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SMALL ANGLE X-RAY SCATTERING MEASUREMENTS FOR EXPANDED FLUID SE NEAR THE CRITICAL POINT

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Abstract

Small angle X-ray scattering (SAXS) measurements have been carried out to investigate density fluctuations near the critical point of expanded fluid Se. The experiments were performed using a polycrystalline sapphire cell of our own design and a high pressure vessel. The vessel has a diamond window for an incident x-ray beam and a Be window for the scattered beams. The absolute value of the scattering intensity was deduced from the measurements on the He gas used as the pressure transmitting medium. The pressure variation of the SAXS intensity for fluid Se at 1630°C shows a maximum intensity at 401 bar just below the isochor of the critical density. This is the first observation of critical scattering for fluid Se and a correlation length of 19 $\pm$ 3 Å was obtained from an Ornstein-Zernike plot.

1 Introduction

Fluid (f-) Se undergoes a semiconductor-metal (SC-M) transition at high temperature and high pressure [1]. Many experimental and theoretical investigations on structural and electronic properties of f-Se have been made so far to understand the SC-M transition [2]–[14]. As is well known, liquid Se has two-fold coordinated chain structure at normal pressure. Structural studies show that the two-fold coordinated structure is largely preserved in the metallic f-Se at high temperature and pressure [7, 10]. The results of nu-

clear magnetic resonance (NMR) measurements [2] suggest that the average chain length becomes short with increasing temperature and pressure. The SC-M transition in f-Se has two characteristic features: the dc conductivity increases with the volume expansion and the transition is correlated with the instability of the chain structure. Recent experimental studies have suggested that the transition occurs around the contour of the dc conductivity of 30 $\Omega^{-1}\mathrm{cm}^{-1}$ [8].

To make the mechanism of the SC-M transition clear, it is interesting to investigate 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 f-Se at high temperature and pressure for the first time [9, 10] and found that the SAXS intensity around 0.1 $\mathrm{\AA}^{-1}$ increases in the transition region [10].

It is significant to study the density fluctuations near the critical point of the supercritical f-Se. When the metallic fluid is further expanded, the conductivity decreases and the fluid finally becomes an insulating vapour consisting of Se dimers, which suggests that metal-non-metal (M-NM) transition occurs in the volume expansion process around the critical point (the critical constants; T_c=1615°C, p_c=385bar and ρ_c=1.85g/cm^3 [13]). In this paper, we report new SAXS data measured near the isochor of the critical density, ρ_c at 1630 °C.

2 Experimental procedure

SAXS measurements for the supercritical f-Se have been carried out using a spectrometer with a slit collimation system. The SAXS spectrometer has three slits to eliminate parasitic scatterings from the first slit. An x-ray beam from a Mo line source provided by a commercial tube with a rotating anode is monochromatized with planar graphite crystal and the Kα_1 line is used. The SAXS intensity is detected by a position sensitive proportional counter (PSPC).

Figure 1 shows the high-pressure vessel for the SAXS measurements. The vessel is made of super-high tension steel and it permits measurements up to 1700 °C and 800 bar. The incident and scattered x-ray beams pass through diamond and Be windows, respectively. In the previous measurements [9, 10], the vessel had a Be window for the

incident beam and the observable k_{min} was limited to 0.08 $Å^{-1}$ due to the large background from the Be window. The background is considerably reduced using the diamond window. The maximum scattering angle is limited by the diameter of the Be window for scattered x-rays. The observable k region in this study is from 0.05$Å^{-1}$ to 0.25$Å^{-1}$.

The Se sample (99.999 %) is contained in a cell made of polycrystalline sapphire, which is resistant to chemical reaction with Se at high temperature. The setup of the cell and heating assemblies are similar to those of our x-ray absorption fine structure (XAFS) [11] and density measurements [13]. The sample thickness was 50 μm for the present measurements. The temperature is measured at three locations by B-type thermocouples (Pt/Rh 30 % , Pt/Rh 6 %) and the difference of the temperatures was within 5 °C at 1630 °C. The vessel was pressurized by high purity grade (99.9999%) He gas and the pressure was measured with a Heise gauge, having an accuracy of $\pm$ 2 bar. The density of f-Se was evaluated from the intensity of transmitted x-ray and its accuracy is within 10%.

