

Calculation of the electronic structure of $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ in terms of the real-space-scattering coherent-potential approximation

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The electronic structure of the Y-Ba-Cu-O system as alloyed by Zn on the Cu(1) and Cu(2) sublattices is calculated for Zn contents up to $x=0.1$. Distinct differences for these two cases of alloy formation are found in terms of partial densities of states (DOS's). The Fermi level and the DOS at the Fermi level, however, vary similarly with the Zn concentration. This behavior can be explained using a description of localization based on integrated local DOS's. In general, calculated spectroscopic properties like x-ray-emission and x-ray photoemission spectroscopy are sensitive with respect to Zn substitution, but too insensitive to resolve differences with respect to the alloy formation on the different sublattices of Cu.

I. INTRODUCTION

One of the most efficient experimental approaches to study the mechanism of high-temperature superconductivity is to investigate compositional perturbations such as nonstoichiometry or selective alloying. Substituting copper with 3d transition metals in the Y-Ba-Cu-O system results in an anomalously large depression of T_c for surprisingly small concentrations. "Doping" with Fe and Co, but also Ga and Al, favors a structural transition from orthorhombic to tetragonal,¹⁻⁴ while Ni (Refs. 3-5) and Zn (Refs. 3, 4, 6-9) do not induce strong structural modifications. Different experimental results are nevertheless more or less contradictory and certainly are very sensitive with respect to the sample preparation. The variation of T_c with the Zn concentration is nearly linear up to $x=0.1$, where the material becomes a semiconductor.^{3,4,6,7,10} Some experiments,^{8,9} however, suggest that in the concentration range $0.02 < x < 0.06$ there exists a plateau in the critical temperature of approximately 50-60 K. There is also considerable disagreement about the preferential "doping" site: extended x-ray absorption fine structure¹¹ (EXAFS) studies and indirect arguments based on formal charge distributions³ support a Cu(2) (plane) site preference, while x-ray diffraction investigations¹² and Néel-temperature measurements⁴ seem to confirm that zinc is alloyed on the Cu(1) (chain) sites. Several types of mechanism, such as filling of *d* holes, localization of copper *d* bands, increasing pair-breaking magnetization, and disorder in the copper-oxygen sublattice but also the formation of new electronic states due to substitution of copper 3*d* bands by zinc 4*s* states⁹ have been proposed to explain the lowering of T_c .

In a recent paper¹³ we described a real-space-scattering cluster coherent-potential approximation (RSSC-CPA) method designed especially to investigate effects of compositional disorder in structurally complex systems. This

method was first applied to the problem of nonstoichiometry in the Y-Ba-Cu-O system. In the present paper the RSSC-CPA method is used to discuss the electronic structure of the $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ system in terms of physical quantities possibly related to the mechanism of superconductivity, such as the variation of the Fermi level ϵ_F , the total DOS at the Fermi level per unit cell $n(\epsilon_F)$, and a model of localization based on integrated local DOS's. In addition, a theoretical study of x-ray emission (XES) and x-ray photoemission (XPS) is also presented.

II. THEORY AND COMPUTATIONAL DETAILS

In a recent review article¹⁴ Pickett stated that finite cluster studies can be expected to be useful for comparisons of *differences* in the electronic structure when dealing with compositional perturbations with respect to the basic periodic system. Concomitantly, he also warned about the breakdown of such methods due to the loss of periodicity and due to possible "surface" effects. The results for the electronic structure and the spectroscopical properties of the nonstoichiometric Y-Ba-Cu-O system¹³ however, imply that cluster calculations, using rather big clusters (about 100 sites), can reproduce the local DOS's (LDOS) fairly well. In the present paper a cluster centered around a chain oxygen site [O(1)] and containing 99 sites within a sphere of radius 13.6 a.u. is used. This cluster has the same point group symmetry as the unit cell in the Y-Ba-Cu-O system.

