

Anomalies of T_c , resistivity, and thermoelectric power in the overdoped region of $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$

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Transport properties of $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ in the overdoped region have been investigated in detail. In a narrow region around $x=0.22$ in $y=0$, we have found anomalously less-metallic behaviors of the electrical resistivity and the thermoelectric power than usual. The value of x around which the anomalies occur decreases through the substitution of Zn; namely, with increasing y . In the anomalously less-metallic samples, superconductivity has been found to be a little suppressed. These anomalies are not connected with the structural phase transition between the tetragonal high-temperature phase ($I4/mmm$) and the orthorhombic midtemperature one ($Bmab$). There is a possibility that an ordering of holes and/or spins is formed or fluctuates in the samples exhibiting the anomalous properties in the overdoped region. [S0163-1829(99)03202-6]

I. INTRODUCTION

The recent discovery of the static order of holes and spins in $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$ by Tranquada *et al.*^{1,2} has thrown new light on the long-standing “1/8 problem:” namely, the anomalous suppression of superconductivity at $x \sim 1/8$ in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (Refs. 3,4) and $\text{La}_{2-x-y}\text{R}_y\text{Sr}_x\text{CuO}_4$ (R : rare earth elements)⁵ in the tetragonal low-temperature (TLT) phase (the space group: $P4_2/ncm$). They have proposed the so-called stripe model on the static order, and have concluded that stripe-patterned dynamical correlations of holes and spins in the CuO_2 plane are pinned by the TLT structure at low temperatures, leading to the stripe-patterned static order of holes and spins and the suppression of superconductivity. This is based on the consideration that the TLT structure is favorable for the pinning of the stripe-patterned order. On the other hand, it is known that the suppression of superconductivity at $x \sim 0.115$ ($\sim 1/8$) in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is enhanced through the partial substitution of Zn for Cu, though the TLT structure does not appear at low temperatures.⁶ According to the stripe model, it is possible to understand the enhancement as being due to the formation of the stripe-patterned static order on account of the pinning by Zn. In fact, we have found anomalies in the thermoelectric power and the Hall coefficient, which are likely to be attributed to the formation of the static order, in the partially Zn-substituted compound $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with $x \sim 0.115$ and $y = 0.005 - 0.025$.⁷⁻⁹

Recently, we have found anomalous suppression of superconductivity at $x = 0.30 - 0.35$, where p (the hole concentration per Cu) $\sim 1/8$, in the partially Zn-substituted compound $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x(\text{Cu}_{1-y}\text{Zn}_y)_2\text{O}_{8+\delta}$ with $y = 0.02 - 0.03$.¹⁰ It is suggested that the stripe-patterned order is pinned by Zn in the Bi-based cuprate as well as in the La-based cuprate.

The stripe model was originally proposed to explain the static order of holes and spins discovered in $\text{La}_2\text{NiO}_{4+\delta}$ or $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$, whose crystal structure is fundamentally the same as that of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. In the nickelates, the stripe-patterned static order has been found at various values of 2δ or $x = 1/n$ ($n = 2, 3, 4$).¹¹⁻¹³ Therefore, there is a possibility

that, besides the order at $x \sim 1/8$, another static order exists in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ as well as in the nickelates. In this paper, in order to search for another static order, we have investigated in detail the superconducting transition temperature T_c , the electrical resistivity, and the thermoelectric power of $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$, focusing on $x \sim 1/4$. Here, Zn atoms are introduced as pinning centers of the possible order. The crystal structure at low temperatures has also been studied by the powder x-ray diffraction measurements.

II. EXPERIMENT

Sintered samples of $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ were prepared by the solid-state reaction method from appropriate powders of dried La_2O_3 , SrCO_3 , CuO , and ZnO . The powders were mixed and pre-fired in air at 900°C for 12 h. After pulverization, the pre-fired materials were mixed, pelletized, and sintered in air at 750°C for 3 h and subsequently at 1050°C for 24 h, followed by furnace cooling. Post annealing was performed in flowing oxygen gas at 500°C for 72 h in order to keep oxygen deficiencies to a minimum. All products were characterized by powder x-ray diffraction to be of the single phase.

