Effect of magnetic and nonmagnetic impurities of the carrier binding energy in Cu–O clusters

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The effect of magnetic and nonmagnetic impurities on the carrier binding energy in a Cu_4O_8 cluster, described by Emery's model, has been studied through an exact diagonalization of the Hamiltonian matrix. This has been done for the cases of *n*-type and *p*-type doping. Nonmagnetic and magnetic impurities in the CuO_2 plane are found to have roughly equal effects on the carrier binding energy, in total agreement with experimental data. The critical impurity concentrations, at which the binding energy vanishes, are close to the experimental values. Those for *n*-type high T_c superconductors are lower by a factor of 3 to 6 than those for *p*-type superconductors. The effective magnetic moment at the copper increases with the concentration of magnetic impurity, while it decreases in the case of replacement by nonmagnetic impurities, again in complete correlation with experimental data. The calculated results show that the cluster approach is promising and that Emery's model is valid for describing the properties of high T_c superconductors.

INTRODUCTION

The transition temperature of high T_c superconductors and the current they carry depend strongly on the presence of structural and radiation-induced defects and magnetic and nonmagnetic impurities. At a certain concentration, the transition temperature and the current drop to zero. Many experimental studies (e.g., Refs. 1–3) support the idea that a superconductor–semiconductor phase transition is induced by defects and impurities. We wish to stress that in this case, in contrast with ordinary superconductors (which are described by the BCS theory), the transition is caused by both magnetic and nonmagnetic impurities and defects (including radiation-induced defects).

There is no generally accepted theory for this transition as yet (or for the high T_c superconductivity itself). Several models have accordingly been proposed. In particular, we have shown in several papers[4] that the binding energy of the carriers in a Cu_4O_8 cluster decreases with increasing degree of Anderson disorder W, and it vanishes at a certain value $W=W_c$. Values of the binding energy Δ have been calculated for *n*- and *p*-doped systems by the exact diagonalization method. The results give a good description of existing data on the effect of radiation-induced defects on high T_c superconductors.

However, an Anderson disorder serves as a model of only nonmagnetic defects and impurities. Furthermore, that type of disorder corresponds best to the situation which arises upon irradiation, in which case the defects appear not directly in the CuO_2 planes, but mostly between these planes. These defects create a random impurity potential, in which the atomic potentials in the plane correspondingly vary in a random way.[4]

A promising method for studying the pairing mechanism in the high T_c superconductors is to partially replace one or more of the chemical elements making up the superconductor.[3,5] This replacement can affect the electronic structure of the superconductor, causing a redistribution of carriers in the unit cell as well as magnetic and superconducting correlations in the system. The most promising approach is to replace the copper and oxygen atoms in the CuO_2 plane, which is a basic structural element of the high T_c superconductors. There is particular interest in replacing the Cu ions, because this replacement alters the magnetic order of the CuO_2 plane. This change has in turn strong effects on the superconducting properties of the high T_c compounds.

It is accordingly of interest to study the effect of point magnetic and nonmagnetic impurities on the binding energy of the carriers in CuO_2 planes by the approach of Ref. 4. We have done this in the study we are reporting here. The impurity consists of the replacement of a copper or oxygen atom in a CuO_2 plane by an atom with a different energy level; this substituent atom may or may not have a magnetic moment (these are the cases of magnetic and normal impurities, respectively). This approach correctly reflects the actual situation, since impurities have a strong effect if they replace copper in the Cu(2) position in the CuO_2 plane (see the detailed analysis of experimental data below). Calculations show that magnetic and nonmagnetic impurities are roughly equally effective in suppressing the binding energy; their effect is greater in the *p*-type high T_c superconductors than in the *n*-type ones.

In Sec. 1 we present the calculation method. The basic results are reported in Sec. 2. Experimental results are reviewed and analyzed in Sec. 3, where conclusions are drawn.

1. CALCULATION METHOD

The most successful model of the electronic structure of the CuO_2 layers is Emery's two-dimensional multiband model.[6] That model incorporates a hybridization of copper and oxygen orbitals, a difference between the atomic ener-

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gies at copper and oxygen sites, and the Coulomb repulsion of the carriers at copper sites, at oxygen sites, and between these sites.

