High-Frequency Dynamics in Metallic Glasses

T. Scopigno,[1] J.-B. Suck,[2] R. Angelini,[1] F. Albergamo,[3] and G. Ruocco[1]

[1]*INFM CRS-SOFT and Dipartimento di Fisica, Universitá di Roma "La Sapienza", I-00185, Roma, Italy*
[2]*Institute of Physics, University of Technology Chemnitz, D-09107 Chemnitz, Germany*
[3]*European Synchrotron Radiation Facility, F-38043 Grenoble, Cedex, France*

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Using inelastic x-ray scattering we studied the collective dynamics of the glassy alloy $Ni_{33}Zr_{67}$ in the first pseudo-Brillouin-zone, an energy-momentum region still unexplored in metallic glasses. We determine key properties such as the momentum transfer dependence of the sound velocity and of the acoustic damping, discussing the results in the general context of recently proposed pictures for acoustic dynamics in glasses. Specifically, we demonstrate the existence in this strong glass of well defined (in the Ioffe-Regel sense) acoustic-like excitations well above the boson peak energy.

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The physics of disordered materials has attracted considerable interest during recent years [1]. This is mainly due to new theoretical concepts that can handle systems lacking long-range order, to large scale computer simulations based on realistic interactions, and to the simultaneous development of new experimental techniques. Disordered materials show several kinds of universal behaviors that differ from those of the ordered state. In particular, great interest has been devoted to their high-frequency (THz) dynamics in respect to the corresponding crystalline counterpart. In this context, inelastic neutron scattering (INS) investigations of the collective dynamics in simple metallic glasses, which may be regarded as model systems, have played a leading role [2–5]. Because of their comparably simple atomic structure and their nearly isotropic interaction, metallic glasses (and glasses with Lennard-Jones interaction) were the first tackled in extended computer simulations, and one-to-one comparisons with experiments were often undertaken. Simple systems like $Mg_{70}Zn_{30}$ belong, however, to the minority of metallic glasses and interest has therefore moved quickly to more abundant and characteristic representatives like the Zr-based transition-metal–transition-metal (TM-TM) or the TM-metalloid glasses, which are characterized by a strong topological and chemical short range order [6].

The TM-TM glass NiZr plays an important role in this context, which can be produced by melt spinning in a large range of compositions. Of these, the Zr-rich concentrations, for which crystalline $NiZr_2$ also exists, have played a prominent role in the investigation of the dynamics of metallic glasses [6,7]. Concerning collective dynamics, in particular, the dispersion of modes around Q_p, (the Q position of the main peak of the static structure factor), i.e., in the region of maximal diffuse umklapp scattering [8], was measured first for glassy $Ni_{24}Zr_{76}$ [9] and then in $Ni_{67}Zr_{33}$ [10]. In these pioneering experiments it was possible to prove the existence of pseudo-Brillouin-zones with clear zone boundaries near the maxima of the static structure factor, these latter acting like "smeared out lattice points" [3]. However, important questions concerning the properties of the collective excitations remained unanswered on the experimental side: the existence of a low-Q linear dispersion, the wave-vector and energy transfer dependence of the velocity, and the damping of the excitations. In this context, of importance here, is the recently proposed existence of a crossover frequency, which should mark the transition between different dynamical regimes [11,12]. This crossover frequency could be identified in different ways. A first possibility (Ω_{IR}) is by the Ioffe-Regel criterion, i.e., by the condition $\Omega/\pi = \Gamma$, Ω being the excitation frequency and Γ the sound attenuation. Furthermore, a crossover (Ω_{co}) could be associated with the frequency where the acoustic damping Γ (i.e., the broadening of the measured excitations) crosses from a $\Gamma \propto \omega^4$ behavior ($\omega < \Omega_{co}$) to a weaker power law, $\Gamma \propto \omega^\alpha$ with $\alpha \simeq 2$ ($\omega > \Omega_{co}$). Finally, the crossover frequency could be identified with the frequency of the boson peak (BP), i.e., the maximum in the excess of vibrational density of states $g(\omega)$ with respect to the Debye behavior of the corresponding crystal, represented as $\frac{g(\omega)}{\omega^2}$. Recently, the coincidence of these three different definition of crossover frequencies has been proposed to hold, at least for the case of strong glasses [11,12].

