PHYSICAL REVIEW B VOLUME 50, NUMBER 14 1 OCTOBER 1994-II

Granular behavior in polycrystalline $Sm_{2-x}Ce_xCuO_{4-y}$ compounds

R. F. Jardim
Instituto de Física, Universidade de São Paulo, Caixa Postal 20516, 01498-970, São Paulo, Brazil

L. Ben-Dor
Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem 91904, Israel

D. Stroud
Department of Physics, The Ohio State University, Columbus, Ohio 43210

M. B. Maple
Department of Physics and Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92093-0075

(Received 16 May 1994)

This work reports a systematic study of polycrystalline samples of $Sm_{2-x}Ce_xCuO_{4-y}$ $(0.15 \leq x \leq 0.18)$ obtained from a sol-gel precursor and subjected to different cooling rates after reduction. A double resistive superconducting transition is a common feature of all samples studied, suggesting that this is an intrinsic property of these polycrystalline compounds. At an upper temperature T_{ci}, there is a fairly sharp drop in the magnitude of the electrical resistivity, which is followed by a well-defined plateau down to a lower temperature T_{cj}. At this temperature, Josephson coupling between superconducting islands is believed to complete the transition to the zero resistance state. From the compositional dependence of electrical resistivity, we infer that T_{ci} decreases slightly from $x = 0.15$ through $x = 0.18$, while T_{cj} shows a maximum for $x = 0.16$. With increasing excitation current, no significant changes in the behavior of the electrical resistivity between T_{ci} and T_{cj} are observed, while a dramatic broadening and a shift of the transition at T_{cj} towards lower temperatures are found. Magnetic-susceptibility measurements reveal appreciable diamagnetism just below the coupling temperature T_{cj} suggesting that superconducting properties are really confined to small regions, with size comparable to the London penetration depth. The average size of these regions are estimated to be between ~ 6 and 300 Å, in good agreement with recent estimates obtained from magnetoresistance measurements on polycrystalline $Sm_{2-x}Ce_xCuO_{4-y}$ $(0.14 \leq x \leq 0.17)$ samples and with both neutron-diffraction studies and Mössbauer spectroscopy measurements in the isomorphic compound $Nd_{2-x}Ce_xCuO_{4-y}$ $(0.0 \leq x \leq 0.18)$. All the observed macroscopic properties, as well as the absence of a peak in the specific heat at T_{ci}, are discussed within the framework of a granular superconductor model. In addition, we give qualitative arguments suggesting the importance of charging effects in the macroscopic properties of these polycrystalline samples.

I. INTRODUCTION

A striking characteristic of polycrystalline samples of electron-doped superconductors $L_{2-x}Ce_xCuO_{4-y}$ (L = Nd, Pr, Sm), produced by mixing simple oxides followed by sintering, is the so-called double resistive superconducting transition.[1-4] This name is applied because electrical resistivity measurements show two well-defined transitions before the zero resistance state is attained. The first transition, which is presumably associated with a genuine superconducting phase, occurs at an upper temperature T_{ci} and is characterized by a drop in the electrical resistivity to a nonzero value. Below T_{ci}, the compound is considered to be comprised of a collection of superconducting grains embedded in a nonsuperconducting matrix, and shows a noticeable plateau in the electrical resistivity down to a lower temperature T_{cj}. At this temperature, it is believed that Josephson coupling develops between the grains and a second rapid drop in the electrical resistivity to the zero resistance state is observed. In fact, the transition at T_{cj} is a transition from phase incoherence, in which the phases of the superconducting order parameter on different "grains" are random, to phase coherence, in which there is long-range phase order. Another interesting feature of these polycrystalline compounds is that significant diamagnetism occurs only below the lower temperature T_{cj}. Previous measurements of magnetic susceptibility $\chi(T)$ on a similar series of materials revealed that no appreciable diamagnetism occurs between T_{ci} and T_{cj}.[1,5] Therefore, in those materials also, an appreciable diamagnetic contribution only occurs below T_{cj}, the weak-coupling temperature of the system. Such an absence of significant diamagnetism just below the superconducting transition at T_{ci} has been attributed to the small size of the superconducting regions (comparable in size to the London penetration depth).[2,3,5] The presence of only small superconducting regions seems to be in complete agreement with specific-heat measurements in $Nd_{2-x}Ce_xCuO_{4-y}$ series, which have revealed no evidence of a jump at ei-

0163-1829/94/50(14)/10080(8)/$06.00

ther T_{ci} or T_{cj}.[6,7]

All these features have been observed mainly in samples prepared with the standard method which consists of mixing together simple oxides L_2O_3 (L =Nd, Pr, Sm, Eu), CeO_2, and CuO, and then sintering the mixture either by solid-state reaction[2] or by liquid-phase sintering.[1,3,4] Recently, similar features were observed in polycrystalline samples of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ obtained from a sol-gel precursor and sintered through the solid-state reaction method.[5] Those results suggested that the double resistive superconducting transition and the absence of significant diamagnetism at T_{ci} are intrinsic properties of polycrystalline samples of electron-doped superconductors.

In this work, we report a systematic study of polycrystalline samples of $Sm_{2-x}Ce_xCuO_{4-y}$ ($0.15 \le x \le 0.18$) produced from a sol-gel precursor. All the samples were sintered below the eutectic temperature through solid-state reaction and subjected to different cooling rates after the reduction process. From measurements of electrical resistivity and magnetic-susceptibility curves, we found that the double resistive superconducting transition is preserved for all samples studied and that significant diamagnetism occurs only below the long-range ordering temperature T_{cj}. This leads us to conclude that these features are really intrinsic to polycrystalline samples of electron-doped superconductors. From an accurate analysis of electrical resistivity data we obtained an estimate of the region where the order parameter is believed to be homogeneous. Such a result reveals that superconducting properties are mainly confined to small regions of typical size between 6 and 300 Å, in excellent agreement with similar estimates obtained from magnetoresistance measurements, neutron-diffraction studies, and Mössbauer spectroscopy measurements. The macroscopic properties of these polycrystalline samples are discussed within the framework of a granular model.

