Low-energy excitation in As_2S_3 glass studied by inelastic X-ray scattering

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Abstract

The low-energy excitation of As_2S_3 glass was measured for the first time by high-resolution inelastic X-ray scattering to obtain an additional insight into the Boson peak. The experiments were performed at room temperature at Q = 1.5 to 63.6 nm^{-1} and ω = -40 to 50 meV. Besides an acoustic-like collective mode in the low-Q region, the low-energy excitation was clearly observed above 20 nm^{-1} around 3 meV, whose intensity increases with increasing Q and exhibits a maximum at 39 nm^{-1} in coincidence with the third peak of the structural factor $S(Q)$. The observations suggest that the low-energy excitation of As_2S_3 glass at Q > 20 nm^{-1} may originate from localized vibrational soft modes associated with the dynamical correlation of S atoms with the nearest-neighboring As atoms.

Keywords: Boson Peak; Low-energy Excitation; Chalcogenide Glass; Amorphous Semiconductors

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1. Introduction

The Boson peak, which appears in the low-energy excitation spectra of glassy materials, has drawn much attention and been extensively studied to explore its origin and features for more than five decades. However, the origin of the Boson peak still remains open to question. Chalcogenide glasses are often called covalent network glasses which can be categorized between fragile (*e.g.*, polymer and molecular glasses) and strong (*e.g.*, silica and other oxides) glasses, and therefore significantly different from silica and polymer/molecular glasses in structural/glassy properties and hence in the origin of the Boson peak. The Boson peak of typical chalcogenide glasses, is observed as an excess peak at about 3 meV in the vibrational density of states. Several models [1-4] have been proposed to explain the origin of the Boson peak in chalcogenide glasses. Features and the origin of Boson peak were often discussed in relation to microscopic and/or intermediate range structure, and sometimes explained together with the origin of the first sharp diffraction peak (FSDP) which is characteristic for the glasses. However, the proposed ideas seem to be still controversial. Besides localized or propagating vibrational modes, the low-energy excitations of glasses can be involved also with relaxational and/or deformational motions of restricted structures. This fact has made the exploration of the low-energy modes (including the Boson peak) of glasses difficult and complicated.

We have studied the low-energy excitations of As_2S_3 glass by far-infrared absorption [5] and Raman scattering measurements [6]. To elucidate the origin of the low-energy excitations, we have tried to apply several models to our results and also to correlate them with the relaxation dynamics of glass transition obtained by differential scanning calorimetry [7]. However, we have not understood fully the origin of low-energy excitations in chalcogenide glasses. The Boson peaks of chalcogenide glasses have been investigated also by inelastic neutron scattering (INS) for Ge-Se glasses [8], but have not yet been studied by inelastic X-ray scattering (IXS). It should be worthy to measure $S(Q,\omega)$ of chalcogenide glasses in the low-energy region in a wide range of momentum transfer Q using the IXS technique, where INS cannot encompass due to its kinematic restrictions, to gain an additional insight into the Boson peak and the low-energy dynamics of the glassy network.

In the present study, the low-energy excitations of As_2S_3 glass were measured for the first time by the high-resolution inelastic IXS to explore their origin and features.

2. Experimental

Bulk As_2S_3 glass was prepared in a sealed quartz ampoule of 1×10^{-4} Pa by a conventional melt-quenching method; quenched from 600 °C to room temperature in air. The resulting ingot was annealed for 3 hours at 170 °C in vacuum, and then sliced with a wire saw and polished down to 150 μm thickness to ensure the penetration of the incident X-ray beam through the sample for IXS experiments (the incident X-ray transmission was 33 %). The sample was put in a vessel in vacuum for IXS experiments.

IXS experiments have been performed at the high-resolution IXS beamline (BL35XU) at SPring-8 in Japan [9]. Since the Boson peak of As_2S_3 glass appears around 3 meV, the energy resolution should be as high as possible. A highly resolved monochromatized X-ray beam of 3.5×10^9 photons/sec at a spot of 0.2 mm in diameter was obtained from a cryogenically cooled Si(111) double-crystal followed by a Si(11 11 11) monochromator operating in a backscattering geometry (21.75 keV). The scattered X-ray photons were collected by four spherically curved Si analyzers with a diameter of 10 cm using the same backscattering geometry. The IXS experiments were carried out at Q values from 1.5 to 63.6 nm^{-1}. A typical energy scan was from -40 to 50 meV and took approximately two hours for one scan. We averaged data over two - six scans, depending on signal intensities, to improve the statistics. The background correction was performed using the data of empty-cell measurements. The spectrometer resolution was about 1.6 meV, determined from the scattering of a 3 mm Plexiglas sample. Even though the Boson peak was located in a low-energy region close to the resolution limit, we were still able to obtain the component of the Boson peak owing to its long tail to the high-energy side. The Q resolution was about ±0.45 nm^{-1}.

