Metallic state in La-doped $YBa_2Cu_3O_y$ thin films with n-type charge carriers

S. W. Zeng,[1,2] X. Wang,[1,2] W. M. Lü,[1,3] Z. Huang,[1] M. Motapothula,[1,2] Z. Q. Liu,[1,2] Y. L. Zhao,[1,2] A. Annadi,[1,2] S. Dhar,[1,3] H. Mao,[4] W. Chen,[2,4] T. Venkatesan,[1,2,3] and Ariando[1,2,*]

[1]*NUSNNI (Nanoscience and Nanotechnology Initiative)–Nanocore, National University of Singapore, Singapore*

[2]*Department of Physics, National University of Singapore, Singapore*

[3]*Department of Electrical and Computer Engineering, National University of Singapore, Singapore*

[4]*Department of Chemistry, National University of Singapore, Singapore*

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We report hole and electron doping in La-doped $YBa_2Cu_3O_y$ (YBCO) thin films synthesized by the pulsed laser deposition technique and subsequent *in situ* postannealing in ambient oxygen and vaccum. The n-type samples show a metallic behavior below the Mott limit and a high carrier density of $\sim 2.8 \times 10^{21}$ cm^{-3} at room temperature (T) at the optimally reduced condition. The in-plane resistivity(ρ_{ab}) of the n-type samples exhibits a quadratic T dependence in the moderate-T range and shows an anomaly at a relatively higher T probably related to pseudogap formation analogous to underdoped $Nd_{2-x}Ce_xCuO_4$ (NCCO). Furthermore, $\rho_{ab}(T)$, T_c, and T with minimum resistivity (T_{min}) were investigated in both p and n sides. The present results reveal the n-p asymmetry (symmetry) within the metallic-state region in an underdoped cuprate and suggest the potential toward ambipolar superconductivity in a single YBCO system.

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I. INTRODUCTION

High-T_c superconductivity in cuprates results from doping charge carriers into Mott insulators. The magnetic and superconducting properties of Mott insulators doped by holes (p-type carriers) are different from those doped by electrons (n-type carriers), showing asymmetry in the phase diagrams.[1] Moreover, their transport properties depend on the type of carriers, for example, in-plane normal-state resistivity exhibits quadratic temperature (T) dependence for n-type cuprates[2] while linear T dependence is seen for p-type cuprates with optimal doping.[3,4] Such comparisons of electron- and hole-doping asymmetry (symmetry) in cuprates should help to further our understanding of the cuprate superconductors.[5,6] The typical electron-hole asymmetry (symmetry) investigation is usually based on cuprates with different crystallographic structures such as NCCO (T′-structure) and $La_{2-x}Sr_xCuO_4$ (T-structure). These materials have different parent Mott insulators and thus exhibit different properties even without doping.[7] Therefore, it is desirable to dope electrons and holes into a Mott insulator without changing the crystallographic structure and address the physics in both sides of such "ambipolar" cuprate.

An ambipolar single-crystal cuprate was first achieved in $Y_{1-z}La_z(Ba_{1-x}La_x)_2Cu_3O_y$ ($x = 0.13$, $z = 0.62$) with charge carriers ranging from 7% of holes per Cu to 2% of electrons per Cu.[8] It was also found that $Y_{0.38}La_{0.62}(Ba_{0.87}La_{0.13})_2Cu_3O_y$ exhibits asymmetric behavior in magnetic ground states and transport properties between electron- and hole-doped sides.[9] However, this asymmetric comparison was limited to insulating state near the zero-doping region due to low carrier density in n-type samples. In order to fully investigate the n-p asymmetry (symmetry), more heavily electron-doped materials in the YBCO system which exhibit metallic and even superconducting behaviors are desirable.

