Joint 20th AIRAPT – 43th EHPRG, June 27 – July 1, Karlsruhe/Germany 2005

Pressure dependence of the structure of liquid II-VI compounds up to 20 GPa

*T. Narushima, T. Kinoshita, T. Hattori and K. Tsuji**

Department of Physics, Keio University, Yokohama, 223-8522, Japan

**tsuji@phys.keio.ac.jp*

X-ray diffraction measurements have been performed for liquid II-VI compounds, HgTe, ZnSe and CdTe up to 20 GPa using a synchrotron radiation. Pressure dependences of the static structure factor $S(Q)$ and the pair distribution function $g(r)$ of the liquids are investigated. For liquid HgTe, the first and second peak positions of $S(Q)$ show different pressure dependences. It suggests that the local structure changes anisotropically with increasing pressure. The first peak position of the pair distribution function $g(r)$ does not change or rather shifts towards a larger r-value and its height increases with increasing pressure. The second peak shifts towards a smaller r-value. With increasing pressure, the local structure of liquid HgTe changes from the NaCl-like structure to the structure similar to that of liquid CdTe at 23 GPa. For liquid CdTe, a remarkable structural change is observed in a narrow pressure region (1.8-3.0 GPa). The local structure in the low pressure region is similar to the zincblende structure, while that in the high pressure region is similar to the rocksalt structure. Another structural transformation occurs above 9 GPa. For liquid ZnSe, the local structure changes from the zincblende-like structure to the NaCl-like structure. These results are discussed in relation to the bonding character. In addition, they are compared with the pressure-induced structural changes in the crystalline phases.

Introduction

In solid phases, crystals transform to high-pressure phases with discontinuous volume contraction at their transition pressures by compression. On the other hand, in the liquid phases, the local structure changes in a different pressure region and in many cases the local structures are different from those of the crystals. In liquid alkali metals the local structure contracts almost uniformly (Tsuji 1990, Tsuji 1996 and Morimoto 1998), whereas those of liquids in which atoms are covalently bonded such as liquid selenium (Tsuji 1988), liquid tellurium (Funamori 2001), and liquid iodine (Tsuji 1999, Katayama 2003) contract anisotropically. In these covalent liquids, the nearest neighbor distance often increases with increasing pressure in spite of volume contraction. In group 14 elements, the local structure of liquid is different from that in the crystal at atmospheric pressure (Waseda 1980) and the pressure dependence is quite different from that of the crystal (Funamori 2002 and Tsuji 2004). In liquid III-V compounds, continuous structural changes occur over 10 GPa. The local structure of the high-pressure phase is different from that of the crystal. The static structure factor and the pair distribution function can be explained by the model of the mixture of the beta-tin structure and body center cubic structure (Hattori 2002, Hattori 2003, Hattori 2004 and Hattori 2005).

In the solid phase, the structure of tetrahedrally bonded material such as group 14 elements, III-V compounds, II-VI compounds and I-VII compounds changes systematically with ionicity in the bonds and pressure. The structure of liquid CdTe and ZnSe is known to have the zincblende-like local structure at ambient pressure (Gaspard 1996, Godlevsky 1998, and Godlevsky 1999). Since the crystalline compounds show a first-order phase transition from the zincblende structure into the highly coordinated rocksalt and the related structures under pressure (McMahon 1993 and Nelmes 1995), these liquids are expected to show the structural transformation with pressure. As the liquids of tetrahedrally bonded materials with less ionicity in the bonds show different pressure dependence from that of crystalline phase, it is interesting to investigate the local structure of liquids of tetrahedrally bonded materials with high ionicity in the bonds. The values of the ionicity f_i are 0 for Si, Ge and Sn, 0.261 for GaSb, 0.321 for InSb, 0.357 for InAs, 0.609 for ZnTe, 0.630 for ZnSe and 0.717 for CdTe.

We have measured X-ray diffraction for liquid II-VI compounds, HgTe, ZnSe and CdTe up to 20 GPa using a synchrotron radiation. The static structure factor *S(Q)* of liquids and the pair distribution function *g(r)* are obtained at various pressures. The pressure dependences of *S(Q)* and *g(r)* are discussed in relation to the bonding character, such as covalency, ionicity and metallicity, and these are compared with the pressure-induced structural changes in the crystalline phases.

