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3d-metal doping of the high-temperature superconducting perovskites La-Sr-Cu-O and Y-Ba-Cu-O

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The structural, magnetic, and superconducting properties of the mixed compounds $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$ $(0<x<0.3)$ $(M=\text{Ni or Zn})$ and $YBa_2Cu_{3-x}Ni_xO_{7-y}$ $(x=0.25 \text{ or } 0.5)$ were studied. dc resistance, Meissner, and shielding measurements have shown that both magnetic Ni and diamagnetic Zn ions destroy the superconductivity in the La-Sr-Cu-O system. Within the Y-Ba-Cu-O system, the replacement of copper by nickel depresses T_c from 93 K $(x=0)$ to 50 K $(x=0.5)$. At higher nickel contents, the phase does not form. The upper critical field $B_{c2}(T)$ of the nickel-doped samples was measured near T_c in dc fields to 23 T. Resistive midpoint transitions yield $dB_{c2}/dT=4.5$ and 1.77 T/K for the Ni-doped La-Sr-Cu-O $(x=0.025)$ and Y-Ba-Cu-O $(x=0.5)$ systems, respectively. We compare doping results for magnetic and nonmagnetic ions, and discuss the origin of the depression in T_c.

I. INTRODUCTION

The oxygen-defect perovskites, of general formula $La_{2-x}M_xCuO_4$ and YBa_2CuO_{7-x} are high-critical-temperature and high-critical-field superconductors. Critical temperatures (T_c) of 40 and 95 K have been reached by several groups for the systems $La_{2-x}Sr_xCuO_4$ $(x=0.15)$ (Refs. 1–3) and $YBa_2Cu_3O_{7-y}$,[4–7] respectively. Critical field onsets (extrapolated to zero temperature) as high as 340 T were also reported for the yttrium phase.[8] An empirical supposition is that the average valence of copper in these materials has to be higher than 2 for superconductivity to exist. The increase in the copper valence can be accomplished either by substitution of divalent ions for trivalent ions, or through the uptake or removal of oxygen atoms as previously reported.[9] (The possibility that the oxygen valence is reduced to less than 2 also exists, but experiments to determine the O and Cu valencies to this point have not proven conclusive.)

This new class of high-T_c superconducting oxides offers new opportunities for the study of the interplay between magnetism and superconductivity, and to further test the Arbrikosov and Gork'ov theory[10] which predicts that T_c should decrease in the presence of magnetic impurities in the lattice. We have investigated two possible ways to introduce magnetic impurities into the perovskite phase. One is to replace La or Y by rare earths, as we previously reported.[9,11] Another is to partially substitute a 3d magnetic transition metal for the copper, such as Ni or Co, as reported here. We also substituted diamagnetic Zn for the copper.

Some of this work has been reported previously.[12] Upon completion of this work, we received copies of recent work by two groups[13,14] who have also studied the substitution of 3d metals for copper in these materials.

II. EXPERIMENT

The mixed compounds $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$ $(0<x<0.3)$ were prepared by mixing appropriate amounts of $SrCO_3$, La_2O_3, CuO, and MO, where $M=$Ni, Co, or Zn. The mixed powders, pressed into pellets, were then reacted at 1140 °C for 48 h under oxygen. A similar process, with a lower heating temperature (950 °C), was followed for the preparation of the $YBa_2Cu_{3-x}Ni_xO_{7-y}$ phases $(x=0.25$ or $0.50)$. In both cases the samples were slowly cooled (5 h) to room temperature.

A part of the pellet was ground to powder for x-ray diffraction and Meissner measurements and, from the remainder, rectangular bars were cut for our resistivity measurements. Resistivity was measured in the standard four-probe configuration; leads attached with silver paint and samples mounted to a tube with the exchange gas and then slowly immersed in liquid helium. Temperatures, measured with a silicon diode, are accurate to ± 0.2 K. Current densities were approximately 0.2 A/cm^2. Contract resistances for both the current and voltage leads were on the order of tens of ohms at room temperature. Powder x-ray diffraction patterns were obtained by means of a Scintag diffractometer using Cu $K\alpha$ radiation. For reasons of simplicity we will denote, in the following, the La-Sr-Cu-O and Ba-Y-Cu-O systems as the 40 and 90 K materials, respectively.

