

Doping n -type carriers by La substitution for Ba in the $\text{YBa}_2\text{Cu}_3\text{O}_y$ system

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Thus far, there is no cuprate system where both n -type and p -type charge carriers can be doped without changing the crystallographic structure. For studying the electron-hole symmetry in an identical structure, we try to dope n -type carriers to $\text{YBa}_2\text{Cu}_3\text{O}_y$ system by reducing oxygen content and substituting La^{3+} ions for Ba^{2+} . Single crystals of La-doped $\text{YBa}_2\text{Cu}_3\text{O}_y$ are grown by a flux method with Y_2O_3 crucibles and it is confirmed that La actually substitutes $\sim 13\%$ of Ba. The oxygen content y can be varied between 6.21 and 6.95 by annealing the crystals in an atmosphere with controlled oxygen partial pressure. The in-plane resistivity ρ_{ab} at room temperature was found to increase with decreasing oxygen content y down to 6.32, but interestingly further decrease in y results in a decrease in ρ_{ab} . The most reduced samples with $y=6.21$ show ρ_{ab} of ~ 30 m Ω cm at room temperature, which is as much as seven orders of magnitude smaller than the maximum value at $y=6.32$. Furthermore, both the Hall coefficient and the Seebeck coefficient of the $y=6.21$ samples are found to be negative at room temperatures. The present results demonstrate that the nondoped Mott-insulating state has been crossed upon reducing y and n -type carriers are successfully doped in this material.

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High- T_c superconducting cuprates are classified into two types in terms of the sign of charge carriers: one has p -type charge carriers (hole-doped system) and the other has n -type ones (electron-doped system).¹ The magnetic and superconducting phase diagrams of these types are known to be different from each other, and thus a whole phase diagram is conventionally drawn by connecting those at the nondoping point. However, discontinuity remains in the low-carrier limit, because there has been no prototypical system in which the type of carriers can be continuously changed from p type to n type while keeping an identical crystallographic structure. In the so-called “214”-type layered cuprates either electrons or holes can be doped; however, hole-doped 214 systems, for example, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO), have T or T^* structure, whereas electron-doped 214 systems like $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (NCCO) have different T' structure.² For the study of electron-hole symmetry in cuprates, it would be very useful if one could change the sign of charge carriers without changing the crystallographic structure unlike the case of 214 systems.

After the failure of various efforts to synthesize electron-doped cuprates, an empirical relation between the doping and crystallographic structures was proposed.³ The coordination number of Cu atoms seems important for determining the sign of carriers; p -type carriers are favored with the coordination number of 5 or 6, while n -type ones are favored for 4-coordinated Cu. Indeed, it seems difficult to dope electrons to LSCO with T structure,⁴ or to dope holes to an infinite-layer system with four-coordinated Cu atoms.⁵ Furthermore, calculations of the Madelung potential⁶ are consistent with the behavior.

In $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO) the oxygen content can be varied in a very wide range from hole-doped compositions to a nondoped insulating one. The doping can be varied also by chemical substitutions;^{7,8} for example, it is well known that substitutions of Ca^{2+} for Y^{3+} in the YBCO system increases the number of holes and shifts the doping range into overdoped regime.⁹ On the other hand, La^{3+} substitution for Ba^{2+} is expected to decrease holes. If the La substitution for Ba is

combined with the reduction of oxygen, the available doping range would shift *across* the nondoping point. This may allow one to study both the electron-doped and the hole-doped regimes in the same system, and the above empirical relation could be scrutinized.

In this work, we explore the ways to change the sign of charge carriers by combining the La substitution for Ba and the oxygen reduction in the YBCO system. In samples where La is substituted for 13% of Ba, we observe that the in-plane resistivity at room temperature becomes maximum at $y \sim 6.32$, and further reduction to $y=6.21$ leads to a decrease in the resistivity down to ~ 30 m Ω cm, which is seven orders of magnitude smaller than the maximum value. Furthermore, these $y=6.21$ samples show both a negative Hall coefficient and a negative thermoelectric power, indicating that electrons are successfully doped.

