Optimal superconductivity in $La_{2-x}Sr_xCuO_4$

J.-S. Zhou and J. B. Goodenough
Texas Materials Science, University of Texas at Austin, Austin, Texas 78712

H. Sato and M. Naito
Material Science Research Laboratory, NTT Basic Research Laboratories, 3-1 Morinosato Wakamiya, Atsugi-shi,
Kanagawa 243-01, Japan

The temperature dependence of the resistivity $\rho(T)$ and the thermoelectric power $\alpha(T)$ have been measured under hydrostatic pressure on a single-crystal film of $La_{1.85}Sr_{0.15}CuO_4$ deposited on a $LaSrAlO_4$ substrate. The compressive biaxial stress built into the film raises T_c at ambient pressure. T_c increased with pressure P < 3.3 kbar, but saturated at a pressure-independent $T_c = 43.7$ at pressures $P > 3.3$ kbar. A low-temperature enhancement of $\alpha(T)$ having a $T_{max} \simeq 140$ K increased with T_c. The data are discussed within the framework of a vibronic model of the superconductive phase.
[S0163-1829(99)07005-8]

$La_{2-x}Sr_xCuO_4$ is the simplest of the superconductive copper-oxide systems. It contains no charge-reservoir layer, which makes unambiguous the number of holes per Cu atom in the superconductive CuO_2 sheets once the doping concentration x and the chemical stoichiometry are established. Systematic study[1] has revealed an evolution with x from antiferromagnetic insulator to superconductor and finally to normal metal, as illustrated by the partial phase diagram of Fig. 1. The superconductive compositions appear to represent a distinguishable thermodynamic state below room temperature,[2] with a maximum critical temperature $T_{max} \simeq 36$ K occurring in an orthorhombic single-phase composition with $x = 0.15$.[3] The distortion from tetragonal to orthorhombic symmetry buckles the Cu-O-Cu bond angle from $180°$ to $(180° - \phi)$ to relieve the compressive stress on the CuO_2 sheets introduced by a mismatch of the (La,Sr)-O and Cu-O equilibrium bond lengths. This distortion decreases with increasing temperature and Sr concentration x. At T_c, the orthorhombic-tetragonal transition occurs at an $x \approx 0.21$.[4]

The charge-carrier concentration of $0.15 \leqslant x \leqslant 0.20$ per Cu in a CuO_2 sheet appears to give the maximum T_c in all cuprate superconductors. An additional feature influencing T_c is the $(180° - \phi)$ Cu-O-Cu bond angle within a CuO_2 sheet. An anomalously large compressibility of the Cu-O bond within a CuO_2 sheet,[5] which is due to a transition from localized to itinerant behavior of the antibonding electrons that σ bond in a CuO_2 sheet,[6] causes hydrostatic pressure to straighten the $(180° - \phi)$ Cu-O-Cu bond angle. Previous measurements[7,8] on ceramic samples with $x \geqslant 0.18$ in Be-Cu pressure cells have shown that T_c initially increases linearly with hydrostatic pressure in the orthorhombic phase, but changes abruptly to a pressure-independent value at a critical pressure P_c that, like the orthorhombic-tetragonal transition temperature T_t, decreases with increasing x. Moreover, a high-pressure x-ray study[9] has shown that pressure stabilizes the tetragonal phase of the 214 structure, so we assume that the change in slope of T_c versus P at P_c reflects the orthorhombic-tetragonal transition. In any case, saturation of

T_c occurs in a phase with flat, or nearly so, CuO_2 sheets as pressure reduces the bending angle ϕ of the $(180° - \phi)$ Cu-O-Cu bond. The dependence of T_c on the bending angle ϕ is also apparent from a comparison of T_c for the same x of the isostructural systems $La_{2-x}Sr_xCuO_4$ and $La_{2-x}Ca_xCuO_4$.[10] However, limitation to pressures $P < 20$ kbar with a Be-Cu cell prevented us from access to critical pressure P_c in an $x = 0.15$ ceramic sample. In this paper we report access to this transition with a Be-Cu pressure cell in an $x = 0.15$ thin-film sample that is under a two-dimensional compressive stress as a result of bond-length mismatch with the substrate. We define optimal superconductivity in the $La_{2-x}Sr_xCuO_4$ system as that having the highest value of T_c obtainable under pressure in the optimally doped ($x = 0.15$) composition.
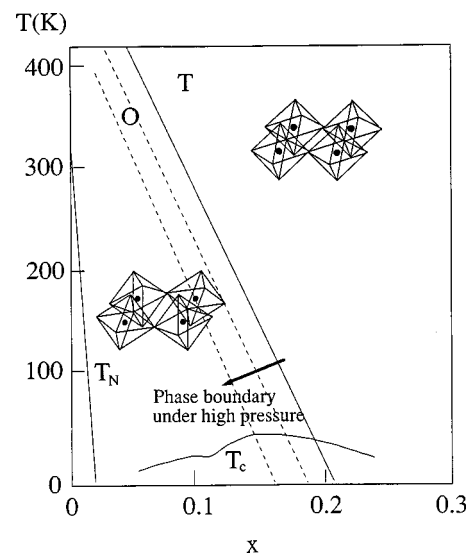
Sato and Naito[11] demonstrated that $La_{2-x}Sr_xCuO_4$ films