The Hamiltonian in Emery's model, in the hole representation, is[4,7]

$$H_1=-t\sum_{\langle ik\rangle,\sigma}(d^{+}_{i\sigma}p_{k\sigma}+\text{H.c.})+\varepsilon\sum_{k,\sigma}n_{k\sigma}+U_d\sum_{i}n_{i\uparrow}\ n_{i\downarrow}$$

$$+U_p\sum_{k}n_{k\uparrow}\ n_{k\downarrow}+V\sum_{\langle ik\rangle,\sigma,\sigma'}n_{i\sigma}n_{k\sigma'}+H_{\text{im}},\qquad(1)$$

where the operators $d^{+}_{i\sigma}$ and $p^{+}_{k\sigma}$ create holes in the $d_{x^2-y^2}$ and p_x, p_y states, respectively; $\langle ik\rangle$ means a summation over nearest neighbors; i, k are the positions of the copper and oxygen, respectively, $n_{i\sigma}=d^{+}_{i\sigma}d_{i\sigma}$; $n_{k\sigma}=p^{+}_{k\sigma}\ p_{k\sigma}$; t is the copper-oxygen hopping matrix element; $\varepsilon=\varepsilon_p-\varepsilon_d$ is the difference between the energies of a hole at oxygen and copper sites; U_d, U_p, and V are the Coulomb repulsion energies of holes at copper sites, at oxygen sites, and between them, respectively; and H_{im} is the impurity Hamiltonian.

When introduced in a CuO_2 plane, magnetic and nonmagnetic impurities shift the site energies ε, between copper and oxygen and change the magnetic surroundings of copper. In other words, these impurities have both nonmagnetic and magnetic components.

The nonmagnetic component of the impurity is modeled by

$$H_{\text{im}}=U^{n}_{\text{im}}\sum_{i_n\sigma}n_{i_n\sigma},\qquad(2)$$

where i_n represents the positions of the impurities, and U^{n}_{im} is the potential of the interaction with the impurity (more precisely, the shift of ε due to the impurity).

For the magnetic component of the impurities, we use the representation

$$H_{\text{im}}=U^{m}_{\text{im}}\sum_{i_n}^{\sigma}(\mathbf{S}_{i_n}\boldsymbol{\sigma})n_{i_n\sigma},\qquad(3)$$

where S_i is the spin of an impurity.

The relations between U_{im} for magnetic and nonmagnetic components differ from one impurity to another. One might assume that the second contribution is essentially zero in the case of a nonmagnetic impurity, but experimentally one frequently observes an antiferromagnetic order and an effective magnetic moment for nonmagnetic impurities.[8]

In this paper we consider a 12-site Cu_4O_8 cluster with periodic boundary conditions.[4,9,10] The cluster is assumed to have the symmetry of the CuO_2 plane.

The interaction of the excess carriers which appear in a Cu–O cluster as a result of doping is characterized by a binding energy Δ.

For p-type doping, the binding energy is

$$\Delta_h=E(N)+E(N+2)-2E(N+1),\qquad(4)$$

while that for n-type doping is

$$\Delta_e=E(N)+E(N-2)-2E(N-1).\qquad(5)$$

These results have been derived by the exact diagonalization method.[7] Here $E(N)$ is the ground-state energy of a cluster with N holes. For a given cluster, an undoped (insulating) state corresponds to $N=4$ (one hole per copper atom).

A value $\Delta<0$ corresponds to an effective attraction of two excess carriers, while a value $\Delta>0$ corresponds to an effective repulsion of these carriers.

When impurities are introduced directly in this comparatively small cluster, one runs into a serious problem in attempting to compare the theoretical results with experimental results on the behavior as a function of the impurity concentration. The reason is that the introduction of even a single copper-replacement impurity is equivalent to a concentration $x=0.25$; the replacement of one oxygen leads to $x=0.125$. In reality, the superconducting properties of the high T_c superconductors have not yet been suppressed at impurity concentrations $x<0.1$–0.2 (Ref. 3). It is thus not possible to find a continuous functional dependence on the impurity concentration in the range $0<x<0.2$ in such a cluster.

To solve this problem, and also to average the impurities over all possible configurations and to extract the dependence of the calculated values on the actual impurity concentration x, we use the following procedure.

1. We calculate the binding energy Δ_m for numbers of impurities $m=1, 2, 3, 4,\ldots$ in a cluster (for the replacement of Cu theses values are $m=1$–4, while for the replacement of oxygen they are $m=1$–8). The results are averaged over all possible distributions of the impurities in the cluster, and the probabilities for the actual realization of the given distributions are taken into account (for the magnetic component of an impurity, we also take an average over the direction of the spin S^z_i).

2. We imagine that an infinite CuO_2 plane (with $N\rightarrow\infty$ atoms) is broken up into 12-site Cu_4O_8 clusters, and i_m randomly distributed impurities are introduced in this plane.

