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NMR Investigation of Pressure Effect on Intermediate Valence Compound SmB_6

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We have carried out ^{11}B-nuclear magnetic resonance (NMR) and X-ray diffraction measurements on the intermediate valence compound SmB_6 under high pressure. The temperature dependence of nuclear quadrupole resonance frequency ν_Q, obtained from the ^{11}B-NMR measurements, is dominantly contributed from on-site charge distribution. By using a relationship between ν_Q and Sm valence at ambient pressure, we have estimated the pressure dependence of the Sm valence up to 6 GPa. The increase of the Sm valence accelerates with pressure and reaches about 10% increase at 6 GPa. The present result suggests that the pressure-induced localization of Sm $4f$-hole is responsible for the long-range magnetic order under pressure.

KEYWORDS: NMR, SmB_6, Kondo insulator, intermediate valence, high pressure

1. Introduction

SmB_6 has been intensively studied for more than forty years because of its notable features: for example, intermediate valence state (Sm valence is ~ 2.6 [see Refs. 1 and 2 and references therein]), and semiconducting property, so-called "Kondo insulator", with a narrow-gap ($50-100$ K [3,4]). The insulating gap of SmB_6 is known to be suppressed by the application of pressure, and subsequently SmB_6 becomes metallic above pressure in the range of $4-7$ GPa [5]. Recently, a new magnetically ordered phase has been found above ~ 6 GPa by a high-pressure ^{149}Sm nuclear forward-scattering measurement, so that interest in this compound has been renewed [6]. The long-range magnetic order in SmB_6 is expected to result from the localization of Sm $4f$ electrons, by considering the general phase diagram of heavy fermion compounds: that is, the magnetic trivalent state of Sm ions (total angular momentum $J = 5/2$) becomes more stable than the divalent state ($J = 0$) under pressure, analogous to the case of Yb-based compounds. However, microscopic understanding of $P - T$ phase diagram has been incomplete due to insufficient experimental information on how electronic configuration (or valence) varies as pressure increases toward the critical pressure P_c of the nonmagnetic-magnetic transition.

To address this problem, we have carried out nuclear magnetic resonance (NMR) measurements at B-site under pressure up to 6 GPa, just below P_c. Since nuclear quadrupole moment couples with the electric-field gradient (EFG) at the nuclear position created by surrounding charges, the mea-

surement of the nuclear quadrupole interaction provides microscopic information on charge distribution. In this paper, we extract essential information by comparing T- and P-dependences of nuclear quadrupole resonance frequency $\nu_{\rm Q}$ with those of the lattice parameter. Therefore, we have also carried out high-pressure X-ray diffraction experiments.

2. Experimental Procedure

A high-quality single crystal of SmB_6 was prepared by the floating melting zone technique. We used a single crystalline sample with dimensions about $1\times1\times1$ mm^3 and a powdered sample for NMR experiments at ambient pressure, while high-pressure NMR measurements were performed with the powdered sample. The high pressures above 3 GPa for the NMR measurements were achieved by using a modified Bridgman anvil cell. A sample container made of Teflon was filled with an equal mixture of Fluorinert FC 70 and FC 77 as a pressure-transmitting medium (PTM). The further information on this pressure cell are given elsewhere [7, 8]. The NMR measurement at 2 GPa was carried out with a conventional piston-cylinder pressure cell made of nonmagnetic NiCrAl/CuBe alloys with polyethylsiloxane as a PTM. The ^{11}B-NMR measurements were carried out at a fixed field of about 7.5 T by using a standard spin-echo technique with a phase-coherent pulsed spectrometer. The high-pressure X-ray diffraction experiment was carried out using a monochromatic synchrotron radiation source on BL10XU station at SPring-8, Hyogo [9]. The high pressure was generated by using a diamond anvil cell with a mixture of 16:3:1 methanol-ethanol-water as a PTM. Powder diffraction patterns of the sample were collected using an angle-dispersive method.