As in Ref. 13, for the ordered system the potentials in this cluster correspond to the *muffin-tin* FLAPW potentials,¹⁵ $V_{MT,i}^{\text{FLAPW}}(r)$, where *i* denotes a particular site. In order to obtain *ad hoc* Zn potentials an impurity construction is used by superposing concentration (*x*) weighted ionic charge densities. The ionicities chosen in the atomic calculations are +2.14 for the Cu and Zn

sites. For the oxygen sites a negative ionicity of -1.78 is used, whereby the negative oxygen ions are stabilized by a Watson sphere radius of 2.5 a.u. The potentials used for the CPA calculation $V_i(r;x)$ are then constructed by choosing $V_{MT,i}^{\text{FLAPW}}(r)$ (corresponding to $x=0$) as a reference, and by including the potentials for the superposed charge densities $V_i^s(r,x)$ in the following way:

$$\Delta_{\text{Cu}(i)}(r) = V_{\text{MT,Cu}(i)}^{\text{FLAPW}}(r) - V_{\text{Cu}(i)}^s(r;x=0),$$

$$V_{\text{Zn}(i)}(r;x) = V_{\text{Zn}(i)}^s(r;x) + \Delta_{\text{Cu}(i)}(r),$$

$$i=1,2.$$

Because the ionicities of all constituents are kept constant for all compositions x , the long-range Madelung-type contributions to the potentials only vary with x due to the x -dependent superposition of the charge densities. It should be noted that by changing the ionicity for Cu and Zn by ± 0.1 and by keeping charge neutrality the difference between the Cu and Zn d resonance energies (energy at which the corresponding phaseshift passes through $\pi/2$) is changed by about ± 0.08 eV. At least for spectroscopical quantities this kind of change seems to be irrelevant.

For the alloy calculations the improved CPA scheme of Ginatempo and Staunton¹⁶ is used guaranteeing rapid convergence for the $\text{Cu}_{1-x}\text{Zn}_x$ subsystem even along the real-energy axis. In all present calculations the energy grid size is 0.1 eV.

III. RESULTS

For a Zn content of $x=0.1$, Fig. 1 shows the d -like component DOS's for both possibly alloyed sublattices,

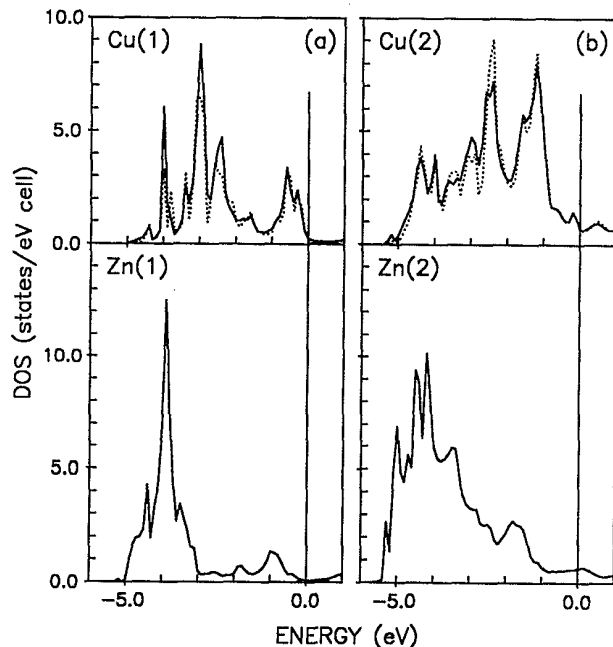


FIG. 1. Partial local d -like DOS's for the disordered sublattices in $\text{YBa}_2(\text{Cu}_{0.9}\text{Zn}_{0.1})_3\text{O}_7$ when "doping" (a) the Cu(1) and (b) the Cu(2) sublattice with Zn. Dotted lines refer to the LDOS's for the ordered case. The zero of the energy scale corresponds to the FLAPW Fermi level (Ref. 15).

