PHYSICAL REVIEW B VOLUME 47, NUMBER 5 1 FEBRUARY 1993-I

Possibility of high-temperature superconductivity in an ordered tetragonal crystal structure in $RBa_2Cu_3O_7$ ($R =$ rare earth) superconductors

Raju P. Gupta
Section de Recherches de Métallurgie Physique, Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette CEDEX, France

Michèle Gupta
Institut des Sciences des Matériaux, Université de Paris-Sud, Bâtiment 415, 91405 Orsay, France

(Received 2 March 1992; revised manuscript received 29 July 1992)

The $RBa_2Cu_3O_{7-\delta}$ compounds are superconducting in the orthorhombic phase but are insulating in the tetragonal case. It is now well understood that while crystal symmetry *per se* does not play any role in the occurrence of superconductivity in these compounds, the orthorhombic phase is superconducting due to the formation of ordered chains that act as dopants for the two-dimensional CuO_2 planes. In the tetragonal phase these chains are destroyed, thus inhibiting the charge transfer from the CuO_2 planes. We propose a fully ordered tetragonal crystal structure for the $RBa_2Cu_3O_7$ ($R =$ rare earth) superconductors with space group $P4/mmm$, which is different from the orthorhombic phase. This structure is formed from the orthorhombic crystal structure of $YBa_2Cu_3O_{6.5}$ but now the chains run along the *a* axis as well. In this structure the Cu(1) atoms in the plane of the chains have twofold, square-planar fourfold, and sixfold coordinations, in contrast to the purely square-planar coordinations in orthorhombic $YBa_2Cu_3O_7$. Such a structure has previously been invoked by Fu *et al.* for the interpretation of their crystal-structure data on $LaBa(Ca,Sr)Cu_3O_{7-\delta}$ compounds. Results of our electronic-structure calculations show that the hole density and the Fermi level in this tetragonal crystal structure are practically identical to those found in the orthorhombic phase. This suggests that this phase, if it could be stabilized by appropriate chemical substitutions and heat treatment, would have a T_c identical to that in the orthorhombic structure, and could be interesting for many technological applications.

There has been a considerable debate in the literature concerning the role of crystal symmetry in the $RBa_2Cu_3O_{7-\delta}$ (where R is a rare-earth element) superconductors.[1–16] These compounds are superconducting in the orthorhombic crystal structure but insulating in the tetragonal case. It is now well understood that the crystal symmetry plays no essential role in the occurrence of superconductivity. The crucial role is instead played by the ordered chains along the *b* axis, which act as electron reservoirs for charge transfer from the two-dimensional CuO_2 planes. This results in an orthorhombic crystal symmetry, since the oxygen sites along the *a* axis are vacant. When the distribution of oxygen atoms in the plane of the chains is completely random and the occupancy of oxygen atoms along both *a* and *b* axes is identical, the overall crystal symmetry is tetragonal. (Note that, since the distribution of oxygen atoms in the plane of the chains is completely random, the structure is truly speaking disordered in this plane and the crystal symmetry is not tetragonal at a local level. However, due to the equal occupation of both type of sites, one can consider the structure to have an overall tetragonal symmetry. This is similar to the case of a disordered alloy.) This random distribution of oxygen atoms results in a complete destruction of the chains. It is in this structure, which has no chains, that the compounds are insulating. 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 occupancy of oxygen atoms along both *a* and *b* axes are equal.[1,5] In this case the true crystal symmetry is orthorhombic although the overall crystal structure is tetragonal.[5] Such a compound is not necessarily an insulator or not a superconductor but the existence of the superconducting state and the T_c depends upon the lengths of the broken chains and their distribution.[14]

On a microscopic scale it is the local environment around the Cu(1) atom in the plane of the chains (see Fig. 1 for notation) that governs the electron transfer and, hence, the hole density and superconductivity in the $RBa_2Cu_3O_{7-\delta}$ family of superconductors for all values of δ. We have shown recently[15,16] that the twofold, threefold, and the non-square-planar fourfold coordinations of the chain site Cu atom are not favorable for electron transfer from the two-dimensional CuO_2 planes to the plane of the chains (hereafter referred to as CuO planes considering the stoichiometry in oxygen), and that a square-planar fourfold configuration facilitates the creation of a significant hole density in the CuO_2 planes and, hence, the occurrence of superconductivity. This shows the vital role that the intact chains, in which the Cu(1) atom has a square-planar fourfold configuration, play in the superconductivity in the $RBa_2Cu_3O_{7-\delta}$ family of superconductors. The destruction of these chains in the tetragonal structure and a completely random occupation of oxygen atoms in the CuO planes results in the elimination of square-planar fourfold coordination of Cu(1) atoms and the occurrence of twofold, threefold,

