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WHAT CAN BE LEARNED ABOUT HIGH T_c FROM LOCAL DENSITY THEORY ?

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The significance of local density band structure results for high T_c compounds is critically discussed. It is pointed out that straightforward application of this method can be misleading because of the correlated nature of these materials. However, with LDA numbers can be derived for the parameters appearing in the models in which correlation is treated explicitely. In this way we arrive at the conclusion that despite a large U the high T_c materials should be viewed as itinerant materials. Turning to ground state properties, we show that the LDA fails to describe the antiferromagnetism of La_2CuO_4 and it is pointed out that this may be cured by the inclusion of self interaction corrections. Finally, using a proposed ozygen defect structure for $YBa_2Cu_3O_{7-x}$ and a simple tight binding model based on band structure calculations, we show that jumps and plateaux in the hole counts in the planes and chains occur as a function of x. These features are perfectly correlated with the occurrence of the antiferromagnetic, as well as of the $60K$ and $90K$ superconducting phases.

1. INTRODUCTION

A fairly common attitude among theorists is to reject results obtained for the high T_c superconducting oxides (HTSO) from bandstructure calculations, based on the local approximation to density functional theory (LDA). This is not groundless : it is expected that the electronic structure of these Cu-oxides should bear a resemblance to that of other $3d$-oxides like NiO, CoO, etc. The LDA is notoriously in error for these materials. According to the LDA calculations of Terakura *et al* [1], the band gap would be small ($0.5eV$) or non-existent, while these systems are in reality insulators with gap magnitudes ranging up to $4eV$ in NiO [2]. It is well established that this discrepancy is due to the large Coulomb interactions between the $3d$-electrons. As explained by Mott and Hubbard [3], if the energy cost (U) of the charge-fluctuation $3d^n + 3d^n \rightarrow 3d^{n+1} + 3d^{n-1}$ exceeds the bandwidth (W), the single particle band picture breaks down completely. Nevertheless, in this paper we shall indicate that density functional calculations can be usefull in several respects.

Based on photoemission data, it has been shown recently ([4,5] and refs therein) that the Mott-Hubbard concept indeed applies to the global electronic structure of these materials. In the simple Mott- Hubbard picture only the d-states are considered. In the real materials, however, also other charge degrees of freedom are present like the $O2p$- and transition metal $4s$- states. In practice these can be quite important, also if one considers low energy properties. Experience shows, that LDA calculations are valuable tools in unravelling these complexities, because they can be used to derive numbers for the different parameters entering in the models used to interpret the photoemission data. In section 2 we will outline the picture as it has emerged for the $3d$-oxides and illustrate the accuracy of the LDA-parameters. Applying this to the HTSO we show that, despite the largeness of U, the d-electrons are probably not localized.

It is often thought that despite the problems with the excitation spectra, LDA calculations give meaningfull results for ground state properties. In section 3 we address this issue by considering the antiferromagnetism of La_2CuO_4 and we will show that according to the LDA this system would be far from being magnetic. One way of improving the density functional is by including self-interaction corrections (SIC). According to a realistic model calculation we find the promising result that upon including SIC an antiferromagnetic ground state is found with a spin polarization of the right order of magnitude.

Finally, in section 4 we show, using a proposed oxygen defect structure for $YBa_2Cu_3O_{7-x}$ and a simple tight binding model based on the LDA-band structure, that sudden jumps in the hole-counts in the $Cu-O$ planes and chains occur as a function of non- stoichiometry, x. These jumps are perfectly correlated with the occurrence of the antiferromagnetic, as well as $60K$ and $90K$ superconducting phases in this system. These findings support the view that the hole count is the controlling parameter for the superconductivity.

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2. HOW LOCALIZED ARE THE *d* ELECTRONS IN THE HTSO ?

