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Acoustic properties of metallic glasses in the mesoscopic regime by inelastic X-ray scattering

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ABSTRACT

The mechanical response of bulk metallic glasses is ultimately controlled by interatomic forces between the randomly distributed atoms. The study of collective dynamics in amorphous systems, either liquid or glassy, opens a window to better understand this interaction. We present here results of recent IXS experiments performed at the ID16 beamline of the European Synchrotron Radiation Facility (ESRF) on a metallic glass. In particular, the high-frequency response of $Pd_{77}Si_{16.5}Cu_{6.5}$ alloys, produced as a ribbon with an ultra-fast quenching rate ($\sim 10^6$ K/s) and as a bulk with a slow one ($\sim 10^2$ K/s), was determined. Previous experiments showed a discrepancy between the sound speed of metallic glasses measured by ultrasounds and by IXS. This was explained as a consequence of density fluctuations in the glass, although other explanations are possible. Here, the dispersion relation of the acoustic modes at room temperature and pressure are measured for both samples, allowing us to compute the sound speed and discuss the differences in the acoustic properties of both samples.

1. Introduction

Metallic glasses are a relatively new class of materials appeared in the 1960s that nowadays are experiencing a revival due the potential applications of the so-called bulk metallic glasses. These materials are characterized by being alloys with an amorphous structure, that is, with lack of crystallinity. Until the 1980s, the production method of metallic glasses was limited to rapid quenching at a rate of 10^6 K/s, thus obtaining alloys with micrometric sections with limited structural applications. The development of new compositions able to be amorphized with low quenching rates has permitted the production of bulk pieces of metallic glasses, thus extending their applicability as structural materials [1]. Therefore, it is of crucial importance to understand the mechanical response of these materials. This cannot be achieved using the same approach than in crystalline materials due to the lack of long range order. At the microscopic level, the mechanical response is controlled by interatomic forces between randomly distributed atoms. The study of collective dynamics in amorphous systems, either liquid or glassy, is a way to gain insight into this interaction. Due to the high longitudinal sound speed usually associated to these materials, inelastic X-ray scattering (IXS) is the only available technique to give access to the high frequency response of metallic glasses, namely, in the THz frequency domain.

Recent IXS results on Pd and Pt-based metallic glasses [2,3] report a positive phonon-dispersion phenomena that has also been observed in other disordered systems like selenium [4]. For metallic glasses, this positive dispersion has been attributed to the existence of spatial inhomogeneities and not to a residual fast relaxation processes in the glass [3,5]. According to that, the structure of these metallic glasses is expected to consist of two different mechanical nanoscale domains corresponding to strongly and weakly bonded regions that globally give to the system its macroscopic properties. In order to check the possible validity of this hypothesis two glasses of the same composition but with different fictive temperatures have been studied. A bulk metallic glass obtained with slow quenching rates of the order of 10^1–10^2 K/s will lie in a different minimum of the potential energy landscape in comparison to the same metallic glass produced this time with ultra-high quenching

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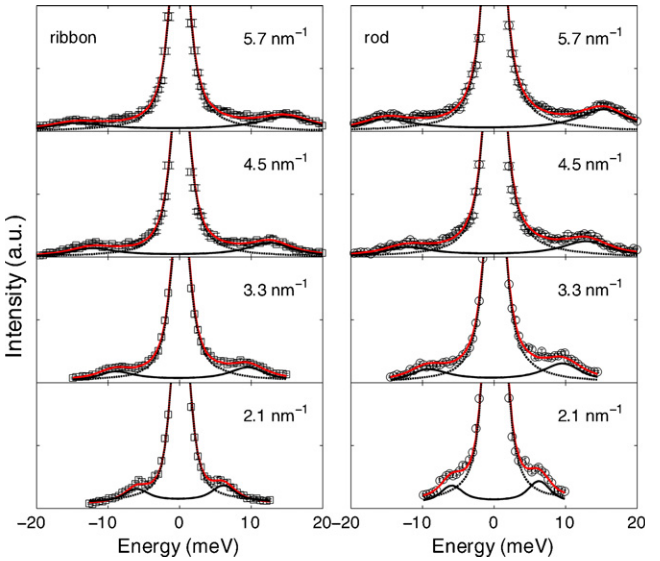

Fig. 1. Selected IXS spectra at several Q-values, for the ribbon (left) and the rod (right). Symbols indicate experimental data and the three curves represent the total best fit to a damped harmonic oscillator and the elastic and inelastic contributions.

rates (10^6 K/s) and, therefore, the degree of spatial homogeneity of both glasses is expected to be different. Moreover, the slightly higher density of the bulk glass with respect to the fast-quenched one, consequence of the suppression of free volume during the cooling process, has a pronounced effect on mechanical behavior shown among others in the increase of the Young and shear modulus [6].

