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Magnetic versus nonmagnetic ion substitution effects on T_c in the La-Sr-Cu-O and Nd-Ce-Cu-O systems

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The effects of a substitution for Cu by other 3*d* metals (Ni, Co, and Zn) on T_c in the Nd-Ce-Cu-O system was studied and compared with effects of the same ions on T_c in the La-Sr-Cu-O system. We found (1) Zn suppresses T_c more slowly in the Nd than in the La systems, so the disorder produced by the nonmagnetic ions is less important in the Nd system, (2) Ni and Co depress T_c more quickly in the Nd than in the La system, showing that the magnetic pair breaking is stronger in the Nd system, and (3) in the La system the magnetism of the dopant has no effect on T_c. Thus, within the same chemical system (cuprates) we find that as the correlation length is increased one obtains more familiar BCS-type behavior. We suggest that much of the behavior of the various high-T_c oxides may be simply a function of the correlation length.

It is well established, both experimentally and theoretically, that within the BCS-type superconductors (e.g., the *A*15 compounds or the Chevrel phases) the presence of magnetic impurities depresses the superconducting critical temperature T_c more effectively than does the introduction of nonmagnetic ions,[1] and this has been ascribed to the breaking of the superconducting pairs by the magnetic ions. In the new high-T_c cuprates superconductivity is confined within CuO_2 planes. To determine whether these materials behave similarly with respect to the presence of magnetic impurities, extensive studies[2–5] involving the substitution for Cu by other 3*d* metals (magnetic or nonmagnetic) were performed on both the La_2CuO_4 and $YBa_2Cu_3O_7$ phases. A result common to all of these studies is that T_c is depressed in the same manner, independent of whether the substituent is magnetic or nonmagnetic, and in contrast to that observed for the BCS-type superconductors. This leads to the conclusion that local structural disorder, rather than magnetism, is the important factor in these materials.

A major difference, however, between the old BCS-type materials and the high-T_c cuprates is the coherence length, which is greater than 300 Å for most of the BCS-type materials and surprisingly short[6] for the new cuprates (10–20 Å). Thus one question to be addressed is whether or not the different behavior with respect to magnetic impurities is typical of the cuprates, or is more related to the difference in coherence lengths between the two types of materials.

Superconductivity at 24 K was recently achieved in the $Nd_{2-x}Ce_xCuO_4$ system[7] by doping the system with electrons instead of holes (all the other known high-T_c cuprate phases are *p*-type). Measurements[8] of H_{c2} on superconducting single crystals of these new materials led to a value of 90 Å for the coherence length, midway between the high-T_c limit where the coherence length is small and the BCS limit where the coherence length is large. With its intermediate coherence length, this new system provides an opportunity to examine whether there is a relationship between the coherence length and magnetic impurity doping effects. Thus we have undertaken a study of substitutions for Cu by magnetic or nonmagnetic 3*d* metals in the Nd-Ce-Cu-O system. To compare our results with those previously obtained[2–3] for the $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$ (M = Ni,Zn) system, we focus our study on similar cation substitutions and, in addition, Co. We note, however, that the oxygen coordination of Cu is different in the two compounds (octahedral in the La-based T phase and square planar in the Nd-based T' phase).

