# Thermoelectric power of $YBa_2Cu_3O_{7-\delta}$

P. J. Ouseph and M. Ray O'Bryan
*Physics Department, University of Louisville, Louisville, Kentucky 40292*
(Received 12 June 1989; revised manuscript received 18 October 1989)

Results of thermoelectric power (TEP) measurements of the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ as a function of oxygen content are reported here. Removal of oxygen produces two distinct changes in TEP versus temperature curves: (1) It raises the TEP curves, and (2) it raises the temperature at which the slope of the curves changes from positive to negative. These changes result from (1) the decrease in the charge carrier density and (2) lattice distortions; both are due to increasing oxygen vacancy. Results of measurements on strontium-substituted compounds show only the second type of change in the TEP versus temperature curves.

## INTRODUCTION

Several experimental techniques have been used to study transport properties of new oxide superconductors. Of all these techniques, the thermoelectric power (TEP) measurements seem to give results that vary both in magnitude and sign from one laboratory to another. Some of the experiments yielded positive thermoelectric power in a temperature range from 300 K down to the transition temperature.[1–12] In other cases negative thermoelectric power was observed in the same temperature range.[13–16] Another feature of the thermoelectric power measurement was the prominent peak in the TEP versus temperature curves observed near the transition temperature. The explanations of the results have also been inconsistent, especially regarding the positive peak. In this paper we report the results of TEP measurements on two sets of samples of 1:2:3 compounds; one set with varying oxygen content and the other with varying amounts of strontium substituted in place of barium.

## EXPERIMENT

The samples of $YBa_2Cu_3O_{7-\delta}$ were prepared by the standard solid-state reaction procedure. A well mixed and ground power of $Y_2O_3$, $BaCO_3$, and CuO was calcinated in air at 950 °C for 10 h or more. The reacted powder was cold pressed into pellets and kept in the furnace at 950 °C for 5 h in flowing oxygen. With the oxygen flow maintained, the furnace was slowly cooled to room temperature in approximately 8 h. Strontium-substituted compounds, $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ with $0<x<1$, were also prepared by the same procedure. Samples thus prepared are found to be single phase, with sharp transition widths of 3 K or less. As strontium content increases the resistivity is found to increase and the transition temperature is found to decrease. The resistance versus temperature curves for these samples were parallel to each other from room temperature to transition temperature within our experimental limits. The variation of transition temperature for compounds used in this study is shown in Fig. 1.

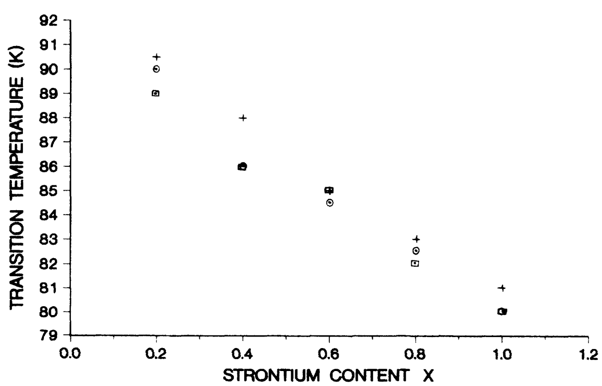


FIG. 1. Variation of transition temperature as a function of strontium content; +, estimated from thermopower; ⊙, from resistance; ⊡, from thermopower of a second set of samples.

The samples were then cut into rectangular-shaped pieces of $10\times4$ mm$^2$ in dimension. For thermoelectric power measurements the samples were kept between two copper blocks. The absolute thermoelectric power is calculated by correcting for the thermoelectric power of copper. The automatic system we used for the measurements consists of a Kiethly meter with a nine-input scanner card controlled by an ITT Courier computer. Only three of the inputs to the scanner card are used for this measurement, two for the thermocouples connected to the copper blocks, and the third for thermoelectric emf. The system is a modification of one we used for resistance measurements.[17] The temperature of the sample is varied by slowly introducing the sample into a liquid nitrogen cryostat.

## RESULTS

The thermoelectric power of $YBa_2Cu_3O_{7-\delta}$ for different oxygen content is shown in Fig. 2. The thermoelectric power is negative for $\delta$ values in the range of 0 to 0.1 (curves 1 through 5) and positive for $\delta$ values above 0.1 (curves 6 through 10). The TEP curves for $\delta$ ranging from 0 to 0.1 are similar, having a positive slope in the temperature range from 300 down to 130 K. In this region the curves are almost parallel to each other and each curve can be obtained by shifting the neighboring curve

 

