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Enhanced superconducting T_c in the immiscible system $(La_{1.85}Sr_{0.15}CuO_4)_x(Lu_2Cu_2O_5)_{1-x}$

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We discovered that the *immiscibility* between $La_{1.85}Sr_{0.15}CuO_4$ and $Lu_2Cu_2O_5$ leads to a micrometer-scale heterogeneous mixture of a superconducting cuprate and an antiferromagnetic insulator. Whereas electronic conduction of the mixture in the normal state exhibits a percolation behavior, superconducting T_c systematically increases with increasing amounts of insulating $Lu_2Cu_2O_5$. The highest onset T_c of 46 K is achieved near the percolation threshold. Even though an unusual magnetic proximity effect cannot be ruled out, a plausible cause for the T_c enhancement is the tensile strain in highly anisotropic $La_{1.85}Sr_{0.15}CuO_4$ induced by the differential thermal contraction of the two phases.

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Since the discovery of high-T_c superconductivity (HTSC), a tremendous number of experimental studies have been performed to determine how the antiferromagnetic (AF) parent compound evolves into the optimum superconducting (SC) phase, which could eventually reveal the mechanism for HTSC.[1] One of the important emerging pictures from these studies is that preformed incoherent SC pairs or localized SC exist(s) below the so-called pseudo-gap temperature, and three-dimensional phase coherence among SC pairs develops at the bulk transition temperature, T_c.[2–4] The difference in magnitude between the preformed SC temperature and T_c is rather significant in the underdoped region and is considerably reduced at the optimum doping range.[5] This picture certainly implies some interrelationship between the AF of the parent compound and HTSC. Related to this scenario, large length-scale tunneling of supercurrent, the so-called giant proximity effect (GPE), was proposed when a HTSC is placed right next to an AF insulator.[6,7]

Chemical phase separation[8] can be utilized to demonstrate the proximity effect in bulk materials between a HTSC and an AF insulator (I). However, any tiny bit of solubility can be disastrous because magnetic as well as nonmagnetic impurities in HTSC tend to suppress SC drastically.[9,10] It has been reported that a wide-range mixture of HTSC and AF-I can be realized in the quasi-binary phase of $YBa_2Cu_3O_7$:Y_2BaCuO_5 (Y123:Y211).[11] In addition to the detailed study of the Y123:Y211 system, we have attempted to find an AF-I cuprate that is immiscible in $(La,Sr)_2CuO_4$. One of the candidates was orthorhombic $R_2Cu_2O_5$ with R = rare earth elements. The structure of $R_2Cu_2O_5$ contains quasi–two-dimensional Cu-O planes with ferromagnetic intraplane and AF interplane interactions, leading to long-range AF ordering below ∼19 K.[12] From our extensive study of the mixture of $(La,Sr)_2CuO_4$ and $R_2Cu_2O_5$, we discovered there exists an almost perfect immiscibility between $La_{1.85}Sr_{0.15}CuO_4$ (LSCO) and $Lu_2Cu_2O_5$ (LCO).[13] Therefore, LSCO:LCO is an ideal system not only to investigate percolative conduction in the SC–I composite, but also to study the proximity effect between a HTSC and an AF-I. To our surprise, we observed a significant increase of T_c in the SC–AF-I composite from our transport measurement, which is maximized near the percolation threshold.

Polycrystalline (x)LSCO:$(1-x)$LCO specimens with about 20 different molar ratios were prepared by using conventional solid-state reaction (see Supplementary Material[37]). For a comparative study, we also prepared polycrystalline (y)Y123:$(1-y)$Y211. Resistivity (ρ) was measured by using the standard four-probe method with the current density of 50 μA/cm^2–0.5 A/cm^2, and a SQUID magnetometer was used for magnetization measurements in 20 Oe. Figure 1(a) and 1(b) shows the x-ray powder diffraction patterns of the mixed specimens at 300 K. Surprisingly, both sets of tetragonal LSCO and orthorhombic LCO peaks are clearly present in the mixtures, and the relative intensity changes systematically without any detectable peak shift with x. These results could imply immiscibility between LSCO and LCO. This poor miscibility of LSCO:LCO probably stems from the extreme difference in ionic radius between La and Lu.[8] The results in Fig. 1(b) indicate the formation of only two end phases in Y123:Y211.[11]

