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Magnetism and electronic structure in $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$

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The influence of oxygen content and magnetic ordering on the electronic structure in $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ is examined. The main difference is the presence in the superconductor, 1:2:3 O_7, of π states on O(2) atoms (in the Ba planes), which are possible carriers of the holes needed for superconductivity. They may also be responsible for the absence of antiferromagnetic ordering in the Cu(2)-O(3,4) planes. The calculated magnetic susceptibility in 1:2:3 O_7 is in satisfactory agreement with experiment. The present calculations show that, for antiferromagnetic ordering of the copper magnetic moments in the Cu(2)-O plane and between the planes, a Slater gap opens in the neighborhood of the Fermi energy, and 1:2:3 O_6 becomes semiconducting. The Cu(1) sites in both systems are not likely to form substantial local magnetic moments and thus probably are not directly involved in the mechanism for superconductivity. The possibility of an anharmonic effect due to magnetic interaction is discussed.

I. INTRODUCTION

The recent discovery[1,2] of superconductors with critical temperatures, T_c, far above those previously considered possible for superconductivity has prompted much interest in the physical properties of these systems. Since many of the proposed mechanisms[3] are based on magnetic interactions between the copper atoms, the magnetic nature of these systems is of interest.

Investigation of possible magnetic phenomena is complicated as it is now known that the local-spin-density-(LSD) functional approach does not account for spontaneous magnetic ordering in these compounds and that non-spin-polarized calculations predict metallic properties for the related insulators.[4] The other approach, from the strong-correlation limit such as the Mott-Hubbard model, leads to an insulating state that is not due to antiferromagnetic (AFM) ordering but rather to strong onsite correlations which are much larger than the bandwidth so that an energy gap is created between spin-up and spin-down electrons.[5] This is in contradiction to another point of view where insulating behavior is due to AFM ordering.[5,6] In previous work[6] we demonstrated that, by performing forced antiferromagnetic ordering calculations for a half-filled band, an AFM "Peierls-type gap" or, the more commonly called, Slater gap,[7] opens up at the Fermi energy due to the doubling of the unit cell. We called[6] the gap a "Peierls gap" as the effect of meta-AFM ordering on the electronic structure is analogous to the Peierls lattice distortion effect. As soon as the gap opens in the iterative process, the density of states close to the gap boundary rises due to flattening of the bands, and the energy lowers. As a result, the external splitting can be removed and the antiferromagnetic ordering becomes stable. Thus, in this case, the insulating state can be obtained in the LSD approximation provided an antiferromagnetic phase can be created.

The consequences of the sharpening of the density of states around the gap for superconductivity should be noted. The sharp peak below the Fermi energy in the density of states for 1:2:3 O_6 has been experimentally observed as well as its disappearance with increasing oxygen content.[8] The gap produced at the Fermi energy is small (~ 0.1 eV) due to a low value of the local moment on the Cu2 sites ($\sim 0.3\mu_B$). The gap calculated within the LSDF approximation cannot be compared with the experimental one because one should take into account an explicit correction[9] due to a discontinuity in the functional derivative of the exchange-correlation energy with respect to density at the gap. It is quite essential to find out what one would obtain in the pure LSD theory before trying to introduce any of the possible corrections to it. This is not an easy task since the expected gap in the bare LSD electronic structure in cuprates is of the order of accuracy of the calculations (0.1 eV). The difficulties of reproducing narrow gaps in numerical calculations has been demonstrated with the analytical example of a hypothetical one-dimensional structure. It has been shown that, unless a large number of terms in the Fourier expansion (10^5) were taken into account, the expected gap in the density of states would not occur.[10] It is interesting that, in numerical calculations for La_2CuO_4 with a plane-wave basis set, it was found that only for a large number (15 625) of plane waves was a gap created.[11]

Since we neglect the spin-orbit interaction, the absolute direction of the moment is not defined. For the half-filled band with a proper nesting at the Fermi surface, the material stays insulating as long as there is antiferromagnetic coupling between spins of copper atoms. Variation of the band filling due to doping lowers the Fermi energy and so, as soon as the metallic state is approached, the local magnetic moment disappears. This stabilization of the magnetic ordering due to the existence of the gap at the Fermi energy explains the strong sensitivity of the magnetic moment to doping which would not be true for spontaneous antiferromagnetism.

