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ZINC SUBSTITUTION EFFECTS ON THE SUPERCONDUCTING PROPERTIES OF $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$

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ABSTRACT

With the discovery of the electron superconductors, a new dimension was added to research in the field of high-temperature superconductivity. Studies of these materials should help elucidate the mechanism responsible for high-temperature superconductivity, as well as improve strategies for finding new superconductors. In this paper, we discuss the superconducting and structural properties of $Nd_{1.85}Ce_{0.15}(Cu_{1-y}Zn_y)O_4$ as a function of the Zn concentration y. Detailed comparisons with previous results of similar substitution studies in the single-CuO_2-layer hole superconductor $La_{1.85}Sr_{0.15}CuO_4$ also are made. We have found that the non-magnetic element Zn has a detrimental effect on the T'-phase electron superconductor, and that this effect is as strong as in the T-phase hole superconductor. Theoretical implications and the question of electron-hole symmetry are also discussed.

1. Introduction

Since the discovery of the new electron-doped superconductors in early 1989,[1] a considerable amount of research has been carried out on these materials. The new electron-doped superconducting materials are particularly interesting because they are the first examples of high T_c oxide

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superconductors in which the charge carriers involved in the superconductivity appear to be electrons rather than holes that reside in the CuO_2 planes.

Prior to 1989, copper-oxide superconductors were hole carriers in which excess positive charge was generated in the CuO_2 layers by substitution of a trivalent metallic ion with a divalent one. Now, excess of negative charge can be created in the CuO_2 layers of RE_2CuO_4 materials (RE = rare earth) with the so-called T' phase, as discovered by Tokura[1] et al. His team discovered that the electron-doped superconductors can be fabricated by substitution of a tetravalent RE for the original trivalent RE in the semiconductor. This has added a new dimension to the quest for understanding the true mechanism of high temperature superconductivity (HTSC).

Although spectroscopic data is not clear,[2-4] Hall coefficient and Seebeck coefficient measurements indicate that electrons,[1,5,6] and not holes, are the carriers in the new materials. These results suggest that there is an electron-hole symmetry in the occurrence of the insulator-metal transition, magnetism, and superconductivity in copper oxides as a function of the concentration charge carriers in the CuO_2 plane. In addition, this suggests that an electron-hole symmetry is missing in all two-band theoretical models,[7] independent of whether a given two-band model ascribes pairing to excitonic or magnetic interactions. Since electron-hole symmetry occurs naturally in the single band Cu-based magnetic models (specifically, the Hubbard model), and since antiferromagnetism has been found[8] in the parent undoped T' RE_2CuO_4 compounds, the weakly doped two dimensional Hubbard model would seem to provide (superficially at least) an appropriate theoretical description for these systems.

Studies of these materials could help elucidate the mechanism of high-temperature superconductivity, as well as improve strategies for finding new superconductors. In order to arrive at the true theoretical model for the superconducting oxides, it is extremely important to ascertain which features of the hole superconductors persist in the electron doped materials. This is particularly so because even at this early stage several differences between electron and hole doped materials are being observed. An example of this is that superconductivity (SC) in the electron carrier $Nd_{2-x}Ce_xCuO_{4-\delta}$ is limited to the very narrow Ce concentration range[1,9] $0.14 \leq x \leq 0.17$, in contrast to the occurrence of SC in $La_{2-x}Sr_xCuO_{4-\delta}$ over the broad regime $0.07 \leq x \leq 0.25$. Similarly, the Néel temperature T_N in $La_{2-x}Sr_xCuO_{4-\delta}$ goes to zero[10] for $x > 0.03$, but $T_N = 210$ K for $x = 0.1$ in

$Nd_{2-x}Ce_xCuO_{4-\delta}$.[8] In addition, the crystal structures and saturation solubilities of dopants are different,[1,9] and all of these differences are considered relevant in at least one theoretical framework.[11,12]