Experimental

Pressure was generated by the cubic-anvil apparatus MAX80 installed on the AR-NE5C beamline at Photon Factory, KEK and the double stage compression apparatus SPEED1500 installed on the BL04B1 beamline at SPring-8. As a sample container MgO or NaCl was used. Heater was made of graphite or TiC and diamond mixture. By using synchrotron radiation with high brightness, high energy and small divergence, x-ray diffraction was measured with an energy-dispersive method. X-ray diffraction intensity was measured at various scattering angles. Measurements were made at temperatures about 50 K above the melting point of each pressure. From the measured diffraction intensities, the static structure factors *S(Q)* of liquids were deduced after some corrections. Details of the procedures are given elsewhere (Tsuji 1989, Funamori 2001, Katayama 2003 and Hattori 2003). The pair distribution functions *g(r)* were obtained by the Fourier transformation of *S(Q)*.

Results and Discussion

Liquid HgTe

The static structure factors, *S(Q)* of liquid HgTe at high pressures are shown in Fig. 1. There exists two main peaks at 2.2 A^{-1} and 3.0 A^{-1} at low pressures. With increasing pressure, the height of the peak at 2.2 A^{-1} increases and the position shifts towards a higher *Q*-value while the height of the peak at 3.0 A^{-1} decreases. On the other hand, the second peak at 4.9 A^{-1} shifts towards a lower *Q*-value in spite of volume contraction. These results show that the local structure of liquid HgTe does not contract uniformly. The pressure dependence of the peak positions of *S(Q)* is shown in Fig. 2.

The ratio of the second peak position to the first peak positions, Q_2/Q_1, decreases with increasing pressure, which is similar to those of group 14 elements and III-V compounds. It changes from 2.25 at 0.3 GPa to 1.95 at 20 GPa. Typical values of the ratio are 2.6-2.7 for liquids with the zincblende-like local structure, 2.09-2.12 for liquids with the NaCl-like local structure and about 1.92 for liquid Sn between 2 GPa to 19 GPa and for liquid InSb above 10 GPa.

The pair distribution functions, *g(r)* at high pressures are shown in Fig. 3. The first peak position, r_1, of *g(r)* does not change or rather shifts towards a larger *r*-value and its height increases with increasing pressure. It suggests that strong covalent bonds between atoms remain under high pressure. The second peak shifts towards a smaller *r*-value with volume contraction. With increasing pressure, a hump, which appears on the right hand side of the first peak, becomes small and approaches the first peak. Peak positions of *g(r)* of liquid HgTe are shown in Fig. 4 as a function of pressure. The coordination number CN_1 of liquid was evaluated by integrating the radial distribution function $4\pi r^2 ng(r)$ in the *r* region of the first peak, where *n* is the number density. In Fig. 5, CN_1 evaluated by two methods are plotted as a function of pressure: Circles show the values obtained by integrating the radial distribution function in the region up to r_1 and multiplying two. Squares are those obtained by integrating

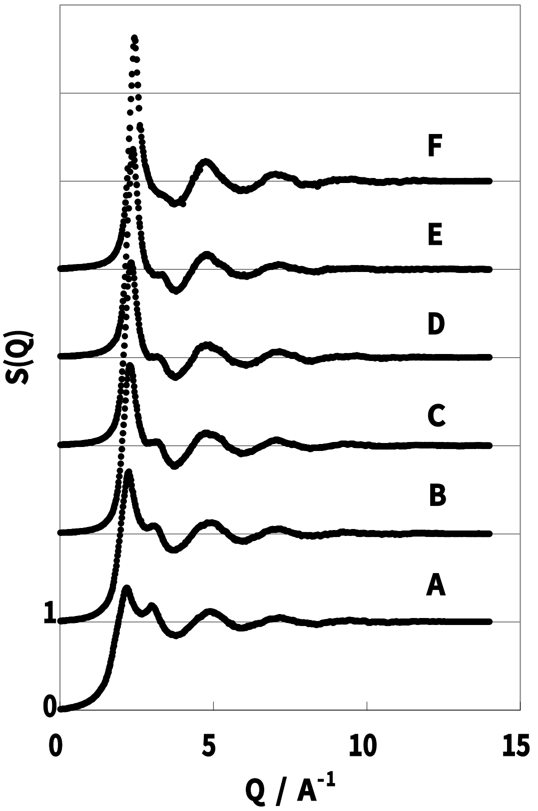

Fig. 1 *S(Q)* of liquid HgTe at various pressures. A: 0.3 GPa, B: 2.7 GPa, C: 5.5 GPa, D: 8.0 GPa, E: 12.4 GPa, F: 18 GPa.

