

Correlation between superconductivity and normal-state properties in the $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ system

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Superconducting and normal-state properties have been studied in the $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ system with $0 \leq x \leq 0.06$. The value of T_c decreases rapidly with the Zn content and vanishes as 2.1 at.% of Zn is doped into the Cu sublattice. Metallic resistivity is observed when superconductivity disappears at $x=0.02$. The suppression of T_c is not caused by the reduction of carrier concentration which should remain constant in the Zn-doped samples, but rather due to the filling of the local Cu $d_{x^2-y^2}$ state. The residual resistivity scales linearly with the Zn content as expected from the impurity scattering due to disorder. Quantitative analysis of the residual resistivity indicates that the mean free path due to disorder is about twice as large as the coherence length when T_c is suppressed to zero. The implication of this finding on the disorder pair-breaking effect will be discussed. The value of T_c is found to strongly correlate with the slope of the resistivity in relation to temperature. Qualitative analysis is carried out in both inelastic and elastic scattering process between carriers and other excitations.

I. INTRODUCTION

High-temperature superconductors of the type $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (the 2:1:4 compound) and $\text{YBa}_2\text{Cu}_3\text{O}_7$ (the 1:2:3 compound) have been the focus of intense theoretical¹ and experimental² studies. The common feature of the two systems is the existence of the two-dimensional Cu-O₂ planes in both structures. In $\text{YBa}_2\text{Cu}_3\text{O}_7$, there also exists a one-dimensional Cu-O chain structure. Understanding the relative importance of the planes and the chains is of fundamental significance. Recently, by doping the Cu sites in the Cu-O₂ planes and the Cu-O chains with Zn and Ga ions, respectively,^{3,4} we have shown that the Cu-O₂ planes are more important than the Cu-O chains in sustaining the high- T_c superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_7$. The conclusion is further confirmed by the recent discovery of the high- T_c Bi-Sr-Ca-Cu-O (Refs. 5 and 6) and Tl-Ba-Ca-Cu-O (Ref. 7) compounds which contain the Cu-O₂ planes only.^{8,9}

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is a unique system for the study of the high- T_c oxides, even though the superconducting transition temperature ($T_c \sim 38$ K) is lower than those of $\text{YBa}_2\text{Cu}_3\text{O}_7$, Bi-Sr-Ca-Cu-O, and Tl-Ba-Ca-Cu-O. It has the simplest layered structure with only one Cu site located on the isolated Cu-O₂ planes.¹⁰ Therefore, the role of the Cu-O₂ planes can be more easily investigated, without the complication of the Cu-O chains or other more complex structures. The parent compound La_2CuO_4 is a semiconductor¹⁰ with a three-dimensional antiferromagnetic ordering among the Cu²⁺ ions ($T_N \sim 220$ K).¹¹ Substituting the trivalent La³⁺ ions by the divalent Sr²⁺ ions introduces free holes^{12,13} (most likely residing at the O sites¹⁴⁻¹⁶) which are the active charge carriers responsible for the superconductivity. Cu is a crucial constituent in all high- T_c superconductors.^{3,4,17-20} Each Cu²⁺ ion, with the configuration of $3d^9$, has one hole in the antibonding $3d_{x^2-y^2}$ band. Doping the Cu sublattice with various impurities affects superconductivity profound-

ly.^{3,4,17-19} Understanding the effect of impurities on superconductivity and normal-state properties is crucial for the elucidation of the superconducting mechanisms. In this study, we have chosen Zn to probe the 2:1:4 compound. Zn ($3d^{10}4s^2$) is divalent, nonmagnetic, and its $3d$ band is completely full. It serves the unique role of eliminating the local $3d$ holes at the Cu sites.

The effect of Zn doping in the 2:1:4 compound has been briefly investigated by other groups.^{19,20} In all cases, only one superconducting Zn-doped sample has been studied. There has been no detailed study of the relationship between the superconducting and normal-state properties of the Zn-doped 2:1:4 compound. Such a study is particularly relevant in view of the theoretical advancement in high- T_c superconductivity.¹ In this paper, we present a systematic study of the structure, normal-state, and superconducting properties of the $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ system in the most critical region ($0 \leq x \leq 0.06$). We investigate to what extent the nonmagnetic disorder affects the high- T_c superconductivity and how T_c is correlated with normal-state transport.

II. EXPERIMENT

Appropriate proportions of La_2O_3 , SrCO_3 , CuO , and ZnO high-purity powders were thoroughly mixed according to the molecular formula $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ ($0 \leq x \leq 0.06$). The powders were pressed into pellet form, and then sintered three times for a total period of about 100 h in an oxygen atmosphere with two intermediate grindings for homogenization. The temperature for the first two sinterings was 1000 °C, and was 1050 °C for the last sintering. The final cooling rate was 3 °C/min.