At this point it is useful to recall the analogy between the influence of lattice distortion and magnetic ordering on the electronic structure.[6] If one takes this analogy further one can conclude that a double-well potential would be created due to local magnetic oscillations which, in turn, may lead to an increase of the effective electron-electron interaction.[12] It has been shown[12] that ω_s, the frequency for quasilocal excitations in a double-well potential, is smaller than ω_D, the characteristic phonon frequency. The following estimate has been obtained[12] for the ratio of the effective electron-electron interaction induced by a two-level system (λ_s) and phonons

$$\lambda_s/\lambda_{\text{ph}} \approx \omega_D/\omega_s^2 \ . \tag{1}$$

In the double-well potential model it is easy to obtain T_c around 100 K, which was predicted before high-T_c superconductors were discovered.[12] It also explains why T_c is actually of the order of 100 K and not 1000 K, as would be expected from simple magnetic interaction pairing. Sensitivity of the effective λ and T_c to the shape of the double-well potential has been discussed recently.[13]

In the present paper we will discuss the important differences in the electronic structure between these two related compounds, one of which is superconducting 1:2:3 O_7 and the other is semiconducting 1:2:3 O_6.

II. LMTO-ASA STUDIES OF MAGNETISM

The LMTO-ASA (linear-muffin-tin-orbital atomic-sphere-approximation) method has been used successfully in explaining electronic and magnetic properties of metals and their alloys.[14] For example, the calculated moment in metallic nickel[15] was in agreement with experiment to within $0.01\mu_B$. It was also predicted that nickel loses magnetic moment during hydrogenation. For the new high-T_c oxides, less approximate methods such as the highly precise full-potential linearized augmented-plane-wave method[16] (FLAPW) should reveal the details of the electronic and magnetic structure better, but the important features in these compounds can be obtained by LMTO-ASA and similar methods with much less computer time required for the computations. The LMTO-ASA method is much faster than most other methods and thus permits the use of a larger number of k points in the Brillouin zone which is essential[6] for magnetic studies in these compounds.

In Fig. 1 we show that present band-structure results in which antiferromagnetic ordering was assumed between the copper-oxide planes in contrast to our previous calculations[6] where ferromagnetic coupling between those planes was assumed. In the present calculations we used the Vosko-Wilk-Nusair[17] exchange-correlation potential which leads to essentially the same results as the von Barth–Hedin[18] potential previously employed, except that convergence is faster. The wave functions were expanded up to $l=2$ (d electrons) for all atoms except oxygen [up to $l=1$ (p electrons)]. Empty spheres (no orbitals were assumed in the empty spheres except from overlapping spheres) were positioned at the oxygen vacancies: one empty sphere per unit cell in 1:2:3 O_7 and two in 1:2:3 O_6 and one additional empty sphere in the yttrium plane.[19] In the self-consistent process, a small mixing parameter of 5% has been used. To obtain convergence within one panel and the minimal basis set approximation (this approximation has been successfully used for electronic structure calculations of transition metals[14]), we had to assume a large value for E_ν (in our case, E_ν is at the center of the band and not at the center of the occupied portion) for p electrons of Y ($5p$) and Ba ($6p$), and s electrons of O ($3s$), around which the expansion is performed, in order to avoid ghost bands, which can be created, for example, by picking up contributions from both $5p$ and $6p$ electrons of Y in the same band.[14]

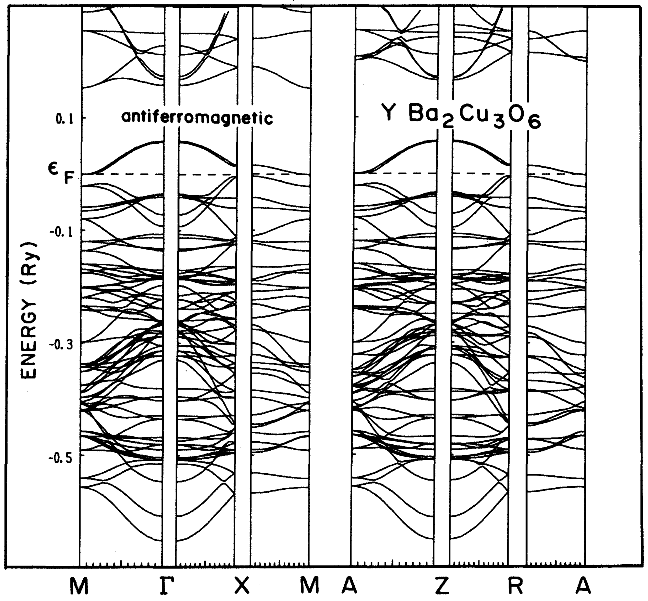

FIG. 1. The calculated band structure for antiferromagnetic 1:2:3 O_6 along the indicated symmetry points in the Brillouin zone [$\gamma=(0,0,0)$, $X=(\pi/a,0,0)$, $M=(\pi/a,\pi/a,0)$, $Z=(0,0,2\pi/c)$, $R=(\pi/a,0,2\pi/c)$, $A=(\pi/a,\pi/a,2\pi/c)$].

