STRUCTURAL RELAXATION: LOW TEMPERATURE PROPERTIES

Francisco de la Cruz

Centro Atómico Bariloche

8400 - S.C. de Bariloche (R.N.), Argentina.

ABSTRACT

We discuss the changes in transport and superconducting properties of amorphous $Zr_{70}Cu_{30}$, induced by thermal relaxation.

The experimental results are used to investigate the relation between the microscopic parameters and the observed physical properties. It is shown that the density of electronic states determines the shift in T_c as well as the variation of the electrical resistivity.

It is necessary to assume strong hybridization between s and d bands to understand the electrodynamic response of the superconductor.

INTRODUCTION

In this lecture I will refer to the research made in the Low Temperature Lab in Bariloche, during the last four years, concerning the normal and superconducting properties of metallic amorphous systems. The title of the talk is misleading. I am not an expert in relaxation and you will see that the heat treatment is only used to induce changes in the physical properties of our samples, in order to study the behaviour of the microscopic parameters of these metals.

The materials investigated are 10μm thick ribbons of $Zr_{70}Cu_{30}$ and $La_{70}Cu_{30}$ alloys, obtained[1] by melt spinning. In most of this talk we will refer to the results obtained from the $Zr_{70}Cu_{30}$ system.

Before we start to show and discuss the experimental results I will remark some properties that are common to all the transition metals amorphous alloys:

a) High electrical resistivity: $\rho \approx 200 \mu\Omega cm$.

b) Non-validity of Matthiessen's rule when applied to the temperature dependence of the electrical resistivity. This result is known as Mooij's criterium.

c) The thermodynamic and transport properties of the amorphous materials at low temperatures are characterized by the presence of the low energy excitations, TLS.

d) Since the electron mean free path ℓ, is of the order of interatomic distances the heat is mainly carried by phonons. As a consequence, amorphous systems are ideal materials to investigate the phonon thermal conduction in metals.

We will now focus our attention in some questions related to the properties we have indicated:

i) Is the high electrical resistivity of these amorphous metals due to the d-electron contribution in transition metals?

ii) Which is the origin of the negative temperature coefficient of $\rho(T)$?

iii) Assuming that in this amorphous metals it is possible to define a Fermi wave vector, it is found that $k_F \cdot \ell \simeq 1$. Is the BCS-Gorkov theory adequate to describe superconductivity in this extreme dirty limit?

iv) Another question related to the previous one is: are the Gorkov equations valid when the d and s electrons contribute to the transport properties and superconductivity?

v) Is there any dependence between the superconducting critical temperature, T_c, and the density of TLS, n(0)?

vi) Is the Matthiessen's rule valid when applied to the phonon thermal conduction in amorphous metals?

THEORETICAL AND EXPERIMENTAL BACKGROUND

Following the BCS scheme, superconductivity arises from the competition between an attractive phonon-electron interaction, characterized by a parameter λ^* and a repulsive Coulomb interaction, μ^*. As a result the critical temperature should be a function of these two parameters

$$T_c = f(\lambda^* \mu^*) \qquad (1)$$

Due to the lack of tunneling data in amorphous metals the electron-phonon parameter can be approached by $\lambda^* = N(0)I^2/\theta^2$, where the symbols are those typically used in the literature. The parameter $\mu^* = 0.1$ is usually accepted for transition metals.

A review of the critical temperature behaviour of amorphous metals can be found in ref.2. There it is indicated that relation (1), with λ^* and μ^* as described previously, is enough to understand most of the experimental data. Nevertheless, I believe there are some questions that have no definite answer. One of the problems is the possibility [3] that the TLS contributes to T_c. If this is the case, T_c should also be a function of n(0) and expression (1) should then be generalized. It is also important to remark that if the TLS can modify[3] the effective λ^*, recent calculations[4] indicate that disorder could increase μ^*. This is an important result[4] since it indicates that T_c, H_{c2} and ρ could be correlated through the degree of electron localization and would indicate that in the extreme dirty limit, the critical temperature should also be a function of the electron mean free path. From the experimental point of view there are no answers to these questions.