FIG. 1. Partial phase diagrams of the system $La_{2-x}Sr_xCuO_4$ showing schematically the shift of the orthorhombic-tetragonal phase boundary with increasing pressure.
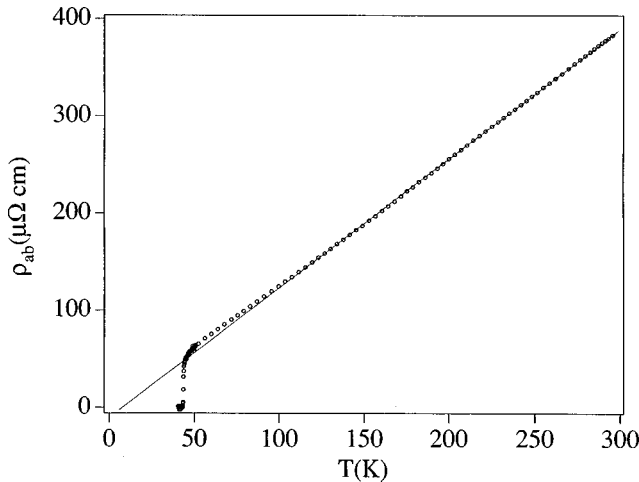
FIG. 2. Temperature dependence of the in-plane resistivity $\rho_{ab}(T)$ of a single-crystal $La_{1.85}Sr_{0.15}CuO_4$ film on a $LaSrAlO_4$ substrate.

FIG. 3. Pressure dependence of the in-plane resistivity $\rho_{ab}(T)$ for the film of Fig. 2.

oriented with the c axis perpendicular to the substrate have T_c reduced by a tensile stress on the CuO_2 sheets if deposited on $SrTiO_3$, and have T_c increased by a compressive stress if deposited on $LaSrAlO_4$. A $La_{1.85}Sr_{0.15}CuO_4$ film on $LaSrAlO_4$ remained orthorhombic at $T = T_0$, but had $T_c \approx 43$ K compared to $T_c \approx 36$ K in an unstressed ceramic or single-crystal specimen. We therefore undertook to investigate whether, with a Be-Cu pressure cell, we could add hydrostatic pressure to the two-dimensional compressive stress already in the film so as to access the orthorhombic to tetragonal transition. Three questions motivated this experiment: (1) Does T_c increase to a maximum value at P_c in an optimally doped sample? (2) What is the maximum value of T_c attainable in the $La_{2-x}Sr_xCuO_4$ system and is it influenced by a biaxial component of the pressure? (3) Does the low-temperature enhancement of the thermoelectric power that we[12] have associated with the superconductive phase increase to a maximum with T_c? Finally, we consider the implications of the observed angular dependence of T_c for a "vibronic" model of the superconductive phase.

The single-crystal $L_{1.85}Sr_{0.15}CuO_4$ film studied was deposited on $LaSrAlO_4$ at NTT, Japan. Details of the procedure for making the films can be found in Ref. 11. The film with $T_0 = 43.8$ K as measured at NTT was found at Austin to have $T_0 = 43.0$ K, where T_0 is the temperature below which no voltage is resolvable with a nanovoltmeter. A higher resolution at Austin revealed a small shoulder at low resistivity that lowered T_0 by 0.4 K. The other 0.4-K discrepancy appears to be due to a difference in the calibration of the thermometers. The measurement error at Austin is $\Delta T_0 < 0.2$ K. The Be-Cu high-pressure apparatus and a description of the measurement of physical properties have been reported elsewhere.[13]

