Hall effect in bulk $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$

G. Ilonca,* M. Mehbod, A. Lanckbeen, and R. Deltour
Physique des Solides, Code Postal 233, Université Libre de Bruxelles, B-1050 Bruxelles, Belgium
(Received 27 July 1992; revised manuscript received 9 December 1992)

The Hall effect and the electrical resistivity have been measured in bulk samples having the general composition $YBa_2(Cu_{1-x}Z_x)_3O_{7-\delta}$ for $0<x<0.06$, in the temperature range 20–300 K, and for magnetic fields up to 5 T. The linear temperature dependence of the resistivity was observed for all the doped samples between 100 and 300 K. The temperature dependence of the carrier concentration and the T^2 dependence of the inverse Hall mobility $[\mu_H^{-1}(T^2)]$ show an anomaly at a temperature around 230 K. These results are discussed in the framework of existing theories.

INTRODUCTION

Atomic substitutions offer an important approach to understanding the superconducting properties of the oxide superconductors. In samples of $YBa_2(Cu_{1-x}M_x)_3O_y$ (where M = Fe, Ni, Zn, Co, and Al) the introduction of these dopants causes the degradation of superconductivity. T_c decreases almost linearly with increasing x and the transition width increases slightly with increasing x, probably due to slight inhomogeneities in the dopant distribution.

To date, there have been many investigations of the solid solution series $YBa_2(Cu_{1-x}Zn_x)_3O_y$.[1-10] Among the interesting properties observed in the cuprate superconductors, mention should be made of the normal-state transport properties. In particular, the temperature dependence of the Hall coefficient, $R_H(T)$ in the normal state of the cuprate superconductors, has been one of the most interesting anomalies.[11-23]

Tamegai and Iye[14] for pure and zinc-doped $YBa_2Cu_3O_{7-\delta}$, and Suzuki[15] for $La_{2-x}Sr_xCuO_4$, where x is within the superconducting range, found that R_H is strongly temperature dependent, monotonically decreasing with temperature. Doping studies by Clayhold *et al.*,[11] Chien and co-workers,[12] and Ong[13] showed that when superconductivity is destroyed in Y-Ba-Cu-O or La-Sr-Cu-O doped with Co and Ni, the slope dn_H/dT shows a corresponding decrease. Kubo *et al.*[16] reported that in the superconducting cuprates, oxygen annealing has a pronounced effect on T_c and R_H. In the case of the Hall data, fluctuation effects in $YBa_2Cu_3O_{7-\delta}$ above T_c give important deviations from the $1/T$ normal-state dependence of the Hall coefficient R_H and there is a similar behavior for R_H in the other cuprates.[12-18] In the literature, there are several theoretical models for these fluctuation effects which, often, involve several parameters and give very good fits of the same data, if some parameters are adjusted.

More recently, Dorsey and Fisher[24] and Ferrell[25] proposed a model to explain, respectively, the Hall effect near the vortex-glass transition in high-T_c superconductors and the Hall voltage sign reversal in thin superconducting films.

In Y-Ba-Cu-O, approximate descriptions of the temperature dependence of the Hall coefficient (R_H) and of the resistivity (ρ) are often given by the relations:

$$1/R_H = aT + b \quad (a,b>0)\ , \qquad (1)$$

$$\rho = \rho(0) + cT \quad (c>0)\ . \qquad (2)$$

Because the Hall data on Y-Ba-Cu-O are rather sparse, Eq. (1) has not been thoroughly tested. Moreover, simultaneous measurements of ρ and R_H are often not available. In the present work, we were careful to simultaneously measure these two independent quantities, the electrical resistivity and the Hall constant, on the same samples of bulk $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$. Zinc, which does not have a magnetic moment, causes a more rapid decrease of T_c than Ni, Co, and Fe. The location of the Zn atoms and their effect on the dynamics of the crystal lattice are, however, still somewhat contradictory; some experimental results indicate that the Cu(1) sites are filled preferentially, while other results show that the Cu(2) sites are preferentially occupied.

