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1998 J. Phys.: Condens. Matter 10 8843

(http://iopscience.iop.org/0953-8984/10/39/019)

J. Phys.: Condens. Matter **10** (1998) 8843–8850. Printed in the UK PII: S0953-8984(98)94386-7

Thermoelectric power of the $Bi_2Sr_{2-x}CuO_y$ system

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Received 18 May 1998, in final form 4 August 1998

Abstract. Single-phase $Bi_2Sr_{2-x}CuO_y$ samples were synthesized by the conventional solid-state reaction method. The normal state transport properties and the behaviour of localized Cu^{2+} spins were investigated by means of resistivity, thermoelectric power and electron paramagnetic resonance. The experimental result shows that with the increase of the fraction of localized Cu^{2+} spins the resistivity increases rapidly and the broad maximum in the TEP curve shifts to high temperature. These results indicate that the variation of resistivity and TEP may be related to localized Cu^{2+} spin scattering.

1. Introduction

To determine the relation between the magnetic properties of the CuO_2 plane and superconductivity, investigations on the effect of elemental doping at Cu sites and non-Cu sites have been carried out extensively, especially for La- and Y-based cuprate superconductors [1–9]. In these studies the unusual normal state properties, such as resistivity (ρ), the Hall coefficient (R_H) and the thermoelectric power (TEP, S), have received wide attention from theoretical and experimental researchers, with the consequent proliferation of new models and a rapid improvement in sample quality. It has been revealed that in various series of copper oxides, the electronic state changes from antiferromagnetic insulating to a normal metallic one through the superconducting state with increasing carrier concentration, and the suppression of elemental doping at Cu sites on superconductivity originates from the magnetic pair-break effect [10]. Since cuprate superconductors are based on an antiferromagnetic background, it is easy to think that the magnetic interaction may influence the normal state properties. In fact, it has already been suggested [11, 12] that the linear temperature dependence of resistivity is caused by spin fluctuation scattering. Up until now, however, how the spin scattering influences TEP has been unclear. Zhou and Goodenough [13] have investigated systematically the TEP of copper oxides with single CuO_2 sheets and found that the doping of magnetic ion at non-Cu sites has little influence on the TEP. For the cases of elemental substitution for a Cu-site, Zn and Ni doped La214 systems have been widely studied [14–16]. The experimental results show that, with increasing dopant concentration, the TEP value increases for the Ni doped system and decreases for the Zn doped system, which may be attributed to the changes

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of carrier concentration by doping. It is known that Ni^{2+} shows a small effective moment ($0.7\ \mu_B$) in the $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_y$ system [1], which is close to that of Cu^{2+} ($0.8\ \mu_B$); therefore, the effect of magnetic scattering on TEP is not understood in the Ni doped La214 system.

Recently, investigations of the transition-metal doped La214 system indicated that Fe^{3+} doping leads to the broad maximum (where the temperature is denoted as T_m) in the $S(T)$–T curve increasing significantly without change to the carrier concentration of the system [17]. This result implies that the hump (T_m) in the $S(T)$–T curve may be closely related to the magnetic mechanism. In order to understand the relationship between spin scattering and T_m, we have employed an electron paramagnetic resonance (EPR) measurement. It is believed that an EPR measurement is effective for determining a localized Cu^{2+} (or other magnetic ions) spin character. Information is obtained on the g value from the resonance field, on the spin relaxation time from the signal width and on the susceptibility from the integrated intensity of the absorption signal. In this paper we chose for study the $Bi_2Sr_{2-x}CuO_y$ system, and systematically investigate the normal state transport properties and magnetic behaviour, as well as their relation.

2. Experimental method

Samples were produced by the conventional solid-state reaction method. Powders of Bi_2O_3, $SrCO_3$ and CuO were mixed with nominal compositions of $Bi_2Sr_{2-x}CuO_y$ ($x = 0.1$, 0.3, 0.4, 0.5, 0.6 and 0.7) and then preheated in air for 20 h at 1103 K. In order to ensure the complete reaction of the reactant oxides, the mixtures were preheated for a total of 70 h with three intermediate grindings. Then the products were pressed into pellets, sintered in air at 1123 K for 40 h, and finally quenched in air.