It is important to mention that, for these materials, which have very nonuniform charge densities and vacancies, the details around the Fermi energy might be sensitive to approximations, such as the values of the atomic sphere radii (influences the Madelung energy contribution), E_ν values (changes the initial hybridization), etc. We find that, in the LMTO-ASA approximation, the initially chosen E_ν values for p electrons of yttrium can change the unoccupied band position by several eV. This is probably the reason why the position of the unoccupied bands in an earlier LMTO-ASA calculation[20(a)] is much lower than in our LMTO-ASA and in highly precise FLAPW calculations.[21] In later work by these authors,[20(b)] the position of the unoccupied bands above the p-$d\sigma$ antibonding band agrees with our calculations. In their spin-polarized calculations there is again an unoccupied band crossing the top of the p-$d\sigma$ antibonding band.[20(b)] It is possible that too low a position of the unoccupied bands might suppress the gap at the Fermi energy. Expansion about the center of the band should give a better description around the Fermi energy for a half-filled band than expansion around the center of the occupied portion. It has been suggested[20(b)] that an increase of the angular-momentum expansion on either oxygen or copper might suppress the moment. Unfortunately, we are about at the limit of our available computer memory and cannot investigate this conjecture. However, this suggestion is very tempting since it might explain why, in the FLAPW calculations in which very large l values are used, not even a semimetallic state could be obtained for this compound.[22] Combined corrections in the LMTO-ASA method might indirectly introduce corrections for higher l values but they were neglected in these calculations.

The electronic structure around the Fermi energy for these high-T_c superconductors can be well described in the tight-binding scheme with consideration of only p electrons of oxygen and d electrons of copper. It has been demonstrated[23] in this model that the (110) nesting (required for stability of antiferromagnetic ordering) is only present when second-nearest-neighbor interactions are neglected. When they are included there is (100) and (010) nesting which is obtained in band-structure calculations for most high-T_c superconductors.[23] Thus, the experimentally observed nonmetallic state with antiferromagnetic ordering[24] cannot be obtained in a tight-binding scheme (equivalent to the LMTO-ASA approximation[14]) when parameterization from self-consistent LSDF calculations is used due to overestimation of overlapping parameters. This indicates that an insulating antiferromagnetic state cannot be created only by artificially increasing the exchange-correlation potential, but that corrections leading to the reduction of overlapping integrals and the proper nesting of the Fermi surface are necessary as well.

In our calculation we obtained an almost spherical Fermi surface for paramagnetic 1:2:3 O_6. It is interesting that, in another related compound $CaCuO_2$, we could not obtain stable magnetic ordering even by forcing it with very high external fields. This is in agreement with the detailed study of this compound by Singh *et al.*[25] These authors[25] found that the Fermi surface does not have any nesting feature that would favor antiferromagnetic ordering even when applying an external field.

One way of creating antiferromagnetic ordering within the present LSD formalism is by application of large external antiferromagnetic fields. To demonstrate the influence of a magnetic field on the Fermi surface, we performed simplified tight-binding-model calculations for a square lattice following Ref. 23 and using the parameters $t_2=0$, $t_2/t_1=0.23$, $t_2/t_1=0.45$,[23] and $\varepsilon_0=0$:

$$\varepsilon(k)=-2t_1[\cos(k_x a)+\cos(k_y a)]+4t_2\cos(k_x a)\cos(k_y a) \ . \tag{2}$$

In the presence of an external field, the paramagnetic band splits, and we represent this effect using rigid-band splitting. In Fig. 2 we show the effect of the rigid-band splitting by $\Delta H=\pm 0.9t_1$ on square and spherical Fermi surfaces: one with $t_2=0$ [as mentioned above, a square Fermi surface with (110) nesting] and one with $t_2/t_1=0.26$ (for our calculations for 1:2:3 O_6). In addition, for $t_2/t_1=0.45$ (which is close to the observed Fermi surface in high-T_c materials),[23] we applied $\Delta H=0.7t_1$. The interesting result is that, after applying a ΔH splitting of the order of 0.1 Ry (t_1 of the order of 1.5 eV), one part of the Fermi-surface nesting vector rotates from the [100] direction towards the [110] direction. This part of the Fermi surface is the one which stabilizes the meta-antiferromagnetic solution.

