

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

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Effects of Ni cation substitution on the copper sites are examined in the Y-Ba-Cu-O system in the concentration range $0 \leq x \leq 0.15$. The ferromagnetic and two types of antiferromagnetic substitution are considered for both copper sublattices. Pronounced differences between these types of "doping" in terms of partial densities of state (DOS), the Fermi level, and the DOS at the Fermi level are found only in the case when the Cu(1) sublattice is "doped." The calculated x-ray emission and x-ray photoemission spectra show distinct differences between chain or plane alloying; however, they are clearly too insensitive to provide information about the preferred type of the "magnetic arrangement."

I. INTRODUCTION

Similarly to Zn, Ni substitution up to $x=0.1$ content maintains the orthorhombic crystal structure of the Y-Ba-Cu-O system within small modifications of the a and b lattice parameters.¹⁻⁷ The reduction of T_C is linear with increasing Ni content and even at $x=0.15$ (at the concentration where the Zn or Fe "doped" systems are no more superconductors) T_C still is about 60 K. The preferential "doping" site is the Cu(2) (plane) site as determined by neutron diffraction⁵ but also as supported by Néel temperature measurements⁷ (at least in the antiferromagnetic state), by thermogravimetry experiments¹ and by Raman spectrometry.⁸ Differential anomalous x-ray scattering (DAS) investigations,⁹ however, indicate that at $x=0.1$ concentration Ni has a 40% fractional Cu(1) (chain) site occupancy. As far as the number n of effective charge carriers is concerned there is, as in the case of Zn substitution, disagreement between different experiments: Hall number measurements (at 100 K)¹⁰ report a rapid increase of n up to $x \approx 0.03$ from where n slowly decreases to a saturation value of about 1 hole/cell at high x (note that for the "undoped" case $n \approx 0.6$ hole/cell). Pauli susceptibility measurements⁷ on the contrary suggest that, in agreement with the decreasing conductivity, n decreases monotonically with increasing x . From the very moderate decrease of T_C with increasing Ni concentration a superconducting pair breaking effect of the local magnetic moments in the Cu-O planes seems to be rather unlikely.^{3,7,11,12} The variation of the oxygen content upon substitution also seems to be of little importance.¹³ It appears that a conventional scattering mechanism for the randomly distributed Ni atoms and on a higher "doping" level a two-dimensional localization is more favorable.^{7,13}

The present study of the electronic structure of $\text{YBa}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_7$ addresses the following questions: (i)

what is the main effect of a small number of magnetic impurities on the electronic structure in this complex system, (ii) whether different positioning of the spin-up and spin-down "doping" atom on the disordered sublattice results in apparent, possibly also spectroscopically detectable changes, and (iii) is it possible to draw conclusions on the superconducting mechanism, considering only the electronic structure.

II. THEORY AND COMPUTATIONAL DETAILS

In two previous papers^{14,15} we applied the real-space-scattering cluster coherent-potential approximation (RSSC-CPA) to the problem of nonstoichiometry and nonmagnetic Zn substitution in the Y-Ba-Cu-O system. A few theoretical and technical modifications are necessary when applying this method in the present context. A particular magnetic substitution is modeled by two different alloying potentials, namely, $V_{\text{Ni}(i)}^{\text{up}}(r;x)$ and $V_{\text{Ni}(i)}^{\text{down}}(r;x)$, for spin-up and spin-down states, respectively, where $i=1,2$ corresponds to the different copper sublattices. These potentials were constructed as described in Ref. 15 by assuming for the ionic charge densities of Ni a magnetic moment, $m=1.7 \mu_B$ which is approximately the experimental value for the Ni cation in NiO.^{16,17} It will be shown in the following that at least for Ni(2) (in plane) this is a very good assumption.

There are several possibilities to place the spin-up and spin-down Ni sites on one of the copper sublattices of the ordered system. In the ferromagnetic case (F) they occupy a subcell containing only one site, in the antiferromagnetic case (AF) a subcell comprising two sites. Possible types of AF arrangements are sketched in Fig. 1. These AF structures can be obtained quite naturally by doubling the unit cell of Y-Ba-Cu-O. All together four cases were considered with 13 (12) inequivalent sites per unit cell in the case of chain "doping" or 12 (11) inequivalent sites per unit cell in the case of plane "doping" for the

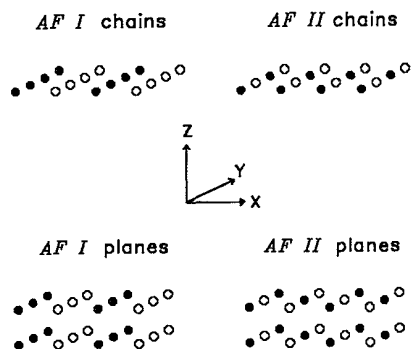


FIG. 1. Different arrangements of antiferromagnetic effective sublattices. Empty and solid circles denote sites alloyed by up-spin and down-spin nickel atoms, respectively.