2. Experiments and Results

We have conducted several experiments on the electron-doped Nd(Ce)CuO in order to ascertain which features of the hole superconductors persist. We report here the effects of zinc substitution on the superconducting properties of $Nd_{1.85}Ce_{0.15}(Cu_{1-y}Zn_y)O_{4-\delta}$ as a function of the concentration level y. Because chemical substitution studies can help elucidate the mechanism of HTSC, substitution studies in the hole superconductors have been pursued by various groups. These reports indicate that the deleterious effect on SC is strongest when Cu,[12-16] (as opposed to a RE atom) is substituted with a different metal atom. Also, the effect of substitution of Cu is strongest when the dopant atom is Zn, and even substitution of magnetic impurities like Fe and Co have a weaker effect on the SC. Such a dramatic effect of Zn-substitution has perplexed many investigators,[13,14] since within the BCS framework nonmagnetic Zn^{2+} with a $3d^{10}$ electronic configuration should have a weak effect on the superconducting properties. As discussed by others[13-16] and us (see below), the effect of Zn-substitution is difficult to understand even within more exotic models. Hence, another motivation of the work presented here is to obtain further information on this aspect.

A series of compounds $Nd_{2-x}Ce_xCuO_{4-\delta}$ with different Ce concentration levels first were prepared. All samples were prepared by solid state reaction of high purity (99.999%) rare earth metal oxides (Nd_2O_3 and CeO_2) and CuO. The mixed powders were calcined in alumina crucibles at 1000 °C for 40 hours in air and then slowly cooled to room temperature in the furnace. X-ray diffraction was used to determine the uniformity of the resulting materials, and then the grinding and firing operations were repeated to ensure the complete homogeneity of the samples. The pressed pellets were then sintered in air at 1100 °C for 18 hours and quenched to room temperature. The samples were reduced by annealing in a stream of flowing nitrogen at various temperatures (800, 900 and 1000 °C) for different times. For the results presented here, we used 36 hours annealing at 800 °C.

Figure 1 is a plot of the normalized resistivity *vs.* temperature for different Ce-concentration levels. We have found that superconductivity is confined to a very narrow Ce concentration range; results that are in agreement with those reported by Tokura *et al.*[1] and others.[9] We also confirmed that the lattice parameters of the undoped and doped T' structures agree with published data.[1] Although it is still not entirely clear (see below), it is believed that the narrowness of the superconducting region in the electron-doped systems may be related to the persistence of Cu-Cu antiferromagnetic (AFM) correlations to much higher dopant concentrations in the electron-doped materials[8] compared with the hole-doped $La_{2-x}Sr_xCuO_4$ compounds.[10] Anyway, the purpose of this figure is to

