

XAFS study on liquid selenium under high pressure

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Using large-volume presses, it is now possible to measure X-ray absorption spectra under a wide range of pressure–temperature conditions. X-ray absorption fine structure (XAFS) has successfully been measured at the *K* edge of crystalline and liquid Se at temperatures up to 1023 K and pressures of about 5 and 8 GPa, and at temperatures up to 1173 K at about 2.5 GPa. Crystalline Se consists of infinite chain molecules. At atmospheric pressure, it is known that the chain structure of Se is largely preserved upon melting. The temperature dependence of the extended X-ray absorption fine structure (EXAFS) at 2.5 GPa indicates that twofold covalent bonds remain upon melting, as at atmospheric pressure. On the other hand, the decrease of EXAFS oscillation upon melting at 8 GPa is larger than that expected from the temperature dependence of EXAFS in the crystalline state, indicating that the covalent bonds are modified in the liquid state. The change of structure of liquid Se is discussed in relation to a proposed semiconductor–metal transition under high pressure.

Keywords: liquid selenium; high pressure; high temperature; phase transitions.

1. Introduction

For the past few decades, pressure-induced structural transitions in crystalline solids have been widely studied and structures of many high-pressure phases have been determined. In general, an element that has an open-packed structure with a low coordination number transforms to a dense-packed structure with a high coordination number under pressure (Young, 1991). Since the local atomic arrangement in the liquid state is similar to that in the crystalline counterpart to some degree, it is reasonable to suppose that the structure of liquids also changes under pressure. However, studies on the structure of liquids under high pressure are limited and details of the structural changes are not as yet well understood. Although the structural changes in liquids are supposed to be smooth and continuous, there is evidence that the changes are sharp for several materials (Endo *et al.*, 1986; Brazhkin *et al.*, 1997; Mishima & Stanley, 1998). In addition, the first *in situ* observation of a first-order liquid–liquid transition in a pure substance has been reported recently (Katayama *et al.*, 2000).

Liquid selenium (l-Se) is one of the candidates that exhibit relatively sharp structural changes. Just above the melting point at atmospheric pressure, l-Se consists of long chain molecules in which each atom is covalently bonded to two nearest-neighbour atoms. The chain molecules are also basic units in crystalline Se (c-Se) and both c-Se and l-Se are semiconductors. Brazhkin *et al.* (1990) have reported a sharp increase of electrical conductivity of l-Se under high pressure. They determined the boundary for the semiconductor–metal (SC–M) transition in the pressure–temperature phase diagram and located the liquid–liquid–solid triple point at 3.6 GPa. They reported that the transition had some features of a first-order phase transition.

To study the structure of liquids under high temperature and pressure, *in situ* methods are essential. Tsuji and co-workers have been developing an X-ray diffraction method using synchrotron radiation to study the structure of liquid under high pressure (Tsuji *et al.*, 1988, 1989; Tsuji, 1990). They measured X-ray diffraction of l-Se under high pressure and found that the structure of l-Se at 8.4 GPa is very different from that at atmospheric pressure. However, it is still unclear if the SC–M transition is accompanied by the structural change or not, because the diffraction measurements were carried out at only two pressures. To investigate the relation between the SC–M transition and the structural change, detailed structural studies on l-Se have been started by our group.

XAFS measurement under high pressure and high temperature is a new tool for such studies. It is a complementary method to X-ray diffraction because the diffraction method under high pressure has limitations, as follows: (i) the range of the wavenumber is narrow as a result of the limited X-ray aperture of high-pressure apparatus; (ii) the accuracy of diffraction intensity is not as good as that at normal pressure. Using large-volume presses, XAFS has been successfully measured at the *K* edge of c- and l-Se at temperatures up to 1023 K and pressures of about 5 and 8 GPa (Katayama *et al.*, 1998), and temperatures up to 1173 K at about 2.5 GPa (Katayama *et al.*, 1999). In this paper, new data at 2.5 GPa are presented, together with the previously reported data. The structural change of l-Se are discussed in connection with the SC–M transition.

