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2008 J. Phys.: Condens. Matter 20 104241

(http://iopscience.iop.org/0953-8984/20/10/104241)

J. Phys.: Condens. Matter **20** (2008) 104241 (4pp) doi:10.1088/0953-8984/20/10/104241

Propagating vibrational modes in the Zr–Be metallic glasses

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Received 16 July 2007, in final form 12 November 2007
Published 19 February 2008
Online at stacks.iop.org/JPhysCM/20/104241

Abstract

The dynamic structure factors, $S(Q, E)$, for the $Zr_{70}Be_{30}$, $Zr_{60}Be_{40}$ and $Zr_{50}Be_{50}$ metallic glasses have been measured using neutron inelastic scattering on the IN4 spectrometer (ILL, Grenoble, France), over the range of momentum transfers $0.7 < \hbar Q$ (Å^{-1}) < 7 and energy transfers $2 < E$ (meV) < 60. The constant-Q cuts through the dynamic structure factor and longitudinal current correlation function, $J_l(Q, E)$, were obtained. The dispersion relations for two representations, $S(Q, E)$ and $J_l(Q, E)$, were derived by fitting a Gaussian to the peaks. The specific low-energy modes (∼5 meV) as well as 'acoustic-phonon like' (∼16 meV) and 'optic-phonon like' excitations (∼47 meV) were observed in these metallic glasses with disparate mass and ionic radius components.

1. Introduction

Very detailed information about the interatomic potentials in disordered matter can be obtained from the measurement of the collective excitations. Some works have been devoted to investigation of propagating vibration modes in metallic glasses. At first only a small part of a dispersion branch with negative slope for Q-values between 1.8 and 2.3 Å^{-1} was measured in the metallic glass $Mg_{70}Zn_{30}$ [1] using thermal neutrons. More recently another metallic glass, $Fe_{85}B_{15}$ [2], has been studied with epithermal neutrons and high resolution. As $Q_p/2$ (Q_p being the position of the main structural peak) for this glass is at a much higher value (1.9 Å^{-1}) than in the case of $Mg_{70}Zn_{30}$ (1.3 Å^{-1}), dispersion with a positive slope was observed, which agrees reasonably well with the slope of elastic modes according to the value of the Young modulus. An 'acoustic-phonon like' dispersion relation up to $Q = 9$ Å^{-1} also was observed in $Ni_{67}Zr_{33}$ metallic glass [3].

Recently we have carried out measurements of the inelastic neutron scattering intensities $I(E, \Omega)$ in binary alloys $Ni_{62}Nb_{38}$ [4]. The isotopes ^{58}Ni, ^{60}Ni and $^{58/64}$Ni with different scattering cross-sections were used for preparation of the samples. A clear isotope contrast was observed which permitted us to separate $I(E, \Omega)$ into partial scattering functions. We indicate that the energy positions of the $I(E, \Omega)$ peaks observed in the three partials show certain differences. This is a clear indication of the sensitivity of the 'partial collective excitations' to the partial atomic distributions and potentials of atomic interactions. The propagating excitations in binary amorphous alloys should be a superposition of such partial excitations, which were observed for the first time in these investigations.

Metallic glasses are typically made up of several different elements. By analogy with many-component crystalline matter, metallic glasses should possess 'acoustic-phonon like' and 'optic-phonon like' vibrational excitations. In the case of the $Ni_{1-x}B_x$ system, for which the ratio of atomic masses is higher ($m_{Ni}/m_B = 5.3$) than for $Mg_{70}Zn_{30}$, $Ni_{67}Zr_{33}$ or $Ni_{62}Nb_{38}$, the density of vibrational states is divided in two distinct parts which can be attributed to 'acoustic' and 'optic' modes [5, 6]. The system Zr–Be is most suitable for investigation of the dispersion of 'acoustic' and 'optic' modes. The ratio of atomic masses is the highest ($m_{Zr}/m_{Be} = 10$) for the existing binary metallic glasses. The structure factors and vibrational densities of states (VDOS) of $Zr_{100-x}Be_x$ ($x =$ 30, 40 and 50) have been studied by neutron scattering and Monte Carlo modeling [7]. It was shown that the partial radial distributions of the atoms in amorphous Zr–Be alloy

