

## HEAT TREATMENT EFFECTS IN AMORPHOUS METALS: $Zr_{70}Cu_{30}$ AND $La_{70}Cu_{30}$

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We measured the electrical resistivity (4–300 K), superconducting critical temperature and thermal conductivity (0.5–7 K) of the amorphous metals  $Zr_{70}Cu_{30}$  and  $La_{70}Cu_{30}$ . Heat treatments below crystallization temperature induced changes in these properties. In particular, in the first stage of the annealing of  $Zr_{70}Cu_{30}$  there are systematic changes in the thermal conductivity and the critical temperature, while the electrical resistivity remains constant. We show that there is no simple correlation between the thermal conductivity processes in the low temperature and plateau regions. We also show that the thermal conductivity of as quenched  $La_{70}Cu_{30}$  is typical of amorphous metals, contrary to information previously reported.

CHANGES IN THE LOW temperature specific heat [1] and thermal conductivity [1–3] of amorphous metals denote that heat treatment below the crystallization temperature reduces the density of states of the two level system (TLS). This result suggests that controlled heat treatment can be used to determine the correlation between the density of states of the TLS and other properties of the material. We think that such studies may help in understanding the origin of the low energy excitations that characterize lattice disorder. In this work we investigate the variation induced by heat treatment in the thermal conductivity of amorphous  $Zr_{70}Cu_{30}$  and  $La_{70}Cu_{30}$  and its relation with the electrical resistivity and superconducting parameters.

Previously [4] we had measured the annealing effects on the resistivity, weak field penetration depth and critical field and temperature of the  $La_{70}Cu_{30}$  amorphous metal. Thermal conductivity measurements in as quenched samples of this system showed [5] that below the critical temperature ( $T_c \approx 3.7$  K) the phonon heat transport was limited by interaction with TLS. The thermal conductivity above  $T_c$  showed, instead of the typical plateau in the phonon conductivity, a  $T^2$  dependence which was attributed [5] to phonon–electron interaction.

Recent measurements [2] in amorphous  $Zr_{70}Cu_{30}$  have shown that the phonon conductivity resembles strongly that of insulating materials, including the nearly temperature-independent region between 5 and 10 K. Results [1] in a similar system,  $Zr_{76}Ni_{24}$ , indicated that annealing increased the thermal conductivity by 50%,

corresponding to a decrease in  $nM^2$  of 35%, where  $n$  is the density of the TLS and  $M$  is an average coupling constant between the TLS and the phonons. Heat treatment produced a nearly parallel displacement of the thermal conductivity curve when represented in a log–log plot [1]. From this result it could be inferred that the thermal conductivity above and below  $T_c$  is predominantly due to disorder, in agreement with the behaviour [3] of other non-superconducting amorphous metals. From this point of view the  $La_{70}Cu_{30}$  system [5] showed anomalous behaviour in that the conductivity above  $T_c$  was limited by the phonon–electron interaction. On the other hand, it was observed [5] that the superconducting transition barely affected the thermal conductivity. The Wiedemann–Franz relation indicated [5] no electric contribution to the heat transport, a fact hard to reconcile with the assumption of phonon–electron interaction dominating the conduction process at  $T_c$ . In order to investigate the origin of the interaction at temperatures higher than  $T_c$ , we have studied the changes in thermal conductivity induced by annealing, thus hoping to separate the low temperature scattering effects from those dominant, above  $T_c$ , that were supposed [5] to be defect independent in this system.

We have also induced systematic changes in the thermal conductivity of  $Zr_{70}Cu_{30}$  amorphous samples by means of heat treatment, to determine the degree of correlation between the TLS and the scattering processes at the plateau region. In addition we measured the effect of heat treatment on the electrical resistivity and critical temperature. X-ray diffraction analysis was used to detect the presence of crystalline nucleation centers.

The samples were prepared from ribbons 0.1 cm wide,  $10^{-3}$  cm thick, obtained by splat cooling [6].

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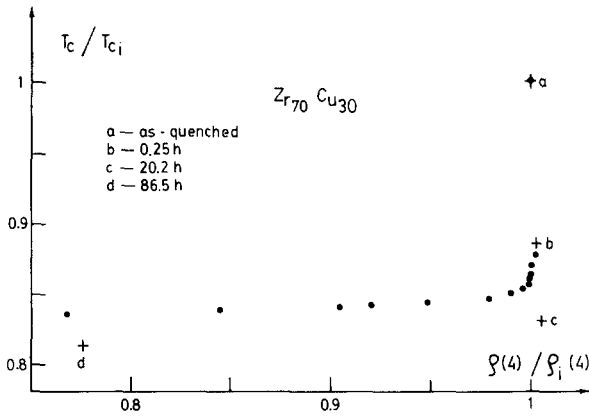


