Lawrence Berkeley National Laboratory
Recent Work

Title
SOME STRUCTURAL FEATURES OF HIGH-T[C] SUPERCONDUCTORS

Permalink
https://escholarship.org/uc/item/3538k0nx

Author
Jou, C.J.

Publication Date
1988-11-01
Some Structural Features of High-\( T_c \) Superconductors

C.J. Jou
(Ph.D. Thesis)

November 1988

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory • University of California
ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
SOME STRUCTURAL FEATURES OF HIGH-\(T_c\) SUPERCONDUCTORS

Chengfong Joseph Jou

Department of Materials Science and Mineral Engineering
University of California
and
Center for Advanced Materials
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
SOME STRUCTURAL FEATURES OF HIGH-\( T_c \) SUPERCONDUCTORS

Chengfong Joseph Jou

Department of Materials Science and Mineral Engineering
University of California
and
Center for Advanced Materials
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720

ABSTRACT

Some structural features of high-\( T_c \) oxide superconductors including Tl-Ca-Ba-Cu-O, Bi-Ca-Sr-Cu-O, Y-Ba-Cu-O, La-(Ba,Sr,Ca)-Cu-O, Ba-K-Bi-O and Ba-Pb-Bi-O systems are systematically examined. Based on common features in these systems in addition to \( \text{CuO}_2 \) layers, an imperfect macro-resonance-cell (MRC) description is proposed that provides a basis for qualitatively understanding the superconductivity in these systems. It is proposed that boundary layer coupling plays a major role in determining the different \( T_c \) values of these systems. The YBCO system is particularly interesting for its unusual linear chain structure at the boundary layer. This chain structure originating from oxygen ordering on the basal plane also results in micro-twinned morphology in orthorhombic phase. A nucleation-and-growth mechanism for this twin formation associated with the second order phase transformation is proposed. An oxygen-depleted twin boundary model is also discussed which explains why stoichiometric, \( \text{YBa}_2\text{Cu}_3\text{O}_7 \), is difficult to achieve.
DEDICATION

To my mother, Chen-Fone Jou (1916–1988),

to my father, Tien-Shih Jou (1916–1984),

ACKNOWLEDGEMENTS

I am indebted to many individuals who have helped me during my studies at Berkeley. I regret I could not name them all and give proper credit (I hope I will be forgiven by those who I have failed to name specifically). I wish to thank the following people:

- Professor Jack Washburn, my research advisor, for his steadfast support, patience, and faith that allowed me to grow and encouraged me to find my own way. I’ll remember all our invaluable discussions in Room 475.

- Professor Ronald Gronsky for reviewing my thesis and making many helpful suggestions. I shall always remember his slides and lectures that were so inspiring.

- Professor Chen-Ming Hu for also reviewing my thesis and providing enjoyable EECS courses.

- Professor Nathan Cheung for allowing me to use the lab to build the ultra-high vacuum system that was an invaluable experience and a memorable event. I will always remember his generosity.

- Professor Eicke R. Weber for many sessions of inspiring discussions and to his wife, Dr. Zuzanna Liliental-Weber, who is also a senior scientist in Prof. Washburn’s group, for many successful collaborations and encouragements.

- Dr. K. Hiraga for sending the high resolution TEM pictures of twin boundaries that enhanced my research.

- Keith Frank for providing technological knowledge and craftsmanship that helped me overcome many difficulties encountered in the flux-pinning experiment.

- MD. Min-Ier Kang for the constant support in many ways during my schooling at Berkeley.

- Professor Frederic Bien of Princeton University for the stimulating discussions on mathematical topics and the very enjoyable companionship during his sabbatical stay at Berkeley’s Advanced Mathematics Research Institute.

- John Van Slyke and Ron Wilson for helping run the SEM and providing many delightful working sessions; John Holthuis and James K. Wu for sharing the working experience of growing
single crystals of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) superconductors.

- Bob Hamilton, James Parrish, and the staff in the microfabrication lab for their technical assistance.