In this work we investigate the high frequency response of a Pd-based alloy with composition $Pd_{77}Si_{16.5}Cu_{6.5}$ and produced as a rod and as a ribbon with a slow and ultra-high quenching rate, respectively. Thus, the acoustic properties of two glasses that lie in different minima of the potential energy landscape are studied shedding some light on how the nanostructure depends on the production method and how it controls the mechanical response.

2. Experimental

The metallic glass $Pd_{77}Si_{16.5}Cu_{6.5}$ was prepared by arc melting of pure raw materials and by two quenching methods: by melt spinning obtaining ribbons of 2 mm width and 22 μm thickness and by copper mould casting obtaining a 1 mm diameter rod. Thus, the ribbons have a higher fictive temperature than the rod due to the higher quenching rate. The amorphous character of the samples was verified using synchrotron radiation X-ray diffraction at beamline BM16 at the ESRF and their density was measured using the Archimedean method with a He pycnometer. IXS experiments were performed at beamline ID16 of the ESRF using monochromatic X-rays of 17.794 keV obtained from the (9 9 9) Si reflection of the monochromator. The obtained energy resolution is of 3 meV and IXS energy scans were performed in the [−40, 40] meV energy range for momentum transfers between 2 and 10 nm^{-1}, with an acquisition time of 150 min per spectrum. Several spectra were added in order to reduce statistical noise and were fitted using a single damped harmonic oscillator function for the excitation convoluted with the experimental resolution function of the corresponding analyzer, as reported elsewhere [7].

3. Results

IXS spectra at selected values of the momentum transfer Q for the ribbon and the rod are shown in Fig. 1. The elastic line at zero energy present at all Q values is due to the frozen density fluctuations present in all glasses. The two inelastic peaks at each side of the elastic line can be ascribed to a single acoustic propagating mode and correspond to the creation and annihilation of this excitation. The simplest model to fit the spectrum is based on the sum of a delta function for the elastic component and a damped harmonic oscillator for the inelastic component to describe the dynamic structure factor $S(Q,\omega)$:

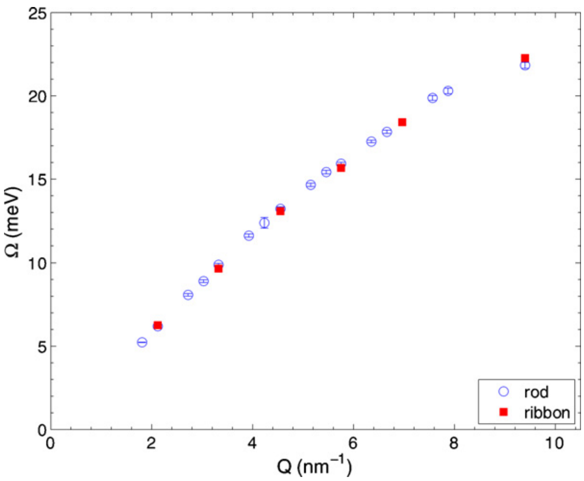

Fig. 2. Longitudinal acoustic dispersion relation obtained from the IXS data for a $Pd_{77}Si_{16.5}Cu_{6.5}$ metallic glass produced as a rod using a low quenching rate and as a ribbon using a high quenching rate.

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

where $S(Q)$ is the static structure factor, Ω is the position of the inelastic peak that corresponds to the maximum of the longitudinal current spectra $C_L(Q,\omega) = (\omega/Q)^2 S(Q,\omega)$, $\Gamma(Q)$ is the broadening of the acoustic-like excitations and f_Q is the non-ergodicity factor. Moreover, this classical expression needs to be corrected to fulfill the detailed balance condition and then to be convolved with the experimental resolution function [7]. The best fitted line shapes obtained with this model are also plotted in Fig. 1. At low Q values the fit has been performed in a limited ω range around the inelastic contribution in order to determine the position of the peak with higher accuracy. At high Q values a second and faint excitation can be observed [8], but fitting the data with two damped harmonic oscillators, although improving the quality of the overall fit, does not produce any significant change in the position and width of the main inelastic peaks. Thus, for simplicity, we have used only one damped harmonic oscillator.