There are nonzero probabilities for 1, 2, 3, etc., impurities to enter a cluster with a given number of atoms at a given concentration. Noting that the probability (i_m) that impurities with a concentration x $(x=i_m/N,\ i_m\rightarrow\infty,\ N\rightarrow\infty)$ will enter a cluster with j_k atoms is

$$P^{i_m}_{j_k}=((1-x)^{j_k-i_m}x^{i_m})/i_m!,$$

we can calculate the binding energy by summing the contributions from the specific realizations of the number of impurities in a cluster with corresponding weights:

$$\Delta(x)=\Delta_0P^{0}_{j_k}+\Delta_1P^{1}_{j_k}+\Delta_2P^{2}_{j_k}+\ldots.\qquad(6)$$

In particular, for the replacement of copper we would have $j_k=4$, while for the replacement of oxygen we would have $j_k=8$.

We thus find the explicit dependence of the binding energy on the impurity concentration. Spin correlation functions are calculated in a corresponding way.

The accuracy of this approach improves as the size of the cluster is raised and also as the number of impurities in

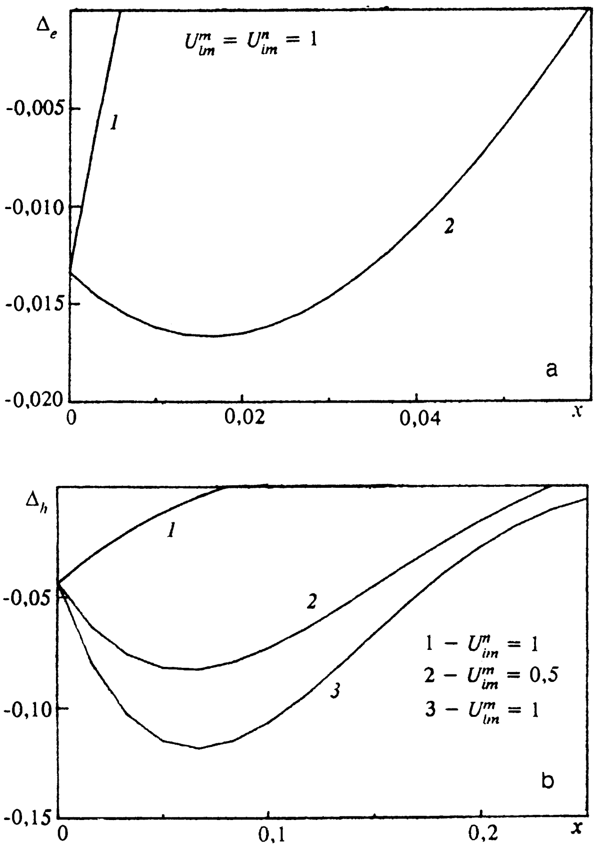

FIG. 1. Binding energy versus the impurity concentration for the occupation of copper sites by magnetic and nonmagnetic components of impurities. a—n-type doping. *1*—Nonmagnetic component; *2*—magnetic component. b—p-type doping. *1*—Nonmagnetic component; *2*, *3*—magnetic component.

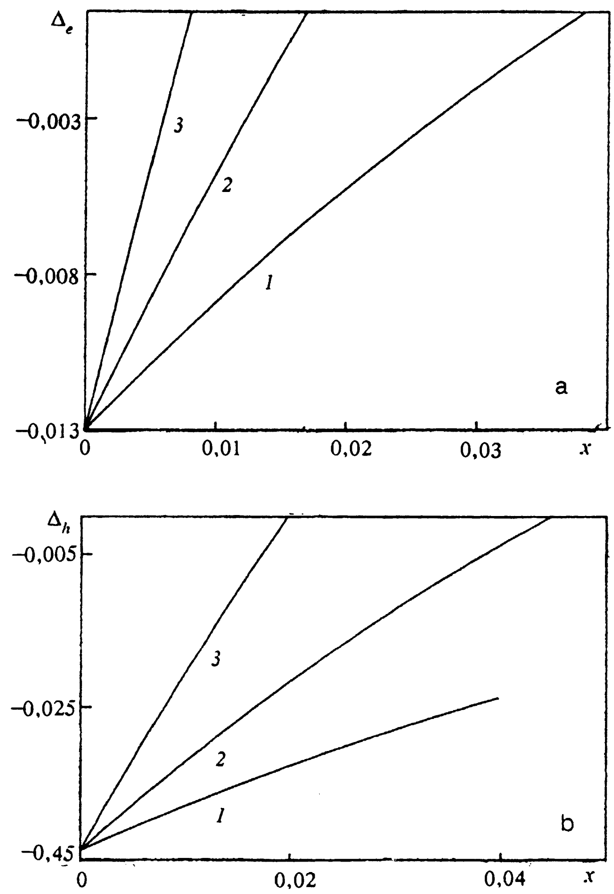

FIG. 2. Binding energy in the case in which oxygen is replaced, for various values of the parameter $U^n_{\rm im}$. a—n-type doping; b—p-type. *1*—$U^n_{\rm im}=0.5$, *2*—$U^n_{\rm im}=1$, *3*—$U^n_{\rm im}=2$.

