Crystal structure and superconductivity in atomic hydrogen: Deformation between $I4_1/amd$ and $Fddd$

T Ishikawa$^1$, H Nagara$^2$, T Oda$^3$, N Suzuki$^4$ and K Shimizu$^1$

$^1$ Center for Science and Technology under Extreme Conditions, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan
$^2$ Department of Applied Mathematics and Physics, Tottori University, 4-104 Koyama-cho-minami, Tottori, Tottori 680-8552, Japan
$^3$ Institute of Science and Engineering, Kanazawa University, Kakuma, Kanazawa, Ishikawa 920-1192, Japan
$^4$ Department of Pure and Applied Physics, Faculty of Engineering Science, Kansai University, 3-3-35 Yamate, Suita, Osaka 564-8680, Japan

E-mail: ishikawa@stec.es.osaka-u.ac.jp

Abstract. We investigated crystal structures of solid metallic hydrogen using the potential energy surface trekking for structure search. We applied this technique to a tetragonal $I4_1/amd$ structure at pressures of 500 and 600 GPa and obtained the transformation into multiple orthorhombic $Fddd$ structures, which are formed by distortions in the $ab$ plane of $I4_1/amd$. The potential barriers are easily surmounted by few trekking steps, which indicates that in solid metallic hydrogen crystal structure is softened with respect to the distortion and is easily fluctuated among the $I4_1/amd$ and $Fddd$ structures. Calculated superconducting critical temperatures show 269 K for $I4_1/amd$ and 263 K for $Fddd$ at 500 GPa. The structures are softened and the electron-phonon coupling are enhanced with pressurization to 600 GPa. As the results, the superconducting critical temperature is increased to 281 K for $I4_1/amd$, whereas it is decreased to 252 K for $Fddd$ owing to its larger phonon softening than that of $I4_1/amd$.

1. Introduction

Solid hydrogen has theoretically been predicted to be a room-temperature superconductor [1–3], and its metallic phases have been explored for decades. High-pressure experimental studies have revealed at least four solid phases in pressure region to 315 GPa [4]. The H$_2$ molecules are in a spherical rotational state on the close-packed lattice (phase I) at low pressures [5], and it transforms into an anisotropic one (phase II) at around 110 GPa owing to the increase of the intermolecular interactions [6]. By further compression below 125 K, another state (phase III) emerges at around 155 GPa [7, 8], accompanying large discontinuities in vibron frequencies. Recently, a phase IV has been discovered at 220 GPa and 300 K by Raman and visible transmission spectroscopy, where the structure has been thought to form a mixture of molecular and atomic hydrogens [4]. Furthermore, it has been found that the phase IV takes the transition into a new phase at around 255 GPa and 480 K, which is possibly based on melting [9]. Above 220 GPa, conductive hydrogen has experimentally been observed [10], but complete metalization has not been obtained.

First-principles calculations predict that a hexagonal $P6_3/m$ is the most stable structure up to around 105 GPa of candidate structures and then a monoclinic $C2/c$ of a layered structure
Figure 1. Projection of crystal structures for solid metallic hydrogen onto the $xy$ plane: (a) tetragonal $I_{41}/amd$ and (b) orthorhombic $Fddd$, in which the H$_2$ molecules are completely dissociated. The unit cells are shown by a broken line and the atoms with different $z$ values are represented by different colors. The structures are characterized by distortion of an angle $\theta$: $\theta = 90^\circ$ for $I_{41}/amd$ and $\theta \neq 90^\circ$ for $Fddd$.

prevails to around 270 GPa [11], whose vibrational spectra agree somewhat well with the experimental Raman data collected from the phase III. The $C2/c$ structure is predicted to transform into an orthorhombic $Cmca$ with a primitive cell containing 12 atoms ($Cmca$-12) at 385 GPa and into another $Cmca$ containing 4 atoms ($Cmca$-4) by further compression [11]. Subsequent transition into an exotic quasi-molecular mC24 structure is expected at around 470 GPa, which has a space group of a monoclinic $C2/c$ [12]. Above 590 GPa an atomic metallic phase of a tetragonal $I_{41}/amd$ is predicted to become the most stable structure [12, 13]. The tetragonal $I_{41}/amd$ prevails over a wide range of pressure and transforms into another atomic phase with a space group of an orthorhombic $Cmcm$, called oC12 structure, above 2100 GPa [12]. A trigonal $R\bar{3}m$ structure with an ABC stacking is also predicted as another higher-pressure structure, which transforms into the face-centered cubic structure near 3500 GPa [13]. In the atomic metallic phase, the superconducting critical temperatures ($T_c$) have been calculated by the use of the Allen-Dynes formula [14], and $T_c$ has been predicted to reach 340 K at around 1000 GPa in $I_{41}/amd$ and 400 K at around 3500 GPa in $R\bar{3}m$ [2].

