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# Study of the structures of solid hydrogen at megabar pressures by means of first-principles calculations

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**Abstract.** A calculation of the Raman- and infrared-active vibrational modes in compressed solid hydrogen is presented and the structures of solid hydrogen at megabar pressures are discussed in the light of the vibrational frequencies and the total energies. We performed band theoretical calculations in the local density approximation (LDA) using a plane-wave basis. The frozen-phonon method was used in the calculation of the vibrational frequencies, where we characterized the modes using group theoretical analysis. The effects of band-gap closure on the vibrational frequencies and those of the gradient correction to the LDA (the generalized-gradient approximation, GGA) for the exchange–correlation energy are also studied. In the structure of the hexagonal close-packed (hcp) lattice for the molecular centres, the mid-lying phonon modes whose frequencies lie in the range  $1500\text{ cm}^{-1}$ – $1900\text{ cm}^{-1}$  at 100–200 GPa and the frequency difference between the in-phase and out-of-phase vibronic modes are in good agreement with experiments. The present study suggests that the most probable lattice of the solid hydrogen is hcp below and beyond the phase transition at 150 GPa, and that the molecules are canted away from the *c*-axis.

## 1. Introduction

A recent x-ray diffraction experiment on compressed hydrogen has determined the lattice of the molecular centres to be hcp up to  $\sim 120$  GPa at room temperature [1] though the molecular orientations are still unclear. And the vibron (intramolecular stretching) and the phonon modes as well as the low-lying rotational and librational modes have also become clearer as a result of infrared (IR) and Raman measurements [2–5]. A recent shock-compression experiment [6] reported a decrease in the resistivity of liquid deuterium and hydrogen, by four orders of magnitude at around 140 GPa (1.4 Mbar). The possible metallic transition was studied on the basis of the Drude model [7], but the evidence for the metallic transition in compressed hydrogen has not been confirmed so far up to around 220 GPa [2, 3] at room and lower temperatures. Meanwhile, a rich phase diagram has been confirmed by optical measurements [8–10].

The vibron, libron, and some phonon modes have been intensively studied experimentally for pure para-hydrogen (p-hydrogen), pure ortho-deuterium (o-deuterium), and mixed ortho–para-systems (o–p-systems) (for hydrogen (deuterium) ‘para-’ designates the species with even (odd) rotational quantum number  $J$  and ‘ortho-’ that with odd (even)  $J$ ), and phase boundaries among three phases (I, II, and III) in the molecular solid hydrogen have been confirmed at megabar pressures [2, 3, 8, 10–12]. However, there have been rather few theoretical studies on the frequencies of those modes at megabar pressures [10,

13–16]. This seems to be due to the complexity of the calculation, which comes from the coexistence of the high-frequency intramolecular modes and the low-frequency librational intermolecular modes. The couplings among these modes are weak at low densities but may be increased at high densities. Extensive theoretical studies of the intramolecular as well as the intermolecular vibrational modes are needed to understand the behaviour of these modes and to help determine the structures in the molecular phase at megabar pressures.

Following the group theoretical analysis by Cui *et al* [10] of the allowed IR and Raman modes, we study the pressure dependences of the frequencies of those modes, for the candidate structures, on the basis of first-principles band theoretical treatments, using the bare Coulomb form of the atomic potential, and the local density approximation (LDA) for the exchange–correlation potential, where the effects of the gradient correction to the LDA, which is usually called the generalized-gradient approximation (GGA) [17], on the frequencies are also studied. We use the frozen-phonon method and the Hellmann–Feynman theorem [18] to calculate the force matrices for some modes specified by the group theory.

Since the lattice of solid hydrogen at low temperature has not been determined experimentally at megabar pressures, we pick out several structures proposed experimentally as well as theoretically. The experimental studies have proposed the hcp lattice for the molecular centre even above  $\sim 150$  GPa [19], where a phase transition characterized by a discontinuous drop of the vibron frequencies occurs [8]. Very recent experimental and theoretical studies reported the possibility of the fcc lattice and other lattices for the molecular centres also.

In this paper, we present calculations of the vibrational frequencies by first-principles treatments and discuss the structures in the molecular phase from the point of view of the vibrational frequencies. We also study the pressure-induced molecular dissociation at megabar pressures, comparing the LDA total energies in the molecular phase as well as the atomic phase. Information on the structures and molecular orientations as well as the structures in the atomic phase is crucial if one is to predict the metallic transition in the compressed hydrogens.