These immiscible two-phase grains in LSCO:LCO are, indeed, discernable under an optical microscope. Optical microscopy images of the polished surfaces of $x = 0.8$ and 0.2 are shown in Fig. 1(c) and 1(d). It turns out that LSCO regions, compared with LCO regions, are mechanically soft and thus tend to be lower in height and show rougher surfaces in the optical images. Within each region of LSCO and LCO, we were able to identify grain structure by using a polarizer/analyzer. From the polarized microscope images (not shown), we found that the grains vary from ∼3 to ∼15 μm in size.

We observed percolative electronic conduction in the micrometer-scale mixture of metallic (M)-LSCO and I-LCO. As shown in Fig. 2(a), ρ systematically increases by ∼5 orders of magnitude when x decreases to 0.32, but the temperature (T) dependence remains metallic in the entire range of $0.32 \leqslant x \leqslant 1$. We found that ρ of $x = 0.29$ is ∼0.8×10^6 Ω-cm at 300 K, exponentially increases upon cooling, and becomes un-measurably large below ∼270 K. Below T_c, a broad $\rho(T)$ hump tends to develop with decreasing x, probably resulting from a weakening of the intergrain coupling of LSCO when the cross-sectional area of the SC path decreases with decreasing x. The change of ρ with x in our M-I mixtures is analyzed in terms of the percolation theory. As shown in

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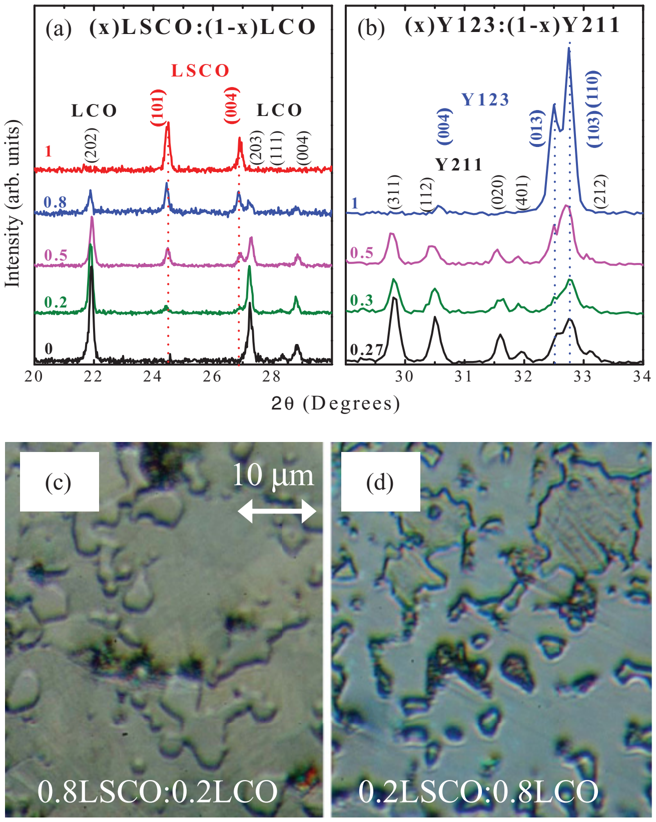

FIG. 1. (Color online) Powder x-ray diffraction intensity vs. 2θ for (a) (x)LSCO:$(1-x)$LCO and (b) (y)Y123:$(1-y)$Y211. Indices for x-ray peaks of tetragonal (I4/mmm) LSCO, orthorhombic (Bmab) LCO, Y123, and Y211 are denoted. (c) (Unpolarized) optical microscope image of $x = 0.8$. The polished surfaces of the mechanically *softer* LSCO grains are lower in height and rougher than those for the *harder* LCO grains. (d) Optical microscope image of $x = 0.2$.

