

ON THE VALIDITY OF THE BAND MODEL FOR HIGH T_c SUPERCONDUCTORS.

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INTRODUCTION

The discovery of high T_c superconductivity in cupric oxides has led, amongst other things, to numerous electronic bandstructure studies of these compounds. The foundation of these calculations is Density Functional Theory (DFT) and they are implemented with the Local Density Approximation (LDA) or Local Spin Density (LSD) approximation. In this article we will review what we have learned from these calculations regarding the electronic structure of the family of high T_c materials. To answer this we have to find out how relevant the LSD/LDA is for the electronic properties of cupric oxides. It is well known that the application of LDA DFT for transition metal oxides is fraught with difficulty and controversy (Anderson, 1987). Although the LDA describes the variation of the equilibrium volume through the 3d transition metal oxides, including the volume expansion associated with Mott insulators (Andersen *et al.*, 1979), the theory fails to describe FeO and CoO as antiferromagnetic insulators, and in the case of NiO and MnO where the LDA does yield an insulating ground state (Terakura *et al.*, 1984 a,b) the band gap is grossly underestimated. Evidently the high- T_c materials are systems that are on the verge of undergoing a Mott transition; consequently, it is necessary to be circumspect regarding the applicability of LDA DFT both in the metallic (superconducting) and magnetic insulating states.

ELECTRONIC STRUCTURE AND BONDING

The electronic groundstate, and hence the bonding, is described in our self-consistent-field (SCF) calculations by the Local Density Approximation to the Density Functional Theory. This has been an extremely successful theory of the bonding properties of solids (Andersen *et al.*, 1985). In Figure 1 we show the variation of the total electronic energy as a function of lattice constant. The calculated equilibrium volumes, in the tetragonal structure, are 188.9 Å for La_2CuO_4 and 181.9 Å for $\text{La}_3\text{SrCu}_2\text{O}_8$ (Stocks *et al.*, 1988). The arrows labelled A and B (see Figure 1) mark the corresponding experimentally determined equilibrium volumes (190.4 Å and 187.7 Å respectively). The differences between theory and experiment are 0.7 and 3.1% respectively. The change in volume upon addition of Sr is overestimated by a factor of 2.6. However, it should be stressed that the experimental volume change is small (1.4%).

In Figure 2 we plot for La_2CuO_4 the partial pressures associated with the different atomic species as a function of lattice spacing. Since the evaluation of the pressure is not as precise as that of the total energy, the equilibrium volume based on the point at which the total pressure vanishes is at a slightly different point than that obtained from the total energy curves. This notwithstanding the plot presents an interesting picture of the stability of the crystal, which is very similar to that found in the early transition metal oxides (Andersen *et al.*, 1979). The partial pressures resulting from oxygen and from copper are positive and the equilibrium is achieved by balancing them against the negative pressure associated with the lanthanum atoms. The oxygen and copper partial pressures are dominated by the 'p' and 'd' contributions respectively, while the lanthanum partial pressure comprises a large, essentially volume-independent 'df' contribution and a positive 'sp' contribution (for the sphere sizes chosen the Madelung contribution is small). In $\text{La}_3\text{SrCu}_2\text{O}_8$ the 'df' pressure is less negative than for lanthanum

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MASTER

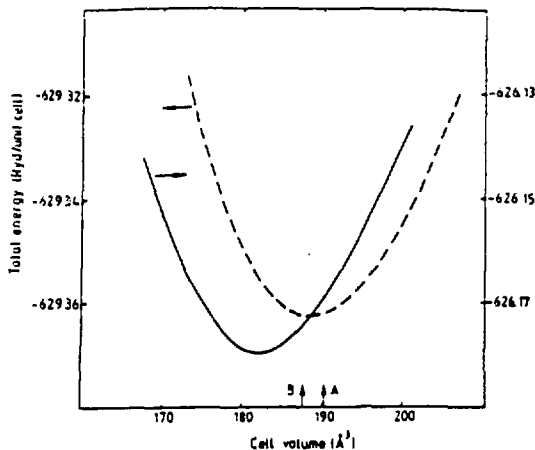


Fig. 1. The calculated volume dependence of the total energy of La_2CuO_4 (broken curve: left-hand scale) and $\text{La}_3\text{SrCu}_2\text{O}_8$ (full curve: right-hand scale). The arrows A and B give the experimentally measured equilibrium volumes of La_2CuO_4 and $\text{La}_{1.5}\text{Sr}_{0.5}\text{CuO}_4$ respectively.