With the combination photoemission - inverse photoemission one measures the probability of removing or adding a single electron at a given energy. In Fig.1*b* the result for *NiO* is shown [2] and compared with the LDA result [1] (Fig.1*c*). It is seen that these experimental data are not reproduced by the LDA, but also the relationship with the simple Mott-Hubbard picture is not clear. Instead, the spectral density can be described in fair detail (see Fig.1*b* [6]) using the Anderson impurity Hamiltonian [7]

$$H = H_0 + H_1,$$

$$H_0 = \sum_{kn\sigma} \varepsilon_{kn} c^\dagger_{kn\sigma} c_{kn\sigma} + \sum_{m\sigma} \varepsilon_{dm} d^\dagger_{m\sigma} d_{m\sigma} + \sum_{ijlm} U(ijlm) d^\dagger_i d_j d^\dagger_l d_m,$$

$$H_1 = \sum_{knm\sigma} V_{knm} (d^\dagger_{m\sigma} c_{kn\sigma} + h.c.). \qquad (1)$$

In H_0 the electronic structure of the isolated *d*-shell, including crystal field splittings and the quasi-atomic Coulomb interactions, as well as the bands arising from the non-*d* states (first term) are gathered. H_1 contains the hybridization between the *d*-states and the non-*d* bands. Upon switching off the hybridization, Fig.1*a* is obtained [6]. The relevant non-*d* bands are the *O2p* valence- and *Ni4s* conduction bands, separated by a large gap. The location of the 3*d*-Hubbard bands with respect to these 'normal' bands is apparently different from what has been hypothesized in the past [8]. If doped, the electrons will go into the d^9 upper Hubbard (UH) band. However, the multiplet-split d^7 lower Hubbard (LH) band is below the bottom of the *O2p* band, and it is far from obvious [9], that the holes can be described with an effective single band Hubbard Hamiltonian. The gap-magnitude is given by the energy cost (Δ) of the charge-transfer fluctuation $3d^n \rightarrow 3d^{n+1}+L$, where L denotes a hole in the ligand band. Concerning the HTSO, if $U < \Delta$ the holes are in the LH band and (for instance) Anderson's resonating valence bond picture [10] would directly apply. If $U > \Delta$, the holes would have *O2p* character, as proposed by Emery [11] and others [12]. Finally, if Δ becomes small compared to the hybridization, the *d* - electrons delocalize, independent of the magnitude of U [13] (mixed-valency) , and weak coupling ideas gain credibility.

From the preceding discussion it is obvious that knowledge of these parameters is an important ingredient in the search for the high T_c mechanism and the LDA has proved to be useful in this respect for other materials. In order to determine Δ or U one sets to zero the hopping between the relevant *d*-orbitals on a particular atom and the remainder of the crystal. By varying the number of *d*- electrons one obtains the desired quantities [14]. Applying essentially this procedure to *NiO*, Norman and Freeman [15] obtained $U = 7.9eV$ and $\Delta = 4.1eV$. From the interpretation of the photoemission data (Fig.1*a*,*b*) one finds $U \simeq 7.0eV$ and $\Delta \simeq 4.0eV$ [6]. Further, we notice that the Δ determined by 'excited state' LDA is very close to the Δ deduced from the ground state calculation (Fig.1*c*). Very recently it was shown by Gunnarsson *et al* [16], that also relevant information about the hybridization matrix elements can be extracted from LDA calculations in the framework of the linear muffin tin orbital (LMTO) method [17]. Using this together with LDA values for Δ and U plus atomic F_2 and F_4 integrals, first principle results for the photoemission spectrum of *Mn* in *CdTe* were obtained [16], being in surprisingly good agreement with experiment.

In Fig.2 we show the orbital composition of the LDA bands of paramagnetic La_2CuO_4 in the vicinity of the Fermi energy (E_F), obtained from a ground state calculation using the LMTO method [17]. The most prominent feature is the band crossing E_F, which is almost of pure $d_{x^2-y^2}$ and in-plane oxygen (O^I) character. Mattheiss pointed out that this band is well described by a simple tight binding model where only the in plane *x*- or *y* *O2p* orbitals and the $d_{x^2-y^2}$ Cu orbitals are taken into account [18]. This band is unusually dispersive (see for instance Fig.1*c*) and tight-binding fits to the LAPW bands [19], as well as first principle tight binding LMTO calculations [20] show that this is due to $\Delta \simeq 0$, while the transfer integrals are of essentially the same order of magnitude ($V \simeq 1.5 - 2.eV$) as in (for instance) *NiO*.

