

Phase behaviours of superionic water at planetary conditions

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Abstract

Most water in the universe may be superionic, and its thermodynamic and transport properties are crucial for planetary science but difficult to probe experimentally or theoretically. We use machine learning and free energy methods to overcome the limitations of quantum mechanical simulations, and characterise hydrogen diffusion, superionic transitions, and phase behaviours of water at extreme conditions. We predict that close-packed superionic phases, which have a fraction of mixed stacking for finite systems, are stable over a wide temperature and pressure range, while a body-centered cubic superionic phase is only thermodynamically stable in a small window but is kinetically favoured. Our phase boundaries, which are consistent with the existing-albeit scarce-experimental observations, help resolve the fractions of insulating ice, different superionic phases, and liquid water inside of ice giants.

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Water is the dominant constituent of Uranus’ and Neptune’s mantle [1], and superionic water is believed to be stable at depths greater than about one-third of the radius of these ice giants [2]. Water superionicity is marked by exceptionally high hydrogen diffusivity and ionic conductivity, as hydrogen atoms become liquid-like while oxygen atoms remain solid-like on a crystalline lattice. Although superionic water was postulated over three decades ago [3], its optical properties (it is partially opaque) and oxygen lattices were only accurately measured recently [2, 4], and many properties of this hot “black ice” are still uncharted.

Amongst the many mysteries regarding superionic water, the location of various coexistence lines over a large range of pressure (P) and temperature (T), including the melting line, the insulating ice to superionic transition line, and the phase boundaries between competing superionic phases, are essential for understanding the formation, evolution, interior structure and magnetic fields of planets [1, 5, 6]. However, these lines and even the possible types of oxygen lattices for superionic water have long been debated. Initial computational studies [3] proposed a face-centered cubic (fcc) oxygen lattice while early first-principles electronic structure molecular dynamics (FPMD) considered a body-centered cubic (bcc) superionic phase as a high temperature analog of ice X [7]. Later FPMD studies re-proposed a fcc [8, 9], suggested a close-packed (cp) [10], and, at pressures higher than 1 TPa, a P21/c [10] oxygen lattice. In the experiments of superionic water [2, 4, 11–13], sample preparation is extremely challenging, hydrogen positions cannot be determined, and temperature measurements in dynamical compression experiments are not straightforward [2, 4]. Notably, recent dynamical compression experiments combined with x-ray diffraction (XRD) found a superionic phase with fcc oxygen lattice, ice XVIII, above 2000 K [2]. Static compression experiments combined with synchrotron XRD suggest a triple point between liquid, ice VII’, and ice VII’’ (a bcc superionic phase) at 14.6 GPa and 850 K [13].

Theoretical modelling of high- P water is also difficult. No reliable empirical force fields are available for this system. FPMD simulations are computationally expensive, and are thus confined to short trajectories and small system sizes, which may introduce artifacts leading to contradictory results on the phase boundaries [5, 7–10, 14–16] and diffusivity [8, 9] between various studies based on the same assumption of the underlying electronic structure. Furthermore, most FPMD simulations treat nuclei as classical point masses and ignore their wave-like nature, even though light elements such as hydrogen can exhibit strong nuclear quantum effects (NQEs). Molecular dynamics (MD) combined with the Feynman path

integral (PIMD) can be used to treat the NQEs, but PIMD multiplies the computational cost by another factor of about 20 [17]. However, machine-learning potentials (MLPs) can help overcome these limits by first learning an accurate data-driven model of atomic interactions from first-principles calculations [18], and then driving large-scale simulations at an affordable computational cost. MLPs have thus helped reproduce the low-P phase diagram of water [19, 20], elucidate the nucleation behaviour of gallium [21], the liquid-liquid transition of high-P hydrogen [22] and the structural transition mechanisms in disordered silicon [23].

In this study, we construct a MLP for high-pressure water using an artificial neural network architecture [24] based on Perdew-Burke-Ernzerhof (PBE) [25, 26] density functional theory (DFT). Combining the MLP with advanced free energy methods, we predict the properties of superionic and liquid water at the PBE level of theory, using large system sizes, long time scales and considering NQEs. We elucidate the mechanisms for ice-superionic transitions and hydrogen transport, map the high-pressure water phase diagram, and probe the kinetics of phase transition.

