Wide and small angle X-ray scattering measurements for expanded fluid Se accompanying the semiconductor-metal and metal-nonmetal transition

M. Inui[1], K. Sato[2], K. Mifune[2], K. Matsuda[2], D. Ishikawa[2,3] and K. Tamura[2]

[1]*Graduate School of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan*

[2]*Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan*

[3] *SPring-8/RIKEN, Sayo-cho, Sayo-gun, Hyogo-ken, 679-5148, Japan*

Corresponding author:

Masanori INUI

Faculty of Integrated Arts and Sciences, Hiroshima University,

Kagamiyama 1-7-1, Higashi-Hiroshima, 739-8521, Japan

TEL:+81-(0)824-24-6555

FAX:+81-(0)824-24-0757

email: inui@mls.ias.hiroshima-u.ac.jp

Abstract

Wide and small angle X-ray scattering measurements for supercritical fluid Se in the wide density region from liquid to dense vapor have been carried out using synchrotron radiation at SPring-8. The large background for the small angle spectra with the previous high-pressure vessel was much suppressed using a new vessel with a large diamond window. We carefully measured wide angle X-ray scattering near the critical density and obtained the structure factor, $S(k)$, and the pair distribution functions, $g(r)$. By small angle X-ray scattering measurements, we succeeded in observing a medium-range fluctuation in the semiconductor-metal transition in expanded fluid Se.

1. Introduction

Liquid Se has a twofold coordinated chain structure where the atoms are covalently bonded. It experiences a semiconductor-metal-insulator (SC-M-I) transition in an expanded fluid state around the critical point (the critical constants of Se [1] : T_c=1888 K , p_c=385 bar, ρ_c=1.85 g cm^{-3}). The first indication of the SC-M transition in fluid Se was found in the electrical conductivity data by Hoshino et al. [2,3]. Many experimental studies on the SC-M transition in expanded fluid Se have been carried out and they are cited in the literature [4]. As a distinct behavior accompanying the SC-M transition, the isochors start to bend at temperatures above 1373 K and pressures above 400 bar [1] near a contour of constant dc conductivity of 30 Ω cm^{-1} [4]. The bending of the isochors was considered to be the onset of a transition to a densely packed structure with defects such as three-fold coordinated centers in the branched chain as assumed by Cabane and Friedel [5]. However, results of neutron diffraction experiments [6] did not give a significant concentration of threefold-coordinated sites up to 1673 K and 265 bar. Tamura and Hosokawa [7] carried out wide angle X-ray scattering (WAXS) measurements for expanded fluid Se up to the metallic region and found that the two-fold coordinated structure is largely preserved in the metallic state while the covalent bond becomes slightly short in the SC-M transition. Recently, WAXS measurements for expanded fluid Se were performed using synchrotron radiation at Spring-8 in Japan and their results were again confirmed by much improved data [8].

The SC-M transition in fluid Se has two characteristic features. First, the transition occurs with volume expansion at constant pressure. Second, the transition promotes the increase of very short chains and it seems to correlate with the instability of the chain structure. Recent molecular dynamics simulations [9-11] have clarified the microscopic picture in the SC-M transition in expanded fluid Se. In the simulation [9], the atoms are actively moving and breaking and branching of the chains frequently occur in the SC-M transition. This process creates one- and three-fold coordinated defects with a short life time and the defect states fill the gap state around the Fermi level, resulting in the metallic state. However there remains a question why the volume tends to contract in the SC-M transition because the simulation assumed the temperature dependence of the density experimentally determined. To understand the SC-M transition in expanded fluid Se more deeply, information on the medium-range correlation may be important. We carried out small angle X-ray scattering (SAXS) measurements for expanded fluid Se in the SC-M transition using a new high-pressure vessel.

When the metallic fluid is further expanded, the conductivity begins to decrease and the fluid finally becomes an insulating vapor consisting of Se dimers, which suggests that the M-I transition occurs upon a further volume expansion around the critical point. Results of SAXS [12] and X-ray absorption fine structure (XAFS) [13] measurements for expanded fluid Se near the critical density indicate that the fluid near the critical density is a mixture of chain molecules and dimers. Now we carried out WAXS measurements for expanded fluid Se and investigated density dependence of the local structure near the critical density.

