Influence of anharmonic modes on the electron spectrum and superconducting properties of $Zr_{70}Be_{30}$ metallic glass

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The low-temperature heat capacity of the metallic superconducting $Zr_{70}Be_{30}$ glass was investigated in two states, freshly prepared and annealed. Additional low-frequency vibrational modes that vanish after annealing were observed. It was established that their vanishing is accompanied by an increase of the band density of the electronic states. The parameters of the spectrum of the electron attraction interaction were also determined and their connection with the observed vibrational modes was analyzed.

INTRODUCTION

Experimental and theoretical investigations of vibrational spectra of amorphous material are being pursued quite intensively. The question of the nature of the excess density of low-frequency vibrational states relative to the Debye spectra of the crystalline analog is actively discussed. It is customary here to distinguish between two excitation regions: the first with very low energies, <0.1 meV, and the second in the wide interval 0.1–10 meV.[1–10]

At the same time, in a number of studies in which the neutron-scattering method was used, the structural and dynamic properties of metallic glasses were compared in two states—freshly prepared and relaxed.[11,12] It was established that the radial distributions of the atoms did not differ greatly. In a quenched specimen, however, an excess density of vibrational states is produced in the energy interval below 5 meV. The intensity of the long-wave "tail" of the spectrum is in fact increased by approximately 40%. Overall, however, the excess density is only about 1–2% of the total density. Note also that the corresponding vibrational modes are spatially localized. It was subsequently indicated[13,14] with the Zr–Cu and Zr–Be systems as examples that the modes present in the quenched specimen are also strongly anharmonic. It was proposed in the same references that these specific modes can play a noticeable role in the formation of the electronic and superconducting properties of metallic glasses.

Our purpose was to investigate the influence the anharmonic modes observed in freshly prepared specimens on the parameters of superconducting glasses. Specifically, we measured the low-temperature heat capacities of two states of a specimen. These measurements made it possible to determine the change of the Sommerfeld parameter γ, as well as the temperture T_c of the superconducting transition and the heat-capacity jump. Information was also obtained on the density of the vibrational states in the low-frequency region. The results made it possible to determine the character of the electronic-state density variation on the Fermi level and simultaneously elucidate the behavior of the parameters of the spectrum of the attracting interelectron interaction, i.e., the coupling constant λ and the effective frequency ω_{ph}. The presence of this information made it possible to consider directly the question of the relation between the specific anharmonic vibrational modes and the electronic and superconducting properties of disordered systems with strong disequilibrium.

Note that the influence of composition variation and structural relaxation on the properties of metallic glasses were investigated in Refs. 15 and 16. The attention there was focused on the electron spectrum. No mention is in fact made there of the existence of anharmonic modes and of their possible role. It can thus be assumed that the question of the interrelation between these modes and the properties of non-equilibrium systems has heretofore been neither raised nor investigated.

EXPERIMENT

A specimen of $Zr_{70}Be_{30}$ metallic glass was obtained by fast quenching from the melt on a rotating copper disk. The heat capacity was measured for one and the same sample—first when freshly prepared and next after annealing at $T = 200$ °C for two hours. The heat capacity was measured by an adiabatic method[16] in the temperature interval 1.6–40 K in magnetic fields 0 and 8 T, with an error on the order of 2%.

RESULTS

The measured heat capacities are plotted in Figs. 1, 2, and 3 and listed in Tables I and II. Figure 1 shows the heat capacities of a freshly prepared specimen and of a heat-treated one in the form of plots of C/T vs T^2. In the absence of a magnetic field the temperature dependences of the heat capacities of both specimens revealed a distinct jump corresponding to the superconducting transition. Both the temperature and the width of the heat-capacity jump were larger in the case of the freshly prepared specimen. To eliminate the influence of the finite width of the jump on its amplitude, the size of the jump was determined by extrapolation to an extremely narrow transition. Account was taken of the entropy balance, meaning equality of the corresponding areas under the plots of C/T vs T.