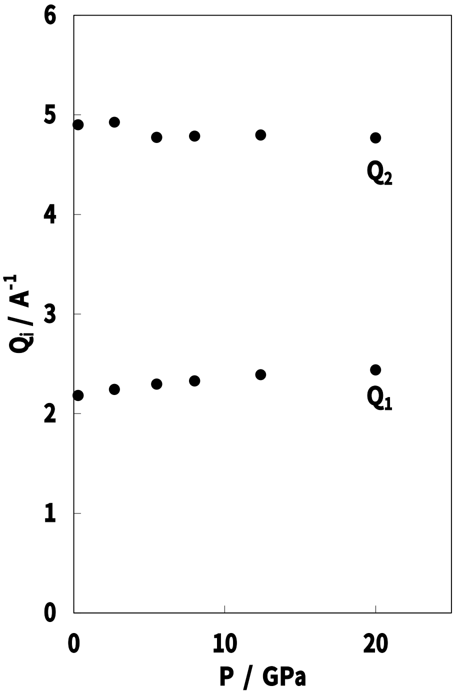

Fig. 2 Peak positions of *S(Q)* of liquid HgTe as a function of pressure.

the radial distribution function up to the first minimum of *g(r)*. Both values show almost the same pressure dependences. They increase continuously from four at 0 GPa to eight at 18 GPa.

These results suggest that the local structure of liquid ZnTe changes continuously from the NaCl-like structure to another high-pressure local structure. Candidates for the local structure may be the CsCl structure, which is a bcc structure without chemical ordering, and the high pressure form of liquid tin or liquid III-V compounds. The mixtures of these structures and the rocksalt structure are also candidates. However, the difference among these models is too small to determine which is appropriate as the local structure.

Liquid CdTe

Fig. 6 shows *S(Q)* of liquid CdTe at several pressures. At 1.8 GPa, two peaks are observed in the *Q* region where the main peak is located in normal liquids. This character also appears in tetrahedrally bonded disordered materials such as amorphous silicon. With increasing pressure, the peak at the lower *Q* value becomes higher. Above 9 GPa, the new peak appears between double peaks. Its height is much higher than those of the double peaks are. In Fig. 7, the peak positions of *S(Q)* are plotted against pressure. There are three pressure regions where the values of peak positions are clearly different: below 1.8 GPa, between 3-7 GPa and above 9 GPa. The pressure width where these values change drastically are quite narrow compared with those of liquid group 14 elements and liquid III-V compounds. In the previous work (Kinoshita 2005), we compared *S(Q)* and *g(r)* with those of typical disorder materials and analyzed the local structure using several structural models. It is concluded that the first structural change originates from the change in the local structure from the zincblende-like form into the rocksalt-like one. The shape of *S(Q)* of liquid HgTe at 8 GPa is similar to that of liquid CdTe in the third pressure region. In Fig. 8, *S(Q)* of liquid HgTe at 8 GPa and *S(Q)* of liquid CdTe at 23.5 GPa are compared. Both *S(Q)* show almost the same shape. It suggests that both liquid II-VI compounds show the similar high-pressure sequence of the local structure.

