

## Superconductivity in Zn-doped tetragonal $\text{LaBaCaCu}_3\text{O}_{7-\delta}$ systems

Rajvir Singh, R. Lal, U. C. Upreti, D. K. Suri, and A. V. Narlikar  
National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi 110012, India

V. P. S. Awana and J. Albino Aguiar  
Departamento de Fisica, Universidade Federal de Pernambuco, Cidade Universitaria 50.670-0-1, Recife PE, Brazil

Md. Shahabuddin  
Physics Department, Jamia Millia Islamia, New Delhi 110025, India  
(Received 11 April 1996; revised manuscript received 18 September 1996)

Resistivity and ac susceptibility of Zn-doped samples of the  $\text{LaBaCaCu}_3\text{O}_{7-\delta}$  (LBCCO) system have been measured for Zn content of 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% at. wt. X-ray diffraction has been used to find the lattice parameters of the samples. The samples remain tetragonal for all the considered concentrations of Zn. Idometry and thermogravimetric analyses have been done to estimate the oxygen content of different samples. Analyzing the resistivity and ac susceptibility data, the following conclusions are drawn about the role of Zn in the LBCCO samples. (1) The conduction mechanism of electrons appears to follow a crossover from the purely metallic regime to the localization regime due to either weak localization or electron-electron interaction effects after about 1.5% Zn. (2) The superconducting transition as revealed by the resistivity vs temperature curves or susceptibility vs temperature curves becomes sharper with Zn increasing content of Zn up to 1.0%. After 1.5% the resistive and ac susceptibility transitions become broader with increasing Zn. (3)  $T_c$  depression up to Zn content of 1.0% seems due to direct suppression of the effective pairing interaction, while at and above 2.5% Zn  $T_c$  depression is expected to be due to disorder effects such as reduction of density of states at the Fermi energy. [S0163-1829(97)07701-1]

### I. INTRODUCTION

Substitutions of metallic dopants in high- $T_c$  superconductors (HTSC's) have played an important role in understanding these systems.<sup>1</sup> Partial substitutions of the HTSC's by impurities like Fe, Co, Ni, Zn, and Ga at the Cu site have been found to shed light on many important features of the normal and superconducting states of these systems.<sup>2-14</sup> On the basis of experimental studies by different groups it has now become clear, for example, that  $T_c$  depression in different cuprate superconductors due to the dopants such as Al, Fe, Co, Ni, Zn, Ga, etc., has no correlation with the magnetic character of these impurity atoms.<sup>1-3</sup> However, the precise cause of occurrence and destruction of superconductivity in doped HTSC's has not yet been satisfactorily understood on the basis of the existing experimental results. Consequently, this field is still open and calls for a systematic study that can provide new insight into the behavior of HTSC systems subjected to metallic dopings. Motivated by this necessity, in this paper, we have investigated the Zn-doped  $\text{LaBaCaCu}_3\text{O}_{7-\delta}$  (LBCCO) system. This system is characterized by a tetragonal crystal structure<sup>15-18</sup> with  $T_c$  around 75 K.<sup>16,18</sup> Unlike the orthorhombic system  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) in which substitutions have been extensively studied, very little substitutional data exist for the tetragonal LBCCO system.

Yamaya *et al.*<sup>18</sup> have studied the oxygen-deficient samples of LBCCO samples and they have found this system to remain tetragonal for all the values of the oxygen content investigated by them. The resistivity behavior of the oxygen-deficient samples is found to be similar to that of the oxygen-deficient YBCO systems.<sup>19</sup>

Studies of various Zn-doped HTSC systems (other than

LBCCO) have been made from different angles by a large number of experimental groups.<sup>1-14</sup> While the local moment formation due to Zn is suggested by most of the studies,<sup>10-12</sup> the role of Zn in strong suppression of superconductivity is still controversial.<sup>5,11,13,20</sup> Some authors believe that suppression of  $T_c$  due to Zn in the HTSC's is due to magnetic pair breaking,<sup>5,13</sup> some suggest that Zn lowers  $T_c$  due to potential scattering,<sup>11</sup> while many attribute this to suppression of the pairing interaction caused by Zn.<sup>13,20</sup>

We will make an attempt to clarify the role of Zn in suppressing  $T_c$  in the LBCCO system. Interestingly, for this system we find the resistivity of the Zn-doped samples to exhibit a crossover in the resistivity slope  $d\rho/dT$  at a particular concentration of Zn. Similar crossover is observed also in the real ( $X'$ ) as well as the imaginary ( $X''$ ) parts of the ac susceptibility  $X' - iX''$  of Zn-doped samples. Occurrence of this crossover has been considered in detail, and possible clues to the role played by Zn in the LBCCO system have been examined.

This paper is organized as follows: In Sec. II we present methods of measurements of x-ray diffraction, mass density, weight loss, oxygen content, resistivity, and ac susceptibility. In Sec. III we present analysis of the experimental data on weight loss, resistivity, and ac susceptibility. In Sec. IV we present a brief discussion on the peculiar behavior of Zn in cuprate superconductors.  $T_c$  depression with increasing Zn content has been discussed in Sec. V. Conclusions are drawn in Sec. VI.

