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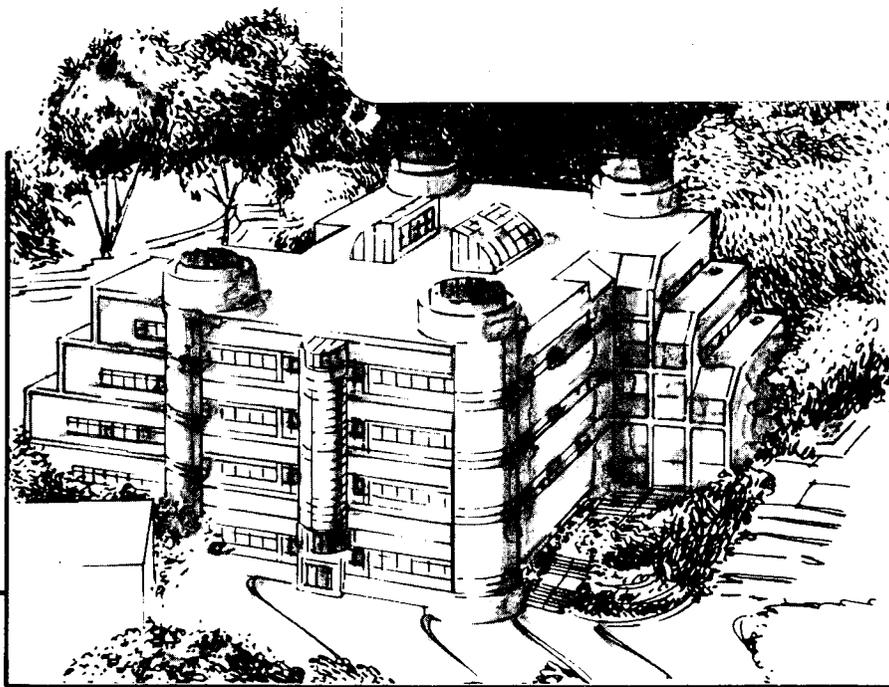
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C.J. Jou and J. Washburn

November 1988

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**A Macro-Resonance-Cell Description
for High- T_c Oxide Superconductors***

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Abstract

A phenomenological macro-resonance-cell description of bonding in high- T_c oxide superconductors based on some common structural features is proposed. In this description, the oxidation states of the cations on the lattice frame are assumed to be oscillating. The oxygen atoms are described as being in a "breathing mode" and coupling is assumed to exist between the CuO_2 layers and the boundary (capping) layers in these quasi two-dimensional systems. The variation of T_c for different materials is attributed in part to the relative effectiveness of the coupling between different kinds of boundary layer(s). Peierl's deformation or Jahn-Teller effect assisted by lattice softening and possibly magnetic ordering is discussed in relation to high T_c superconductivity in these oxides.

1. Introduction

Since the discovery of the La-Ba-Cu-O (LBCO) system of high- T_c oxide superconductors with $T_c \sim 28^\circ \text{K}$ in 1986,^[1] a world-wide search for other oxide superconductors has resulted in the discovery of the Y-Ba-Cu-O (YBCO) system with $T_c \sim 93^\circ \text{K}$ in 1987,^[2] two new classes in 1988, i.e., the Bi-Ca-Sr-Cu-O (BCS) system^[3] and the Tl-Ca-Ba-Cu-O (TCB) systems,^[4] with the highest reported $T_c \approx 110^\circ \text{K}$ and 125°K respectively. Also, a perovskite-related Ba-K-Bi-O (BKBO) system^[5] with $T_c \sim 30^\circ \text{K}$ became the first known high- T_c oxide superconductor in the bismuth oxide family. The discovery of each class provided a new challenge to the fundamental understanding of superconductivity. For example, the discovery of the YBCO system initiated a race to find a superconducting mechanism related to the oxygen-ordered Cu-O chain structure. When the BCS and TCB systems were discovered, which did not contain the linear chain structure of the YBCO system but had even higher T_c , emphasis shifted to the CuO_2 layers that were common to all known high T_c copper oxide superconductors.

A heavily twinned microstructure is a unique property of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ among all known high- T_c ceramic superconductors. Orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ with oxygen content ranging from about 6.5 to 7.0 has bad metallic properties at temperature higher than T_c and becomes superconducting below T_c . In contrast, the higher symmetry parent structure, tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $6.0 \leq x \leq 6.5$ exhibits electrical properties ranging from insulator to semiconductor at all temperatures and does not have the twinned morphology. The oxygen-ordered b-chain and perhaps the twinning in the orthorhombic phase apparently play an important role in the dramatic transition of the properties from insulator-semiconductor to superconductor.

A clear explanation of the mechanism of this superconductivity should be able to explain why orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ is a superconductor and tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x$ is not. Although many speculative theories currently coexist, none can satisfactorily explain all the observed superconducting phenomena. A qualitative phenomenological description is proposed here, based on the observation that certain features of the bonding are common to all the high- T_c oxide superconductors that are not present in closely related nonsuperconducting phases such as tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x$.

2. Various Oxidation States, Breathing Modes and Macro Resonance Cells

All the presently known high- T_c oxide superconductors except BKBO share a common pseudo-two-dimensional structure with CuO_2 layers sandwiched between metallic layers. This structure appears to play a critical role for the observed superconductivity. In all of these materials the structure can be described by stacked perovskite-related unit cells. They all show poor metallic properties above T_c and are all oxygen-deficient because of doping with randomly distributed dopants. For the YBCO, BCS and TCB systems, Cu^{III} , Bi^{III} and Tl^{III} can be considered as substitutional dopants in the three-dimensional Cu^{II} lattice which result in randomly distributed oxygen vacancies in the capping layers, i.e., $\text{Cu}^{\text{III}}\text{O}$ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{Bi}_2^{\text{III}}\text{O}_2$ in BCS and $\text{Tl}_2^{\text{III}}\text{O}_2$ in TCB systems. The result of this doping is that the uniformity of the oxidation state (III) of cations in the capping layer(s), which is also a common feature in copper oxide superconductors, is destroyed.

