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Structures of hydrogen at megabar pressures

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The atomic and molecular phases of hydrogen at megabar pressures are studied with use of the band theoretical calculation based on the local density approximation. The free energies, in the atomic phase of the hydrogen, of structures in a tetragonal diamond family are calculated and compared with those of structures studied earlier. The Cs-IV structure is of lowest free energy at pressures from 360 GPa to 1.7 TPa. And the stable region for the β-Sn structure is narrow, which lies in the region from 260 GPa to 360 GPa. At pressures lower than 260 GPa, the molecular phase becomes stable. Possibilities of the metallization in the molecular phase are briefly discussed. [S0163-1829(97)05029-7]

Recently, from the Raman and infrared spectra,[1,2] important information on the phase diagram in the molecular phase has been obtained and the phase boundaries have become clearer in the molecular phase.[3] Very recently the crystal lattice has been determined at pressures up to 119 GPa,[4] although orientations of the molecule in the lattice are still vague.

Pressure induced molecular dissociation and the insulator-metal (IM) transition at megabar pressures have long been the central interest and the possibility of metallization in the molecular phase due to the band overlapping has also attracted much experimental and theoretical interests.[5–7] Recent experiments,[1,2] however, show no sign of the metallic transition up to about 220 GPa at low temperatures. The predicted pressures for the molecular dissociation lie in the region from 300 GPa to 600 GPa.[8,9]

The crystal structures in both molecular and atomic phases are fundamental to the prediction of the pressures for the possible band overlapping in the molecular phase and for the molecular dissociation at low temperatures. Many recent theoretical studies have been done mainly by the band theoretical approach[8,10,11] based on the local density approximation (LDA) and the quantum Monte Carlo (QMC) calculation.[12–14] However, vanishingly small energy differences among structures in both molecular and atomic phases together with the possible large effects of the zero point motion of the atoms make the prediction of the transition pressures difficult.

At pressures of celestial interests, the dominant contribution to the structural energy is from the Madelung energy, which prefers the densely packed structures, for which the bcc structure is lowest. As the pressure decreases the electronic energy begins to play a significant role which leads the structure to less densely packed ones, and the possibilities of the anisotropic structures was pointed out based on the structural expansion.[15,16] However, stable regions of the predicted structures in the atomic phase are still diversified.

According to our LDA calculation[17] in the atomic phase, the bcc structure becomes stable beyond 4 TPa and the hexagonal-close-packed (hcp) structure in the region 2–4 TPa. These pressure regions are high compared with other results,[11,13] which is due to the presence of the region of ''planar'' structures.[17] In their early studies, Brovman *et al.*[15] predicted the ''filamentary'' structure in the atomic phase, and Barbee *et al.*[11] supported its stability and showed the possibility of high temperature superconductivity.[18] Recently Natoli, Martin, and Ceperley[13] performed the QMC and LDA calculations for atomic phases of compressed hydrogen at zero temperature, and reported no region of the anisotropic structures and the diamond structure to be stable in the atomic phase.

In this paper we present the results of the detailed study of the total energy for the structures of compressed hydrogen using a band theoretical calculation based on the LDA, with special concern for the structures in the tetragonal diamond family . We compare the free energies with those of structures studied earlier[8,17] and with those of calculated structures in the molecular phase.

We use the bare Coulomb form of the atomic potential and set the number of the plane-wave basis at $\sim 130\times n$ (where n is the number of atoms in the primitive cell) which corresponds to the energy cutoff of ~ 60 Ry at $r_s=1.6$ and ~ 90 Ry at $r_s=1.3$, where r_s denotes the radius of a sphere of volume per electron in units of Bohr radius a_0. The use of the plane-wave basis will avoid the errors originating from the ambiguities in the construction of basis functions when the shape of the unit cell is changed.[16] We take energy corrections due to the cutoff of the plane waves into account using the second-order perturbational treatment[19] for the correction to the one electron energy, which improves the convergence of the total energy. The number of the **k** points sampled in the Brillouin zone is set at $\sim$ 4000/n for the molecular phase, which is proved to be sufficient for the accuracy of the energy differences among the structures studied. For the atomic phase, twice the number of the **k** points is sampled. We used the exchange-correlation potential by Barth and Hedin.[20,21]

