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Pressure dependence of the structure of liquid copper halides

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Abstract

X-ray diffraction of liquid CuI, CuBr and CuCl has been measured up to 19 GPa using synchrotron radiations. Static structure factor $S(Q)$ and pair distribution function $g(r)$ were obtained. For liquid CuI, CuBr and CuCl, $S(Q)$ and $g(r)$ change their shapes continuously with increasing pressure, indicating anisotropic compression of the local structures. The pressure dependence of the peak position ratio r_2/r_1 of $g(r)$ shows that Cu atoms are located in a tetrahedral site at low pressures and then in an octahedral site at high pressures in these liquid copper halides. At higher pressures, the local structure of liquid CuCl is similar to the intermediate structure between NaCl and CsCl structures. These results are compared with the pressure-induced structural transformation in the crystalline phase.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The pressure dependence of the local structure of liquid group 14 elements and liquid III–V compounds is different from that of the crystal. The structural change occurs continuously in a wide pressure width below the transition pressure of the crystal. Moreover, the local structure at high pressures is different from that of the crystal [1–6]. On the other hand, in liquid CdTe with large ionicity ($f_i = 0.717$) in the bonding between atoms a drastic structural transformation occurs in a narrow pressure width around the transition pressure of the crystal [7, 8]. Copper halides also have a large ionicity in the bonding: f_i is 0.692 for CuI, 0.735 for CuBr and 0.746 for CuCl. Their partial structure in the liquid phase is different from that of the typical ionic liquid such as liquid NaCl [9–14]. The Cu–Cu correlation penetrates into the first peak of the pair distribution function of copper–halogen atoms. The structure of the high pressure phase of tetrahedrally bonded materials depends on the ionicity in the bonding between atoms. Group 14 elements and III–V compounds with small ionicity transform from a zinc-blende structure to a beta-Sn structure, while I–VII compounds, II–VI compounds and some III–V compounds with large ionicity transform to an NaCl structure. At high temperatures, crystalline copper halides have several super ionic conducting phases, in which Cu atoms distribute with disordered structures [15]. In the

zinc-blende structure, halogen atoms form a fcc sublattice and copper atoms situated at the tetrahedral site form another fcc sublattice. There are eight tetrahedral sites in the zinc-blende structure and copper atoms enter four tetrahedral sites. In the NaCl structure, copper atoms are located in the octahedral site, forming another fcc sublattice. There are 12 sites in the fcc sublattice of halogen atoms; eight tetrahedral sites and four octahedral sites. In the alpha-AgI structure, halogen atoms form a bcc sublattice and copper atoms distribute among 24 tetrahedral sites with a disordered distribution.

It is interesting to measure the pressure dependence of the structure of liquid copper halides to see how the structural transformation occurs in the liquid phase and compare the results with those of crystals. X-ray diffraction was measured at high pressures up to 19 GPa for liquid CuI, liquid CuBr and liquid CuCl.

2. Experimental details

Pressure was generated by the cubic-anvil apparatus MAX80 installed on the AR–NE5C beamline at the Photon Factory, KEK, Japan and the double stage apparatus SPEED1500 installed on the BL04B1 beamline at SPring-8, Japan. By using synchrotron radiations with high brightness, high energy and small divergence, x-ray diffraction was measured

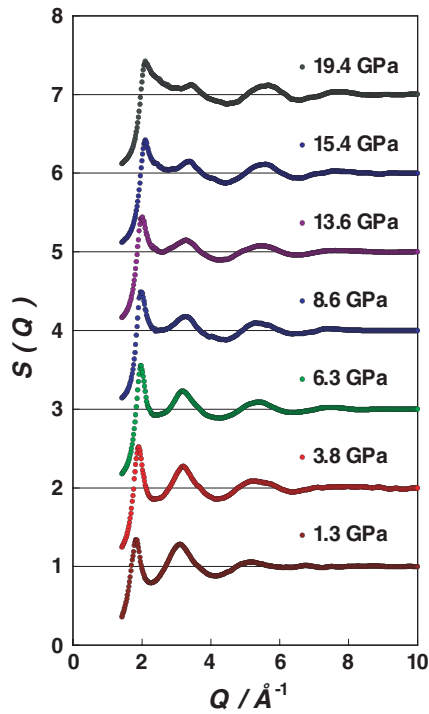


Figure 1. $S(Q)$ of liquid CuI at various pressures.

with an energy-dispersive method. A powdered mixture of crystalline sample and MgO was placed in an MgO capsule. Measurements were made at temperatures about 50 K above the melting point of each pressure. Energy-dispersive diffraction profiles were measured typically at 10 different scattering angles, 2θ , between 2.5° and 20° (MAX80) and between 3° and 15° (SPEED1500) with white x-rays of 30–140 keV. From the measured diffraction intensities, the static structure factors $S(Q)$ of liquid metals were deduced up to $Q = 17 \text{ \AA}^{-1}$ after some corrections. Details of the procedures are given elsewhere [16, 17].

