

Superconducting and normal-state properties of $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$

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We have studied the superconducting and normal-state properties of $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ ($0 < x < 0.03$). T_c decreases essentially linearly with the Ga content and reaches 0 K for only 2.2 at. % of Ga, while the carrier concentration reduces by approximately 20% in the doping range studied. The T_c suppression is analogous to that observed by us in the $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ system. The disappearance of superconductivity is most likely due to the complete filling of the Cu local 3d band and not due to the pair-breaking effect induced by nonmagnetic disorder. The Ga doping induces localization of the Cu 3d holes as evidenced from the susceptibility measurements. The normal-state resistivity exhibits a minimum followed by a logarithmic increase as the temperature is lowered. The temperature of the minimum increases linearly with the Ga content. The logarithmic upturn in the resistivity indicates that neither an activation process nor variable range hopping is responsible for the low-temperature electronic transport. Among two other possible mechanisms, the Kondo effect and effect of localization and correlation, the Kondo effect gives a much better description of the temperature dependence of the resistivity in the whole temperature range (4–300 K) and for all of the samples.

I. INTRODUCTION

Since the discovery of high- T_c superconductors understanding of their structures and properties has been rapidly advancing due to the vigorous efforts of both experimentalists¹ and theorists.² It is now well known that a proper concentration of charge carriers is essential for sustaining high- T_c superconductivity. The carrier concentration may be changed by adjusting the oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (1:2:3 compound)³ or by the substitution of the Sr^{2+} ions for La^{3+} in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (2:1:4 compound).⁴ The nature of the superconducting pairing mechanism itself is much less clear. Some insight was provided by the discovery of the long-range antiferromagnetic ordering in the insulating parent compounds $\text{La}_2\text{CuO}_{4-\delta}$ (Refs. 5 and 6) and $\text{YBa}_2\text{Cu}_3\text{O}_6$ (Ref. 7) as well as in the superconducting oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$.⁸ The presence of strongly correlated spin fluctuations in both $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (Ref. 9) and $\text{La}_2\text{CuO}_{4-\delta}$ (Refs. 6 and 9) has also been established. All of these experimental results indicate that some kind of exchange interactions within the CuO_2 planes may play a role in the superconducting pairing mechanism.

One way to probe the superconducting mechanism is to substitute Cu^{2+} ions by transition metals or other elements. Many experimental studies performed on both $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Refs. 10–13) and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (Refs. 11, 14–16) reveal that such substitutions suppress T_c to varying degrees. Most clear in this respect is the study on the substitution of the nonmagnetic Zn (Refs. 12 and 13) and Ga ions¹² into $\text{YBa}_2\text{Cu}_3\text{O}_7$. Ga^{3+} ions with a 3d¹⁰ configuration substitute for Cu in the Cu-O chains. This lowers T_c to 70 K when the level of Ga content approaches 10 at. %. Zn^{2+} (3d¹⁰), on the other hand, substitutes for Cu in the Cu-O₂ planes and destroys supercon-

ductivity far more effectively: T_c is completely suppressed with 13 at. % of Zn. Recently, we have completed a detailed study on the Zn substitution into $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$,¹⁶ where the effect of Zn substitution on T_c is even more drastic. The $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ system ceases to be superconducting for $x=0.02$ while maintaining approximately the same carrier concentration. It is clear that the Zn substitution affects the superconducting pairing mechanism itself without lowering the carrier concentration. As we have shown in Ref. 16 the strong suppression of T_c cannot be explained solely by the pair-breaking effect due to nonmagnetic disorder. Rather it is the complete filling of the local Cu 3d band that affects superconductivity so severely.

In the present work we have studied for the first time the effect of Ga substitution on superconductivity and normal-state properties of the 2:1:4 compound. The result is remarkably different from the one seen in $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_7$ in that Ga doping affects superconductivity in the 2:1:4 compound detrimentally, while it only has a small effect on T_c in the 1:2:3 compound. In fact, T_c is suppressed in $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ in a fashion similar to the one observed in the $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ system. The implication of this finding will be one of the topics of this paper. We will present interesting behaviors in the normal-state properties of the Ga-doped 2:1:4 compound. Among them a logarithmic temperature dependence of the resistivity in the low-temperature region is particularly intriguing. Such a behavior, which has not been observed or claimed in any other study, provides valuable insight into the electronic transport mechanism of the high- T_c superconductors. In addition, the influence of Ga doping on the lattice parameters, magnetization, and susceptibility of the 2:1:4 compound will be presented and discussed.

II. EXPERIMENTAL DETAILS

Ceramic $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ samples with $0 \leq x \leq 0.03$ were prepared by thoroughly mixing appropriate proportions of high purity La_2O_3 , SrCO_3 , CuO , and Ga_2O_3 powders, pressing them into pellet forms and sintering them in an oxygen atmosphere for a total period of 150 h. Three intermediate grindings for homogenization were used. The annealing temperatures were 1000, 1000, 1050, and 1050°C. The final cooling rate was 3°C/min.

