamond-anvil cell and analysed with a range of *ex situ* experimental techniques before and after heating/compression as well as *in situ* during compression.

Transmission electron microscopy (TEM) images and diffraction patterns of pristine material and material recovered from 54 GPa are shown in Fig. 1. Permanent alteration to the material's microstructure after compression is clearly observed. Corresponding Raman spectroscopy shows a decrease in structural order, but strong retention of the sp^2 content after compression. TEM measurements thus show solely a permanent increase in density after room temperature compression. Additionally, changes to the sp^2:sp^3 bonding composition occurs upon heating during compression, including the appearance of the Lonsdaleite structure.

Thus, room temperature compression of glassy carbon in a DAC does alter the microstructure of the material permanently without inducing any changes to the bonding composition. In contrast, static high pressure under moderate-temperature conditions can induce additional conversion to metastable sp^3 bonded structures with high degrees of hexagonality.

Figure 1: (a) TEM image of unpressurised glassy carbon. (inset) Electron diffraction pattern (indexed to graphite) showing graphitic structures with no preferred structural orientation. (b) TEM image of recovered glassy carbon after room temperature compression to 54 GPa. (inset) Electron diffraction pattern (indexed to graphite) showing preferred structural orientation.

Figure 1



O 9.2

Does amorphous germanium exhibit polyamorphism?

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The phase behavior of amorphous germanium (a-Ge) remains under considerable debate. Some studies suggest that a-Ge crystallizes into the same crystalline metallic phases as does crystalline Ge upon compression. Other studies suggest that a-Ge undergoes a polyamorphic transition to a high density amorphous (HDA) phase. This discrepancy appears tied to the fact that the structure of amorphous covalent networks is critically dependent on their formation method and thermal history. To shed light on this possible polyamorphism, this study aims to correlate the high pressure behavior of different forms of a-Ge with their exact structural characteristics.

Therefore, two different forms of a-Ge were studied. The first was made via molecular beam epitaxy (MBE) under ultra-high vacuum conditions for high purity films. Its properties were assessed by electron microscopy and secondary ion mass spectrometry. The second was made via a cold-temperature decompression pathway that turns crystalline Ge into pure a-Ge. Semiconductor-grade, undoped prime Cz-grown Ge (99.9999%) was used as precursor to eliminate any uncertainty regarding the purity. The a-Ge structure was studied by *ex situ* neutron diffraction and *ex situ* neutron spectroscopy.

The MBE a-Ge was compressed in a diamond anvil cell (DAC) at room temperature to 20 GPa. *In situ* synchrotron X-ray diffraction reveals crystallization into the metastable four-fold coordinated r8-Ge form accompanied by a small portion of the metallic crystalline (β-Sn) phase. No evidence of HDA Ge was detected. The same transition sequence was observed under high shear and quasi-hydrostatic conditions. This r8-Ge can however, only nucleate at temperatures above ~77 K thus not excluding the formation of HDA Ge at low temperatures. To fully resolve this question, the ultra-high purity a-Ge will be studied at temperatures below 77 K. Therefore, *in situ* neutron diffraction in a DAC up to 15 GPa is currently in progress. Recent development in the geometry of neutron DACs allows for capture of a very large diffraction angle, thus enabling highest *Q in situ* structural data.

Our study thus demonstrates that sufficiently pure a-Ge crystallizes upon room temperature compression, but will also shed significant new light on the role of impurities and stress conditions in the polyamorphism of Ge.

O 9.4

Polarized Raman spectroscopy of v-SiO_2 under rare gas compression

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High-pressure polarized Raman spectra of vitreous silica are measured up to 8 GPa in a diamond-anvil cell at room temperature [1]. The combined use of either a non-penetrating pressurizing medium, argon, or a penetrating one, helium, allows to separate density from stress effects on the Raman frequencies. In the framework of a simple central force model, the results emphasize the distinct role played by the shrinkage of the inter-tetrahedral angle Si-O-Si and the force-constant stiffening during the compression. The polarization analysis further reveals the existence of an additional isotropic component in the high frequency wing of the Boson peak. The pressure dependence of the genuine Boson peak frequency is found to be much weaker than previously reported and even goes through a minimum around 2 GPa in a remarkable coincidence with the anomalous compressibility maximum of silica.

[1] C. Weigel, M. Foret, B. Hehlen, M. Kint, S. Clément, A. Polian, R. Vacher, B. Rufflé, Polarized Raman spectroscopy of v-SiO_2 under rare gas compression, submitted (2016)

O 9.5

Impact of high pressure on glass-forming soft matter nanocomposiates

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The glass transition is one of the most important unsolved problems in 21st century. Glassy dynamics in soft matter can be studied by various methods but the commonly used one is the broadband dielectric spectroscopy. Combining linear and nonlinear (strong electric fields) measurements it is possible to describe collective motions in soft matter systems. Pressure or temperature evolution of relaxation times is mostly illustrated via Arrhenius and Vogel-Fulcher-Tammann (VFT) equations. In this work relaxation processes in glass-forming soft matter composites doped nanoparticles are discussed. Pretransitional effects in liquid crystalline nanocomposites, amorphous solids and supercooled liquids with nanoparticles dispersion are very interesting from the scientific point of view and the modern industry. Studying dielectric properties of nanoparticles dispersed composite materials permits to peek into nature of glass transition and full characterize systems. The dependence of relaxation time were carried out in wide range of frequency (10^{-6} - 10^{9} Hz), temperature (-150°C - 400°C) and pressure (0.1 MPa - 2 GPa). All electric properties like conductivity, dielectric constant and molecular relaxation processes strongly depend on nanoparticles concentration. New properties of materials (higher hardness, density), changes in phase transitions, emerging new relaxation processes there were obtained in this study.

O 9.6

Electronic origin of melting T-P curves for alkali metals with flat, negative slope and minimum

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Group I elements - alkali metals from Li to Cs - are examples of *simple* metals with 1*s* electron in the valence band. Under pressure they display unusually complex structural behaviour transforming from close-packed to low symmetry open structures [1]. Unexpectedly complex form was found for melting curves of alkalis under compression with initial increasing in accordance to Lindemann criterion and further decreasing to very low melting point [2,3]. To explain complex and low symmetry structures in compressed alkalis the model of the Fermi sphere (FS) - Brillouin zone (BZ) interaction was applied [4,5]. Within this model one can understand the complex melting curves of alkalis.

Flat and negative slope of melting curve may result from a strong increase of band structure energy where the nearly spherical Fermi spheres of alkalis assume necks attracted to BZ planes. This attraction is reciprocal and leads to contraction of BZ and to expansion in real space. FS - BZ interactions exist also for liquids with spherical BZ and non-directional attraction to FS. FS-BZ interactions produce remarkable effect that liquid state become denser than crystal at some pressure. Similar effects may be responsible for flattening of T-P curves found for transition metals [6].

Deep minimum on melting curves is related to overlap of valence electron band and core electrons similar to suggested transfer for the structures Na-*oP*8 and K-*oP*8 assuming that Na and K become divalent metals at compression [4,5]. Electron transfer may occur in liquid state and even at lower pressure. The only one liquid metal is known at ambient conditions - the divalent metal Hg. Experimental diffraction data on liquid alkalis near the minimum of T-P melting curve display deformation of the first diffraction peak with appearance of shoulder like for liquid Hg (as shown for liquid K [7]). Non-simple behaviour in melting of alkali metals on compression is connected with the essential changes of the electron state in the valence band.

[1] M. I. McMahon, R. J. Nelmes, *Chem Soc Rev* **35** 943 (2006)

[2] E. Gregoryanz, O. Degtyareva, M. Somayazulu *et al*, *Phys Rev Lett* **94** 185502 (2005)

[3] C. L. Guillaume, E. Gregoryanz, O. Degtyareva *et al*, *Nature Phys* **6** 211 (2011)

[4] V. F. Degtyareva, O. Degtyareva, *New. Phys **11** 063037 (2009)*

[5] V. F. Degtyareva, *Solid State Sci* **36**, 62 (2014)

[6] S. Japel, B Schwager, R. Boehler and M. Ross, *Phys Rev Lett* **95** 167801 (2005) [7] O. Narygina *et al*, *Phys Rev B* **84** 054111 (2011)

O 9.7

Pressure-induced liquid-liquid transition in early transition metal Ti with a positive melting slope

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Pressure-induced amorphous-amorphous or liquid-liquid phase transitions (AAPT or LLPT) have been discovered in many material systems. Moreover, some elemental materials show the transitions between disordered structures. So far, the polyamorphisms have been found in either *sp*-valent materials, or *f*-valent rare-earth elements with maximum or a negative slope in the melting line, but not in *d*-valent transition metals. Here we study the pressure-induced LLPT in liquid Ti using *ab-initio* molecular dynamics calculations, supported by diamond-anvil-cell (DAC) measurements. Structure factor, pair distribution, microstructural analysis, DOS, and velocity auto-correlation function show the signal of LLPT. This behavior appears to be characteristic of the early transition metals. In contrast, the late transition metal liquid Ni does not show the LLPT with pressure, which suggests that the possibility of the LLPT decreases from early to late transition metals due to electronic structural difference. In addition, the polyamorphism in liquid Ti may be responsible for the low melting slope and the following characteristic knee at high pressure as measured in DAC that is absent in the melting curve for Ni up to the highest pressure 120 GPa.

O 9.8

Water and methane: when models fail to explain newly discovered phenomena

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We presented last year a novel quantitative imaging technique that allows accurate determination of the solubility in various binary-mixtures, and how we successfully applied this to the case of methane and water under extreme conditions. This revealed an unexpected increase in the solubility of methane in water in the 1-2 GPa range, followed by a saturation concentration of 41(2) mol % above 2 GPa.

These changes have a profound effect on modelling planetary interiors (such as those of Neptune, Titan or Uranus), since the value of the miscibility determines whether the planet exhibits differentiated layers or a single, multi-component one, which impacts convections, magnetic properties and many others.

In this talk we will present our results from applying classical molecular dynamics to this specific problem, and critically asses what they tell us and whether that is about the real behaviour or the shortcomings in our computational models. A range of water potentials has been tried, and we will report on their similarities and differences in what concerns their behaviour in the presence of methane. The results likely suggest that in order to reproduce the experimentally observed better models are needed, possibly both for water and methane, also highlighting the limits of some vastly used potentials.

O 9.9

Reporting on the high pressure thermal decomposition of *2,4,6*-triamino-*1,3,5*-trinitrobenzene (TATB)

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TATB is an insensitive high-energy-density $C_6H_6N_6O_6$ molecule of significant global and technological importance. Since 1980, there have been 800+ published papers on TATB; in 2015 there were nearly 7,000 TATB energetic material citations (Web of Science^{TM}, March, 2016). And yet, there are only a handful of peer-reviewed papers communicating experimental-based quasi-static high-pressure (GPa) TATB thermal decomposition results. The accuracy of numerous first-principle and thermochemical (equilibrium) calculations of extreme P-T condition decomposition of TATB is hampered because intermediate carbon-based species delay the release of chemical energy or end-state products formation, -carbon specie kinetics play a central role in TATB decomposition. Here we report chemical stability and decomposition results in the pressure range of 2-35 GPa. We use diamond-anvil cells to encapsulate samples and laser heating (highly localized) and electrical/resistive heating (highly uniform) methodologies to initiate decomposition chemistry. Our *in situ* measurements are conducted using µ-Raman (CW probe) and in-house (tabletop) µ -FTIR vibrational spectroscopy diagnostics.

On the basis of our spectroscopic results we find that very few of the measured ambient pressure products [1] are produced at GPa pressures. For example, (up to this writing), we have no definitive spectral signature of H_2O: most theoretical and semi-empirical studies conclude it should be a measurable equilibrium product. We do measure carbon, N_2, and CO_2 spectral peaks up to 15 GPa. It is plausible that carbon and water intermediates react to form additional CO_2; however, intense laser heating does not appear to decompose TATB above 20-25 GPa, -at least when ~10 µm grains are suspended in solid argon and a near-IR wavelength laser heating beam is used. In the absence of a pressure transmitting medium, pressurized TATB deflagrates violently when irradiated with a single visible wavelength 10 ns, 10-µJ laser pulse [2].

Figure 1. Temperature dependent µ -FTIR spectra from thermally (uniformly heated) decomposed TATB.

Figure 2. Pressure dependent µ -Raman spectra from 1064 nm laser-heated TATB.

[1] T.B. Brill and K.J. James, *J. Phys. Chem.*97, 8752 (1993).

[2] M. Francis Foltz, *PEP*18, 210 (1993).

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Figure 1

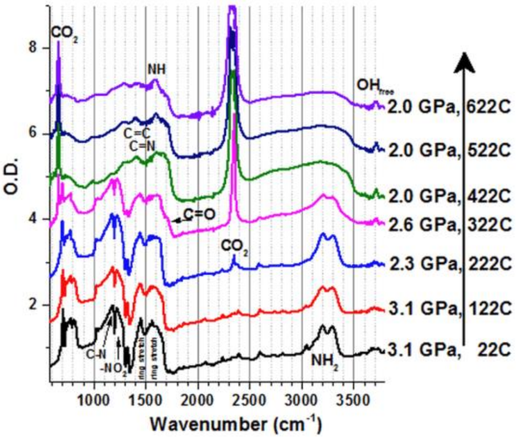
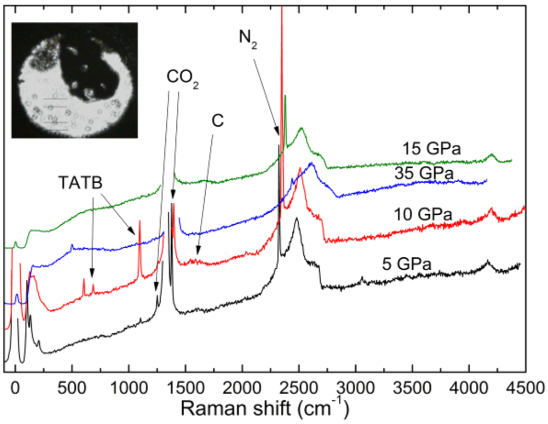


Figure 2



O 9.10

Phase relations, reactivity and new materials landscapes in alloys, nitrides using extreme conditions, X-ray, precession electron diffraction and electron microscopy

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We induce changes in crystal symmetry, atomic radii, melting points and metallicity with pressure and temperature to transform existing and prepare new materials landscapes with targeted properties. We make these changes using the collective advantages of laser-heated diamond cell, multianvil and piston cylinder devices. Effective characterization of the new material territory is made possible by exploiting the complementary merits of precession electron diffraction, X-ray diffraction and electron microscopy for structural, chemical and morphological analysis. We present here results for group IV alloys as well as metal nitrides which have a clean energy, mechanical and planetary science remit.

O 9.12

Mid-ocean ridge basalt - serpentinized mantle interaction producing primary tholeiitic melts is fast-rate

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Mid-ocean ridge basalt (MORB) is frequently considered to be derived from depleted endmember MORB-mantle component (DMM). This paradigm implies the MORB isotopic compositions to be representative for the upper mantle source region. However, finding of oceanic boninites and depleted mafic cumulates that crystallized from a silica-enriched and incompatible elements-depleted melts, frequently with radiogenic $^{87}Sr/^{86}Sr$ ratios, advocates MORB interaction with overlaying serpentinized lithosphere. We report results of piston cylinder experiments constraining mechanisms and rates of mid-ocean ridge basalt (MORB) - hydrous mantle (serpentinite) interaction from 0.5 to 1.0 GPa at 1300°C with varying initial water contents. The data imply that the reaction is controlled by a two-stage mechanism: (1) initial incongruent melting of serpentinite with instantaneous crystallization of chromitebearing wehrlite in association with hydrous basaltic andesite to andesite melts (53 - 61 wt% of SiO_2 and 3 - 6 wt.% of MgO contents) and (2) the following congruent dissolution of the produced minerals with formation of primitive mafic melts (50 - 52 wt% of SiO_2, 10 - 13 wt.% of MgO contents), sometimes associated with dunite (Fo_{89-94}). The produced first series of hydrous melts is chemically similar to oceanic andesites and boninites. The produced second series of primitive melts demonstrates similarity to primary MORB melts. Our data indicate that natural basaltic melts, if produced by the investigated reaction with serpentinized mantle lithosphere, may be distinguished from "normal" MORB melts by an excess of H_2O, halogens and unusual isotope composition (e.g., radiogenic $^{87}Sr/^{86}Sr$, non-mantle $\delta^{18}O$ and low $^{3}He/^{4}He$). We experimentally demonstrate that chemical evolution of MORB depends on how fast the basaltic melt is transported from its anhydrous mantle source and how long it interacts with the overlaying hydrous mantle lithosphere. Our study prevents routine interpretation of variably enriched primary MORB melts and primitive basalts as uniquely derived from upper mantle DMM component, especially those produced in slow spreading ocean ridges.

P 9.1

Influence of the hydrogen bonding degree on the elastic properties of propylene glycol oligomers under high pressure

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Hydrogen bonds play an important role in the intermolecular interaction of molecular glassformers. Molecules of the investigated substances (mono-, di- and tripropylene glycol) have different weights and lengths, but the number of the hydroxyl OH groups remains constant and equals 2 [1,2]. We have studied the elastic properties of the oligomers of propylene glycol under high pressure in liquid and glassy state, and at the glass-liquid transition in order to determine the effect of the specific amount of hydrogen bonding on the elastic properties.

Elastic properties of propylene glycol oligomers were studied under high pressure up to 1 GPa in liquid state (at room temperature) and up to 1.8 GPa in glass (T=77 K). Experiments were carried out using a high-pressure ultrasonic piezometer based on the piston-cylinder device. Measurements of the changes in the transit times of longitudinal (10 MHz) and transverse (5 MHz) ultrasonic pulses were performed by the pulsed method using *x*-cut and *y*-cut $LiNbO_3$ plates as piezoelectric sensors. Bulk and shear moduli and Poisson's ratio were calculated from the ultrasonic data on transit time and length of the sample using approximation of homogeneous isotropic medium.

All three investigated substances have similar compressibility both in liquid and glassy state. Di- and tripropylene glycol have close values of the shear modulus G and the bulk modulus B, but both are considerably lower than the elastic moduli of monopropylene glycol (Fig. 1). Isobaric warming from 77 to room temperature revealed a monotonic dependence of the elastic moduli and glass transition temperature Tg from the mass of the molecules (Fig. 2). We can conclude that a high intermolecular connectivity, due to the large specific number of hydrogen bonds (like in propylene glycol), leads to strengthening of elastic moduli.

Literature

[1] Casalini R., Roland C. M., Phys. Rev. B, 2004, № 69, 094202

[2] Leo´n C., Ngai K. L., Roland C. M., J. Chem. Phys., 1999, № 110 (23), 11585

Figure 1. Pressure dependence of the shear and the bulk modulus of glassy propylene glycol oligomers (T = 77 K)

Figure 2. Temperature dependence of the elastic moduli of propylene glycol oligomers during glass-liquid transition (P = const = 0.05 GPa)

Figure 1

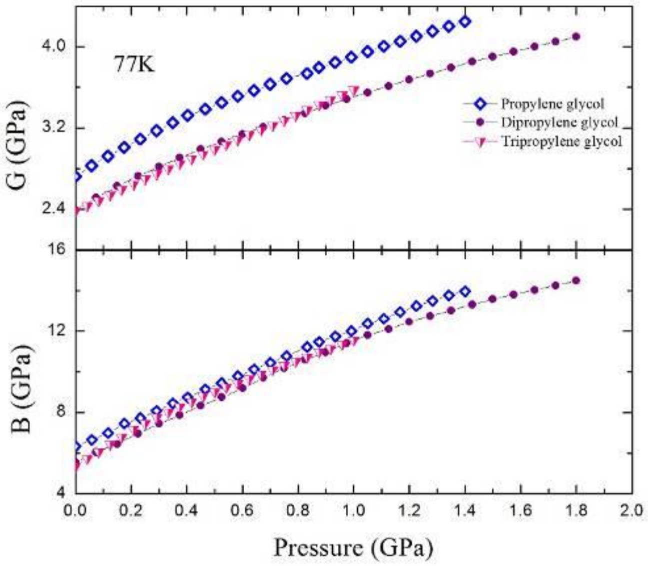
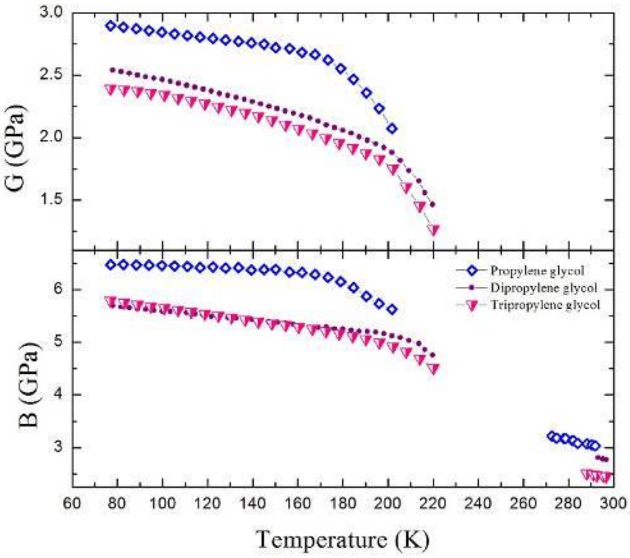


Figure 2



P 9.2

Probing fluid CH_4 deep into the supercritical region: Raman and X-ray diffraction measurements

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Recently the understanding that there is no discontinuous transition between gas-like and liquid-like states beyond the critical point (CP) has been questioned. A crossover between liquid-like and gas-like regions emanating from the CP and extending a finite distance from it, the Widom line, was observed experimentally [1]. Then a different crossover line was proposed, extending to arbitrarily high P, T and existing even in systems with no CP, the Frenkel line [2,3].

The Frenkel line is due to crossover between the time periods for the propagation of shear waves through the sample and atom/molecule hopping between adjacent atomic/molecular sites. On liquid-like side of the line the atoms/molecules stay stationary for long enough for shear waves to propagate, on the gas-like side they do not. Viscosity, thermal conductivity and specific heat capacity are expected to change when the line is crossed [2,3] so its existence would have wide ranging consequences.

We conducted a series of high P Raman spectroscopy and X-ray diffraction experiments on fluid CH_4 at T from 300 K to 520 K, nearly 3x the critical T (190 K). In our Raman experiments, we observe evidence of discontinuous transition between liquid-like and gas-like states at 300 K, but no evidence at higher T. In our X-ray diffraction experiments, we observe no discontinuous change in any property of the structure factor S(Q) at any T.

Our findings contrast to a recent diffraction study on supercritical Ar [4], claiming discontinuous change in properties of S(Q), including peak position, is observed at 400 K. We attribute the lack of similar observation in our own work to the continuous nature of our path through P-T space and conclude that the experimental methods utilized so far in the search for the Frenkel line cannot conclusively prove its existence (or otherwise). We will discuss alternate methods that may be utilized.

[1] Nat Phys **6**, 503 (2010)

[2] PRE **85**, 031203 (2012)

[3] Sci Rep **2**, 421 (2012)

[4] Sci Rep **5**, 15850 (2015)

P 9.4

High pressure Raman study of perfluorotripentylamine (FC70)

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Introduction

Perfluorotripentylamine (FC70 Fluorinert^{TM}) is an important liquid with a wide range of applications in electronics, including vapor phase soldering and thermal management, as well as material science because of its unique properties (thermal and chemical stability, compatibility with sensitive materials etc.). Furthermore, it has been widely used in high pressure diffraction or Raman studies as pressure-transmitting medium. Consequently, knowledge of its Raman spectrum and pressure evolution is particularly useful for high pressure spectroscopic experiments.

Objectives

In this work, the pressure response and stability of the FC70 is studied by means of Raman spectroscopy up to ~5 GPa.

Materials and methods

High pressure on FC70 (3M) was generated by means of a diamond anvil cell (DAC), while pressure was calibrated by the well-known ruby method. Raman measurements were conducted using a LabRam HR (HORIBA) spectrometer. A laser beam at 515 nm at a power of ~1 mW on the DAC was used for excitation and focused on the sample by means of a 50x objective.

Results

In the Raman spectrum of the FC70, 24 peaks can be resolved and followed with pressure. With increasing pressure, all the Raman peaks shift to higher energies, while no significant changes in the general spectrum profile occur up to 5 GPa with respect to the number of the Raman peaks, their linewidths and relative intensities. The only exception is the lowest frequency peak at 108 cm^{-1} that exhibits a continuous broadening and intensity attenuation with pressure. Previous studies have shown that FC70 becomes non-hydrostatic for P> 0.6 GPa due to its solidification. However, the pressure evolution of the frequencies of all the observed Raman peaks is quasilinear up to the maximum pressure attained in our experiments (5 GPa) with the corresponding pressure slopes ranging between 1.1 and 5.8 $cm^{-1}GPa^{-1}$. Moreover, the pressure-induced shifts of the frequencies of the Raman peaks are fully reversible upon pressure release.

Conclusion

The high pressure response of the FC70 Fluorinert^{TM} was studied by Raman spectroscopy. Despite its solidification, the pressure response of the frequencies of the Raman peaks and the overall spectrum profile remain unaffected for pressures at least up to 5 GPa, justifying its use as a pressure transmitting medium.

Invited Talk

Theory of the liquid-liquid phase transition in high pressure hydrogen

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The phase diagram of high pressure hydrogen is of great interest for fundamental research, planetary physics, and energy applications [1]. A first-order phase transition in the fluid phase between a molecular insulating fluid and a monoatomic metallic fluid has been predicted [2,3,4]. The existence and precise location of the transition line is relevant for planetary models. Recent experiments reported contrasting results about the location of the transition [5,6,7]. Theoretical results based on density functional theory are also very scattered [7]. We report highly accurate coupled electron-ion Monte Carlo calculations of this transition finding results that lie between the two experimental predictions, close to that measured in diamond anvil cell experiments but at 25-30 GPa higher pressure. The transition along an isotherm is signaled by a discontinuity in the specific volume, a sudden dissociation of the molecules, a jump in electrical conductivity and loss of electron localization[8].
We discuss the difference observed with respect to the predictions of a different Quantum Monte Carlo method [9,10].

References

[1] J.M. McMahon, M.A. Morales, C. Pierleoni and D.M. Ceperley, "The properties of hydrogen and helium under extreme conditions", Review of Modern Physics 84, 1607 (2012).

[2] M.A. Morales, C. Pierleoni, E. Schwegler and D.M. Ceperley "Evidence for a first-order liquid-liquid transition in high-pressure hydrogen from ab initio simulations", PNAS 107, 12799 (2010).

[3] M.A. Morales, J.M. McMahon, C. Pierleoni, D.M. Ceperley, "Nuclear quantum effects and nonlocal exchange-correlation functionals applied to liquid hydrogen at high pressure", Phys. Rev. Lett. 110, 065702 (2013).

[4] W. Lorenzen, B. Holst, R. Redmer, "First-order liquid-liquid phase transition in dense hydrogen" Phys. Rev. B 82, 195107 (2010).

[5] Zaghoo M, Salamat A, Silvera IF, "A first-order phase transition to metallic hydrogen", (2015) arXiv:1504.00259

[6] Ohta K et al." Phase boundary of hot dense fluid hydrogen" Scientific Reports 5:16560 (2015).

[7] Knudson MD et al." Direct observation of an abrupt insulator-to-metal transition in dense liquid deuterium" Science 348, 1455 (2015).

[8] C. Pierleoni, M.A. Morales, G. Rillo, M. Holzmann and D.M. Ceperley, "Liquid-liquid phase transition in hydrogen by Coupled Electron-Ion Monte Carlo Simulations", PNAS (2016), in print.

[9] G. Mazzola, Yunoki S, Sorella S "Unexpectedly high pressure for molecular dissociation in liquid hydrogen by electronic simulation", Nature Communications 5, 3487 (2014).

[10] Mazzola G, Sorella S, "Distinct metallization and atomization transitions in dense liquid hydrogen", Phys Rev Lett 114, 105701 (2015).

O 10.1

Equations of state for solids under strong compression and effects of wrong constraints

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Equations of state (EOS) in thermodynamics are constraint by the thermodynamic model used to describe all the thermo-physical properties of the system. Even in simple solids, like Cu, Ag, and Au, anharmonicity of the phonons must be taken into count when one is interested in modeling the thermo-physical properties in wide ranges of temperature [1], where by the temperature dependence of the heat capacity, the thermal expansion, the isothermal bulk modulus, and its isothermal pressure derivative, all at ambient pressure, constrain the physical parameters of the thermodynamic model. On the other hand shock-wave-reduced-isotherms (SWRI) are deduced from Hugoniot-data typically by unrealistic quasi-harmonic phonon approximations leading to systematic errors especially at compression where the Hugoniot crosses the melting curve [2-4], Inappropriate EOS-forms, which diverge with respect to the well know behavior of solid under strong compression, lead to additional errors in the parameters fitting these forms to the data. Detailed thermodynamic modeling of all the thermo-physical properties at ambient pressure for Cu, Ag, Au, Ni, Pt, W, and Ne result in reliable EOS which are used to illustrate the deficiencies of EOS derived with wrong constraints from shock-wave data and with correspondingly wrong reference isotherms derived in static compression experiments.

[1] "Equations of State for Solids over Wide Ranges of Pressure and Temperature" W.B. Holzapfel, Chapter 5 p. 81-94 in "High-Pressure Physics" ed. John Loveday, CRC Press, Boca Raton, Fl. U.S.A. (2012)

[2] “Anharmonicity in the EOS of Cu, Ag, and Au and related Uncertainties in the Realization of a Practical Pressure Scale” W.B. Holzapfel, J. Phys.: Condens. Matter14, 10525-10531 (2002)

[3] "Effects of Phonon Dispersion and Anharmonicity on Thermophysical Properties of Solids” W.B. Holzapfel, Z. Naturforsch. 63b, 718-724 (2008)

[4] "Equations of State for Cu, Ag, and Au and problems with shock wave reduced isotherms" W.B. Holzapfel, High Press. Res., 30, 372-394 (2010)

O 10.2

Electronic correlations and transport properties of ε-Fe at extreme conditions

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The electronic state and transport properties of iron at high-temperature/high-pressure conditions are of fundamental interest for the condensed matter theory and especially important for understanding of the physics of Earth's inner core.

We apply an *ab initio* theoretical framework combining the density functional and dynamical mean field theories (DFT+DMFT) to study electronic and transport properties of the hexagonal close-packed ε phase of Fe in the vicinity of the α→ε transition [1] as well as at the extreme pressure and temperature conditions expected for the inner core of Earth [2]. We find a significant enhancement of electronic correlations across the α→ε transition as evidenced by a step-wise enhancement of the effective mass and electron-electron scattering at the transition point. This is due to absence of the static exchange splitting in paramagnetic ε-Fe leading to an increase in the dynamical part of the electronic self-energy as compared to ferromagnetic α-Fe. This enhancement of correlations has a direct impact to the ground state properties of ε-Fe. Our DFT+DMFT calculations correct a significant over-binding of the paramagnetic ε phase obtained with standard DFT methods [1].

We have performed calculations using the same framework for ε-iron at the Earth's core volume and for temperatures up to 7000K [2]. We find that highly compressed ε-Fe behaves as a nearly perfect Fermi liquid with the corresponding Fermi-liquid temperature scale T_{FL} of about 14000 K, i.e. much higher than the possible temperature range for the core. The calculated electron-electron-scattering contribution to the electrical resistivity is rather insignificant compared to the electron-phonon one. However, we find that the electron-electron-scattering is still quite important for the thermal resistivity of ε-Fe, which is greatly enhanced due to the Fermi-liquid quadratic frequency dependence of the scattering rate. Hence, the Fermi liquid behavior causes the calculated thermal resistivity to be of comparable magnitude to the electron-phonon one. This effect might be important for the geodynamo stabilization.

[1] L. V. Pourovskii, J. Mravlje, M. Ferrero, O. Parcollet, I. A. Abrikosov Phys. Rev. B 90, 155120 (2014)

[2] L. V. Pourovskii, J. Mravlje, A. Georges, S.I. Simak, I. A. Abrikosov arXiv:1603.02287

O 10.3

Thermodynamic analysis of solid solutions of Fe-H system at hydrogen pressures of several gigapascals

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Iron forms hydrides at high hydrogen pressures. Their structural and magnetic properties have been studied by X-ray and neutron diffractions [1-4], and Mössbauer and X-ray absorption spectroscopies [4, 5]. Three hydrides are known at temperatures of 300-1000 K and pressures of 0-10 GPa: ferromagnetic a phase with a bcc metal lattice, ferromagnetic e' phase with a dhcp metal lattice, and paramagnetic g phase with an fcc metal lattice. Although ferromagnetism has been theoretically predicted for monohydride fcc-FeH [6], its experimental evidence has not been reported yet.

Hydrogen composition x is essential for understanding the structural and magnetic properties of Fe-H system. Neutron diffraction measurement is the most effective experimental tool for determining hydrogen composition [7], but not applicable for phase study requiring observation over a wide temperature and pressure span. The thermodynamic and magnetic properties of dhcp and fcc FeH_x at high temperatures remain an area not yet explored.

The aim of this study was to derive the enthalpy of solution of hydrogen DH_s and magnetic transition composition x_m for dhcp and fcc FeH_x at temperatures of 300-1000 K and hydrogen pressures up to 10 GPa. Hydrogen composition x was estimated from the volume expansion of a metal lattice due to hydrogen absorption and magnetic ordering. Arrhenius plotting of x vs $1/T$ allowed us to derive DH_s and x_m. The enthalpies of both solid solutions increased with pressure at a rate of 3 kJ/H-mol/GPa, while x_m showed pressure insensitive behavior. Pressure dependence of DH_s was interpreted in terms of hydrogen-induced volume expansion.

References

[1] V. E. Antonov *et al*, J. Alloys Comp., **264** (1998), 214-222.

[2] T. Hiroi *et al*, J. Alloys Comp., **404-406**(2005)252-255.

[3] Tatsuya Sakamaki *et al*, Phys. Earth Planet Int., **174**(2009)192-201.

[4] Olga Naryginaa *et al*, Earth Planet. Sci. Lett., **307** (2011) 409-414.

[5] N. Ishimatsu *et al*, Phys. Rev. B 86(2012)104430.

[6] C Elsässer *et al*, J. Phys.: Condens. Matter **10** (1998) 5113-5129.

[7] A. Machida *et al*, Nature Commun., **5**(2014)5063.

O 10.4

Computational phase diagrams of gas hydrates under pressure

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Gas hydrates are molecular host-guest mixtures where guest gas species are encapsulated in host water networks. They play an important role in gas storage in aqueous environments at relatively low pressures, and their stability is determined by weak interactions of the guest species with their respective host water frameworks. Thus, the size and amount of the guest species vary, depending on the size of the empty space provided by the host water structures. The systems studied here are noble gas (He, Ne, Ar) and diatomic (H_2 and O_2) hydrates. Because of the similar guest sizes, the noble gas hydrates act as simple models for the diatomic gas hydrates.

We use first-principles calculations to obtain the formation enthalpies of each gas hydrate, as function of host network, guest stoichiometry, and pressure. Graph invariant topology is used to assign protons to proton-disordered water host structures. In diatomic hydrates, molecular stretch frequencies are used as structural fingerprints and compared to experimental data.

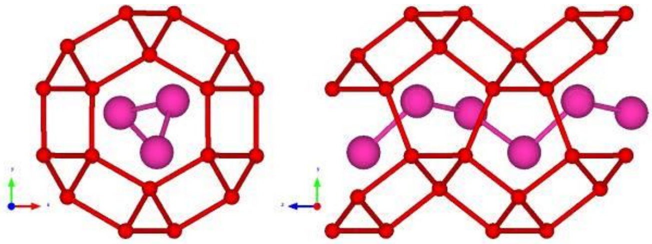
Our calculations predict stable phases for noble gas compound systems based on four host water networks, namely, ice I_h, II and I_c, and the new water network C_0. The He-water system adopts ice I_h, II and I_c networks upon increasing pressure. In the Ne-water system, we find a sequence of C_0/ice-I_h, II and Ic with a competitive hydrate phase in the C_0 host network at very low pressure. This is similar to the phase evolution of the H_2-water system. For the Ar-water mixture, only a partially occupied hydrate in the C_0 host network was found stable. This C_0 phase becomes metastable if we take the traditional clathrates (CS-I and CS-II) into account.

For the diatomic guest gas compound systems, we consider three more host water networks, namely, the standard clathrate structures CS-I, CS-II, and CS-T. We verify the phase sequence seen in H_2 hydrate, and predict a succession of new O_2 hydrates to emerge as pressure is increased.

We determine computationally the low-temperature phase diagrams of noble gas and diatomic gas hydrates under pressure. We find new water networks (such as C_0) stable in systems other than those known so far, and that the little-studied O_2-hydrate has a succession of high-pressure phases beyond the phase known to date.

Figure 1. Two views of the fully-filled Ne-C_0 hydrate, along (left) and perpendicular (right) to the channels in the C_0 structure water network.

Figure 1



O 10.5

Pressure-induced phonon freezing in the Percolation-type Zn(Se, S) mixed crystal: Phonon-polaritons and *ab initio* calculations

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Introduction

Recently, we have shown that the short Zn-S bond of $ZnSe_{1-x}S_x$ exhibits a percolation-type Raman doublet. This distinguishes between Zn-S vibrations depending on their ZnS- or ZnSe-like environments. Such sensitivity is attractive because it offers the possibility to investigate how the Zn-S vibrations of $ZnSe_{1-x}S_x$ behave versus various stimuli depending on their local environment.

Objectives

In this work we study the pressure dependence of the Zn-S Raman doublet of $ZnSe_{1-x}S_x$ at the approach of its pressure-induced zincblende→rocksalt transition, identical in every respect to that of its parents. The actual study completes an earlier one done with the percolation-type Be-Se Raman doublet of $Zn_{1-x}Be_xSe$ [1], with a large contrast in the pressure-induced structural transitions of its parents (regarding both the transition pressure and the final phase). At this occasion we found that the lower Be-Se sub-mode progressively collapses and converges onto the upper Be-Se one as the pressure increases, until coincidence/disappearance. Ultimately, the lower sub-mode remains 'frozen', only the upper one survives. Our aim is to elucidate whether the trend is specific to $Zn_{1-x}Be_xSe$, or not.

Materials & Methods

As the Zn-S Raman doublet of $ZnSe_{1-x}S_x$ is poorly resolved (the frequency gap hardly reaches ~15 cm^{-1}), we cannot study its pressure dependence by using the standard backscattering geometry (operating in 'reflection'), as for Be-Se. We adopt the near-forward scattering geometry (operating in 'transmission'), giving access to the phonon-polaritons (PP), with mixed phonon-photon character. The reason is that the Zn-S frequency gap is magnified in the PP regime. The discussion is supported by *ab initio* phonon calculations done at different pressures in the 'pure-phonon' regime, and by contour modeling of the PP-Raman lineshapes within the linear dielectric approach.

Results

We find that the Zn-S doublet of $ZnSe_{1-x}S_x$ behaves as the Be-Se one of $Zn_{1-x}Be_xSe$ under pressure [2].

Conclusion

We deduce that the pressure-induced "phonon freezing" is intrinsic to the percolation doublet, at least in ZnSe-based mixed crystals, and not due to any contrast between the pressure-induced structural transitions of its parents.

[1] G.K. Pradhan *et al.*, *Phys. Rev. B* **81**, 115207 (2010)
[2] R. Hajj Hussein *et al.*, http://arxiv.org/abs/1603.00606, *J. Phys.: Condens. Matter* (to be published).

O 10.6

High pressure phase diagram of MgO and FeO

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The state of matter (e.g. temperatures and pressures) inside super-Earths, i.e., planets in the mass range 1-10 ME, is much more extreme than in the interior of the Earth so that current experiments are not able to cover the whole density-temperature range directly [1]. In order to improve the understanding of the interior of exoplanets and their physical properties [2], *ab inito* calculations for the planetary materials are needed.

Typical representatives are MgO and FeO, which are abundant materials in the Earth's mantle. Both are expected to be also important for the mantle of exoplanets as well as for the rocky cores of gas giants such as Jupiter [3]. Using *ab initio* molecular dynamic simulations (VASP [4]), we have determined the phase diagram for MgO up to 20000 K and 1.5 TPa. In particular, the transition from the solid to the molten salt has been studied using diffusion analyses and pair distribution functions. The transition from the NaCl (B1) to the CsCl (B2) structure in solid MgO is determined by calculating the respective free enthalpies. The phase diagram of MgO is constructed based on the accurate equation of state (EOS) data. We compare with experimental results from (decaying) shock and ramp compression experiments [5, 6]. The B1-B2 and the liquid-solid transition line are compared with earlier simulation and experimental results [7].

The more complex phase diagram of FeO is under investigation, first results with DFT+U calculations show agreement with experimental results for the B1 phase. Using the quasi-harmonic approximation, the EOS is calculated and compared against available experimental data [8].

References

[1] D. Valencia, R.J. O'Connell and D. Sasselov, Icarus 181, 545 (2006).

[2] V. Stamenkovic, D. Breuer and T. Spohn, Icarus 216, 2 (2011).

[3] F.H. Wilson and B. Militzer, Phys. Rev. Lett., 108, 111101 (2012).

[4] G. Kresse and J. Hafner, Phys. Rev. B 48, 13115 (1993).

[5] R.S. McWilliams, D.K. Spaulding, J.H. Eggert et al., Science, 338, 1330 (2012).

[6] F. Coppari, R.F. Smith, J.H. Eggert et al., Nature Geoscience, 6, 926 (2013).

[7] D. Cebulla and R. Redmer, Phys. Rev. B, 89, 134107 (2014).

[8] R.A. Fischer, A.J. Campbell, O.T. Lord et al., Geophys. Res. Lett. 38, (2011).

O 10.7

Pressure-induced site-selective mott transition and local moment collapse in Fe_2O_3

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We report a combined theoretical and experimental (57Fe Mössbauer spectroscopy and X-ray diffraction) investigation of the electronic and structural properties of Fe_2O_3 at pressures up to 100 GPa. On the theory side, we employ the LDA+DMFT approach for the computation of materials with strongly interacting electrons to study the electronic structure and phase stability of Fe_2O_3 near a pressure-induced Mott metal-insulator transition. To explore structural transformations as a function of pressure, we use the experimentally determined atomic positions for the metallic and insulating phases, respectively, and calculate the total energy as a function of volume. We find that the structural stability depends very sensitively on changes of the lattice volume. In contrast to the classical case of Mott transition, in which insulator-to-metal transition concurs with a complete collapse of magnetism, we observe a new scenario of Mott transition characterized by a site-selective correlation breakdown. Our results reveal the existence of a site-selective Mott phase, in which only half of the Fe sites is metallic, while the rest remain insulating. In agreement with experiment, we observe that the insulator-to-metal transition is accompanied by a remarkable site-selective collapse of local moments and concomitant structural transformation from corundum to a double perovskite lattice structure. Our results indicate that the site-selective Mott transition scenario appears to be a broadly applicable concept of the description of pressure-induced insulator-to-metal transitions in correlated materials, particularly, which start out in the corundum crystal structure.

O 10.8

First-principles prediction of superconducting H_5S_2 phase in sulfur-hydrogen system

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Recently, Drozdov *et al.* discovered high critical temperature (T_c) superconductivity in compressed hydrogen sulfide (H_2S) [1]. The T_c value shows 30-70 K in pressure range of 100-170 GPa (low-T_c phase) and increases to 203 K, which sets a record for the highest T_c, by the heating of the sample to room temperature in pressure region above 150 GPa and the cooling again (high-T_c phase). First-principles calculations [2,3] and the x-ray diffraction measurements [4] clarified that the high-T_c phase can be explained by H_3S stoichiometric compounds. For the low-T_c phase, H_2S is considered as the candidate, while calculated T_c values do not reproduce the experimental data completely. Therefore, further studies are required for the understanding of the superconductivity mechanism in sulfur-hydrogen system.

Here we present a new superconducting phase with a H_5S_2 stoichiometric compound in sulfur-hydrogen system under high-pressure, obtained by first-principles calculations and the genetic algorithm technique for crystal structure search [5]. The H_5S_2 compound takes a mixed structure of H_2S and H_3S molecules and is thermodynamically stable at around 110 GPa. The T_c values calculated within the harmonic approximation show 50-70 K in pressure range of 100-150 GPa, which is in a good agreement with the data of the experimentally observed low-T_c phase.

References

[1] A. P. Drozdov *et al.*, Nature **525**, 73 (2015).

[2] D. Duan *et al.*, Sci. Rep. **4**, 6968 (2014).

[3] I. Errea *et al.*, Nature **532**, 81 (2016).

[4] M. Einaga *et al.*, Preprint at http://arXiv.org/abs/1509.03156v1 (2015).

[5] T. Ishikawa *et al.*, Sci. Rep. **6**, 23160 (2016).

O 10.9

A proton disorder-order transition in ice look-like Ammonium Fluoride

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The structural phase diagram of ice is known to be rich and unique, and is attributed to its hydrogen-bonded open structure. A close analog however exists, surprisingly, in the ionic solid NH_4F, which displays intriguing parallels with ice despite its apparently ionic character. Earlier work [1-3] has used mainly X-ray diffraction and Raman scattering in the 0-16 GPa region to establish the low pressure room temperature phase diagram of NH_4F.

Figure 1: Temperature-Pressure phase diagram of ammonium fluoride. We have detected the new low temperature NH_4F-Vt phase and established the phase boundary of the order-disorder NH_4F-Vt to NH_4F-IIIc transition by Raman scattering and structure search calculations. The full symbols indicate our X-ray diffraction and Raman measurements while the empty circles and solid lines are from earlier work. The dashed line indicates a measured anomaly in the equation of state of the cubic phase. The unit cell shown is the predicted cubic NH_4F-IIIc structure with the two possible configurations for the central ammonium ion which can give rise to orientational disorder.

In this study [4] we investigate its phase diagram (Fig. 1) in so far unexplored low temperature and high pressure regions using the *Ab Initio* Random Structure Search method [5], calculations of Raman spectra, X-ray diffraction, and Raman scattering. We discovered a low temperature proton ordered phase (NH_4F-V) and the disorder-order transition to it from the high temperature cubic NH_4F-IIIc phase, perfectly analogous to the Ice VII-Ice VIII transition. Our theoretical findings, supported by our experiments, point to a richness in the NH_4F phase diagram which, despite its ionic nature, is strikingly similar to the one observed in ice, and thus indicate the possibility of a better understanding of the ice phase diagram through the study in this system.

References

[1] H. W. W. Adrian and D. Feil, *Acta Crystallogr.* **A25**, 438 (1969)

[2] L. G. Dowell and A. P. Rinfret, *Nature*, **188**, 1144 (1960)

[3] A. K. Kuriakose and E. Whalley, *J. Chem. Phys.*, **48**, 2025 (1968)

[4] C. Bellin, A. Mafety, C. Narayana, P. Giura, G. Rousse, J-P Itié, A. Polian, A. M. Saitta, and

A. Shukla, *Nat. Mater.* submitted for publication (2016).

[5] C. J. Pickard, R. J. Needs, *J. Phys. Condens. Matter.* **23**, 053201 (2011)

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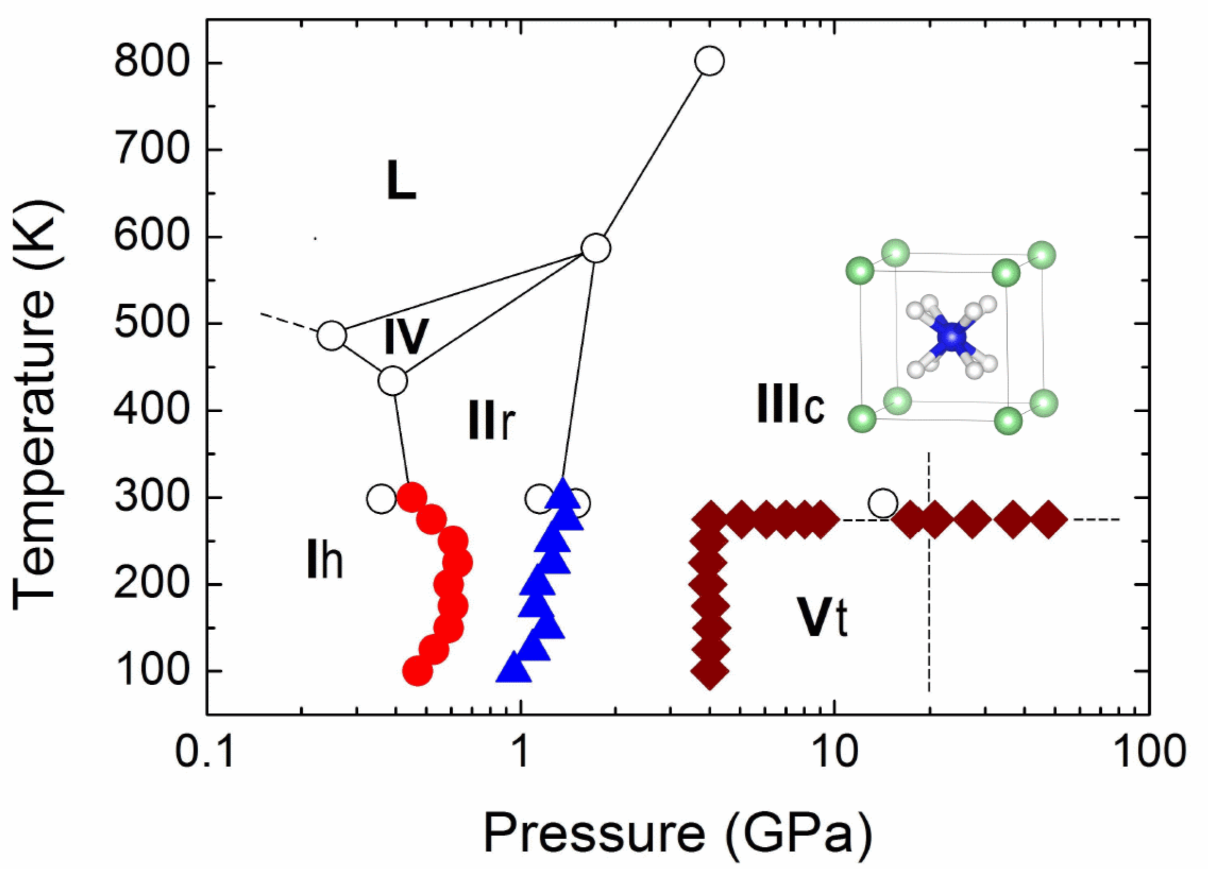
Keywords: ices, ammonium fluoride, order-disorder, *ab initio,* Raman scattering, X-ray diffraction

Figure 1


800
700
600
500
400
300
200
100
Temperature (K)
L
IV
IIr
IIIc
Ih
Vt
0.1
1
10
100
Pressure (GPa)

O 10.10

Understanding the non-existence of the cd→β-Sn phase transition for carbon by the quantum chemical topology approach

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Phase transitions are difficult to understand without the knowlenge about the corresponding changes in the bonding character. Here the quantum chemical topology (QCT) approach is useful, even when the QCT indicators don't have a direct connection to the energy. To use such indicators for the investigation of the reasons for phase transitions, at least empirical correlation between their change and the structure stabilization is required.

We compare changes of few QCT indicators along the cd→β-Sn transition for the group 14 elements, which is observed for Si, Ge and Sn, but not for the carbon. Both cd and β-Sn structures can be described by the body-centered tetragonal lattice, where $c/a=\surd 2$ for the cd and $c/a\approx 0.5$ for the β-Sn phase. The cd→β-Sn transition is simulated by a smooth decrease of the c/a ratio. During the transition, the coordination of atoms changes from 4 to 4+2.

It was shown that, although the increase of the number of bond critical points (BCPs) of electron density (ED) is caused by the change of the symmetry, in terms of energy, this change can be indeed attributed to the increase of the number of bonds per atom.

The ED value at the bond critical point (ρ_b) is a suitable measure of a bond strength for these structures, the sum of them being correlated with the energy and havimg maxima along the transformation pathway for the stable structures. The character of change of this sum depends on the volume change during the transition and reveals the low compressibility of the carbon structures as the main factor for the absence of the phase transformation.

The delocalization indexes reflect the change in the bonding character during the transition, but the interaction energies based on them don't correlate with the energy change.

The electron localizability indicator (ELI-D) for stable structures shows compact valence domains, shared between the neighbors (4 for the cd and 6 for the β-Sn structures), the split of the maxima into two parts being a signature of the structure instability.

Thus, the non-existence of the cd→β-Sn phase transition for carbon is reflected by the absence of the maximum of the sum of the ρ_b values and the split of the ELI-D maxima for the β-Sn-like structure.

Figure 1. Change of the total energy and the sum of the ρ_b values per bond along the transition

Figure 2. Change of the ELI-D distribution along the transition

Figure 1

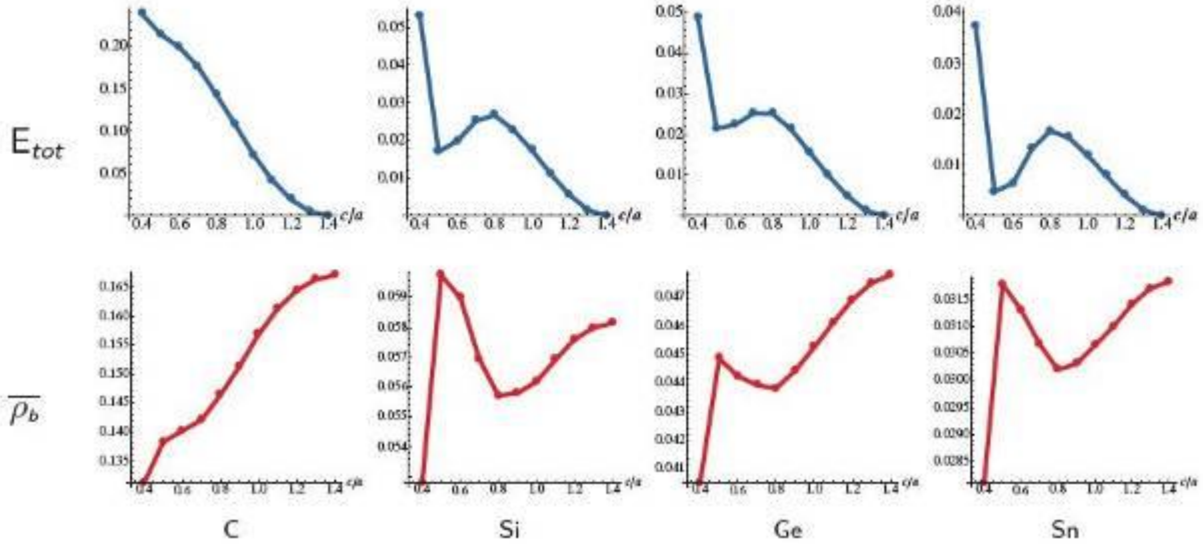
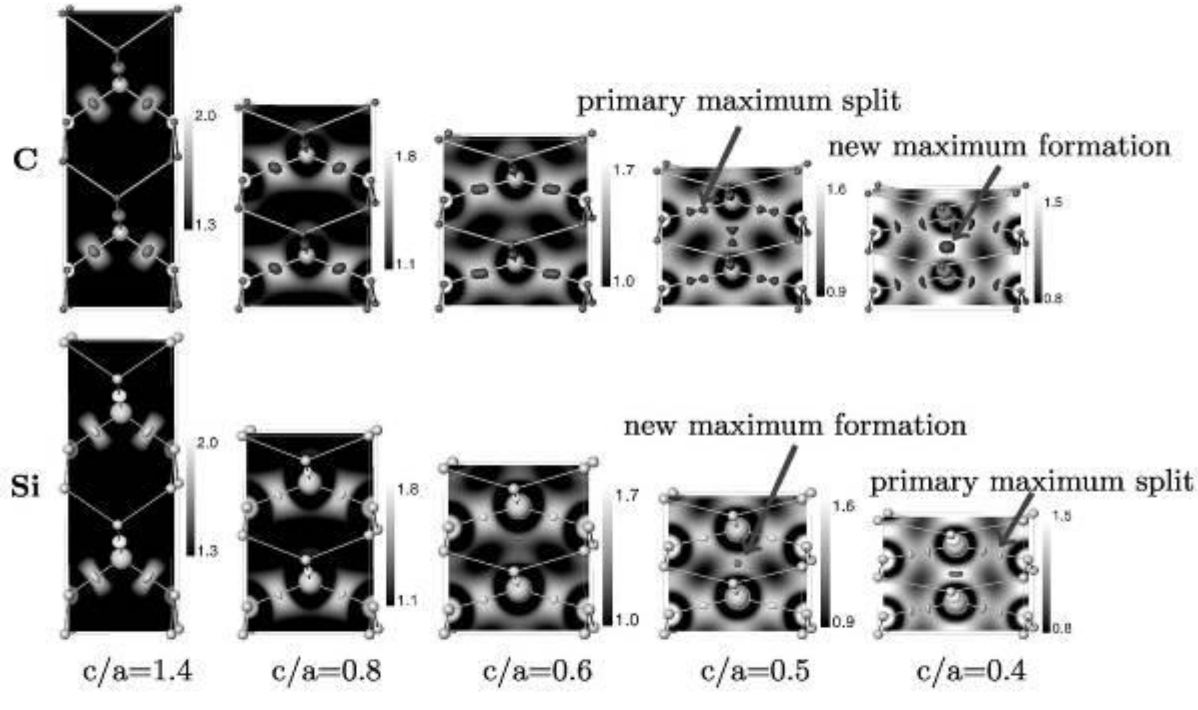


Figure 2



P 10.1

Impact of stress on structure and stability of selected group-IV crystalline materials

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Understanding the stability limit of crystalline materials under variable tensile-stress conditions is of capital interest for their technological applications. Quantum-mechanical simulations can provide useful and accurate information on this limit by computing stress-strain curves. In this contribution we perform such first-principles density functional theory calculations to quantitatively account for the response of selected crystalline materials to general stress conditions. In particular, we have evaluated the ideal strength of different polymorphs of binary group IV compounds along several crystallographic directions. The effect of hydrostatic stress on the shear stress and transverse stress on the tensile stress were taken into account in order to evaluated how the critical strength is affected by these conditions. The stability limit of the compounds is interpreted using the spinodal equation of state.[1] The resulting structures after the critical point are analyzed to identify potential new phases and/or bond breaking transition paths. Our preliminary study on the cubic 3C-SiC polytype is consistent with previous theoretical results by Umeno *et al.*[2] Our simulations have been extended to graphite and other MX_2 laminar compounds where tensile strains perpendicular and along the atomic layers are expected to provide very different results.