The dependence of the inelastic peak energy on the momentum transfer Q is referred to as the acoustic dispersion relation and is displayed in Fig. 2. At Q values approaching zero a linear behavior is

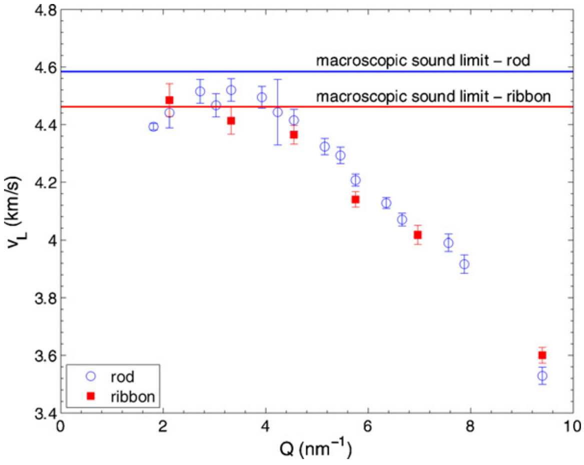

Fig. 3. Q dependence of the apparent longitudinal phase velocity derived from the IXS experiment. The horizontal lines correspond to the macroscopic sound limit obtained from ultrasound methods for the rod and from the elastic constants for the ribbon.

Table 1
The density (ρ), bulk (B) and shear (G) modulus, longitudinal (v_L) and transverse (v_T) sound velocities and Debye energy (E_D) for the rod and the ribbon.

Sample	ρ (g cm^{-3})	B (GPa)	G (GPa)	v_L (km s^{-1})	v_T (km s^{-1})	E_D (meV)
Rod	11.19 (1)	174.7 (5)	32.9 (1)	4.58 (5)	1.78 (5)	21.76 (6)
Ribbon	10.94 (4)	–	24.6 (5)	4.46 (5)	1.54 (5)	18.8 (2)

observed and the slope of the dispersion is closely proportional to the macroscopic sound velocity measurable, for example, by ultrasound spectroscopy. At high Q values a deviation from linearity is observed. This is expected when Q approaches the boundary of the pseudo-Brillouin zone defined as half the value of the maximum of $S(Q)$, which in this glass appears at $Q = 28\,\mathrm{nm}^{-1}$ [9]. There are no strong differences between the ribbon and the glass dispersion relations, however, a closer look at the dispersion data can be obtained plotting the apparent longitudinal phase velocity defined as $v_L(Q) = \Omega(Q)/(\hbar Q)$. As shown in Fig. 3, both rod and ribbon phase velocities display the same pattern: at low Q values the phase velocity reaches a plateau that it is expected to coincide with the macroscopic sound velocity whereas at high Q values it begins to bend, similar to the behavior found in crystalline materials. However, two features can be distinguished: (i) at the low Q limit there is a distinct decrease of the rod phase velocity that it is not observed for the ribbon sample and (ii) the sound speed of the ribbon for intermediate Q values is slightly lower than that of the rod. We can compare the apparent sound speed of the samples with the macroscopic one; in the case of the rod there are ultrasounds measurements [10] yielding the values of both the longitudinal and the transverse velocities. The longitudinal one is also plotted in Fig. 3 as a horizontal line and the values are in Table 1. On the contrary, due to geometrical considerations, ultrasounds measurements cannot be carried out in thin ribbon samples. Therefore, we will estimate the macroscopic velocities from the Debye energy (E_D) [11]. The Debye energy can be calculated following the Debye approximation for the density of states at energies tending to zero:

$$\frac{3}{E_D^3} = \frac{1}{6\pi^2\hbar^3 n}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right) \tag{2}$$

where n is the number density and v_T and v_L the transverse and longitudinal sound velocities, respectively, that can be expressed as a function of the bulk modulus B, the shear modulus G, and the density ρ:

$$v_L = \sqrt{\frac{B + \frac{4}{3}G}{\rho}} \qquad v_T = \sqrt{\frac{G}{\rho}} \tag{3}$$

