Negative thermopower of $YbBa_2Cu_3O_{7-y}$

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We have measured the thermopower of $RBa_2Cu_3O_{7-y}$ for R=Yb, Er, Y, Dy, and Gd as a function of temperature with further details on the Yb compound. We find that the Yb compound has a negative thermopower at all temperatures above T_c unlike the other compounds, whereas its temperature dependence is similar to that of the others. We also find that as the oxygen deficiency increases, the thermopower of $YbBa_2Cu_3O_{7-y}$ increases and becomes positive, while the whole shape of the thermopower-versus-temperature curve remains nearly unchanged. The observed insensitivity of the thermopower-versus-temperature profile to the sign of the thermopower or to the carrier concentration indicates that the electronic structure of the 1:2:3 compounds cannot be adequately explained within a single-conduction-band framework.

Ever since the discovery of the new high-T_c superconductors, the electronic structure of the materials has been intensively studied. Despite a great deal of effort, the electronic band structure, knowledge of which is essential to understand the superconducting mechanism in the materials, is not known in detail. In such a situation, the thermopower of the materials draws particular attention since it sensitively reflects the underlying electronic structural configuration. Measurements on selected high-T_c materials reveal that the thermopower has an unusual temperature dependence[1-5] and is highly sensitive to the oxygen concentration or sample doping.[5-10] For $YBa_2Cu_3O_{7-y}$, it is found that the thermopower has positive maxima at two different temperatures and its magnitude increases by more than a factor of 90 as the oxygen concentration decreases.[5] These experimental findings are indeed interesting, but they do not seem to provide enough specifics yet on the electronic structures except that the major charge carriers in the compounds are holes. More detailed measurements of the thermopower as functions of various parameters will shed more light on the problem.

In this paper, we report detailed measurements of the thermopower of $RBa_2Cu_3O_{7-y}$ ceramic samples for R =Yb, Er, Y, Dy, and Gd with special emphasis on the Yb compound. For $YbBa_2Cu_3O_{7-y}$, the thermopower is negative, unlike the others. As the oxygen deficiency increases, the thermopower of the Yb compound increases and becomes positive while the whole shape of the temperature-dependence curve (S-T curve) remains nearly unchanged. We also find that the S-T curves are all similar in shape for every 1:2:3 compound including the Yb compound.

The samples were prepared by the solid-state-reaction method. Different amounts of oxygen deficiency could be introduced to the samples by baking the ones with the least oxygen deficiency in the air at different temperatures. A higher baking temperature induces a higher oxygen deficiency. The thermopower was measured by employing the dc method described in Ref. 5.

The temperature dependence of the thermopower of $RBa_2Cu_3O_{7-y}$ ceramic samples for R=Yb, Er, Y, Dy, and Gd is shown in Fig. 1. As we mentioned earlier, all the samples share certain features in common in the S-T curves; a truncated peak at T_c, a broad peak at ~300 K, and a negative dS/dT at high temperatures. The observed temperature dependence is rather unusual and more complicated than can be explained under the assumption of a single conduction-band model. At high temperatures, in a single-band theory, S is linear in T and dS/dT has the same sign as S. We realize that both the temperature (T_p) at which the broad peak occurs and the magnitude of the thermopower S are related to the 3+ ion radius r of the rare-earth element in the material. The larger the r, the lower the T_p is and the larger the magnitude of S. The correlation between r and the magnitude of S was first reported with different magnitudes by Lee *et al.*[11] from measurements at room temperature. However, it is known that S is very sensitive to the oxygen content in the 1:2:3 compounds and that a larger r makes it easier to create the oxygen deficiencies. We cannot directly tell if the effect of changing r on S is intrinsic or not because we did not make systematic measurements to determine the oxygen deficiency in those five compounds. Nevertheless, the correlation between r and T_p seems to be intrinsic since for $YBa_2Cu_3O_{7-y}$ (Ref. 5) the sample with a larger oxygen deficiency is found to have a higher T_p as well as a larger S.

