# Stable Phases of Solid Hydrogen at Megabar Pressures and at Zero Temperature

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We have explored the stable phases of solid hydrogen by calculating band-theoretical energies in the local density approximation, for the system of oriented molecules at Mbar pressures and at zero temperature. It is shown that the hexagonal-close-packed lattice persists up to $\sim 300$ GPa with a structure of space group $Pca2_1$, which has wide band gaps. The subsequent phase is still molecular with a rutile structure with $c/a \sim 0.9$ which must be conducting. The molecular phase terminates at $\sim 600$ GPa, where the atomic phase with a planar structure appears.

Remarkable studies are in progress for clarifying the properties of solid hydrogen at Mbar pressures, with a strong interest shown in the insulator-to-metal (IM) transition [1,2]. In 1988 Hemley and Mao [3] observed a discontinuous shift to lower frequency for the vibron (intramolecular vibration) at $\sim 150$ GPa (1.5 Mbar). Hemley, Mao, and Shu (HMS) [4] studied the low-frequency rotational and lattice-phonon spectra, concluding that the hexagonal-close-packed (hcp) lattice persists above 150 GPa. The new phase is molecular, and likely to be orientationally ordered at low temperature according to Silvera and co-workers [2,5] and others [3].

The nature of the new phase has been controversial. Mao and Hemley [6] proposed that metallization occurs in molecular phases; an IM transition may occur at Mbar pressures through a closing of the gap between the valence and conduction bands [7]. Subsequently Mao, Hemley, and Hanfland (MHH) [8] measured the optical reflectance and predicted the IM transition to occur at 149 GPa by utilizing a Drude model. However, Eggert *et al.* [9] later provided optical data inconsistent with the Drude model, making MHH's prediction inconclusive. The metallization of hydrogen remains an open question.

Theoretically, Barbee, Garcia, Cohen, and Martins (BGCM) [10] studied hcp molecular hydrogen oriented along the $c$ axis, by calculating band-theoretical energies in the local density approximation (LDA). BGCM's m-hcp phase is more stable than the $Pa3$ structure which was studied in the LDA earlier by Min, Jansen, and Freeman [11]. The $Pa3$ structure is known to occur for solid nitrogen $(\alpha\text{-}N_2)$ in the face-centered-cubic (fcc) lattice (Fig. 1) with molecular axes along body diagonals of the cubic unit cell. BGCM's result was consistent with HMS regarding the persistence of the hcp lattice. The m-hcp phase must be metallic above 150 GPa according to Chacham and Louie's quasiparticle calculation of band gaps [12]. Very recently, Kaxiras, Broughton, and Hemley (KBH) [13] reported that new hcp structures exist with lower energies and with much wider band gaps than the m-hcp phase, in the LDA. Unfortunately their search for the lowest-energy structure (LES) was confined to structures of two molecules in a unit cell. More recently Ashcroft [14] suggested a layered structure of four molecules in a unit cell as the LES, by a certain reasoning. The LES of the hcp lattice remains unsettled.

Knowledge of the LES is fundamental for clarifying the properties of compressed solid hydrogen at low temperatures. In this Letter we report the LES at Mbar pressures. Our main result is the prediction that rutile structures occur at pressures higher than the stability region of the hcp lattice, whose LES is also reported, with a much lower energy than those of KBH. It is not feasible to cover all possible structures in first-principles calculations. There must be a guiding principle in searching for the LES. We shall use a new principle in identifying the LES, and explain it first for the hcp lattice.

At low density, the orientation-dependent energy comes mainly from the electric quadrupole-quadrupole (EQQ) interactions. The LES of the EQQ system is known to be Kitaigorodskii and Mirskaya's structure of space group $Pca2_1$ [15]. In this structure, the molecular axes orient
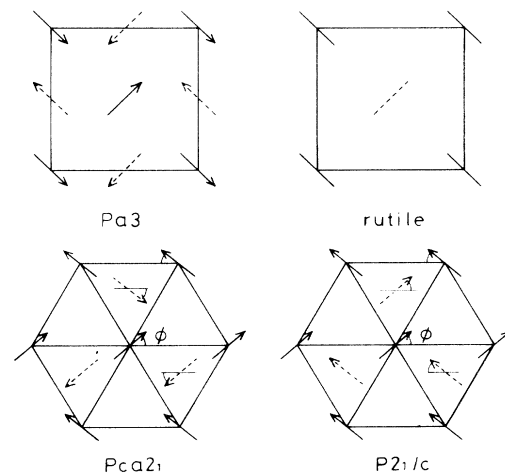


