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Order-disorder-driven change in hole concentration and superconductivity in $YBa_2Cu_3O_{6.5}$

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The results of electronic-structure calculations for the compound $YBa_2Cu_3O_{6.5}$ are presented in order to understand the role that the ordering of oxygen atoms in the plane of the chains plays in the charge transfer from the CuO_2 planes to the plane of the chains. Three models of crystal structure for $YBa_2Cu_3O_{6.5}$ have been considered for this purpose: (a) an alternate-chain model where each alternate chain is fully intact and the adjacent one fully empty, (b) an identical-chain model where all chains are identical but broken, and (c) a tetragonal crystal structure. We find that practically no charge transfer occurs from the CuO_2 planes towards the plane of the chains in the latter two models, while in the first ~ 0.16 electrons/CuO_2 plane are transferred. This shows that ordered chains are important for hole creation and superconductivity.

I. INTRODUCTION

One of the most interesting features of the $YBa_2Cu_3O_{7-\delta}$ family of superconductors is the vital role that the stoichiometry of oxygen δ plays in determining the superconducting transition temperature T_c of these materials. For $\delta = 1$ the compounds are nonmetallic and nonsuperconducting while for $\delta = 0$ a maximum $T_c \sim 90$ K is observed.[1-6] Indeed, as δ increases from 0 to 1, T_c decreases continuously going through a well-known two-plateau behavior. T_c remains constant at ~ 90 K for $\delta < 0.2$ but for $\delta > 0.2$ there is a sharp drop until it stabilizes at ~ 60 K for $0.3 < \delta < 0.55$. For $\delta > 0.55$ there is again a rapid decline until the material becomes nonmetallic and nonsuperconducting for $\delta > 0.6$. The transition from the superconducting to the nonsuperconducting state is accompanied by an orthogonal-to-tetragonal phase transition and the onset of antiferromagnetism.[7]

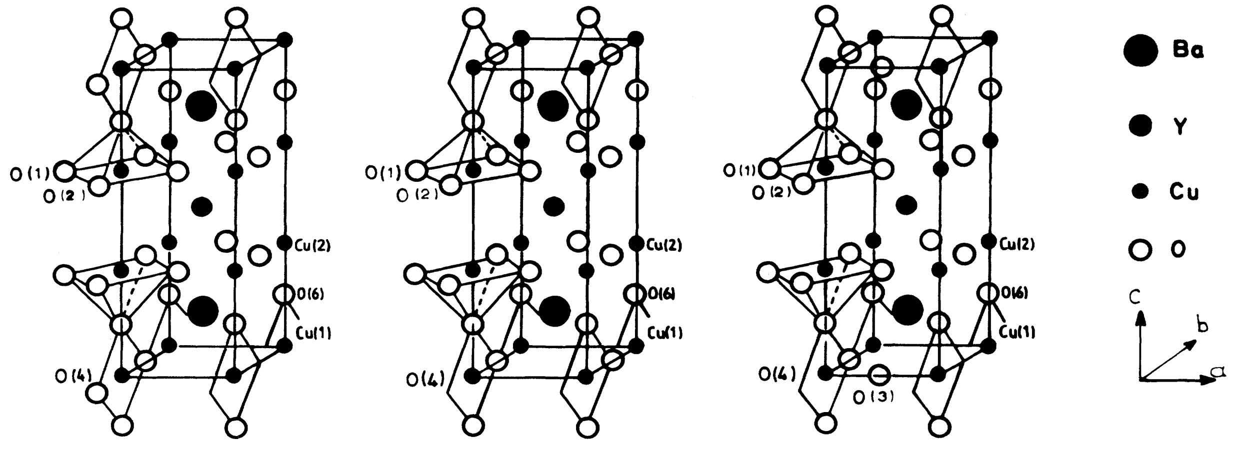
There is a considerable debate in the literature about this occurrence of superconductvity in the orthorhombic phase only and its complete disappearance in the tetragonal phase.[1-13] Although the exact mechanism for the occurrence of superconductivity in the cuprate superconductors is still not understood, it is nonetheless well established that the superconductivity in these compounds arises only when the two-dimensional CuO_2 planes are conducting and that there is a direct correlation between the hole concentration in these CuO_2 planes and T_c.[14] In the insulating $YBa_2Cu_3O_6$ compound the lack of oxygen atoms at the chain sites isolates the CuO_2 planes from the chains and renders them nonconducting. In the fully stoichiometric superconducting $YBa_2Cu_3O_7$ compound the presence of oxygen atoms on the chain sites couples the CuO_2 planes to the CuO chains which act as electron reservoirs for electron transfer from the planes to the chains.[15]

