Communication: Are metallic glasses different from other glasses? A closer look at their high frequency dynamics FREE

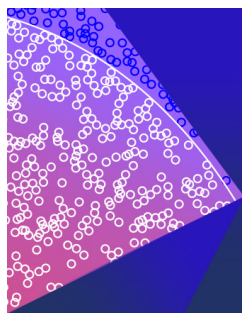P. Bruna; G. Baldi; E. Pineda; J. Serrano; J. B. Suck; D. Crespo; G. Monaco

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Communication: Are metallic glasses different from other glasses? A closer look at their high frequency dynamics

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Using high resolution inelastic x-ray scattering we studied the collective dynamics of the $Pd_{77}Si_{16.5}Cu_{6.5}$ metallic glass, focusing on the energy-momentum region where the boson peak appears. The dispersion relation and the width of the acoustic excitations are determined showing how the longitudinal acoustic modes maintain their dispersive character for frequencies well above the boson peak frequencies. Moreover, we prove that close to these frequencies there is a softening of the apparent sound speed indicating a failure of the Debye continuum approximation at the boson peak frequencies and challenging previous results on other metallic glasses. © *2011 American Institute of Physics*. [doi:10.1063/1.3640002]

The glassy state is far from being completely understood. The absence of periodicity makes the determination of its structure by both simulation and experimental methods rather cumbersome. Thousands of atoms must be considered for simulations in order to yield realistic atomic configurations. From the experimental side, the combination of probes such as x-ray absorption, neutron, and x-ray diffraction are required, together with simulation techniques such as reverse Monte Carlo for the determination of the most likely atomic arrangements. There is also a longstanding debate in the literature about the origin of the low temperature anomalies in the thermal properties of amorphous materials with respect to their crystalline counterparts, namely, the excess of specific heat over the T^3 temperature dependence of the Debye prediction[1] and the plateau in the thermal conductivity.[2] These anomalies are usually associated with two level systems below 1 K and with the boson peak (BP) near and above 10 K, the latter being an excess of vibrational states displayed as a maximum in the reduced vibrational density of states, $g(E)/E^2$. The BP is generally considered the signature of some sort of disorder in the glass, though there is no consensus on its physical origin.[3,4] In the study of the BP and its relation to the acoustic attenuation in glasses, besides the existence of distinct models (see references in Refs. 5 and 6), several controversial issues have arisen: (i) the acoustic or non-acoustic nature of the BP,[5] (ii) the possible relation of the BP frequency to a limiting frequency for the propagating nature of the acoustic modes (Ioffe-Regel limit),[6] (iii) the existence of a particularly strong damping for the acoustic modes with a Ω^4 frequency dependence (Rayleigh-like scattering) in the low momentum transfer region, i.e., near and below the BP,[7–10] being Ω the excitation frequency, and (iv) the way the apparent sound speed approaches the low-frequency value, i.e., uniformly or with either positive or negative dispersion, in the mesoscopic scale.[10–14] Previous studies on the BP are mainly devoted to network, molecular, and polymeric glasses where intramolecular, reorientational, and translational motions of molecules can contribute to the BP, possibly screening the underlying physics by numerous degrees of freedom. In this respect, metallic glasses (MGs) may be a simpler model system to shed further light on the mechanisms involved in the BP and the glass transition, given the greater simplicity of their glassy structure derived from the metallic, dominantly radial bonding.

Inelastic x-ray scattering spectroscopy (IXS) is the only method to gain information on the high frequency collective dynamics in MGs due to their usually high longitudinal sound speed. IXS has only been applied to few of these systems[10,11,15–17] and the cases of $Ni_{33}Zr_{67}$,[10] Pd-based,[11] and Pt-based[17] MGs are of special relevance here. NiZr IXS data show a sound attenuation (Γ) with a Ω^2 frequency dependence for small values of the momentum transfer q, with no indications of a possible transition towards a Ω^4 dependence at low q. This transition frequency was recently observed in a lithium diborate glass[7] and identified with the BP energy and the Ioffe-Regel limit, although it is still a matter of debate.[8,9] On the contrary, in the NiZr glass well defined acoustic-like excitations exist in the Ioffe-Regel sense well above the energy corresponding to the BP. For Pd- and Pt-based MGs, the IXS sound speed exceeds at low q, the macroscopic sound speed determined by ultrasounds, i.e., a positive dispersion exists in the low q region. This phenomenon has been attributed to topological disorder that modifies the sound