Single crystals of La-doped YBCO are grown by a flux method using Y_2O_3 crucibles.¹⁰ In the starting material, La_2O_3 is substituted for BaO_2 by 10%, and Y_2O_3 is provided by the crucibles. The purity of the raw material is 99.99% for CuO and 99.9% for BaO_2 , La_2O_3 , and Y_2O_3 (crucibles). The actual composition of the grown crystals is analyzed by the inductively coupled plasma atomic-emission spectroscopy (ICP-AES) and is found to be $\text{Y}_{0.38}\text{Ba}_{1.74}\text{La}_{0.88}\text{Cu}_3\text{O}_y$. Hence, La is substituted for both 13% of Ba and 62% of Y, so we express the composition as $\text{Y}_{1-z}\text{La}_z(\text{Ba}_{1-x}\text{La}_x)_2\text{Cu}_3\text{O}_y$ with $x=0.13$ and $z=0.62$. Since Y and La ions have the identical valence number of +3, the carrier density should not depend on z . In this paper, we denote the specific composition of our single crystals of $\text{Y}_{0.38}\text{La}_{0.62}(\text{Ba}_{0.87}\text{La}_{0.13})_2\text{Cu}_3\text{O}_y$ by YLBCO_y for simplicity. The lattice parameters of as-grown crystals are determined to be $a=3.901$ Å and $c=11.763$ Å by the x-ray diffraction, where, interestingly, a is much longer than pristine YBCO. In addition, no signal of any other phase is observed. The annealing is performed under various conditions shown in Table I by using a home-made furnace which can control the gas flow with a precise oxygen partial pressure. It should be noted that the oxygen

TABLE I. Annealing conditions for YLBLCO crystals. y is the measured oxygen content.

| y | T_{anneal} (°C) | Duration time | Atmosphere | T_c (K) |
|------|--------------------------|---------------|---------------------------------------|-----------|
| 6.95 | 485 | ≤ 7 days | 1 atm O ₂ | 25 |
| 6.78 | 550 | 40 hours | 0.06 atm O ₂ | |
| 6.43 | 550 | 40 hours | 2×10^{-4} atm O ₂ | |
| 6.32 | 700 | 12 hours | 2×10^{-5} atm O ₂ | |
| 6.29 | 750 | 12 hours | 2×10^{-5} atm O ₂ | |
| 6.21 | 890 | 6 hours | 2×10^{-5} atm O ₂ | |

control in our YLBLCO crystals is completely reversible between $y=6.21$ – 6.95 . Also, no structural transition, except for the ordinary orthorhombic-to-tetragonal transition, was reported for samples with similar compositions;¹¹ therefore, crystallographically our samples are essentially unchanged down to $y=6.21$. The oxygen content is determined mainly by iodometric titration for polycrystalline samples with the identical composition to YLBLCO single crystals annealed at the same time, which yields an error of less than ± 0.02 . The titration result is corroborated by precision measurements of the mass of single crystals. Twinned structures are observed only in $y=6.95$ samples, but no detwinning is performed. The in-plane resistivity and the Hall coefficient are measured by the six-probe method,¹² but a two-wire method is employed for measuring the resistivity of samples with very high resistance. At least two samples are measured for each composition in order to check for reproducibility, and the accuracy of the present result is $\sim 20\%$ for the six-probe measurements, and $\sim 50\%$ for the two-wire measurements.

Figure 1(a) shows the temperature dependence of the in-plane resistivity for YLBLCO with $y=6.95$ together with the data for pristine YBCO with $y=6.55$. The zero-resistance T_c of the YLBLCO sample is ~ 25 K. The temperature dependence of the Hall coefficient [Fig. 1(b)] in YLBLCO_{6.95} is found to be very close to that in YBCO_{6.55}, and this result suggests that the hole concentration of YLBLCO_{6.95} corresponds to that of YBCO_{6.55}, which was suggested to be $\sim 7\%$ per Cu (Ref. 13). Corroboratively, the slope of the temperature dependence of ρ_{ab} in the YLBLCO_{6.95} is similar to that in YBCO_{6.55}. In the YBCO system, there is no simple relation between the oxygen content and the exact hole concentration, because the latter depends also on the oxygen ordering in the Cu-O chain layers,¹⁴ as well as on how the positive charge is transferred from the Cu-O chains to the CuO₂ planes. Therefore, it is not simple to understand how the above two compositions produce an identical hole concentration. Nevertheless, the present result might be helpful for estimating the hole concentration of optimally doped YBCO_{6.95}, because the effect of the oxygen ordering is quite modest in nearly fully oxygenated samples. As mentioned above, the hole concentration of YLBLCO_{6.95} is likely to be $\sim 7\%$ /Cu, and thus in YBCO_{6.95} it is inferred to be $\sim 20\%$ /Cu by simple calculation (if so, the average valence of Cu in the Cu-O chain layers would be +2.50). We note that the actual hole concentration in the CuO₂ planes can be

