Changes in the superconducting properties of the $Zr_{75}Rh_{25}$ system on becoming amorphous

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The heat capacity (from 2 to 700 K), magnetic susceptibility (from 2 to 300 K) and electrical resistivity (from T_c to 300 K) have been measured for the superconducting system $Zr_{75}Rh_{25}$ in the amorphous and metastable crystalline states. A simultaneous analysis of the results obtained enabled the temperature dependence of the phonon heat capacity and its anharmonic component to be determined. An anomalous increase in phonon heat capacity and an increase in the electron density of states at the Fermi surface was found for the amorphous phase of $Zr_{75}Rh_{25}$ compared with the crystalline phase. The contributions to the change in T_c connected with rearrangement of the phonon and electron spectra and the electron-phonon interaction, when the $Zr_{75}Rh_{25}$ system becomes amorphous, are discussed. The main contribution to the change in T_c comes from the rearrangement of the electron spectrum: the product of the density of states $N(\varepsilon_F)$ and the mean square matrix element of the electron-phonon interaction $\langle J^2\rangle$. The change in the phonon spectrum is small and is not a determining factor in the change of T_c.

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INTRODUCTION

The first studies of amorphous superconductors were carried out over twenty five years ago on thin films of simple metals formed by vapor deposition onto a cold substrate.[1,2] The investigation was later broadened to transition metals[3,4] and quite recently to amorphous metals formed by rapid quenching from the liquid state.[5,6]

In spite of the great scientific and practical interest aroused by amorphous superconducting systems because of their unusual physical properties, and the appreciably increased amount of work on them, many questions about the nature of the change in superconducting properties on becoming amorphous are unsolved so far. The absence of long-range order and the local disorder in amorphous metals has an appreciable influence in the phonon and electron spectra and also on the electron-phonon interaction and, consequently, on their T_c. The quantitative relations between these changes require, in the first instance, an accurate experimental investigation for the case of amorphous alloys which do not, in general, have crystalline analogs.

The greatest progress has been achieved in understanding the reasons for the change of T_c in amorphous films of transition metals evaporated onto a cold substrate.[1,2,7] The main result of the work carried out so far[7] was the discovery of a relative growth in the low-frequency part of the phonon spectrum of an amorphous compared with a crystalline system and a change in T_c on becoming disordered. Comparison of the results of measuring the tunneling characteristics, the low-temperature heat capacity and the Mössbauer effect made it possible to understand the main reasons for the change in the Éliashberg function $\alpha^2(\omega)F(\omega)$, which determines superconductivity: the change in the electron-phonon interaction $\alpha^2(\omega)$ or in the phonon spectrum $F(\omega)$. The results of measuring, for example, the Mössbauer effect on the films and on amorphous films of Sn + (10 to 18%)Cu (Ref. 8) provide evidence for the determining role of the change in the parameter $\alpha^2(\omega)$ on the transition from the crystalline to the amorphous state. However, in so far as the temperature variation of the Debye-Waller factor is stronger in amorphous films, this indicates a change not only in the electron-phonon interaction but also in the phonon spectrum on becoming amorphous. Measurements of heat capacity and tunneling characteristics[9-11] also confirm this conclusion.

Amorphous transition metals are superconductors with weak or intermediate coupling ($\lambda < 0.8$) as distinct from amorphous non-transition metals which are in general superconductors with strong coupling ($\lambda \gtrsim 2$). The reasons for such a difference are not very clear.

The main reason for the change in T_c for transition metals and alloys on becoming amorphous is considered to be the deformation of the electron spectrum, leading to a change in the density of states at the Fermi surface, although the phonon spectrum changes simultaneously, and as the inelastic neutron scattering studies showed,[12] this is quite noticeable. The spectrum is broadened as a whole in the amorphous state with an increase in the phonon density of states in the region of low and high frequencies and a shift of the limiting frequency into the high frequency region. Such a deformation must be reflected in a change of T_c.

The state of the theoretical understanding is considerably worse here than in the case of amorphous non-transition metals for which the free electron approximation is applicable as for liquid non-transition metals.

The model representations developed in Refs. 13 and 14 lead to the conclusion that for the given class of materials (b. c. c. transition metals and alloys), in the McMillan expression for the electron-phonon interaction constant[15]

$$\lambda = N(\varepsilon_F)\langle J^2\rangle / M\langle\omega^2\rangle$$

[M is the mean atomic mass, $\langle\omega^2\rangle$ is determined from

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Eq. (4), see below], and $\langle J^2\rangle/\langle\omega^2\rangle$ is constant, so that the change in λ is determined by a change in $N(\varepsilon_F)$. This is evidently not satisfied for a number of transition metal alloys.[16]

It is apparent that because of the absence of a consistent theory of transition metals in general and of amorphous transition metal alloys in particular, a comparison of normal and superconducting transition metals alloys with their crystalline analogues takes on a special importance. Unfortunately, of all the known amorphous superconducting systems of transition metals (except for pure metals), only $Nb_{60}Ni_{40}$ goes over on crystalline to a stable single-phase system. It is therefore necessary for studying changes in physical properties (including superconducting) on becoming amorphous, to look for single-phase metastable crystalline phases with the same short-range order as in the amorphous phase. Structural studies of amorphous systems indicate the existence of such phases among a number of alloys, a typical representative of which can be considered to be the well studied compound Fe_3B (Ref. 17) with trigonal structure.

