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Ground-State Structures of Atomic Metallic Hydrogen

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Ab initio random structure searching using density functional theory was used to determine the ground-state structures of atomic metallic hydrogen from 500 GPa to 5 TPa. Including proton zero-point motion within the harmonic approximation, we estimate that molecular hydrogen dissociates into a monatomic body-centered tetragonal structure near 500 GPa ($r_s = 1.23$) that remains stable to 1 TPa ($r_s = 1.11$). At higher pressures, hydrogen stabilizes in an ...*ABCABC*... planar structure that is similar to the ground state of lithium, but with a different stacking sequence. With increasing pressure this structure compresses to the face-centered cubic lattice near 3.5 TPa ($r_s = 0.92$).

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Since the first prediction of an atomic metallic phase of hydrogen by Wigner and Huntington over 75 years ago [1], there have been many theoretical efforts aimed at determining the crystal structures of the ground-state phases as a function of density [2–11]. Such interest is understandable, considering the importance to astrophysics, predictions of high- T_c superconductivity [12], and the possibility of a low or even zero-temperature metallic liquid [13]. Despite the importance and corresponding efforts, there is still no conclusive understanding of this most basic and fundamental aspect. These efforts have been hindered by the fact that experiments have only been able to reach pressures of just over 300 GPa [14], which is lower than that of the atomic phase(s).

Previous studies have taken the approach of simply proposing candidate structures, leading to diverse and contradictory predictions. In some cases isotropic structures have been predicted as the ground state [2, 5–7], while in other cases anisotropic ones have [3, 4, 8–11]. This diversity is related to the primary disadvantage of such an approach, in that only a few select structures can be considered at any one time. It is apparent that, in analogy with the other alkali metals, even an elemental solid can have a rather complex structure [15]. Recently, however, more robust methods for determining crystal structures have been proposed, such as the *ab initio* random structure searching (AIRSS) method by Pickard and Needs [16]. In this approach, a number of random initial configurations are each relaxed to the ground state at constant pressure. After enough trials, a good sampling of the atomic configuration space is obtained and the ground-state structure is generated with a high probability. Such an approach has been used to accurately predict a number of structures, including more complicated ones than considered here, such as silane [16] and the highest pressure molecular phase of hydrogen [17].

In this Letter, we use AIRSS to resolve these contradictory predictions and determine the ground-state structures of atomic metallic hydrogen. Our calculations were performed using the Quantum ESPRESSO *ab initio* density functional theory (DFT) code [18]. A norm-conserving Troullier–Martins pseudopotential [19] with a cutoff radius of 0.5 a.u. was used to replace the actual $1/r$ Coulomb potential [see the Supplementary Information (SI) for a justification of this approximation], along with the Perdew–Burke–Ernzerhof exchange and correlation functional [20]. A basis set of plane-waves with a cutoff of 2721 eV was used for the random structure searching, and then increased to 2993 eV for recalculating detailed enthalpy vs. pressure curves. For Brillouin-zone sampling, 14^3 k -points were used for the structure searching and then significantly increased for recalculating the enthalpy curves. While both the plane-wave cutoff and number of k -points may seem exceedingly high, such values were found necessary to ensure convergence of each structure to better than 1.5 meV/proton in energy and the pressure to 0.1 GPa/proton. Phonons were calculated using density functional perturbation theory as implemented within Quantum ESPRESSO, and were converged to a similar level of accuracy as the DFT calculations. Typical relaxations included at least 100 random structures at each pressure considered. In most cases this appeared to be enough to generate the low-enthalpy structure(s) multiple times. At pressures where the results were considered inconclusive (e.g., a low-enthalpy structure generated only once or twice), additional relaxations were performed. Below we refer to each structure by its Hermann–Mauguin space-group symbol (international notation), but also provide more common lattice names, where applicable.