Fig. 1. Variation of the superconducting critical temperature as a function of the residual resistivity induced by heat treatment at  $250^{\circ}\text{C}$  for two amorphous samples of  $Zr_{70}Cu_{30}$ , normalized to the values of the samples as quenched.  $\bullet$  Sample I [7] with  $T_{ci} = 2.758\text{ K}$ ,  $\rho_i(4) = 182\ \mu\Omega\text{-cm}$ ,  $\Delta T_{ci} = 0.09\text{ K}$ ;  $+$ , Sample II,  $T_{ci} = 2.730\text{ K}$ ,  $\rho_i(4) = 182\ \mu\Omega\text{-cm}$ ,  $\Delta T_{ci} = 0.1\text{ K}$ . Annealing periods are indicated for some points.

The transition temperature, critical field and resistivity of similar  $La_{70}Cu_{30}$  samples have been already reported [4]. The results shown in this paper correspond to an as quenched sample with a negative resistance temperature coefficient  $1/\rho\ d\rho/dT = -6.7 \times 10^{-5}\text{ K}^{-1}$ ,  $T_{ci} = 3.583\text{ K}$  and a transition width  $\Delta T_c = 28\text{ mK}$ . Other samples with negative and zero temperature coefficients were measured; their thermal conductivity did not differ by more than 15% from those reported here.

The changes in electrical resistivity and critical temperature of several samples of  $Zr_{70}Cu_{30}$  were measured as a function of heat treatment. The behaviour was similar in all samples. The only difference among them was the annealing period required to produce a given change in  $\rho$  and  $T_c$ . Similar behaviour was also reported [4] for the  $La_{70}Cu_{30}$  system. Figure 1 shows the change in critical temperature as a function of the variation of the residual resistivity, induced by heat treatment.

The thermal conductivity measurements were done in a  $He^3$  cryostat between 0.3 and 7 K, using the standard stationary technique with two thermometers and one heater. The sample support was designed to permit the heat treatment to be made without changing the sample geometrical factor, thus avoiding the uncertainty introduced by changes in the sample geometry. Since different ribbons might respond differently [4] to heat treatment and considering that even different regions of the same ribbon might give slightly different results we decided to use only three short pieces of the same ribbon connected in parallel with an effective geometrical factor of approximately  $1/3(2.3 \times 10^3)\text{ cm}^{-1}$ .

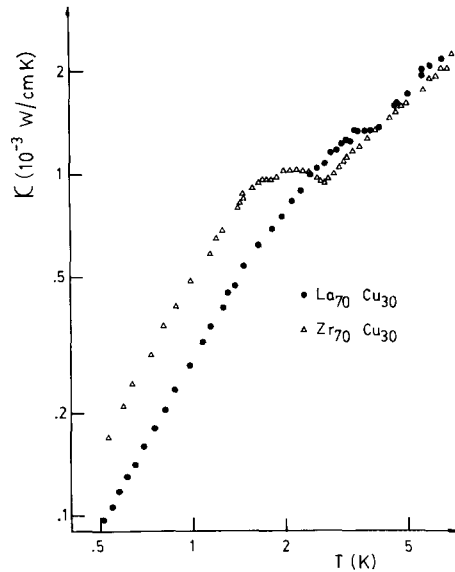


Fig. 2. Thermal conductivity  $\kappa$  as a function of temperature  $T$  for the  $La_{70}Cu_{30}$  and  $Zr_{70}Cu_{30}$  amorphous systems.

The thermal shunt due to leads and sample support was measured in the whole temperature range, and found to be less than 20% of the sample conductance. The thermometers, slices of Speer carbon resistors, were calibrated against a Ge thermometer in thermal contact with the  $He^3$  bath. The error in the absolute value of the conductivity, mainly due to errors in the determination of the sample geometry, was 15%.

Figure 2 shows the thermal conductivity  $\kappa$ , of the as quenched  $La_{70}Cu_{30}$  amorphous system. The thermal conductivity between 0.4 and 1 K is fitted by  $\kappa_s = aT^n$ , with  $a = 2.85 \times 10^{-4}\text{ W cm}^{-1}\text{ K}^{-(n+1)}$  and  $n = 1.63$ . The results for  $T > T_c$  are well represented by  $\kappa_n = bT^m$  with  $b = 4.05 \times 10^{-4}\text{ W cm}^{-1}\text{ K}^{-(m+1)}$  and  $m = 0.90$ . The thermal conductivity in the low temperature region is six times smaller than that reported in [5] and what is more important, the thermal conductivity for temperatures higher than  $T_c$  is not quadratic in  $T$ .

