PHYSICAL REVIEW B VOLUME 36, NUMBER 10 1 OCTOBER 1987

Effect of magnetic impurities on high-temperature superconductivity in $La_{1.85}Sr_{0.15}CuO_4$

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(Received 29 May 1987)

We have investigated the effect of magnetic impurities on the two-dimensional high-T_c superconductor $La_{1.85}Sr_{0.15}CuO_4$ by replacing La with Nd. We find a decrease in T_c and $dH_{c2}/dT\,|_{T_c}$ and an increase in the normal-state resistivity with increasing Nd content. We use the Werthamer, Helfand, and Hohenberg equations to derive the effect of an exchange field, magnetic polarization, nonmagnetic impurity scattering, and changes in the density of states on T_c and $dH_{c2}/dT\,|_{T_c}$. We find no evidence of an exchange interaction between the magnetic moments and the conduction electrons. We explain the changes in the superconducting properties in terms of the van Hove singularity in the density of states near the Fermi level.

INTRODUCTION

The superconductivity in $La_{2-x}M_xCuO_{4-\delta}$ depends on a wide variety of structural, electronic, and lattice-defect parameters. Recent works[1-5] have shown that the substitution of $M=$Ba, Sr, or Ca into $La_{2-x}M_xCuO_{4-\delta}$ produces a high superconducting transition temperature in this K_2NiF_4 structure, with $x=0.15$ producing the highest T_c. The fact that Ba, Sr, and Ca produce different T_c's is interesting because all three ions have identical 2^+ valences and therefore should not alter the electronic structure of the material. This suggests that a size effect may be involved in producing the high T_c observed with Sr substitution. More recently, it has been found that oxygen defects[6,7] in the Cu-O plane play an important role in affecting both T_c and the normal-state resistivity. In order to further probe the nature of high-T_c superconductivity, we address the role of magnetic ion impurities in this compound. Previous work on magnetic superconductors[8] has shown that the magnetic ions break the Cooper pairs and often lead to interesting phenomena like a reduction in T_c, reentrant superconductivity, the coexistence of superconductivity and magnetism, and the Jaccarino-Peter effect. In this paper, we study the effect of doping $La_{1.85}Sr_{0.15}CuO_4$ with a rare-earth ion. We use the Werthamer, Helfand, and Hohenberg (WHH) equations to derive the expected effects of an exchange interaction, a magnetization field, nonmagnetic impurity scattering, and the density of states on T_c and $(dH_{c2}/dT)\,|_{T_c}$. We have measured the resistivity, susceptibility, magnetoresistance, and critical field of $La_{1.85-x}Sr_{0.15}Nd_x\,CuO_4$ for $x=0$, 0.03, and 0.4. We find a depression in T_c and $(dH_{c2}/dT)\,|_{T_c}$ with increasing x and attribute this result to a density-of-states effect rather than to a magnetic effect. A preliminary report of this work has been presented elsewhere.[9] In a separate paper we address the dependence of T_c on the size of substituted Nd and Eu ions and on the structural phase transition induced by alloying.[10]

SAMPLE PREPARATION AND MEASUREMENTS

The samples were prepared by evaporating nitrate solutions containing the appropriate metal ion ratios. The nitrates were fired at 1000 °C, ground, and refired. Pellets were then pressed, and the samples fired a final time at 1000 °C overnight. The samples were characterized by powder x-ray diffraction, resistivity, magnetoresistance, dc magnetization, and critical-field measurements. Lattice-constant measurements and checks for impurity phases were made by powder x-ray diffraction on a Scintag powder diffractometer employing Cu K_α radiation. Resistivity was measured by a four-wire ac technique using 2.5-mA measuring current at 100 Hz. Magnetoresistance and critical fields were measured up to 8 T in a superconducting solenoid. dc magnetization curves were measured in a SHE superconducting quantum interference device magnetometer in fields up to 10 kG.

