Transport mechanism in $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ $(0 \leqslant x \leqslant 1)$

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The transport properties of the $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ $(0 \leqslant x \leqslant 1)$ solid solution series have been investigated by means of electric resistivity and thermoelectric power (TEP). The TEP measurements reveal that the Ni doping at the Cu site brings about an anomalous change in the TEP. The TEP value $S(T)$ increases with increasing Ni content for the samples with low dopant levels ($x < 0.3$) and reaches a maximum at $x = 0.3$, but decreases rapidly with the further increase of Ni content for $x > 0.3$ and becomes negative at $x = 1.0$. The resistivity measurements show that the character of the conductivity for the samples with $x \geqslant 0.1$ changes from thermally activated at high temperature to hoppinglike at low temperature. By the comparison of the thermal activation energy derived from the resistivity with that from the TEP, we find that the transport mechanism in $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ can be understood in terms of the polaron model. [S0163-1829(98)00745-0]

INTRODUCTION

It is known that the transport properties at the normal state of high-T_c superconductors exhibit anomalies. Many authors believed that two-dimensional antiferromagnetic spin correlation with a short range plays an important role in determining the anomalous characteristics of the transport properties and that the origin of high-T_c superconductivity is also related to this type of spin correlation. Nevertheless, at present there have been few experiments to reveal the intrinsic relation that exists between the short-range spin correlation and the charge transport in the CuO_2 plane.

In order to gain more information on the above relation, Ishikawa *et al.*[1] investigated the magnetism and transport properties of the $La_{2-x}Sr_xCuO_{4+\delta}$ superconductors doped with different $3d$ and sp metals (Fe, Co, Ni, Zn, and Ga). One of the important results of these researches is that the Ni doping has the least effect on the spin correlation in the CuO_2 plane compared with the doping by Fe, Zn, and Ga, thus producing a weak influence on T_c. This result is obtained from the measurements of the samples with low-Ni dopant levels (<10 at. %). For the samples with high dopant levels (>10 at. %), our earlier work showed that the Ni doping increases the resistivity much more rapidly compared with the doping by Mg and Zn.[2] This suggests that the Ni doping has much stronger influence on the transport properties of the CuO_2 plane in the case of high dopant level. In the present paper, we systematically studied the transport properties in the $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ with $0 \leqslant x \leqslant 1$, by the measurements of resistivity and TEP. An anomalous change in the TEP with x is observed, i.e., the $S(T)$ increases with Ni concentration for the samples with $x \leqslant 0.3$, but decreases dramatically with a further increase of Ni content for $x > 0.3$. From the comparison of thermal activation energy derived from the resistivity with that from the TEP, we found the evidence for polaronic transport in the $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ solid solution series, as well as the expansion of the polaron caused by substitution of Cu for Ni.

EXPERIMENTAL METHOD

Samples of $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ with $x = 0-1$ were prepared by the standard ceramic techniques, starting from high-purity La_2O_3, $SrCO_3$, CuO, and Ni_2O_3. Since La_2O_3 is strongly hygroscopic, it was dried at 900 °C in a furnace before weighing. Initially, the appropriate mixture of these powders was well ground and preheated in air at 1020–1250 °C for 20 h with an intermediate grinding. The loose powder was reground and pressed into disk-shaped pellets. The pellets were sintered in flowing oxygen at the temperature range of 1050–1320 °C for one day, then cooled down to and kept at 800 °C in the furnace for another day.

X-ray-diffraction (XRD) analysis was carried out with a Rigaku-D/max-γA diffractometer using monochromatic high-intensity Cu-$K\alpha$ radiation at room temperature. The lattice parameters were determined from the d values of XRD by a standard least-squares refinement method. Resistivity was measured using a standard four-probe method in a closed-cycle helium cryostat C50W. The measuring current was provided by a constant-current source and the voltage was measured by a Keithley 182 nanovoltmeter. The data were collected automatically by a computer. The TEP of the sample was measured by a differential method. Calibrated by pure Pb, the error of the TEP measurement system is smaller than 0.1 μV/K.