II. EXPERIMENTAL PROCEDURE

Polycrystalline samples of $Sm_{2-x}Ce_xCuO_4$ ($0.15 \le x \le 0.18$) were obtained from a sol-gel prescursor. While details of the experimental procedure concerning the sol-gel route are amply described elsewhere,[5] it is important to mention that these samples were sintered at 1000 °C, which is below the eutectic temperature of ~1050 °C,[8] i.e., through the solid-state reaction method. Chemical reduction, which is necessary to obtain superconducting properties in these compounds, was carried out in flowing He gas at 950 °C for 20 h, followed by cooling either for 1 h (fast-cooled) or 2 h (slow-cooled). Phases were identified by means of powder x-ray diffractometry using Cu $K\alpha$ radiation on a Rigaku "Rotaflex" RU-200B diffractometer. The lattice parameters were obtained from corrected peak positions, using MgO as an internal standard. All samples proved to have the T' structure. Vestiges of an additional phase $Sm_{1-x}Ce_xO_y$ ($x \approx 1$) (Ref. 9) were detected in the $Sm_{1.82}Ce_{0.18}CuO_{4-y}$ sample, which has Ce concentration slightly higher than the Ce solubility limit obtained in these series.[1]

Four-wire electrical resistivity measurements were performed using a Linear Research Model LR-400 ac resistance bridge operating at a frequency of 16 Hz. Copper electrical leads were attached to Au film contact pads on $2 \times 2 \times 6$ mm^3 parallelepiped-shaped samples using Ag epoxy. Current densities of 2.3 to 23 mA/cm^2 were employed in these experiments. The temperatures T_{ci} and T_{cj} have been defined as the onset temperatures where either the genuine superconducting phase or the Josephson coupling develops, respectively. Magnetic-susceptibility measurements were made with a Quantum Design commercial variable temperature superconducting quantum interference device susceptometer. Zero-field-cooled (ZFC) and field-cooled (FC) curves were obtained from 5 to 30 K in magnetic fields as high as 10 Oe. Meissner fractions were estimated from the theoretical density of the $Sm_{1.85}Ce_{0.15}CuO_{4-y}$ unit cell with no demagnetizing corrections.

III. RESULTS AND DISCUSSION

Previous electrical resistivity measurements on polycrystalline samples of $Sm_{2-x}Ce_xCuO_{4-y}$ ($0.13 \le x \le 0.20$), produced by mixing of simple oxides and liquid-phase sintering at 1100 °C before the reduction process,[1] revealed four interesting features: (1) a double resistive superconducting transition for the entire series of samples studied; (2) a nearly constant drop in the electrical resistivity at T_{ci} of order of 30%; (3) a constant upper critical temperature $T_{ci} \approx 20.5$ K for samples with $0.13 \le x \le 0.20$; and (4) a maximum in T_{cj} at $x = 0.15$. These results elicited several possible explanations, including phase separation,[1] which had been claimed to occur in the $Nd_{2-x}Ce_xCuO_{4-y}$ ($0.0 \le x \le 0.20$) series.[10,11] It was argued that phase separation occurs because of a nonequilibrium process which results in only one superconducting stoichiometry for $x \approx 0.165$. Our electrical resistivity results at low temperatures, made on polycrystalline samples of $Sm_{2-x}Ce_xCuO_{4-y}$ ($0.15 \le x \le 0.18$) prepared from a sol-gel, reveal additional aspects, calling for a more elaborate discussion. These results are shown in Fig. 1, where transport critical current densities of these samples were estimated by varying the excitation current used to measure the electrical resistivity.

The first point to be addressed in this discussion is the double resistive superconducting transition. This double resistive transition persists, even when polycrystalline samples of electron-doped superconductors are prepared from a sol-gel precursor and sintered below the eutectic temperature at 1000 °C. From results shown in Fig. 1, evidently all of the resistive curves display such a feature. This seems to be a very important point, since it suggests that one can separate two distinct contributions in transport properties of polycrystalline samples, one arising from an intrinsic superconducting phase (the so-called intragranular component), and the other arising from the Josephson coupling (the so-called intergranular component). This separation has been shown to be very difficult experimentally in other high-T_c superconductors cuprate, as in polycrystalline samples of $YBa_2Cu_3O_{7-\delta}$

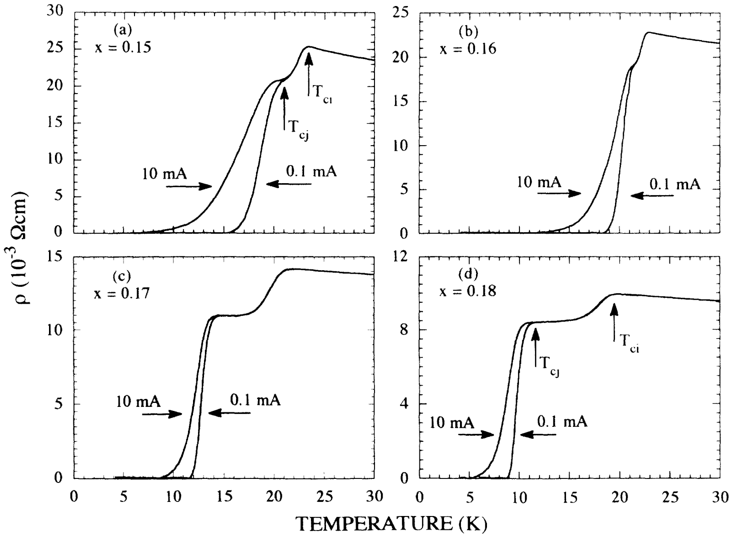

FIG. 1. Temperature dependence of the electrical resistivity in polycrystalline samples of $Sm_{2-x}Ce_xCuO_{4-y}$, $x=0.15$ (a), 0.16 (b), 0.17 (c), and 0.18 (d). All of the samples were obtained from a sol-gel precursor and cooled for 2 h after the reduction process. The superconducting transition temperature of the islands T_{ci} and the weak-coupling temperature T_{cj} are marked in (a) and (d). Changes in the excitation current in all curves are also marked.