Resistivity as a function of temperature for the $x=0.0$ and 0.4 samples is plotted in Fig. 1 and summarized in Table I. The normal-state resistivity for $x=0.4$ is 4800 $\mu\Omega$ cm, a factor of 4.9 higher than the 980 $\mu\Omega$ cm observed for $x=0.0$. There is a shallow minimum in resistivity occurring at $T=70$ K for the $x=0.4$ sample while the $x=0.0$ and $x=0.03$ samples are metallic with a nearly

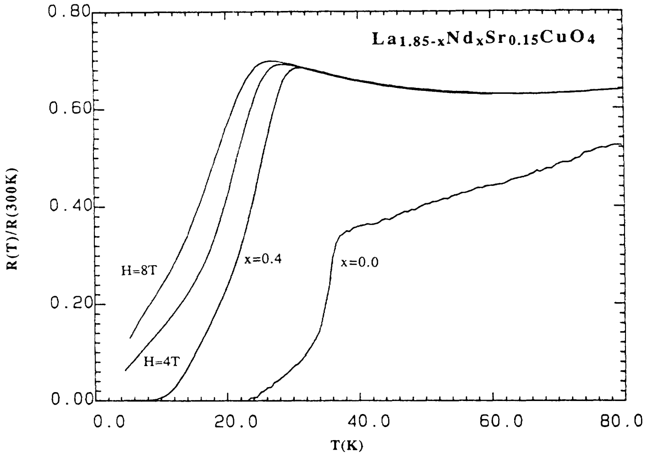

FIG. 1. Resistivity vs temperature of $La_{1.85-x}Nd_xSr_{0.15}CuO_4$ normalized by the room-temperature value for $x=0.0$ and $x=0.4$. The behavior of the $x=0.4$ sample in fields of 4 and 8 T is also shown.

TABLE I. Measured superconducting and normal-state properties of $La_{1.85-x}Nd_xSr_{0.15}CuO_4$.

x	Onset (K)	Midpoint (K)	Zero (K)	$\left.\frac{dH_{c2}}{dT}\right\|_{T_c}$ (T/K)	ρ ($\mu\Omega$ cm)	μ_{eff} (μ_B/Nd)
0.0	37.0	34.4	24.0	−1.33	980	
0.03	38.0	34.2	28.0	−1.26		
0.4	30.0	22.5	9.0	−0.97	4800	3.9

linear resistivity from T_c to room temperature. The superconducting transitions for $x=0.0$ and $x=0.4$ samples are rather broad with onsets, midpoints, and zero resistance values for $x=0.0$ and $x=0.4$ of 37, 34.4, and 24 K and 30, 22.5, and 9 K, respectively. Both transitions are asymmetric with a low-temperature tail. The $x=0.03$ sample has a much sharper transition without the low-temperature tail. The onset, midpoint, and zero resistance values for $x=0.03$ are 38, 34.2, and 28 K, respectively.

The presence of a field considerably broadens the superconducting transition for the $x=0.4$ sample as seen in Fig. 1. This broadening is attributed to anisotropy of the critical field in these two-dimensional materials. Magnetoresistance data were taken at 18 temperatures between 1 and 30 K for the $x=0.4$ sample, at 14 temperatures between 1 and 40 K for the $x=0.0$ sample, and at 13 temperatures between 10 and 36 K for the $x=0.03$ sample. No appreciable magnetoresistance was seen in the normal state for any of the samples.

From the magnetoresistance data and from the temperature dependence of the resistivity in fields of 4 and 8 T, we constructed the critical field versus temperature curves shown in Fig. 2. Transition temperatures were taken at the midpoint of the transition curves. The critical-field curves for all three samples determined in this way are linear from 0 to 8 T. The critical-field slopes at T_c, $(dH_{c2}/dT)|_{T_c}$, for $x=0.0$ and 0.03 are nearly identical, -1.33 and -1.26 T/K, respectively. The $x=0.4$ sample has a considerably smaller slope, -0.97 T/K.

The magnetization of the $x=0.4$ sample was measured at $T=50$ and 250 K and found to be linear up to 1 T. The susceptibility as a function of temperature was determined from the magnetization at 1 T at 16 temperatures between 35 and 300 K. The Curie plot determined in this way is shown in Fig. 3. It is linear at high temperature with a slight downturn below 100 K. From the slope of the high-temperature portion of the curve, we determined the moment per Nd to be $3.9\mu_B$. This compares with a free-ion moment of $3.6\mu_B$ implying a moment of $0.12\mu_B$ per Cu in the host material $La_{1.85}Sr_{0.15}CuO_4$. A summary of all the experimental results is given in Table I.