In the present work we report the results of measuring the heat capacity, magnetic susceptibility and electrical resistivity of the superconducting system $Zr_{75}Rh_{25}$ in the amorphous and metastable crystalline states. The choice of this system was determined by the existence of a metastable crystalline phase for it. The amorphous system $Zr_{75}Rh_{25}$ with $T_c = 4.23$ K goes over, after annealing, to a metastable crystalline single-phase system of $E9_3$ structure and $T_c = 2.90$ K (Ref. 8). The purpose of this work is to study the effect of becoming amorphous on the electron and phonon spectra and on the electron-phonon interaction, and to establish a correlation between these changes and other physical properties, in the first place with superconductivity.

EXPERIMENT

1. Sample preparation

The $Zr_{75}Rh_{25}$ system was prepared from electrolytically pure zirconium (99.99%) and pure rhodium (99.95%). The specimens were melted in an induction furnace in a suspended state under a small helium pressure, and were quenched from the liquid state through a metering system onto the outer surface of a rotating copper disc. The quenching rate, according to estimates was $\sim 10^6$ K·s^{-1}.

The amorphous specimens prepared in this way are 1.5 to 2 mm wide strips, 0.03 mm thick. The specimens were etched for 1 to 2 min in a mixture of hydrochloric and nitric acids and then dried in a vacuum of 10^{-3} Torr to remove traces of crystalline phase which might arise during the process of becoming amorphous. The electrical resistivity measurements were carried out on the strip specimens. The strips were pressed into 5 mm diameter and 2 mm high pellets for measuring the heat capacity and magnetic susceptibility. The pressed pellets were used as the specimens. Measurements were carried out simultaneously on four pellets of total weight 0.8 g. After the measurements the amoprhous specimens were annealed at a temperature of 530 °C for 10 min to obtain the metastable crystalline state. The transition to the metastable phase was recorded by the appearance of a jump (~10%) in the temperature dependence of the resistivity.

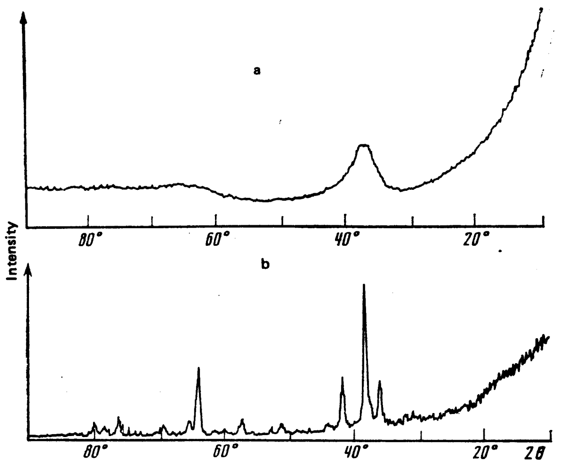

FIG. 1. X-ray diffraction pictures from $Zr_{75}Rh_{25}$ specimens in the amorphous (a) and metastable crystalline (b) states.

After this the whole array of investigations was repeated on the specimens in the metastable crystalline state.

2. Specimen characteristics

The structure of the specimens was studied by x-ray and electron diffraction. Identification of the phases and determination of the lattice parameters was carried out by x-ray diffraction. The x-ray picture of a $Zr_{75}Rh_{25}$ specimen quenched from the liquid state is shown in Fig. 1(a). The overall form of the curve is typical for an amorphous metal and shows the absence of long-range order. The first broad maximum is localized around $2\Theta = 37°$ and the breadth of the maximum at half height, $\Delta 2\Theta = 5°$ (Cu K_α radiation). Using the standard formula for the distance between nearest neighbors

$$d_{\text{eff}} \approx \left(\frac{3}{2}\right)^{1/2}\frac{\lambda}{2\sin\theta},$$

where $\lambda = 1.54$ Å for Cu K_α radiation, the value of the effective distance was found to be 3.03 Å, which is in good agreement with earlier measurements.[18]

Analysis of the x-ray and electron diffraction on specimens after annealing indicate the appearance of the metastable crystalline state with the $E9_3$ structure.[20] The structure is a complicated face-centered cubic lattice of the Fe_3W_3C type with lattice parameter $a_0 = 12.447$ Å. An x-ray diffraction picture for the metastable crystalline phase is shown in Fig. 1(b). An electron diffraction photograph for a $Zr_{74}Rh_{25}$ specimen in the amorphous and metastable crystalline states is shown in Fig. 2.