Hydrogen diffusivity in superionic phases

The H diffusion coefficient D_H is the key feature of superionic water, and can be used to derive the ionic conductivity [27] which is crucial for modelling the magnetic field geometry of Uranus and Neptune [6]. We consider the aforementioned bcc and fcc lattices of oxygen, and a hexagonal close-packed (hcp) lattice that has a low-T ice analog with the Pbcm space group. The insulating structures become superionic when the temperature rises, as marked by the rapid increase of D_H (Fig. 1) at about 2000 K. The dashed lines in Fig. 1 indicate the associated transition temperatures T_s defined by a cutoff of 10^{-4} cm²/s in D_H . The bcc phase has a higher T_s compared to fcc and hcp. At $T \gg T_s$, D_H in all three superionic phases show no distinct difference, which is in agreement with Ref. [9] and in contrast with Ref. [8]. The distributions of hydrogen positions are shown in the contour plots of Fig. 1: at low T hydrogen atoms are confined to their equilibrium sites, while in the superionic phases only a fraction are.

We focus on the hydrogen diffusion in the fcc lattice at 300 GPa, as the results at other pressures and for bcc and hcp are similar (Supplementary Information Sec.VI D). When

the lattice remains stable, Fig. 2a shows that D_{H} changes rapidly but smoothly across the ice-superionic transition region, and increases gradually as a function of T when the system is fully superionic. To rationalize such behaviour, we use an interstitial formation model [28] to describe the free energy of the system:

$$f(x, T) = (\epsilon_0 - Ts_0)x - \frac{\lambda}{2}x^2 + k_{\text{B}}T[x \ln x + (1 - x) \ln(1 - x)], \quad (1)$$

where x is the fraction of the conducting hydrogen, s_0 is the entropy gain for creating a conducting atom in the unit cell from a confined atom, as the former has a higher accessible volume, and ϵ_0 and λ are the energy scales for interstitial formation and interaction, respectively. Upon equilibration, Eqn. (1) reaches a minimum and the equilibrium fraction $x(T) = \arg \min_x f(x, T)$. We use a Speedy-Angell power-law [29]

$$D = D_0 [(T/T_0) - 1]^\nu \quad (2)$$

to model the diffusivity of conducting hydrogen atoms in the lattice, and assume that the confined hydrogen have negligible diffusivity, so that overall $D_{\text{H}}(T) = x(T)D$. We fit this $x(T)D$ to the computed H diffusion coefficients for bcc, fcc and hcp at various conditions (one example is shown as the black curve in Fig. 2a, all fits are in the Figure S13 of Supplementary Information), and the fits are excellent over the entire range of thousands of kelvin considered. Fig. 2b shows $x(T)$ from the fits for fcc at different pressures, which exhibits rapid increase at $T \approx 2000$ K corresponding to the ice-superionic transitions. At $T > T_{\text{s}}$, $x(T)$ increases slowly and reaches about 0.8 at 3000 K, consistent with the observation in Fig. 1 that a fraction of hydrogen atoms are close to the equilibrium sites even in fully superionic phases.

The interstitial model (Eqn. (1)) sheds light on the driving force of the superionic transition: the entropy gain s_0 competes with the energetic cost ϵ_0 of interstitial formation and wins at high T . The interaction between interstitial λ affects the nature of the transition: $x(T)$ will exhibit a smooth crossover, which is the case observed here, when $\lambda \leq 4\epsilon_0/(2 + s_0)$, and a first-order phase transition in T otherwise. The smooth crossover in this case explains the facile ice-superionic transitions and the lack of hysteresis. A similar framework can be used to understand how to tune the conductivity of ambient pressure superionic materials used for solid-state fuel cells and solid electrolyte applications [30, 31].