An 8 T magnetic field suppressed the superconductivity, making it possible to measure the heat capacity of the specimens in the normal (non-superconducting) state down to the very lowest temperatures. Below 12 K, the temperature dependence of the heat capacity is well described by the relation

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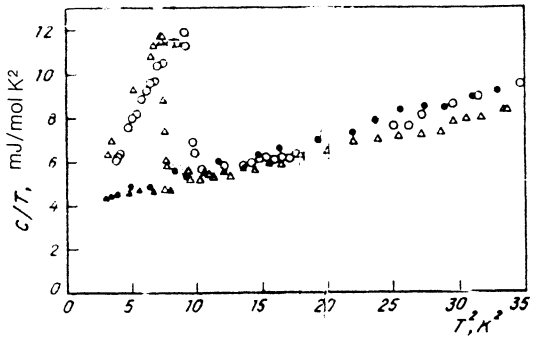

FIG. 1. Temperature dependences of the heat capacity of metallic glass $Zr_{70}Be_{30}$ without a magnetic field (○, △) and in an 8 Tl magnetic field (●, ▲). Freshly prepared (○, ●) and annealed (△, ▲) specimens.

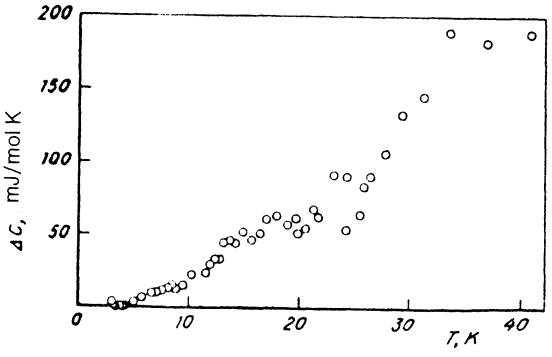

FIG. 3. Difference between the heat capacities of fresh and annealed samples vs temperature.

$$C=\gamma T+\beta T^3+\alpha T^5.$$

The values obtained by least squares for the parameters γ, β, and α are listed in Table II. This table contains also data on the superconducting-transition temperatures T_c widths ΔT_c, and the corresponding heat-capacity jumps $\Delta C/\gamma T_c$, extrapolated to the extremely narrow transitions. The values we obtained for the parameters γ, β, T_c, and $\Delta C/T_c$ are somewhat lower than those in Refs. 18 and 19, possible as a result of differences in the specimen compositions and preparation methods.

DISCUSSION

The heat-capacity data obtained for the normal state make it possible to separate the electron and phonon contributions. It is assumed here, as usual, that the electron contribution in the investigated temperature range is linear in the temperature. Generally speaking, the so-called two-level states can cause also a linear temperature dependence in metallic glasses. The contribution of such states, however, is usually small in the considered temperature interval, and we have neglected it. As to the phonon component C_{ph} of the thermal conductivity, it was determined as the difference between the measured total heat capacity of the specimen and the linear contribution γT.

Figure 2 shows the phonon heat capacities as plots of C_{ph}/T^3 vs T for freshly prepared and annealed specimens. It is seen directly from the figure that the heat capacity of a freshly prepared specimen exceeds that of an annealed one, and in the region below 10 K the relative difference reaches 30% and decreases slowly as the temperature rises. Figure 3 shows the difference ΔC between the total heat capacities of the freshly prepared and heat-treated samples. It is practically equal to the difference between the phonon contributions, since the electron heat capacity changes insignificantly. Below 20 K, the value of ΔC first increases with temperature and then saturates. We propose that this difference between the vibrational heat capacities is due to the presence, in the fresh sample, of specific anharmonic-type modes due to soft atomic configurations that become restructured (by external action) in the course of the heat treatment.

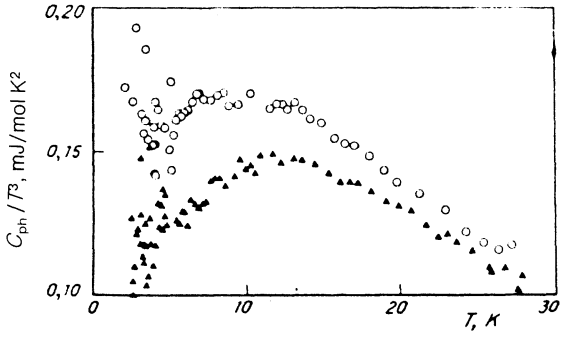

FIG. 2. Temperature dependences of photon heat capacity of metallic $Zr_{70}Be_{30}$ glass expressed in coordinates C_{ph}/T^3. Fresh (○) and annealed (▲) samples.

