Hydrogen occupation and hydrogen-induced volume expansion in Fe$_{0.9}$Ni$_{0.1}$D$_x$ at high P-T conditions

Chikara Shito$^1$, Hiroyuki Kagi$^{1*}$, Sho Kakizawa$^2$, Katsutoshi Aoki$^1$, Kazuki Komatsu$^1$, Riko Iizuka-Oku$^1$, Jun Abe$^3$, Hiroyuki Saitoh$^4$, Asami Sano-Furukawa$^{5,6}$, Takanori Hattori$^5$

$^1$Geochemical Research Center, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

$^2$Earth and Planetary Systems Science Program, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-3-1, Kagamiyama, Higashi-Hiroshima-Shi, Hiroshima, 739-8526, Japan

$^3$Neutron Science and Technology Center, Comprehensive Research Organization for Science and Society, 162-1, Shirakata, Tokai-mura, Naka-gun, Ibaraki 319-1106, Japan

$^4$Quantum Beam Science Research Directorate, National Institutes for Quantum and Radiological Science and Technology, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo, 679-5148, Japan

$^5$J-PARC Center, Japan Atomic Energy Agency, 2-4, Shirakata, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan

$^6$Institute of Materials Structure Science, KEK, 203-1 Shirakata, Tokai-mura, Naka-gun, Ibaraki, 319-1195, Japan

*Corresponding author: kagi@eqchem.s.u-tokyo.ac.jp (Hiroyuki Kagi)
Abstract

The density of the Earth’s core is several percent lower than that of iron–nickel alloy under conditions of pressure and temperature equivalent to the Earth’s core. Hydrogen is one of the most promising constituents accounting for the density deficit, but hydrogen occupation sites and density decrease of iron–nickel alloy caused by hydrogenation have never been investigated. In this study, the phase relation and crystal structure of Fe$_{0.9}$Ni$_{0.1}$H$_x$(D$_x$) at high pressures and temperatures up to 12 GPa and 1000 K were clarified by in-situ X-ray diffraction and neutron diffraction measurements. Under the $P$-$T$ conditions of the present study, no deuterium atoms occupied tetragonal (T) sites of face-centered cubic (fcc) Fe$_{0.9}$Ni$_{0.1}$D$_x$ although the T site occupation was previously reported for fcc FeH$_x$(D$_x$). The deuterium-induced volume expansion per deuterium $v_D$ was determined to be 2.45(4) Å$^3$ and 3.31(6) Å$^3$ for fcc and hcp Fe$_{0.9}$Ni$_{0.1}$D$_x$, respectively. These $v_D$ values are significantly larger than the corresponding values for FeD$_x$. The $v_D$ value for fcc Fe$_{0.9}$Ni$_{0.1}$D$_x$ slightly increases with increasing temperature. This study suggests that only 10% of nickel in iron drastically changes the behaviors of hydrogen in metal. Assuming that $v_D$ is constant regardless of pressure, the maximum hydrogen content in the Earth’s inner core is estimated to be one to two times the amount of hydrogen in the oceans.
Keywords: neutron diffraction, high pressure, metal hydride, Earth’s core

Introduction

Cosmochemical studies suggested that the iron in the Earth’s core contains 5–15 wt% of nickel (e.g. Anderson 1989). It has been a long-standing subject that the core would contain light elements (H, C, N, O, Si, and S) because the density of the Earth’s core is about 10% lower in the outer core and about 5% lower in the inner core than that of pure iron (e.g. Birch 1952). Hydrogen, the most abundant element in the solar system, is thought to be the most plausible candidate among the light elements. According to Fricker and Reynolds (1968), a deep magma ocean, which once existed on the primordial Earth’s surface, would have dissolved about 1 wt% of water. Okuchi (1997) suggested that most of the dissolved water was incorporated into metallic iron by metal–silicate partitioning in the lowermost of the magma ocean. Iizuka-Oku et al. (2017) directly observed the formation process of iron hydride through the reaction between iron and water using high-pressure and high-temperature (high-PT) neutron diffraction. The H-bearing iron at the base of the magma ocean formed through such processes would sink to form the current core because of the gravitational instability. Tagawa et al. (2021) found that the partition coefficient of hydrogen between molten iron and silicate melt is greater than 29 and
hydrogen is strongly siderophile at the conditions of core formation. Kato et al. (2020) determined the stability of stoichiometric $f_{cc}$ FeH up to 137 GPa and showed that $f_{cc}$ FeH is stable at the P-T conditions of the Earth’s core. Ohta et al. (2019) indicated that the resistivity of stoichiometric $f_{cc}$ FeH is smaller than that of $f_{cc}$ Fe by measuring resistivity of iron hydrides at high pressures up to 65 GPa and high temperatures up to 2100 K. The chemical composition of the Earth’s core has been estimated by comparing density (e.g. Anderson and Isaak 2002) and sound velocity measurements (e.g. Sakamaki et al. 2016) of prospective constituent phases to the 1-D averaged seismic models such as PREM (Dziewonski and Anderson 1981). However, the definitive chemical composition has not been determined because the behavior of light elements in the core is unknown.

