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Low-Temperature Properties of a Superconducting Disordered Metal

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Specific heat C_p and thermal conductivity κ measurements between 0.1 and 10 K on the superconducting ($T_c = 2.53$ K) and structurally disordered metal $Zr_{0.7}Pd_{0.3}$ exhibit an approximately linear term in C_p and a $T^{1.9}$ dependence of κ below T_c. The magnitudes of these terms are close to those found for insulating glasses, thereby suggesting that disorder-induced localized excitations exist at similar densities in very different classes of disordered solids.

Metallic glasses present a unique opportunity for understanding how the basic low-temperature thermodynamic properties and phonon and electron transport of metals are affected by structural disorder. For example, although there is direct evidence[1] for a preferential softening of transverse phonons in the disordered state relative to the crystal, leading to an enhanced phonon specific heat at low temperatures, there is no way to predict with any certainty the corresponding changes of the electronic specific heat. Recent measurements of thermal conductivity,[2] sound velocity,[3,4] and resonant acoustic absorption[4] in metallic glasses indirectly suggest that there may exist extra localized excitations at energies below 1 K similar to those found in insulating glasses.[5-7] Direct evidence in disordered metals for these excitations, usually described as two-level configurational or tunneling systems,[8,9] would support the intrinsic nature of these states in the amorphous phase,[10] particularly since metallic glasses, unlike insulators, possess rather closely packed structures with mass densities only a few percent lower than those in their crystalline phases.

In the present work, we have measured the specific heat C_p of a bulk disordered metallic alloy,[11,12] a-$Zr_{0.7}Pd_{0.3}$, between 0.1 and 10 K. Since this material is *superconducting below 2.53 K*, it is possible to evaluate the individual contributions to C_p in this temperature region. We find that the observed specific heat *cannot* be accounted for solely by the phonon and electron contributions. An additional contribution, approximately linear in T, is observed, whose magnitude is strikingly similar to that observed below 1 K for insulating glasses. In addition, we observe a thermal conductivity in the superconducting state whose temperature dependence is $T^{1.9}$, also remarkably similar to that found in insulating glasses. We suggest that there are no fundamental differences between the disorder-induced excitations found in this disordered metal and those found in insulating glasses.

The sample of $Zr_{0.7}Pd_{0.3}$ was prepared in bulk form from the melt[13] as a ribbon of cross section 0.085×0.0032 cm. X-ray diffraction measurements yielded results similar to those found previously.[11] A 1.2 m length of ribbon (0.259 g) was wound into a spiral of 1 cm o.d. and glued with a minimum amount of GE 7031 varnish onto the sapphire-plate sample holder of a calorim-

eter[14] in a ^{3}He-^{4}He dilution refrigerator for low-temperature C_p measurements, $T<2$ K, or a pulse calorimeter for $T>1.5$ K. Good agreement was obtained in the region of overlap. The addendum contributed ~20% of the total heat capacity at the lowest temperatures. The onset of superconductivity was observed at $T_c=2.53\pm0.01$ K with a (10–90)% resistive transition width of 10 mK and a C_p width of 30 mK. The thermal conductivity of a 0.5 cm length of ribbon was measured by a two-heater one-thermometer technique.[15] The carbon thermometer was calibrated during each run against a cerium magnesium nitrate–superconducting quantum interence device (SQUID) thermometer.[16] Because of the very low thermal conductance of the sample, the electrical leads had to be of extremely low thermal conductance to avoid short thermal paths to the bath. Each of the six 8-cm-long leads consisted of a few ~5-μm filaments extracted from NbTi filamentary wire. The ambient magnetic field was less than 1 Oe.

The specific heat (Fig. 1) varies over more than four orders of magnitude between 0.1 and 10 K. Below the discontinuity at T_c, C_p drops rapidly until $T\approx0.4$ K, below which a roughly linear T dependence is visible. The data were fitted above T_c by the expression

$$C_p=AT+BT^3+CT^5, \tag{1}$$

and below T_c by

$$C_p=DT+BT^3+E\exp(-F/T)+G[T/T_c]^{(4+T/T_c)}. \tag{2}$$

In Eq. (1), the first term accounts predominantly for the normal electronic contribution, while the second and third terms describe the phonon specific heat. The first term in Eq. (2) is included as the simplest representation of the extra specific heat at the lowest temperatures. We take the same phonon T^3 term above and below T_c, but neglect the (small) T^5 term in the superconducting state. The third and fourth terms in Eq. (2) represent the contribution of the electrons below T_c. The analytical form of the fourth term was found to be a convenient representation of the deviations of the Mühlschlegel numerical calculations[17] from a simple exponential. The fourth term is significant only for $1.5<T<2.53$ K.

