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1996 J. Phys.: Condens. Matter 8 9347

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## X-ray diffraction and small-angle x-ray scattering measurements on expanded fluid selenium

M Inui†, T Noda‡§, K Tamura† and C Li‡||

† Faculty of Integrated Arts and Sciences, Hiroshima University, Higashihiroshima 739, Japan

‡ Graduate School of Biosphere Sciences, Hiroshima University, Higashihiroshima 739, Japan

Received 15 July 1996

**Abstract.** To investigate the structural change in the semiconductor-to-metal transition in expanded fluid selenium, x-ray diffraction and small-angle x-ray scattering (SAXS) measurements at high temperatures and pressures up to 1650 °C and 1500 bar have been carried out. The results of the x-ray diffraction study show that the twofold-coordinated structure is largely preserved in the metallic fluid. The covalent bond becomes short at around 1200 °C, where the metallic character starts to be enhanced. These results suggest that the local structure of chain molecules changes with the transition. Since the semiconductor-to-metal transition occurs near the liquid–gas critical point, it is important to study how the critical density fluctuations are concerned with the transition. The SAXS spectra at 400 bar show that a broad peak appears at around  $0.12 \text{ \AA}^{-1}$  above 1200 °C, which may suggest density fluctuations with a correlation length of about 50 Å in the metallic fluid.

### 1. Introduction

A great deal of effort has been made to study the semiconductor-to-metal (SC-to-M) transition of Se which occurs in the supercritical region near the liquid–gas critical point [1–8]. (The critical constants are  $T_c = 1615 \text{ °C}$ ,  $p_c = 385 \text{ bar}$  and  $\rho_c = 1.85 \text{ g cm}^{-3}$  [6].) However, there have been few structural studies on the SC-to-M transition because of the experimental difficulties at high temperature and pressure. Tamura and Hosokawa [8] carried out energy-dispersive x-ray diffraction measurements for supercritical fluid Se up to 1500 °C and 815 bar for the first time using a sapphire cell of their own design. (The measured points in the phase diagram of fluid Se are shown in figure 2(b)—see later—by open squares.) They found that the twofold-coordinated chain structure is largely preserved even in the metallic region where the optical gap disappears.

To make the mechanism of the SC-to-M transition clear, it is of importance to study the correlation between Se chains in the fluid as well as the local structure. We have performed a small-angle x-ray scattering (SAXS) measurement for the supercritical fluid Se at high temperature and pressure to investigate the density fluctuations accompanying the SC-to-M transition [9, 10]. In this paper, we report new structural data obtained from x-ray diffraction measurements up to 1500 °C and 1420 bar and the results of SAXS measurements at 400 bar.

§ Present address: Nippon Electric Glass Co. Inc., Otsu 520, Japan.

|| Permanent address: Institute of Physics, Chinese Academy of Science, Beijing 100080, People's Republic of China.

## 2. Experimental procedure

### 2.1. X-ray diffraction

X-ray diffraction measurements for supercritical fluid Se have been carried out using the energy-dispersive method. We used a sample cell made of single-crystalline sapphire similar to that used in the previous study [8]. A new type of high-pressure vessel has been developed for the measurements of expanded fluid mercury [11] and this apparatus permits measurements up to 1700 °C and 2000 bar. The vessel was pressurized by high-purity-grade (99.9999%) He gas. The details and the procedure of the data analysis are described in previous papers [8, 11]. In the present study, white x-rays are generated by operating a commercial W tube of a special model at 70 kV and 20 mA. As a result, spectra are obtained over a wider energy region than in the previous study and the statistical errors in the high- $k$  region are reduced (where  $k$  is the scattering vector).

### 2.2. SAXS

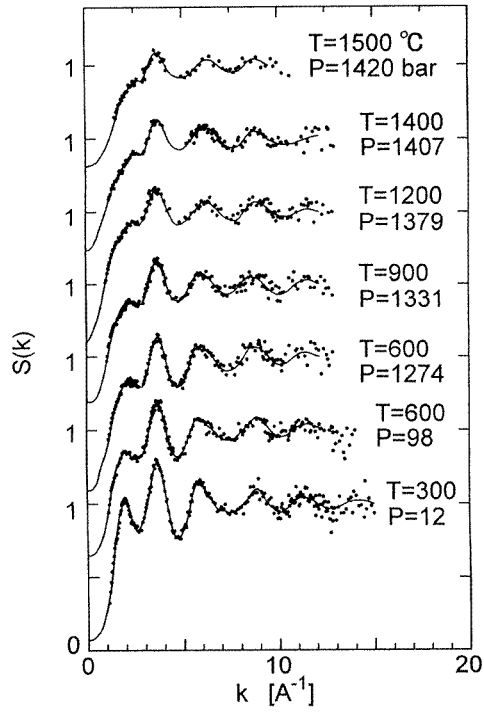
SAXS measurements for supercritical fluid Se have been carried out using a three-slit spectrometer. The x-ray beam from a Mo line source is monochromatized with planar graphite crystal and the  $K\alpha_1$  line obtained is used. The SAXS intensity is detected by a position-sensitive proportional counter (pspc).