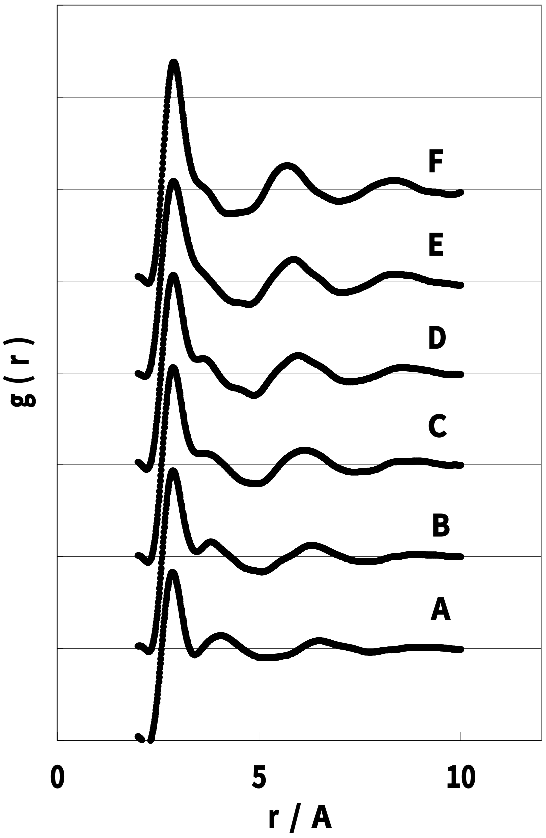

Fig. 3 *g(r)* of liquid HgTe at various pressures. A: 0.3 GPa, B: 2.7 GPa, C: 5.5 GPa, D: 8.0 GPa, E: 12.4 GPa, F: 18 GPa.

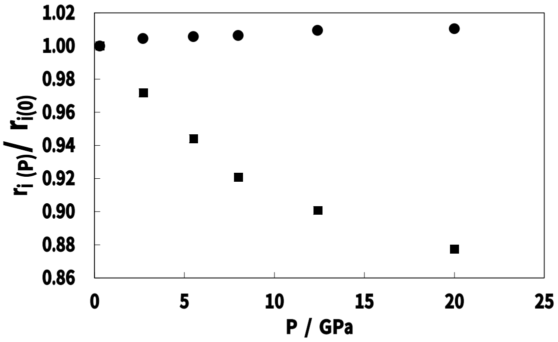

Fig. 4 Peak positions of *g(r)* of liquid HgTe as a function of pressure. The values are scaled to the value at 0 GPa.

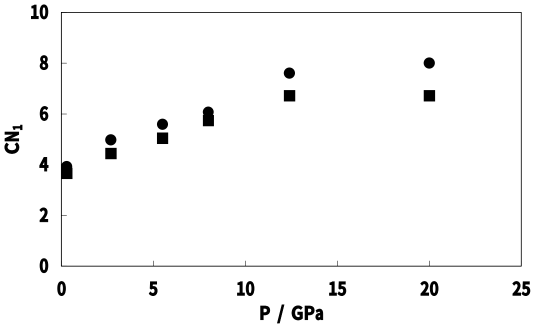

Fig. 5 Coordination number CN_1 of liquid HgTe as a function of pressure. Circle: coordination number obtained by integrating the radial distribution function up to r_1 and multiplying two; square: coordination number obtained by integrating the radial distribution function up to the first minimum of *g(r)*.

Liquid ZnSe

In Fig. 9, *S(Q)* of liquid ZnSe at several pressures are compared with those of liquid CdTe. At 1.7 GPa and 4.3 GPa, *S(Q)* of liquid ZnSe have double peaks in the Q region between 1 A^{-1} and 4 A^{-1}, which is similar to those of liquid CdTe in the first pressure region with the zincblende-like local structure(D and E in the figure). Unfortunately, the curve C of liquid ZnSe at 14 GPa is deduced from the data taken at a limited scattering angle. However, it shows the sharp main peak between the double peaks, which is similar to those of liquid CdTe in the second pressure region. In Fig. 10, *g(r)* of liquid ZnSe at 1.7 GPa and 4.3 GPa is compared with that of liquid CdTe at 0.5 GPa. This figure also reveals that the local structure of liquid ZnSe at low pressures is the zincblende-like structure as well as that of liquid CdTe in the first pressure region.