[1] Y. Umeno, A. Kubo, S. Ngao, Computational Materials Science 109 (2015)

[2] V. García Baonza, M. Caceres, J. Nuñez, Phys. Rev. B 51, 28 (1995)

P 10.2

Exploring solids with chemical pressure maps – from prototype to technological materials

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The concept of chemical pressure (CP) is useful for explaining mechanical and electronic properties of crystalline materials, although a quantitative account of this concept has been scarcely reported. In last years, a first principles procedure has been proposed to construct chemical pressure maps and to integrate atomic-level pressures, with the possibility of projecting them onto spherical harmonics.[1] These maps can be designed with a new computational tool developed by Fredrickson *et al.*[1] that uses Khon-Sham total energy contributions (kinetic energy and local potential energy terms) obtained by means of the ABINIT package.[2] As a result, the overall pressure exerted by interatomic contacts on each atom can be revealed and crystalline directions with particular tensions are identified. This is a successful approach in the identification and characterization of the chemical bonding nature of prototype crystals as metallic Na, ionic NaCl, covalent C-diamond and molecular CO_2. Our contribution also shows distinctive features of other technologically interesting materials as graphite, graphene, and 3C-SiC. The raw data for the CP analysis were obtained through three single-point crystal energy calculations spanning a volume range of 3 % around the equilibrium geometry. These quantum-mechanical calculations were performed within the LDA exchange-correlation approximation using HGH atomic pseudopotentials.[3] Overall, chemical pressure maps contain positive (repulsive) pressure regions around atomic cores that counterbalance the negative (attractive) pressures of the interatomic regions, leading to a net zero pressure. Moreover, the CP analysis shows that the graphite layers are connected by negative pressure regions due to the delocalized electron density representing van der Waals forces. It turns to be in the other way around when each single isolated graphene layer is analyzed. In this latter case, an accumulation of positive pressure above and below the graphene layer is obtained, resembling the π-type electron density. CP maps along the pressure-induced B3-B1 transition path of 3C-SiC will be analyzed.

[1] D. C. Fredrickson, J. Am. Chem. Soc. **134**, 5991 (2012)

[2] X. Gonze et al., Comput. Phys. Commun. **180**, 2582 (2009)

[3] C. Hartwigsen, S. Goedecker, Hutter, J. Phys. Rev. B **58**, 3641 (1998)

P 10.3

Elasticity and phase stability of transition metals under extreme static compression

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In this work we consider connection of phase stability of transition metals under pressures exceeding their bulk modulus value and their elastic properties. The methodological part of the work is targeted on the development of the elastic consatns calculation technique from the finite strain under high pressures.

The possibility of longwave instability is analyzed using the theoretical approach, based on Landau theory of phase transitions. For this purpose, the elastic constants, including higher order elastic constants, are calculated *ab initio* using technique, based on finite strains theory of deformation. At the same time, we discuss precursor events of phase transition with other mechanism and impact of near phase transition state on elastic, dynamic and electronic properies of studied metals.

Our technique correctly describes the phase transition in vanadium at 69 GPa and allows to determine the high pressure low symmetry phase. Combining the approach with soft mode theory we were able to describe phase transition in tungsten and molybdenum at 400 and 700 GPa respectively.

P 10.4

Machine learning interatomic potential

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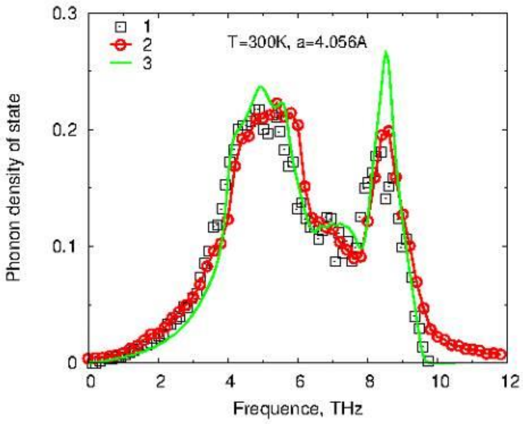
Classic interaction potentials are commonly used in modern computational methods. However, for various applications the accuracy of these potentials is insufficient. DFT methods could replace classic potentials but they are much more computationally expensive. Machine learning (ML) algorithms are known to possess both high accuracy and high operating speed. The aim of our study was to build machine learning potential that can predict interatomic forces (e.g. during molecular dynamics (MD) run) with high accuracy.

As a descriptor of the crystal structure that does not depend on translations and rotations we used the idea presented in [Li, Kermode, De Vita, PRL 114 (2015)]. The key point there is that forces are predicted on the basis of internal vectors, which are uniquely constructed based on the local atomic configuration. As a result, each atom is described by a matrix and a vector of the force acting on it. We used linear regression as a machine learning technique to reproduce the relation between the atomic descriptor and the force. The resultant vector of the parameters works as interatomic potential. The machine learning potential was implemented in LAMMPS code.

We studied aluminum systems. Forces acting on atoms in crystalline configurations were predicted within the error of 0.04 eV/atom, in the liquid - 0.08 eV/atom. Being trained on Al with a particular density and at a particular temperature, the resulting potential is also able to predict forces for structures with other densities and temperatures. Using the machine learning potential phonon density of states (PDOS) (Fig. 1), vibrational entropy and the melting point of Al were calculated. The calculated values are in good agreement with experimental data.

Figure 1. The PDOS dependence on temperature, 1 - experimental data, 2 - calculation via MD with ML potential, 3 - calculation via frozen phonon method (using DFT)

Figure 1



P 10.5

Electronic topological transition in niobium under pressure and its relation to Hooke's law

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Electronic topological transitions, which take place under extreme compressions are responsible for many unique effects. Among the transition metals, the 5-th group elements are of special interest in this respect. One reason for this is an outstanding combination of properties, which make V, Nb and Ta important components of superconducting, functional and refractory materials. At the same time, the behaviour of these materials under pressure is interesting on its own. For example, vanadium demonstrates high pressure phase transition to low symmetry phase. While the presence of electronic topological transition in both vanadium and niobium are quite evident, studies of electronic structure in literature are usually dedicated to the former.

We present qualitatively new picture of electronic topological transition (ETT) in pure niobium, achieved in theoretical simulations of this metal subjected to hydrostatic loading and homogeneous deformation. Carefull *ab initio* calculations were performed to figure out the impact of electronic structure picularities on the character of stress-strain relations in the material. While there is no sign of phase instability with increasing pressure, a peculiarity of the elastic properties of Nb is clearly observed in the pressure range of 0-100 GPa. In particular, we show that the range of strains in which the Hook's low holds is rapidly shrinking upon the approach to the ETT at high pressure, and effectively vanishes at the ETT. The role of the electronic structure modification upon deformation under non-uniform strain in this effect can be clearly distinguished.

The support from the Grant of Ministry of Education and Science of the Russian Federation (Grant No. 14.Y26.31.0005) is gratefully acknowledged. Calculations were preformed on the Computational Cluster of NUST MISIS "Cherry".

P 10.6

Interface pinning for the study of melting – the case of MgO

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Modern studies of Earth's origin led to the idea of an initial magma ocean from which, through a cooling process, core, mantle, crust, and atmosphere originated. Thus chemical evolution of deep Earth materials is directly connected to crystallisation and melting processes, and the understanding of such processes in the depths of Earth is strictly related to the understanding of the origin of our planet.

However, the study of melting is not straightforward because it is difficult to reproduce the extreme temperatures and pressures at the Earth's mantle in the lab. Also the coexistence of different minerals and different phases makes the theoretical description of these systems non-trivial. In order to study such a complex melting process, known as incongruent melting, control over the different phases of the minerals is needed.

Here we predict the melting curve of MgO, one of the most abundant oxides in the Earth's mantle, using *ab initio* molecular dynamics and our multi-atom implementation of the interface pinning (IP) method. [U. R. Pedersen, F. Hummel, G. Kresse, C. Kahl, C. Dellago, *Phys. Rev. B*, 2013, **88**, 094101.]

The IP method, originally developed for mono-atomic systems by Pedersen *et al.*, allows to compute Gibbs free energy differences between different phases by forcing the system to find a configurational equilibrium where the two phases coexist at given pressure and temperature. In addition to the conceptual simplicity of the IP method, the other main advantage is related to the explicit representation of the solid-liquid interface that also allows direct access important information such as crystal growth rates by simply looking at the fluctuations of the structure factor.

Our encouraging preliminary results show that the IP method can be used to look at the incongruent melting of more complex minerals, like $MgSiO_3$, in order to study properties such ascrystal growth rates and buoyancy of liquid and solid components and their relevance for the formation of the mantle.

P 10.7

The anion in metallic matrices model in the light of the chemical pressure formalism

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Under the Anions in Metallic Matrices (AAM) model, the crystal structure of an inorganic compound consists of a metallic matrix playing the role of a host lattice in which the non-metallic atomic constituents are located. Actual positions of these guest atoms can be microscopically interpreted in terms of the topological features of the electron density of the metallic sub-lattice. Besides the electron density, the electron localization function (ELF) has also provided successful support to the AAM model in a variety of examples. Different phases of Ca (*fcc*, *bcc* and *sc*) show ELF attractors at the same positions as those occupied by the O-atoms in the rocks-salt (B1) and cesium chloride (B2) phases of CaO. Similar results were also observed for the pairs Ca/CaF_2 and BaSn/$BaSnO_3$.[1] Interestingly enough, we show in this contribution how the DFT-Chemical Pressure (DFT-CP) approach developed by Fredrickson *et. al.*[2] provides an straightforward interpretation of these findings using DFT calculations carried out with the ABINIT package.[3] CP data are obtained after three single-point calculations spanning a volume range of 3% around the equilibrium crystal structure. Our results are quite similar to the ELF plots. Using different geometries for the metallic sub-lattice, CP maps are able to display negative (attractive) pressure regions at the positions of the anions in CaO B1 and B2 phases, and fluorite CaF_2. CP map of *fcc*-Ca with the same dimension of the B1 CaO phase (a = 4.83 Å) shows a maximum (attractor) of negative pressure at the oxygen positions of the B1 CaO phase (see Fig. 1). The same is obtained with *sc*-Ca having the dimension of B2 CaO phase with a = 2.64 Å. Moreover, CP analysis of the high pressure phase of BaSn shows localization of negative pressure regions at the oxygen positions in $BaSnO_3$ forming an octahedral-like isosurface around each Sn atom. In addition, the very recent SH_3 superconducting structure has been analyzed within the AMM-CP framework finding equivalences between SH_3 and K atoms that are still under a deeper analysis.

[1] A. Vegas and M. Mattesini, Acta Cryst. B **66**, 338-344, (2010)

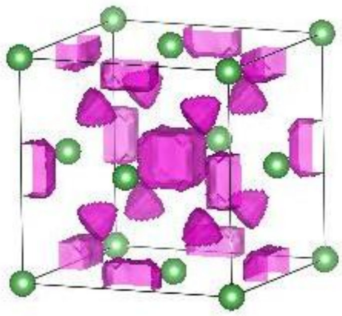
[2] D. C. Fredrickson, J. Am. Chem. Soc. **134**, 5991 (2012)

[3] X. Gonze et al., Comput. Phys. Commun. **180**, 2582 (2009)

[4] K. Momma, F. Izumi. J. Appl. Crystallogr. **44**, 1272 (2011)

Fig. 1 CP map of *fcc*-Ca unit cell (VESTA-3[4]).

Figure 1



P 10.8

Ab initio high pressure study of $NaNb_3O_8$

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The semiconductor sodium niobate $NaNb_3O_8$, is a novel lamellar array [1-2], with interesting technological applications in water decomposition [3] and self-cleaning glasses [4]. However, few experimental and theoretical data are available. In this work we present an *ab initio* study of NaNb3O8 (space group *Pmnm*), in the framework of the density function theory (DFT) [5] as implemented in the VASP code, with the projector-augmented waves, PAW [6]. For the exchange correlation energy functional, we used the generalized gradient approximation (GGA) in the form of Perdew- Burke-Ernzerhof (PBEsol) [7]. The structural and electronic properties under pressure were obtained. The calculated structural parameters are in very good agreement with experimental data [1]. The bulk modulus is 56 GPa. The band gap is direct with a value of 2.56 eV at zero pressure and the orbital composition is analyzed. Calculations of the vibrational properties: Raman and Infrared phonons, phonon dispersion, and phonon density of states, were carried out. The range of stability under pressure is discussed; a dynamical instability is found at 5.7 GPa.

References

[1] Nedjar R. (1); Borel M. M.; Leclaire A.; Raveaux B. *Journal of solid state chemistry1987, vol. 71, n°1, pp. 182-188 (16 ref.)*

[2] Range, K. J.; Wildenauer, M.; Heyns, A. M.*AngewandteChemie* (**1988**). 100, 973-975

[3] J. Wu and DongfengXue.*CrystEngComm,* (**2011**). 13, 1752-1754

[4] Ken-ichi Katsumata, Sohei Okazaki, Christopher E. J. Cordonier, Tetsuya Shichi, Takayoshi SasakiandAkira Fujishima, ACS Appl. Mater. Interfaces, 2010, 2 (4), pp 1236-1241

[5] P. Hohenberg, and W. Kohn, *Phys. Rev.***136,** 3B, B864-871 (1964).

[6] P.E. Blöchl, *Phys. Rev. B***50**, 17953-17979, (1994).

[7] J. P. Perdew, A. Ruzsinszky, G.I. Csonka, O. A. Vydrow, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Phys. Rev. Lett*. **100**, 136406 (2008).

P 10.9

Structural and electronic behaviour of $MoSe_2$ at Mbar pressures

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We study the structural and electronic evolution of MoSe2 at high pressure up to 2 Mbar. At normal conditions the stable phase of MoSe2 is the layered 2Hc structure which is semiconducting with indirect band gap of 1.1 eV. Upon increasing pressure this structure metalizes at 41 GPa [1,2] but does not undergo the layer sliding transition to the 2Ha phase, known from structurally similar MoS2 [3,4]. The behaviour of MoSe2 upon compression beyond 60 GPa is unknown.

Employing ab initio calculations and evolutionary algorithms [5] we predict new stable and metastable phases of MoSe2 at high pressure. We find that the 2Hc phase is stable up to pressure of 120 GPa where a new stable metallic tetragonal phase (P4/mmm) appears. Around 150 GPa the system becomes unstable with respect to chemical decomposition into MoSe and Se, similarly to scenario previously predicted for MoS2 [6]. At even higher pressure of 160 GPa another tetragonal phase (I4/mmm) with 8-fold coordination of Mo atoms (similar to CaC2) becomes stable with respect to the 2Hc phase. While the transition to P4/mmm or chemical decomposition require atomic diffusion which might be difficult at high pressure, the transition to the I4/mmm phase might be easier to observe due to it closer relation to the 2Hc phase. We analyze the electronic properties and electron-phonon interaction of the new metallic structures and predict the superconducting critical temperature Tc.

References

[1] Michaela Riflikova, Roman Martonak, and Erio Tosatti, Phys. Rev. B 90, 035108 (2014)

[2] Z. Zhao et al, Nat. Comm. 6, 7312 (2015)

[3] Liliana Hromadova, Roman Martonak, and Erio Tosatti, Phys. Rev. B 87, 144105 (2013)

[4] Z.-H. Chi et al., Phys. Rev. Lett. 113, 036802 (2014)

[5] D. C. Lonie and E. Zurek, Comput. Phys. Commun. 182, 372 (2011)

[6] Oto Kohulak, Roman Martonak, and Erio Tosatti, Phys. Rev. B 91, 144113 (2015)

P 10.10

Dynamical properties under pressure of CdGeP2 pictinide semiconductor from ab initio simulations

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Due to the possible technological interest and applications on photo-voltaic detectors, light emitting diodes, solar cells, and their use in nonlinear optics, the pictinide semiconductors semiconductor have been widely studied. These ternary compound crystallize in the chalcopyrite structure, derived from the binary analogs, zinc-blende, III-V and II-VI semiconductors compounds. In the chalcopyrite two different groups of cations are tetrahedrally bonded to the anion, which lead to a reduction in symmetry, and typically smallest band-gaps than those corresponding to the binary analogs.

Although $CdGeP_2$ chalcopyrite belongs to the pictinide family, very few experimental or theoretical data are available, even at ambient pressure, for this compound [1-4]. In this work we present an *ab initio* simulation study of the structural, and dynamical properties of $CdGeP_2$ chalcopyrite under high pressure. We perform the simulations using density functional theory [5], DFT, with the pseudopotential method with the projector-augmented waves, PAW [6], and the generalized gradient approximation (GGA) in the PBEsol prescription [7] for the exchange-correlation energy. It is well known that first principles simulations provide accurate results with predictive character. We show the pressure evolution of the structural parameters and the equation of state, EOS, of this material, reporting some thermodynamic properties. We study also the vibrational properties under pressure of this system: Raman and infrared phonons, their pressure evolution, and Grüneissen parameters. Moreover, the dynamical stability of this chalcopyrite under pressure will be discussed.

[1] L. Artús et al. *Phys. Rev. B* **43**, 2088 (1991).

[2] Sho Shirakata, *J. Appl. Phys*. **85**, 3294 (1999).

[3] V.L. Shaposhnikov, et al. *Phys. Rev. B*, **85**, 205201 (2012).

[4] F. Chiker, et al. u, Physica B, 349, 181 (2004).

[5] P. Hohenberg, et al. *Phys. Rev.* **136,** 3B, B864-871 (1964).

[6] P.E. Blöchl, *Phys. Rev. B* **50**, 17953-17979, (1994).

[7] J. P. Perdew, et al. *Phys. Rev. Lett*. **100**, 136406 (2008).

P 10.11

New high-pressure phases predicted for SiS$_2$

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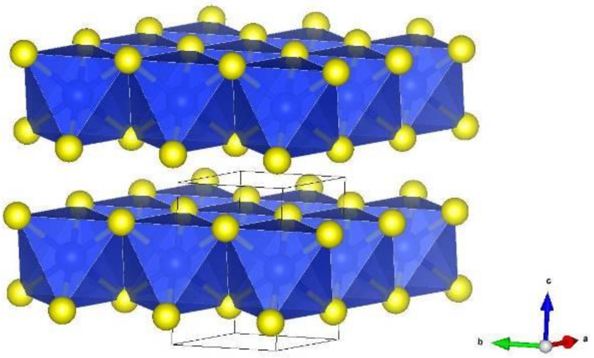
SiS$_2$ is member of the archetypal family of IV-VI AB$_2$ compounds made of light elements, which includes important systems such as CO$_2$, SiO$_2$, GeO$_2$ and CS$_2$. [1] The high-pressure phase diagram of SiS$_2$ is, however, currently known only up to cca. 6 GPa, featuring several phases (NP, HP1, HP2, HP3) whose common property is tetrahedral coordination of the Si ion which occasionally, such as in HP1, leads to a layered structure. [2] Nothing seems to be known about the structural and electronic evolution of SiS$_2$ at higher pressures. By means of *ab initio* calculations combined with evolutionary structure searching [3] and molecular dynamics (MD), we predict new stable and metastable phases of SiS$_2$ above 6 GPa and focus on three lowest-enthalpy phases with space groups P-3m1, P6$_3$mc and R-3m. In all three phases, the Si coordination has switched from 4 to 6 and, surprisingly, the structures are layered, consisting of sheets formed by edge-sharing octahedra (SiS$_6$ units). Six-fold coordination is an expected property at high pressure and mimicks the structural evolution in SiO$_2$. The most stable P-3m1 phase (one SiS$_2$ layer per unit cell) is isostructural to CdI$_2$, where all sheets are directly above each other (Fig. 1), while in P6$_3$mc the two SiS$_2$ layers in the unit cell are mutually staggered. Finally, R-3m contains three sheets per unit cell and the structure is the same as for CdCl$_2$. Beyond 6 GPa the enthalpies of the three new octahedral phases are lower than the enthalpy of HP3, which is currently the highest-pressure known phase. All newly predicted phases are semiconducting with indirect band gaps at low pressures, all of which close with increasing pressure leading to metallization around 30 GPa. We calculated phonon dispersions at several pressures and analyzed the dynamical stability of the phases. We also determined elastic constants at zero pressure and found the materials to be highly anisotropic. Finally, constant-pressure MD simulations were performed in order to analyze possible transformation pathways from tetrahedral to octahedral phases. These results may also be useful in order to compare the future experimental compression products with the ideal phases which we found in the structure search.

[1] S. Naghavi et al., *Phys. Rev. B* **91**, 224108 (2015)

[2] J. Evers et al., *Inorg. Chem.* **54**, 1240 (2015)

[3] D. Lonie and E. Zurek, *Comput. Phys. Commun.* **182**, 372 (2011)

Figure 1



P 10.12

First-principles study on anharmonic effects in simple cubic calcium under high-pressure

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Calcium is experimentally observed to take a simple cubic structure in pressure range of 32-119 GPa at room temperature. However, first-principles calculations show that the simple cubic phase is energetically and mechanically unstable at static condition [1-3]. The discrepancy between the experimental and theoretical results suggests that calcium shows large anharmonicity in the simple cubic phase, and the inclusion of thermal effect is considered to be a way to solve this problem.

Self-consistent harmonic approximation (SCHA) has been used as an approach based on non-perturbative theory, which enables us to treat anharmonic potentials and discuss the structural stability at finite temperatures [4]. The SCHA stands on the idea that the anharmonic potential can be renormalized to the harmonic potential minimizing the free energy of the system.

In this study, we implemented stochastic SCHA (SSCHA) proposed by Errea *et al.* [5], which is derived from SCHA and evaluates several operators stochastically, to the Quantum ESPRESSO code, and applied it to the simple cubic calcium. As the results, the imaginary phonon frequency, observed within the harmonic approximation, was disappeared at 300 K in pressure range of 30-60 GPa and the simple cubic phase was mechanically stabilized, which are consistent with those reported by Errea *et al.* [6] and Gennaro *et al.* [7]. In the presentation, we will also discuss free energies among simple cubic structure and other candidate structures.

References

[1] G. Gao, Y. Xie, T. Cui, Y. Ma, L. Zhang, and G. Zou, *Solid State Commun.* 146, 181 (2008).

[2] A. M. Teweldeberhan and S. A. Bonev, *Phys. Rev. B* **78**, 140101 (2008).

[3] T. Ishikawa, H. Nagara, N. Suzuki, T. Tsuchiya, and J. Tsuchiya, *Phys. Rev. B* **81**, 092104 (2010).

[4] D. J. Hooton, *Phil. Mag.* **46**, 422 (1955).

[5] I. Errea, M. Calandra, and F. Mauri, *Phys. Rev. B* **89**, 064302 (2014).

[6] I. Errea, B. Rousseau, and A. Bergara, *Phys. Rev. Lett.* **106**, 165501 (2011).

[7] M. D. Gennaro, S. K. Saha, and M. J. Verstraete, *Phys. Rev. Lett.* **111**, 025503 (2013)

P 10.13

Ionic ammonia-water mixtures at high pressures

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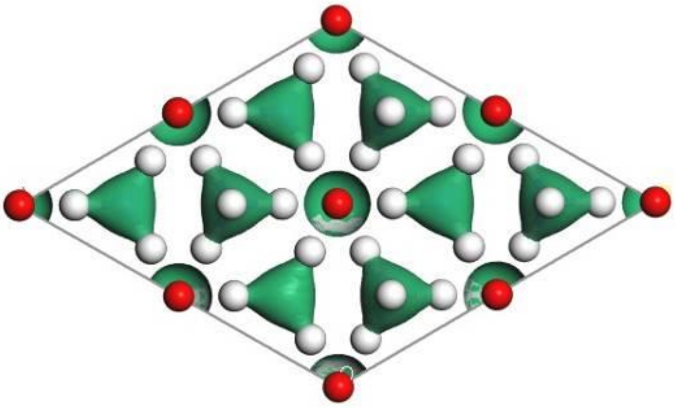
Mixtures of simple molecular ices (water, ammonia, and methane) at high pressure and temperature are proposed to dominate the outer layers of icy planets such as Uranus and Neptune. Experimental studies on such mixtures have so far been restricted to simple mixing ratios and pressures up to 30 GPa. Computational studies on the stability fields of various phases are thus very valuable, but hitherto tend to focus on individual compounds, with few results on mixtures. Here, we present new phase diagrams for ammonia-water mixtures at high pressure, constructed by using crystal structure prediction and density functional theory.

We observe that the three canonical mixing ratios of 2:1, 1:1, and 1:2 form the convex hull at 300 GPa against many more mixing ratios, and thus remain the most stable forms of solid ammonia water mixtures. We confirm stability of pseudo-BCC structures in the pressure range of 25-60 GPa, where the BCC disordered molecular alloy has been observed for all three mixing ratios. These structures offer repeating cubic units distorted by the hydrogen-bonding network similar to that of ice VII.

We also find intriguing new stable phases in all compounds at higher pressures, before they eventually de-mix into separate NH3 and H2O phases above 500 GPa. These are dominated by increased de-protonation of water, leading to structures dominated by ionic bonding. The hemihydrate $(H_2O)(NH_3)_2$ dominates the convex hull at high pressures and is predicted to resist de-mixing until 550 GPa in a sequence of $O^{2-}(NH_4^+)_2$ structures, which maximize ionic NH^{4+}-O^{2-} interactions.

Figure 1. Electron density of an ionic high-pressure phase of ammonia hemihydrate.

Figure 1



P 10.14

Molecular mixtures at high pressures

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The interiors of the giant planets Uranus and Neptune are dominated by a mixture of the molecular compounds water, ammonia and methane. Many observable properties of these planets, such as luminosity, gravitational moments and magnetic fields, are thought to be determined by the physical and chemical properties of matter within this ice layer. Hence, the phase diagrams, equations of state and structural properties of these materials and their respective mixtures are of great interest. [1]

In particular, the superionic phases of water and ammonia, characterized by highly mobile hydrogen ions diffusing through a lattice of oxygen and nitrogen ions, respectively, have gained much attention. For water, the influence of such a phase on the properties of the giant planets as well as on exoplanets has been discussed widely [2,3], while it is an open question how the properties of such a water layer change when other compounds are introduced.

To address this question we performed ab initio simulations based on density functional theory using the VASP code [4] for a variety of molecular mixtures starting with a 1:1 water-ammonia mixture. Heating up structures which we had found from evolutionary random structure search calculations with XtalOpt [5] we find superionic water- ammonia structures present up to several Mbar. Adding methane to the water-ammonia mixtures we observe amorphous structures of nitrogen and oxygen while carbon forms short chains. Evaluating the equation of state and structural properties such as diffusion coefficients and bond autocorrelation functions for varying mixing ratio we discuss general trends with respect to the N:O:C concentration. The obtained results are essential to construct new interior models for Uranus and Neptune as well as Neptune-like exoplanets. [6]

References

[1] R. Chau, S. Hamel and W. J. Nellis, Nature Communications 2, 203 (2011).

[2] R. Redmer, T.R. Mattsson, N. Nettelmann and M. French, Icarus 211, 798 (2011).

[3] L. Zeng and D. Sasselov, Astrophysical Journal 784, 96 (2014).

[4] G. Kresse and J. Hafner, Physical Review B 47, 558 (1993).

[5] D. C. Lonie and E. Zurek, Computer Physics Communications 182, 372 (2011).

[6] N. Nettelmann, R. Helled, J. J. Fortney and R. Redmer, Planetary and Space Science 77, 143 (2013).

P 10.15

Hydrates on the high pressure range up to 1 GPa

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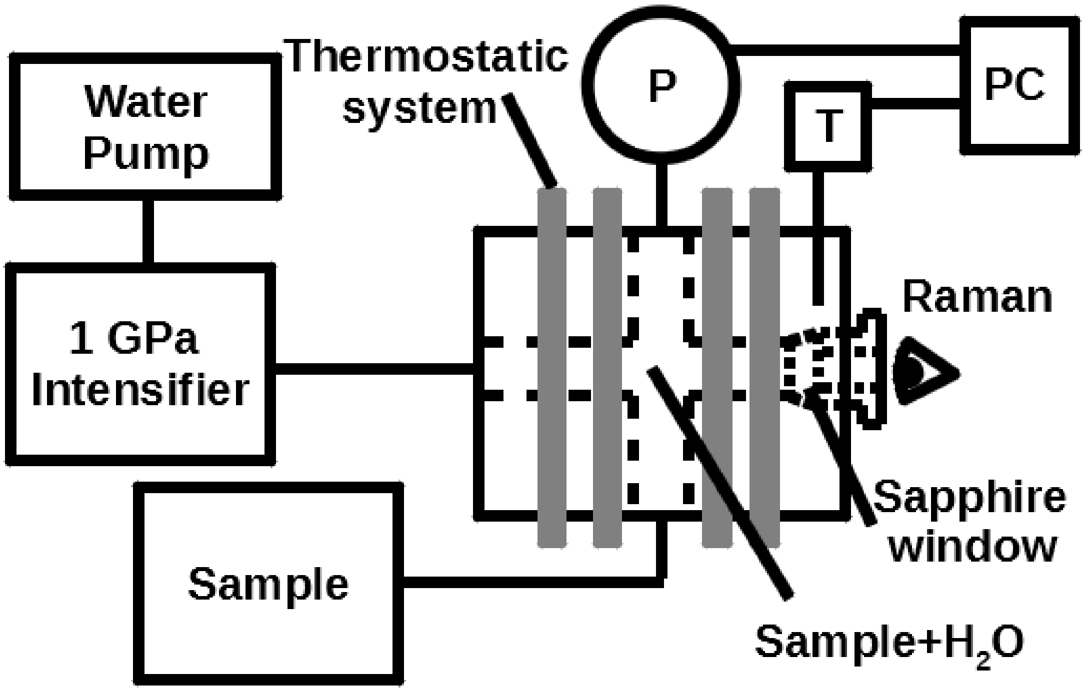
Clathrate hydrates are of primary importance in several fields of knowledge as exploitation of natural resources, origin of life, planetology or climate change. These crystalline compounds accommodate guest molecules (usually of a non-polar gas) within the framework of a host tridimensional web of water cages or channels. Although it depends on the guest molecule, clathrate hydrates generally need high pressure and low temperature to be stabilized. They show wide pressure and temperature ranges of stability, displaying pressure-induced phase transitions between the main types of known clathrate structures: cubic sI and sII, hexagonal sH and orthorhombic FIS (from Filled Ice Structure). Our contribution addresses the modelization of structural, energetic and mechanical properties of CO2@sI, CO2@FIS and N2@sII clathrates using ab initio DFT methodologies under periodic boundary conditions. We obtain structural and equation of state parameters providing a microscopic decomposition of the bulk compressibility in terms of cage contributions. Calculated vibrational frequencies inform on the energetic barriers associated with some restricted movements of CO2 molecules in specific cages. In addition to the simulations, we synthesise CO2@sI and CO2@FIS on a newly developed Very High Pressure Planetological Chamber (VHPPC, see Figure 1). Raman scattering measurements are programmed.

Figure 1



P 10.16

Topological transitions of the Fermi surface of Osmium under pressure - An LDA+DMFT study

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Influence of pressure on electronic structure has attracted substantial attention recently due to reports on isostructural electronic transitions in this metal. Here, we theoretically investigate the Fermi surface of Os from ambient to high pressure, using density functional theory combined with dynamical mean field theory. We provide a detailed discussion of the calculated Fermi surface and its dependence on the level of theory used for the treatment of the electron-electron interactions. Although we confirm that Os can be classified as weakly correlated metal, the inclusion of local quantum fluctuations between 5d electrons beyond the local density approximation explains the most recent experimental reports regarding the occurrence of ETTs in hcp-Os.

P 10.17

Theoretical investigation of disordered Ir-Os alloys under pressure

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The aim of this work is to theoretically investigate disordered alloys of the Ir-Os system under pressure in the whole concentration range. For the calculations of the total energy E of disordered alloys we used the Exact Muffin-Tin Orbitals (EMTO) method in combination with the coherent potential approximation [1]. The lattice parameter obtained for fcc and hcp alloys changes very slowly with increasing concentration of Os because the lattice parameters of Ir and Os are close. Calculations performed in the local density approximation (LDA) give slightly lower results compared with the experiment, but the theoretical values and the experimental data agree well with each other. The bulk modulus depends on the composition of alloys and increases with increasing osmium content. The experiment [2] demonstrated that the fcc $Ir_{80}Os_{20}$ alloy did not undergo structural transformations at pressures up to 55 GPa, however the dependence of the compressibility on the pressure had a peculiarity at 20 GPa. Such a peculiarity may be caused by the presence of the so-called electronic topological transition, associated with a change of the Fermi surface topology. To investigate this possibility, we have calculated the Fermi surface for this alloy at different pressures. It can be seen that the Fermi surface at pressure 0, 20 and 35 GPa are almost identical, suggesting that the pressure induced electronic topological transition in this alloy is not seen within state-of-the-art computational approaches. The study of new type of electronic transition (CLC) [3] in the system Ir-Os alloys may give an explanation of the peculiarities in the behavior of compressibility fcc $Ir_{80}Os_{20}$ alloy.

The support from the Grant of Ministry of Education and Science of theRussian Federation (Grant No. 14.Y26.31.0005) is gratefully acknowledged.

[1] L. Vitos, I.A. Abrikosov, and B. Johansson, Phys. Rev. Lett. **87**, 156401 (2001).

[2] K.V. Yusenko, E.A. Bykova, M. Bykov, et all, J. Alloys Compounds. **622**, 155 (2015)

[3] L. Dubrovinsky, N. Dubrovinskaia, E. Bykova, M. Bykov, V. Prakapenka, C. Prescher, K. Glazyrin, H.-P. Liermann, M. Hanfland, M. Ekholm, Q. Feng, L. V. Pourovskii, M. I. Katsnelson, J. M. Wills, and I. A. Abrikosov, Nature **525**, 226-229 (2015)

Invited Talk

New forms of silica and aluminosilicates from hydrothermal environments at gigapascal pressures

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Hydrothermal processing - utilizing aqueous media at elevated temperature and pressure - provides excellent possibilities for synthesizing advanced ceramic materials, whether they are bulk single crystals, fine particles, or nanoparticles. Hydrothermal processing is normally performed at subcritical conditions (that is at p, T conditions below the critical point of water (T = 374 °C and p = 22.1 MPa)). However, water can exist at very high pressures and temperatures, and it is interesting to imagine the extension of hydrothermal processing to extreme conditions, involving gigapascal pressures and temperatures up to 1000 °C. Water's physicochemical properties will be drastically changed and new prospects can be envisioned for chemical/materials synthesis, with water exhibiting novel behaviors as solvent, reactant, and catalyst. Large-volume high pressure methodology using multi anvils enable handling of pressurized aqueous environments up to 10 GPa. In this presentation we show some of the potential of extreme hydrothermal environments for creating truly new and unique materials. In particular, hydrothermal crystallization of silica and aluminosilicate glasses at high pressures yields a new form of stishovite, hydrous stishovite with significant amounts of structural water, and new types of dense hydroxy-oxide materials, respectively.

O 11.1

Unexpected high pressure and high temperature chemistry in Xe-N_2 mixtures

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Question

Recent numerical simulations predict that xenon and nitrogen, two inert gases under ambient conditions, chemically react at high pressures to form an intriguing covalently-bonded high energy density xenon nitride.[1] In this study, we present a thorough investigation of Xe-N_2 mixtures to high pressures (184 GPa) and high temperatures (2500 K).

Methods

Xe-N_2 mixtures were characterized using visual observations, Raman spectroscopy as well as synchrotron X-ray diffraction and X-ray absorption spectroscopy (XAS). The gas mixtures were loaded into a membrane diamond anvil cell with a high pressure gas charger after sufficient homogenization time (~12 h). High temperatures were achieved by laser-heating the sample with a YAG laser while a thin layer of either LiF or Al_2O_3 was used to thermally insulate the diamond anvils. XAS experiments were carried out with nanopolycrystalline diamond anvils.

Results

The Xe-N_2 binary phase diagram was determined at 300 K from the pressure evolution of 14 different concentrations. Above 4.9 GPa, the $Xe(N_2)_2$ van der Waals compound was found stable, adopting the $MgCu_2$-type Laves phase structure (cubic, *Fd-3m*) with N_2 molecules spherically disordered. At 10 GPa, $Xe(N_2)_2$ undergoes a martensitic phase transition into a tetragonal (*I41/amd*) unit cell, due to the growing N_2-N_2 quadrupole-quadrupole interaction inducing a partial ordering of the N_2 molecules. No other phase transition was detected in $Xe(N_2)_2$ up to 184 GPa, even when heating it to 2500 K. Its great stability is explained by an intriguing bondless redistribution of electronic density between N_2-N_2 and Xe-N_2 entities. However, for Xe-N_2 mixtures in excess of nitrogen with respect to $Xe(N_2)_2$, a novel compound was produced above 1500 K and 140 GPa along with $Xe(N_2)_2$. Previously unobserved low frequency Raman modes and XAS measurements suggest the new compound to be a Xe-N covalently-bonded solid. Surprisingly, this xenon nitride does not correspond to the predicted XeN_6, but instead seems to be of even greater nitrogen concentration.

Conclusions

Under the thermodynamic conditions where XeN_6 is predicted, a $Xe(N_2)_2$ compound with bondless Xe-N_2 interactions and a xenon nitride with a higher than anticipated nitrogen concentration were instead observed.

Reference

[1] F. Peng, Y. Wang, H. Wang, Y. Zhang, and Y. Ma, Phys. Rev. B **92**, 094104 (2015).

O 11.2

Reaction between nickel or iron with xenon under high pressure

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Xenon has a rich chemistry under pressure: several new stable Xe-containing compounds such as xenon oxides have been theoretically predicted (using density functional theory) and/or synthesized in the Mbar range. Here, Xe-Ni and Xe-Fe systems are studied in a pressure range relevant to the Earth's core (117-200 GPa) using laser-heated diamond anvil cells. Xenon has been predicted to react with nickel and iron to form several metal-rich intermetallic compounds, above 155 and 190 GPa, respectively [1]. Indeed, we have synthesized $XeNi_3$ above 150 GPa and identified its structure which is different from the prediction. In addition, a disordered $Ni_{1-x}Xe_x$ alloy is observed to form prior to the compound, which might be interesting in the perspective of a possible storage of xenon in the Earth's core. Such a storage could explain the anomalously low Xe content in the atmosphere. Despite three trials, we have not observed any reaction between Xe and Fe up to 200 GPa, a pressure at which a reaction is predicted. This might be related to an unefficient laser heating in the Xe-Fe samples assemblies.

[1] L. Zhu et al., Reactions of xenon with iron and nickel are predicted in the Earth’s inner core, Nat. Chem. 6, 644, 2014

O 11.3

Rapid polycyclic polymerization of linear dicyanoacetylene activated by pressure

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Pressure-induced polymerization has been documented for a wide variety of crystalline molecular solids, yet precise mechanistic details of the reactions are not fully understood and the direct characterization of recovered products is lacking. Here we study the high-pressure behavior of linear dicyanoacetylene (C_4N_2) up to 10 GPa in diamond anvil cells. Pressure-induced polymerization was observed above 6 GPa and a novel amorphous C_4N_2 extended network with five and six-membered ring was recovered to ambient conditions. This product was characterized by Raman, IR and XRD, XPS, EELS, and MD simulations. The mechanism is computationally rationalized from the formation of bulked molecular chains into cis and trans specices, which spontaneously assemble into multiple-membered rings. This understanding offers valuable mechanistic insights into design guidelines for the next-generation carbon nitride materials with unique structures and compositions.

O 11.4

Synthesis of highly transparent triclinic Al_2SiO_5 kyanite

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State-of-the-art high pressure technologies allow synthesizing novel nano-scaled polycrystalline materials, in particular ceramics with premium physical properties made from Earth's highly abundant geomaterials.

Composites of Al_2SiO_5 (kyanite) with small amounts of Al_2O_3 (corundum) were synthesized from glasses with Al_2SiO_5 composition produced by container-less processing in an aerodynamic levitation furnace under high pressure and temperature. These composites have a high optical transparency and high resolution X-Ray powder diffraction shows that Al_2SiO_5-glass completely transformed into Al_2SiO_5 (kyanite) with small amounts of Al_2O_3 (corundum) (Fig. 1).

Transmission electron microscopy observations show that highly transparent Al_2SiO_5 (kyanite) + small amount of Al_2O_3 (corundum) exhibits nano-sized grains (Fig. 2). Furthermore, in-line transmission measurements were performed revealing an unexpected in-line transmission behaviour. Kyanite is triclinic that is the lowest symmetry of crystals. The results indicate that oxide polycrystalline materials can be transparent even with the lowest symmetry. This is the first example of transparent ceramics with triclinic symmetry. Our results present that poly-nanocrystalline geomaterials made from low-cost raw substances like SiO_2 and Al_2O_3 are suitable and very promising for the production of materials with exceptional optical properties.

References

[1] Nishiyama N, Taniguchi T, Ohfuji H, Yoshida K, Wakai F, Kim B-N, Yoshida H, Higo Y, Holzheid A, Beermann O, Irifune T, Sakka Y, Funakoshi K (2013) *Scr. Mater.*, 69, 362-365.

[2] Nishiyama N, Wakai F, Ohfuji H, Tamenori Y, Murata H, Taniguchi T, Matsushita M, Takahashi M, Kulik E, Yoshida K, Wada K, Bednarcik J, Irifune T (2014) *Sci. Rep.*, 4.

[3] Riello P, Canton P, Comelato N, Polizzi M, Verita M, Fagherazzi G, Hofmeister H, Hopfe S (2001) *J. Non-Cryst. Solids*, 288, 127-139.

[4] Comodi P, Zanazzi PF, Poli S, Schmidt MW (1997) *Am. Mineral.,* 82, 452-459.

Figure 1

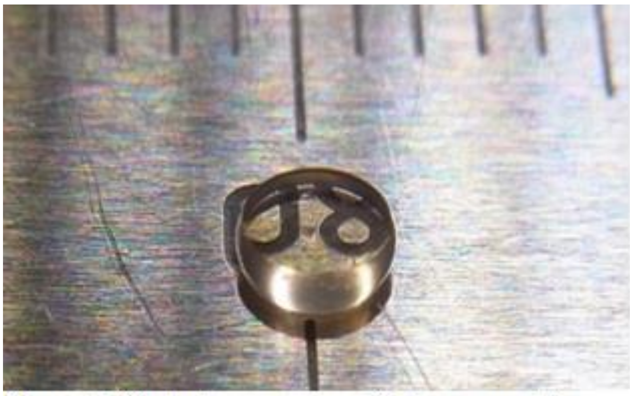

Figure 1: Optical appearace of the composite

Figure 2

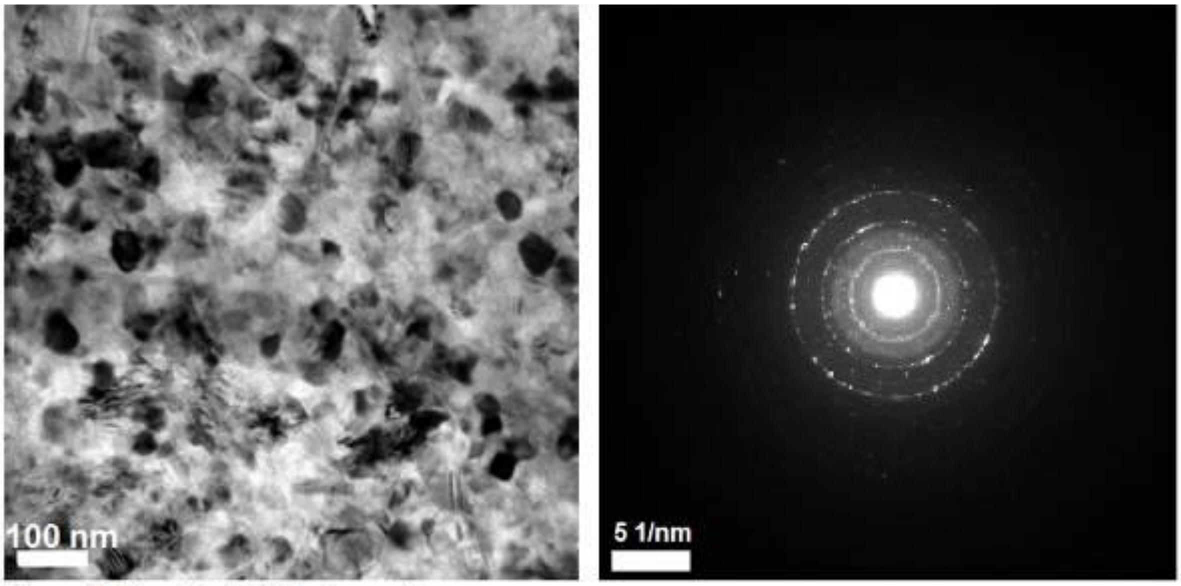

Figure 2: Results of TEM observations

O 11.5

Oriented growth and grain size reduction during phase transitions in hydrous Mg_2SiO_4: Implications for slab strength variations at transition zone depth

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We report, on microstructural changes (grain size and textural relationships) in hydrous Mg_2SiO_4 during the series of *α-β-γ* phase transformations with data acquired *in situ* at high pressure and temperature using multi-grain crystallography. Detailed knowledge on transformation related microstructural changes in the Earth's mantle major constituent ($(Mg,Fe)_2SiO_4$) is important to understand the descending behaviour of subducted slabs as well as observations of seismic anisotropy. Diffraction experiments were carried out using synchrotron radiation combined with a resistively heated diamond anvil cell up to 40 GPa and 850 °C. The experiment was conducted over 2 days and at a low strain rate of $2*10^{-6}$ $s^{-}1$.

We monitored the orientations of hundreds of grains and grain size variations during the succession of the transformations. Obtained transformation micro-textures reveal the absence of orientation relationships between the parent *α*-phase and the daughter phase at each stage of the transformations, suggesting an incoherent growth through the nucleation and growth mechanism. During all transformations we observed significant grain size reductions and only little grain growth of newly formed phases. Such grain size reductions in cold slabs may lead to a change of the plastic deformation behaviour, from dislocation creep to grain sensitive diffusion creep and may therefore result in slab strength weakening and their stagnation. The new results are important for understanding the mechanical behavior of subducting slabs, seismic anisotropy in the Earth's mantle, and phase transformation mechanisms in olivine.

O 11.6

High pressure synthesis and study of layered Cr^{4+} based oxides

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Question

After 25 years of research on the superconducting cuprates, the discovery of high T_c superconductivity in related iron based pnictides in 2008 has stimulated the search of new compounds. In particular, antiferromagnets (AFM) with high Néel temperature and moderate magnetic moments with crystallographic 2D layers could be good candidates. In this context we have started the study of the n=1 and n=2 members of the $Sr_{n+1}Cr_nO_{3n+1}$ Ruddlesden-Popper series which can be only synthesized at high pressure - high temperature (HP-HT).

Methods

To synthesize these phases we use our large volume presses at the Néel Institute, the Conac-type and the Belt-type. The mixture of SrO + CrO_2 in stoichiometric proportion, placed in a gold (or platinum) capsule, is treated at 8 GPa and 1500°C.

Results

Our samples of Sr_2CrO_4 (Sr214) and $Sr_3Cr_2O_7$ (Sr327) are quasi monophasic. We measured the magnetization, specific heat and Neutron Powder Diffraction of Sr327. We find an antiferromagnetic ordering at $T_{Néel}$=210K with the magnetic structure (Fig.1b), that agrees with our DFT calculations. We observed a huge magneto-structural coupling, resulting in an increase of the a-axis by 0.33% and a decrease of the c-axis by 1.33% at $T_{Néel}$ (Fig.1a). The CrO_6 octahedron, almost ideal at ambient temperature, distorts along the apical oxygen from the Néel temperature down to 4K (Fig.2). While for S214, the CrO_6 octahedron, distorted at ambient temperature, becomes almost ideal at 4K.

We have recently synthesized (4 GPa and 1000°C) quasi monophasic samples of Ca_2CrO_4 (Ca214) and $Ca_3Cr_2O_7$ (Ca327). Our magnetization measurements clearly suggests an AFM ordering (Fig.3) and a strong magneto-structural coupling below T_N=150K for Ca327.

Conclusions

We have studied the magnetic and structural properties of the n=1 and n=2 members of the $Sr_{n+1}Cr_nO_{3n+1}$Ruddlesden-Popper series. Doping has been tried, but phases still remain insulating, even under pressure. So we tried chemical pressure and have synthesized under high pressure, for the first time, the corresponding ones for $Ca_{n+1}Cr_nO_{3n+1}$.

Figure 1 :(a) Temperature dependence of $Sr_3Cr_2O_7$ lattice parameters (b) Magnetic structure of $Sr_3Cr_2O_7$.

Figure 2 : Temperature dependence of interatomic distances in CrO_6 octahedron of $Sr_3Cr_2O_7$.

Figure 3 : Temperature dependence of the magnetization of $Ca_3Cr_2O_7$.

Figure 1

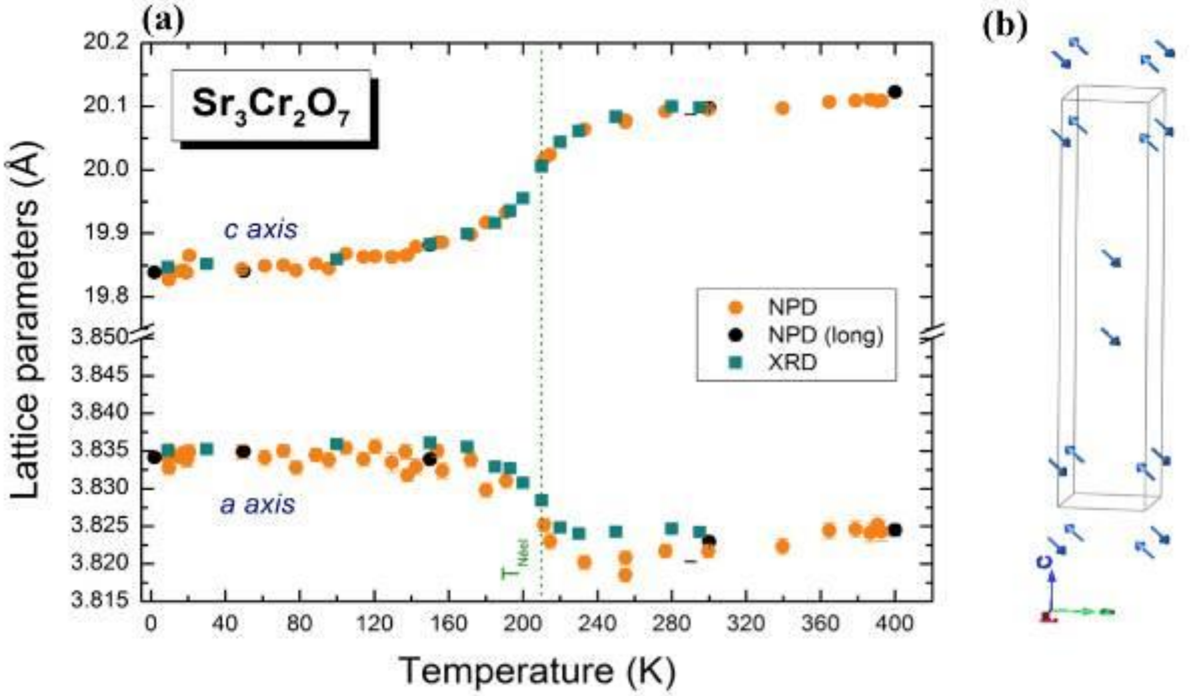


Figure 2

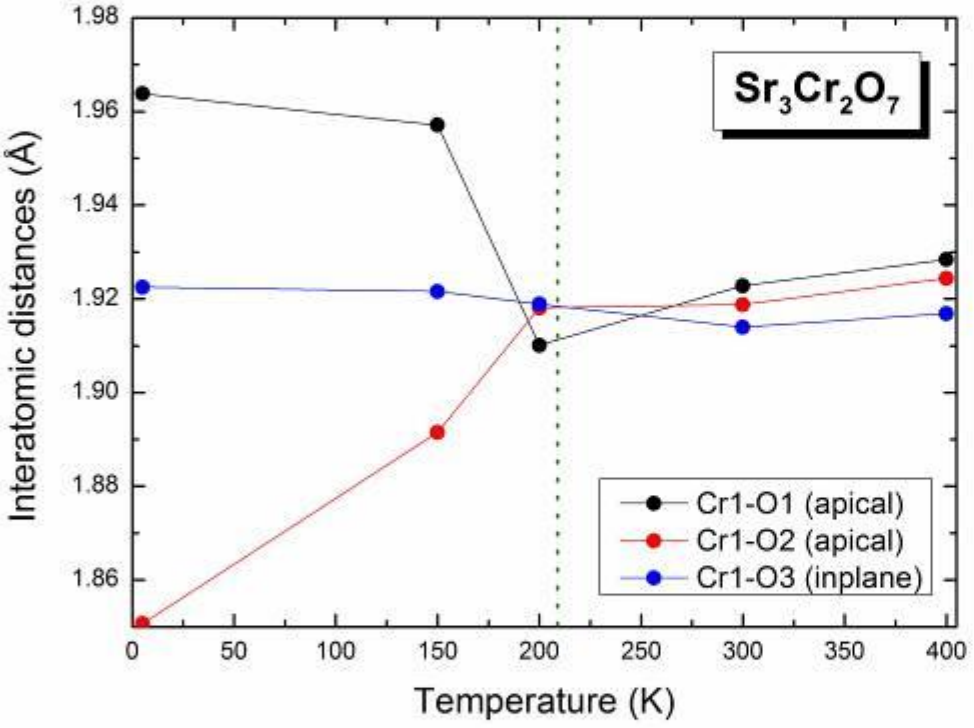
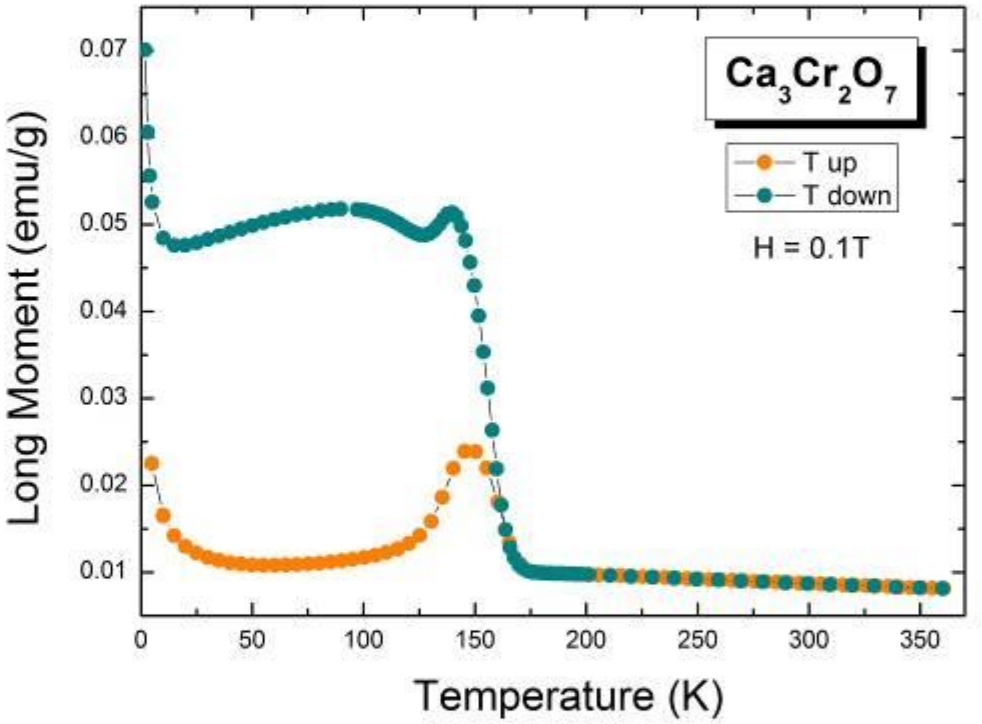


Figure 3



$Ca_3Cr_2O_7$
T up
T down
H = 0.1T
Long Moment (emu/g)
Temperature (K)
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0
50
100
150
200
250
300
350

O 11.7

High-pressure synthesis, crystal structure and physical properties of *A*-site-ordered perovskite $BiCu_3Cr_4O_{12}$

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Many 3*d*-transition metal perovskites exhibit various interesting phenomena. A-site-ordered perovskites with a chemical formula of $AA'_3B_4O_{12}$ crystallize in an *Im* cubic lattice. The structure with cubic cell of 2*ap* x 2*ap* x 2*ap* (*ap* is the simple perovskite lattice parameter) is a largely distorted variant of the perovskite structure. *A*' site is of a pseudosquare planar coordination suited to Jahn-Teller active ions such as Cu^{2+} and Mn^{3+}, while *A* site is occupied by typical large *A*-site ions such as alkaline earth and rare earth metal ions. In this case, *B* site is occupied by a 3*d*-transition metal. They provide an opportunity for the mixed valence state of *B* site. *B* cations should be in the mixed valence state $B^{+3.75}$, when *A* and *A*' sites occupy 3+ cations and Cu^{2+} ions. We have obtained new *A*-site ordered perovskite $BiCu_3Cr_4O_{12}$ using high-pressure and high-temperature synthesis. Ferrimagnetic transition with a structural distortion was observed at around 185K. The resistivity exhibits an anomaly at the transition, but metallic behavior persists even in the magnetic phase. We have revealed an unusual charge disproportionation below the transition from the structural analysis. It is considered that the origin of the transition is the local distortion of the BiO_{12} polyhedron for Bi 6*s*-O 2*p*-Bi 6*p* hybridization. The structural distortion stabilizes the Cr-O hybridization of the $Cr^{4+}O_6$ octahedra. As the result, the two kinds of $Cr^{3.5+}O_6$ and $Cr^{4+}O_6$ chains ordered in a rocksalt-type substructure in ac plane in the low-temperature phase. This is the first observation of the charge disproportionation transition in chromium oxides.