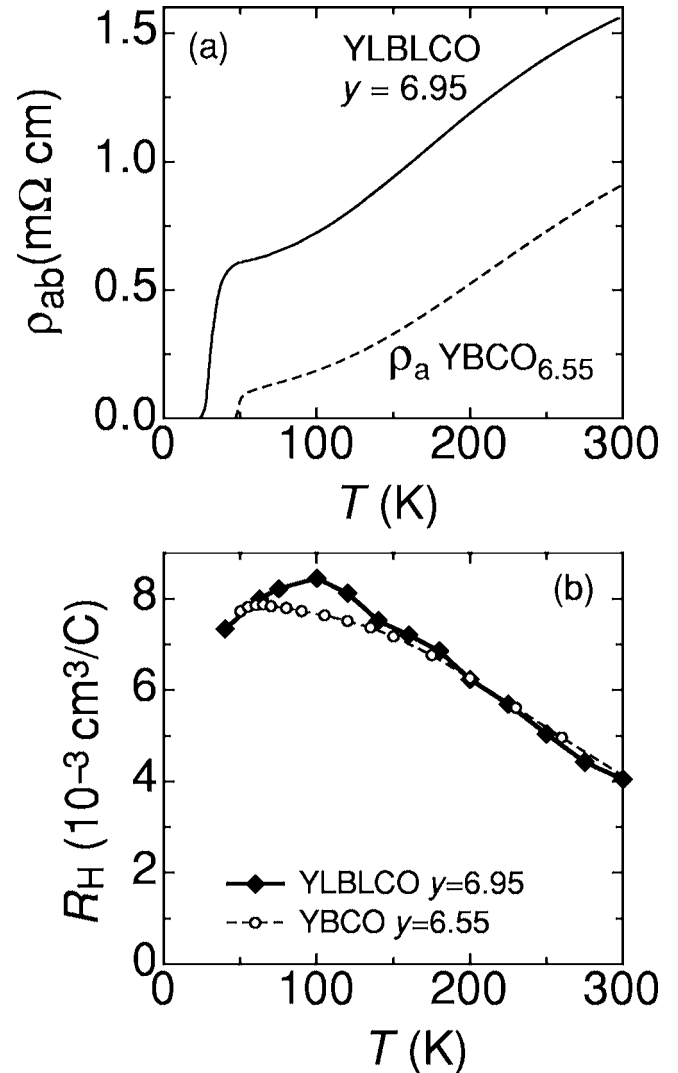


FIG. 1. The temperature dependences of (a) the in-plane resistivity and (b) the Hall coefficient in YLBLCO with $y=6.95$, together with those for YBCO with $y=6.55$.

different from $\sim 20\%$ /Cu, if the La substitution affects the charge transfer from the chains to the planes.

The oxygen content of YLBLCO crystals can be decreased by reduction annealings. Figure 2 shows the evolution of the temperature dependence of the in-plane resistivity upon changing y in a semilog plot. ρ_{ab} increases significantly with decreasing y down to 6.32. In samples with $y=6.32$, ρ_{ab} at room temperature becomes as large as $\sim 10^5 \Omega \text{ cm}$, which is about five orders of magnitude larger than that of La₂CuO₄ (Ref. 15). We emphasize that the observed insulating behavior is not due to decompositions, because the samples can be reannealed to another composition and give consistent results. When the oxygen content is decreased further from 6.32, interestingly, we observe a *decrease* in resistivity with decreasing y (broken lines in Fig. 2).

Figures 3(a)–3(c) show temperature dependences of the transport properties in the most reduced YLBLCO crystals with $y=6.21$. The in-plane resistivity in YLBLCO_{6.21} becomes 30 mΩ cm at room temperature [Fig. 3(a)], which is seven orders of magnitude smaller than that in YLBLCO_{6.32}.