Among these parameters, the two elastic constants of the ribbon are unknown. As it has been found in other metallic glasses [6], the effect of structural relaxation, and even crystallization, in the elastic constants is basically to modify the Young and the shear modulus while the bulk modulus remains nearly constant. Therefore, we can make the assumption that the bulk modulus of the rod and the ribbon are the same and then calculate G for the ribbon using Eqs. (2) and (3), obtaining a value of 24.6 (5) GPa. Thus, the longitudinal and transverse sound speeds for the ribbon can be readily calculated using Eq. (3) and the results are shown in Table 1. The longitudinal sound speed of the ribbon is slightly lower (~3%) than the corresponding value for the rod and it is also plotted in Fig. 3 as a horizontal line.

4. Discussion

The comparison between the apparent phase velocity and the macroscopic one, either measured by ultrasonic methods or calculated from the elastic constants, yields a lower velocity for the ribbon compared with the rod, as it would be expected due to the lower density of the ribbon. Moreover, in both cases the macroscopic speed is higher than the phase velocity though the two estimations are very close at low Q values. Therefore, in any case, a positive dispersion of the sound speed as found in [2,3] is not present in the PdSiCu glass, neither in the rod nor in the ribbon. As the rod has been produced with a slow quenching rate, it is in a non-equilibrium state of lower energy than the ribbon and, thus, its structure should be more homogeneous than in the case of the ribbon, where the stresses induced in the material by the high-quenching rate can lead to larger inhomogeneities. Therefore, the hypothesis made by Ichitsubo et al in [2,3] that the presence of a positive dispersion will imply the existence of elastic inhomogenities seems to be contradicted by the present results where the same glass but with different elastic properties (specifically in the shear modulus) shows a phase velocity always below the macroscopic sound speed.

Further discussion is required by the observed decrease of the apparent phase velocity of the rod for $Q \leq 2\,\mathrm{nm}^{-1}$. This softening of the velocity at low Q values has been reported in other systems like vitreous silica and glycerol [12,13] and in molecular dynamics simulations [14]; the presence of a minimum in the velocity has been related to the boson peak, an excess of vibrational modes over the Debye level that appears at energies of few meV in the vibrational density of states. The energy at which the boson peak appears depends on several parameters, in particular on the quenching rate, being lower for rapidly quenched glasses. In the $Pd_{77}Si_{16.5}Cu_{6.5}$ under study the energy of the boson peak for the rod is 3.59 (10) meV and 2.32 (7) meV for the ribbon [11]. This means, using the dispersion relations to convert energies into wavenumbers, that the boson peak appears approximately at $1.2\,\mathrm{nm}^{-1}$ and $0.8\,\mathrm{nm}^{-1}$ Q values for the rod and the ribbon, respectively, assuming a longitudinal acoustic character for these excess modes. These values explain why a decrease in the phase velocity of the ribbon is not observed while its signature can be seen in the rod. In order to detect these features, IXS experiments with better resolution in energy are required to allow higher accuracy at very low Q values and to separate the inelastic and the elastic contributions.

Moreover, the results presented here and in [12–14] offer a possibility to explain the positive dispersion observed in [2,3]. When analyzed with the highest available energy resolution, the softening of the velocity at low Q values, around $1\,\mathrm{nm}^{-1}$, appears to be a universal feature of all the glasses studied up to now and the results presented here on a metallic glass point in the same direction. Therefore, the positive dispersion observed in [2,3] must be validated with higher energy resolution experiments at the lowest achievable momentum transfer.

5. Conclusions

Inelastic X-ray scattering experiments have been performed on two metallic glasses of the same composition produced with different quenching rates. The acoustic dispersion relation of both samples did not show significant differences while a lower longitudinal sound speed is found in the fast quenched glass. The longitudinal phase velocity has been compared with the macroscopic speed of sound measured by ultrasound techniques for the rods and estimations based on the Debye energy for the ribbons. This comparison did not evidence any positive dispersion, thus contradicting the model of strong and weak zones presented in [2,3].

The softening of the sound speed in the rod sample signals to a universal feature of all glasses related to the existence of the boson peak that can only be observed in very high energy resolution IXS measurements.

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