EXPERIMENT

A series of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ compounds were prepared by the following standard solid-state powder processing technique. Powders of $BaCO_3$ and the oxides Y_2O_3, CuO, and ZnO, were stirred together in water, in stoichiometric quantities, and in polyethylene jars with ZrO_2 beads for 2 h. The powder was then dried and pressed at 300 bars in order to obtain pellets which were calcined at 905 °C during 160 h under O_2 flow (heating rate 3° C/min and cooling rate 0.5° C/min). The pellets were then ground in SiO_2 jars with SiO_2 balls. The powders were sieved (25 μm mesh), pressed into 4-cm-diam pellets and fired at 930° C under O_2 flow for 12 h (heating rate 3° C/min and cooling rate 0.5° C/min). This process was repeated twice, and the pellets were then sintered at 950° C under O_2 flow (heating rate 3° C/min and cooling rate 0.5° C/min) for 12 h and oxygenated at 500° C during 72 h.

Careful examinations of x-ray diffraction (XRD), thermogravimetric analysis (TGA), energy dispersion x-ray analysis (EDAX), scanning electron microscopy (SEM),and optical microscopy were performed to control the grain distribution and the contamination of the samples. The oxygen content was determined by an odometric titration method. Single-phase material was obtained with impurity phase concentration lower than 1%, and homogeneity of the zinc distribution in the grain was checked at the resolution level of the EDAX analysis.

In order to perform precise Hall measurements, it was essential to minimize the misalignment of the Hall arms and also to achieve low contact resistances. For this purpose, a sample was cut from a pellet into a five terminal Hall-bar shape. Five pads were painted with silver-epoxy adhesive onto the Hall-bar shape and successively tempered at 400° C in air for 20 min. Finally gold wires were attached with silver paste. The contact resistance depended on the bulk resistivity of the sample, but was typically less than 0.2 Ω for surfaces smaller than 10^{-4} cm^2.

We have measured the resistivity and the Hall voltage (ac current) with a lock-in technique (Princeton Applied Research, Model 5210) in magnetic field sup to 5 T, in the temperature range 20–300 K. For dc measurements, we used a Keithley 220 programmable current source, a Keithley 182 sensitive digital voltmeter and a Keithley 181 nanovoltmeter. The current intensity which passed through the sample was between 1 and 10 mA. The standard procedure of taking data for both polarities of the current and the magnetic field, to cancel out thermal emf and resistive components was followed. The temperature dependence of the resistivity in zero field was measured simultaneously as well as in a separate run.

RESULTS AND DISCUSSION

The Hall coefficient and electrical resistivity measurements were made as a function of the temperature for bulk $YBa_2(Cu_{1-x}Zn_x)_3O_y$, with $x=0$ and $y=6.91, x=0.02$, and $y=6.91$, $x=0.039$ and $y=6.90$, $x=0.053$ and $y=6.89$, and $x=0.058$ and $y=6.89$ and are similar to those of Chien and co-workers[12] for Zn-doped Y-Ba-Cu-O single crystals. They show an increase in the Hall coefficient and a decrease in the transition temperature as a function of x. We also observed an anomaly in the temperature dependence of the Hall coefficient in bulk material at high temperature. The values of the Hall coefficient do not change appreciably with x, but increase monotonically from room temperature down to just above T_c. From the Hall coefficient value R_H, we calculated $n_H V$, the Hall number, defined as $V/R_H e$ (where V is the unit-cell volume, 173.2 Å^3). Figure 1 shows the temperature dependence of $n_H V$ for the pure and the Zn-doped samples.

As for the undoped $YBa_2Cu_3O_{6.9}$ sample, for the doped sample with $x=0-0.02$, $n_H V$ shows a linear temperature dependence between 100 and 300 K with a change in the slope at 230–240 K. For the concentration range $x=0.039-0.058$, it was found that the temperature dependence is less linear near T_c, in partial agreement with theoretical results presented by Nagaosa and Lee[26] and Ioffe, Kalmeyer, and Wiegmann.[27] The same behavior can be seen in data reported by Chien and co-workers.[12]