Figure 2 shows the temperature dependence of the resistivity within the basal plane, $\rho_{ab}(T)$; it is identical to single-crystal data[14] and to independent measurements on films.[15] Above 100 K, $\rho(T)$ can be fit perfectly to a linear relationship that extrapolates to zero near $T = 0$ K. Hydrostatic pressure does not alter this linear temperature dependence, but it increases T_0 from 43 to 43.7 K within 3.3 kbar. T_0 saturates for $P \gtrsim 3.3$ kbar (Figs. 3 and 4) indicative of a $P_c \approx 3.3$ kbar in our film.
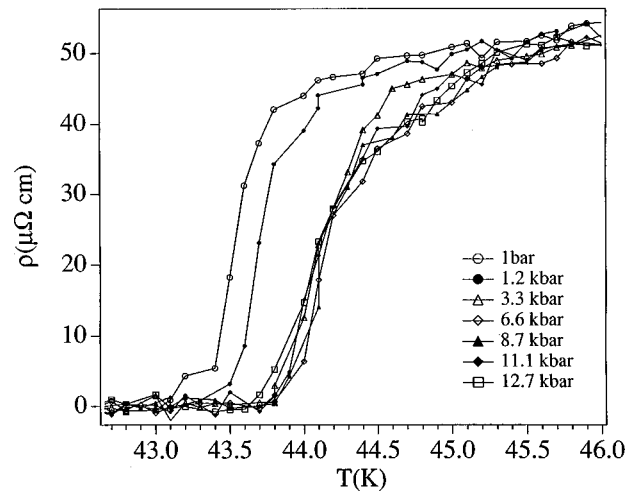
At ambient pressure, the temperature dependence of the thermoelectric power $\alpha(T)$ of Fig. 5 is similar to that found for ceramic samples.[16] Also as in the ceramic samples, the low-temperature enhancement of $\alpha(T)$ with a $T_{max} \approx 140$ K increases significantly with T_c below 3.3 kbar. In the $x = 0.15$ ceramic samples, T_c and the enhancement do not saturate within the pressure range accessible in a Be-Cu pressure cell. However, in the films the enhancement increases only weakly with P at $P > 3.3$ kbar, where T_c is pressure independent (Fig. 4).

The T_c-P curve in Fig. 4 suggests that the film is still orthorhombic under ambient pressure but much closer to the transition at P_c than a ceramic specimen, which is orthorhombic for $P < 20$ kbar.[7] Figure 4 confirms that the film is under the epitaxial stress caused by the lattice mismatch with the substrate. our estimation for the in-plane epitaxial stress of about 16 kbar[11] shows good agreement with the difference between $P_c \approx 3.3$ kbar for the film and $P_c \gtrsim 20$ kbar for the ceramic sample.[7] Moreover, the low-temperature enhancement of $\alpha(T)$, which is not due to phonon drag, is found to increase with T_c in the pressure range $0 \leq P \leq 3.3$ kbar; it
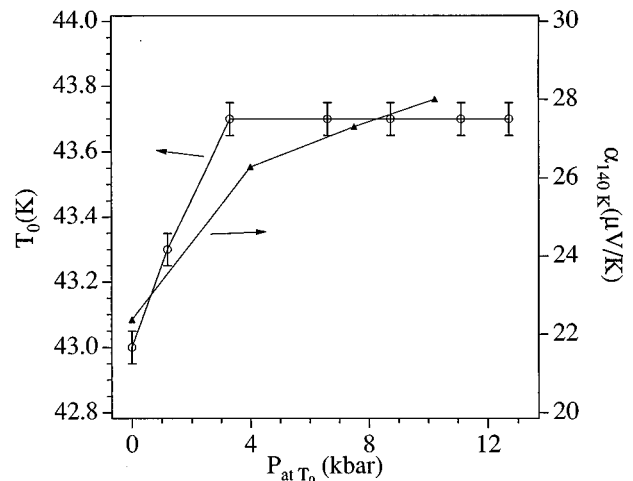

