Nonmonotonic resistivity transitions in granular superconducting ceramics

A. Gerber, T. Grenet, M. Cyrot, and J. Beille
Laboratoire Louis Néel, C.N.R.S., 166 X, 38042 Grenoble CEDEX, France
(Received 14 December 1990)

Nonmonotonic forms of resistive superconducting transition as a function of temperature and magnetic field have been observed in granular high-T_c ceramics of the electron-type family $L_{2-x}M_x\mathrm{CuO}_{4-y}$. The behavior is compared with that of low-temperature granular superconductors and is treated by the conventional terms of the energy gap and Josephson and quasiparticle tunnelings. The values of the intragranular upper critical field H_{c2} perpendicular to the a-b plane of Sm-Ce-Cu-O are extracted. We find evidence for the appearance of superconductivity in individual grains at temperatures significantly higher than the resistance onset temperature.

INTRODUCTION

It is generally recognized now that the intrinsic short coherence length[1] and granular structure of the high-temperature superconductors are the essential parameters limiting the potential applications of these materials. Unlike the classical superconductors, the intergranular boundaries of high-T_c ceramics are the sites of a depressed order parameter and operate like Josephson-type weak links.[2] As a result, the critical current of the polycrystalline samples is usually found to be strongly dependent on magnetic field and unsatisfactorily low for large-scale applications.

The study of granular superconductivity is not, however, new. A lot of theoretical and experimental work has been devoted to the subject, especially after the discovery of a universal threshold value R_Q (Ref. 3) of the normal-state sheet resistance of two-dimensional films, which divides films that show complete superconducting transitions to zero resistance from those that do not. In a granular film, superconductivity is destroyed by a loss of long-range phase coherence when the film's resistance exceeds the value R_Q of the order of $h/4e^2$. In this case a so-called "quasireentrant" behavior can be observed[4–6] in which the resistivity falls at the onset transition temperature, then passes through a minimum before rapidly increasing at the lower temperatures. The behavior appears not to be restricted to two-dimensional systems, but was also found in thicker three-dimensional samples of granular metals.[7] Moreover, the resistivity of three-dimensional films of granular aluminum very close to the metal-insulator transition was found[7] to show quasireentrant behavior also in the magnetic-field dependence. One of the explanations of the quasireentrant behavior in the temperature dependence arises from a combination of quasiparticle and Josephson tunnelings between isolated superconducting islands. The normal-state resistance of the metallic grains themselves in the system near the metal-insulator threshold is negligible compared to that of the intergranular spacings. The drop of resistivity below the onset can then be associated with the creation of a finite nonpercolating chain of intergranular 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 resistance of the sample then increases when the temperature is further decreased because of the reduction in the quasiparticle density.

The application of the conventional superconductivity apparatus to high-T_c superconductors became even more valuable after the discovery of the remarkable similarity between the properties of "classical" homogeneous Bi films[8] and ultrathin films of $\mathrm{DyBa_2Cu_3O_7}$ (Ref. 9) and $\mathrm{YBa_2Cu_3O_7}$.[10] In both systems superconductivity was found only when the normal-state sheet resistance is below 6450 Ω. It is therefore attractive to find how far the similarity between the low- and high-T_c granular superconductors may extend.

EXPERIMENTAL TECHNIQUES

We concentrated our study on the family of electron-type superconducting ceramics $L_{2-x}M_x\mathrm{CuO}_{4-y}$ (L = Pr, Nd, Sm, and Eu; M = Ce and Th). Polycrystalline samples were prepared by a solid-state reaction as described in Refs. 11 and 12. The existence of macroscopic superconductivity in these compounds is limited within a narrow range of doping concentrations x and of oxygen deficiency y.[13] The maximum values of the transition temperature of the order of 20 K were found for x = 0.15–0.16 and y = 0.02. Resistance of the samples was measured by an ac four-probe technique in an applied magnetic field up to 6 T. Susceptibility was measured in a superconducting quantum interference device (SQUID) magnetometer. The sample topology was studied by a scanning electron microscope (SEM).

EXPERIMENTAL RESULTS

We shall start by a presentation of the topological structure of the materials studied. The structure of all the family of electron-type materials $L_{2-x}M_x\mathrm{CuO}_{4-y}$ is very similar. We show in Fig. 1 the SEM micrographs of Nd-Th-Cu-O and Pr-Ce-Cu-O samples, the typical representatives of this class of materials. The samples are built of large grains tightly pressed one to another. The

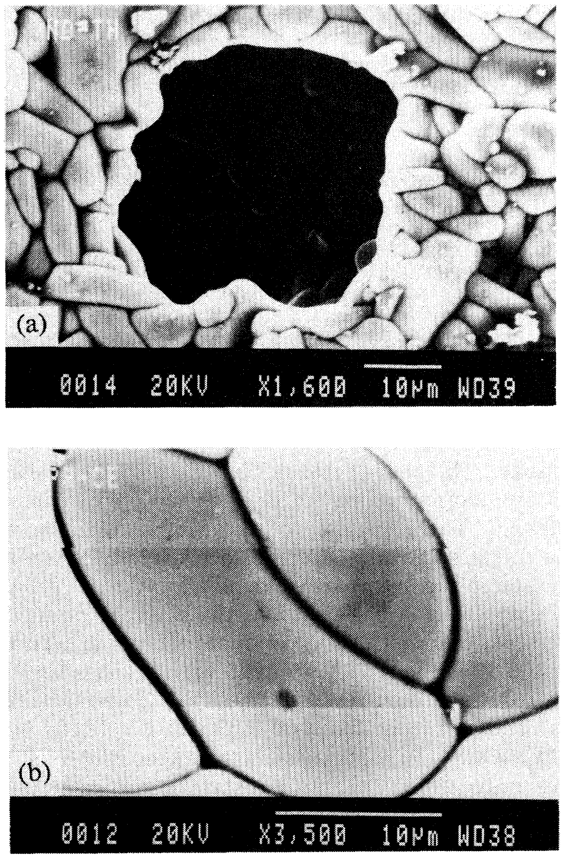

FIG. 1. SEM micrographs of (a) Nd-Th-Cu-O and (b) Pr-Ce-Cu-O samples. The grains are large and tightly packed.