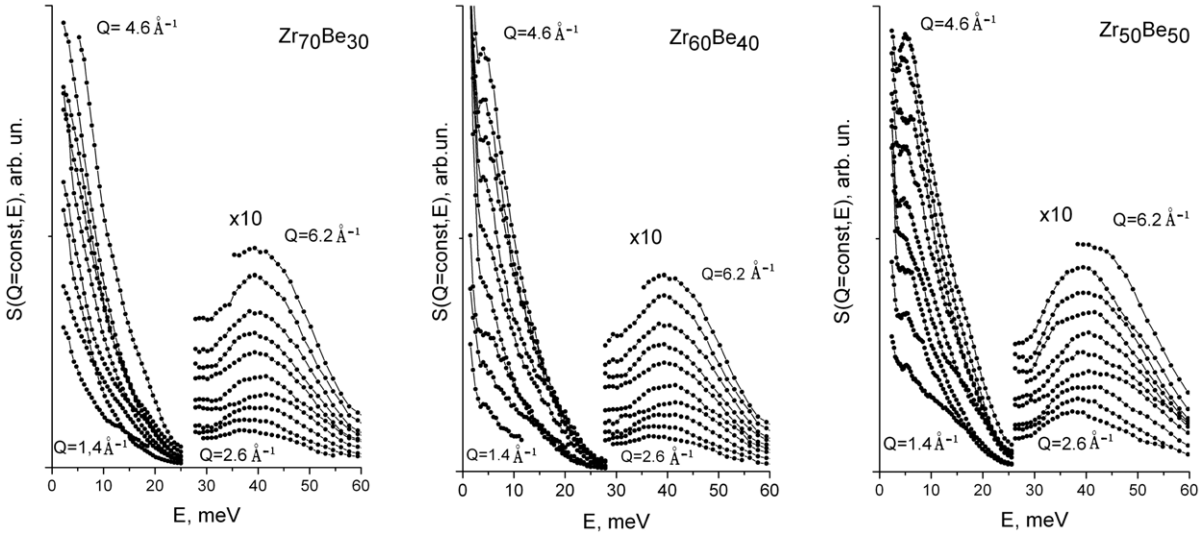

Figure 1. Cuts through the dynamic structure factors, $S(Q, E)$, of the $Zr_{70}Be_{30}$, $Zr_{60}Be_{40}$ and $Zr_{50}Be_{50}$ samples at different Q values. The cut width $\Delta Q = 0.4$ Å^{-1}. The statistical errors are of the order of 3%.

strongly differ due to the disparate ionic radii of the two components. The VDOS spectra consist of the two frequency bands centered at about 18 meV and 51 meV, respectively. For the $Zr_{70}Be_{30}$ sample the low-frequency band reveals no visible substructure. However, with increasing concentration of the light atoms a shoulder (∼9 meV) appears in the low-frequency band of the $Zr_{60}Be_{40}$ and $Zr_{50}Be_{50}$ samples. At the same time the Monte Carlo modeling shows a clear low-energy kink at ∼9 meV for all three samples. In the present work we carried out an inelastic neutron scattering investigation of the dynamic structure factors of Zr–Be metallic glasses.

2. Experiment and data treatment

The metallic glass samples were prepared by melt spinning. Inelastic neutron scattering intensities, $I(\Omega, t)$, were measured on the time-of-flight neutron spectrometer IN4 (ILL, Grenoble, France). The experiment was performed with an incident energy of 16.9 meV at room temperature. The energy resolution (FWHM) at the elastic position was 0.85 meV. Measurements of the background scattering from the empty container and a sample of vanadium were carried out under the same conditions. The measured spectra $I(\Omega, t)$ were transformed to dynamic structure factors, $S(Q, E)$, taking into account corrections for background, detector efficiency, multiple scattering and Debye–Waller factors.

