# Thermal Expansion of Amorphous $Pd_{0.775}Si_{0.165}Cu_{0.06}$

W. Kaspers and R. Pott
*II. Physikalisches Institut der Universität Köln, D-5000 Köln 41, West Germany*

and

D. M. Herlach[a] and H. v. Löhneysen
*II. Physikalisches Institut der Rheinisch-Westfälischen Technischen Hochschule Aachen, D-5100 Aachen, West Germany*

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The thermal expansion of an amorphous metal ($Pd_{0.775}Si_{0.165}Cu_{0.06}$) has been measured between 1.5 and 350 K. A negative thermal-expansion coefficient is observed at low temperatures. This arises from a huge negative Grüneisen parameter which is attributed to tunneling states.

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The scientific and technological interest in amorphous (or glassy) metals has increased considerably during the past few years.[1] However, comparatively little is known about the thermal expansion of these materials. While at high temperatures (but still below the glass transition temperature) the thermal expansion of glassy metals behaves rather as "expected," i.e., like that of their crystalline counterparts,[1] it is their low-temperature behavior which should be particularly interesting, but—to our knowledge—this has not been investigated at all up to now. At low temperatures, glasses reveal characteristic differences with respect to crystals in their thermal and acoustic properties. These differences are attributed to low-energy excitations in the glass which presumably arise from tunneling transitions of atoms or groups of atoms between the two states of a double-well potential.[2,3] The few thermal-expansion measurements[4,5] carried out so far on insulating glasses have shown rather large negative Grüneisen parameters $\Gamma$, reaching values of about $-20$ at 1.5 K. These large values of $|\Gamma|$ are attributed to the above-mentioned two-level tunneling systems (TLS). Recent measurements below 1 K showed, however, that the magnitude and the sign of $\Gamma$ in insulating glasses are not universal.[6]

Evidence has accumulated that TLS exist not only in insulating glasses but also in amorphous metals.[7] It is therefore highly desirable to measure the thermal expansion of an amorphous metal at low temperatures, even more so because the direct correlation between $\Gamma$ and the pressure dependence of the energy splitting of the TLS might eventually provide a key to understand their microscopic nature, which is still unknown in both insulating and metallic glasses. In addition to this problem, it seemed worthwhile to investigate the electron and phonon contributions to the thermal expansion of an amorphous metal.

We chose the metallic glass $Pd_{0.775}Si_{0.165}Cu_{0.06}$ (PdSiCu hereafter) for this investigation because it is easily obtained in the amorphous state in rigid bulk form suitable for dilatometry. Stoichiometric ingots were prepared by inductive melting of the constituents (99.999% Pd and Cu, 99.9999% Si) in high vacuum, followed by a homogenizing heat treatment (700 °C, 6 h). The samples were then remelted *in situ* and water quenched. The resulting rods (length 1 cm, diam 1 mm) were checked to be amorphous by x-ray diffraction. Also, the resistivity ratio $R(300\text{ K})/R(4.2\text{ K}) = 1.02$ indicated a homogeneous amorphous state.[8]

The linear thermal-expansion coefficient $\alpha$ was measured with a capacitance dilatometer between 1.5 and 350 K as described in detail elsewhere.[9] The resolution of $\alpha$ is $\pm 3\times 10^{-9}\text{ K}^{-1}$ at low temperature. Several runs were performed for $T < 5$ K, and the Cu dilatometer cell was recalibrated with a Cu thermal-expansion standard[10] between each of these runs. The low-temperature data to be presented below are smoothed averages of a total of five runs. The dispersion from run to run remained within the stated error bar. Because the thermal expansion increases rapidly with $T$, only one run was necessary above 5 K. Here, too, the cell was calibrated with the thermal expansion of Cu.

Figure 1 shows the linear thermal-expansion coefficient $\alpha = (d\ln l/dT)_p$ of PdSiCu as a function of temperature. Earlier data for PdSiCu taken above room temperature[11] agree rather well with

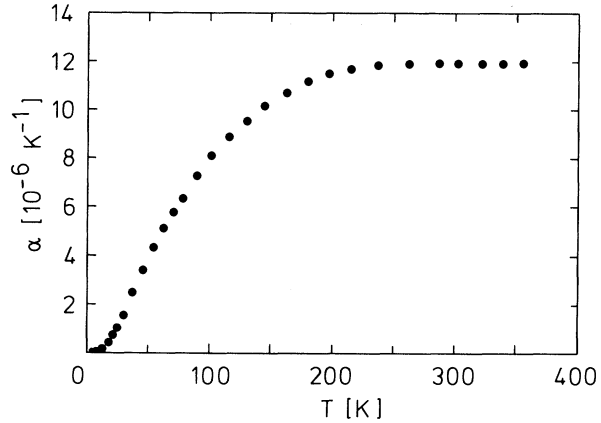

FIG. 1. Linear thermal-expansion coefficient $\alpha = (d\ln l/dT)_p$ of amorphous $Pd_{0.775}Si_{0.165}Cu_{0.06}$ as a function of temperature $T$.

