Site occupancy of interstitial deuterium atoms in face-centred cubic iron

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Hydrogen composition and occupation state provide basic information for understanding various properties of the metal-hydrogen system, ranging from microscopic properties such as hydrogen diffusion to macroscopic properties such as phase stability. Here the deuterization process of face-centred cubic Fe to form solid-solution face-centred cubic FeD_x is investigated using in situ neutron diffraction at high temperature and pressure. In a completely deuterized specimen at 988 K and 6.3 GPa, deuterium atoms occupy octahedral and tetrahedral interstitial sites with an occupancy of 0.532(9) and 0.056(5), respectively, giving a deuterium composition x of 0.64(1). During deuterization, the metal lattice expands approximately linearly with deuterium composition at a rate of 2.21 Å³ per deuterium atom. The minor occupation of the tetrahedral site is thermally driven by the intersite movement of deuterium atoms along the 〈111〉 direction in the face-centred cubic metal lattice.
At high hydrogen pressures (several GPa), metals react with hydrogen (H) to form hydrides, with the hydrogen atoms occupying the interstitial sites of metal lattices. Iron hydrides have been intensively studied for many decades and the diagram of the Fe–H system is well established at temperatures up to 2,000 K and pressures up to 20 GPa. Three hydride forms exist: body-centred cubic (bcc)-FeH₃, double hexagonal close-packed (dhcp)-FeH₄ and face-centred cubic (fcc)-FeH₅, which correspond to the bcc, dhcp and fcc phases of pure Fe, respectively (Fig. 1); in the hydride, the stacking of the closed-packed metal plane of dhcp Fe is slightly modified into dhcp stacking.

Knowledge of hydrogen composition is essential for interpreting the physical and chemical properties of hydrides. The solubility of hydrogen in bcc Fe is very low (that is, <10⁻⁶ H/Fe) at ambient temperature in hydrogen pressure of 0.1 GPa. The hydrogen solubility in iron increases drastically as the gas pressure increases above several GPa and a nearly stoichiometric hydride dhcp FeH₄ is obtained above 3.5 GPa at ambient pressure. The high-temperature phase of fcc Fe is reacted yet with deuterium fluid above 870 K and approximately at 6 GPa, and the deuterization process is monitored by in situ neutron diffraction measurements. The crystal structures are refined using the Rietveld refinement by employing the diffraction profiles measured during deuterization and for a completely deuterized product. In addition to the dominant O site occupation, the slight occupation of D at the T site is unexpectedly observed and interpreted in terms of thermally activated intersite movement of D atoms by quantum mechanical calculation.

Results

Deuterium composition and site occupancies of fcc FeDₓ. Solid solution of fcc FeDₓ was prepared by heating bcc Fe in the presence of an internal deuterium source (that is, AlD₃) at an initial pressure of 7.4 GPa. The bcc–fcc transition of Fe occurred approximately at 800 K. Deuterization started at 870 K concurrently with decomposition of the inner deuterium source AlD₃, and proceeded on further heating to 988 K, at which the temperature was maintained constant to form the equilibrium state of fcc FeDₓ. Diffraction profiles used for structural analysis were required to be free from grain growth and chemical contamination, which were carefully examined by in situ neutron diffraction measurement at 988 K and 6.3 GPa (Supplementary Figs 1 and 2 and Supplementary Table 1), X-ray diffraction and chemical analysis of the recovered specimen at ambient conditions (Supplementary Figs 3 and 4 and Supplementary Methods).

