Double-Peak Superconducting Transition in Granular L-M-Cu-O (L = Pr,Nd,Sm,Eu; M = Ce,Th) Superconductors

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An unusual form of superconducting transition has been observed in some of the superconducting compounds $L_{2-x}M_xCuO_{4-y}$ (L=Pr,Nd,Sm,Eu; M=Ce,Th) under low magnetic fields. When the temperature is reduced below the critical one, the sample's resistance first increases, then drops to a nonzero value, increases again, and finally decreases at low temperature, creating a characteristic double-peak transition. The behavior is explained in terms of intragranular and intergranular superconducting transitions.

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Superconductivity in granular and disordered systems has attracted a lot of attention during the last years. This interest has been further enhanced since the discovery of high-temperature superconductors because of the intrinsic granular structure of the sintered samples commonly prepared. The resistivity of classical discontinuous systems, like thin metallic films[1] or thicker samples of granular metals[2] near the metal-insulator transition, can vary nonmonotonically with temperature, in contrast to what is observed in microscopically disordered systems[3] and in ordinary superconductors. As the temperature is lowered, the resistivity typically first falls, then passes through a minimum, before finally rapidly increasing at the lowest temperatures. This local superconducting transition is usually called "quasireentrant" since it appears to be an incomplete version of the theoretically predicted[4] reentrant transition in granular superconductors. A more complicated nonmonotonic transition was reported in random arrays of tin particles,[5] in which $R(T)$ decreases in two steps and finally increases with lowering temperature. We wish to report here a remarkable "double-peak" superconducting transition, in which a quasireentrantlike behavior is followed by the development of macroscopic superconductivity and a reduction of resistance at lower temperatures.

One of the explanations of the quasireentrant behavior in the resistivity temperature dependence of regular superconductors is that it arises from a combination of quasiparticle and Josephson tunnelings between isolated superconducting islands. The normal-state resistance of the metallic grains themselves in these systems is negligible compared to that of the intergrain spacings. A long-range superconducting order at $T=0$ appears possible only if the normal-state junction resistance is less than $R_Q=\alpha^{-1}h/4e^2$, where α is a constant that depends on the theoretical approach but is such that R_Q is of the order of 10 kΩ. The drop of resistivity below T_c can then be associated with the creation of a finite nonpercolating chain of intergrain Josephson couplings across the low-resistance (smaller than R_Q) junctions. The charge transfer across the high-resistance junctions (larger than R_Q) is governed by quasiparticle tunneling. The resistivity of the sample then increases when the temperature is further decreased due to the reduction in the quasiparticle density of states.

Samples with an infinite percolating chain of Josephson couplings can demonstrate another behavior below T_c. Zero resistance can be achieved by a monotonic two-step transition[6] in which the first resistance drop is associated with the transition of well coupled grains and a second transition at a lower temperature T_{cJ} is due to Josephson tunneling between the weakly coupled grains, which makes the whole sample superconducting. T_{cJ} is lower than T_c when the Josephson coupling energy E_J of the grain to its neighbors is smaller than kT_c.[7]

We studied the effects of granular structure on the superconducting transition of polycrystalline electron-doped superconducting ceramics $L_{2-x}M_xCuO_{4-y}$ (L =Pr,Nd,Sm,Eu; M=Ce,Th). The samples were prepared by a solid-state reaction.[8] Some of the transport and magnetization properties and x-ray characterization have recently been reported.[9] We show in Fig. 1 a scanning electron micrograph (SEM) of a Nd-Th-Cu-O sample, a typical representative of this class of materi-

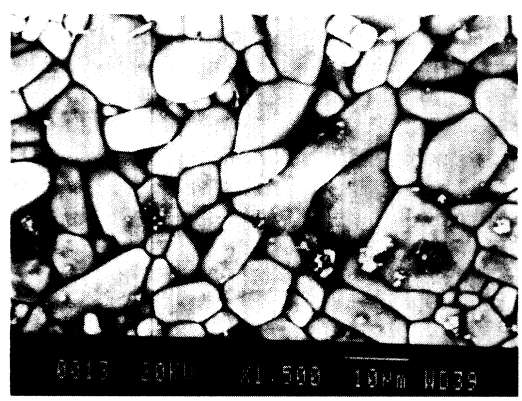

FIG. 1. SEM micrograph of a $Nd_{1.85}Th_{0.15}CuO_{3.98}$ sample.