Resistivity as a function of temperature was measured on regularly shaped samples by using a standard four-probe method. The magnetization of the samples were measured by using a dc superconducting quantum in-

TABLE I. Various parameters determined for the $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ system: (1) lattice parameters a and c ; (2) superconducting transition temperature T_c ; (3) residual resistivity $\rho(0\text{ K})$ extrapolated from normal-state resistivity; (4) resistivity at 40 K, $\rho(40\text{ K})$; (5) resistivity at 297 K, $\rho(297\text{ K})$; and (6) slope of the resistivity at 297 K, $d\rho/dT$.

x (%)	a (Å)	c (Å)	T_c (K)	$\rho(0\text{ K})$ ($\mu\Omega\text{ cm}$)	$\rho(40\text{ K})$ ($\mu\Omega\text{ cm}$)	$\rho(297\text{ K})$ ($\text{m}\Omega\text{ cm}$)	$d\rho/dT$ ($\mu\Omega\text{ cm/K}$)
0	3.7763(1)	13.2368(5)	37.8	104	372	1.80	5.67
0.5	3.7766(3)	13.2303(16)	35.1	177	464	1.64	5.00
1.0	3.7773(3)	13.2300(17)	30.1	208	505	1.56	4.61
1.5	3.7778(2)	13.2286(11)	22.1	234	545	1.55	4.40
2.0	3.7785(1)	13.2214(8)	6.5	338	669	1.50	3.91
3.0	3.7800(3)	13.2209(15)	0	392	761	1.64	4.19
4.0	3.7794(3)	13.2202(16)	0	483	788	1.48	3.40

terference device (SQUID) magnetometer. The lattice parameters of the samples were determined with a Philips APD 3720 automated x-ray powder diffractometer. The diffraction peaks were fitted by modified Gaussian functions, and the lattice parameters were then determined by fitting the positions of at least seventeen diffraction peaks by using a standard least-squares reduction method.

Various structural, superconducting, and normal-state resistivity parameters obtained from measurements are summarized in Table I and will be discussed in the following sections.

III. RESULTS

The Zn ion has a definite valence state of $2+$, same as the Cu valence state in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. Its ionic size (0.75 Å) is also similar to that of Cu^{2+} (0.73 Å).²¹ Neutron-diffraction measurement has shown that Zn substitutes exclusively the Cu(2) site in the Cu-O₂ planes of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ system.³ It is expected to be true in the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ system also.

θ - 2θ x-ray diffraction indicated that all of the samples were single-phase with good quality in our Zn doping level ($0 \leq x \leq 0.06$), having the same tetragonal perovskite phase of the parent $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ compound. The lattice parameters a and c obtained are shown in Fig. 1 for different Zn doping levels. The a axis increases with Zn composition, while the c axis decreases. Both parameters change by about 0.1% up to $x=0.06$. The variation of the lattice parameters is caused by the Jahn-Teller effect.^{19,22} The Cu^{2+} ions [$d^9:(t_{2g})^6(d_{z^2})^2(d_{x^2-y^2})^1$] exhibit a strong Jahn-Teller effect; the octahedron around Cu^{2+} is elongated along the c axis and contracted in the plane. Consequently, in $\text{La}_{1.85}(\text{Sr},\text{Ba})_{0.15}\text{CuO}_4$, the length of the Cu-O bond (2.428 Å) along the z direction is much longer than that of the Cu-O bond (1.894 Å) in the plane.¹⁰ However, the octahedron around Zn^{2+} is not distorted, since Zn^{2+} is in the d^{10} state. Doping the Cu sites with Zn will reduce the local Jahn-Teller distortion, and hence reduces the c axis and increases the a axis. Interestingly, the variation of the lattice parameters (a, c) as shown in Fig. 1 seems to correlate with T_c . The parameters a and c vary approximately linearly with the Zn content, and then they level off as T_c goes to zero. If the

correlation is real, the Jahn-Teller distortion may play an important role in the superconductivity. It is noted that the main interest of this study is in those samples with Zn content less than 3 at. %.

The temperature dependence of the normalized resistivity is shown in Fig. 2 for $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ ($x=0.0, 0.005, 0.01, 0.015, 0.02, 0.03, \text{ and } 0.04$). The resistivity at room temperature is shown in the inset of Fig. 2. All of the samples up to $x=0.06$ show metallic behavior in the normal state. The value of T_c decreases rapidly with the Zn content. For Zn doping level above 2%, samples are no longer superconducting, but remain metallic. The slope of the resistivity ($d\rho/dT$) decreases steadily with the Zn content. However, the resistivity of the samples remains relatively constant at room temperature.

The values of T_c as a function of the Zn content are presented in Fig. 3. The bars represent the superconducting transition width obtained from resistivity measurement (90%–10% resistivity drop), and the dots are mid-point resistive transition temperatures. T_c reduces to zero at a very small critical Zn doping level of only 2.1%. The

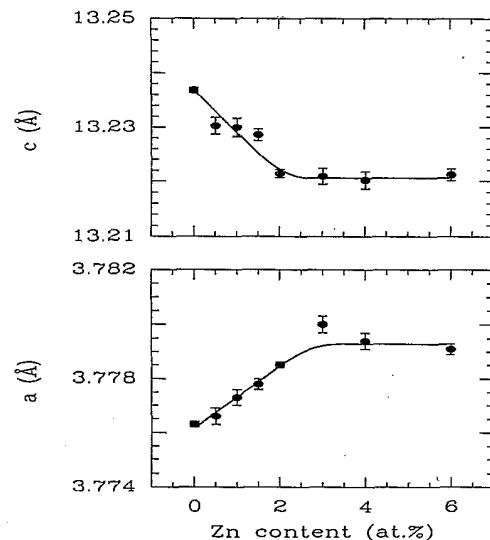


FIG. 1. The lattice parameters a and c vs the Zn content for $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$.

