

Influence of structural relaxation on the low-temperature properties of glassy metals

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The thermal conductivity κ of glassy metals is shown to change reversibly with heat treatment at temperatures T_A near the glass transition. If the change in κ is interpreted as resulting from a change in the density $n(E)$ of the two-level states found in amorphous solids, the observed dependence of $n(E)$ on T_A is in qualitative agreement with a prediction of a free-volume model for the glass transition.

The structure of a glass can be manipulated by subjecting the glass to heat treatment near the glass transition temperature T_g . The resulting changes in atomic configuration modify the spectrum of low-energy excitations¹ which are responsible for the anomalous and universal properties of amorphous solids at temperatures $T \leq 1$ K. The purpose of our work has been to observe the effect of "reversible" heat treatment² on the low-temperature properties of a glass so as to obtain information concerning the structural origin of the unknown excitations.

A successful phenomenological model for glasses³ considers the localized, low-energy excitation to be a two-level state (TLS) having an energy splitting of E . A density $n(E)$ of such states, with $n(E)$ nearly independent of E , explains the observed specific heat, which is roughly linear in T , the phonon thermal conductivity κ , which is roughly proportional to T^2 , and other properties.¹ It is speculated that the TLS arise because of the tunneling of some entity between neighboring potential-energy wells associated with the disorder in the solid.

For our study of the TLS we have selected glassy metals since changes in atomic configuration can be produced in relatively short times⁴ at furnace temperatures ≤ 600 K, since the thermal relaxation of glassy metals has been studied extensively,⁵ and since theories of atomic relaxation have been suggested for glassy metals,⁶⁻⁸ including computer modeling.^{6,9,10} The response of a glassy metal to a series of isochronal "anneals" is exemplified by the data for Pd-Si-Cu shown in Fig. 1. The sample was quenched from an annealing temperature of T_A , then the electrical resistance R was measured at 4.2 K. As T_A increases, R decreases irreversibly along the sequence AB . The line CB may then be traced essentially reversibly as long as the temperature at B is not exceeded.¹¹ If the temperature at B is exceeded, the irreversible curve AB continues to D . Then line ED may be traced reversibly as long as the temperature at D is not exceeded. Other properties of glassy metals also respond reversibly to heat treatment.^{5,12-15} Oxide glasses^{12,16,17} and amorphous polymers¹⁸ exhibit analogous behavior.

The effect of irreversible annealing (line ABD of Fig. 1) on the TLS density of states, $n(E)$, has been studied previously.¹⁹⁻²¹ Irreversible changes in atomic configuration appeared to reduce the magnitude of $n(E)$. Our purpose was to observe the effect on $n(E)$ of reversible changes as

represented by curve CB of Fig. 1. A change in $n(E)$ is monitored most directly by measuring the specific heat C , since $C \propto n(E)$. However, we chose to measure the phonon thermal conductivity $\kappa \propto 1/n(E)$ since κ can be measured with greater precision and since sample mounting arrangements are more compatible with high-temperature heat treatment.

We used two different types of metallic glasses and observed similar results in each. One was the well-studied transition-metal-metalloid-based glass, $\text{Pd}_{0.775}\text{Si}_{0.165}\text{Cu}_{0.06}$ in the form of a wire of 2.9×10^{-2} cm diameter. The phonon thermal conductivity κ was extracted from the total conductivity by using the Wiedemann-Franz law and measured resistances. The other sample was a 3.7×10^{-3} -cm-thick, 0.17-cm-wide ribbon of the simple-metal-transition-metal alloy Zr_3Rh . This alloy contains no "glass formers" and also is superconducting below ≈ 4.1 K, thereby avoiding

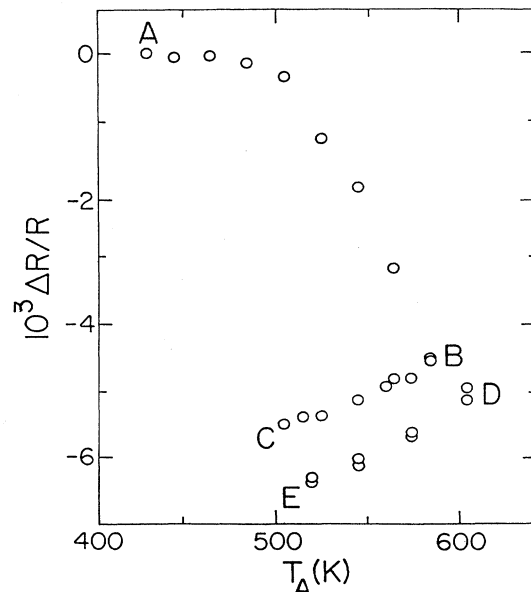


FIG. 1. Fractional change in electrical resistance R , measured at 4.2 K, of glassy Pd-Si-Cu following a series of 15-min isochronal anneals at temperature T_A . This sample is not that used for Fig. 2(a).