Resistivity measurements were carried out by the dc four-point probe method. The magnetic susceptibility was measured using a SQUID magnetometer in a magnetic field of 10 Oe during warm-up after field cooling, to determine T_c . The thermoelectric power was measured by the dc method with a temperature gradient of ~ 0.5 K across the sample. The powder x-ray diffraction measurements at low temperatures were made using a conventional diffractometer (Rigaku Co., RAD-C) with a curved graphite monochromator in the scattering beam path for $\text{CuK}\alpha$ radiation. The data were analyzed after $\text{CuK}\alpha_2$ stripping.

III. RESULTS

Figure 1 displays the temperature dependence of the electrical resistivity ρ for various x values in $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with $y = 0$, $y = 0.005$, and $y = 0.01$. In the overdoped region of $x \geq 0.15$, it is well known that the

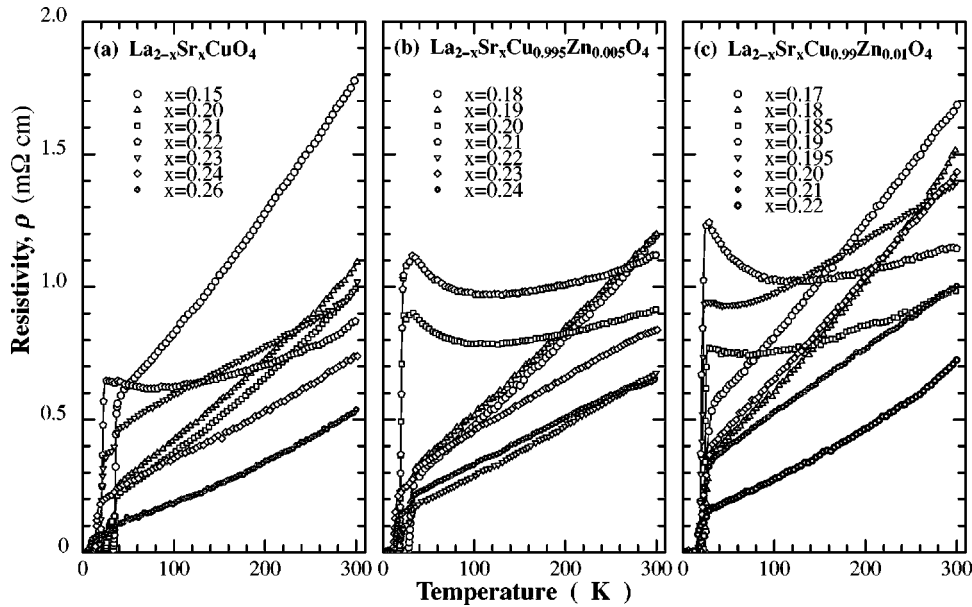


FIG. 1. Temperature dependence of the electrical resistivity ρ for various x values in $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with (a) $y = 0$, (b) $y = 0.005$, (c) $y = 0.01$.

resistivity in the normal state usually exhibits a metallic behavior, namely, $d\rho/dT > 0$. At $x = 0.22$ of nonsubstituted samples with $y = 0$, however, the resistivity exhibits a minimum around 100 K and $d\rho/dT < 0$ at low temperatures. As for Zn-substituted samples with $y = 0.005$ and 0.01 , such anomalous behaviors are observed at $x = 0.20 - 0.21$ and $0.185 - 0.195$, respectively. The value of x around which the anomaly occurs decreases with increasing y .

