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Effect of Zn and Ni substitution on the local electronic structure of the $YBa_2Cu_3O_7$ superconductor

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Embedded cluster calculations at the MP2 electron correlation level of pure and Zn- and Ni-doped $YBa_2Cu_3O_7$(Y123) ceramics reveal great changes of the local charge distribution and crystal bonding in the vicinity of impurities. In the Zn-doped ceramics the obtained changes are stronger and more extended than in the Ni-doped ceramics. This can be one of explanations of the stronger depression of T_c due to Zn. The calculated increase of positive charge for both impurities, comparing with substituted Cu, indicates that the impurity atoms lose more negative charge than Cu. As a result, all nearest CuO_2 units around impurity lose their holes: completely in the Zn case and partly in the Ni case. This leads to the breaking of the hole pairs in the vicinity of impurity and correlated with an increase of the coherence length in Zn- and Ni-doped Y123 crystals measured by Timomoto *et al.* [Phys. Rev. B **60**, 114 (1999)]. Both Zn and Ni impurities, the latter to a less extent, act as effective pair breakers due to the elimination of holes on adjacent CuO_2 groups.

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I. INTRODUCTION

It is now well documented (see Refs. 2–7 and references therein) that a small amount of Zn and Ni impurities substituted for Cu in the $YBa_2Cu_3O_7$(Y123) ceramics destroys the superconductivity. The detrimental effect of the Zn substitution is about three times as much as that due to Ni.[2] The substitution of only 8–10% of Cu by Zn results in the full suppression of the superconductivity. This experimental finding is in a sharp contrast with the impurity effect in the conventional superconductors,[8,9] where nonmagnetic impurities such as Zn depress the transition temperature T_c much less than magnetic impurities such as Ni.

Both Ni and Zn have a valence shell $4s^2$; however, Ni has a magnetic moment, created by $3d$ electrons, and Zn is a nonmagnetic atom. The comparative study of Zn and Ni action can help to elucidate the nature of pairing in high-T_c superconductors or, at least, to exclude some pairing hypotheses.[10] The mechanisms that might be responsible for the depression of T_c by Zn and Ni were extensively discussed in the literature.[6,7,11–15] Most of the proposed scenarios are consistent with a $d_{x^2-y^2}$ symmetry of the order parameter. But the reasons for such an exceptionally large depression of T_c by Zn are still unclear. Experimental observations of localized magnetic moments on Cu sites around each Zn (Refs. 16–19) further complicate the issue, adding some extra enigma in the mechanism of the T_c suppression by the Zn impurity.

It is well known that the effects of the unusually strong localization in the oxides of transition metals make the task of performing electron structure calculations very difficult.[20] To reveal the peculiarities of electronic structure, sophisticated band structure calculations (see Refs. 21–23), have to be supplemented by a calculation of local electron configurations. A suitable approach for this is the embedded cluster method (ECM).[24,25] There are many published studies of copper oxides based on the application of the ECM,[26–33] but in most of them the electron correlation effects were not taken into account.

In previous studies,[34–36] we elaborated on the version of the ECM in the framework of the Gaussian package. This allows one to take into account the electron correlation, at least, at the second order of the Møller-Plesset perturbation theory (MP2). That approach was denoted as the ECM-MP2.

For a low concentration of impurities, modifications in the electronic structure of pure Y123 ceramics are localized in the neighborhood of the impurity. To study these changes, the cluster approach with the cluster built around the impurity atoms is most appropriate. Recently, Gupta and Gupta[37,38] used the tight-binding recursion method for calculating a large cluster around isolated Ni and Zn atoms. Their approach allows one to employ a cluster of more than 10 000 atoms, but the method is very approximate. In calculations[37,38] only p functions at the oxygen sites and d functions at other sites were considered and, certainly, the tight-binding model does not take into account the electron correlation. The latter plays an extremely important role in the copper-oxide ceramics.[39] As shown in our studies[34,35] of Y123 ceramics, the electron correlation effects calculated at the ECM-MP2 level essentially change the noncorrelated charge and spin distributions, e.g., the magnitude of the electron correlated MP2 charge on copper ions decreases by a factor 1.5 in comparison with the charge, calculated at the restricted Hartree-Fock (RHF) level.[35]