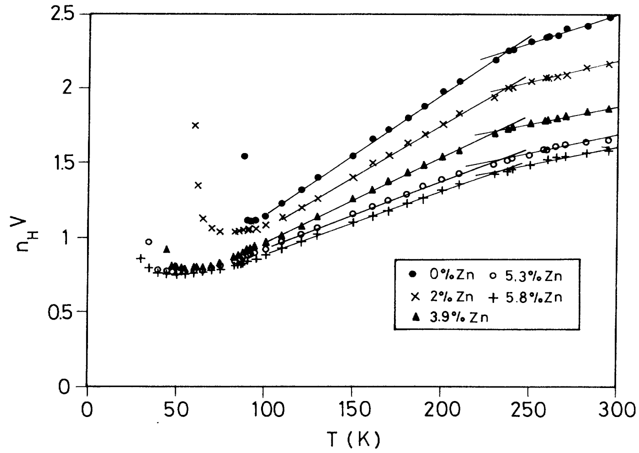

FIG. 1. Temperature dependence of the Hall number $n_H V$ (defined as $V/R_H e$, where V=unit cell volume) in $YBa_2(Cu_{1-x}Zn_x)_3O_y$. The lines are a guide for the eyes.

Figure 2 shows the variation of the Hall number with x at four temperatures ($T=100$, 150, 200, and 300 K). The lowest values correspond to the linear extrapolation of the data to $T=0$ K. For the doped samples, the negative slope $d(n_H V)/dx$ decreases with temperature from 0.17 for $T=300$ K to 0.04 for $T=100$ K.

The slope, $d(n_H V)/dT$, of the linear dependence of $n_H V$ on T, as discussed previously, is given in the inset of Fig. 2. It decreases with x from 0.0084 hole/K unit cell for $x=0$ to 0.0043 hole/K per unit cell for $x=0.058$.

Figure 3 shows the temperature dependence of the electrical resistivity on the Zn content. With increasing dopant concentration, the electrical resistivity curves are shifted upwards, in agreement with the results reported

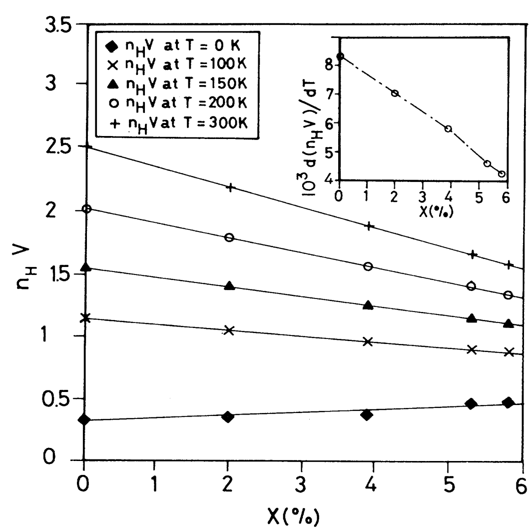

FIG. 2. The Hall number $n_H V$ vs x (%) in bulk $YBa_2(Cu_{1-x}Zn_x)_3O_y$, at $T=0$, 100, 150, 200, and 300 K. In the inset, the slope $d(n_H V)/dT$ vs the zinc concentration. The lines are a guide for the eyes.

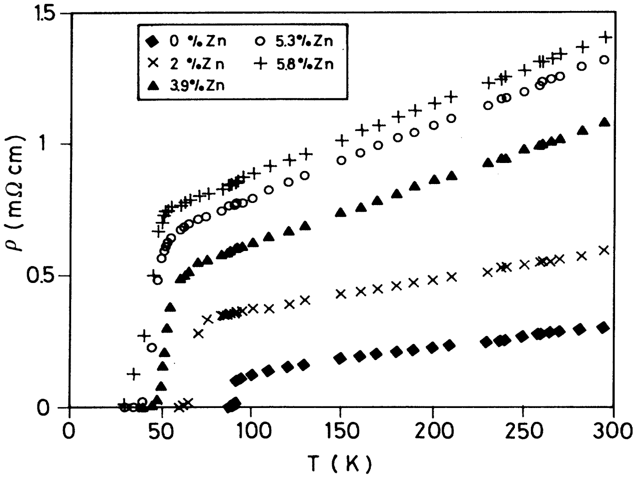

FIG. 3. Temperature dependence of the electrical resistivity in bulk $YBa_2(Cu_{1-x}Zn_x)_3O_y$.

