Transport studies of $La_{2-x}Sr_xCuO_4$ near the insulator-metal-superconductor transition

B. Ellman, H. M. Jaeger, D. P. Katz, and T. F. Rosenbaum
The James Franck Institute and Department of Physics, The University of Chicago, Chicago, Illinois 60637

A. S. Cooper and G. P. Espinosa
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 27 October 1988)

We have measured the temperature-dependent resistivities of a series of samples of $La_{2-x}Sr_xCuO_4$ with $0.02 \leq x \leq 0.1$ over the temperature range $0.05 \leq T \leq 300$ K. We find the onset of superconductivity as x is increased to be correlated with a substantial drop in the magnitude of the normal-state resistivity. We observe no change, however, in the qualitative shape of the resistivity as the superconducting threshold is crossed. We also find that the low-temperature ($T \leq 8.0$ K) resistivities of the least concentrated samples can be described by variable range hopping, with a crossover between Coulomb gap and single-particle behavior occurring as x is increased.

Since the discovery of high-temperature superconductivity in the La-Ba-Cu-O system,[1] there has been intense interest in the properties of these layered perovskites. Several classes of such materials have been found and superconducting transition temperatures of up to 125 K have been reported.[2] Most of the work on these materials, however, has focused on samples with dopant and oxygen concentrations near that required for an optimal superconducting transition temperature with comparatively little work being done on samples at the crossover to the nonsuperconducting regime. Such studies are of fundamental interest, though, both to increase our understanding of the approach to and the nature of the superconducting state, and also to provide basic information on the normal-state properties of these systems.

In order to address these issues, we have carried out transport measurements on $La_{2-x}Sr_xCuO_4$ for values of Sr concentration x in the vicinity of the insulator-metal-superconductor transition. $La_{2-x}Sr_xCuO_4$ was studied in considerable detail[3] even before it was first shown[4] to be a high-T_c superconductor, and it is now known to be perhaps the simplest such system, possessing only one low-dimensional structure in the form of a single Cu-O plane per unit cell. The material possesses orthorhombic symmetry at room temperature for $x \leq 0.10$, switching over to tetragonal for higher concentrations.[5] $La_{2-x}Sr_xCuO_{4-\delta}$ is a superconductor in the $x=0$ limit under certain conditions (probably related to the concentration of oxygen deficiencies δ)[6] as well as in the strontium concentration window[7] $0.05 \lesssim x \lesssim 0.30$. The highest transition temperatures are obtained[8] for $x \approx 0.15$. We present here resistivity measurements on a series of samples with $0.02 \leq x \leq 0.10$, a range allowing the investigation of the normal, superconducting, and low-temperature insulating regimes of this system. We find the onset of superconductivity as x is varied to be correlated with a large change in the magnitude of the normal-state resistivity.

The samples used were sintered ceramic pellets prepared using standard techniques[5] with a final thermal history consisting of cooling from 1060 to 550 °C in pure O_2 and then annealing in O_2 at 550 °C overnight. The material was stored in dry nitrogen, with no other measures taken to alter or control oxygen concentration. X-ray crystallographic data[9] show single-phase orthorhombic material with no sign of the more concentrated tetragonal structure.[5] The x-ray results, along with the fact that semiquantitative electron-microprobe measurements[10] conducted on two of the samples ($x=0.05$ and 0.055) find no spatial variations in Sr density at the 500-ppm level, make it unlikely that a small volume fraction of more concentrated material is acting as a superconducting short in the $x > 0.05$ samples. Multiple measurements on a given sample indicated little or no degradation due to repeated temperature cycling. Resistance measurements were made on roughly bar-shaped samples of cross-sectional area 0.05 cm^2 using a four-probe ac technique at 17 Hz. Electrical contacts were made using silver paint, either on the surface of the sample (which was scraped to remove any surface layer) or in grooves cut into it. The absolute accuracy of our resistivities is largely determined by uncertainties in the geometry of these painted contacts and by variations in the densities of the sintered samples, and is estimated to be better than 30%. Data on very low concentration ($x < 0.02$) samples are not presented as resistivity measurements indicated the existence of regions of superconducting La_2CuO_4. For low-temperature (≤ 2 K) measurements, the samples were either top-loaded into or mounted on the mixing chamber of a helium dilution refrigerator. Special care was taken on all low-T data to verify that the contacts had linear I-V characteristics and to avoid Ohmic heating due to the measuring current.

