

Metallic Nonsuperconducting Phase and *D*-Wave Superconductivity in Zn-Substituted $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$

K. Karpińska,¹ Marta Z. Cieplak,^{1,2} S. Guha,² A. Malinowski,¹ T. Skośkiewicz,¹ W. Plesiewicz,¹ M. Berkowski,¹ B. Boyce,³ Thomas R. Lemberger,³ and P. Lindenfeld²

¹*Institute of Physics, Polish Academy of Sciences, 02 668 Warsaw, Poland*

²*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019*

³*Department of Physics, The Ohio State University, Columbus, Ohio 43210-1106*

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Measurements of the resistivity, magnetoresistance, and penetration depth were made on films of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, with up to 12 at. % of Zn substituted for the Cu. The results show that the quadratic temperature dependence of the inverse square of the penetration depth, indicative of *d*-wave superconductivity, is not affected by doping. The suppression of superconductivity leads to a metallic nonsuperconducting phase, as expected for a pairing mechanism related to spin fluctuations. The metal-insulator transition occurs in the vicinity of $k_F\ell \approx 1$, and appears to be disorder driven, with the carrier concentration unaffected by doping.

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Although there is strong evidence for *d*-wave symmetry of the order parameter in high- T_c superconductors [1], earlier experiments do not distinguish between mechanisms that lead to pure $d_{x^2-y^2}$ symmetry [2] and others that allow an admixture of *s*-wave pairing [3].

In this Letter we describe the suppression of superconductivity by disorder, with the conclusion that pure *d*-wave symmetry continues until the superconductivity disappears. The experiment is based on the fact that disorder strongly suppresses *d*-wave pairing, and may therefore lead to a transition from the superconducting state to a normal-metal state. Any *s*-wave pairing would be less strongly affected, so that in its presence superconductivity would be expected to persist until, with greater disorder, it is destroyed at the metal-insulator transition.

Studies of the T_c suppression in electron-irradiated $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) [3] or in Zn-doped YBCO and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) [4] did not address the question of the nature of the nonsuperconducting phase. Our previous study showed the existence of a metallic nonsuperconducting phase in LSCO with various impurities [5], but was subject to criticism because it was done on polycrystalline, ceramic specimens.

We studied a series of single-crystalline $\text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ films, with zinc content, y , from 0 to 0.12. We find that with increasing y the transition from the superconducting state is to a metallic state, with the carrier concentration unaffected by the addition of the zinc. This is in contrast with the carrier-driven transition that is observed with a change in the strontium content. We also measured the superconducting penetration depth (λ), and find that it remains proportional to T^2 when y is increased, suggesting that there is no *s*-wave component. As y increases to 0.12, the metal-insulator transition is approached in the vicinity of $k_F\ell = 1$, where k_F is the Fermi wave vector and ℓ is the electronic mean free path, suggesting that the transition is disorder driven.

The *c*-axis oriented films, with thicknesses between 5000 and 9000 Å, were grown by pulsed laser deposition on LaSrAlO_4 substrates. The films were patterned by photolithography and wires were attached with indium to evaporated silver pads. Standard six-probe geometry was used to measure the Hall voltage and the magnetoresistance. The specimens were mounted in a dilution refrigerator, and cooled to 20 mK without a magnetic field, and to 45 mK in the presence of a field. The magnetoresistance was measured with low-frequency ac, in magnetic fields up to 8.5 T, and in the longitudinal (field parallel to the *ab* plane) and transverse (field perpendicular to the *ab* plane and to the current) configurations. A second set of specimens was prepared for penetration depth measurements. $\lambda(T)$ was obtained from the mutual inductance of two coaxial coils fixed on opposite sides of the superconducting film [6].

The zinc content in the films was checked to confirm that it is the same as that of the targets [7]. The films have some substrate-induced strain, and varying amounts of oxygen vacancies so that they had a range of resistivities at each value of y [7]. For each y a group of 6 to 10 films was made, and it was possible to select films with residual resistivities within 30% of those for bulk single crystals [4]. In these selected films superconductivity persists to $y_c = 0.055$, while for larger resistivities T_c vanishes earlier. In ceramic specimens $y_c = 0.03$ [8].