by Chien and co-workers[12] and Ong[13] for single crystals of the same system, and by Mehbod *et al.* for bulk samples.[1]

The slope $d\rho/dT$ is affected by impurity scattering as shown in Fig. 4, where we also plotted the "residual resistivity" versus the x content. This last quantity was obtained by the extrapolation of the electrical resistivity curves at $T=0$ K. The slope $d\rho/dT$ increases from 0.96 ($\mu\Omega$ cm/K) to 2.73 ($\mu\Omega$ cm/K). As in all our samples, the oxygen concentration is almost the same, $\delta \sim 0.1$, so these effects can be attributed, in part, to a decrease in carrier concentration caused by the zinc. [It is known that a lack of oxygen also increases the residual resistivity and the slope $d\rho/dT$ (Ref. 20)].

The superconducting transition temperature T_c together with its width ΔT_c, taken from the resistivity data, are plotted in the inset of Fig. 4. The bars indicate the width of the transition defined by the 10% and the 90% values of the resistivity. Over the measured concentration range, T_c decreased sharply from 91 to 46 K, in agreement with previous work.[1] The reduction of T_c by the Zn impurities seems to be related to the decrease in the "Hall slope" $d(n_H V)/dT$ and the increase in the slope $d\rho/dT$. A similar correlation as been observed in $YBa_2(Cu_{3-x}M_x)O_{7-\delta}$ (where $M=$Ni, Co),[11] in $La_{2-x}Sr_xCuO_4$, when the Sr content is varied,[15] and in $Tl_2Ba_2CaCu_2O_{8-\delta}$ when the oxygen content is varied.[21]

From the Hall constant and the electrical resistivity data (measured during the same experimental run), the Hall mobility was calculated (using the relation $\mu_H=R_H/\rho$) for the different Zn-doped samples and is given in the inset of Fig. 5. The Hall mobility decreases with the addition of Zn at any fixed temperature in agreement with Ghorayeb *et al.*[10] and with an analysis of the data from Chien and co-workers.[12]

Figure 5 shows the dependence of the inverse Hall mobility (μ_H^{-1}) on the square of the temperature. For all the samples, the data fall on straight lines in the temperature range from approximately 100 to 230 K, at which temperature the slope of the curves changes. (The values of the slope are slightly dependent on the Zn content.) This result may indicate a change in the scattering mechanism of the carriers at about 230–240 K. This deviation from the T^2 dependence can also be seen in the Zn-doped YBaCuO single-crystal data,[12] which were interpreted in the frame of the Anderson theory.[28] More recently, Mott[29] suggested that, in zinc-doped Y-Ba-Cu-O, the current carriers are fermions forming a degenerate gas (a Fermi liquid), with an effective mass depending on the phonon frequency.

The experimental results on the Hall effect in Zn-doped Y-Ba-Cu-O are also very difficult to interpret in the framework of the Bloch-Boltzmann theories, which try to explain the temperature dependence of $n_H V$ using cancellation effects of multiple bands. Furthermore, a compensational mechanism[23] may be suggested but would as-

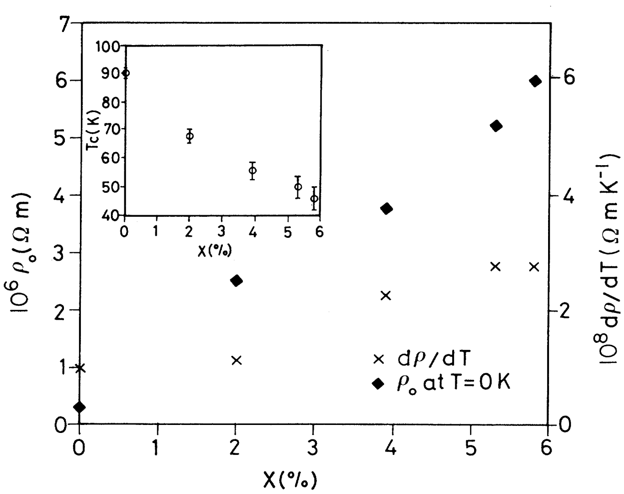

FIG. 4. The residual resistivity ρ_0, the slope $d\rho/dT$ and, in the inset, the superconducting transition temperature T_c, vs the zinc concentration x (%) in bulk $YBa_2(Cu_{1-x}Zn_x)_3O_y$.

