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THERMOELECTRIC POWER IN THE NORMAL STATE OF HIGH-T_c SUPERCONDUCTORS $RBa_2Cu_3O_x$ (R = YTTRIUM OR RARE EARTH)

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We report measurements of the thermoelectric power S and resistivity ρ of high-T_c superconductors $RBa_2Cu_3O_x$. For R = Y or a rare earth and $x \simeq 7$, S is positive and nearly temperature independent but its magnitude can vary depending on R. We have systematically varied the oxygen stoichiometry ($6 < x \leqslant 7$) and find that changes in x have a far more dramatic effect on S and ρ than does R. When x approaches 6.5, there is a cross-over to new behavior with S approximately linear in temperature. This metallic-like behavior does not appear in the resistivity. The thermopower results suggest that $RBa_2CU_3O_x$ compounds have strong on-site Coulomb correlations.

Among recent measurements on high-T_c copper-oxide superconductors, to the best of our knowledge, no systematic study of the thermopower has been reported. We have performed thermopower measurements on $RBa_2Cu_3O_x$ (where R = Y, Eu, Gd, Ho) and studied the effect on resistivity as well as thermopower due to oxygen deficiency. This study was motivated in part by the large discrepancies between several groups reporting measurements on the normal state properties of nominally comparable materials [1]. We believe that several factors complicate the issue: chemical stoichiometry, the density of polycrystalline material, and expected anisotropy of the transport properties. Hall effect experiments [2] indicate that the carrier concentration changes with oxygen stoichiometry suggesting that other transport properties may be affected similarly.

All samples were prepared by conventional ceramic powder techniques. To vary the oxygen stoichiometry, we heated samples of the same batch to 300–600°C in various oxygen pressures for 2 to 24 hours, then allowed the sample to cool slowly to room temperature. Assuming the weight loss incurred by heating resulted solely from the removal of oxygen provided a semiquantitative estimate of the oxygen content.

The electrical resistivity was measured by a standard dc 4-probe method and the Seebeck effect was detected through copper reference wires. The absolute thermopower of the sample was obtained by correcting the measured Seebeck coefficient with the absolute thermopower of copper at various temperatures. We used a differential Au–0.07%Fe/Chromel–P thermocouple to detect the temperature gradient of ≈ 0.5 K across the sample. Our apparatus was calibrated with constantan wires and the measured Seebeck coefficient agreed with NBS values to within 5% accuracy.

The thermopower S of $RBa_2Cu_3O_x$ samples is shown in fig. 1. That S is positive suggests conduction is dominated by holes, which is confirmed by Hall effect measurements [2, 3]. The room temperature values of S are similar to that predicted by the free electron approximation if one allows the carriers to be positively charged. ($S_d = \pi^2 k^2 T / e\varepsilon_F \approx 10$ µV/K with $\varepsilon_F \approx 2$ eV). However, this is not consistent with the temperature independence of S above T_c, which for a metal is expected to increase linearly with temperature. Within experimental uncertainty, S goes to zero below T_c, as expected.

A first glance at fig. 1 might suggest that S

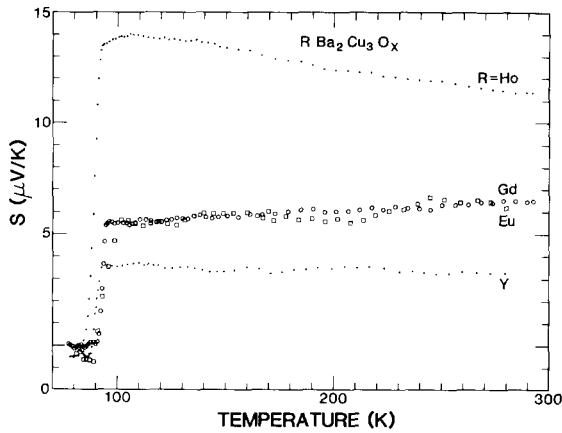* Permanent address: Physics Department and Solid State Science Center, UCLA.

Fig. 1. Absolute thermopower versus temperature for $RBa_2Cu_3O_x$ where R = Y, Eu, Gd, Ho.

Fig. 3. Resistivity versus temperature for $EuBa_2Cu_3O_x$ where $x > 6.45$. The inset shows the resistivity at 250 K and T_c as functions of x.

increases as the mass of R increases. However, the oxygen stoichiometry of these compounds has far more influence on the thermopower and resistivity because the values can vary significantly from one batch to another. We have systematically varied the oxygen stoichiometry of $YBa_2Cu_3O_x$ and $EuBa_2Cu_3O_x$ for $6 < x \leqslant 7$. The results for both are similar and we discuss our observations in the Eu compound below.

The thermopower and resistivity are plotted in fig. 2 for the starting material $EuBa_2Cu_3O_x$ (where $x \approx 7.0$ as determined by chemical analysis). As x decreases (see fig. 3), the resistivity increases and the mid-point T_c decreases.
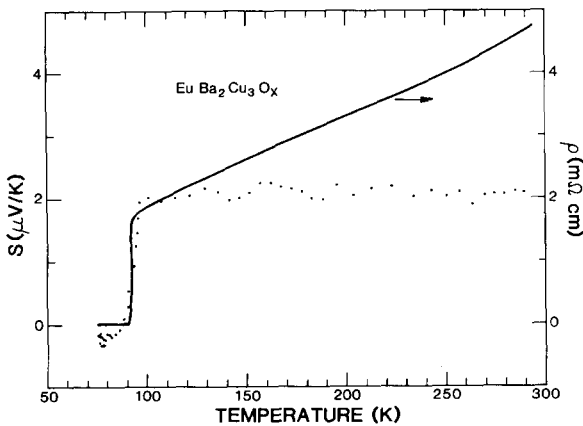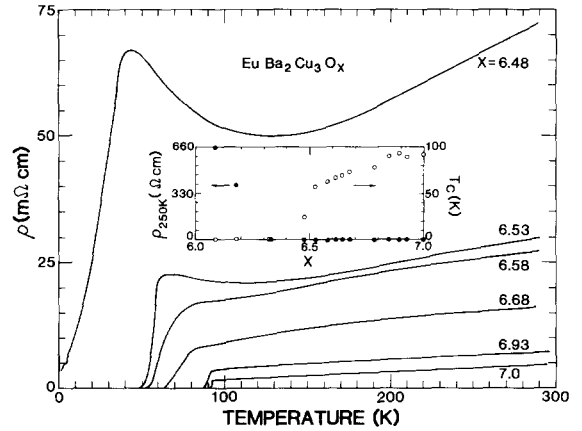

