Solubility of deuterium and hydrogen in fcc iron at high pressures and temperatures

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An isobar $x(T)$ of deuterium solubility in iron is constructed at $P = 6.3$ GPa and $100 \leqslant T \leqslant 800\,^{\circ}\mathrm{C}$ based on the results of thermal desorption analysis of FeD_x samples produced by quenching under high D_2 pressure to the temperature of liquid nitrogen. The experiment confirms the value of $x = 0.64$ at $T = 715\,^{\circ}\mathrm{C}$ proposed previously in a neutron diffraction work [Machida *et al.*, Nature Commun. **5**, 5063 (2014)] for γ iron deuteride under the assumption that deuterium atoms occupy both octa- and tetrahedral interstices in its fcc metal lattice. An estimate of $\Delta V/x = 2.2\,\mathrm{\AA}^3$/atom D made in that work for the deuterium-induced volume expansion $\Delta V(x)$ of fcc iron is also confirmed. To prove that the absorption of protium leads to a similar volume expansion, we constructed an isotherm $x(P)$ of hydrogen solubility in fcc iron at $T = 600\,^{\circ}\mathrm{C}$ and H_2 pressures from 4.3 to 7.4 GPa. The available $\Delta V(P, T)$ data of *in situ* x-ray diffraction studies of iron hydrides [T. Hiroi *et al.*, J. Alloys Compd. **404–406**, 252 (2005); H. Saitoh *et al.*, J. Alloys Compd. **706**, 520 (2017)] agree with this isotherm under the assumption that $\Delta V/x = 2.2\,\mathrm{\AA}^3$/atom H. The transformation between the high-temperature fcc (γ) and low-temperature dhcp (ε') deuterides of iron is shown to occur at 260 °C, which is approximately 100 °C lower than the temperature of the $\gamma \leftrightarrow \varepsilon'$ transformation in the Fe-H system at the same pressure of 6.3 GPa.

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I. INTRODUCTION

Metal hydrides have long been studied due to their unusual physical properties, such as the anomalously high diffusion rates (in many Me-H systems, phase equilibrium is quickly reached at room or even lower temperatures) [1]; superconductivity with a strong inverse isotope effect (observed in the Pd-H/D [2,3], Ti-H/D [4], and Mo-H/D [5] systems) and superconductivity with a very high critical temperature (to date, a record value of $T_c = 250$–260 K has been achieved in the La-H system [6,7]); the formation of "superabundant" vacancies (with concentrations up to 10%–30%) in the metal lattice of d-metal hydrides at high pressure and temperature [1]; the giant tunneling effect of hydrogen in α-Mn (one of very few quantum effects persisting at temperatures above the boiling point of nitrogen) [8,9]. Metal hydrides also find technical applications as hydrogen and energy storage materials, the binary hydrides being of importance as part of decomposition reactions for other hydrides (see, for example, Ref. [10]).

High pressure is a powerful tool for the synthesis of new hydrogen compounds, since it greatly increases the Gibbs free energy of gaseous hydrogen, thereby increasing the thermodynamical stability of new hydrogen-rich phases. The fundamental properties of hydrides are dominated by the high-frequency optical phonons of hydrogen vibrations, which particularly leads to the record-high superconducting transition temperatures, reaching 243 K in the yttrium-hydrogen system [11] and 250–260 K in the lanthanum-hydrogen system [6,7]. In turn, the vibrational properties of a hydrogen atom in hydrides are determined by the type of the interstitial site that it occupies.

Most high-pressure hydrides of d metals with H-to-metal atomic ratios of $x < 3$ synthesized so far had close-packed metal lattices [fcc (face centered cubic), hcp (hexagonal close packed), or double hcp] with two types of interstitial sites, octahedral (O) and tetrahedral (T) ones, which could accommodate all absorbed hydrogen atoms. Particularly, H atoms are expected to occupy T sites, or both O and T sites in many hydrides with $1 < x < 3$ synthesized in recent years using diamond anvil cells (fcc-RhH_2 [12], fcc-CoH_2 [13], hcp-MoH_{1+x} [14], hcp-WH_{1+x} [15,16], hcp-$\mathrm{Cr}_2\mathrm{H}_3$ and hcp-CrH_2 [17], hcp-$\mathrm{TaH}_{2.2}$ [18], hcp-NbH_2 and dhcp-$\mathrm{NbH}_{2.5}$ [19]), because there are two T sites and only one O site per metal atom in the close-packed metal lattices. It should be noted, however, that neither the positions of H atoms in the metal lattice, nor the hydrogen content of the above hydrides have ever been determined experimentally (with the exception of the H content of hcp-$\mathrm{TaH}_{2.2}$ [18]). Instead, these parameters were derived from a comparison of the experimentally measured baric dependences of atomic volume with the results of *ab initio* calculations. The results of such a comparison can only be considered as preliminary, because the calculations are performed for stoichiometric compounds, whereas the hydrides of d metals can have a nonstoichiometric composition, which varies widely depending on the pressure and temperature of the surrounding H_2 gas [1].

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Until recently, the hydrogen content and the positions of H atoms in the crystal structure have only been determined experimentally for the high-pressure hydrides with $x \leqslant 1$ (fcc-NiH; fcc-CoH; fcc-PdH; fcc-RhD; fcc-MnD$_{0.41}$; hcp-CrH; hcp-MnH$_{0.83}$; hcp-FeD$_{0.42}$; hcp-CoH$_x$ and CoD$_x$ with $x \leqslant 0.5$; hcp-MoH; hcp-TcH$_{0.45}$; hcp-ReH$_{0.23}$; dhcp-FeH). The full crystal structures of these hydrides were determined *ex situ* by powder neutron diffraction (ND) at ambient pressure and room or cryogenic temperatures using, in many cases, deuterated samples synthesized at high pressures and elevated temperatures, and then quenched to the liquid N$_2$ temperature to prevent H or D losses during the subsequent pressure release (see Refs. [1,20] for results and references). The experiments showed that hydrogen atoms invariably occupied only octahedral interstitial sites in all these hydrides.

At the same time, the increase in the ground-state energy of the H atom, which jumped from the O site to a T site is likely to be less than 1 eV (see, e.g., *ab initio* calculations of Ref. [21] for PdH; Ref. [22] for NiH and FeH; Ref. [23] for RhH) and this opens the possibility of a partial Boltzmann occupancy of the T sites at elevated temperatures. The partial filling of the T sites should dramatically change the thermodynamics of the hydride, the spectrum of its optical vibrations and the physical properties (such as superconductivity) that depend on these vibrations.

Approximately ten years ago, a considerable T occupancy reaching about 1/3 of all D atoms was first observed in fcc deuterides of palladium with $x \sim 0.6$ at a temperature of 310 °C and a deuterium pressure of 9 MPa using *in situ* neutron diffraction [24,25]. Some evidence has also been obtained that the T occupancy can significantly enhance the superconductivity in the Pd-H (D) system [26].

In 2014, another *in situ* ND investigation showed that about 1/6 of the D atoms are likely to occupy the T sites in fcc (γ) deuteride of iron at $T = 715\,^{\circ}$C and $P = 6.3$ GPa [27]. This result is of great interest to geophysics, since it is believed that the Earth's core consists mainly of iron and contains light elements, including a significant amount of hydrogen [1]. The quality of the ND pattern of γ-FeH$_x$ collected in Ref. [27] was not however sufficient to establish the presence of D atoms on the T sites with certainty. On the other hand, modeling this pattern under the assumption that D atoms could fill only O sites and, alternatively, allowing them to occupy both O and T sites gave noticeably different total D/Fe ratios of $x = 0.47$ and 0.64, respectively [27]. This provided the opportunity to check whether or not the D atoms occupy T sites in FeD$_x$, by measuring the hydrogen content of the deuteride.