The resistivities so obtained for $x=0.02$, 0.05 and $x=0.055$, 0.065, 0.075, and 0.10 are shown in Figs. 1 and 2, respectively. Qualitatively, the general shape of $\rho(T)$ for $x \leq 0.05$ and above T_c for $x \geq 0.055$ is independent of x in that it displays two types of behavior: an essentially linear drop in ρ for $T > T_{min} \approx 100$ K, followed by a steep rise in ρ at lower temperatures. This generic shape is similar to that seen by other groups,[11] with the linear high-T behavior seemingly a ubiquitous property of high-

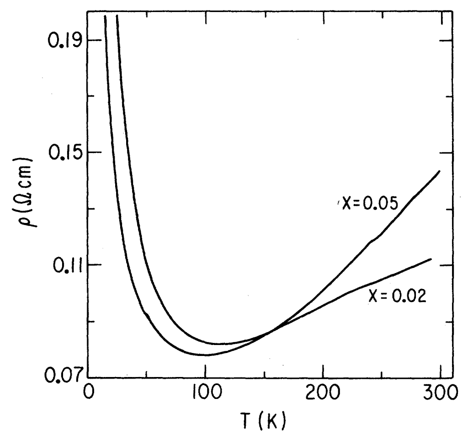

FIG. 1. Resistivity of $La_{2-x}Sr_xCuO_4$ for $x=0.02$ and 0.05 as a function of temperature.

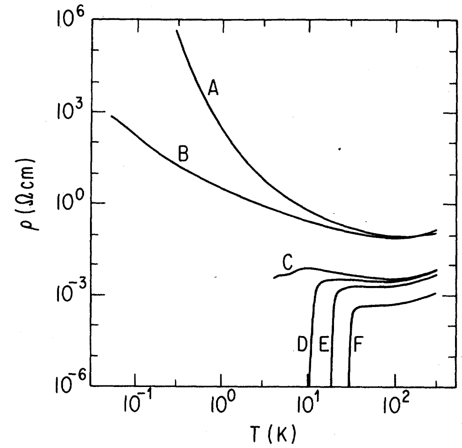

FIG. 3. Resistivity of $La_{2-x}Sr_xCuO_4$ for all measured concentrations. Curves A, B, C, D, E, and F are the data from the $x=0.02$, 0.05, 0.055, 0.065, 0.075, and 0.10 samples, respectively. Superconductivity in the $x \gtrsim 0.055$ samples coincides with a drop in normal-state resistivity (see also Fig. 4).

T_c superconductors.[12,13] The superconducting transitions are moderately sharp with widths (10%–90%) of 4.4, 7.4, and 6.0 K, respectively, for the $x=0.065$, 0.075, and 0.10 samples, and show no signs of steps in $\rho(T)$ that would indicate gross inhomogeneities. This, combined with the x-ray characterization, implies that random inclusions of more concentrated material with higher transition temperatures are absent. Therefore, it is particularly notable that even the superconducting samples display both of the regimes in resistivity: metallic at high temperatures, they apparently behave as insulators just above their T_c's as shown by obvious minima in $\rho(T)$ for $x=0.055$ and 0.065 and a shallow minimum for $x=0.075$. The single exception is the $x=0.10$ sample, whose resistivity flattens off, but never rises as T is lowered. One interpretation, which is attractive in view of the behavior of the other samples, is that the flattening off is indicative of the onset of the insulating regime but that the upturn for $x=0.10$ at low T is cut off by a superconducting transition. Thus, a linear metallic resistivity at high T, resistive behavior for lower T, and superconductivity all seem intrinsic to these polycrystalline materials, with all three coexisting for $x \gtrsim 0.055$.

A striking feature of our data when viewed as a function of strontium concentration is that, as x is increased above 0.05, the onset of superconductivity coincides with a strong drop in the normal-state resistivity (Fig. 3). We have verified the existence of this feature using a number of sample from separate production runs with Sr concentrations o both sides of $x_c=0.055$. In Fig. 4 we show $\rho(300\ \mathrm{K})$ as a function of x. While $\rho(300\ \mathrm{K})$ changes by a factor of order 2 between $x=0.01$ and 0.05, it drops by a factor of 23 as x is increased 10% in crossing x_c.