X-ray diffraction (XRD) analysis was carried out by a Rigaku-D/max-γA diffractometer using high-intensity Cu Kα radiation. The lattice parameters were determined from the d-values of XRD peaks by a standard least-squares refinement method. Resistivity as a function of temperature for all the samples was measured using a standard four-probe method in a closed-cycle helium cryostat. The TEP of the samples was measured by a differential method [18]. The temperature at the two ends of the measured sample was controlled automatically within a precision of 0.01 K. The emf of the sample was indicated by a Keithley 181 nanovoltmeter with an error of less than 0.2 μV. The EPR experiments were carried out at 100 K by a Bruker (ER-200D-SRC) reflection x-band-type spectrometer. The frequency counter and magnetic field were measured using a frequency counter and a proton NMR gaussmeter, respectively.

3. Experimental results

XRD analysis shows that all the prepared samples remain single phase. Figure 1 shows the lattice parameters for samples $Bi_2Sr_{2-x}CuO_y$ ($x = 0.1$, 0.3, 0.4, 0.5, 0.6 and 0.7) obtained from a least-squares refinement. From figure 1 one can clearly see that, with decreasing Sr content, the a and b axes lengths increase, while the length of c decreases rapidly.

Figure 2 shows the temperature dependence of resistivity for samples $Bi_2Sr_{2-x}CuO_y$. Although all the samples exhibit the ideal single phase, the charge transport properties reflected in figure 2 are noticeably different. The sample with $x = 0.1$ shows metallic behaviour within the measured temperature range and no superconducting transition was detected down to 11 K. The $\rho(T)$–T curve exhibits an obvious downturn below 120 K

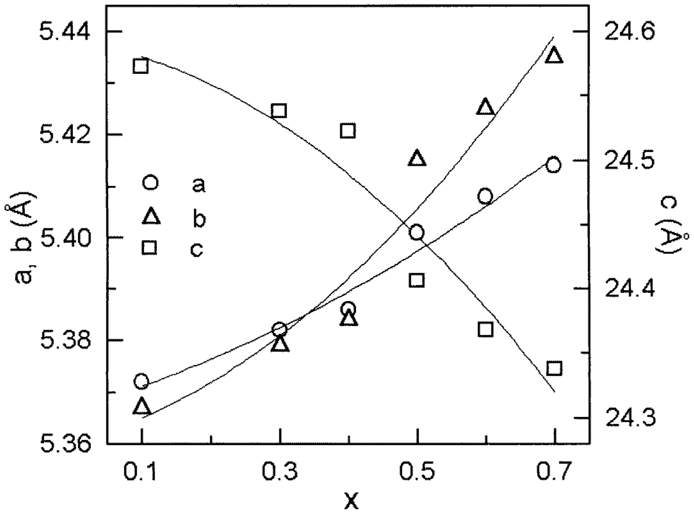

Figure 1. Lattice parameters a, b and c as a function of x in the $Bi_2Sr_{2-x}CuO_y$ system. The lines are a guide for the eye.