3 Results

We first investigate the pressure and temperature dependence of SAXS from the empty cell. Parasitic scattering from the sapphire cell is found to be negligible even at high temperatures but the scattering intensity from pressurized He gas is clearly observed, which was not observable under the large parasitic scattering from the Be window in the previous experiments [9, 10].

Figure 2 shows the scattering intensity, $I(k)$, of the pressurized He gas in the vessel with the sapphire cell at 27 °C and at pressures of 98 bar, 196 bar and 392 bar, as a function of a wave number, k. The scattering intensity from the cell, the diamond and Be windows are subtracted using $I(k)$ at 4 bar. The dots denote the experimental data and the solid curves are calculated ones described in the next paragraphs. Although the experimental data may not have enough quality due to the small statistics, a clear pressure dependence is observed. The maximum of the scattering intensity is proportional to the pressure. It is found that the pressurized He gas has little temperature dependence because of a very small hot area compared with the size of the vessel.

The scattering intensity of x-ray is given by,

$$I(k) = CNf(k)^2 S(k) \quad , \tag{1}$$

where N and $f(k)$ are number of atoms and the atomic form factor, respectively. $S(k)$ is the structure factor and C is a constant which depends on the apparatus. We can determine C from the observed $I(k)$ if N and $S(k)$ of the pressurized He gas are estimated.

In SAXS measurements, $S(k)$ can be approximated by $S(0)$ while $S(k)$ is considered to be almost 1 for a rarefied monatomic gas. Here $S(0)$ of pressurized He gas is estimated from the equation, $S(0) = n_0 k_B T \kappa_T$, where n_0 and κ_T are a number density and an isothermal compressibility of He gas at each pressure, respectively, and k_B the Boltzmann's constant. In calculating $I(k)$ of the pressurized He gas, it should be considered that the He atoms in the vessel are distributed along the x-ray path. After dividing the path into infinitesimal parts, the equation (1) can be used to evaluate the scattering intensity from each part. Consequently we obtain the observed $I(k)$ from the scattering intensity of each part by carrying out numerical integration, considering the geometric arrangement between the vessel and the PSPC detector.

The calculated $I(k)$ is denoted by solid curves in Fig. 2. The constant C is determined to be $(5\pm1)\times10^{-19}$ by adjusting the experimental and calculated spectra at 392 bar. The pressure dependence of the calculated spectra agrees well with that of the experimental ones, which suggests that the determined C is reasonable. The calculated $I(k)$ have a plateau near $k = 0$ because at a small enough scattering angle N is constant, corresponding to n_0 times the volume of x-ray path in the vessel. The calculated $I(k)$ decreases with increasing k because the scattered x-rays are shaded with the flange of the vessel on increasing the scattering angle. The observed spectra agree with the calculated ones besides the difference around 0.2 Å^{-1}, which is considered due to the approximation that the divergence of the incident x-ray beam is neglected in the calculation.

SAXS measurements for f-Se in the critical region were carried out using the same sapphire cell. The observed $I(k)$ became larger with decreasing pressure to the isochor of ρ_c. After subtracting the scattering intensity of pressurized He gas, the absolute values of $S(k)$ for f-Se were deduced for the first time using the obtained C. Figure 3 shows the deduced $S(k)$ of f-Se at 1630 °C and at various pressures near the isochor of ρ_c. Dots

denote the experimental data. The signal to noise ratio of the spectra is not good and there are oscillations in the spectra which may come from some electrical noise by the thermo-regulator. However the spectra behave like the critical scattering because the scattering intensity increases as the isochor of ρ_c is approached.