In this paper, we report new results of WAXS and SAXS measurements.

2. Experimental

WAXS and SAXS experiments were carried out using synchrotron radiation at SPring-8. The storage ring at SPring-8 was operated at 8 GeV with 100 mA during the present experiments. We have performed energy-dispersive WAXS measurements for expanded fluid metals using high-pressure gas apparatus installed at BL28B2. A new diffractometer was installed and the sample position could be more exactly adjusted at the beam center. The high-pressure vessel for WAXS measurements had seven Be windows for the scattered X-ray beams. These windows were located at the scattering angles of 2θ of 4, 7, 11.5, 15, 20, 25 and 33 degrees, to cover a wide range of the modulus of the scattering vector k, ($k=4$ $\pi E \sin\ \ /hc$, where h is Planck's constant, c is the velocity of light and E is the energy of the X-ray). The Se sample (99.999%) was contained in a single-crystalline sapphire cell with the sample thickness of 1.5 mm. Shift of the onset of WAXS spectra to lower energy was observed with decreasing density of fluid sample. We calibrated the density of fluid Se using the magnitude of this shift. Details of the high-pressure gas apparatus for WAXS experiments were described in the literature [14].

SAXS measurements were carried out at the BL04B2 beamline whose details are shown in the paper [15]. Monochromatized 38 keV X-rays were incident on the sample and the scattered X-rays were detected with an imaging plate. Here k is calculated from $k=4$ πsin $/\lambda$, where λ is the wave length of the X-ray. An ionization chamber was put in front of the

imaging plate before and after a SAXS measurement to measure the X-ray transmission for the absorption correction. We installed a new high-pressure vessel with a diamond window of 6 mm in diameter for scattered X-rays. Using a synthetic diamond with the highest quality, the background was significantly suppressed compared to the previous vessel with a Be window. The Se sample was contained in a poly-crystalline sapphire cell with the sample thickness of 0.5 mm. No parasitic scattering was observed from the poly-crystalline cell, even at the highest temperature. In both of WAXS and SAXS measurements, the vessels were pressurized by He gas (99.9999%). SAXS intensity of compressed He gas was measured and compared with a calculated one to deduce the scaling factor for the calibration of the absolute SAXS intensity of fluid Se [12].

3. Results

To obtain the structure factor, $S(k)$, of the expanded fluid Se from the WAXS spectra, we made several data corrections. The details of the data analysis are described in the literature [14]. Figure 1 shows selected $S(k)$ for expanded fluid Se at temperatures and pressures indicated in the figure. The quality of $S(K)$ in vapor phase at 1923 K becomes much better than the previous data [8]. Figure 2 shows the pair distribution function, $g(r)$, obtained from the Fourier transform of $S(k)$ in Fig.1. In the data analysis of SAXS, we subtracted the background intensity of compressed He gas from the observed spectra of fluid Se after being scaled for sample transmission. Then the SAXS intensity of the fluid was normalized with the scaling factor and $S(k)$ was deduced from the formula, $I(k)=Nf(k)^2S(k)$, where N is

the number of atoms depending on the density, $f(k)$ the atomic form factor. The density of

the fluid at each spectrum was estimated from the intensity of the transmitted X-rays. $S(k)$

of expanded fluid Se near the SC-M transition obtained from SAXS measurements is

shown in Fig.3.

4. Discussion

4.1 Local structure in the SC-M-I transition

To see the density variation in the nearest neighbor distance and the first coordination

number, N_I, of fluid Se, we calculated the radial distribution function, $4 \pi n_0 r^2 g(r)$, from

$g(r)$ and number density, n_0. We calculated N_I using two methods because the present $g(r)$

has the first shell merged into the second one. First, we defined the nearest neighboring

coordination number, N_A, twice area in the range from the minimum distance to r_1 , the first

peak position of $g(r)$. Next, we defined the coordination number N_B from the area of 4

$\pi n_0 r^2 g(r)$ up to r_{min} in g(r) as shown in the inset of Fig.4 (a). For the first peak in $g(r)$, we

deduced the full width at the half maximum, Δ, and a skew parameter, μ, as

$\mu = (N_B - N_A)/N_A$. We plot N_A, N_B, r_1, Δ and μ as a function of density in Fig.4.