Intriguingly, both of the current known high T_c oxide families, copper oxide and bismuth oxide, have a common feature, i.e., more than one charge state with a difference of charge equal to two on the cations located at the frames, i.e., the cations at the centers of the oxygen octahedral sites, of their lattices, e.g., Cu with valence I, II, and III, Bi with III and V, Tl with I and III, and Pb with II and IV. The lowest one is designated in the following description as the fundamental oxidation state. These charge states represent cations in different environments of oxygen bonding,^[6] e.g., the Cu(I) oxidation state has two characteristic shortest Cu-O bonds on opposite sides at about 1.85 Å distinguishable from the other longer orthogonal Cu-O bonds, the Cu(II) oxidation state has four characteristic shortest bonds of about 1.90 Å in a cross arrangement with two other longer Cu-O bonds perpendicular to the plane and the Cu(III) oxidation state has four characteristic shortest bonds of 1.85 Å in the same cross arrangement as in Cu(II) but with the perpendicular Cu-O bonds even longer.

In an octahedron with Cu in the center and O at the six corners, the oxidation state of Cu could be considered to vary continuously between I and III as the four oxygens on the same plane harmonically oscillate in phase and the other two oxygens 180° out of phase, i.e., when the former move toward Cu simultaneously, the latter move away from Cu and vice versa. It is suggested here that this type of harmonically oscillating oxygen induces the variation of the Cu oxidation state and is referred to as the “breathing mode” of oxygen as in the perovskite structure of bismuth oxide $\text{Ba}(\text{Pb}_{0.7}\text{Bi}_{0.3})\text{O}_{3.8}$ ^[7] and the perovskite-

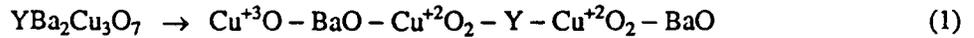
related 2-1-4 structure of $(La_{2-x}A_x)CuO_{4-\delta}$ with $A = Ba, Sr, \text{ or } Ca$. Other variations of the oxygen breathing mode include the CuO_5 pyramid configuration with Cu near the center of the square base and the CuO_4 square configuration with Cu at the center. The last two configurations are found in the $YBa_2Cu_3O_{7-\delta}$ orthorhombic structure but only the pyramid arrangement is found in the tetragonal structure because its oxygen on the basal plane is randomly distributed, i.e., disordered. Neutron diffraction^[8] reveals the equilibrium distance between Cu1 and O1 matches the characteristic bond length for Cu(I)-O and the equilibrium distances of Cu2-O2 and Cu2-O3 are slightly larger than the characteristic bond length for Cu(II)-O in the octahedron configuration.

Among all known classes of high- T_c oxide superconductors, the YBCO system has the most unusual features in its structure. The cation in its capping layer, CuO, is the same as that of the CuO_2 layers. Hence, the Cu cations in this structure form a three-dimensional frame similar to the Bi frame in the BKBO system. The stacking sequence of the YBCO system has only a single period and single boundary layer, unlike the other systems, all of which have a double period with phase shift as the stacking sequence is followed through the center of the double boundary layers (see Table 1). Also, oxygen atoms in the capping layer of the YBCO system are ordered forming a linear chain structure on the basal plane. This oxygen (vacancy) ordering mechanism results in an orthorhombic structure which in turn results in a finely twinned microstructure which is formed when the structure changes from tetragonal to orthorhombic on cooling.

Table 1. Stacking sequence of layers in unit cell.

$\text{YBa}_2\text{Cu}_3\text{O}_7$	(n=2)	<table style="border-collapse: collapse; margin: auto;"> <tr> <td style="border: 1px solid black; padding: 2px;">Ba</td> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">Y</td> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">Ba</td> <td style="border: 1px solid black; padding: 2px;"></td> <td style="padding: 2px;">← center</td> </tr> <tr> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">O₂</td> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">O₂</td> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="padding: 2px;">← edge</td> </tr> <tr> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;">Cu</td> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">Cu</td> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;">Cu</td> <td style="padding: 2px;">← corner</td> </tr> </table>	Ba		Y		Ba		← center		O ₂		O ₂		O	← edge	O	Cu		Cu	O	Cu	← corner																								
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$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	(n=2)	<table style="border-collapse: collapse; margin: auto;"> <tr> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;">Sr</td> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">Ca</td> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">Sr</td> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;"> </td> <td style="border: 1px solid black; padding: 2px;">Bi</td> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;">Cu</td> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">Cu</td> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;">Bi</td> </tr> <tr> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;">O₂</td> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">O₂</td> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;">Bi</td> <td style="border: 1px solid black; padding: 2px;"> </td> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;">Sr</td> <td style="border: 1px solid black; padding: 2px;">O₂</td> <td style="border: 1px solid black; padding: 2px;">Ca</td> <td style="border: 1px solid black; padding: 2px;">O₂</td> <td style="border: 1px solid black; padding: 2px;">Sr</td> <td style="border: 1px solid black; padding: 2px;">O</td> </tr> <tr> <td style="border: 1px solid black; padding: 2px;">Bi</td> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;">Cu</td> <td style="border: 1px solid black; padding: 2px;"></td> <td style="border: 1px solid black; padding: 2px;">Cu</td> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;">Bi</td> <td style="border: 1px solid black; padding: 2px;"> </td> <td style="border: 1px solid black; padding: 2px;">O</td> <td style="border: 1px solid black; padding: 2px;">Sr</td> <td style="border: 1px solid black; padding: 2px;">Cu</td> <td style="border: 1px solid black; padding: 2px;">Ca</td> <td style="border: 1px solid black; padding: 2px;">Cu</td> <td style="border: 1px solid black; padding: 2px;">Sr</td> <td style="border: 1px solid black; padding: 2px;">O</td> </tr> </table>	O	Sr		Ca		Sr	O		Bi	O	Cu		Cu	O	Bi		O	O ₂		O ₂	O	Bi		O	Sr	O ₂	Ca	O ₂	Sr	O	Bi	O	Cu		Cu	O	Bi		O	Sr	Cu	Ca	Cu	Sr	O
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A consideration of charge balance in stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_7$ shows Cu_3 should have a total charge of +7 which can reasonably be distributed as Cu^{+2} , Cu^{+2} and Cu^{+3} , or in layer-stacking sequence as:



where Cu^{+3}O is the boundary (capping) layer or the basal plane containing O4-Cu1-O4 b-chains, and Cu^{+2}O_2 is the layer containing the base of the pyramid configuration near the central plane. Cu^{+3} could be further expressed as $\text{Cu}^{+3} \rightarrow \text{Cu}^{+1} + 2h$ with the electronic holes (h) located at the overlapped orbitals of $\text{O} : 2p_z$ and $\text{Cu} : 3d_{3z^2-r^2}$ along the c-axis direction or $\text{O} : 2p_y$ and $\text{Cu} : 3d_{x^2-y^2}$ along the b-chain direction and oscillating between Cu and O regulated by the vibration of O. The breathing mode which describes the overall Cu oxidation state oscillating between I and III in $\text{YBa}_2\text{Cu}_3\text{O}_7$ could be realized by the synchronized harmonic oscillation of the two neighboring O4 (b-chain) oxygens and two neighboring O1 (on c-axis) oxygens (see Fig. 1a). Note the oxidation states of neighboring Cu1 atoms on the same b-chain would be oscillating out-of-phase due to the breathing mode of oxygen and that the Cu cation on the basal plane of

tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$ has the fundamental oxidation state, Cu^1 , hence could not oscillate harmonically. Similarly, the Cu^{+2}O_2 plane could be presented as shown in Fig. 1b with $\text{Cu}^{+2} \rightarrow \text{Cu}^{+1} + \text{h}$ and holes are assumed to resonate between two lobes of the $\text{O} : \text{p}$ orbitals on opposite sides of oxygen according to Pauling's resonating bond model.^[6] The oscillation of the oxidation state of Cu2 on the CuO_2 plane is implemented by the breathing mode of two O2 and two O3 on the plane as well as O1 and Cu2 oscillating along the c-axis direction. The oxidation states of the neighboring Cu2 on the CuO_2 plane would then be oscillating 180° out-of-phase. The central four oxygens at corners of the shaded square in Fig. 1b would undergo a Peierl's deformation assuming oxygens vibrate in the breathing mode, which would break the degeneracy, lower the energy and symmetry of the system and create the Jahn-Teller gap at the Fermi level^[9] necessary for the stabilization of superconducting pairs.

The Cu cations in the $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ crystal form a three dimensional frame. Assuming the oxidation states of the neighboring Cu cations, along the c-axis direction, are oscillating 180° out-of-phase, due to the polarization fluctuation, a macro resonance state (MRS) could be established in the whole lattice. A repeating unit of the macro resonance cell (MRC) would be composed of eight unit cells ($2a \times 2b \times 2c$) with double periods along the c-axis direction as in the BCS, TCB and LSCO systems. The role of oxygen on the O1 sites could be to force, together with ordered oxygen on the O4 (b-chain) sites, the oxidation state of Cu1 to oscillate and to couple it to that of Cu2 in the neighboring CuO_2 plane yielding a macro resonance of the whole crystal lattice. However, the Cu2-O1 distance is too long for strong coupling, the coupling (Fig. 2) is possibly assisted by a soft mode of lattice vibration as evidenced by electron energy loss spectroscopy^[10] (EELS) and electron diffraction at low temperature.^[11] The $\text{YBa}_2\text{Cu}_3\text{O}_x$ tetragonal phase does not have the ordered oxygen on O4 sites. Thus macro resonance of the whole lattice could not be achieved. The boundary layer with its deficient and disordered oxygen would be expected to damp the resonance. Regularity at the boundary layers is probably necessary to achieve the MRS in the YBCO system as well as in other systems which will be discussed later.

The production of holes by the demotion of copper in the higher oxidation states into the lowest (fundamental) one, i.e., $\text{Cu}^{+3} \rightarrow \text{Cu}^{+1} + 2\text{h}$ in the CuO boundary layer and $\text{Cu}^{+2} \rightarrow \text{Cu}^{+1} + \text{h}$ in the CuO_2 layers, could provide an antiferromagnetic correlated background necessary for the coupling of superconducting pairs.^[12] The calculated hole counts^[13] for the superconducting phase $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $x = 7.0 - 6.3$ fol-

lows the same trend as T_c as a function of x ^[14] in the same range of oxygen content suggesting that hole pairs indeed relate to the superconductivity. Experimentally, a strong electronic transition in the visible-near-uv optical spectra of nonsuperconducting, tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $6.0 \leq x < 6.33$ is associated with the existence of a highly localized Cu^{+1} complex^[15] as would be expected in the description: $\text{Cu}^{+3} \rightarrow \text{Cu}^{+1} + 2h$ and $\text{Cu}^{+2} \rightarrow \text{Cu}^{+1} + h$, and is coincident with the antiferromagnetic phase in the same range of oxygen content.^[16] Also, EELS experiments on superconducting YBCO material show an enhanced broad peak, on a nonsuperconducting background, appearing in the frequency range of the breathing modes of the oxygen vibrations.^[17] A similar enhanced breathing-mode peak is observed in superconducting $(\text{La}_{1.85}\text{Sr}_{0.15})\text{CuO}_{4-\delta}$ over nonsuperconducting La_2CuO_4 .^[16] The large charge oscillations of Cu between I and III could be enhanced by a longitudinal optical (LO) phonon mode, similar to the soft mode observed in La_2CuO_4 , and yield a strong attractive force acting on the pair (Fig. 2).^[17] A MRS of oxidation states on the Cu frame oscillating in LO frequency assisted by the breathing mode of oxygen vibration could enhance the coupling of the hole pairs^[17] as all these observations suggest. These pre-existing free pairs could condense into coherent superconducting pairs when the temperature drops to T_c .^[18]

3. Pseudogap, Delocalization and Mott's I-M Transition

All the known high- T_c oxide superconductors have poor metallic properties in the normal conducting state, i.e., they tend to occur near a metal-insulator transition into an odd-electron insulator with peculiar magnetic properties as pointed out by Anderson.^[12] According to Anderson's RVB theory, a perfect resonance lattice would lead to an insulator,^[19] e.g., La_2CuO_4 and BaBiO_3 ($\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$), instead of a superconductor. Friedel and Noguera^[20] have shown that if the resonant states form a periodic lattice, i.e., a perfect resonance lattice, there will be a real gap splitting the peak of the density of states (DOS) from the middle into two peaks thus yielding an insulator. But if these resonant states, e.g., macro resonance cells, are distributed at random in three dimensions, a pseudo gap will exist at the DOS peak resulting in poor metallic properties. A similar situation that can cause this type of Mott's insulator-metal (I-M) transition could be to have the perfect resonance lattice doped with randomly distributed, isolated impurities (or charged defects) which could result in local disorder or unsynchronized resonance and delocalization of the charge carriers changing the insulating state into the conducting state. From a mean field RVB theory

point of view,^[12] these oxides would become superconductors as soon as they are doped to become metalized, i.e., the bounded or localized hole pairs would become delocalized or free pairs.