The β-Sn, the cubic diamond, and the Cs-IV structure belong to the tetragonal diamond family. They transform into each other by the stretch or compression along the c axis of the rectangular unit cell. The quasireciprocal relation between the β-Sn and the Cs-IV structure has been pointed out and they have almost the same Madelung energy at the local minima[22] when the Madelung energy is plotted as a function of c/a. The Madelung energy of the diamond is located at the local maximum. In Fig. 1 our results of the total energies

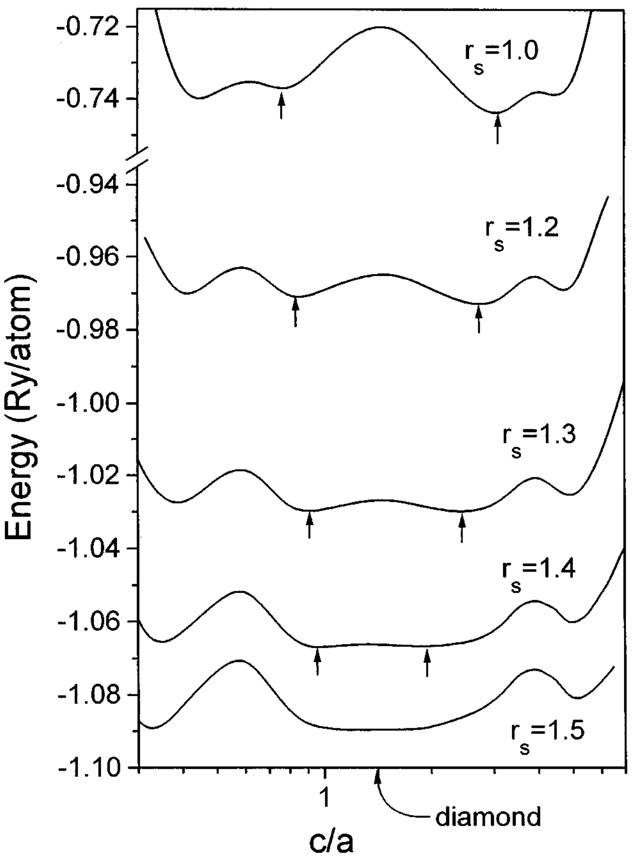

FIG. 1. Total energies for the tetragonal diamond structure as functions of c/a. The arrows point to the places of the local minima.

for the tetragonal diamond family are shown as functions of c/a. As is shown in the figure, at lower densities $r_s>1.50$, there are three local minima: the first is located near $c/a\sim 0.32$, the second $c/a\sim 1.4$ which is near the cubic diamond, and the third near $c/a\sim 5.1$. At higher densities $r_s<1.50$, the local minimum near the diamond disappears and turns into a local maximum and two new local minima appear at both sides of the new maximum.

Let us look into the above transition of local minima from the viewpoint of coordination of the structure. For $c/a<2/\sqrt{15}=0.516$, the structure has two nearest neighbor atoms lying in the c direction, which implies the structure has ''filamentary'' character, and at $c/a=2/\sqrt{15}$, the structure has six nearest neighbor atoms. For $2/\sqrt{15}<c/a<\sqrt{12}=3.464$, including the cubic diamond, the structure has four nearest neighbors. At $c/a=\sqrt{12}$ the structure has eight nearest neighbors and for $c/a>\sqrt{12}$ it has again four nearest neighbors lying in the c plane, which implies the ''planar'' character of the structure made of sheets of the square lattice. So the first minimum near $c/a\sim 0.32$ corresponds to the ''filamentary'' structure and the third near $c/a\sim 5.1$ corresponds to the ''planar'' one, which is similar to other families, for example, the rhombohedral, etc.[17]