Measurements in the Zr_xCu_{1-x} system indicate that the increase in x induces a rise in T_c together with a decrease in ρ. The behaviour of T_c has being explained taking into account the measured[5] behaviour of N(0). The decrease in ρ has also been related[9,10] to the increase in the density of states due to contribution of the d-Zr band. In those experiments it is difficult to separate the contribution of TLS (if any) and/or, of localization. There is not enough systematic investigation of a possible direct correlation between T_c and n(0). In this lecture we will discuss some results related to this topic.

Other superconducting parameter related to the electronic properties of the material is the upper critical field, H_{c2}. Within the Gorkov theory and for the dirty limit

$$H_{c2} = 4k \frac{e}{\pi} N(0) \rho f(T). \tag{2}$$

To obtain (2) it has being used the Ginzburg-Landau coherence length in the dirty limit, given by $\xi^2(0,\ell) = \xi_0 \ell$, with $\xi_0 = 0.18\ hv_F/kT_c$, $v_F = k^2 S/6h\gamma$, $\rho^{-1} = (2/3)e^2 v_F N(0)\ell$, and $\gamma = (2/3)(\pi k)^2 N(0)$. Here ξ_0 is the BCS coherence lengths, S is the area of the Fermi sphere, ℓ the electron mean free path and γ the coefficient of the electron heat capacity. All these expressions have been obtained assuming that $k_F\ell \gg 1$. As was mentioned before this limit is not adequate for the amorphous samples used in our experiments.

Within the same approximation the superconducting response to the presence of a low magnetic field is determined by the superconducting penetration depth

$$\lambda(\ell,t) = \lambda_L(0)(\xi_0/\ell)^{1/2}f(t). \qquad (3)$$

For T near T_c

$$\lambda(\ell,T) = \frac{\lambda'(0)}{2}(1-t)^{-1/2} = 0,644\ 10^{-2}(\rho/T_c)^{1/2} \qquad (3')$$

where the London penetration depth $\lambda_L(0) = 3h\pi^{1/2}\gamma^{1/2}/ekS$. It is interesting to recall that $\lambda_L(0)$ is only related to the normal properties of the material and that expressions (3) and (3') indicate a correction to $\lambda_L(0)$ through the square root of the ratio of two distances. Superconductivity only appears through the definition of ξ_0. Expressions (2) and (3') can be verified since all physical quantities that appear in them are experimentally accesible. Although the verification of expressions (2) and (3') is interesting from the point of view of the effects induced by an extreme short ℓ, we believe that there is other related point that has to be considered when studying transition metals. It was realized by Bergmann[6] that expression (2) should not be valid when applied to metals that can be characterized by the presence of two bands (d and s, in our case). Following the same arguments we will see that it is difficult to justify the validity of expression (3'). The coherence length ξ_0 is strongly associated to the interaction energy necessary to form the Cooper pairs (kT_c). The critical temperature in a d and s band superconductor, is believed to be determined by the d band density of states, N_d. On the other hand in an independent two band model the s electrons contribution should at least be competitive with the d electrons[7,8].

Recent work[9,10] gives the experimental results of the resistivity of Zr_xCu_{1-x} as a function of x. The concentration dependence has being explained[9], on the basis of a two band model, where the contribution to ρ from d and s electrons are found to be comparable. We believe that if this is the correct explanation expression (3') should not be applicable.

Until here we have referred to changes in the physical properties of the amorphous material induced by changing concentration. We have other available experimental technique to change the behaviour of the material at constant concentration. It has being shown in the last years that thermal heat treatment[11-16] modifies the normal and superconducting properties of these materials. In the case of Zr_xCu_{1-x} it has being suggested[5] that the superconducting critical temperature is determined by the electronic density of states, in agreement with Varma and Dynes.[17] This result has being obtained from the analysis of the variation of T_c and N(0) with concentration[5]. If the analysis is correct the change in T_c induced by thermal relaxation should also be determined[15] by a corresponding change in N(0).

