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Effect of nickel and zinc substitutions on the electronic charge-density redistribution in a $YBa_2Cu_3O_7$ superconductor

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It is shown, on the basis of our electronic structure calculations, that the nature of the perturbations created by Ni and Zn impurities in a $YBa_2Cu_3O_7$ superconductor is quite different although both impurities are divalent. While the charge-density redistribution due to Ni in its neighborhood is weak and well localized, the one due to Zn is very strong and extended. This indicates that the mechanisms of the degradation of T_c by these two impurities are quite different. The extended nature of the perturbation due to Zn substitution results in strong electron scatterings not only from Zn but also from the neighboring atomic sites. The hole carrier density, which is determined by the distribution of the electronic charge, is as a result also modified locally and becomes nonuniform in the neighborhood of the Zn impurity, although there is no overall change in the carrier density. In contrast, in the case of Ni substitution it is primarily the magnetic moments at the Ni site which may be considered as the primary source for the deterioration of the superconducting transition temperature. [S0163-1829(99)07205-7]

The elements Ni and Zn substitute primarily at the Cu(2) sites in the two-dimensional CuO_2 planes in a $YBa_2Cu_3O_7$ superconductor, and have an extremely detrimental effect[1] on the superconducting transition temperature T_c. In conventional superconductors nonmagnetic impurities such as Zn depress the T_c far less than the magnetic ones such as Ni. Considering the fact that both Ni and Zn are divalent, one expects the depression of T_c due to Zn to be much less than due to Ni. In contrast to this expectation one finds Zn to be much more detrimental to T_c in $YBa_2Cu_3O_7$ where the rate of depression of T_c due to Zn is nearly three times as much as due to Ni.[2–5] In the single CuO_2 plane superconductors the effect of the two impurities are nearly the same. The lower depression of T_c due to Ni in $YBa_2Cu_3O_7$ superconductor has, therefore, been attributed to a partial substitution of Ni at the chain copper Cu(1) sites.[1] Indeed, recent results[6,7] indicate that when one corrects for the concentration of the impurity that does not go to the CuO_2 planes, then both Ni and Zn depress the T_c at practically the same rate in $YBa_2Cu_3O_7$ also. Nevertheless, the depression of T_c due to Zn in cuprate superconductors remains exceptionally large. This has led to an intense debate concerning the mechanisms that might be responsible for the depression of T_c by these impurities. In fact, the case of Zn has been used as a test case for the symmetry of the order parameter for which, on the basis of the unusual depression of T_c by Zn, a $d_{x^2-y^2}$ symmetry has been proposed.[8–11]

In general, an impurity modifies the electronic structure of the host matrix in its neighborhood, the extent of which depends upon the nature of the impurity. This perturbation serves as a source of electron scattering, and thus the degradation of T_c, and contributes to the transport properties such as the electrical resistivity, etc. An impurity can also modify the carrier density in these superconductors and this depends upon the nature of the impurity and its concentration. The change in the carrier density can affect the T_c since the two are very intimately related in the cuprates.[12] It is known that Ni and Zn impurities do not appreciably change the overall carrier density.[3,13–15] A calculation[16] of the carrier density in $YBa_2Cu_3O_7$ in the presence of a substantial concentration of Zn at which superconductivity is fully destroyed in this compound also showed that the overall carrier density is not altered in a significant manner from its value in the superconducting compound. However, it was found to be very nonuniformly distributed. This nonuniformity in the carrier density perturbs considerably the electronic integrity of the CuO_2 planes, and thus contributes to the degradation of the superconducting transition temperature.

For low concentrations of an impurity, the overall carrier density in the compound remains unaffected since the contribution of the impurity is rather small due to its very small concentration, and can be neglected. In this limit, the modifications in the electronic structure and the associated changes in the carrier density locally in the neighborhood of the impurity, and not the overall changes in the carrier density, are essentially responsible for the changes in the superconducting transition temperature. In fact a large number of experiments have been performed with low concentrations of these impurities. With this in mind we have investigated the effect of isolated Ni and Zn impurities on the electronic structure of $YBa_2Cu_3O_7$ in the vicinity of these impurities which we hope will shed some light on the mechanisms that control the depression of T_c by these impurities. We have used the tight binding recursion method for this purpose, as in our previous work,[17] and employed clusters of more than 13 000 atoms with p functions at the oxygen sites and d at other sites. This method has the advantage that this is a real-space method and therefore does not require periodicity, and

