Thermoelectric power and resistivity measurements on oxygen-annealed $HgBa_2Ca_2Cu_3O_{8+\delta}$ superconductors

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The thermopower and resistivity of bulk superconducting $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) have been measured for 15 samples (prepared from two batches) subjected to various annealing treatments in oxygen or nitrogen; all but two samples had values of zero-resistance T_c of approximately 134 K. In the normal state, the thermopower of the annealed samples shows a similar shape as a function of temperature: it decreases as temperature increases, with the rate of decrease slowing down at higher temperatures. The thermopower remains positive up to room temperature in all of our samples despite the high T_c values and annealing in oxygen, suggesting that the samples remain slightly underdoped.

The cuprate superconductor $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) (Refs. 1–4) currently has the highest known value of superconducting transition temperature: $T_c \sim 134$ K, which can be increased to more than 150 K under pressure.[5–7] The properties of this superconductor, and those of other members of the superconducting family $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$, e.g., Hg-1201 ($n=1$) and Hg-1212 ($n=2$), are therefore of particular interest.

The thermoelectric power of the cuprate superconductors has attracted attention because it tends to show a "universal" systematic pattern that shows a surprisingly good correlation with the superconductivity of the material.[8–10] So far, few data are available on the thermopower of the Hg-based cuprates. For a sample of $(Hg,Pb)_xBa_2Ca_2Cu_3O_{8+\delta}$ (Pb-doped Hg-1223), Isawa *et al.*[11] found a very small thermopower that showed a decrease as temperature increased; little change was caused by annealing in argon, but annealing in oxygen caused the thermopower to become negative almost down to T_c. This behavior is similar to that seen in the Tl- and Bi-based cuprate superconductors.[8,9] Ren *et al.*[12] measured the thermopower of a sample of $HgBa_2CaCu_2O_{6+\delta}$ (Hg-1212) with $T_c \sim 120$ K, as grown and after each of two anneals, finding a somewhat larger positive thermopower that also decreased with temperature. We have previously published the thermopower of two samples of $HgBa_2CuO_{4+\delta}$ (Hg-1201) subjected to different annealing treatments, finding a thermopower that became negative with approximately linear slope as the oxygen content increased.[13]

In this paper, we present the thermopower of 15 bulk samples of nearly phase-pure $HgBa_2Ca_2Cu_3O_{8+\delta}$ without Pb doping. Two master samples (labeled 1a and 2a) were prepared by a solid-state reaction from stoichiometric mixtures of HgO, BaO, CaO, and CuO. The as-sintered samples were then stored in a vacuum desiccator. Sample 2 was post annealed in oxygen at 300°C for 6 h and slow cooled to room temperature in oxygen. Detailed descriptions of sample preparation and the characterization of the samples have been given elsewhere.[4]

Portions of samples 1 and 2 were subsequently subjected to annealing treatments in flowing oxygen (or nitrogen) at atmospheric pressure or at 1 atm excess pressure to produce 15 different samples as listed in Table I. The resistivity was measured using a conventional four-probe technique. The thermopower was measured on pellets of about 1 mm thickness, using a setup similar to that described elsewhere.[13] A Keithley 181 nanovoltmeter was used in both sets of measurements. The thermopower measured in polycrystalline sintered samples is strongly dominated by the in-plane thermopower,[8] since the in-plane conductivity is very much larger than the c-axis conductivity in the cuprate superconductors.

The results of our measurements of thermopower and resistivity are shown in Figs. 1 and 2. Although its thermopower was measured, the nitrogen-annealed sample deteriorated to the extent that resistivity data could not be obtained. The resistivity of sample 1f is not shown since it was extremely large at room temperature (about 300 mΩ cm) and dropped sharply at about 220 K to about 10 mΩ cm. The resistivity of sample 2c was also anomalous. When it was first measured it showed a very sharp drop around 210 K, its magnitude decreasing to less than half. As temperature decreased further below 200 K, the anomalous resistivity resumed normal behavior with a slope similar to that seen above 210 K, and the usual superconducting transition was seen around 135 K. However, when the measurement was re-

TABLE I. Annealing treatment of master samples 1a and 2a of $HgBa_2Ca_2Cu_3O_{8+\delta}$.

