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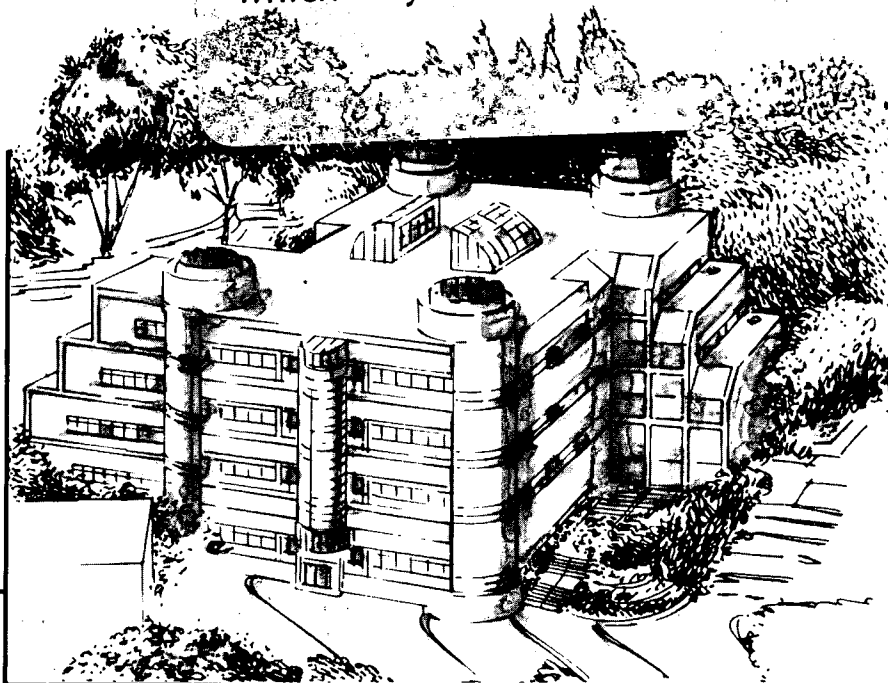
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June 1987

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**Concentration-Wave Representation of the
Structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$**

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ABSTRACT

The structures of many complex oxides can be derived by imposing a simple set of ordering concentration waves on a parent NaCl lattice. The present paper shows how this description can be applied to the structure of the high-temperature superconducting oxide $\text{YBa}_2\text{Cu}_3\text{O}_7$. It is obtained from the NaCl lattice in three steps, beginning with the replacements $\text{Na} = [\text{Cu}\Delta_3]_{1/3}$ and $\text{Cl} = [\text{YBa}_2\text{O}_7\Delta_2]_{1/9}$, where the symbol Δ represents a vacancy. The first step is an ordering of the $L1_2$ type (A_3B) generated by the star of the wavevector $\mathbf{k}^1 = (2\pi/a_0)[100]$. It divides the Na-sites into Cu and Δ sublattices, and the Cl sites into sublattices occupied by the compound atoms $(\text{YBa}_2)_{1/3}$ and $(\text{O}_7\Delta_2)_{1/3}$. The resulting structure is the classic perovskite structure. In the second step this structure is ordered according by the wavevector $\mathbf{k}^2 = (2\pi/3a_0)[001]$, which triples the unit cell along the c-axis, orders Y and Ba onto separate sublattices, and divides the oxygen atoms between O and $\text{O}' = [\text{O}\Delta_2]_{1/3}$ sublattices. The final ordering is generated by the vector $\mathbf{k}^3 = (2\pi/a_0)[100]$, and separates the O' sublattice into oxygen and vacancy sites, creating copper chains along the basal plane of the unit cell. This description clarifies the relation between the superconducting oxide structure and that of other complex oxides, and suggests alternate compositions for the oxide phase.

1. Introduction

The recent discovery of high-temperature superconductivity in Y-Ba-Cu oxides [1] has generated an intense interest in the crystal structures of this and similar materials. The superconducting phase has the composition $\text{YBa}_2\text{Cu}_3\text{O}_x$, where $x \sim 7$, and a structure that is a derivative of the perovskite structure [2]. Recent studies [3-5] have shown that the unit cell is slightly orthorhombic, and identified a transition from the tetragonal to the orthorhombic structure at approximately 750°C . The best available neutron diffraction evidence [4] suggests the stoichiometric formula $\text{YBa}_2\text{Cu}_3\text{O}_7$ and the structure shown in Figure 1.

Recently, one of us [6,7] showed that the crystal structures and transformations of many metal-oxide ceramics, including such complex oxides as the homologous series $\text{Ti}_n\text{O}_{2n-1}$ and $\text{Mo}_n\text{O}_{3n-1}$, can be predicted or understood by using the method of concentration waves [8]. In this approach the oxide is regarded as an interstitial solid solution on a simple oxygen host lattice with an FCC, BCC or HCP structure. The metal cations order on the interstitial sublattice, and may also partly substitute for oxygen, to achieve a structure that is both electrically neutral and fully ordered. The method has the additional advantage that it identifies important similarities between seemingly dissimilar structures.