The upper critical field $B_{c2}(T)$ was measured resistively with a standard four-probe method in transverse dc magnetic fields up to 23 T in water-cooled Bitter magnets in the Francis Bitter National Magnetic Laboratory facility. Leads were attached with silver paint and current densities were kept low. Tests were made to assure that $B_{c2}(T)$ was not sensitive to the applied dc current. The specimens were rectangular polycrystalline slabs with good mechanical integrity. The resistive measurements were made in a small He gas cryostat having variable temperature control (capacitance and carbon-glass thermometers). Most of the data were taken at fixed values of T and swept B_0, and selected points were taken at fixed B_0 while varying T.

III. RESULTS

The 40 K materials were single phase as determined by x-ray diffraction with all the Bragg diffraction peaks completely indexed on the basis of a tetragonal unit cell. The x-ray data are summarized in Table I, and Figs. 1(a), 1(b), and 1(d) show the variation of the tetragonal lattice parameters a, c, and V as a function of nickel and zinc content. In both cases the cell length a increases continuously as a function of x while c decreases. We recall that an opposite trend was observed when replacing La by Sr in the $La_{2-x}Sr_xCuO_4$ system.[3] The large magnitude of these changes is somewhat surprising, since nickel, copper and zinc are about the same size 0.83, 0.87, and 0.88 Å, respectively, in an octahedral environment. A simple explanation to account for the large lattice change may result from the release of the Jahn-Teller distortion in going from a d^9 ion (Cu^{2+}) to a d^{10} ion (Zn^{2+}). For the pure La-Sr-Cu-O phase, the Cu—O bonds along the c axis are longer than those within the basal (a,b) plane. As the non-Jahn-Teller ion Zn^{2+} is substituted for copper in the lattice the CuO_6 octahedron is progressively squeezed along the c axis leading to an increase of the Cu—O bonds within the basal plane and a decrease of those parallel to the c axis. As a result, one would expect an increase of the unit cell length a and a decrease of c as observed experimentally. The c/a ratio can also be used to characterize this distortion. Like Zn^{2+}, Ni^{2+} should affect the structure in a similar way. This is consistant with the fact that the c/a ratio varies in a similar way for both Ni and Zn-doped materials [Fig. 1(c)]. Finally, another interesting feature [Fig. 1(d)] is the variation of the unit cell volume (V) as a function of Ni and Zn content. Note that V increases when M =Zn whereas it decreases when M =Ni as expected from the ionic radii since Ni is smaller than copper which is smaller than Zn.

The 90 K nickel-doped materials (x =0.25 or 0.5) were also single phase. The lattice parameters of the orthorhombic unit cell are reported in Table I. Note that the cell lengths a, b, and c slightly decrease with x within the accuracy of the data. The shrinkage of the cell is better shown by the cell volume which decreases from 173.28 to 171.75 Å^3 upon nickel substitution. An attempt to insert more nickel into this compound resulted in a multiphase material. Thus, the value of x =0.5 may overestimate the upper limit of the nickel solubility in the 90 K phase.

The temperature dependence of the resistivity for the Ni and Zn 40 K-doped samples is shown in Fig. 2. For

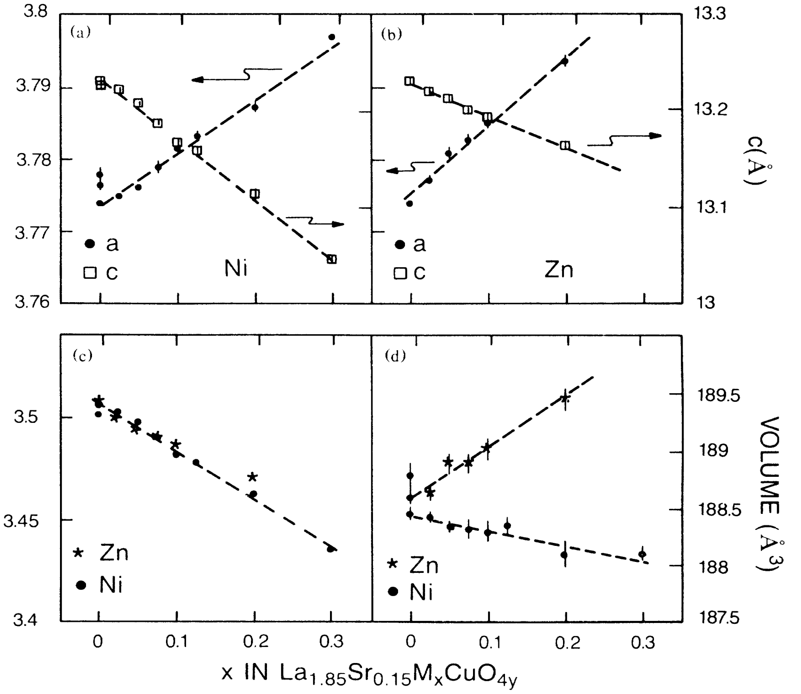

FIG. 1. Tetragonal unit cell parameters a, c, and V are reported for the $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$ series: (a) a and c are shown when M =Ni, (b) a and c are shown when M =Zn, (c) c/a ratio for both M =Ni and Zn, and (d) V is shown for both M =Ni and Zn.