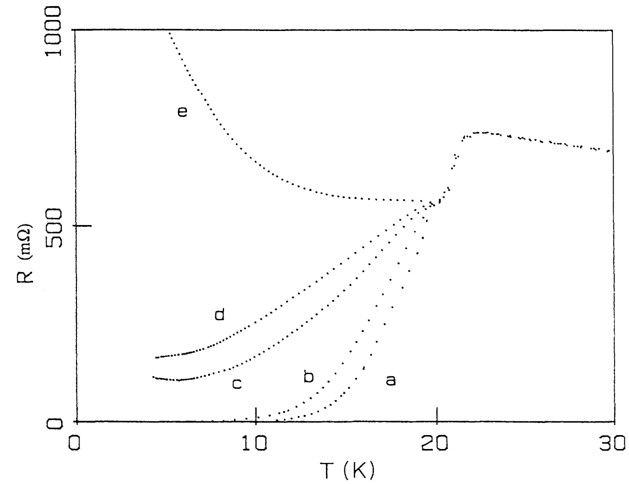

FIG. 2. Resistance of $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ sample as a function of temperature measured with different current levels at zero applied field. (a) 1 mA, (b) 2 mA, (c) 4 mA, (d) 5 mA, and (e) 10 mA. An initial current-independent resistance drop can be related to the intragranular transition, when the current-dependent stage is a property of intergranular boundaries.

grains are large, and their dimensions vary between 1 and 10 μm. The surfaces of the neighboring grains are smoothly adjusted; the material fills almost all the volume. The intergranular spacings are narrow and of approximately constant width. The structure seen inside the porous cavity is identical to that on the surface; thus a three-dimensional picture can be imagined. This topology is very different from, for example, granular aluminum,[7] Al-Ge,[14] or random array of tin particles,[15] extensively studied near their metal-insulator transition. The latter are the systems of diluted small metallic grains with a typical size of 100 Å embedded in an insulator matrix.

Study of the granularity effects means separation and identification of the intra- and intergranular properties. In the transport measurements we tried to reach this by tuning the superconducting transition by current and applied magnetic field. We show in Fig. 2 the resistivity of a $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ sample as a function of temperature measured with different current levels at zero magnetic field. The transition consists of two clearly separated stages: an initial current-independent drop of constant value and a resistance tail, which character changes dramatically by varying the measuring current. Zero resistance is achieved by a smooth monotonic transition when the current is lower than a few μA. A wide "knee" tail is developed for higher currents, which gradually upturns when the current is further increased. The different current dependences of the two transition stages can be related to two different components of the polycrystalline samples: the grains themselves and the intergranular boundaries.

This assumption is confirmed by the transport measurements under applied magnetic field. We show in Fig. 3 the resistance of the same $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ sample (as in Fig. 2) measured with a low current under different

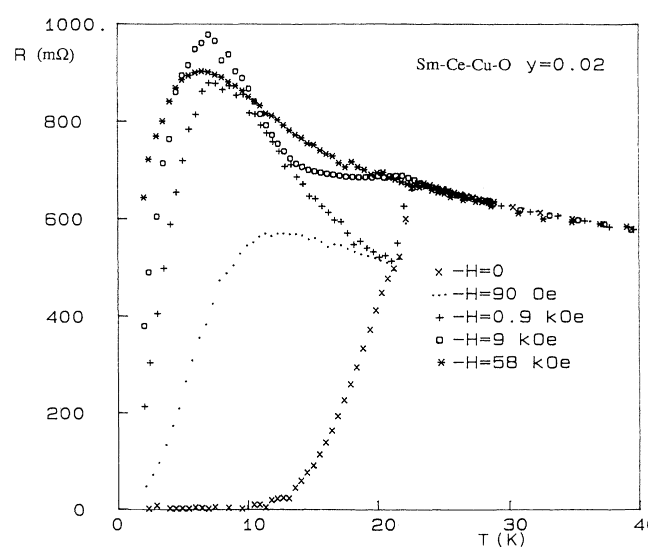

FIG. 3. Resistance of $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ sample as a function of temperature under different applied magnetic fields. The measured current is 100 μA. Nonmonotonic resistive transition is emphasized under $H = 0.9$ kOe.

applied magnetic fields. The two-stage separation of the transition becomes evident under a field as low as 10 Oe. An extraordinary form of transition is developed under the field in the range 50 Oe$<H<$10 kOe. Resistance drops to a nonzero minimum below the onset transition temperature and increases when the temperature is further reduced. In contrast to the known quasireentrant behavior,[4] it reaches a maximum and decreases under additional reduction of temperature. The height and sharpness of the peak increase with the value of the applied field. The high-temperature resistance drop becomes progressively smeared when the field exceeds several kOe, and the anomaly disappears under fields above 10 kOe. The resistance measured under a higher magnetic field monotonically increases until an onset temperature and reduces with additional cooling. It is important to note that the high-temperature resistance drop unsensitive to the increase of the current (Fig. 2) is of the same value as that observed under low magnetic field (Fig. 3).

