

Signature of rigidity transition in liquid As_2Se_3 observed by inelastic X-ray scattering

$\text{As}_x\text{Se}_{1-x}$ is an interesting glass-forming system where the glass-forming ability is maximized for $x=0.4$ or As_2Se_3 . This has been discussed in terms of rigidity theory, which focuses on the nearest-neighbor coordination number of the atoms, suggesting that the system will be most stable when the number of mechanical constraints per atom is equivalent to the number of spatial degrees of freedom, 3 [1], which corresponds to an average coordination number of 2.4. The idea of a rigidity transition has been used to account for the relatively high glass-forming ability of As_2Se_3 , and to suggest that in the glassy state there can be a stiffness transition from inflexible to flexible structures when the average coordination number drops below 2.4.

As_2Se_3 also has interesting and typical properties as a liquid. Investigation of the local structure of liquid As_2Se_3 in a wide temperature range at high pressures [2] revealed that the average coordination number exceeded 2.4 near the melting point and *decreased* with increasing temperature, whereas, more often, the average coordination number of a liquid increases with increasing temperature. This correlates with the rather unusual semiconductor-metal transition in liquid As_2Se_3 (see the atomic configurations of crystalline and liquid As_2Se_3 in Fig.1). Usually, the semiconductor-metal transition occurs when the valence electron density increases with compression of the material at high pressures; closing the band gap and delocalization of conduction electrons are the main processes for metallization. Liquid As_2Se_3 , however, acquires metallic properties during volume expansion with increasing temperature. This suggests

that atomic motion induced by the thermal energy may play an important role in the semiconductor-metal transition in this liquid.

Considering these unusual properties, it is interesting to directly investigate the atomic dynamics of liquid As_2Se_3 via measurement of the dynamic structure factor, $S(Q, E)$, where Q and E are momentum and energy transfer, respectively. In particular, there was interest in the mesoscale region, corresponding to nanometer-order correlation lengths, where one may begin to see the onset of the impact of the local atomic structure.

In the present study, inelastic X-ray scattering experiments were carried out at temperatures from 1073 to 1673 K at 6 MPa and at momentum transfers Q from 1.6 to 11 nm^{-1} using the high-pressure apparatus installed at SPing-8 BL35XU [4]. Highly brilliant X-rays with high energy resolution were incident onto the sample with the scattered X-rays received by an array of analyzer crystals. The energy and momentum transfer resolutions were 1.5 meV and 0.45 nm^{-1} , respectively. The As_2Se_3 sample of 99.999% purity and 0.1 mm thickness was mounted in a single-crystal sapphire cell that was placed in a high-pressure vessel. The vessel was filled with He gas (99.999% purity) at 6 MPa to stabilize the liquid state. The background spectra were measured at 1273 K and 6 MPa using an empty cell. After background subtraction with the absorption correction and integration with respect to E , we deduced the normalized dynamic structure factor $S(Q, E)/S(Q)$ of liquid As_2Se_3 from the observed spectra. Figure 2 shows $S(Q, E)/S(Q)$ of liquid As_2Se_3 at

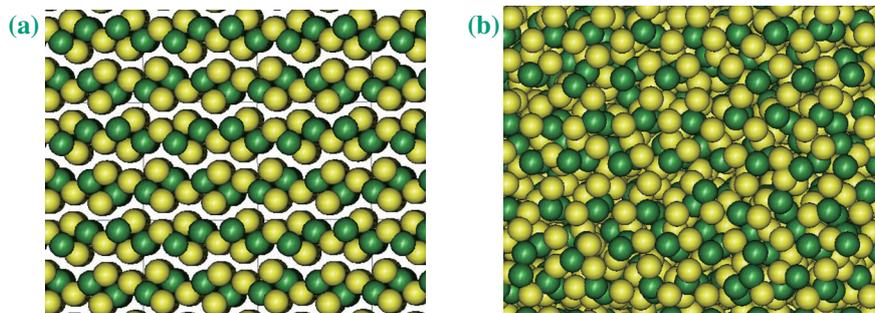


Fig. 1. Atomic configurations of As (green) and Se (yellow) in monoclinic crystalline As_2Se_3 [3] (left) and in liquid As_2Se_3 (right) near the melting point. The liquid structure was obtained by reverse Monte Carlo simulation [2].