and bismuth cuprates.[12-14] In fact, such a separation would permit a detailed study of both contributions in these electron-doped superconductors. It is clear from Fig. 1 that changing the excitation current does not modify the upper drop in $\rho(T)$ at T_{ci}, but dramatically alters the $\rho(T)$ behavior below T_{cj}. Increasing the excitation current broadens the lower superconducting transition, shifting either T_{cj} or the zero resistance state towards lower temperatures. This effect is more pronounced in polycrystalline $Sm_{1.85}Ce_{0.15}CuO_{4-y}$, as shown in Fig. 1(a). There, a change from 0.1 to 10 mA, corresponding to increasing the current density from 3.8×10^{-2} Å/cm^2 to 3.8×10^{-1} Å/cm^2, shifts the zero resistance temperature from ~15 to ~7 K. Similarly, T_{cj} is also shifted towards lower temperatures. Figure 1 reveals that these features occur in all samples studied. This strongly suggests that Josephson coupling develops below T_{cj}, because such coupling is known to be very sensitive to both changes in the excitation current and small applied magnetic fields.[3-5,15] These results, as well as previous ones on electron-doped superconductors, show that there are not two superconducting phases in these samples.[1-5,15]

The second point regarding Fig. 1 refers to the upper fractional drop in $\rho(T)$ at T_{ci}. From previous electrical resistivity measurements on polycrystalline samples in the systems Sm-Ce-Cu-O,[1,15] and Nd-Ce-Cu-O,[2,4] it seems that the upper fractional drop in the electrical resistivity is always close to 30% and nearly for concentrations of Ce in the range $0.13\leq x\leq0.20$. However, there is an anomaly in Fig. 1; the relative drop in $\rho(T)$ increases slightly with increasing concentration of Ce up to $x=0.17$, but then *decreases significantly* for the sample with $x=0.18$. This behavior is important for understanding the phase separation in $Nd_{2-x}Ce_xCuO_{4-y}$ series as has been discussed in Refs. 10 and 11, based on high-resolution neutron-diffraction studies on polycrystalline samples of $Nd_{2-x}Ce_xCuO_{4-y}$ $(0.0\leq x\leq0.20)$. It was proposed that phase separation, associated with some nonequilibrium process, occurs in these materials. In such circumstances, the entire series should be comprised of two very similar crystallographic phases, one superconducting phase with $x\approx0.165$ and a nonsuperconducting phase with a different Ce concentration.

Our electrical resistivity results seem to be in agreement with this proposition, i.e., that all of the samples are comprised of at least two different phases, one responsible for the superconducting properties, and the other nonsuperconducting. In order to put this point in perspective, it is necessary to assume that the first drop in $\rho(T)$ is due only to a genuine superconducting phase. In this picture, a given sample does not attain the zero resistance state just below T_{ci} because the superconducting volume fraction is below the percolation threshold. However, the fractional drop in $\rho(T)$ at T_{ci} in a given sample would be strongly dependent on the superconducting volume fraction present in that sample. Additionally, according to the effective-medium approximation,[16] the relative drop in $\rho(T)$ would increase linearly with increasing superconducting volume fraction up to the Ce composition of the probable superconducting phase of $x\approx0.165$. For higher Ce concentrations, a linear decrease in $\rho(T)$ should be observed, since the nonsuperconducting phase volume would increase notably. From observations of Fig. 1, the fractional decreases in $\rho(T)$ at T_{ci} are about 17, 18, 23, and 15% for Ce concentrations of $x=0.15$, 0.16, 0.17, and 0.18, respectively. The fractional drop has a maximum for $x=0.17$, which is very close to the stoichiometric composition of $x=0.165$ proposed in Refs. 10 and 11. While our results for the relative drop at T_{ci} agree qualitatively with the above neutron-diffraction results for polycrystalline samples of $Nd_{2-x}Ce_xCuO_{4-y}$ $(0.0\leq x\leq0.20)$,[10,11] they would not be inconsistent with the existence of a true Ce solid solution observed in similar series, as proposed by Cava *et al.*[17]

Figure 2 displays $T_{ci}(x)$ and $T_{cj}(x)$ for polycrystalline $Sm_{2-x}Ce_xCuO_{4-y}$ $(0.15\leq x\leq0.18)$, subjected to two different post-reduction cooling rates. In both cases, T_{ci} decreases slightly with x, while T_{cj} has a maximum at $x=0.16$. By contrast, in polycrystalline $Sm_{2-x}Ce_xCuO_{4-y}$,[1] T_{ci} remains constant ~20.5 K for samples $0.13\leq x\leq0.20$. The negative dT_{ci}/dx shown in

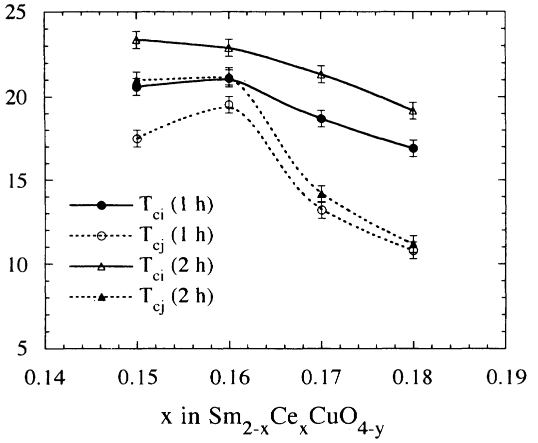

FIG. 2. Compositional dependence of T_{ci} and T_{cj} for a series of polycrystalline samples of $Sm_{2-x}Ce_xCuO_{4-y}$ ($0.15 \leq x \leq 0.18$). The data display results obtained in two series cooled for either 1 or 2 h after the reduction process. T_{ci} and T_{cj} are defined in Fig. 1.

