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Vibrational excitations of glass observed using helium atom scattering

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Abstract
In this paper we demonstrate a new application of helium atom scattering: the investigation of amorphous solids. Recently, we observed an excess density of states in the vibrational spectrum of the vitreous silica surface using inelastic He atom scattering. A surface phonon spectral density was readily extracted from the recorded data and the excess density of states was attributed to the surface manifestation of the boson peak phenomenon of disordered structures. Here we present further data analysis and show that the intensity of the surface boson peak at constant energy, i.e., $\rho_{zz}(\Delta E = \text{const}, \Delta\underline{K})/\rho_{\text{Debye}}$, strongly depends upon the parallel momentum transfer with a maximum in the neighborhood of $\approx$1 nm^{-1}. In contrast, the position of the maximum intensity of the surface boson peak shows negligible $\Delta\underline{K}$ dependence and is seen as a dispersionless mode at 3.7 ± 0.4 meV. Measurements of the width of the surface boson peak are also presented.

1. Introduction

Helium atom scattering (HAS) is a strictly surface sensitive technique with no penetration into the bulk. While experimental investigation of surface dynamics is difficult in general and even more challenging in the case of insulator surfaces, HAS has proven to be very well suited for looking at surface vibrational properties [1–3]. The probing He atoms impinge on the surface with kinetic energy in the range of the lowest energy phonons, and thus are especially sensitive to these modes. Despite the inert nature of the He atoms and the outstanding applicability of HAS for studying insulator surfaces, most investigations using HAS have been reported for metal surfaces in the past and far fewer for insulator surfaces [4–8].

Essentially all previously published results using HAS have been obtained on crystalline surfaces or on molten metals. Here we demonstrate the usefulness of HAS as a tool for studying surface dynamics of disordered solid materials. Recently, a fundamental phenomenon of amorphous structures was observed at the surface of vitreous silica in inelastic HAS experiments [9]. A dispersionless mode at $\approx$4 meV was seen in recorded time-of-flight data which was ascribed to the presence of excess modes over the Debye limit in the low energy region of the extracted surface phonon spectral density. An excess density of states compared to the Debye model, commonly termed the 'boson peak' (BP) [10, 11], has been observed in bulk measurements for a long time [12, 13]; however, it has not yet been observed at the surface. Despite all the progress made in modeling the BP recently [14–18], the nature of the BP is still a matter of considerable discussion.

A much debated topic in current BP research is the speculation about an 'end of the acoustic branch'. Inelastic x-ray spectroscopy experiments on densified silica (d-SiO_2) are consistent with a picture where the acoustic modes experience a crossover at a certain frequency Ω_{co} beyond which plane waves cease to exist [19]. The corresponding crossover wavevector, $q_{\text{co}} = \Omega_{\text{co}}/c_0$, where c_0 is the sound velocity, or equivalently the crossover wavelength, λ_{co}, should mark the 'end of the branch'. However, no such experimental data are available for vitreous silica (v-SiO_2) due to the present capabilities of inelastic x-ray scattering [20]. Whereas experimental investigation of d-SiO_2 is possible ($\Omega_{\text{co}} = 9$ meV, $q_{\text{co}} = 2.2$ nm^{-1}, $\lambda_{\text{co}} = 2.9$ nm), for v-SiO_2 only the

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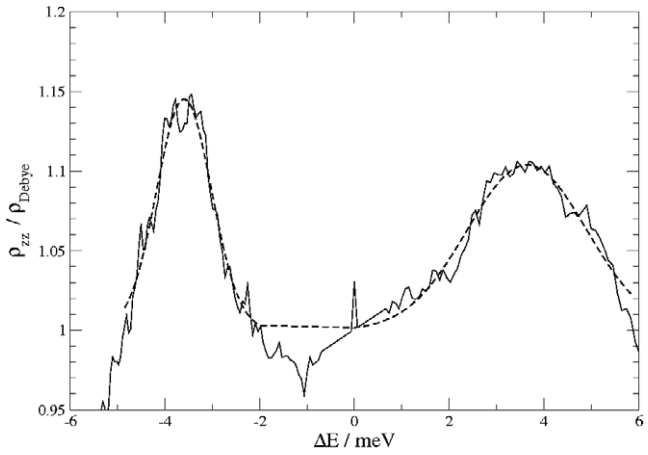

Figure 1. The BP feature is best seen in a depiction of the surface phonon spectral density divided by the Debye spectral density. The dashed line is a fit to the data from which BP position and the width of the BP are extracted (experimental conditions: $\theta_i = \theta_f = 45°$).

