PHYSICAL REVIEW B VOLUME 47, NUMBER 13 1 APRIL 1993-I

Anisotropic transport properties of single-crystal $La_{2-x}Sr_xCuO_4$: Evidence for the dimensional crossover

Y. Nakamura* and S. Uchida
Superconductivity Research Course, The University of Tokyo, Yayoi 2-11-16, Bunkyo-ku, Tokyo 113, Japan
(Received 29 December 1992)

The anisotropic normal-state transport properties, resistivity and thermopower, are investigated for high-quality single crystals of $La_{2-x}Sr_xCuO_4$ in the compositional range $0.10 \leq x \leq 0.30$. The results indicate that charge transport in the material with superconducting compositions is two-dimensional. A crossover from two to three dimensions is observed at high temperature or on entering the nonsuperconducting overdoped region.

Besides unprecedentedly high T_c the most surprising fact about the copper oxide superconductors[1] was probably the metallic temperature dependence of the normal-state resistivity of doped La_2CuO_4. Previously, none of the oxides with layered structures had shown a truly metallic behavior at all temperatures. Subsequent progress in single-crystal study has established that the in-plane resistivity (ρ_{ab}) is proportional to temperature for optimally doped cuprates[2] whereas the resistivity between CuO_2 planes (ρ_c) is nonmetallic in many cases.[3] However, the understanding of charge transport processes in the CuO_2 plane as well as that between the planes is still far from complete. This is partly because most experimental studies have so far been conducted on the optimally doped, maximum-T_c materials. Here we show how the normal-state resistivities, both ρ_{ab} and ρ_c, and thermoelectric power, S_{ab} and S_c, evolve with dopant concentration. At present this type of study is possible only on the $La_{2-x}Sr_xCuO_4$ system where large high-quality single crystals are now available over a wide compositional range and ambiguity does not arise from structural complexity, as it does because of the CuO chains in the $YBa_2Cu_3O_{6+x}$ system. The present results address a basic question concerning charge transport processes in the high-T_c cuprates which has not been clearly answered yet: What can we say about the dimensionality of the electronic state and the conduction process between the planes from the variation of the anisotropy with x and T?

Single crystals of $La_{2-x}Sr_xCuO_4$ were grown by the traveling-solvent-floating-zone (TSFZ) method.[4] This method for growing single crystals of compounds which show incongruent melt has some advantages over the conventional flux method with use of a crucible. The first advantage is that there is no impurity contamination from the crucible material because the melting zone is supported only by its surface tension in the TSFZ method. In the case of flux-grown $La_{2-x}Sr_xCuO_4$, Pt contamination from the crucible severely degrades the superconducting properties and it is highly probable that the normal-state transport properties are affected as well. Another advantage is in the steady-state process of the crystal growth in the TSFZ method. Unlike the flux method in which the composition of the liquid phase gradually changes as the crystals grow, we can keep the La-Sr-Cu ratio in the melting zone at a fixed point on the ternary phase diagram through the whole growth process.

We first prepared a polycrystalling rod. Powders of La_2O_3 (dehydrated at 1000 °C for 10 h), $SrCO_3$, and CuO with purities higher than 99.9% were mixed in the nominal ratios, well ground, and then sintered at 950 °C for 10 h in an alumina crucible. After regrinding the powder we isostatically pressed it into a rod shape ($\sim$5 mm$\phi \times$80 mm) and sintered it again at 1200 °C for 20 h to get a high-density rod. Solvent material was also prepared in the same way except that the final sintering temperature was lower ($\sim$950 °C). In the TSFZ method the solvent composition is a key factor to control the composition of the single crystal obtained. We determined it from the ternary phase diagram, which has been reported previously.[5] Decreasing Cu concentration in the solvent as the target Sr content x increases is the most important factor to control x in a wide range up to 0.30. We used a single crystal of La_2CuO_4 grown by the conventional flux method as a seed, which had a typical cross section of 4×4 mm^2 perpendicular to the [100] direction.

Single-crystal growth was done using an infrared furnace with two halogen lamps and double ellipsoidal mirrors (a Nichiden machine S-15HD). An appropriate quantity ($\sim$600 mg) of solvent was sandwiched between the polycrystalline rod and the seed crystal and melted to form a liquid zone. During the growth the rod and the seed, rotating opposite each other to stir the liquid zone, were slowly fed down at the speed of 1.0 mm/h and a single crystal was grown epitaxially on the seed. We kept the atmosphere of 3 atm O_2 as in the previous work, which was also effective to reduce oxygen vacancies especially in the highly Sr-doped crystals. Indeed further oxygen annealing showed no improvement of transport properties of those crystals. The typical single-domain crystal was column-shaped along the a axis with the size of 5 mm$\phi \times$20 mm and thus allowed for reliable and easy measurements of the c-axis properties.

