Structural and electronic properties of liquid InAs under pressure

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Abstract. The structural and bonding properties of liquid InAs under pressure are investigated by ab initio molecular-dynamics simulations. The calculated structure factors are in good agreement with the recent X-ray diffraction measurements over a wide range of pressure. It is shown that the pressure dependence of the spatial correlation between atoms depends on the species of atomic pairs reflecting the strength of the covalent bonding. A detailed investigation of the pair distribution functions confirms that different pressure-induced structural changes occur below and above 6∼10 GPa. It is suggested that such structural changes are related to the reduction of the covalent nature under pressure.

1. Introduction
The structural properties of liquid III-V compounds under pressure have been extensively investigated by an energy-dispersive x-ray diffraction method using a synchrotron radiation source [1, 2, 3]. It was suggested that, when the pressure is relatively lower \( P < 9 \) GPa, liquid InAs contracts almost uniformly with increasing pressure, while liquid GaSb and InSb contract nonuniformly. In this way, the contraction behavior of these liquids is different from each other, although they consist of the same group elements. It is very interesting to consider these structural differences under pressure in relation to the bonding properties of these liquids. For this purpose, theoretical studies based on first-principles calculations would be indispensable.

Recently, the structure of liquid InAs under higher pressure up to about 20 GPa has been measured by the x-ray diffraction experiments [4]. It was found that the contraction behavior changes qualitatively at about 9 GPa; the liquid contracts nonuniformly and the coordination number increases above 9 GPa, while there occurs a uniform compression below 9 GPa. In this study, we carry out ab initio molecular-dynamics (MD) simulations for liquid InAs under pressure to explain the pressure dependence of the structure observed experimentally.

2. Method of calculation
The electronic structure calculations were performed using the projector-augmented-wave (PAW) method [5] based on density functional theory within the generalized gradient approximation [6]. The plane-wave cutoff energies for the pseudo-wavefunctions and the pseudo-electron density were 11 and 70 ry., respectively. The energy functional was minimized using an
iterative scheme based on the preconditioned conjugate-gradient method [7]. The Γ point was used for the Brillouin zone sampling. We used a cubic supercell which contains 192 (96In+96As) atoms. The MD simulations were carried out at six thermodynamic states; the temperatures $T$ [K] and number densities $\rho$ [Å$^{-3}$] are $(T, \rho) = (1150, 0.0348)$, $(1100, 0.0395)$, $(1100, 0.0420)$, $(1350, 0.0452)$, $(1450, 0.0479)$, and $(1500, 0.0508)$. The pressures calculated for these states are 0.1, 3.0, 6.0, 10.6, 15.0, and 21.7 GPa, respectively. The equations of motion for the canonical ensemble were solved with a time step of $\Delta t = 3.1 \sim 3.6$ fs. The quantities of interest were obtained by averaging over about 12 ps after the initial equilibration taking about 6 ps.

3. Results and discussion

3.1. Structure factor

In Fig. 3, the calculated structure factors $S(k)$ (solid lines) are compared with the experimental results (open circles). It is seen that the pressure dependence of $S(k)$ is successfully reproduced by our $ab$ $initio$ simulations, although some small discrepancies are recognized above 10 GPa. The positions of the first and second peaks shift toward larger $k$ values in both $S(k)$. It is found from partial structure factors that the hump at about $k = 3.5$ Å$^{-1}$ is mainly contributed by the As-As correlation.

![Figure 1](image1.png)

**Figure 1.** Pressure dependence of the structure factor $S(k)$. The solid lines and open circles show the theoretical and experimental results, respectively.

![Figure 2](image2.png)

**Figure 2.** Pressure dependence of the partial pair distribution functions $g_{\alpha\beta}(r)$.

3.2. Pair distribution function

Figure 2 shows the pressure dependence of the partial pair distribution functions $g_{\alpha\beta}(r)$. The three correlations are largely different from each other at 0.1 GPa, and their pressure dependence is dissimilar to one another, which reflects the strength of the covalent bonding for each atomic pair. The nearest-neighbor distance $r_{\text{AsAs}}$ (the position of the first peak) for As-As is shortest among the three correlations up to 20 GPa, and increases slightly with increasing pressure, while
The pressure dependence of the distributions $Q_{\alpha}$ (see Fig. 3). These structural changes would be related to the fact that the covalent bonding for As-As pairs is stronger compared with those for In-In and In-As as will be shown later. At higher pressures, all $g_{\alpha\beta}(r)$ have similar profiles at larger $r \geq 4$ Å; they have minima at about 4.0 and 6.5 Å, and maxima at about 5.5 and 8.0 Å.

