Thermopower anisotropy of highly underdoped and slightly overdoped $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ single crystals

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The thermoelectric power (S) for a series of $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ (R=Y, Gd, Dy) single crystals were measured in the ab plane and along the c direction. The doping level of these crystals changes from highly underdoped (T_c=44 K), through optimally doped (T_c=90 K) to slightly overdoped (T_c=88 K). Both S_{ab} and S_c change linearly with the doping level, but S_{ab} reverses its sign near the optimal doping stoichiometry, as it was observed for polycrystalline materials, whereas S_c remains positive for the whole series. In contrast to the results of electrical resistivity, the anisotropy of S was found to decrease with both increasing oxygen deficiency and decreasing temperature. A brief overview of thermopower results for single crystals of various high-temperature superconducting families is also presented. [S0163-1829(98)06102-5]

I. INTRODUCTION

The electronic transport properties of high-T_c superconductors (HTSC's) in the normal state still remain to be fully understood. Thermopower (S, TEP) measurements are useful for examination of the electronic structure of HTSC's and should be an important help in the understanding of superconductivity. Obertelli *et al.*[1] showed that $T_c/T_{c,\max}$ is a universal function of the TEP measured at room temperature (S_{300}) for polycrystalline samples of high-T_c superconductors, which evidenced a strong relationship between normal-state transport properties and superconductivity ($T_{c,\max}$ is a maximal critical temperature observed for a specific family). However, the thermopower exhibits a significant anisotropy, showing not only quantitative differences, but also a general distinction in temperature dependences and even opposite signs of in-plane and out-of-plane TEP values, as was reported for nearly optimally doped Y-Ba-Cu-O.[2,3] Such unusual anisotropy was also observed in Hall-effect experiments for Y-Ba-Cu-O,[2,4] where both changes in sign and in general temperature characteristics for ab and c directions were observed. Despite the crucial influence of doping on high-temperature superconductivity, up to now the in-plane vs out-of-plane anisotropy of both the Seebeck and Hall effects has been reported in literature only for nearly optimally doped samples.

In this paper we report the out-of-plane and in-plane thermopower for highly underdoped as well as nearly optimally doped crystals of HTSC's. The measurements were performed on a series of eight $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ (R=Y, Gd, and Dy) single crystals. The doping level of these crystals encompasses a wide region from highly underdoped (T_c =44 K) to optimally doped (T_c=90 K) and even slightly overdoped (T_c=88 K). A comparison of results to TEP measurements of other single crystals of HTSC's is also presented.

II. SAMPLES AND EXPERIMENTAL

$R\mathrm{Ba_2Cu_3O_{7-\delta}}$ (R=Y, Gd, and Dy) single crystals were grown using a self-flux technique described earlier[5] (2–5 mm^2 of area, 0.3–0.5 mm thick). The crystals were annealed at temperatures between 450 and 660 °C for 5 days (and then quickly cooled to room temperature) in order to obtain the oxygen content corresponding to various T_c val-

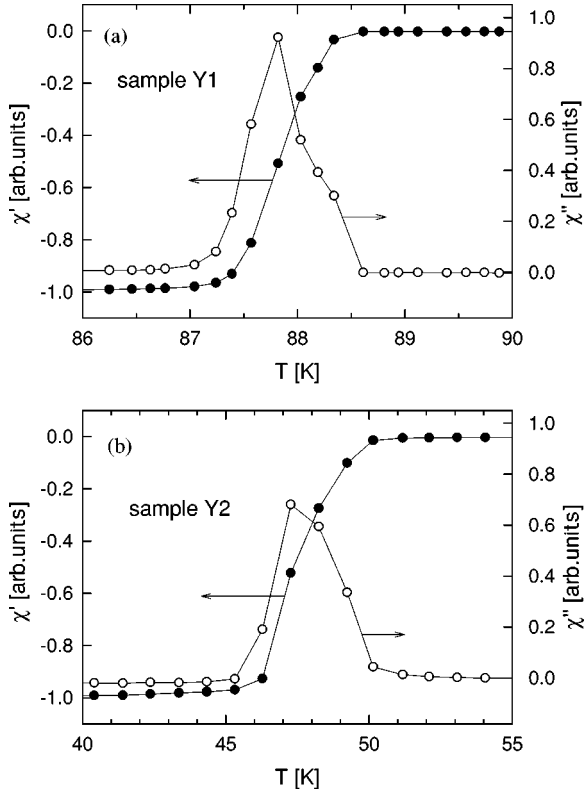

FIG. 1. The selected temperature dependences of the ac susceptibility of $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ single crystals: (a) sample Y(1) [R=Y,(7−δ]=6.90), (b) sample Y(2) [R=Y, (7−δ)=6.48].

