PHYSICAL REVIEW B VOLUME 37, NUMBER 13 1 MAY 1988

Observations on the thermopower of the high-T_c superconductors

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(Received 10 February 1988)

Measurements of the thermopower of the high-temperature superconductor ceramics in the normal state have generally shown a positive, almost temperature-independent Seebeck coefficient, which has been interpreted by several authors in terms of the correlated hopping of the carriers as would be found in the strong Coulomb interaction limit of the Hubbard model. In this case the thermopower has a contribution from spin entropy which can be quenched by a large magnetic field. On the contrary, we measure a field-independent thermopower to 30 T. Moreover, in single crystals we find that the thermopower in the Cu-O planes is negative, while the perpendicular thermopower is positive.

The transport properties of the new high-T_c oxide superconductors have been intensively studied ever since the discovery of these materials. Despite a great deal of activity both on theories and experiments, the resistivity, Hall coefficient, thermal conductivity, and thermopower have yet to be consistently understood in any model. The thermopower of the ceramic samples has drawn particular[1-9] attention since measurements indicate that it is largely independent of temperature, positive, and very sensitive to the sample doping or oxygen concentration. In such a situation it is tempting to associate the sign of the carriers with the sign of the thermopower, and to regard the absence of a large temperature dependence as the result of hopping transport with the magnitude simply related to the carrier concentration. In particular, several authors[3,4,8] have found that the high-temperature thermopower (100–300 K) can be semiquantitatively explained by a model based on hopping in a strongly Coulomb correlated system.[10] In this case, the thermopower arises from a configurational entropy term, $(k_B/e)\ln[(1-\rho)/\rho]$ related to the number of carriers per site, ρ, and a spin entropy term, $(k_B/e)\ln 2$, related to the free spin associated with the carriers which have sufficient on-site repulsion that no two carriers occupy the same site. This picture is accessible to a simple test; the spin entropy can easily be reduced in the presence of a large applied magnetic field.[11] It is also important to determine the thermopower in single-crystal samples since it should be expected that these materials are highly anisotropic.

In this paper we report measurements on the magnetic field dependence of the thermopower of a $Sr_{0.15}La_{1.85}CuO_{4-\delta}$ ceramic sample and the thermopower on the Cu-O plane of a single-crystal $Ba_2YCu_3O_{7-\delta}$ sample. The ceramic sample was chosen so that we could attain a large value of H/T above the superconducting transition, hence we require a low T_c. We find that the thermopower of the ceramic is almost independent of magnetic field up to 30 T at 42, 53, and 90 K. For the single-crystal $Ba_2YCu_3O_{7-\delta}$ sample we find that the thermopower in the Cu-O plane is small, negative, and almost temperature independent, while the thermopower in the direction perpendicular to the Cu-O plane is large, temperature dependent, and positive.

The high-field experiments were carried out at the Francis Bitter National Magnet Laboratory at MIT using the hybrid magnet. We used $Sr_{0.15}La_{1.85}CuO_{4-\delta}$ and $Ba_2YCu_3O_{7-\delta}$ ceramic samples. The single-phase samples were prepared by the method described in Ref. 12 and were characterized by x-ray analysis and resistivity and susceptibility measurements. They exhibited a sharp transition temperature at 35 and 92 K, respectively, with less than 1.0 K in transition width. The samples were cut into pieces with dimension $3\times0.5\times0.3$ mm^3. The experimental setup was arranged in such a way that we could measure both samples at the same time. For each sample, one end was attached to a single-crystal quartz block in thermal contact with a copper block which was part of a copper vacuum can. Another end was attached by General Electric 7031 varnish to a 1.0-kΩ thin-film resistor which served as a heater. The temperature difference was monitored by a Chromel-Constantan thermocouple with junctions mounted to the two ends of the sample by General Electric varnish without shorting the sample electrically. 25-μm gold wires were attached to the ends of the sample with silver paint to measure the thermal emf.

The temperature was periodically modulated at about one cycle per minute by alternately applying a voltage across the thin-film resistor. The sample copper can was placed in a stainless-steel tube which can either serve as a vacuum can or exchange-gas tube. The entire apparatus

was immersed in liquid helium. The temperature was controlled and measured by a capacitance temperature controller calibrated in zero field versus a silicon diode. When the temperature was stabilized (typical temperature drift was less than 0.1 K/h), we increased the magnetic field to 30 T with a sweep time of 20 min. At the same time, we recorded the temperature difference and thermal voltage across the sample as the thin-film resistance heater was turned on and off. The same procedure was repeated for the down sweep of the field. During the entire magnetic field sweep, the temperature of the sample can be changed less than 0.1 K. With an applied temperature difference across the sample of 3 K, the typical thermal voltage signal ranged from 10 to 100 μV. By using two low-pass filters and considerable care, we were able to limit the noise level to less than 2 μV.