Fig. 2(b), the ρ change with x obeys the scaling law of $\rho \propto (p - p_c)^{-t}$ for $0.32 \leqslant x \leqslant \sim 0.6$, where p is the M volume ratio, p_c is the percolation threshold of the M phase, and t is the scaling exponent. p is calculated from the LSCO molar ratio and its unit cell volume. p_c is 0.26(2) for $x_c = 0.30(1)$, which is close to the predicted percolation threshold ($p_c = 0.25$) for a continuum model.[14] However, the critical exponent t is estimated to be 3.4(5) from the least square fit, which is significantly larger than the classical value of 2.0.[15] Note that a similarly large magnitude of t has been observed often when tunneling-type conduction dominates electronic transport.[8,16] However, the origin of our enhanced value of t remains to be unveiled.[17]

Any slight cross-contamination in the mixture (e.g., a slight replacement of La by Lu in LSCO) will naturally influence its physical properties, particularly phase transition temperatures. Thus, we have carefully examined how the SC T_c of LSCO and the AF Néel temperature (T_N) of LCO in the mixture change with x. Figure 3(a) and 3(b) exhibit $\rho(T)$ and magnetic susceptibility (χ) below 50 K for $x = 1$ (Fig. 3(a)) and 0.6 (Fig. 3(b)). In $\chi(T)$ of all specimens, SC transitions seem apparent, and there appears to be little change of T_c in the 1–K-step data, which is close to the literature value (38–39 K) for LSCO.[20] (More detailed observation on $\chi(T)$ with 0.1 K steps, shown in the inset of Fig. 3(b), will be discussed later.) The feature at 17 K for $x = 0.6$ results from an AF transition, and this transition is certainly present in our pure LCO. This T_N is also close to the literature value for LCO.[12] No observable change of T_c and T_N in the entire mixing range of $x = 0$–1 corroborates the existence of a complete chemical phase separation in LSCO:LCO. However, the most unusual behavior is evident in $\rho(T)$ in Fig. 3(a) and 3(b): whereas T_c in $\rho(T)$ for $x = 1$ is very close to that in the literature, the onset T_c in $\rho(T)$ for $x = 0.6$ is significantly higher than that in $x = 1$. The onset T_c in $\rho(T)$ of $x = 0.6$ is $\sim$45 K, which is almost 13% higher than the pure LSCO T_c. On the other hand, there is no evidence of T_c change in $\rho(T)$ in the mixture of Y123:Y211, as shown in Fig. 3(c).