### II. EXPERIMENT

Samples with composition  $\text{LaBaCa}(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$  (where  $x=0.0-0.3$ ) were prepared by thoroughly mixing and

TABLE I. Values of the density, lattice parameters  $a$  and  $C$ , oxygen content  $7 - \delta$  in the pure and doped samples of LBCCO system: The lattice parameter  $b$  is found equal to  $a$  for all the sample.

Sample	Density (g/cc)	$a$ (Å)	$c$ (Å)	$(7 - \delta)$ (idometry)	$(7 - \delta)$ (TGA)
Pure	4.92	3.869	11.645	6.86	6.85
0.5% Zn	4.92			6.86	6.89
1.0% Zn	4.97	3.866	11.645	6.86	6.90
1.5% Zn	4.88	3.868	11.645	6.84	6.80
2.0% Zn	5.10	3.868	11.645	6.82	6.83
2.5% Zn	5.17	3.868	11.646	6.86	6.81
3.0% Zn	4.94	3.867	11.645	6.86	6.84

grinding  $\text{La}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{CuO}$ , and  $\text{ZnO}$  (as the case may be) in stoichiometric ratio and firing at  $975^\circ\text{C}$  for 12 h. The samples were cooled to room temperature by air quenching. Then the powders were reground and heated at  $975^\circ\text{C}$  in air for 12 h before furnace cooling to room temperature. After grinding a second time, the powders were pressed into pellets. These pellets were annealed at  $575^\circ\text{C}$  in flowing  $\text{O}_2$  for 24 h and were furnace cooled to room temperature.

The dc resistivity measurements were carried out in a closed-cycle refrigerator using the conventional four-probe technique. The temperature of the samples was monitored using a standard PRT 100 in conjunction with a Keithley 195A DMM with an accuracy of 0.1 K in the temperature range 30–300 K. The entire measurement system comprising the nanovoltmeter, a constant current source and temperature controller and indicator was hooked onto a HP 216 system controller for automatic data acquisition and control. The x-ray diffraction (XRD) was obtained and used to determine the phase purity of the samples using a Siemens D-500 diffractometer with  $\text{Cu } K\alpha$  radiation. The XRD of all the samples were characteristic of a single-phase tetragonal structure. The lattice parameters  $a$  and  $c$  of the pure and Zn-doped samples were practically invariant, as may be seen from Table I. ac susceptibility measurements were carried out using a SQUID-Quantum Design Magnetometer in a rms field of 0.01 Oe and frequency of 31 Hz in the temperature range of 4.2–100 K.

We have estimated the mass density of all the samples. The values are shown in Table I. It is clear that while the density vary only little (up to 6%) from sample to sample, it is about 30% smaller than the ideal density of the YBCO-based samples.

The oxygen content for pure and doped LBCCO samples was determined both by iodometry and thermogravimetry. The estimated values are given in Table I. The latter was done by using a Perkin Elmer TGA-7 thermogravimetric analyzer. The measurements were carried out at the rate of  $20^\circ\text{C}/\text{min}$  under nitrogen atmosphere. The weight-loss variation with temperature is plotted in Fig. 1 for all the samples. The weight loss was studied up to  $950^\circ\text{C}$ , except for the 1.5% Zn sample where the loss was found to occur relatively rapidly as compared to other samples. Because of this the weight loss of the 1.5% Zn sample was studied up to  $830^\circ\text{C}$  only.

The weight loss shown in Fig. 1 has different variations with temperature than that found by Peng *et al.*<sup>17</sup> In particu-

lar, Peng *et al.* have observed a weight-loss saturation after about  $800^\circ\text{C}$ . The main reason of difference between our observations and that of Peng *et al.*<sup>17</sup> lies in the fact that we have not used hydrogen gas in measuring the weight loss. The other point regarding the weight loss is that for a given sample different observations lead to different values of weight losses. However, the qualitative variation of weight loss remains similar in all the different observations. In particular, the shape of weight loss for the 2.0% Zn sample is reproduced every time. The average weight loss is shown in Fig. 1 for different samples. In extracting the oxygen content we have taken average of different values of weight losses observed by us for a sample of given Zn content. The value of the oxygen content thus determined from the TGA measurements agree with those obtained by using iodometric method within 1.0%. The oxygen content is estimated from the TGA measurements in the following manner. Let  $m_1(x)$  denote the molecular weight of the starting sample  $\text{LaBaCa}(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$ . When heated up to  $950^\circ\text{C}$  or  $830^\circ\text{C}$  this sample loses an amount of  $(1 - \delta)$  of the oxygen atoms. The weight of the oxygen lost in this manner is  $16(1 - \delta)$ . Then if  $L$  denotes the experimentally observed % weight loss, we get  $16(1 - \delta)/m_1 = L/100$ . This formula helps us in extracting the oxygen content from the observed weight losses.

### III. WEIGHT LOSS, RESISTIVITY, AND ac SUSCEPTIBILITY

#### A. Weight loss

The weight loss shows a peculiar trend in the samples considered. As we move from the pure sample, increasing the Zn concentration, it is seen from Fig. 1 that below about  $400^\circ\text{C}$  the rate of weight loss increases in the order: 0.5% Zn, pure, 1.0% Zn, 2.5% Zn, 2.0% Zn, 3.0% Zn, and 1.5% Zn. This shows that the binding of the oxygen atoms in the chains (wherefrom it is released on heating) is lowest for the 1.5% Zn sample. Zn concentration above 1.5% makes the oxygen tightly bound. Below we shall see that this kind of change of oxygen binding in the  $\text{CuO}$  chains at a particular Zn concentration is visible in almost every property of LBCCO system considered here.

