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Negative Hall coefficients of heavily overdoped $La_{2-x}Sr_xCuO_4$

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The Hall coefficient (R_H) is investigated along the in-plane direction of carefully prepared $La_{2-x}Sr_xCuO_4$ thin films from $x=0.08$ to 0.40. It is found that R_H becomes almost temperature independent around room temperature for $x \geqslant 0.24$, and its sign smoothly changes from positive to negative between $x=0.28$ and 0.32, showing contrasting behavior to previously reported results. This result indicates that the carrier can be doped smoothly across the hole- to electron-dominant regions. According to the sign change of R_H, superconductivity disappears for $x \geqslant 0.32$ films, which suggests that a positive R_H is one of the necessary conditions for superconductivity in *p*-type cuprates.

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Evolution of superconductivity according to carrier doping is an essential feature of high-temperature (high-T_c) cuprate superconductors. All high-T_c cuprates have a two-dimensional square-lattice CuO_2 plane in common, on which the electronic ground state drastically changes from insulator to doped semiconductor, superconductor, and normal metal.[1] One of the key concepts needed to reveal the mechanism of high-T_c superconductivity is understanding how superconductivity occurs by carrier doping. For that purpose, people started extensive studies on the carrier doping effect in the underdoped region soon after the discovery of high-T_c cuprates. Due to an incredible amount of studies, we have now come to believe that a strong coupling among charge, spin, and lattice plays a significant role in the physical properties of underdoped cuprates, even though its direct relation to the occurrence of superconductivity is still veiled. On the other hand, physical properties of the overdoped metallic region have not been fully investigated mainly due to difficulty in preparing high-quality samples. Even for well-studied $La_{2-x}Sr_xCuO_4$ (LSCO), for example, it is known that the oxygen deficiency becomes significant in the overdoped side, typically when x exceeds 0.28.[2] Thus, the experimental approach to superconductivity from the overdoped side using high-quality single crystals or thin films is limited to only two systems: LSCO,[1,3,4] and $Tl_2Ba_2CuO_{6+\delta}$ (Tl2201),[5,6] and, because of the toxicity of Tl, LSCO has been and is still the most important compound for the study from the *nonsuperconducting* overdoped side.

It is still an open question whether or not heavily overdoped LSCO is really a normal Fermi liquid. Takagi *et al.*[3] reported for $x=0.34$ single-crystal thin films that the in-plane resistivity (ρ) does not follow simple T^2 behavior but is well fitted by $T^{1.5}$. Nakamae *et al.*[4] has recently found ideal T^2 resistivity behavior below ~55 K for $x=0.30$ in a single crystal, but the resistivity in the higher-temperature region followed $T^{1.6}$ behavior. Similar temperature dependence has been reported for overdoped Tl2201 single crystals.[5,6] The situation mentioned above means that there is a difficulty in judging whether or not heavily overdoped high-T_c cuprates merge into a normal Fermi liquid from only a resistivity measurement.

The Hall coefficient (R_H) is a more robust parameter than resistivity, and is used to obtain direct information about carriers. However, the R_H data for heavily overdoped LSCO is still controversial. The first systematic study on the Hall effect of LSCO was done by Takagi *et al.*[1] immediately after the discovery of high-T_c cuprates. They reported for polycrystalline LSCO that R_H possibly becomes negative at $x=0.32$ and 0.34. However, they also described in the same paper that an $x=0.34$ single crystal shows a positive R_H. Such an unclear situation was reported also by Hwang *et al.*[7] for polycrystalline sintered samples and single-crystal thin-film samples. They reported that the room-temperature R_H becomes almost zero for both $x=0.30$, and 0.34; R_H does not obviously go to a negative side, but seems to stay around zero. Suzuki[8] has reported the R_H for LSCO thin films prepared by sputtering; he found that the $x=0.36$ sample shows a positive R_H, which is clearly inconsistent with the above two results.[1,7] These three results suggest the presence of two hurdles when we study the Hall effect of heavily overdoped LSCO. The first hurdle is that we must be very careful about the sample misalignment and orientation. In particular, we need to align the current direction perfectly parallel to the CuO_2 plane, because even a slight misalignment may seriously influence the sign of the Hall coefficients. As was demonstrated by Tamasaku *et al.*,[9] for the $x=0.30$ crystal, R_H is positive for $i \parallel CuO_2$ plane while it is negative for $i \perp CuO_2$ plane. Thus it becomes very important to reduce the misalignment between the CuO_2 plane direction and the current path direction as much as possible, especially when the magnitude of R_H is very small as in the overdoped samples. The other hurdle is the oxygen deficiency as was mentioned before.[2,10] It is partially helpful to anneal the samples for a very long time under high oxygen pressure.[2–4] However, high-pressure annealing is not possible everywhere, and is hardly applicable to thin-film samples.