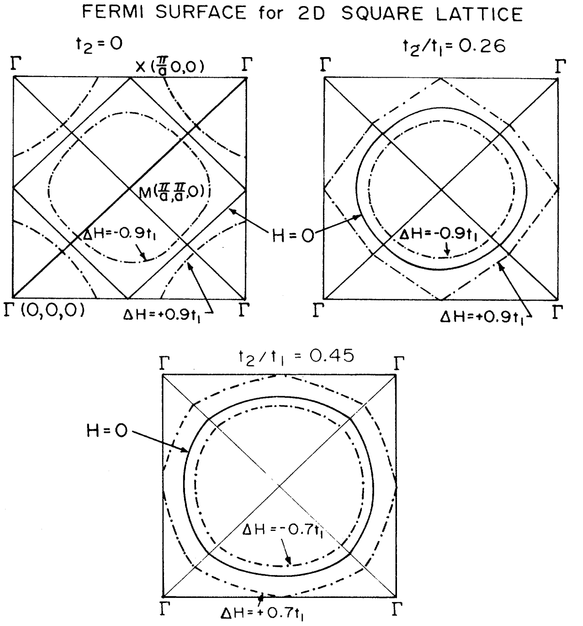

FIG. 2. The Fermi surface for the two-dimensional (2D) square lattice (Ref. 17) with different t_2/t_1 ratios as indicated (t_1 nearest-neighbor hopping integral, t_2 next-nearest-neighbor hopping integral). The applied field rigid-band splitting as indicated.

In our calculations we apply this field (0.05 Ry–0.1 Ry) to all atoms with the restriction that the sign of the field was opposite on nearest-neighbor copper atoms. Hundreds of iterations (initially with small numbers of k points) have been performed until a gap opened up around the Fermi energy. Then the external field has been removed and further iterations have been performed with a large number of k points and low mixing (5%) of the new with the previous charge density. There is an evident analogy between our calculations and those previously performed for the metamagnetic[26] state in Pd. In both cases, a large number of k points were needed in order to eliminate artificial fluctuations at the Fermi energy. We used 108 k points in the irreducible wedge of the Brillouin zone.

At this point, a comment about the sensitivity of antiferromagnetic solutions to the number of k points employed is in order. According to Guo *et al.*,[27] the moment for the antiferromagnetic solution is La_2CuO_4 decreases smoothly for increasing number of k points and the opposite behavior is found for La_2NiO_4 where the moment is present only for more than 105 k points.[27] In later work they claim[20(b)] that their results agree with ours for 1:2:3 O_6 only when a small number of k points (30) is used. We do not find for 1:2:3 O_6 a smooth dependence of the value of the moment on the number of k points. The value varies quite randomly from higher to lower values for small numbers of k points and becomes relatively stable for 108 and more k points where, for example, there is essentially no difference ($<0.01\mu_B$) between our calculations with 108 and 135 k points. The magnetic moment for the antiferromagnetic solution is more sensitive to the number of k points than for the ferromagnetic solution. This is mainly due to interpolation errors for spin-up and -down electrons which, in the antiferromagnetic case, do not subtract as in the ferromagnetic case where the spin-up and -down electron density of states are almost rigidly shifted and the detailed features of the density of states are not important. The sharpening of the density of states around the gap boundary demonstrates the sensitivity of the results to the number of k points employed. We should, however, point out that our solution for 1:2:3 O_6 is consistent with the other LMTO-ASA calculations,[20(b),27] where it was demonstrated that the LMTO-ASA method can lead to a semimetallic solution in contrast to the FLAPW (in principle, a more accurate method) calculations where such solutions have not yet been obtained.

In Table I we present our results from the present calculations for the charge distribution. We use the notation of Kamaras *et al.*[28] for the atomic positions. The calculated moment of the Cu2 sites is equal to $0.31\mu_B$, which is lower than obtained experimentally[24] (about $0.5\mu_B$). As noted by Slater,[29] the exchange potential is dependent on the momentum and energy of the electrons, while the Kohn-Sham exchange potential used in the LSD approximation (for electrons at the top of the Fermi surface) is $\frac{2}{3}$ of the Slater potential (which is averaged over the Fermi distribution). Because of this we also performed calculations with a factor 1.5 introduced in the exchange part of the exchange-correlation potential. The moment increased to $0.41\mu_B$ with almost the same shape of the band structure and the same value ($\sim$0.1 eV) of the band gap. This indicates that a simple rescaling of the exchange-correlation potential is not sufficient to describe the magnetic properties and the band gap in these compounds.

The calculated value of I_{Stoner} (Ref. 30) ($I=\Delta/M$, where Δ is the band splitting due to magnetic ordering and M is the local magnetic moment) from Table I yields, for fivefold degenerate d electrons, a U value equal to 5.3 eV. The valence electron distribution presented in Table I is dependent on the assumed atomic sphere radii, but the predominantly p and d character of the band electrons is not affected. The presented values of intrinsic band mass enhancement (m^*/m) (Ref. 14) for d electrons of copper and p electrons of oxygen are much larger than one because of the two-dimensionality (reduction of the overlap in the z direction) of this compound which causes narrowing of the band and its seen as the effective-mass enhancement.