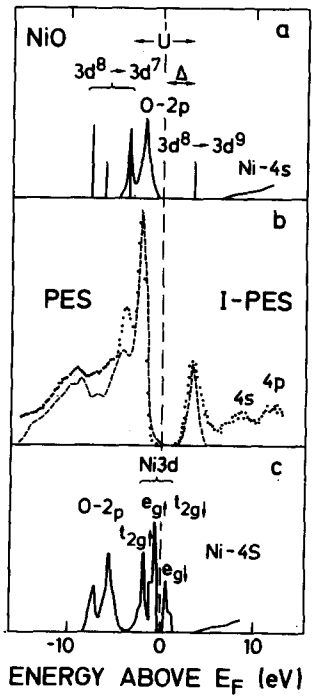

FIGURE 1

Spectral densities for NiO. a: Theory for fully localized d - electrons. b: The experimental (inverse) photoemission spectra [2] compared with a result obtained from the Anderson impurity model [6]. c: LDA densities of states [1].

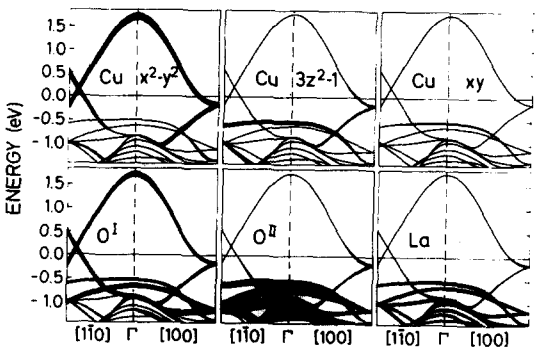

FIGURE 2

LDA bands of La_2CuO_4 in the vicinity of E_F in the folded (AF) Brillouin zone. The thickness of the lines indicates the orbital character of the bands.

Using a $4[La_2CuO_4]$ supercell and the LMTO-ASA method [17] we calculated Δ and U in the LDA. For Δ we use the transition state technique [21]. Thus we have $E(d^{10}L) - E(d^9) \simeq \varepsilon_d - \varepsilon_p$, where ε_d and ε_p refer to the energies of the Cu $3d$ and O $2p$ orthogonal LMTO's, calculated for the $3d$-occupancy 9.5. From these calculations we deduced $\Delta = 0 - 1eV$, depending on computational details. We again find, that the ground- and excited state LDA Δ's are very similar.

The value of U was obtained from $U = \delta^2 E[n_d]/\delta n_d^2$, where the energy E is the energy of a neutral system with n_d $3d$-electrons. Note that since the hopping from the $3d$ state is included explicitely in the Hamiltonian, the rather important renormalization effects on U from this hopping should *not* be included in the calculation of U. From the total energy we deduced $U = 8eV$.

In the valence band photoemission spectra of the HTSO one always observes a feature located at 9 - 11 eV below E_F [22,23,24]. According to the band calculations there is no density of states in this region and this structure can be identified with the multiplets of the d^8 LH band [6]. Additional evidence is supported by resonance photoemission where one finds the typical and well understood resonance behaviour of a d^8 satellite [25]. This confirms that U is as large as suggested by our calculation and it shows that the LH band is well removed from E_F. Also our small Δ is confirmed by experiment. Several groups have analyzed the core-XPS spectra, where the d - hole count in the ground state is measured, and they arrive at $< n_d > \simeq 0.5$ [26], indicative of $\Delta < V$ [27]. It has also been argued that the anomalous high energy scale for the (two dimensional) antiferromagnetism can be interpreted as an indication for small Δ/V [22]. Finally, the most direct evidence in favour of small Δ/V comes from inverse photoemission. In localized materials like NiO (Fig.1*b*) one finds always a distinct feature above E_F corresponding to the narrow d^{n+1} UH band. In the data of the HTSO such a feature seems to be absent and instead one finds instead a rather broad band around E_F [23,28].