EXPERIMENTAL RESULTS AND DISCUSSION

We have measured the thermal conductivity of $Zr_{70}Cu_{30}$ amorphous ribbons, in the range of temperature between 0.4°K and 7°K. The results are shown in Fig.1. Experimental details can be found in ref. 12. It is clearly seen that the thermal conductivity below the critical temperature of the alloy is monotonically increased with annealing. Further annealing is not possible because the sample starts to crystallize as indicated by X-ray diffraction analysis and electrical resistivity measurement[11]. The critical temperature is decreased[11] when annealing, as it is also indicated by the structure of the thermal conductivity[12] plot in Fig.1.

The T^2 dependence of the thermal conductivity at low temperature is characteristic of phonon-TLS resonant scattering. Since annealing does not change the temperature dependence but increases the thermal conductivity we conclude that annealing increases the coefficient of the T^2 dependence. That is to say, it decreases the product of the number of scattering centers, n(0), times the square of the coupling matrix between the phonon and TLS. Considering only thermal conductivity measurements that is all we can say. In any event, these measurements indicate that these mild heat treatments can modify considerably the TLS behaviour. In Fig.2 we plot the thermal conductivity of the amorphous sample taken at T=0.5K, normalized by the value of the as quenched one, as a function of the critical temperature, also normalized by the critical temperature of the as quenched sample. From these results it is tempting to say that there is a correlation between the TLS behaviour and the critical temperature. We will see later that this is not necessarily true and that the change in T_c can be explained without involving the assistance of the TLS.

In Fig.3 we show the effect[11] of annealing in the critical temperature and electrical resistivity. In the plot of T_c vs ρ, normalized by the respective values of the non annealing sample, we can clearly distinguish two regions. First, the critical temperature decreases at almost constant ρ, later there is a rapid decrease in ρ without major changes in T_c. This indicates two thermally induced processes. To detect structure changes during annealing we have investigated the X-ray diffraction pattern. In the first region, we were not able to distinguish any change within our experimental error, in the second when $\rho(4k)/\rho_i(4k) = 0.8$ it was detected[11] a weak structure typical of crystallization. All the results we discuss here, including the thermal conductivity measurements, correspond to thermal heat treatment in the first region.

As was mentioned in the Introduction, if there is only one microscopic parameter that determines T_c, the change in the parameter that corresponds to a given ΔT_c should be independent of the method used to vary T_c.

From specific heat and H_{c2} measurements[5] the change in density of states as a function of concentration is known. From these data we obtain that the change we should expect from the ΔT_c induced by annealing is only a few percent. Since it is very difficult to achieve the necessary precision by measuring specific heats we decided[15] to use the H_{c2} and ρ measurements, together with expression (2), to determine the relation between N(0) and T_c when annealing. There is experimental evidence[5,18] indicating that this expression is valid when applied to splat cooled samples. In this work we assume the validity of expression (2) and we will discuss later some related experimental results, obtained in our laboratory.

Figure 4 shows the results of N(0) obtained from H_{c2} as a function of T_c. The dotts correspond[15] to the variation of N(0) with T_c, induced by annealing and the full line is an interpolation from the data[5] obtained by changing concentration. We see that the data obtained by thermal heat treatment are quite similar to that obtained from the change in concentration. As a consequence, the correlation suggested by Fig. 2 is not more than spurious, indicating that there is no direct relation between T_c and n(0). It would be intereting to understand why the thermal relaxation changes the electronic density of states as well as that of the TLS.