3. Results and discussion

3.1. Liquid CuI

Figure 1 shows the static structure factor $S(Q)$ of liquid CuI at various pressures. At 1.3 GPa, there are peaks at 1.8 and 3.1 \AA^{-1} . With increasing pressure these peaks shift towards higher Q . Figure 2 shows the ratio Q_2/Q_1 , which indicates the anisotropy of the local structure of the liquid, as a function of pressure. Here, Q_1 and Q_2 are the positions of the first and the second peaks, respectively. The Q_2/Q_1 ratio decreases with increasing pressure. Above about 6 GPa the ratio is almost kept constant and remains at 2.7, which is still larger than the typical value, 1.86, for simple liquids. Above 6 GPa a new peak appears between 1.8 and 3.1 \AA^{-1} and its height increases with increasing pressure.

Figure 3 shows the pair distribution function $g(r)$ of liquid CuI at various pressures. The peak position of the first peak is almost kept constant with increasing pressure in spite of the volume contraction. Instead a remarkable shift of the

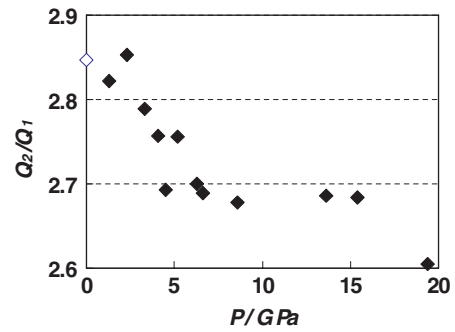


Figure 2. Q_2/Q_1 ratio of $S(Q)$ of liquid CuI as a function of pressure. Open square at ambient pressure [10] is shown for reference.

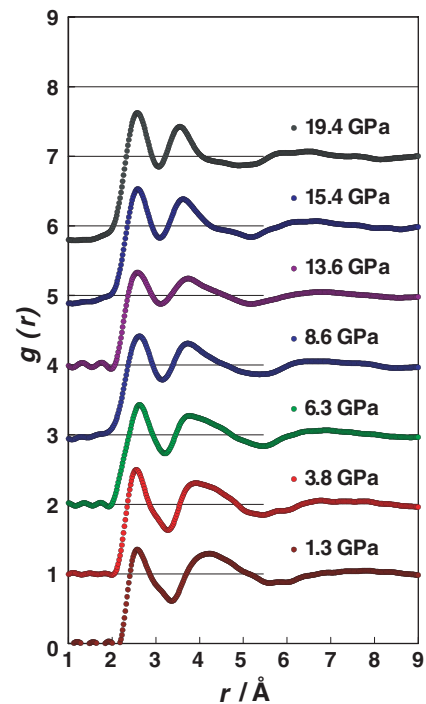


Figure 3. $g(r)$ of liquid CuI at various pressures.

second peak towards smaller r was observed with increasing pressure. This indicates the decrease of the bond angle of copper–halogen atoms. The ratio of r_2/r_1 is plotted in figure 4. When the copper atom locates in the tetrahedral site of the fcc sublattice of the anions (zinc-blende structure), the ratio of r_2/r_1 is 1.63. The ratio is 1.55 for the tetrahedral site of the bcc sublattice (alpha-AgI structure) and is 1.41 for the octahedral site of the fcc sublattice (NaCl structure). The coordination number of copper atoms is four in the zinc-blende structure and the alpha-AgI structure and six in the NaCl structure. The r_2/r_1 ratio of liquid CuI decreases from 1.64 at 1.3 GPa to 1.48 at 6 GPa. Above 6 GPa it gradually decreases and approaches the value of NaCl. In liquid CdTe, a drastic structural change occurs at about 2 GPa [7, 8]. The local structure of liquid below 2 GPa is similar to that of the zinc-blende structure with a coordination number of four and that above 2 GPa is similar to that of the NaCl structure with coordination number six. Similar structural change occurs in liquid AgI around