2. Experimental and data analysis

For structural studies under pressure, several types of apparatus have been developed. Although the most popular apparatus is a diamond anvil cell (DAC), it has a disadvantage in X-ray absorption measurements (Shimomura *et al.*, 1978). In conventional geometry, an X-ray passes through single-crystal diamonds that may satisfy the diffraction condition during the energy scan. Diffraction causes glitches in the X-ray absorption spectra. To avoid this problem, large-volume presses were employed. They are capable of generating moderate high-pressure/high-temperature conditions in a relatively large volume. For example, a cubic-type multi-anvil press is capable of generating pressures up to 15 GPa and temperatures up to 1800 K. A typical sample dimension is about 1 mm. There is no single crystal in the X-ray path, so the spectra can be measured without glitches. Shimomura & Kawamura (1987) carried out the first XAFS measurement using a multi-anvil press. XAFS measurements of isolated Se chains (Katayama *et al.*, 1994), c-Se (Katayama *et al.*, 1995) and amorphous Se (Katayama *et al.*, 1996) were subsequently carried out. Recently, large-volume presses of Paris–Edinburgh type have been used for synchrotron radiation studies (Mezouar *et al.*, 1996). The apparatus is compact and lightweight, so it can be installed in conventional XAFS beamlines (Katayama *et al.*, 1997).

The temperature dependence of EXAFS at about 5 and 8 GPa was studied using a cubic-type multi-anvil apparatus (MAX90) installed at station BL13B1 in the Photon Factory, Japan. The measurements were carried out in transmission mode. Details of the experimental conditions were given in a previous paper (Katayama *et al.*, 1998). Measurements at 2.5 GPa were performed using a press of Paris–Edinburgh type at an XAFS station (BL01B1) at SPring-8, Japan. The gasket was made of a mixture of boron and epoxy resin. Se powder was mixed with boron nitride (BN) powder and then the mixture was put into a sample capsule made of BN. Graphite heaters inside the sample assembly were used to raise the temperature. The temperature was measured by a thermocouple. The pressure was estimated from the lattice constants of c-Se. The X-ray beam was mono-

chromated using Si(111) reflection. Mirrors were used for rejection of higher harmonics and focusing. The size of the X-ray beam was reduced to about 0.3×0.2 mm.

Data analysis was performed using the *UWXAFS* package (Stern *et al.*, 1995). Theoretical EXAFS parameters were calculated by *FEFF7* code (Zabinsky *et al.*, 1995) with atomic positions in c-Se at atmospheric pressure. Parameter fitting was performed in *R* space within a harmonic approximation.

3. Results and discussion

Fig. 1 shows experimental paths in the pressure–temperature phase diagram of Se. The solid curve indicates the melting temperature and the dashed curve indicates the proposed boundary for the SC–M transition (Brazhkin *et al.*, 1990).

To see the relation between the structural change and the proposed SC–M transition, measurements were performed along a path that is across the reported boundary. Preliminary data were reported in a previous paper (Katayama, *et al.*, 1999). Here, new improved data are presented, which were measured after the commissioning period of the XAFS station BL01B1 at SPring-8. Fig. 2 shows the EXAFS function $\chi(k)$ of c- and l-Se as a function of wavenumber, k , at about 2.5 GPa and various temperatures. The solid lines represent experimental data and the dashed lines represent results of parameter fits. The signal to noise ratio of the data is excellent in spite of the extreme pressure–temperature conditions: clear EXAFS oscillation is seen even at the highest temperature, 1173 K, except for some spikes around $k = 10 \text{ \AA}^{-1}$. The amplitude of the EXAFS oscillation becomes smaller with increasing temperature. The melting of the sample was detected by a change in X-ray absorption near-edge structure (XANES). Although the sample melts between 773 and 873 K, no significant change was observed in the EXAFS upon melting.

Fig. 3 shows the radial distribution function, $|F(r)|$ obtained from the Fourier transform of k -weighted $\chi(k)$ for c- and l-Se at about 2.5 GPa as a function of temperature. The first peak corresponds to intra-chain covalent bonds. The change in intensity of the first peak is smooth and continuous in the entire temperature range.