O 11.8

High-pressure synthesis of novel electrocatalysts

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Transition metal perovskite oxides, ABO_3, have been investigated because of their excellent catalytic properties for electrochemical reactions like oxygen evolution reaction (OER) [1] and oxygen reduction reaction [2]. Sutivich et al. proposed that the e_g orbital occupancy for B-site cations dominates OER catalytic activity, in which $e_g^{1.2}$ for $(Ba,Sr)(Co,Fe)O_{3-\delta}$ has the highest catalytic activity for OER [1]. We recently reported that the Fe^{4+}-based simple and quadruple perovskite oxides, $(Ca/Sr)FeO_3$ and $CaCu_3Fe_4O_{12}$, synthesized under high-pressure nad high-temperature conditions (>10 GPa, ~1000 °C) display high catalytice activity for OER in alkaline conditions [3]. Here, we show the Fe-valency dependence of the OER catalytic activity for $Fe^{3+/4+}$ compounds, $Ca_{1-x}La_xFeO_3$ and $ACu_3Fe_4O_{12}$ (A = Ca, Y, La, Ce) synthesized under high pressure. The OER catalytic activity monotonically increased when Fe valence increased from +3 to +4, confiming that the Fe^{4+}-oxides have highest catalytic activity. In our presentation, we will show structure-activity relationship for the Fe^{4+}-perovskite oxides.

References

[1] J. Suntivich et al., Science 334, 1383 (2011)

[2] J. Suntivich et al., Nat. Chem. 3, 546 (2011)

[3] S. Yagi et al., Nat. Commn. 6, 8249 (2015)

O 11.10

Extending the field of nickel borates *via* high-pressure synthesis

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When comparing the systems Fe–B–O(–H), Co–B–O(–H), and Ni–B–O(–H), it is striking that the number of published high-pressure borates in each system decreases from five (Fe-borates), to four (Co-borates), to two (Ni-borates). Since the transition metals Fe, Co, and Ni have similar chemical properties and thus often form isotypic compounds, one would also expect that a similar number of corresponding transition metal borates exist. Therefore, the small number of already known nickel borates motivated us to further investigate the system Ni–B–O(–H).

Within this system, six compounds are known so far. Three hydrous phases and three anhydrous phases. Two of these anhydrous compounds were formed during high-pressure experiments at 7.5 GPa/680 °C (HP-NiB_2O_4)[1] and 7.5 GPa/1150 °C (⍰-NiB_4O_7)[2], respectively.

Here, we present the crystal structures of another four nickel borates synthesized at elevated pressures using a Walker-type multianvil apparatus. The compositions, reaction conditions, and space groups are listed in Table 1.

Table 1. Compositions, reaction conditions, and space groups of the new nickel borates.

Composition	*p* /GPa	*T* /°C	Crucible	Space group
$NiB_3O_5(OH)$	3.5	750	BN	$P2_1/c$
"$Ni_3B_{18}O_{32}$" [a)]	5	750	BN	$P\bar{6}2m$
γ-NiB_4O_7	5	900	BN	$P6_522$
$Ni_6B_{22}O_{39} \cdot H_2O$	5	900	Pt	$Pmn2_1$

a) The exact composition could not be determined yet

We were able to extend the field of nickel borates by synthesizing four new compounds. The fact that these compounds were synthesized within the narrow pressure range of 3.5–5 GPa emphasizes once more the importance of the parameter pressure in solid state chemistry.

References

[1] Knyrim, J. S.; Roessner, F.; Jakob, S.; Johrendt, D.; Kinski, I.; Glaum, R.; Huppertz, H., *Angew. Chem. Int. Ed.* **2007**, *46*, 9097-9100.

[2] Knyrim, J. S.; Friedrichs, J.; Neumair, S.; Roessner, F.; Floredo, Y.; Jakob, S.; Johrendt, D.; Glaum, R.; Huppertz, H., *Solid State Sci.* **2008**, *10*, 168-176.

P 11.1

Niamond: superhard diamond-cBN alloy formed under high pressure and high temperature

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Diamond and cubic boron nitride (cBN) are super-hard materials that have been widely used in industry for over half a century, but both have inherent limitations. Diamond is neither stable in the presence of oxygen, even at moderate temperatures of about 900 K, nor is it suitable for machining ferrous alloys, while cBN is only about half as hard as diamond. The structural similarity between diamond and cBN has stimulated the synthesis of a new hybrid compound consisting of the three elements boron, carbon and nitrogen, which can potentially fill the performance gap. However, the idea has never been demonstrated because samples obtained in the previous studies were too small to be tested for their practical performance. Here, the bulk diamond-cBN alloy compacts were synthesized at pressures of 11-20 GPa and temperatures of 1300-2600K**,** whose diameters (3mm) are sufficiently large for all kinds of performance testing. The testing results show that the diamond-cBN alloy has superior chemical inertness over polycrystalline diamond and higher hardness than single crystal cBN. High-speed cutting tests on hardened steel and granite suggest that diamond-cBN alloy is a universal cutting material.

P 11.2

The synthesis of nanocrystalline diamond balls to generate ultra-high pressures in diamond anvil cells

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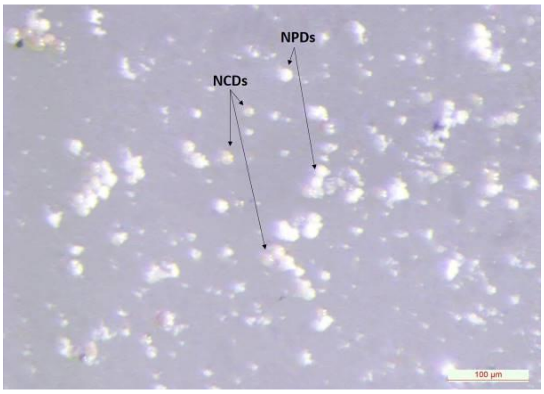
Until recently conventional diamond anvil cells have been facilitated to succeed pressures up to 4 Mbar. However, the necessity to study materials at extreme conditions has led to the implementation of alternative anvils such as the nano-polycrystalline diamonds (NPDs) or the nanocrystalline diamond balls (NCDs). Using NCDs pressures above 750 GPa were generated leading to the investigation of extremely incompressible materials [1]. However, the synthesis of NCDs is a challenging and not well constrained procedure yet [2, 3]. Thus, with our work we present key factors for their successful synthesis. A mechanical mixture of MgO and glassy carbon balls (GCs) (10-20 μm) (MgO:GCs = 10:1) was prepared and kept at 130 °C for 24 hrs prior to its use. The synthesis was carried out in a multi anvil apparatus using a BN capsule at 18 GPa and 2100 ± 100 °C for 1 min. All assembly parts were fired at 1000 °C for 4 hrs before their assemblage. The assembly was then kept in a vacuum furnace at 130 °C overnight and later was quickly placed in the apparatus. The intensive drying procedure is essential for the successful NCDs synthesis. The produced sample was thoroughly washed by hot HCl acid forming $MgCl_2$, which is solved by H_2O, thus, leaving the NCDs, NPDs or GCs unreacted to be observed by an optical microscope (Fig. 1). By these experimental conditions, we obtain significant amounts of NCDs coexisting with NPDs. Shorter heating times result in an assemblage of mainly untransformed GCs coexisting with small amounts of NPDs and NCDs, while longer heating times result in higher amounts of NPDs coexisting with NCDs. XRD patterns of the untransformed GCs shows amorphous material suggesting that GCs transform directly to NCDs. Finally, we found that the capsule material strongly affects the synthesis. Using MgO or Re capsules at the same experimental conditions produces mostly NPDs and untransformed GCs, respectively. Our investigation for the perfection of NCDs synthesis continues.

Figure 1. Optical image of the washed sample.

[1] Dubrovisnky et al. (2015), Nature, 525, 226-229; **[2]** Dubrovisnky et al. (2012), Nat. Commun., 3, 1163; **[3]** Solopova et al. (2014), JCG, 412, 54-59.

Figure 1



P 11.3

Ordering of interstitial nitrogen in hcp iron under high pressure

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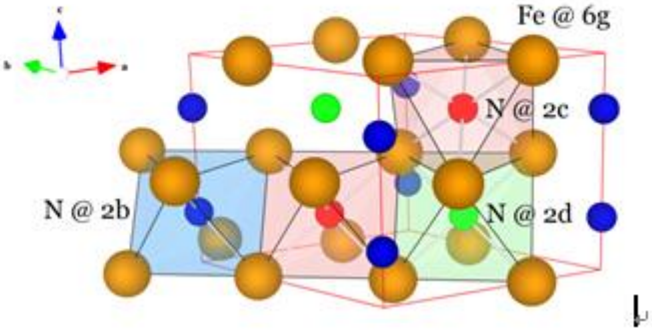
The Earth's inner core is composed primarily of Fe element. Fe transforms from a bcc α-Fe at ambient conditions to an hcp ε-Fe over a wide range pressure (13-300 GPa) and temperature conditions (<3000 K). Iron nitrides are classified as metallic interstitial nitrides with variable amounts of nitrogen. The introduction of interstitial nitrogen stabilizes hcp arrangement of Fe at lower pressure and temperature condition, such as 5 GPa and 1673 K. ε-$Fe_3N_{1+\delta}$ is a rare nitrogen and iron mineral in natural, under the name of "Siderazot". In the ideal ε-$Fe_3N_{1+\delta}$ with space group $P6_322$, as depicted in Figure 1, Fe(6g) atoms form a hcp arrangement with N(2c) atoms occupying one-third of voids inside Fe_6 octahedral in an ordered fashion. Each Fe(6g) atom is coordinated by two nearest-neighbor N(2c) atoms, and the interstitial lattice 2c site is the only occupation site for N atoms. Our neutron powder diffraction (NPD) experiments showed that the high-pressure confining environment allows nitrogen to occupy the higher potential barrier lattice 2b and 2d sites in binary ε-$Fe_{3-x}N_{1.098}$, and 2b site in ternary ε-$Fe_{2.322}Co_{0.678}N_{0.888}$. Both binary ε-$Fe_{3-x}N_{1.098}$ and ternary ε-$Fe_{2.322}Co_{0.678}N_{0.888}$ have metallic Fe^0 characters. The content of metallic Fe^0 can be determined by NPD and XPS methods. This work has implications to our understanding of the ordering of interstitial N in hcp iron under high pressure.

Figure 1



P 11.4

Nitrogen pentafluoride accessed via high-pressure synthesis - evidence for hexacoordinated N(V)

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Pentavalent nitrogen(V) is found in a variety of compounds (e.g. nitric acid), but in all of these connections each nitrogen atom forms bonds to no more than four other atoms. Many attempts have been made to synthesize species with nitrogen(V) coordinated by five atoms (hypercoordinated nitrogen), with nitrogen pentafluoride (NF_5) being the most promising candidate for such a compound. Yet despite many efforts NF_5 has not been obtained under ambient conditions.

In recent years the high-pressure chemistry of fluorine [1-4] has attracted considerable attention. Even at low pressure several exotic species have been predicted to form, such as CsF_n ($n > 1$) [2,3] or ArF_2[4]. On the other hand our recent experimental investigation [5] indicated that nitrogen trifluoride (NF_3) is a promising reagent for high-pressure reactions.

Motivated by the above-mentioned findings we have studied theoretically the possibility of obtaining NF_5 by means of a high-pressure reaction between NF_3 and F_2. Based on previous observations that standard GGA functionals may fail to quantitatively describe the thermodynamic stability of weakly bound systems [4] we used the HSE06 hybrid DFT functional for geometry and enthalpy calculations.

Our results indicate that the proposed reaction pathway should result in synthesis of NF_5 already at a pressure of 40 GPa. We find that nitrogen pentafluoride exhibits a rich high-pressure polymorphism with a variety of phases exhibiting both covalent and ionic bonds (Figure 1). Interestingly, NF_5-containing structures are not stable up to 300 GPa. Instead we find that above 34 GPa all the ground state structures contain a novel NF_6^- anion with hexacoordinated nitrogen(V).

Our findings indicate that NF_5 should be readily accessible at high pressures and also possibly metastable at ambient conditions, due to its ionic nature.

Figure 1. High-pressure phases of NF_5: (A) $NF_3 \cdot F_2$, (B) $NF_4^+F^-$, (C) $(NF_4^+)(NF_6)^-$, (D) $(NF_4^+)_2(NF_6)^-F^-$.

References

[1] J. Botana, X. Wang, C. Hou, D. Yan, H. Lin, Y. Ma, M. Miao, *Angew. Chemie Int. Ed.* **2015**, *54*, 9280.

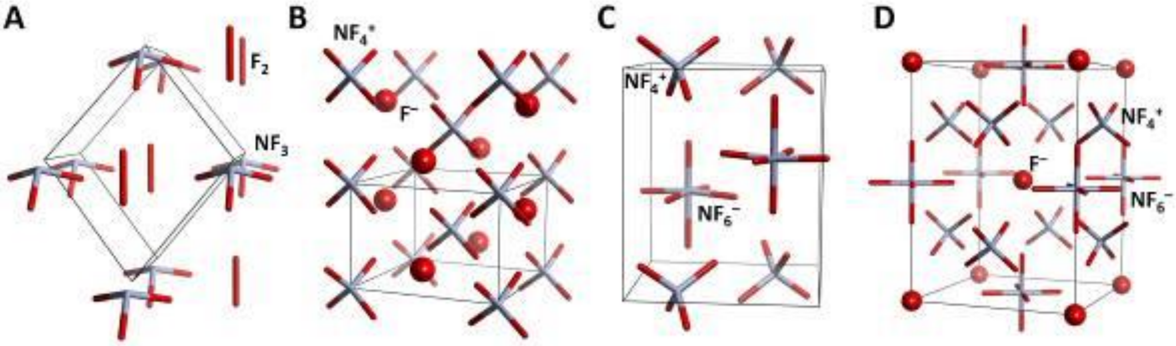
[2] M. Miao, *Nat. Chem.* **2013**, *5*, 846.

[3] Q. Zhu, A. R. Oganov, Q. Zeng, *Sci. Rep.* **2015**, *5*, 7875.

[4] D. Kurzydłowski, P. Zaleski-Ejgierd, *Phys. Chem. Chem. Phys.* **2016**, *18*, 2309.

[5] D. Kurzydłowski, H. B. Wang, I. A. Troyan, M. I. Eremets, *J. Chem. Phys.* **2014**, *141*, 064706.

Figure 1



P 11.5

Synthesis and crystal structure of the new high-pressure indium borate $In_{19}B_{34}O_{74}(OH)_{11}$

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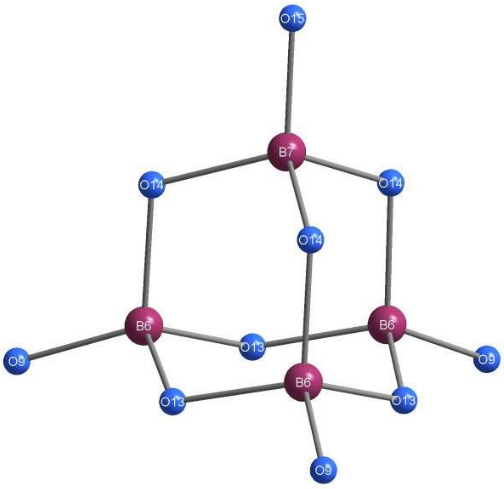
In the system In–B–O(–H) there are three compounds known up to now: $InBO_3$[1], $H_2InB_5O_{10}$[2] and its dehydrated equivalent InB_5O_9[2]. All three compounds were synthesized either in autoclaves or at ambient pressure. This motivated us to apply high-pressure conditions to explore the field of indium borates in more detail.
With the successful high-pressure synthesis of $In_{19}B_{34}O_{74}(OH)_{11}$ we were able to find the second hydrated indium borate which is also the first borate showing the structural motif of a T2-supertetrahedron.
The synthesis of $In_{19}B_{34}O_{74}(OH)_{11}$ was carried out under high-pressure/high-temperature conditions of 12.8 GPa and 1100 °C in a Walker-type multianvil apparatus. Its crystal structure was solved and refined based on single-crystal X-ray diffraction data. $In_{19}B_{34}O_{74}(OH)_{11}$ crystallizes in the trigonal space group $R\overline{3}$ (Z = 12) with the lattice parameters $a = 1802.49(6)$, $c = 1340.46(5)$ pm, and $V = 0.37716(3)$ nm^3. The complex structure of $In_{19}B_{34}O_{74}(OH)_{11}$, which could be refined to R-values of $R_1 = 0.0195$ and $wR_2 = 0.0366$ (all data), is mainly built up of InO_6 octahedra, corner-sharing BO_4 tetrahedra and hydroxyl groups. Additionally, the structure of $In_{19}B_{34}O_{74}(OH)_{11}$ includes adamantane-like B_4O_{10} groups which form the above mentioned T2-supertetrahedra.

To conclude, with the synthesis of the second hydrated indium borate $In_{19}B_{34}O_{74}(OH)_{11}$ we were able to expand the substance class of indium borates opening up a promising new field for high-pressure syntheses.

[1] Cox, J. R.; Keszler, D. A., *Acta Crystallogr., Sect. C: Struct. Chem.* **1994**, *50*, 1857-1859.

[2] Cong, R.; Yang, T.; Li, H.; Liao, F.; Wang, Y.; Lin, J., *Eur. J. Inorg. Chem.* **2010**, *2010*, 1703-1709.

Figure 1



P 11.6

High pressure synthesis of geometric frustrated rare earth pyrochlores $RE_2Ge_{2-x}Si_xO_7$ with multianvil technique

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The magnetic Rare Earth (RE) ions in compounds with pyrochlore structure (Fd-3m, 227) of the general formula $RE_2B_2O_7$ (e.g. RE = Tb, Dy und B = Ti, Ge) build a network of corner sharing tetrahedra. The nature of the magnetic coupling, together with this special mutual arrangement of the RE-ions in the pyrochlore lattice creates a geometrically frustrated system from which at low temperatures <10 K unusual magnetic states like Spin-Ice [1,2] or magnetic monopole quasiparticles [1] emerge. Materials with particularly short distances between the magnetic centers are most promising to have new interesting properties, due to high correlation of the magnetic spins [1]. Hence pyrochlore compounds with especially small lattice constants are of great interest. The germanate pyrochlore $Dy_2Ge_2O_7$ possesses the smallest known lattice constant (a = 9.929 Å) so far [1], requiring high pressures over 5 GPa for its synthesis.

While the magnetic properties of the rare earth ions need to be preserved, further contraction of the lattice can only be achieved by the "chemical pressure concept", i.e. incorporation of yet smaller B-cations, without leaving the bounds for pyrochlore structural stability [3].

Here we present partial substitution of germanium by silicon in rare earth germanate pyrochlores $RE_2Ge_2O_7$ via high pressure-high temperature solid state synthesis at pressures > 10 GPa using the multianvil technique. With increasing pressure, solid solutions of $RE_2Ge_{2-x}Si_xO_7$ with increasing silicon content x and decreasing lattice constant can be obtained. First results on the evolution of magnetization and magnetic susceptibility down to cryogenic temperatures will be reported.

Website: http://www. http://tu-dresden.de/forschung/forschungskompetenz/sonderforschungsbereiche/sfb1143/projekte/b02

References

[1] Zhou, H. et al. *nature communications*, DOI: 10.1038/ncomms1483, **2011**, s. 1-5.

[2] Hallas, A., et al. *Phys. Rev. Lett.*, 113, **2014**, s. 267205-1-6.

[3] Mouta, R., et al. *Acta Cryst*., B69, **2013**, s. 439-445

P 11.8

High pressure synthesis of Li_2IrO_3

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The 5d transition metals, especially iridium, have strong spin-orbit interactions. These lead to effective angular momentum of J_{eff}=½. Due to these correlations, iridates with a honeycomb-like arrangement of IrO_6-octahedra are considered as candidate materials for frustrated magnetism with spin liquid behavior as predicted by the famous Kitaev-Heisenberg model. [1] Alkaline iridates of the type A_2IrO_3, A = Li, Na are of particular interest. [1] However, samples of Li_2IrO_3 phases realized so far show magnetic ordering at low temperature. It is still unknown which process leads to this magnetic ordering while a disordered state is expected [2]. For magnetic studies single crystals with high purity are needed, but for the synthesis of Li_2IrO_3 so far only ambient-pressure methods, resulting in polycrystalline bulk samples, have been reported. Until now, single crystal synthesis of honeycomb-type Li_2IrO_3 phases meets experimental difficulties due to the high volatility of both Li-O and Ir-O species. Moreover, many polytypes of honeycomb-Li_2IrO_3 are predicted, which could further complicate synthesis of a phase-pure product. At ambient pressure, g-Li_2IrO_3 could already be realized as single crystals by Modic et al. [2]. While this phase shows orthorhombic symmetry, the monoclinic, denser, alpha-phase seemed furthermore interesting.

Here we show a high pressure approach on the synthesis of Li_2IrO_3 materials using multianvil, as well as toroid-type high pressure technology. Iridium oxide IrO_2 together with different lithium source materials, such as Li_2CO_3, LiOH and $LiNO_3$, Li_2O and Li_2O_2 enclosed in noble metal capsules were tested at pressures between 2 and 10 GPa and temperatures up to 1100°C. It is shown that the formation of Li_2IrO_3 is indeed very sensitive on the starting material. So far, synthesis of the interesting alpha-Li_2IrO_3 in polycrystalline bulk form has been achieved. High pressure synthesis may lead to a reduction of impurities, stacking faults and other crystal defects, necessary to probe the true magnetic properties of the material. Efforts, to extend the method towards single crystal growth via appropriate pressure cell and furnace design are presented. This will lead to new possibilities in the studies of frustrated magnetism.

[1] Chaloupka et al., Phy. Rev. B, 92 (2), 024413

[2] Cao et al.; *Cond. Mat. Str. el.* **2013** 1-8.

[3] Modic et al.*; Cond. Mat. Mtrl sci* **2014** 1-16.

P 11.9

Hidden face of Silicon-III BC8 allotrope: Study of samples obtained in the Na-Si system at recordly low pressures

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Strain-free metastable high-pressure allotrope of silicon, Si-III or BC-8, has been synthesized in the Na-Si system at 9.5 GPa by quenching from high temperatures above 1000 K. Pure sintered polycrystalline grains up to 500 µm can be easily extracted. Such chemical route also allowed us strongly decrease the synthetic pressure down to 7 GPa, while pressures required for complete direct phase transition in the silicon element, are remarkably higher. *In situ* control of synthesis using synchrotron radiation allowed us to observe the mechanism of underlying chemical interactions and phase transformations in the Na-Si system. The large volume synthesis allowed to perform the detailed characterization of Si-III using ^{29}Si NMR spectroscopy and IR-Vis-UV reflectance and transmission measurements.

P 11.10

Hydrothermal synthesis of GTS-type sodium titanosilicate and temperature dependence of Er^{3+} ion exchange

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Grace titanosilicates (GTS), represented by pharmacosiderite, have three dimensional tunnel-type structures. Na-GTS ($Na_4Ti_4Si_3O_{16}\cdot 6H_2O$) crystallizes as a rhombohedral phase (space group; a = 7.812 Å, α = 88.79°) close to cubic system. In this structure, four TiO_6 octahedra linked by edge-sharing form a Ti_4O_4 cubic cluster; the clusters are linked through SiO_4 tetrahedra to form a three-dimensional framework with an interconnected pore system of 8-ring channels, occupied by the alkali-metal ions and adsorbed water molecules. The rare-earth ions exchanged GTS-type titanosilicates are of interest as promissing optical and catalytic materials, as well as the rare-earth ions exchanged forms of A-type zeolites, with microporous structure. In the present study, Er^{3+}-exchanged forms [$Na_{4(1-x)}Er_{4/3x}Ti_4Si_3O_{16}$] of Na-GTS are investigated to examine temperature dependence of Er^{3+} ion exchange and the occupied positions of Er^{3+} by powder XRD.

The starting materials were NaOH, amorphous SiO_2 fine powder and aqueous solution of $TiCl_4$ and HCl. For the synthesis of Na-GTS, the starting mixtures with the molar ratios of SiO_2/TiO_2 = 3.125 and Na_2O/TiO_2 = 5.625 were hydrothermally heat-treated at 0.23MPa and 100 °C. The Er^{3+}-exchanged forms were obtained by shaking of Na-GTS in the aqueous solutions of $ErCl_3$ at 25, 40 and 60 °C for 24 hours. The concentration of Er^{3+} (C_{Er}) in the aqueous solution was varied in the range from 0.01 to 0.5 M. The obtained samples were filtrated, washed, and dried at 80 °C. The Er concentration in the supernatant solutions was analyzed with atomic absorption spectrometry to evaluate the ion-exchange amount. The obtained products were characterized by powder XRD and TG-DTA.

The sample with the composition x = 0.98, very close to x = 1.0 corresponding to the complete Er-exchange, was successfully obtained after the treatments of Na-GTS in 0.5 M $ErCl_3$ aqueous solution at 40 °C. The increase in treatment temperatures and concentration of the $ErCl_3$ aqueous solution increases the exchange amounts. The increase in the exchange amount decreases the lattice parameter a and increases the lattice parameter α to decrease the unit-cell volume V. The site distribution of Er^{3+} in the cavities of GTS framework will be discussed on the basis of the simulations of XRD patterns.

P 11.11

Conversion of graphene and fullerenes to diamond, and diamondlike phases

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Due to the industrial importance of diamond synthesis [1], the carbon phase diagram has been of enormous interest historically. However, there is now a need to update our understanding of the phase diagram to include the behaviour at extreme conditions of the nanostructured allotropes of carbon: Fullerenes, single walled carbon nanotubes and graphene. In addition, nanodiamond is expected to exhibit exciting applications (optoelectronics, drug delivery) different to those of its bulk counterpart.

We will present an overview of the field, focussing on two topics in particular.

Firstly, the conversion of monolayer and fewlayer graphene to nanodiamond, or diamondlike phases. The conversion of fewlayer graphene to nanodiamond in inert atmosphere is impeded by the high energetic cost of creating the broken sp^3 bonds on the surface of the nanodiamond, but potentially the opposite is true if the process takes place in hydrogen atmosphere as the hydrogen can terminate the broken bonds on the surface of the nanodiamond [2]. We have already demonstrated the most basic case of this (conversion of monolayer graphene to hydrogenated graphene) using very modest high pressure and temperature [3] but obtained negative preliminary results on the conversion of fewlayer graphene to nanodiamond in a hydrogen atmosphere at high pressure and temperature.

Secondly, we will discuss the possibility to convert (in inert atmosphere) fullerenes and nanotubes to diamond, or diamondlike phases, at more modest pressure and temperature than that required to convert graphite to diamond. This has already been proposed [4], due to the fact that the bonding in these materials is already partially sp^3 (or diamondlike) in nature. However, we will present our findings suggesting that, in fact, C_{60} converts to a diamondlike phase less readily than graphite.

[1] Bundy *et al*, Nature **176**, 51 (1955)

[2] Kvashnin *et al*, Nano Lett. **14**, 676 (2014)

[3] Smith *et al*, ACS Nano **9**, 8279 (2015)

[4] Regueiro *et al*, Nature **355**, 237 (1992)

P 11.12

Stable solid and aqueous H_2CO_3 from CO_2 and H_2O at high pressure and high temperature

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Carbon dioxide (CO_2), when dissolved in water, readily reacts to form carbonic acid (H_2CO_3), but which dissociates so rapidly under ambient aqueous conditions to bicarbonate (HCO_3^-) and H_3O^+ that neutral aqueous H_2CO_3(aq) is usually not considered as a relevant species in investigations of the CO_2/H_2O system in geological applications. In this work, we studied H_2O/CO_2 mixtures experimentally at high pressure and temperature in a diamond anvil cell (DAC) by IR-absorption and Raman spectroscopy, looking for evidence of increased stability of molecular H_2CO_3 in aqueous solution inside celestial bodies. We present a novel method to synthesize solid H_2CO_3 by heating CO_2/H_2O mixtures at high pressure with a CO_2 laser. Furthermore, we found that, contrary to present understanding, neutral H_2CO_3 is a significant component in aqueous CO_2 solutions above 2.4 GPa and 110 °C. This is highly significant for speciation of deep C-O-H fluids with potential consequences for fluid-carbonate-bearing rock interactions. As conditions inside subduction zones on Earth appear to be most favorable for production of aqueous H_2CO_3, a role in subduction related phenomena is inferred.

P 11.13

Synthesis of a new high pressure polymorph of potassium iridate

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Introduction

The synthesis of new iridate compounds has recently attracted much attention. Not only as model systems for high pressure transitions of silicate perovskites like $CaIrO_3$, but mainly due to interesting electronic states and related non-trivial magnetic phenomena of *5d* elements. For iridates, especially the interplay between spin-orbit coupling and coulomb repulsive interaction leads to unexpected phenomena like metal-insulator transitions or spin-liquid ground states and e.g. correlated magnetic frustration as a consequence.

Objectives

The focus of this study is related to the search for high pressure polymorphs of $KIrO_3$. Despite several known phases of e.g. lithium or sodium bearing Ir^{4+} compounds, examples of alkali-bearing Ir^{5+} compounds are still rare, although these compounds are discussed in the context of interesting spin states. The only known examples are a $NaIrO_3$ post-perovskite synthesised at 4.5 GPa, a triclinic $NaIrO_3$ layered honeycomb structure and an ambient pressure phase of $KIrO_3$ ($KSbO_3$ structure type), in which 8 K^+ ions are enclosed in cavities of a three-dimensional octahedrally coordinated iridate framework. The existence of $KIrO_3$ high pressure polymorphs appears plausible, because the packing of a potential $KIrO_3$ perovskite structure would be at least 12% denser, whereas its tolerance factor is only slightly higher than for cubic $BaIrO_3$, which exists above 25 GPa.

Results and discussion

Several synthesis trials have been performed in a Walker-type multi-anvil apparatus at pressures between 2.5 and 20 GPa and temperatures of 800° to 1400°C. Despite experimental difficulties in oxidising sufficient amounts of iridium to the pentavalent state, a new iridate phase is recovered from experiments at nearly 20 GPa in addition to a high pressure polymorph of IrO_2 and alkali oxides. The new phase is characterised by X-ray powder diffraction and electron microscopic techniques. Crystallographic data are obtained from Rietveld refinements and compared to crystallographically related phases.

Invited Talk

Systems with correlated electrons at high pressure

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Materials with strongly correlated electrons display astonishing variety of properties, which in addition can be strongly modified by external factors such as change of composition, temperature etc. Pressure, in particular can be very useful tool for that. In this talk I will give general overview of several phenomena in systems with correlated electrons, mostly transition metal compounds, which can be strongly modified by pressure. Among the topics to be considered there will be: magnetic and orbital ordering; charge ordering and spontaneous charge disproportionation; spin-state transitions; insulator-metal transitions.

Invited Talk

Strongly enhanced magnetic ordering temperatures in lanthanides at extreme pressure

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Lanthanide metals order magnetically at temperatures T_o well below ambient, the only exception being Gd where T_o = 292 K. A significant enhancement of T_o would greatly broaden the number of potential applications, one example being superior permanent magnet materials.

At ambient pressure all lanthanides except perhaps Ce exhibit stable, highly localized 4*f* magnetic moments, the magnetic ordering temperature T_o following standard de Gennes scaling. Under sufficient pressure, however, this magnetic state will eventually become unstable. This first occurs in Ce metal as signaled by an abrupt 16% volume collapse and apparent loss of magnetism under only 0.7 GPa pressure. The pressure necessary to destabilize the magnetic state of the other lanthanides is much higher. Possible scenarios to account for such changes in magnetism under pressure include: (1) increase in valence accompanied by a decrease in the number of 4*f* electrons, (2) magnetic local-to-itinerant transition due to 4*f*-orbital overlap, (3) emergence of Kondo physics as the 4*f* level approaches the Fermi energy.

We present the results of four-point electrical resistivity and, in some cases, synchrotron spectroscopy (XANES, XES, SMS) measurements on the lanthanide metals Dy, Tb, Gd, Eu, Nd, and Pr to pressures as high as 160 GPa. For Dy, Tb, and Nd the pressure dependence of T_o is highly non-monotonic, soaring above 60 GPa to unexpectedly high values. For Dy, in fact, T_o extrapolates to approximately 400 K at 160 GPa (1.6 Mbar), a record high value for a lanthanide. In addition, dilute concentrations of magnetic Dy, Tb, and Nd impurities in superconducting Y show a dramatic increase in pair breaking ΔT_c in the same region of pressure where T_o increases dramatically. These and further high-pressure experiments utilizing synchrotron spectroscopy will be critically discussed.

We suggest that the anomalously high values of T_o for Dy, Tb, and Nd may arise from their entering a Kondo lattice state for pressures above 60 GPa. These results would appear to contradict conventional wisdom that Kondo phenomena only serve to weaken, not strengthen, magnetic ordering phenomena.

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O 12.1

Intriguing electrical-transport behavior in the high pressure phase of the hybridization gapped semiconductor $FeGa_3$

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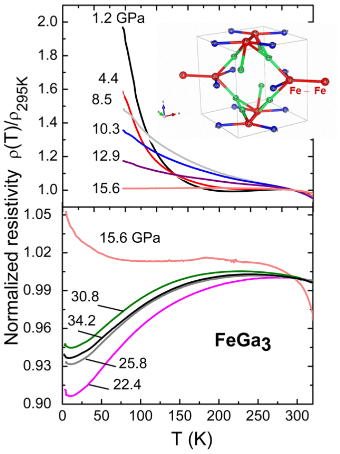
The metallic elements Fe and Ga may be combined to render a hybridisation gapped semiconductor $FeGa_3$ with a band gap of ~0.4 eV. This is in analogy to other ruthenium and iron-based semiconducting compounds (e.g., $RuAl_2$, $RuGa_3$, FeSi, $FeSb_2$) [1]. The energy gap, of the order of 0.1 eV, is formed by the hybridization between transition metal *d* states and *p* states of group 13 or 14 elements. They may constitute *3d* analogues of such hybridisation effects in highly correlated *4f* electron systems. The distinction between such a hybridisation gapped semiconductor and one with a conventional band gap (from the periodic lattice potential), is that in the former the gap disappears already at temperatures (k_BT) lower than the energy gap. These systems also show highly sensitive doping tunability of their transport and magnetic properties [2]. $FeGa_3$ also exhibits interesting structural characteristics. It crystallizes in the tetragonal lattice space group $P4_2/mnm$ (No. 136) and has Fe-Fe dimer configurations along (110) and (11-0) directions. These have been predicted to occur as antiferromagnetic singlets. We have tuned the *3d-4p* hybridisation by pressure applied to samples in a diamond anvil cell and monitored the structural, magnetic and electrical-transport response to $P > 30$ GPa. A semiconductor-metal transition ensues at ~19 GPa in accord with band structure calculations. X-ray diffraction pressure studies show a structural transition to an as yet unidentified high pressure (HP) phase onset at ~16 GPa and reaching completion by ~30 GPa. In the high temperature limit of the HP metallic phase the resistivity exhibits a smeared maximum, uncharacteristic of a conventional Bloch metal. At low temperatures, below ~15 K, a definitive minimum in the resistivity occurs. Static ordered magnetic moments have not been detected in the P-T phase diagram using the Fe Mössbauer magnetic probe of associated magnetic hyperfine structure. Do these data sets taken together indicate Kondo screening of magnetic moments by the electron gas in the HP metallic phase?

References

[1] J. M. Tomczak, K. Haule, and G. Kotliar, Proc. Natl. Acad. Sci. USA **109**, 3243 (2012).
[2] M. B. Gamza, J. M. Tomczak, C. Brown, et al., Phys. Rev. B **89**, 195102 (2014).

Figure 1



O 12.2

Competing magnetic and structural states in multiferroic RMn_2O_5 at high pressure

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The multiferroic materials demonstrating a coexistence of magnetic order and ferroelectric polarization are at the current focus of extensive scientific research due to challenging physical phenomena such as magnetoelectric effects, generation of electromagnons, etc, and prospects for development of novel electronic devices. In the RMn_2O_5 improper multiferroics ferroelectricity is induced by modulated magnetic order due to lattice inversion symmetry breaking. These compounds demonstrate colossal magnetoelectric effects and complex variation of modulated magnetic states, tuning the polarization. Most of RMn_2O_5 (except for Bi and Gd) exhibit general sequence of low temperature magnetic transformations between incollinear and collinear antiferromagnetic (AFM) states with propagation vector $q = (q_x \sim 1/2, 0, q_z \sim 1/4)$ below $T_N \sim 45$ K.

The magnetic and structural properties of RMn_2O_5 multiferroics (R=Y, Bi) have been studied by means of neutron diffraction at pressures up to 7 GPa [1]. In YMn_2O_5, at $P > 1$ GPa a gradual suppression of the commensurate and incommensurate AFM phases with a propagation vector $q = (1/2, 0, q_z \sim 1/4)$ and appearance of the novel commensurate AFM phase with $q_1 = (1/2, 0, 1/2)$ was evidenced. This observation is sharply contrasting to general trend towards stabilization of commensurate AFM phase with $q = (1/2, 0, 1/4)$ found in other RMn_2O_5 compounds upon lattice compression. Moreover, comparison with behavior of ferroelectric polarization points to reversal of its sign and absolute value increase due to magnetic state modulation change. As exception, $BiMn_2O_5$ with expanded lattice compared to YMn_2O_5 has the AFM state with $q_1 = (1/2, 0, 1/2)$ at ambient pressure. No changes in its modulation was detected upon compression.

Complementary X-ray diffraction and Raman spectroscopy experiments up to 30 GPa evidence a structural transformation at $P \sim 16$ GPa in YMn_2O_5 accompanied by anomalies in lattice compression and behaviour of vibrational modes. The comparative analysis of high pressure and R-cation radius variation effects clarified a role of particular magnetic interactions in the formation of the magnetic states of RMn_2O_5 compounds.

The work was supported by RFBR, grant 15-02-03248.

[1] D.P. Kozlenko et al., Phys. Rev. B 92, 134409 (2015).

O 12.3

Pressure-induced superconductivity in iron-based spin-ladder compound $BaFe_2S_3$ and related materials

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Iron-based superconductor was discovered as a high-T_c superconductor in 2008, whichhas a two-dimensional iron lattice as a common feature and exhibits characteristic magnetic phases next to the superconducting phase. A stripe-type magnetic order is observed in the 1111, 122, 111 and 11 type iron-based superconductors, and a block-type magnetic order is observed in 245 type ones.

Recently, quasi-one-dimensional iron-based spin-ladder compounds have attracted much attention. These compounds exhibitseveralkinds of magnetic orderingphase, which are one-dimensional analog of both stripe and block magnetismrelated to the iron-based superconductors [1,2]. Due to such a similarity of magnetic propertiy, superconductivity was much expected in these compounds. However, these compounds show insulating behavior.

Here we report the pressure-induced superconductivity in the spin-ladder compound $BaFe_2S_3$. Intensive high pressure studies, mainly electrical resistivity measurements, have been carried out to find superconductivity. The insulator-metal transition was observed at ~11GPa, and just after appearance of metallic phase, superconductivity was observed. The dome-shaped superconducting phase was obtained in the *P-T* phase diagram, as shown in Fig.1, in which the maximum *T*c was 17 K [3]. The results of high pressure studies for substituted compounds $Cs_{1-x}Ba_xFe_2S_3$ and Ba $(Fe_{1-x}Co_x)_2S_3$, which correspond to the hole and electron doped compound, respectively, will be presented.

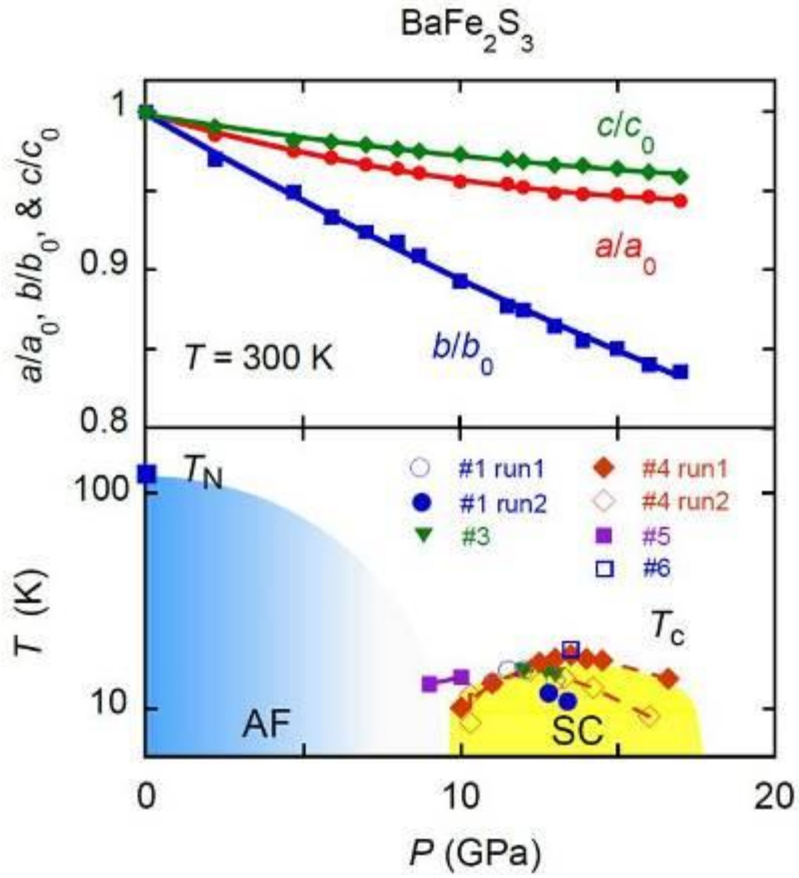
[1] Y. Nambu *et al.*, Phys. Rev. **B85**, 064413 (2012).

[2] F. Du *et al.*, Phys. Rev. **B85**, 214436 (2012).

[3] H. Takahashi et al., Nat.Mater. **14**, 1008 (2015).

Figure 1: P-T phase diagram of $BaFe_2S_3$, which shows antiferromagnetic phase at ambient pressure. Superconducting transiton appears above 10 GPa and disappears above 17 GPa. The maximum T_c ia ~17 K. (H. Takahashi et al., Nature Materials **14**, 1008 (2015)

Figure 1


BaFe$_2$S$_3$
a/a_0, b/b_0, & c/c_0
1
0.9
0.8
c/c_0
a/a_0
b/b_0
T = 300 K
T (K)
100
10
T_N
T_c
AF
SC
○ #1 run1
● #1 run2
▼ #3
◆ #4 run1
◇ #4 run2
■ #5
□ #6
0
10
20
P (GPa)

O 12.4

Spin-libron coupling in solid oxygen under pressure

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Di-oxygen (O_2, usually simply called oxygen) forms at low temperatures and high pressures one of the most remarkable molecular solids. Contrary to its closest neighbour, N_2, oxygen has an open 2p shell with two unpaired electrons, hence a spin S=1. The resulting intermolecular magnetic interactions are of similar magnitude to the van-der-Waals forces and lead to a profound modification of the low-temperature phase diagram compared to other diatomic elemental molecules [1]. In this contribution we focus on the high pressure delta ('orange') phase, stable between 6 and 8 GPa, between 180 and 0 K. Previous high pressure neutron diffraction measurements have revealed the existence of three different magnetic structures within the same crystallographic phase [2]. We report unpublished Raman data which investigate the influence of magnetic long-range order on the lattice dynamics of solid O_2, more precisely the librational motions of O_2-molecules, in both a- and d-O_2. We find strong spin-libron coupling in these phases, demonstrated by strong changes in the libron spectra associated with the three magnetic phases. The experiments reveal the existence of 4 libron modes in d-O_2, as predicted by theory [3], and clarify many of the hitherto incoherent reports on the dynamics of low-energy excitations in solid oxygen.

[1] Y. Freiman and H.J. Jodl, Physics Reports 401, 1 (2004)

[2] S. Klotz, Th. Strässle, A.L. Cornelius, J. Philippe, Th. Hansen, Phys. Rev. Lett. 104, 115501 (2010)

[3] R.D. Etters, K. Kobashi, J. Belak, Phys. Rev. B 32, 4097 (1985)

O 12.5

Magnetism and valence in the CsCl-phases of EuO, EuS and EuSe at extreme pressures

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The magnetic properties and the valence state of initially divalent Eu-ions were probed in the Eu-chalcogenides EuO, EuS and EuSe in the CsCl-type (B2) high-pressure phases at pressures up to 120 GPa using ^{151}Eu nuclear forward scattering (NFS) of synchrotron radiation [1]. Together with previous data on EuTe [2], we present a magnetic phase diagram of EuX (X = O, S, Se, Te) in their B2-phases and compare it with the corresponding data in the NaCl-type B1-phases, studied most intensively with ^{151}Eu-Mössbauer effect and ^{151}Eu-NFS in the last decades [2-7]. Beside the magnetic ordering temperatures, important information is obtained on the Eu valence state and magnetic exchange mechanism from the observed isomer shifts and hyperfine fields, respectively. We observe for all EuX systems in the B2-phase ferromagnetic order, reaching T_C = 165 K for EuO at 75 GPa, followed by a decrease of T_C at higher pressures connected with the onset of mixed valence. EuS exhibits a steep increase of T_C with pressure, which saturates around 295 K at 120 GPa, connected with a mixed valence also saturating at v(IS) = ~2.5 at 120 GPa. For EuSe we observe an even steeper increase of T_C in the B2-phase starting from 110 K at 25 GPa and reaching T_C = 300 K at 77 GPa without any sign of saturation. These findings demonstrate that the strength of magnetic interactions, which is highest for EuO in the B1-phases, is now reversed in the B2-phases, being larger for the heavier chalcogen members. This behaviour is attributed to a strong ferromagnetic J_2 (Eu-X-Eu) exchange in the B2-phase, obviously enhanced by the covalency of the Eu-X bonds as well as by the different coordination and neighbour numbers, when compared to the B1-phase.

[1] O. Leupold et al., Europhys. Lett. 35, 671 (1996).

[2] O. Leupold, K. Rupprecht, G. Wortmann, Structural Chemistry 14, 97 (2003).

[3] U.F. Klein, G. Wortmann, G.M. Kalvius, J. Magn. Magn. Mat. **3**, 50 (1976).

[4] J. Moser, G. Wortmann, et al., J. Magn. Magn. Mat. **12**, 77 (1979).

[5] M.M. Abd-Elmeguid, R.D. Taylor, Phys. Rev. B 42, 1048 (1990).

[6] I.N. Goncharenko, I. Mirebeau, Phys. Rev. Lett. 80, 1082 (1998).

[7] N.M. Souza-Neto et al., Phys. Rev. Lett. 108, 026403 (2012).

O 12.6

Ferrromagnetic criticality of uranium intermetallics under pressure

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The critical behavior of U itinerant electron ferromagnets (IEF) on the verge of the long range magnetic order is a subject of intensive experimental and theoretical studies [1]. Hydrostatic pressure (*p*) is ideal tuning parameter since it usually decreases the interatomic distances. While T_C of IEF by rule rapidly decreases with increasing *p*, the *p*-*T* magnetic phase diagrams illustrate various types of critical behavior. At ambient pressure the ferromagnet-paramagnet phase transition at T_C is of the 2nd order type. However, the evolution of this phase transition with increasing *p* at low temperatures has more possible scenarios in the zero temperature limit where a quantum phase transition may take place. At low temperatures and in clean systems two scenarios avoiding single quantum critical point are possible: a) the ferromagnetic fluctuations become critical and the ferromagnet-to-paramagnet transition is first-order; b) inhomogeneous magnetic phases may appear between the uniform ferromagnetic phase and the paramagnetic phase. Global detailed investigation of both options is rather rare in literature and still open problem.

The talk will be devoted to the discussion of the critical ferromagnetic behavior of selected high quality single crystals of U compounds using magnetization, ac-susceptibility, and resistivity measurements at hydrostatic pressure up to about 10 GPa and down to 30 mK. Novel findings of pressure-induced variations of ferromagnetism in uranium intermetallics will be presented dealing with two cases: a) the hexagonal ZrNiAl-type compounds exhibiting huge uniaxial anisotropy, namely UCoGa ($T_C \approx 50$ K at ambient *p*) and U $(Co_{1-x}Ru_x)Al$ compounds undergoing first order transition at low temperatures; and b) cubic magnetically almost isotropic $U_4Ru_7Ge_6$ ($T_C \approx 7.5$ K at ambient *p*) in which the 2nd order phase transition is observed at about 2 GPa down to 30 mK. The discussion of the results concerning the case a) will be drawn in the context of earlier published data on the UCoAl [2] and URhAl [3]. Reasons of the strikingly different magnetic behavior of $U_4Ru_7Ge_6$ will be discussed.

[1] M. Brando, D. Belitz, F. M. Grosche, and T. R. Kirkpatrick, Rev. Mod. Phys. (accepted 2016).

[2] D. Aoki, J. Flouquet, J. Phys. Soc. Jpn. 81, 011003 (2012).

[3] Y. Shimizu et al., Phys. Rev. B 91, 125115 (2015).

O 12.7

Magnetism and superconductivity in UGe2

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The talk will present high pressure studies of the utlrasound veclocity and attenuation, magnetoresistance and Hall effect in UGe2.

UGe2 is a ferromagentic superconductor. The superconductivity is linked to a magentic transition within the ferromagentic state. The nature of the magnetic transition will be discussed in the light of the above measurements along with the implications for the pairing mechanism giving superconductivity.

O 12.8

Correlated states near electronic and structural instabilities

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Many complex materials display an interesting interplay between structural and electronic instabilities, which can often be studied effectively under applied pressure. We present some recent examples, including

(i) a structural quantum critical point and its consequences for conventional superconductivity in the quasi-skutterudite system $Sr_3(Ir/Rh)_4Sn_{13}$,

(ii) the evolution of quantum oscillations with pressure in the pressure-metallised Mott insulator NiS_2, and

(iii) unconventional superconductivity in YFe_2Ge_2 and its connection with superconductivity in the high-pressure collapsed tetragonal phase of alkaline-metal iron arsenides.

These and other examples underline the need for joint structural and electronic studies and suggest new tools for manipulating the correlated states of complex metals.

O 12.9

Electronic structure of Eu^{2+}-doped KBr: volume and bondlength dependences in phases B1 and B2

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Eu^{2+} ($4f^7$) is one of the most studied luminescent ions due to its high oscillator strength associated with the electric-dipole *f-d* transition and efficient blue photoluminescence (PL) [1,2]. It is a fundamental ingredient in highly efficient phosphors due to its capability to emit at different wavelengths form blue to infrared by adequate modification of the Eu^{2+} crystal environment [3]. The knowledge of the electronic structure and its dependence with the crystal-field acting at Eu^{2+} site results crucial to predict and eventually tailoring novel phosphors with given PL specifications. This work investigates the Eu^{2+} electronic structure associated with the $5d^14f^6$ configuration in Eu^{2+}-doped KBr and its pressure dependence. In particular, we focus on the effect of the NaCl-type (B1) to CsCl-type (B2) structural phase transition at about 2.3 GPa [4] and how the change of the substituted K$^+$ site coordination from 6-fold to 8-fold affects Eu^{2+} and its blue luminescence. Interestingly, KBr, unlike other chloride, fluoride or oxide hosts, is a unique system for measuring the crystal-field splitting of 5d orbitals (e_g + t_{2g}) directly from optical absorption spectroscopy with DAC. The figure shows the variation of $10Dq$ for Eu^{2+} in KBr with pressure. It must be noted that $10Dq$ decrease abruptly at the B1 ® B2 phase transition although increases with pressure in each phase. An account of the volume and bondlength dependences on $10Dq$ using equation of state for B1 and B2 KBr [4] as well as the effect of change of coordination will be presented at the Meeting.

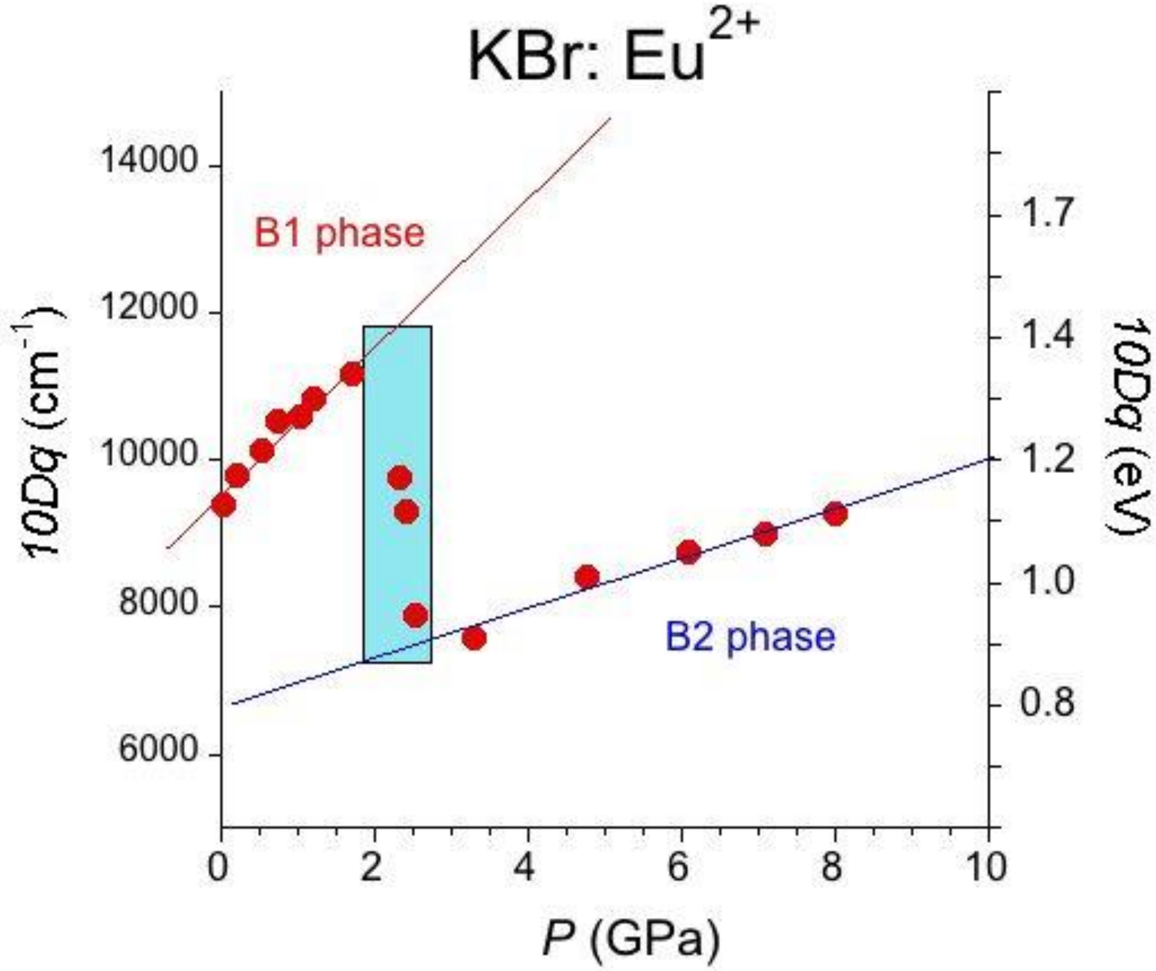
[1] G. Blasse and A. Bril, *Philips Tech. Rev.* **31**, 304 (1970).

[2] M. Suta, P. Larsen, F. Lavoie-Cardinal, C. Wickleder, J. Lumin. **149**, 35-44 (2014).

[3] E.V. Mejía-Uriarte, R. Castañeda-Guzmán, M. Villagrán-Muniz, E. Camarillo, J. Hernández A, H. Murrieta and M. Navarrete, *J. Phys.: Condens. Matter* **15**, 6889 (2003).

[4] A. Dewaele, A. B. Belonoshko, G. Garbarino, F. Occelli, P. Bouvier, M. Hanfland, and M. Mezouar, *Phys. Rev. B* **85**, 214105 (2012)

Figure 1


KBr: Eu^{2+}
B1 phase
B2 phase
14000
12000
10000
8000
6000
10Dq (cm^{-1})
1.7
1.4
1.2
1.0
0.8
10Dq (eV)
0
2
4
6
8
10
P (GPa)

P 12.1

Superconductivity mediated by polar phonons in $SrTiO_3$

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Weakly electron doped SrTiO3 is well known as the most dilute superconductor. The mere fact that superconductivity occurs at charge carrier densities at least as low as 10^{17} cm^{-3} can be seen as proof of an exorbitant interaction strength generating an attractive force between the electrons. Thus, although the material exhibits a critical temperature of approximately 1 K or less, it is of great interest in the search for superconductors with higher transition temperatures. Here, we present a combined experimental and theoretical work, which clearly demonstrates that polar optical phonons might act as the glue between electrons. Our measurements of Tsc under pressure shows a behaviour that agrees very well with the predictions of our theory of electron pairing via polar modes that exist close to a ferroelectric quantum critical point. These results provide routes to discovering new superconductors that exhibit the same or similar pairing mechanisms.

P 12.2

Metal-insulator-type transition in a high-pressure iron oxide polymorph Fe_4O_5 involving dimer and trimer formation

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Using multi-anvil high-pressure high-temperature (HP-HT) facilities, we have synthesized single-crystalline samples of the recently discovered new iron oxide, Fe_4O_5 [1]. Fe_4O_5 contains equal amounts of Fe^{2+} and Fe^{3+} ions, and in a similar manner to magnetite, Fe_3O_4 [2,3], it might undergo a charge-ordering transition at relatively low temperatures. At ambient conditions Fe_4O_5 crystallizes in an orthorhombic $CaFe_3O_5$-type crystal structure. The crystal structure of Fe_4O_5 comprises linear chains of octahedrally-coordinated iron ions occupying two slightly different crystallographic positions, Fe2 and Fe3 and linear chains of trigonal-prismatically coordinated Fe1 cations along the *a*-axis. Therefore, Fe_4O_5 is expected to be a good model system to trace the charge-ordering process. We examined the physical properties of Fe_4O_5 by means of single-crystal X-ray diffraction, by measurements of electronic transport properties and magnetization, and by neutron diffraction. We found that on cooling below ~150 K Fe_4O_5 undergoes an unusual charge-ordering transition which involves competing dimeric and trimeric ordering within the chains of Fe ions. This transition is concurrent with a significant increase in electrical resistivity. We discuss possible mechanisms of this transition and compare it with the trimeronic charge ordering observed in magnetite below the Verwey transition temperature [3].