The comparison between the $R(T)$ curves measured under different applied magnetic fields reveals additional interesting details. For most of the samples, the resistance measured under low fields starts to exceed the value observed under high applied field at temperatures significantly higher than the resistance reduction onset temperature.[16] We illustrate the phenomenon with three $R(T)$ curves measured in the $Sm_{1.85}Ce_{0.15}CuO_{3.97}$ ($y=0.03$) sample under fields of 0, 900 Oe, and 50 kOe, respectively (Fig. 4). The zero field resistance drops to zero below the onset temperature; however, when measured under a low applied field, a characteristic "double-peak" transition[17] is developed. An enhancement of the resistance at temperature above the reduction onset was also found in the Nd-Ce-Cu-O sample which shows a metal-like resistance temperature dependence $dR/dT>0$ in its normal state (Fig. 5).

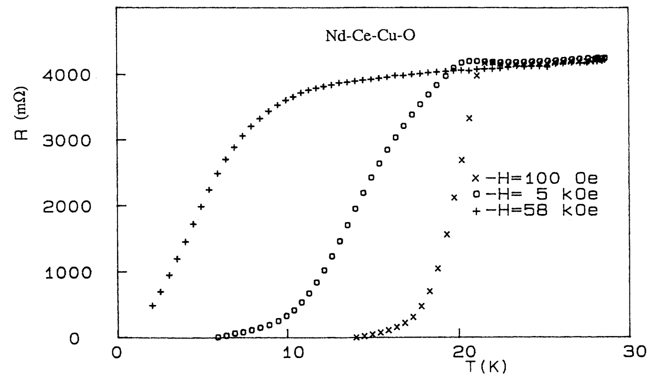

FIG. 5. Resistance of $Nd_{1.85}Ce_{0.15}CuO_{3.98}$ sample as a function of temperature under different applied magnetic fields. The measuring current is 100 μA. Enhancement of resistance below T_{cg} measured under low field is observed also in this sample with a metal-like normal-state behavior ($dR/dT>0$).

The nonmonotonic form of the R-versus-T transition reflects itself also in the magnetoresistance curves. Negative magnetoresistance is found in all the samples studied in the temperature range $T_{int}<T<T_{cg}$, where T_{cg} is defined as the temperature at which the resistance measured under strong fields deviates from that measured at zero field, and T_{int} is the temperature of their intersection (see Fig. 4). At temperatures below T_{int}, the resistance varies nonmonotonically as a function of applied magnetic field: it increases at low fields and decreases at higher ones (Fig. 6, $T=15$ K). In several samples, such as $Sm_{1.85}Ce_{0.15}CuO_{3.98}$, one can find a temperature range in which a double-peak resistive transition is observed as a function of magnetic field (Fig. 6). Resistance measured

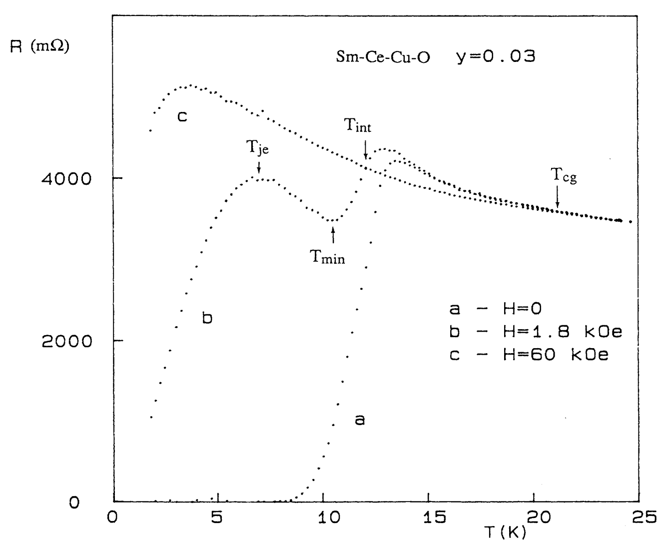

FIG. 4. Resistance of $Sm_{1.85}Ce_{0.15}CuO_{3.97}$ sample as a function of temperature under different applied magnetic fields. The measuring current is 100 μA. Double-peak transition including the resistance enhancement below T_{cg} is pronounced under $H=1.8$ kOe.

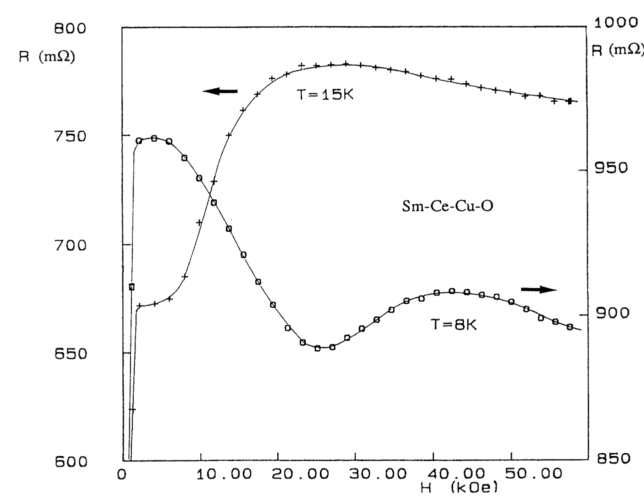

FIG. 6. Resistance of $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ sample as a function of applied magnetic field at two temperatures 8 and 15 K. The measuring current is 100 μA. Double-peak magnetoresistance transition is seen at 8 K.

at $T=8$ K increases sharply at low field and passes local maximum, minimum, and maximum, respectively, as the field increases.