In this paper, we propose to solve these two problems by using epitaxial thin films combined with a strong oxidation technique, and carry out Hall-effect measurements to demonstrate that a sufficient amount of holes can be doped in LSCO at least up to $x=0.40$. We pay attention to the following two points in particular: (a) whether R_H indeed becomes negative above a certain x, or just stays at zero, and (b) how the temperature dependence of R_H varies with increasing x, or, in other words, whether an ordinary Fermi liquid (T-independent R_H) indeed can be observed in the heavily overdoped LSCO.

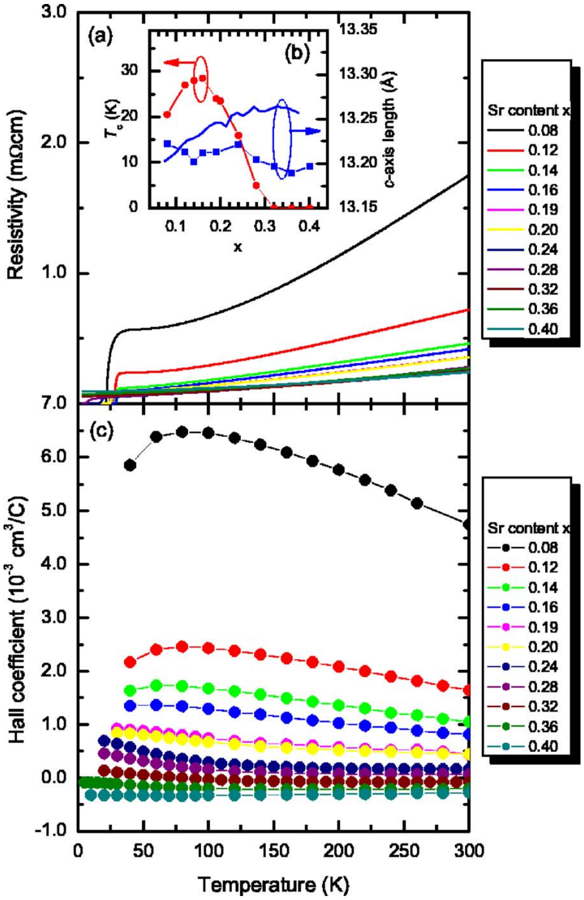

FIG. 1. (Color online) (a) Temperature dependence of dc resistivity for $0.08 \leqslant x \leqslant 0.40$. (b) The line with red filled circles shows the x dependence of T_c (left axis). It shows a smooth change with x. The line with blue filled squares shows the x dependence of the c-axis length which shows shorter values than those of bulk crystals (Ref. 16) (blue solid line) for $x \geqslant 0.12$. (c) Temperature dependence of R_H. The data were taken by sweeping the magnetic field between ±1 T for $0.08 \leqslant x \leqslant 0.22$, and ±6 T for $0.24 \leqslant x \leqslant 0.40$.