Fig. 4 shows the temperature dependence of bond length, r , the mean-square displacement, σ^2 , and the coordination number, N , for the first nearest-neighbour obtained by the parameter fit. The fit was

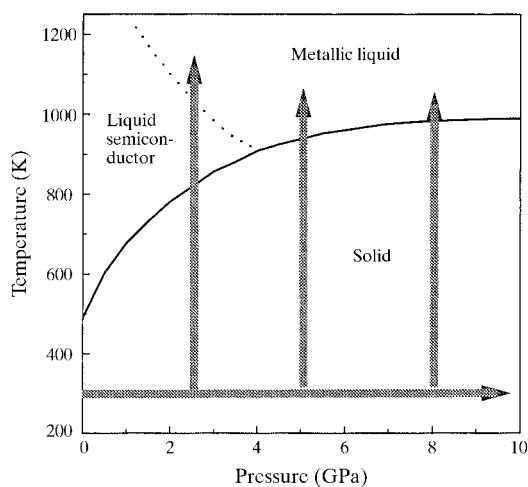


Figure 1

Experimental paths in the pressure–temperature diagram of Se. The solid and dashed curves indicate the melting curve and a boundary for a semiconductor–metal transition in liquid Se.

performed including first to fourth neighbours for c-Se. The fit range was 1.75–4.25 \AA in *R* space. For l-Se, only the first neighbour (1.75–3 \AA) was included in the fit. The bond length decreases with increasing temperature. The decrease may be consistent with the contraction of the crystallographic *c* axis, which is parallel to the chain molecules, with increasing temperature. There is, however, a possibility that the harmonic approximation gives incorrect temperature dependence of r . The bond length decreases discontinuously upon melting. The mean-square displacement increases linearly with increasing temperature, while the coordination number is almost constant in both the crystalline and the liquid state. The linear temperature dependence of σ^2 and little change in N indicate that the twofold covalent bonds are almost fully preserved in the liquid state, as in the case at atmospheric pressure.

The temperature dependence of EXAFS measured above 5 GPa is different from that at 2.5 GPa. The data were collected at the Photon Factory and were published in a previous paper (Katayama *et al.*, 1998). The results of the previous analysis may be summarized as follows: (i) the decrease of EXAFS oscillation upon melting is larger than that expected from the temperature dependence of the EXAFS for c-Se, indicating that the covalent bonds are modified in the liquid state; (ii) results of the parameter fits by a one-shell harmonic model indicate that the coordination number decreases with increasing pressure, while the mean-square displacement is almost constant; (iii) the bond length in the liquid state is shorter than that of c-Se at the same pressure; it increases with increasing pressure. For the present study, a re-analysis of the data in a similar manner to the analysis of the data at 2.5 GPa was performed. Data for thin-film samples were omitted in the present analysis because the samples were not held stably when it melted. In the course of the analysis, it was found that

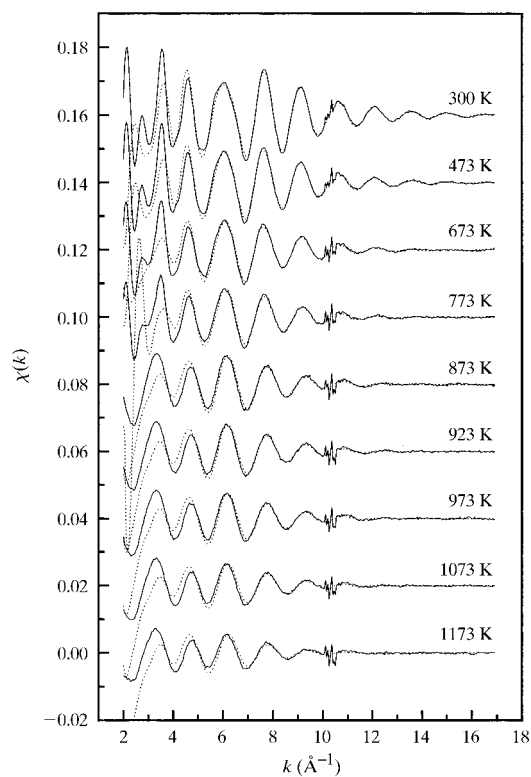


Figure 2

EXAFS function $\chi(k)$ for crystalline and liquid Se at 2.5 GPa and various temperatures. Solid lines indicate experimental data and dashed lines indicate results of parameter fits.