## 2. Calculations

We used the bare Coulomb form of the atomic potential and the exchange–correlation potential of the form of von Barth and Hedin [20] in the LDA band theoretical calculations. We calculate force matrices in the harmonic approximation at the  $\Gamma$  point in the Brillouin zone (BZ). The vibrational frequencies at other points in the BZ are obtained through similar calculations using a supercell which consists of several original unit cells contained in the period of the wave vector.

In the calculation of the force matrix, we first transform the force matrix into the reduced form which consists of submatrices on the diagonal, using the symmetry coordinates for the displacements corresponding to the representation of the space group. The symmetry coordinates are obtained by the use of projection operators [21]. Using ambiguities in the definition of the symmetry coordinates, we tentatively define those which correspond to the vibronic (stretching), librational, phonon-like, and uniform translational motions, by which we can easily specify the characteristics of the modes. In table 1, we show the symmetry coordinates used in the calculation for the  $Cmc2_1$  structure described in figure 1. The normal coordinates and the frequencies of the vibrational modes are obtained through the diagonalization of the submatrix. In this treatment we need to treat only submatrices of small dimensions and need not treat all degrees of freedom of the motion in the unit cell together.

**Table 1.** Symmetry coordinates for vibrational modes at the  $\Gamma$  point used in the calculation of vibrational frequencies for the  $Cmc2_1$  structure.  $\theta$  is the polar angle of the molecule at the equilibrium orientation, and the subscripts to the displacements denote the atom numbers given in figure 1. The  $Cmc2_1$  structure contains four atoms in the primitive cell, and hence it has twelve vibrational modes altogether. The ‘IR’ and ‘Raman’ in parentheses indicate the IR and Raman activity of the mode.

Representation: (IR or Raman activity) Symmetry coordinate	Characteristic <sup>a</sup>
<b>A<sub>1</sub>: (IR, Raman)</b>	
$(1/2)[\sin \theta\{(y_1 - y_2) - (y_3 - y_4)\} + \cos \theta\{(z_1 - z_2) + (z_3 - z_4)\}]$	Vibron (in-phase)
$(1/2)[\cos \theta\{(y_1 - y_2) - (y_3 - y_4)\} - \sin \theta\{(z_1 - z_2) + (z_3 - z_4)\}]$	Libron
$(1/2)[(y_1 + y_2) - (y_3 + y_4)]$	Phonon
$(1/2)[(z_1 + z_2) + (z_3 + z_4)]$	Translation
<b>A<sub>2</sub>: (Raman)</b>	
$(1/2)[(x_1 - x_2) - (x_3 - x_4)]$	Libron
$(1/2)[(x_1 + x_2) - (x_3 + x_4)]$	Phonon
<b>B<sub>1</sub>: (IR, Raman)</b>	
$(1/2)[(x_1 - x_2) + (x_3 - x_4)]$	Libron
$(1/2)[(x_1 + x_2) + (x_3 + x_4)]$	Translation
<b>B<sub>2</sub>: (IR, Raman)</b>	
$(1/2)[\sin \theta\{(y_1 - y_2) + (y_3 - y_4)\} + \cos \theta\{(z_1 - z_2) - (z_3 - z_4)\}]$	Vibron (out-of-phase)
$(1/2)[\cos \theta\{(y_1 - y_2) + (y_3 - y_4)\} - \sin \theta\{(z_1 - z_2) - (z_3 - z_4)\}]$	Libron
$(1/2)[(z_1 + z_2) - (z_3 + z_4)]$	Phonon
$(1/2)[(y_1 + y_2) + (y_3 + y_4)]$	Translation

<sup>a</sup> The column headed ‘Characteristic’ shows the attributes of the modes. ‘Vibron’ means the stretching motion of the molecule, ‘Libron’ the librational motion, ‘Phonon’ the phonon-like motion of the centre of the molecule, and ‘Translation’ the uniform translation of the system. Note that those attributes have their literal meanings when the couplings among the modes in the same representation are negligibly small.