The present results reconfirm that the twofold coordinated structure is averagely preserved

in the metallic fluid around 3 g cm^{-3}. As seen in Fig.4(b), r_1 is almost constant in the SC-M

transition within the error bars. The maximum in Δ and broad maximum in μ in the SC-M

transition at about 3.2 g cm^{-3} may be related to the enhancement of inter-chain interaction

predicted by the molecular dynamics simulations. The distribution in the first peak of $g(r)$

is extending to larger distance and results in slightly large μ. We believe that the enhancement in $g(r_{min})$ seen in Fig.2 is strongly correlated with the metallic properties.

N_A and N_B gradually decreases with decreasing density towards insulating vapor, which is qualitatively in agreement with the XAFS results [13]. With decreasing density, the r_1 remains about 2.34 A, a covalent bond length of chain molecules, to 2 g cm^{-3} and it starts to decrease to 2.2 A with further volume expansion. The r_1 of about 2 2 A and N_1 of about 1 around 0.5 g cm^{-3} is consistent with the molecular structure of a Se dimmer. These results suggest that dense Se vapor at 0.5 - 1 g cm^{-3} consists of dimeric molecules, which agrees with results by an *ab initio* molecular dynamics simulation for Se vapor [16]. Gradual change of the r_1 and N_1 from the metallic fluid to insulating vapor in the present results strongly hint that expanded fluid Se near the critical density are a mixture of chain and dimeric molecules. In this density region, there appears a clear sub-peak around r_{min}. We carefully investigated it and concluded that it is a spurious one because the termination effect brought a peak at the corresponding r and its height strongly depends on the statictics of $S(k)$. It should be noticed that the density region where the r_1 and N_1 gradually changes are located in the insulating region of the dc conductivity less than 0.1 Ω cm^{-1}. We speculate that the real M-I transition in expanded fluid Se should occur at the dc conductivity of 30 Ω cm-1 which is located near the isochors of 3 – 2 g cm^{-3} in the phase diagram [12], where N_1 shows rapid decrease from 2 but no anomaly in r_1 was observed.

4.2 Medium-range fluctuations in the SC-M transition

We discuss new results of SAXS near the SC-M transition. To observe SAXS in this region was hard and different conclusions have been deduced [17, 18]. In the present result, as shown in Fig.3, we found that $S(k)$ obtained from SAXS increases in the SC-M transition around 1473 K [19]. The enhancement of $S(k)$ at small k seems to be correlated with the increase of $S(0)$ calculated from the thermodynamic quantities. The profile of the spectra does not follow the Ornstein-Zernike equation, $S(k)= S(0)/(1+ \xi^2 k^2)$, which is usually applied to the large SAXS spectra near the critical point. The appearance of weak SAXS hints that there appear dense and rare domains in the SC-M transition, which may be correlated with volume contraction induced by the SC-M transition. Shimojo et al. [9] investigated the SC-M transition in fluid Se by means of an *ab initio* molecular-dynamics simulation and found that the chain-like structure persists even in the metallic state, although the chain structure is substantially disrupted. The broad maximum around 0.12 Å^{-1} in $S(k)$ corresponds to a correlation length of 50 Å, which is a medium-range structure that the *ab initio* molecular-dynamics simulation cannot assess. From these evidences, we speculate that the observed SAXS in the SC-M transition is related to the density fluctuation that the simulation does not predict. The observation of dynamic structure in expanded fluid Se may clarify this medium-range fluctuation.

5. Conclusion

We could observed the density dependence in the local structure in fluid Se by means of WAXS. Molecules in fluid Se gradually transform from chain to dimeric ones with volume expansion. Thanks to a new high-pressure vessel with a large diamond window for SAXS

measurements, we found that $S(k)$ has a broad maximum at 0.12 Å^{-1}, suggesting a medium-range fluctuation induced by the SC-M transition.

References

[1] S. Hosokawa, T. Kuboi and K. Tamura, Ber. Bunsenges. Phys. Chem. **101** (1997) 120.

[2] H. Hoshino, R. W. Schmutzler and F. Hensel, Ber. Bunsenges. Phys. Chem. **80** (1976) 27.

