Oxygen-deficiency dependence of the thermopower of $YBa_2Cu_3O_{7-y}$

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We have measured the thermopower of $YBa_2Cu_3O_{7-y}$ as a function of oxygen deficiency. We found that both the magnitude and the temperature dependence of the thermopower strongly depend upon the oxygen deficiency. As the oxygen deficiency increases, the magnitude at 273 K increases by more than a factor of 90 and the large positive peak observed at the superconducting transition temperature moves toward a higher-temperature region with its width broadening. We found that there exist some discrepancies between our observation and the models suggested by others. As a plausible explanation for the experimental results, a magnon-drag effect is considered.

Since the discovery of high-T_c superconductors, there have been a large number of experimental and theoretical efforts to understand the mechanism of superconductivity. However, a satisfactory explanation is still lacking. The difficulties come mainly from insufficient current knowledge of the electronic and ionic properties of the new materials. The transport properties of the material which are important to understand the electronic properties have not yet been consistently understood in any model. The thermopower draws particular attention, since the experimental results as well as their interpretations differ from one to another.[1-14] The thermopower measurement has been thought to be a fine probe to study the electronic properties of conductors because of its sensitivity to the electron energy-band structure and the electron-excitation interactions. This would, however, be true only if the obtained experimental result was comprehensive and interpreted properly. It is well known that the oxygen concentration in an oxide material is an important parameter to determine its electronic and sometimes ionic properties. Hence, it is important to determine the thermopower of the new oxide superconductors as a function of the oxygen concentration for a proper interpretation.

In this paper we report measurements on the oxygen-deficiency dependence of the thermopower of $YBa_2Cu_3O_{7-y}$ ceramic samples. We found that both the magnitude and the temperature dependence of the thermopower strongly depend upon the oxygen deficiency. As the oxygen deficiency increases, the magnitude increases by more than a factor of 90 and the large positive peak observed at the superconducting transition temperature moves toward a higher temperature region with its width broadening. The magnitude of the thermopower as a function of deficiency is found to vary consistently with the change of the conduction electron concentration. We have checked the significance of the contributions of phonon drag, superconducting fluctuations, and variable hopping to the thermopower and found that they are irrelevant. As an alternative, the magnon-drag effect is considered.

The samples were prepared by the solid-state reaction of Y_2O_3, $BaCO_3$, and CuO. A mixture of fine powders of the starting materials was first calcinated at 930 °C for 5 h in O_2 atmosphere and for 5 h in air, and cold-pressed into six 13-mm-diam pellets. The pellets were sintered at 950 °C for 10 h and finally submitted to heat treatment in O_2 atmosphere, 3 h at 700 °C , 5 h at 500 °C, and then 2 h at 350 °C. Different amounts of oxygen deficiency could be introduced to the six pellets by subsequently baking five of them in air, each at a different temperature (450 °C, 550 °C, 650 °C, and 750 °C for 3 h, and 900 °C for 6 h), keeping one unbaked. The thermopower was measured by employing the dc method. A sample with a typical size of $11\times2\times0.2$ mm^3 was mounted on two copper blocks, one of which was heated by a nichrome wire. The temperature gradient across the sample was monitored by a Chromel-Constantan thermocouple mounted independently on the copper blocks. The resistivity was measured through the low-frequency ac four-probe method.

The oxygen deficiency dependence of the thermopower and the resistivity measured at 273 K is summarized in Table I. A higher baking temperature introduces a higher oxygen deficiency. The magnitude of resistivity of the unbaked sample with the least oxygen deficiency is in agreement with other works. The thermopower at 273 K is positive for all the baking temperatures we have examined. As the baking temperature increases, or as the oxygen deficiency increases, the thermopower increases by more than a factor of 90 and the resistivity by more than a factor of 20. In Fig. 1, we show the temperature dependence

TABLE I. Resistivity and thermopower at 273 K of $YBa_2Cu_3O_{7-y}$ samples baked at different temperatures. A higher baking temperature introduces a higher oxygen deficiency.

