



## Study of the electronic structure of Zn-doped Y123 ceramics

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The electronic structure of undoped and Zn-doped Y123 ceramics is studied by means of the embedded cluster method at the MP2 electron correlation level. The Zn impurity is found to be a source of nonhomogeneity in the hole density distribution in the CuO<sub>2</sub> planes which acts as an extended and strong scattering center. In Zn-doped ceramics the orbital symmetry of holes on nearest-neighbor oxygens is changed: in addition to the 2p $\sigma$  symmetry which characterizes the pure material, a 30% contribution of the 2p $\pi$  (in plane) symmetry is revealed. The latter can hinder the hole-pair formation on oxygen ions.

### 1. Introduction.

Zn and Ni substitution in copper oxide superconductors is known to have a strong influence on electrical properties of these materials which depend also on the oxygen concentration [1], and can also induce local magnetic moments [2]. On the other hand, the comparison of the efficiency of these impurities to suppress the superconductivity is considered as a good test of the mechanisms proposed for the formation of charge carrier pairs in the superconducting state [3].

The study of impurity effect in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> has been tackled recently by R.P. Gupta and M. Gupta [4] in the case of Ni and Zn substitutions using a recurrent tight binding approximation. This approach allows to employ clusters with more than ten thousand atoms but it does not take into account the electron correlation. The latter plays an extremely important role in copper-oxide ceramics [5]. As was shown in our previous calculations [6], it essentially changes the charge and spin distributions (the magnitude of the electron correlated charge on copper ions decreases by a factor 1.5 in comparison with the Hartree-Fock charges).

In the present work the electronic structure of undoped and Zn-doped ceramics is studied by an elaborated version of the embedded cluster method [6,7] which allows to take into account the electron correlation effects in the frame of the Gaussian program. A comparative study of the obtained results allows a description of electronic

density variation as well as the hole orbital symmetry analysis.

### 2. Methodology

The self-consistent embedded-cluster method used is characterized by two aspects: (i) a computational method describing the cluster at the quantum mechanical level; in our case, it is provided by the *Gaussian 94* program; (ii) an embedding scheme which couples the cluster to its environment and has to represent an infinite crystal; it is described elsewhere [6,7].

The *ab initio*, full electron calculations are carried out using the restricted Hartree-Fock method with the triply split valence basis set 6-311G. In order to take into account the electron correlation, the second order Moller-Plesset perturbation theory (MP2) is used. To calculate the charge distribution we use Mulliken population analysis along with the natural bond orbital (NBO) option provided by the program.

### 3. Results and discussion

The charge distribution calculated at the MP2 level is presented in Table 1 for the undoped and Zn-doped clusters. The calculation of NBO charges takes into account a small electronic density in excited states which is not included in the valence orbital population shown in Table 1.

**Table 1.**  
Self-consistent charge distribution at the MP2 level for the clusters  $Cu_4O_{12}$  and  $Cu_2Zn_2O_{12}$

|                     | NBO value | Valence orbital population |
|---------------------|-----------|----------------------------|
| a) $Cu_4O_{12}$     |           |                            |
| Cu2                 | +1.37     | $4s^{0.29}3d^{9.26}$       |
| O2                  | -1.28     | $2s^{1.93}3p^{5.42}$       |
| O3                  | -1.28     | $2s^{1.93}3p^{5.42}$       |
| b) $Cu_2Zn_2O_{12}$ |           |                            |
| Zn                  | +1.68     | $4s^{0.26}3d^{9.97}$       |
| Cu2                 | +1.41     | $4s^{0.28}3d^{9.22}$       |
| O2                  | -1.48     | $2s^{1.93}2p^{5.62}$       |
| O3                  | -1.51     | $2s^{1.94}2p^{5.65}$       |

The substitution of Cu2 by Zn in a  $CuO_2$  plane results in small increase of the nearest neighbor Cu2 charge and in a large increase of the electronic charge on oxygen sites closed to the impurity. In the case of Cu2 ion, the charge variation (+0.04e) is distributed on the s and d shells whereas in the case of oxygen ions, the charge variation (-0.20e for O2, -0.23e for O3) corresponds essentially to an increase of the electron population in the p shell.

A modification of the electron hole symmetry at oxygen sites closed to the Zn impurity is revealed: the  $2p\sigma$  symmetry in the undoped material becomes  $0.7\ 2p\sigma + 0.3\ 2p\pi$  in the Zn-doped ceramics. The hole symmetry on oxygen sites which are not adjacent to a Zn impurity are not modified, this is also the case of holes on Cu2 sites, which have the  $3d_{x^2-y^2}$  symmetry. The  $2p\sigma$ - $2p\sigma$  hole pair formation on oxygen ions can be hindered by the  $2p\pi$  contribution which appears in the hole orbitals on oxygen ions in the vicinity of the Zn atom.

The d shell of the Zn impurity is found completely filled. As it substitutes a Cu ion with a partially filled d shell, Zn doping results in a local decrease of hole density available for pair formation on cationic sites. The reduction of hole count in the  $CuO_2$  unit close to the impurity with respect to a  $CuO_2$  unit of the pure material is about 0.4.

According to Table 1, the charge variation

along the a axis is as follow: -0.71e on the Zn site (in d-shell), -0.2e on the oxygen site and +0.04e on the nearest neighbor Cu2 site. This distribution is consistent with the Friedel charge oscillation observed in reference [3]. More detailed presentation of the results obtained will be published in [8].

#### 4. Conclusions

The perturbation associated to the Zn impurity is not localized on a cationic site, it is extended and consists of 3 types of scattering centers (Zn, O, Cu) with different effective charges. A non-uniform hole density in the  $CuO_2$  planes is created, which contributes to a mechanism responsible for the degradation of superconductivity in this material. In the case of oxygen holes, a modification of their orbital symmetry is revealed. The latter have to be taken into account when the Zn impurity is considered as the Cooper pairs breaker.

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1. Y. Fukuzumi, K. Mizuhashi, K. Takenaka and S. Uchida, *Phys. Rev. Lett.* 76 (1996) 684.
2. A.V. Mahajan, H. Alloul, G. Collin and J.F. Marucco, *Phys. Rev. Lett.* 72 (1994) 3100
3. M. Sigrist and K. Ueda, *Rev. Mod. Phys.* 63 (1991) 239.
4. R.P. Gupta and M. Gupta, *Phys. Rev.* B49 (1999) 3381. *Physica C* 305 (1998) 179.
5. W. Brenig, *Phys. Rep.* 251 (1995) 153.
6. I.G. Kaplan, J. Soullard, J. Hernández-Cobos and R. Pandey, *J. Phys.: Condens. Matter.* 11 (1999) 1049.
7. I.G. Kaplan, J. Hernández-Cobos and J. Soullard, *Progress in Theoretical Chemistry and Physics*, series B, vol. 1 (2000) 145, Kluwer Acad. Press.
8. I.G. Kaplan and J. Soullard, *Intern. J. Quant. Chem.* (in Press).