In this work, we investigated charge transport in $La_{2-x}Sr_xCuO_4$ single crystals with $x = 0.10$, 0.12, 0.15, 0.20, and 0.30, covering both superconducting and nonsuperconducting metallic regions. Sr content x was checked by the electron-probe microscope analysis and no inhomogeneity was observed either along the radial or the axial direction within our precision of analysis ($\Delta x \sim 0.01$). dc magnetization measurement of the shielding effect under a magnetic field of 10 Oe parallel to

the c axis showed almost perfect diamagnetism for superconducting samples ($0.10 \leq x \leq 0.20$) and no appreciable signals of superconductivity for $x = 0.30$ (Fig. 1). Evidence for the high quality of the present crystals is given by a sharp superconducting transition of width less than 2 K and by the fact that the x dependence of T_c coincides exactly with that established for the best-characterized ceramic samples.[6]

For the transport measurements we cut the column-shaped ingot into two parallelepiped samples with a diamond blade. We prepared two samples for each x, which had nearly the same dimensions ($\sim 1 \times 1 \times 4\text{mm}^3$) but had different orientations of crystal axis: one had the longest dimension parallel to the c axis and the other had the one perpendicular to that. Highly anisotropic transport properties of these cuprates were reliably and reproducibly measured. Resistivity was measured by the standard four-probe method in the temperature range 4.2–800 K. Dots of gold paste were fired as electrodes on the samples at 900 °C in oxygen. In the high-temperature measurement above room temperature Au lead wires were wound around the sample tightly and bonded with heat-treated Au paste.

To monitor the temperature gradient (typically 0.3 K) in the measurement of thermoelectric power, Chromel-Constantan differential thermocouples were attached. The thermoelectric power was measured across two additional copper leads. The contribution of the copper wires was determined by smooth interpolation between the low-temperature data obtained by measuring the thermoelectric power of polycrystalline $YBa_2Cu_3O_7$ below T_c and the previously reported high-temperature data. Subtracting this contribution from the raw data, we got the absolute thermoelectric power of the sample.

The in-plane resistivity shown in Fig. 2(a) rapidly decreases with increasing x, which is in accord with an evolution of a Drude term in the optical conductivity spectrum[5] as well as the x dependence of the Hall coefficient.[6] These experimental results demonstrate a rapid development of itinerant states as the dopant concentration increases. Note that the resistivities at the optimal composition ($x = 0.15$), $\rho_{ab} = 400\ \mu\Omega$ cm at 300 K, are larger by a factor of 2 than those for fully oxygenated $YBa_2Cu_3O_{6+x}$.[2,3] This factor coincides with the ratio of the carrier density between the two systems, as estimated

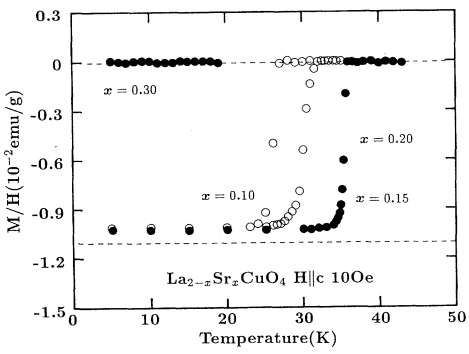

FIG. 1. Temperature dependence of the shielding signal (zero-field cooling) for magnetic field ($H = 10$ Oe) applied parallel to the c axis.

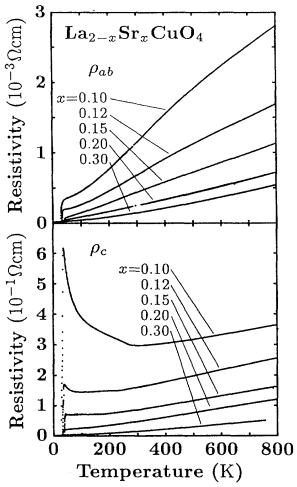

FIG. 2. Temperature dependence of the in-plane (upper panel) and out-of-plane (lower panel) resistivity for single crystals with various compositions in the metallic phase.

from the Drude weight in the optical spectrum[5,7] and from the zero-temperature values of the magnetic penetration depth, which is a measure of the carrier density condensed in the superconducting state.[8] This fact is suggestive of the existence of a common scattering time in all the high-T_c cuprates.