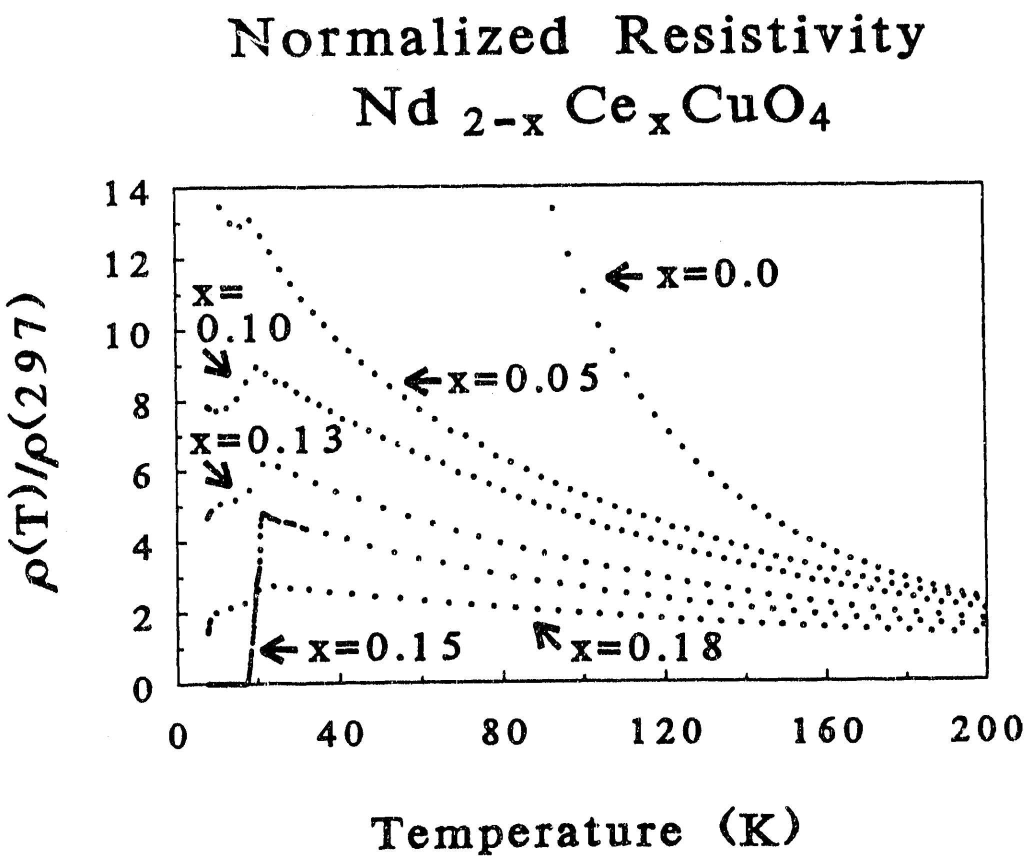

Figure 1. Normalized resistivity *vs.* temperature of $Nd_{2-x}Ce_xCuO_{4-\delta}$ samples with different Ce-concentration levels $0 < x < 0.18$.

convince of our results before the Zn substitution is shown. Our undoped $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ has an onset superconducting T_c of 22 K, in agreement with published data.[1,9] A weak tendency to a resistivity drop at ≈21 K is also seen in our $Nd_{1.9}Ce_{0.1}CuO_{4-\delta}$ sample (Fig. 1), although the material remained weakly semiconducting.

After selecting the composition for which the superconducting temperature transition is a maximum, we started doping with zinc. Thus, our Zn-substitution studies were done with the electron superconductor $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ as the starting material. This selection also allowed us to directly compare our results with the previously done Zn-doping studies[13,14] of the single CuO_2 layer hole superconducting material $La_{1.85}Sr_{0.15}CuO_{4-\delta}$. We used the procedure described above to synthesize the Zn substituted compounds $Nd_{1.85}Ce_{0.15}(Cu_{1-y}Zn_y)O_{4-\delta}$. We choose 0.0, 0.005, 0.01, 0.015, 0.02, 0.03, 0.04 and 0.05 for the y values, which are exactly the same Zn concentration values that were used by Xiao *et al.*[14] in their study of the hole superconductor. This was done so direct comparisons could be made.

Figure 2 shows the resistivity *vs.* temperature for our various Zn-doped materials. Here we see that there is a rapid drop in T_c with increasing of the doping level y, followed by the disappearance of SC. We can also see from Fig. 2 that onset T_c's are 15.5 K, 14.1 K, 13.6 K and less than 7 K for $y = 0.005$, 0.01, 0.015 and 0.02, respectively. An inset in this figure shows the T_c *vs.* y behavior. All $y > 0.02$ materials are nonsuperconducting and weakly semiconducting. A strong semiconducting behavior, with activation energy nearly the same as in antiferromagnetic Nd_2CuO_4, is seen for $y = 0.05$ (not shown). What is noticeable is that SC vanishes at exactly the same Zn concentration[14] in the electron-doped materials as in the hole doped $La_{1.85}Sr_{0.15}(Cu_{1-y}Zn_y)O_{4-\delta}$. We note that this result was predicted within a theoretical model proposed by one of us[12] (see below).

In order to confirm that all compositions had the same single-phase (Nd_2CuO_4)-type structure, we did x-ray diffraction studies of the $Nd_{2-x}Ce_xCuO_{4-\delta}$ ($0 < x < 0.15$ in steps of 0.03) and $Nd_{1.85}Ce_{0.15}(Cu_{1-y}Zn_y)O_{4-\delta}$. Figure 3, shows the powder x-ray diffraction patterns for the superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ and two of the Zn-substituted samples; one superconducting and the other a highly doped nonsuperconducting material. Clearly, the structure remains unaltered on Zn-substitution, and supports our conclusion that our samples are single phase.

We performed lattice parameter calculations from the experimental x-ray diffraction data to confirm that the structure is indeed unaltered. X-ray diffraction data on the samples were collected on a Philips automated x-ray powder diffractometer using Cu-Kα radiation. The diffracted peaks were fitted by modified Cauchy functions and the lattice parameters were then determined by fitting the positions of at least nineteen diffraction peaks using a standard least square reduction (Cohen's) method. As the Zn content is varied, and within our experimental error, we found no appreciable variation in the lattice parameters *a* and *c*.