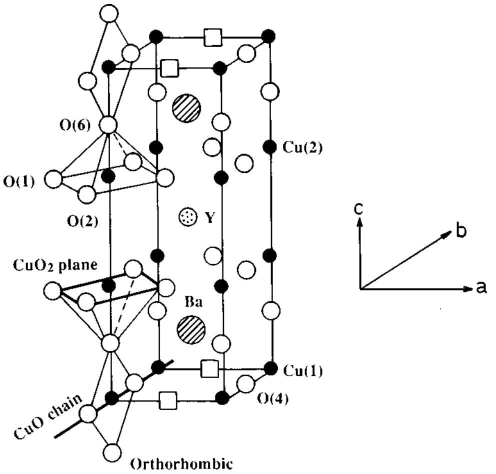

FIG. 1. Crystal structure of $YBa_2Cu_3O_7$ which shows the notation used in this paper.

is thus well suited for studying the electronic structure of defects, especially when the perturbation created by them is of long range. The impurity, Ni or Zn, is placed at the center of the cluster at an in-plane Cu(2) site in $YBa_2Cu_3O_7$, the crystal structure of which is shown in Fig. 1 in order to clarify the notation for the various atomic positions that we have used in this paper. The electronic densities of states (DOS) are obtained at various atomic sites with and without the impurity. Since we are dealing with the case of an isolated impurity in this work, the Fermi level remains practically unchanged from its value in the impurity-free compound.

The superconductivity in the cuprate superconductors is controlled by the electronic structure of the two-dimensional CuO_2 planes,[17] and that in turn depends upon the antibonding band formed by the interaction between the planar $Cu(2)d_{x^2-y^2}$ and $O(1)p_x$, $O(2)p_y$ orbitals. The substitution of a transition-metal impurity at the Cu(2) site perturbs the electronic structure of this band, and the nature of this perturbation depends mainly upon the difference in energy between the *d* levels of the impurity and those of the Cu(2) site. If this difference is small, the perturbation in the neighborhood of the impurity will be small and localized. On the other hand, if this difference is large the perturbation can be very large and, as a consequence, also very extended. The two impurities, Ni and Zn, fall respectively in these two categories. The *d* levels of Ni (Ref. 18) are just 1.5 eV above those of Cu(2), so that the antibonding band is pushed slightly higher in energy. This results in a slight depletion of the electronic charge from the neighboring oxygen sites but most of the perturbation remains otherwise quite confined to the impurity site. In contrast, in the case of Zn substitution at the Cu(2) site the perturbation is very severe and extended since the *d* levels of Zn lie far too low in energy, and are fully filled with a d^{10} configuration. This completely severs the interaction between a Zn impurity and the neighboring oxygen atoms. Due to this, the oxygen orbitals that were previously participating in the formation of the antibonding band with a given Cu(2) atom now no longer participate in this interaction and fall below the Fermi energy to lower energies, and charge accumulation therefore occurs at these sites. Due to this rather drastic modification the electronic structure is affected not only at the Zn site but at the neighboring atomic sites as well.

TABLE I. Change in the electronic charge at different copper sites at different CuO_2 planes due to Ni and Zn impurities.

Site	Ni	Zn
CuO_2 plane of impurity		
First neighbor Cu(2)	0.0047	0.0195
Second neighbor Cu(2)	−0.0084	0.0004
CuO_2 plane across Y		
First neighbor Cu(2)	0.0020	0.0168
CuO_2 plane across the Chain		
First neighbor Cu(2)	−0.0069	−0.0096

In Tables I and II we have shown the changes in the electronic charges at various Cu(2) and O(1), O(2) sites in the CuO_2 planes due to Ni and Zn impurities in their neighborhoods. These charge differences have been obtained by integrating the local densities of states (LDOS) at these sites upto the Fermi level with and without the impurity. We should note here that changes also occur at the chain, apical oxygen, Y, and Ba sites but these are relatively small and will not be the subject of discussion in this paper.