TABLE I. Lattice parameters, transition temperatures, and resistivities for the materials studied. The midpoint temperature T_{cm} is the temperature where the resistance has fallen to half its extrapolated value. Also reported are the parameters obtained from a fit to the Curie-Weiss law. Show are the effective magnetic moment per M atom $\mu_{\text{eff}}(\mu_0)$ derived from the Curie constant C, the Weiss constant Θ, the rms deviation σ of the data from the Curie-Weiss law (in percent), and the temperature interval over which the fit was determined T_{fit}. (VA) refers to vacuum-annealed $YBa_2Cu_3O_{7-y}$ sample ($y \cong 1$).

Compounds	a (Å)	b (Å)	c (Å)	ρ_{3000} ($\mu\Omega$ cm)	V (Å)^3	T_{cm} (K)
$La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$						
M = Ni						
x = 0	3.777(3)		13.226(1)	2300	188.60(1)	
x = 0.025	3.7749(2)		13.222(1)	2380	188.42(2)	
x = 0.05	3.7761(2)		13.2078(9)	3500	188.33(2)	
x = 0.075	2.7789(4)		13.187(1)	4000	188.31(4)	
x = 0.1	3.7915(3)		13.1671(3)	4200	188.29(6)	
x = 0.125	2.7833(3)		13.1582(3)	9300	188.36(3)	
x = 0.2	3.7873(4)		13.1138(2)	· · ·	188.09(6)	
x = 0.3	3.7971(3)		13.0460(1)	· · ·	188.10(3)	
M = Zn						
x = 0.025	3.7772(2)		13.2213(1)	3500	188.663(4)	
x = 0.05	3.7809(1)		13.135(3)	3000	188.86(3)	
x = 0.075	3.7927(3)		13.2014(2)	15 000	188.892(2)	
x = 0.10	3.7850(4)		13.1940(1)	10 500	189.017(5)	
x = 0.2	3.7936(3)		13.1638	20 000	189.442(6)	
$YBa_2Cu_{3-x}Ni_xO_7$						
x = 0	3.8237(8)	3.8874(3)	11.657(3)	1800	173.28(6)	
x = 0.25 (VA)	3.8589(8)		11.800(4)	· · ·	175.72(8)	
x = 0.25	3.8191(8)	3.8857(8)	11.6571(3)	1360	172.98(7)	
x = 0.5	3.8197(7)	3.8832(4)	11.6470(5)	2500	172.75(8)	

Compounds	T_{cm} (K)	$\mu_{\text{eff}}(\mu_0)$		Θ (K)	σ (%)	T_{fit} (K)
		(per mole of Cu)	(per mole of M)			
$La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$						
M = Ni						
x = 0	39.3	· · ·	· · ·	· · ·	· · ·	· · ·
x = 0.025	22.6	· · ·	· · ·	· · ·	· · ·	· · ·
x = 0.05	4.2	· · ·	· · ·	· · ·	· · ·	· · ·
x = 0.075	No	0.21	0.74	1	0.93	15–300
x = 0.1	No	0.28	0.83	2	0.27	20–300
x = 0.125	No	0.43	1.14	9	0.9	20–300
x = 0.2	No	· · ·	· · ·	· · ·	· · ·	· · ·
x = 0.3	No	1.14	1.72	14	0.76	10–300
M = Zn						
x = 0.025	15	· · ·	· · ·	· · ·	· · ·	· · ·
x = 0.05	No	· · ·	· · ·	· · ·	· · ·	· · ·
x = 0.075	No	0.16	0.56	11	0.85	10–300
x = 0.10	No	0.17	0.50	8	0.73	10–300
x = 0.2	No	0.23	0.46	9	0.71	10–300
$YBa_2Cu_{3-x}Ni_xO_7$		(per mole of 3d metal)				
x = 0	91.6	0.29		−21	0.5	100–300
x = 0.25 (VA)	No	0.66		−3	0.18	15–300
x = 0.25	63.9	0.62		14	0.13	80–300
x = 0.5	52.3	0.87		−4	0.23	60–300

