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Anisotropic normal-state magnetothermopower of superconducting $Nd_{1.85}Ce_{0.15}CuO_4$ crystals

Wu Jiang, X. Q. Xu, S. J. Hagen,* J. L. Peng, Z. Y. Li, and R. L. Greene
Center for Superconductivity Research, Department of Physics, Univeristy of Maryland, College Park, Maryland 20742

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We report measurements of the normal-state in-plane thermopower S of superconducting $Nd_{1.85}Ce_{0.15}CuO_4$ crystals in magnetic fields (B) up to 9 tesla. When the magnetic field is parallel to the CuO_2 planes, we find that S is B independent indicating the absence of spin entropy effects. As B is oriented perpendicular to the CuO_2 planes, a giant negative magnetothermopower is found suggesting an orbital effect which cannot be understood within existing models. The normal-state thermopower tends to vanish as T goes to zero when superconductivity is destroyed by a large magnetic field, consistent with thermal transport in conventional metals.

The normal-state properties of the high-T_c oxide superconductors are very unconventional in many respects and may be the most important clue to the mechanism of superconductivity. The well-known anomalous temperature dependence of the in-plane conductivity, Hall coefficient,[1] and thermoelectric power[2] seem to be incompatible with a conventional Fermi-liquid description. There have been suggestions of various models[3-5] based on strongly correlated electrons in the CuO_2 planes. However, none of them has yet been able to explain all the transport properties consistently. New insights into the charge dynamics in the CuO_2 planes are therefore highly desirable.

Thermopower (S) is a probe sensitive to the carrier balance, carrier-phonon interaction, and the energy dependence of the scattering rate at the Fermi surface. It has thus attracted considerable experimental and theoretical attention.[2] Measurements to date on well-characterized materials of untwinned $YBa_2Cu_3O_7$,[6] $Bi_2Sr_2CaCu_2O_8$,[7] $Tl_2Ba_2CaCu_2O_8$,[8] and $Nd_{2-x}Ce_xCuO_4$ (Ref. 9) suggest a possible "universal behavior" in the T dependence of S for the CuO_2 planes, i.e., a nearly T-linear contribution with a negative slope plus a positive offset which is extremely sensitive to the carrier density. Some authors[7,10] have interpreted this as due to an anomalously large electron-phonon enhancement effect, while another approach[9,11] proposes a hopping model[12] for a strongly correlated electron system. In this latter picture, the thermopower consists of a configurational entropy term, $(k/e)\ln[(1-f)/f]$ related to f, the filling fraction per site (so it is T independent), and a spin entropy term $-(k/e)\ln 2$. A crucial test for the validity of the correlated hopping picture in the cuprate superconductors is the magnetic field dependence of the normal-state thermopower since one expects the spin entropy term to be significantly suppressed "*isotropically*" in a large B field. An early measurement[13] on a $La_{1.85}Sr_{0.15}CuO_4$ ceramic sample showed that S is nearly B independent up to 30 tesla, suggesting the possibility of Bose-type charge carriers in the normal state rather than correlated hopping. However, the polycrystalline nature of the sample made it difficult to separate spin and orbital effects.

In this paper, we present the first observation of a very *anisotropic* magnetothermopower $S(B)$ in the normal state of superconducting $Nd_{1.85}Ce_{0.15}CuO_4$ (NCCO) single crystals. Since NCCO crystals have lower T_c (~ 24 K), a relatively large value of B/T, a key parameter in magnetothermopower measurements, is accessible in a moderate magnetic field ($B \approx 9$ tesla). We find that $S(B)$ (e.g., at $T = 30$ K) is field independent when B is parallel to the CuO_2 planes but decreases in magnitude with increasing B for magnetic field perpendicular to the a-b plane, indicating a *giant orbital effect* which is quite anomalous and might be related to the other unusual properties of high-T_c cuprates in the normal and superconducting states. These results may have significant implications for possible theoretical models of charge transport as we will discuss later in this paper.

