Interstitial hydrogen atoms in face-centered cubic iron in the Earth’s core

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Hydrogen is likely one of the light elements in the Earth’s core. Despite its importance, no direct observation has been made of hydrogen in an iron lattice at high pressure. We made the first direct determination of site occupancy and volume of interstitial hydrogen in a face-centered cubic (fcc) iron lattice up to 12 GPa and 1200 K using the in situ neutron diffraction method. The transition temperatures from the body-centered cubic and the double-hexagonal close-packed phases to the fcc phase were higher than reported previously. At pressures $<5$ GPa, the hydrogen content in the fcc iron hydride lattice ($x$) was small at $x<0.3$, but increased to $x>0.8$ with increasing pressure. Hydrogen atoms occupy both octahedral (O) and tetrahedral (T) sites; typically $0.870(±0.047)$ in O-sites and $0.057(±0.035)$ in T-sites at 12 GPa and 1200 K. The fcc lattice expanded approximately linearly at a rate of $2.22(±0.36)$ Å³ per hydrogen atom, which is higher than previously estimated ($1.9$ Å³/H). The lattice expansion by hydrogen dissolution was negligibly dependent on pressure. The large lattice expansion by interstitial hydrogen reduced the estimated hydrogen content in the Earth’s core that accounted for the density deficit of the core. The revised analyses indicate that whole core may contain hydrogen of $80(±31)$ times of the ocean mass with $79(±30)$ and $0.8(±0.3)$ ocean mass for the outer and inner cores, respectively.

The Earth’s core has supposed to be constituted by iron with ~10% nickel and some light elements. Hydrogen is one of the most probable candidates among the light elements in the Earth’s core. In order to estimate the hydrogen contents in the inner and outer cores, previous studies have determined phase relations, equations of state, magnetic properties, and the sound velocity of iron hydride FeHₓ by using synchrotron X-ray¹–⁷ and theoretical works⁸. Despite intensive studies of iron hydride by X-ray diffraction, precise in situ direct determination of the volume expansion by interstitial hydrogen in metallic iron has not yet been conducted using in situ high pressure and high temperature neutron diffraction studies, except the neutron diffraction of recovered iron hydrides at 90 K and ambient pressure⁹. Therefore, we need to use the volume of hydrogen estimated empirically from many metal hydride compounds¹⁰. To date, neutron diffraction experiments at high pressures have been conducted for deuterides¹¹,¹², but not for hydrides. However, the experimental results for deuterium (D) compounds cannot be directly applied to discuss the behaviors of hydrogen compounds in the lower mantle and core because physical and thermodynamic properties of deuterium and hydrogen compounds differ with each other.

In this study, we directly determined the crystallographic positions of hydrogen atoms and their effects on cell volumes for a high-pressure polymorph, fcc iron hydride, using neutron powder diffraction measurements. This technique provided a precise determination of the hydrogen content in the samples used in previous studies on the phase relations and equation of state of iron hydride. Thus, we can estimate precisely the hydrogen content in the core by comparison with the seismic model of the Earth’s core.

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Results

We determined the volume expansion by interstitial hydrogen atoms in the fcc iron hydride lattice by neutron diffraction at various pressures and temperatures for the first time. The phase transition and hydrogenation of iron were observed in both the fcc FeH\textsubscript{x} and the double-hexagonal close-packed (dhcp) FeH\textsubscript{x} phases. We conducted four separate runs from 3.5 to 12 GPa and in the temperature range from the ambient to 1200 K by using the cubic press (ATSUHIME)\textsuperscript{13} installed at high-pressure neutron beamline PLANET\textsuperscript{14} in J-PARC. The phase diagram determined by the present \textit{in situ} neutron diffraction experiments and the pressure-temperature paths of our experiments are shown in Fig. 1. The phase boundaries of FeH\textsubscript{x} compounds determined in this study were significantly different from those estimated previously by using electrical resistivity change due to the phase transitions\textsuperscript{15,16}; that is, the transition temperature from body-centered cubic (bcc) to fcc was higher than that previously reported in the Fe-H system (Fig. 1). This discrepancy in the phase boundary might be caused by the reaction kinetics of the fcc-bcc-dhcp reactions in FeH\textsubscript{x}. We conducted time studies at the conditions of the phase boundaries (Fig. 2). We also observed through the neutron diffraction patterns the phase transitions of forward and reverse reactions \textit{in situ} by increasing and decreasing the temperature at a constant press load condition.