As the density is increased the contribution from the Madelung energy becomes important and a hump appears near $c/a\sim 1.4$ and consequently the local minimum at the diamond splits into two local minima at $c/a\sim 0.9$ and $c/a\sim 1.9$. The smaller value of the c/a's for the local minima decreases and the larger one increases as the hump grows up, respectively. At extremely high density, $r_s<0.9$, the energy curves approach the shape of double minima, i.e., that of the Madelung energy. We show in Table I our LDA energy at several densities for the structures of interest with c/a values for the β-Sn and the Cs-IV structure. Our results of slightly lower energies than those of Natoli *et al.*[13] is attributed mainly to the inclusion of the energy correction which improves the equation of states but the energy differences between structures are in good agreement.

From our energies, we calculate the Gibbs free energy at $T=0$ (the enthalpy), and in Fig. 2, we plotted the differences among structures in comparison with those studied earlier.[8,17] The β-Sn structure is the lowest at pressures lower than 360 GPa and the Cs-IV structure becomes the lowest in the region 360 GPa $<P<$ 1700 GPa. There are no stable regions for the rutile (γ-nitrogen) structure which Nagara *et al.*[8] predicted to be stable. At 1700 GPa, the Cs-IV structure transforms into another ''planar,'' rh(II), structure.[17] The c/a of the above Cs-IV structure does not grow beyond $c/a=\sqrt{12}$ at pressures up to 1700 GPa, which means that the number of the nearest neighbor atoms remains four and they form a tetrahedron in the stable region like the diamond although it is stretched along the c direction to more than twice the c/a of the diamond. There are no stable regions for the new ''planar'' structure with a square lattice,

TABLE I. Total energy per atom in units of rydberg.

	$P6_3/mmc$ [a]	$Pca2_1$ [b]	$P2_1/b$ [c]	Diamond [d]	β-Sn		Cs-IV	
r_s	$E_{\rm tot}$	$E_{\rm tot}$	$E_{\rm tot}$	$E_{\rm tot}$	$E_{\rm tot}$	c/a	$E_{\rm tot}$	c/a
1.2	−0.96449	−0.96757	−0.96715	−0.96451	−0.97113	0.865	−0.97258	2.712
1.3	−1.02767	−1.02833	−1.02776	−1.02646	−1.02998	0.902	−1.02981	2.422
1.4	−1.06872	−1.06957	−1.06911	−1.06564	−1.06693	0.941	−1.06653	1.965
1.5	−1.09603	−1.09756	−1.09722	−1.08913	−1.08889	0.980[e]	−1.08890	1.960[e]
1.6	−1.11456	−1.11621	−1.11586	−1.10188	−1.10077	1.020[e]	−1.10054	1.960[e]

[a] The m-hcp structure in Refs. 11 and 17, in which the direction of the molecule is along the c axis.

[b] Molecules sit on the ideal hcp lattice sites. The direction of the central molecule is set at $(\theta,\phi)=(55°,43.5°)$.

[c] Molecules sit on the ideal hcp lattice sites. The direction of the central molecule is set at $(\theta,\phi)=(59.3°,37.6°)$.

[d] The value of c/a for the diamond is equal to $\sqrt{2}$.

[e] There are no local minima around these c/a, as is seen in Fig. 1. These values are taken tentatively to obtain the free energy curves for the structures.