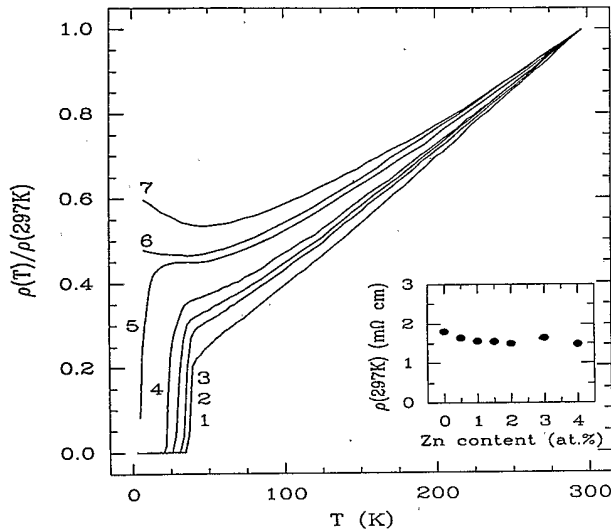


FIG. 2. The temperature dependence of normalized resistivity $[\rho(T)/\rho(297\text{ K})]$ of samples with various Zn content, (1) $x=0$, (2) 0.005, (3) 0.01, (4) 0.015, (5) 0.02, (6) 0.03, and (7) 0.04. Inset: The room-temperature resistivity $[\rho(297\text{ K})]$ vs Zn content. The experimental error in ρ is about $\pm 5\%$.

deleterious effect of Zn on superconductivity far exceeds that of magnetic ions such as Fe (Ref. 20), Co (Ref. 20), and Ni (Refs. 19, 20, and 23). Similar behavior has also been observed in the 1:2:3 compound.^{17,18} Among all of the 3d transition-metal elements and some of the sp elements, Zn produces the strongest suppression of T_c in $\text{YBa}_2\text{Cu}_3\text{O}_7$.^{3,4,17,18,24} The critical Zn composition beyond which the system ceases to be superconducting is about 12 at. %.

The solid curve in Fig. 3 represents the relation $T_c = C(x_c - x)^{1/2}$ with $C=28.8\text{ K}$ and $x_c=0.0205$. Although, the limited number of data does not allow us to firmly establish such a dependence, this relation does give

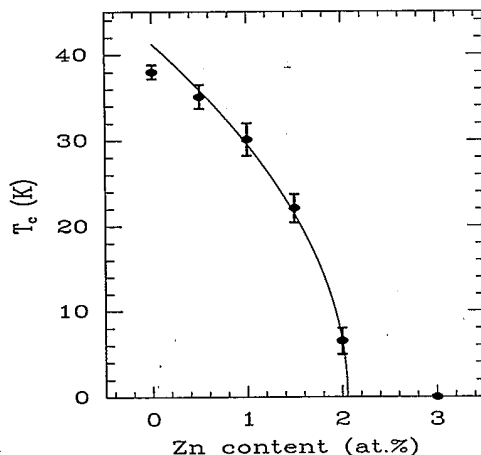


FIG. 3. Variation of T_c with Zn content for $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$. The bars represent 90–10% resistive superconducting transition, and the dots are the midpoint resistive transition temperature. The curve is a fit to the data using $T_c = C(x_c - x)^{1/2}$ ($C=28.8$ and $x_c=2.05\%$).

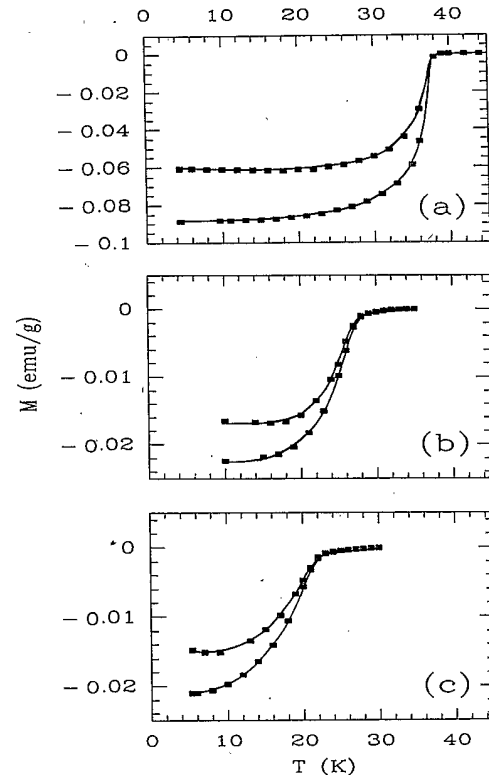


FIG. 4. Magnetization as a function of temperature in zero-field-cooled (increasing temperature) and field-cooled (decreasing temperature) modes for samples with (a) $x=0$, (b) 0.01, and (c) 0.015.