If our claim, i.e. large U/V and small Δ/V, turns out to be true this can have important consequences with respect to the nature of the superconductivity. At least on the level of the 'bare' d-electrons one has to account for the charge degrees of freedom. However, one can also question the validity of the localized picture on the quasi-particle level. According to the T-matrix [29] or Gutzwiller [30] pictures one expects an electronic mass renormalization of only ~ 1.5, if $< n_d > \simeq 0.5$. Of course, complications arise because of the antiferromagnetism found when the $d_{x^2-y^2}$-band is half filled, and the insulating nature of the antiferromagnets La_2CuO_4 and $YBa_2Cu_3O_6$ is often put forward as evidence for having a local gap. However, one should keep in mind that the gap magnitude $(1.5 - 2.eV)$ is in fact quite small compared to the overall dispersional width ($\sim 10.eV$, see Eq.(4)) of the plane band. One way to obtain more clarity about the locality of the gap could be by considering the electronic structure of the doped systems. Both for large and small Δ/V it is expected that states, induced by the excess of holes, are found in the charge excitation gap. In the localized regime the energy scale of the gap itself (Δ) is much larger than the interactions giving rise to self-localization ($V^2/\Delta, V^2/(U-\Delta)$ [9]). These hole states will therefore be in the neighborhood of the valence band edge (Fig.3*b*). However, if $\Delta < V$ these energy scales cannot be separated and therefore the new hole states can be located everywhere in the gap (Fig.3*a*). In this latter situation, Schrieffer's spin-bag concept [31] seems to be a more natural 'generic' picture. We notice that the EELS data of Nücker *et al* [23] seem to favour this uniform gap filling.

3. LDA AND ANTIFERROMAGNETISM IN La_2CuO_4.

At half filling, the plane band has a near nesting instability for $\vec{q} = [110]$ (Fig.2 and Eq. (4)). The associated breathing mode was instrumental in conventional transport theory based on the electron-phonon interaction and the LDA for $La_{2-y}Sr_yCuO_4$ [32]. This theory could account for $T_c \simeq 40K$, but in order to explain the temperature dependence of the resistivity above T_c, an unreasonable short mean free path had to be assumed [33]. For the superconductivity of $YBa_2Cu_3O_7$ the theory failed completely [34].

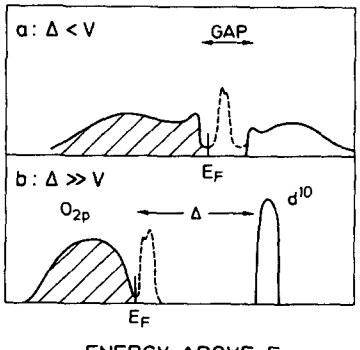

FIGURE 3

Artist's impression of the filling of the gap by dopant induced states in (a) the mixed-valent and (b) the localized regime.

The proper ground state of La_2CuO_4 is antiferromagnetic with the above mentioned $\vec{q}$-vector and a moment of $\simeq 0.4\mu_B$. In the past, the spin-unrestricted LDA (LSDA) has been successful in yielding realistic magnetic moments for numerous transition-metal systems. However, the LSDA solution for La_2CuO_4 is not spin polarized [20,35]. The size of the discrepancy is best seen from Fig.4 where we show the unenhanced $\chi_0^{-1} \equiv 2\mu_B H/m_{LDA}$ and enhanced $\chi^{-1} \equiv 2\mu_B H/m_{LSDA}$ inverse susceptibilties calculated by applying an external staggered magnetic field H on the Cu sites. The sublattice magnetizations m_{LDA} and m_{LSDA} were obtained, respectively, without and with including the internal exchange-correlation field. From the susceptibility curves we find the effective Stoner parameter $I = \chi_0^{-1} - \chi^{-1}$. This is seen to be at least a factor 5 to small to account for the moment, although its magnitude ($\simeq 0.7-1.0$) is of the same order as commonly accepted for Cu and Ni metals. In these LMTO calculations the $s-, p-$, and $d-$orbitals were included on all atoms, as well as the La f-orbitals, and extreme care was taken in performing the Brillioun zone integration (tetrahedron method with 300 irreducible k points). One possible source of error could be the spherically averaging of the spin density, but this can account for a factor of 2 at most.

In the LSDA an electron has an unphysical interaction with itself which may be explicitly subtracted. This gives rise to the so-called SIC LDA [36]. For many properties these two density functionals have a comparable accuracy [37]. In an application to the one-dimensional Hubbard model it was, however, found that the SIC gives a substantially better moment than the LSDA [38]. It is therefore interesting to see if a similar improvement is obtained also for La_2CuO_4.