4 Discussion

The quality of the spectra shown in Fig. 3 is not good and it may be difficult to discuss the long range structure of f-Se in the critical region. However we could estimate the correlation length, ξ, and fluctuations in number-density, $S(0)$, for f-Se near ρ_c, using the Orenstein-Zernike equation.

$$S(k) = \frac{S(0)}{1 + \xi^2 k^2} \quad , \tag{2}$$

To estimate the critical parameters, a curve fitting was carried out and the fitted spectra are denoted by solid curves in Fig. 3. Due to the noise, the results of the fitting have large ambiguity and we estimate large errors of ξ and $S(0)$ using Orenstein-Zernike plots, $1/S(0)$ vs. k^2. In the plots, the experimental data points are scattered but change certainly with pressure. The optimized parameters and the errors are listed in Table 1 together with the density, ρ.

The experimental data at 400 bar and 401 bar show similar behavior as seen in Fig. 3 but the optimized ξ and $S(0)$ are 19 $\pm$ 3 Å and 15 $\pm$ 3, respectively, at 401 bar, while they are 10 $\pm$ 2 and 7.3 $\pm$ 2, respectively, at 400 bar. Taking the quality of the data into acount, it is difficult to discuss the difference in the fitting results. However the density isotherm at 1630 °C in the critical region shows that the density changes largely with pressure [13] and the difference in the SAXS spectra between 400 bar and 401 bar may be reasonable.

The SAXS spectrum at 401 bar behaves like the critical scattering and the density of 1.6 g/cm^3 at 401 bar is the nearest to ρ_c. We can estimate the average number and its fluctuations of atoms at 401 bar and we consider the fluctuation in the intermolecular distance under the density fluctuations. As is well known,

$$S(0) = \frac{| < \Delta N > |^2}{< N >} \quad , \tag{3}$$

where $< N >$ and $< \Delta N >=< N - < N >>$ are the average number and its fluctuation, respectively. For the cubic cell with a side length of 19 Å, $< N >$ and $| < \Delta N > |$ of Se dimers are estimated to be 44 and 26, respectively, from the values of 1.6 g/cm^3 and $S(0) = 15$. As the result the cubic cell contains 70 dimers in the dense state in the fluctuation. The average distance between the dimers is 5.47 Å at 1.6 g/cm^3 while the average distance becomes 4.69 Å in the dense state, corresponding to 2.54 g/cm^3. On the other hand, the cell contains 18 dimers in the rare state in the fluctuation and the average distance is 7.37 Å, corresponding to 0.66 g/cm^3. In the latter case, f-Se in the cell is considered to consist mainly of Se dimers. It is, however, difficult to believe that most of molecules are Se dimers in the dense state. Chain molecules are expected to be formed because of intermolecular interaction between the dimers.

Since the estimated $< N >$ and $| < \Delta N > |$ have large ambiguity, the estimated intermolecular distances have large errors and the above idea may not be supported. However we have another experimental data on the pressure dependence of the bond length in f-Se. In fact, our XAFS results of the supercritical f-Se show that dense Se vapour below ρ_c consists mainly of Se dimers and other chain molecules are formed in the density ranging from ρ_c to about 3 g/cm^3 [15].

Recently *ab initio* molecular-dynamics simulations using the generalized-gradient-corrected density functional theory were carried out by Shimojo et al. [14]. New results of their simulation for f-Se with the densities of 1 g/cm^3 and 2 g/cm^3 where spin effects are taken into account [16] support our idea. The results show that in f-Se with 1 g/cm^3 most of molecules are Se dimers and a rate of chain molecules is small while in that with 2 g/cm^3 most of Se atoms form chain molecules. It is difficult to investigate the density fluctuation in f-Se by the simulation at the present stage because the supercell used in their simulation is as small as the observed ξ near ρ_c.

As seen in the pressure-temperature phase diagram of f-Se with the contours of the constant dc conductivity [2], the isochor of ρ_c is located near the contour of 0.1 Ω^{-1}cm^{-1}, which suggests the insulating property of f-Se near ρ_c. However the density fluctuation near the critical point may induce fluctuations of the conductivity in a microscopic level because the conductivity must strongly depend on the density. The results of SAXS mea-

surements together with the XAFS and simulation results give a picture on structural change in the process condensing rare Se vapour into dense f-Se exceeding ρ_c. The density fluctuations in the supercritical region can induce forming chain molecules from Se dimers. The chain molecules may be seeds of metallic f-Se. It is speculated that when the region consisting of the chain molecules percolate over the whole fluid, the insulating fluid becomes metallic.