The composition of hydrogen $x$ in a metal hydride (MH$_x$) can be estimated from the increase of unit cell volume, if the volume expansion per hydrogen $v_H$ is defined by the following equation:

$$ v_H = \frac{V_{MH_x} - V_M}{x} \quad (1) $$

where $V_{MH_x}$ and $V_M$ are volume per metal atom of metal hydride and pure metal, respectively. Hydrogen atoms incorporated into metal occupy interstitial sites of the metal lattice. Metals with a close-packed structure have one octahedral (O) site and two tetrahedral (T) sites per metal atom (Figure 1): the composition of hydrogen $x$ is
calculated from the occupancy \((O)\) of each site by \(x = O_O + 2O_T\). Hydrogen atoms dominantly occupy the O site that has a larger free space than the T site.

Iron hydride is formed only at hydrogen pressure higher than several gigapascals (Antonov et al., 1982). In the iron–deuterium system, Machida et al. (2014) clarified for the first time that the D atoms in face-centered cubic \((fcc)\) FeD\(_x\) occupied not only O site but also T site with occupancies of 0.532(9) and 0.056(5), respectively, using in-situ high-\(PT\) neutron diffraction. Afterwards, a similar T site occupancy of 0.057(35) was observed for FeH\(_x\) by Ikuta et al. (2019) at pressures lower than 5 GPa. It should be noted that the O-site occupancy (0.87) reported by Ikuta et al. (2019) was slightly higher than that reported by Machida et al. (2014).

Recent experiments clarified that even approximately 10% of nickel in iron affects phase relations and density of iron under high-\(PT\) conditions (Torchio et al. 2020; Sakai et al. 2014). However, the iron–nickel–hydrogen system has been poorly investigated under high-\(PT\) conditions. In this study, we have investigated the \(P–T–x\) phase diagram of Fe\(_{0.9}Ni_{0.1}H_x\) using X-ray diffraction (XRD) and the relation between unit cell volumes and hydrogen occupancies of Fe\(_{0.9}Ni_{0.1}D_x\) using neutron diffraction. The obtained results were compared with those of FeH\(_x\)(D\(_x\)) to clarify the effect of nickel on hydrogen occupation sites and hydrogen-induced volume expansion.
Methods

Synthesis of Fe\(_{0.9}\)Ni\(_{0.1}\) alloy

Fe\(_{0.9}\)Ni\(_{0.1}\) alloy was prepared using an arc melting furnace (Nisshin Giken Corporation NEV-ADR). Iron and nickel powders were mixed in a molar ratio of 9:1 and pelletized into a cuboid (15×15×10 mm\(^3\)). The chamber of the melting furnace was flushed by Ar and then the sample was melted for approximately one minute under Ar pressure of 0.04 MPa. The molten ingot was turned over and then melted again. The rotating and melting process was repeated 5 times. The recovered sample was observed using a scanning electron microscope (SEM) (Hitachi S-4500) equipped with an energy-dispersive X-ray spectrometer (EDS). A back scattered electron (BSE) image of the recovered sample is shown in Figure S1. Dark and light areas were observed, although the chemical compositions in the two regions were identical. According to the phase diagram of iron–nickel system, body-centered cubic (bcc) and fcc phases should coexist in the Fe\(_{0.9}\)Ni\(_{0.1}\) sample (e.g. Swartzendruber et al. 1991); however, only the bcc phase was identified from our XRD measurements. This may be due to the fast transition from fcc to bcc via diffusion-less mechanism by rapid cooling (Gilbert and Owen 1962). The different colors of the two regions in Figure S1 were not caused by the coexistence of the two phases,
but by difference in crystal orientation, suggesting that large grains grew during the crystallization. Preliminary neutron diffraction measurements on a crescent-shaped fragment of the synthesized Fe$_{0.9}$Ni$_{0.1}$ alloy were carried out to check the orientation of the grains. Diffraction profiles of the alloy were measured at two geometries perpendicular to each other. The peak intensities in the two profiles were significantly different (Figure S2). Therefore, the sample for the high-$PT$ experiments was prepared by pelleting the shavings after lathing the bulk alloy in order to obtain less-orientated sample.

