HIGH-FREQUENCY DYNAMICS IN GLASSY SELENIUM

The investigation of short wavelength acoustic modes in glasses has stimulated a sizeable number of studies in the last decades. The reason for such interest lies in the close link between these high-frequency excitations and some well-known anomalies, such as the excess of the vibrational density of state (the so-called Boson Peak) or the thermal conductivity plateau observed in the 1<T<10 K region, which mark remarkable differences from the crystalline state. In glassy selenium the competition between two energetically similar local configurations allows for excellent glass-forming ability, a very rare feature in a monatomic system. This explains why g-Se has been intensively investigated in the past, though some crucial aspects related to the features of its microscopic collective dynamics at a wavelength comprising few atomic units are still unknown.

The aim of this experiment is to determine the coherent dynamic structure factor by inelastic X-ray scattering (IXS) in g-Se [1]. The experiment was carried out at the high resolution inelastic scattering beamline **BL35XU** [2]. High resolution was obtained using the (11 11 11) reflection of perfect silicon crystals in an extreme backscattering geometry. The use of four analyzer crystals, placed with 0.78 degree spacing on the 10 m two-theta arm (horizontal scattering plane), and four independent detectors, allowed to collect four momentum transfers simultaneously. Slits in front of the analyzer crystals limited their acceptance to 0.24 nm^{-1} on the scattering plane. The overall resolution of the spectrometer was about 1.5 meV. Elemental Se was prepared in flakes with thicknesses between 50 µm and 100 µm, which are very close to the optimum for matching the absorption length of the X-rays μ^{-1} = 50 µm.

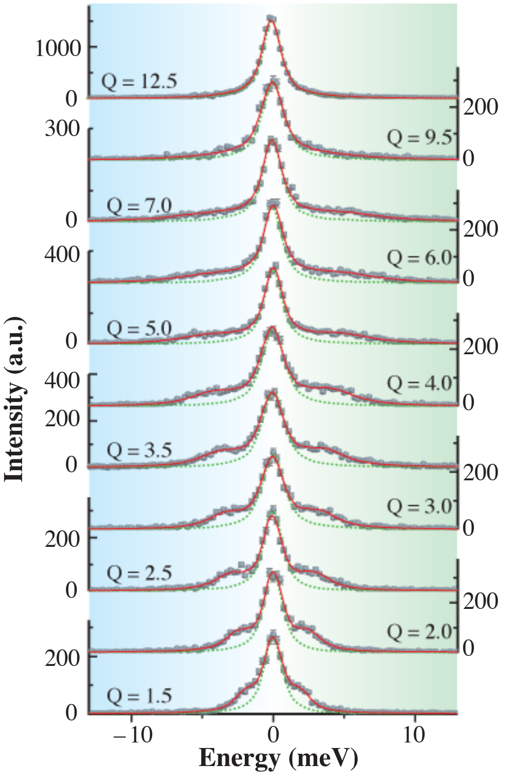

Fig. 1. IXS spectra of g-Se (solid circles) for several momentum transfers, indicated by labels in units of nm^{-1}. The instrument resolution (dotted line) and the best fit lineshape (continuous line) according to the model discussed in the text (corrected for resolution broadening and detailed balance factor) are also indicated.

In Fig. 1, we report the measured spectra for several fixed momentum transfers. Clear evidence of an inelastic mode, at the wings of the elastic peak, can be observed. The behavior of the energy shift of this mode *vs* the momentum transfer strongly resembles a phonon-like propagating mode. The high inelastic/elastic ratio allows for a less ambiguous detailed analysis of this mode than that in previously studied glasses.

Following the prescription of generalized hydrodynamics and modeling the vibrational dynamics as a Markovian process with an instantaneous second order memory function (an appropriate approximation for a glassy system), one ends up with a damped harmonic oscillator line shape to represent the dynamic structure factor:

$$\frac{S(Q,\omega)}{S(Q)} = f(Q)\delta(\omega) + \frac{1-f(Q)}{\pi}\,\frac{\Omega^2(Q)\Gamma(\omega)}{(\omega^2-\Omega^2(Q))^2-\omega^2\Gamma^2(Q)}$$

The parameters Ω and Γ are the characteristic frequency and attenuation of the mode, respectively, while S(Q) is the static structure factor.

The results of the present IXS experiment are summarized in Fig. 2. Compelling evidence for the existence of an acoustic-like longitudinal branch, which is well defined up to the higher investigated momentum transfer, is shown in Figs. 2(a) and 2(b). No evidence of localization is found at Q = 3 nm^{-1} as it has been suggested in ref. [3]. Moreover, the dispersion curve extends well beyond the boson peak frequency ($E_{BP} \cong$ 1.7 meV in g-Se at T = 300 K), confirming earlier observations reported in other glasses [4]. The extrapolated low Q limit of the apparent sound velocity (2000 m/s) falls above the hydrodynamic value (c_0 = 1800 m/s), suggesting the presence of a mild positive dispersion effect. As recently reported for other glassy systems [5], this effect may be due to a residual relaxation process related to the positional disorder intrinsic of the glassy phase.