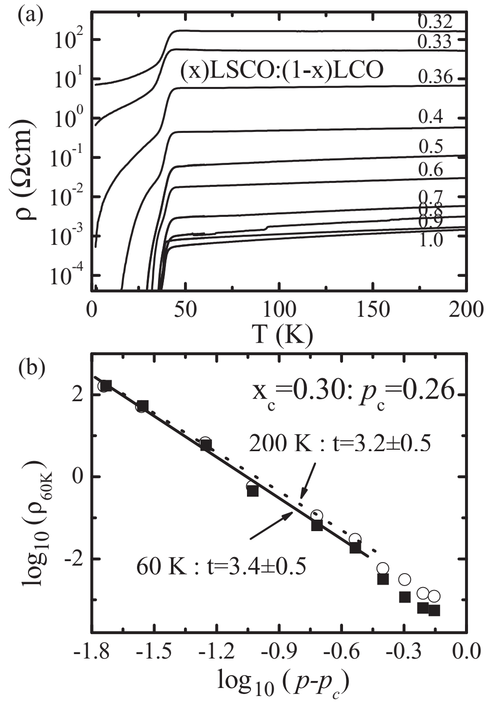

FIG. 2. (Color online) (a) Resistivity of (x)LSCO:$(1-x)$LCO as a function of temperature with the current density of about 50 mA/cm^2. $\rho(T)$ of all specimens in the figure shows a metallic temperature dependence in the normal state, and $\rho(T)$ of $x = 0.29$ (not shown) is highly insulating. (b) $\log_{10}(\rho)$ vs. $\log_{10}(p - p_c)$ at 60 K and 200 K. The solid and dashed lines indicate the results of least squared fit with $p_c = 0.26(1)$ for 60 K and 200 K, respectively.

The systematics of this unexpected behavior of LSCO:LCO is clearly demonstrated in $d\rho/dT$ near T_c in Fig. 4(a). An effect of LCO mixing is a broadening of the $d\rho/dT$ peak width, indicating the broadening of the SC transition.[21] However, the unusual results are: (1) the peak position shifts to a higher T and (2) the T, where the $d\rho/dT$ peak starts at the high-T end, significantly shifts to a higher T with decreasing x, clearly indicating the increase of the onset T_c for SC.[23] As shown in Fig. 4(b), the electric onset T_c increases rather abruptly just below $x = 1$, then almost saturates below $x = 0.7$, giving the maximum at $x = 0.32$ near the percolation threshold. The peak T_c also shows a similar trend, but the increase is relatively small. The maximum changes in the onset T_c and the peak T_c are 6.2 K and 2.5 K, respectively.

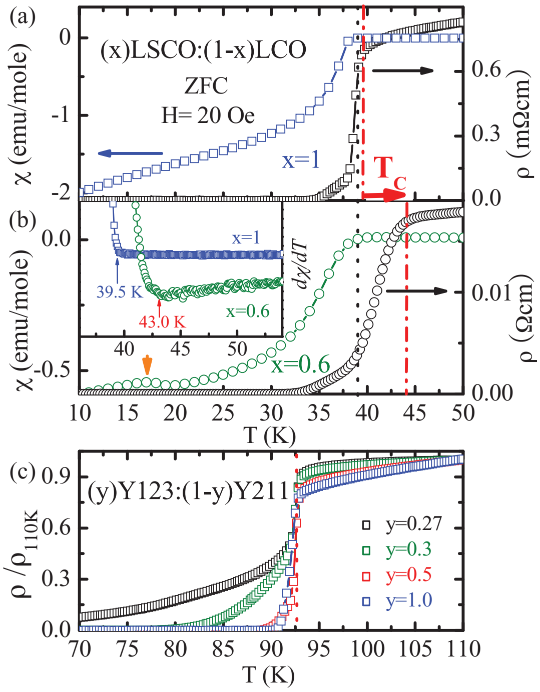

FIG. 3. (Color online) Resistivity and magnetic susceptibility vs. temperature for (a) $x = 1$ (pure LSCO) and (b) $x = 0.6$. The small yellow/gray arrow in the main figure indicates $T_N \approx 17$ K. The inset shows the temperature derivatives of magnetic susceptibilities with steps of 0.1 K near the SC transitions for both $x = 1$ and $x = 0.6$. $\chi(T)$ was measured while warming the samples from 5 K in 20 Oe after zero field cooling. (c) Normalized resistivity vs. temperature for the (y)Y123:$(1 - y)$Y211 mixture with $y = 0.27$, 0.3, 0.5, and 1.0.