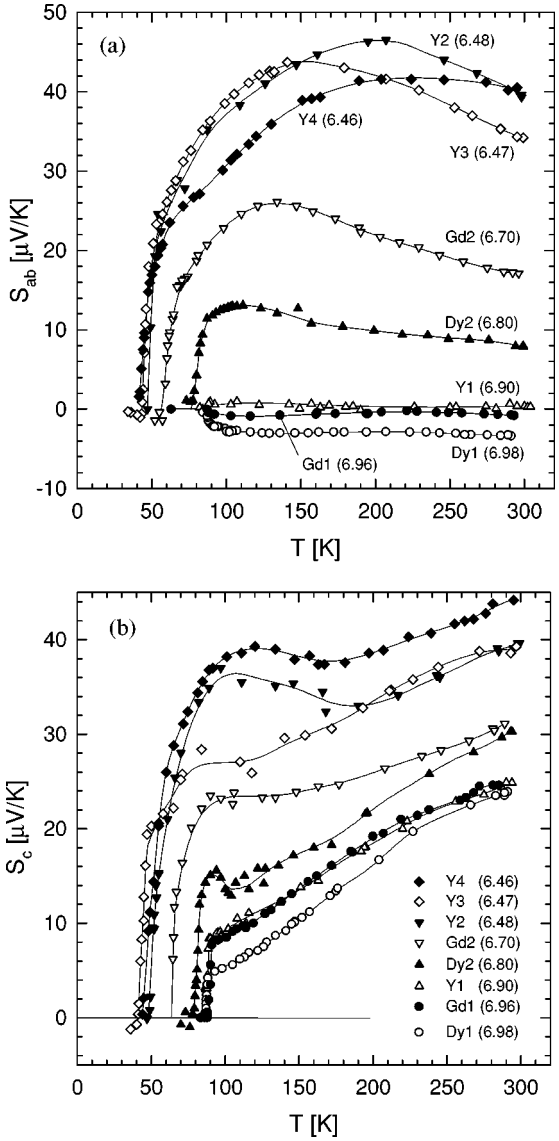

FIG. 2. The thermopower of $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ single crystals (R=Y, Gd, Dy) measured parallel to the ab plane (a) and along the c direction (b). Sample symbols denoting the curves contain the rare-earth name. Oxygen content ($7-\delta$) is given in parentheses.

ues. The critical temperature was measured by means of ac susceptibility and the results are presented in Table I. The selected temperature dependences of ac susceptibility are presented in Fig. 1. The last column in Table I shows the oxygen concentration assessed by comparison of the T_c values with literature data.[6–11] Since there is a maximum in T_c vs δ dependence for optimally doped R-123 samples ($\delta \approx 0.07$)[7] the sign of S_{ab} was additionally used to determine the oxygen content.

During the thermopower measurements the samples were clamped between two copper blocks, one of which was kept at a temperature a few degrees higher than the other ($1<\Delta T<4$ K). The quality of the contacts was checked by their resistance which was below a few Ohms in all cases. The temperature gradient and absolute temperature were determined by two copper wire thermometers. The signal was measured by copper gauge wires soldered to the copper blocks. The absolute TEP was obtained relative to the See-