It is also interesting that the Yb compound, which has the smallest r, is found to have a negative S, considering that the sign of the thermopower determines the nature of the charge carriers in simple metals. What particularly attracts our attention is the fact that the Yb compound with negative S has more or less the same S-T curve shape as that with a positive S, since we would expect within a single-band theory that the negative S would show the opposite temperature dependence with an inverted S-T curve. In Fig. 2, we see that S of the Yb compound increases from negative to positive with the shape of its S-T curve unchanged as the baking temperature or the oxygen deficiency increases. For the baking temperature of 250 °C, S changes its sign at 170 K. We expect that the S-T curve will change sign again at higher temperatures, as we have confirmed in other samples which

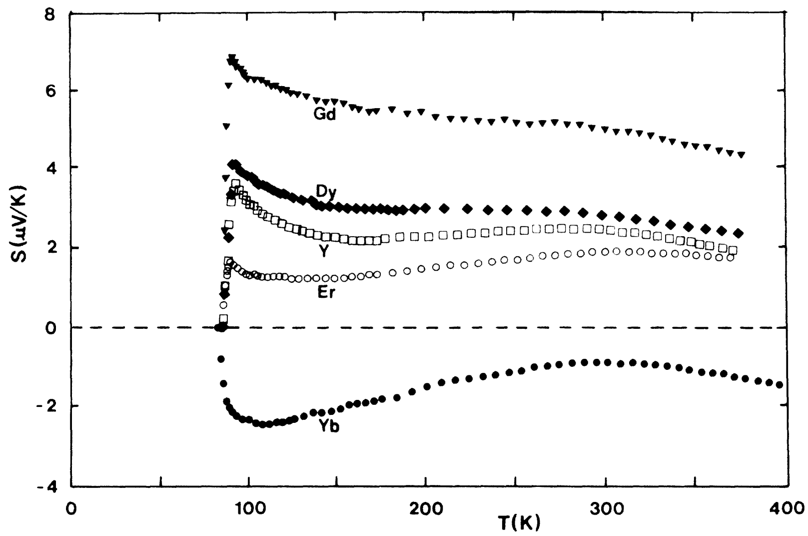

FIG. 1. Temperature dependence of the thermopower of $RBa_2Cu_3O_{7-y}$ ceramic samples for R =Yb, Er, Y, Dy, and Gd.

are not shown in Fig. 2. Upon comparing Fig. 2 with its counterpart for the Y compound shown in Ref. 5, we notice that, apart from their magnitudes, the two plots look very similar. The small wiggles appearing in the S-T curves between 100 and 300 K for the samples baked at lower temperatures seem to be associated with the structural transitions observed in sound-velocity[12-14] and specific-heat[15,16] measurements.

In the following, we focus our attention on the common shape of the S-T curves. Thermopower is a result of charge redistribution due to the diffusion or excitation drag of electrons in the presence of the temperature gradient across the sample. In a single-band system, the diffusion thermopower has the same sign as the charge carrier. Therefore, when the electron concentration increases and, as a result, the nature of charge carriers changes from electrons to holes, the thermopower should increase from negative to positive with the shape of its temperature profile inverted about the T axis so that at some point S becomes zero at all temperatures. The same holds for the drag thermopower as well except that in the Umklapp process the drag term changes sign. Hence, when the increase of oxygen deficiencies induces the growing electron concentration and, therefore, a sign change of the thermopower as observed in the Yb compound, the S-T curve is expected to become increasingly flat as it draws near the T axis and eventually becomes inverted when it lies above the T axis. However, what we see in Fig. 2 is in clear contrast to the picture given above based on the single-band theory.

In the presence of certain impurities in a host material which is single banded, as we can see in the silver-gold alloy system,[17] such a complicated temperature dependence and a rigid shift of the S vs T profile with variation in the amount of impurities may occur. However, there is no intentionally substituted impurity in this material and the oxygen deficiency is not known to create any impurity state in the conducting CuO_2 planes in the material. Moreover, for superconducting $YBa_2Cu_3O_{7-y}$, which has positive S, observations of similar temperature dependence of S have been reported by several other experimental groups working independently with their own ceramic or single-crystal samples.[2-4] The negative dS/dT at high temperatures and the sign change of S in temperature are observed not only in the 1:2:3 compounds but also in other high-T_c superconductors such as $La_{2-x}Sr_xCuO_4$ (Ref. 1) and $Bi_2Sr_2CaCu_2O_8$.[18] All these facts indicate that the nature of the S vs T profile of our samples is intrinsic and not an impurity effect.

