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Nonlinear temperature dependence of resistivity in $Bi_2Sr_2CuO_y$ crystals

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We have measured the *ab*-plane resistivity on a number of $Bi_2Sr_2CuO_y$ crystals from 4.2 K to 300 K. The as-grown crystals usually exhibit a minimum in their normal-state resistivity. The low-temperature electronic transport can be described by a hopping conduction. As the crystals were annealed in the ambient flowing oxygen, they could become metallic over the whole temperature range. A nonlinear temperature-dependent resistivity was observed and found to be sample dependent. Some $\rho(T)$ curves can be fitted to a power law with the exponent slightly greater than 1, while others appear with a Bloch-Grüneisen-like shape. A discussion of the experimental results is presented.

The understanding of the unusual normal-state transport properties in layered cuprates has been widely recognized to be the first step towards the understanding of high-temperature superconductivity. Among these properties, the linear increase in the resistivity has commonly been observed in most high-T_c systems and is discussed in a lot of literature. This T-linear resistivity is seen over a wide range of temperature. For the high-temperature side, it extends up to ~ 1000 K in the case of $La_{1.86}Sr_{0.15}CuO_4$.[1] This is unusual if one expects the resistivity saturation to occur as happens in the strong electron-phonon-coupled conventional superconducting materials such as Nb_3Sn. For the low-temperature side, on the other hand, the linearity extends down to ~ 10 K in the $Bi_2Sr_2CuO_6$ materials, which is also quite unusual.[2] Martin *et al.* have demonstrated that if fitting the observed $\rho(T)$ data to the Bloch-Grüneisen formula, one would get a transport Debye temperature $\theta_D^* \sim 35$ K, which may be unphysically low.

The linear temperature-dependent resistivity, though common, is not universal. The nonlinear T-dependent resistivity in $YBa_2Cu_4O_{8+y}$ has been reported by several groups and can be accounted for by the classical Bloch-Grüneisen theory of metallic conduction.[3,4] $Nd_{1.85}Ce_{0.15}CuO_{4+y}$ is an electron-doped superconductor, which exhibits a quadratic T-dependent resistivity.[5,6] Even in the case of $YBa_2Cu_3O_7$, it has been found that the resistivity goes more rapidly than linear as the temperature is higher than 200 K.[7] Takagi *et al.* have studied the systematic evolution of temperature-dependent resistivity on $La_{2-x}Sr_xCuO_4$ single-crystal thin films. They demonstrated that the T-linear resistivity existed only in the narrow composition region associated with optimal superconductivity. In the overdoped region ($x > 0.2$), the resistivity follows a power-law dependence with the exponent of 1.5 over the entire temperature range up to 1000 K.[8]

In this work, we present a measurement of the *ab*-plane resistivity on $Bi_2Sr_2CuO_{6+y}$ crystals. The motivation to study this system is that the Bi 2:2:0:1 has a rather low superconducting transition temperature and the normal state extends to a sufficiently low temperature so that we can see rather clearly if there is a crystal exhibiting nonlinear T-dependent resistivity. Our experimental results indicate that the resistivity is sample dependent. Several kinds of nonlinear T dependence of resistivity were observed.

Single crystals with different starting composition were grown from a copper-oxide-rich melt in Al_2O_3 crucibles. Typical dimensions are of 4 mm$\times$2 mm$\times$(10$\sim$40) μm. The 2:2:0:1 structure has been characterized by x-ray diffraction. Gold electrodes were evaporated in the standard four-probe configuration and copper leads were softly soldered to the electrodes. This procedure ensures low contact resistances. A current of 100 μA from the Lake Shore Cryotronics 120 current source was passed through the sample and the voltage was measured with a Keithley 181 nanovoltmeter.