The increase in the residual resistivity, $\Delta\rho_0$, as a function of y is shown in the inset of Fig. 1. The residual resistivity is determined by extrapolation to zero temperature of the linear high-temperature resistivity, and $\Delta\rho_0$ is calculated with respect to a zinc-free film with $\rho_0 = 36.5 \mu\Omega \text{ cm}$ and $T_{c0} = 35.2 \text{ K}$. It is seen that $\Delta\rho_0$ increases linearly with y at a rate of $3.3 \mu\Omega \text{ cm per at. \%}$ of Zn until y reaches 0.1. For larger concentrations the rate increases rapidly, signaling the approach to the metal-insulator transition. The resistivity in a two-dimensional

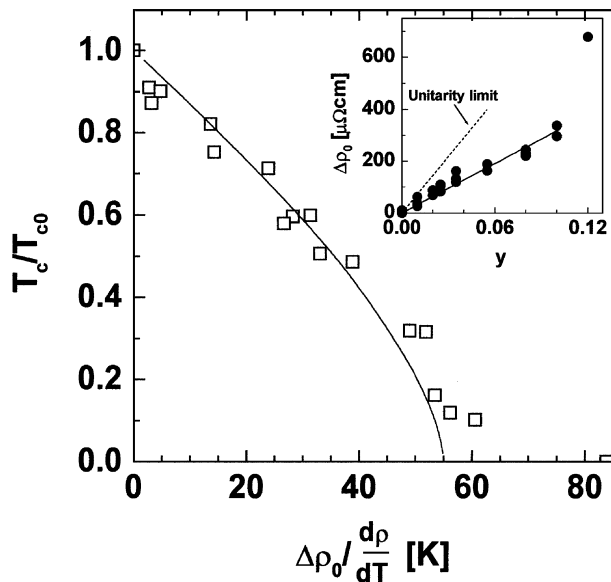


FIG. 1. The normalized critical temperature, T_c/T_{c0} , as a function of $\Delta\rho_0/(d\rho/dT)$ for a set of Zn-doped LSCO films, with $0 < y < 0.055$. The solid line shows the best fit to the AG formula with $\lambda_{TR} = 0.18$. Inset: The dependence of $\Delta\rho_0$ on y . The solid line is a fit to the experimental points for $0 < y < 0.10$. The dashed line indicates the unitarity limit.

system from s -wave impurity scattering follows the formula $\Delta\rho_0 = 4(\hbar/e^2)(y/n) d \sin^2\delta_0$, where n is the carrier concentration, d is the distance between the CuO_2 planes (6.5 Å in LSCO), and δ_0 is a phase shift [9]. The dashed line shows the unitarity (maximal) limit corresponding to $\delta_0 = \pi/2$. We use $n = 0.15$, as the carrier concentration is shown by Hall-effect measurements to be almost independent of y [10]. It is seen that the scattering is about half as effective as in the unitarity limit. This result is close to the result for Zn-doped YBCO single crystals [9], but differs from that reported for single crystals of Zn-doped LSCO where the scattering was claimed to exceed the unitarity limit [4]. In fact, the discrepancy seems to be primarily the result of a difference in the method of calculating the residual resistivities [11].

The scattering rate for nonmagnetic impurities, $1/\tau_{\text{IMP}}$, is related to the residual resistivity, $\Delta\rho_0$, by the formula $1/\tau_{\text{IMP}} = 2\pi\lambda_{\text{TR}}k_B\Delta\rho_0/\hbar(d\rho/dT)$, where λ_{TR} is an electron-boson transport coupling constant, and the value of $d\rho/dT$ is from the temperature range 200 to 300 K where the resistivity is boson mediated. We display the T_c suppression by plotting the ratio $\Delta\rho_0/(d\rho/dT)$, since the errors related to uncertainties of size and homogeneity of the specimens cancel in this ratio [3]. This is shown in Fig. 1, where T_c is normalized to $T_{c0} = 35.2$ K. The solid line shows the best fit to the Abrikosov-Gorkov (AG) formula [12], $\ln\frac{T_{c0}}{T_c} = \Psi\left(\frac{1}{2} + \frac{\hbar}{4\pi\tau k_B T_c}\right) - \Psi\left(\frac{1}{2}\right)$ (where Ψ is the digamma function), with the pair-breaking scattering rate $1/\tau$ equal to $1/\tau_{\text{IMP}}$ [13,14] and the fitting parameter λ_{TR} equal to 0.18. There is a slight deviation of the theoretical curve from the experimental