the cluster is raised. It thus becomes possible to study not only isolated impurities but also an interaction of impurities. For our cluster, the maximum number of copper replacements is correspondingly 4, and the maximum number of oxygen replacements 8. These numbers are quite sufficient for a study of correlation effects which may occur in interactions of impurities with each other and with charge carriers. The calculations using Eq. (6) were restricted to four possible impurities in a cluster for both copper and oxygen, since at low concentrations x the probability for finding five or more impurity atoms simultaneously in our cluster ($P^i_{j_k}$, $i > 4$) is extremely small.

2. BASIC RESULTS AND CONCLUSIONS

Figures 1–5 show the binding energy Δ and the mean square spin versus the dimensionless impurity concentration for some typical values of the parameters in Emery's model: $t \approx \varepsilon \approx 1$ eV, $U_d \approx 8$ eV, $U_p = 0$. At these parameter values the carriers undergo pairing by virtue of an antiferromagnetic ordering.[4,7]

It can be seen from Fig. 1b that Δ_h falls off roughly linearly with the concentration of a nonmagnetic impurity replacing copper, and vanishes at $x_c \approx 0.07$. When a magnetic impurity (more precisely, the magnetic component of an impurity) replaces copper, on the other hand, with the same time scale for scattering by the impurity ($U^m_{\rm im} = U^n_{\rm im}$), there is in fact an increase in Δ at small values of x. Later, Δ decreases, and it vanishes at $x_c \approx 0.2$. Qualitatively the same behavior is found for n-type doping (Fig. 1a), but the corresponding critical concentrations are smaller by a factor of about 3–6.

In the interval $0 < x^h < 0.07$ and $0 < x^e < 0.01$ the magnetic contribution thus causes essentially no suppression of the binding energy (it in fact stimulates this energy), while the nonmagnetic component leads to a linear decrease and a disappearance of carrier pairing.[1)]

Figure 2 shows curves of $\Delta_{e,h}(x)$ for the replacement of oxygen by a nonmagnetic impurity. We see that both Δ_e and Δ_h fall off linearly with x, and they vanish at approximately the same concentrations as in the case of replacement of copper.

Figure 3 shows Δ_h versus x for the case in which the magnetic and nonmagnetic components of the impurity are operating simultaneously [$U^n_{\rm im} = U^m_{\rm im} = 1$ (in units of t)]. We see that Δ falls off nearly linearly with x, for both n-type and p-type doping. This result is explained on the basis that at small values of x the nonmagnetic component is predominant, while at higher values of the magnetic component becomes predominant. As can be seen from

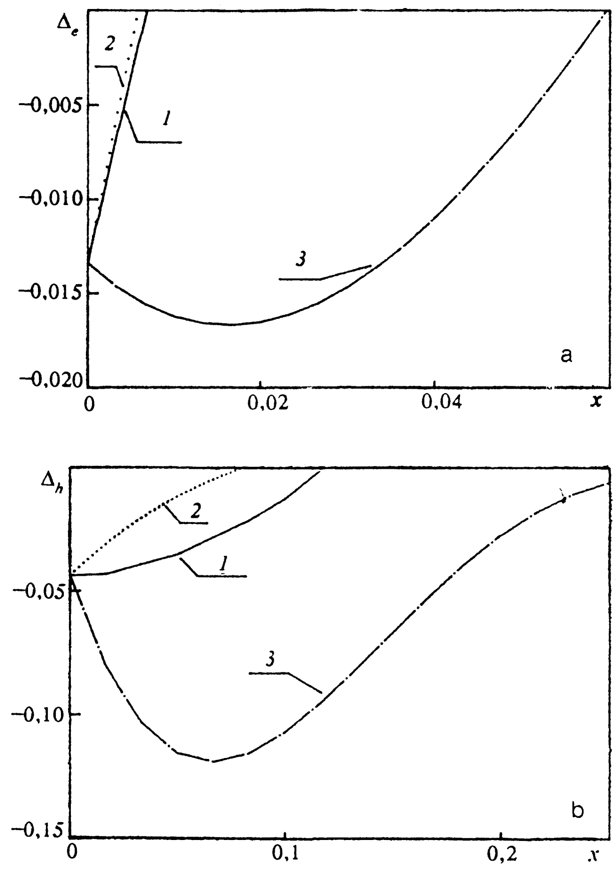

FIG. 3. Binding energy upon the filling of copper sites—the resultant effect of the magnetic and nonmagnetic components of the impurities (curve *1*)—for $U^m_{\rm im} = U^n_{\rm im} = 1$. a—*n*-type doping. b—*p*-type. Shown for comparison are the nonmagnetic component (*2*) and the magnetic one (*3*).