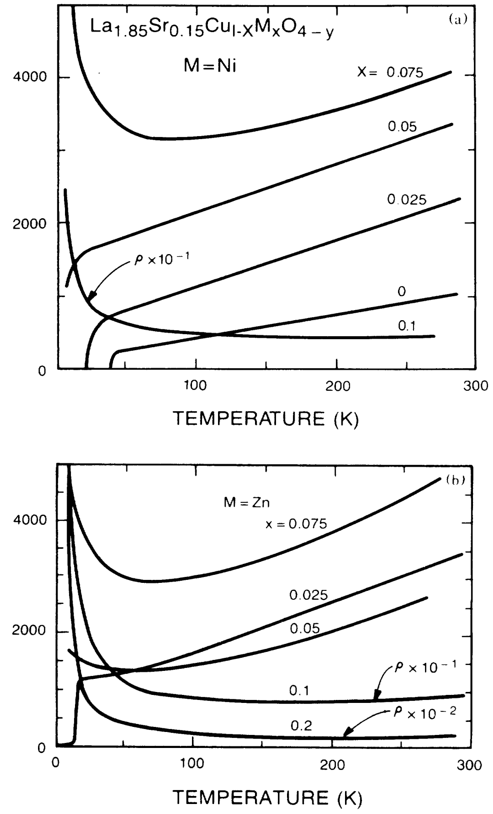

FIG. 2. The resistivity vs temperature for several nickel and zinc-doped perovskites is given from 300 K to below T_c: (a) Resistivity data for the $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_4$ series, and (b) resistivity data for the $La_{1.85}Sr_{0.15}Cu_{1-x}Zn_xO_4$ series.

the nickel-doped samples the superconducting transition temperature is depressed from 40 K ($x=0$) to 22 K ($x=0.025$) and about 4.2 K for $x=0.05$. For these Ni concentrations a metallic character (defined as resistance decreasing with decreasing temperature) is observed having a linear resistivity temperature dependence at temperatures above the onset of superconductivity. At higher nickel contents the low-temperature resistivity increases with decreasing temperature, indicating a semiconductinglike behavior. As x increases the temperature at which the resistivity reaches a minimum also increases. This trend is consistent with the semiconducting behavior over this entire temperature range previously reported for La_2NiO_4. A surprising result is that the diamagnetic ion (Zn^{2+}) suppresses T_c more rapidly than does nickel. T_c decreases from 40 K ($x=0$) to 15 K ($x=0.025$) and below 4.2 K for $x=0.05$. At higher concentrations the compounds do not superconduct but superconducting-semiconducting behavior is observed for the nickel samples.

Figure 3 shows the transport properties for the 90 K nickel-doped phases. In this case the superconductivity is less affected by introducing nickel than for the 40 K system, so that T_c is still 50 K for $x=0.5$. The complete loss of a superconducting transition, like in the 40 K system, cannot be observed because of the inability to prepare a single-phase material at higher x.

A resistance going to zero only proves that there is a superconducting path between the voltage leads. To ensure that there is bulk superconductivity in the mixed phases, Meissner and shielding measurements were performed by means of a superconducting quantum interference device (SQUID) magnetometer. For the $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$ series, 58% and 42% Meissner effects were observed for $x=0.025$ with $M=$Ni (Fig. 4) and Zn, respectively, supportive of bulk superconductivity. No sign of superconductivity was detected at higher x. For the 90 K phases, $YBa_2Cu_{3-x}Ni_x$, 25 and 20% Meissner signals were measured for $x=0.25$ and $x=0.5$ respectively.

Figure 5(a) shows the $B_{c2}(T)$ for a nickel-doped 40 K specimen (x = 0.025). The values of $B_{c2}(T)$ are midpoint values which are influenced somewhat by a problem in the determination of the normal resistance at high fields because the Ni introduces a slight rise in the resistance with increasing temperature just above the transition. The $B_{c2}(T)$ data are roughly linear and the extrapolation of this straight line to $B_{c2}=0$ yields a transition temperature of 20 K. The value of $dB_{c2}/dT=4.5$ T/K, which is a very high slope, is determined from the highest field (lowest T) data, but this value may be somewhat higher if measurements are extended above 20 T. Using the above values and the WHH theory[15] for a dirty type-II superconductor, one obtains $B_{c2}=64$ T. A surprising result here is that the value of (dB_{c2}/dT) is two times larger than that obtained for the undoped La-Sr-Cu-O phase,[16] so that with a superconducting critical temperature two times smaller, $B_{c2}(0)$ is similar for both doped or undoped materials. We also found that the introduction of a rare earth into the La-Sr-Cu-O system at the lanthanum site affects the critical field. These results will be presented elsewhere.