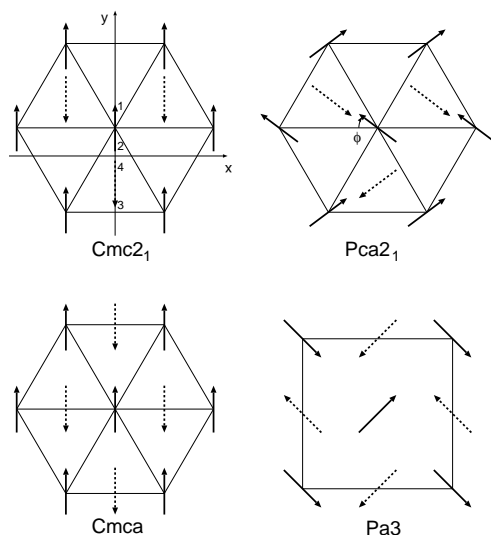
In the band theoretical treatments, we set the energy cut-off of the plane wave at  $\sim 60$  Ryd at the lowest density,  $r_s = 1.6$  ( $P \sim 70$  GPa), which is sufficient for the calculation of the frequencies, and fixed the number of plane waves in our calculation. Above, the density parameter,  $r_s$ , denotes the radius of a sphere whose volume is equal to the volume per electron in units of the Bohr radius  $a_0$ . We sampled 512  $k$ -points in the BZ, and optimized the bond length and the molecular orientation at each density.

For the evaluation of the forces, we set the amplitude of the symmetry coordinate at values sufficiently small that the forces remain harmonic, and set different values for each symmetry coordinate. We have checked the anharmonicity in the force by inverting the signs of the displacements or by halving the magnitudes of the amplitudes depending on the character of the mode.

We also checked the accuracy of the force by comparing the Hellmann–Feynman forces with those calculated from the second derivatives of the total energy with respect to the displacement.

### 3. Pressure dependences of the vibrational frequencies

Experimental studies [1, 19, 22] suggested that the hcp lattice is the most probable one for the molecular centres, and theoretical studies [16, 23–26] have supported the hcp lattice.



**Figure 1.** An illustration of the structures: the  $Cmc2_1$ , the  $Pca2_1$ , the  $Cmca$ , and the  $Pa3$  forms. For the  $Cmc2_1$  form, the  $x$ - and  $y$ -axes are shown, together with the numbering of the atoms in the primitive cell. Arrows indicate the directions of the molecular axes whose direction cosines with the  $z$ -axis are positive. For the m-hcp ( $P6_3/mmc$ ) form, we set the polar angle at  $\theta = 0^\circ$ .

A very recent Raman experiment [22], however, has indicated the possibility of the  $Pa3$  structure for phase II, in which the molecular centres form a fcc lattice, on the basis of the Raman activity of a peak for phase II. Furthermore, recent total-energy calculations within the LDA report that the shift of the molecular centres from the hcp sites [16, 27] leads to lower energy at high densities. We study the structures proposed by experimental as well as theoretical studies.

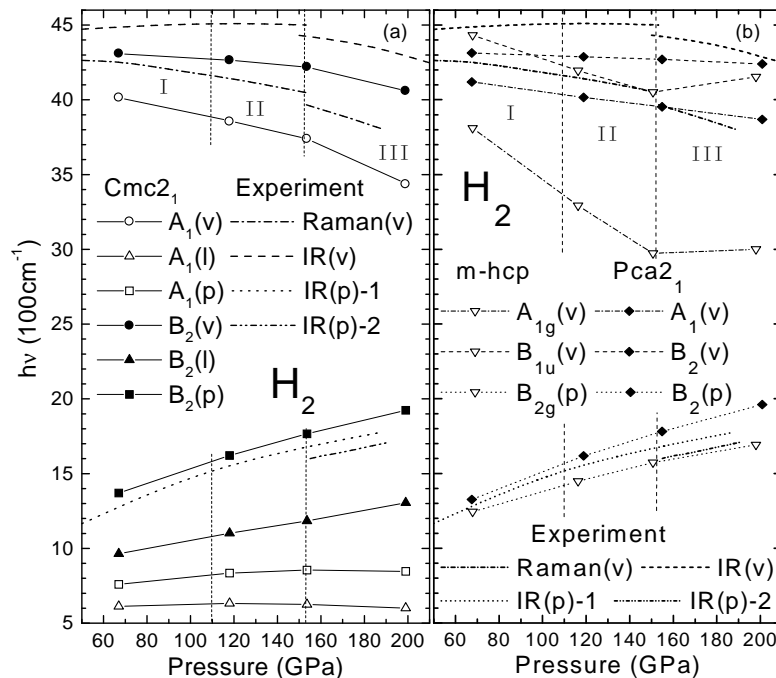
At low pressures and at low temperatures, the molecules in para-hydrogen are in an orientationally isotropic state. However, as the pressure is increased, the molecules are thought to order in some orientationally ordered structure [4, 8, 26]. The predicted pressures of the ordering transition have been controversial, in close connection with the metallization caused by band overlap in the molecular phase [23, 24, 28].

