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Electronic transport in highly doped $La_{2-x}Sr_xCuO_4$ superconductors

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The thermoelectric power, Hall coefficient, and resistivity have been measured on two samples of $La_{2-x}Sr_xCuO_4$ with a strontium content of $x=0.2$ and $x=0.25$. We observe typical metallic behavior with a strong electron-phonon interaction and a low density of carriers. A large positive peak at a temperature of more than twice the respective superconducting transition temperature suggests a strong phonon-drag contribution to the thermopower. At higher temperatures the thermopower changes sign from positive to negative, a trend that increases with increasing Sr content. A positive Hall coefficient combined with a negative diffusion thermopower implies the presence of more than one type of carrier.

The recent discovery[1-4] of high-T_c superconductivity in the oxygen-deficient perovskitelike structures has generated tremendous excitement in the scientific community and continues to stimulate vigorous research activity in this field. A plethora of experimental techniques has been used to elucidate the important structural and electronic properties underlying the spectacularly high transition temperatures observed in this class of materials. Most recently the scope of studies has expanded to include the thermal transport effects and, in particular, the behavior of the thermopower.

Grant *et al.*[5] measured the thermopower in undoped sintered La_2CuO_4, finding a very large value (~ 200 μV/K) which is consistent with the nonmetallic behavior of the normal-state resistivity (that is extremely large and decreases with temperature above a temperature of about 50 K). Similar thermopower behavior was seen[6] in La_2CuO_4 lightly doped with Sr and Ba (doping concentration $x=0.1$), and interpreted in terms of strong correlations and hopping conduction by d electrons.

In this paper we concentrate on the behavior of the thermopower in the opposite case, that of the heavily Sr-doped regime of $La_{2-x}Sr_xCuO_4$ with $x=0.2$ and $x=0.25$, in which the transport properties are rather different from those in the lightly doped regime. Chen, McEwan, Wenger, and Logothetis[7] measured the thermopower in a $La_{1.8}Ba_{0.2}CuO_4$ sample and concluded that conduction was by positive (holelike) carriers. We demonstrate here, however, that this conclusion is not warranted by the data, and have in fact shown by extending our measurements to higher temperatures that the *diffusion* thermopower in the most heavily Sr-doped compounds is negative (the first report of this behavior in high-T_c superconductors, to our knowledge). Since in this concentration range there are conflicting reports on the sign of the carriers,[8,9] we also decided to measure the Hall effect to settle this issue. In contrast to the lightly doped systems, we are able to form a consistent picture of transport in these highly doped samples in terms of ordinary metallic conduction via low densities of holes *and* electrons in the presence of a large carrier-phonon interaction.

Samples used for the study were prepared in a way similar to the recipes stated elsewhere. The only notable difference is in one of the starting materials $La(NO_3)_3 \cdot 6H_2O$ instead of the usual La_2O_3. This necessitated heating of the mixture in alumina crucibles at about 600 °C until the NO_2 emission stopped, typically a 5 min procedure. After grinding and heating again in air at 1000 °C for one day, samples were furnace cooled and pressed into pellets of 13 mm diameter and 2 mm thickness under a pressure of about 1.5 kbar. Overnight annealing at 1000 °C in flowing O_2 was followed by cooling in O_2. We wish to stress that both the $x=0.2$ and $x=0.25$ samples were prepared simultaneously and were treated identically in all respects. No attempt was made to further optimize the properties of these samples. X-ray data indicate that both samples are single-phase materials. Rectangular bars of 12 mm by 2 mm by 2.5 mm were cut with a diamond wheel and electrical contacts were prepared with the aid of silver epoxy.

Each sample was cooled down to liquid-helium temperatures twice, in the first round to measure the resistivity and Hall coefficient under the isothermal conditions and, after a pause of about 5 weeks, the resistance measurements were repeated under adiabatic conditions in the process of the thermopower investigations. We find no significant difference between the transition temperatures of either sample within this time period, indicating a high stability of the structure.