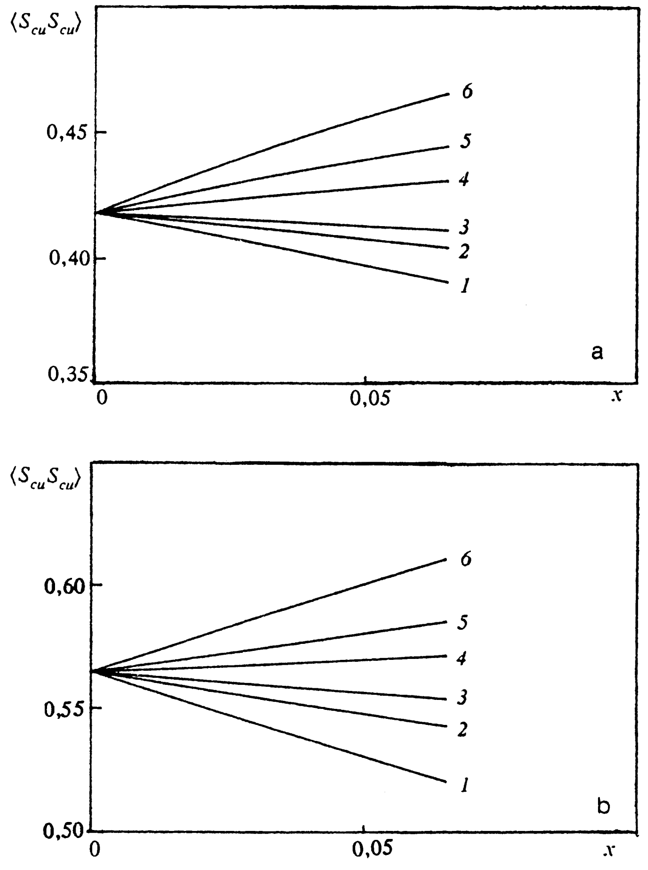

FIG. 4. Mean square spin in the copper sublattice versus the impurity concentration and the parameter $U_{\rm im}$. a—*n*-type doping (one excess electron per cluster). b—*p*-type doping (one excess hole). *1*—$U^n_{\rm im}=2$, *2*—$U^n_{\rm im}=1$, *3*—$U^n_{\rm im}=0.5$, *4*—$U^m_{\rm im}=0.5$, *5*—$U^m_{\rm im}=1$, *6*—$U^m_{\rm im}=2$; *1*, *2*, *3*—nonmagnetic impurities; *4*, *5*, *6*—magnetic impurities.

Fig. 3, the resultant effect is not the simple sum of the contributions from the magnetic and nonmagnetic components (this situation is particularly noticeable for the case of *p*-type doping; Fig. 3b). Judging from all the evidence, the interplay between these two mechanisms is such that even if there is only a single initial interaction constant ($U^n_{\rm im} = U^m_{\rm im}$) the magnetic component ultimately acquires a renormalized effective interaction constant which is much smaller than that of the nonmagnetic component. As a result, the magnetic component has essentially no effect on the carrier pairing. It is apparently this resultant value $\Delta(x)$ which should be compared with experimental data. In this case, as can be seen from Fig. 3, curves *2* and *1* nearly coincide, and we can say that the magnetic and nonmagnetic impurities are almost identically effective.

We also calculated the mean square values of the spin in the copper sublattice. The results are shown as a function of x in Figs. 4 and 5. At small values of x there is an increase in $\langle S^2\rangle$ for the magnetic impurities; later, saturation sets in, and there is even a decrease at large values of x (Fig. 5). We wish to stress that this behavior is also characteristic of the resultant effect of the magnetic and nonmagnetic contributions, so it is the magnetic component of the impurity which has the primary effect on the correlation functions.

In the case of nonmagnetic impurities, there is a monotonic decrease. This behavior is found for both the *n*-type (Fig. 4a) and *p*-type (Fig. 4b) high T_c superconductors.

The results of these calculations can be summarized as follows.