AIRSS was carried out for unit cells containing 4 and 6 atoms at pressures from 500 GPa to 4.5 TPa in intervals of 500 GPa. Such relaxations implicitly include searches over unit cells of their factors – i.e., those with 1, 2, or 3 atoms. While structures with unit cells of 5, 7, 8 ... atoms are certainly possible, based on comparisons with other elemental structures they are unlikely to occur. For example, lithium, the closest element to monatomic hydrogen, has a ground-state structure consisting of a 3 atom unit cell [15]. Detailed enthalpy vs. pressure curves were calculated

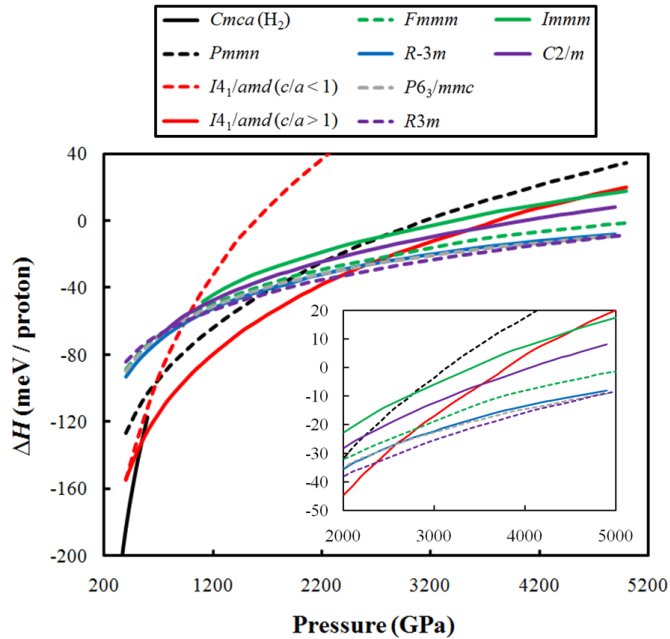


FIG. 1: (color online). Ground-state enthalpies of the crystal structures of atomic metallic hydrogen relative to fcc, not including proton zero-point energy. The inset shows an expanded view of the ultrahigh pressure region.

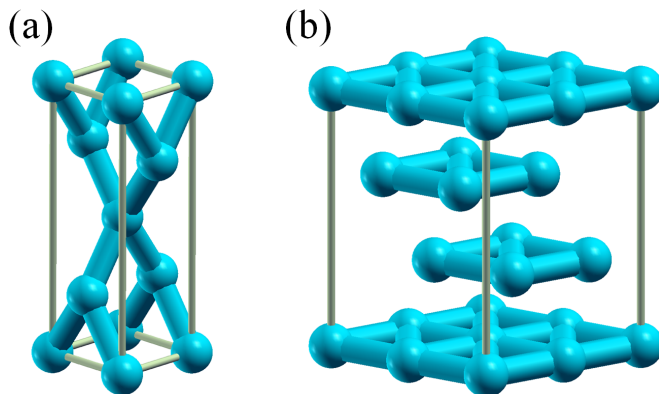


FIG. 2: (color online). Structures of the ground-state phases of atomic metallic hydrogen. (a) Unit cell of $I4_1/amd$ ($c/a > 1$). (b) $2 \times 2 \times 1$ supercell of $R-3m$. Fictitious bonds have been drawn for clarity.

for each structure found, giving the results in Fig. 1. Note that the enthalpy H is plotted relative to the face-centered cubic (fcc) lattice (space-group $Fm-3m$). Also note that the body-centered cubic (bcc) lattice (space-group $Im-3m$), which was assumed to be the structure of dense hydrogen originally proposed by Wigner and Huntington [1], is not shown in Fig. 1 for clarity but it is less stable than fcc by approximately 11 meV/proton over the entire pressure range considered.

