Thermoelectric power and resistivity of $La_{1.8}Sr_{0.2}CaCu_2O_{6-\delta}$ and the effects of O_2 hot-isostatic-press annealing

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We have measured the resistivity and thermoelectric power of $La_{1.8}Sr_{0.2}CaCu_2O_{6-\delta}$ for $15 \le T \le 340$ K. For the as-sintered sample heated under one atmosphere of oxygen, a minimum resistivity occurs at ca. 100 K, and the conductivity can be fitted to the form $\exp(T^{-1/2})$ or $\exp(T^{-1/4})$ for $30.3 \le T \le 86.8$ K. The thermoelectric power varies as $T^{1/2}$ for $20 \le T \le 200$ K and exhibits a saturated value of ca. 100 μV/K for $T \ge 230$ K. Upon O_2 HIP (hot isostatic press) treatment, the upturn of resistivity (metal-nonmetal transition) is suppressed and superconductivity ensues, and the thermoelectric power decreases in magnitude and displays a broad maximum at ca. 190 K in a manner similar to $La_{2-x}Sr_xCuO_{4-\delta}$. It is conceivable that the O_2 HIP treatment suppresses the metal-nonmetal transition as a result of increasing carrier concentration and possibly enhancing cation ordering. The possible origin of the metal-nonmetal transition is discussed.

I. INTRODUCTION

The conduction behavior for the "326" cuprates $(La,Sr,Ca)_3Cu_2O_{6-\delta}$ appears to be very sensitive to the synthesis conditions, particularly the annealing temperature and the oxygen partial pressure. Some 326 cuprates behave like a semiconductor or a semimetal, while others exhibit a minimum resistivity at around 100 K for those materials synthesized at 1 atm of oxygen.[1-3] Superconductivity in this system was confirmed by Cava *et al.*[4] using a sophisticated processing technique involving sample annealing at a moderately high pressure of oxygen. Both of the subtle structural differences caused by oxygen stoichiometry and cation ordering were suggested to be associated with the occurrence of superconductivity in the 326 materials, based on combined x-ray and neutron powder diffraction data.[5] For superconducting $La_{1.8}Sr_{0.2}CaCu_2O_6$ samples, the smaller divalent Ca has a preferential occupation on the 2*a* site, which is coordinated by eight oxygen atoms, whereas both La and Sr have preferential occupation on the 4*e* site, which is coordinated by nine oxygen atoms. In addition, superconducting $La_{1.85}Ca_{1.15}CuO_{6-\delta}$ was reported to have a La/Ca ratio of 0.88/0.12 at the 4*e* site, and 0.85/0.15 for the nonsuperconducting counterpart.[6]

The upturn of resistivity at low temperatures (metal-nonmetal transition) has been observed over a wide variety of compounds by decreasing the carrier concentration, ion-beam bombardment, or metal substitution for Cu in the parent high-T_c compounds.[7-9] The conductivity in the nonmetallic regime could be described by the form $\exp(T^{-\upsilon})$ with $\upsilon = \frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{4}$. Therefore the transport behavior has been discussed in a manner similar to the impurity band conduction in a disordered system.[7-14] In this paper, we present the effects of O_2 HIP (hot isostatic press) treatment on the resistivity and thermoelectric power (TEP) for $La_{1.8}Sr_{0.2}CaCu_2O_{6-\delta}$. Upon O_2 HIP treatment, our general finding is that (1) the metal-nonmetal transition at low temperatures is suppressed and superconductivity ensues, and (2) the TEP decreases in magnitude and displays a broad maximum at ca. 190 K. For the sample sintered at 1 atm of oxygen, the conductivity data can be well fitted to the form $\exp(T^{-1/2})$ or $\exp(T^{-1/4})$ at $30.3 \le T \le 86.8$ K, and the TEP nicely follows the form of $T^{1/2}$. The possible origin of the metal-nonmetal transition for a disordered system is discussed.

II. EXPERIMENT

Material with the composition of $La_{1.8}Sr_{0.2}CaCu_2O_{6-\delta}$ was prepared by a conventional solid-state reaction method. Appropriate amounts of high-purity La_2O_3, $SrCO_3$, and CuO were quantitatively mixed. The mixed powders were ground by ball milling using zirconia balls. The ground mixture was then dried at temperatures between 60 and 80 °C in five stages. The resulting powder was then pressed into bars and fired at 900 °C for 150 h in flowing oxygen with intermediate grindings. The as-prepared samples were annealed at 1090 °C under a total pressure of 1000 atm (oxygen 200 atm and argon 800 atm) by using O_2 HIP techniques.