5 Conclusion

SAXS measurements for dense Se vapour near the isochor of ρ_c have been carried out and the absolute values of $S(k)$ have been deduced using scattering intensity of pressurized He gas. The number-density fluctuations and its correlation length of f-Se are deduced using Orenstein-Zernike equation though the quality of the spectra is not good. The large density fluctuation near the critical point may enhance the formation of chain molecules with metallic character due to strong intermolecular interaction. The results of XAFS measurements [15] and the computer simulation [16] support above idea.

Acknowledgments

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Figure Captions

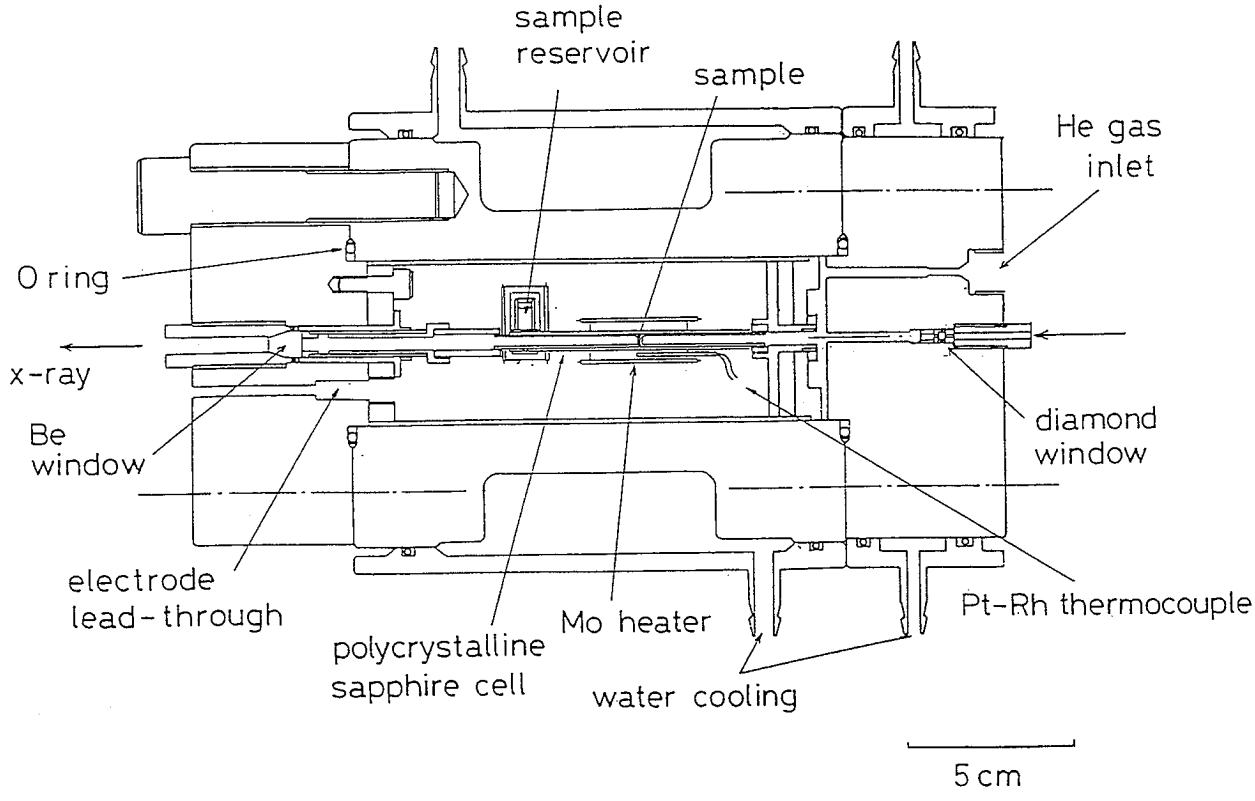
Figure 1 The side view of the high pressure vessel for SAXS measurements.