Given that our calculations span a large range in pressure, and also much higher than previously considered, Fig. 1 contains a significant number of structures. Below 500 GPa ($r_s = 1.23$), the most stable structure is the molecular phase $Cmca$, which has previously been predicted by both theoretical calculations [21] and an earlier AIRSS study [17]. Near 500 GPa, $Cmca$ dissociates into a monatomic body-centered tetragonal structure of space-group $I4_1/amd$ with a c/a ratio greater than unity (e.g., $c/a = 2.59$ at 500 GPa) as is shown in Fig. 2(a). This transition is also consistent with previous calculations that predicted the stability of $I4_1/amd$ above 490 GPa [17]. Our searches also generated another $I4_1/amd$ structure with a c/a ratio less than unity (e.g., $c/a = 0.88$ at 500 GPa). However, while both structures are close in enthalpy near 500 GPa, the latter quickly becomes much less stable with an increase in pressure.

$I4_1/amd$ is found to remain stable until approximately 2.5 TPa ($r_s = 0.97$), resisting compression along the c axis

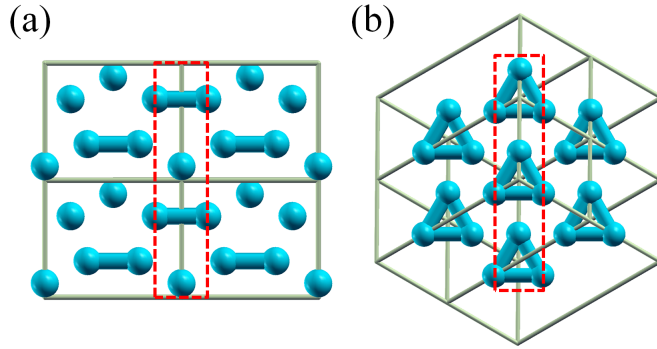


FIG. 3: (color online). Structures of (a) $Pmmn$ and (b) $R3m$. Note that the unit cells shown in (b) are actually $2 \times 1 \times 1$ supercells. The dotted lines border linear chains, which stick out of the plane relative to their neighbors.

(e.g., $c/a = 2.99$ at 2.5 TPa). This result is similar to the conclusion of a previous study that considered a family of tetragonal structures [7]. The only other structure close in enthalpy generated during our searches was $Pmmn$, which is still 15 meV/proton less stable over the entire pressure range considered. Although relatively unstable, $Pmmn$ does form an intriguing structure. Below 1.9 TPa ($r_s = 1.01$) it is monatomic. With increasing pressure, a pairing between atoms then occurs forming a mixture of molecular and atomic hydrogen that arranges in linear chains; see Fig. 3(a).

Near 2.5 TPa, four additional structures with similar enthalpies become important. The least stable is a face-centered orthorhombic structure with space-group $Fmmm$, which is planar with $\dots ABAB\dots$ stacking and is similar to the fcc lattice except elongated along both the b and c axes (e.g., $b/a = 1.72$ and $c/a = 2.02$ at 3 TPa). Slightly more stable by 5 – 6 meV/proton are two structures nearly equal in enthalpy. One is $P6_3/mmc$, a planar hexagonal structure with $\dots ABAB\dots$ stacking, and is similar to the hexagonal close-packed (hcp) lattice (also of space-group $P6_3/mmc$) except elongated along the c axis (e.g., $c/a = 2.01$ at 3 TPa). Note that hcp is not shown in Fig. 1 for clarity, but it is more stable than fcc by about 4.5 meV/proton over the entire pressure range considered, although becomes unstable when proton zero-point energy (ZPE) is included (see the SI). The other structure is $R-3m$, which is hexagonal and planar with $\dots ABCABC\dots$ stacking (e.g., $c/a = 3.03$ at 3 TPa) as is shown in Fig. 2(b). (Note that fcc forms a close-packed version of this stacking sequence.) The most stable structure of this group (e.g., by a further 2 – 3 meV/proton at 3.5 TPa) is $R3m$, which is formed from a rhombohedral unit cell consisting of triatomic structures; see Fig. 3(b). Interestingly, this structure can be considered analogous to a metallic state based on a compressed H_3^+ ion (e.g., at 3 TPa the interatomic distances are 1.52 and 1.53 a.u. compared to 1.65 a.u. for the isolated equilateral ion [22]). At zero pressure, such a structure would actually form the unstable H_3 molecule. However, at high pressure the close proximity to neighboring molecules leads to a partial charge delocalization, resulting in a metallic state consisting of stable H_3^+ ions immersed in a background of negative charge. A similar scenario appears in a different context in Ref. [23].