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properties at wavelengths comparable with the mean interparticle distances. On the contrary, in recent IXS experiments in glycerol,[12] sorbitol,[13] and vitreous silica[14] performed with high energy resolution and reaching q values as low as 1.0 nm^{-1}, the sound velocity shows a rapid decrease on increasing q followed by a plateau. The metallic systems studied so far thus seem to behave differently in this sense with respect to other glasses. The question that immediately arises is whether this distinct behavior stems from the metallic bonding or, on the contrary, they are universal features of the glassy state and a higher energy resolution is required to unveil them in the case of MGs.

In this Communication we present the study of the high-frequency dynamics of a Pd$_{77}$Si$_{16.5}$Cu$_{6.5}$ MG, focusing on the low q region between 1.0 and 2.0 nm^{-1}, aiming at answering these questions and contributing to the understanding of the nature of acoustic-like excitations in glasses. This system has been chosen because of its high glass forming ability and extensive results available in the literature, as well as the excellent inelastic-to-elastic signal ratio exhibited in previous low energy resolution IXS experiments,[16] allowing reliable measurements at low q to be carried on. The experiment was performed at room temperature at the IXS beam line ID16 of the European Synchrotron Radiation Facility in the q range between 1.0 and 10 nm^{-1}. Two Si reflections of the monochromator and crystal analyzers were used in order to optimize simultaneously the energy resolution and photon flux. For $q \leq 3.0$ nm^{-1} the Si (12 12 12) Bragg reflection was used with an energy resolution of 1.5 meV whereas for $q > 3.0$ nm^{-1} a lower energy resolution of 3.0 meV was obtained using the Si (9 9 9) Bragg reflection. Several scans in the -40 meV $\leq \hbar\omega \leq 40$ meV energy range were added in order to improve the statistical accuracy. The Pd$_{77}$Si$_{16.5}$Cu$_{6.5}$ sample was produced by arc melting the pure elements and copper mould casting, obtaining a 1 mm diameter rod. Two discs were cut with thicknesses of ~40 μm and ~80 μm in order to match the photoelectric absorption length of the sample at the chosen incident energy. The quality of both discs was checked by x-ray diffraction prior to the IXS experiment. Similar rods were employed at the Institute Laue Langevin to obtain the reduced density of vibrational states (GVDOS) by time-of-flight inelastic neutron scattering (INS). The GDVOS was obtained using the neutron gain spectra and taking a mean value over a wide range in q space (from 8 to 50 nm^{-1} for the elastically scattered neutrons).

Figure 1 shows the IXS intensity at selected q values after normalization for the incident photon flux. The central elastic line is due to frozen density fluctuations. The measured inelastic signal can be ascribed to a single acoustic propagating mode for $q \leq 4$ nm^{-1} whereas for higher q values a faint peak at around 8 meV can be observed and related to a second almost non-dispersing acoustic mode. Also in the low q range ($q \leq 4$ nm^{-1}) the spectra present a second weak inelastic feature around 15–25 meV, which is described by a second peak in the fitting function. The position of this weak excitation is almost constant with q and can be identified as the lowest optic branch. The IXS intensity is proportional to the dynamic structure factor, $S(q, \omega)$, that, at low q values, can
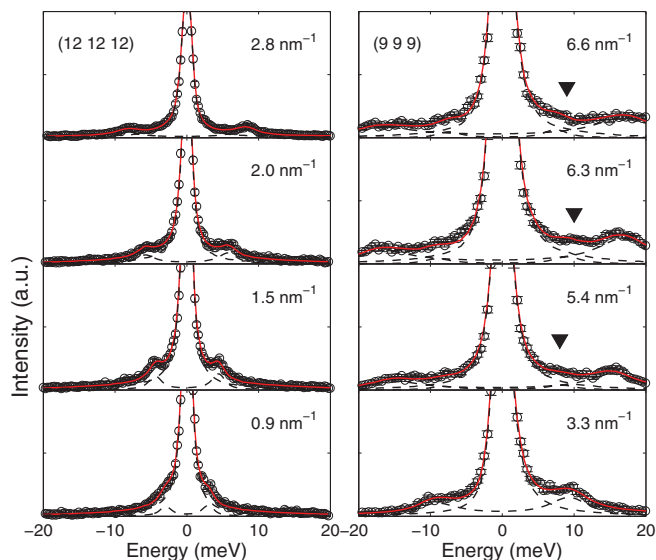