1) Nonmagnetic point impurities consisting of the replacement of Cu and O reduce the binding energy, causing it to vanish at concentrations higher by a factor of 3–6 in the *p*-type high T_c superconductors than in the *n*-type ones.

2) Purely magnetic point impurities consisting of the replacement of Cu (the magnetic components of the impurity) increase Δ at small values of x and later reduce it, causing it to vanish at concentrations higher than for nonmagnetic impurities (the nonmagnetic components).

3) The "resultant" effect of a "real" magnetic impurity is a nearly linear decrease in Δ. The critical values x_c in this case are approximately the same as for a nonmagnetic impurity.

4) The effective magnetic moment in the copper sublattice increases with increasing concentration of magnetic

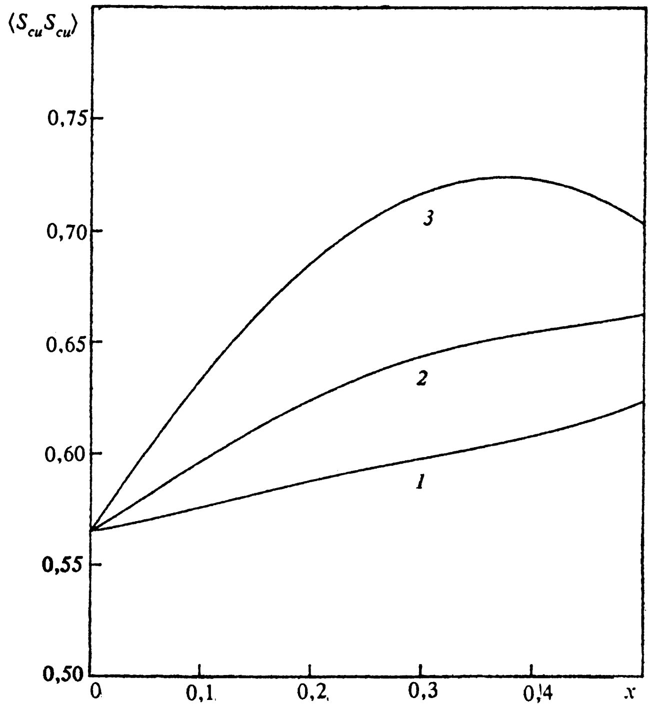

FIG. 5. Mean square spin in the copper sublattice in the case of p-type doping and a magnetic impurity at high concentrations x. A nonlinear behavior of $\langle S^2\rangle$ is seen at $x>0.3$. 1—$U^m_{\rm im}=0.5$, 2—$U^m_{\rm im}=1$, 3—$U^m_{\rm im}=2$.

impurities (and later falls off at high values of x). It decreases in the case of nonmagnetic impurities.

These results were derived, and reported at conferences,[9,10] at a time when the positions occupied by substitutional impurities had not yet been established reliably by experiments. The corresponding experimental data are now available, and we will go through a detailed analysis of the experimental results and compare them with our calculations.

3. COMPARISON WITH EXPERIMENT; DISCUSSION OF RESULTS

In order to carry out a detailed analysis of the effect of impurity atoms in specific experiments, we need to know the positions of the impurities: Do they replace copper atoms in CuO_2 layers [do they occupy Cu(2) sites in the 1-2-3 compounds], or does the replacement occur in Cu–O chains [do they occupy Cu(1) sites]? From this standpoint, the best compounds to look at are the Bi-containing high T_c superconductors,[11,12] in which the layered structure is quite obvious, and there is no problem in the arrangement of impurities at copper atoms. In the lanthanum[3] and neodymium[13] compounds, all the Cu sites are again equivalent, simplifying a comparison with theoretical results.

However, the case which has been studied most thoroughly is the replacement of the copper subsystem in the 1-2-3 compounds, in which there are several nonequivalent sites for copper atoms. For example, detailed data have been obtained on the replacement of copper by Fe (Refs. 14–20), Co (Refs. 15–17), Zn (Refs. 15, 16, 21–24), Ni (Refs. 16, 17, 21), Mg (Ref. 24), and Mn (Refs. 25 and 26) in the M–Ba–Cu–O (M=Y, Eu, Ga) system,[14,16,17,19,20,22-26] the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system,[15] the $CaBaLaCu_3O_{7-\delta}$ system,[21] and the $Y_{1-z}Ca_zBa_2Cu_3O_{6+y}$ system.[18]