If the stoichiometry in oxygen is the dominant criterion for electron transfer from the planes to the chains, the compound $YBa_2Cu_3O_{6.5}$ should remain superconducting in both orthorhombic and tetragonal crystal structures, which is obviously not the case since the compound is superconducting only in the orthorhombic phase when the chains are fully intact. The only major difference between the two crystal structures is the local rearrangement of oxygen atoms in the plane of the chains. In the orthorhombic structure the arrangement of oxygen atoms is such that the alternate chains are fully ordered and completely intact, as in the superconducting compound $YBa_2Cu_3O_7$, while the adjacent ones are fully empty as in the insulating nonsuperconducting compound $YBa_2Cu_3O_6$; in the tetragonal structure, however, the chains are broken and the oxygen atoms are equally distributed along the *a* and the *b* axes.

In this paper we present the results of our electronic-structure calculations for the compound $YBa_2Cu_3O_{6.5}$ which shows that the oxygen ordering in the Cu-O chains plays a vital role in the charge-transfer interplay between the CuO_2 planes and the CuO chains and thus in determining the hole concentration in the CuO_2 planes. We find that in the $YBa_2Cu_3O_{6.5}$ compound ~ 0.16 hole/CuO_2 planes are created when the alternate chains are fully intact and the adjacent ones fully empty while practically no charge is transferred from the CuO_2 planes when the chains are broken or disordered. The effect of the oxygen stoichiometry, oxygen defects, and the fragmentation of the chains has been previously considered by Goodenough *et al.*,[10] Burdett, *et al.*,[11] Whangbo *et al.*,[12] Zaanen *et al.*,[13] and Cava *et al.*[5].

II. DETAILS OF CALCULATION

Three different models of crystalline arrangements (shown in Figs. 1 and 2) have been considered in this work; the first two of them retain the orthorhombic symmetry while the third one is tetragonal. In model I the



ACM ICM TETRAGONAL

FIG. 1. Three models of crystal structure of $YBa_2Cu_3O_{6.5}$: (a) alternate chain model (ACM); (b) identical chain model (ICM); (c) tetragonal. Note that only 1/4 of the unit cell is shown in the basal plane.

order of the chains is fully preserved so that each alternate chain is fully intact as in $YBa_2Cu_3O_7$, and the adjacent one fully empty as in $YBa_2Cu_3O_6$. The structure remains orthorhombic as in $YBa_2Cu_3O_7$ but there is a doubling of the lattice parameter along the a axis. This alternate-chain model (ACM) with full-empty-full-$\cdots$ chain configuration has been found experimentally[2-5] for the 60-K plateau region. In model II we consider the case where all of the chains are identical (ICM). In this case all of the chains are quite clearly broken since an alternate oxygen atom on each chain is missing. The orthorhombic crystal symmetry is, however, retained since there are no oxygen atoms on the O(3) sites along the a axis. In model III the crystal symmetry is tetragonal so that the O(4) sites along the b axis and the O(3) sites along the a axis have identical occupancies. It should be noted that in none of the three models considered above is the distribution of oxygen atoms in the plane of the chains completely random. It is only the manner in which the oxygens order which is different.

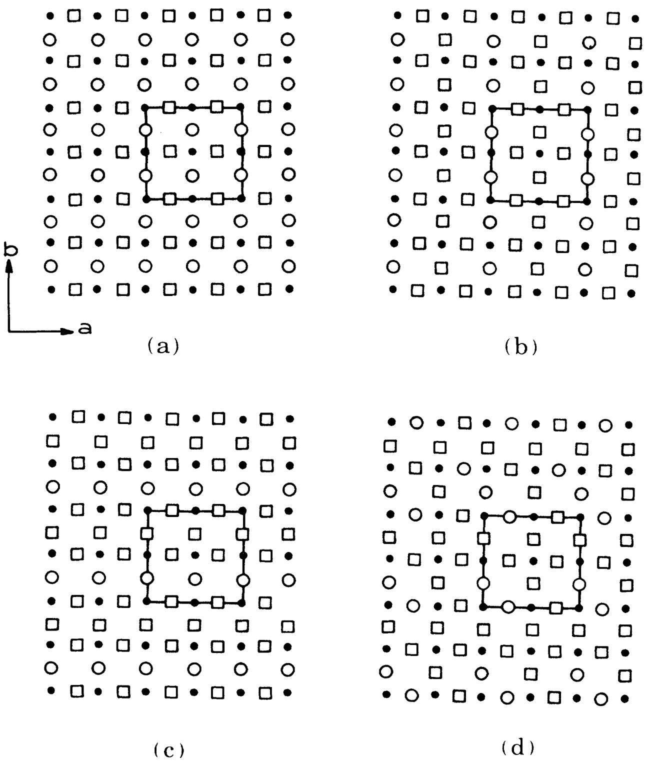


FIG. 2. Distribution of the oxygen atoms in the plane of the chains with filled circles representing Cu atoms, open circles oxygen atoms, and the open squares vacancies in (a) $YBa_2Cu_3O_7$, and in $YBa_2Cu_3O_{6/5}$ in (b) alternate chain model, (c) identical chain model, and (d) tetragonal-crystal structure.