The deuterium content of the FeD$_x$ sample studied in Ref. [27] could not be measured experimentally because the sample could only be taken out of the high-pressure cell at room temperature, whereas the iron deuteride decomposes in a few seconds if heated above –60 °C at ambient pressure (see Sec. IIIA). In order to examine which of the two predicted x values better agrees with experiment, an isobar of deuterium solubility in iron at $P = 6.3$ GPa was constructed in the present paper using a quenching technique. Each iron sample loaded with deuterium at given temperature and pressure was then rapidly cooled (quenched) together with the high-pressure chamber to the liquid nitrogen temperature; the pressure was released; the chamber was disassembled under liquid nitrogen; the sample was retrieved from the reaction cell and its deuterium content was determined by thermal desorption.

Constructing the isobar at a D$_2$ pressure of 6.3 GPa and $100 \leqslant T \leqslant 800\,^{\circ}$C (see Sec. III A) increased the statistical accuracy and reliability of determining the deuterium content of the iron deuteride at $T = 715\,^{\circ}$C. Additionally, the isobar revealed a step-wise increase in the deuterium solubility in iron with the decrease in the synthesis temperature below $T_0 \approx 260\,^{\circ}$C due to the transition from the high-temperature fcc (γ) Fe-D phase with a variable composition to the low-temperature stoichiometric dhcp (ε') FeD phase (this is discussed in Sec. III B).

Our experiment confirmed the value of $x = 0.64(3)$ for the γ iron deuteride at $T = 715\,^{\circ}$C resulting from the O+T model [27]. According to Ref. [27], such a value of x corresponds to the deuterium-induced volume expansion of fcc iron equal to 2.21(4) Å^3/atom D; therefore, this estimate has also been confirmed. To prove that absorption of protium leads to a similar volume expansion, we also constructed an isotherm of hydrogen solubility in fcc iron at $T = 600\,^{\circ}$C and H$_2$ pressures from 4.3 to 7.4 GPa and compared it with isotherms derived from *in situ* synchrotron x-ray diffraction experiments [28,29] (Sec. III C).

Assuming that the partial volume $\beta_{\rm H}^{\rm O} = dV_a/dx$ of hydrogen occupying O sites in fcc and hcp 3d metals monotonically depends on their atomic number, the available literature data [1] give a value of $\beta_{\rm H}^{\rm O} = 1.9\,\text{Å}^3$/atom H for iron (particularly, this value of $\beta_{\rm H}$ was used in Ref. [28] to estimate the hydrogen content of the solid γ solutions FeH$_x$ studied *in situ* by x-ray diffraction.) The noticeably larger experimental value of $\beta_{\rm H}^{\rm exp} = 2.2\,\text{Å}^3$/atom H for the fcc Fe hydrides can be explained by the presence of H atoms on the T sites. Based on the literature data, we arrived at a reasonable [1] value of $\beta_{\rm H}^{\rm T} \approx 3.1\,\text{Å}^3$/atom H for the hypothetical fcc iron hydrides with H atoms sitting only on the T sites. This gave us the fraction $y^{\rm T} \sim 0.25$ of such atoms in the fcc Fe hydrides with $\beta_{\rm H}^{\rm exp} = 2.2\,\text{Å}^3$/atom H in fair agreement with $y^{\rm T} \sim 1/6 \approx 0.17$ proposed for fcc FeD$_{0.64}$ at $P = 6.3$ GPa and $T = 715\,^{\circ}$C [27]. The agreement between these two estimates is indirect, but independent evidence in favor of the noticeable occupancy of tetrahedral interstices in fcc iron hydrides at elevated temperatures (Sec. III D).

Taken together, the results of Secs. III A and III D provided convincing evidence in favor of the noticeable occupancy of tetrahedral interstices in the fcc iron hydrides at elevated temperatures, as was proposed in Ref. [27]. However, the origin of this effect was not entirely clear. In analogy with the palladium deuterides [24,25], the authors of Ref. [27] ascribed the partial T site occupancy in the fcc iron deuteride to the Boltzmann distribution $2\exp(-\Delta E/k_BT)$ of the dissolved D atoms between the O and T sites, which differed in the ground-state energy by $\Delta E = E_{\rm tetra} - E_{\rm octa}$. We performed *ab initio* calculations for the fcc hydrides and deuterides of Pd, Fe, Ni, and Rh in order to see whether the estimates of ΔE made in Refs. [24,25,27] for Pd and Fe could be reproduced and whether a considerable Boltzmann occupancy of T sites could be expected for other hydrides. The nickel and rhodium hydrides were chosen for the latter purpose, because they are the closest physical and chemical analogues of the palladium hydrides [1,20]. It is also important that the differences $\Delta E^{\mathrm{bottom}}$ in the minima of potential energy for H atoms at the O and T sites in the fcc NiH and RhH hydrides have been calculated earlier [22,23], and a comparison with these results could serve as an independent test for the accuracy of our *ab initio* calculations (Sec. III E).

More recently [30], fcc iron hydrides were studied *in situ* by neutron diffraction similarly to the fcc iron deuterides in Ref. [27]. The obtained results were interpreted as confirming the partial occupancy of the T sites with hydrogen atoms at temperatures above 750 °C and pressures of a few GPa. However, due to the large incoherent neutron scattering length of hydrogen [31], the quality of the ND patterns obtained in Ref. [30] was much poorer than in Ref. [27] and was insufficient for reliable conclusions about the occupancy of the T sites. In particular, the result of Ref. [30] (see their Table S1) that the T sites are not filled in fcc iron hydrides with $\mathrm{H/Fe} \sim 0.5$–0.7 is inconsistent with the previous ND results for fcc deuterides of iron [27] and palladium [24,25].

II. EXPERIMENT

The starting material was a polycrystalline foil made of carbonyl iron melted under an Ar atmosphere, cold rolled to a thickness of 0.12 mm, annealed in vacuum at 800 °C for 15 min and quenched in water. Platelets of about 5 mm in diameter cut out of this foil were placed into a copper reaction cell together with AlD_3, separated from the sample with a layer of hexagonal BN. The cell was compressed in a Toroid-type high-pressure apparatus [32] to ∼1.5 GPa and heated to 350 °C for 10 min in order to decompose the AlD_3 powder used as an internal source of gaseous D_2. The pressure was then raised to 6.3 GPa, the temperature set to the pre-selected value and kept constant for a period of time ranging from 3 days at 100 °C to 20 min at 800 °C. After that, the sample was cooled (quenched) together with the high-pressure apparatus to room temperature in 15–20 s and further to approximately –190 °C in 20–30 min. The pressure was then reduced to atmospheric; the sample was removed from the reaction cell and stored in liquid N_2 until the measurements. The quantity of AlD_3 placed in the reaction cell was large enough to ensure that the amount of the released D_2 gas always exceeded the amount of deuterium absorbed by the sample by 2–3 times. The procedure of synthesis of iron hydrides was similar except that AlH_3 or NH_3BH_3 were used instead of AlD_3 to produce gaseous H_2 in the reaction cell. The pressure in the cell was estimated with an accuracy of ±0.3 GPa using the pressure/ram load dependence determined in separate experiments. The temperature was measured using a Chromel-Alumel thermocouple with an accuracy varying from ±10 °C at 100 °C to ±20 °C at 800 °C. The method of high-pressure hydrogenation is described in more detail in Ref. [33].

The hydrogen content of the samples was determined with a relative accuracy of 3% by thermal desorption of hydrogen into a pre-evacuated measuring system in the regime of heating from –190 to 440 °C at a rate of 10 °C/min. The mass of the analyzed probe was a few milligrams. A more detailed description of the method can be found in Ref. [34].

