Classification

Physics Abstracts

74.40+k — 74.70Vy — 64.60Fr

Intragranular and intergranular transitions in Y-Ba-Cu-O ceramics

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(Reçu le 28 mai 1989, accepté le 31 juillet 1989)

Résumé. — Nous pouvons décrire quantitativement la transition résistive en fonction de la température (de $\rho \approx \rho_N$ à $\rho = 0$) de céramiques Y-Ba-Cu-O en considérant successivement la transition supraconductrice intragrain à $T = T_{cs}$ et la transition intergrain à la cohérence de phase à $T_c < T_{cs}$ induite par le couplage Josephson entre les grains. La transition à la cohérence est analogue à la transition paramagnétisme-ferromagnétisme d'un ferromagnétique X-Y désordonné (3D). Dans la région paraconductrice $T > T_{cs}$, les fluctuations de l'amplitude du paramètre d'ordre supraconducteur des grains individuels conduisent à une conductivité supplémentaire calculée d'après les théories d'Azlamazov et Larkin et/ou de Lawrence et Doniach. Dans la région paracoherente $T_c < T < T_{cs}$, les fluctuations de phase dans les grains sont responsables du comportement critique de la conductivité. Les résultats expérimentaux concernant la paraconductivité d'échantillons de degrés de granularité différents suggèrent l'existence d'une structure lamellaire dans les grains. Par contre au voisinage de T_c , le comportement de $\rho(T)$ et des caractéristiques $V(I)$ est toujours déterminé par la transition à la cohérence.

Abstract. — We describe quantitatively the whole resistive transition (from $\rho \approx \rho_N$ to $\rho = 0$) of Y-Ba-Cu-O ceramics as two successive phase transitions : the intragrain superconducting transition at T_{cs} and the intergrain coherence transition induced by the Josephson coupling between neighbouring grains at $T_c < T_{cs}$. The coherence transition is similar to the paramagnetism-ferromagnetism transition in a 3D disordered X-Y ferromagnet. In the paraconductive region $T > T_{cs}$, the fluctuations in the amplitude of the superconducting order parameter in the grains lead to an excess conductivity given by the Azlamazov-Larkin and/or the Lawrence-Doniach theories. In the paracoherent region $T_c < T < T_{cs}$, phase fluctuations result in critical behaviour of the excess conductivity. Above T_{cs} , the paraconductivity of samples with different degrees of granularity reflects a layered structure, while near T_c the behaviour of $\rho(T)$ and $V(I)$ characteristics is always determined by the 3D coherence transition.

1. Introduction.

In previous work we have extensively studied the made of weakly coupled superconducting grains (Nb or Ta) imbedded in epoxy resin. Now, it is well known that granularity plays an important role in determining the transport and magnetic properties of high- T_c compounds. But in opposition to « simple » granularity found in bulk granular superconductors, in high- T_c ceramics we have evidence of a multiple-level granularity [5]. In this paper we study the resistive transition of Y-Ba-Cu-O ceramics ; our results can be quantitatively described by a simple model involving two phase transitions : the intragrain

superconductive transition at T_{cs} and the intergrain coherence transition at $T_c < T_{cs}$.

Above the superconducting critical temperature T_{cs} , can be explained by fluctuations in the amplitude of the superconducting order parameter in the grains giving an excess conductivity (paraconductivity) for $T > T_{cs}$. This effect has been calculated for Gaussian fluctuations by Azlamazov and Larkin (AL) for d-dimensional superconductors [6] and by Lawrence and Doniach (LD) for very anisotropic layered materials [7].

On the other hand, below T_{cs} the amplitude of the superconducting order parameter is no longer a fluctuating quantity. But the phases in the grains

may fluctuate inducing the Josephson effect across the barriers and these fluctuations lead to an excess conductivity. The transition to phase coherence at $T_c < T_{cs}$ is analogous to the paramagnetic-ferromagnetic transition of 3D X-Y ferromagnets, where the Josephson coupling plays the role of an exchange energy between 2D spins [2]. In the critical region $T \geq T_c$ and $T \leq T_c$ physical quantities should be governed by power laws in $t = |T - T_c|/T_c$ characterized by the critical exponents of a 3D disordered X-Y model. In particular the paracoherent excess conductivity is expected to display critical behaviour.

A great number of papers have studied the paraconductivity in high T_c superconductors (HTS). Measurements on polycrystalline samples [8-12], oriented thin films [13] and single crystals [14, 15] were fit to the 3D or 2D Azlamazov and Larkin model or to the Lawrence and Doniach model. These fits indicate agreement for the temperature dependence of the excess conductivity but the amplitude differs from that predicted by theories and a sample-dependent correction factor C is sometimes needed [13]. This factor depends on the normal resistivity ρ_N of the samples and in the high temperature region $C^{-1} d\rho_N/dT \sim 0.5-0.6 \mu\Omega \cdot \text{cm} \cdot \text{K}^{-1}$. Furthermore the multiplication of adjustable parameters and correction factors brings about considerable ambiguity in determining whether superconductivity fluctuations are 2D or 3D.