Our treatments can handle only structures with orientational order. However, we can calculate the frequencies of some modes approximately for structures in which the molecules are rotating, because the dependence of the frequencies on the orientation are weak, as shown below, at low pressures for the vibronic and the mid-lying phonon-like modes. Thus we can show results for phase III and those for phases I and II as well.

### 3.1. The structures of the hcp lattice

We studied the hcp lattice for the molecular centres intensively, changing the molecular orientation [29]. For the structures containing two molecules in the primitive cell, we calculate the  $Cmc2_1$  structure using symmetry coordinates given in table 1.

In this structure, the band gap closes at  $\sim 150$  GPa. The pressure dependences of the calculated frequencies are shown in figure 2 together with those of the experimental values. The total number of vibrational modes is nine, except for the uniform translation, in the  $Cmc2_1$  structure. Both the vibronic modes and the  $B_2$  phonon mode are IR active



**Figure 2.** Pressure dependences of the vibrational frequencies for the (a)  $Cmc2_1$  and (b) m-hcp and  $Pca2_1$  structures. The symbols show our data points, and lines connecting those points are guides to the eye. (v), (l), and (p) denote the vibronic, librational, and phonon-like modes. The experimental data are taken from reference [2] (p-H<sub>2</sub>) for IR(p)-2 and from reference [8, 12] (mixed o-p-H<sub>2</sub>) for the others. The vertical broken lines show the boundaries between the phases I, II, and III taken from references [8, 39].

as well as Raman active. The mid-lying B<sub>2</sub> phonon mode whose frequency lies in the range 1500 cm<sup>-1</sup>–1900 cm<sup>-1</sup> at 100–200 GPa, and the frequency difference between the A<sub>1</sub> and A<sub>2</sub> vibronic modes are in good agreement with the experiments, if we assign the B<sub>2</sub> phonon mode to the experimentally observed mid-lying phonon mode, and also assign the B<sub>2</sub> vibronic and the A<sub>1</sub> vibronic modes to the observed IR and Raman modes respectively. The pressure dependences of the frequencies of the vibronic modes are also in good agreement with the experiments, though the frequencies themselves are lower than those from the experiments by ~5%. We note here the effect of the decrease of  $c/a$  on the frequencies. The vibron frequencies decrease slightly and that of the mid-lying phonon-like mode increases by a very small amount, as long as the decrease of  $c/a$  is in the range observed in the experiments.

By setting the polar angle  $\theta = 0^\circ$ , we can study the m-hcp structure. In this structure, the band gap closes at a considerably lower pressure. We made the same calculations as those for the  $Cmc2_1$  form using the same symmetry coordinates as are given table 1. The calculated vibron frequencies are considerably lower than those of the other structure of the hcp lattice, as shown in figure 2. The frequencies of the mid-lying phonon-like mode are very close to those for the  $Cmc2_1$  form. We note that in this structure there are no IR-active phonon and vibron modes [10].

Lastly we studied the  $Pca2_1$  form, which is the structure containing four molecules in the unit cell. In this structure, orientationally, the neighbouring molecules keep away from

each other to a higher degree than in the  $Cmc2_1$  structure, and the band gap persists near  $\sim 180$  GPa. The equilibrium bond length decreases with increasing pressure. The LDA bond length is  $1.412 a_0$  at  $r_s = 1.40$ .

There are 21 modes, except for the uniform translation. We show in figure 2 the pressure dependences of the frequencies for some modes connected with the modes studied for the  $Cmc2_1$  structure when we set the azimuthal angle  $\phi = 0^\circ$ . The difference between in-phase and out-of-phase vibronic modes lies in the degree of agreement with the experiments, though the calculated vibron frequencies are slightly lower at pressures lower than  $\sim 150$  GPa. The frequencies of the mid-lying phonon-like mode are very close to those for the structures studied above.