A series of $Nd_{1.85}Ce_{0.15}Cu_{1-x}M_xO_4$ samples (M = Ni, Co, Zn and vacancies) were prepared using solid-state reactions of stoichiometric amounts of the starting oxides. To improve homogeneity, the samples were heated at successive temperatures of 900, 950, 1000, 1050, and 1100 °C (in air) and throughly groundup after each heating treatment. The powders were then pressed into a pellet, annealed at 1100 °C in air for four days, reground and repressed and finally annealed a second time at the same temperature for five more days. After such a heat treatment, part of the pellet was reground to perform powder x-ray measurements, and the rest was sliced into 1-mm thick rectangular bars for further characterization. X-ray diffraction measurements indicate that the range of solubility x of the dopants in the T' phase is very small and does not exceed 0.005, 0.005, and 0.01 for Ni, Co, and Zn, respectively. This is in contrast to the range of solubility observed for the same $3d$ metals in the La-Sr-Cu-O system which can exceed 0.3 for Zn and extend up to 1 for both Co and Ni. The difference in the coordination of the Cu is likely at the origin of the smaller solubility for these dopants in the T' phase than in the T phase. A square planar coordination (in contrast to the sixfold coordination generally observed for these $3d$-metal ions, e.g., Co) is not very common. Thus it may be that the cationic substitution for Cu by Co in the Nd-Ce-Cu-O system is accompanied by the insertion of oxygen atoms into the empty apex positions such that the substituted cation ends up to be octahedrally coordinated. However, the small dopant cation solubility range implies a small change in oxygen content that we have, so far, failed to detect using chemical or thermogravimetric analysis.

From the x-ray diffraction powder patterns, the values of the a and c lattice parameters were determined. The main result is that the observed changes, as expected, remain constant (within our limit of resolution), since the ionic radius of fourfold coordinated Cu^{2+} ions (0.71 Å) is about the same as that of fourfold coordinated Ni^{2+} (0.69 Å), Zn^{2+} (0.74 Å), and Co^{2+} (0.72 Å). Possibilities we consider unlikely but that cannot be ruled out from our x-ray data alone (with samples having such small doping amounts) are as follows: (1) The $3d$-metal ions may enter the structure by occupying an interstitial site instead of substituting for the copper. One possible interstitial site in the structure is the apex position that is surrounded by cations. However, the occupancy of this site, because of large Coulomb repulsions, is energetically unattractive. (2) It is possible that the $3d$-metal ions do not enter the structure at all but instead exist as a small amount of a second phase (Cu deficient samples plus $3d$-metal oxides) not detected by x rays. To investigate this possibility, we have prepared Cu deficient, (i.e., vacancy doped) samples for x ranging from 0 to 0.1 in steps of 0.02 and characterized them for their structural and physical properties. Over the range of x examined, the samples were single phase and no change in the lattice parameters could be detected.

The $3d$-metal-doped samples were further investigated by transmission electron microscopy (TEM). This technique, which can characterize the $3d$-metal content in different areas of the sample as small as 200 Å, indicates that the substituents are uniformly distributed throughout the sample (resolution 200 Å) without evidence of a Ni, Zn, or Co segragation for these samples up to a doping content x of 0.01. For samples with x greater than 0.01 there are islands having a composition rich in dopant (Zn, Ni, or Co) and indicating, in agreement with the crystal data, that beyond that concentration the samples are multiphase.

For each series, those compositions that were determined to be single phase by x-ray diffraction were selected, and one piece of each sample (1-mm-thick rectangular bar) was then heated under nitrogen at 900 °C for 12 h in order to induce superconductivity. To prevent any temperature or ambient processing effects on the physical property differences between the different series of samples, the Co, Ni, Zn and vacancy doped Nd-Ce-Cu-O samples were always treated together. Also, because of the large difference in the maximum x between the $3d$-metal substituted $Nd_{1.85}Ce_{0.15}Cu_{1-x}M_xO_y$ $(0<x<0.01)$ and $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_y$ $(0<x<0.3)$ compounds, we prepared a low-content $3d$-metal-doped La-Sr-Cu-O series in order to better compare the effects of $3d$ metals on T_c within these two systems. These samples, with Ni, Zn, and Co as the dopants, were synthesized from oxide mixtures annealed in an oxygen ambient at 1100 °C for 48 h and then furnace cooled.

The two sets of samples (the $3d$-metal or vacancy doped Nd-based materials after the treatment under nitrogen, and the La-based samples after the 1100 °C treatment) were investigated for their superconducting properties by temperature dependent resistivity, as well as dc- and ac-susceptibility measurements.

