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Pressure-induced drastic structural change in liquid CdTe

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We investigate the structure of liquid CdTe at pressures up to 6 GPa by synchrotron x-ray diffraction. The structure factor, $S(Q)$, and the pair distribution function, $g(r)$, change drastically within a small pressure interval of about 1 GPa (between 1.8 and 3 GPa). The $S(Q), g(r)$, and other structural parameters, such as the average coordination number, CN, and the ratios of peak positions in $S(Q)$ or $g(r)$, reveal that the change originates from the pressure-induced modification in the local structure from the zinc-blende-like form into the rocksaltlike one. The liquid CdTe shows a high-pressure behavior similar to that in the crystalline counterpart in terms of the sharpness of the structural change and the high-pressure sequence in the local structure.

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Crystalline matter often shows pressure-induced first-order phase transitions accompanied by drastic structural changes. On the contrary, it is believed that liquid matter does not show such transitions due to the absence of the periodicity in the atomic arrangement and due to the resultant large degree of freedom in the structure. The transition is unlikely to occur especially in the liquids in a thermodynamically stable state due to the large structural fluctuation caused by thermal activation, although the transition may occur in metastable states, such as supercooled liquid[1] and an amorphous state.[2] However, the recent discoveries of the liquid-liquid phase transition (LLT) in several substances[3,4] contradict this view. Now much attention has been paid for the existence of the first-order phase transition in liquid phases.[5–8]

The LLT is predicted to take place for several substances, such as Si, Ge, C, S, Se, Te, I, SiO_2, GeO_2, and H_2O (Ref. 9). Among these, tetrahedrally bonded materials, such as light group 14 elements and liquid III-V compounds, are the most probable candidates because of their open local structure. Indeed, the crystalline counterparts show the first-order phase transition from the fourfold-coordinated diamond/zinc-blende structure into the highly coordinated β-Sn and/or the related structures, accompanied by a large volume change. In spite of the prediction of LLT for these substances, none of the clear experimental evidence has been shown. One of the reasons is that, in these liquids, the drastic structural changes corresponding to those observed in the crystalline phases are already completed at ambient pressure. In fact, liquids of Si, Ge, and GaSb are denser than the crystalline phases at ambient pressure, and the structural parameters, such as the structure factor $S(Q)$, the pair distribution function $g(r)$, and the coordination number (CN) are known to be similar to those in the high-pressure crystalline form (β-tin structure), rather than those in the ambient form (diamond/zinc-blende structure).[10] Contrary to these substances, several liquid II-VI compounds, such as CdTe and ZnSe, are known to have the zinc-blende-like local structure at ambient pressure.[11–13] Since the crystalline counterparts show a first-order phase transition from the zinc-blende structure into the highly coordinated rocksalt and the related structures under pressure,[14,15] these liquids are expected to show LLT on the application of pressure. On the basis of this motivation, we investigate the pressure dependence of the structure of liquid CdTe (l-CdTe) by synchrotron x-ray diffraction.

High-pressure and high-temperature conditions were generated with a multianvil high-pressure apparatus, MAX80, installed on a bending magnet beam line, NE5C at PF-AR in KEK. The reagent graded CdTe with a purity of 99.9% was finely grounded and mixed with boron nitride so that μt becomes equal to 2 against an incident x-ray beam of 40 keV to avoid too much absorption of x ray by the sample. Here μ and t are an average absorption coefficient and the sample thickness, respectively. The cell assembly used in this study was almost the same as that described in Ref. 16. The pellet of the mixture was enclosed in a container made of boron nitride. The container was encased in a cubic-shaped pressure transmitting medium made of boron-epoxy resin mixture. The temperature was increased with a graphite tube heater surrounding the sample container. The generated temperature was estimated from the electric power applied to the heater, where the temperature-electric power relation was determined beforehand. The pressure was determined from the lattice parameter of magnesia put in the high-pressure cell on the basis of the equation of state.[17] The uncertainties of the temperature and pressure were within 50 K and 0.1 GPa, respectively.