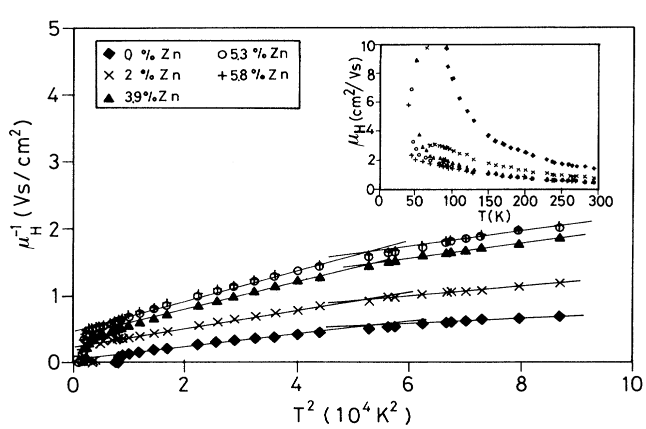

FIG. 5. The square temperature dependence of the inverse Hall mobility [$\mu_H^{-1}(T^2)$]. (In the inset is the temperature dependence of the Hall mobility) in bulk $YBa_2(Cu_{1-x}Zn_x)_3O_y$. The lines are a guide for the eyes.

sume a rather symmetric band structure. If, however, we suppose that, in $YBa_2Cu_3O_{3-\delta}$, only one band contributes to the hole transport, the observed anomalous Hall effect cannot be explained using only conventional Fermi-liquid theory. At present, there is no theoretical model which can explain the transport mechanism in Zn-doped Y-Ba-Cu-O over the entire temperature range.

CONCLUSIONS

We report an investigation of Zn substitution effects in bulk $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$, prepared by a standard solid-state reaction, for $0<x<0.06$. The fact that the Zn doping causes the same anomalies to occur in (1 2 3) and (2 1 4) systems, in the Hall number and in the electrical resistivity, suggests that Zn goes preferentially in the planes. The linear temperature dependence of the resistivity was observed for all doped samples between 100 and 300 K. The temperature dependence of the carrier concentration shows the following two anomalies.

Below room temperature, the carrier concentration decreases linearly with the temperature down to $T \sim 230-240$ K, where there is a change in the slope of $n_H(T)$ and a further linear decrease towards a minimum value at a temperature $T > T_c$. This variation could be caused by a subtle change in the "ionic lattice" rather than a modification of the electronic structure. The T^2 dependence of μ_H^{-1}, with a change in the slope around 230–240 K, observed over the entire doping range, is strongly correlated with the T dependence of the carrier concentration.

Note added in proof. We recently became aware of the work of Kremer and co-workers showing, by susceptibility measurements, the existence of an electronic phase separation in the CuO_2 planes, starting around $T=230$ K, in the La-cuprates.[30] The anomalies around 230 K, described here, could be an indication for such a phase separation in the Y-Ba-Cu-O system.

ACKNOWLEDGMENTS

This research was supported by the Belgian National Program on high temperature superconductivity under Grant No. SU 02/09.

---

*Permanent address: University of Cluj-Napoca, Faculty of Physics, 3400 Cluj-Napoca, Romania.

