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LETTER TO THE EDITOR

SUPERCONDUCTING WEAK LINKS IN $YBa_2Cu_3O_{7-\delta}$ AN AC MAGNETIC SUSCEPTIBILITY STUDY

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AC magnetic susceptibility, χ' and χ'', and ac resistivity, ρ, of two different samples of superconducting $YBa_2Cu_3O_{7-\delta}$ have been measured. The results show a strong non-linear behaviour and are very sensitive to the exciting amplitudes. From the analysis of the data and comparison with appropriate models and other superconducting compounds, evidence for the existence of weak superconducting links is inferred. Finally, the utility of ac χ measurements for detection of different superconducting phases is made evident.

1. Introduction

Superconductivity on $YBa_2Cu_3O_{7-\delta}$ and on related systems has been often assessed by means of ac magnetic susceptibility, since their associated diamagnetism is easily detected in bulk (sintered) or powdered samples. The ceramic nature of the compounds and the coexistence of different superconducting phases complicate the phenomenology associated with the phase transition, which is less sharply defined than in usual low temperature superconductors. Moreover, the presence of superconducting regions or grains coupled by weak links or Josephson type junctions [1] and with different transition temperatures complicates the analysis of the data. Furthermore, as the oxygen deficiency structure reflects the valence state of the Cu ions, which is certainly related to the superconducting state, the physical behaviour changes from one sample to another, depending on the synthesis method and on the sinterization treatment. As a consequence, there are differences in the measurements depending on the sample, and caution should be paid to derive meaningful results. In the present contribution a careful study of the ac magnetic susceptibility $\chi = \chi' -$ iχ'' (χ' = in-phase and χ'' = out-phase components) has been undertaken for samples obtained by two different methods. In addition, ac resistivity measurements on the same samples have been performed, to correlate the magnetic and electrical conduction properties. Finally, the observed superconducting behaviour has been compared with available phenomenological theory and with the behaviour of other high and low temperature superconductors.

2. Experimental

Two different samples have been studied. Sample I was prepared mixing fine powders of $BaCO_3$, Y_2O_3 and CuO in stoichiometric proportions according to the formula $YBa_2Cu_3O_7$ [2]. The mixture was heated at 900 °C for 15 h, quenched in air, reground and sintered at 800 °C for 12 h. Finally, the compound was slowly cooled (10 h) to 300 °C under an oxygen flow. Sample II was obtained by the citrate route [3]. The same starting materials were solved in nitric acid, to which citric acid was added, and neutralized with ammonia.

nm), which underwent the same procedure described above. Sample II was characterized (except for indetermination of oxygen content), and X-ray diffraction showed to be mostly a single phase system [3]. Both samples were cut into $0.11 \times 0.12 \times 0.55$ and $0.18 \times 0.17 \times 0.62$ cm^3 bars with apparent densities of 4.28 and 6.51 g cm^{-3}, respectively.

According to ac resistivity measurements, $\rho(T)$, on sample I ($\nu = 3$ Hz and 2 mA amplitude), the onset of superconductivity appears at $T_0(\rho) = 87$ K, whereas the resistance becomes zero at $T_c = 75$ K. Similar $\rho(T)$ data on sample II give zero resistivity at $T_c = 91.2$ K. Thus, quite obviously, sample I contains a superconducting phase (or phases) somewhat out of stoichiometry with respect to the now well established $YBa_2Cu_3O_{7-\delta}$ optimal composition [4].

Measurements of χ' and χ'' as a function of temperature for both samples were conducted in a computer controlled susceptometer described elsewhere [5] with the ac field applied in the longer dimension of the bars. Since no attempt to shield the earth magnetic field was done, χ' is only a quasi-initial susceptibility. The frequency applied was $\nu = 121$ Hz, and the exciting field amplitude, h_0, ranged from 1.1 mOe to 11 Oe.