A full *ab initio* SIC calculation is difficult to perform, since the one-particle solutions are not automatically orthogonal. To predict the outcome of such a calculation, we have studied a simple model of the CuO_2 planes, including the Cu x^2-y^2 orbital as well as the O $2p$ orbital pointing towards the nearest Cu neighbors. Mattheiss' value for the hopping integral $V = 1.6$ eV between these orbitals was used. Each orbital was furthermore assumed to have an on-site Coulomb interaction. We used 'spectroscopic' values for these interactions, i.e. $8eV$ (Cu) and $6eV$ (O) [39]. The exchange-correlation energy was described in an analogous way to our earlier work [38], taking into account the Cu and O charges and moments. The parameters in the exchange-correlation energy expression were deduced from atomic and band structure calculations to simulate an *ab initio* SIC calculation as closely as possible. The orthogonality of the one-particle solutions was enforced explicitly.

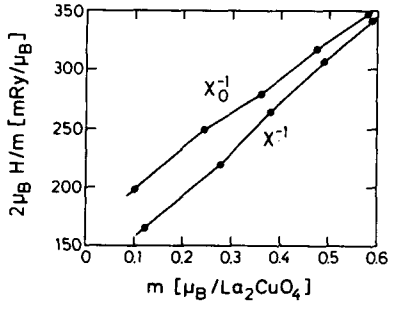

FIGURE 4
Inverse staggered susceptibilities vs. sublattice magnetization according to LDA calculations for La_2CuO_4.

For this model SIC calculation We find an antiferromagnetic solution, with the moment 0.3 μ_B and with Cu hole count 0.5. In the LSDA one finds, as in the full LMTO calculation, that the moment is very close to zero, while the small deviation from zero is due to the two-dimensional nature of the model. We conclude that the description of the antiferromagnetism in La_2CuO_4 is greatly improved in the SIC approximation compared with the LSDA approximation.

4. OXYGEN VACANCY STRUCTURE AND THE PHASE DIAGRAM OF $YBa_2Cu_3O_{7-x}$.

An important theme in the theories about high T_c is the hole concentration in the perovskite planes. This is based on the phase diagram of $La_{2-y}Sr_yCuO_4$. For $y = 0$ the $d_{x^2-y^2}$ band is half filled, giving rise to antiferromagnetism. For $y > 0$ holes are introduced, which destroy the antiferromagnetic state and stabilize the superconducting state. It has even been claimed that T_c is directly proportional to the hole count in these materials [40]. In this light, the phase diagram of $YBa_2Cu_3O_{7-x}$ as a function of the oxygen non-stoichiometry, x, is at first sight mysterious [41,42,43] (see top of Fig.5). For $0 \leq x \leq 0.2$ the $90K$ superconductors are found. At a critical concentration $x \simeq 0.25$, T_c decreases suddenly to $60K$, where it remains up to $x \simeq 0.5$. Beyond $x \simeq 0.5$, T_c gradually detoriates [41] and it has been established that the $x = 0.85$ and $x = 1$ materials are antiferromagnets with high Neél temperatures [43]. Considering the oxygen vacancies merely as donors of electrons, neither the AF state for $x = 1$, nor the sudden jumps between the different phases can be explained. However, it has recently been shown that the vacancies are not distributed randomly through the crystal, but instead form well defined defect structures [44]. The oxygen vacancies break the chains up in fragments. We will argue, using a simple tight binding model based on the LDA bands, that these chain fragments act as the doping agents and that in this system the same correlation exists between hole count and superconductivity as in the La-cuprates.

For $x = 0$, the structure is well known [45], consisting of two planes and one chain per $YBa_2Cu_3O_7$ unit cell. As x increases, the planes remain intact, while oxygen vacancies appear in the chains. The chains run along the b-direction and consist of oxygen linked CuO_2 -units directed along the c-axis. At $x = 1$, all the oxygen links are removed and the structure comprises intact planes and isolated CuO_2-units (empty chains) [45]. Based on the observations of Chaillot *et al* [44], we use the following defect-structural model for $0 \leq x \leq 1$. In a unit cell, which is doubled along the a-axis, we regard the two chains as inequivalent. One of the chains will be either intact ($0 \leq x \leq 0.5$) or empty ($0.5 \leq x \leq 1$). The other chain will then