Baking temperature (°C)	Resistivity at 273 K (10^{-4} Ω cm)	Thermopower at 273 K (μV/K)
No baking	3.8	2.5
450	12	9.2
550	19	14
650	34	36
750	38	94
900	91	230

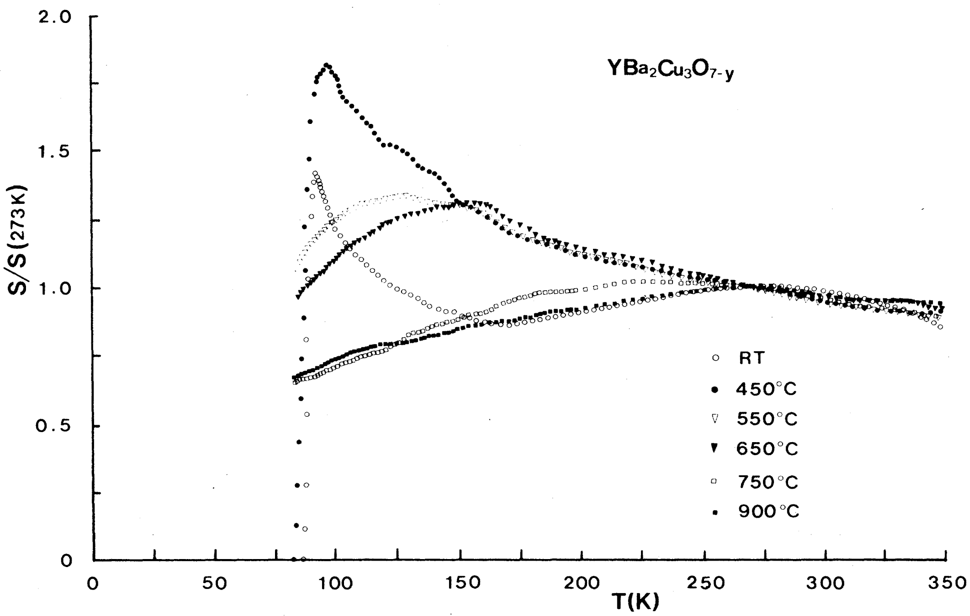

FIG. 1. Temperature dependence of the thermopower of $YBa_2Cu_3O_{7-y}$ samples baked at different temperatures.

of thermopower of the samples baked at six different temperatures. The thermopower of each sample is normalized in such a way that its value at 273 K is to be 1. We see that there exist two peaks in the curve of the unbaked sample, a large and sharp peak at the superconducting temperature and a broad peak at around 280 K. For the baked ones, there exists only one peak, which moves to a higher-temperature region with its width broadening as the baking temperature increases. We believe that the peaks in the baked samples correspond to the lower-temperature peak observed in the unbaked sample. The higher-temperature peak observed in the unbaked one is not seen for the baked samples at temperatures up to 350 K.

The oxygen-deficiency dependence of the thermopower can be understood within a simple theory of thermopower. From a direct counting of electrons, we know that for $0 \leq y \leq 0.5$ the oxygen deficiency in $YBa_2Cu_3O_{7-y}$ enhances the electron concentration, or reduces the hole concentration in the conduction band corresponding to the copper $3d_{x^2-y^2}$ level. From the sign of the measured thermopower, we see that the major charge carrier of $YBa_2Cu_3O_{7-y}$ is a hole. According to the theory, the thermopower of conductor is approximately inverse proportional to the carrier concentration. Hence, it is natural that the positive thermopower of the material increases along with the oxygen deficiency.

The magnitude of thermopower at 273 K of the sample baked at 900 °C is as large as 230 μV/K, which corresponds to about $2.8k_B/e$. This implies that the conduction in the material with a high oxygen deficiency is not metallic, but through the activated carriers. This conjecture seems to be consistent with the result of the resistance measurement shown in Fig. 2. The temperature curves of the resistance of the samples baked at and above 650 °C show an upturn curvature at low temperatures, which is a characteristic feature of an activated system.

The temperature dependence of the thermopower is more difficult to explain. Several different explanations have been proposed for the temperature dependence; phonon drag,[3,5,9,10] superconducting fluctuations,[12] variable hopping,[11] and a correlated hopping[2,6,13] due to a strong Coulomb interaction in a Hubbard model. It is tempting to relate the positive peak in the thermopower curve to the phonon drag, since the appearance of a bump caused by phonon drag is common in metals. However, the phonon-drag peak is known to appear at about $\frac{1}{5}$ the Debye temperature, which does not change much even if the conduction electrons vanish altogether. In Fig. 1, we see that the lower-temperature peak moves from below 95 to 275 K as the oxygen deficiency increases. If we accept the phonon drag is responsible for the peak, the Debye temperature is supposed to vary from below 500 to above 1300 K, which can hardly be the case. It is not likely either that the superconducting precursor effect is the explanation. We believe that the lower-temperature peak of the unbaked sample and the peaks of the baked ones come from the same origin. If the superconducting precursor effect is the origin, it implies that superconducting fluctuations persist even to above 270 K in a nonsuperconducting sample while in the sample superconducting at 92 K the fluctuations persist only up to even a lower temperature. It does not seem to be realistic. For a variable hopping conduction, the resistance varies with temperature as

$$R = R_0 \exp(T_0/T)^{1/4} \tag{1}$$

and the thermopower varies in proportion to $T^{1/2}$, which does not fit into any of our observations. The correlated hopping model was tested by Yu *et al.*[14] They report experimental evidence against the model. Our observation of the strong temperature dependence of the thermopower

