

Magnetism of Fe, Ni, and Zn in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$: Comparison of experiment and theory

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We have studied the magnetic and superconducting properties of Fe-, Ni-, and Zn-substituted $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ bulk materials. The normal-state magnetic susceptibility of all samples is found to follow the Curie-Weiss law between 50 and 300 K. The magnitude of local moments deduced for Fe and Ni are $2.2\mu_B$ and $2\mu_B$, respectively. The observed moment on Ni is attributed to Ni in a $3+$ valency state. A magnetic moment of $0.8\mu_B$ is obtained in Zn-substituted samples. This is ascribed to the localized Cu^{2+} spins. The T_c vs $3d$ ion concentration (x) curves indicate that Ni inhibits the T_c of this system at an anomalously higher rate. In an effort to understand the correlation between the magnitude of the magnetic moment on the $3d$ ion and its role in the suppression of superconductivity, we have performed density-functional cluster calculations under local-spin-density approximations. The calculations support the following inferences drawn from the experiments: (i) Ni is in a $3+$ state, (ii) the moment of $0.8\mu_B$ observed in Zn-substituted samples is due to localized Cu^{2+} spins, and (iii) Zn induces a moment of almost the same magnitude in both the electron-doped and the hole-doped $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ systems. We have also attempted to explain qualitatively the observed T_c vs x behavior in the above systems using the effective single-band t - J model.

The $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta}$ systems are a convenient set of model materials to explore the physical properties pertaining to magnetism and superconductivity. The fact that the character of the charge carriers is electronlike in the former and holelike in the latter provided a means to evaluate the veracity of various competing theoretical models in explaining the underlying features related to superconductivity in these materials.¹ A number of crucial studies have been performed to understand the crystal structure,² band structure,³ magnetic ordering,⁴ electronic phase diagram,⁵ and so on. In an effort to gain a better insight into the role of Cu-O clusters in obtaining high- T_c superconductivity, the possibility of substitution at the Cu site has been exploited.⁶ The substituted ions were used to probe the local electronic⁷ and magnetic properties⁸ and to unravel various factors that are relevant to superconductivity.⁹ These studies served well in establishing the correlation between the magnetic character of the ions occupying the Cu site and their effect on superconductivity. The observed systematics of T_c variation have been used to assess the relevant theoretical models.^{6,10} The indications are, although there exist a lot of similarities between the hole-doped and the electron-doped superconductors, the basic mechanism of superconductivity perhaps is different in these systems.⁶ The phonon density of states measurements by neutron-scattering¹¹ as well as tunneling studies¹² seem to suggest the dominance of a phonon-mediated electron pairing mechanism for super-

conductivity in the electron-doped superconductor.

We have undertaken a comprehensive study that encompasses experiment and theory of a Fe-, Ni-, and Zn-substituted $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ system to explore the relation between the local magnetic moment and the valency of the substituted ions and their effect on T_c . Density-functional cluster calculations were performed under local-spin-density approximations to determine the local electronic configuration of the $3d$ ions and the effective magnetic moments. The results were compared with the analogous hole-doped $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta}$ compound to understand the effect of differing crystal fields on the magnitudes of the magnetic moments. We have used the effective single-band model (t - J model) to explain the apparent anomalies found in T_c variation of electron-doped and hole-doped superconductors.

Samples of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{M}_x\text{O}_{4-\delta}$, where M is Fe, Ni, or Zn were synthesized by a solid-state reaction of stoichiometric amounts of the constituent oxides. To improve homogeneity, well-mixed materials were reacted in air for 24 h at 900, 1000, and 1100°C, respectively. The reacted materials were pelletized and sintered at 1100°C for 18 h. Subsequently, the samples were annealed for 36 h under flowing nitrogen gas. Depending on the substitution, the optimum annealing temperature varied in the range 840–900°C. X-ray powder-diffraction patterns were recorded to ascertain the phase purity of the samples. All peaks in the pattern could be indexed using the tetragonal T' phase structure. To determine the super-

conducting transition temperature (T_c), magnetization measurements were made using a Quantum Design Superconducting quantum interference device magnetometer, in a field of 10 G, in the zero-field-cooled and field-cooled modes. T_c represents the temperature corresponding to the onset of diamagnetic susceptibility. To collect susceptibility data in the normal state the samples were cooled in a field of 10 kG. Resistivity data were collected in the temperature range 4.2–300 K on rectangular slab samples using the standard four-probe configuration.