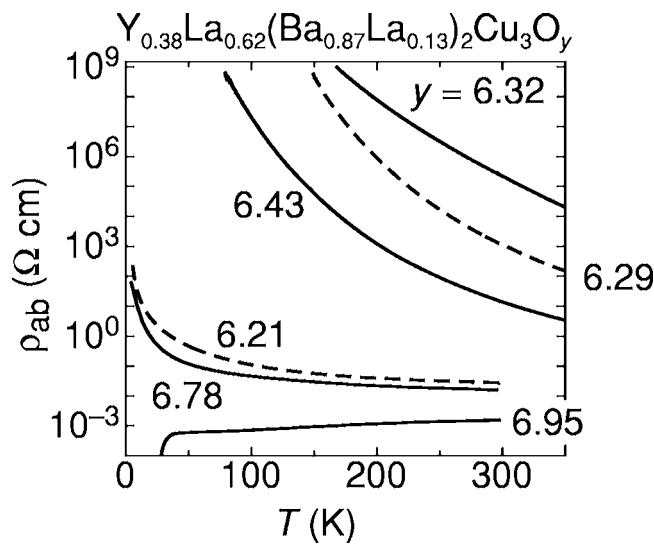


FIG. 2. Semilog plot of the temperature dependence of ρ_{ab} in YLBCO with various oxygen contents. The broken lines are for $y < 6.32$, and the solid lines are for larger y .

The temperature dependence of ρ_{ab} shows an insulating behavior below 300 K. The Hall coefficient shown in Fig. 3(b) is negative all the way below 300 K. The temperature dependence of R_H is quite modest except at low temperatures, which gives confidence in estimating the carrier concentration from the 300 K value of R_H to be $\sim 2\%$ per Cu (Ref. 16). Furthermore, the Seebeck coefficient also shows a negative sign [Fig. 3(c)]. These results clearly show that the sign of the charge carriers in this sample is *negative*. At the moment we cannot rule out the possibility that the *n*-type carriers are doped to the Cu-O chain layers rather than to the CuO_2 planes; however, such a possibility is very unlikely because the Hall mobility in $\text{YLBCO}_{6.21}$, which is obtained to be $1.0 \text{ cm}^2/\text{Vs}$ at 300 K, is comparable to that in $\text{YLBCO}_{6.95}$ ($2.7 \text{ cm}^2/\text{Vs}$) and pristine YBCO (Ref. 13); such a high mobility of *n*-type carriers would not be expected in the Cu-O chain layers at $y=6.21$, at which the chains are very disordered and fragmented.

Figures 4(a) and 4(b) show the y dependences of ρ_{ab} and S_{ab} at fixed temperatures. ρ_{ab} shows a steep maximum at $y \sim 6.32$, where apparently there are few carriers. The Hall coefficient in this sample measured at room temperature is positive and $\sim 5 \times 10^4 \text{ cm}^3/\text{C}$ within an error of $\sim 50\%$, which corresponds to the hole concentration of $\sim 1 \times 10^{-6}$ per Cu. These observations indicate that $\text{YLBCO}_{6.32}$ is very close to the nondoped state. The sign of S_{ab} correspondingly changes from positive to negative with decreasing y across ~ 6.3 [Fig. 4(b)]. The absolute value of S_{ab} appears to increase upon approaching the nondoped composition. Probably, S_{ab} for $y=6.32$ is in the middle of a jump from positive to negative and happens to be intermediate. Similar behavior of the Seebeck coefficient is observed also in the $\text{GdBaCo}_2\text{O}_{5+x}$ system, where continuous ambipolar doping is possible.¹⁷

As discussed above, about 2% of electrons per Cu is successfully doped to YBCO system, but the system still remains insulating. Doping more electrons to this system is