Effective reduction of the as-grown materials is necessary to dope n-type carriers in cuprates.[10] In general, the bulk single crystals are annealed at high T (850–1080 °C) in low oxygen partial pressure (P_{O2}) for tens of hours to several days. For the thin-film growth, oxygen can be removed uniformly and efficiently with postannealing for several tens of minutes, since oxygen diffusion along the c axis is much easier and the diffusion lengths are comparable to the film thickness.[1] Recently, an electrochemical technique was used to remove oxygen in pure YBCO thin films and achieve n-type metallic states.[11] However, carrier density of the n-type sample was still low ($\sim 2.5 \times 10^{20}$ cm^{-3}) and the metallic state was only observed above 120 K. Chemical doping is necessary for achieving higher electron density. Since La^{3+} possesses a higher valence state than Ba^{2+}, La substitution for Ba in YBCO is expected to provide additional electrons.[8] Therefore, one can expect that more electrons can be doped by varying the La content in $Y_{1-z}La_z(Ba_{1-x}La_x)_2Cu_3O_y$ and efficiently removing oxygen using a thin-film growth method. In this work, we grow the $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$ thin films using a pulsed laser deposition (PLD) process and shift the materials from p-type superconducting to n-type metallic states by postannealing in low P_{O2}. The resistivity of n-type samples exhibits a Fermi-liquid behavior and an anomaly at a certain T below which the resistivity begins to decrease rapidly. This behavior is similar to that of the underdoped nonsuperconducting NCCO, suggesting the potential of n-type superconductivity in a YBCO system if electrons are further doped.

II. EXPERIMENTAL

The starting materials for the preparation of the ceramic target were pure cation oxides powders of Y_2O_3 (99.999%), La_2O_3 (99.999%), $BaCO_3$ (99.997%), and CuO (99.9999%). These were weighed and mixed according to the chemical formula of $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$. The mixture was then fired at 850, 900, and 900 °C for 10 h each and at 980 °C for 20 h in air and ground between each firing. On the final firing, the powder was pressed into a disk-shaped pellet for the PLD process. Thin films with thickness of

~260 nm were grown on (001) $LaAlO_3$ (LAO) substrates by a PLD system using the prepared target. The deposition T and P_{O2} for all samples were 760 °C and 200 mTorr, respectively. Since we cannot accurately measure the oxygen content, we label the films annealed at different conditions by carriers per Cu atom which is determined by the carrier densities (from Hall measurements) and volume of primitive cell of YBCO. Three p-type samples with carrier densities (at 300 K) of $p = 0.019$, 0.034, and 0.055 holes/Cu were obtained by *in situ* postannealing in the PLD chamber at 560 °C for 20 min in $P_{O2} = 0.02$, 0.2, and 3 Torr, respectively. A p-type sample with higher carrier doping of $p = 0.068$ holes/Cu was obtained by reannealing in a tube furnace at 600 °C for 30 min in air. N-type samples with carrier densities of $n = 0.02$, 0.029, 0.034, and 0.038 electrons/Cu were obtained by *in situ* postannealing at 640 °C in a vacuum ($P_{O2} < 10^{-5}$ Torr) for 10, 30, 50, and 80 min, respectively, and then cooling down to room temperature at 30 °C/min. In order to obtain higher electron dopings of $n = 0.087$ and 0.166, the samples annealed for 80 min were reannealed in a vaccum at 380 °C with a ramp rate of 30°C/min for 0 min (with immediate cooling at $T = 380$ °C) and 10 min, respectively. Note that this reannealing process is critical for reduction of oxygen as confirmed by expansion of the c axis. The composition of the grown films was analyzed by the Rutherford backscattering spectrometry (RBS) and was found to approximately be the same as that of the target. The crystallographic structure of the thin films was measured by x-ray diffraction (XRD). The transport property measurements were made using a Quantum Design Physical Property Measurement System (PPMS) at temperatures ranging from 2 to 400 K. The resistivity was measured by the four-probe method and Hall effects by Van der Pauw geometry with the magnetic field swept from −5 to 5 T.