**High-$PT$ XRD measurements of Fe$_{0.9}$Ni$_{0.1}$ and Fe$_{0.9}$Ni$_{0.1}$H$_x$**

Energy-dispersive XRD measurements at high-$PT$ conditions were conducted using the multi-anvil (MA) high pressure apparatus (MAX-III) at NE7A beamline of the Photon Factory Advanced Ring (PF-AR), KEK. MAX-III is a 700-ton uniaxial press, with a DIA type guide-block. Pressure was generated by the double-stage system, the MA 6-8 cell assembly, consisting of six outer anvils (MA6) and eight truncated cubic anvils (MA8). The truncation edge length (TEL) of the second-stage anvils was 5 mm. The details of the high-pressure cell are shown in Figure S3. The cell assembly consists of a thermally insulating ZrO$_2$ sleeve and an X-ray transparent boron epoxy pressure medium. Energy-
dispersive XRD using white X-ray beam was adopted, and diffraction angle $2\theta$ was fixed at $6^\circ$. Two experiments with and without hydrogen sources were conducted to obtain the volumes of hydrogenated and non-hydrogenated samples at high-PT conditions. In the experiments of $\text{Fe}_{0.9}\text{Ni}_{0.1}$, the sample was mixed with BN powder in a volume ratio of 2:3 to prevent the grain growth at high temperatures. In the experiments of $\text{Fe}_{0.9}\text{Ni}_{0.1}\text{H}_x$, ammonia borane ($\text{NH}_3\text{BH}_3$) as the hydrogen source (Antonov et al. 2017) was included in the high-pressure cell. In both experiments, the pelletized sample was enclosed in a NaCl capsule that enables quasi-hydrostatic compression and seals H$_2$ fluid released from NH$_3$BH$_3$ (Machida et al. 2014). To avoid contamination of boron to the sample, a gold foil was placed between NH$_3$BH$_3$ and $\text{Fe}_{0.9}\text{Ni}_{0.1}$. A mixture of NaCl and BN powder in a volume ratio of 1: 1 was placed as a pressure marker above the NaCl capsule. The temperature was measured using a W5\%Re–W26\%Re thermocouple, and the pressure was determined from lattice parameter of NaCl based on the equation of state (EoS) by Brown (1999). Although new equations of state for NaCl have been published (Dorogokupets and Dewaele 2007; Dewaele 2019), we adopted Brown (1999) which has been conventionally used by many researchers. The maximum pressure error was estimated to be ~0.3 GPa. Unit cell volumes of fcc $\text{Fe}_{0.9}\text{Ni}_{0.1}$ at high-PT conditions were fitted to the following third-order Birch–Murnaghan (BM) EoS:
\[ P = \frac{3}{2} K(0, T) \left[ \left( \frac{V(0, T)}{V(P, T)} \right)^{\frac{7}{3}} - \left( \frac{V(0, T)}{V(P, T)} \right)^\frac{5}{3} \right] \left\{ 1 - \frac{3}{4} (K' - 4) \left[ \left( \frac{V(0, T)}{V(P, T)} \right)^\frac{2}{3} - 1 \right] \right\} \]  

(2)

\[ K(0, T) = K(0, T_0) + \frac{dK}{dT}(T - T_0) \]  

(3)

where \( K(0, T) \) is the temperature dependent bulk modulus and \( K' \) is its pressure derivative, respectively. \( K' \) was assumed to be independent on temperature. The volume expansion with temperature is expressed as follows:

\[ V(0, T) = V(0, T_0) \exp \left[ \int_{T_0}^{T} \alpha(T) dT \right] \]  

(4)

\[ \alpha(T) = a + bT \]  

(5)

where \( \alpha \) is a temperature-dependent thermal expansion parameter defined by two constants \( a \) and \( b \) (Fei 1995). Least squares fitting was performed using EoSFit7 GUI software (Gonzalez-Platas et al. 2016).

In the hydrogenated experiments, pressure was increased up to 3.5 GPa under a load of 100 tons, and then the temperature was increased up to 800 K over 1.5 hours. The completion of hydrogenation was confirmed from the unit cell volume.

**High-PT neutron diffraction measurements of Fe_{0.9}Ni_{0.1}D_x**

Neutron diffraction measurements of Fe_{0.9}Ni_{0.1}D_x under high-PT conditions were conducted at high-pressure neutron beamline, PLANET (BL11), in MLF, J-PARC (Hattori et al. 2015). High pressure and high temperature were generated with a six-axis
multi-anvil press ATSUHIME (Sano-Furukawa et al. 2014) using a 6-6 cell assembly. Second-stage anvils with TEL 7 mm and 10 mm were used in the experimental Runs A560–561 and A578–580, respectively. A typical cell assembly is depicted in Figure 2. A Cr-doped MgO cube was used as a pressure-transmitting medium and pyrophyllite gaskets were used to prevent the pressure medium from flowing out. High temperatures were generated using a graphite heater embedded in the pressure medium. The temperature was estimated from the electric power applied to the heater based on the power–temperature relation pre-calibrated using a W3%Re–W25%Re thermocouple. Two ND$_3$BD$_3$ pellets were placed below and above the Fe$_{0.9}$Ni$_{0.1}$ pellet. About two-thirds of deuterium in ND$_3$BD$_3$ is released by heating above 400 K at ambient pressure (Frueh et al. 2011). Table 1 summarizes the initial sample size and amount of deuterium loaded in the cell. Run A578 was conducted under the condition in which deuterium would be released above the solubility limit of Fe$_{0.9}$Ni$_{0.1}$. NaCl was used as a deuterium-sealing capsule and pressure marker. Pressure was estimated from the lattice parameter of NaCl based on the EoS by Brown (1999). Pressure uncertainty was estimated to be ~0.2 GPa. 