This kind of composition-controlled I-M transition has been observed in perovskite-related oxides of the type $(\text{La}_{1-x}\text{Sr}_x)\text{BO}_3$ and $\text{La}(\text{Ni}_{1-x}\text{B}_x)\text{O}_3$ with $\text{B} = \text{Ti}^{+3}, \text{V}^{+3}, \text{Cr}^{+3}, \text{Mn}^{+3}, \text{Fe}^{+3}, \text{Co}^{+3}$ and Ni^{+3} .^[21] In high- T_c oxides, Mott's I-M transition could be accomplished (I) by creating disorder with a randomly distributed A-site substitutional dopant having different charge, e.g., hole acceptor K^{I} in three-dimensional 1-1-3 perovskite-related $(\text{Ba}_{0.6}^{\text{II}}\text{K}_{0.4}^{\text{I}})\text{Bi}^{(\text{III},\text{V})}\text{O}_{3.8}$ (undoped BaBiO_3 ($\text{Ba}_2^{\text{II}}\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$) is an insulator), or by doping elements, A^{II} , in quasi-two-dimensional 2-1-4 perovskite-related $(\text{La}_{1-x}^{\text{III}}\text{A}_x^{\text{II}})_2\text{Cu}^{(\text{II},\text{III})}\text{O}_{4.8}$ with $\text{A} = \text{Ba}, \text{Sr}$ or Ca where $\text{La}_2^{\text{III}}\text{Cu}^{(\text{II},\text{III})}\text{O}_4$ is an insulator; or (II) by creating disorder through changing the exchange potential with a B-site substitutional dopant having the same (average) charge but different $3d^n$, e.g., Bi in $\text{Ba}(\text{Pb}_{0.7}^{\text{IV}}\text{Bi}_{0.3}^{\text{IV}})\text{O}_{3.8}$ where BaPbO_3 becomes superconducting only below 0.5° K; or (III) by absorbing oxygen (or sulfur, fluorine, etc.) at interstitial sites on the boundary (capping) layer(s) with some disordered oxygen vacancies confined on the boundary layer(s), e.g., nonmetallic tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$ absorbs oxygen at the boundary layer to become superconducting orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$. These oxygens acting as hole donors are expected to pull down the Fermi level to intersect more $E(k)$ bands and promote the cation in the boundary layer(s) from a fundamental oxidation state, e.g., $\text{Cu}^{\text{I}}, \text{Tl}^{\text{I}}$, to a higher (nominal) oxidation state, e.g., $\text{Cu}^{\text{III}}, \text{Tl}^{\text{III}}$, which in turn could provide holes as charge carriers and oscillate about the average oxidation state II. In YBCO and in the TCB systems, oxygen vacancies that are required to create disorder in the perfect MRS naturally exist due to an equilibrium vacancy concentration. In the YBCO system, some of these vacancies could be concentrated at twin boundaries to reduce the system energy. Otherwise, they would be randomly distributed on capping layer(s). In both systems, oxygen is absorbed to promote most of the cations on the capping layer(s). In the BCS system, however, the cations in the fully oxidized boundary layers would have oxidation state Bi^{III} , which is the fundamental oxidation state of Bi and could not provide charge carriers. Similar to the case in which Cu^{II} is promoted to Cu^{III} through shortening the length of the four Cu-O bonds in the CuO_4 plane of the CuO_6 octahedral structure,^[6] promotion of Bi^{III} to Bi^{V} is probably accomplished by removing some of the oxygen, or by limiting absorption of oxygen through fast cooling or quenching, so that the Bi^{III} nearest to the oxygen vacancies could attract some of its first neighboring oxygens (two on the Cu-O-Bi-O-Sr chain along the c-axis direction and

two others on the Bi-O-Bi-O-Bi chain at about right angles to the c-axis direction), yielding a Bi^V oxidation state by decreasing certain bond lengths. Thus in the BCS system, only partial oxidation is necessary which would promote part of Bi to Bi^V rather than Bi^{III}. These oxygen vacancies in the BCS system could be necessary to yield metallic properties as discussed above and could be produced by a quench-in process. However, oxygen vacancies in systems with substitutional dopants, i.e., case (I) and (II), could also be formed due to the requirement of charge balance. Once the critical doping level is exceeded,^[18] the charge carrier could be delocalized and the material would become metallic.

It is interesting to note that in all the presently known high-T_c oxide superconductors the cations in the centers of the oxygen octahedra or its variations all have more than one oxidation state with a charge difference of two. Assuming the lowest oxidation state is the fundamental one, then all these cations at the boundary layer(s) would be in high oxidation states which can drop back to the fundamental oxidation state by contributing a pair of holes, e.g., Cu^{III} → Cu^I + 2h, Bi^V → Bi^{III} + 2h, Tl^{III} → Tl^I + 2h and Pb^{IV} → Pb^{II} + 2h, and then have their oxidation state oscillating about the average. Also, each pair of copper ions, Cu⁺², in the square lattice of CuO₂ plane could contribute a pair of holes by 2Cu⁺² → 2Cu⁺¹ + 2h. These holes as determined by Hall measurement^[22] are the charge carriers in the normal conducting state and as discussed above could condense into superconducting pairs in the imperfect or defected MRS (DRS) when the system is doped to create enough local disruptions, and become metallic.

4. Quasi-Two-Dimensionality, Boundary Layers, and Layer Coupling

As shown by many calculated energy band structures using various methods, all high T_c copper oxide superconductors have quasi-two-dimensional characteristics,^[23] i.e., the total N(E_F) can be dissociated into the sum of the partial ΔN(E_F) due to individual CuO₂ layers, the capping boundary layers and a correction term representing the coupling between CuO₂ layers and the capping layers:

$$N(E_F) = n_{\text{CuO}_2} \cdot \Delta N_{\text{CuO}_2}^{\text{ave}}(E_F) + n_{\text{cap}}^{\text{eff}} \cdot \Delta N_{\text{cap}}^{\text{ave}}(E_F) + \Delta N_{\text{coupling}}(E_F) \quad (2)$$

where n_{CuO_2} is the number of CuO₂ layers and $n_{\text{cap}}^{\text{eff}}$ is the effective number of capping layers. When an energy band in the E(k) diagram does not intersect the zone E_F ± Δ, this branch will not contribute to the N(E_F), i.e., ΔN(E_F) = 0. When there are double boundary layers, the number of energy bands related to these boundary layers is doubled but the contribution due to each band is not exactly the same. Thus $n_{\text{cap}}^{\text{eff}}$

represents this effect. The same effect also exists in CuO_2 layers but much less significantly, since $E(\mathbf{k})$ s of these layers are very close to E_F and to each other due to degeneracy. The correction coupling-term may have strong influence on the total $N(E_F)^{[24]}$ and thus cannot be omitted. This term represents the coupling power of the boundary layer(s) which reflects the coupling strength of boundary layer(s) to CuO_2 layers and the interference between or at boundary layers.