The invariance of lattice parameters is in sharp contrast to what is

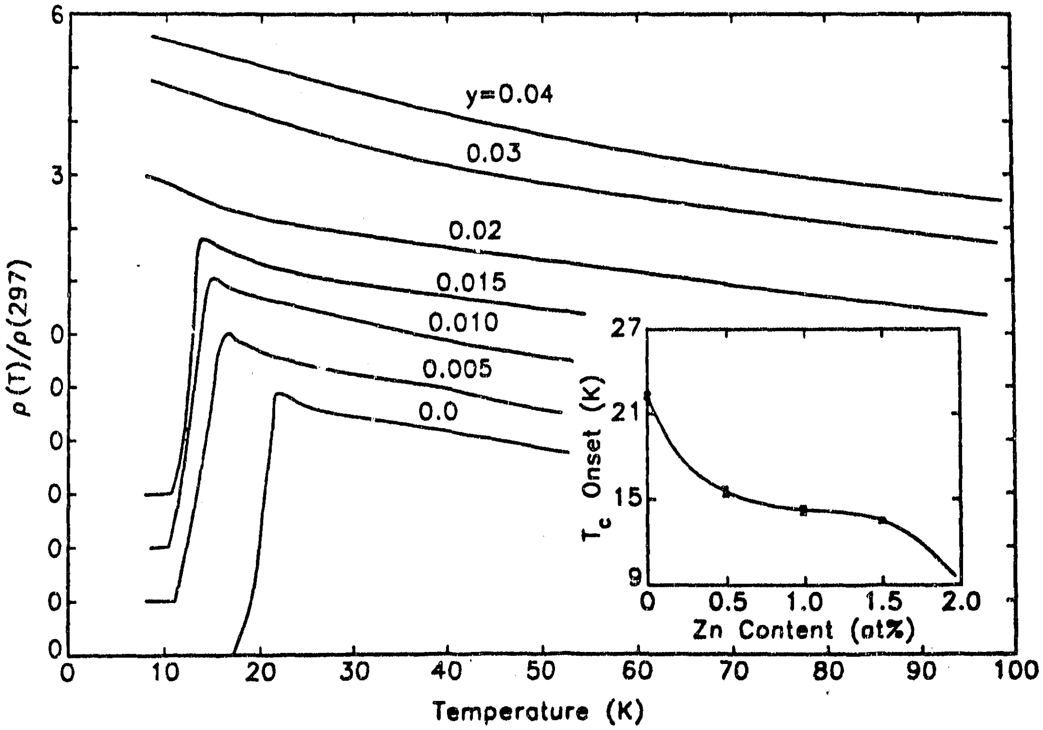

Figure 2. Normalized resistivity *vs.* temperature of Nd$_{1.85}$Ce$_{0.15}$(Cu$_{1-y}$Zn$_y$)O$_{4-\delta}$ samples with Zn content $0 < y < 0.04$. Inset: T$_c$ onset *vs.* Zn content.

seen[14] in $La_{1.85}Sr_{0.15}(Cu_{1-y}Zn_y)O_{4-\delta}$. Both parameters change up to 0.1% in the latter material, with the *c* parameter decreasing and the *a* parameter increasing as the Zn content is increased. The effect of both variations in the latter material was explained in terms of the Jahn-Teller effect. The Jahn-Teller distortion of a pure Cu^{2+} system makes the apical Cu-O bonds longer than the layer Cu-O bonds, while substitution with Zn will have a tendency to equalize the bond lengths since the $3d^{10}$ configuration of Zn^{2+} does not allow this distortion.

In Nd_2CuO_4, however, there are no apical oxygens and the Nd^{3+}-Cu^{2+} linkage is ionic. Therefore, a Jahn-Teller effect, as in La_2CuO_4, is not

