The anomalous thermoelectric power of the La doped Bi-2201 phase

1997 J. Phys.: Condens. Matter 9 1261

(http://iopscience.iop.org/0953-8984/9/6/012)

J. Phys.: Condens. Matter **9** (1997) 1261–1265. Printed in the UK PII: S0953-8984(97)76919-4

The anomalous thermoelectric power of the La doped Bi-2201 phase

Xu Gaojie†, Mao Zhiqiang†, Wang Ruiping†, Tian Mingliang† and Zhang Yuheng†‡

† Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China
‡ Chinese Centre of Advanced Science and Technology (World Laboratory), PO Box 8730, Beijing, People's Republic of China

Received 5 August 1996

Abstract. Samples of the $Bi_{1.9}Sr_{1.6}La_{0.4}CuO_y$ system with different oxygen contents have been obtained by annealing the as-grown samples at different temperatures and oxygen partial pressures. The results of resistivity and thermoelectric power (TEP) measurements of these samples are reported here. Some anomalous phenomena in transport for the underdoped sample of $Bi_{1.9}Sr_{1.6}La_{0.4}CuO_y$ were observed, i.e., below a characteristic temperature, the TEP exhibits a significant enhancement and the temperature dependence of the resistivity deviates downward from linearity. These results imply that a spin gap exists in the La doped Bi-2201 system. By comparison with the results reported previously, we suggest that the microstructural characteristics are another important factor in determining the spin excitation spectrum.

1. Introduction

A great deal of experimental and theoretical work has been devoted to the understanding of the normal state properties of the high-temperature superconducting oxides. Several experimental techniques have been used in the study of the normal state transport properties. Of all these techniques, thermoelectric power (TEP) measurement is believed to be most effective in revealing the scattering mechanism of charge carriers. The Bi-based 2201 system is a good candidate material for studying the normal state transport properties of high-temperature superconductors, because it allows one to measure the properties to lower temperature than do other high-T_c materials. Previous investigations on the TEP of the Bi-2201 phase mainly focused on the La doped $Bi_2Sr_2CuO_y$ system [1–3], in which the optimally doped and underdoped samples can be obtained. Recently, we successfully obtained both overdoped and underdoped samples by annealing sintered samples of $Bi_{1.9}Sr_{1.6}La_{0.4}CuO_y$ at different conditions, and some anomalous behaviours in transport were observed for the underdoped samples.

2. Experimental details

The samples of $Bi_{1.9}Sr_{1.6}La_{0.4}CuO_y$ were synthesized by a conventional solid state reaction method using high-purity powders of Bi_2O_3, $SrCO_3$ and CuO. First, the appropriate mixture of these powders was well ground and calcined at about 850 °C for 24 h in air with an intermediate grinding; then, the loose powder was pressed into pellets and sintered at 880 °C in air for another 2 days; finally, the sample was cooled down to room temperature in the furnace. Sets of samples with different oxygen concentrations were obtained by annealing the sintered samples at various temperatures and oxygen partial pressures. The details of the annealing conditions are listed in table 1.

Table 1. Different annealing conditions of $Bi_{1.9}Sr_{1.6}CuO_y$.

Sample	Annealing conditions
A	O_2 25 atm 550 °C × 24 h
B	quenched in air from 850 °C
C	O_2 10^{-5} atm 550 °C × 2.5 h
D	O_2 10^{-8} atm 550 °C × 4 h

Powder x-ray diffraction (XRD) patterns were obtained on a Rigaku-D/max-γ A rotating target x-ray diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm). The resistivity was measured by a standard four-probe method in a closed-cycle helium cryostat, in which the lowest available temperature is 11 K. The TEP, $S(T)$, was measured by a differential method [4]. The temperature at two ends of the measured sample was controlled automatically within a precision of 0.01 K, and the temperature gradient between the ends of the sample was 2 K. The emf of the sample was indicated by a Keithley 181 nanovoltmeter with an error of TEP measurement smaller than 0.1 μV K^{-1}

3. Results and discussion

XRD analysis showed that the sintered sample was free of impurity phase and all the samples used in the measurement still remained single phase after annealing under different conditions. Furthermore, a progressive structure change accompanied by the variation of the oxygen content in $Bi_{1.9}Sr_{1.6}La_{0.4}CuO_y$ was also detected in the XRD patterns and electron diffraction patterns, which will be discussed elsewhere.

The temperature dependence of the resistivity for samples A–D is displayed in figure 1. Sample A exhibits a metallic behaviour with a small slope over the whole measured temperature range, and no superconducting transition is observed down to 11 K. The quenched sample B is superconducting with a T_c of 35 K (midpoint in the transition) and shows a linear temperature dependence of resistivity above T_c, while for sample C superconductivity appears at 23 K and the $\rho(T)$–T curve exhibits an obvious downturn below 180 K, which is denoted by the arrow in figure 1. Sample D with a T_c of 17 K shows a semiconductor-like behaviour above T_c. From the variation of normal state resistivity, one can easily speculate that the oxygen content decreases gradually from sample A to D.