The resistivity versus temperature measurements on the Ni, Co, and Zn doped Nd-Ce-Cu-O series were made at constant current (0.1 mA/cm^2) in a standard four-probe configuration. Figure 1 shows the results only for the Co-doped series. Note that T_c decreases with increasing x and that the width of the superconducting transition does not exceed 2 K at any x (indicative of a homogeneously distributed dopant throughout the sample). For each sample, above T_c, the resistivity temperature dependence is slightly semiconductinglike as is usually observed on polycrystalline ceramics[7] and in contrast to the metalliclike behavior measured on single crystals.[8,9] Both features (sharp transition at any x and semiconductinglike behavior above T_c) were observed in all the $3d$-metal-doped Nd series investigated.

To confirm superconductivity in the $3d$-metal-doped Nd-Ce-Cu-O samples, we measured the magnetic-field screening and expulsion using a SQUID magnetometer. The samples were warmed in a field of 10 G after having been cooled in zero field (shielding effect), and cooled in 10 G (Meissner effect). Figure 2 shows the Meissner and shielding traces for all the superconducting members of the Co, Ni, and Zn doped Nd-Ce-Cu-O series. In agree-

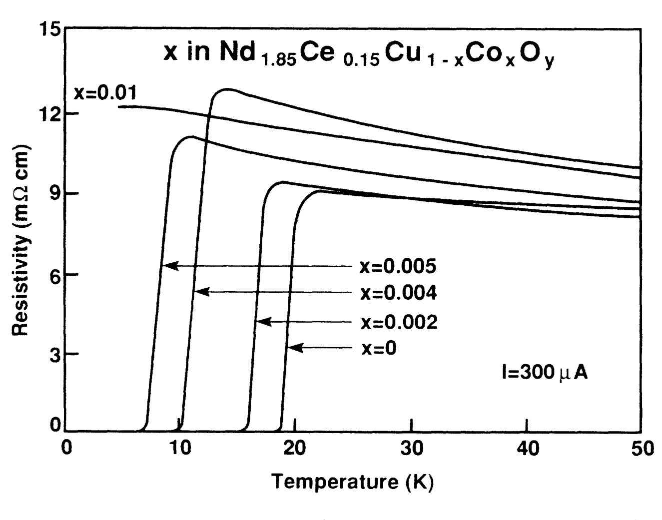

FIG. 1. The resistivity as a function of the temperature and x is shown for the $Nd_{1.85}Ce_{0.15}Cu_{1-x}M_xO_Y$ series with M=Co.

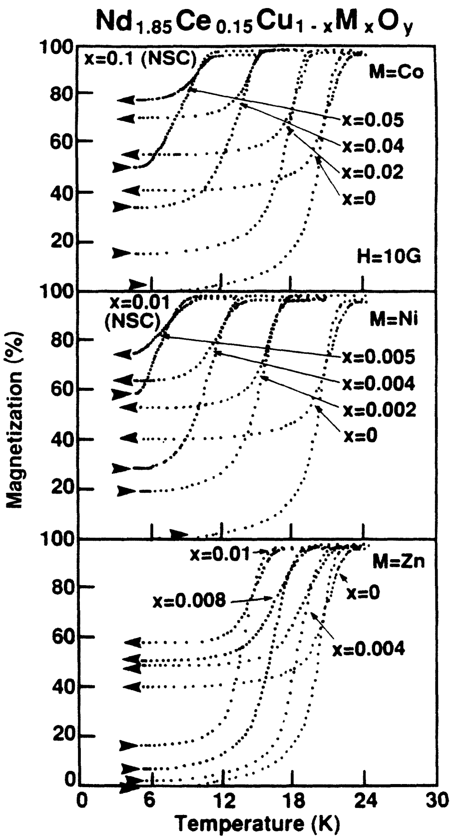

FIG. 2. Temperature-dependent susceptibility for the $\mathrm{Nd_{1.85}Ce_{0.15}Cu_{1-x}}M_x\mathrm{O}_y$ series (M=Co, Ni and Zn). In all cases the down arrow denotes cooling in a field of 10 G; the up arrow denotes warming in 10 G after cooling in zero field. In this figure the Meissner effect for the doped materials have been normalized to that measured for the undoped (30%).