We notice from Table I that there is a small increase in the charge at the nearest-neighbor Cu(2) sites both due to Ni and Zn impurities but the increase due to Zn is larger. This increase in charge reflects a tendency toward the Cu^{2+} ionic state at these sites, and is thus consistent with the development of a small magnetic moment of less than $0.2\mu_B$ observed in optimally doped $YBa_2Cu_3O_7$ upon Zn substitution.[19] Since the increase in charge due to Ni at the nearest-neighbor Cu(2) sites is much smaller, the magnitude of the magnetic moment due to this perturbation due to Ni is also expected to be much smaller. The intrinsic magnetic moment at the Ni site may, however, induce a small moment at these sites. We also see from Table I that the increase in the electronic charge due to Zn at the Cu(2) sites across the

TABLE II. Change in the electronic charge at different oxygen sites at different CuO_2 planes due to Ni and Zn substitutions.

	Ni		Zn	
Site	*a*-axis oxygen	*b*-axis oxygen	*a*-axis oxygen	*b*-axis oxygen
CuO_2 plane of the impurity				
First neighbor oxygen	−0.0458	−0.0557	0.2052	0.1752
Second neighbor oxygen	−0.0090	−0.0094	−0.1200	−0.0734
Third neighbor oxygen	−0.0062	−0.0060	0.0048	0.0006
Fourth neighbor oxygen	−0.0010	−0.0019	0.0268	0.0209
CuO_2 plane across Y				
First neighbor oxygen	−0.0057	−0.0041	0.0278	0.0226
CuO_2 plane across the chain				
First neighbor oxygen	−0.0024	−0.0021	0.0220	0.0162

plane of Y is as large as at the nearest-neighbor Cu(2) sites in its own plane, which is not the case with Ni. This is a manifestation of the extended nature of the perturbation created by Zn. An increase in the hyperfine field at the Cu(2) sites neighboring a Zn impurity has been observed by Mahajan *et al.*[13] and is clearly related to this change in the electronic structure.

The largest perturbation due to Ni or Zn impurities is, however, felt by the oxygen atoms on the CuO_2 plane in the neighborhood of the impurity, as can be seen from Table II which shows a depletion of the electronic charge at these sites due to Ni and a large pileup due to Zn. We should note that the charge deficits or pileups at the *a*-axis O(1) and *b*-axis O(2) sites are different due to the chains along the *b* axis. We again notice that the perturbation due to Ni is rather localized since it is mainly the four nearest-neighbor oxygen atoms surrounding the Ni atom that are the most affected. In contrast, Zn perturbs many oxygen sites that are nearest to it, including those at the CuO_2 plane across the plane of Y and the one just across the chain, where a small increase in charge occurs. However, the most important changes occur at the oxygen sites in the CuO_2 plane of Zn where a Friedel-type of oscillation can be noticed. We should mention that there is much less charge at the Ni site itself compared to the Cu(2) site that it replaces, and has a charge deficit of roughly 0.80 electron. This difference combined with the decrease in charge at the neighboring oxygen sites accounts for the fact that Ni has one electron less than Cu. Similarly, at the Zn site there is approximately 0.65 of an electron more than at the Cu(2) site that it substitutes for due to the fact that the *d* band is completely filled. This increase in charge at the Zn site together with the charge differences at the sites in its vicinity account for an extra electron that a Zn impurity brings compared to copper. All those sites where a significant modification in charge occurs act as potential scattering centers in addition to the impurity itself. Since the hole carrier density is determined by the distribution of the electronic charge, this charge redistribution also modifies the carrier density locally and makes it nonuniform, although the overall carrier density remains unchanged for very low impurity concentrations. These effects need to be included in the interpretation of the experimental data. In particular, these results are relevant also to the understanding of the local suppression of the pseudogap[14] at the sites neighboring Zn in $YBa_2Cu_3O_{7-\delta}$ superconductors, and the fact that no such suppression occurs in the vicinity of Ni. We believe that the large inhomogeneity in the local charge redistribution in the vicinity of Zn plays an important role in the suppression of this pseudogap.

Our calculations are also relevant to the understanding of the transport properties in the presence of these impurities. The residual resistivity ρ_0 in the presence of, for example, Zn has been usually expressed[19] in terms of a single *s*-wave phase shift δ_0 in two dimensions in the form