The high-pressure vessel is made of super-high-tension steel and the sample cell made of polycrystalline sapphire. The set-up of the cell and heating assemblies is similar to those of our XAFS [12] and density measurements [6]. The maximum scattering angle is limited by the diameter of the Be window while the minimum one is limited due to the SAXS intensity from the Be window for an incident beam. The observable  $k$ -region was from  $0.08 \text{ \AA}^{-1}$  to  $0.25 \text{ \AA}^{-1}$ .

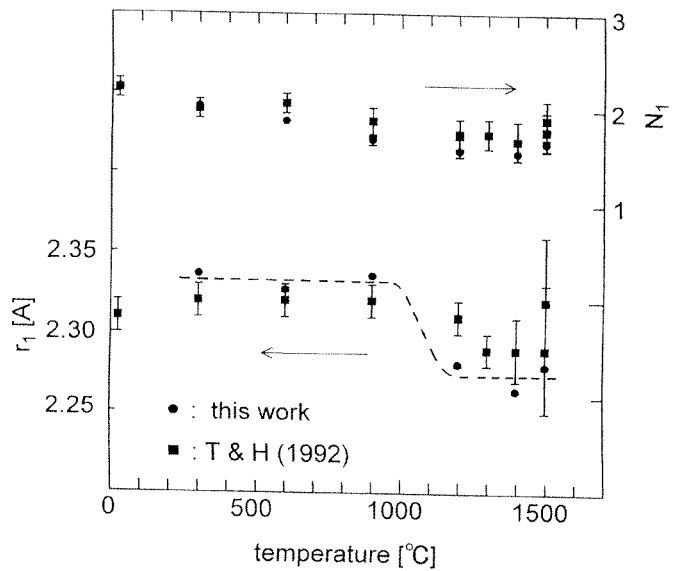
## 3. Results

Figure 1(a) shows the structure factor,  $S(k)$ , of the expanded fluid Se at temperatures and pressures up to 1500 °C and 1420 bar, respectively. Dots represent the experimental data and the solid curves show  $S(k)$  after a smoothing procedure.  $S(k)$  below  $1 \text{ \AA}^{-1}$  is interpolated to the  $S(0)$ -value estimated from the thermodynamic values of fluid Se. The results of 300 °C and 600 °C obtained at lower pressure agree well with those of the previous measurements [8]. It is noticed that the period of the oscillations abruptly changes above 1200 °C, where metallic properties are enhanced.

The pair distribution function,  $g(r)$ , is obtained from Fourier transformation of the  $S(k)$  shown in figure 1(a). From  $g(r)$  and density data,  $n_0$ , we can calculate the radial distribution function,  $4\pi n_0 r^2 g(r)$ , and obtain the first-nearest coordination number,  $N_1$ . Figure 1(b) shows  $N_1$  together with the first peak position in  $g(r)$ ,  $r_1$ , as a function of temperature. Solid circles and squares show the results of this work and the previous one [8], respectively. The results agree well qualitatively and quantitatively. The error bars in this work are within  $\pm 0.14$  for  $N_1$ , and within  $\pm 0.01 \text{ \AA}$  for  $r_1$ . The results of this work have smaller error bars because the oscillations in  $S(k)$  are observed up to higher  $k$ . As is clearly seen in the figure, it is confirmed again that  $N_1$  remains almost equal to 2 over a wide temperature and pressure range and it slightly decreases at temperatures higher than 1200 °C. It is noteworthy that  $r_1$  becomes short at around the temperatures where the electrical conductivity increases progressively and the optical gap disappears.