In the following, we show that the concept of granularity is essential to describe the resistive transition of ceramics; in this way we study the resistivity $\rho(T)$ in the paracoherent region $T_c < T < T_{cs}$, the $V(I)$ characteristics at $T \approx T_c$ and the paraconductivity at $T > T_{cs}$. Furthermore we discuss in section 2 the conditions for the observation of granularity in the normal and superconducting states.

2. Normal — and superconducting — state granularity.

An interesting feature of granularity, which in our opinion has been overlooked in the past, is that it may have spectacular effects in the superconducting and in the normal state, but not necessarily in both of them for the same sample. To illustrate this idea, let us consider grains made of a free-electron metal, coupled by ideal Josephson tunnel junctions in the limit $T \rightarrow 0$.

It is well-known [16] that the size a of the grains has a minimum value a_0 compatible with superconductivity :

$$a > (N(0) \Delta)^{-1/3} \approx a_0 \approx 3 \text{ nm} \quad (1)$$

which simply expresses the fact that the superconducting energy gap Δ must be larger than the average level distance as obtained from the density

of states at the Fermi energy $N(0)$. The Josephson coupling energy is [17]

$$J = R_0 \Delta / R_J = R_0 a \Delta / \rho_b, \quad (2)$$

where $R_0 = \pi \hbar / 4 e^2 = 3 \, 230 \, \Omega$ and $\rho_b = R_J a$ is the barriers' contribution to the total resistivity. This may be compared to the grain condensation energy

$$E_c = \frac{1}{2} N(0) \Delta^2 a^3 > E_{G0} = \frac{\Delta}{2} \quad (3)$$

to give the parameter $J/E_c < 2 R_0/R_J$. It is interesting to point out here — although the coincidence may be purely fortuitous — that superconductivity disappears in 2D granular films with resistance per square $R \approx 2 R_0$ [18]. Another limitation, $J/E_c < 1$, simply comes from the fact that J is a first-order perturbation effect. Therefore values of $J/E_c > 1$ [19] only indicate the disappearance of granular behaviour, replaced by the properties of homogeneous superconductors. Equations (2) and (3) are of course valid for low-temperature superconductors (LTS). They are based however on very general physical ideas, like phase coherence and the existence of an energy gap; the latter should be independent of the pairing mechanism and in particular applicable to HTS. The same applies to the characteristic coherence length

$$\xi_0 = \frac{\hbar v_F}{\pi \Delta}. \quad (4)$$

In the normal state, the parameter measuring the importance of granularity is $x = \rho_b/\rho_N$, where the normal resistivity $\rho_N = \rho_{GN} + \rho_b$ with

$$\frac{1}{\rho_{GN}} = \frac{1}{3} e^2 N(0) v_F^2 \tau \quad (5)$$

for a free-electron model. The mean free path is $\ell = v_F \tau$.

Combining equations (2) to (5), we obtain

$$x^{-1} = 1 + \frac{6}{\pi^2} \frac{a^2}{\xi_0 \ell} \frac{J}{E_c}, \quad (6)$$

where $a/a_0 > 1$ for superconductivity. Typical values in granular LTS thin films are $a \approx 10 \text{ nm}$, $\xi_0 \approx 100 \text{ nm}$, $\ell \approx 200 \text{ nm}$, so $a^2/\xi_0 \ell \approx 5 \cdot 10^{-3}$ while in HTS $a \geq 10^2 \text{ nm}$, $\xi_0 \approx 1 \text{ nm}$, $\ell \approx 1 \text{ nm}$, giving $a^2/\xi_0 \ell \geq 10^4$. The two behaviours are shown schematically in figure 1 putting, for the sake of clarity, $a^2/\xi_0 \ell \approx 1$ for LTS, 100 for HTS: while LTS which are granular in the superconducting state ($J < E_c$) are also granular ($\rho_b/\rho_N \geq 0.5$) when normal, HTS may have ρ_b/ρ_N small, and still display granular superconducting behaviour.

Fig. 1. — Phase diagramme illustrating normal- and superconducting-state granularity. The LTS and HTS curves have been calculated using $a^2/\xi_0 \ell = 1$ and 100 respectively. The arrows indicate the direction in which granular (G) or homogeneous (H) behaviour prevails in the normal (N) or superconducting (S) state.