Figure 1. The experimental pressure and temperature conditions and observed phase(s) of FeH\textsubscript{x} in this study. (a) The solid circles and open squares represent the experimental conditions of Rietveld refinement for fcc FeH\textsubscript{x} and phase observation, respectively. The yellow and blue arrows indicate the heating and cooling paths, respectively. (b) The observed phase(s) in all experimental conditions. The uncertainties in temperature are estimated to be ±50 K. The overall uncertainties in pressure are estimated to be <0.5 GPa; this includes the differences in pressure of 0.2–0.3 GPa before and after neutron diffraction measurement and experimental errors of ~0.1 GPa. Colored symbols show the observed phase(s). Gray star: bcc + dhcp + fcc, blue solid diamonds: bcc, magenta open diamonds: bcc + fcc, red solid squares/triangles: fcc (in heating/cooling paths, respectively), yellow open squares/triangles: fcc + dhcp (in heating/cooling paths, respectively), green solid circles: dhcp/hcp, light blue open circles: dhcp/hcp + bcc. The hcp phase was observed under low temperature conditions where no hydrogen was released from the hydrogen source, NH\textsubscript{3}BH\textsubscript{3}. The magenta bold line represents the phase boundary of FeH\textsubscript{x} phases obtained in this study. The green dotted line and the blue dashed line represent the phase boundaries of FeH\textsubscript{x} and Fe as reproduced from previous studies, respectively\textsuperscript{15,16,26}. 
The site occupancies of hydrogen in O- and T-sites are similar to those reported by Machida and 1200 K, and at 4 GPa and 1175 K, the occupancy is 0.140 (Fig. 1). The single fcc FeH

Figure 2. Typical examples of the phase transition for FeH

Hydrogen atoms generally occupy interstitial O-sites of the iron lattice with a small number of T-sites, therefore the iron lattice expands by hydrogenation. The volume expansion of the iron lattice can be calculated from following formula:

$$\Delta V(H) = \frac{V(FeH_x) - V(Fe))}{x},$$

where \(x\), \(V(FeH_x)\), \(V(Fe)\), and \(\Delta V(H)\) are the hydrogen concentration, atomic volumes of iron hydride and pure iron, and the volume expansion per hydrogen atom, respectively. We used the equation of state of fcc iron reported by Tsujino et al. for \(V(Fe)\). Here, \(V(FeH_x)\) and the hydrogen concentration \(x\) at each pressure and
Temperature were directly determined by powder neutron diffraction combined with Rietveld refinement, and we could determine the volume expansion per hydrogen atom, $\Delta V(H)$, in this study. To date, there have been a limited number of experiments on the determination of $\Delta V(H)$ in the fcc lattice of metals, such as the neutron diffraction study of the quenched iron-rich hydride alloy, Fe$_{0.65}$Mn$_{0.29}$Ni$_{0.06}$H$_{0.95}$, synthesized by Antonov et al. at 7 GPa, and recovered to atmospheric pressure at liquid N$_2$ temperature. They determined the hydrogen concentration by degassing after recovery. The $\Delta V(H)$ value of 1.9 Å$^3$ that they obtained is consistent with that of other 3d transition-metal hydrides with fcc crystal structure (e.g., $\gamma$ -MnD$_{0.45}$: 1.85 Å$^3$, $\gamma$ -CoH: 1.9 Å$^3$). The present measurement of a volume increase by a hydrogen atom, $\Delta V(H)$, can be compared with this value and is discussed later.

The pressure dependence of the volume increase in the fcc iron lattice by hydrogen dissolution, $V(\text{FeH}_x) - V(\text{Fe})$, and its hydrogen content, $x$, are shown in Fig. 4. As can be observed, both $V(\text{FeH}_x) - V(\text{Fe})$ and $x$ increase with increasing pressure; $V(\text{FeH}_x) - V(\text{Fe})$ depends very weakly on temperature, whereas $x$ decreases with increasing temperature.