A nonlinear least-squares fit of Eqs. (1) and (2) to the data was performed with $T_c=2.53$ K. The various terms[18] are indicated by broken lines in Fig. 1 and the sum by the solid line. Good agreement with the data is obtained except for a few points at the lowest temperatures which lie no more than 10% above the calculated fit. Data were not taken below 90 mK because of long internal equilibration times, which may also account for the high values of the last few points. The three contributions below T_c are comparable at $T=0.5$ K but the linear term rapidly dominates at lower T. We note that the coefficient of this term is 2.2% of the coefficient of the linear term above T_c. We assume that the linear term below T_c is not due to normal-state electrons,[19] and thus it should also be present above T_c. The electronic term is therefore 2.2% less than A, which, for comparison, is 4.3 times larger than that of Cu. The T^3 coefficient corresponds to a Debye temperature θ_D of 180 K. The ratio of superconducting- to normal-state electronic specific heat

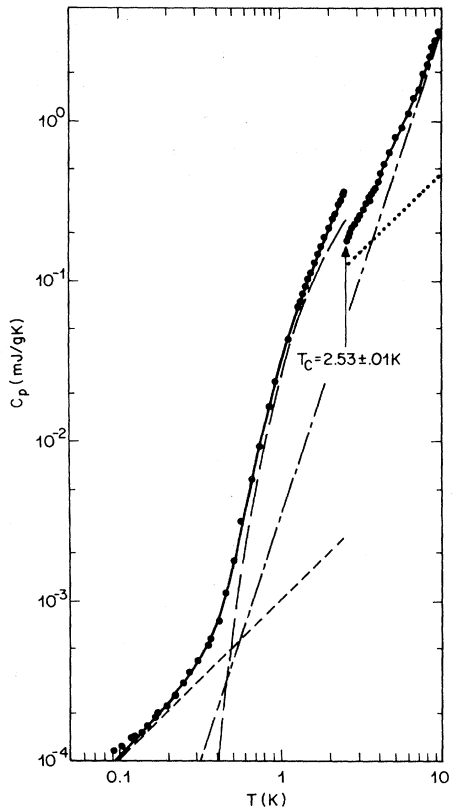

FIG. 1. Heat capacity of the superconducting disordered metal $Zr_{0.7}Pd_{0.3}$. The solid line is a fit to the data using Eqs. (1) and (2). The individual components are indicated as follows: ...., electrons above T_c; – –, electrons below T_c; –·–·, phonons; and – – – –, extra contribution linear in T.

at T_c is 2.61, or only 7% larger than expected from theory.[17] Alternatively, the exponent F can be identified with Δ_0/k_B, where Δ_0 is the energy gap at $T=0$, yielding $\Delta_0 = 1.47 k_B T_c$, or 16% less than the theoretical value. The material therefore seems to be a fairly well-behaved superconductor.

The thermal conductivity (Fig. 2) is described quite well below 1 K by a single power law,

$$\kappa\,(\mathrm{W\ cm^{-1}\ K^{-1}}) = [(8.6 \pm 1)\times 10^{-4}]T^{1.9\pm 0.05},$$

for over an order of magnitude in temperature. Above T_c, the data vary linearly as κ (W cm^{-1} K^{-1}) $= (6.7\times 10^{-4})T$. The Wiedemann-Franz law predicts an electronic thermal conductivity which is only one-sixth of the observed κ, indicating that κ is dominated by phonon conduction above T_c. The observed κ above T_c agrees both in magnitude, within 50%, and in temperature dependence, linear in T, with the phonon conductivity expected from normal electron-phonon interactions.[20] The rise in κ just below T_c can then be understood as decreased phonon-electron scattering due to the rapidly decreasing number of normal-state electrons below T_c. The $T^{1.9}$ dependence of κ must therefore arise from some other scattering mechanism. Even though we expect the phonon mean free path to become comparable with the sample thickness below 0.3 K, we do not observe behavior characteristic of boundary scattering.[2,21]