FIG. 1. Illustration of the structures: $Pa3$, rutile structure, $Pca2_1$, and $P2_1/c$ (projection on the $c$ plane). Solid lines represent molecules lying in a $c$ plane and broken ones in the next $c$ plane. Arrows indicate the direction of molecular axes whose direction cosine with the $+z$ axis is positive. Polar and azimuthal angles of the molecular direction at the origin are $(\theta,\phi) = (55.0°,43.5°)$ for the $Pca2_1$ and $(\theta,\phi) = (59.3°,37.6°)$ for the $P2_1/c$, in accordance with Ref. [15].

along four directions as shown in Fig. 1, according to the combinations of $\cos\theta \sim \pm 1/\sqrt{3}$ and $\cos\phi \sim \pm 1/\sqrt{2}$, with the polar angle $\theta$ of orientation measured from the $c$ axis and the azimuthal angle $\phi$ from the line to the nearest molecule in the $c$ plane.

As the density is increased, the electron distribution is modified, with a tendency toward one that is uniform throughout the crystal, where the proton separation in a molecule does not appreciably change in our density region if the structure is stable, as proved later. (Our density extends up to roughly 10 times the density of solid hydrogen at zero pressure.) When such modification occurs in the electron distribution, we inquire whether or not the LES changes. Then we consider a limiting case where the electron distribution is uniform in a lattice of pairs of protons with fixed separation. This hypothetical system is a molecular one-component plasma (M-OCP) in the solid state. For the hcp lattice, the energies of the M-OCP, the Madelung energies, are contours in the $\theta$-$\phi$ plane for an ordered family of structures with $Pca2_1$ symmetry. In Fig. 2, the lowest-energy point $K$ and its equivalent points are very close to the LES of the EQQ system. The line $B$ for $\theta = 0$ represents m-hcp, which is a local maximum. Of the saddle points seen in Fig. 2, the point $L$ and its equivalents represent a layered structure with symmetry $Pbcm$. The Madelung energy becomes higher in the order of $K$, $L$, and $B$. This order is identical with that of the EQQ energies, whose contours are quite similar to those in Fig. 2.

Thus, for a given lattice the LES of the M-OCP must be identical with that of the EQQ system. Accordingly we conjecture that *for a given lattice the LES of solid hydrogen is identical with that of the EQQ system and M-OCP*. This conjecture will be confirmed by calculations of energies at relevant densities.

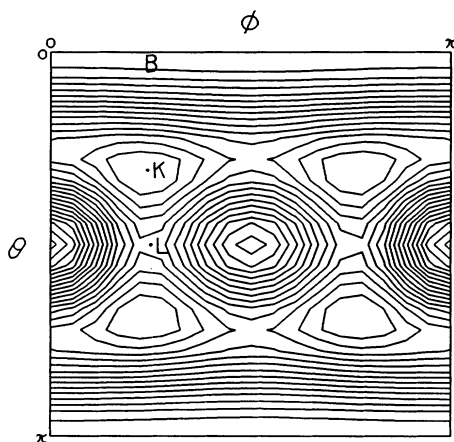For the series of structures marked before, we calculate



FIG. 2. Energy contours of the molecular one-component plasma for a family of space group $Pca2_1$. Contours are drawn at $V = 3.06$ cm$^3$/mole, with proton separation in a molecule fixed to be $1.4a_0$. The lowest energy is located at point $K$ and its equivalents.

band-theoretical total energies within LDA, using plane-wave basis states [10]. The number of plane-wave basis states is $\sim 130 \times n$ (with $n$ denoting the number of atoms in a unit cell), and we use 60 Ry for the cutoff energy of the plane waves at $r_s = 1.6$ and $\sim 45$ Ry at $r_s = 1.8$. The density parameter $r_s$, denoting the radius (in units of bohr radius $a_0$) of a sphere of volume per electron, is related to the molar volume $V$ (in cm$^3$) by $V = 0.7476r_s$ [3]. For the $k$-space integration the number of $k$ points is set to $\sim 8000/n$ in the Brillouin zone. The accuracy of the resultant energies depends mostly on the number of plane-wave basis states, with an error of 0.001 Ry/atom in our density region. Energy corrections for the cutoff of the plane waves are accounted for partially by applying second-order perturbation theory to the occupied one-electron states, improving the convergence [16].