namely, (a) the chain and (b) the plane positions. For a comparison we also plotted the LDOS's for the "undoped" case. The most obvious effect is the very strong hybridization of Cu and Zn d -states. As one can see from Fig. 1 the two types of alloys are remarkably different. For "chain site" alloys the Zn d -like DOS has a virtual bounded-statelike peak at -3.9 eV, which is also reflected in the Cu(1) d -like DOS. The situation is completely different when Zn alloys the Cu(2) sublattice. Because of the wide dispersion of electronic states related to the Cu(2)-O(2)-O(3) planes in the stoichiometric compound (attributed to strong " $d\rho\sigma$ " bonding,^{15,17} the Zn d -like DOS shows mostly effects of back scattering ("hybridization").

To get more insight into the modification of the electronic structure upon alloy formation, we calculated as a function of x the differences of the integrated LDOS's, $\Delta N(E)$, with respect to the stoichiometric cluster. These differences are plotted in Figs. 2(a) and 2(b) for both cases of alloy formation. The shape of these curves provides direct information about energy regimes where characteristic changes for the on-site located charges, i.e., where "localization" or "delocalization" occur. Strong localization is observed for the Cu(1) site around -3.9 eV (virtual bound state) when substituted partially by Zn. Localization is also observed between -3 and -2 eV (non-bonding states)—an energy regime where also some excess charge is formed on the Cu(2) sites. Substitution in the plane results in a moderate charge localization at the host [Cu(2)] site, but surprisingly also on the Cu(1) sublattice with features similar to those of the chain substitution. This enlightens the important role of the O(4) sites situated between the chains and planes obviously creating a *channel* for charge compensation: even when zinc substitutes for the copper sites in the plane, the excess charge will be localized preferably in the chains. As a very illustrative comparison we show in Fig. 3 the $\Delta N(E)$ for the copper sites for the case of oxygen vacancies in the chain [O(1)] and the plane [O(2)]. Figure 3 clearly

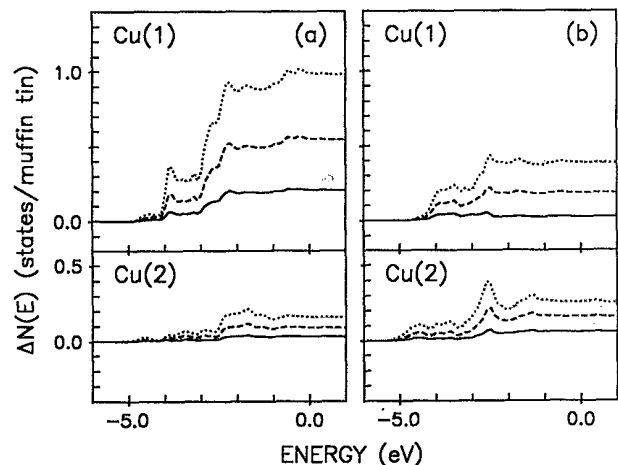


FIG. 2. Difference of the integrated partial local d -like DOS's with respect to the "undoped" system when "doping" (a) the Cu(1) and (b) the Cu(2) sublattice with Zn. (Solid line $x=0.01666$, dashed line $x=0.05$, dotted line $x=0.1$.)

