Low-Temperature Specific Heats of Glassy $Pd_{1-x-y}Si_xCu_y$ Alloys

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Measurements are reported of low-temperature specific heats in a number of binary and ternary amorphous Pd-Si and Pd-Si-Cu alloys. The results indicate that the linear-term temperature coefficient, γ, changes with electron concentration and shows a pronounced maximum near $e/a = 1.6$. The glassy alloys are also characterized by a large T^5-term coefficient and a relatively low limiting Debye temperature. The hypothesis of a minimum in the density of states at the Fermi level within the glassy range has not been confirmed.

Numerous metallic alloys can be obtained in the amorphous (glassy) form following rapid cooling from the melt.[1] Among the models that seek an explanation as to why the particularly stable metallic glasses are restricted mainly to certain groups of alloys,[2,3] a recent proposal by Nagel and Tauc[4-7] considers the contribution to stability from the interaction of the conduction electrons with the tightly packed ionic assemblage. By analogy with liquid metals and alloys,[8] the Fermi surface of the conduction electrons in an alloy glass is expected to be spherical, and the theory of Nagel and Tauc suggests that a strong interaction occurs when the Fermi sphere nearly coincides with the wave number q_p, representing the first maximum in the structure factor $S(q)$, i.e., when $q_p = 2k_F$; here q_p corresponds to the inverse of the average nearest-neighbor distance $\bar{a}$. It has been proposed further that in this situation a minimum should occur in the density of states $N(E)$ at the Fermi level. The most direct test of the above possibility can be provided through a careful measurement of the electronic specific heats, which can reveal the form of the $N(E)$ curve in the vicinity of the Fermi level.[9-11] The low-temperature specific heat of a glassy $Pd_{0.775}Si_{0.165}Cu_{0.06}$ alloy, which can be produced in bulk form, has been measured recently.[12,13] The present work reports for the first time on the composition dependence of the electronic specific heats in a range of amorphous Pd-Si and Pd-Si-Cu alloys.

The specific heats were measured in the temperature range between 1.5 and 7 K, employing a semidifferential calorimeter described elsewhere.[10,14] Samples were prepared from very pure materials in the form of a ribbon, 1.5–2.0 mm in width and 0.03 mm thick, by rapid quench-

ing from the melt utilizing the "chill block casting" technique.[15] The amount of ferromagnetic impurities present in both the Pd and Si was determined by neutron activation analysis to be less than 1 ppm. Alloy compositions (verified by microprobe analysis) were chosen to cover the metastable glass region in each alloy system. Electrical resistance measurements, as well as transmission electron microscopy, x-ray diffraction, and differential scanning calorimeter studies, confirmed the amorphous structure of the samples. Specimens suitable for specific-heat measurements were fabricated by winding the amorphous ribbon into tightly packed disks on a copper spool.

A typical C_p/T vs T^2 plot is shown in Fig. 1 for the amorphous alloy $Pd_{0.75}Si_{0.16}Cu_{0.09}$. The data points in the flat middle portion of this curve

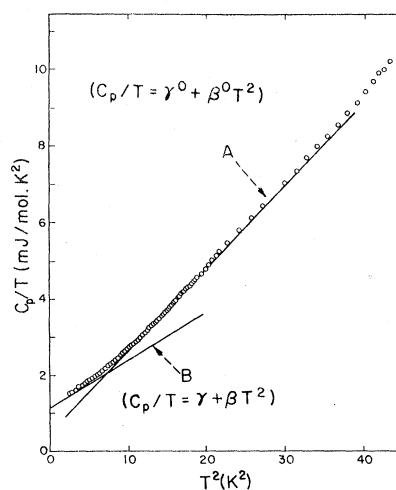FIG. 1. C_p/T vs T^2 relationship for amorphous $Pd_{0.75}Si_{0.16}Cu_{0.09}$.

fall on an apparently straight line over a wide temperature range, $12 < T^2 < 50$ K^2 (see the line marked A in Fig. 1). If one assumes that this general behavior confirms a simple relationship between the specific heat at constant pressure and the absolute temperature

$$C_p/T = \gamma^0 + \beta^0 T^2, \qquad (1)$$

then, at temperatures below $T^2 \approx 12$ K, a clear positive deviation from the straight line is evident. We can define this deviation as an "excess" specific heat $\Delta C_p{}^0$, as was done by Chen and Haemmerle[12] in an earlier study on a bulk $Pd_{0.775}Si_{0.165}Cu_{0.06}$ sample. Such a departure from an assumed linear behavior could be ascirbed to ferromagnetic impurity contributions,[12] or to glassy-state effects.[16] We believe, however, that in the present case such an interpretation is unwarranted and would lead to wrong conclusions. The reasons for this are as follows:

Suppose we assume a linear relationship given by Eq. (1), and fit the data in the long, nearly linear region to this expression. $\Delta C_p{}^0$ then represents the difference between the experimental data and the above fitting equation and becomes appreciable at temperatures below $T^2 \approx 12$ K^2 and above $T^2 \approx 35$ K^2. If a Schottky-type specific-heat anomaly is ascribed to $\Delta C_p{}^0$ below 1.5 K, its high-temperature tail should obey a T^{-2} dependence.[17] However, as is seen in Fig. 2, the observed excess $\Delta C_p{}^0$ trend does not agree with either a T^{-2} or a T^{-n} fitting. It is therefore not justifiable to fit the experimental data to an equation of the

form

$$C_p = \gamma^0 T + \beta^0 T^3 + H^0 T^{-n}. \qquad (2)$$

On the other hand, if the complete data are assumed to fit an equation of the form

$$C_p = \gamma T + \beta T^3 + \delta T^5, \qquad (3)$$

as was done by Golding, Bagley, and Hsu,[13] then in a plot of C_p/T vs T^2, a positive and different deviation, ΔC_p, occurs throughout the whole range of the measurements, from a curve such as that given by line B in Fig. 1. Line B corresponds to the first two terms of Eq. (3). A corresponding plot of $\ln\Delta C_p$ vs $\ln T$ confirms this excess specific heat to be consistently proportional to T^5. Thus, the appropriate fitting equation for the present results is well approximated by Eq. (3), at least in the He^4-temperature range.

The coefficients obtained from the least-squares fitting of the present data to Eq. (3) are summarized in Table I. The presence of the relatively large δ coefficient points to a substantial deviation of the phonon spectrum from the Debye model, occurring at relatively low temperatures in glassy alloys. At the same time the Debye temperature for the $Pd_{0.772}Si_{0.168}Cu_{0.06}$ alloy derived from the β coefficient ($\Theta_D = 236$ K), agrees well with $\Theta_D = 250$ K derived from acoustic measurements for an alloy of similar composition.[13]

The linear–temperature-term coefficient, γ, is plotted in Fig. 3, as a function of electron concentration e/a, which we define as Nagel and Tauc did,[4] by assuming that the valences of Pd, Cu, and Si are 1, 1, and 4, respectively. The γ value obtained by Golding, Bagley, and Hsu[13] is also included and agrees well with the present work. The γ values fall on a single master curve, which shows a maximum at about 1.58–1.60 electrons per atom. This is surprising in view of the recent measurements of photoemission spectra in Pd-Si and Nb-Ni alloys,[18,19] and the temperature dependence of resistivity,[20] which can be interpreted as indicating that a minimum exists in the density of states at the Fermi level. A similar conclusion is also indicated by the recent calculation of the d-band spectrum in liquid copper.[21] The magnitude of the γ values is almost twice as large as the values typically observed in Hume-Rothery alloys with noble metals.[10] The XPS (x-ray photoemission spectroscopy) spectrum for the glassy $Pd_{0.775}Si_{0.165}Cu_{0.06}$ alloy clearly shows that the Pd d band is completely filled by electrons donated by Si, and that the Fermi level is located at about 0.5 eV above the top of the d
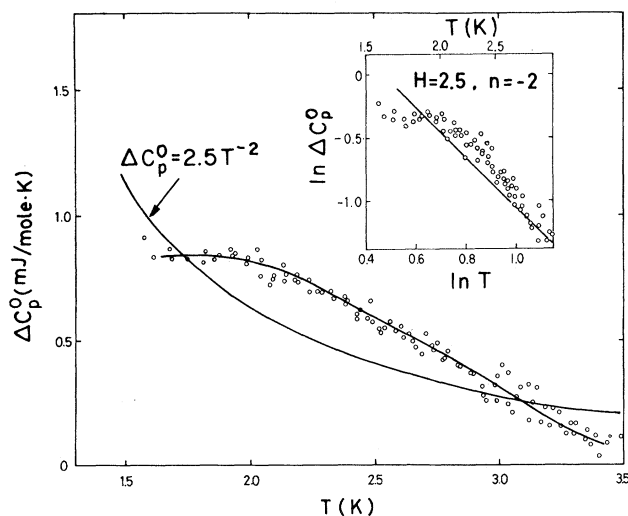

FIG. 2. "Excess" specific heat, $\Delta C_p{}^0$, vs temperature for amorphous $Pd_{0.75}Si_{0.16}Cu_{0.09}$.

TABLE I. Low-temperature specific-heat data for amorphous Pd-Si-Cu alloys. The coefficients γ, β, and δ were derived from fitting the data with $C_p = \gamma T + \beta T^3 + \delta T^5$ for $T < 4.2$ K.