The θ - 2θ x-ray diffraction spectrum of the samples was checked with a Philips APD 3720 powder diffractometer. The quality of the samples was very good, without any detectable impurity phases. The shapes of the diffraction peaks were fitted by a modified Gaussian function. The lattice parameters were then calculated from the positions of at least 22 diffraction peaks using a standard least-squares reduction method.

Resistivity versus temperature was measured using a standard four-probe method. The temperature dependence of the magnetization was measured with a SQUID magnetometer in both zero-field-cooled and field-cooled modes.

III. EXPERIMENTAL RESULTS

A. Lattice parameters

The θ - 2θ x-ray diffraction spectrum reveals that all of the samples are single phase with a tetragonal perovskite structure of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. The lattice parameters a and c depend linearly on the Ga content as displayed in Fig. 1. The a parameter increases by about 0.1% and c decreases by about 0.17% in the composition range studied. Such a behavior, similar to those observed in $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ni}_x)\text{O}_4$ (Ref. 15) and $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$,^{11,16} can be explained by the reduction of the local Jahn-Teller distortion. Due to the $3d^9$ electronic

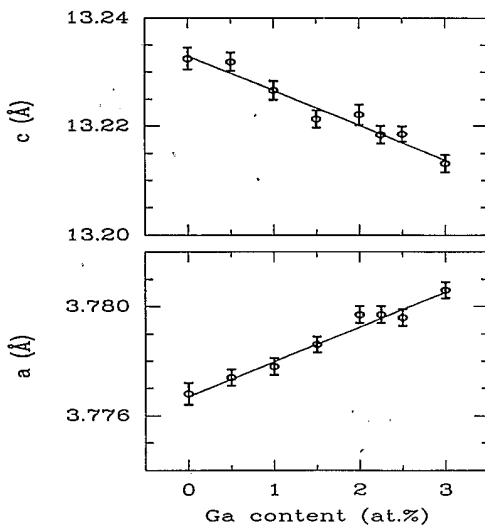


FIG. 1. The lattice parameters a and c vs Ga content in $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$.

configuration of the Cu^{2+} ions, the Jahn-Teller effect is present in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. The Cu-O bond in the CuO_2 plane is shorter than the one perpendicular to the plane (1.894 and 2.428 Å, respectively¹⁷). On the other hand, Ga ions with a well-defined valence of 3+ and in the $3d^{10}$ configuration do not exhibit Jahn-Teller effect. Therefore, the difference in the bond lengths is reduced in the octahedron surrounding a Ga impurity. This causes the increase of the a and the decrease of the c lattice parameters.

B. Resistivity

The temperature dependence of the resistivity for a series of Ga-doped samples (doping level: 0–3 at.%) is shown in Fig. 2. The resistivity increases steadily with the Ga doping level. For samples doped with more than 1 at. % of Ga, resistivity has a well-defined minimum followed by an upturn at low temperatures. Ga has one more valence electron than Cu in the 2:1:4 compound. Doping with Ga therefore reduces the free-hole concentration. If we assume that one Ga ion removes one free hole, the hole concentration in $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ is $(0.15 - x)/V$, where V is the volume of the unit cell. The ratio of the hole concentration in Ga-doped samples to the concentration in the undoped 2:1:4 compound n_x is then equal to $(0.15 - x)/0.15$. For the sample with $x = 0.03$, the relative change in the hole concentration $1 - n_x$ amounts to 20%. In Fig. 3(a) we plot the room-temperature resistivity multiplied by n_x as a function of the Ga content. Such a “rescaled” room-temperature resistivity still increases with the Ga content, indicating that the increase in the resistivity is not due to the reduction in the carrier concentration alone.

The high-temperature resistivity data in the region from 200 to 300 K are essentially linear in T . We have attempted to fit those data with the following relation:

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

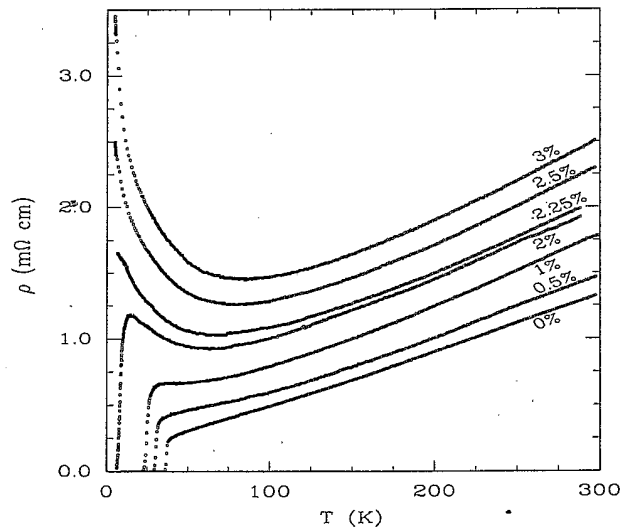


FIG. 2. The temperature dependence of resistivity for samples with various Ga content (in at. %).