The powder x-ray diffraction (XRD) patterns were obtained by using a diffractometer equipped with Cu $K\alpha$ radiation (MAC Science model MXP^{18}). Electrical resistivity was measured using a standard four-probe technique. Thermoelectric power was measured by employing two pairs of copper-Constantan thermocouples. Data were taken only after the system reached thermal equilibrium, which was monitored by a calibrated Si diode and the voltage response across Cu Seebeck probes. Temperature gradients were typically between 0.3 and 0.4 K. The uncertainty of measurements was ± 0.1 μV/K.

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III. RESULTS

As shown in Fig. 1, the XRD patterns indicate that the as-sintered material is virtually a single phase of the 326 structure with the tetragonal lattice constants of $a=3.818(3)$ Å and $c=19.69(2)$ Å. As shown in Fig. 1, the material prepared at 900 °C at 1 atm of oxygen (designated as *A*) displays a minimum resistivity at ca. 100 K, and a relatively rapid drop of resistance at ca. 26.5 K. The upturn of resistivity is suppressed by post-anneal using the O_2 HIP technique at 1090 °C at a total pressure of 1000 atm (oxygen 200 atm and argon 800 atm). The O_2 HIP treated sample (designated as *H*) shows an onset of superconducting transition at ca. 58 K and $T_{c,0}=46$ K. In Fig. 2 we replot $\ln\sigma$ against $T^{-1/4}$ and also against $T^{-1/2}$ on a semilog scale between 86.8 and 30.3 K from the resistivity data given in Fig. 1. We find that the fit to $T^{-1/2}$ is slightly favored over $T^{-1/4}$; the former implies the presence of electron-electron interactions with a soft Coulomb gap near the Fermi energy (E_F) and the latter a variable-range-hopping process for a three-dimensional system.[10] The TEP data shown in Fig. 3 have been corrected for the contribution of the Cu leads. Both samples *A* and *H* show positive TEP at all investigated temperatures, $15\le T\le 340$ K. The TEP for sample *A* decreases with decreasing temperature for $T\le 230$ K, and shows a saturated value of ca. 110 μV/K for $T\ge 230$ K. This behavior resembles that for underdoped samples of $La_{2-x}Sr_xCuO_{4-\delta}$. The TEP for sample *H* apparently becomes smaller in magnitude as compared to sample *A*, and displays a broad maximum at ca. 190 K. The change of the TEP behavior from sample *A* to sample *H* resembles that for $La_{2-x}Sr_xCuO_{4-\delta}$ as a result of increasing carrier concentration. Note that their structures are also quite similar. All these facts indicate that the hole carrier concentration increases as a result of the O_2 HIP treatment. In Fig. 4 we replot the TEP data against $T^{1/2}$ and find a reasonably good linear relationship, which will be discussed as follows.

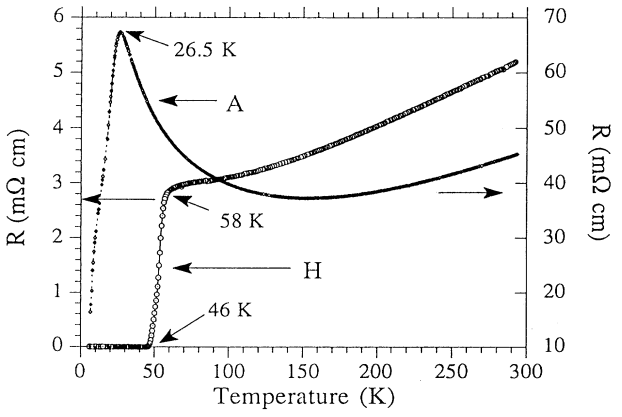

FIG. 1. Temperature dependence of dc resistivity for $La_{1.8}Sr_{0.2}CaCu_2O_{6-\delta}$ prepared at 900 °C in 1 atm of oxygen (sample *A*) and by O_2 HIP post treatment (sample *H*).

