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Low-temperature specific heat of Zr-Rh-Pd metallic glasses

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The specific heat of glassy Zr-Rh-Pd alloys at low temperatures is investigated. The results are interpreted within the framework of the model of soft atomic potentials (Karpov *et al.*, Solid State Commun. **44**, 333 (1982); Zh. Eksp. Teor. Fiz. **84**, 760 (1983) [Sov. Phys. JETP **57**, 439 (1983)]). Using the experimental data for the normal and superconducting states, low-energy vibrational excitation parameters are obtained.

I. INTRODUCTION

Low-temperature thermal properties are very important for understanding of the nature and properties of low-energy excitations in glasses. This is why there are many papers concerning this topic. Most of the investigations were performed with dielectric glasses where the specific heat C is due to vibrational excitations. The situation in metallic glasses is not so simple because of electronic degrees of freedom. Their contribution, however, can be separated in amorphous superconductors with high enough transition temperature T_c. In such materials at low temperature electronic degrees of freedom freeze out and the remainder is due to vibrational excitations.[1] According to the results of numerous experiments (for a review see Ref. 2) at low temperatures the vibrational contribution to the specific heat is virtually linear in the temperature T. This has been explained in the framework of the well-known model of two-level systems (TLS's).[3,4] At higher temperatures the situation becomes more complicated. Along with the contribution of conduction electrons there exists an extra temperature-dependent contribution which is natural to ascribe to common vibrational degrees of freedom.

The traditional way to describe the low-temperature specific heat of dielectric crystals is to use the Debye expression for the specific heat (see, e.g., Ref. 5),

$$C(T) = \alpha T^3, \quad \alpha(T) = \frac{12\pi^4 k_B}{5M_0\Theta^3} F\left(\frac{T}{\Theta}\right), \tag{1}$$

where M_0 is the atomic unit of mass while

$$F(z) = \frac{15}{4\pi^4}\int_0^z dx \frac{x^4 e^x}{(e^x-1)^2}, \quad F(0) = 1.$$

The reason is that at low temperatures the thermodynamics of a crystal is dominated by low-frequency phonons having a linear dispersion law. To describe experimental data it is natural to use Eq. (1) as a *definition* of an effective temperature-dependent *caloric* Debye temperature $\Theta(T)$. For *metallic glasses* it is known that at low enough temperatures $\Theta(T)$ decreases with increasing of the temperature (see, e.g., Refs. 6 and 7).

The decreasing temperature dependence of Θ means that there are excess low-frequency modes in comparison with the density of phonon states given by the Debye model. Such a dependence was also observed in some polycrystalline metals (see Refs. 8 and 9 for a review) and was also ascribed to excess low-frequency modes.

The purpose of this paper is to report the results of an experimental study of the low-temperature specific heat in Zr-Rh-Pd metallic glasses which also exhibit a temperature-dependent effective Debye temperature. The varying size of this temperature dependence for different samples identifies it as a glass property resulting from differing preparation conditions of the glass.

To interpret the experimental data we use the macroscopic model of quasilocal vibrational states in glasses developed in Ref. 10 (see Ref. 11 for a review). This model was successfully employed to analyze thermodynamics and kinetics in dielectric and semiconducting glasses.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Aspects for the choice of Zr-Rh-Pd glasses were the almost equal vapor pressures of the constituents near the melting temperature, assuring that the composition of the alloys would not differ much from their ingot compositions, and the thermal stability of the glasses up to 700 K.[12] Physically, their rather high transition temperatures to superconductivity would favor the detection of linear contributions to the heat capacity due to two-level systems[2–4] at very low temperatures while normal excitations are being frozen out in the superconducting state. In a different study,[13] a correlation of the density of TLS's and the phonon contribution to the specific heat has been found. We will use those results in the present work.