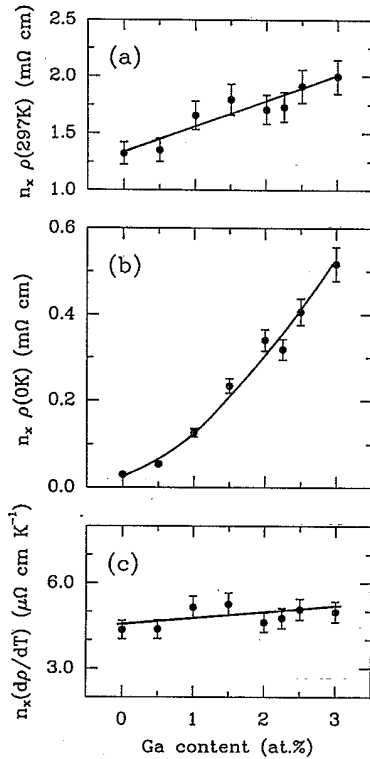


FIG. 3. (a) The room-temperature resistivity (at $T=297\text{ K}$) multiplied by $n_x = (0.15 - x)/0.15$ (see text) as a function of Ga content. (b) Residual resistivity $\rho(0\text{ K}) = \rho_0 + \rho(x)$, as obtained from the fit of Eq. (1) to the resistivity data in the 200–300 K temperature range, multiplied by n_x , as a function of Ga content. (c) The resistivity slope $d\rho/dT$ obtained from the same fit, multiplied by n_x , as a function of Ga content.

where $\rho(x)$ is the residual resistivity due to impurity scattering induced by Ga, ρ_0 is the residual resistivity due to other defects, and $\alpha(x)$ is the slope of the resistivity $d\rho/dT$. The obtained values of $\rho(0\text{ K}) = \rho_0 + \rho(x)$ and $\alpha(x)$ are shown in Figs. 3(b) and 3(c), again rescaled by n_x . The rescaled residual resistivity increases nonlinearly with Ga doping and the rescaled slope of the resistivity is almost constant versus Ga content. Those results differ from the ones observed by us in the Zn-doped 2:1:4 compound with constant carrier concentration,¹⁶ where the residual resistivity is linearly dependent on Zn doping and the slope decreases with Zn content. It should be pointed out that relation (1) is strictly adequate for the description of the high-temperature resistivity only in low Ga-doped samples (less than 1 at. %). For higher doping levels the temperature dependence of resistivity is increasingly nonlinear even at high temperatures. However, the above crude analysis provides an upper limit of the residual resistivity in the Ga-doped 2:1:4 compound which will be useful in the discussion below.

Let us now turn our attention to the superconducting properties of the $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ system. The values of T_c as a function of the doping level for both Ga- and Zn-doped 2:1:4 compounds are shown in Fig. 4. The bars represent the superconducting transition width (90% to 10% resistivity drop), and the points are midpoint

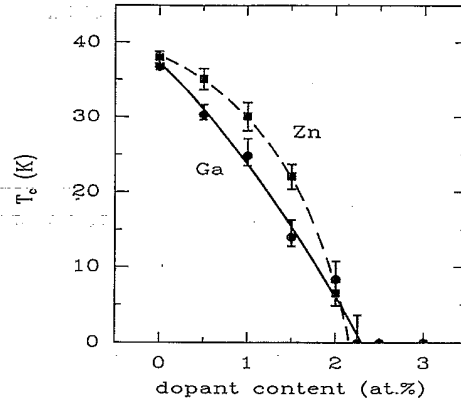


FIG. 4. Variation of T_c with Ga content in $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ (circles) and with Zn content in $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ (squares). The bars represent 90–10% resistive superconducting transition, and the points are the midpoint resistive transition temperatures. The curves are guides to the eye.

resistive transition temperatures. The T_c suppression is very similar for both systems, and it is very effective. T_c drops to zero at a doping level of only 2.1–2.2 at. %. There is a slight difference in the initial slope of the T_c vs x dependence resulting from the decrease of carrier concentration in the Ga-doped samples. However, what we would like to stress here is the striking similarity with which both Zn and Ga suppress the superconductivity. The deleterious effect of Zn on superconductivity in both $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$, is well known to be the strongest among all the 3d transition metal and some of the *sp* elements investigated so far, despite the fact that Zn does not carry a magnetic moment.^{10–16} Ga was found to substitute the Cu(1) chain sites in $\text{YBa}_2\text{Cu}_3\text{O}_7$, its effect on T_c being very small.¹² The results presented here show that Ga can suppress T_c just as effectively as Zn if it is substituted into the Cu-O₂ planes. This finding further reinforces our earlier conclusion¹² that the integrity of the planes is much more important than that of the chains in sustaining high- T_c superconductivity. The fact that superconductivity disappears in the $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ and in $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ at almost the same doping level proves that such substitutions affect the pairing mechanism. The change in the carrier concentration in the Ga-doped 2:1:4 compound, although slightly affecting the shape of the $T_c(x)$ curve, is not the main reason for the observed drastic T_c suppression.

