Ab initio molecular-dynamics study of pressure-induced structural change in liquid cadmium telluride

Y Miyata, F Shimojo, T Sugahara, and M Aniya
Department of Physics, Kumamoto University, Kumamoto 860-8555, Japan
E-mail: 061d8079@atud.kumamoto-u.ac.jp

Abstract. The pressure dependence of structural and electronic properties of liquid CdTe is studied by means of ab initio molecular-dynamics simulation. It is confirmed that there occur drastic structural changes in two pressure regions, 1.2 – 3.1 and 5.9 – 9.7 GPa. It is found that these structural changes are strongly related to like atom correlations. The Cd-Cd and Te-Te correlations appear above 3.1 and 9.7 GPa, respectively, in the first coordination shell. The pressure dependence of Mulliken charges is discussed in relation to that of the structure.

1. Introduction

III-V and II-VI compounds have a partially covalent and partially ionic bonding between atoms. At ambient pressure, the solid phases [1] of these compounds have a tetrahedrally coordinated structure (zinc-blende or wurtzite). It is known that the sequence of pressure-induced structural transformations in solids depends on ionicity. In small ionicity compounds (GaSb, InSb, InAs, etc.), the tetrahedrally coordinated structure transforms into a five-fold coordinated structure (β-tin) before a six-fold coordinated structure (rock-salt) appears. On the other hand, large ionicity compounds (CdTe, ZnSe, AgI etc.) change their structures from the tetrahedrally coordinated structure to the six-fold coordinated structure directly.

It is natural to consider that a similar sequence of structural changes would occur in the liquid phases under pressure. Hattori et al. [2] have examined the pressure dependence of the structural properties of liquid CdTe by X-ray diffraction experiments. They found that the structure of liquid CdTe exhibits drastic changes in two pressure regions, 1.8 – 3.0 and 7.0 – 9.0 GPa, which means that there exist at least three stable liquid forms. They explained that the lowest- and intermediate-pressure forms have a similar local structure to the crystalline counterparts, while the highest-pressure form has a different local structure form that in the crystal. To investigate the pressure-induced structure changes in more detail, computer simulations based on first principles theory would be useful. So far, the structure of liquid CdTe at ambient pressure has been studied by first principles calculations [3, 4]. However, no theoretical study on the pressure dependence has been reported. In this paper, we investigate the structure of liquid CdTe under pressure in detail by ab initio molecular-dynamics (MD) simulations. The purposes of our study are to compare the calculated structure with the experiments and to clarify the detailed mechanism of compression of the liquid under pressure.

2. Method of calculation

We used the projector-augmented-wave (PAW) method [5] to calculate the electronic structure based on density functional theory (DFT). The exchange-correlation energy was treated by the generalized gradient approximation (GGA) [6]. The electronic pseudo-wavefunctions and the pseudo-charge
density were expanded in plane waves with cut off energies of 13 and 90 Ry, respectively. The cubic supercell contains 192 atoms (96 Cd + 96 Te). The MD simulations were carried out for several pressures from 0.5 to 19.5 GPa. The time step was $\Delta t = 3.6$ fs. The $\Gamma$ point was used for the Brillouin zone sampling. The quantities of interest were obtained by averaging over 14.4 ps after the initial equilibration taking at least 1.8 ps.

3. Results and discussion

3.1. Structure factors

Figure 1 shows the pressure dependence of the structure factor $S(k)$ for liquid CdTe. The solid lines and open circles show the calculated and experimental $S(k)$, respectively. It is seen that the calculated results are in good agreement with experiments in a wide range of pressure. Below 1.2 GPa, there is a plateau from 2 to 3 Å$^{-1}$ in the profile of $S(k)$. At 3.1 GPa, there appears a peak at about 2.3 Å$^{-1}$ followed by a shoulder around 3 Å$^{-1}$, and the profile of $S(k)$ is clearly different from those below 1.2 GPa. We see from the partial structure factors that the appearance of the first peak comes mainly from the Cd-Cd correlation. Up to 5.9 GPa, the first peak shifts toward larger $k$ values slightly, and the peak height is almost unchanged. However, upon further compression up to 9.7 GPa, the first peak becomes higher, and its position shifts from 2.3 to 2.4 Å$^{-1}$. These changes in the first peak originate mainly from the Te-Te correlation. Also, the shoulder disappears. Up to 19.5 GPa, no drastic changes are observed. In this way, liquid CdTe exhibit two drastic structural changes in narrow pressure ranges of 1.2-3.1 and 5.9-9.7 GPa.