The sound attenuation parameter $\Gamma(Q)$ (Fig. 2(c)) is found to be compatible with the Q^2 law, up to Q values where the dispersion relation is. This coincidence suggests a simultaneous breakdown of the linear and quadratic laws for $\Omega(Q)$ and $\Gamma(Q)$, respectively, which is expected to be caused by structural effects, i.e., by the Q dependence of the static structure factor. In order to remove this structural dependence we show the value of the sound attenuation parameter plotted against the excitation frequency for all measured Q values in Fig. 2(d). As can be observed, a simple power law relation now extends up to the entire explored momentum region. The best fitted law turns out to be $\Gamma = \Omega^{\alpha}$ with $\alpha = 2.15 \pm 0.10$. The present observation emphasizes another aspect that needs to be encompassed in the explanation of the ubiquitous Q^2 (or Ω^2) dependence which is not yet fully explained.

Finally, the data from the INS experiment [2] are shown in Fig. 3 (full dots), alongside with our IXS data (open dots). As can be observed, the two sets of data are in reasonable agreement. The small differences at the base of the elastic peak are expected, given the difference between the INS and IXS resolution functions: while both have 1.5 meV FWHM, the IXS resolution is approximately Lorentzian, while the INS resolution is Gaussian. The INS measurements, even pushing the limit of the technique at its maximum, span only a limited energy range due to kinematic restrictions.

Summing up, we presented an accurate measurement of the dynamic structure factor in g-Se, exploiting the state of the art capabilities of a new IXS facility. The favorable inelastic/elastic signal, the lack of kinematic constrains and the very good statistics allowed us to perform intensive study in an extended and previously unexplored momentum-energy region. Evidence for a well-defined longitudinal acoustic mode was found, extending all the way beyond the first pseudo-Brillouin zone through the boson peak frequency, thus suggesting a link between this universal feature of glasses and the reported high-frequency acoustic excitation. Moreover, the presence of such a well defined mode allowed us to obtain new insight into the high-frequency sound attenuation issue. Specifically, the quadratic dependence of the sound attenuation on the mode frequency corroborated the Q^2 law holding in a smaller range and observed in other glass formers.

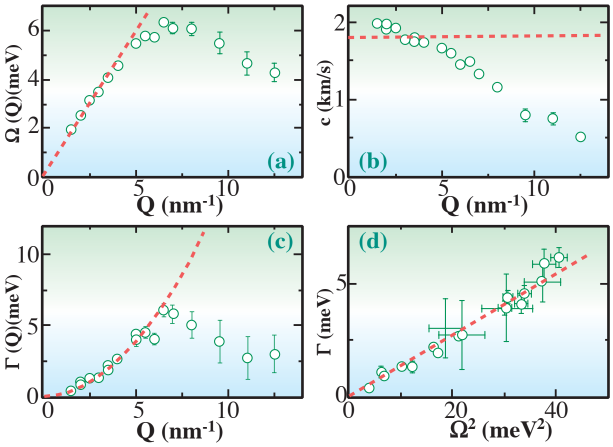

Fig. 2. Dynamical parameters obtained by IXS measurements. **(a)** Excitation frequency (open circles) and hydrodynamic dispersion (dotted line). **(b)** Apparent sound velocity, $\Omega(Q)/Q$ (open circles) and hydrodynamic value (dotted line). **(c)** Sound attenuation (open circles) with the best Q^2 fit $\Gamma(Q) = 0.15Q^2$; Γ and Q expressed in meV and nm^{-1}, respectively (dotted line). **(d)** Sound damping *vs* square of the excitation frequency. The quadratic dependence on the wavevector Q^2 shown in the panel **(c)** turns out to be the low Q limit of the more general dependence shown here.

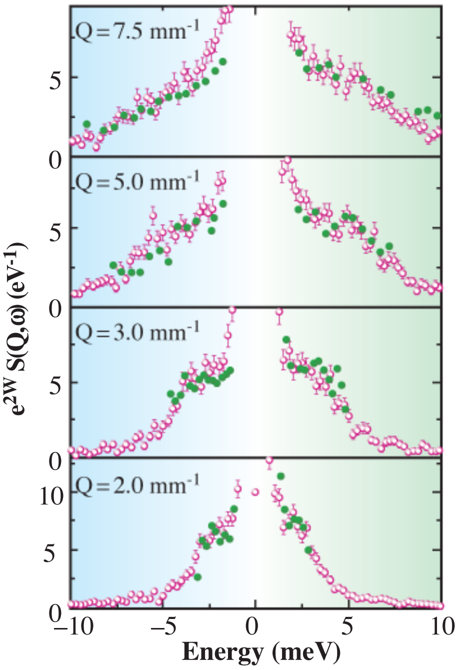

Fig. 3. Comparison between the IXS results (open circles and error bar) and previous INS measurements from ref. [3] (solid circles).

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