The pressure dependence of $r_{\alpha\beta}$ and the coordination number $N_{\alpha\beta}$ is shown in Fig. 3. We also calculated $r_X$ and $N_X$ from the total pair distribution function $g_X(r)$ obtained by the X-ray scattering factors to compare them with the experimental results. $N_{\alpha\beta}$ and $N_X$ were obtained by the integration of the radial distribution functions $G_{\alpha\beta}(r) = 4\pi r^2 \rho_\alpha g_{\alpha\beta}(r)$ and $G_X(r) = 4\pi r^2 \rho g_X(r)$, respectively, up to the positions of their respective first peaks. It is seen from Fig. 3 that different pressure-induced structural changes are observed below and above 6 ~ 10 GPa. Especially, $N_X$ has weak pressure dependence below 6 GPa, and it increases from about 6 to 8 around 10 GPa, which agrees qualitatively with the experimental observations [2, 4]. However, the pressure dependence of $N_{\alpha\beta}$ seems not to correspond to this behavior of $N_X$. This contradictory behavior can be understood from the profiles of $G_{\alpha\beta}(r)$ and $G_X(r)$ shown in Fig. 4. At lower pressures, the first-peak position of $G_{\text{InIn}}(r)$ is at larger distances than that for $G_X(r)$, and $G_{\text{InIn}}(r)$ does not contribute so much to form the first peak of $G_X(r)$. With increasing pressure, the first peak of $G_{\text{InIn}}(r)$ approaches that of $G_X(r)$, and the contribution of $G_{\text{InIn}}(r)$ becomes larger. Moreover, the minimum of $G_{\text{AsAs}}(r)$ becomes shallower with pressure, which also makes $N_X$ larger.

![Figure 3](image1.png)

**Figure 3.** (a) Pressure dependence of the first-peak positions $r_{\alpha\beta}$ of $g_{\alpha\beta}(r)$ and $r_X$ of $g_X(r)$. (b) Pressure dependence of the coordination numbers $N_{\alpha\beta}$ and $N_X$ obtained by the integration of $4\pi r^2 \rho_\alpha g_{\alpha\beta}(r)$ and $4\pi r^2 \rho g_X(r)$, respectively.

![Figure 4](image2.png)

**Figure 4.** Pressure dependence of the radial distribution functions $G_{\alpha\beta}(r) = 4\pi r^2 \rho_\alpha g_{\alpha\beta}(r)$ and $G_X(r) = 4\pi r^2 \rho g_X(r)$

### 3.3. Population analysis

To discuss the atomic charges and bonding properties, we utilized the population analysis [8]. Figure 5 shows the pressure dependence of the Mulliken charges $Q_\alpha$. With increasing pressure, $|Q_\alpha|$ increase. The increasing rate changes largely around 10 GPa corresponding to the structural variations. The pressure dependence of the distributions $P_{\alpha\beta}(\overline{O})$ of the bond-overlap population is displayed in Fig. 6. Below 6.0 GPa, $P_{\text{InAs}}(\overline{O})$ and $P_{\text{AsAs}}(\overline{O})$ have clear peaks at about $\overline{O} = 0.3$ and 0.6, respectively, while $P_{\text{InIn}}(\overline{O})$ have no peaks except at $\overline{O} = 0.0$. $P_{\text{AsAs}}(\overline{O})$ distributes...
over larger $\bar{O}$, which means that As-As pairs have stronger covalent bonding in the liquid. Above 10 GPa, the peaks of $P_{\text{InAs}}(\bar{O})$ and $P_{\text{AsAs}}(\bar{O})$ become unclear. This behavior of $Q_\alpha$ and $P_{\alpha\beta}(\bar{O})$ reflects the fact that the covalency becomes weak under pressure. The structural changes described in the previous subsection are considered to be related to the reduction of the covalent nature in the liquid.

![Figure 5](image1.png) ![Figure 6](image2.png)

**Figure 5.** (a) Pressure dependence of the Mulliken charges $Q_\alpha$.

**Figure 6.** Pressure dependence of the distribution $P_{\alpha\beta}(\bar{O})$ of the bond-overlap population.

4. Summary
The structural and bonding properties of liquid InAs under pressure have been investigated by *ab initio* molecular-dynamics simulations. We have shown that the calculated structure factors $S(k)$ are in good agreement with the recent X-ray diffraction measurements. The pressure dependence of the structure has been discussed based on the detailed investigation of the pair distribution functions. The population analysis has been utilized to examine the atomic charges and bonding properties.

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References
[1] Hattori T, Tsuji K, Taga N, Takasugi Y and Mori T 2003 *Phys. Rev. B* **68** 224106
[2] Hattori T, Kinoshita T, Narushima T and Tsuji K 2004 *J. Phys. Condens. Matter* **16** S997
[3] Hattori T, Kinoshita T, Taga N, Takasugi Y, Mori T and Tsuji K 2005 *Phys. Rev. B* **72** 064205
[4] Hattori T and Tsuji K *private communication*
[5] Böchl P E 1994 *Phys. Rev. B* **50** 17953
[6] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[7] Shimojo F, Kalia R K, Nakano A and Vashishta P 2001 *Comp. Phys. Comm.* **140** 303
[8] Shimojo F, Hoshino K and Zempo Y 2003 *J. Phys. Soc. Jpn.* **72** 2822