Thermopower was determined by a standard steady-state technique with one end of the samples fastened to a slotted cold tip of the helium cryostat using Stycast and the same method was applied to attach a metal-film resistor (heater) to the other end. The temperature gradient was monitored by a combination of a Au/Fe-chromel differential thermocouple and a pair of calibrated glassy-carbon sensors, with care being taken to limit heat loss along the wires. For thermopower leads we have used thin

(0.03 mm diameter) and long (0.2 m) copper wires. With its small and only weakly temperature-dependent thermopower, the copper is quite convenient as a Seebeck probe above about liquid-nitrogen temperature. In this regime we rely on the data of Crisp, Henry, and Schroeder[10] to correct for the thermopower of the copper leads. At lower temperatures copper is generally considered unsuitable as a material for the thermopower leads due to the interference of phonon-drag and Kondo-effect mechanisms, which vary from spool to spool and, thus, render the tabulation of the low-temperature thermopower of copper impractical. With the advent of high-T_c superconductors the precise metrology becomes a very simple procedure. Using the fact that the thermopower of a superconductor is zero, one can determine the absolute thermopower of any section of wire that forms a thermoelectric circuit with a superconducting element to high precision up to the transition temperature. We use this feature to calibrate our copper spool up to 92 K, the transition temperature of $YBa_2Cu_3O_7$.

In Fig. 1 our sample resistivities and their temperature dependence are shown. Both samples have features similar to those reported in the literature:[8] approximately linear temperature dependence, resistance change between room temperature and close to the transition of about a factor of 4, and a rather high resistivity of the order of 200–300 $\mu\Omega$ cm just before the transition. Amorphous metal-metal alloys with this magnitude of resistivity have electronic mean free paths of the order of the interatomic spacing. This is not the case, however, for high-T_c superconductors since their conduction-electron density is smaller by at least an order of magnitude. Assuming a simple metallic picture, we therefore expect the mean free path to be some tens of Å just above T_c in our samples. This picture is confirmed by the strong linear temperature dependence of the resistivity (i.e., the standard behavior for scattering by phonons), which is very difficult to reconcile with any model of conductivity by hopping.[6] Assuming the usual interpretation, the "residual" resistivity is large ($\sim$200 $\mu\Omega$ cm), but at higher temperatures the scattering of carriers by phonons is dominant. A corollary of this conclusion is that phonon-drag thermopower, which is essentially completely suppressed in amorphous metals,[11] may well be present in high-T_c superconductors, particularly since phonon drag is more important in systems with a low density of carriers,[12] such as the group-V semimetals[13] or graphite.[14]

The thermopower S of the samples is presented in Fig. 2. The behavior observed above the transition temperature is typical of metallic thermopower: a large peak ascribed to phonon drag at about $T_D/5$ (where T_D is the Debye temperature), followed by a slow decay of the phonon-drag component (as T^{-1} in the simplest model[12]) to leave an approximately linear diffusion thermopower. Because the phonon spectrum extends to high energies in the high-T_c superconductors[15] (the root-mean-square energy corresponds to $T_D \sim 600$ K), we expect the phonon-drag effect to extend to higher temperatures than in most metals, and to be still significant at room temperature (in contrast to a statement in Ref. 7). The peak location shows only a small shift as the Sr concentration x increases from 0.2 to 0.25, in spite of T_c changing by about a factor of 2, and occurs at a temperature well above T_c, and well above any superconducting precursor effects in the resistivity. It seems likely, therefore, that the location of the peak reflects more the intrinsic phonon-drag effect rather than a peak at lower temperature truncated by the onset of superconductivity.

