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Thermoelectric power of $Nd_{2-x}Ce_xCuO_4$ crystals

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We report the in-plane thermopower S of $Nd_{2-x}Ce_xCuO_4$ $(0.01 \le x \le 0.22)$ crystals for $4 \le T \le 300$ K. In the weakly doped $(x \sim 0.01-0.025)$ samples S is large and negative at high temperature, consistent with electron doping of the CuO_2 planes, and approaches zero at low T. Crystals of superconducting and highly doped compositions $(x \ge 0.15)$ show a small positive thermopower, with $dS/dT < 0$. The thermopower of these samples is therefore surprisingly similar, in sign and T dependence, to that of the hole-doped cuprate superconductors.

A controversial problem in superconductivity has been the nature of the charge carriers in the electron-doped cuprates $R_{2-x}M_xCuO_{4-y}$ (R = Nd,Sm,Pr and M = Ce,Th), where $x \approx 0.15$ produces superconductivity at temperatures as high as ~ 25 K. Initial observations[1,2] of negative thermoelectric power and the Hall coefficient in $Nd_{2-x}Ce_xCuO_{4-y}$ appeared to confirm that Ce contributes electronlike carriers to the CuO_2 planes, as expected if Ce^{4+} is formed. Thus it appeared that high-T_c superconductivity can occur in cuprates for both electron and hole doping of the CuO_2 planes. However, there has lately been some question as to whether this is correct: Recent reports of a *positive* Hall effect and thermopower[3,4,5] suggest that the dominant carriers are in fact positively charged, as in other superconducting cuprates. We recently reported[6] that the Hall coefficient R_H in well-characterized crystals of $Nd_{2-x}Ce_xCuO_4$ is negative for $x \le 0.2$ and decreases in magnitude as the Ce concentration increases until $R_H > 0$ for $x \approx 0.2$. This is consistent with electron doping in the CuO_2 planes, but raises questions as to the intrinsic sign of the thermopower S. We present here a study of the in-plane S in crystals, which shows how S varies systematically as Ce concentration x increases. We find that in well-characterized superconducting crystals there is a sign difference between S and the Hall coefficient R_H, demonstrating that the effect of Ce doping is more complicated than the simple donation of electron carriers.

The sign of the carrier-diffusion thermopower in a metal is often taken to indicate the sign of the charge carriers. However, this thermopower, obtained from the Mott formula[7]

$$S = -\frac{\pi^2 k_B^2}{3e} T \left[\frac{\partial}{\partial E} [\ln \sigma(E)] \right]_{E_F} , \tag{1}$$

is sensitive to properties of the relaxation time $\tau(\mathbf{k})$ and Fermi surface, and so interpretation of S is difficult in many cases. Thermopower in the high-T_c cuprates has been a persistent problem:[8] the flat or weakly T-dependent S is atypical of metals, and in many cases even the sign of S is sample or temperature dependent. Nevertheless, thermopower is a fundamental probe of electronic properties and electron-phonon interactions; reliable thermopower data are necessary for a full understanding of the electronic state in the superconducting cuprates.

We grew $Nd_{2-x}Ce_xCuO_4$ crystals using a directional solidification technique; details of growth and characterization appear in Ref. 9. The measured crystals were typically $\sim 2 \times 1 \times 0.02$ mm.[3] X-ray diffraction showed them to be single phase, with the CuO_2 planes parallel to the broad faces. Sample quality was also tested by dc magnetization and resistivity measurements: The T_c for the superconducting samples is typically ~ 24 K, and the magnetic transition widths are ~ 1 K.

We used a slow ac method to measure the thermopower. With one end of the crystal epoxied to a copper sink, a metal-film resistor attached to the other end generates a slowly oscillating temperature gradient (~ 0.5 K/mm) parallel to the crystal *ab* plane. Two Chromel-Constantan thermocouples glued to the crystal measure this gradient, and a pair of Au leads detect the sample voltage. [The gold leads were in turn calibrated against Pb foil ($>99.999\%$ pure) by using the Pb data of Roberts.[10]]