[1] B. Lavina, *et al.* Proc Nat. Acad. Sci. US **108**, 17281 (2011).

[2] 3. E. J. W. Verwey, Nature **144**, 327 (1939).

[3] M. S. Senn, J. P. Wright, & J. P. Attfield, Nature **481**, 173 (2012).

[4] S.V. Ovsyannikov et al., Nature Chemistry **8**, DOI: 10.1038/NCHEM.2478 (2016).

P 12.3

Linear-in-temperature resistivity close to a topological metal insulator transition in ultra-multi valley fcc-Ytterbium

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The semimetal-to-semiconductor transition in fcc-Yb under modest pressure can be considered a picture book example of a metal-insulator transition of the Lifshitz type. We have performed transport measurements at low temperatures in the closest vicinity to the transition and DFT calculations of the Fermi surface. Our low-temperature resistivity measurements show a linear dependency with an unusually low $d\rho/dT$ at low temperatures approaching the MIT. Our calculations suggest fcc- Ytterbium being an ultra-multi valley system with 24 electron- and 6 hole pockets in the Brilloun zone. Such a multi-valley naturally supports the appearance of strongly correlated phases. The scattering rate is by orders of magnitude lower than in other materials which exhibit linear-in-T behavior at a quantum critical point, if not the effective mass enhancement at the critical point accounts for at least two orders of magnitude.

P 12.4

High pressure Raman and *ab initio* study of $TlGaSe_2$

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The $TlGaSe_2$ compound with monocline structure belongs to the family of layered ternary chalcogenide semiconductors with the basic chemical formula $A^3B^3C^6_2$ and have attracted a lot of attention as perspective material for application in optoelectronics due to complex physical effects caused of the peculiarity of their crystal structures.

The nature of the pressure induced phase transition(s) in $TlGaSe_2$ are still extensively debated and demands further investigations. In order to clarify role of the intralayer interactions in pressure induced structural phase transition, we have performed a study of vibrational spectra of $TlGaSe_2$ by means of Raman spectroscopy in the pressure range up to about 10 GPa. We also perform additional theoretical calculations of baric dependences of vibration frequencies and elastic constants for this compound using the density functional theory approach as implemented in software ABINIT.

Raman spectra at ambient temperature and selected pressures up to 10.3 GPa were collected using a LabRam spectrometer (Ne-He excitation laser) with wavelength of 632.8 nm, 1800 grating, confocal hole of 1100 mm, and a 50x objective. The BX90 type diamond anvil cell was used for the X-ray diffraction and Raman experiments. The sample was loaded into the hole of the 125 μm diameter made in the Re gasket indented to about 20 μm thickness. The diamonds with culets of 250 μm were used. A methanol-ethanol mixture was used as a pressure transmitting medium. The pressure was determined by the ruby fluorescence technique.

The theoretical analysis predict for the $TlGaSe_2$ with monoclinic symmetry (*C2/c*) 24 Raman active modes, Γ=10Ag + 14Bg. All observed vibrations modes can be divided on intralayer and low frequency interlayer (Ag+2Bg) vibrations. The frequencies of vibration modes increase nearly linearly under pressure up to P = 0.9 GPa. Close to this pressure the values of mode Gruneisen parameters for all observed intralayer modes decrease. The modes with n_{i0} = 230 cm^{-1} and n_{i0} = 250 cm^{-1} demonstrate at the same time a sharp reduction of frequences. These effects testifies of the re-arrangement of intralayer configuration at phase transition under pressure.

Baric dependence of vibration frequencies and elastic constants of $TlGaSe_2$ studied using *ab initio* calculation are in good agreement with experimental observations and in pressure range 0.9-1.0 GPa show the first-order phase transition wihout symmetry change and characterized by reconstruction ofthe structure of a layers.

P 12.5

Structural and electronic properties of hcp-Os at ultrahigh pressure

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Studying materials at ultra-high pressure is interesting from the perspective of fundamental physics. Moreover, the generated knowledge is highly relevant for a design of novel functional materials, capable of withstanding extreme conditions during operation.

It was recently shown [1] in a combined experimental and theoretical study that Os has an anomaly in the c/a lattice parameters ratio at ultrahigh pressure (440 GPa). This anomaly is unrelated to any topological transition of the Fermi surface. However, it coincides with the crossing of the deep lying 4f and 5d electron states, which are normally assumed to be frozen, unaffected by external conditions such as pressure. The core level transition can in fact be shown to be a general effect going through the 5d series of the periodic table [2]. However, relating this anomaly to the lattice parameters is a highly non-trivial task. In addition, the experimental equation of state is not well reproduced by the local density approximation (LDA) or semi-local generalized gradient approximations of density functional theory [1].

We report the results of our study of the interplay between these core states and their in influence on the valence electrons in hcp-Os at ultra-high pressure, using a variety of theoretical approaches. In addition, we calculate the equation of state for Os using more advanced treatment of local Coulomb correlation effects, provided by dynamical mean-field theory (DMFT) in combination with LDA (the LDA+DMFT method).

References

[1] L. Dubrovinsky, N. Dubrovinskaia, E. Bykova, M. Bykov, V. Prakapenka, C. Prescher, K. Glazyrin, H. P. Liermann, M. Han and, M. Ekholm, Q. Feng, L. V. Pourovskii, M. I. Katsnelson, J. M. Wills, and I. A. Abrikosov. The most incompressible metal osmium at static pressures above 750 gigapascals. Nature, 525(7568):226{229, 09 2015.

[2] A. A. Tal, M. I. Katsnelson, M. Ekholm, J. J•önsson, L. Dubrovinsky, N. Dubrovinskaia, and I. A. Abrikosov. Pressure induced crossing of the core-levels in 5d metals. ArXiv e-prints, Sept. 2015.

P 12.6

Susceptibility measurement under pressure for the low-dimensional spin systems: $Cu(C_8H_{16}O_4)$ Cl_2 and $Cu(C_{10}H_{20}O_5)Br_2{\cdot}2H_2O$

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[1]*Paul Scherrer Institut, LNS, Villigen, Switzerland*

The synthesis with flexible molecules like crown ether [1] in low dimensional systems is of great interest, to be able to study the modification of physical properties depending on the structural variations of such materials [2], as it leads to additional dimerized and chain compounds in the metal organic material class. It is notable that in such systems a different magnetic behavior ranging from ferromagnetic to antiferromagnetic interactions has been found. The project‘s aim is to study under pressure the continuous tuning within the isotropic or isolated chain limits. Due to a weaker coupling of the molecules of metalorganic compounds than those of inorganic materials, even a moderate pressure is sufficient to vary the distance between atoms. The pressure acts as control parameter to cause magnetic interaction between the involved magnetic ions, even if such magnetic ions haven’t shown an interaction before.

The material $Cu(C_8H_{16}O_4)Cl_2$ (1) and $Cu(C_{10}H_{20}O_5)Br_2{\cdot}2H_2O$ (2) have been prepared to investigate the low dimensional spin system of compounds with a comparable flexibility based on the crown ether molecule [3]. The composition (1) (see Fig. 1a)) has a orthorhombic structure with space group $P2_12_12_1$ and lattice parameters a = 7.017(3)Å, b = 12.262(6)Å, c = 13.552(6)Å. The composition (2) (see Fig. 1b)) has a monoclinic structure with space group $P2_1$ and lattice parameters a = 8.698(4)Å, b = 13.740(7)Å, c = 8.019(4)Å and β = 116.31(3)°. The magnetic behavior of $Cu(C_8H_{16}O_4)Cl_2$ without pressure shows an antiferromagnetic interaction, the development of the susceptibility can be described with S = 1/2 quasi 1D spin chain system. The exchange coupling constants of this latter compound are J_{chain}= -0.29 meV (-2.32 cm^{-1}). The magnetic behavior of $Cu(C_{10}H_{20}O_5)Br_2{\cdot}2H_2O$ without pressure shows paramagnetic behavior. We will present the first results of the susceptibility measurements under pressure for the compounds (1) and (2).

a) b)

Fig. 1: Typical example of crystals of a) $Cu(C_8H_{16}O_4)Cl_2$ b) $Cu(C_{10}H_{20}O_5)Br_2{\cdot}2H_2O$

[1] C. J. Pedersen, H. K. Frensdorff, Angew.Chem. 84 (1972), 16

[2] A. Escuer, G. Aromi, Eur. J. Inorg. Chem. (2006), 4721-4736

[3] N. van Well, Innovative und interdisziplinäre Kristallzüchtung, Springer Spektrum (2016), Wiesbaden

Figure 1

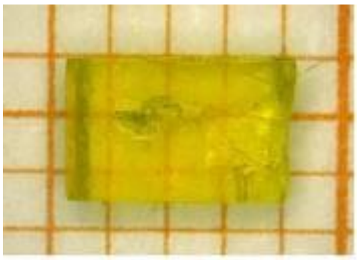

Figure 2

P 12.7

Anomalous field dependence of the susceptibility in Cd_3As_2

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In a Dirac semimetal like Cd3As2, the conduction and valence band touch at discrete points within the Brillouin zone only. This gives rise to a relativistic dispersion of charge carriers which is responsible for a large charge carrier mobility [1,2]. Cd3As2 has already shown a series of unexpected physical phenomena from linear magnetoresistance, chiral anomaly and even signatures of superconductivity [3-5]. Here, we will present recent experimental data from Cd3As2 measured using a tunnel diode oscillator (TDO) technique in pulsed magnetic fields up to 60T at 4.2K. We observe a strong anomaly in this signal as a function of both magnetic fields and sample orientation which does not seem to correspond to any known thermodynamic phase transition. Moreover, clear quantum oscillations can be observed not only at higher fields, but also across the unusual diamagnetic-like transition. We will discuss these findings in light of the putative formation of possible charge puddles on the sample surface, and we will compare them to similar findings in the topological insulator Sb2Te3 and the archetypical 2D system graphene.

[1] Neupane et al., Nat. Commun. 5:3786 (2014)

[2] Borisenko et al., PRL 113, 027603 (2014)

[3] Narayanan et al., PRL 114, 117201 (2015)

[4] Zhang et al., arXiv:1504.07698 (2015)

[5] Wang et al., Nat. Mat. 15, 38-42 (2016)

P 12.8

Coexistence of site- and bond-centered electron localization in the high pressure phase of the $LuFe_2O_4$ multiferroic

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[2]*Institut Néel, CNRS and Université Joseph Fourier, Grenoble, South Africa*
[3]*National Research Nuclear University (MEPHI), Sarov Physics and Technology Institute, Sarov, Russian Federation*
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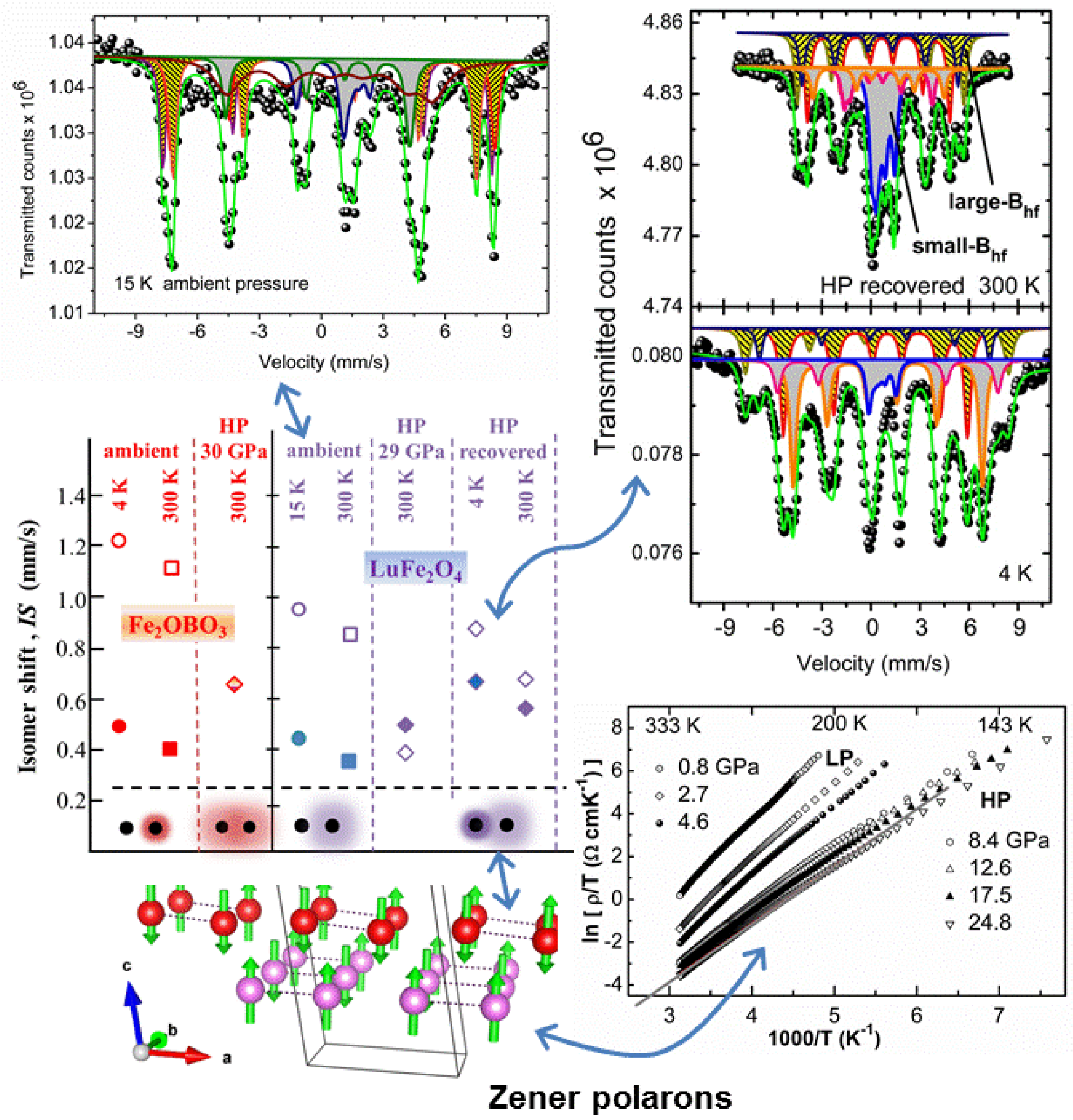
Charge order (site centered CO) normally refers to spatial localization of charge carriers at periodic lattice sites, which may result in a superstructure of mixed valences. In $LuFe_2O_4$ there are controversial claims for CO (electronically) instigated ferroelectricity at ambient pressure. There are also claims for CO in a high pressure (HP) polymorph of this compound stabilized at P > 8 GPa, and recovered in metastable form from high pressure processing to at least ~12 GPa [1]. The magnetic-electronic pressure response of $LuFe_2O_4$ up to 30 GPa and the recovered metastable HP polymorph has been investigated by temperature dependent Fe Mössbauer spectroscopy (MS) as well as ab initio electronic structure calculations. In the MS spectra of $LuFe_2O_4$ under ambient conditions at variable cryogenic temperatures, we find evidence of site-centered CO at the majority of sites in the charge and spin frustrated triangular Fe sublattice where magnetic ordering is onset at ~260 K. Previous structural pressure studies show that the monoclinic C2/m (LP) phase transforms to a monoclinic Pm (HP) polymorph in the range 4 - 8 GPa [1]. This HP polymorph recovered to ambient conditions evidences Bragg satellites in electron diffraction (ED) patterns. At P > 10 GPa in the HP phase, new magnetic hyperfine structure is observed at room temperature implying $T_{Neel} > 300$ K. This suggests a change of the ambient pressure phase to a new HP magnetic state with ‘reduced frustration’ in its rectangular Fe sublattice. We demonstrate from the Mössbauer spectral analysis and band-structure calculations of the HP phase that coexistence of site and bond-centered electron localization occurs [2]. These manifest as asymmetric dimers at neighboring Fe sites along the a-axis. In this direction atomic spins are ferromagnetically aligned and alternating long and short Fe-Fe interatomic distances occur. Such a superstructure may be responsible for the Bragg satellites discerned in the ED patterns of the recovered HP polymorph. This potential intermediate-state CO has the requisite inversion symmetry breaking for $LuFe_2O_4$ it its HP form to be rendered a new electronically instigated ferroelectric.

References

[1] F. Damay, M. Poienar, M. Hervieu, et al., Phys. Rev. B **91**, 214111 (2015).

[2] G.R. Hearne, E. Carleschi, W. Sibanda et al., Phys. Rev. B **93**, 105101 (2016).

Figure 1


Transmited counts x 10^6
1.04
1.04
1.03
1.03
1.02
1.02
1.01
15 K ambient pressure
-9 -6 -3 0 3 6 9
Velocity (mm/s)
Transmitted counts x 10^6
4.86
4.83
4.80
4.77
4.74
large-B_{hf}
small-B_{hf}
HP recovered 300 K
0.080
0.078
0.076
4 K
-9 -6 -3 0 3 6 9
Velocity (mm/s)
Isomer shift , IS (mm/s)
ambient
HP 30 GPa
ambient
HP 29 GPa
HP recovered
4 K
300 K
300 K
15 K
300 K
300 K
4 K
300 K
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Fe_2OBO_3
$LuFe_2O_4$
c
b
a
ln [ρ/T (Ω cmK^{-1})]
333 K
200 K
143 K
0.8 GPa
2.7
4.6
LP
HP
8.4 GPa
12.6
17.5
24.8
8
6
4
2
0
-2
-4
3 4 5 6 7
1000/T (K^{-1})
Zener polarons

P 12.9

Pressure effects on weakly anisotropic magnetism in $U_4Ru_7Ge_6$

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Ferromagnetic U intermetallics usually exhibit very strong magnetocrystalline anisotropy due to the strong spin-orbit coupling of the U ions and participation of U 5*f* orbitals in anisotropic covalent bonding. $U_4Ru_7Ge_6$ appears to be a striking exception of this general feature. We have grown a high quality single crystal of $U_4Ru_7Ge_6$ by Czochralski method and measured the magnetization, AC susceptibility and electrical resistivity in various conditions including high pressure. X-ray diffraction (XRD), specific heat, thermal expansion (TE) and magnetostriction were measured at ambient pressure. Our data confirmed that this cubic (Im-3m space group) compound is ferromagnetic (T_C = 7.5 K) with the easy magnetization axis along the [111] direction. The anisotropy field for the [110] and [100] directions is only of ~ 0.2 T, which is at least two orders of magnitude smaller than in other U ferromagnets. TE shows a positive length change below T_C for the [100] direction and almost no response along [111]. It can be interpreted in terms of a spontaneous rhombohedral distortion with the lattice angle > 90° which leads to two crystallographically inequivalent U sites. This is in agreement with results of our XRD experiments performed down to 2.8 K.

At 1.9 K we observed a negative (tiny positive) longitudinal [100] ([111] magnetostriction in magnetic fields up to 9 T. Inspection of Ehrenfest relations with TE data suggested strong negative pressure dependence of T_C. Measurements of resistivity and AC susceptibility under hydrostatic pressure up to about 3 GPa in a 3He/^{4}He dilution fridge down to 30 mK revealed a suppression of T_C towards 0 K at a critical pressure around 2.1 GPa. We observed a low-temperature tail in the p-T magnetic phase diagram expected for strongly disordered systems. The magnetization decreases up to 1 GPa decreases by ~ 20 %.

We also performed relativistic first-principle calculations based on the DFT theory providing the total magnetic moment of 1 μ_B/f.u. being in good agreement with experiment (1.0 μ_B/f.u. at 7 T). The spin-orbit coupling yields 2 crystallographically inequivalent U positions which is in agreement with XRD results. The U ions at the first site bear almost negligible magnetic moment due to the cancelation of S and L components. The second site has uncompensated S and L moment dominating the total moment.

P 12.10

Phase diagram of UCoAl doped with low amount of Ru

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Phase diagrams of some ferromagnetic compounds show interesting behavior. Instead of suppressing the second order ferromagnetic transition (FT) into quantum critical point (QCP), the second order FT is suppressed until it changes into the first order FT. This point of change of order is called tricritical point (TCP). After that the first order FT is quickly suppressed to 0 K. At TCP first order metamagnetic transition (MT) appears. Point where first order MT appears is called critical endpoint and is suppressed by external parameters until QCP is reached. Compounds who have same or similar phase diagram are $ZrZn_2$, URhAl, UGe_2 or UCoAl.

Our objective was to investigate immediate vicinity of TCP with focus on change of character of FT and appearance of MT by the doping and application of hydrostatic pressure.

We prepared three $UCo_{1-x}Ru_xAl$ single crystals, where parent compound UCoAl is paramagnet with MT and doping by already small concentration of Ru induces ferromagnetism. Concentration of these single crystals was 1%, 0.5%, 0.25% of Ru. Magnetic, electric transport and dilatometry measurements were done in ambient and hydrostatic pressure.

$UCo_{0.99}Ru_{0.01}Al$ is ferromagnet with T_C = 16 K. $UCo_{0.995}Ru_{0.005}Al$ is metamagnetic and exhibits first order FT around 4 K. $UCo_{0.9975}Ru_{0.0025}Al$ is paramagnet with MT, similar to parent compound UCoAl. All single crystals have phase diagram similar to one described above with hydrostatic pressure as tuning parameter.

We present investigation of ferromagnetic phase diagram, mainly focused on area around TCP done on set of single crystals of $UCo_{1-x}Ru_xAl$ by macroscopic measurements.

P 12.11

Effect of pressure and temperature on lattice dynamics of ZrB_{12} and LuB_{12}

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ZrB_{12}, exhibiting relatively high superconducting transition temperature T_c of 6 K, is a member of metal dodecaborides family. The results of thermal spectroscopy experiments [1, 2] suggest that superconductivity in ZrB_{12} and YB_6 is explained by the dominating electron-phonon coupling with low energy phonon modes associated with the vibration of weakly bonded metal atoms within boron cages. The obtained estimates of overall Gruneisen parameter showed their strong dependence on phonon frequency.

In order to get direct estimates of Gruneisen parameters in this work we investigated pressure (up to 10 GPa) and temperature (10-650K) behaviour of different phonon modes in ZrB_{12} and its low-T_c (0.42 K) structural analog LuB_{12} using Raman spectroscopy. Acoustic phonons in ZrB_{12} were observed both in forbidden first order Raman scattering and allowed second order scattering and exhibited anomalous softening with a decrease in the temperature. The positive isothermal Gruneisen coefficient of these modes was several times lower than the absolute value of the negative isobaric coefficient, which indicates the dominating role of temperature effects. Both the isothermal and isobaric Gruneisen parameters showed a strong increase with decrease of the acoustic phonon energy that implies temperature and pressure dependent anomalies in phonon dispersion.

No such effects was found in LuB_{12}; its acoustic phonon frequencies, concentrated in a narrow energy range, show only negligible temperature changes. High-frequency boron vibrations in both materials demonstrated softening under temperature increase and hardening under pressure increase with average Gruneisen parameter$\gamma \sim 1$.

[1] R. Lortz, Y. Wang, S. Abe, C. Meingast, Yu. B. Paderno, V. Filippov, and A. Junod, Phys. Rev. B72, 024547 (2005).

[2] R. Lortz, Y. Wang, U. Tutsch, S. Abe, C. Meingast, P. Popovich, W. Knafo, N. Shitsevalova, Yu. B. Paderno, and J. Junod, Phys. Rev. B 73, 024512 (2006).

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P 12.12

Evidence for a pressure-induced magnetic quantum transition in UCoGa

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In recent years, the investigation of the critical behavior of itinerant ferromagnets under pressure has attracted considerable interest. Particularly, the evolution of the ferromagnetic (FM) to paramagnet transition at low temperatures has been discussed within different scenarios, where a quantum phase transitions (QPT) may take place. In the clean systems at low temperatures, there are two possible scenarios: Either a first-order ferromagnetic to paramagnetic transition, or the appearance of an inhomogeneous magnetic phase between the ferromagnetic and paramagnetic state. There is only few known U-based ferromagnetic compounds displaying the change of the order of transition, demonstrating the appearance of the first order transition by driving the system close to the loss of the long range magnetic order. In this respect, the FM UCoGa compound (T_C= 48K), crystalizing in the hexagonal ZrNiAl-type structure /1/, is such system, where this behavior would be expected with the application of hydrostatic pressure. This allows one to investigate the evolution of ferromagnetic order using different experimental techniques. High quality single crystal of UCoGa has been prepared by Czochralski method and carefully characterized by means of powder x-ray diffraction, element specific analysis, heat capacity, thermal expansion and electrical transport measurements. The behavior under pressure has been studied by magnetization (in SQUID magnetometer) and resistivity measurements, both utilizing a diamond anvil cell to generate the hydrostatic pressures up to about 10 GPa. Our high pressure experiments demonstrate that the ferromagnetic order in UCoGa is suppressed at pressures ~ 5.5 GPa, where the ordered magnetic moment is reduced by about 30 % at about 4GPa. The observed pressure-induced QPT are compared with those observed in related isostructural hexagonal UTX compounds, in particular URhAl /2/. The above mentioned scenarios for the observed QPT in UCoGa are discussed.

[1] Nakotte, F. R. de Boer, L. Havela, P. Svoboda, V. Sechovsky, Y. Kergadallan, J. C. Spirlet, and J. Rebizant, J. Appl. Phys. **73**, 6554 (1993).

[2] Y. Shimizu, D. Braithwaite, B. Salce, T. Combier, D. Aoki, E. N. Hering, S. M. Ramos, J. Flouquet, Phys. Rev. B **91**, 125115 (2015)

P 12.13

High-pressure studies for hydrogen doped $SmFeAsO_{1-x}H_x$ and related materials

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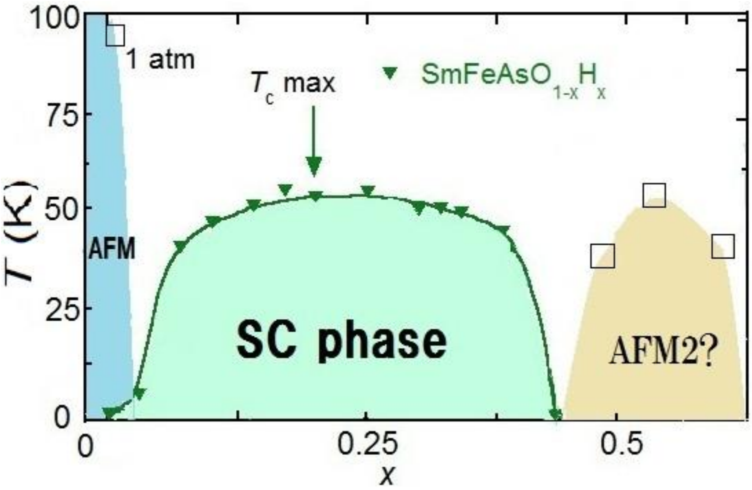
Iron-based superconductors have attracted much attention because of inclusion of typical magnetic element iron, showing high T_c and wide variety of materials. In these materials, the undoped 1111-type iron-based materials show antiferromagnetic ordering phase (AFM1), which is suppressed with carrier doping. With further carrier doping, the superconductivity appears, whose maximum T_c is more than 50 K. Hydrogen doped 1111-type LnFeAsO$_{1-x}$H$_x$ (*Ln* = La,Ce,Sm,Gd,) was successfully synthesized up to x~ 0.5 [1]. The x-T phase diagrams show dome-shape $T_c(x)$ and the T_c domes shift to the lightly-doped side as the ionic radius of *Ln* decreases in the order La to Gd [1]. Recent high-pressure experiments reveals that the x-T phase diagram of $LaFeAsO_{1-x}H_x$ tends to be similar to the one of $SmFeAsO_{1-x}H_x$ under high pressure [2]. Such results indicate that physical pressure effect has chemical pressure-like effect, that is, the $T_c(x)$ dome shifts to the lightly-doped side with applying pressure. In the highly doped region beyond superconducting phase, the second antiferromagnetic phase (AFM2) was observed for $LaFeAsO_{1-x}H_x$, and also found another phase in the over-doped side of $SmFeAsO_{1-x}H_x$ (Figure 1.) It is interesting to study the interplay between superconducting phase and AFM2 phase, and further doping materials beyond AFM2 phase. The pressure effect is might be a good tool to study the highly doped region beyond the AFM2 phase. In this study, electrical resistivity measurements under high pressure were carried out for $SmFeAsO_{1-x}H_x$, especially for the overdoped region. High-pressure effect for the related materials will be presented in the conference.

Figure 1**.** The phase diagrams of $SmFeAsO_{1-x}H_x$

Figure 1



P 12.14

Quantum criticality in CeRh($Si_{1-x}Ge_x$)$_3$ compounds under pressure

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$CeRhSi_3$ crystallizes in the $BaNiSn_3$-type non-centrosymmetric tetragonal crystal structure (space group I4mm). The compound reveals antiferromagnetic below T_N = 1.6 K at ambient pressure and superconductivity already appears at 0.2 GPa below T_c = 0.1 K [1]. At higher pressures T_N first increases to a maximum and then decrease to zero at about 2.4 GPa, pointing to the existence of a QCP [1, 2]. T_c also increases with pressure, so that the T_N (p) -and T_c (p)-curves meet at about 2 GPa, indicating that QCP at 2.4 GPa is hidden inside the superconducting state. In contrast, the isostructural compound $CeRhGe_3$ displays antiferromagnetic ordering below T_N = 14.6 K [3] and no superconductivity has been observed in pressures up to 8 GPa [4].

In order to visualize the magnetic QCP and separate the magnetic and superconducting transitions in $CeRhSi_3$ we have doped this compound with Ge. Since Ge doping causes expansion of the $CeRhSi_3$ lattice volume, it is expected that the superconducting transition would be shifted to higher pressures and thereby uncover the QCP. This allows us to study the quantum criticality for different Ge concentrations of CeRh($Si_{1-x}Ge_x$)$_3$ compounds.

We have succeeded to prepare high quality CeRh($Si_{1-x}Ge_x$)$_3$ single crystals for x = 0, 0.027, 0.07. First measurements of electric resistivity were performed on these samples under hydrostatic pressures up to 3 GPa and low temperatures down to 0.3 K . The measured data show decreasing tendency of T_N with increasing pressure up to 0.9 GPa (e.g. T_N^{0GPa} = 3 K and $T_N^{0.9GPa}$ = 1.8 K for x = 0.027). The superconducting transition is observed at 1.9 GPa for x = 0.027 and 0.07 while the temperature of superconducting transition is at 0.4 K and 0.36 K for x = 0.027 and x = 0.07, respectively. Increasing pressure causes moving of the superconducting transitions to higher temperature up to at least 2.8 GPa (T_c = 0.83 K and 0.78 K for x = 0.027 and x = 0.07, respectively). These results together with data in progress will be presented and discussed in a (T, p)-phase diagram.

[1] N. Kimura, Y. Muro and H. Aoki, *J. Phys. Soc. Jpn.*, **76** 051010 (2007)

[2] N. Egetenmeyer, J.L. Gavilano et al., *Phys. Rev. Lett.*, **108** 177204 (2012)

[3] Y. Muro, D Eom, N. Takeda and M. Ishikawa, *J. Phys. Soc. Jpn.*, **67** 3601 (1998)

[4] T. Kawai, M Nakashima et al., *J. Phys. Soc. Jpn.*, **76** Suppl A, pp. 166 (2007)

P 12.15

Pressure effect on the antiferromagnetic transition of UIrGe

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UIrGe belongs to a family of uranium UTX compounds crystallizing in the orthorhombic TiNiSi-type crystal structure and displays magnetic non-collinear antiferromagnetic structure below the Néel temperature T_N ~ 16 K with strongly reduced U-magnetic moment (0.36 μ_B/U at 1.8 K) [1]. The reduced value of U-moment points to its itinerant character which leads to a high sensitivity to external conditions like applied magnetic field or external pressure. Studies on a single crystal of UIrGe revealed anisotropic behavior along principal axes with *a*-axis as a hard magnetization direction. A different sensitivity to external magnetic field applied along various directions was observed [2]. Large difference in the resistivity curves with the current passing along principal crystallographic directions was observed, including semiconducting-like behavior above ~30 K along *a* or *c* with a sharp upturn near T_N.

The aim of the present work was to investigate the evolution of T_N with increasing pressure. For this purpose, we have performed high-pressure experiments on UIrGe single crystal up to about 10 GPa between 300 K and 4 K using a Bridgman anvil pressure cell with a pyrophyllite gasket ring and a steatite as a pressure-transmitting medium. To obtain information about the expected trend of the initial change of T_N with pressure, we have measured the heat capacity and the linear thermal expansion along each of the three crystallographic axes in the temperature range 2-40 K. From the data analysis we find a small expected change of T_N with pressure ($dT_N/dp = -0.55$ K/GPa). From the first high pressure resistivity data up to 8 GPa we find a small shift of the anomaly connected with T_N to lower temperatures corresponding to a decrease of T_N ($dT_N/dp^{exp} \approx -0.6$ K/GPa) in a good agreement with that obtained from our thermal expansion data. Further high pressure resistivity measurements with current along the *a*-axis and up to about 12 GPa are in progress.

[1] K. Prokeš. H. Nakotte, V. Sechovský et al., *Physica B* **350**, e199 (2004)

[2] V. Sechovský, J. Vejpravová, A.V. Andreev et al., *Physica B* **359-361**, 1126 (2005)

P 12.16

Novel physical phenomena at high pressures and low temperatures

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Novel physical phenomena at high pressures and low temperatures

P 12.17

Stress-strain research on sintering polycrystalline diamond under high pressure

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In the field of super-hard materials, it has been a fundamental and hard problem for stress-strain of fine diamond particles in sintering polycrystalline diamond under high pressure and high temperature. Recently, polycrystalline diamond and polycrystalline cubic boron nitride (c-BN) by sintering without binder phase have been prepared [1],[2] , but the sintering mechanism need to be explored[3] . We investigated the stress-strain of diamond particles under high pressure by the diamond anvil cell(DAC) and synchrotron radiation x-ray diffraction for high-pressure in-situ. We obtained the relationship between the shape of diamond diffraction peak and pressure. The peaks were widened and the shapes of the peak were asymmetric. There are a high-pressure zone and low-pressure zone in diamond particles. Diamond-diamond bonding is formed in high-pressure zone and diamond graphitizing happen in low-pressure zone.

References

[1] H. Sumiya, T. Irifune, Diamond & Related Materials, 2004, 13: 1771 -1776.

[2] Guoduan Liu, Zili Kou, Xiaozhi Yan, Li Lei, Fang Peng, Qiming Wang, Kaixue Wang, Pei Wang, Liang Li, Yong Li, Wentao Li, Yonghua Wang, Yan Bi, Yang Leng and Duanwei He, Applied Physics Letters ,2015,106, 121901.

[3] Guerold Sergueevitch Bobrovnitchii, Oleksandr Sergueevitch Osipov, Marcello Filgueira, International Journal of Refractory Metals & Hard Materia, 2003,21:251-258.

Keywords: synchrotron radiation, polycrystalline diamond, high temperature and high pressure sintering, Stress-Strain

P 12.18

X-ray emission spectroscopy at extreme conditions at beamline P01, PETRA III, DESY

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Recently, a new experimental set-up was tested to record in-situ X-ray emission spectra of samples at high pressure and high temperature with acquisition times from several minutes to several dozens of minutes. The recordable energy range from about 6.4 to 14.5 keV covers K- and L-emission energies of a large number of elements.

The beamline P01 with two 5 m undulators delivers very high flux of up to $7x10^{13}$ ph/s [1]. The von-Hamos-type spectrometer is equipped with 16 slots for exchangeable cylindrically bent analyzers of 0.5 m bending radius [2]. The energy-dispersed signal of each analyzer is detected on a 2D 100k Pilatus detector. We use panoramic diamond-anvil cells (DAC) which allow the emission signal to be collected in the highly desirable 90° scattering geometry, which minimizes both the elastically scattered background and the path of the emission signal through attenuating diamond and/or gasket material. The mobile laser-heating system of beamline P01 follows in basis the layout of Boehler et al. [3]. The use of panoramic DAC required modification from off-axis to on-axis heating.

We will discuss the set-up and show acquired Fe K_b spectra of reference iron-containing oxide, sulfide and carbonate samples at high pressure from ambient temperature and high temperature.

[1] Wille H.C. et al., 2010. J. Phys. Conf. Ser. 217, 012008.

[2] Alonso-Mori R. et al., 2012. Rev. Sci. Instr. 83, 073114.

[3] Boehler R. et al., 2009. Rev. Sci. Instr. 80, 045103.

P 12.19

Development of the EXAFS diagnostic on the National Ignition Facility

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The use of lasers to induce extreme compression states has enabled the study of material properties and equations of state at unprecedented pressures and temperature conditions [1]. The combination of laser-driven compression and x-ray diagnostics provides a unique picture of the transformations taking place in high energy density matter in nano-second time scales. In static high pressure experiments, X-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) are the principal diagnostics used to characterize structural properties and document the occurrence of phase transitions. Recently we have developed these capabilities at the Omega laser (University of Rochester, NY) to look at phase transitions of matter dynamically driven to high pressure and high temperature [2, 3, 4, 5]. Here we present the first attempt at developing XAS measurements at the National Ignition Facility (NIF) (Lawrence Livermore National Laboratory, CA) where much higher compressions can be achieved. We use 128 laser beams and about 400 kJ to implode a 1.5 mm diameter plastic capsule acting as x-ray source. As the capsule implodes it becomes hot and eventually generates a bright, smooth and broad-band x-ray flash (bang time). A flat crystal spectrometer is used to disperse the x-rays generated by the implosion in the 7 keV range and an image plate detector is used to record EXAFS spectra at the Fe Kedge [6]. Different capsule sizes and materials have been studied to optimize the x-ray source. Their brightness is compared and discussed together with the achieved spectral resolution. These measurements represent the first attempt at measuring EXAFS spectra on the NIF. Future experiments will allow us to extend the measurements to laser-driven samples and to look at different materials, by changing the dispersive crystal in the spectrometer.

This work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract No. DE-AC52-07NA27344

References

[1] R. Smith et al, Nature 511, 330 (2014)

[2] J. R. Rygg et al, Review of Scientific Instruments 83, 113904 (2012)

[3] F. Coppari et al, Nature Geoscience 6, 926 (2013)

[4] Y. Ping et al, Review Scientific Instruments 84, 123105 (2013)

[5] Y. Ping et al, Physical Review Letters 111, 065501 (2013)

[6] D. B. Thorn et al, abstract at the High-Temperature Plasma Diagnostic

P 12.20

Ultrafast dynamics in VO_2 under high pressures

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Vanadium dioxide (VO_2) is a classic example of a strongly correlated system demonstrating a sharp insulator-to-metal transition (IMT) at T_c = 340 K. Since the IMT occurs just above room temperature, VO_2 has a high potential for applications in optoelectronic and electrical devices. Nevertheless, the microscopic mechanism of the IMT in VO_2 is not yet fully understood. In particular, the roles played by the electronic correlation and the lattice distortion during the IMT are still under debate.

A pressure-induced metallization of VO_2 above 10 GPa has been reported by Arcangeletti et al. using infrared spectroscopy.[1] Remarkably, high-pressure Raman spectra do not reveal qualitative changes indicating that the pressure-driven IMT in VO_2 is not coupled to any structural distortion. Recently, the first time-resolved pump-probe study of VO_2 under pressure has, indeed, revealed a nonequilibrium metallic phase with the monoclinic structure inherent to the insulating phase.[2]

Here, we report a systematic study of ultrafast pump-probe response in VO_2 under pressure at different excitation fluences in order to clarify the nature of the pressure-induced changes in this material. The pump-probe measurements with 400 nm pump and 800 nm probe wavelengths were performed on single VO_2 crystals mounted inside a diamond anvil cell. CsI has been used as a pressure-transmitting medium in order to ensure contact between the sample and the diamond anvil.

At low pressures of a few GPa, the photoexcited electrons relax on a time scale of about 0.5 ps. With increasing pressure, the relaxation time gradually becomes faster reaching the value of about 0.15 ps beyond 10 GPa. Furthermore, the application of pressure reduces the amount of pump energy which is required to induce a metastable metallic state. However, even close to 12 GPa, the sample demonstrates a dynamics typical of the insulating VO_2. These preliminary results agree with recent high-pressure resistivity measurements that show a gradual crossover to the metallic state which is reached only above 30 GPa.[3]

References

[1] E. Arcangeletti et al., *Phys. Rev. Lett.* **98**, 196406 (2007).

[2] W.-P. Hsieh et al., *Appl. Phys. Lett.* **104**, 021917 (2014).

[3] L. Bai et al., *Phys. Rev. B.* **91**, 104110 (2015).

Invited Talk

Process induced relaminarization during high pressure processing

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Laminar and turbulent flow regimes play an important role in technical high pressure processes among others due to the specific different mixing behavior. The present contribution is showing on the one hand the importance of the different mixing properties and its effect on (bio)chemical reactions. On the other hand the contribution proves experimentally and theoretically that the pressure ramps are able to induce a transition of fully developed turbulence towards a stable laminar regime.

Reverse transition from the turbulent towards the laminar flow regime was investigated experimentally and theoretically by progressively increasing the pressure up to 400 MPa in a fully developed pipe flow operated with glycerol and silicone oil as the working fluid. The experimental investigation is based on special high pressure adapted Laser-Doppler-Anemometry and Hot Wire Anemometry (operated in constant-temperature and constant-current modes). The theoretical consideration makes use of theanisotropy invariant map.

During the compression phase laminar and turbulent flow regime was observed at low and moderate Reynolds numbers. Measurements of the velocity and temperature fluctuations at the axis of the pipe show a transition from turbulent to laminar regime at Reynolds numbers typically governed by turbulent flow. Using theoretical considerations regarding the wall turbulence it is derived that due to the rapid changes of the fluid density relaminarization is expected. The compression phase reduces the turbulent dissipation and, thus, the spectral separation between large and small scale motion. This effect leads to a complete relaminarization. [1-4]

References

[1] J. Jovanovic, R. Hillerbrand, *J. Thermal Sci.*, **9**, 3-12 (2005).

[2] K. Song, C. Rauh, A. Delgado, *Proc. Appl. Math. Mech.*, **8**, 10603-10604 (2008).

[3] K. Song, W. Regulski, J. Jovanovic, C. Rauh, A. Delgado, *High Press. Res.*, **29**, 739-745 (2009).

[4] K. Song, A. Al-Salaymeh, J. Jovanovic, C. Rauh, A. Delgado, *Ann. New York Acad. Sci.*, **1189**, 24-33 (2010).

Keywords: Process uniformity, mixing, bio thermo fluid dynamics, turbulence, anisotropy invariance map, relaminarization

Invited Talk

Triggering Dynamic Structural Changes in Lipid Membranes

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Lipid membrane structural dynamics and micromechanics are vitally important to a wide range of cellular processes including mediating protein activity, signaling, material transport and apoptosis (programmed cell death). Developing model systems to study the structural and energetic behavior of membranes, and methods to trigger changes in these parameters are essential to understanding the contributions of the many components that make up biological membranes.

We have recently developed a range of novel instruments for studying soft matter and biological system at non-ambient conditions and out-of-equilibrium. Amongst these, our new platforms for high pressure and pressure-jump microscopy, small angle X-ray diffraction (SAXS) and spectroscopy have led to a series of exciting studies of the pressure dependence of key micromechanical membrane parameters and membrane structural behaviour.

Of particular interest are our recent first measurements of the lateral structure of membranes under pressure. This has allowed us to measure changes in the bending rigidity of lipid bilayers, and rapidly trigger membrane domain growth in both model lipid membranes and plasma membrane vesicles. In addition, hydrostatic pressure has played a key roll in the generation and control of highly swollen interconnected cubic lipid structures which have enormous potential for encapsulation and controlled release of bioactive molecules, and large membrane protein crystalisation.

Figure 1. Pressure induced lipid phase separation in a giant unilamellar vesicle (GUV)

References

[1] N. McCarthy, O. Ces, R. Law, J. Seddon and N. Brooks, *Chem. Commun.* **51** (2015) 8675-8678

[2] H. Barriga, A. Tyler, N. McCarthy, E. Parsons, O. Ces, R. Law, J. Seddon and N. Brooks, *Soft Matter* **11** (2015) 600-607

[3] A. Tyler, H. Barriga, E. Parsons, N. McCarthy, O. Ces, R. Law, J. Seddon and N. Brooks, *Soft Matter* **11** (2015) 3279-3286

[4] S. Purushothaman, P. Cicuta, O. Ces and N. Brooks, *J. of Phys. Chem. B* **119** (2015) 9805-9810

[5] H. Barriga, R. Law, J. Seddon, O. Ces and N. Brooks *Phys. Chem. Chem. Phys.* **18** (2016) 149-155

Figure 1

Invited Talk

Anomalous compression of crystals

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At hydrostatic conditions the compression of crystals reflects their structure and interactions. Therefore, the compression measurements can be used for understanding the structural features of crystals and specific properties of the chemical compounds. The crystals can be compressed in monotonic and discontinuous way, when phase transitions take place. Hydrostatically compressed crystals in most cases shrink in all directions, but occasionally they expand in one direction (so called negative linear compression, NLC) and very rarely in two directions (negative area compression, NLC) can occur. Different structural mechanisms lead to such transformations. Some examples of the NAC materials will be discussed [1,2]. The compression of some crystals is so large that it can be easily followed by naked eyes [2]. The relation between the compression and thermal expansion of materials is usually reverse, i.e. the effect of increased pressure corresponds to that of reduced temperature. However, exceptionally rare positive effects of pressure and temperature effects are also possible [3]. The effects of compression and expansion can be further modified by the molecular conformation, as will be exemplified by the ferrocene crystals [4].

References

[1] Zieliński W., Katrusiak A., *Cryst.Growth Des.* **2014,** *14*, 4247.

[2] Cai W., Gładysiak A., Anioła M., Smith W., Barbour L., Katrusiak A., *J. Am. Chem. Soc*. **2015**. 137, 9296.

[3] Cai W., Katrusiak A., *Nature Commun.* **2014,** *5*, 4337.

[4] Paliwoda D., Kowalska K., Hanfland M., Katrusiak A., *J. Phys. Chem. Lett*. **2013**, *4*, 4032.

O 14.1

Bacterial survival following shock compression in the GigaPascal range

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The possibility that life might exist within previously unconsidered habitats on Earth or elsewhere is causing us to expand our understanding of potential planetary biospheres. Significant populations of living organisms are now identified in subsurface habitats extending up to several km below the planetary surface and laboratory experiments show that microbial species can survive following exposure to pressures into the Gigapascal (GPa) range. Potential transport of biological organisms between planetary systems is also of interest for spreading life forms throughout the cosmos. This implies survival during the dynamic shock processes encountered during impact of the bolide carrying the organisms in active or dormant states with the planetary surface. Pascalization strategies *via* static and shock compression are also becoming increasingly important in food, pharmaceuticals and agricultural technologies. Our present results compare the survival of *Shewanella oneidensis* bacteria exposed to static and dynamic pressurization into the GPa range. The results indicate that shock compression results in significantly greater survival of both wild type and survivor populations that had previously been exposed to static pressurization. The shorter exposure timescale of the shock compression may play a significant role in determining survival of the microbial species. If temperatures achieved during a bolide impact do not exceed approximately 120-130˚C it is likely that organisms contained within the rocky matrix could survive implantation on the new host planet.

O 14.2

Process stability of Listeriophage P100 towards high pressure processing

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As an environmental friendly and minimal processing technology, high pressure processing (HPP) became a potential technology to combine with bacteriophage P100, because after exposure to mild pressures, pathogenic bacteria present in foods become injured and, as a consequence, more susceptible to bacteriophage infection. The aim of this work was to evaluate the pressure stability of bacteriophage P100 in PBS buffer (pH 7.4).

Solutions of bacteriophage Listex™ P100 in PBS buffer (10^8 PFU mL^{-1}) were freshly prepared and subsequently pressurized, from 200 MPa to 700 MPa (5 min, 10°C). Isothermal pressure inactivation kinetics of phage P100 was also investigated within the range of 200 to 400 MPa. Phage titer was determined using the soft agar overlay method using *Listeria monocytogenes* as the host. The data was statistically analyzed using the ANOVA with Turkey HSD post hoc test.

At 200 MPa, the stability of bacteriophage P100 was not significantly affected (*P 0.05*) when compared with untreated samples, but when submitted to 300 MPa, a 2.50±0.12 log PFU/mL reduction was observed. For pressures > 300 MPa, the phage was inactivated up to values below the detection limit (10 PFU/mL) of the enumeration technique. During refrigerated storage (4ºC), pressurized samples at 200 MPa did not present significant (*P 0.05*) reduction in the phage titers in comparison with the untreated ones, whereas the 300 MPa HPP treated samples had a reduction just after pressurization, and maintained stable during the storage period. Tailing was observed in the three kinetic curves, indicating that the Weibull model could produce good fits to the curves. The obtained results have shown that bacteriophage P100 suffered severe inactivation for pressures higher than 300 MPa, but afterwards it remained stable under refrigerated storage. This evidence seems to support that the combination of HPP with bacteriophage P100 could be a promising way to control *L. monocytogenes* as a hurdle technology in the food industry.

O 14.3

Pressure-responsive organic compounds: Beauty at the lower end of the high-pressure scale

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Advances in static and dynamic compression techniques allowing access to the Mbar and TPa pressure regimes have opened up a myriad of research avenues in Physics, Chemistry, Materials Science, Earth and Planetary Science. [1-2]

Within molecule-based materials, wonderful opportunities for probing and tuning structural, mechanical, electronic, magnetic and vibrational properties lie at the lower end of the high-pressure scale, with most studies being performed below 10 GPa. Materials as diverse as biomolecules, molecular magnets, metal-organic frameworks and pharmaceuticals have demonstrated exceptional structural response at these modest high pressures, enabling for instance a better understanding of intermolecular interactions and the derivation of structure-property relationships. [3-7]

This contribution will provide some examples of organic-based compounds for which a considerable number of polymorphs have been obtained by direct compression and/or *in situ* high-pressure crystallisation below 1 GPa. It will be shown how high-pressure experiments, coupled with ambient-pressure studies and computer simulations, can help forming a more complete picture of the crystallisation and structural landscape of these compounds, giving clues as to how and why phase transitions and structural changes occur. Examples will also be given of how this type of research might resonate within an industrial context, *e.g.* in the development and processing of pharmaceuticals.

[1] L. Dubrovinsky, N. Dubrovinskaia, V. B. Prakapenka and M. Abakumov, *Nat. Commun.*, 2012, 3, 1163.

[2] R. F. Smith, J. H. Eggert, R. Jeanloz, T. S. Duffy, D. G. Braun, J. R. Patterson, R. E. Rudd, J. Biener, A. E. Lazicki, A. V. Hamza, J. Wang, T. Braun, L. X. Benedict, P. M. Celliers and G. W. Collins, *Nature*, 2014, 511, 330-333.

[3] K. Kurpiewska, K. Dziubek, A. Katrusiak, J. Font, M. Ribò, M. Vilanova, K. Lewiński, *Chem. Phys.*, 2016, 468, 53-62.

[4] B. A. Zakharov, N. A. Tumanov and E. V. Boldyreva, *CrystEngComm*, 2015, 17, 2074-2079.

[5] J. P. Tidey, H. L. S. Wong, M. Schröder and A. J. Blake, *Coord. Chem. Rev.*, 2014, 277-278, 187-207.

[6] S. C. McKellar and S. A. Moggach, *Acta Cryst.*, 2015, B71, 587-607.

[7] M. A. Neumann, J. van de Streek, F. P. A. Fabbiani, P. Hidber and O. Grassmann, *Nat. Commun.*, 2015, 6, 7793.

O 14.4

The stability hierarchy of trimorphic piracetam solved through high-pressure analysis

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[3]*Polytechnical University or Catalonia, Barcelona, Spain*

Introduction

The stability hierarchy of polymorphs is often based on transition temperature measurements by DSC. However, it may happen that this approach is incomplete and the trimorphism of piracetam is such a case. It is known for over a decade that forms II and III both transform endothermically into form I on heating; however, the onset temperatures of the two solid-solid transitions at equilibrium are not known, as they appear to depend on the sample. In this paper, it will be demonstrated how the stability hierarchy can be inferred from experimental pressure-temperature diagrams.

Materials and Methods

Piracetam forms II and III of medicinal grade were obtained from Isochem, France. The samples have been studied by differential scanning calorimetry, high resolution X-ray powder diffraction, piezo-thermal analysis (constructed in-house), high-pressure differential thermal analysis (constructed in-house), sublimation-condensation, and volumetry of the melt of piracetam.

Results and Conclusions

High-pressure measurements (isothermal pressure dependent, and isobaric temperature dependent) have provided the I-II-III triple point and the two equilibria II-I and III-I with which the position of the third solid-solid equilibrium III-II could be determined.

The inequalities between the slopes of the solid-solid equilibrium curves involving forms I, II and III were experimentally obtained and obey the sequence $dP/dT_{\text{I-II}} > dP/dT_{\text{I-III}} > dP/dT_{\text{II-III}}$. These three slopes intersect each other at positive pressure leading to the conclusion that the inequality in the temperatures of triple points I-II-vap, I-III-vap and II-III-vap (i.e. at $P = 0$ MPa) must be $T_{\text{I-II-vap}} > T_{\text{I-III-vap}} > T_{\text{II-III-vap}}$.

Thus, the *P*-*T* diagram for the phase relationships involving the three solid forms (I, II, and III) of piracetam can be topologically drawn as presented in figure 1, in which all two-phase equilibria are present, or in figure 2 in which only stable equilibria and subsequent stable phase regions are present.

Figure 1. Complete pressure-temperature phase diagram of trimorphic piracetam

Figure 2. The domains of the stable phases in the pressure-temperature phase diagram of trimorphic piracetam

Figure 1

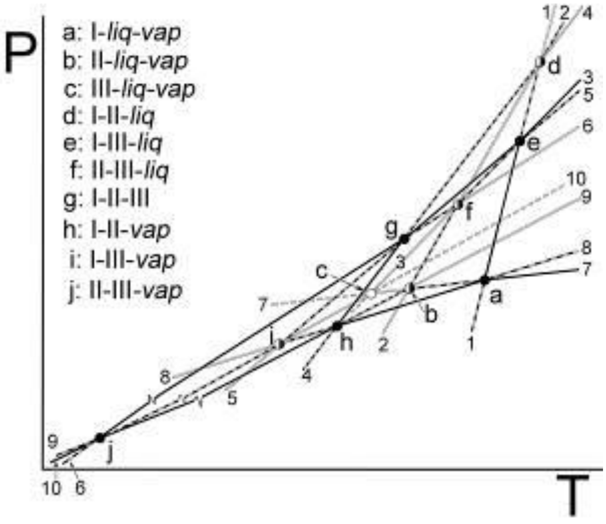
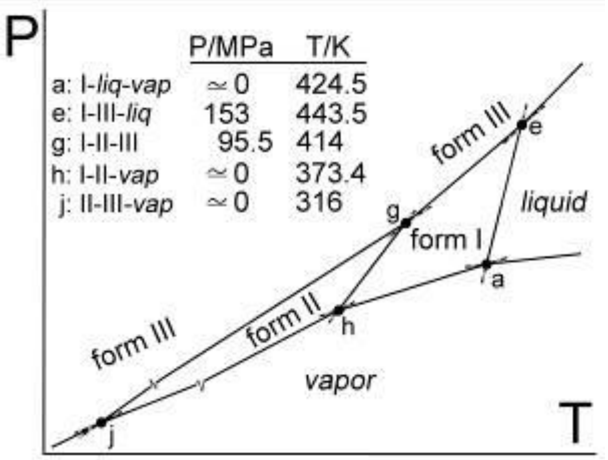


Figure 2



	P/MPa	T/K
a: I-*liq*-*vap*	≃ 0	424.5
e: I-III-*liq*	153	443.5
g: I-II-III	95.5	414
h: I-II-*vap*	≃ 0	373.4
j: II-III-*vap*	≃ 0	316

O 14.5

5-aminotetrazole monohydrate up to 51 GPa: pressure-induced phonon softening and phase transitions

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At extreme conditions, novel compounds with unusual structural features and interesting properties can be obtained [1]. Within the framework of a DFG-funded project, we are particularly interested in polymerisation reactions of molecules with different N:C ratios. We chose 5-aminotetrazole monohydrate (ATM, $CH_3N_5 \cdot H_2O$) for our investigations because of its high N:C ratio. Recent studies of the anhydride reported 3 different phases upon temperature increase at ambient pressure [2] and no phase transition up to 12 GPa at ambient temperature [3]. The high-pressure behaviour of ATM has not been reported in the literature, yet. In this study, we performed Raman spectroscopy up to 51 GPa, second harmonic generation (SHG) measurements up to 17 GPa as well as X-ray diffraction up to 16 GPa at PETRA III (DESY). We used single crystalline and powdered ATM loaded in diamond anvil cells. DFT-based model calculations, including the calculation of Raman intensities, were performed. Figure 1 shows the experimental Raman spectra of ATM. Between 9 and 11 GPa discontinuities indicate a phase transition. Furthermore, there was a phonon which softened and broadened upon pressure increase before the transition took place. This red shift was confirmed by DFT calculations which revealed that this mode is predominantly a combination of N-H bending and stretching. The observed phase transition was confirmed by the X-ray diffraction data (figure 2). Up to around 17 GPa the SHG signal was around zero and comparable to centrosymmetric crystals. In conclusion, in contrast to the anhydride, we found a structural phase transition of ATM between 9 and 11 GPa. Further studies will now focus on inducing chemical reactions by heating the sample at high pressures.

Financial support from the DFG (project RA 2585/1-1) and the BMBF (project 05K13RF1) is gratefully acknowledged.

Figure 1: Raman spectra of ATM from 0 to 16 GPa.

Figure 2: Diffraction images of ATM at 5.4(1) GPa (left) and 15.9(3) GPa (right).

[1] R. Bini, M. Ceppatelli, M. Citroni, and V. Schettino, Chem. Phys., 398, 262 (2012).

[2] S. Obata, S. Takeya, H. Fujihisa, K. Honda, and Y. Gotoh, J. Phys. Chem. B, 114, 12572 (2010).

[3] H. Fujihisa, K. Honda, S. Obata, H. Yamawaki, S. Takeya, Y. Gotoha, and T. Matsunaga, CrystEngComm, 13, 99 (2011).