In our calculations the most complicated case is for the structure $K$ ($Pca2_1$ in Fig. 1), which has four molecules in an orthorhombic unit cell and whose form factor is a complex quantity. For this case, we first calculate the energy difference between two structures, $K$ and $B$, for the identical orthorhombic lattice, with a small cutoff energy of the plane waves ($\sim 40$ Ry at $r_s = 1.6$) and with a small number of sampling points ($\sim 500$) in the Brillouin zone. Then we add this difference to the more accurate energy of the structure $B$, which is obtained above, to estimate the energy of the structure $K$. The same procedure is applied to $L$.

The calculation shows that the total energy becomes higher in the order of $K$, $L$, and $B$ throughout our density region, in parallel with the EQQ system and the M-OCP. In the hcp lattice we have several local minima of EQQ energy [15], of which one is the $P2_1/c$ of a monoclinic structure (Fig. 1). A similar LDA calculation [17] shows that it has energy higher than $Pca2_1$, as should be the case, although they are very close to each other. Thus the LES of the EQQ and M-OCP continues to be the lowest for the hcp lattice at relevant densities. Similarly the LES of fcc hydrogen must be the $Pa3$, which is the LES of the EQQ and M-OCP. In the following we use the same principle to discover the LES for the other lattices.

In the body-centered-cubic (bcc) lattice the lowest EQQ energy appears in a rutile form (Fig. 1), where nearest-neighbor molecules orient vertically to each other, lying in the $c$ plane. This structure occurs in a high-pressure phase of solid nitrogen ($\gamma$-$N_2$) [18]. Ceperley and Alder [19] found it unfavorable in the cubic form, by a quantum Monte Carlo method. It appears that tetragonal deformation lowers the total energy significantly. Figure 3 shows the total energy of the rutile structure as a function of $c/a$ at several values of $r_s$. Here we have a minimum at $c/a < 1$ and/or another one at $c/a > 1$, of which the former is lower at high density and limits the stable region of the $Pca2_1$ structure.

We mention briefly a family of molecular rhombohedral structures (m-rh) when the fcc lattice deforms with molecular axes parallel to the [111] direction. With
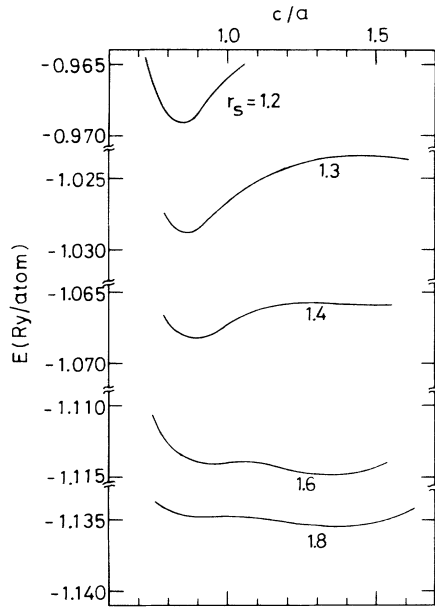
FIG. 3. Total energies for the rutile structure as a function of $c/a$ at several densities. The proton distance in a molecule, $R_b$, is fixed at $1.4a_0$. $r_s = 1.2$, 1.3, 1.4, 1.6, and 1.8 correspond respectively to molar volumes of 1.29, 1.64, 2.05, 3.06, and 4.36 cm$^3$.
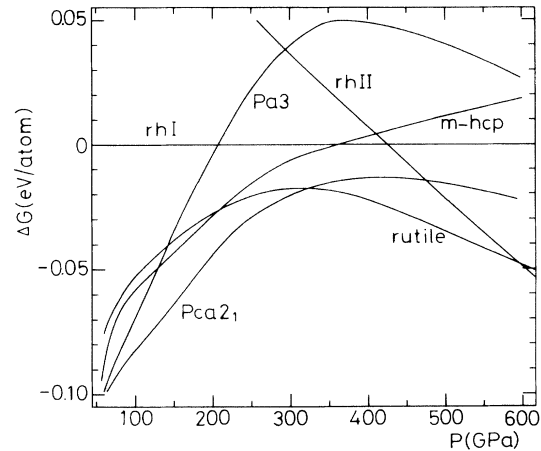


