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The conductivity threshold for superconductivity in copper oxides: effect of localization and strong correlations

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Abstract. We report evidence for a conductivity threshold for superconductivity in copper oxide systems. For samples with an electrical conductivity below this threshold, no superconducting transition is observed. We discuss a possible explanation for this threshold based on the combined effects of localization and strong correlations between charge carriers.

It has been experimentally established that high-temperature superconductivity in copper oxide materials involves pairing of two charge carriers, each with charge e [1]. While the pairing phenomenon is consistent with our knowledge on superconductivity, the surprisingly high superconducting transition temperature brings about a central question, i.e. whether the pairing theory based on the Fermi liquid picture is still applicable but with a tremendously large pairing interaction or a completely different theoretical treatment (for instance a quantum spin liquid picture) has to be adopted. In the formal approach, pairing in the copper oxide family is, similar to other superconducting systems, a result of a delicate balance between the repulsive Coulomb interaction and an attractive interaction (due to mechanisms such as electron–phonon interaction, charge fluctuation or superexchange interaction of magnetic origin) between the charge carriers. In the second approach, however, Bose condensation of single-boson excitations (such as bipolarons or holons) is considered. The exact mechanism of high-T_c superconductivity is still unclear to date although much progress has been made in understanding the 'parent state' ($La_{2-x}Sr_xCuO_4$ with $x = 0$ and $Y_1Ba_2Cu_3O_{7-\delta}$ with $\delta = 1$). In the framework of interacting Fermi particles, it is well established that superconductivity can be appreciably suppressed by the localization effect. In ultra-thin films a threshold for superconductivity has been reported extensively. It is shown [2] that in many ultra-thin films (such as Mo–C, Bi, Pb, Sn and Ga) a sheet conductance of the order of $4e^2/h$ (about $1.6 \times 10^{-4}\,\Omega^{-1}$, corresponding to a sheet resistance of $6 \times 10^3\,\Omega$) is the threshold normal conductance below which global superconductivity is not found. The nature of this superconductivity threshold still remains an open question [2].

In this paper we report the existence of a similar conductivity threshold for superconductivity in the copper oxide family. When electrical conductivity at room temperature is below this threshold, no superconducting transition is observed. This concept of a threshold for superconductivity in copper oxides has not been reported previously, even though there have been a large number of experiments [3] to study the

Table 1. Preparation method and thermal history of our samples.

Samples	1: $La_{1.8}Ba_{0.2}CuO_4$ 2: $YBa_2Cu_3O_{7-\delta}$ 3: $Bi_2Sr_2CaCu_2O_8$ 4: $Tl_2Ba_2Ca_2Cu_3O_{10}$
Starting powders	1: La_2O_3, $BaCO_3$, CuO 2: Y_2O_3, $BaCO_3$, CuO 3: Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO 4: Tl_2O_3, $BaCO_3$, $CaCO_3$, CuO
Preparation	1: Mixing and sintering all starting powders with two intermediate grindings; followed by a slow cool in O_2 2: Same as 1 3: Mixing all starting powders and sintering them in air; followed by air quench 4: Making precursor first by mixing and sintering $BaCO_3$, $CaCO_3$, CuO; then add Tl_2O_3 to the precursor in a short time (5 min) followed by a slow cool in O_2
Thermal history	1: 900 °C for 12 h; 900 °C for 12 h; 925 °C for 12 h; 500 °C for 12 h 2: 940 °C for 12 h; 940 °C for 12 h; 950 °C for 12 h; 500 °C for 12 h 3. 820 °C for 12 h; 820 °C for 12 h; 840 °C for 12 h 4: 900 °C for 12 h; 900 °C for 12 h; (add Tl) 900 °C for 5 min

correlation between superconductivity and electrical conductivity. Since the destruction of superconductivity is in general not directly related to the conductivity of a three-dimensional system, there is no universal connection between superconductivity and the behaviour of conductivity. In fact there are indications that a direct transition from the insulating state to superconducting state is feasible [4]. Therefore we attribute the existence of the conductivity threshold for superconductivity in copper oxides to the unique characteristics of these materials. To explain this result, we shall examine the interplay between superconductivity, localization and strong correlations in copper oxides.

