

Soft anharmonic vibrational states in metallic glasses

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The temperature dependence of the vibrational spectra of $Zr_{67}Cu_{33}$ and $Zr_{60}Be_{40}$, in freshly prepared and annealed states, has been studied by neutron scattering. Analysis of the experimental data leads to the conclusion that there are specific anharmonic low-energy excitations in the energy interval up to ≈ 5 meV in metallic glasses in a highly nonequilibrium state.

INTRODUCTION

Numerous studies of the dynamic properties of amorphous systems have established that the vibrational spectra of these systems are quite different from those of crystals. Measurements of the specific heat and thermal conductivity at liquid-helium temperature have led to the assertion that there are tunneling states with an energy on the order of 1 K (Refs. 1 and 2). It follows from experiments on neutron scattering and optical scattering, as well as from data on the low-temperature behavior of the specific heat and the thermal conductivity, that the vibrational spectra of amorphous materials have a density of low-energy excitations with energies up to ~ 10 meV which is in excess of that in the vibrational spectra of the crystalline analogs of these materials.^{3–5}

The vibrational spectra of metallic glasses in their as-synthesized state (i.e., in a highly nonequilibrium state) were recently compared^{6,7} with the vibrational spectra of the same materials in an annealed state. It was found that a structural relaxation causes a decrease in the spectral density of low-energy excitations. The restructuring of the vibrational spectrum has been attributed to the existence of regions in these amorphous materials in which there are soft atomic configurations. Specifically, after annealing near the crystallization temperature T_{cr} , a certain fraction of the soft configurations disappear, with the result that the spectrum is deformed. Since the dynamic properties of atoms belonging to soft configurations are sensitive to the temperature, a study of the vibrational spectra over a broad temperature range below T_{cr} should shed further light on the nature of the low-energy excitations.

We have accordingly studied the temperature dependence of the vibrational spectra of as-synthesized and annealed samples of $Zr_{67}Cu_{33}$ and $Zr_{60}Be_{40}$.

EXPERIMENTAL PROCEDURE

Samples of the metallic glasses $Zr_{67}Cu_{33}$ and $Zr_{60}Be_{40}$ were prepared by rapid quenching from the melt on a rotating copper disk. Double differential neutron-scattering cross sections were recorded on a time-of-flight spectrometer with a source of cold neutrons.⁸ These cross sections were recorded at temperatures of 135, 300, and 450 K for as-synthesized and heat-treated samples. The heat treatment was carried out directly in the spectrometer. This procedure made it possible to avoid systematic error.

Information on the static structure factor could be obtained on this interferometer in a narrow interval of momentum transfer (from ≈ 0.8 to $\approx 2.1 \text{ \AA}^{-1}$). It was found that after the first heat-treatment cycle ($T = 450 \text{ K}$, $t = 2 \text{ h}$) the

intensity of the elastically scattered neutrons falls off by $\approx 8\%$; it falls off by another $\approx 1.5\%$ after a second heat-treatment cycle. The structure of the glass thus essentially stabilizes after two cycles.

The data on the inelastic neutron scattering were analyzed with the help of a quasiharmonic model of an interatomic dynamic interaction for these systems. It was also assumed that the double differential scattering cross section can be written in the incoherent approximation,⁹ i.e.,

$$\frac{d^2\sigma}{dE d\Omega} = \frac{\mathbf{k}_1}{8\pi\mathbf{k}_0} \frac{\kappa^2}{E} \frac{1}{\exp(E/kT) - 1} \times \sum_i c_i \sigma_i \exp(-2W_i) \langle u_i(t) u_i(0) \rangle_E, \quad (1)$$

where \mathbf{k}_0 and \mathbf{k}_1 are the momenta of the incident neutron and of the scattered neutron, $\kappa = \mathbf{k}_1 - \mathbf{k}_0$, c_i and σ_i are the concentration and scattering cross section of the nuclei of the constituent elements, and the parameter $-2W_i$ is the Debye-Waller factor. The quantity $\langle u_i(t) u_i(0) \rangle_E$ is a temporal Fourier component of the binary correlation function found in terms of the operators representing dynamic atomic displacements [to within an inverse mass, this correlation function is the same as the partial vibrational spectrum of atom i : $\langle u_i(t) u_i(0) \rangle_E = g_i(E)/M_i$].

Using expression (1), we can extract from the experimental data a generalized vibrational spectrum $G(E)$ for the test sample. This spectrum is a sum, with corresponding weight factors, of the partial vibrational spectra of the elements making up the sample. For the $Zr_{67}Cu_{33}$ system, the generalized spectrum $G(E)$ is approximately the density of vibrational states, $g(E)$. For the $Zr_{60}Be_{40}$ system, in contrast, the generalized spectrum is approximately the partial density of vibrational states of the Be atoms.