ELECTRONIC AND MAGNETIC PAIR-BREAKING EFFECTS

We observe a depression of T_c and a decrease in the critical-field slope with an increase in Nd concentration. There are several possible sources for these effects. Magnetic impurities are well known to depress T_c and affect the shape of the critical-field curve through their exchange coupling with the conduction electrons. The in-

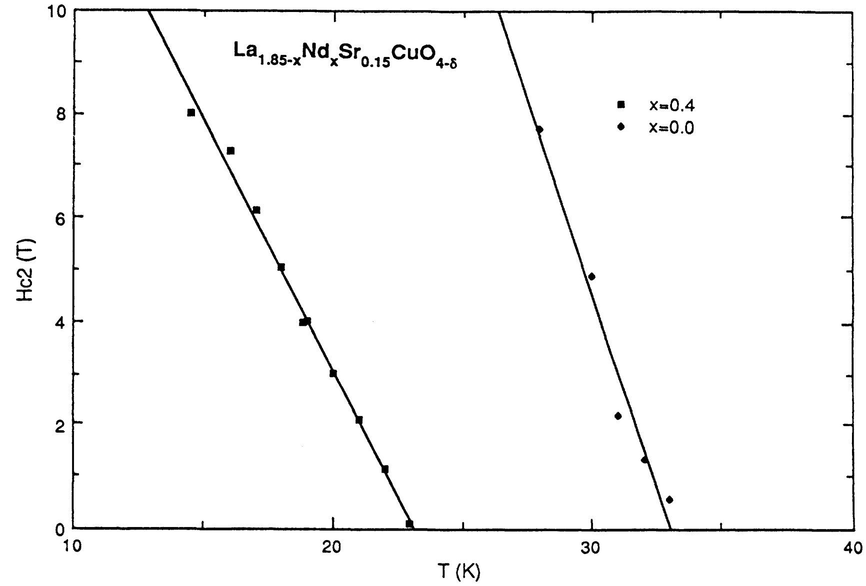

FIG. 2. Critical field vs temperature for $x=0.0$ and $x=0.4$ samples. Solid lines are linear least-squares fits to the data.

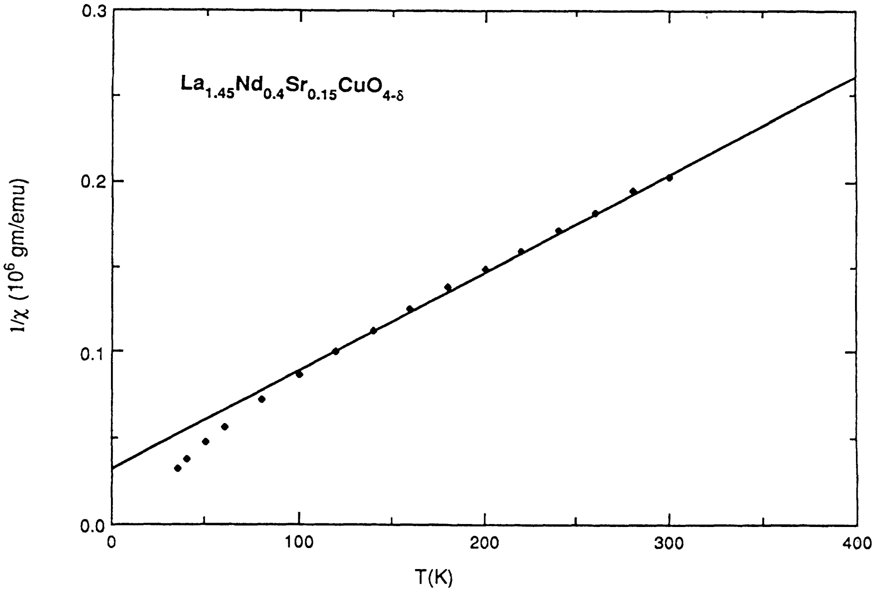

FIG. 3. Curie plot for $La_{1.45}Nd_{0.4}Sr_{0.15}CuO_4$. The solid line is a least-squares fit to the high-temperature points.