a reasonable fit to the data specially for x close to x_c . Such behavior remains to be explained theoretically.^{25–27}

Magnetization as a function of temperature in both the zero-field-cooled and field-cooled modes is shown in Fig. 4 for samples with $x=0, 0.01$, and 0.015 . The $x=0$ sample has a well-defined superconducting transition at $T=38\text{ K}$, while the values of T_c for the Zn-doped samples are lower. The result of T_c obtained from magnetization measurement is in good agreement with that from resistivity measurement. The magnetization reduces significantly as the Zn doping level increases. It should be pointed out that the reduced Meissner effect here does not imply the presence of a nonsuperconducting phase. It is an intrinsic property of the samples. Doping with Zn reduces the coherence length and increases the penetration depth in the oxide superconductors. A similar example is the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system, where the T_c and Meissner effect are maximized around $x=0.15$. Reducing the Sr content ($x < 0.15$) not only reduces the T_c , but also the Meissner effect. Definitely, such a behavior is not due to the presence of nonsuperconducting phase.

IV. ANALYSIS AND DISCUSSION

The La_2CuO_4 compound is an antiferromagnetic insulator.¹¹ Doping with Sr introduces free hole carriers,^{11,12} and it has been established that T_c scales approximately linearly with the carrier concentration which is deter-

mined by the Sr content²⁸ [the oxygen content is insensitive to the Sr doping for $x_{\text{Sr}} < 0.2$ (Ref. 29)]. In $\text{YBa}_2\text{Cu}_3\text{O}_7$, T_c also increases with carrier density which is controlled by the oxygen content.^{30,31} The $3d$ holes of the Cu^{2+} are believed to be crucial in the superconducting mechanism. Since Zn ions are in the same valence state as Cu^{2+} , they will not change the formal charge balance in the compound. Thus, doping with Zn will not change the oxygen content, especially when the Zn doping level is low. The carrier concentration should remain approximately unchanged, but the number of d holes is reduced. This very property makes $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ a unique system in that the disappearance of superconductivity is not mainly caused by the reduction of carrier concentration.

A closely related observation in the Zn-doped 2:1:4 system is that the disappearance of superconductivity does not seem to be associated with a metal-insulator transition.^{32,33} In this system, T_c drops to zero at about $x = 0.021$, but the room-temperature resistivity remains approximately constant up to at least 6 at. % of Zn. The slopes of the resistivity ($d\rho/dT$) are all positive in a wide temperature range, reflecting the metallic nature of the samples. At low temperatures, there is a small resistivity upturn in the nonsuperconducting samples. Preliminary analysis indicates that it is not caused by an activation or a variable range hopping mechanism. Whether it is due to a localization effect or a new scattering mechanism is currently under investigation. The main advantage of this system over other impurity-doped systems is that Zn strongly affects the superconducting mechanism, but has a relatively small effect on the carrier density.

As indicated in this study and others, the holes in the $3d$ band of Cu^{2+} are the necessary ingredients of oxide superconductors. There are many proposals on how the existence of the Cu $3d$ holes provides the coupling mechanism.^{1,33-42} Doping Zn into the Cu sublattice has two main effects. First, it distorts the local lattice, because of the different Zn-O and Cu-O bond strengths. However, the lattice distortion at the low doping level provides only a marginal disturbance to the system (see Fig. 1). Secondly, Zn generates random topological point defects such that the neighboring $3d$ holes or free carriers cannot hop into the Zn site with a $3d^{10}$ structure, because the unfilled s, p bands of Zn are much higher than the Fermi level. The Zn sites effectively prevent the $3d$ holes from hopping and therefore hinder the antiferromagnetic correlation (exchange interaction J is of the order of t^2/U , where t is the hopping integral and U the on-site Coulomb repulsion) or the formation of spin-density-wave state.³⁸ The proximity of the appropriate Cu and O ionization levels is also lost at the Zn site, which reduces the tendency for charge transfer fluctuations.⁴³ The Zn sites also affect the mobility of the free hole carriers by providing scattering centers which may be pair breaking. It is instructive to compare the results of the Ni-doped 2:1:4 system with that of the Zn-doped 2:1:4 system.^{19,23} The Ni^{2+} has a $3d^8$ electronic structure. Although doping Ni into the Cu sublattice will affect the local hopping parameter t , other Cu $3d$ holes as well as free carriers can still hop into the Ni sites. T_c should reduce much more slowly with Ni

doping as opposed to Zn doping. Indeed the critical Ni concentration for $T_c = 0$ is above 4%, much higher than the critical Zn concentration. It thus indicates that the *itinerancy* of the Cu $3d$ holes and the free carriers is crucial to the high- T_c superconductivity.