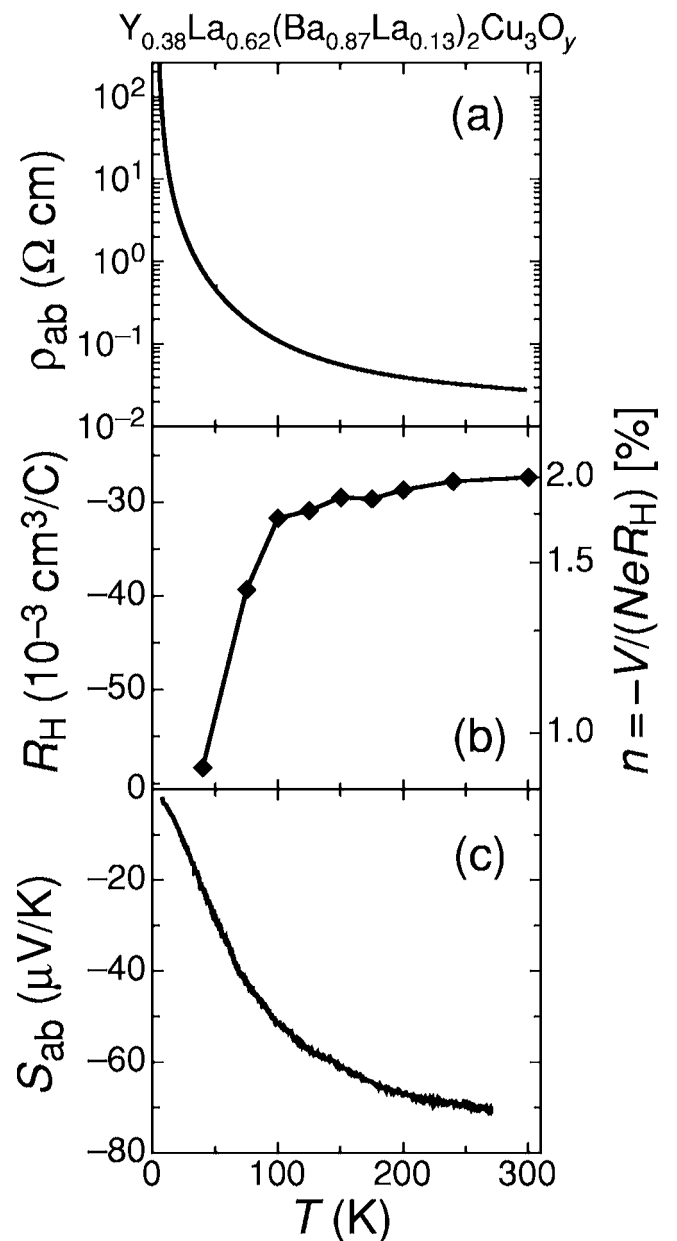


FIG. 3. The temperature dependences of three transport properties, (a) the in-plane resistivity, (b) the Hall coefficient, and (c) the Seebeck coefficient, in YLBCO with $y=6.21$.

desirable, but unfortunately further reduction of YLBCO has not been successful yet.¹⁸ One may guess that increasing x is helpful for increasing *n*-type carriers. In this respect, we have also grown crystals with larger x ($=0.18$ and 0.32), but it turns out that low enough y cannot be achieved in those high- x samples. Hence, there is apparently a delicate balance between the x value and the lowest achievable y value. This is probably the main reason why this system has not been discovered as an electron-doped system. There still remains a possibility that optimizing the x value allows further electron doping to make the system metallic and/or superconducting.

Figure 4(c) shows a speculative phase diagram for YLBCO. In principle, one would be able to draw the phase diagram without discontinuity at the nondoping point just by