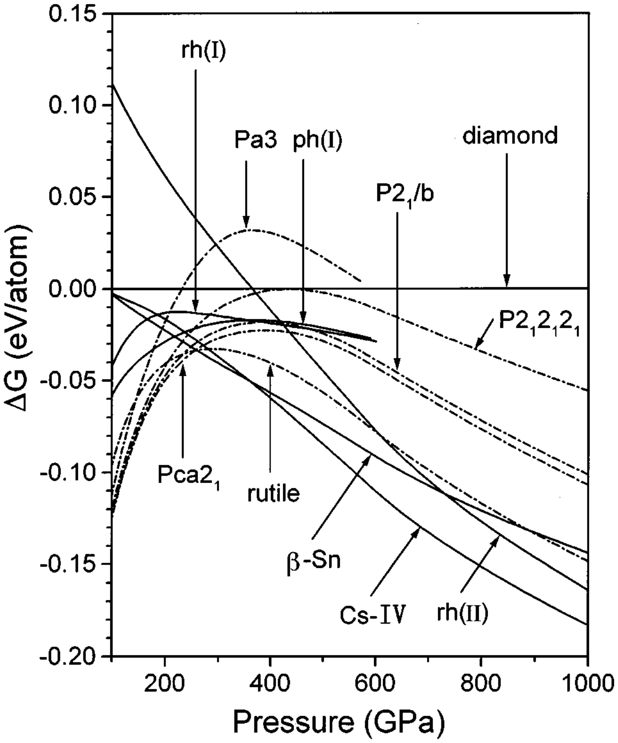

FIG. 2. Gibbs free energy differences, $\Delta G = G - G_{\mathrm{diamond}}$, per atom. The solid lines represent the curves for the atomic phase and the dot-broken lines for the molecular phase. The diamond structure is taken to be the reference. The namings of the structures are in conformity with Refs. 8 and 17.

and no stable region for the new ''filamentary'' one either because of the stable molecular phases which are discussed below.

In the molecular phase, the center of the molecule in the solid hydrogen occupies the hcp site with slightly decreased c/a at pressures lower than 119 GPa, according to the recent experiment.[4] At low pressures the molecules are in an isotropic rotating state. However, as the pressure is increased, the molecules are thought to order in some orientationally ordered structure[3,23,24] which has been controversial in close connection with the metallization by the band overlapping in the molecular phase.[7,11] Miyagi and Nakamura[25] studied the molecular orientation in the hcp lattice assuming the electric quadrupole-quadrupole (EQQ) interaction between molecules. The EQQ interaction favors the $Pca2_1$ structure most, then $P2_1/b$ and the $P2_12_12_1$ [these structures correspond to (a), (b),and (c) of Fig. 3 in Ref. 25, respectively, all of which have four molecules in the primitive cell]. Our preliminary calculations for the hcp lattice show that the lower the EQQ energy is, the lower the total energy is.

Then for the $P2_1/b$ and $P2_12_12_1$ structure, we perform the same full calculations. The molecular orientations are fixed at values given in Fig. 3 of Ref. 25 and the values of c/a is fixed at an ideal hcp structure. We searched the energy minimum, changing the atomic distance R_b in the molecule. The energy minimum is located around $R_b \sim 1.45 a_0$ for all molecular structures at $r_s \sim 1.8$ but the R_b increases or decreases slightly at higher density, depending on the structure. The LDA can be blamed for slightly larger R_b as pointed out by Averill *et al.*[26] Throughout our calculations for the molecular hcp structures, we fixed the atomic distance at $R_b = 1.45 a_0$. The energy difference between $Pca2_1$ and $P2_1/b$ or $P2_12_12_1$ is very small. Their free energy differences are plotted also in Fig. 2. The free energy differences among these structures are less than 10 meV/atom at pressures lower than 200 GPa. For these structures, we did not deform the lattice. However, the symmetry of the space group for the structures allows the deformation of the hcp lattice, which may slightly lower the energy of the structures (see Edwards *et al.*[27]). As is shown in Fig. 2, the stable region of the molecular phase terminates at 260 GPa where the β-Sn structure becomes stable.