Results found by x-ray diffraction and Mössbauer spectroscopy indicate that Zn, Ni, and Mg in these compounds occupy predominantly Cu(2) sites, while Mn occupies predominantly Cu(1) sites.[26] At low concentrations, Fe and Co occupy predominantly Cu(1) sites, while at sufficiently high concentrations they occupy predominantly Cu(2) sites.[14-17] For example, Mössbauer spectroscopy of the $Y_{1-y}Pr_yBa_2Cu_{3-x}M_xO_y$ system (M=Fe, Co, Zn) has revealed that Fe and Co lie primarily at Cu(1) sites at $x<0.2$, while at $x>0.2$ they also occupy Cu(2) sites to some extent.[15] The value $x=x_c=0.4$—the critical concentration of iron and cobalt impurities, at which T_c vanishes—is considerably higher than that of Zn in the same compound ($x_c=0.2$). The dependence of T_c on the Fe or Co concentration is as follows: at $x<0.2$, T_c remains essentially unchanged. At $x>0.2$, there is a decrease in T_c, to the point that the superconductivity is completely suppressed at $x_c=0.4$ (Refs. 15 and 16). The correlation between the substitution of Fe or Co for copper in Cu(2) sites with the $T_c(x)$ dependence is obvious: The Fe and Co have a substantial effect on the transition temperature (specifically, they cause it to decay sharply) only at concentrations at which the Fe and Co begin to replace copper in Cu(2) sites.

Convincing proof of this fact was demonstrated in Ref. 18 for the $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ system. Smith *et al.*[18] established that a change in the concentration of calcium displaces ion atoms from Cu(1) sites to Cu(2) sites. At $z=0$, for example, with a critical iron concentration $x_c=0.15$ ($T_c=0$), only 13% of the iron atoms are replacing copper in Cu(2) sites, while at $z=0.05$ the critical concentration is $x_c=0.10$, and 47% of the Fe atoms are in Cu(2) sites. With increasing fraction of the Fe atoms in Cu(2) sites, the $T_c(x)$ dependence becomes progressively more nearly linear [with a slight decrease in the original value $T_c(0)$], and the critical value x_c decreases.

Compounds in which the substituent atoms (whether magnetic or not is unimportant) are predominantly in Cu(2) sites (this is the case, for example, of Fe in the compound[19] $EuBa_2Cu_3O_y$ and of Mg and Zn in the compound[15,24] Y–Ba–Cu–O) usually have a linear $T_c(x)$ dependence and a low critical concentration ($x_c=0.01$–0.05). The replacement of copper in the compound $CaBaLaCu_3O_{7-\delta}$ by magnetic Ni or nonmagnetic Zn thus leads to a linear $T_c(x)$ dependence and to the value $x_c=0.03$ in both cases.[21]

When impurities are added to a system with different possible copper sites, one sees a strong dependence of the carrier density on the impurity concentration.[27-29] This comment applies to such impurities as Fe (Refs. 27 and 29) and Co (Ref. 28), which undergo a redistribution from the chains [Cu(1)] to the planes [Cu(2)]. If the impurities are instead in the CuO_2 planes [this is true of Ni (Ref. 28) and Zn (Ref. 30)], the Hall density is essentially independent of x. Furthermore, as the impurity concentration is raised, and Fe moves to Cu(2) sites, the carrier density tends toward a constant value[27] (just when the effect on T_c is at a maximum). All these results show that when the impurities are in the CuO_2 planes the carrier density is not altered by an increase in the impurity concentration. This important experimental fact means that we can compare experimental data with our calculated results found at a constant density of excess carriers [for the Cu_4O_8 cluster, the number of excess carriers Δn (electrons or holes) in the calculation of the binding energy from expressions (4), (5) is, on the average, $\Delta n^{e,h}=0.25$].

In compounds in which the copper sites are equivalent and lie exclusively in CuO_2 planes (this is the case of the Bi-containing high T_c superconductors[11,12] and lanthanum[3] and neodymium[13] compounds), the effect of the impurities is at its greatest [for example, when copper is replaced by Co in $Nd_{1.85}Ce_{0.15}CuO_4$ (Ref. 13) or when copper is replaced by Ni, Fe, Co, or Ga in $Bi_2CaSr_2Cu_2O_8$ (Ref. 12)], and the effects of magnetic and nonmagnetic impurities are approximately the same. In this case the $T_c(x)$ dependence is linear. Furthermore, the curves of $T_c(x)$ found during the substitution of Zn (nonmagnetic) and Fe (magnetic) are essentially the same [in $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$].[31] There is essentially no dependence of the carrier density on the impurity concentration in this case (as in[32] $La_{2-y}Sr_yCu_{1-x}Ni_xO_4$), in total agreement with data on the 1-2-3 systems.[27–30]

These data are at odds with the conclusions reached by Arai *et al.*,[33] who attributed the change in T_c in the $(La_{1-x}Sr_x)_2Cu_{0.99}M_{0.01}O_{4-z}$ system (M=Ga, Fe) to a change in the density of excess carriers in the CuO_2 plane (there were no data on the Hall density in Ref. 33). However, the change in T_c with the Fe and Ga concentration in Ref. 33 can be explained completely on the basis of a change in the antiferromagnetic order near the impurity, which was also observed in Ref. 33.