In sample I, the onset of diamagnetism starts at $T_0(\chi') \approx T_0(\rho)$, independently of h_0. However, the strong decrease in χ' takes place at a lower temperature and depends on h_0 (see figs. 1a and b). For the lowest value, $h_0 = 1.1$ mOe, χ' decreases at 75 K, in coincidence with T_c determined from resistivity. At low temperature χ' reaches an asymptotic value of -21.1×10^{-3} emu/g. The χ' curves become smoother for increasingly higher h_0 values while the low temperature limit increases dramatically. For all measured h_0 values χ'' shows a peak, which starts at T_c (see fig. 1c), and has its maximum approximately located at the inflexion point of χ'. As h_0 increases, the height of the χ'' peak increases too, but reaches a maximum value of about 15% of $-\chi'$ ($T \approx 0$ K, $h_0 \approx 1$ mOe). Finally, a minor hysteresis (0.2 K) was observed between warming and cooling determinations, in spite of the care paid to reach thermal equilibrium for every point.

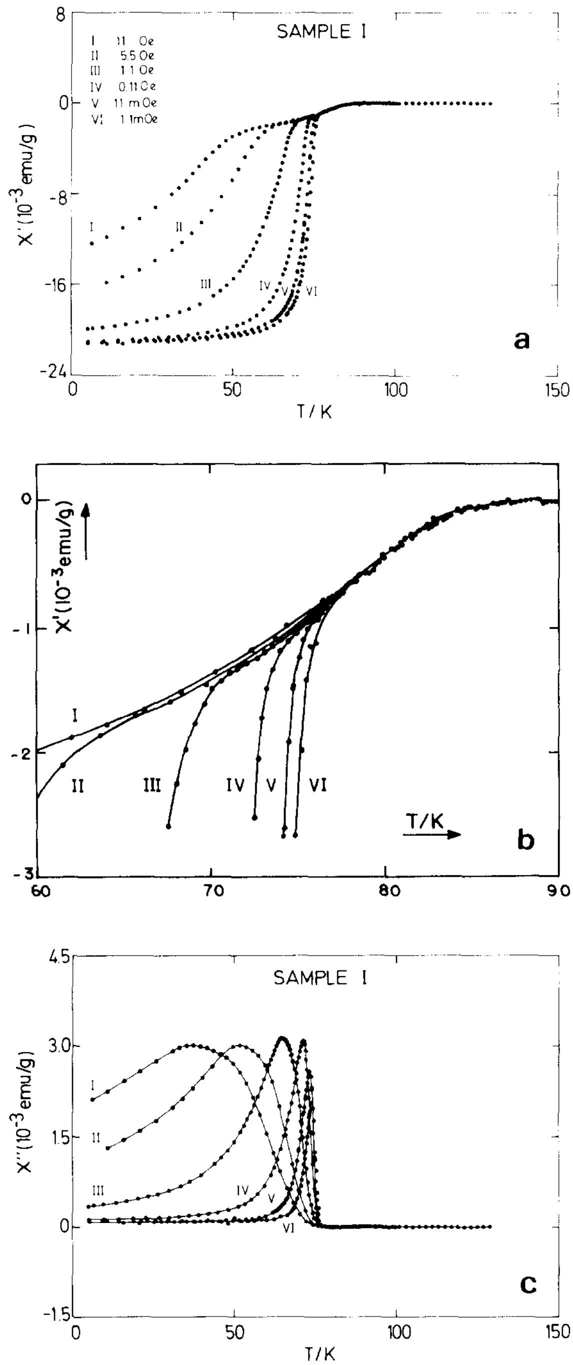

Fig. 1. In-phase (a) and out-phase (c) ac magnetic susceptibility of $YBa_2Cu_3O_{7-\delta}$, sample I, for $\nu = 121$ Hz. The curves labeled I to VI correspond to different exciting amplitudes. In (b) the region close to the superconducting percolative transi-

sample II and the results were somewhat different, as shown in fig. 2. Though the diamagnetism onset temperature ($T_0(\chi') = 91.8$ K) is quite satisfactory, one clearly observes a marked change in the

