Observation of the Boson Peak at the Surface of Vitreous Silica

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The boson peak is an excess in the phonon density of states compared to the Debye model that appears in almost all glasses. It has been repeatedly measured in the bulk by a variety of methods, but its origin is still highly debated. Here we present first experimental evidence of the boson peak on the v-SiO_2 surface. The measurements were obtained by helium atom scattering. The boson peak appears as a dispersionless mode of ≈ 4 meV in the recorded time-of-flight spectra. It is clearly identified as an excess contribution to the low energy Debye-like region in the surface phonon spectral density which is extracted from the time-of-flight spectra using a straightforward theoretical model.

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An excess contribution to the usual bulk Debye density of phonon states in glasses has been observed at terahertz frequencies by a variety of optical, neutron, and thermal measurements [1–4]. This so-called ''boson peak'' (BP) is observed as a broad peak in the vibrational density of states divided by ω^2, at frequencies about 10–100 times smaller than the corresponding Debye frequency ω_D. In the case of surface sensitive measurements, we show in this Letter that a peak is likewise seen when plotting the surface projected density of states (i.e., the surface phonon spectral density) divided by ω. Until now this feature in the dynamics of amorphous structures has been reported only as a bulk property and has never been measured on the surface.

The BP is a general feature of glassy materials, but its spectral signature varies considerably between materials. However, despite numerous efforts, the nature of the vibration modes leading to the BP still remains unclear. Several authors treat the BP as resulting from acoustic phonon instabilities in the framework of elastic statistical physics models of disordered matter [5–7]. Another approach is based on the mode coupling theory of glasses [8]. Neither of these models has yet been able to fully predict the excess over the Debye value of the BP peak.

Another interpretation explains the BP as arising from modes that are not of acoustic nature [9]. The BP is related to a vibrational instability of the spectrum of weakly interacting quasilocal harmonic modes which causes a complete reconstruction of the vibrational density of states below a certain frequency, proportional to the strength of interaction. This model agrees with observations of the BP in amorphous silica where the BP is related to strongly localized modes owing to librations of SiO_4 tetrahedra with optical mode nature [1,10,11].

Here we present measurements that clearly show evidence of a dispersionless phonon band on the surface which is identified as the BP. Recently a BP was predicted in a molecular dynamics study of the amorphous silica surface [12]. Experimental investigation of surface dynamics is difficult in general and even more challenging in the case of insulator surfaces. However, scattering experiments with neutral helium atoms upon surfaces have proven to be very well suited for studying surface dynamics [13–15]. The technique is strictly surface sensitive with no penetration into the bulk, and the energy of the probing He atoms is in the range of the lowest-energy phonons, thus especially sensitive to these modes.

In the course of the experiment time-of-flight (TOF) data of scattered He particles were recorded and the features observed in the spectra consisted of a dominant elastic peak and two inelastic humps, one each on the phonon creation side and phonon annihilation side, respectively, as shown in Fig. 1. The inelastic features are interpreted as a dispersionless mode, i.e., one whose energy is independent of parallel momentum transfer, which in this experiment at constant incident beam energy is changed by varying the final angles. The mode energy is at about 4 meV (1 THz = 4.136 meV) in qualitative agreement with the simulations of Wang *et al.* [12] who predicted a slightly higher energy. As conclusive evidence that the observed mode is really a surface boson peak, we show in this Letter that the spectral density can readily be extracted from the TOF spectra with the use of straightforward theoretical models [16] and that the spectral density thus obtained clearly reveals the characteristic boson inelastic feature.

A theory of atom-surface scattering in the single-phonon limit is obtained in the kinematic approximation [16], and this theory has demonstrated its usefulness in interpreting He atom scattering data [13]. The result is expressed as a differential reflection coefficient, $d^2R(\underline{k}_f, \underline{k}_i)/d\Omega dE_f$, which is the fraction of the incident particles scattered into a small solid angle of $d\Omega$ and an energy interval dE_f and is given in its simplest form by

$$\frac{d^2R(\underline{k}_f, \underline{k}_i)}{d\Omega dE_f} = N\frac{|\underline{k}_f|}{k_{iz}}|\tau_{fi}|^2 e^{-2W(\Delta\underline{k})}\{\begin{matrix} n(\omega) \\ n(\omega)+1 \end{matrix}\}\Delta\underline{k}\cdot\underline{\underline{\rho}}\cdot\Delta\underline{k}, \quad (1)$$