FIG. 1. Selected IXS spectra of a Pd$_{77}$Si$_{16.5}$Cu$_{6.5}$ MG measured using the (12 12 12) (left) and (9 9 9) (right) Si Bragg reflection. The thick line corresponds to the fit using Eq. (1), whereas the dashed lines display the individual elastic and inelastic contributions. Note the faint signal corresponding to the transverse mode (black triangle), appearing for q larger than 4.0 nm^{-1}.

be fitted with the sum of a delta function for the elastic component and a damped harmonic oscillator (DHO) function for the inelastic component:[10]

$$\frac{S(q, \omega)}{S(q)} = f_q \delta(\omega) + \frac{1 - f_q}{\pi} \frac{\Gamma(q)\Omega^2(q)}{(\omega^2 - \Omega^2(q))^2 + \omega^2\Gamma^2(q)}. \tag{1}$$

Here $S(q)$ is the static structure factor and Ω is the excitation frequency of the inelastic peak that corresponds to the maximum of the longitudinal current spectrum $C_L(q, \omega) = (\omega/q)^2 S(q, \omega)$. $\Gamma(q)$ is the broadening of the acoustic peaks and corresponds to the sound attenuation, and f_q is the spectral fraction of elastic scattering. In addition, Eq. (1), prior to be fitted to the experimental data (fits shown in Fig. 1), needs to be adapted to fulfill the detailed balance condition and to be convolved with the instrumental function. For $q > 4$ nm^{-1} a second DHO function has been added to Eq. (1) to describe the second, non-dispersive excitation. The excitation frequency of the inelastic peaks Ω as a function of q yields the dispersion relation, plotted in Fig. 2. Two acoustic-like excitations are clearly observed for $q > 4$ nm^{-1}. Based on the shape of this dispersion curve and on comparison with results from computer simulations,[18] we can ascribe the dispersive excitations to longitudinal modes and the almost q-independent excitations to transverse ones.[19] At low q-values, the dispersion of the longitudinal modes tends to the macroscopic limit set by the longitudinal sound speed, accessible using low frequency techniques such as ultrasound. At high q values the longitudinal dispersion begins to bend in the proximity of the boundary of the pseudo-Brillouin zone, as found previously in crystals.