3. Critical behaviour.

A development of the analogy with the X-Y model leads to the excess conductivity at $T \approx T_c$ [4] :

$$\sigma_s(T, I_s) = t^{-\gamma} f^{\pm} \left(\frac{I_s - I_c}{t^{\varphi}} \right) \quad (7)$$

where I_s is the supercurrent flowing in the sample, I_c the critical current ($I_c \neq 0$ for $T < T_c$), φ a crossover exponent and $f^{\pm}$ are scaling functions for $T > T_c$ and $T < T_c$. In the limit $I_s \rightarrow 0$ we obtain :

$$\sigma_s \sim t^{-\gamma}. \quad (8)$$

Taking into account the behaviour of f^- for $T \rightarrow T_c^-$ and the scaling relations, the integration of equation (7) gives :

$$V \sim (I_s - I_c)^{a(T)} \quad (9)$$

with $a(T_c) = 1 + \gamma/\varphi \approx 2$ for 3D bulk granular superconductors.

We measure the resistive transition and the

samples with different degrees of granularity [20] : two ceramics pressed into pellets made with a standard technique [21] but with different porosity referred to as SP (stoichiometric polycrystalline) sample and HP (high porosity) sample ; and a sample with induced granularity (IG) obtained by thinning HP material in the presence of water. This probably results in the formation of hydroxides at the surface of the grains [22]. The three types of samples are characterized by their resistivity at 250 K (see Tab. I) ; the SP and HP samples display

Table I. — Characteristic parameters of the samples.

Sample	SP	HP	IG
ρ_{250} (m Ω .cm)	2.27	10	28
T_c (K)	89.4	86.9	76.9
T_{cs} (K)	90.6	90.6	90.9
x	0.75	0.795	0.9
LD fit d (nm) $\xi_c(0)$ (nm)	1.17 0.2	1.17 0.35	
AL fit $\xi(0)$ (nm)			0.56

$d\rho_N/dT > 0$, while the IG sample has $d\rho_N/dT < 0$. A distinctive feature of granularity in our samples is their sensitivity to low magnetic fields (< 50 $\text{\AA}$) in the region $\rho \rightarrow 0$ [3] (in increasing order : HP and IG samples, the resistive transition of the SP sample being unaffected by low fields).

In our model, we consider two contributions to the resistivity of the sample : the resistivity of the grain's material ρ_G and the resistivity of the barriers ρ_b [23] ; so the measured resistivity is $\rho(T) = \rho_G(T) + \rho_b(T)$. Now, in the para coherent region $T < T_{cs}$, the grains are superconductors ($\rho_G = 0$), and the resistivity $\rho_b(T)$ is assumed to be affected by phase fluctuations in the grains. The resulting excess conductivity $\sigma_s = 1/\rho - 1/\rho_b$ (with $\rho_b = \rho_b(T_{cs})$) is compared to the predictions of equation (8). From figure 2 it appears that the three types of samples behave similarly and the critical exponent $\gamma \approx 2.7$ coincides with the value found in bulk granular samples. T_c has been determined by a linear extrapolation of $(\rho/(\rho_b - \rho))^{1/\gamma}$ as a function of T , with ρ_b the value which optimizes the fit in figure 2.

From a fit of equation (9) to log-log plots of V against $I_s - I_c$ with $I_s = I - V/R_b$, we obtain $a(T)$. I_c is the fitting parameter and R_b is determined from the value of ρ_b . The results for the three samples are shown in figure 3. Using T_c found from figure 2, we find $a(T_c) = 1.9 \pm 0.2$ in good agreement with similar measurements on granular Ta samples. Below T_c the fit to equation (9) with $I_c = 0$ is rather worse but it becomes reasonable with $I_c \neq 0$. The exponent $a(T_c)$ is strongly dependent on the space dimensionality, so we conclude that for $T \leq T_c$ the behaviour of Y-Ba-Cu-O ceramics is determined by 3D granularity ; the X-Y coherence transition prevents the observation of a possible 2D Kosterlitz-Thouless transition [24] where the vol-

Fig. 2. — Scaling behaviour of the resistivities of the SP, HP and IG samples (the upper scale is relative to the IG sample). The same exponent $\gamma = 2.7$ applies for the three types of samples.

Fig. 3. — Critical exponent $a(T)$ of the HP and IG samples obtained from fitting the experimental data to equation (9).

tage-current characteristics are $V \sim I_s^a$ with $a(T_{KT}) = 3$ [25]. Furthermore, up to now the complex multiple-level granularity of Y-Ba-Cu-O does not seem to affect the critical behaviour.