It may be noted that the behavior of weight loss with different contents of Zn in the LBCCO sample is different from that observed by Tarascon *et al.*<sup>2</sup> in the Zn-doped YBCO systems. There are two main reasons for such a difference. First, our base system LBCCO is different from the

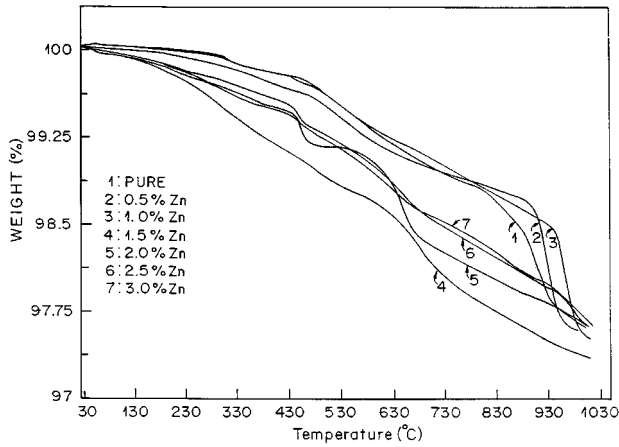


FIG. 1. Weight loss measured by the thermogravimetric analysis for all the samples.

YBCO sample in crystal structure. Second, we have used only low concentration of Zn in our samples. As the weight loss observed by us for the samples of increasing Zn content (cf. curves 5, 6, and 7 in Fig. 1) tend to coverage into one curve, we hope that for higher concentration of Zn the behavior of Zn-doped LBCCO samples may be similar to that observed by Tarascon *et al.*<sup>2</sup> in the Zn-doped YBCO sample.

### B. Resistivity

The resistivity vs temperature plots of all the samples of  $\text{LaBaCa}(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$  are shown in Fig. 2. A few degrees above the onset transition temperature, the resistivity appears to be linear at least up to  $x=0.02$ . In particular, there is no signature of the so-called spin gap<sup>21</sup> in the resistivity behavior (up to  $x=0.02$ ). We therefore assume that (for  $x \leq 0.02$ ) the normal state resistivity is given by

$$\rho_n = \rho_0 + \rho_1 T. \quad (1)$$

Here  $\rho_0 = \rho_n(T=0)$  is the residual resistivity and  $\rho_1$  is the resistivity slope in the normal state. Equation (1) presents the usual behavior of resistivity in the optimally or near to optimally doped cuprates.<sup>22</sup> There are many different explanations given for this behavior in literature.<sup>23</sup>

The values of  $\rho_0$  and  $\rho_1$  are estimated and presented in Table II for all the samples. For  $x=0.025$  and  $0.03$  samples, the linear- $T$  fit is made for the  $T > 130$  K portion of the  $\rho_n$ - $T$  curves. From these values it is clear that the pure system ( $x=0$ ) does not have zero residual resistivity. Similar behavior has been observed by Carim *et al.*<sup>16</sup> and Yamaya *et al.*<sup>18</sup> This is most likely due to the oxygen disorder as the oxygen content in all the samples is less than the stoichiometric value of 7.0. Partial substitutions of Cu by Zn increases the residual resistivity gradually with  $x$ . However, the resistivity slope increases with increasing Zn content first up to  $x=0.01$ ; thereafter, it decreases for  $x=0.015$ , followed by a fresh increase for  $x=0.02$ .

Samples with  $x=0.025$  and  $0.03$  cannot be satisfactorily fitted with Eq. (1), especially below 130 K (cf. Fig. 2). This means that the origin of resistivity for  $x=0.025$  and  $0.03$  is different from that of the  $x \leq 0.02$  samples. Activation behavior,<sup>24</sup> variable range hopping<sup>24</sup> (VRH), Kondo effect,<sup>25</sup> and localization<sup>26</sup> may be considered as possible origins. However, it was impossible to fit our resistivity curves by the  $\exp(1/T^\alpha)$  law. Thus possibilities due to activation behavior ( $\alpha=1$ ) and variable range hopping [ $\alpha=1/(1+d)$  with  $d$  as dimension of the VRH] may be ruled out. We found that the  $T$  dependence of resistivity for  $x=0.025$  and  $x=0.03$  is best fitted by

$$\rho_n(T) = \rho_0 + \rho_1 T - \rho_2 \ln T, \quad (2)$$

up to about 250 K. The fitting is shown by solid lines in Fig. 2. Presence of the  $-\ln T$  term in Eq. (2) indicates that the resistivity behavior (for  $x=0.025$  and  $0.03$ ) appears to be due to either Kondo effect,<sup>25</sup> weak localization,<sup>26</sup> or interaction effect.<sup>27</sup> However, Kondo effect appears to be unlikely because according to Walstedt *et al.*<sup>11</sup> Kondo temperature in