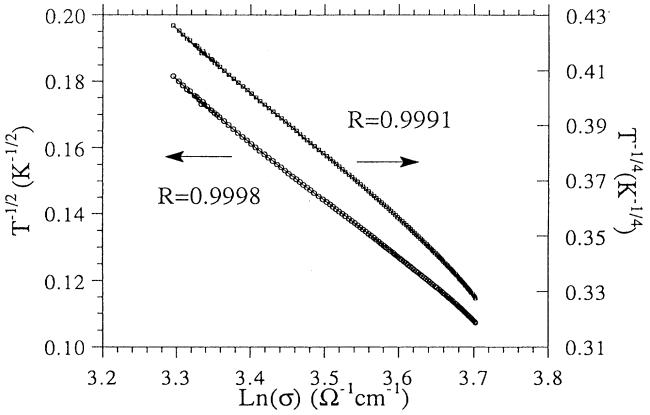

FIG. 2. Conductivity $\ln(\sigma)$ for sample *A* at $30.3\le T\le 86.8$ K replotted against $T^{-1/2}$ and $T^{-1/4}$; the former is slightly favored over the latter.

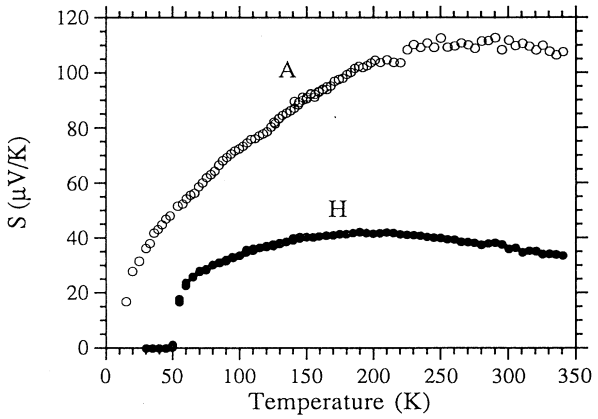

FIG. 3. Temperature dependence of thermoelectric power for samples *A* and *H*. The sample labels are the same as in Fig. 1.

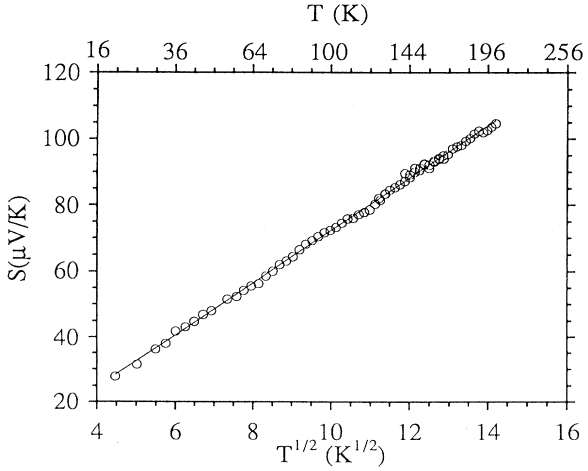

FIG. 4. Thermoelectric power for sample *A* at $20\le T\le 200$ K varies as $T^{1/2}$, suggestive of variable-range hopping in three dimensions, instead of the presence of a "soft" Efros and Shklovskii Coulomb gap due to electron-electron interactions.

IV. DISCUSSION

For nonmetallic cuprate analogs, the conductivity σ has been frequently found to obey the equation[10]