$P$-$T$ conditions of the neutron diffraction measurements are shown in Figure S4. Neutron diffraction intensities of the sample were corrected using those of a vanadium rod and empty cell in order to subtract scattering from the surrounding cell assembly (Hattori et
al. 2015). Lattice parameters and crystal structure of Fe$_{0.9}$Ni$_{0.1}$D$_x$ including the O and T site occupancies of deuterium atoms were refined by the Rietveld method using GSAS/EXPGUI software (Larson and Von Dreele 2004; Toby 2001).

**Results and Discussion**

**Equation of state of fcc Fe$_{0.9}$Ni$_{0.1}$**

$P$-$V$-$T$ data of fcc Fe$_{0.9}$Ni$_{0.1}$ obtained from XRD measurements are summarized in Table S1. The $P$-$V$ plots and the fitting result by third-order BM EoS of fcc Fe$_{0.9}$Ni$_{0.1}$ are depicted in Figure 3. The results indicate that the unit cell volume of fcc Fe$_{0.9}$Ni$_{0.1}$ is about 1% smaller than that of pure iron in the $P$-$T$ range of this study. Only the data points where the single phase of fcc was observed were used for EoS fitting to exclude effects of variations in iron–nickel composition. Because the number of data points is limited, some thermoelastic parameters were fixed to the following values of pure iron (Tsujino et al. 2013): $\frac{dK}{dT} = -0.0288$ GPaK$^{-1}$, $K' = 5.3$ and $b = 1.81 \times 10^{-8}$ K$^{-2}$. Thermoelastic parameters refined by the least squares method are listed in Table 2. The bulk modulus of fcc Fe$_{0.9}$Ni$_{0.1}$ is comparable to that of fcc Fe at 300–900 K, but the thermal expansion coefficient is slightly larger than that of fcc Fe. The EoS obtained in this study was used to estimate the deuterium-induced volume expansion per deuterium $v_D$ of Fe$_{0.9}$Ni$_{0.1}$D$_x$. 

11
Phase diagram of $\text{Fe}_{0.9}\text{Ni}_{0.1}$ and $\text{Fe}_{0.9}\text{Ni}_{0.1}H_x$

The phase boundary between $\text{bcc} + \text{fcc}$ and $\text{fcc}$ $\text{Fe}_{0.9}\text{Ni}_{0.1}$ was determined using in-situ XRD measurements. Phase identification was performed using 111, 200, 220, 311, and 222 reflections for the $\text{fcc}$ phase and 111, 200, 211, and 220 reflections for the $\text{bcc}$ phase. Figure S5 shows the experimental $P$-$T$ conditions and the observed phases. Each XRD profile was obtained for 150 or 300 seconds to investigate a dominant phase (Figure S6). Considering the composition–temperature phase diagram at ambient pressure, the Fe/Ni ratios of coexisting $\text{bcc}$ and $\text{fcc}$ phases can be different. The $P$-$T$ conditions under which the phase transition occurred were plotted for both heating and cooling processes (Figure 4). The transition temperatures during heating and cooling were notably different; thus, the midpoints between the two was defined as the transition temperature. The phase boundary is drawn so that it passes through the transition temperatures at ambient and high pressures. The results from the present study first indicate that the phase boundary between $\text{bcc} + \text{fcc}$ and $\text{fcc}$ of $\text{Fe}_{0.9}\text{Ni}_{0.1}$ was about 300 K lower than that of pure Fe.

Figure 5 shows the phase diagram of $\text{Fe}_{0.9}\text{Ni}_{0.1}$–H(D) system up to 12 GPa and 1000 K obtained in this study. In the XRD experiments, one $\text{bcc}$ phase and two $\text{fcc}$ phases with different lattice parameters were observed during the cooling process below 450 K.
(Figure 6, Figure 7). In the heating process, the two fcc phases with different hydrogen (deuterium) concentrations coexisted with the bcc phase up to 600 K and then they merged into a single phase with fcc structure. Moreover, the stability region of fcc phase was slightly expanded compared with the pure iron system reported by Machida et al. (2019). In Run A561, the hcp phase unexpectedly appeared probably due to the deficit of deuterium in the high-pressure cell. Under such deuterium-undersaturated ($x < 1$) conditions, the hcp phase with $x < 0.5$ was observed below 600 K. This result is consistent with Machida et al. (2019) reporting the appearance of hcp phase of FeH$_x$ with $x < 0.5$.

Representative neutron diffraction profiles are depicted in Figure S7. Most of the peaks from the dhcp phase were broader than those of the fcc phases. However, dhcp 110 reflection that appeared near fcc 220 was sharp presumably because the stacking layers of fcc (220) and dhcp (110) are preserved during the phase transition.