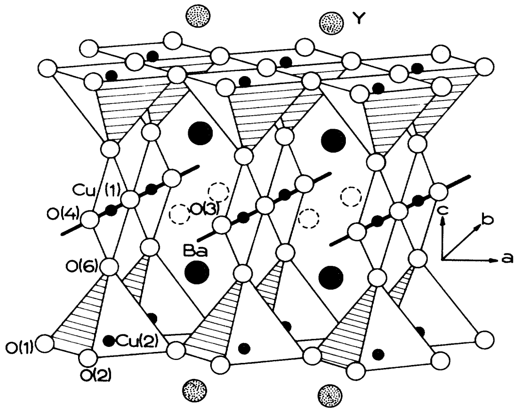
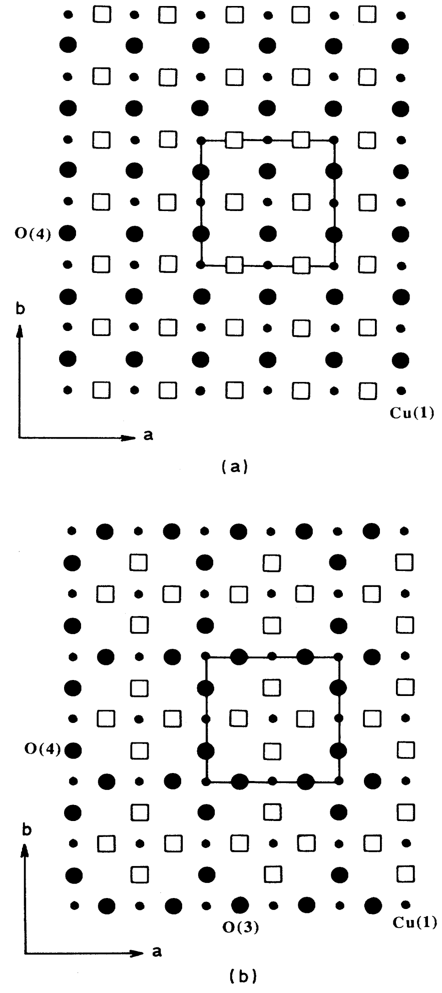


FIG. 1. Crystal structure of orthorhombic $YBa_2Cu_3O_7$, which shows the notation used in this paper.

and non-square-planar fourfold coordinations and, hence, the destruction of superconductivity.

In this paper we present a fully ordered crystal structure for the $RBa_2Cu_3O_7$ family of superconductors, which has a full tetragonal symmetry, and is a promising candidate for high-temperature superconductivity if it could be stabilized through some chemical treatment or by some other means. In this structure shown in Fig. 2 the oxygen atoms in the CuO planes have an ordered distribution (space group $p4mm$), which results in a tetragonal crystal structure with space group $P4/mmm$. One can immediately recognize from Fig. 2 that this structure is formed from the full-empty-full chain sequence along the b-axis model of $YBa_2Cu_3O_{6.5}$ but with the sequence of chains now running along both a and b axes, resulting in an ordered tetragonal $YBa_2Cu_3O_7$. In this structure, Cu(1) atoms have three types of coordinations, twofold as in $YBa_2Cu_3O_6$, square-planar fourfold as in $YBa_2Cu_3O_7$ but along both a and b axes, and sixfold. The square-planar fourfold coordinations are twice as numerous as either the twofold or the sixfold coordinations. This structure was, in fact, suggested previously by Fu *et al.*[11] for the $LaBaACu_3O_{7-\delta}$ (A = Ca,Sr) family of superconductors on the basis of their x-ray-diffraction and electron microscopy investigations. De Fontaine[12] showed that, although for $YBa_2Cu_3O_7$ the orthorhombic structure is the stable one, the tetragonal crystal structure could indeed be the stable one for this family of superconductors, since the interaction parameters in the two-dimensional Ising model used in the construction of the phase diagram do depend upon the nature of the ions involved in the lattice. A tetragonal crystal structure with $P4/mmm$ symmetry has also been suggested recently by Arabi *et al.*[13] for $HoBa_2Cu_3O_{7-\delta}$. Our electronic structure calculations, which were performed for $YBa_2Cu_3O_7$ as an example, although the orthorhombic phase is the stable crystal structure for this compound,[14] show that the hole density in the two-dimensional CuO_2 planes in this compound is essentially the same as in the orthorhombic $YBa_2Cu_3O_7$ with $T_c \sim 90$ K and much higher than in the orthorhombic $YBa_2Cu_3O_{6.5}$ with $T_c \sim 55$ K. These calculations were performed using the tight-binding recursion method, as described earlier,[15,16] with clusters of more than 2500 atoms including p functions at oxygen sites and d at other sites. Increasing the size of the cluster did not change the results significantly, indicating the convergence of the calculations. Considering the direct correlation between T_c and the hole density,[17,18] one therefore expects a value of $T_c \sim 90$ K in the tetragonal crystal structure proposed in this paper. Note that the superconducting tetragonal crystal structure, which is proposed here, is entirely different from the one that will be obtained, for instance, by the chemical substitution of Ca at the Y site in the insulating tetragonal $YBa_2Cu_3O_{7-\delta}$ crystal structure.[19] In the latter, the hole density in the CuO_2 planes is obtained by a chemical replacement similar to the case of the insulating La_2CuO_4. On the other hand, the tetragonal crystal structure proposed in this paper is self-doped as is the case with orthorhombic $YBa_2Cu_3O_7$.