Fig. 2 is seemingly incompatible with phase separation, as proposed in Refs. 10 and 11, which would seem to imply a constant T_{ci}, corresponding to a unique superconducting stoichiometry. However, a negative dT_{ci}/dx could be consistent with a phase separation. To see this, first note that these two-phase polycrystalline samples are believed to have a superconducting volume fraction below the percolation threshold, i.e., probably below 30%,[16] presumably in the form of superconducting particles randomly distributed throughout with a wide volume distribution and randomly dispersed through the sample. If T_{ci} decreases with average particle size, and if that size decreases with increasing x, this would account for the negative dT_{ci}/dx.[18] In agreement with our results, this decrease would be more pronounced for $x > 0.16$ (the apparent Ce solubility limit).[1] Similar results have been reported in the hole-doped superconductor heavily doped $La_{2-x}Sr_xCuO_{4-y}$ ($x \geq 0.20$), with a similar interpretation.[19]

Why is this series effectively a two-phase system? The reduction process which induces superconductivity removes ~0.02 oxygen per formula unit,[20] suggesting that superconductivity may be confined mainly to sites near the removed oxygen. Now, increasing Ce content decreases the amount of removed oxygen,[21] and hence may produce smaller phase-coherent superconducting regions. It may also create different phases with different types of oxygen ordering,[21] only one of which may be superconducting. As evidence for the role of oxygen ordering, we find that the reducing process and hence superconductivity occurs only in samples rapidly cooled from temperatures as high as 950 °C.

There is considerable evidence in the literature for short-range composition or orthorhombic fluctuations in these cuprates. For example, in the $La_{2-x}Sr_xCuO_{4-y}$ series,[19] a crystallographic phase transition near $x = 0.2$ is thought to produce fluctuations of this kind. Such short-range fluctuations, being difficult to detect by x rays, are most easily observed in the macroscopic properties of the sample. In particular, one expects a systematic decrease in the diamagnetic signal, and a disappearance of the specific-heat jump at T_{ci},[16] because of the small size of the superconducting regions. Such behavior of both properties is observed in polycrystalline samples of both electron- and hole-doped superconductors.[1,5,6,19]

The existence of small superconducting regions, or more appropriately short-range compositional order, in a series of polycrystalline samples of $Nd_{2-x}Ce_xCuO_{4-y}$, $x = 0.165$ and $x = 0.20$, has been also proposed by Billinge and Egami.[22] From analysis of the atomic pair-density function, obtained from neutron powder-diffraction data, these authors proposed that the CuO_2 planes are spatially inhomogeneous, generating two different domains or phases. Their estimate of the size of these domains, within which the crystallographic properties are believed to be coherent, was extremely small—about 6 Å. Their result also suggests that superconducting properties are confined to very small regions in these polycrystalline samples and that the superconducting phase coexists with one or more nonsuperconducting phases. From systematic Mössbauer effect spectroscopic studies on lightly Co-doped polycrystalline samples of $Nd_{2-x}Ce_xCuO_{4-y}$ ($0.0 \leq x \leq 0.18$), a coexistence of superconducting and nonsuperconducting regions was deduced.[23] It was estimated that nonsuperconducting regions are mainly confined within clusters of typical size ~25–250 Å and that these regions coexist with superconducting ones. From these observations, one concludes that both superconducting and nonsuperconducting phases are confined to small regions. Considering all these features, one concludes that a higher Ce content in electron-doped superconductors, combined with the removal of oxygen, should result in smaller regions where the order parameter of the superconducting phase is coherent. In our view, these small regions, closely spaced, are interspersed with occasional large regions. Such a morphology accounts for the observed decrease of T_{ci} with increasing Ce concentration, and the observed absence of a peak in the specific heat at T_{ci}.

From the data shown in Figs. 1 and 2, it is evident that the oxygen removal has little effect on T_{cj}, i.e., the coupling temperature T_{cj} is mainly governed by the Ce doping implying that one can experimentally control the Josephson coupling temperature just by the Ce doping. This means that the Josephson coupling temperature can be adjusted and the coupling can be studied separately from the genuine superconducting phase. Figure 2 also shows that the coupling temperature T_{cj} assumes a maximum value for a Ce concentration of $x = 0.16$; i.e., 21 and 19.5 K in samples cooled for 2 and 1 h, respectively.

Considering all of these results, we tentatively conclude that electron-doped superconductors are described by the physics of granular superconductors.[18] The experimental results and their possible explanation imply that these polycrystalline samples are comprised of small superconducting regions, closely spaced, and embedded in a nonsuperconducting host—a structure analogous to a composite. The structure is apparently granular, and superconductivity is destroyed by the depression of the long-range phase coherence across the sample.

The results shown in Fig. 1 can be interpreted in terms of the physics of granular superconductors, yielding estimates for several parameters. Our picture of the superconducting transition is that it occurs in two well-defined stages. The upper superconducting transition, T_{ci}, is the resistive transition of a genuine superconducting phase. At this temperature, there is a fairly sharp drop in the resistivity as a part, but not all, of the material in the composite becomes superconducting. Below this temperature, the material consists of a collection of superconducting grains in a nonsuperconducting host. At a low enough temperature, these grains begin to interact with one another via Josephson coupling, leading eventually to a superconducting transition at a lower temperature T_{cj}. The Josephson coupling temperature T_{cj} is the transition from phase incoherence, in which the phases of the superconducting order parameter on different grains are random, to phase coherence, in which there is long-range phase ordering. For simplicity, let us assume that the superconducting grains are all the same size, distributed on a diluted simple cubic network of lattice parameter a, such that a fraction p of the sites of the network are occupied by grains, which are Josephson coupled. With $p > p_c$, the percolation threshold, the Josephson junctions form an infinite connected cluster.