C. Magnetization and susceptibility

We have also investigated the magnetic properties of the $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ system. Examples of the low-temperature magnetization in both the zero-field-cooled and field-cooled modes under a magnetic field of 10 Oe (for two samples: 0.5% and 1.5 at. % of Ga) are displayed in Fig. 5. The magnitude of the Meissner and diamagnetic effects reduces significantly with increasing Ga content. The values of T_c obtained from the magneti-

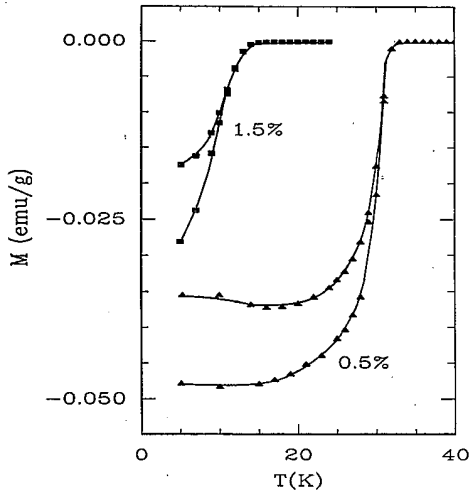


FIG. 5. Magnetization as a function of temperature in the zero-field-cooled (increasing temperature) and field-cooled (decreasing temperature) modes for two samples with Ga content of 0.5 and 1.5 at. %.

zation measurements are in good agreement with those from resistivity measurements.

In Fig. 6 the temperature dependence of the susceptibility measured in a field of 5 kOe is presented. For clarity, only the results of three samples (0, 2, and 3 at. % of Ga) are shown. The normal-state susceptibility of the samples remains relatively constant above $T=250$ K. But as the Ga concentration is increased, the susceptibility reduces gradually as shown in the inset of Fig. 6. The relative reduction in the high-temperature susceptibility [$\chi(3\%) - \chi(0\%)$]/ $\chi(0\%)$ is equal to 21% in the investigated range of Ga content. The relative change in the hole concentration, assuming that substitution of one Ga ion removes one free hole, is also equal to 20% for the same Ga-doping range. This result strongly indicates that the

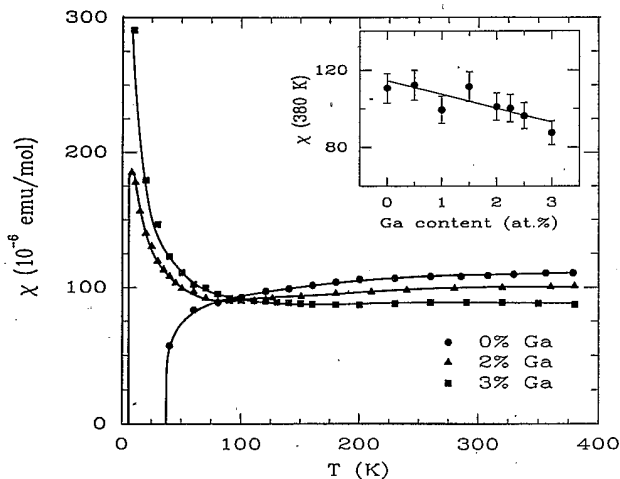


FIG. 6. The temperature dependence of the susceptibility for samples with Ga content of 0, 2, and 3 at. %. The inset shows the values of susceptibility (in units of 10^{-6} emu/mol) measured at the temperature 380 K, as a function of the doping level.

change in the high-temperature susceptibility originates from the variation in the free-carrier concentration. We did not measure directly the oxygen content in our samples. However, since the Ga-doping level is rather small, the oxygen content should not be affected much. The observed change in the high-temperature susceptibility suggests that this is indeed the case. In the low-temperature region an upturn in the susceptibility is induced by the Ga doping. With increasing Ga content this upturn increases steadily. Such a behavior may seem surprising at first glance because Ga^{3+} is a nonmagnetic ion. But, as will be discussed in Sec. IV, the local moment induced by the Ga doping actually resides on the Cu sites.

IV. DISCUSSION

A. The T_c suppression

In our view, the deleterious effect of Ga and Zn on high- T_c cuprate superconductors is an important fundamental question. There are no other known dopants that cause a stronger suppression of T_c . A possible cause proposed in the literature is the pair-breaking effect due to nonmagnetic disorder. This effect in high- T_c superconductors has been studied by Coffey and Cox.¹⁸ They have found that the value of T_c should be reduced to half of its original value, when the mean-free path due to disorder (l) decreases to half of the superconducting coherence length. Using a coherence length of 20 Å for the 2:1:4 compound, Coffey and Cox estimated that a 50% T_c reduction will require an increase in the residual resistivity of about 1000 $\mu\Omega$ cm. We have previously shown that the increase of the residual resistivity due to disorder in the Zn-substituted samples is only about 250 $\mu\Omega$ cm when T_c drops to 0 K.¹⁶ We can make a similar comparison in the Ga-doped system. From the analysis in Sec. III we have obtained an upper limit on the resistivity due to disorder, $\rho(x) = \rho(0 \text{ K}) - \rho_0$. The correlation between T_c and $\rho(x)$ is presented in Fig. 7. T_c is completely suppressed when the residual resistivity increases to about 400 $\mu\Omega$ cm, a value much smaller than the critical value estimated by Coffey and Cox. The upper scale in Fig. 7 displays the values of the mean free path due to disorder (l) calculated from the expression¹⁹