Each decoupled plane has its partial density of states (DOS), which is proportional to the inverse of the slope of $E(\mathbf{k})$ with proportional constant B , contributing to the total $N(E_F)$. Approximately, each band intersecting the zone $E_F \pm \Delta$ at $(k_F - m''\Delta k, E_F + \Delta)$ and $(k_F + m'\Delta k, E_F + \Delta)$ will have contribution:

$$\Delta N(E_F) = \int_{E_F - \Delta}^{E_F + \Delta} \text{DOS}(E) dE = \int B \frac{dE}{\left[\frac{dE(\mathbf{k})}{dk} \right]} \approx \int_{k_F - m''\Delta k}^{k_F + m'\Delta k} B' dk = B'(m' + m'') \Delta k = B'm \Delta k \quad (3)$$

where $m\Delta k$ is the total expansion length of k where $E(\mathbf{k})$ intersects the zone $E_F \pm \Delta$ on Fermi surface, with

$$\Delta k = \frac{\pi/b}{N_A} = \frac{\pi}{V_o} ac \quad (4)$$

in three dimensional lattice. N_A , a , b , c , and V_o are Avogadro number, lattice constants and the molar volume, respectively.

Assuming a simplified BCS expression of $T_c = A\langle\omega\rangle \exp(-1/N(E_F)V)$ with constant A and interaction parameter V , then

$$\begin{aligned} \ln T_c &= A' + \ln \langle\omega\rangle - \frac{1}{N(E_F)V} \\ &= A' + \ln \langle\omega\rangle - \frac{V_o}{B'\pi a V} \left[\frac{1}{n_{\text{CuO}_2} \cdot m_{\text{CuO}_2}^{\text{ave}} \cdot c_{\text{CuO}_2} + n_{\text{cap}}^{\text{eff}} \cdot m_{\text{cap}}^{\text{ave}} \cdot c_{\text{cap}} + \text{coupling term}} \right] \end{aligned} \quad (5)$$

where c_{CuO_2} and c_{cap} are the thickness of CuO_2 and cap (boundary) layer, respectively. When n_{CuO_2} in the equation increases, T_c should increase consistent with the trend in Table 2. When $n_{\text{CuO}_2} \rightarrow \infty$, there is a limit for T_c . However, without a capping layer E_F could shift into a real bandgap or a half-filled band before T_c reaches the limiting value, e.g., $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$, with infinite stacking sequence, has strong electron correlation effects to result in localized spin, antiferromagnetic exchange and semiconducting

behavior.^[25]

Both TCB and BCS systems show T_c increasing when the number (n) of CuO_2 layers increases, no matter if the material has a single boundary layer (SBL) or a double boundary layer (DBL) (see Table 2).

Table 2. T_c of TCB and BCS systems with various number of CuO_2 layers.

	n_{CuO_2}	SBL	DBL
TCB System	1		80 K
	2	90 K*	110 K
	3	110 K	125 K
	4	122 K 162 K [†] (?)	
BCS System	1	25 K [‡]	38 K
	2	75 K	95 K
	3		110 K
YBCO	2	93 K	80 K [§]

*Data from Ref. 26.

[†] $\text{TlCa}_2\text{Ba}_3\text{Cu}_4\text{O}_{11.8}$ with $T_c \approx 162$ K is not confirmed. (High T_c update.)

[‡]Data from Ref. 27.

[§]Datum from Ref. 28. Also an alternation of SBL and DBL ($\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15.8}$) in sequence yield $T_c \approx 40$ K.^[29]

This trend of increasing T_c in the same class with increasing n could be due to the increasing total number of energy states near the Fermi level, $N(E_F)$, as shown in Eq. (5).

As shown in the calculated $E(k)$ of the BCS system,^[24] a flat double layer arrangement of the boundary layers Bi_2O_2 , i.e., BiO-BiO, shows little contribution to the total $N(E_F)$, but a puckered triple layer arrangement, i.e., $\text{Bi-O}_2\text{-Bi}$, shows enhanced coupling between these capping layers and the CuO_2 layers, yielding much higher total $N(E_F)$ by causing the CuO_2 bands to move up and the Bi_2O_2 bands to move down, yielding more intersection with the $E_F \pm \Delta$ zone. The Bi- O_2 -Bi configuration could momentarily exist, assuming oxygens in $\text{O}_{\text{Sr}}\text{-Bi}^{\text{V}}\text{-O}_{\text{Bi}}$ chains are oscillating along the c -axis direction; O_{Sr} and O_{Bi} are the oxygens on the SrO and BiO layers, relatively, and Bi^{V} could demote to Bi^{III} and $2h$. As a consequence, both m_{CuO_2} and $m_{\text{Bi}_2\text{O}_2}$, as well as the coupling term would be all increased. According to Eq. (5), this configuration could thus result in a higher T_c than that of the BiO-BiO flat double layer arrangement. The quasi-two-dimensional character of all high T_c copper oxide superconductors shown from the $E(k)$

band structure allows the separate evaluation of partial number of state, e.g., $\Delta N_{\text{CuO}_2}(E_F)$ and $\Delta N_{\text{cap}}(E_F)$, due to the individual planes. However, various arrangement of Bi_2O_2 boundary layers in the BCS system^[24] shows a dramatic coupling effect between these capping layers and CuO_2 layers. Similar coupling effects could exist in other copper oxide superconductors, e.g., oxygens in $\text{O}_{\text{Ba}}-\text{Tl}^{\text{III}}-\text{O}_{\text{Tl}}$ chains ($\text{Tl}^{\text{III}} \rightarrow \text{Tl}^{\text{I}} + 2h$) are oscillating along the c-axis direction.

