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Title: The Synthesis of Pu₆Fe from Plutonium Deuteride and Iron Powders

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Introduction

In order to make contemporary measurements of Pu₆Fe properties, an effort, described here, was made to create small high purity samples. The intermetallic compound Pu₆Fe was successfully synthesized from blended PuD_{2.7} and iron powders followed by thermal vacuum treatment at 420°C to remove the deuterium. The quality of the product was confirmed by differential scanning calorimetry (DSC), which indicated a 90% yield. During the thermal desorption of deuterium the equilibrium D₂ pressure exhibited a plateau (two phase behavior) with an equilibrium pressure well below the expected PuD₂ equilibrium pressure indicating a Pu₆FeD_x intermediate compound existed during the synthesis.

The resulting Pu₆Fe intermetallic compound will be used for further property measurements including hydrogen interactions.

Sample Preparation

The sample was prepared as follows:

The iron powder used was Alpha Aesar (P/N 10621), -22 mesh, 800 micron (maximum, but actually much smaller), 99.998% metals basis purity. The plutonium deuteride powder was prepared from a sample of doubly electrolytically refined plutonium (9x9x1mm) that was vacuum annealed at 450°C and flushed with deuterium and subsequently deuterided at room temperature to a stoichiometry of PuD_{2.7}. The deuteriding of alpha-Pu takes much longer than for delta-Pu, and so equilibrium took about five hours, but the large lattice parameter change and transformation to the fluorite structure (from the monoclinic alpha phase) results in a fine black powder. The resulting powder was removed from its cell and weighed in a pure argon atmosphere.

After the plutonium deuteride was weighed, a quantity of the iron powder was weighed out. The quantity of iron was such that the stoichiometry of Pu₆Fe was met, in this case 1.6g Pu to 62 mg Fe. The powders were thoroughly blended manually and placed into a tantalum foil sample boat. The sample boat was attached to three type K thermocouples ($\pm 1^\circ\text{C}$ accuracy) which act to hold the sample and measure its temperature and then that configuration is wrapped in aluminum foil to guarantee uniform temperature and placed into a vacuum furnace.

Thermal Desorption of Deuterium

Following a leak check the vacuum furnace (a Sieverts type apparatus) was taken to 412-420°C and the pressure and composition of desorbed gas was monitored. After about two hours the pressure decreased to an equilibrium value. At this point the vacuum was isolated from the sample to allow measurement of the equilibrium D₂ pressure. The equilibrium pressure was much lower than the expected PuD₂ plateau [1, 2] (two phase region) pressure for that temperature. Additional gas was evacuated using known volumes but the equilibrium pressure remained the same, confirming two phase behavior.

To confirm the possibility that a new compound was binding the deuterium more tightly, the free energy was measured by varying temperature over a range and measuring equilibrium pressures. The free energy was calculated using equation (1) and the values in Table I.

$$\Delta G = R \cdot T \cdot \ln(P/P_0) \quad (1)$$

Figure 1 shows the deuterium equilibrium pressure free energy result. The D₂ is bound more tightly in Pu₆FeD_x than in PuD₂ by 3 kJ/mol.

