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Theoretical study of atomic phases of metallic hydrogen

T. W. Barbee III* and Marvin L. Cohen
Department of Physics, University of California, Berkeley, Berkeley, California 94720
and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

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Several structures are considered as candidates for the predicted high-pressure (above 400 GPa) atomic phase of metallic hydrogen. Results for the cubic phases are found to agree well with previous calculations. Two particularly interesting structures are the primitive hexagonal (ph) and rhombohedral (9*R*), which are found to be particularly stable and may be good candidates for the structure of atomic metallic hydrogen.

In this paper we present a study of possible high-pressure monatomic structures of solid metallic hydrogen. Predictions of the transformation of solid molecular hydrogen into a metal at very high pressures date from the 1930's.[1] Recent theoretical studies[2–6] estimate the transition pressure to be in the range of a few hundred GPa. In addition, theoretical studies suggest the possibility of high-temperature superconductivity in the metallic phase and, in some cases, provide estimates of the electron-phonon coupling and superconducting transition temperature. Detailed experimental data[7–9] are available for the 0–50-GPa pressure range. Despite the fact that the highest pressure achieved in solid hydrogen,[10] above 200 GPa, is within the range of some of the predictions for metallization, it is not yet generally agreed that metallic hydrogen has been observed. Some evidence for a structural phase transition in solid hydrogen was deduced[10] from a sudden drop in the vibron frequency observed at 150 GPa. Optical studies above this pressure have reported increases in absorption and reflectivity which are cited as evidence[10,11] for metallization; however, at this time this interpretation is controversial. For example, another study[12] found no such increase in reflectivity, and it has been proposed that the reflectivity seen resulted from a reaction of the hydrogen with ruby in the pressure cell[13] rather than from the formation of metallic hydrogen. Recent theoretical calculations[14,15] indicate that, for some candidate structures, a transition at 150 GPa due to metallization via band overlap within the molecular phase is possible.

The usual picture of the atomic metallic phase of hydrogen is that of a densely packed univalent solid, much

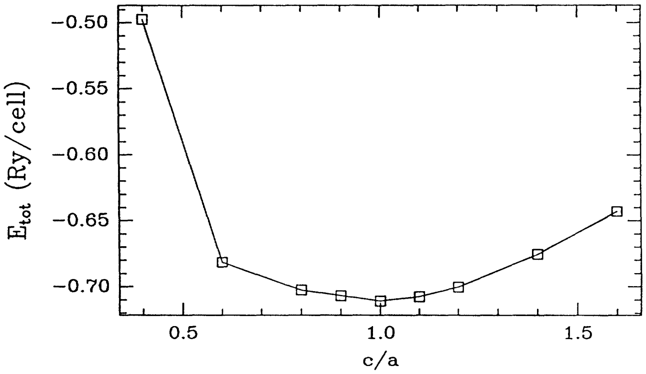


FIG. 1. The total energy E_{tot} is shown as a function of the ratio of the axes c/a for hydrogen in the simple hexagonal structure at the density corresponding to $r_s = 1.0$. The most stable structure has a nearly ideal $c/a = 0.995$.

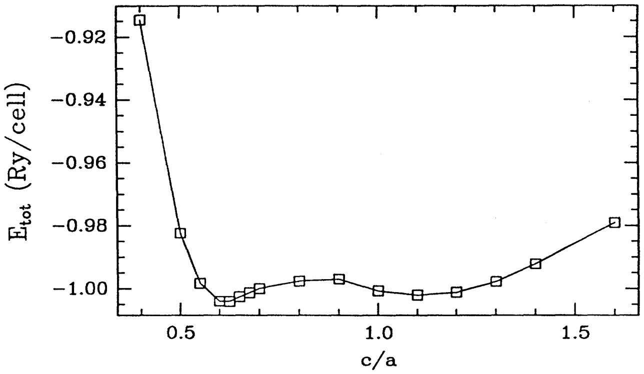


FIG. 2. The total energy E_{tot} is shown as a function of the ratio of the axes c/a for hydrogen in the simple hexagonal structure at the density corresponding to $r_s = 1.3$. The most stable structure is a filamentary structure with $c/a = 0.618$.