To use the method of concentration waves to predict the crystal structure of an ordered compound one must know the effective interatomic potentials between the various species present. However, in the absence of that knowledge the structure may often be inferred from a few simple rules, particularly if some of the dominant ordering vectors are known. The theory is described in some detail in reference [7], and leads to the conclusion that the preferred low-temperature structures will ordinarily have dominant ordering vectors that correspond to the Lifshitz special points of the parent lattice, supplemented, if necessary, by secondary or tertiary ordering according to one of a finite set of secondary ordering vectors. In accordance with the Nernst principle,

the minimum-energy structure is a state of complete order, and ordinarily includes the minimum set of secondary ordering vectors that is necessary to achieve this result.

In the following we show how the method of concentration waves can be applied to describe the proposed structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The analysis suggests that the structure given in Figure 1 is the most plausible perovskite derivative that is consistent with the overall stoichiometry of the compound, and naturally leads to a transformation from an orthorhombic to a tetragonal structure at high temperature. The representation of the structure is relatively straightforward and may help to clarify its relation to the structures of similar phases.

2. The Perovskite Structure

The perovskite structure is a simple ordered derivative of the rocksalt (NaCl) structure. The latter can be regarded as a pair of interpenetrating FCC lattices, in which one species, which may be arbitrarily chosen to be Na, occupies the sites of the FCC lattice while the other (Cl) fills the octahedral voids. If the atom sites are described by the vector

$$\mathbf{R} = a_0 [x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z] \quad (1)$$

in a Cartesian coordinate frame with axes parallel to the cube axes, the Na-lattice (FCC) contains all points whose coordinates (x,y,z) have integral or half-integral values with an integral sum $(x+y+z)$. The Cl-lattice (octahedral voids) contains all points of the type

$$\mathbf{R}_\mathbf{I} = \mathbf{R}_\mathbf{M} + (a_0/2)[\mathbf{e}_x + \mathbf{e}_y + \mathbf{e}_z] \quad (2)$$

or, equivalently, all points whose coordinates (x,y,z) are integers or half-integers with a half-integral sum $(x+y+z)$.

One of the most common orderings of the FCC lattice is the $L1_2$ -type order that creates a structure with the stoichiometric formula AB_3 , where component A occupies the corners of the FCC unit cell and B fills the face-centered positions (Figure 2). The ordering vectors for the $L1_2$ structure are associated with the Lifshitz special point at $[100]$ in the FCC reciprocal lattice, and are the three members of the star of the vector

$$\mathbf{k}^1 = (2\pi/a_0)[100] \quad (3)$$

The distribution of a component (A) can be described by the function, $c_A(\mathbf{R})$, defined on the lattice sites, which has the value 1 if component A is present at \mathbf{R} and the value zero if it is not. Since the vectors $[100]$, $[010]$, $[001]$ and $[000]$ appear in the star of $[100]$, the distributions of the A and B atoms in the ordered structure created by this star are

$$c_A(x,y,z) = (1/4)\{1+\exp(2\pi ix)+\exp(2\pi iy)+\exp(2\pi iz)\}$$

$$c_B(x,y,z) = 1 - c_A(x,y,z) \quad (4)$$

where (x,y,z) are the coordinates of the FCC lattice sites. The distribution functions (4) fill the FCC lattice in precisely the pattern shown in Figure 2.

If the same ordering wave acts on the NaCl lattice both the Na and Cl sublattices order in the $L1_2$ pattern, and the stoichiometric formula is replaced by the formula $[AB_3][ab_3]$ where the first bracket gives the decomposition of the FCC lattice and the second is the decomposition of the associated lattice of octahedral voids. The distribution of A and B over the Na-lattice is given by equations (4). In the FCC primitive cell the octahedral interstitial site associated with the corner site at (000) is $(1/2,1/2,1/2)$. The distribution functions

$$c_a(x,y,z) = c_A(x-1/2,y-1/2,z-1/2)$$

$$= (1/4)\{1-\exp(2\pi ix)+\exp(2\pi iy)+\exp(2\pi iz)\}$$

$$c_b(x,y,z) = 1 - c_a(x,y,z) \quad (5)$$

where (x,y,z) are the coordinates of the octahedral voids, give the arrangement of a and b over the sites of the octahedral void lattice.

Using the generalization that the components on a lattice may be vacancies (Δ) or composite atoms as well as discrete atoms, and may be slightly displaced in the final state, equations (4) and (5) describe a variety of crystal structures. One of the most common is the classic perovskite (CaTiO_3) structure (Figure 3). The stoichiometric formula CaTiO_3 may be rewritten $[\text{Ti}\Delta_3][\text{CaO}_3]$, in which case the $L1_2$ ordering of disordered NaCl lattice gives the identifications $A=\text{Ti}$, $B=\Delta$, $a=\text{Ca}$, $b=0$. Given the distribution of vacancies on the B-sublattice the stoichiometric compound CaTiO_3 precisely fills the ordered lattice, and no further ordering is required to satisfy the Nernst principle for a minimum energy state.

Several other simple oxide structures are simply related to the perovskite structure. The classic example is the ReO_3 structure, shown in Figure 4, which is obtained from the perovskite structure by replacing Ti by Re on the A-sublattice and Ca by vacancies on the a-sublattice.