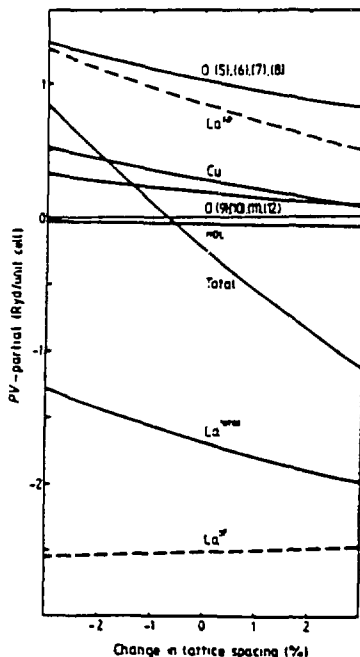


Fig. 2. Total and species decomposed partial pressures in La_2CuO_4 . The ordinate is in terms of the percentage deviation in the lattice spacing from $a=3.7817 \text{ \AA}$, which corresponds to a volume of 189.47 \AA^3 . The broken curves show the results of further decomposing the partial pressure associated with the La sites into 'sp' and 'df' angular momentum components. The curve marked MDL gives the Madelung contribution to the pressure (Andersen *et al*, 1979).

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However, this is more than compensated for by a reduction in the lanthanum 'sp' pressure and in the 'p' pressure of the oxygen at the octahedron apex closest to the plane of Sr atoms. These compensating effects produce the overall slight reduction in volume over that of La_2CuO_4 referred to previously. That the bonding is highly 3 dimensional can be inferred from Figure 3a where the experimental change in c/a as a function of pressure is plotted (Akhtar *et al.*, 1988). In Figure 3b we compare our calculated P-V curve with the measurements. The agreement is excellent. The calculated variation in volume follows experiment almost exactly, and with only a small (about 0.5%) difference between the absolute values of calculated and measured volumes. These results strongly support the quantitative reliability of LDA calculations for the bonding properties of high T_c materials.

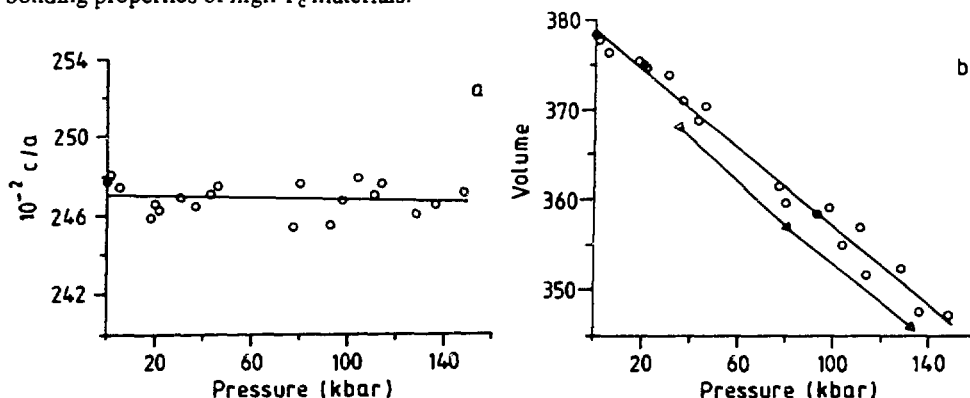


Fig. 3. The effect of pressure on La_2CuO_4 . (a) The effect of pressure on c/a . Open circles: experimental results; full line: fitted line. (b) The variation of volume with pressure. Open circles: experimental results; open triangles: theoretical results; full lines: fitted lines.