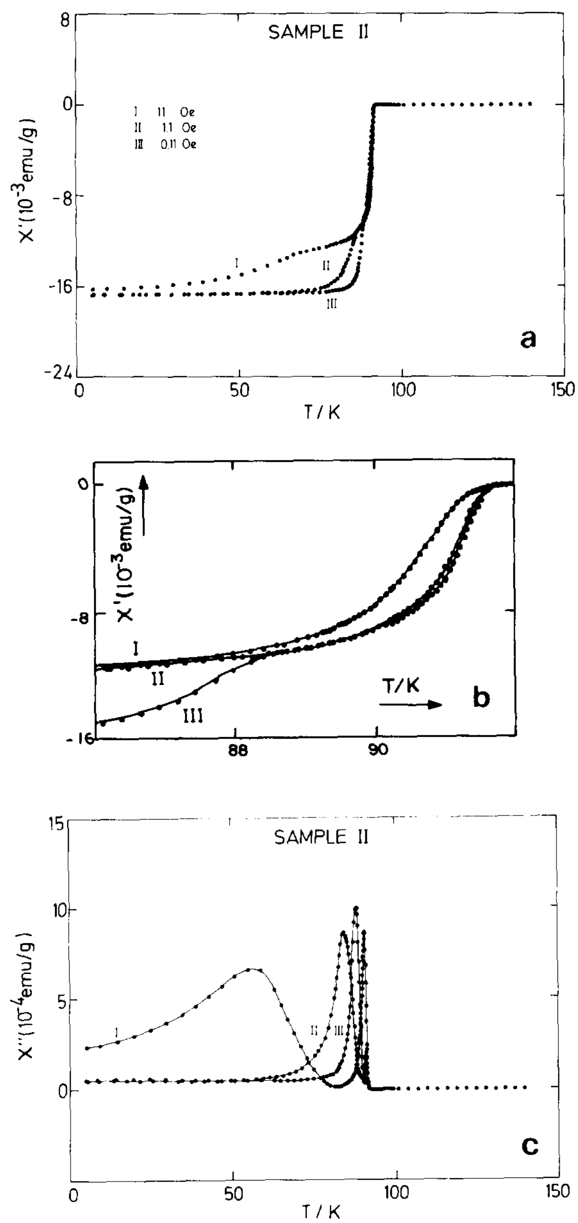

Fig. 2. In-phase (a) and out-phase (c) ac magnetic susceptibility of $YBa_2Cu_3O_{7-\delta}$, sample II, for $\nu = 121$ Hz. The curves correspond to different exciting amplitudes. In (b) the region

χ' slope at 85 K, which is close to the onset point of superconductivity [$T_0(\rho)$] for sample I. The χ'' measurements show more dramatically the presence of two peaks, each centered at the midpoints of the two segments of the $\chi'(T)$ anomalous curve. Both χ'' peaks depend on h_0, but the one corresponding to 91.5 K has a smaller height and is sharper than the lower temperature peak. These results clearly indicate the presence of different superconducting phases in the same sample, most probably due to inhomogeneities in the oxidation process after sinterization. At low temperatures $\chi'(T)$ reaches a constant value of -16.7×10^{-3} emu/g which, considering the apparent densities and approximate demagnetizing factors, $D(\mathrm{I})/4\pi \approx 0.059$ and $D(\mathrm{II})/4\pi \approx 0.090$, gives differences of 13%.

The h_0 dependence of χ' and χ'' depicted in figs. 1 and 2 has been previously reported for La–Sr–Cu–O systems [6,7] and for $YBa_2Cu_3O_{7-\delta}$ [8]. The diamagnetism detected below T_0 is undoubtedly caused by the Meissner effect, but, following Hein [9], one avoids any interpretation of the extrapolated $\chi'(T = 0)$ value as a measure of the amount of superconducting volume, because ac χ measurements do not discern between bulk and non-bulk superconductivity.

On sample I, ac voltage versus intensity was measured, for temperatures below T_0 (see fig. 3), and the existence of a critical current of $I_0 \approx 12$

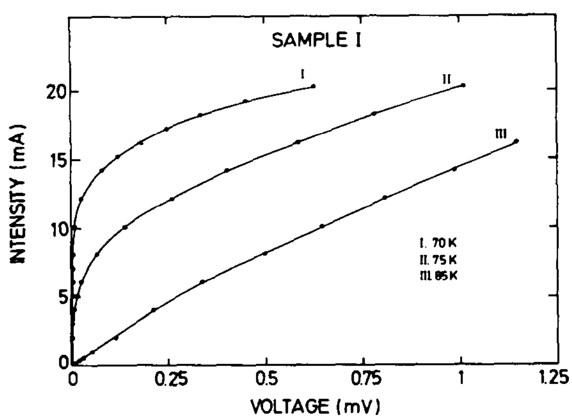

Fig. 3. AC current amplitude versus voltage of $YBa_2Cu_3O_{7-\delta}$ (sample I) for $\nu = 3$ Hz and temperatures above and below