The structure of l-CdTe was investigated by an energy-dispersive x-ray diffraction (EDX) method. The melting of the sample was judged from the appearance of the halo pattern, as well as the disappearance of all the Bragg peaks. The x-ray diffraction pattern of l-CdTe was taken at several 2θ angles of 3°, 4°, 5°, 6°, 8°, 10°, 12°, 15°, and 20° to obtain the $S(Q)$ over a wide Q region up to about 20 Å^{-1}. The structure of l-CdTe was investigated at six pressure points at 50 K above the melting points at each pressure. We observed no degeneration of the sample, such as the reaction to the sample container and the preferential evaporation of Cd or Te. The diffraction intensity in the energy range typically between 40 and 120 keV was used in the analyses. The diffraction profiles taken at several 2θ angles were normalized and connected to each other for obtaining $S(Q)$ (Ref. 18). The detailed procedures are described in Ref. 19. The $g(r)$ was obtained by Fourier transformation of $S(Q)$ (Ref. 18). We used Kaplow's method to minimize the error introduced in this procedure.[20] The number density of the liquid, ρ_0, was estimated from the volume of the crystalline phase just before the melting and the volume change on melting, which

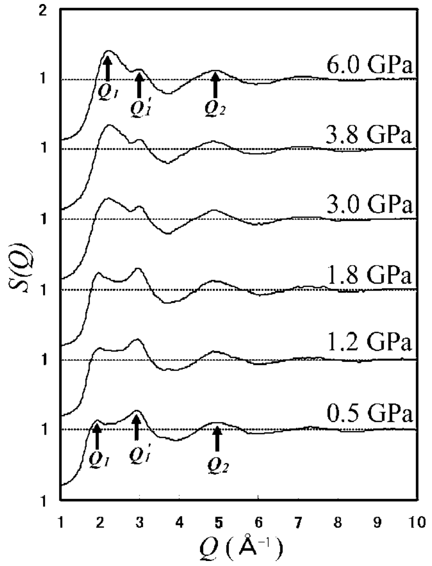

FIG. 1. Structure factor of *l*-CdTe at high pressures. Here we show the profile only up to $Q=10$ Å^{-1} to observe the pressure dependence easily. For making $g(r)$, we used the data in the Q region up to 13 Å^{-1}.

was estimated from the slope of the melting curve on the basis of Clausius-Clapeyron equation. The average CN (Ref. 21) was obtained from the radial distribution function RDF $[=4\pi r^2\rho_0 g(r)]$. The error of CN was within 10%.

The pressure dependence of the $S(Q)$ for *l*-CdTe is shown in Fig. 1. At pressures below 1.8 GPa, $S(Q)$ has the first peak, the hump, and the second peak at wave numbers of 2.0 , 2.9, and 5.0 Å^{-1}, respectively. Hereafter, the respective positions are represented by Q_1, Q_1', and Q_2. The $S(Q)$ below 1.8 GPa is almost the same as that at ambient pressure.[11] With increasing pressure from 0.5 to 1.8 GPa, the $S(Q)$ shifts toward high Q values without changing the shape of the profile. However, on further compression up to 3.0 GPa, the shape of the profile drastically changes: the first peak and the hump disappear and new peaks appear at 2.25 and 3.0 3.0 Å^{-1} (Ref. 22). By further compression, the $S(Q)$ shifts toward high Q values without changing the shape of the profile again. To confirm the sharpness of the change quantitatively, the pressure dependence of the ratio in the wave numbers between the first and second peaks, Q_2/Q_1, and that in the wave numbers between the hump and the first peak, Q_1'/Q_1, is shown in Fig. 2. Both ratios jump between 1.8 and 3.0 GPa. These results strongly suggest that the structure of *l*-CdTe drastically changes within the pressure interval of about 1 GPa. The same conclusion is also obtained from the pressure dependence of $g(r)$ (Fig. 3). With increasing pressure up to 1.8 GPa, no marked change in the shape of the profile was observed. On the other hand, with increasing pressure up to 3.0 GPa, the shape of the profile drastically changes: the second and third peaks abruptly shift toward small r values and the height of the second peak decreases. The r value of the first peak abruptly increases by 2% (Table I). The ratio of the positions at the first and second peaks, r_2/r_1, jumps between 1.8 and 3.0 GPa (Table I). The average CN also jumps from 3.7 to 4.8 in this pressure interval (Fig. 2). These findings suggest that the structure of *l*-CdTe changes from a low-coordinated form into a highly coordinated one within a relatively small pressure interval (less than 1.2 GPa).