AF I (AF II) types, respectively. We should emphasize that, since all of our investigations are for the *normal metallic* state, this type of notation (F, AF) *does not* label different *thermodynamical states* of the system but denotes merely different possibilities for the Ni “doping.”

For the AF cases our RSSC-CPA program was extended to solve the CPA condition [see Eq. (7) of Ref. 14] for two sites simultaneously, one referring to the spin-up to the other to the spin-down Ni potential. Technically this implies to solve the CPA condition for a diagonal block of doubled size. In the present calculations we chose the same cluster, namely, containing 99 sites as in Ref. 15. All calculations have been performed along the real energy axis. In order to calculate the integrated DOS sufficiently accurate an inequidistant energy scale of more than 200 points was used. The accuracy of the cluster local DOS's with respect to the FLAPW muffin-tin projected DOS's has been discussed in Ref. 14 and partially also in Ref. 15.

III. RESULTS

In order to see what primary effect is caused by the exchange splitting we also performed calculations alloying with Ni potentials corresponding to the zero magnetic moment. This case will be referred to as the paramagnetic (P) case. The *d*-like partial local density of states (PDOS) for the Ni(1) and Ni(2) sites are presented for $x=0.1$ in Figs. 2 and 3, respectively. The Ni states show a rather large dispersion in the valence band. Apparently, a large contribution of these states is found close to the Fermi level, i.e., in an energy regime related to the antibonding part of covalent σ bonding between Ni *d*-like and O *p*-like states (as interpreted from their Cu-O counterparts by the FLAPW calculations for the ordered system^{18,19}). The exchange splitting of about 1.5 eV pushes the spin-up states toward lower energies. These states show similar features as the corresponding copper states. The spin-down states of Ni(2) are localized mainly around the Fermi level, those of Ni(1) beyond the Fermi level. The Ni(1) spin-down states are therefore filled only partially ($\sim 65\%$), which in turn gives rise to the higher magnetic moment for Ni(1) (see Table I). As can be seen

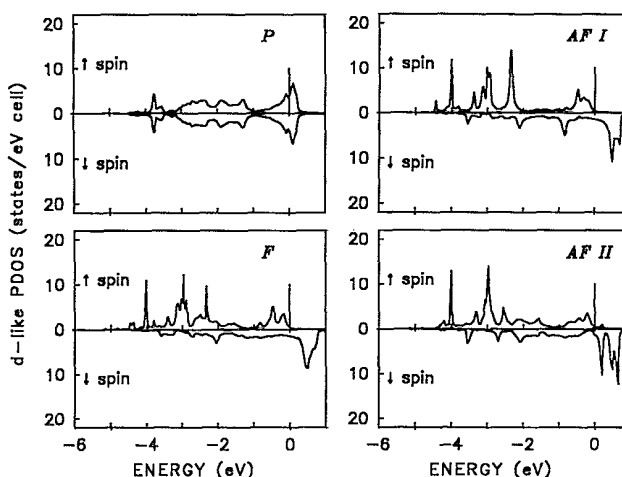


FIG. 2. Partial local *d*-like DOS's of Ni in $\text{YBa}_2(\text{Cu}_{0.9}\text{Ni}_{0.1})_3\text{O}_7$ when the Cu(1) (chain) sublattice is disordered. The different sheets refer to different “doping” cases (P: paramagnetic, F: ferromagnetic, AF: antiferromagnetic). The zero of the energy scale corresponds to the FLAPW Fermi level (Ref. 18).

in Fig. 3, the Ni(2) PDOS shows only moderate changes upon the ferromagnetic or antiferromagnetic types of “doping,” indicating that in this case correlations between spin states are in fact negligible. From Fig. 4 it is obvious that the large peaks in the Ni(1) spin-down *d*-like PDOS at about 0.5 eV above the (FLAPW) Fermi level are derived from hybridization with the O(4) [and partially O(1)] *p*-like states, whereas the spin-up states show no back-scattering in this region. In the AF II case—when spin-up and spin-down nickel atoms alternate within one chain—an additional back-scattering effect happens: Ni spin states are interplaying through the O(1) sites, giving rise to the peak at 0.2 eV above the Fermi level of the or-