In both Bi-Ca-Sr-Cu-O (BCS) and Tl-Ca-Ba-Cu-O (TCB) systems with double boundary layers the stacking sequence of the cations shifts when crossing these double boundary layers (Table 1). However, the double-layered two-dimensional arrays of $\text{O}-\text{Bi}^{\text{V}}-\text{O}$ and $\text{O}-\text{Tl}^{\text{III}}-\text{O}$ along the c-axis direction in $\text{Bi}^{\text{V}}\text{O}_6$ and $\text{Tl}^{\text{III}}\text{O}_6$ octahedra in the double boundary layers of the BCS and TCB systems, respectively, apparently couple the resonance of the cation-lattice even more strongly than does the one-dimensional chain of $\text{Cu}^{\text{III}}\text{O}_4$ in the single boundary layer of the YBCO system. This could be attributed to the dimensions of the octahedra network of BiO_6 and TlO_6 , which matches that of the CuO_2 planes above and below better than the one-dimensional square chain does in $\text{YBa}_2\text{Cu}_3\text{O}_7$, so the interference due to the charge oscillation of the neighboring cations in the boundary layers is smaller. The fact that the BCS system has a lower T_c (~ 110 K) in the 2-2-2-3 phase, than that (~ 125 K) of the TCB system in the same phase may be qualitatively understood on the basis of the model. There are several reasons why a resulting macro-resonance-state in the BCS system is less stable, i.e., smaller Δ , than that in the TCB systems according to Eq. (5): (1) the very weak bonding between two BiO boundary layers (i.e., the cleavage plane); (2) the incommensurate bonding lengths between Bi-O and Cu-O; and more importantly, (3) the oxidation state of Bi at the boundary layers being the fundamental oxidation state III (only a small fraction of Bi^{III} is promoted to Bi^{V} by oxygen vacancies resulting in a smaller carrier concentration than in the TCB system).

The calculated energy band structures of $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $x = 6, 7, 8$, using the self-consistent pseudofunction method,^[30] show that major features of the lower complex of valence and conduction bands near E_F are mainly determined by the three Cu : $3d^5$ orbitals and the six, seven, or eight sets, respectively, of O : $2s^2 2p^6$ orbitals. Changing from $\text{YBa}_2\text{Cu}_3\text{O}_6$ to $\text{YBa}_2\text{Cu}_3\text{O}_7$, two important energy bands across E_F evolve. One broad anisotropic band across E_F sharply is due to the antibonding Cu : $3d-\text{O} : 2s$ orbitals in one-dimensional O4-Cu1-O4 b-chain and has little contribution to the total $N(E_F)$. The other narrow band across and staying close to E_F is from the nonbonding Cu : $3d-\text{O} : 2p$ orbitals in the same b-chain. This

narrow band has a large portion intersecting the zone $E_F \pm \Delta$ which stabilizes or pins the E_F position and contributes largely, together with the two-dimensional antibonding band from the CuO_2 planes, to the total $N(E_F)$.

Structures with double layers of the CuO plane in $\text{YBa}_2\text{Cu}_4\text{O}_8$ (1-2-4-8 structure) films have a lower $T_c \approx 80$ K,^[28] compared to $T_c \approx 93$ K of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ (1-2-3-7 or 1-2-3 structure) with a single layer of CuO. This lowering of T_c with a double CuO layer could be attributed to the mismatch of the dimensionality of the chain structure in the boundary layers to that in CuO_2 layers. The reason is that either of the two CuO layers would act as a damping boundary and phase shifter on the other layer, posing difficulty in the coupling of the oscillation of the oxidation state of Cu1 in those layers. The difficulty could be because O in the double boundary layers of 1-2-4-8 structure is bonded to three Cu atoms and has less freedom to oscillate compared to O bonded to two Cu atoms in 1-2-3-7 structure, and all the neighboring Cu1 in the different layers of the double boundary Cu_2O_2 layers, unlike the BCS and TCB systems, are closely linked to each other with the rigid network of Cu-O bonds. The MRS of the 1-2-4-8 structure might thus be expected to be less stable, i.e., Δ of 1-2-4-8 structure is smaller, than that of the 1-2-3-(7) structure.

It is interesting to compare the case $n_{\text{CuO}_2} = 2$ (Table 3) of all three systems in Table 2. For single boundary layer (SBL), BCS system has T_c (75 K) lower than the other two (90 ~ 93 K). This could be due to the incompatibility of the Bi-O bond to the Cu-O bond, yielding a weak coupling. For the structure with double boundary layers (DBL), the TCB system has $T_c \approx 110$ K, followed by the BCS system with $T_c \approx 95$ K and then the YBCO system with $T_c \approx 80$ K. For the double layers of interwoven BiO_6 octahedra network, it seems that more freedom (due to the weak bonding between two BiO layers, i.e., the cleavage plane) allows rearrangement of those incommensurate Bi-O bonds into a wavy configuration, while the single boundary layer is constrained by the two rigid CuO_2 layers. Its coupling strength becomes stronger though it is still weaker than that of the Ti_2O_2 layers which match better to the CuO_2 layers. On the other hand, double-layered linear chains in $\text{YBa}_2\text{Cu}_4\text{O}_8$ have a strong disadvantage due to dimensional incompatibility with the two-dimensional CuO_2 plane. The coupling strength is weaker than that for the single layer and T_c drops. Table 3 also shows tentatively assigned coupling strengths of the boundary layer(s) according to the T_c measured for $n_{\text{CuO}_2} = 2$ of these systems and the analysis of the bonding compatibility between the boundary layer(s) and CuO_2 layers. For comparison, $(\text{La}_{1.85}\text{Sr}_{0.15})\text{CuO}_{4.8}$ (LSCO system, $n_{\text{CuO}_2} = 1$),

(Ba_{0.6}K_{0.4}) BiO_{3-δ} (BKBO system) and Ba (Pb_{0.7}Bi_{0.3}) O_{3-δ} (BPBO system) without boundary layer (NBL) are also listed. It appears that the boundary layer(s) in copper oxide with less overlapping, therefore less interference and more flexibility, and thus better coupling to the CuO₂ layers yield stronger overall layer coupling and higher T_c. On the other hand, a high concentration of dopant randomly distributed in the rigid, three dimensional cation frame of the bismuth oxide family results in an irregular three-dimensional charge-network of cations and low T_c. In contrast, dopants in the copper oxide family are at a much lower level than in the bismuth oxide family and are confined in the boundary layer(s). The integrity of the two-dimensional CuO₂ layers is well preserved. In addition, magnetic ordering on the copper sublattice, which is absent in the bismuth/lead sublattice,^[31] together with LO mode of lattice softening may strongly enhance the boundary layer coupling yielding quasi-two-dimensionality, free pair condensation and superconductivity at T_c higher than that of the bismuth oxide family.