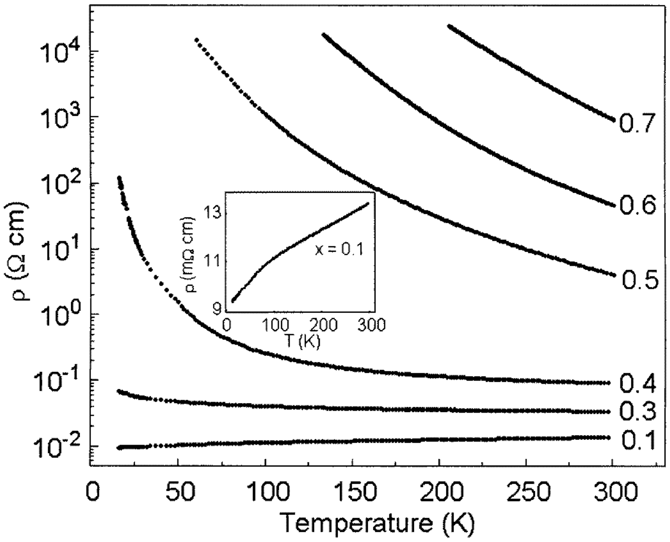

Figure 2. Temperature dependence of resistivity in $Bi_2Sr_{2-x}CuO_y$. The value of x is shown in the figure. The inset shows the $\rho(T)$–T curve of the $x = 0.1$ sample.

(see the inset of figure 2), which may be related to an opening of a spin gap [19]. The samples with $x > 0.1$ all exhibit semiconductivity. Moreover, the resistivity of the samples increases rapidly with decreasing Sr content. Obviously decreasing Sr content causes a metal–insulator (MI) transition in this system.

Figure 3 displays the TEP as a function of temperature for the samples $Bi_2Sr_{2-x}CuO_y$. The $S(T)$ value increases progressively with decreasing Sr content from the sample with

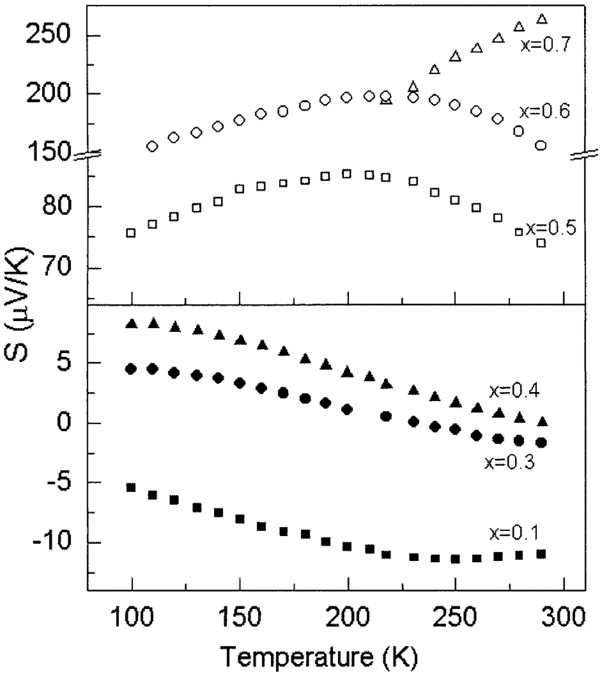

Figure 3. Temperature dependence of thermoelectric power for the $Bi_2Sr_{2-x}CuO_y$ (x = 0.1, 0.3, 0.4, 0.5, 0.6 and 0.7) system.

$x = 0.1$ to the sample with $x = 0.7$. The $x = 0.1$ sample has negative values in the TEP over the whole measured temperature region, and above 250 K a positive slope behaviour in $S(T)$ is observed, while the samples with $x = 0.4$, 0.5, 0.6 and 0.7 show positive values within the temperature range. The $S(T)$–T curve shows a positive slope below room temperature for the sample with $x = 0.7$, and no broad maximum appears below room temperature (unfortunately, we cannot obtain the TEP for the low temperature). For the $x = 0.3$ sample, the $S(T)$ changes sign from negative to positive around 230 K. All the samples, except for $x = 0.1$ and 0.7, show a broad peak in the $S(T)$–T curve, and the temperature (T_m) increases with increasing x. The T_m is 110 K, 120 K, 200 K and 220 K for the samples with $x = 0.3$, 0.4, 0.5 and 0.6 respectively.