3. Results and Discussion

The inset of Fig. 1 shows the representative NMR lines central lines ($-1/2 \leftrightarrow 1/2$ transition) and quadrupole satellites ($1/2 \leftrightarrow 3/2$ transition) at ambient pressure. When magnetic field is applied along the [001] direction of a boron-octahedron B_6, two sets of three resonance lines are observed: one is from two apical borons of a boron-octahedron (denoted by $B^{\parallel}$ in the inset of Fig. 1(a)) and the other is from four plane borons ($B^{\perp}$). $\nu_{\rm Q}$ was evaluated by measuring intervals between the two sets of resonance lines indicated by solid and broken arrows. Figure 1(a) shows the T-dependence of $\nu_{\rm Q}$, where we plot the mean frequencies of these splits. Generally $\nu_{\rm Q}$ is expressed as $\nu_{\rm Q} = 3eQV_{zz}/2I(2I+1)$, where V_{zz} is the largest principal axis component of the EFG tensor and I is the nuclear spin ($I = 3/2$ for ^{11}B nucleus). Here, EFG at the B nuclear position consists of two contributions; one comes from ionic charges on all the other lattice sites surrounding the observing B-site and the other comes from intra-atomic charge distribution at the B-site, *i.e.*

$$V_{zz} = V_{zz}^{\rm lattice} + V_{zz}^{\rm onsite}. \tag{1}$$

If $V_{zz}^{\rm lattice}$ is dominant in the T-dependence of V_{zz}, $\nu_{\rm Q}$ ($\propto V_{zz}$) will vary roughly as $\nu_{\rm Q} \propto 1/V$ from a point charge model, where V is the unit cell volume. However, by comparing the T-dependence of $1/V$ from previous reports [10, 11] (see Fig. 1(a) and (b)), this is obviously contrary to the present case.

On the other hand, we find a resemblance between the T-dependences of $\nu_{\rm Q}$ and the valence of the boron-octahedron B_6 [see Fig. 1(a) and (c)]. This is natural because, considering Eq. (1), the on-site charge distribution is an alternative physical parameter governing the T-variation of V_{zz}. Recently, Mizumaki *et al.* have precisely measured the T-dependence of the Sm valence at ambient pressure by the X-ray absorption spectroscopy [12]. We assume $\upsilon(B_6) = -\upsilon(\rm Sm)$ from charge neutrality consideration, where $\upsilon(\rm Sm)$ and $\upsilon(B_6)$ are the valences of Sm and B_6, respectively. If we describe $\upsilon(\rm Sm) = 2 + n_f$ with n_f as the number of $4f$-hole in the $J = 5/2$ multiplet, $1 - n_f$ is a parameter reflecting $\upsilon(B_6)$. In Fig. 1(c), we show the plot of $1 - n_f$ vs T at ambient pressure. Both