3. Results

In Fig. 1 are shown the IXS spectra, normalized to the intensity at ω=0, for As_2S_3 glass at the indicated fixed Q values. At Q < 9 nm^{-1}, a shoulder both in stokes and anti-stokes shifts can be seen, indicating an acoustic-like propagating mode. Its collective dynamics will be reported elsewhere [10]. Here, we should mention that the Boson peak is not appreciable in the low-Q region below 15 nm^{-1}. On the other hand, above 20 nm^{-1} the component of low-energy excitation appears around 3 meV with a long tail to higher energies in the IXS spectra. This is clearly realized after the subtraction of the resolution function from the experimental data, as shown in Fig. 2 for Q = 59.7 nm^{-1} as an example. Here, we assume that the resolution function is identical with the elastic component of this glass. The component after subtraction, referred to as the low-energy excitation spectrum hereafter, exhibits a peak around 3 meV and a long tail to 20 meV both in stokes and anti-stokes shifts, being identified as the Boson peak of this glass. Changes in the low-energy excitation spectrum with Q are shown in Fig. 3. The Boson peak does not change in energy and lineshape but in intensity with Q. In Fig. 4, the intensity of the Boson peak at 3 meV is plotted as a function of Q together with the structural factor $S(Q)$ obtained by neutron diffraction [11]. The Q-dependence of the elastic scattering component $S(Q,0)$, *i.e.* the IXS intensity at ω=0 meV, is also shown for comparison. It is found that the Boson peak, which starts to appear around 15 nm^{-1}, increases in intensity with Q and exhibits a maximum at 39 nm^{-1} which is in coincidence with the third peak of $S(Q)$. With a further increase in Q above 40 nm^{-1}, the intensity of the Boson peak oscillates as $S(Q)$. It is noteworthy that the low-energy excitation is not appreciable in the Q region of FSDP. We also observed a S-As-S bending mode in the energy region of 20-25 meV and a weak but appreciable As-S stretching mode at 45 meV. The Q-dependence of those local modes in a glassy state is also interesting and will be reported elsewhere.

4. Discussion

In the low-energy region where the Boson peak is observed, some vibrational contributions may have to be considered as the low-energy excitations in glasses. One is the low-lying optical modes of the counterpart crystal which are broadened due to disorder in glasses, *e.g.* the rigid layer modes at 36 cm^{-1} and 25 cm^{-1} in crystalline As_2S_3 [12]. Debye-like as well as highly-damped ~~transverse~~ acoustic modes would also contribute to the low-energy excitation spectra [4, 13]. Indeed, we have observed the acoustic-like propagating mode in a low-Q region (Q < 9 nm^{-1}). The acoustic-like collective mode increases in energy with Q, and reaches a ceiling of about 9 meV with significant damping, and then becomes almost inappreciable above 9 nm^{-1}. On the other hand, the Boson peak appears at 3 meV above 20 nm^{-1}. The observation suggests that it is hard to relate the highly-damped acoustic-like mode to the vibrational excitation causing the Boson peak in the high-Q region. In addition, the Boson peak exhibits no dispersion, *i.e.* no Q-dependence of energy, indicating that the low-energy excitation mode due to the Boson peak is localized. Thus, the Boson peak in high-Q region is not in favor for a simple picture of a damped acoustic nature.

Disorder-induced localized soft mode, in which atoms vibrate in soft atomic configurations, is another candidate for the Boson peak, and some “disorder-induced” mechanisms have been proposed [14, 15]. In the Raman scattering spectra of glasses, both the Debye-like acoustic and the localized soft modes are believed to contribute to the Boson peak [16], which makes an analysis of the Boson peak complicated. In our IXS spectra, these two contributions are separated into different Q-regions. We consider that the Boson peak observed in the high-Q region above 20 nm^{-1} originates purely from localized vibrational modes. As represented by the solid line in Fig. 2, the lineshape of the Boson peak is well reproduced with a soft-potential model in which the vibrational instability of weakly interacting quasi-localized harmonic modes is taken into account to explain the Boson peak

[15].