The importance of the intergranular coupling is well illustrated by the properties of Eu-based ceramics. We show in Figs. 7 and 8 two sets of measurements obtained from two samples, the second sample being a small piece cut from the first one. The general properties of the large sample (sample 1), such as the appearance of the double-peak transition at low fields [Fig. 7(a)] and nonmonotonic magnetoresistance transition [Fig. 7(b)] are similar to the rest of the family. However, zero-resistance global superconductivity is never achieved in the small sample (sample 2). Instead, a classical quasireentrant behavior is observed under low magnetic fields [Fig. 8(a)]. The magnetoresistance of this sample includes a double-peak nonmonotonic variation in the temperature range $3\ \mathrm{K}<T<6$ K [Fig. 8(b)]. The absence of global superconductivity in the small sample indicates explicitly that the network of superconducting couplings in this material is very diluted and an infinite cluster of Josephson intergranular couplings does not pass the volume of the small sample.

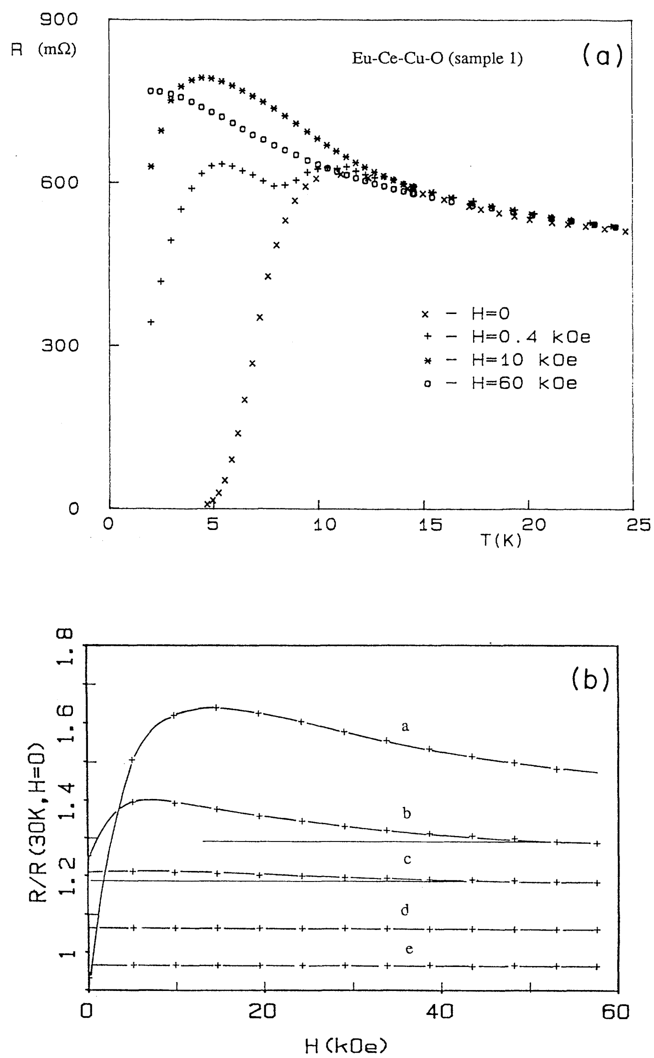

FIG. 7. (a) Resistance of a large $Eu_{1.85}Ce_{0.15}CuO_{3.98}$ sample as a function of temperature under different applied magnetic fields. The measuring current is 100 μA. (b) Normalized resistance of a large $Eu_{1.85}Ce_{0.15}CuO_{3.98}$ sample as a function of applied magnetic field at temperatures: (a) 5 K, (b) 10 K, (c) 14.5 K, (d) 24 K, and (e) 33 K.