Analysis of the temperature dependence of the heat-capacity difference ΔC makes it possible to determine the characteristic frequencies ω_s of these modes as well as their fraction x of the total number of vibrational states. The point is that the ratio of the excess heat capacity ΔC to the heat capacity of the heat-treated sample should be a maximum at $T_s = 4.93\omega_s$. Its approximate value is[20]

$$\frac{\Delta C(T_s)}{C_{ph}(T_s)} = 0.91\left(\frac{\omega_D}{\omega_s}\right)^3 x. \qquad (1)$$

Taking the foregoing into account and using the experimental results, we obtained $\omega_s = 6$ meV and a density $x = 0.8\%$ for the localized oscillations. These conclusions agree with the previously observed features of the density of the vibrational excitations. Namely, additional modes were obtained[14] for fresh $Zr_{60}Be_{40}$ metallic glass by the method of inelastic neutron scattering at energies up to 5 meV. The concentration fraction of these modes was 1–2% of the total number of vibrational states, with both low- and high-frequency excitations taken into account.

The onset of anharmonic modes is due apparently to the appearance of some excess volume typical of quenched systems. The condensation of a substance by annealing suppresses the anharmonic effects significantly.

We proceed now to analyze the electronic heat capacity. Note that according to the data of Table II the value of the

TABLE I. Smoothed values of the heat capacity of the metallic glass $Zr_{70}Be_{30}$ in the normal (non-superconducting) state.

T, K	Heat capacity, J/mol·K		T, K	Heat capacity, J/mol·K	
	Quenched	Annealed		Quenched	Annealed
2	0.0091	0.0072	15	0.592	0.550
3	0.0164	0.015	20	1.20	1.13
4	0.0250	0.0238	25	1.97	1.88
5	0.039	0.036	30	2.95	2.78
6	0.058	0.0052	35	4.02	3.84
8	0.118	0.0103	40	5.08	4.91
10	0.209	0.185			

Sommerfeld parameter γ of $Zr_{70}Be_{30}$ decreases after relaxation. Knowing the critical temperature T_c and the parameters γ we can determine the relaxation-induced variation of the electronic-states band density. In fact, in critical temperatures in the superconducting Zr–Be system are quite low, so that this system can be regarded as superconducting with weak or intermediate coupling. The change of T_c of such superconductors is determined primarily by the renormalization of the coupling constant λ. Since T_c drops after annealing, this means in fact that λ decreases, or in other words that $\lambda_{\rm fr} > \lambda_{\rm ann}$. At the same time we have by definition

$$\gamma = N_{\rm band}(1+\lambda).$$

Taking into account the experimentally established inequalities

$$\gamma_{\rm fr} < \gamma_{\rm ann}, \lambda_{\rm fr} < \lambda_{\rm ann},$$

we conclude that annealing increases the density of the electronic states in the conduction band.

It is customarily assumed that electrons are autolocalized in regions with dynamically soft configurations. External effects, particularly annealing, cause these configurations to vanish and return the electrons simultaneously to the conduction band. A similar opinion is held usually with respect to semiconductors,[21] but it turns out to have a more general character.

Next, using the experimental data on the heat-capacity jump and using the critical temperature one can calculate, within the framework of the phonon model, the principal parameter of the attractive-interaction spectrum, i.e., the coupling constant λ and the characteristic frequency $\omega_{\rm ph}$, averaged over the spectrum, of the electron-phonon interaction. The main formulas for the heat-capacity jump and for T_c are

$$\Delta C/\gamma T_c = 1.43\left\{1 + a\left(\frac{T_c}{\omega_{ph}}\right)^2 \ln\left(\frac{\omega_{ph}}{bT_c}\right)\right\}, \quad (2)$$

$$T_c = 1.13\omega_{ph}\exp\left(-\frac{1}{g-\mu^*}\right), \quad g = \frac{\lambda}{1+\lambda}. \quad (3)$$

The values of a and b are estimated respectively at 18 and 1 (Ref. 22) and 27 and 2 (Ref. 23). μ^* denotes the Coulomb pseudopotential ($\mu^* = 0.1$).