duced magnetic moment of the Nd ions supplements the applied field by an amount $4\pi M$ that lowers the orbital critical field relative to the zero-magnetization case. Nonmagnetic impurities have little effect on T_c but reduce the mean free path and in the dirty limit raise the orbital critical field. Finally, both T_c and H_{c2} are affected by changes in the conduction-electron density of states at the Fermi level. We will consider each of these four effects with the aid of the dirty-limit pair-breaking formula of de Gennes[11] and Maki.[12]

The reduction in T_c caused by any of the pair-breaking mechanisms listed above can be described in the dirty limit[13] with the equation

$$\ln\left[\frac{1}{t}\right]=\psi\left[\frac{\rho}{2t}+\frac{1}{2}\right]-\psi\left[\frac{1}{2}\right] , \qquad (1)$$

where t is the reduced temperature T/T_c, T_c is the transition temperature in the absence of pair-breaking, ρ is the pair-breaking parameter, and ψ is the digamma function. The pair-breaking parameter which describes the effect of an applied field[14] is (in the limit $\lambda_{so} \gg 1$)

$$\rho=h+\frac{\alpha^2}{\lambda_{so}}h^2 , \qquad (2)$$

where

$$h=\frac{2ev_F^2\tau}{6\pi k_B T_c}H,\ \ \alpha=\frac{3\hbar}{2mv_F^2\tau},\ \ \lambda_{so}=\frac{2\hbar}{3\pi k_B T_c \tau_{so}} .$$

In the above expressions, α is the Maki parameter, v_F is the Fermi velocity, τ is the transport scattering lifetime, and τ_{so} is the spin orbit scattering lifetime. The first term in Eq. (2) describes the pair-breaking due to the orbital motion of the electrons in the applied field. The solution of Eq. (1) with only this term is called the orbital critical field H_{c2}^*. The second term in Eq. (2) describes pair breaking due to the Pauli spin polarization of the electrons in the applied field.

The pair-breaking parameter describing the effect of magnetic impurities[15] is given by

$$\rho_{AG}=x\frac{(g-1)^2}{8k_B T_{c0}}N(0)J(J+1)\Gamma^2 , \qquad (3)$$

where x is the concentration of the impurity, $T_{c0}=T_c(x=0)$, g is the Lande g factor, $N(0)$ is the conduction-electron density of states at the Fermi level, J is the total angular momentum of the magnetic impurity, and Γ is the exchange coupling between the local moment and the conduction electrons. The effect of all of the above pair-breaking mechanisms is described by Eq. (1) with ρ set equal to the sum of all the pair-breaking parameters. If the critical field is to be determined in the presence of magnetic impurities, the field affecting the orbital motion of the electrons includes a contribution M from the magnetizing field of the sample so that H in the first term in Eq. (2) should be replaced by $H+M$. In addition, there is an exchange field acting on the spin of the conduction electron through its exchange coupling to the local moment given by

$$H_J=\frac{(g-1)\Gamma}{gg_eN\mu_B^2}M(H,T) , \qquad (4)$$

where N is the number of magnetic ions and g_e is the conduction-electron g factor. In the second term of Eq. (2), H should be replaced by $H+H_J$.

The solution to Eq. (1) is a unique function of ρ, the pair-breaking parameter. Therefore, the solution in the presence of all the pair-breaking mechanisms, H_{c2}, can be written[13] in terms of the solution for the orbital critical field H_{c2}^* (in SI units):

$$H_{c2}(T)=H_{c2}^*(T)-4\pi M(H_{c2},T)-3.56\rho_{AG}H_{c2}^*(0)$$
$$-0.22\frac{\alpha}{\lambda_{so}T_{c0}}[H_{c2}(T)+H_J(H_{c2},T)]^2 . \qquad (5)$$

There is a temperature dependence to all the above terms

TABLE II. Effect on T_c and $(dH_{c2}/dT)|_{T_c}$ of various magnetic and nonmagnetic mechanisms affecting superconductivity.

