Determination of charge carriers in superconducting La-Ba-Cu-O by thermoelectric measurements

J. T. Chen, C. J. McEwan, and L. E. Wenger
Department of Physics, Wayne State University, Detroit, Michigan 48202

E. M. Logothetis
Research Staff, Ford Motor Company, Dearborn, Michigan 48121
(Received 2 March 1987)

Majority-charge carriers in high-T_c superconducting La-Ba-Cu-O are shown to be positive (holelike) carriers as determined by thermoelectric measurements in the temperature range of 300 to 28 K, the superconducting transition temperature.

Recently, reports of superconductivity with high transition temperatures[1-6] in the range of 30 to 50 K and high critical fields[7] have been reported in La-Ba-Cu-O and La-Sr-Cu-O compounds prepared under various annealing conditions. Experimental results seem to indicate that multiple phases of crystalline structure, mixed valence states of Cu^{3+} and Cu^{2+}, and the concentrations of Ba and Sr substituted for La play important roles. Percolation near the metal-insulator transition and interfacial effects due to layered structures in the mixed phases or between grains were also suggested to be important in influencing the onset of superconductivity as well as the sharpness of resistive transition.[2] Kresin[8] suggested that low dimensionality and the presence of groups with high density of states may be the cause of the high T_c. In this Brief Report, we present evidence which shows that the majority carriers in La-Ba-Cu-O are positive (holelike).

The compound investigated had a nominal composition of $La_{1.8}Ba_{0.2}CuO_{4-y}$, where y is undetermined. It was prepared by the solid-state reaction method.[2,9] The appropriate mixture of La_2O_3, $BaCO_3$, and CuO powders was first heated to 900 °C for 8 h in air, then pulverized, and reheated at the same temperature for another 6 h. The thoroughly reacted mixture was again pulverized and pressed into a flat disk for final sintering at 1100 °C for 4 h in air. The x-ray diffraction pattern of this compound indicates a K_2NiF_4-type structure, identical to that reported in the literature.[2-4] In addition, a minor phase ($<5\%$) of the perovskite $CuLaO_3$ phase was observed. From measurements of both the in-phase (dispersive) and out-of-phase (absorptive) components of the ac susceptibility [250 Hz and 42 mOe(rms)], we have observed the onset of diamagnetism at 33 K with the full superconducting phase occurring at 28 K and estimated the in-phase susceptibility to be $\sim 80\%$ of the ideal diamagnetic limit at 4.2 K. Resistive transitions and current-voltage characteristics were also taken for the temperature range of 4.2 to 300 K. The best sample had a continuous superconducting path at 28 K as determined by the zero-voltage current I_0 in the I-V characteristics. I_0 was greater than 1.2 A at 4.2 K, gradually decreased with increasing temperature, and disappeared at 29 K. This temperature correlates well with the onset of diamagnetism observed in the ac susceptibility. More detailed results of these measurements will be reported elsewhere.

The sign of the charge carriers can be determined by the thermoelectric effect as follows. If a temperature gradient exists between the two ends of a sample, charge carriers will diffuse from the higher- to the lower-temperature side until a steady-state potential difference is established. The sign of this thermoelectric voltage depends on the sign of the charge carriers. For negative charge carriers, the potential and temperature gradients have the same sign; for positive charge carriers, the opposite sign. The experimental arrangement is shown in the inset of Fig. 1. The sample was sandwiched between two copper blocks. The one on the left was part of the sample holder with a large thermal mass. The one on the right had a much smaller thermal mass. Embedded in each copper block was a calibrated diode thermometer for temperature measurements. When the sample was cooled down at a steady rate, about 10 K/min, the larger block on the left showed a thermal lag; i.e., the sample surface on the right was colder during the cooling. During the warming cycle, the temperature gradient was reversed. When the temperature was stabilized to allow thermal equilibrium, the thermoelectric voltage disappeared. The

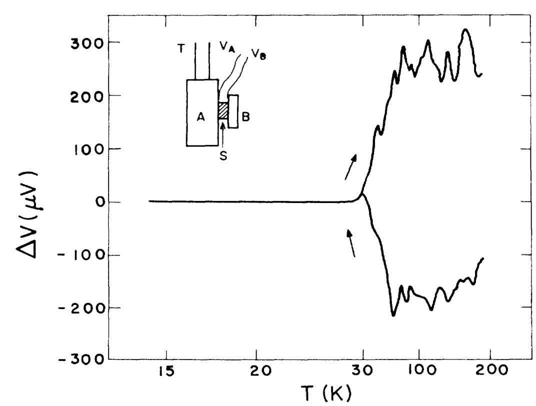

FIG. 1. The thermoelectric voltage ΔV ($=V_A - V_B$) vs temperature for both (lower) cooling and warming (upper) cycles. Note that the temperature scale is not linear and the small oscillations are nonreproducible fluctuations. In the inset, A and B are two copper blocks with diode thermometers, V_A and V_B are voltage leads, S is the sample, and T is stainless-steel tubing.