3. The Structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$

The structure of the superconducting compound $\text{YBa}_2\text{Cu}_3\text{O}_7$ can also be referred to the perovskite lattice if some of the components are composite atoms. If we collapse the structure into an FCC unit cell, i.e., into one of the three stacked cells shown in Figure 1, it fits the perovskite pattern with the identifications $A=\text{Cu}$, $B=\Delta$, $a=(\text{Y}_{1/3}\text{Ba}_{2/3})$, $b=(\text{O}_{7/3}\Delta_{2/3})$. However, the collapsed structure does not satisfy the

Nernst principle, and must undergo at least secondary and tertiary ordering to achieve a stoichiometric configuration.

a. The Distribution of Y and Ba

First consider the ordering of Y and Ba on the b-sublattice of the perovskite structure. It was shown in reference [7] that the wave-vectors of secondary ordering that lead to the most stable ordered superstructures are reciprocal lattice vectors, \mathbf{k}^2 , of one of the types

$$\mathbf{k}^2 = 2\pi\mathbf{K}/2, 2\pi\mathbf{K}/3, 2\pi\mathbf{K}/4 \quad (6)$$

where \mathbf{K} is a reciprocal lattice vector of the parent, disordered structure and \mathbf{k}^2 is reduced into the first Brillouin zone. This requirement should be satisfied so that the superstructure can be generated by concentration waves that belong to the same optimal star. The resulting superstructures are one-dimensional, layered structures since the sum or difference of vectors of the type (8) along orthogonal axes would introduce concentration waves that correspond to other stars with higher energies. While the number of reciprocal lattice vectors is infinite, reduction into the first Brillouin zone produces a finite series of possible wave vectors, and hence a finite number of possible structures.

The simplest vector of the type (8) that provides a stoichiometric distribution of Y and Ba over the sites of the a-sublattice is the vector

$$\mathbf{k}^2 = (2\pi/3a_0)[001] \quad (9)$$

which creates the observed pattern ...BaYBaBaYBa... in the a-sites along the z-axis (Figure 1). Its consequence is to divide the a-sublattice into Y and Ba sublattices whose distributions can be written

$$c_Y = (1/3)\{1+\exp[(2\pi i/3)(z-3/2)]+\exp[(4\pi i/3)(z-3/2)]\}$$

$$= (1/3)\{1+2\cos[(4\pi/3)(z-3/2)]\}$$

$$c_{Ba} = 1 - c_Y$$

$$= (2/3)\{1-\cos[(4\pi/3)(z-3/2)]\} \quad (10)$$

where z gives the vertical positions of the a-sites and the phase of the wave has been adjusted to place the yttrium atom in the center of a vertical stack of three FCC cells (Figure 5a).

b. The Distributions of Oxygen and Vacancies

The same ordering wave must be reflected in the other sublattices of the perovskite structure. The b-sublattice is filled by a mixture of oxygen and vacancies, $[O_{7/3}\Delta_{2/3}]$, with oxygen predominant. Dividing the bracket into sets that are compatible with the ordering vector k^2 we have

$$[O_{7/3}\Delta_{2/3}] = [O'O_2] \quad (11)$$

where the composite component, O' is $(O_{1/3}\Delta_{2/3})$. The ordering of O and O' over the sites of the b-sublattice is given by equation (10), where the values of z are now the vertical components of the sites of the b-lattice. The result is shown in Figure 5a.

However, equations (10) do not complete the ordering on the b-sublattice since they do not yield a stoichiometric distribution of oxygen and vacancies. The oxygen and vacancies on the O' -sublattice must undergo tertiary ordering into a stoichiometric configuration. A straightforward examination of the possible ordering vectors shows that there is only one ordering vector that can accomplish this without requiring other vectors or increasing the size of the unit cell. It is the wavevector

$$\mathbf{k}^s = (2\pi/a_0)[100] \quad (12)$$

(or, equivalently, $(2\pi/a_0)[010]$), which modulates the distribution (10) on the O'-sublattice by the composition waves

$$c_0 = (1/2)[1 - \exp(2\pi i x)]$$

$$c_\Delta = 1 - c_0 \quad (13)$$

Both the Cu and Y-Ba sublattices already satisfy equations (13), and are hence unaffected by the tertiary ordering wave. The distribution (13) therefore completes the description of the simplest derivative of the perovskite structure that is compatible with the stoichiometric formula $\text{YBa}_2\text{Cu}_3\text{O}_7$. The structure is shown in Figure 5b.

c. Lattice Displacements: The Tetragonal-Orthorhombic Transition

The ordering wave $\mathbf{k}^s = (2\pi/a_0)[100]$ destroys the symmetry between the x- and y-axes of the unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and makes it orthorhombic. The ordering wavevector is degenerate with the vector $\mathbf{k}^{s'} = (2\pi/a_0)[010]$, and should mix with it to maximize entropy at higher temperature. The intermixing of the vectors \mathbf{k}^s and $\mathbf{k}^{s'}$ disorders the oxygen atoms in the basal plane of the unit cell without affecting the basic atomic arrangement in any other plane, and should, therefore, produce a tetragonal structure, as is observed [4].