In the present work, we carried out the calculation at the

ECM-MP2 level of the local electronic structure of a pure crystal $YBa_2Cu_3O_7$ and of the crystal doped with Ni or Zn. Although, according to some experimental data,[40–43] Zn and, especially, Ni substitute for Cu not only in the CuO_2 planes, the main detrimental effect of the impurity is caused by the substitution in the CuO_2 planes. That is why we considered clusters located in the CuO_2 planes. The preliminary results for the Zn-doped ceramics were published in Refs. 36 and 44. In the present study, we used a more representative clusters, Cu_5O_{16}, Cu_4NiO_{16}, and Cu_4ZnO_{16}, and performed a comparative study of Ni and Zn action on the local electronic structure in the CuO_2 planes.

II. METHODOLOGY

The ECM-MP2 methodology was described in details in Refs. 34 and 35; the peculiarities, arising in the case where the symmetry of cluster does not coincide with the point symmetry of the crystal, were summarized in Ref. 36. Hence only the relevant features of the methodology relatives to the studied Cu_5O_{16} cluster (see Fig. 1) are presented.

The methodology is based on a procedure originally proposed by Kelires and Das,[45] which consists of adjusting the external charges of an array that embeds the cluster under study in order to reproduce the correct value of the Madelung potential on each cluster site. This is realized by solving a system of $n+1$ linear equations if the potential on n cluster sites has to be reproduced; an additional equation is needed to express the electrical neutrality. The number of point-symmetry operations of the Cu_5O_{16} cluster (the C_{2v} symmetry) is less than that of the Cu_3O_{12} cluster[34,35] (the latter possesses the same point symmetry D_{2h} as the $YBa_2Cu_3O_7$ crystal) and the number of cluster sites to be adjusted has been increased from 15 to 21. As a consequence, the number of linear equations which allow to adjust the Madelung potential of the embedding charges to that of the infinite crystal has been increased from 7 (as in Refs. 34 and 35) up to 14 in the case of the Cu_5O_{16} cluster. As one equation is left to express the electrical neutrality of the charge array (cluster plus background charges), 13 sites were directly adjusted, but a very satisfactory agreement between the Madelung potential of the infinite crystal and the background charges was found on 17 sites (the difference being less than 10^{-13}) and only on the four external oxygen ions (Fig. 1) was a less satisfactory agreement found, the Madelung potential difference being less than 37% in that case. These four oxygen ions were introduced into the cluster in order to reproduce the correct bonding of the four external coppers. Furthermore, due to the boundary effects which occur when the bonds between cluster and background atoms are not taken into account, the charge of these outermost oxygens is different from that of the oxygen ions inside the cluster, and the results relative to the former ions are not taken into account in this study. But, as follows from our results, these boundary effects have a small influence on the external Cu charge; the modification of the external Cu charges is only 6% in comparison with the central Cu [see Fig. 1(a)].

The charge array (background) has to possess the point symmetry of the crystal. It was found that it is sufficient to