Sample	Temperature (°C)	Gas	Duration (h)
1a as sintered			
1b	500	oxygen	24
1c	500	1 atm oxygen	24
1d	480	1 atm oxygen	48
1e	480	1 atm oxygen	96
1f	480	1 atm oxygen	124
1g	500	oxygen	240
2a as received (after annealing at 300°C in oxygen for 6 h)			
2b	400	oxygen	24
2c	400	oxygen	48
2d	400	oxygen	72
2e	400	oxygen	120
2f	500	oxygen	24
2g	500	oxygen	48
2h	400	nitrogen	24

peated the following day with reestablished contacts, no anomaly was seen, the resistivity closely following the same initial decrease with temperature but continuing with a similar slope down to the onset of the usual superconducting transition as in Fig. 2(b). The thermopower of this sample 2c [Fig. 1(b)], which had been measured (with different contacts) prior to both resistivity measurements, showed no anomaly around 200 K, however, indicating that the resistivity anomaly was an extrinsic effect. Sharp resistivity drops at elevated temperatures have been noted earlier in this material.[14]

The resistivity (Fig. 2) generally follows the standard pattern seen in the cuprate superconductors, namely, an approximately linear increase as temperature increases,

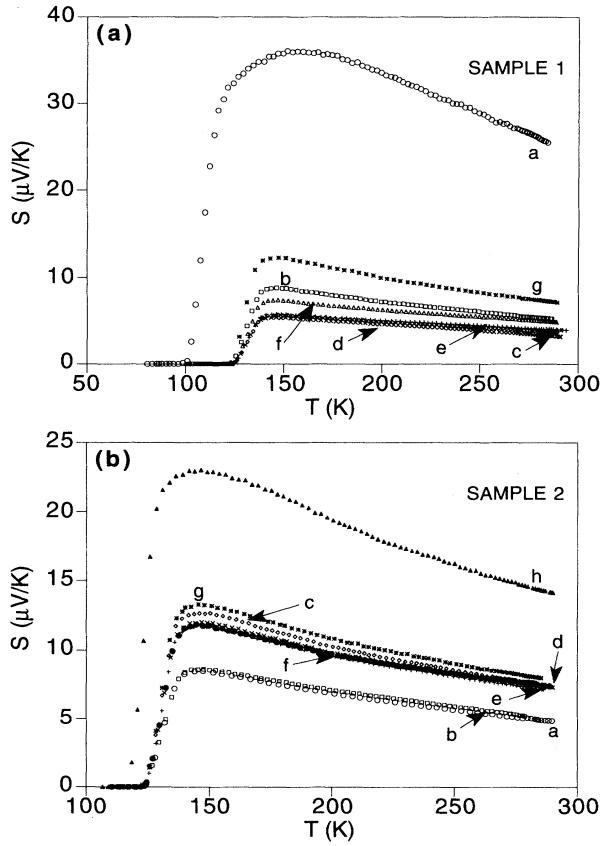

FIG. 1. Variation of the thermopower as a function of temperature for $HgBa_2Ca_2Cu_3O_{8+\delta}$ as sintered (sample 1a) and after various annealing treatments in nitrogen (sample 2h) or oxygen (all other samples), as listed in Table I.

