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MODEL RELATING SUPERCONDUCTIVE PENETRATION DEPTH AND METALLURGICAL PHASE SEPARATION IN AMORPHOUS $La_{70}Cu_{30}$

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A model is proposed to account for the large increase in the measured penetration depth of superconducting, amorphous $La_{70}Cu_{30}$ when the specimens are annealed sufficiently long near, but below, the crystallization temperature. It is suggested that a metallurgical phase separation occurs with domain dimensions in the submicrometer range. Penetration depth measurements as a function of temperature in a weak magnetic field are a useful tool to detect changes in phase separation in high-κ materials.

THE RESISTIVITY ρ of amorphous $La_{70}Cu_{30}$ above the superconductive transition temperature T_c (≈ 3.7K) is about 170 $\mu\Omega$-cm, implying that the electron mean free path l is of the order of the interatomic distance. It is of interest to find out if the mean free path corrections to the theory of superconductivity by Gor'kov [1] are valid for such small values of l. In $La_{70}Cu_{30}$ the value of l is much smaller than the BCS coherence length ξ_0, the Ginzburg–Landau (GL) coherence length $\xi(t = T/T_c)$ and the GL penetration depth $\lambda(t)$. λ is a suitable parameter to test the l dependence of the theory. To this effect we have performed weak field penetration depth measurements on amorphous $La_{70}Cu_{30}$.

In the dirty limit λ is directly related to ρ and T_c, both of which can be readily measured:

$$\lambda = \lambda_L(\xi_0/l)^{1/2} = 1.296 \times 10^{-2}(\rho/T_c)^{1/2}, \quad (1)$$

where

$$\lambda_L = (c\sqrt{3})/[2\sqrt{2\pi N(0)}ev_F],$$

$$\rho = 3/[2e^2 l v_F N(0)],$$

and

$$\xi_0 = (0.18\hbar v_F)/(kT_c)$$

have been used.

In equation (1) ρ is in Ω-cm, T_c in K and λ in cm. $N(0)$ is the density of states per unit energy at the Fermi surface for one spin direction and v_F is the Fermi velocity.

It has been shown [2] that heat treatment below the crystallization temperature (390 K) modifies ρ and T_c, although the resistive transition width, ΔT_c, remains sharp during the whole annealing process. It was then concluded [2] that the system can be considered as homogeneous from a superconducting point of view. Consequently, the measurements of ρ, T_c and λ as a function of heat treatment permits verification of equation (1).

The samples were ribbons 13 μm thick, 0.1 cm wide and 3 cm long obtained by ultrarapid cooling from the molten alloy, using a rotating cylinder technique [3]. The present results were obtained on three different samples, all of which had similar initial critical temperatures ($T_c \approx 3.70$ K). The difference in T_c among the samples was less than 200 mK. The transition width of the as-quenched samples was less than 30 mK. Their resistivity before heat treatment increased slightly as the temperature was decreased. The annealing procedure and the behavior of the three samples was similar to that reported for samples 2 and 3 in [2]. The total reduction in ρ produced by heat treatment was about 30%, with a corresponding decrease in T_c of about 20%. Further annealing at constant temperature (330 K) did not change ρ nor T_c on a time scale of several hours. Partial results for one of the samples have already been reported [4].

The experimental penetration depth $\delta(t)$ was measured by means of a SQUID. Details of the apparatus and measuring techniques are given in [5]. The values of $\delta(t)$ were obtained in the range of field and temperature at which the magnetic flux expulsion was a

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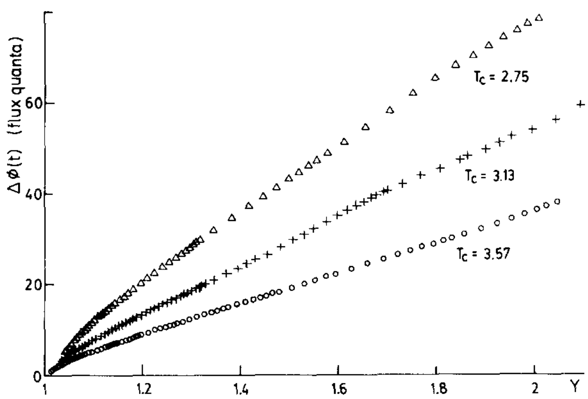

Fig. 1. Expelled flux for $H_0 = 1$ Oe as a function of $y = (1 - t^4)^{-1/2}$ for one of the samples. The different curves correspond to different stages of annealing.