The room-temperature resistivity ($\rho(290)$) and TEP ($S(290)$) for the samples $Bi_2Sr_{2-x}CuO_y$ are given in figure 4. With decreasing Sr content, both $\rho(290)$ and $S(290)$ increase rapidly. According to a common opinion about the relation between room-temperature TEP and charge carrier concentration, it can be speculated that the carrier concentration of the $Bi_2Sr_{2-x}CuO_y$ system decreases progressively with the increase of x.

The EPR signals at 100 K for the samples of $Bi_2Sr_{2-x}CuO_y$ are shown in figure 5. The g-factor corresponding to these lines is approximately 2.1, indicating the dominance of Cu^{2+} spins. Ishida and co-workers [20] found that the EPR signal coming from localized Cu^{2+} spins reproduced the intrinsic susceptibility of high-T_c superconducting phase. From figure 5 one can see that the relative intensity of the EPR line increases rapidly with the decrease of Sr content, which indicates that the fraction of localized Cu^{2+} spins increases strikingly with a decrease in Sr content.

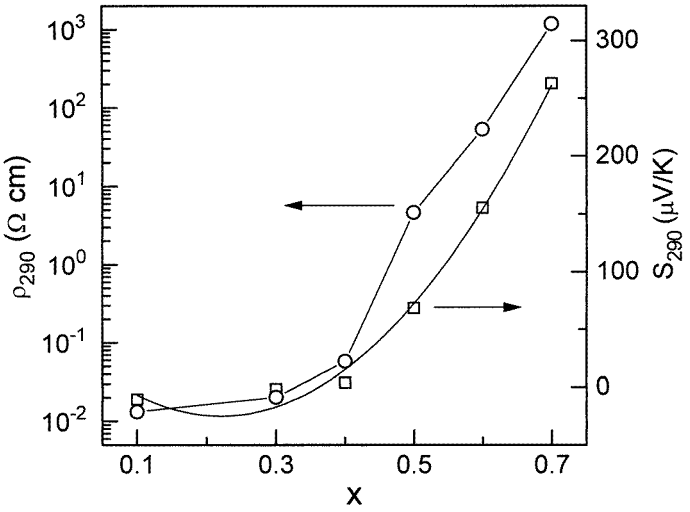

Figure 4. Room-temperature resistivity ($\rho(290)$) and TEP ($S(290)$) as a function of x in the $Bi_2Sr_{2-x}CuO_y$ system.

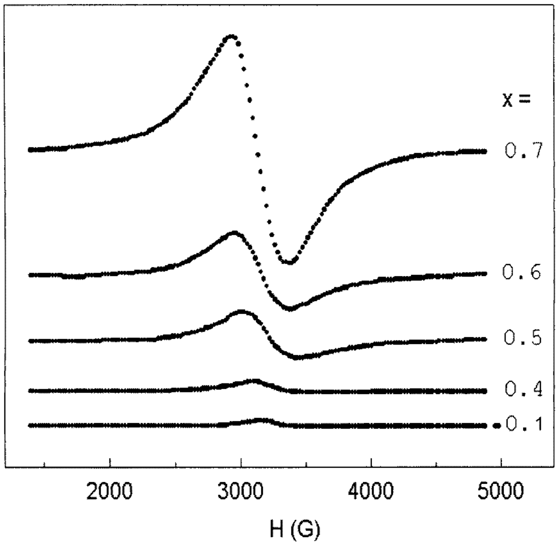

Figure 5. EPR spectra at 100 K of the $Bi_2Sr_{2-x}CuO_y$ ($x = 0.1$, 0.4, 0.5, 0.6 and 0.7) system.

4. Discussion

Previous studies [11, 12] have pointed out that spin scattering plays an important role in determining the normal state resistivity. Our experimental results analysed above are in accordance with this point of view. It has been indicated that the decrease of Sr content in the $Bi_2Sr_{2-x}CuO_y$ system leads to an intensification of incommensurate modulation [21]. The modulation wave causes the deviation of the Cu-atom positions from the *a*–*c* plane. The relative displacements of Bi, Sr and Cu certainly enhance the local structural distortion, and this distortion causes the Cu 3d electrons to change from a partially delocalized to a localized state, which accounts for the MI transition in this system. Accompanied by this MI transition, the fraction of localized Cu^{2+} spins increases markedly. So it can be assumed that the MI transition also results from the increase of the fraction of localized Cu^{2+} spins.