In this Letter we report the determination of the collective dynamics in a metallic glass ($Ni_{33}Zr_{67}$), focused to the region below Q_p, where the excitations are still very well defined, aiming to answer some of the questions on the nature of these high-frequency modes, unanswered up to now by INS investigations. Using inelastic-x-ray scattering (IXS), we exploited the lack of any kinematic restrictions in the accessible Q-E region which, combined with the good resolution, allowed us to investigate previously inaccessible dynamics in metallic glasses. A well-defined acoustic branch has been observed up to $Q \simeq Q_p$, and the Ioffe-Regel criterium indicates that Ω_{IR} is close to $\Omega(Q_p)$, i.e., well above the BP frequency. The behavior of the sound attenuation can be rationalized in terms of a relaxation process related to the structural disorder, similarly to what was found in simple monatomic systems [13,14]. No evidence for a Rayleigh regime ($\Gamma \propto \omega^4$) could be observed in the explored Q range, thus concluding that $\hbar\Omega$co, if existing, is well below 5 meV. Finally, the fragility value ($m = 26$), as deduced by the temperature dependence of the nonergodicity parameter, agrees well with independent viscosity determinations [15], thus corroborating the recent proposed correlation between the low temperature vibrational regime and the high temperature diffusive dynamics in glass formers [16], and extending it to a class of systems not considered so far. The whole scenario reported here does not indicate the existence in this system of a single crossover frequency marking the BP position ($\hbar\Omega_{\mathrm{BP}} \simeq 3$ meV), the Ioffe-Regel criterium ($\hbar\Omega_{\mathrm{IR}} \simeq 8$ meV), and the end of Rayleigh scattering of phonons regime (which, if it exists, has to be confined at energies $\hbar\Omega\mathrm{co} < 5$ meV).

The experiment was performed at room temperature ($T = 297$ K) at the IXS beam line ID16 of ESRF [17,18] at fixed scattering angle (and therefore fixed Q values) in a region between 1.5 and 20 nm^{-1}. The Q resolution (FWHM) was set to $\delta Q \approx 0.35$ nm^{-1} and improved to $\delta Q \approx 0.1$ nm^{-1} at the lowest Q's. Using the (9 9 9) reflection for the Si monochromator and crystal analyzers the overall energy resolution (FWHM) was $\delta\hbar\omega = 3.0$ meV. A five-analyzer bench, operating in horizontal scattering geometry, allowed the simultaneous collection of spectra at five different values of Q. Each energy scan from $-50 < \hbar\omega < 50$ meV, where $\hbar\omega$ is the energy transfer ($E_0 - E$), with E_0 and E being the energy of the incident (17 794 eV) and the scattered x ray, took approximately 300 min, and several scans have been summed up to improve the statistical accuracy. The $Ni_{33}Zr_{67}$ sample was freshly prepared by melt spinning techniques, its structure was checked by x-ray diffraction before (and during) the measurement.

In Fig. 1 we report all the measured spectra in absolute counts, after proper normalization for the incident monitor. The elastic line is an effect of the nonergodicity typical of the glassy state (scattering from static disorder) and possibly to incoherent scattering from concentration fluctuations. Most reasonably the measured inelastic signal can be ascribed to a single acoustic propagating mode. The low energy ($E \approx 8$ meV) peak observed around $Q \approx 11$ nm^{-1} in the energy loss side is due to the elastic scattering from the kapton window located in the incoming beam before the sample. This peak, which is due to the sample environment geometry and is only present in the range $9 < Q < 13$ nm^{-1}, is also present in the empty cell measurements and totally disappears when the empty cell is subtracted from the data. The fitting procedure is performed by adding the empty cell with the proper transmission normalization factor to the model line shape used to represent the data. Following generalized hydrodynamics, the simplest model function to get the basic features of collective glassy dynamics is the damped harmonic oscillator, based on the assumption of an instantaneously decaying memory function for vibrational dynamics, typical of Markovian processes, plus an elastic contribution due to the arrested diffusive dynamics and to incoherent scattering [19]. We have checked that fitting the data with a more refined model (Debye-like memory functions), while improving the quality of the overall fit, does not produce significant variation in the peak width and position. Therefore, for simplicity, we use the damped harmonic oscillator model function:

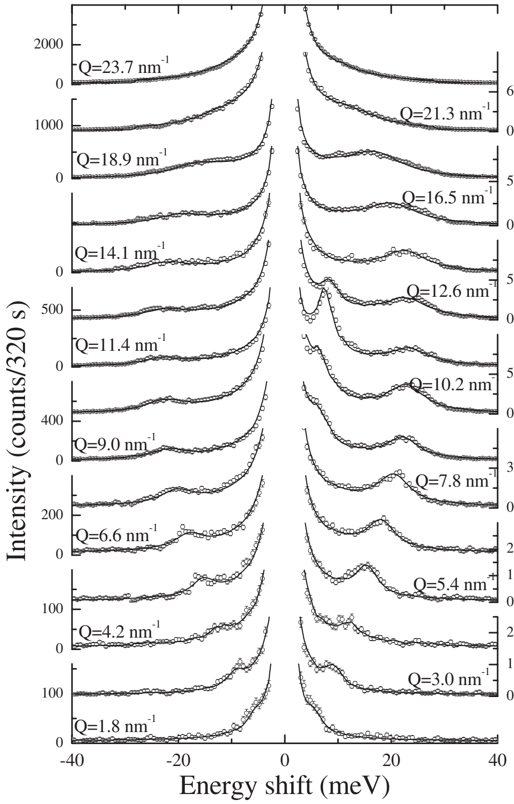

FIG. 1. IXS spectra of $Ni_{33}Zr_{67}$ at the indicated fixed Q values (open dots). Also reported are the best-fit line shapes (continuous lines; see text). The low energy structures at $E \approx 8$ meV observed around $Q \approx 11$ nm^{-1} are spurious scattering from the kapton windows of the sample container.

$$\frac{S(Q,\omega)}{S(Q)} = \left[A(Q)\delta(\omega) + \frac{1 - A(Q)}{\pi} \times \frac{\Omega^2(Q)\Gamma(Q)}{[\omega^2 - \Omega^2(Q)]^2 + \omega^2\Gamma^2(Q)} \right]. \quad (1)$$

This function needs to be adapted to satisfy the detailed balance condition and to be convoluted with the instrumental energy resolution. The characteristic frequency of the acoustic mode, Ω, corresponds to the maximum of the longitudinal current spectra $C_L(Q,\omega) = (\omega/Q)^2 S(Q,\omega)$. Its Q dependency defines the dispersion relation of the mode. The parameter $\Gamma(Q)$ is related to the sound attenuation, while $A(Q)$ is the intensity of the elastic scattering relative to the total intensity of the spectrum at the Q under consideration.

Based on the form of the dispersion reported in Fig. 2, we ascribe the corresponding excitations to longitudinal

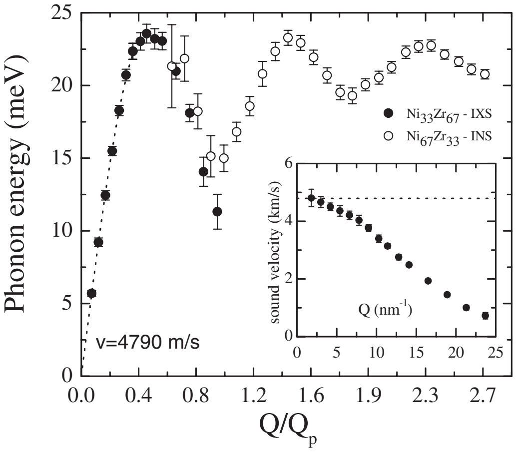

FIG. 2. Dispersion curve $\hbar\Omega(Q)$ of the NiZr alloy as obtained from the IXS and INS experiments. The momentum transfers have been scaled to Q_p to account for the different structural properties due to the different compositions ($Q_p^{(\mathrm{Ni_{33}Zr_{67}})} = 25.7\ \mathrm{nm}^{-1}$ and $Q_p^{(\mathrm{Ni_{67}Zr_{33}})} = 29\ \mathrm{nm}^{-1}$). Inset: Q dependence of the sound velocity $v = \Omega/Q$ as measured by IXS.