Pure starting materials (99.99% Zr and Pd, Material Research Corp.; 99.9% Rh, Ventron Corp.) were arc molten on a flat polished copper plate in high purity argon atmosphere and quenched by shooting a flat polished copper hammer at 40–50 ms^{-1} speed through the burning arc onto the molten alloy sphere. Splats of 40–50 μm thickness resulted. Due to the cooling conditions in the hammer-and-anvil device, the central and circumferential parts of the circular splats were not always fully amorphous, as inspection by x-ray analysis showed. These parts were cut away. The samples were then investigated for crystalline inclusions by electron diffraction, with no indications within the limits of resolution of ca. 0.5% of volume. Further, measurements of the angle of the x-ray diffraction maxima for estimates of the nearest neighbor distance and direct measurements of the mass density were made. Both types of measurement yield similar findings with respect to characteristic differences of the packing density for the metallic glasses. This is exemplified in Fig. 1 where the density is plotted vertically over part of a Zr-Rh-Pd composition triangle. (Note that not all ternary alloys shown are identical with those for which calorimetric data were taken.) For binary $\mathrm{Zr}_{100-x}\mathrm{Pd}_x$ alloys density ρ vs concentration x data lie quite close to a straight line which at $x = 0$ extrapolates well to the density of hcp zirconium (6.44 $\mathrm{g\,cm}^{-3}$). For binary $\mathrm{Zr}_{100-x}\mathrm{Rh}_x$ alloys there are *nonsystematic* deviations from a straight line far outside the experimental resolution ($\Delta\rho \pm 0.03$ $\mathrm{g\,cm}^{-3}$). For the ternary $\mathrm{Zr}_{75}\mathrm{Rh}_{25-x}\mathrm{Pd}_x$ alloys a more systematic density minimum near x=10 was observed ($\Delta\rho \approx 20 \times 10^{-2}$ $\mathrm{g\,cm}^{-3}$). This may be interpreted as an enhanced tendency of forming a "free volume" in the middle of the ternary alloy series, superimposed by an uncontrollable influence of the preparation conditions, notably in the Rh-containing glasses. This, in turn, may originate from different ingot sizes, different piston speeds, and/or different temperatures of the molten sample before quenching.

The heat capacity C of the small samples (mass 10–60 mg) was measured using a heat pulse method. The apparatus is fully automatized and computer controlled. Samples, heater, and thermometer were mounted on a 100 μm thick sapphire support. Heat capacities of the addenda were measured separately and accounted for. Direct calibration of the equipment was performed with a high purity platinum sample of dimensions similar to the sample sizes. Good agreement with the literature data[14] within 0.5%–1% was obtained.

In a magnetic field of 6 T practically identical C data were obtained for temperatures between 2 and 10 K. From this fact it is estimated that the thermometer calibrations in such fields are correct to within 1%, and that the apparatus is capable of determining the Sommerfeld parameter γ and Θ with and without a magnetic field with an absolute accuracy of 1% and 2%, respectively. We also note that the decay of the heat pulse signal is purely exponential for both Pt and the amorphous metal alloys. Characteristic decay times are between 1 and 20 s. No time-dependent heat capacities at our scale of times were observed for the metallic glasses, as expected.

In Fig. 2 a typical C/T vs T^2 plot is shown for $\mathrm{Zr}_{75}\mathrm{Rh}_{13}\mathrm{Pd}_{12}$ both without and with a 6 T magnetic field (field data omitted above T_c for clarity). Note the curvature in the normal state, indicative of a contribution of higher power than T^3 in $C(T)$. Also note here the small upward curvature below 2 K, this being due to precursors of superconductivity as magnetic field dependence showed.