Figure 3a shows the magnitude of the volume expansion $V(\text{FeH}_x) - V(\text{Fe})$ for the fcc iron lattice increases with increasing the hydrogen content, $x$. The volume expansion $V(\text{FeH}_x) - V(\text{Fe})$ of the lattice seems to increase...
linearly up to $x \sim 0.8$, at a rate of $\Delta V(H)$ of $\sim 2.22(\pm 0.36) \text{Å}^3$ at high temperatures, which is comparable with that of deuterium ($\Delta V(D) \sim 2.21 \text{Å}^3$) determined at 988 K and 6.3 GPa by Machida et al.\textsuperscript{11}. Figure 5b shows the pressure dependence of the volume increase of the fcc lattice as a result of hydrogen dissolution for one hydrogen atom, $\Delta V(H)$. The figure indicates that $\Delta V(H)$ is almost independent of pressure at least up to 12 GPa.

**Discussion**

Several high pressure polymorphs of iron hydride and superhydride phases were reported by using in situ X-ray diffraction method. Hirao et al.\textsuperscript{5} observed dhcp FeH\textsubscript{x} phases up to 80 GPa and 300 K. Peppin et al.\textsuperscript{6,7} observed iron hydride, FeH\textsubscript{2} and FeH\textsubscript{3} at around 60–80 GPa, and iron superhydride phase, FeH\textsubscript{5} toward to 130–160 GPa after temperature quenching at room temperature. In theoretical work, the presence of further superhydride phase FeH\textsubscript{6} has been suggested\textsuperscript{8}. However, these studies were conducted only at room temperature conditions, and had not observed the behavior of hydrogen and its volume in situ. Therefore, our data provide important information for evaluation of the effect of hydrogen dissolution on the compression behavior of the fcc iron lattice that is a high pressure and high temperature phase of FeH\textsubscript{x}, and for reliable estimation of the hydrogen content in the Earth’s core by comparison with the density of the PREM (Preliminary Reference Earth Model) Earth’s core\textsuperscript{22}. Chakravarty et al.\textsuperscript{23} made ab initio calculations for hydrogen in the iron lattice and showed the pressure effect on the volume of interstitial hydrogen at high pressure. The interstitial volume $\Delta V(H)$\textsuperscript{24} fitted using the Vinet equation of state by Fukai\textsuperscript{19} (Fig. 5b) was very weakly dependent on pressure, which is consistent with the present work.

The volume increase per hydrogen atom, $\Delta V(H)$, in fcc FeH\textsubscript{x} has not been determined previously, and the value of $\Delta V(H) = 1.9 \text{Å}^3$ per hydrogen atom that is conventionally used for fcc FeH\textsubscript{x} was estimated by the neutron
Sakamaki et al. used this value of volume expansion and reported that fcc FeH$_x$ approaches superstoichiometric composition with $x = 1.0–1.2$ immediately below the melting temperature at 11.5–20 GPa. The present results of lattice expansion per hydrogen atom, $\Delta V(H) = (V(\text{FeH}_x) - V(\text{Fe})) / x$, is $2.22(\pm 0.36) \text{ Å}^3$ shown as a magenta dotted line. (b) Pressure dependence of the volume expansion of the fcc lattice due to dissolution of one hydrogen atom, $\Delta V(H)$. The pressure dependence calculated theoretically$^{4,11}$ is shown as a green dashed line. The abbreviations of symbols and the errors are the same as those in Fig. 4.