We should note that when measuring the heat capacity of the metastable crystalline phase, the presence of amorphous phase (~10%) was found, its heat capacity

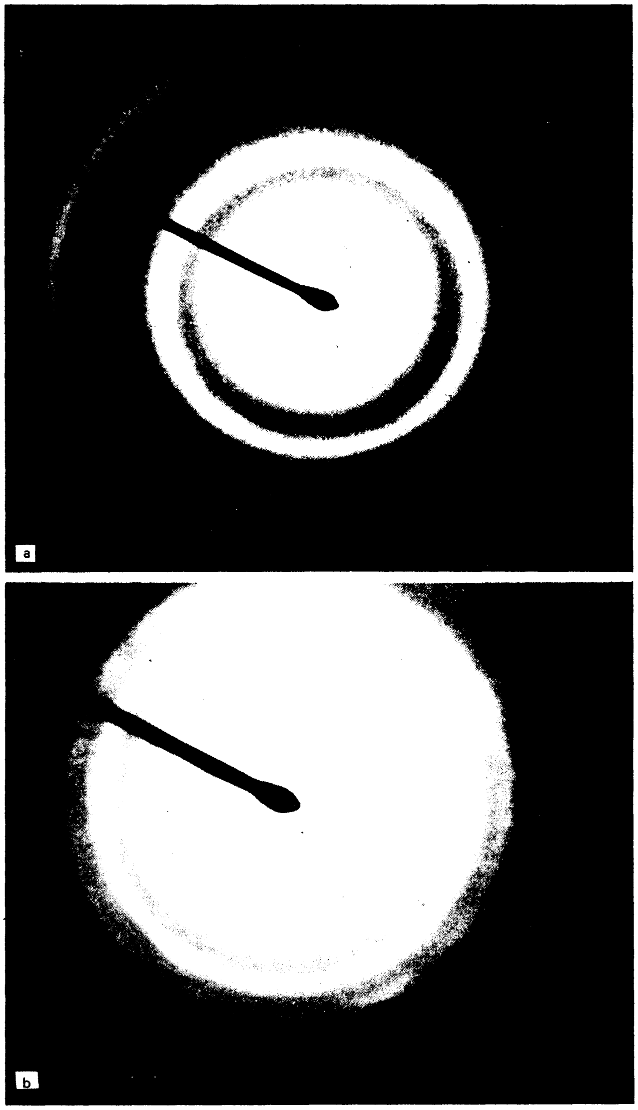

FIG. 2. Electron diffraction photographs from $Zr_{75}Rh_{25}$ specimens in the amorphous (a) and metastable crystalline (b) states.

being calculated from the total capacity, taking normalization into account.

3. Experiments

The heat capacity of the specimens was measured in the temperature range from 2 to 700 K in the absence of a field and from 2 to 15 K in a magnetic field produced by a ~6 T superconducting solenoid. The method of measuring heat capacity is described in detail in earlier papers.[21,22] The random error in determining the molar heat capacity was 2% in the range from 2 to 5 K and 1% from 5 to 100 K. Measurements above 100 K were carried out with a differential scanning calorimeter and the error did not exceed 1.5%.

Magnetic susceptibility was measured on the same specimens in the temperature range from 2 to 300 K. The susceptibility was measured with a string magnetometer in the field of a ~7 T superconducting solenoid. The design of the apparatus was similar to that described by Alekseevskiĭ *et al.*[23] Systematic errors in measuring susceptibility were 3% and random errors not more than 0.5%.

The electrical resistance of amorphous and crystalline specimens of $Zr_{75}Rh_{25}$ was measured by a four-lead system with constant current in the temperature range from T_c to 300 K. It should be noted that the main error in determining the absolute specific resistivity is introduced by uncertainty in the geometrical dimensions s/l of the specimen, which is ~10%.

The density was calculated by weighing the specimens in distilled water and in air in order to determine the molar volume. The isothermal bulk modulus was determined by measuring the longitudinal and transverse velocities of sound in amorphous and crystalline specimens. The coefficient of volume thermal expansion was determined by measuring the coefficient of linear expansion in the range from 4 to 300 K.

4. Results of the measurements and discussion

Results of measuring the heat capacity of the same $Zr_{75}Rh_{25}$ specimen in the amorphous and metastable crystalline states from 2 to 700 K are shown in Figs. 3 and 4.

Figure 3 shows the behavior of the low-temperature heat capacity from 2 to 7 K without and with a field of ~6 T, using C/T and T^2 as coordinates. The Debye temperature, $\Theta(0)$, and the coefficient of the electronic heat capacity, $\gamma(0)$, were deduced from these data. The temperature of the transition into the superconducting state. T_c, and the width of the transition, ΔT_c, and also the value of the normalized jump in the heat capacity, $\Delta C/\gamma T_c$, were determined from the jump in the heat capacity in the absence of a field.