**Deuterium release from ND$_3$BD$_3$ and hydrogenation of Fe$_{0.9}$Ni$_{0.1}$**

The hydrogenation process of Fe$_{0.9}$Ni$_{0.1}$ was observed by high-PT neutron diffraction measurements. At 6–7 GPa, ND$_3$BD$_3$ thermally decomposed during heating from 500 K to 600 K in Run A578 (Figure 8). However, neither the notable volume expansion of Fe$_{0.9}$Ni$_{0.1}$ nor the phase transition from bcc to fcc was observed up to 600 K. The phase
transition from bcc to fcc occurred on further heating from 600 K to 700 K. The deuterium content ($x$) of $\text{fcc Fe}_{0.9}\text{Ni}_{0.1}\text{D}_x$ at 700 K was estimated to be about 0.1. After increasing the temperature from 700 K to 900 K in Run A578, we observed a clear volume expansion of $\text{fcc Fe}_{0.9}\text{Ni}_{0.1}$ (see Figure 8), and the volume expansion completed in about an hour (Figure 9). In Run A580, however, a longer time was needed for homogeneous hydrogenation over the entire sample presumably because the sample was longer than that used in A578 (see Table 1). After the neutron diffraction measurements, SEM-EDS observation was conducted on the recovered sample. The result confirmed that the chemical composition did not change, indicating that the disproportionation reaction associated with the phase transition did not occur.

**Site occupancies of deuterium atoms in Fe$_{0.9}$Ni$_{0.1}$D$_x$**

A representative result of the Rietveld refinement of $\text{fcc Fe}_{0.9}\text{Ni}_{0.1}\text{D}_x$ is shown in Figure 10. For the Rietveld refinement, only the data after the volume expansion had stabilized were used. The obtained neutron diffraction profiles and the fitting results are summarized in Figure S8. The result of structure refinements and the estimated $v_D$ value are listed in Table 3. Machida et al. (2014) clarified that deuterium atoms in fcc FeD$_x$ occupy O and T sites with an occupancy of 0.532(9) and 0.056(5), respectively, at 988 K.
and 6.3 GPa. On the other hand, no T site occupation was observed in $fcc$ Fe$_{0.9}$Ni$_{0.1}$D$_x$.

**Deuterium-induced volume expansion: Effects of nickel on deuterization of iron**

Deuterium-induced volume expansion per deuterium, $v_{Dx}$, of $fcc$ Fe$_{0.9}$Ni$_{0.1}$D$_x$ was determined from the volume expansion and deuterium concentration obtained by the Rietveld refinements. **Figure 11a** plots deuterium-induced volume expansion ($V_{MDx} - V_M$) versus the deuterium content in $fcc$ Fe$_{0.9}$Ni$_{0.1}$D$_x$. The plots have an almost linear relation with a slope $v_D$ of 2.45(4) Å$^3$, where data at 6.3–11.7 GPa and 300–950 K were also used for the least-squares fitting. As shown in **Fig. 11b**, the $v_D$ of $fcc$ Fe$_{0.9}$Ni$_{0.1}$D$_x$ was notably larger than that of $fcc$ FeD$_x$ (2.21(4) Å$^3$, Machida et al. 2014). This study indicates that introduction of 10% nickel into iron increases the hydrogen(deuterium)-induced volume expansion. The $v_D$ of $fcc$ Fe$_{0.9}$Ni$_{0.1}$D$_x$ is also larger than that of $fcc$ NiD$_x$ (2.09(13) Å$^3$, Saitoh et al. 2020), while it is in the range of $v_H$ in other transition metals such as Cr, Mn, Co, Mo, Tc, Rh, and Pd (1.7–2.5 Å$^3$, e.g. Fukai, 2005).

Temperature dependence of $v_D$ of iron hydride has been poorly investigated in previous studies. We suggest for the first time that $v_D$ of $fcc$ Fe$_{0.9}$Ni$_{0.1}$D$_x$ slightly increases with temperature at the ratio of about 0.0005 Å$^3$/K (see **Figure 11b**). However, due to the limited number of data points, additional experiments at higher-PT conditions would be
needed to confirm it.

The \( \nu_D \) of \( \text{hcp Fe}_{0.9}\text{Ni}_{0.1}\text{D}_x \) was determined to be \( 3.31(6) \, \text{Å}^3 \) at 6.3 GPa and 500 K. The \( \nu_D \) values of \( \text{fcc Fe}_{0.9}\text{Ni}_{0.1}\text{D}_x \) and \( \text{hcp Fe}_{0.9}\text{Ni}_{0.1}\text{D}_x \) obtained in this study were \( \sim 11\% \) and \( \sim 33\% \) larger than the corresponding values for \( \text{FeD}_x \), respectively. Therefore, the effects of nickel cannot be ignored in studying hydrogen and other light elements contained in the Earth’s core. However, it is unclear why 10\% nickel in iron has such a significant effect on hydrogen volume expansion of iron. Theoretical calculations and additional high-pressure experiments are needed to clarify the mechanism and the detailed effects of nickel.