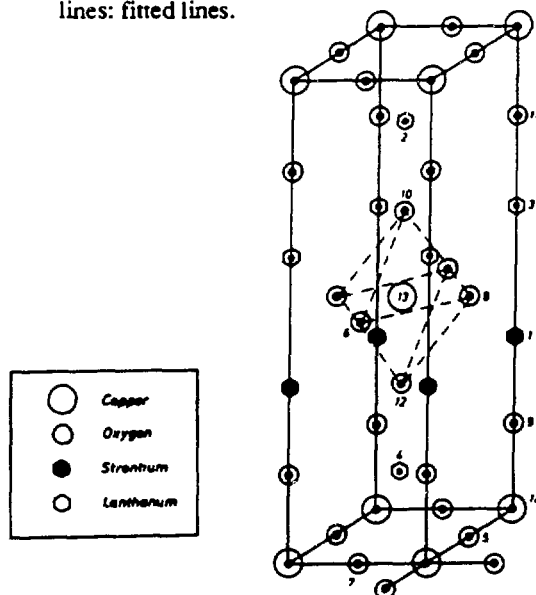


Fig. 4. A schematic representation of the simple tetragonal unit cell used in the $\text{La}_3\text{SrCu}_2\text{O}_8$ calculation. Replacement of the Sr atom (labelled 1) by La gives the unit cell used in the La_2CuO_4 calculation.

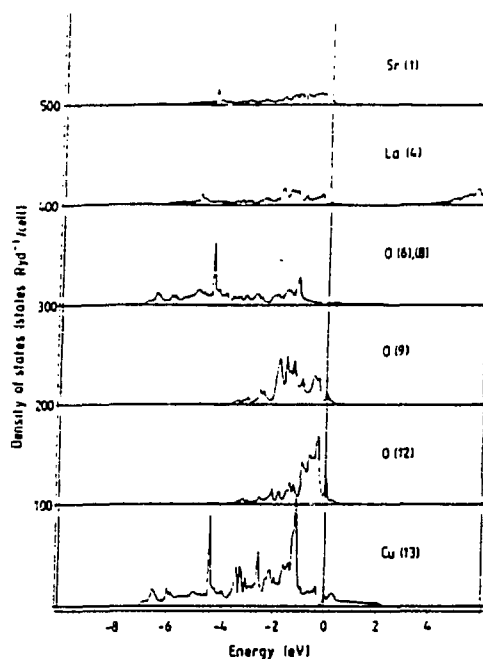


Fig. 5. Atomic-species-decomposed densities of states of $\text{La}_3\text{SrCu}_2\text{O}_8$ for Sr and for atoms in the planes neighbouring the Sr layer. The species labelling is according to Fig. 4.

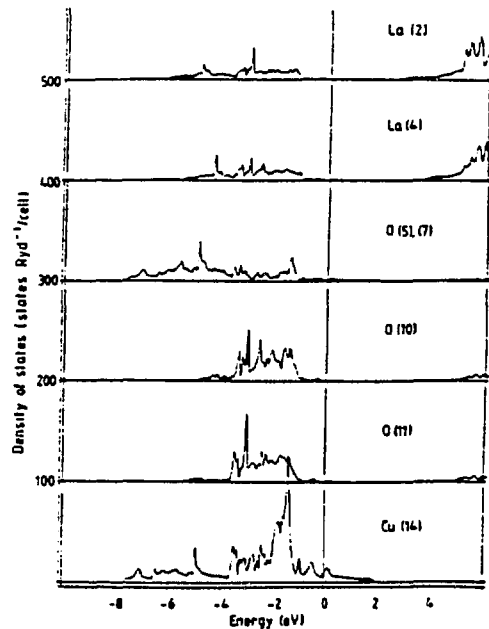


Fig. 6. Atomic-species-decomposed densities of states of $\text{La}_3\text{SrCu}_2\text{O}_8$ for atoms in the next-nearest-neighbour planes to the Sr layer. The species labelling is according to Fig. 4.

