Meso-scale fluctuations in liquid chalcogens near the metal-nonmetal Transition

Y. Ohmasa, K.Fujii, T.Hoshino and M.Yao
Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan
E-mail: ohmasa@scphys.kyoto-u.ac.jp

Abstract. Liquid Te-Se mixtures exhibit a metal-nonmetal (M-NM) transition, which is accompanied by various anomalies in thermodynamic properties such as the thermal expansion coefficient, compressibility and sound attenuation coefficient. These anomalies may be explained by the coexistence and the relaxation of the metallic and non-metallic regions in the liquid, and it is interesting to study the space and time-structure of the meso-scale fluctuations. In the present work, we performed small angle neutron scattering (SANS) and neutron spin-echo (NSE) measurements for liquid Te-Se mixtures near the M-NM transition. We observed that SANS intensity increases with temperature. The NSE intermediate scattering function can be expressed by a superposition of fast and slow exponential relaxation process, whose relaxation times are estimated as $\tau_{\text{fast}} \sim 0.1$ nsec and $\tau_{\text{slow}} > 10$ nsec, respectively. The slow component becomes dominant in the low-Q region, and this process may be related to the anomalous sound attenuation.

1. Introduction

Liquid Te-Se mixtures exhibit a metal-nonmetal (M-NM) transition in a relatively narrow temperature range [1]. This transition is accompanied by anomalies in thermodynamic properties such as the thermal expansion coefficient and compressibility. Recently, sound attenuation measurements for liquid Te-Se mixtures revealed that there occur dynamic anomalies in the M-NM transition region [2, 3]. From the frequency dependence of the sound attenuation coefficient $\alpha$, their relaxation time is estimated to be of the order of nano-seconds. These anomalies may be related to the relaxation between the metallic and non-metallic states in the liquid, and it is interesting to study the space- and time-structure of the mesoscale fluctuations. Neutron spin-echo (NSE) is a powerful technique which gives information on the intermediate scattering function $I(Q, t)$. However, to our knowledge, there is no NSE measurement under such high temperature conditions.

In the present work, we measured the mesoscale space-time structure of liquid Te-Se system by using Small Angle Neutron Scattering (SANS) and Neutron Spin-Echo (NSE) measurements.

2. Experimental

SANS measurements were performed on the SWAN spectrometer in KEK Neutron Scattering facility (KENS) [4]. SWAN spectrometer is equipped with a small-angle, a middle-angle and a high-angle detector banks, and these three detector banks cover a wide $Q$ range from 0.007 to 12Å$^{-1}$. Its $Q$-resolution is $\Delta Q/Q = 0.3$ at 0.007Å$^{-1}$. The size of the neutron beam is 20mm $\times$ 20mm.
We developed a new electric furnace which can be used up to 700~800°C. In order to reduce the back ground, a BN mask is set just in front of the sample cell. We measured liquid Te$_{0.7}$Se$_{0.3}$ at the temperature of 410°C (semiconductor region), 490°C (transition region) and 580°C (metallic region), and liquid Te$_{0.7}$Se$_{0.3}$ at 410°C (semiconductor region), 500°C (transition region), 600°C (metallic region) and 690°C (metallic region). The sample was sealed in a evacuated cylindrical fused quartz cell with inner diameter of 11mm and outer diameter of 11.6mm.

In addition to the scattering intensity from the cell containing liquid sample, $I_{\text{sample+cell}}$, we measured the empty quartz cell, $I_{\text{cell}}$, and the back ground intensity $I_{BG}$. In order to measure $I_{BG}$, a cadmium mask was inserted in front of the BN mask, and the neutron beam path was blocked by the cadmium mask. We also measured transmission of the sample and the cell, $I_T$, measured the empty quartz cell, $I_{cell}$, and that of the empty quartz cell, $I_{cell}$. Then, we calculated the scattering cross sections of the sample, $d\Sigma_s/d\Omega$, and the cell, $d\Sigma_c/d\Omega$ by using

$$I_{\text{sample+cell}} = AT_{s+c} \left( \frac{d\Sigma_s}{d\Omega} + \frac{d\Sigma_c}{d\Omega} \right) + I_{BG}$$

and

$$I_{\text{cell}} = AT_c \frac{d\Sigma_c}{d\Omega} + I_{BG}.$$

NSE measurements were performed at the iNSE spectrometer in the guide hall of the JRR-3M research reactor of the Japan Atomic Energy Research Institute. This spectrometer has a wide detector area, and the echo signal for various $Q$-values can be measured simultaneously by using the spatial distribution of the integrated magnetic field. Detail of this technique will be given elsewhere [5].