$$\sigma=\sigma_0\exp\left[\frac{T_0}{T}\right]^{v}, \tag{1}$$

where σ_0 is weakly temperature dependent but barely influences the value of the index v, and T_0 is associated with the localization length. When the charge transport is governed by variable-range hopping, the index v should be given by $1/(d+1)$, where d is the dimensionality, provided the density of states near E_F is constant. When a "soft" Efros and Shklovskii Coulomb gap[11] exists in the density of states near E_F as a result of electron-electron interactions, v should be given by $\frac{1}{2}$ for both two- and three-dimensional systems, and the density of states in the vicinity of E_F varies as $|E-E_F|^n$, where $n=1$ for two dimensions (2D) and $n=2$ for 3D. Nevertheless, it seems to be quite ambiguous, based on the value of v determined only from the resistivity data, to determine the dimensionality or to answer the question of whether the Coulomb gap is present for hopping conduction between localized states. Different values of v have been reported for nonmetallic cuprate analogs.[7-9,12-14] For nonmetallic $La_{2-y}Sr_yCu_{1-x}Li_xO_{4-\delta}$ single crystals and ceramics,[12] the value of $v=\frac{1}{4}$ has been observed. For both ceramics and epitaxial films of $PrBa_2Cu_3O_{7-\delta}$,[13] the difference between $v=\frac{1}{3}$ and $\frac{1}{4}$ was not distinguishable. For $La_{2-x}Sr_xCu_{1-y}M_yO_{4-\delta}$ (M=Fe, Co, Ni, Zn, and Ga),[9] both $v=\frac{1}{4}$ and $\frac{1}{2}$ have been obtained in the hopping-conduction regime, depending on the composition and temperature range. For $YBa_2Cu_3O_{7-\delta}$ films damaged by ion-beam irradiation with high ion fluences, $v=\frac{1}{2}$ was found.[8] It has been argued[9] that the Coulomb gap will gradually disappear when the metal-nonmetal transition regime is approached from the insulating side because the Coulomb interaction between carriers is screened. This argument seems plausible in view of the variation of the index v from 0.5 ($z=0.0$) to 0.2 ($z=0.4$) with increasing carrier concentration for $Bi_2Sr_2(Ca_zY_{1-z})Cu_2O_{8+\delta}$.[7] However, Forro[14] argued that a Coulomb gap should become less significant for hopping with increasing the charge separation by a factor of 2–3, in view of the fact that the value of v changes from $\frac{1}{4}$ to $\frac{1}{2}$ on annealing a single crystal of $Bi_2Sr_2YCu_2O_8$ in argon at 600 °C. In addition, for a single crystal and a ceramic sample of $Bi_2Sr_2YCu_2O_8$, both of which were annealed at 600 °C in argon, the index $v=\frac{1}{2}$ is obtained for the single crystal and v is close to $\frac{1}{4}$ for the ceramic sample, suggesting that the resistance network of the grain boundaries should also be considered. Taking all these experimental data into account, the problem seems to be rather confused regarding the temperature dependence of conductivity in the hopping regime for cuprate analogs.

Burns and Chaikin[15] calculated the effect of electron-electron interactions on the thermoelectric power for hopping transport in two- and three-dimensional systems in the low-temperature limit. They concluded that in a disordered system the TEP will reflect the presence of electron-electron interactions and is much more sensitive than conductivity to the presence of the Efros and Shklovskii Coulomb gap in the single-particle density of states. For a disordered system, the temperature dependence of the TEP, as described by variable-range hopping, should follow the form

$$S(T)\propto T^{(d-1)/(d+1)}, \tag{2}$$

where d is the dimensionality. The TEP should follow the form of $T^{1/2}$ for 3D, and of $T^{1/3}$ for 2D. As seen in Eq. (2), the TEP will decrease with decreasing temperature and tends to zero as T approaches absolute zero. When a soft Efros and Shklovskii Coulomb gap exists in the single particle density of states and T drops to a certain temperature T_{ES} where the states within the Coulomb gap become extremely important, the TEP below T_{ES}, according to Burns and Chaikin,[15] will be given as follows instead of the relation given by Eq. (2):

$$S(T)=\frac{k_Be}{K}\alpha\left[\frac{\partial\ln D_0(E)}{\partial E}\right]_{E=E_F}, \tag{3}$$

where K is the dielectric constant of the medium, $1/\alpha$ the decay length of the localized wave function, and $D_0(E)$ the "noninteracting" density of states. Consequently, when an interacting system is described by Efros and Shklovskii's model, the TEP will follow Eq. (2) in the same manner as the variable-range hopping in a noninteracting system for $T>T_{ES}$, and then should be governed by Eq. (3) for $T\ll T_{ES}$, leveling off to a nonzero constant instead of decreasing to zero as T approaches zero.