The lattice parameters and the atomic positions in the $YBa_2Cu_3O_{7-\delta}$ family of superconductors depend quite sensitively on the oxygen stoichiometry and the crystal structure. Cava *et al.*[5] have performed a systematic study of the crystal structure of $YBa_2Cu_3O_{7-\delta}$ as a function of δ. Their data for four oxygen stoichiometries most relevant to the present investigation are given in Table I. In the orthorhombic crystal structure we have used their data corresponding to $\delta=0.05$ for $YBa_2Cu_3O_7$ and $\delta=0.55$ for $YBa_2Cu_3O_{6.5}$ while in the tetragonal case the data corresponding to $\delta=0.65$ for $YBa_2Cu_3O_{6.5}$ and $\delta=1.0$ for $YBa_2Cu_3O_6$ have been used. Generally speaking, there are always some minor differences in the crystal-structure data for the same oxygen stoichiometry from two different sources. Thus our use of the crystal structure data for all oxygen stoichiometries from the same source helps avoid such errors and should result in a proper representation of the charge distribution as a function of the stoichiometry of oxygen and the crystal structure.

The electronic-structure calculations were performed using the tight-binding recursion method with clusters of more than 2500 atoms. Increasing the cluster size to 3500 atoms did not affect the results, indicating the con-

TABLE I. Crystal-structure data from Cava *et al.* (orthorhombic space group *Pmmm*, $Z = 1$) for $YBa_2Cu_3O_{7-\delta}$ for various oxygen stoichiometries. Cu(1) is located at $1a(0, 0, 0)$, Y at $1h(1/2\ 1/2\ 1/2)$, Ba at $2t(1/2\ 1/2\ z)$, Cu(2) at $2q(0\ 0\ z)$, O(1) at $2s(1/2\ 0\ z)$, O(2) at $2r(0\ 1/2\ z)$, and O(6) at $2q(0\ 0\ z)$.

	Orthorhombic structure		Tetragonal structure	
Parameter	$\delta=0.05$	$\delta=0.55$	$\delta=0.65$	$\delta=1.00$
a (Å)	3.8136	3.8293	3.8580	3.8544
b (Å)	3.8845	3.8750	3.8580	3.8544
c (Å)	11.6603	11.7101	11.7913	11.8175
z(Cu(2))	0.3546	0.3573	0.3603	0.3602
z(O(1))	0.3781	0.3781	0.3788	0.3791
z(O(2))	0.3777	0.3768	0.3788	0.3791
z(O(6))	0.1572	0.1541	0.1515	0.1511
z(Ba)	0.1843	0.1878	0.1931	0.1944

vergence of calculations. In this method one works directly in real space without the need of a periodic structure, in contrast to the usual reciprocal-space methods which are based on Bloch's theorem and require periodicity. The densities of states are calculated directly at individual atomic sites through the recursion technique amounting essentially to an outward integration. A given atom interacts directly with its neighbors which in turn interacts with theirs, leading to an indirect interaction of the central atom with distinct neighbors. This technique has been described in detail elsewhere.[16] The $2s$ orbitals of oxygen lie at much lower energies than the oxygen $2p$ orbitals, and hence play no essential role in bonding. Thus p functions at the oxygen sites and d at other sites were included in our calculation. The important parameters are those involving Cu-O interactions which have been taken from the work of Mattheiss.[15,17] These parameters do not vary significantly in cuprate superconductors, including those with different local environments, and are thus transferable to many different problems of interest. A $1/d^2$ dependence, where d is the interatomic separation,, is used to take into account the distance dependence of the parameters. The densities of states obtained with this method for several cuprate compounds[18] are in good agreement with more elaborate *ab initio* calculations,[15,17,19] and demonstrate the reliability of this method and the transferability of the parameters in the study of cuprate superconductors. A similar conclusion concerning the transferability was reached by Zaanen *et al.*[13] who found in their study on the effect of chain fragments on doping that the tight-binding parameters obtained by fitting to their LDA (local-density approximation) results were insensitive to the stoichiometry in oxygen.