mA at $T = 70$ K (which implies a critical current density of $J_0 \approx 0.75$ A/cm^2) is evident. This critical current is quite low, but of the order of that found for a sample obtained with the same preparation technique [10]. However, it should be noted that for 85 K (i.e. between T_c and T_0) the $I-V$ characteristic is non-linear, which is ascribed to the presence of connected (out of percolation) superconducting regions. Even more, $\rho(T)$ measurements with 20 mA do not reproduce, below 130 K, the data recorded with 2 mA, and $\rho(T)$ becomes zero at a different temperature, $T_c' = 64$ K.

3. Discussion

The χ' and χ'' results described above can be understood in terms of a model proposed by Ishida and Mazaki [11] to predict the response of a superconducting multiconnected structure to a small ac field. The mechanism involved is the creation of an increasing number of weakly linked superconducting loops, as the temperature becomes lower than the percolative zero resistance $T_c(\rho = 0)$. The model treats any number of loops as an equivalent weakly connected single loop, in which a current density necessary to shield the loop against the external exciting field is induced. When this current reaches the critical value J_0, a magnetic quantum flux, Φ_0, penetrates into the effective loop, and the time dependent magnetization, $m(t)$, changes by $\Phi_0/4\pi S$ (S = loop area) and loses the sinusoidal shape of the excitation signal. The average J_0 value for each temperature, $J_0(T)$, is then the parameter that shapes the wave form of the off-balance signal in the susceptometer. Since the measured $\chi(T)$ is the first-harmonic of the time Fourier expansion of $m(t, T)$, for fixed h_0, $\chi'(T)$ is a magnitude directly related to $J_0(T)$, while $\chi''(T)$ is related to the energy absorption. Thus, the fundamental χ' and χ'' become very sensitive to the h_0 amplitude and its increase gives rise to a broadening of the T_c transition. The χ'' peak becomes broad with increasing h_0, while the diamagnetism onset temperature is h_0 independent. Ishida and Mazaki [11] deduce Josephson tunnel or microbridge type, a symmetric or asymmetric disposition of $\chi'(T)$ and $\chi''(T)$ with respect to its midpoint, respectively, is expected.

For the new high temperature superconductors the Ishida and Mazaki model has been applied and qualitatively explains the χ' and χ'' dependence on h_0 for $La_{1.9}Sr_{0.1}CuO_{4-\delta}$ [6]. Moreover, the χ' and χ'' asymmetry observed is leant towards T_c rather than the Meissner limiting asymptotic temperature (χ' constant). Since the broadening of both the χ' variation to perfect diamagnetism and of the χ'' peak with h_0 are obviously related, a plot (fig. 4) of χ' versus χ'' for different h_0 values will enhance this fact. The curves of fig. 4 have been obtained by scaling to 1 the χ' span between the normal state (almost zero) and the χ' ($T = 0$ K) asymptotic value. The curve obtained is asymmetric and increases its maximum with h_0 for low fields. For $h_0 \geq 0.11$ Oe the respective curves merge to an approximately common one, thus giving a limit to the response of the system to high h_0 fields. Of course this result is directly observable in the direct χ'' measurements, where the peak is observed first to increase for increasing h_0 and then to reach a constant maximum value for $h_0 > 0.11$ Oe.

The height of the peak predicted by the Ishida and Mazaki model is h_0 independent ($4\pi\chi''_{max} =$

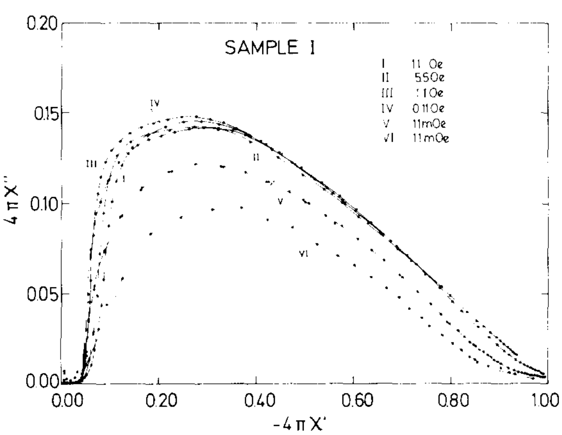

Fig. 4. χ'' versus χ' magnetic susceptibility of $YBa_2Cu_3O_{7-\delta}$ (sample I; $\nu = 121$ Hz) for temperatures below $T_c = 75$ K. Both axes have been normalized so that for the lowest exciting