Besides the changes in the bonding properties upon Sr doping, there are also major changes to the electronic structure and charge distributions. The densities of states for each of the twelve inequivalent atoms in the $\text{La}_3\text{SrCu}_2\text{O}_8$ supercell (Figure 4) are plotted in Figures 5 and 6. We have divided these into two groups, according to the effect of the Sr addition. Figure 5 comprises the densities of states for those sites that are affected, i.e. those atoms immediately above and below the Sr plane: (La(4)-O(9) plane, Cu(13)-O(6)-O(8) plane, Sr-O(12) plane itself). Figure 6 comprises the densities of states of those atoms that are not substantially affected, i.e. atoms in the next-nearest-neighbour planes to the Sr plane (La(2)-O(11), La(3)-O(10), Cu(14)-O(5)-O(7) planes). From Figures 5 and 6 it is clear that the extra structure in the density of states in $\text{La}_3\text{SrCu}_2\text{O}_8$ in the first 1.5 eV below the Fermi energy E_f is Sr induced and arises primarily from the atoms in the nearest neighbour planes to the Sr. The densities of states for the more distant atoms are almost identical with those of pure La_2CuO_4 . It is the density of states associated with O(12) and, to a somewhat lesser extent, O(9) that are most affected by the Sr substitution. Both of these oxygen atoms have structure in the densities of states at and just below E_f that is not present in La_2CuO_4 . Also it should be noted that the Fermi energy peak in $\text{La}_3\text{SrCu}_2\text{O}_8$ is different in nature from the peak just below E_f in La_2CuO_4 . In La_2CuO_4 the peak arises from the saddle point at X and Y and is dominated by the Cu component; in $\text{La}_3\text{SrCu}_2\text{O}_8$ octahedral apex oxygen atoms (O(9) and O(12)) adjacent to the Sr atoms dominate. Indeed a small saddle-point peak in the densities of states of $\text{La}_3\text{SrCu}_2\text{O}_8$ that results from the unperturbed Cu-O₂ plane can still be seen in figure 6 just above E_f .

ELECTRONIC STRUCTURE AND ANTIFERROMAGNETISM

The cupric oxides La_2CuO_4 (Freltoft *et al.*, 1987) and also $\text{YBa}_2\text{Cu}_3\text{O}_6$ (Tranquanda *et al.*, 1988) are antiferromagnetic insulators. It is a remarkable result that the bonding and the doping properties of these compounds can be described on the basis of a non-magnetic and metallic groundstate. The other issue, of course, is to see whether the LSD approximation to DFT can obtain this antiferromagnetic state. The results of our calculations are summarized in Figure 7 (Guo *et al.*, 1988a). Whilst the total energy converges within about 1 mRyd when 80 or more k-points inside the irreducible Brillouin zone wedge are included in the tetrahedral Brillouin zone integration, the antiferromagnetic moment decreases significantly with increasing

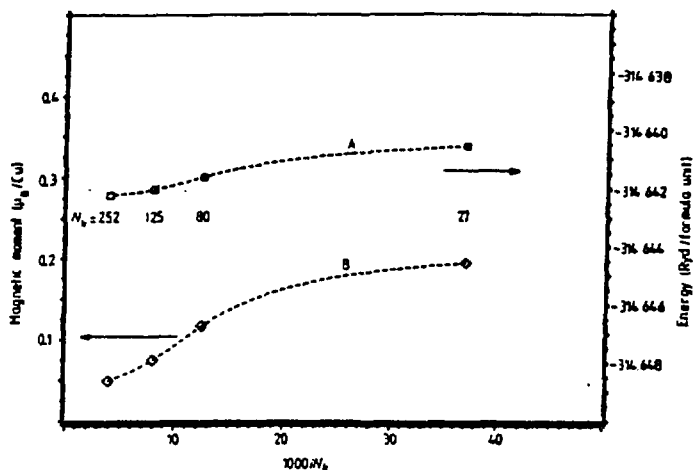


Fig. 7. The self-consistent antiferromagnetic moment on each Cu site (B), and the total energy (A), versus the number of k-points N_k inside the irreducible (1/8) Brillouin zone wedge for the orthorhombic structure. The curves are merely a guide to the eye.