To study further the T_c suppression due to Zn doping, it is worthwhile to examine the correlation between the superconductivity and normal-state resistivity. In the normal state, the resistivity of the high- T_c oxides can be approximately described by the following relation:

$$\rho = \rho_0 + \rho(x) + \alpha(x)T, \quad (1)$$

where ρ_0 is the residual resistivity due to the non-Zn defects (e.g., grain boundary, dislocation, point defects, etc.), $\rho(x)$ is the residual resistivity due to impurity scattering induced by Zn, and the $\alpha(x)T$ term is the temperature-dependent part of the resistivity, where $\alpha(x)$ is the slope of the resistivity. ρ_0 which exists in every sample can be assumed to remain constant for different Zn doping. The second term can be written as⁴⁴

$$\rho(x) = \frac{m^*}{ne^2\tau} = \frac{4\pi v_F}{\omega_p^2 l}, \quad (2)$$

where $1/\tau$ is the elastic scattering rate between electron and impurity, l is the associated mean free path, n is the carrier concentration, m^* is the effective mass, v_F is the Fermi velocity, and $\omega_p = (4\pi ne^2/m^*)^{1/2}$ is the plasma frequency. $1/\tau$ is proportional to the impurity concentration.⁴⁴ In Fig. 5, we present the residual resistivity [$\rho_0 + \rho(x)$] extrapolated from the normal state resistivity to $T = 0$ K as a function of the Zn impurity content. The data can be well described by a straight line. The linear relationship between the residual resistivity and impurity content is consistent with the result expected from impurity scattering mechanism.⁴⁴ This indicates that the Zn impurities are uniformly distributed in the samples. As the Zn concentration is reduced to zero, the residual resistivity intercepts at a finite value ρ_0 due to the existence of the

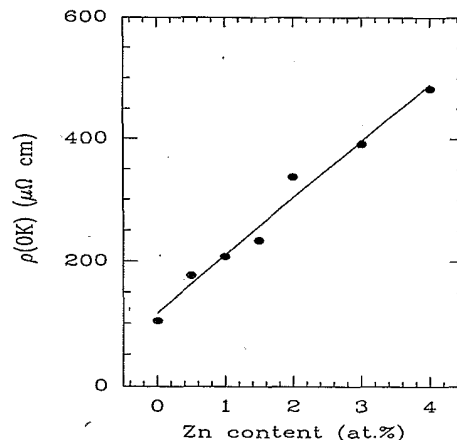


FIG. 5. Variation of residual resistivity due to impurity scattering with Zn content. The straight line is the result of a least square fit to the data. The residual resistivities were obtained from extrapolating normal-state resistivity to $T = 0$ K.

intrinsic structural defects.

In conventional isotropic superconductors, magnetic impurities have a large effect on T_c because of the magnetic pair-breaking mechanism.^{26,27} However, nonmagnetic impurities have no effect on T_c of an isotropic superconductor.^{45,46} In the high- T_c oxides, both magnetic (e.g., Fe, Co) and nonmagnetic (e.g., Zn) impurities suppress T_c greatly, of which nonmagnetic Zn affect the T_c the most.^{3,4,17-20} Coffey and Cox⁴⁷ have calculated the suppression of T_c due to nonmagnetic disorder in the resonating-valence-bond (RVB) model. They have found that nonmagnetic disorder is detrimental to T_c in this model, and the nonmagnetic pair-breaking effect results from the energy dependence of the order parameter over the energy band where pairing takes place. Because of this result, the effect of Zn on T_c has been attributed to the disorder by Coffey and Cox,⁴⁷ and others.¹⁹ According to the model, the value of T_c will be reduced to half of its original value T_{c0} , when the mean free path due to disorder decreases to half of the coherence length. Using a coherence length of 20 Å for the 2:1:4 compound,⁴⁷ Coffey and Cox estimated that T_c will be reduced to half of its original value T_{c0} for an increase in $\rho(x)$ of 1000 $\mu\Omega$ cm due to disorder.

Figure 6 shows the correlation between T_c and residual resistivity $\rho(x)$ in the Zn-doped 2:1:4 system. Indeed, the value of T_c decreases with increasing resistivity. However, even when T_c is completely suppressed at $x=0.021$, the resistivity due to impurity scattering increases only by an amount of 250 $\mu\Omega$ cm. Such an increase in resistivity should reduce T_c by no more than 10 K in Coffey and Cox's estimation.⁴⁷ One can also calculate the mean free path from relation (2), if the parameters v_F and ω_p are known. Gurvitch and Fiory⁴⁸ have obtained the v_F and ω_p for the 2:1:4 compound ($v_F \approx 0.95 \times 10^7$ cms⁻¹, $\hbar\omega_p \approx 0.4$ eV from resistivity and 0.85 eV from penetration depth). Using the v_F and the average value $\hbar\omega_p \approx 0.63$ eV, we have calculated the mean free path ac-

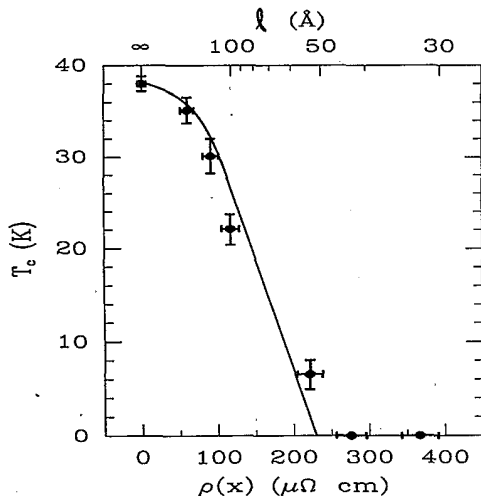


FIG. 6. Superconducting transition temperature (T_c) vs residual resistivity [$\rho(x)$]. The upper scale is the mean free path (l) associated with impurity scattering. l was calculated from relation (2).