The preparation method and the thermal history of our copper oxide samples are given in table 1. Electrical resistivity measurements were performed using the standard four-probe AC technique. In figure 1 we show resistivity ρ as a function of temperature measured on four superconducting samples. A common feature of all these superconducting samples is that their conductivity σ at room temperature is in the range 200–1000 $\Omega^{-1}\,cm^{-1}$ (ρ in the range 1–5 mΩ cm). Besides these superconducting samples, we have also fabricated a large number of non-superconducting copper oxide samples with high room-temperature resistivity. While some of these samples such as $CeBa_2Cu_3O_x$ and $ScBa_2Cu_3O_x$ do not form the correct structural phase for superconductivity, many of them have the known structures for superconductivity but possess severe disorder resulting from oxygen deficiency, incorrect stoichiometry or impurity doping. It is this observation that motivated our present investigation on the threshold for superconductivity.

In order to determine the threshold quantitatively, we have specifically performed experiments on a series of $YBa_2Cu_3O_{7-\delta}$ (1:2:3) samples as follows. First, superconducting 1:2:3 pellets with $T_c = 92$ K were made using the standard solid state reaction

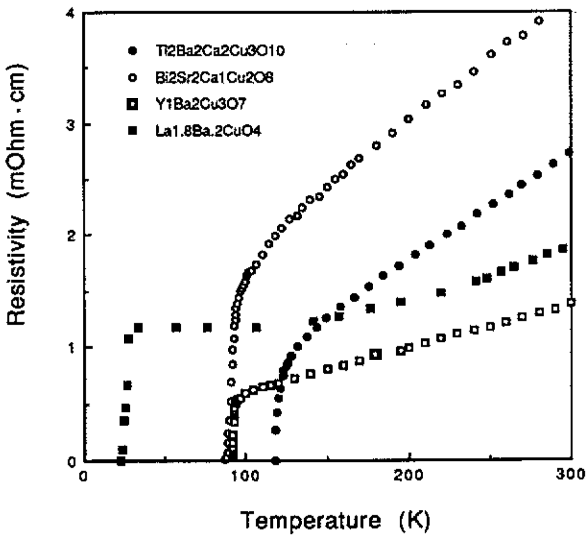

Figure 1. The temperature dependence of resistivity ρ measured on four superconducting samples. The conductivity σ at room temperature is in the range 200–1000 $\Omega^{-1}\,cm^{-1}$ (ρ in the range 1–5 mΩ cm).

method. Then they were heated to various final temperatures ranging from 200 to 940 °C. They were kept at each final temperature in air for at least 5 h in order to reach the equilibrium distribution of oxygen content. After that they were quenched in liquid nitrogen. In figure 2 we plot normalized resistivity as a function of temperature measured on these quenched 1:2:3 samples. In the inset we present the room-temperature conductivity of these samples as a function of the quenching temperature. It can be seen clearly from the inset that room-temperature conductivity is suppressed rapidly when the quenching temperature is increased. The samples quenched at 200, 600 and 750 °C show a clear superconducting transition. The sample quenched at 900 °C has a metallic behaviour near room temperature indicated by the positive temperature coefficient of resistance. At lower temperatures ($T < 170$ K) its resistivity has a negative temperature coefficient which suggests the development of weak localization in the system. This sample shows a superconducting transition with onset temperature at 48 K even though the transition remains incomplete until 4.2 K. The samples that were quenched at 920 and 940 °C have a low room-temperature conductivity and they show no sign of a superconducting transition. From figure 2 (and the inset) we find our conductivity threshold for superconductivity to be 10 $\Omega^{-1}\,cm^{-1}$ [5]. Although this threshold value has been determined from just the data presented here on 1:2:3 copper oxides, it is consistent with the observations that we made on hundreds of samples of all types of copper oxide material. Therefore we believe that this threshold is applicable to all types of copper oxide superconductor.

We now discuss possible explanations for the superconductivity threshold. The direct consequence of quenching in the experiments is to introduce disorder into oxygen sites. If we neglect the effect of interaction between charge carriers, we are dealing with a problem of non-interacting particles in an aperiodic potential as a result of the disorder. Anderson [6] and Gorkov [7] showed that the superconducting transition temperature