The lattice parameters and the atomic positions used in our calculations are the same[15] as in orthorhombic



(a)

(b)

FIG. 2. Distribution of oxygen atoms in the CuO planes in (a) orthorhombic phase, and (b) ordered tetragonal phase in $RBa_2Cu_3O_7$, with small circles representing the Cu(1) atoms, large circles oxygen atoms, and open squares vacancies.

$YBa_2Cu_3O_7$, except that a mean value of *a* and *b* lattice parameters was used for the lattice parameter *a*. This choice was dictated by the preponderance of the square-planar fourfold configurations of the Cu(1) atom, as found in the orthorhombic $YBa_2Cu_3O_7$. In a true tetragonal crystal structure the lattice parameters and the atomic positions are expected to be somewhat different, and this difference will affect the hole density in the CuO_2 planes. We, however, expect this to be small and to not alter our conclusions, considering the large hole density obtained in our calculations. Further the sixfold coordinated Cu(1) may be expected to undergo a Jahn-Teller distortion. This will also affect the hole density. To assess the effect of this distortion, preliminary calculations were performed for $YBa_2Cu_3O_7$ with lattice parameters appropriate for $YBa_2Cu_3O_6$, where the Cu(2)-apical oxygen bond is $\sim 7\%$ longer than in $YBa_2Cu_3O_7$. The hole density was found to decrease by less than 10%. We therefore expect the effect of the Jahn-Teller distortion to be small. We should note that the lattice parameters obtained by Fu *et al.*[11] for tetragonal $LaBa(Ca,Sr)Cu_3O_{7-\delta}$ and by Arabi *et al.*[13] for tetragonal $HoBa_2Cu_3O_{7-\delta}$ are similar to the ones used in the present work. Further, Fu *et al.* did not invoke the possibility of a Jahn-Teller distortion in the interpretation of their data. Arabi *et al.*[13] determined for $HoBa_2Cu_3O_{7-\delta}$ with $T_c = 91.5$ K the atomic positions as well in the tetragonal space group *P*4/*mmm* and their values are quite close to the ones found in the orthorhombic crystal structure. However, these authors did not propose a model for the distribution of oxygen atoms in the CuO plane. In any event, our calculations done for $YBa_2Cu_3O_7$ as an example, are only indicative and the true hole density will necessarily depend upon the nature of the ions involved and the true atomic positions and lattice parameters.

In orthorhombic $YBa_2Cu_3O_7$ the planar Cu(2)-apical O(6) atom bond length is approximately 25% longer than the Cu(1)-O(6) bond length or the average Cu-O bond length in the crystal. 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, conferring on the crystal a layered character. In fact the Cu(1)—O(6) bond length is approximately equal to the Cu(1)—O(4) and the Cu(1)—O(3) bond lengths. Here O(3) and O(4) represent oxygen atoms along *a* and *b* axes. This leads to the formation of two separate antibonding band complexes in the vicinity of the Fermi level, as has been discussed by several authors:[6,8] (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_y orbitals and (b) the bands formed between the Cu(1) d orbitals, and the apical oxygen O(6) p_z and the O(3) p_x and O(4) p_y orbitals in the CuO plane. The charge transfer from the CuO_2 planes depends in a delicate manner on the relative positions of these two-band complexes. (Note that we have aligned the crystal *a*, *b*, and *c* axes along the cartesian *x*, *y*, and *z* axes).