In addition to the orthorhombic distortion, neutron diffraction studies [4] reveal small vertical displacements of the atoms, which are shown in Figure 1. The vertical displacements are most pronounced in the O-lattice at $z=c/3$, $2c/3$ and lead to a pronounced "pucker" in the atom positions in this plane. The measured displacements appear to be a natural consequence of local deviations from charge neutrality, and are consistent with the \mathbf{k}^s ordering wavevector.

d. The Cu-Sublattice

The ordering wavevector k^z also affects the Cu-sublattice, even though all points on the lattice are occupied by Cu. The result is to divide the sublattice into two distinct types of Cu-site (Cu^1 , Cu^2) that are differently coordinated. The distribution functions can be written

$$c_{\text{Cu}^1} = (1/3)[1+2\cos(2\pi z/3)]$$
$$c_{\text{Cu}^2} = 1 - c_{\text{Cu}^1} \quad (14)$$

where z is the vertical component of the Cu-sublattice site. The distinct sites are labelled in Figure 5b. Cu^1 sites sit midway between planes containing Ba; Cu^2 sites lie between planes containing Ba and Y.

The ordering of the Cu-sublattice may couple to the Cu valence in important ways. If the Cu ions were restricted to have integral charge the stoichiometric requirement for an average valence of 2.3 would require the pattern $\dots\text{Cu}^{+3}\text{Cu}^{+2}\text{Cu}^{+2}\dots$, which can be accommodated quite simply by placing Cu^{+3} in the Cu^1 sites. However, because of the localization of the charge the resulting compound would probably be an insulator. There are several features of the lattice that oppose the development of a pattern based on integral Cu valence, including the charge separation that would result between the planes at $z=0$ and those near $z=c/2$ and the preference of Cu for the +2 oxidation state. These factors likely spread the Cu charge, consistent with the $(1/3)[001]$ ordering vector, to create the fractional Cu valence that is favorable for conductivity.

4. Discussion

a. Other Compatible Stoichiometries

It is interesting to note that there are two other arrangements of the oxygen atoms that are consistent with the ordering pattern given here. The first is obtained by reversing the oxygen and vacancy ordering on the O' -sublattice, equation (13). This arrangement yields a stoichiometric formula $YBa_2Cu_3O_8$ and is consistent with a uniform Cu^{+3} ionic charge. The formation of this structure is opposed by the preference of Cu for the +2 oxidation state.

The second alternate stoichiometry is obtained by emptying the O-sites on the O' sublattice. This creates the compound $YBa_2Cu_3O_6$, and removes the need for the k^3 ordering wave. The compound would have an average copper valence of 1.67, which corresponds to mixed Cu^{+2} and Cu^{+1} states in a $Cu^{+1}Cu^{+2}Cu^{+2}$ pattern. Given that this stoichiometry eliminates one ordering step and leads to preferred oxidation states of the Cu ion, it is perhaps surprising that it is not more commonly observed. The reason may lie in the openness of the resulting structure, which easily accommodates an excess of oxygen, or in physical effects that are not accounted for here.

b. Other Compatible Compositions

The possibility that the Y-Ba-Cu-O phase has structural relatives with still better superconducting properties has generated an interest in modifications of the compound. It is perhaps useful to note that, in light of the ordering scheme of the basic compound, its compositional modifications can be systematically divided into four basic types.

(1) Complete substitution for one element of the compound, as, for example, substitution of a trivalent rare earth for Y or divalent Sr for Ba. The $YBa_2Cu_3O_7$ structure is at least a possible structure of the substituted oxide.

(2) Complete substitution on a sublattice of the ordered oxide. If all of the atoms on any sublattice of the oxide are replaced then a new compound is created that can have the same structure. The obvious possibilities include the substitution of an anion (X) for all oxygens on the O' sublattice to create the stoichiometric compound $\text{YBa}_2\text{Cu}_3\text{O}_6\text{X}$, or for the oxygen atoms in the $x=0$ and $x=1$ faces in the planes at $c/3$ and $2c/3$ to create the stoichiometric compound $\text{YBa}_2\text{Cu}_3\text{O}_5\text{X}_2$ (Figure 6), and the substitution of a cation (M) on either the Cu^{+2} or Cu^{+3} sites, which creates, respectively, the compounds $\text{YBa}_2\text{Cu}_2\text{MO}_7$ and $\text{YBa}_2\text{CuM}_2\text{O}_7$.

(3) Incomplete substitution for the atoms on a sublattice to create a solid solution or "alloy". Since the alloy does not satisfy the Nernst principle, at low temperature it is at least metastable with respect to a transition that completes its order, which may be a quaternary ordering on the parent oxide lattice or a decomposition that separates the alloy into discrete ordered phases.

c. Possible Relations between Structure and Superconductivity

While the mechanism of superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_7$ is not fully understood, there is general agreement that the high critical temperature is associated with the ordering of oxygen atoms and vacancies on the O' sublattice in the planes at $c = 0.1$ in Figure 5. The k^2 -order in this plane provides rows of Cu atoms in the [010] direction that are separated by vacancies. In addition, the k^2 -order has the probable consequence that there is an accumulation of positive charge on the Cu-ions in this plane; if the crystal were strictly ionic they would be in the +3 oxidation state.