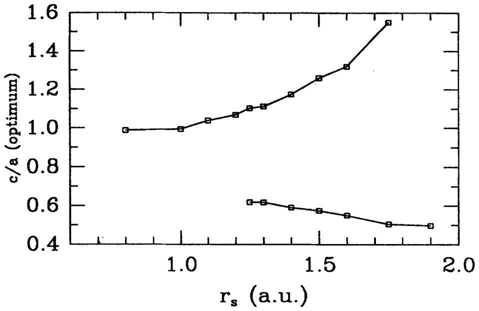


FIG. 3. The optimum values for c/a are shown as a function of r_s for hydrogen in the simple hexagonal structure. The upper curve represents layered structures at low densities (larger r_s) which transform smoothly into a structure with an ideal c/a at high density. The lower curve represents the filamentary structure which is only stable for $r_s \geq 1.25$.

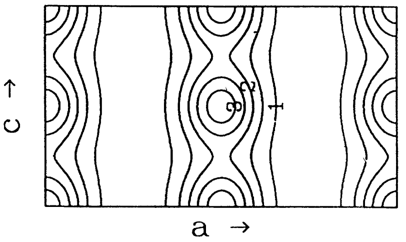


FIG. 4. Charge density $\rho(\mathbf{r})$ for hydrogen in the simple hexagonal structure discussed in the text in a plane containing the hexagonal axis c. The electrons are concentrated in filamentary structures along the hexagonal axis, resulting in anisotropic and covalent bonding. The charge density is given in units of electrons per primitive cell and the spacing between adjacent contours is 0.5 electrons per primitive cell.

like the alkali metals. Wigner and Huntington[1] proposed that molecular hydrogen could transform under pressure into a low-coordination structure, and our calculations lend support to this proposal.[16] The results presented here extend our earlier study[16] of possible high-pressure structures. Previously we showed that a filamentary primitive hexagonal (ph) phase was most stable among the structures tested in the pressure range of 380±50 to 860±100 GPa. At lower pressures, a molecular hexagonal-close-packed (*m*-hcp) phase was found to be the most stable, while above 860 GPa the body-centered-cubic (bcc) phase was preferred. Here we report on more calculations for the atomic structures considered before[16] and results for the 9*R* rhombohedral structure not considered previously. We believe that the 9*R* structure is a good candidate for pressures in the range 420–1090 GPa.

The calculations of the properties of hydrogen in atomic structures are performed using the *ab initio* total-energy method with a plane-wave basis[17] for the wave functions and the local-density approximation (LDA) for the exchange and correlation energy of the interacting electrons. Prior studies using this method together with pseudopotentials have been successful in predicting the structural and electronic properties[18] of insulators, semiconductors, and metals under pressure.

Because of the lack of core electrons, the true potential $1/r$ for hydrogen is used instead of a pseudopotential together with the Ceperley-Alder[19] exchange and correlation energy functional for electron-electron interactions. The results reported here were obtained with a basis set of plane waves[17] with kinetic energy up to 36 Ry. The total energy for each of the selected crystal structures were calculated for several volumes, and the resulting data points were fit with the Murnaghan[20] and Birch[21] equations of state. Increasing the energy cutoff to 64 Ry causes only slight changes in the calculated bulk moduli and equilibrium volumes, and the energy differences between the structures change by less than 0.2 mRy/atom for both the cubic and the more open structures studied. The total energies are also similarly converged with respect to the number of **k** points used for the Brillouin-zone integrals.

Since the contribution to the total energy of solid hydrogen from the zero-point-motion (ZPM) energy cannot be neglected, we add an estimation of the harmonic ZPM energy at each volume; that is, we use the quasiharmonic

TABLE I. The calculated bulk modulus B_0, equilibrium Wigner-Seitz radius r_s^0, and equilibrium value of the total energy E_0 are shown for several nonmolecular structures. The results of a previous calculation (Ref. 5) are also shown. Good agreement is found with these previous results, except that we find a reversal in the ordering of the fcc and bcc phases at equilibrium. At the equilibrium density, the molecular phase lies much lower in energy than any of the structures listed here.