reversible function of temperature and proportional to the applied field, indicating that the sample remained in the Meissner state. The experimental penetration depth is defined by

$$\delta(t) = \frac{1}{H_0}\int_0^d H(x, t)\,\mathrm{d}x, \qquad (2)$$

where H_0 is the applied magnetic field. In our experiments H_0 was applied parallel to the surface of the ribbons and the temperature was swept from $t \approx 0.5$ to well above T_c. The change in magnetic flux, $\Delta\Phi(t)$, produced by the temperature dependence of $\delta(t)$ was measured as a function of temperature. Since the sample remained in the Meissner state $\Delta\Phi(t)$ is

$$\Delta\phi(t) = 2wH_0[\delta(t) - \delta(t \simeq 0)]. \qquad (3)$$

At $t = 1$ this becomes

$$\Delta\phi(1) = 2wH_0[d/2 - \delta(t \simeq 0)]. \qquad (3a)$$

where w is the width and d the thickness of the ribbon. In equation (3) it is assumed that $\delta(t \simeq 0) \ll d \ll w$. $\delta(t \simeq 0)$ can be obtained from equation (3a) if w and d are known. On the other hand it can also be obtained from equation (3) if the phenomenological relation $\delta(y) = \delta(0)y$ is assumed to apply, where $y = (1 - t^4)^{-1/2}$. In any event, since heat treatment is performed on the same sample, the variation of $\delta(0)$ was obtained with good precision.

Figure 1 shows $\Delta\Phi(y)$ as a function of y for one of the samples. The different curves correspond to different T_c values obtained by annealing. It can be seen that the temperature dependence is well described by $\delta(y) = \delta(0)y$. The values for $\delta(0)$ were obtained from equation (3).

Figure 2 shows $\delta(0)/\delta_i(0)$ as a function of $T_c/T_{ci} = \tau$, where $\delta_i(0)$ and T_{ci} are the initial values obtained in the as-quenched samples. In the same figure the dashed

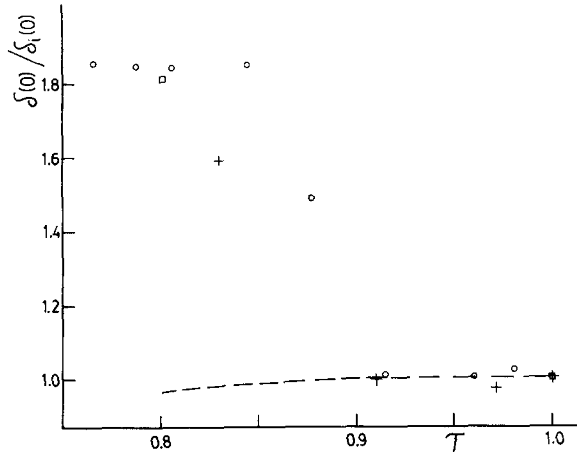

Fig. 2. Annealing effect on the penetration depth, normalized by the value of the as-quenched samples, as a function of $\tau = T_c/T_{ci}$ for three different samples. Sample 1: ×, $T_{ci} = 3.75$ K. Sample 2: □, $T_{ci} = 3.65$ K. Sample 3: ○, $T_{ci} = 3.57$ K. The dashed line represents typical values of $(\rho/T_c)^{1/2}$ normalized by those of the non-annealed sample.

line represents, within 15% accuracy, the values of $(\rho/T_c)^{1/2}$ normalized by that of the non-annealed material for all measured samples. It is seen that equation (1) describes well the penetration depth when $\tau \gtrsim 0.9$. For $\tau < 0.9$, the value of $\delta(0)$ increases although $(\rho/T)^{1/2}$ remains practically constant. What is more important is that over the whole range of τ-values $\rho \propto T_c$ and neither ρ nor T_c show any unusual behavior in the vicinity of $\tau = 0.9$. The average value calculated from $1.296 \times 10^{-2}(\rho/T_c)^{1/2}$ is 0.9×10^{-4} cm in good agreement with the measured value $\delta_i(0) \simeq 1.07 \times 10^{-4}$ cm for $\tau \gtrsim 0.9$.

Equation (1) describes then quantitatively the behavior of the penetration depth for $\tau \gtrsim 0.9$. This is surprising, not only because of the extremely short mean free paths, but also because superconductivity in La is complex [6]. We plan to investigate equation (1) for other amorphous materials.

In order to explain $\delta(0)$ for $\tau < 0.9$ we want to point out that great interest has lately been focused on non-homogeneous superconductors. Quite recent measurements of the upper critical field, H_{c2}, in amorphous materials have been interpreted [7] on the basis of a non-homogeneous distribution of electron diffusivity in the bulk of the specimens. We propose that annealing produces a metallurgical phase separation in the submicrometer range. Penetration depth measurements as a function of temperature in a weak magnetic field are a useful tool to detect such changes in high-κ materials. The behavior of $\delta(0)$ for $\tau < 0.9$ can be interpreted as being characteristic of inhomogeneous superconductors. The penetration depth will be affected

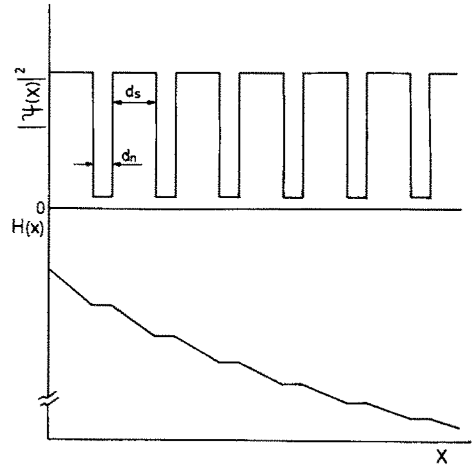

Fig. 3. Shown is the superfluid density and the local magnetic field near the surface of the specimen after phase separation has occured. This is a schematic plot of the simple model.

by inhomogeneities whose characteristic parameters are different from those of the matrix in which they are embedded.

