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Relationship between radiation-induced orthorhombic-tetragonal phase transformation and loss of superconductivity in $YBa_2Cu_3O_7$

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Under low-temperature ion irradiation, the superconductor $YBa_2Cu_3O_7$ transforms into an insulator at relatively low doses ~ 0.04 displacement per atom. This change to the insulating state is accompanied by a crystallographic phase transition from the orthorhombic to tetragonal symmetry. There is no loss of oxygen and this phase transition has been attributed to the disordering of the oxygens in the plane of the chains. Results of electronic-structure calculations are presented in this paper which show that the ordering of the oxygen atoms in the plane of the chains plays a crucial role in the charge transfer from the CuO_2 planes. Two models for the disordering of the oxygen atoms in the plane of the chains have been considered for this purpose. In each case, an alternate oxygen atom from the chains along the *b* axis is missing and is assumed to populate the originally vacant oxygen sites along the *a* axis, leading to a complete distruction of the chains and an identical population of the oxygen atoms along both the *a* and *b* axes in the irradiated sample. Our calculations show that this destruction of the chains under irradiation results in a drastic reduction of the electron transfer from the CuO_2 planes to the planes of the chains, although the stoichiometry in oxygen remains unchanged. This reduction in the hole density renders the compound insulating. Our calculations also point out the vital role which the local coordination geometry of the chain-site Cu atom plays in controlling the charge transfer from the CuO_2 planes. Displacement of the oxygen atoms from the chains to the originally vacant sites along the *a* axis in the two models of the irradiated crystal structure considered in the present work results in the transformation of the square-planar coordination of the chain-site Cu atom into a non-square-planar fourfold coordination. We find that it is this change in the coordination geometry that results in a drastic reduction of the hole-carrier density in the CuO_2 planes.

I. INTRODUCTION

The effects of irradiation in high-T_c cuprate superconductors have been investigated quite intensively.[1–14] The compound $YBa_2Cu_3O_7$ with a $T_c \sim 90$ K stands out as a promising candidate for technological applications, and it has thus been the most widely studied. The electronic properties of this high-T_c superconductor are highly sensitive to irradiation. The effect of irradiation is to create defects and the nature of these defects depends upon the particle and the energy employed for irradiation. But in general, at low temperatures and low doses there is a gradual decrease in the superconducting transition temperature T_c, a gradual broadening of the transition width ΔT_c, and an increase in the normal-state resistivity as a function of increasing dose.[1–3] At higher doses, in the $YBa_2Cu_3O_7$ compound, there is a sharp drop in T_c and an exponential increase in the resistivity, and then a transformation from the superconducting to the insulating state occurs at doses which correspond to ~ 0.02–0.04 displacement per atom (dpa).[1–6] This transformation is direct and the material never passes through a nonsuperconducting metallic state. This is in contrast to the case of conventional non-oxide superconductors where the effect of irradiation is to depress the T_c or to supress it altogether, but the material nevertheless remains metallic.[1,2] Furthermore, the doses which are required to drive the superconductor→insulator transition are roughly two orders of magnitude lower than those which are needed for the suppression of T_c in the conventional superconductors.[1,2] The transformation from the superconducting to the insulating state is accompanied by an orthorhombic→tetragonal (*O-T*) crystallographic phase transition.[1–6] This *O-T* phase transition is reversible if the level of dose does not exceed a certain critical value, and the material partly or completely recovers the T_c after simply annealing in air at room temperature. This recovery of T_c in ambient atmosphere indicates that the oxygen is not lost from the sample during irradiation. At even higher doses or with highly energetic ions the structure becomes highly disordered and amorphization occurs[7–9] at >0.15 dpa.

In conventional superconductors, the lattice disorder caused by defect production under irradiation is primarily responsible for the increase of resistivity. However, this increase in resistivity is linear as a function of dose, and eventually saturates when defects begin to overlap.[1] The underlying electronic structures of these superconductors are such that even in their highly disordered states they remain metallic, although the disorder can result in a lowering of T_c or the loss of superconductivity. The simultaneous loss of metallicity and superconductivity is a property which is quite unique to the oxide superconductors,[1-3] and in particular to the cuprate superconductors.[2] This indicates that the effect of irradiation on the electronic properties of these compounds is rather subtle. A clue to understanding the effect of irradiation in the $YBa_2Cu_3O_7$ superconductor comes from the low level of dose needed to destroy superconductivity and the rapid recovery of the superconducting properties by annealing at room temperature. It is true that under irradiation all types of atoms are displaced, but this displacement depends upon the mass of an atom and its location in the lattice. A lighter atom is easier to displace. Furthermore, if the atom is loosely bound in the lattice and has vacant lattice sites nearby, it will be ejected rather easily from its lattice site. This makes the oxygen atoms along the chains in the $YBa_2Cu_3O_7$ superconductor the dominant source of atomic displacement under irradiation. Furthermore, the easy recovery of the superconducting properties at room temperature indicates that there is probably only a disordering of the oxygen atoms in the chains, so that the sites along the *a* axis which were empty in the unirradiated compound now begin to populate.[1-5,11-14] Eventually one reaches a situation where the populations along both the *a* and the *b* axes are equal. In this case, there is a complete disordering of the chains, and necessarily a crystallographic phase transformation from the orthorhombic to the tetragonal crystal symmetry. Note that the degradation of the superconducting properties in $YBa_2Cu_3O_7$ is much more sharper and happens at much lower doses[2,3] than in $La_{1.85}Sr_{0.15}CuO_4$, in which there are no chains. This comparison also indicates that in $YBa_2Cu_3O_7$ it is primarily the complete destruction of the chains that is responsible for the loss of superconductivity.