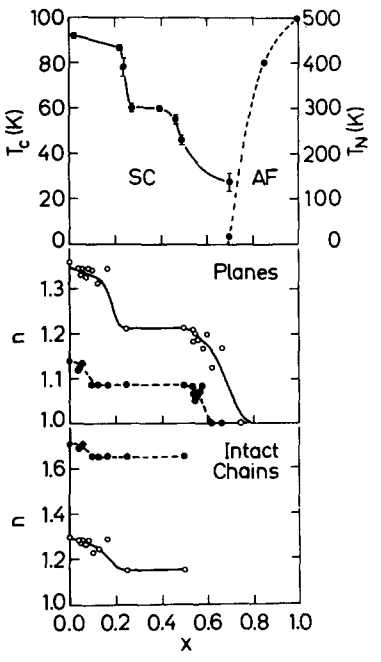

FIGURE 5

Phase diagram of $YBa_2Cu_3O_{7-x}$ as a function of x [41,43] compared to the hole counts in planes and chains derived from the model discussed in the text.

have oxygen vacancies arranged with a regular spacing so as to satisfy the non-stochiometry. In the simplest case, this broken chain will then comprise lengths of ν CuO_2-units connected by $(\nu-1)$ oxygen links, where for $0 < x \leq 0.5$ $x = 1/(2\nu)$, and for $0.5 < x \leq 1$ $x = 0.5 + 1/(2\nu)$. For values of x for which $1/(2x)$ is not an integer, the broken chains will be made up of two different lengths such that the oxygen-vacancies are kept as far apart as possible and form the simplest possible defect structure. This model agrees with the findings of Chaillot *et al* for $x = 1/8, 1/2$ and $7/8$.

It is expected that the LDA gives a reasonable picture of the ground state charge distribution. We have performed LMTO calculations [17] for $Y_2Ba_4Cu_6O_{13}$ $= 2(YBa_2Cu_3O_{6.5})$. Per primitive cell there are 2 planes with 2 CuO_2 units each, one intact chain, and one broken chain with $\nu = 1$. We find 2 doubly degenerate plane-bands which are very similar to the band in La_2CuO_4 (Fig.2) . The intact chain band is also highly dispersive and can be very well described in the tight binding approximation as the antibonding band obtained from the $Cu\ d_{z^2-y^2}$ orbital, the z-orbitals on the two oxygens in the c-direction, and the y-orbital on the oxygen along the chain. One finds for the dispersion of the antibonding band [46]

$$E(k) = \frac{-\Delta}{2} + \sqrt{(\frac{\Delta}{2})^2 + 2V^2(\alpha^2 + 1 - cosk)}. \quad (2)$$

Here $-\pi < k \leq \pi$ is the b-projection of $b\vec{k}$. The hopping integral from Cu to an oxygen along the chain is V, and to one of the oxygens in the c-direction, which are 5 per cent closer, is αV. Δ is as before the $p-d$ level splitting. The parameter values $\Delta \simeq 0eV$, $V = 2.4eV$ and $\alpha \simeq 1.3$ describe the antibonding LDA band. With n holes in this band, $k_F = \pi(1-n/2)$ and $E_F = E(k_F)$.

According to the band structure calculation the dispersionless antibonding band corresponding with the empty chain is below E_F, indicating that this Cu is formally monovalent. The most convenient way to describe the electronic structure of a broken chain is to remove the linking oxygens, without changing the values of the parameters. In this approximation the states for a fragment of length ν, with oxygens at positions $y = 1,...,(\nu-1)$ and with CuO_2-units at $y = 1/2,...,(\nu-1/2)$ simply equal those states in the intact chain which have the Bloch factor $cos(ky)$ and the wave vectors $k = q\pi/\nu$ with integer values of q from 0 to $\nu-1$ The reason is that these infinite-chain states have equal amplitudes at the z^2-y^2 orbitals at $y = \pm 1/2, \nu \pm 1/2$, so that they cannot couple via the missing O orbitals. The antibonding states of a fragment with length ν thus have the discrete energy spectrum $E(0), E(\pi/\nu), .., E(\pi(\nu-1)/\nu)$, as indicated in figure 6. Starting with the empty chain, each time we add an oxygen, we create one additional antibonding level and two holes. As long as the level is above E_F it will absorp the two holes and no doping occurs. The length ν_c of the longest non-donor fragment is therefore given by $E(\pi/(\nu_c+1)) < E_F \leq E(\pi/\nu_c)$. This fact, that fragments less than or equal to a critical one do not act as dopants, leads to the characteristic plateaux in the hole counts vs. oxygen vacancy concentration curves. Starting at $x = 1$, the plane band is half-filled($n_{pl} = 1$), exactly as in La_2CuO_4, and addition of oxygen does not change the hole count before the first fragment of length $\nu_c(1)+1$ occurs at $x_c(1) = 1/2+1/(2\nu_c(1))$. This is repeated beginning at $x = 1/2$, giving rise to the $60K$ plateau, although the jump position $(x_c(1/2))$ can in principle be different from $x_c(1)$, because E_F has shifted down. However, because it can be expected that the change in E_F is relatively small compared to the discrete level splittings, $x_c(1)$ and $x_c(1/2)$ will be similar (see Fig.5), in