All films were grown by the pulsed laser deposition (PLD) technique with low-pressure pure ozone as an oxidant.[11] The films were all highly c-axis oriented as confirmed by x-ray diffraction. We used $SrTiO_3$ (100) as a substrate in order to not only compare our data with several published data but also decrease the influence of a strong epitaxial-strain effect.[12] It is known that LSCO is highly susceptible to lattice mismatch, and it is almost impossible to perfectly reproduce the transport properties of bulk crystals in thin-film samples.[13–15] However, it has been experimentally shown[12] that the epitaxial strain in LSCO is not as large on $SrTiO_3$ (100) as on $LaSrAlO_4$ (001) and LSAT (100). We actually confirm that the effect of epitaxial strain is not destroyed completely even using $SrTiO_3$ (100), and the present films indeed have shorter c axes than the bulk crystals have[16] for almost the entire x range [Fig. 1(b)], which indicates that finite tensile strain survives in our films. Substrate temperature during the deposition was set around 820–840 °C, and the film thickness was kept around 1500–2500 Å. Samples are separated into two groups; the films for $x = 0.08–0.20$ were processed into a small six-terminal shape using photolithography and wet etching,[17] while those for $x = 0.24–0.40$ were prepared using a metal mask (six-terminal shape) in order to omit any post-heat-treatments. Ozone is indispensable for two reasons. First, we can keep the chemical composition of the films identical to the targets. It is known that in the usual PLD or sputtering technique excess Cu must be added to the target in order to compensate the Cu deficiency in the films.[8] However, this procedure makes the relation between Sr concentration and real hole density unclear and uncontrollable. Because the reduction of gas pressure can make the mean free path of each ablated species longer than the target-substrate distance, the deviation of chemical composition is automatically suppressed as a result.[18] We set the ozone pressure to 10 mPa during the film deposition, and increase it to 15 mPa during the cooling down procedure. Second, we can utilize the stronger oxidation ability of ozone than high-pressure oxygen. It is known that the activity of ozone at $T = 300$ K is 10^{19} times larger than that of oxygen,[19] implying an efficient compensation for oxygen deficiency. In the present case, we suppress the oxygen deficiency by supplying ozone until the film temperature decreases by 60–65 °C. This procedure is applied for the samples with $0.20 \leqslant x \leqslant 0.40$. The other films with lower x are annealed after growth under the same conditions applied to bulk single crystals.[20]

The temperature dependence of the in-plane resistivity of all the films is summarized in Fig. 1(a). The figure shows a systematic change in magnitude and T_c. The magnitude of the resistivity in moderately doped films is slightly higher than that of bulk single crystals,[21] which is frequently observed when films are grown on $SrTiO_3$,[8,13,22] and considered to be one of the effects of the remanent epitaxial strain. The zero-resistivity temperature (T_{c0}) is plotted as a function of x in Fig. 1(b), and the conventional dome-shaped curvature is properly reproduced. The temperature dependence of Hall coefficients for these films is shown in Fig. 1(c). In contrast to the resistivity data, R_H shows better coincidence for $x \leqslant 0.16$ with that of bulk single crystals;[21] R_H moderately increases toward low temperatures, shows a peak between 50 and 100 K, and rapidly decreases toward the superconducting transition. The room-temperature values are plotted in the inset of Fig. 3 below, which shows a smooth evolution of low-field R_H by Sr doping.

We focus on the heavily overdoped region in more detail. We again plot the resistivity and Hall data for $x \geqslant 0.24$ in Figs. 2(a) and 2(b). As is easily seen, superconductivity is clearly observed for $x = 0.24$ and 0.28, while zero resistivity is no longer observed for $x \geqslant 0.32$, which is consistent with the results of Torrance *et al.*[2] The transition width of $x = 0.28$ is far wider than that of $x = 0.24$, which indicates that the oxygen distribution becomes inhomogeneous with increasing x. The onset of superconductivity observed in the $x = 0.32$ film may be caused also by oxygen inhomogeneity. It is intriguing that the room-temperature R_H changes its sign in accordance with the disappearance of superconductivity. For $x = 0.28$, R_H keeps a very small but positive value of the order of 10^{-5} cm^3/C from 300 to 200 K, and begins increasing toward the lower temperatures. The boundary between positive and negative R_H is found between $x = 0.28$ and 0.32. For $x = 0.32$, R_H(300 K) is no longer positive but its temperature

