Influence of relaxation on the vibrational spectrum of metallic glass $Zr_{67}Cu_{33}$

G. F. Syrykh

I. V. Kurchatov Institute of Atomic Energy, Moscow

(Submitted 12 May 1989)
Zh. Eksp. Teor. Fiz. **96**, 1454–1458 (October 1989)

The method of scattering of cold neutrons was used in an investigation of the metallic glass $Zr_{67}Cu_{33}$ before and after relaxation. Experimental evidence indicated an excess density of low-energy vibrational excitations in the freshly prepared sample, compared with that in a sample subjected to a heat treatment.

INTRODUCTION

Freshly prepared metallic glasses formed by rapid quenching from the melt are in a state far from equilibrium. The structure of a glass eventually relaxes to a more stable state. This relaxation is accompanied by changes in many physical properties including mechanical, magnetic, thermodynamic, kinetic, etc.[1] Relaxation processes may be accelerated by brief annealing at temperatures below the crystallization point T_x of glass. This makes it possible to study properties of glasses of practical importance (particularly their stability) as well as fundamental properties of disordered systems.

The low-energy range of the vibrational spectra of disordered systems is of special interest. This is because such systems exhibit not only the usual vibrational excitations, but also specific low-energy excitations which are manifested, for example, in the temperature dependence of the specific heat and thermal conductivity.[2,3] Physical models intended to explain the low-energy dynamics of amorphous systems have been proposed in several theoretical papers.[4,5] They are based in the concept of soft anharmonic potentials in disordered systems. This approach leads to a prediction tunnel modes and specific anharmonic low-frequency modes with a spectrum extending right down to ~ 50 K. The structural basis of the soft potential concept is a model of noncoincident sites in clusters within an amorphous body.[6]

Annealing of freshly prepared metallic glasses usually increases the density because of the release of trapped free volume. It is usual to assume that this alters the number of local regions where soft anharmonic potentials exist. This is supported indirectly by experiments on the low-temperature specific heat and thermal conductivity.[7,8]

An attempt to investigate directly the influence of relaxation on the vibrational spectrum of a metallic glass was reported in Ref. 9, where a study was described of a $Mg_{70}Zn_{30}$ system by the method of inelastic scattering of cold neutrons. This method required the temperature of a sample to be maintained near 300 K. However, the crystallization temperature of metallic glass $Mg_{70}Zn_{30}$ was known to be fairly low ($T_x = 353$ K). Therefore, as the heat treatment was carried out at temperatures only 15–20 K below T_x, the observed changes in the densities of the vibrational states could be due to the appearance of nuclei of the crystalline phase.

We used the method of cold neutron scattering to investigate the influence of relaxation of the vibrational spectrum of metallic glass $Zr_{67}Cu_{33}$ with a much higher crystalline temperature $T_x \sim 630$ K.

EXPERIMENTS AND DISCUSSION OF RESULTS

A sample of $Zr_{67}Cu_{33}$ was prepared by fast quenching of a melt on a rotating copper drum (drum diameter 200 mm, revolving at 4000 rpm) in an atmosphere of purified Ar. Heating was provided by an hf oscillator and a boron nitride crucible was used. The starting materials were Cu and Zr of purity 99.98 and 99.90% purity, respectively. Heat treatment of a freshly prepared sample took place in an evacuated chamber at $T = 450$ K and lasted 1 h (only two cycles were carried out). X-ray and neutron diffraction data indicated that the sample was in the amorphous state before and after the heat treatment.

The double differential neutron scattering cross section of $Zr_{67}Cu_{33}$ (before and after the heat treatment) was determined using a time-of-flight spectrometer with a cold neutron source.[10] The energy of the incident neutrons was $E_0 \approx 4.8$ meV and the scatter of this energy was $\Delta E_0/E_0 \approx 10\%$. The heat treatment was carried out directly during exposure to the neutron beam so as to avoid disturbing the experimental conditions. The double differential neutron scattering cross section of a polyatomic solid, considered in the incoherent approximation, was described by[11]

$$\frac{d^2\sigma}{d\Omega\, dE} = \frac{k}{8\pi k_0}\frac{\varkappa^2}{E}\frac{1}{\exp(E/kT)-1}\sum_i \frac{c_i\sigma_i}{m_i}\exp(-2W_i)\,g_i(E) = \frac{k\varkappa^2}{8\pi k_0 E}\frac{1}{\exp(E/kT)-1}G(E), \qquad (1)$$

where c_i, σ_i, and m_i are concentrations, scattering cross sections, and the masses of the nuclei of the elements present in the sample; $g_i(E) = g(E)|\mathbf{e}_i(E)|^2$ are the partial densities of the vibrational states. The rest of the notation is standard. An analysis of the experimental results could be used to reconstruct the generalized density of the vibrational states $G(E)$, which represents a sum of the partial vibrational densities with the weighting factors

$$\frac{c_i\sigma_i}{m_i}\Big/\sum_i \frac{c_i\sigma_i}{m_i}.$$

In the investigated case we have

$$G(E) = 0.52 g_{Zr}(E) + 0.48 g_{Cu}(E).$$

The density of the vibrational states in the $Zr_{67}Cu_{33}$ system is $g(E) = 0.67 g_{Zr}(E) + 0.33 g_{Cu}(E)$. Thus, it follows that the experimental function $G(E)$ is close to $g(E)$ and represents satisfactorily the changes in the latter.