FIG. 4. Gibbs free-energy difference, $\Delta G = G - G_{rhI}$, per atom, as a function of pressure. The curve for the rutile structure refers to that with $c/a \sim 0.9$. A filamentlike structure rhI is taken to be the reference for the sake of convenience.

this direction taken to be $c$ axis we have two local minima of energy at $c/a \sim 0.6$ and $\sim 2.4$, where the first minimum (m-rhI) is close to the bcc lattice and the second one (m-rhII) is close to the fcc lattice. Here the m-rhII has lower energy for $1.3 \le r_s \le 1.8$. In the above, $c$ denotes treble the separation of layers and $a$ the distance to the nearest molecule in a layer.

We minimize the energy by relaxing the proton distance $R_b$ in a molecule for ordered structures, apart from $Pca2_1$, for which we fixed $R_b$ at $1.45a_0$. At low density ($r_s = 1.8$) the energy minimum is located at $R_b \sim 1.45a_0$ for all structures investigated. As the density is increased, $R_b$ at the minimum tends to increase although the increments are less than 10%. Curves for the energy as a function of $R_b$ become much broader for the rutile structure and m-rhI at high density ($r_s \lesssim 1.4$), with an asymmetric form, suggesting the presence of large anharmonicity in the vibron [19]. This indicates a tendency for molecular dissociation into atoms. Thus, the m-rhI transforms into a filamentlike structure, rhI, in accord with Nagara's RH(I) [16], when $R_b$ is equal to one-half of the molecular distance along a line parallel to the $c$ axis. This is the atomic-phase LES which Brovman, Kagan, and Kholas predicted to appear at low density [20].

Interpolating the energy values at local minima for several values of $r_s$, we obtain the pressure $P$ and then the Gibbs free energy $G$. The resultant EOS (equation of state) is nearly independent of structure, where typical values are $P \sim 70$, 120, 200, and 340 GPa at $r_s = 1.6$, 1.5, 1.4, and 1.3, respectively. In Fig. 4 we plot $G$ as a func-

tion of $P$, where rhI is taken to be the reference. The orthorhombic $Pca2_1$ structure persists as the lowest-energy one up to $\sim 320$ GPa. Then $Pca2_1$ is replaced by a rutile structure. The molecular phase terminates at $\sim 600$ GPa with the appearance of a planar structure rhII [16], which is derived from rhI by stretching along the $c$ axis. The atomic phase of filamentlike structure, whose high-$T_c$ superconductivity was predicted recently [21], becomes unstable owing to the new phases, the $Pca2_1$ and rutile structures.

On the low-pressure side of Fig. 4, the $Pa3$ energy decreases more rapidly than that of $Pca2_1$ as the pressure lowers, and eventually those curves would cross at $\sim 50$ GPa, below which $Pa3$ must be stable. This is in agreement with what one observes for solid hydrogen at low temperature, when orthohydrogen (in $J = 1$ rotational states) is concentrated [2].

We have examined band gaps, which are much wider for $Pca2_1$ and $Pa3$ than for rutile structures. The critical values of $V$ and $P$ (GPa units) for the band gaps to close are estimated as $V_c = 2.37$, $P_c = 135$ for $Pca2_1$ and $V_c = 3.53$, $P_c = 45$ for rutile structures, with $R_b$ fixed to be $1.4a_0$. We mention the values $V_c = 2.13$, $P_c = 190$ for $Pa3$ and $V_c = 3.42$, $P_c = 55$ for m-hcp, which are fairly close to previous estimates: $P_c = 170$ and 40, respectively [10,11]. In general, the LDA underestimates band gaps considerably, and specifically for solid hydrogen the critical pressure ($P_c$) must be higher than the LDA value by a factor of 2-3 according to Chacham and Louie [12]. Our result suggests that solid hydrogen must be conducting at least in the phase of the rutile structure where band closing occurs at a remarkably low pressure. Thus the structural transformation of the $Pca2_1$ into a rutile structure may be an IM transition, if the $Pca2_1$ remains insulating up to the phase boundary.

