Harmonic behavior of metallic glasses up to the metastable melt

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In two amorphous alloys ZrTiCuNiBe and ZrAlNiCu coherent neutron scattering has been measured over five decades in energy, including measurements in the metastable melt of a metallic alloy more than 80 K above T_g. In the vibrational spectra a pronounced ''boson'' peak is found: Even in crystallized samples the density of states exceeds the Debye ω^2 model, and in the amorphous state low-frequency vibrations are further enhanced. The peak position shows no dispersion in q, while intensities are strongly correlated with the static structure factor. Over the full energy range the temperature dependence is strictly harmonic. From high-energy resolution measurements we establish lower bounds for the temperatures at which structural α and fast β relaxation become observable. [S0163-1829(96)01218-0]

I. INTRODUCTION

The low-energy vibrational spectra of many glasses deviate in a characteristic way from Debye's plane-wave density of states, the excess modes being designated as the ''boson peak.'' On heating towards and above the glass transition, a sequence of additional relaxational modes sets in. Very similar behavior is observed in chemically quite dissimilar samples,[1] and there is an ongoing discussion about possible interrelations between the strength of the chemical bonds, the width of the first diffraction peak, the spectral broadening of structural relaxation, and the temperature dependence thereof.[2–4]

So far it is not known how *metallic glasses* accomodate within these schemes. Conventional alloys inevitably crystallize on approaching the glass transition. Only recently[5,6] four- and five-component glasses have been developed that open the possibility of performing day long experiments in the metastable melt far above the calorimetric glass transition. By means of broad band inelastic neutron scattering we have studied the vibrational properties and searched for relaxational motion in two different metallic glasses.

II. EXPERIMENTAL

The formula $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ was taken from the literature;[5] the other alloy's composition $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ was improved with respect to pre-

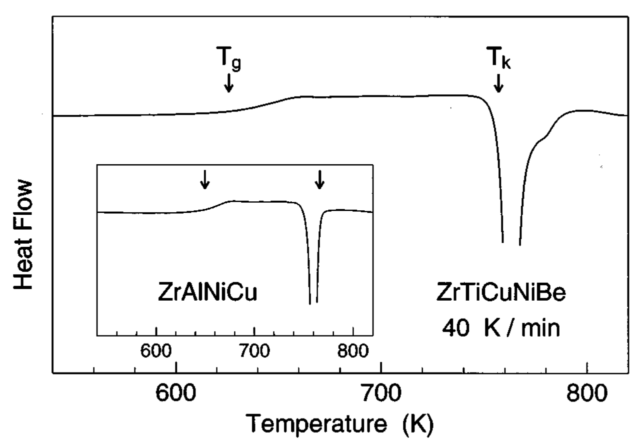

FIG. 1. DSC scans of the glassy alloys with a heating rate of 40 K/min using a Netzsch STA 409 scanning calorimeter.

TABLE I. Calorimetric glass transition T_g and crystallization temperature T_k vs heating rate.

	ZrTiCuNiBe		ZrAlNiCu	
	T_g (K)	T_k (K)	T_g (K)	T_k (K)
40 K/min	626	757	643	757
20 K/min	613	741	643	739
2 K/min	596	706	624	700
Quasi-stationary	582		605	

vious publications[6] and has an even wider range of stability in the melt. More than 75 m of ZrAlNiCu ribbons with a section of about $2.5\times0.06\ \mathrm{mm}^2$ were prepared by conventional melt spinning. For preparing amorphous ZrTiCuNiBe relatively low cooling rates are required so that bulk material could be obtained by casting the melt into copper molds and by suiting the ingot to $35\times5\times1.1\ \mathrm{mm}^3$. The sample material was characterized by x-ray diffraction and thermal analysis. The x-ray structure factor behaved as expected for an amorphous solid and showed no traces of crystallization. By differential scanning calorimetry (DSC) we found that the samples can be heated more than 100 K above T_g before crystallization sets in (Fig. 1). Both the glass transition T_g and the crystallization temperature T_k depend of course on the heating rate. Table I gives a summary of thermal properties, including an estimation for the quasistationary situation of neutron-scattering experiments (scans of about 5 h duration at a given temperature).

Preliminary experiments had shown that surface oxidation is a main cause for precocious crystallization. The samples were therefore sealed under He atmosphere in Al containers. For neutron scattering a hollow cylinder geometry (height 52 mm, diameter 22 mm, thickness 1.1 mm) was chosen. Three samples of each composition were prepared, all of them being deliberately crystallized at the end of the measuring campaign. To determine the melting point of the alloys, DSC scans were performed with samples sealed under He atmosphere in Gold pans. For ZrTiCuNiBe the melting point is 908 K, while for ZrAlNiCu $T_m=1098$ K is much higher. Comparing the interval T_m-T_g with the stability range T_k-T_g of the undercooled melt, we anticipate that ZrTiCuNiBe is the more promising candidate for the search of relaxational processes.

