Dynamical structure in liquid Te using inelastic x-ray scattering: from semiconductor-metal transition to metallic regime

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Abstract. We have carried out inelastic x-ray scattering measurements of liquid Te at SPring-8 in Japan and obtained the dynamic structure factors $S(Q, \omega)$ at 500, 650 and 800 °C in $Q$-range from 1.3 to 43 nm$^{-1}$ and $\omega$-range from -40 to 40 meV, respectively. Collective excitation is ascertained in each $S(Q, \omega)$. Dynamical velocity $v_Q$ of the excitation mode decreases with increasing temperature, which is normal but contradicts to the behaviour of the ultrasonic sound velocity $v_s$ that anomalously increases against temperature. This contradiction means that the ultrasonic anomaly is not derived from the dynamics in this $Q$-region and larger-size (> a few nm) structural relaxation process exists. The value of ‘positive dispersion’ $(\equiv (v_Q - v_s)/v_s)$ decreases from 70% at 500 °C to 15% at 800 °C. Large positive dispersion is also observed at the nonmetal-metal transition regime in other liquids such as supercritical Hg, which imply that this is a common phenomenon concerning with nonmetal-metal transition.

1. Introduction

Liquid Te is known to exhibit semiconductor-metal (SC-M) transition on melting (melting temperature $T_m$=450 °C) and to show many anomalous thermodynamic behaviours near the temperature: temperature dependence of the density [1] shows maximum at around $T_m$; ultrasonic sound velocity increases with increasing temperature up to around 800 °C [2, 3] which is a rare behaviour because ordinary liquids become softer and their sound velocity decreases with increasing temperature. These anomalies are believed to relate the gradual semiconductor-metal (SC-M) transition of Te.

Many researchers have carried out neutron or x-ray diffraction measurements and determined the static local structure [4, 5, 6]. In summary of these studies, semiconducting solid Te forms 2-fold coordinated covalently bonded structures but in liquid Te there appears a longer bond and it partially forms 3-fold coordinated structures. With increasing temperature, the ratio of this 3-fold coordinated atoms gradually increases, which is closely related to the gradual increase of metallic nature in liquid Te. They could partially explain the SC-M transition [7] but could not mention the thermodynamic anomalies of liquid Te.
Several researchers have obtained the dynamical structure factors $S(Q, \omega)$: some have carried out inelastic neutron scattering (INS) measurements in high-$Q$ region [8, 9, 10] and others have focused on the collective dynamics in low-$Q$ region by inelastic x-ray scattering (IXS) [11] and INS [12]. In the former papers, the discussions were restricted, mainly due to the kinematical restrictions of neutron, to the vibrational density of states or diffusive nature of the particle, and in the latter, the temperature dependences of the data were not reported in detail. The discussion about temperature dependence of the collective dynamics and the origin of thermodynamic anomaly has not yet been concluded. The purposes of the present work are to obtain these data and to discuss its relation to the SC-M transition accompanying thermodynamic anomalies.

2. Experiment
The experiments were carried out at high-resolution inelastic scattering beamline BL35XU of SPring-8 in Japan [13]. The energy of incident x-ray is highly monochromatized to 21.748 keV by Si(11 11 11) back scattering monochrometer and the final energy resolution of the measurements was 1.5-1.8 meV FWHM.

Liquid Te sample with a thickness of 290 $\mu$m was contained in a thin-walled single-crystalline sapphire cell [14]. The cell was located in a vessel [15] equipped with single-crystal Si windows capable of covering scattering angle between 0$^\circ$ and 25$^\circ$. The vessel was filled with about 2bar He gas of 99.9999% purity in order to reduce evaporation of liquid Te. The IXS spectra were measured at 500, 650 and 800 $^\circ$C and the momentum transfer ranges between 1.3 and 43 nm$^{-1}$ at 500 and 800 $^\circ$C and between 1.3 and 27 nm$^{-1}$ at 650 $^\circ$C. Empty cell and and polymethyl methacrylate (PMMA) measurements were separately carried out for background corrections and resolution function determination, respectively.

3. Results and Discussions
Figure 1 shows the representative background-subtracted spectra at 500 $^\circ$C. Each spectrum corresponds to the one at each momentum transfer indicated beside the spectrum. Solid line is a typical resolution spectrum obtained by the PMMA measurement. With increasing momentum transfer, the spectrum becomes broader from 1.3 to 8 nm$^{-1}$, shows so-called de Gennes narrowing at around 20 nm$^{-1}$ where the static structure factor $S(Q)$ shows maximum, and becomes broader again at larger momentum transfer region. There are no clear inelastic peaks in the spectra but small shoulders, indicated by the arrows in the figure, can be seen.