FIG. 4. Pressure dependence of the critical temperature T_0 and of the thermoelectric power at $T_{max} \approx 140$ K.
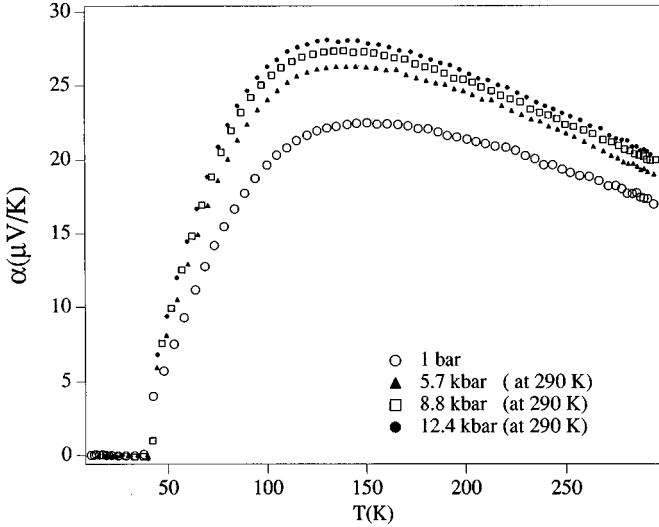
FIG. 5. Temperature dependence of the in-plane thermoelectric power $\alpha_{ab}(T)$ under different hydrostatic pressures of the film of Fig. 2.

retains a smaller pressure dependence for $P > 3.3$ kbar, even though the films already appear to be tetragonal at a $T_{max} \approx 140$ K at ambient pressure. We suggest that this observation indicates that the transition from orthorhombic to tetragonal symmetry is not sharp in the normal state, short-range orthorhombic distortions persisting well above the long-range ordering temperature. $T_c = 43.7$ K for the film in the tetragonal phase is nearly 2 K higher than the maximum $T_c \approx 42$ K obtained under hydrostatic pressure for the bulk.[17] This gain in T_c is associated with the two-dimensional component of the stress on the film, which has $T_c = 43$ K at ambient pressure. Even higher T_c is expected for a tetragonal sample with higher compressive stress in the a-b plane and large c-axis extensions. In fact, $T_c = 49$ K was recently reported for a thin film of La$_{1.9}$Sr$_{0.1}$CuO$_4$ with a large compression of the a-b plane and a large c-axis extension by the epitaxial strain.[18]

To interpret the significance of this dependence on the angle ϕ, we turn finally to a *vibronic* model of the superconductive phase. The superconductive phase in La$_{2-x}$Sr$_x$CuO$_4$ appears at a crossover from localized-electron behavior in the antiferromagnetic insulator La$_2$CuO$_4$ to Fermi-liquid electronic behavior in the overdoped compositions with $x \geq 0.30$. The equilibrium Cu-O bond length for localized electrons is larger than that for itinerant electrons,[6] and a double-well potential for the Cu-O bond length at crossover is responsible not only for the large compressibility of the Cu-O bond in the superconductive phase, but also for phase segregation between the antiferromagnetic phase and clusters or stripes rich in charge carriers. Two of us have shown[2,19] that in the underdoped compositions $0 < x < 0.10$, a mobile charge carrier is confined to a cluster of five copper centers by interaction with the antiferromagnetic matrix. We have also argued[20] that in the optimally doped compositions these clusters form a strongly interacting ''polaron gas'' at high temperatures that condenses into a ''polaron liquid'' below room temperature. At that time we did not specify the nature of this liquid, but later experiments[21,22] indicated that the hole-rich regions become ordered below T_l into stripes separated by localized-electron magnetic-stripes that, in the

La$_{2-x}$Sr$_x$CuO$_4$ structure, are oriented alternately along tetragonal [100] and [010] directions, the $(\pi,0)$ and $(0,\pi)$ directions of the CuO$_2$ sheet on traversing the c axis. In the low-temperature-tetragonal (LTT) phase of La$_{1.88}$Ba$_{0.12}$CuO$_4$, these stripes are pinned and are therefore directly detectable with neutron diffraction.[22] Superconductivity is suppressed where the stripes are stationary;[23,24] it reappears in the LTT phase if the stripes are depinned under pressure, and T_c increases with pressure.[25] It follows that superconductivity is associated with mobile stripes and that these stripes are to be distinguished from a conventional charge-density wave that introduces an energy gap at the Fermi energy. These stripes appear to be the consequence of a phase segregation that is accomplished by cooperative oxygen-atom displacements in the CuO$_2$ sheets rather than by any atomic diffusion.[21] Clearly the charge carriers must couple strongly to the oxygen displacements for phase segregation into the stripes to occur. This strong electron-lattice coupling would be retained with mobile stripes as well as with mobile clusters of five copper centers. The linear temperature dependence of $\rho_{ab}(T)$ extends to 1000 K without saturation,[15] which indicates that the mobility of the charge carriers is not determined by a Boltzmann scattering mechanism. Strong electron coupling to mobile stripes or clusters would make the normal-state charge carriers move diffusively, but with any activation energy $E_a \ll kT$ for $T > T_c$, thereby giving a charge-carrier mobility $\mu \sim T^{-1}$ and $\rho_{ab} \sim T$. The problem is to find a way to describe the transformation from cluster molecular orbitals to itinerant charge carriers coupled to mobile stripes.