Here we discuss the low-lying phonon-like and librational modes. The low-lying phonon-like modes strongly couple with the librational modes. The calculated frequencies of these modes have pressure dependences somewhat different from those found in the experiments, and some are shown in figure 2. The large orientational fluctuations, which are expected in phase II as well as in phase III, may affect the frequencies and their pressure dependences.

### 3.2. The structure of the fcc lattice

Next, we calculated the vibrational frequencies in the  $Pa3$  structure as a structure for the fcc lattice of the molecular centres. The structure is shown in figure 1. The vibron frequencies calculated in the LDA are slightly lower than the experimental values at pressures lower than 150 GPa, though at higher pressures they are higher than the experimental ones. In this structure too, molecular orientations are such that they keep the neighbouring molecules away from each other to a high degree, and the band gap persists to over  $\sim 200$  GPa. The frequency of the mid-lying phonon-like mode is near the experimental value. The results are given in figure 3. We note that there are no IR vibron and Raman phonon modes for this structure [10].

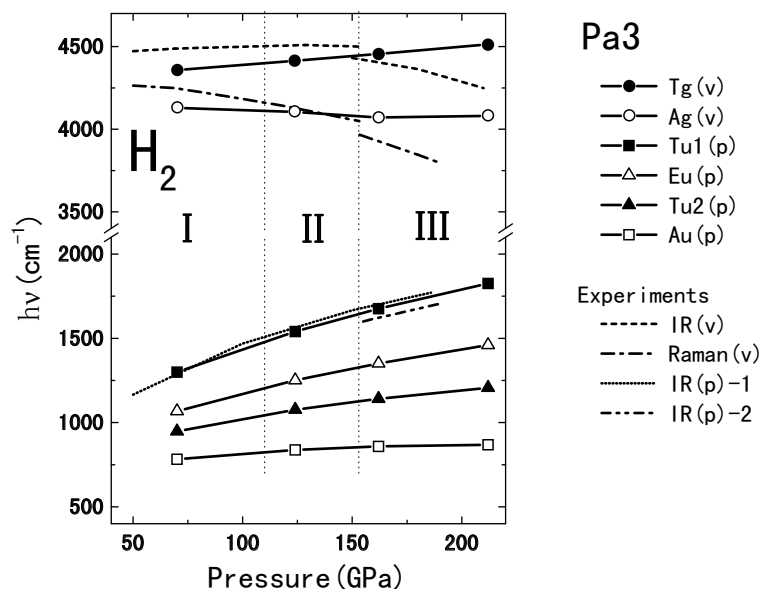


Figure 3. Pressure dependences of the vibrational frequencies in the  $Pa3$  structure.

### 3.3. Other structures

Edwards *et al* [27] studied the  $Cmca$  structure and showed that the  $Cmca$  structure is of lower energy than the  $Pca2_1$  structure, which is a structure of the hcp lattice. The  $Pca2_1$  structure studied above changes into the  $Cmc2_1$  structure at a special value of the azimuthal angle. And the  $Cmc2_1$  structure further allows the shift of the molecular centre in certain directions without changing the symmetry, and the  $Cmca$  structure corresponds to special values of the shift of the molecular centre in the  $Cmc2_1$  structure, as is shown in figure 1. So we studied the  $Cmc2_1$  form by shifting the molecular centre.

In such structures, however, the band gap is already closed at the lowest densities that we studied here, and the calculated vibron frequencies are much lower than the experimental values, as is expected from the closed band gap, and the mid-lying phonon-like mode is higher than those of the hcp structures.

In the above three subsections, we have shown the results of the LDA calculations made without the GGA. Applying the GGA to the exchange–correlation energy has some effects on the vibron frequencies, which are discussed in the following subsection.

### 3.4. Effects of the band-gap closure and the GGA for the exchange–correlation energy

Underestimation of the band gap is one of the well known shortcomings of electronic structure calculations made using the LDA. The band gaps of the structures in which the molecules orient to keep away from neighbouring molecules, like the  $Pca2_1$  and the  $Pa3$  structures studied above, persist to higher pressures than those in which the molecules orient to stay close to neighbouring molecules. The band-gap closure leads to considerably lower frequencies of vibronic modes, while it has small effects on the mid-lying phonon-like modes, as shown in the above subsection. In the m-hcp and  $Cmca$  structures, the vibronic frequencies are considerably lower than the experimental ones, while those of the mid-lying phonon-like modes remain near the experimental values.