Figure 2 $I(k)$ of pressurized He gas at 27 °C. Dots and solid curves denote experimental data and calculated ones, respectively.

Figure 3 $S(k)$ of f-Se at 1630 °C. Dots denote the experimental data and the optimized Ornstein-Zernike curve is denoted by solid curves.

Table 1. The correlation length of density fluctuations, ξ, and the fluctuation of number density, $S(0)$, obtained from the Ornstein-Zernike equation for f-Se at 1630 °C, together with the estimated density, ρ.

p[bar]	ρ [g/cm^3]	ξ [Å]	$S(0)$
427	2.4	5.2 ± 0.8	2.0 ± 0.4
412	2.3	7.0 ± 1.1	2.6 ± 0.5
407	2.2	11. ± 2	4.1 ± 0.8
401	1.6	19. ± 3	15. ± 3
400	1.4	10. ± 2	7.3 ± 2
399	1.3	9.0 ± 2	7.0 ± 2
396	1.2	8.7 ± 2	5.1 ± 2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He gas
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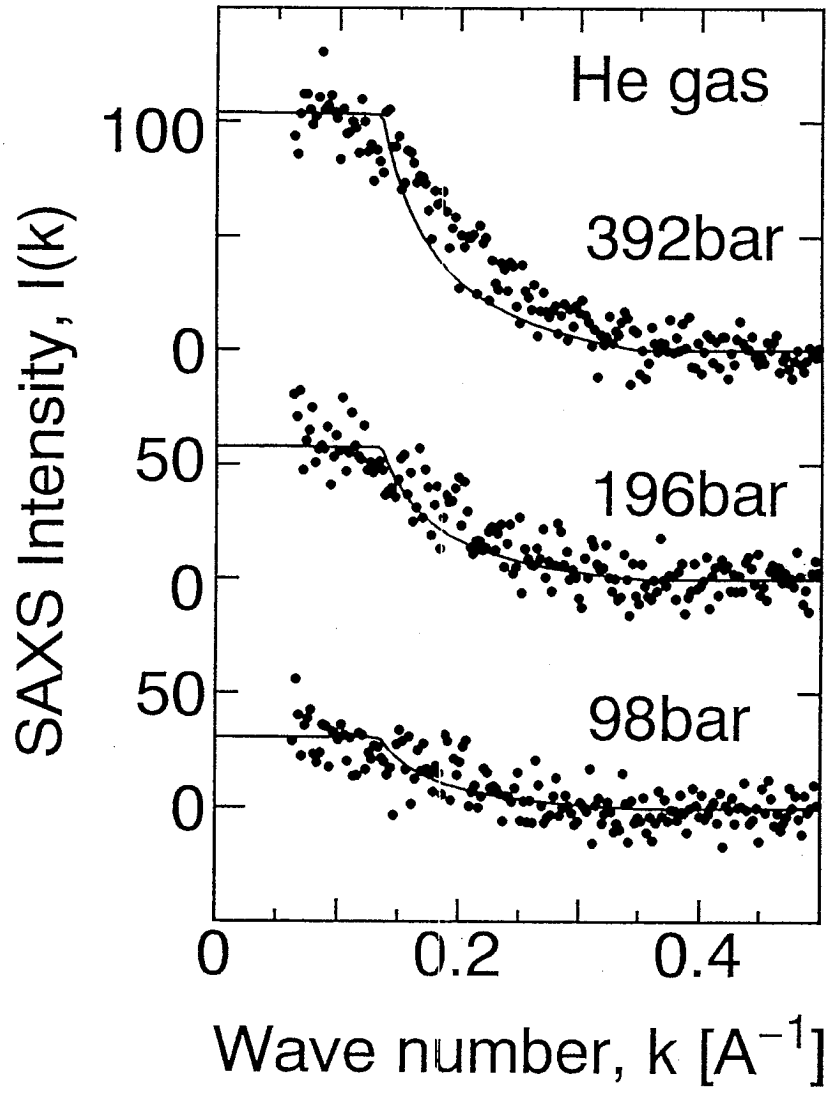
window
diamond
window
electrode
lead-through
polycrystalline
sapphire cell
Mo heater
Pt-Rh thermocouple
water cooling
5 cm