Results obtained in the temperature range from 1.5 to 12 K are summarized by the least-squares fit coefficients of the polynomial $C = \sum_n a_n T^n$ given in Table I, with n = 1, 3, 5, and 7. For reasons to be discussed below, fits are also included within the temper-

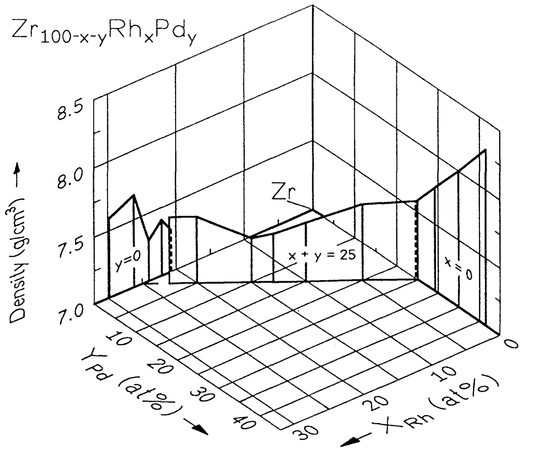

FIG. 1. Mass density for binary and ternary amorphous Zr alloys. For the latter, Zr concentration is fixed at 75 at %.

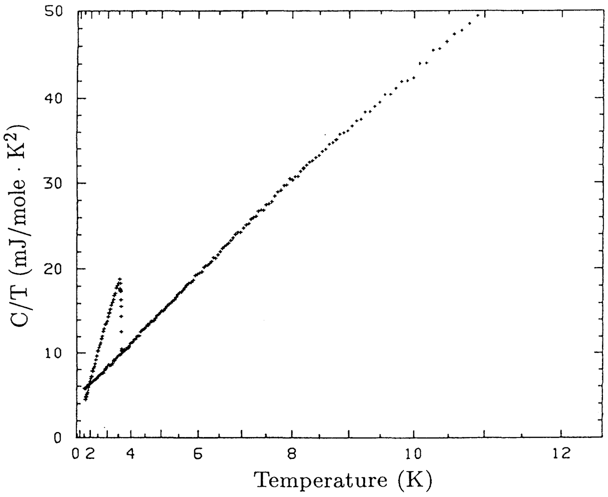

FIG. 2. Example of calorimetric data (metallic glass $\mathrm{Zr}_{75}\mathrm{Rh}_{13}\mathrm{Pd}_{12}$).

TABLE I. Results of calorimetric data fitting and parameters of the model. Atomic weights are 91.22, 102.905, and 106.4 for Zr, Rh, and Pd, respectively. Included are calibration data obtained for Pt and comparison is made with literature data (Ref. 14). Parameters of the model are calculated for $t_{\mathrm{expt}} = 1.5$ s, $t_0 = 10^{-6}$ s.

$\mathrm{Zr_{75}Rh_xPd_{25-x}}$ x	Interval (K)	$a_1 \equiv 10^3\gamma_{\mathrm{el}}$ (J/K^{2}mol)	$10^4 a_3$ (J/K^{4}mol)	$10^7 a_5$ (J/K^{6}mol)	$10^9 a_7$ (J/K^{9}mol)	Θ_0 (K)	$10^{5\,\mathrm{a}}\gamma_{\mathrm{TLS}}$ (J/K^{2}mol)	w/k_B (K)	E (eV)	Na^2 (Å^2)	N
2.5	1.5–6.5	4.99±0.03	3.02±0.04	9.43±2.0		186	0.30	4.2	88	13	18
	1.5–10.0	5.03±0.03	2.94±0.04	15.70±1.8	−13.1±0.7	188		3.7	133	19	26
7.5	1.5–6.5	4.99±0.03	3.43±0.04	6.19±1.5		178	0.20	4.2	73	12	26
	1.5–12.0	4.96±0.04	3.43±0.04	9.36±1.1	−8.9±0.6	178		3.8	100	16	21
13.0	1.45–6.5	4.98±0.05	2.26±0.07	21.10±1.7		205	0.70	4.2	128	15	21
	1.48–10.0	4.98±0.03	2.45±0.04	22.40±1.1	−17.3±0.8	200		4.2	118	15	21
17.5	1.5–6.1	4.99±0.03	3.20±0.04	9.63±1.1		182	0.30	4.2	83	13	27
22.5	1.88–10.0	4.94±0.04	3.26±0.04	11.30±1.5	−10.3±0.7	182	0.30	4.0	91	14	19
25	1.8–8.0	4.94±0.04	3.08±0.04	12.70±0.9	−10.9±2.8	185	0.35	4.0	95	14	19
Pt	1.41–7.0	6.55±0.02	1.49±0.02	1.9 ±0.2		235					
Pt$^{\mathrm{b}}$	0.30–30	6.492±0.01	1.430±0.01	3.27 ±0.1		238.7					