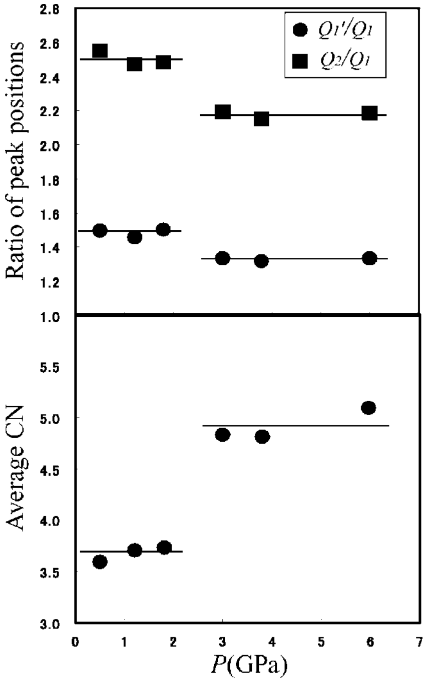

FIG. 2. Ratio of peak positions in $S(Q)$ and the average CN for *l*-CdTe at high pressures. Thin lines are only guides for the eye.

To reveal the microscopic origin of the structural change, the local structures of *l*-CdTe are identified. It is natural to consider that the low- and high-pressure forms in *l*-CdTe are similar to those in the crystalline CdTe (*c*-CdTe), that is, the zinc-blende and the rocksalt structures. Therefore, we compare the structure of *l*-CdTe with that of the disorder materials with the zinc-blende-like and rocksaltlike local structures. As for the typical disordered materials with the zinc-blende-

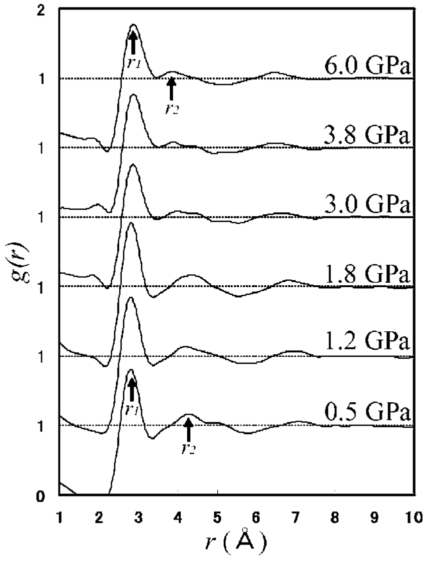

FIG. 3. Pair distribution function of *l*-CdTe at high pressures.

TABLE I. Structural information on *l*-CdTe at high pressures.