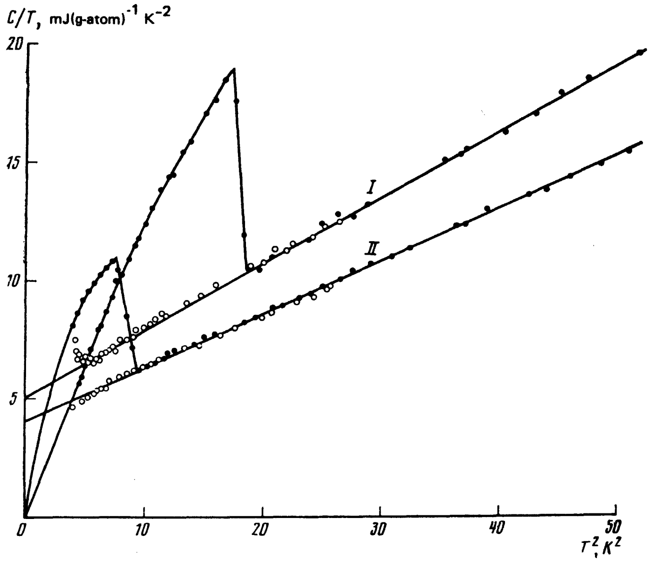

FIG. 3. Heat capacity of amorphous (I) and metastable crystalline (II) specimens of $Zr_{75}Rh_{25}$ specimens in the absence of a field (full circles) and in a field ~ 6*T* (open circles) in the temperature range from 2 to 7 K.

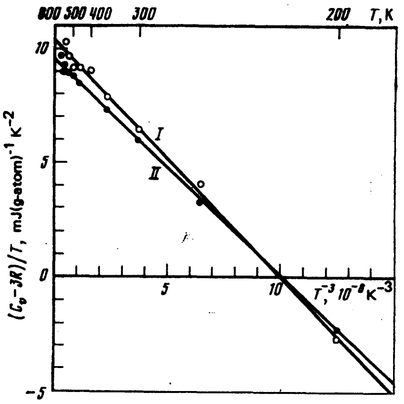

FIG. 4. High-temperature heat capacity of amorphous (I) and metastable crystalline (II) specimens.

The results of measuring the heat capacity from 100 to 700 K are shown in Fig. 4 as the relation between $(C_v - 3R)/T$ and $1/T^3$.

The high-temperature parameters, the Debye temperature Θ_{ht}, and the combined term $A + \gamma$ were obtained from the expression[24]

$$\frac{C_v-3R}{T}=-\frac{3R\Theta_{ht}^2}{20T^3}+(A+\gamma),$$

where C_v is the total heat capacity at constant volume obtained by separating out from C_p the contribution connected with thermal expansion, γ is the coefficient of the electronic heat capacity at high temperatures and A is the anharmonicity parameter. The electronic heat capacity coefficient at high temperatures was calculated from results on the magnetic susceptibility and the low-temperature heat capacity.

The experimental results obtained are shown in Table I. It follows from a comparison of them that the temperature T_c increases 1.5-fold when the $Zr_{75}Rh_{25}$ system becomes amorphous; $\gamma(0)$ also increases then and the Debye temperature falls. At high temperatures, Θ_{ht} is greater for the amorphous phase. These changes indicate rearrangement of the phonon spectrum, an increase in the phonon density of states both in the low-frequency and also in the high-frequency parts of the spectrum, which is characteristic for amorphous metals, and an increase in the electron density of states at the Fermi surface for the $Zr_{75}Rh_{25}$ system.

TABLE I.

	T_c, K (by heat capacity)	Transition width, K	T_c, K (by inductance)	$\frac{\Delta C}{\gamma T_c}$	$\Theta(0)$ $\pm 1.5\%$, K	$\gamma(0)\pm 1\%$, $\frac{\text{mJ}}{\text{g-atom}\cdot\text{K}^2}$	λ according to Ref. 15
$Zr_{75}Rh_{25}$ amorphous	4.23	0.15	4.37	1.76	190	5.1	0.66
$Zr_{75}Rh_{25}$ metastable crystalline	2.92	0.22	2.95	1.23	204	4.0	0.59
Relative change in %	44.9		48.1	43	7	28	13

	$\Theta_{ht}\pm 3\%$, K	$\gamma\pm 10\%$, $\frac{\text{mJ}}{\text{g-atom}\cdot\text{K}^2}$	$(A+\gamma)$ $\pm 2\%$, $\frac{\text{mJ}}{\text{g-atom}\cdot\text{K}^2}$	$A\pm 10\%$, $\frac{\text{mJ}}{\text{g-atom}\cdot\text{K}^2}$	χ, $\frac{\text{emu}}{g}\cdot 10^{-6}$	$N(\varepsilon_F)$, $\frac{\text{states}}{\text{eV}\cdot\text{atom}}$	$\rho(T_c)$, ohm·cm
$Zr_{75}Rh_{25}$ amorphous	289	3.1	10.4	7.3	1.18	0.65	182
$Zr_{75}Rh_{25}$ metastable crystalline	277	2.5	9.5	7.0	1.05	0.53	129
Relative change in %	4	17	10	7	12	22	41

It follows from a comparison of the values of $\Delta C/\gamma T_c$ that the crystalline phase is a superconductor with weak coupling and that this coupling becomes stronger on becoming amorphous. An intermediate coupling character is observed for the amorphous phase.

The magnetic susceptibility was measured on the same specimens as for measurement of heat capacity. It was found that the magnitude of the magnetic susceptibility, $\chi(T)$ was constant, independent of temperature, over the whole temperature range studied, from 2 to 300 K. However, $\chi(T)$ for the amorphous specimens was 11% greater than the susceptibility of the metastable crystalline phase. This confirms the result of an increase in the electron density of states on becoming amorphous, obtained from measurements of heat capacity.