points on Fig. 1 for $T_c/T_{c0} < 0.25$. The value of λ_{TR} of 0.18 (indicating the weak-coupling limit) is a factor of 2 smaller than the value we estimate from high-temperature resistivity data, for $d\rho/dT$ equal to the average of the experimental values, $2.5 \mu\Omega \text{ cm/K}$, and $\hbar\omega_P = 0.8$ eV [15,16].

Both the deviation of the curve for small T_c and the reduced value of λ_{TR} may be related to effects which are not included in the AG formula, such as the anisotropy of the impurity scattering (which leads to a difference between $1/\tau$ and $1/\tau_{\text{IMP}}$ [17]) and the spatial variation of the order parameter [18,19]. The dependence of T_c/T_{c0} on $\Delta\rho_0$ by itself does not allow us to distinguish between these effects. The deviations could also be caused by the presence of an s -wave component of the superconducting order parameter, and this possibility is examined below.

Figure 2 shows the temperature dependence of the penetration depth for four films with values of y between 0 and 0.03, and values of T_c from 28 to 6.2 K. The specimen with the lowest T_c has T_c/T_{c0} equal to 0.18 which is in the regime where the AG formula begins to deviate from the experimental data (see Fig. 1). For d -wave symmetry of the order parameter, disorder leads to a quadratic temperature dependence $\lambda^{-2}(T) - \lambda^{-2}(0) \propto T^2$ for $T \ll T_c$, while exponential behavior, $\lambda^{-2}(T) - \lambda^{-2}(0) \sim \exp(-\Delta_{\text{min}}/kT)$, is expected for $T \ll \Delta_{\text{min}}$ in an s -wave superconductor [20,21]. Here the magnitude of the minimum of the energy gap, Δ_{min} , is expected to increase with disorder for anisotropic s -wave pairing [22,23]. The quadratic temperature dependence is well documented for zinc-free LSCO films with different amounts of intrinsic disorder [24]. It is evident from Fig. 2 that the quadratic

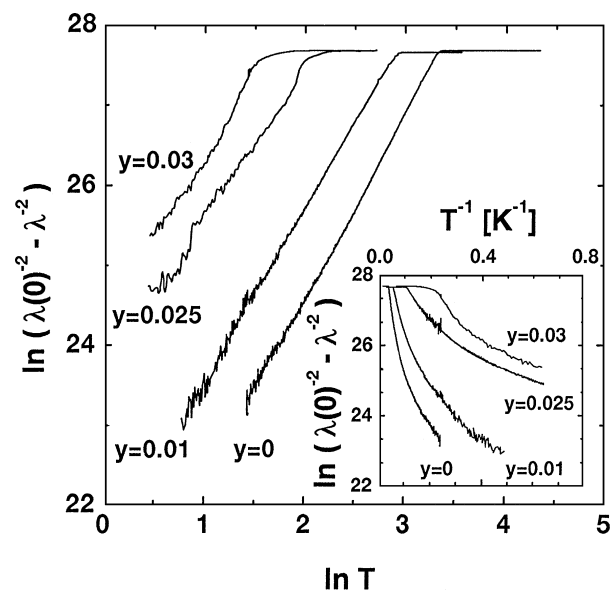


FIG. 2. Penetration depth results: log-log graph of $\ln(\lambda(0)^{-2} - \lambda^{-2})$ versus temperature, for films with $y = 0, 0.01, 0.025$, and 0.03 and $\lambda(0) = 9800, 10000, 16000$, and 19300 Å, respectively. Inset: $\ln[\lambda(0)^{-2} - \lambda^{-2}]$ versus $1/T$ for the same films.