Determination of the neutron fraction arriving at the detector after being scattered more than once requires the exact energy- and momentum-dependent cross-section, i.e. the scattering law, which, however, is the subject of the investigation and is *a priori* unknown. Therefore the preferred method is the Monte Carlo simulation of the scattering experiment. Here, a dedicated simulation program for time-of-flight spectrometers, PRANA [8], was used. The most critical question was how to obtain a good model for the dynamic structure factor $S(Q, E)$. The idea was therefore to produce a suitable model $S^{\mathrm{mod}}(Q, E)$ by fitting the experimental scattering law $S^{\mathrm{exp}}(Q, E)$. As the dynamic range in $S(Q, E)$ needed for the simulation is larger than the experimentally accessible one, the incoherent approximation have then to be extrapolated to smaller and larger Q. For calculations of the partial scattering laws in the incoherent approximation for Zr and Be we used the theoretical partial frequency distributions [7]. The obtained results show that the ratio of total to single scattering varied from 1.03 to 1.12, being a slowly increasing function of energy transfer. Estimation of the two-phonon scattering using the Gaussian approximation [9] gives a 3–4% correction at the boundary of the vibration spectrum.

3. Experimental results, analysis and discussions

Constant-Q cuts through the (Q, E) intensity maps of dynamic structure factors $S(Q, E)$ of the $Zr_{70}Be_{30}$, $Zr_{60}Be_{40}$ and $Zr_{50}Be_{50}$ samples obtained by averaging within 0.4 Å^{-1} around the central Q values are displayed in figure 1. They reveal a characteristic two-band structure with a gap near ∼25 meV. For the $Zr_{70}Be_{30}$ sample the low-energy band in $S(Q, E)$ looks like an extended intensity tail aside the elastic line decreasing towards higher energy transfers, and reveals no visible features. The high-energy band (multiplied by a factor of 10 for clarity) is represented by a peak with the center of gravity varying as a function of momentum transfer. Similar to the previous results on VDOS for Ni–B [5, 6] and Zr–Be [7], the low-energy band (below 25 meV) can be associated with motions involving Zr–Zr bonds, while the high-energy band (25–60 meV) corresponds to the modes in which mostly the light Be atoms are moving. Apart from that, an additional low-energy mode (∼5 meV) arises and increases in intensity with increasing Be atom content. It can be easily seen in $S(Q, E)$ for the $Zr_{60}Be_{40}$ and $Zr_{50}Be_{50}$ samples.

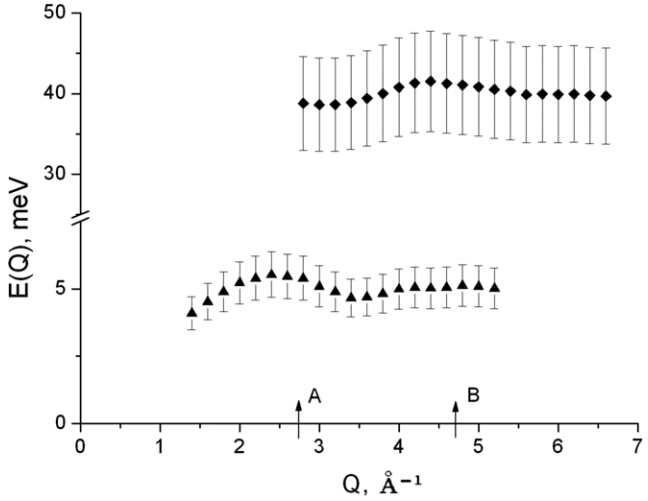

Figure 2. Peak positions in Q-cuts through the scattering function $S(Q, E)$ of the $Zr_{50}Be_{50}$ sample obtained by Gaussian fitting. The 'additional' ∼5 meV mode is shown together with the high-energy 'optical' band. Vertical bars indicate the FWHM of Gaussians.