acoustic modes. In spite of the fact that we were able to measure at rather low-Q values, where the longitudinal acoustic and optic branch should be well separated and the excitations still well defined, we did not observe longitudinal optic modes within the energy range covered in our experiment. This is most likely due to the fact that the intensity of the opticlike modes is expected to vanish in the $Q \rightarrow 0$ limit. Moreover, the dynamic structure factor measured by the IXS is heavily dominated by the density-density correlations, while the concentration-concentration contribution is negligible: approximating the form factors of Ni and Zr by their $Q \rightarrow 0$ values, i.e., their atomic numbers, one has $I_{\mathrm{IXS}}(Q, \omega) \propto 2.25 S_{\rho\rho}(Q, \omega) + 0.25 S_{\mathrm{cc}}(Q, \omega) - 1.5 S_{\rho c}(Q, \omega)$. In the same figure, we report the energy of the high-frequency mode previously measured with INS in $\mathrm{Ni_{67}Zr_{33}}$. Because of the different concentrations and cross sections of the two species in the neutron and x-ray investigations, leading to different weighting factors in the total dynamic structure factor measured in each of the two experiments, some difference in the measured excitation is observed. Nevertheless normalizing the momentum transfer scale to Q_p, one obtains a good overlap.

The sound attenuation, reported in Fig. 3(a), shows a power law dependence, with a change of slope around $Q \approx 7\ \mathrm{nm}^{-1}$ ($E \approx 4$ meV) being proportional to Q^2 below this value (full line) and to a lower Q dependence above (dashed line). In the same figure we also report the peak position $\Omega(Q)$ divided by π (small full dots and thin full line). The intersection of this line with $\Gamma(Q)$ define the Ioffe-Regel limit, which is found here at $Q_{\mathrm{IR}} = 14 \pm 2\ \mathrm{nm}^{-1}$ or $\hbar\Omega_{\mathrm{IR}} = 7 \pm 1$ meV. The boson peak energy, on the contrary, is $\hbar\Omega_{\mathrm{BP}} = 3$ meV [6,20]. This observation clearly indicates that in the present glass there exist well defined (in the Ioffe-Regel sense) acoustic excitations well above the boson peak energy. Furthermore, no transition towards the Rayleigh Q^4 dependence is observed in the investigated Q range, thus posing an upper limit to the crossover energy, $\hbar\Omega\mathrm{co} < 4.5$ meV. We can therefore conclude that neither the boson peak energy, nor the crossover energy, coincide with the Ioffe-Regel energy.

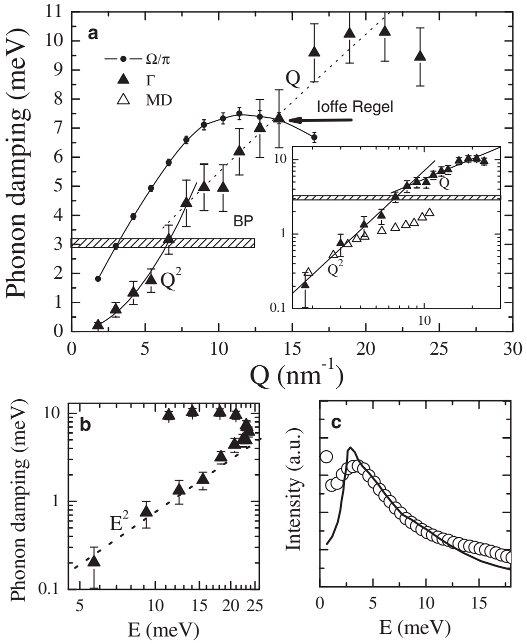

FIG. 3. (a) Q dependency of the damping of the observed excitation (full triangles). A transition from the Q^2 to a linear dependence of the damping around $Q = 7\ \mathrm{nm}^{-1}$ can be observed. Values of Ω/π are also reported to identify the Ioffe-Regel crossover (full circles), together with the boson peak energy. Open triangles show the sound attenuation calculated by means of molecular dynamics in a simple metal, which shows a qualitatively similar behavior [14]. (b) Energy dependence of the damping: the breakdown of the quadratic dependence is shifted to higher energies but not completely removed. (c) reduced vibrational density of states $g(\omega)/\omega^2$ for $\mathrm{Ni_{33}Zr_{67}}$ as measured by INS [20] and calculated by molecular-dynamic simulations [6].