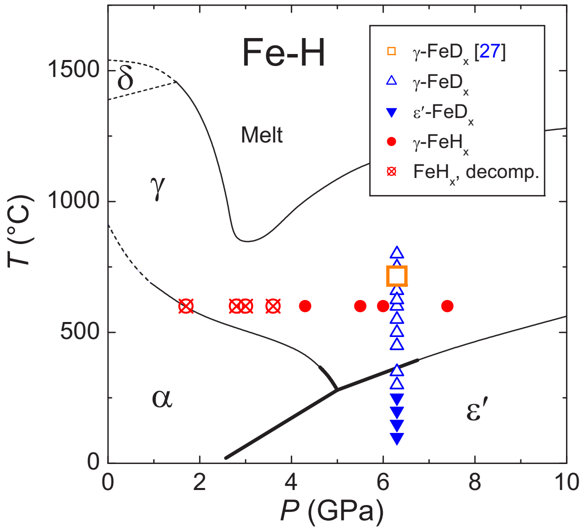

FIG. 1. *T-P* phase diagram of the Fe-H system [35] (black lines). α stands for dilute solid solutions of hydrogen in body centered cubic α-Fe with atomic ratios H/Fe of $x < 0.01$ [36]; ε' is the approximately stoichiometric FeH hydride with a double hcp metal lattice; γ is the hydride with an fcc metal lattice and variable hydrogen concentration. The open orange square indicates the point ($P_{D2} = 6.3$ GPa, $T = 715$ °C) chosen for the *in situ* ND experiment in Ref. [27]. The blue triangles show the temperatures of synthesis of Fe-D samples along the isobar at $P_{D2} = 6.3$ GPa. The open up-triangles refer to the γ deuterides; the solid down-triangles are for the ε' ones. The red circles indicate the H_2 pressures of synthesis of Fe-H samples along the isotherm at $T = 600$ °C. The solid circles refer to the samples, which retained hydrogen during their quenching to the liquid N_2 temperature; the crossed circles are for the samples decomposed in the course of the quenching while crossing the α field of dilute hydrogen solutions at high temperatures.

Some deuterated samples were examined by x-ray diffraction at 85 K with a Siemens D500 diffractometer using Cu K_α radiation selected by a diffracted beam monochromator. The diffractometer was equipped with a home-designed nitrogen cryostat that permitted the samples to be loaded without any intermediate warming. The obtained diffraction patterns were analyzed using POWDERCELL2.4 software.

III. RESULTS AND DISCUSSION

A. Deuterium solubility in fcc iron at 6.3 GPa.

Figure 1 shows the *T-P* phase diagram of the Fe-H system from Ref. [35] (thin black lines) slightly corrected to better represent the position $P = 5$ GPa and $T = 280$ °C of the point of invariant phase equilibrium $\alpha + \varepsilon' + \gamma$ in the low-temperature portion of the diagram determined in Ref. [36] and later more accurately redrawn in the review paper [37] (thick black lines). The *T-P* diagram of the Fe-D system is not yet known, but it is likely to be similar, since the phase diagrams of most metal-hydrogen systems change little when protium is replaced by deuterium [1].

As seen from Fig. 1, the isobar at $P = 6.3$ GPa lies in the *T-P* region where cooling the γ phase with $x < 1$ should

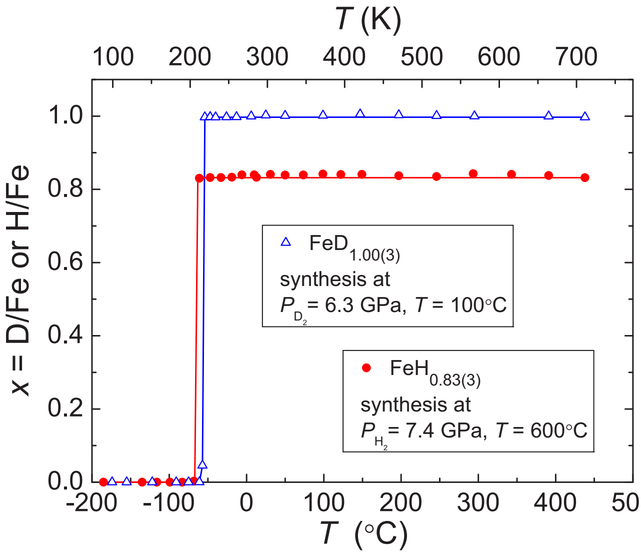

FIG. 2. Hydrogen release from the quenched $FeD_{1.00(3)}$ and $FeH_{0.83(3)}$ samples heated in vacuum at a rate of 10 °C/min.

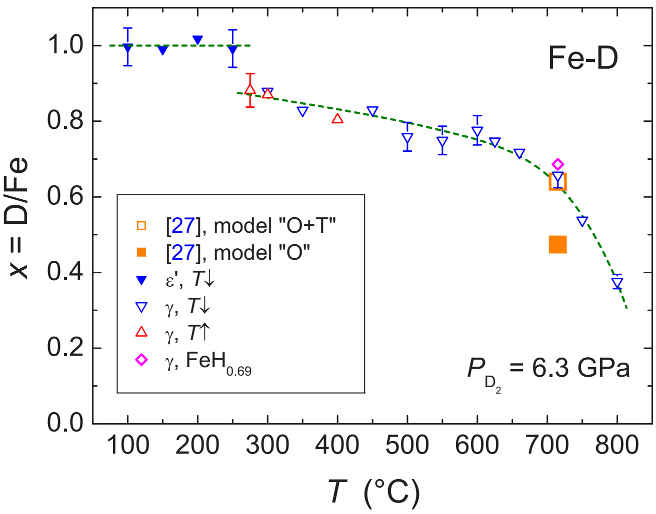

FIG. 3. Experimental isobar of deuterium solubility in iron at a D_2 pressure of 6.3 GPa presented as triangles interpolated with dashed curves for use as a guide for the eyes. The solid triangles stand for the low-temperature stoichiometric monodeuteride ε'-FeD with a dhcp metal lattice. Open triangles are for the high-temperature γ-FeD_x with an fcc metal lattice and variable composition. The orange squares show results of Ref. [27] of modeling the neutron diffraction pattern of a γ-FeD_x sample assuming that D atoms could fill only octahedral O sites in its fcc metal lattice (solid square) or occupied both O sites and tetrahedral T sites (open square). The open magenta diamond shows the hydrogen content $x = H/Fe$ of a γ-FeH_x sample synthesized in an H_2 atmosphere at the same $P = 6.3$ GPa and $T = 715$ °C as the γ-FeD_x sample in Ref. [27].

transform it to the ε' phase with a higher value of $x = 1$. This transformation is very fast and the γ phase cannot be supercooled much below the line of the $\gamma \leftrightarrow \varepsilon'$ equilibrium and transforms to a mixture of the ε' phase with $x = 1$ and α phase with $x < 0.01$ [36]. Such a phase separation, however, cannot lead to the loss of hydrogen from the sample, because the equilibrium hydrogen content is higher. In our experiments with deuterides, the absorption of a noticeable additional amount of deuterium during quenching the γ samples was also unlikely. Our auxiliary experiments showed that achieving the equilibrium deuterium content of Fe-D samples at $P_{D2} = 6.3$ GPa at $T = 400$ °C required a few hours and exposing Fe-D samples to room temperature for a few hours did not change their deuterium content at all. We therefore believe that the quenching procedure used in the present paper (cooling the sample to room temperature in 15–20 s and further to approximately –190 °C in 20–30 min) ensured that the deuterium content reached at the synthesis temperature was not changed.

A typical curve of deuterium desorption from a single-phase sample of ε'-FeD is shown in Fig. 2. When the sample is heated in vacuum at a rate of 10 °C/min, almost all of the deuterium leaves it abruptly in a narrow temperature interval near –60 °. The jumplike deuterium release from the two-phase $(\alpha + \varepsilon')$ samples with $x < 1$ occurs at the same temperature. The iron hydrides also studied in the present paper decompose at a slightly lower temperature of approximately –65 °C. Consequently, in our experiments, cooling the synthesized samples of Fe-D and Fe-H to approximately –190 °C, before lowering the pressure, was to warrant the absence of D or H losses.