Figure 1

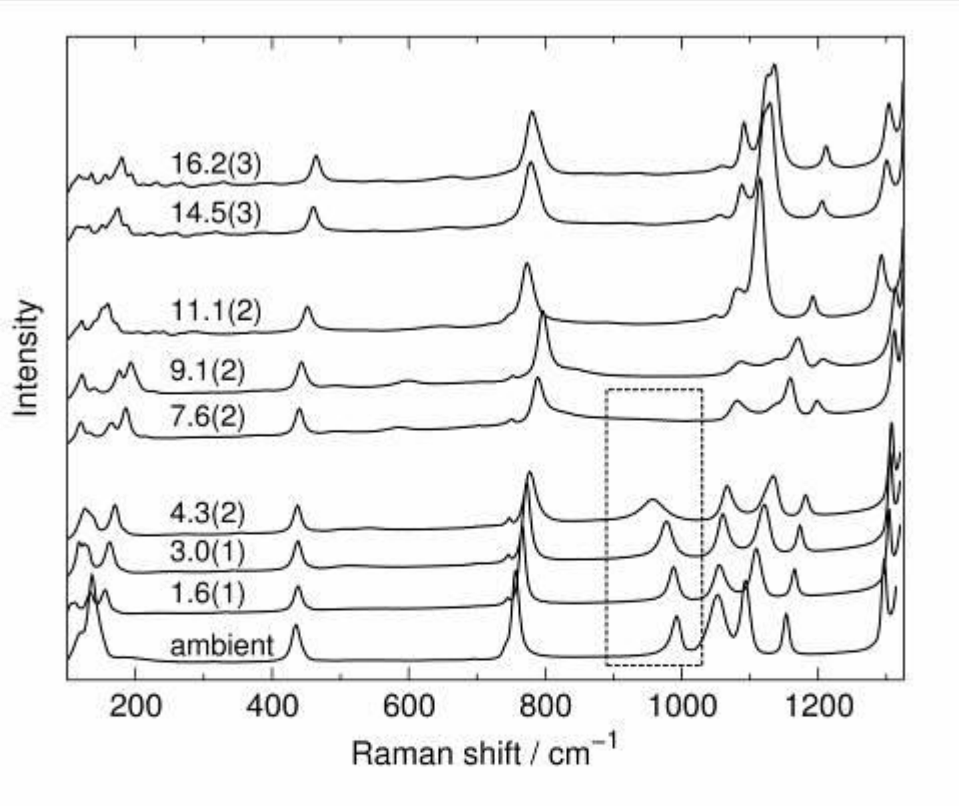
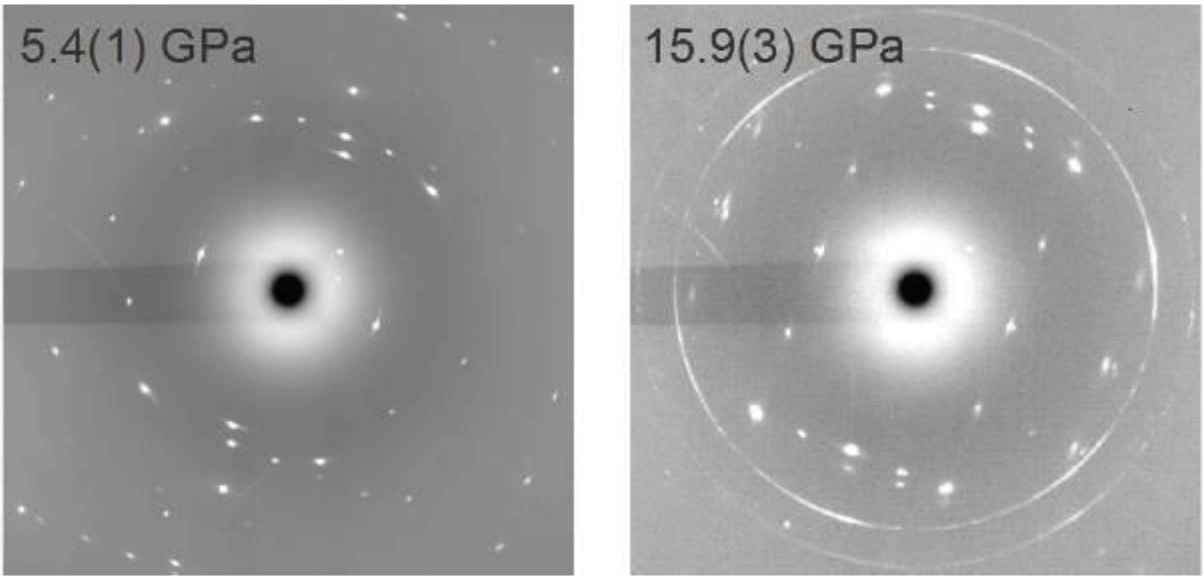


Figure 2



O 14.6

High pressure structural properties of functionalized imidazolium salts

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[2]*ALBA-CELLS Synchrotron Light Source, Barcelona, Spain*
[3]*Institut de Ciència de Materials de Barcelona (CSIC), UAB, Bellaterra, Spain*
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The positively charged imidazolium ion (Figure 1) is usually employed as the basic unit in many ionic-liquid related compounds in which the functionalized imidazolium cation coordinates with halides or more complex anions. With many possible chemical variations, including the imidazolium functionalization at different positions, a rich variety of combinations allows a complex interplay of rigid and flexible units and ionic interacting across H-bonding, anion-π and other van de Waals interactions [1]. This causes a wide span of melting points and structural features which, together with other propertieslike magnetism, optical properties, etc. that can be achieved with suitable choice of components favour their use or potential use in a of industrial applications [1].

Often, simple functionalization of the imidazolium, for instance with methyl and ethyl (namely Dimim, Emim or Edimim (dimethyl, ethyl-methyl, or ethyl-dimethyl imidazolium, respectively)), yield surprising results. For instance, the imidazolium salt Edimim chloride displays a colossal and highly anisotropic positive thermal expansion (TE) along the *b*-axis of their monoclinic centrosymmetric structure [2]. Moreover, replacing Cl with Br anions in the same crystal structure increases the value of the colossal positive TE in response to temperature changes and induces a biaxial negative TE in the other two directions.

In this work we will present the structural behavior of some of these salts as studied by Raman spectroscopy and X-ray diffraction under temperature and pressure and will discuss the results in terms of the different units, interactions and anisotropies, including observed phase transitions.

Figure 1. Left: Imidazolium basic unit showing radicals at given positions. Right: XRD patter of Edimim Cl as a function of temperature, showing the large and negative displacements for given planes.

Figure 2. Selected Raman modes of Dimim chloride as a function of pressure in the low frequency range. Observe phase transitions and mode softening between 100 and 150 cm-1 below 2 GPa.

[1] J. Dupont, *Acc. Chem. Res*. 2011, 44, 1223- 1231

[2] I. De Pedro et al., Cryst.Growth Des., 2015, 15, 5207-5212

Figure 1

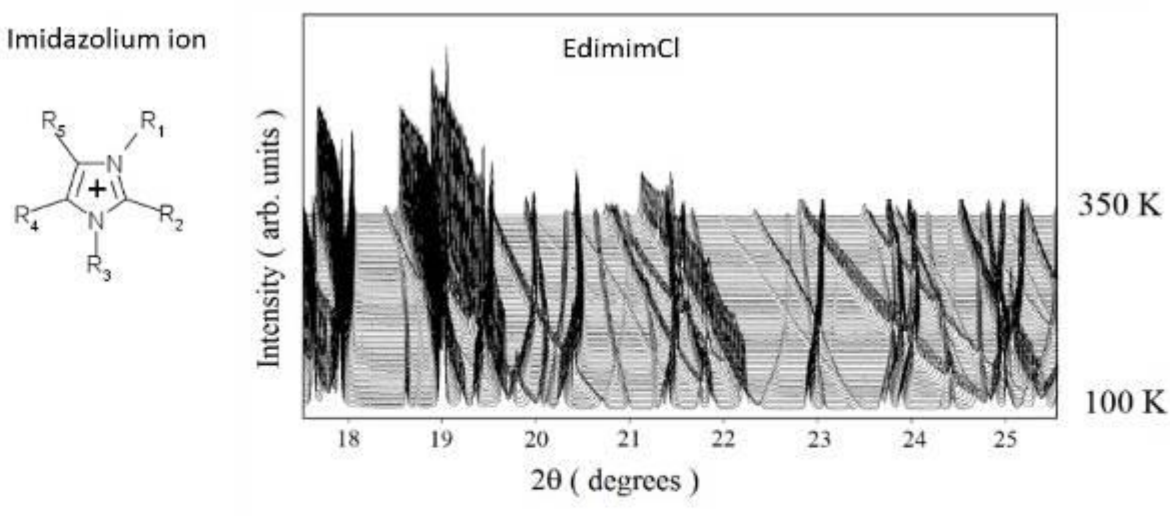
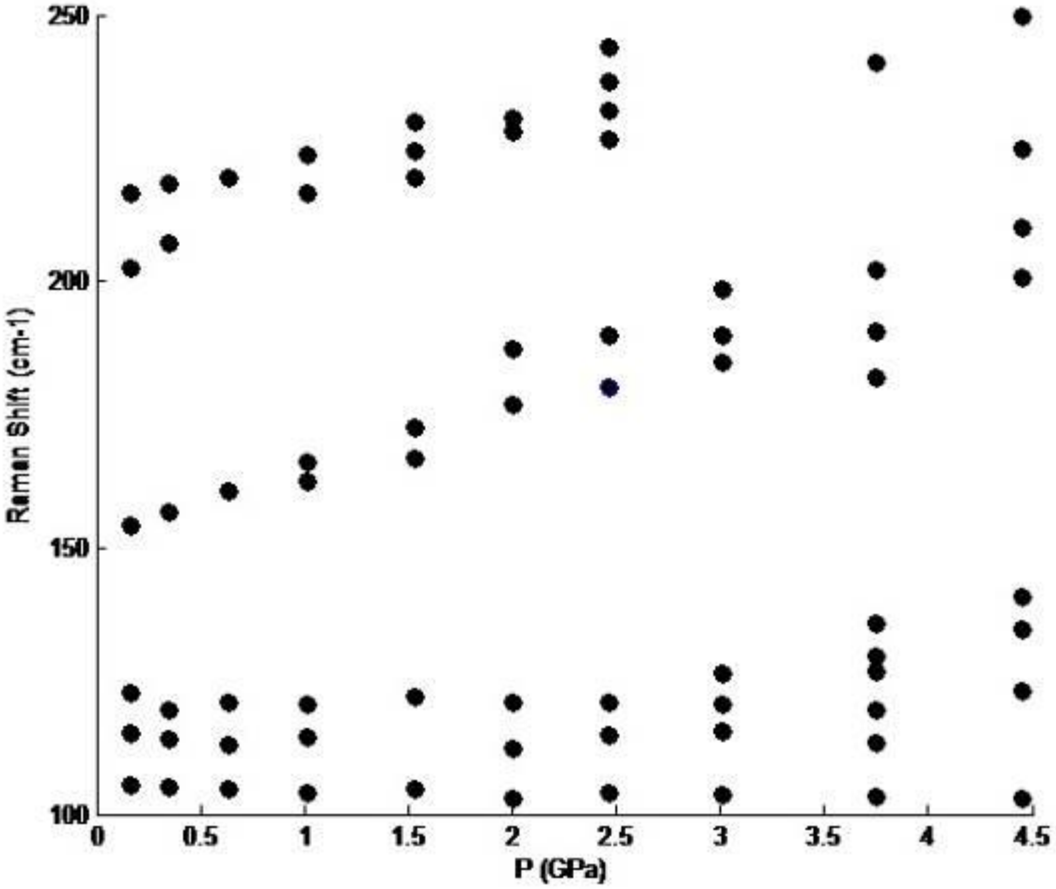


Figure 2



O 14.7

Role of pressure transmitting media in structural transformations of molecular crystals at high pressures

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Molecular compounds are interesting both from fundamental and applied point of view since many of them are promising as materials with piezoelectric, ferroelectric and non-linear optical properties. Some of them can serve as biomimetics. Due to these facts studies of polymorphism of molecular compounds are important for crystal engineering and crystallization theory. High pressure is one of the most powerful tools to influence polymorphism of molecular compounds. However, the control of high-pressure polymorphism is not a trivial task. Generally, it is not possible to predict which phase will be formed at a selected (T, P) point based on a thermodynamic phase diagram. As a result of the kinetic control of nucleation and nuclei growth, different phases can form, depending on the choice of the starting polymorph, the hydrostatic medium, the compression/decompression protocol and the choice of pressure transmitting media. The last effect is the most intriguing due to the fact that proper pressure transmitting media do not react chemically with studied molecular compound. Despite that pressure transmitting medium was shown to influence the product of high-pressure transformation of molecular compounds. In this contribution we illustrate this phenomenon in relation to an antidiabetic drug, chlorpropamide. In addition to the commercially available α polymorph, which is thermodynamically stable, four other polymorphs (β-, γ-, δ-, ε-) can be preserved indefinitely long under ambient conditions. The variety of polymorphs makes chlorpropamide very interesting for high-pressure research. The chlorpropamide polymorphs were studied by diffraction and spectroscopic techniques. We compared the phase transitions in solid polymorphs immersed in different pressure transmitting media. We also studied the effects of pressure, when several different polymorphs were present simultaneously in the same diamond anvil cell. A plethora of interesting effects was observed. The same polymorph of chlorpropamide was shown to undergo transformations into different polymorphs depending on selected pressure transmitting medium (without recrystallization), as well as to recrystalize into other forms, depending on the presence of other polymorphs in the same diamond anvil cell.

The work was supported by a grant from RSF (14-13-00834).

O 14.8

Energetic materials under pressure

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[4]*Australian Nuclear Science and Technology Organisation, Bragg Institute, Sydney, Australia*

Explosives and propellants, known generically as energetic materials, are widely used in applications that include mining, munitions, and automotive safety. Key properties of these materials include: reliable performance under a range of environmental conditions; long-term stability; environmental impact; processability; sensitivity to accidental initiation through stimuli such as impact, shock, friction, and electrostatic discharge. Many of these properties are affected by the crystal structure of the energetic material. Explosives experience elevated pressures and temperatures under detonation conditions - such conditions often induce phase transitions in the energetic material. Hence detailed studies of pressure-induced structural changes in these materials are essential in order to understand and model fully their behaviour.

This presentation will describe some recent high-pressure studies (using a combination of X-ray and neutron diffraction techniques) on selected high explosives including NTO (nitrotriazolone), CL-20, and TATB (triaminotrinitrobenzene). The often highly anisotropic compressibility behaviour of these materials can be correlated with their crystal structures. The presentation will also describe the interplay between experiment and theory, which will be illustrated by experimental and computational high-pressure studies of CL-20. In particular, we will highlight the potential effects of X-ray damage on these materials and how this issue can be overcome through the use of neutron diffraction.

P 14.1

High pressure Raman study of polyvinyl-toluene

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[2]BARC, radiation and photo chemistry Division , Mumbai, India

Investigating pressure, volume and temperature behavior of polymers and polymer composites under high pressures would be valuable, particularly for EOS measurement, constitutive models for modeling and predicting polymers response under extreme pressure and temperature conditions. Vibrational spectroscopy is an effective tool to examine high pressure effects such as molecular orientation and conformation, and phase transitions. Polyvinyl-toluene (PVT) is a potential high temperature plastic scintillator and widely used for gamma-ray detection. In the present study, we examined the dependency of the vibrational frequencies of PVT under static and dynamic pressure.

Raman spectrum of PVT at various static pressures was measured in diamond anvil cell using Jobi-Yvon triple stage Raman spectrometer T64000.

Figure 1 shows shift of the fundamental modes of PVT as a function of static pressure in the range 200-3250 cm^{-1}. All of the observed modes show shift to higher wavenumber and decrease in intensity, as the pressure is increased. The position of these modes is fitted by linear least square fit. The observed vibrational modes show a proportional relation with pressure except for 1456 cm^{-1} mode (δCH_2 mode). This suggests that the δCH_2 mode is much more intact up to 3.2 GPa, after which the intensity of the mode is difficult to observe under the present experimental conditions. Vibrational modes at 223, 2903 and 3057 cm^{-1} are found to be more sensitive to pressure change. It will be discussed in more details in the presentation. The low frequency modes (e.g. 223 cm^{-1} in our case) are found to be important for the examination of crystalline state such as phase transitions [1]. These low frequency modes are extremely sensitive to changes in the chain conformation of the polymers [2]. However, no evidence is found for any change in plot for present pressure range. By considering the monotonical change of all vibrational modes of PVT it can be concluded that PVT does not changes it's conformation up to 5 GPa.

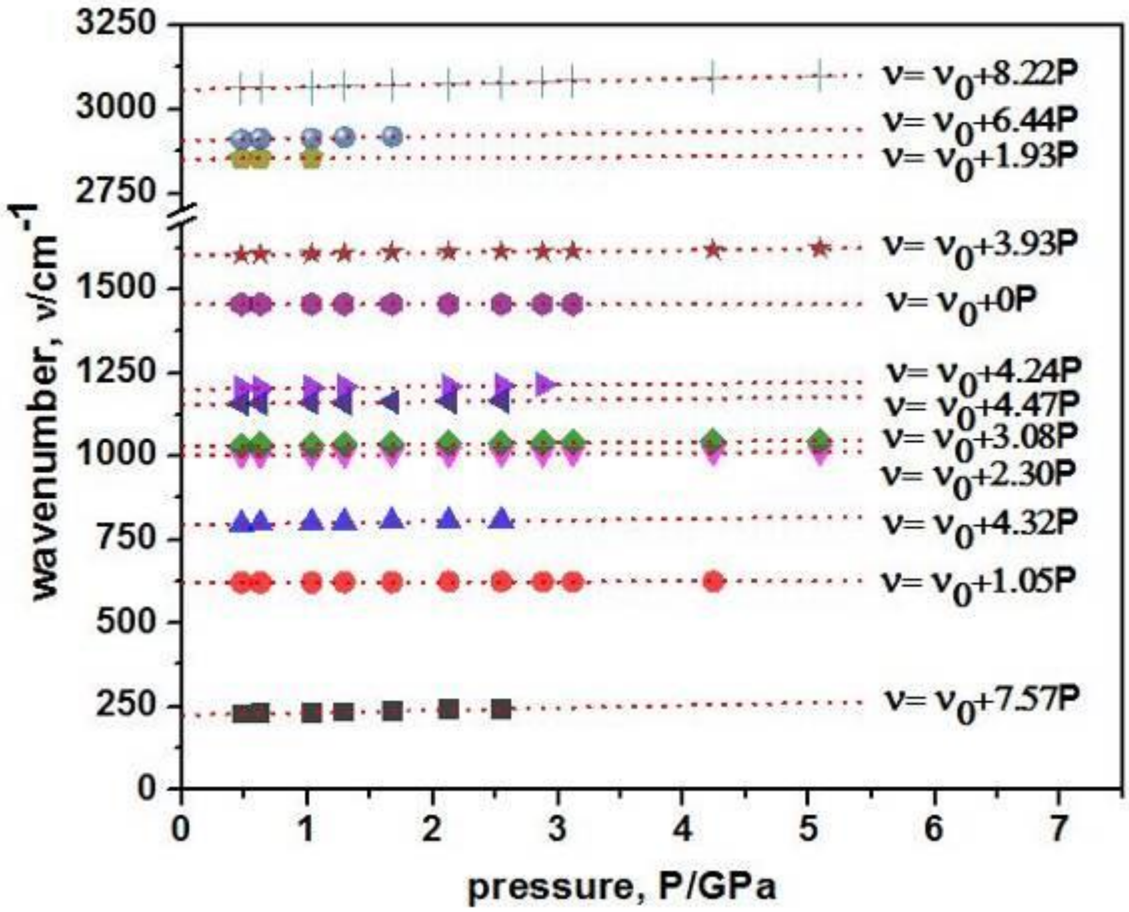
References

[1] C.N. King et al. Phys. Rev. Lett., 32 (1974), p. 538.

[2] Y. Furushima et al. *Solid State Commun.*, vol. 140, no. 5, pp. 240-244, 2006.

Figure. 1 Shift of different Raman modes of PVT under static compression.

Figure 1


wavenumber, v/cm^{-1}
pressure, P/GPa
3250
3000
2750
1500
1250
1000
750
500
250
0
0
1
2
3
4
5
6
7
ν= ν$_0$+8.22P
ν= ν$_0$+6.44P
ν= ν$_0$+1.93P
ν= ν$_0$+3.93P
ν= ν$_0$+0P
ν= ν$_0$+4.24P
ν= ν$_0$+4.47P
ν= ν$_0$+3.08P
ν= ν$_0$+2.30P
ν= ν$_0$+4.32P
ν= ν$_0$+1.05P
ν= ν$_0$+7.57P

P 14.3

Experimental studies of gas hydrate formation-dissociation under submarine conditions

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[2]Technical University of Berlin, Department of Food Biotechnology and Food Process Engineering, Berlin, Germany
[3]University of Erlangen-Nuremberg, Institute of Fluid Mechanics, Erlangen, Germany

During the last decade, Gas Hydrate (GH) formation-dissociation processes have attracted attention from the scientific community in terms of bio-engineering applications. However, the transport phenomena involved in the physical-chemical processes taking place under submarine conditions are not yet fully understood. An exhaustive study is required to ensure a safe and ecological manipulation of GH in deep ocean deposits.

We experimentally study how fluctuations in the environment, as derived from changes on pressure, temperature or the sediment geometry, affect the stability of GH inside a pressure vessel with optical access which simulates the submarine conditions of GH in deep oceanic deposits. Particle Image Velocimetry (PIV) measurements are performed to qualitative study the onset of GH dissociation. The flow velocity generated as a consequence of the gas relief into the bulk of water can be characterized as a function of the deviation degree from gas hydrate stability conditions (GHSC).

Besides, we study the influence of geometry of the sediment bed during GH formation-dissociation. For that purpose, we study the kinetics of the process within substrates made of uniformly sized beads regularly arranged according to triangular or quadratic symmetries. Experimental results showed a strong impact of the sediment arrangement: Under the same initial conditions, depending only on the substrate symmetry, we observed a favoured kinetics of MH formation, by a factor up to 3, for the triangular substrate as compared to the quadratic one. Similarly, we observed dissociation phases in quadratic geometries but not in triangular substrates under the same initial conditions [1].

[1] Agudo J. R., Park J., Luzi G., Williams M., Rauh C., Wierschem A. and Delgado A. 2016, *J. Phys.: Conf. Ser. (Accepted)*

P 14.4

Production of kefir under high pressure - a case-study of fermentation under innovative conditions

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Kefir is a lightly carbonated, low-alcohol and creamy consistency dairy beverage [1], with several benefits for health and peculiar sensory properties. High pressure (HP) technology has been suggested as a novel approach to change the performance of microbial fermentations under sub-lethal pressures. This new application can bring novel characteristics and features to the fermentative process and/or to the final product.

The aim of this study was to evaluate the application of HP for kefir production at room temperature (≈17.0 ºC). For this purpose, reconstituted milk was inoculated with a commercial starter culture, which was composed of both bacteria (*Lactococcus lactis subsp. lactis*, *Lactococcus lactis subsp. cremoris*, *Lactococcus lactis subsp. lactis biovar. diacetylactis*, *Leuconostoc mesenteroides subsp. cremoris*, *Lactobacillus acidophilus*, *Streptococcus thermophilus*, *Lactobacillus kefyr*) and yeasts (*Kluyveromyces marxianus* and *Saccharamyces unisporus*). The fermentation process was performed under different pressure conditions (0.1 - 50 MPa) and variation of pH, titratable acidity and reducing sugars concentration were evaluated over time.

Results showed that kefir production was slower under pressure but kefir could be obtained by prolongation of fermentation time, since the final pH values achieved were in the range of those reported in literature for kefir (≈ 4.2 - 4.6) [2]. Regarding kinetic analysis, activation volumes (Va, cm^3/mol) were calculated and positives values were observed for the different parameters so far quantified (pH, titratable acidity and reducing sugars), indicating that in general fermentation were slowed down by pressure.

These results show a good potential for kefir production under pressure, with a higher fermentation rate and different characteristics. Experiments are being performed in order to understand the possible effects of fermentation under HP on kefir texture and chemical composition.

[1] Kök-Taş T, Seydim AC, Özer B, Guzel-Seydim ZB. Journal of Dairy Science. 2013;96(2):780-9.

[2] Otles S, Cagindi O. Pakistan Journal of Nutrition. 2003;2(2):54-9.

P 14.5

High pressure processing pasteurization of raw sheep cheese

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[2]*Catholic University of Portugal, Faculty of Biotechnology, Porto, Portugal*

Serra da Estrela cheese is a Portuguese traditional cheese with Protected Designation of Origin (PDO), which is manufactured from raw sheep's milk, salt and cardoon flower extract (as plant rennet). The raw milk has in its composition several microorganisms, some of which may be of spoilage or eventually pathogenic nature.

High-pressure processing (HPP) has emerged as a commercially viable food manufacturing tool that satisfies consumers' demand and food processors for mildly processed food, with nutritional and textural advantages over thermal processing while assuring pathogenic and spoilage bacteria, yeasts and moulds inactivation.

This work aimed to study the effect of HPP on Serra da Estrela cheese after pressure processing and storage at 5 ºC for 225 days on: endogenous microflora, proteolysis indexes, sensorial characteristics and physicochemical parameters.

Cheeses with 45 days of ripening were HPP at 600 MPa/6 minutes (P1), 450 MPa/6 minutes (P2) and 450 MPa/9 minutes (P3) at 8 ºC. Non-processed samples were used as controls (NonP).

After pressurization and during storage, lactococci, lactobacilli and total aerobic mesophilic counts were reduced in about 4 Log CFU/g in P1 cheeses and about 2 Log CFU/g in P2 and P3 cheeses. Between cheeses P2 and P3 only small differences in viable cell numbers were detected. Thus, the more intense pressure treatment (P1) caused a greater impact on microflora's viability, than the time under pressure (by comparing P2 with P3). *Enterobacteriaceae* and *Pseudomonas* spp. counts showed > 4 log cycle reductions, to numbers below detection limit for all HPP cheeses.

The pH values were slightly higher in Non-P than in HPP cheeses. Non-P, P2 and P3 chesses revealed similar titratable acidity, and lower values were determined for P1 cheeses. HPP cheeses revealed total colour variation lower than 5 and more yellowness on its surface and core than Non-P cheeses. The ripening extension indexes of P1 treated chesses revealed values closer to those of Non-P cheeses at 45 days of ripening.

The results obtained enabled concluding on the good potential of HPP to render Serra da Estrela cheese microbiologically safe with increased shelf-life and a proteolytic index similar to the unpasteurized cheese.

P 14.6

Holding time of HHP as affecting parameter on quality of liquid whole egg

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HHP is investigated in case of many food products. The two most important parameters of HHP are pressure and holding time. Most common attention is paid to pressure, not to holding time, although holding time of pressure processing is neglected, it has similar importance as applied pressure.

In our study liquid whole egg (LWE) was treated at 400 MPa for 1, 3, 5, 7 and 10 min in Resato FPU 100-2000 HHP equipment. The aim of our experiment is to examine the effect of holding time to certain properties of liquid whole egg.

Physical-chemical attributes (pH-value and colour), microbiological state (mesophyll aerobic cell count) were measured in LWE and texture and sensorial quality were examined in product (omelettes) made from LWE.

Results show that neither HHP treatment, nor holding times don't influence pH-value significantly (one-way ANOVA, α=0,05), in contrast colour of LWE is significant changed. Colour of samples became brighter (CIELab colour-system). L* became higher, a* and b* lower by increasing of holding time. Colour change may be caused by denaturation of proteins.

Mesophyll aerobe cell count decreased proportional to increasing holding time. HHP reached two orders of magnitude decreasing of cell count in 10 minutes at 400 MPa, but it is not enough to produce microbiological safe LWE. Acceptable microbiological safety can be provided through combination of HHP and other preservation methods.

For investigation of texture omelettes were cooked. We examined texture instrumental (Stable Micro System) and sensorial (12 untreated panellists). Results of the two methods show similarity: samples with instrumental measured same textures showed equal popularity of panellists. Sensorial test shows that HHP treated samples have better texture, smell, taste and overall quality. Longer treated samples were preferred by the panellists. The top rated omelettes were cooked from 420 s HHP treated LWE.

Summarising our results show that different holding times of HHP at 400 MPa cause significant changes in examined properties (excepted pH-value). It means that it is not sufficient to study pressure range in studies, in applied research we have to focus on holding time same extent as pressure.

P 14.7

Evaluation of quality changes of beetroot juice after high hydrostatic pressure (HHP) processing

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[1]*1Prof. Wacław Dąbrowski Institute of Agricultural and Food Biotechnology, Department of Fruit and Vegetable Product Technology, Warsaw, Poland*
[2]*2Institute of High Pressure Physic of Polish Academy of Sciences, Warsaw, Poland*

In the last years in juice and beverage industry the new non - thermal preservation technologies are increasingly used. These technologies allow to obtain drinks with nutritious and sensory characteristics similar to the fresh product.

Betalains, water-soluble nitrogen-containing pigments, found in high concentration in red beets (*Beta vulgaris*), are responsible for their attractive red colour. Betalains have antimicrobial and antiviral effects, can inhibit the cell proliferation of human tumor cells and, due to their antioxiadant properties, can contribute to protection from age-related diseases. Freshly-squeezed commercially available beetroot juice, a popular beverage in Poland, is a good source of betalains, but as a root vegetable can contain undesirable microflora from the soil.

The objective of this study was to investigate the effect of new preservation technique, high hydrostatic pressure (HHP), on the beetroot juice quality. The impact of processing was evaluated on the basis of betalain pigments content and on microbial quality of the processed samples.

Samples of beetroot juice were treated with HHP 300, 400 and 500 MPa/20°C/up to 10 min. High Pressure Single Vessel Apparatus U 4000/65 (Unipress Poland) was used. Total count of spoilage microorganisms was determined by pour plate on OSA agar (according to IFU No. 2 Method). Pigment content was determined using HPLC-DAD system with detection at 538 nm and 476 nm for betacyanins and betaxanthins, respectively.

Total count of spoilage microorganisms (including lactic acid bacteria, yeasts, moulds and acetic acid bacteria) after pressurization decreased by 3.8, 4.1 and 4.5 log cfu/mL, depending on the pressure. HHP treatment of beetroot juice resulted in 11.3-12.2 % decrease in betacyanins content and 7.7 - 8.9 % in betaxanthins.

A significant reduction of the number of spoilage microorganisms with a slight degradation of pigments, indicates the possibility of industrial application of HHP to preservation of beetroot juice. Further research during refrigerated storage will be conducted.

Acknowledgements

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P 14.8

The analysis of protein and physico-chemical changes in high hydrostatic pressure or heat treated whole milk

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High pressure treatment affects proteins and the individual protein groups in different ways. The changes of a product can depend on a lot of factors for example the environmental conditions (temperature, pH or nutritional properties of the product). It was our goal to detect the physio-chemical changes and changes of proteins in sterilized (121 °C, 15 min) or pasteurized (72 °C, 42 sec) or treated (on pressure 300, 400, 500, 600 MPa, 5 min) whole milk and to analyse the microbial stability of the samples. Native-PAGE and SDS-PAGE were used to determine the changes of proteins. Color, pH, apparent viscosity and microbiological properties were also examined. It could be observed that the L* (lightness) values decreased, so the color of samples got darker as a result of the various treatments. In case of the values of a* and b* significant changes could be noticed between the pasteurized and the high pressure treated samples, but the sterilized samples totally differed from these because melanoidins formed in the milk due to the high heat dose. It could be established that the pH values decreased proportionally to the temperature increase. In case of the pressure treated and pasteurized samples the decreasing tendency of pH was similar. The apparent viscosity of the pressure treated milk samples increased by the increasing heat dose. Compared to raw milk, two-three magnitude decrease could be achieved in the total aerobic mesophilic cell count by pasteurization and pressure treatments, while the results were be under the detection limit by sterilization. During the electrophoretic analysis partial denaturation of β-lactoglobulin B was experienced in case of treatment by 300 MPa. The higher pressure values caused complete denaturation of β-lactoglobulin B. In case of β-lactoglobulin A similar changes were experienced. The α-lactalbumin did not change during the high pressure treatment and pasteurization, respectively, but the proteins of sterilized milk samples completely denatured. Both native-PAGE and SDS-PAGE gels show these phenomena, but on the SDS-PAGE gels the rate of denaturation was less pronounced due to the strong detergent.

It can be concluded that the high pressure treatment increased the microbial safety of the whole milk and did not largely influence the proteins and the examined properties of milk.

P 14.9

Pressure-induced structural phase transition of L-phenylalanine studied by Raman spectroscopy

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Introduction

Amino acids are biologically important compounds, constituting the building blocks of all proteins. Amino acids form molecular crystals where the interplay between van der Waals interactions and hydrogen bonds determine their structure. Phenylalanine is an essential amino acid that is hydrophobic, non-polar and aromatic and is the precursor of tyrosine, melanin and important neurotransmitter molecules. Raman spectroscopy can provide valuable insight in the vibrational and structural properties of biomolecules.

Objectives

In this work, Raman spectroscopy is used to probe the structural stability and possible phase transitions of L-phenylalanine crystals subjected to hydrostatic pressure.

Materials and methods

L-phenylalanine crystals where pressurized (up to 5 GPa) by means of a diamond anvil cell, using the 1:1 FC70-FC77 Fluorinert^{TM} mixture as pressure transmitting medium. Raman measurements were conducted using a LabRam HR or a T64000 spectrometer. A laser beam at 515 nm was used for excitation, focused on the sample by means of a 50x objective at a power of ~1 mW.

Results

The Raman spectrum of the studied system is very rich, owing to the low symmetry of the phenylalanine molecule and the monoclinic crystal structure. The intermolecular modes appear in the low frequency region (-1), while the intermediate region contains the backbone, aromatic and side-chain vibrational modes and the high frequency region (>2800 cm^{-1}) is dominated by C-H and N-H stretching vibrations. The pressure dependence of the frequencies of all the Raman peaks is quasi-linear up to ~2 GPa with pressure slopes 1.6-16.2 cm^{-1}GPa^{-1}. However, above 2 GPa, significant changes occur with respect to the number of the Raman peaks, their frequencies and pressure slopes. These changes signal a structural phase transition of the crystalline L-phenylalanine at ~2 GPa. The new high pressure phase is stable to pressure application up to 5 GPa. Nevertheless, the phase transition is reversible and the initial phase is recovered during the downstroke experiments below 2 GPa.

Conclusion

L-phenylalanine undergoes a structural phase transition at ~2 GPa accompanied by molecular conformation modifications. This transition is reversible and the initial phase is recovered upon pressure release.

P 14.10

Tuning a colourful organic crystal with pressure

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5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile is known to crystallise in at least 10 different forms, all under ambient conditions.[1] This is strongly evident in the visual appearance of the crystals, having different morphologies and a bright red, orange, or yellow colour; they are colloquially referred to as the 'ROY' system. The forms are conformational polymorphs—all possessing different torsion angles between the aromatic groups at either end of the molecule (see Figure), to which the crystal colour is attributed. [2]

Our aim is to explore the extent to which the planarity of the molecule, and thus its colour, can be controlled with hydrostatic pressure, and to start investigating the high-pressure phase diagram of this highly-polymorphic system for the very first time.

On compression of a single 'Y'-phase (yellow) crystal, using a diamond anvil cell, we exploit the flexibility in molecular conformation, finding that the crystal continuously turns orange, and then red—observed by microscope and UV-Vis spectroscopy—consistent with increased co-planarity of the aromatic groups, determined via structure refinement against X-ray data. [3] Moreover, the colour change occurs in the absence of a crystallographic phase transition. Our spectroscopic results suggest that Y-form ROY exhibits one of the strongest known, visible, piezochromic responses in the organic solid state under hydrostatic conditions—a desirable feature in high-pressure sensing applications.

References

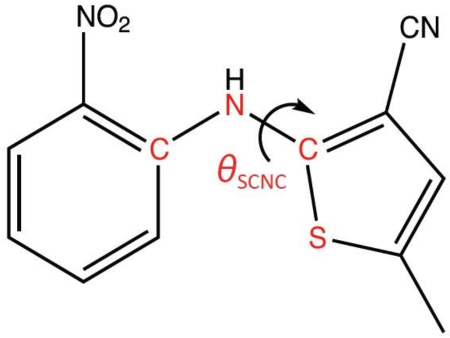
[1] L. Yu, *Acc. Chem. Res.,* 2010, **43**, 1257

[2] J. R. Smith, W. Xu and D. Raftery, *J. Phys. Chem. B,* 2006, **110**, 7766

[3] E. L. Harty, A. R. Ha, M. R. Warren, A. L. Thompson, D. R. Allan, A. L. Goodwin and N. P. Funnell, *Chem. Commun.,* 2015, **51**, 10608

Figure caption: The molecular structure of 'ROY', indicating the rotatable torsion angle

Figure 1



P 14.11

Alternatives to “co-crystal - salt” transitions in glycine co-crystals at low temperature and high pressure: two new examples as a follow-up to a glycine-glutaric acid study

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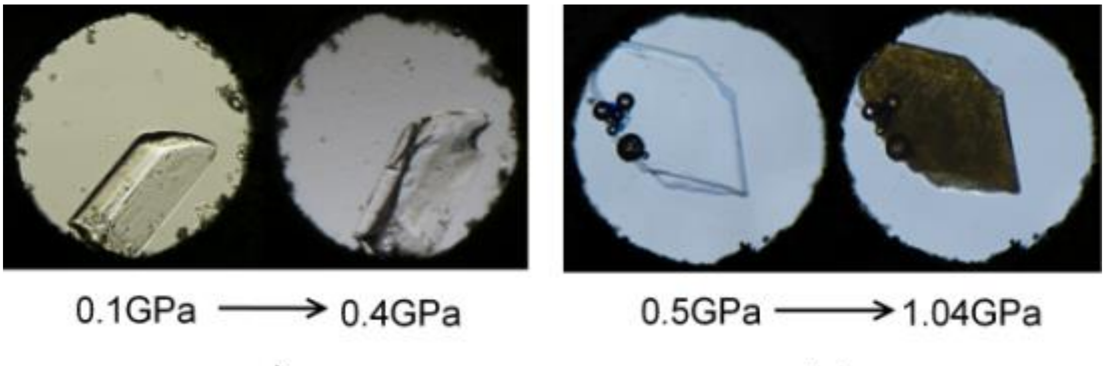
The effects of temperature and pressure on the co-crystals of glycine with DL-tartaric and phthalic acids (**GT** and **GP**, respectively) have been studied by X-ray diffraction and Raman spectroscopy in a comparison with those in glycine-glutaric acid co-crystal (**GG**). Like for **GG**, for both **GT** and **GP** neither cooling nor increasing pressure resulted in a co-crystal to salt transition. On cooling, no phase transitions were observed in **GT** or **GP**, contrasting the situation with **GG**. On hydrostatic compression both **GT** and **GP** underwent reversible phase transformations, accompanied by fracture (Fig.1a and Fig.1b, respectively). In the high-pressure phases the main structural framework was preserved, the number of crystallographicaly independent molecules in the unit cell increased; the type of intermolecular H-bonds linking DL-tartaric molecules into dimers in **GT** changed in every second dimer from hydroxyl-group to hydroxyl-group in the low-pressure phase for the hydroxyl-group - carboxyl-group in the high-pressure phase.

The work was supported by the Russian Foundation for Basic Research (RFBR) (Grants No. 14-03-31866 mol_a, 16-33-60089 mol_a_dk), and RAS (Project 44.3.4).

Figure 1



P 14.12

How do isoenergetic polymorphs behave under pressure? – A case study of tolazamide

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Polymorphism of organic compounds is of high interest for academia and industry. An intriguing case of polymorphism is isoenergetic polymorphism, when one form transforms into another without a measurable heat effect. Our recent study has shown the polymorphs of tolazamide - an antidiabetic drug - to be isoenergetic despite a significantly different molecular packing [1]. When crystallised from solution at ambient pressure, the nuclei of the two polymorphs, I and II, form simultaneously, then the crystals of polymorph II grow much faster than those of polymorph I. However, if the crystals of polymorph II are stored in solution, they eventually recrystallise into polymorph I. DSC revealed no thermal effects corresponding to the II to I transformation. Model calculations also supported the conclusion that the two polymorphs are isoenergetic [1].

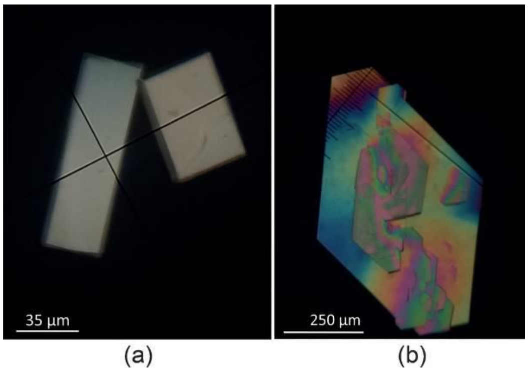
The two polymorphs differ radically in molecular packing and, slightly, in densities. Therefore, one could expect that pressure could favour the II to I transformation in the crystals of tolazamide, or, if nucleation in the solid state is hindered, a recrystallisation of polymorph II into polymorph I when pressure is increased. The aim of this study was to follow the effect of pressure on polymorphs I and II in two types of hydrostatic fluids: a) the one which can dissolve tolazamide, so that a solvent-assisted transformation / recrystallisation were possible (methanol), or b) the fluid in which tolazamide is not soluble (equimolar pentane / isopentane mixture). In this work the experimental study using single crystal X-ray diffraction in different fluids (dissolving or not dissolving tolazamide) was complemented by DFT-D calculations of optimized structures and energies for both forms of tolazamide over a wide pressure range. Neither of the two forms transforms into another on increasing pressure (at least up to 6 GPa) not only in the solid state (in pentane-isopentane), but also when a recrystallization is possible (in methanol). This phenomenon is rationalized based on the analysis of experimental and computationally optimized crystal structures.

This work was supported by Russian Science Foundation (14-13-00834).

[1] Boldyreva, E.V., et al. Isoenergetic Polymorphism: The Puzzle of Tolazamide as a Case Study (2015) Chemistry - A European Journal, 21 (43), pp. 15395-15404.

Figure 1. Crystals of tolazamide a) Form I and b) Form II.

Figure 1



(a) (b)

Invited Talk

Structure of silicate glasses up to 172 GPa

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The physical properties of silicate melts at temperature and pressure conditions of the Earth’s mantle have a fundamental influence on the chemical and thermal evolution of the Earth. However, direct investigations of melt structures at these conditions are experimentally very difficult or even impossible with current capabilities. In order to still be able to obtain an estimate of the structural behavior of melts at high pressures and temperatures, amorphous materials have been widely used as analogue materials.

Here we report experimental investigationsof the structural behavior of glasses ofSiO_2 up to 172 GPa, $MgSiO_3$ up to 135 GPa, and Mg_2SiO_4 up to 140 GPa using X- ray total scattering and pair distribution function analysis. To further understand ultra high pressure behavior we have investigated GeO_2 glass, as an analogue for SiO_2 glass, up to 85 GPa. The very high pressure range for these measurements were enabled by the newly commissioned multichannel collimator setup at GSECARS, APS, which significantly reduces the amount of diamond Compton scattering. This facilitates the collection of total x-ray diffraction patterns up to a maximum Q of 15 A^{-1} at very high pressures.

The data clearly shows changes from 4- to 6-fold coordination of Si, which is completed around 40-60 GPa, depending on composition, in agreement with previous reports. GeO_2 shows an increase to 6-fold coordination already about 25-30 GPa. At higher pressures, after the change to 6-fold coordination, the glasses show smooth changes in structure factors S(Q) and pair distribution functions g(r). The Si coordination number gradually increases to about 7.2 at 172 GPa for SiO_2 with no apparent discontinuity.

We will present experimental data, discuss densification mechanisms and differences of the various glass compositions at high pressures. The goal is to establish a framework for silicate glass structures as analogue materials for silicate melts to understand the deep Earth's interior.

O 15.1

Crystal structure of MgO along the shock Hugoniot

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Of the more than 6,000 confirmed and candidate extrasolar planets discovered to date those that are 1-4 times the radius of the Earth are found to be the most abundant. The silicate compounds that dominate the Earth's mantle likely dissociate into component oxides at the extreme pressures (200-2,000 GPa) and temperatures (5,000-10,000 K) corresponding to conditions of super-Earth mantles. Magnesium oxide (periclase), an end-member of the ferropericlase solid solution (Mg,Fe)O and an important component the Earth's mantle, has been studied under static compression in the pressure and temperature range found within the Earth (~135 GPa, 2500-4000 K). However, as static compression techniques are typically limited to peak pressures of < 200 GPa, much less is known about its behavior under high-pressure and -temperature conditions.

In this study, the structure of MgO upon shock compression over the 200-700 GPa pressure range was examined at the Omega-EP Laser facility at the Laboratory for Laser Energetics, University of Rochester. Laser drives of up to 2 kJ over 10 ns focused onto a polyimide ablator were used to shock compress 50-µm thick polycrystalline or single-crystal MgO. At peak compression, the sample was probed with He-α X-rays from a laser-plasma source. Diffracted X-rays were collected using the PXRDiP diagnostic which consists of image plates lining the inner walls of a box attached to the target package. For each pressure we measure pressure (velocity interferometry), density (x-ray diffraction) and shock temperature (pyrometry). Along the shock Hugoniot MgO transforms from B1 to the B2 structure at ~400 GPa and melts at ~700 GPa.

O 15.2

Deformation of polyphase aggregates, forsterite+MgO, at high pressures and temperatures

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Modeling the solid-state flow of the upper mantle requires a thorough understanding of its rheology and therefore necessitates to perform deformation experiments on mantle rocks (or analogues) at very high pressures and temperatures. Minerals other than olivine constitute up to 40 vol% of upper mantle rocks and may have a significant effect on the rheological behavior of these rocks. Nevertheless, most experimental studies to date have focused on the deformation properties of olivine single crystals or monomineralic olivine aggregates.

In this study, and as a first step before focusing on more realistic mantle-like compositions, we have performed deformation experiments on polymineralic model aggregates of forsterite and MgO, at high pressures and temperatures. Commercial powders of Mg_2SiO_4 and MgO were mixed and ground in WC grinders and dried in a one-atmosphere furnace at 1000°C. Powders with different volume proportions of the two phases were sintered by spark plasma sintering (SPS) at temperatures of 1300-1400°C and 100 MPa for a few minutes, resulting in dense pellets 8 mm in diameter and 3-4 mm in length. Microstructural analysis by SEM reveals equilibrated microstructures with forsterite and MgO grain sizes of a few microns.

Deformation experiments were performed at 3-8 GPa and 1000-1300°C in a D-DIA apparatus coupled with synchrotron X-ray radiation at beam line X17B2 (NSLS, Brookhaven, NY, USA). The technique permits in situ measurement of macroscopic strain rates as well as stress levels sustained by different subpopulations of grains of each phase. Typically, two specimens, respectively a monomineralic and a polyphase aggregate, were deformed concurrently in order to minimize the relative uncertainties in temperature and pressure and to facilitate the comparison of their rheological properties. The samples were deformed to total strains of 15-25%.

As expected, the harder phase, forsterite, sustains much higher stress levels than MgO, in agreement with numerical models for two-phase flow. Results on stress and strain partitioning in polyphase aggregates and on the effect of the presence of a weak phase on the rheology of forsterite-rich aggregates will be discussed. In addition to stress-strain data, we will also present the microstructures observed by SEM on deformed samples.

O 15.3

Understanding transformational faulting as a deep focus earthquake mechanism: correlating in-situ acoustic emission locations at high pressure and temperature with post-mortem fault imaging using synchrotron X-Ray microtomography

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One of the possible mechanisms responsible for deep focus earthquakes occurring at depths below 350 km is faulting triggered by phase transformations from mineral olivine to its high-pressure phases (wadsleyite and ringwoodite, both are related to the general spinel structure) in the Earth's mantle. We have studied transformational faulting from olivine to spinel in Mg_2GeO_4, which is a close analog of the silicate olivine $(Mg,Fe)_2SiO_4$, using a high-pressure deformation apparatus in conjunction with in-situ acoustic emission (AE) monitoring [1]. Synchrotron X-ray microtomography (XMT) [2] was used to image the samples recovered from high-pressure deformation experiments, with spatial resolution of ~0.005 mm. In this study, we establish spatial correlations between AE events observed in-situ during deformation and faults imaged by XMT post-mortem. The nature of high-pressure experiments limits the sample size to the order of 2 mm in linear dimensions, and the acoustic system has a maximum sampling rate of 50 MHz (i.e., 20 ns between adjacent sampling points), which limits spatial resolution of AE locations to about 0.3 mm. This makes it difficult to locate AE events accurately. A cross-correlation (CC) algorithm (hypoDD - [3]), developed for seismological studies, has been adapted in the analysis of AE locations, improving AE allocation spatial resolution by a factor of ~10. This algorithm also helps separate events with various waveforms, which are related to different fault planes and faulting directions. The CC algorithm classifies AE events into various groups. Events within each share common characteristics and can be considered occurring within a same fault plane. These groups of events display excellent correlations with faults imaged by XMT, with two major groups of AE events correlating well with two conjugated faults in XMT images. These results help understand the dynamic process of transformational faulting.

References

[1] A. Schubnel *et al.*, Deep-Focus Earthquake Analogs Recorded at High Pressure and Temperature in the Laboratory. *Science* **341**, 1377 (2013).

[2] M. L. Rivers, Y. Wang. (2006), *Developments in X-Ray Tomography V*, U. Bonse (ed.), *Proc. SPIE* vol. 6318, pp. 63180J-63180J-15

[3] F. Waldhauser, W. L. Ellsworth, A Double-Difference Earthquake Location Algorithm: Method and Application to the Northern Hayward Fault, California. *Bulletin of the Seismological Society of America* **90**, 1353 (2000).

O 15.4

Iron carbide and iron hydride from hydrocarbons during slab subduction

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An important role of hydrocarbon fluids in subducting slabs became evident recently[1]. Oceanic lithosphere together with petroleum deposits located both in sediment layer and in basement rocks is transferred into the Earth by subduction[2]. At the same time possible transformations of hydrocarbon fluids during subduction have never been studied. To get information about possible transformations of hydrocarbons in the subducting slab, the chemical reactions in the mixture of hydrocarbons and rock-forming iron substance were investigated in the range of thermobaric conditions corresponding with the depth down to 290 km (2.6-9.5 GPa, 1200-2300 K).

The experiments were carried out employing a laser-heated diamond anvil cell. ^{57}Fe-inreached powdered pyroxene glass $Mg_{0.91}Fe_{0.09}Si_{0.91}Al_{0.09}O_3$, powdered ferropericlase $(Mg_{0.8}Fe_{0.2})O$, and powdered iron oxide $Fe_{0.94}O$ were used as iron compounds. Astrakhan petroleum and synthetic paraffin oil were used as hydrocarbon systems. X-ray diffraction, Raman and Mössbauer spectroscopy were used to analyse the sample. The formation of iron hydride from hydrocarbons was observed at pressure 2.5-6.9 GPa and temperature 1400-1800 K, and the mixture of iron hydride and iron carbide was observed at pressure 7.5-9.5 GPa and temperature 1400-2300 K.

Our study shows that iron hydride (FeH) and iron carbide (Fe_7C_3) may be formed from interaction between hydrocarbons and the rock-forming iron materials at the mantle thermobaric conditions at the depth of 200-290 km. These substances may be present in mantle and take part in abyssal hydrocarbons formation[3].

[1] Sverjensky D.A., Stango V. and Huang F. Important role for organic carbon in subduction-zone fluids in the deep carbon cycle (2014) Nature Geoscience

[2] Plank T. and Langmuir C.H. The chemical composition of subducting sediment and its consequences for the crust and mantle (1998) Chemical Geology

[3] Kutcherov V.G. and Krayushkin V.A. Deep-seated abiogenic origin of petroleum: From geological assessment to physical theory (2010) Reviews of Geophysics

O 15.5

Novel stable Xe compounds of Fe and Ni at the pressure-temperature conditions of the Earth's core

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The lower Xe abundance in Earth's atmosphere, in comparison to other noble gases like Ar and Kr, is one of the most challenging open questions in geosciences [1]. The origin of the so-called "missing Xe paradox" is usually attributed to the inclusion of Xe in the interior of Earth [2]. Although Xe is known to form compounds (e.g. with hydrogen, oxygen), none of them can be related with Earth's interior. Indeed, only a very low amount of Xe can be incorporated in silica at <1 GPa and 500K [3]. On the other hand, experimental attempts to trace possible formation of Fe-Xe compounds up to 155 GPa and bellow 2500K have failed [4]. A very recent theoretical study, suggests that Xe-Ni and Xe-Fe compounds can form at thermodynamic conditions representative for the Earth's outer core [5].

Here we explored the possible formation of stable compounds in the Xe-Fe/Ni system at thermodynamic conditions representative for the Earth's core starting from the following mixtures: a) Xe-Fe, b) Xe-Ni and c) Xe-Fe/Ni alloy representative for the Earth's core (ca 6% Ni). Using in situ synchrotron X-ray diffraction and Raman spectroscopy we report the formation of: a) a $XeNi_3$ compound, in the form of a $CrNi_3$-type FCC solid solution, above 150 GPa and 1500K, b) a $Xe(Fe/Ni)_3$ compound, tentatively characterized as an orthorhombic $NbPd_3$-type solid solution, above 190 GPa and 2000K and c) a still not completely characterized $XeFe_x$ compound above 180 GPa and 2000K. This work provides a plausible explanation of the "missing Xe paradox" and underscores the importance of understanding of novel high-pressure chemistry rules for the better understanding of the structure and chemistry of the Earth's core.

[1] E. Anders, E. and T. Owen, Science 198, 453 (1977).

[2] Caldwell, W. A. et al., Science 277, 930 (1997).

[3] C. Sanloup et al., Science 310, 1174 (2005).

[4] D. Nishio-Hamane et al., Geophys. Res. Lett. 37, L04302 (2010).

[5] L. Zhu et al., Nature Chemistry 6, 664 (2014)

O 15.6

Origin of lower-mantle diamonds and associated minerals

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On mineralogical evidence, lower-mantle diamonds and their primary inclusions have been originated in common growth melts. The key problems for lower-mantle diamond genesis may be formulated as follows: 1) to determine the chemical nature and compositions of growth melts of diamonds and paragenetic inclusions; 2) to reveal the physico-chemical mechanisms of diamonds and primary inclusions syngenesis; 3) to unravel the phase reactions responsible for formation of discrete ultrabasic and basic parageneses among the diamond-hosted mineral inclusions. The principal diamond-producing $(MgO{\cdot}FeO)_{ss}$-CaO-SiO_2-(Mg-Fe-Ca-Na-carbonate)-carbon system was studied in physico-chemical experiments at 24 -26 ГПа. Boundary compositions of the multicomponent system are chemically-justified in accordance with the primary inclusions in lower-mantle diamonds. Combined experimental and mineralogical data allow to substantiate the silicate-oxide-carbonate melts with dissolved carbon as the parental media for the lower-mantle diamonds and associated phases. Generation of the oversaturation of dissolved carbon in respect to diamond in the completely miscible silicate-oxide-carbonate melts represents the physico-chemical mechanism responsible for diamond nucleation and crystallization. In such an event, diamond growth is accompanied with formation of paragenetic mineral phases in the common growth melts. During this process, the primary mineral inclusions are fragmentarily trapped by the growing diamonds. Along with this, the fractional ultrabasic-basic evolution of diamond-parental melts is run. The chemically contrasting evolution has been made possible due to the peritectic reaction of bridgmanite $(Mg,Fe)SiO_3$ and melt with formation of the association of periclase-wustite solid solution phases (MgO·FeO)ss and stishovite SiO_2 (the mechanism of "stishovite paradox"). During the evolution, a sequential paragenetic transition from ultrabasic ferropericlase-bridgmanite-bearing assemblages to basic magnesiowustite-stishovite-bearing ones takes place. Based on experimental and mineralogical data, the mantle-carbonatite conception of lower-mantle diamonds origin and genetic classification of mineral inclusions in them are worked out.

O 15.7

Phase transitions in Group-I and -II hydroxides under pressure: predictions and confirmations

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Alkali and alkaline earth hydroxides are intriguing compounds stabilised by a combination of ionic, covalent, and hydrogen bonding. The nature of the hydrogen bond networks, formed by hydroxyl groups in all cases, and their response to external pressure, has been the subject of numerous studies, as they influence mechanical strength, elasticity, and internal ionic diffusion. Group-II hydroxides are relevant as water-carrying phases in Earth's mantle.

We have performed first-principles calculations and neutron powder diffraction experiments on several group-I and group-II hydroxides under pressure. Calculations used particle swarm and evolutionary algorithms to predict structural candidates, experiments used the Paris-Edinburgh cell.