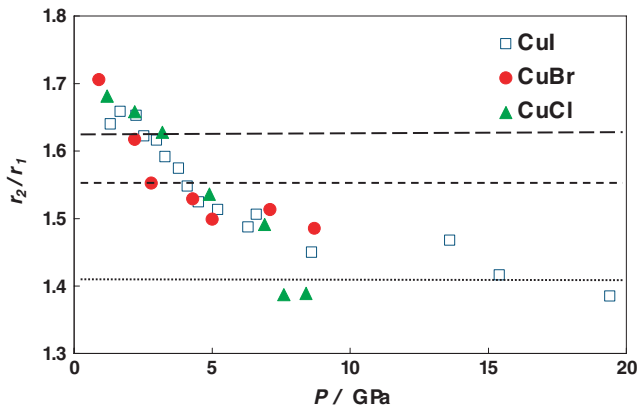


Figure 4. Pressure dependence of r_2/r_1 of liquid CuI, liquid CuBr and liquid CuCl. The chain line: the value for the tetrahedral site in the fcc sublattice (zinc-blende structure). The dashed line: the value for the tetrahedral site in the bcc sublattice (alpha-AgI structure). The dotted line: the value for the octahedral site in the fcc sublattice (NaCl structure).

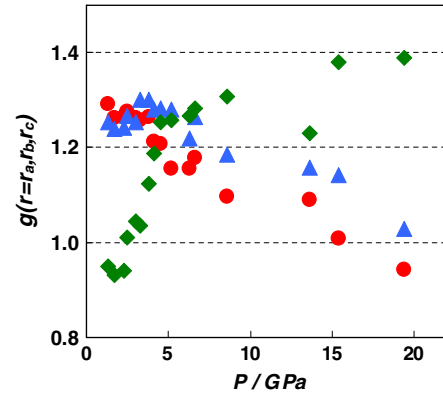


Figure 6. The values of $g(r)$ at $r_a = 1.63 r_1$ (circle), $r_b = 1.55r_1$ (triangle) and $r_c = 1.41r_1$ (square) of liquid CuI.

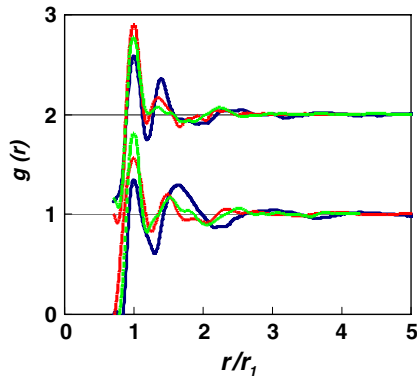


Figure 5. Comparison of $S(Q)$ of liquid CuI with other liquids. Upper; $g(r)$ of liquid CuI at 19.4 GPa (solid line) is similar to those of liquid AgI at 4.6 GPa (dotted line) and liquid CdTe at 3.8 GPa (dashed line). Lower; $g(r)$ of liquid CuI at 1.3 GPa (solid line) is different from those of liquid AgI at 1.4 GPa (dotted line) and liquid CdTe at 0.5 GPa (dashed line).

2 GPa [18]. In figure 5, $g(r)$ s of liquid CuI are compared with those of liquid CdTe and liquid AgI. The local structure of liquid CuI at 19.4 GPa is similar to that of an NaCl-like structure with coordination number six. On the other hand, that of liquid CuI at 1.3 GPa is different from those of zinc-blende-like structures.

As the value of $g(r)$ at the first minimum increases with increasing pressure, it is difficult to evaluate the coordination number from the integration of the radial distribution function. Therefore, to analyze the local structure, the value of $g(r)$ at $1.41r_1$, $1.55r_1$ and $1.63r_1$ are plotted in figure 6. Below 6 GPa, the value at $1.41r_1$ for a tetrahedral site of the fcc sublattice and the value at $1.55r_1$ for a tetrahedral site of the bcc sublattice have large values and begin to decrease at about 6 GPa. Above 6 GPa, the value at $1.63r_1$ for an octahedral site of the fcc sublattice has a large value, suggesting a six-fold coordination structure.