number of k-points. Figure 7 indicates that the converged antiferromagnetic moment would be non-existent or negligibly small. The total energy of the 'antiferromagnetic state' corresponding to 80 k-points and a moment of $0.117 \mu_B$ is only 1 mRyd lower than the total energy of the corresponding non-magnetic calculation. The value of this moment is only slightly dependent on the structure: $0.117 \mu_B$ in the orthorhombic structure with tilted CuO_6 octahedra and $0.109 \mu_B$ in the tetragonal structure. Moreover the spin band splitting is always too small to produce a semiconducting gap at the Fermi level. The energy bands of the orthorhombic and 'anti-ferromagnetic' (80 k-points) compound are shown in Figure 8 (Temmerman *et al.*, 1988). The bandsplitting across the Brillouin zone varies from $D_1=0.08 \text{ eV}$ to $D_2=0.15 \text{ eV}$. A periodic lattice distortion (PLD) of a 3.4% modulation of the planar $\text{Cu}-\text{O}$ bond lengths would give rise to similar band splittings: $D_1=0.0 \text{ eV}$ and $D_2=0.23 \text{ eV}$.

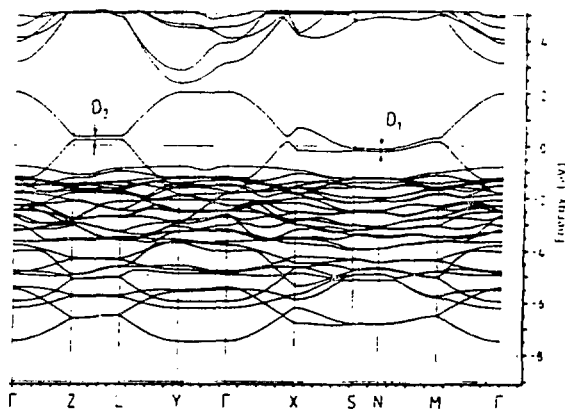


Fig. 8. The energy bands of orthorhombic and 'antiferromagnetic' $\text{La}_4\text{Cu}_2\text{O}_8$.

The tendency towards magnetism can usually be enhanced by expanding the lattice. This narrows the bands (the band width W decreases), whilst leaving the on-site inter-electronic d-d Coulomb repulsion U more or less constant; therefore the ratio U/W increases. Uniformly expanding the La_2CuO_4 lattice up to 10% and squeezing it down to 9% failed to increase the magnetic moment significantly. The results show that the moment slightly decreases as the lattice expands. In the 10% expanded lattice the Cu-O planar bond lengths have increased from 1.89 Å to 2.08 Å and the Cu-O apex bond length from 2.42 Å to 2.66 Å. Whilst this narrows the occupied Cu d and O p bands, there is hardly any narrowing of the Cu d and O p anti-bonding bands that cross the Fermi energy E_F . Expanding La_2CuO_4 non-uniformly by increasing just the c axis by 5%, and hence isolating the CuO_2 planes even more, does not alter the bandstructure in the vicinity of E_F . This demonstrates that the dispersion of the Cu $d_{x^2-y^2}$ and O $p_{x,y}$ anti-bonding bands is nearly completely dominated by the intra-layer interactions.

What seems to control the tendency towards moment formation is the charge on the O and Cu sites. In Figure 9 we show the energy bands of $\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{12}$ for two different basis sets. In both cases the resulting band structures are semi-metallic, differing in their separation of the Cu d and O p bands. In Figure 9a the Cu planar sphere has a charge of 28.12 electrons, the planar O has 7.72 electrons. In Figure 9b, for a different basis set, the charge on the O site is reduced to 7.67 electrons whilst the charge on the Cu site has remained unchanged. The effect is to separate the O p band from the Cu d bands, increasing the d character at E_F and slightly increasing the antiferromagnetic tendency.