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

where v_F is the Fermi velocity, $\omega_p = [(4\pi n e^2)/m^*]^{1/2}$ is the plasma frequency, m^* and n are the effective mass and the carrier concentration, respectively. We have assumed that $\hbar\omega_p(x) = \sqrt{n_x} \hbar\omega_p(x=0)$ and used $v_F = 0.95 \times 10^7 \text{ cm s}^{-1}$ and $\hbar\omega_p(x=0) = 0.63 \text{ eV}$.²⁰ One can see from Fig. 7 that the mean free path due to disorder decreases to about 35 Å when the samples cease to be superconducting. This mean-free-path value is almost twice as high as the superconducting coherence length. Therefore, it is unlikely that the nonmagnetic pair-breaking effect is the dominant reason for the T_c suppression in Ga-doped $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$.

Most likely, the strong effect on T_c results from the

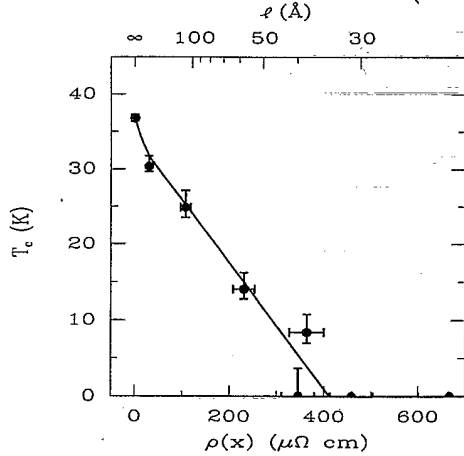


FIG. 7. Superconducting transition temperature T_c vs the upper limit of the residual resistivity due to Ga-induced disorder $\rho(x) = \rho(0 \text{ K}) - \rho_0$ obtained from the fit of Eq. (1) to the resistivity data in the 200–300 K temperature range. ρ_0 is the residual resistivity of the 0 at. % sample. The upper scale is the mean free path due to disorder, l , calculated from Eq. (2).

same closed-shell $3d^{10}$ configuration of the Zn^{2+} and Ga^{3+} ions. As we have argued before,¹⁶ the filling of the local Cu $3d$ band prevents both the free carriers and the d holes at the neighboring Cu^{2+} site from hopping into the impurity site. Ni^{2+} with a configuration $3d^8$ does not fill the $3d$ band, and, therefore, has a much weaker effect on superconductivity (T_c drops to zero at a Ni-doping level of more than 4 at. %¹⁵).

B. The Curie-Weiss law

The low-temperature region of the susceptibility for samples with Ga content above 1.5 at. % can be fitted by the Curie-Weiss law of the form

$$\chi = \chi_0 + \frac{Np_{\text{eff}}^2\mu_B^2}{3k_B(T - \Theta)} \quad (3)$$

Here χ_0 is the temperature independent part of the susceptibility, N is the number of magnetic ions, p_{eff} is the effective moment in the units of Bohr magneton μ_B , and Θ is the Curie-Weiss temperature. We have fitted relation (3) to the susceptibility data in the temperature region up to 100 K. The fitted parameter Θ is close to 1 K for all of the samples. In Fig. 8(a) an example of $1/(\chi - \chi_0)$ dependence on the temperature is shown for 3 samples together with the straight lines which represent Eq. (3). The fit is good and the slope of the straight lines changes consistently with Ga content. Assuming that the effective moment resides on the Cu sites, we can extract the p_{eff} values. They are presented in Fig. 8(b). The effective moment is small, equal to $0.14\mu_B$ in the sample with 3 at. % of Ga. It decreases consistently with the decrease of the Ga content. The extrapolation of this dependence to 0% sample does not give a zero effective moment but a value of $(0.03 \pm 0.015)\mu_B$.