In Figs. 3 and 4 the local density of states of d electrons for 1:2:3 O_6 is show for Cu2 and Cu1 sites, respectively. It is easy to understand why no magnetic moment

TABLE I. The calculated contributions for the antiferromagnetic solution to the spin moment (μ_B), charge distribution (E), I_{Stoner} parameter (Ry), and intrinsic band mass enhancement ratio (m^*/m) for the semiconductor 1:2:3 O_6.

Atom	Quantity	Electron type		Calculated values on different sites	
	Site		Two (up)		Two (down)
Copper	Spin moment	s	−0.004		0.004
		p	−0.003		0.003
		d	0.313		−0.313
	I_{Stoner}	d	0.078		0.078
	Site		One	Two (up)	Two (down)
Copper	Charge	s	0.604	0.340	0.340
		p	0.444	0.511	0.511
		d	9.600	9.365	9.367
Copper	m^*/m	$s\uparrow$	0.798	0.813	0.812
		$s\downarrow$	0.798	0.812	0.814
		$p\uparrow$	0.934	0.951	0.949
		$p\downarrow$	0.934	0.949	0.951
		$d\uparrow$	12.351	13.776	13.413
		$d\downarrow$	12.351	13.412	13.778
	Site		Two		Three, four
Oxygen	Charge	p	4.550		4.514
Oxygen	m^*/m	$p\uparrow$	3.368		3.371
		$p\downarrow$	3.368		3.370

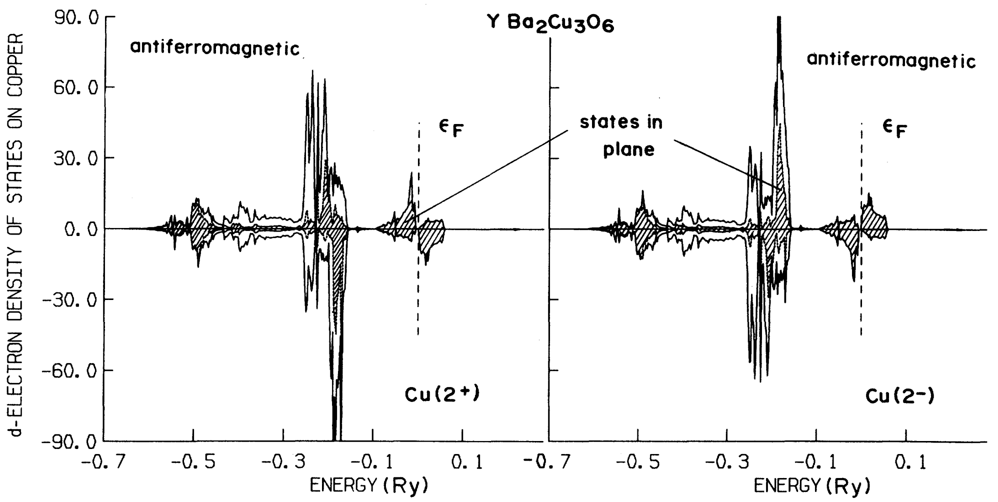

FIG. 3. The calculated, local density of states for 1:2:3 O_6 for antiferromagnetic ordering on the Cu2 sites for Cu2 atoms with moment up and down, respectively. The shaded area represents in-plane states, i.e., states projected onto the Cu2-O plane.

is present on Cu1 sites since almost all (except some 1 eV above the Fermi energy) Cu1 states fall below the Fermi energy due to strong localization effects for the assumed idealized structure with the absence of oxygen atoms in the Cu1 layer.

The moment on Cu2 sites is quite well localized as can be seen in Fig. 5 with the maximum of the spherical spin density at 0.56 a.u. We find some sensitivity of the moment to the atomic radii employed. This is due to the tails of the muffin-tin orbitals. We cannot judge the stability of the antiferromagnetic solution based on calculated total energies in the nonmagnetic and antiferromagnetic states as they are the same within the accuracy of our calculations. It has been shown by Freeman *et al.*[31] and independently by us[32] that spontaneous magnetic ordering is possible for isolated copper-oxygen planes. For the full structure of 1:2:3 O_6, the Stoner criterion[30] $[I\rho(\varepsilon_F)\geq 1$, where $\rho(\varepsilon_F)$ is the density of states at the Fermi energy per spin and I is the Stoner parameter defined above] is not fulfilled and there is only a stable "metamagnetic" type of antiferromagnetic solution.