The revised analyses indicate that whole core may contain hydrogen of 80(±31) times of the ocean mass with 79(±30) and 0.8(±0.3) ocean mass for the outer and inner cores, respectively.
Methods
The high-pressure and high-temperature neutron diffraction experiments were conducted at the high-pressure PLANET beamline (BL11) at the Material and Life Science Experimental Facility (MLF) in J-PARC. The PLANET beamline has the capability to obtain low background and including incoherent scattering from hydrogen due to the excellent collimation of the incident beam and scattered neutron with narrow incident and receiving collimators. A six-axis multi-anvil high-pressure apparatus (ATSUHIME) installed at this beamline was used for high-pressure generation. An iron disc specimen was placed in the center of a hydrogen-sealing capsule made of NaCl with internal hydrogen sources of NH₄BH₄ pellets above and below. To seal hydrogen, the NaCl capsule was inserted in a cylindrical graphite heater and embedded in a pressure-transmitting medium made of Cr-doped MgO [a 10.5 mm edge cube for the anvil with a 7 mm truncated edge length (TEL), and a 15 mm edge cube for the anvil with a 10 mm TEL]. Neutron diffraction data were collected at high pressure and high temperature. The generated pressure was determined by the neutron powder diffraction profile of the capsule material of NaCl. The NaCl-B₁ pressure scale used in this experiment was based on Brown. The experimental temperature was evaluated based on the heating power using a power-temperature calibration curve which was determined by the separate runs with a Pt-Pt 13% Rh thermocouple. The accuracy of the temperature calibration curve was confirmed by the bcc-fcc transition of iron. The uncertainty of the temperature determination was ±50 K. Neutron diffraction profiles were collected during increasing and decreasing temperatures for 5 min. The temporal evolution of the diffraction profile was monitored at several fixed temperatures near the phase boundaries above the decomposition temperature of NH₄BH₄, which is considered to be < 500 K as examples shown in Fig. 2. In addition, no unknown phases were observed except Fe, FeH₅, and NaCl in both heating/cooling paths (Figs. 2 and 3). This indicates that the reaction had been occurred only by iron and hydrogen, and there was no contamination with a hydrogen sample by boron or nitrogen from the hydrogen sources. The composition and site occupancy of hydrogen atoms in the fcc lattice of FeH₅ were determined for the equilibrium state of fcc FeH₅ at a fixed pressure based on Rietveld analysis of the diffraction profiles. The temperature was kept constant and the temporal evolution of the diffraction profile was monitored to confirm that FeH₅ reached equilibrium with the surrounding H₂ fluid. High-pressure and high-temperature neutron diffraction experiments were conducted at pressures in the range 3–12 GPa and at temperatures in the range 900–1200 K. Two runs (Runs 1 and 4) were conducted in the pressure range 3.5–6 GPa using cubic anvils with a 10 mm truncated edge. The other two runs (Runs 2 and 3) were conducted at pressures in the range 8–12 GPa using anvils with a 7 mm truncated edge. The schematic diagram of the multianvil apparatus with the high-pressure and high-temperature cell assembly and the neutron scattering geometry is given in Machida et al. The diffraction intensity of the sample was corrected using the data obtained for a vanadium pellet and an empty cell of a dimension similar to that used in sample data collection. The detailed cell assembly of the present cubic apparatus is given in Supplementary Fig. 2.

Data Availability
All data supporting the findings of this study are available within the paper, Methods and Supplementary Information. The crystallographic data are available from the corresponding authors upon request.