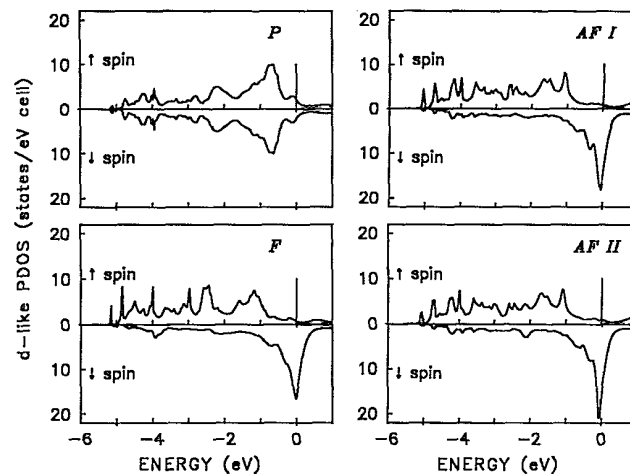


FIG. 3. Partial local *d*-like DOS's of Ni in $\text{YBa}_2(\text{Cu}_{0.9}\text{Ni}_{0.1})_3\text{O}_7$ when the Cu(2) (plane) sublattice is disordered. The different sheets refer to different “doping” cases (P: paramagnetic, F: ferromagnetic, AF: antiferromagnetic). The zero of the energy scale corresponds to the FLAPW Fermi level (Ref. 18).

TABLE I. Variation of the Fermi level, $\Delta\varepsilon_F$ (eV) and the DOS at ε_F , $\Delta n(\varepsilon_F)$ (states/eV cell) with respect to the ordered system and the magnetic moment, m (units of μ_B) of Ni per corresponding subcell in $\text{YBa}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_7$ for the different "doping" cases.

"Doping"	x	$\Delta\varepsilon_F$	$\Delta n(\varepsilon_F)$	m
Ni(1)	0.05	0.079	-1.256	3.68
	0.10	0.168	-1.662	3.45
	0.15	0.270	-1.553	3.21
AF I	0.05	0.147	-1.398	3.54
	0.10	0.235	-1.346	3.37
	0.15	0.319	-0.908	3.24
AF II	0.05	0.118	-1.080	3.73
	0.10	0.185	0.047	3.32
	0.15	0.245	-0.504	2.98
Ni(2)	0.05	0.045	0.040	1.78
	0.10	0.051	0.783	1.78
	0.15	0.062	1.276	1.76
AF I	0.05	0.027	0.602	1.79
	0.10	0.037	1.427	1.77
	0.15	0.048	2.055	1.73
AF II	0.05	0.024	0.682	1.82
	0.10	0.036	1.437	1.75
	0.15	0.052	1.951	1.66

dered system. Although this situation could be changed due to self-consistency, it can be expected that the spins should be more correlated when nickel substitutes in chain than in plane.

In Table I the variation of the Fermi level, $\Delta\varepsilon_F$ and the variation of the DOS at ε_F , $\Delta n(\varepsilon_F)$ as related to the corresponding quantities of the ordered system are listed together with the Ni magnetic moment per corresponding subcell as a function of the concentration x for all investigated "doping" cases. Table I can be interpreted using a simple picture of bonding and antibonding. Substitution of nickel partially destroys covalent bonding between copper and oxygen atoms and new bonding is formed between nickel and oxygen sites. Spin-up nickel sites simply replace the broken copper—oxygen bonds, while—especially in the case of substitution in the chains—the antibonding states related to spin-down nickel and the oxygen atoms lie significantly higher in energy than those for the copper and the oxygen atoms. For F and AF I type "doping" in the chains therefore ε_F increases and $n(\varepsilon_F)$ decreases rapidly, while for AF II "doping" in the chains ε_F passes through the sharp peak at 0.2 eV with a corresponding maximum for $n(\varepsilon_F)$ at $x=0.10$. When substituting in the planes ε_F remains approximately constant for all considered cases with a steady increase of $n(\varepsilon_F)$.