In Fig. 5 we plot the positions $T_{\min}$ of the resistivity minimas and the slopes of fits to the linear regions of ρ scaled by $\rho(300\ \mathrm{K})$. The slopes have been so scaled in order to remove their trivial dependence on the global change in $\rho(T)$ at x_c. No obvious qualitative change is

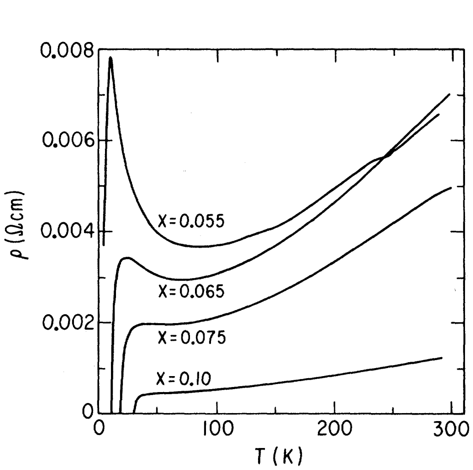

FIG. 2. Resistivity of $La_{2-x}Sr_xCuO_4$ for $x=0.055$, 0.065, 0.075, and 0.10 as a function of temperature.

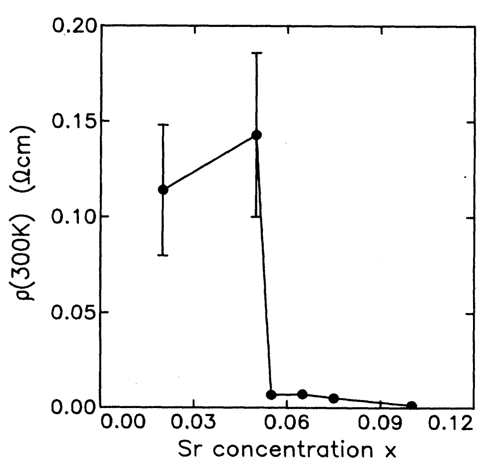

FIG. 4. Room-temperature resistivity $\rho(300\ \mathrm{K})$ as a function of Sr concentration. The resistivity drops by a factor of 23 when x exceeds 0.05.

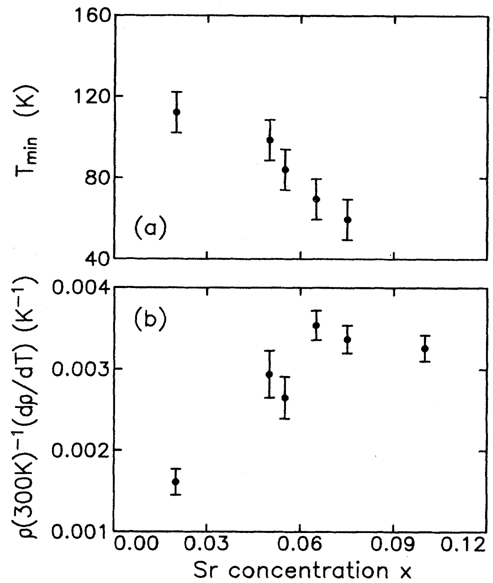

FIG. 5. (a) Temperature T_{min} at which $\rho(T)$ has its minimum in the normal state. (b) Slope of the high-temperature resistivity scaled by $\rho(300\text{ K})$. Neither quantity exhibits changes correlated with the resistivity drop in Fig. 4.

seen in either plot as x crosses x_c. This suggests that the mechanisms which account for the normal-state resistivity for $x > x_c$ and for $x < x_c$ are *qualitatively* the same. In the superconducting samples, however, the overall magnitude of ρ is sharply reduced.