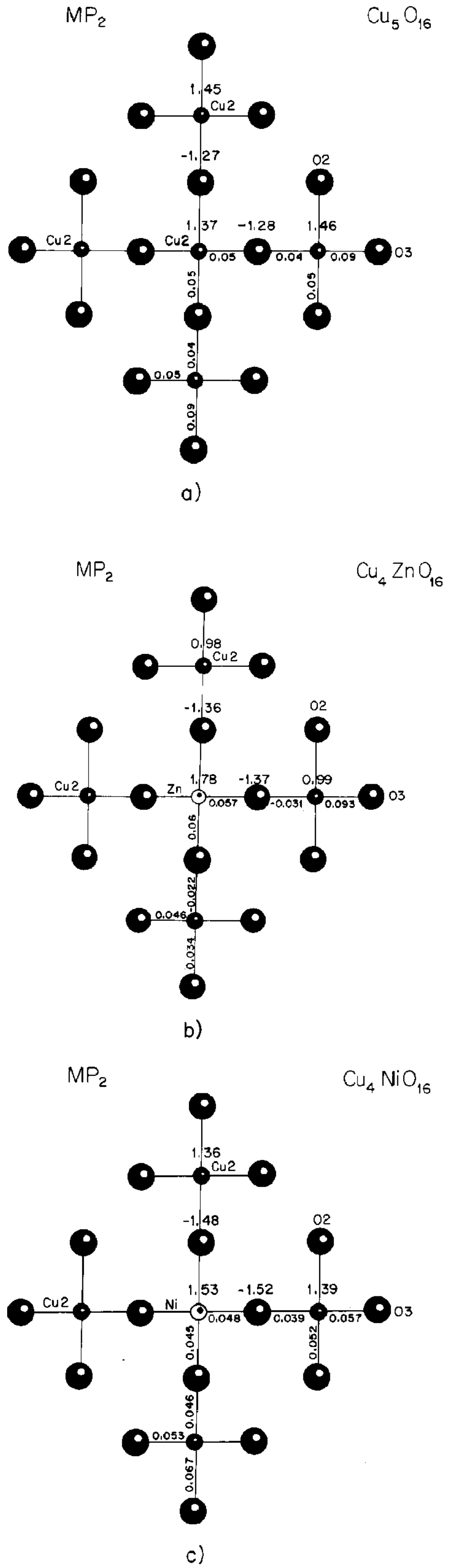

FIG. 1. Charge distribution at the MP2 level on clusters embedded into $YBa_2Cu_3O_7$ obtained from the Mulliken charge matrix: (a) Cu_5O_{16}, (b) Cu_4ZnO_{16}, and (c) Cu_4NiO_{16}.

use not very large charge arrays. In our case it contains 322 charges.

The second point, which characterizes the methodology, is to obtain a consistent set of charges between cluster and background for the perfect crystal represented in this case by the Cu_5O_{16} cluster. This is achieved through a series of calculations where the charges obtained as a result of a quantum-mechanical calculation are taken as background charges for the next calculation. The starting values of charges were taken from Ref. 46, which gives a cluster charge $q=-16$.

For the pure Y123 we have to consider a singlet state in the CuO_2 planes.[34] When the charge of the Cu_5O_{16} cluster is $q=-16$, the singlet state cannot be constructed because the total number of electrons is odd. In order to consider a singlet state in the CuO_2 planes the following procedure was used: two series of RHF calculations were performed, one with $q=-15$ and the other one with $q=-17$, the average of the two final results after convergence being considered as representing the Cu_5O_{16} cluster when its charge is $q=-16$. In each case, three cycles were sufficient to obtain consistency. As a consequence of the previous procedure, the calculations of clusters with impurity atoms (Cu_4ZnO_{16} and Cu_4NiO_{16}, with the charge $q=-16$) have to be performed with two backgrounds for the pure crystal corresponding to the cluster charges $q=-15$ and -17. The final result is obtained by taking the average of the results for each background, although, as follows from the calculations, the difference between these two cases is rather small. The RHF and MP2 calculations were performed with the standard triply split valence 6-311G basis set of the GAUSSIAN 94 program.[47] All core electrons were included in the *ab initio* calculations without using any pseudopotential. A finite array of background charges was introduced as solvent charges using the Charge keyword of the GAUSSIAN program. To calculate the charges on atoms we used the natural bond orbital (NBO) analysis, the charges on bonds were obtained from the Mulliken charge matrix, both at the MP2 level. In order to determine the symmetry of holes on cluster atoms, the NBO population data were used.

III. RESULTS AND DISCUSSION

The *ab initio* quantum-mechanical calculation of clusters, discussed above, was performed in the Madelung field of the perfect crystal mimicked by the finite charge array. As shown in our previous studies,[34–36] the influence of the crystal field on the charge distribution is very strong. For the Cu_4O_{12} and $Cu_2Zn_2O_{12}$ clusters studied in Ref. 36, the comparative calculation of the isolated clusters and clusters embedded into the Madelung potential field revealed, after embedding, an increase of the Cu charge by a factor 3–3.4 and an increase of the oxygen charge by a factor 1.6–1.7. The Zn charge undergoes a relatively smaller increase: 1.2. This indicates that the results obtained for the isolated cluster cannot be extended to the local crystal structure.

