



EFFECTS OF Cu SUBSTITUTION BY Zn ON TRANSPORT PROPERTIES OF $Y_1Ba_2Cu_3O_{7-\delta}$

M. Affronte, D. Pavuna, O. Martin,
Department de Physique, I.M.O., Ecole Polytechnique Fédérale,
CH - 1015 Lausanne, Switzerland,

F. Licci, T. Besagni, S. Cattani
Istituto MASPEC, C.N.R., I-43100, Parma, Italy

(Received 20 February 1989 by P. Bulet)

We report the temperature dependence of resistivity and the Hall coefficient R_H of a series of $Y_1Ba_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ ceramics with x up to 0.075. In all our samples we have observed linear temperature dependence of $(eR_H)^{-1}$. The slope, $d(eR_H)^{-1}/dT$, decreases with the increase in Zn concentration, while the intercept $(eR_H)^{-1}$ at $T=0$ increases. These changes, together with a decrease of $\alpha=(\partial\rho/\partial T)\rho^{-1}$ due also to the Cu substitution, provokes the flattening in the temperature dependence of the Hall mobility. The analysis of the data shows that one cannot consider Zn as a simple charge donor for $Y_1Ba_2Cu_3O_{7-\delta}$, but more complex change in the mechanism of transport seems to be introduced by the Cu substitution.

The reduction of T_c due to the Cu substitution by Zn in $Y_1Ba_2Cu_3O_{7-\delta}$ ("YBCO") ceramics was reported by several groups [1-3]. The origin of this effect is still controversial. Unlike other substitutions, Zn seems to introduce very few changes in YBCO superconducting phase. In fact we know that the crystal structure remains orthorhombic for Cu substitution by Zn up to ≈ 11 at.% [2], with lattice parameters very close to those of pure YBCO. Moreover, the oxygen content is almost unaffected [4,5] by the presence of Zn. Zn has valence 2+, the most likely valence of Cu in YBCO, and it is a non-magnetic impurity. On the other hand an important change introduced by Zn is the complete filling of the 3d-orbitals of Zn^{+2} , unlike in Cu^{+2} and Cu^{+3} . Therefore the substitution of Cu by Zn seems to be an ideal tool to study the role of 3d-orbitals of Cu in YBCO.

In this Communication we present a study of the temperature dependence of resistivity and Hall coefficient in $Y_1Ba_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ ceramics with $x = 0, 0.025, 0.05$ and 0.075 . The aim of this work is to elucidate main changes in the normal state introduced by the Cu substitution that provoke the reduction of T_c .

The samples were prepared by high temperature solid state reaction. Stoichiometric amounts of Y_2O_3 , $BaCO_3$, CuO , ZnO were mixed under ethanol for a few hours in agata container by means of a ball-mill, dried at $\approx 70^\circ C$ and reacted at $920^\circ C$ in flowing oxygen for 50 hours, with two intermediate

mixing and grinding steps. Powders were then pressed at 2500 Kg/cm^2 and sintered at $950^\circ C$, in flowing oxygen for 24 hours. Final cooling was done in oxygen, at spontaneous furnace cooling rate. X-ray diffractograms, taken with a Siemens D500 powder diffractometer and $Co K\alpha$ radiation, indicate that all the samples are orthorhombic with lattice parameters, reported in Table 1, faintly dependent on x. In Table 1 we also report the density of all our samples.

Table 1 : Lattice parameters and density of our samples :

Zn (x)	a (Å) ± 0.002	b (Å) ± 0.002	c (Å) ± 0.006	density g/cm^3
0	3.820	3.889	11.672	5.3
0.025	3.820	3.890	11.673	5.2
0.05	3.820	3.885	11.671	5.05
0.075	3.826	3.893	11.689	4.95

Secondary phases were not detectable. However, in agreement with Mehbod et al. [4], we cannot exclude that for the highest concentrations of Zn the Cu substitution is incomplete and small amount of secondary phases is present, which we estimate to be within the sensitivity limits of the x-ray measurements (a few weight percents). Our preparation is similar to that