At first sight it is not clear why the destruction of the chains should result in the loss of metallicity and superconductivity since the stoichiometry in oxygen of the material remains unchanged. The stoichiometry in oxygen has been considered to be the crucial parameter governing the superconducting transition temperature T_c of the $YBa_2Cu_3O_{7-\delta}$ family of superconductors. Indeed the T_c depends so strongly on the stoichiometry δ in oxygen[15,16] that the highest $T_c \sim 90$ K is obtained only for $\delta \leq 0.1$. For $\delta > 0.2$ there is a sharp drop in the T_c and one obtains a $T_c \sim 60$ K for $0.3 < \delta < 0.5$. For $\delta > 0.5$ there is again a sharp drop until the material becomes nonsuperconducting for $\delta > 0.65$. The transition from the superconducting to the nonsuperconducting state is accompanied by a metal-insulator transition. There is also a crystallographic phase transformation since the crystal structure in the superconducting phase is orthorhombic but changes to tetragonal in the nonsuperconducting phase.

Thus the crystallographic phase transformation from the orthorhombic-tetragonal crystal structure that takes place under irradiation is in certain respects similar to the one that occurs as a function of oxygen stoichiometry. In both cases the compound is superconducting only in the orthorhombic phase and turns insulating and nonsuperconducting in the tetragonal phase. One could therefore be tempted to attribute the orthorhombic-tetragonal transition under irradiation to the loss of oxygen. However, the recovery of the superconducting properties after annealing at room temperature indicates that the oxygen is not lost from the sample.[1-4]

The role of orthorhombicity in the superconducting properties of the $YBa_2Cu_3O_{7-\delta}$ family of superconductors has been discussed quite extensively in the literature.[15-28] A large portion of the experimental work[15-18] has, however, been concerned with establishing a correlation between the decrease in orthorhombicity and T_c as a function of increasing δ. On the other hand, the theoretical investigation[19,20] of the phase diagram of $YBa_2Cu_3O_{7-\delta}$ as a function of δ has shown that the orthorhombic phase in which the chains are ordered is favored thermodynamically in the superconducting region. Two types of orthorhombic phases have been proposed to exist predominantly in the superconducting region: ortho-I consisting of $YBa_2Cu_3O_7$ and ortho-II consisting of $YBa_2Cu_3O_{6.5}$ The latter is a fully ordered phase in which again the chains are completely ordered in an alternate fashion with full, empty, full, . . . sequence. This results in a doubling of the lattice parameter along the *a* axis and gives rise to a superstructure which has been identified experimentally.[21,22] The 60-K plateau region appears to result primarily from the ortho-II phase, although an overlap with the ortho-I phase may also be present.

From these investigations it is clear that it is really not the orthorhombicity that is of interest for superconductivity; it is rather the formation of fully ordered chains that is more relevant, and this chain formation along the *b* axis (see Fig. 1) is reflected in an orthorhombic distortion. Clearly when the chains are completely broken and disordered and the oxygens have a random distribution so that the populations along both *a* and *b* axes are equal, the overall crystal symmetry is tetragonal. It is in this structure which has no chains that the compounds are insulating and not superconducting. On the other hand, a tetragonal diffraction pattern can also result from orthorhombic domains consisting of broken chains but which are oriented in a manner so that the occupancies of oxygens atoms both along *a* and *b* axes are equal.[22] In this case the true crystal symmetry is really orthorhombic although the overall crystal symmetry is tetragonal.[16] Such a compound is not necessarily an insulator or not a superconductor, but the existence of superconductivity and T_c depends upon the lengths of the broken chains and their distribution.

A remarkable property of all cuprate superconductors is the presence of the two-dimensional CuO_2 planes. The ground state of these compounds is insulating and antiferromagnetic. Superconductivity arises when they are doped either chemically or structurally, which creates carriers in the CuO_2 planes thus rendering them metallic. Although the mechanism of superconductivity in these cuprate superconductors is still not understood, it is nonetheless clear that a relationship exists between T_c and the concentration of carriers in the CuO_2 plane.[29] We have recently[27] shown that the ordering of the oxygen atoms in the chains plays a crucial role in controlling the carrier concentration in the CuO_2 planes in $YBa_2Cu_3O_{6.5}$. For this purpose three models of the crystal structures were considered, the first two of which are orthorhombic: an alternate chain model (ACM) where each alternate chain is fully intact and the adjacent one fully empty (this is the ortho-II phase discussed above), an identical chain model (ICM) where all chains are identical but broken since an alternate oxygen atom from each chain is missing (notice that the crystal symmetry of this model is orthorhombic since there are no oxygens along the *a* axis), and a crystal structure in which also there are no chains and the oxygen sites along both *a* and *b* axes are equally populated. It was found that practically no charge transfer occurs from the CuO_2 planes in the latter two models which have no chains (despite the fact that the crystal symmetry in ICM's is orthorhombic), and thus the CuO_2 planes remain insulating. Our results are in agreement with those of Lambin,[26] who considered a tetragonal structure with a random distribution of oxygen atoms and also found almost no charge transfer from the CuO_2 planes. On the other hand, in ACM's where the alternate chains are fully ordered ~0.16 hole/CuO_2 (as compared to ~0.28 hole/CuO_2 in superconducting $YBa_2Cu_3O_7$) in each CuO_2 plane were obtained. This hole carrier density, which is quite significant, renders it superconducting although with a reduced $T_c \sim 52$ K due to a reduction in the hole density. This value of T_c agrees quite well with the one found in the second plateau region. This shows that it is not the crystal symmetry (orthorhombic or tetragonal crystal structure) which is of interest for superconductivity but rather the presence of intact chains, and that the complete destruction of chains can render this compound nonmetallic and nonsuperconducting. At a local level it is the coordination geometry around the chain-site Cu atom that plays the critical role in controlling the charge transfer form the CuO_2 planes. We found that the twofold, threefold, and the non-square-planar fourfold coordinations of the chain-site Cu atom are not favorable for charge transfer from the CuO_2 planes, and that the fourfold square planar coordination was essential for a significant hole carrier density and hence superconductivity to occur.

