Thermal emf of $YBa_2Cu_3O_{7-\delta}$ single crystals

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(Submitted 11 April 1988)
Pis'ma Zh. Eksp. Teor. Fiz. **47**, No. 11, 578–580 (10 June 1988)

The differential thermal emf S of $YBa_2Cu_3O_{7-\delta}$ single crystals in the (ab) plane has been measured over the temperature range 400–90 K. The sign of S corresponds to a positive charge of the current carriers. The temperature dependence of this emf below ~ 300 K is anomalous and similar to the temperature dependence of the Hall voltage.

Since the appearance of single crystals of the high-temperature superconductors, these systems have attracted increased research interest as being the best known physical entities. In this letter we report the first results of a study of the differential thermal emf S of $YBa_2Cu_3O_{7-\delta}$ single crystals. Previous measurements on ceramics[1-7] have yielded contradictory results in terms of the sign of S (Refs. 1–3, 5),its magnitude,[4,6,7] and its temperature dependence $S(T)$ (Refs. 2, 4, and 5).

Our measurements of the thermal emf were carried out on samples of orthorhombic $YBa_2Cu_3O_{7-\delta}$ single crystals ($\delta \lesssim 0.1$) synthesized at the Institute of Crystallography, Academy of Sciences of the USSR.[8] The samples were faceted parallel-plane wafers of rectangular shape with a dimension of 10–30 μm along the c axis and a dimension of 0.2–0.6 mm in the ab plane. Their parameter values were similar to those described in Ref. 8: $T_c = 90$–93 K, a superconducting width <0.5 K, ρ_{300} (in the ab plane) ≈ 300 $\mu\Omega\cdot$cm, and $\rho_{300}/\rho_{95} \approx 4$.

The cell used to measure the thermal emf consists of a fused quartz plate to which two blocks of MgO single crystals are attached, separated by a 300-μm gap.[1)] The sample is mounted on these blocks with silver paste (see the inset in Fig. 1). The junctions of a calibrated differential copper-constantan-copper thermocouple are placed in the immediate vicinity of the sample. A local heater, attached to one of the blocks, changes the temperature of one block with respect to the other by $\Delta T = 0$–1 K. The contact resistance to the sample at $T = 90$–400 K is ~ 1 Ω ($\sim 10^{-4}$ $\Omega\cdot$cm^2) (Ref. 9). The potentiometric leads are made of silver wire.

At a given temperature we change the current through the local heater, and on a chart recorder we record the thermal emf V as a function of the voltage across the differential thermocouple, V_1. At $T > T_c$, the curves of $V(V_1)$ are linear. From their slope we find the difference between the differential thermal emf's of Ag and $YBa_2Cu_3O_{7-\delta}$: $V/\Delta T = S_{Ag} - S$. From the known values[10] of S_{Ag} we then calculate[2)] S.

For the three test samples, the value of S was positive and exhibited the reproducible temperature dependence shown in Fig. 1. At $T \gg 300$ K, $S(T)$ is metallic; i.e., $S(T)$ is roughly proportional to T. As the temperature is lowered below 280–300 K, we observe an increase in S, a saturation at $T \sim 140$ K ($S_{140}/S_{300} \approx 1.7$),and then a

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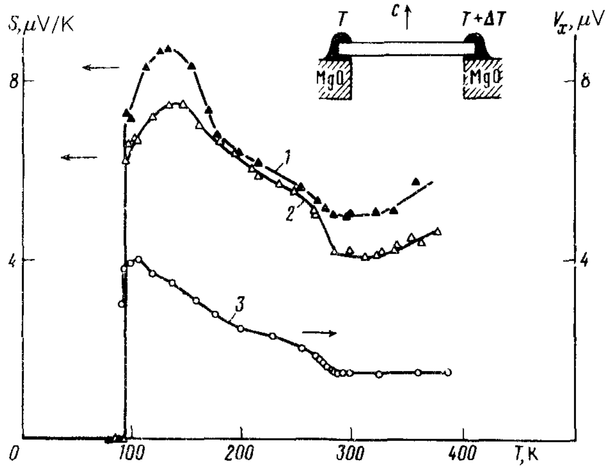

FIG. 1. Temperature dependence of (1,2) the differential thermal emf S and (3) the Hall voltage V_H of $YBa_2Cu_3O_{7-\delta}$ single crystals. 2,3—Sample 1; 1—sample 2. The error in the $S(T)$ measurements is 3%. The position and orientation of the sample in the measurement cell are shown schematically in the inset.

smooth decay and a sharp drop to zero in a narrow temperature interval ~0.5 K near T_c. In the course of these measurements we noted that holding the sample at $T \sim 400$ K for several hours would smooth out the nonmonotonic behavior $S(T)$ considerably and would shift the $S(T)$ minimum up the temperature scale (Fig. 2) The apparent explanation is the partial loss of oxygen from the sample.