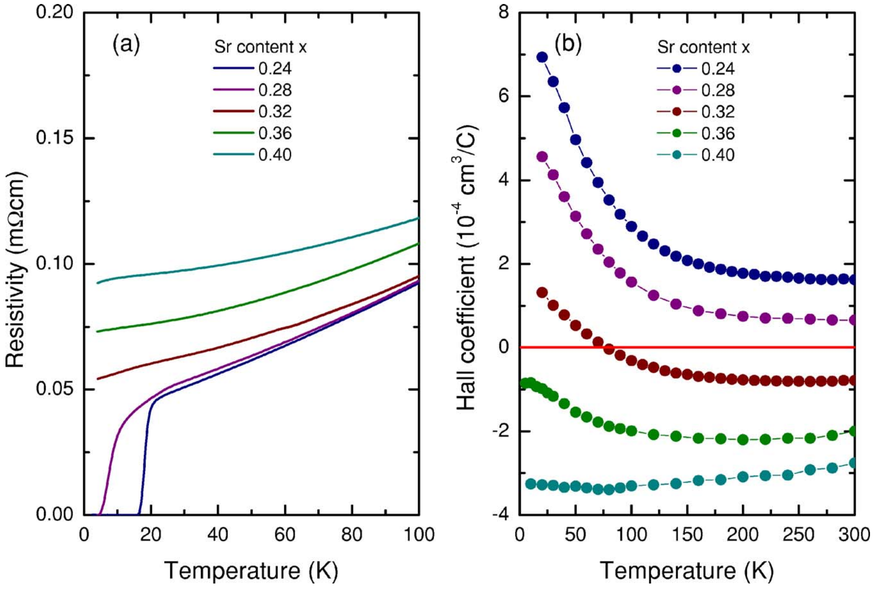

FIG. 2. (Color online) Closeup of data for resistivity (a) and R_H (b) for $x \geqslant 0.24$.

dependence looks similar to that of the $x=0.28$ film, and also to that reported for $x=0.30$ bulk single crystals.[9] What is interesting here is the R_H behavior of $x=0.36$ and 0.40 films. For $x=0.36$, $R_H(300\text{ K})$ increases its magnitude to the negative side, is no longer positive down to $T=0$ K, and dR_H/dT turns positive at room temperature, suggesting that the high-temperature limit of R_H is much closer to zero. To our knowledge, these features have not been reported for LSCO. For $x=0.40$, the low-temperature upturn behavior is no longer observed and R_H behaves as in a typical metal. The doping dependence of the $R_H(T)$ behavior reminds us of the doping dependence of *n*-type cuprates $(Nd_{2-x}Ce_x)CuO_4$ (NCCO) and $(Pr_{2-x}Ce_x)CuO_4$ (PCCO),[23–25] in which R_H changes its sign from negative to positive with increasing Ce^{4+} substitution for Nd^{3+} or Pr^{3+}. Therefore, the present data strongly indicate the similarity of electronic states between LSCO and NCCO (PCCO) in heavily overdoped regions.

It should also be noted that the occurrence of superconductivity and the sign change of R_H are not always correlated. We should remember that overdoped nonsuperconducting Tl2201 has a positive R_H,[5] which is one piece of counterevidence. Moreover, we have recently revealed that strong epitaxial strain can destroy superconductivity completely in any doping region,[26] which also indicates that superconductivity can disappear even when $R_H > 0$. To reveal how the epitaxial strain influences the sign of R_H is our next subject.