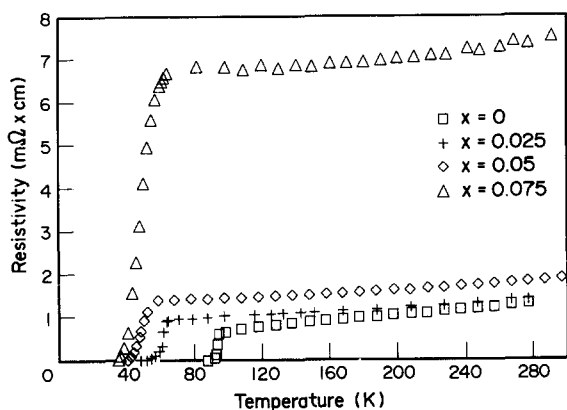


Fig.1 : Temperature dependence of resistivity of $Y_1Ba_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$.

used by Xiao et al. [6] and Mehdod et al. [4]. Using neutron diffraction measurements, they have independently found that Zn replaces Cu preferentially in the planes. However, a different result has been found by Kitijani et al. [7] who found that the substitution occurs mainly on the chains.

We measured resistivity and Hall effect simultaneously on samples of typical size of $8 \times 2 \times 0.3 \text{ mm}^3$. For resistivity we used the 4 probe a.c. method with currents of 2-5 mA peak to peak. Contacts were made by attaching Ag wires with silver paint on Ag metallized samples [8]. Typical resistance for each contact was 0.2-1 Ohm. For Hall effect measurements, we used the 5 probe method with a.c. currents of 30, 50 and 70 mA peak to peak and magnetic fields up to 5 Tesla. Hall voltage always showed a linear dependence on current and magnetic field.

Fig.1 shows the temperature dependence of resistivity of $Y_1Ba_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ with $x = 0, 0.025, 0.05$ and 0.075 . In Table 2 we resume the results of transport measurements made on these samples. The shape of the resistance transitions indicates good homogeneity of the samples and the dependence of T_c (midpoint) and $\rho(280K)$ on Zn concentration is in a good agreement with data reported in the literature

[2]. The reduction of T_c measured on our samples indirectly confirms the inclusion of Zn in the YBCO structure. We observe that the effect of Cu substitution on resistivity is to increase $\rho(280K)$ and to flatten the ρ vs T curve. This is evident from Fig.1 and also from data of the temperature coefficient of resistivity $\alpha = (\partial\rho/\partial T)\rho^{-1}$ reported in Table 2. We also present in Table 2 values of the effective number of carriers $(eR_H)^{-1}$ measured at 120K and 280K. At 120K, $(eR_H)^{-1}$ increases with the Zn addition in agreement with what has been found by Shafer et al. [5] and Zhenhui et al. [9]. This result is quite surprising because, a priori, we would not expect Zn^{+2} to introduce some holes when it replaces bivalent Cu. On the other hand, we observe that values of $(eR_H)^{-1}$ at 280K indicate an inverse situation, i.e. Zn reduces $(eR_H)^{-1}$. Because values of $(eR_H)^{-1}$ at only one temperature do not give sufficient information about the mechanism of transport, we have studied the temperature dependence of $(eR_H)^{-1}$ and of the Hall mobility $\mu_H = R_H/\rho$, which we estimated from combined resistivity and Hall coefficient. Fig.2 shows the temperature dependence of $(eR_H)^{-1}$ for samples of $Y_1Ba_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ with $x = 0, 0.025, 0.05$ and 0.075 . Linear temperature dependence of $(eR_H)^{-1}$, observed also in the ab planes of YBCO single crystal [10], has been found in all the samples. The effect of Zn is to change progressively the parameters of the straight line, i.e. the slope $d(eR_H)^{-1}/dT$ and the intercept $(eR_H)^{-1}(T=0)$. The values of these parameters, obtained by fitting the temperature dependence of $(eR_H)^{-1}$ in the range 100K - 300K, are reported in Table 2. The change is towards more temperature independent $(eR_H)^{-1}$, which is a typical characteristic of an ordinary non-superconducting metal. An immediate consequence of the flattening of ρ vs T and $(eR_H)^{-1}$ vs T curves due to Zn is clearly visible in the temperature dependence of the Hall mobilities μ_H as reported in Fig.3.