Figure 1 shows ρ and S vs T for two nonsuperconduct-

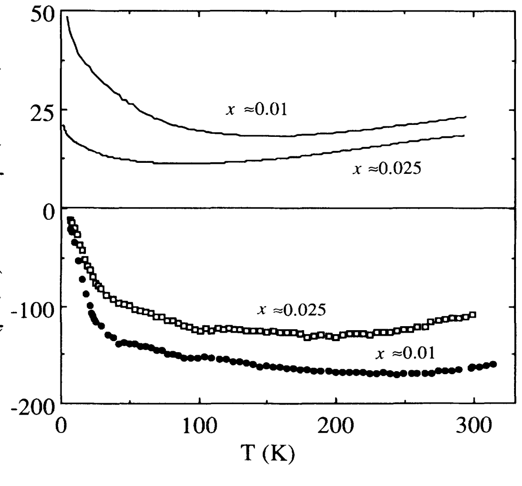

FIG. 1. In-plane resistivity ρ and thermopower S vs T for two $Nd_{2-x}Ce_xCuO_4$ crystals with $x \approx 0.01$ (solid circles) and $x \approx 0.025$ (open squares).

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ing crystals with $x \approx 0.01$ and 0.025. Both samples show insulating behavior in ρ at low T. The large thermopower ($|S| \sim 100$ μV/K) of these samples is negative over the full temperature range $T \leq 300$ K, consistent with electron doping. At low T, S approaches zero and ρ shows a weak upturn. Magnetoresistance measurements[11] at low T show that this rise in ρ is due to localization of a two-dimensional conducting system, not to the appearance of any energy gap.

Figure 2 shows the resistivity ρ and Hall coefficient R_H of two $x \approx 0.15$ crystals ($T_c \approx 24$ K). Both have metallic resistivity, but at low T the slopes $d\rho/dT$ decrease and the resistivity of sample A flattens just above T_c. The room-temperature resistivities are 600 $\mu\Omega$ cm (sample A) and 300 $\mu\Omega$ cm (sample B), and the resistivity ratios of the two crystals are $\rho(300)/\rho(T_c) \approx 2$ and 6, respectively. For both samples we find $R_H < 0$, although crystal B shows a weak trend toward positive R_H at low T. We previously reported[6] that increased Ce doping x strongly suppresses the resistivity in $Nd_{2-x}Ce_xCuO_4$ crystals and drives R_H to positive values. The transport data therefore suggest that, while both crystals have nominal composition $x \approx 0.15$, sample B may in fact have slightly higher Ce content.

Figure 3 shows S vs T for crystals A and B and for an overdoped ($x \approx 0.22$) nonsuperconducting crystal. The small magnitude of S is typical of metals, and the T dependence is similar for all samples. S is nearly linear at high T, with negative slope $dS/dT \sim -0.01$ $\mu V/K^2$. This linear S does not extrapolate to zero for $T \rightarrow 0$, however, because of a positive offset of 2–4 μV/K. In the superconducting crystals, S falls abruptly to zero at T_c, while for higher doping, S shows a peak at $T \sim 50$ K and then falls to zero as $T \rightarrow 0$. Although $S > 0$ was observed in ceramic samples by Lim *et al.*,[3] the negative slope of S is not visible in their data. This negative slope, which causes a zero crossing of S in some samples at $T < 300$ K, may have led some groups[2] measuring S at $T = 300$ K to report $S < 0$, while others found $S > 0$.

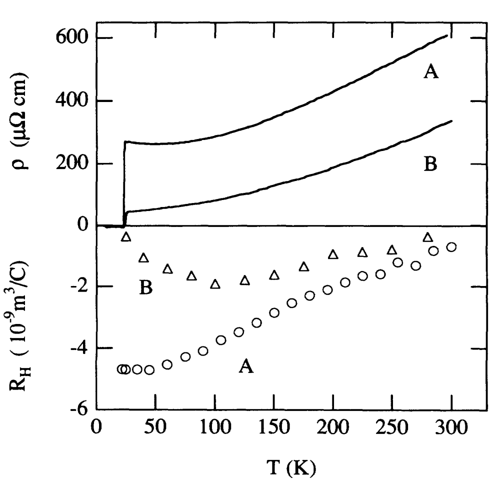

FIG. 2. Resistivity and Hall coefficient vs T for two superconducting $Nd_{1.85}Ce_{0.15}CuO_4$ crystals.

