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# High frequency dynamics of BMG determined by synchrotron radiation: A microscopic picture

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ABSTRACT

Mechanical properties are becoming the focus in research on bulk metallic glasses (BMG), as they are the limiting factor for structural applications. A wide range of experimental techniques gives complementary macroscopic data that are often difficult to correlate with the microscopic structural knowledge of the same materials. Recently, high resolution inelastic X-ray scattering (IXS) was applied to determine the high frequency dynamics of BMG [T. Scopigno, J.-B. Suck, R. Angelini, F. Albergamo, G. Ruocco, Phys. Rev. Lett. 96 (2006) 135501]. This technique offers a new approach to the mechanic properties helping to bridge the gap between the microscopic and the macroscopic picture. Here we will present results of IXS experiments on bulk metallic glasses with different fragility values, obtained at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France).



## 1. Introduction

Mechanical properties of metallic glasses (MGs) have distinct features from those of crystalline materials, thus offering the possibility of new applications and posing also new challenges. The lack of long range order as well as the non-existence of lattice defects, largely responsible for the mechanical properties of crystalline materials, forces us to seek for new approaches when modelling the mechanical response of MGs. At the microscopic level, this response is controlled by interatomic forces between randomly distributed atoms. The study of collective dynamics in amorphous systems, either liquid or glass, is a way to gain insight into this interaction. However, due to the intrinsic randomness of these systems even the most basic physical entities present in crystalline materials, such as phonon branches and Brillouin zones have to be reassessed [2,3].

For quite a long time inelastic neutron scattering (INS) experiments were the main source of information about the collective dynamics in metallic glasses [4–7]. However, the availability of third generation Synchrotrons allowed the design of inelastic X-ray scattering (IXS) experiments that, free of the kinematic restrictions of INS, enable the study of a much larger range of alloy compositions.

Besides the determination of longitudinal sound speeds, sound attenuation coefficients and elastic moduli, IXS has proved to be an outstanding technique for testing different aspects of the glass transition and the glassy state [8,9] as well as liquid metals [10]. One parameter easily derived from IXS spectra is the non-ergodicity factor of a glass, $f_0(T) = f(Q \to 0, T)$, $Q$ being the momentum transfer, which corresponds to the relative weight of the elastic contribution in the dynamic structure factor. The non-ergodicity factor was found to be related to the fragility, $m$, of the corresponding glass-forming liquid [8], thus evidencing a link between the structure frozen-in in the glass and the viscous behaviour of the liquid. Scopigno et al. modelled the temperature dependence of the non-ergodicity factor as [8]:

$$f(Q \to 0, T) = \lim_{Q \to 0} \frac{S_{\text{elast}}(Q, \omega)}{S(Q, \omega)}\bigg|_{T \ll T_g} = \left[1 + \alpha \frac{T}{T_g}\right]^{-1}, \quad (1)$$

where $T_g$ is the glass transition temperature, $S(Q,\omega)$ the dynamic structure factor, $S_{\text{elast}}(Q,\omega)$ the elastic contribution to $S(Q,\omega)$, both obtained at temperature $T$, and $\alpha$ a dimensionless constant parameter. Furthermore, the empirical correlation $m \approx 135\alpha$ was found for very different kinds of glass-forming substances.

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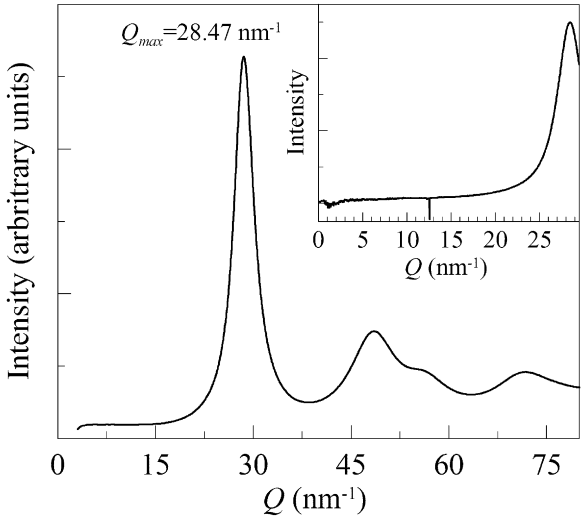


**Fig. 1.** Scattered X-ray intensity of $Pd_{77}Si_{16.5}Cu_{6.5}$. The inset displays the low $Q$ tail of the diffraction intensity, measured above 3 nm$^{-1}$.