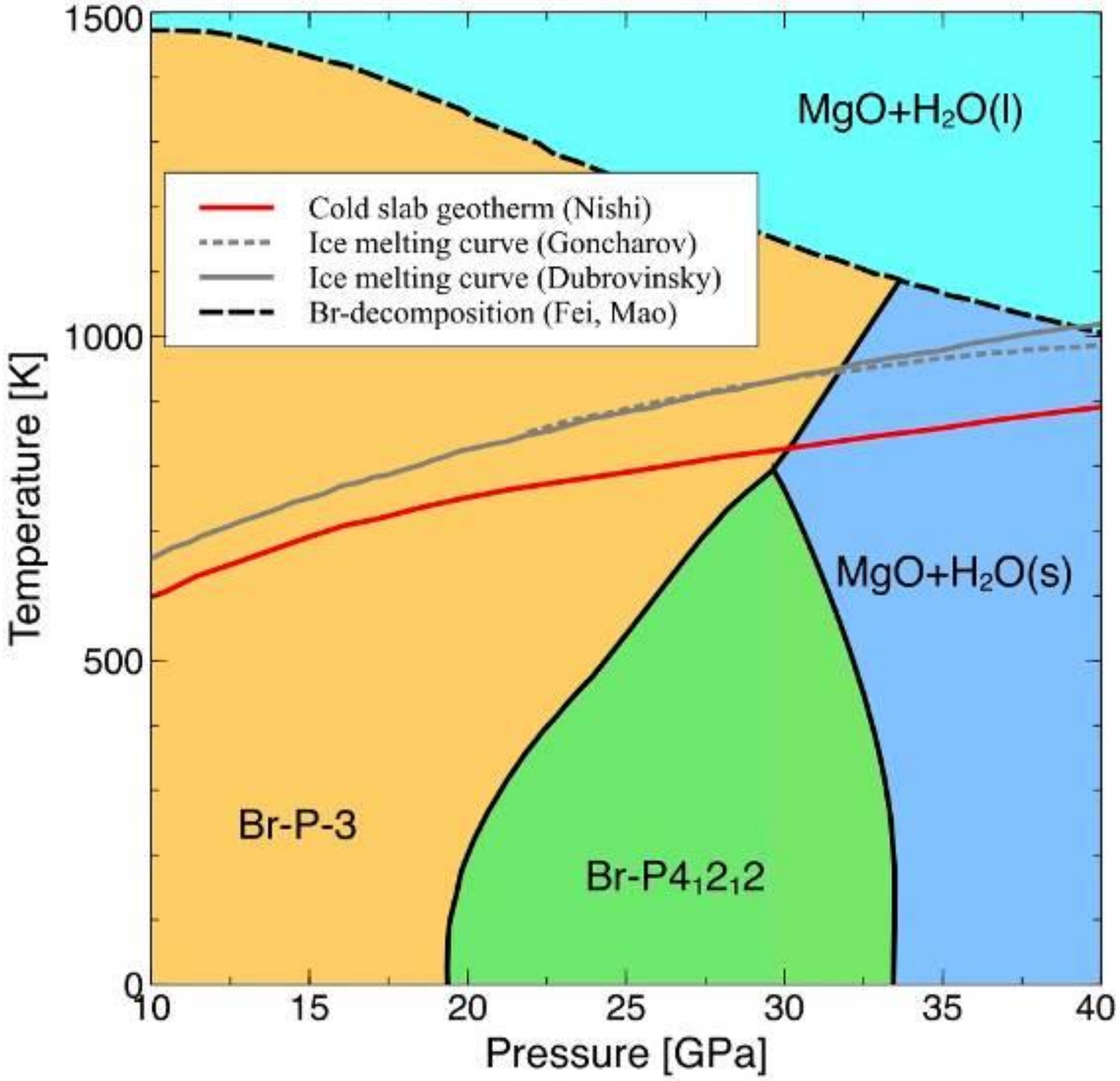
For various alkali hydroxides, we suggest a re-interpretation of previously assigned high-pressure phases. LiOH-III, stable above 0.7GPa, is found to be tetragonal with linear hydroxyl chains, and a new high-pressure phase, LiOH-V is predicted to be stable above 17GPa. KOH-VI and RbOH-VI, stable above 7GPa, feature localised $(OH)_4$ units. And we predict that CsOH-VII is a prediction for an isosymmetric phase transition around 10GPa.

For geologically relevant magnesium hydroxide $Mg(OH)_2$, brucite, we find computational evidence for a new high-pressure phase relevant at lower mantle conditions, P=20-40GPa and $T \leq 800K$, which marks the transition from layered to three-dimensional network structures. We also studied the high-pressure phase evolution of portlandite, $Ca(OH)_2$, in search for similar phase transitions.

A fruitful interaction of experiment and computation allowed us to re-draw the high-pressure phase diagrams of group-I and -II hydroxides. A much larger variability in the hydrogen-bond networks is found than previously thought, with far-reaching consequences: we show that brucite can be stable at much lower depths than previously thought, and could thus play a role in water storage and transport in cold subduction slabs in the mantle.

Figure 1. Phase diagram of brucite obtained from DFT calculations (except for high-T decomposition curve), including the stability field of predicted tetragonal brucite.

Figure 1


1500
1000
500
0
Temperature [K]
10
15
20
25
30
35
40
Pressure [GPa]
MgO+H$_2$O(l)
Cold slab geotherm (Nishi)
Ice melting curve (Goncharov)
Ice melting curve (Dubrovinsky)
Br-decomposition (Fei, Mao)
MgO+H$_2$O(s)
Br-P-3
Br-P4$_1$2$_1$2

O 15.8

Synthesis of high-pressure $MgSi(OH)_6$ hydroxide perovskite via decomposition of '10Å phase'

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Introduction

An enigmatic '3.65Å phase' observed among high-pressure / moderate temperature run products in MgO-SiO_2-H_2O system was only recently identified as $MgSi(OH)_6$ with hydroxide perovskite structure (Wunder *et al.* 2011). The $MgSi(OH)_6$ hydroxide perovskite is the most hydrous high-pressure silicate known; it also can play a role of water reservoir in the coldest parts of subducting slabs.

Objectives

Earlier Wunder *et al.* (2011) noted the sluggish kinetics of $MgSi(OH)_6$ growth: only a minor amount of starting oxides transformed into hydroxide perovskite even after 114 hours at 10 GPa / 400°C; in the case of gel at least 77 hours was needed for the transformation. The run products was studied by Wunder *et al.* (2011) at ambient conditions. We tried to synthesize $MgSi(OH)_6$ hydroxide perovskite in a diamond-anvil cell for *in situ* measurements using fast reaction of '10Å phase' ($Mg_3Si_4O_{10}(OH)_2{\cdot}H_2O$) with water.

Materials & Methods

We used a Bassett diamond anvil cell (DAC) with resistive heating for generation of high-pressure / high-temperature conditions and *in situ* synchrotron X-ray diffraction on the BL10XU beamline of the SPring8 lightsource for sample monitoring. We used natural talc ($Mg_3Si_4O_{10}(OH)_2$) and distilled water as initial reagents to synthesize first the '10Å phase', then pressure were increased to enter the stability field of hydroxide perovskite (Fig. 1).

Figure 1. Crystal structure of $MgSi(OH)_6$ hydroxide perovskite (inset) and its constrained stability field (highlighted). En - enstatite; Coe - coesite; St - stishovite.

Results

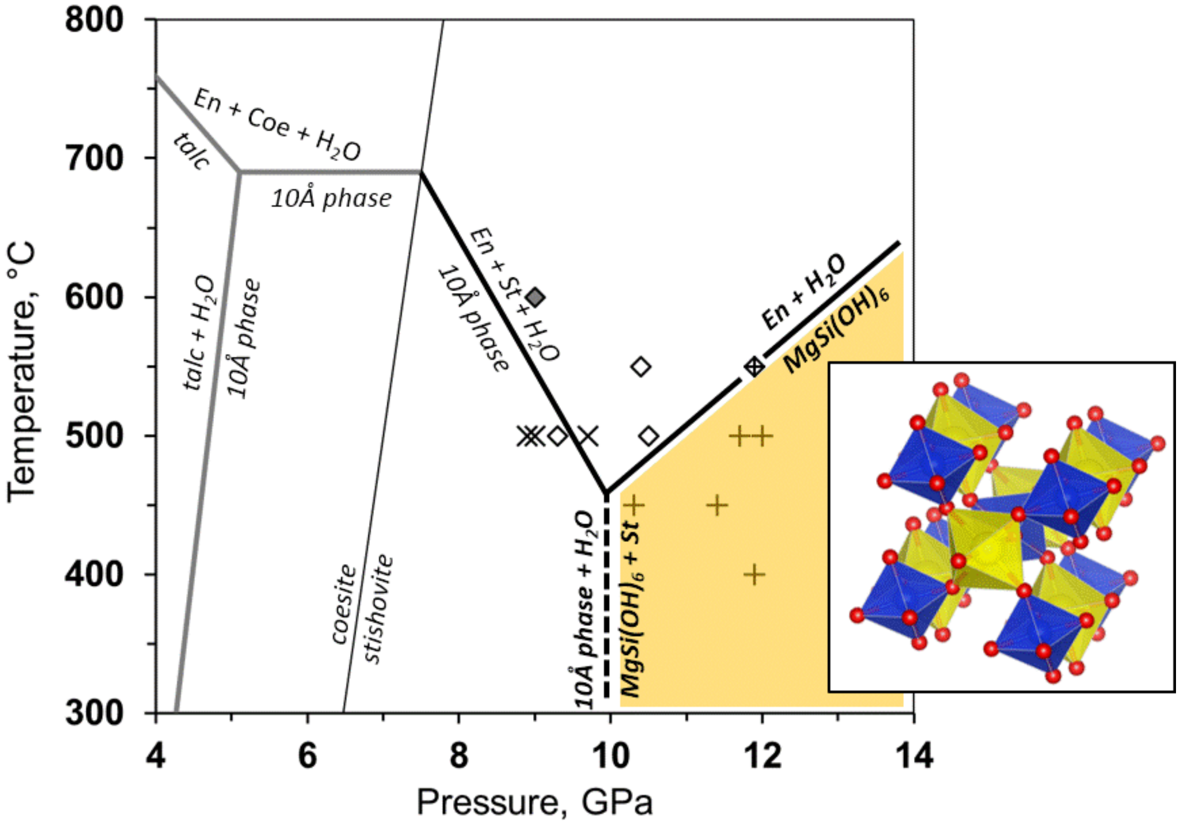
The reaction '$Mg_3Si_4O_{10}(OH)_2{\cdot}H_2O + 8H_2O \rightarrow 3MgSi(OH)_6 + SiO_2$' observed near 10 GPa at 400-500°C was characterized by very fast kinetics: a complete transformation took place in a half an hour, which is hardly comparable with 77- and 114-hours runs of Wunder *et al.* (2011). The obtained diffraction data allowed for the first time measure the unit cell of $MgSi(OH)_6$ at simultaneous high-pressure and high-temperature conditions, and also constrain the position of nonvariant point near 10 GPa and 450°C (Fig. 1).

This work was supported by the Russian Ministry of Education and Science (grant #14.B25.31.0032), and the Russian Scientific Fund (grant #14-13-00834).

References

Wunder *et al.* (2011). American Mineralogist 96, 1207-1214.

Figure 1



800
700
600
500
400
300
Temperature, °C
4
6
8
10
12
14
Pressure, GPa
En + Coe + H_2O
talc
10Å phase
talc + H_2O
10Å phase
coesite
stishovite
En + St + H_2O
10Å phase
En + H_2O
$MgSi(OH)_6$
10Å phase + H_2O
$MgSi(OH)_6$ + St

O 15.9

Nanoconfined water in porous zeolites under extreme conditions

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The intrusion and extrusion of water and its properties in porous solids, such as zeolites, are very important as it modifies the properties of its host material, possibly leading to new technological applications. In the case of water insertion in microporous zeolites, super-hydration effects and hindering of pore collapse are observed, with a consequent major change in the mechanical properties of the system, which indicate that zeolitic water plays a relevant role in the overall response of the zeolite framework to pressure. Concerning the water's properties, super-diffusion effects have been predicted for water nanoconfined in unidimensional pores under high-pressure (HP). Oppositely, some studies have shown that water confined in hydrophobic nanopores crystallizes for temperatures below the bulk freezing point or at HP. Here we present the effect of low temperatures (LT) and HP in water nanconfined at $AlPO_4\text{-}54{\bullet}xH_2O$ zeolite. $AlPO_4\text{-}54{\bullet}xH_2O$ (hexagonal VFI structure, space group $P6_3$, a=18.9678(13) Å and c=8.0997(4) Å, $Al_{18}P_{18}O_{72}{\bullet}47H_2O$) exhibits 1-D pores along the **c** direction, which are among *the largest pores known for zeolites and aluminophosphates*, with a diameter of 12.7 Å, in which H_2O molecules form a disordered hydrogen-bonded network at ambient temperature, is an ideal system to probe nanoconfined water under extreme conditions. From single-crystal X rays diffraction (XRD) and Molecular Dynamics simulations (MD) studies in $AlPO_4\text{-}54{\bullet}xH_2O$ at LT it was observed that while the pore surface induces orientational order of water in contact with it, water inside the pore does not crystallize at T down to 173 K. Both the experimental and simulated data show that water ordering (ice-like orientational order) and site occupancies are more marked as T decreases, especially for molecules in the vicinity of the pore surface. Oppositely, when HP is applied in $AlPO_4\text{-}54{\bullet}xH_2O$ at ambient T, synchrotron single-crystal XRD and MD results shows that water in the pore is highly disordered and, with increasing pressure, suggests that is too mobile exhibiting a high-density liquid-like structure. New results have been recently obtained on water dynamics in $AlPO_4\text{-}54{\bullet}xH_2O$ zeolite nanopores by IINS, QENS, Far- and Mid-IR spectroscopy, at both LT and HP, elucidating water diffusive and vibrational behaviour at the nanoscale.

O 15.10

Solid product of hydrocarbon formation from inorganic minerals

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Deep abiogenic formation of hydrocarbons may be a significant part of the Earth's global carbon cycle. It was experimentally confirmed that a complex hydrocarbon mixture with the composition of natural gas forms from inorganic carbon and hydrogen containing minerals at pressures and temperatures corresponding to the Earth's deep layers (Kucherov et al. 2010). Composition of the gas hydrocarbon product from these experiments is well studied (Chen et al. 2008; Kucherov et al. 2010; Scott et al. 2004). The yield of gaseous hydrocarbons usually did not exceed 5% and no carbon solid or liquid compounds were observed.

This work was aimed to discover unknown details of the solid product composition of hydrocarbons formation reaction under pressure and temperature conditions similar to the Earth's deep layers-P = 6 GPa and T = 1200K.

The large reactive volume high pressure apparatus with "Toroid" type chamber was used to perform the experiments. X-ray powder diffraction, Raman spectroscopy and IR spectroscopy were employed for the analysis of the solid phase. Hydrocarbons with the composition similar to natural gas was observed before the solid product analysis by means of gas chromatography.

Investigation showed that the solid products of the reaction are $CaCO_3$ (remained, aragonite), FeO (remained), Fe_3O_4 and C (graphite). No heavy hydrocarbons were observed. No $Ca(OH)_2$ or CaO were observed. These results suggest that the carbon product could be formed as amorphous soot, like in the work [1], or as crystalline graphite like in our work, which made it possible to be detected by X-ray diffraction. The detection of the graphite allows to complete the carbon balance of the process. The knowledge about composition of the solid product of the reaction will help to fully understand the process of deep hydrocarbon generation, including thermodynamic and kinetic aspects.

O 15.11

Phase diagram of hydrides of ron at pressures up to 200 GPa

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Iron hydride system is currently actively pursued topic (1,2,3) related to an old problem of hydrogen presence in the Earth's core (4). Recent theoretical predictions of stable phases of higher hydrides (polyhydrides) of iron above 100 GPa (1) pose new constraints related to their stability at the conditions of the Earth core. We performed synthesis of iron hydrides at high P-T conditions to clarify the remaining questions related to the phase diagram of the most stable FeH (2,5,6), FeH_2, and FeH_3 (3) phases. We searched also for new phases in laser-heating experiments (see Ref. 7 for the description of experimental methods) up to 200 GPa. We will report the equations of state of fcc FeH, FeH_2, and FeH_3, and preliminary results on higher polyhydride phases of iron. Our use of pure hydrogen-iron chemistry favors creation of iron polyhidrides and provides insights into new chemical scenarios that pose constraints on the hydrogen content in the Earth's core and may be relevant for the chemistry of iron in giant planets or super-Earth exoplanet interiors.

[1] Z. G. Bazhanova et. al., *Physics-Uspekhi* **55**, p.489 (2012)

[2] O. Narygina et. al., *Earth and Planetary Sci. Lett.* **307**, p.409 (2011)

[3] C. M. Pepin, *Phys. Rev. Lett.* **113**, 265504 (2014).

[4] D. J. Stevenson, *Nature* **268**, p.130 (1977).

[5] N. Hirao et. al., *Geoph. Res. Lett.* **31**, p.L06616 (2004).

[6] V. E. Antonov et. al., *J. Phys. Condens. Matter* **14**, p.6427 (2002)

[7] V. V. Struzhkin et. al., arxiv.1412.1542

O 15.12

Ultrahigh-pressure synthesis and characterization of transparent nano-polycrystalline silicate garnet

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Transparent oxide ceramics have been mostly synthesized at relatively low pressures below 1 GPa, using Hot Isostatic Pressing (HIP) and Sparkling Plasma Sintering (SPS) techniques. However, synthesis of highly transparent ceramics with nano-crystals (<100 nanometers) has been difficult using these conventional sintering techniques, although it is predicted that the optical transparency and mechanical strength of such ceramics are significantly enhanced if transparent ceramics composed of nano-crystals without residual pores are available. We used Kawai-type multianvil apparatus and bulk glass starting material, and succeeded in synthesis of pore-free nano-polycrystalline grossular ($Ca_3Al_2Si_3O_{12}$) garnet in a limited temperature range around 1400ºC at pressures greater than 10 GPa for 2 hours under very dry conditions. In contrast, significant crystal growth to the micrometer range was observed with decreasing pressure to 5 GPa and at relatively low temperature of 1200ºC rather independent on pressure, where nucleation rates of garnet from glass starting material should be low. Thus synthesized nano-polycrystalline grossular has transmittance of light almost equivalent to that of the corresponding single crystal (~88%) in the visible light region. Moreover, its Knoop hardness becomes higher with decreasing grain size by ~30%, particularly for the grain sizes less than 200 nm, showing that the Hall-Petch effect is valid in the nano-crystalline regime. We also succeeded in making highly transparent nano-polycrystalline garnet samples having compositions between grossular and uvarovite ($Ca_3Cr_2Si_3O_{12}$) and those between pyrope ($Mg_3Al_2Si_3O_{12}$) and knorringite ($Mg_3Cr_2Si_3O_{12}$) at the similar P,T conditions, suggesting that the present ultrahigh-pressure conversion method is important in synthesizing novel transparent nano-polycrystalline ceramics. Transparent nano-crystalline samples of high-pressure minerals should also be important for the measurements of sound velocities by Brillouin scattering method and GHz ultrasonic interferometry.

O 15.13

Phase relations in the system $MgSiO_3$-Al_2O_3 in the lower mantle

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Introduction

Aluminum behavior in bridgmanite can be investigated by the phase relations in the system $MgSiO_3$-Al_2O_3 at high pressure and high temperature, which is a simplified model most relevant to the chemical composition of the lower mantle (Irifune et al., 1996). However, phase relations in the system is not well constrained at pressure higher than 27 GPa and various temperature. Thus we will determine phase relations in the system $MgSiO_3$-Al_2O_3 in the lower mantle conditions using the sintered diamond anvils in the multi-anvil appratus.

Objectives

We will clarify the pressure and temperature effect on the aluminum solubilities in bridgmanite in the lower mantle conditions, and further constrain the physical and chemical properties of bridgmanite such as the cation substitution mechanism and crystal structure.

Materials&Methods

The starting materials: $En_{50}Cor_{50}$ nanosized-oxide mixing and pyrope glass

Methods: high pressure and high temperature generation in the multi-anvil apparatus, X-ray diffraction, Raman spectroscopy and electron microprobe

Results

A wide two-phase region of garnet and corundum is found to exist up to 27 GPa, while a phase assemblage of aluminous bridgmanite and corundum is stabilized at higher pressures.

The Al_2O_3 solubility in bridgmanite and the $MgSiO_3$ solubility in corundum are highly dependent on pressure and temperature, and the Al_2O_3 content in bridgmanite increases with increasing pressure and temperature. The pyropic bridgmanite is formed at about 45 GPa, which is significantly higher than the result of the earlier study (~ 37 GPa) on the pyrope composition. The alumina content in bridgmanite increase from 9 mol% at 1700 K to 12 mol% at 2000 K at pressure of 27 GPa.

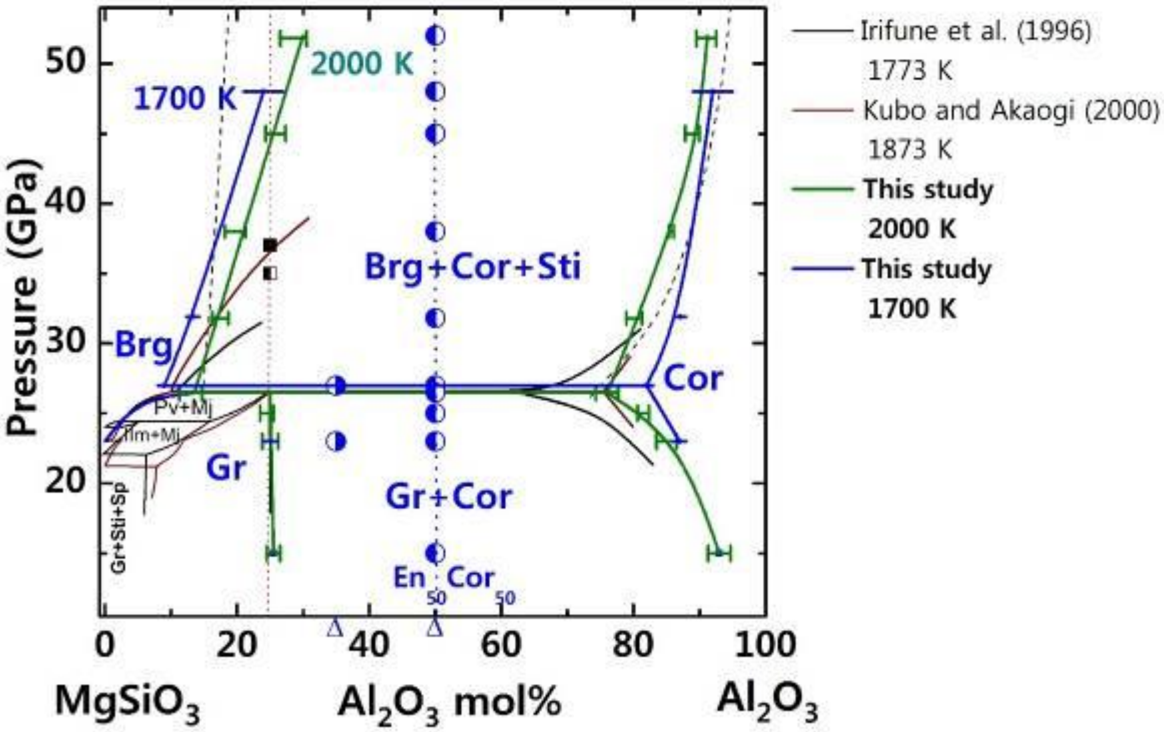
Conclusion

Phase relations in the system $MgSiO_3$-Al_2O_3 have been determined at 15-52 GPa and at temperature of 1700 and 2300 K in a multi-anvil apparatus combined with hard tungsten carbide anvils and sintered diamond anvils.

The present results suggest the Al_2O_3 content in bridgmanite and the $MgSiO_3$ content in corundum are good pressure indicators in the mixed phase region at pressures higher than 27 GPa at various high temperatures, where virtually no pressure references are available for the quench experiments.

The new phase diagram in the system $MgSiO_3$-Al_2O_3 confirms that bridgmanite is the dominant host mineral for Al_2O_3 in the Earth's lower mantle.

Figure 1



Pressure (GPa)
50
40
30
20
1700 K
2000 K
Brg
Brg+Cor+Sti
Pv+Mj
Ilm+Mj
Gr
Gr+Sti+Sp
Gr+Cor
Cor
En_{50} Cor_{50}
0
20
40
60
80
100
$MgSiO_3$
Al_2O_3 mol%
Al_2O_3
Irifune et al. (1996)
1773 K
Kubo and Akaogi (2000)
1873 K
This study
2000 K
This study
1700 K

O 15.14

Combined Ni K-edge x-ray absorption and Raman spectroscopic investigation of nickel hydroxide under high pressure

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In the last decades 3d metal oxides and hydroxides have attracted many interests because of their potential applications. In this context, the β-form of nickel hydroxide, β-Ni(OH)2 remains a very resourceful material [1]. β-$Ni(OH)_2$ crystallizes in the trigonal structure [2]. Ni atoms are sandwiched between two sheets of oxygen atoms forming a NiO_6 octahedron. Each OH bond lies along the three-fold axis perpendicular to these layers. The simplicity of β-$Ni(OH)_2$ makes the system a prototype for stability study of hydrous minerals which are of considerable importance for geophysical and geochemical phenomena [3]. X- ray diffraction [4-7], Raman and Infrared [8,9] have been largely used to determine long range order and dynamics properties.

Here, we present a combined high pressure Ni K-edge x-ray absorption and Raman spectroscopic investigation of β-$Ni(OH)_2$. EXAFS analysis reveal a shrinking of the bond-distances. The corresponding Debye Waller factors showed an abrupt change around 8 GPa, indicating the presence of a local anomaly. Raman data show a continuous hardening of the Ni-O phonon modes, whereas a systematic frequency softening is displayed by the O-H stretching mode. This behavior implies a gradual development of a lattice instability. The results suggest that the hydrogen bond becomes unstable under pressure mainly because of the displacement of H atoms, influencing the electronic properties.

References

[1] J. W. Lee et al., Chem. Commun., 47, 6305-6307 (2011)

[2] A. Szytula et al., Phys. Status Solidi B, 43, 125 (1971)

[3] J.B. Parise et al. Am. Mineral. 79, 193 (1994)

[4] J. L. Bantignies et al. J. Phys. Chem. C, 112, 2193 (2008)

[5] D. S. Hall et al., J. Phys. Chem. A, 116, 6771 (2012)

[6] A M. Scheidegger et al., J. Synchrotron Rad. 8, 916, (2001)

[7] J.-L. Bantignies et al., J. Phys. Chem. C, 112, 2193 (2008)

[8] E. F. De Oliveira et al. Vib. Spectrosc., 31, 19 (2003)

[9] S. Deabate et al., Electrochim. Acta, 51, 5430 (2006)

O 15.15

Pyrolite during and in the aftermath of the giant impact

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We model the physical properties of liquid pyrolite at the pressures and temperatures attained during the giant impact that generated the Earth's moon. We model the speciation and the structure of the liquid. We pay special attention to the determination of the transport properties both atomic diffusion and viscosity. Then we focus on the lower temperatures, characteristic to the magma ocean.

We show that the dynamics of the crystallization of the magma ocean is highly dependent (i) on extrinsic parameters, like pressure at the core-mantle boundary and temperature profile through the magma ocean, and (ii) on intrinsic parameters, like relative density relations between the melt and the crystals and vigor of the stirring. Formation of a solid layer in the middle of the magma ocean is possible, which can lead to the eventual formation of a basal magma ocean.

For our study we employ first-principles molecular-dynamics calculations to determine the density of the magmas. Then we use diamond-anvil cell experiments to trace the chemical evolution of the silicate liquids during cooling and crystallization. We build a grid of pressure and temperature points, following the chemical evolution during the entire fractional crystallization of perovskite. Then we construct a geodynamical model of the evolving magma fully taking into account the density and chemistry of the melts and crystals.

O 15.16

Neutron diffraction experiment on δ-AlOOH and investigation of symmetrization of hydrogen bond

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A few hydrous minerals are known to be stable under lower mantle conditions so far; for example, phase D, phase H and δ-AlOOH. Theoretical studies indicate that all these minerals have a "symmetric hydrogen bond" at high pressure (e.g. Tsuchiya et al., 2002), in which hydrogen locates at the midpoint between two oxygen atoms. The symmetrization has been considered as a potential cause of changes of the compressibility and sound velocities (Sano-Furukawa et al., 2009; Mashino et al., 2016). However, it is unquenchable to ambient conditions thus in-situ experiment is necessary to determine the hydrogen bond geometry. In this study, we have investigated the pressure response of hydrogen bond in distorted rutile type hydrous mineral δ-AlOOH and its deuterated compound δ -AlOOD by neutron diffraction experiment. Neutron powder diffraction experiments with a Paris-Edinburgh press were carried out at the high-pressure neutron diffractometer PLANET in the J-PARC. Deuterated methanol-ethanol mixture was used as a pressure transmitting medium and TiZr encapsulating gasket was used to seal the sample. Diffraction patterns were collected for 4 to 6 hours at the pressures up to 18 GPa. The atomic positions were refined by Rietveld method. We observed the disappearance of 021 reflection at high pressure in δ-AlOOH which indicates the transition from the structure with asymmetric hydrogen bond ($P2_1nm$) to that with disordered or symmetric hydrogen bond (*Pnnm*), in agreement with previous single crystal X-ray diffraction study (Kuribayashi et al., 2014). On the other hand the transition pressure is higher in δ-AlOOD, which was determined to be 12 GPa. The detail about the hydrogen distribution around the transition pressure and its relevance to the change of compressibility and anomalies in sound velocities will be discussed.

O 15.17

Thermal expansion of coesite: A synchrotron X-ray diffraction study from 100 K up to 1000 K

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The dense SiO_2 polymorph coesite has been studied by X-ray powder diffraction at 1 bar in a temperature range from 100 K up to 1000 K. Coesite along with other polymorphs of silica are investigated due to their geophysical importance, as well as for understanding and modelling properties of framework silicates with the polyhedral approach. Coesite is the densest silica polymorph in which silicon is tetrahedrally coordinated by oxygen. In addition, contrary to other low pressure forms of SiO_2, coesite does not undergo α-β transition at least up to 1776 K. It also exhibits anomalous elastic properties and has much smaller thermal expansion than quartz and cristobalite. However, the thermal behavior of coesite was considered just in few works, where either a very limited temperature range was used or due to an insufficient data quality a high-temperature structure of coesite had been simulated by lattice and molecular dynamics.

In this work we have focused on a high-temperature structural features of coesite and its behavior at the microscopic level. Therefore, we performed X-ray powder diffraction study of a synthetic coesite sample using the large Debye-Scherrer camera at BL02B2 beamline (Spring-8). XRD patterns were collected with a high-angular resolution in a temperature range from 100 K up to 1000 K with 50 K step. The high and low temperature N_2 gas flow systems were used.

According to our results, the thermal expansion of coesite is strongly anisotropic. It is almost 6 times greater along the *a* axis than along the *c* axis and 3 times greater than along the *b* axis.

We also observed a slightly negative thermal expansion along the *c* axis. This gives a very low volume expansion by only 0.7% in the considered temperature range. With increasing temperature, coesite tends to enhance the symmetry and becomes more hexagonal. The biggest changes in structure caused by a rotation of the Si2 tetrahedron around the [001] direction and the Si1-O5-Si2 angle rise. This rotation also leads to a significant deformation of the Si1 and Si2 tetrahedrons accompanied by almost opposite changes in the tetrahedrons' volume.

Very low expansion materials are not only interesting from a scientific point of view. For the material research and ceramic industry, the importance of such materials is in their widespread use in high anti-thermal shock applications.

O 15.18

Pressure-induced phase transitions in anilite and digenite

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Cuprous sulfides ($Cu_{2-x}S$; $0 \leq x \leq 0.25$) have been the focus of numerous studies for several decades due to their outstanding physical properties and their geoscientific relevance as one of the most important copper ores on Earth. However, because of the high mobility of copper atoms and vacancies within the sulfur sublattice, their crystal structures and phase relations are complex. Our knowledge of the crystal structures of this compound family as a function of pressure is limited to two recent high pressure studies [1,2] on monoclinic ($P2_1/c$) chalcocite, Cu_2S, reporting two pressure-induced phase transitions up to 25 GPa.

The aim of this study is to increase our knowledge of the influence of pressure on the crystal structures of copper sulfides by determining the crystal structure of anilite, Cu_7S_4, [3] and digenite, $Cu_{2-x}S$, [4] as a function of pressure by means of single crystal and powder X-ray diffraction (XRD).

We synthesized single crystals and powders of anilite and digenite from the elements at elevated temperatures. The samples were characterized by in-house XRD. The evolution of the crystal structure as a function of pressure was investigated by *in situ* XRD in diamond anvil cells using synchrotron radiation at the PETRA III beamline P02.2 [5].

Powder diffraction shows that anilite undergoes three pressure-induced phase transitions up to 11 GPa (Fig. 1). The first structural phase transition takes place below 1.1(2) GPa. At this pressure, orthorhombic anilite transforms into digenite. Single crystal data confirm the anilite-digenite transition and suggest an orthorhombic and monoclinic symmetry for the two other high pressure phases. Upon further compression up to 26 GPa another structural phase transition takes place leading to a high pressure phase which is stable up to ~ 75 GPa (Fig. 2).

The authors gratefully acknowledge financial support by the DFG (Wi 1232 & BA 4020 /2-1) and the BMBF (05K13RF1).

Figure 1: PXRD patterns of anilite on increasing pressure (25 keV).

Figure 2: PXRD patterns of digenite on increasing pressure (43 keV)

[1] S. Wang *et al.* (2002). *Mater. Chem. Phys.* **75**, 32.

[2] D. Santamaría-Pérez *et al.* (2014). *J. Alloys Compd.* **610**, 645.

[3] K. Koto, N. Morimoto (1970). *Acta Cryst.* **B26**, 915.

[4] G. Donnay *et al.* (1958). *Am. Mineral.* **43**, 228

[5] H.-P. Liermann *et al.* (2015). *J. Synchrotron Radiat.* **22**, 908.

Figure 1

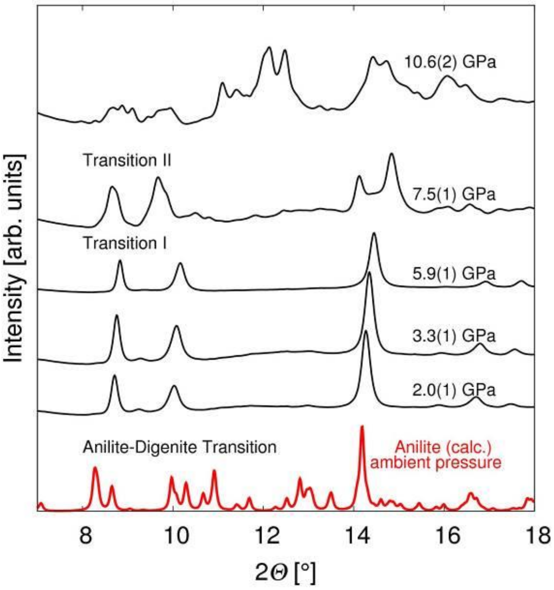
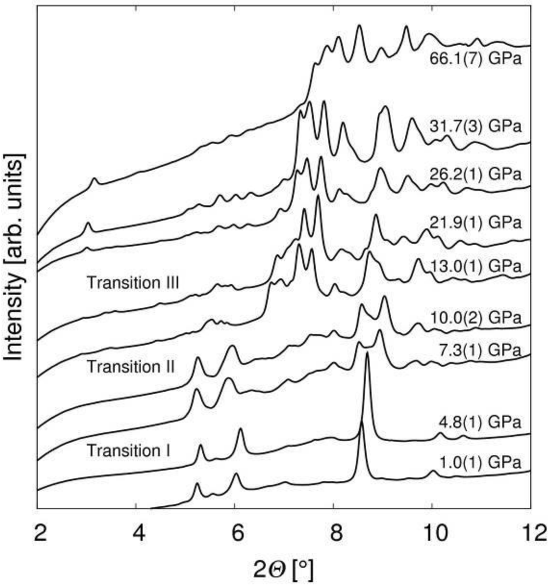


Figure 2



P 15.1

X-ray diffraction study of FeOOH under high pressures and high temperatures

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Water (hydrogen) plays important roles in dynamics in the Earth's interior. It is expected that hydrogen is transported from the surface to the interior by the subducting slab. Hydrogen is also a candidate of the light element of outer core. Therefore, the study of the hydrogen in the Earth's interior is quite important. We carried out X-ray diffraction study and X-ray absorption measurement in the Photon Factory, Tsukuba, Japan. Goethite (alpha-FeOOH) is stable at ambient condition. However, we showed that the alpha phase transformed to the epsilon phase at 7.8+-0.5 GPa and 873K. Our previous study showed that epsilon-FeOOH was stable under the condition of the lower mantle. We suggest that epsilon-FeOOH can transport hydrogen to the core-mantle boundary and supply hydrogen to the outer core.

P 15.2

Deformation behaviour of ferropericlase (Mg,Fe)O in a graphite heated diamond anvil cell under lower mantle conditions

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Earth's lower mantle is the largest geochemical reservoir for many elements and is dominated by the phases bridgmanite (silicate-perovskite) and ferropericlase ((Mg,Fe)O). Although bridgmanite has a larger share in terms of volume, the rheology of the lower mantle of the Earth might be dominated by ferropericlase, because it is plastically the weakest phase[1]. For this reason (Mg,Fe)O can play a key role for global dynamics. It has, for instance, been suggested that a rheology change in ferropericlase causes slabs to stagnate in the uppermost lower mantle as indicated by seismic tomography results[2,3] Furthermore, the shear wave anisotropy observed in the lowermost mantle might be caused by lattice preferred orientation of ferropericlase[4,5], but our understanding of the slip system activities of (Mg,Fe)O at condition of the lowermost mantle is incomplete. In-situ measurements on powders of $(Mg_{0.2},Fe_{0.8})O$ in a graphite heated DAC using angle dispersive synchrotron x-ray diffraction (XRD) in a radial geometry provide the possibilities of deformation experiments at simultaneously high pressure and temperature. In our previous experiments, texture development and stress measurements were made up to a pressure of 75 GPa at a temperature of 1200 K. Details of the experimental setup will be shown and results will be discussed with regard to the state and dynamics of Earth's lower mantle.

[1] Girard, J., Amulule, G., Farla, R., Mohiuddin, A. & Karato, S. *Science* **351,** 144-147 (2016).

[2] Fukao, Y. & Obayashi, M. *J. Geophys. Res. Solid Earth* **118,** 5920-5938 (2013).

[3] Marquardt, H. & Miyagi, L. *Nat. Geosci.* **8,** 311-314 (2015).

[4] Yamazaki, D. *Phys. Earth Planet. Inter.* **131,** 251-267 (2002).

[5] Marquardt, H. *et al. Science* **324,** 224-226 (2009).

P 15.3

Mechanical and dynamical stability of As_4O_6 and As_4O_6:2He at high pressures

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Arsenic oxide (As_2O_3) belongs to the sesquioxide family of group-15 elements, which also includes P_2O_3, Sb_2O_3, and Bi_2O_3. In particular, As_2O_3 crystallizes either in a cubic structure [space group (SG) 227, Fd-3m, Z=16] (which gives the name to the mineral arsenolite)[1] or in monoclinic structures [SG 14, $P2_1/c$, Z=4] (which are known as minerals claudetite I and claudetite II).[2-4] Arsenolite is one of the few polymorphs of group-15 sesquioxides that constitute a molecular solid, in this case with molecular cages of As_4O_6 stoichiometry. Here, we present a theoretical study of the elastic constants and phonon dispersion curves at different pressures of arsenolite (As_4O_6) and As_4O_6:2He, which is a recently discovered compound formed by He trapping at 16d sites in arsenolite at pressures above 3 GPa.[5,6] Experimental x-ray diffraction and Raman scattering measurements under pressure showed a pressure-induced amorphization above 15 GPa for pure arsenolite but not in the case of As_4O_6:2He.[5] We will evaluate this result in the framework of the mechanical and dynamical stability of both compounds at high pressures.

References

[1] F. Pertlik, *Czech. J. Phys. B* **28**, 170 (1978).

[2] A.J. Frueh, *Am. Mineralogist* **36**, 833 (1951).

[3] W.B. White, F. Dachille, R. Roy, Z. Kristall. **125**, 450 (1967).

[4] F. Pertlik, *Monatsh. Chem.* **109**, 277 (1978).

[5] J.A. Sans, F.J. Manjón, C. Popescu, V.P. Cuenca-Gotor, O. Gomis, A. Muñoz, P. Rodríguez-Hernández, J. Contreras-García, J. Pellicer-Porres, A.L.J. Pereira, D. Santamaría-Pérez, and A. Segura, Phys. Rev. B **93**, 054102 (2016).

[6] P. A. Gunka, K.F. Dziubek, A. Gladysiak, M. Dranka, J. Piechota, M. Hanfland, A. Katrusiak, and J. Zachara, Cryst. Growth Des. 15, 3740 (2015).

P 15.4

Quantum effects in diamond isotopes at high pressures

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An influence of quantum effects on the equation of states and phase transitions in compressed matter is of primary interest in the physics of giant planets and in astrophysics. The isotope effects manifest themselves rather clearly in diamond because of its small atomic mass as well as extremely high Debye temperature (2200 K). Among numerous studies of diamond there are examples of both enhancement and attenuation of quantum effects under pressure. Nevertheless, the question on a role of quantum effects in diamond under pressure remains open.

The present research is aimed at a significant extension of the pressure range and an increase in the measurement precision in hydrostatic conditions at clarifying the behavior of quantum effects in diamond isotopes under pressure.

We report accurate measurements of Raman scattering for diamonds ^{12}C, ^{13}C, and $^{12.5}C$ over the extended pressure range up to 75 GPa at room temperature and of isotopically pure ^{12}C and ^{13}C samples at pressures up to 17 GPa at 80 K. High pressure was generated by a original diamond anvil cell with helium as the best pressure-transmitting medium.

It was found that the ratio of Raman frequencies of ^{12}C and ^{13}C diamonds, which differs from the classical value (1.0408), change up to 60 GPa slightly, but nonmonotonically. Examination of the isotopically mixed $^{12.5}C$ diamond shows that the effective mass determining the Raman frequency varies under compression from 12.38 a.u. at ambient pressure to 12.33 a.u. at pressure of 73 GPa.

We can conclude that the precision measurements of the Raman spectra in different diamond isotopes under hydrostatic conditions in the record pressure range revealed inversion of the pressure dependence of quantum isotope effects under compression. Diamond seemingly behaves like a Coulomb system at moderate pressures, however, measurements over higher pressures show different features, which can be tentatively connected with the repulsive non-Coulomb part of the interaction. The data of the present study were obtained in an extended pressure range with the use of the hydrostatic medium and can be also employed for high-pressure measurements as pressure sensors in the construction for high-pressure scale.

P 15.5

Interaction of carbonate melts and lower-mantle materials: role in diamond genesis

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Carbonate minerals among the lower-mantle diamond-hosted primary inclusions are indicative for a Mg-Fe-Ca-Na-carbonate constituent of the lower-mantle diamond-producing silicate-oxide-carbonate-carbon system. High-pressure high-temperature experiments on the multicomponent $MgCO_3$-$FeCO_3$-$CaCO_3$-Na_2CO_3 carbonate system demonstrate its eutectic melting and complete liquid miscibility under the transition zone and lower mantle conditions. It is of significant importance that *PT*-conditions of partial melting of the carbonate system are noticeably lower in comparison with the geothermal ones. Such a positive superposition of geothermal and melting conditions for the multicomponent carbonate system may be a determining factor for origin and operation of the diamond-parental silicate-oxide-carbonate-carbon melts at the deeper mantle horizons. The diamond-parental melts make possible the processes of nucleation and mass crystallization of the deeper-mantle diamonds and a joint formation together with diamonds of minerals trapped by them as primary inclusions. Therewith, melting phase relations of the diamond-parental silicate-oxide-carbonate (MgO-FeO-CaO-SiO_2)-Carb* system (where Carb* corresponds to the $MgCO_3$-$FeCO_3$-$CaCO_3$-Na_2CO_3 system) are studied in physico-chemical experiments at 24-26 GPa. A peritectic reaction of bridgmanite $(Mg,Fe)SiO_3$ with carbonate-bearing melt L resulting in the paradoxical assemblage of periclase-wustite solid solution phases $(MgO{\cdot}FeO)_{ss}$ and stishovite SiO_2 has been revealed. The reaction is of primary importance for formation of the quasi-invariant multiphase peritectic point L+$(Mg,Fe)SiO_3$+$(MgO\ {\cdot}FeO)_{ss}$+SiO_2+$CaSiO_3$+Carb*, where Ca-perovskite $CaSiO_3$ and Carb* components are involved into the melt and form their own phases without any additional reactions. The peritectic reaction has made it possible the process of ultrabasic-basic evolution of the diamond-parental melts and sequential going in the series formation from ultrabasic bridgmanite-ferropericlase-bearing assemblages to basic stishovite-magnesiowustite-bearing ones.

P 15.6

Experimental evidence for ultrabasic-basic evolution of upper-mantile magma: role of olivine garnetization

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The upper-mantle eclogite rocks including their diamond-bearing varieties are presented among the mantle xenoliths in kimberlites. The problem of their origin is debatable for years. The upper-mantle *in situ* version has perceived as unlikely for reasons of the “eclogitic thermal barrier”, that is a temperature maximum for the univariant cotectic curve between the ultrabasic olivine-saturated and basic silica-saturated compositions. Also, it was unknown a natural reaction capable to remove olivine at ultrabasic-basic magma evolution. Reaction of forsterite garnetization have been experimentally revealed in experiments at pressures higher 4.5 GPa (Gasparik, Litvin, 1997). It turned out that forsterite can react with jadeite to form pyrope, enstatite and a low-melting Na-Mg-silicate. The result initiates physico-chemical experimental investigation at 7 GPa of melting relations of the quasi-ternary multicomponent olivine $(Mg,Fe)_2SiO_4$ - clynopyroxene $(Ca,Fe)MgSi_2O_6$ - jadeite $NaAlSi_2O_6$ system with the use of the methodology of polythermal sections. The main result lies in the establishment of qusi-invariant point Ol+Grt+Cpx+L at the liquidus surface combining the primary crystallization fields Ol+L, Grt+L, Cpx+L and univariant cotectics Ol+Grt+L, Ol+Cpx+L, Grt+Cpx+L. In these physico-chemical conditions the clynopyroxene solid solution phases are compositionally variable in respect to diopside/jadeite ratio. As a result, the consecutive conversion of Ol-bearing ultrabasic assemblage with Jd-poor Cpx into the Ol-free basic assemblage with Jd-rich omphacitic clinopyroxene Omph takes place. The experimental physico-chemical mechanism of olivine garnetization can be used for explanation of the ultrabasic-basic evolution of primary ultrabasic magma, generated on melting of the upper-mantle garnet peridotite, with the resulting formation *in situ* of basic eclogitic rocks. The upper-mantle ultrabasic-basic magmatic evolution must be accompanied by the formation of peridotite-eclogite rocks series that can be realized exclusively within the regime of fractional crystallization.

P 15.7

Metallization of Silica Analogs: high pressure behavior of $PbCl_2$ and $SnCl_2$

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In this study, we show using high-pressure x-ray diffraction and infrared absorption spectroscopy, along with first-principles calculationsthat $PbCl_2$ and $SnCl_2$ compounds which are structural analogs of silica become more conducting with increasing pressure, in support of the conclusion that silicates become metallic at conditions relevant to large exo-planet interiors and meteorite impacts.

Silica belongs to a large group of materials classified as AX_2 compounds, which are widely believed to follow a structural sequence with increasing pressure, which includes the cottunite structure at relatively high pressure. This qualifies materials with this structure at ambient conditions useful as high-pressure analogs of silica. We study $PbCl_2$ and $SnCl_2$ under pressure, which crystalize in the cotunnite (*Pnam*) structure and observe their transformation to the orthorhombic (*Pnma*) structure, challenging previous structural measurements of Leger et al. (PRB, 51, 3902 (1995)) on these materials. We also document the closure of the bandgap to <1-2 eV of these materials and predict they become fully metallic at 80-100 GPa. This suggests that materials in the AX_2 structural sequence may become metallic in the orthorhombic, cotttunite structure (*pnma*) structure at extreme conditions (~750 GPa for silica). A metallic state of silica would have serious implications for the dynamics and magnetic field generation of such planets, as well as chemical bonding in early planet formation.

P 15.8

Bulk modulus of Fe-rich olivines

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Olivine, a solid-solution between end-members forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) is one of the most abundant minerals in the mantles of terrestrial planets. A good knowledge of its physical properties, in particular thermo-elastic parameters, is thus essential to understand and model planetary interiors. Because the accepted average composition of Earth's mantle olivines is around $[Fe_{0.1},Mg_{0.9}]_2SiO_4$, Mg-rich olivines have been extensively studied. In comparison Fe-rich olivines have received little attention. The goal of this study is to measure equations of state of olivines with compositions ranging from $[Fe_{0.4},Mg_{0.6}]_2SiO_4$ to Fe_2SiO_4 in order to to better constrain the effect of Fe content on elastic properties of olivines. We will present here our results obtained on compositions $[Fe_{0.9},Mg_{0.1}]_2SiO_4$ (Fa80) and Fe_2SiO_4 (Fa100).

Our fayalite samples have been synthesized from nano-size powders of elementary oxides mixed with the proper stoichiometries and reacted at room pressure and 1000°C under controlled atmosphere (~ Fe/FeO buffer). The fully reacted powders were then sintered using Spark Plasma Sintering in order to minimize the porosity of our samples. The resulting olivine aggregates have fairly homogeneous grain sizes from ~300 nm to ~2 µm depending on their Fe content. High-pressure high-temperature experiments coupled with synchrotron X-ray diffraction and X-radiographic imaging were conducted using the DIA apparatus at the X17B2 beamline at NSLS (Brookhaven, N.Y., U.S.A). We also performed ultrasonic interferometry measurements in order to obtain P- and S-wave travel times using the DIASCoPE setup at X17B2. The sample density was determined in situ using X-ray diffraction, the sample length was measured under extreme conditions using the X-radiographic image, and the acoustic travel times were measured using the ultrasonic interferometer. The travel times combined with sample lengths yield the P and S wave velocities in the sample, and these data combined with the density gives a direct measurement of the elastic bulk and shear moduli under all conditions of the experiment.

Our presentation will focus on results obtained at room temperature on Fa80 and Fa100 samples. The bulk modulus and its pressure derivative for each composition were calculated by two methods: 1. the traditional way, using NaCl as pressure gauge, 2. using the ultrasonic acoustic velocity measurements. This will allow to compare different methods but most importantly to discuss the effect of deviatoric stress on our results.

P 15.9

Is electrical resistivity constant on the pressure-dependent melting boundary?

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Introduction

The Earth's core cools by heat transport to the top of the core and removal of heat from the core-mantle boundary. Understanding core heat transport requires knowledge of the thermal and electrical conductivity of solid and liquid Fe and its relevant alloys. It has been proposed that electrical resistivity of a pure metal is constant along its P-dependent melting boundary (Stacey and Anderson, PEPI, 2001). If confirmed, this invariant behavior could serve as a practical tool for low P studies to assess electrical resistivity of Earth's core, a property that has major implications for the geodynamo and thermal evolution of the core via related thermal conductivity. Since Earth's inner core boundary (ICB) is a melting boundary of mainly Fe, measurements of electrical resistivity of Fe at the melting boundary, under any P, would serve as a proxy for the resistivity at the ICB. A revised treatment (Stacey and Loper, PEPI, 2007) accounted for s-d scattering in transition metals with partially filled d-bands and limited the proposal to metals with electrons of the same type in filled d-band metals.

Objectives

To test this proposal, we made high P,T measurements of electrical resistivity of d-band filled (Cu, Ag) and partially filled (Ni) transition metals in solid and liquid states.

Materials and Methods

Experiments were carried out in 1000 ton cubic anvil and 3000 ton multi-anvil presses up to 5 GPa and 1973K. Two thermocouples placed at opposite ends of the wire sample served as T probes as well as 4-wire resistance electrodes in a switched circuit. A polarity switch was also used to remove any bias associated with current flow and voltage measurement using thermocouple legs. Electron microprobe analyses were used to check the composition of the recovered sample.

Results

The observed large jump in resistivity at the high P melting T of each metal is consistent with its known phase diagram and with post-run compositional analyses. The expected resistivity decrease with P and increase with T were found and comparisons with 1atm data are in very good agreement. Within the error of measurement, the resistivity value at the melting T at high P of each metal appears to mimic its 1 atm value.

Conclusion

Resistivity values measured to date support the hypothesis of constant resistivity along the melting boundary.

P 15.10

Equation of state, phase diagram and melting iron at earth core conditions

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Formalism from Dorogokupets et al. [2014; 2015] was used to constrain the revised equations of state for solid and liquid Fe phases. Reference *P-V-T* data from experimental works were recalculated using pressure scales from Sokolova et al. [2013] and Dorogokupets et al. [2015]. Calibration of the Gibbs energy was performed using critical points from high temperature and high pressure experimental data corrected for thermal pressure and adjusted for self-consistent pressure scales, along with the Anzellini et al. [2013] data on the melting curve of Fe. The calculated triple points have following parameters: bcc-fcc-hcp is located at 7.3 GPa and 820 K, bcc-fcc-liquid at 5.2 GPa and 1998 K, fcc-hcp-liquid at 106.5 GPa and 3787 K. Melting curve of fcc = liquid is very close to hcp=liquid one when extrapolated to high pressure conditions (for more details of shocked iron see Brown and McQueen, [1986]). If magnetic moment for hcp-Fe is B_0 = 0.04 then melting line of hcp=liquid Fe is shifted up in temperature (red squares on the Figure).

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References

Dorogokupets, P.I., Dymshits, A.M., Sokolova, T.S., Danilov, B.S., Litasov, K.D., *Russian Geology and Geophysics* **56**, 172-189 (2015).

Dorogokupets, P.I., Sokolova, T.S., Litasov, K.D, *Geodynamic and Tectonophysics* **5**, 1033-1044 (2014). http://dx.doi.org/10.5800/GT-2014-5-4-0166

Sokolova T.S., Dorogokupets P.I., Litasov K.D., *Russian Geology and Geophysics* **54**, 181-199 (2013).

Anzellini, S., Dewaele, A., Mezouar, M., Loubeyre, P., Morard, G., *Science* **340**, 464-466 (2013).

Brown, J.M., McQueen, R.G., *Journal of Geophysical Research: Solid Earth*, **91**, 7485-7494 (1986).

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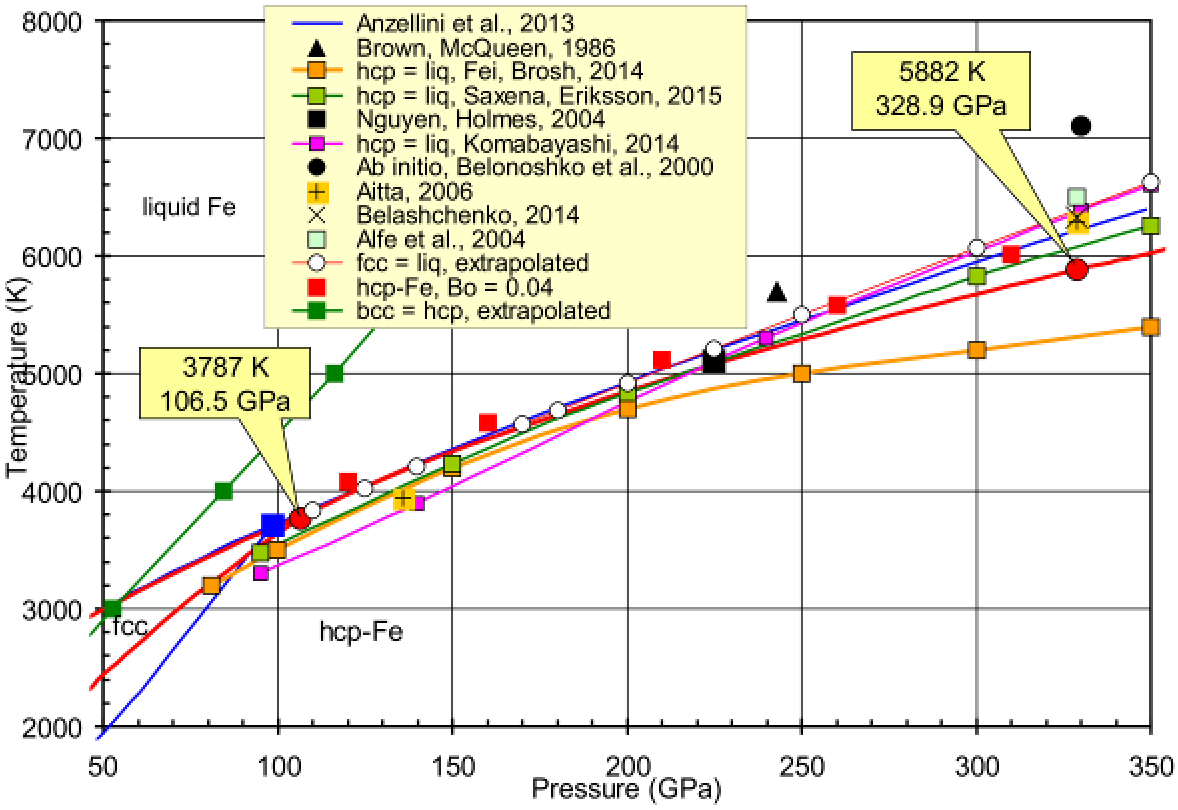
Keywords: Iron, equation of state, phase diagram, melting

Figure 1



Anzellini et al., 2013
Brown, McQueen, 1986
hcp = liq, Fei, Brosh, 2014
hcp = liq, Saxena, Eriksson, 2015
Nguyen, Holmes, 2004
hcp = liq, Komabayashi, 2014
Ab initio, Belonoshko et al., 2000
Aitta, 2006
Belashchenko, 2014
Alfe et al., 2004
fcc = liq, extrapolated
hcp-Fe, Bo = 0.04
bcc = hcp, extrapolated
5882 K
328.9 GPa
3787 K
106.5 GPa
liquid Fe
fcc
hcp-Fe
Temperature (K)
Pressure (GPa)
8000
7000
6000
5000
4000
3000
2000
50
100
150
200
250
300
350

P 15.11

The effect of iron content and hydration state on the elastic moduli of single-crystal ringwoodite at high pressure

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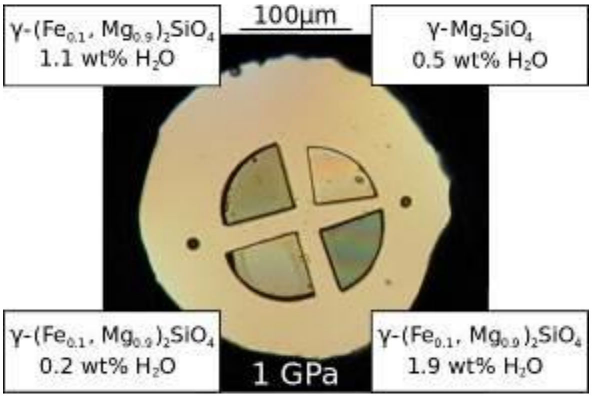
The most abundant minerals in the earth's upper mantle are olivine and its high-pressure polymorphs wadsleyite and ringwoodite. It is known that ringwoodite can incorporate hydrogen as OH-defects in its nominally anhydrous structure and may contribute to the water budget of Earth's mantle. To detect hydrous mantle regions from seismic data, quantitative knowledge about the effects of water on ringwoodite elasticity is necessary. The elastic tensor of ringwoodite does not only depend on the hydration state, but also on the Fe/Mg ratio. Differences in experimental set-ups and sample characterisation between published studies make it difficult to reliably quantify the separate effects of these chemical variations at high pressures and high temperatures.