Table 2

Zn(x)	$\rho(280K)$ mΩxcm	$\alpha(280K)$ $\times 10^{-3} K^{-1}$	$(eR_H)^{-1} \times 10^{21}/cm^3$ (280K)	$(eR_H)^{-1} \times 10^{21}/cm^3$ (120K)	T_c (K)	$(eR_H)^{-1}(T=0)$ $\times 10^{21}/cm^3$	$\frac{\partial(eR_H)^{-1}}{\partial T}$ $\times 10^{19}/cm^3K$
0	1.33	3.4	8.31	3.43	91	-0.024	3.0
0.025	1.43	2.3	7.31	4.30	59	2.1	1.9
0.05	1.88	1.8	7.05	4.63	49	3.0	1.5
0.075	7.37	0.9	5.94	4.19	46	2.7	1.2

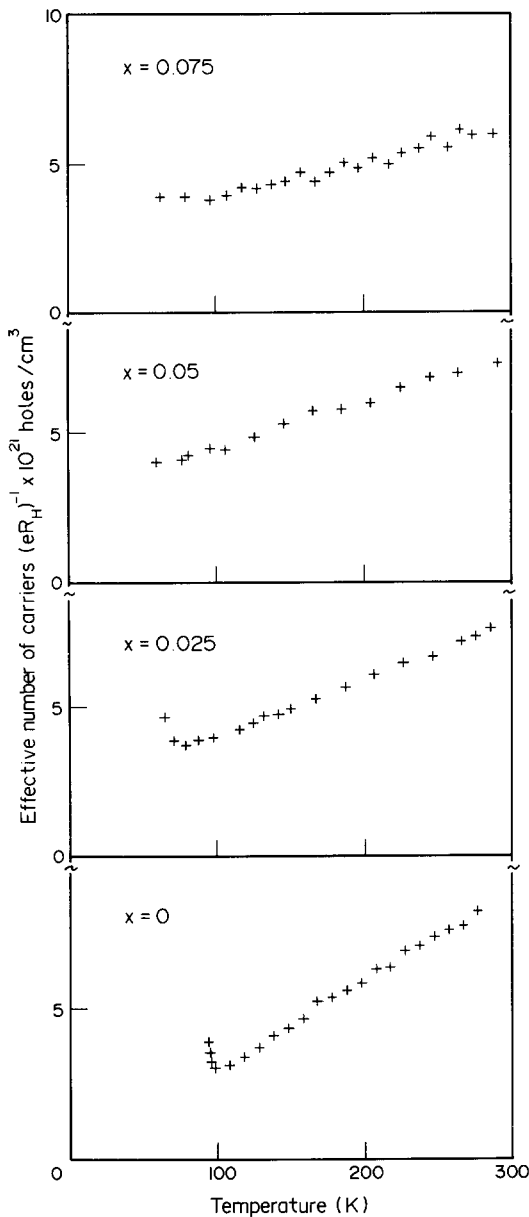


Fig.2 : Temperature dependence of the effective number of carriers $(eR_H)^{-1}$ of $YBa_2(Cu_{1-x}Zn_x)O_{7-\delta}$.

From the aforementioned facts we deduce that Zn cannot be regarded as a simple charge donor for a system with only one type of carriers because this would imply a temperature independent change in $(eR_H)^{-1}$. A more consistent physical picture can be imagined if we consider for YBCO two bands with a delicate

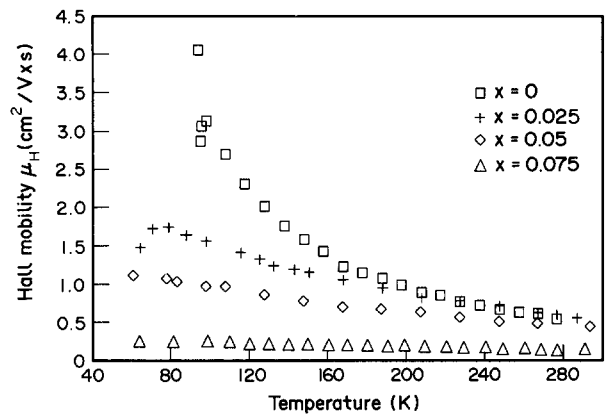


Fig.3 : Temperature dependence of Hall mobility of $YBa_2(Cu_{1-x}Zn_x)O_{7-\delta}$.