**Implications**

The density deficit estimated in the Earth’s inner core depends on the temperature at inner core boundary (ICB), nickel content and compositions of light elements contained in the core. The ICB temperature was estimated to be 5150–6200 K from eutectic temperatures of Fe, Fe–C, Fe–O, Fe–Si and Fe–S systems at high pressures (e.g., Terasaki and Fischer 2016; Anzellini et al. 2013; Fei and Brosh, 2014; Seagle et al., 2008; Fischer et al., 2013; Mori et al., 2017). In the Fe–H system, however, melting temperature was clarified only up to pressures of 20 GPa (Sakamaki et al., 2016); therefore, it is difficult
to estimate the hydrogen content from melting temperature at the ICB pressure. Using the thermal EoS of hcp Fe (Fei et al., 2016) and hcp Fe$_{0.9}$Ni$_{0.1}$ (Sakai et al., 2014), the density deficits range from 3.3 to 5.0% and from 3.4 to 6.3%, respectively, given that the ICB temperature is 5150–6200 K.

Maximum hydrogen content in the Earth’s inner core was previously estimated to be 0.12(5)wt% using the $v_H$ value of fcc FeH$_x$ (Ikuta et al., 2019). In this study, $v_D$ of Fe$_{0.9}$Ni$_{0.1}$, which is close to the metal composition of the Earth’s core, was determined for the first time. This study indicates that the deuterium-induced volume expansion of fcc Fe$_{0.9}$Ni$_{0.1}$ is more than 10% greater than that of fcc Fe (e.g. Machida et al., 2014). In the hcp phase, which is likely to be comprised of the Earth’s inner core, the $v_D$ value of Fe$_{0.9}$Ni$_{0.1}$ was about 33% larger than that of pure Fe (Machida et al., 2019). Assuming that the density deficit of the Earth’s inner core is 3.4–6.3%, the hydrogen content $x$ in hcp Fe$_{0.9}$Ni$_{0.1}$H$_x$ is calculated to be 0.07–0.14, which corresponds to 0.13–0.25wt% of hydrogen in Fe$_{0.9}$Ni$_{0.1}$. If the whole inner core contains this amount of hydrogen, it would be equivalent to one-to-two times the amount of hydrogen contained in the oceans.

In this study, the maximum value of hydrogen content was estimated assuming pressure independent $v_D$ because of the limited pressure range of this study. The $v_D$ would have the pressure dependence; thus, it needs to be further investigated to estimate the
hydrogen contents in the core more accurately. Caracas (2015) obtained equations of state of pure hcp Fe and hcp FeH up to 400 GPa based on first-principles calculations. According to his results, the $v_H$ value decreases with increasing pressure. Recently, Tagawa et al. (2022) obtained experimentally the high-temperature equation of state of fcc FeH (FeH$_x$, $x=1$) and also showed that the $v_H$ value decreases with increasing pressure in the range up to 142 GPa. For further discussion, it is necessary to conduct neutron diffraction measurements on Fe and Ni-containing Fe at much higher-PT conditions corresponding to the core, which is a far-reaching goal.

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**Figure captions**

**Figure 1.** Crystal structure of (a) face-centered cubic (fcc) MH$_x$($D_3$) and (b) hexagonal close-packed (hcp) MH$_x$. Large gray spheres indicate metal atoms. Small spheres indicate O sites and T sites occupied by hydrogen atoms. The figures were produced using VESTA (Momma and Izumi, 2011).

**Figure 2.** Cell assembly for high-PT neutron diffraction experiment using TEL 7 anvils.

**Figure 3.** P-V plots of fcc Fe$_{0.9}$Ni$_{0.1}$. Solid and dashed lines indicate isothermal compression curves of fcc Fe$_{0.9}$Ni$_{0.1}$ (this study) and fcc Fe (Tsujino et al., 2013), respectively. The error of the plots without bars is smaller than the size of the symbol.

**Figure 4.** Phase boundaries of Fe$_{0.9}$Ni$_{0.1}$ in this study and pure Fe by Bundy, 1965.

**Figure 5.** Observed phases in Fe$_{0.9}$Ni$_{0.1}$–H system at P-T conditions using XRD and neutron diffraction measurements in the (a) heating and (b) cooling paths. Dashed lines indicate phase boundaries of FeH$_x$ by Fukai et al. (2003).
**Figure 6.** XRD patterns of Fe$_{0.9}$Ni$_{0.1}$–H system obtained at 4.3–5.1 GPa during the cooling process. Inverted filled/opened triangles indicate the peak positions of H-rich/H-poor fcc phases, respectively.

**Figure 7.** $x$-$T$ diagrams of Fe$_{0.9}$Ni$_{0.1}$H$_x$(D$_x$) determined by high-PT XRD and neutron diffraction. (a)–(c) X-ray diffraction. (d) and (e) Neutron diffraction (Run A561). Hydrogen (deuterium) content $x$ of fcc and hcp (dhcp) Fe$_{0.9}$Ni$_{0.1}$H$_x$(D$_x$) were calculated from the excess volume using the $v_{H(D)}$ of 2.45 Å$^3$ determined in this study and 2.48 Å$^3$ reported by Machida et al. (2019), respectively.