Figure 2 shows $S(T)$ plotted against temperature for samples A–D. Sample A has negative values in the TEP over the whole measured temperature, while samples B–D have positive values. All the samples have a similar slope for the $S(T)$–T curves at high temperature. Nevertheless, the shapes of the $S(T)$–T curves exhibit an obvious difference. For sample A the TEP increases almost linearly with decreasing temperature above 110 K. For samples B–D, each of the $S(T)$–T curves exhibits a clear broad peak and the temperatures corresponding to these peaks are 106, 120 and 130 K respectively. Furthermore, there is another quite interesting feature in the $S(T)$–T curves of the samples C and D, i.e., the $S(T)$ shows a significant enhancement below 180 and 200 K respectively

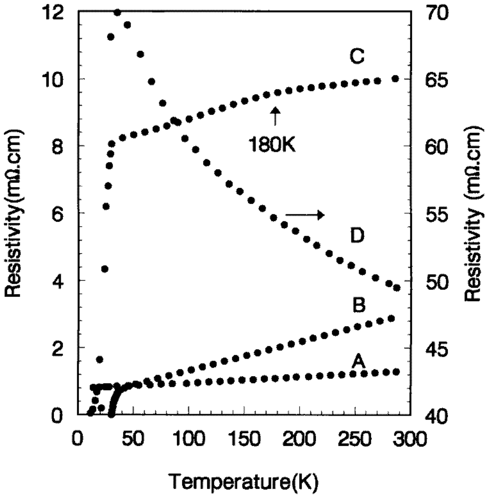

Figure 1. The temperature dependence of the resistivity for the $Bi_{1.9}Sr_{1.6}La_{0.4}CuO_y$ samples annealed under different conditions.

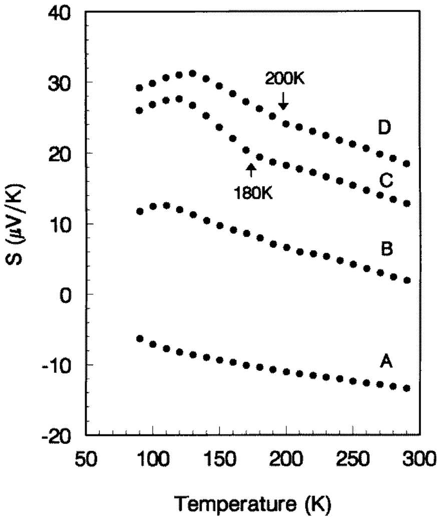

Figure 2. The temperature dependence of the TEP for the $Bi_{1.9}Sr_{1.6}La_{0.4}CuO_y$ samples annealed under different conditions.

(denoted by arrows in figure 2). Such a steep enhancement in $S(T)$ below a certain characteristic temperature is very similar to the behaviour observed in the underdoped Y-123 [5, 6] and stoichiometric Y-124 [5] systems.

From the above analyses of the resistivity and TEP data, it can be seen that sample B has the highest T_c and shows a linear temperature dependence of resistivity above T_c, which can be believed to lie in (or nearly lie in) the optimal doped region in the phase diagram. Sample A, annealed at an oxygen pressure of 25 atm, has smaller room-temperature resistivity and

TEP than sample B and does not show superconductivity down to 11 K. Clearly, it lies in the overdoped region. In contrast, the samples C and D with lower T_c and larger values in resistivity and TEP must lie in the underdoped region.

Tallon *et al* [5] indicated that the anomalies of TEP in the underdoped Y-123 and Y-124 systems were closely related to the smooth opening of the spin gap. That is, the TEP undergoes significant enhancement as the spin gap opens. In accordance with the argument of Tallon *et al*, we can believe that the steep enhancement of the TEP below 180 and 200 K observed in samples C and D (figure 2) originates from the opening of the spin gap in the normal state spectrum. Moreover, the downturn behaviour in the $\rho(T)$–T curves associated with the opening of spin gap was clearly observed in sample C. From figure 2, it can also be clearly seen that the temperature of the opening of the spin gap, T_g, increases with decreasing oxygen content. For sample D, a steep enhancement in $S(T)$ below 200 K is observed, but the corresponding anomaly in the $\rho(T)$–T curve is not detected. The reason for this may be that the TEP reflects the modification in the spin excitation spectrum more sensitively than the resistivity.