Recently, we have obtained an orthorhombic $Fddd$ structure in the metallic atomic phase using the genetic algorithm technique for crystal structure search [15]. The obtained structure is formed by a slight distortion in the $ab$ plane of the tetragonal $I_{41}/amd$, and the crystal symmetry is lowered. The structures are characterized by distortion angle $\theta$ as shown in Fig. 1: $\theta = 90^\circ$ for $I_{41}/amd$ and $\theta \neq 90^\circ$ for $Fddd$. In pressure region of 1800-2000 GPa, where $Fddd$ mainly emerges as the most stable structure, the electron-phonon coupling is enhanced and $T_c$ calculated by the Allen-Dynes formula reaches 350 K.

In the present study, we focus on the two atomic phases of solid hydrogen, $I_{41}/amd$ and $Fddd$, at pressures of 500 and 600 GPa. We perform further investigations on the structural stability and the superconductivity of the two structures via another structure search technique, which we have developed and called the potential energy surface trekking (PEST) [16, 17].

2. Methods
In the PEST technique, the system is forced to ascend the potential energy surface to its ridges through various trekking paths following by the inversion of restoring force (ascent-run) and then to descend toward neighboring local minima by the release from the inversion (descent-run) [16, 17]. Since the trekking paths are independent from each other, many stable
structures existing around a target structure can be simultaneously and rapidly obtained. We have combined our PEST code with the Quantum ESPRESSO code [18], in which electronic structures are calculated within the density functional theory (DFT) by the use of plane waves and pseudopotentials.

In the DFT calculations, the generalized gradient approximation by Perdew, Burke and Ernzerhof [19] was used for the exchange-correlation functional, and the Rabe-Rappe-Kaxiras-Joannopoulos ultrasoft pseudopotential [20] was employed. The supercell including $4 \times 4 \times 2$ $I4_1/amd$ primitive cells, including 128 hydrogen atoms, was employed as the starting structure for the PEST simulations. The $k$-space integration over the Brillouin zone was performed on a $6 \times 6 \times 4$ grid, and the energy cutoff of the plane wave basis was set at 72 Ry. We created 64 starting directions for the trekking by adding the distortions to the $I4_1/amd$ supercell, i.e. adding either $-0.2$ or $+0.2$Å to six independent elements of a cell matrix $\mathbf{h} = (\mathbf{a}, \mathbf{b}, \mathbf{c})$, where $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ are lattice vectors of the supercell. In the ascent-run, the matrix $\mathbf{h}$ is updated by the inversion of the restoring force $F$ as follows: $h_{ij}^{t+1} = h_{ij}^t - (\delta h_{ij}) F_{ij}^{t} / | F_{ij}^{t} |$, where $t$ is the number of trekking steps and $\delta h_{ij}$ stepping parameters. The restoring force $F$ is defined as a set of derivatives of the Gibbs free energy $G(\mathbf{h})$ with respect to the six parameters of $\mathbf{h}$: $F_{ij} = -\partial G / \partial h_{ij} = V \{ [ (\mathbf{p} - P \mathbf{I} ) h^{-1} ]_{ij} + [ (\mathbf{p} - P \mathbf{I}) h^{-1} ]_{ji} \} (1 - \delta_{ij} / 2)$, where $V$ is volume, $\mathbf{p}$ an averaged stress tensor, $P$ a given pressure, $\mathbf{I}$ the unit tensor, and $\delta_{ij}$ the Kronecker delta [21].

Figure 2. Evolution of cell angles in the PEST simulations: (a) a trekking path at 500 GPa and (b) a trekking path at 600 GPa. The structural transformations obtained through the trekking are shown on the right side.
Table 1. Results of the PEST simulations at pressures of 500 and 600 GPa. \( N_{\text{tp}} \) represents the number of the trekking paths leading to the corresponding structure.