One should note the T-linear resistivity over a wide temperature range is observed only in a narrow compositional range near $x = 0.15$ in agreement with the result by Takagi *et al.*[9] on epitaxial films. ρ_{ab} for the overdoped material ($x = 0.30$) shows a superlinear temperature dependence, $\rho_{ab} \sim T^{\alpha}$ with $\alpha > 1$ as would be expected for Fermi-liquid-type behavior. On the other hand, underdoped materials ($x = 0.10$ and $x = 0.12$) exhibit a complicated temperature dependence. The resistivity shows an inflexion at 300–400 K. Since the measurements were done under constant pressure, there might be an appreciable correction to the resistivity under constant volume, which is the quantity of theoretical interest. The correction estimated from the pressure dependence of the resistivity of the same crystals,[10] however, become appreciable only at temperatures higher than 800 K.

A similar T-dependent resistivity is observed in $YBa_2Cu_3O_{6+x}$ with various oxygen content.[11] Particularly the temperature dependence for an underdoped material, 60-K Y-Ba-Cu-O with $x = 0.65$–0.80, is basically the same as that observed here for $x = 0.10$ and $x = 0.12$. The normal-state resistivity of 60-K Y-Ba-Cu-O is proportional to T in the high-temperature region but deviates downward from the T linearity below about 150 K. This temperature incidentally coincides with that below which a gap presumably opens in the spin excitation spectrum as suggested by NMR (Ref. 12) and neutron-scattering studies.[13,14] It is tempting to speculate that the resistivity is determined by scattering of charge carriers due to spin fluctuations which would be suppressed when a "spin gap" opens, leading to a reduction of resistivity. It is, however, an open question whether a spin gap exists in the $La_{2-x}Sr_xCuO_4$ systems. A recent neutron study has given no indication of a gap in the normal

state for incommensurate spin fluctuations.[14]

Temperature dependence of the c-axis resistivity (ρ_c) is shown in Fig. 2(b) for the same compositions as in Fig. 2(a). The values of ρ_c are by two orders of magnitude larger than those of ρ_{ab} for every x and decrease with increasing x as in the case of ρ_{ab}. Since the results, both magnitude and T dependence, were reproducible among several samples cut from the same ingot, the decrease of ρ_c with x is a genuine effect, not an artifact arising from misorientation of the sample. Actually, this has been confirmed to be a general trend that all the known high-T_c cuprates show.[3]

In the case of $La_{2-x}Sr_xCuO_4$, the Sr substitution introduces a disorder in the LaO layers which intervene between CuO_2 planes, contrary to the case of $YBa_2Cu_3O_{6+x}$ where the increase in hole density reduces the disorder in the intervening CuO-chain layers. Moreover, the increase in the distance between adjacent CuO_2 planes with x would be unfavorable for electron transfer between the planes in the band picture. Hence, in an ordinary sense, the effect of Sr substitution would operate to reduce the c-axis conductivity. Thus, the decrease of ρ_c with x, inherent to the high-T_c cuprates, signals a remarkable change in the overall electronic structure as doping proceeds.

As regards the T dependence, ρ_c for $x<0.15$ is characterized by a kink which is seen at temperature T_0 in coincidence with the high-temperature tetragonal (HTT) to low-temperature orthorhombic (LTO) structural phase transition.[16] T_c rapidly decreases with x and the LTO phase is completely suppressed when $x>0.20$. The fact that superconductivity is observed only in the orthorhombic phase in an important issue to be pursued.[9] As most evident for $x=0.10$, the T dependence of ρ_c changes at T_0, metallic at $T>T_0$ but nonmetallic at $T<T_0$. For the superconducting compositions there is a region where the conduction is metallic in the a and b directions whereas it is nonmetallic in the c direction, so that the material may be regarded as a two-dimensional metal in this region. Actually a recent c-axis-polarized optical study has shown that the c-axis conductivity is severely suppressed over a wide energy range up to ~ 1 eV.[17]

It has been suggested that nonmetallic ρ_c as well as non-T-linear ρ_{ab} may be linked to the presence of a spin gap in the underdoped region. In the resonating-valence-bond theory,[18] charge carriers along the c axis are electrons which are produced by the recombination of a holon with a spinon. If there were a gap for the spinon excitation, then the probability of spinon-holon recombination or scattering would be suppressed, leading to a reduction of the c-axis conductivity and an enhancement of the in-plane conductivity.

It is interesting to compare these data with band-structure calculations. The band-structure theory predicts an anisotropic three-dimensional metal for any x.[19] Assuming the same scattering process in all directions, the anisotropy in resistivity is estimated to be $\rho_c/\rho_{ab}\sim 28$ and not very dependent on x. In the actual material the anisotropy is larger even in the overdoped region and is much enhanced in the superconducting regime. This suggests that a certain mechanism is working to confine electrons in the CuO_2 plane and thus to make the electronic system two-dimensional.