Until now, the spin gap phenomenon has been suggested in the following systems: $YBa_2Cu_3O_y$ [7, 8], $YBa_2Cu_4O_8$ [9, 10], Bi-2212 [11], $La_{2-x}Sr_xCuO_y$ [12] and $Tl_2Ba_2CuO_y$ [13]. Although attempts have been made to examine the spin gap behaviour in the Bi-2201 system, there is no successful report. It is known that underdoped samples [1–3] in the Bi2201 system can be obtained by substitution of La for Sr, but the resistivity and TEP do not show the features associated with the spin gap behaviour [2, 3, 14]. Why do two different kinds of results exist in resistivity or TEP measurement? We think this may be attributed to the different microstructures of the samples. It is known that La substitution for Sr in the Bi-2201 phase increases the extra oxygen in the Bi_2O_2 layer and decreases the modulation period, thus enhancing the local structural distortion [15]. Inversely, removal of oxygen from the Bi-2201 phase, namely, decreasing oxygen in the Bi_2O_2 layer, lowers the structural distortion, which has been clarified by our present experimental results. Strong structural distortion seriously influences the interplay of Cu^{2+} spins and suppresses the spin gap appearance. Although De Silva *et al* [16] also investigated the resistivity and TEP of the La doped Bi-2201 system by annealing samples in N_2 at different temperatures, no anomaly was observed in the measurement. We think it may be that the oxygen concentration is still higher or the structural distortion of their samples is stronger than that of ours. One knows that in the Bi-2201 system Bi content has a strong influence on the crystal microstructure and superconductivity. For example, for the $Bi_{2+x}Sr_{1.6-x}La_{0.4}CuO_y$ system, the superconducting transition temperatures are 16 and 27 K for $x = 0.1$ and 0 respectively [17]. In our samples, the Bi nominal composition is 1.9, so the modulation is weaker than that with a Bi nominal composition of 2.0. From above analysis, one can easily think that besides carrier concentration, the microstructural characteristics are also an important factor in determining the spin excitation spectrum.

4. Conclusion

The results of resistivity and TEP measurements for $Bi_{1.9}Sr_{1.6}La_{0.4}CuO_y$ samples annealed at different conditions have been reported. From the analyses of anomalous normal state transport properties, as well as the comparison of our results with those reported previously, some suggestions were made: (i) a spin gap exists in the La doped Bi-2201 phase; (ii) the crystal microstructural characteristics are another important factor in determining the spin excitation spectrum.

References

[1] Sera M, Tanaka S, Sato M and Fujishita H 1992 *Solid State Commun.* **81** 415

[2] Devaux F, Manthiram A and Goodenough J B 1990 *Phys. Rev.* B **41** 8723

[3] Wang N L, Chong Y, Wang C Y and Huang D J 1993 *Phys. Rev.* B **47** 3347

[4] Ruan Y 1988 *Chinese J. Low Temp. Phys.* **10** 161

[5] Tallon J L, Cooper J R, de Silva P S I P N, Williams G V M and Loram J W 1995 *Phys. Rev. Lett.* **75** 4114

[6] Ouseph P J and O'Brien M R 1990 *Phys. Rev.* B **41** 4123

[7] Alloul H, Ohno T and Mendels P 1989 *Phys. Rev. Lett.* **63** 1700

[8] Rossat-Mignod J, Regnault L P, Vettier C, Burlet P, Henry J Y and Lapertot G 1991 *Physica* B **169** 58

[9] Bucher B, Steiner P, Karpinski J, Kaldis E and Wachter P 1993 *Phys. Rev. Lett.* **70** 2012

[10] Machi T, Tomeno I, Miyatake T, Tai K, Koshizuka N, Tanaka S and Yasuoka H 1991 *Physica* C **185–9** 1147

[11] Walstedt R E, Bell R E and Mitzi D B 1991 *Phys. Rev.* B **44** 7760

[12] Kitaoka Y, Ishida K, Ohsugi S,Fujiwara K and Asayama K 1992 *Physica* C **185–189** 98

[13] Fujiwara K, Kitaoka Y, Ishida H, Asayama K, Shimakawa Y, Manako T and Kubo Y 1990 *J. Phys. Soc. Japan* **59** 3459

[14] Allgeier C, Neumeier J J and Schilling J S 1992 *Physica* C **194** 227

[15] Mao Z, Tian Mingliang, Ji Mingrong, Zhu Jingsheng, Zu Jian and Zhang Yuheng 1994 *Phys. Rev.* B **49** 9857

[16] De Silva P S I P N, Sinclair D C, Flower N E, Tallon J L and Cooper J R 1994 *Physica* C **235–40** 1531

[17] Maeda A, Hase M, Tsukada I, Noda K, Takebayashi S and Uchinokura K 1990 *Phys. Rev.* B **41** 6418