[3] H. Hoshino, R. W. Schmutzler, W. W. Warren Jr. and F. Hensel, Philos. Mag. **33** (1976) 255.

[4] K. Tamura, J. Non-Cryst. Solids, **205-207** (1996) 239 and references therein.

[5] B. Cabane and J. Friedel, J. Phys. (Paris) **32** (1971) 73.

[6] M. Edeling and W. Freyland, Ber. Bunsenges. Phys. Chem., **85** (1981) 1049.

[7] K. Tamura and S. Hosokawa, Ber. Bunsenges. Phys. Chem., **96** (1992) 681.

[8] M.Inui, X. Hong, T. Matsusaka, D. Ishikawa, M. H. Kazi, K. Tamura, K. Funakoshi and W. Utsumi, J. Non-Cryst. Solids, **312-314** (2002) 274.

[9] F. Shimojo, K. Hoshino, M. Watabe and Y. Zempo, J. Phys.: Condens. Matter, **10** (1998) 1199.

[10] F. Kirchhoff, G. Kresse and M.J. Gillan, Phys. Rev. B **57** ,(1998) 10482.

[11] J.Y. Raty, J.P. Gasperd and C. Bichara, Phys. Rev. B **60** (1999) 2441.

[12] M. Inui, Y. Oh'ishi, I. Nakaso, M. H. Kazi and K. Tamura, J. Non-Cryst. Solids, **250-252** (1999) 531.

[13] M. Inui, K. Tamura, J.L. Hazemann, D. Raoux, Y. Soldo, R. Argoud, J.F. Jal, J.Non-Cryst. Solids, **250-252** (1999) 525.

[14] K.Tamura and M.Inui, J. Phys.: Condens. Matter **13** (2001) R337.

[15] M.Isshiki, Y.Ohishi, S.Goto, K.Takeshita and T.Ishikawa, Nuclear Inst. and Methods in Physics Research, A, **467-8** (2001) 663.

[16] F.Shimojo, K.Hoshino, M.Watabe, Y.Zempo, J.Phys.: Condens. Matter, **11** (1999) 8829.

[17] M. Inui, T. Noda, K. Tamura and C. Li, J. Phys.: Condens. Matter , **8** (1996) 9347.

[18] M-.V. Coulet, V. Simonet, Y. Calzavara, D., Testemale, J.-L. Hazemann, D. Raoux, F. Bley, and J.-P. Simon, J. Chem. Phys. **118** (2003) 11235.

[19] M. Inui, K. Matsuda, K. Tamura, K. Satoh, A. Sobajima and H. Tada, to be published in J. Appl. Crystallogr.

Figure Captions

Figure 1

S(k) of supercritical fluid Se including the critical density region. Temperature, pressure and density are shown in the figure. The spectra are displaced by 1 for clarity.

Figure 2

g(r) of supercritical fluid Se obtained from Fourier transform of *S(k)* shown in Fig.1. The curves are displaced by 1 for clarity.

Figure 3

S(k) obtained from small angle X-ray scattering for expanded fluid Se in the SC-M transition region at 600 bar. Also shown is *S(0)* calculated from the thermodynamic quantities by symbols as indicated in the figure.

Figure 4

(a) Coordination number N_1 (N_A:open squares, N_B:closed squares),   (b) the nearest neighbor distance r_1 , (c) the full width at the half maximum of the first peak in *g(r)*, Δ, and (d) skew parameter, $\mu=(N_B-N_A)/N_A$, for expanded fluid Se as functions of density ρ. The inset in (a) shows the definition of Δ, r_1 and r_{min}. The critical density and density where the SC-M transition occurs are indicated by ρ_c and SC-M, respectively.

T	p	ρ
[K]	[bar]	[gcm^{-3}]
1923	200	0.29
1923	250	0.36
1923	300	0.47
1923	350	0.62
1923	400	0.75
1923	420	0.84
1923	450	1.01
1923	470	1.17
1923	480	1.37
1923	491	1.68
1923	500	1.91
1923	552	2.59
1873	609	2.88
1773	605	3.04
1673	602	3.13
1473	594	3.19
573	10	3.91

S(k)

k [Å^{-1}]