| Structure     | \( N_{\text{tp}} \) | Structure     | \( N_{\text{tp}} \) |
|---------------|----------------------|---------------|----------------------|
| \( I_{41}/\text{amd} \) (\( \theta = 90.0^\circ \)) | 2                    | \( F_{\text{ddd}} \) (\( \theta = 91.5^\circ \)) | 5                     |
| \( F_{\text{ddd}} \) (\( \theta = 91.2^\circ \)) | 1                    | \( F_{\text{ddd}} \) (\( \theta = 92.9^\circ \)) | 1                     |
| \( F_{\text{ddd}} \) (\( \theta = 91.8^\circ \)) | 1                    | \( F_{\text{ddd}} \) (\( \theta = 94.5^\circ \)) | 1                     |
| \( F_{\text{ddd}} \) (\( \theta = 92.6^\circ \)) | 2                    | \( F_{\text{ddd}} \) (\( \theta = 97.6^\circ \)) | 2                     |
| \( F_{\text{ddd}} \) (\( \theta = 95.4^\circ \)) | 2                    | \( F_{\text{ddd}} \) (\( \theta = 101.2^\circ \)) | 2                     |
| \( F_{\text{ddd}} \) (\( \theta = 96.8^\circ \)) | 1                    | \( F_{\text{ddd}} \) (\( \theta = 102.4^\circ \)) | 1                     |
| \( \text{Cmca-4} \) | 2                       |                      |                      |

For the stepping parameters, \( \delta h_{11} \), \( \delta h_{22} \), and \( \delta h_{33} \) were set at 0.4 Å, and \( \delta h_{12} \), \( \delta h_{13} \), and \( \delta h_{23} \) at 0.2 Å. An molecular dynamics (MD) run of 0.2 ps (200 MD steps) was carried out at each trekking step, and \( p \) was obtained by the average of the stress tensors for the last half of the MD steps. In the descent-run, the matrix \( h \) is updated by \( h_{ij}^{t+1} = h_{ij}^t + (\delta h_{ij})F_{ij}/|F_{ij}| \). Pressure-temperature conditions for the simulations are 500 GPa and 300 K, and 600 GPa and 300 K.

The superconducting \( T_c \) was calculated by the use of the Allen-Dynes formula [14],

\[
T_c = \frac{\omega_{\log}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right].
\]  

In Eq. 1, the parameters of electron-phonon coupling constant \( \lambda \) and logarithmic-averaged phonon frequency \( \omega_{\log} \) represent a set of characters for the phonon-mediated superconductivity. Using the QE code, we calculated these parameters with a 4 \( \times \) 4 \( \times \) 4 \( q \)-point grid. The \( k \)-space integration was performed on a 48 \( \times \) 48 \( \times \) 24 grid, and the energy cutoff of the plane wave basis was set at 80 Ry. The effective screened Coulomb repulsion constant \( \mu^* \) was assumed to be 0.089, which is deduced as a reasonable value for atomic metallic hydrogen [22].

3. Results

Figure 2 (a) shows the evolution of three cell angles, \( \alpha \), \( \beta \), and \( \gamma \), obtained in a trekking path at 500 GPa. The ascent-run was switched to the descent-run at the second trekking step, and finally \( \alpha \) decreased from 90° to about 82°, and \( \beta \) and \( \gamma \) increased to around 94°. We carried out the structural optimization at the 10th trekking step and obtained the structure consisting of H\(_2\) molecules (see the rightmost structure in the figure). This structure is consistent with the earlier-predicted \( \text{Cmca-4} \) structure, which has been considered as a candidate of the molecular phase in lower pressure region. The similar results obtained by another trekking path at 600 GPa are shown in Fig. 2 (b). This trekking path also shows the switching from the ascent-run to the descent-run at the second trekking step. The angles, \( \alpha \) and \( \beta \), remained at 90°, whereas \( \gamma \) increased to about 104° through 10 trekking steps. In contrast to the results shown in Fig. 2 (a), the atomic structure remained through the simulation, and the final structure became the \( F_{\text{ddd}} \) structure predicted as a candidate of the metallic phase.

Table 1 lists the obtained structures and the number of the trekking paths leading to them at 500 and 600 GPa. At 500 GPa, the structure returns to the starting \( I_{41}/\text{amd} \) with \( \theta = 90^\circ \) through two trekking paths, whereas it transforms into the \( F_{\text{ddd}} \) structure with \( \theta \neq 90^\circ \) through eight trekking paths. The \( F_{\text{ddd}} \) structure takes six stable states with respect to the change of
Table 2. Density of states at the Fermi level $N(E_F)$, electron-phonon coupling constant $\lambda$, logarithmic-averaged phonon frequency $\omega_{\log}$, and superconducting critical temperature $T_c$ for $I4_1/amd$ and $Fddd$.