Since vacancies on the oxygen sublattice behave as if they were local positive charges the wave-functions of the copper atoms that are not involved in covalent bonding are pointed at vacancies and aligned along the [010] rows. Their overlap may provide quasi-one-dimensional metallic or semimetallic conductivity along the rows. This

situation is favorable for superconductivity because the density of states of quasi-one-dimensional metals near the Fermi level is very high. This suggests that the exceptional T_c of the oxide is largely due to the k^3 -order of the oxygen sublattice, which changes the dimensionality of conduction in the basal plane.

There are, however, two well-known phenomena that have an adverse effect on one-dimensional superconductivity: the Peierls transition and Verwey ordering (formation of charge density waves). Both open gaps at the Fermi level that result in metal-insulator transitions. The appearance of superconductivity is governed by a competition between the superconducting transition and these transitions to insulating states, which may be affected by small changes in composition or order.

ACKNOWLEDGMENTS

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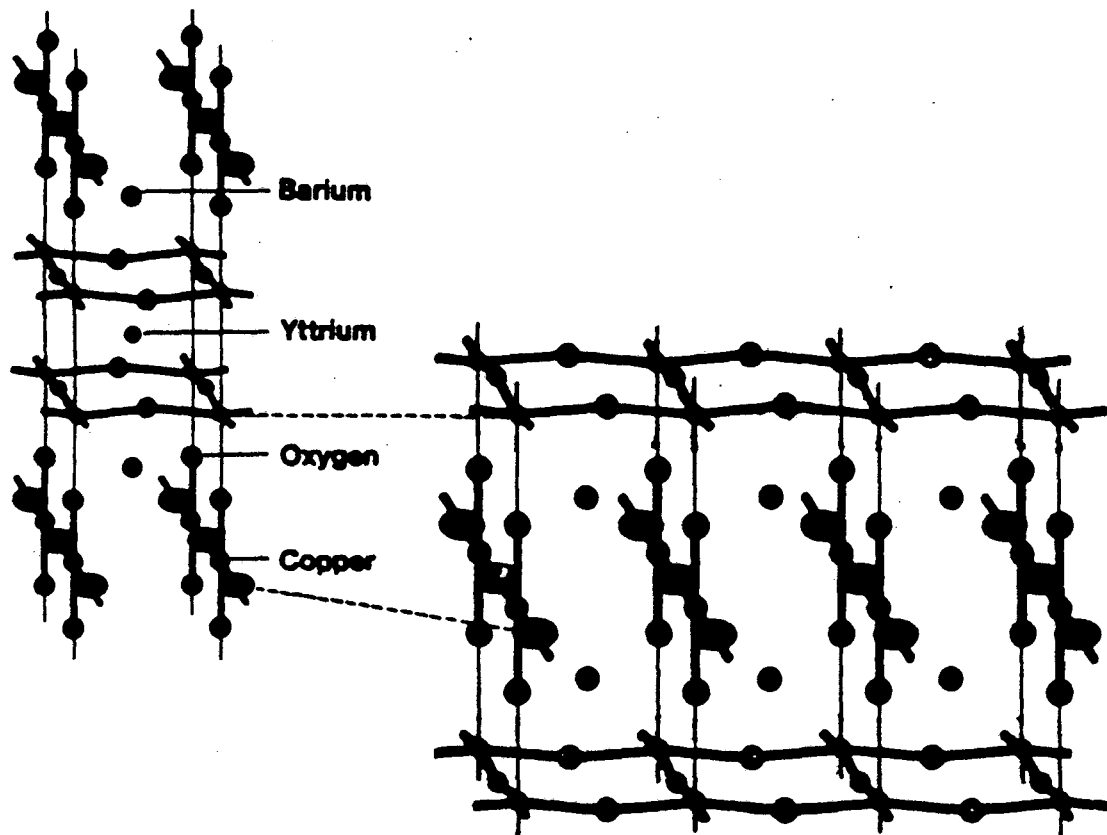
REFERENCES

1. M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang and C.W. Chu, *Phys. Rev. Lett.*, **58**, 908 (1987)
2. R.M. Hazen, L.W. Finger, R.J. Angel, C.T. Prewitt, N.L. Ross, H.K. Mao, C.G. Hadjidakos, P.H. Hor, R.L. Meng and C.W. Chu, *Phys. Rev. Lett.*, (in press)
3. R.J. Cava, B. Batlogg, R.B. van Dover, D.W. Murphy, S. Sunshine, T. Siegrist, J.P. Remeika, E.A. Reitman, S. Zahurak and G.P. Espinosa, *Phys. Rev. Lett.*, (submitted)

4. M.A. Beno, L. Soderholm, D.W. Capone II, D.G. Hinks, J.D. Jorgenson, I.K. Schuller, C.U. Segre, K. Zhang and J.D. Grace, **Appl. Phys. Lett.**, (submitted)
5. I.K. Schuller, D.G. Hinks, M.A. Beno, D.W. Capone II, L. Soderholm, J.-P. Locquet, Y. Bruynseraede, C.U. Segre and K. Zhang, **Solid State Comm.**, (submitted)
6. B.I. Pokrovskii and A.G. Khachaturyan, **J. Solid State Chem.**, **61**, 137 (1986); *ibid.*, 154 (1986)
7. A.G. Khachaturyan and B.I. Pokrovskii, **Prog. Mat. Sci.**, **30**, 1 (1986)
8. A.G. Khachaturyan, **Prog. Mat. Sci.**, **22**, 1 (1978); **The Theory of Structural Transformations in Solids**, J. Wiley, New York (1983)