Further information can be extracted from the q dependence of the apparent longitudinal phase velocity, defined as $v_L(q) = \Omega(q)/(\hbar q)$, also shown in Fig. 2. At low q values a
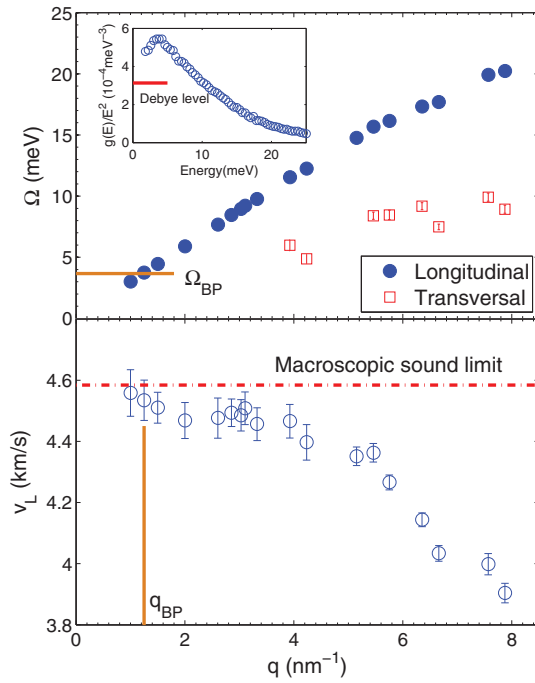
FIG. 2. (Top) Acoustic dispersion relations of a Pd$_{77}$Si$_{16.5}$Cu$_{6.5}$ MG. The reduced vibrational density of states is shown in the inset. (Bottom) Apparent longitudinal phase velocity as a function of momentum transfer q.
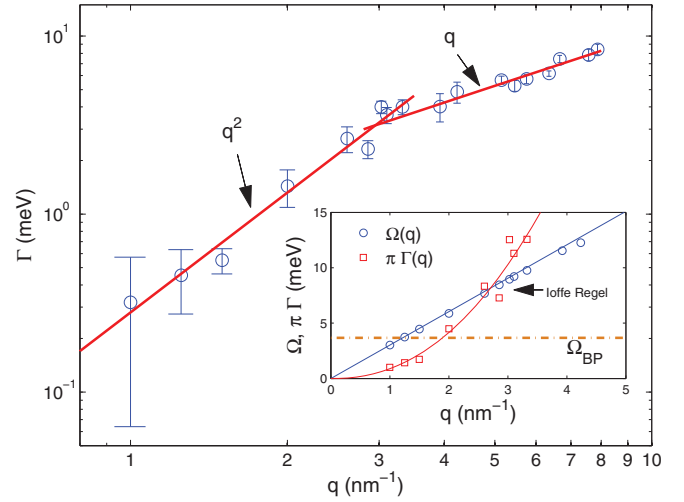

FIG. 3. Sound attenuation as a function of momentum transfer q. The inset shows the dispersion relation of the longitudinal modes together with $\pi\Gamma$, their intersection marking the Ioffe-Regel limit (Ref. 7). Solid lines are the best fits to experimental data and the horizontal dashed line corresponds to the BP frequency.

lower sound velocity is observed with respect to the ultrasonic sound speed.[20] The decrease of the sound speed between 1 and 2 nm^{-1} is not due to structural features because the measured static structure factor at q tending to zero is flat,[16] similar to what has been observed in other glassy systems such as glycerol, sorbitol, and vitreous silica.[12–14] Thus, this result is at odds with the positive dispersion found in the Pd- and Pt-based systems. Two explanations for this result are possible. On the one hand, in Ref. 17 the explored region does not cover the q-range around 1 nm^{-1} where the softening of the sound speed could be expected. On the other hand, in Ref. 17 results are reported for two classes of systems: Zr-based alloys, where no positive dispersion is observed, and Pd- and Pt-based glasses, where this effect appears. The common feature of the latter compositions is the presence of a significant amount of P ($\sim$20 at.%), the solely non-metallic element of all the metallic systems studied by IXS. Therefore, these systems can present partially covalent P–P bonds that may give rise to structural inhomogeneities possibly responsible for the positive dispersion.

Analogously to the sound speed, two different regions are also observed when displaying the q-dependence of the damping of the acoustic excitations (Fig. 3). For high q values, the sound attenuation follows a linear dependence while, for low q values, there is a stronger dependence compatible with a quadratic power law, thus not showing any indication of Rayleigh-like scattering. The transition between these two regimes occurs at $q = 3$ nm^{-1}, where the sound speed begins to show the typical behavior found in crystals (Fig. 2). The inset of Fig. 2 displays the GVDOS as a function of energy, obtained using INS. The BP is observed at 3.6 meV, as an excess of vibrational states over the Debye level. According to the dispersion relation of Fig. 2, the q value corresponding

to the frequency of the BP (q_{BP}) is 1.25 nm^{-1}. The longitudinal acoustic modes thus maintain their dispersive character for frequencies well above the BP frequency. Moreover, the Ioffe-Regel limit for the longitudinal mode is reached at 8.2 meV, i.e., at frequencies much higher than the BP frequency (inset of Fig. 3). This is similar to what is found in NiZr MG (Ref. 10) and also in simulations[6] where it is shown that the Ioffe-Regel limit coincides with the BP frequency only for the transverse modes.