III. RESULTS AND DISCUSSION

Before discussing the results of our calculations in a few remarks concerning certain noteworthy features of the crystal structures of these $YBa_2Cu_3O_{7-\delta}$ compounds are in order. In Table II we present, based on the crystal-structure data given in Table I from Cava *et al.*,[5] several important bond-length parameters for the oxygen stoichiometries of interest in this work. Neglecting for the moment the variation of these bond lengths as a function of stoichiometry or crystal structure, it is quite clear from Table II that, despite a square pyramidal coordination, the planar Cu(2) atom retains in reality a fourfold square planar coordination since the apical O(6) oxygen atom to which it is connected is ~20% further away than the four O(1),O(2) oxygen atoms in its plane. This much longer Cu(2)-O(6) bond length renders the interaction of the planar Cu(2) atom with the apical O(6) atom much weaker as compared to that with the oxygens in its plane. This interaction is also much weaker in comparison to the one between the chain Cu(1) atom and the api-

TABLE II. Variation of certain bond lengths (in Å) as a function of stoichiometry in oxygen in $YBa_2Cu_3O_{7-\delta}$. The last two horizontal rows are the ratios of the bond lengths indicated.

Bond-length	Orthorhombic structure		Tetragonal structure	
parameter	$\delta=0.05$	$\delta=0.55$	$\delta=0.65$	$\delta=1.00$
Cu(2)-O(1)	1.9261	1.9301	1.9413	1.9401
Cu(2)-O(2)	1.9608	1.9509	1.9413	1.9401
Cu(2)-O(6)	2.3018	2.3795	2.4620	2.4710
Cu(1)-O(6)	1.8330	1.8045	1.7864	1.7856
Cu(1)-O(4)	1.9423	1.9375	1.9290	
$\frac{\text{Cu(2)-O(6)}}{\text{Cu(1)-O(6)}}$	1.2558	1.3186	1.3782	1.3838
$\frac{\text{Cu(2)-O(6)}}{\text{Cu(2)-O(1),O(2)}}$	1.1844	1.2262	1.2682	1.2736

cal O(6) atom since the bond length Cu(2)-O(6) is at least ~25% longer than the bond length Cu(1)-O(6) depending upon the stoichiometry. Indeed, it is this rather weak Cu(2)-O(6) interaction which confers on these materials a two-dimensional character. As Table II shows the chain Cu(1) atom forms a natural partner of the apical O(6) atom since the Cu(1)-O(6) bond length is the shortest. Actually, in $YBa_2Cu_3O_7$ the bond length Cu(1)-O(6) is even slightly shorter than the Cu(1)-O(4) bond length. But on the whole these bond lengths are such that the Cu(1) atom has a natural square planar coordination of its own in the *bc* plane. This leads to the formation of two separate sets of antibonding band complexes in the vicinity of the Fermi level as has been discussed by several authors:[10-13] (a) planar CuO_2 bands formed between the planar Cu(2) $d_{x^2-y^2}$ and the planar O(1) p_x and O(2) p_x orbitals, and (2) the chain CuO_3 bands formed between the chain Cu(1) $d_{z^2-y^2}$ orbital and the apical O(6) p_z orbital and the chain oxygen O(4) p_y orbital. The bond-length considerations, which we discussed above, are reflected in detailed electronic-structure calculations[13,15] which show a negligibly small hybridization between the planar CuO_2 bands and the chain CuO_3 bands. The relative positions of these band complexes determine the charge flow between the CuO_2 planes and the CuO_3 units, and the neglect of the hybridization between the two allows one to calculate this charge transfer, as also pointed out by Zaanen *et al.*[13] Note that in what follows, for convenience, we will use the name "CuO_3 unit" to designate the chain Cu(1) and the oxygen atoms associated with it, independent of the stoichiometry in oxygen or the arrangement of oxygens although the name is appropriate only for $YBa_2Cu_3O_7$.