In this work, we have combined four setups on three spectrometers to cover energy transfers from less than 1 μeV up to at least 100 meV: the thermal neutron time-of-flight machine DN6 of the Kernforschungszentrum Karlsruhe at the Centre d'Études Nucléaires de Grenoble (wavelength $\lambda=2.2$ Å, resolution full width at half maximum $\delta E=950\ \mu$eV, wave number range at zero energy transfer $q=1.2-4.3$ Å^{-1}); the cold neutron time-of-flight spectrometer Mibémol at the LLB, Saclay, with $\lambda=5$ Å for maximum flux ($\delta E=140\ \mu$eV, $0.8-2.4$ Å^{-1}) and in another setup with $\lambda=8.5$ Å for higher resolution ($\delta E=30\ \mu$eV, $q=0.5-1.4$ Å^{-1}); and the backscattering instrument IN10 at the ILL, Grenoble [$\lambda=3.27$ Å, $\delta E=4.2\ \mu$eV, $q=1.7-3.7$ Å^{-1} (Ref. 7)].

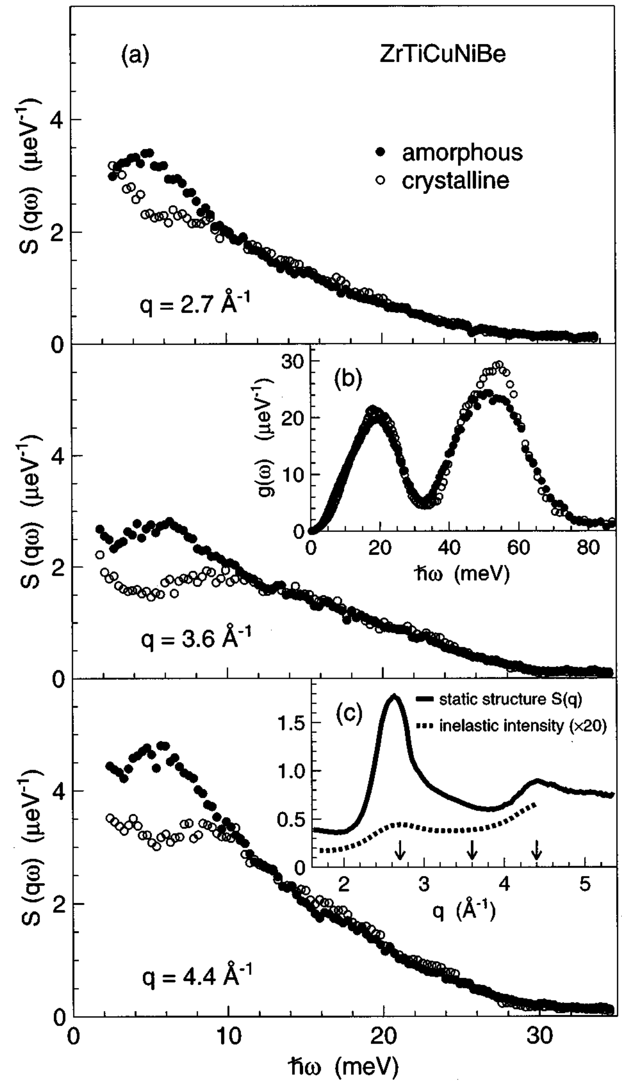

FIG. 2. Vibrational spectra of ZrTiCuNiBe before and after crystallization, measured at room temperature on DN6. (a) Scattering law $S(q\omega)$ for different q. (b) Density of vibrational states $g(\omega)$ evaluated in incoherent approximation. The total number of states was normalized to 1. (c) Static structure factor $S(q)$ compared to the inelastic intensity integrated over the interval $2.4-10$ meV. The arrows in (c) indicate the wave numbers chosen in (a).

III. VIBRATIONAL PROPERTIES

Vibrational modes are studied by time-of-flight spectroscopy in the meV range. In some simple experimental situations incoherent neutron scattering yields a fiducial density of vibrational states (DOS) $g(\omega)$. However, our samples contain four or five different elements with predominantly (about 90%) coherent scattering so that a DOS can be determined only in a very first approximation. Treating $S(2\theta,\omega)$ as if it were an incoherent scattering law, we obtain for every detector angle 2θ another $g(\omega)$. By averaging over the full accessible q range ($2\theta=23°\ldots99°$) (incoherent approximation[8]) we obtain a $g(\omega)$ which may give at least a rough idea of the spectral distribution of vibrational modes [Figs. 2(b), and 3(b)].