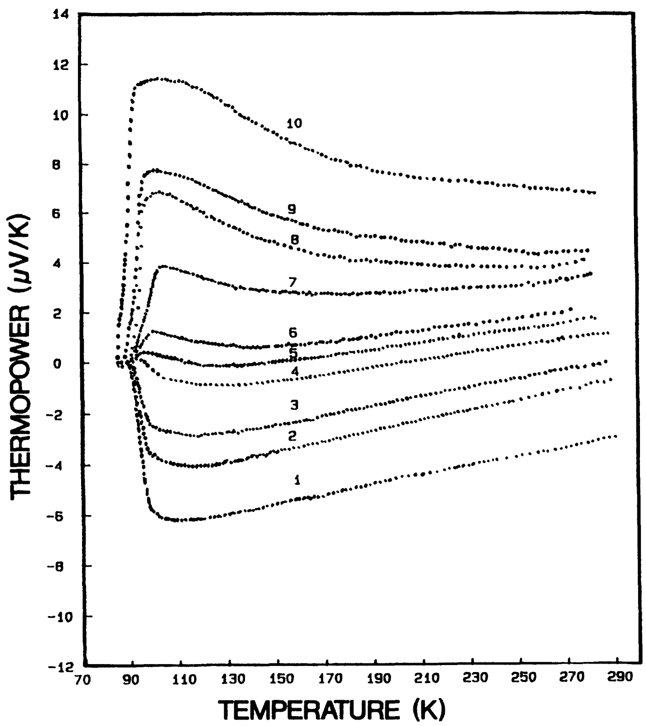


FIG. 2. Variation of thermoelectric power as a function of temperature for $YBa_2Cu_3O_{7-\delta}$ compounds with different oxygen content. Oxygen content, $7-\delta$, for curve 1 is 7; for curve 2, 6.98; for curve 3, 6.94; for curve 4, 6.93; for curve 5, 6.91; for curve 6, 6.90; for curve 7, 6.86; for curve 8, 6.84; for curve 9, 6.83; and for curve 10, 6.81.

up or down. Another important feature of these curves is an upward turn (negative slope) at low temperatures. In the negative TEP cases, this upward turn continues until the curve reaches the transition temperature. In the positive TEP cases the upward turn stops several degrees above the transition temperature and then decreases reaching 0° at the transition temperature. The high-temperature side of the peak near the transition, seen by almost all TEP studies, is due to this upward turn.

The results in Fig. 2 have been reproduced with other samples prepared by the same method. In addition, the sample used for the data in Fig. 2 was reoxidized and TEP measurements were repeated. The results were reproduced several times by repeating the oxidation reduction cycle. The amount of oxygen removed is arrived at by gravimetric measurements and the values of oxygen content (7-$\delta$) indicated in Fig. 2 could be off by $\pm0.01$. As mentioned earlier, the positive TEP curves have been obtained by several groups[1–12] and curves similar to those numbered 4, 5, and 6 have been obtained by some other groups.[13–16] In single-crystal studies Yu *et al.* obtained data similar to those in curve 3 for measurements in the *a-b* plane.[15]

Figure 3 shows the results of thermoelectric power measurements of $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ samples with $x=0.2$, 0.4, 0.6, 0.8, and 1.0. The room-temperature thermoelectric power is the same for all of the samples.

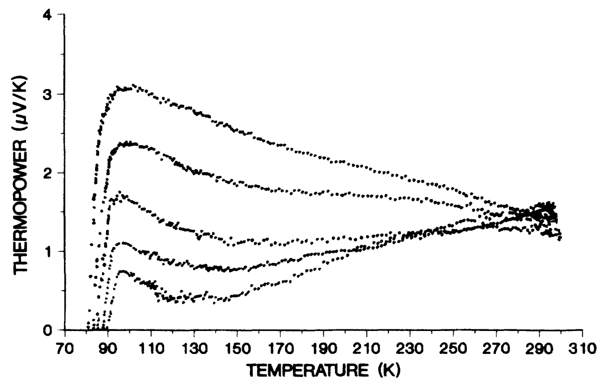


FIG. 3. Variation of thermoelectric power of strontium-substituted samples as a function of temperature. The curves are for $x=0.2$ (bottom), 0.4, 0.6, 0.8, and 1.0 (top).

The thermoelectric power for temperatures below room temperature increases with $x$ and all the curves show peaks above transition.

## DISCUSSION

As indicated earlier, curves for $\delta=0-0.14$ have a linear section where TEP is proportional to $T$. This fact along with the very small values of TEP demonstrate the metallic nature of the superconductor. The linear section is longest for $\delta=0$. The deviation from linearity takes place at successively higher temperatures as oxygen vacancy increases. This result is consistent with the observation of W. N. Kang *et al.*, who measured the TEP of samples with greater $\delta$ values than 0.3.[12]

The removal of oxygen produces two types of changes in the TEP versus temperature curves. Removal raises the temperature at which the slope of the curves change from positive to negative and shifts the TEP curves up. The first of these changes is similar to what we observe in strontium-substituted compounds (Fig. 3). As the strontium content increases, the slope of the TEP curves changes from positive to negative at successively higher temperatures. However, the room-temperature value of TEP did not change with strontium content. Results in Fig. 2 show that the room-temperature thermoelectric power of 1:2:3 samples increases by approximately 1 $\mu$V/K for a change in $\delta$ of 0.03. The fact that the room-temperature thermoelectric power of the strontium-substituted samples do not change suggests that strontium substitution does not increase oxygen vacancy as suggested in earlier papers.[18,19]