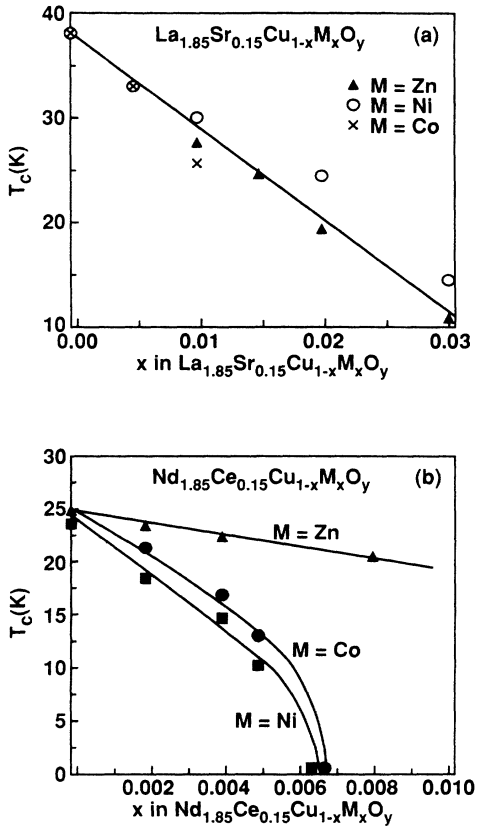

FIG. 3. The variation of the superconducting critical temperatures, as determined by ac-susceptibility measurements, are reported as a function of dopant content x in (a) for the $\mathrm{La_{1.85}Sr_{0.15}Cu_{1-x}}M_x\mathrm{CuO_4}$ series and in (b) for the $\mathrm{Nd_{1.85}Ce_{0.15}Cu_{1-x}}M_x\mathrm{O}_y$ series.

ment with the resistivity data, T_c decreases with an increasing amount of the 3d metal and this decrease is faster for Ni and Co than for Zn. Meissner and shielding measurements were also performed on the Cu vacancy doped series, with the result being that T_c remains a constant independent of x (and therefore the Meissner and shielding traces are not included in Fig. 2). This is clear evidence that the observed T_c depression is caused by the 3d-metal doping. A second observation (from Fig. 2) is that, with increasing x and independent of the nature of the 3d metal, the Meissner fraction (which is about 30% in the undoped sample) continuously decreases. This is typical of the doping studies done, thus far, on the high-T_c cuprates and an explanation for this effect has been proposed by Junod *et al.*[10]

The superconducting transitions were also characterized by ac-susceptibility measurements. The T_c values obtained were in agreement (to ±2K) with the values obtained from resistivity or dc-squid measurements. Figure 3 shows the variation of T_c as a function of x. For the La-based series [Fig. 3(a)], and in agreement with previous work, T_c decreases with x in a similar manner, independent of whether the dopant is magnetic (Ni,Co) or nonmagnetic (Zn). This behavior is in contrast to that shown in Fig. 3(b) for the 3d-metal-doped Nd series where the rate at which T_c decreases with x is strongly dependent upon whether the dopant is magnetic or nonmagnetic, with a faster decrease observed for the magnetic dopants. Also, we note that for the same x (e.g., $x = 0.01$), the nonmagnetic Zn ion suppresses T_c two times faster in the La system ($\Delta T_c = 10$ K) than in the Nd system ($\Delta T_c = 5$ K). However, magnetic ions (Ni,Co), at the same concentration, depress T_c three times faster in the Nd than in the La system.