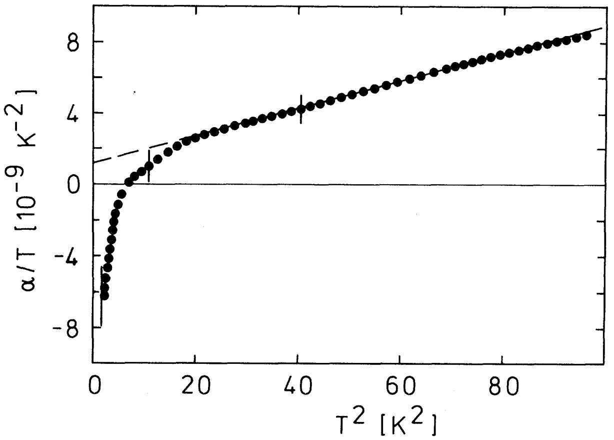

FIG. 2. Low-temperature thermal-expansion data for $Pd_{0.775}Si_{0.165}Cu_{0.06}$ plotted as $\alpha/T$ vs $T^2$.

our results, as do data for crystalline Pd[12] over an extended temperature range. The latter comparison shows that $\alpha$ of PdSiCu at high temperatures ($T > 10$ K) behaves rather normally. For $T = 300$ K, we calculate $\Gamma = 3\alpha V B_T/C_v = 2.33$ for PdSiCu. Here $V$ is the molar volume,[13] $B_T$ the isothermal bulk modulus,[13] and $C_v = 23.85$ J/mole K the molar heat capacity.[14] The above room-temperature $\Gamma$ of PdSiCu is in good agreement with $\Gamma = 2.37$ for crystalline Pd.[12]

The low-temperature thermal-expansion data are shown in Fig. 2 in a plot of $\alpha/T$ vs $T^2$ in order to facilitate the separation of electron and phonon contributions. Between 4.5 and 10 K, $\alpha = aT + bT^3$ is inferred from the straight line in this plot, with $a = (1.2 \pm 0.2)\times 10^{-9}$ K$^{-2}$ and $b = (7.3 \pm 0.5)\times 10^{-11}$ K$^{-4}$. The most important observation, however, is the dramatic fall of $\alpha$ below $\approx 4$ K. $\alpha$ turns negative at 2.5 K and reaches $-(1 \pm 0.3)\times 10^{-8}$ K$^{-1}$ at 1.5 K. This behavior bears resemblance to the negative thermal expansion observed in insulating glasses and hence suggests a contribution by TLS. Before discussing this feature in detail, however, we have to treat the electron and phonon contributions to $\alpha$.

Neglecting, therefore, the anomalous contribution to $\alpha$ below 4.5 K temporarily, we can write $\alpha = \Gamma(\gamma T + \beta T^3)/3VB_T$, where $\gamma T$ and $\beta T^3$ are the electron and phonon specific heats. With the low-temperature specific-heat data for PdSiCu,[13] we obtain $\Gamma_{el} = 4.7$ and $\Gamma_{ph} = 2.8$ when evaluating electron and phonon contributions to $\alpha$. The relatively large value of $\Gamma_{el}$ as compared with crystalline Pd[12] ($\Gamma_{el} = 2.22$) implies that the reduction of the electronic density of states at the Fermi level by a factor of $\approx 8$ when going from crystalline Pd to amorphous PdSiCu is not totally cancelled by a corresponding reduction of the electronic contribution to $\alpha$. Thus our data add one more item to the long list of physical quantities that show strong deviations from free-electron behavior in amorphous transition metals, for which $\Gamma_{el} = 0.67$.

The value of $\Gamma_{ph}$ for PdSiCu is close to that for Pd[12] ($\Gamma_{ph} = 2.18$). The small difference could be due to the fact that we have fitted the phonon contribution to $\alpha$ with a $T^3$ dependence up to 10 K while the phonon specific heat shows positive deviations from $\beta T^3$ already well below that temperature.[13, 15] As a result of the limited accuracy of our measurement, a possible corresponding behavior of $\alpha$ could not be resolved. In brief, our data suggest that the electronic and phonon contributions to the thermal expansion in a metallic glass behave quite similarly to those of the crystalline counterpart.