The magnetization of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{M}_x\text{O}_4$ samples, where M is Fe, Ni, or Zn, was measured under a field of 10 G in both the zero-field-cooled and field-cooled modes. Figure 1 shows the observed dependence of T_c on the concentration of $3d$ ions (x) substituted at the Cu site. As shown, the T_c for all the substitutions studied varies smoothly with x . To confirm the T_c values determined by magnetization measurements, resistivity of samples was measured in the temperature region 4.2–300 K. The T_c values were in agreement with that obtained by magnetization measurements. Figure 1 clearly demonstrates the anomalous deleterious effect of Ni substitution on the superconductivity of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$. Comparing the rates of T_c depression (dT_c/dx) with the substitution of Ni, Fe, and Zn, it can be seen that in the case of Ni the dT_c/dx is twice that of Fe and almost ten times the rate found for Zn substitution. The concentrations corresponding to complete suppression of superconductivity for Ni and Zn substitution are $x=0.85$ and 9 at. %, respectively. Whereas for Fe substitution this could not be established as the x-ray powder-diffraction pattern indicated the presence CaFeO_3 as a secondary phase for $x > 1$. The concentrations of $3d$ ions corresponding to complete suppression of T_c are in agreement with that published in the literature.

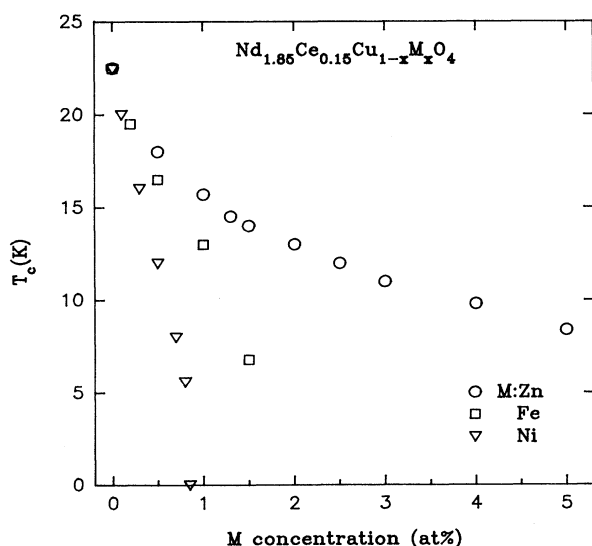


FIG. 1. Variation of T_c of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{M}_x\text{O}_4$, where M is Fe, Ni, and Zn. Concentration (x) of M corresponding to $T_c \sim 0$: $x(\text{Ni})=0.85$ at. % and $x(\text{Zn})=9$ at. %.

The electron-doped superconductor $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, except for the lack of apical oxygens for the Cu atoms in the CuO_2 planes, possesses a very similar structure to that of the hole-doped superconductor $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. Therefore, it will be an interesting exercise to compare the above results with that found in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. For this purpose we have replotted the results of Xiao *et al.* in Fig. 2.⁸ They have carefully studied the variation of T_c with the substitution of various ions including Fe, Ni, and Zn in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. Comparing Figs. 1 and 2, striking differences in the behavior of T_c depression can be seen. A number of factors, including about an order of magnitude difference in the zero-temperature coherence lengths, change in the valency and/or magnetic moment due to differing crystal-field symmetries, and a difference in the fundamental characteristics between these systems, may account for this behavior. In $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ the Cu ions are octahedrally coordinated to oxygen ions, whereas the oxygen coordination in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ is square planar. Since the crystal-field effects dominate the magnetic properties of $3d$ ions, a significant difference in the moment can be expected between these two systems.