We present first results of internally consistent single-crystal elasticity measurements of chemically diverse ringwoodite crystals at high pressure. Single-crystals of ringwoodite were synthesised in multi-anvil experiments with chemical compositions ranging from Mg_2SiO_4 to $(Mg_{1.8},Fe_{0.2})SiO_4$ and in the range of 0.2 - 1.9 wt%H_20 at ambient conditions. Four ringwoodite single-crystals with different compositions were oriented, double-side polished and cut into quarter-circles with a FEI Scios Focused Ion Beam (FIB). To ensure the same temperature and pressure conditions for all crystals, four different samples were loaded in the pressure chamber of one diamond anvil cell (DAC), ruby spheres were added as a pressure marker (see figure). We measure comparative elasticity of these single-crystals by x-ray diffraction (XRD) and Brillouin spectroscopy at high pressure.

XRD at 1 GPa shows that the incorporation of OH-defects equivalent to ~ 3.2 mol/L H_2O in Fo90 ringwoodite leads to an increase in the unit cell volume by ~ 2.8 Å³. A decrease in unit cell volume of ~ 3 Å³ is observed in low water containing Mg-endmember ringwoodite compared to a Fo90 ringwoodite with comparable water content. Brillouin spectroscopy shows a reduction of all elastic moduli with increasing water content in iron bearing ringwoodite at 1 GPa. The dependency is in the order of ~ -5 GPa/(mol/L) and ~ -3 GPa/(mol/L) for the bulk and shear modulus respectively.

Figure: Pressure chamber of a diamond anvil cell loaded with four samples of single-crystal ringwoodite with different chemical compositions at 1 GPa pressure.

Figure 1



P 15.12

Effect of composition on compressibility of skiagite-Fe-majorite garnet

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Garnets are among the most abundant phases in the upper mantle and transition zone; hence data on their behavior under extreme conditions is important for understanding the composition, structure, and dynamics of the deep Earth's interior. Natural garnets are usually complex solid solutions because the garnet structure can accommodate a number of different divalent and trivalent cations. While most major cations in garnet occur in only a single oxidation state (Al^{3+}, Ca^{2+}, Mg^{2+}, Si^{4+}), iron occurs as both Fe^{2+} and Fe^{3+}.

Skiagite garnet ($Fe^{2+}_3Fe^{3+}_2Si_3O_{12}$) contains iron in two oxidation states and as a component in peridotitic garnet, it can be used as a redox sensor to determine mantle fO_2 from $Fe^{3+}/\sum Fe$. With increasing pressure/depth the $Fe^{3+}/\sum Fe$ ratio increases due to the higher solubility of Fe^{3+} in garnet, hence expanding the stability field of skiagite. At greater depth skiagite garnet is expected to accommodate an excess of Si, forming a solid solution with the iron majorite endmember ($Fe_4Si_4O_{12}$).

Skiagite-Fe-majorite garnets were synthesized using a multianvil apparatus at 7.5-9.5 GPa and 1400-1600 K. Single-crystal X-ray diffraction at ambient conditions revealed that synthesized garnets contain 23 to 76 % of an Fe-majorite component. We found that the substitution of Fe^{2+} and Si^{4+} for Fe^{3+} in the octahedral site decreases the unit-cell volume of garnet at ambient conditions. Analysis of single-crystal X-ray diffraction data up to 90 GPa of garnets with different compositions reveals that with increasing majorite component the bulk modulus increases from 164(3) to 169(3) GPa. Extrapolation of our data for the pure Fe-majorite composition gives a value of bulk sound velocity of 6.2 km/s, which is significantly lower than any estimates for the Mg-majorite end member. Our results for majoritic garnets firmly establish that the total iron content and the Fe^{2+}/Fe^{3+} ratio notably affect its elastic properties and the bulk sound velocity.

P 15.13

Internally consistent single-crystal elasticity of (Mg,Fe)2SiO$_4$ wadsleyite at high pressures and high temperatures

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The elastic properties of mantle minerals at relevant pressure and temperature conditions control the propagation of seismic waves through the Earth's deep interior. At a depth of about 410 km, (Mg,Fe)2SiO4 olivine is predicted to transform to the orthorhombic high-pressure polymorph wadsleyite. Depending on the bulk composition, wadsleyite can contribute to the mineral assemblage of a transition zone rock with up to 60 vol-% for a pyrolitic upper mantle. This entails a remarkable water storage capacity of the upper transition zone through incorporation of hydrogen into wadsleyite [1] and the potential to induce seismic anisotropy by deformation [2].

We will present internally consistent measurements of single-crystal elastic constants for wadsleyite with a relevant chemical composition (Fe/(Mg+Fe) = 0.11, 0.2 wt-% H2O) to transition zone pressures and at elevated temperatures. Focused ion beam cut single-crystal segments [3] of tailored dimensions and complementary crystallographic orientations were loaded together in the same pressure chamber of resistively heated diamond anvil cells (DAC). In this way, the complete elasticity tensor can be determined on a single DAC loading using Brillouin spectroscopy in combination with X-ray diffraction. This novel multi-sample approach ensures uniform conditions during data acquisition, a prerequisite for an internally consistent description of the elastic behavior of wadsleyite at high pressures and high temperatures.

The pressure evolution of the elastic constants as captured by our room temperature experiments helps to clarify the effect of chemical variability due to incorporation of iron and hydrogen on the equation of state and sound wave velocities of wadsleyite.

[1] Inoue, Yurimoto, and Kudoh (1995) Geophys. Res. Lett. 22:117-120.

[2] Kawazoe, Ohuchi, Nishihara, Nishiyama, Fujino, and Irifune (2013) Phys. Earth Planet. Inter. 216:91-98.

[3] Marquardt and Marquardt (2012) Am. Mineral. 97:299-304.

P 15.14

Combination of laser ultrasonics and Raman spectroscopy in the laser heated diamond anvil cell

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Understanding of the elastic behavior of minerals under high pressure is a crucial factor for developing a model of the Earth structure since the information about Earth interior comes mainly from seismological data. Laboratory measurements of velocities and other elastic properties of minerals are the key for understanding observed seismic information, allowing us to translate it into quantities such as chemical composition, mineralogy, temperature, and preferred orientation of minerals. Laser ultrasonics (LU) combined with diamond anvil cell (DAC) demonstrated to be an appropriate technique for direct determination of the acoustical properties of solids under high pressure. The use of lasers generating subnanosecond acoustical pulses in solids allows measurements of the velocities of shear and longitudinal waves propagated in opaque materials *in-situ* at high pressure and temperature [1-4]. Absorption of the incident laser pulse energy and the associated temperature gradients induces a rapidly changing strain field. This strain field, in turn, radiates energy as elastic (ultrasonic) waves. At low pulse power, this is an entirely thermoelastic process resulting in no damage to the sample. The acoustic echo arriving at the probed surface causes both the displacement of the surface (a few nanometers) and the strain in the subsurface material, which might be detected through its influence on the optical reflectivity of the material, i.e. through the acousto-optic effect.

The details of the advanced system including laser ultrasonics in a point-source-point-receiver configuration coupled with Raman spectroscopy and laser heating techniques in the DAC for studying elastic properties of materials *in-situ* at high pressure and temperature will be demonstrated. Future combination of this innovative system with high-resolution synchrotron micro-diffraction at GSECARS (sector 13, APS) for full structural characterization of materials at extreme conditions will be discussed.

[1] N. Chigarev, P. Zinin, L.C. Ming, G. Amulele, A. Bulou, V. Gusev., *Appl. Phys. Lett.* **93,** 181905 (2008).

[2] P. Zinin, V. Prakapenka, K. Burgess, D. Velikovsky, *Scientific Notes of the Physics Department of Moscow State University*. **6,** 146314 (2014).

[3] K. Burgess, V. Prakapenka, E. Hellebrand, P. Zinin, *Ultrasonics.* **54**, 963 (2014)

P 15.15

Study of the single-crystal elasticity of $Mg_{0.9}Fe_{0.1}Si_{0.9}Al_{0.1}O_3$ - bridgmanite up to lower mantle pressures

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MgSiO3 bridgmanite is widely accepted to be the dominant phase in the Earth's lower mantle where it coexists with ferropericlase. Chemical substitutions in $MgSiO_3$ bridgmanite involving Al and Fe may contribute to seismic velocity anomalies observed in the Earth's lower mantle [1-3]. The effect of these substitutions on the elastic properties of bridgmanite at high pressures and temperatures need to be better constrained experimentally in order to interpret seismic data.

In this study two differently oriented single-crystals of magnesium silicate brigmanite containing some Fe and Al have been double-side polished and cut using the focused ion beam (FIB) technique as two semi-disks. Both semi-disks were loaded in one diamond anvil cell with helium as a pressure medium. Simultaneous measurements of density and sound velocities have been made on both crystals at high pressures and room temperature using single-crystal X-ray diffraction and Brillouin spectroscopy in order to obtain self-consistent data, which do not depend on a pressure scale. The data at each pressure were fitted for both crystals simultaneously in order to reduce correlations of Cij constants. The orientation matrix and cell parameters for each crystal at every pressure point were refined using in-situ x-ray diffraction measurements. From sample densities obtained from x-ray diffraction data and simultaneous measurements of the adiabatic bulk modulus obtained from Brillouin measurements, it was possible to calculate the absolute pressure for all our experimental points. This approach allowed the elastic properties of bridgmanite to be determined as a function of primary pressure, i.e. without resort to a secondary pressure standard. This consequently provides a more reliable data set to be compared with seismic data for the lower mantle.

[1] Ni et al. (2005), Geophys. J. Int. 161, 283-294.

[2] Masters et al. (2000), AGU Monograph Series, 117, 63-87.

[3] Garnero et al. (2005), The Geological Society of America Special Paper, 430, 79-101.

Invited Talk

Challenge of generating pressures beyond the limit of diamond anvil: Double stage anvils fabricated using FIB

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In order to extend the pressure range of static high-pressure experiments beyond the limit of current diamond anvils, we have been making various efforts using double stage diamond-anvil technique with the aid of FIB (Focused Ion Beam). This technique makes it possible to fabricate micron size paired anvils precisely in very reproducible manner. However, there are still many parameters to be optimized to generate very high pressures. X-ray diffraction technique also needs many improvements to study the very tiny samples of micron size. Technical problems in such experiments will be reviewed.

O 16.1

Toroidal diamond anvil cell to reach multi-Mbar

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Since the early 2000’s, the pressure reached in diamond anvil cells was saturating to ~350 GPa. Recent efforts to imagine new diamond anvils designs, such as double-stage anvils consisting of nano-diamond hemispheres placed on conventional anvils, have approximately doubled the pressure range reachable by this instrument [1]. The alignment and the stability of these hemispheres are instrumental to performing successful experiments, which is difficult to ensure. Here we present an alternative way of tailoring anvils using focused ion beam machining. With this technique, we have cut toroidal grooves in beveled diamond anvils, which forms smaller tips with an almost cylindrical geometry. After several tests and shape modifications, we have reached 590 GPa on a gold sample [2]; the non-hydrostatic stress on the sample directly compressed between the anvils was high (~15 GPa). The relatively large sample size (4 microns) and the use of a standard alignment procedure allow to consider loading with soft pressure media to reach quasi-hydrostatic compression in the Multi-Mbar range.

[1] Dubrovinsky *et al.*, Implementation of micro-ball nanodiamond anvils for high-pressure studies above 6 Mbar, Nat. Comm. 3, 1163, 2012

[2] ESRF report ME-1380

O 16.2

Progress in ds-DAC design: Gasketed ds-DACs extend the capabilities of investigation of matter at ultra-high pressures

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In high pressure (HP) research, an achievable static pressure limit is imposed by available strong materials and design of HP devices. Achieving higher and higher pressures will open new horizons for a deeper understanding of matter and the discovery of new physical and chemical phenomena at extreme conditions. Recently we developed a new technique of ultra-high static pressure generation in a double-stage diamond anvil cell (ds-DAC). Nanocrystalline diamond (NCD) balls synthesized from glassy carbon were employed as secondary anvils. This technique allowed us to reach pressures beyond 1 TPa and to study the behavior of a number of materials at such extreme conditions.

So far ds-DACs were used without gaskets and samples were compressed directly between secondary anvils. This limited the application of the technique only to materials solid at ambient conditions. In combination with our novel transparent NCD material, able to sustain much larger stresses compared to strong materials known before, we also introduced an internal gasket for ds-DACs and conducted a number of pilot experiments in gasketed ds-DACs. These results along with characterization of the NCD material will be presented.

Keywords: Nanocrystalline diamond (NCD); double-stage ds-DAC; ultra-high static pressures; high strength materials; gasketed ds-DAC

P 16.1

High pressure and high temperature generation using multianvil apparatus with sintered diamond anvils

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The Kawai-type multianvil apparatus (KMA) is widely used to investigate the structure and state of mantle minerals. The KMA have the ability in producing high pressures and high temperatures with large volume of samples, and with small thermal gradient in the sample chamber.Sintered diamond (SD) anvils are useful to generate higher pressures corresponding to deeper mantle conditions.To date, technical developments of the high pressure generation using SD anvils have expanded the experimental pressures to the deep lower mantle.However, few experiments were conducted to determine the phase relation of major mantle minerals above pressures of 50 GPa because it is difficult to generate high temperature corresponding to mantle geotherm at those pressure regions. In this study, we conducted high pressure and high temperature generation using SD anvils.

High pressure and high temperature experiments were made in the 1500-ton KMA (SPEED-Mk.II) at the beamline BL04B1, SPring-8. The KMA (MADONNA II) at GRC, Ehime University was also used. The SD anvils of 14 mm with truncated edge length of 1.5 mm were used. A semi-sintered Cr-doped MgO (5 wt% Cr_2O_3) and a semi-sintered Al_2O_3 corundum were used as a pressure medium. Ca-doped $LaCrO_3$ heater and Re foil heater were used.

Pressure generations using the Al_2O_3 pressure medium were reached to 60 GPa, which is ~20% higher than those of the Cr-doped MgO. The efficiencies of pressure generation substantially changed by changing the pressure medium because of the high hardness of the Al_2O_3 compared to the Cr-doped MgO. The heating with the Al_2O_3 pressure medium was conducted at higher pressure region than those of the Cr-doped MgO pressure medium. We successfully generated 2300 K up to 60 GPa. Temperature fluctuation was about 5 K during heating without any large scattering, and the sample was heated for at least 30 minutes. The pressure and temperature conditions in this study correspond to mantle geotherm at the middle part of lower mantle. Those techniques would solve the difficulties of high temperature generation at pressures above 50 GPa.

Invited Talk

High pressure high temperature X-ray studies in the laser heated diamond anvil cell – Problems and solutions

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The laser-heated diamond anvil cell (DAC) is the only static technique that can create extreme temperatures at extreme pressures (P>200 GPa). Temperatures in excess of 5000K can be achieved for samples under pressure in diamond cells by heating with high-power infrared lasers. Because of their low absorption by the diamond anvils, hard X-rays are ideal for probing micro-samples subjected to such extreme conditions. The array of X-ray techniques that was initially restricted to structural measurements using X-Ray diffraction is now extended to include several others such as inelastic X-ray Scattering, Mossbauer spectroscopy and EXAFS. As a direct consequence, many scientific breakthroughs have been achieved across fields ranging from Earth and planetary sciences to fundamental physics, chemistry and materials science. However, despite these important technical and scientific achievements, this kind of experiments still remains very challenging. The difficulties originate from multiple factors including undesired chemical reactions, inaccurate high P-T metrology, and uncertainty in the relative alignment of X-ray and laser beams. In melting studies using X-rays, additional problems can occur such as the use of an unambiguous melting criterion. In this presentation, these problems will be discussed and possible solutions proposed.

O 17.1

Iron melting at megabar pressures determined by x-ray absorption spectroscopy

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The determination of iron melting temperature at the conditions in which the solid core of the Earth becomes liquid is one of the main concerns in geophysics as this value represents a fixed point in the thermal profile of our planet. There is a long-standing controversy over the melting curve of Fe at inner core boundary and in this work we have used x-ray absorption spectroscopy (XAS) as a criterion to detect melting under pressure.

XAS is sensitive to changes in the electronic structure through the features close to the absorption edge, provides structural information within a few angstroms around the photoabsorbing atom, and therefore maintains the same sensitivity and accuracy regardless of the physical state of the investigated sample. The melting criterion here adopted is based on changes occurring in the near-edge region of the absorption spectrum (XANES) that is known to be less affected by thermal damping and by the noise associated with extreme conditions. The modifications of the features of the experimental spectra attributed to the solid-to liquid phase transition are reproduced in XANES calculations.

The combination of XAS and elevated pressure and temperature conditions offers great potential to probe Earth's deep interior. In addition, the experiment reported here holds promise for studies related to the structure and phase diagram of compressed melts such as the investigation of polyamorphism in the liquid phase, the analysis of which has been limited until now to ambient conditions.

O 17.2

Melting of iron alloys in Laser-Heated Diamond Anvil Cell: converging results using different in situ and ex-situ diagnostics

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Planetary cores are mainly constituted of iron and nickel, alloyed with lighter elements (Si, O, C, S or H). Understanding how these elements affect the physical and chemical properties of solid and liquid iron provides stringent constraints on the composition of the Earth's core. In particular, melting curves of iron alloys are key parameter to establish the temperature profile in the Earth's core, and to asses the potential occurrence of partial melting at the Core-Mantle Boundary.

As today, throughout the literature, we can observe an overall agreement on the melting temperature of many iron alloys under extreme conditions, with results within mutual uncertainties, irrespectively of the melting diagnostics However, a controversy has been recently pointed out on the case of pure iron, with XANES measurements (Aquilanti et al, PNAS, 2015) in open disagreement with previous results by x-ray diffraction (Anzellini et al, Science, 2013).

Here I will present results of experiments carried out by in situ X-ray diffraction, in situ X-ray absorption, and analysis on recovered samples using FIB and SEM on various samples within many binary systems (Fe-O, Fe-C, Fe-S and Fe-Si alloys). Provided the systematic use of the same, optimized sample configuration, all experiments show a remarkable agreement. Therefore, the discrepancy observed for the case of pure iron cannot be explained by the dissimilar melting diagnostic, as proposed in Aquilanti et al., but is most likely related to sample reaction with diamonds or other experimental issues.

On the contrary, the complementarity between x-ray diffraction and absorption measurements can be exploited, so to probe the local arrangement and the liquid structure of the investigated iron alloys, offering a unique opportunity to better constrain how the light elements affects the liquid properties under Earth's core conditions.

O 17.3

Local structure of molten 3d metals under extreme conditions of pressure and temperature by means of X-ray absorption spectroscopy

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The local structure of a liquid metal, far from the periodicity of a solid crystal but still not purely random, has not only fundamental but also geophysical interest; the metals under analysis, i.e. iron and nickel, are in fact major alloying constituents of the outer core of Earth [1] in the liquid phase at the P-T conditions that we try to reach. Nevertheless, very little can be found in the literature on the local structure of these metals under extreme conditions [2].

With its short order sensitivity X-ray Absorption Spectroscopy is the ideal technique to study the local structure of a liquid [3], as well as to detect the transition to the molten phase.

Absorption spectra are measured on a laser heated sample compressed in a diamond anvil cell at the energy-dispersive XAS beamline ID24 at ESRF [4]. The XAS spectrum and the temperature of the laser heated liquid sample can be measured at the same time in a fraction of seconds [5], making possible the study of the liquid under extreme conditions.

The flattening of the edge and post-edge in the XANES (X-ray Absorption Near Edge Structure) as well as a change in the XANES derivative, Fig. 1 left and middle panel, are good indications of the transition to the liquid phase [6]. The determination of the melting temperature at different pressures will be here presented for the Ni case [7], (Fig.1 right panel). Moreover, a first EXAFS (Extended X-ray Absorption Fine Structure) study of the nearest neighbor shell of liquid Ni as a function of pressure and temperature gives promising results and encourages us to proceed with further analysis.

Fig.1 Ni K-edge XANES at 50 GPa in KCl (left), derivative of the spectra shown in the left panel (middle), Nickel melting curve detected by absorption (right).

References

[1] J. Li, Geochimica et Cosmochimica Acta 65, 1821 (2001)

[2] C. Sanloup et al., Europhysics Letters 52, 151 (2000)

[3] A. Di Cicco et al., PRB 89, 060102(R) (2014)

[4] S. Pascarelli et al. J. Synchrotron Rad. (2016). 23, 353-368

[5] I. Kantor, J.-C. Labiche, E. Collet et al., J. Synch. Rad. 21, 1240 (2014)

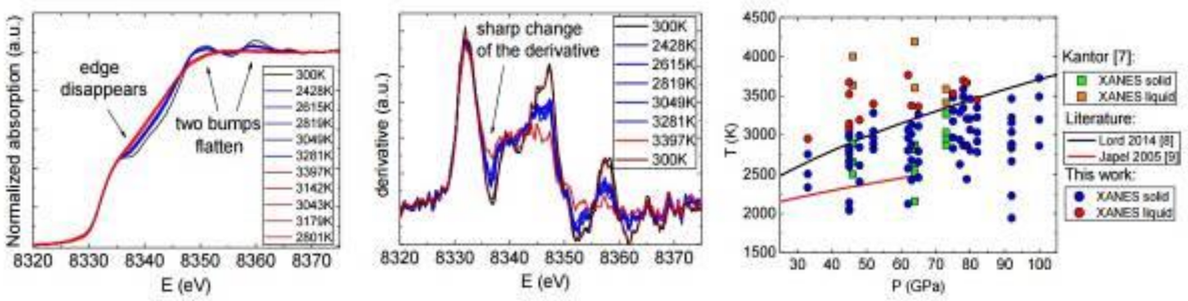
[6] G. Aquilanti et al. PNAS 112, 12042 (2015)

[7] I. Kantor et al., submitted

[8] O. Lord et al., Earth and Planetary Science Letters 408, 226 (2014)

[9] S. Japel et al. Phys. Rev. Lett. 95, 167801 (2005)

Figure 1



O 17.4

Melting and structure of light molecular fluids using synchrotron X-ray diffraction

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The structure and dynamics of fluids, although a long standing matter of investigations, is still far from being well established. In particular, with the existence of a first order liquid-liquid phase transition (LLT) discovered in liquid phosphorus at 0.9 GPa and 1300 K [1] it is now recognized that the fluid state could present complex structural changes. At present, very few examples of LLTs have been clearly evidenced, which may mean that a larger range of densities must be probed. First order transitions between a molecular and a polymeric liquid have been recently predicted by first principles calculations in liquid nitrogen at 88 GPa and 2000 K [2]. The only experimental information collected in the high PT region of the nitrogen phase diagram are from optical [4] and Raman [5,6] measurements performed in a laser heated diamond anvil cell. They highlighted a maximum on the melting curve at respectively 50 and 70 GPa, the origin of which is still matter of debate since there is no Raman evidence of the polymeric fluid.

In this contribution, we present recent developments performed in order to measure the melting curve and the static structure factor S(Q) of simple molecular fluid under extreme condition of pressure and temperature using synchrotron X-ray diffraction. First, we have designed new sample geometry where the sample is enclosed in an opaque diamond capsule that absorbs the YLF laser. This geometry provides a uniform heating of the sample volume probed by the x-ray beam. Second, we have implemented a double-sided laser heating system and a multichannel collimator (MCC) in the EH2 of the ID27 beamline in order to extract the weak liquid diffraction signal of a laser heated sample in the megabar range. Finally, we have developed a method of analysis that allows to quantitatively determine the density, structure factor and radial distribution function of a fluid in a diamond anvil cell. Measurement on cryogenic fluid hydrogen and laser heated fluid nitrogen will be presented to illustrate these developments.

[1]. Y. Katayama et al. Nature 403, 170 (2000).

[2]. B. Boates and S. A. Bonev. Phys. Rev. Lett. 102, 015701, (2009).

[3] G. D. Mukherjee and R. Boehler, Phys. Rev. Lett. 99, 225701 (2007).

[4] A. Goncharov, J. Crowhurst, V. Struzhkin and R. Hemley, Phys. Rev. Lett. 101, 095502 (2008).

[5] D. Tomasino, Z. Jenei, W. Evans, C. Yoo, J. Chem. Phys. 140, 244510 (2014)

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Keywords: (Liquid, X-ray diffraction, simple molecular system)

O 17.5

The existence of a density maximum in fluid tin tetraiodide

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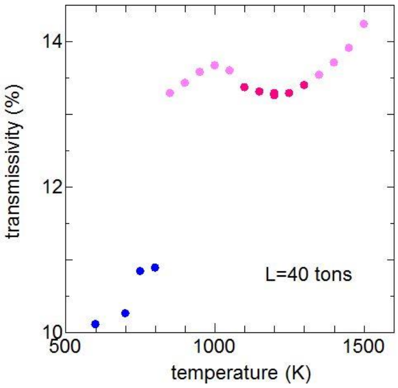
Tin tetraiodide exhibits water-type polyamorphic nature; it has low-density amorphous (LDA) and high-density amorphous (HDA) states [1]. Unlike water, their liquid counterparts, low-density liquid (LDL) and high-density liquid (HDL) states, can be observed in the bulk; their local structures [2] and densities [3] were measured in situ using synchrotron x-ray diffraction and absorption, respectively. The measurements were performed using multianvil press installed at BL22XU, SPring-8, and at NE5C and NE7A, KEK-AR, Japan.

Not only the pseudo-binary regular-solution model but also a coarse-grained Potts model and the Franzese—Stanley (FZ) model [4] could capture equally well the location of these states and phases on the pressure—temperature phase diagram [5]. It should be stressed that all these models support the existence of the liquid—liquid critical point, whose location was predicted to be close to the breakpoint (at ~ 1.5 GPa and 950 K) of the melting curve of the crystalline phase [5]. This prediction has indeed been confirmed by recent x-ray absorption measurement [6]. That is, the liquid—liquid critical region will never be "no-man’s land" for tin tetraiodide.

The other feature worth examining is a temperature of maximum density, whose existence was suggested by the FZ model for tin tetraiodide [7]. The predicted region of the density anomaly extends from 1200 K to 1400 K below 1 GPa. Because of this rather low pressure, it was difficult to keep liquid tin tetraiodide for a long time. Very recently, we have succeeded in detecting a slight increase in x-ray absorptivity (or a slight decrease in transmissivity, see Fig.1), introducing a newly-devised sample container, in the region between 1100 K and 1400 K just below 1 GPa (calibrated from another experiment), which is quite consistent with the theoretical prediction. The reproducibility of the result was confirmed.

[1] N. Hamaya *et al.*, Phys. Rev. Lett. **79**, 4597 (1997). [2] K. Fuchizaki *et al.*, J. Chem. Phys. **130**, 121101 (2009). [3] K. Fuchizaki *et al.*, J. Phys. Soc. Jpn. **82**, 033003 (2013). [4] G. Franzese and H. E. Stanley, J. Phys.: Condens. Matter **14**, 2201 (2002). [5] K. Fuchizaki *et al.*, J. Chem. Phys. **135**, 091101 (2011). [6] K. Fuchizaki *et al.*, to be presented at StatPhys26. [7] K. Fuchizaki, read at the JPS meeting, 22 March 2010; in preparation.

Figure 1



O 17.6

Melting and liquid structure of ammonia at high pressure and temperature

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Ammonia is believed to be an essential component of outer icy planets and their moons. Studying the structure of ammonia is important to clarify astrophysical measurements and to further understand properties ofcelestial objects. New and exotic properties of solid ammonia have been found [1] and predicted [2], but liquid ammonia has been less explored and poorly described.

A major difficulty in studying liquids of low-Z elements using x-ray diffraction in the DAC is the large incoherent background due to diamonds' scattering. A new setup has been implemented at ESRF on ID27 which greatly reduces the Compton diffusion from the diamond anvils [3]. This setup was used to measure the melting curve and fluid structure factor of ammonia using resistive or CO_2 laser heating. The structure factor, radial distribution function and density of liquid ammonia will be presented. Partial dissociation of NH_3 into N_2 and H_2 was observed by Raman scattering, in accordance with [4].

References

[1] Ninet, S., F. Datchi, and A. M. Saitta, *Phys. Rev. Lett.* 108,16 (2012); S. Ninet, F. Datchi, P. Dumas, M. Mezouar, G. Garbarino, A. Mafety, C. J. Pickard, R. J. Needs and A. M. Saitta, *Phys. Rev. B* 89, 174103 (2014)

[2] Cavazzoni, C., Chiarotti, G. L., Scandolo, S., Tosatti, E., Bernasconi, M., & Parrinello, M., *Science* 283,5398 (1999).

[3] Weck, G., Garbarino, G., Ninet, S., Spaulding, D., Datchi, F., Loubeyre, P., & Mezouar, M., *Rev. Sci. Instr* 84,6 (2013).

[4] Ojwang, J. G. O., McWilliams, R. S., Ke, X., & Goncharov, A. F., *J. Chem. Phys.,* 137,6 (2012).

P 17.1

Phase relations of CuBr under high pressure and temperature

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Copper halides (CuCl, CuBr, CuI) are the most ionic crystals with a zinc-blende structure. On Phillips scale, these compounds have ionicities of around 0.7. This is very close to the critical value of 0.785 which marks the idealized boundary between compounds characterized by fourfold-coordinated structures (zinc blende, wurtzite) and those with sixfold coordination (rocksalt). As a result of this near structural instability, a large number of pressure-induced polymorphism are possible. Indeed, these copper halides undergo a number of structural phase transitions under pressure before attaining the rocksalt structure (Hull and Keen, 1994). Since the *P-T* phase diagram of CuBr has not been determined to date, we have performed both *in situ* XRD and XAFS observations of CuBr under high pressure and high temperature up to 8 GPa and 1400 K to investigate the phase relations and crystal structures including the local structure of liquid phase using multi-anvil high-pressure devices and synchrotron radiation.

XRD measurements were performed by using energy dispersive mode using the MAX 80 high-pressure devices installed at the Photon Factory in the High Energy Accelerator Research Organization, while XAFS experiments for Br *K*-edge were executed using the SMAP2 system at BL14B1 in the SPring-8. X-ray absorption spectra near Br *K*-edge were measured.

Figure 1 summarizes the newly obtained *P-T* phase diagram. Several phase boundaries are determined and phases with sixfold coordination (rocksalt type) appear above 6 GPa. We found that the melting curve shows broad maximum. The pressure variation of the first-neighbor bond length in liquid CuBr at various temperatures obtained by EXAF analysis is shown in Figure 2. The bond distances gradually increase with pressure indicating that higher fold coordination than 4 fold is introduced by compression. Pressure induced local structure change in liquid CuBr occurs over a wide range of pressure and 6 fold coordination is almost fully achieved above 5 GPa which pressure is higher than that of the temperature minimum in the melting curve of 3-4 GPa.

Fig. 1 *P-T* phase diagram of CuBr determined by the present XRD and XAFS studies.

Fig.2 Pressure variation of the first-neighbor bond length in liquid CuBr at various tempetarures. For comparison, the values of low pressure solid phases (4 fold coordination) and high pressure solid phase (6 fold coordination) at room temperature are also shown by solid lines.

Reference

Hull S. and Keen D.A., 1994. Phys.Rev. B, 50 (9), 5868-5885.

Figure 1

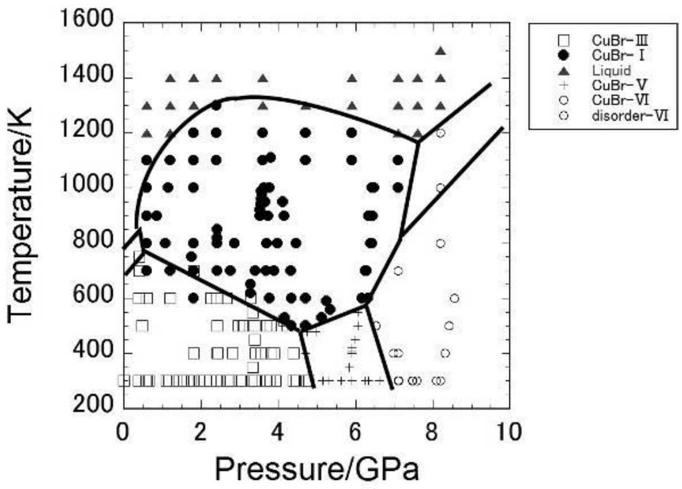
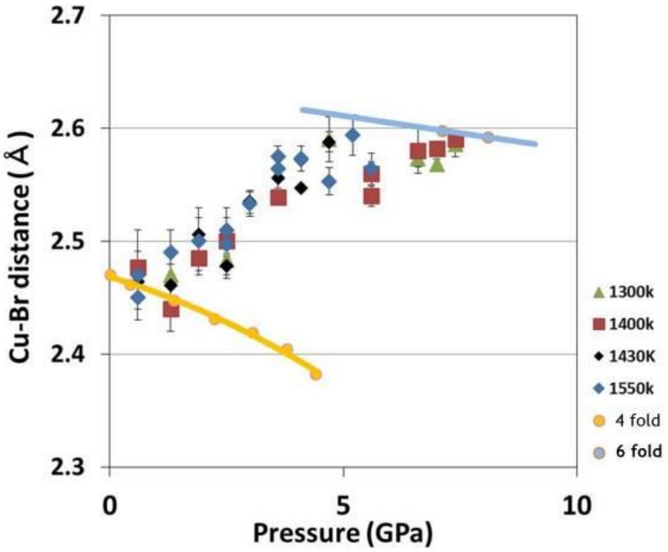


Figure 2



P 17.2

The influence of wavelength-dependent absorption and temperature gradients on temperature determination in laser-heated diamond-anvil cells

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In situ temperature measurements in high-pressure/temperature experiments using the laser-heated diamond-anvil cell (LHDAC) are among the most fundamental measurements undertaken in high-pressure science. Despite its importance, few efforts have been made to examine the alteration of thermal radiation spectra of samples by wavelength-dependent absorption of the sample itself and temperature gradients within samples upon laser heating and their influence on temperature measurements. In this study, we take ferropericlase as an example and systematically measure its absorption spectra under different high-pressure conditions. Iron-rich ferropericlase shows strong wavelength dependent absorption in the wavelengths of light used to determine temperature, which, together with the temperature gradient can account for largely deviated apparent temperatures (e.g., 800 K deviation for a 4000 K melting temperature) in some experiments obtained by Wien fitting intensities of light detected. In general, wavelength-dependent absorption and temperature gradients are two key factors in order to obtain rigorously constrained temperatures, while unfortunately, to our best knowledge, ignored in all the previous LHDAC studies.

P 17.3

Melting curves of metals with excited electrons in the quasiharmonic approximation

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In this work we used ab initio calculations (VASP [1]), based upon the density functional theory, the quasiharmonic appoximation and Lindemann [2] criterion to build melting curves in wide region of pressures. This approach allows to calculate the total free energy of electrons and phonons, so it is possible to obtain all thermodynamic properties in the crystalline state.

All calculations were performed for aluminum, copper and nickel. Results for aluminum and copper are in good agreement with available experimental data, but there is a discrepancy between our calculations and static experimental points for nickel.

Also we studied the influence of electronic temperature on melting curves. It turned out that the melting temperature increases with the rise of electron temperature at normal and reduced density and has non-monotonic behavior at higher densities.

[1] Kresse, G., and Hafner, J., Phys. Rev. B., 47, 558 (1993).

[2] F.A. Lindemann, Phys. Z. 11, 609 (1910).

Invited Talk

Dynamic high temperatures in the diamond cell: pump-probe measurements of optical and transport properties at extremes

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High pressure and temperature experiments on materials in the diamond anvil cell are limited by problems including undesirable reactions, sample loss, and anvil failure. By controlling time at high temperature with pulsed heating, and combining this with real time measurements of sample conditions and character, higher temperatures can be achieved, samples better preserved, and new types of measurement enabled. This talk will cover recent developments in dynamic heating of the diamond cell using a pump (laser heat) and probe (by optical spectroscopy) methodology (McWilliams et al. 2015). Thermally induced insulator-conductor transformations have been studied under pressure, documenting decreasing transformation temperature with pressure, and conducting states with optical character of semiconductors, indicating a dominant role of bound rather than free electrons in hot insulators. Tracking of the propagation of temperature perturbations across heated samples allows direct *in-situ* determination of thermal conductivities at high pressure and temperature, which were tested on the metals Pt and Fe. The thermal conductivity of Pt shows close agreement with estimates based on earlier data, whereas the thermal conductivity of Fe is most consistent with empirical estimates from in-situ resistivity measurements (Seagle et al. 2013) and earlier theories (Stacey and Loper 2007). These results support a low thermal conductivity in Earth and terrestrial planet cores, and suggest Earth's magnetic field can be long-lived without the need for unusually high historic temperatures or additional energy sources beyond thermal convection.

McWilliams, R. S. et al. Opacity and conductivity measurements in noble gases at conditions of planetary and stellar interiors. *Proceedings of the National Academy of Sciences* **112**, 7925 (2015).

McWilliams, R. S. et al. A flash heating method for measuring thermal conductivity at high pressure and temperature: application to Pt. *Phys. Earth Planet. Inter.* **247**, 17-26 (2015).

Seagle, C. T. et al. Electrical and thermal transport properties of iron and iron-silicon alloy at high pressure. *Geophysical Research Letters* **40**, 5377-5381 (2013).

Stacey, F. D. & Loper, D. E. A revised estimate of the conductivity of iron alloy at high pressure and implications for the core energy balance. *Phys. Earth Planet. Inter.* **161**, 13-18 (2007).

Invited Talk

Melting and Solidification as a Planetary Phenomenon

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The melting curve represents a tremendous rheological transition, from a material with strength to one without. This transition is critical to the evolution of the Earth, as the latent heat from solidification of Earth's inner core helps to drive the magneto-dynamo in the liquid outer-core. Efforts to use diamond anvil cell measurements to constrain the melting curves of important engineering and planetary materials are often limited in pressure and temperature. The sound velocity along the shock Hugoniot has been used as a diagnostic of melting, however, the interpretation of the data has sometimes come into question. I will present initial results and the development of techniques to constrain the ultra-high pressure melting curve using tailored pressure drives and in-situ x-ray diffraction. I will discuss how we use x-ray diffraction as a diagnostic of melting along the principal Hugoniots of iron and tantalum. I will also present the first evidence for re-crystallization of tin on the nanosecond timescale after re-compression from the molten Hugoniot state. Finally, I will present preliminary results from our in-situ x-ray diffraction campaign at the National Ignition Facility to constrain the ultra-high-pressure melting curve of iron at super-Earth core conditions, which will help constrain the types of exoplanets that could be habitable.

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Invited Talk

Planetary physics and warm dense matter research

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The behaviour of warm dense matter (pressures up to the TPa region and temperatures up to several eV) is of paramount importance for understanding the interior, evolution and magnetic field of solar and extrasolar planets. While the light elements H and He are the main components of gas giants like Jupiter, mixtures of C-N-O-H-He are relevant for Neptune-like planets, and minerals of the MgO-FeO-SiO2 complex are the building blocks of rocky planets (Earth, super-Earths). The high-pressure phase diagram of these elements and mixtures has to be known in order to develop corresponding models (see [1] for H/He). Of special interest in this context is the location of the melting line (Fe: [2]), the occurrence of de-mixing effects (H/He: [1,3], (Mg,Fe)SiO3 [4]) and of metal-insulator transitions (H/He: [1,5]). These high-pressure phenomena have a strong impact on interior, evolution, and dynamo models for planets and, simultaneously, constitute a major challenge to computational physics.

Molecular dynamics simulations based on finite-temperature density functional theory are used to predict the equation of state, the high-pressure phase diagram, and the transport properties of warm dense matter for a wide range of densities and temperatures as typical for the interior of planets (H/He: [6,7], H2O: [8], NH3: [9], MgO: [10]). These data are benchmarked against DAC and shock-wave experiments and then applied to construct interior and evolution models for giant planets like Saturn [11] and Uranus [12]. The treatment of more complex mixtures such as H-He, H2O-NH3, or MgO-FeO is in progress. Furthermore, new high-pressure techniques such as double-stage [13] and dynamic DACs [14] but also dynamic quasi-isentropic compression experiments will extend the pressure-temperature range studied at synchrotron [15] and free electron laser facilities [16]. These combined efforts will lead to a better understanding of the physics of warm dense matter and of planetary interiors.

References

[1] J.M. McMahon et al., Rev. Mod. Phys. 84, 1607 (2012).
[2] S. Anzellini, A. Dewaele, M. Mezouar, P. Lobeyre, G. Morard, Science 340, 464 (2013).
[3] W. Lorenzen, B. Holst, R. Redmer, Phys. Rev. Lett. 102, 115701 (2009).
[4] L. Zhang et al., Science 344, 877 (2014).
[5] M.D. Knudson et al., Science 348, 1455 (2015).
[6] M. French et al., Astrophys. J. Suppl. 202, 5 (2012).
[7] A. Becker et al., Astrophys. J. Suppl. 215, 21 (2014).
[8] R. Redmer, T.R. Mattsson, N. Nettelmann, M. French, Icarus 211, 798 (2011).
[9] M. Bethkenhagen, M. French, R. Redmer, J. Chem. Phys. 138, 234504 (2013).
[10] D. Cebulla, R. Redmer, Phys. Rev. B 89, 134107 (2014).
[11] R. Püstow, N. Nettelmann, R. Redmer, Icarus 267, 323 (2016).
[12] N. Nettelmann et al., Icarus (accepted).
[13] L. Dubrovinsky et al., Nat. Commun. 3, 1163 (2012).
[14] W.J. Evans et al., Rev. Sci. Instr. 78, 073904 (2007).
[15] M.I. McMahon, J. Synchr. Rad. 21, 1077 (2014).
[16] K. Appel et al., Plasma Phys. Contr. Fusion 57, 014003 (2015).

O 18.1

Fast compression and decompression capabilities and experiments at HPCAT, APS

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Materials behavior and phase transformation pathways are strongly influenced by the time dependence of the driving mechanism (compression, thermal transfer, strain, irradiation, etc). While shock compression and static compression are well established techniques available for a long time, the techniques filling the compression rate gap and studying materials behavior as a function of compression rates at intermediate rates remain scarce.

Recent advances in synchrotron sources, x-ray optics, fast area detectors, and sample environment control have enabled many time-resolved experimental techniques for studying materials at extreme pressure and temperature conditions. The High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source has made a sustained effort to develop and assemble a powerful collection of high-pressure apparatus for time-resolved research and developing techniques for collecting high-quality time-resolved x-ray scattering data at compression rates intermediate between static and shock compression experiments. In this talk we will outline recently developed capabilities at HPCAT for synthesis of metastable and amorphous materials and studying properties (EOS, lattice relaxation, etc.) and phase transition mechanisms of materials using fast unidirectional and cyclic compression-decompression with variable strain rates up to extreme compression of tens of TPa per second.

O 18.2

Sub-millisecond time-resolved XAS as a probe of the dynamics of structural phase transitions

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X-ray Absorption Spectroscopy (XAS) is a powerful technique to characterize the local and electronic structure around a probed atomic species. The Energy Dispersive XAS (EDXAS) beamline at the European Synchrotron (ID24) has been recently reconstructed to create a facility dedicated to time-resolved and extreme-conditions XAS (Pascarelli 2016). On ID24, the energy dispersive spectrometer allows to record a full XAS spectrum in a single detector acquisition. Coupled to a high flux undulator source, this beamline provides a powerful tool to study matter under extreme conditions in particular when short integration times are required. Examples are studies of chemical reactions (Kantor 2014), of melts at very high pressure and temperature (Marini 2014), or of dynamically compressed matter under laser shock compression (Torchio, submitted).

Here we present very recent results where sub-millisecond resolved EXAFS has been coupled to a dynamic Diamond Anvil Cell device and employed to probe the changes in local and electronic structure that occur at structural phase transitions. The example of the a α->ω phase transition in Zr metal will be shown as an example.

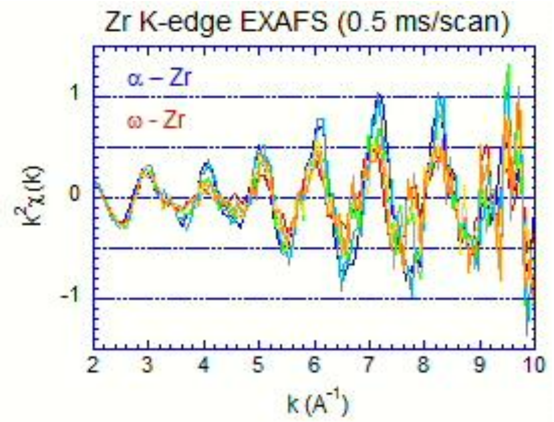
[Pascarelli 2016] Pascarelli, S., et al., The Time-resolved and Extreme-conditions XAS (TEXAS) facility at the European Synchrotron Radiation Facility: the energy-dispersive X-ray absorption spectroscopy beamline ID24. Journal of Synchrotron Radiation 23, 353 (2016)

[Kantor 2014] Kantor, I., et al., A new detector for sub-millisecond EXAFS spectroscopy at the European Synchrotron Radiation Facility. Journal of Synchrotron Radiation 21, 1240 (2014)

[Marini 2014] Marini, C., et al., A microsecond time resolved x-ray absorption near edge structure synchrotron study of phase transitions in Fe undergoing ramp heating at high pressure. Journal of Applied Physics 115, 093513 (2014)

[Torchio 2016] Torchio R. (submitted)

Figure 1



O 18.3

Laser shock experiments at ESRF: developments and first results

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Two years ago a first laser shock experiment was performed on iron at the ESRF, coupling a 40J portable laser to the X-ray absorption spectroscopy beamline ID24[1]. This experiment demonstrated the possibility to investigate the atomic structure of iron exposed to ns dynamic compression, using single x-ray pulses and with a data quality comparable to static experiments[1].

This year a second campaign has been carried on iron and other systems (FeO and Ta).

We present here the new developments that have characterized this second campaign, i.e. the test of different synchrotron timing modes and the implementation of VISAR and SOP diagnostics, and first results obtained on Tantalum.

[1] S. Pascarelli et al. JSR 2016

[2] R. Torchio et al, Scientific Reports 2016

O 18.4

Double-sided pulsed laser heating system for time resolved geoscience and materials science applications

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The Laser Heated Diamond Anvil Cell (LHDAC) technique seems to be the most effective experimental method in the studies of materials at extreme conditions of both high temperature and pressure. Constant Wave laser heating is a reliable method which still has a number of disadvantages. Pulsed laser heating is an improvement of this technique, capable to provide information on the dynamics of the heated material, allow time-resolved studies and increase the heating stability. In this way, new fields of studies can be introduced, including thermally induced dynamic response of materials under high pressure, thermal conductivity characterization, melting point determination, etc. A new double-sided pulsed laser heating system for DACs has been developed in the University of Bayreuth, able to stably produce laser pulses as short as a few microseconds with repetition frequencies up to 100 kHz. *In-situ* temperature determination is possible by collecting and fitting the thermal radiation spectrum for a specific wavelength range, in our set up at approximately 650 nm - 850 nm, to the Planck function. Surface temperature information can also be time-resolved by using a gated detector that is synchronized with the laser pulse modulation, and space-resolved with the implementation of a novel multi-point thermal radiation collection technique. The system can be easily coupled with similar laser heating set ups at synchrotron facilities. Examples of application include both *in house* investigations of high-pressure high-temperature behavior of different materials inside a DAC, as well as a Synchrotron Mössbauer Source study of iron-bearing compounds at the Nuclear Resonance (ID18) beamline of the European Synchrotron Radiation Facility (ESRF).

O 18.5

X-ray diffraction measurements of phase transitions and melting in shock-compressed scandium

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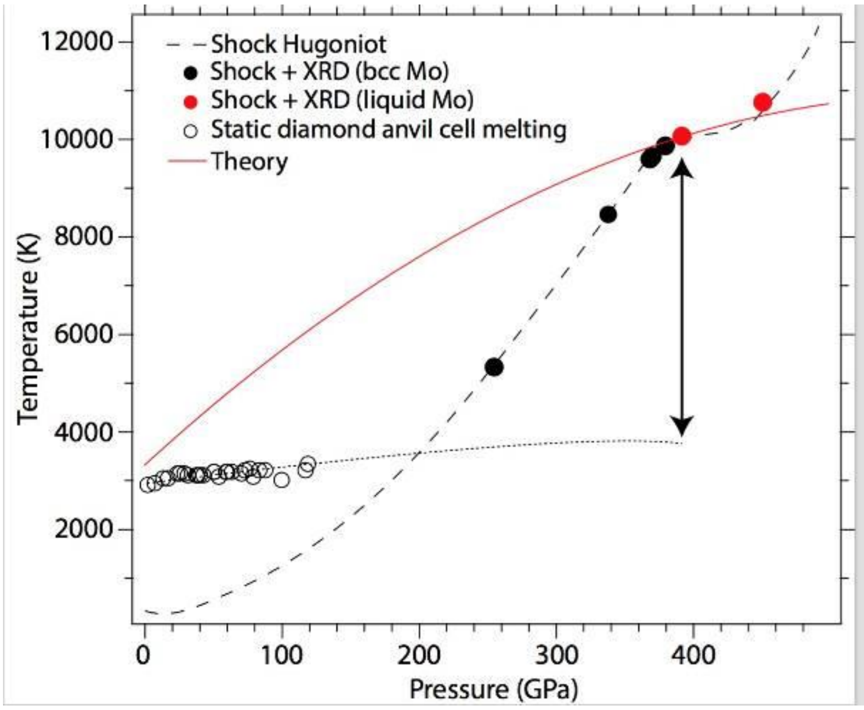
Scandium is the lightest transition metal and undergoes a transition, at room temperature, from the basic hexagonally closed packed crystal structure to the complex incommensurate host-guest crystal structure at ~ 22 GPa. In previous studies using dynamic shock compression, a transition to a mixed phase region between 16.5 and 38 GPa was observed, with a further transition near 53 GPa thought to be melting or another high-pressure phase transition of unknown origin. However, no in situ characterisation of the crystalline state of the material could be carried out in those experiments and the transitions to particular phases are assumed. Here, using X-ray diffraction at the MEC end-station of the LCLS x-ray free electron laser in Stanford, we have carried out femtosecond X-ray diffraction during shock compression of scandium to unambiguously identify the phase transitions (including melting) along the shock Hugoniot.

Figure 1



O 18.6

X-ray diffraction of water dynamically compressed to 4 Mbar and evidence for a new crystalline ice phase

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The study of water at extreme conditions is important for planetary science, water being thought to dominate the interiors of Neptune, Uranus and extrasolar mini-Neptunes. At the extreme pressures and temperatures deep inside these bodies water has been predicted to become superionic with a solid lattice of oxygen and diffusing hydrogen. Optical measurements[1] combined with previous electrical conductivity experiments[2] reveal high ionic electrical conduction near 1.5 Mbar and 4000 K, consistent with the predictions for superionicity. However, no direct experimental evidence exists so far documenting a solid oxygen lattice at these conditions. Nano-second x-ray diffraction measurements of matter dynamically compressed to multi-megabar pressures are now routinely collected at the Omega laser facility[3,4,5]. However extending the technique to measure diffraction of low-Z solids remains extremely challenging. It requires optimization of the laser drive pulse shape (to follow a low-entropy compression path) and maximization of the signal-to-background. Here we present diffraction data on water dynamically compressed into dense ice. A specifically designed stack of laser pulses was used to compress liquid water through small shocks. The laser power was tuned to follow the pressure-temperature compression path to explore conditions approaching Neptune's core mantle boundary near 4 Mbar and 5000-6000 K. The new data evidence a solid oxygen lattice demonstrating that we succeeded in compressing water into crystalline dense ice. Our data suggest the existence of a temperature-driven solid-solid phase transition in the predicted stability domain of superionic water ice and they indicate that water melting temperature increases quickly above 70 GPa and might exceed the interior temperature of large icy planets. Therefore, the stability of a new crystalline phase of water at extreme conditions has broad implications for planetary science[6].

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[1] M. Millot et al., under revision
[2] R. Chau et al., JCP, 114, 1361 (2001).
[3] J. R. Rygg, et al., Review of Scientific Instruments 83, 113904 (2012).
[4] F. Coppari et al., Nature Geoscience 6, 929 (2013).
[5] A. Lazicki et al, Physical Review Letters 115, 075502 (2015).
[6] N. Nettelmann, et al., Planetary and Space Science, 77, 143 (2013).

O 18.7

Shock induced phase transformations in bismuth probed using femtosecond X-Ray diffraction

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The ability to characterise atomic structure at extreme conditions and on the timescale of laser-driven shock experiments is vital for our understanding of how materials behave under rapid pressure loading. A key finding in recent static high-pressure studies has been that many materials adopt complex crystal structures at high-pressure such as incommensurate host-guest structures (Pickard *et al*. Nature Mater. **9**, 624-627, 2010)

However, it is uncertain whether such complex structures are able to form on the timescales of laser shock experiments due to the highly reconstructive nature of the phase transformation mechanisms, leading to the possibility of non-equilibrium phases forming. Studying such shock-induced phenomena using *in situ* X-ray diffraction is experimentally challenging, and requires ultra bright, sub-nanosecond X-ray pulses. The low symmetry of the complex crystal structure also tends to produce diffraction patterns with many weak Bragg reflections, the observation of which is essential to determining the structure correctly.

Fortuitously, the advent of free-electron lasers (XFELs) has resulted in a billion-fold increase in X-ray brightness, sufficient that even complex crystal structures can be resolved from a single 50 fs exposure. Here we describe the use on an XFEL to study the behavior of bismuth under dynamic compression. Bismuth exists in 5 different solid phases below 10 GPa and 600K, and has been reported to melt along the Hugoniot from 17-28 GPa. Several of bismuth's high-pressure phases adopt complex crystal structures - most notably the incommensurate host-guest structure of Bi-III found between 3 and 7 GPa. Bismuth thus affords an ideal system to study the formation of complex structural forms on nanosecond timescales at modest pressures and temperatures.

We present X-ray diffraction measurements that characterise the structure of several solid phases of Bi including one new phase, which is not reported in the equilibrium phase diagram. Diffraction measurements on molten Bi will also be presented, and the melting P-T conditions compared to equilibrium studies.

O 18.8

Crystal structure of Fe-Si alloys at TPa pressures

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The recent discovery of thousands of planets outside our Solar System has prompted research into the material properties of geologically-relevant minerals at pressures well in excess of those found in the interior of Earth. As super-Earths - rocky extrasolar planets with masses up to 10 times that of Earth - have core pressures that are predicted to be as high as 4000 GPa (4 TPa), a better understanding of the high pressure and temperature response of the constituent materials is essential to understanding the internal structure and properties of these planets.

Recently developed dynamic compression techniques with high-powered lasers allow solid-state material properties to be measured at TPa pressures [5, 6]. The ramp compression approach and associated low temperature compression path is key to studying materials at pressures relevant to planetary interiors while maintaining the solid state. Here, we discuss experiments conducted on the Omega laser facility located at the University of Rochester’s Laboratory for Laser Energetics, where we measured the crystal structure of Fe-Si alloy with the goal of understanding the effect of silicon on the structure and density of exoplanetary cores.

Using up to twenty five beams of the Omega laser we combine the techniques of ramp compression and nanosecond x-ray diffraction to measure the structure of Fe-7wt%Si and Fe-15wt%Si alloys to 1250 GPa. High pressures were achieved by focusing temporally-shaped laser drives onto target packages containing Fe-Si alloys, while in situ x-ray diffraction probed the structure at maximum compression.

O 18.9

Moving beyond feasibility in ultrafast shock chemistry experiments

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Although ultrafast hydrodynamic methods to investigate the chemistry of shocked materials on ps to ns time scales are generally mature, questions about the interpretation of such experiments remain. Most ultrafast experiments employ shock etalon methods whose interpretation depends on assumptions about the index of refraction of the shocked state. Further, although signatures for chemistry in longer time scale time-of-flight (ToF) experiments are well understood, ultrafast chemistry experiments have not typically employed ToF methods. The use of ToF methods in ultrafast experiments would enable a more straightforward connection to longer time scale data, and would generally provide more information than shock etalon methods. Finally, ultrafast experiments have not been performed over time scales greater than a few hundred of picoseconds, significantly limiting the scope of experiments to observe shocked chemistry under typical conditions at larger length scales. Here we address all of these issues by presenting data from shocked polymers obtained using both ToF and shock etalon methods, using a 1 ns pump and observation window. We compare the results of these two methods to reconcile data from these different methods and strengthen the interpretation of both types of experiment.

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O 18.10

Universal Hugoniot of fluid metals in WDM regime up to 20 TPa

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Question

Warm dense matter (WDM) exists at high pressures *P*, densities *r* and temperatures *T* such that T/T_F ~ 1, where T_F is the Fermi temperature of itinerant electrons. Such extreme conditions are achieved by dynamic compression and all materials are metals at sufficiently extreme conditions. In WDM potential energy of electron-ion interactions is comparable to kinetic energies of electrons. The challenge of WDM is to understand the correlated-electron-ion physics of partially ionized fluids to develop theoretical equation-of-state (EOS) models for Inertial Confinement Fusion (ICF) and EOS models of deep interiors of giant exoplanets.

Methods

Because of the challenge of WDM, experimental data are needed to suggest possible directions for theory of WDM. An enormous published database of measured Hugoniot data was accumulated for WDM in the last decades of the 20th Century. The bulk of that shock-compression data is in the range ~0.3 to 20 TPa (200 Mbar). That data was analyzed to determine what could be learned systematically from that substantial database.

Results

Below ~0.3 TPa residual effects of ambient structures are evident. Just above ~0.3 TPa Hugoniots of dense fluids have curvature but no definitive distinct features. Above 20 TPa substantial effects of electron shells are predicted. In the range just above ~0.3 TPa most materials with initial density r_0 such that $2.5 < r_0 < 10$ g/cm^3 have a common linear Hugoniot $u_s = C + Su_p$, where C = 5.9 km/s and S=1.22. This common universal Hugoniot is essentially satisfied by Al, Fe, Cu, Mo, Kr, Xe, SiO_2, $Gd_3Ga_5O_{12}$, etc. For a free-electron gas S = 1.33, which is significantly greater than 1.22 of WDM, which suggests this difference in S might be caused by electron correlations in WDM.

