Phonon transport in glassy metals below 100 K

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The phonon thermal conductivities of glassy metals, whether quenched from the melt or electrodeposited, have the same magnitude and temperature dependence as nonmetallic amorphous materials. For glassy Pd-Si, the temperature dependences of the acoustic velocities below 4 K are also similar to those found in dielectric glasses. The thermal conductivity deduced from these velocity measurements using the theory of tunnel states does not agree with the measured thermal conductivity.

I. INTRODUCTION

At low temperatures the properties of a variety of amorphous materials are remarkably similar, both in magnitude and temperature dependence.[1] As one example appropriate to this paper, the thermal conductivity decreases with decreasing temperature below room temperature, becomes only weakly temperature dependent near 10 K (often referred to as the plateau), then attains a nearly T^2 dependence below ≈1 K. This behavior, shown in Fig. 1, occurs for fused quartz, epoxy, rubber, frozen grease, etc., thus indicating that it is the glassy structure which is important rather than the chemical composition of the material.

An explanation for the unusual behavior of glassy materials is provided by a model which assumes that atoms or groups of atoms reorient via quantum-mechanical tunneling.[2,3] The resulting localized excitations would scatter phonons and limit the thermal conductivity, would provide a specific heat in excess of that provided by phonons, and would in general affect most low-temperature properties of amorphous materials.[1] It has been shown that the additional excitations present in glassy materials are highly localized[4]; more importantly phonon echos,[5] saturation of attenuation,[6,7] and other acoustical phenomena predicted by the theory can be observed.

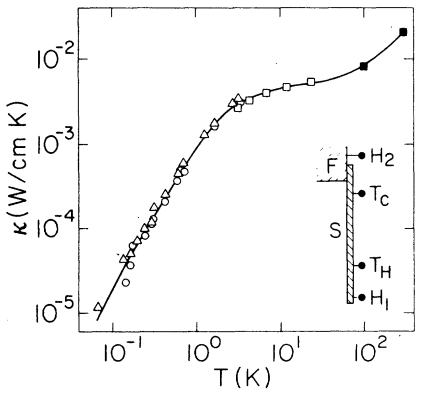

FIG. 1. Phonon thermal conductivity κ of gla Pd-Si vs temperature. The magnitude and temperature pendence of the conductivity is characteristic of non metallic amorphous materials. Open data from Refs. 16 and 17; closed data from Ref. 18. The inset shows schematically the experimental arrangement. S, sample; F, heat sink; T_C, T_H, thermometers; H_1, H_2, electr al heaters.

Even though the tunneling theory has achieved notable success, a physical description of the entity which undergoes tunneling remains uncertain. There is some evidence that the tunneling entity is rather large or massive,[8] and there is evidence that different classes of localized excitations contribute to different physical properties.[9] We felt that the glassy metals might provide additional information on these questions. The glassy metals are tightly packed, having a ≈2% difference in density between the glassy and crystalline states (cf. ≈20% for quartz), and voids as large as vacancies occur infrequently in these metals.[10,11] Hence, if tunneling can occur, a theoretical treatment should be simpler than for a covalently bonded glass or a polymer.

Specific-heat measurements[12,13] on glassy metallic alloys quenched from the melt failed to detect the characteristic excess specific heat found in amorphous dielectrics (which varies as T^n at low temperatures,[1] $n \approx 1$); the nonelectronic portion of the specific heat appeared to be accounted for by a Debye-phonon specific heat calculated using measured sound velocities. The term in T^n was also absent[14] in the specific heat of vapor-quenched amorphous metallic alloys. Finally, acoustic measurements[15] on electrodeposited glassy Ni-P initially did not exhibit the saturation of attenuation nor the temperature-dependent velocity found in dielectric glasses.

These differences between glassy metals and other amorphous materials led us previously to measure the phonon thermal conductivity of glassy Pd-Si. Glassy Pd-Si was selected since it is relatively simple to glassify and is nonmagnetic. The

thermal conductivity was measured because it is less difficult to extract the phonon contribution as compared to the specific heat. We found[16-18] that the phonon thermal conductivity of glassy Pd-Si has the behavior typical of other amorphous materials, see Fig. 1. The results were quite independent of quenching technique (rate), size of sample, etc. But since Pd-Si is unique in that it forms the glassy state so readily, we have in the present paper examined several amorphous alloys which quench from the melt with greater difficulty. In addition we have investigated glassy metals formed by an entirely different technique, room-temperature electrodeposition. We have found that all of the glassy metal samples have a phonon thermal conductivity similar to that in amorphous dielectric materials.