Table II shows that the largest variation with oxygen stoichiometry occurs in fact in bond-length parameters that are associated with the apical oxygen, namely Cu(1)-O(6), and Cu(2)-O(6). This was noticed by Cava *et al.*[5] and has been related to the interplay of charge transfer between the CuO_2 planes and the CuO_3 units. These bond lengths are expected to play an important role in determining the relative positions of the two band complexes,[11] and hence in determining the charge transfer. These bond-length variations are, however, explicitly included in our calculations, since we use the crystal-structure data given in Table I from Cava *et al.*[5]

We now first discuss the results for the superconducting compound $YBa_2Cu_3O_7$ and compare them with the nonsuperconducting compound $YBa_2Cu_3O_6$ in which the oxygen atoms from the chain sites are missing. Table III gives the effective charges (number of electrons) at different atomic sites obtained by integrating the partial densities of states at these sites up to the Fermi level. We notice from Table III that both Y and Ba atoms are essentially ionic, acting as electron donors and retaining only a very small charge at their sites. This small charge arises from a very weak hybridization with the neighboring oxygens, and is in agreement with the generally accepted chemical description of these elements being of ionic nature in these compounds. As Table III shows, the charges at Y and Ba sites are nearly independent of the stoichiometry in oxygen since the charges at these two sites are essentially the same in the two compounds $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$. Indeed, as shown below, we obtain practically the same charges in the compound $YBa_2Cu_3O_{6.5}$, which remains essentially unaffected by the order or disorder at the chain site oxygens. In fact the largest change (±0.01 electron) occurs at Ba sites that are closer to the chain site oxygen atoms. This indicates that the major effect of the stoichiometry or the ordering of the chain site oxygens is to influence the charge balance between the CuO_2 planes and the CuO_3 units containing the CuO chains and the bridging (apical) oxygens.

Table III shows that in the nonsuperconducting $YBa_2Cu_3O_6$ the chain site Cu(1) and the apical oxygens

TABLE III. Effective charges (*p* at oxygen sites and *d* at other sites) at different atomic sites in nonsuperconducting tetragonal $YBa_2Cu_3O_6$ and superconducting orthorhombic $YBa_2Cu_3O_7$ compounds. The hole count is obtained by taking the total charge on a CuO_2 plane in $YBa_2Cu_3O_6$ corresponding to the half-filled-band situation as a reference.

Site	$YBa_2Cu_3O_6$	$YBa_2Cu_3O_7$
CuO_2 plane		
Cu	9.515	9.371
O(1)	5.587	5.496
O(2)	5.587	5.539
Total CuO_2 plane	20.689	20.406
Hole count	0.000	0.283
CuO_3 unit		
Apical oxygen	5.945	5.658
Chain Cu	9.957	9.428
Chain oxygen	Absent	5.612
Total CuO_3 unit	21.847	26.356
Y	0.423	0.425
Ba	0.176	0.202
Total	64.000	68.000

O(6) are in their insulating Cu^+ and O^{2-} ionic states, respectively. In fact $YBa_2Cu_3O_6$ is an antiferromagnetic insulator, and a Mott-Hubbard description is certainly more appropriate. Nevertheless, as pointed out by Mattheiss[15,17] and others,[10–13] we expect the overall charge distributions to be well described by the local-density approximation. Because of the insulating character of $YBa_2Cu_3O_6$ the total charge on a CuO_2 plane in $YBa_2Cu_3O_6$ provides a natural reference for calculating the charge transfers from the CuO_2 planes in different crystallographic situations; this charge transfer corresponds to the hole concentration in the CuO_2 planes with respect to the insulating ground state. Thus taking the calculated charge on a CuO_2 plane in $YBa_2Cu_3O_6$ in Table III as a reference we obtain a hole count of $0.283/CuO_2$ plane in $YBa_2Cu_3O_7$, a result which is in good agreement with the available experimental data[14] and previous calculations.[11,13,17]

The charge transfer from the CuO_2 planes in $YBa_2Cu_3O_7$ with respect to $YBa_2Cu_3O_6$ results from a rather delicate balance between the CuO_2 planes and the CuO_3 units, and can be understood qualitatively on chemical grounds[11] by considering the local coordination and geometry. Table III shows that the chain Cu(1) and apical oxygen O(6) atoms are no longer in their insulating ionic states in $YBa_2Cu_3O_7$ but participate covalently with the chain O(4) oxygen atoms to facilitate electron transfer. Essentially in $YBa_2Cu_3O_6$ the absence of oxygens along the chains puts the Cu(1) d_{z^2} level [interacting only with the apical oxygen O(6) p_z orbitals] below the Fermi level so that the planar $CuO_2\, d_{x^2-y^2}$ band (interacting with planar oxygen p_x and p_y orbitals) is half full. In $YBa_2Cu_3O_7$ the presence of O(4) oxygens along the chains brings two nonbonding O(4) p_x, p_z levels below the Fermi level. Further, the p_y interaction with the occupied Cu(1) d_{z^2} orbital (now properly designated as a $d_{z^2-y^2}$ orbital) results in an occupied bonding O(4) p_y–Cu(1) $d_{z^2-y^2}$ level, and the corresponding antibonding part in the vicinity of the Fermi level of $YBa_2CU_3O_6$. The O(4) oxygen brings only four electrons per unit cell. Thus the two additional lower levels being filled, the charge transfer depends in a crucial way on the position of the antibonding Cu(1) $d_{z^2+y^2}$–O(4) p_y state. If this state is completely above the Fermi level there will be no charge transfer. In $YBa_2Cu_3O_7$ this band is dispersed but the bottom of this band falls below the Fermi level. This leads to electron transfer from the CuO_2 planes so that the Fermi level is equalized. We find a downward shift in the Fermi level of ~ 0.2 eV in $YBa_2Cu_3O_7$ relative to $YBa_2Cu_3O_6$.