Figure 2 shows the temperature dependence of the mag-

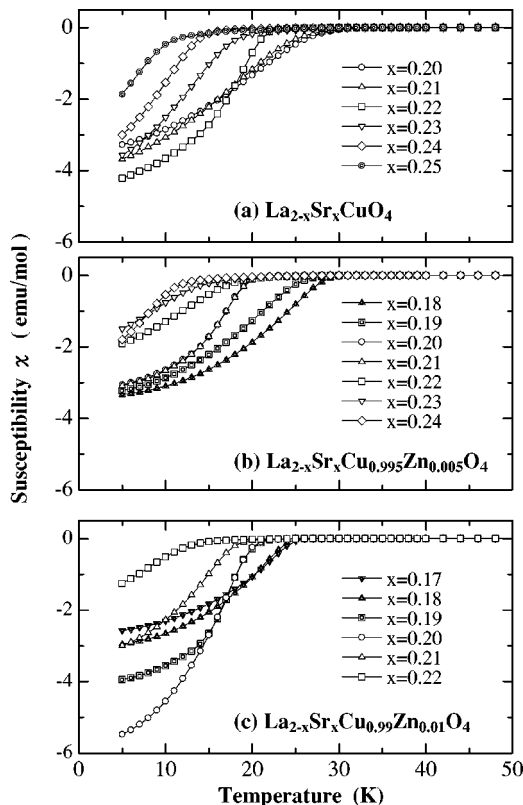


FIG. 2. Temperature dependence of the magnetic susceptibility χ , measured in a magnetic field of 10 Oe during warm-up after field cooling, for various x values in $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with (a) $y = 0$, (b) $y = 0.005$, (c) $y = 0.01$.

netic susceptibility χ . The value of T_c , defined as the temperature where the extrapolated line of the steepest part of the χ vs T plot reaches the normal-state value of χ , is shown in Fig. 3. The value of T_c , defined as the midpoint of the superconducting transition curve in the ρ vs T plot, is also

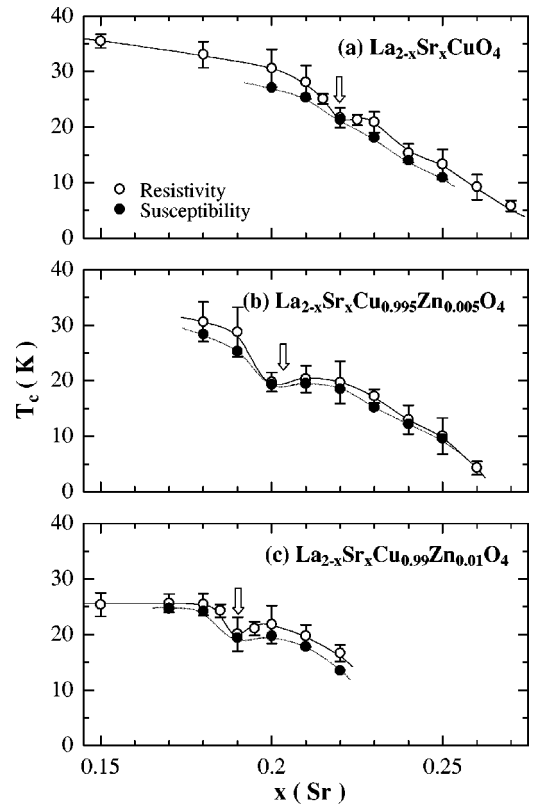


FIG. 3. Sr-concentration x dependence of T_c , estimated from the magnetic susceptibility (closed circles) and the electrical resistivity (open circles) measurements, for $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with (a) $y = 0$, (b) $y = 0.005$, (c) $y = 0.01$. From the resistivity measurements, T_c is defined as the midpoint of the superconducting transition curve. Bars indicate the temperatures where ρ drops to 90 and 10% of the normal-state resistivity. Arrows indicate x values of the samples exhibiting the most anomalous properties.