From the analyses of the thermoelectric power and EPR results, one can see that with decreasing Sr content the broad maximum in the $S(T)$–T curve moves to high temperature gradually and the fraction of localized Cu^{2+} spins increases. Furthermore, a great variation in T_m between $x = 0.4$ and $x = 0.5$ samples can be clearly observed, which is consistent with the change of ESR signals of the corresponding samples, see figure 5. These results suggest that the interaction between charge carrier and Cu^{2+} spins may play an important role not only in determining resistivity, but also in influencing TEP. The T_m may be closely related to the spin scattering.

A similar phenomenon about the increase of T_m can be observed in $La_{2-x}Sr_xCuO_y$ [14], $Bi_2Sr_{2-2y}La_2yCuO_{6+x}$ [22], $Nd_{1+z}Ba_{2-y}Cu_3O_{6+x}$ [22] and $(Yb, Ca)(BaSr)_2Cu_3O_z$ $(6.1 \leqslant z \leqslant 6.78)$ [23] systems. Analysing these systems, one can find easily that, accompanied by the shift of the broad peak, the carrier concentration of these systems all decrease. It is known that decreasing carrier concentration will change the hybridization of the Cu 3d and O 2p orbitals, and will lead to the Cu–O bond changing from being covalent to ionic. On the other hand, the change of carrier concentration will increase the fraction of Cu^{2+} spins or change the spin correlation of a system. Is carrier concentration a direct factor influencing the broad maximum in the $S(T)$–T curve? The answer is negative. Recently the transport properties of sp-metal (Ga and Al) and transition-metal (Fe, Co etc) doped La 214 systems have been investigated [17]. It was found that, with constant carrier concentration (or slightly increasing carrier concentration), Fe or Co doping led to the broad maximum moving to high temperature, while Ga or Al doping only modified T_m slightly, similar to the results of the Zn doped La214 system. Figure 6 shows the $S(T)$–T curves of some Fe doped samples. It is known that the Fe^{3+} ion is in a high-spin state $S = 5/2$ with an effective moment of 4.9 μ_B. Since Fe lies in the conducting CuO_2 plane, Fe doping should strongly change the spin correlation and directly influence the conductivity. Analysing these experimental results one can find that what causes the variation of T_m is spin scattering and not carrier concentration.

For high-T_c superconductors a more general formula for the Seebeck coefficient should be used [24],

$$S(T) = -\frac{k}{e}\int \mathrm{d}\varepsilon \frac{(\varepsilon - \varepsilon_F)}{kT}\frac{\sigma(\varepsilon)}{\sigma} \tag{1}$$

where $\sigma(\varepsilon) = f(\varepsilon)[1 - f(\varepsilon)]g(\varepsilon)\mu(\varepsilon)$, $g(\varepsilon)$ is the density of the one-particle state, $\mu(\varepsilon)$ is the particle mobility at an energy ε relative to a band edge, $f(\varepsilon)$ is the Fermi distribution function. ε and ε_F are the energy of electrons and the Fermi energy, respectively. $\sigma = \int \sigma(\varepsilon)\,\mathrm{d}\varepsilon$ is the total conductivity. Equation (1) is applicable where there is no singularity or abrupt change in the density of states near ε_F. Since Equation (1) does not include the correction term due to the interaction of the charge carrier with another medium, we must add a term $D(\varepsilon, T)$; thus we have

$$S(T) = -\frac{k}{e}\int \mathrm{d}\varepsilon \frac{(\varepsilon - \varepsilon_F + D(\varepsilon, T))}{kT}\frac{\sigma(\varepsilon)}{\sigma}. \tag{2}$$

In the systems discussed above, the interaction between the spins of Cu^{2+} or Fe^{3+} and the charge carriers is included in the term $D(\varepsilon, T)$. This interaction will change the shape of the ε against k curves near ε_F as a function of temperature so as to give a hump in the S against T curve.