dependence gives a much better description of the data for all values of y . An attempt to fit a straight line to the low-temperature portion of the data, as shown in the inset, leads to energy gaps decreasing with increasing y , inconsistent with the expectations for anisotropic s -wave symmetry. A similarly negligible effect of zinc doping on the T dependence of λ has also been reported for YBCO [25]. We note that nonmagnetic disorder should produce a rapid decrease of the zero-temperature value of the superfluid density, $n_S(0) \sim \lambda(0)^{-2}$, together with a steep decrease of T_c [26]. Our results show that $n_S(0)$ decreases by a factor of 1.3% of impurity, which is slightly slower than the rate reported for YBCO [25] but close to the theoretical predictions for a d -wave superconductor [26].

Figure 3 shows the temperature dependence of the resistivity down to 20 mK for several films with large amounts of zinc. The film with $y = 0.055$ is still superconducting, with a transition whose midpoint is at 3.5 K. The films with larger values of y (0.08, 0.10, and 0.12) are nonsuperconducting, and their resistivity increases approximately as $\rho_{ab} \sim \ln(1/T)$ as T is lowered, but below about 300 mK the increase slows down and the resistivity is clearly finite in the $T = 0$ limit. This behavior is markedly different from the evolution of the ab -plane resistivity with strontium content, where nonsuperconducting specimens exhibit hopping conductivity indicative of insulating behavior in the $T = 0$ limit.

The inset of Fig. 3 shows the temperature dependence of the Hall coefficient, R_H , for three nonsuperconducting

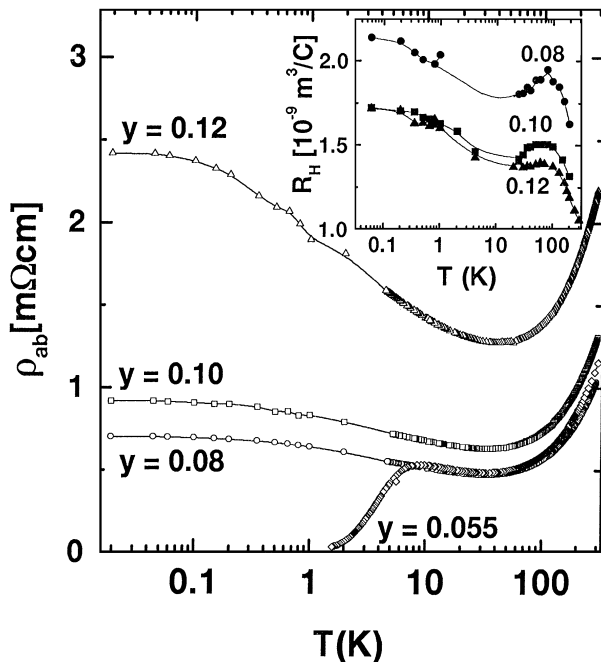


FIG. 3. The temperature dependence of the resistivity for four films with values of y of 0.055, 0.08, 0.1, and 0.12. Inset: Hall coefficient for films with $y = 0.08, 0.1,$ and 0.12 as a function of temperature. All lines are guides to the eye.

films. A slow increase of R_H followed by saturation below 300 mK is seen in the low-temperature region. The magnitude of R_H is close to that observed for $y = 0$ [27], indicating that the specimens remain metallic up to the highest doping level, $y = 0.12$, without any change in the carrier concentration.

The saturation of the resistivity shown in Fig. 3 could signal some remanence of the superconducting phase. We examined this possibility by magnetoresistance measurements. Figure 4 shows the resistivity as a function of magnetic field, applied in the longitudinal and transverse configurations, for two films, with y equal to 0.055 and 0.08, which are superconducting and nonsuperconducting, respectively, in the absence of the field. The curves are for constant temperatures from 2 K to 45 mK. The magnetoresistance is positive for the film with $y = 0.055$ for both field configurations. This is similar to the magnetoresistance in LSCO without zinc [28] and is clearly caused by the suppression of superconductivity by the magnetic field. On the other hand, the magnetoresistance of the film with $y = 0.08$ is negative for both configurations, with the magnitude of the transverse magnetoresistance about twice as large as the longitudinal. If we attribute the longitudinal magnetoresistance entirely to spin-related isotropic scattering, the difference between the transverse and longitudinal magnetoresistance gives the orbital part, which is then also negative. This result demonstrates that superconducting fluctuations are absent in the specimen with $y = 0.08$ and that the metallic nonsuperconducting phase is uniform without any macroscopic superconducting inclusions.