In Fig. 1, we present the charges on atoms and bonds obtained from the condensed two-atom Mulliken charge matrix calculated at the MP2 electron correlation level for the pure $YBa_2Cu_3O_7$ ceramics and ceramics doped with the Zn and Ni impurities. Charges on bonds are given as fractions of the electron charge; thus they are negative. The cluster Cu_5O_{16} is more representative than the cluster used in Ref. 36. It consists of the central atom Cu and two shells of nearest neighbors: four O atoms and four Cu atoms that are not on the cluster boundary because they are surrounded by 12 outermost oxygen atoms. Thus these oxygen atoms shield the inner ions from the point-charge background. In Fig. 1, the charges are indicated only on inner ions of the clusters. In this study, we consider the case of a small impurity concentration. Therefore, only the central Cu atom was substituted for by Zn or Ni, and the cluster with an impurity was embedded into the Madelung field of the pure crystal.

TABLE I. Self-consistent charge distribution at the MP2 level obtained from the NBO population analysis for clusters Cu_5O_{16}, Cu_4ZnO_{16}, and Cu_4NiO_{16} with charge $q=-16$ embedded into Y123 ceramics.

	Charges on atoms	Valence orbital population
(a) Cu_5O_{16}		
Cu(centr.)	1.21	$4s^{0.31}3d^{9.37}$
Cu(a)	1.25	$4s^{0.30}3d^{9.35}$
Cu(b)	1.27	$4s^{0.30}3d^{9.34}$
n.n.O(2)[a]	-1.39	$2s^{1.93}2p^{5.38}$
n.n.O(3)	-1.40	$2s^{1.93}2p^{5.39}$
(b) Cu_4ZnO_{16}		
Zn	1.75	$4s^{0.34}3d^{9.73}$
Cu(a)	0.97	$4s^{0.41}3d^{9.43}$
Cu(b)	0.99	$4s^{0.44}3d^{9.37}$
n.n.O(2)	-1.44	$2s^{1.93}2p^{5.42}$
n.n.O(3)	-1.43	$2s^{1.94}2p^{5.41}$
(c) Cu_4NiO_{16}		
Ni	1.41	$4s^{0.33}3d^{8.16}$
Cu(a)	1.21	$4s^{0.32}3d^{9.37}$
Cu(b)	1.18	$4s^{0.33}3d^{9.39}$
n.n.O(2)	-1.58	$2s^{1.92}2p^{5.58}$
n.n.O(3)	-1.62	$2s^{1.93}2p^{5.61}$

[a] The notation n.n refers to the nearest neighbors of the central ion of the cluster.

In Table I, charges on atoms and the valence orbital population, obtained from the NBO analysis, are presented. The central atom of the cluster and the two neighbor shells are considered. In the valence orbital population, the small populated excited orbitals are not included, although their population is taken into account in the presented values of atomic charges. The charges on atoms represented in Fig. 1 correspond to the diagonal elements of the Mulliken charge matrix. If we take into account the charges on bonds, usually negative, the difference with the NBO charges (Table I) will diminish. As follows from our calculations at the MP2 level, the Mulliken total charges on most of atoms differ from the more precise NBO charges by less than 0.1e.

According to the valence orbital population in crystal (Table I), both $3d$ and $4s$ copper electrons are involved into

TABLE II. Change in the electric charge due to the impurity, $\Delta q = q$ (doped crystal)$-q$(pure crystal).

	Zn	Ni
Central atom	0.54	0.20
n.n. O(2)[a]	-0.05	-0.19
n.n. O(3)	-0.03	-0.21
n.n. Cu(a)	-0.28	-0.04
n.n. Cu(b)	-0.28	-0.09
n.n.n. O(2)	-0.20	-0.04
n.n.n. O(3)	-0.18	-0.02

[a] The notation n.n and n.n.n. refer to the nearest neighbors and to next-nearest neighbors of the central ion of the cluster, respectively.