In this paper, we present the results of our electronic structure calculations for the compound $YBa_2Cu_3O_7$, which show that, in this compound as well, the criterion of the maximum stoichiometry in oxygen is not of sufficient value for attaining the maximum T_c, and that the ordering of the oxygen atoms along the chains plays a crucial role. We find that the destruction of the chains in $YBa_2Cu_3O_7$ results in a drastic decrease in the hole carrier density in the CuO_2 planes. Displacement of an oxygen atom from the chains along the *b* axis to the originally vacant sites along the *a* axis changes the local coordination geometry of the chain-site Cu atom from the fourfold square planar to fourfold non-square-planar. It is this change in the coordination geometry that destroys the hole density in the CuO_2 planes. Our results thus suggest that the observed loss of metallicity and superconductivity in $YBa_2Cu_3O_7$ under irradiation can be accounted for by the suppression of the hole carriers in the CuO_2 planes caused by the destruction of chains.

II. DETAILS OF CALCULATION

A schematic representation of the crystal structures of $YBa_2Cu_3O_7$ in the superconducting and the irradiated phases is shown in Fig. 1. While several models for the distribution of the oxygen atoms in the plane of the chains in the irradiated crystal can be envisaged, two of them have been considered in the present work in the absence of detailed structural information, and are shown in Fig. 2. In each case an alternate oxygen atom in each chain along *b* axis is missing and transferred to the previously unoccupied sites along the *a* axis. (Note that the models shown in Fig. 2 are the simplest and have an ordered arrangement of oxygen atoms. They differ in the local environment of the oxygen atoms.) Thus in each case the chain Cu(1) atom is fourfold coordinated with the oxygen atoms: two apical oxygens and two in the plane of the chains. However, in neither case is this coordination square planar as observed in the superconducting crystal structure. The lattice parameters and atomic positions were taken from the work of Cava *et al.*[17] Since no crystal structure measurements exist in the irradiated crystal structure of $YBa_2Cu_3O_7$ the *a* or *b* lattice parameter was taken to be an average of the *a* and *b* lattice parameters in the orthorhombic phase and the *c* lattice parameter was kept unchanged. It is known[1-3] that there is a slight expansion in the lattice parameters under irradiation. However, since precise information concerning the atomic positions is not available, this expansion of the lattice parameters was not taken into consideration.

The electronic structure calculations were performed using the tight-binding recursion method with clusters of more than 2500 atoms and included *p* functions at oxygen sites and *d* functions at other sites. The techniques has been described in detail elsewhere[30] where the mathemat-

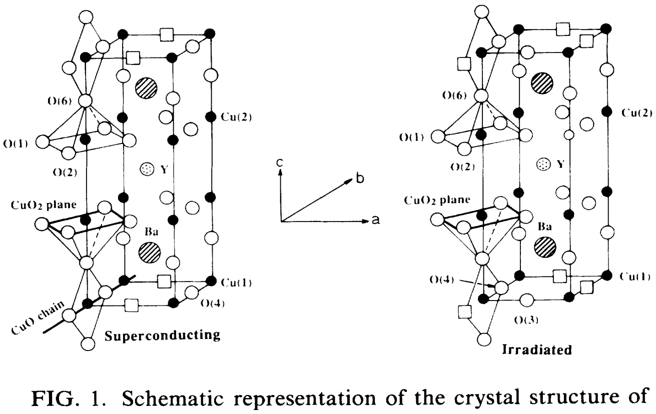

FIG. 1. Schematic representation of the crystal structure of $YBa_2Cu_3O_7$ in the superconducting and irradiated phases. Open squares represent the vacant oxygen sites.