The temperature dependence of the electrical resistivity, $R(T)/R(300\text{ K})$ of the system in the amorphous and metastable crystalline states is shown in Fig. 5. The resistivity of an amorphous specimen of $Zr_{75}Rh_{25}$ hardly changes with temperature. The decrease in resistivity when the temperature increases between 5 and 300 K is ~5%. On the other hand, the resistivity of the crystalline specimen depends appreciably on temperature and is less than that of the amorphous specimen in absolute magnitude. The values of $\rho(T_c)$ for the specimens studied are also shown in Table I.

The experimental results obtained were used to extract the temperature dependence of the phonon heat capacity of the $Zr_{75}Rh_{25}$ system in the amorphous and crystalline states. For this purpose it was essential to calculate the electronic heat capacity correctly from the magnetic susceptibility and low-temperature heat capacity results. On the assumption that the diamagnetic and orbital contributions to the susceptibility are independent of temperature, and using the low-temperature electronic heat capacity coefficient $\gamma(0)$ and the

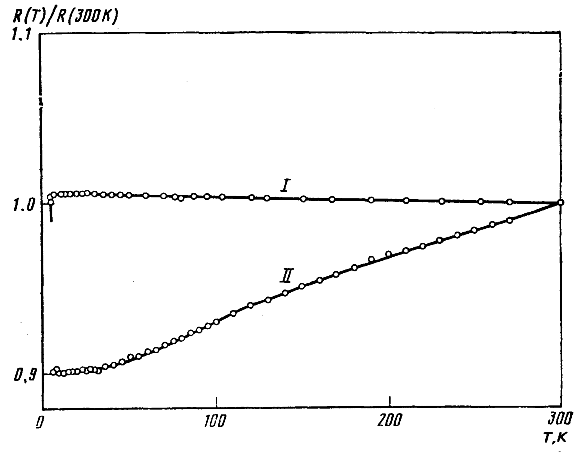

FIG. 5. Temperature dependence of the electrical resistance of a specimen of $Zr_{75}Rh_{25}$ in the amorphous (I) and metastable crystalline (II) states.

electron-phonon interaction parameter λ, determined as in Ref. 15 and obtained from the calorimetric experiment, the electron density of states at the Fermi surface, $N(\varepsilon_F)$, was determined for both systems.

The temperature dependence of $\lambda(T)$ for the temperature tange from 2 to 300 K was determined from the values of $\Theta(0)$ and $\lambda(0)$ obtained from the low-temperature calorimetric experiments and from the theoretical dependence of $\lambda(T)/\lambda(0)$ on T/Θ obtained in Ref. 25. The combination of the results on the electron density of states $N(\varepsilon_F)$ and on the temperature dependence of $\lambda(T)$ enables the total electronic contribution to the heat capacity to be calculated:

$$C_e={}^2/_3\pi^2k_B{}^2N(\varepsilon_F)(1+\lambda(T))T.$$

The heat capacity at constant volume, C_v, and the measured heat capacity at constant pressure, C_p, are connected by the well-known thermodynamic relation

$$C_v=C_p-V\beta^2B_TT,$$

where V is the gram-atomic volume, β is the isobaric volume coefficient of thermal expansion, and B_T is the isothermal bulk compression modulus.

The heat capacity, C_v, of the systems studied can as usual be represented by the sum

$$C_v=C_h^v+C_{\text{anh}}^v+\Delta C_v+C_e,$$

where C_h^v is the phonon heat capacity in the harmonic approximation, ΔC_v is the correction to the heat capacity resulting from reduction of the volume $V(T)$ to a fixed volume V_0 at 0 K (the estimate of this correction[26] is not more than 0.2%), and C_{anh}^v is the anharmonic contribution to the heat capacity at high temperatures ($T>100$ K), which in this range can be represented by

$$C_{\text{anh}}^v=AT.$$

The anharmonic component of the heat capacity was calculated from the results of measuring the high-temperature heat capacity and the magnetic susceptibility.

The analysis made it possible to calculate the temperature dependence of the phonon heat capacity and to compare the phonon heat capacities of the amorphous and crystalline specimens.

Figure 6 shows the temperature dependence of the relative difference between the phonon heat capacity of an amorphous specimen compared with a crystalline specimen:

$$\Delta C_{\text{ph}}/C_{\text{ph}}=(C_{\text{ph}}^{\text{am}}-C_{\text{ph}}^{\text{cr}})/C_{\text{ph}}^{\text{cr}}.$$

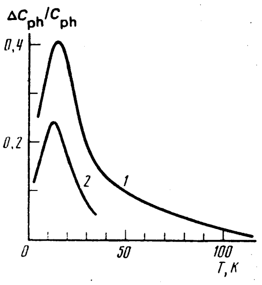

FIG. 6. Temperature dependence of the relative change in phonon heat capacity of an amorphous specimen of $Zr_{75}Rh_{25}$ (1) compared with the metastable crystal and, for comparison, an alloy of V with 1 at. % of heavy U impurities.