It is known that both strontium substitution and oxygen deficiency produce lattice distortion.[19] The variation from linearity of the TEP curves, therefore, may be a result of lattice distortion caused by strontium substitution or oxygen vacancy in these samples. Increasing oxygen vacancy above $\delta=0.16$ decreases the transition temperature. Strontium substitution also produces similar decrease in $T_c$. The transition temperatures for these samples were determined by resistance measurements. Even though small changes in the transition temperature are seen, as determined from the thermoelectric curves for $\delta=0$ to 0.14, the resistance measurements did not show such changes, agreeing with the earlier work.[20]

The fact that the sign of the thermoelectric power changes from negative to positive supports the view that the oxide superconductors are multicarrier systems. As $\delta$ changes, the relative number of negative to positive charge carriers changes. The changes in the carrier density and associated changes in the Fermi level may contribute to the continuous shift of the thermoelectric power with $\delta$. We are presently attempting an analysis based on band-structure changes associated with changes in oxygen content.

The TEP curves of strontium-substituted and oxygen deficient ($\delta > 0.1$) 1:2:3 compounds show peaks near the transition temperature. The presence of this peak is not yet fully understood even though several explanations such as phonon drag magnon drag have been suggested.[4,10,11]

## CONCLUSION

In conclusion, we have reproduced the results of thermoelectric power measurements by almost all researchers in this field. The variations in magnitude of TEP and in the shape of the TEP curves are the result of small variations in the oxygen content. It is extremely difficult to control the oxygen content during preparation of samples by the solid-state reaction. The matter is further complicated by the fact that small variations in oxygen content do not produce changes in the transition temperature. This could explain why TEP measurements lacked agreement from laboratory to laboratory. It also appears that strontium substitution does not increase oxygen vacancy in 1:2:3 compounds.


[1]C. Uher and A. B. Kaiser, Phys. Rev. B **36**, 5680 (1987).

[2]H. J. Trodahl and A. Mavdsley, Phys. Rev. B **36**, 881 (1987).

[3]H. Ishii, H. Sato, N. Kanazawa, H. Takagi, S. Uchida, K. Kitazawa, K. Kishio, K. Fueki, and S. Tanaka, Physica **148B**, 419 (1987).

[4]R. Srinivasan, V. Sankaranarayanan, N. P. Raju, S. Natarayan, U. V. Varadaraju, and G. V. Subboa Rao, Pramana—J. Phys. **29**, 225 (1987).

[5]S. Yan, P. Lu, H. Ma, Q. Jia, and X. Wang, Solid State Commun. **64**, 537 (1987).

[6]P. K. Davies, J. A. Stuart, D. White, C. Lee, P. M. Chaikin, M. J. Naughton, R. C. Yu, and R. L. Ehrenhaufer, Solid State Commun. **644**, 1441 (1987).

[7]N. Mitra, J. Trefny, M. Young, and B. Yarar, Phys. Rev. B **36**, 5581 (1987).

[8]I. M. Tsidilkovski and V. I. Tsidilkovski, Solid State Commun. **66**, 51 (1988).

[9]Rnan Yaozhong, Hu Xuelong, Zhao Yong, Qian Yitai, Chen Zuyao, Wang Ruiping, and Zhang Quiri, Solid State Commun. **64**, 467 (1987).

[10]A. B. Kaiser, Phys. Rev. B **37**, 5924 (1988).

[11]Ch. Laurent, S. K. Patapis, M. Laguesse, H. W. Vanderschueren, A. Rulmont, P. Tarte, and M. Austoos, Solid State Commun. **66**, 445 (1988).

[12]W. N. Kang, K. C. Cho, Y. M. Kim, and Mu-Yong Choi, Phys. Rev. B **39**, 2763 (1989).

[13]U. Gottwich, R. Held, G. Sparn, F. Steglich, H. Rietschel, D. Ewert, B. Renker, W. Bauhoffer, S. Von Molnar, M. Wilhelm and H. E. Hoenig, Europhys. Lett. **4**, 1183 (1987).

[14]S. C. Lee, J. H. Lee, B. J. Suh, S. H. Moon, C. J. Lim, and Z. G. Khim, Phys. Rev. B **37**, 2285 (1988).

[15]R. C. Yu, M. J. Naughton, X. Yan, P. M. Chikin, F. Holtzberg, R. L. Greene, J. Stuart, and P. Davis, Phys. Rev. B **37**, 7963 (1988).

[16]Shousheng Yan, Peixiang Lu, and Qi Li, Solid State Commun. **65**, 355 (1988).

[17]P. J. Ouseph, D. Bruning, M. Ray O'Bryan, John P. Ouseph, and S. Carter, Rev. Sci. Instrum. **60**, 511 (1989).

[18]B. W. Veal, W. K. Kwok, A. Umezawa, G. W. Crabtree, J. D. Jorgensen, J. W. Downey, L. J. Novicki, A. W. Mitchell, A. P. Paulikas, and C. H. Sowers, Appl. Phys. Lett. **51**, 279 (1987).

[19]W. F. Huang, P. J. Ouseph, K. Fang, and X. J. Xu, Solid State Commun. **66**, 283 (1988).

[20]R. J. Cava, Int. J. Mod. Phys. B **1**, 813 (1987).