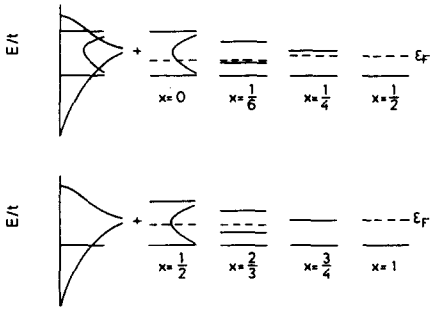

FIGURE 6

Intact chain and plane bands vs. the energy levels of the chain fragments for $\Delta_{pl} = 0$ and $\alpha = 1$. The jumps of E_F (dashed lines) at $x = \frac{1}{6}$ and $\frac{2}{3}$ are seen to be due to the filling of the $i = 2$ fragment level.

agreement with experiment. We notice that the $60K$ plateau in the data indicated in Fig.5 extends merely from $x \simeq 0.40$ to 0.25 which is undoubtly due to crystal imperfections. The data of Tokumoto *et al* [42], on the other hand, show this plateau to extend from $x \simeq 0.65$ to 0.40.

Provided we can use Eq.(2) both for the hole donor levels and the intact chain we can derive bounds for the hole counts in the intact chain and planes in the $60K$ material given the length of the $60K$ plateau. We find for the hole count in the intact chain $4L \leq n(1/2) < (1-L)^{-1}$, where $L = 1/2 - x_c(1/2)$ is the length of the plateau. Using $x_c(1/2) \simeq 0.25$ we find $1 \leq n(1/2) < 4/3$ and for the hole count in the plane ($n_{pl}(1/2) = 3/2 - n(1/2)/4$) we find $7/6 < n_{pl}(1/2) \leq 5/4$. In order to be more specific we have to make assumptions about the quasiparticle densities of states in the chain and plane bands [46], which cannot be claimed to be known. As a model, we can take the dispersion Eq.(2) for the chain band and for the planes the tight binding band proposed by Mattheiss [18]

$$E_{pl}(k) = \Delta_{pl} - \frac{\Delta}{2} + \sqrt{(\frac{\Delta}{2})^2 + 2V^2(2 - cosk_a - cosk_b)}. \quad (3)$$

where $-\pi < (k_a, k_b) \leq \pi$ and where Δ_{pl} gives the position of the plane band with respect to the chain band. The hopping integral V as well as Δ have been taken the same as in the chain. In Fig.5 we compare results for the hole- counts obtained from LDA parameter values ($\Delta_{pl} = \Delta = 0, \alpha = 1.3$) with a 'most likely' result ($\Delta_{pl} = \Delta = 0, \alpha = 1$). In particular, for the latter values there is a striking correlation between the hole counts in the planes and the chains and the occurrence of the SC and AF phases. It is obvious that the effect on the hole counts of the increased c-hopping suggested by the LDA calculations is essentially the same as using the off-set $\Delta_{pl} \simeq V(\sqrt{2\alpha^2 + 2} - 2)$. This points to some serious error in the LDA ground state charge distribution. It can be well imagined that Coulomb effects beyond the LDA could bring the hole counts back towards those obtained with our second parameter choice. Finally, we assumed small Δ in our calculation. Strictly speaking our findings in this chapter are rather insensitive to the choice of Δ and they cannot be used to discriminate between the localized and itinerant pictures. At least as long as Δ takes the same value in the chains and planes, increasing Δ will result in a rescaling of the bandwidth's with little effect on the positions where the jumps occur.

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