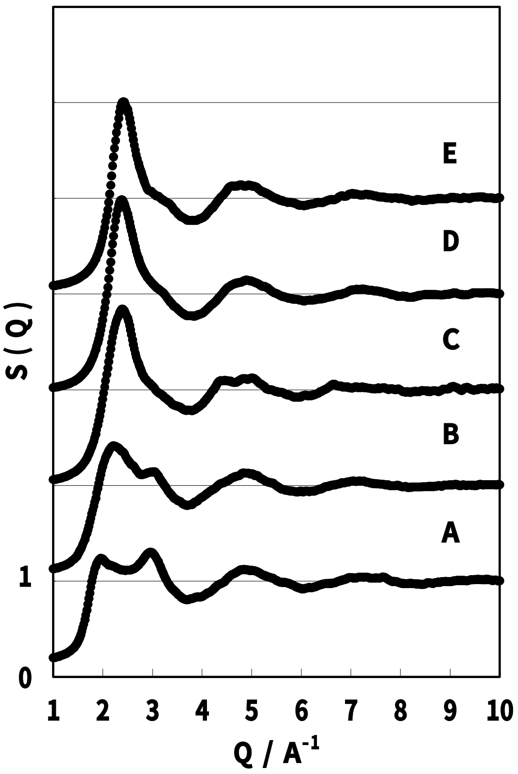

Fig. 6 *S(Q)* of liquid CdTe at various pressures. A: 1.8GPa, B: 6.0GPa, C:12.1GPa, D: 18.7GPa and E: 23.5GPa.

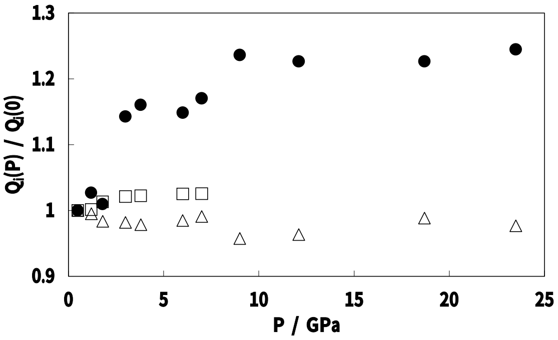

Fig. 7 Peak positions of *S(Q)* of liquid CdTe as a function of pressure.

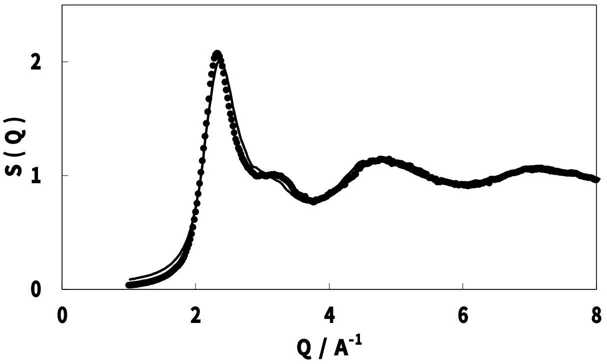

Fig. 8 Comparison of *S(Q)* between liquid HgTe and liquid CdTe. Circles: liquid HgTe at 8 GPa, solid line: liquid CdTe at 23.5 GPa. *Q*-value for liquid CdTe is reduced so that both *S(Q)* are overlapped.

Comparison with II-VI compounds

With increasing pressure, the crystalline HgTe transforms from the zincblende structure to the cinnabar structure at 1.5 GPa, then to the rocksalt structure at 8 GPa and finally to the Cmcm structure at 11 GPa. The last structure can be regarded as a distorted form of the rocksalt structure. The crystalline CdTe transforms from the zincblende structure to the cinnabar structure at 2.7 GPa, and then to the rocksalt structure at 3.6 GPa. The cinnabar phase appears in a very narrow pressure region. The crystalline ZnSe shows almost the same high-pressure structural sequence as that in the crystalline CdTe. The transition pressure to the rocksalt phase is 12 GPa for ZnSe.

In liquid CdTe, three kinds of shapes for the main peak of *S(Q)* are observed: Double peaks are observed in the pressure region between 0.5-1.8GPa. Asymmetric double peaks are observed between 3-7 GPa. Above 9 GPa a sharp main peak are observed. Several structural parameters, such as Q_{i}, Q_2/Q_1, r_{i}, r_2/r_1, CN_1, have different values in each pressure region. From the comparison of them to the typical disorder materials, it is concluded that the local structure of the liquid is the zincblende-like structure in the first pressure region and the rocksalt-like structure in the second pressure region. It is noted that the transition pressure is almost the same as that in the crystalline phase. Furthermore, the local structure of liquid is similar to that in the crystalline phase. These features may originate from the presence of the chemical order in the liquid with high ionicity in the bonding character. The pressure dependence of the structure of liquid CdTe is in contrast with those of liquid group 14 elements and liquid III-V compounds. In liquid ZnSe, the structural change from the zincblende-like structure to the rocksalt-like structure occurs similarly.