Let us compare the present negative Hall coefficients with previously published data. Hwang *et al.*[7] analyzed the temperature dependence of the Hall coefficient of LSCO with $0.15 \leqslant x \leqslant 0.34$ using a scaling function expressed as $R_H(T) = R_H^\infty + R_H^* f(T/T^*)$. In this manner, R_H^∞ gives the value of the high-temperature T-independent part of R_H, and in our case $R_H(300\text{ K})$ for $x \geqslant 0.24$ is a good approximation of R_H^∞. Figure 3 shows the x dependence of $R_H(300\text{ K})$ of our films with R_H^∞ shown in the inset of Fig. 2 of Ref. 7. In contrast to Hwang *et al.*'s data, our $R_H(300\text{ K})$ data show no saturation even above $x=0.30$; the value keeps decreasing to the negative side while keeping the gradient dR_H/dx unchanged. This result strongly indicates that the carrier doping proceeds smoothly across the hole- to electron-dominant regions. It should be noted that this smooth sign change is consistent with the theoretical prediction by Shastry *et al.*,[27] in which the ac Hall coefficients were proposed to be a better measure of carrier concentration. If our R_H around 300 K can be regarded as an approximation of the ac Hall coefficient at a sufficiently high-frequency limit, our data look consistent with these predictions in the following two points: (1) the sign change occurs at $x=0.30-0.35$, and (2) there is no saturating behavior at the sign-change concentration. The smooth sign change at similar Sr content was also predicted in a different theory constructed by Stanescu and Phillips,[28] which again supports that the smooth sign change is a natural consequence of the *p*-type doping in LSCO.

Comparison with the results of angle-resolved photoemission spectroscopy (ARPES) measurements is also intriguing. Doping dependence of the Fermi surface in LSCO has been systematically investigated by Ino *et al.*[29] According to them,

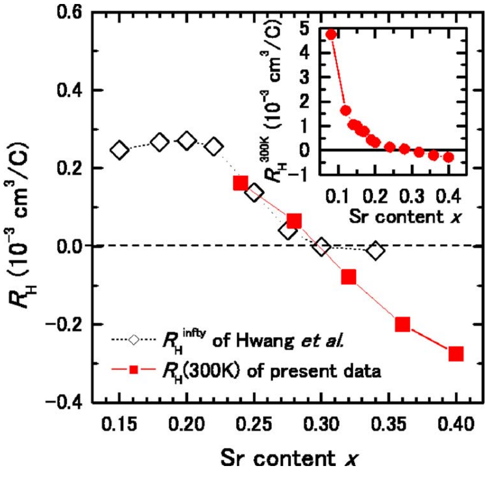

FIG. 3. (Color online) Plot of R_H at 300 K of the present work for $x \geqslant 0.24$ with R_H^∞ from Ref. 7. Inset shows the x dependence of R_H at 300 K for the entire doping range.

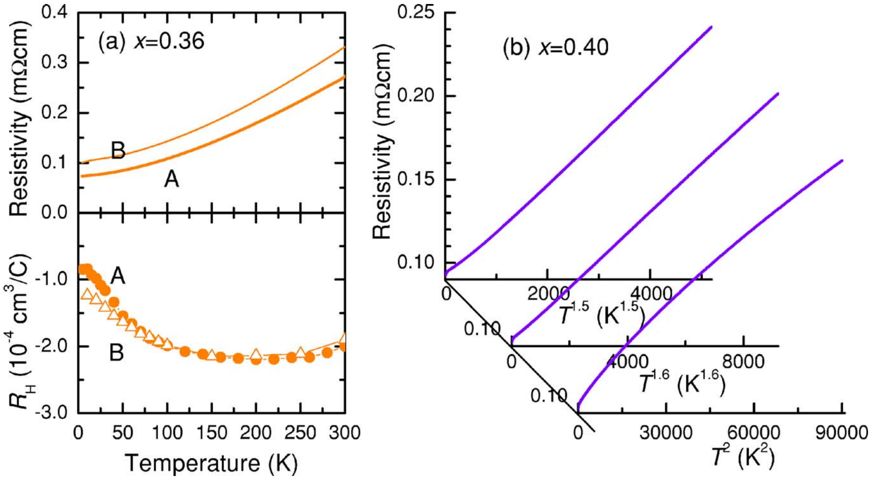

FIG. 4. (Color online) (a) Temperature dependence of resistivity and Hall coefficients for the two $x=0.36$ films. (b) $T^{1.5}$, $T^{1.6}$, and T^2 plots of the resistivity data for $x=0.40$.