the interaction with the nearest oxygen neighbors. The interaction Cu$(3d)$–O$(2p)$ leads to an antibonding state,[48,49] while the interaction Cu$(4s)$–O$(2p)$ stabilizes the crystal, forming a covalent bond with an electron density equals to 0.05e [Fig. 1(a)]. The $4s$ electrons of Zn and Ni are to a great extent involved in crystal interactions. The $4s^2$ population of the isolated atoms in crystal becomes $4s^{0.34}$ for Zn and $4s^{0.33}$ for Ni. On the other hand, the $3d$ electrons of Zn and Ni practically do not participate in the binding. The $3d$ subshell of Zn is unfilled only on 0.17e, and in Ni there is a small increase of the d-electron population on 0.16e, compared with the $3d^8$ population in the isolated atom. This means that the antibonding state Cu$(3d)$–O$(2p)$ almost vanishes at the sites of impurity substitution. The bonds Zn-O and Ni-O are more ionic than the corresponding Cu-O bond (in the case of Zn to a great extent), although the covalent nature of $4s$-$2p$ bonding is still preserved. In the case of Zn, the negative electron density on the Cu-O bond adjacent to impurity [see Fig. 1(b)] indicates a completely antibonding character, while the same bond in the case of Ni is still covalent [Fig. 1(c)].

The substitution of the central Cu atom by the Zn or Ni atoms results in a large change of the net charge on the central atom, and changes of the net charge on neighbor atoms which are different for the Zn and Ni substitutions. In Table II we present these changes for the central atom, the nearest copper atoms, and nearest-neighbor (n.n.) and next-nearest-neighbor (n.n.n.) oxygen atoms. In the case of the Zn substitution, there is a large increase (0.54e) of the positive charge on Zn. This means that, in crystal, in spite of the extra electron, Zn loses more negative charge than Cu. The additional negative charge is distributed relatively far from Zn. There is a small increase of negative charge on the n.n. O atoms, and a large transfer of negative charge to the more distantly located Cu atoms and n.n.n. O atoms.

In the Ni-doped crystal there is also an increase of positive charge on Ni in comparison with the substituted Cu, but 2.8 times less than that on the Zn atom. Ni, like Zn, has a $4s^2$ valence shell and, though the Ni atom possesses one electron less than the Cu atom, it still donates more electrons than the $4s^1$ valence shell of Cu to the crystal chemical bonding. In contrast to the Zn case, the Ni substitution causes a less extended perturbation. The largest changes of charge take place on the n.n. oxygens; on the n.n. coppers and on n.n.n. oxygens the decrease of the positive charge is rather small. Thus the Zn substitution results in stronger and more extended changes of the charge distribution than the Ni substitution.

The comparison of the data in Table II with the Gupta-Gupta calculation[38] indicates large discrepancies, although their qualitative conclusion about the extended charge changes in the Zn-doped crystal coincides with our calculation result. Almost zero charge changes were reported in Ref. 38 for the Ni doping. These discrepancies may be attributed to the approximate nature of the approach used in Ref. 38. The authors of Ref. 38 did not take into account the valence $4s$ electrons of Cu and impurities, involved in the charge-transfer processes and in the covalent bonding with $2p$ oxygen electrons, as well as the electron correlation effects. The latter is evident, because the tight-binding model is based on the one-electron approximation.

It is well established that Y ceramics are characterized by the hole conductivity; the charge carriers are the hole pairs. According to experimental data,[50,51] the superconductivity in Y123 ceramics is achieved when the mean hole density ρ_h is in the range of $(0.10–0.25)e$ per CuO_2 unit. In Ref. 50 chemical methods indicate $T_{c,max}$ at $\rho_h = 0.22e$, Tallon *et al.*[51] obtained $T_{c,max}$ at $\rho_h = 0.16e$. Let us estimate the changes of the hole concentration cause by the impurity doping.

According to Table II, a loss of negative charge on Zn and Ni leads to an increase of negative charge on the CuO_2 units adjacent to the impurities and, consequently, to a decrease of the hole density on these units. The estimation of hole density decrease, $\Delta\rho_h$, per adjacent CuO_2 amounts $-0.52e$ for the Zn impurity and $-0.26e$ for the Ni impurity. We should compare these $\Delta\rho_h$ values with the value of ρ_h in the pure crystal. A comparison has to be done in the framework of one model. In the pure crystal, for the plane cluster used in this study, we obtain $\rho_h = 0.49e$. This value is larger than reported experimental values,[50,51] but for a study of impurity effects the comparative changes in ρ_h are more important than the absolute values.[60] Thus all the nearest CuO_2 units around the Zn impurity completely lose their holes, and the mean density of charge carriers in the vicinity of impurity drops down. The Zn impurity acts as an effective breaker of the hole pairs. For the Ni impurity there is only a decrease in the hole density. The hole-pair breaking action of Ni is much less pronounced than that of Zn.