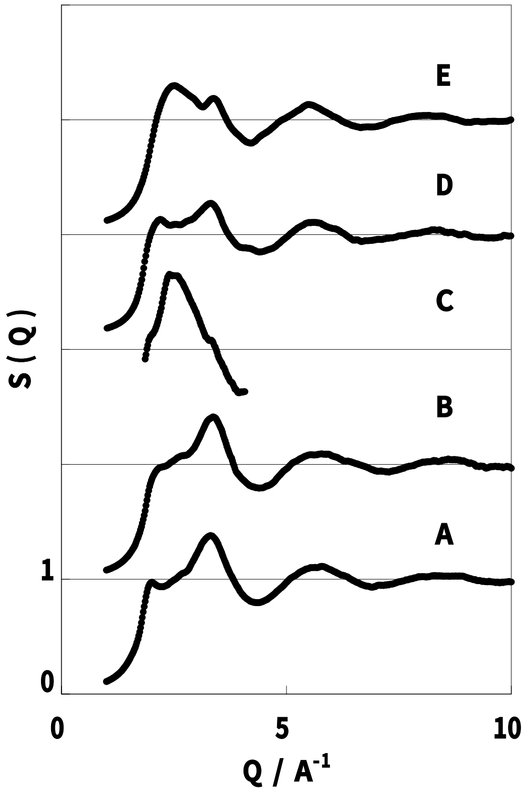

Fig. 9 Comparison of *S(Q)* between liquid ZnSe and liquid CdTe. A: liquid ZnSe at 1.7 GPa, B: liquid ZnSe at 4.3GPa, C: liquid ZnSe at 14 GPa, D: liquid CdTe at 0.5GPa and E: liquid CdTe at 3.0 GPa.

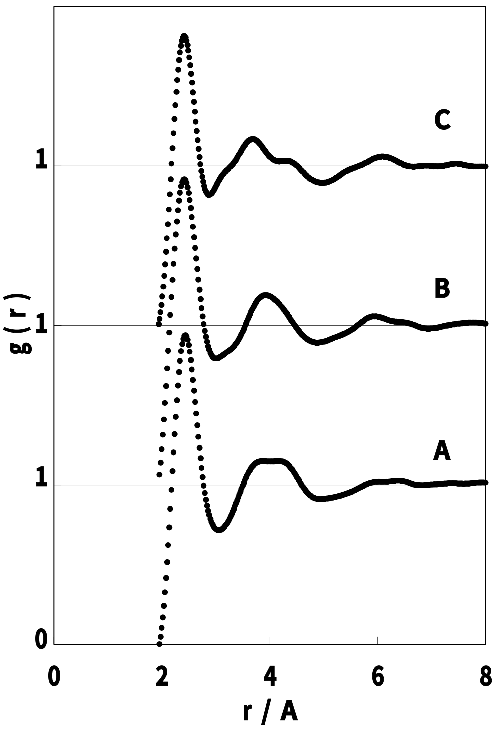

Fig 10 Comparison of *g(r)* between liquid ZnSe and liquid CdTe. A: liquid ZnSe at 1.7 GPa, B: liquid ZnSe at 4.3 GPa and C: liquid CdTe at 0.5 GPa

On the other hand, the local structure of liquid HgTe changes continuously over the wide pressure region. The local structure changes from the rocksalt-like structure to that of another high-pressure form with increasing pressure. The continuous structural change may be related to the narrow pressure region of the rocksalt phase in the solid phase.

Conclusion

Systematic studies of the structure of liquid II-VI compounds under high pressure reveal that the pressure dependence of the local structure is alike among liquid HgTe, CdTe and ZnSe, although the pressure width where structural changes occur is different. The local structure changes from the zincblende-like structure to the NaCl-like structure, and then into another high-pressure form. The pressure dependence of the local structure of liquid compounds with high ionicity in the bonds is similar to those of crystals. This is in contrast with the quite different pressure dependence of the liquids from that in the crystals with less ionicity in the bonds.