It can be seen from Fig. 6 that a maximum is observed in the temperature dependence of $\Delta C_{\text{ph}}/C_{\text{ph}}$ at $T\sim12$ K with the maximum difference in phonon heat capacities of ~40%. Since the low-temperature phonon heat capacity is sensitive to the low-frequency changes in $F(\omega)$, the anomalous growth in phonon heat capacity on becoming amorphous indicates a rearrangement of the phonon spectrum in the low-frequency region.

For comparison, the results of measuring the heat capacity of an alloy of vanadium with heavy uranium atom impurity (1 at.%) is also shown[27] in Fig. 6. The introduction of heavy impurity atoms into vanadium and the weakening of the force constants which results, leads to a deformation of the phonon spectrum and the appearance of quasilocalized modes in the spectrum, which in turn leads to the appearance of a maximum in the temperature dependence of the relative change in phonon heat capacity.

Calculations[28] showed that an increase in low-temperature heat capacity on becoming amorphous can be explained by the existence of low-frequency singularities in $F(\omega)$ connected with the change in force constants. Localized fluctuations in force constants in a disordered system lead, on the one hand, to an increase in the low-frequency density of states, and on the other to a shift of the limiting frequency towards high frequencies. These two effects lead to a smearing out of $F(\omega)$. A maximum is obtained in the frequency dependence of the relative change in phonon density of states $F_{\text{am}}(\omega)/F_{\text{cr}}(\omega)$ at $\omega/\omega_{\text{lim}}\approx0.15$, which leads to the anomalous behavior of the phonon heat capacity observed by us experimentally.

We shall pass directly to consideration of the effect on T_c of becoming amorphous. In order to establish the scale of the change in the contributions to T_c from the rearrangements of the phonon and electron spectra and the electron-phonon interaction, we carried out calculations using the experimental results and those of other workers.[15,29] According to McMillan,[15]

$$T_c=\frac{\langle\omega\rangle_\omega}{1.2}\exp\left\{-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right\},\tag{1}$$

$$\lambda=\frac{N(\varepsilon_F)\langle J^2\rangle}{M\langle\omega^2\rangle_\omega},\tag{2}$$

$$\mu^*=\mu\Big/\left(1+\mu\ln\frac{\varepsilon_F}{\langle\omega\rangle_\omega}\right),\tag{3}$$

where the symbol $\langle\ldots\rangle_\omega$ here and in what follows is to be interpreted as:

$$\langle f\rangle_\omega=\int\limits_0^\infty\frac{d\omega}{\omega}f(\omega)\alpha^2(\omega)F(\omega)\Big/\int\limits_0^\infty\frac{d\omega}{\omega}\alpha^2(\omega)F(\omega).\tag{4}$$

In Eq. (4), $\alpha^2(\omega)$ was considered constant. The error in such an approximation is small since $\alpha^2(\omega)$ enters into both integrals.

On the basis of Butler's work[30] we calculated $\varepsilon_F=6.79$ eV. It was assumed that ε_F does not change on becoming amorphous. We may note that the value of ε_F has a weak influence on the final result. For example, a 20% change in ε_F leads to a 1 or 2% change in λ, while the relative change $(\lambda_{am}-\lambda_{cr})/\lambda_{cr}$ is an order of magnitude smaller.

For evaluating the screening parameter μ we used the expression

$$\mu=\frac{1}{\pi K_F a_B}\int_0^2\frac{dx}{x\varepsilon(x)}, \tag{5}$$

$$\varepsilon(x)=1+\frac{2}{\pi K_F a_B}\left[1+\frac{4-x^2}{x}\ln\left|\frac{2+x}{2-x}\right|\right]\Big/ x^2 \tag{6}$$

(a_B is the Bohr radius).

The value of K_F was determined from a quasi-free electron model from the relation

$$\varepsilon_F=p_F^2/2m^*, \quad N(\varepsilon_F)={}^4/{}_3\pi V(2m^*)^{3/2}\varepsilon_F^{1/2}. \tag{7}$$

Calculation of the parameters μ, μ^*, λ, $N(\varepsilon_F)$ and K_F was carried out by a self-consistent iterative method based on the solution of the system of equation (1), (5), to (9) and

$$\gamma={}^2/{}_3\pi^2 k_B^2 N(\varepsilon_F)(1+\lambda);$$

and a second iteration already sufficed to obtain the final result.

The experimental phonon spectrum obtained for the $Zr_{54}CU_{46}$ system in the amorphous and crystalline states[12] was used as a model for an approximate determination of the characteristic phonon frequencies. For this system the low-temperature calorimetric Debye temperature $\Theta(0)$ (Ref. 13) and the calculated high-temperature $\Theta_{ht}=\langle\omega^2\rangle_\omega^{1/2}$ practically coincide with the experimental values for $Zr_{75}Rh_{25}$. The calculated results obtained are shown in Table II.