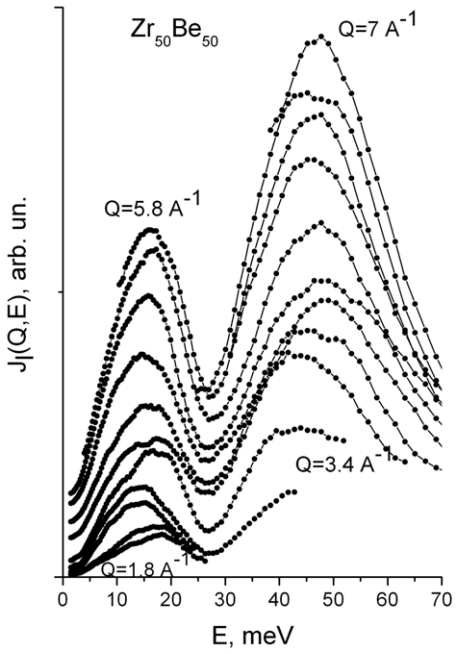

Figure 3. Cuts through the longitudinal current correlation functions, $J_l(Q, E)$, of the $Zr_{50}Be_{50}$ sample for selected ranges of momentum transfer. The cut widths $\Delta Q = 0.4$ Å^{-1}. The statistical errors are of the order of 3%.

The peak positions in $S(Q, E)$, obtained by fitting a Gaussian to the low-energy (∼5 meV) and high-energy (∼42 meV) peaks, are shown in figure 2. One clearly sees that their positions depend on the momentum transfer and they oscillate with Q apparently 'in phase'. The positions of the first and second peaks in the static structure factor $S(Q)$ are indicated by arrows A and B.

In order to characterize energy parameters of the whole low-energy acoustic-like band we use the longitudinal current-correlation function $J_l(Q, E) \propto (E/Q)^2(Q, E)$ [10]. In this representation the measured spectra consist of two broad but distinct energy bands separated by a pseudogap at ∼28 meV, as shown for different Q values in figure 3 for the $Zr_{50}Be_{50}$ sample.

The acoustic-like energy band arising from the slowly decreasing intensity tails in the low-energy (<25 meV) sector of $S(Q, E)$ is now seen as well-shaped peaks slightly oscillating, as a function of the Q-value, around the average energy of ∼16 meV. The above mentioned specific 5 meV mode is transformed to a shoulder at around 9 meV with very little effect on the overall peak position. The high-energy 'optic-like' band is equally well formed in both $S(Q, E)$ and $J_1(Q, E)$ presentations.

Due to the fact that the energy widths of the observed bands is comparable to their central energy, the position of the peaks appears to be sensitive to the representation of the spectra, for example the average position of the 'optic-like' band is shifted from ∼42 meV in $S(Q, E)$ to ∼47 meV in $J_1(Q, E)$. The other possible representation of the measured spectra with a linear energy pre-factor [11] will result in the other peak energies. However, the relative positions of the peaks in the cuts at different Qs, or the shape of the excitation dispersion which is depicted on the figure 4, appear to be less sensitive to the specific form of the pre-factor.

We notice that the positions of the low-energy peak, as derived from the $J_l(Q, E)$ representation of the spectra,