We now discuss some of the implications of the observed differences in the behavior of the Nd-Ce-Cu-O (T') and La-Sr-Cu-O (T) systems. In both materials, the superconductivity occurs in basically identical Cu-O planes. Whereas one material is made conducting by doping with electrons (T') and the other by doping with holes (T), both have a positive Hall coefficient.[11] There are, however, a number of factors that should be considered in accounting for the difference in their sensitivity to magnetic impurities: (1) In the T' material the added electrons are primarily on the Cu sites, whereas in the T material the holes are predominantly on the oxygen sites. If the holes form a tightly bound singlet with a central oxygen, then both materials can be represented by an effective t-J model[12] and this difference in microscopic structure should be unimportant. If, on the other hand, the basic carriers in the hole-type superconductors are hole quasiparticles[13] whose spin is strongly correlated with that of adjacent copper holes and the pairing force results from the enhanced superexchange of the associated spins on the Cu sites ($S=\frac{1}{2}$), then this might account for some of the difference between the two materials. This picture predicts a similar effect on T_c for any $3d$-metal dopant that substitutes for Cu and has a spin different than $S=\frac{1}{2}$, such as Zn with $S=0$ or Ni with $S=1$. For the Nd-based supercondcutors there are observed[14,15] magnetic correlations similar to those observed in the p-type materials, and therefore these materials may behave in a way similar to p-type with respect to magnetic or nonmagnetic impurities. This is not what we observe experimentally, which suggests that the origin of the pairing force might be different in the two types of materials. (2) There is a large, and conceivably important, difference in the magnitude of the zero-temperature superconducting coherence length (which we will refer to loosely as the pair radius) in the two materials. In the T' material the pair size is large ($\xi_0 \approx 90$ Å) compared to a lattice constant (a) and there are many $[(\xi_0/a)^2 0.15 \approx 100]$ charge carriers in a pair area, whereas in the T material the pair size is small ($\xi_0 \approx 20$ Å) and there are few $[(\xi_0/a)^2 0.15 \approx 4]$ charge carriers in a pair area. We tentatively propose that the qualitative differences between the behavior of the two classes of materials, which are otherwise microscopically so similar, is due to this difference in the correlation lengths.

In the weak-coupling limit pairing and condensation occur simultaneously, and thus a BCS mean-field theory is reliable. An important qualitative feature of BCS superconductors, which is largely independent of microscopic details, is that the pair binding energy is the smallest energy in the problem and therefore even weak magnetic scattering (i.e., scattering that breaks time-reversal symmetry) leads to pair breaking and hence a strong suppression of T_c (the pairing itself is a delicate coherent effect that is easily disrupted). However, nonmagnetic scattering is only effective in suppressing T_c when it is strong enough to destroy the coherence between different regions of the material, i.e., when the electronic wave functions are localized on length scales of order ξ_0. The drastic difference between the effect of magnetic and nonmagnetic impurities in the T' material is thus consistent with the expectation that a weak-coupling theory is applicable in these materials. It should be noted that other properties of the T' material also look considerably more like those of typical BCS superconductors than do the same properties in the T material. For instance, the tunneling curves[16] in the superconducting state exhibit a clean gap of magnitude roughly $3.5kT_c$ and have the characteristic peaks at the gap edge which, in a BCS superconductor, are produced by the divergent density of quasiparticle states. Moreover, the normal-state resistance in single crystals appears to level off above T_c as if approaching a finite residual value at low temperatures, as it does in normal metals, rather than exhibiting the anomalous linear temperature dependence observed in the T material.

In the hole-doped T material, the fact that $(\xi_0/a)^2 0.15$ is of order 1 is incompatible with a weak-coupling theory. That magnetic and nonmagnetic impurities have a similar and weak effect (in comparison to magnetic impurities in the electron-doped material) on T_c adds to the list of properties of these materials that are inconsistent with the basic tenets of a weak-coupling BCS mean-field theory. Based on our observations that, in these materials, T_c is independent of whether or not the impurity is magnetic or not and that local structural disorder can destroy superconductivity, we believe that their behavior is more consistent with the existence of a larger pair binding energy. With a large pair binding energy there could be a temptation to assume that the hole-doped materials are close to the strong-coupling limit. Although this is an interesting approach, there is, as yet, no experimental evidence for the existence of pairing at temperatures higher than the condensation temperatures (T_c) to support the strong-coupling limit. With respect to the doping studies reported here, however, it is unambiguously clear that upon increasing the correlation length a more BCS-like behavior obtains.

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