The values of the conductivity at $T = 20$ mK, σ_0 , for three metallic films with $y = 0.08, 0.10,$ and 0.12 , are equal to $1430, 1098,$ and $436 (\Omega \text{ cm})^{-1}$, respectively.

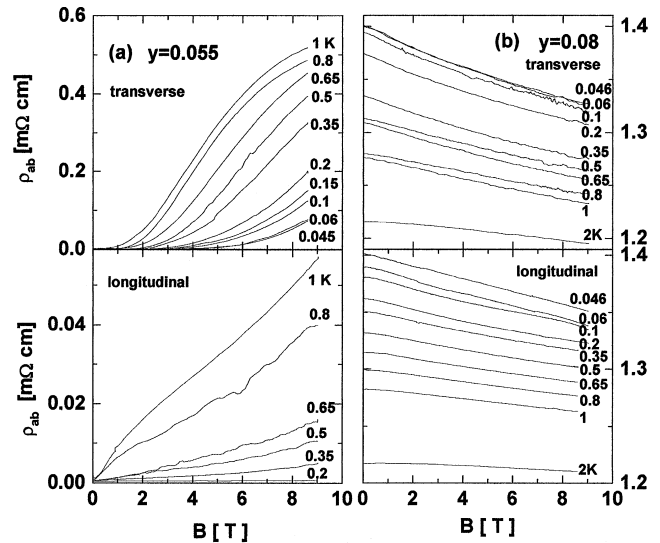


FIG. 4. Transverse and longitudinal magnetoresistance for films with $y = 0.055$ (a) and $y = 0.08$ (b) versus magnetic field. The labels show the temperatures at which the measurements were made.

Using a linear extrapolation to $\sigma_0 = 0$ we estimate that the metal-insulator transition occurs at $y_{\text{MI}} \approx 0.14$. We also estimate the magnitudes of $k_F \ell$ for these specimens as equal to 2.4, 1.8, and 0.7, respectively, from the relation for a 2D free-electron system, $k_F \ell = \hbar d \sigma_0 / e^2$. We see that the metal-insulator transition occurs in the vicinity of $k_F \ell = 1$, as expected for disorder-induced localization [29] in contrast to suggestions that the superconductor-insulator transition in this system occurs at $\hbar/4e^2 = 6.5 \text{ k}\Omega$ [4]. The value of y_{MI} is remarkably small compared to the fraction of the nonmetallic constituent required for the metal-insulator transition in amorphous systems [30], showing that the Zn creates extremely effective localization centers in the CuO_2 plane (see, e.g., Ref. [31]) and that in addition to the effect of disorder, the scattering by Zn impurities is enhanced by electron-electron interactions in this strongly correlated system.

In related work we have shown that with increasing y the high-temperature susceptibility of the ceramic targets evolves toward the Curie-Weiss relation, $\chi = C/(T + \Theta)$, with Θ reaching about 40 K at $y = 0.14$ [32]. This result indicates that large Zn-doping, while removing Cu spins, restores some antiferromagnetic ordering in LSCO. It has been suggested before on the basis of neutron scattering experiments that substitution of a small amount of zinc in LSCO ($y = 0.012$) may stabilize a short-range-order spin-density-wave state [33], and our result appears to be consistent with this suggestion. Related magnetic effects are presumably responsible for the large negative magnetoresistance and for the saturation of the resistivity at low temperatures.

The experiments described here indicate that the suppression of superconductivity by Zn doping in LSCO proceeds without a change of the symmetry of the order parameter, up to the point where superconductivity disappears and the normal metallic phase is reached. This result favors models that predict pure d -wave symmetry, as, for example, the spin-fluctuation exchange model. With further doping the metal-insulator transition occurs in the vicinity of $k_F \ell = 1$, showing that it is disorder driven.

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