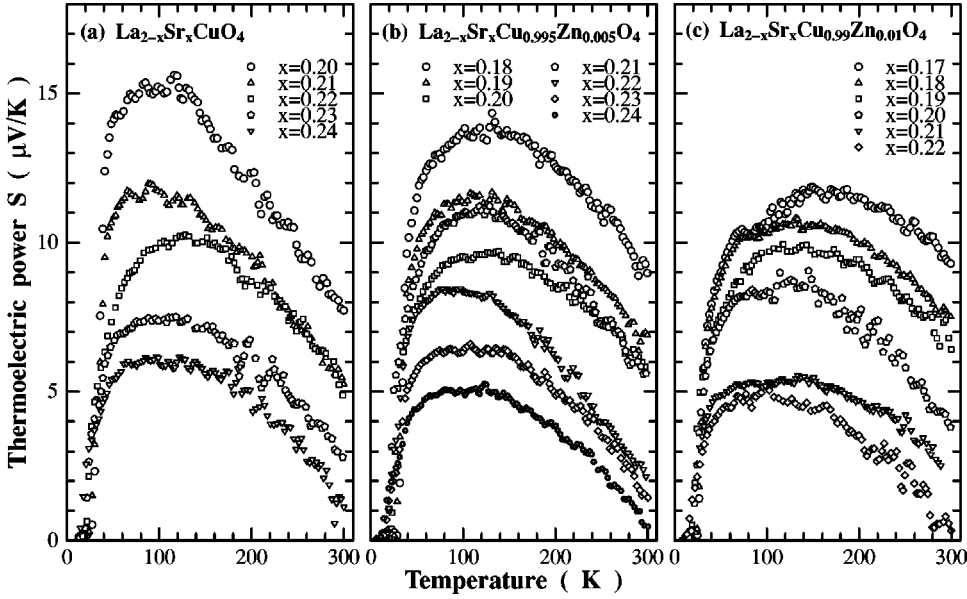


FIG. 4. Temperature dependence of the thermoelectric power S for various x values in $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with (a) $y = 0$, (b) $y = 0.005$, (c) $y = 0.01$.

shown in Fig. 3. A local minimum in T_c is observed at the composition of x where the abovementioned anomaly of ρ occurs.

Figure 4 displays the temperature dependence of the thermoelectric power S . Although the temperature dependence of S has not yet been understood clearly for the high- T_c cuprates, it is empirically known that S at 290 K ($S_{290\text{K}}$) decreases with increasing p universally for the high- T_c cuprates.^{14,15} In fact, one can confirm that this empirical law holds good for nonsubstituted samples with $y = 0$. That is, $S_{290\text{K}}$ decreases with increasing x , namely, with increasing p . It is found that the value of S in the normal state decreases through the Zn substitution, namely, with increasing y , though the reason has not yet been settled. No anomalous behavior of S is observed for the samples exhibiting the anomalous behaviors of ρ and T_c , but it is remarkable that values of S in the normal state of these samples are almost the same. It may be said, at least, that the electronic states of these samples are almost the same.

Figure 5 shows the powder x-ray diffraction profiles of the $(110)_{\text{THT}}$ and $(220)_{\text{THT}}$ reflections at various temperatures. The suffix THT indicates an index in the tetragonal

high-temperature (THT) phase (the space group: $I4/mmm$). For $x = 0.22$ and $y = 0$, it is found that the $(110)_{\text{THT}}$ and $(220)_{\text{THT}}$ peaks do not split in the measured temperature region, meaning that this sample is kept in the THT phase at temperatures between 12 and 300 K. For $x = 0.19$ and $y = 0.01$, on the other hand, the $(220)_{\text{THT}}$ peak is found to clearly split into two, meaning that this sample undergoes a structural phase transition from the THT phase to the orthorhombic midtemperature (OMT) phase (the space group: $Bmab$) at a temperature above 12 K. The THT-OMT transition temperature T_{d1} is estimated from the temperature dependence of the full width at half-maximum (FWHM) of the $(110)_{\text{THT}}$ and $(220)_{\text{THT}}$ peaks, as shown in Fig. 6. The value of T_{d1} , defined as the temperature where the FWHM begins to increase markedly with decreasing temperature, is estimated as 165 K for $x = 0.19$ and $y = 0.01$, and the sample with $x = 0.20$ and $y = 0.005$ is also found to undergo the THT-OMT transition at 120 K. These values of T_{d1} are consistent with those of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ obtained from the detailed study by Takagi *et al.*,¹⁶ as shown in Fig. 7, because it is known that the value of T_{d1} increases through the Zn substitution.¹⁷ In any case, what is important is that the