In an effort to unravel the magnetic character of the $3d$ ions substituted at the Cu site, we have measured the susceptibility of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-x}\text{M}_x\text{O}_4$ ($M=\text{Fe, Ni, and Zn}$) samples with $0 \leq x \leq 0.1$, in the normal state. The temperature variation of susceptibility of all samples followed the Curie-Weiss law, above about 50 K. We have subtracted the susceptibility of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, $\chi(0, T)$, from the data of $3d$ ion substituted samples, $\chi(x, T)$, to eliminate the contributions due to Nd^{3+} moments as well as the effects of Ce substitution. The differential susceptibility $\Delta\chi(x, T) = \chi(x, T) - \chi(0, T)$. Figure 3 displays the temperature dependence of the inverse susceptibility for

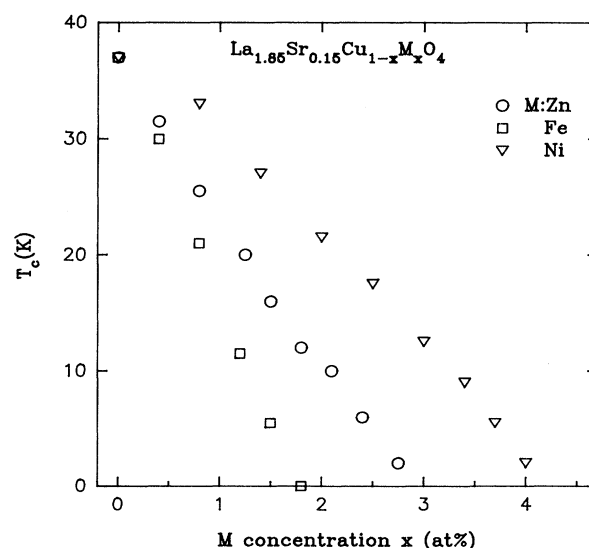


FIG. 2. Variation of T_c of $\text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_{1-x}\text{M}_x\text{O}_4$, where M is Fe, Ni, and Zn. Concentration (x) of M corresponding to $T_c \sim 0$: $x(\text{Fe})=1.8$ at. % $x(\text{Ni})=4$ at. % and $x(\text{Zn})=3$ at. %. Above $T_c(x)$ data are reproduced from Ref. 8.

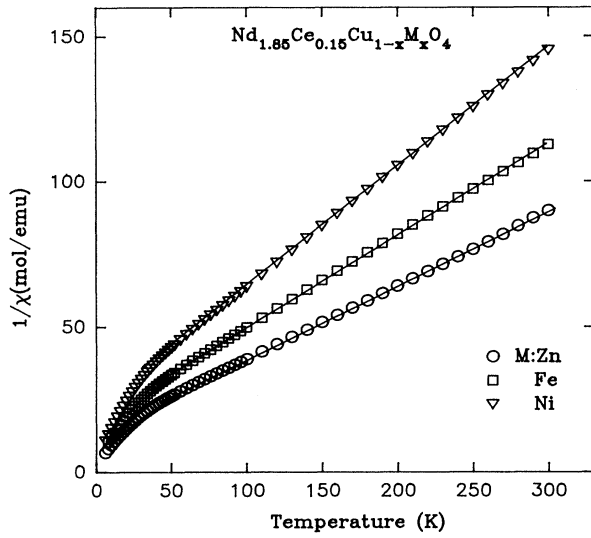


FIG. 3. Variation of χ^{-1} with temperature for some representative samples. Solid lines are the Curie-Weiss law fit to the data. Fe data represented by (\square) are scaled by a factor of 1.25 in order to display the data clearly.

some representative samples. We have used the following Curie-Weiss relation to deduce the effective moment on the $3d$ ion occupying the Ce site:

$$\Delta\chi(x, T) = \frac{NP_{\text{eff}}^2\mu_B^2}{3k_B(T - \theta_C)},$$

where N is the number of $3d$ ions per mole, θ_C is the Curie-Weiss temperature, and k_B is the Boltzmann constant. In Zn-substituted samples the P_{eff} values obtained from the fit to the above equation remained around $0.8\mu_B$, independent of the concentration x . This value is attributed to the localized Cu^{2+} spins, as Zn^{2+} is a non-magnetic ion. On the other hand, in the case of Ni or Fe substitution, the effective magnetic moment (P_{eff}) deduced from the fit contains contributions from the magnetic ions along with the Cu^{2+} ions. To alienate the magnetic moment on Ni from that of the P_{eff} value, we have written $NP_{\text{eff}}^2 = N_{\text{Cu}}P_{\text{Cu}}^2 - N_{\text{Ni}}P_{\text{Ni}}^2$. Since $N_{\text{Ni}} = Nx$ and $N_{\text{Cu}} = N(1-x)$ the relation reduces to $P_{\text{eff}}^2 = P_{\text{Cu}}^2 - (P_{\text{Cu}}^2 + P_{\text{Ni}}^2)x$. By fitting the P_{eff} and Ni content x to this equation the effective moments $P_{\text{Cu}} = 0.8\mu_B$ and $P_{\text{Ni}} = 1.96\mu_B$ are obtained. By following a similar procedure we have obtained $P_{\text{Cu}} = 0.8\mu_B$ and $P_{\text{Fe}} = 2.2\mu_B$ for Fe-substituted samples. In Fig. 4 we have plotted the effective moment (P_{eff}) values as a function of the $3d$ ion concentration (x). The paramagnetic Curie temperature as shown in Fig. 4 increased with increasing x .

Now we will compare the P_{eff} values of Fe, Ni, and Zn observed in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ with that in the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ system. As mentioned earlier the effective magnetic moment ($0.8\mu_B$) observed in Zn-substituted samples is attributed to the localized Cu^{2+} spins. This value compares favorably with the value ($1\mu_B$) obtained by Xiao *et al.* for Zn-substituted $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$.⁸ The effective magnetic moment (P_{eff})

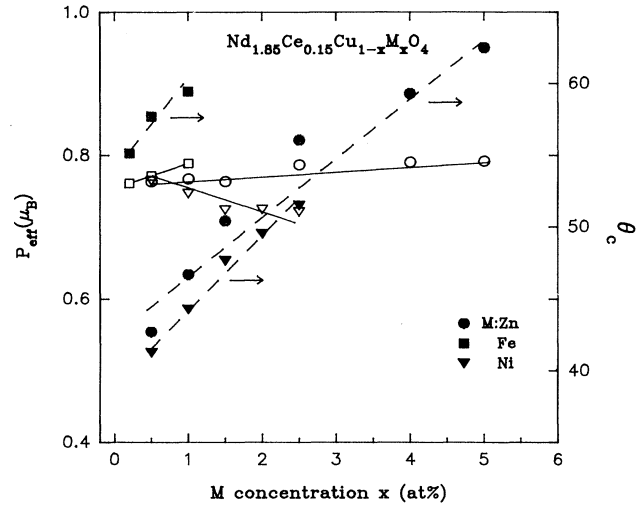


FIG. 4. Dependence of the effective magnetic moment (P_{eff}) on the concentration (x) of the $3d$ ions substituted at the Cu site in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$. The solid and dashed lines are a guide to the eye.

of Ni and Fe in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ is about $2\mu_B$ and $2.2\mu_B$, respectively. The P_{eff} values of these ions in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ are $0.6\mu_B$ and $4.9\mu_B$, respectively.⁸

In order to explain the observed magnetic moment in Zn-substituted samples, it is imperative to have *a priori* knowledge of the effect of substitution of Sr and Ce on the antiferromagnetic order of the parent compounds La_2CuO_4 and Nd_2CuO_4 . In the case of La_2CuO_4 , long-ranged antiferromagnetic order is destroyed at 2% Sr, however, short-ranged correlations are found to survive into the superconducting state. On the other hand, in Nd_2CuO_4 , the μSR measurements demonstrate that the effect of Ce substitution is to reduce the antiferromagnetic ordering temperature (T_N) gradually with complete suppression of $T_N \rightarrow 0$ occurring close to 15% Ce, where the material is a superconductor.⁵ This difference is understood in terms of greater effectiveness of frustration relative to dilution in destroying the magnetic order. Irrespective of the mechanism by which the long-ranged order is destroyed it is evident that short-ranged antiferromagnetic correlations persist into the superconducting regime. The effect of Zn substitution then is to create a localized spin vacancy that only dilutes the short-ranged spin order further.¹³ The region surrounding the spin vacancy gives rise to a net moment.