For the remainder of this article, we want to discuss the anomalous behavior of $\alpha$ at low temperatures under the assumption that electron and phonon parts of $\alpha$ as determined above can be extrapolated to below 4.5 K. The negative $\alpha$'s below 2.5 K strongly hint at a contribution by TLS whose existence in PdSiCu has already been proven with ultrasonic experiments.[16] The value $\Gamma = -(20 \pm 6)$ for $T = 1.5$ K inferred from our $\alpha$ measurement is of the same magnitude as those found in insulating glasses. This coincidence is, however, circumstantial, because in amorphous metals the Grüneisen parameter arising from TLS has to be evaluated according to $\Gamma = \sum_i \Gamma_i C_i / \sum_i C_i$ where $i$ denotes the contributions by electrons, phonons, and TLS, respectively. Unfortunately, $C_{\mathrm{TLS}}$ can only be accurately determined in amorphous superconductors and therefore is not available for PdSiCu. We estimate $\gamma_{\rm TLS} = 1 \times 10^{-4}$ J/mole K$^2$ for the linear specific coefficient due to TLS in PdSiCu, i.e., the value for superconducting $\rm Pd_{0.30}Zr_{0.70}$.[17] Taking the above values for $\Gamma_{\rm el}$ and $\Gamma_{\rm ph}$, we then obtain $\Gamma_{\rm TLS} = -(350 \pm 100)$ at 1.5 K. This is unusually large even for glasses, where $\Gamma_{\rm TLS} \approx -20$ has been observed in vitreous silica.[4-6] $|\Gamma_{\rm TLS}|$ in PdSiCu decreases strongly with increasing temperature ($\Gamma_{\rm TLS} \approx -60$ at 3 K). This temperature dependence is stronger than that of $\Gamma$ in vitreous silica.[6,18]

While $\Gamma$'s of the order of $10^4$ are conceivable for a single tunneling system[5] (values of up to $\approx 300$ are indeed observed for some tunneling centers in alkali halides), the necessary averaging over the ensemble of tunneling systems in glasses reduces $\Gamma_{\rm TLS}$ remarkably. For a given energy splitting $E = (\Delta_0^2 + \Delta^2)^{1/2}$ of a subset of TLS, there is a distribution of both the tunneling splitting $\Delta_0$ and the asymmetry $\Delta$ of the double-well potential. It has been suggested[5] that the large negative $\Gamma$'s observed in glasses arise mostly from asymmetric TLS ($E \approx \Delta$) although this is not universally accepted.[4,19] The very large value of $|\Gamma_{\rm TLS}|$ in PdSiCu is only explicable if one assumes a correlation[20] between $\Delta$ and $\partial\Delta/\partial V$ and rules out an explanation in terms of symmetric TLS for which $|\Gamma| \approx 20$ at most is conceivable.[19]

In the absence of a detailed microscopic model for TLS we cannot at present give a more specific account of our observations. In particular, future work should show if the large $|\Gamma_{\rm TLS}|$ in PdSiCu is unique to this material or representative for a wider class of amorphous metals. In the latter case, our results would hint at considerable differences in the microscopic structure of TLS in metals as compared with insulating glasses.

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(a)Also at Labor für Tieftemperaturphysik der Universität Duisberg, Lotharstrasse 65, D-4100 Duisberg, West Germany.

[1] See, e. g., H. S. Chen, Rep. Prog. Phys. 43, 353 (1980).

[2] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. 25, 1 (1972).

[3] W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).

[4] G. K. White, Phys. Rev. Lett. 34, 204 (1975); K. G. Lyon, G. L. Salinger, and C. A. Swenson, Phys. Rev. B 19, 4231 (1979); G. J. Morgan, G. K. White, and J. G. Collins, Philos. Mag. B 43, 1039 (1981).

[5] W. A. Phillips, in *Amorphous Solids: Low Temperature Properties*, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981), p. 53.

[6] D. A. Ackerman and A. C. Anderson, Phys. Rev. Lett. 49, 1176 (1982).

[7] J. L. Black, in *Glassy Metals I*, edited by H.-J. Güntherodt and H. Beck (Springer-Verlag, Berlin, 1981), p. 167; H. v. Löhneysen, Phys. Rep. 79, 161 (1981).

[8] D. M. Herlach, J. Kästner, and E. F. Wassermann, to be published.

[9] R. Pott and R. Schefzyk, to be published.

[10] F. R. Kroeger and C. A. Swenson, J. Appl. Phys. 48, 853 (1977).

[11] H. S. Chen, J. Appl. Phys. 49, 3289 (1978).

[12] G. K. White and A. T. Pawlowicz, J. Low Temp. Phys. 2, 631 (1970).

[13] B. Golding, B. G. Bagley, and F. S. L. Hsu, Phys. Rev. Lett. 29, 68 (1972).

[14] L. R. Testardi, J. T. Krause, and H. S. Chen, Phys. Rev. B 8, 4464 (1973).

[15] H. S. Chen and W. H. Haemmerle, J. Non-Cryst. Solids 11, 161 (1972).

[16] B. Golding, J. E. Graebner, A. B. Kane, and J. Black, Phys. Rev. Lett. 41, 1487 (1978).

[17] J. E. Graebner, B. Golding, R. J. Schutz, F. S. L. Hsu, and H. S. Chen, Phys. Rev. Lett. 39, 1480 (1977).

[18] O. B. Wright and W. A. Phillips, Physica (Utrecht) 108B, 859 (1981).

[19] B. Fischer and M. W. Klein, Solid State Commun. 35, 37 (1980).

[20] W. A. Phillips, J. Low Temp. Phys. 11, 757 (1973).