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Study on the in-plane electrical resistivity and thermoelectric power in single crystals of $La_{2-x}Ba_xCuO_4$ *

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The in-plane electrical resistivity and thermoelectric power have been measured on single crystals of $La_{2-x}Ba_xCuO_4$ at around x=0.125. The room temperature resistivity and thermopower have their maximum values at x=0.125, indicating that the carrier concentration is the minimum and the carriers are most strongly localized at x=0.125. The observed semiconductor-like behaviour can be well described by the weak-localized quasi-two-dimensional state. The steep rise in electric resistivity of the sample at x=0.125 below 70K is attributed to the formation of static stripe-order of holes and spins, which are pinned by the low-temperature tetragonal (LTT) structure, as discovered in $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$. The temperature dependence of electric resistivity below 70K is still well described by the formula $\rho \propto \ln T$. A definite change in the slope of thermopower is observed at the low-temperature orthorhombic–LTT structural phase transition temperature. The origin of the 1/8 anomaly is discussed in the text.

Keywords: resistivity, thermopower
PACC: 7430F, 7220P

1. Introduction

Since the discovery of $La_{2-x}Ba_xCuO_4$ (LBCO), the first high-T_c cuprate,[1] much effort has been made to elucidate the structural phase transitions and transport properties of $La_{2-x}M_xCuO_4$ (M=Ba, Sr) and other high-T_c copper oxides.[2–18]

As is known, the charge carrier concentration of $0.10 \leq x \leq 0.20$ per Cu atom in a CuO_2 sheet appears to give the optimal T_c in 214 cuprate superconductors. However, in the $La_{2-x}Ba_xCuO_4$ system, it was found that T_c has a complicated x dependence, reaching a maximum (about 25K) near x=0.10 and 0.15, with an intervening sharp drop (down to below 5K) near x=0.12,[4] the so-called "1/8 anomaly". Soon after the 1/8 anomaly was recognized, there were many experiments that tried to investigate the fundamental mechanism of the 1/8 anomaly. It was found that the LBCO system shows a structural phase transition from a low-temperature orthorhombic (LTO) phase to a low-temperature tetragonal (LTT) phase, which appears below 60K at around x=0.125.[13,14] It was reported that high pressure suppresses the phase transition from LTO to LTT and restores the superconductivity in bulk samples of LBCO.[5–10] Furthermore, the $La_{2-x}Sr_xCuO_4$ (LSCO) system, which has the same crystal structure as LBCO at room temperature and has no structural phase transition from LTO to LTT at around x=1/8, does not show the suppression of T_c.[19,20] It is generally believed that the phase transition from LTO to LTT is responsible for the suppression of T_c in LBCO.

After it was found that the same structural modification can be induced in $La_{2-x}Sr_xCuO_4$ by partial substitution of Nd and Zn/Ni for La,[6,7] intensive efforts have focused on this system, and the properties of $La_{2-x-y}Nd_ySr_xCuO_4$ (Nd-doped LSCO) are quite similar to those of LBCO. However, in Nd-doped LSCO system, it was reported[21] that there is a structural phase transition from LTO to LTT at 71K, and the superconductivity is almost completely destroyed for x=0.12. There also remains a bulk superconductivity (with x=0.20), where the structural phase transition to LTT appears at 79K. This suggests that the occurrence of the LTT phase does not necessarily mean a destruction of superconductivity. Thus, it is

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still unclear whether the suppression of T_c at around 1/8 can be prevented only by structural modifications.

Because of the difficulty in growing single crystals of LBCO, the anisotropic resistivity and the thermoelectric power of this system have not been well studied and especially the "1/8 anomaly" is not well understood.

In this paper, we report on our measurement of the in-plane electrical resistivity and thermoelectric power of the LBCO system, and discuss the behaviour of these properties in single crystals of $La_{2-x}Ba_xCuO_4$. Finally, the origin of the 1/8 problem is discussed.

2. Experiment

The single-crystal samples of $La_{2-x}Ba_xCuO_4$ were synthesized by the flux method from an appropriate mixture of powders of dried La_2O_3, $BaCO_3$, CuO, with the weight ratio: $La_{2-x}Ba_xCuO_4$(g):CuO(g)=100(g):40(g). The powders were well mixed and then melted at 1280°C in air in an Al_2O_3 crucible for about 10 min. Afterwards, it was rapidly cooled to 1250°C for 5min and then cooled to 1220°C at a constant cooling rate of $10°Ch^{-1}$. The samples were annealed at 500°C for 72h in air in order to reduce the oxygen defect.