Special thanks go to the library staff: Denise Jones, Carol Backhus, Rita LaBrie, and Richard Robinson for their efficient help in reducing time in searching the literature; Wanda Capece and Carole James of the MSME and Learr English of the MCSD, whose help made the paper work move smoothly; and the Technical Information Department for helping prepare this manuscript at various stages and, in particular, my special thanks to Connie Silva for her patience in coping with the endless revisions and providing efficient word processing efforts that made the thesis filing possible.

Lastly, thanks go to my friends Julia and John, Marie and Bruno, Nathalie, Leith, Leslie and Greg, L.S. Fan, and many others with whom I experience the warm friendship and share the memorable times together.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
# TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................... 1
DEDICATION .......................................................................................................................................... i
ACKNOWLEDGEMENTS ..................................................................................................................... iii
INTRODUCTION ...................................................................................................................................... 1
1. FORMATION OF COHERENT TWINS IN YBa$_2$Cu$_3$O$_{7-\delta}$ SUPERCONDUCTORS ........................................... 4
   1.1 Nucleation .................................................................................................................................... 5
   1.2 Growth ......................................................................................................................................... 7
   1.3 Coarsening ................................................................................................................................... 7
REFERENCES ........................................................................................................................................... 9
FIGURES ................................................................................................................................................ 10
2. MODELS AND SIMULATIONS OF OXYGEN-DEPLETED TWIN BOUNDARIES .................................................. 14
   2.1 Models of Oxygen-Depleted Twin Boundaries ............................................................................. 14
   2.2 Calculations and Experimental Values .......................................................................................... 15
   2.3 Simulations ................................................................................................................................... 16
   2.4 Discussion .................................................................................................................................... 18
REFERENCES ......................................................................................................................................... 19
FIGURES ................................................................................................................................................ 21
3. A HYPOTHESIZED MACRO-RESONANCE-CELL DESCRIPTION FOR HIGH-T$_c$ OXIDE SUPERCONDUCTORS ... 26
   3.1 Various Oxidation States, Breathing Modes and Macro Resonance Cells ...................................... 26
   3.2 Pseudogap, Delocalization and Mott's I-M Transition ..................................................................... 31
   3.3 Quasi-Two-Dimensionality, Boundary Layers, and Layer Coupling .............................................. 33
   3.4 Substitution, Doping and Isotope Effect ......................................................................................... 38
REFERENCES ......................................................................................................................................... 42
FIGURES ................................................................................................................................................ 46
4. EFFECTS OF OXYGEN-DEPLETED TWIN BOUNDARIES ON SUPERCONDUCTING PROPERTIES .................. 50
   4.1 SIS Josephson Junction and Glassy States ....................................................................................... 50
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 Flux Pinning and Vortex State</td>
<td>52</td>
</tr>
<tr>
<td>4.3 Superlattice, Band-folding and Minigaps</td>
<td>54</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>56</td>
</tr>
<tr>
<td>FIGURES</td>
<td>58</td>
</tr>
<tr>
<td>CONCLUSIONS</td>
<td>60</td>
</tr>
<tr>
<td>APPENDIX A</td>
<td>63</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>66</td>
</tr>
<tr>
<td>FIGURES</td>
<td>67</td>
</tr>
</tbody>
</table>
FIGURES

Fig. 1.1. (a) Total oxygen content, $x$, in $\text{YBa}_2\text{Cu}_3\text{O}_x$ increases monotonically when cooled slowly from sintering temperature in 1 atm $O_2$ ambient. Note there is a kink at the structure transition temperature $T_p$. Data deduced from Ref. 1. Scale of $O_x$ is for (a) only.

(b) The differentiation of the curve in (a) reveals a peak at $T_p$ forming the characteristic "$\lambda$" curve of a second order phase transformation. Oxygen ordering on the basal plane is in progress starting at $T_p$.