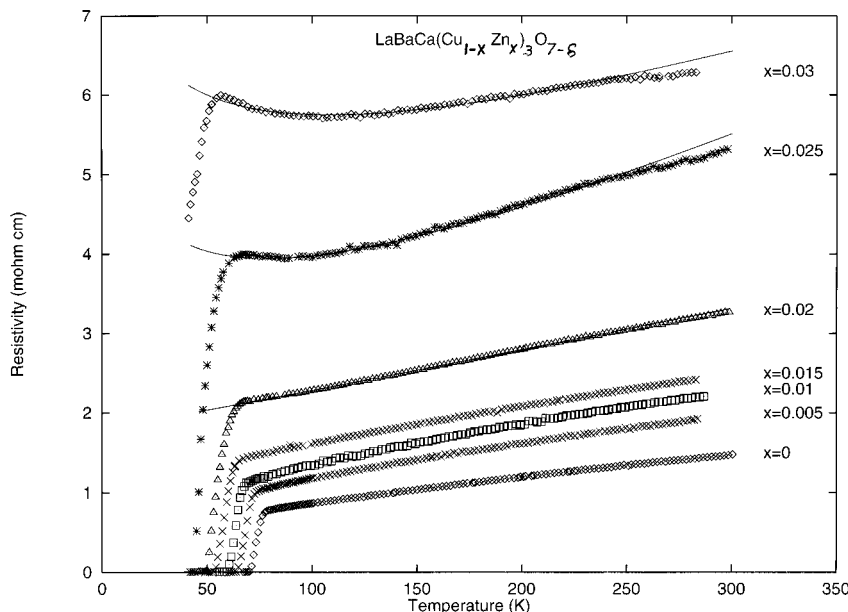


FIG. 2. Resistivity vs temperature plots for the pure, 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% Zn-doped LBCCO samples. Solid curves for 2.0%, 2.5%, and 3.0% Zn are fits to Eq. (2).

TABLE II. Values of the fitting parameters  $\rho_0$  and  $\rho_1$  (Eq. 1),  $T_{c,R=0}$ ,  $T_c$  [from  $(d\rho/dT)_{\text{peak}}$ ],  $T_{c,X}$  (from  $X'$  vs  $T$  plots), and  $T_p/T_c$  for different samples of LBCCO. Values of  $\rho_0$  and  $\rho_1$  for  $x \geq 0.02$  in parentheses correspond to Eq. (2).

Sample	$\rho_0$ (m $\Omega$ cm)	$\rho_1$ ( $\mu\Omega$ cm/K)	$T_{c,R=0}$ (K)	$T_c$ (K)	$T_{c,X}$ (K)	$T_p/T_c$
Pure	0.60	2.93	67.7	72.6	68	0.81
0.5% Zn	0.87	3.72	62.9	68.8		
1.0% Zn	0.94	4.52	58.0	63.7	58	0.85
1.5% Zn	1.17	4.47	52.4	57.7	53	0.85
2.0% Zn	1.78 (1.86)	5.03 (5.30)	48.3	51.6	44	0.64
2.5% Zn	3.16 (7.47)	7.27 (13.42)	40.3	47.1	34	0.18
3.0% Zn	5.23 (9.68)	3.88 (9.88)		32.2	15	

Zn-doped cuprates is very small, of order of mK. The observed behavior may therefore most reasonably be attributed to localization arising due to weak localization<sup>26</sup> or electron-electron interaction effects.<sup>27</sup> Our data is not adequate enough to clarify whether weak localization or electron-electron interaction effect is dominating in the present case. In fact, we require experiments like magnetoresistance to resolve this issue.

It may furthermore be noted that above  $T \approx 250$  K Eq. (2) does not fit well with the observed curves. A better fit below and above 250 K is obtained when contribution due to spin gap is used in place of the linear term in Eq. (2). Since the pure LBCCO samples does not show a spin gap effect in resistivity (Fig. 2), and since Zn is known either not to alter the spin gap (for low Zn content), or to suppress it,<sup>28</sup> presence of spin gap in the  $x=0.025$  and 0.03 samples is to be taken carefully. In fact other experiments like inelastic neutron scattering are needed to resolve the issue.

From the values of the density of the different samples presented in Table I it is clear that these densities are not much different for the samples considered here. Then, since  $\rho_n \propto [d(x)/d(0)]^{1/3}$  (Ref. 9) we do not expect any significant change in the relative variation of the resistivity behavior for samples of different Zn content. [Here  $d(x)$  is the density of the LBCCO sample for Zn content  $x$ .] We will thus limit the following analysis on the basis of the resistivities presented in Fig. 2 only.

The resistivity curves are used to specify the transition temperature  $T_c$ . There are numerous ways in literature for estimating  $T_c$ . We have adopted the one where  $T_c$  is defined as the temperature for which  $d\rho/dT$  is maximum. The values of  $T_c$  obtained in this way are presented in Table II. Below [cf. Eq. (7)] we shall treat  $T_c$  as the mean-field transition temperature.

### C. ac susceptibility

A peculiar feature of the HTSC systems is that they are granular systems.<sup>29</sup> This became clear ever since the discovery of superconductivity in these systems.<sup>30</sup> Thus in general a high- $T_c$  superconductor contains two regions—the region of superconducting grains and the region of weak links where the grain boundary regions essentially serve as weak

links. The weak-link region may acquire a weak superconductivity due to proximity effects. As a consequence, the lower critical field of this (weak-link) region will be low. In fact, at  $T=0$ , the value of the lower critical field of the weak links,  $H_{C1}(o)$ , is of the order of 1G (Refs. 31 and 32). This is much smaller than that for the intragranular region. The typical value of lower critical field for the intragranular region,  $H_{C1g}(o)$ , is 140G at  $T=0$  (Refs. 31 and 32).