In the case of the overdoped compound, ρ_c shows basically the same T dependence as ρ_{ab}. This is demonstrated in Fig. 3 where the anisotropic resistivity ratio ρ_c/ρ_{ab} is plotted as a function of T. The anisotropy of $x=0.30$ is almost constant (~ 100) over the whole temperature range, giving evidence for the same conduction mechanism in all directions and thus for a three-dimensional metal. This seems also the case with the superconducting compositions ($x\leq 0.20$) in the high-temperature region where ρ_c/ρ_{ab} is nearly T independent ($\rho_c/\rho_{ab}\sim 150$–200) and depends little on the composition x in contrast to the behavior in the low-temperature region. In this regard, Fig. 3 demonstrates a crossover from a three-dimensional metal to a two-dimensional one as temperature is lowered.

One should note that the change in the T dependence of ρ_c/ρ_{ab} does not take place abruptly at T_0 and even for $x=0.20$, where the HTT→LTO transition is not clearly defined, the crossover is seen at about 200 K. Basically the same temperature dependence of ρ_c/ρ_{ab} has been observed for superconducting $YBa_2Cu_3O_{6+x}$, including both 90-K and 60-K phases.[3] In this system the corresponding structural phase transition does not occur and ρ_c of the fully oxygenated compound is metallic at all temperatures in the sense that $d\rho_c/dT>0$. Nevertheless, $\rho_c(T)/\rho_{ab}(T)$ of 90-K Y-Ba-Cu-O follows a trajectory like that of $x=0.20$. A similar T dependence of ρ_c/ρ_{ab} is commonly observed for other known cuprates showing bulk superconductivity regardless of the presence or otherwise of structural phase transition. Hence the HTT→LTO structural change is not a primary driving force for the 3D→2D crossover. Perhaps the gradual change in the electronic structure or in the spin or charge fluctuations which readily couple to the rigid rotation of oxygen octahedra in La 2:1:4 would be more relevant to the crossover. Then one might conclude that the high-T_c superconductivity is realized when the electronic states tend to be two-dimensional or equivalently when the carriers tend to be confined within the CuO_2 plane as temperature is lowered.

Finally, we present another evidence for unconventional charge transport in the cuprates. The thermopower, which is related to the energy-current correlation, displays a different aspect of charge transport. The results, both a-b and c components, are shown in Fig. 4.

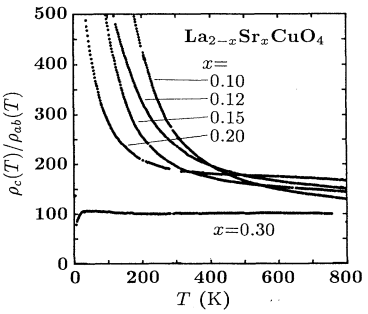

FIG. 3. Anisotropic resistivity ρ_c/ρ_{ab} plotted against temperature for various compositions.

The a-b component, S_{ab}, exhibits a broad maximum and then slowly decreases with increase of temperature for every x. S_{ab} in the superconducting phase is positive and rapidly decreases in magnitude as x increases. For an overdoped compound ($x=0.30$) the sign becomes negative above 250 K in agreement with the result of the Hall effect.[6]

In the present work it is found that the out-of-plane thermopower, S_c, is always positive and decreases with x as in the case of S_{ab}. However, the temperature dependence of S_c is quite different. S_c increases with temperature like that expected for ordinary metallic-diffusion thermopower. Similar temperature dependence of S_c, as well as that of S_{ab}, is commonly observed for all the known high-T_c cuprates, but the magnitude of S_c and S_{ab} in the present system is by almost an order larger than that in $YBa_2Cu_3O_7$ (Ref. 20) and Bi- or Tl-based cuprates.[21]

Both sign and T dependence of S_c for the optimal $x=0.15$ are consistent with the Bloch-Boltzmann result of Allen, Picket, and Krakauer,[22] but the calculated S_{ab} is negative in contradiction to the observation. Kaiser and Mountjoy[23] tried to overcome the discrepancy in S_{ab} by taking into account the T-dependent enhancement due to strong electron-photon coupling. Actually, they were successful in fitting both S_{ab} and S_c of $YBa_2Cu_3O_7$ and Tl- and Bi-based cuprates with smaller values of the order $0.1k_B/e$ or less. It is, however, far from clear whether the marked x dependences can be explained in their context.