The possibility of localized/preformed SC far above the bulk T_c in HTSC, as well as its connection with the pseudo-gap state, especially in the underdoped region, has been extensively discussed.[2–4] Because our observation could be related to the stabilization of the localized/preformed SC and/or the pseudo-gap state in our SC–AF mixture, we have investigated how the onset T_c of our mixture varies with Sr doping level for a fixed ratio of LSCO/LCO (see Supplementary Material[37]). Our results indicate that, even though the rate of the T_c enhancement is slightly higher in the underdoped region, the optimum onset T_c in the mixture occurs at the Sr concentration of 0.15–0.17, similar to the behavior in pure LSCO. Thus, the connection between our T_c enhancement and the localized/preformed SC is not evident. Additionally, the diamagnetic precursor domains in optimally doped LSCO and YBCO have been reported to appear in a similar temperature range up to ∼5 K above T_c.[3] However, as shown in Fig. 3, only the LSCO:LCO mixture provides meaningful evidence of T_c enhancement, whereas the same effect is not observed in Y123:Y211. Other related topics in the field of HTSC are the magnetic origin of HTSC and GPE between a HTSC and an AF insulator. In this sense, we have carefully looked for any transport anomaly near the AF transition T (17 K), which is far below the SC onset T_c. Our results do not show any detectable anomaly in $\rho(T)$ near 17 K for any x, even though the AF transition at 17 K is evident in $\chi(T)$ of our mixed specimens (see Figs. 2 and 3). Furthermore, GPE naturally induces the reduction of p_c for SC from the value for the normal state, but we do not see any indication for it (see Fig. 2(a)).[24] These observations possibly indicate little connection between GPE and the transport properties of our mixtures.

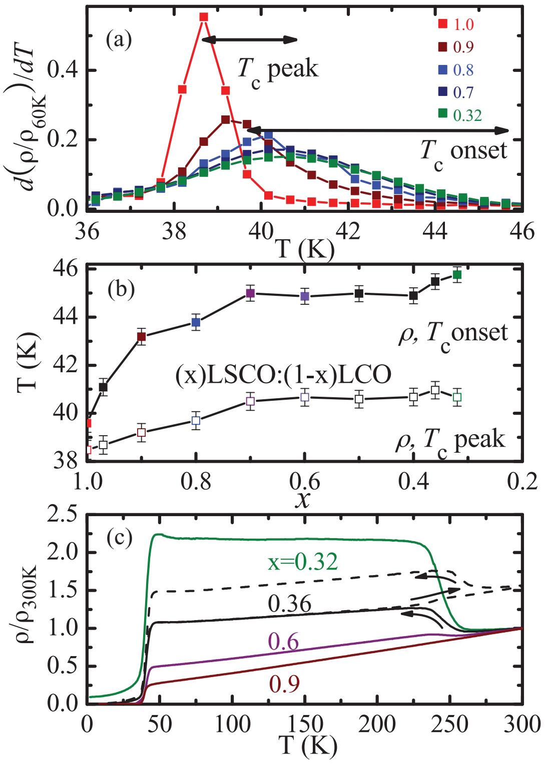

FIG. 4. (Color online) (a) Temperature derivative of normalized resistivity vs. temperature for selected compositions. (b) Onset T_c and T_c from the $d\rho(T)/dT$ peak vs. x. The solid lines are guides for the eyes. (c) Normalized resistivity vs. temperature up to 300 K upon cooling. The dotted line shows $\rho(T)$ for $x = 0.36$ with thermal cycles.

Significant strain appears to exist because of the differential thermal contraction between LSCO and LCO. Whereas orthorhombic $Y_2Cu_2O_5$ (isostructural with $Lu_2Cu_2O_5$) has been reported to show a negligible change of lattice constants (0.02 ∼ 0.04%) on cooling,[12,25] the lattice constant change for LSCO from 300 K to 40 K is 0.30% for c and 0.13% for $(a + b)/2$, which is about one order of magnitude larger than that of LCO.[26,27] Compared with LCO, the larger thermal contraction of LSCO is certainly consistent with the softer mechanical property of LSCO grains. Thus, in our mixture of LSCO:LCO, where two types of grains are tightly interlocked to each other, LCO can provide significant tensile strain on LSCO at low T. The tensile strain effect is especially strong along the c axis because of the large thermal contraction of LSCO along the c axis. This tensile strain naturally exists at the interfacial regions between LSCO and LCO and relaxes in the bulk regions of LSCO and LCO.