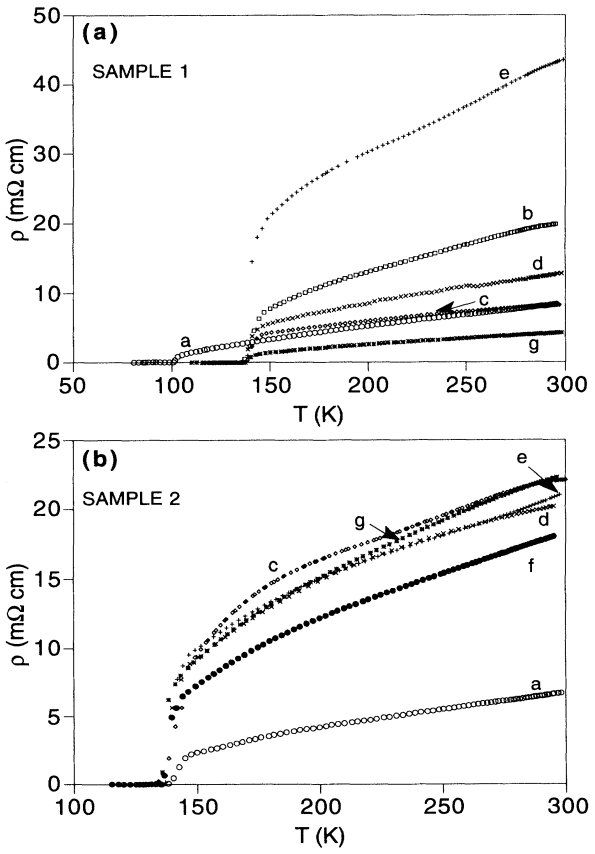

FIG. 2. Variation of the resistivity as a function of temperature for $HgBa_2Ca_2Cu_3O_{8+\delta}$ for the samples as listed in Table I.

and annealing in oxygen increases T_c from around 100 K in the as-sintered sample to approximately 134 K. The influence of superconducting fluctuations apparently extends to temperatures up to near 200 K, and there is evidence for changes in slope at higher temperatures, consistent with earlier data for Hg-1223.[15] The resistivity intercept at zero temperature obtained by extrapolating the resistivity between room temperature and 200 K varies considerably: it has a small negative value for the three samples with lowest resistivity (1a, 1g, 2a), is approximately zero for some samples (1b, 1d, 2e, 2g), and is positive for the other samples shown in Fig. 2.

The thermopower data are shown in Fig. 1. The as-sintered thermopower (sample 1a) is large, with a broad peak around 150 K reminiscent of that in many underdoped cuprates.[8] After annealing in oxygen, the thermopower for all samples lies between 3 and 13 μV K^{-1}, and shows a decrease as temperature increases. This pattern is somewhat similar to that seen in the Tl- and Bi-based cuprates (e.g., Refs. 16, 17), and for sample 2 of Subramaniam, Paranthaman, and Kaiser.[13] However, in none of our Hg-1223 samples were we able to attain a negative thermopower as usually seen in overdoped cuprates, and as seen in Pb-doped Hg-1223 by Isawa *et al.*[11] and in Hg-1201.[13] In terms of the "universal" correlation[10,17] indicating that room-temperature thermopower changes sign near the carrier density for maximum T_c, these data therefore suggest that our samples are still on the underdoped side of maximum T_c. As expected, annealing in nitrogen (sample 2h) increased thermopower, corresponding to reduced carrier density, but prolonged annealing in oxygen also had this effect. The value of T_c for the nitrogen-annealed sample, like that for the as-sintered sample 1a, is considerably smaller than for the oxygen-annealed samples.

We find only a very small decrease in T_c upon further annealing in oxygen of the "optimum" sample 2a for which $T_c \sim 134$ K [Fig. 2(b)], consistent with the results of Morosin *et al.*[18] The fact that our thermopower data become more positive as sample 2 is further annealed suggests strongly that the small decrease in T_c that does occur is not due to overdoping after passing the carrier density for maximum T_c, but due to underdoping. The trend for the resistivity to increase with further annealing for sample 2 [Fig. 2(b)] also indicates reversion to the underdoped state. Further support is provided by the thermopower for sample 1, which is large in the as-sintered state, initially decreases with annealing (1a→1b→1c→1d) to reach a minimum of about 3 μV/K near 290 K, but then increases with further annealing (1e→1f→1g). The resistivity decrease (1b→1c) and then increase (1c→1d→1e) is also consistent with an increase and then decrease in carrier density, as suggested by thermopower, but the relatively small resistivities for samples 1a and 1g do not fit the pattern. We note that thermopower is often a more reliable indicator of intrinsic behavior than an extrinsic parameter like resistivity when material defects are introduced.[19]

As shown in Fig. 3 for the annealed samples, the temperature dependence of the thermopower of Hg-1223 is not linear, but shows curvature as the magnitude of the