As our ac measurements are done at a field  $H_a=0.01$  Oe, we do not expect this field to penetrate the grains unless  $T \approx T_c$ . In fact,  $H_{C1g}(T)$  varies like<sup>31</sup>

$$H_{C1g}(T) = H_{C1g}(o) [1 - T^2/T_c^2] \quad (3)$$

so that it will be quite small only very close to  $T_c$ . We have not observed any peaks in the  $X''$  vs  $T$  plots near  $T_c$  in any of the samples studied by us (Fig. 3). This absence of a peak near  $T_c$  in our  $X''$  vs  $T$  plots may be understood in the fol-

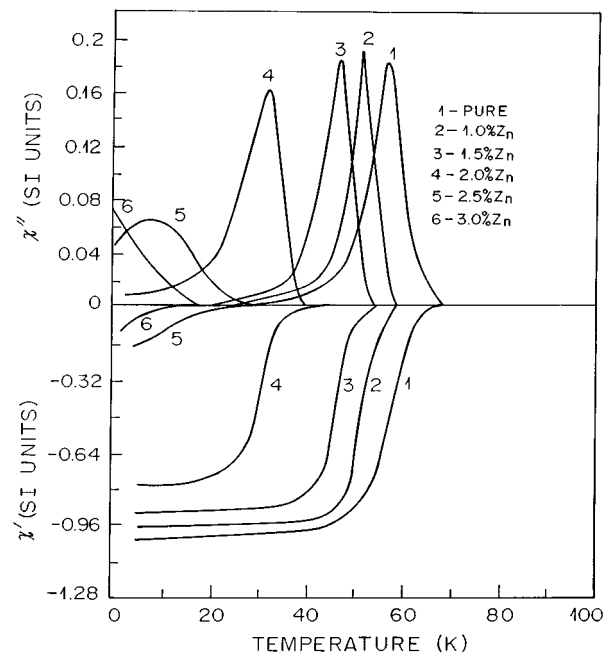


FIG. 3. ac susceptibility curves for the pure, 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% Zn-doped samples.

lowing way. The temperature required to penetrate the granular region by the low field of 0.01 Oe may be too close to  $T_c$  that it is not accessible practically. Since  $H_{C1J}$  is rather small we expect the applied magnetic field of 0.01 Oe to enter in the intergranular (weak-link) regions. This is indeed observed for all the samples as is seen in Fig. 3 in the  $X''$  vs  $T$  plots.

We turn to the detailed features of the real and imaginary parts of the ac susceptibility,  $X'$  and  $X''$ . Using the  $X'-T$  plots of Fig. 3 we have estimated the superconducting transition temperature  $T_{c,x}$ . Values of  $T_{c,x}$  are presented in Table II. These values agree reasonably well with the  $T_{c,R=0}$  values extracted from the  $\rho-T$  curves of Fig. 2 (cf. Table II). The real part of the ac susceptibility,  $X'$ , represents the flux excluded jointly by the intragranular and the intergranular regions. We consider features of  $X'$  from the viewpoint of the relative effects of different contents of Zn. From Fig. 3 it is clear that flux is excluded rather sharply in the case of the  $x=0.01$  sample. This behavior corroborates with the narrow resistive transition observed for the  $x=0.01$  sample [cf.  $(d\rho/dT)_{\text{peak}}$  vs  $x$  plot in Fig. 4].

The imaginary part of the ac susceptibility,  $X''$ , is the result of the absorption of the flux inside the weak-link regions formed by the intragranular space. Looking at the  $X''$  vs  $T$  plots of Fig. 3 we find that the peak height of the  $X''$  vs  $T$  plot,  $X''_{\text{peak}}$  which represents the flux absorption is relatively maximum in case of the  $x=0.01$  sample (cf. Fig. 4). This corroborates well with the behavior of the  $(d\rho/dT)_{\text{peak}}$  as shown in Fig. 4.

In order to further understand the  $X''$  behavior we have calculated  $T_p/T_c$ , where  $T_p$  is the temperature where  $X''$  has its maximum value. This ratio ( $T_p/T_c$ ) is given in Table II. It is clear that  $T_p/T_c$  is relatively higher for the  $x=0.01$  and  $x=0.015$  samples than that of the pure and other samples. Assuming that  $H_{C1J}(T)$  has a  $T$  dependence similar to that of  $H_{C1g}(T)$ , i.e.,  $H_{C1J}(T) = H_{C1J}(0)[1 - T^2/T_c^2]$ , we may say that for the same applied field, higher values of  $T_p/T_c$  imply higher values of  $H_{C1J}(0)$ . In this sense,  $H_{C1J}(0)$  appears to be higher in the cases of the  $x=0.01$  and  $x=0.015$  samples. In order to understand how it can be so, we proceed as follows. We estimate the transition width from the  $\rho-T$  and the  $X''-T$  curves separately. From the  $\rho-T$  curves we define the transition width as the difference between the onset and the  $R=0$  temperatures, i.e.,  $\Delta T_{c,R} = T_{c,on} - T_{c,R=0}$ . On the other hand, from the  $X''-T$  plots we estimate the transition width in terms of the full-width at half-maximum (FWHM) of the  $X''-T$  curves. This gives us the transition widths  $\Delta T_{c,X}$ .