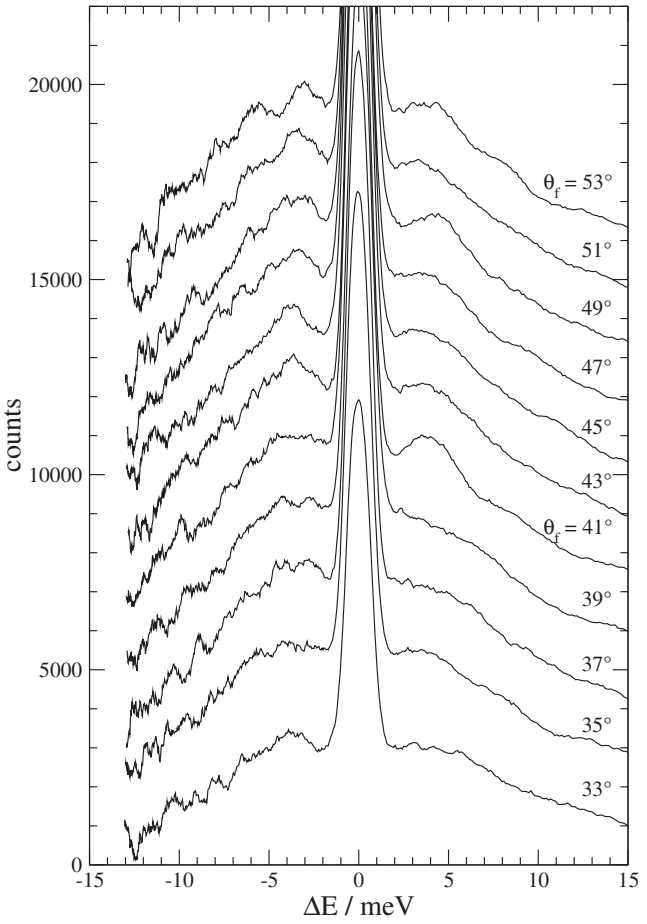

FIG. 1. Energy converted TOF experiments showing the dispersionless mode as a function of the energy transfer of the He projectile. The ordinate depicts the differential reflection coefficient. For the sake of clarity, successive plots are shifted by 1500 counts.

where $\underline{\underline{\rho}}(\omega, \Delta\underline{K})$ is the surface phonon spectral density, a tensor of rank two and a function of phonon frequency ω and parallel momentum $\Delta\underline{K}$ which is essentially the surface projection of the phonon density of states [17]. A detailed discussion of all components involved in Eq. (1) is given in [13].

Equation (1) shows that in helium atom scattering the energy and momentum dependence of the observed spectra is dominated by the squared transition matrix element $|\tau_{fi}|^2$ and the Debye-Waller factor $2W$. Both of these have strong energy dependence because the momentum transfer is large especially in the surface-normal direction because of the large total scattering angles. The scattering spectra are strongly dependent on the interaction potential, and the transition matrix element decreases rapidly with decreasing final energy. It is this latter effect that is most important in causing the intensity spectra to be smaller on the phonon creation side (negative energy transfer in Fig. 1) than would be expected from simple arguments based only on the Bose-Einstein factor, i.e., $n(\omega)$ versus $n(\omega) + 1$.

Equation (1) is the starting point for the derivation of the spectral density from the measured TOF record. The differential reflection coefficient is directly proportional to the number of counts measured in the experiment. If, with the exception of $\underline{\underline{\rho}}$, expressions for each of the factors appearing in Eq. (1) are determined, then $\underline{\underline{\rho}}$ can be extracted through comparison with sufficient experimental data.

The final wave vector $|\underline{k}_f|$ is experimentally determined and the form factor amplitude τ_{fi} (i.e., the inelastic transition matrix determined from the interaction potential) is approximated by the Mott-Jackson matrix element [18,19]: i.e., the matrix element of an exponentially repulsive potential $V(z) = V_0 \exp(-\beta z)$ taken with respect to its proper wave functions where z is the direction perpendicular to the surface. The range parameter is chosen to be $\beta = 25\ \mathrm{nm}^{-1}$, a value that is appropriate for insulator surfaces [13]. The Debye-Waller exponent is used in its common expression, i.e., $2W = C\Delta\underline{k}^2 T$ where C is a constant depending inversely on mass and the surface Debye temperature squared, and it can be determined from measurements of the temperature dependence of the Debye-Waller factor. In the single quantum limit $\hbar\omega = E_f - E_i$ and the Bose-Einstein distribution $n(\omega)$ reduces to $k_B T/|E_f - E_i|$ for $\hbar\omega \ll k_B T$. In these experiments the parallel momentum transfer $\Delta\underline{K}$ is more than an order of magnitude smaller than the perpendicular momentum transfer Δk_z so for both the Debye-Waller factor and in Eq. (1) it can be neglected, thus the experiment is preferentially sensitive only to the normal surface spectral density element $\rho_{zz}(\omega, \Delta\underline{K})$.