Chemical potentials of superionic and liquid water

The thermodynamic stability of different phases is governed by their chemical potentials μ . However, computing the μ of the superionic phases is difficult, because these phases are half-solid-half-liquid, and because the thermodynamic integration (TI) method cannot be applied across first-order boundaries that might exist between a number of phases (ice VII, VII', VII'', X) all sharing the bcc oxygen lattice [13, 16]. To circumvent these difficulties, we instead compute their relative chemical potentials to the liquid, $\mu_{\text{fcc/bcc/hcp}}^{\text{MLP}} - \mu_{\text{l}}^{\text{MLP}}$, in umbrella sampling [35] simulations on superionic-liquid coexistence systems (illustrated in Fig. 3) at different pressures between 15 and 200 GPa and temperatures close to melting points using the MLP. In these coexistence systems, oxygen atoms in the liquid phase diffuse around, and the ones in the superionic phase stay on the bcc, fcc or hcp lattices. Meanwhile, hydrogen atoms travel in and out between the two phases, as illustrated by a few H trajectories in Fig. 3.

The difference in μ between two superionic phases is just, e.g. $\mu_{\text{bcc}}^{\text{MLP}} - \mu_{\text{fcc}}^{\text{MLP}} = (\mu_{\text{bcc}}^{\text{MLP}} - \mu_{\text{l}}^{\text{MLP}}) - (\mu_{\text{fcc}}^{\text{MLP}} - \mu_{\text{l}}^{\text{MLP}})$. We use TI along isotherms and isobars to calculate the chemical potential differences at other conditions where the two phases remain metastable. We then promote the MLP results to the PBE level by adding $\mu - \mu^{\text{MLP}}$ computed from free-energy perturbation, which removes the small residual errors in the MLP partly due to its lack of long-range electrostatics [19, 36]. Finally, we perform PIMD simulations using the MLP, and obtain $\mu_{\text{fcc/bcc/hcp}}$ at the PBE level that include NQEs.

The melting curves (T_{m}) of bcc and fcc, indicated using the purple and the blue lines in Fig. 4a,b, respectively, are similar to each other at $P \geq 40$ GPa, and noticeably different from previous single-phase melting and solidification FPMD calculations [5]. At $P < 100$ GPa (Fig. 4b), our T_{m} are roughly in between the experiments based on laser-heated diamond anvil cell with XRD at $P \leq 45$ GPa [13], and the direct observation of motion in the laser-speckle pattern at $P \leq 90$ GPa [32, 33]. Our T_{m} are presented up to 220 GPa, and agree with a single point at about 190 GPa and 4800 K in the precompressed shockwave experiment [4].

Fig. 4a shows $\mu_{\text{bcc}} - \mu_{\text{fcc}}$, and the hatched area indicates the statistical uncertainty bounds of the coexistence line $T(\mu_{\text{fcc}} = \mu_{\text{bcc}})$. The bcc lattice is stable at low T as well as low $P \lesssim 75$ GPa, and this stability region includes both the insulating ice and the superionic bcc, which are separated by the aforementioned ice-superionic transition line T_{s} (the solid green

line in Fig. 4a). The superionic bcc phase has a narrow stability region, and becomes less stable at higher P . Previous calculations of the boundary between competing superionic phases were conflicting and scattered: TI calculations using FPMD at 3000 K [8] (the brown line), constant-pressure single-phase FPMD at 2200 K and 3000 K [10] (the pink line with the bounds of transition pressure between bcc and cp), and analytic models combined with FPMD [9] (the gray curve). Our boundary has small statistical uncertainty thanks to the large-scale simulations. Notably, our boundary is fully compatible with the pressure–temperature conditions where bcc (red circles) and fcc (orange circles) phases were observed in the XRD measurements [2].

Fig. 4c shows that hcp becomes more favourable at higher pressure, and is slightly more stable than fcc above ≈ 400 GPa. Overall, the magnitude of $\mu_{\text{hcp}} - \mu_{\text{fcc}}$ is very small across $100 \text{ GPa} \leq P \leq 800 \text{ GPa}$ and $2000 \text{ K} \leq T \leq 5500 \text{ K}$, of less than 10 meV per H_2O formula unit, compared with the thermal energy of 0.3 eV per degree of freedom at a few thousands of kelvin. This hints that fcc and hcp can coexist at these conditions, which has been observed in FPMD simulations at $P > 280$ GPa in Ref. [10]. To further confirm this, we simulate superionic water growing from liquid water supercooled at 3000 K, 100 GPa (one example shown in Fig. 4d). The starting configuration has a pure hcp oxygen lattice with close-packed planes parallel to the interface, and the oxygen lattice gradually grows into a state of mixed stacking. This indicates that, for a system of finite sizes, the equilibrium oxygen lattice in the fcc region of stability (shown in Fig. 4a) may have a finite fraction of mixed stacking. Such stacking can be revealed from XRD measurements, and we provide the simulated diffraction patterns (Figure S21 in Supplementary Information) as a guide.