Electron coupling to mobile stripes would be to the phonons with propagation vector $\mathbf{q}$ parallel to the vector $\mathbf{Q}$ of the stripe periodicity in a CuO$_2$ plane. These phonons would have the same symmetry as an itinerant electron of wave vector $\mathbf{k}$ having a component in the direction $\mathbf{Q}$, so we can expect an admixture of phonons and electrons to give *itinerant vibronic states* traveling in the direction of $\mathbf{Q}$. The admixture of traveling electronic and phononic states would transform the electronic heterogeneity of mobile clusters or static stripes into a homogeneous system as required by the theories of vortex formation and pinning. Moreover, it would give a stabilization energy $\Delta\varepsilon \sim (\mathbf{k}\cdot\mathbf{Q})^2$ in a given CuO$_2$ sheet. Averaging over successive sheets, the stabilization would go as $(\cos\theta + \sin\theta)(\cos\theta - \sin\theta) \sim \cos2\theta$, which corresponds to d-wave symmetry. Moreover, the number of states so stabilized would increase with the ordering of the mobile stripes, and hence with decreasing temperature, in the polaron-liquid phase appearing in the interval $T_c < T < T_l \approx 300$ K. A transfer of spectral weight from (π,π) to the $(\pi,0)$ and $(0,\pi)$ directions with decreasing temperature would flatten the $\varepsilon_\mathbf{k}(\mathbf{k})$ curves in the $(\pi,0)$ and $(0,\pi)$ directions, so as to enhance $\alpha(T)$ to a maximum value at T_{max}. The onset of Cooper-pair fluctuations in the interval $T_c < T < T_{max}$ would increasingly lower $\alpha(T)$ as T approached T_c in the interval $T_c < T < T_{max}$. Consistent with this model is the quite spectacular observation of a progressive transfer of spectral weight from the (π,π) to the $(\pi,0)$ and $(0,\pi)$ directions in the CuO$_2$ sheets on lowering the temperature from 300 K to T_c.[26,27] In this model, the d-wave superconductivity below T_c reflects a coupling between itinerant vibronic states. The itinerant electrons with $\mathbf{k}$ parallel to the stripes

are not coupled to the phonons and may give a measurable s-wave component to the superconductive energy gap Δ.

Within this model, the influence of the Cu-O-Cu bond angle on T_c might be attributed to (1) a change in the oxygen vibrational frequency ω_O within a bond, (2) an enhanced Cu-O covalent mixing, or (3) a weaker pinning and hence greater mobility of the stripes. Although there is strong evidence that ω_O would increase with the Cu-O-Cu bond angle, we rule out the first alternative as there is little effect on T_c of $^{18}O/^{16}O$ isotope exchange in optimally doped copper oxides. We might rule out the second alternative because T_c is unchanged by pressure in the tetragonal phase even though pressure should continue to increase the Cu-O covalent mixing after the Cu-O-Cu bond angle is straightened. Indeed, T_c has been reported[17] to decrease at high pressures $P > 4$ GPa in overdoped tetragonal samples. On the other hand, an anisotropic compressibility may invalidate this deduction, since a large c-axis compression under hydrostatic pressure may make the increase in c-axis covalent bonding compete with any increase in covalence in the a-b plane. With only a two-dimensional compressive stress, T_c appears to be higher in the tetragonal phase. A maximum $T_c = 42$ K under hydrostatic pressure[17] is to be compared with a $T_0 = 43.7$ K in the film samples, and a $T_c > T_0$ makes the difference even larger. Finally, the increase with pressure in the enhancement of $\alpha(T)$ would, in the vibronic model, signal a more facile coherence of stripe segments within the polaron-liquid normal state, which would be compatible with achieving the long-range coherence needed for superconductivity at a higher T_c. We are thus led to the conclusion that bending of the Cu-O-Cu bond angle makes more difficult the long-range ordering of the mobile stripes that is required for superconductivity.