Structure	B_0 (GPa)	r_s^0 (atomic units)	E_0 (Ry/atom)
	This calculation		
Simple cubic	106	1.712	−1.0703
Body-centered cubic	103	1.675	−1.0605
Face-centered cubic	118	1.680	−1.0610
Diamond	92	1.777	−1.0907
	Ref. 5		
Simple cubic	112	1.707	−1.0878
Body-centered cubic	107	1.677	−1.0775
Face-centered cubic	125	1.683	−1.0763

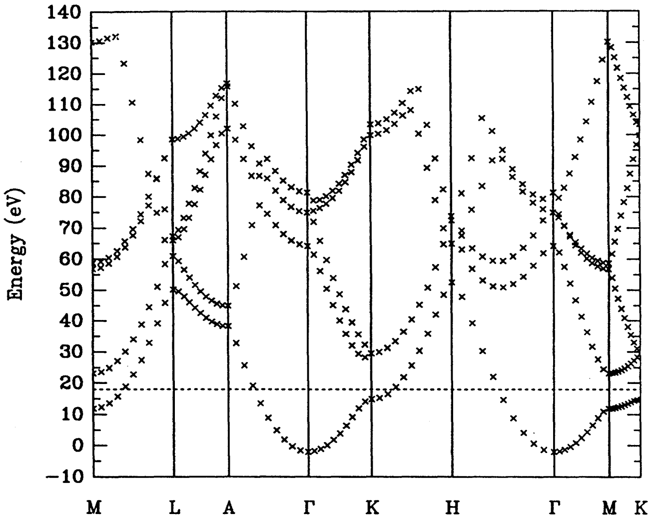
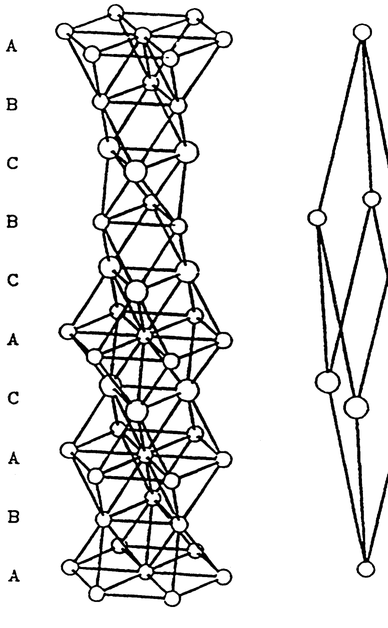


FIG. 5. Band structure of metallic hydrogen in the simple hexagonal structure at a density corresponding to $r_s=1.5$. The dotted line represents the Fermi level. Γ is at the center of the Brillouin zone (BZ) with *M* at the center of the rectangular face and *K* on the edge. *A*, *L*, and *H* are on the hexagonal face of the BZ directly above Γ, *M*, and *K*, respectively.

approximation. The energies of several phonons in each structure were calculated[22] from first principles using the frozen-phonon method.[18] For the cubic structures, a simple isotropic dispersion relation was fitted to the calculated frequencies at each volume. For the hexagonal and rhombohedral structures, an extensive study of the phonon frequencies was done at one volume ($r_s=1.3$). For other volumes, the results from $r_s=1.3$ were scaled using two calculated frequencies at each volume. The ZPM energy per atom is then estimated at $E_{\mathrm{ZPM}}=\frac{3}{2}\hbar\omega_{\mathrm{av}}$, where ω_{av} is the average phonon frequency.



(a) (b)

FIG. 6. The 9*R* structure described in the text. The structure can be viewed as either rhombohedral with a basis of three atoms or as hexagonal layers with the stacking sequence $\cdots[ABACACBCB]\cdots$. The hexagonal layers are shown in (a). For the layers in the *A* position, seven atoms are shown. The *B* and *C* layers have only three atoms, and the *C* layers are distinguished by larger atoms. The rhombohedral unit cell is shown in (b). The basis consists of three atoms at (0,0,0), $(\frac{2}{9},\frac{2}{9},\frac{2}{9})$, and $(\frac{4}{9},\frac{4}{9},\frac{4}{9})$.

The structural phase transitions are found by comparing the Gibbs free energy *G* calculated for the different structures. Since our calculations are performed at zero temperature, we can alternatively compare the enthalpies

TABLE II. The optimal c/a ratio(s) are shown for the 9*R* and sh structures for each r_s. At lower densities (larger r_s), there are two possible values for c/a, corresponding to a filamentary structure with $c/a<1$ (1) and a layered structure with $c/a>1$. At high densities, there is only one possible value of c/a and it lies near 1.