[a] Reference 13.

[b] Reference 14.

ature interval 1.5–6.5 K and for $n \leq 5$. The electronic term $a_1 \equiv \gamma$ is remarkably constant, independent of alloy composition and also of the order of fit. The term a_3T^3 is identified with the Debye contribution and yields $\Theta_0 \equiv \Theta(T \to 0)$ [if C is measured in J/mol K^4, we have $\Theta_0 = (1943/a_3)^{1/3}$]. Θ_0 ranges from 178 to 200 K; it is weakly dependent on the order of fit. There is substantial variation of the a_5 term within different alloys, well outside its dependence on fit order, but with a clear correlation to the a_3 term. It is illuminating to discuss these data in terms of a temperature dependence of the caloric Debye temperature. In the region of our fit, $\Theta(T) = \Theta_0\left[1 + (T^2/a_3)(a_5 + a_7T^2)\right]^{-1/3}$. Figure 3 shows this function for four of the ternary alloys investigated. For two of them original data taken directly from the heat capacity measurements according to the formula $\Theta(T) = T\left[1943/(C_{\mathrm{meas}} - a_1T)\right]^{1/3}$ are presented (triangles). In this representation, because of the dominating contribution of the electronic term to C_{meas}, there will be rather high uncertainties at low temperatures. Also, traces of superconductivity will be exaggerated. Nevertheless, it is seen that the data are well described by the above four-parameter fit with a very clear minimum of $\Theta(T)$ near $T = 7.5$ K. Above 9 K the data might have been better represented by adding one or two more terms to the polynomial for $C(T)$. With respect to the interpretation below, this is not necessary.

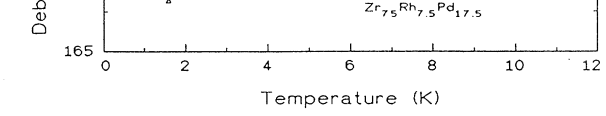

FIG. 3. Temperature variation of the effective Debye temperature for four metallic glasses. Investigated Rh concentrations x= 2.5, 7.5, 13.0, 25.0. For clarity, direct experimental data (triangles) are shown for two alloys only. Solid lines represent least-squares four parameter fits. Parameters are given in Table I.

It is clear that the success of such a procedure crucially depends on the quality of knowledge of a_1T. Here we take advantage of the independence of this term of the fit procedure and even of the alloy chosen.[15]

The interesting feature of the graphical presentation of Table I is that at temperatures around the minimum of $\Theta(T)$, common to all alloys, the phonon contribution to C is almost the same [as revealed by $\Theta(T)$], amounting to $\Theta(T)_{\mathrm{min}}$ from 175 to 182 K. In the limit $T \to 0$, however, strong variations of Θ_0 occur, ranging from 178 to 200 K. Thus, near $T = 7.5$ K the difference $\Delta\Theta(T)_{\mathrm{min}}$ amounts to 7 K while at $T \to 0$ it has risen to 22 K. It is to be noted that the strongest variation of $\Theta(T)$, i.e., the largest value of a_5, is measured for $\mathrm{Zr_{75}Rh_{13}Pd_{12}}$. This is in the middle of the ternary alloy series. For these alloys a minimum density has been measured, as reported above.