The upper critical field $B_{c2}(T)$ for a $YBa_2Cu_{2.5}Ni_{0.5}O_{7-y}$ specimen is shown in Fig. 5(b). The $B_{c2}(T)$

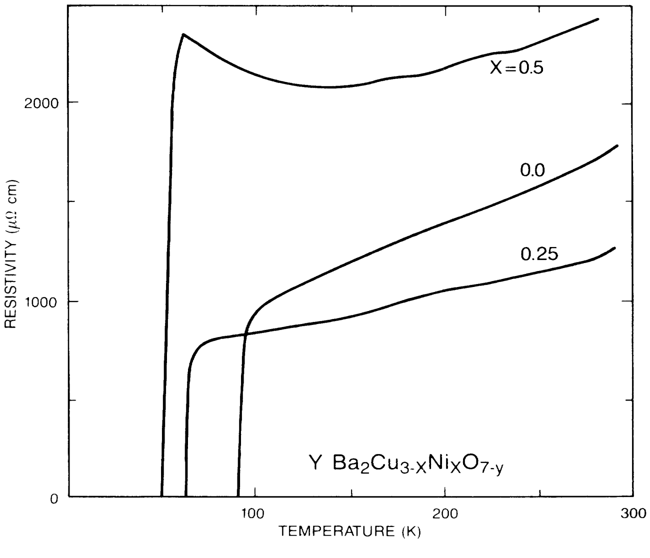

FIG. 3. The resistivity vs temperature is given for several members of the $YBa_2Cu_{3-x}Ni_xO_{7-y}$ series.

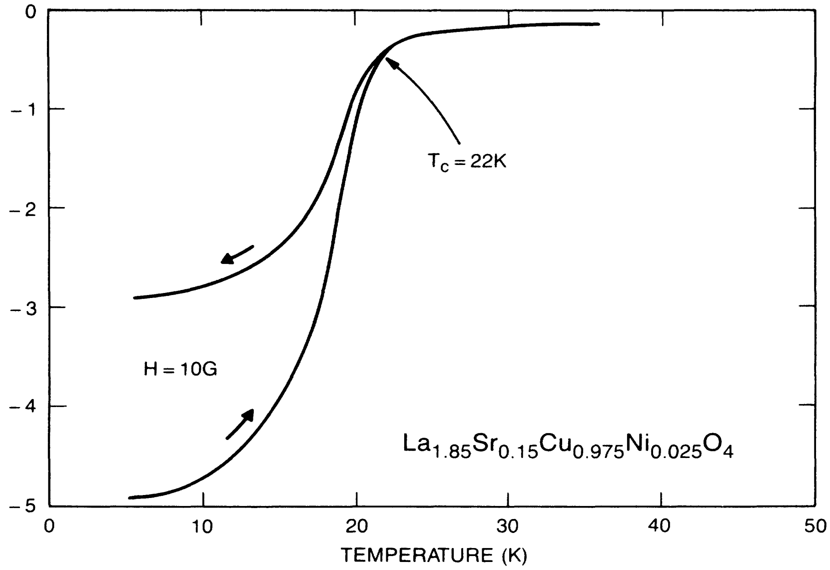

FIG. 4. Magnetic susceptibility vs temperature for the nickel doped 40 K phase with $x = 0.025$. The upper curve is for cooling in a field of 10 G (Meissner); the lower curve is for warming in 10 G after cooling in zero field (shielding).

data are clearly nonlinear with a substantial positive curvature of B_{c2} vs T. Using the same procedure as above we define $T_c = 47.7$ K as the midpoint of the superconducting transition, and $dB_{c2}/dT = 1.7$ T/K so that $B_{c2}(0) = 56$ T. Due to the large positive curvature of the B_{c2} curve the value of the slope is here les accurate than in Fig. 4(a). The introduction of nickel reduces T_c markedly whereas the values of dB_{c2}/dT remain about the same as that for pure $YBa_2Cu_3O_{7-y}$. In contrast, recent studies have shown that the introduction of rare earth atoms on the yttrium sites do not affect the critical temperatures and the critical fields.[17]

In an attempt to determine the oxidation state of the nickel in these materials, magnetic measurements from 4.2 K to room temperature have been performed. In Fig. 6 are shown our results for the 40 K system. Note that for the undoped material the susceptibility decreases slightly with decreasing temperature suggesting that there is no contribution of the Cu ions to the susceptibility. The substitution for copper by nickel modifies the susceptibility in such a manner that beyond a nickel content of 0.05, the susceptibility increases with decreasing temperature in a Curie-type manner. The data were least-squares fitted to the Curie-Weiss formula $\chi_g = C_g/(T+\Theta)+\chi_0$ as previ-