Calculation of the partial components of $\delta T_c=\Delta T_c/T_c$ on changing the magnitudes of $\tilde{\omega}$, $\langle\omega\rangle_\omega$, $N(\varepsilon_F)$, $\langle J^2\rangle$ and μ^* [where, according to Eq. (4), $\tilde{\omega}=\langle\omega^2\rangle_\omega/\langle\omega\rangle_\omega$] was carried out by varying the parameters:

$$\delta T_c=\sum_{i=1}^{5}A_i\delta x_i,$$

$$A_1=1+A_2,\quad A_2=A_3=A_4=-\{\ldots\}\frac{1.04+\lambda-0.62\mu^*\lambda}{\lambda-\mu^*(1+0.62\lambda)}, \tag{8}$$

$$A_5=-\{\ldots\}\frac{1+0.62\lambda}{\lambda-\mu^*(1+0.62\lambda)},$$

where $\{\ldots\}$ is the argument of the exponential in Eq. (1) and δx_i is the relative change in $\tilde{\omega}$, $\langle\omega\rangle_\omega$, $N(\varepsilon_F)$, $\langle J^2\rangle$ and μ^* corresponding to $i=1$ to 5.

TABLE II.

	$N(\varepsilon_F)$, states/eV·atom	m^*, 10^{-28} g	K_F, 10^{-8} cm^{-1}	μ	μ^*	$\langle\omega\rangle_\omega$, K	$\tilde{\omega}$, K	$\langle\omega^2\rangle_\omega^{1/2}$, K	$(\tilde{\omega}^2)^{1/2}$, K	$\langle\omega^2\rangle^{-1}$, 10^3 eV^{-2}	$\langle J\rangle^2$, 10^{-3} rel. units	λ	T_c, K
$Zr_{75}Rh_{25}$ amorphous	0.69	20.0	2.07	0,151	0.078	170.2	223.4	195.0	297	3.542	2.69	0,57	4.23
$Zr_{75}Rh_{25}$ metastable crystalline	0.56	17.9	1.95	0.155	0.079	176.3	212.3	193.4	287	3.601	2.87	0,50	2,92
Relative change in %	22	15.5	6	−2,6	−1.3	−3.5	5.2	0.8	3,5	−1.6	−6.1	13.4	45

The orders of magnitude of the partial contributions (in %) of the various factors to ΔT_c on becoming amorphous are shown below

$\langle\omega\rangle_\omega$	$\tilde{\omega}$	$N(\varepsilon_F)$	$\langle J^2\rangle$	μ^*
2.6	−26.6	113	−29	40 .

As was shown above, an anomalous increase in the phonon density of states in the low-frequency region is observed on becoming amorphous. Renormalization of λ due to electron interaction with this type of low-frequency modes leads to a small positive contribution to T_c. However, as a result of the increase in Θ_{ht}, the phonon spectrum as a whole becomes stiffer and this fact leads to a negative contribution to T_c. As a result, the change in the phonon spectrum of the $Zr_{75}Rh_{25}$ system on becoming amorphous leads to a reduction in T_c (~24%).

The increase of T_c when the $Zr_{75}Rh_{25}$ system is amorphous is mainly due to an increase in the electron density of states at the Fermi surface. Because of a reduction in μ^* connected with the weakening of the electron-phonon interaction, a positive contribution is then introduced into ΔT_c. The contribution of the mean square matrix element of the electron-phonon interaction $\langle J^2\rangle$ to ΔT_c is negative.

A second analysis of the nature of the change in T_c when amorphous was carried out on the basis of the work of Zhernov *et al.*,[29] by taking explicit account of the frequency dependence of the energy gap Δ (the parameter η). Results were obtained for an irregular isotropic superconductor with intermediate coupling, without any assumption about the nature of the electron-phonon interaction and the form of the phonon spectrum. In this work the following relations are given which determine T_c:

$$T_c=1.14\omega_c\exp\{-1/(g-\tilde{\mu}^*)\},$$

$$\omega_c=\exp\langle\ln\omega\rangle_\omega,\ g=\frac{\nu}{1+\eta\nu/2},\ \nu=\frac{\lambda}{1+\lambda},\ \tilde{\mu}^*=\frac{\mu^*}{1+\lambda},\ \mu^*=\frac{\mu}{1+\mu\ln(\varepsilon_F/\omega_c)}, \tag{9}$$

$$\eta=\left\langle\left\langle\frac{\omega^2}{\omega^2-\omega'^2}\ln\frac{\omega^2}{\omega'^2}\right\rangle_\omega\right\rangle_{\omega'}.$$

Calculation of the parameters determining T_c can be carried out using these relations and an iterative procedure. Their values are shown in Table III. As can be seen from the results for the partial contributions (in %) of the various parameters to the change in T_c on becoming amorphous given below, a reduction in the preexponential ω_c leads to a reduction in T_c, while a corresponding change in μ^* leads to a small increase in T_c:

TABLE III.

	μ	μ^*	$\tilde{\mu}^*$	λ	ν	g	$N(\varepsilon_F)$, states/eV·atom	K_F, 10^{-8} cm^{-1}	ω_c, K	η
$Zr_{75}Rh_{25}$ amorphous	0.152	0.077	0.046	0.697	0.411	0.323	0.637	2.02	136.3	1.32
$Zr_{75}Rh_{25}$ metastable crystalline	0.155	0.079	0.051	0.555	0.357	0.295	0.546	1.93	154.5	1.18
Relative change in %	−2,0	−2,6	−10	23	15	9.5	16	4.6	−12	12

ω_c	λ	η	μ^*
-3.5	157	-26	4 .