The variation in the theoretical Cu L_3 XES and XPS

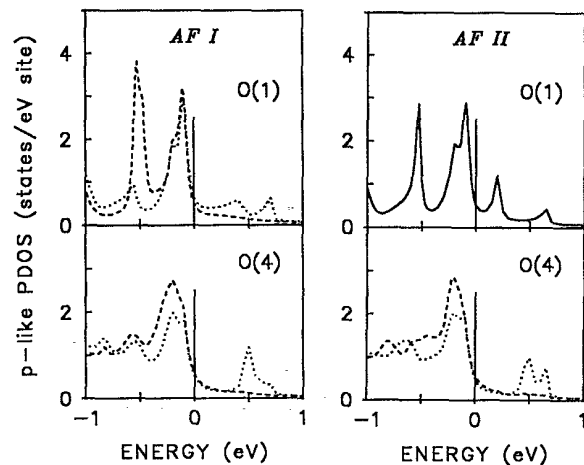


FIG. 4. Partial local p -like DOS's of the O(1) and the O(4) sublattice in $\text{YBa}_2(\text{Cu}_{0.9}\text{Ni}_{0.1})_3\text{O}_7$ in the vicinity of the Fermi level for the two different antiferromagnetic types of "doping" when the Cu(1) sublattice is alloyed. For AF I "doping" there are two inequivalent O(1) sites, namely, those in the chains alloyed by up-spin nickel ions (dashed line) and those by down-spin nickel ions (dotted line). For the AF II case all O(1) sites are equivalent (solid line). For both antiferromagnetic arrangements there are two inequivalent O(4) sites.

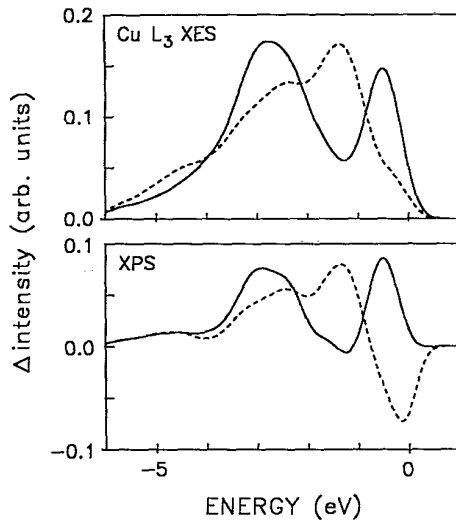


FIG. 5. Differences of the calculated Cu L_3 x-ray emission (upper sheet) and the Al $K\alpha$ x-ray photoemission (lower sheet) spectra with respect to the ordered system [$\Delta i = (i_{\text{ordered}} - i_{\text{disordered}}) / i_{\text{ordered}}^{\text{max}}$] for $\text{YBa}_2(\text{Cu}_{0.85}\text{Ni}_{0.15})_3\text{O}_7$, when "doping" the Cu(1) (solid line) or the Cu(2) (dashed line) sublattice with Ni.

(Al $K\alpha$ line) spectra, displayed in Fig. 5 for $x=0.15$ as corresponding differences relative to the ordered system, show mainly the effects of the reduced copper contribution. Direct nickel related contributions can be seen only in the XPS when nickel substitutes in the plane: the large contribution below ϵ_F is derived from the nickel spin-down d -like PDOS. However, the theoretical spectra are completely insensitive with respect to the different types "magnetic arrangements" (see also Fig. 1).

IV. CONCLUSIONS

The spin moments of "doped" Ni atoms create a weakly correlated spin lattice especially on the Cu(2) sublattice. Fairly important modifications in the electronic structure have been found close to the Fermi level due to the hybridization between Ni d -like and O p -like states. In partial agreement with available Hall number data, this gives rise to an increase of $n(\epsilon_F)$ with increasing Ni content when the Cu(2) sublattice is "doped." However, "doping" the Cu(1) sublattice results in a decreasing $n(\epsilon_F)$.

As compared to the chains, modifications (non-stoichiometry or substitutions) of the Cu-O planes in the Y-Ba-C-O system have minor influence on the electronic structure (see, also, Refs. 14 and 15). In general this can be interpreted in terms of the rather delocalized states related to the Cu(2)-O(2)-O(3) (planar) complex and the more localized states related to the Cu(1)-O(1)-O(4) (ribbonlike) complex near to ϵ_F and by the dominant contribution to $n(\epsilon_F)$ associated with the chains.¹⁸⁻²⁰ This is correlated to the fact that, as recorded in a large number of experiments for different substituting (magnetic or nonmagnetic) elements, modifications in the chains are more effective in suppressing the superconductivity in Y-Ba-Cu-O. Impurity magnetic moment formation, however, seems to have little importance for T_C .

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