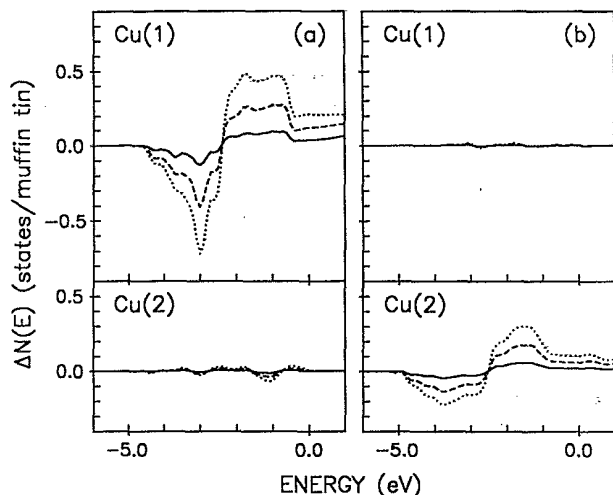


FIG. 3. Difference of the integrated partial local d -like DOS's in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with respect to the stoichiometric system ($\delta=0$) when (a) the O(1) and (b) the O(2) sublattice is disordered. (Solid line $\delta=0.1$, dashed line $\delta=0.3$, and dotted line $\delta=0.5$.)

shows that by breaking the Cu— d and O— p bonds, charge is moved mainly to the nonbonding $\text{Cu}d$ -like states, whereby the interplay between chains and planes is negligible.

Using a procedure discussed previously¹³ for the calculation of ϵ_F within the cluster approach, we computed ϵ_F and $n(\epsilon_F)$ for the zinc-“doped” Y-Ba-Cu-O system. Figure 4 shows that for both types of Cu-Zn alloys there are

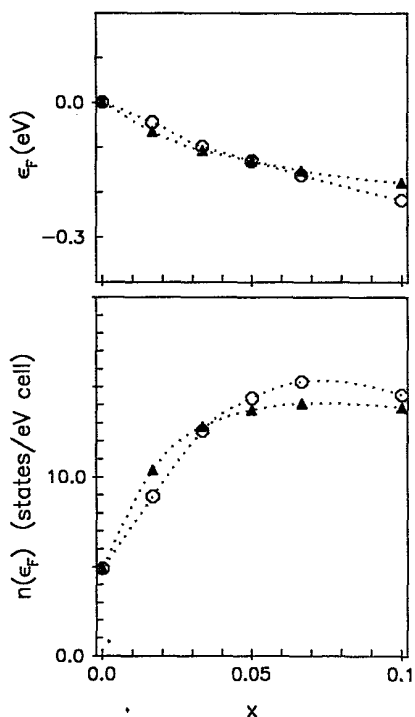


FIG. 4. Variation of the Fermi level (upper part) and the total DOS at the Fermi level (lower part) with respect to the Zn concentration. Triangles and open circles denote Zn substitution on the Cu(1) and Cu(2) sublattice, respectively. The dotted lines serve as a guide for the eye.

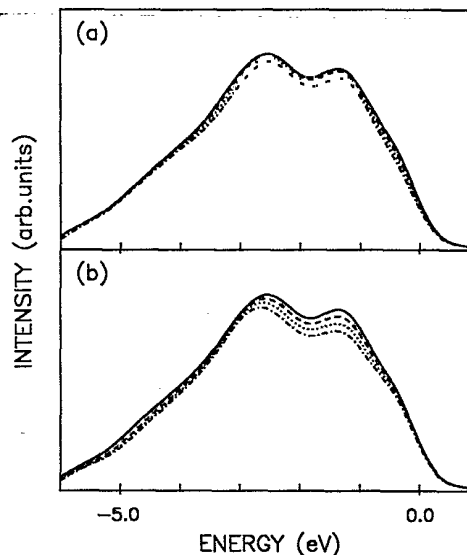


FIG. 5. Calculated Cu-L_3 x-ray emission spectra for different Zn concentrations when “doping” (a) the Cu(1) and (b) the Cu(2) sublattice with Zn. (Solid line $x=0$, dashed line $x=0.0333$, dotted line $x=0.0666$, dashed-dotted line $x=0.1$.)