RESULTS

The powder XRD revealed the formation of single-phase products for all x with $0 \leqslant x \leqslant 1$ in $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$. All the doped samples in this series crystallize in the tetragonal lattice. The lattice parameters of different members are shown in Fig. 1(a). It is seen that the lattice parameter a increases continuously as a function of x while the c parameter decreases. The lattice parameter changes clearly show that the doping of Ni definitely substitutes for the Cu sites. Besides, one knows that the c/a ratio is generally used to characterize the Jahn-Teller distortion of the oxygen octahe-

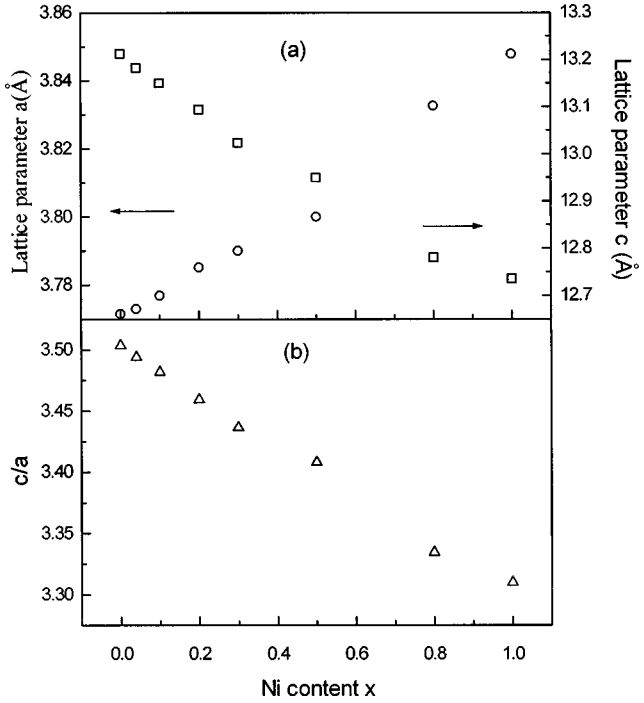

FIG. 1. (a) The lattice parameters as a function of Ni content in $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$. (b) The c/a ratio as a function of Ni content.

drons around Cu^{2+}. From Fig. 1(b), we can see that the c/a ratio decreases with increasing Ni content, indicating that the Ni doping leads to a release in the Jahn-Teller distortion of the CuO_6 octahedrons. This result is consistent with the data reported in Refs. 3 and 4.

The temperature dependence of resistivity for the $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ solid solution series is shown in Fig. 2. The T_c almost decreases linearly with increasing Ni concentration and the superconductivity disappears around $x=0.05$, as reported by other groups.[3–5] For the samples showing superconductivity, a metallic character is observed having T-linear resistivity at temperature above T_c. As the Ni concentration increases to $x=0.1$, the sample exhibits a semiconductinglike behavior. Figure 3 gives the room-temperature resistivity $\rho(290)$ as a function of Ni content. It can be seen that $\rho(290)$ starts to deviate from a linearity at

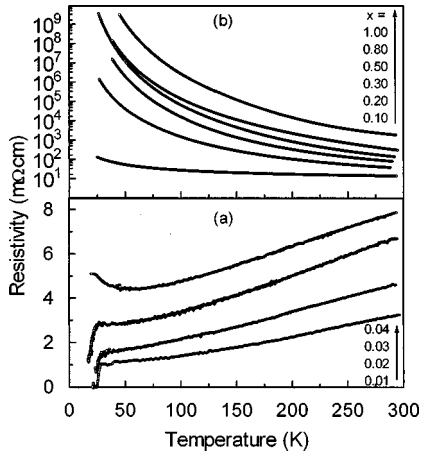

FIG. 2. The temperature dependence of the resistivity for $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$.

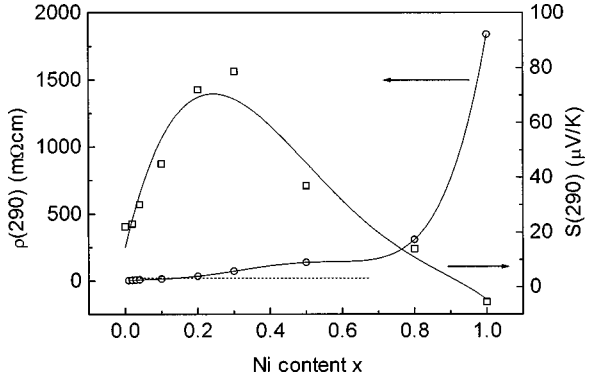

FIG. 3. The room-temperature (290 K) resistivity and TEP as a function of Ni content.

$x=0.2$ and increases dramatically as $x>0.8$.