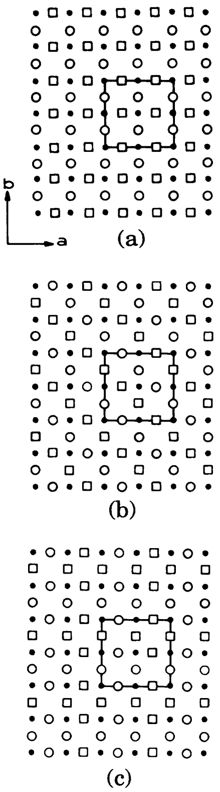

FIG. 2. Distribution of the oxygen atoms in the plane of the chains in $YBa_2Cu_3O_7$, with filled circles representing Cu atoms, open circles oxygen atoms, and the open squares vacancies in (a) superconducting, and in irradiated crystal structures (b) model I, and (c) model II.

ical formulation is also given. Increasing the cluster size did not affect the results significantly, indicating the convergence of the calculations. The important parameters are those involving Cu-O interactions, which have been taken from the work of Mattheiss and Hamann.[31] These parameters do not vary significantly in cuprate superconductors, including those with different local environments, and are thus transferable for investigating many different problems of interest. A $1/d^2$ dependence, where d is the interatomic separation, is used to account for the distance dependence of the parameters. The densities of states obtained with this method for several cuprate superconductors[32] are in good agreement with more elaborate *ab initio* calculations,[33] which demonstrates the reliability of this method and the transferability of the parameters in the study of the cuprate superconductors.[26]

III. RESULTS AND DISCUSSION

In the $YBa_2Cu_3O_{7-\delta}$ family of superconductors the planar Cu(2) atom has a square pyramidal coordination (see Fig. 1 for notation). However, the apical O(6) oxygen atom to which a Cu(2) atom is bonded is $\sim 20\%$ further away than the four O(1), O(2) oxygen atoms in its plane.[17] This much longer Cu(2)-O(6) bond length renders the interaction of the planar Cu(2) atom with the apical O(6) oxygen atom much weaker in comparison to that with the oxygens in its plane, so that in reality the planar Cu(2) atom retains a fourfold square-planar coordination. In fact, the chain Cu(1) atom forms a rather natural partner of the apical O(6) oxygen atom since the Cu(1)-O(6) bond length is the shortest, independent of the stoichiometry.[17,27] Actually, in superconducting $YBa_2Cu_3O_7$ Cu(1)-O(6) and the Cu(1)-O(4) bond lengths are such that the chain Cu(1) atom has a square-planar coordination of its own in the *bc* plane. Indeed, it is this rather weak Cu(2)-O(6) interaction that confers on these materials a two-dimensional character. This leads to the formation of two separate sets of antibonding band complexes in the vicinity of the Fermi level with a rather negligibly small hybridization between them, as has been discussed by several authors:[23-27,31] (1) planar CuO_2 bands formed between the planar Cu(2) $d_{x^2-y^2}$ orbital and the planar O(1) p_x and O(2) p_y 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 in orthorhombic $YBa_2Cu_3O_7$ (note that we have aligned a, b, and c along the Cartesian x, y, and z axes). The relative positions of these band complexes determine the charge transfer between the CuO_2 planes and the CuO_3 units. The neglect of the hybridization between the two allows one to calculate the charge transfer, as also discussed by Zaanen *et al.*[26]

The calculation of the charge transfer requires a knowledge of the electronic charge distribution at different atomic sites. This can be obtained by integrating the local densities of states at these sites up to the Fermi level. In Table I we have given the effective charges at different atomic sites calculated in this manner for the insulating compound $YBa_2Cu_3O_6$ and the compound $YBa_2Cu_3O_7$ in the superconducting and the irradiated crystal structures. Note that we use the name "CuO_3 unit" to designate the chain Cu(1) atom and the oxygens associated with it [apical O(6) oxygen atoms and the O(3), O(4) oxygen atoms in the plane of Cu(1)], independent of the stoichiometry in oxygen or the arrangement of oxygens although the name is appropriate for only $YBa_2Cu_3O_7$.

Table I shows that Y and Ba 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 ionic in nature in these compounds. We also see from Table I that in the insulating $YBa_2Cu_3O_6$ the chain site Cu(1) and the apical O(6) oxygen atoms are in their insulating Cu^+ and O^{2-} ionic states, respectively, so that the planar CuO_2 bands are half filled. In fact $YBa_2Cu_3O_6$ is an antiferromagnetic insulator, and a Mott-Hubbard description is certainly more appropriate. However, as pointed out by Mattheiss and Hamann[31] and others,[23-27,33] we expect the overall charge distribution 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 this compound provides a natural reference for calculating the charge transfers from the CuO_2 planes in different

TABLE I. Effective charges (p at oxygen sites and d at other sites) at different atomic sites in insulating $YBa_2Cu_3O_6$ compound, and in $YBa_2Cu_3O_7$ in the superconducting and irradiated crystal structures. The hole count is obtained by taking the total charge on a CuO_2 plane in $Yba_2Cu_3O_6$ as a reference. Chain oxygen is an oxygen atom in the plane of the chains.