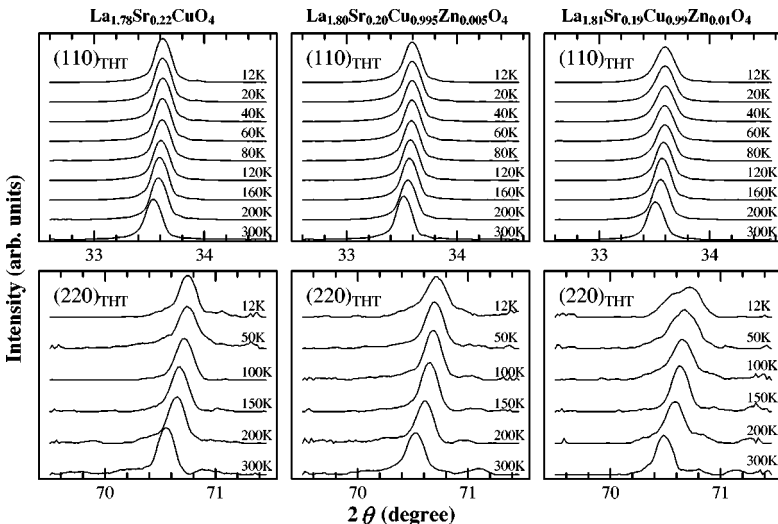


FIG. 5. Powder x-ray diffraction profiles of the $(110)_{\text{THT}}$ and $(220)_{\text{THT}}$ reflections due to $\text{CuK}\alpha_1$ radiation at various temperatures for $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with $[x = 0.22$ and $y = 0]$, $[x = 0.20$ and $y = 0.005]$, and $[x = 0.19$ and $y = 0.01]$.

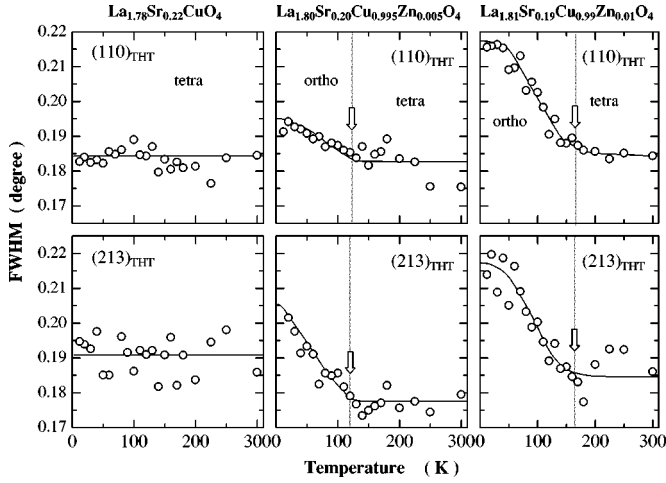


FIG. 6. Temperature dependence of the FWHM of the $(110)_{\text{THT}}$ and $(213)_{\text{THT}}$ peaks due to $\text{Cu}K_{\alpha 1}$ radiation for $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with $[x=0.22$ and $y=0]$, $[x=0.20$ and $y=0.005]$, and $[x=0.19$ and $y=0.01]$. Arrows indicate the THT-OMT transition temperature T_{d1} .

sample with $x=0.22$ and $y=0$ exhibiting the anomalous behaviors is kept in the THT phase in the measured temperature region, while the samples with $[x=0.20$ and $y=0.005]$ and $[x=0.19$ and $y=0.01]$ exhibiting the anomalous behaviors are in the OMT phase at low temperatures. This means that the anomalous behaviors of ρ and T_c are independent of the THT-OMT structural phase transition.

IV. DISCUSSION

First, we discuss the experimental results of the resistivity and the thermoelectric power. In order to highlight the