Since oxygen coordination of Cu is square planar in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, the crystal-field symmetry experienced by $3d$ ions substituted at Cu sites is lower compared to that in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. The square planar (octahedral) crystal field stabilizes ions having spin configuration $3d^4$ and greater in the low (high) spin state. Following this criterion the expected magnetic moment on Ni^{2+} in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ is zero, since the effective spin of low-spin Ni^{2+} is zero; on the other hand in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, it should display a large moment ($\geq 2.8\mu_B$), corresponding to the high-spin state.¹⁴ The value of $P_{\text{eff}}(\text{Ni}) = 2\mu_B$ obtained in the $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ is not compatible with

Ni^{2+} in the low-spin state. This discrepancy can be accounted for by considering two plausible scenarios: (i) The crystal field is distorted to tetrahedral symmetry with the replacement of Cu by Ni. In this situation Ni^{2+} will attain the high-spin state. Then the difference that exists between the expected and the observed P_{eff} values can be ascribed to a strong hybridization of Cu $3d$ orbitals with the O $2p$ orbitals. (ii) Highly electronegative ions such as O^{2-} tend to stabilize Ni in a $3+$ state. The effective moment (P_{eff}) of Ni^{3+} in square planar coordination is found to be $1.7\mu_B$.¹⁵ The proximity of Ni^{2+} and Cu^{2+} ionic radii seems to preclude the possibility of local structural distortions. Considering this and the agreement of observed P_{eff} of Ni with the Ni^{3+} , it is tempting to speculate that Ni, contrary to the general expectation, enters the $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ lattice in a $3+$ state.

Recently Chen and Callaway performed density-functional calculations to study the local electronic structure and the magnetism of $3d$ ions substituted in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$.¹⁶ In this approach TMO_6 clusters, where TM stands for transition-metal ion, are embedded in an array of point charges to simulate the crystalline environment. This cluster approach is considered to be the simplest and most effective method to probe the local properties. The calculated values of local moments for Ni^{2+} ($1.56\mu_B$), Co^{2+} ($1\mu_B$), and Fe^{3+} ($3.48\mu_B$) are in general agreement with the experimentally obtained values $0.6\mu_B$, $1.2\mu_B$, and $4.9\mu_B$, respectively. Consequently, we have used this method to calculate the moment on Ni and Fe in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$.

Following an identical approach used for the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, a theoretical study was carried out based on density-functional cluster calculations under the local-spin-density (LSD) approximations. The method is described only briefly here, as the detailed account of it was published earlier.¹⁷ A realistic crystal environment is simulated by embedding the $3d$ O_4 clusters in an array of point charges. A total of 2156 point charges were placed on atomic sites of the Nd_2CuO_4 crystal structure, surrounding the central CuO_4 cluster. When the central Cu ion was replaced by other $3d$ ions (Fe and Ni), the cation-anion distance was fixed at 3.7249 bohr corresponding to the original Cu-O distance. Very little information regarding the Nd_2CuO_4 crystal relaxation due to substitution is available at the present time. For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ there is only a marginal change of lattice constants at low levels of substitution.¹⁸ Local electronic

structure and magnetism of CuO_4 , NiO_4 , and FeO_4 clusters were then obtained through the all-electron LSD calculations using a program package developed by Chen, Callaway, and Misra.¹⁷ Wave functions were expanded into localized Gaussian functions and a form of the local exchange-correlation potential as parametrized by Vosko, Wilk, and Nusair was used in these calculations.¹⁹

Each cluster was studied in -7 , -6 , and -5 charge states. Assuming that the oxygen ion charge state is fixed at -2 , the $3d$ cations in $3d\text{O}_4^{-6}$ should have $+2$ charge. Consequently, -7 charge state of the CuO_4 cluster represents the electron doping situation. Results of these calculations are summarized in Table I, where the charge-density distribution is studied by the Mulliken population analyses. The values in the column $N_d \uparrow - N_d \downarrow$ represent the local magnetic moments. As expected, Fe possesses the largest moment, $3.72\mu_B$ in FeO_4^{-6} , which compares favorably with $3.96\mu_B$ observed for Fe^{2+} in the square planar coordination.¹⁴ This value reduces to $2.82\mu_B$ when an extra electron is removed from the cluster, i.e., when Fe is in a $3+$ state. The moment on Fe in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ obtained from susceptibility measurements is $2.2\mu_B$. This agrees well with $2.18\mu_B$ obtained for low-spin Fe^{3+} in $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$, where it occupies the Cu(1) chain site having a square planar crystal field.²⁰ Consequently, it is reasonable to attribute the observed moment to low-spin Fe^{3+} . Interestingly, the agreement between $P_{\text{eff}} = 2\mu_B$ obtained for Ni from susceptibility measurements and the value ($2\mu_B$) calculated for Ni in a $3+$ state is excellent. Similarly, the calculated P_{eff} value ($=0.76\mu_B$) for Cu^{2+} also agrees well with $0.8\mu_B$ obtained in Zn-substituted samples. This agreement found between experiment and theory substantiates our contention that (i) Ni in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ is in a $+3$ state, (ii) the magnetic moment observed in Zn-substituted samples can be attributed to localized Cu^{2+} spins, and (iii) P_{eff} of Cu^{2+} is almost the same in both electron-doped and hole-doped superconductors.