Fig.1


He gas
392bar
196bar
98bar
100
0
50
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50
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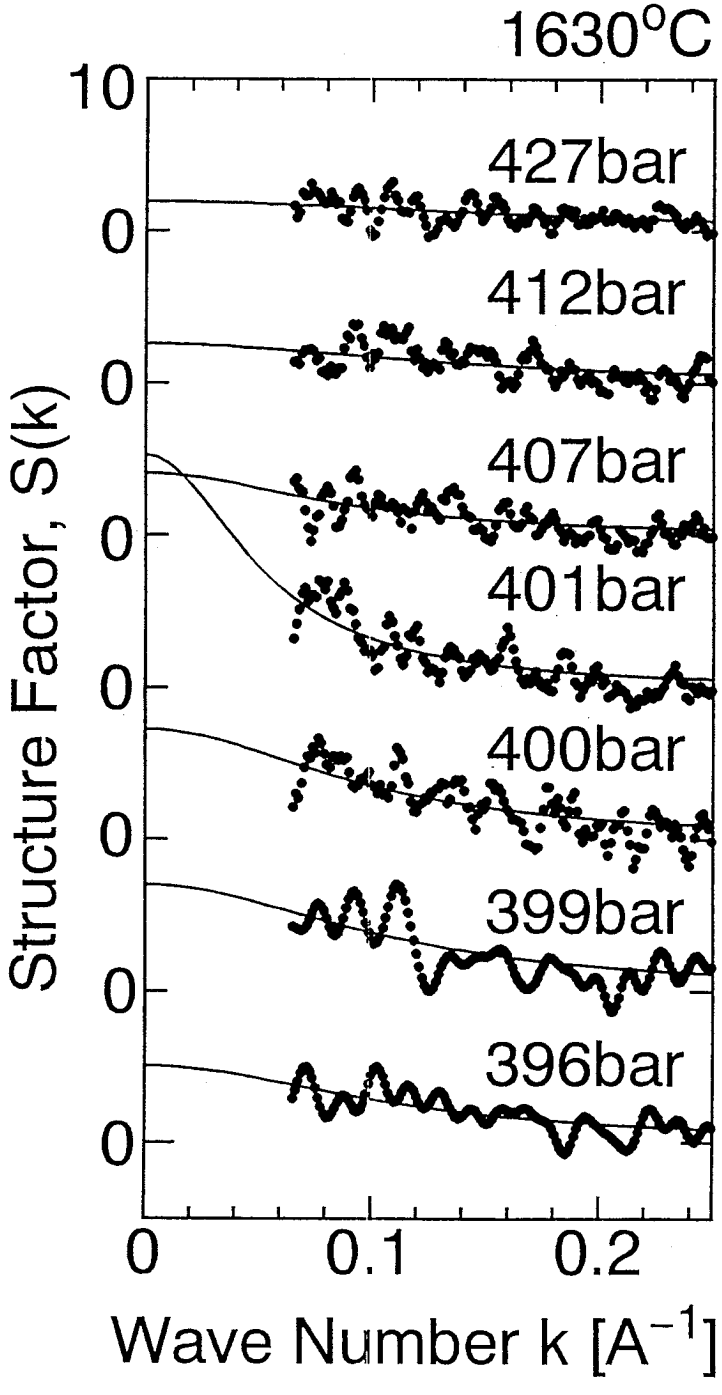
SAXS Intensity, I(k)
0
0.2
0.4
Wave number, k [A^{-1}]

Fig.2


1630°C
10
427bar
0
412bar
0
407bar
0
401bar
0
400bar
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399bar
0
396bar
0
0
0.1
0.2
Structure Factor, S(k)
Wave Number k [A⁻¹]

Fig.3