Contrary to the metallic-diffusion theory, the gauge theory of Nagaosa and Lee[24] based on the uniform resonating-valence-bond (RVB) ground state predicts correct signs of S_{ab} and S_c as well as the T and x dependences, in overall agreement with the results shown here.[25] According to this theory the charge transport mechanisms are totally different between the two directions. The major contribution to S_{ab} comes from bosons (holons) while S_c is determined by the incoherent part of the electron quasiparticle which gives rise to a positive and T-linear thermopower.

In summary, we have presented an extensive set of data for single crystals of $La_{2-x}Sr_xCuO_4$ demonstrating a remarkable evolution of anisotropic transport properties with T and x. The anisotropy in the normal-state resistivity is much enhanced in the superconducting compositional region, by more than an order larger than that in the band theory, and the conduction mechanisms appear to be different between a-b and c directions. The results are indicative of a two-dimensional electronic state in the CuO_2 plane, showing many features in coincidence with the normal-state properties predicted by the gauge theory of the uniform RVB state. It is clearly demonstrated that a crossover from two to three dimensions takes place as temperature becomes higher and when one enters the nonsuperconducting overdoped region. These features will be common with all the known high-T_c cuprates.

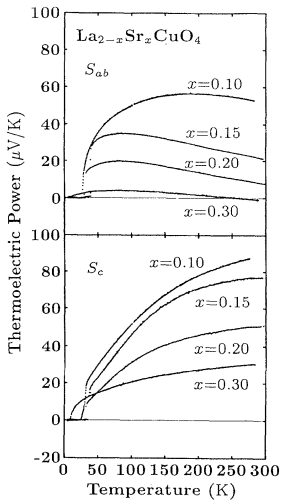

FIG. 4. Temperature dependence of in-plane (S_{ab}) and out-of-plane (S_c) thermopower.

We gratefully acknowledge N. Nagaosa and H. Takagi for many discussions and T. Kimura and K. Kishio for helpful advice in crystal growth. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, "Science of High T_c Superconductivity" from the Ministry of Education, Science, and Culture of Japan.

*Present address: Fundamental Research Laboratories, NEC Corporation, Tsukuba, Ibaraki 305, Japan.

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2] N. P. Ong, in *Physical Properties of High-Temperature Superconductors,* edited by D. M. Ginsberg (World Scientific, Singapore, 1990), Vol. 2, p. 459.
[3] T. Ito *et al.*, Nature **350**, 596 (1991).
[4] I. Tanaka and H. Kojima, Nature **337**, 21 (1989).
[5] S. Uchida *et al.*, Phys. Rev. B **43**, 7942 (1991).
[6] H. Takagi *et al.* Phys. Rev. B **40**, 2254 (1989).
[7] S. L. Cooper *et al.*, Phys. Rev. B **45**, 2549 (1992).
[8] Y. J. Uemura *et al.*, Phys. Rev. Lett. **62**, 2317 (1989).
[9] H. Takagi *et al.*, Phys. Rev. Lett. **68**, 3777 (1992).
[10] T. Ito, H. Eisaki, S. Uchida, C. Murayama, and N. Mori (unpublished).
[11] T. Ito, K. Takenaka, and S. Uchida (unpublished).
[12] M. Takigawa *et al.*, Phys. Rev. B **43**, 247 (1991).
[13] J. Rossat-Mignod *et al.*, Physica (Amsterdam) C **185-189**, 86 (1991).
[14] J. M. Tranquada *et al.*, Phys. Rev. B **46**, 5561 (1992).
[15] S-W. Cheong *et al.*, Phys. Rev. Lett. **67**, 1791 (1991).
[16] S. Kambe *et al.*, Physica C **160**, 243 (1989).
[17] K. Tamasaku, T. Hinatsu, and S. Uchida (unpublished).
[18] P. W. Anderson and Z. Zou, Phys. Rev. Lett. **60**, 132 (1988).
[19] W. E. Picket, Rev. Mod. Phys. **61**, 433 (1989).
[20] Z. Z. Wang and N. P. Ong, Phy. Rev. B **38**, 7160 (1988).
[21] M. F. Crommie *et al.*, Physica C **162-164**, 1397 (1989).
[22] P. B. Allen *et al.*, in *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 489.
[23] A. B. Kaiser and G. Mountjoy, Phys. Rev. B **43**, 6266 (1991).
[24] N. Nagaosa and P. A. Lee, Phys. Rev. Lett. **64**, 2450 (1990); Phys. Rev. B **43**, 1233 (1991).
[25] N. Nagaosa (private communication).