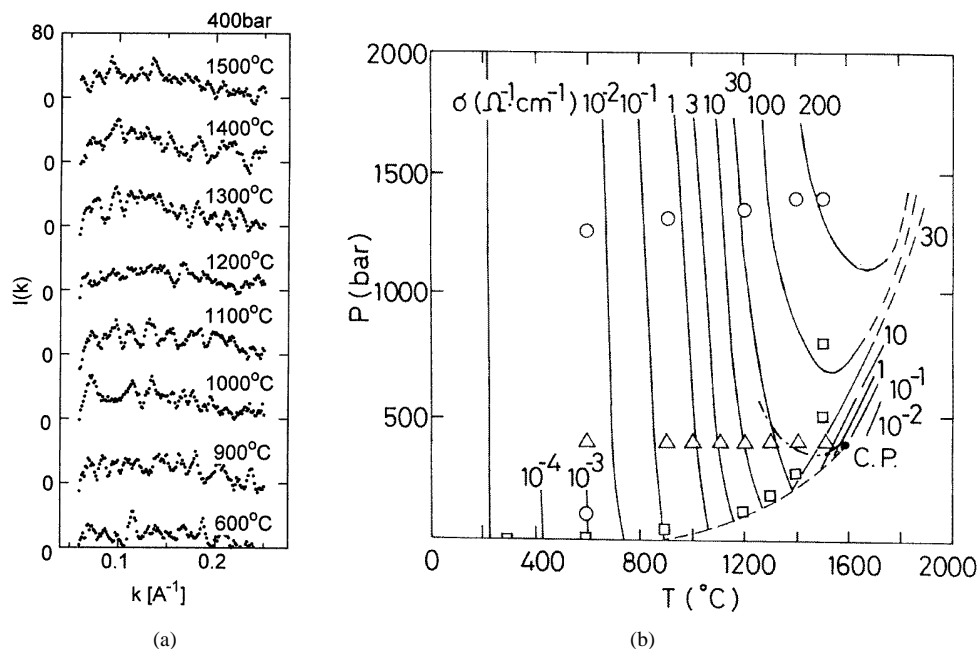


(a)



(b)

**Figure 1.** (a) The structure factor,  $S(k)$ , of fluid Se including supercritical fluid. The temperatures and pressures are shown in the figure. (b) The coordination number,  $N_1$ , and the first-nearest-neighbour distance,  $r_1$ , of fluid Se as functions of temperature. Solid circles show the results of this work and solid squares show those of the previous one [8]. The broken line is to guide the reader's eye.



**Figure 2.** (a) The SAXS intensity,  $I(k)$ , of the supercritical fluid Se at 400 bar. (b) The pressure–temperature phase diagram of Se showing contours of the electrical conductivity. The measured points from SAXS, and x-ray diffraction in the present and previous [8] studies are denoted by triangles, circles and squares, respectively. The chain curve denotes the boundary where the optical gap is closed.

Figure 2(a) shows the temperature dependence of the SAXS spectra for supercritical fluid Se at 400 bar. The measured points in the pressure–temperature phase diagram are shown in figure 2(b) by triangles. The spectra are noisy and a smooth line drawn through the data seems to have a maximum at around  $0.15 \text{ \AA}^{-1}$  at each temperature below  $1200 \text{ }^\circ\text{C}$ . It has been observed that the SAXS intensity at around  $0.12 \text{ \AA}^{-1}$  becomes large above  $1200 \text{ }^\circ\text{C}$  and it looks like a broad peak.

#### 4. Discussion

To explain the anomaly that the isochores bend near the SC-to-M transition region, it has been speculated that threefold-coordinated centres in branched chains are largely created in the high-temperature and high-pressure region and they cause the volume contraction [13]. However, as shown in figure 1(b), the present results give no evidence for the existence of threefold-coordinated centres and show that the twofold-coordinated structure is largely preserved in the metallic region. The most interesting result is that the nearest-neighbour distance decreases when metallic properties are enhanced. The results of our XAFS measurements for supercritical fluid Se show similar contraction of the covalent bond in such a region [9].

A possible mechanism of the SC-to-M transition for supercritical fluid Se should be considered as follows. According to theoretical studies on an isolated Se chain [14], a Se chain with infinite length has an electronic conformation with overlapping of valence and conduction bands in the planar zigzag geometry. In the semiconducting liquid, a helical

chain structure similar to that in crystalline Se is considered to be stable while the sign of the dihedral angle along the chain should be randomly distributed in the liquid state. At higher temperature, the planar zigzag conformation may easily be stabilized because the chain molecule becomes short [2], and the effect of dangling bonds and that of the thermal excitation of a lone-pair electron to the conduction band easily extend over the chain. The covalent bonds become strong due to the formation of a  $\pi$ -bond in the planar zigzag chain.

The metallic behaviour of fluid Se with twofold-coordinated structure may be attributed to the short-chain molecules with the planar zigzag conformation. The SAXS results give information on the density fluctuations in the metallic fluid. The broad peak at around  $0.12 \text{ \AA}^{-1}$  indicates that there are density fluctuations with a correlation length of about  $50 \text{ \AA}$  in the SC-to-M transition. The fluctuations may arise from the mixture of the metallic region consisting of the short-chain molecules and the semiconducting one consisting of relatively long molecules. More accurate SAXS spectra are necessary for discussing the detailed structure of the density fluctuations.

### Acknowledgments

The authors are grateful to Professor S Hosokawa for valuable discussion. Rigaku Co. Ltd and High Pressure Chemical Co. Ltd are acknowledged for their technical support. This work was partly supported by the Grant-in-Aid for Scientific Research Fund of the Ministry of Education, Science and Culture of Japan.

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