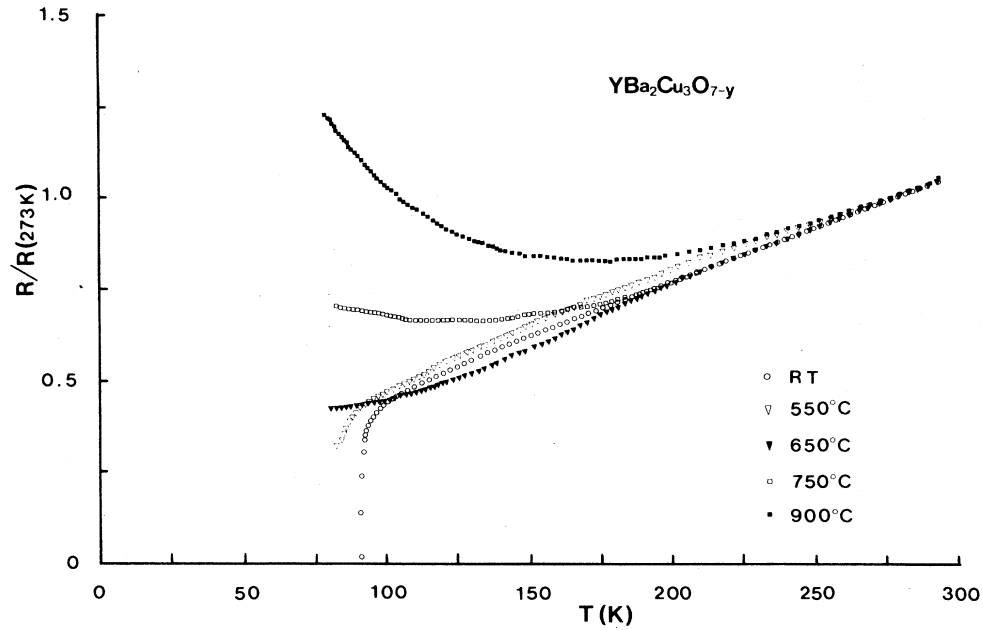

FIG. 2. Temperature dependence of the resistance of $YBa_2Cu_3O_{7-y}$ samples baked at different temperatures.

is also inconsistent with the expected temperature independent thermopower[15,16] for the correlated hopping.

We have examined four different models suggested by others and found significant discrepancies between the models and our observations. We now consider other possibilities. The neutron scattering experiments[17,18] and the muon-spin-rotation experiments[19,20] indicate that there exists an antiferromagnetic transition in $YBa_2Cu_3O_{7-y}$ for $y > 0.5$ as well as in La_2CuO_{4-y}. The Néel temperature is found to be lowered as the oxygen deficiency is enhanced.[17,19] In the presence of antiferromagnetic transition, there should exist the corresponding magnetic excitations, which make an extra contribution to the thermopower as a result of interaction with electrons. The magnetic excitation contribution which we tentatively call a magnon-drag thermopower is expressed as

$$S_m = \frac{C_m}{ne} A(T) , \qquad (2)$$

similar to the phonon-drag contribution. C_m is a magnetic specific heat, n a charge carrier concentration, and $A(T)$ a quantity determined by the magnon-magnon collision rate and the magnon-charge carrier collision rate. A magnetic specific heat associated with an antiferromagnetic transition diverges at the transition temperature, and therefore, it is expected that the magnon-drag thermopower of $YBa_2Cu_3O_{7-y}$ has a peak at the Néel temperature and the peak moves toward the higher-temperature region as the oxygen deficiency increases. Since the muon-spin-rotation experimental result[19] shows that the antiferromagnetic transition width becomes broader as more oxygen deficiency is introduced, we also expect that the peak width in the thermopower curve gets broader too. These expectations agree qualitatively well with our observations summarized above. If the magnon-drag effect is indeed responsible for the thermopower peak, then the long tail above the peak temperature in the thermopower curve is supposedly from the antiferromagnetic fluctuations. For La_2CuO_{4-y}, such strong two-dimensional antiferromagnetic fluctuations have been proved to exist.[18] The truncated peak at the superconducting temperature of the unbaked sample may then suggest that the antiferromagnetic fluctuations exist even in the superconducting samples. However, the experimental confirmation has yet to be made. Equation (2) tells also that the positive magnon-drag thermopower should increase as the hole concentration is enhanced along with the oxygen deficiency increment. This expectation is also qualitatively consistent with the observation.