It is interesting to note that three out of the four structures in this pressure range are anisotropic and planar, consistent with previous work [4, 9]. Perhaps more interesting is that $R-3m$ is also the space-group of the ground state of lithium [15], the structure of which, termed $9R$, differs primarily by its packing efficiency and stacking sequence ($\dots ABCBCACAB\dots$). In fact, the $9R$ structure has been previously predicted as the ground-state of atomic metallic hydrogen [8]. Relative to $R-3m$, however, $9R$ is unstable. This can be inferred by comparing their relative stabilities to bcc. $9R$ is predicted to transform to bcc at 1090 ± 100 GPa [8], while $R-3m$ is stable even above 5 TPa (as it is more stable than fcc; see Fig. 1).

Two additional structures with significantly higher enthalpies were also generated during our searches in the pressure range 2 – 3 TPa, $Immm$ and $C2/m$. Both structures are qualitatively very similar, and interestingly have recently been suggested as likely candidates for the ultrahigh pressure ground-state structure of hydrogen [23]. Below 3 TPa, they are very similar to $Pmmn$ and are comprised of chains of atomic and molecular hydrogen. However, their behavior with increasing pressure is different. $Pmmn$ compresses both along and between linear chains, forming triatomic molecules connected to their counterparts in neighboring planes. $Immm$ and $C2/m$, on the other hand, resist compression along the c axis and form molecular chains.

By approximately 4 TPa our searches began generating the “simple” lattices, such as fcc. This suggests that the entire pressure range from 500 GPa to 5 TPa is well mapped out, with the result that the molecular phase $Cmca$ dissociates into the body-centered tetragonal structure $I4_1/amd$ near 500 GPa ($r_s = 1.23$), transforming to a planar

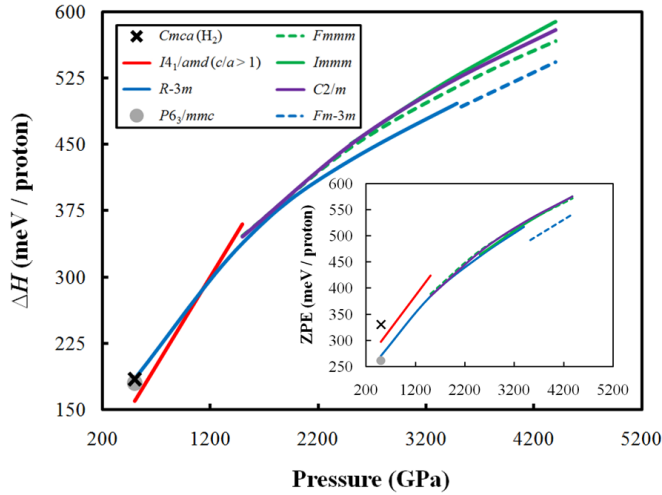


FIG. 4: (color online). Ground-state enthalpies of the crystal structures of atomic metallic hydrogen including proton ZPE (shown in the inset). Enthalpies shown are relative to fcc without ZPE. Note that results are not shown in cases where the structures are predicted to be unstable (see the text).

($R-3m$, $P6_3/mmc$, or $Fmmm$) or triatomic ($R3m$) structure near 2.5 TPa ($r_s = 0.97$), which then either compresses or transforms to a close-packed lattice (fcc or hcp) above 5 TPa ($r_s < 0.86$).

The scenario outlined above is based on lattices of infinitely massive protons. It therefore actually describes the ground-state structures of the isotopes of hydrogen with heavier nuclei, including tritium and possibly deuterium. The light proton mass, however, causes hydrogen to have a large ZPE that must be estimated in order to determine the most stable ground-state structures. Accurately estimating the full magnitude of the ZPE is particularly challenging because proton zero-point motion in atomic metallic hydrogen exhibits anharmonic effects that are difficult to describe using DFT, but which could stabilize some of the structures [2]. A full analysis of this is beyond the scope of this work, but it is nonetheless possible to make reliable predictions based on the harmonic ZPE and symmetry arguments (see below).