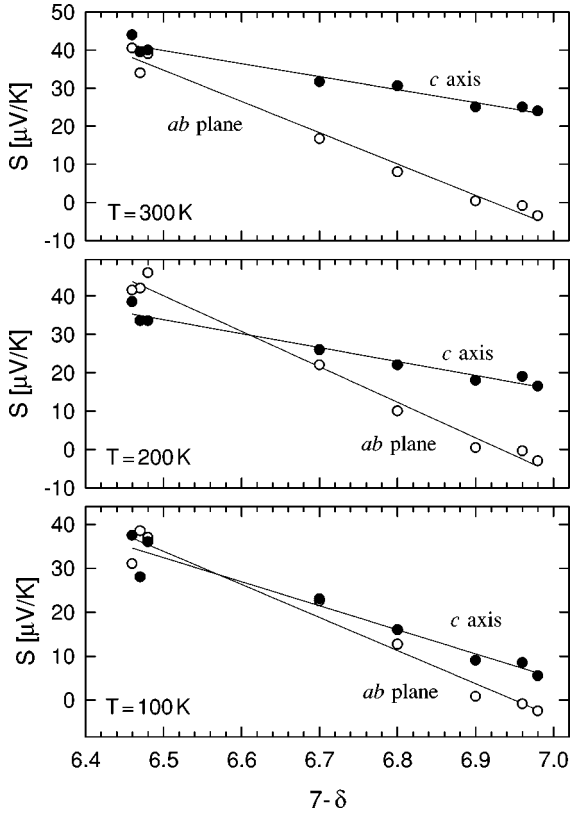

FIG. 3. The in-plane and out-of-plane thermopower of $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ single crystals (R=Y, Gd, Dy) versus oxygen content ($7-\delta$) at different temperatures. Straight lines are guides for the eyes only.

beck coefficient of copper. The crystals were not untwinned so the in-plane results should be regarded as an average of a and b directions.

III. RESULTS AND DISCUSSION

The in-plane and out-of-plane thermopower vs T for the series of $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ single crystals is shown in Fig. 2. The temperature variation and values of S_{ab} [see Fig. 2(a)] are much the same as TEP measured for polycrystalline samples, including a change of sign for overdoped samples. A wide maximum observed for underdoped crystals tends, like ceramic samples, toward higher temperatures with increasing oxygen deficiency. On the other hand, the behavior of S_c [Fig. 2(b)] resembles a classic metal, namely, it does not change sign upon changes in doping and varies approximately linearly with temperature for $\delta<0.5$. Surprisingly, the c axis TEP seems to be independent of the type of R ions located between two adjacent CuO_2 planes.

The dependences of the in-plane and out-of-plane TEP vs oxygen content at various temperatures are shown in Fig. 3. It is striking that the anisotropy of the thermopower is distinct for highly oxygenated samples (see the sign reversal for overdoped ones), whereas it almost disappears for samples with lower oxygen content. This observation is opposite to the behavior of electrical resistivity for R-123, the anisotropy of which strongly increases with decreasing both the oxygen content and the temperature.

Figure 4 shows the variation of S_{ab} and S_c measured at

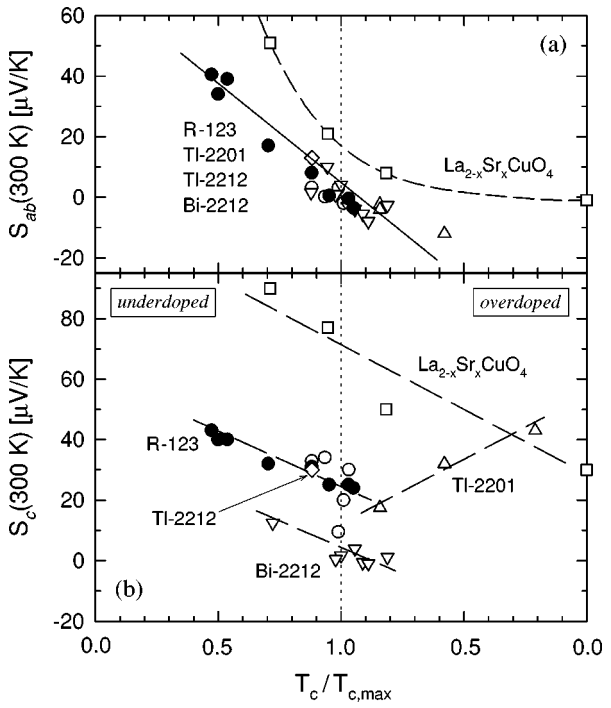

FIG. 4. The thermopower at room temperature measured parallel to the ab plane (a) and along the c direction (b) versus $T_c/T_{c,\max}$ for single crystals of HTSC's. Solid circles denote data for the R-123 family from the present work, open symbols indicate literature data: (○) Y-123 (Refs. 2, 3, 18, and 19); (△) Tl-2201 (Refs. 20,21); (▽) Bi-2212 (Refs. 22–26); (◇) Tl-2212 (Ref. 27); and (□) $La_{2-x}Sr_xCuO_4$ (Ref. 28).