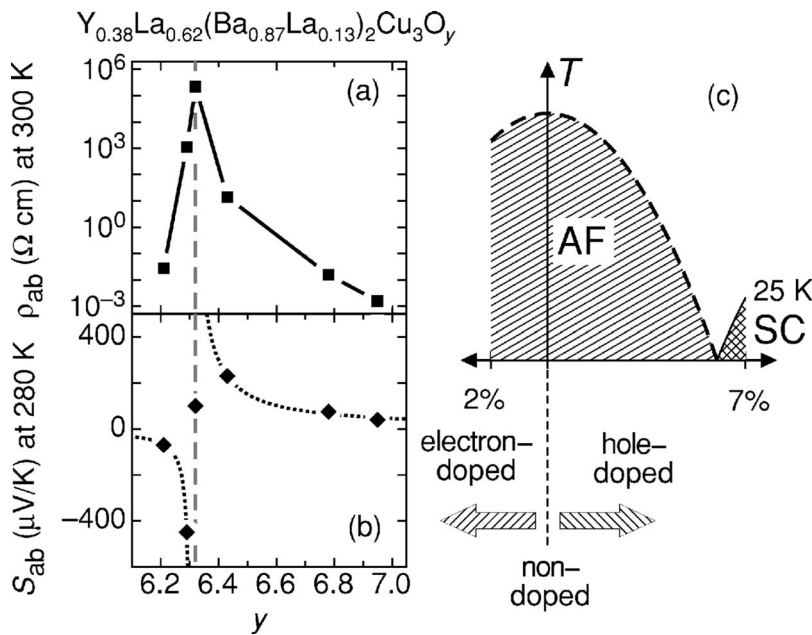


FIG. 4. Oxygen-content dependence of (a) the in-plane resistivity at 300 K and (b) the Seebeck coefficient at 280 K in YLBLCO. (c) Speculative phase diagram of YLBLCO.

determining the Néel temperature T_N by a suitable means. We would like to emphasize that, to the best of our knowledge, this system is the first bilayer cuprate having n -type carriers.

Since the Cu atoms in the CuO_2 planes in the so-called “123” structure are five-coordinated, it appears that the coordination number of Cu does not play a prohibitive role for determining the sign of charge carriers. Instead, the Cu-O bond length in the CuO_2 planes may be important, because that length in the present system ($\approx 1.95 \text{ \AA}$) is notably longer than that in other hole-doped cuprates and is almost equal to the NCCO system.

In conclusion, about 2% of n -type carriers are successfully doped in a Y-based bilayer cuprate in which La is substituted for Ba by 13%. In this system one can change the doping from p type to n type by reducing the oxygen content. Thus, we have spanned a doping range from negative to positive across the nondoping state in the same crystal. This opens a new avenue for studying the electron-hole symmetry (asymmetry) in cuprates.

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- ¹Y. Tokura, H. Takagi, and S. Uchida, *Nature (London)* **337**, 345 (1989).
- ²Y. Tokura, A. Fujimori, H. Matsubara, H. Watabe, H. Takagi, S. Uchida, M. Sakai, H. Ikeda, S. Okuda, and S. Tanaka, *Phys. Rev. B* **39**, 9704 (1989).
- ³Y. Tokura and T. Arima, *Jpn. J. Appl. Phys., Part 1* **29**, 2388 (1990).
- ⁴A. Tsukada, H. Yamamoto, and M. Naito, *Physica C* **426-431**, 454 (2005).
- ⁵K. I. Kubo and H. Yamauchi, *Phys. Rev. B* **49**, 1289 (1994).
- ⁶Y. Ohta, T. Tohyama, and S. Maekawa, *Phys. Rev. B* **43**, 2968 (1991).
- ⁷Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzari, *Phys. Rev. B* **38**, 7156 (1988).
- ⁸A. Tokiwa, Y. Syono, M. Kikuchi, R. Suzuki, T. Kajitani, N. Kobayashi, T. Sasaki, O. Nakatsu, and Y. Muto, *Jpn. J. Appl. Phys., Part 2* **27**, L1009 (1988).

- ⁹J. L. Tallon, C. Bernhard, H. Shaked, R. L. Hitterman, and J. D. Jorgensen, *Phys. Rev. B* **51**, 12911 (1995).
- ¹⁰K. Segawa and Y. Ando, *Phys. Rev. B* **59**, R3948 (1999).
- ¹¹T. B. Lindemer, E. D. Specht, C. S. MacDougall, G. M. Taylor, and S. L. Pye, *Physica C* **216**, 99 (1993).
- ¹²K. Segawa and Y. Ando, *Phys. Rev. Lett.* **86**, 4907 (2001).
- ¹³K. Segawa and Y. Ando, *Phys. Rev. B* **69**, 104521 (2004).
- ¹⁴B. W. Veal, A. P. Paulikas, H. You, H. Shi, Y. Fang, and J. W. Downey, *Phys. Rev. B* **42**, 6305 (1990).
- ¹⁵S. Ono, S. Komiya, and Y. Ando (unpublished).
- ¹⁶Y. Ando, Y. Hanaki, S. Ono, T. Murayama, K. Segawa, N. Miyamoto, and S. Komiya, *Phys. Rev. B* **61**, R14956 (2000).
- ¹⁷A. A. Taskin, A. N. Lavrov, and Y. Ando, *Phys. Rev. B* **71**, 134414 (2005).
- ¹⁸The surface of the samples with $y=6.21$ showed indications that further reduction would cause decompositions.