If the antiferromagnetic groundstate is not a LSD solution to DFT, the question arises how far away is the LSD approximation from obtaining an anti-ferromagnetic groundstate? The study of the q and ω RPA-LSD spin susceptibility (Stenzel and Winter, 1985) should provide us with that information. Preliminary results suggest that there is a peak in the spin susceptibility

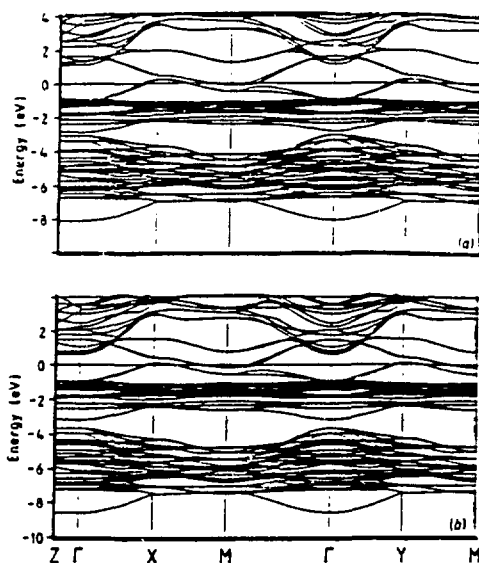


Fig. 9. The energy bands of $\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{12}$; (a) antiferromagnetic with up to $l=3$ on Cu and $l=2$ on O; (b) antiferromagnetic with up to $l=3$ on Cu and $l=1$ on O.

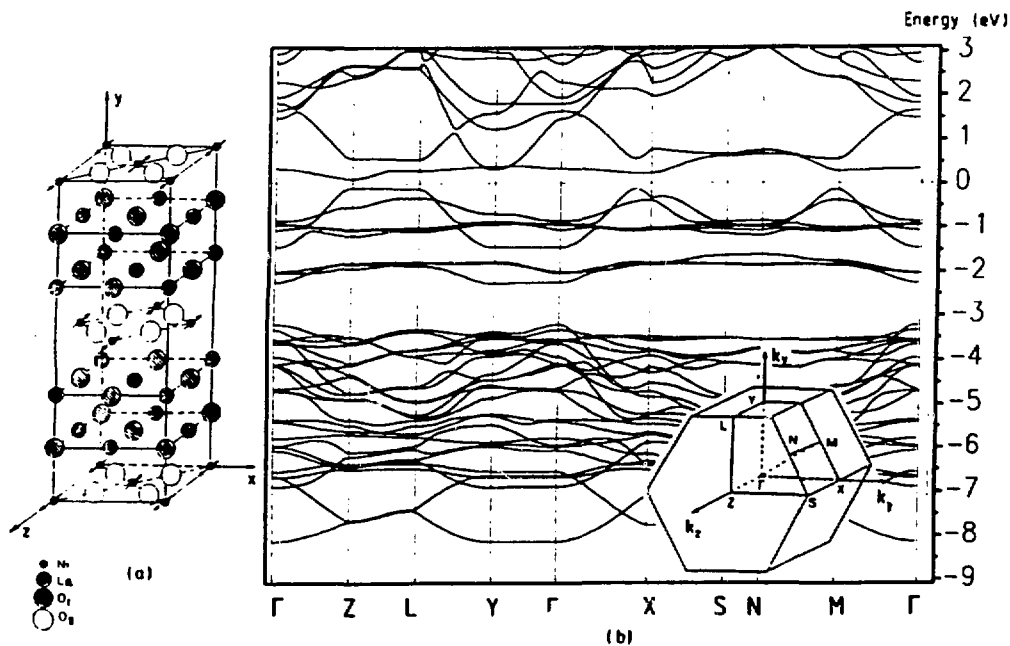


Fig.10. (a) The antiferromagnetic spin structure of La_2NiO_4 used in the present calculation and (b) the band structure of the antiferromagnetic La_2NiO_4 at the experimental lattice constant, with the Brillouin zone shown in the inset.