In addition, we have performed calculations for *forced* ferromagnetism of an idealized structure of 1:2:3 O_7 (Ref. 28) where 100% occupancy of oxygen in the O1 site of the chain was assumed. In that case, a small moment appeared on the Cu1 sites. The absolute value of the mo-

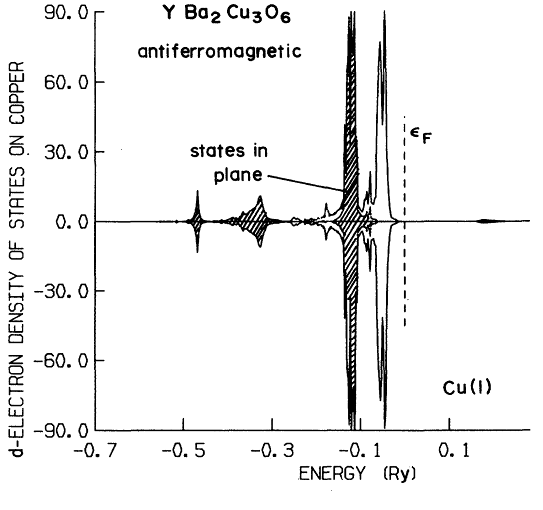

FIG. 4. The local density of states of spin-up and spin-down d electrons on Cu1 sites in 1:2:3 O_6. The shaded area represents in-plane states, i.e., states projected onto the Cu2-O plane.

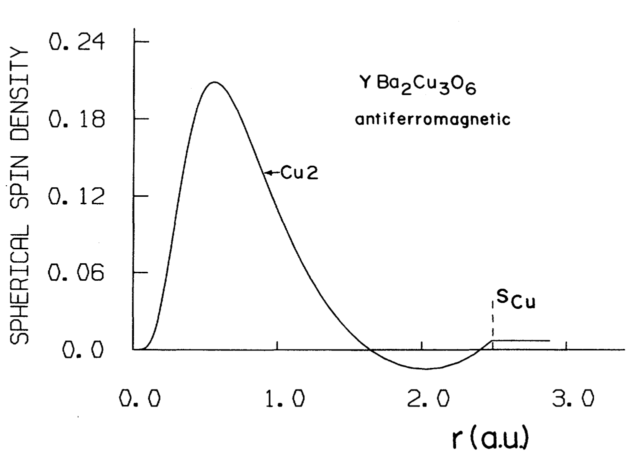

FIG. 5. Spherical spin density on the Cu2 atom in AFM 1:2:3 O_6 as a function of radial distance r.

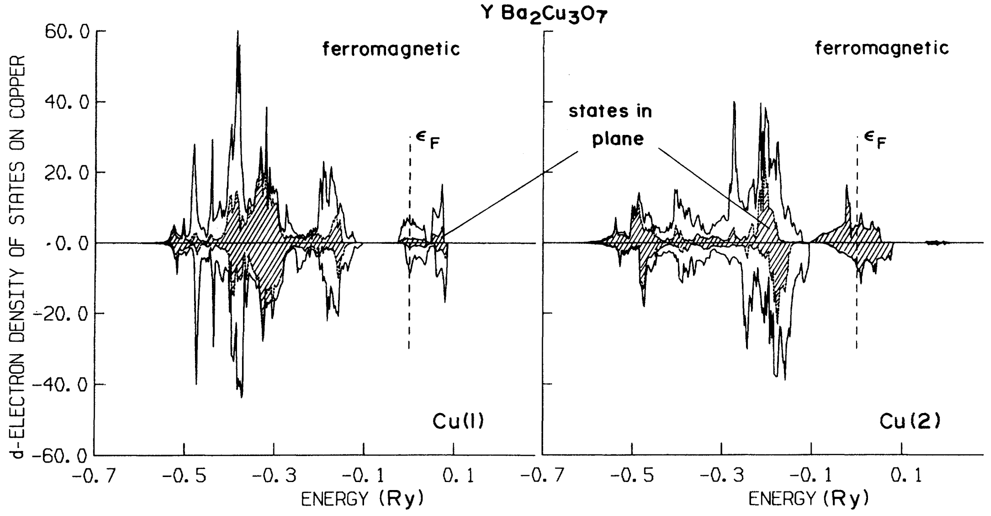

FIG. 6. The local density of states of spin-up and spin-down d electrons for *forced* ferromagnetic 1:2:3 O_7 on Cu1 and Cu2 sites. The shaded area represents in-plane states, i.e., states projected onto the Cu2-O plane.