The rock curve of x-ray diffraction (taken with a diffractometer of Rigaku D/Max γA, λ=0.15405nm Cu $K_{\alpha 1}$ radiation) is sharp and the full width at half maximum (FWHM) is less than 1°. Unfortunately, the energy dispersive x-ray (EDX) analysis shows that all the samples contain about 3% Al in contrast with Cu atom number (just see the peak caused by Al), which is the common problem in using the flux method for the La-based compounds. The rock curve and the EDX analysis show that all the samples are single crystals of good quality. The actual composition for all the samples is consistent with the nominal composition within an error about 0.01. The x-ray diffraction shows that the CuO_2 planes are parallel to the broad faces. The measured crystals are of a typical size of $3\times1.5\times0.3mm^3$.

Resistivity measurements were carried out by the dc four-probe method. The thermoelectric power S was measured with a method similar to that by Goodenough *et al.*[22] The temperature gradient ΔT of 0.3–1K across the samples was delicately controlled in the temperature range between 8–300K. The average thermal voltage ΔV was taken after stabilizing the temperatures of both copper blocks and two thermal shields; 200 points for a run were taken to produce the average value at the speed of 1 point·s^{-1}.

3. Experimental results

Figure 1 shows the temperature dependence of the electrical resistivity ρ_{ab} of $La_{2-x}Ba_xCuO_4$ single crystals for x=0.08, 0.122, 0.125, 0.128 and 0.131. None of the samples show superconductivity at low temperatures, whereas they show semiconductor-like behaviour. The in-plane electrical resistivity ρ_{ab} at room temperature increases with increasing x and reaches a maximum at x=0.125 in the range from 0.08 to 0.125, and then decreases with increasing x.

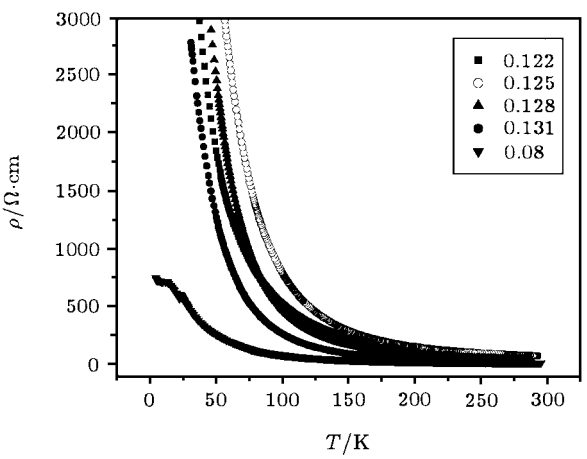


Fig.1. The temperature dependence of in-plane resistivity ρ_{ab} (T) for the single crystals of $La_{2-x}Ba_xCuO_4$ with x=0.08, 0.122, 0.125, 0.128 and 0.131.

Figure 2 shows the plot of the in-plane resistivity ρ_{ab} versus ln$T$ for different values of x in $La_{2-x}Ba_xCuO_4$. The in-plane resistivity ρ_{ab} of the samples at around x=0.125 is well described by the formula of $\rho \propto \ln T$. The slope of the samples at around x=0.125 changes near 60K and becomes steeper in the low-temperature region. The slope of the sample of x=0.125 shows a maximal change among all the samples.

Figure 3 shows the temperature dependence of in-plane thermoelectric power $S_{ab}(T)$ for single crystals of $La_{2-x}Ba_xCuO_4$ with x=0.08, 0.125 and 0.131. The S_{ab} versus T curve shows an obvious change of slope below 70K and then a very weak temperature dependence above 70K. For all samples, the room-temperature thermoelectric power S_{ab} value reaches a maximum at x=0.125.

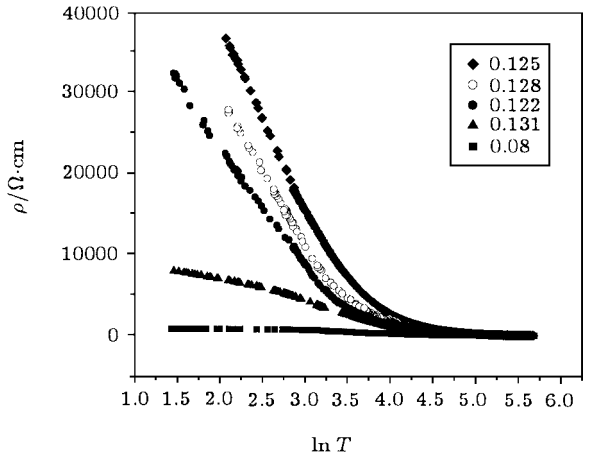


Fig.2. The plots of the in-plane resistivity ρ_{ab} versus ln$T$ in $La_{2-x}Ba_xCuO_4$ with x=0.08, 0.122, 0.125, 0.128 and 0.131. The plots at around x=0.125 indicate an obvious change near 60K.