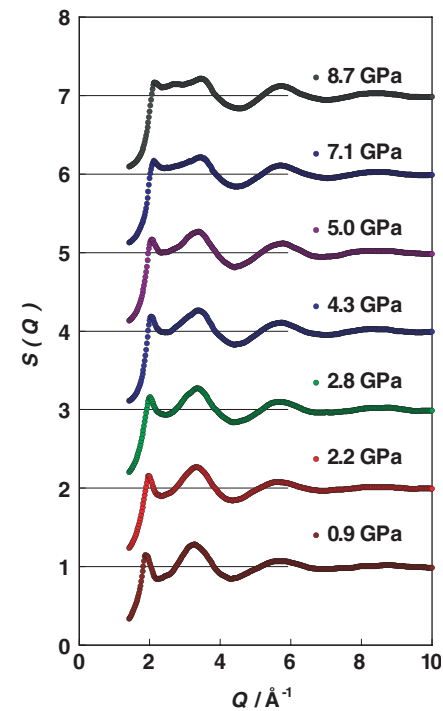


Figure 7. $S(Q)$ of liquid CuBr at various pressures.

With increasing pressure in the crystalline phase, the structure of CuI just below the melting temperature changes sluggishly from superionic conducting phase with an fcc sublattice of anions to an alpha-AgI structure with a bcc sublattice of anions, and then disordered rocksalt structure with an fcc sublattice of anions [15]. The wide pressure width of the structural transformation in liquid CuI should correspond to the stability of the crystal structures with a disordered distribution of copper ions.

3.2. Liquid CuBr

Figure 7 shows $S(Q)$ of liquid CuBr at various pressures. At 0.9 GPa, there are peaks at 1.9 and 3.3 \AA^{-1} . With increasing pressure these peaks shift towards higher Q . With increasing

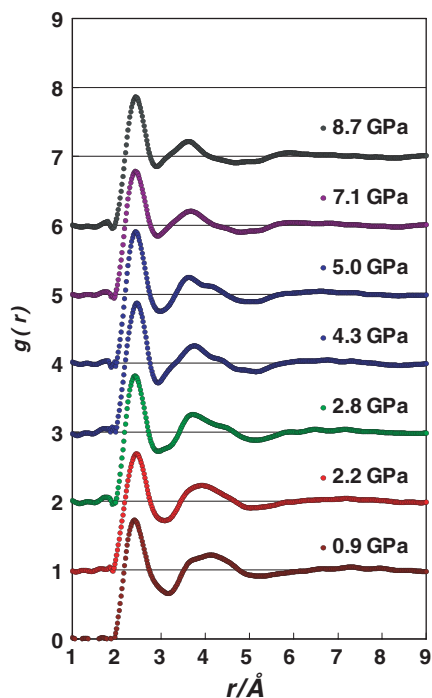


Figure 8. $g(r)$ of liquid CuBr at various pressures.

pressure a new peak appears between 1.9 and 3.3 \AA^{-1} and its height increases with increasing pressure, similar to the liquid CuI. Figure 8 shows $g(r)$ of liquid CuBr at various pressures. The peak position of the first peak is almost kept constant with increasing pressure in spite of the volume contraction. Instead a remarkable shift of the second peak towards smaller r was observed with increasing pressure. This indicates the decrease of the bond angle of copper–halogen atoms. This pressure dependence of the local structure is similar to that of liquid CuI. In figure 4, the ratio of r_2/r_1 of liquid CuBr is also plotted. The value of the ratio decreases from the value for tetrahedral structures but is still larger than the value for the NaCl structure. The coordination number deduced from the integration of the first peak of the radial distribution function increases from 2.6 at 0.9 GPa to 3.5 at 8.7 GPa.

3.3. Liquid CuCl

Figure 9 shows $S(Q)$ of liquid CuCl at various pressures. At 1.2 GPa, there are peaks at 2.0 and 3.4 \AA^{-1} . In liquid CuCl, two peaks are broad and overlap, in contrast to those of liquid CuI and liquid CuBr. With increasing pressure the heights of the two peaks become small and a new peak appears between two peaks and its height increases with increasing pressure. Above 13.1 GPa, the peak position is almost kept constant but its height changes with increasing pressure. This behavior suggests the different pressure dependence of the local structure above 13.1 GPa. Figure 10 shows $g(r)$ of liquid CuCl at various pressures. The peak position of the first peak is almost kept constant with increasing pressure in spite of the volume contraction. Instead a remarkable shift of the second peak towards smaller r was observed with increasing pressure.