Table 3. T_c and tentatively assigned coupling strength of boundary layer(s) of various systems.

	n _{CuO₂} = 2	NBL	SBL	DBL	(S+D) BL
Quasi-two-dimensional copper oxide	TCB System		medium 90 K	strong 110 K	
	BCS System		medium-weak 75 K	medium (BiO-BiO) 95 K	strong (Bi-O ₂ -Bi) ?
	YBCO System		medium 93 K	medium-weak 80 K	weak 40 K
	LSCO System			weak (n=1) 38 K	
Isotropic three-dimensional bismuth oxide	BKBO System	weak 30 K			
	BPBO System	very weak 13 K			

5. Conclusions

An imperfect macro-resonance-cell description suggested by other common features in addition to CuO₂ layers of the currently known high-T_c oxide superconductors is proposed, which leads to the

following conclusions:

- It is suggested by this comparative study that oxygen doping in the boundary layers of the YBCO, TCB and BCS systems promotes the oxidation state of the cations in the boundary layer(s), thus making possible macro-resonance in these systems.
- The fact that superconductivity is observed in the orthorhombic phase of YBCO and not in the tetragonal phase is explained by the proposed macro-resonance cell description.
- Variations in T_c corresponding to different numbers of CuO_2 layers in BCS and TCB systems can be rationalized.
- Differences of T_c in various systems of oxide superconductors having the same number of CuO_2 layers can be understood in terms of different efficiency of coupling through the boundary layer(s).
- T_c changes due to different numbers of boundary layer, e.g., SBL and DBL, in the same systems can also be interpreted as a variation of coupling efficiency and interference between boundary layer(s) and CuO_2 layers.

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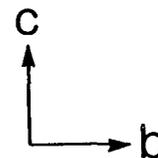
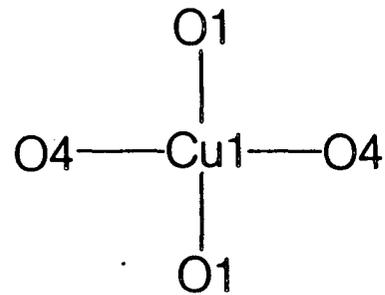
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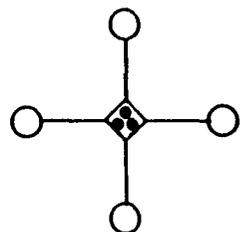
FIGURE CAPTIONS

- Fig. 1. (a) Cu in CuO basal plane of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with nominal charge +3 can be dissociated into the fundamental charge state Cu^{+1} and two holes located at the overlapped orbitals of $\text{O} : 2p_z$ and $\text{Cu} : 3d_{3z^2-r^2}$ along the c-axis direction or $\text{O} : 2p_y$ and $\text{Cu} : 3d_{x^2-y^2}$ along the b-chain direction. When oxygen oscillates in breathing mode, holes join or leave Cu^{+1} yielding a continuous variation of Cu oxidation state between III and I. Spacewisely, Cu in CuO layer still has +3 stoichiometric charge required in a unit cell. But timewisely, Cu owns only the fundamental +1 charge during most of the oscillating cycle. Note the oxidation states of neighboring Cu in the same chain are oscillating out-of-phase. (The diamond, circle, dot and small open circle represent copper, oxygen, hole, and alternative hole position, respectively.)
- (b) Similarly, Cu in CuO_2 plane with +2 charge can be dissociated into Cu^{+1} and one hole. This hole can resonate between two lobes of $\text{O} : p$ on the opposite sides of oxygen. Breathing mode of oxygen is probably encouraged by the Jahn-Teller effect as shown by the shaded area, which breaks the symmetry, lowers the energy and created a gap at E_F . The oxidation states of neighboring Cu on CuO_2 plane are oscillating out-of-phase. The holes located at the oxygen sites are only meant to be at the average positions.
- Fig. 2. A possible coupling mechanism between CuO plane (center line) and CuO_2 planes (top and bottom lines) enhanced by lattice softening mode at LO frequency shows Peierl's deformation of oxygen which lowers the system energy similar to that on CuO_2 plane (Fig. 1b). (The atomic distances in the figure are exaggerated and small details like the puckered structure on the CuO_2 plane are not shown.)

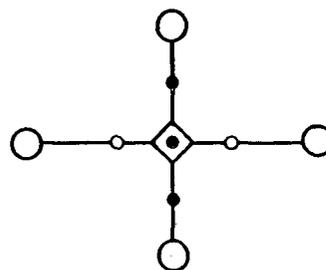
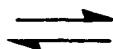
(a) Cu^{+3}O chain:



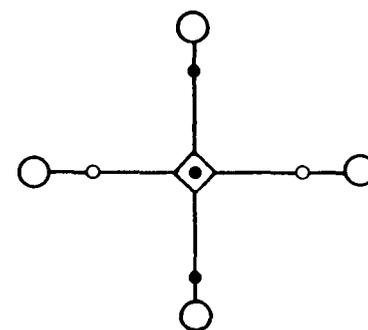
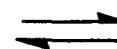
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Oxidation state III