Let us focus our attention on the behaviour of the electrical resistance. We have found that the resistivity increases[11] when the sample is annealed. Since we will not discuss the kinetics of the relaxation process and it is found that T_c is strongly correlated with the behaviour of the resistivity, we plot the resistivity change as a function of the variation of T_c, see Fig.5. The increase in resistivity found for these alloys seems to be characteristic of amorphous transition metals and, to my knowledge, there is no explanation for such behaviour.

It is interesting to remark that in the range of concentration[9,10] we investigate T_c decreases with N(0) and ρ increases when N(0) is diminished. Since we know[5] the experimental relation between concentration and N(0) we can determine $\Delta\rho/\Delta N(0)$ in the range of concentration of interest. It is found[19] that the $\Delta\rho/\Delta N(0)$ obtained from Figs. 4 and 5 is smaller by a factor between 1.3 and 2.2 when compared with that obtained from the change in concentration[9,10]. The range in the slope values is due to the difference between the experimental values of refs. 9 and 10. Considering the difficulties in determining the geometrical factor of amorphous ribbons, we think that the similarity found[19] between the $\Delta\rho/\Delta N(0)$ obtained from the change in concentration and annealing experiments, is strongly indicating that N(0) is also the fundamental parameter determining the behaviour of ρ.

Let us now discuss the results obtained from the penetration depth measurements. Details on the experimental technique used to measure $\lambda(t)$ can be found in reference 20. We will not discuss here the temperature dependence of $\lambda(t)$. We will refer only to the relations between $\lambda(0)$, ρ and T_c, as given by expression (3). We have measured[19,20] $\lambda(0)$, T_c and ρ for different amorphous alloys, the results are shown in table I. We see that expression (3) is verified within a 10% error. Since the error in the geometrical factor is not less than 10% we find the agreement surprising and good. These results are important since until now we have indicated that N(0) is the main microscopic parameter determining the behaviour of several properties of the $Zr_{70}Cu_{30}$ systems.

In a two band model the density of electronic states should be mainly related to the d contribution. As we said in the introduction, expression (3) seems to be incompatible with a two band model since the correction due to a finite mean free path is given by a ratio of two lengths, one characteristic of the superconducting state, ξ_0, the other, ℓ, related to the transport properties in the normal state. In a two band model T_c is determined by the d density of states but the ℓ that appears in (3) should not be the one that determines the measured electrical conductivity.

The experimental verification of expression (3) is strongly suggesting that in these transition amorphous metal there is a single type of carriers contributing to the thermodynamic and transport properties. These results are in agreement with those[5,18] supporting the verification of expression (2). We believe that the suggestion made by tenBosch and Bennemann[8] concerning to hybridization of d and s bands is of fundamental importance for a correct understanding of transport properties in amorphous transition metals.

We have not been able to complete the discussion proposed at the introduction but I hope that future work will serve to verify the ideas exposed previously and will clarify the rest of the remarks made at the beginning of this lecture.

ACKNOWLEDGEMENTS

I want to thank M.E. de la Cruz for her help during the preparation of the manuscript. The results that have been discussed here were obtained at the Low Temperature Group in Bariloche. I gratefully acknowledge many suggestions and discussions with the staff of the group. Many points discussed in the lecture become clearer after useful conversations with C. Balseiro.

REFERENCES

1 H. Tutzauer, P. Esquinazi, M.E. de la Cruz and F. de la Cruz, Rev. Sci. Instrum. 51, 546 (1980).

2 W.L. Johnson, in Glassy Metals I, Vol. 46 of Topics in Applied Physics, edited by H.J. Güntherodt and H. Beck (Springer, N.Y. 1981).

3 R. Harris, L.J. Lewis and M.J. Zuckermann, J. Phys. F 13, 2323 (1983), S.V. Maleev, Sov.Phys. JETP, 57, 149 (1983).

4 P.W. Anderson, K.A. Muttalib, and T.V. Ramakrishnan, Phys. Rev. B 28, 117 (1983); Liam Coffey, K.A. Muttalib and K. Levin, Phys. Rev. Lett. 52, 783 (1984).