A large number of experimental works of the pressure-strain effect on HTSC have been reported for the last two decades.[28] Hydrostatic compressive pressure of 1.5 GPa was reported to enhance the onset T_c up to ∼43 K in LSCO.[22,29] However, careful experiments of uniaxial pressure on single crystals or epitaxial strain in thin films indicate that T_c of LSCO does increase with the contraction of a/b lattice constants, but the most significant increase of T_c results from the c-axis expansion.[30–32] Because it can start from a T much higher than 300 K, the tensile strain due to the interlocking thermal contraction of LSCO grains and LCO grains can be greater than 0.3%, which can readily produce the 6 K increase of T_c if the tensile strain is applied along the c direction.[31] However, this tensile strain on the interfacial regions of LSCO is expected to be random in direction, so that it produces a broadening of the electric T_c in addition to a sharp increase of the electric onset T_c. The contribution of this interfacial effect to transport properties naturally becomes dominant when x approaches x_c. Meanwhile, the little change of magnetic T_c indicates that the bulk region of LSCO, where the strain is relaxed, is dominant in volume. In any case, as shown in the inset of Fig. 3(b), a careful observation of the T derivative of $\chi(T)$ for $x = 0.6$ clearly shows that even the magnetic onset T_c is significantly enhanced. In Y123:Y211, the strain induced by the differential thermal contraction of the two phases has also been reported.[11] On the other hand, pure Y123 shows little hydrostatic pressure effect of T_c, consistent with the observed minimal change of T_c in Y123:Y211.[33] Note that Welp *et al.* reported that the small hydrostatic pressure effect on fully oxygenated Y123 stems from the cancellation of opposite effects along the a and b directions, whereas the c axis changes little under pressure.[34]

The presence of this significant tensile strain is also reflected in the behavior of a $\rho(T)$ anomaly at ∼250 K [Fig. 4(c)], which becomes large when x approaches x_c. The ρ anomaly starts to appear below $x = 0.6$, and absent for $x \geqslant 0.7$. Additionally, as shown for $x = 0.36$, $\rho(T)$ shows a systematic increase with thermal cycle around 250 K. These $\rho(T)$ behaviors are probably associated with the orthorhombic-tetragonal structural transition in LSCO. In pure LSCO, the structural transition temperature (T_o) is known to be ∼180 K, but $\rho(T)$ does not show any anomaly at T_o. Because a/b lattice constants in low-T orthorhombic phase, compared with those in high-T tetragonal phase, tend to expand on cooling, a tensile strain naturally induces the increase of T_o.[26] Thus, the enhancement of T_o from 180 K to 250 K is consistent with the existence of a significant tensile strain.[35] The systematic increase of $\rho(T)$ with thermal cycle at ∼250 K and the enhancement of the $\rho(T)$ anomaly with decreasing x suggest the local, nonreproducible cracking in the strained interfacial regions when the structural transition sets in.

In summary, we have found excellent immiscibility between HTSC LSCO and AF-I LCO. In this completely phase-separated system, the percolative electronic conduction occurs with the percolation threshold of $p_c = 0.26(1)$ and the scaling exponent of $t = 3.4(5)$. This phase mixture, surprisingly, exhibits a systematic enhancement of onset T_c with increasing volume fraction of AF-I LCO. This T_c enhancement possibly stems from the tensile strain due to the differential thermal contraction of the LSCO and LCO, as well as the highly anisotropic change of SC with the variation of lattice constant.

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[1] See, for example, J. Orenstein and A. J. Millis, Science **288**, 468 (2000).

[2] Z. A. Xu *et al.*, Nature **406**, 486 (2000).

[3] I. Iguchi *et al.*, Nature **412**, 420 (2001).

[4] A. Lascialfari *et al.*, Phys. Rev. B **68**, 100505(R) (2003).