Thermal Desorption of Deuterium

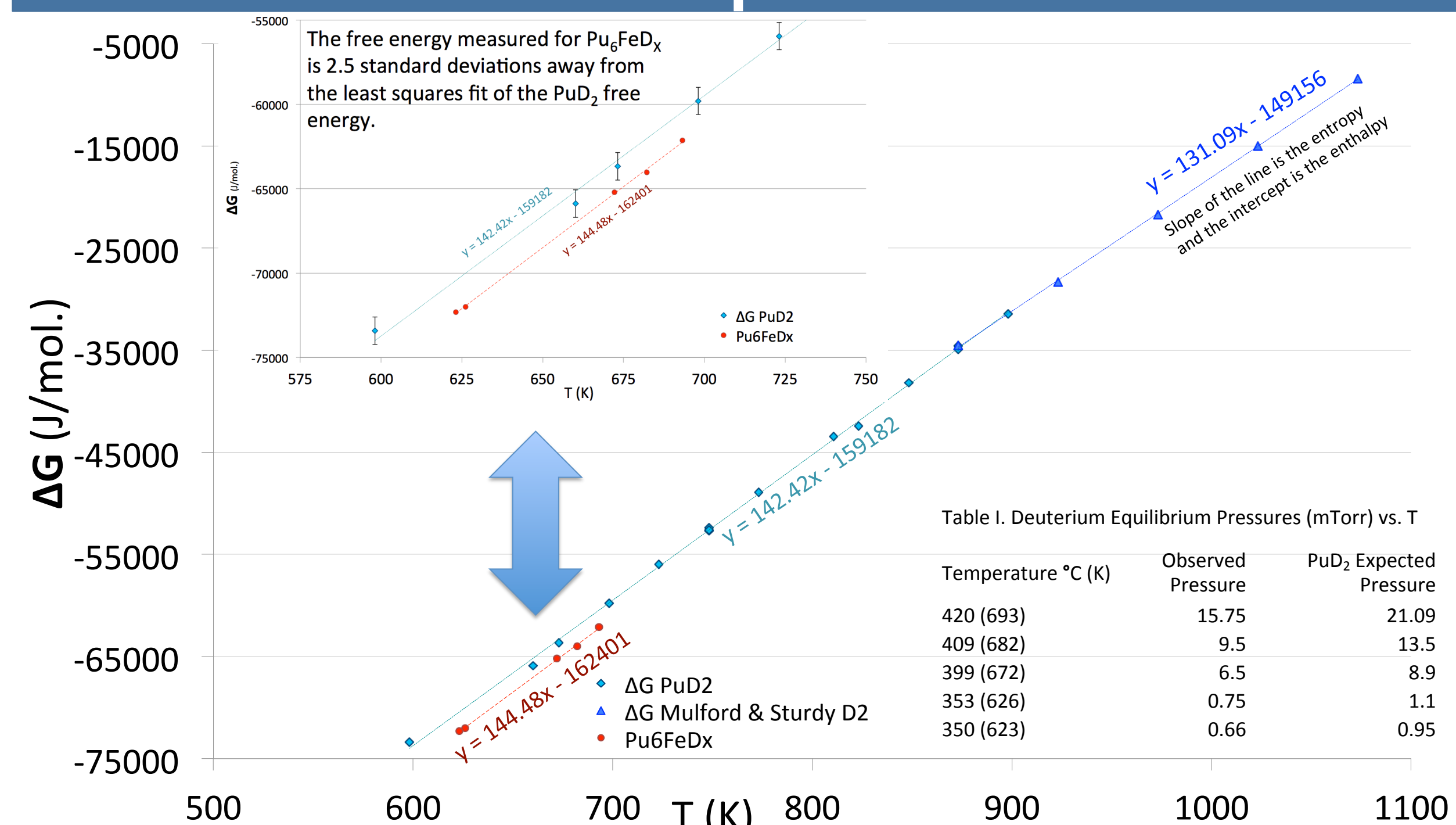


Figure 1. Free energy plot of PuD₂ and Pu₆FeD_x. The red line for the Pu₆FeD_x equilibrium lies 2.5 standard deviations below PuD₂. D₂ is bound more tightly in Pu₆FeD_x than in PuD₂ by 3 kJ/mol.

The remainder of the deuterium was evacuated from the sample. Figure 2 shows the dehydrated Pu₆Fe sample.



Figure 2. Resulting Pu₆Fe sample.

DSC Analysis

A 30 mg sample of the material was loaded into the DSC. The sample was heated from RT to 450°C, then cooled to RT. The cycle was repeated three times. The result of the 3rd cycle is shown in Figure 3. It is evident in Figure 3 that heat absorption is seen for the $\alpha \rightarrow \beta$ solid-state transformation. This indicates that we had excess Pu in the Pu-Fe mixture (α -Pu+Pu₆Fe)

The data indicates that the Pu₆Fe melting enthalpy is approximately 41.7 kJ/mol. This is fairly high and is comparable to high-melting intermetallics. Evaluation of the data indicates Pu₆Fe yield was ~90%.