The spectrometer was used to detect scattered neutrons at angles of 15, 30, 45, 60, 75, and 90° relative to the direction

 0038-5646/89/100824-03$04.00

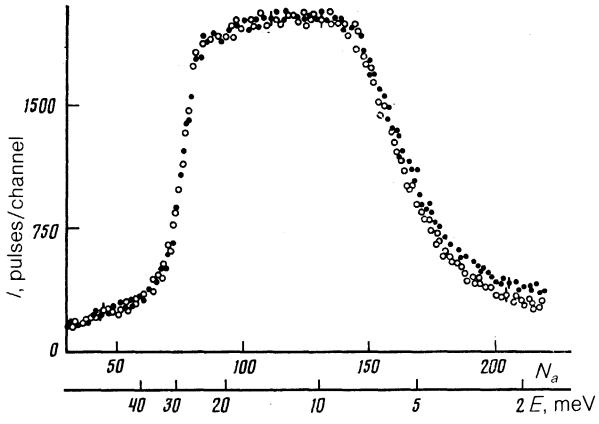

FIG. 1. Time-of-flight neutron scattering spectra of the metallic glass $Zr_{67}Cu_{33}$: ●) freshly prepared sample; ○) sample subjected to a heat treatment at $T = 450$ K for $t = 2$ h (N_a is the number of the channel in an analyzer).

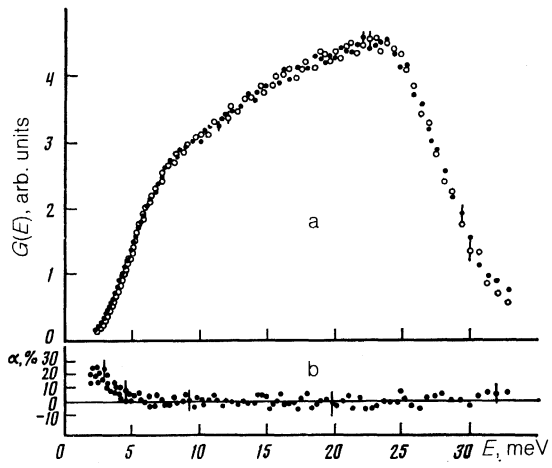

FIG. 2. a) Generalized densities of vibrational states of the metallic glass $Zr_{67}Cu_{33}$ before and after relaxation: ●) $G_{fr}(E)$; ○) $G_{rel}(E)$. b) Relative change in the density $\alpha = [G_{fr}(E) - G_{rel}(E)]/G_{fr}(E)$.

of the incident beam. This made it possible to analyze the changes in the static structure factor in a narrow interval of the transferred momenta (0.8–2.1 $Å^{-1}$), i.e., to the left of the first peak located near 2.62 $Å^{-1}$. It was established that after the first heat treatment cycle the intensity of the peak representing the elastically scattered neutrons fell by $\sim 8\%$. The second heat treatment cycle lowered the intensity by a further $\sim 1.5\%$. Consequently, the structure of the glass had become stabilized. We observed this deformation in the structure factor, in agreement with the results published elsewhere.[12]

Information on the inelastic neutron scattering is presented in Fig. 1 in the form of normalized (relative to the incident flux) time-of-flight spectra for the scattering angle 75° before and after the heat treatment. Clearly, at low energies ($E < 5$ meV) the probability of neutron scattering was reduced by the heat treatment. Elsewhere in the spectrum the changes were slight. The second treatment produced practically no changes in the scattered neutron spectrum. On the other hand, it was reported in Ref. 9 that changes in the density of the vibrational states in the $Mg_{70}Zn_{30}$ system increased when the annealing lasted longer.

Figure 2 shows the generalized densities of the vibrational states of metallic glass $Zr_{67}Cu_{33}$ before and after relaxation, which were obtained by simultaneous analysis of the time-of-flight spectra obtained for all the scattering angles of the freshly prepared $G_{fr}(E)$ and heat-treated, i.e., relaxed $G_{rel}(E)$, samples, and also the relative change $[G_{fr}(E) - G_{rel}(E)]/G_{fr}(E)$. The energy spread of the incident neutron line limited the vibrational spectrum to $E_{min} \approx 2$ meV on the low-energy side. Note that

$$\int_{E_{min}}^{E_{max}} [G_{fr}(E) - G_{rel}(E)]dE \int_{E_{min}}^{E_{max}} G_{rel}(E)dxE \approx 0.02 .$$

The excess density of the vibrational states exhibited by the freshly prepared sample was concentrated in the low-energy range $E < 5$ meV. At energies $E > 5$ meV the density of the vibrational states changed only slightly and only the edge of the spectrum shifted toward lower energies.