| $P$ (GPa) | Structure          | $N(E_F)$ (states/Ry/proton) | $\lambda$ | $\omega_{\log}$ (K) | $T_c$ (K) |
|-----------|--------------------|----------------------------|-----------|----------------------|-----------|
| 500       | $I4_1/amd$ ($\theta = 90^\circ$) | 0.2272                     | 2.2332    | 1706                 | 269.3     |
|           | $Fddd$ ($\theta = 92.88^\circ$) | 0.2391                     | 2.0774    | 1743                 | 263.2     |
| 600       | $I4_1/amd$ ($\theta = 90^\circ$) | 0.2288                     | 2.6920    | 1610                 | 280.8     |
|           | $Fddd$ ($\theta = 91.42^\circ$) | 0.2241                     | 2.5663    | 1477                 | 251.5     |

The angle $\theta$: 91.2°, 91.8°, 92.6°, 95.4°, 96.8°, and 102.4°. The enthalpy differences among them are less than 0.4 mRy/proton. In addition, two trekking paths lead to $Cmca-4$ with the molecular structure as shown in Fig. 2 (a). The other trekking paths lead to unstable structures obtained by disorderly freezing of H atoms in the course of the trekking, on which we have no further discussion in this paper. The transformation into multiple $Fddd$ structures was also obtained at 600 GPa. 11 trekking paths lead to the $Fddd$ structures, which show five stable $\theta$ values, 91.5°, 92.9°, 94.5°, 97.6°, and 101.2°. The number of the stable $\theta$ values including $\theta = 90^\circ$ decreases from seven to five by pressurization from 500 to 600 GPa, which indicates that the potential wells get to be shallow with the pressurization and few local minima of the potential surface disappear. In addition, the potential barriers between $I4_1/amd$ and $Fddd$ are easily surmounted by few trekking steps. These results of the PEST simulations suggest that in metallic hydrogen crystal structure is softened with respect to the distortion of the angle $\theta$ and is easily fluctuated among the $I4_1/amd$ and $Fddd$ structures. The molecular $Cmca-4$ structure got to be unstable with pressurization and was not obtained by the structure search at 600 GPa.

We investigated the superconductivity of $I4_1/amd$ and $Fddd$ (Table 2). Though the $I4_1/amd$ structure was not obtained by the PEST simulations at 600 GPa, its superconducting parameters were calculated at the pressure for comparison. The two structures are metallic at the pressures, and the values of the density of states at the Fermi level $N(E_F)$ are in good agreement with each other. At 500 GPa, $T_c$ shows the almost same value between the two structures: 269.3 K for $I4_1/amd$ and 263.2 K for $Fddd$. Both the structures are softened with pressurization to 600 GPa, and $\omega_{\log}$ decreases by 5.6% for $I4_1/amd$ and by 15.3% for $Fddd$. This pressure-induced phonon softening is related to the results of PEST, the shallowing of the potential wells. The parameter $\lambda$ increases by 0.46 for $I4_1/amd$ and 0.49 for $Fddd$ by the pressurization. However, there is a difference between the two structures with respect to the pressure dependence of $T_c$. The superconducting $T_c$ increases by 11 K for $I4_1/amd$, whereas it decreases by 12 K for $Fddd$. This is caused by the difference of the phonon softening magnitude between $I4_1/amd$ and $Fddd$. The phonon softening involves the decrease of $\omega_{\log}$ and the increase of $\lambda$. If the effect of the $\omega_{\log}$ decreasing is smaller than that of the $\lambda$ increasing, then $T_c$ is enhanced by the softening. On the other hand, if the effect of the $\omega_{\log}$ decreasing is larger, then $T_c$ is decreased. Thus, $I4_1/amd$ corresponds to the former and $Fddd$ the latter.

