The Effects of Ferromagnetism and Interstitial Hydrogen on the Physical Properties of hcp and dhcp FeH_x: Implications for the Density and Magnetism of a Hydrogen-bearing Core.

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Introduction: Hydrogen plays an important role in the evolution of our Solar System, and is potentially incorporated in the iron-dominant cores of the Earth and other planets. Hydrogen and iron form non-stoichiometric FeH_x at high pressure. The maximum abundance of hydrogen in the Earth's core has been estimated to be $0.3 \leq x \leq 0.5$ [1]. Furthermore, recent experimental study on hcp Fe-Si-H ternary alloys, suggests that the abundance of alloying hydrogen is found to be $x = 0.17$ [2]. Reliable estimate of the H content is critically depended on our knowledge of the non-stoichiometric FeH_x. It is chellenging to investigate non-stoichiometric FeH_x experimentally or theoretically.

Conventional first-principles calculations require large supercells to calculate arbitrary concentration of hydrogen. The calculated results are influenced by the geometry of the super cell [3]. Here we report results of the total energy of FeH_x alloys obtained by means of first-principles calculations based on the Korringa-Kohn-Rostoker method (KKR). The coherent potential approximation (CPA) is adopted to deal with the alloying effect, which is a complementary approach with the super cell method. The results demonstrate the non-linear volume change at a certain amount of hydrogen content. The magnetism and interstitial hydrogen also affect the electrical resistivity of FeH_x, that has important consequence for thermal evolution of a H-bearing core.

Methods: We conducted static first-principles calculations of hcp and dhcp iron-hydrogen alloys. The KKR method was used as implemented in the AkaiKKR code [4]. Perdew-Burke-Ernzerhof (PBE) type of generalized gradient approximation (GGA) was used for the exchange-correlation functional [5]. The relativistic effects are taken into account within the scalar relativistic approximation. The wave functions are calculated up to $l = 2$, where l is the angular momentum quantum number. The CPA was used to represent hydrogen atoms, which randomly occupied the octahedral interstitial site. The hydrogen content x was ranging from 0.0 (pure iron) to 1.0 (hydrogen saturated iron hydrides) with 0.1 step. The axis ratio is optimized by the total energy minimum at each volume. The number of k-points is set to be at least 312 in the irreducible Brillouin zone. Both of spin polarized and non-spin polarized calculations were carried out to represents ferromagnetic and non-magnetic states, respectively. The volume-energy relationship is then fitted to the Birch-Murnaghan Equation of state (EoS). The local moment disorder (LMD) state is also simulated, which is an analog of the paramagnetic state above the Curie temperature [6]. The energy difference between ferromagnetic and LMD state indicates the relative stability of the ferromagnetism with regards to temperature. Applying the Heisenberg model, the energy difference gives rough value of the Curie temperature: $T_c = 2*(E_{LMD}-E_{ferro})/(3k_B)$, where T_c is the Curie temperature, k_B is the Boltzmann constant, E_{LMD} and E_{ferro} are total energies of LMD and ferromagnetic states, respectively [6].

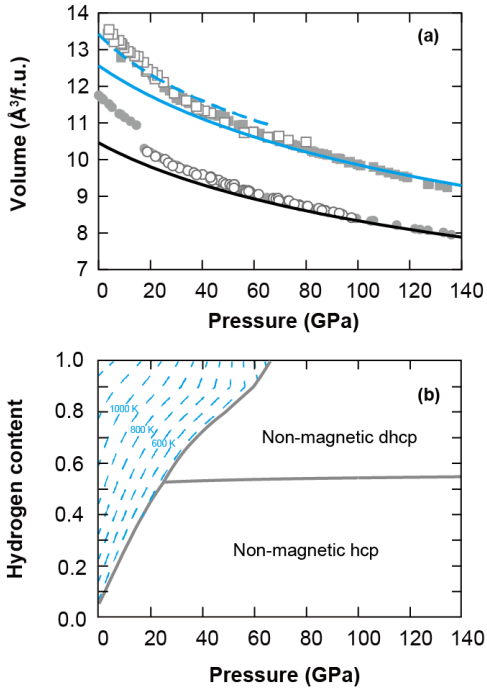

Fig.1 (a) Compression curves of dhcp FeH and hcp Fe. Blue broken line indicates ferromagnetic dhcp FeH. Blue and black solid lines are nonmagnetic dhcp FeH and hcp Fe, respectively. Previous DAC measurements (open square; [7], filled square: [8], open circle: [9], filled circle: [10]) are also shown for comparison. (b) Stable crystal and magnetic structure of FeH_x as function of pressure at given hydrogen content.