P (GPa)	Q_1 (Å^{-1})	Q_1' (Å^{-1})	Q_2 (Å^{-1})	Q_1'/Q_1	Q_2/Q_1	r_1 (Å)	r_2 (Å)	r_2/r_1	CN
0.5	1.95	2.92	4.98	1.50	2.55	2.81	4.29	1.53	3.6
1.2	2.01	2.93	4.96	1.46	2.47	2.82	4.27	1.52	3.7
1.8	1.97	2.96	4.90	1.50	2.48	2.82	4.34	1.54	3.7
3.0	2.23	2.99	4.89	1.34	2.19	2.88	4.01	1.39	4.8
3.8	2.26	2.99	4.87	1.32	2.15	2.89	3.90	1.35	4.8
6.0	2.24	3.00	4.91	1.34	2.19	2.89	3.87	1.34	5.1

like and rocksaltlike local structures, the amorphous Si (*a*-Si) (Ref. 23) and liquid NaCl (*l*-NaCl) (Ref. 24) are selected, respectively.[25] The comparison of the $S(Q)$ is shown in Fig. 4, where the horizontal axes for $S(Q)$ of *a*-Si and *l*-NaCl are scaled so that the positions of the peaks become almost the same as those for *l*-CdTe. The figure shows that the shape of the profile of $S(Q)$ for the low-pressure form of *l*-CdTe is similar to that for *a*-Si not only in the relative position of the peaks and the hump but also in the relative height of the peaks, although the peaks for *l*-CdTe are much lower and broader due to the larger structural fluctuation in the liquid state. On the other hand, the shape of the profile of $S(Q)$ for the high-pressure form of *l*-CdTe is similar to that for *l*-NaCl: the positions of the first peak and the hump are relatively close and the height of the first peak is much smaller than the typical value for simple liquid metals. The CNs for the low- and high-pressure forms in *l*-CdTe show a good agreement with those for the zinc-blende-type (CN=4) and the rocksaltlike local structures (CN=6), respectively.[26] These findings suggest that the local structure in *l*-CdTe changes from the zinc-blende-like form into the rocksaltlike one on application of pressure.

Next, let us compare the pressure-induced change in *l*-CdTe with that in other liquids. We can find that the structural change in *l*-CdTe is much sharper than that in the liquids of tetrahedrally bonded materials. The liquid light group 14 elements and liquid III-V compounds are known to change their local structures gradually by application of pressure.[19,27,28] The pressure interval of the structural change for *l*-Si is within 6 GPa (Ref. 27), that for *l*-Ge is more than 10 GPa (Ref. 28), and that for *l*-GaSb is more than 20 GPa (Ref. 19). The value for *l*-CdTe (less than 1.2 GPa) is much smaller than these values. Although a relatively sharp structural change was reported in liquid I-VII compounds, the structural change is less sharp compared to that in *l*-CdTe [ΔP≈ several gigapascals for liquid KCl (Ref. 29)]. The sharp structural change in *l*-CdTe is considered to be attributed to the different nature of the chemical bonding between the low- and high-pressure forms. In *l*-CdTe, the nature of the chemical bonding changes from a covalent type into an ionic one during the structural change. The coexistence of two local structures with different chemical bonding in liquid increases the potential energy, and therefore, the coexistence is not preferable. On the other hand, in the structural changes in *l*-Ge, *l*-GaSb, and *l*-KCl, the nature of the chemical bonding does not change[19,29,30] (from a metallic type into a metallic one or from an ionic type into an ionic one). In that case, the coexistence of low- and high-pressure forms is realized (i.e., the structural change occurs over a wide pressure region). Besides the sharpness of the structural change, *l*-CdTe shows a unique character in the onset pressure of the structural change. Generally, in a liquid state, the local structure starts to change at pressure much lower than that for the corresponding transition in the crystalline phase.[31] However, in *l*-CdTe, the onset pressure is almost the same as that in *c*-CdTe.