Finally, as a test of the applicability of the tunneling theory to glassy metals, we have measured the temperature dependence of the velocity of sound in Pd-Si below 4 K to determine if the interaction of phonons with the localized excitations is of the same magnitude as that deduced from the thermal conductivity data. Although this temperature dependence is similar to that found in nonmetallic glasses, the magnitude is smaller than predicted from the thermal conductivity measurements using the tunneling theory. Additional discussion is presented in Sec. III.

II. TECHNIQUE AND RESULTS

The samples are listed in Table I. The Ni-P and Fe-P were obtained from Logan,[19] the Pd-Si wire, Fe-Ni, and Ti-Be materials were obtained from a commercial source,[20] and the Pd-Si rods were formed in our laboratory.[16] All samples were quenched from the melt except the Ni-P and Fe-P which were electrodeposited. Electron diffraction studies of the Fe-P, Fe-Ni, Pd-Si wire and Pd-Si rod gave no evidence for the presence of crystallinity.

In earlier work[16] on samples of Pd-Si wire and Pd-Si rod we concentrated on different measurement and quenching techniques to be certain the data were reliable and representative of amorphous Pd-Si. Thus in the present measurements only the most convenient experimental arrangement has been used. For data obtained below $\approx$2 K, the arrangement is shown in the inset of Fig. 1. The resistance thermometers were chips cut from Matsushita resistors[21] and mounted on Pt tabs. The tabs were spot welded to the samples; they were also used as potential leads for electrical resistivity measurements. The lower thermometer (T_H) was calibrated against a magnetic thermometer[22] which in turn had been calibrated against ^{3}He vapor pressure and a set of superconducting fixed points.[23] The uncalibrated thermometer (T_C) was maintained at constant temperature during a measurement through electronic control of heater H_2. Heater H_1, a strain gauge, provided the measured heat flux. Electrical leads of superconducting 7-μm NbTi filaments[24] were used to provide sufficient thermal isolation, since the thermal conductance of the samples was very small.

At temperatures above $\approx$2 K the samples were mounted within the vacuum chamber of a simple ^{4}He cryostat. Thermometers T_C and T_H (Fig. 1) were chromel-constantan thermocouples. The heat sink F was held at a different, though constant, temperature for each measurement. The thermocouples were referenced to a separate heat sink which was maintained at a fixed temperature. The thermocouples were calibrated in place against Ge resistance thermometers. The reversing switches for the thermocouple measurements were immersed in the ^{4}He bath to eliminate problems of thermal emf in the electrical leads. As a test of both the low- and high-temperature techniques, several samples of the Fe-Ni were measured and found to reproduce within the $\approx$5% scatter in the data and to agree in the region of overlap.

TABLE I. Characteristics of the glassy metal samples. The electrical residual-resistivity ratios are referenced to 4.2 K, but are essentially independent of temperature.

Sample	Composition	Cross section (cm)	Residual-resistivity ratio
Ni-P	$Ni_{0.86}P_{0.14}$	0.03 × 0.27	0.978
Fe-P	$Fe_{0.84}P_{0.16}$	0.014 × 0.41	0.973
Fe-Ni[a]	$Fe_{0.32}Ni_{0.36}Cr_{0.14}P_{0.12}B_{0.06}$	0.0053 × 0.29	1.015
Ti-Be[b]	$Ti_{0.50}Be_{0.40}Zr_{0.10}$	0.005 × 0.076	1.06
Pd-Si wire[c]	$Pd_{0.775}Si_{0.165}Cu_{0.06}$	0.025 diam	0.964
Pd-Si rod	$Pd_{0.775}Si_{0.165}Cu_{0.06}$	0.2 diam	0.963

[a]Allied Chemical 2826A ribbon.
[b]Allied Chemical 2204 ribbon.
[c]Allied Chemical 4614 wire.

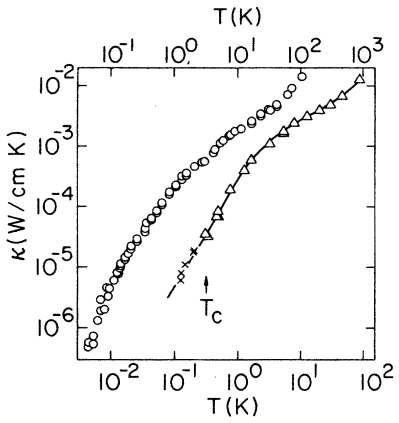

FIG. 2. Phonon thermal conductivity κ of Fe-Ni (○, top scale) and Ti-Be (△, bottom scale) vs temperature. The Ti-Be becomes superconducting at T_c; the data indicated by × were obtained in the superconducting state.