In the interpretation (see below) the TLS contribution γ_{TLS} to the linear term a_1T is needed, which cannot be obtained from the present measurement. We have access to γ_{TLS} from very-low-temperature calorimetry on the binary metallic glasses $\mathrm{Zr_{100-x}Rh_x}$, $21 < x < 29$.[13] These measurements that cover the temperature range 170–1000 mK as reported above uncovered a correlation between γ_{TLS} and Θ_0. The correlation can be expressed as $\gamma_{\mathrm{TLS}} = (a_0 - a_3)/b$, where $a_0 = (3.93 \pm 0.5) \times 10^{-4}$ J/mol K^4, $b = (2.4 \pm 0.5)$ K^{-2}, and $a_3 = 1943/\Theta_0^3$.

Thus, γ_{TLS} can be estimated from a_3, as obtained in the present work. We have no explanation for such a big "hardening" of phonons due to the introduction of TLS's. We note, however, that it appears to be inherently essential for the present model, as it causes the quantity $\Theta(T)_{\mathrm{min}}$ to become almost constant, even when the degree of disorder is different. Apparently, in all samples, the nature of the disordered entities seems to be the same.

III. INTERPRETATION AND DISCUSSION

In this section we present the interpretation of the experimental results which is close to the one used for dielectric glasses in Ref. 16.

According to the model[10] of soft atomic vibrational states low-frequency atomic modes can be described in a one-mode approximation by an effective anharmonic potential

$$V(x) = \mathcal{E}[\eta(x/a)^2 + \xi(x/a)^3 + (x/a)^4], \qquad (2)$$

with random parameters η and ξ. Here x is a generalized coordinate corresponding to the soft mode, and a is of the order of interatomic distance, while $\mathcal{E}$ is an energy of atomic scale. We are interested in low-energy excitations which correspond to $\mid \eta \mid, \mid \xi \mid \ll 1$. In this case anharmonic terms can be important.

To analyze characteristic parameters of soft modes let us assume that all the items in Eq. (2) have the same order of magnitude. In this case one can extract the characteristic parameters from the Schrödinger equation by making it dimensionless. Following Ref. 10 we get that the characteristic displacement is of the order of $a\eta_L^{1/2}$ where $\eta_L = (\hbar^2/2Ma^2\mathcal{E})^{1/3} \approx (\hbar\omega_c/\mathcal{E})^{2/3} \ll 1$, and M is the effective mass of a soft atomic mode, while ω_c is the characteristic frequency of atomic vibrations. This frequency is of the order of the Debye frequency $k_B\Theta_0/\hbar$. The characteristic range of interlevel spacings is

$$w = \mathcal{E}\eta_L^2 \approx \hbar\omega_c\eta_L^{1/2} \approx 10 \text{ K}. \qquad (3)$$

Such a spacing exists between the energy levels in the potential (2) at $\eta \approx \eta_L$, $\xi \approx \eta_L^{1/2}$. At $\eta < 0$ the potential (2) has a two-well shape. As was shown in Ref. 10 at $\mid \eta \mid > \eta_L$, $\mid \xi \mid < \mid \eta \mid^{1/2}$, the lowest states represent a doublet of levels with the spacing $E = (\Delta^2 + \Delta_0^2)^{1/2}$ where

$$\Delta = \frac{w \mid \xi \mid\mid \eta \mid^{3/2}}{\sqrt{2}\eta_L^2}, \; \Delta_0 \approx w \exp\left(-\frac{\sqrt{2}}{3}\left|\frac{\eta}{\eta_L}\right|^{3/2}\right). \qquad (4)$$

Thus we see that the model under consideration for low energies ($E < w$) describes two-level configurations.