The sharp rise in $\rho(T)$ may be followed to $T \ll 1$ K in the nonsuperconducting samples. At sufficiently low temperatures ($T \leq 8$ K for $x = 0.02$ and $T \leq 2.5$ K for $x = 0.05$), both concentrations display a stretched exponential form

$$\rho(T) = \rho_0 \exp(T_0/T)^{\beta} . \tag{1}$$

A best fit of the $x = 0.02$ data gives $\beta = \frac{1}{2}$ and $T_0 = 74$ K (Fig. 6), while the $x = 0.05$ sample gives $\beta = \frac{1}{4}$ with $T_0 = 645$ K (Fig. 7). An exponent $\beta = \frac{1}{4}$ is indicative of Mott variable range hopping (VRH) in three dimensions.[14] If, in the presence of interactions between carriers, screening is sufficiently weak, then the VRH result is modified to $\beta = \frac{1}{2}$ in two as well as three dimensions.[15] Both forms have been proposed for the description of $\rho(T)$ in strongly disordered metals[16] and in semiconductors.[14,15] In general, a crossover from $\beta = \frac{1}{2}$ to $\beta = \frac{1}{4}$ with increasing carrier densities is believed to take place.[17] In $La_{2-x}Sr_xCuO_4$ the carriers are holes contributed by the Sr, and we interpret the change in β as an indication that at $x = 0.05$ the hole concentration has increased sufficiently to provide screening even to the lowest temperatures measured (0.05 K).[18]

We may use our value of T_0 for $x = 0.05$ to estimate the localization length α^{-1} in the screened regime. α^{-1} is given by the approximate VRH relation[14,19]

$$\alpha^{-1} \approx [k_B T_0 N(E_F)/16]^{-1/3} , \tag{2}$$

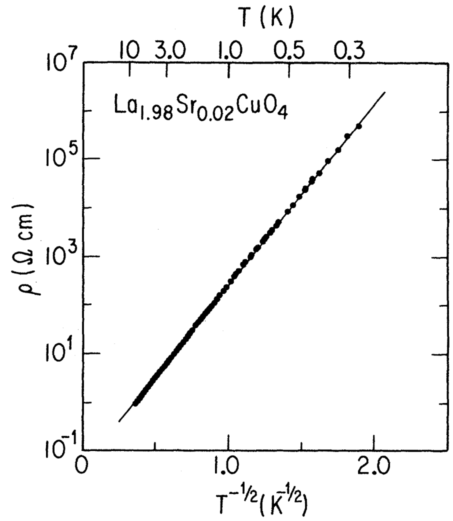

FIG. 6. Logarithm of low-temperature resistivity of the $x = 0.02$ sample as a function of $T^{1/2}$ indicating variable-range-hopping conduction in the presence of carrier interactions.

where the density of states, $N(E_F)$, with dimensions of states/eV cell, has been measured to be in the range[20] 2–13. Using $T_0 = 645$ K, we find $16 \leq \alpha^{-1} \leq 30$ Å, which equals from 4 to 8 in-plane or 1 to 2.5 out-of-plane lattice spacings. This large localization length may imply that the system is near a metal-insulator transition, a conclusion also reached by Uher and Kaiser[21] in a somewhat different context. We may also try to estimate α^{-1} for the $x = 0.02$ sample using an expression from theories of the Coulomb gap[15]

$$\alpha^{-1} \approx \frac{e^2}{k_B T_0 \kappa} \approx \frac{2200}{\kappa}\text{ Å} , \tag{3}$$

where κ is the dc dielectric constant of the material and

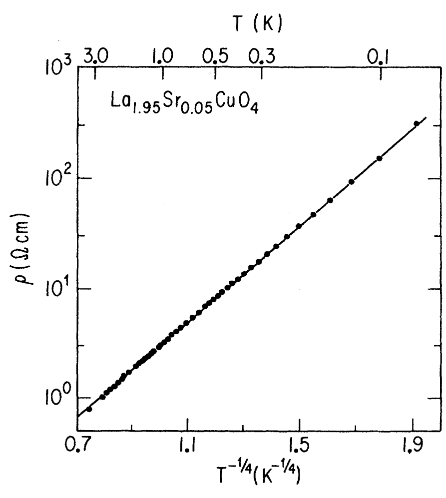

FIG. 7. Logarithm of low-temperature resistivity of the $x = 0.05$ sample as a function of $T^{1/4}$, indicating variable range hopping in the case of sufficiently screened carrier interactions.