[1]M. Mehbod, W. Biberacher, A. G. M. Jansen, P. Wyder, R. Deltour, and P. H. Duvigneaud, Phys. Rev. B **38**, 1181 (1988).
[2]G. Xiao, M. Z. Cieplak, D. Musser, A. Gavrin, F. H. Streitz, C. L. Chien, J. J. Rhyne, and J. A. Gotaas, Nature **332**, 238 (1988).
[3]M. F. Yan, W. W. Rhodes, and P. K. Gallagher, J. Appl. Phys. **63**, 821 (1988).
[4]J. M. Tarascon, P. Barboux, P. E. Miceli, L. H. Greene, G. W. Hull, M. Eibschut, and S. A. Sunshine, Phys. Rev. B **37**, 7458 (1988).
[5]T. J. Kistenmacher, Phys. Rev. B **38**, 8862 (1988).
[6]M. W. Shafer, T. Penney, B. L. Olson, R. L. Greene, and R. H. Koch, Phys. Rev. B **39**, 2914 (1989).
[7]K. Westerholt, H. J. Wüller, H. Bach, and P. Stauche, Phys. Rev. B **39**, 11 680 (1989).
[8]L. Szunyogh, U. König, P. Weingberger, P. Podloucky, and P. Herzig, Phys. Rev. B **42**, 432 (1990).
[9]H. Zhenhui, Z. Han, S. Shifang, C. Zuyao, Z. Qirui, and X. Jiansheng, Solid State Commun. **70**, 951 (1989).
[10]A. M. Ghorayeb, M. Rateau, H. Pankowska, R. Suryanarayanan, and O. Gorochov, J. Less-Common. Met. **151**, 221 (1989).
[11]J. Clayhold, N. P. Ong, Z. Z. Wang, J. M. Tarascon, and P. Barboux, Phys. Rev. B **39**, 7324 (1989).
[12]T. R. Chien, Z. Z. Wang, and N. P. Ong, Phys. Rev. Lett. **67**, 2088 (1991); T. R. Chien, D. A. Brawner, Z. Z. Wang, and N. P. Ong, Phys. Rev. B **43**, 6242 (1991).
[13]N. P. Ong, in *Proceedings of the Toshiba International School of Superconductivity (ITS²)*, Kyoto, Japan, 1991, edited by S. Mackawa and M. Sato (Springer, Berlin, 1991), p. 247.
[14]T. Tamegai and Y. Iye, Phys. Rev. B **44**, 10 167 (1991).
[15]M. Suzuki, Phys. Rev. B **39**, 2312 (1989).
[16]Y. Kubo, Y. Shimakwa, T. Manako, and H. Igarashi, in *Advances in Superconductivity II,* edited by T. Ishiguro and K. Kajimura (Springer, Tokyo, 1990), p. 505; Physica C **197**, 378 (1992).
[17]Y. Iye, S. Nakamura, and T. Tamegai, Physica C **159**, 616 (1989).
[18]J. P. Rice, J. Giapintzakis, D. M. Zinzberg, and J. M. Mochel, Phys. Rev. B **44**, 10 158 (1991).
[19]M. Affronte, D. Pavuna, O. Martin, F. Licci, T. Besagni, and S. Cattami, Solid State Commun. **70**, 951 (1989).
[20]J. R. Cooper, S. D. Obertelli, A. Carrington, and J. W. Loram, Phys. Rev. B **44**, 12 086 (1991).
[21]Y. Kubo and T. Manako, Physica C **197**, 375 (1992).
[22]O. Laborde, M. Potel, P. Gougeon, J. Padiou, J. C. Levet, and H. Noel, Phys. Lett. **147**, 525 (1990).
[23]A. Davidson, P. Santhanam, A. Palevski, and M. J. Brady, Phys. Rev. B **38**, 2828 (1988).
[24]A. T. Dorsey and M. P. A. Fisher, Phys. Rev. Lett. **68**, 694 (1992).
[25]R. A. Ferrell, Phys. Rev. Lett. **68**, 2524 (1992).
[26]N. Nagaosa and P. Lee, Phys. Rev. B **43**, 1233 (1991).
[27]L. B. Ioffe, V. Kalmeyer, and P. B. Wiegmann, Phys. Rev. B **43**, 1219 (1991).
[28]P. W. Anderson, Physica C **185-189**, 11 (1991).
[29]N. F. Mott, Physica C **196**, 369 (1992).
[30]R. K. Kremer, E. Sigmund, V. Hizhnyakov, F. Hentsch, A. Simon, K. A. Müller, and M. Mehring, Z. Phys. B **86**, 319 (1992); R. K. Kremer, V. Hizhnyakov, E. Sigmund, A. Simon, and K. A. Müller, Z. Phys. B (to be published).