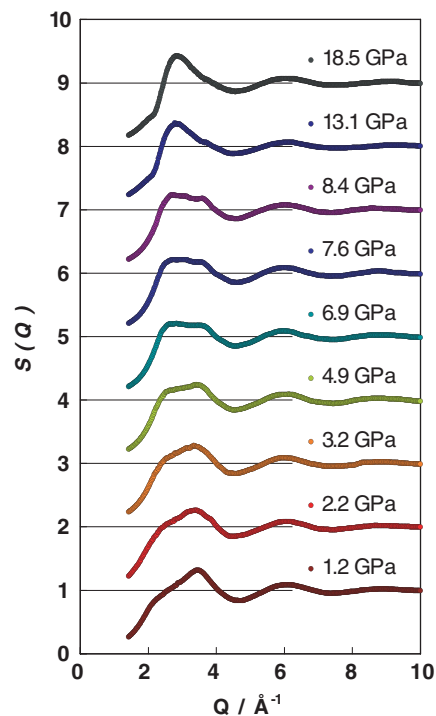


Figure 9. $S(Q)$ of liquid CuCl at various pressures.

Above 13.1 GPa the second peak overlaps with the first peak and forms a shoulder. Such a shape of $S(Q)$ and $g(r)$ was not observed in liquid CuI and liquid CuBr. In figure 4, the ratio of r_2/r_1 of liquid CuCl is also plotted. The value of the ratio decreases from the value for tetrahedral structures to a smaller value than that of the NaCl structure. With increasing pressure, the coordination number CN increases from 3.7 at 1.2 GPa to 5.6 at 18.5 GPa.

From the two species model with distorted crystalline structures [4], good agreement between the calculated $S(Q)$ and the experimental $S(Q)$ at 18.5 GPa was obtained when a mixture of 69% of NaCl structure and 31% of CsCl structure was applied.

3.4. Pressure-induced structural transformation in liquid copper halides

In the crystalline phase, the transition pressure to the NaCl structure just below the melting temperature is about 12 GPa for CuI and 6 GPa for CuCl. In the liquid phase, the structural transformation to the six-fold structure is completed at about 19 GPa for CuI and 8 GPa for CuCl. In an ionic crystal, the larger anion size causes the lower transition pressure from the zinc-blende structure to the NaCl structure. In the liquid state, the transition pressure of CuI is higher than that of CuCl and its width of CuI (19 GPa) is wider than that of CuCl (6 GPa). Cations with smaller size should move easily between anions and prefer a disordered distribution. This causes a wide pressure width of the structural transformation.

In liquid copper halides, the copper atom transforms from the tetrahedral site to the octahedral site and the transformation occurs continuously around the transition pressure in the

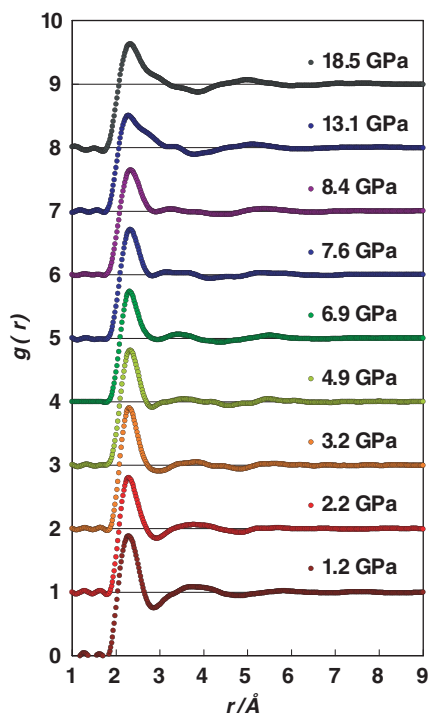


Figure 10. $g(r)$ of liquid CuCl at various pressures.

crystalline phase. Its width is narrower than the liquid III–V compounds and the local structures in the liquid before and after the transition are similar to those of crystals, in contrast to the different structures in III–V compounds.

4. Conclusion

X-ray diffraction measurements at high pressures using synchrotron radiations show that copper atoms are located in the tetrahedral site at low pressure and change their position continuously to the octahedral site. The transition pressure increases from liquid CuCl to liquid CuI due to the difference in the size of the cation and the anion. The transition from the tetrahedral site to the octahedral site in liquid copper halides occurs continuously, in contrast with the liquid CdTe. However, these materials with large ionicity in the bonding between atoms show similar pressure-induced

structural changes of liquids to those of crystals, in contrast with the different structural change between the liquid and crystalline phase in III–V compounds and group 14 elements.

Acknowledgments

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