$T_0=74$ K is determined from the data of Fig. 6. Thus, if the localization lengths of the $x=0.02$ and 0.05 samples are of the same order of magnitude, κ for the latter must be large (≈ 100).[22]

Our results may be contrasted with those of Osquiguil *et al.*,[23] who measured $\rho(T)$ for $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ as a function of oxygen deficiency δ. They found that all of their samples obeyed Eq. (1) with $\beta=\frac{1}{4}$, even though the normal-state behavior varied from largely metallic (like our $x=0.10$ sample) to highly insulating, with no crossover to $\beta=\frac{1}{2}$ evident. One possible explanation is that all of their deoxygenated samples have enough carriers to be in the screened regime. Osquiguil *et al.* also find that the slope of $\rho(T)$ at high T is invariant under changes in δ, while we find it to be a strong function of x for the lower concentrations [see Figs. 1 and 5(b)], a feature also noted by other workers.[13,24] Following the analysis of Fiory *et al.*,[12] who treat the linear part of ρ within a diffusive conduction model, we can write

$$\rho(T)=C_1+C_2\langle v_F^2\rangle^{-1}T\,, \qquad (4)$$

where v_F is the Fermi velocity and C_1 and C_2 are temperature independent. Thus, within this simple model, the fact that the slope of ρ changes with x but not with δ implies that the valence-band curvature, and therefore v_F, also change with x but not with δ. In any case, the model-independent implication of the differences between our work and that of Osquiguil *et al.* is that varying hole concentration by changing x is not the same as doing so by varying δ.

Our observation of three-dimensional VRH is somewhat surprising in view of the essentially two-dimensional nature of these materials. Some insight may be gained, however, from in-plane ρ_{ab} and out-of-plane ρ_c resistivity measurements by Cheong *et al.*[11] on single crystals of semiconducting La_2CuO_4. They find that while the anisotropy ρ_c/ρ_{ab} may be as large as 1000 for $T\approx 70$ K, it falls sharply as T is reduced further. If this trend continues to the low temperatures used here, our low-T data may reflect three-dimensional behavior in the sense that out-of-plane conduction is comparable to in-plane hopping. Careful low-temperature studies of high-quality single crystals of $La_{2-x}Sr_xCuO_4$ with $x\neq 0$ are necessary to test this explanation.

The data for $x<0.05$ (Fig. 2) are consistent with an insulator-to-superconductor transition at low temperature. Due to the polycrystalline nature of our samples, we cannot distinguish between in-plane and out-of-plane contributions to the resistivity. However, if ρ_{ab} is metallic for the superconducting concentrations,[25] then our results imply that ρ_c exhibits an insulator-to-superconducting transition as a function of temperature.

Our finding that superconductivity first appears at a Sr concentration $x_c=0.055$ is consistent with phase diagrams obtained from specific-heat[26] and magnetic-susceptibility studies.[27] Our data, however, suggest that the appearance of superconductivity in the transport properties of $La_{2-x}Sr_xCuO_4$ is primarily correlated with a value of the normal-state resistivity. This is supported by the fact that, qualitatively, the shape of $\rho(T)$ above T_c does not change as x crosses x_c. Within this picture, the suppression of superconductivity is driven by an increase in normal-state resistivity, leading to a vanishing of T_c as $\rho(300\text{ K})$ approaches 0.007 Ω cm. If indeed the resistivity ρ is the control variable, then for x close to x_c superconductivity could be induced by changing ρ at fixed x. An investigation of this possibility is currently underway.

We thank J. Pluth and I. Steele for invaluable technical assistance. We have benefited from illuminating conversations with J. Kim, K. Levin, and G. Zimanyi. The work at the University of Chicago was supported by National Science Foundation Grant No. DMR 85-17478. One of us (H.M.J) acknowledges support from the Materials Research Laboratory at the University of Chicago under Grant No. DMR 85-19460.