We are interested in the thermal conductance contributed by the phonons, while the measurements provide the total thermal conductance of phonons and electrons. The electronic contribution is subtracted off using the Wiedemann-Franz law since the electrical residual resistivity ratio is near unity (Table I). The resulting thermal conductivity due to phonons is plotted in Figs. 1–3.

A qualitative test of the subtraction procedure is provided by the Ti-Be samples, which undergo a superconducting transition near $T_c \simeq 0.315$ K as determined from the electrical resistivity and the ac magnetic susceptibility measurements shown in Fig. 4. The electronic contribution to the thermal conductivity decreases rapidly as the temperature is reduced below T_c. Yet when the calculated value[25] of the electronic contribution is subtracted, the resulting curve, Fig. 3, is a smooth extrapolation of data taken above T_c. In brief, we have evidence that the subtraction procedure does provide the thermal conductivity associated only with the thermal phonons.

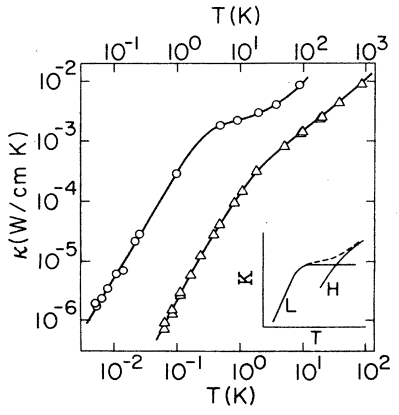

FIG. 3. Phonon thermal conductivity κ of glassy Ni-P (○, top scale) and Fe-P (△, bottom scale) vs temperature. The inset indicates how the phonon thermal conductivity (dashed line) comprises two contributions, that from low-frequency phonons (L) plus that from high-frequency phonons (H).

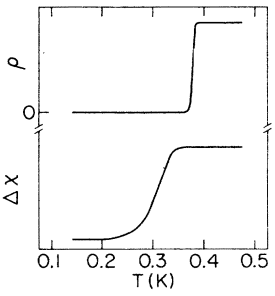

FIG. 4. Electrical resistivity ρ and magnetic susceptibility χ vs temperature for Ti-Be near the superconducting transition at 0.315 K. Both ρ and χ are plotted in arbitrary units. The χ was measured at 400 Hz.

Changes in the acoustic velocities of Pd-Si rod were measured in a second dilution refrigerator using quartz transducers in a pulse-echo-overlap method.[26] The results are displayed in Fig. 5.

III. DISCUSSION

The phonon scattering which causes the relatively small thermal conductivity shown in Figs. 1–3 could conceivably arise from four sources: the conduction electrons, domain boundaries or other magnetic excitations in the magnetic samples, nonspecular boundary scattering, or the localized states of the amorphous structure. It has been argued previously[16] that electron scattering enters only near 1 K, and then only to order 10%. This conclusion is supported by the results shown in Fig. 3 for the Ti-Be; the phonon scattering is essentially the same in the superconducting state as in the normal state. The possibility of magnetic scattering was checked by applying a magnetic field[27] of $10^{-2}T$ to the Fe-Ni. The thermal conductivity was unchanged within ≈1% at 0.1 and at 10 K. Hence magnetic scattering appears not to be important.

Nonspecular boundary scattering is characterized by a T^3 temperature dependence. The data below 0.1 K for Fe-Ni, Fig. 2, do appear to follow a T^3 dependence which could result from boundary

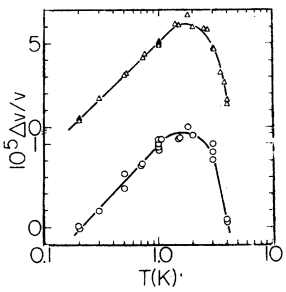

FIG. 5. Relative change in acoustic velocity v of glassy Pd-Si rod at 47 MHz, vs temperature. △, transverse mode; ○, longitudinal mode.

scattering, either from the surfaces of the ribbon or from crystallites within the ribbon. However, nonspecular boundary scattering of phonons is usually absent at the surface of a glassy material.[16,28] On the other hand, if crystallites (or clusters) were present similar to those observed in other glassy metals,[29] only 10^{-6} of the sample would have to be crystallized to explain the T^3 behavior. This is well below the resolution of our electron diffraction studies. Finally, the apparent T^3 behavior might be ascribed to a small systematic error; at 0.05 K the phonon conduction is only ≈10% of the total thermal conduction.

We therefore suggest that, with the possible exception of the Fe-Ni below 0.1 K, phonon scattering in metallic glasses is dominated by the localized states which are intrinsic to amorphous materials. There are three additional arguments to support this hypothesis.