For the samples exhibiting semiconductinglike behaviors with $x\geqslant 0.1$, we investigated the possibility of a thermally activated conduction or hoppinglike process. The resistivity associated with the thermally activated conduction mechanism shows temperature dependence as

$$\rho(T)=\rho_0\exp(\varepsilon_a/kT). \tag{1}$$

By analyzing the data in Fig. 2(b), we found that the resistivity of the samples with $x\geqslant 0.1$ follows a thermal activation law above a temperature of about 140 K, as shown in Fig. 4. The thermal activation energy ε_a derived from the slope of straight lines in Fig. 4 is summarized in Fig. 8. It shows that the ε_a increases from 10 meV with $x=0.1$ to 117 meV with $x=1.0$.

In variable-range hopping (VRH) model, the resistivity shows the temperature dependence as

$$\rho\propto\exp[(T_0/T)^{\alpha}], \tag{2}$$

with $\alpha=\frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{4}$. The value of α depends on both the dimension of the system and the behavior of the density of state at the Fermi level. The VRH model predicts $\alpha=\frac{1}{4}$ in the three dimensions and $\alpha=\frac{1}{3}$ in two dimensions. Formula (2) is applied to fit the resistivity data in Fig. 2(b). The results show that for the sample with $x\geqslant 0.1$, the best fitting is obtained at $\alpha=\frac{1}{4}$ at low temperature, as shown in Fig. 5.

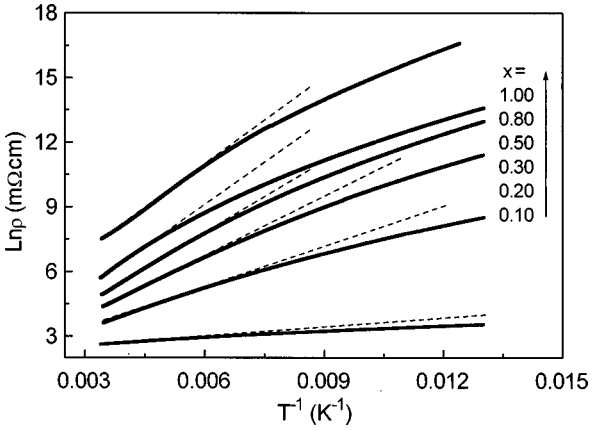

FIG. 4. Resistivity in logarithmic scale vs $1/T$ for $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ samples. The thermal activation energy ε_a^{ρ} has been derived from the straight lines in this figure.

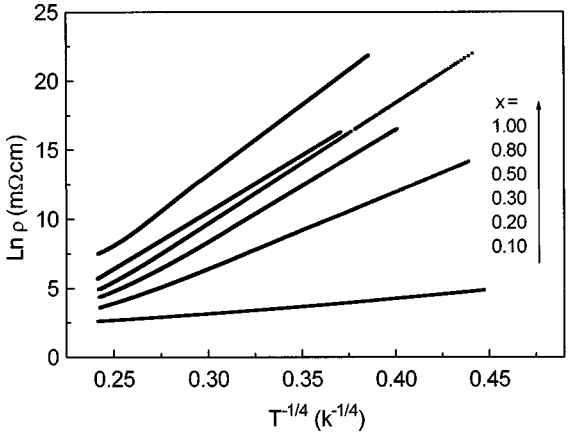

FIG. 5. Resistivity in logarithmic scale vs $1/T^{1/4}$ for $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ samples.

This suggests that at low temperature the $\rho(T)$ deviates from the thermally activated form and becomes dominated by hoppinglike process.

Figure 6 shows the TEP of the samples with different Ni contents as a function of temperature. The TEP of $La_{1.85}Sr_{0.15}CuO_{4+\delta}$ shows weak temperature dependence, while the Ni doping produces a rather significant change of the temperature-dependent TEP. The TEP value $S(T)$ increases with increasing Ni content for the samples with low dopant levels ($x \leqslant 0.3$), which is in agreement with the result reported in Ref. 6. However, it is interesting that the $S(T)$ decreases rapidly with a further increase of x for $x > 0.3$, and become negative at $x = 1.0$. The temperature dependence of the TEP for the $x = 1.0$ sample exhibits a similar behavior as observed in $La_{2-x}Sr_xNiO_{4+\delta}$ with $x \sim 0.15$,[7] i.e., a minimum occurs in the S-T curve around 190 K. The room-temperature TEP, $S(290)$, a function of Ni content is also shown in Fig. 3. The $S(290)$ shows a maximum at $x = 0.3$.