For elucidating the mechanism of the hole-pair formation, it is important to know the symmetry of holes. This problem has a long history. In the early band calculations,[52,53] the $2p\sigma$ symmetry of the holes on oxygen ions was obtained. Later, in the generalized valence bond calculations,[54] without taking into account the crystal field, the $2p\pi$ symmetry of the holes on oxygen ions was reported. In our recent studies[34–36] of $YBa_2Cu_3O_7$ ceramics by the ECM-MP2 approach, we obtained the $2p\sigma$ symmetry of the holes on the oxygens in the CuO_2 plane. We confirm these results in the present calculations; see Fig. 2. This information was extracted from the NBO analysis data after calculation at the MP2 level of the Cu_5O_{16} embedded cluster. The holes on the

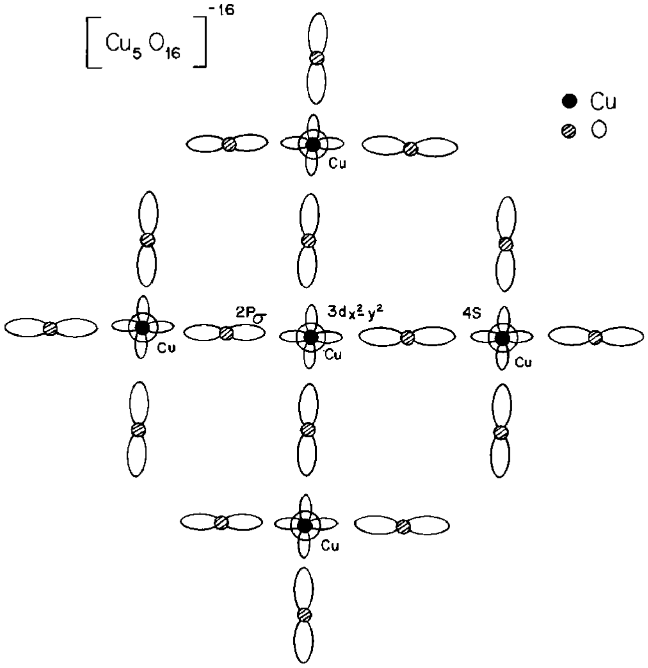

FIG. 2. Symmetry of holes in a pure $YBa_2Cu_3O_7$ crystal from a NBO population analysis at the MP2 level.

O atom are estimated with reference to O^{-2}, i.e., they are real holes in the solid estimated with respect to the filled oxygen band, while the holes on the Cu atom are estimated with reference to the isolated neutral Cu atom and reflect an electron deficit. The quantitative measure of the electron deficit can be found from the valence shell population presented in Table I. As follows from the NBO analysis, the main contribution to the hole density in the d subshell has a $d_{x^2-y^2}$ origin.

It is interesting to note that a qualitative picture, similar to that represented in Fig. 2, was proposed without any rigorous treatment by Zhang and Rice.[55] They assume that on the CuO_2 planes of superconducting ceramics the hybridization of $3d$ (Cu) and $2p$ (O) electrons is realized, and all spins are paired (the so called Zhang-Rice singlet). Their hypothesis was substantiated by our ECM-MP2 calculations in Ref. 34, where it was shown that there are no unpaired spins in the CuO_2 planes. The results about the $2p\sigma$ hole symmetry presented in Fig. 2 give to the hybridization hypothesis an additional support. These theoretical results are in a good agreement with the NMR experiments[56,57] and x-ray absorption spectroscopy studies.[58]

The NBO analysis gives the following mean orbital contributions to the hole density on oxygens in the pure crystal: $0.07\ 2s+0.51\ 2p\sigma+0.07\ 2p\pi$ ($\perp$ to plane). In the doped material for the oxygens adjacent to the Zn impurity we have $0.06\ 2s+0.50\ 2p\sigma+0.06\ 2p\pi$ ($\perp$ to plane), whereas in the case of the oxygens adjacent to the Ni impurity we have $0.08\ 2s+0.37\ 2p\sigma+0.06\ 2p\pi$ ($\perp$ to plane).