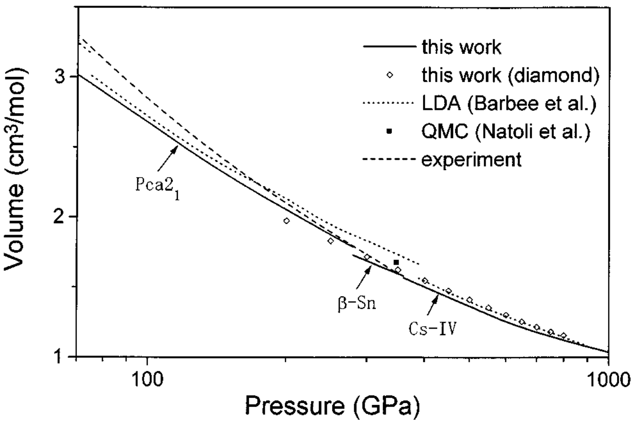

FIG. 3. The equation of state for hydrogen. The solid line represents the present results; the broken line the experimental EOS by Loubeyre *et al.* (Ref. 4); the dotted line the LDA results by Barbee *et al.* (Ref. 11); the filled square QMC (Ref. 13); the open diamond our results for the cubic diamond. None of our results contain zero-point energy.

Recent experiments cannot detect signs of the metallization up to over ~ 220 GPa.[1,2] The band gaps for $Pca2_1$ close at ~ 140 GPa, according to our LDA calculation at $R_b = 1.4 a_0$. However the LDA generally underestimates band gaps, and the band gaps must close at much higher pressures: by a factor of 2–3 higher than the LDA estimates according to Chacham and Louie.[7] Then it can be probable that the metallization occurs with the molecular dissociation.

In Fig. 3, we show our equation of states (EOS) with those of the experimental one. In the low pressure region $P < 100$ GPa, the discrepancy between our EOS and the experimental one becomes large. This is partly because our cutoff energy of the plane-wave basis decreases with decreasing density, though the energy correction has been taken into account. Our results do not include the zero-point energy of the proton motion. The contribution of the zero-point energy to the pressures, which is estimated to be $\sim 6\%$ at 100 GPa by the use of Mie-Gruneisen-Debye model according to Loubeyre *et al.*,[4], improves the results.

Finally, we discuss Natoli, Martin, and Ceperley's[13,14] results of QMC and LDA calculations for both atomic and molecular phases of compressed hydrogen at zero temperature. They reported a small difference in the zero-point energy between two structures in the molecular phase when the lattice of the centers of the molecule is the same.[14,28] They also reported a large difference in the zero-point energy between β-Sn structure and the cubic diamond in the atomic phase. However, we point out that in Barbee *et al.*'s[11] free energy curves, which include the zero-point energy within the quasiharmonic approximation, the free energy crossing of m-hcp and ph occurs at 380 GPa while Nagara *et al.*'s[8] crossing of m-hcp and rh(I) occurs at 360 GPa (Ref. 29) without zero-point energy. We mention here that the present Cs-IV structure ($c/a \sim 3.0$) is on the way from the cubic diamond to the eight-nearest-neighbor structure of $c/a = 3.464$. The structure might not be as anisotropic as the ''planar'' or ''filamentary'' structure for which Straus and Ashcroft[30] reported the large difference in the zero-point motion energy. We mention also the Loubeyre *et al.*'s reports[4] of a significantly small difference of the EOS between H_2 and D_2.

Our conclusion is that the Cs-IV structure is stable in the wide region of the pressure in the atomic phase. The diamond structure becomes a local maximum of the energy when plotted as a function of c/a. The energy differences among structures with the hcp lattice of molecules tilted from the c axis are very small regardless of the molecular orientations. It is probable that the metallic transition is caused by the molecular dissociation at ~ 300 GPa which will be within the range of current static techniques.[4]

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[1] N. H. Chen, E. Sterer, and I. F. Silvera, Phys. Rev. Lett. **76**, 1663 (1996).