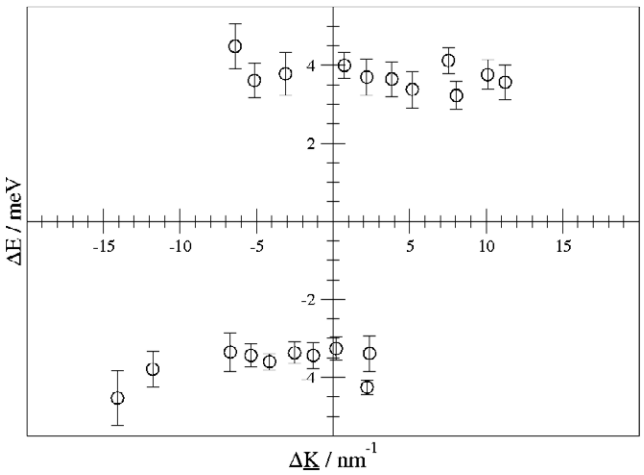

Figure 2. Dispersion relation of the observed surface BP. Data points were obtained from fittings of $\rho_{zz}/\rho_{\mathrm{Debye}}$ with two Gaussian functions; see figure 1.

regions near and above the crossover are accessible (estimated crossover: $\Omega_{co} \approx 4$ meV, $q_{co} \approx 1$ nm^{-1}, $\lambda_{co} \approx 6.3$ nm). In contrast, HAS is not limited to a lowest scattering vector. As seen in figure 4, a strong dependence of the BP intensity at constant energy, $\rho_{zz}(\Delta E = \text{const}, \Delta\underline{K})/\rho_{\mathrm{Debye}}$, is observed in these first helium scattering experiments for vitreous silica.

2. Experiment

2.1. Surface preparation

A 1 × 1 cm^2 silica sample was cut from polished Spectrosil®. The sample was sonicated in a detergent solution (10% Alconox®), and rinsed and sonicated in deionized water three times before drying and final UV-O_3 cleaning. To eliminate residual scratches from the polishing process, the sample was heated in a platinum crucible to 1708 °C under 1 bar of O_2. This treatment leads to a smooth surface with typical RMS roughness values of 0.27 nm over scan areas of 1 μm^2, a value which compares with roughness properties of a freshly melted glass surface [21]. The surface roughness was investigated using atomic force microscopy before a final UV O_3 cleaning to remove residual carbon contamination. Then the sample was transferred to an ultrahigh vacuum chamber equipped with an x-ray photoelectron spectroscopy instrument and the chemical composition of the surface was checked. A slight C 1s peak remained. The sample was heated under the equivalent of 10^{-2} mbar of O_2 until complete disappearance of the C 1s peak occurred. Finally, the sample was transferred using a glove box under argon into a transport chamber and was shipped from Saint Gobain to the helium scattering facility in Graz.

2.2. Scattering experiments

The experiments were all carried out in the MAGIE apparatus [22] with a base pressure in the 10^{-9} mbar region. Before starting experiments the surface was exposed to an initial cleaning *in situ* similar to the one described in [23]. An almost monochromatic beam was created by supersonic expansion with an energy around 20 meV and a spread of $\delta E/E \approx 2\%$ for all experiments. The scattered helium atoms were ionized by electron bombardment, sent through a magnetic mass selector and detected by a channeltron. The detector entrance was 1618 mm from the sample surface. For the experiments presented here the incident angle was kept fixed at 45° and the detector was rotated in the scattering plane (the plane containing the incident beam, the detector and the surface normal) leading to parallel momentum transfers $\Delta\underline{K}$ at the sample surface between −15 and 15 nm^{-1}. All experiments were carried out with the sample temperature at ≈127 K.

3. Results

The recorded time-of-flight data feature a dominant elastic peak and some smaller structure. Small humps are seen on both phonon creation and phonon annihilation sides at ≈4 meV (for a depiction of the differential reflection coefficient versus energy transfer we refer the reader to figure 1 of our previous publication [9]). As we have shown in [9], a surface phonon spectral density can readily be extracted from the experimental data. The small features at ≈4 meV appear as an excess density to the Debye density of states in the extracted surface phonon spectral density. This excess density of states is thus assigned to the surface manifestation of the BP. The BP is even better seen in a depiction of the surface phonon spectral density divided by the Debye spectral density, as shown in figure 1. The dashed line in figure 1 is a fit of two Gaussian functions to the data. The sum of the two Gaussian functions describes the BP rather well and allows the determination of the full width at half-maximum (FWHM) of the BP and the position of the BP maximum in a straightforward way. The energy positions of the BP maxima obtained in this manner appear as a dispersionless mode in the energy versus momentum graph shown in figure 2.