Interestingly, the samples of iron hydrides and deuterides, which we studied earlier, were less thermally stable and decomposed when heated in vacuum to approximately –120 °C (see, e.g., Ref. [38]). Most likely, the thermal stability of these polycrystalline materials strongly depends on their microstructure (the key role of grain boundaries and other lattice defects was previously demonstrated only for the thermal decomposition of nickel hydrides under ambient conditions [39,40] due to the complexity of studying most other high-pressure hydrides decomposing at cryogenic temperatures).

An X-ray diffraction study at $T = 85\ K = -188$ °C and ambient pressure showed that the ε' phase in both single-phase and two-phase $(\alpha + \varepsilon')$ Fe-D samples had a dhcp metal lattice with parameters $a = 2.676(2)$ Å and $c = 8.76(1)$Å. These parameters are somewhat larger than $a = 2.668$ Å and $c = 8.75$ Å of the ε' phase in the Fe-D sample, which was previously studied by neutron diffraction at $T = 90$ K [38]. The ε' phase in the two-phase Fe-H samples had $a = 2.682(2)$ Å and $c = 8.785(10)$ Å in fair agreement with $a = 2.679$ Å and $c = 8.77$ Å determined for a Fe-H sample in Ref. [38]. The α phase in our two-phase Fe-D and Fe-H samples had a bcc metal lattice with $a = 2.863(3)$ Å, which did not differ from $a = 2.8606$ Å of pure Fe at T = 79 K [41].

The obtained isobar $x(T)$ at $P_{D2} = 6.3$ GPa is shown in Fig. 3. As one can see, our experimental results (open blue down-triangles) agree with the point $x = 0.64(3)$ at $T =$ 715 °C (open orange square) resulting from the O+T model [27] and lie far from the point $x = 0.47(3)$ (solid orange square) followed from the O model. Thus the estimate $x =$ 0.64 of Ref. [27] for the content of deuterium in γ-FeD_x at $P_{D2} = 6.3$ GPa and $T = 715$ °C was unequivocally confirmed. We will return to the discussion of the O- and T-site occupancies in the γ iron deuteride in Sec. III D.

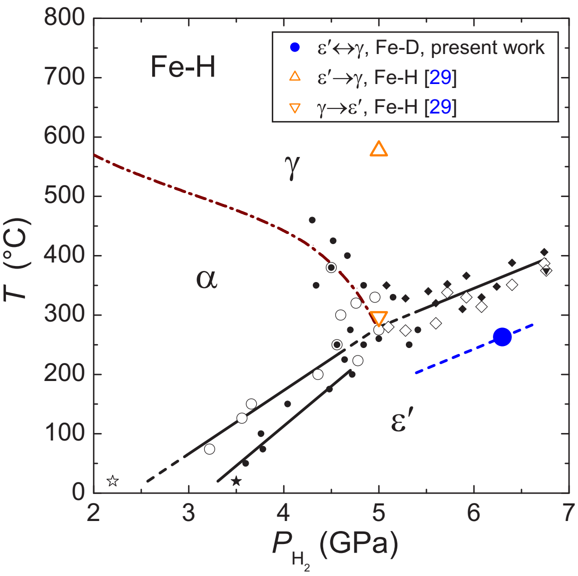

FIG. 4. *T-P* phase diagram of the Fe-H system [37] with the line of the $\alpha \leftrightarrow \gamma$ transformation (dash-dot brown curve) taken from Ref. [35]. The small solid black symbols indicate positions of the $\alpha \rightarrow \varepsilon'$ and $\alpha \rightarrow \gamma$ and $\varepsilon' \rightarrow \gamma$ transitions, while the small open black symbols stand for the corresponding reverse transitions. Large open orange triangles show the positions of the $\varepsilon' \rightarrow \gamma$ and $e \rightarrow \varepsilon'$ transitions observed in Ref. [29]. The large solid blue circle represents the point of the $\varepsilon' \leftrightarrow \gamma$ equilibrium in the Fe-D system determined in the present work. The dashed blue line crossing this circle shows a tentative position of the phase boundary $\varepsilon' \leftrightarrow \gamma$ in the Fe-D system.

B. Temperature of the $\varepsilon' \leftrightarrow \gamma$ transformation in the Fe-D system at 6.3 GPa

The isobar in Fig. 3 demonstrates a step-wise increase in the deuterium solubility in iron from D/Fe ≈ 0.9 to D/Fe = 1.0 at $T_0 \approx 260\,^\circ\mathrm{C}$ due to the transition from the high-temperature fcc (γ) Fe-D phase with a variable composition to the low-temperature stoichiometric dhcp (ε') FeD phase.

Since direct synthesis of single-phase samples of ε'-FeD from α-Fe at a pressure of 6.3 GPa is not possible for kinetic reasons [38], the points at $T \leqslant 350\,^\circ\mathrm{C}$ shown by blue triangles were obtained with the samples, which were first transformed to γ-FeD$_x$ at 500 °C and then cooled and exposed to a lower temperature for a period varying from 1 day at 350 °C to 3 days at 100 °C. To determine the temperature hysteresis of the $\gamma \leftrightarrow \varepsilon'$ transformation, three single-phase ε'-FeD samples formed at 6.3 GPa and 200 °C were further heated again and exposed for 1 day to a higher temperature (red open up-triangles in Fig. 3). The equilibrium temperature T_0 of the $\gamma \leftrightarrow \varepsilon'$ transformation should be in between the highest temperature of formation of the ε' phase (solid blue triangles) and the lowest temperature of formation of the γ phase (open red triangles). As one can see, the $\varepsilon' \leftrightarrow \gamma$ transformation at $T_0 \approx 260\,^\circ\mathrm{C}$ showed no hysteresis within the experimental accuracy of ±15 °C.

The obtained point of the $\varepsilon' \leftrightarrow \gamma$ transformation in the Fe-D system is shown with a large solid blue circle in the T-P diagram of the Fe-H system presented in Fig. 4. As seen from the figure, this point lies approximately 100 °C below the line of the $\varepsilon' \leftrightarrow \gamma$ transformation in the Fe-H system. As can also be seen, the experimental points of the $\varepsilon' \rightarrow \gamma$ and $\gamma \rightarrow \varepsilon'$ transitions in the Fe-H system (solid and open diamonds, respectively) [36] demonstrate a rather large scatter, but do not show a systematic temperature hysteresis. Consequently, the hysteresis of the $\varepsilon' \leftrightarrow \gamma$ transformation both in the Fe-D system and in the Fe-H system is less than the experimental error.

Interestingly, the hydrogen content x = H/Fe of a Fe-H sample synthesized in the present work at $P_{\mathrm{H2}} = 6.3$ GPa and $T = 715\,^\circ\mathrm{C}$ (open magenta diamond in Fig. 3) turned to be close to the content of x = D/Fe of the γ iron deuterides, which were synthesized in a D_2 atmosphere at the same pressure and temperature in Ref. [27] and in the present paper. This suggests similar $x(T)$ dependences of the γ phases in the Fe-D and Fe-H systems at a pressure of 6.3 GPa, despite the considerable difference in the temperatures of the corresponding $\varepsilon' \leftrightarrow \gamma$ transformations (Fig. 4).

With regard to phase transitions in the Fe-H system, it can also be mentioned that the $\varepsilon' \leftrightarrow \gamma$ transformation showed a large temperature hysteresis of about 300 °C at P_{H2} = 5 GPa in the recent work [29] using *in situ* x-ray diffraction. This hysteresis turned to be highly asymmetric, because the point of the $\gamma \rightarrow \varepsilon'$ transition (open orange down-triangle in Fig. 4) was in good agreement with previous equilibrium results [36,37], whereas the $\varepsilon' \rightarrow \gamma$ transition (open orange up-triangle) occurred only at a temperature that was 300 °C higher. The reason for the strongly nonequilibrium behavior of the $\varepsilon' \rightarrow \gamma$ transition in Ref. [29] is unclear. The $\varepsilon' \rightarrow \gamma$ and $\alpha \rightarrow \gamma$ phase transitions in the Fe-H system at temperatures exceeding the equilibrium values by 250 °C –300 °C were also observed in the *in situ* ND experiments conducted in Ref. [30].