Site	$YBa_2Cu_3O_6$	Superconducting $YBa_2Cu_3O_7$	Irradiated $YBa_2Cu_3O_7$ Model I	Model II
CuO_2 plane				
Cu(2)	9.515	9.371	9.460	9.447
O(1)	5.587	5.496	5.577	5.586
O(2)	5.587	5.539	5.577	5.586
Total CuO_2 plane	20.689	20.406	20.614	20.619
Hole count	0.000	0.283	0.075	0.070
"CuO_3" unit				
Apical oxygen O(6)	5.945	5.658	5.632	5.630
Chain Cu(1)	9.957	9.430	9.287	9.256
Chain oxygen O(4),O(3)	Absent	5.613	5.389	5.372
Total "CuO_3"	21.847	26.359	25.940	25.888
Y	0.423	0.425	0.426	0.424
Ba	0.176	0.202	0.203	0.225
Total	64.000	68.000	68.000	68.000

crystallographic situations, and 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 I as a reference we obtain a hole count of $0.283/CuO_2$ in $YBa_2Cu_3O_7$ in the superconducting phase, a result that is in good agreement with the available experimental data[29] and previous calculations.[23,26,32] On the other hand, we find from Table I that in $YBa_2Cu_3O_7$ this hole count is dramatically reduced in the irradiated phase from its value in the superconducting phase. Although there is a slight difference in the charge redistribution in the two models of the irradiated crystal structure considered in this paper, we obtain nonetheless in each case a very small hole count of $\sim 0.07/CuO_2$ in the CuO_2 planes. This shows that the stoichiometry in oxygen is not a sufficient condition for determining the hole concentration in the CuO_2 planes, and that the local coordination geometry around the chain-site Cu(1) atom plays a deciding role in controlling its value.

This can be understood on physical grounds. The charge transfer from the CuO_2 planes in these compounds depends on a rather delicate balance between the positions of the antibonding band complexes formed by the CuO_2 planes and those by the CuO_3 units. In $YBa_2Cu_3O_6$ the chain Cu(1) atom interacts essentially with the P_z orbitals of the apical O(6) atoms through its d_{z^2} orbital. The antibonding band which is formed through this interaction falls below the Fermi level. This leaves the antibonding bands formed by the planar Cu-O interactions exactly half full. In the superconducting $YBa_2Cu_3O_7$ the addition of the O(4) oxygen atoms to form chains along the b axis leads to the formation of two nonbonding O(4) p_x and O(4) p_z levels which lie below the Fermi level. Further, the interaction of the O(4) p_y level with the Cu(1) d_{z^2} level, which was occupied in $YBa_2Cu_3O_6$ and now properly designated as Cu(1) $d_{z^2-y^2}$, gives rise to an occupied bonding Cu(1)$d_{z^2-y^2}$–O(4)p_y level, and the corresponding antibonding part in the vicinity of the Fermi level. Thus the presence of the chain O(4) oxygen atoms results in the formation of three additional bands. However, an O(4) oxygen atom brings only four p electrons [note that there is only one O(4) oxygen atom per unit cell in the chains]. This leaves the antibonding band in the vicinity of the Fermi level nearly empty. If this band was fully empty falling above the Fermi level, there will again be no charge transfer from the planar CuO_2 antibonding band, which will remain half filled as in $YBa_2Cu_3O_6$. However, in superconducting $YBa_2Cu_3O_7$ the bottom of this band falls below the Fermi level. This leads to a lowering of the Fermi level and an electron transfer from the planar CuO_2 bands so that the Fermi level can be equalized. We find a downward shift of ~ 0.2 eV in the Fermi level in superconducting $YBa_2Cu_3O_7$ with respect to $YBa_2Cu_3O_6$.

The situation is somewhat different for the irradiated $YBa_2Cu_3O_7$. In this case, although the chain Cu(1) atom remains fourfold coordinated, this coordination is very different from the one which is found in the superconducting case, and the chain Cu(1) atom no longer has the square-planar coordination in the bc plane. The removal of an oxygen atom along the b axis and its presence along the a axis transforms a nonbonding occupied oxygen p_x orbital in the superconducting structure into an occupied and a partially occupied antibonding orbital in the irradiated structure. Further, it establishes direct interaction between the two O(4) and O(3) oxygen atoms in the plane of the chains,which are now only a distance $b/\sqrt{2} \sim 2.7$ Å apart rather than $b \sim 3.8$ Å in the superconducting structure. This direct interaction pushes the Cu-O states of the "CuO_3" unit, which were originally in the vicinity of the Fermi level, to higher energies. Thus the net result of having a chain Cu(1) atom triangularly coordinated in the CuO plane in the irradiated structure rather than with a linear coordination of the superconducting structure, is that there is an upward shift in the Fermi level in the irradiated crystal structure with respect to the superconducting one. We find an upward shift in the Fermi level of ~ 0.2 eV in the irradiated phase relative to the superconducting one, which puts the Fermi energy in this case at essentially the same level as found in the insulating $YBa_2Cu_3O_6$. This leads to an electron transfer from the plane of the chains back to the two-dimensional CuO_2 planes, and thus a filling of the holes in the CuO_2 planes. From Table I we notice that there is hardly any change in the electronic charges at the apical oxygen O(6) sites or the ionic Y and Ba sites with the change in the crystal symmetry. But there is a depletion of electronic charge at the Cu(1) and O(3),O(4) sites in the irradiated crystal structure, which is directly compensated by a corresponding increase of electronic charge at the planar Cu(2) and O(1),O(2) sites. This shows that there is a direct relationship between the hole carrier density in the CuO_2 planes and the degree of order in the CuO chains. The number of holes $\sim 0.07/CuO_2$ found in our calculation in the irradiated crystal structure falls in the limit where electron localization is expected to occur[29] and one expects the compound to be insulating. Note that in our calculation we have ignored the lattice expansion which occurs under irradiation. Preliminary calculations show that the inclusion of this expansion in the calculation reduces even further the number of holes.