In Table IV we present the effective charges for the compound $YBa_2Cu_3O_{6.5}$ in the alternate chain model (ACM) and identical chain model (ICM) and in Table V in the tetragonal-crystal structure. In ICM, all Cu atoms in the plane of the chains are threefold *T*-shaped coordinated with oxygen atoms (two apical oxygen atoms and one oxygen atom in the plane of the chains) and are all equivalent. This makes all Cu atoms in CuO_2 planes also equivalent. In ACM on the contrary, there are two types of Cu atoms in the plane of the chains, namely, those where the chains are complete and have a fourfold square planar coordination as in $YBa_2Cu_3O_7$ and those where the chains are empty and are only twofold linearly coordinated as in $YBa_2Cu_3O_6$. This difference in coordination results in two different types of apical oxygens and two different types of Cu atoms on the CuO_2 planes. These are differentiated in Table IV in columns designated as full chains and empty chains, respectively. In the tetragonal-crystal structure, three types of Cu atoms exist in the plane of the chains: (1) fourfold-coordinated Cu

TABLE IV. Effective charges (*p* at oxygen sites and *d* at other sites) at different atomic sites in orthorhombic $YBa_2Cu_3O_{6.5}$ in the alternate chain (ACM) and identical chain (ICM) models. The hole count is obtained by taking the total charge on a CuO_2 plane in $YBa_2Cu_3O_6$ corresponding to the half-filled-band situation as a reference.

	Alternate chain model			Identical chain
Site	Empty chain	Full chain	Average	model
CuO_2 plane				
Cu	9.415	9.433	9.424	9.501
O(1)	5.542	5.542	5.542	5.587
O(2)	5.558	5.566	5.562	5.603
Total CuO_2 plane	20.515	20.541	20.528	20.691
Hole count	0.174	0.148	0.161	~ 0.0
CuO_3 unit				
Apical oxygen	5.915	5.675	5.795	5.712
Chain Cu	9.927	9.571	9.749	9.603
Chain oxygen	Absent	5.616	5.616	5.528
Total CuO_3 unit	21.757	26.537	24.147	23.791
Y	0.421	0.421	0.421	0.423
Ba	0.188	0.188	0.188	0.202
Total	63.584	68.416	66.000	66.000

TABLE V. Effective charges (p at oxygen sites and d at other sites) at different atomic sites in tetragonal $YBa_2Cu_3O_{6.5}$ corresponding to different coordinations of the chain site Cu. Note that for each twofold-coordinated chain Cu, there is one fourfold-coordinated chain Cu and two threefold-coordinated chain Cu atoms. The hole count is obtained by taking the total charge on a CuO_2 plane in $YBa_2Cu_3O_6$ corresponding to the half-filled-band situation as a reference.

Site	Twofold	Threefold	Fourfold	Average
CuO_2 plane				
Cu	9.519	9.495	9.497	9.501
O(1)	5.593	5.594	5.594	5.594
O(2)	5.593	5.594	5.594	5.594
Total CuO_2 plane	20.705	20.683	20.685	20.689
Hole count	~0.0	~0.0	~0.0	0.000
CuO_3 unit				
Apical oxygen	5.885	5.701	5.653	5.735
Chain Cu	9.907	9.544	9.368	9.591
Chain oxygen	Absent	5.484	5.481	5.483
Total CuO_3 unit	21.677	23.688	26.155	23.802
Y	0.422	0.422	0.422	0.422
Ba	0.199	0.199	0.199	0.199
Total	63.907	65.874	68.345	66.000

atoms (two apical oxygen atoms and two in the plane of the chains), however, this fourfold coordination is not the same as in $YBa_2Cu_3O_7$ since the oxygen atoms in the plane of the chains are not linear, (2) threefold-coordinated Cu atoms, and (3) twofold-coordinated Cu atoms. Again this difference in coordination makes the environment of Cu atoms on the planes just above or below different. These are differentiated in Table V in columns marked as fourfold-, threefold-, and twofold-coordinated chain Cu atoms in the plane of the chains. It should be noted that in a unit cell the number of twofold-coordinated chain Cu atoms is the same as the number of fourfold-coordinated chain Cu atoms but the threefold-coordinated chain Cu atoms are twice as numerous (see Fig. 2).