The increasing moment is presumably caused by the in-

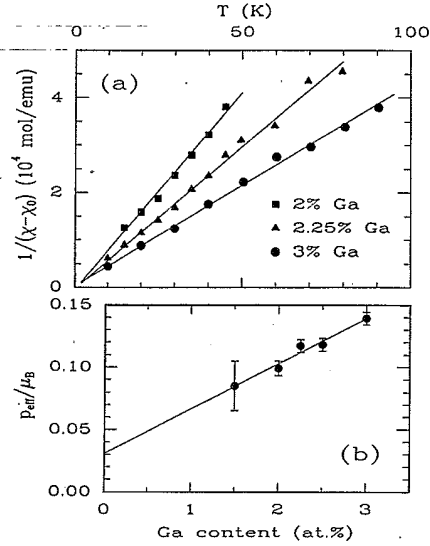


FIG. 8 (a) The inverse of the Curie-Weiss susceptibility $\chi - \chi_0$ vs temperature for 3 samples: 2, 2.25, and 3 at. % of Ga content. Straight lines represent Eq. (3) with the best-fitted parameters. (b) The dependence of the calculated effective moment on the Ga content.

duced localization of Cu $3d$ holes as the Ga concentration grows. This interpretation is also consistent with two other experiments in which similar effects have been observed. Recently we have observed the Curie-Weiss law in the susceptibility of $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$.²¹ In $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$, a jump in the value of the magnetic moment was observed as the Zn-doping level was increased.¹³ This effect was also attributed to the increasing localization of d -holes at the Cu sites.

C. The low-temperature resistivity minimum and upturn

La_2CuO_4 is an anisotropic insulator with a small carrier concentration in the Cu-O planes of the order of $5 \times 10^{19} \text{ cm}^{-3}$.^{22,23} The resistivity in the Cu-O planes displays variable range hopping behavior at low temperatures.²³ The substitution of the divalent Sr^{2+} for La^{3+} in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ creates free holes with a concentration approximately equal to the Sr concentration.⁴ After an insulator-metal transition the samples become increasingly metallic with a linear temperature dependence of resistivity in a wide temperature range above T_c .^{20,24} Mechanisms such as electron-phonon scattering,^{20,25} electron-electron scattering,²⁶ and holon-spinon elastic scattering in the resonating-valence-bond (RVB) theory²⁷ have been proposed to explain the linear temperature dependence of the resistivity. As we have shown earlier, doping of the 2:1:4 compound with Ga affects the normal-state resistivity both in the low- and the high-temperature regions. There is a low-temperature resistivity upturn which increases with the Ga content. Also, in the high-temperature region the dependence of the resistivity becomes increasingly nonlinear. Such a behavior has been observed, to a smaller or larger degree, in many

transition-metal-doped 2:1:4 or 1:2:3 compounds.¹⁰⁻¹⁶ The low-temperature upturn was usually labeled as evidence of semiconducting behavior or localization effects.

Let us first examine the possibility that the resistivity upturn is due to the opening of an energy gap. There are examples in the literature that the resistivity minimum in reduced-dimensionality systems is due to the formation of charge-density waves.²⁸ Although the early suggestions of oxygen-breathing-mode charge-density waves in cuprate oxides²⁹ were not confirmed by recent experiments,³⁰ there are still some indications that mechanical lattice instabilities or spin-density waves may influence the transport properties in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$.³¹ The activation process associated with the opening of an energy gap would result in the temperature dependence of the resistivity of the form $\rho \sim \exp(1/T)$ at low temperatures. In Fig. 9 we plot $\ln(\rho - \rho_l)$ vs $1000/T$, where the values of ρ_l , as described by Eq. (1), have been obtained from the high-temperature part of the resistivity. Clearly the exponential dependence is not found in any of the samples. Therefore, the low-temperature transport is not a simple activation process, and there is no opening of a gap. We have performed a similar analysis assuming variable range hopping conduction as observed in the parent compound La_2CuO_4 .²³ Our analysis indicates that the resistivity upturn is not caused by that mechanism either.

There are other mechanisms which produce resistivity minimum and upturn. One of them is localization and correlation in the presence of disorder in two-dimensional systems. The conductivity due to those effects is given by $D \ln[(T/T_0)]$, where the coefficient D is a sum of the localization term dependent on the dominant scattering mechanism and the Coulomb interaction term.³² We have assumed that the total conductivity has the form

$$\sigma(T) = \sigma_0 + D \ln \left(\frac{T}{T_0} \right), \quad (4)$$

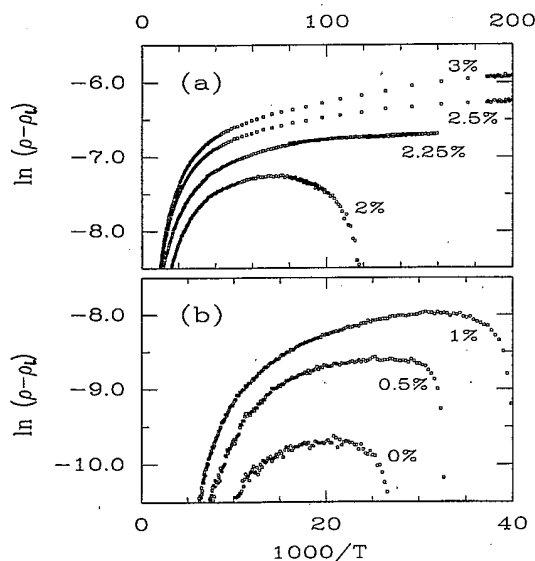


FIG. 9. Logarithm of the nonlinear part of the resistivity $\rho - \rho_l$ as a function of $1000/T$ for samples with different Ga content: (a) samples with 2-3 at. % and (b) samples with 0-1 at. %.