	Exchange field	Magnetization field	Nonmagnetic scattering	Density of states
T_c	Decreases	No change	No change	Increases/decreases
$\left.\frac{dH_{c2}}{dT}\right\|_{T_c}$	No change	Decreases $\sim\frac{1}{1+\chi}$	Increases $\sim\frac{1}{\tau}$	Increases/decreases

except that involving ρ_{AG}. The effect of this term is simply to lower the critical field without altering its shape. The initial slope of the critical field can be obtained from Eq. (5) by differentiating with respect to T and evaluating the derivative at T_c:

$$\left.\frac{dH_{c2}}{dT}\right|_{T_c} = \left.\frac{dH_{c2}^*}{dT}\right|_{T_c} \frac{1}{1+\chi} . \tag{6}$$

The terms in the exchange field are zero at T_c and therefore do not contribute to the initial slope. The magnetic susceptibility decreases the initial slope because the polarization of the impurity moments increases the effective field acting on the orbital motion of the electrons. The orbital critical-field slope may be obtained from the solution of Eq. (1) for orbital pair breaking by the applied field:

$$-\left.\frac{dH_{c2}^*}{dT}\right|_{T_c} = 3.81\frac{k_B}{ev_F^2\tau} . \tag{7}$$

The above analysis can be used to determine the effect of each of the pair-breaking mechanisms on the measurable quantities T_c and $(dH_{c2}/dT)|_{T_c}$. These are summarized in Table II. Magnetic impurities affect superconductivity through the contribution of their magnetic polarization to the magnetic field and through their exchange coupling to the conduction electrons. The first contribution is described by Eq. (6) and leads to a reduction of the critical-field slope at T_c but not to a reduction of T_c itself. The exchange coupling leads to a reduction in T_c through the Abrikosov-Gorkov pair breaking described by Eq. (3). This term does not lead to any change in the critical-field slope, but only to a uniform lowering of the critical field. Exchange coupling also contributes an additional term H_J to the second term of Eq. (2). This term is responsible for a strong modification of the critical field in magnetic superconductors leading to the Jaccarino-Peter effect and field-induced superconductivity if the exchange field opposes the applied field. However, there is no effect on the initial slope of the critical field, because M and H_J are zero at T_c.

The effect of nonmagnetic impurities on T_c and $(dH_{c2}/dT)|_{T_c}$ is well known from the dirty limit WHH formulas.[13,16] In principle, T_c is not affected by nonmagnetic impurities, although in practice there is often a slight reduction. The critical-field slope is increased as τ in Eq. (7) is reduced by potential scattering.

Finally, we consider the effect on T_c and the initial critical-field slope of a change in the density of states due to a shift in the Fermi level or a change in the band structure. T_c depends exponentially on the density of states and increases or decreases as the density of states increases or decreases. $(dH_{c2}^*/dT)|_{T_c}$ depends inversely on v_F^2 which can be related to the density of states by an integral over the Fermi surface. As the density of states increases the initial slope of the critical field also increases. Thus, both T_c and the initial slope of the critical field increase or decrease with the density of states.

ANALYSIS OF RESULTS

Comparing the observed behavior in T_c and the initial slope of the critical field with the expected behavior in Table II, we see that none of the magnetic effects qualitatively agrees with our observations. The reduction in the initial critical-field slope cannot be due to the contribution of the magnetization to the orbital pair-breaking field because the magnitude of the magnetic susceptibility is too small. According to Eq. (6) our measured value of 1.38×10^{-4} (dimensionless units) for χ at 50 K will not noticeably affect the initial slope. Our measuring field of 8 T limits our critical-field results to the region close to T_c and our curves for $H_{c2}(T)$ are linear to within experimental accuracy, indicating that they represent the initial slope where exchange effects cannot be observed. Thus, there is no mechanism involving the Nd moments which can explain the reduced initial critical-field slope which we observe. Apparently, the exchange interaction between the Nd moments and the conduction electrons is very weak, a conclusion supported by the absence of any measurable magnetoresistance in the normal state. Further support for a weak exchange interaction comes from Mössbauer isomer shift measurements. In a separate experiment,[10] we substituted Eu for La in $La_{1.85-x}Eu_x$-$Sr_{0.15}CuO_4$ for $0.0 \le x \le 0.4$; Eu suppresses T_c at a faster rate than does Nd. Mössbauer measurements on ^{151}Eu show isomer shifts typical of strongly ionic Eu^{3+} with little contribution from any conduction-electron density at the Eu site. This experimental result shows directly that the conduction electrons avoid the La position, and this provides a natural explanation for the weak exchange interaction.