The values of  $\Delta T_{c,R}$  and  $\Delta T_{c,X}$  obtained in these manners are plotted in Fig. 4 for various Zn concentrations  $x$ . It is clear that both  $\Delta T_{c,R}$  and  $\Delta T_{c,X}$  have similar qualitative variation with  $x$  and both are minimum for  $x=0.01$ . Reduced values of  $\Delta T_{c,R}$  implies strongly defined Cooper pairs. When this is so (for  $x=0.01$ ), the weak-link region is expected to experience a rather sharp effect of superconductivity. That is to say, the weak-link region of the  $x=0.01$  sample is expected to be relatively more superconducting than that of other samples. When this is so,  $H_{C1J}$  is certainly likely to be higher for the  $x=0.01$  sample. This is what is inferred above on the basis of the relative variation of the  $T_p/T_c$  values. In

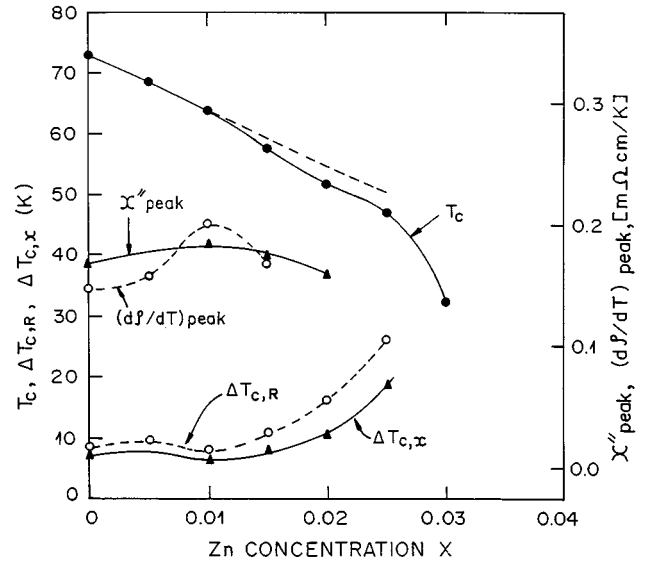


FIG. 4.  $T_c$ ,  $\Delta T_{c,R}$ ,  $\Delta T_{c,X}$ ,  $(d\rho/dT)_{\text{peak}}$  and  $X''_{\text{peak}}$  for different Zn concentrations  $x$ .

this way, the resistivity behavior and the ac susceptibility behavior of the different samples corroborate with each other reasonably well.

#### IV. CROSSOVER EFFECT OF Zn

We have seen from the resistivity slope,  $X'$  slope,  $(d\rho/dT)_{\text{peak}}$ ,  $X''_{\text{peak}}$ ,  $\Delta T_{c,R}$ , and  $\Delta T_{c,X}$  that in the Zn-doped samples of LBCCO, the effect of Zn appears to be optimal for the particular concentration  $x=0.01$ . This raises a question: has such an optimal effect of Zn for a particular concentration been observed earlier in any of the HTSC systems? After going through literature we have found that although no one has specifically reported such an effect, it is evident in the existing experimental data of some groups. For example, in the Raman study on the Zn-doped  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (YBCO) system Shin *et al.*<sup>8</sup> have found a dip in the effect of Zn on the FWHM of the  $\text{Cu}(2) A_{1g}$  mode. While Fig. 8 of Shin *et al.*<sup>8</sup> shows a clear dip in the FWHM of the  $\text{Cu}(2) A_{1g}$  mode for a particular Zn concentration, these authors have overlooked this (dip). A careful fitting of the FWHM data presented in Fig. 8 of Shin *et al.* shows that Zn shows its smallest effect on the FWHM of the  $\text{Cu}(2) A_{1g}$  mode for the Zn concentration corresponding to  $T_c = 76$  K. According to Licci and Raffo<sup>5</sup> this value of  $T_c$  corresponds to a Zn content of about 1.3%. This is somewhat similar to the  $x=0.01$  value in the present case. In fact in the present case of the Zn-doped LBCCO systems the optimal effect of Zn is expected between  $x=0.01$  and  $x=0.015$ .

The FWHM of the  $A_{1g}$  mode may be ascribed to the scattering of charge carriers by Zn in the  $\text{CuO}_2$  planes. Thus, the FWHM measurements of Shin *et al.* indicate that up to about 1.3% Zn, the effect of scattering of charge carriers with Zn become relatively weaker with increasing  $x$ . In the present case, the scattering of charge carriers with Zn is characterized by  $\rho_0$  (Table II). It is seen from Table II that with increasing  $x$  the relative increase of  $\rho_0$  is relatively slower up to 1.0% Zn. After  $x=0.01$ , the relative increase of  $\rho_0$  becomes faster with increasing  $x$ . Combining this with the

above result obtained on the basis of the work of Shin *et al.* it may be argued that the scattering of charge carriers with Zn has qualitatively similar behavior in the LBCCO and YBCO systems. A very recent observation on the optimal role of Zn in HTSC's is given by the  $ab$  direction coherence length  $\xi_{ab}$  inferred by Axnas *et al.*<sup>33</sup> According to Fig. 3 of these authors Zn shows an optimum effect on  $\xi_{ab}$  for  $x=0.01$ . However, no such peculiarity in  $\xi_{ab}$  as a function of  $x$  was observed by Semba *et al.*<sup>34</sup> Even so, it is desired to further investigate the peculiar role of Zn in cuprate superconductors. Our results and those of Shin *et al.* and Axnas *et al.* serve only as a signal to such a peculiarity.

