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X線小角散乱測定による超臨界流体セレンの密度ゆらぎの研究

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A Study of Density Fluctuations in Supercritical Fluid Selenium by Small Angle X-ray Scattering Measurements

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Abstract

Small angle X-ray scattering (SAXS) measurements for dense Se vapour have been carried out to investigate the characteristics of density fluctuations near the critical density region. The correlation lengths of density fluctuations and the number-density fluctuations have been measured precisely at different temperatures and pressures near the critical point. We have also estimated the densities at those temperatures and pressures by using absorption method of X-ray intensities at the same time. In this paper we have also described how we have overcome many difficulties to improve our experimental condition and finally achieved less noisy spectra with better fitting condition to calculate correlation lengths of density fluctuations. Larger values of correlation length of density fluctuations (and also the number density fluctuations) are obtained near the critical density region. The correlation length of density fluctuations as well as number density fluctuations increases as we approach the critical point of fluid Se along the path of critical density region.

Introduction

We know that density, in general, is very important for the physical and thermodynamic properties of materials. However, the deviation from mean density i.e. density fluctuations play an important role for understanding the physical properties of supercritical fluids. Specially, in the case of metallic fluids such as Hg, Se and alkali metals, it is expected that the electronic properties are very sensitive to the density fluctuations. The main aim of this study is to investigate the correlation between density fluctuations and electronic properties of metallic fluids. Fluid Se is chosen in this study to carry out small angle X-ray scattering (SAXS) measurements which give important information about density fluctuations.

Elemental selenium is the third and middle element in chalcogen group. The crystal structure of trigonal Se

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consists of helical chains. Each atom within a chain is covalently bonded to two neighbours, and the bonding between chains is week compared with the interchain bonding. The distance of covalently bonded atoms within the chain is 2.37 A, and the bond angle is about 103^0. The electronic configuration of atomic Se is $4s^24p^4$. The two s electrons are sufficiently low in energy that they do not participate in bonding; two p electrons form covalent σ bonds, one to each neighbours on the chain, and the remaining two p electrons enter the nonbonding lone pair (LP) state. The LP states are the highest filled state and form the valence band, while the empty antibonding σ^* states form the conduction band. Hence trigonal Se behaves as a semiconductor. When Se is melted, a twofold coordinated chain structure is largely preserved and liquid Se shows semiconducting properties as well. From the measurements of viscosity, magnetic susceptibility and nuclear magnetic resonance (NMR), near the melting point, an average chain length of 10^4-10^5 atoms can be estimated. With increasing temperature and pressure the average chain length becomes small and near the critical point (the critical constants: T_c = 1615^0C, P_c =385 bar and ρ_c = 1.85 g/cm^3) it approaches only about ten atoms which was estimated by NMR study. At the same time, the electrical conductivity increases gradually with increasing temperature and pressure and a high conductivity region appears in the immediate vicinity of the critical point. Many experimental and theoretical investigations on structural and electronic properties of fluid Se have been made so far to understand the semiconductor-metal (SC-M) transition. Structural studies show that the twofold-coordinated structure is largely preserved in the metallic fluid Se and the nearest-neighbour distance decreases slightly when the SC-M transition occurs. The SC-M transition in fluid Se has two characteristic features; (1) the dc conductivity increases with volume expansion and (2) the transition occurs when the chain length becomes very short, which seems to correlate with the instability of the chain structure. When the metallic fluid is further expanded, the conductivity turns to decrease, and the fluid finally becomes an insulating vapour consisting of Se dimers, which suggests that the metal-Insulator (M-I) transition occurs in the further expansion process around the critical point.

It is an important point to state that Se experiences SC-M-I transition around the critical point. So it is plausible to think that the electronic properties of fluid Se are very sensitive to the density fluctuations. To make the mechanism SC-M-I transition clear, it is interesting to study how the electronic properties of fluid Se correlate with the density fluctuations near the critical point. For this purpose we need a clear mapping of density fluctuations around the critical point. So it is essential to measure correlation lengths of density fluctuations as well as number density fluctuations at many points in a wide region around the critical point. For this reason we should first investigate the nature of density fluctuations near the critical point of fluid Se.

To understand the properties of density fluctuations of fluid Se we have performed SAXS measurements for supercritical fluid Se near the critical point and have measured the correlation lengths of density fluctuations and the number density fluctuations at different temperatures and pressures.

Experimental procedure and data analysis

Here a brief history of the development of our experimental condition is described. In the previous experiments the high-pressure vessel had Be windows both for incident and scattered X-ray beams. As polycrystalline Be gives rise to background for SAXS spectra, the minimum wave vector k_{min} becomes large due to the peak from the further Be window and the observable k_{min} was limited to 0.08 A^{-1} because of large background from the Be window. The background was much reduced by using the diamond window for the incident X-ray and the observable k_{min} becomes 0.05 A^{-1}.

Initially, X-ray from a Mo Kα source provided by a commercial tube with a rotating anode was monochromatized with a planar graphite crystal and SAXS intensity was detected by a position sensitive proportional counter (PSPC). Although our primary result was obtained for the first time, the signal to noise ratio of the spectra was poor. To improve the X-ray intensity we used a multi-layered mirror for Mo Kα to focus and monochromatize for the first time. It was found that the intensity is increased three to four times using old X-ray generator. Finally SAXS measurements for the supercritical fluid Se have been carried out using a newly installed high brilliant x-ray source. Using the new source, the performance of the multi-layered mirror is much improved and we get parallel beam with high brilliance. The SAXS intensity is detected by Imaging Plate instead of PSPC.