ording to relation (2), and the results are shown as the upper scale in Fig. 6. When T_c is reduced to 0 K ($x=0.021$), the mean free path due to disorder is reduced to 50 Å which is twice as large as the coherence length. Such a sizable mean free path should not drastically change T_c in the theory of Coffey and Cox.⁴⁸ On the other hand, the mean free path associated with disorder is not large enough to completely rule out the possibility of disorder-induced pair-breaking effect. However, we feel it is inadequate to attribute the suppression of T_c to the effect of disorder alone, because as will be shown later doping with Zn seems to have a profound effect on the dynamical mechanism leading to high- T_c superconductivity.

Another important quantity to superconductivity is the slope of the resistivity (α), which may provide information about the coupling strength between the carriers and the excitations in a system.⁴⁹ The correlation between T_c and $d\rho/dT$ at room temperature in the Zn-doped 2:1:4 system is shown in Fig. 7. There exists a critical $(d\rho/dT)_c \approx 4$ $\mu\Omega$ cm/K above which the system becomes superconducting, and then T_c increases monotonically with $d\rho/dT$. A saturation in T_c is seen at larger $d\rho/dT$ values.

We first consider the case in which the normal-state resistivity is caused by an inelastic scattering process,^{48,49-52} $\rho = (4\pi/\omega_p^2)(1/\tau_{in})$. For example, in electron-boson scattering, $\hbar\tau_{in}^{-1} \approx 2\pi\lambda k_B T$, for $k_B T \geq \hbar\omega_0$ (characteristic boson energy). Therefore, the slope of the linear temperature dependence of resistivity gives a measure of the coupling strength (λ) between electrons and other excitations. With λ , one can compute T_c according to the McMillan formula⁵³

$$T_c = \Theta \exp \left\{ - \left[\left(\frac{1}{1 + \lambda} \right) - \mu^* \right]^{-1} \right\}, \quad (3)$$

where μ^* is an adjustable parameter (of the order of 0.1-0.2) which represents the Coulomb repulsion. Qualitatively, the above equation provides the general trend in Fig. 7. Specially, it gives a critical $\lambda_c(\mu^*)$ value below which superconductivity will not occur, consistent with the

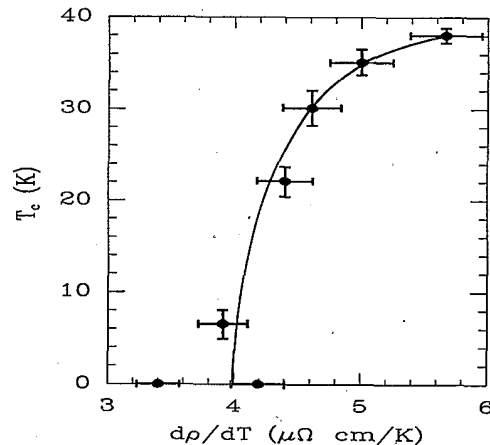


FIG. 7. Correlation between T_c and the slope ($d\rho/dT$) of the resistivity. The experimental error in $d\rho/dT$ is about $\pm 5\%$.

existence of a critical slope of the resistivity in Fig. 7. Quantitatively, however, it would be difficult to fit the data in Fig. 7 to Eq. (3), because of the lack of knowledge on how to extract λ from $d\rho/dT$.

Anderson and Zou⁵⁰ have investigated the normal-state transport in the RVB model. They argue that the conduction in the Cu-O₂ planes is an *elastic* scattering process between the charged bosons (holons) and the spin fermions (spinons). From the Drude formula, they obtained the resistivity in the plane

$$\rho_{ab} = \frac{m_B^* \pi(U/t)}{32\hbar \Delta n e^2} T, \quad (4)$$

where m_B^* is the holon effective mass, n is the carrier density, and Δ is a constant ($4/\pi^2$). The resistivity along the c axis (ρ_c) is very large and has a $1/T$ dependence.⁵⁴ In polycrystalline samples, if $\rho_{ab} \ll \rho_c$, an effective-medium model⁴⁸ leads to a correction factor of $\rho/\rho_{ab} = 2$. Relation (4) indicates $d\rho/dT$ is proportional to $m_B^*/n(U/t)$. Since n does not change with the Zn²⁺ doping and m_B^* is proportional to t^{-1} , $d\rho/dT$ is therefore proportional to $1/J (=U/t^2)$. Thus, $d\rho/dT$ would scale with $1/J$, i.e., doping with Zn would increase J . Figure 7 then becomes a superconducting phase diagram which shows the dependence of T_c on J . There exists a critical value of J for the appearance of superconductivity, and small J is favorable for high T_c . However, Zn is expected to reduce the hopping parameter t , hence, the value of J . Therefore, the observed relation between $d\rho/dT$ and J in the Zn-doped samples seems to be inconsistent with the prediction of Eq. (4). On the other hand, the reduction of T_c in the

Zn-doped samples is consistent with the prediction of the RVB theory^{34-37,55} In the mean-field approximation of RVB theory, T_c scales with J as observed in our study.