**Figure 8.** Neutron diffraction profiles (raw data) obtained during the first heating from 300 K to 900 K in Run A578. Phase transition of ND$_3$BD$_3$ was observed at temperature between 300 K and 500 K.

**Figure 9.** Time dependence of (a) unit cell volume and (b) deuterium content of fcc Fe$_{0.9}$Ni$_{0.1}$D$_x$ at 7.2 GPa and 900 K. The deuterium content was calculated from the unit cell volume using $v_D$ value of fcc Fe$_{0.9}$Ni$_{0.1}$D$_x$ determined in this study (described below).
The horizontal axis represents the elapsed time after the temperature reaches 900 K. The error of the data points without bars is smaller than the size of the symbol.

**Figure 10.** Neutron diffraction profile of $f_{cc}$ Fe$_{0.9}$Ni$_{0.1}$D$_{x}$ (Run A578) after intensity correction and the result of the Rietveld fitting. The triangles show the expected peak positions.

**Figure 11.** (a) Relation between deuterium content and deuterium-induced volume expansion in $f_{cc}$ Fe$_{0.9}$Ni$_{0.1}$D$_{x}$. (b) Temperature dependence of $v_D$. $V_{MD_x}$: Volume of $f_{cc}$ MD$_x$ (M = Fe$_{0.9}$Ni$_{0.1}$ (this study) and Fe (Machida et al., 2014)) per metal atom. $V_M$: Volume of $f_{cc}$ Fe$_{0.9}$Ni$_{0.1}$ (this study) and $f_{cc}$ Fe (Tsujino et al., 2013) per metal atom. The error of the plots without bars is smaller than the size of the symbol.
Table 1. Initial sample size of Fe_{0.9}Ni_{0.1} and expected deuterium content added as ND_3BD_3. *Deuterium content x, is described in molar ratio assuming that all the deuterium is released from ND_3BD_3.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>TEL (mm)</th>
<th>Sample size (mm)</th>
<th>*Deuterium content, x</th>
</tr>
</thead>
<tbody>
<tr>
<td>A560</td>
<td>7</td>
<td>φ3.0 × 3.7</td>
<td>0.48</td>
</tr>
<tr>
<td>A561</td>
<td>7</td>
<td>φ3.0 × 2.9</td>
<td>0.78</td>
</tr>
<tr>
<td>A578</td>
<td>10</td>
<td>φ4.0 × 2.5</td>
<td>2.00</td>
</tr>
<tr>
<td>A580</td>
<td>10</td>
<td>φ4.0 × 4.7</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Table 2. Thermoelastic parameters obtained from least squares fitting to BM EoS. The parameters at $T_0 = 1273$ K are shown for comparison with those of pure Fe by Tsujino et al. (2013). Numbers in parentheses represent errors in last digit(s).