Thus the $2p\sigma$ symmetry of holes on adjacent oxygens is preserved for both impurities, although to a less extent in the Ni case. The $2p\pi$ (in-plane) symmetry contribution to the hole symmetry on the oxygens atoms adjacent to Zn, revealed in Ref. 36, proceeds from the two Zn atoms substituted in one small cluster. In the case of the single impurity atom in cluster considered in this study, Zn and Ni impurities do not change the qualitative picture of the hole symmetry on oxygen atoms.

According to Table I, there is an increase of electron population on the d subshell of Cu close to the impurities; it is equal to $0.08e$ and $0.03e$ in the case of Zn and to $0.05e$ and $0.02e$ in the Ni case. Although in the Zn case the increase has a slightly larger magnitude, it is difficult to conclude if this increase in the d electron charge of the Cu nearest to Zn can explain the small local magnetic moments observed on Cu in the experiments[16–19] upon Zn substitution.

IV. CONCLUSIONS

The ECM-MP2 approach developed in our previous works[34–36] allows one to make calculation of the local electronic structure of doped crystals at the electron correlation level provided by the GAUSSIAN package. One of the advantages of the methodology developed is the possibility to use the rather precise NBO population analysis at the electron correlation level. The application of this approach to the comparative study of the local electronic structure of pure Y123 ceramics and ceramics doped with Zn and Ni reveals that the antibonding state $Cu(3d)$–$O(2p)$ almost vanishes at the sites of impurity substitution. The bonds Zn-O and Ni-O are more ionic than the corresponding Cu-O bond (in the case of Zn to a great extent), although the $4s$-$2p$ covalent nature of the bond is still preserved.

For both Zn and Ni impurities there is an increase of positive charge at sites of substitution (in the case of Zn of 2.8 times) and changes in the net charge of neighbor oxygens and coppers. The Zn doping causes stronger and more extended changes of neighbor atom charges and of their bonding than the Ni doping. These stronger and more extended perturbations of electronic structure in the neighborhood of a Zn impurity can be the reason for the stronger depression of T_c due to Zn. The study of Zn-substitution effects on the normal-state charge transport in $YBa_2Cu_3O_7$ ceramics has revealed a large scattering cross section of the Zn impurities.[59] According to Fukuzumi *et al.*,[5] the primary effect of Zn doping is to produce a large residual resistivity as a potential scattering center in the unitary limit. As follows from our results, this is not a pointlike scattering center located on Zn; it is rather delocalized in the vicinity of impurity.

The increase of positive charge on the impurities means that impurity atoms lose more negative charge than copper atoms. The additional negative charge is distributed on neighboring O and Cu atoms. As a result, all the nearest CuO_2 units around the impurity lose their holes, completely in the Zn case and partly in the Ni case. In the normal state, an increase in the slope of the electrical resistivity versus the temperature as a function of the Zn concentration is observed experimentally, and may be attributed to a decrease of carrier density.[59] This experimental fact is consistent with our result: a decrease of hole concentration is expected in the presence of a Zn impurity. In the superconducting state the decrease of the hole concentration provokes the breaking of hole pairs in the vicinity of the impurity, and is correlated with an increase of the superconductivity coherence length of Zn- and Ni-doped Y123 single crystal, as measured in Ref. 1. In agreement with our calculation results, the rate of the measured coherence length increase in the Zn-doped crystal is larger than that due to Ni. The measured increase of the in-plane coherence length, as noted by the authors of Ref. 1, is in an excellent agreement with the prediction of the pair-breaking theory in the *d*-wave superconductivity.[13] Thus the Zn and Ni impurities, the latter to a less extent, act as effective pair breakers, and the elimination of holes on adjacent CuO_2 groups can be considered as a possible mechanism responsible for the pair breaking.

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