Application of IXS to metallic glasses is very recent and, at present, it has been reported only for $Ni_{33}Zr_{67}$ [1], $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ [11] and $ZrCu_2$ [12]. In $Ni_{33}Zr_{67}$ the validity of the empirical relationship between the non-ergodicity factor and the fragility was checked for MGs and the obtained "dynamic fragility" ($m$ = 26) was in good agreement with experimental data available from viscosity measurements [1]. The sound speed determined in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ by IXS, i.e. on a nanometer length scale, was found to exceed the macroscopic sound speed determined by ultrasound measurements, i.e. on a millimetre length scale [11]. This fact was linked to the existence of an upward bending of the acoustic dispersion, considered to be an evidence for the existence of regions with mechanical inhomogeneities at the nanoscale level, though other phenomena may lead to the same result. The available experimental data are far to be enough to describe the general features of the collective atomic excitations in MGs. One of the most relevant issues is to elucidate how the collective dynamics in MGs changes with the fragility of the glass.

We report here IXS data on a fragile metallic glass, $Pd_{77}Si_{16.5}Cu_{6.5}$ ($m$ = 75). The analysis of the fragility of this MG in terms of the non-ergodicity factor confirms the validity of the empiric relation observed in other kinds of glasses and in $Ni_{33}Zr_{67}$. This confirmation encourages the use of IXS as a suitable technique to investigate the fragility of MGs from a microscopic point of view.

## 2. Experimental

The experiments were performed on beamline ID28 at the European Synchrotron Radiation Facility (ESRF). To this aim, monochromatic X-rays of 17.794 keV were utilised, in order to achieve an energy resolution of 3 meV and a momentum transfer resolution of 0.27 nm$^{-1}$. The X-ray beam dimension at the sample position was of 270 × 60 (horizontal × vertical) μm$^2$. A multi-analyser setup was exploited to obtain nine spectra, corresponding to different momentum transfers, simultaneously. The experiments were performed at room temperature in a specially designed vacuum chamber in order to avoid scattering from air and the kapton windows.

Samples of composition $Pd_{77}Si_{16.5}Cu_{6.5}$ were prepared by arc-melting of pure raw materials and by rapidly quenching by melt spinning. The resulting ribbons, of 2 mm width and 22 μm thickness, were cut in pieces of 20 mm length. Two of them were employed, attached on top of each other, in order to achieve the optimal thickness and therefore maximum scattering intensity in transmission geometry for the selected composition and X-ray incident energy. The amorphous structure of the ribbons was assessed prior to the IXS experiment by X-ray diffraction using Synchrotron radiation on beamline CRG-BM16 at the ESRF. Fig. 1 displays the scattered X-ray intensity $I(Q)$ obtained from those measurements, where the maximum of $I(Q)$ was observed at 28.51 nm$^{-1}$.

IXS energy scans were performed in the [−50, 50] meV energy range for momentum transfers between 1.5 and 20 nm$^{-1}$, with a typical acquisition time of 300 min per spectrum. Several spectra were added in order to reduce statistical noise. Each spectrum represents the dynamic structure factor $S(Q,\omega)$ at a given momentum transfer $Q$, and was fitted with a standard least-squares procedure using a single damped harmonic oscillator function for the excitation convoluted with the experimental resolution function of the corresponding analyser, similar to what was reported in ref. [8]. The characteristic frequency of the excitation corresponds to the maximum of the longitudinal current spectrum, defined as $C_L(Q,\omega) = (\omega/Q)^2 S(Q,\omega)$.