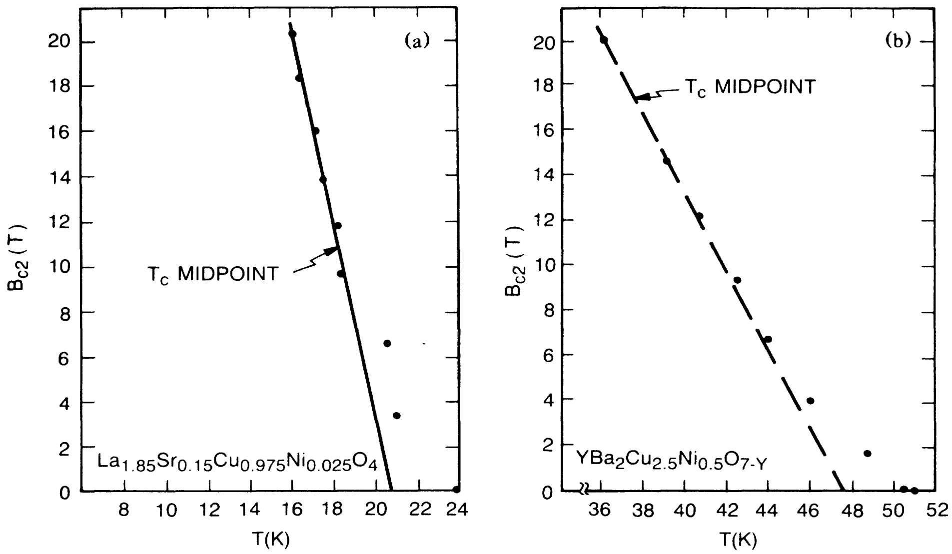

FIG. 5. Upper critical fields B_{c2} vs temperature for the nickel-doped superconducting perovskites. The values of $B_{c2}(T)$ for midpoint resistivity are shown for the (a) La-Sr-Cu-O ($x = 0.025$), and (b) Y-Ba-Cu-O ($x = 0.5$) compounds.

ously described.[18] Table I shows the results of such a fit along with the temperature interval over which the fit was made and the magnetic moment of the substituted element (Ni). (The values of μ_{eff} are also given per mole of Cu atoms.) Note that the moment obtained increases with increasing x reaching a value of 1.73 at $x = 0.3$. Simultaneously, we observed that the Weiss constant (Θ) becomes more positive with increasing nickel concentration as expected since pure La_2NiO_4 has a Weiss constant of 500 K. Singh, Ganguly, and Goodenough[19] have shown, by means of high-temperature magnetic measurements, that in the $La_2Ni_{0.25}Cu_{0.75}O_4$ phase the nickel ions with a μ_{eff} of $3.0\mu_B$ are unambiguously divalent, as in most oxides. For the same compound at temperatures below 310 K, their data obeyed different Curie-Weiss behavior leading to a moment of $1.83\mu_B$ per nickel ion as we have observed in our $x = 0.3$ nickel-doped 40 K materials. Thus, it is reasonable to assume that nickel replaces copper as a divalent ion. When $M = \text{Zn}$, Fig. 6(b), the susceptibility remains temperature independent up to $x = 0.025$ and then follows a Curie-Weiss law at higher concentrations. Since zinc is diamagnetic, the copper atoms are most likely responsible for the observed Curie-type behavior. Using a Curie-Weiss fit as described above the magnetic moment per Cu atom can be extracted. The values are reported in Table I. Note that the moment thus obtained, increases slightly with increasing zinc content, most likely due to some copper atoms becoming magnetically active. It is also important to note that in both cases the changes in transport and magnetic properties occur between $x = 0.05$ and 0.075 for Ni and between $x = 0.025$ and 0.05 for Zn. For Ni and Zn, respectively, and for $x \leq 0.05$ and 0.025, the compounds are superconductors and exhibit a Pauli paramagnetism, while for $x > 0.075$ and 0.05 the materials are semiconductors with a paramagnetic susceptibility.