With all the above approximations the spectral density ρ_{zz} is given by

$$\rho_{zz} \propto \frac{[dR(\underline{k}_f, \underline{k}_i)/d\Omega dE_f]^{\mathrm{expt.}} |E_f - E_i|}{|\tau_{fi}|^2 E_f^{3/2} e^{-C\Delta\underline{k}^2 T}}, \qquad (2)$$

where the superscript expt. denotes the measured differential reflection coefficient. The linear term in $|E_f - E_i|$ is the characteristic signature for the small frequency region of Debye-model behavior in the surface phonon spectral density.

In the present experiments a $10 \times 10 \times 1\ \mathrm{mm}^3$ sample was cut out of polished Spectrosil® glass. The sample was cleaned in a soap solution and by UV-O_3 and was annealed to 1700 °C under an oxygen atmosphere to eliminate residual scratches from the polishing process. This treatment leads to a smooth surface with roughness properties of freshly melted glass surfaces as described in [20]. For a detailed description of the preparation protocol we refer to a previous publication (see [21]) where elastic helium atom scattering results were reported for the crystalline silica surface. The experiments were all carried out in the MAGIE apparatus [22] with a base pressure in the

10^{-9} mbar range. Before starting experiments the surface was exposed to an initial cleaning *in situ* similar to the one described in [21]. 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 so that the final angle measured with respect to the surface normal ranged from 33° to 53° in steps of 2°; see Fig. 1. A final angle 45° corresponds to specular reflection. All experiments were carried out with the sample at ≈ 127 K. In a second series (not shown herein) the Debye-Waller behavior of the elastic peak intensity was measured at the specular position with final angle 45° in a temperature range between 103.7 and 368.5 K. All TOF plots presented herein are converted to an energy-transfer scale for the x axis and to the differential reflection coefficient for the y axis, respectively. TOF data were obtained with a bin width of 0.05 ms at a total recording time of 1.7 ms.

The TOFs shown in Fig. 1 feature a dominant elastic peak (FWHM ≈ 2 meV) and some smaller structure which is rather similar in all curves shown. A broad hump is seen on the phonon annihilation side ($\Delta E > 0$) at ≈4 meV in all plots and this is quite accentuated for $\theta_f = 41°$ and 49°. Two plots, obtained at $\theta_f = 41°$ and 53° show onsets of shoulders at ≈ 8 meV which may be indications of a small double quantum excitation of the 4 meV feature. On the phonon creation side ($\Delta E < 0$) a pronounced hump is seen at ≈ −4 meV in all data. These peaks are attributed to the dispersionless mode, the energies of which are plotted in Fig. 2. While the dispersionless nature of the phonon mode follows directly from Fig. 1, the peak positions can be determined more accurately by extracting the surface phonon spectral density from the individual TOFs as described in the next paragraph. The higher noise level on the phonon creation side of the energy-resolved spectra shown in Fig. 1 is an artifact due to the conversion of the data from TOF to energy transfer.

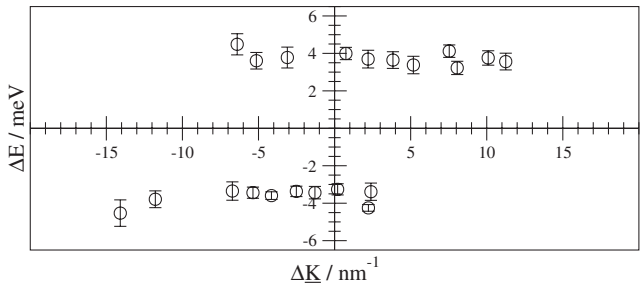

FIG. 2. Dispersionless BP mode at approximately 4 meV plotted as a function of parallel momentum transfer.

Figure 3 shows a typical surface phonon spectral density extracted from the TOF at $\theta_f = 45°$ in Fig. 1. The measured spectral density is proportional to the energy transfer for small values but drops away from linearity for surface phonons of higher energy. An excess contribution to states as compared to the Debye-model approximation is seen and this becomes more apparent when plotting the experimental surface phonon spectral density divided by the Debye limit as shown in the top panel of Fig. 3. From this depiction the dispersion relation of the BP (shown in Fig. 2) was obtained by fitting with two Gaussian functions, one each for the BP on the annihilation and the creation side. The smooth segment with nonzero slope between ±1 meV in the upper panel of Fig. 3 is an artifact of the elastic peak subtraction procedure. Ideally, $\rho_{zz}/\rho_{zz\mathrm{Debye}}$ would take the constant value 1 here. It is important to note that this peak subtraction does not alter the appearance of the BP, nor does it affect the slope of the Debye density of states. The Debye limit shown in the lower panel of Fig. 3 (dashed line) was obtained by a linear fit to the data for phonon energies in the ranges $[-2, -1]$ and $[1, 2]$ meV.