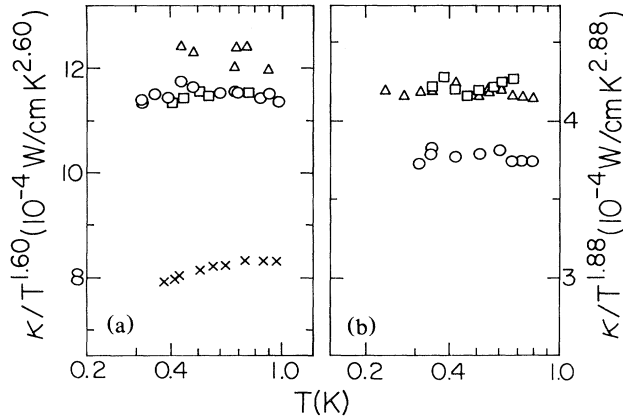


FIG. 2. Phonon thermal conductivity κ for two glassy metals, divided by T^n to allow expansion of the vertical scale. (a) Pd-Si-Cu ($T_g = 636$ K): \times , as received; \circ , $T_A = 570$ K for 50 min (irreversible change in κ); Δ , $T_A = 520$ K for 20 min (reversible change); \square , $T_A = 570$ K for 15 min (reversible change). (b) Superconducting Zr-Rh ($T_g \approx 700$ K), reversible changes in κ : Δ , $T_A = 548$ K for 40 h to establish a quasiequilibrium state (Ref. 15); \circ , $T_A = 615$ K for 0.33 h; \square , $T_A = 545$ K for 43 h.

the complication of conduction electrons. To heat treat a sample similarly supported at both ends, the thermometers were removed and the sample and holder placed in a furnace above a He cryostat. The anneals were carried out in a He atmosphere, the samples were then quenched to 300 K in He vapor at rates up to 10^3 K/sec. They could be lowered into the liquid He to observe the new resistance (Fig. 1) or, for ZrRh, the new superconducting transition temperature.^{14,15} Thus we could be certain that the desired change in atomic configuration had occurred. Thermometers were then remounted at precisely the same positions, and the samples placed in the dilution refrigerator. The relative accuracy of the measurements was $\approx 1\%$.

The data are displayed in Fig. 2. Figure 2(a) shows both the irreversible increase in κ observed previously¹⁹ for Pd-Si-Cu and, for the first time, a reversible change occurring within the equivalent range CB of Fig. 1. Figure 2(b) shows a similar 10% reversible change in κ for Zr-Rh. An inverse relationship between κ and T_A is consistent with our data as shown in Table I.

The phonon thermal conductivity depends on several parameters, $\kappa \propto (A/L)v[n(E)M^2]^{-1}$, where A/L is the dimensional factor for the sample, v is an average phonon velocity, and M is a deformation potential representing the strength of TLS-phonon coupling.¹ The observed changes in κ most likely arise from changes in $n(E)M^2$. The mass density, and hence A/L , changes by less than 1%. The ultrasonic velocity v of Pd-Si-Cu changes^{13,22} less than 2% during the entire irreversible change in κ shown in Fig. 2(a). A number of measurements²⁰ on Zr-Ni and Zr-Cu have found the same fractional change in κ as in the specific heat following (irreversible) anneals, which suggests that changes in κ are, in fact, dominated by changes in $n(E)$. However, recent measurements²³ on Zr-Cu detected irreversible changes in κ but not in specific heat. Thus at present we can only conclude that the product $n(E)M^2$ changes by $\approx 10\%$ as a consequence of our heat treatment, and therefore that the dependence $n(E)M^2 \propto T_A$ is consistent with

TABLE I. Phonon thermal conductivity at 0.5 K, $\kappa_{0.5}$, multiplied by heat-treatment temperature T_A for two glassy metals. For Pd-Si-Cu, $\kappa_{0.5}$ could be $\approx 30\%$ larger if electron-phonon scattering were subtracted. The corrected $\kappa_{0.5}T_A$, however, remains constant.

Sample	T_A (K)	$\kappa_{0.5}T_A$ (W/cm)
Pd-Si-Cu	570	0.217
	520	0.211
	570	0.216
Zr-Rh	548	0.0622
	615	0.0630
	545	0.0625

our results.

An explanation for a T_A dependence of $n(E)$ is found in a free-volume model of a glass.⁷ This free-volume model was originally developed to explain relaxation phenomena near T_g . It is suggested⁷ that the TLS should be assigned to tunneling of atoms adjacent to voids, the voids arising naturally within the model. The free volume V_F establishes the total number of voids or TLS [i.e., $\int n(E)dE$] present in a sample, thus $n(E) \propto V_F$, while T_g determines the energy scale or breadth of $n(E)$ and hence $n(E) \propto 1/T_g$. Experimental evidence for the dependence of $n(E)$ on $1/T_g$ was noted²⁴ in literature data for specific heat and thermal conductivity, and has found further support in recent measurements of specific heat²⁵ and ultrasonic properties.^{26,27} Our present interest is in the dependence of $n(E)$ on free volume. The authors⁷ estimate

$$V_F = G \{ (T - T_0) + [(T - T_0)^2 + HT^2]^{1/2} \}$$

with G , H , and T_0 constants. For the materials considered in Ref. 7, $T_0 > T_g$. With $T \ll T_0$, $V_F \propto T$. Hence, in this limit $n(E) \propto T$. The temperature T refers to the temperature at which the free volume is established. Thus we equate T of the model to our T_A , the temperature from which the sample was quenched. In this approximation $n(E) \propto T_A$, which is consistent with the experimental results of Table I, provided that M^2 remains constant.

In summary, we have shown that the thermal conductivity κ of glassy metals can be changed reversibly by appropriate heat treatment at temperatures T_A near the glass transition. The change in κ can be interpreted as resulting either from a change in the density $n(E)$ of TLS, or a change in the coupling M between TLS and phonons. The observed behavior should occur also in other amorphous solids, such as polymers and oxide glasses, since a "reversible" response to thermal treatment near T_g is common to these materials.

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