C. Partial volume of deuterium and hydrogen in fcc iron

According to Ref. [27], the value of $x = 0.64(3)$ at P_{D2} = 6.3 GPa and $T = 715\,^\circ\mathrm{C}$ confirmed in the present paper, corresponds to the deuterium-induced volume expansion of fcc iron equal to $dV_a/dx = 2.21(4)$ Å^3/atom D. This dV_a/dx value (also called the partial volume of deuterium and denoted as β_D hereafter) was obtained from the difference $\Delta V_\mathrm{a}(x) = V_\mathrm{a}(x) - V_\mathrm{a}(0)$ of the atomic volume $V_\mathrm{a}(0.64) = a^3/4$ of fcc iron deuteride determined in Ref. [27] and literature data for the atomic volume $V_\mathrm{a}(0)$ of pure γ-Fe under the same P and T in inert medium corrected for the thermal expansion as suggested in Ref. [42]. The partial volume of deuterium was set equal to $\Delta V_\mathrm{a}/x$ assuming a linear dependence $\Delta V_\mathrm{a}(x)$ at the given pressure and temperature.

In order to see whether the partial volume β_H of hydrogen in fcc iron is similar, we synthesized a few Fe-H samples at $T = 600\,^\circ\mathrm{C}$ and H_2 pressures from 1.7 to 7.4 GPa (see Fig. 1), determined their hydrogen content by thermal desorption analysis and compared it with the $x(P_{\mathrm{H2}})$ data derived from results of previous *in situ* synchrotron x-ray studies [28,29] under the assumption that $\beta_\mathrm{H} = 2.2$ Å^3/atom H. The results are presented in Fig. 5.

As seen from Fig. 5, at pressures above 4.5 GPa, the experimental points of the present paper and calculated points of Refs. [28,29] satisfactorily agree with the dashed blue curve

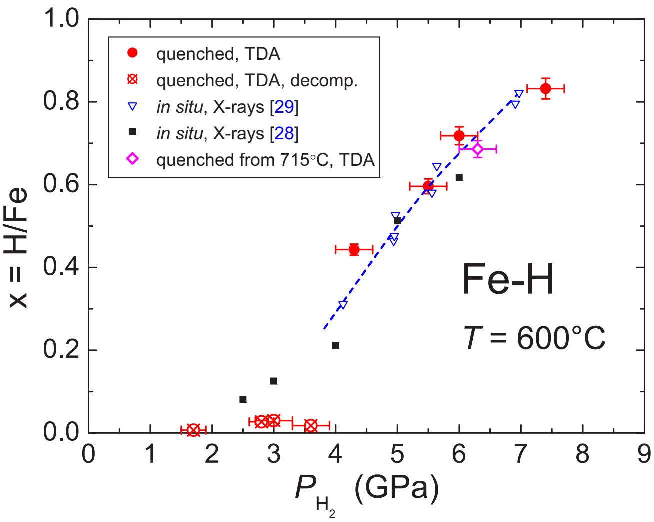

FIG. 5. Atomic ratios $x = \mathrm{H/Fe}$ of Fe-H samples loaded with hydrogen at 600 °C and pressures indicated along the horizontal axis. The ratios shown with the red circles are determined by thermal desorption analysis (TDA) in the present paper; the synthesis conditions of the samples are indicated in Fig. 1 using the same symbols. The open magenta diamond stands for the sample hydrogenated at $P_{\mathrm{H2}} = 6.3$ GPa and 715 °C; a point for this sample is indicated in Fig. 3 with the same symbol. All other data are derived from the results of previous *in situ* synchrotron x-ray diffraction studies [28,29] (see text).

interpolating the points of Ref. [29]. Taking into account the scatter of the points, the partial volume of hydrogen in fcc iron hydrides at $T = 600\,^{\circ}\mathrm{C}$ and $4.5 \leqslant P_{\mathrm{H2}} \leqslant 7.5$ GPa can roughly be estimated as $\beta_{\mathrm{H}} = 2.20(5)\ \mathring{\mathrm{A}}^3/\mathrm{atom\ H}$.

At pressures below 4.5 GPa, the isotherm $x(P_{\mathrm{H2}})$ is considerably nonlinear due to the proximity to the critical point at $P_{\mathrm{cr}} = 4.0$–4.5 GPa [28,29] and $T_{\mathrm{cr}} = 400 \pm 100\,^{\circ}\mathrm{C}$ [28] of the isomorphous phase transformation $\gamma_1 \leftrightarrow \gamma_2$ occurring in the Fe-H system at lower temperatures (γ_1 and γ_2 are, respectively, the hydrogen-poor and hydrogen-rich phases of fcc iron hydrides). Regretfully, the quenching technique did not allow us to study this pressure interval because the Fe-H samples synthesized at 600 °C lost nearly all hydrogen in crossing the stability region of dilute α solutions at high temperatures (see Fig. 1). The low content of residual hydrogen in these decomposed Fe-H samples is shown in Fig. 5 with the crossed red circles.

The hydrogen content of γ iron hydrides in Refs. [28,29] was estimated as $x = \Delta V_{\mathrm{a}}/\beta_{\mathrm{H}}$, where the ΔV_{a} values were calculated as the difference between the measured atomic volume of the fcc hydride and the atomic volume of pure fcc Fe at the same P and T taken from the literature. The points $\mathrm{x}(P_{\mathrm{H2}})$ shown with the solid black squares in Fig. 5 are recalculated from the isobars in Fig. 3 of Ref. [28] using $\beta_{\mathrm{H}} = 2.2\ \mathring{\mathrm{A}}^3/$atom H instead of $\beta_{\mathrm{H}} = 1.9\ \mathring{\mathrm{A}}^3/\mathrm{atom\ H}$ used in Ref. [28].

In Ref. [29], the $\mathrm{x}(P_{\mathrm{H2}}, T)$ points were calculated from the x-ray data using the correct value of $\beta_{\mathrm{H}} = 2.2\ \mathring{\mathrm{A}}^3/\mathrm{atom\ H}$ but were only presented in Fig. 7 of that paper as functions of both temperature and pressure along the experimental paths at a few constant ram loads. The pressure noticeably varied with increasing and decreasing temperature due to the thermal expansion of the high-pressure cell, and the starting and ending pressures of the heating and cooling runs were only given in Table I of Ref. [29]. The $x(P_{\mathrm{H2}})$ points at $T = 600\,^{\circ}\mathrm{C}$ shown in Fig. 5 with the open blue down-triangles are derived from these data under the assumption that the temperature dependences of the hydrogen pressure were linear.

As follows from Refs. [28,29], the $\mathrm{x}(P_{H2})$ isotherms in the Fe-H system at $\mathrm{H_2}$ pressures from 4 to 7 GPa do not change much with the temperature in the range 600 °C –700 °C. This agrees with the position of our point for the Fe-H sample hydrogenated at $P_{\mathrm{H2}} = 6.3$ GPa and 715 °C (open magenta diamond in Fig. 5), which does not depart from the dependences $x(P_{\mathrm{H2}})$ at 600 °C within the experimental scatter. At the same time, the hydrogen content of the γ iron hydrides rather steeply grows with increasing pressure. Assuming a similar $x(P, T)$ dependence for the γ iron deuterides, our inaccuracy of ±0.3 GPa in determining the hydrogen pressure should have led to an increase to approximately 5% in the uncertainty in determining the $x(T)$ values along the isobar at $P_{\mathrm{D2}} = 6.3$ GPa. The error bars in Fig. 3 are expanded correspondingly.

D. Volume expansion of fcc and hcp 3*d* metals due to hydrogen atoms on the octahedral and tetrahedral interstices

This section is mainly intended to estimate the volume expansion of fcc iron due to the hydrogen atoms occupying the T sites and to further evaluate the contribution due to the T site occupancy to the overall volume increase accompanying the formation of fcc iron hydrides with partially filled O and T sites at high pressures and temperatures. In view of the lacking experimental data for the fcc iron hydrides, such an estimate could only be done by comparison with the results obtained for hydrides of other 3*d* metals.