Acknowledgement

This work is supported by Grant-in-Aid for Scientific Research from Japanese Government. Synchrotron x-ray diffraction experiments were carried out at SPring-8 and PF using SPEED-1500 and MAX80 systems.

References

Funamori N. and Tsuji K., 2001. Structural transformation of liquid tellurium at high pressures and temperatures. Phys. Rev. B **65**, 014105-1-5.

Funamori N. and Tsuji K., 2002. Pressure-induced structural change of liquid silicon, Phys. Rev. Lett. **88**(25), 255508-1-4.

Gaspard J. P., Raty J. Y., Ceolin R. and Bellissent R., 1996. Local orders in II-VI liquid compounds. *J. Non-cryst. Sol.* **205**, 75.

Godlevsky V. V., Derby J. J. and Chelikowsky J. R., 1998. *Ab initio* molecular dynamics simulation of liquid CdTe and GaAs: Semiconducting versus metallic behavior. *Phys. Rev. Letters* **81**, 4959.

Godlevsky V. V. Jain M., Derby J. J. and Chelikowsky J. R., 1999. First-principle calculations of liquid CdTe at temperatures above and below the melting point. *Phys. Rev. B* **60**, 8640.

Hattori T., Taga N., Takasugi Y., Mori T. and Tsuji K., 2002. Structure of liquid GaSb under pressure. *J. Non-Cryst. Solids* **312-314**, 26-29.

Hattori T., Tsuji K., Taga N., Takasugi Y. and Mori T., 2003. Structure of liquid GaSb at pressures up to 20 GPa. *Phys. Rev. B* **68**, 224106-1-17.

Hattori T., Kinoshita T., Narushima T. and Tsuji K., 2004. Pressure dependence of the structure of liquid InAs up to 13 GPa. *J. Phys.: Condens. Matter* **16,** S997–S1006

Hattori T., Kinoshita T., Taga T., Takasugi Y., Mori T. And Tsuji K., 2005. Pressure and temperature dependence of the structure of liquid InSb. *Phys. Rev. B*, in press.

Katayama Y. and Tsuji K., 2003. X-ray structural studies on elemental liquids under high pressures. *J. Phys.; Condens. Matter* **15**, 6085-6103.

Kinoshita T., Hattori T., Narushima T. and Tsuji K., 2005, Pressure-induced drastic structural change in liquid CdTe, submitted.

McMahon M. I., Nelmes R. J. , Wright N. G. and Allan D. R., 1993.Phase transitions in CdTe to 5 GPa. *Phys. Rev. B* **48**, 16246.

Morimoto Y., Kato S., Toda N., Katayama Y., Tsuji K., Yaoita K. and Shimomura O., 1998. Structure of liquid rubidium and liquid sodium under pressure. Rev. *High Pressure Sci. Technol.* **7**, 245-247.

Nelmes R. J., McMahon M. I., Wright N. G. and Allan D. R., 1995. *Phys. Rev. B* **51**, 15723.

Tsuji K., Shimomura O., Tamura K. and Endo H., 1988. Structure of liquid Se under high pressure. *Z. Phys. Chem. Neue Folge* **156**, 495-499.

Tsuji K., Yaoita K., Imai M., Shimomura O. and Kikegawa T., 1989. Measurements of x-ray diffraction of liquid metals under high pressure. *Rev. Sci. Instrum*. **60**, 2425-2428.

Tsuji K., 1990. Structure of liquid metals under high pressure. *J. Non-Cryst. Solids* **117&118**, 27-34.

Tsuji K., Katayama Y., Morimoto Y. And Shimomura O., 1996. Structure of liquid rubidium under high pressure. J. Non-Cryst. Solids **205-207**, 295-298.

Tsuji K. and Ohtani M., 1999. Structure of liquid iodine under pressure. *Proc. AIRAPT 17 Conference, Hawaii,* pp.514-517.

Tsuji K., Hattori T., Mori T., Kinoshita T., Narushima T. and Funamori N., 2004. Pressure dependence of the structure of liquid group 14 elements. *J. Phys.: Condens. Matter*, **16**, S989-S996.

Waseda Y., 1980. The Structure of Non-Crystalline Materials (New York: McGraw-Hill).