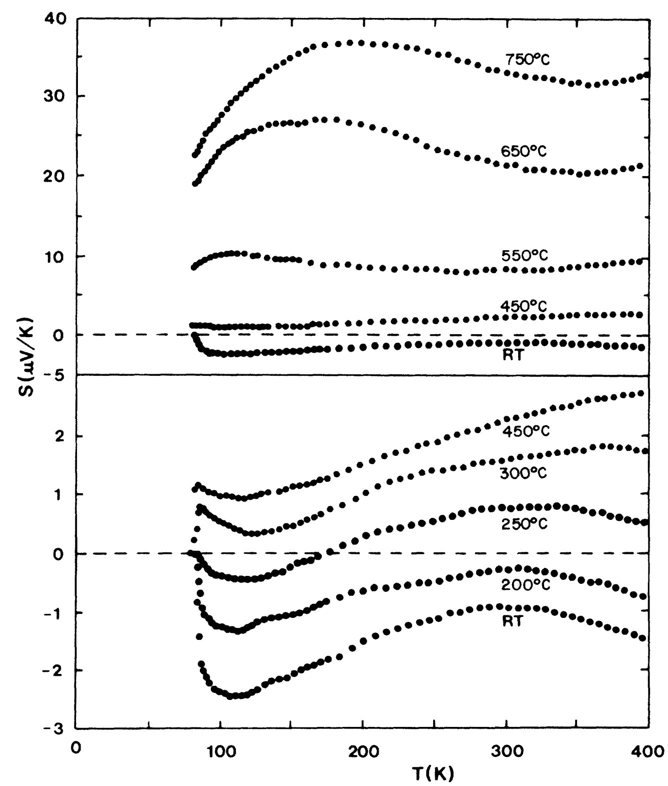

FIG. 2. Temperature dependence of the thermopower of $YbBa_2Cu_3O_{7-y}$ samples baked in air at different temperatures.

We now consider a multiband model as an alternative. In transition metals which have multiple conduction bands with *s* and *d* characters and, therefore, a multiple-sheet Fermi surface, frequent sign changes of S or dS/dT in temperature is not unusual.[19] The thermopower of a system with multiple conduction bands is a weighted sum of the contribution from each band. For a system with two conduction bands, electron and hole, as a simplest case, the thermopower is given as

$$S=\frac{\sigma_h S_h+\sigma_e S_e}{\sigma_h+\sigma_e}, \qquad (1)$$

where σ is the conductivity and the subscripts h and e indicate hole and electron contribution, respectively. In Eq. (1), the sign of S is determined by the ratio $|\sigma_e S_e/\sigma_h S_h|$, which is certainly a function of temperature or oxygen deficiency. Therefore, when the ratio changes with temperature, the S-T curve may have a complicated shape and even show a change in sign. When extra oxygen deficiency is introduced in the sample, the thermopower at a given temperature changes in magnitude and also possibly in sign, but the qualitative features of the S vs T profile should not change as long as the order of the relative importance of each band in temperature does not change.

Recent angle-resolved spectroscopy measurements[20,21] clearly show that $YBa_2Cu_3O_{7-y}$ and $Bi_2Sr_2CaCu_2O_8$ are multibanded. The observed temperature-dependent Hall coefficients[22–27] also imply the possibility of the existence of multiple conduction bands in every high-T_c superconductor. With these supporting facts, it still remains to be proven, by direct computation, that the observed behavior of the thermopower is truly due to the multibandedness. For this, we need a detailed knowledge of the dispersion of the whole Fermi surface, which is not available at the moment.

In summary, we find that the shape with two peaks and negative dS/dT at high temperatures in the S-T curve observed first in $YBa_2Cu_3O_{7-y}$ is common in the 1:2:3 compounds, regardless of the sign of the thermopower, the carrier concentration, and the rare-earth element in the material. We also find that a single-banded electronic structure does not provide an adequate explanation of our observations.

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