We will now attempt to rationalize the marked differences found in the T_c variation of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ systems with the $3d$ ion concentration (x). Although the value of P_{eff} in Zn-substituted samples is found to be almost the same, from Figs. 1 and 2 it is obvious that Zn is less effective in suppressing the T_c of the former compared to that of the latter. In the case of hole-doped superconductors it is argued that the

TABLE I. Mulliken charge population analyses for $3d$ O_4 clusters in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$. N_{tot} is the total number of electrons inside the cluster.

$3d$ O_4 clusters	$N_{\text{tot}} \uparrow$	$N_{\text{tot}} \downarrow$	$N_d \uparrow$	$N_d \downarrow$	$N_d \uparrow - N_d \downarrow$	P_{eff} (Expt.)
FeO_4^{-5}	33	30	4.41	1.59	2.82	2.2
FeO_4^{-6}	34	30	4.93	1.21	3.72	
FeO_4^{-7}	35	30	4.92	1.18	3.74	
NiO_4^{-5}	34	31	4.98	2.98	2.00	2.0
NiO_4^{-6}	34	32	4.97	3.16	1.81	
NiO_4^{-7}	34	33	4.83	3.75	1.08	
CuO_4^{-6}	34	33	4.97	4.21	0.76	0.8
CuO_4^{-7}	34	34	4.8	4.8	0.0	

magnetic moment observed in Zn-substituted samples acts similar to the pair-breaking field, and would inhibit T_c in the same way that a magnetic impurity suppresses T_c of a conventional superconductor. Then the issue of why the superconductivity of both systems is not inhibited at the same rate needs to be resolved. A possible explanation for this lies in the effective single-band model for superconductivity proposed by Zhang and Rice.²¹ In this model the array of Cu^{2+} arrays are magnetically bound into singlets by nearest-neighbor exchange interaction of strength J . The strong hybridization between the Cu and O orbitals is presumed to be the source of the singlet binding. Holes doped into this array are bound into local singlets on each CuO_4 square. Because of their ability to hop from square to square by the exchange of an electron (this process is represented by a matrix element t in the theory), the doped holes are mobile. According to this scenario the CuO_4 square containing two holes which are bound in a mobile singlet configuration represents a spin polaron. The spatial extent of the spin-polaronic wave function is expected to be much larger in hole-doped systems compared to the electron-doped superconductors.¹⁰ Consequently, the pair-breaking field produced as a result of Zn substitution would affect the T_c of hole-doped superconductors more effectively than electron-doped superconductors. Comparing the magnitudes P_{eff} of Ni and Fe in both systems and following the above arguments, it is possible to place these ions in an order of decreasing effectiveness in suppressing the superconductivity: Fe in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ ($P_{\text{eff}}=4.9\mu_B$) $>$ Fe in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($P_{\text{eff}}=2.2\mu_B$) $>$ Ni in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($P_{\text{eff}}=2\mu_B$) $>$ Ni in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ ($P_{\text{eff}}=0.6\mu_B$). There are two anomalies in this sequence: (i) From Fig. 1, it may be noted that the rate of T_c suppression is lower for Fe compared to that of Ni. It should be pointed out that because of the presence of a CaFeO_3 secondary phase observed for $x \geq 0.01$, the actual concentration of Fe in the grains can be much lower than the nominal composition suggests. Therefore, the nominal concentration (x) used here should be considered as an overestimate of the actual Fe concentration. (ii) Comparing Figs. 1 and 2 it is obvious that Ni is most effective in inhibiting the superconductivity of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, since the rate of T_c depression is higher than in the case of Fe in the hole superconductor where it is found to possess a moment as high as $4.9\mu_B$. This fact can be accounted for by considering the $3+$ valency state of Ni in the $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ system. Ni^{3+} substitution would reduce the mobile electron concentration, because it is equivalent to the addition of holes to (i.e., removal of electrons from) the Cu-O planes. The fact that the T_c of cuprates is very sensitive to the variation of carrier concentration is well established.²²