In the above discussions, we assumed that $YBa_2Cu_3O_{7-y}$ has a single conduction band and that the sample studied was homogeneous and single phased. And also we ignored the ceramic nature of the sample. However, if any of the assumptions is not adequate, then we have to include additional contributions coming from additional conduction bands, impurities, or electron conductions perpendicular to the Cu-O plane. To consider all these effects in the analysis, we need detailed information of each of them, which, however, is currently not available.

In summary, we have measured the thermopower of $YBa_2Cu_3O_{7-y}$ as a function of oxygen deficiency and found a strong oxygen-deficiency dependence of the thermopower. This result shows that the contribution of phonon drag, superconducting fluctuations, variable hopping, and correlated hopping are not significant in the material. We also considered the magnon-drag effect associated with the observed antiferromagnetic transition. The qualitative features of the magnon-drag contribution in the material appears to agree well with our experimental result. We conclude that the magnon-drag effect should be considered seriously for the further studies on the thermopower of $YBa_2Cu_3O_{7-y}$.

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[1]J. T. Chen, C. J. McEwan, L. E. Wenger, and E. M. Logothetis, Phys. Rev. B **35**, 7124 (1987).
[2]J. R. Cooger, B. Alavi, L-W. Zhou, W. P. Beyermann, and G. Grüner, Phys. Rev. B **35**, 8794 (1987).
[3]M. F. Hundley, A. Zettl, A. Stacy, and Marvin L. Cohen, Phys. Rev. B **35**, 8800 (1987).
[4]P. M. Grant, S. S. P. Parkin, V. Y. Lee, E. M. Engler, M. L. Ramirez, J. E. Vanquez, G. Lim, and R. D. Jacowitz, Phys. Rev. Lett. **58**, 2482 (1987).
[5]Z. G. Khim, S. C. Lee, J. H. Lee, B. J. Suh, Y. W. Park, C. Park, I. S. Yu, and J. C. Park, Phys. Rev. B **36**, 2305 (1987).
[6]S-W. Cheong *et al.*, Phys. Rev. B **36**, 3913 (1987).
[7]D. C. Johnston, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski, Phys. Rev. B **36**, 4007 (1987).
[8]N. Mitra, J. Trefny, M. Young, and B. Yarar, Phys. Rev. B **36**, 5581 (1987).
[9]C. Uher, A. B. Kaiser, E. Gmelin, and L. Walz, Phys. Rev. B **36**, 5676 (1987).
[10]C. Uher and A. B. Kaiser, Phys. Rev. B **36**, 5680 (1987).
[11]R. C. Budhani, Sin-Mo H. Tzeng, and R. F. Bunshah, Phys. Rev. B **36**, 8873 (1987).
[12]H. J. Tordahl and A. Mawdsley, Phys. Rev. B **36**, 8881 (1987).
[13]A. P. Goncalves, I. C. Santos, E. B. Lopes, R. T. Henriques, M. Almeida, and M. O. Fingueiredo, Phys. Rev. B **37**, 7476 (1988).
[14]R. C. Yu, M. J. Naughton, X. Yan, P. M. Chaikin, F. Holtzberg, R. L. Greene, J. Stuart, and P. Davis, Phys. Rev. B **37**, 7963 (1987).
[15]P. M. Chaikin and G. Beni, Phys. Rev. B **13**, 647 (1976).
[16]J. F. Kwak and G. Beni, Phys. Rev. B **13**, 652 (1976).
[17]J. M. Tranquada *et al.*, Phys. Rev. Lett. **60**, 156 (1988).
[18]G. Shirane, Y. Endoh, R. J. Birgeneau, M. A. Kastner, Y. Hidaka, M. Oda, M. Suzuki, and T. Murakami, Phys. Rev. Lett. **59**, 1613 (1987).
[19]J. H. Brewer *et al.*, Phys. Rev. Lett. **60**, 1073 (1988).
[20]Y. J. Uemura *et al.*, Phys. Rev. Lett. **59**, 1045 (1987).