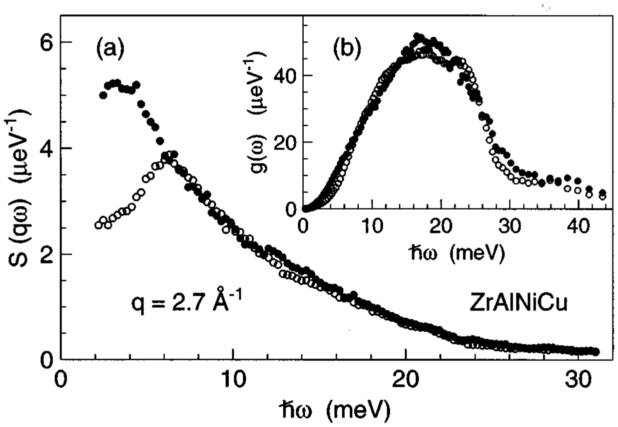

FIG. 3. Vibrational spectra of ZrAlNiCu before and after crystallization, measured and plotted as in Figs. 2(a) and 2(b).

Up to about 30 meV both alloys show similar behavior, with a broad maximum around 20 meV. A second peak around 50 meV that occurs only in ZrTiCuNiBe may be ascribed to vibrations of the light Be atoms. Above 10 meV the spectra of amorphous and crystallized samples nearly coincide: the eigenfrequencies of high-lying modes in which near neighbors oscillate against each other appear rather insensitive to the presence or absence of long-range crystalline order.

Below 10 meV vibrational modes are studied better in terms of $S(q\omega)$ which in one-phonon approximation is proportional to $g(\omega)/\omega^2$. Assuming a Debye DOS, a constant $S(q\omega)$ should be expected. Instead, as most other amorphous substances, our metallic glasses show a ''boson'' maximum of $S(q\omega)$ [Figs. 2(a) and 3(a)] that reveals an excess of low-energy modes with respect to a Debye solid. In ZrTiCuNiBe the boson peak is located at about 5 meV and shows no dispersion in q; the intensity modulates weakly in phase with

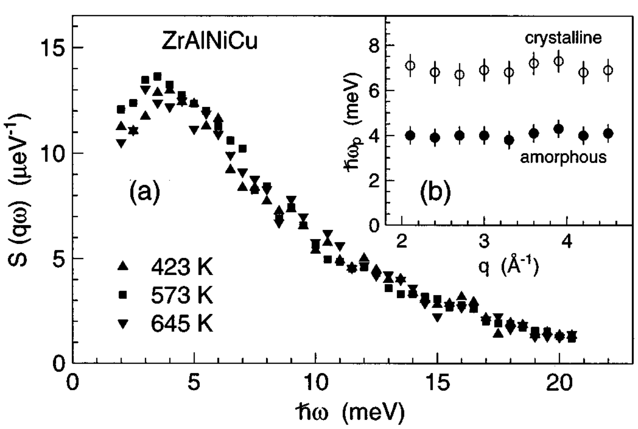

FIG. 4. (a) Vibrational spectra of ZrAlNiCu in the amorphous state, measured on Mibémol at $q=2.6$ Å^{-1}, at different temperatures up to the metastable melt, rescaled with the Bose occupancy $n(\omega,573\text{ K})/n(\omega,T)$ in order to demonstrate harmonic behavior over the full frequency range. (b) Frequency ω_p of the inelastic maximum of $S(q\omega)$ as function of q. Within experimental error, no dispersion could be detected.

$S(q)$ [Fig. 2(c)]. ZrAlNiCu behaves similarly.

In this context one should note that a peak in $S(q\omega)$ is observed not only in the amorphous samples but also (at somewhat higher frequencies) in their crystalline counterparts (at 6 meV in ZrAlNiCu, and less pronounced at 9 meV in ZrTiCuNiBe). Above this peak which shows also no dispersion in q [Fig. 4(b)] amorphous and crystalline spectra merge as discussed before: above a certain frequency, vibration modes do not change much when a disordered system crystallizes into a complicated unit cell.

Up to here, our observations resemble those made in conventional, binary glasses like $Cu_{46}Zr_{54}$ (Ref. 9) and $Mg_{70}Zn_{30}$,[10,11] where, however, the boson peak either showed dispersion in q (Ref. 11) or could not be fully resolved.[9] In these studies, an inelastic peak in the crystalline phase's $S(q,\omega)$ has been ascribed to the onset of dispersion near the lowest zone boundary.[11,12] This interpretation seems to be in conflict with the absence of q dispersion in our measurements. On the other hand, one might argue that boundaries of pseudo-Brillouin zones are considerably smeared out in complicated structures.