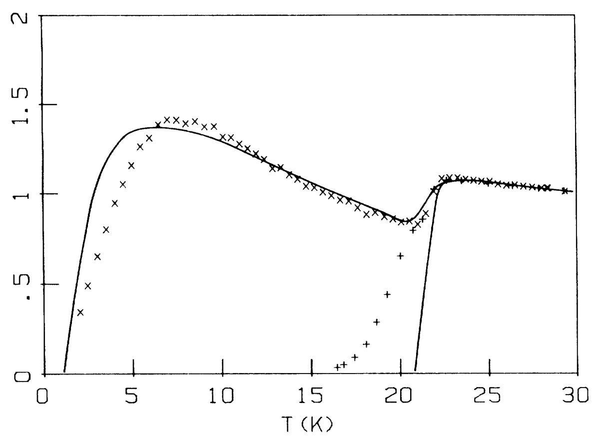

FIG. 2. Resistance of the $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ sample as a function of temperature measured at zero (+) and under 0.9-kOe applied magnetic field (×). Solid lines are numerically calculated.

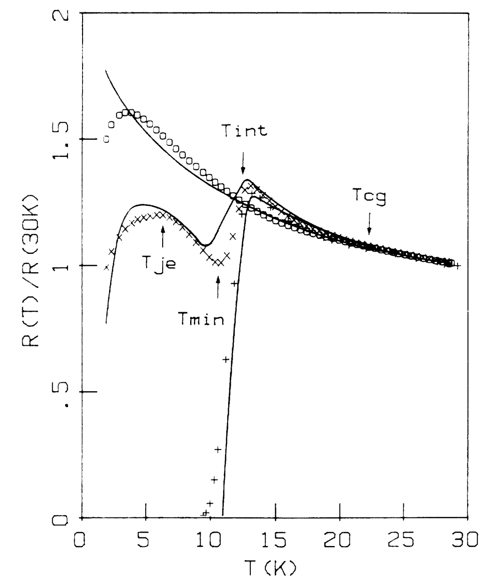

FIG. 3. Resistance of the $Sm_{1.85}Ce_{0.15}CuO_{3.97}$ sample as a function of temperature measured at zero (+) and under applied magnetic fields of 0.9 kOe (×) and 50 kOe (o). Solid lines are numerically calculated.

als. The topology of the sample is quite different from, for example, granular aluminum[2] or Al-Ge (Ref. 10) systems, extensively studied near their metal-insulator transitions. In contrast to the system of diluted small metallic grains (typical size 100 Å) embedded in an insulator matrix, the samples studied here are built of large grains tightly pressed one to another. The grains are very large, and their dimensions vary between 1 and 10 μm, 3 μm being an average value. The surfaces of the neighboring grains are smoothly adjusted, and the material fills almost all the volume. The intergranular spacings are narrow and of approximately constant width, which enables the creation of multiple weak links between the neighboring grains.

An extraordinary behavior of the samples studied is demonstrated in Fig. 2 in which we show the resistance of a $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ sample measured as a function of temperature at zero and under 900-Oe applied magnetic field. In its normal state at temperatures above ≈ 23 K the sample's resistance increases moderately with temperature reduction. Below the superconducting transition temperature and at zero field the resistance drops to zero; however, when measured under a low magnetic field, it drops to a nonzero minimum and increases sharply when the temperature is further reduced. In contrast to the known quasireentrant behavior,[1,2] the resistance reaches its maximum at $T \approx 8$ K and decreases to zero under additional reduction of temperature. The height and sharpness of the peak depends on the value of the applied field, and the anomaly disappears at fields above 9 kOe. The resistance measured under high magnetic field (50 kOe) monotonically increases until $T \approx 4$ K and decreases at lower temperatures.

The behavior reported above was observed in the majority of the samples studied which showed a negative resistance temperature coefficient in their normal state. The details of the pattern are unique for different materials, with an additional interesting property which was found to be especially pronounced in the $Sm_{1.85}Ce_{0.15}CuO_{3.97}$ sample (Fig. 3). At temperature T_{cg} (see Fig. 3) the sample's resistance measured at zero or low magnetic field increases and in the temperature range $T_{int} < T < T_{cg}$ the resistance measured at zero field is significantly higher than that measured under high field.[11] The zero-field resistance drops to zero under further reduction of temperature; however, when measured under a low magnetic field it demonstrates a double-peak transition.

Results qualitatively consistent and interesting in themselves have been obtained by studying the current effect on the superconducting transition. Some of the curves of the resistance temperature dependence measured at 0.4-kOe field for different current levels, observed in the same $Sm_{1.85}Ce_{0.15}CuO_{3.97}$ sample, are presented in Fig. 4. The high-temperature resistance peak was found to be uninfluenced by the current increase from 10 μA to 5 mA, in contrast to the low-temperature one. Macroscopic superconductivity is suppressed by the strong currents and the transition gradually passes from the double-peak (low current) to the quasireentrant form (strong current).