poor data quality, together with the strong coupling between the mean-square displacement and the coordination number, prevent the separation of the two contributions. To illustrate the modifications in the covalent bonds, a tentative fit of the data has been performed under a constraint that the coordination number for the first neighbour is two. This assumption is adequate for c-Se, but it may not be adequate for l-Se, for which no information about the coordination number is available. Thus, the resultant mean-square displacement, $\sigma_{N=2}^2$, for l-Se is a rough measure of the intensity of the EXAFS oscillation. In Fig. 5, the circles, squares and triangles represent $\sigma_{N=2}^2$ at 2.5, 5 (4.4) and 8 (7.4) GPa, respectively. The values within parentheses are pressures adopted in the previous paper, in which they were underestimated. The filled and unfilled symbols indicate values for c-Se and l-Se, respectively. In the crystalline states, $\sigma_{N=2}^2$ increases linearly with temperature. The change upon melting is continuous at 2.5 GPa, while it is discontinuous at 5 and 8 GPa; the values for l-Se at 5 and 8 GPa are larger than those expected from the linear relation in c-Se. The change at 8 GPa is larger than that at 5 GPa. On the other hand, the interpolated value for $\sigma_{N=2}^2$ at 2.5 GPa and 1023 K is lower than $\sigma_{N=2}^2$ at 5 GPa. The difference in $\sigma_{N=2}^2$ at the same temperature indicates that additional disorder in l-Se increases with increasing pressure. At high temperatures, above 1073 K, at 2.5 GPa, there is a positive deviation from the linear relation. The positive deviation suggests additional disorder in the high-temperature region. There is, however, a possibility that the deviation is caused by the effect of anharmonicity, which is not included in the present analysis.

The behaviour of $\sigma_{N=2}^2$ indicates that the twofold covalent bonds are preserved upon melting up to pressures of 2.5 GPa, while they are

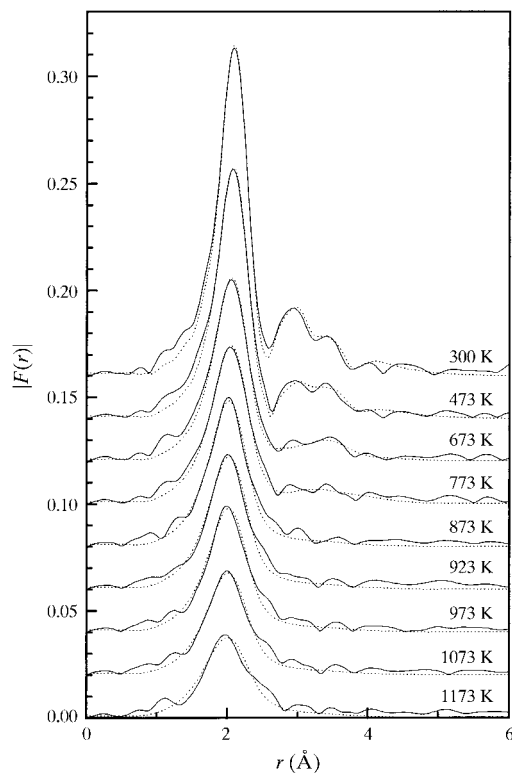


Figure 3 Radial distribution function $|F(r)|$ obtained by Fourier transform of k -weighted $\chi(k)$ for crystalline and liquid Se at 2.5 GPa and various temperatures. Solid lines indicate experimental data and dashed lines indicate results of parameter fits.

modified above 5 GPa. This result is consistent with the view that the SC–M transition is accompanied by the structural change because the proposed liquid–liquid–solid triple point is located at 3.6 GPa. In addition, the slope of $\sigma_{N=2}^2$ at 2.5 GPa changes around the boundary for the SC–M transition (Fig. 1).