compensation between holes and electrons. We expect the Hall coefficient to be very sensitive to such compensation [10-12]. We can suppose first that the Cu substitution by Zn fills or empties a rigid band structure. This provokes a change in $N_e(T)/N_h(T)$ and also a non negligible variation in $\mu_e(T)/\mu_h(T)$. As a consequence the delicate compensation is altered when Zn is introduced in YBCO. However, for this picture of compensated carriers, rigid electronic band model should not be a realistic framework to analyse the effect of Zn doping. In fact, we expect that, if Zn replaces Cu in the planes, at least partially [4,6,7], the substitution of 3d-orbitals of Cu with 4s ones of Zn introduces a new type of electronic states. In particular we would suggest in a microscopic picture, that when the Zn_x replaces Cu it suppresses the "exotic" $[Cu-O]$ holes and creates another type of more "ordinary" holes. This could also be the origin of the lowering of T_c in $YBa_2(Cu_{1-x}Zn_x)O_{7-\delta}$.

In conclusion we have presented a study of temperature dependence of the resistivity and the Hall coefficient in a series of $YBa_2(Cu_{1-x}Zn_x)O_{7-\delta}$ ceramics with x up to 0.075. We have observed a simultaneous flattening of ρ vs T and $(eR_H)^{-1}$ vs T curves.

Our data indicate that Zn does not play only a role of charge dopant in YBCO, but it alters the mechanism of transport in YBCO in a complex way.

ACKNOWLEDGEMENTS : This work was in part supported by General Direction of PTT Bern, Switzerland, which we gratefully acknowledge. We acknowledge stimulating discussions with Professors F.K. Reinhart (E.P.F.L.) and Ø. Fischer (University of Geneva) and Drs. M. Decroux, B. Dwir and M.G. Doss. We also thank A. Morenza for his experimental help.

REFERENCES

- [1] Chan-So Jee , D. Nichols , A. Kebede , S. Rahman , J.E. Crow , A.M. Ponte Gongalves , T. Mihalisin , G. H. Myer , I. Perez , R.E. Salomon , P. Schlottmann , S.H. Bloom , M. V. Kuric , Y.S. Yao , R.P. Guertin , J. of Supercond. , Vol. 1 , No. 1 , p.63 (1988) .
- [2] G. Xiao , M.Z. Cieplak , A. Garvin , F.H. Streitz , A. Bakhshai , and C.L. Chien , Phys. Rev. Lett. 60 , 14 , p.1446 (1988) ;
- [3] B. Jayaram , S.K. Agarwal , C.V. Narasimha Rau , and A.V. Narlikar , Phys. Rev. B 38 , 4 , p.2903 (1988) ;
- [4] M. Mehbod , W. Biberaker , A.G.M. Jansen , P. Wyder , R. Deltour and P.H. Duvigneaud , Phys. Rev. B 38 , 16 , p. 11813 (1988) ;
- [5] M.W. Shafer , T. Penney , B.L. Olson , R.L. Greene and R.H. Koch , Phys. Rev. B 39 , 4 , p.2914 (1989) (more detailed results were also presented at the fall M.R.S. meeting in Boston, Nov. 1988) ;
- [6] G. Xiao , M.Z. Cieplak , D. Musser , A. Garvin , F.H. Streitz , C.L. Chien , J.J. Rhyne and J.A. Gotaas , Nature Vol. 332 p. 238 , (1988) ;
- [7] T. Kajitani , K. Kusaba , M. Kikuchi , Y. Syono and M. Hirabayashi , Jpn. J. Appl. Phys., 27 , 354 (1988) ;
- [8] a similar method was presented in J. van der Maas , V.A. Gasparov and D. Pavuna , Nature 328 , 603 (1987) ;
- [9] H. Zhenhui , Z. Han, S. Shifang , C. Zuyao, Z. Qirui and X. Jiansheng , Solid State Comm. , Vol. 66 , No. 12 , pp. 1215-1218 (1988) ;
- [10] T. Penney , S. von Molnar , D. Kaiser , F. Holtzberg , and A.W. Kleinsasser , Phys. Rev. B Vol. 38 , 4 , p.2918 (1988) .
- [11] see for example , C.M. Hurd " Hall effect in metals and alloys " , Plenum Press , New York - London 1972 .
- [12] D.M. Eagles , Solid State Comm. Vol.69 , No.3 , p.229 (1989) .