The pressures of the band-gap closure are sensitive to the bond length. The GGA improves the bond length for the isolated hydrogen molecule, although it does not necessarily improve the bond lengths for other diatomic molecules [30].

Let us examine the effects of the GGA for the  $Cmc2_1$  structure. We tried the simplified version of the GGA [31]. In the LDA, the equilibrium bond length in this structure at  $r_s = 1.45$  ( $P \sim 150$  GPa) is  $1.427 a_0$ , at which point the band gap is closed. When the GGA is applied to the exchange–correlation energy, the equilibrium bond length decreases to  $\sim 1.38 a_0$ , at which point the GGA band gap is  $\sim 0.05$  Ryd. The GGA seems to widen the band gap in molecular hydrogen. Without the GGA, the band gap in the  $Cmc2_1$  structure is  $0.042$  Ryd, while with the GGA it is  $0.083$  Ryd, when the bond length is set at  $1.323 a_0$  for both cases at  $r_s = 1.45$ .

The GGA results for the vibron frequencies increase by about 10% at most, at the pressure  $\sim 200$  GPa, while the shift of the frequency of the mid-lying phonon-like modes is very small. With the GGA, the vibron frequencies in the  $Cmc2_1$  structure are in quite good agreement with the experimental results, while those without the GGA were lower than the experimental ones. In the  $Pca2_1$  structure, the GGA shifts the vibron frequencies upward further, to values higher than the experimental ones by  $\sim 7\%$  at  $P \sim 200$  GPa.

We compare here our bond length and the frequency within the GGA with those calculated by Kohanoff *et al* [16] for the  $Pca2_1$  structure. At  $r_s = 1.40$  our bond length of  $1.38 a_0$  is close to that obtained by Kohanoff *et al* [16], namely  $1.373 a_0$ , while our GGA results for the vibron frequencies, especially that for the in-phase vibron, decrease as the



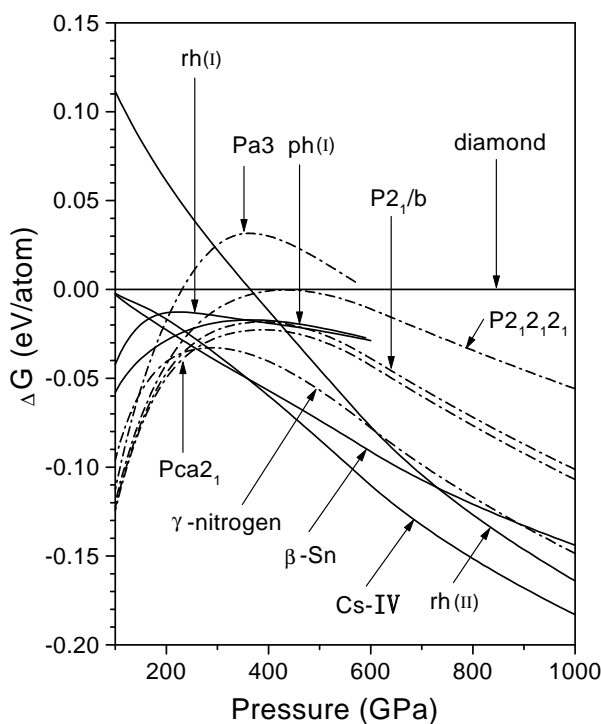
pressure is increased, which contradicts the results by Kohanoff *et al*. We note that we used the bare Coulomb form of the atomic potential while they used their pseudopotential.

#### 4. Total-energy consideration

In the preceding section, we studied the structures of the hcp and fcc lattices as well as another lattice for the molecular centres. We briefly review the structures, comparing their total energies.

The  $Cmc2_1$  structure—which was first studied by Kaxiras *et al* [24] in their study of low-energy structures—corresponding to the  $Pca2_1$  structure with the azimuthal angle  $\phi = 90^\circ$ , has been shown to have slightly higher energy than the  $Pca2_1$  structure [25, 26]. It is possible that the large fluctuation of the azimuthal angle in the  $Pca2_1$  structure results in the  $Cmc2_1$  structure being produced. We refer the reader to Mazin and Cohen's [26] study of the fluctuation of the azimuthal angle of the molecules in the  $Pca2_1$  structure, though it is preliminary.