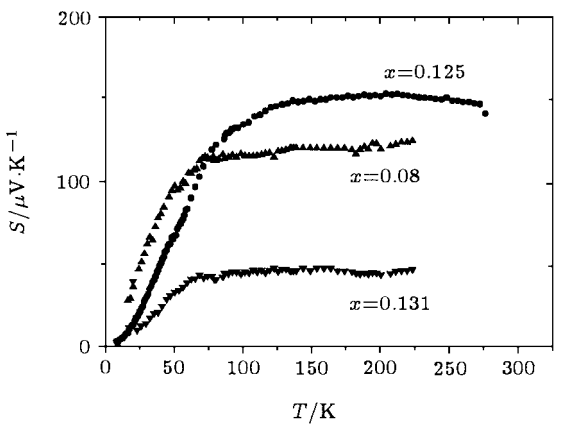


Fig.3. The temperature dependence of in-plane thermoelectric power $S_{ab}(T)$ for the single crystals of $La_{2-x}Ba_xCuO_4$ with x=0.08, 0.125 and 0.131.

4. Discussion

4.1. In-plane electric resistivity

None of the samples show superconductivity at low temperatures. The suppression of the superconductivity of the samples is due to the small amount substitution of Al for Cu. Similarly, it was found that partial substitution of Zn, Ni, etc, for Cu could suppress superconductivity and induce the localization of the charge carrier.[23,24] The semiconductor-like behaviour indicates that the charge carriers in all the samples are localized. The in-plane electrical resistivity ρ_{ab} of the sample with x=0.125 reaches a maximum, indicating that the charge carrier in the sample with x=0.125 is localized most strongly among the samples.

Since the charge carriers in the LBCO system are localized, it is necessary to know what kind of localization behaviour they belong to. While the carrier is strongly localized, the temperature dependence of the electrical resistivity ρ_{ab} is semiconductor-like, and can be fitted reasonably well to the following Mott formula for variable range hopping (VRH) conduction[25]

$$\rho = \rho_0 \exp\left[(T_0/T)^{1/n}\right], \qquad (1)$$

where ρ_0 is a constant. T_0 is given by the expression T_0=2.8$e^2/(4\pi\varepsilon\varepsilon_0 k_B a_H)$, with ε being the dielectric constant of the material and a_H the localization length; $n = 1 + D$ is related to the dimensionality D. While the carrier is weakly localized in a quasi-two-dimensional system, the electrical resistivity ρ will manifest itself as a sublogarithmic temperature dependence as described by the formula of $\rho \propto \ln T$.[26] Also, we find that the temperature dependence of the in-plane electrical resistivity ρ_{ab} can only be well described by the formula $\rho \propto \ln T$ (see Fig.2). In other words, the behaviour of carriers is affected by the weak localization. Since all the samples have a similar Al content, the localization effect caused by Al is expected to be similar among the samples. Supposing the semiconductor-like behaviour for the samples of x=0.08 and 0.131 is induced by the Al contamination, a stronger localization effect at around x=0.125 is certainly induced not only by the Al contamination but also by the 1/8 anomaly. Compared with the two types of effect of carrier localization, as shown in Fig.2, it is clear that the stronger carrier localization is related to the "1/8 anomaly", and the effect caused by Al contamination is negligible compared to the intrinsic localization effect at x=0.125. Although the behaviour of the carriers in the sample with x=0.125 shows the strongest localization among all the samples, the behaviour still belongs to the weak localization.

Furthermore, the ρ_{ab} versus ln$T$ curve shows that there is an obvious change of slope near 60K. The slope becomes steeper below 60K, also indicating that the carriers are localized more strongly below 60K. The change of slope is corresponds well to the structural phase transition from LTO to LTT near 60K, which was confirmed by x-ray diffraction measurements for polycrystalline samples of LBCO.[13,14] It is generally believed that the carriers are more strongly localized after the structural phase transition from LTO to LTT.