NCCO crystals were grown by a directional solidification technique which has been described in a previous publication.[14] The two high-quality crystals used in this study were characterized by x-ray diffraction, dc susceptibility using a superconducting quantum interference device (SQUID) magnetometer and resistivity measurements. They have dimensions of $2.0 \times 1.0 \times 0.02$ mm^3 and $3.0 \times 0.8 \times 0.01$ mm^3, respectively. The superconducting transition temperature T_c determined by dc magnetization and resistivity is about 24 K with transition width $\Delta T_c \sim 1$ K.

A steady-state method was employed to measure the in-plane thermopower, as schematically illustrated in the inset to Fig. 1. With one end of the crystal epoxied to a copper sink (at T_0), a metal-film resistor attached to the other end generates a temperature gradient (~ 0.2 K/mm) parallel to the crystal a-b plane. Two Chromel-Constantan thermocouples glued to the crystal measure this temperature gradient and a pair of 50 μm diameter Au leads were soldered with indium-silver alloy onto the crystals (just next to the thermocouple tips) to measure the Seebeck voltage. Since the thermocouple reading $\Delta V_{TC}(B)$ and the Seebeck coefficient of the Au wire $S_{Au}(B)$ depend on the magnetic field, it is necessary to calibrate $\Delta V_{TC}(B)$ and $S_{Au}(B)$ in order to determine $S_{samp}(B) = S_{meas}(B) + S_{Au}(B)$. In the early work on La-Sr-Cu-O,[13] the calibration of the thermopower of the Au wires against a $YBa_2Cu_3O_7$ (YBCO) superconductor in a high magnetic field was possibly inaccurate because the magnetothermopower of YBCO in the mixed state is

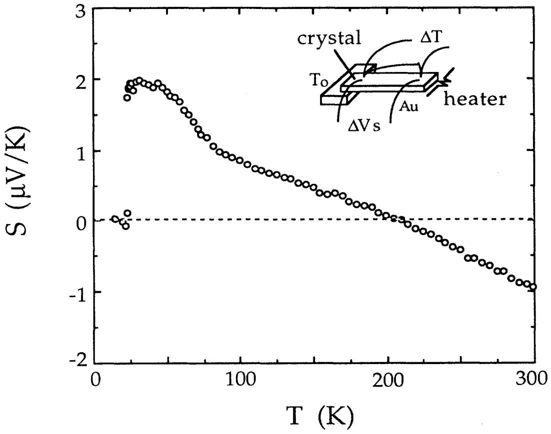

FIG. 1. The temperature dependence of the in-plane thermopower of a typical $Nd_{1.85}Ce_{0.15}CuO_4$ crystal.

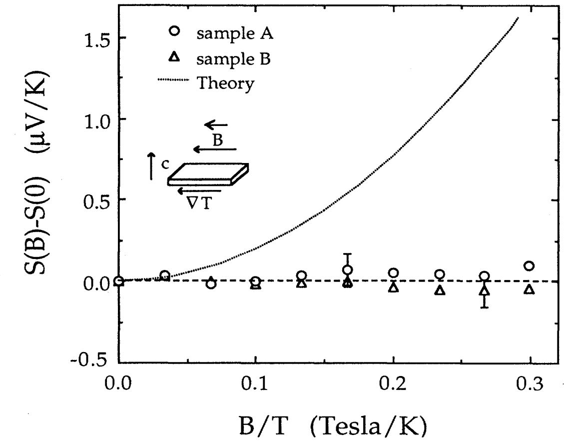

FIG. 2. Magnetothermopower vs B/T at $T=30$ K with $B \| a$-b plane.