The crystal structure of fcc FeDₓ at equilibrium has been refined using the 988 K–6.3 GPa profile by employing the Rietveld refinement within the Z-Rietveld software (version 0.9.42.2). We examined two structural models: the fcc metal lattice with D atoms only at the O sites (model 1), and with D atoms occupying both the T and O sites (model 2). As seen in Fig. 2a,b, the profile seems to be satisfactorily reproduced by the two models. However, as obvious by the enlargement of the 220 reflection-peak profiles (Fig. 2c,d), a slight misfit remained for the 220 reflection peak in model 1. The structure factors of fcc FeDₓ were given by the sum or difference of the scattering lengths of the constituent Fe and D atoms: $F_{D_{k+l}} = \sum \left( b_{Fe} - g_{D(O)} \right) b_{D}$ for odd-indexed reflections and $F_{D_{k+l}} = \sum \left( b_{Fe} + 2g_{D(T)} \right) b_{D}$ for even-indexed reflections, where $b_{Fe} = 9.45$ fm and $b_{D} = 6.67$ fm, and $g_{D(T)}$ and $g_{D(O)}$ indicate the T- and O-site occupancies, respectively. The T-site occupation provided additional intensity to the 220 reflections; therefore, the deficit of the 220 peak intensity in model 1 was attributed to the exclusion of the T-site occupancy. A best fit result was obtained with model 2. The optimized fitting parameters were as follows: lattice constant $a = 3.71686(5)$ Å, isotropic atomic displacements $b_{Fe} = 1.44(3) Å^2$ for Fe, $B_{D} = 4.12(1) Å^2$ for D, $g_{D(O)} = 0.532(9)$ and $g_{D(T)} = 0.056(5)$. Assuming the Boltzmann distribution $exp(-\Delta E/kT)$, the site occupancy ratio $g_{D(T)}/g_{D(O)} = 0.056/0.532 = 0.08$ K yielded an energy difference between the two sites of 0.19 eV. The deuterization composition, $x = g_{D(O)} + 2g_{D(T)}$, was 0.64(1), which gave the chemical formula FeD₀.₆₄₋₀.₄₆.

Figure 1 | Compression and heating path of the deuterization of iron. Pressure-temperature phase diagram of FeHₓ (red lines) and Fe (grey lines), which are reproduced from those presented in refs 2–4 for FeHₓ and ref. 17 for Fe, respectively. In situ neutron diffraction measurements were made along the compression and heating paths indicated by the light-blue arrows.
Volume expansion by deuterium absorption. The diffraction profiles obtained during deuterization are displayed in Fig. 3a,b. Low-intensity peaks appeared at the large-\( d \) spacing sides of the original peaks at 873 K, indicating possible deuteride formation on the specimen surface at the early stage of deuterization. The original dominant peaks gradually shifted to large-\( d \) spacing with significant change in peak intensity with time and further increase in temperature. For instance, the 111 reflection peak at \( \sim 2.1 \) Å

### Figure 2 | Experimental and calculated diffraction profiles of fcc Fe\(_D\) at 988 K and 6.3 GPa.** Refined profiles calculated using the fit parameters optimized for (a) model 1 and (b) model 2. The crystal symmetry is cubic (\( Fm\overline{3}m, Z = 4 \)). The atomic sites are Fe 4\( a \)(0,0,0), D(O) 4\( b \)(1/2,1/2,1/2) and D(T) 8\( c \)(1/4,1/4,1/4). The refined structure parameters are given in the main text. Reliable values for the parameters \( R_{wp} \) and \( \chi^2 \) are given in the panels. The enlarged 220 reflection peak profiles are displayed in c,d, in which the experimental errors, which are from counting statistics, are given as vertical bars. A best fit is obtained for model 2 with D atoms at the O sites (dark-blue sphere) and T sites (light-blue sphere), as illustrated in the inset of b, where the O sites surrounding the occupied T site are vacant to avoid the violation of the 2-Å rule (ref. 28).

### Figure 3 | Neutron diffraction profiles and obtained parameters. (a) Neutron diffraction profiles measured with a 2-min accumulation for the deuterization process of fcc Fe at an initial pressure of 7.4 GPa. The profiles of bcc Fe are omitted to clearly display the profile change due to deuterization. (b) Selected profiles showing bcc–fcc transition of Fe and successive deuterization of fcc-Fe. (c) Lattice constant \( a \) (top), D composition \( x \) (middle) and volume expansion rate \( v_D \) (bottom) plotted with time after the start of deuterization. Solid and open circles represent the parameters derived with the refinement analysis using the dominant and shoulder peaks, respectively. Errors are estimated based on the s.d. of Rietveld analysis.
showed almost twice the peak height of the 200 reflection peak at ~1.8 Å, whereas the 873 K profile displayed approximately equal peak heights from 16 to 18 min after the initiation of deuterization. Upon further heating, the dominant peaks merged with the shoulder peaks and formed single peaks, and the 111 peak height reverted approximately to two-thirds of the height of the 200 peak. These profile changes arose from the successive volume expansion caused by D-atom occupation at the specific interstitial site of the metal lattice as described above.