Our understanding of the results reported here is based on the unique properties of sintered high-temperature superconducting compounds. The samples are built of well adjusted large grains. Unlike the behavior of classical superconductors, grain boundaries in high-T_c materials have been found to act like Josephson-type weak links; however, due to their topological structure

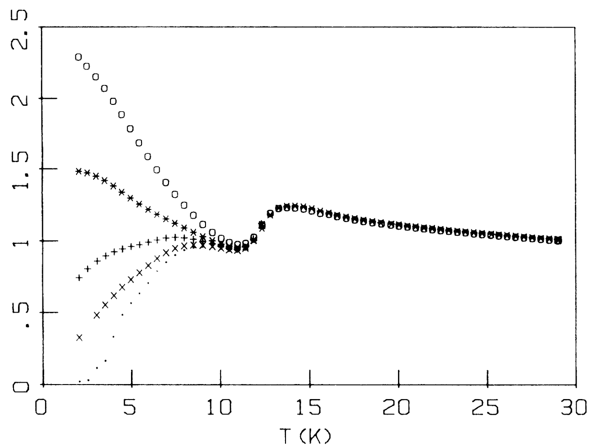

FIG. 4. Resistance of the $Sm_{1.85}Ce_{0.15}CuO_{3.97}$ sample as a function of temperature measured under 0.4-kOe field for different values of currents: (●) 10 μA, (×) 100 μA, (+) 200 μA, (*) 500 μA, (○) 5 mA.

(see Fig. 1), the number of these links between the neighboring grains can be large. As a result, in contrast with classical superconductors in the vicinity of the metal-insulator transition, the normal resistance of the grains themselves can be of the same order of magnitude as the intergranular or sample's total resistance, and the intragrain superconducting transition can influence significantly the overall resistance. At the temperature[11] T_{cg} (see Fig. 3), which we define as the temperature at which the resistance measured at zero field deviates from that measured at high field, some of the grains become superconducting. The critical temperatures of different grains can vary strongly because of the extreme sensitivity of the n-doped superconductors to the values of electron doping (x) and oxygen deficiency (y).[12] A slight inhomogeneity of these parameters in different grains can cause a wide distribution of T_c across the sample. Actually, we estimate the width of this distribution ΔT_c to be $\Delta T_c = T_{cg} - T_{\min} \approx 10$ K ($T_{\min}$ is defined in Fig. 3). The charge transfer between neighboring normal and superconducting grains is governed by quasiparticle tunneling, which is sensitive to the value of the energy gap in the superconducting grain. The reduction of this gap by an applied magnetic field leads to the progressive reduction of the resistance to its normal value. This process can explain the enhancement of resistance measured at zero field and the strong negative magnetoresistance observed in the temperature range $T_{\rm int} < T < T_{cg}$ ($T_{\rm int}$ is defined in Fig. 3). The number of superconducting grains increases with temperature reduction and causes a steep resistance drop. At zero applied magnetic field the superconducting transition in the grains is associated with the creation of percolating chains of Josephson intergrain couplings, and zero resistance is achieved. Application of a low magnetic field (or increase in the measuring current) does not have much effect on the intragranular transition temperatures; however, it strongly reduces the Josephson coupling temperatures. The resistance drop, in this case, reflects the superconducting transition of the grains alone. At temperatures below $T_{\min}$ the charge transfer is again governed by single electrons tunneling between the superconducting grains. The resistance of the sample then steeply increases with a reduction in temperature, due to the decrease of the unpaired electron density in the superconducting grains. In the absence of charging effects the junction is expected[7] to become Josephson coupled, when its coupling energy E_J exceeds the thermal energy (of the order of kT). In previously studied systems like Al-Ge (Ref. 10) or tin particles networks[5] with typical grain sizes of 120 and 300 Å, respectively, the activation of Josephson coupling at temperatures below the critical one was hardly observed because of strong charging effects in small grains of metal. In our systems built of large grains of the order of 10 μm, the charging effects are minimized and Josephson coupling becomes efficient at T_{Je} (Figs. 2 and 3). The macroscopic transition from temperature-activated to Josephson-coupled conductivity occurs at this temperature and the sample's resistance starts to decrease.

The double-peak transition was not observed under magnetic fields higher than 10 kOe. This can be explained by the broadening of the intragranular-critical-temperature distribution under field, caused by the high-critical-field anisotropy of the randomly oriented grains.