quite large and should not be ignored.[15] We did a careful calibration by measuring ΔV_{TC} for a constant temperature gradient in the B field and evaluated the relative change $\delta(\Delta V_{TC})/\Delta V_{TC}$ vs B. Then $S_{Au}(B)$ was determined at fixed T over the range of 5–30 K by measuring $S(B)$ against a $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10}$ superconductor (i.e., $S=0$ in the superconducting state) which has a T_c ($R=0$) of ~105 K in zero field and ~35 K in $B=9$ tesla. We also checked that $S_{Au}(B)$ is independent of the B direction as anticipated. Each data point was measured 20 times to minimize experimental error. After this procedure, we were able to determine the absolute thermopower of the NCCO crystals in the magnetic field with the uncertainty of about 5% ($\Delta S_{max} \sim \pm 0.08$ μV/K in 9 tesla at 30 K). For B perpendicular to the a-b plane, we measured $S(B)$ of NCCO under both positive and negative directions of the magnetic field and then averaged them in order to eliminate any Nernst voltage[16] resulting from a possible misalignment of the Seebeck leads. All results are reproducible on warming to room temperature, remounting, and remeasuring.

In Fig. 1 we show S vs T for a typical superconducting NCCO crystal similar to the two used in the present study. The thermopower of our two samples at $T=30$ K are $+2.7$ μV/K (sample A) and $+1.9$ μV/K (sample B), respectively. NCCO is generally considered to be a quasi-two-dimensional system with the motion of charge carriers confined to the CuO_2 planes. The most direct way to distinguish spin and orbital effects is to measure the in-plane thermopower with the magnetic field applied parallel to the CuO_2 planes since spin effects are isotropic and orbital effects would be minimal in this situation. Figure 2 shows the change of the absolute thermopower of both crystals as a function of B/T at $T=30$ K with B parallel to the a-b plane and parallel to the temperature gradient. Within the experimental uncertainty, this figure indicates that any spin-dependent part of S is essentially B independent (at least up to $B=9$ tesla).

According to the theory[12] of thermoelectric power for a narrow-band system where the correlated hopping model can be applied, an *isotropic* and positive magnetothermopower should be observed at high T due to the suppression of the spin entropy as the magnetic field is applied. This model was found to be in good agreement with the experimental data in organic salts.[17] The functional form of the spin entropy term for a single electron in a magnetic field is given by

$$S(B)=(-k/e)[\ln(e^{-\mu B/kT}+e^{\mu B/kT}) -(\mu B/kT)\tanh(\mu B/kT)] , \quad (1)$$

where μ is the electronic magnetic moment and k is Boltzmann's constant. The theoretical change of the spin term $\Delta S=S(B)-S(0)$ from Eq. (1) (assuming $\mu=\mu_B$) is shown as the dotted line in Fig. 2 for comparison.

The observation of the null magnetothermopower as B is applied parallel to the CuO_2 planes has a significant impact on theoretical models of the charge transport in high-T_c oxides. The spectroscopic and transport studies in most cuprates suggest that the normal-state electrons are strongly correlated. If carriers do not form a degenerate electron gas as suggested by some thermopower data,[11] the most probable transport process is some kind of correlated hopping. Thus it is plausible that a measurable magnetothermopower might be observed if the carriers have free spins. However, Eq. (1) was derived at extreme conditions, i.e., for $kT \gg t$ and J (t is the bandwidth and J is the antiferromagnetic coupling), which is not true in the hole-doped cuprates or in NCCO (for NCCO, $J \sim 0.1$ eV, $t \sim 0.2$ eV$\gg$300 K).[18] Therefore, our results do not rule out the correlated hopping model but only suggest that the spin entropy effect is too small to be observed or that the charge carriers have no net spin.

In the two-dimensional (2D) Luttinger-liquid model of Anderson,[3] electrons are decoupled into holons and spinons. Starting from the same 1D Hubbard model as used in correlated hopping, Stafford[19] recently found that both holons and spinons contribute to the in-plane thermopower but with opposite signs. This calculation gives the same result in the high-T limit as that of the correlated hopping model. At low T, however, both holon and spinon terms vary linearly with T. Since $J \approx 1500$ K for NCCO, any spin entropy effect associated with spinons [estimated to be $\approx (k/e)(kT/J)(\mu B/kT)^2$] will be unobservable in the temperature and field range we studied in this paper.