$$\rho_0=(4h/e^2)(n_i/n)\sin^2\delta_0, \tag{1}$$

where n_i is the impurity concentration, and *n* the carrier hole density per CuO_2 unit. In this expression a CuO_2 plane is treated as a two-dimensional electron gas and Zn as an *s*-wave impurity with a charge $+1$ in this jellium. While such a treatment might be considered to be more appropriate for a Zn impurity in Cu metal, it is abundantly clear that such an approximation is an enormous oversimplification of both the true electronic structure of a CuO_2 plane and the perturbation that a Zn impurity creates in its vicinity. The electronic structure of the CuO_2 planes is determined primarily by the hybridization between the Cu(2)-*d* and O(1), O(2)-*p* orbitals, and the *s* orbitals hardly enter in this electronic structure. This can hardly be represented by a free-electron gas. Further, by the substitution of Ni or Zn at the Cu(2) site it is essentially the *d* band that is affected at the Cu(2) site, if one ignores the perturbation at the neighboring atomic sites. Admittedly, a full-fledged calculation of the residual resistivity is difficult since it requires a detailed knowledge of the perturbation by the impurity and the wave functions at the Fermi surface of the host. Even with this information, the calculation for these compounds is extremely laborious due to the complicated nature of the integrals that have to be numerically evaluated. Nonetheless, an approximate expression that takes into account the electronic structure of the host has been proposed[20] for the residual resistivity ρ in the single-site approximation in which

$$\rho=(4h/e^2)(n_i/n)(0.5/k_F)\sum_{\ell}(\ell+1)\sin^2(\delta_{\ell+1}-\delta_{\ell}). \tag{2}$$

Here k_F is an average Fermi wave vector, and

$$\delta_{\ell}=\delta^{i}_{\ell}-\delta^{h}_{\ell}, \tag{3}$$

where δ^{i}_{ℓ} and δ^{h}_{ℓ} are the phase shifts of ℓ-type angular momentum associated with the impurity and the host atom potentials evaluated at the Fermi level. Note that Eq. (2) is slightly different from Eq. (1), since Eq. (2) corresponds to the residual resistivity in a three dimensional solid while Eq. (1) is the residual resistivity in two dimensions. The term δ^{h}_{ℓ} in Eq. (3) corrects in an approximate manner for the fact that the host background in which the impurity is immersed is not a free-electron gas (for which $\delta^{h}_{\ell}=0$) but has a finite phase shift δ^{h}_{ℓ}. In the limit $\delta^{h}_{\ell}=0$ we recover the formula for the residual resistivity of defects in a jellium matrix derived by Friedel.[21]

As we have discussed previously, the states involved at the Fermi level for both Ni and Zn impurities are mainly of *d*-type at the impurity site. Thus if we retain only the $\ell=2$ phase shift and ignore the others, Eq. (2) can then be simplified and written in terms of a single phase shift δ_2:

$$\rho=(4h/e^2)(n_i/n)(0.5/k_F)5\sin^2\delta_2. \tag{4}$$

Note that while Eq. (4) is quite similar to Eq. (1) for *s*-wave scattering, the contribution from the *d*-wave scattering is five times as large for a similar value of the phase shift. In the case of Zn the contribution to scattering at the Zn site arises mainly from the absence of the host potential since the *d* shell of Zn is filled and lies well below the Fermi level. Thus in a first-order approximation we can write $\delta_2=-\delta^{h}_2$.

Since the perturbation in the case of Ni substitution is quite localized and mainly confined to the impurity site, a single *d*-wave phase shift should constitute an adequate approximation for the interpretation of the experimental data. In the case of Zn the perturbation is, in contrast, quite extended so that the single site approximation to the residual resistivity is not appropriate and contributions from the neighboring sites should also be included using Eq. (2).

The localized and weak nature of the perturbation due to Ni as compared to Zn clearly indicates that the depression of T_c due to Ni is expected to be much smaller than due to Zn. However, the magnetic nature of the Ni ion has not been included in this discussion. Since the rate of depression of T_c due to Ni is nearly of the same order as due to Zn in the single CuO_2 layer superconductors; we can attribute this depression of T_c due to Ni in large part to the formation of large magnetic moments[4,22] at the Ni site and the resulting scattering from these moments. On the other hand, the magnitude of the magnetic moments at the neighboring Cu(2) sites in Zn substituted optimally hole doped $YBa_2Cu_3O_{7-\delta}$ superconductors is quite small[19,23] so that the depression of T_c in this case owes its origin largely to the extended nature of the perturbation that it creates in its neighborhood.