III. RESULTS AND DISCUSSION

Figure 1 shows the θ-2θ XRD patterns of four $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$ samples annealed in air and vacuum. Only (00l) peaks of thin films and LAO substrates [indicated with S(00l)] were clearly observed, where l is an integer, confirming the c-axis-oriented epitaxial growth. The c-axis lattice constant, d, of the sample annealed in air

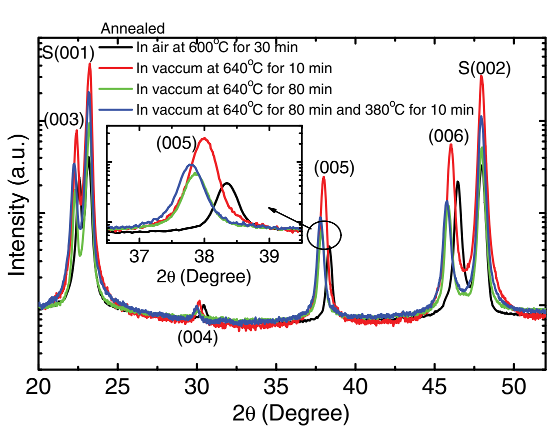

FIG. 1. (Color online) X-ray diffraction patterns of $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$ thin films. Inset: (005) peaks.

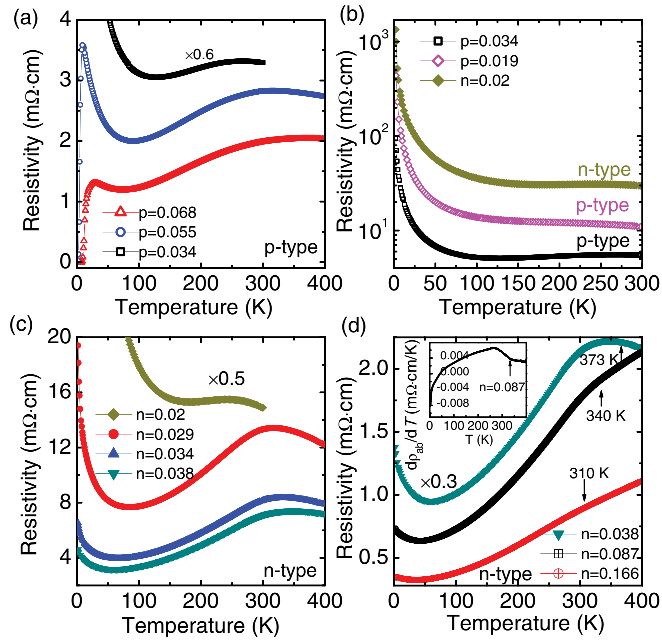

FIG. 2. (Color online) The in-plane resistivity ρ_{ab} as a function of temperature for p-type and n-type thin films. The samples were labeled by the hole (p) and electron (n) doping at 300 K (per Cu atom), which is obtained by Hall measurement. Inset of panel (d) is the temperature derivative of ρ_{ab} for the sample with $n = 0.087$.

was determined to be 11.728 Å which is less than that of the as-grown (in air) crystal $Y_{0.38}La_{0.62}(Ba_{0.87}La_{0.13})_2Cu_3O_y$ (11.763 Å).[8] This indicates that our samples have larger La composition substituted for Ba and thus possess smaller d, which is in fair agreement with the established empirical relation.[12] The (00l) peaks of the samples annealed in a vacuum shift to smaller angles compared with those of the sample annealed in air, suggesting an expansion of the c axis. It is known that d of $YBa_2Cu_3O_y$ increases as y decreases.[13,14] This supports the fact that oxygen was removed as $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$ films were annealed in low P_{O2} and vacuum.