FIGURE CAPTIONS

- Fig. 1 The structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (after Beno, et al., [4])
- Fig. 2 The L1_2 ordered FCC-structure.
- Fig. 3 The perovskite structure.
- Fig. 4 The ReO_3 structure.
- Fig. 5 (a) The structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ after secondary ordering. (b)
The structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ after tertiary ordering.
- Fig. 6 The structure of the hypothetical compound $\text{YBa}_2\text{Cu}_3\text{O}_5\text{X}_7$.



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Fig 1 The structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (after Beno, et al., [4]).

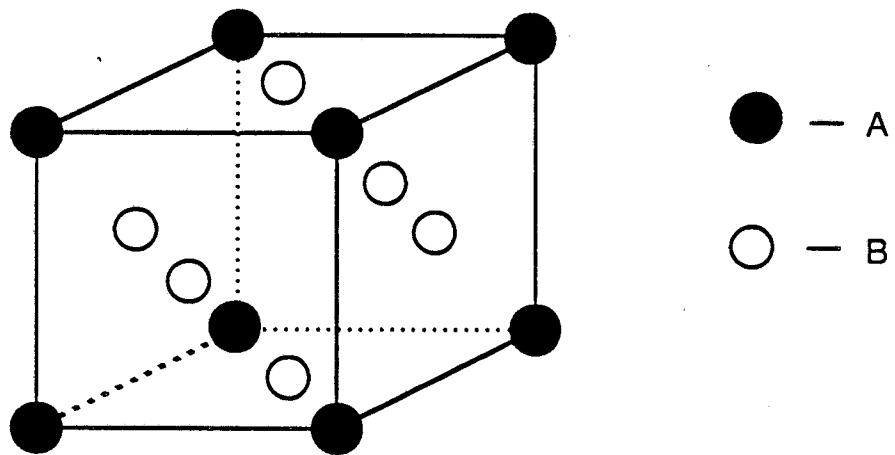


Fig. 2 The L₁₂ ordered FCC-structure.

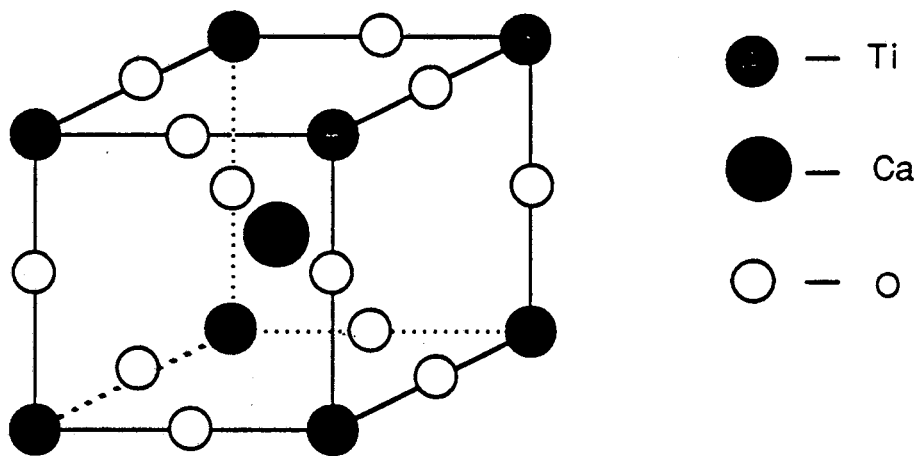


Fig. 3 The perovskite structure.

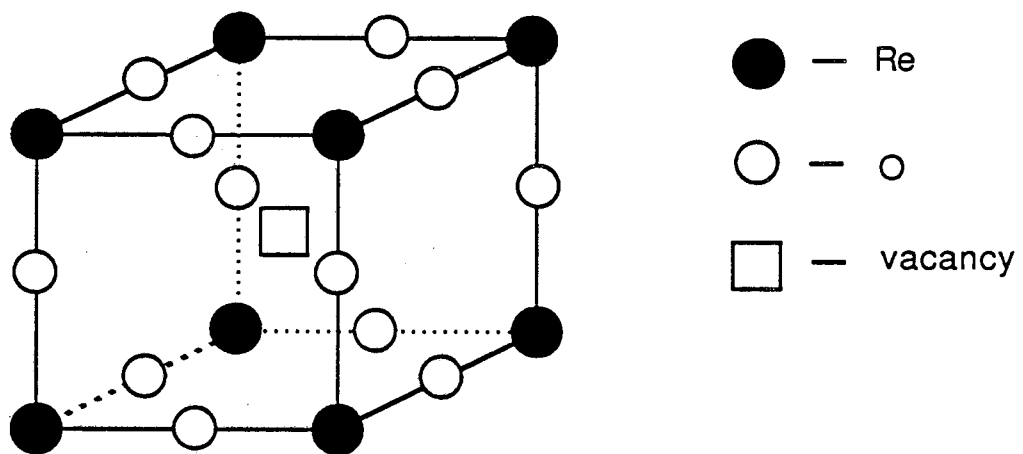


Fig. 4 The ReO_3 structure.