![Figure 1](image)

**Figure 1.** The pressure dependence of the structure factor $S(k)$ of the liquid CdTe. The calculated and experimental [2] results are shown by the solid lines and open circles, respectively.
3.2. Pair distribution functions

The partial pair distribution functions, $g_{\alpha\beta}(r)$, for the liquid CdTe are shown in figure 2. At 0.5 GPa, $g_{\text{Cd-Te}}(r)$ has the clear first peak at about 2.9 Å, around which there are no peaks in $g_{\text{Cd-Cd}}(r)$ and $g_{\text{Te-Te}}(r)$. In $g_{\text{Te-Te}}(r)$, a broad peak exists at about 3.8 Å. When the pressure is increased to 3.1 GPa, a peak appears in $g_{\text{Cd-Cd}}(r)$ near the first-peak position of $g_{\text{Cd-Te}}(r)$, and it grows with increasing pressure. The broad peak in $g_{\text{Te-Te}}(r)$ shifts to smaller $r$ gradually up to 9.7 GPa, and it keeps its position at about 3.5 Å under further compression. The profile of $g_{\text{Te-Te}}(r)$ above 9.7 GPa is dissimilar to that below 7.6 GPa, and has a clear peak. It is found from these results that the two drastic structural changes are related to the appearances of short-range correlations between like atoms.

To compare the calculated real space correlations with the experimental observations, we calculated the total pair distribution function $g_X(r)$ obtained from $g_{\alpha\beta}(r)$ using the X-ray scattering factors. We confirmed that the calculated $g_X(r)$ is in reasonably good agreement with the experimental results. Also, we obtained the coordination numbers $N_X$ by the integration of $4\pi r^2 \rho g_X(r)$ up to the peak position. We saw that the pressure dependence of $N_X$ agrees qualitatively with the experimental observations [2].

![Figure 2. Pressure dependence of the partial pair distribution functions $g_{\alpha\beta}(r)$. The solid, dashed, and dotted lines show $g_{\alpha\beta}(r)$ for Cd-Te, Cd-Cd, and Te-Te, respectively.](image)

3.3. Mulliken charges

The Mulliken charge is a quantity to measure the ionicity of atoms. Figure 3 shows the pressure dependence of the Mulliken charges $Q_\alpha$ averaged over $\alpha$-type atoms. We see that $Q_\alpha$ have three pressure regions; the lowest-pressure region of 0.5-3.1 GPa, the intermediate-pressure region of 3.1-7.6 GPa, and the highest-pressure region of 7.6-19.5 GPa. In the lowest-pressure region, $|Q_\alpha|$ decreases with increase pressure. In the intermediate-pressure region, the decreasing rate of $|Q_\alpha|$ becomes smaller. In the highest-pressure region, $|Q_\alpha|$ increases with compression. This pressure dependence of $Q_\alpha$
corresponds to those of $S(k)$ and $g(r)$, which means that the structural changes are accompanied by the changes of the chemical properties.

Figure 3. Pressure dependence of the averaged Mulliken charges $Q_{\alpha}$ for Cd and Te atoms.

4. Conclusion
The pressure dependence of the structure and electronic states of liquid CdTe has been investigated by ab initio molecular-dynamics simulations. The structure factor is well reproduced in a wide range of pressure. It has been confirmed that liquid CdTe exhibit two drastic structural changes in narrow pressure ranges of 1.2-3.1 and 5.9-9.7 GPa. These structural changes are strongly related to like atom correlations. Below 1.2 GPa, there exist almost no short-range correlations between like atoms. Above 3.1 GPa, Cd-Cd correlations appear in the first coordination shell. Moreover, above 9.7 GPa, Te-Te correlations appear in the first coordination shell. The pressure dependence of Mulliken charges corresponds very well to that of the structure.

Acknowledgments
The authors acknowledge the financial support of a Grant-in-Aid for Scientific Research on Priority Area, “Nanoionics (439)” from the MEXT, Japan. The authors thank the Supercomputer Center, ISSP, University of Tokyo for the use of facilities.

References
[1] Nelmes R J, McMahon M I, Wright N G, and Allan D R 2006 Phys. Rev. B 51 15723
[2] Hattori T, Kinoshita T, Narushima T, Tsuji K, and Katayama Y 2006 Phys. Rev. B 73 054203
[3] Godlevsky V V, Derby J J, and Chelikowsky J R 1998 Phys. Rev. Lett. 81 4959
[4] Godlevsky V V, Jain M, Derby J J, and Chelikowsky J R 1999 Phys. Rev. B 60 8640
[5] Blöchl P E 1994 Phys. Rev. B 50 17953
[6] Perdew J P, Burke K, and Ernzerhof M 1996 Phys. Rev. Let.. 77 3865