Figure 6 compares the experimental value of $\beta_{\mathrm{H}} = 2.2\ \mathring{\mathrm{A}}^3/\mathrm{atom\ H}$ for fcc iron hydrides (open red star) with the available β_{H} values for other fcc (solid symbols) and hcp (open symbols) hydrides of 3*d* metals. The blue diamonds represent the experimental $\beta_{\mathrm{H}}^{\mathrm{O}}$ values for the monohydrides with hydrogen atoms filling only octahedral interstitial sites [1]; the olive circles show the expected volume effect $\beta_{\mathrm{H}}^{\mathrm{T}}$ of hydrogen atoms occupying tetrahedral sites in dihydrides. In most cases, the partial hydrogen volume β_{H} was estimated as the ratio $\Delta V_{\mathrm{a}}/\Delta x$, where ΔV_{a} is the difference between the atomic volumes of two phases and Δx is the difference in the hydrogen contents of those phases. In view of the dependence of atomic volume on the symmetry of the metal lattice of the phase, the β_{H} values can unambiguously be estimated only for the metal-hydrogen systems, in which the metal and its hydride(s), or two hydrides with different H contents have metal lattices of the same symmetry, fcc or hcp. Since only a tetragonal *I*4/*mmm* modification of iron dihydride has been synthesized so far [43,44], the $\beta_{\mathrm{H}}^{\mathrm{T}}$ value for its fcc modification cannot be determined directly.

The atomic number of the hydrogenated metal used as the *X* coordinate in Fig. 6 should be a good parameter for comparing the $\beta_{\mathrm{H}}^{\mathrm{O}}$ and $\beta_{\mathrm{H}}^{\mathrm{T}}$ values for both fcc and hcp hydrides of different 3*d* metals. First, these values are mainly determined by the interaction of H atoms with the neighboring metal

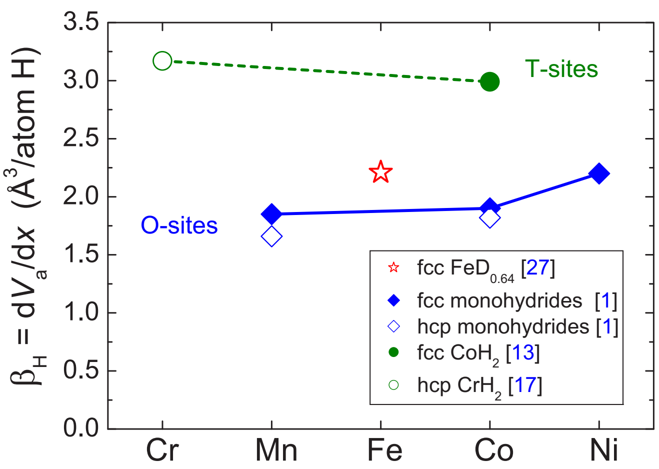

FIG. 6. Partial volume $\beta_H = dV_a/dx$ of hydrogen at ambient pressure and room or lower temperature in the O sites of fcc hydrides $MnH_{0.41}$, CoH, and NiH [1] (solid blue diamonds); in the O sites of hcp hydrides $MnH_{0.65–0.96}$, and $CoH_{0–0.5}$ [1] (open blue diamonds); in the T sites of fcc dihydride CoH_2 [13] (solid olive circle) and in the T sites of hcp dihydride CrH_2 [17] (open olive circle). The open red star shows the experimental β_H value at elevated temperatures for fcc $FeD_{0.64}$ [27] and for fcc iron hydrides (result of the present paper).

atoms [1] and therefore should not differ much for the fcc and hcp modifications of the same metal, since the O and T sites are formed similarly in each of the two structures. Second, the strength of the metal-hydrogen interaction monotonically increases from right to left along the transition metal rows in the periodic table due to the less efficient screening of the ionic core charges with the decreasing number of valence electrons (this effect was theoretically predicted by C. Elsässer [22,45] and later experimentally confirmed in Refs. [46,47]).

As seen from Fig. 6, the experimental point $\beta_H^{exp} = 2.2\,\mathring{A}^3$/atom H for the fcc Fe hydrides is noticeably shifted upward from the dependence for the fcc hydrides with H atoms on the O sites (solid blue diamonds). Assuming this dependence to be linear in the interval between the points for Mn and Co (solid blue line in Fig. 6) predicts $\beta_H^O \approx 1.9\,\mathring{A}^3$/atom H for the fcc FeH_x hydrides. Similarly, a linear approximation of the dependence for H atoms on the T sites (dashed olive line connecting the points for Cr and Co in Fig. 6) gives $\beta_H^T \approx 3.1\,\mathring{A}^3$/atom H for the hypothetical iron hydrides, in which hydrogen atoms sit only on the T sites. If the increase in the experimental value of β_H^{exp} compared to the predicted β_H^O is attributed to the partial filling of the T sites, then the fraction H(tetra)/{H(octa) + H(tetra)} of H atoms occupying the T sites in the studied fcc iron hydrides can be estimated as $y^T = (\beta_H^{exp} - \beta_H^O)/(\beta_H^T - \beta_H^O)$ ~0.25. This value rather well agrees with $y^T \sim 1/6 \approx 0.18$ proposed for fcc $FeD_{0.64}$ [27].

We find the agreement encouraging in view of the large uncertainty in the β_H^T values for dihydrides of Cr and Co (olive circles in Fig. 6) used to estimate the above y^T value. In the first place, the hydrogen content of these dihydrides has never been determined experimentally and could significantly differ from $x = 2$ (for example, the only high-pressure dihydride with the measured hydrogen content—the dihydride of tantalum—had $x = 2.2$ [18]). Secondly, the positions of H atoms in these dihydrides were not experimentally determined and were only predicted by *ab initio* calculations (all H atoms in the T sites of fcc CoH_2 [48] and equal numbers of H atoms in the T and O sites of hcp CrH_2 [17,49]). Third, the effect of pressure on the β_H values becomes significant at $P >$ 10 GPa (see, e.g., Ref. [17]) that necessitated extrapolating the experimental $V_a(P)$ dependences for CoH_2 [13] and CrH_2 [17] to $P = 0$ over wide pressure intervals of instability of these high-pressure hydrides.

In addition, fcc Co and fcc CoH are ferromagnetic, whereas fcc-CoH_2 is predicted to possess no magnetic order [48]; therefore, the estimated β_H^T value for the Co-H hydrides includes a contribution from magnetostriction. Chromium has a body centered cubic structure and does not form a fcc dihydride, so one can only estimate β_H^T by comparing the atomic volumes of the hcp CrH and hcp CrH_2 phases [17]. As seen from Fig. 6, the β_H^O values for the hcp hydrides (open blue diamonds) are close to those for the fcc hydrides (solid blue diamonds). This gives hope that the β_H^T values for the hcp and (hypothetical) fcc dihydrides of chromium do not differ much as well, but the uncertainty in estimating the required latter value increases again.

On the other hand, our DFT calculations, which are described in the next Section, predict a value of $\beta_H^T \approx 2.94\,\mathring{A}^3/$atom H for the fcc iron hydrides, and this value is close to the estimate of $3.1\,\mathring{A}^3$/atom H, interpolated from the experimental data for the Cr and Co dihydrides. After weighing all the pros and cons, we came to the conclusion that $\beta_H^T = 3.1\,\mathring{A}^3/$atom H is the most likely value of the volume increase of fcc Fe caused by H atoms occupying the T sites. This suggests that the fraction $y^T \sim 0.25$ of these H atoms, which was estimated above using this value of β_H^T, can be considered as evidence in favor of the noticeable population of tetrahedral interstices in the fcc iron hydrides at high pressures and elevated temperatures.