Results: EoS of ferromagnetic and nonmagnetic dhcp $FeH_{1.0}$ and nonmagnetic hcp Fe are shown in Fig. 1a. Our calculated results of ferromagnetic dhcp $FeH_{1.0}$ are consistent with previous results obtained from dia-

mond-anvil cell (DAC) experiments at low pressure [7, 8]. However, the calculated volume of ferromagnetic dhcp $FeH_{1.0}$ deviates at about 30 GPa, and the non-magnetic result approaches to the experimentally determined volumes at around 60 GPa. This behavior is consistent with previous calculations [e.g. 8]. Similarly, our hcp Fe results broadly reproduce a compression curve of hcp Fe determined by previous DAC studies [9, 10]. The same procedure was applied to non-stoichiometric FeH_x alloys calculated by using the CPA. Fig. 1b indicates the most stable crystal/magnetic structure among these four combinations as functions of pressure and hydrogen content. Within the ferromagnetic dhcp stability field, the Curie temperature is also shown by broken lines (Fig. 1b).

Discussion: In-situ XRD measurement is the most common way to determine the volume of FeH_x at high pressure (e.g., P > 10 GPa). In order to estimate the hydrogen content from the measured volume, the following linear volume-composition relationship is widely used, $x = (V_{FeHx} - V_{Fe})/\Delta V_H$, where x is hydrogen content, V_{FeHx} is the volume of FeH_x per formula, V_{Fe} is the atomic volume of iron, and ΔV_H is volume increase per hydrogen atom. The ΔV_H has been assumed to be independent of x. This relationship is applicable to several face-centered cubic (fcc) metal-hydrogen alloys [11]. To test the applicability of our first-principles calculations, we first calculated the equilibrium volume of fcc metal-hydrogen alloys (PdH_x, NiH_x, $Ni_{0.8}Fe_{0.2}H_x$ and $Fe_{0.65}Ni_{0.29}Mn_{0.06}H_x$). Our first-principles results are broadly consistent with previous experimental results [11], which show nearly linear volume expansion as a function of hydrogen content (Fig. 2a). Fig. 2b shows a plot of the volume of the most stable phase and non-magnetic phase of FeH_x at 20 GPa, which clearly shows the violation of linearity. At small x, where non-magnetic hcp FeH_x is the most stable, the volume increases almost linearly. However, a discontinuous increase of volume occurs across the phase transition from non-magnetic hcp to ferromagnetic dhcp phase. Within the ferromagnetic phase, the volume is almost independent of hydrogen content, suggesting that the volume of FeH_x phase is mostly controlled by ferromagnetism.

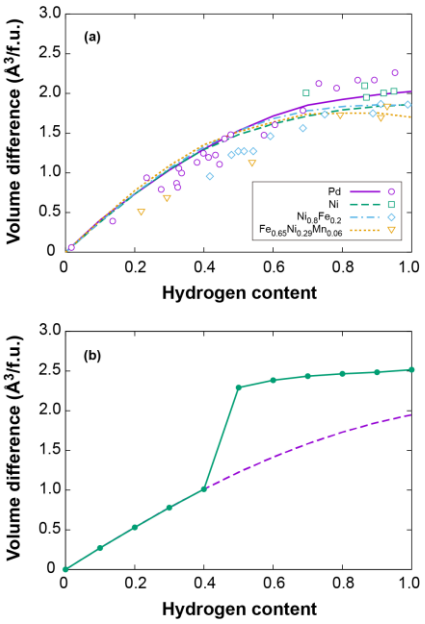

Fig. 2 Increase of volume of metal-hydrogen alloys as functions of hydrogen content, x. (a) fcc metal-hydrogen alloys at ambient pressure. Our first-principles results (purple solid line: Pd, green dashed line: Ni, blue dotted-dashed line: $Ni_{0.8}Fe_{0.2}$, yellow dotted line: $Fe_{0.65}Ni_{0.29}Mn_{0.06}$) are consistent with previous experiments (purple circle: Pd, green square: Ni, blue diamond: $Ni_{0.8}Fe_{0.2}$, yellow triangle: $Fe_{0.65}Ni_{0.29}Mn_{0.06}$) [11]. (b) FeH_x alloys at 20 GPa. Green solid line with circle indicates FeH_x of stable phase, whereas purple broken line represents FeH_x in non-magnetic state. Note that magnetic transition violates the linear volume-hydrogen content relation, which observed in nonmagnetic FeH_x and many fcc metal-hydrogen alloys.

In addition to the density change, many physical properties such as thermal conductivity may change significantly at the magnetic transition. Therefore, the effect of ferromagnetism may play an important role in smaller planets and satellites, if their iron-dominant cores contain hydrogen. For example, such a situation likely occurs at the interior of the Ganymede, which contains large amount of hydrogen as the thick icy mantle, and hence, coexisting iron may react to form iron hydrides. Our prediction of the Curie temperature is comparable to the temperature of interior of these smaller bodies [12]. If the internal temperature is below the Curie temperature, the FeH_x alloy has spontaneous magnetism and could be a source of remnant magnetism of the bodies [13].

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