	9*R* structure $(c/a)/(c/a)_{\mathrm{ideal}}$		sh structure c/a	
r_s (a.u.)	(1)	(2)	(1)	(2)
0.8				0.988
1.0	0.95			0.995
1.1	0.71	1.33		1.039
1.2	0.70	1.38		1.069
1.25			0.619	1.103
1.3	0.71	1.41	0.618	1.112
1.4	0.70	1.43	0.591	1.174
1.5	0.68	1.57	0.575	1.260
1.6	0.65	1.60	0.550	1.320
1.7		1.65		
1.75			0.505	1.550
1.8		1.76		
1.9			0.497	

$H(P)=E+PV$ of the structures, since $G=H$ at $T=0$.

The first candidates considered for the structure of hydrogen in a monatomic state are the simple-cubic (sc), body-centered-cubic (bcc), and face-centered-cubic (fcc) structures. Although it is not strictly a monatomic structure, the diamond structure is also considered. For each structure, the total energy was computed at a number of different specific volumes and the results were fit to the Murnaghan[20] and Birch[21] equations of state. The equilibrium properties were calculated by fitting the equations of state to the data for a number of volumes near the equilibrium volume. The results for the bulk modulus B_0, the equilibrium Wigner-Seitz radius r_s^0, and the total energy E_0 are shown in Table I. Our calculated bulk moduli are a few percent lower than those found in an earlier calculation[5] using a different method. The equilibrium Wigner-Seitz radius (and therefore the lattice constant) agrees to within half a percent. For the total energies, both calculations show that the sc structure is lowest of the three cubic structures. We find that the fcc structure is more stable than bcc while the order is reversed in Ref. 5, but the energy differences are small and only slightly larger than the numerical error inherent in the calculations.

It should be noted that, at the densities considered here, the molecular phase of hydrogen has much lower total energy than any of the atomic phases considered, so atomic metallic hydrogen is not thermodynamically stable at zero pressure. The question of metastability remains open, and we point out that some metastable structures can be extremely long lived. Hence, it is possible that metallic hydrogen could exist at zero pressure. One calculation[23] predicts that atomic metallic hydrogen would be stable above pressures of 10 GPa, but nucleation of H_2 molecules at surfaces[24] could provide a pathway for decay back to the molecular state.

Several other candidate structures were considered for the atomic phase of metallic hydrogen. The simple hexagonal (sh) and rhombohedral 9*R* structures were chosen for detailed study. For a uniaxial structure such as sh, the ratio c/a of the lattice constant along the symmetry axis to that perpendicular to the symmetry axis is a free parameter. At each volume, the total energy was minimized as a function of c/a. For most other materials, the values of c/a found differ only slightly from the ideal c/a, and this is the case for hydrogen in the sh structure at extremely high density.

In Fig. 1, the total energy for hydrogen in the sh structure is plotted as a function of c/a at $r_s=1.0$. At this density, the pressure from the calculated equation of state is near 2000 GPa. At this extremely high pressure, it is energetically favorable for simple hexagonal hydrogen to assume a nearly isotropic structure with a coordination number of eight. By fitting a parabolic curve to the minimum in the E_{tot} versus c/a curve, we find the optimum $c/a=0.995$ where the "ideal" $c/a=1$. At lower densities and pressures, however, a surprising result is found. Instead of one minimum in the E versus c/a graph, two minima are found. Figure 2 shows the total energy for hydrogen in the sh structure as a function of c/a at $r_s=1.3$. In contrast to the higher density results, two minima are found at $c/a=0.618$ and 1.112. These correspond to a filamentary structure with a coordination number of two and a layered structure with coordination number six, respectively. Similar behavior of E versus c/a was found for all $r_s \geq 1.25$, and a summary of the results appears in Fig. 3. The structure with near ideal c/a found at high density undergoes a continuous transition to the layered structure with increasing r_s. At $r_s=1.25$, the filamentary $(c/a<1)$ structure becomes stable and remains the more stable structure for all $r_s \geq 1.25$ studied. Figure 4 shows the charge density at $r_s=1.3$ and $c/a=0.6$, revealing the bonding along the hexagonal axis and the filamentary nature of the structure. For $r_s \geq 1.6$, we find that the filamentary structure is unstable, and adjacent atoms along the hexagonal axis will dimerize, leading to a "pseudomolecular" structure.