In seeking a conventional interpretation of $S(B)$, a zero $\Delta S(B \| a\text{-}b)$ is not readily understandable. For example, phonon drag was commonly found to be strongly affected by a magnetic field in transition metals,[20] although a theoretical explanation is still lacking. The existence of dilute magnetic impurities would cause a negative and isotropic magnetothermopower due to the suppression of spin-flip scattering as reported for a Au-0.03 at. % Fe alloy.[21]

Figure 3 shows the change of S as a function of B at $T=30$ K when the magnetic field is applied perpendicular to the CuO_2 planes. In contrast to Fig. 2, the magnitude of S decreases as B increases. The relative change $\Delta S/S$ is about -8% for sample A and -13% for sample B in the field of 9 tesla. At lower T ($T \le 16$ K), a similar behavior of S was also observed when B was high enough to drive the sample into the normal state, but the effect becomes less observable as T decreases. This orbital effect is quite remarkable and has never been observed in the cuprates before.

In a standard two-band model,[22] a transverse magnetic field may influence the carriers of the two types differently and result in a nonvanishing $S(B)$, in analogy to classical magnetoresistance. For simplicity, if we assume the bands have equal numbers of electrons and holes and equal electrical and thermal conductivities, then a transverse magnetothermopower is given by[22]

$$\frac{\Delta S}{S_0} = \frac{-\alpha[1+(L_0/L_n)]B^2}{1+\alpha(L_0/L_n)B^2} , \qquad (2)$$

where $L_n = (\pi k/e)^2/3$ is the Lorentz number, $L_0 = \lambda_0/\sigma_0 T$ is the value in zero magnetic field, $\alpha = (L_0/L_n)(\sigma_0/2ne)^2$, and λ_0, σ_0 are the thermal and electrical conductivities, respectively. Equation (2) states that $\Delta S/S_0$ varies as $\sim B^2$ in low fields and saturates in a high field. Assuming the Wiedemann-Franz law is obeyed (i.e., $L_n \approx L_0$), we estimate the electronic thermal conductivity λ_0 to be ~ 1.6 W/mK for sample B at 30 K. Using the measured σ_0 of $\sim 1/40$ $\mu\Omega$ cm and the Hall coefficient R_H of 1×10^{-9} m^3/C at 30 K, we obtain $\alpha \approx 6.25 \times 10^{-6}$ T^2. This gives rise to a relative change $\Delta S/S_0$ of only -0.1% in 9 tesla, which is about 100 times smaller than our observed value. We conclude that our observed negative magnetothermopower is unlikely to be accounted for by a standard two-band effect.

Since a 2D weak localization effect (WL) exists in low-doped NCCO (Ref. 23) and as-prepared NCCO with $x \sim 0.15$,[24,25] we now explore the possibility of a localizaton correction to the thermopower in the presence of the magnetic field. Within the framework of linear-response theory, the diffusion thermopower S_d can be expressed in terms of the diffusive component of the thermoelectric coefficient (η_d) and the conductivity σ as $S_d = \eta_d/\sigma$. The destruction of quantum interference by the magnetic field will enhance the electrical conductivity [i.e., negative magnetoresistance (MR)] and thus a negative magnetothermopower $\Delta S/S \approx \Delta S_d/S = \Delta\eta_d/\eta - \Delta\sigma/\sigma$ might be possible if the change of η_d is much smaller than that of σ. There was a recent report[26] on the observation of such a localization correction to the thermopower in a 2D electron gas system. However, this approach seems to be inappropriate for NCCO because a positive MR was observed at 30 K (see the inset to Fig. 3 for sample B) which should lead to a positive $\Delta S/S$. Even if a WL effect exists (a positive MR could result from strong spin-orbit scattering), we estimate $\Delta S/S$ ($\approx \Delta\sigma/\sigma$) to be not more than 1% at 30 K in 9 T based on our MR results[24] in as-grown $x \sim 0.15$ NCCO crystals.