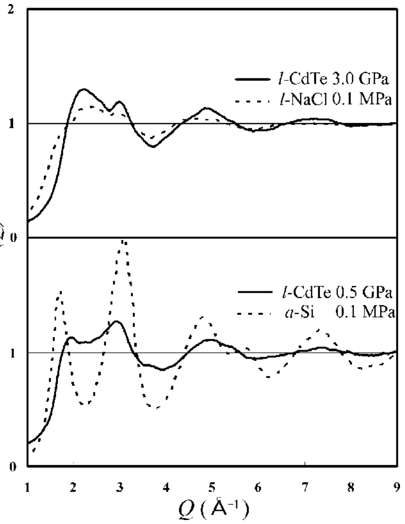

FIG. 4. Comparison of the $S(Q)$ for *l*-CdTe with those for *a*-Si (Ref. 23) and *l*-NaCl (Ref. 24).

Even though the drastic structural change between two liquid forms has been reported already in *l*-P, it differs from that observed in *l*-CdTe in terms of the connectivity of the local structures; in *l*-CdTe the local structure changes from a three-dimensional network into another three-dimensional one, while in *l*-P the structure changes from a molecular liquid into a polymerized one.

So far, the existence of the LLT has been suggested for the liquid of tetrahedrally bonded materials, such as Si, Ge, and C (Ref. 9). However, there are few studies showing clear evidence for LLT on the basis of the (microscopic) structural information. The present study indicates the LLT-like behavior on the basis of the microscopic structural information. It is, however, still unknown whether the observed structural change is a true first-order type or not. Our recent results are suggestive of the continuous structural change while the pressure interval is very small. In spite of the uncertainty, the present results will help us understand the nature of LLT and amorphous-amorphous phase transitions observed in other materials, such as amorphous ice[32] and silica glass.[33]

In summary, we find the drastic pressure-induced structural change in *l*-CdTe. The structure change is completed within the small pressure interval of 1.2 GPa. The drastic change originates from the change in the local structure from the zinc-blende-like form into the rocksaltlike one. The high-pressure sequence in the local structure and the onset pressure of the structural change is common between the liquid and the crystalline phases. This is a unique example showing the drastic structural change in the liquids of tetrahedrally bonded materials.

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$$\mathrm{CN} = c_{\mathrm{Cd}}\frac{f_{\mathrm{Cd}}^2}{\langle f\rangle^2}\mathrm{CN}_{\mathrm{CdCd}} + c_{\mathrm{Cd}}\frac{f_{\mathrm{Cd}}f_{\mathrm{Te}}}{\langle f\rangle^2}\mathrm{CN}_{\mathrm{CdTe}} + c_{\mathrm{Te}}\frac{f_{\mathrm{Te}}f_{\mathrm{Cd}}}{\langle f\rangle^2}\mathrm{CN}_{\mathrm{TeCd}} + c_{\mathrm{Te}}\frac{f_{\mathrm{Te}}^2}{\langle f\rangle^2}\mathrm{CN}_{\mathrm{TeTe}}.$$

Here, $\mathrm{CN}_{\mathrm{ij}}$ is the number of j atoms around an i atom.

[22] A new hump is considered to appear at 3.0 GPa because the height for the hump discontinuously changes, although the position for the hump does not change significantly.

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[25] In discussing the shape of $S(Q)$, we must take the difference in the atomic scattering factor for chemical species into account because the total $S(Q)$ is the sum of the partial $S_{\mathrm{ij}}(Q)$ weighted by atomic scattering factors. However, the weight factors for $S_{\mathrm{ij}}(Q)$ in *l*-CdTe become almost the same as those in *l*-Si (i.e., unity) due to the small difference in the atomic scattering factor between Cd and Te. Therefore, the comparison in the shape of $S(Q)$ between *l*-CdTe and *a*-Si is meaningful. The comparison between *l*-CdTe and *l*-NaCl is also meaningful because the weight factors for $S_{\mathrm{ij}}(Q)$ of like-ion and unlike-ion pairs are almost the same between both liquids.

[26] The CN for the low- and high-pressure forms in *l*-CdTe are a little smaller than those for the zinc-blende-like and rocksaltlike local structures, respectively. It is attributed to the existence of voids in the liquid states (Ref. 35).

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