What is the reason for the rapid increase of the

electrical resistivity ρ_{ab} at around x=1/8 below the LTO–LTT phase structural transition with decreasing temperature? Recently, in Nd-doped LSCO with x=0.12, Tranquada *et al.*[27−29] observed an elastic magnetic superlattice peak of the type (1/2± $\in$, 1/2, 0) and the charge-order peaks at (2±2 $\in$, 0, 0), where $\in$=0.118 at low temperatures. They have concluded that the stripe-patterned dynamical correlation of holes and spins in the CuO_2 plane are pinned by the LTT structure at low temperatures, leading to the stripe-patterned static order of holes and spins, and the suppression of superconductivity. Correspondingly, spin and charge stripe ordering in LBCO have been found by techniques such as nuclear quadruple resonance (NQR).[30] The spin and charge stripe are expected to be pinned and stabilized in the LTT structure at low temperatures, leading to the rise in resistivity (still well described by the formula $\rho_{ab} \propto \ln T$ in our experiments), and the suppression of superconductivity.[27−30] Furthermore, we do not observe any trace of the phase structural transition from HTT to LTO at about 180 K for x=0.125 by means of electrical resistivity and thermoelectric power measurements. This suggests that the behaviour of the carriers is still quasi-two-dimensional both in the LTO and HTT phase regions.

4.2. Thermoelectric power

Although the temperature dependence of S has not yet been understood clearly for high-T_c cuprates, it is empirically known that the absolute thermoelectric power S at room temperature usually decreases with increasing carrier concentration for high-T_c cuprates.[31,32] The measurements on the thermoelectric power S_{ab} for the three samples with x=0.08, 0.125 and 0.131 show that the maximal room-temperature value of thermoelectric power S_{ab} occurs at x=0.125. It is believed that the carrier concentration in the sample with x=0.125 will be minimal in all of the samples. This also reflects that the carriers in the sample with x=0.125 are most strongly localized. These are consistent with the observation in resistivity measurements.

It was also found that the Seebeck coefficient for the underdoped $La_{2-x}Sr_xCuO_4$ system is temperature-independent at temperatures $T > T_F$ (T_F=crossover temperature below which the spin-fluctuation time is longer than the hole-transfer time),[22,33,34] which is similar to the behaviour of $S_{ab}(T)$ in our experiments. However, such a large value of the Seebeck coefficient α ($\alpha > 40\mu V \cdot K^{-1}$) in the underdoped LSCO system has not been found to be associated with itinerant charge carriers. Goodenough *et al.*[22,34] considered that the temperature-independent Seebeck coefficient $\alpha(T)$ for $T > T_F$ is a typical case of polaronic hopping. The polaronic motion in a narrow-band mixed-valence oxide contains a transport contribution. The dominating configuration term is given by[35]

$$\alpha = -\frac{k_B}{e} \ln\left[\frac{\beta(1-p)}{p}\right], \qquad (2)$$

where β=2 is a spin-degeneracy factor and p is the hole concentration per Cu atom in CuO_2 sheets. In the same way, it seems that the temperature-independent behaviour of $S_{ab}(T)$ in the LBCO system should also be introduced by the polaronic hopping. Furthermore, Eq.(2) also indicates that the carrier concentration in the sample with x=0.125 is minimal among all the samples. On the other hand, the behaviour of $S(T)$ in LBCO at x=0.125 is different from that in the LSCO system. It is suggested that the difference should be induced by both the crystal structure and the carrier concentration.

The S_{ab} versus T curve shows that there is a change of slope occurring at around 70K, which is similar to the observation in the ρ_{ab} versus T, indicating that the change should correspond to the structural phase transition from LTO to LTT, and the formation of charge and spin stripe at low temperatures.

In comparison to the LSCO system, the typical hump between 100 and 250K is not observable in LBCO compounds. Since the hump is supposed to be due to the competition of the superconducting fluctuation and the polaron liquid states[22,34] (the temperature-independent thermopower above 300K is attributed to the polaron gas state), the absence of the hump suggests that neither the superconducting fluctuation or the polaron liquid state exist in the LBCO system at x=0.125.