In the case of $Mg_{70}Zn_{30}$ there were no changes in the density of the vibrational states in the low-energy range and the changes elsewhere in the spectrum were similar to the changes typical of a transition amorphous to the crystalline state.

The excess density of the vibrational states in our freshly prepared metallic glass $Zr_{67}Cu_{33}$ can be explained on the basis of the theoretical models mentioned above.[4,5] The amplitude of the atomic vibrations in a soft anharmonic mode may be an order of magnitude higher than the amplitude of vibrations of the usual phonon modes. The inelastic neutron scattering cross section is proportional to the square of the ratio of the displacement of an atom to the interatomic distance so that the anharmonic modes can appear in the elastic neutron scattering spectra with a large weighting factor. After relaxation the fraction of the atoms participating in the anharmonic vibrations decreases; this is manifested by a reduction in the intensity of the inelastic neutron scattering.

The soft anharmonic modes should contribute to the mean square values of the displacements of the atoms. We therefore investigated the temperature dependence of the intensity of the elastic neutron scattering peak before and after relaxation (heat treatment). Measurements were carried out at temperatures of 100 and 300 K. The Debye–Waller factor of the freshly prepared sample varied in this range of temperatures by an amount which was $\sim 30\%$ greater than in the case of the sample subjected to the heat treatment. The result clearly indicated that in the case of the freshly prepared sample the classical temperature dependence of the mean-square value of the displacements of the atoms was reached earlier because of the low value of the Debye temperature of soft anharmonic modes.

The results obtained led us to the following conclusion. The structural relaxation processes influences the vibrational spectrum of metallic glass $Zr_{67}Cu_{33}$ mainly in the low-energy range. Relaxation destroys the excess density of the low-energy excitations typical of the freshly prepared state. The changes in the density of the vibrational states become stabilized after a heat treatment of a certain duration i.e., the metallic glass then reaches a state of "quasiequilibrium." The effects observed provide qualitative support for the hypothesis of the existence of soft anharmonic potentials in a disordered system which is far from equilibrium. Further investigations are necessary in order to determine how general is the validity of the results obtained and to make a

quantitative comparison with the theoretical models.

The author is grateful to A. P. Zhernov for valuable discussions, and to N. T. Bezobrazov, Yu. Yu. Bulanovskiĭ, V. Ya. Vasyuta, V. G. Omel'yanenko, and V. G. Fedorov for their help in the experiments.

[1]S. Steeb and H. Warlimont (eds.), *Rapidly Quenched Metals* (Proc. Fifth Intern. Conf., Würzburg, West Germany, 1984) Vol. 1, North-Holland, Amsterdam (1985).
[2]H. Von Loehneysen, M. Platte, W. Sander, *et al.*, J. Phys. (Paris) **41**, Colloq. 8, C8-745 (1980).
[3]H. von Löhneysen, D. M. Herlach, E. F. Wassermann, and K. Samwer, Solid State Commun. **39**, 591 (1981).
[4]N. M. Plakida, Proc. Fifth Intern. School on Neutron Physics, Alushta, 1986 [in Russian], Joint Institute for Nuclear Research, Dubna (1987), p. 259.
[5]V. G. Karpov, M. I. Klinger, and F. N. Ignat'ev, Zh. Eksp. Teor. Fiz. **84**, 760 (1983) [Sov. Phys. JETP **57**, 439 (1983)].
[6]A. S. Bakaĭ, *Polycluster Amorphous Materials* [in Russian], Énergoatomizdat, Moscow (1987), p. 195.
[7]P. Esquinazi, M. E. de la Cruz, A. Ridner, and F. de la Cruz, Solid State Commun. **44**, 941 (1982).
[8]A. Ravex, J. C. Lasjaunias, and O. Béthoux, Solid State Commun. **40**, 853 (1981).
[9]J.-B. Suck, H. Rudin, and H.-J. Guntherodt, J. Non-Cryst. Solids **61/62**, 295 (1984).
[10]M. G. Zemlyanov, A. E. Golovin, S. P. Mironov, *et al.*, Prib. Tekh. Eksp. No. 5, 34 (1973).
[11]N. A. Chernoplekov, M. G. Zemlyanov, E. G. Brovman, and A. G. Chicherin, Fiz. Tverd. Tela (Leningrad) **5**, 112 (1963) [Sov. Phys. Solid State **5**, 78 (1963)].
[12]P. Garoche, Y. Calvayrac, W. Cheng, and J. J. Veyssie, J. Phys. F **12**, 2783 (1982).

Translated by A. Tybulewicz