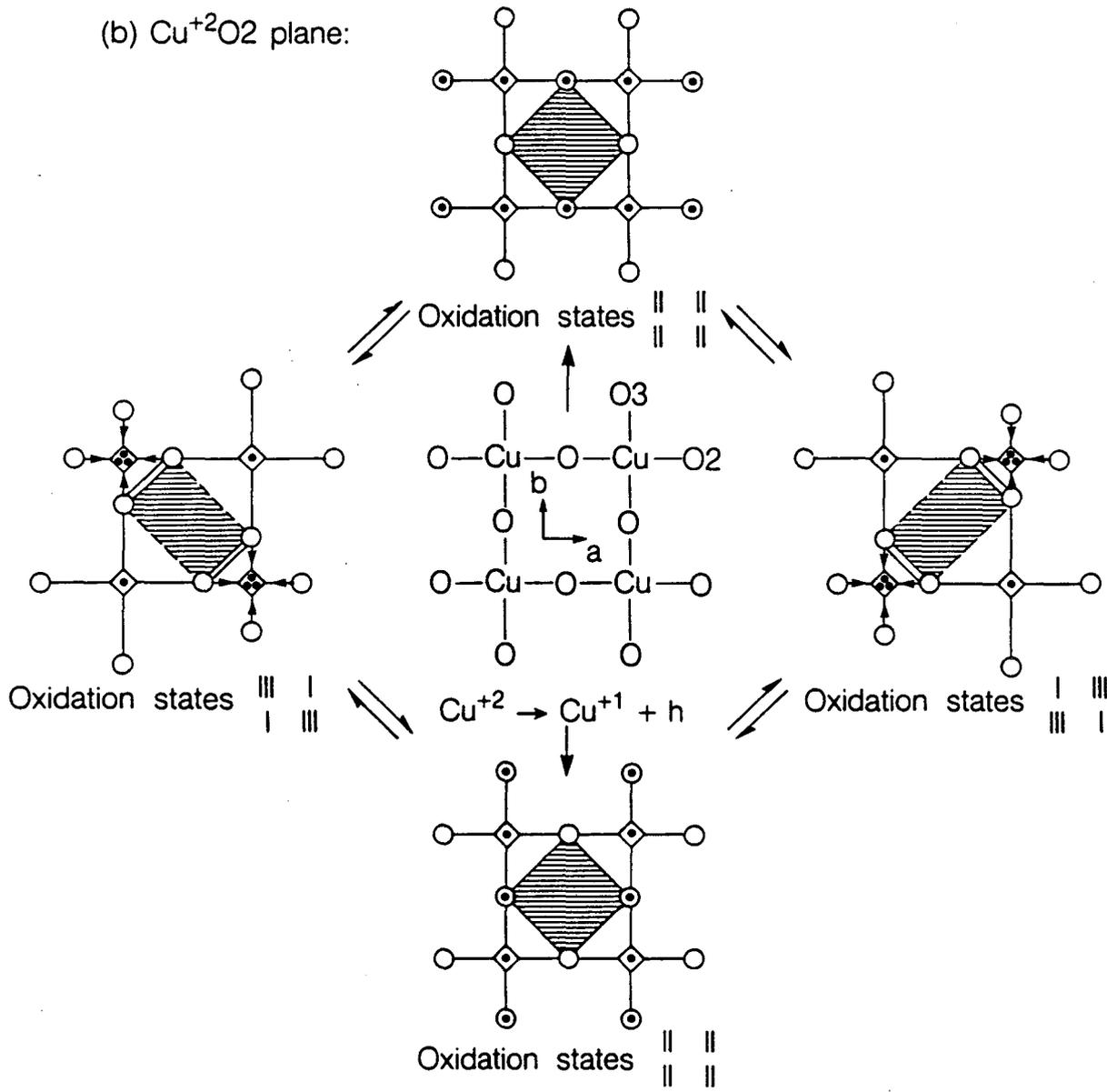
Oxidation state II



Oxidation state I

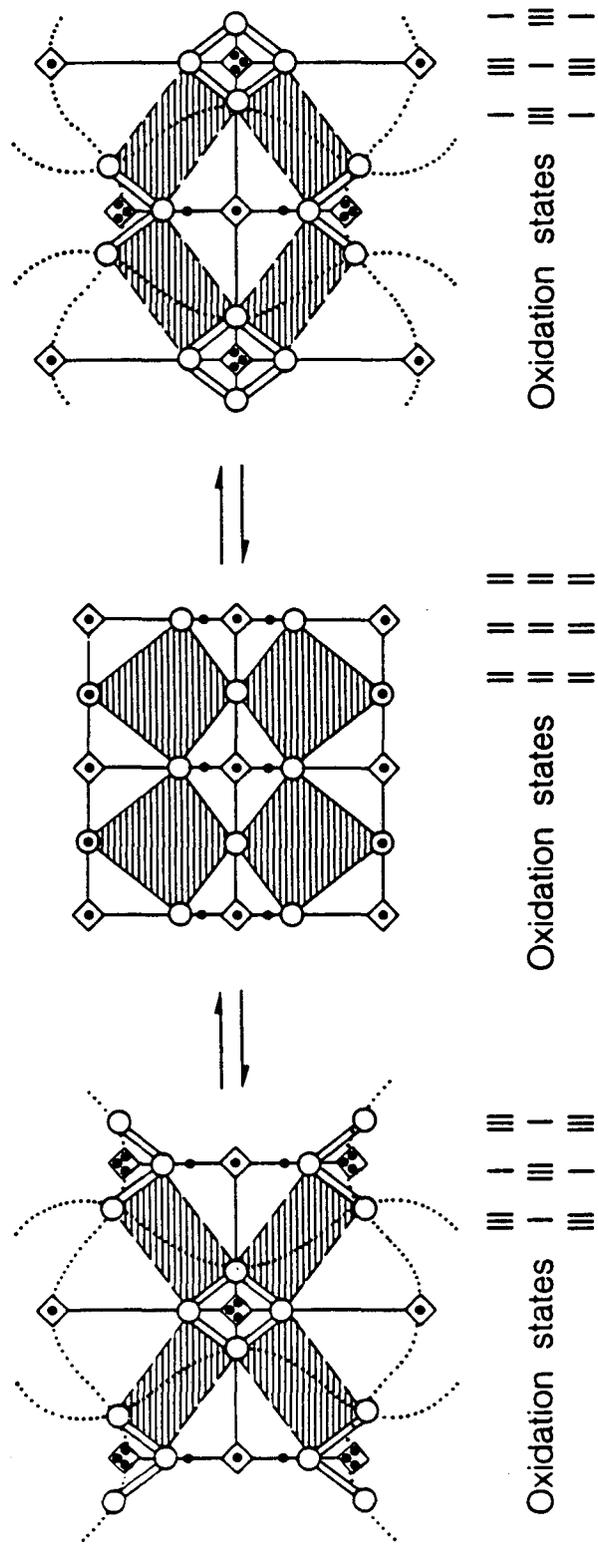
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Figure 1A



XBL 8810-8550

Figure 1B



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Figure 2

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