4.3. The 1/8 anomaly

Since the 1/8 anomaly was recognized, there have been many experiments that have tried to demonstrate the mechanism of the 1/8 anomaly. After all, the true nature of the 1/8 anomaly is the key to establishing a unified picture of the hole-doped CuO_2 planes. These observations in recent experiments[27,30] are compatible with the viewpoint that the stripe fluctuations near the critical hole concentration x=1/8

have a connection with the mechanism of high-T_c superconductivity.[36]

However, the normal state properties such as ρ_{ab} versus T and ρ_{ab} versus ln$T$ in our experiments also present the 1/8 anomaly obviously in the sample with x=0.125, having the highest value and the steepest temperature dependence above the phase structural transition from LTO to LTT. Previous high-pressure studies[5,6,8−11] have suggested that there are other unknown origins of the 1/8 anomaly. High pressure suppresses the phase transition from LTO to LTT and restores the superconductivity, and can also suppress the resistivity ρ upturn in LBCO at around x=0.125 below the LTO–LTT phase transition. But the recovery of T_c seems to be incomplete; T_c remains around 15K or lower.[5−10] Recently, it was reported that the 1/8 anomaly is absent in strained thin films of $La_{2-x}Ba_xCuO_{4+\delta}$; the absence of the 1/8 anomaly in the strained films is due to the c-axis expansion, as well as the in-plane compression.[37] So it seems that the origin of the 1/8 anomaly is not directly related to the structural features of the LTT phase. Whether the origin of the 1/8 anomaly is connected with the charge and spin stripe ordering or the stripe fluctuations, is a matter of debate.

In the LBCO system, the La_2O_2 planes separate the CuO_6 octahedra. When the nominal concentration is 1/8, it means that one corner of the La_2O_2 tetragon will be occupied by the doped Ba atom. In this case, Ba doping introduces the local structural distortions that severely change the corrugation pattern of CuO_2 planes and the octahedra tilts near the Ba site, so that the distortion results in a large Fermi surface. The CuO_6 octahedra tilts of the LTT phase result in major changes in La–O_z configuration and the inequivalent O_{xy} (O_{xy} are oxygen forming the basal plane of CuO_6 octahedra) sites that promote charge transfer and the charge-density-wave (CDW) state formation, which stabilizes in the LTT phase and competes with superconductivity for the Fermi surface.[38] On the other hand, Pickett *et al.*[39] suggested a model based on local-density-functional calculations, which shows that in the LTT phase a gap occurs along a Brillouin zone edge at the Fermi energy (E_F) for $x \approx 0.125$, destroying much of the Fermi surface. The redistribution of electronic states splits a van Hove singularity (VHS), which can explain qualitatively the T_c suppression. Furthermore, the possible origin of an energy gap near E_F in the middle of the band for $x \approx 0.125$ was discussed by Zhou and Goodenough,[34,40] it can introduce the rise in electrical resistivity when going from the LTO phase to the LTT phase.[4,15] Recently, it was found[41] that the local LTT tilt angle of CuO_6 octahedra exhibits a large, random fluctuation with root mean square (rms) $[< (\theta - < \theta >)^2 >]^{1/2} \approx 2 < \theta >$, $< \theta >$ being the average tilt angle. The fluctuations originate from the large random static disorder introduced by Ba doping. This may create a mobility gap along a Brillouin zone edge. The density of mobile states at E_F for x=0.125, which will be reduced when the long-range LTT order appears, would not contribute to superconductivity, leading to T_c suppression. So it is reasonable to suggest that the origin of the 1/8 anomaly should be related to the local crystal structure.

Finally, the problem of the 1/8 anomaly is not yet completely understood. For example, it is still indistinct whether the patterned static order could be regarded as a type of pinned CDW and/or spin-density-wave (SDW).[29]

5. Conclusion

We have discussed the semiconductor-like behaviour of the electrical resistivity of single crystals of $La_{2-x}Ba_xCuO_4$ with x= 0.08, 0.122, 0.125, 0.128 and 0.131, and the thermoelectric power for samples with x=0.08, 0.122 and 0.131. We found that the carrier in $La_{2-x}Ba_xCuO_4$ with x=0.125 is the most strongly localized among all the samples, and the semiconductor-like behaviour can be well described by the weak-localized quasi-two-dimensional state. The steep rise in electrical resistivity for the x=0.125 sample below the LTO–LTT structural phase transition is probably due to the formation of static stripe-ordering of holes and spins which are pinned by the LTT structure, as discovered in $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$.

The resistivity and thermoelectric power data also show the 1/8 anomaly above the LTO–LTT structural phase transition. We speculate that the origin of the 1/8 anomaly can be related to the local crystal structure.

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