The observed reduction in the initial critical-field slope is opposite to that expected for dirty superconductors. The addition of Nd impurities reduces the scattering lifetime as seen in the increased resistivity for the $x=0.4$ sample over the $x=0$ sample. This reduced lifetime would increase the critical-field slope in the absence of other effects, as shown by Eq. (7).

To explain both the reduction in T_c and the reduction in the critical-field slope we turn to a nonmagnetic mechanism, a reduction of the density of states. Band-structure calculations[17,18] show that there is a van Hove singularity in the density of states of La_2CuO_4 which occurs at the Fermi level in the composition $La_{1.85}Sr_{0.15}CuO_4$. The change in the density of states between these two compounds is significant, nearly a factor of two. Thus any change in the Fermi level or the underlying band structure will move the Fermi level off the peak in the density of states and will cause a reduction in T_c and the initial critical-field slope. The mechanism for a change in the Fermi level or band structure of $La_{1.85}Sr_{0.15}CuO_4$ upon alloying with Nd is not obvious, since Nd has the same valence as the La ion it replaces. The slight decrease in the lattice constants[10] from

$$a=3.7777(9),\ c=13.2222(38)$$

for $x=0.0$ to

$$a=3.7682(14),\ c=13.1732(75)$$

for $x=0.4$ leads to a reduction in the density of states, which is far too small to explain the decrease in T_c. However, we note that there is a substantial reduction in T_c of $La_{1.85}Sr_{0.15}CuO_4$ when Sr is replaced with Ba or Ca, even though the valence of these atoms is identical. The origin of this effect must be the differing sizes of the ions, leading to local distortions around the impurity site which alter the Cu—O bonding and the resulting band structure. In addition to distortions of the atomic positions, the presence of an impurity can alter the number of oxygen vacancies occurring in the Cu-O two-dimensional networks which control the metallic and superconducting properties of these systems. The number of oxygen vacancies affects both the Fermi level by changing the charge balance of the formula unit and the band structure by altering the Cu-O overlap. Oxygen vacancies have a strong effect on the superconducting properties of these materials, as shown most dramatically by the fact that La_2CuO_4 can be made superconducting by the proper oxygen treatment without alloying with 2^+ ions.[7]

Regardless of the exact mechanism by which the Nd impurities alter the electronic structure, their influence on the effective density of states can be estimated from the increase in the resistivity with Nd content. The resistivity of the $x=0.4$ compound, combined with the mean free path and Fermi velocity derived earlier[3] for $La_{1.85}Sr_{0.15}CuO_4$, can be used to estimate the scattering lifetime due to Nd impurities. Using the uncertainty principle, an energy spread over which the density of states is smeared by the impurity scattering may be determined. For the $x=0.4$ sample, this energy spread is approximately 0.26 eV, a significant fraction of the width of the peak in the density of states due to the van Hove singularity. At 0.13 eV from the van Hove singularity the density of states has fallen[17] from 1.0 states/eV cell to 1.2 states/eV cell. Thus, the increased scattering due to the Nd impurities implies a substantial reduction in the effective density of states due to lifetime smearing, consistent with the observed reduction in T_c and $(dH_{c2}/dT)|_{T_c}$.

CONCLUSION

We have examined the effect of magnetic impurities on the superconducting system $La_{1.85}Sr_{0.15}CuO_4$. Although our studies were restricted to Nd impurities, the effect of magnetic impurities is mainly dependent on the crystal and electronic structure of the K_2NiF_4 system and should apply generally to superconductors in this class. We do not find any evidence for an effect of the exchange interaction on superconductivity. The reductions in T_c and the initial critical-field slope are due to a lowering of the effective density of states from its maximum value obtained in the $La_{1.85}Sr_{0.15}CuO_4$ composition.

ACKNOWLEDGMENT

This work was supported by the U. S. Department of Energy, Basic Energy Sciences-Materials Sciences and Chemical Sciences under Contract No. W-31-109-ENG-38.

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