Comparing the critical impurity concentrations for p-type[34] and n-type[13] high T_c superconductors, we generally find $x_c^h/x_c^e=3$–6. In other words, the suppression of superconductivity is much stronger in the n-type superconductors. This conclusion agrees with the results of our calculations.

Few of the papers reporting results on the replacement of copper by such elements as Sb (Ref. 35), Sn (Ref. 36), and Ag (Ref. 37) (we have in mind data on the M–Ba–Cu–O systems) have contained information on the distribution of impurities among sublattices. As a result, an analysis for comparison with calculations is much less effective.

The replacement of the second component of the CuO_2 plane, i.e., oxygen, by F (Ref. 3), I (Ref. 38), or S (Ref. 39) in Y–Ba–Cu–O does not have any important effect on the T_c's, since these dopants primarily occupy oxygen vacancies in the basal plane. However, a quite different effect arises when a neodymium ceramic is doped with fluorine ($Nd_2CuO_{4-x}F_x$; Ref. 40): There is a sharp, linear degradation of T_c, and T_c vanishes at $x_c=0.3$. Again, this result is in total agreement with the results of our calculations.

With regard to magnetic properties, we note that the average moment at copper (and also the antiferromagnetic ordering temperature T_N) usually increases upon doping by a magnetic impurity (Fe, Ni, Co), while it usually decreases upon doping by a nonmagnetic impurity (Ga, Zn) (Ref. 34; cf. our data in Fig. 4).

When nonmagnetic Zn is introduced into a 1-2-3 compound, one sometimes observes the appearance of an effective magnetic moment and of an antiferromagnetic order.[8,41] This observation does not contradict our interpretation that every impurity (magnetic or not) has both magnetic and nonmagnetic components. Furthermore, a decay of the effective magnetic moment with increasing concentration of the magnetic dopant cobalt in a neodymium ceramic was found in Ref. 13. This case is a clear example of the suppression of the magnetic contribution against the background of the nonmagnetic one (which a cobalt dopant undoubtedly has), and it is clearly demonstrated by our results (see the x dependence of $\langle S^2\rangle$ in Fig. 4a for the case of a nonmagnetic impurity, with n-type doping).

The experimental data discussed above lead to the following generalizing conclusions regarding the effect of substitutional impurities on high T_c superconductors:

1) Nonmagnetic and magnetic impurities have the same effects in terms of the degradation of the superconducting properties of high T_c superconductors when they lie in CuO_2 planes.

2) When the Cu is replaced, the Cu(2) sites in CuO_2 planes are the most important ones.

3) When O is replaced, the oxygen sites in CuO_2 planes also become important.

4) The critical impurity concentrations for the n-type high T_c superconductors are lower by a factor of 3–6 than those in the p-type superconductors.

5) The plot of $T_c(x)$ is usually linear for both magnetic and nonmagnetic impurities. Only if there are several nonequivalent sites for the impurity can the plot become nonlinear. This effect is usually attributed to a nonlinearity of the increase in the "true" impurity concentration in the CuO_2 plane.

6) The effective magnetic moment at the copper sites increases upon the introduction of magnetic impurities, while it decreases in the case of nonmagnetic substitutional impurities.

7) The carrier density in the CuO_2 plane does not depend on whether impurities enter this plane. All the changes observed result from redistributions of impurities between the planes and the Cu–O chains.

Comparing conclusions 2 and 3, we see that there is a good qualitative agreement (the agreement is even quantitative in several cases) between the results of these calculations and experimental data (for example, even the calculated critical concentrations x_c are close to those seen experimentally). This agreement allows us to conclude that the cluster approach holds promise and that Emery's model is valid for explaining the set of unusual properties of high T_c superconductors.

We wish to stress that the primary result of this study—the conclusion that magnetic and nonmagnetic impurities have equivalent effects on the superconducting properties of *n*- and *p*-type high T_c superconductors—is supported by experimental data. Marsiglio[42] reached the same conclusion (for *p*-type high T_c superconductors only).

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1) We have also noticed that as calculations show, in the case of a nonmagnetic compound the result does not depend on the sign of the impurity potential, $(\Delta(U^n_{\rm im})=\Delta(-U^n_{\rm im}))$.

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