Amorphous Alloy Composition	Electron/Atom Ratio	γ (mJ/mole·K²)	β (mJ/mole·K⁴)	θ_D (K)	δ (mJ/mole·K⁶)
$Pd_{0.835}Si_{0.165}$	1.495	1.201 ± 0.017	0.1554 ± 0.0034	231.1 ± 1.6	0.0025 ± 0.0002
$Pd_{0.82}Si_{0.18}$	1.54	1.282 ± 0.015	0.1490 ± 0.0028	234.4 ± 1.5	0.0034 ± 0.0001
$Pd_{0.80}Si_{0.20}$	1.60	1.290 ± 0.013	0.1441 ± 0.0026	236.9 ± 1.4	0.0034 ± 0.0001
$Pd_{0.78}Si_{0.22}$	1.66	1.175 ± 0.015	0.1714 ± 0.0031	223.7 ± 1.4	0.0027 ± 0.0001
$Pd_{0.80}Si_{0.17}Cu_{0.03}$	1.51	1.234 ± 0.014	0.1429 ± 0.0027	237.6 ± 1.5	0.0037 ± 0.0001
$Pd_{0.772}Si_{0.168}Cu_{0.06}$	1.504	1.193 ± 0.012	0.1463 ± 0.0022	235.8 ± 1.2	0.0035 ± 0.0001
$Pd_{0.75}Si_{0.16}Cu_{0.09}$	1.48	1.151 ± 0.006	0.1267 ± 0.0012	247.4 ± 0.8	0.0031 ± 0.00005
$Pd_{0.775}Si_{0.165}Cu_{.06}$			0.122	252.	0.00374

^{a} Additional sample. ^{b} Golding et al. (Ref. 13).

band.[18] Therefore, the overall large γ value may be attributed at least in part to the possible presence of a tail of the Pd d band at the Fermi level in these alloys. The occurrence of a maximum in the γ values, in the range of the glassy alloys, suggests that the condition $q_p = 2k_F$ need not necessarily lead to a minimum in the density of states, as proposed by Nagel and Tauc. The analogy with crystalline Hume-Rothery alloys, where an interaction of the Fermi surface with the Brillouin zone produces measurable peaks and valleys in the density of states,[10,11] cannot be carried too far without additional studies. However, it can be shown in the latter case that the contribution of such features in the conduction band to the relative stability constitutes only a fraction of one percent of the total electronic energy.[10] If this is also the case in glassy alloys, the significance of a particular trend in the density of states may be less important than has been proposed.

The coefficient γ may incorporate not only the band-structure term, proportional to the density of states at the Fermi level, but also contributions from the electron-phonon interactions, and the nonelectronic contribution observed generally in glassy materials. The latter of these two possible contributions has been reported to be of the order of 0.05 mJ/g atom K²,[22,23] which is negligibly small in comparison with the γ value presently measured. Furthermore, the electron-phonon interaction in the crystalline alloys characteristic of the noble metals is relatively small and changes monotonically with composition.[10,11] Thus, we may reasonably assume that the observed γ trend reflects the change in the density of states of the conduction band in the glassy Pd-Si-Cu alloys.
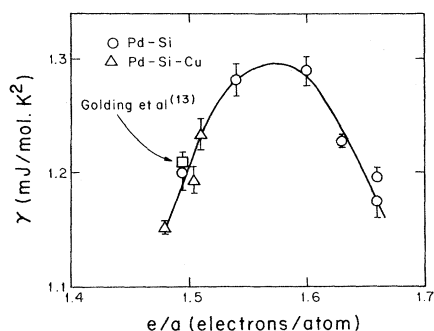
FIG. 3. The relationship between γ and e/a within the amorphous range.

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Comparison between the Amorphous and Crystalline (*A*-15) Phases on Nb₃Ge

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A comparative study on the superconducting and the normal-state properties of the amorphous, low-T_c (3.9 K) and the crystalline, high-T_c (2.18 K) phases of Nb₃Ge suggests that changes in the strength of electron-phonon interaction account, in large part, for the drastic reduction in T_c. This result is consistent with a dehybridization between Nb $4d$ and Ge $4p$ orbitals at E_F in amorphous Nb₃Ge as shown by recent x-ray photoemission spectroscopy measurements and a microscopic theory of dielectric screening and lattice dynamics.

In the crystalline state (with the *A*-15 structure), the intermetallic compound Nb₃Ge exhibits superconductivity with the highest onset transition temperature ($T_c \sim 23$ K) attained to date.[1] On the other hand, the amorphous phase of Nb₃Ge becomes superconducting at a much lower temperature ($T_c \sim 4$ K).[2] To obtain a better understanding of superconductivity in the high-T_c crystalline (*c*) and the low-T_c amorphous (*a*) phases of Nb₃Ge, it may be fruitful to compare the superconducting and the normal-state properties of these phases. Efforts along these lines have already resulted in a variety of studies, e.g., x-ray photoemission,[3] x-ray absorption fine structure,[4]

and superconductive tunneling.[5] In this note, we present the results of low-temperature specific-heat measurements on an amorphous Nb₃Ge film (~ 8 μm thick). With this new piece of information, together with the existing data, we will then show, by a comparison between the amorphous and crystalline phases of Nb₃Ge, that changes in the strength of the electron-phonon interaction account in large part for the drastic reduction in transition temperature.

The amorphous state of Nb₃Ge was achieved by rf sputtering from a Nb₃Ge target onto a substrate (sapphire or fused quartz) held at liquid-nitrogen temperature. The noncrystallinity of the sput-