E. *Ab initio* calculations

In Ref. [27], the composition $FeD(octa)_{0.532}D(tetra)_{0.112}$ of the fcc iron deuteride at $T = 988$ K (=715 °C) derived from the *in situ* ND investigation was ascribed to the Boltzmann distribution of the dissolved D atoms between the O and T sites,

$$D(tetra)/D(octa) = 2\exp(-\Delta E/k_B T), \qquad (1)$$

where k_B is the Boltzmann constant and $\Delta E = E_{tetra} - E_{octa}$ is the difference in the ground-state energies of the D atoms occupying these sites. The "experimental" value of $\Delta E = 0.19$ eV per D atom obtained from Eq. (1) was also confirmed by *ab initio* calculations (using a method described in Ref. [50]), which gave a similar value of $\Delta E = 0.22$ eV per D atom. These estimates did not however agree with the value of $\Delta E^{bottom} = 0.5$ eV per H (or D) atom obtained previously for fcc FeH [22] in the framework of the density-functional theory (DFT) for the difference in the minima of the potential wells for the H or D atoms in the T and O sites. Since ΔE should be greater than ΔE^{bottom}, the result of Ref. [22]

TABLE I. Calculated differences ΔE^{bottom} in the minima of potential energy and calculated ($T = 0$ K, ZPE-corrected) and experimental differences ΔE in the ground-state energies of H and D atoms occupying tetrahedral (tetra) and octahedral (octa) interstitial sites in the fcc metal lattices of hydrides and deuterides of Fe, Ni, Pd, and Rh.

	$\Delta E^{\text{bottom}} = E^{\text{bottom}}_{\text{tetra}} - E^{\text{bottom}}_{\text{octa}}$ (eV/atom H or D)		$\Delta E = E_{\text{tetra}} - E_{\text{octa}}$ (eV/atom H or D)		ΔE^{ZPE} (eV/atom H or D)
System	DFT calculation, present paper	DFT calculation, literature results	Calculation, present paper & [27]	Experiment, literature results	Calculation, present paper
Fe-H	0.42	0.5 [22]	0.52	–	0.10
Fe-D	0.42	0.5 [22]	0.49		0.07
		–	0.22 [27]	0.19 at 988 K [27]	
Ni-H	0.18	0.2 [22]	0.28	–	0.10
Ni-D	0.18	0.2 [22]	0.25	–	0.07
Pd-H	−0.07	0.1 [21]	0.04	–	0.11
Pd-D	−0.07	0.1 [21]	0.01	0.12 at 582 K [24]	0.08
				0.08 at 583 K [25]	
Rh-H	0.37	0.542 [23]	0.48	–	0.11
Rh-D	0.37	0.542 [23]	0.45	–	0.08

actually makes the Boltzmann mechanism completely ineffective for filling the T sites in fcc Fe. In fact, substituting $\Delta E = 0.19$ eV per D atom in Eq. (1) gives 17.7% or 1/6 of the D atoms occupying T sites at $T = 988$ K in agreement with the ND results [27], whereas $\Delta E = 0.5$ eV per D atom reduces this number to a vanishingly small value of 0.6%.

From the works [27] and [22] themselves, it is not possible to deduce whose results are more accurate, because the uncertainties in the *ab initio* calculations of ΔE^{bottom} and ΔE cannot be reliably estimated. On the other hand, the ΔE^{bottom} values have already been calculated in different works for H atoms in the fcc hydrides NiH [22], FeH [22], PdH [21], and RhH [23]. This provides the opportunity to recalculate these ΔE^{bottom} values using a similar approach, and roughly estimate the uncertainty in ΔE^{bottom} typical of such calculations by comparing the obtained values with those from the literature. The ΔE value for each hydride can further be determined by adding the difference in the zero-point energies (also calculated) of H atoms on the T and O sites to the obtained ΔE^{bottom} value.

In the present work, we carried out DFT calculations aimed at the determination of the ground-state energy difference for the hydrogen (deuterium) atom at the T and O sites in hydrides (deuterides) of Fe, Ni, Pd, and Rh. The calculations were based on the plane-wave pseudopotential method as implemented in the CASTEP code [51,52]. We used ultrasoft pseudopotentials with a plane-wave cutoff of 300 eV. The calculations were performed with the PBE approximation for exchange and correlation. All systems were treated as non-spin-polarized in order that results of the calculations, which were all performed for $T = 0$ K, were better applicable to the state of these systems at high temperatures, when no magnetic order could survive. All structural and lattice parameters were relaxed simultaneously, so that the residual forces experienced by the atoms were less than 0.01 eV/Å and the residual pressure was below 0.02 GPa. The valence electron configurations were $\text{H} - 1s^1$, $\text{Fe} - [\text{Ar}]3d^6 4s^2$, $\text{Ni} - [\text{Ar}]3d^8 4s^2$, $\text{Pd} - [\text{Kr}]4d^{10}$, and $\text{Rh} - [\text{Kr}]4d^8 5s^1$. To estimate the contribution of the zero-point energy (ZPE) to the formation enthalpy of the hydrides and deuterides, we performed phonon calculations within the finite displacement approach with the displacements of about 0.005 Å for the supercells defined by a cutoff radius of 5 Å.

The calculations were made for stoichiometric MeH(octa) and MeH(tetra) hydrides and for $\text{Me}_2\text{H(octa)}$ and $\text{Me}_8\text{H(octa)}_4\text{H(tetra)}$ compounds, i.e., for the compositions similar to those observed in experiment [24,25,27]. More details are given in Ref. [53]. In particular, Fig. S1 shows the calculated phonon dispersion curves and densities of states for the MeH(octa) and MeH(tetra) hydrides. These hydrides are all dynamically stable.

The calculated values of ΔE^{bottom} and ΔE are presented in Table I together with the literature data. The bottom energies of the potential wells were calculated as

$$E^{\text{bottom}}_{\text{octa}} = 2\{H[\text{fcc-MeH(octa)}] - H[P4/nmm\text{-Me}_2\text{H(octa)}]\}$$

and

$$\begin{aligned} E^{\text{bottom}}_{\text{tetra}} = 8\{&H[P\bar{4}2m\text{-Me}_8\text{H(octa)}_4\text{H(tetra)}] \\ &- H[P4/nmm\text{-Me}_2\text{H(octa)}]\}, \end{aligned}$$

using the calculated enthalpies H at $T = 0$ K listed in Table SI of Ref. [53]. The ground state energies E for the hydrogen atoms were obtained from the bottom well energies E^{bottom} by adding $\frac{3}{2}\langle\hbar\omega\rangle^{\text{H}}$, where $\langle\hbar\omega\rangle^{\text{H}}$ is the mean energy of optical hydrogen vibrations for the given interstitial type. The calculated values of $\langle\hbar\omega\rangle^{\text{H}}_{\text{octa}}$ and $\langle\hbar\omega\rangle^{\text{H}}_{\text{tetra}}$ for the corresponding fcc MeH phases are listed in Table SI. The differences $\Delta E^{\text{ZPE}} = \frac{3}{2}[\langle\hbar\omega\rangle_{\text{tetra}} - \langle\hbar\omega\rangle_{\text{octa}}]$ to be added to ΔE^{bottom} to get ΔE are presented in the rightmost column of Table I. For the deuterium atoms, we used a harmonic approximation $\langle\hbar\omega\rangle^{\text{D}} = \langle\hbar\omega\rangle^{\text{H}}/\sqrt{2}$.

As seen from Table I, the ΔE^{bottom} values calculated in the present paper are systematically lower than those in the literature. The difference is smaller than 0.1 eV for the hydrides FeH and NiH of $3d$ metals and increases to 0.17 eV for the hydrides PdH and RhH of $4d$ metals. In any case, the uncertainty in determining ΔE^{bottom} from the DFT calculations is unlikely to exceed ±0.1 eV.