To analyze the thermodynamics one should specify the distribution of the random parameters η and ξ, $P(\eta,\xi)$. This distribution cannot be calculated in the framework of the macroscopic model and one should introduce it phenomenologically. (In principle such a distribution can be calculated from some microscopic model or with the help of computer simulations. For example, computer modeling of a-Si and a-SiO$_2$ was performed in Refs. 17 and 18. The model close to the situation in metallic glasses was numerically analyzed in Refs. 19 and 20). It is natural to assume that the distribution of the asymmetry ξ is even because there is no preferred direction in a glass. More interesting is the distribution of the force constant η. As was shown in Ref. 21 (see also Ref. 22), at $\mid \eta \mid \ll 1$ the distribution should be proportional to $\mid \eta \mid$. The vanishing of $P(\eta,\xi)$ as $\eta \to 0$ in fact corresponds to the destruction of the soft potentials as a result of small random perturbations due to interaction with the environment. The influence of such perturbations is of great importance for soft potentials. The second fact that should be taken into account is that the dominant part of atomic potentials have parameters close to the standard value $\eta \approx 1$ for atomic (nonsoft) potentials in solids. Thus $P(\eta,\xi)$ should have a maximum at $\eta \approx 1$ and should rapidly decrease at as $\eta \to -\infty$. The soft modes we are interested in belong to the "tail" of the distribution. To describe low-temperature properties it is enough to express $P(\eta,\xi)$ in the form

$$P(\eta,\xi) = \mid \eta \mid P_0(\eta,\xi), \qquad (5)$$

where $P_0(\eta,\xi)$ is some nonsingular function that is finite at $\eta = 0$.

For two-well configurations with low interlevel spacing we can assume that $\mid \eta \mid \approx \eta_L \ll \delta\eta$, $\mid \xi \mid \approx \eta_L^{1/2} \ll \delta\xi$, where $\delta\eta$ and $\delta\xi$ are characteristic widths of the decrease of $P_0(\eta,\xi)$. In this case we can approximate $P_0(\eta,\xi)$ by the constant $P_0(0,0)$. As a result, combining Eqs. (4),(5) we get the following expression for the density of states (DOS) of two-level modes:[16]

$$n_0(E) = \frac{2^{5/2}\eta_L^2(\delta\eta)^{1/2}}{w}P_0(0,0) \equiv n_{\text{TLS}}. \qquad (6)$$

Thus the model of soft atomic potentials reproduces results of the model of two-level systems introduced in Refs. 3 and 4. The corresponding expression for the contribution of TLS's to the specific heat has the form[3,4]

$$C_{\text{TLS}}/T = \gamma_{\text{TLS}}, \quad \gamma_{\text{TLS}} = (\pi^2/6)n_{\text{TLS}}k_B^2. \qquad (7)$$

To be more accurate we should note that Eq. (7) makes use of the assumption that all the TLS's had enough time to relax during the measurement of the specific heat. At the same time it is well known that there is an exponentially wide distribution of relaxation rates in glasses and some TLS's would remain in a nonequilibrium state. To take this fact into account following Ref. 21 one should replace $\delta\eta$ in Eq. (6) by

$$\eta_c \equiv \min(\delta\eta, \eta_m), \quad \eta_m \equiv \frac{3^{2/3}}{2}\eta_L \ln^{2/3}\left(\frac{t_{\text{expt}}}{\tau_0(k_BT)}\right).$$

Here t_{expt} is the time of measurement while $\tau_0(E)$ is the relaxation time of a symmetric TLS with interlevel spacing E. In metallic glasses this relaxation is due to interaction with electrons in the normal state and with phonons in the superconducting one. In what follows we shall be interested in the last case where $\tau_0(E) = \hbar^4\rho s^5/D^2E^3$, and D is the characteristic value of the deformation potential of TLS's, while s is the sound velocity.