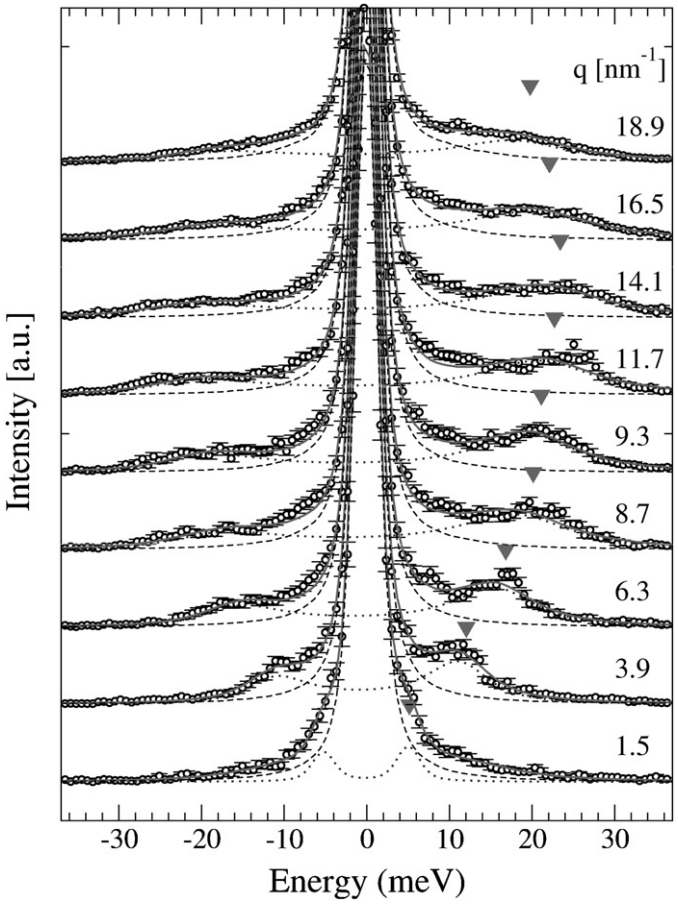


**Fig. 2.** Inelastic X-ray scattering spectra for selected momentum transfers. The inverted triangles display the maximum of the longitudinal current correlation function in the damped harmonic oscillator model, the dashed and dotted curves show the elastic and inelastic contributions, respectively, and the solid (light grey) curves correspond to the best fit to the spectra.

## 3. Results

Fig. 2 displays selected IXS spectra as a function of the momentum transfer. Beside a central elastic line, two excitations are observed at positive and negative energy, corresponding to the creation and annihilation of longitudinal acoustic modes, respectively. No excitations related to transverse acoustic modes similar to those reported in ref. [13] were observed in these experiments. The observed excitations increase linearly in energy with increasing momentum transfer at low $Q$, whereas they decrease in energy for $Q > 14$ nm$^{-1}$. They thus follow a dispersion relationship similar to that expected for a crystal, with a Brillouin zone size defined by the momentum transfer of the maximum in the diffraction pattern, shown in Fig. 1.

The microscopic or high frequency limit of the sound speed can be obtained as the limit for vanishing $Q$ of the slope of a sinusoidal fit of the dispersion. For $Pd_{77}Si_{16.5}Cu_{6.5}$, this fit yields a longitudinal sound speed of $v_l$ = 5.07(10) km/s, i.e. significantly larger than the value of 4.6 km/s derived from ultrasound experiments [13] in a very similar composition (Pd77.5Si16.5Cu6). A similar result was reported also from IXS experiments on a Pd-based bulk metal-

**Table 1**
Values of $\alpha$, fragility determined by IXS ($m_{IXS} = [135 \pm 10]\alpha$), and fragility obtained by viscosity measurements ($m_{visc}$), for bulk metallic glasses.

| | $\alpha$ | $m_{IXS}$ | Ref. | $m_{visc}$ | Ref. |
|---|---|---|---|---|---|
| $Ni_{33}Zr_{67}$ | 0.19(4) | 26(9) | [8] | 24 | [17] |
| $Pd_{77}Si_{16.5}Cu_{6.5}$ | 0.47(4) | 63(9) | This work | 75 | [15] |

lic glass (Pd42.5Ni7.5Cu30P20) and was attributed to nanosized elastic inhomogeneities [11] and at present, all MGs investigated with IXS exhibit a larger sound speed in the high frequency limit than that obtained with the aid of ultrasounds. The origin of this distinct behaviour is under debate, one explanation being the existence of nanosized domains with stronger and weaker bonds while keeping similar stoichiometry [11]. However, other explanations such as topological disorder and residual fast relaxation in the glass have been also proposed and observed in conventional glasses, and further experimental data are needed to ascertain the mechanism responsible for these differences. The density fluctuations or the weak–strong bonding domains in a glass are expected to have sizes in the *nanometre* scale. Ultrasound probes, with a wavelength in the *millimetre* scale, give us the response of the material as homogeneous system, while the IXS experiment probes collective vibrations with wavelengths of about 1–10 nm, i.e. in the same length scale as the glass inhomogeneities. The different response of the material to low frequency (MHz range) and high frequency (THz range) probes, such as ultrasound and X-rays respectively, thus implies different mechanic behaviour at microscopic and macroscopic scales, thus making IXS a unique technique to ascertain the microscopic origin of mechanical properties in MGs.

The increase in excitation energy with increasing momentum transfer is accompanied with an increase of the excitation linewidth, related to the sound attenuation in the glass. This has been previously observed in many types of conventional glasses [14] and in $Ni_{33}Zr_{67}$ [1]. The dependence of linewidths on momentum transfer is still a matter of controversy [14] and will be addressed for the $Pd_{77}Si_{16.5}Cu_{6.5}$ alloy elsewhere.