Here, the question is what microscopically the “quasi-localized harmonic vibrational mode” in this glass is. Let us discuss the quasi-localized mode originating in the Boson peak in the high-Q region in the microscopic structural and dynamical aspects. Firstly, the low-energy excitation is inappreciable in the Q region of the FSDP (Q=10~15 nm^{-1}), as shown in Fig. 4. This implies that the intermediate-range structural correlations resulting in the FSDP, *e.g.* As-As and S-S correlations as suggested by anomalous X-ray scattering [17], are not associated with the Boson peak. Secondly, the intensity of the Boson peak makes a maximum at 39 nm^{-1} in coincidence with the third peak of $S(Q)$ and oscillates as $S(Q)$ in the higher Q region. This observation indicates that the dynamical correlation of S atoms with the nearest –neighbor As atoms should be associated with the occurrence of the Boson peak. However, how such a mode becomes soft and interacts weakly with each other is still open to question. It should be noteworthy that the relative intensity of the Boson peak to the elastic scattering component follows $I_r(Q) \sim Q^{2.4}$. This would provide another clue for the nature of such a vibrational excitation.

5. Conclusion

To explore the low-energy excitation, the so called Boson peak, in chalcogenide glasses, we have measured for the first time the high-resolution inelastic X-ray scattering of As_2S_3 glass. We have qualitatively examined our results for its origin and relation to microscopic and/or intermediate-range structure. Our observations suggest that the low-energy excitation of As_2S_3 glass at Q > 20 nm^{-1} may originate from localized vibrational soft modes associated with the dynamical correlation of S atoms with the nearest–neighbor As atoms. Further analyses are now in progress.

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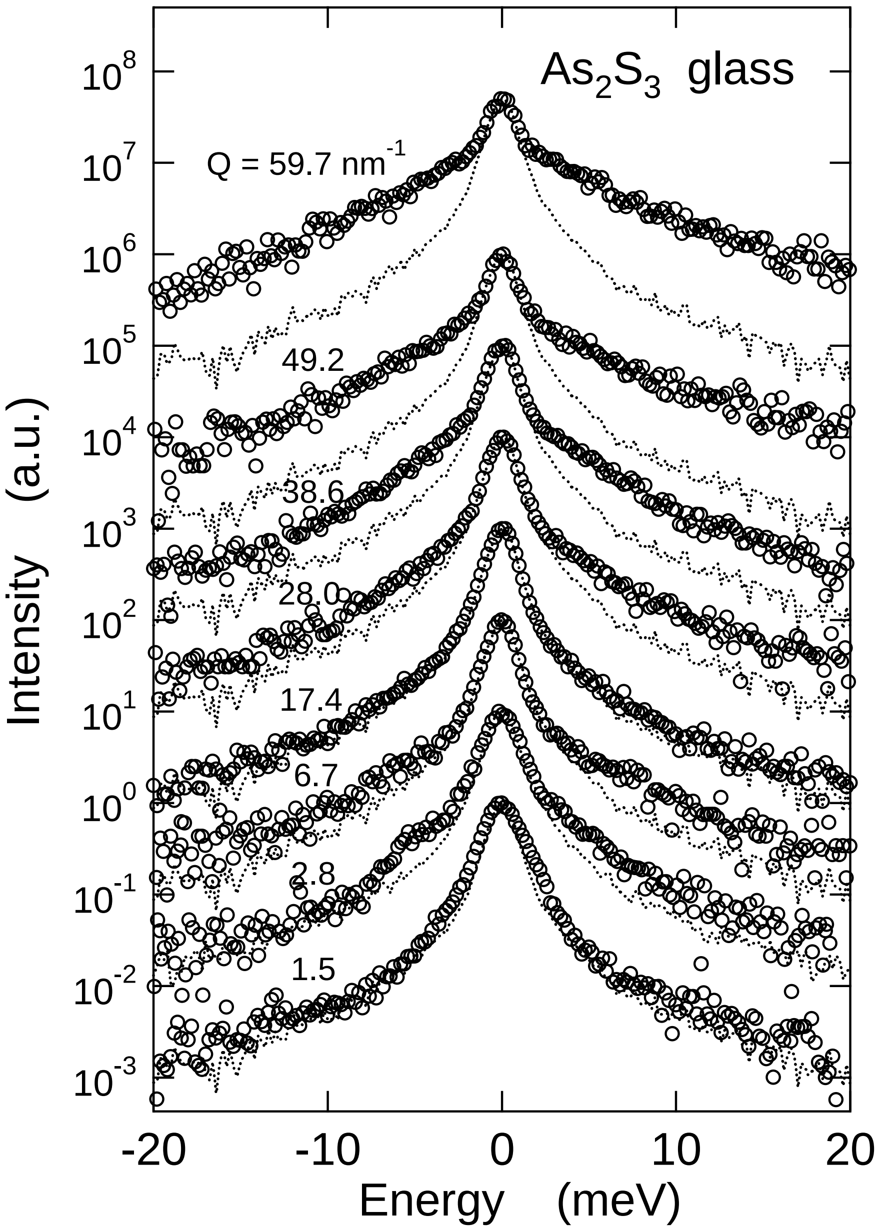
Figure captions

Fig. 1. Normalized IXS spectra (open circles) of As_2S_3 glass at the indicated fixed *Q* values. The instrumental resolution function is also represented by the dotted line.