It is seen then that the temperature dependence above and below  $T_c$  is similar to that measured [1, 2] in the  $Zr_{76}Ni_{24}$  and  $Zr_{70}Cu_{30}$  systems. Since the electrical resistivity is approximately the same ( $175\ \mu\Omega\text{-cm}$ ) as that used in [5], the electron contribution calculated by means of the Wiedemann–Franz law cannot be disregarded anymore, being 40% of the total conductivity at  $T_c$ . In the same figure we plotted our results for as quenched  $Zr_{70}Cu_{30}$ . It is worthwhile to mention that in spite of the difference in the origin of the materials used to prepare the samples and the difference in the splat cooling technique the results coincide with those of Löhneysen *et al.* [2], within experimental error. As a consequence we believe that the present results

for the thermal conductivity of  $La_{70}Cu_{30}$  supersede those of [5].

The thermal conductivity of  $La_{70}Cu_{30}$  below  $T_c$ , see Fig. 2, is lower than that of amorphous  $Zr_{70}Cu_{30}$ . The fitting of the low temperature data to commonly used theoretical expressions [8] gives  $nM^2 \approx 7 \times 10^7$  erg  $cm^{-3}$  for  $La_{70}Cu_{30}$ , 10% larger than for  $Zr_{70}Cu_{30}$  and 30% smaller [1] than that of  $Zr_{76}Ni_{24}$ . We note that most of the difference in the thermal conductivity shown in Fig. 2 is due to the difference in the Debye temperatures of the two metals (due to the lack of specific heat data for  $La_{70}Cu_{30}$  we have used  $\theta_D = 120$  K, obtained from specific heat measurements [9] in LaGa).

The thermal conductivity of metals can be expressed by

$$\kappa = \kappa_e + \kappa_{ph} \quad (1)$$

with

$$\frac{1}{\kappa_{ph}} = \frac{1}{\kappa_{ph}^D} + \frac{1}{\kappa_{ph}^e}, \quad (2)$$

where  $\kappa_e$  and  $\kappa_{ph}$  are the electron and phonon contributions respectively,  $\kappa_{ph}^D$  and  $\kappa_{ph}^e$  are the phonon-defect and phonon-electron contributions to the phonon thermal conductivity. Since  $\kappa_e$  in  $La_{70}Cu_{30}$  is of the order of 40% of the total conductivity at  $T = T_c$  it follows that below  $T_c$ , the decrease in  $\kappa_e$  and the increase in  $\kappa_{ph}$  must cancel almost exactly for the superconducting transition to have no noticeable effect in  $\kappa$ .

Figure 3 shows the effect of heat treatment on the thermal conductivity of amorphous  $Zr_{70}Cu_{30}$  (Sample II). The thermal conductivity increases for longer annealing times. The heat treatment of the sample discussed in this paper refers to the region represented in Fig. 1 by the sharp change in  $T_c$  at approximately constant  $\rho$ . X-ray analysis did not show any indication of crystalline nucleation in this annealing region. This result is also supported by the behaviour of the transition width, which decreases from 100 mK in the as quenched sample to 5 mK in curve D in Fig. 3.

It is also interesting that the first relaxation was obtained by annealing the sample at room temperature during four weeks. This relaxation did not change either  $\rho$  or  $T_c$  within the experimental error but it produced a noticeable change in the thermal conductivity, as shown by curve B in Fig. 3.

The electrical resistivity and  $T_c$  were measured after each annealing process. The critical temperature so obtained coincide with those obtained from the thermal conductivity measurements. The behaviour of this sample is in agreement with results for samples obtained from other ribbons [7], as shown in Fig. 1.

The critical temperature of superconducting materials is usually related to the electron-phonon

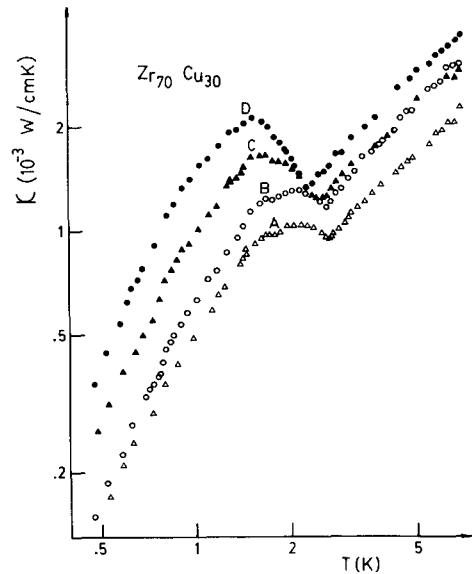


Fig. 3. Thermal conductivity  $\kappa$  as a function of temperature  $T$  for amorphous  $Zr_{70}Cu_{30}$ .  $\Delta$  as quenched (point *a*, Fig. 1);  $\circ$ , annealed at room temperature during 28 days;  $\blacktriangle$ , annealed at 250°C during 0.25 hr (point *b*, Fig. 1);  $\bullet$ , annealed at 250°C during 20.2 hr (point *c*, Fig. 1).