## V. SUPERCONDUCTIVITY

Let us now see in what way we can understand the superconducting transition in the Zn-doped LBCCO samples. First of all, we consider the variation of the superconducting transition temperature  $T_c$  with the Zn content  $x$ . This variation is presented in Fig. 4. On the basis of this figure we can divide the variation of  $T_c$  with  $x$  in three parts. The first part extends from the pure sample to the 1.0% Zn sample. This part belongs to an almost linear decrease of  $T_c$  with Zn. The second part belongs to the Zn concentrations from  $x=0.01$  to  $x=0.02$ . In this part the rate of decrease of  $T_c$  is reduced with increasing  $x$ . In the third and last part which lies somewhat after  $x=0.02$ , the rate of decrease of  $T_c$  increases with increasing  $x$ .

Combining the variations of  $T_c$  with  $x$  from all the three parts we find that at  $x=0.01$  and  $x=0.025$  this variation shows crossover effects. Let us consider the crossover at  $x=0.01$ . We note the following facts. (1) The oxygen content does not change much from sample to sample (Table I). Thus, from  $x=0.00$  to  $x=0.01$  we expect no additional effect on the superconductivity due to the oxygen disorder. So, the reduction of  $T_c$  from  $x=0.00$  to  $x=0.01$  samples is not likely to be due to oxygen disorder (or, equivalently, due to reduction of carrier density). (2) If  $T_c$  depression from  $x=0.00$  to  $x=0.01$  were due to the disorder effects of Zn ions, there would have been increasing broadening of the resistive transition with  $x$ . Our experimental results ( $\Delta T_{c,R}$ ,  $\Delta T_{c,X}$  vs  $x$  in Fig. 4) show the opposite effect. Thus  $T_c$  reduction for the  $x=0.00$  to  $x=0.01$  samples is not expected due to the Zn disorder also. (3) No trace of localization is found up to  $x=0.01$  (Fig. 2). Thus, we cannot expect the density of states at the Fermi energy,  $N_F$ , to decrease at least up to  $x=0.01$ . So, the reduction of  $T_c$  up to the samples of  $x=0.01$  is not expected due to the density of states effect also.

In view of the above, it may be argued that at least up to

the  $x=0.01$  samples the degradation of  $T_c$  will be due to a mechanism different from those mentioned above. One of such a mechanism in the cases of the Zn-doped HTSC's is the direct suppression of the effective pairing interaction.<sup>13,20</sup> The situation changes in samples having Zn concentration above  $x=0.01$ . Now, the resistive transition starts to broaden and after  $x=0.02$  localization (due to weak localization or electron-electron interaction) starts to show dominating effect near  $T_c$  (see above). Thus, as we move beyond the Zn concentration  $x=0.015$ , disorder effects (e.g., reduction of  $N_F$ ) may start to take part in suppression of  $T_c$ .

The above conclusions are based on the measurements of the resistivity of the polycrystalline samples. It is therefore desired to know how far the above results will hold in a single crystal. In a very recent paper Lal *et al.*<sup>4</sup> have demonstrated that from the viewpoint of qualitative variation of the resistivity, there is no significant difference between the behavior of the single crystalline and polycrystalline samples. We thus hope that the qualitative essence of the above results will not be drastically altered in the single crystals of LBCCO.

## VI. CONCLUSIONS

We have presented measurements of weight loss, resistivity, and ac susceptibility of the Zn-doped samples of the LBCCO system. Unlike the YBCO system, this system possesses a tetragonal crystal structure in the undoped as well as Zn-doped conditions. Analysis of the weight loss, resistivity, and ac susceptibility shows that Zn has its optimal effect for specific concentration lying between 1.0% and 1.5%. Occurrence of this kind of optimal behavior of Zn has been further found in the resistive transition width and in the  $X''$  vs  $T$  shape. Guided by this discovery, we have pointed out that such an effect was observed earlier also, although it was overlooked. The Zn-doped LBCCO samples appear to provide a clear-cut case for the optimal behavior of Zn for a specific concentration.

The impact of the optimal behavior of Zn on  $T_c$  depression has been analyzed. It is argued, in particular, that up to the concentration required for optimal behavior of Zn, the decrease of  $T_c$  is mainly due to the direct suppression of the effective pairing interaction. The situation remains less clear for higher concentration of Zn.

## ACKNOWLEDGMENTS

The authors at NPL would like to thank Professor S. K. Joshi for his keen interest in the present work. Thanks are also due to Deepak Varandani for help in different calculations.

<sup>1</sup>A. V. Narlikar, C. V. N. Rao, and S. K. Agarwal, in *Studies of High Temperature Superconductors*, edited by Anant Narlikar (Nova Science, New York, 1989), Vol. 1, p. 341.

<sup>2</sup>J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, and G. W. Hull, *Phys. Rev. B* **37**, 7458 (1989).

<sup>3</sup>Y. Xu, R. L. Sabatini, A. R. Moodenbaugh, Y. Zhu, S. G. Shyu,

and M. Suenaga, *Physica C* **169**, 205 (1990).

<sup>4</sup>Ratan Lal, V. P. S. Awana, S. P. Pandey, V. S. Yadav, Deepak Varandani, A. V. Narlikar, A. Chhikara, and E. Gmelin, *Phys. Rev. B* **51**, 539 (1995).