Figure 1 shows the temperature dependence of the inplane resistivity for two 2:2:0:1 crystals. The shape of $\rho(T)$ curvelike crystal A is commonly observed in the as-grown crystals in our measurements. They show metallic behavior at high temperature but insulating behavior at low temperature. These two regions are separated by a shallow minimum $\rho_{\min}$. For sample A, $\rho_{\min}$ occurs at $T_{\min} \sim 70$ K. Though it is insulating at low temperatures, the high-temperature resistivity of this crystal indeed increases linearly with T. A similar situation in Bi 2:2:0:1 crystals was also reported previously.[2,9] In fact, this kind of temperature-dependent resistivity is often seen in other high-T_c superconducting systems when their CuO_2 layers are doped by impurities or their carrier concentrations are reduced.[10-15] It is also seen in other strong electron-correlation systems showing the metal-insulator transitions with the change of the carrier concentration, e.g., $R_{1-x}Sr_xMO_3$(R=rare-earth element, M=Ti, V, and others).[16]

The $\rho(T)$ curve exhibiting a minimum is similar to the

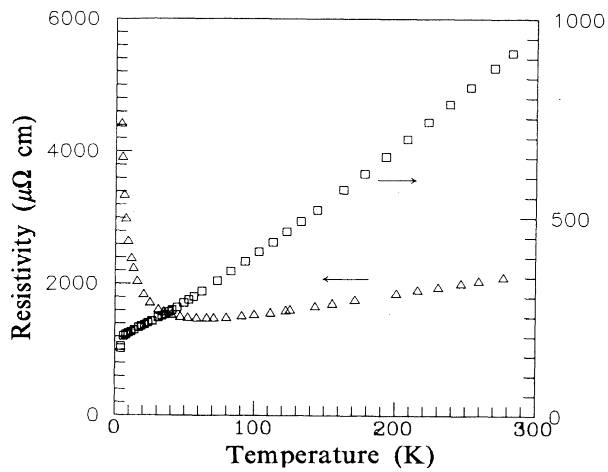

FIG. 1. Two different temperature dependences of the *ab*-plane resistivity of 2:2:0:1 crystals growing from the starting composition of $Bi_2Sr_2Cu_3O_y$. △: crystal *A*; □: crystal *B*.

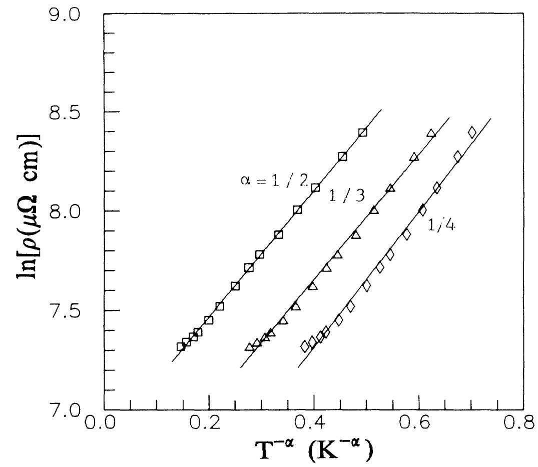

FIG. 2. Variable-range hopping $\rho=\rho_0\exp(T_0/T)^\alpha$ fits to the low-temperature resistivity of crystal *A* in Fig. 1 with $\alpha=\frac{1}{2}$, $\frac{1}{3}$, and $\frac{1}{4}$. The $\alpha=\frac{1}{2}$ exponent gives the best straight line fit.

case of the Kondo effect. Some authors indeed interpreted their resistivity data in terms of the Kondo effect.[14,15] However, the $\rho(T)$ curve of crystal *A* cannot be fitted well to the formula of $\rho(T)=A+BT+C\ln T$. This is because the resistivity increases rather sharply at low temperature. In fact the explanation of the Kondo effect is based on the exchange interaction between the spins of the conduction electrons and the localized magnetic moments of the impurities. In cuprates, though, the Cu in CuO_2 layers is divalent, i.e., $3d^9$, these Cu^{2+} cations do not show an isolated magnetic moment because they are antiferromagnetically correlated through the oxygen ions. Therefore, it is reasonable that the minimum in the $\rho(T)$ curve is not associated with the Kondo effect.