Now let us turn to the region of higher energies where

$$\hbar\omega_c \gg E \gg w. \qquad (8)$$

To get such an interlevel spacing one should consider a quasilocal mode due to a one-well potential with $\eta > 0$, $\eta \gg \eta_L$, $\mid \xi \mid < (32\eta/9)^{1/2}$ (see Refs. 11, 16, and

21). If inequality (8) holds, the anharmonicity of the potential (2) is small and one can omit the items proportional to $(x/a)^3$ and $(x/a)^4$. At the same time to take into account soft modes we are interested in the region $\eta \ll 1$. The density of states $n_H(E)$ corresponding to low-frequency quasiharmonic modes can be calculated straightforwardly from the definition $n(E) = \langle\delta[E - E(\eta,\xi)]\rangle$.

Such a calculation[21] (see also Refs. 16 and 23), assuming the validity of Eq. (2), yields

$$n_H(E) = \frac{1}{24} n_{\text{TLS}} \left(\frac{\eta_L}{\eta_c}\right)^{1/2} \left(\frac{E}{w}\right)^4 . \tag{9}$$

The corresponding contribution to the specific heat has the form

$$\frac{C_H}{T} = \beta T^4, \quad \beta = \frac{30 n_{\text{TLS}} k_B^6}{w^4} \left(\frac{\eta_L}{\eta_c}\right)^{1/2} . \tag{10}$$

Thus we have come to the important conclusion that the coefficients γ_{TLS} in Eq. (7) and β both are proportional to the quantity n_{TLS} and thus are related to each other. If both are known from the experiment, one can determine the quantity w which is very important to the model. Combining Eqs. (7) and (10) we get

$$w/k_B = (180\gamma_{\text{TLS}}/\pi^2\beta)^{1/4}(\eta_L/\eta_c)^{1/8}. \tag{11}$$

Note that this quantity is almost insensitive to the time of measurement.

Unfortunately the expression (7) is only applicable if the temperature is low enough. There are several sources of its violation. The first one is that if η is big enough one cannot replace the function $P_0(\eta,\xi)$ by a constant. The second one is more fundamental. As was shown in Ref. 23 the interaction between quasilocal modes drastically increases with the increase of their frequencies. This is natural because the density of these states increases with their frequency as ω^4. Several experiments concerning phonon propagation (though in dielectric glasses) show that such interaction should be important at frequencies of the order of 1 THz that corresponds to the temperature $\approx$6–7 K. (Note that $n_H \propto E^4$ and the characteristic value of E is several k_BT.) One can make similar conclusions from the results of computer simulations of vibrational modes.[19,20] According to estimates given in Ref. 23 at higher energies the energy dependence of the density of vibrational states should be smoother than the energy dependence of the Debye DOS. As a result, the temperature dependence of the caloric Debye temperature, $\Theta(T)$, should be nonmonotonous: At very low temperatures it should be constant; then it should decrease with increasing temperature due to the fast increase of the density of quasilocal modes with their energy and at higher temperatures it should increase due to the weaker (than E^4) energy dependence of the vibrational DOS. This qualitative behavior is in reasonable agreement with the experimental data (see Fig. 3).

Now let us turn to a quantitative interpretation of the experimental data. According to the considerations given above at very low temperatures where the samples are in the superconducting state the specific heat is determined by TLS's and described by Eq. (7). Another simple expression for C/T exists at $T > T_1 \approx w/5k_B$. In this region there are three important contributions to the specific heat which are due to conduction electrons, to long wavelength extended vibrational modes (phonons) which we shall describe by the Debye model, and to quasilocal, nearly harmonic vibrational modes. In this region we have

$$C/T = \gamma_{\text{el}} + \alpha T^2 + \beta T^4. \tag{12}$$

Here αT^2 is the usual Debye term $\alpha \equiv a_3$, $\beta \equiv a_5$. It can be shown that the electron-induced anharmonic correction to the quantity C/T [which is proportional to $(T/\epsilon_F)^2$] is much smaller.