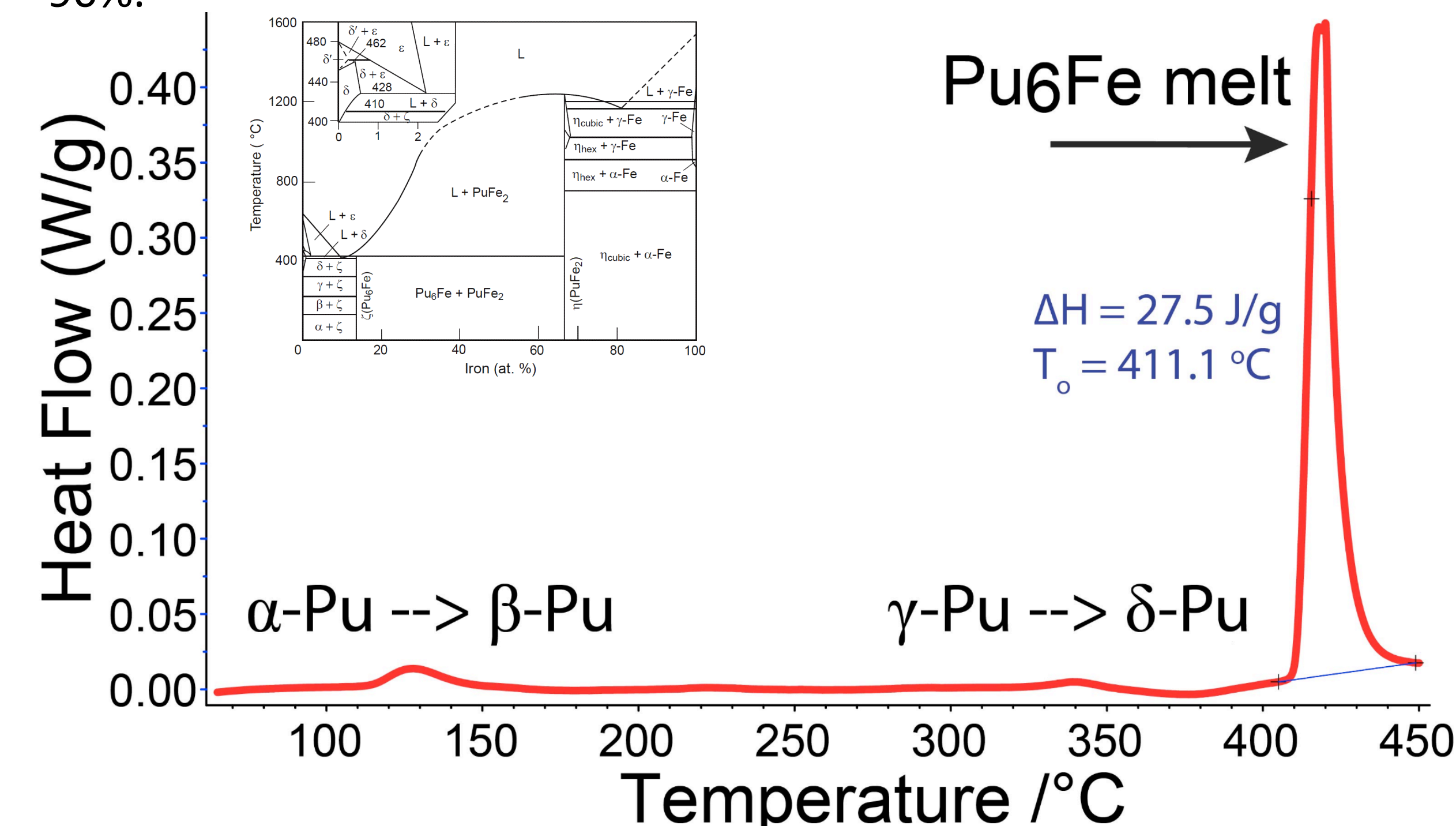


Figure 3. Differential Scanning Calorimetry of Pu₆Fe. Pu-Fe phase diagram [3] inset for reference.

Conclusions

The heat of fusion for Pu₆Fe has been measured for the first time. This new synthesis method was successful in producing a small sample of Pu₆Fe with high yield. A surprising result was that hydrogen was more strongly bound in the Pu₆FeD_x. Since the material also showed two phase behavior the thermodynamic evidence indicates an intermediate compound, Pu₆FeD_x, is likely where X remains unknown.

Future Work

Because Pu₆Fe shares the same composition and structure as U₆Fe we anticipate Pu₆FeD_x is analogous to U₆FeH₁₅ identified by Drulis [4], and so we will remake the presumed compound and measure its properties and structure (figure 4). If the Pu₆FeH_x compound is produced and it has a greater affinity for hydrogen than PuH₂, then we will examine the implications for iron impurities in Pu metal (Figure 5).