where $\sigma_0 = 1/\rho_l$ and ρ_l can be obtained from the linear fit of the resistivity in the high-temperature range. In Fig. 10 we plot the value $\sigma_0 - \sigma$ as a function of $\ln(T)$. Only for samples with Ga content 0 and 0.5 at. % can the conductivity be described by relation (4) in the temperature region just above T_c . The linear fit shown in Fig. 10 gives the values of $D = 1.23 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ and $2.08 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ and $T_0 = 90$ and 95.4 K for 0 and 0.5 at. % samples, respectively. The logarithmic term in the conductivity increases substantially after substitution of only 0.5 at. % of Ga. When the Ga content is increased to above 0.5 at. % the temperature dependence of $\sigma_0 - \sigma$ no longer follows $\ln(T)$, and the value of $\sigma_0 - \sigma$ decreases. However, this decrease is most likely an artifact due to the assumption that σ at high temperatures is equal to σ_0 . We observe that the high-temperature resistivity is increasingly nonlinear when the Ga content grows. It strongly indicates that for samples with more than 0.5 at. % of Ga the correction to σ_0 is large and that it affects the conductivity even at high temperatures. It should be noted that Eq. (4) was obtained via the perturbation theory and it is valid only in the weak localization limit.³² Therefore, we cannot expect relation (4) to be applicable for the Ga-doping level higher than 0.5 at. %. Unfortunately there is no theoretical prediction for the temperature dependence of the conductivity in the case of strong or intermediate localization.

Another possible explanation for the observed resistivity upturn is the Kondo effect. The Kondo effect was first realized in the case of spin-flip scattering of conduction electrons by magnetic impurities in metallic alloys.³³ There the presence of the s - d exchange interaction introduces an additional term to the resistivity of the form $C \ln(T)$. The constant C is proportional to the s - d exchange integral. The negative sign of C leads to the minimum in the low-temperature resistivity. We have assumed the following temperature dependence of the

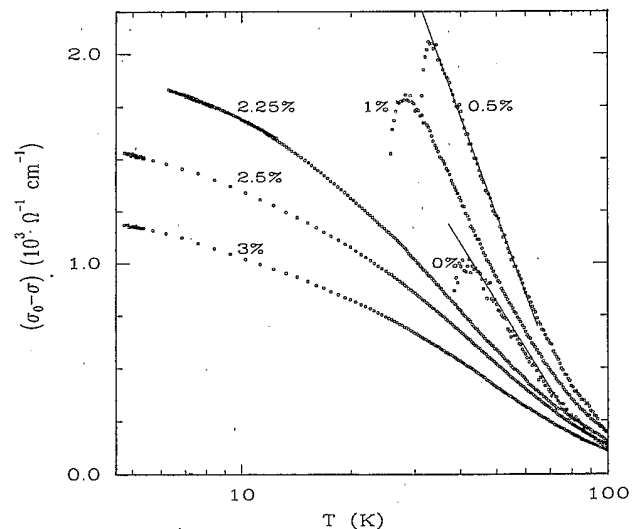


FIG. 10. The correction term to the conductivity $\sigma_0 - \sigma$ as a function of $\ln(T)$. The straight lines display the fit of Eq. (4) to the data for 0 and 0.5 at. % samples.

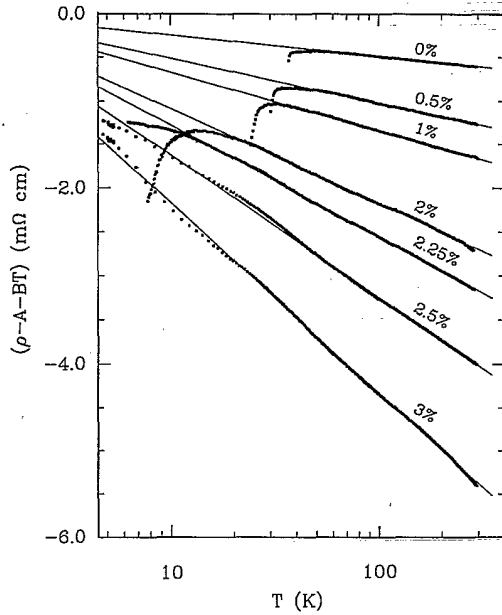


FIG. 11. The dependence of the nonlinear part of the resistivity $\rho - A - BT = -C \ln(T)$ on the $\ln(t)$ [see Eq. (5)]. Lines represent the best fit of Eq. (5) to the experimental data.