4. Paraconductivity, Gaussian fluctuations.

In the paraconductive region ($T > T_{cs}$), our model assumes that fluctuations are localised in the grains and do not affect the barrier resistivity. So the resistivity of the system can be written as: $\rho = \rho_b + 1/(\sigma_{GN} + \sigma')$, where σ_{GN} is the normal conductivity of the grains and σ' the excess conductivity due to the fluctuations of the amplitude of the

superconducting order parameter. Considering Gaussian fluctuations, the Lawrence and Doniach expression for the latter quantity is :

$$\sigma'_{LD} = g(d^2\varepsilon^2 + 4\xi_c^2(0)\varepsilon)^{-1/2} \quad (10)$$

where $g = e^2/16\hbar = 1.52 \cdot 10^{-5} \Omega^{-1}$, d is the distance between the layers, $\xi_c(0)$ the coherence length perpendicular to the layers at $T \rightarrow 0$ and $\varepsilon = (T - T_{cs}^{mf})/T_{cs}^{mf}$ is a reduced temperature. The mean field transition temperature T_{cs}^{mf} is found to be very close to T_{cs} in LTS so we shall consider $T_{cs}^{mf} \approx T_{cs}$ by analogy. At sufficiently high temperatures, the expression (10) will diverge as ε^{-1} and coincides with the 2D Azlamazov and Larkin expression σ'_{AL} (2D), while near T_{cs} , we get the $\varepsilon^{-1/2}$ dependence of σ'_{AL} (3D).

Our model gives the deviation due to the superconducting fluctuations of the measured resistivity $\rho(T)$ from the normal resistivity $\rho_N(T) = \rho_{GN}(T) + \rho_b(T)$

$$\delta\rho = \rho_N(T) - \rho(T) = \frac{\sigma' \rho_{GN}^2(T)}{1 + \sigma' \rho_{GN}(T)}. \quad (11)$$

We test these predictions for SP, HP and IG samples. The calculation of σ' requires the determination of T_{cs} ; this parameter, as defined from the fit in figure 2 by $\rho(T_{cs}) = \rho_b$ is practically the same for the three samples. We estimate $\rho_N(T)$ by linearly extrapolating the behaviour of $\rho(T)$ from the high temperature region. We also assume that the ratio $\rho_{GN}(T)/\rho_N(T)$ is slowly varying with temperature and take it independent of T . Notice that the quantity $x = 1 - \rho_{GN}(T)/\rho_N(T) = \rho_b(T)/\rho_N(T)$

Fig. 4. — Deviation of the measured resistivity from the normal resistivity as a function of reduced temperature for the SP, HP and IG samples. The solid lines are predictions of the Lawrence and Doniach theory (SP and HP samples) and of the Azlamazov and Larkin theory (IG sample). The fitting parameters are listed in table I.

measures the amount of granularity of the sample. We have analyzed the measured resistivity in terms of AL and LD theories. Experimental results are shown in figure 4 together with calculations from equation (11). We obtain a rather good fit to the LD model for SP and HP samples with $\xi_c(0) = 0.2$ nm, $d = 1.17$ nm and $\xi_c(0) = 0.35$ nm, $d = 1.17$ nm respectively. However for the IG sample we find no evidence of a 2D behaviour and the results are described by the 3D AL model with $\xi(0) = 0.56$ nm. The characteristic parameters of the samples are listed in table I.

So, analysis of the paraconductivity data gives informations about the dimensionality of the superconducting transition in the grains. Our results reflect a layered structure but this 2D character disappears in the presence of strong disorder.

5. Discussion.

We have shown that the resistive transition of Y-Ba-Cu-O ceramics can be described by considering: 1) the excess conductivity due to Gaussian fluctuations above the intragranular transition at T_{cs} ; 2) the excess conductivity due to phase fluctuations in the critical region above T_c . The intergranular coherence transition is always 3D while the intragranular transition seems to be strongly influenced by disorder. The consistency of our approach is demonstrated by the fact that the parameters

determined in the paracoherent region need no further adjustment in the paraconductive and coherent regions.

Our description shows that the correction factor introduced to explain some experimental results on paraconductivity is due to the granular structure of the samples. In our calculation [20] we have found $C = (1 - x)^{-2}$. By the same token the correlation between the temperature derivative of the normal resistivity and the correction factor has been established.

In conclusion we emphasize the importance of the granular structure in determining the behaviour of the resistive transition of high T_c ceramics. But the granularity in these compounds is a much more complex phenomena than that encountered in bulk granular superconductors. While in the last systems highly conductive homogeneous grains are connected through highly resistive barriers ($\rho_{GN} \ll \rho_b$) in ceramics ρ_{GN} and ρ_b are of the same order of magnitude.

Acknowledgments.

We would like to thank O. Peña, C. Perrin and A. Perrin of the Laboratoire de Chimie Minérale B, for preparing and analysing the samples. This work has been supported by the Ministère de la Recherche et de l'Enseignement Supérieur, under contract N° 88F 1701.

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