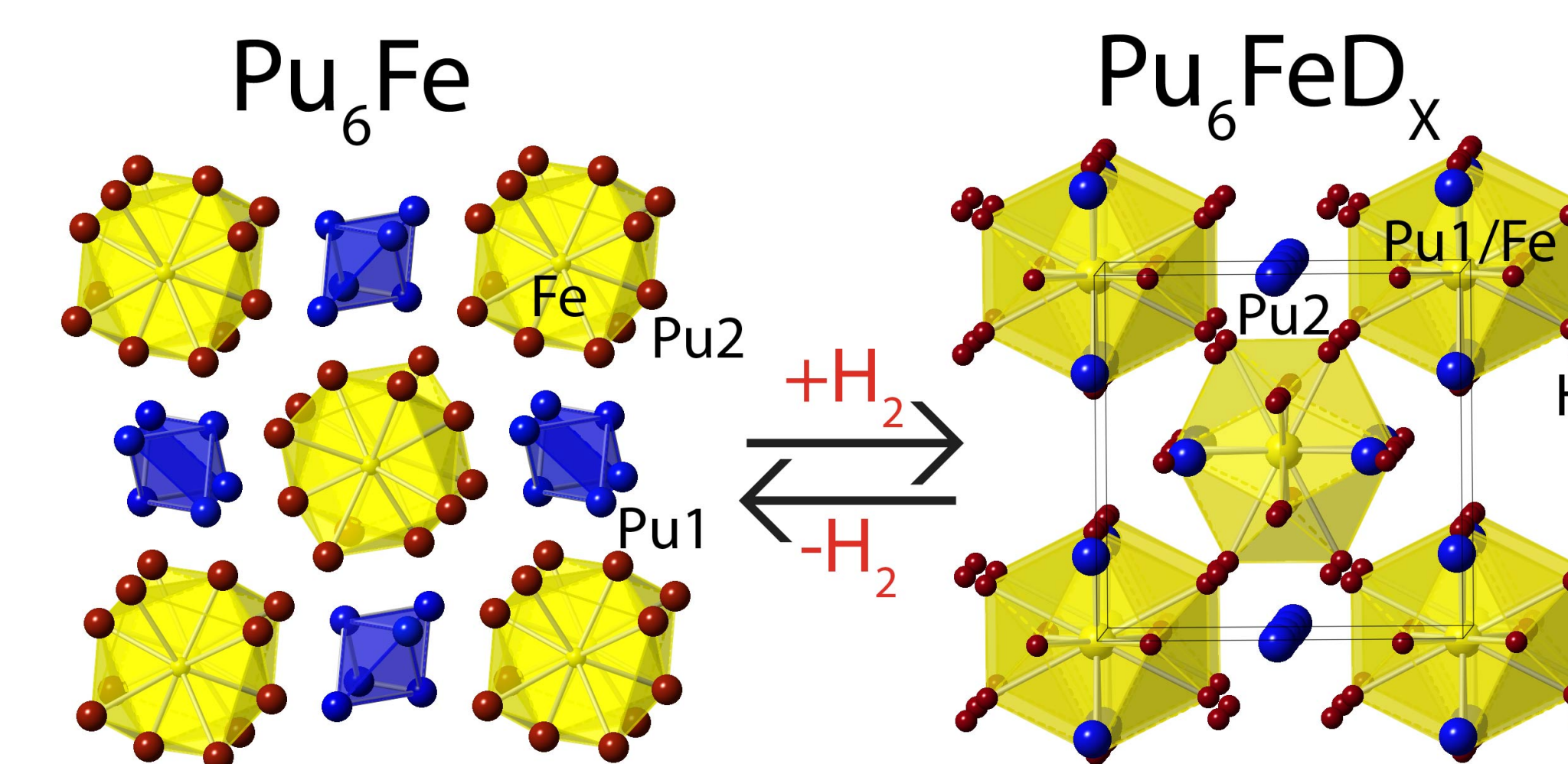


Figure 4. The proposed crystal structure of Pu₆Fe and Pu₆FeD₁₅ showing the change of a tetragonal lattice to a cubic lattice. Because Pu₆Fe is the structural analog of U₆Fe, we hypothesize Pu₆FeH_x to be analogous to the U₆FeH₁₅ compound identified by Drulis [4].