References
1. Sakamaki, K. et al. Melting phase relation of FeH₅ up to 20 GPa: Implication for the temperature of the Earth’s core. Phys. Earth Planet. Inter. 174, 192–201, https://doi.org/10.1016/j.pepi.2008.05.017 (2009).
2. Narygina, O. et al. X-ray diffraction and Mossbauer spectroscopy study of fcc iron hydride FeH₅ at high pressures and implications for the composition of the Earth’s core. Earth Planet. Sci. Lett. 307, 409–414, https://doi.org/10.1016/j.epsl.2011.05.015 (2011).
3. Thompson, E. C. et al. High-Pressure Geophysical Properties of fcc Phase FeH₅. Geochim. Geophys. Geosys. 19, 305–314, https://doi.org/10.1002/2017GC007168 (2018).
4. Shibazaki, Y. et al. Sound velocity measurements in dhcp-FeH₅ up to 70 GPa with inelastic X-ray scattering: Implications for the composition of the Earth’s core. Earth Planet. Sci. Lett. 313–314, 79–85, https://doi.org/10.1016/j.epsl.2011.11.002 (2012).
5. Hirao, N. et al. Compression of iron hydride to 80 GPa and hydrogen in the Earth’s inner core. Geophys. Res. Lett. 31, L06616, https://doi.org/10.1029/2003GL019380 (2004).
6. Pepin, C. M. et al. New Iron Hydrides under High Pressure. Phys. Rev. Lett. 113, 265504, https://doi.org/10.1103/PhysRevLett.113.265504 (2014).
7. Pepin, C. M. et al. Synthesis of FeH₅: A layered structure with atomic hydrogen slabs. Science 357, 382–385, https://doi.org/10.1126/science.aao9961 (2018).
8. Kavshin et al. Iron Superhydrides FeH₅ and FeH₆: Stability, Electronic Properties, and Superconductivity. J. Phys. Chem. C 122, 4731–4736, https://doi.org/10.1021/acs.jpcc.8b01270 (2018).
9. Antonov, V. E. et al. Neutron diffraction investigation of the dhcp and hcp iron hydrides and deuterides. J. Alloy Compd. 264, 214–222, https://doi.org/10.1016/S0925-8388(97)02988-3 (1998).
10. Fukai, Y. et al. Evidence of copious vacancy formation in Ni and Pd under a high hydrogen pressure. Ipn J. Appl. Phys. 32, L1256–L1259, https://doi.org/10.1143/IJAP.32.L1259 (1993).
11. Machida, A. et al. Site occupancy of interstitial deuterium atoms in face-centred cubic iron. Nat. Commun. 5, 5063, https://doi.org/10.1038/ncomms6083 (2014).
12. Izuka-Ooku, R. et al. Hydrogenation of iron in the early stage of Earth’s evolution. Nat. Commun. 8, 14096, https://doi.org/10.1038/ncomms14096 (2017).
13. Sano-Furukawa, A. et al. Six-axis multi-anvil press for high-pressure, high temperature neutron diffraction experiments. Rev. Sci. Instrum. 85, 113905, https://doi.org/10.1063/1.4901095 (2014).
14. Eltorai, T. et al. Design and performance of high-pressure PLANET beamline at pulsed neutron source at J-PARC. Nucl. Instrum. Methods. Phys. Res. A 780, 53–67, https://doi.org/10.1016/j.nima.2015.01.059 (2015).
15. Antonov, V. E. et al. High-pressure hydrides of iron and its alloys. J. Phys. Condens. Matter. 14, 6427–6445, https://doi.org/10.1088/0953-8984/14/25/311 (2002).
16. Fukai, Y. et al. The phase diagram and superabundant vacancy formation in Fe–H alloys under high hydrogen pressures. J. Alloy Compd. 348, 105–109, https://doi.org/10.1016/S0925-8388(02)00906-X (2002).
17. Fukai, Y. The Metal-Hydrogen System 2nd Edition, https://doi.org/10.1007/3-540-28883-X (Springer-Verlag, Heidelberg, 2005).
18. Pitt, M. P. & Gray, E. M. Tetrahedral occupancy in the Pd-D system observed by neutron powder diffraction. Europhys. Lett. 64, 344–350, https://doi.org/10.1209/epl/i2003-00187-x (2003).
19. Fukai, Y. Some properties of the Fe-H system at high pressures and temperatures, and their implications for the Earth’s core. In High Pressure Research: Application to Earth and Planetary Sciences, edited by Syono, Y. & Manghnani, M. H., pp. 373–385, https://doi.org/10.1029/GM067 (Terra Scientific Publishing Company, Tokyo, 1992).

20. Tsujino, N. et al. Equation of state of γ-Fe: Reference density for planetary cores. Earth Planet. Sci. Lett. 375, 244–253, https://doi.org/10.1016/j.epsl.2013.05.040 (2013).

21. Antonov, V. E. et al. Magnetic properties of hydrogen solid solutions in Fe-Ni-Mn alloys. Phys. Stat. Sol. (a) 52, 703–710, https://doi.org/10.1002/pssa.2210520243 (1979).

22. Dziewonski, A. M. & Anderson, D. L. Preliminary reference Earth model. Phys. Earth Planet. Inter. 25, 297–356, https://doi.org/10.1016/0031-9201(81)90046-7 (1981).

23. Chakravarty, S. et al. Theory of dense hydrogen. Phys. Rev. B 24, 1624–1635, https://doi.org/10.1103/PhysRevB.24.1624 (1981).

24. Nylen, J. et al. Thermal decomposition of ammonia borane at high pressures. J. Chem. Phys. 131, 104506, https://doi.org/10.1063/1.3230973 (2009).

25. Brown, J. M. The NaCl pressure standard. J. Appl. Phys. 86, 5801–5808, https://doi.org/10.1063/1.371596 (1999).

26. Klotz, S. et al. The α-γ-ε triple point of iron investigated by high pressure-high temperature neutron scattering. Appl. Phys. Lett. 93, 091904, https://doi.org/10.1063/1.2976128 (2008).

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Author Contributions
E.O. devised the project. A.S.-F. and T.H. developed the new in situ neutron powder diffraction system at the PLANET Beamline in J-PARC. All authors participated in the experiments. D.I. analyzed the data. All authors discussed the results. D.I. and E.O. wrote the paper with input from all authors.

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