the Fermi surface turned to an electronlike shape at $x=0.30$, i.e., closed the Fermi surface around the Γ point. The valence band clearly crosses the Fermi energy between the (0,0) and $(\pi,0)$ points (antinodal direction), and the Fermi surface approaches that of a conventional metal. This is roughly consistent with the negative Hall coefficients in our films. One may wonder if the consistency between R_H and ARPES data is invalid because the latest ARPES measurements by Yoshida *et al.*[30] reveal that even at $x=0.22$ the Fermi surface has a closed shape. However, we should remember that the sign of R_H is not determined simply by the topology of the Fermi surface. It is widely known based on Ong's argument[31] that R_H is mainly determined by the portion of the convex and concave parts of the Fermi surface, and the Fermi surface of the $x=0.22$ crystal[30] mostly consists of the convex part, which is consistent with positive R_H at $x=0.22$. Kontani *et al.*[32] calculated R_H more rigorously. According to them, the vertex correction (backflow process) should be taken into account when calculating R_H, and the portion of the Fermi surface inside and ouside the magnetic Brillouin zone is important. Even according to their conclusion, the ARPES data for the $x=0.22$ single crystal look consistent with positive R_H. One may suspect that the ARPES data were taken at $T=20$ K, and hence should be compared with the R_H also at $T=20$ K. However, we think that the low-temperature upturn of R_H is not a good measure of hole concentration, because it is strongly influenced by impurity scattering. To give an example, we show resistivity and Hall data for two different $x=0.36$ films in Fig. 4(a). One can see that a lower-resistivity sample (A) shows a stronger upturn in R_H at low temperatures, while the magnitude of R_H at room temperature is insensitive to a difference of resistivity. Thus, we may regard the room-temperature R_H as a more direct measure of carrier concentration.

After seeing the increase of $|R_H|$ to the negative side, we may reasonably understand the increase of resistivity when x exceeds 0.32 to be intrinsic. In previous studies, the oxygen deficiency which becomes remarkable in the heavily overdoped region was believed to be the main reason for this resistivity increase.[1,2,21] The present result indicates that the Fermi surface starts to shrink once the doping exceeds $x \approx 0.3$, which leads to a decrease in electron concentration. Thus, the resistivity may increase if the effective mass of the electron is kept unchanged. It would be interesting to perform an optical reflectivity measurement, with which we can estimate the density of the free carriers summed up to a finite frequency.

We briefly mention the temperature dependence of resistivity of the $x=0.40$ film. Figure 2(b) suggests absence of a special Sr concentration at which R_H strictly becomes temperature independent. However, the R_H for $x=0.40$ shows weaker temperature dependence than the others. Thus, it is meaningful to analyze the temperature dependence of the resistivity of this film. The result is shown in Fig. 4(b). We do not observe perfect T^2 behavior as in previous results.[3] The temperature dependence is better expressed as $T^{1.5}-T^{1.6}$, which indicates a mixture of T-linear behavior with the T^2 one. We do not know whether further doping realizes pure T^2 behavior or not. However, the presence of a T-linear term at $x=0.40$, where R_H becomes almost temperature independent, indicates that the electron-electron scattering is not the only scattering process even in heavily overdoped LSCO.

In summary, we measured the Hall coefficients of LSCO thin films grown under ozone atmosphere, which effectively suppresses the oxygen deficiency. These films demonstrate a smooth change of the Hall coefficient from positive to negative at $T=300$ K, which shows a clear contrast to previously reported results. The temperature dependence of the Hall coefficient almost disappears at $x=0.40$ while the temperature dependence of resistivity still follows $T^{1.5}-T^{1.6}$. The sign change of R_H is consistent with the shape of the Fermi surface determined by an ARPES measurement.

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