[5] M. Oda *et al.*, J. Phys. Chem. Solids **65**, 1381 (2004).

[6] G. Alvarez *et al.*, Phys. Rev. B **71**, 014514 (2005).

[7] R. S. Decca *et al.*, Phys. Rev. Lett. **85**, 3708 (2000).

[8] S. Park *et al.*, Phys. Rev. Lett. **92**, 167206 (2004).

[9] M. K. Crawford *et al.*, Phys. Rev. B **44**, 7749 (1991).

[10] H.-H. Klauss *et al.*, Phys. Rev. Lett. **85**, 4590 (2000).

[11] H.S. Gamchi *et al.*, Phys. Rev. B **50**, 12950 (1994). P. Diko *et al.*, Physica C **247**, 169 (1995).

[12] J. Aride *et al.*, Solid State Commun. **72**, 459 (1989).

[13] Different insulating phases of $Tb_2(MoO_4)_2$, CuO, $Sc_2Cu_2O_5$, and $Er_2Cu_2O_5$ have been tested and showed phase intermixing and reduction of SC T_C.

[14] S. Kirkpatrick, Rev. Mod. Phys. **45**, 574 (1973).

[15] M. B. Isichenko, Rev. Mod. Phys. **64**, 961 (1992).

[16] Z. Rubin *et al.*, Phys. Rev. B **59**, 12196 (1999). .

[17] Earlier work on *artificial* mixtures of SC cuprates, in which the materials were separately prepared and then mixed, showed classical percolation behavior with $p_c \approx 0.18\sim0.21$ and $t \approx 1.7\sim2.5$.[18,19]

[18] J. Koshy *et al.*, Phys. Rev. B **51**, 9096 (1995).

[19] J. J. Lin *et al.*, Physica C **210**, 455 (1993).

[20] J. M. Tarascon *et al.*, Science **235**, 1373 (1987).

[21] A similar effect was reported from a hydrostatic pressure experiment in $La_{1.84}Sr_{0.16}CuO_4$ and was interpreted in terms of the anisotropy of the stress dependence of T_c.[22]

[22] N. Tanahashi *et al.*, Jpn. J. Appl. Phys. **28**, L762 (1989).

[23] We arbitrarily defined the electric onset T_c as T, where $d\rho/dT$ becomes 10% of its peak value and the peak T_c as T for the $d\rho/dT$ peak.

[24] In fact, the $\rho(T)$ data in Fig. 2(a) suggest that p_c for SC is larger than p_c (0.26 for $x = 0.30$) for the normal state, which could be (partially) due to the finite magnitude of the applied electric current.

[25] J. L. Garcia-Muñoz *et al.*, Phys. Lett. A **149**, 319 (1990).

[26] H. Maeta *et al.*, J. Phys. Chem. Solids **65**, 1445 (2004).

[27] F. Gugenberger *et al.*, Phys. Rev. B **49**, 13137 (1994).

[28] B. Lorenz and C. W. Chu, e-print arXiv:condmat/0410367.

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

[30] F. Nakamura *et al.*, Phys. Rev. B **61**, 107 (2000).

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

[32] J.-P. Locquet *et al.*, Nature **394**, 453 (1998).

[33] P. H. Hor *et al.*, Phys. Rev. Lett. **58**, 911 (1987).

[34] U. Welp *et al.*, Phys. Rev. Lett. **69**, 2130 (1992).

[35] $\Delta T_o \sim 70$ K would be consistent with the presence of ∼0.58 GPa of tensile strain,[36] and this tensile strain would induce T_c enhancement of ∼2.6 K according to $dT_c/dP \sim -4.5$ K/GPa,[30] which is in agreement with our observation. However, the detailed mechanism of the tensile strain on the structural transitions has not been unveiled.

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

[37] See supplemental material at [http://link.aps.org/supplemental/10.1103/PhysRevB.83.220509] for information on material preparation and a supplementary figure.