Figures 2(a)–2(d) show the evolution of the T dependence of ρ_{ab} upon changing carrier doping levels at 300 K. (The p- and n-type charge carriers were confirmed by Hall effects measurements in Fig. 4.) Samples with high hole-doping level show superconductivity; for example, the sample with $p = 0.068$ exhibits zero-resistance T_c of ~8 K. As p decreases, and thus the oxygen content in the sample is reduced, T_c decreases, ρ_{ab} increases and the samples show evolution from superconductors to insulators [Fig. 2(b)]. To further reduce oxygen content and obtain electron doping, thin films were annealed in a vacuum. For low-electron-doping level, the sample exhibits insulating behavior [Fig. 2(b)]. As doping increases, ρ_{ab} goes down and the samples show metallic behavior at high T [Figs. 2(c) and 2(d)], although ρ_{ab} shows an upturn at low T. For n-type samples with $n < 0.087$, the magnitude of ρ_{ab} within the metallic region is above the Mott limit.[15] Moreover, the metallic behavior is already established at doping $n = 0.029$ (5.0×10^{20} cm^{-3}) near the Mott insulating state[9], and electron-electron scatterings are dominant in transport behavior, which is discussed in the

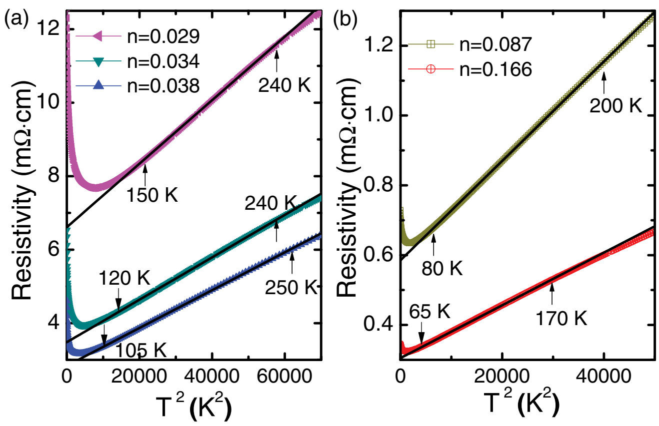

FIG. 3. (Color online) ρ_{ab} of n-type samples as a function of T^2 for the same data shown in Fig. 2. Solid line is the fitting to the data. Arrows indicate the T where ρ_{ab} deviates from Fermi-liquid behavior.

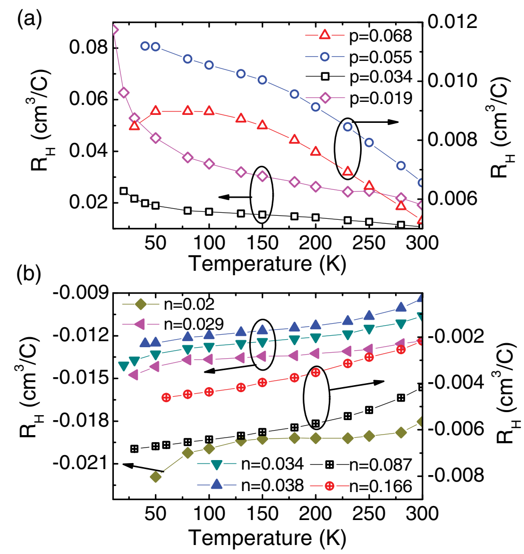

FIG. 4. (Color online) The Hall coefficients R_H of p-type (a) and n-type (b) thin films as functions of temperature.

following text. This suggests a bad metal behavior at low doping.[17–19] However, the sample with $n = 0.166$ is obviously metallic since ρ_{ab} is below the Mott limit from ~300 K down to the lowest T measured. The ρ_{ab} of the sample with highest doping (~0.88 mΩ cm at 300 K), to the best of our knowledge, is the lowest resistivity in n-type YBCO system.[8,9,11]