Conventional thermopower measurements such as this one are relative: sample thermopower minus that of the gold leads. Since there is a lack of high-field thermopower data for gold wires, and since the magnetothermopower of gold is sensitive to impurities, the Ba-Y-Cu-O (123) sample was used to calibrate the magnetothermopower of the gold wire leads in the region $T < T_{c123} \sim 90$ K. The thermopower of the superconductor is zero, allowing an absolute calibration of the thermopower of the other member of the thermocouple. Also, we had to take into account the magnetic field dependence of Constantan-Chromel thermocouple. Since there were no high-field data available, we extrapolated the low-field data (up to 16 T) from Ref. 13. Taking all these into account, we find the total uncertainty in our measurement to be about +1.0 to −1.5 μV/K in 30 T.

The temperature dependence of thermopower of the samples in zero field is shown in Fig. 1. The measured change of thermopower of the $Sr_{0.15}La_{1.5}CuO_{4-\delta}$ ceramic sample versus B/T is shown in Fig. 2.

We first consider the magnetic field dependence. There are three sets of data taken at 42, 53, and 90 K, respectively. From Fig. 2 we can set an upper limit for the change in thermopower with magnetic field. At 30 T, the total change of thermopower of $Sr_{0.15}La_{1.5}CuO_{4-\delta}$ can be set to +1 to −1.5 μV/K. In the model of correlated hopping[10] the spin entropy term, which is $(-k/|e|)\ln 2$ in the absence of a magnetic field, decreases as the magnetic field is applied. The functional form is given by[11]

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

where μ is the electronic magnetic moment, and k_B is Boltzmann's constant. The change of thermopower due to this quenching of the spin entropy contribution is $\Delta S = S(B) - S(0)$, which is plotted in the dashed line in Fig. 2. In this figure it is clear that the limits on the observed changes in thermopower are much smaller than the calculated change due to spin entropy effects. While it is possible that orbital effects might have precisely canceled the spin effects, it is exceedingly unlikely that this unfortuitous cancellation might have occurred. This is especially true in light of the absence of any significant magnetoresistance in the field and temperature range studied. Therefore, the conclusion we draw is that the carriers do not have a free-spin degree of freedom; the correlated hopping model is not appropriate for this system.

The observation that the thermopower is independent of magnetic field to 30 T at temperatures as low as 42 K is quite remarkable in itself. The large magnitude of the thermopower coupled with its lack of a substantial temperature dependence (and particularly the absence of a substantial decrease) from room temperature to ~40 K suggests that the carriers do not form a degenerate electron gas. The most probable transport process is some form of hopping. In this case one might expect a sizable magnetothermopower in any model in which the carriers have spin and magnetic moments. Thus our negative result on the magnetothermopower lends support to models in which the carriers are Bose type, either lacking spin as suggested by Anderson,[14] or moving only as pairs with a total spin of zero.

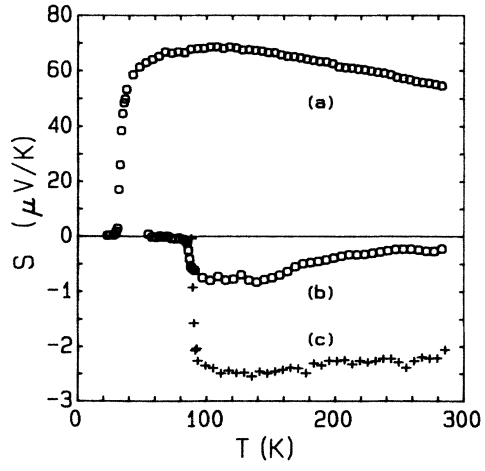

FIG. 1. Temperature dependence of the thermopower of (a) a ceramic sample of $Sr_{0.15}La_{1.85}CuO_{4-\delta}$, (b) a ceramic sample of $YBa_2Cu_3O_{7-\delta}$, and (c) the a-b plane of a $YBa_2Cu_3O_{7-\delta}$ single-crystal sample. Note the different scales on the positive and negative parts of the y axis.