In tetragonal $YBa_2Cu_3O_6$ the Cu(1) atom is only twofold coordinated (by the two apical oxygens) and thus forms a CuO_2 unit (due to the considerations of stoichiometry). In this structure the 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, leading to no charge transfer from the CuO_2 planes to the CuO_2 units. 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[20] and others[6-10] we expect the overall charge distribution to be well described by the local-density approximation. Due to the insulating nature 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 crystallographic environments, and this charge-transfer corresponds to the hole concentration in the CuO_2 planes with respect to the insulating ground state.

The addition of the O(4) oxygen atoms to form chains along the *b* axis in orthorhombic $YBa_2Cu_3O_7$ leads to the formation of square-planar fourfold coordination of the Cu(1) atom with stoichiometry CuO_3. This results in 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) $d_{z^2-y^2}$ level 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 with respect to $YBa_2Cu_3O_6$. Since an oxygen atom brings only four *p* electrons, 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 would 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 the orthorhombic $YBa_2Cu_3O_7$ the bottom of this band falls below the Fermi level. This leads to a lowering of the Fermi level by ~ 0.2 eV, and consequently an electron transfer from the planar CuO_2 bands.

In the tetragonal crystal structure shown in Fig. 2(b) the Cu(1) atom has three types of coordinations as pointed out earlier, twofold, square-planar fourfold, and sixfold, resulting in the formation of CuO_2, CuO_3, and CuO_4 units. The charge-transfer from the CuO_2 planes therefore depends intricately on the positions of the three-band complexes with respect to the position of the antibonding CuO_2 band. The three-band complexes are not isolated but intimately linked to each other. A general insight can, however, be gained by considering three separate band complexes. The addition of O(3) atoms along the *a* axis to the square-planar fourfold coordinations of the Cu(1) atom in orthorhombic $RBa_2Cu_3O_7$ to obtain a sixfold coordinated Cu(1) atom gives rise to two additional nonbonding O(3) p_y and O(3) p_z states below the Fermi level, as compared to the orthorhombic $RBa_2Cu_3O_7$. The interaction of the O(3) p_x level with the Cu(1) $d_{z^2-x^2}$ orbital gives rise to an occupied bonding

Cu(1) $d_{z^2-x^2}$–O(3) p_x state, and the corresponding antibonding part in the vicinity of the Fermi level. Thus an octahedral configuration generates three additional bands over a fourfold coordination. Again, since an oxygen atom brings only four electrons, this leaves an extra antibonding band in the vicinity of the Fermi level nearly empty. Assuming that the two antibonding bands are similarly placed in energy and have similar densities of states, this would result in a further downward shift in the Fermi level and, hence, an increased hole density in the CuO_2 planes, with a sixfold coordination over a purely square-planar fourfold coordination.

The true Fermi level, and hence the true hole density, can be obtained only when all three coordinations are treated together. As we have discussed above, a twofold configuration tends to push the Fermi level up and hence decrease the hole density, while a sixfold configuration tends to pull it down and hence increase the hole density with respect to a square-planar fourfold configuration. Our calculations show that the net result of this competition is that in the tetragonal $RBa_2Cu_3O_7$ the Fermi level is placed at approximately the same energy as in the orthorhombic $RBa_2Cu_3O_7$. This placement of the Fermi level leads to practically the same hole densities in the two structures.

An actual calculation of the charge transfer requires a knowledge of the electronic charge distributions at different atomic sites. This can be obtained by integrating the local densities of states at these sites up the Fermi level. In Table I we have given the effective charges at different atomic sites calculated in this manner for $RBa_2Cu_3O_7$ in both orthorhombic and tetragonal crystal structures. By comparing the total charge on a CuO_2 plane with the one in the insulating $YBa_2Cu_3O_6$ one can obtain an estimate of the hole density. With this we[15] obtain 0.283 hole/CuO_2 in orthorhombic superconducting $RBa_2Cu_3O_7$, as shown in Table I. This is in good agreement with the available experimental data[17,18] and previous calculations.[8–10] The mean value of the hole density and the effective charges at different atomic sites in the tetragonal crystal structure is practically the same as in the orthorhombic crystal structure. In the insulating $YBa_2Cu_3O_6$ compound Cu(1) and apical O(6) atoms are in their ionic Cu^+ and O^{2-} states, respectively, Table I shows that this is not the case for the twofold coordinated Cu(1) and the associated O(6) atoms in tetragonal $RBa_2Cu_3O_7$, where one finds slightly less electronic charge than was found in their ionic states.[15] This is due to a downward shift in the Fermi level, which puts the top of the antibonding band, which was previously filled, just above the Fermi level. What is interesting to notice from Table I is that the effective charges associated with the square-planar fourfold geometry differ only marginally in the two crystal structures due to the placement of the Fermi level at essentially the same energy, and thus emphasizing again the role of the local coordination geometry in the charge transfer from the CuO_2 planes. Table I also shows that R 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. The amount of charge at these sites is the same in the two crystal structures.