We propose a very simple model to explain the observed behavior of $\delta(0)$. For $\tau \gtrsim 0.9$ the material is homogeneous on the scale of $\delta(0)$. When $\tau \simeq 0.9$ a phase separation starts to occur which nucleates "normal" (weakly superconducting) regions within the superconducting matrix whose dimensions are comparable to or smaller than $\lambda(t)$. The thickness of the superconducting regions must be larger than $\xi(t)$ since measurements of (dH_{c2}/dt) at T_c do not show any significant change when passing through $\tau \approx 0.9$. We visualize a simplified two-dimensional periodic structure with "normal" and superconducting regions of thickness d_n and d_s, respectively. In Fig. 3 we show schematically the distribution of the square of the order parameter and the local magnetic flux density as a function of the distance x from the surface. Notice that we have taken $|\psi|^2$ finite in the "normal" region although much smaller than in the superconducting matrix. Therefore, the flux can penetrate continuously and reversibly into the "normal" regions and the magnetic field is for all practical purposes uniform over d_n. $H(x)$ must have the shape shown in Fig. 3.

The experimental penetration depth is then

$$\delta(t) = \lambda(t)(1 + (d_n/d_s)f(z(y))), \qquad (4)$$

where $\lambda(t) = \lambda(0)y(t)$, $f(z) = z/[\exp(z) - 1]$ and $z = d_s/\lambda(t)$. Equation (4) shows the following limiting values:

(a) for $d_n \to 0$, $\delta(t) \to \lambda(t)$;
(b) for $d_s \gg \lambda(t)$, $\delta(t) \to \lambda(t)$; and
(c) for $d_s \lesssim \lambda(t)$,

$$\delta(t)/\lambda(t) \approx 1 + (d_n/d_s)[1 - z(y)/2 + z^2(y)/12 + \ldots] \qquad (4a)$$

We notice that if $z(y)$ is small the temperature dependence of $\delta(t)$ is similar to that of $\lambda(t)$. Equation (4a) indicates that precise measurements of the temperature dependence of $\delta(t)$ allow an independent determination of d_n and d_s provided $\lambda(0)$ is obtained from the data for $\tau > 0.9$. Experimentally, small differences in the temperature dependence between the as-quenched and heat treated sample are found [4, 5]. Unfortunately, it is difficult to determine the correction term in equation (4a) since the approximation $\lambda(t) = \lambda(0)y$ has intrinsic deviations that might also change with annealing. Considering this and the experimental error, equation (4a) is used only to indicate that for $\tau \leqslant 0.9$, $d_n/d_s \approx 0.8$.

Until further metallographical information is available the proposed model should be interpreted to be more of a qualitative than quantitative nature. X-ray diffraction analyses in the as-quenched samples are typical of amorphous metals [8]. Preliminary data for heat treated samples show modification in the X-ray spectra. Further studies are in progress to identify the origin of the modifications. It is interesting to notice that the time evolution of ρ and T_c with annealing is consistent [9] with a nucleation and growth process.

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REFERENCES

1. P.L. Gor'kov, *Zh. Eksp. Teor. Fiz.* **37**, 1407 (1959); [Engl. Trans.: *JETP* **10**, 998 (1960)].
2. P. Esquinazi, M.E. de la Cruz & F. de la Cruz, *Physica* **108B**, 1215 (1981).
3. H. Tutzauer, P. Esquinazi, M.E. de la Cruz & F. de la Cruz, *Rev. Sci. Instrum.* **51**, 546 (1980).
4. R. Arce, F. de la Cruz & P. Esquinazi, *Physica* **108B**, 1253 (1981).
5. R. Arce, F. de la Cruz & P. Esquinazi, *Solid State Commun.* **38**, 1253 (1981).
6. C. Probst & J. Wittig, *Handbook on the Physics and Chemistry of Rare Earths* (Edited by K.A. Gschneidner and L. Eyring), Chapter 10. North-Holland, Amsterdam (1978).
7. W.L. Carter, S.J. Poon, G.W. Hull, Jr. & T.H. Geballe, *Solid State Commun.* **39**, 41 (1981).
8. P. Esquinazi, Licenciatura Thesis (1980) (unpublished). The authors thank Dr Iris Torreani from UNICAMP, Brasil, for her collaboration in the X-ray analysis of the samples.
9. B. Guillet & P. Esquinazi (private communication).