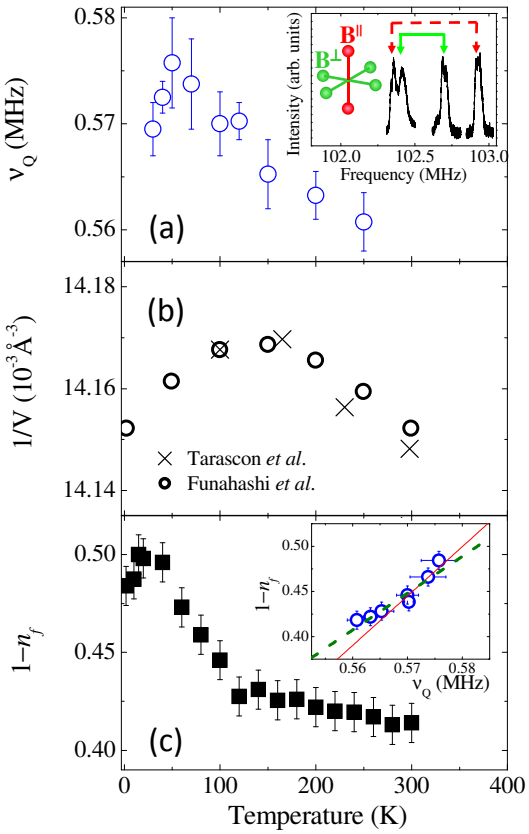

Fig. 1. (Color online) (a) T-dependences of ν_Q. Inset: ^{11}B-NMR spectrum of the single crystalline sample for $H \parallel [001]$ at 100K and ambient pressure. (b) T-dependence of $1/V$ from Refs. [10, 11] (c) T-dependence of $1 - n_f$ estimated from Ref. [12]. Inset: the plot of $1 - n_f$ vs ν_Q with temperature as an implicit parameter. The solid and broken lines are least squares linear fits to the data. See text for details.

ν_Q and $1 - n_f$ increase with decreasing temperature, and exhibit a maximum below 50 K. We see a slight difference between the temperatures for the maxima, which might be due to the difference in experimental method. The temperature at which ν_Q shows the maximum corresponds to the gap energy estimated from the T-dependence of nuclear spin-lattice relaxation rate $1/T_1$ [4]. As shown in the inset of Fig. 1(c), where we plot the data for $T \geq 50$ K, ν_Q depends roughly linearly upon $1 - n_f$ within error bars (dotted line) except the data point at 120 K. However, there seems a slight difference in the slope of the linear fit between in the high- and low-temperature regions. This might suggest that, in the semiconducting state, the contributions to ν_Q and/or $1 - n_f$ from conduction electrons differs from those in the metallic state. We therefore adopt a linear fit in the relatively lower-temperature region (solid line) for the following analysis.

Next, as we did in the study at ambient pressure, we compare the data of ν_Q and V in the high pressure region. First, we show the results of the high-pressure X-ray diffraction experiment. Figure 2(a) shows the X-ray diffraction patterns of SmB_6 at different pressures up to 9.9 GPa. The P-dependence of V is shown in Fig. 2(b), along with the data from Ref. [13]. Obviously, the accuracy of the present measurement is markedly improved compared to the previous data reported in 1980s [13]. A bulk modulus $B_0 = 144$ GPa and its pressure derivative $B_0' = 6.4$ have been obtained by fitting the present

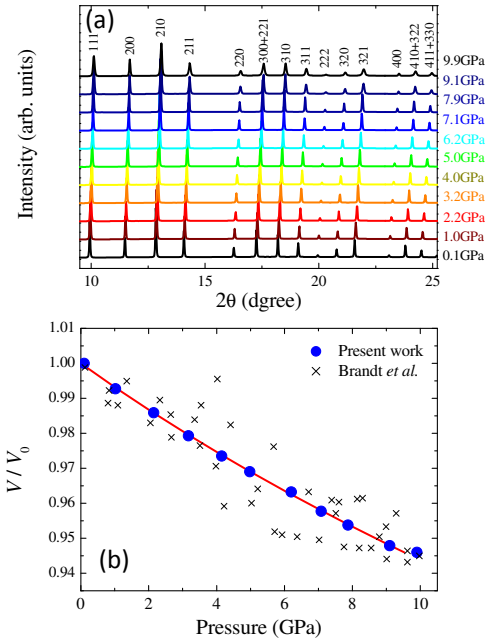

Fig. 2. (Color online) (a) Powder x-ray diffraction patterns of SmB_6 at room temperature and at different pressures up to 9.9 GPa. (b) P-dependence of V estimated from the data in Fig. 2(a), together with previous data [13] for comparison. The solid line is a least-square fit to the Murnaghan-Birch equation.

data for $P \leq 9.1$ GPa to the Murnaghan-Birch equation [14],

$$P = \frac{3}{2}B_0\left[\left(\frac{V}{V_0}\right)^{-\frac{7}{3}} - \left(\frac{V}{V_0}\right)^{-\frac{5}{3}}\right]\left\{1 - \frac{3}{4}(4 - B_0')\left[\left(\frac{V}{V_0}\right)^{-\frac{2}{3}} - 1\right]\right\}, \quad (2)$$

Present B_0 is rather consistent with the value described in Ref. [6] than in Ref. [13].