Fig. 2. Low-energy excitation spectrum (solid circles) of As_2S_3 glass after subtraction of the resolution function (dashed line) from the experimental IXS spectrum (open circles) for $Q = 59.7$ nm^{-1}. The solid line is the best fit to the low-energy excitation spectrum by the soft-potential model [15].

Fig. 3. Changes in the low-energy excitation spectrum, obtained as represented in Fig. 2, with *Q*. Error bars are put on the data.

Fig. 4. Intensity of the Boson peak at 3 meV (solid circles) as a function of *Q*. The structural factor $S(Q)$ obtained by neutron diffraction [11] and the *Q*-dependence of the elastic scattering component (*i.e.*, the intensity at $\omega = 0$ meV) are also shown by the solid line and open circles, respectively, for comparison. The line for the open circles is drawn as guide for the eye.



As$_2$S$_3$ glass
Q = 59.7 nm^{-1}
49.2
38.6
28.0
17.4
6.7
2.8
1.5
Intensity (a.u.)
Energy (meV)

Fig. 1

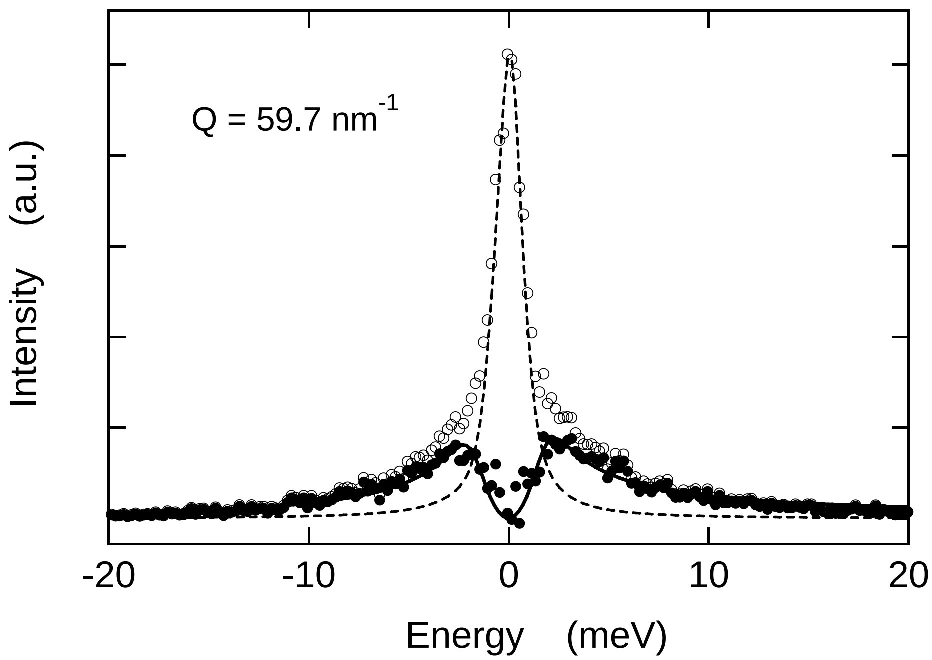
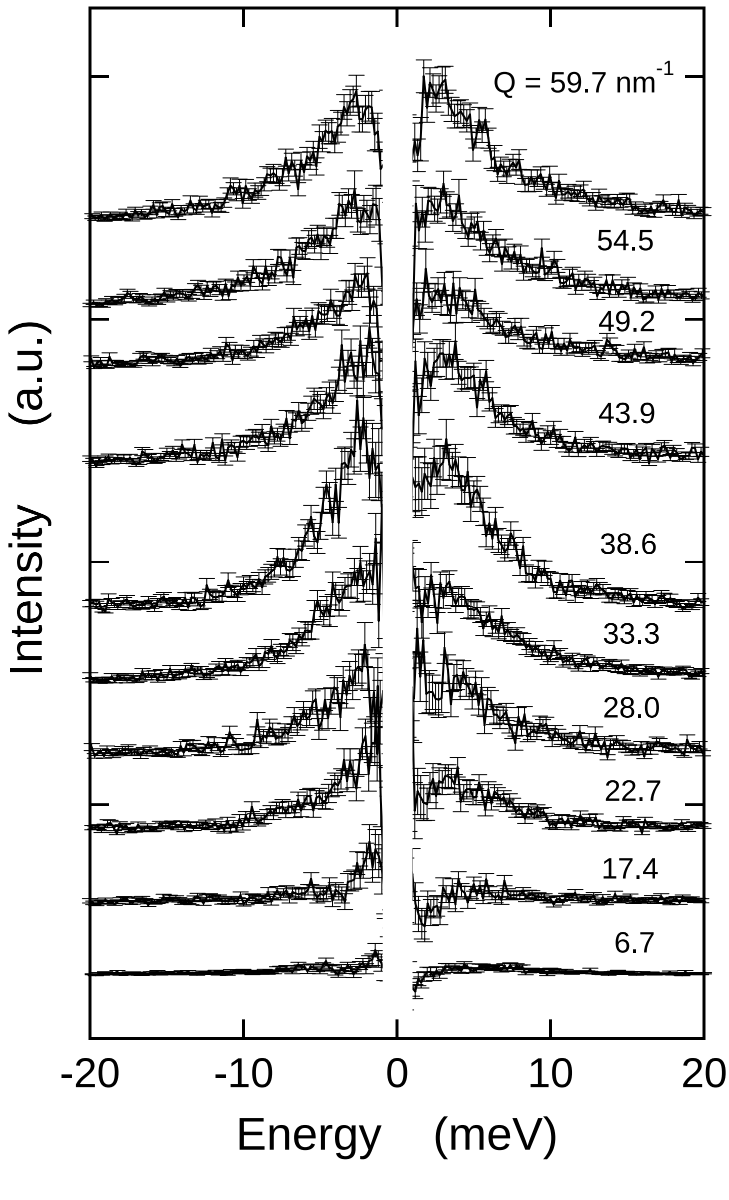