From Table I we may calculate the valence of Cu in different crystal structures since it is quite common in cuprates to associate a valence of +2 with the insulating state and to express the hole concentration in terms of a Cu valence greater than +2 It is quite clear from Table I that the Cu-O interactions are, truly speaking, of covalent nature and the charges at the two types Cu(1),Cu(2) sites are not significantly different from each other in $YBa_2Cu_3O_7$. The discussion in terms of a Cu valence, however, implicitly assumes all elements to be completely ionic. In our calculation, we find that Y and Ba atoms are not completely ionic but retain a small charge at their sites due to hybridization with the neighboring oxygens. The closest neighbors of a Ba atom are the four apical O(6) oxygens in its plane, four planar oxygens O(1),O(2) in the CuO_2 plane, and two O(4),O(3) oxygen atoms in the plane of the chains, while the closest neighbors of a 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 share the charges on Y and Ba atoms equally with all of the neighboring oxygen atoms. The total charges thus obtained on the CuO_2 planes and the CuO_3 units are given in Table II. Assuming further the ionic configuration O^{2-} for oxygens to arrive at a completely ionic picture, we can calculate the ionic charge at a Cu site and thus the ionic valence of Cu. These are also shown in Table II. We see in Table II that in insulating $YBa_2Cu_3O_6$ the valence of Cu in the CuO_2 planes is $\sim +2$ and in the chains $\sim +1$. In the superconducting $YBa_2Cu_3O_7$ the valence at Cu(2) and Cu(1) sites are quite close with values of $+2.3$ and $+2.4$, respectively. In the irradiated crystal structure we find that there is a drastic reduction in the valence of Cu at the planar Cu(2) sites where it is essentially stabilized at $\sim +2$. This results in the chain site Cu(1) with a valence $\sim +3$. With this we expect both the CuO_2 planes and the plane of the chains to be insulating.

This drastic reduction in the hole density found in our calculation in the irradiated crystal structure may be considered to be in disagreement with the carrier density obtained from the Hall-effect measurements,[6] which show a decrease only by a factor of 2 in the carrier density at 300 K in the irradiated insulating $YBa_2Cu_3O_7$. This has been interpreted to mean that the carrier density does not change much with damage and instead carrier localization occurs which leads to the insulating behavior. The carrier density n from the Hall-effect measurements is calculated from the standard formula $R_H = 1/nec$, which is valid only in the free-electron limit. Further, in $YBa_2Cu_3O_7$ the carrier density thus obtained varies strongly with temperature, in contrast with the constant

TABLE II. Total charges at the CuO_2 planes and the CuO_3 units in insulating $YBa_2Cu_3O_6$ compound, and in $YBa_2Cu_3O_7$ in the superconducting and irradiated crystal structures, obtained by a sharing of charges at Y and Ba sites with the neighboring oxygens, as explained in the text. Also given are the valence of Cu obtained from these charges assuming an ionic model.

Site		Superconducting	Irradiated $YBa_2Cu_3O_7$	
	$YBa_2Cu_3O_6$	$YBa_2Cu_3O_7$	Model I	Model II
CuO_2 plane				
Total charge	20.989	20.699	20.908	20.921
Valence Cu(2)	+2.011	+2.301	+2.092	+2.079
CuO_3 unit				
Total charge	22.023	26.601	26.184	26.158
Valence Cu(1)	+0.977	+2.399	+2.816	+2.842

value predicted by the free-electron formula. This anomalous temperature dependence, the origin of which is still not understood, makes the calculation of the carrier density from the Hall coefficient of dubious value.[34] It should be noted in this connection that in the double-chain compound $YBa_2Cu_4O_8$ with a $T_c = 80$ K one expects a value of the carrier density in the CuO_2 planes that is similar to what is found for $YBa_2Cu_3O_7$. The Hall-effect measurements, on the other hand, yield a value which is ten times higher.[35] It was therefore concluded[35] that the role of the double chains has to be considered in the interpretation of the Hall data. In the irradiated $YBa_2Cu_3O_7$, a significant contribution to the Hall voltage may arise from the plane of the chains which no longer have one-dimensional chains.

IV. CONCLUSION

We have shown that this irradiation-induced destruction of chains and change in the local coordination geometry of the chain-site Cu atom from fourfold square planar to fourfold non-square-planar leads to a drastic reduction in the hole carrier density in the two-dimensional CuO_2 planes. The hole density of ~ 0.07 hole/CuO_2 obtained in our calculation in the irradiated phase is extremely low and falls in the limit of the electron localization so that the irradiated $YBa_2Cu_3O_7$ compound loses superconductivity and becomes insulating. In our calculation we have neglected the small expansion of the lattice parameters which occurs under irradiation since precise information concerning these changes is lacking. Inclusion of the lattice parameter expansion will further lower the hole density in the CuO_2 planes. The models of the irradiated crystal structure considered in this paper are the simplest. In a truly disordered structure obtained after irradiation, many local coordination defects, such as the ones formed uniformly in the structures shown in Figs. 2(b) and 2(c), will be formed. Since the calculated hole density in these structures is very low, we expect it to be very low in the disordered structures as well. Since the irradiation reduces the hole density it is natural, on the basis of the T_c versus hole density curve,[29] that the material loses metallicity and superconductivity simultaneously. For the compound to remain metallic but not superconducting after irradiation, the hole density has to increase, which is not the case. Our calculations also suggest that there may be substantial contribution to the Hall voltage from the plane of the chains when the chains are fully disordered.