In order to confirm our interpretation of the behavior observed, we have reproduced qualitatively the resistivity-temperature curves using a simple effective-medium model. By analogy with Yoshida,[13] we modeled the samples as assemblies of elementary cells consisting of a spherical core representing a real grain, and a spherical shell whose conductivity reflects the intergranular charge transfer. The intergranular connections are normal resistances if the grains are metallic, and Josephson junctions if they are superconducting and kT is lower than the Josephson coupling energy E_J. In the intermediate cases (connection between normal and superconducting grains, or between superconducting grains with $kT > E_J$), we assume that a given fraction of the connections are normal weak links while the other ones are single-particle tunneling junctions. Therefore, the cores of the cells can be either normal or superconducting, and the shells can have either normal, infinite, or thermally activated conductivities, the relevant combinations defining the different types of cells (denoted "i" below).

The global resistivity of the sample was calculated as a function of temperature and magnetic field by solving numerically a self-consistent equation of the form

$$\sum_i \int_{T_c} \int_{T_{cJ}} X_i(T_c, T_{cJ}, H) S_i(\sigma_c^i, \sigma_s^i, \sigma^*) dT_c \, dT_{cJ} = 0 \,,$$

where $X_i(T_c, T_{cJ}, H)$ is the fraction of i-type cells with core critical temperature T_c and Josephson coupling energy kT_{cJ}, and $S_i(\sigma_c^i,\sigma_s^i,\sigma^*)$, which is a "normalized" conductivity[13] integrated over the i cell's volume, depends on the core, shell, and global sample conductivities, respectively. Two parameters are magnetic-field dependent: the fraction of superconducting cores (the upper-critical-field anisotropy has been taken into account) and the Josephson coupling temperatures since they were taken proportional to the junction critical currents.

The following characteristics of the junctions were used as fitting parameters: normal conductivity, average thickness, rectangular distribution of sizes, and fraction of weak links versus tunnel junctions. The Josephson coupling energies are a function of the junctions' normal resistances and their distributions at zero field arise from those of the junction sizes. The zero-field distributions of T_c, which extend from $T_{\min}$ to T_{cg}, have been chosen rectangular.

Some calculated curves are shown in Figs. 2 and 3 (solid lines). For both samples the shells' normal resistivity is 2 orders of magnitude higher than that of the cores. In the first case (Fig. 2), the junction sizes are 0.25 ± 0.15 μm and the fraction of tunnel-like junctions is 35%. In the second case, these values are respectively 0.18 ± 0.13 μm and 20%. For the second sample, separate distributions of intragranular critical temperatures have been chosen for the cores associated with weak-link-type and tunnel-type junctions: 11.5 ± 1.5 and 19 ± 6 K, respectively. In both cases, the distributions of T_{cJ} are broad and typically range from $\frac{1}{2}$ to 5 times the average T_c of the cores.

The general features of the resistivity curves (increase of resistivity below T_{cg} and low-temperature peak) are well described by the model. Moreover, the obtained values of junction sizes, which govern the magnetic-field effect on the low-temperature peak, are consistent with the sizes of the grains (a few microns). Unfortunately, the fractions of tunnel-like junctions cannot be directly compared with experimental values. In Fig. 2, the difference between the calculated and experimental curves below the onset at zero field can be assigned to the destruction of some Josephson junctions by the current on its percolating paths. The resulting effect can be important, as illustrated in Fig. 4. In Fig. 3, the resistivity reduction observed at low temperature under high applied field may correspond to the formation of a partial percolation path across the sample, developed by a small percentage of Josephson couplings.

To conclude, we report here the first observation of a nonmonotonic double-peak superconducting transition in the family of electron-doped superconducting compounds $L_{2-x}M_x\mathrm{CuO}_{4-y}$. In contrast with other systems demonstrating quasireentrant behavior in the vicinity of the metal-insulator threshold, the samples studied are free of charging effects and their intragranular normal resistance is of the same order of magnitude as the total sample's resistance. The resistance transition can be tuned by application of low magnetic fields and three clearly separated stages can be observed with temperature reduction: (a) the intragranular transition, (b) temperature-activated quasiparticle tunneling, and (c) Josephson-like intergranular coupling. The experimental results have been reproduced qualitatively by numerical calculations based on a simple effective-medium model.

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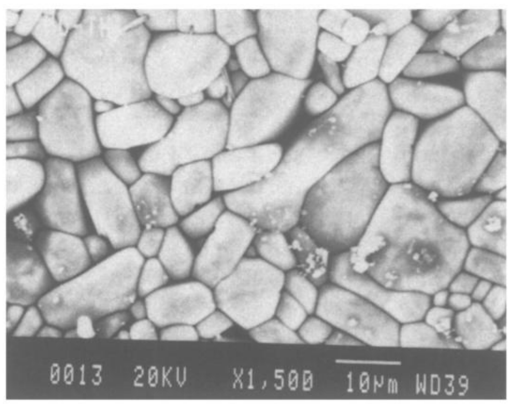

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