One of the most interesting aspects of the experiment is the change in the nature of $S(T)$in the region 280–300 K and the increase in S with decreasing temperature below 280 K. The growth of $S(T)$in this region is not monotonic. The sharpest increase in S occurs in the intervals 260–280 K and 180–140 K. Typically, the entire $S(T)$ dependence in the region 150–400 K, including the nonmonotonic increase, is similar to the temperature dependence of the Hall voltage $V_H(T)$ measured for these and similar samples in the *ab* plane[9] (line 3 in Fig. 1) As the temperature is lowered, the difference between the temperature dependences of V_H and S comes into play at

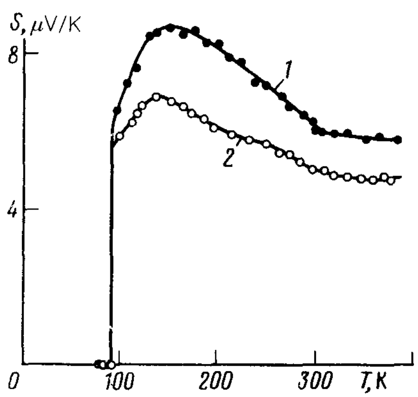

FIG. 2. Temperature dependence of S of $YBa_2Cu_3O_{7-\delta}$ single crystals after a prolonged hold at 400 K in a helium atmosphere. 1—Sample 3; 2—sample 1.

$T \lesssim 140$–150 K: The quantity $S(T)$ reaches saturation in this region and begins to decrease, while $V_H(T)$ continues to increase, all the way to $T \approx 105$ K.

The similarities in the behavior of $S(T)$ and $V_H(T)$ in the temperature range 140–400 K apparently make it possible to rule out a phonon drag as a possible mechanism for the anomalous growth of $S(T)$in the $YBa_2Cu_3O_{7-\delta}$ system,[1] since the Hall measurements were carried out under isothermal conditions. The results on $S(T)$ and $V_H(T)$ thus seem to provide independent evidence that the $YBa_2Cu_3O_{7-\delta}$ system undergoes a transition at $T < 280$–300 K from a metallic state to some other state at a temperature long before the superconducting transition. In Ref. 9 this state was linked with the onset of a Peierls instability, which precedes the superconducting state. It has been mentioned elsewhere[11] that the onset of specifically a Peierls instability could be the main factor stimulating superconductivity at high temperatures. The data obtained on $S(T)$ do not contradict that hypothesis, since a structural Peierls transition is usually preceded by a significant increase in the thermal emf.[12] Evidence in favor of these arguments comes from the recent observation in electron diffraction at $T < 300$ K of some additional diffuse lines corresponding to a superperiod[13] $b^*/2$. These lines can be linked with fluctuations in a superlattice which has formed with a doubled period along Cu-O chains. Yet further evidence comes from results of the observation of anomalies in the Mössbauer spectra of $YBa_2Cu_3O_{7-\delta}$ at temperatures below[14] 250 K. Our data on the Hall carrier density $p_{300} = 6 \times 10^{21}$ cm^{-3} (Ref. 9) correlate with the results of structural measurements.[13] This Hall carrier density is close to the density of 5.74×10^{21} cm^{-3} which corresponds to the half-filled $YBa_2Cu_3O_{7-\delta}$ band.[7]

The apparent reason for the decrease in $S(T)$ below 140 K is the proximity to the superconducting transition, although we did not observe any changes in $S(H)$ in magnetic fields H up to 10 kG ($H \| c$) at temperatures $T - T_c \geqslant 2$ K. Another point which remains unexplained is the difference between the behavior of $S(T)$ and $V_H(T)$ in this temperature range.

We are indebted to S. M. Stishov, I. N. Makarenko, and O. K. Mel'nikov for furnishing the samples and for a discussion of this study; V. N. Gubankov and R. N. Sheftal' for support of this study; and A. F. Volkov, E. V. Chenskiĭ, and V. M. Yakovenko for useful comments offered in the course of a discussion of these results.

[1)]The thermal conductivity of MgO single crystals is more than two orders of magnitude higher than that of fused quartz in the working temperature range.

[2)]The correspondence between the temperature difference ΔT determined from the differential thermocouple, on the one hand, and the actual temperature difference between the ends of the sample, on the other, was checked at $T < T_c$, where the measured value of $V/\Delta T$ agreed within 0.03 μV/K with the tabulated value of S_{Ag} (0.8 μV/K) At higher temperatures, it was also checked on the basis of special calibration measurements with TaS_3 samples ($S_{TaS} \gg S_{Ag}$). We also verified that the thermal emf of the silver-(silver-paste) circuit was negligible in the temperature range studied.

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Translated by Dave Parsons