We discuss KBH's [13] results. The energy of their

LES, KBH's $c$, at $V = 3.06$ is lower than that of m-hcp by about 12 meV/atom, which is to be compared with our estimate 22.6 meV/atom for the energy difference between m-hcp and $Pca2_1$. Thus their LES has a much higher energy than ours. Despite such energy difference, KBH's band gap is comparable to ours. We note here that their exchange-correlation potential is different from ours [22].

Throughout our study we neglected the zero-point energy (ZPE) of protons. It has been taken into account approximately by BGCM [10]. Their EOS are very close to each other with and without ZPE, in accordance with the small isotope effect as observed for the EOS at high pressure [23]. BGCM's transition between the m-hcp and the ph (primitive hexagonal) phases occurs at $\sim380$ GPa, which is comparable to our transition pressure $\sim370$ GPa between the m-hcp and the rhI, a structure nearly identical with the ph. The effect of the ZPE seems to be small according to the above comparison, although the ZPE itself has a considerable magnitude.

[1] R. J. Hemley, H. K. Mao, and M. Hanfland, in *Molecular Systems under High Pressure*, edited by R. Pucci and G. Piccitto (Elsevier, Amsterdam, 1991), p. 223, and references therein.

[2] I. F. Silvera, J. H. Eggert, K. A. Goettel, and H. E. Lorenzana, in *Molecular Systems under High Pressure* (Ref. [1]), p. 181, and references therein.

[3] R. J. Hemley and H. K. Mao, Phys. Rev. Lett. **61**, 857 (1988).

[4] R. J. Hemley, H. K. Mao, and J. F. Shu, Phys. Rev. Lett. **65**, 2670 (1990).

[5] H. E. Lorenzana, I. F. Silvera, and K. A. Goettel, Phys. Rev. Lett. **64**, 1939 (1990).

[6] H. K. Mao and R. J. Hemley, Science **244**, 1462 (1989).

[7] D. E. Ramaker, L. Kumar, and F. E. Harris, Phys. Rev. Lett. **34**, 812 (1975); C. Friedli and N. W. Ashcroft, Phys. Rev. B **16**, 662 (1977).

[8] H. K. Mao, R. J. Hemly, and M. Hanfland, Phys. Rev. Lett. **65**, 484 (1990); Phys. Rev. B **43**, 8767 (1991).

[9] J. H. Eggert, F. Moshary, W. J. Evans, H. E. Lorenzana, K. A. Goettel, I. F. Silvera, and W. C. Moss, Phys. Rev. Lett. **66**, 193 (1991).

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

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

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

[13] E. Kaxiras, J. Broughton, and R. J. Hemley, Phys. Rev. Lett. **67**, 1138 (1991).

[14] N. W. Ashcroft, in Proceedings of the Conference on Frontiers of High Pressure Research, Colorado State University, July 1991 (to be published).

[15] H. Miyagi and T. Nakamura, Prog. Theor. Phys. **37**, 641 (1967), and earlier references therein. Space groups were given by James [H. M. James, Phys. Rev. **167**, 862 (1968)].

[16] H. Nagara, J. Phys. Soc. Jpn. **58**, 3861 (1989); H. Nagara, in *Strongly Coupled Plasma Physics*, edited by S. Ichimaru (Elsevier/Yamada Science Foundation, 1990), p. 663.

[17] S. Matsubara (private communication).

[18] A. F. Schuch and R. L. Mills, J. Chem. Phys. **52**, 6000 (1970).

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

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

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

[22] Our exchange-correlation potential is taken from U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[23] J. van Straaten and I. F. Silvera, Phys. Rev. B **37**, 1989 (1988).