In the moderate-temperature range, ρ_{ab} of the n-type samples is approximately proportional to T^2, as is demonstrated in Fig. 3, indicating a conventional Fermi-liquid (FL) behavior due to electron-electron scattering.[2] By fitting the data to the equation $\rho_{ab}(T) = \rho_0 + A_2T^2$, we can obtain the quadratic scattering rate A_2. A_2 decreases rapidly from $\sim 8.6 \times 10^{-5}$ to $\sim 7.5 \times 10^{-6}$ mΩ cm K^{-2} with increasing electron doping, as is shown in Fig. 5. This behavior of A_2 is similar to those in NCCO as electron doping increases.[20] Interestingly, the magnitudes of A_2 in our films are of the order of 10^{-6} to 10^{-5} mΩ cm K^{-2}, which is comparable to those of NCCO.[2,20] The similarity in magnitude and evolution of A_2 between $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$ and NCCO hint at the possibility that the electron-electron scattering in n-type cuprates is governed by essentially the same physics, regardless of the different crystallographic structures. As is marked by arrows, the FL regimes shift to lower T as the electron doping increases. It has been demonstrated that the ground state of heavily overdoped n-type cuprates is dominated by FL behavior.[21] The shift of FL regimes probably suggests the same ground state in n-type YBCO system if electrons are overdoped. In contrast, the quadratic dependence with T of ρ_{ab} is not observed in p-type samples.

At T above ~250 K, weakening of the quadratic dependence of ρ_{ab} is observed for electron-doped samples.[2] ρ_{ab} even saturates and becomes nonmetallic at higher T for $n < 0.087$. For $n = 0.087$ and 0.166, ρ_{ab} tends to saturate at higher T although it is metallic up to 400 K. The saturation of ρ_{ab} can also be observed in p-type samples. On close examination, for samples with $n \geqslant 0.038$, ρ_{ab} begins to decrease rapidly at around the T marked by arrows (T_ρ) with decreasing T. T_ρ can be obtained by the T derivative of ρ_{ab} and is around the T where $d\rho_{ab}/dT$ starts to increase,[22] as is shown in inset of Fig. 2(d). The steep decrease of ρ_{ab} is also observed in underdoped $Nd_{2-x}Ce_xCuO_4$ with $x = 0.025$–0.075 and is related to the formation of pseudogap confirmed by optical spectra.[22,23] In $Nd_{2-x}Ce_xCuO_4$, T_ρ decreases as x increases and disappears at optimal doping of $x = 0.15$. In our samples, T_ρ also decreases with increasing electron doping. Importantly, this anomaly in ρ_{ab} become less noticeable at higher electron doping, which is similar to NCCO. Whether the pseudogap begins to evolve below T_ρ requires further investigation by optical spectroscopy. Nevertheless, the anomalies in ρ_{ab} of n-type films suggest the possibility of its being a precursor of superconductivity.

Figure 4 shows the Hall coefficients (R_H). The samples annealed in a vacuum exhibit negative R_H all the way below 300 K, indicating electron doping. The electron density of optimally reduced sample is $\sim 2.87 \times 10^{21}$ cm^{-3} ($R_H \sim -0.00217$ cm^3/C) at 300 K, which is one order of magnitude higher than those in $Y_{0.38}La_{0.62}(Ba_{0.87}La_{0.13})_2Cu_3O_y$ single crystal ($\sim 2.2 \times 10^{20}$ cm^{-3}, $R_H \sim -0.028$ cm^3/C)[8] and pure YBCO film ($\sim 2.5 \times 10^{20}$ cm^{-3}).[11] The magnitude of R_H in insulating film with $n = 0.02$ ($R_H \sim -0.018$ cm^3/C at 300 K) increases more sharply at low T, which is similar to that of the single crystal with near electron doping ($R_H \sim -0.028$ cm^3/C at 300 K).[8] Futhermore, ρ_{ab} at 300 K of the insulating thin film exhibits a similar value (~29 mΩ cm) to that in single crystals (~30 mΩ cm).[8] These suggest that the crystal quality of our thin films is comparable to that of a single crystal. As is shown in Fig. 5, d continuously increases by hole depletion and electron doping across the zero-doping state, although it is moderate at the higher electron-doping region, which indicates that electrons were continuously doped as oxygens were removed. Therefore, high carrier density and low ρ_{ab} in n-type thin films are caused by electron doping.