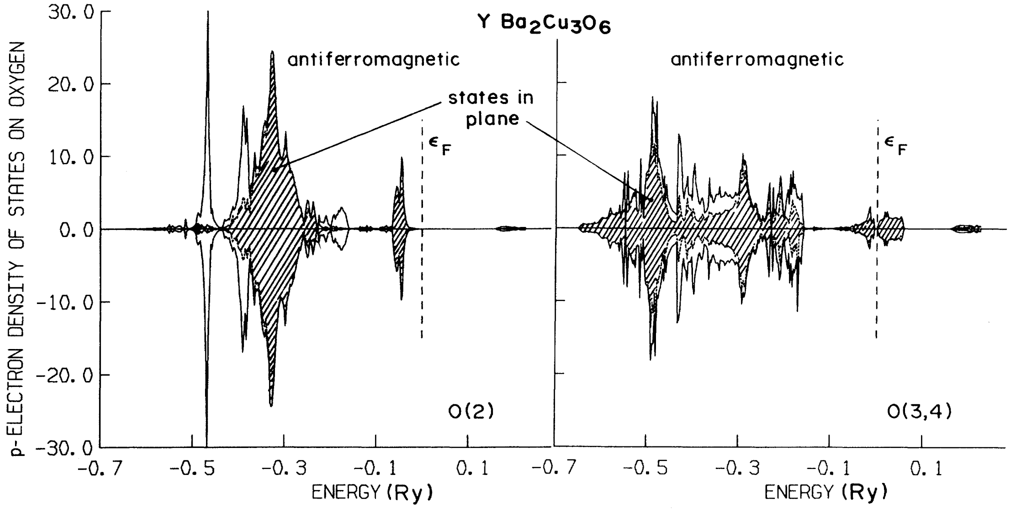

FIG. 7. The local density of states of spin-up and spin-down p electrons for antiferromagnetic 1:2:3 O_6 on O2 and O3, O4 sites. The shaded area represents in-plane states, i.e., states projected onto the a-b plane.

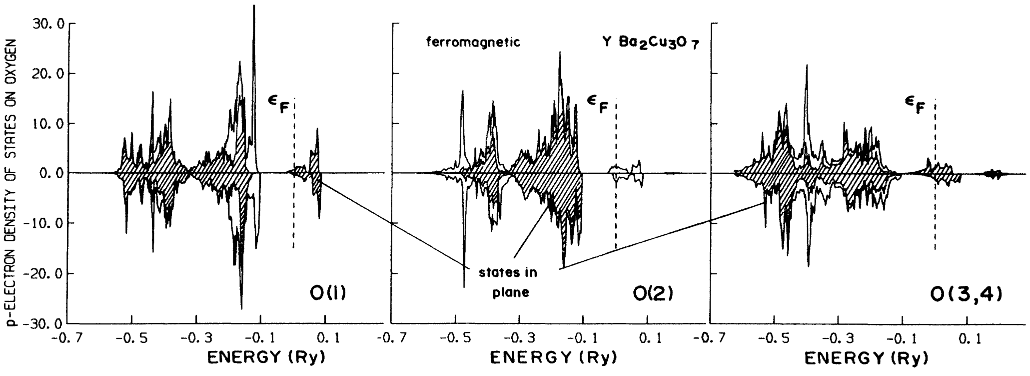

FIG. 8. The local density of states of spin-up and spin-down p electrons for *forced* ferromagnetic 1:2:3 O_7 on O1, O2, and O3, O4 sites.

ment is irrelevant as it is dependent on the value of the external field and all moments disappear when the field is removed (please notice that, in our earlier paper, we also did not mention the value of the moment in the presented *forced* ferromagnetic solution[6] and it should not be interpreted as a *stable* ferromagnetic solution[22]). However, it is interesting that the moment on the Cu1 sites was more than four times smaller than the moment on the Cu2 sites. In a recent paper,[33] neutron-diffraction measurements show that, in 1:2:3 O_{6+y}, there is a phase present with a small moment $0.012\pm0.007\mu_B$ on the Cu1 sites. On the basis of our results, we suggest that the phase with the moment on the Cu1 sites must have more oxygen present in the Cu1 layer than the phase which is nonmagnetic.