The Q^2 dependence is a well documented feature of the high-frequency attenuation in glasses, while the breakdown of this dependence at intermediate Q (around $Q = 7\ \mathrm{nm}^{-1}$ here) has not been well understood until now. In some systems, the breakdown of the quadratic dependence is simply an effect of the modulation of the structure of $S(Q)$, which can be wiped out reporting the attenuation versus the excitation energy. In such cases, it seems more significant to describe the sound attenuation as a Ω^2 law [21]. This does not seem to be the case here, where the $S(Q)$ is almost flat up to $10\ \mathrm{nm}^{-1}$, while the change of slope is around $7\ \mathrm{nm}^{-1}$, where the dispersion leaves its linear slope. Indeed, in Fig. 3(b) one can observe a deviation from the $\Gamma \propto \Omega^2$ law above $\Omega \approx 20$ meV ($Q \approx 8\ \mathrm{nm}^{-1}$). The observed transition might be possibly related to a dynamical effect, as reported in the molecular dynamics simulation of a simple metallic glass [open triangles in

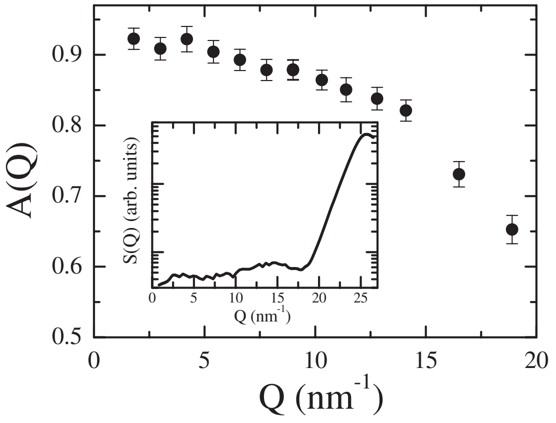

FIG. 4. Q dependence of the elastic/total scattered intensity ratio. Inset: static structure factor; note the prepeak at $Q \approx 14\ \mathrm{nm}^{-1}$), where $A(Q)$ changes its slope.

Fig. 3(a)], scaled by an arbitrary factor for presentation reasons [14].

In Fig. 4, the elastic/total intensity ratio $A(Q) = I_{\mathrm{el}}/I_{\mathrm{tot}}$ is reported. Generally speaking, the elastic signal comes from the relaxation processes active over a time scale longer than the inverse of the phonon frequency. In systems, where the dominant elastic contribution comes from the structural relaxation, $A(Q)$ is a measure of the so-called nonergodicity factor, $f(Q)$. It has been recently proposed [16] that the low temperature behavior of the nonergodicity factor in a T/T_g plot is closely correlated to the so-called Angel plot, i.e., to the temperature behavior of viscosity on approaching the glass transition in a T_g/T scale. More specifically, in terms of the fragility index $m = \lim_{T\to T_g}[d\log(\eta)/d(T_g/T)]$ and of the parameter $\alpha = \lim_{T\to 0}[df(Q\to 0, T)/d(T/T_g)]$ one has $m \approx 135\alpha$. At the same time, the temperature dependence of the nonergodicity parameter in the $T \to 0$ limit is well described by the functional form $f(Q, T \to 0) = 1/1 + \alpha T/T_g$. The glass transition temperature of $\mathrm{Ni}_{33}\mathrm{Zr}_{67}$ is about $T_g = 652$ K, and using our determination of $A(Q \to 0, T) \approx 0.92$ at room temperature one has $\alpha = 0.19$, which would lead to a fragility of about $m = 26$, indicating $\mathrm{Ni}_{33}\mathrm{Zr}_{67}$ to be a strong glass. Though this value of fragility has to be taken as a lower estimate, due to possible elastic contribution from concentration fluctuations, it is in very good agreement with independent high temperature viscosity determination, which would give $m = 24$ [15].

Summing up, we have studied the high-frequency dynamics of the strong metallic glass $\mathrm{Ni}_{33}\mathrm{Zr}_{67}$ in a range of momentum transfer below the first maximum of the static structure factor. Evidence of a longitudinal-acoustic–like branch has been reported, which is the extension into the sensible low-Q region of the high-frequency excitations observed a few years ago by means of INS. The analysis of the nonergodicity factor allows us to classify—in agreement with previous determination [15]—this glass as "strong" ($m = 26$). At low Q, the sound attenuation exhibits a Q^2 behavior, with no hint of a possible transition towards a Q^4 dependence. Finally, we determine the Ioffe-Regel limit, that is reached close to the top of the acoustic branch, at $E_{\mathrm{IR}} = 7 \pm 1$ meV, thus well above the boson peak energy, $E_{\mathrm{BP}} = 3$ meV. In the present strong glass, there exist well-defined (in the Ioffe-Regel sense) acoustic-like excitations well above the boson Peak energy. These findings are not in accordance with recent models proposed for the acoustic properties in strong glasses [11,12] that predict $E_{\mathrm{IR}} = E_{\mathrm{BP}}$.

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