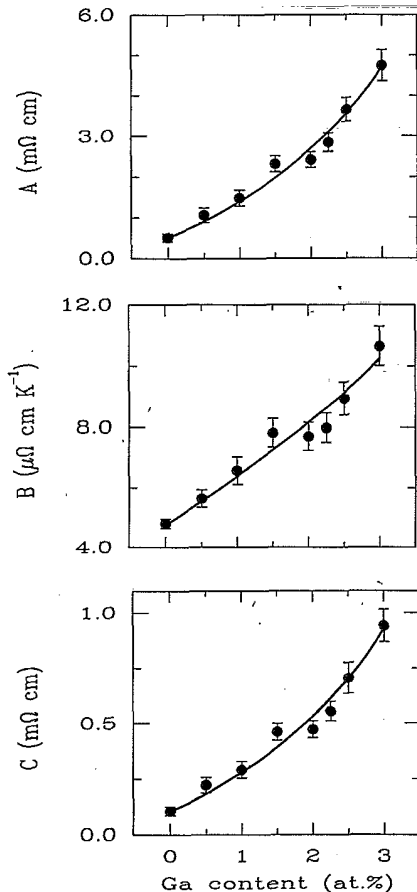


FIG. 12. Variation of the fitted A , B , and C parameters with the Ga content.

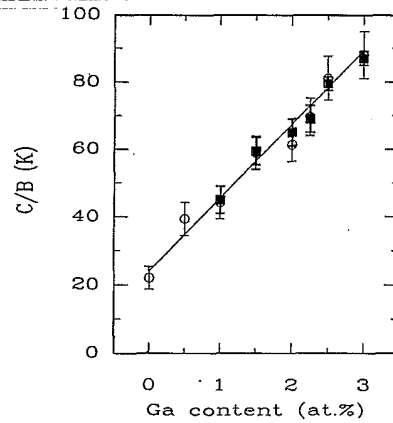


FIG. 13. The ratio C/B as obtained by the fitting (open circles) and experimental values of T_m (filled squares) as a function of the Ga-doping level. Note that the fitted values and the experimental values coincide with each other very well.

resistivity:

$$\rho(T) = A + BT - C \ln(T). \quad (5)$$

From the fit of Eq. (5) to resistivity data in the *whole* temperature range (4.5–300 K) we have obtained the parameters A , B , and C . In Fig. 11 we plot $\rho - A - BT$ versus temperature on the logarithmic scale. Equation (5) describes the experimental results remarkably well for *all* of the samples, including 0 at.% Ga. To the best of our knowledge, this is the first observation of a logarithmic temperature dependence of resistivity in the normal state of a high- T_c superconductor. We believe such a behavior provides an important insight into the electronic transport of cuprate oxides. The dependence of the parameters A , B , and C on Ga content is shown in Fig. 12. Interestingly, C/B is a linear function of the Ga content as shown in Fig. 13. It follows from Eq. (5) that C/B is equal to the temperature T_m , at which the resistivity has a minimum. In Fig. 13 we plotted the values of C/B obtained by our fitting as well as the experimental values of T_m . The excellent agreement between those two sets of data indicates that the use of relation (5) accurately describes the electronic transport in our samples.

The electronic transport on the Cu-O₂ planes is an interesting process. It is generally agreed that the charge carriers (holes) reside in the p states at the O sites.³⁴ The carriers are believed to strongly interact with the Cu d band. It is possible that under some conditions such interaction may lead to a Kondo-like behavior. In the La_{1.85}Sr_{0.85}CuO₄ compound the localized moment is very small and Kondo-like behavior is not apparent. However, doping the Cu sites with Ga impurities induces a localized moment in those neighboring Cu sites next to Ga ions. In effect, the Ga-doped Cu-O₂ planes are in many respects similar to a Kondo system. There are some recent attempts to explore theoretically the Kondo-type d - p exchange interactions in the high- T_c cuprate oxides.³⁵ We plan further experiments to investigate this interesting electronic transport behavior.

V. SUMMARY AND CONCLUSIONS

We have investigated $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ with x in the range of 0–0.03. T_c is strongly suppressed by Ga substitution into the CuO_2 planes: Samples with a Ga-doping level higher than 2.2 at. % cease to be superconducting. Such a T_c suppression is not likely to be caused by the pair-breaking mechanism due to nonmagnetic disorder. The filling of the local Cu $3d$ band due to the $3d^{10}$ configuration of the Ga ions seems to be associated with this strong quenching of the superconductivity. The Curie-Weiss behavior observed in the susceptibility gives evidence of the Cu $3d$ -holes localization induced by the Ga doping.

The suppression of T_c due to Ga substitution is very similar to the one observed in the Zn-doped 2:1:4 compound, despite the fact that the carrier concentration in the $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ drops about 20% in the investigated x range whereas it is approximately constant in the Zn-substituted samples. In contrast to the superconducting properties, the normal-state resistivity is strongly affected by the change in the carrier concentration. The

resistivity of $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ depends nonlinearly on the temperature at high temperatures and displays a minimum followed by a logarithmic increase when the temperature is lowered. This indicates that neither the activation process nor the variable range hopping mechanism are responsible for the electronic transport in the Ga-doped 2:1:4 compound. We have investigated the effect of localization and correlation and the Kondo effect as possible causes of the logarithmic increase in the resistivity. The Kondo effect appears to be the better explanation since it is an excellent description of the resistivity in the whole temperature range (4–300 K) for all of the samples.

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