The  $Pa3$  structure is known to have the lowest energy in the orientational patterns of the molecules on the fcc lattice sites, when only the electric quadrupole–quadrupole (EQQ) interaction is taken into account. The free energy is higher than those of the hcp lattice, as shown in figure 4.



**Figure 4.** Gibbs free-energy differences among structures in the molecular phase as well as the atomic phase,  $\Delta G = G - G_{\text{diamond}}$ , per atom. The solid lines represent the curves for the atomic phase and the dot-dash lines those for the molecular phase. The diamond structure is taken to be the reference. The namings of the structures are in conformity with references [36] and [25].

Lastly, we compare the total energy of the  $Cmca$  structure with that of the  $Cmc2_1$  structure. The total energy of the  $Cmca$  structure becomes lower than that of the  $Cmc2_1$  structure at pressures higher than  $P \sim 150$  GPa [27].

## 5. Molecular dissociation

Finally, we discuss molecular dissociation on the basis of the LDA total-energy calculation. The predicted pressures for the molecular dissociation are scattered over the range from 300 GPa to 600 GPa [25, 32].

We performed additional calculations for some of the structures in the atomic phase, following the prediction made by Natoli *et al* of the cubic diamond structure being that of lowest energy in the atomic phase [33, 34]. This denies the possibility of anisotropic structures in the atomic phase [35, 36]. In the anisotropic structures the possibility of high-temperature superconductivity had been proposed [37].

We have carried out first-principles calculations of the total energy for the structures in the tetragonal diamond family, varying the value of  $c/a$  for the lattice [38], and found that the energy of the cubic diamond structure is the lowest at low pressures less than  $\sim 120$  GPa. However, as the density is increased the energy of the  $\beta$ -Sn ( $c/a \sim 0.9$ ) or the Cs-IV structure ( $c/a \sim 3.0$ ) becomes the lowest.

In figure 4 we compare the Gibbs free energies with those of other structures that we had calculated before for both atomic and molecular phases. For the structures for the molecular phase, we have assumed the fcc lattice and the ideal hcp lattice. Our results do not contain the zero-point energy of the nuclear motions. The free-energy curves for the molecular phase cross those for the atomic phase at large angles at around 300 GPa, which implies a rather small change of the transition pressure due to the ambiguities of the free energy in the molecular phase.

The molecular phase persists up to  $\sim 260$  GPa and transforms into the  $\beta$ -Sn structure of the atomic phase, which transforms then into the Cs-IV structure at  $\sim 340$  GPa. There are no stable regions for the cubic diamond structure [38]. And the region of the anisotropic structure almost disappears, owing to the appearance of the Cs-IV structure.

The correction from the GGA favours the molecular phases, and shifts the dissociation pressure upward to around 350 GPa for the transition from the  $Pca2_1$  to the  $\beta$ -Sn structure.

## 6. Summary and concluding remarks

We performed a first-principles calculation of the vibrational frequencies and the total energy for some of the candidate structures.

The pressure dependences of the vibron and the mid-lying phonon mode suggest that the  $Cmc2_1$  structure is the most probable. The  $Pca2_1$  structure, however, cannot be ruled out, because very recent experiments [5, 22] have reported more low-lying modes than would be expected for  $Cmc2_1$  structure.

For the  $Pa3$  structure, the frequencies of the mid-lying phonon-like modes lie near the experimental values, although the LDA total energy is much higher than those of the structures of the hcp lattice. This structure has no Raman-active phonon modes nor any IR-active modes for pure para-crystal.

The pressure dependences of the frequencies of the low-lying phonon-like and librational modes do not agree with those from the experiments [22].

The energy differences among structures with hcp lattices of molecules tilted away from

the *c*-axis are rather small regardless of the molecular orientations.

Here we mention that we have not taken the effects of the quantum fluctuation of the molecular orientation into account. The effects of the fluctuation may be expected for low-lying phonon and librational modes, which are coupled with each other at high densities. We mention also that our total-energy calculations do not include the zero-point energy of the proton motion, though Natoli *et al* [33, 34] reported a small difference between the zero-point energies of the two structures for the molecular phase when the lattices of the centres of the molecules are the same. The above effects remain as subjects for investigation in future studies.

Our results predict that it is probable that the metallic transition is caused by molecular dissociation at  $\sim 300$  GPa, which is accessible to current techniques of static compression [1, 8].

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