Using the data on ΔC, γ, and T_c and relation (2) we found, first, that the characteristic frequency $\omega_{\rm ph}$ is about 40 K (*sic*). After relaxation this frequency increases about 5%. This result can be attributed to the vanishing of low-frequency anharmonic modes. After determining the characteristic phonon frequencies $\omega_{\rm ph}$ and knowing the corresponding values of T_c we easily determine from Eq. (3) the coupling parameter λ. For freshly proposed and annealed samples we obtain

$$\lambda_{\rm fr} = 0.88, \quad \lambda_{\rm ann} = 0.80.$$

TABLE II. Characteristics of superconducting transitions and of the phonon and electron spectra of the metallic glass $Zr_{70}Be_{30}$.

Characteristic	Quenched	Annealed	[19]	[18]
T_c, K	3.10	2.75	3.05	3.50
ΔT_c, K	0.15	0.10	–	0.15
$\Delta C/T_c$, mJ/mol²·K²	7.2	7.0	7.2	–
γ, mJ/mol²·K²	3.85	4.00	3.71	4.44
$N_{\rm band}$, mJ/mol²·K²	2.65	2.22	–	–
β, mJ/mol·K⁴	0.161	0.121	0.169	0.152
α, mJ/mol·K⁶	$9.4\cdot10^5$	$28\cdot10^5$	–	–
θ, K	229	252	228	234
$\Delta C/\gamma T_c$	1.87	1.75	–	1.61
ω_{ph}, K	42	44	–	–
λ	0.68	0.80	–	–
g	0.47	0.44	–	–

It is thus established that the parameter λ decreases by 10% after annealing. In has been furthermore confirmed that the system $Zr_{70}Be_{30}$ is really a superconductor with intermediate coupling.

Let us consider the main cause of the change of the coupling constant λ by relaxation. According to McMillan

$$\lambda = \frac{N(\varepsilon_F)J^2}{M\omega_{ph}^2}, \tag{4}$$

where J^2 is the squared electron-ion interaction matrix element. The value of λ should remain practically constant following the obtained changes of the electron density $N(\varepsilon_F)$ and of the effective frequency ω_{ph}. Actually, however, the coupling parameter λ decreases substantially. To resolve the ensuing contradiction it is necessary to propose a signficant change of the electron-ion factor. Such a change may be due to the presence of soft atom configurations and their restructuring.

Namely, if direct account is taken of the role of soft atomic configurations and of the modes associated with them,[24,25] the expression for λ is a sum of two contributions:

$$\lambda \approx N_{\text{band}} \left\{ (1-x) J_h^2 \frac{\langle u_h^2 \rangle}{\omega_h} + x J_s^2 \frac{\langle u_s^2 \rangle}{\omega_s} \right\}. \tag{5}$$

The subscripts h and s label here quantities pertaining to the harmonic and anharmonic modes and $\langle u^2 \rangle$ denotes the mean squared atomic displacements.

Although the role of soft modes is relatively small, the large amplitude of the vibrations of the anharmonic type may make the contribution to λ large if the matrix elements J_h and J_s are of the same order. The amplitudes of atoms belonging to soft configurations exceed by an order of magnitude more than the amplitudes of the displacements in the harmonic modes. Annealing relaxes the soft configurations, whose number decreases noticeably. The effective coupling parameter can therefore be decreased by 10–15%, and it is this which explains the observed change of λ.

We have already noted that the transition temperature T_c is defined primarily in terms of the parameter λ. Taking into account the foregoing discussion of λ we can state that electron interaction with soft anharmonic configurations influences directly the value of T_c. It is important here that it increases.

The results of the present paper lead to the following conclusions.

1. It has been confirmed that soft anharmonic configuration exist, having characteristic frequencies up to 5 meV. They relax after heat treatment.

2. It has been established that when the soft atomic configurations vanish the band density of the electronic states increases.

3. The character of the renormalization via interaction of electrons with anharmonic configurations of the main parameters of the attractive interaction spectrum has been elucidated. Namely, the coupling parameter λ increases and the effective frequency ω_{ph} of the spectrum decreases. The scale of variation of the parameter λ is more pronounced here than the change of the frequency of the spectrum.

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