[2] R. J. Hemley *et al.*, Phys. Rev. Lett. **76**, 1667 (1996).

[3] A. F. Goncharov *et al.*, Phys. Rev. Lett. **75**, 2514 (1995); L. Cui, N. H. Chen, S. J. Jeon, and I. F. Silvera, *ibid.* **72**, 3048 (1994); L. Cui, N. H. Chen, and I. F. Silvera, Phys. Rev. B **51**, 14 987 (1995).

[4] P. Loubeyre *et al.*, Nature (London) **383**, 702 (1996).

[5] E. Wigner and H. B. Huntington, J. Chem. Phys. **3**, 764 (1935).

[6] H. K. Mao, R. J. Hemley, and M. Hanfland, Phys. Rev. Lett. **65**, 484 (1990).

[7] H. Chacham and S. G. Louie, Phys. Rev. Lett. **66**, 64 (1991).

[8] H. Nagara and T. Nakamura, Phys. Rev. Lett. **68**, 2468 (1992).

[9] N. W. Ashcroft, Phys. Rev. B **41**, 10 963 (1990), and references therein.

[10] B. I. Min, H. J. F. Jansen, and A. J. Freeman, Phys. Rev. B **33**, 6383 (1986).

[11] T. W. Barbee III, A. Garcia, M. L. Cohen, and J. L. Martins, Phys. Rev. Lett. **62**, 1150 (1989).

[12] D. M. Ceperley and B. J. Alder, Phys. Rev. B **36**, 2092 (1987).

[13] V. Natoli, R. M. Martin, and D. M. Ceperley, Phys. Rev. Lett. **70**, 1952 (1993).

[14] V. Natoli, R. M. Martin, and D. M. Ceperley, Phys. Rev. Lett. **74**, 1601 (1995).

[15] E. G. Brovman, Yu. Kagan, and A. Kholas, Zh. Éksp. Teor. Fiz. **62**, 1492 (1972) [Sov. Phys. JETP **35**, 783 (1972)].

[16] H. Miyagi, T. Hatano, and H. Nagara, J. Phys. Soc. Jpn. **57**, 2751 (1988).

[17] H. Nagara, J. Phys. Soc. Jpn. **58**, 3861 (1989).

[18] T. W. Barbee III and M. L. Cohen, Phys. Rev. B **43**, 5269 (1991).

[19] H. Nagara (unpublished).

[20] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[21] Another choice of the exchange-correlation potential by Ceperley and Alder [D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980) and J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981)] gives no significant energy differences among structures.

[22] K. Ebina and T. Nakamura, Phys. Rev. B **32**, 2614 (1985), and references therein.

[23] A. F. Goncharov *et al.*, Phys. Rev. B **54**, R15 590 (1996).

[24] I. I. Mazin *et al.*, Phys. Rev. Lett. **78**, 1066 (1997).

[25] H. Miyagi and T. Nakamura, Prog. Theor. Phys. **37**, 641 (1967).

[26] F. W. Averill and G. S. Painter, Phys. Rev. B **24**, 6795 (1981).

[27] B. Edwards, N. W. Ashcroft, and T. Lenosky, Europhys. Lett. **34**, 519 (1996); the free energy curves for the molecular phase cross those of the β-Sn and the Cs-IV with large angles around 300 GPa, which implies that the change of the transition pressure due to the ambiguities of the molecular phase is rather small.

[28] This result contradicts that of M. P. Surh *et al.* [Phys. Rev. Lett. **70**, 4090 (1993)] in which only the vibron zero-point energy has been taken into account.

[29] Around these pressures, the free energy of the rh(I) is very close to that of ph(I). (See Fig. 2.) Compare also the free energy crossings of $Pa3$ and ph.

[30] D. M. Straus and N. W. Ashcroft, Phys. Rev. Lett. **38**, 415 (1977).