The above analyses have revealed that for the samples with $x \geqslant 0.1$ the resistivity follows the thermally activated conduction mechanism at high temperature. For a thermally activated single-band charge-transport process with the activation energy ε_a, the temperature dependence of TEP (see Ref. 8) is

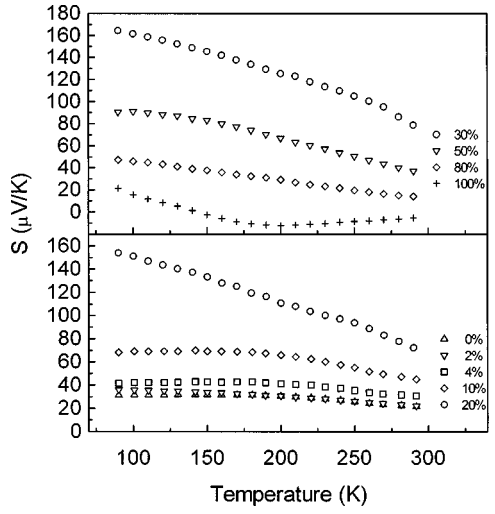

FIG. 6. The temperature dependence of TEP for $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ samples.

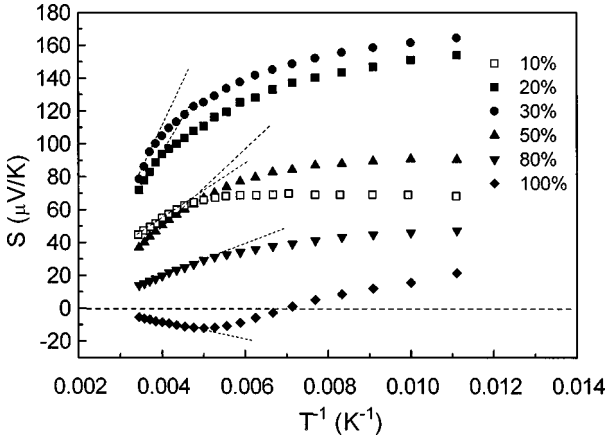

FIG. 7. Thermoelectric power $S(T)$ vs the reciprocal temperature for $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ samples. The straight dashed lines in the figure give the thermal activation energy ε_a^s in Fig. 8.

$$S(T) = \pm (k/e)(\varepsilon_a/kT + A). \tag{3}$$

The + and − signs correspond to hole-type and electron-type of conduction, and the constant A is determined by the energy dependence of scattering time. It is obvious that the ε_a can also be evaluated using formula (3). In Fig. 7 we plotted S as a function of $1/T$. The ε_a derived from the slope of straight lines at high temperature is also given in Fig. 8 in order to be compared with those derived from the resistivity. Here, we use ε_a^ρ and ε_a^s to denote the thermal activation energy derived from resistivity and TEP, respectively. One finds that the ε_a^s accrues remarkably as x increasing from 0.1 to 0.3. The $x = 0.1$ sample has nearly the same value between ε_a^s and ε_a^ρ, whereas for the samples with $x = 0.2$ and 0.3, the ε_a^s is slightly smaller than the ε_a^ρ. However, for the samples with $x > 0.3$, contrary to the behavior of ε_a^ρ, the ε_a^s decreases gradually with increasing x, i.e., the discrepancy between the ε_a^ρ and ε_a^s becomes more and more appreciable with increasing Ni content. This difference reaches as high as ~110 meV with $x = 1.0$.

DISCUSSION

Strangfeld, Westerholt, and Bach[7] have studied the charge transport of the system $La_{2-x}Sr_xNiO_{4+\delta}$ with $0 \leqslant x \leqslant 0.5$. They also found that the thermal activation energy derived from the TEP is systematically lower than that derived from the resistivity. The explanation they gave for the discrepancy in ε_a is the polaron character of the charge carriers, i.e., the charge carriers in $La_{2-x}Sr_xNiO_{4+\delta}$ are small polarons. The so-called small polarons are the self-localized states induced by the large magnetic coupling between Ni and hole spins.[9–11] Chen, Cheong, and Cooper[12] reported experimental evidence for the small polarons from the electron diffraction at low temperature. They found that the small polarons form superlattice at low temperature, thus producing quasi-two-dimensional, macroscopic charge modulation. Furthermore, recently Blumberg, Klein, and Cheong[13] experimentally observed the opening of the pseudogap in the electron-hole excitation spectrum associated with the charge ordering.