We developed a new electric furnace which can be used for NSE measurements up to ~600°C. In order not to disturb the magnetic field around the sample, we used non-inductive resistance heaters. By using this furnace, we measured NSE signals for liquid Te$_{0.7}$Se$_{0.3}$ mixture at 410°C (semiconductor region), 490°C (transition region) and 570°C (metallic region). The sample was encapsulated in a quartz cell and then sealed off under vacuum. The quartz cell has a rectangular parallelepiped shape with sample length of 8mm and the thickness of the quartz wall is 0.5mm.

3. Result and Discussion

3.1. SANS measurements

The SWAN spectrometer is equipped with small-angle, middle-angle and high-angle detector banks, and these three detector banks cover the wide $Q$ range. In the present work, however, we discuss the structure of liquid Te-Se system using the data of only the middle-angle detector bank ($Q \geq 0.25$ Å$^{-1}$) because the scattered neutron intensity detected by the small-angle detector bank was very weak and statistical error is inevitable.

Figures 1(a) and 1(b) show the observed structure factors $S(Q)$ of liquid Te$_{0.6}$Se$_{0.4}$ and (b) liquid Te$_{0.7}$Se$_{0.3}$, respectively. $S(Q)$ measured in the high temperature metallic region (690°C for liquid Te$_{0.6}$Se$_{0.4}$ and 580°C for liquid Te$_{0.7}$Se$_{0.3}$) are indicated by closed circles and those in the low temperature semiconductor region (410°C for both samples) are by open squares. When the temperature is increased, the first peak positions of both samples shift toward high $Q$ value, and this feature coincides with that reported in literatures [6].

It is noticed from these figures that, in the low-$Q$ region below 0.7Å$^{-1}$, $S(Q)$ is larger in the high temperature metallic region than that in the low temperature semiconductor region. Figures 2(a) and 2(b) show the structure factors $S(Q)$ in the small-angle region in more detail. In this $Q$ region, $S(Q)$ increases with temperature monotonously. Especially, in the high temperature metallic region (690°C and 600°C for Te$_{0.6}$Se$_{0.4}$ and 580°C for Te$_{0.7}$Se$_{0.3}$), it is observed that
$S(Q)$ increases with decreasing $Q$, and this result indicates the existence of the long-wavelength fluctuations in this temperature range.

Figure 1. The observed structure factors $S(Q)$ of (a) liquid Te$_{0.6}$Se$_{0.4}$ at 690°C (closed circles) and 410°C (open squares), and (b) liquid Te$_{0.7}$Se$_{0.3}$ at 580°C (closed circles) and 410°C (open squares).

The observed long-range limit of the structure factor, $S(Q \to 0)$, is much larger than the number density fluctuation $\theta = n_0 k_B T \kappa_T$, where $\kappa_T$ is the isothermal compressibility and $n_0$ is the averaged number density. Indeed, $\theta$ is estimated to be around $\sim 0.1$ from the literature value of $\kappa_T$ [7] while the extrapolation of $S(Q)$ to $Q = 0$ seems to be larger than 0.3 at $T = 690°C$ for Te$_{0.6}$Se$_{0.4}$ sample. This result suggests that the concentration fluctuation contributes to the small angle scattering intensity. In addition, the observed monotonous temperature dependence of $S(Q \to 0)$ cannot be explained by temperature dependence of $\kappa_T$, which shows a maximum around the transition region between the semiconductor and the metallic region [7]. This may be explained by the assumption that the concentration fluctuations keep growing with temperature in the metallic region.

Figure 3 shows the difference $\Delta S(Q)$ between the structure factors observed at 690°C and 410°C for Te$_{0.6}$Se$_{0.4}$ sample. The $Q$-dependence of $\Delta S(Q)$ can well be explained by the Ornstein-Zernike form

$$\Delta S(Q) = \frac{\Delta S(0)}{1 + \xi^2 Q^2},$$

where $\Delta S(0)$ is the long-wavelength limit of $\Delta S(Q)$ and $\xi$ is the correlation length. The solid line in Fig.3 is the fitting curve. From the fitting procedure, we obtained $\Delta S(0) \sim 0.2$ and $\xi \sim 3 \sim 4\AA$ as fitting parameters.