Referring to Fig. 2 we have inquired whether the decreasing thermopower on the high-temperature side would eventually change sign or whether it would flatten and remain positive. To this end we have extended the measurements on a sample with $x=0.25$ up to near 380 K. Without any doubt the thermopower changes sign at 310 K and becomes substantially negative at higher temperatures. We expect the same crossover on the sample with a Sr content $x=0.2$ above 400 K. Note that the data have been corrected for the (positive) thermopower of the copper leads; without this correction the thermopower would have been even more negative. Based on these high-temperature observations it thus appears that the diffusion thermopower, at least for the most heavily doped Sr compounds, has a negative sign. We suggest this is also true for the somewhat similar data[7] on a Ba-doped compound, in spite of the opposite conclusion drawn in that paper, where it was assumed that phonon drag usually does not change the sign of thermopower. We must emphasize that the phonon-drag contribution does not

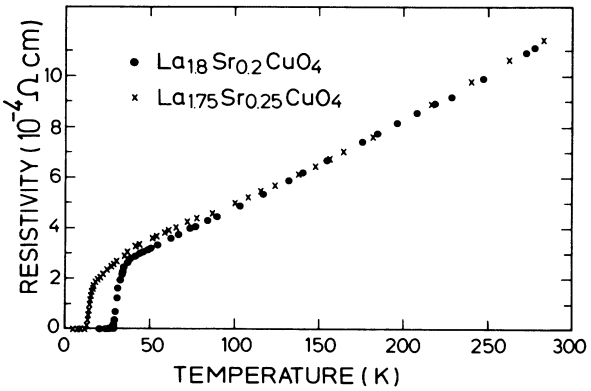

FIG. 1. Resistivity of our $La_{2-x}Sr_xCuO_4$ samples.

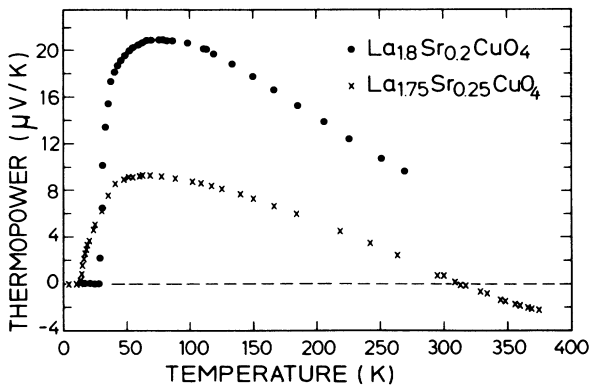

FIG. 2. Thermopower of the same samples as in Fig. 1.

necessarily have the same sign as the diffusion thermopower, depending on the topology of the Fermi surface and the relative contributions of different carriers. Experimental examples where the sign is opposite are Pd, Pt,[16] and the Chevrel compounds (Ref. 17) $Cu_{1.8}Mo_6S_{8-y}Se_y$. The latter compounds are particularly interesting, because one can see the decrease of the phonon-drag peak as structural scattering increases, the suppression being virtually complete for a residual resistivity ρ_0 more than 0.85 times the room-temperature resistivity ρ_{RT}. The fact that ρ_0/ρ_{RT} in our samples is only about 0.2 emphasizes the likelihood of significant phonon drag.

Our conclusion that the diffusion thermopower in the more highly doped region is dominated by electrons rather than by holes raises the question of the carrier sign in these materials. As follows from the chemical formula of these compounds and a simple picture of the band structure, one expects p-type, i.e., hole-dominated transport. This has been confirmed recently by Hall effect studies on $La_{2-x}Sr_xCuO_4$ compounds for $x<0.17$ by Ong *et al.*[9] These authors report that above $x=0.15$ the Hall constant R_H falls precipitously and becomes undetectable for $x>0.18$. On the other hand, for their $x=0.2$ sample, Panson *et al.*[8] report a *negative* (electron) carrier sign. We have determined R_H by dc Hall effect measurements at 50 K in a magnetic field of 7 T using a Keithley 181 nanovoltmeter and currents of 20 mA. Our two samples show Hall constants R_H of 1.7×10^{-9} and 0.45×10^{-9} m^3/C for $x=0.2$ and $x=0.25$, respectively, which would correspond to carrier densities of 3.7×10^{21} cm^{-3} and 1.4×10^{22} cm^{-3} assuming strictly one-band conduction. (We argue below, however, that these values, particularly the $x=0.25$ sample, are overestimates.) The former value has a 10% confidence level while the latter corresponds to a much weaker signal and consequently only about 20% accuracy is claimed. The rapid fall in R_H with increasing doping is in accord with the trend observed by Ong *et al.*[9] The magnitudes of our Hall constants are, however, larger and certainly measurable. Invariably, the sign is positive.