If λ is written in the form $\lambda = \lambda_e \lambda_{ph}$, where

$$\lambda_{ph} = \int_0^\infty \frac{d\omega\, F(\omega)}{\omega},$$

and we consider the contributions of both quantities to T_c, then it turns out that the increase in T_c in the $Zr_{75}Rh_{25}$ system is mainly related to an increase in the electron component of λ. The contribution of λ_e to the change in T_c is about six times greater than the corresponding contribution of λ_{ph}.

The increase in the parameter η in the amorphous state is evidence, as for λ_{ph}, of the growth in the role of the low-frequency part of the phonon spectrum. Since η in the denominator of the exponent in Eq. (9) enters as the product $\eta\nu\tilde{\mu}^*$, while in the numerator it is without $\tilde{\mu}^*$, where $\tilde{\mu} < 1$, in the upshot its change leads to a negative contribution to T_c. Taking account of the change in all the phonon characteristics ω_c, λ_{ph} and η on becoming amorphous gives a negative contribution to ΔT_c. Consequently the increase in T_c in the amorphous system is mainly due to changes occuring in the electron spectrum.

Both analysis of the experimental results carried out on the basis of McMillan's work[15] and relations (9) and (10) thus lead to one and the same result.

A similar analysis based on McMillan's work[15] was carried out for the $La_{78}Zn_{22}$ system in the amorphous and metastable crystalline states for which the results of measurements carried out have been reported.[16] The experimentally observed doubling of T_c on becoming amorphous is accompanied by a reduction in the coefficient of the electronic heat capacity, $\gamma(0)$, as distinct from the $Zr_{75}Rh_{25}$ system. Just because of this it would be interesting to carry out an analysis of the reasons for the change in T_c in the $La_{78}Zn_{22}$ system and to compare the results with the $Zr_{75}Rh_{25}$ system.

Calculation of the influence of the phonon spectrum on the change in T_c was made on the basis of Eq. (1) with the preexponential factor $\Theta(0)/1.45$ using two phonon characteristics: $\Theta(0)$ and $\langle\omega^2\rangle_\omega^{-1}$ which are more like integral features than the variables $\langle\omega\rangle_\omega$ and $\tilde{\omega}$. $\langle\omega^2\rangle_\omega$ was estimated from the similar change which takes place in it when the $Zr_{75}Rh_{25}$ system is amorphous and the value of $\Theta(0)$ for $La_{78}Zn_{22}$. The results of the analysis are shown below (contributions of the different factors to ΔT_c, given in %):

$\Theta(0)$	$\langle\omega^2\rangle$	$N(\varepsilon_F)$	$\langle J^2\rangle$	μ^*
-9	45	-62	110	16 .

It is found that the pronounced softening of the phonon spectrum in the low-frequency region due to the preexponential gives a negative contribution to the change in T_c; the change in $\langle\omega^2\rangle_\omega$ gives a positive contribution. As a result, the rearrangement of the phonon spectrum on becoming amorphous leads, overall, to an increase in T_c.

It follows from experiment[16] that the coefficient of the electronic heat capacity of the amorphous $La_{78}Zn_{22}$ system is 30% less than in the crystalline system. This difference leads to a large negative contribution due to the electrons, to the change in T_c on becoming amorphous.

The calculations carried out show that the increase in T_c observed experimentally when the $La_{78}Zn_{22}$ system becomes amorphous is apparently mainly connected with the strong increase in the electron-phonon interaction, which confirms earlier work.[16] The weakening of the electron-electron interaction on becoming amorphous leads to a small increase in T_c.

The following conclusions can be drawn as a result of the analysis of experimental results obtained in the present work for $Zr_{75}Rh_{25}$ and earlier work[16] on $La_{78}Zn_{22}$. In spite of the considerable softening of the phonon spectrum in the low-frequency region on becoming amorphous, the overall change in the phonon spectrum is small and is not the determining factor in the change in T_c. The main changes in T_c are due to rearrangement of the electron spectrum and the electron-phonon interaction: the electron-phonon interaction weakens with an increase in the electron density of states at the Fermi surface, as in the case of $Zr_{75}Rh_{25}$, while on the contrary, a strengthening of the electron-phonon interaction is observed with a reduction in the electron density of states, as in the case of $La_{78}Zn_{22}$. For both systems $N(\varepsilon_F)\langle J^2\rangle$ then gives the main contribution to the change in T_c (~80%).

We note finally that there is theoretical[32,33] and experimental[34,35] work in which the existence of phonon excitations of low energy and high momentum in an amorphous system is shown, leading to the appearance of a heat-capacity term linear in temperature. In addition, it has been shown[36,37] that a stronger electron-phonon interaction is assumed for these specific phonons (of the so-called roton type).

Unfortunately the temperature range in which the experimental studies of the $Zr_{75}Rh_{25}$ system were carried out did not allow any conclusions to be drawn about the existence of specific phonon excitations in the system investigated. Further work is essential for a deeper understanding of the change of superconducting properties on becoming amorphous. A study of tunneling characteristics and of phonon spectra obtained by inelastic scattering of neutrons would be of great interest in this connection, as would a more precise measurement of structure factors.

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