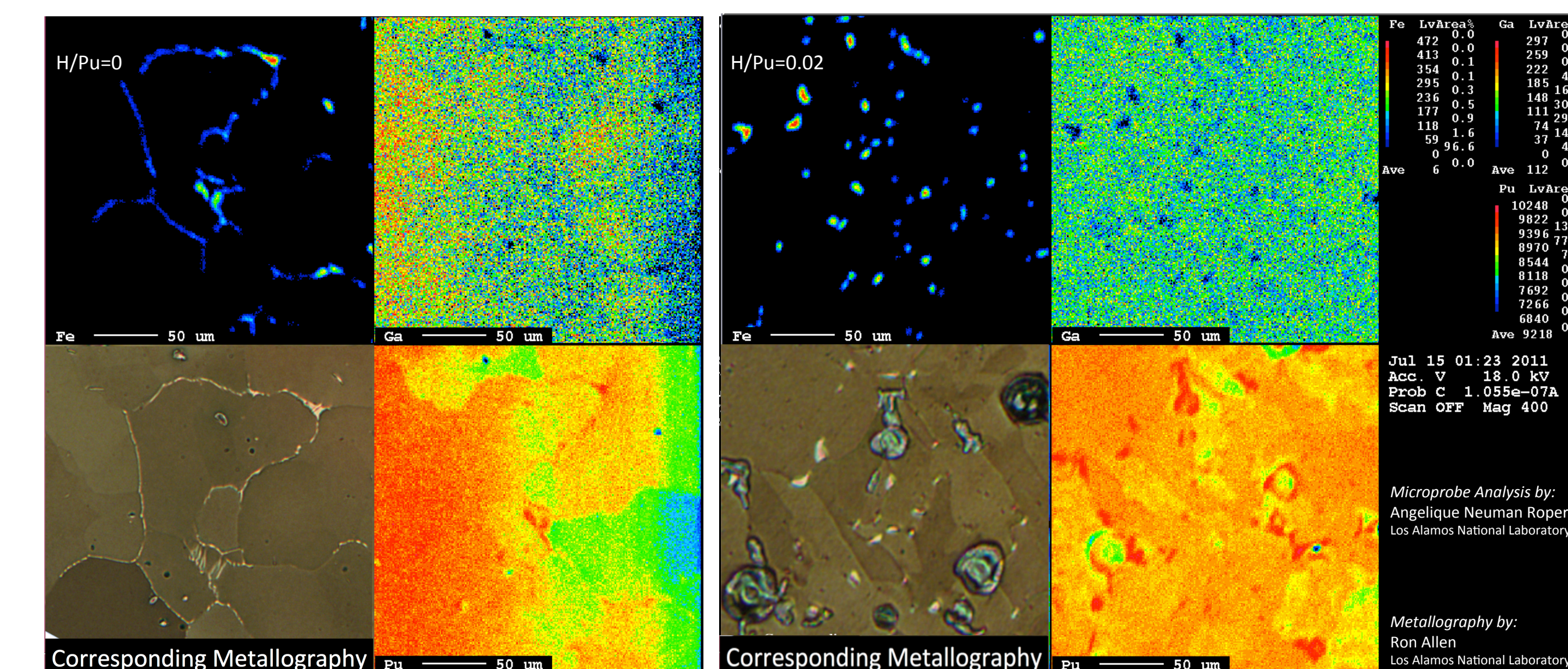
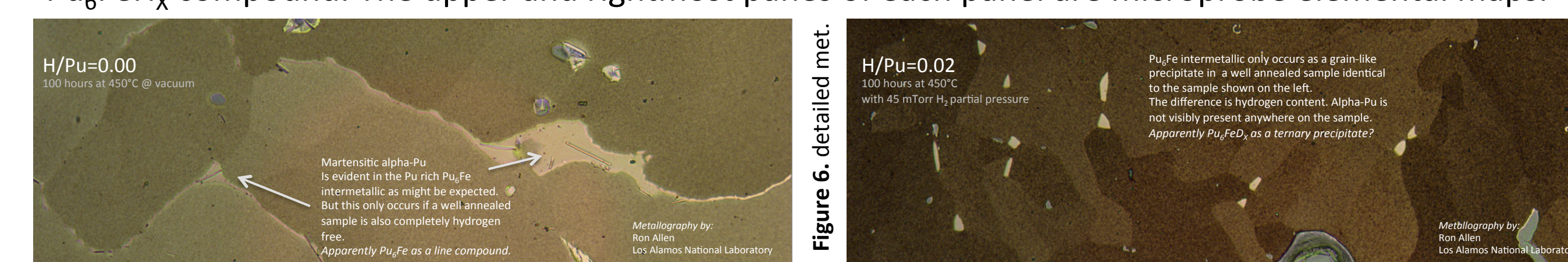


Figure 5. Morphological variation in Pu₆Fe for hydrogen free (left) and H/Pu 0.02 (right) of otherwise identical δ -Pu metal. The source sample was split and H concentration set in a vacuum furnace at 450°C. In the future we will determine if this difference depends on hydrogen precipitating as the Pu₆FeH_x compound. The upper and rightmost panes of each panel are microprobe elemental maps.



Acknowledgements

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