5 F.P. Missell, S. Frota-Pessoa, J. Wood, J. Tyler and J.E. Keem, Phys. Rev. B 27, 1596 (1983); K. Samwer and H.v. Lohneysen, Phys. Rev. B 26, 107 (1982).

6 G. Bergmann, Phys. Rev. B 7, 4850 (1973).

7 G.F. Weir and G.J. Morgan, J. Phys. F. 11, 1833 (1981).

8 A. ten Bosch and K.H. Bennemann, J. Phys. F. 5, 13?3 (1975).

9 D. Pavuna, J. of Non Cryst. Sol. - in print.

10 M.N. Baibich, W.B. Muir, Z. Altounian and Tu Guo-Hua, Phys. Rev. B 27, 619 (1983).

11 J. Guimpel and F. de la Cruz, Solid State Commun. 44, 1045 (1982).

12 P. Esquinazi, M.E. de la Cruz, A. Ridner and F. de la Cruz, Solid State Commun. 44, 941 (1982).

13 H.J. Schink, S. Grondey and H.v. Löhneysen, in Phonon Scattering in Condensed Matter, Ed. W. Eisenmenger and S. Döttinger (Springer Series in Solid State Sciences, Vol. 51, 1984).

14 J.C. Lasjaunias, A. Ravex, and O. Béthoux, in Phonon Scattering in Condensed Matter, Ed. W. Eisenmenger and S. Döttinger (Springer Series in Solid State Sciences, Vol.51, 1984).

15 L. Civale, F. de la Cruz and J. Luzuriaga, Solid State Commun, 48, 389 (1983).

16 P.H. Kes and C.C. Tsuei, Phys. Rev. B 29, 5126 (1983).

17 C.M. Varma and Dynes, in Superconductivity in d and f-band Metals, edited by D.H. Douglass (Plenum, N.Y., 1976).

18 M.G. Karkut and R.R. Hake, Phys. Rev. B 28, 1396 (1983).

19 F. de la Cruz, M.E. de la Cruz, L. Civale and R. Arce, to be published.

20 R. Arce, F. de la Cruz and J. Guimpel, Solid State Commun. 47, 885 (1983).

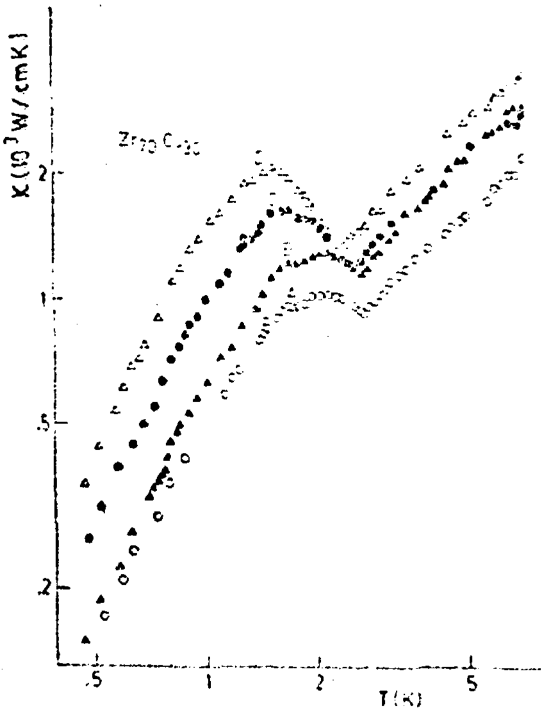

Fig.1 - Thermal conductivity, k, as a function of temperature, T, for amorphous $Zr_{70}Cu_{30}$, for different heat treatments. See ref.12.