Fig. 2. Thermopower S and resistivity ρ (solid line) versus temperature for $EuBa_2Cu_3O_7$.

For $x < 6.45$, the resistivity increases drastically as a power law of decreasing temperature. The mid-point T_c and resistivity at 250 K are shown in the inset of fig. 3. It is clear that the scattering mechanism changes near $x = 6.45$ which is about the stoichiometry where an orthorhombic–tetragonal structural phase transition occurs [4].

The thermopower for $EuBa_2Cu_3O_x$ (where $6 < x \leqslant 7$) is plotted in fig. 4 with different scales. As x decreases, S increases and shows a slight temperature dependence above T_c for $x > 6.45$ [5]. For $6.1 < x < 6.45$, the thermopower shows a metallic-like behavior, i.e. $S = AT + BT^3$ for $T < 40$ K, while the resistivity behaves otherwise. The values of S at room temperature have a similar dependence on oxygen stoichiometry as the Hall coefficient [2]. At $x = 6.1$, the thermopower is semiconductor-like with a large negative value at room temperature. The sign change at $x = 6.1$ suggests that conduction is now dominated by electron-like carriers for $T \geqslant 100$ K.

It has been proposed [3] that the Hubbard model well describes the transport properties of these compounds. We plot S at 250 K in the inset of fig. 4 along with the Heikes expression [6] for a system with strong on-site electron–electron repulsion, i.e. $S = (k/e) \ln[2(1 - \rho)/\rho]$, where ρ is the number of free electrons per site. Here, $\rho = (13 - 2x)/3$ per Cu-site for $x < 6.5$ and $\rho =$
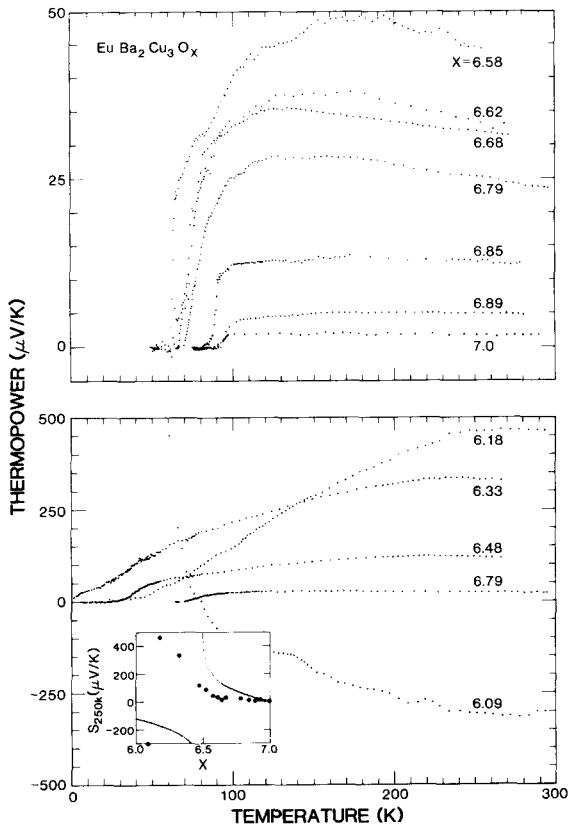
Fig. 4. Absolute thermopower versus temperature for $EuBa_2Cu_3O_x$ where $6 < x \leqslant 7$. The inset shows the thermopower at 250 K as a function of x, along with Heikes expression (small dots) for a system with strong on-site electron–electron repulsion.

$1 - (2x - 13)/3$ per Cu-site for $x > 6.5$. We see that Heikes expression qualitatively accounts for our observations, including the sign change in S.

In conclusion, the resistivity and thermopower depend strongly on the oxygen stoichiometry and little on various rare earth substitutions. A simple two-band model seems inadequate to explain the temperature independence of S together with the observed effects of oxygen stoichiometry. Further, thermopower measurements suggest that these compounds have strong on-site Coulomb correlations.

Acknowledgement

References

[1] See, for example, papers in Japan. J. Appl. Phys. 26, nos. 4 and 5 (1987); and Proc. of the Berkeley Conf. on Novel Mechanisms for High-T_c Superconductivity (1987).
[2] N.P. Ong et al. (preprint).
[3] S-W. Cheong et al., Phys. Rev. B 36 (1987) 3913.
[4] P.K. Gallagher et al. (preprint).
[5] Qualitatively similar behavior is reported on $YBa_2Cu_3O_x$ by S. Uchida et al. (preprint).
[6] P.M. Chaikin and G. Beni, Phys. Rev. B 13 (1976) 647.
R. Heikes, in: Buhl International Conference on Materials, E.R. Shatz, ed. (Gordon and Breach, New York, 1979).