<sup>5</sup>F. Licci and L. Raffo, *Supercond. Sci. Technol.* **8**, 245 (1995).

<sup>6</sup>S. Ikegawa, T. Yamashita, T. Sakurai, R. Ltti, H. Yamauchi, and

- S. Tanaka, *Phys. Rev. B* **43**, 2885 (1991).
- <sup>7</sup>D. -S. Jeon, M. Akamatsu, H. Ikeda, and R. Yoshizaki, *Physica C* **253**, 102 (1995).
- <sup>8</sup>H. -S. Shin, I. S. Yang, and W. -C. Lee, *Physica C* **250**, 275 (1995).
- <sup>9</sup>S. Zagaulaev, P. Monod, and J. Jegoudez, *Phys. Rev. B* **52**, 10 474 (1995).
- <sup>10</sup>H. Alloul, P. Mendels, H. Casetta, J. F. Masucco, and J. Arabrki, *Phys. Rev. Lett.* **67**, 3140 (1991).
- <sup>11</sup>R. E. Walstedt, R. F. Bell, L. F. Schneemeyer, J. V. Waszczak, W. W. Warren, Jr., and R. Dupree, *Phys. Rev. B* **48**, 10 646 (1996).
- <sup>12</sup>A. V. Mahajan, H. Alloul, G. Collin, and J. F. Marucco, *Phys. Rev. Lett.* **72**, 3100 (1994).
- <sup>13</sup>G. V. M. Williams, J. L. Tallon, and R. Meinholds, *Phys. Rev. B* **52**, 7034 (1995).
- <sup>14</sup>G. Ilonca, M. Mehbod, A. Lanchbeen, and R. Deltour, *Phys. Rev. B* **47**, 15 256 (1993).
- <sup>15</sup>W. T. Fu, H. W. Zandbergen, C. J. Van Der Beek, and L. J. De Jongh, *Physica C* **156**, 133 (1988).
- <sup>16</sup>A. H. Carim, A. F. de Jong, and D. M. de Leeuw, *Phys. Rev. B* **38**, 7009 (1988).
- <sup>17</sup>J. L. Peng, P. Klavins, and R. N. Shelton, *Phys. Rev. B* **39**, 9074 (1989).
- <sup>18</sup>K. Yamaya, T. Yagi, and Y. Okajima, *Solid State Commun.* **87**, 1113 (1993).
- <sup>19</sup>M. Buchgeister, W. Hiller, S. M. Hosseini, K. Kopitzki, and D. Wagener, in *Transport Properties of Superconductors*, edited by Roberts Nicosky (World Scientific, Singapore, 1990), p. 511; G. Kallias, I. Panagiotopoulos, D. Niarches, and A. Kostikas, *Phys. Rev. B* **48**, 15 995 (1993); A. Carrington, D. J. C. Walber, A. P. Mackenzie, and J. R. Cooper, *ibid.* **48**, 13 051 (1993).
- <sup>20</sup>Ratan Lal, *Phys. Rev. B* **51**, 640 (1995).
- <sup>21</sup>S. K. Tolpygo, J. Y. Lin, M. Gurvitch, S. Y. Hou, and J. M. Phillips, *Phys. Rev. B* **53**, 12 454 (1996).
- <sup>22</sup>B. Wuyts, V. V. Moshchalkov, and Y. Bruynseraede, *Phys. Rev. B* **51**, 6115 (1995).
- <sup>23</sup>N. Nagaosa and P. A. Lee, *Phys. Rev. Lett.* **64**, 2450 (1990); Q. Si and K. Levin, *Phys. Rev. B* **44**, 4727 (1991); J. Ruvalds and A. Virosztek, *ibid.* **43**, 5498 (1991); C. M. Verma, *Phys. Rev. Lett.* **75**, 898 (1995).
- <sup>24</sup>N. F. Nott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed. (Clarendon, Oxford, 1979).
- <sup>25</sup>J. Kondo, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 183.
- <sup>26</sup>P. A. Lee and T. V. Ramakrishnan, *Rev. Mod. Phys.* **57**, 287 (1985); D. Belitz and T. R. Kirkpatrick, *ibid.* **66**, 261 (1994).
- <sup>27</sup>B. L. Altshuler and A. G. Aronov, *Solid State Commun.* **39**, 115 (1979).
- <sup>28</sup>G. V. M. Williams, J. L. Tallon, R. Meinhold, and A. Janossy, *Phys. Rev. B* **51**, 16 503 (1995).
- <sup>29</sup>J. R. Clem, *Physica C* **153-155**, 50 (1988).
- <sup>30</sup>J. G. Bednorz and K. A. Muller, *Z. Phys. B* **64**, 189 (1986).
- <sup>31</sup>B. Schulz, B. Schliepe, W. Wisny, and K. Baberschke, *Solid State Commun.* **80**, 111 (1991).
- <sup>32</sup>R. Puzniak, R. Usami, and H. Yamauchi, *Phys. Rev. B* **53**, 86 (1996).
- <sup>33</sup>J. Axnas, W. Holm, Yu. Eltsev, and O. Rapp, *Phys. Rev. B* **53**, 3003 (1996).
- <sup>34</sup>K. Semba, A. Matsuda, and T. Ishii, *Phys. Rev. B* **49**, 10 043 (1994).