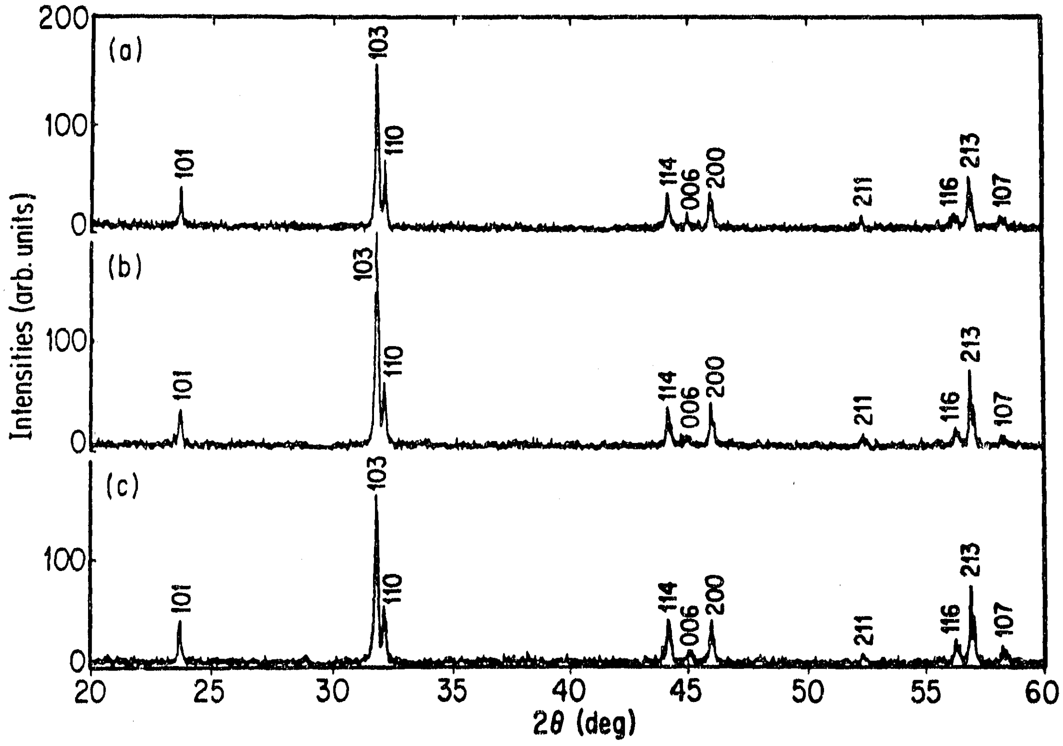

Figure 3. X-ray powder diffraction spectra of three $Nd_{1.85}Ce_{0.15}(Cu_{1-y}Zn_y)O_4$ samples: (a) superconducting, $y = 0$; (b) superconducting, $y = 0.005$; and (c) non-superconducting, $y = 0.02$.

expected, even in the undoped semiconductor. Hence, in the undoped $Nd_{1.85}Ce_{0.15}CuO_{4-y}$, it is tempting to ascribe this absence of Jahn-Teller distortion to the very small change in *a* and *c* on Zn-substitution. However, a recent study[17] of antiferromagnetic $La_2(Cu_{1-y}Zn_y)O_4$ (i.e., no Sr) also found that the lattice parameters remain essentially unaltered as a function of *y*, so that care should be taken with any such interpretation.

The above structural data, as well as the large differences in ionic radii between Nd^{3+} (1.25 Å) and Ce^{4+} (1.11 Å) on one hand, and Zn^{2+} (0.73 Å) on the other, indicate that the Zn enters the Cu sites. For a more convincing proof, neutron diffraction studies will have to be performed. However, we assume that Zn enters the Cu sites selectively. This assumption is also based on the previous work on Zn-substitution in LaSrCuO and YBaCuO.

3. Theoretical Implications

We have found that our results are difficult to explain within the existing simple models, including the Hubbard model. Several plausible arguments[12,14] have been offered to explain the surprisingly strong deleterious effect of Zn-substitution on SC. We next give a summary of those arguments.

3.1 *Structural Disorder*

Since changes in the lattice parameters are larger in the hole-superconducting materials, T_c in our substitution should have been only weakly suppressed. The very small lattice parameter change in the electron-doped material precludes structural disorder being the dominant cause of SC suppression.

3.2 *Creation of Oxygen Vacancies*

Oxygen vacancies have different effects in the hole and electron superconductors. Furthermore, the effects are opposite: in the hole superconductors, vacancies suppress the SC and can induce a semiconducting behavior; in the electron superconductors, the vacancies enhance the SC (presumably by creating excess negative charge in the CuO_2 layer).

Therefore, if indeed Zn created oxygen vacancies when it is introduced into the electron superconductor, the effects on T_c would have to be different from those reported on the hole superconductor.