In Fig. 3(a), we shows the P-dependence of ν_Q up to 6 GPa evaluated from the measurement of NMR spectra at 2 K. We also plot the P-dependence of $1/V$ in Fig. 3(b). ν_Q reveals a more rapid decrease with increasing pressure, which is against the expectation from the scenario that $V_{zz}^{\rm lattice}$ is dominant in the P-dependences of V_{zz}. Thus, both P- and T-dependences of ν_Q indicate that $1/V$ is not a proper parameter of determining ν_Q. We apply the linear relationship between ν_Q and $1 - n_f$ obtained at ambient pressure to the P-variation of ν_Q and roughly estimate υ(Sm) under pressure. From Fig. 3(a), ν_Q is reduced by about 9 % as pressure increases from ambient pressure to 6 GPa. Then, $1 - n_f$ at 6 GPa is estimated to be 0.23 ± 0.08 from the present assumption, corresponding to $\upsilon(\mathrm{Sm}) = 2.77 \pm 0.08$. According to the previous measurement of Raman scattering spectrum under pressure [15], the Sm ions of SmB_6 is expected to be trivalent above 20 GPa and at room temperature. Our estimation of υ(Sm) at 6 GPa is consistent with the extrapolated value (~ 2.78 at 6 GPa) using the Raman scattering data. However, as seen in Fig. 3(c), the present result indicates that the pressure-induced variation of υ(Sm) accelerates with increasing pressure, rather than changes linearly against pressure as reported in Ref. [15]. The discrepancy may arise from the difference in experimental conditions: namely, present measurement of ν_Q was carried out at 2 K, much lower than the Kondo temperature of SmB_6, while the Raman scattering was performed at room temperature.

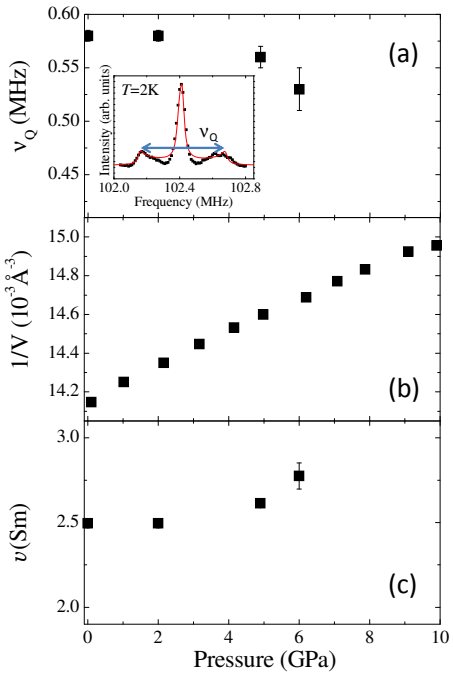

Fig. 3. (Color online) (a) P-dependence of ν_Q estimated by fitting the powder patterns as shown in the inset. Inset: ^{11}B-NMR spectrum at 6 GPa. (b) P-dependence of $1/V$ evaluated from the data in Fig. 2(b). (c) P-dependence of Sm valence estimated by using the linear relationship ν_Q and $1 - n_f$.

4. Conclusion

We have carried out ^{11}B-nuclear magnetic resonance (NMR) and X-ray diffraction measurements on SmB_6 under high pressure. The X-ray diffraction pattern does not show any anomaly up to 9.1 GPa, and the P-dependence of the lattice constant was precisely determined with advantage of recent improved experimental techniques using the synchrotron facility. The T-dependence of ν_Q is dominantly contributed from the on-site charge distribution, rather than that from the lattice. By applying the relationship between ν_Q and Sm valence at ambient pressure to the P-variation of ν_Q, we have found that the Sm valence increases by about 10% at 6 GPa. The present result supports the scenario that the pressure-induced localization of Sm $4f$-hole gives rise to the long-range magnetic order in SmB_6, similar to the general phase diagram for Kondo lattice systems.

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