Investigations of vibrational spectra in conventional glasses have most often been performed at room temperature. In the context of our search for relaxational modes (Sec. IV) we extended our measurements over a wider temperature range. The thermal stability of our four- and five-component samples allowed vibrational spectroscopy above T_g. Over the full temperature range, scattering intensities grew as expected from Bose-Einstein statistics. In Fig. 4, rescaled spectra $S(q\omega)/n(\omega,T)$ are shown to coincide within the experimental noise level of about 5%. Even more precise evidence for strictly harmonic behavior over a wide temperature range reaching far into the metastable melt was obtained from elastic measurements as described in the next section.

The vibrational spectra of amorphous materials are often decomposed into a Debye component plus an excess contribution that is ascribed to ''glass-typical'' modes, fitted by some model function, and possibly brought into connection with the onset of relaxational modes at higher temperatures.[13] The presence of non-Debye components in the polycrystalline spectra and the strictly harmonic temperature dependence of all excitations recommend more caution: the vibrational spectra may eventually turn out to be less universal and less strongly correlated with the glass transition dynamics than used to be thought.[14] Our observations rather support a picture in which the boson peak is ascribed to localized vibrations that do not show more anharmonicity than any other phonon mode.

IV. SEARCH FOR RELAXATIONAL MOTION

With high-energy resolution measurements we have searched for the onset of relaxational motion. Structural (α) relaxation should become observable as quasielastic broadening on IN10. In previous studies on organic liquids, the linewidth of structural relaxation was found to increase strongly with q;[15] therefore the new configuration of IN10 with a maximum $q=3.7$ Å^{-1} was particularly valuable. A broadening of 1/10 of the resolution width would easily have been detected in $S(q\omega)$. Nevertheless, up to 653 K in ZrTiCuNiBe no quasielastic broadening was observed [Fig. 5(a)].

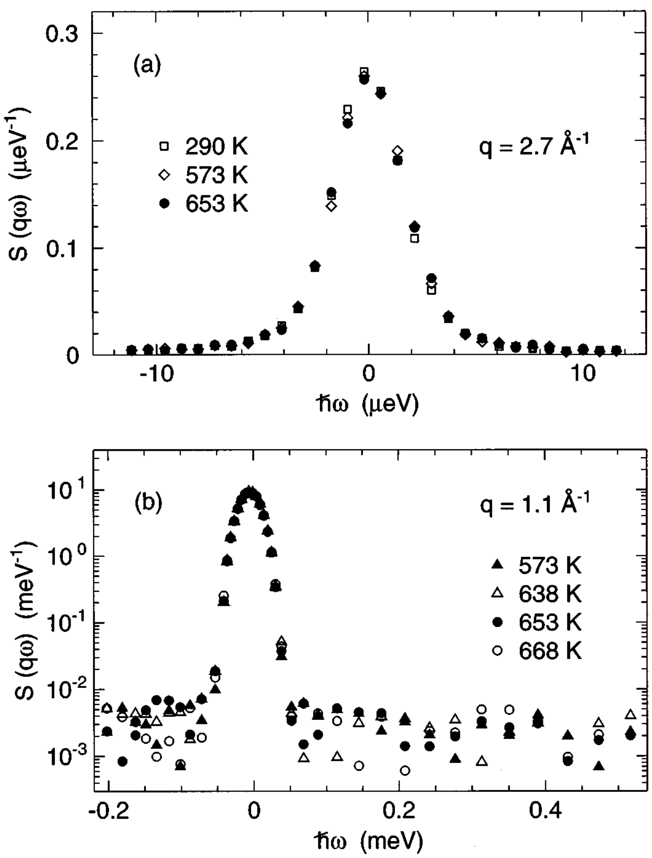

FIG. 5. Search for relaxational broadening in $S(q\omega)$ of ZrTiCuNiBe. (a) High-resolution spectra at IN10, rescaled to equal areas under the peak. At 653 K we could measure 7 h before the sample showed first signs of crystallization. No quasielastic broadening was observed. (b) Time-of-flight measurements at Mibémol. Within the noise level of 3×10^{-4} no fast relaxation is observed. At 668 K, we could measure 2.5 h before crystallization set in. Similar results were obtained for ZrAlNiCu up to $T=657$ K.