The good quality of the obtained IXS spectra allowed us to evaluate the contribution of elastic scattering to the dynamic structure factor and hence obtain the non-ergodicity factor. According to Eq. (1) and ref. [8], the parameter $\alpha$ can be then derived and compared with the fragility index $m$, obtained either from viscosity or calorimetric measurements. The $m$ values obtained from viscosity measurements are typically slightly larger than those obtained from calorimetric measurements of $T_g$ at different heating rates. The viscosity at $T_g$ used in the calorimetric fragility determination is usually one or two orders of magnitude lower than the defined glass transition viscosity $10^{12}$ Pa s, this leading to the differences between the two values for the fragility [15]. Table 1 gives the values of the $\alpha$ parameter defined in Eq. (1) as determined from IXS measurements of bulk metallic glasses, using a value of $T_g = 620$ K for the glass transition of the studied alloy [15], and compares them to the fragilities determined from viscosity measurements. The value of $\alpha$ for $Q = 0$ was assumed to be that obtained for the lowest momentum transfer, since $f(Q)$ is known to saturate near $Q = 0$. This value defines an upper limit for $\alpha$. A lower limit would be then given by the linear extrapolation at $Q = 0$ from the experimental data, which yields $\alpha = 0.40(4)$.

The experimental values of $m_{visc}$ and $\alpha$ in Table 1 are plotted in Fig. 3, together with data obtained in a similar way for other glass-forming systems, taken from ref. [8]. There is a slight deviation from the expected behaviour of $m = 135\alpha$, in line with other deviations displayed by selenium and salol glasses. The agreement improves if we compare our data with the calorimetric fragility, $m = 61$ [15]. In addition to possible uncertainties in the few fragility measurements available in literature, this deviation can be attributed to either a specific behaviour of the Pd-based compositions or a special behaviour shown by metallic glasses. Higher resolution IXS data at lower $Q$ values would also improve the reliability of the value of $\alpha$. Note also that slight changes in composition of Pd–Cu ratio allow for significant changes in the fragility (e.g. for $Pd_{77.5}Si_{16.5}Cu_6$ a fragility of 73 has been reported [16]). Nevertheless, there is indeed good agreement with the general trend observed in glasses. More IXS data are required in order to pinpoint the relation between fragility and non-ergodicity factor in the case of metallic glasses.

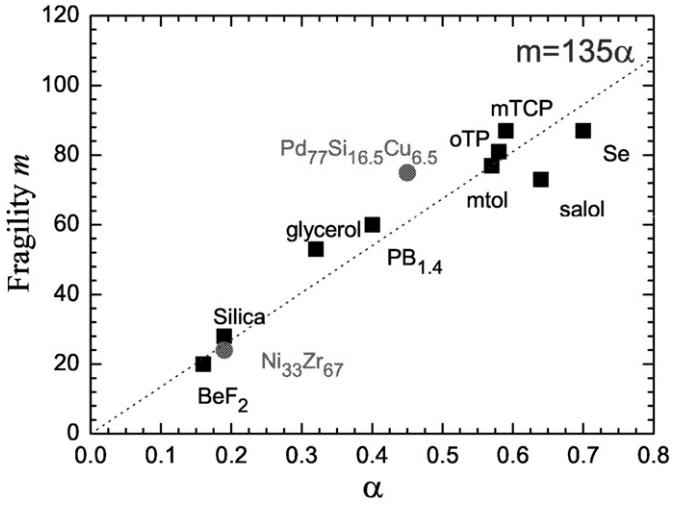


**Fig. 3.** Comparison of the empiric relation between fragility and non-ergodicity factor for conventional glasses and metallic glasses. The data for conventional glasses have been taken from Table 1 in ref. [8] and the data for $Ni_{33}Zr_{67}$ were taken from ref. [1] ($\alpha$) and [17] ($m$).

## 4. Conclusions

We performed inelastic X-ray scattering experiments on $Pd_{77}Si_{16.5}Cu_{6.5}$ bulk metallic glass. This technique offers a microscopic description of the collective dynamics and mechanical properties both for crystalline and amorphous phases. Basic physical concepts such as Brillouin zones and phonon branches, well defined for crystalline materials, have their counterparts in amorphous materials where pseudo-Brillouin zones are defined from the first peak of the static structure factor. Among other properties, sound speed, elastic moduli and sound attenuation coefficients can be easily derived from IXS spectra. The sound speed obtained from the IXS spectra is larger than that reported from ultrasounds measurements. The origin of this discrepancy is still unknown and further experiments are under way to ascertain the responsible mechanism.

Fragility was also computed from the IXS data, in semi-quantitative agreement with the value reported from viscosity measurements in the literature. The previous measurements in a strong glass, $Ni_{33}Zr_{67}$, and the present results for one of the most fragile metallic glasses sustain the hypothesis that the correlation between non-ergodicity factor and fragility, proposed as general relation in glasses, also holds for metallic glasses.

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