It is found that in all the samples with metallic state, even in superconducting p-type samples, ρ_{ab} exhibits insulating-like behavior below T with minimum ρ_{ab} ($T_{\min}$). This behavior has been investigated in underdoped cuprates but its origin is still unclear.[24–26] We also show T_c and $T_{\min}$ as a function of carrier density at 300 K (n_{300K}) in Fig. 5. $T_{\min}$ was found to share the

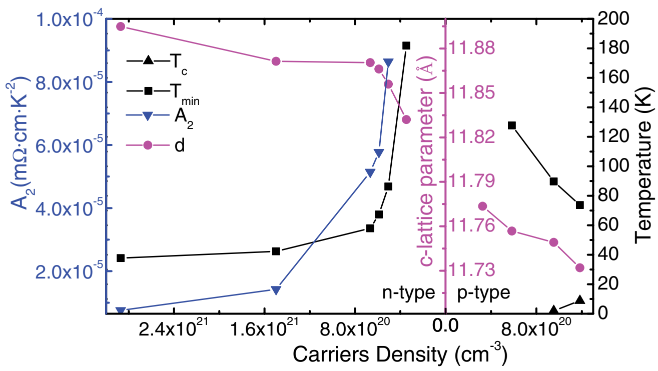

FIG. 5. (Color online) Superconductivity transition temperature T_c, temperature with minimum resistivity $T_{\min}$, c-lattice parameter d, and quadratic scattering rate A_2 as a function of carriers density at 300 K. $T_{\min}$ is obtained by calculating the derivatives $d\rho_{ab}/dT$ and is the temperature when $d\rho_{ab}/dT = 0$. A_2 is obtained from fitting $\rho_{ab}(T) = \rho_0 + A_2T^2$ to data within $\rho_{ab} \propto T^2$ region shown in Fig. 3.

same evolution as a function of doping in both n- and p-type thin films, mainly decreasing with increasing n_{300K}. However, $T_{\min}$ decreases much more rapidly in n-type samples, from 181.8 K at $n_{300K} \approx 3.46 \times 10^{20}$ cm^{-3} to 57.9 K at $n_{300K} \approx 6.65 \times 10^{20}$ cm^{-3}, than that in p-type samples, from 127.7 K at $n_{300K} \approx 5.8 \times 10^{20}$ cm^{-3} to 73.7 K at $n_{300K} \approx 1.18 \times 10^{21}$ cm^{-3}. At higher electron doping, $T_{\min}$ exhibits a slight drop and tends to saturate. Superconductivity emerges at $n_{300K} \approx 9.5 \times 10^{20}$ cm^{-3} ($T_c = 2$ K) when $T_{\min} =$ 89.7 K in p-type samples and T_c increases with decreasing $T_{\min}$. However, superconductivity was not observed in n-type samples even if $T_{\min}$ was much lower than 89.7 K and the doping level of electrons was higher than that of holes. Interestingly, it was found that the amplitude of A_2 exhibits the same evolution as $T_{\min}$ with electron doping, suggesting an intimate relationship between electron-electron scattering and the metal-insulator transition in n-type YBCO system.

IV. CONCLUSION

In conclusion, metallic n-type La-doped YBCO thin films were successfully obtained by PLD technique and postannealing in a vacuum. Above around T of the metallic-insulating transition, the n-type samples exhibited T^2-dependent resistivity. At relatively higher T, ρ_{ab} showed an anomaly probably due to the formation of a pseudogap, which has been observed in underdoped NCCO. P-type samples were also investigated and showed different evolutions with doping in $\rho_{ab}(T)$, T_c, and $T_{\min}$. The present work could be a significant step toward ambipolar superconductivity in a YBCO system.