V. CONCLUSIONS

Doping Zn ions into the Cu site of the La_{1.85}Sr_{0.15}CuO₄ compound affects superconductivity detrimentally, even though the carrier concentration remains approximately unchanged. Nonmagnetic pair-breaking mechanism induced by disorder alone cannot adequately account for the deleterious effect of Zn on T_c . The filling of the local Cu $d_{x^2-y^2}$ state due to the full d band of Zn ions significantly affects the superconducting mechanism. As a result of a nearly constant carrier concentration, a metal-insulator transition is absent near the critical Zn doping level for the disappearance of superconductivity. The value of T_c is found to correlate with the slope of the normal state resistivity. The change of the slope is mainly resulted from the change in the scattering rate. In both the inelastic and elastic scattering processes, the scattering rate is related to various fundamental parameters such as coupling strength λ . Our result shows that T_c can be correlated with these parameters if the nature of the scattering process is known.

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¹See e.g., *Theories of High Temperature Superconductivity*, edited by J. W. Halley (Addison, Redwood City, 1988).

²See e.g., *High-Temperature Superconductors*, edited by B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller (Materials Research Society, Pittsburgh, 1988).

³Gang Xiao, M. Z. Cieplak, D. Musser, A. Gavrin, F. H. Streitz, C. L. Chien, J. J. Rhyne, and J. A. Gotaas, *Nature (London)* **328**, 512 (1988).

⁴Gang Xiao, M. Z. Cieplak, A. Garvin, F. H. Streitz, A. Bakhshai, and C. L. Chien, *Phys. Rev. Lett.* **60**, 1446 (1988).

⁵M. Maeda, Y. Tanaka, M. Fukutomi, and T. Asaro, *Jpn. J. Appl. Phys.* **27**, L209 (1988).

⁶C. W. Chu, J. Bechtold, L. Gao, P. H. Hor, Z. J. Huang, R. L. Meng, Y. Y. Sun, Y. Q. Wang, and Y. Y. Xue, *Phys. Rev. Lett.* **60**, 941 (1988).

⁷Z. Z. Sheng and A. M. Hermann, *Nature (London)* **332**, 138 (1988).

⁸J. M. Tarascon, Y. Le Page, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon, G. W. Hull, M. Giroud, and D. M. Hwang, *Phys. Rev. B* **37**, 9382 (1988).

⁹M. A. Subramanian, J. C. Calabrese, C. C. Torardi, J. Gopalakrishnan, T. R. Askew, R. B. Flippen, K. J. Morrissey, U. Chowdhry, and A. W. Sleight, *Nature (London)* **332**, 420 (1988).

¹⁰J. D. Jorgensen, H.-B. Schüttler, D. G. Hinks, D. W. Capone II, K. Zhang, M. B. Brodsky, and D. J. Scalapino, *Phys. Rev.*

Lett. **58**, 1024 (1987).

¹¹D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinya, and H. E. King, Jr., *Phys. Rev. Lett.* **58**, 2802 (1987).

¹²N. P. Ong, Z. Z. Wang, J. Clayhold, J. M. Tarascon, L. H. Greene, and W. R. McKinnon, *Phys. Rev. B* **35**, 8807 (1987).

¹³M. F. Hundley, A. Zettl, A. Stacy, and M. L. Cohen, *Phys. Rev. B* **35**, 8800 (1987).

¹⁴A. Fujimori, E. Takagama-Muromachi, Y. Uchida, and B. Okai, *Phys. Rev. B* **35**, 8814 (1987).

¹⁵P. Steiner, S. Hufner, V. Kinsinger, I. Sander, B. Siegwart, H. Schmitt, R. Schulz, S. Junk, G. Schwitzgebel, A. Gold, C. Politis, H. P. Müller, R. Hoppe, S. Kemmler-Sack, and C. Kunz, *Z. Phys. B* **69**, 449 (1988).

¹⁶N. Nücker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Temmerman, *Phys. Rev. B* **37**, 5158 (1988).

¹⁷Gang Xiao, F. H. Streitz, A. Gavrin, Y. W. Du, and C. L. Chien, *Phys. Rev. B* **35**, 8782 (1987).

¹⁸Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. Aoki, K. Hoshino, A. Minami, and T. Fujita, *Nature (London)* **328**, 512 (1987).

¹⁹J. M. Tarascon, L.H. Greene, P. Barboux, W. R. McKinnon, G. W. Hull, T. P. Orlando, K. A. Delin, S. Foner, and E. J. McNiff, Jr., *Phys. Rev. B* **36**, 8393 (1987).

²⁰T. Hasegawa, K. Kishio, M. Aoki, N. Ooba, K. Kitazawa, K. Fueki, S. Uchida, and S. Tanaka, *Jpn. J. Appl. Phys.* **26**, L337 (1987).