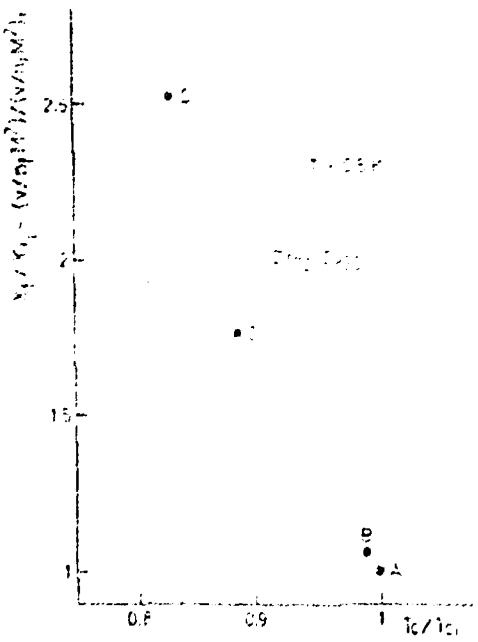

Fig.2 - Thermal conductivity at 0.5k as a function of the change in T_c, induced by annealing.

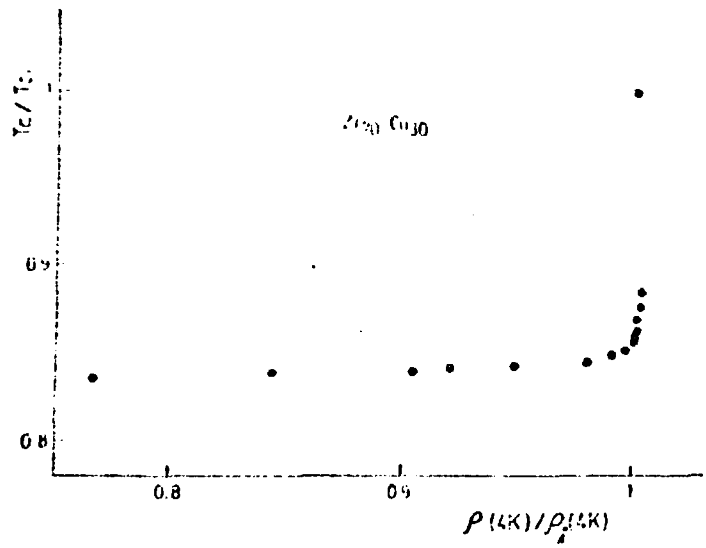

Fig.3 - Variation of the critical temperature as a function of the change in resistivity, induced by annealing.

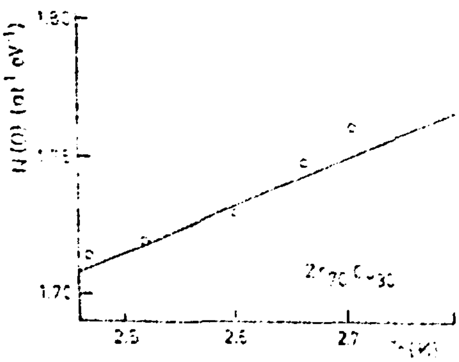

Fig.4 - Density of states, N(0), as a function of T_c. Open circles correspond to the value obtained by annealing, the full curve is an interpolation from ref.5.

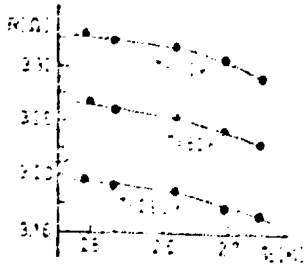

Fig.5 - Variation of the electrical resistance as a function of the critical temperature.

	ρ	[illegible]	N(0)	[illegible]
[illegible]	170	[illegible]	[illegible]	[illegible]
" "	"	[illegible]	[illegible]	[illegible]
" "	"	[illegible]	[illegible]	[illegible]
[illegible]	150	[illegible]	[illegible]	[illegible]
" "	"	[illegible]	[illegible]	[illegible]
[illegible]	170	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
" "	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 1