Intuitively one could think of the ACM to be a mixture of the $YBa_2Cu_3O_6$ (empty chains) and $YBa_2Cu_3O_7$ (full chains) compounds. If this was so the charge transfer would be expected only from the CuO_2 units above or below the full chains. Table IV shows that this is not the case. While one finds the Cu and the apical oxygen atoms associated with the empty chains to be approximately in the Cu^+ and O^{2-} states respectively and a comparison with $YBa_2Cu_3O_6$ in Table III shows that there are only minor differences in charges at these sites relative to $YBa_2Cu_3O_6$, the situation is quite different for the full chains. Further, in contrast to the case of $YBa_2Cu_3O_6$, charge is also transferred from the CuO_2 units above or below the empty chains, which now have holes. This hole count is approximately the same as on the CuO_2 units associated with full chains where there is a significant decrease in the number of holes as compared to $YBa_2Cu_3O_7$. Thus empty- and full-chain columns cannot be considered to be isolated or separate and there is some interaction between them. As shown in Table IV the empty-chain column unloads ~0.42 electrons on the full-chain column and the full chains alone now act as electron reservoirs. This charge transfer equalizes the hole concentration in the entire CuO_2 plane. The hole concentration $\sim 0.16/CuO_2$ in $YBa_2Cu_3O_{6.5}$ found for ACM compared to $\sim 0.28/CuO_2$ in $YBa_2Cu_3O_7$ is expected to result, on linear extrapolation, in a critical temperature $T_c \sim 52$ K in this compound which is in good agreement with experiment.

The mechanism of this charge transfer is the same as discussed previously for $YBa_2Cu_3O_7$. However, since the Cu(1) and O(6) atoms associated with the empty chains are in their nonconducting ionic states, due to the d_{z^2} level falling below the Fermi level, the antibonding Cu(1) $d_{z^2-y^2}$–O(4) p_y band associated with the full chains has to accommodate the charge transfer from twice as many CuO_2 planes as in $YBa_2Cu_3O_7$. Thus there is a lowering in the Fermi level but the depression in the Fermi level is not as much as in $YBa_2Cu_3O_7$ from $YBa_2Cu_3O_6$. We find a lowering of the Fermi level of ~0.1 eV in $YBa_2Cu_3O_{6.5}$ in ACM with respect to $YBa_2Cu_3O_6$ which is half as much as in $YBa_2Cu_3O_7$. This difference in behavior between the empty- and full-chain states leaves the empty chains insulating while the full chains are conducting and accommodate slightly more electrons than in $YBa_2Cu_3O_7$.

The situation is quite different for ICM or when the crystal symmetry is tetragonal. In both cases the charge transfer from the CuO_2 planes to the plane of the chains is quite insignificant, and one obtains essentially the same charge on a CuO_2 plane as in $YBa_2Cu_3O_6$. Although in the tetragonal-crystal structure both twofold- and fourfold-coordinated Cu atoms are present in the plane of the chains as in ACM, the local geometry of the fourfold-coordinated Cu is different—it no longer forms chains in the plane of the chains as in ACM but rather triangles. This change in geometry of the Cu atom, in addition to the presence of threefold-coordinated Cu atoms, results in a substantially reduced charge transfer to the fourfold-coordinated CuO_3 units as compared to that in ACM. A comparison of the charges in ICM (Table IV), where all Cu atoms are threefold coordinated in the plane of the chains, with the sites associated with the threefold-coordinated Cu in the tetragonal case (Table V), shows that there are only minor differences in charges at different atomic sites in the two cases. This can be interpreted to mean that the local coordination geometry of Cu atom plays a crucial role and that neither a threefold-coordinated Cu nor a fourfold-coordinated Cu with a triangular coordination in the plane of the chains are favorable configurations for the charge transfer from the CuO_2 planes to the planes of the chains, as also discussed by Burdett *et al.*[11]