Below ≈1 K the thermal conductivity of the alloys varies approximately as T^2, which is characteristic of nonmetallic glasses. The phonon mean free path can be estimated using the dominant phonon and Debye approximations

$$\kappa = 4.1 \times 10^{10} l T^3 v^{-2} \ (\mathrm{W/cm\,K}), \tag{1}$$

where $v^{-2} = \frac{1}{3}(v_l^{-2} + 2v_t^{-2})$, and v_l and v_t represent the longitudinal and transverse-phonon velocities. Near 0.2 K ($\approx 2 \times 10^{10}$ Hz), where the $\approx T^2$ behavior is well established, Eq. (1) gives[30] 9×10^{-3} cm for Pd-Si and 4×10^{-3} cm for Ni-P. These values may be compared with the similar mean free paths of 6×10^{-3} and 3×10^{-3} cm observed for fused quartz[1] and borosilicate glass.[4]

A well-resolved plateau near 10 K, another characteristic of nonmetallic glasses, occurs for glassy Pd-Si rod (or Pd-Si wire), Ni-P, and Ti-Be. For Fe-Ni and Fe-P, however, only a slight inflection is apparent. This can be explained with the help of the inset in Fig. 3. The thermal conductivity κ, the dashed curve, is obtained from two nearly independent contributions,[4] that from low-frequency phonons (roughly $< 10^{11}$ Hz) labeled L plus that from high-frequency phonons labeled H. The breadth of the plateau depends simply on the relative magnitudes of L and H. Taking a value of κ at 100 K as being representative of H, and a value of κ at 0.1 K as being representative of L, the ratio of L/H decreases progressively through Pd-Si, Ni-P, Ti-Be, Fe-Ni, and Fe-P. From Figs. 1–3, this is also the order in which the breadth of the plateau decreases. In brief, all the samples of glassy metal measured here have the same behavior in the plateau region as nonmetallic amorphous materials.

Finally, the temperature dependence of the acoustic velocities in glassy metals is similar to that observed in amorphous dielectrics. Our results on quenched Pd-Si rod are shown in Fig. 5; Bellessa *et al.*[31,32] have carried out measurements on electrodeposited Ni-P and Co-P.

The $\approx T^2$ behavior and plateau in the thermal conductivity, the magnitude of the mean free paths, and the temperature dependence of the sound velocity lead us to the conclusion that the localized states found in dielectric glasses are also present in metallic glasses. This is true whether the metallic sample is quenched from the melt or prepared by room-temperature electrodeposition. The relatively close atomic packing of the metallic glasses is apparently not a significant factor in determining the presence and behavior of these states.

Assuming the existence of localized states, the tunneling model can be used to compare the results of the velocity variation and the thermal conductivity data. In the tunneling model the low-temperature phonon mean free path l for mode i is[33]

$$l_i = [\beta_i \omega \tanh(\hbar\omega/2kT)]^{-1}, \tag{2}$$

where ω is the phonon (angular) frequency and β is an empirical constant which includes the magnitude of the interaction between a phonon and the localized excitations. Using Eq. (2) in the Debye approximation gives, in units of W/cm K,

$$\kappa = 4.0 \times 10^{-2} T^2 [(\beta_l v_l^2)^{-1} + 2(\beta_t v_t^2)^{-1}]. \tag{3}$$

Very-low-intensity acoustic-attenuation measurements may be used to obtain β. Alternatively β may be obtained from the temperature variation of the acoustic velocity[34]

$$(\Delta v/v)_i = (v_i \beta_i/\pi) \ln(T/T_0). \tag{4}$$

Table II compares the measured magnitudes of the thermal conductivity at 0.2 K with magnitudes predicted using Eqs. (3) and (4). Included are comparisons for fused quartz and borosilicate glass.[35] The agreement for the metallic glasses is not as good as that for the dielectric glasses. This might indicate that a constant density of localized excitations, as a function of energy, is not as good an approximation for glassy metals as for the silicate glasses.

In conclusion it has been noted that the phonon

TABLE II. Phonon thermal conductivity of glasses at 0.2 K as calculated from the tunneling model κ_C and measured κ_M in units of 10^{-5} W/cm K.

Glass	κ_C	κ_M
Fused quartz	1.2	1.1
Borosilicate	1.1	0.9
Pd-Si rod	38	6.5
Ni-P	13	1.9

thermal conductivity and the variation of sound velocity with temperature in metallic glasses show behavior characteristic of dielectric glasses. This indicates the presence of a broad spectrum of localized excitations. Quantitative agreement with the predictions of the tunneling-states theory is not as good for the metallic glasses as for dielectric glasses.

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