We also calculated the unenhanced Pauli susceptibility $[\chi=\mu_B^2\rho(\varepsilon_F)]$ at the magnetic field strength (35 kG) corresponding to thermal fluctuations at the Néel temperature (0.0015 Ry) and obtained $\chi=3.6\times10^{-5}$ cm^3/g Cu(2) atom, 4.1×10^{-5} cm^3/g Cu (1) atom, and 3.77×10^{-5} cm^3/g Cu atom. These results are in agreement with the value which we calculated from the results of Massida *et al.* $[\rho(\varepsilon_f)=1.13$ states/eV per Cu atom];[34] $\chi=3.65\times10^{-5}$ cm^3/g Cu atom. The corresponding susceptibility per g of material measured experimentally[35] is $\chi=2\times10^{-7}$ cm^3/g, which is slightly lower than our value $\chi=2.5\times10^{-7}$ cm^3/g. We also calculated the maximal susceptibility: $\chi_m=\Delta m/\Delta H$, which is $\chi_m=10\times10^{-5}$ cm^3/g Cu (1) atom and $\chi_m=43\times10^{-5}$ cm^3/g Cu(2) atom.

In Fig. 6 we present the calculated *d*-electron density of states for Cu1 and Cu2 sites in 1:2:3 O_7. The feature which appears is a small contribution of *d*-electron states of Cu1 atoms in the *a*-*b* plane and perpendicular to the plane (along the *c* axis) at the Fermi energy. Of particular interest is the effect of the occupancy of the O1 oxygen on the bonding. In Figs. 7 and 8 we compare the variation in the population of states around the Fermi energy due to the *p* electrons of oxygen. The appearance of out-of-plane (*a*-*b*) states of O2 atoms at the Fermi energy for 1:2:3 O_7 is important and explains the experimentally observed[36] sensitivity of T_c to the variation of the Cu1-O2 bond length in the *c* direction [note in Ref. 30, O2 is designated as O(4)]. These O2 states are probably responsible for creating the magnetic instabilities in 1:2:3 O_7, which are essential for superconductivity. They might also carry holes as they are weakly bonded. We cannot rule out the possibility of supercurrents due to holes on π electrons of O2 atoms. The Cu2-O(3,4) planes might be the source of attraction for holes (electrons) due to spin or charge fluctuations.

In Fig. 9 we present the spherically averaged spin density for *forced* ferromagnetic ordering in 1:2:3 O_7. It is most interesting that the spin density on the Cu2 site (Fig. 9) remains almost the same as for antiferromagnetic ordering (Fig. 5) with the values slightly higher due to the applied field. It is tempting to suggest that, in the superconducting phase where no static moment is present, an oscillating moment would exist. The tail spin polarization on the O(3,4) sites should be noted as well as the small contribution from the Cu1 site.

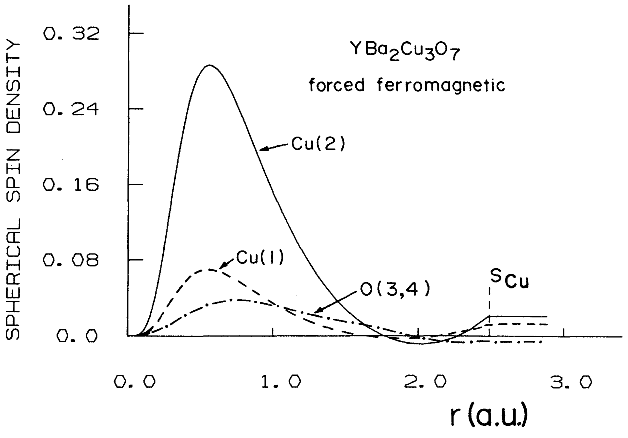

FIG. 9. The spherical spin density per corresponding atom as noted for *forced* ferromagnetic ordering in 1:2:3 O_7.

III. SUMMARY

We have performed a detailed analysis of the electronic interactions in these two compounds (1:2:3 O_6 and 1:2:3 O_7) with a focus on directional dependences. It is interesting that it has been argued that the observed plateau in T_c at 60 K between $y=0.55$ and 0.63 in 1:2:3 O_{6+y} can be explained with the coexistence of these two phases.[37]

The possible magnetic instabilities in correlation with oxygen content have been analyzed. We performed calculations for antiferromagnetically ordered copper-oxygen planes for 1:2:3 O_6 and showed that a "metamagnetic solution" is possible as in our previous calculations[6] and that it leads to an insulating state but with too small a gap at the Fermi energy. The smallnesses of the gap is characteristic of the LSD method.[8]

The calculated magnetic susceptibility in 1:2:3 O_7 is in good agreement with experimental measurements.[35]

Note added in proof. In addition, we performed LMTO-ASA calculations in the conventional way with expansion around the center of gravity of the band and spin polarizability introduced by variation of charge occupation for spin-up and spin-down electrons. The *p* electrons on yttrium and barium were downfolded.[38] We were unable to stabilize antiferromagnetic ordering. The moment disappears very rapidly even with a small mixing parameter, independent of the number of *k* points employed.

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