²¹A. F. Wells, *Structural Inorganic Chemistry* (Clarendon, Ox-

- ford, 1975), p. 259.
- ²²L. E. Orgel, *An Introduction to Transition-Metal Chemistry: Ligand-Field Theory* (Methuen, London, 1960).
- ²³W. Kang, H. J. Schulz, D. Jerome, S. S. P. Parkin, J. M. Bas-sat, and Ph. Odier, *Phys. Rev. B* **37**, 5132 (1988).
- ²⁴C. L. Chien, Gang Xiao, M. Z. Cieplak, D. Musser, J. J. Rhyne, and J. A. Gotaas, in *Superconductivity and Its Appli-cations*, edited by H. S. Kwok and D. T. Shaw (Elsevier, New York, 1988), p. 110.
- ²⁵ $T_c \sim (x_c = x)^{1/2}$ is a functional dependence predicted by the Abrikosov-Gor'kov theory (Ref. 26) of the impurity pair-breaking effect in conventional superconductors.
- ²⁶A. A. Abrikosov and L. P. Gor'kov, *Zh. Eksp. Teor. Fiz.* **39**, 1781 (1960) [*Sov. Phys. JETP* **12**, 1243 (1961)].
- ²⁷P. B. Allen and B. Mitrovic, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1982), Vol. 37, p. 1.
- ²⁸M. W. Shafer, T. Penney, and B. L. Olson, *Phys. Rev. B* **36**, 4047 (1987).
- ²⁹D. G. Hinks, B. Dabrowski, K. Zhang, C. U. Segre, J. D. Jor-gensen, L. Soderholm, and M. A. Beno, in *High-Temperature Superconductors*, edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller (Materials Research Society, Pittsburgh, 1988), p. 9.
- ³⁰R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, *Nature (London)* **329**, 423 (1987); *Phys. Rev. B* **36**, 5719 (1987).
- ³¹Z. Z. Wang, J. Clayhold, N. P. Ong, J. M. Tarascon, L. H. Greene, W. R. McKinnon, and G. W. Hull, *Phys. Rev. B* **36**, 7222 (1987).
- ³²A. W. Sleight, in *High-Temperature Superconductors*, edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller (Materials Research Society, Pittsburgh, 1988), p. 3.
- ³³A. Aharony, R. J. Birgeneau, A. Coniglio, M. A. Kastner, and H. E. Stanley, *Phys. Rev. Lett.* **60**, 1330 (1988).
- ³⁴P. W. Anderson, *Science* **235**, 1196 (1987).
- ³⁵Z. Zou and P. W. Anderson, *Phys. Rev. B* **37**, 627 (1988).
- ³⁶X. G. Wen and R. Kan, *Phys. Rev. B* **37**, 595 (1988).
- ³⁷J. M. Wheatley, T. C. Hsu, and P. W. Anderson, *Phys. Rev. B* **37**, 5897 (1988).
- ³⁸J. R. Schrieffer, X. G. Wen, and S. C. Zhang, *Phys. Rev. Lett.* **60**, 944 (1988).
- ³⁹V. J. Emery, *Phys. Rev. Lett.* **58**, 2794 (1987).
- ⁴⁰C. M. Varma, S. Schmitt-Rink, and E. Abrahams, *Solid State Commun.* **62**, 681 (1987).
- ⁴¹J. Hirsch, S. Tang, E. Loh, and D. Scalapino, *Phys. Rev. Lett.* **60**, 1668 (1988).
- ⁴²Z. Tesanovic, A. R. Bishop, and R. L. Martin, *Solid State Commun.* **68**, 337 (1988).
- ⁴³C. M. Varma, in *Proceedings of the Schloss Mautendorf Meeting on High Temperature Superconductivity*, edited by H. W. Weber (Plenum, New York, in press).
- ⁴⁴J. M. Ziman, *Principles of the Theory of Solids* (Cambridge Univ. Press, Cambridge, 1979), p. 220.
- ⁴⁵P. W. Anderson, *J. Phys. Chem. Solids* **11**, 26 (1959).
- ⁴⁶A. A. Abrikosov and L. P. Gor'kov, *Zh. Eksp. Teor. Fiz.* **35**, 1558 (1958) [*Sov. Phys. JETP* **8**, 1090 (1959)].
- ⁴⁷L. Coffey and D. L. Cox, *Phys. Rev. B* **37**, 3389 (1988).
- ⁴⁸M. Gurvitch and A. T. Fiory, *Phys. Rev. Lett.* **59**, 1337 (1987).
- ⁴⁹P. A. Lee and N. Read, *Phys. Rev. Lett.* **58**, 2691 (1987).
- ⁵⁰P. W. Anderson and Z. Zou, *Phys. Rev. Lett.* **60**, 132 (1987).
- ⁵¹R. Micnas, J. Ranninger, and S. Robaszkiewicz, *Phys. Rev. B* **36**, 4051 (1987).
- ⁵²P. B. Allen, W. E. Pickett, and H. Krakauer, *Phys. Rev. B* **37**, 7482 (1988).
- ⁵³W. L. McMillan, *Phys. Rev.* **167**, 331 (1968).
- ⁵⁴S. W. Tozer, A. W. Kleinsasser, T. Penney, D. Kaiser, and F. Holtzberg, *Phys. Rev. Lett.* **59**, 1768 (1987).
- ⁵⁵G. Baskaran, Z. Zou, and P. W. Anderson, *Solid State Com-mun.* **63**, 973 (1987).