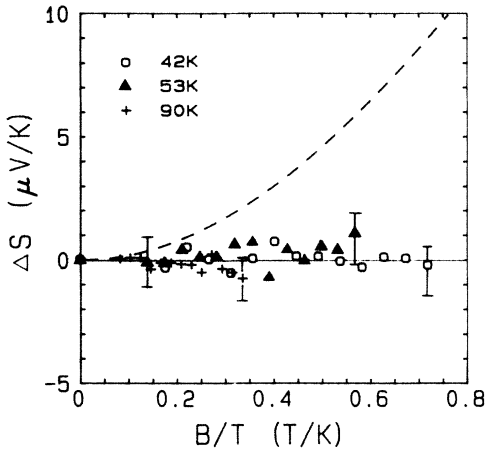

FIG. 2. Magnetothermopower $[S(B) - S(O)]$ vs magnetic field for the $Sr_{0.15}La_{1.85}CuO_{4-\delta}$ ceramic sample at 42, 53, and 90 K.

We now turn our attention to the anisotropy of the thermopower and its value in single crystals. Previous single-crystal measurements have revealed anisotropic transport coefficients.[15-17] For this study we used a single-crystal $Ba_2YCu_3O_{7-\delta}$ sample from IBM, Yorktown Heights, NY. The procedure for making the sample was presented elsewhere.[18] The platelike sample had dimensions $1.0 \times 0.35 \times 0.04$ mm^3 with the *a-b* plane along the plate. The ac magnetic susceptibility showed a sharp transition at 91 K. The technique used for the thermopower measurement in the *a-b* plane was similar to the measurement described above for the ceramics. The *a-b* plane thermopower is shown in Fig. 1. The thermopower in this Cu-O plane is negative in sign and almost temperature independent from 300 to 100 K.

The thermopower in the direction perpendicular to the *a-b* plane was much more difficult to obtain since the sample was very thin. We used the following techniques. The sample was sandwiched between the tips of two shaped copper blocks. The sandwich was clamped by two nylon screws. One of the copper blocks was wrapped with Manganin wire serving as a heater. The two tips on the copper blocks served as voltage leads and the blocks served as constant temperature platforms on which the junctions of a Constantan-Chromel differential thermocouple were glued by General Electric varnish to measure the temperature difference across the sample. Accurate measurements were difficult as the contact between the Cu tips and the sample changed as temperature changed. However, we were able to get some rough values of the thermopower at specific temperatures. The thermopower in the *c* direction perpendicular to Cu-O planes was positive at all temperatures measured and was about 20 μV/K at 300 K, and 6 μV/K at 91 K, and near zero at 90 K. Thus the thermopower in this direction seems much more like a conventional metallic thermopower (that is decreasing with decreasing temperature, albeit with a high value at room temperature), than the in-plane thermopower. This behavior should be contrasted to that of the resistivity which is "metallic" (positive temperature coefficient) in the *a-b* plane and "nonmetallic" (negative coefficient) along the *c* axis.

The negative sign of the in-plane thermopower is in marked contrast to the positive thermopower observed for most of the ceramics previously reported. It should be noted, however, that there have been reports[6,9] of negative thermopowers for $Ba_2YCu_3O_{7-\delta}$ ceramics when $\delta \sim 0$, including the sample we used as a reference for the magnetothermopower measurements (see Fig. 1). We suggest that the sign of the carriers is not to be determined from these thermopower measurements, but rather it is to be inferred that the intrinsic *a-b* plane thermopower of the stoichiometric material $\delta = 0$ is essentially at a symmetry point in the band which produces a thermopower of zero. Extrinsic effects then may account for the small thermopower of either sign observed in different samples.

It should be noted that the signs of the thermopower from these measurements, negative along *a-b* and positive along *c*, are those which occur in the band-theory calculations of Allen, Pickett, and Krahauer,[19] who also have the correct sign for the Hall tensor. Whether the band theory alone is sufficient to explain the transport properties is far from confirmed.

In conclusion, we have measured the thermopower of a $Sr_{0.15}La_{1.5}CuO_{4-\delta}$ sample and found a null magnetic field dependence of the thermopower to 30 T. This result shows that models of correlated hopping in the large-U limit of the Hubbard model are not appropriate for the CuO superconductors. It further shows that the carriers do not retain a spin degree of freedom and lends credence to models with Bose-type carriers. Our measurements of the thermopower on single-crystal $Ba_2YCu_3O_{7-\delta}$ showed a highly anisotropic behavior with a small, negative, temperature-independent thermopower in the *a-b* plane and a large, positive, thermopower along *c* which decreased markedly with reduced temperature. We suggest that the intrinsic thermopower in the *a-b* plane is essentially zero for stoichiometric samples ($\delta = 0$).

We would like to acknowledge useful discussions with N. P. Ong and his group, who have also measured the anisotropic thermopower of single-crystal samples. This work was supported by the National Science Foundation under Grants No. DMR8710332 (R.C.Y., P.M.C.), No. DMR8316999 (P.K.D.), and No. DMR8519059.

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