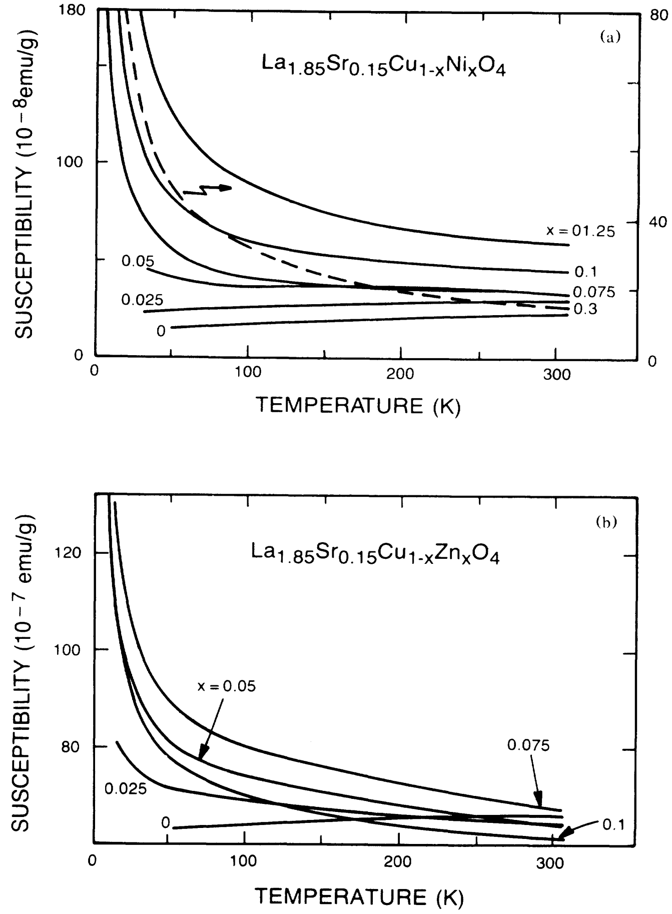

FIG. 6. The magnetic susceptibility in a field of 10 kG as a function of the temperature is given for several members of (a) $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_4$ and (b) $La_{1.85}Sr_{0.15}Cu_{1-x}Zn_xO_4$ series.

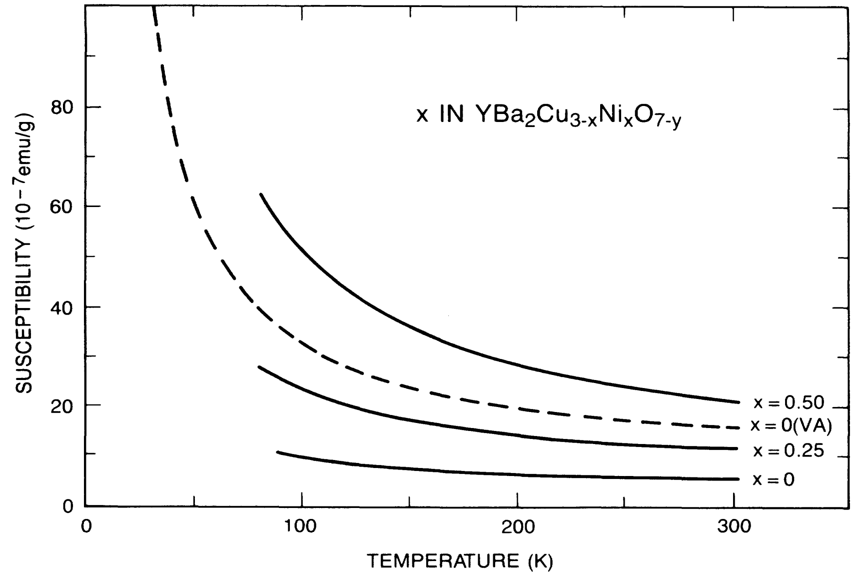

FIG. 7. The magnetic susceptibility in a field of 10 kG is shown as a function of the temperature for several members of the $YBa_2Cu_{3-x}Ni_xO_{7-y}$ series. The dashed line refers to the vacuum-annealed $YBa_2Cu_3O_{7-y}$ ($y \cong 1$) sample.

Our magnetic results for the nickel-doped 90 K phases are summarized in Fig. 7. Note the large temperature dependence of the susceptibility for the undoped sample, suggesting, in this case, a contribution from the Cu ions. The introduction of nickel atoms enhances the paramagnetic signal and in all cases the susceptibility increases in a Curie-type manner upon cooling the sample down to its superconducting temperature. The data have been fitted (as described previously) and the results are summarized in Table I. The moment per mole of 3*d* transition metal, as well as the Weiss constant, increases with increasing nickel content. However, the contribution of the copper ions to the susceptibility prevents attributing a valence to the substituted nickel ions. It is important to note also in Table I that removal of oxygen from pure $YBa_2Cu_3O_{7-x}$ increases the moment per copper ion from 0.24 to 0.66.