Additional conclusions can be drawn from the apparent longitudinal sound speed. Interestingly, the observed negative dispersion is in this case of only about a 5% with respect to the ultrasound value, much lower than for non-metallic glasses.[12] Moreover, it appears precisely around q_{BP}, thus directly implying the existence of vibrational acoustic modes in excess with respect to the Debye level in the nanometer length scale at the BP frequency. Moreover, the plateau observed between 2 and 3 nm^{-1} appears in the same q range where the scattering of the sound waves follows a quadratic dependence on q. At higher q values a linear dependence of the sound attenuation is obtained, consistent with recent observations in liquid metals[21] and in the NiZr MG.[10] At low q, the present results are qualitatively compatible with a recent theoretical model by Schirmacher[22] as it predicts a q dependence of the sound attenuation with a lower than 4 power law. However, we are not able to discern a possible q^4 dependence predicted by the model up to the onset of the BP as we only have two experimental points in this region.

More in general, our results point to the following scheme. At a wavelength of a few nanometers, a sudden decrease of the sound speed appears. This might come together with a Rayleigh-like scattering of the sound waves, though we do not have enough points for $q < q_{BP}$ to be able to discern its existence. On increasing q, there is a transition region characterized by a plateau in the sound speed and a quadratic dependence in the acoustic damping. The transition

between these two regimes occurs at $q = 3$ nm^{-1}. Above this wavevector, the sound speed decreases because the dispersion curve is bending towards the first pseudo-Brillouin zone boundary, similar to what happens in crystals.[23] Here a second peak, likely transverse in nature, appears in the spectrum at an energy comparable to that of the BP. According to recent simulations[24] the negative dispersion in the longitudinal apparent sound velocity may be a signature of a similar softening that takes place on the transverse branch, i.e., it should be a consequence of changes in the shear modulus (G). Our results are consistent with the assumption that the bulk modulus is constant over the considered energy range and that the changes in the longitudinal velocity are due to changes in G that may imply the corresponding changes in the transverse one. This would explain why the decrease in the sound velocity with respect to the ultrasonic one is small in MGs in comparison to other inorganic glasses: the ratio between the bulk (K) and shear modulus (G) in MGs ($K/G \sim 3$–6) is relatively higher than in other inorganic ones ($K/G \sim 1$–2.5).[25] The longitudinal velocity is thus mainly dominated by the bulk modulus contribution that is likely constant. Therefore, in order to detect this phenomenon in a MG it is necessary to use the best possible energy and momentum resolution and explore the region below and around 1 nm^{-1}. In order to check this assumption it would be interesting to study MGs containing lanthanoids or magnesium as main elements, as they have a small K/G ratio comparable to other inorganic and organic glasses.[25] Moreover, the study with high energy and momentum resolution of metallic systems containing P will allow us to discern whether or not the non-metallic character of this element introduces some kind of disorder or interatomic forces that can be held responsible for the positive dispersion reported in such systems.[17]

In conclusion, the exploitation of the latest developments of the IXS technique in the study of a wide range of glassy systems (glycerol, sorbitol, vitreous silica, and a MG) evidences a common feature in all glasses, namely, a softening of the apparent sound speed in the q region where the BP appears, indicating a failure of the Debye continuum approximation at frequencies close to that of the BP. Our results challenge previous observations on Pd-based alloys performed with lower energy resolution and call for a reassessment of the high frequency dynamics in MGs in the mesoscopic range.

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