This leads to an apparent conflict with the high-temperature thermopower that, as we have indicated, is negative. The different polarities of the Hall effect and the thermopower indicate the presence of more than one type of carrier. We propose that the carrier spectrum of the highest Sr-doped $La_{2-x}Sr_xCuO_4$ superconducting compounds consists of relatively mobile (~5 $cm^2V^{-1}s^{-1}$ at 77 K) holes, which are responsible for superconductivity, and somewhat heavier electrons. The standard two-band expressions for thermopower and Hall constant are[12,16]

$$S=\frac{\sigma_1}{\sigma}S_1+\frac{\sigma_2}{\sigma}S_2\ , \tag{1}$$

$$R_H=\left(\frac{\sigma_1}{\sigma}\right)^2R_{H1}+\left(\frac{\sigma_2}{\sigma}\right)^2R_{H2}\ , \tag{2}$$

where σ is the conductivity and the subscripts denote the values for each band. It is seen immediately from the weighting factors that heavier carriers make a larger contribution to the thermopower than to the Hall constant, and this is accentuated by the fact that the characteristic thermopower S_i for heavier carriers is usually large because of the larger energy dependence of their mobility. Thus, the heavier electrons can dominate the thermopower while lighter holes dominate the Hall constant. We suggest that the density of electrons increases more strongly than that of holes for larger Sr content, bringing about the overall tendency of the thermopower crossover from positive to negative values to occur at lower temperatures as the Sr concentration increases.

The similarity of the resistivity for the $x=0.2$ and $x=0.25$ samples implies that the smallness of the Hall constant for the latter sample arises more from a cancellation of hole and electron contributions than from an increase in the overall carrier density n.[18] Besides, if n were really larger than 10^{22} cm^{-3}, the size of resistivity would require such a small mean free path that Mooij correlation effects, such as seen in amorphorous metals,[19] would be important and only a small temperature dependence would be expected. Thus, values of carrier density deduced from Hall constants using a one-band model should be treated with caution, and we can say only that the transport properties indicate that n is significantly less than 10^{22} cm^{-3}.

We can check the consistency of our picture of metallic conduction with the size of resistivity temperature dependence ($d\rho/dT\sim3.6$ $\mu\Omega\,cm\,K^{-1}$ at higher temperatures) using the expression of Allen *et al.*[20] for a phonon-limited metallic resistivity:

$$\frac{d\rho}{dT}\approx\frac{2\pi k_B}{\hbar e^2}\left(\frac{m}{n}\right)_{\rm eff}\lambda_{\rm tr}\ , \tag{3}$$

where m is the carrier mass and $\lambda_{\rm tr}$ the electron-phonon coupling constant for transport. Using $n\sim10^{21}$–10^{22} cm^{-3}, we find

$$\frac{m_{\rm eff}}{m}\lambda_{\rm tr}\sim1.2\text{–}12\ ,$$

where $m_{\rm eff}/m$ is an appropriate average mass enhancement at higher temperatures. These values are of the right order of magnitude, being consistent with a large carrier-phonon coupling and possibly a modest mass enhancement due to the band effects or correlations.[21] The novel suggestion[22] that electron-electron scattering contributes to the linear temperature dependence of resistivity is not excluded, but the large size of $d\rho/dT$ appears explicable by the small density of carriers without exotic mechanisms.

In conclusion, the thermopower of the two heavily Sr-doped samples of $La_{2-x}Sr_xCuO_4$ shows a pronounced peak at temperatures well above the respective superconducting transition temperatures. Such extrema are likely to have their origin in the phonon drag of holes and would indicate a strong carrier-phonon interaction. Above room temperature the thermopower has a tendency to change sign from positive to negative. This trend, coupled with the positive sign of the Hall constant, indicates that, in addition to dominant holes, the carrier spectrum of the high Sr-concentration compounds also contains negative carriers. The contribution of these electrons increases with increasing Sr content.

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