A positive MR could also come from the suppression of superconducting fluctuations[27] above T_c which may affect S as well. However, since the Cooper pairs (which carry zero entropy) tend to short the thermal current, one should probably expect $\Delta S/S$ to be positive. If the superconducting fluctuations contribute only to the negative linear part of S but not to the positive offset (see Fig. 1), one could get a negative sign for $\Delta S/S$, but this is

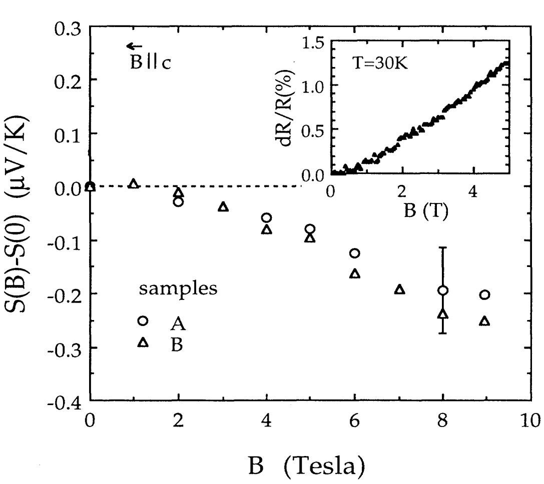

FIG. 3. Magnetothermopower vs magnetic field at $T=30$ K with $B \| c$ axis. Inset: magnetoresistance vs B at 30 K for sample B.

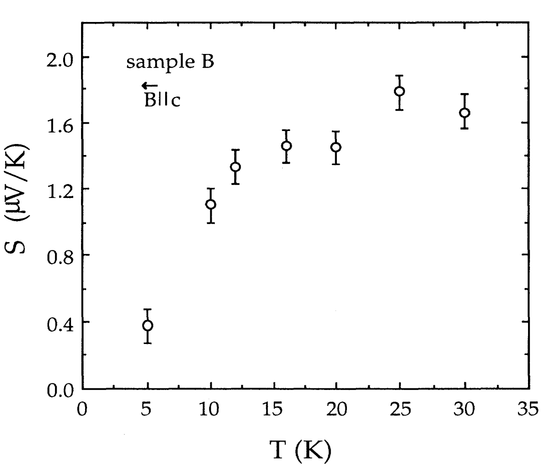

FIG. 4. The normal state thermopower S vs T in $B=8$ tesla for sample B. The magnetic field is applied perpendicular to the CuO_2 plane.

rather speculative and cannot be justified. At this stage, we think the origin of this giant negative orbital magnetothermopower is still not understood.

It is of interest to look at the low-temperature behavior of the normal-state S of superconducting cuprates since conventional transport theories of metals state that $S \rightarrow 0$ as T goes to zero. Experimentally it is very difficult to measure S at low T for the optimally hole-doped cuprates because of their high $H_{c2}(0)$, but for NCCO we were able to measure S (with an 8 T field applied parallel to the c axis) down to 5 K due to its much lower $H_{c2}(0)$ (~ 9 T). Figure 4 clearly shows that S tends to vanish as T decreases, indicating a behavior similar to that in normal metals.

In summary, we have measured the in-plane normal-state thermopower of superconducting $\mathrm{Nd_{1.85}Ce_{0.15}CuO_4}$ crystals in the presence of a magnetic field. When the magnetic field is parallel to the $\mathrm{CuO_2}$ planes, the thermopower is field independent indicating that no spin-entropy effects exist in the temperature and field range studied. For the magnetic field perpendicular to the $\mathrm{CuO_2}$ planes, a giant negative magnetothermopower is observed. This indicates an orbital effect associated with carrier conduction in the $\mathrm{CuO_2}$ planes but its origin remains unclarified. We also find that the normal-state thermopower of NCCO tends to vanish as T goes to zero similar to that of conventional metals.

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*Present address: NIDDK-LCP, Bldg. 2/Rm. B1-03, NIH, Bethesda, MD 20892.

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