We now interpret our electrical resistivity measurements in terms of this picture. First of all, let us assume that the resistive drop just below T_{ci} is of the order of 25%, as shown in Fig. 1. An effective-medium picture of the composite[16(a)] would suggest that about 20% of the composite by volume is comprised of superconducting grains. To estimate the Josephson-coupling transition temperature in zero magnetic field, we note that the Josephson coupling energy $J(T)$ of a superconductor-insulator-superconductor junction at temperature T is given by[24] $J(T)=(23.1/2\pi)k_B T_{ci}(1-T/T_{ci})(R_c/R)$, where R is the normal state of the junction, or the intergrain resistance, and $R_c=\hbar/e^2=4114\ \Omega$. In the diluted array picture, a relationship between T_{cj}, T_{ci}, and the normal resistance of the array at zero magnetic field is obtained by using a relationship given by Harris *et al.*[25]

$$T_{cj}/T_{ci}=1/[1+\alpha(R/R_c)] , \tag{1}$$

where we estimate the dimensionless constant $\alpha=0.12$. This result follows from the relationship $k_B T_c \approx 2.21 J(T_c)$ for the transition temperature T_c of a three-dimensional xy model with coupling constant J to which our Josephson-junction model corresponds.[26] From Fig. 1, one can see that T_{cj}/T_{ci} is typically of order 0.7 at zero applied magnetic field, which gives $R \approx 15\ \mathrm{k}\Omega$.

Our next step is to connect R to the normal-state resistivity ρ, i.e., the plateau resistivity at zero magnetic field, in the temperature range between T_{ci} and T_{cj}. From Fig. 1, one might estimate $\rho \approx 10\ \mathrm{m}\Omega\,\mathrm{cm}$. For the percolating model just described, the desired relation is[27]

$$\rho=Ra[(p-p_c)/(1-p_c)]^{-t} , \tag{2}$$

where a is the lattice constant of the diluted lattice of Josephson junctions, $p_c(\approx 0.31)$ is the percolation threshold,[16] and $t(\approx 1.9)$ is the three-dimensional conductivity exponent describing the conductivity of a diluted lattice of resistors R. When we estimate a on the basis of this expression, assuming p in the vicinity of 0.5, we obtain the remarkable small value of ≈ 6 Å. This suggests that the "grains" involved in the normal-to-superconducting transition are much smaller than the morphological grains of about 5 μm seen in photomicrographs of these materials.[2,15] Therefore, such a result is in excellent agreement with those obtained by Billinge and Egami,[22] as discussed above.

An alternative procedure for estimating the size of the superconducting regions in this model relies on discussion of Eq. (1), which is a mean-field expression valid for BCS-like superconductors in the dirty limit. As first noted by Beasley, Mooij, and Orlando[28] for granular Al/Al_2O_3 thin films, T_{cj} is depressed as R approximates the critical value R_c. In such a picture it is reasonable to estimate the dimension of the superconducting regions directly from Eq. (1). This can be made by assuming that the intergrain resistance $R=\rho_n/a$, where ρ_n is the electrical resistivity of the plateau observed between T_{ci} and T_{cj}. For the results shown in Fig. 1, $\rho_n \approx 10\ \mathrm{m}\Omega\,\mathrm{cm}$, and if one crudely estimates $T_{cj}/T_{ci} \approx 0.9$, one then obtains an estimate $a \approx 300$ Å. Again, the estimated size of the superconducting regions in these series is very small and quantitatively agrees with the ones obtained in Ref. 23. Similarly, small superconducting regions have been obtained from magnetoresistance measurements on the series $Sm_{2-x}Ce_xCuO_{4-y}$ $(0.14 \le x \le 0.17)$.[3] In addition, from the difference between field-cooled and zero-field-cooled magnetoresistance curves, a superconducting glass state has been proposed. All these estimates are consistent with the presence of small superconducting regions in these materials.

The small sizes of the superconducting regions obtained from the above estimates would affect the magnetic properties of these samples. The temperature dependence of both the magnetic susceptibility and the electrical resistivity obtained in samples of $Sm_{2-x}Ce_xCuO_{4-y}$ with $x=0.17$ and $x=0.18$ are shown in Fig. 3. We have selected these two samples because the coupling temperatures T_{cj} are well separated from T_{ci}—an important characteristic for the following discussion. The first important result shown in Fig. 3 is that appreciable diamagnetism is only observed below the coupling temperature T_{cj}. This feature, while present in the $Sm_{1.83}Ce_{0.17}CuO_{4-y}$ sample, is more pronounced in the $Sm_{1.82}Ce_{0.18}CuO_{4-y}$ sample, in which $T_{ci} \approx 20$ K and $T_{cj} \approx 11$ K. Furthermore, there is no evidence that either the absolute moment or the diamagnetism increases considerably with decreasing temperature between these two temperatures.

As discussed above, the transition at T_{ci} appears to be associated with a genuine superconducting phase and not, for example, a structural transition. One might also imagine that such a drop in $\rho(T)$ just below T_{ci} could be due to an insulator-metal (I-M) transition as observed, for example, in $Nd_{2-x}Sr_xNiO_{4+y}$ (Ref. 29) and $PrNiO_3$.[30] If this were the case, no significant diamagnetism would be observed between T_{ci} and T_{cj}, which is consistent with

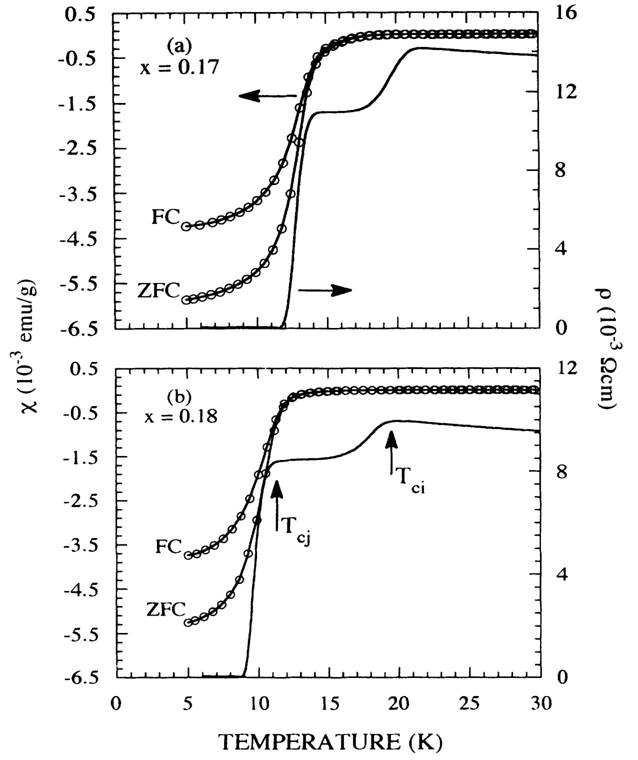

FIG. 3. Temperature dependence of magnetic susceptibility χ and electrical resistivity ρ in polycrystalline samples of $Sm_{2-x}Ce_xCuO_{4-y}$, $x=0.17$ (a), and $x=0.18$ (b). Magnetic-susceptibility measurements were performed in an applied field of 1 Oe. The critical temperatures T_{ci} and T_{cj} are marked in (b).