We analyzed the spectra by a damped harmonic oscillator (DHO) model: in this model, the quasi-elastic line of a simple Lorentzian is assumed, and the inelastic mode is expressed by DHO given as,

$$\frac{S(Q, \omega)}{S(Q)} = \left(\frac{\hbar \omega/k_B T}{1 - e^{-\hbar \omega/k_B T}}\right) \frac{A_0}{\pi} \frac{\Gamma}{\omega^2 + \Gamma_0^2} + \left(\frac{1}{1 - e^{-\hbar \omega/k_B T}}\right) \frac{A_Q}{\pi} \frac{4\omega \Gamma Q \sqrt{\omega_Q^2 - \Gamma_Q^2}}{\left(\omega^2 - \omega_Q^2\right)^2 + 4\Gamma_Q^2 \omega^2}. \quad (1)$$

Here $A_0$ and $\Gamma_0$ are the amplitude and the width of the central quasi-elastic line and $A_Q$, $\Gamma_Q$ and $\omega_Q$ are the amplitude, width and energy of the inelastic mode, respectively. The above model function is convoluted by the measured resolution function and the parameters were optimized by the non-linear least square method.

Figure 2 shows the $Q$-dependence of the optimized $\omega_Q$ at (a) 500, (b) 650 and (c) 800 $^\circ$C. Dashed lines are dispersion curves calculated from the ultrasonic sound velocity [3]. Solid lines are the static structure factor $S(Q)$ obtained by neutron scattering measurements [6]. In the high-$Q$ region, $\omega_Q$ show dips at around quasi-Brillouin zone boundary $hQ \approx 19$ and 33 nm$^{-1}$ where $S(Q)$ shows maxima. In the small-$Q$ region, $\omega_Q$ almost linearly disperses at each temperature, which demonstrates acoustic-like mode.
We calculate the dynamical velocity of this acoustic mode defined by $v_Q \equiv \omega_Q/Q$ in the small-$Q$ region where the $\omega_Q$ linearly disperses. The results are plotted by circles in Fig. 3. Velocities deduced by other authors are also plotted: triangle and crosses denote the dynamical velocities obtained from the previous IXS [11] and INS [12], respectively. The consistency between these dynamical velocities is good. Dashed line is the adiabatic value measured directly from the ultrasonic method [3]. The important experimental facts indicated in this figure are two: first, $v_Q$ decreases with increasing temperature while the adiabatic sound velocity increases. This different temperature dependence between $v_Q$ and adiabatic one indicates that the ultrasonic sound anomaly, and we also believe other thermodynamic anomalies accompanying SC-M transition, are not derived from the $Q$-range dynamics observed in the present IXS observe. Namely the thermodynamic anomalies arise from structural relaxation processes with larger sizes ($2\pi/Q > \text{a few nm}$), which hints the existence of mesoscopic inhomogeneity at SC-M transition region in liquid Te. Second point is that the value of ‘positive dispersion’ defined by $(v_Q - v_s)/v_s$, substantially changes from 70% at 500 °C to 15% at 800 °C. The latter value is normal for liquid metals but the former is considerably large as a liquid metal. This large increase of positive dispersion at SC-M transition indicates that the viscosity of the above mentioned mesoscopic relaxation process increases due to the transition. A large increase of positive dispersion is also

Figure 1. IXS spectra at 500 °C. Each spectrum corresponds to each momentum transfer beside the spectrum and is shifted each other for clarity. Solid line shows the resolution spectrum. Arrows indicate the positions of the small shoulder.

Figure 2. Dispersion curves at (a)500, (b)650 and (c)800 °C. Dashed lines indicate the dispersion curves calculated from the ultrasonic sound velocities [3]. Solid lines are the static structure factors $S(Q)$ by neutron diffraction measurements [6].
Figure 3. Velocities of liquid Te obtained from various methods. Circles, triangle and crosses are the dynamical values deduced from $S(Q, \omega)$ of the present IXS, previous IXS [11] and INS [12] measurements, respectively. A solid line is a guide for the eyes. A dashed line is the adiabatic value by the ultrasonic sound measurement [3]. The SC-M transition region is denoted by a hatch around 400 °C.

observed near the metal-nonmetal transition in supercritical fluid mercury [16]. We believe that it is intrinsic feature for fluid metal-nonmetal transition systems.

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