As can also be seen from Table I, the values of $\Delta E^{\rm ZPE} = \frac{3}{2}[\langle\hbar\omega\rangle_{\rm tetra} - \langle\hbar\omega\rangle_{\rm octa}]$ are all positive, small compared to $\Delta E^{\rm bottom}$ and almost independent of the hydrogenated metal, amounting to about 0.1 eV for all studied hydrides and about 0.07 eV for the deuterides. Consequently, the uncertainty in the calculation of $\Delta E = \Delta E^{\rm bottom} + \Delta E^{\rm ZPE}$ should remain approximately the same as that of $\Delta E^{\rm bottom}$ and do not exceed ±0.1 eV.

To date, a noticeable population of the T sites at high temperatures has only been observed in the Pd-D [24,25] and Fe-D [27] systems. As for the Pd-D system, the reported compositions PdD(octa)$_{0.394}$D(tetra)$_{0.066}$ at 582 K [24] and PdD(octa)$_{0.43}$D(tetra)$_{0.19}$ at 583 K [25] substituted in Eq. (1) give "experimental" values of $\Delta E = 0.12$ and 0.08 eV per D atom indicated in Table I. A ZPE-corrected value of $\Delta E = \Delta E^{\rm bottom} + \Delta E^{\rm ZPE} = 0.1 + 0.08 = 0.18\,{\rm eV/atom}$ D from Ref. [21] and $\Delta E = 0.01\,{\rm eV/atom}$ D from the present paper, respectively, overestimate and underestimate these "experimental" values, but the discrepancy is within the calculation error limit of ±0.1 eV. Thus the calculations confirmed the Boltzmann mechanism of T-site occupancy in palladium deuterides proposed in Refs. [24,25].

In the case of iron deuterides, both the ZPE-corrected value $\Delta E = 0.5 + 0.07 = 0.57\,{\rm eV/atom}$ D from Ref. [22] and the value of $\Delta E = 0.49\,{\rm eV/atom}$ D calculated in the present paper proved to be much higher than the "experimental" value of $\Delta E = 0.19\,{\rm eV/atom}$ D [27] obtained from Eq. (1) under the assumption of the Boltzmann distribution of D atoms over the O and T sites in fcc Fe. With $\Delta E \approx 0.5$ eV/atom D, the Boltzmann mechanism of T-site occupancy in fcc iron deuterides is completely ineffective. The lower value of $\Delta E = 0.22\,{\rm eV/atom}$ D corroborating this mechanism was calculated in Ref. [27] using the method [50], which has not been studied as thoroughly as the DFT methods, and is likely to be less accurate.

Table SII in Ref. [53] presents the values $\beta_{\rm H}^{\rm O}$ and $\beta_{\rm H}^{\rm T}$ of hydrogen-induced volume expansion, which were also calculated in this paper for the fcc hydrides of Fe, Ni, Pd, and Rh. These values can only be considered as very approximate due to the limited accuracy of the DFT calculations [54]. For our calculations, we used the GGA-PBE functional, which gave the most accurate lattice parameters for the 3d metals Fe and Ni compared to other functionals. As one can see from Table SII, our calculated value of $\beta_{\rm H}^{\rm O} = 2.10\,{\rm \AA}^3$/atom H for fcc NiH is in fair agreement with the experimental $\beta_{\rm H}^{\rm O} = 2.20\,{\rm \AA}^3$/atom H at $T = 120$ K [1,20]. This suggests that similar calculations for the fcc iron hydrides can also be trusted.

Our calculations gave $\beta_{\rm H}^{\rm O} = 1.86\,{\rm \AA}^3$/atom H and $\beta_{\rm H}^{\rm T} = 2.94\,{\rm \AA}^3$/atom H for the fcc FeH(octa) and FeH(tetra) phases, respectively. These values proved to be close to $\beta_{\rm H}^{\rm O} = 1.9\,{\rm \AA}^3$/atom H and $\beta_{\rm H}^{\rm T} = 3.1\,{\rm \AA}^3$/atom H for fcc iron obtained by interpolating the experimental results for fcc and hcp hydrides of other 3d metals (see Sec. III D and Fig. 6). Therefore the calculations corroborate the conclusion that the hydrogen-induced volume expansion $\beta_{\rm H} = 2.2\,{\rm \AA}^3$/atom H of fcc Fe observed in high-temperature high-pressure experiments cannot be caused by filling the O sites alone because of the considerably lower value of $\beta_{\rm H}^{\rm O}$. A partial filling of the T sites accompanied with a much larger volume expansion may explain the experimental findings.

If the partial filling of the T sites in the fcc iron deuterides discovered in Ref. [27] were due to the thermal excitations, the D(tetra)/D(octa) ratio would exponentially increase with temperature according to Eq. (1) causing an increase in $\beta = dV_a/dx$. However, a large value of $\Delta E = 0.49\,{\rm eV}$ per D atom (and even larger value of $\Delta E = 0.52\,{\rm eV}$ per H atom) calculated in the present paper suggest that the T occupancy in fcc Fe should be of some other origin. One could expect that a non-Boltzmann mechanism of filling the T sites (as yet unknown) would lead to a less steep increase in the T-site occupancy with increasing temperature. Accordingly, the β values will moderately vary with the temperature, too, so the value $\beta = 2.20(5)\,{\rm \AA}^3$ per D or H atom determined at temperatures of 600 °C –700 °C is likely to apply to a much larger temperature interval.

IV. CONCLUSIONS

Despite the large number of papers devoted to high-pressure investigations of the iron-hydrogen system (see, for example, recent experimental papers [27,29,30,43,44] and references therein), it is for the first time that the hydrogen content of the high-pressure high-temperature γ iron hydrides and deuterides has been determined experimentally.

Constructing the isobar $x(T)$ of deuterium solubility in iron at $P_{\rm D2} = 6.3\,{\rm GPa}$ and $100 \leqslant T \leqslant 800\,^{\circ}{\rm C}$ made it possible to choose between the predictions of $x = 0.64$ and 0.47 of two different models used to interpret results of an *in situ* neutron diffraction study of a γ-FeD$_x$ sample formed at $P_{\rm D2} = 6.3\,{\rm GPa}$ and $T = 715\,^{\circ}{\rm C}$ [27]. Our experiment unequivocally confirmed the estimate $x = 0.64$ of the model assuming that 5/6 of the deuterium atoms filled the usual octahedral interstices in the fcc iron lattice of the iron deuteride, whereas 1/6 of the D atoms occupied the tetrahedral sites. The possibility of partial filling the T sites at high temperatures is important for many hydrides with closed-packed metal lattices, because this will greatly affect their thermodynamical and physical properties.

It should however be mentioned that results of our *ab initio* calculations rather well agree with the literature data on the filling of T sites in fcc Pd deuterides [25], but do not confirm the theoretical estimate $\Delta E = E_{\rm tetra} - E_{\rm octa} = 0.22\,{\rm eV}$ per D atom, which was made in Ref. [27] for the difference between the ground state energies of the D atoms sitting on the T and O sites in the fcc lattice of γ iron deuterides. With $\Delta E = 0.22\,{\rm eV}$ per D atom, the presence of 1/6 of the D atoms on T sites in the γ-FeD$_{0.64}$ sample at $T = 715\,^{\circ}{\rm C}$ could fully be ascribed to the Boltzmann population of these sites due to thermal excitations. With our calculated value of $\Delta E = 0.49\,{\rm eV}$ per D atom, the Boltzmann population of the T sites at $T = 715\,^{\circ}{\rm C}$ should be vanishingly small. Most likely, the partial filling of the T sites (if it exists) in γ-FeD$_{0.64}$ studied in Ref. [27] should be of some other origin.

Combining the $x(P, T)$ values for γ deuterides and hydrides of iron obtained in the present paper with the structural results of previous neutron diffraction [27] and x-ray diffraction [28,29] studies, respectively, made it possible for the first time to make an experimental estimate of

$dV_a/dx = 2.20(5)$ Å^3 per D or H atom for the hydrogen-induced volume expansion of fcc iron. Consequently, from now on, the hydrogen content of γ hydrides of iron studied by *in situ* x-ray diffraction in many previous and, we believe, many future works can be calculated from the value of their lattice parameter.

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