No clear dependence of the FWHM of the BP upon the parallel momentum transfer is observed, as shown in figure 3. The values obtained fluctuate around a value of ≈2.6 meV;

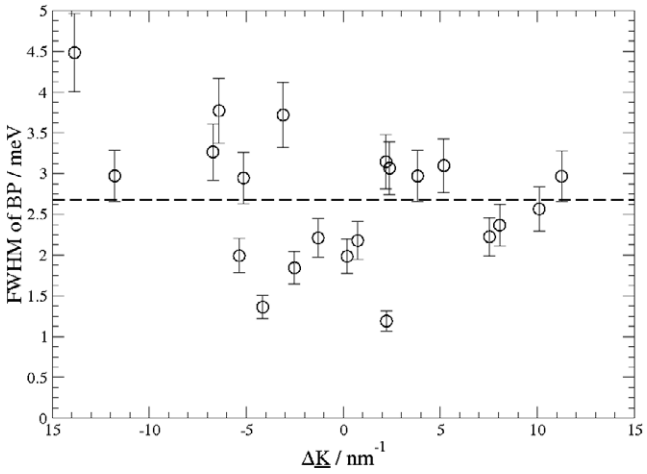

Figure 3. Full width at half-maximum of the surface boson peak as a function of the parallel momentum transfer $\Delta\underline{K}$.

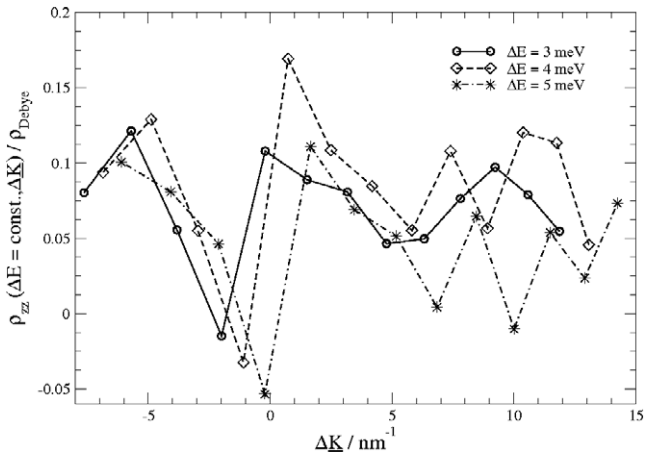

Figure 4. Dependence of the surface boson peak intensity upon the parallel momentum transfer $\Delta\underline{K}$. The lines connect points of same energy values ΔE.

the origin of these fluctuations is presumably the high noise level in the recorded time-of-flight data. In contrast to the lack of dispersion in the FWHM and maximum position of the BP, its intensity strongly depends upon the parallel momentum transfer. Figure 4 depicts the progression of the BP intensity, i.e., $\rho_{zz}(\Delta E = \text{const}, \Delta\underline{K})/\rho_{\text{Debye}}$, as a function of the parallel momentum transfer $\Delta\underline{K}$ for energy transfer values of 3, 4, and 5 meV. For all energy transfers shown, the intensity strongly increases between 0 and 1 nm^{-1} and then roughly remains at a constant level to the end of the accessible wavevector range of the experiment. The putative maximum in the neighborhood of 1 nm^{-1} may lend further support for the heavily discussed question of the 'end of the acoustic branch'; however, the present data set is not sufficiently dense to establish the precise position of this peak. Further experiments are needed in order to resolve this point.

4. Conclusion

In conclusion, new inelastic HAS experiments on a silica glass surface point out the strengths of He scattering techniques for probing the low energy vibrational properties of disordered solids. In contrast to well-established methods like inelastic x-ray scattering and inelastic neutron scattering, experiments using HAS are not limited to a lowest value of the scattering vector and, furthermore, the best achievable wavevector resolution of $\Delta\underline{K} \approx 1 \times 10^{-3}$ nm^{-1} is unsurpassed. A strong dependence of the BP intensity as a function of parallel momentum transfer is observed in the measurements presented here. This work suggests directions for future investigations of the intriguing surface vibrational dynamics of amorphous solids.

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