<table>
<thead>
<tr>
<th></th>
<th>This study</th>
<th>This study</th>
<th>Tsujino et al. (2013)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$ (K)</td>
<td>300</td>
<td>1273</td>
<td>1273</td>
</tr>
<tr>
<td>$V_0$ ($\text{Å}^3$)</td>
<td>45.73(11)</td>
<td>48.77(8)</td>
<td>49.026(25)</td>
</tr>
<tr>
<td>$K_0$ (GPa)</td>
<td>139(7)</td>
<td>111(7)</td>
<td>110.8(18)</td>
</tr>
<tr>
<td>$K'$</td>
<td>5.3 (fix)</td>
<td>5.3 (fix)</td>
<td>5.3(2)</td>
</tr>
<tr>
<td>$dK/dT$ (GPa/K)</td>
<td>$-0.0288$ (fix)</td>
<td>$-0.0288$ (fix)</td>
<td>$-0.0288$ (fix)</td>
</tr>
<tr>
<td>$a$ ($\times 10^{-5} \text{ K}^{-1}$)</td>
<td>5.18(23)</td>
<td>5.18(23)</td>
<td>4.50(36)</td>
</tr>
<tr>
<td>$b$ ($\times 10^{-8} \text{ K}^{-2}$)</td>
<td>1.81 (fix)</td>
<td>1.81 (fix)</td>
<td>1.81(30)</td>
</tr>
</tbody>
</table>
Table 3. Crystal structural parameters refined by the Rietveld method. The T site occupancy was fixed at 0 because it converged to a small negative value between ~0.004 and ~0.018. $V_M$ was calculated using the EoS of Fe$_{0.9}$Ni$_{0.1}$ determined in this study and those for fcc Fe (Tsujino et al. 2013) and hcp Fe (Fei et al. 2016). Isotropic atomic displacement parameters of iron ($U_{Fe}$) and nickel ($U_{Ni}$) were constrained to the same value. The temperature error is estimated to be ~50 K.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$P$ (GPa)</th>
<th>$T$ (K)</th>
<th>Phase</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ ($Å^3$)</th>
<th>$U_{Fe,Ni}$ ($×10^{-2}Å^2$)</th>
<th>$U_{DO}$ ($×10^{-2}Å^2$)</th>
<th>$ω_0$</th>
<th>$σ_T$</th>
<th>$R_{wp}$ (%)</th>
<th>$χ^2$</th>
<th>$v_D$ ($Å^3$)$^*$</th>
<th>$v_D$ ($Å^3$)$^**$</th>
<th>Wt. Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>A560</td>
<td>11.7</td>
<td>950</td>
<td>fcc</td>
<td>3.62293(5) –</td>
<td>–</td>
<td>47.553(2)</td>
<td>1.46(4)</td>
<td>4.1(2)</td>
<td>0.356(9)</td>
<td>0</td>
<td>5.62</td>
<td>1.343</td>
<td>2.50(6)</td>
<td>2.25(6)</td>
<td>1</td>
</tr>
<tr>
<td>A560</td>
<td>11.7</td>
<td>900</td>
<td>fcc</td>
<td>3.61995(6) –</td>
<td>–</td>
<td>47.436(2)</td>
<td>1.45(5)</td>
<td>3.83(19)</td>
<td>0.348(8)</td>
<td>0</td>
<td>5.62</td>
<td>1.329</td>
<td>2.57(6)</td>
<td>2.29(5)</td>
<td>1</td>
</tr>
<tr>
<td>A578</td>
<td>7.2</td>
<td>900</td>
<td>fcc</td>
<td>3.74415(3) –</td>
<td>–</td>
<td>52.488(1)</td>
<td>1.80(3)</td>
<td>4.62(7)</td>
<td>0.714(6)</td>
<td>0</td>
<td>3.32</td>
<td>1.356</td>
<td>2.56(2)</td>
<td>2.47(2)</td>
<td>1</td>
</tr>
<tr>
<td>A580</td>
<td>7.2</td>
<td>900</td>
<td>fcc</td>
<td>3.67584(2) –</td>
<td>–</td>
<td>49.667(1)</td>
<td>1.73(3)</td>
<td>4.87(9)</td>
<td>0.459(4)</td>
<td>0</td>
<td>3.51</td>
<td>1.724</td>
<td>2.44(2)</td>
<td>2.30(2)</td>
<td>1</td>
</tr>
<tr>
<td>A580</td>
<td>6.7</td>
<td>700</td>
<td>fcc</td>
<td>3.66481(2) –</td>
<td>–</td>
<td>49.221(1)</td>
<td>1.30(2)</td>
<td>3.73(7)</td>
<td>0.464(4)</td>
<td>0</td>
<td>4.05</td>
<td>1.993</td>
<td>2.40(2)</td>
<td>2.198(19)</td>
<td>1</td>
</tr>
<tr>
<td>A580</td>
<td>6.3</td>
<td>500</td>
<td>fcc</td>
<td>3.65052(3) –</td>
<td>–</td>
<td>48.648(1)</td>
<td>0.833(15)</td>
<td>2.77(6)</td>
<td>0.464(4)</td>
<td>0</td>
<td>4.56</td>
<td>2.624</td>
<td>2.33(2)</td>
<td>2.062(18)</td>
<td>0.776(3)</td>
</tr>
<tr>
<td>&amp;h;cp &amp; 2.58166(11)</td>
<td>4.2007(3)</td>
<td>24.247(2)</td>
<td>0.363(6)</td>
<td>0</td>
<td>4.56</td>
<td>2.624</td>
<td>–</td>
<td>3.31(6)</td>
<td>0.224(3)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

*The value calculated using the volume of Fe$_{0.9}$Ni$_{0.1}$ determined in this study.

**The value calculated using the volume of pure Fe determined by Tsujino et al. (2013) and Fei et al. (2016).
Figures

Figure 1
Figure 2
Figure 3
Figure 4
Figure 5

(a) Heating

(b) Cooling
Figure 6

4.3–5.1 GPa cooling

- fcc
- bcc

Intensity (a.u.)

Energy (keV)

- 700 K
- 500 K
- 400 K
- 300 K

40 60 80 100 120
Figure 7
Figure 8

The figure shows a series of intensity plots against time of flight (µsec) for different temperatures (300 K to 900 K). The plots represent different crystal structures: fcc Fe₀.₉Ni₀.₁Dₓ, bcc Fe₀.₉Ni₀.₁Dₓ, NaCl, Graphite, and ND₃BD₃. Each temperature level is marked with distinct symbols and intensity peaks corresponding to the crystal structures.

Figure 8
Figure 9
Run A578 HPN65936
7.2 GPa, 900 K
\( \sigma_0 = 0.714(6) \)
\( R_{wp} = 3.32\% \)
\( \chi^2 = 1.356 \)

Figure 10
Figure 11