For each structure, the phonon density of states $g(\omega)$ was calculated using a 2^3 grid of q -points in the Brillouin zone and the ZPE was estimated using the harmonic approximation: $E_{\text{ZPE}} = \int d\omega g(\omega) \hbar\omega/2$. We estimate that a q -point grid of this density is sufficient to converge ZPE differences between structures to within a few percent (see the SI). Calculating the ZPEs from 500 GPa to 4.5 TPa in intervals of 500 GPa and adding them to the enthalpies in Fig. 1 gives the modified diagram shown in Fig. 4. Results are not shown in cases where the structures exhibit imaginary phonon frequencies, which are unphysical and indicate instability in a structure. Note that although they are not shown, $I4_1/amd$ ($c/a < 1$), $Pm\bar{m}n$, and $R3m$ are all borderline stable (the former two only near 500 and the latter over the entire pressure range) but even their inclusion does not change the predictions based on Fig. 4. The exclusion of the unstable structures significantly simplifies the picture originally presented in Fig. 1. Furthermore, the fact that we found at least one stable structure at all pressures considered provides an indication that our searches were exhaustive.

Actual ZPEs for each structure are shown in the inset of Fig. 4. It is found that they are quite high, ranging from approximately 270 meV/proton near 500 GPa to over 550 meV/proton at higher pressures. This can be attributed to high-frequency phonon modes that can exceed, for example, 6000 cm^{-1} at high pressure (see the SI). The inclusion of ZPE is found to affect the relative stabilities of the structures, as expected. The near degeneracy of the ultrahigh-pressure structures is lifted, with $R-3m$ becoming the clear ground state. Additionally, the transitions of $I4_1/amd$ to $R-3m$ and $R-3m$ to fcc are found to be shifted to much lower pressures of approximately 1 TPa ($r_s = 1.11$) and 3.5 TPa ($r_s = 0.92$), respectively.

While the ZPEs are quite high, they are roughly half of those reported in Ref. [2] because of our neglect of anharmonic effects. However, it is known that these favor symmetric structures [2], which turn out to be the ones already predicted as the ground states in Fig. 4. For example, between 1 and 3.5 TPa $R-3m$ is the most symmetric structure out of those predicted (as is fcc at even higher pressures). At lower pressures, $I4_1/amd$ is also highly symmetric (only slightly less so than $R-3m$ and $P6_3/mmc$, the latter which quickly becomes unstable with increasing pressure), and so this prediction is probably correct as well. Therefore, Fig. 4 likely gives an accurate prediction of the ground-state structures of atomic metallic hydrogen. (However, precise transition pressures could still be affected

by anharmonic effects.)

In summary, we performed AIRSS to resolve previous contradictory predictions and determine the ground-state structures of atomic metallic hydrogen at pressures from 500 GPa to 5 TPa. While consistent with some previous predictions [4, 7, 9, 17, 21], our calculations revealed a number of new structures. We estimate that molecular hydrogen dissociates into a monatomic body-centered tetragonal structure near 500 GPa ($r_s = 1.23$) that remains stable to 1 TPa ($r_s = 1.11$). At higher pressures, the most stable structure becomes a planar hexagonal one with $\dots ABCABC\dots$ stacking. With increasing pressure this structure compresses with a continuous change to fcc near 3.5 TPa ($r_s = 0.92$), analogous to the situation proposed in Ref. [11]. An estimation of the impact of proton zero-point motion was given in the harmonic approximation, and based on Ref. [2] and symmetry arguments we suggested that anharmonic effects are unlikely to affect our conclusions. However, a more accurate estimation will be necessary to confirm these predictions, which could be obtained from coupled electron-ion Monte Carlo calculations [24], for example. The fact that we found a significant number of possible ground-state structures with similar enthalpies suggests that many of them will become important at finite temperature when their relative free energies depend not only on enthalpy but also on entropy.

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