The upturn in the resistivity at low temperature indicates that the carriers tend to be localized. There is no doubt that this case is located near the border of the metal-insulator transition. Jing *et al.*[17] have studied the magnetoresistance of a $Bi_2Sr_2CuO_{6+y}$ crystal in which the resistivity minimum occurs at the temperature about 10 K. Because its resistivity below $T_{\min}$ follows the relationship of $\rho(T)\propto -\ln T$, the crystal is demonstrated to be in the weak-localization regime. However, the crystal *A* in this study does not obey such a relationship. As the temperature decreases, it shows a faster than $-\ln T$ increase in resistivity below $T_{\min}$. This indicates definitely that the crystal is in the strong-localization regime at low temperature. The temperature-dependent resistivity in this regime is generally analyzed within the context of variable-range hopping with the form of $\rho(T)=\rho_0\exp(T_0/T)^\alpha$. In Fig. 2, the data are plotted as $\ln\rho$ vs $T^{-\alpha}$ with $\alpha=\frac{1}{2}$, $\frac{1}{3}$, and $\frac{1}{4}$ to show the hopping behavior. The straight lines represent a linear fit to the experimental data. It can be seen that the $\alpha=\frac{1}{2}$ exponent gives the best straight-line fit. This result is a little different from the report of Fiory *et al.* on the 2:2:0:1 crystal, where they get the best fit with $\alpha=\frac{1}{3}$.[9] In fact, the exponent is in close relationship to the carrier density. As the carrier density increases, a crossover from $\alpha=\frac{1}{2}$ to $\frac{1}{4}$ is demonstrated to take place.[10,18] Thus the result may indicate that this crystal has a lower carrier density.

What we should stress is, it is quite unusual that the charge conduction is metallic at high temperature but insulating at low temperature. Although such a shape of the $\rho(T)$ curve is reported in various systems and its low-temperature resistivity follows the hopping conduction, the conduction mechanism for the whole process is still not fully understood. It is notable that even in the antiferromagnetic region, for example, $La_{1-x}Sr_xCuO_4$ with $x\le 0.02$, the samples still display both of the regimes in resistivity with the $T_{\min}$ lower than 200 K.[8,12] One should keep in mind that the charge-transfer energy gap for La_2CuO_4 is about 1.5 eV, which is much greater than the temperature $T_{\min}$ of the resistivity minimum. It is reported that in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ series, with the increase of Y content, the superconducting transition temperature falls sharply and the sample soon becomes insulating at low temperature, however, its high-temperature (> 100 K) slope, $d\rho(T)/dT$, even increases.[13] We believe that this kind of charge transport is a common feature of a strong electron-correlation system under the low carrier concentration region and deserves to be further studied.

When the as-grown crystals were annealed in air or ambient flowing oxygen for a period, say 12 h, they could become metallic in the whole temperature range with a much smaller resistivity. The crystal represented by *B* in Fig. 1 is metallic in the whole temperature range measured. A superconducting transition appears at the temperature about 5 K, but its resistivity in the normal state is not exactly linear temperature dependent. In Fig. 3, we plot the resistivity as $\ln(\rho-\rho_0)$ vs $\ln(T)$. One can see that the resistivity approximately follows a simple power law $\rho-\rho_0=aT^n$. A best fit of the data gives $n\sim 1.1$ and $\rho_0=192\ \mu\Omega$ cm. As it has been realized from many high-T_c cuprate systems, when the system changes from the optimally doped superconductor with the highest T_c to

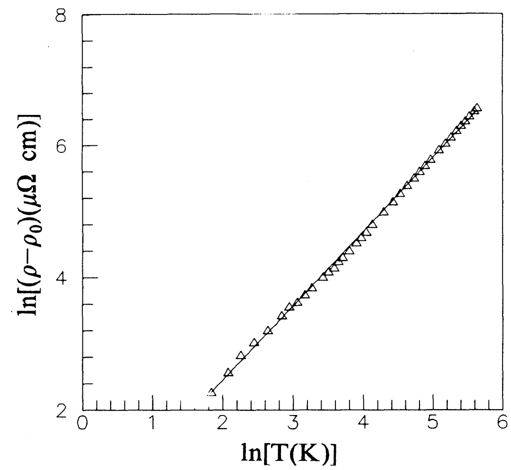

FIG. 3. ln-ln plot of the temperature-dependent resistivity of crystal B in Fig. 1. The solid line gives the best fit.

the overdoped nonsuperconducting metal, the electrical resistivity changes from a linear temperature dependence to a power-law temperature with the exponent greater than 1, and this crystal showing a faster than linear increase in resistivity may be in the slightly overdoped region. It should be mentioned that in Pb-doped $Bi_2Sr_2Cu_2O_y$ ceramics, we have observed the resistivity vs temperature as $T^{1.5}$ in 30–300 K accompanied by a comparatively smaller Hall coefficient and even negative thermoelectrical power.[19] But in these crystals we do not find the exponent higher than 1.1.