The volume expansion rate \( \nu_T \) was derived from the D composition and the volume expansion because of deuterium absorption. After correction of the thermal expansion of the Fe lattice\(^{17} \), we obtained a value of 2.21(4) Å\(^3\) per H at 988 K and 6.3 GPa, which was significantly larger than the value of 1.9 Å\(^3\) per H conventionally used for fcc FeH\(_x\), but rather close to 2.4 Å\(^3\) per H\(^4\) reported for dhcp-FeD recovered at 90 K and ambient pressure\(^{18} \). According to Fukai\(^{19} \), \( \nu_T \) of other 3-d transition metals such as Cr, Mn, Co, Ni and Mo, with O-site occupancy of H atom ranges from 1.85 to 2.3 Å\(^3\) per H. Especially, fcc-NiH, (Ni,Mn)H and MoH give values of 2.2–2.3 Å\(^3\) per H, which are close to 2.21(4) Å\(^3\) per D obtained in the present study.

The volume expansion rate \( \nu_T \) can be considered constant over a wide range of deuterium compositions. The lattice constant of the fcc metal lattice and the site occupancies of D atoms have been obtained for each profile measured during the deuterization process by Rietveld analysis, where the occupancy ratio of D atom, in spite of the significant difference in the wave function of sites O and T. The wave functions of the first-excited states display a sine-function-like shape with nodes at the origin, and their maxima are located slightly apart from the O-site centre. The wave functions extend very slightly to the T sites even for the first-excited state, thus, giving negligible probability of T-site occupation.

Another possible origin of the T-site occupation is the intersite movement of the D atom by thermal activation. The potential barrier between the O and T sites along the \( \langle 111 \rangle \) direction is ~0.3 eV high, allowing some migration of the D atom by thermal activation. Adding a deformation energy of 0.031 and 0.136 eV to the O-site ground-state energy (that is, 0.0025 eV) and T-site ground-state energy (that is, 0.117 eV), respectively\(^{19} \), yields an energy difference of 0.22 eV between the two sites, which agrees with the experimental value of 0.19 eV; the accuracy of the calculated energies is within 0.0001 eV. Similar calculation for the H atom provides the ground-state energies of 0.0378 (O site) and 0.1849 eV (T site), and the energy difference corrected for the deformation energies becomes 0.25 eV (data not shown). The energy difference of the H atom is close to that of the D atom, in spite of the significant difference in the wave function and, hence, in the site ground-state energies between H and D atoms.

**Discussion**

We have investigated the deuterization process of fcc-Fe and the occupation state of D atoms in fcc-FeD\(_x\) at high temperatures and hydrogen pressures by *in situ* neutron diffraction measurements. Rietveld refinements of diffraction profiles reveal that D atoms predominantly occupy the octahedral interstitial sites \( g_{D(O)} = 0.532 \), with slight occupancy of the tetrahedral interstitial site \( g_{D(T)} = 0.056 \) in the equilibrium state of fcc FeD\(_x\) achieved at 988 K and 6.3 GPa. Quantum-mechanical calculations show that the ground-state energy level of the D atoms at the T site is located 0.22 eV higher than that at the O site, and D atoms can move from the O site to the T site by thermal activation along the \( \langle 111 \rangle \) direction of the fcc metal lattice, at high temperatures of ~1,000 K. The calculated energy difference of 0.22 eV is in agreement with an experimental value of 0.19 eV, which is derived from the site occupancy ratio of \( g_{D(T)}/g_{D(O)} \) using the Boltzmann distribution exp(–\( \Delta e/k_B T \)). The occupation state of D atoms, including the intersite movement, in Fe metal provides an insight into the various properties of metal–hydrogen/deuterium systems such as H/D atom diffusion and phase stability of hydrides/deuterides.