4. Conclusion

We explored crystal structures in metallic hydrogen by applying PEST to the supercell of the tetragonal $I4_1/amd$ structure including 128 atoms. The angle $\theta$, corresponding to a cell angle in the $ab$ plane and characterizing the structure, was easily changed from 90° through few trekking steps and the following angles were obtained as stable states: $\theta = 91.2^\circ$, 91.8°, 92.6°, 95.4°, 96.8°, and 102.4° at 500 GPa, and 91.5°, 92.9°, 94.5°, 97.6°, and 101.2° at 600 GPa. The
number of the stable states decreases by the pressurization from 500 to 600 GPa, which indicates that the potential wells get to be shallow with the pressurization. These results suggest that crystal structure is softened with respect to the distortion and is easily fluctuated among the $I4_1/amd$ and $Fddd$ structures at the pressures. Bonev et al. predicted the decrease of melting temperature in hydrogen above 90 GPa [23], and Eremets and Trojan observed it by laser heating diamond anvil cell experiments, in which the melting temperature takes the maximum value of $1050 \pm 60 \text{ K}$ at 160 GPa and decreases to $880 \pm 50 \text{ K}$ by compression to 146 GPa [24]. In 2013, Chen et al. investigated the melting of hydrogen in higher pressure region using first-principles path-integral molecular dynamics simulations and predicted the transition from the metallic atomic solid phase into a low-temperature metallic atomic liquid phase at around 800 GPa [25]. Therefore, our results could be interpreted as the sign of the pressure-induced melting of the atomic solid hydrogen reported earlier.

The superconducting $T_c$ shows 269.3 K for $I4_1/amd$ and 263.2 K for $Fddd$ at 500 GPa. These structures both show the pressure-induced phonon softening, and $\omega_{log}$ is decreased by 5.6% for $I4_1/amd$ and by 15.3% for $Fddd$. On the other hand, $\lambda$ is increased by 0.46 for $I4_1/amd$ and 0.49 for $Fddd$. As the results, $T_c$ is enhanced to 280.8 K for $I4_1/amd$, whereas it is decreased to 251.5 K for $Fddd$ owing to the effect of the larger phonon softening than that in $I4_1/amd$.

**Acknowledgments**

This work was supported by JSPS KAKENHI, Grant-in-Aid for Specially Promoted Research (26000006) and Grant-in-Aid for Young Scientists (B) (15K17707).

**References**

[1] Ashcroft N W 1968 *Phys. Rev. Lett.* 21 1748  
[2] McMahon J M and Ceperley D M 2011 *Phys. Rev. B.* 84 144515  
[3] McMahon J M and Ceperley D M 2012 *Phys. Rev. B.* 85 219902(E)  
[4] Howie R T, Guillaume C L, Scheler T, Goncharov A F and Gregoryanz E 2012 *Phys. Rev. Lett.* 108 125501  
[5] Loubeyre P, LeToullec R, Hausermann D, Hanand M, Hemley R J, Mao H K and Finger L W 1996 *Nature* 383 702  
[6] Cui L, Chen N H and Silvera I F 1995 *Phys. Rev. B* 51 14897  
[7] Hemley R J and Mao H K 1988 *Phys. Rev. Lett.* 61 857  
[8] Goncharov A F, Hemley R J, Mao H K and Shu J 1998 *Phys. Rev. Lett.* 80 101  
[9] Howie R T, Dalladay-Simpson P and Gregoryanz E 2015 *Nat. Mater.* 14 495  
[10] Eremets M I and Trojan I A 2011 *Nat. Mater.* 10 927  
[11] Pickard C J and Needs R J 2007 *Nature Physics* 3 473  
[12] Liu H, Wang H and Ma Y 2012 *J. Phys. Chem. C* 116 9221  
[13] McMahon J M and Ceperley D M 2011 *Phys. Rev. Lett.* 106 165302  
[14] Allen P B and Dynes R C 1975 *Phys. Rev. B* 12 905  
[15] Ishikawa T, Nagara H, Oda T, Suzuki N and Shimizu K 2014 *Phys. Rev. B* 90 104102  
[16] Ishikawa T, Suzuki N and Shimizu K 2014 *J. Phys.: Conf. Ser.* 500 162003  
[17] Ishikawa T 2014 *Comput. Mater. Sci.* 92 36  
[18] Giannozzi P *et al.* 2009 *J. Phys.: Condens. Matter* 21 395502-395520  
[19] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* 77 3865  
[20] Rappe A M, Rabe K M, Kaxiras E and Joannopoulos J D 1990 *Phys. Rev. B* 41 1227-1230  
[21] Allen M P and Tildesley D J (eds) 1989 *Computer Simulation of Liquids* (Oxford University Press)  
[22] Richardson C F and Ashcroft N W 1997 *Phys. Rev. Lett.* 78 118  
[23] Bonev S A, Schweger E, Ogitsu T and Galli G 2004 *Nature* 431 669  
[24] Eremets M I and Trojan I A 2009 *JETP* 89 174  
[25] Chen J, Li X Z, Zhang Q, Probert M I J, Pickard C J, Needs R J, Michaelides A and Wang E 2013 *Nat. Commun.* 4 2064