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*ariando@nus.edu.sg

[1] N. P. Armitage, P. Fournier, and R. L. Greene, Rev. Mod. Phys. **82**, 2421 (2010).

[2] C. C. Tsuei, A. Gupta, and G. Koren, Phys. C (Amsterdam, Neth.) **161**, 415 (1989).

[3] M. Gurvitch and A. T. Fiory, Phys. Rev. Lett. **59**, 1337 (1987).

[4] 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).

[5] E. Dagotto, Rev. Mod. Phys. **66**, 763 (1994).

[6] P. A. Lee, N. Nagaosa, and X. G. Wen, Rev. Mod. Phys. **78**, 17 (2006).

[7] M. A. Kastner, R. J. Birgeneau, G. Shirane, and Y. Endoh, Rev. Mod. Phys. **70**, 897 (1998).

[8] K. Segawa and Y. Ando, Phys. Rev. B **74**, 100508 (2006).

[9] K. Segawa, M. Kofu, S.-H. Lee, I. Tsukada, H. Hiraka, M. Fujita, S. Chang, K. Yamada, and Y. Ando, Nat. Phys. **6**, 579 (2010).

[10] Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989).

[11] T. Nojima, H. Tada, S. Nakamura, N. Kobayashi, H. Shimotani, and Y. Iwasa, Phys. Rev. B **84**, 020502 (2011).

[12] X. S. Wu and J. Gao, Phys. C (Amsterdam, Neth.) **315**, 215 (1999).

[13] R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck Jr., and L. W. Rupp Jr., Phys. C (Amsterdam, Neth.) **165**, 419 (1990).

[14] J. D. Jorgensen, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, H. Claus, and W. K. Kwok, Phys. Rev. B **41**, 1863 (1990).

[15] In a quasi-two-dimensional system, the Mott limit for metallic transport requires that the resistivity should satisfy the condition $\rho_{ab} \leqslant hd/e^2$, where d is the interlayer distance.[16] This suggest a condition $\rho_{ab} \leqslant 0.82$ mΩ cm for metallic conduction in YBCO system with a distance between CuO_2 planes of 0.318 nm.

[16] Y. Ando, *Mott Limit in High-Tc Cuprates* (Springer, Berlin, 2007).

[17] V. J. Emery and S. A. Kivelson, Phys. Rev. Lett. **74**, 3253 (1995).

[18] Y. Ando, A. N. Lavrov, S. Komiya, K. Segawa, and X. F. Sun, Phys. Rev. Lett. **87**, 017001 (2001).

[19] N. E. Hussey, K. Takenaka, and H. Takagi, Philos. Mag. **84**, 2847 (2004).

[20] N. A. Babushkina, L. M. Belova, and A. P. Zhernov, Phys. C (Amsterdam, Neth.) **282**, 1163 (1997).

[21] K. Jin, N. P. Butch, K. Kirshenbaum, J. Paglione, and R. L. Greene, Nature (London) **476**, 72 (2011).

[22] Y. Onose, Y. Taguchi, K. Ishizaka, and Y. Tokura, Phys. Rev. B **69**, 024504 (2004).

[23] Y. Onose, Y. Taguchi, K. Ishizaka, and Y. Tokura, Phys. Rev. Lett. **87**, 217001 (2001).

[24] S. J. Hagen, X. Q. Xu, W. Jiang, J. L. Peng, Z. Y. Li, and R. L. Greene, Phys. Rev. B **45**, 515 (1992).

[25] P. Fournier, J. Higgins, H. Balci, E. Maiser, C. J. Lobb, and R. L. Greene, Phys. Rev. B **62**, R11993 (2000).

[26] Y. Dagan, M. C. Barr, W. M. Fisher, R. Beck, T. Dhakal, A. Biswas, and R. L. Greene, Phys. Rev. Lett. **94**, 057005 (2005).