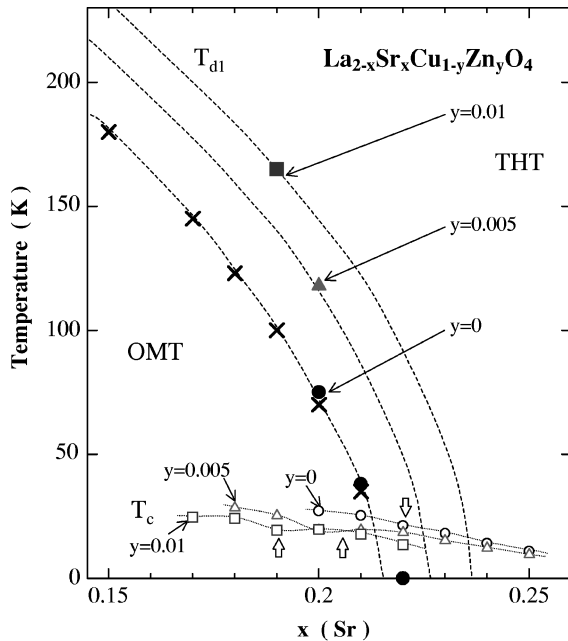


FIG. 7. Sr-concentration x dependences of T_{d1} and T_c for $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with $y=0$ (closed circles, open circles), 0.005 (closed triangle, open triangles), and 0.01 (closed square, open squares). Crosses are data of T_{d1} of $y=0$ by Takagi *et al.* (Ref. 16). Large arrows indicate x values of the samples exhibiting the most anomalous properties. Lines are guides to the eye.

anomalous behaviors, $S/\rho T$ vs T is plotted in Fig. 8. It is noteworthy that $S/\rho T$ tends to increase with decreasing temperature on a universal line independent of x , while values of $S/\rho T$ of the samples exhibiting anomalous behaviors deviate from the universal line and are lower than the line. It is well known that the thermoelectric power in the Fermi-liquid region is given by the Mott formula,¹⁸

$$S = - \frac{\pi^2 k_B^2 T}{3|e|} \left(\frac{d \ln \sigma(\epsilon)}{d\epsilon} \right)_{\epsilon=\mu}, \quad (1)$$

where k_B , e , μ , and $\sigma(\epsilon)$ are the Boltzmann constant, the electric charge, the chemical potential, and the contribution of electrons with energy ϵ to the electrical conductivity, respectively. Assuming that $\sigma(\mu)=1/\rho$, $S/\rho T$ is given by

$$\frac{S}{\rho T} = - \frac{\pi^2 k_B^2}{3|e|} \left(\frac{d\sigma(\epsilon)}{d\epsilon} \right)_{\epsilon=\mu}. \quad (2)$$

Although it is not clear that this formula is applicable to $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ in the overdoped region, it may be reasonable that $S/\rho T$ is universal in the overdoped region, because $S/\rho T$ does not depend on $\sigma(\mu)$ directly but depends only on $[d\sigma(\epsilon)/d\epsilon]_{\epsilon=\mu}$. Taking account of the fact that values of $S/\rho T$ of conventional semiconductors are smaller than those of conventional metals, the samples exhibiting the anomalous behaviors of ρ and T_c and their neighboring ones are inferred to be less metallic than others. As already pointed out, the electronic states of the samples exhibiting the anomalous behaviors are guessed from values of S to be almost the same. Consequently, there is a possibility that an ordering of holes and/or spins is formed or fluctuates in these samples, leading to the less-metallic behaviors and the slight suppression of superconductivity.

For nonsubstituted samples with $y=0$, the value of x around which the anomalies occur is neither the simply expected one $1/4$ nor $1/5$ but 0.22 . This may be explained as follows. In the overdoped region, holes may be supplied to not only oxygen in the CuO_2 plane but also the apical oxygen or the so-called blocking layer.^{19,20} Consequently, it is possible that the value of p in the CuO_2 plane is $1/5$, $1/6$, or $1/7$ at $x=0.22$. This inference is supported by the experimental result of inelastic neutron scattering.²¹

Another possibility to explain the magic number 0.22 is that $2/3^2=0.22$. As $2/4^2=1/8$, $2/n^2$ (n : integer) may be magic numbers. Formerly, it was pointed out by Maeno *et al.* that the equation $2/4^2=1/8$ was a key to solve the so-called $1/8$ problem in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$.²² They imagined localized hole pairs forming a 4×4 square superlattice in the CuO_2 plane of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with $x=1/8$. By analogy, there is a possibility that not the stripe order but the 3×3 square superlattice of hole-pairs is formed or fluctuates at $x=0.22$.