Now we can turn to our resistivity and TEP data for $La_{1.8}Sr_{0.2}CaCu_2O_{6-\delta}$ given in Figs. 1 and 2. As seen in Fig. 2, the conductivity data for sample A can be well fitted to $v=\frac{1}{2}$ or $\frac{1}{4}$ in Eq. (1) for $30.3\le T\le 86.8$ K. The index $v=\frac{1}{2}$ is found to be slightly favored. This situation is fundamentally different from the transition of the state with $v=\frac{1}{2}$ to the one with $v=\frac{1}{4}$ due to the screening of the Coulomb interaction and makes one ask whether the charge transport in the nonmetallic regime in Fig. 1 is of the Mott type or the Efros and Shklovskii type. For polycrystalline samples, the electrical resistance between grains has less effect on the TEP than the bulk electrical resistivity. Therefore the TEP measurements seem to be useful to clarify these confusions. As shown in Fig. 4, the TEP decreases with increasing temperature for $15\le T\le 200$ K and the temperature dependence of the TEP for $20\le T\le 200$ K follows the $T^{1/2}$ law quite nicely, suggesting a variable-range-hopping process in a three-dimensional network. It is therefore quite evident that the good fit of $\ln\sigma$ to $T^{-1/2}$ cannot be ascribed to Efros and Shklovskii's Coulomb gap, for which the TEP should drop to a minimum at $T=T_{ES}$ and then increase with decreasing temperature down to the T ($\ll T_{ES}$) where the TEP becomes a nonzero constant according to Burns and Chaikin's calculation. The metal-like temperature dependence of resistivity ($d\rho/dT>0$) for $T>100$ K seems to

indicate the coexistence of itinerant states and localized states. This could arise if the mobility of localized states is very small compared to itinerant states so that the itinerant states dominate the electrical conduction at sufficiently high temperatures. Upon O_2 HIP treatment, the magnitudes of both electrical resistivity and TEP decrease for sample *H*. The metal-nonmetal transition is also suppressed and superconductivity occurs. The temperature dependence of the TEP displays a broad maximum at ca. 190 K. The TEP behavior for $La_{1.8}Sr_{0.2}CaCu_2O_{6-\delta}$ is very similar to that for $La_{2-x}Sr_xCuO_{4-\delta}$, and so are their structures.

The suppression of the metal-nonmetal transition at low temperatures by O_2 HIP treatment can be qualitatively explained as follows by considering a simple disordered system in terms of Anderson localization. When the random field V generated by disorder exceeds a certain extent for a given bandwidth B, e.g., $(V/B)_{crit}$, the carriers in such a medium will be localized. In such disordered lattices the charge transport is governed by the variable-range-hopping process at low temperatures. As mentioned previously for $La_{1.8}Sr_{0.2}CaCu_2O_{6-\delta}$, the hole concentration increases and the occupation of cation sites seems to become more ordered after O_2 HIP treatment. This might imply that the bandwidth B increases and V decreases, both of which would cause localized carriers to become itinerant. For sample *A*, the carrier concentration is most likely in the vicinity of the critical concentration where the metal-nonmetal transition takes place. A study of the electronic density of states as a function of oxygen content derived from ultraviolet photoemission spectroscopy is desirable in order to confirm whether the metal-nonmetal transition is of the Anderson type.

V. CONCLUSIONS

The 326 cuprate, $La_{1.8}Sr_{0.2}CaCu_2O_{6-\delta}$, prepared at 1 atm of oxygen displays a minimum resistivity at ~ 100 K, and the conductivity varies as $\sigma=\sigma_0\exp(T_0/T)^v$ with $v=\frac{1}{2}$ or $\frac{1}{4}$ for $30.3 \le T \le 86.8$ K. The thermoelectric power is proportional to $T^{1/2}$ for $20 \le T \le 200$ K and displays a saturated value of ca. 110 μV/K for $T \ge 230$ K. Upon O_2 HIP treatment, the metal-nonmetal transition is suppressed and superconductivity occurs. The thermoelectric power displays a broad maximum at ca. 190 K. This behavior is similar to that reported for $La_{2-x}Sr_xCuO_{4-\delta}$. According to Burns and Chaikin's calculation using Efros and Shklovskii's interacting model, the transport behavior for the as-sintered $La_{1.8}Sr_{0.2}CaCu_2O_{6-\delta}$ sample should be dominated by Mott's variable-range hopping, but not by the presence of a "soft" Efros and Shklovskii Coulomb gap. The effect of O_2 HIP treatment is believed to increase the hole carrier concentration. The metal-nonmetal transition can be explained in the sense of Anderson localization.

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