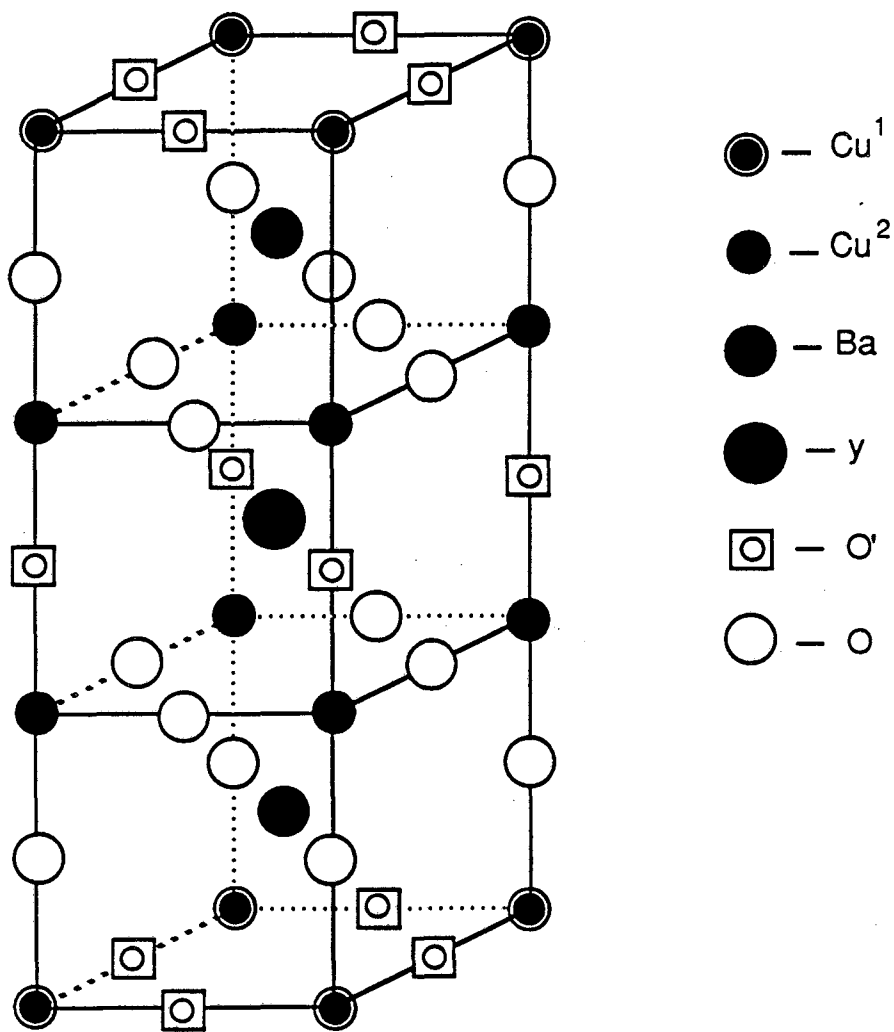


Fig. 5(a) The structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ after secondary ordering.