our magnetic data. However, if there were an I-M transition at T_{ci}, the electrical transport data would be expected to be hysteretic because of the first-order nature of the I-M transition. Such behavior has been not observed in our electrical resistivity measurements suggesting that the transition observed at T_{ci} is really associated with a genuine superconducting phase.

Since the transition at T_{ci} is associated with superconductivity, there are several possible explanations for the absence of significant diamagnetism between T_{ci} and T_{cj}. First, there may be an insufficient total superconducting grain volume, which would drastically decrease the diamagnetic contribution. This assumption is also consistent with the very low superconducting fraction as estimated above from electrical resistivity data, and from magnetization measurements at temperatures as low as 5 K.[1,5] However, even if the superconducting grain volume is small but there were superconducting regions as large as 5 μm, appreciable diamagnetism would be observed since the Meissner signal is robust. Hence, the small total superconducting grain volume by itself it is not a reasonable explanation for the absence of appreciable diamagnetism between T_{ci} and T_{cj}. It is also possible that the grain size, or more appropriately, the region where the order parameter is not depressed, may be of order of the London penetration depth λ_L. Such an assumption would be consistent with no appreciable diamagnetism just below T_{ci} since λ_L diverges as the critical temperature T_{ci}.

Another possibility is that the 5-μm physical grains have a shell-core morphology, in which the superconducting properties are confined to a thin shell which is evidently comparable to λ_L. This kind of morphology has been proposed for these polycrystalline samples of electron-doped superconductors together with a very broad distribution of either Josephson resistance and critical temperatures.[15] The magnetic data shown in Fig. 3 seem to be inconsistent with such an assumption. Let us assume that 5–10 μm grains have a thin superconducting shell with size comparable to the London penetration depth λ_L. It is reasonable that the diamagnetic contribution would be very small during the field-cooled (FC) measurements since the field penetration would then be deeper. On the other hand, data taken during zero-field-cooled measurements (ZFC) would reveal completely different results, mostly in the temperature interval between T_{ci} and T_{cj}. This is because the area enclosed by the supercurrents would be, at least, as large as 5–10 μm and, hence, a robust diamagnetic contribution would be observed, even within the temperature interval between T_{ci} and T_{cj}. This is not observed in our experimental results.

Alternating current magnetic-susceptibility (ac) χ_{ac} measurements made in these series also confirms that superconducting properties are primarily confined to small regions.[31] It was found that the resistive component χ''_{ac} shows only one peak and that this peak occurs only at T_{cj}. Such an experimental result corroborates the ones shown in Fig. 3 and strongly suggests the presence of small superconducting regions in these series. In any event, the absence of appreciable diamagnetism between T_{ci} and T_{cj} can be fully understood if there is a combination of insufficient superconducting grain volume, i.e., a very low superconducting fraction, and that the superconducting properties are confined to small regions with size comparable to the London penetration depth λ_L. Below T_{cj} the long-range order is established and the absolute moment or diamagnetism increases considerably with decreasing temperature, as shown in Fig. 3.

The results of Fig. 3 also call for a discussion regarding the nature of the transition at T_{cj}. Let us distinguish further between previous experimental results and those presented in Figs. 1 and 3. Previous measurements in these cuprates have mainly been carried out on what might be called true percolative systems.[16] In such a true percolative system, one expects an extremely broad distribution of individual junction critical currents. When the temperature falls below T_{ci}, one might expect the simultaneous formation of both small and large connected networks of junctions, through which supercurrent can flow. The number and size of such pathways might be expected to increase as the temperature decreases below T_{ci}. One would also expect this increase to be mirrored in macroscopic measurements, such as electrical resistivity and magnetic susceptibility. Indeed, in such systems, it is observed that the electrical resistivity decreases with decreasing temperature just below T_{ci}, often followed by a long tail near the temperature where the system attains zero resistivity. Magnetic-susceptibility measurements also reveal such behavior. Namely, the absolute moment of diamagnetism increases considerably with decreasing temperature and saturates for temperatures below that for which the system attains the zero resistance state. These features characterize a true percolative system and are extensively discussed in the literature. One example of this has been carefully discussed by Goldfarb, Lelental, and Thomspon.[32] Let us concentrate on Fig. 4 of this reference, which displays the ac magnetic susceptibility χ_{ac} and ac resistance data as a function of temperature for polycrystalline $YBa_2Cu_3O_{7-\delta}$ with a broad and weak intergranular coupling. Below $T_{ci} \approx 92.1$ K, a systematic decrease in the electrical resistance down to $T_{cj} \approx 13.9$ K is observed. This behavior has its counterpart in the ac magnetic-susceptibility (χ_{ac}) data. There is a fairly rapid drop at T_{ci} in the ac magnetic susceptibility χ'_{ac} and the diamagnetic signal decreases with decreasing temperature down to T_{cj}. At the latter temperature, there is another fairly sharp drop in the χ'_{ac} component which corresponds to the zero resistance state in $R(T)$.