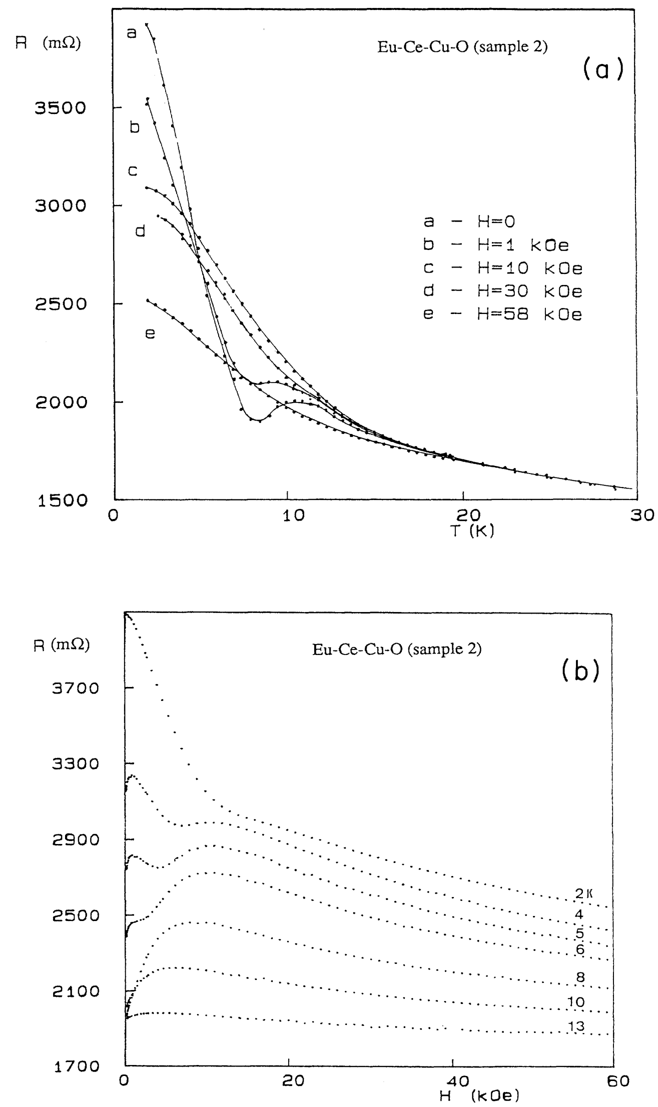

FIG. 8. (a) Resistance of a small $Eu_{1.85}Ce_{0.15}CuO_{3.98}$ sample as a function of temperature under different applied magnetic fields. The measuring current is 100 μA. Behavior of this sample is similar to that of conventional granular superconductors below the percolation threshold. (b) Resistance of a small $Eu_{1.85}Ce_{0.15}CuO_{3.98}$ sample as a function of applied magnetic field at different temperatures. Nonmonotonic double-peak magnetoresistance is observed at 4, 5, and 6 K.

DISCUSSION

We have presented here a variety of unusual superconducting transition forms observed in the family of the electron-type high-T_c superconducting ceramics. We argue that in spite of their extraordinary behavior, compared to the conventional "low-T_c" systems, it can be understood qualitatively using the classical terms, such as superconducting energy gap, Josephson and quasiparticle tunneling, etc.

Our understanding of these results is based on the morphological structure of the material. The samples are built of well-adjusted large grains (see Fig. 1), which defines two important properties: (1) the normal resistance of the grains themselves can be of the same order of magnitude as the intergranular or total sample's resistance because of the large contact surface (or multiple parallel weak links) between the neighboring grains; (2) charging effects of insulated large grains are minimized. This situation is very different from the one usually found in the conventional systems of granular superconductors in the vicinity of the metal-insulator threshold.

We now concentrate the discussion on curve B (Fig. 4) in which the nonmonotonic double-peak transition is emphasized. We divide the curve into two temperature intervals: above and below $T_{\rm min}$, temperature at which the local minimum resistance $R_{\rm min}$ is reached. We argue that the behavior above this temperature, including the enhancement of resistance below T_{cg} and its drop to $R_{\rm min}$, which was found to be weakly dependent on variation of measuring current and low applied field, is determined by the intragranular superconducting transitions mainly and does not involve the creation of intergranular Josephson couplings. The low-temperature part of the transition (below $T_{\rm min}$), which is highly sensitive to the measuring conditions, is governed by the interplay between the Josephson and quasiparticle tunneling between the superconducting grains.

The critical temperature of electron-type superconductors has been reported to depend strongly on the level of electron doping (x) and oxygen deficiency (y). The highest transition temperature of 24 K for the Nd-Ce-Cu-O sample was claimed for $x=0.15$ and $y=0.02$.[11] However, an onset transition temperature as high as 31 K has recently been reported[18] in a Nd-Ce-Cu-O sample with a quite different value of oxygen deficiency $y=0.07$. Therefore, we suppose that because of some inhomogeneous treatment a number of grains can become superconducting at temperatures significantly higher than the resistance drop onset $T_{\rm con}$. The appearance of superconducting grains between the normal ones can give two opposite contributions to the total sample's resistance. The total intragranular resistance reduces; however, the intergranular resistance can increase. The charge transfer between the neighboring normal and superconducting grains separated by an insulating layer is governed by quasiparticle tunneling. The increase of the gap in the superconducting grain decreases the probability of the quasiparticle tunneling, which leads to the enhancement of resistance above its normal-state value. The predominance of this mechanism can explain the enhancement of

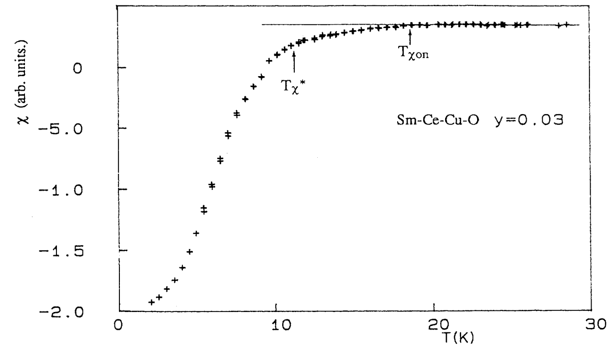

FIG. 9. Field-cooled magnetic susceptibility of $Sm_{1.85}Ce_{0.15}CuO_{3.97}$ sample as a function of temperature measured under 28 Oe applied field. Moderate signal variation below $T_{\chi\rm on}$ becomes much steeper at T_χ^*.

the resistance below T_{cg} and the strong negative magnetoresistance in the temperature range $T_{\rm int} < T < T_{cg}$ (Fig. 4). The existence of superconducting grains at temperatures above the resistance onset $T_{\rm con}$ is supported by the SQUID measurements. We show in Fig. 9 the susceptibility of the same $Sm_{1.85}Ce_{0.15}CuO_{3.97}$ sample as a function of temperature under an applied field of 28 Oe. The diamagnetic signal onset is found at temperature $T_{\chi\rm on}=19$ K, which is lower than T_{cg}, but significantly higher than $T_{\rm con}$ (see Fig. 4). The moderate variation of the susceptibility below $T_{\chi\rm on}$ becomes much steeper at temperature T_χ^*, which corresponds exactly to the resistance drop onset $T_{\rm con}$.