A high-pressure vessel made of super-high tension steel is used for SAXS measurements. The vessel permits the measurements up to 1700°C and 800 bar. The incident and scattered X-ray beams pass through diamond and Be windows, respectively. The observable wave number, k (where $k=(4\pi/\lambda)sin\theta)$, in this study is ranging from 0.05 A^{-1} to 0.25 A^{-1}. The high-purity-grade (99.999%) Se sample is contained in a cell made of polycrystalline sapphire which is resistant to chemical reaction with Se at high temperatures. The sample thickness and camera length are 75 μm and 384 mm for the present measurements. The temperature is measured at three locations by two W-Re thermocouples (Re/W 5%, Re/W 26%) and one B-type thermocouple (Pt/Rh 30%, Pt/Rh 6%) and the difference of the temperatures is within 10°C. The vessel is pressurized by high purity grade (99.9999%) He gas and the pressure is measured with Heise gauge, having an accuracy of ±2 bar.

We obtained the absolute intensity of SAXS spectra and a structure factor, $S(k)$, of fluid Se in the small angle region, using the following way. We have investigated the scattering intensity of compressed He gas from the vessel with sapphire cell at room temperature and pressures 199 bar, 400 bar and 595 bar. We get the calculated spectra using the scattering intensity of X-ray that is given by the equation: $I(k) = CNf(k)^2S(k)$ where $f(k)$ is the atomic form factor. We can obtained the constant C from the observed $I(k)$ if number of atoms N and structure factor $S(k)$ of the pressurized He gas are estimated. The constant C is determined to be 3.85×10^{-19} by adjusting the experimental spectra. We have deduced $S(k)$ of fluid Se by using the constant C .

The SAXS spectra of liquid and fluid Se at different temperatures and pressures were obtained after absorption correction. To carry out the correction, we measured the transmission of x-ray. The spectrum at 600°C and 400 bar of liquid Se is used to subtract scattering intensity of compressed He gas. The larger scattering intensities of fluid Se are found near the critical density region. It is also observed that the intensity of critical scattering becomes larger as we approach the critical point with decreasing temperature.

Results and discussion

To investigate correlation lengths of density fluctuations ξ and the number density fluctuations $S(0)$ for the fluid Se near the critical density, the Ornstein-Zernike equation $S(k) = S(0)/(1+\xi^2k^2)$ is used. We have obtained the larger value of ξ as well as $S(0)$ near the critical density region. We also observed that the largest value of ξ as well as $S(0)$ at a constant temperature increases as we approach the critical point closely along the path of critical density region. This behavior may agree with the fact that the density fluctuations become larger as the critical point is approached.

As is well known $S(0) = \Delta N^2/<N>$, where $<N>$ and $\Delta N = N - <N>$ are the average number and its fluctuation, respectively. At temperature 1647°C and pressure 415 bar it is found that $\xi$and *S(0)* are 56 A and 81 respectively where the density is estimated 1.53g/cm^3. These results mean that the density fluctuations induce a few dense regions with an average size of 56 A. When the cubic cell with a side length of 56 A is considered, the average Se dimers N and its fluctuations ΔN are estimated to be 1039 and 290 respectively. The average distance between the dimers is 5.6 A at 1.53g/cm3. In the dense state the cubic cell contain 1329 dimers and the average distance between the dimers is 5.1 A. The density in the dense state becomes 2.0g/cm^3. On the other hand, in rare state the average distance is 6.2 A, corresponding to density 1.10g/cm^3. It is however difficult to believe that the most of molecules are Se dimers in the dense state; chain molecules are expected to be formed because of strong intermolecular interaction between the dimers. The results of an *ab initio* molecular-dynamics simulation by Shimojo *et al.* for fluid Se show that most molecules are Se dimers and the fraction of chain molecules is small in the fluid with 1g/cm^3, while with 2 g/cm^3 most Se atoms form chain molecules with metallic character. This simulation support our speculation that chain molecules are formed in the dense state under the density fluctuations. In practice, our X-ray absorption fine structure (XAFS) experiments show that fluid Se is a mixture of Se dimers and chain molecules above the critical density. This result can be explained by the fact that XAFS spectroscopy observes the superposition of the dense and rare regions under the density fluctuations.

The results of the XAFS and SAXS measurements together with the simulation results give a picture of the structural change in the process of condensing rare Se vapour into dense fluid Se exceeding the critical density. Density fluctuations in the supercritical region near the critical point can induce the formation of chain molecules from Se dimers, where the chain molecules must be the seeds of metallic fluid Se. Hence density fluctuations may induce fluctuations of conductivity at a microscopic level. The insulating property of fluid Se near the critical density, whose isochore is located near the contour of 0.1 Ω^{-1}cm^{-1}, correlates with such fluctuations. It is speculated that when the region consisting of the chain molecules percolates over the whole fluid, the insulating fluid becomes metallic. It is confirmed that such process can occur in the wide supercritical region around the critical density by the present SAXS measurements.

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