DISCUSSION OF RESULTS

A comparison of the generalized vibrational spectra $G(E)$ found at 300 K for the as-synthesized and annealed samples (Figs. 1 and 2) shows that the density of low-energy excitations (to ≈ 5 meV) decreases by some 20–30% after heat treatment, although it remains higher than the density of vibrational excitations of a crystalline sample. We should stress that for both of the systems studied here the integrated density of states $\int_0^{E_{\max}} G(E) dE$ for the as-synthesized sample is about 2% higher than for the annealed sample. For the $Zr_{67}Cu_{33}$ system, the changes in the main part of the spectrum are insignificant. There is a slight softening at the spectral boundary. Beyond the boundary of one-phonon scatter-

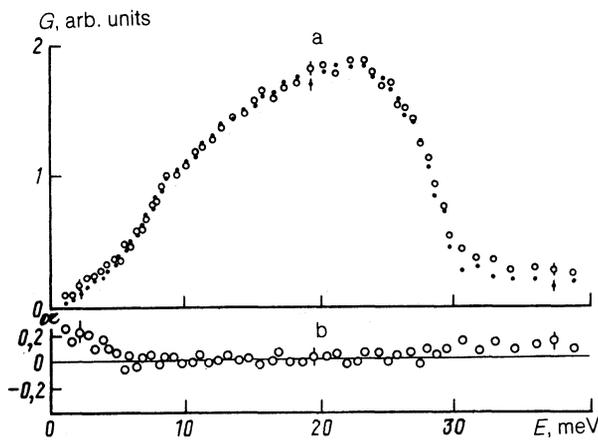


FIG. 1. a: Generalized density of vibrational states $G(E)$ of the metallic glass $Zr_{67}Cu_{33}$. \circ — G_{as} (as synthesized, i.e., before relaxation); \bullet — G_{rel} (after relaxation). b: Relative change $\alpha(E) = [G_{as}(E) - G_{rel}(E)]/G_{as}(E)$ as a result of the relaxation.

ing we observe a decrease in the intensity of the anharmonic tail.¹⁰ The experimental results on the vibrational spectrum of the $Zr_{60}Be_{40}$ system show that the high-frequency part of the spectrum $G(E)$ shifts slightly in the direction of higher frequencies.

In the quasiharmonic approximation the spectrum $G(E)$ should be independent of the sample temperature. A comparison of $G(E)$ for these two amorphous systems at sample temperatures of 135 and 300 K, before and after relaxation, shows that the low-energy part of the spectrum is quite sensitive to the temperature in the as-synthesized systems. After relaxation, this dependence weakens noticeably. Figure 3 shows corresponding data on the $Zr_{67}Cu_{33}$ system.

From data on elastic neutron scattering at various temperatures we determined the intensities $I_0(T)$ (which are listed in Table I). It follows from these results that the temperature dependence $I_0(T)$ is stronger in the as-synthesized samples.

The set of experimental results can be explained on the basis of theoretical models which assume the existence of

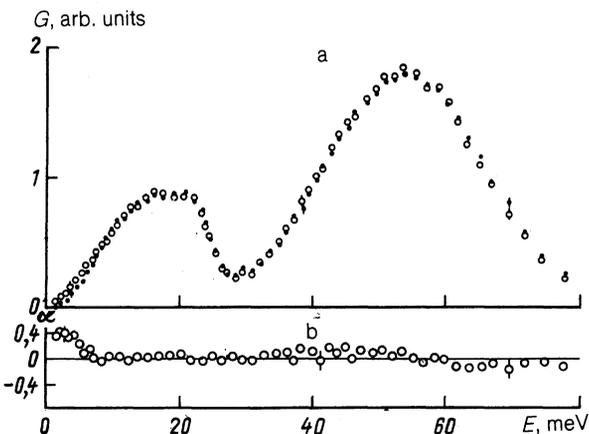


FIG. 2. a: Generalized density of vibrational states $G(E)$ of the metallic glass $Zr_{60}Be_{40}$. \circ , \bullet —Respectively before and after relaxation. b: Relative change $\alpha(E)$ as a result of the relaxation.