interaction parameter,  $\lambda$ . Quite recently [10] it has been argued that the  $T_c$  of amorphous Zr based alloys is determined by this parameter, given by  $\lambda = k \, d\rho/dT$  at 280 K. Precise electrical resistivity measurements [7] in our samples show that in the annealing range of interest in this work,  $d\rho/dT$  decreased by 10%. Following the procedure of [10] we can relate the  $\lambda$  obtained from  $T_c$  with the experimental  $d\rho/dT$ . If the Debye temperature is taken as constant [10], we obtain  $k \sim -2 \mu\Omega^{-1} \text{ cm}^{-1} \text{ K}$ , smaller than that of [10] by one order of magnitude, and a finite  $\lambda \approx 0.5$  at  $d\rho/dT = 0$ . This shows that the change in  $T_c$  at the beginning of the annealing processes has a different origin than that induced by alloying different metals. Variations in  $\theta_D$  of the order of 15% would be sufficient to explain the change of  $T_c$  observed in these measurements [11]. It will then be interesting to measure the specific heat of  $Zr_{70}Cu_{30}$  as a function of heat treatment so as to determine whether the change of  $T_c$  at constant  $\rho$  is due to variation in  $\lambda$  or if the disorder has some intrinsic influence on the superconducting critical temperature.

The thermal conductivity below 1 K is almost entirely due to  $\kappa_{ph}^D$ , since at these temperatures the number of electronic excitations approaches zero exponentially and, as a consequence,  $\kappa_e \approx 0$  and  $\kappa_{ph}^e \gg \kappa_{ph}^D$ . Changes in  $\kappa_{ph}^D$  in this temperature region are then associated with relaxation effects. The increase in  $\kappa_{ph}^D$ , (Fig. 3), can be explained [1, 3] by a corresponding decrease in the density of scattering centers (TLS). This

is consistent with the observation that the change in  $\kappa$  induced by the superconducting transition increases when going from curve *A* to *D*.

The analysis of the thermal conductivity above  $T_c$  is difficult but, since the electrical conductivity remains constant throughout the relaxation range studied here, and assuming that the change in  $\theta_D$  is not larger than 15% (as observed in a similar system [1]) we expect  $\kappa_{ph}^e$  to remain approximately constant within our annealing region. The results in Fig. 3 show that the changes induced in the low and high temperature regions are different indicating that there is no simple correlation between the resonant phonon interaction with the TLS and the conduction process at the plateau region. Assuming a change in  $\theta_D$  of 15% we find that going from curve *A* to curve *D* (Fig. 3) the value of  $nM^2$  decreased by a factor 2.2.

Further annealing induces changes in both  $\rho$  and  $T_c$ , while X-ray analysis [7] shows the presence of small crystalline nucleation centers. The thermal conductivity is lower in the whole temperature range while the temperature dependence for  $T < 1$  K is steeper.

The behaviour of the  $La_{70}Cu_{30}$  alloy under heat treatment, is quite different: its thermal conductivity is lowered when the material is heat treated below the crystallization temperature. Even mild annealing (inducing a 2% decrease in  $T_c$  and  $\rho$ ) reduces  $\kappa$  in 10% in the whole temperature range. Although we have no explanation for this behaviour it is interesting to recall that the increase in  $\kappa$  observed in  $Zr_{70}Cu_{30}$  occurs in the annealing region where  $T_c$  changes at constant  $\rho$ . An equivalent region has not been observed in  $La_{70}Cu_{30}$ . The similarity of behaviour between  $La_{70}Cu_{30}$  and  $Zr_{70}Cu_{30}$  in the region where changes in  $\rho$  and  $T_c$  are correlated [4] might suggest a common origin for the decrease in  $\kappa$  in both samples. On the other hand the exponent in the temperature dependence of the low temperature thermal conductivity of  $La_{70}Cu_{30}$  does

not change even after heat treatments that reduce  $\rho$  and  $T_c$  by more than 20%.

In conclusion, we have studied the thermal conductivity of two amorphous superconductors. The thermal conductivity of  $Zr_{70}Cu_{30}$  can be systematically increased by heat treatment; in this way we have shown that there is no simple correlation between the thermal conduction processes in the low temperatures and plateau regions. We have found that the thermal conductivity of as quenched amorphous  $La_{70}Cu_{30}$  and  $Zr_{70}Cu_{30}$  shows the same behaviour as that of other amorphous metals.

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