It is quite common in cuprates to associate a valence of +2 with the insulating state, and to express the hole density in terms of a Cu valence greater than +2. It is quite clear from Table I that truly speaking, the Cu-O interactions are of covalent nature. The discussion in terms of a Cu valence, however, implicitly assumes all elements to be completely ionic. In our calculation we find, as discussed above, that Y and Ba are not completely ionic and retain a small charge at their sites due to the hybridization with the neighboring oxygens. This charge will have to be transferred back to these oxygens to arrive at an

TABLE I. Effective charges (p at oxygen sites and d at other sites) at different atomic sites in $RBa_2Cu_3O_7$ (R = rare earth) in orthorhombic and tetragonal 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.

	Orthorhombic	Tetragonal $RBa_2Cu_3O_7$			
Site	$RBa_2Cu_3O_7$	Twofold Cu(1)	Fourfold Cu(1)	Sixfold Cu(1)	Average
CuO_2 plane					
Cu(2)	9.371	9.335	9.376	9.364	9.363
O(1)	5.496	5.516	5.525	5.525	5.523
O(2)	5.539	5.516	5.525	5.525	5.523
Total CuO_2 plane	20.406	20.367	20.426	20.414	20.408
Hole count	0.283	0.322	0.263	0.275	0.281
CuO_n unit	CuO_3	CuO_2	CuO_3	CuO_4	CuO_3
Apical oxygen O(6)	5.658	5.862	5.671	5.593	5.699
Cu(1)	9.430	9.858	9.433	8.952	9.419
O(3)	Vacant	Vacant	5.537	5.537	5.537
O(4)	5.613	Vacant	5.537	5.537	5.537
Total CuO_n	26.359	21.582	26.312	31.212	26.355
R	0.425	0.425	0.425	0.425	0.425
Ba	0.202	0.202	0.202	0.202	0.202
Total	68.000	63.145	67.993	72.869	68.000

TABLE II. Total charges at the CuO_2 planes and the CuO_n units in $RBa_2Cu_3O_7$ (R = rare earth) in orthorhombic and tetragonal crystal structures obtained by a sharing of charges at R 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.

	Orthorhombic	Tetragonal $RBa_2Cu_3O_7$			
Site	$RBa_2Cu_3O_7$	Twofold Cu(1)	Fourfold Cu(1)	Sixfold Cu(1)	Average
CuO_2 plane					
Total charge	20.699	20.661	20.720	20.707	20.702
Valence Cu(2)	+2.301	+2.339	+2.280	+2.293	+2.298
CuO_n unit	CuO_3	CuO_2	CuO_3	CuO_4	CuO_3
Total charge	26.601	21.744	26.554	31.535	26.597
Valence Cu(1)	+2.399	+1.256	+2.446	+3.465	+2.403

ionic model. The closest neighbors of a Ba are the four apical O(5) oxygens in its plane, four planar oxygens O(1),O(2) in the CuO_2 plane, and four O(3),O(4) oxygens in the CuO plane, while the closest neighbor of an R atom are the eight O(1),O(2) oxygen atoms in the two CuO_2 planes above and below it. Thus to obtain a picture closest to the ionic model, which neglects hybridization, we might, as a first approximation, share the charges on R and Ba sites equally with all the neighboring oxygen atoms. The total charges thus obtained on the CuO_2 planes and the CuO_n units are shown 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. This is also given in Table II. This table shows that the mean ionic valence of Cu(1) and Cu(2) in the two crystal structures are practically identical. The valence of Cu(2) is found to be $\sim +2.3$, which corresponds to a hole density of ~ 0.3 hole/CuO_2, in good agreement with the one presented in Table I, and with experimental data.[17,18] Note that this hole density has been calculated completely independently from the effective charges of the compound and without referring to the charge on a CuO_2 plane in the insulating $YBa_2Cu_3O_6$.