An interesting $\rho(T)$ curve is shown in Fig. 4. The $\rho(T)$ curve is approximately linear at high temperature, but deviated from the straight line rather obviously at the temperature below 100 K. A drop in resistivity near 4.2 K suggests it would be superconducting below the liquid-helium boiling temperature. The starting composition for growing this crystal is $Bi_{1.95}Pb_{0.05}Sr_2Cu_3O_y$. However, similar $\rho(T)$ curves are also observed in several crystals including that with the starting composition

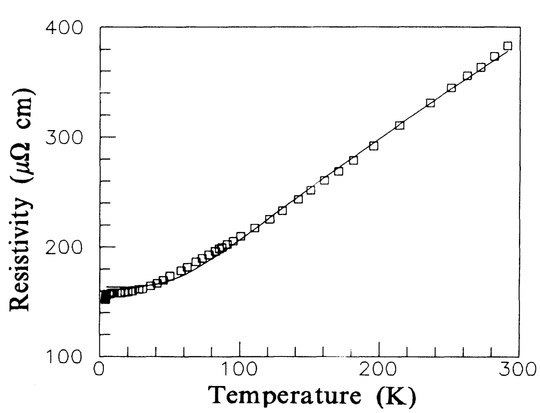

FIG. 4. The in-plane temperature-dependent resistivity of a 2:2:0:1 crystal growing from the starting composition of $Bi_{1.96}Pb_{0.05}Sr_2Cu_3O_y$. The solid curve represents a least-squares fit to the Bloch-Grüneisen formula.

without Pb at all. The shape in the $\rho(T)$ curve may suggest that the resistivity crosses over to a higher power of T at low temperature, which may be similar to that of a phonon-limited resistivity of an ordinary metal. We thus fit the $\rho(T)$ curve to the Bloch-Grüneisen formula with the transport Debye temperature θ_D^* as an adjustable parameter. In Fig. 4, the solid curve represents a least-squares fit to Bloch-Grüneisen formula with $\theta_D^* \sim 350$ K. One can see that only a small deviation of the experimental data from the solid curve appears at low temperature. This result is very different from previous reports.[2,20] For one thing, the transport Debye temperature θ_D^* used here is one order higher than the one that Martin *et al.* could use to fit linear $\rho(T)$. This situation is analogous to the $\rho(T)$ curve observed in $YBa_2Cu_4O_8$.[3]

An alternative explanation of the above experimental data may be that the sample is in fact in the slightly underdoped region. The tendency towards a temperature-independent resistivity at low temperature is really just the beginning of an upturn such as is seen in sample A of Fig. 1. The transport behavior for this crystal might in reality be a combination of metallic and insulating behavior, similar to, but less pronounced than crystal A. Because the sample is barely superconducting and definitely not optimally doped, this possibility cannot be ruled out.

We should emphasize here that all these crystals in the measurements have essentially the same Bi 2:2:0:1 structure, and no clear difference could be drawn out from their x-ray diffraction patterns. The main difference among these crystals may be that they have different oxygen contents during the process of crystal growth and the annealing treatments, so that they lie at different doping levels. We have only observed the above three kinds of $\rho(T)$ curves, all of them are nonlinear temperature dependent. We have not found any crystal exhibiting a superconducting transition temperature higher than a few Kelvin. We suggest that the linear temperature-dependent resistivity reported previously is just connected with the optimally doped sample, and our experimental data could serve as a compensatory one.

Then what could we learn from the above transport properties? Can we accept Fig. 4 as showing that the phonon scattering dominates the charge transport process? We suggest that the answer still is no. Because if this was the case, how could we understand the linear T-dependent resistivity commonly observed, as well as the $\rho(T)$ curves in Fig. 1 from the same transport mechanism? A single experimental data may well be explained away, but a correct theory must be able to explain all these unusual experimental results. We believe that the electron-correlation effect plays an important role in these materials and cannot be ruled out from the charge transport mechanism. Due to the correlation effect, the charge carriers in superconducting cuprates are near the border of the localization and delocalization. The insulator-metal transition can easily take place as the doping level changes. The metallic state seems to be marginal, and can easily be destroyed by doping or by impurities. Further efforts to elucidate the charge dynamics in the layered cuprates are still needed.

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