3.2. NSE measurements

Figure 1 shows a representative result of the NSE intermediate scattering function $I(Q,t)/I(Q,0)$ observed at 490°C for the Te$_{0.7}$Se$_{0.3}$ sample. Similar results were obtained at other temperatures.

It is noticed from the figure that $I(Q,t)/I(Q,0)$ increases with decreasing $Q$ at the same Fourier time $t$. In addition, $I(Q,t)/I(Q,0)$ drops sharply at small $t$ and then it decreases gradually with time.

In order to fit the observed data, we adopted a superposition of two exponential relaxation processes as follows:

$$I(Q,t)/I(Q,0) = A_{\text{fast}} \exp(-t/\tau_{\text{fast}}) + A_{\text{slow}} \exp(-t/\tau_{\text{slow}}).$$  \hspace{1cm} (1)

Here $A_{\text{fast}}$ and $A_{\text{slow}}$ represent the fraction of the fast and slow components, satisfying $A_{\text{fast}} + A_{\text{slow}} = 1$, and $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ are the relaxation times of the fast and slow dynamics,
respectively. We assumed that $A_{\text{fast}}$ is a linear function of $Q$, and $\tau_{\text{slow}}$ is proportional to $Q^2$. The solid lines in Fig.3 represent the fitting curves.

From this analysis, the relaxation times are estimated to be $\tau_{\text{fast}} \sim 0.1 \text{nsec}$ and $\tau_{\text{slow}} \geq 10 \text{nsec}$ in the $Q$-range of the observation. This value of $\tau_{\text{slow}}$ nearly coincides with the relaxation time obtained from the sound attenuation measurements, $\tau \simeq 15 \pm 3 \text{nsec}$ [2, 3]. The slow component becomes dominant in the low-$Q$ region, and this process may be related to the anomalous sound attenuation.

**Figure 3.** The difference $\Delta S(Q)$ between the structure factors observed at 690$^\circ$C and 410$^\circ$C for Te$_0.6$Se$_0.4$ sample. The solid line indicates the fitting curve using the Ornstein-Zernike formula.

**Figure 4.** The NSE intermediate scattering functions for liquid Te$_0.7$Se$_0.3$ at 490$^\circ$C measured at various momentum transfer $Q$. The solid lines indicate the fitting curves expressed as a superposition of two exponential relaxation functions.

4. Summary

We performed small angle neutron scattering (SANS) and neutron spin-echo (NSE) measurements for liquid Te-Se mixtures near the M-NM transition. We observed that SANS intensity increases with temperature, and this result indicates the existence of the long-wavelength fluctuations. This increase in the SANS intensity cannot be explained solely by the density fluctuation, which is related to the isothermal compressibility, and the contribution from the concentration fluctuation have to be taken into account.

We also observed the relaxation process of the NSE intermediate scattering function. The intermediate scattering function can be expressed by a superposition of fast and slow exponential relaxation process, whose relaxation times are estimated as $\tau_{\text{fast}} \sim 0.1 \text{nsec}$ and $\tau_{\text{slow}} > 10 \text{ nsec}$, respectively. The slow component becomes dominant in the low-$Q$ region, and this process may be related to the anomalous sound attenuation.

Acknowledgments

The authors are grateful to Professors Toshiya Ohtomo and Hitoshi Endo, and Mr. Noboru Osaka for their collaboration on this work. This work is partially supported by the Grant-in-Aid for Scientific Research on Priority Area "Soft Matter Physics" and "Science of Ionic Liquids" from the Ministry of Education, Culture, Sports, Science and Technology, and the Grant-in-Aid for the 21st Century COE "Center for Diversity and Universality in Physics" from the Ministry of Education, Culture, Sports, Science and Technology.

[1] M. Yao and H. Endo, J. Non-Cryst. Solids 205-207 (1996) 85, and references therein.
[2] M. Yao, N. Itokawa, H. Kohno, Y. Kajihara and Y. Hiejima, J. Phys.: Condens. Matter 12 (2000) 7323.
[3] H. Kajikawa, Doctoral thesis (Kyoto University, 2007)
[4] T. Otomo et al.: J. Phys. Chem. Solids, 60 (1999) 1579-1582.
[5] S. Yamada et al., to be published.
[6] S. Takeda, S. Tamaki, and Y. Waseda, J. Phys. Soc. Jpn., 55 4283 (1986)
[7] Y. Tshuchiya, J. Phys. Soc. Jpn, 60 (1991) 960.