The dispersionless mode of 4 meV can thus be identified as the BP. Wang *et al.* predicted the BP on the surface of amorphous silica at roughly this energy [12] in their molecular dynamics study. Furthermore, the surface phonon spectral density drops away from the Debye model at energies beyond 6 meV (as seen in Fig. 3) in qualitative agreement with their predicted density of states.

Although not shown here, clear Debye-Waller behavior of the specular elastic peak intensity was measured in the series of temperature-dependent experiments. The Debye-Waller exponent was found to be significantly smaller than 1 at surface temperatures below 150 K. Since the

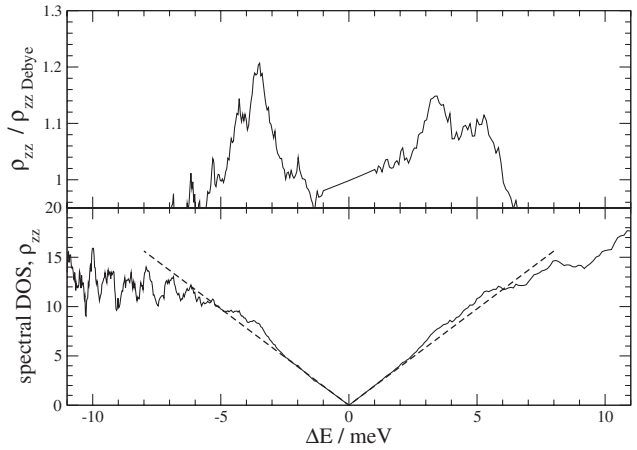

FIG. 3. Lower panel: Typical plot of the experimentally obtained surface phonon spectral density (from TOF curve $\theta_f = 45°$ in Fig. 1) showing an excess contribution to states compared to a Debye model (dashed line). Upper panel: The BP is better seen in the depiction of measured spectral density divided by Debye limit.

value of the Debye-Waller exponent roughly corresponds to the number of phonons created or destroyed in a surface collision, this indicates that experiments are clearly in the single-phonon regime. This conclusion is consistent with Buchenau *et al.* [1] who found from inelastic neutron scattering experiments that multiphonon scattering is still negligibly small compared to single-phonon scattering at beam energies below 20 meV even for a glass sample at room temperature.

The only apparent structure seen in the TOF spectra is a dispersionless BP mode at about 4 meV. The intensity of the BP shows a strong $\Delta\underline{K}$ dependence; however, the amount of data available is not sufficient to clearly identify the positions of the maxima and minima in the intensity structure. Not shown herein, as a function of $\Delta\underline{K}$ the intensity increases strongly between 0 and 1 nm^{-1} and then remains roughly at the same level to the end of the accessible wave vector range of the experiment. Owing to the extraordinary sensitivity of helium atom scattering, more features in the TOF spectra might have been anticipated. At low beam energies, such as used in this experiment, a Rayleigh peak on the flat surface would be expected but was not observed. Clear evidence for the existence of a long-wavelength Rayleigh mode on the crystalline $SiO_2(0001)$ surface has been obtained in a separate set of experiments [23].

The absence of the Rayleigh mode at large wavelengths for the amorphous glass surface studied cannot be fully explained yet. An analysis of the diffuse elastic peak intensity observed in the energy-resolved TOF spectra [23] indicates that the glass surface exhibits a roughness at the 3 nm scale with a distribution of slopes of up to 7° with respect to the surface plane. For parallel wave vectors corresponding to wavelengths shorter than 3 nm, a given scan curve would intersect the dispersion curve from all slopes within the coherence region of the incident He atom beam, thus smearing out the signal due to the Rayleigh mode and making it unobservable. Only for wavelengths significantly larger than the characteristic size of 3 nm would a clear Rayleigh mode be observable, and that corresponds to parallel momentum vectors of order 0.2 nm^{-1}, which is below the sensitivity of the present experiment.

In conclusion, these experiments show first experimental evidence on the surface of vitreous silica of an excess contribution to the surface phonon spectral density as compared to the Debye limit, and this can be identified as the surface manifestation of the boson peak observed in the bulk. The BP appears in the recorded TOF spectra as a dispersionless mode of ≈ 4 meV in qualitative agreement with a recent molecular dynamics study. This dispersionless feature is clearly identified in the surface phonon spectral density where it is seen as an excess of states in the small frequency region.

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