$1/\pi$). On the contrary, the present results and previous ones [8] for $YBa_2Cu_3O_{7-\delta}$ show increasing peaks for increasing h_0 approaching a constant value much lower than predicted. The same increase was observed for $La_{1.9}Sr_{0.1}CuO_{4-\delta}$ [6] though the limiting peak height reach $4\pi\chi'' \approx 0.3$ in agreement with the model. This type of discrepancy is found commonly in ac susceptibility studies of superconductors, and is associated to rounding effects of the actual B–H hysteresis loop which reduces its area to the model one. In this particular case, Oda et al. [6] argued that the cause of it is the increase of flux fluctuations with h_0, which in turn implies that the convergent curve obtained for the highest values is related to the better fulfilment of the condition $h_0 \gg \phi_0/S$ [11]. To ascertain this interpretation, multiple harmonic analysis of the response signal is in progress.

The remarkable non-linearity of χ' and χ'' with the ac field amplitude agrees with the model of Ishida and Mazaki [11], and from this comparison the presence of weak links between superconducting regions is inferred. The weak links may be located at the grain surface, but as they have been detected in samples derived with very different methods, they may also be located inside the grains.

The absence of linearity with the amplitude of the exciting current, as observed in the $\rho(T)$ ac measurements, together with the small values of the critical current, also points out the existence of superconducting weak links.

The height of the maximum of the normalized χ' versus χ'' curve resembles very closely the values achieved in the $(SN)_x$ superconductor [12], and both, in turn, are smaller than the curve obtained for technetium imbedded in alumina [11]. This points towards lower dimensionality in the setting of loops in $YBa_2Cu_3O_{7-\delta}$ as happens $(SN)_x$ superconductors. This aspect agrees with the observed structural layer disposition of Cu ions, coordinated by four oxygen, although it requires a deeper study. Between the layers the Cu ions are arranged in a chain-like fashion via oxygen ions, and the superconducting currents will probably flow by these two paths. Finally, above T_0 and up to 130 K, $\rho(T)$ is non-linear with the ac intensity, whereas χ' and χ'' do not show any anomalous behaviour. This phenomenology has been already observed [1] and ascribed to granular superconductivity [13].

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References

[1] J.T. Chen, L.E. Wenger and C.J. McEwan, Phys. Rev. Lett. 58 (1987) 1972.
[2] J.G. Bednorz and K.A. Muller, Z. Phys. B64 (1986) 189.
[3] D.H.A. Blank, J. Flokstra, G.J. Gerritsma, L.J.M. van de Klundert and G.J.M. Velders, Physica 145B (1987) 222.
[4] T. Takabatake, H. Takeda, Y. Nakazawa and M. Ishikawa, Japan. J. Appl. Phys. 26 (1987) L502.
[5] C. Rillo, Ph. D. Thesis, University of Zaragoza, Spain (1986).
[6] H. Mazaki, M. Takano. R. Kanno and Y. Takeda, Japan. J. Appl. Phys. 26 (1987) L780.
[7] Y. Oda, I. Nakada, T. Kohara, H. Fujita, T. Kaneko, H. Toyoda, E. Sakagami and K. Asayama, Japan. J. Appl. Phys. 26 (1987) L481.
[8] Y. Oda, I. Nakada, T. Kohara and K. Asayama, Japan. J. Appl. Phys. 26 (1987) L608.
[9] R.A. Hein, Phys. Rev. B 33 (1987) L327.
[10] I. Iguchi, H. Watanabe, Y. Kasai, T. Mochiku, A. Sugishita, S. Narumi and E. Yamaka, Japan. J. Appl. Phys. 26 (1987) L798.
[11] T. Ishida and H. Mazaki, J. Appl. Phys. 52 (1981) 6798.
[12] Y. Oda, H. Takenaka, H. Nagano and I. Nakada, Solid State Commun. 32 (1979) 659, 35 (1980) 890.
[13] X. Coi, R. Joynt and D.C. Larbalestier, Phys. Rev. Lett. 58 (1987) 2798.