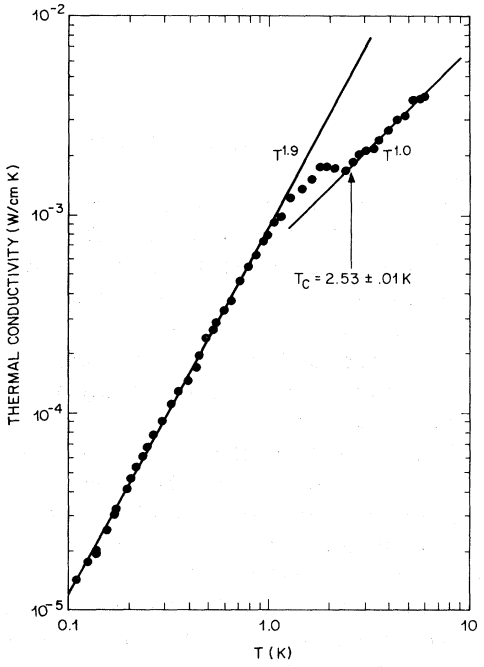

FIG. 2. Thermal conductivity of the superconducting disordered metal $Zr_{0.7}Pd_{0.3}$.

The linear specific heat and approximately quadratic thermal conductivity of this material below T_c are strikingly similar to those properties in typical insulating glasses,[6] for which the coefficient of the linear term in C_p lies in the range $(0.4\text{–}6)\times 10^{-3}$ mJ/gK^2 and the coefficient of the $T^{1.9}$ thermal conductivity is in the range 10^{-4}–10^{-3} W cm^{-1} K^{-3}. The present values are thus near the low end of the C_p range and the high end of the κ range. If we interpret the linear specific heat as arising from two-level configurational systems as in amorphous insulators, we obtain a density of states[8,9]

$$n_0 = \frac{6D\rho}{\pi^2 k_B{}^2} = 2.7\times 10^{33}\ \mathrm{erg^{-1}\ cm^{-3}}.$$

In the Debye approximation[22] we find $\Theta_D = 180$ K and estimate a transverse phonon velocity $v_T \cong 1.6\times 10^5$ cm/sec. We can then use the expression for phonon conductivity as limited by resonant scattering from two-level states,[23]

$$\kappa(T) = 1.645(\rho k_B{}^3/\pi^3\hbar^2)(v_L/\tilde{n}\gamma_L{}^2 + 2v_T/\tilde{n}\gamma_T{}^2)T^2,$$

to determine $\tilde{n}\gamma_T{}^2$ if we make the reasonable assumptions that $v_L = 2v_T$ and $\gamma_L{}^2 = 2\gamma_T{}^2$, where γ_L and γ_T are the deformation potentials for the two-level systems coupled to longitudinal and transverse phonons, respectively. Here, $\tilde{n}$ is the density of two-level systems which are active in resonantly absorbing phonons and which for fused silica is[24] approximately 4% of n_0, the density of states calculated from the linear heat capacity. We calculate $\tilde{n}\gamma_T{}^2 \cong 5\times 10^7$ erg cm^{-3} for a-$Zr_{0.7}Pd_{0.3}$. This value is surprisingly close to the value of 9×10^7 erg cm^{-3} found in fused silica.

We conclude that the anomalous specific heat and thermal conductivity of this disordered metal below 1 K are due to the intrinsic defects characteristic of the disordered state. While the microscopic nature of these two-level states is yet unknown, it is surprising that their density and their coupling to acoustic phonons in a densely packed disordered metal are so similar to those properties in the much more loosely packed network structures of dielectric glasses.

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[19]We have considered the possibility that normal-state regions may exist in our sample below 2.5 K. An upper limit of 0.1% can be imposed on the volume of any *crystalline* second phase as a result of a Siemen-Bollins x-ray study of a 1 cm section of ribbon adjacent to the C_p sample. Furthermore, we note that the crystalline phase which is stable at 600°C is superconducting below ~1 K (Ref. 13). Regions of normal-state *disordered* material seem unlikely in view of the sharpness of the superconducting transition.

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