We therefore suggest that at zero applied field the distribution of intragranular critical temperatures has a wide tail until high temperature (even above T_{cg}, which is defined within the experimental accuracy) and a sharp peak near $T_{\rm con}$. As a result, the relative balance between the intra- and intergranular contributions to the total sample's resistance can change drastically and resistance can drop at an effective onset temperature. An opposite situation with a very wide distribution of intragranular critical temperatures is met under high applied fields (above 1 T). The anisotropy of the upper critical field in directions parallel and perpendicular to the a-b planes of electron-type single crystals was found[19,20] to be very large. The grains in the polycrystalline samples are randomly oriented, which broadens the intragranular critical-temperature distribution under field. As a result, the relative balance between the intra- and intergranular contributions does not change, and the resistance measured under lower fields (larger intergranular superconducting energy gap) is higher than the one measured under larger fields (lower gap) (see high-field curves in Figs. 3, 7, and 8).

The high-temperature resistance drop unsensitive to the variation of the current (Fig. 2) and low applied magnetic field (Fig. 3) can then be explained by the partial shunting of the sample by the superconducting grains themselves. For the $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ sample, it gives a ratio between the normal-state intragranular and total sample resistances at 20 K of $R_{\text{intragran}}/R_{\text{total}}=0.25$.

We imagine the system of intergranular boundaries to be built of two independent networks of *S-N-S* (superconductor-normal-superconductor) and *S-I-S* (superconductor-insulator-superconductor) type. The resistance of the weak link of *S-N-S* type is supposed to be almost temperature independent. Following the analogy with low-T_c superconductors, we divide the system of *S-I-S* boundaries into two classes: Josephson-like junctions with normal-state resistances below the critical value R_Q^* and insulator-like junctions with normal resistances above R_Q^*, their charge transfer being governed by quasiparticle tunneling. The vicinity of every network to its percolation threshold is individual to every sample and depends on its chemical treatment and dimensions. For example, the network of Josephson-like *S-I-S* junctions in the small Eu-based sample is *below* its percolating threshold and the sample's resistance does not reach zero. The low-temperature resistance increase can be explained by quasiparticle tunneling across the high-resistance (above R_Q^*) junctions. The rest of the samples discussed have an infinite cluster of Josephson-like junctions, and zero resistance is achieved at zero applied magnetic field.

In the absence of charging effects, a low-resistance junction is expected to carry Josephson currents when the thermal energy (of the order of kT) becomes lower than its coupling energy E_j. Both Josephson coupling energy E_j and the junction's critical current J_c are depressed by magnetic flux. As a result, for a given applied external field the junction's coupling temperature defined as $kT_j=E_j$ is shifted down. In the temperature range $T_{je}<T<T_{\min}$, the charge transfer is governed by quasiparticle tunneling between the superconducting grains and the total resistance increases with temperature reduction due to an exponential decrease of quasiparticle density. At temperature T_{je} a sufficient number of junctions becomes Josephson coupled and the sample's resistance starts to decrease. We are not familiar with a similar behavior in the classical low-T_c superconductors, possibly because of the strong charging effects in the usually small (about 100 Å) grains of the studied systems.[5,7,13]

The mechanism of low-temperature peak development described above is based on the assumption that the applied field is low enough that the grains themselves remain superconducting. The effect of strong magnetic fields is twofold: (1) the intergranular critical-temperature distribution broadens, which smears down the high-temperature resistivity drop; (2) the temperature of the effective transition from quasiparticle to Josephson-like charge transfer is shifted to lower values.

The interpretation of the magnetoresistance curves is based on the same arguments. Two general features should be noted (see Fig. 6): a sharp resistance increase at low fields and a decrease at high fields. The first one corresponds to the destruction of Josephson couplings by the flux penetrating through the junctions, the second to the enhancement of the quasiparticle tunneling due to the suppression of the intragranular gap. The transition from low- to high-field regime can give rise to a double-

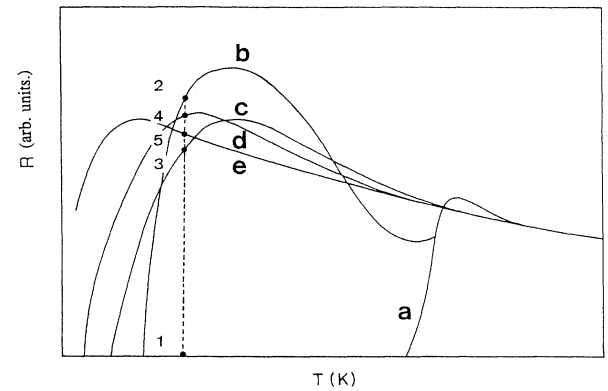

FIG. 10. Schematic presentation of $R(T)$ curves measured under different applied fields (after experimental curves in Fig. 3). The curves *a*, *b*, *c*, *d*, and *e* correspond, respectively, to the increasing fields. Magnetoresistance measured at temperature T passes the values 1, 2, 3, 4, and 5, respectively.

peak magnetoresistance transition ($T=8$ K curve, Fig. 6). We illustrate this development schematically in Fig. 10. As the magnetic field is increased, the sample's resistance varies along the vertical isotherm and successively passes the numbered positions. The saddle point of the double-peak pattern is developed if position 2 (low magnetic field) exceeds the high-field curves (positions 3,4,. . .). This condition is not necessarily met in all the samples.