From the discrepancy between ε_a^ρ and ε_a^s as shown in Fig. 8, we found that the transport mechanism in the

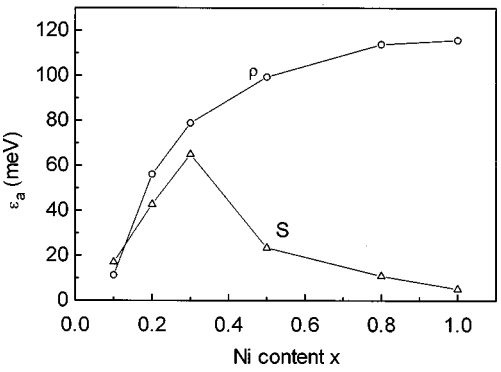

FIG. 8. Thermal activation energy derived from the resistivity measurements and thermoelectric power measurements vs the Sr concentration x for $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ samples.

$La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ series can also be understood in terms of the small polaron model. From this model, one can deduce that the polaron formation energy ε_p is twice as much as the difference between ε_a^ρ and ε_a^s, i.e., $\varepsilon_p = 2(\varepsilon_a^\rho - \varepsilon_a^s)$. For the $x=1.0$ sample, $La_{1.85}Sr_{0.15}NiO_{4+\delta}$, we can see from Fig. 8 that the difference of ε_a^ρ and ε_a^s is ~110 meV. If the conduction in this material is through small polarons, the ε_p of this material should be ~220 meV. This is close to the ε_p value 240 meV, determined by optical conducting measurements for $La_{1.85}Sr_{0.15}NiO_{4+\delta}$ (Ref. 10) and also very close to the ε_p value, 204 meV, observed in $La_{2/3}Ca_{1/3}MnO_3$.[14] This suggests that the charge carriers in the $x=1.0$ sample substantially have the characteristic of small polarons.

The polaron behavior of charge carriers in $La_{2-x}Sr_xCuO_{4+\delta}$ is also detected by optical conductivity measurement.[10] But it shows different characteristics compared with $La_{2-x}Sr_xNiO_{4+\delta}$. The ε_p of $La_{1.85}Sr_{0.15}Cu_xO_{4+\delta}$ is ~60 meV, which is only a quarter of ε_p of $La_{1.85}Sr_{0.15}NiO_{4+\delta}$. The polaron size of the former is almost ten times as much as the latter. Therefore, for the $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ solution series, it can be expected that the polaron formation energy reduces with decreasing Ni content and its size tends to expand correspondingly. The difference between ε_a^ρ and ε_a^s shown in Fig. 8 demonstrates a good agreement with this expected tendency.

From the argument of Chen, Cheong, and Cooper,[12] as described above, the small polarons are supposed to form a superlattice with x increasing to 1.0, thus giving rise to a charge modulation at low temperature (<235 K). Nevertheless, we did not see any anomaly in $\rho(T)$ associated with charge ordering below 235 K for all the members of x. But we observed that the character of the conductivity changes from activated at high temperature to hoppinglike at low temperature, as revealed by Figs. 4 and 5, which suggests localization of small polarons at low temperature. The drastic increase in $\rho(290)$ with $x>0.8$ reflects the conspicuous reduction in polaron size.

On the other hand, the study of optical conductivity has also revealed that in $La_{2-x}Sr_xCuO_{4+\delta}$ both bandlike carriers and polarons exhibit contribution to conductivity from bandlike carriers. As a matter of fact, we can apply the two-carrier model of $La_{2-x}Sr_xCuO_{4+\delta}$ to interpret the maximum behavior of TEP at $x=0.3$ shown in Fig. 3. In the case of the lower Ni-dopant level with $x<0.3$, the bandlike carriers probably have more contribution to TEP than the polarons. It is known that the Ni doping reduces the carrier concentration,[6] which certainly results in the increase of TEP. However, with a further increase of Ni content for $x>0.3$, the polarons should show a main contribution to TEP so that the value of TEP decreases.

In summary, we have measured the transport properties of $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ and compared the ε_a derived from the resistivity with that from the TEP. Based on the difference of ε_a^ρ and ε_a^s, which develops rapidly with increasing x for $x>0.1$, we discussed the transport mechanism of $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4+\delta}$ using the polaron model. It is found that the conduction in this solution series is by polarons and that the polarons expand with decreasing Ni content.

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