3.2 *Magnetic Pair Breaking*

A more plausible explanation seems to be magnetic pair breaking, especially in view of the electron-hole symmetry within the Hubbard model. However, there are several problems with this. First, T_c in our substituted samples does not decrease as $(y_c - y)^{1/2}$, where y_c is the critical Zn concentration, which would in be in accordance with the Abrikosov-Gorkov model of magnetic pair breaking.[14] This is not the case in the hole superconductors. In addition (see discussion below) the extent of magnetic pair breaking could also have been expected to be different in the hole and electron superconductors. To confirm the above differences, more careful and quantitative magnetic susceptibility measurements would be necessary.

The ordered magnetic moment per Cu remains the same for $y \leq 0.03$ Zn doping, as shown by recent investigation of $La_2(Cu_{1-y}Zn_y)O_4$,[17] even though there is a considerable lowering of T_N. As also suggested by the authors of the above paper,[17] the most reasonable explanation for this is that Zn^{2+} adds vacancies that are immobile in the two dimensional antiferromagnet, so that the surrounding Néel order is very weakly affected.[18] It may be argued that the net moment due to the vacancy can inhibit SC, since a spin vacancy in the antiferromagnet will have an effective moment.[17] Whether such a <u>local</u> defect would inhibit SC equally in the hole and electron superconductors would then strongly depend on the spatial extents of the spin polaronic wave functions in the two cases (particularly for Zn concentrations as low as a few atomic percent). We believe that the spatial extents are very different in the hole and the electron superconductors.

The hole-doped superconductors contain O^{1-} and not Cu^{3+}. A dopant-induced oxygen hole forms a local singlet with a Cu^{2+} spin, and the composite acts as a mobile double occupancy according to the effective single-band model.[19] It can be expected that the spatial extent of such a spin polaron would be much larger (as it extends over at least one CuO_4 unit) than the spin polaron obtained by electron doping, a single Cu^{1+} ion. Therefore, the pair breaking field due to local immobile Zn defects should be much larger in the case of holes than for electrons. In view of the short coherence lengths in the oxide superconductors, this assortment could be true. Hence, observable differences in the effects on T_c might have been expected within magnetic models. It should be added that it is still not entirely clear whether there is persistence of short-range antiferromagnetic correlations in the superconducting phase of the hole superconductors,[20] while current data would seem to preclude such correlations in the electron superconductor.[8]

4. Discussion

One of us has proposed a different theoretical model.[11] In this model, a dopant-induced valence transition mechanism is proposed in which a first-order valence transition, such as $Cu^{2+} \rightarrow Cu^{1+}$, accompanies the antiferromagnetic to superconductor transition in the copper oxides; both hole- and electron doped materials.

The ionization energy of closed shell Cu^{1+} is unusually large, and only the large Madelung energy gives a Cu^{2+} configuration in the undoped semiconductors. Doping reduces the Madelung energy and drives the valence transition, generating a large number of O^{1-}. Observation of O^{1-} in the electron superconductors[3,4] is then expected.

Based on this theoretical mechanism, a large number of explicit, testable experimental predictions[12] were made for the normal state of Nd(Ce)CuO. In particular, predictions of experiments involving chemical substitution were made. Unlike Cu, Zn is most stable in its closed shell bivalent Zn^{2+} state. Even a minute quantity of Zn^{2+} converts neighboring O^{1-} in the superconductors to O^{2-} and increases the Madelung energy again. This then drives a reverse valence transition $Cu^{1+} \rightarrow Cu^{2+}$, destroying superconductivity.

Within the proposed model, it was predicted[12] that disappearance of SC should occur for the same y doping level in both $La_{1.85}Sr_{0.15}(Cu_{1-y}Zn_y)O_{4-\delta}$ and $Nd_{1.85}Ce_{0.15}(Cu_{1-y}Zn_y)O_{4-\delta}$. Although our experimental work certainly does not prove the validity of the model, it is suggestive that the critical Zn concentration is the same, and further work is in progress.

5. Conclusions

In conclusion, substituting Zn ions onto the Cu site of the T'-phase electron superconductor $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ compound affects the superconducting properties detrimentally. In addition, this effect is as strong as in the T-phase hole superconductors, and T_c goes to zero at exactly the same Zn concentration levels. Both results are in accordance with a recent prediction made by one of us. We believe that the disappearance of SC at the same Zn concentration suggests that the origin of pair breaking is not magnetic, but further work needs to be done. The Zn-substitution made here does not appreciable change the lattice parameters, and any dopant-induced oxygen vacancies would have had opposite effects on the hole and electron superconductors.

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