Based on the mechanism described above, some qualitative information can be extracted. We show in Fig. 11 the low-field magnetoresistance curves of a $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ sample measured at several temperatures between 12 and 20 K in the vicinity of the double-peak saddle point $R_{\min}$ (see Fig. 3). The curves consist of

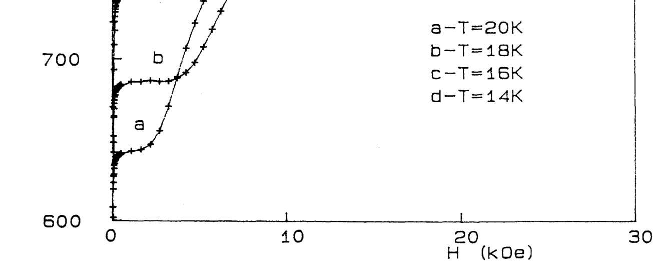

FIG. 11. Low-field magnetoresistance of $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ sample measured at several temperatures in the vicinity of $T_{\min}$. Identification of H_{c2} is discussed in the text.

three clear stages: (1) sharp low-field increase (destruction of Josephson coupling), (2) a range of moderate almost zero variation, and (3) a high-field increase due to the suppression of the intragranular superconductivity (the following decrease is not seen in this field scale). We identify the high-field increase onset as the lowest of the intragranular critical fields H_{c2}, i.e., H_{c2} parallel to the c axis. The values of H_{c2} can be accurately defined in the vicinity of $T_{\min}$ and are presented in Fig. 12 as a function of temperature. The variation is linear near T_c with the slope $dH_{c2}/dT = 0.1$ T/K, which is in a perfect agreement with the one found in $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ single crystal.[20]

The value of T_{cg} has been determined for all the compounds of the electron-type family.[15] The most striking feature of the results is that within the accuracy of this determination, T_{cg} is almost independent of the rare-earth component and is of the order of 20 K. A similar property is observed for the diamagnetic signal onset $T_{\chi on}$. This is in a sharp contradiction with the variation of the resistive transition middle point T_{cmid}, which was shown to fall down for heavy rare-earth-based compounds and was suggested to be related to the size of the rare-earth ions. If our understanding of the physical meaning of T_{cg} is correct, some grains that got the "best" treatment become superconducting at temperatures even higher than T_{cg}. We speculate that if these optimum conditions could be realized for all the material, the transition onset of all the family could be increased significantly.

The results presented here have been obtained by the study of the electron-type family $L_{2-x}M_xCuO_{4-y}$. We believe, however, that the general features of the nonmonotonic behavior are not restricted to this class of materials only and can be met in other granular superconductors. Some evidence for this can be found in the literature. Negative magnetoresistance and a diamagnetic signal at temperatures above the resistance onset have been reported in Ba-K-Bi-O ceramic.[21] Double-peak-like behavior has been observed in Bi-Pb-Sr-Ca-Cu-O films under certain treatment conditions.[22] The anomalous increase of low-temperature resistance reported for Ba-K-Bi-O samples[23] under pressure and high measuring currents can be understood in the same framework.

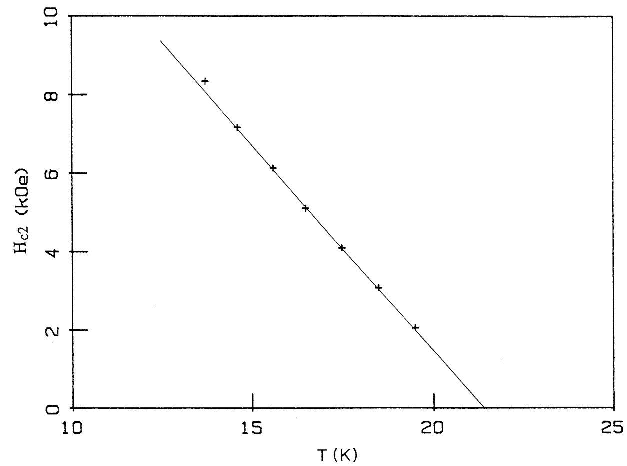

FIG. 12. Upper critical field H_{c2} in direction parallel to the c axis of $Sm_{1.85}Ce_{0.15}CuO_{3.98}$ as a function of temperature.

CONCLUSIONS

Unusual forms of nonmonotonic resistive transitions as a function of temperature and magnetic field have been observed in high-T_c superconducting ceramics of the electron-type family $L_{2-x}M_xCuO_{4-y}$. The behavior can be understood qualitatively in the framework of intra- and intergranular superconducting transitions, using the conventional terms of energy gap, Josephson and quasiparticle tunneling, etc. The systems studied are morphologically different from the low-T_c granular superconductors in the vicinity of metal-insulator threshold. The grains' large sizes and their tight packing minimize the charging effects and make the intragranular normal resistance comparable to the intergranular one. As a result the intragranular and intergranular transitions can be separated and identified, and the value of the intragranular upper critical field can be extracted.

Evidence has been found for the existence of superconducting phase in individual grains at higher temperatures than the resistance onset one. We speculate that under optimum treatment the critical temperatures of the electron-type family can be increased significantly.

The granularity effects described here are believed not to be restricted to electron-type ceramics, but can manifest themselves in other polycrystalline superconductors.

ACKNOWLEDGMENTS

We are grateful to J. Markert, T. Early, and M. B. Maple for providing the samples, and to Th. Fournier for the electron microscopy work. We acknowledge fruitful discussions with B. Barbara, D. Pavuna, and S. Pinol, and thank J. C. Jenna, P. Lethuillier, and A. Draperi for their technical support.