In conclusion, our calculations show that despite the fact that both Ni and Zn are divalent, the mechanisms of the depression of T_c due to these impurities in $YBa_2Cu_3O_7$ superconductor are quite different. In the case of Ni substitution at the Cu(2) site the perturbation in the vicinity of Ni is small and localized, and this should affect the T_c only marginally. Thus the depression of T_c in this case can be attributed essentially to the magnetic moments formed at the Ni site. This is not the case with the Zn substitution where, in contrast, the perturbation in its neighborhood is very strong and extends much further. Thus although Zn is not magnetic and induces only weak moments at the neighboring Cu(2) sites, the exceptionally large depression of T_c in this case owes its origin mainly to the extended nature of this perturbation that plays a major role in the breaking of the cooper pairs. This difference in the nature of the perturbation generated by these impurities is clearly reflected in the response of the normal-state spin pseudogap. While this pseudogap is suppressed by Zn in its neighborhood, no such suppression occurs due to Ni impurities.[22] The long-range perturbation created by Zn also shows up in the hole carrier density in the CuO_2 planes affected by this perturbation where the carrier density is no longer uniform in the neighborhood of a Zn impurity although the overall carrier density remains practically unchanged. This nonuniformity in the hole density is an important factor in the degradation of T_c, and is a distinguishing feature of the cuprate superconductors from the classical superconductors where T_c is not so intimately related to the carrier density as in the cuprate superconductors. We believe that it is important to include this long-range nature of the perturbation in the analysis of the experimental data, and also in models for the determination of the symmetry of the order parameter.

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[1] J. L. Tallon, C. Bernhard, G. V. M. Williams, and J. W. Loram, Phys. Rev. Lett. **79**, 5294 (1997).

[2] S. Zagoulaev, P. Monod, and J. Jegoudez, Phys. Rev. B **52**, 10 474 (1995).

[3] D. Goldschmidt, Y. Direktovitch, A. Knizhnik, and Y. Eckstein, Phys. Rev. B **54**, 13 348 (1996).

[4] K. Ishida, Y. Kitaoka, N. Ogata, T. Kamino, K. Asayama, J. R. Cooper, and N. Athanassopoulou, J. Phys. Soc. Jpn. **62**, 2803 (1993).

[5] J. A. Hodges, P. Bonneville, P. Imbert, D. Colson, Genand-Riondet, and A. Pinatel-Phillipot, Physica C **218**, 272 (1993).

[6] H. A. Blackstead and J. D. Dow, Europhys. Lett. **41**, 659 (1998).

[7] F. Bridges, G. Li, J. B. Boyce, and T. Claeson, Phys. Rev. B **48**, 1266 (1993).

[8] R. Fehrenbacher, Phys. Rev. Lett. **77**, 1849 (1996).

[9] R. Fehrenbacher and M. R. Norman, Phys. Rev. Lett. **74**, 3884 (1995).

[10] S. Borkowski and P. J. Hirschfeld, Phys. Rev. B **49**, 15 404 (1994).

[11] Y. Sun and K. Maki, Phys. Rev. B **51**, 6059 (1995).

[12] M. W. Shafer and T. Penney, Eur. J. Solid State Inorg. Chem. **27**, 191 (1990).

[13] A. V. Mahajan, H. Alloul, G. Collin, and J. F. Marucco, Phys. Rev. Lett. **72**, 3100 (1994).

[14] J. L. Tallon, J. R. Cooper, P. S. de Silva, G. V. M. Williams, and J. W. Loram, Phys. Rev. Lett. **75**, 4114 (1995).

[15] G. V. M. Williams, J. L. Tallon, and R. Meinhold, Phys. Rev. B **51**, 16 503 (1995).

[16] R. P. Gupta and M. Gupta, Physica C **305**, 179 (1998).

[17] R. P. Gupta and M. Gupta, Phys. Rev. B **44**, 2739 (1991).

[18] L. F. Mattheiss, Phys. Rev. B **48**, 4352 (1993).

[19] Y. Fukuzumi, K. Mizuhashi, K. Takenaka, and S. Uchida, Phys. Rev. Lett. **76**, 684 (1996).

[20] R. P. Gupta, Phys. Rev. B **35**, 5431 (1987).

[21] J. Friedel, Adv. Phys. **3**, 446 (1954).

[22] G. V. M. Williams, J. L. Tallon, R. Dupree, and R. Michalak, Phys. Rev. B **54**, 9532 (1996).

[23] C. Panagopoulos, J. R. Cooper, N. Athanassopoulos, and J. Chrosch, Phys. Rev. B **54**, 12 721 (1996).