induced thermoelectric voltage, ΔV ($=V_A-V_B$) for both cooling and warming cycles, is shown in Fig. 1. The ΔV shows that the potential V_B on the right side of the sample was more positive during the cooling cycle when it was at a lower temperature. It became more negative during the warming cycle when it was at a higher temperature. This means that charge carriers are positive. Figure 2 shows the absolute thermoelectric power, defined as $-\Delta V/\Delta T$ versus the temperature. As can be seen, it decreases in magnitude very quickly to zero at a temperature where the sample becomes superconducting. This indicates that the observed thermoelectric power was from the sample and not in the leads outside the sample. These types of materials are generally granular and porous, and consequently the thermoelectric power may be affected by a large phonon drag.[10] However, the phonon drag is usually only important at low temperatures and normally does not change the sign of the thermoelectric power. Thus the negative thermoelectric powers result from positive charge carriers. If the same charge carriers (holes instead of electrons) are responsible for the superconductivity below the transition temperature, this result and the fact that the range of T_c being reported for this class of oxides is so wide suggest that a very different mechanism may be involved. We speculate that Ba and La may form a hybrid band of *d* electrons and the superconductivity is related to the vacant states in this band. Spectroscopic analyses of the Ba and La atoms in this compound may provide evidence to check this speculation.

On further note, Zhao *et al.*[5] have reported observations of nonreproducible resistivity decreases and increases near 70 K in some of their experiments where samples were cooled at a steady rate. We suggest that the thermoelectric effect was the cause of these observations. We have found in numerous occasions that if a small bias current was used to study the superconducting transition of a high-resistivity sample not in thermal equilibrium, the thermoelectric voltage could lead to "apparent" zero or even negative resistivity at a much higher temperature than the true T_c. Thus, reporting of new high-T_c superconductors based solely on resistivity measurements without collaborative measurements that independently deduce transition temperatures from the occurrence of diamagnetism or the flow of supercurrent should be viewed with caution. Since these new high-T_c superconducting materials are oxides with fairly high resistivities and porosities, information about the resistivity in both polarities, the magnitude of the zero-voltage current, and the nature of the I-V characteristics near T_c would be very beneficial.

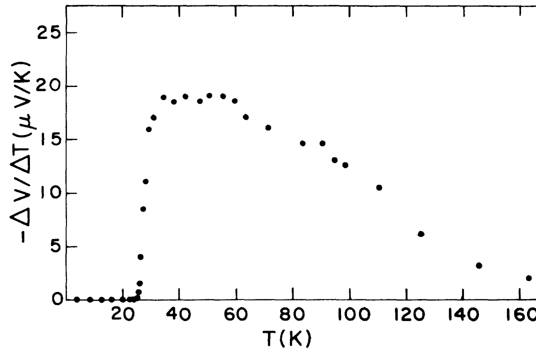

FIG. 2. The absolute thermoelectric power $-\Delta V/\Delta T$ vs temperature.

In conclusion, measurements of the thermoelectric power above the superconducting transition temperature in La-Ba-Cu-O show that the charge carriers are positive.

We wish to thank David Allred, Henry V. Bohm, Y. W. Kim, Carl F. Foiles, Stanford R. Ovshinsky, and Rosa Young for useful discussions and W. Win, R. Soltis, and M. Hurley for their technical assistance. This work is supported in part by the Institute for Manufacturing Research and the Industrial Productivity and Projects Research Institute of Wayne State University and the National Science Foundation under Grant No. DMR-8400711.

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987); Science **235**, 567 (1987).

[3] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).

[4] S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Lett. (to be published).

[5] Zhao Zhongxian, Chen Liquan, Cui Changgneg, Huang Yuzhen, Liu Jinxiang, Chen Genghua, Li Shanling, Guo Shuquan, and He Yeye, Ke Xue Tongbao (unpublished).

[6] M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987).

[7] T. P. Orlando, K. A. Deling, S. Foner, E. J. McNiff, Jr., J. M. Tarascon, and L. H. Greene, Phys. Rev. B **35**, 5347 (1987).

[8] Vladimir Z. Kresin (unpublished).

[9] C. Michel, L. Er-Rakho, and B. Raveau, Mater. Res. Bull. **20**, 667 (1985).

[10] O. I. Shklyarevskii, A. G. M. Jansen, J. G. H. Hermsen, and P. Wyder, Phys. Rev. Lett. **57**, 1374 (1986).