Superionic-liquid interfacial free energies

The phase synthesized in experiments may not be the stable phase suggested by the phase diagram (Fig. 4a,c), but a metastable phase with lower activation barrier to nucleate [37]. The interfacial free energy γ dominates the nucleation rate by entering as an exponential of a cubic power [38] and is a key quantity in the modelling of kinetics of phase transition during dynamical compression experiments [39, 40]. We compute fcc/bcc-liquid interfacial free energies γ for the $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ interfaces at $T = 3250 \text{ K}$ and $P = 100 \text{ GPa}$ (on the T_{m}) using the capillary fluctuation method (see Supplementary Information Sec.Vi F

and Ref. [41]). For bcc, $(\gamma_{100}, \gamma_{111}, \gamma_{110}) = (16.7 \pm 0.3, 17.0 \pm 0.2, 16.8 \pm 0.2) \text{ meV}/\text{\AA}^2$, and for fcc, $(24.5 \pm 0.4, 24.1 \pm 0.4, 24.2 \pm 0.4) \text{ meV}/\text{\AA}^2$. We assume that hcp is likely to have similar γ as fcc, due to their shared close-packing.

Both bcc and fcc have small anisotropy in γ , suggesting that the equilibrium shapes of superionic nuclei in liquid water are near-spherical. The bcc superionic phase has much lower γ compared to fcc at the given condition, suggesting that bcc is easier to nucleate and thus kinetically favoured. Crucially, dynamic compression experiments [2, 4], pulsed laser heating in the diamond anvil cell [42, 43] and FPMD simulations have short time scales, so in these settings the bcc superionic phase may form even at conditions where it is not as stable as fcc. Such kinetic effect can shed light on the discrepancy between recent experimental measurements [2, 43].

Our phase boundaries of water at planetary conditions can be used to determine the fraction of insulating ice, superionic, and liquid water in the interior of ice giants. Compared with previous theoretical results shown in Fig. 4, which are sparse and contradictory, we are able to quantitatively map the phases of superionic water across a large part of the phase diagram ($10 \text{ GPa} \leq P \leq 800 \text{ GPa}$, $500 \text{ K} \leq T \leq 5500 \text{ K}$), along with mechanistic understanding of the ice-superionic transition. Our results suggest that for finite systems a close-packed superionic phase with mixed stacking is stable over a wide temperature and pressure range (Fig. 4), while the superionic bcc phase is stable in a small region at $P \lesssim 75 \text{ GPa}$ and $T \lesssim 2500 \text{ K}$, but may be kinetically favoured due to its lower interfacial free energy with the liquid. As planets have billions of years to evolve and to reach equilibrium, but dynamic compression experiments and FPMD simulations are bound to have short time scales, the kinetic factors probed in our study help bridge the gap. The planetary interior models illustrated in Fig. 4a combined with our phase diagram imply a transition from liquid water to superionic water deep inside the ice giants. This transition zone will see a liquid-superionic water interface, with hydrogen atoms diffusing across the interface between the two phases like what we see in Fig. 3, carrying electrical charges and heat across such interfaces in the icy planets.

Our quantitative understanding of superionic water sheds light into the interior structure, evolution and the dynamo process of planets such as Uranus and Neptune and also of the increasing number of icy exoplanets [44]. We suggest future static and dynamic compression experiments to discover the close-packed phase with mixed stacking, and to investigate

the preferential nucleation of bcc. Furthermore, our framework can be used to discover and characterise superionic electrolyte materials, as well as new superionic phases of other components such as ammonia, salts and related mixtures that are relevant for planetary science.

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Authors contributions: B.C., M.B. and S.H. conceived the study; B.C. performed the simulations related to the MLP; M.B., C.J.P. and S.H. performed the FP calculations; B.C. M.B. and S.H. analysed the data; All wrote the paper.

Competing interests: All authors declare no competing interests.