Finally, we discuss the shift of the value of x , around which the anomalies occur, through the Zn substitution. This is not what we have expected, because Zn atoms have simply been regarded as pinning centers at $p \sim 1/8$ in the La-based cuprate and also in the Bi-based cuprate, and no clear shift is observed around $p \sim 1/8$ through the Zn substitution.^{6,10} However, it is supposed that the holes are not transferred to the nearest neighbor sites of oxygen around Zn^{2+} , because the Zhang-Rice singlet-pair²³ is not formed between Zn^{2+}

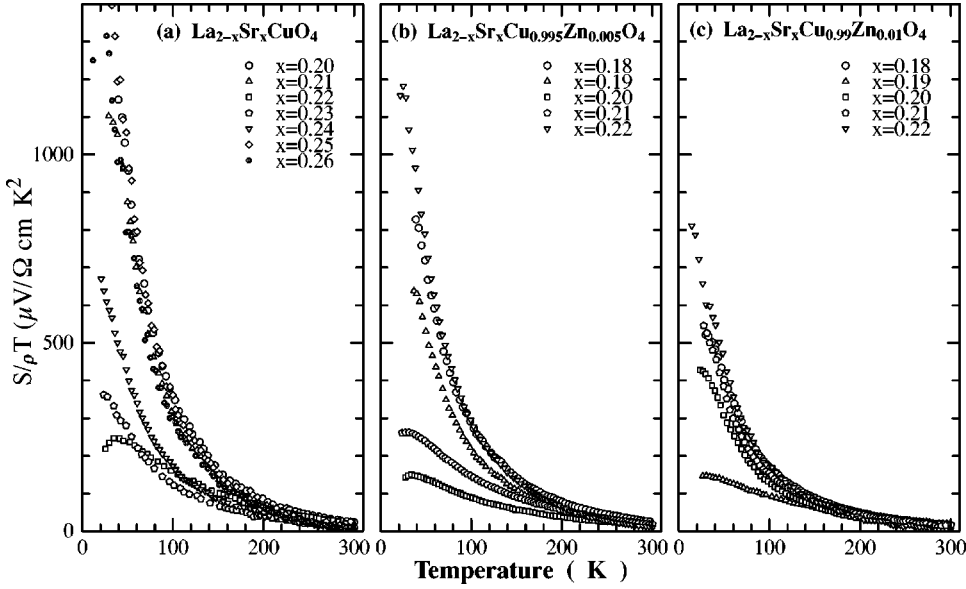


FIG. 8. Temperature dependence of $S/\rho T$ for various x values in $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with (a) $y=0$, (b) $y=0.005$, (c) $y=0.01$.

and O^- . This exclusion of holes from the neighbors of Zn^{2+} leads to the local enhancement of the hole concentration in the region far from Zn^{2+} . Therefore, the local hole concentration in the region far from Zn^{2+} will increase with increasing y in $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$. As the amount of holes increases with increasing x , the local hole concentration in the region far from Zn^{2+} may be almost the same between the samples with [$x=0.22$ and $y=0$] and [$x=0.20-0.21$ and $y=0.005$] and [$x=0.185-0.195$ and $y=0.01$]. This speculation is supported by the experimental result that values of S in the normal state of these samples are almost the same. As for the fact that there was no clear shift of the x value around $p \sim 1/8$ through the Zn substitution, it may be due to the small influence of the exclusion of holes from the neighbors of Zn^{2+} , because the amount of holes is small in the underdoped region. The discussion mentioned above is very speculative and must be substantiated by other measurements.

V. CONCLUSION

In the overdoped region of $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$, we have found anomalously less-metallic behaviors of the electrical resistivity and the thermoelectric power at [$x=0.22$ and $y=0$] and [$x=0.20-0.21$ and $y=0.005$] and [x

$=0.185-0.195$ and $y=0.01$] than usual. In the anomalously less-metallic samples, values of the thermoelectric power in the normal state are almost the same, meaning that the electronic states of these samples are almost the same. Moreover, superconductivity is a little suppressed in these samples. These anomalies are not connected with the structural phase transition between the tetragonal high-temperature phase and the orthorhombic midtemperature one. There is a possibility that an ordering of holes and/or spins, such as the so-called stripe order or the 3×3 square superlattice of hole pairs, is formed or fluctuates in these samples in the overdoped region.

In order to clear up the possible order, further experiments such as electron diffraction and neutron diffraction are necessary in the samples exhibiting the anomalous properties.

ACKNOWLEDGMENTS

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