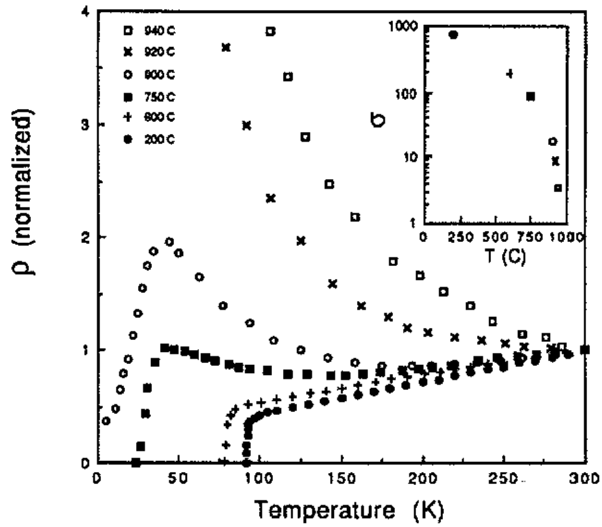

Figure 2. Resistivity normalized to its value at 300 K as a function of temperature measured on a series of $YBa_2Cu_3O_x$ samples which were held at different temperatures for at least 5 h and then quenched in liquid nitrogen. The inset shows the conductivity σ (Ω^{-1} cm^{-1}) of these samples measured at 300 K as a function of quenching temperature. The samples that were quenched at 920 and 940 °C show no sign of a superconducting transition and this leads to a critical value of conductivity of 10 Ω^{-1} cm^{-1} (corresponding to ρ = 100 mΩ cm) for the superconductivity threshold.

of a superconductor is not affected by static and non-magnetic disorder. In their theories the interplay of the electron–electron interaction and disorder was neglected. These theories, valid in the limit of weak localization ($k_F l \gg 1$ where k_F is the Fermi momentum and l is the mean free path), successfully explained superconductivity in many disordered systems [8]. In a system where the combined effect of disorder and interactions between charge carriers is large, superconductivity may persist when the repulsive interaction (such as Coulomb interaction) is weakened by the screening effect of free charge carriers. As localization develops, however, charge carriers are more and more localized and this gives rise to a reduction in the screening effect. Therefore an effective growth of the repulsion interaction is induced which in turn leads to destruction of superconductivity. The localization can be induced by strong disorder in the system or by other mechanisms such as antiferromagnetic ordering of spins [9]. The copper oxide materials are highly correlated systems [10]. Band-structure calculations have shown that without considering the correlation effect both La_2CuO_4 and $YBa_2Cu_3O_6$ have an antibonding band which crosses the Fermi surface [11], but resistivity measurements indicate that these 'parent' materials have semiconducting behaviour. Furthermore magnetic studies indicate that both of these materials are antiferromagnetic. A large electron–electron Coulomb interaction or interaction of magnetic origin may lead to insulating behaviour near half-filling in the Hubbard [12] model. The electronic and magnetic correlation is found to extend to the superconducting phase, even though the spatial extension of correlation is reduced [13]. Experiments indicate that in $YBa_2Cu_3O_{7-\delta}$ the hole concentration n is essentially unchanged when the oxygen content δ is changed from 7.0 to 6.6, corresponding to a change in T_c from 90 to 60 K, and n decreases by only 30% when

δ changes from 6.6 to 6.3, leading to the disappearance of superconductivity. This fact further supports the idea that the suppression of superconductivity in copper oxide materials is due to localization effect rather than to a change in charge carrier concentration.

Our numerical value of the conductivity threshold for superconductivity is obtained on polycrystalline samples. An ideal determination of this threshold should be carried out on single-crystal samples although significant experimental difficulties would be encountered [14]. One may use single crystals to study the anisotropic behaviour of conduction in copper oxide superconductors. Experiments have shown that the conductivity σ_{a-b} in the a–b plane is much larger than the conductivity σ_c along the c axis and the reported anisotropic ratios σ_{a-b}/σ_c range from 10^2 to 10^3 [15]. Our experiments on polycrystalline samples therefore detect an 'effective conductivity' σ_{eff} that is an average of the a–b plane component and the c axis component of the conductivity tensor. How this average is determined is not clear to us, but we recognize that the main contribution comes from the a–b plane component since the anisotropic ratio is very large. It has been suggested that $\sigma_{eff} = \beta^{-1}\sigma_{a-b}$ with $\beta \simeq 2$ [16]. We should point out that other complexities such as grain boundaries and sample voids present in polycrystalline samples seriously prevent us from pursuing further quantitative discussion on the superconductivity threshold.

Finally we emphasize that firstly the concept of superconductivity threshold that we discuss here does not apply to macroscopically inhomogeneous systems which because of percolative or multiphased structures may have very low conductivity but still possess superconductivity and secondly this threshold is a necesary rather than a sufficient condition for superconductivity.

In summary, we have observed in polycrystalline copper oxide materials the existence of a conductivity threshold for superconductivity. When conductivity at room temperature is below this threshold which is $10\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for polycrystalline samples, no superconductivity is observed in these copper oxides. We propose that the existence of such a threshold is due to the combining effect of localization and the strong correlation between charge carriers.

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