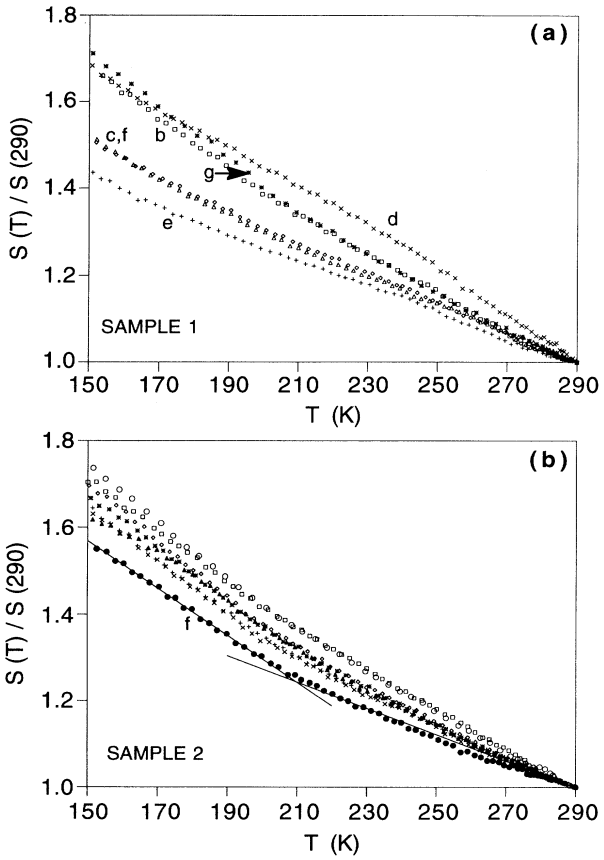

FIG. 3. Thermopower of samples 1 and 2 after various annealing treatments as in Table I normalized by their room-temperature thermopower, showing the increase in slope as temperature decreases. The lines are linear fits to the data for sample 2g below and above 200 K, and the letters identify some of the samples as in Fig. 1 and Table I.

negative gradient decreases above about 200 K [the effect is smaller for some of the sample 1 data, and one case (sample 1d) is anomalous in showing an increased slope above 230 K]. By contrast, our Hg-1201 data (when not linear) tended to show an increase in the magnitude of the gradient as temperature increases.[13] A decreasing slope as temperature increases such as we find in Hg-1223 was seen by Ren *et al.*[12] in their Hg-1212 samples, and has also been seen in $YBa_2Cu_3O_{7-\delta}$ (123) superconductors.[8] However, the data of Isawa *et al.*[11] for Pb-doped Hg-1223 were approximately linear in temperature, a difference possibly associated with the Pb doping, which appears to shift these materials to the overdoped regime.

Obviously, our observed increase in the magnitude of the gradient as temperature decreases is opposite to the change required to produce a gradual transition to zero thermopower below T_c. In addition, the change in slope of thermopower does not appear to be related to the onset of superconductivity (at least in a simple way) because there is evidence in Fig. 3(b) that an increase in slope as temperature decreases also occurs near room temperature, and rather than gradually increasing, the slope changes most near 200 K and then shows little increase

nearer T_c itself.

Another significant feature of the data revealed by Fig. 3 is that the normalized thermopower is similar for all the samples, although the absolute magnitude varies significantly (particularly for sample 2h). Thus the magnitude of the temperature gradient of the thermopower tends to be larger for samples with a larger magnitude of thermopower. This suggests that the negative gradient represents the decay as temperature increases of whatever effect[8,9] is the main origin of the thermopower for these samples. This is also consistent with data of Ren *et al.*[12] for Hg-1212. In several previous investigations of Bi- and Tl-based cuprate thermopower (e.g., Refs. 8,9,16,17,20), the negative gradient appears to stay approximately constant while the thermopower varies in magnitude or even changes sign, suggesting a negative linear term adding to a positive temperature-independent term of different magnitude in different samples.[9] This latter case seems to be more closely applicable for the Pb-doped Hg-1223 data of Isawa *et al.*[11] It is also more applicable to our data for maximum-T_c and overdoped Hg-1201 samples,[13] although the slope in this case is reduced in the underdoped and as-sintered samples.

In conclusion, our data indicate that $HgBa_2Ca_2Cu_3O_{8+\delta}$ has a positive thermopower and remains underdoped on annealing in oxygen as listed in Table I, unlike our previous data[13] for Hg-1201 and data[11] for Pb-doped Hg-1223. There is also an intriguing difference in the temperature dependence: the thermopower in Hg-1223 has a slower rate of decrease as temperature increases above 200 K. The magnitude of the gradient is larger for samples with larger thermopower magnitudes, so that normalizing the thermopower by its value at room temperature yields a rather uniform variation as a function of temperature (Fig. 3).

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