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[1] B. Raveau, C. Michel, M. Hervieu, and D. Groult, *Crystal Chemistry of High-T_c Superconductors* (Springer-Verlag, New York, 1991); A. English, A. D. Marwick, J. M. Poate, H. Bernas, G. J. Clark, and O. Meyer (unpublished).

[2] O. Mayer, in *Studies of High Temperature Superconductors,* edited by A. V. Narlikar (Nova Science, New York, 1989), Vol. I, p. 139.

[3] G. Xiong, H. C. Li, G. Linker, and O. Meyer, Phys. Rev. B **38**, 240 (1988); B. Egner, J. Geerk, H. C. Li, G. Linker, O. Meyer, and B. Strehlau, Jpn. J. Appl. Phys. **26**, (Suppl. 26-3), 2141 (1987); O. Meyer, B. Egner, G. C. Xiong, X. X. Xi, G. Linker, and J. Geerk, Nucl. Instrum. Methods B **39**, 628 (1989); O. Meyer, B. Egner, J. Geerk, R. Gerber, G. Linker, F. Weschenfelder, X. X. Xi, and G. C. Xiong, *ibid.* **37-38**, 917 (1989).

[4] H. Bernas, J. Lesueur, P. Nedellec, M. O. Ruault, and L. Dumoulin, Nucl. Instrum. Methods B **46**, 269 (1990); M. O. Ruault, H. Bernas, J. Lesueur, L. Dumoulin, M. Nicolas, J. P. Burger, M. Gasgnier, H. Noel, P. Gougeon, M. Potel, and J. C. Levet, Europhys. Lett. **7**, 435 (1988); M. O. Ruault, H. Bernas, and M. Gasgnier, Philos. Mag. B **60**, 801 (1989).

[5] A. D. Marwick, G. J. Clark, D. S. Yee, R. B. Laibowitz, G. Coleman, and J. J. Cuomo, Phys. Rev. B **39**, 9061 (1989); A. D. Marwick and G. J. Clark, Nucl. Instrum. Methods B **37-38**, 910 (1989).

[6] J. M. Valles, Jr., A. E. White, K. T. Short, R. C. Dynes, J. P. Garno, A. F. Levi, M. Anzlowar, and K. W. Baldwin, Phys. Rev. B **39**, 11 599 (1989); A. E. White, K. T. Short, D. C. Jacobson, J. M. Poate, R. C. Dynes, P. M. Mankiewich, W. J. Skocpol, R. E. Howard, M. Anzlowar, K. W. Baldwin, A. F. Levi, J. R. Kwo, T. Hsieh, and M. Hong, *ibid.* **27**, 3755 (1988); A. E. White, K. T. Short, J. P. Garno, J. M. Valles, Jr., R. C. Dynes, L. F. Schneemeyer, J. Waszczak, A. F. Levi, M. Anzlowar, and K. W. Baldwin, Nucl. Instrum. Methods B **37-38**, 923 (1989).

[7] H. Vichery, F. Rullier-Albenque, H. Pascard, M. Konczykowski, R. Kormann, D. Favrot, and G. Collin, Physica C **159**, 697 (1989); F. Rullier-Albenque, A. Legris, S. Bouffard, E. Paumier, and P. Lejay, *ibid.* **175**, 111 (1991).

[8] D. Bourgault, S. Bouffard, M. Toulemonde, D. Groult, J. Provost, F. Studer, N. Nguyen, and B. Raveau, Phys. Rev. B **39**, 6549 (1989).

[9] B. Hensel, B. Roas, S. Henke, R. Hopfengärtner, M. Lippert, J. P. Ströbel, M. Vildic, G. Saemann-Ischenko, and S. Klaumünzer, Phys. Rev. B **42**, 4135 (1990).

[10] M. A. Kirk, M. C. Frischherz, J. Z. Liu, L. R. Greenwood, and H. W. Weber, Philos. Mag. Lett. **62**, 41 (1990).

[11] D. B. Chrisey, J. S. Horwitz, H. S. Newman, M. E. Reeves, B. D. Weaver, K. S. Grabowski, and G. P. Summers, J. Supercond. **4**, 57 (1991).

[12] S. N. Basu, T. E. Mitchell, and M. Natassi, J. Appl. Phys. **69**, 3167 (1991).

[13] S. Vadlamannati, P. England, N. G. Stoffel, R. Ramesh, T. S. Ravi, D. M. Hwang, A. Findikoglu, Q. Li, T. Venkatesan, and W. L. McLean, Appl. Phys. Lett. **57**, 2265 (1990).

[14] Y. Li, C. Ren, G. Chen, J. Chen, and S. Zou, J. Appl. Phys. **69**, 7915 (1991).

[15] R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M Zahurak, and D. Werder, Phys. Rev. B **36**, 5719 (1987); R. J. Cava, Science **247**, 656 (1990).