Another plausible scenario that we should consider in order to explain the observed differences in T_c suppression is the difference in the symmetry of the superconducting order parameter. In the case of hole-doped superconductors there is a growing consensus that the symmetry of the pair wave function is d wave,²³ despite the fact that the results of some careful measurements do not rule out other possibilities, such as anisotropic s -wave²⁴ or the conventional s -wave²⁵ symmetries. The situation with the electron-doped superconductor $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, on the other hand, is quite clear. Temperature dependence of the penetration depth and the surface resistance²⁶ as well as the tunneling data¹² clearly establish the fact that the superconducting state in this class of cuprates is very similar to that of conventional s -wave superconductors. From this point of view, the Fe and Ni ions that are observed to carry large magnetic moments are expected to suppress the T_c of the electron-doped superconductor due to the pair-breaking effect. However, relevance of this magnetic interaction and its implication in the suppression of T_c in hole superconductors is yet to be properly understood. Furthermore, the differing symmetries of the pair wave function impose additional restrictions on any attempts to understand the origin of superconductivity in cuprates, as the systems that are almost identical should lead to differing superconducting states.

In conclusion, we have studied the susceptibility of Fe-, Ni-, and Zn-substituted $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ system in the superconducting as well as the normal state. The observed T_c variation with the $3d$ ion concentration is compared with the hole-doped $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ superconductor. In an attempt to understand the discrepancies in the observed rates of T_c depression, the effective moment carried by these ions is determined from the normal-state susceptibility measurements. The results indicate that Zn substitution produces the same magnitude ($0.8\mu_B$) moment in both electron- and hole-doped superconductors. The $P_{\text{eff}}=2\mu_B$ observed for Ni is consistent with Ni in a $3+$ state. Density-functional cluster calculations support the magnitudes of the magnetic moments and the valency states inferred from the experiment. Further, we have found that the variation of T_c with the $3d$ ion concentration (x) in both the electron-doped and hole-doped systems can be explained, roughly qualitatively, in a unified manner using the t - J model.

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¹V. J. Emery, *Nature* (London) **337**, 306 (1989); T. M. Rice, *ibid.* **337**, 686 (1989).

²Y. Tokura, H. Takagi, and S. Uchida, *Nature* (London) **337**, 345 (1989); G. H. Kwei, S.-W. Cheong, Z. Fisk, F. H. Garzon,

J. A. Goldstone, and J. D. Thompson, *Phys. Rev. B* **40**, 9370 (1989).

³S. Massida, N. Hamada, Jaeeun Yu, and A. J. Freeman, *Physica C* **157**, 571 (1989); M. Alexander, H. Romberg, N. Nücker,