Simple arguments based on electron counting indicate that hydrogen in the sh structure should be metallic. Figure 5 shows the band structure $E(\mathbf{k})$ for hydrogen in the filamentary sh structure at $r_s=1.5$. It is clear that hydrogen is indeed metallic in the sh structure. The energy bands in the $\Gamma-A$ direction show strong dispersion, reflecting the bonding between the atoms along the hexagonal axis, while along the Γ-M and Γ-K directions the energy bands show less dispersion, reflecting the weaker bonding between the filamentary structures.

Since hydrogen has one valence electron and can be considered to be grouped with the alkali metals, the structures of the alkali metals may be good candidates for the structure of atomic hydrogen. One such structure is the 9*R* rhombohedral structure, which was recently found to be the low-temperature structure of lithium. This structure is shown in Fig. 6. In this structure, the c/a ratio must also be varied to optimize the total energy for each density. The "ideal" c/a is $\frac{9}{2}$ times the ideal c/a for the hcp structure, or $(c/a)_{\text{ideal}}=6^{1/2}$. The behavior of the total energy as a function of c/a is similar to that found for the sh structure. At $r_s=1.0$, only one significant minimum in E_{tot} versus c/a is found with a c/a ratio of 0.95 of the ideal value. This structure is nearly a close-packed structure. For $r_s=1.3$, two minima are again found as shown in Fig. 7. In this case, how-

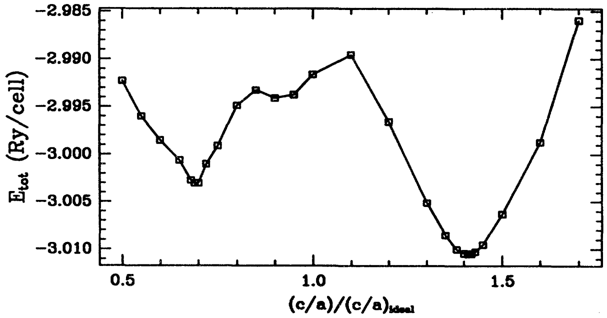


FIG. 7. The total energy E_{tot} is shown as a function of the ratio of the axes c/a for hydrogen in the 9*R* structure at the density corresponding to $r_s=1.3$. The c/a ratio is given in units of the ideal ratio $(c/a)_{\text{ideal}}=6^{1/2}$. There are two minima in the curve, and the most stable structure has $c/a=1.41$, indicating a layered structure.

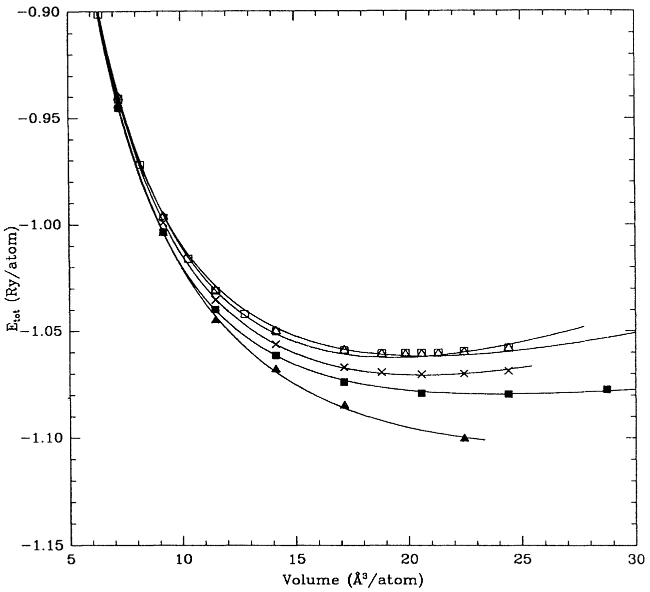


FIG. 8. The static total energies (points) and equations of state (lines) are shown for hydrogen in the atomic structures studied. Results for the bcc (open squares), fcc (open triangles), simple cubic (×), 9*R* (solid squares), and simple hexagonal (solid triangles) structures are shown. The lines are the equations of state for the various structures obtained by fitting to the Murnaghan (Ref. 20) equation of state. The simple hexagonal structure is the most stable of those studied.