Having in mind that the characteristic energy of the excitations in the region (8) is of the order of (4–5)k_BT [because $n_H(E) \propto E^4$] it is reasonable to fit the experimental data by Eq. (7) only in the region 1.5–6.5 K. This fit allows to determine the coefficients in Eq. (12). The quantity γ_{TLS} can be determined from the experimental data for very low temperatures where the specific heat is almost linear in T while the sample is in its superconducting state and electronic degrees of freedom are frozen out. Having the quantities α, γ_{TLS}, and β one can determine the effective Debye energy Θ_0 and the characteristic energy w for the quasilocal vibrations. It can be shown that in a realistic situation $\delta\eta > \eta_m$, and we come to the following expression for w:

$$\frac{w}{k_B} = \left(\frac{180\gamma_{\text{TLS}}}{\pi^2\beta}\right)^{1/4} \left[\frac{2^{3/2}}{3\ln\left(t_{\text{expt}}/\tau_0\right)}\right]^{1/12} . \tag{13}$$

One can also determine other characteristic parameters of the model (see Ref. 16): the energy $\mathcal{E}$

$$\mathcal{E} = (\hbar\omega_c/16)(\hbar\omega_c/w)^3 \tag{14}$$

and the characteristic number of atoms which participate in a typical soft mode,

$$N = (\hbar^2\omega_c)^2/16Ma^2w^3. \tag{15}$$

It is not so easy to estimate the characteristic frequency ω_c of atomic vibrations because in real materials there are important corrections to the Debye model at high frequencies. In Ref. 16 the frequency of the lowest DOS maximum was taken for ω_c. This frequency appears to be about 2/3 times the Debye frequency determined from the sound velocity measurements. The Debye temperature Θ_0 can be also estimated from Eq. (1). At the same time, according to many experiments [see e.g., Fig. 1 in the review article (Ref. 24) where the dependences C/T vs T^2 are plotted and Refs. 7 and 25] in amorphous materials there exists an additional contribution to the specific heat which is proportional to T^3 and could be interpreted as the Debye one. One can understand this fact qualitatively having assumed that some anharmonic quasilocal modes also contribute to the T^3 term in the specific heat. As a result, the effective Debye frequency determined from the specific heat data should be greater than the one obtained from the sound velocity.

In our estimates it would be reasonable to assume that ω_c corresponds to the most pronounced peak in the vibrational DOS (see Ref. 16). Unfortunately we do not have results of a neutron analysis of Zr-Rh-Pd metallic glasses. This is why in the following for rough estimates we put $\omega_c = k_B\Theta_0/\hbar$ where Θ_0 is determined from the specific heat data. The reason for this assumption is an analogy with other glasses where the data on the neutron scattering and sound velocity are accessible. The other quantity we need is the characteristic length a. Following Ref. 16 we assume here $a \approx d/2$ where d is the interatomic spacing determined from the sample's density.

The result of such a fit is given in Table I. One should have in mind that the quantity w is the one that is determined directly while the others (E, ω_c, and N) are calculated under the assumption that $\omega_c \approx k_B\Theta_0/\hbar$. The number of atoms ($N \approx 20$) participating in a soft mode appears to be of the same order of magnitude as obtained with the help of computer simulations for a model glass (in Refs. 19 and 20). Note that the estimates given above provided a reasonable order of magnitude for all the characteristic parameters of soft modes which are not far from the corresponding parameters in dielectric glasses (see Ref. 16).

It is very interesting that there is a correlation between the values of γ_{TLS} and a_3, such that the increase of the first quantity is followed by an increase of the effective Debye temperature Θ_0. Such a correlation was also observed for some dielectric glasses while for other ones the correlation is quite opposite [see Fig. 3 in the review article (Ref. 24)].

IV. CONCLUSION

Finally we summarize that the temperature dependence of the specific heat in Zr-Rh-Pd metallic glasses can be reasonably well explained in the framework of the model[10] of soft atomic vibrational states. According to our interpretation, the physical nature of soft vibrational modes in all the glassy alloys investigated is the same while their number is dependent on preparing conditions.

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