1073 and 1473 K. At 1073 K, the inelastic excitations at 2.6 nm^{-1} merge into a broad single peak as a result of the spectrometer resolution while they are clearly separate at 2.9 nm^{-1} , indicating a discrete increase in the excitation energies between these Q values. On the other hand, the acoustic excitations at 1473 K disperse with increasing Q without such a discrete energy change. An anomaly in the acoustic mode energy at 2.7 nm^{-1} was observed below 1373 K, as shown in Fig. 3, where black circles denote the excitation energy of the model function of the damped harmonic oscillator.

The Q dependence of the excitation energy is reminiscent of an anti-crossing phenomenon in a solid. A linear chain model presenting an anti-crossing dispersion curve to the black circles is applied to describe in Fig. 3 and obtained the optimized dispersion curves indicated by the red broken lines. Comparison with structural information obtained by reverse Monte Carlo modeling of X-ray diffraction data [2] indicates that the disappearance of the anomaly at higher temperatures ($>1373 \text{ K}$) is associated with a drop in the average coordination number, reminiscent of the threshold applicable for glass-forming in rigidity theory. Thus, the surprising jump in the dispersion in the liquid may be analogous to the stiffness transition in network glasses.

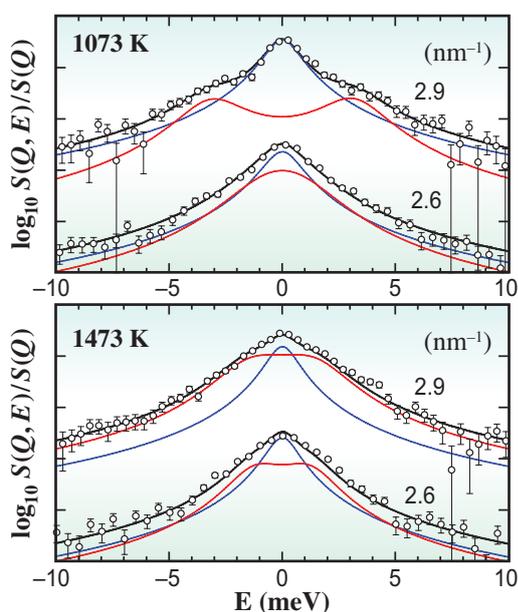


Fig. 2: $S(Q, E)/S(Q)$ of liquid As_2Se_3 at 1073 K (upper graph) and 1473 K (lower graph) at 6 MPa. Open circles and solid lines denote the experimental results and the optimized fits, respectively. Also shown are the quasielastic/Lorentzian component (blue) and inelastic excitation/damped harmonic oscillator (red) of the model function convoluted with the spectrometer resolution function.

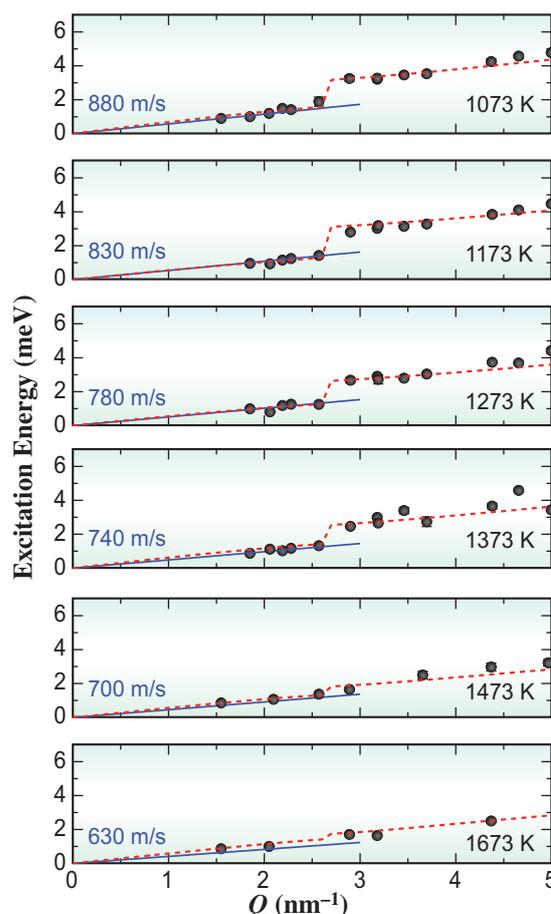


Fig. 3. Excitation energies of the acoustic mode as a function of Q at the indicated temperature. The red broken lines indicate optimized fits using a linear chain model. The energy corresponding to the ultrasonic sound speed indicated in each panel is also shown by a blue line from the origin.

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