We have also substituted Co for Cu in the $La_{1.85}Sr_{0.15}Cu_{1-x}Co_xO_4$ ($0 < x < 0.3$ in 0.05 steps) system. Like nickel, cobalt rapidly suppresses superconductivity. For example, the phase with a cobalt content of 0.05 was not superconducting down to 4.2 K.

IV. DISCUSSION

For conventional type superconductors, it is well known from the Arbrikosov and Gork'ov[10] theory that the direct interactions of magnetic ions with the superconducting electrons breaks the Cooper pairs and suppresses T_c. As an example, it has been found for the Chevrel phase $PbMo_6S_8$ that T_c decreases dramatically from 15 K down to less than 1 K when 3*d* magnetic ions (Ni, Fe, . . .) are substituted for Pb in the structure while it is slightly affected by 3*d* nonmagnetic ions such as Cu^{1+}.[20,21]

Band structure calculations performed by Mattheiss and Hamann[22] on these new high T_c perovskites have indicated that the Cu 3*d*–O 2*p* electrons are most likely responsible for superconductivity. We have previously reported that the substitution of rare-earth magnetic ions on the lanthanum site (40 K materials),[11] or on the yttrium sites (90 K materials)[10] have little effect on T_c. It was suggested that the distance between magnetic ions and superconducting electrons was too large to uncouple Cooper pairs. Here we have shown that the replacement of Cu by Ni in the 90 K phase decreases T_c rapidly, but from x-ray data we were not able to determine whether the nickel ions are equivalently distributed over the two copper sites present in the structure. For the 40 K type material there is only one copper site, and we found that the chemical doping of the Cu–O plane in this phase suppresses T_c and promotes semiconducting behavior. Furthermore, this is independent of the nature of the 3*d* metal, either magnetic (Ni, Co) or nonmagnetic (Zn). Thus we conclude that the depression of T_c in these new oxides is not necessarily of a magnetic origin. It might be argued that the moment induced by Zn (Table I) is responsible for suppressing T_c, but that moment is smaller than the moment induced by Ni in the Ni-doped compound, and yet T_c drops faster with Zn doping than with Ni doping.

We consider four interrelated explanations, discussed below, for the reduction of T_c with 3*d* metal doping in the Cu–O planes; structural disorder, oxygen vacancies, the dopants inducing a different oxidation state in the copper and magnetic pair breaking. The replacement of 3*d* metals for Cu can be seen as the introduction of defects (which may act as electron traps) within the Cu–O plane, perturbing the conducting path for the Cu 3*d*–O 2*p* electrons. As the disorder within the Cu–O plane increases, the compound becomes semiconducting and, simultaneously, the susceptibility increases. The phase La_2NiO_4 exists in the same structure as La_2CuO_4 whereas the La_2ZnO_4 has a different structure,[23] leading to the expectation that Zn should introduce more disorder than Ni in the compound, thus suppressing T_c faster. This is consistent with our data. But we also observe that the introduction of oxygen vacancies (i.e., defects) suppresses T_c in the 40 K material and induces a semiconducting behavior similar to that produced by Ni or Zn. And in fact, we cannot rule out the possibility that introducing Zn or Ni changes the oxygen content as occurs with Sr doping in $La_{2-x}Sr_xCuO_4$.[3] The 3*d* metal dopants may also induce a different oxidation state in the copper. Finally, magnetic pair breaking must be considered. The introduction of magnetic species directly, as that associated with the dopant Ni^{2+}, or that induced by the localization associated with the structural disorder, as indicated by the introduction of a magnetic moment in the Zn-doped material, may be equally efficient as magnetic pair breakers.

Several new superconductivity mechanisms, including those which propose Cooper pairing mediated either by excitons[24] or antiferromagnetic interactions (RVB model),[25] have been proposed to explain the unexpectedly high T_c in these materials. Recent theoretical work by Coffey and Cox[26] has shown that the RVB order parameter, and thus the T_c, is suppressed by disorder more strongly than occurs in the phonon-mediated BCS theory. Our results then could be consistent with an RVB-type mechanism. On the other hand, we do not know the effect of disorder within the framework of the excitonic model.

In summary, we have shown that the superconducting properties of both $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-x}$ systems are extremely sensitive to the chemical doping of the Cu–O planes. The replacement of Cu by Ni and Zn as well as the oxygen doping suppresses T_c, promotes semiconducting behavior and enhances magnetism for both systems.

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