Fig. 2



Q = 59.7 nm-1
54.5
49.2
43.9
38.6
33.3
28.0
22.7
17.4
6.7
Intensity (a.u.)
-20
-10
0
10
20
Energy (meV)

Fig. 3

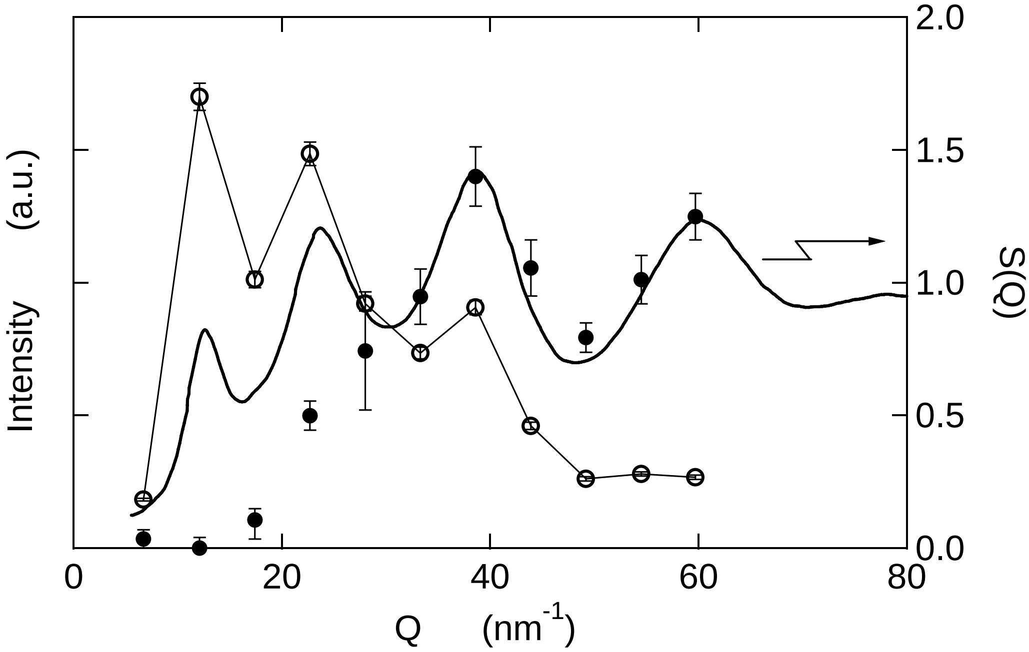


Fig. 4