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2]S. S. P. Parkin, V. Y. Lee, E. M. Engler, A. I. Nazzal, T. C. Huang, G. Gorman, R. Savoy, and R. Beyers, Phys. Rev. Lett. **60**, 2539 (1988).
[3]N. Nguyen, F. Studer, and B. Raveau, J. Phys. Chem. Solids **44**, 389 (1983); K. K. Singh, P. Ganguly, and J. B. Goodenough, J. Solid State Chem. **52**, 254 (1984).
[4]R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).
[5]R. M. Fleming, B. Batlogg, R. J. Cava, and E. A. Rietman, Phys. Rev. B **35**, 7191 (1987).
[6]P. M. Grant, S. S. P. Parkin, V. Y. Lee, E. M. Engler, M. L. Ramirez, J. E. Vazquez, G. Lim, R. D. Jacowitz, and R. L. Greene, Phys. Rev. Lett. **58**, 2482 (1987); S. A. Shaheen, N. Jisrawi, Y. H. Min, H. Zhen, L. Rebelsky, M. Croft, W. L. McLean, and S. Horn, in *Novel Superconductivity*, edited by Stuart A. Wolf and Vladamir Z. Kresin (Plenum, New York, 1987).
[7]J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Parkin, Phys. Rev. Lett. **61**, 1127 (1988).
[8]R. B. van Dover, R. J. Cava, B. Batlogg, and E. A. Rietman, Phys. Rev. B **35**, 5227 (1987).
[9]J. Pluth (private communication).
[10]I. Steele (private communication).
[11]S. W. Cheong, Z. Fisk, R. S. Kwok, J. P. Remeika, J. D. Thompson, and G. Gruner, Phys. Rev. B **37**, 5916 (1987).
[12]A. T. Fiory, M. Gurvitch, R. J. Cava, and G. P. Espinosa, Phys. Rev. B **36**, 7262 (1987).
[13]J. M. Tarascon, L. H. Greene, B. G. Bagely, W. R. McKinnon, P. Barboux, and G. W. Hull, in *Novel Superconductivity*, edited by Stuart A. Wolf and Vladamir Z. Kresin (Plenum, New York, 1987).
[14]N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed. (Oxford Univ. Press, London, 1979); N. F. Mott, Philos. Mag. **19**, 635 (1969).
[15]A. L. Efros and B. I. Shklovskii, J. Phys. C **8**, L49 (1975); B. I. Shklovskii and A. L. Efros, Zh. Eksp. Teor. Fiz. **81**, 406 (1981) [Sov. Phys. JETP **54**, 218 (1981)].
[16]T. Chui, G. Deutscher, P. Lindenfield, and W. L. McLean, Phys. Rev. B **23**, 6172 (1981); P. Sheng, B. Abeles, and Y. Arie, Phys. Rev. Lett. **31**, 44 (1973).
[17]A. M. Glukhov, N. Ya. Fogel, and A. A. Shablo, Fiz. Tverd,

Tela (Leningrad) **28**, 1043 (1986) [Sov. Phys. Solid State **28**, 583 (1986)]; W. N Shafarman and T. G. Castner, Phys. Rev. B **33**, 3570 (1986); S. L. Weng, S. Moehlecke, M. Strongin, and A. Zangwill, Phys. Rev. Lett. **50**, 1795 (1983).

[18]This is in contradiction to work indicating variable-range-hopping behavior at high temperatures with a T_0 three orders of magnitude greater than ours. See R. J. Birgeneau, C. Y. Chen, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, T. Thio, T. R. Thurston, and H. L. Tuller, Phys. Rev. Lett. **59**, 1329 (1987).

[19]V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. B. **4**, 2612 (1972).

[20]R. L. Greene, H. Maletta, T. S. Plaskett, J. G. Bednorz, and K. A. Müller, Solid State Commun. **63**, 379 (1987); Shin-ichi Uchida, Hidenori Takagi, Kohji Kishio, Koichi Kitazawa, Kazuo Fueki, and Shoji Tanaka, Jpn. J. Appl. Phys. **26**, L443 (1987).

[21]C. Uher and A. B. Kaiser, Phys. Rev. B **37**, 127 (1988).

[22]Extrapolations of far-infrared reflectivity measurements to the dc limit in single crystals of La_2CuO_4 grown in lead flux do indeed indicate a κ of order 50 to 100 [G. A. Thomas (private communication)].

[23]E. J. Osquiguil, L. Civale, R. Decca, and F. de la Cruz, Phys. Rev. B **38**, 2840 (1988); E. J. Osquiguil, R. Decca, G. Nieva, L. Civale, and F. de la Cruz, Solid State Commun. **65**, 491 (1988).

[24]Minoru Suzuki (unpublished).

[25]P. W. Anderson and Z. Zou, Phys. Rev. Lett. **60**, 132 (1988).

[26]M. Kato, Y. Maeno, and T. Fujita, Physica C **152**, 116 (1988); R. A. Fisher, J. E. Gordon, and N. E. Phillips (unpublished).

[27]L. F. Schneemeyer, J. V. Waszczak, E. A. Rietman, and R. J. Cava, Phys. Rev. B **35**, 8421 (1987).