Conclusions

The theoretical challenge is to determine why so many materials have a common universal Hugoniot of fluid metals (UHFM) in the WDM regime and why the C and S have the values they do.

O 18.11

Release behavior and equation of state models for high density carbon at the national ignition facility

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Research to achieve controlled thermonuclear fusion gain in the laboratory is on-going at the National Ignition Facility (NIF), the world's largest laser facility at Lawrence Livermore National Laboratory in California. The main approach investigated is the indirectly driven laser compression of a Deuterium-Tritium (DT) ice shell surrounded by an *ablator* material which is ablated away to launch accurately tuned compression waves in the DT shell by *rocket-effect*.

While CH polymers are the most generally used ablator materials, nanocrystalline diamond, or High Density Carbon (HdC), has many advantages due to its higher density and incompressibility. Extended knowledge about its equation of state and transport properties at extreme densities, pressure and temperatures is critical to help design and analyze integrated inertial confinement fusion (ICF) experiments using HdC ablator at the NIF.

We will report shock and release impedance matching measurements between HdC and liquid deuterium using ultrafast Doppler velocimetry (VISAR) to track the velocity of strong shocks transmitted from a HdC capsule into fluid liquid deuterium up to ~ 15 Mbar in HdC.

We will discuss how the new data compare with the current equation of state tabular models used in radiative-hydrodynamic simulations of ICF experiments as well as with advanced density-functional-theory based molecular dynamics simulations and previous experimental data on dynamically compressed diamond.

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O 18.12

Investigating the hydrogen plasma phase transition on the national ignition facility

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New dynamic-compression techniques allow scientists to recreate the material states expected to exist in the deep interiors of planets, including the newly discovered extra solar planets.

At the conditions existing deep inside stars and planets, pressure produces highly degenerate conditions (strong quantum effects), with atoms brought closer than the Bohr radius. State-of-the-art calculations indicate that such strong degeneracy effects induce the insulator-conductor transition in fluid hydrogen to become first-order, i.e. discontinuous, at temperatures below about 2500 K. This phase transition is called the Plasma Phase Transition (PPT). This problem challenges the most advanced simulations and theories resulting in a span of proposed conditions for the PPT from 1 to 5 Mbar, between 1000 and 2500 K. At higher temperature the metallization onset is thought to be continuous.

We will present recent experiments using a reverberation compression scheme on the National Ignition Facility to compress cryogenic deuterium up to several megabars while keeping the temperature much lower than using single shock compression.

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P 18.1

In situ observation of high-pressure phase transition in silicon carbide under shock loading using ultrafast x-ray diffraction

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The behavior of silicon carbide (SiC) under shock loading was investigated through a series of time-resolved pump-probe diffraction measurements reaching stresses up to 200 GPa. SiC is an important high-strength ceramic material used for a range of technological applications, including lightweight impact shielding and abrasives. SiC is also relevant to geology and planetary science. It may be a host of reduced carbon in the Earth's interior and also occurs in meteorites and impact sites. SiC has also been put forward as a possible major constituent in the proposed class of extra-solar planets known as carbon planets. Understanding the high-pressure response of SiC is pertinent to improving the design and performance of impact shielding. Additionally, these measurements determine the phase stability at pressures exceeding one megabar and provide information that is relevant to understanding the role of SiC in planetary interiors. Previous studies have used wave profile measurements to identify a phase transition under shock loading near 1 Mbar, but lattice-level structural information was not obtained. Our experiments were conducted at the Materials in Extreme Conditions beamline of the Linear Coherent Light Source. *In situ* x-ray diffraction data on shock-compressed SiC was collected using a free electron laser source combined with a pulsed high-energy laser. These measurements allow for the determination of time-dependent atomic arrangements, demonstrating that the hexagonal wurtzite phase (4H) of SiC transforms directly to the B1 structure. Our measurements also reveal details of the material texture evolution under shock loading.

Invited Talk

Candidate carbonate minerals at Earth's mantle conditions

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Carbonate may act as carbon host phase in the Earth's mantle, and the presence of carbonate as diamond inclusion confirm that, at least in the upper mantle, they coexist with elemental carbon (and/or with c-bearing fluids). However, the knowledge of the possible form of carbonate was unclear. In the last decade, theoretical and experimental works have significantly addressed the question about the structures adopted by carbonates at high pressure. The results are overviewed. The most significant results achieved indicate the following.

1) calcite-type structure may transform into denser and thermodynamically stable polymorphs at lower mantle conditions for all the compositions between the end-member $CaCO_3$-$MgCO_3$-$FeCO_3$. Dolomite, $CaMg(CO_3)_2$ is stable and does not decompose into pure component.

2) Fe-carbonate may transform into complex stoichiometries featuring Fe^{3+} and silicate-like topology with tetrahedral carbon at lower mantle conditions.

3) above the Mbar is predicted and experimentally observed a carbonate with cyclo-carbonate rings. The scenario is getting clear and the experimental data may constitute a robust reference for ab-initio thermodynamical computing of the possible actual stability in equilibrium with mantle rocks.

Invited Talk

Carbon species in silicate melts and glasses

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We study the speciation and behaviour of carbon species in forsterite and pyrolite melts from molecular dynamics simulations. We consider several species: atomic carbon, molecular carbon dioxide and carbonate ions. We followed the carbon speciation as a function of pressure and its entry state in the system. The general tendency is to increase coordination by O with increasing pressure. The natural series of coordination is CO - CO_2 - CO_3 - CO_4. However, the exact sequence depends on the state of the carbonaceous molecule that is introduced in the melt.

When atomic C is introduced in the melt as an isolated atom, it goes through several coordination states with increasing pressure. Around 0 GPa it sticks from outside to an O atom of a SiO_4 tetrahedron; together they form a SiO_4C complex. Under pressure the coordination changes first to CO_2, which is an isolated molecule, free to diffuse in the melt, then to CO_3 groups. When CO_2 is introduced in the system as a molecule its integrity is preserved at low pressure. With increasing pressure carbon increases its coordination number forming first CO_3 groups, which are quasi-planar, and then CO_4 tetrahedra. This happens well beyond the megabar pressures. Finally, when CO_3^{2-} is introduced it shows only the last two states - CO_3 and CO_4.

The compressibility of glasses clearly depends on the thermodynamic path of obtaining them. Just as in experiments annealing helps removing stresses and enhances polymerization.

O 19.1

Transition metal carbonates ($MnCO_3$, $CoCO_3$) at extreme conditions

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Many studies have examined the behavior of the carbonates $CaCO_3$, $MgCO_3$ and $FeCO_3$ at extreme conditions, motivated by the many natural samples that prove carbonates to be present in the Earth's deep interior. However, these carbonates present distinct behaviors to each other at mantle conditions. Studying the rarer transition metal carbonates, such as rhodochrosite ($MnCO_3$) and spherocobaltite ($CoCO_3$), can therefore be useful to identify systematics in carbonate behavior at high pressures and high temperatures. Therefore, we synthesized pure single crystals of $MnCO_3$ and $CoCO_3$ and studied them to 57 and 65 GPa, respectively, in diamond anvil cells using single crystal synchrotron X-ray diffraction (XRD) and Raman spectroscopy. Although no new Raman peaks appear for $CoCO_3$ up to 55 GPa, suggesting regular behavior, many new Raman peaks appear for $MnCO_3$ above 40 GPa, indicating a structural transformation (Fig. 1). Indeed, XRD reveals that $MnCO_3$ (R-*3c*) transforms to $MnCO_3$-II (P-*1*) above 43 GPa, which is equivalent to the $CaCO_3$-IV structure [1]. In contrast, $CoCO_3$ is stable in the structure up to 56 GPa, even after heating at 1200 K. We determined the equation of state (EoS) for $CoCO_3$ (K=130.1(1) GPa, K'=4.34) and $MnCO_3$-II (K=93.0(1) GPa, K'=4) and found that the EoS of $MnCO_3$ (K=106.9(1) GPa, K'=4) in [1] also fits our data (Fig. 2). We observed that the CoO_6 and $MnCO_6$ octahedra become regular at 16 and 15 GPa, respectively. Furthermore, our results so far do not indicate any spin transitions in the studied pressure ranges. Finally, we observed partial thermal decomposition of $CoCO_3$ into CoO at 57 GPa and above 2000 K, while MnCO3-II decomposed into a monoclinic $MnCO_3$-phase and a coexisting Mn_5O_7 phase. Our results provide insight into the high-pressure crystal chemistry of carbonates and the effect of alkaline-earth cation (i.e., Ca^{2+}, Mg^{2+}) substitution by a 3d transition metal on the stability field of carbonates.

[1] Merlini et al. (2015), Am. Min., 100, 2625-2629

Figure 1. Raman spectra of $CoCO_3$ and $MnCO_3$.

Figure 2. Equation of state for $CoCO_3$ and $MnCO_3$.

Figure 1

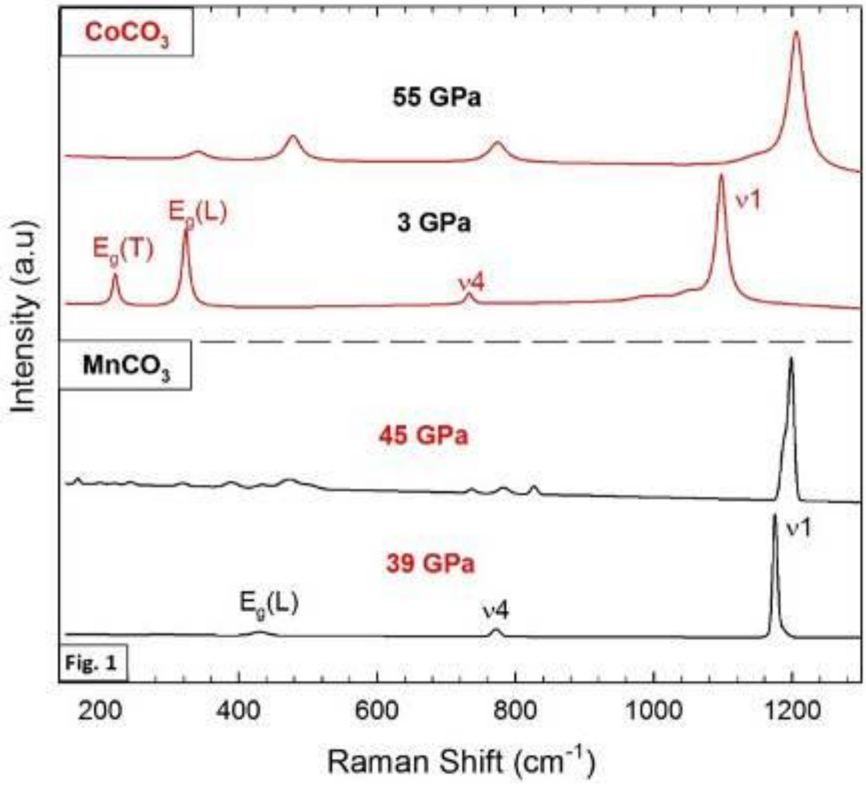
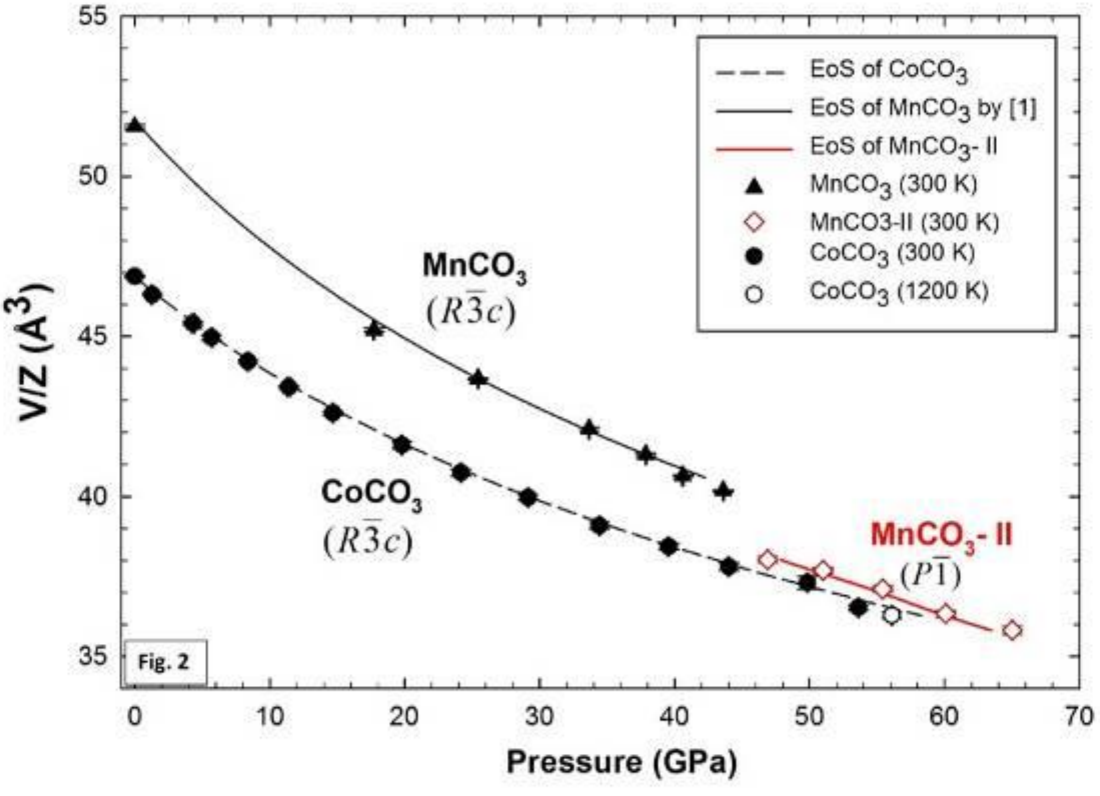


Figure 2



O 19.2

High pressure studies on carbonate crystals using coherent anti-Stokes Raman Spectroscopy

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Spontaneous Raman spectroscopy is one of the main tools for unambiguous sample characterization in diamond anvil cell (DAC) based experiments, but it has its shortcomings for investigations at simultaneous high pressure and temperature. Coherent anti-Stokes Raman spectroscopy (CARS) might overcome these problems, due to the fact that the signal intensity can be enhanced by several orders of magnitude and therefore eliminate the influence of thermal radiation or fluorescence effects [1-3].

CARS relies on a nonlinear optical process, in which a laser beam of a fixed pump frequency ω_{pump} interacts with a tunable laser ω_{probe}. If the probe laser equals a Stokes frequency ω_{Stokes} the corresponding anti-Stokes signal ω_{CARS} is enhanced (Fig. 1).

The aim of this study is to employ coherent anti-Stokes Raman spectroscopy on carbonates in DACs at ambient temperature and high pressures and to determine the pressure dependence of the Raman modes of carbonates detected by CARS.

Our CARS setup consists of a pulsed Nd: YAG laser to pump the CARS signal (ω_{pump} = 532 nm) and additionally to pump an optical parametric oscillator (OPO) with ω = 355 nm. The OPO output is tuned in a range from 532 to 570 nm and is used as the probe laser.

In this study we present CARS spectra of different natural and synthetic carbonate single crystals, such as siderite, calcite and other geological important representatives (Fig. 2). The pressure dependence of the Raman modes of carbonates are measured and compared to results of spontaneous Raman spectroscopy [4].

Our results show the feasibility of CARS for high pressure measurements on carbonates. For future work we will focus on CARS at simultaneous high pressures and temperatures in order to get new insights on the phase relations of carbonate minerals under upper mantle conditions.

Fig. 1 CARS energy diagram

Fig. 2 Typical spectrum of calcite, dashed line: filter transmittance

Financial support from the DFG (FOR2125) is gratefully acknowledged.

[1] Baer et al., *Rev. Sci. Inst.* **76** 13907 (2005).

[2] Baer et al., *Phys. Rev. Lett.* **98** 235503 (2007).

[3] Hellwig et al., *J. Chem. Phys.* **115** 10876 (2001).

[4] Farfan et al., *Am. Mineral.* **97** 1421-1426 (2012).

Figure 1

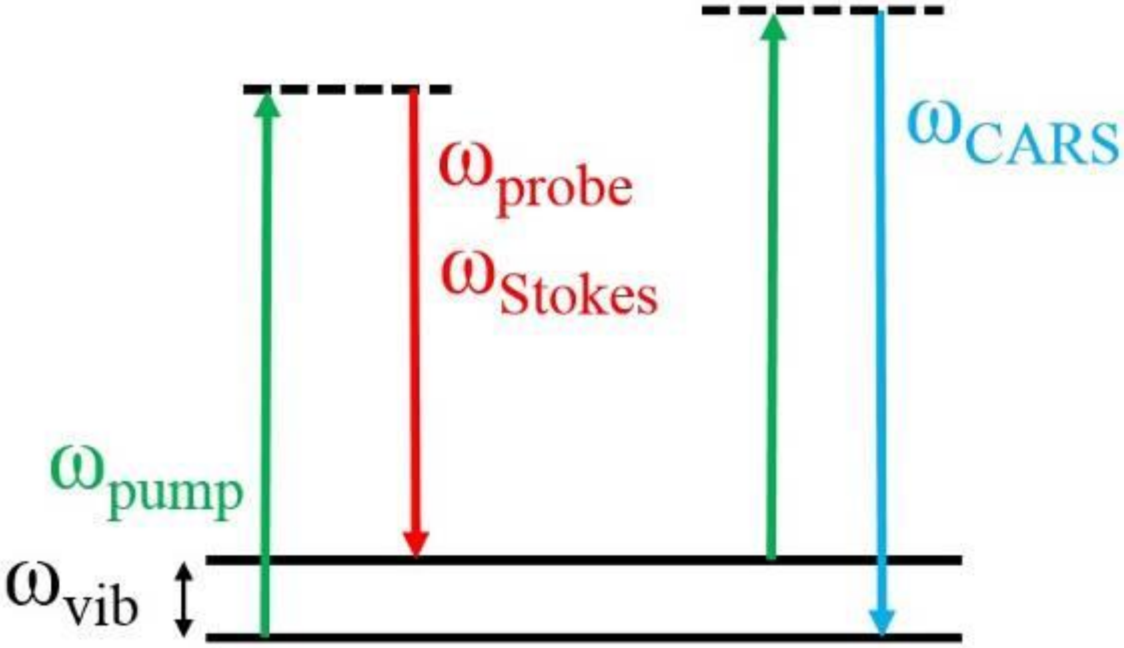
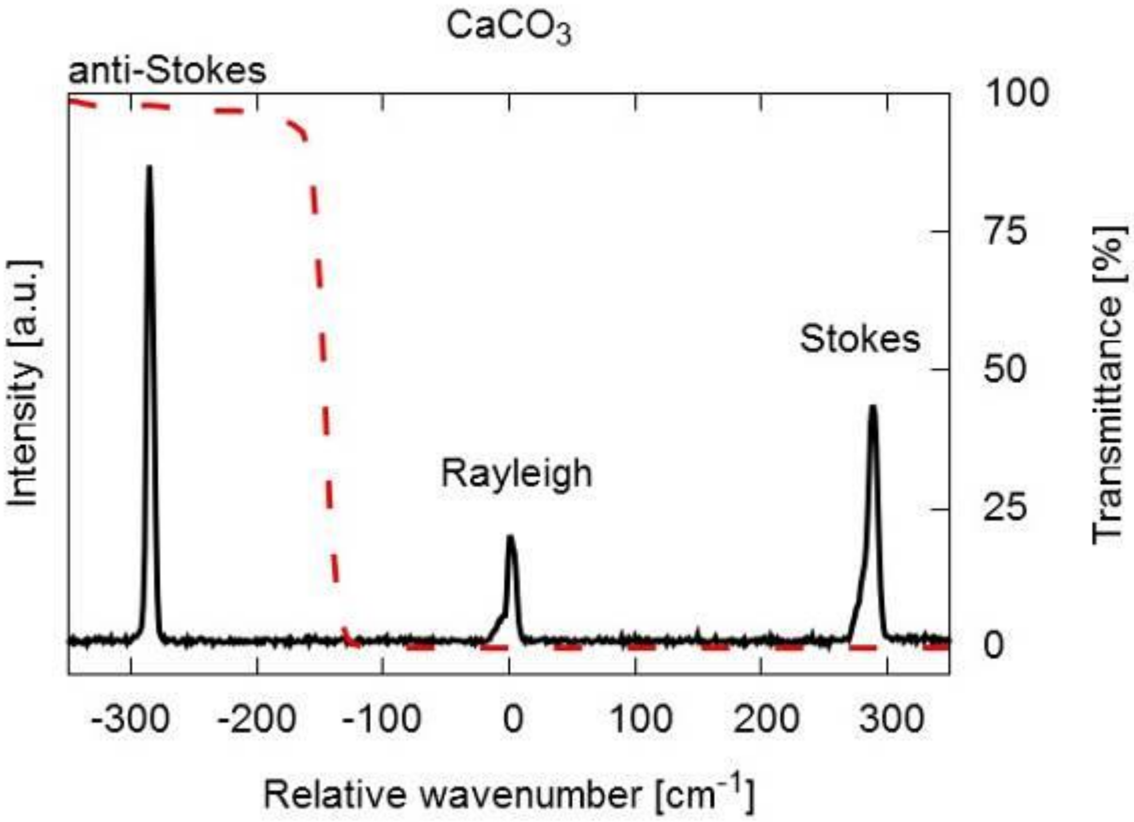


Figure 2



O 19.3

Melting relations in the system $CaCO_3$-$MgCO_3$ at 6 GPa: A comparison between anhydrous and hydrous conditions

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Buob et al. (2006) performed sub- and super-solidus experiments in the anhydrous system $CaCO_3$-$MgCO_3$, using the multi-anvil press at 6 GPa. In comparison to the low pressure experiments by Byrnes & Wyllie (1981) and Irving & Wyllie (1975) in the system $CaCO_3$-$MgCO_3$, Buob et al. (2006) showed how higher pressures have a large impact on the topology of the phase diagram. However, Buob et al. (2006) reported quenching problems, which made the determination of the phase relations at the Mg-rich side of the phase diagram at 6 GPa impossible. Furthermore, the melting point of magnesite at 6 GPa is controversially reported. Buob et al. (2006) estimate it to 1650 °C based on experiments of Irving & Wyllie (1975), while Shatskiy et al. (2014) propose to 1900 °C based on experiments of Katsura & Ito (1990).

In order to determine liquidus and solidus in the Mg-rich part of the system we performed rotating multi-anvil experiments in the super-solidus field on the Mg-rich side of the phase diagram under anhydrous and hydrous conditions. By the use of the rotating press we were able to overcome the quenching problems as we could separate crystals and melt. In order to determine the melting point of the pure endmember we performed falling sphere experiments also under anhydrous and hydrous conditions.

Under anhydrous conditions the shape of the two-phase field where melt and crystals co-exist is significantly different from that estimated by Buob et al. (2006). The melting point of magnesite at 6 GPa and anhydrous conditions could be narrowed down between 1750 and 1800 °C. Under hydrous conditions liquidus and solidus moved to lower temperatures as expected.

References

Buob et al. (2006), *Am. Min.* **91**, 435-440.

Byrnes, A. & Wyllie, P. (1981), *Geochim. Chosmochim. Acta* **45**, 321-328.

Irving, A. & Wyllie, P. (1975), *Geochim. Chosmochim. Acta* **39**, 35-53.

Katsura, T. & Ito, E. (1990), *Earth Planet. Sci. Lett.* **99**, 110-117.

O 19.4

High pressure elastic properties of $FeCO_3$

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Iron carbonate, $FeCO_3$, is an endmember of carbonates occurring in Earth's mantle. Therefore, it is interesting from geophysical point of view to understand the elastic properties of this material at high pressures. At 45 GPa siderite undergoes a spin transition associated with 10% volume collapse [1], no symmetry change is associated with this transition.

Synthetic $FeCO_3$ powder was synthesized in two steps by the hydrothermal method, single crystals were grown from powder in a multi-anvil press. Inelastic X-ray scattering experiment of $FeCO_3$ in a diamond anvil cell was performed at ID28 at the ESRF. Phonon excitations were measured with 3 meV energy resolution at different Brillouin zone points.

Phonon dispersion curves were measured at different pressures, below and above the spin transition. Transverse and longitudinal acoustic phonons were observed. By measuring their velocities and using Christoffel's equation, elastic stiffness coefficients were calculated. The data analysis is currently ongoing and will be complemented by DFT based calculations.

The study is supported by project DFG-ANR WI1232/41-1.

[1] B. Lavina et al., *Geophys. Res. Lett.,* vol. 36, pp. L23306, 2009.

O 19.5

Vibrational properties of dolomite at extreme conditions

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Carbonates are the most abundant carbon-bearing minerals and widely considered as major candidates for carbon subduction processes into the deep Earth [1]. As one of the most common carbonates, the behavior of dolomite $CaMg(CO_3)_2$ under variant pressure and temperature conditions has attracted significant attention over the years [2]. It was only recently, however, that two structural polymorphs could be identified at 17 GPa (dolomite-II) and 35 GPa (dolomite-III) at room temperature [3]. Interestingly, dolomite-III was reported to be stable up to 2400 K, thus making this phase a viable candidate for carbon subduction into the Earth's mantle [3]. Despite the determination of the structural response, however, the vibrational signature of the dolomite high-pressure phases remains elusive.

Here we present our high-pressure infrared and Raman investigation of an iron-free natural dolomite [4]. Our studies reveal two phase transitions near 17 GPa and 35 GPa, consistent with the aforementioned XRD results [3]. Spectroscopic measurements at combined high-pressure and high-temperature conditions allowed us to detect the stability regions of both dolomite high-pressure phases over an extended *P-T* range. Preliminary results indicate a positive *P-T* slope for the phase boundary between the dolomite and dolomite-II structures, whereas a negative slope was resolved for the dolomite-II and dolomite-III phase boundary. We discuss the implications of the Fe content on the structural stability of the various dolomite phases, as well as compare our results with relevant studies on carbonates.

[1] Dasgupta R., Hirschmann M. M., 2010, Earth Planet. Sci. Lett. 298, 1-13 and refs therein.

[2] Mao Z., Armentrout M., Rainey E., Manning C. E., Dera P., Prakapenka V. B., Kavner A., 2011, Geophys. Res. Lett. 38, L22303 and refs therein.

[3] Merlini M., Crichton W. A., Hanfland M., Gemmi M., Muller H., Kupenko I., Dubrovinsky L., 2012, Proc. Natl. Acad. Sci. 109, 13509-13514.

[4] Heinrich W., Metz P., Bayh W., 1986, Contrib. Mineral. Petrol. 93, 215-221.

O 19.6

Stability of high-pressure polymorph of topaz-OH

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Water is considered to be transported into the deep interior of the Earth by hydrous minerals in a subducting slab. Topaz-OH has been considered to be one of water carriers in the sediment layer of subducting slabs [1,2]. Recent experimental studies showed that Topaz-OH transforms to a high-pressure polymorph, Topaz-OH II [3]. However, the stability field of Topaz-OH II has not been constrained precisely yet. Here, we report on the stability field of Topaz-OH II determined by high-pressure and -temperature experiments.

The starting material was prepared in the MgO-Al_2O_3-SiO_2-H_2O (MASH) systems. Experiments were carried out using a 1000-ton Kawai type multi-anvil apparatus at Tohoku University, Japan. The pressure was calibrated by using the β-γ phase boundary of Mg_2SiO_4. We collected the X-ray diffraction patterns of samples recovered from high-pressure and high-temperature conditions to identify the experimental products at Photon Factory in KEK, Japan. Chemical composition was analyzed by an electron probe microanalyzer at Tohoku University.

δ-AlOOH and phase egg ($AlSiO_3OH$), which could be hydrous phases in the sediment layer of slabs penetrated to the mantle transition zone, and Topaz-OH II were found in the samples recovered from 18-20 GPa and 1000-1300 °C and from 18 GPa and 1400 °C, respectively. Those results show that Topaz-OH II has broader stability field than that reported by previous studies and suggest that Topaz-OH II could be a potential candidate of the water carrier at the middle of the mantle transition zone.

References

[1] Wunder, B., Medenbach, O., Krause, W., Schreier, W. (1993) *Eur. J. Mineral.* **5**, 637-649.

[2] Ono, S. (1998) *J. Geophys. Res*. **103**, 18253-18267.

[3] Kanzaki, M. (2010) *Am. Mineral.* **95**, 1349-1352.

O 19.7

Ammonia monohydrate at high pressure

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Knowing the properties of H_2O, NH_3 and their mixtures under high pressure and temperature is important for planetary science because these H-bonded ices are present in Jovian planets and their satellites under a wide range of pressure (P) and temperature (T) conditions. The high P-T properties of the pure ice compounds have been the focus of many investigations, which have revealed a rich polymorphism. By contrast with the pure components, there are rather few information available on the properties of the dense phases of H2O/NH3 mixtures, although the latter are crucial for the description of icy planets.

Depending on the mixture concentration, three types of ammonia/water compounds can be obtained: ammonia monohydrate (H_2O,NH_3) (noted AMH), ammonia hemihydrate ($H_2O,2NH_3$) and ammonia dihydrate ($2H_2O,NH_3$). Experimental high-pressure studies on AMH have been done up to 10 GPa and a large polymorphism has been observed : six phases of AMH have been reported (170 Kab initio calculations. Only the structure of the three phases, I, II and VI, have been determined. Actually, AMH is the simplest system to contain O-H…N and N-H…O heteronuclear hydrogen bonds. The structure of phase VI [1] is of particular interest as it is a substitutionally-disordered molecular alloy whose simple BCC structure is related to that of H_2O ice VII. A recent theoretical study [2] has suggested that the ammonia monohydrate (AMH) molecular solid transforms into an ionic solid composed of NH_4^+ and OH^- ions, in a similar fashion as the self-ionization observed in pure ammonia [3,4], but at much lower pressures (10 GPa instead of 150 GPa), thus much easier to reach in experiments.

In this presentation, we will present new experimental and theoritical investigations of the phase diagram of AMH. In particular, to test this surprising prediction, we have performed infrared absorption studies, Raman scattering and X-ray diffraction of AMH up to 40 GPa. We will discuss the existence of the molecular/ionic phase transition.

[1] J. S. Loveday and R. J. Nelmes, Phys. Rev. Lett. **83**, 4329 (1999)

[2] G. I. G. Griffiths, A. J. Misquitta, A. D. Fortes, C. J. Pickard, and R. J. Needs, J. Chem. Phys. **137**, 64506 (2012)

[3] S. Ninet, F. Datchi, P. Dumas, M. Mezouar, G. Garbarino, A. Mafety, C.J. Pickard, R.J. Needs and A.M. Saitta, Phys. Rev. B, **89**, 174103 (2014)

[4] T. Palasyuk, I. Troyan, M. Eremets, V. Drozd, S. Medvedev, P. Zalesky-Ejgierd, E. Magos-Palasyuk, H. Wang, S. Bonev, D. Dudenko et P. Naumov, Nat. Comm., 5, 3460 (2014)

O 19.8

Shock-wave treatment of carbonates at pressures beyond 100 GPa - new possibilities for an old method?

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Question

For the high-pressure treatment of sensitive phases shock-wave methods doesn't play a role for the synthesis of new interesting phases. Will it be possible to develop a new method for pressures beyond 100 GPa and high temperatures, which allows the synthesis of new phases, with this method too?

Methods

In the shock-wave lab of the TU Bergakademie Freiberg new methods were developed to solve especially these problems for the synthesis in the pressure range beyond 100 GPa. This include the impedance correction of the sample recovery capsule, a better control of the melting behavior along the release path [1] and the "halide based method of shock-wave treatment of fluid rich natural phases" at pressures up to 116 GPa [2].

Results

An example of shocked calcium carbonate at 116 GPa and approx. 4600 K (single ramp compression) is given in figure 1. In its NaCl-matrix the crystals are free of fractures and indications of degassing (fig. 1A). The crystallites without decay reactions shows a smooth surface and the products of recrystallization (secondary $CaCO_3$) shows a very fine grained rough crystal shape (fig. 1B).

Conclusions

With the new methods the shock wave treatment of carbonates up to p>100 GPa is now possible. This will open new future possibilities for the shock wave synthesis, because the behavior of these kinds of materials under shock in this pressure range is not yet known.

Acknowledgements

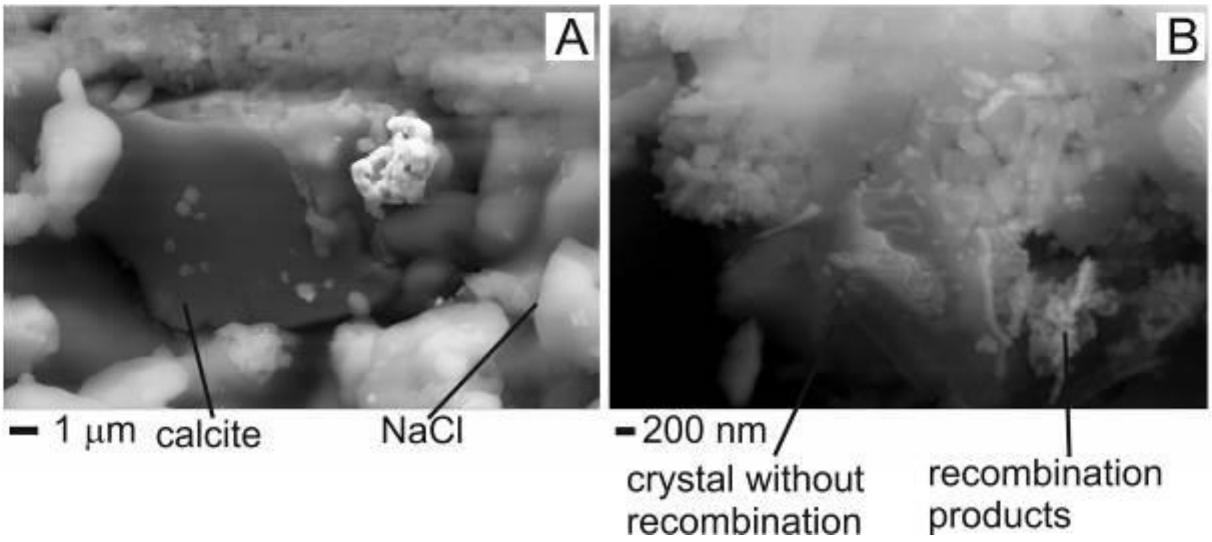
The build-up of the shock-wave-lab at the TU Bergakademie Freiberg was completely funded by the Dr. Erich-Foundation. This work was funded by the DFG-research group FoGru2125 "Carbonates ax high temperatures and pressures" CarboPaT.

References

[1] Schlothauer T., Schimpf C., M. R. Schwarz, Kroke E. and Heide G., in *Equations of State for Matter Elbrus 2016*, edited by Fortov V.E., Karamurzov B.S., Efremov V.P., Khishchenko K.V., Sultanov V.G., Kadatskiy M.A., Andreev N.E., Dyachkov L.G., Iosilevskiy I.L., Kanel G.I., Levashov P.R., V. B. Mintsev, Savintsev A.P., Shakhray D.V., and Shpatakovskaya G.V. (Moskwa, Cernogolovka, Nalchik, 2016), p. 130.

[2] T. Schlothauer, C. Schimpf, E. Brendler, K. Keller, E. Kroke and G. Heide, Journal of Physics: Conference Series **653** (2015) 012033.

Figure 1


A
B
1 µm
calcite
NaCl
200 nm
crystal without recombination
recombination products

P 19.1

From the crust to the core, $FeCO_3$ stability field in the deep Earth

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Carbonates play a fundamental role in the recycling of carbon inside our planet due to their presence in oceanic slabs that sink through the Earth's interior. Through this process, iron carbonates are potential stable carbon-bearing minerals in the deep mantle in part due to spin crossover of ferrous iron. Our goal is to identify which minerals may be the dominant carriers of carbon into the deep mantle at the relevant conditions of fO_2, P and T. All experiments were performed using synthetic $FeCO_3$ and $MgFeCO_3$ single crystals in laser heated diamond anvil cells up to 100 GPa and 2500 K in order to simulate the conditions prevailing in the Earth's lower mantle. Transformation and decomposition products of the original carbonates were characterized at different synchrotron facilities by means of single-crystal XRD, synchrotron Mössbauer source spectroscopy and XANES techniques. At deep lower mantle conditions, we observed the transformation of $FeCO_3$ to two new HP-carbonate structures, monoclinic $Fe_2^{2+}Fe_2^{3+}C_4O_{13}$ and trigonal $Fe_4^{3+}(CO_4)_3$, both characterized by the presence of CO_4 tetrahedra with different degrees of polymerization. At shallower depths in the lower mantle where temperatures are lower following the geotherm, Fe-carbonates decompose to different Fe-oxides instead of new HP-carbonates. However, at slab temperatures several hundred degrees lower than the surrounding mantle, carbonates could be stabilized until reaching conditions that trigger their transformation to HP-structures. We postulate that Fe-rich carbonates could exist in regions down to the core-mantle boundary in the proximity of subducting slabs, i.e., a "cold" environment with relatively high fO_2.

P 19.2

Elastic properties of iron-bearing carbonates and implications for the deep Earth

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Current models predict the occurrence of carbonates in subducting slabs, yet their presence may be challenging to detect using geophysical methods due to their low abundance relative to other phases. One of the important parameters in deciphering seismic data is the elastic properties of iron-bearing carbonates at high pressure and temperature, particularly the anisotropy and the effect of the high-spin to low-spin transition reported in the literature to occur in Fe^{2+} around 50 GPa. Up to now, however, elastic wave velocities of iron-bearing carbonates have not been measured through the spin transition. To address this problem, we undertook a diamond anvil cell study of iron-bearing carbonates on the Nuclear Resonance beamline (ID18) at the European Synchrotron Radiation Facility in Grenoble, France. Elastic wave velocities were derived from nuclear inelastic scattering data, and results show a substantial increase in shear wave velocity through the spin transition. We will present our latest results and discuss implications for the detectability of carbonate in the deep Earth.

P 19.3

Single-crystal elasticity of $SrCO_3$ by Brillouin spectroscopy and density functional theory calculations

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Carbonates are key carriers of carbon into the deep mantle and they were found to be stable at conditions of the lower mantle. They are present as inclusions in transition-zone diamonds [1]. Strontianite ($SrCO_3$), which is a component in all natural carbonates, is isostructural to aragonite, a major high-pressure polymorph of $CaCO_3$, and therefore a model material to investigate the stability and physical properties of carbonates at high pressure and high temperature. The available data on the elastic properties of aragonite-type carbonates are still scarce. The present study provides the first experimental data for the stiffness tensor C_{ij} of $SrCO_3$. Strontianite was synthesized at 4 GPa and 1273 K for 24h in a multi-anvil apparatus. We used Brillouin spectroscopy to investigate the elastic properties of synthetic $SrCO_3$ single-crystals at ambient conditions (293 K, 1 bar). An inversion procedure based on Christoffel's equation was used to determine the 9 independent elastic coefficients of orthorhombic strontianite from previously measured acoustic velocities along 69 different crystallographic directions. The linear compressibilities of *a*, *b* and *c* axis at ambient conditions are 3.1 x 10^{-3}, 3.8 x 10^{-3} and 10.0 x 10^{-3} GPa^{-1}. The adiabatic bulk modulus is 63 ± 1 GPa. A comparison with the elastic moduli of other aragonite-type carbonates confirms a systematic linear relationship between cation radius and bulk modulus. The shear modulus for $SrCO_3$ is 32.0 ± 5 GPa, which is about 10 % smaller in comparison to aragonite [2]. The experimental study was complemented by density functional theory based calculations. Using a stress-strain approach, the full elastic stiffness tensor was obtained. The agreement between the experimental and the theoretical data is generally very good. Deviations between the two data sets are likely due to limitations of the experimental set-up and will be discussed in the presentation.

References

[1] Brenker, F. et al., Earth Planet. Sci. Lett., 260, 1, 2007.

[2] Liu, L.-G. et al., Phys. Chem. Minerals, 32, 97, 2005.

P 19.4

High-pressure phase behavior of $SrCO_3$ – an experimental and computational Raman scattering study

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Carbonates are key-phases in the chemistry and dynamics of our planet. They are present from marine environments down to the lower mantle. Carbonate inclusions in kimberlitic diamonds have been shown to carry significant amounts of Sr [1,2]. Very little is known about the carbonate stability of pure endmember minerals. Therefore, we have studied the high-pressure phase behavior of the endmember $SrCO_3$ by Raman spectroscopy and density functional theory (DFT) based calculations. Strontianite ($SrCO_3$) is a component in all natural carbonates and is isostructural to aragonite, a high-pressure polymorph of $CaCO_3$. Strontianite was synthesized at 4 GPa and 1273 K for 24h in a multi-anvil apparatus. We compressed single-crystals or powder samples in the diamond anvil cell, and measured Raman spectra up to 78 GPa. We observed a transition at 25 ± 2 GPa during compression to a new high-pressure structure, which is accompanied by significant changes in the vibrational spectrum. The very satisfactory agreement between the observed and computed frequencies and intensities implies that the high pressure polymorph has space group *Pmmn* which is in agreement with previously published high-pressure structures for other aragonite-type carbonates [3-5]. The transition pressure from the aragonite to a post-aragonite structure linearly depends on the cation radius for (Ca,Ba,Pb,Sr)-carbonates.

References

[1] Brenker, F. et al., Earth Planet. Sci. Lett., 236, 579, 2005.

[2] Brenker, F. et al., Earth Planet. Sci. Lett., 260, 1, 2007.

[3] Ono, S. et al., Phys. Chem. Minerals 32, 8, 2005.

[4] Oganov, A. et al., Earth Planet. Sci. Lett., 241, 95, 2006.

[5] Ono, S., Phys. Chem. Minerals 34, 215, 2007.

P 19.5

The elastic stiffness tensor of natural dolomite

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Mg,Ca,Fe-carbonates are important carriers of carbon to the deep Earth interior. They are stable at conditions of the deep mantle, and are present as inclusions in natural diamonds [1]. The compressibility of simple and binary carbonates is a key parameter for thermodynamic modeling of complex carbonates in the deep Earth. However, the number of extant experimental studies of the elastic properties is extremely limited. The elastic tensor of dolomite $CaMg(CO_3)_2$ has been determined in two studies, which show clear disagreement [2,3]. To solve this disagreement, we have determined the full tensor of a natural dolomite single-crystal by Brillouin scattering sampling a larger range of crystal orientations than the previous studies. We have prepared two platelets with orientations (-8 -2 10) and (9 -10 2) from a natural crystal from the Eugui metamorphic complex [4]. We have determined 114 individual acoustic wave velocities in 72 different crystallographic directions. We have then fitted the 7 independent coefficients (C_{ij}) of the elastic tensor and calculated linear compressibilities (β_a, β_c) and the aggregate bulk and shear moduli (K, G). K and G are 84 ± 1 and 39 ± 1 GPa; β_a and β_c are 2.52 ± 0.05 x 10^{-3} and 6.85 ± 0.05 x 10^{-3} GPa^{-1}. G is in excellent agreement with the previous elasticity studies, while K, β_a and β_c are only marginally consistent, confirming the need of a large dataset of velocities. Both β_a and β_c determined in our Brillouin scattering study are larger than those determined by a recent X-ray diffraction study of single crystals from the same source (1.71 ± 0.03 x 10^{-3} and 5.21 ± 0.05 x 10^{-3} GPa^{-1}; ref. [5]). The apparent disagreement is caused by the strong correlation between elastic moduli and their pressure derivative fitted from X-ray diffraction data. The same X-ray diffraction study of dolomite at high pressures [5] has documented a change of β_a and β_c associated to cation disordering. We have then thermally disordered our sample (at 1500 K and 3 GPa) and measured Brillouin scattering of the recovered material. Our first, partial results show that the effect of cation disordering is negligible for the constants C_{11}, C_{12} and C_{44} while constants C_{33} and C_{13} stiffen.

References

[1] Brenker, F. et al., Earth Planet. Sci. Lett., 260, 1, 2007.

[2] Humbert, P., F. Plique, Comp. Rend. Acad. Sci. Paris, Ser. B, 275, 391, 1972.

[3] Chen, P.-F. et al., Phys. Earth Planet. Inter., 155, 73, 2006.

[4] Pilger, A. Clausthaler Geol. Abh., 12, 95, 1979.

[5] Zucchini, A. et al., Phys. Chem. Minerals, 41, 783, 2014.

P 19.6

Deformation of water ice VI: a single-crystal X-ray diffraction study

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High-pressure polymorphs of water ice form significant portion of outer space icy sattelites that are of particular interest to planetary science. Different processes of accretion, differentiation and early evolution followed by each sattelite are governed by the elastic and rheological propeties of the constituent materials. In order to obtain insight in the deformation mechanism of these high-pressure ices, we adopted a novel approach which make use of single-crystal X-ray diffraction (SCXRD).

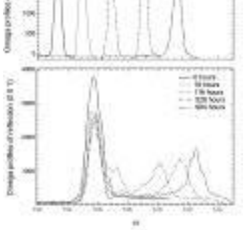
Two single crystals of ice VI have been grown *in situ* inside a four-screw diamond anvil cell at room temperature. The single-crystal X-ray diffraction experiments were performed at 1.2-1.4 GPa and room temperature. The crystals of ice VI were studied using a Huber 4-circle diffractometer to investigate broadening effects due to the applied pressure. Selected reflections profiles were measured repetitively over months in order to monitor their broadening with time.

After c.a. 20 hours, the appearance of an additional peak in the omega profiles of several reflections of one of the crystals, crystal 1, was observed. The difference in the positions of the two peaks of the omega profiles, $\Delta\omega$, increases with time (Fig. 1). A different behavior is observed for the (0 2 1) reflection which remains sharp during the whole experiment at 1.2 GPa (Fig. 1). The larger $\Delta\omega$ was observed for planes oriented perpendicular to the (0 2 1) plane (*e.g.* (400), (201)), whereas planes with smaller interplanar angles to the (0 2 1) have smaller $\Delta\omega$ value. A further increase in pressure to 1.3 GPa also led to significant broadening of the reflections of the second crystal, crystal 2, similar to what observed for crystal 1 at 1.2 GPa.

The uniaxial compression of the DAC leads to bending of the crystals resulting in broadening of the initial ω-profiles and indicates the formation of randomly distributed dislocations. The energy associated with the elastic bending of the crystal lattice is reduced by rearranging the dislocations into a vertical wall to form low angle boundaries. The slip system, deformation mechanism and microstructural evolution of ice VI single crystal will be discussed.

Fig. 1. Evolution of ω-profiles of reflections (201) and (021) of crystal 1

Figure 1



P 19.7

Coupled substitution of Fe^{3+} and H^+ for Si in wadsleyite: a study by polarized infrared and Mössbauer spectroscopies and single-crystal X-ray diffraction

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Wadsleyite is the most abundant mineral in the upper part of the mantle transition zone. Incorporation of water (or hydrogen) in wadsleyite significantly influences its physical properties. Therefore, determination of substitution mechanisms of hydrogen in wadsleyite is fundamentally important to addressing the effects of water on the properties of the upper mantle transition zone. Coupled substitution of Fe^{3+} and H^+ for Si in wadsleyite was studied by polarized infrared and Mössbauer spectroscopies and single-crystal X-ray diffraction. Single crystals of Fe-bearing hydrous wadsleyite were synthesized at 16 GPa and 1870 K using a Kawai-type multianvil apparatus. Water and Fe contents of the sample were 0.19-0.26 wt% H_2O and Fe/(Mg + Fe) of 0.099(2), respectively. Mössbauer spectra showed 13(4) % $Fe^{3+}/\Sigma Fe$ and Fe^{3+} at the tetrahedral site with 5(3) % $^{IV}Fe^{3+}/\Sigma Fe$. Crystal structure refinement by single-crystal X-ray diffraction indicated that Fe (presumably Fe^{3+}) occupied 4.9(5) % of the tetrahedral site. Infrared light polarized with the electric vector **E** // **a** and **c** was absorbed at 3477(2) cm^{-1} while no absorption was observed at the region in spectra with **E** // **b**. The pleochroic behavior of the 3477 cm^{-1} band can be interpreted as protonation of silicate oxygen O3 in Fe-bearing hydrous wadsleyite. The protonation of O3 together with the presence of Fe^{3+} at the tetrahedral site confirms the coupled substitution of Fe^{3+} and H^+ for Si in Fe-bearing hydrous wadsleyite.

P 19.9

Experimental approach for the stability fields of hydrous minerals in the Earth's lower mantle

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[2]*V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Science, Novosibirsk, Japan*
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[4]*Japan Synchrotron Radiation Research Institute, Sayo, Japan*

Introduction

New hydrous silicate ($MgSiO_4H_2$), named Phase H, was discovered by recent first principles calculations and experiments using a multianvil apparatus [1,2]. Phase H is stable at pressures up to 60 GPa [3] and can form solid solution with δ-AlOOH [4,5], which is only hydrous mineral stable at the base of the mantle pressure [6]. In MgO-Al_2O_3-SiO_2-H_2O system, the simplified composition of hydrous peridotite and oceanic crust in a slab, the solid solution can contain δ-AlOOH enough to exist stably at the whole lower mantle [4,5].

However, there is no study showing the possible existence of hydrous phases including Phase H - δ-AlOOH solid solution in actual compositions of a hydrous peridotite and a hydrous oceanic crust at the whole lower mantle *P, T* conditions. To address the stability of the solid solution in natural hydrous rocks, *in-situ* high *P, T* XRD measurements and chemical analyses of recovered sample were conducted at the lower mantle conditions.

Methods

Gel samples having the compositions of hydrous peridotite, and hydrous oceanic crust were used as starting materials. *In-situ* XRD measurements using a laser heated diamond anvil cell were conducted at BL10XU beamline at the SPring-8 synchrotron facility in Japan. Slices of recovered samples were prepared by FIB system and analyzed using FE-SEM/EDS and STEM/EDS at Tohoku university.

Results

In the peridotite system containing 1.0 wt.% H_2O, Phase H - δ-AlOOH solid solution coexists with anhydrous lower mantle minerals at 49-53 GPa and 1550-2210 K. At 76 GP and 1970 K, however, Phase H - δ-AlOOH solid solution was not formed.

Conclusion

The solid solution formed in a hydrous peridotite layer of a slab subducted to the lower mantle may decompose at about 1,500-1,650 km depth. In the session, we will also discuss the stability field of the solid solution formed in a hydrous oceanic crust and its role in the water cycle in the lower mantle.

References

[1] Tsuchiya (2013) *Geophys. Res. Lett.*, **40**, 4570-4573.
[2] Nishi *et al.* (2014) *Nature Geosci.*, **7**, 224-227.
[3] Ohtani *et al.* (2014) *Geophys. Res. Lett.*, **41**, 8283-8287.
[4] Ohira *et al.* (2014) *Earth Planet Sci. Lett.*, **401**, 12-17.
[5] Walter *et al.* (2015) *Chem. Geol.*, **418**, 16-29.
[6] Sano *et al.* (2007) *Geophys. Res. Lett.*, **35**, L03303.
[7] Nishi *et al.* (2015) *Phys. Earth Planet Inter.*, **245**, 52-58

P 19.10

Raman study of methane to 160 GPa

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We present a Raman study of methane (CH_4) to 160 GPa at 300 K. Our data supports the previous reports of several phase transitions at pressures up to 90 GPa in X-ray diffraction studies [1] but does not support the theoretical prediction that methane will dissociate into ethane (C_2H_6) at ultra-high pressures, commencing at 95 GPa [2]. we observe no further phase transitions above 100 GPa. In particular, we observe no evidence for the presence of free hydrogen produced by the dissociation of CH_4; the hydrogen (H_2) vibron was not observed.

[1] L. Sun *et al.*, Chem. Phys. Lett. **473**, 72 (2009)

[2] G. Gao *et al.*, J. Chem. Phys. **133**, 144508 (2010)

Invited Talk

Light complex hydrides: an overview of the recent progress

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The demand for materials with high energy density has driven the research from metal hydrides, having by now excellent cycling properties and the thermodynamics, to much lighter systems based on light *p*-elements bound to hydrogen atoms. The need to break and form strong covalent bonds raises difficulties in the design of these truly "chemical" hydrogen storage systems. Advances in this area started with the discovery of catalysts for the reversible dehydrogenation of alanates [1], and this success inspired the research on even more sturdy borohydrides. A combination of different metals was used to tune the decomposition temperature in the wide range recently [2]. Also, formation of borohydride complexes has been recognized as a design principle, opening the door to the discovery of many new metal borohydrides. I will present design of light complex hydrides based on aluminium chemistry, where Al^{3+} serves as a template for H-conversion [3]. To achieve the ultimate goal of the reversible hydrogen storage using light complex hydrides, the reactive hydride composites (RHCs) have to be explored, considering many combinations of the high H-capacity materials.

An unexpected outcome of the directional metal-borohydride interaction are the porous [4, 5] and dense (obtained at high pressures) [4, 6, 7] frameworks containing less electropositive Mg and Mn, where the BH_4 units serve as linear linkers. The dense phases with high volumetric hydrogen density can be obtained by relatively modest hydrostatic pressure. Already at pressures of 1 GPa, achievable in laboratory steel dies, the amorphous $Mg(BH_4)_2$ can be synthesized, as well as the dense form of $Mn(BH_4)_2$. Both phases can be quenched to the ambient pressure. The porous hydrides can be obtained by chemical methods [4, 5]. I will present the strategy of obtaining porous hydridic MOFs and new unusual properties discovered so far.

[1] B. Bogdanovich, M. Schwickardi, *J. Alloys Compd.* **1997**, *254-256*, 1.

[2] D. B. Ravnsbæk et al., *Angew. Chem. Int. Ed.* **2009**, *48*, 6659.

[3] I. Dovgaliuk et al., *Chem. Eur. J.* **2015**, *21*, 14562; I. Dovgaliuk et al., *Chem. Mater.* **2015**, *27*, 768.

[4] Y. Filinchuk et al., *Angew. Chem. Int. Ed.* **2011**, *50*, 11162.

[5] B. Richter et al., *Dalton Trans.* **2015**, *44*, 3988.

[6] V. Ban et al., *J. Phys. Chem. C* **2014**, *118*, 40, 23402.

[7] N. Tumanov et al., *Chem. Mater.* **2016**, 28, 274.

O 20.1

Ca-H and Y-H systems under high pressure

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Hydrogen - rich compounds remain to be the subject of great interest primarily due to the issue of high - temperature superconductivity which was first suggested theoretically for hydrogen - dominant metallic alloys [1] and then found experimentally in suffer hydride [2]. From the structure search algorithms when combined with the density functional theory calculations it appears that at sufficiently high pressures a number of metal - hydrogen compounds MeH_n with $n>3$ should become enthalpically stable with respect to their less abandoned counterparts. Among those CaH_6 and YH_6 compounds is predicted to posses superconductivity with T_c even higher than that for suffer hydride: ~220 K at P > 150 GPa [3] and ~260 K at P = 120 GPa [4] respectively.

Here we present experimental electrical resistivity and Raman scattering study of Ca - H and Y -H systems to maximum pressures of ~230 GPa. The results obtained are discussed in context of the issue of superconductivity.

References

[1] N. W. Ashcroft, *Phys. Rev. Lett*., **92**, p. 187002 (2004)

[2] A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov & S. I. Shylin, *Nature*, **525**, p.73 (2015)

[3] H. Wang, J. S. Tse, K. Tanaka, T. Litaka, Y. Ma, *Proc. Nat. Acad. Sci. U.S.A.*, **109**, p. 6463 (2012)

[4] Y. Li, J. Hao, H. Liu, J. S. Tse, Y. Wang & Y. Ma, *Sci. Rep.*, **5**, p. 9948 (2015)

O 20.2

New melting line and direct liquid-liquid transition evidence for hydrogen up to 300 GPa

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Hot-dense hydrogen studies have been conducted under static compression by using external resistive heating diamond anvil cells. In-situ Raman spectroscopic measurements were used for obtaining both intra-molecular vibration and lattice libron-phonon spectra at the pressure-temperature (PT) space of 0 ~ 300 GPa and 300 ~ 900K. Results indicate that this simplest element may have unexpected rich phases in the higher PT region. The new melting line is different from the previous extrapolations. Particularly, two pressure-induced transition points on the melting line may relate the new solid molecular phases to the liquid-liquid transitions.

O 20.3

Determination of the phase diagram of H2/D2 above 300 GPa via synchrotron infrared measurements

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Disclosing the phase transformations of solid hydrogen under very high pressures, with ultimately the observation of metal hydrogen, is a very challenging and fascinating problem. First principle simulations are predicting a complex phase diagram, with an entropy stabilization of more anisotropic structures at 300K than below 100K [1]. Few experimental studies have recently been published on the structural changes in hydrogen isotopes in the 300 GPa - 400 GPa range from Raman and infrared measurements [2, 3, 4]. However, discrepancies exist between these studies that highlight the need for further experimental investigations.

The aim of our measurements is to extend our previous infrared synchrotron measurements in H2 and D2 up to 290 GPa at 300K [5], over the 300 GPa - 400 GPa range and at 77K. These measurements are coupled to online Raman measurements.

Measurements have been achieved up to 380 GPa on D2 and 320 GPa on H2 at 77K. Excellent quality data are obtained. No sign of phase transition, nor metallization is observed. A strong isotopic shift is observed. We will compare our data to other recent studies. Sources of uncertainty and discrepancies will be discussed.

Finally, it is clear now that to observe metal hydrogen, pressures in excess of 400 GPa will have to be generated. A promising route could be to use the newly designed toroidal shape anvils.

[1] Jeffrey M. McMahon, Miguel A. Morales, Carlo Pierleoni, and David M. Ceperley, Rev. Mod. Phys. 84, 1607 (2012).

[2] Philip Dalladay-Simpson, Ross Howie and Eugene Gregoryanz. Nature 529, 63 (2016).

[3] M.I. Eremets, I.A. Troyan and A.P. Drozdov, Arxiv

[4] Ranga Dias, Ori Noked and Isaac Silvera, Arxiv.

[5] Paul Loubeyre, Florent Occelli and Paul Dumas, Phys. Rev. B 87, 134101 (2013).