**Figure 4** | Potential curves and wave functions along the \( \langle 100 \rangle \), \( \langle 110 \rangle \) and \( \langle 111 \rangle \) directions in an fcc metal lattice. D atom is located at the (a) O site and (b) T site. Wave functions are shown for the ground state (broken lines), first-excited states (solid lines) of the vibrational states of D atom at the O site, and ground state (broken line) at the T site. The distance from the original point of the O-site centre is scaled by the fcc lattice constant \( a \) (that is, 3.720 Å), which was obtained from the neutron diffraction profile observed at 988 K and 6.3 GPa.
Methods

Neutron-diffraction measurements. The experimental setup for high-pressure neutron-diffraction measurements is illustrated in Fig. 5. A high-pressure cell was designed based on the conventional design used for in situ X-ray diffraction.\(^{22,23}\) An Fe rod specimen (3 mm in diameter and 2.5 mm in height) was placed at the centre of a deuterium-sealing capsule made of NaCl (3.5 mm in diameter and 8 mm in height) with internal deuterium sources of AlD\(_3\) pellets above and below. The NaCl capsule was inserted in a cylindrical graphite heater and embedded in a pressure-transmitting medium made of ZrO\(_2\) (17-mm-edge cube). The cell was compressed at ambient temperature to 7.4 GPa and then heated to 988 K at a rate of ~40 K per min in a six-axis multi-anvils press, each with a maximum load of 5,000 kN, equipped with an electric power supply system.

The AlD\(_3\) deuterium source decomposed upon heating, providing fluid deuterium to the iron specimen to initiate the deuteration reaction. The loading force of each six-axis was held at 1,300 kN during heating. However, the pressure in the NaCl capsule decreased to ~6.3 GPa on heating to 988 K. The sample pressure was estimated on the basis of the relation between the generated pressure and press load, which had been calibrated in advance by neutron diffraction measurement on a volume–pressure standard substance NaCl at pressures up to 10 GPa.\(^{24}\) To estimate the sample pressure, besides the pressure calibration relation, we used the lattice constants of the Fe specimen and NaCl capsule derived from the observed diffraction profiles using the equations of state\(^{25,26}\). The sample temperature was estimated from the relation between the generated temperature and input electric power, calibrated with a Pt–Pt 13% Rh thermocouple.

Neutron-diffraction profiles were accumulated every 2 min during the heating process. The temporal evolution of the diffraction profile was monitored at several fixed temperatures above the deuteration-initiating temperature (~780 K).

Finally, 1-h accumulated diffraction profile was taken at 988 K and 6.3 GPa for the equilibrium state of fcc-FeD\(_2\)\(^{\text{988 K}}\). We here describe the general formulation for calculating the self-trapped states of light interstitial atoms in a metal lattice. A method to calculate the wave function depend on the displacements of the metal atoms for the adiabatic potential (equation (1)) is obtained taking the lowest value as a function of displacements of metal atoms.

\[
\frac{\partial E}{\partial \mathbf{u}_i} = 0.
\]

This defines the self-trapped state, providing the wave function and energy eigenvalue for the interstitial atom. Here we assume the displacements of metal atoms because of self-trapped D (H) atoms to be appropriate values, and calculate the U by the equation (3). Using obtained U, we numerically solve the equation (2) and obtain the wave function and energy eigenvalue. The detailed procedure for the calculation has been published elsewhere.\(^{21}\)

Quantum-mechanical calculations. We here describe the general formulation for calculating the self-trapped states of light interstitial atoms in a metal lattice. A system is supposed to consist of a light interstitial atom, here H or D, and N host metal atoms. The interstitial atom is assumed to follow the motion of the metal atoms adiabatically within the Born–Oppenheimer approximation. Therefore, the energy of the whole system can be written as

\[
E\left(\{\mathbf{u}_i\}, \mathbf{r}\right) = E_i\left(\{\mathbf{u}_i\}\right) + E_N\left(\{\mathbf{u}_i\}\right).
\]

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Author contributions

A.M., H.S., T.H., A.S.-F. and R.I. performed the high-pressure neutron diffraction experiment. H.S., N.E. and Y.K. developed the high-pressure cell for this experiment. A.M. analysed the neutron diffraction data. T.H. and A.S.-F. developed the high-pressure neutron diffractometer PLANET. H.Su performed the theoretical calculations. T.S., M.M. and S.O. prepared the AlD3. A.M., H.S and K.A. wrote the manuscript. K.A. directed this study.

Additional information

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