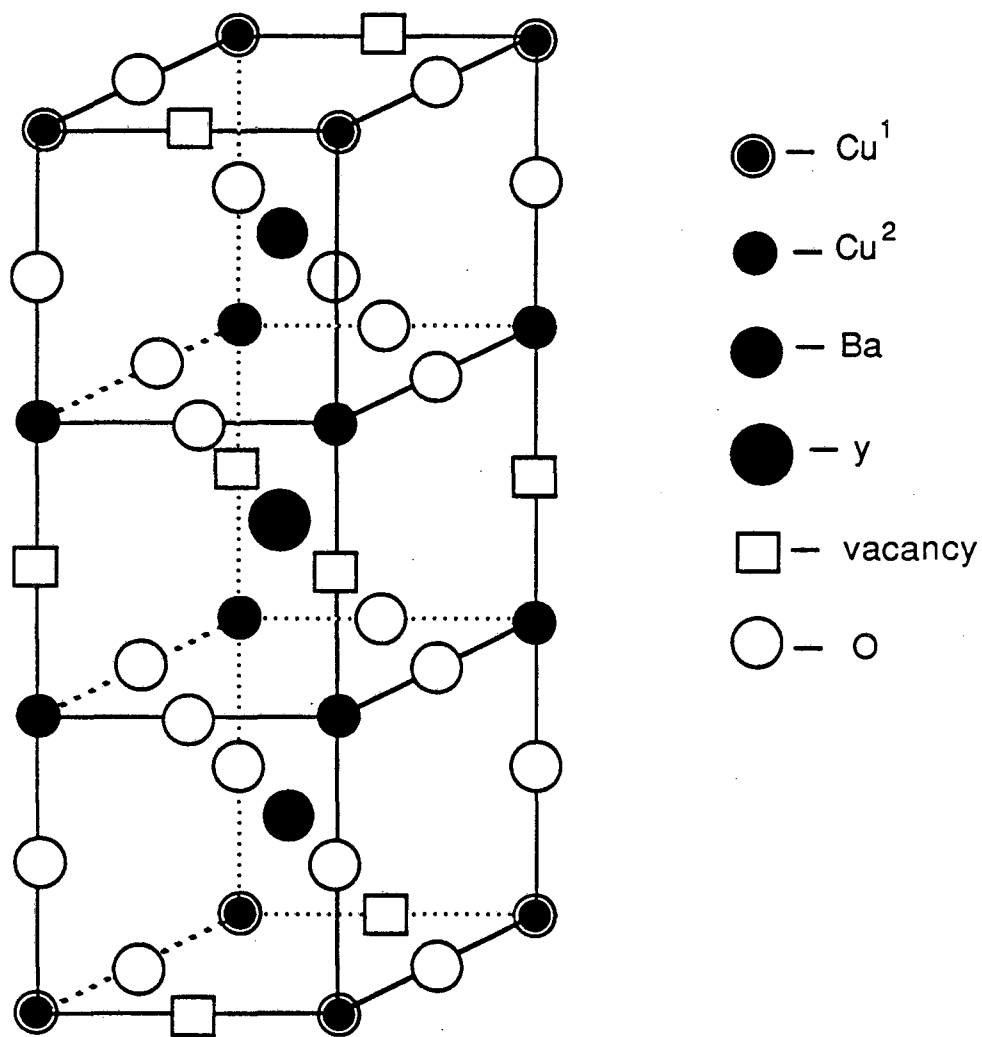


Fig. 5(b) The structure of YBa₂ Cu₃ O₇ after tertiary ordering.

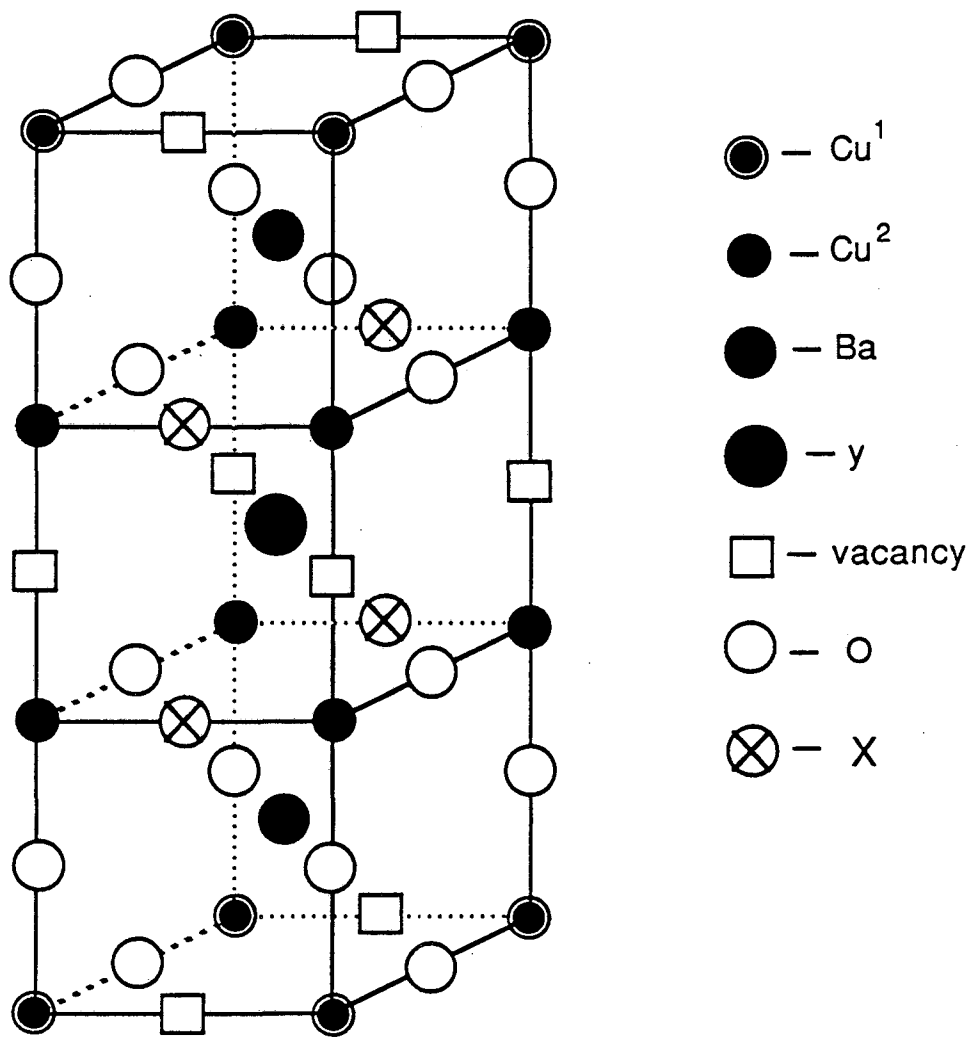


Fig. 6 The structure of the hypothetical compound $\text{YBa}_2\text{Cu}_3\text{O}_5\text{X}_7$.

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