In our calculation we find that there is essentially no shift in the Fermi level in $YBa_2Cu_3O_{6.5}$ in ICM and tetragonal-crystal structures with respect to $YBa_2Cu_3O_6$. Alternatively, there is an upward shift of ~ 0.2 eV with respect to the orthorhombic $YBa_2Cu_3O_7$. This can be understood qualitatively in terms of the local coordination of the chain Cu(1) atom. Removal of the alternate oxygen atoms along the *b* axis from $YBa_1Cu_3O_7$ to obtain ICM results in a T-shaped coordination of Cu(1). This removes two occupied states [two nonbonding O(4) p_x and p_y levels] and affects a bonding Cu(1) $d_{z^2-y^2}$–O(4) p_y level and a partially occupied antibonding Cu(1) $d_{z^2-y^2}$–O(4) p_y level per unit cell doubled along the *b* axis while removing only four electrons associated with that oxygen. The result is an upward shift in the Fermi level with respect to $YBa_2Cu_3O_7$ despite a downward shift in the $d_{z^2-y^2}$-p_y antibonding band. The situation is the same for a threefold-coordinated Cu(1) in the tetragonal model of $YBa_2Cu_3O_{6.5}$. The twofold-coordinated Cu(1) in the tetragonal structure has a situation comparable to that in $YBa_2Cu_3O_6$. The case of the fourfold-coordinated Cu(1) is somewhat different. In this case the presence of oxygen atoms both along the *a* and *b* axes transforms a nonbonding oxygen p_x orbital in $YBa_2Cu_3O_7$ into an occupied bonding orbital and a partially occupied antibonding orbital. This raises the Fermi level so that it can be equalized throughout the crystal, and results in the elimination of holes in the planar CuO_2 bonds. It should be noted that this is only a qualitative description and the Fermi level is not determined separately for each coordination geometry but rather for the crystal as a whole with all coordination geometries treated simultaneously. A comparison of Tables IV and V shows that the average valence of Cu(1) in tetragonal structure is essentially the same as in ICM and is really close to Cu^{2+}, which makes them nonconducting. Note that in a purely ionic model one would expect a total charge of 24 electrons on a CuO_3 unit in $YBa_2Cu_3O_{6.5}$ [a CuO_3 unit here has a Cu(1), two O(6) atoms, and on the average 0.5 oxygen atoms in the plane of the chains and has a formal electronic configuration $(CuO_{2.5})^{3-}$]. However, because Y and Ba atoms are not fully ionic and retain a small charge at their sites due to hybridization with neighboring oxygen atoms we obtain a slightly smaller charge. The closest neighbors of a Ba atom are the four oxygen atoms O(6) in its plane, four oxygen atoms O(1), O(2) in the CuO_2 plane, and an oxygen atom in the plane of the chains, while the closest neighbors of an Y atom are the eight oxygen atoms in the two CuO_2 planes above and below it. Thus to obtain a picture closest to the ionic model which neglects the hybridization, we might as a first approximation partition the charge on a Ba atom equally on the nine neighboring oxygen atoms. With this we find an average of ~ 24 electrons on a CuO_3 unit in both ICM and tetragonal-crystal structures, which shows that the average valence of Cu(1) in these structures is essentially Cu^{2+}, the same as on a CuO_2 plane. This renders both the CuO_2 planes and the plane of the chains in these structures insulating.

IV. CONCLUSION

Our calculations show that the ordered chains are essential for charge transfer from CuO_2 planes and hence for superconductivity in $YBa_2Cu_3O_{6.5}$ and the disorder in the chains inhibits the charge transfer and renders the CuO_2 planes insulating. These results can be used to explain qualitatively the recent results of Jorgensen *et al.*[6] who observed the appearance of superconductivity in an originally nonsuperconducting $YBa_2Cu_3O_{6.41}$ sample after annealing at room temperature. We believe that in their original sample the oxygen atoms in the plane of the chains are randomly distributed. In this case, the local coordinations around Cu atoms in the plane of the chains are either twofold, threefold, or nonplanar fourfold and, as we have discussed above, all these coordinations are unfavorable for charge transfer from the CuO_2 planes to the plane of the chains. The material is thus nonmetallic and nonsuperconducting. Thermodynamically, an ordered state is, however, favored. For this, diffusion lengths of $b/\sqrt{2} \sim 3$ Å are required so that the oxygen atoms on the *a* axis can jump onto the empty sites on the *b* axis to form chains. If the chains were complete, a $T_c \sim 35$–40 K would be expected for $YBa_2Cu_3O_{6.41}$ taking into account roughly the effect of stoichiometry in oxygen. The lower $T_c \sim 20$ K quite likely results because of the formation of short, fragmented chains. A Cu atom at the end of a fragmented chain is only threefold coordinated. As we have discussed above, this threefold coordination inhibits the charge transfer from the planes to the chains. The result is an overall decrease in the number of holes in the CuO_2 planes, and hence a decrease in T_c.

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