$\chi(q,0)$ around the (1,1,0) point (Lueng *et al.*,1988 and Chui *et al.*,1988), but reliable estimates of the magnitude of the peak of the interacting susceptibility based on the RPA-LSD formalism are not available yet. Moreover the q and ω behaviour of the spin susceptibility would provide the coherence length of the spin fluctuations. Unfortunately, those calculations are not available yet. However, from LSD bandstructure calculations of systems structurally and chemically close to La_2CuO_4 , such as K_2NiF_4 , K_2CuF_4 and La_2NiO_4 , some conclusions regarding the validity of LSD in cupric oxides can be inferred.

Kubler *et al.*,1988, find K_2NiF_4 to be an anti-ferromagnetic insulator with a moment of $1.5\mu_B$ and 0.5 eV gap, whilst K_2CuF_4 is ferromagnetic with a moment of $0.4\mu_B$. In these fluorides the metal d bands are more separated from the fluoride p bands, and therefore the states at the Fermi energy would be more of metallic d character than in La_2CuO_4 . We studied La_2NiO_4 (Guo *et al.*,1988b and Guo *et al.*,1988c) which we find to be an anti-ferromagnetic insulator with a moment of $1.0\mu_B$ and a gap of 0.2 eV. In Figure 10 we show this bandstructure; first we note that the O p bands are well separated from the Ni d bands. Secondly the metal d bands are split by approximately 0.5 eV: the Ni t_{2g} and both of the Ni e_g bands, i.e. the Ni $3d_{z^2} - \text{O } 2p_z$ and the Ni $3d_{x^2-y^2} - \text{O } 2p_{x,y}$. The majority and minority t_{2g} bands are occupied, whilst only the majority of the e_g bands are occupied, and the energy gap separates the majority from the minority e_g bands. For a gap to open up it is crucial that the e_g orbitals pointing along the z-axis occur at the same energy as the x^2-y^2 e_g orbitals. We find for example that increasing the ratio of the Ni-O apex to Ni-O planar bond length from 1.04 to 1.08 would take us from an insulator to a metal. This is a consequence of a charge transfer from the Ni to the La which pulls the minority Ni $3d_{z^2} - \text{O } 2p_z$ below E_F . Also, the tilting of the Ni-O₆ octahedra gives rise to charge transfers which in turn affects the magnetic properties, increasing the moment slightly.

ELECTRONIC STRUCTURE AND XPS/EELS SPECTROSCOPY

Numerous spectroscopic studies with electrons and photons have been performed to determine the electronic structure of high T_c materials. From these experiments a model of the electronic structure has emerged which is rather different than the results of the bandstructure calculations. Whilst in the band picture the Cu and O bands are strongly hybridized, from spectroscopic studies it is deduced that the Cu bands are localized and are split in a lower and upper Hubbard Cu d band with the O p band sandwiched in between (Fuggle *et al.*,1988). In Figure 11 we compare the experimental XPS and BIS with our one electron calculations. The calculated XPS peak is much too narrow and occurs at a binding energy of 2eV instead of the observed binding energy of 4 eV. The XPS spectra are dominated by the Cu 3d states and therefore the principal reason for the discrepancy between experiment and theory is the strong electron-electron interaction in the Cu 3d states, as is also found in transition metal compounds.

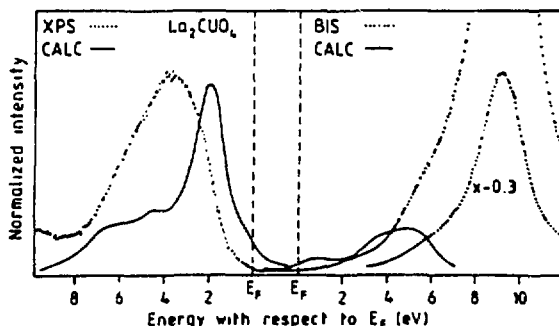


Fig.11. Experimental and calculated XPS and BIS spectra at 1486.7 eV for La_2CuO_4 .