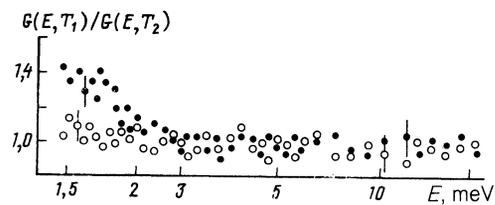


FIG. 3. Temperature dependence of the generalized density of vibrational states of the metallic glass $Zr_{67}Cu_{33}$ (\bullet) before and (\circ) after relaxation ($T_1 = 300$ K, $T_2 = 135$ K).

soft local atomic configurations between hard dynamic clusters in the glasses. If some atom belongs to an unstable soft configuration, one can assume that it moves in an anharmonic potential (Ref. 11, for example)

$$u = \frac{m\omega_0}{2}x^2 + \frac{m\alpha}{3}x^3,$$

where α is the third-order anharmonic parameter in the expansion of the potential in small displacements x . In the simplest approximation, the correction to the fundamental frequency ω_0 is then

$$\Delta\omega = -\frac{5\alpha^2}{12\omega_0^3}\langle x^2 \rangle,$$

where $\langle x^2 \rangle$ is the square of the vibration amplitude, with the standard temperature dependence. It follows from this expression for $\Delta\omega$ that the density of low-frequency states increases with increasing temperature. Furthermore, since the square of the displacements, $\langle x^2 \rangle$, is expressed in terms of the frequency $\bar{\omega} = \omega_0 + \Delta\omega$, its temperature dependence is nonlinear.

As we have already mentioned, the experimental data show that the as-synthesized samples have a more than 2% excess of vibrational modes corresponding to the low-frequency interval, $\omega \leq 3$ meV. Let us see how they influence the Debye–Waller factor:

$$W \propto u_h^2 + c_a u_a^2,$$

where u_h^2 and u_a^2 are the mean square displacements of the atoms moving in respectively harmonic and anharmonic potentials. Here $c_a \sim 10^{-2}$, and the characteristic frequencies ω_h and ω_a differ by more than an order of magnitude. In order to explain the differences which we observe in the values of W for the as-synthesized and annealed samples (Table I), we should assume that the vibrational amplitudes of the atoms belonging to the soft configurations can be an order of magnitude or more greater than the amplitudes of the displacements in harmonic modes. In other words, the corresponding atomic potentials are highly anharmonic.

A systematic analysis can be carried out in a self-consistent theory. However, the qualitative conclusions reached on the basis of this simplified model should generally remain in force.

We wish to stress that a study of the dynamic properties of a sample in its as-synthesized state requires satisfaction of a condition relating the sample temperature (T_0) to the temperature of the transition to a crystalline state (T_{cr}): $T_0 \leq (2/3)T_{cr}$. If this condition is not satisfied, relaxation processes become intense. Furthermore, if the scat-

TABLE I.

System	State	$I_0(T)$, arb. units		
		135 K	300 K	450 K
$Zr_{67}Cu_{33}$	As synthesized	1,00	0,95	0,89
	Relaxed	1,00	0,96	0,94
$Zr_{60}Be_{40}$	As synthesized	1,00	0,94	0,88
	Relaxed	1,00	0,96	0,94

tered-neutron spectrum has a significant component from the anharmonicity, it becomes difficult to determine how the relaxation affects the upper boundary of the spectrum. We know that an anharmonic contribution can be essentially ignored if the sample temperature is below the Debye temperature T_D : $T_0 \leq (1/2) T_D$. In other words, under the inequality $T_D > T_{cr}$, the anharmonic contribution is seen only weakly.

For the $Zr_{60}Be_{40}$ system the condition $T_D > T_{cr}$ holds. Consequently, the increase in the density of vibrational states observed in the high-frequency part of the spectrum for this system is not a consequence of anharmonic processes. It can be explained in terms of a restructuring during the heat treatment, which results in an increase in the density of the sample (because of a liberation of excess volume). For the $Zr_{67}Cu_{33}$ system, in contrast, the opposite condition holds: $T_D < T_{cr}$. For this system, the anharmonicity is thus important at both low and high frequencies. The softening of the spectral boundary in the $Zr_{67}Cu_{33}$ system can evidently be attributed to a decrease in the contribution of the anharmonic tail.

We can draw the following conclusions from this study of the dynamic properties of the two metallic glasses $Zr_{67}Cu_{33}$ and $Zr_{60}Be_{40}$.

1. Vibrational modes of an anharmonic type exist in metallic glasses (particularly in a state far from equilibrium) in the energy interval to ≈ 5 meV. These modes arise from the presence of soft local atomic configurations in the disordered systems; the structure of these configurations changes with the temperature.

2. The large amplitudes of the atomic displacements in the soft modes, even if these modes are present in only a

relatively low concentration, make a significant contribution to the Debye–Waller factor.

3. The decrease in the number of soft atomic configurations due to the annealing results in a substantial decrease in the intensity of the anharmonic tail in the $Zr_{67}Cu_{33}$.

4. For the $Zr_{60}Be_{40}$ system, for which the anharmonic tail is seen only slightly in the scattering cross section, we observe an effect of relaxation processes on the partial vibrational spectrum of the beryllium atoms.

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