[1]G. Deutscher and K. A. Müller, Phys. Rev. Lett. **59**, 1745 (1987).
[2]P. Chaudhari, J. Mannhart, D. Dimas, C. C. Tsuei, C. C. Chi, M. M. Oprysko, and M. Scheuermann, Phys. Rev. Lett. **60**, 1653 (1988).
[3]B. G. Orr, H. M. Jaeger, A. M. Goldman, and C. G. Kuper, Phys. Rev. Lett. **56**, 378 (1986).
[4]B. G. Orr, H. M. Jaeger, and A. M. Goldman, Phys. Rev. B **32**, 7586 (1985); H. M. Jaeger, D. B. Haviland, A. M. Goldman, and B. G. Orr, Phys. Rev. B **34**, 4920 (1986).
[5]S. Kobayashi, Physica B **152**, 223 (1988).
[6]B. I. Belevtsev, Yu. F. Komnik, and A. V. Fomin, Fiz. Nizk. Temp. **11**, 1143 (1985) [Sov. J. Low Temp. Phys. **11**, 629 (1985)].

[7]M. Kunchur, Y. Z. Zhang, P. Lindenfeld, W. L. McLean, and J. S. Brooks, Phys. Rev. B **36**, 4062 (1987).
[8]D. B. Haviland, Y. Liu, and A. M. Goldman, Phys. Rev. Lett. **62**, 2180 (1989).
[9]T. Wang, K. M. Beauchamp, D. D. Berkeley, J. X. Liu, B. R. Johnson, and A. M. Goldman, Physica B **165&166**, 1463 (1990).
[10]A. F. Hebard, R. H. Eick, T. Siegrist, and E. Coleman (unpublished).
[11]Y. Tokura, H. Takagi, and S. Uchida, Nature **337**, 345 (1989).
[12]H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989).
[13]N. Y. Ayoub, J. T. Markert, E. A. Early, C. L. Seaman, L. M. Paulius, and M. B. Maple, Physica C **165**, 469 (1990).
[14]Y. Shapira and G. Deutscher, Phys. Rev. B **27**, 4463 (1983).
[15]S. Kobayashi, Y. Tada, and W. Sasaki, Physica **107B**, 129 (1981).
[16]A. Gerber, J. Beille, T. Grenet, and M. Cyrot, Europhys. Lett. **12**, 441 (1990).
[17]A. Gerber, T. Grenet, M. Cryot, and J. Beille, Phys. Rev. Lett. **65**, 3201 (1990).
[18]G. H. Hwang, T. H. Her, and H. C. Ku, Chin. J. Phys. **28**, 453 (1990).
[19]Y. Hidaka and M. Suzuki, Nature **338**, 635 (1989).
[20]Y. Dalichaouch, B. W. Lee, C. L. Seaman, J. T. Markert, and M. B. Maple, Phys. Rev. Lett. **64**, 599 (1990).
[21]C. Chaillout, C. Berger, F. Cyrot-Lackmann, C. Escribe-Filippini, G. Fourcaudot, G. Deutscher, J. Beille, M. Cyrot, H. Dupendant, M. Godinho, and J. L. Tholence, Physica C **162-164**, 935 (1989).
[22]H. Nakano, S. Nicoud, M. Suzuki, G. Burri, and L. Rinderer, J. Less-Common Met. **164-165**, 679 (1990).
[23]Z. J. Huang, C. Y. Huang, P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Y. Y. Xue, C. W. Chu, B. Dabrowski, and D. G. Hinks, Int. J. Mod. Phys. B **3**, 935 (1989).

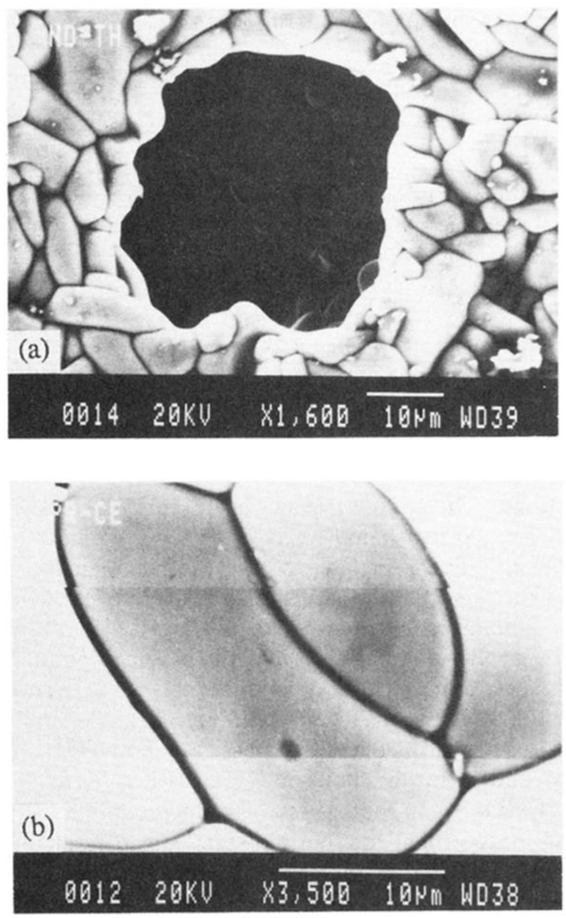

FIG. 1. SEM micrographs of (a) Nd-Th-Cu-O and (b) Pr-Ce-Cu-O samples. The grains are large and tightly packed.