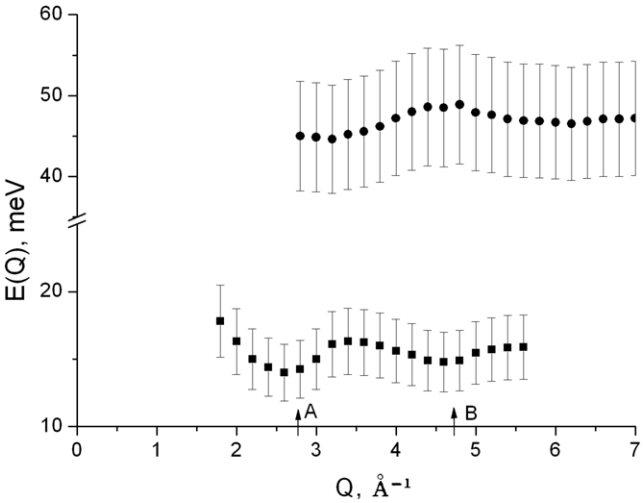

Figure 4. Peak positions of the 'acoustic' and 'optical' bands in the cuts through the longitudinal current function $J_l(Q, E)$ of the $Zr_{50}Be_{50}$ sample obtained by Gaussian fitting. Vertical bars indicate the FWHM of Gaussians. Arrows A and B as in figure 2 correspond to positions of the first two maxima in the static structure factor $S(Q)$.

oscillate as a function of momentum transfer around the average band energy of ∼16 meV. The two minima visible in the experimental range closely correspond to the positions of the maxima in the static structure factor (figure 4) similarly to earlier observations at Q_p (position A) in the other metallic glasses ($Mg_{70}Zn_{30}$ [1], $Ni_{67}Zr_{33}$ [3], $Ni_{62}Nb_{38}$ [4]). Such behavior of the low-energy excitations closely resembles acoustic phonon branches in ordered crystals and permits us

to identify this band as an 'acoustic-like' mode involving predominantly Zr–Zr bonds.

The high-energy excitations at around ∼47 meV (figure 4) could be rather thought of as the 'optic-like' mode due to vibrations of light Be atoms. Indeed, its energy scales with that of the low-energy mode roughly as the mass ratio $(m_{Zr}/m_{Be})^{1/2} = 3.15$ and the Q-dependences of these two modes exhibit apparent out-of-phase behavior. This resembles the energy spectrum of a two-component regular crystal with clear optical and acoustic bands.

It was shown [12] that the partial excitations are governed by partial structure factors. From this point of view the observed different dispersion of the 'acoustic-like' and 'optic-like' modes can be interpreted in accord with considerations [14] on the basis of significant difference of partial structure factors in amorphous Zr–Be, namely $S(Q)_{ZrZr}$ and $S(Q)_{BeBe}$ [7]. As we noticed earlier, the dispersion curve of the specific mode at ∼5 meV in Zr–Be appears to be in phase with the 'optical' dispersion curve and it does not show a minimum at Q_p (figure 2). Such a 'non-acoustic-like' behavior contrasts with the other similarly low-energy modes observed in $Mg_{70}Zn_{30}$ (∼4.5 meV) [13] and $Ni_{24}Zr_{76}$ (∼3 meV) [14] metallic glasses where they display a minimum near Q_p. Based on the dispersion of this specific mode in Zr–Be glass and the fact that it emerges upon an increase in concentration of the light atoms (figure 1) we suggest that this mode is related predominantly to the vibrations of Be atoms, as the high-energy 'optic-like' mode. In order to clarify the nature of this specific mode we plan the high-resolution measurements extending to the Q-range below $Q_p/2$.

4. Conclusion

The dynamical structure factors $S(Q, E)$ of $Zr_{100-x}Be_x$ ($x =$ 30, 40 and 50) metallic glasses with disparate atomic masses and ionic radii have been measured by inelastic neutron scattering. The 'acoustic-phonon like' and 'optic-phonon like' dispersion relations were observed. The 'optic' dispersion curve is out-of-phase with the 'acoustic' dispersion curve. A specific low-energy mode (∼5 meV) arises upon increasing Be atom content with the dispersion in-phase with the 'optic' mode, suggesting a dominant role of the light atom correlations in this mode.

Acknowledgments

G F Syrykh thanks ILL for hospitality and the use of its facilities. This work was supported by RFBR grant no. 07-02-01042-a.

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