The data shown in Fig. 3 show completely different features. First, all of our samples show a striking double resistive superconducting transition, which is not observed in the percolative systems mentioned in the previous paragraph. Specifically, there is a ~25% drop in electrical resistivity at the upper temperature T_{ci}, followed by a well-defined plateau and no evidence of a zero resistance state down to a lower temperature T_{cj}, where there is a very sharp drop of about 75% in $\rho(T)$ down to the zero resistance state. Thus, there is no evidence of decrease in the magnitude of the electrical resistivity between T_{ci} and T_{cj}. The remarkable plateau in $\rho(T)$ data suggests that there is no continuous increase in superconducting fraction with decreasing temperature, i.e., that percolation ideas, in the sense of the previous paragraph, are not applicable here. Similarly, our magnetization measurements show no evidence of significant diamagnetism between T_{cj} and T_{cj} or even a systematic increase in the magnitude of the moment in the same temperature interval. All of these macroscopic measurements point towards a nonpercolative phase transition at T_{cj}, in contrast with previous measurements obtained on polycrystalline samples of high-T_c superconductors.[32]

The evidence of small superconducting regions in these series has focused our attention on the possible importance of charging effects[33,34] for the phase-ordering transition in these polycrystalline samples.[35] Such Coulomb effects arise from Cooper-pair exchange between superconducting grains, which causes the deviation of a single metal grain from charge neutrality.[33,34] The charging energy is defined as $E_c = e^2/2C$, where C is the grain capacitance. The possibility of reentrance into the normal state below T_{cj} because of Coulomb-induced zero-point phase fluctuations has been raised within mean-field theory.[36] Such an effect, which is important when $E_c \geq E_j = 2eI_{cj}/\hbar$, where E_j is the Josephson energy and I_{cj} is the Josephson critical current, has been neglected by Gerber and co-workers[15] in their analysis. These authors have observed a quasireentrant behavior in magnetoresistance measurements made in polycrystalline $Sm_{1.85}Ce_{0.15}CuO_{4-y}$ and attributed the observed increase in $\rho(T,H)$ between T_{ci} and T_{cj} to thermally activated quasiparticle tunneling. Their analysis assumes that charging effects are weak because of the large physical grain size of the order of 10 μm. From the above discussion, however, the dimension of the physical grains of the order of μm in these polycrystalline samples is not an appropriate size to consider for the problem. Instead, it has been proposed here that physical grains of the order of 5–10 μm are comprised of small superconducting regions with dimension between 6 and 300 Å. In addition, recent transport measurements made on polycrystalline $(Nd_{1-x}Gd_x)_{1.85}Ce_{0.15}CuO_{4-y}$ samples[37] have demonstrated not only the relevance of charging effects in these electron-doped superconductors but also evidence for macroscopic quantum tunneling[38] at low temperatures.

While our results, and previous ones, suggest that Josephson coupling develop at T_{cj}, and that these polycrystalline samples of electron-doped superconductors can be understood within the framework of a superconducting granular scenario, there are few points which need to be clarified for a better understanding of these materials. For example, from Fig. 1, we see that while T_{cj} occurs at lower temperatures for $x > 0.16$, there is a substantial decrease in the magnitude of the normal electrical resistivity in these samples. This seems to be in contradiction with the discussion made throughout the text. A "more metallic behavior" in the normal electrical resistivity would imply both a higher T_{cj} and a better coupling at low temperatures, since resistance across the junctions would be smaller in magnitude. However, a more detailed discussion based on our experimental results is also complicated by the proximity effect. This effect will cause superconducting regions to grow a distance of order of ξ into the surrounding normal region, where ξ is the temperature-dependent normal-metal coherence length. On the other hand, as discussed above, we have found evidence for a decrease in the size of the superconducting regions with increasing Ce content. Thus, it seems that there is a competition between the size of the superconducting islands and the coherence length ξ which describes the penetration of superconductivity into the normal region.

To summarize, we have studied polycrystalline samples of $Sm_{2-x}Ce_xCuO_{4-y}$ ($0.15 \leq x \leq 0.18$) obtained from a sol-gel precursor and subjected to different cooling rates after the reduction process. From the electrical resistivity data, all the samples show a double resistive superconducting transitions, which seems to be an intrinsic property of these polycrystalline compounds. Magnetic-susceptibility data show that appreciable diamagnetism only occurs below the long-range order temperature T_{cj}. From the discussion of these results within the framework of granular superconductivity, it was found that superconductivity exists in these polycrystalline samples in a volume fraction below the percolation threshold and is confined to small spatial regions. Such a result accounts for several macroscopic properties of these polycrystalline samples of electron-doped superconductors: (1) the double resistive superconducting transition, (2) the absence of appreciable diamagnetism between the mean-field critical temperature and the Josephson coupling temperature; and, (3) the absence of a jump in the specific heat at the mean-field critical temperature T_{ci}. Finally, we have argued that charging effects can be relevant in macroscopic properties of these materials.

ACKNOWLEDGMENTS

We have benefited from stimulating discussions with E. A. Early and R. C. Dynes. This work was supported in part by the United States Department of Energy under Grant No. DE-FG03-86ER45230. Research at The Ohio State University was supported by the Midwest Superconductivity Consortium (MISCOM) at Purdue University through the Department of Energy Grant No. DE-FG90-02 ER45427 and NSF Grant No. DMR90-20994. One of us (R.F.J.) acknowledges support from the Brazilian agency Fundação de Amparo à Pesquisa do Estado de Sáo Paulo (FAPESP) under Grant Nos. PD-EXT91/2743-0 and 93/4204-4, and the Brazilian agency CNPq under Grant No. 304647/90-0. L.B.D. was supported by the Sabbatical Fund of the Hebrew University during her stay in San Diego where part of this work was done.

---

[1] E. A. Early, C. C. Almasan, R. F. Jardim, and M. B. Maple, Phys. Rev. B **47**, 433 (1993).

[2] R. F. Jardim, E. A. Early, and M. B. Maple (unpublished).

[3] R. F. Jardim, M. C. de Andrade, E. A. Early, M. B. Maple, and D. Stroud (unpublished).

[4] V. B. Barbeta, C. H. Westphal, R. F. Jardim, M. B. Maple, and X. Obradors, J. Appl. Phys. **73**, 6639 (1993).