room temperature (300 K) with doping level for our $RBa_2Cu_3O_{7-\delta}$ series of single crystals (solid circles) together with the literature data (empty symbols), including other families of HTSC's (only single crystals). The doping level was measured by the ratio $T_c/T_{c,\max}$, where $T_{c,\max}$ denotes a maximal critical temperature observed for a specific family. The in-plane values of TEP [Fig. 4(a)] follow the universal relation described by Obertelli *et al.*,[1] with the exception of the series of $La_{2-x}Sr_xCuO_4$ single crystals, which revealed higher values and no clear change of the sign in the superconducting composition region.[12]

As one would expect the differences between the S_c values of different families [Fig. 4(b)] are much more significant than for the case of the in-plane TEP. That is because not only CuO_2 planes but also the remaining construction elements of HTSC structures (i.e., insulating, interface, and separating layers[13]) contribute to TEP along the c direction. Separate linear dependences may be distinguished for different families, most of them, however, reveal a very similar slope (-35 μV/K for $La_{2-x}Sr_xCuO_4$, R-123, and Bi-2212). This slope is of the same sign but approximately two times lower than for the S_{ab} dependence on the doping level (-68 μV/K). The Tl-2201 family looks like an exception exhibiting opposite slope ($+42$ μV/K), but there are only three points from two papers, so some additional proof seems necessary. A group with a conducting block consisting of a single CuO_2 layer ($La_{2-x}Sr_xCuO_4$, $T_{c,\max}=38$ K) reveals the highest values of S_c. Both Tl families with single (Tl-2201, $T_{c,\max}=95$ K) and double (Tl-2212, $T_{c,\max}=118$ K) CuO_2 layers show medium values of S_c. Medium values of S_c are revealed also in a group of R-123 ($T_{c,\max}=93$ K), with double CuO_2 layers, but contrary to Tl-2212 the CuO_2 planes are separated by R atoms instead of Ca ones and additionally they are associated by CuO chains. A group with double CuO_2 layers (Bi-2212, $T_{c,\max}=90$ K) exhibits the lowest values of S_c. It is worth noting that the doping dependence of S_c of the last family seems also to show a sign change near optimal doping, as for the S_{ab} dependence. The anisotropy of TEP for the Bi-2212 family is the lowest.

As described above, there is no apparent connection between values of S_c for a particular family and the $T_{c,\max}$ value or details of crystallographic structure, like the number of CuO_2 layers within the conducting block. The insensitivity of S_c on the R type in R-123 indicates, however, that some layers may not contribute to the out-of-plane TEP. The same slope of S_c vs $T_c/T_{c,\max}$ lines for most families (Tl-2201 seems to be an exception) suggests a common influence of doping level on the c-axis transport.

The anisotropy of TEP for $RBa_2Cu_3O_{7-\delta}$ is most distinct for overdoped samples (i.e., with negative S_{ab} values). It leads not only to quantitative differences, but also to a difference in sign and temperature dependence. Experiments showing the anisotropy of Hall coefficient (which is also strongly dependent on Fermi-surface geometry) for Y-Ba-Cu-O lead to similar differences.[2] For in-plane direction ($B\perp ab$, $U_H||ab$) the Hall coefficient (R_H) is positive and approximately inversely proportional to temperature and is nearly like the $R_H(T)$ curves measured on the polycrystalline samples. Surprisingly, R_H in the out-of-plane direction ($B\perp c$, $U_H||c$) remains negative and constant over a wide temperature range (from T_c up to 300 K). This type of temperature dependence is characteristic for a normal metal described by the Fermi-liquid theory. A similar R_H sign change between different crystallographic directions was also reported for Bi-2201 and Bi-2212 (Ref. 14) as well as for $La_{2-x}Sr_xCuO_4$ single crystals.[15] Moreover, the negative R_H in the c direction for the above compounds is also temperature independent ($La_{2-x}Sr_xCuO_4$) or only weakly depends on temperature (Bi-2201 and Bi-2212).

