Stability of fcc phase FeH to 137 GPa

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ABSTRACT

We examined the crystal structure of FeH2 (X~1) (FeH hereafter) at high pressure and temperature by X-ray diffraction up to 137 GPa. Results show that FeH adopts a face-centered cubic (fcc) structure at pressures of 43 to 137 GPa and temperatures of ~1000 to 2000 K. Our study revises a phase diagram of stoichiometric FeH in which fcc has a wider-than-expected stability field at high pressure and temperature. Based on our findings, the FeH end-member of the Fe-FeH system is expected to be stable in the fcc structure at the P-T conditions of the Earth’s core, rather than in the double-hexagonal close packed (dhcp) structure as previously reported. We compared the experimentally determined unit-cell volumes of FeH with those from ab initio calculations. Additionally, we observed a change in compressibility at ~60 GPa, which could be attributed to a magnetic transition—an interpretation supported by our ab initio computations.

Keywords: FeH, fcc structure, Earth’s core, X-ray diffraction, ab initio calculation

INTRODUCTION

Hydrogen is a possible constituent light element within the Earth’s predominantly iron-nickel core (e.g., Poirier 1994). Therefore, evaluation of the Fe–FeH system under the high-pressure (P) and high-temperature (T) conditions of the Earth’s deep interior is important in the discussion of chemical and physical properties of the core. An end-member of this system, stoichiometric FeH with double-hexagonal close packed (dhcp) structure, has been observed in iron loaded in a hydrogen pressure medium at pressures exceeding 3.5 GPa at room temperature (e.g., Badding et al. 1991). The temperature-induced phase transition from dhcp to face-centered cubic (fcc) was observed up to 20 GPa in a multi-anvil apparatus (Ikuta et al. 2019; Saitoh et al. 2017; Sakamaki et al. 2009). Locations of the melting curve and the dhcp/fcc phase boundary predict the triple point of dhcp, fcc, and liquid phases FeH at about 60 GPa and 2000 K, and the disappearance of the fcc stability field at higher pressures. Room-temperature compression experiments showed no structural change in dhcp FeH up to 136 GPa, but they did not involve thermal annealing during compression, thus lacking direct evidence for the stability of dhcp at this pressure range (Badding et al. 1991; Hirao et al. 2004; Pépin et al. 2014; Shibazaki et al. 2012). On the other hand, there are experimental and theoretical studies that suggest fcc FeH is stable above 80 GPa and up to 1800 K (Isaev et al. 2007; Thompson et al. 2018). Free-energy calculations suggested that, at room temperature, FeH undergoes a structural transition from dhcp to hexagonal close packed (hcp) at 37 GPa, and a second transition from hcp to fcc occurs at 83 GPa (Isaev et al. 2007). They also found that a ferromagnetic-paramagnetic transition takes place at ~60 GPa in metastable fcc FeH, which leads to the change in compressibility.

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In addition to the end-member FeH, non-stoichiometric FeH(X < 1) has been identified in both the fcc structure (Thompson et al. 2018) and the dhcp structure (Antonov et al. 1998; Yuan et al. 2018; Machida et al. 2019). Additionally, Fe polyhydrides with the compositions FeH2, FeH3, and FeH4 have been reported (Pépin et al. 2014, 2017), and FeH4 and FeH6 have also been suggested as potential Fe-H compounds at high pressure (Bazhanova et al. 2012; Kvasnin et al. 2018).

In this study, we performed in situ synchrotron X-ray diffraction experiments at high P-T in a laser-heated diamond-anvil cell (LHDAC) to determine the stability field of stoichiometric fcc FeH. These experiments confirmed that fcc FeH is stable up to 137 GPa and about 1000 K. We also determined the unit-cell volumes of fcc FeH as a function of pressure and found anomalous compression behavior at ~60 GPa. Based on our ab initio calculations, the magnetic transition in fcc FeH reasonably explains the observed change in compressibility.

METHODS

We employed the LHDAC technique to generate high P-T conditions. Diamond anvils with 300 or 120 μm diameter culets were used, and gaskets were pre-indented rhenium plates. We used two different methods to supply hydrogen to the iron foil starting material (99.999% purity). In runs 1–3, iron hydride was formed by loading an iron foil with a paraffin (CnH2n+2, n > 5) pressure medium to the iron foil starting material (99.999% purity). In runs 1–3, iron hydride was formed by loading an iron foil with a paraffin (CnH2n+2, n > 5) pressure medium into the LHDAC with ruby or KCl as the pressure markers (Narygina et al. 2011; Ohta et al. 2019; Thompson et al. 2018; Hirose et al. 2019). In runs 4–8, liquid H2 was introduced into the LHDAC and compressed with an iron foil and a NaCl inner gasket at ~20 K in a helium refrigerator (Chu et al. 2011; Ohma et al. 2015; Tagawa et al. 2016). The NaCl inner gasket prevents hydrogen embrittlement of the Re gasket and the escape of hydrogen from the sample chamber. The surface of the diamond anvils was coated with a thin Ti film to prevent the hydrogen from escaping into the anvils. Supplemental Figure S1 shows the sample chamber after the liquid H2 injection.

In situ angle-dispersive X-ray diffraction (XRD) measurements were performed at BL10XU, SPring-8. XRD patterns were collected on a flat panel detector. The...