[16] D. Jorgensen, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, H. Claus, and W. K. Kwok, Phys. Rev. B **41**,

1863 (1990); H. Shaked, B. W. Veal, J. Faber, Jr., R. L. Hitterman, V. Balachandran, G. Tomlins, H. Shi, L. Morss, and A. P. Paulikas, *ibid.* **41**, 4173 (1990).

[17] R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck, Jr., and L. W. Rupp, Jr., Physica C **165**, 419 (1990).

[18] C. N. R. Rao, R. Nagarajan, A. K. Ganguli, G. N. Subbanna, and S. V. Bhat, Phys. Rev. B **42**, 6765 (1990).

[19] J. T. Wille, A. Berera, and D. de Fontaine, Phys. Rev. Lett. **60**, 1065 (1988); L. T. Wille and D. de Fontaine, Phys. Rev. B **37**, 2227 (1988); D. de Fontaine, M. E. Mann, and G. Ceder, Phys. Rev. Lett. **63**, 1300 (1989); G. Ceder, M. Asta, and D. de Fontaine, Physica C **177**, 106 (1991); D. de Fontaine, G. Ceder, and M. Asta, Nature **343**, 544 (1990): G. Ceder, M. Asta, W. C. Carter, M. Kraitchman, D. de Fontaine, M. E. Mann, and M. Sluiter, Phys. Rev. B **41**, 8698 (1990); G. Ceder, R. McCormack, and D. de Fontaine, *ibid.* **44**, 2377 (1991).

[20] H. F. Poulson, N. H. Andersen, J. V. Andersen, H. Bohr, and O. G. Mouritsen, Nature **349**, 594 (1991); J. D. Jorgensen, *ibid.* **349**, 565 (1991).

[21] C. Chaillout, M. A. Alario-Franco, J. J. Capponi, J. Chenavas, P. Strobel, and M. Marezio, Solid State Commun. **65**, 283 (1988); M. A. Alario-Franco, C. Chaillout, J. J. Capponi, J. Chenavas, and M. Marezio, Physica C **156**, 455 (1988); R. Beyers, B. T. Ahn, G. Gorman, V. Y. Lee, S. S. P. Parkin, M. L. Ramirez, K. P. Roche, J. E. Vazquez, T. M. Gür, and R. A. Huggins, Nature **340**, 619 (1989).

[22] G. Van Tendeloo, H. W. Zandbergen, and S. Amelinckx, Solid State Commun. **63**, 389 (1987); **63**, 603 (1987); S. Amelinckx, G. Van Tendeloo, and J. Van Landuyt, in *Oxygen Disorder Effects in High-T_c Superconductors,* edited by J. L. Moran-Lopez and I. K. Schuller (Plenum, New York, 1990), p. 9.

[23] J. K. Burdett and G. V. Kulkarni, Phys. Rev. B **40**, 8908 (1989); J. B. Goodenough, Supercond. Sci. Technol. **3**, 26 (1990).

[24] M. H. Whangbo, M. Evain, M. A. Beno, U. Geiser, and J. M. Williams, Inorg. Chem. **26**, 2566 (1987).

[25] J. Zaanen, A. T. Paxton, O. Jepsen, and O. K. Andersen, Phys. Rev. Lett. **60**, 2685 (1988).

[26] Ph. Lambin, in *Oxygen Disorder Effects in High-T_c Superconductors* (Ref. 22), p. 101.

[27] R. P. Gupta and M. Gupta, Phys. Rev. B **44**, 2739 (1991).

[28] J. D. Jorgensen, S. Pei, P. Lightfoot, H. Shi, A. P. Paulikas, and B. W. Veal, Physica C **167**, 571 (1990); H. Claus, S. Yang, A. P. Paulikas, J. W. Downey, and B. W. Veal, *ibid.* **171**, 205 (1990); B. W. Veal, H. You, A. P. Paulikas, H. Shi, Y. Fang, and J. W. Downey, Phys. Rev. B **42**, 4770 (1990); B. W Veal, A. P. Paulikas, H. You, H. Shi, Y. Fang, and J. W. Downey, *ibid.* **42**, 6305 (1990); R. J. Cava, Nature **346**, 110 (1990).

[29] J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Parkin, Phys. Rev. Lett. **61**, 1127 (1988); Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzal, Phys. Rev. B **38**, 7156 (1988); M. W. Shafer and T. Penney, Eur. J. Solid State Inorg. Chem. **27**, 191 (1990).

[30] R. Haydock, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35, p. 216.

[31] L. F. Mattheiss and D. R. Hamann, Solid State Commun. **63**, 395 (1987).

[32] R. P. Gupta and M. Gupta, Solid State Commun. **67**, 129 (1988); J. Phys. Condens. Matter **1**, 1543 (1989); Physica C **160**, 129 (1989); **171**, 465 (1990).

[33] W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989).

[34] A. T. Fiory, A. F. Hebard, R. H. Eick, P. M. Mankiewich, R. E. Howard, and M. L. O'Malley, Phys. Rev. Lett. **65**, 3441 (1990).

[35] R. A. M. Van Woerden, H. J. Terpstra, C. F. Van Bruggen, M. Kraan, and D. M. De Leewo, Physica C **170**, 112 (1990).