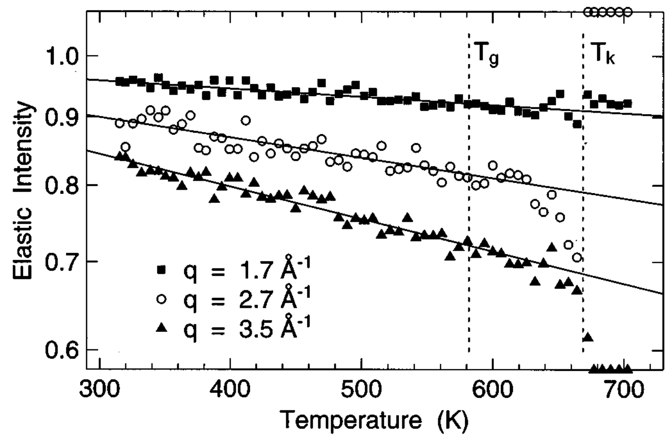

FIG. 6. Elastic scattering intensity $I(q,T)$ of ZrTiCuNiBe measured on IN10 with a constant heating rate of 0.2 K/min and normalized to $I(q,T=0)=1$. Solid lines show the regular temperature dependence of a harmonic Debye-Waller factor; dashed vertical lines indicate the approximative temperatures of glass transition and crystallization. While the vibrational behavior does not change at T_g, we possibly observed the onset of relaxational motion at the structure factor maximum $q=2.7$ Å^{-1} in a 20 K interval before the sample crystallized at $T_k=670$ K.

This negative result is fully consistent with recent measurements of viscosity[16] and self-diffusion[17] that revealed a rather moderate temperature dependence as compared to fragile systems.[4] A crude estimate indicates that structural relaxation will fall into the window of neutron spectrometers only some 100 K above the highest temperature we could attain.

More promising is the search for a dynamic precursor of the glass transition, the fast β relaxation, a localized rattling motion predicted by mode-coupling theory[18] and found in neutron and light scattering spectra of molecular liquids on a psec scale. Recent molecular-dynamics simulations of a $Ni_{50}Zr_{50}$ melt strongly suggest that β relaxation as a precursor of structural relaxation occurs also in metallic alloys.[19] By neutron scattering the onset of anharmonic localized motion can be recognized even without measuring full spectra from a nonlinear decrease in elastic intensity. We have therefore performed two experiments: high-resolution spectral measurements on Mibémol, and elastic scans on IN10.

On the Mibémol spectrometer, an exceptionally good signal-to-noise ratio, better than 1000:1, could be achieved. Nevertheless, up to the highest temperatures [668(657) K for ZrTiCuNiBe (ZrAlNiCu)] elastic peaks coincide with the instrumental resolution, and there is no additional inelastic intensity [Fig. 5(b)]. The β-relaxation amplitude is expected to increase with q. The search for the onset of β relaxation was therefore continued by measuring the elastic scattering intensity $I(q,T)$ on IN10 with its extended q range. In Fig. 6, a perfectly exponential decay $I\propto\exp-q^2\langle u^2\rangle$ with $\langle u^2\rangle\propto T$ is found. This corroborates a main conclusion drawn from the inelastic spectra discussed before: our *metallic glasses show even stronger harmonic behavior than most crystalline solids*.

At the crystallization temperature T_k the intensities at different detector angles suddenly increase or decrease as the static structure factor becomes sharply peaked. For $q=2.7$ Å^{-1} this change is preceded by an inflection of $I(q,T)$ in the opposite direction, beginning about 20 K below T_k. On the basis of the available data we can neither affirm nor exclude that this is an indication of fast liquid dynamics reaching the experimental window.

V. CONCLUSION

To summarize, the vibrational spectra of two amorphous metals show a pronounced low-frequency maximum that can be assigned to localized, strictly harmonic vibrations. Any physical interpretation of this ''boson peak'' should be able to cope with the fact that part of these modes are present also in the crystalline phase. With high-energy resolution spectroscopy, we have established a lower bound for structural relaxation falling into the dynamic range of neutron scattering that is consistent with macroscopic measurements of transport coefficients. The occurrence of β relaxation can be excluded up to at least $1.14T_g$. This is in contrast to a fragile liquidlike *o*-terphenyl where the anharmonic decrease of $I(qT)$ begins even below T_g,[20] and where at $T_c = 1.18T_g$ the full critical dynamics of mode-coupling theory falls into the window of available neutron spectrometers.[21] It appears that metallic melts are much less fragile than one would expect for a simple mixture of hard spheres; local structure and microscopic dynamics probably cannot be understood without proper consideration of the long-range and relatively strong metallic interaction.[22]

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