In conclusion, the (tetragonal) phase having a pressure-independent T_c has been approached under hydrostaitc pressure in an optimally doped $La_{2-x}Sr_xCuO_4$ thin film. The flat CuO_2 sheets have been shown to give a maximum T_c under ambient or hydrostatic pressure. In contrast to the maximum T_c of a ceramic sample under hydrostatic pressure, the two-dimensional stress on the CuO_2 sheets of a film give an extra gain in T_c, which points to a way to increase T_c in these anisotropic materials. The enhancement at $T \approx 140$ K in the thermoelectric power has been confirmed to change with T_c regardless of whether the gain in T_c is due to a flattening of the CuO_2 sheets or to a two-dimensional stress.

[1] H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida, and Y. Tokura, Phys. Rev. B **40**, 2254 (1989).

[2] J. B. Goodenough, J.-S. Zhou, and J. Chan, Phys. Rev. B **47**, 5275 (1993).

[3] P. G. Radaelli, D. G. Hinks, A. W. Mitchell, B. A. Hunter, J. L. Wagner, B. Dabrowski, K. G. Vandervoort, H. K. Viswanathan, and J. D. Jorgensen, Phys. Rev. B **49**, 4163 (1994).

[4] 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).

[5] H. Takahashi, H. Shaked, B. A. Hunter, P. G. Radaelli, R. L. Hitterman, D. G. Hinks, and J. D. Jorgensen, Phys. Rev. B **50**, 3221 (1994).

[6] J. B. Goodenough, Ferroelectrics **130**, 77 (1992).

[7] N. Yamada and M. Ido, Physica C **203**, 240 (1992).

[8] J.-S. Zhou, H. Chen, and J. B. Goodenough, Phys. Rev. B **49**, 9084 (1994).

[9] H. J. Kim and R. Moret, Physica C **156**, 363 (1988).

[10] B. Dabrowski, Z. Wang, K. Rogacki, J. D. Jorgensen, R. L. Hitterman, J. L. Wagner, B. A. Hunter, P. G. Radaelli, and D. G. Hinks, Phys. Rev. Lett. **76**, 1348 (1996).

[11] H. Sato and M. Naito, Physica C **274**, 221 (1997).

[12] J.-S. Zhou and J. B. Goodenough, Phys. Rev. Lett. **77**, 151 (1996).

[13] J.-S. Zhou and J. B. Goodenough, Phys. Rev. B **54**, 13 393 (1996).

[14] G. S. Boebinger, Y. Ando, A. Passner, T. Kimura, M. Okuya, J. Shimoyama, K. Kishio, K. Tamasaku, N. Ichikawa, and S. Uchida, Phys. Rev. Lett. **77**, 5417 (1996).

[15] H. Takagi, B. Batlogg, H. L. Kao, J. Kwo, R. J. Cava, J. J. Krajewski, and W. F. Peck, Jr., Phys. Rev. Lett. **69**, 2975 (1992).

[16] J.-S. Zhou and J. B. Goodenough, Phys. Rev. B **51**, 3104 (1995).

[17] N. Mori *et al.* Physica C **185-189**, 40 (1991).

[18] J.-P. Locquet, J. Perret, J. Fompeyine, E. Machler, J. W. Seo, and G. Van Tendeloo, Nature (London) **394**, 453 (1998).

[19] J.-S. Zhou, G. I. Bersuker, and J. B. Goodenough, J. Supercond. **8**, 541 (1995).

[20] J. B. Goodenough and J.-S. Zhou, Phys. Rev. B **49**, 4251 (1994).

[21] A. Bianconi, N. L. Saini, A. Lanzara, M. Missori, T. Rossetti, H. Oyanagi, H. Yamaguchi, K. Oka, and T. Ito, Phys. Rev. Lett. **76**, 3412 (1996).

[22] J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, Nature (London) **375**, 561 (1995).

[23] J. D. Axe, A. H. Moudden, D. Hohlwein, D. E. Cox, K. M. Mohanty, A. R. Moodenbaugh, and Y. Xu, Phys. Rev. Lett. **62**, 2751 (1989).

[24] Y. Nakamura and S. Uchida, Phys. Rev. B **46**, 5841 (1992).

[25] J. B. Goodenough and J.-S. Zhou, J. Supercond. **10**, 309 (1997).

[26] Z.-X. Shen, P. J. White, D. L. Feng, C. Kim, G. D. Gu, H. Ikeda, R. Yoshizaki, and N. Koshizuka, Science **280**, 259 (1998).

[27] M. R. Norman, H. Ding, M. Randena, J. C. Compuzano, T. Yokoya, T. Takeuchi, T. Takahoushi, T. Mochiku, K. Kadowaki, P. Guptasarma, and D. G. Hinks, Nature (London) **392**, 157 (1998).