In summary, we have shown that in a hypothetical fully ordered tetragonal crystal structure of $RBa_2Cu_3O_7$ one can obtain the same value of the hole density and T_c as in the orthorhombic phase. The stabilization of this tetragonal phase could be helpful for technological applications.

We would like to thank Dr D. de Fontaine for bringing Refs. 11 and 12 to our attention.

---

[1] B. Raveau, C. Michel, M. Hervieu, and D. Groult, in *Crystal Chemistry of High-T_c Superconductors* (Springer-Verlag, New York, 1991); R. Beyers and T. M. Shaw, Solid State Phys. **42**, 135 (1989).

[2] G. Xiao, M. Z. Cieplak, A. Gavrin, F. H. Streitz, A. Bakhshai, and C. L. Chien, Phys. Rev. Lett. **60**, 1446 (1988); X. Jiang, P. Wochner, S. C. Moss, and P. Zschack, *ibid.* **67**, 2167 (1991); E. Suard, A. Maignan, V. Craignaert, and B. Raveau, Physica C **200**, 43 (1992); X. Z. Wang, P. L. Steger, M. Reissner, and W. Steiner, *ibid.* **196**, 247 (1992).

[3] J. 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).

[4] R. J. Cava, B. Batlogg, K. M. Rabe, E. A. Rietman, P. K. Gallagher, and L. W. Rupp, Jr., Physica C **156**, 523 (1988).

[5] G. Van Tendeloo, H. W. Zandbergen, and S. Amlinckx, Solid State Commun. **63**, 389 (1987); **63**, 603 (1987); S. Amlimckx, 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.

[6] J. K. Burdett and G. V. Kulkarni, Phys. Rev. B **40**, 8908 (1990).

[7] J. B. Goodenough, Supercond. Sci. Technol. **3**, 26 (1990); M. H. Whangbo, M. Evain, M. A. Beno, U. Geiser, and J. M. Williams, Inorg. Chem. **26**, 2566 (1987).

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

[9] P. Lambin, in *Oxygen Disorder Effects in High-T_c Superconductors,* edited by J. L. Moran-Lopez and I. K. Schuller (Plenum, New York, 1990), p. 101; T. Minerva and C. Calandra, Physica C **170**, 532 (1990); F. Lopez-Aguilar and J. Costa Quintana, Phys. Rev. B **42**, 4150 (1990); A. Largé, E. V. Anda, and J. L. Moran-Lopez, *ibid.* **42**, 4288 (1990); W. Zhang, M. Avignon, and K. H. Bennemann, *ibid.* **42**, 10 192 (1990).

[10] T. Bjornholm, I. K. Schuller, E. A. Early, M. B. Maple, B. Wuyts, J. Vanacken, and Y. Bruynseraede, Phys. Rev. B **41**, 11 154 (1990); J. L. Peng, P. Klavins, R. N. Shelton, H. B. Radousky, P. A. Hahn, L. Bernardez, and M. Costantino, *ibid.* **39**, 9074 (1989).

[11] W. T. Fu, H. W. Zandbergen, C. J. Van Der Beek, A. A. Verheijen, L. J. de Jongh, and V. A. M. Brabers, J. Less Common Metals **151**, 213 (1989).

[12] D. de Fontaine, J. Less Common Metals **160**, L5 (1990).

[13] H. Arabi, D. A. Ciomartan, M. E. Clamp, P. W. Mitchell, J. W. Ross, D. J. Sandiford, O. S. Mills, and R. H. Fenn, Physica C **193**, 90 (1992).

[14] G. Ceder, R. Mc Cormack, and D. de Fontaine, Phys. Rev. B **44**, 2377 (1991); A. Berera and D. de Fontaine, *ibid.* **39**, 6727 (1989).

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

Gupta and R. P. Gupta, J. Phys. (Paris) **2**, 175 (1992).

[16] R. P. Gupta and M. Gupta, Phys. Rev. B **45**, 9958 (1992).

[17] 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, Europ. J. Solid State Inorg. Chem. **27**, 191 (1990).

[18] Z. Z. Wang, J. Clayhold, N. P. Ong, J. M. Tarascon, L. H. Greene, W. R. Mc Kinnon, and G. W. Hull, Phys. Rev. B **36**, 7222 (1987).

[19] R. P. Gupta and M. Gupta, Solid State Commun. **67**, 129 (1988).

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