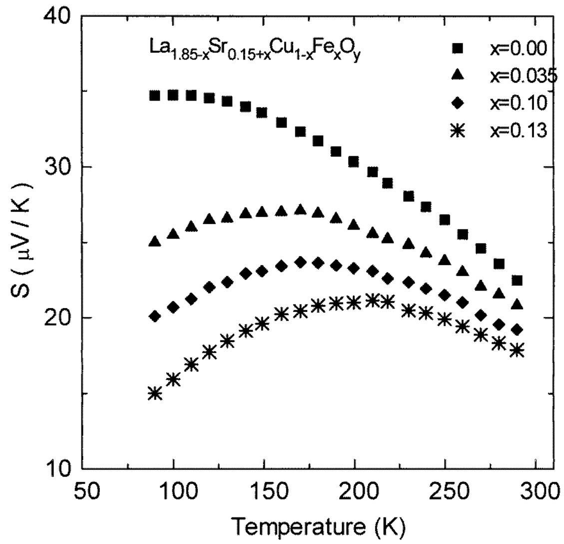

Figure 6. Temperature dependence of TEP for the $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_y$ ($x = 0$, 0.035, 0.1, 0.13) system.

Besides magnetic scattering, decreasing carrier concentration or Fe^{3+} doping modifies the hybridization state of Cu 3d–O 2p and changes the electronic structure near the Fermi level, thus influencing the ε against k dispersion curve.

In the above discussion we only suggest a relation between T_m and the localized spin scattering, while the origin of the broad peak cannot be well clarified by these experimental results. Yu *et al* [25] and Zhou and Goodenough [13] have investigated the TEP of the $La_{2-x}Sr_xCuO_4$ system under a magnetic field and pointed out that the magnetic field only influences the TEP slightly. This seems to rule out the magnetic mechanism for the broad maximum in the $S(T)$–T curve. However, in the systems they studied, the structural distortion is weak and the fraction of localized spins is small, so the spin scattering may have a weak influence on the TEP. For $Bi_2Sr_{2-x}CuO_6$ and $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_y$ systems, the localized spin scattering is so strong that it demonstrates a marked influence on the TEP.

It should be noted that in figure 3 we observe a positive slope behaviour in $S(T)$ for the $x = 0.1$ sample. It is known that the TEP shows a negative slope for most HTSCs, which is characteristic of the CuO_2 planes. The positive slope in $S(T)$ data was observed only in Y-based superconductors [26, 27], which is believed to arise from the contribution of the oxygenated Cu–O chains [26, 15]. It is obvious that the positive slope behaviour in $S(T)$ in our $x = 0.1$ sample should similarly be related to the transport in non-CuO_2 planes. For Bi-based superconductors, band structure calculations show that the Bi_2O_2 layers are metallic and play a similar role to the Cu–O chains. Our data seem to support the results of the band structure calculations. The Bi_2O_2 layers for the heavily overdoped Bi2201 phase are metallic and make a contribution to the TEP, while for the Bi2201 system with low carrier concentration the contribution of Bi_2O_2 layers to the TEP can be neglected.

In conclusion, the transport properties and ESR signal of the Bi2201 system with Sr deficiency have been investigated. The shift of the broad maximum in the $S(T)$–T curve is consistent with the variation of the EPR signals. A close relation between T_m and localized spin scattering is suggested.

Acknowledgments

This work was supported by the National Foundation for Outstanding Young Scientists, China Postdoctoral Science Foundation, the National Center for Research and Development on Superconductivity, the National Education Ministry Foundation for Outstanding Young Teachers and the President Foundation of Chinese Academia Sinica.

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