Data availability statement The authors declare that the data supporting the findings of this study are available within the paper, and detailed description of the calculations are included in Supplemental Information. All original data generated for the study, and the machine learning potential for high-pressure water constructed in this study are in the Supplementary Information and repository <https://github.com/BingqingCheng/superionic-water>.

Code availability statement All necessary input files for simulations and a Python notebook for data analysis are in the Supplementary Information.

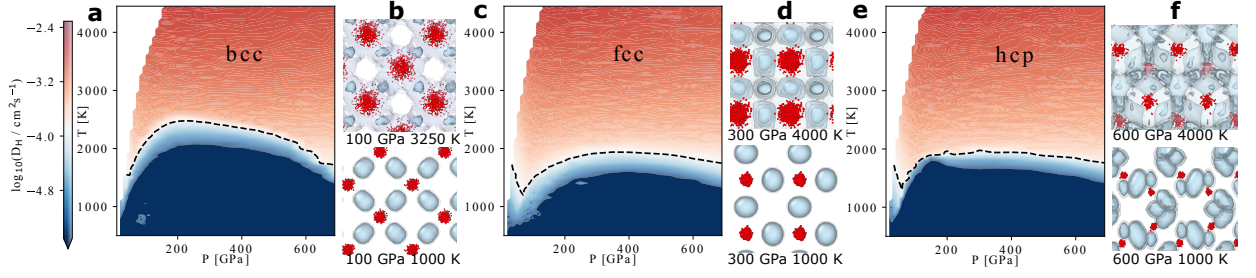


FIG. 1. The diffusion of hydrogen in water with bcc, fcc, and hcp lattice of oxygen.

Panel **a**, **c**, **e**: The diffusion coefficients of hydrogen (D_H) in bcc, fcc and hcp are shown logarithmically as a function of pressure (P) and temperature (T). The dashed lines illustrate the ice to superionic transition temperatures T_s defined by $D_H = 10^{-4} \text{ cm}^2/\text{s}$. Panel **b**, **d**, **f**: A low-temperature ice structure (lower) and a high-temperature superionic structure (upper) are separately shown for bcc, fcc, and hcp lattices. The gray contours of different shapes indicate the isosurfaces of the distributions of hydrogen atoms, and the instantaneous positions of oxygen atoms are indicated using red spheres.

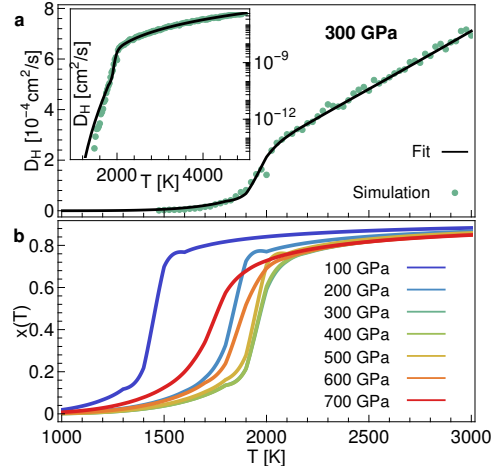


FIG. 2. modelling the hydrogen diffusion in water with the fcc oxygen lattice.

Panel **a**: The diffusion coefficients of hydrogen D_H at 300 GPa. The black curves are the fits to $x(T)D$ as described in the text. The inset shows D_H on the log scale.

Panel **b**: The equilibrium fraction of conducting hydrogen atoms $x(T)$ at different pressures.

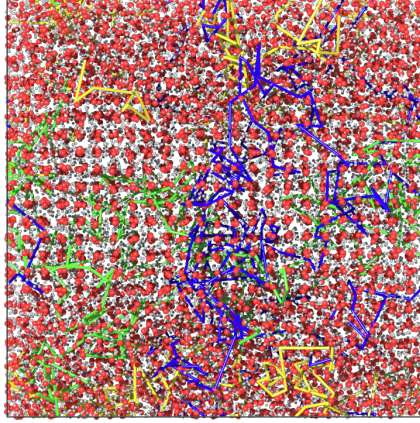


FIG. 3. Hydrogen atoms diffuse easily between the superionic and the liquid phases. Liquid-fcc superionic interface of a water system with 20,736 atoms at 100 GPa and 3250 K (on the melting line). The oxygen atoms are in red and the hydrogen atoms are in white. The yellow, green and blue lines show the trajectories of three hydrogen atoms during a 75 ps MD simulation run using the MLP.