TABLE I. The basic data for investigated single crystals of $RBa_2Cu_3O_{7-\delta}$. Sample symbol contains the rare-earth name and crystal number. The critical temperature (T_c) and the width of transition (ΔT_c) were obtained from ac suceptibility measurements. The oxygen content ($7-\delta$) was estimated from T_c and literature data (Refs. 6–11).

Sample symbol	T_c (K)	ΔT_c (K)	$7-\delta$ (± 0.02)
Dy(1)	88.3	1.6	6.98
Gd(1)	90.2	1.2	6.96
Y(1)	88.5	0.9	6.90
Dy(2)	82	3	6.80
Gd(2)	65.5	2	6.70
Y(2)	50	4	6.48
Y(3)	46.5	3	6.47
Y(4)	44	4	6.46

The comparison between the anisotropy of S and R_H for overdoped 123 compounds leads to some striking conclusions. The characteristic temperature dependences of both S and R_H along the c axis is purely metallic (S is T linear, R_H is temperature independent) in terms of Fermi-liquid theory. On the other side, the S and R_H along the ab plane reveal clearly nonclassical behavior. This picture is complicated by signs of these effects: S_{ab} and $R_{H,c}$ are negative, whereas S_c and $R_{H,ab}$ are positive.

An explanation of the opposite signs for the in-plane thermopower and Hall effect was proposed by Kubo.[16] The observations of some universal laws for polycrystalline HTSC's (the temperature dependence of Hall mobility $\mu_H \sim T^{-2}$;[17] S_{300} versus $T_c/T_{c,\max}$ relation[1]) led to the conclusion that electronic structure of HTSC's have to be described within a single-band picture.[16] Such a two-dimensional tight-binding model applied to transport phenomena in overdoped HTSC's anticipates exotic features of electronic transport. The most striking feature of this state is the effective-mass tensor, which is separated into a transport component $m_{\rm tr}$ (perpendicular to the Fermi surface and responsible for thermopower) and a cyclotron component m_H (parallel to the Fermi surface and responsible for the Hall effect). Stressed in this model is that $m_{\rm tr}$ is electronlike ($m_{\rm tr}>0$) and m_H is holelike ($m_H<0$) for a wide region of model parameters. Thus, this effective-mass dualism may qualitatively clarify opposite signs of in-plane TEP and Hall effect, but it does not explain the signs for out-of-plane transport phenomena.

IV. SUMMARY

In this paper we have presented TEP measurements for a series of $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ single crystals (44 K$\leqslant T_c \leqslant$90 K) for a wide range of doping level. It was revealed that not only S_{ab} but also S_c (as well as the anisotropy of S) are very sensitive to slight changes of oxygen stoichiometry. In contrast to the results for electrical resistivity, the anisotropy of S was found to decrease with increasing oxygen deficiency, almost disappearing for samples with $T_c \leqslant 50$ K. The anisotropy of S tends also to decrease with temperature, again in opposition to resistivity behavior.

Our data have demonstrated that S_{ab} follows the same common linear dependence on the doping level, including sign reversal near optimal stoichiometry, which was revealed by Obertelli *et al.*[1] for polycrystalline samples. The available literature data on thermopower measured on HTSC single crystals, which concern, however, only nearly optimally doped crystals, support this conclusion ($\mathrm{La_{2-x}Sr_xCuO_4}$ is an exception). The S_c values for our series of R-123 samples also exhibit linear dependence on the doping level, as was shown for several different temperatures. However, this dependence differs from that shown in Fig. 4(b) for other families of HTSC's. Still, the same slope of these lines (except the Tl-2201) may suggest a common origin of the S_c variation due to the changes of doping level.

Comparison with literature data for the Hall effect (R_H), another quantity sensitive to the sign of charge carriers, indicated that for overdoped Y-123 a striking situation is observed: R_H in ab plane and S along the c axis are positive, whereas R_H along the c axis and S in ab plane are negative. Moreover, temperature dependences of both S and R_H along the c axis behave strictly as a Fermi metal , whereas in the ab plane they reveal a clear non-Fermi behavior.

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