no distinct differences in the variation of ϵ_F and $n(\epsilon_F)$ with respect to the concentration. Despite the increasing number of valence electrons with increasing Zn content, ϵ_F decreases. Concomitantly, due to the large O(1)-O(4) [and partially Cu(1)] peak in the DOS, $n(\epsilon_F)$ rises very rapidly with the concentration up to about $x=0.04$, where $n(\epsilon_F)$ becomes approximately constant. Note that plane-related states actually do not interplay in the increase of $n(\epsilon_F)$ in either of both cases. The rather similar behavior of charge redistribution, emphasized previously in connection with Fig. 4, accounts for a similar variation in ϵ_F with respect to the two cases of Zn substitution:

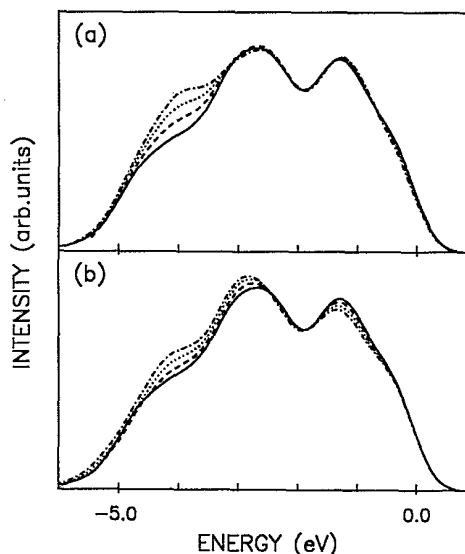


FIG. 6. Calculated x-ray photoemission when “doping” (a) the Cu(1) and (b) the Cu(2) sublattice with Zn. (Solid line $x=0$, dashed line $x=0.0333$, dotted line $x=0.0666$, dashed-dotted line $x=0.1$.)

the strong localization on the copper sites [mainly on Cu(1)] pushes the spectral weight of the DOS towards lower energies which in turn results in a decrease of ϵ_F .

In Figs. 5 and 6 the theoretical Cu- L_3 XES and XPS (Al- K_α line) spectra are displayed for different values of x . As can be seen from Fig. 5, XES is more sensitive to Zn substitution in the planes than in the chains. Figure 6 implies that even for small concentrations of Zn the XPS is sensitive on the energetic position of Zn states. The corresponding shoulder, however, is probably too insensitive to distinguish between the two types of alloy formation.

IV. DISCUSSION

Despite the enormous interest of experimentalists towards substitutions in superconducting ceramics very little theoretical work has been published in this field—in particular, concerning the Zn substitution. In Ref. 18 one or the other copper sublattices is replaced by the corresponding Zn sublattice and therefore no information is provided about effects of disorder.

The variation of $n(\epsilon_F)$ (or at least the amount of the effective charge carriers at ϵ_F) with respect to compositional disorder is usually strongly correlated with the variation of T_c . According to conventional explanations the dramatic suppression of T_c with increasing Zn content would imply also a rapidly decreasing $n(\epsilon_F)$. As can be seen from FLAPW calculations^{15,17} such rapid decrease can not be expected. Low-temperature specific-heat mea-

surements^{6,7} in fact report an increasing value of the linear coefficient of the specific heat (γ) in the superconducting state which indeed suggests an increasing value of $n(\epsilon_F)$. Our results for the variation of $n(\epsilon_F)$ with respect to the Zn content agree surprisingly well with the order of the observed variation for γ , namely from 5.6 mJ/Cu mol K^2 at $x=0.0$ to 10.6 mJ/Cu mol K^2 at $x=0.025$.⁷ The increasing effective number of carriers up to $x=0.05$ as deduced from Hall effect measurements at 120 K (Ref. 9) is also supported by our results. Pauli susceptibility measurements, however, predict a decreasing number of charge carriers similar to the non-stoichiometric system with increasing number of vacancies.⁴ Spectroscopical investigations for $YBa_2(Cu_{1-x}Zn_x)_3O_7$ have not yet been presented in the literature. Since our calculations of theoretical spectra show that in particular XPS seems to be sensitive with respect to substitution in very small concentrations, it would indeed be very desirable to see such experimental investigations in the near future.

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