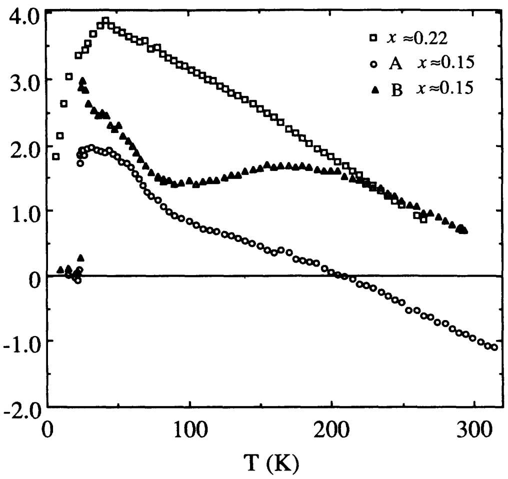

FIG. 3. In-plane thermopower S vs T for the superconducting samples A and B and for a highly doped ($x \approx 0.22$) crystal.

The clear trend in our data is that increased Ce doping drives the in-plane thermopower from large negative to small positive values. In the low-doped crystals of Fig. 1, S is very similar in its large magnitude and weak T dependence to that of hole-doped $La_{2-x}Sr_xCuO_4$, $Bi_2Sr_2CaCu_2O_8$, and $YBa_2Cu_3O_7$ at low carrier concentration.[8] The negative sign of S in Fig. 1 is qualitatively consistent with a negative R_H and appears to verify that Ce doping contributes electrons to the CuO_2 planes. However, in the superconducting material ($x \approx 0.15$), we find positive S, in apparent conflict with the negative R_H. Thus the simple relation between carrier charge and the sign of the thermopower and Hall effect does not hold in $Nd_{2-x}Ce_xCuO_4$. This is unlike the hole-doped cuprates, for which both S and R_H are generally positive (although excess doping[12] can cause $S < 0$).

It is interesting to compare the $x \approx 0.15$ data of Fig. 3 to the in-plane thermopower reported in the hole-doped cuprates. In $Bi_2Sr_2CaCu_2O_8$ and $Tl_2Ba_2CaCu_2O_8$, S has a small positive offset ($\sim$few μV/K) and a negative slope $dS/dT \sim -0.03$ $\mu V/K^2$. In $YBa_2Cu_3O_7$ the thermopower is also small and (generally) positive, with weak T dependence. Despite a qualitatively different means of doping, the thermopower in $Nd_{1.85}Ce_{0.15}CuO_4$ is nearly identical in magnitude and T dependence to that of these hole-doped cuprates. Therefore, although R_H indicates that electronlike carriers are present in $Nd_{2-x}Ce_xCuO_4$ and holelike carriers are present in, e.g., $Bi_2Sr_2CaCu_2O_8$, the thermopower reveals a similarity of the electronic states in the two materials once the superconducting composition is attained.

Understanding S therefore presents a similar problem in the hole- and electron-doped superconductors. In the p-type cuprates, the small and weakly T-dependent thermopower has been variously attributed to phonon drag, strong electron-phonon coupling, two-band behavior, and correlation effects.[8] Phonon drag, or enhancement of thermopower due to interaction between carrier and phonon heat currents, could account for some of the curvature in S near 100 K in the superconducting samples.

However, if the negative slope dS/dT is due to diffusion thermopower (linear in T) of n-type carriers, phonon drag is probably not responsible for the overall positive offset in S. This is because phonon drag generally decreases as $1/T$ at high temperatures,[7] while in Fig. 3 the thermopower is very nearly linear. That is, the offset in S is essentially T independent. Also, the size of a phonon-drag contribution should *decrease* as the carrier density and impurity-scattering rate increase. However, we find the positive offset growing with Ce content. Thus it appears unlikely that the thermopower of $Nd_{2-x}Ce_xCuO_4$ represents a simple sum of diffusion and phonon-drag components.

Kaiser and Mountjoy[13] have argued that strong electron-phonon (e-ph) coupling can account for unusual thermopower in the cuprate superconductors. In the presence of strong e-ph coupling, the slope of the diffusion thermopower [Eq. (1)] $S=AT$ is enhanced, $dS/dT \gg A$ at low T, but approaches A again at higher T. Therefore holelike carriers with strong e-ph coupling but small A would cause a large increase of S to positive values at low T and a flat, weakly T-dependent behavior at high temperatures. To explain $S>0$ (but $dS/dT<0$) in this picture then requires that both electronlike and holelike carriers exist, where the electronlike carriers have weaker e-ph coupling but a larger A, giving $dS/dT<0$ at high T.