- P. Adelman, J. Fink, J. T. Market, M. B. Maple, S. Uchida, H. Takagi, Y. Tokura, A. C. W. P. James, and D. W. Murphy, *Phys. Rev. B* **43**, 333 (1991).
- ⁴G. M. Luke, B. J. Sternlieb, Y. J. Uemura, J. H. Brewer, R. Kadono, R. F. Kiefl, S. R. Krietzman, T. M. Riseman, J. Gopalakrishnan, A. W. Sleight, M. A. Subramanian, S. Uchida, H. Takagi, and Y. Tokura, *Nature (London)* **338**, 49 (1989).
- ⁵G. M. Luke, L. P. Le, B. J. Sternlieb, Y. J. Uemura, J. H. Brewer, R. Kadono, R. F. Kiefl, S. R. Krietzman, T. M. Riseman, C. E. Stronach, M. R. Davis, S. Uchida, H. Takagi, Y. Tokura, Y. Hidaka, T. Murakami, J. Gopalakrishnan, A. W. Sleight, M. A. Subramanian, E. A. Early, J. T. Market, M. B. Maple, and C. L. Seaman, *Phys. Rev. B* **42**, 7981 (1990).
- ⁶J. M. Tarascon, E. Wang, S. Kivelson, B. G. Bagley, G. W. Hull, and R. Ramesh, *Phys. Rev. B* **42**, 218 (1990).
- ⁷Jun Sugiyama, Shinya Tokuono, Shin-ichi Koriyama, H. Yamauchi, and Shoji Tanaka, *Phys. Rev. B* **43**, 10 489 (1991).
- ⁸Gang Xiao, Marta Z. Cieplak, J. Q. Xiao, and C. L. Chien, *Phys. Rev. B* **42**, 8752 (1990).
- ⁹J. Sugiyama, J. H. Brewer, G. D. Morris, C. Niedermayer, T. M. Riseman, I. Shinkoda, H. Zhou, E. J. Ansaldo, H. Glucker, H. Yamauchi, and S. Tanaka, *Physica C* **193**, 449 (1992).
- ¹⁰C. Barlingay, Valentin Garcia-Vazquez, Charles M. Falco, S. Mazumdar, and S. H. Risbud, *Phys. Rev. B* **41**, 4797 (1990).
- ¹¹J. W. Lynn, I. W. Sumarlin, D. A. Neumann, J. J. Rush, J. L. Peng, and Z. Y. Li, *Phys. Rev. Lett.* **66**, 919 (1991).
- ¹²Q. Huang, J. F. Zasadzinski, N. Trishawala, K. E. Gray, D. G. Hinks, J. L. Peng, and R. L. Greene, *Nature (London)* **347**, 369 (1990).
- ¹³A. Chakraborty, A. J. Epstein, M. Jarrell, and E. M. McCarron, *Phys. Rev. B* **40**, 5296 (1989).
- ¹⁴A. F. Wells, *Structural Inorganic Chemistry* (Clarendon, Oxford, 1984).
- ¹⁵D. A. Owen and M. F. Hawthorne, *J. Am. Chem. Soc.* **92**, 3194 (1991).
- ¹⁶H. Chen and J. Callaway, *Phys. Rev. B* **44**, 2289 (1991).
- ¹⁷H. Chen, J. Callaway, and P. K. Misra, *Phys. Rev. B* **38**, 195 (1988); H. Chen, Ph.D. thesis, Louisiana State University, 1988.
- ¹⁸C. Y. Yang, A. R. Moodenbaugh, Y. L. Wang, Y. Xu, S. M. Heald, D. D. Welch, M. Suenaga, D. A. Fischer, and J. E. Penner-Hahn, *Phys. Rev. B* **42**, 2231 (1990).
- ¹⁹S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- ²⁰L. Nunez, R. D. Rogers, G. W. Crabtree, U. Welp, K. Vandervoort, A. Umezawa, and Y. Fang, *Phys. Rev. B* **44**, 4526 (1991).
- ²¹F. C. Zang and T. M. Rice, *Phys. Rev. B* **37**, 3759 (1988).
- ²²J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezing, T. C. Huang, and S. S. P. Parkin, *Phys. Rev. Lett.* **61**, 1127 (1988).
- ²³W. N. Hardy, D. A. Bonn, D. C. Morgan, Ruixing Liang, and Kuan Zhang, *Phys. Rev. Lett.* **70**, 3999 (1993); Jian Mao, D.H. Wu, J. L. Peng, R. L. Greene, and Steven M. Anlage, *Phys. Rev. B* **51**, 3316 (1995).
- ²⁴S. Chakravarty, A. Subdo, P. W. Anderson, and S. Strong, *Science* **261**, 337 (1993).
- ²⁵P. Chaudhari and Shawn-Yu Lin, *Phys. Rev. Lett.* **72**, 1084 (1994); M. R. Beasley, in *Proceedings of the 1994 Applied Superconductivity Conference* [IEEE Trans. Appl. Supercond. (to be published)].
- ²⁶D. H. Wu, Jian Mao, S. N. Mao, J. L. Peng, X. X. Xi, T. Venkatesan, R. L. Green, and Steven M. Anlage, *Phys. Rev. Lett.* **70**, 85 (1993).