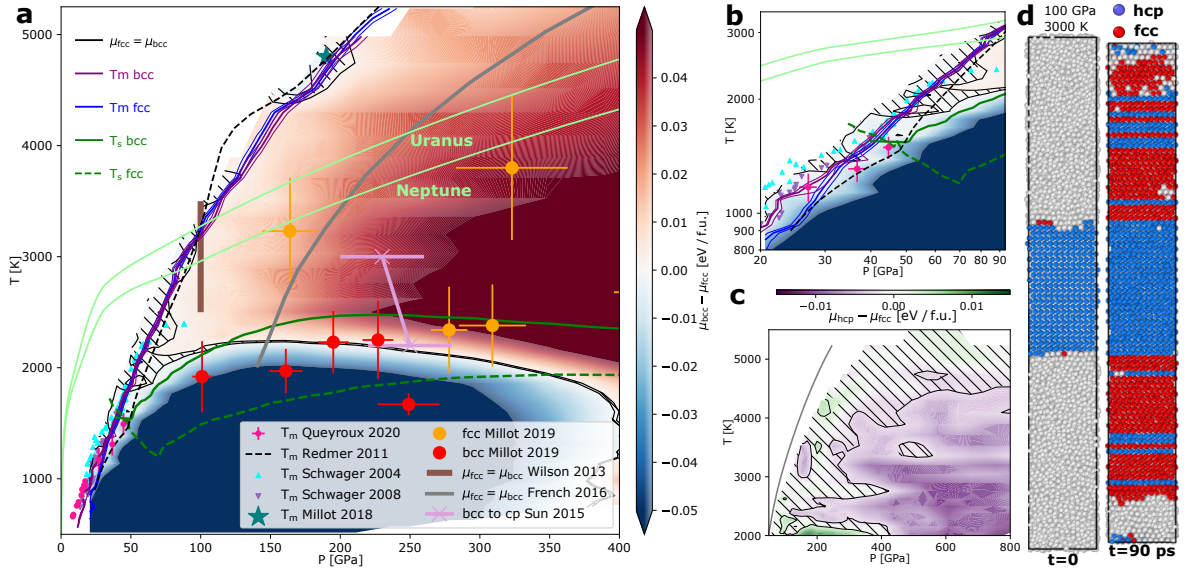


FIG. 4. **The phase stabilities for bcc, fcc, hcp and liquid water.**

Panel **a**: The chemical potential difference $\mu_{\text{bcc}} - \mu_{\text{fcc}}$ per formula unit (f.u.) between bcc and fcc at different pressure (P) and temperature (T) conditions. The blue and the purple lines are the melting lines T_m for fcc and bcc, respectively, with the statistical uncertainties indicated by the upper and lower thin lines. The green lines are the superionic-ice transition lines T_s for fcc (dashed lines) and bcc (solid lines). The black lines show the $\mu_{\text{bcc}} = \mu_{\text{fcc}}$ coexistence region, and the hatched area indicates the statistical uncertainty of this region estimated from the standard error of the chemical potentials. Experimental results, including the error estimations, are from Schwager 2004 [32], Schwager 2008 [33], Millot 2018 [4], Millot 2019 [2], and Queyroux 2020 [13], and theoretical predictions are from Redmer 2011 [5], Wilson 2013 [8], Sun 2015 [10], and French 2016 [9]. Planetary interior conditions for Neptune and Uranus (bright green lines) are from Ref. [34]. The zoom-in of the low-pressure region is shown in panel **b**.

Panel **b**: A zoom-in at $P < 100$ GPa of the panel **a** with P and T both on the log scale. Legends are shared.

Panel **c**: The chemical potential difference $\mu_{\text{hcp}} - \mu_{\text{fcc}}$ between the hcp and fcc superionic phases. The uncertainties in the coexistence line are indicated by the hatched area, which were estimated from the standard error of the chemical potentials.

Panel **d**: At $t = 0$, the system contains a pure hcp oxygen lattice slab with closed-packed planes parallel to the interface with liquid water. At $t = 90$ ps, the oxygen lattice grows into a mixed-stacking state. The gray atoms are not identified as either fcc or hcp.