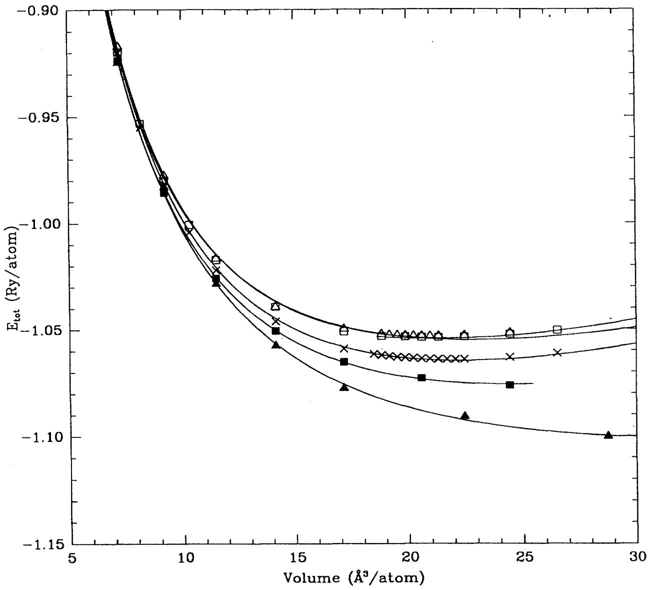


FIG. 9. The total energies including zero-point motion (points) and equations of state (lines) are shown for hydrogen in the atomic structures studied. Results for the bcc (open squares), fcc (open triangles), simple cubic (×), 9*R* (solid squares), and simple hexagonal (solid triangles) structures are shown. The lines are the equations of state for the various structures obtained by fitting to the Murnaghan (Ref. 20) equation of state. The simple hexagonal structure is the most stable of those studied at lower pressures, but will transform into the 9*R* structure at higher pressures (see text).

ever, the layered structure is more stable than the filamentary structure. In the 9*R* structure, the filaments are bent into twisted chains since atoms in adjacent layers do not lie directly above/below each other, which could result in lower stability for the filamentary structure. In Table II, a summary of the optimum c/a found for both of the uniaxial structures considered (sh and 9*R*) is presented.

For all the atomic structures considered, the data for total energy as a function of volume are fit to the Murnaghan[20] equation of state. The results are shown in Fig. 8. These calculations do not include the contribution of the zero-point energy. The difference between the fcc and bcc structures is negligible near the equilibrium volume. At low densities, the sh structure is the most stable, while at higher densities, the bcc structure is more stable. In the intermediate region, the 9*R* structure may be the stable structure of metallic hydrogen. The transition pressure from the sh to the 9*R* structure is found to be 440±50 GPa when the contributions of zero-point motion are neglected.

The zero-point energy can be important for comparisons of the relative stability of candidate structures of atomic hydrogen. The ZPM energy is estimated by using the calculated energies of several phonons in each structure from a frozen-phonon method.[22] A model spectrum is then used to estimate the energy from zero-point motion. Figure 9 shows the equation of state including the zero-point energy as a function of volume for the sc, bcc, fcc, sh, and 9*R* structures. The behavior of the estimated zero-point energy is very similar for the cubic structures. For the sh structure, the zero-point energy was calculated for the layered structure for $r_s < 1.25$, while for larger r_s, the value for the filamentary structure was used. At the largest r_s considered for the filamentary hexagonal structure, the zero-point energy is found to increase due to the dimerization discussed above and the hardening of the "intramolecular" vibrational mode. With the inclusion of the zero-point energy, the primitive hexagonal structure remains the most stable of the atomic structures considered at low pressures. Between 420±50 and 1090±100 GPa, the 9*R* structure is more stable than sh, and the bcc structure is predicted to be stable above 1090 GPa.

In summary, a general feature of our calculations is that for $P \lesssim 1090$ GPa open structures of atomic phases of metallic hydrogen with low coordination (sh, 9*R*, sc) are more stable than the higher coordination, densely packed structures (bcc, fcc, and hcp), indicating the preference for molecular hydrogen to transform into low-coordination structures under pressure. The charge density in these structures reveals a large covalent contribution to the bonding, and calculations of the electron-phonon interaction indicate that hydrogen in these structures may be a high-temperature superconductor.

Two transitions are expected for hydrogen under pressure, a structural phase transition to a more densely packed structure and a metal-insulator transition. Up to now only an unspecified phase transition has been observed[10] at 150 GPa. Our calculations suggest that the structural phase transition will be from a molecular phase to a layered or filamentary phase with low coordination at 380±50 GPa. The sh and 9*R* structures studied here are good candidates for this high-pressure phase. At still higher pressures, we predict a transition to a densely packed structure (bcc) at 1090±100 GPa.

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[*] Present address: L-412, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550.

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