X-ray absorption/emission and EELS experiments provide local probes of the electronic structure. X-ray emission spectroscopy confirmed the conclusion drawn from the XPS experiments regarding the Cu 3d binding energy of 4-eV (Bamole *et al.*, 1988). The O p bands on the other hand has been seen in the spectroscopy which probes the unoccupied bands such as the EELS (Nucker *et al.*, 1988) and the X-ray absorption (Kuiper *et al.*, 1988). These experiments demonstrate the presence of O holes on doping the insulating state. One would expect the band picture to give a better description of the band-like O p states. In Figure 12 we show the calculated EELS spectra. At threshold the calculations predict wrongly for undoped La_2CuO_4 a finite intensity due to holes in the two-dimensional Cu $3d_{x^2-y^2}$ - O $2p_{x,y}$ band. Upon doping with Sr an increase in the intensity is predicted by the calculation for $x=0.5$ due to states on both the planar and apex O. This increase in intensity near threshold is caused by large increases in the Fermi energy densities of states on the apex O sites, i.e. O(12) and O(9) closest to the 'Sr' doping. Calculations for other concentrations such as $x=0.25$ and 0.125 together with the symmetry analysis of the O p holes would be extremely useful for further analysis of the EELS and X-ray absorption experiments.

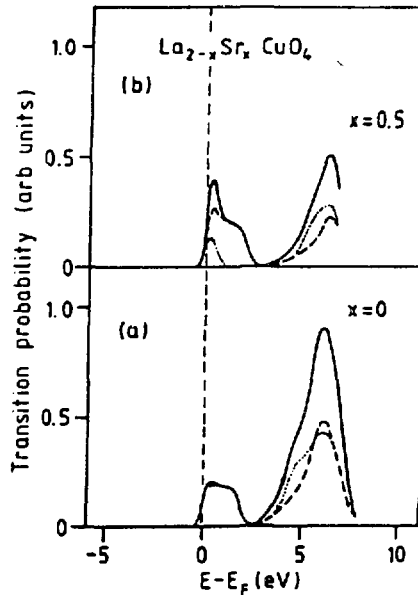


Fig.12. Calculated oxygen 1s absorption edges for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$: (a) $x=0$ (b) $x=0.5$. Total: solid curve, dashed curve: planar O, dotted curve: apex O.

CONCLUSIONS AND OUTLOOK

As has been mentioned before, the LDA gives a very good description of the bonding properties of the high T_c materials. It describes not only the lattice constant and the P-V curve very well, but it also determines highly accurately the position of the La and apex O atoms in the unit cell (Cohen *et al.*, 1988 and Krakauer *et al.*, 1988). Since these results are obtained from a metallic and non-magnetic groundstate which is in marked contrast to the experimental insulating and antiferromagnetic groundstate, one may expect that those two states are energetically not so far away from each other.

It is well known that electron-electron interactions are important in transition metal oxides. The band picture determines the d states to be too band like and this leads to too small a lattice

constant in the late transition metal oxides (Andersen *et al.*, 1979). Allowing for these systems to become magnetic within LSD leads to a volume expansion as a consequence of narrowing and localizing the d states. This volume expansion brings the theory in close agreement with the experiment. It is therefore an important result that the LSD gives a very good description of the bonding in the high T_c cupric oxides on the basis of a non-magnetic, strongly Cu-O hybridized, groundstate, and this contrasts with the calculations of the late transition metal oxides.

We also find that the bonding is dominated by the La and O planes, whilst the antiferromagnetic interactions are constrained to the CuO_2 planes. The energy scales of the bonding and antiferromagnetic interaction are very different: a convergence of 1mRyd is more than sufficient to describe the bonding, but on this energy scale the moment still varies by 0.12 μ_B . We also obtain that charge transfer is a more important quantity than U/W to describe the magnetic interactions.

In short, the LSD calculations indicate that the electronic structure of the high T_c cupric oxides is different from the late transition metal oxides and the bonding gives no strong indications, as is the case in transition metal oxides, that the calculated Cu 3d states are too band like. Also, the magnetic properties seem to be different from the late transition metal oxides. In this context, q, ω spin susceptibility studies would be of great interest for high T_c cupric oxides.

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