The modification of covalent bonds has been observed in a SC–M transition in tellurium (Te). Although Te has the same crystal structure as Se, it transforms from crystalline semiconductor to metallic

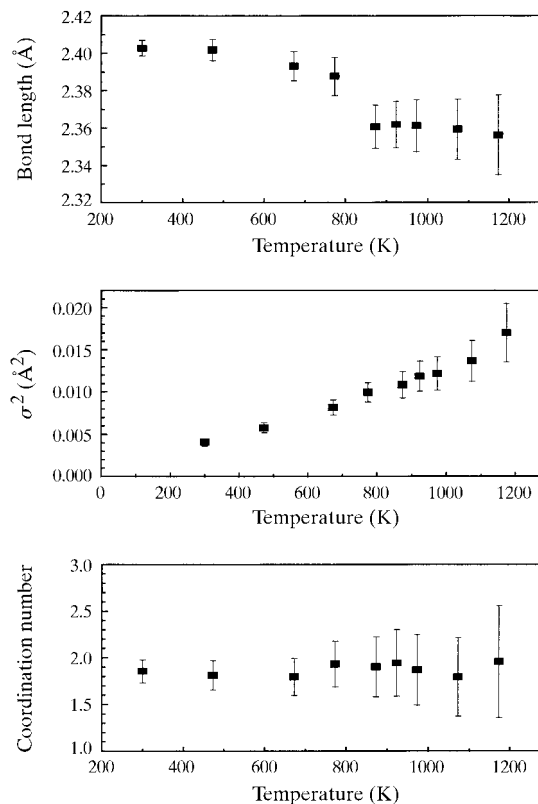


Figure 4 Temperature dependence of (a) bond length, (b) mean-square displacement, σ^2 , and (c) coordination number for crystalline and liquid Se at 2.5 GPa.

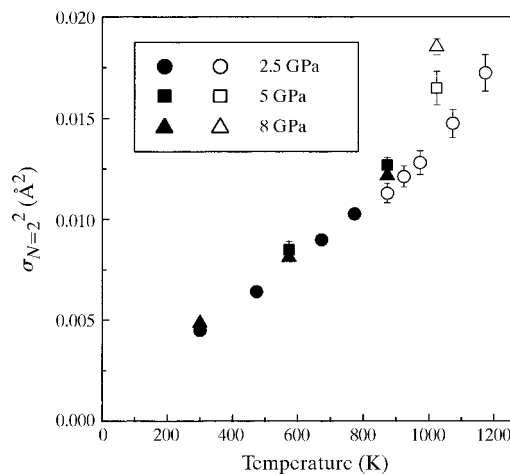


Figure 5 Mean-square displacement, $\sigma_{N=2}^2$, for Se at 2.5, 5 and 8 GPa, obtained from fits under an assumption that the coordination number is 2. Filled and unfilled symbols correspond to crystalline and liquid Se, respectively. Pressures are indicated.

liquid when it melts. A previous EXAFS study revealed that the EXAFS oscillation for Te discontinuously decreased upon melting (Tamura *et al.*, 1991). The change in EXAFS upon melting for Se under high pressure resembles that for Te. It is consistent with the fact that the structure factor for l-Se obtained by X-ray diffraction at 8.4 GPa is similar to that of l-Te (Tsuji *et al.*, 1988). The structure factor at 4.4 GPa, above the reported triple point, is already different from that at atmospheric pressure (Tsuji, 1990).

From these results, it is certain that the structure of l-Se starts to change around the boundary of the SC–M transition. The covalent bonds are preserved in the liquid semiconductor, whereas they are modified in the metallic liquid. However, it is still not clear how sharp the change is. The difference in $\sigma_{N=2}^2$ for l-Se at different pressures suggests that the structure change continues in the metallic region. In order to clarify this point, measurements over a wide pressure–temperature region, together with refined analysis to give the correct radial distribution function, are necessary (Kawakita, *et al.*, 1999). As presented in this paper, the recent improvements in the quality of the data encourage us to proceed with the study.

4. Conclusions

XAFS at the *K* edge of c- and l-Se has been measured at temperatures up to 1023 K and at pressures of about 5 and 8 GPa, and at temperatures up to 1173 K at about 2.5 GPa. By combining a large-volume press and a stable XAFS beamline, high-quality data can be obtained under such extreme conditions. Analysis of EXAFS data for liquid Se indicates that the twofold covalent bonds are modified in the high-pressure metallic region.

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