[5] R. F. Jardim, L. Ben-Dor, and M. P. Maple, J. Alloys Compounds **199**, 105 (1993).

[6] M. B. Maple, N. Y. Ayoub, T. Bjørnholm, E. A. Early, S. Ghamaty, B. W. Lee, J. T. Markert, J. J. Neumeier, and C. L. Seaman, Physica C **162-164**, 296 (1989).

[7] C. Geibel, A. Vierling, P. V. Aken, R. Eichert, A. Gravel, M. Rau, S. Horn, G. Weber, and F. Steglich, Physica C **185-189**, 591 (1991).

[8] K. Oka and H. Unoki, Jpn. J. Appl. Phys. **28**, L937 (1989).

[9] R. F. Jardim and M. B. Maple, Mater. Lett. **18**, 5 (1993).

[10] P. Lightfoot, D. R. Richards, B. Dabrowski, D. G. Hinks, S. Pei, D. T. Marx, A. W. Mitchell, Y. Zheng, and J. D. Jorgensen, Physica C **168**, (1990) 627.

[11] J. D. Jorgensen, P. Lightfoot, S. Pei, B. Dabrowski, D. R. Richards, and D. G. Hinks, in *Advances in Superconductivity III,* Proceedings of the 3rd International Symposium on Superconductivity, edited by K. Kajimura and H. Hayakawa (Springer-Verlag, Tokyo, 1991).

[12] P. P. Freitas, C. C. Tsuei, and T. S. Plaskett, Phys. Rev. B **36**, 833 (1987).

[13] M. Ausloos and Ch. Laurent, Phys. Rev. B **37**, 611 (1988).

[14] P. Pureur, J. Schaf, M. A. Gusmão, and J. V. Kunzler, Physica C **176**, 357 (1991).

[15] A. Gerber, T. Grenet, M. Cyrot, and J. Beille, Phys. Rev. Lett. **65**, 3201 (1990); A. Gerber, T. Grenet, M. Cyrot, and J. Beille, Phys. Rev. B **43**, 12 935 (1991).

[16] (a) See, for example, D. J. Bergman and D. Stroud, *Solid State Physics: Advances in Research and Applications,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1992), Vol. 46, p. 148; (b) C. Ebner and D. Stroud, Phys. Rev. B **25**, 5711 (1982).

[17] R. J. Cava, H. Takagi, R. M. Fleming, J. J. Krajewski, W. F. Peck, Jr., P. Bordet, M. Marezio, B. Batlogg, and L. W. Rupp, Jr., Physica C **199**, 65 (1992).

[18] For a review and series of experimental and theoretical studies, see articles in *Inhomogeneous Superconductors-1979,* edited by T. L. Francavilla, D. V. Gubser, J. R. Leibowitz, and S. A. Wolf, AIP Conf. Proc. No. 58 (AIP, New York, 1980).

[19] H. Takagi, R. J. Cava, M. Marezio, B. Batlogg, J. J. Krajewski, W. F. Peck, Jr., P. Bordet, and D. E. Cox, Phys. Rev. Lett. **68**, 3777 (1992).

[20] J. T. Markert, N. Y. Ayoub, T. Bjørnholm, E. A. Early, C. L. Seaman, P. K. Tsai, and M. B. Maple, Physica C **162-164**, 957 (1989).

[21] E. Wang, J.-M. Tarascon, L. H. Greene, G. W. Hull, and W. R. McKinnon, Phys. Rev. B **41**, 6582 (1990).

[22] S. J. L. Billinge and T. Egami, Phys. Rev. B **47**, 14 386 (1993).

[23] V. Chechersky, N. S. Kopelev, Beom-hoam O, M. I. Larkin, J. L. Peng, J. T. Markert, R. L. Greene, and A. Nath, Phys. Rev. Lett. **70**, 3355 (1993).

[24] J. E. Mooij, in *Percolation, Localization, and Superconductivity,* Vol. 109 of NATO Advanced Study Institute Series B: Physics, edited by A. M. Goldman and S. A. Wolf (Plenum, New York, 1983), p. 325.

[25] D. C. Harris, S. T. Herbert, D. Stroud, and J. C. Garland, Phys. Rev. Lett. **67**, 3606 (1991).

[26] M. Ferer, M. A. Moore, and M. Wortis, Phys. Rev. B **8**, 5205 (1973); A. Garg, R. Pandit, S. A. Solla, and C. Ebner, Phys. Rev. B **30**, 106 (1984); Y. H. Li and S. Teitel, Phys. Rev. B **40**, 9122 (1992).

[27] C. Ebner and D. Stroud, Phys. Rev. B **28**, 5053 (1983).

[28] M. R. Beasley, J. E. Mooij, and T. P. Orlando, Phys. Rev. Lett. **42**, 1165 (1979).

[29] X. Granados, J. Fontcuberta, J. Alonso, M. Vallet, and J. M. Gonzalez Calbet, Physica C **191**, 371 (1992).

[30] X. Granados, J. Fontcuberta, X. Obradors, and J. B. Torrance, Phys. Rev. B **46**, 15 683 (1992).

[31] R. F. Jardin, C. H. Westphal, C. H. Cohenca, L. Ben-Dor, and M. B. Maple, J. Appl. Phys. **75**, 6720 (1994).

[32] R. B. Goldfarb, M. Lelental, and C. A. Thompson, in *Magnetic Susceptibility of Superconductors and Other Spin Systems,* edited by R. A. Hein, T. L. Francavilla, and D. H. Liebenberg (Plenum, New York, 1992).

[33] B. Abeles, Phys. Rev. B **15**, 2828 (1977).

[34] E. Simanek, Phys. Rev. B **22**, 459 (1980).

[35] Z. Q. Wang and D. Stroud, Phys. Rev. B **44**, 9643 (1991).

[36] E. Simanek, Phys. Rev. B **23**, 5762 (1981).

[37] R. F. Jardim, C. H. Westphal, C. C. Becerra, and A. Paduan-Filho (unpublished).

[38] M. P. A. Fisher, Phys. Rev. Lett. **57**, 885 (1986).