Rather than attempt to evaluate such a model for S in $Nd_{2-x}Ce_xCuO_4$, we consider whether two-carrier effects in general could cause the unusual transport behavior of this material. If two bands have conductivities σ_1 and σ_2 (with $\sigma \equiv \sigma_1+\sigma_2$), the thermopower and Hall coefficient are given by the weighted sum[7]

$$S=(\sigma_1/\sigma)S_1+(\sigma_2/\sigma)S_2 \ ,$$

$$R_H=(\sigma_1/\sigma)^2R_{H1}+(\sigma_2/\sigma)^2R_{H2} \ .$$

While it is arguable whether the complicated T dependences of S, ρ, and R_H could all be accounted for in a realistic two-band model, a more immediate difficulty is simply understanding how two bands would arise. Local-density-approximation band-theory calculations[14] indicate that metallic conduction is due to a free-electron-like O $2p$–Cu $3d$ level in the CuO_2 planes. However, no other bands cross the Fermi level in these calculations; the only states approaching E_F are an O p_z band (connecting oxygen atoms in the z direction) and an O p_x-p_y band connecting oxygen atoms in the Nd_2O_2 interlayer. Both bands lie $\sim$0.4 eV below E_F for $x=0$. If one of these bands actually crossed E_F, it could contribute carriers: For example, recent photoemission data[15] indicate that in $Bi_2Sr_2CaCu_2O_y$ a band with BiO_2 character crosses the Fermi level, generating an electronlike pocket to supplement the CuO_2 plane holes.

However, there is presently no spectroscopic evidence for a second band in $Nd_{2-x}Ce_xCuO_4$. The nature of the conduction levels and the effects of doping in $Nd_{2-x}Ce_xCuO_4$ remain controversial, but the x-ray photoemission data[16] appear to confirm that the Ce dopant enters the 4+ state, thus donating electrons to the system. X-ray-absorption[17] and electron-energy-loss[18] spectroscopies show that the donated electrons enter states of largely Cu $3d$ character lying in the CuO_2 planes: There is presently no firm evidence for additional conduction states. Therefore two-carrier models for transport must be regarded as speculative.

An interesting possibility for explaining the near-constant S in the hole-doped cuprates is a correlated electronic system in the O $2p$–Cu $3d$ levels. The thermopower is then T independent, as given by the Heikes[19] formula $S=-(k_B/e)\ln[(1-f)/f]$ [with a term $-(k_B/e)\ln 2$ if the carriers have a spin degree of freedom]. Here f is the filling fraction of the upper or lower Hubbard band in the CuO_2 planes, so such a thermopower in $Nd_{2-x}Ce_xCuO_4$ would change from negative to positive as Ce was added. If a second electronlike band were also present, it would contribute a negative diffusion thermopower to this correlation term and result in $S>0$ with $dS/dT<0$.

We therefore speculate that S in $Nd_{2-x}Ce_xCuO_4$ contains contributions both from a highly correlated system in the CuO_2 planes and from electronlike carriers residing (possibly) in the Nd_2O_2 layers. At low doping the CuO_2 planes generate a large, negative, T-independent thermopower. Increasing the Ce content (i.e., f) to optimize superconductivity raises this correlation contribution to a small positive value, while the diffusion thermopower of the electron band contributes a negative slope to S. Both R_H and ρ are dominated by the higher conductivity of the electronlike carriers, and so $R_H<0$ is observed, and ρ vs T shows a more conventional curved profile than the $\rho \propto T$ seen in $YBa_2Cu_3O_7$, where only the correlated holes are observed.

In summary, we have measured the in-plane thermopower S of crystals of the n-type superconductor $Nd_{2-x}Ce_xCuO_4$ over a range of Ce concentration x. In the low-x samples, S is large and negative, consistent with electron conduction. However, in superconducting crystals, S is positive below $\sim$200–300 K (but $dS/dT<0$), in apparent conflict with the negative Hall coefficient. These data show that the Ce doping process is more complicated than the simple addition of electronlike carriers. However, a picture of the charge carriers that is consistent with both transport and spectroscopic data has not yet emerged.

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