Fig. 1.2. Proposed nucleation of ordered oxygen clusters starts at grain surfaces, i.e., grain boundaries or pore surfaces, where the stress due to structural transformation can be partially relaxed. When two neighboring clusters with orthogonal b-chain directions meet, coherent twin boundaries with an oxygen-depleted zone are formed. Twin nuclei (insert at lower left corner) are formed later in the interior of the grain. They consume most of the available oxygen content in the grain at $T_p$ forming a heavily interpenetrated tweed structure (Fig. 1.3a). An oxygen concentration gradient between the grain surface and the grain interior is set up. Further growth of the twin laths in the grain is limited by diffusion of oxygen into the grain center. The twin nuclei at the grain surfaces can grow faster with the oxygen supplied directly from ambient via the pore-grain boundary network and the oxygen-depleted twin boundaries. During the growth, twin laths in the grain interior are incorporated at the growth front.

Fig. 1.3. (a) Interpenetrated twin laths leave the untransformed matrix oxygen-depleted inside the grain. (b) A fully grown tweed structure would form a two-dimensional mutually-modulated regular pattern, possibly observed in some in-situ transmission electron microscopy observations during cooling from high temperature. The electron diffraction pattern of this structure may reveal an effective unit cell with $\sqrt{2}a \times \sqrt{2}a \times -3a$. However, the structure contains both twin boundaries and high energy 90°-rotation boundaries, therefore it would be a metastable intermediate product.
Fig. 2.1. Oxygen vacant twin boundary models for (a) 1 vacant layer (j=1), (b) 3 vacant layers (j=2), and (c) 5 vacant layers (j=3). Note: The angle at twin boundaries and the length difference between the lattice constants (a) and (b) are exaggerated. For simplicity, only oxygen atoms (black dots) are shown.

Fig. 2.2. Simulated HREM [001] images of twin boundaries. Simulation parameters are chosen to correspond to the operating conditions in the JEOL 4000 FX electron microscope. Sample thickness is 100Å and objective lens defocus is -800Å unless specified otherwise.

(a) Changes with respect to j from j = 0 (no oxygen depleted layer, top) to j = 3 (bottom).

(b) Variation with respect to objective lens defocus; -400Å (top) to -1600Å (bottom) in increments of -400Å, j = 3.

(c) Variation with respect to sample thickness; 50Å (top) to 200Å (bottom) in increments of 50Å, j = 3.

(d) Total oxygen atom number fixed, but abrupt concentration changes at twin boundaries are gradually relaxed (j = 3).

Fig. 2.3. High resolution electron micrograph of a twin boundary in YBa$_2$Cu$_3$O$_x$ material reveals significant contrast across the twin boundary. (Photo courtesy of Dr. K. Hiraga.)

Fig. 2.4. A proposed twin-refining mechanism during a short pulse of electron beam heating.

(a) Originally, twin boundary (TB) has oxygen depleted with oxygen content of stoichiometric O$_6$ and twin domains, α and β, with oxygen content O$_{7-x}$.

(b) Electron beam bombards the specimen activating the diffusion of oxygen in b-chain near twin boundary and causing an oxygen-disordered zone, i.e., tetragonal structure (T).

(c) The counterparts of the remaining twin domains are nucleated at the thin edge of the specimen where cooling is more efficient after beam is removed. (d) New twin boundaries and domains are formed. Twin refining always occurs at twin boundaries and appears as pairs as observed in TEM.

Fig. 3.1. (a) Cu in CuO basal plane of YBa$_2$Cu$_3$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
O : 2p\(_2\) and Cu : 3d\(_{2x^2-r^2}\) along the c-axis direction or O : 2p\(_1\) and 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. Space-wisely, Cu in CuO layer still has +3 stoichiometric charge required in a unit cell. But timewise, 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.)

Fig. 3.1. (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 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 \(E_p\). 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. 3.2. 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. 3.1b). (The atomic distances in the figure are exaggerated and small details like the puckered structure on the CuO\(_2\) plane are not shown.)

Fig. 4.1. Critical current density as a function of oxygen content, \(x\), in YBa\(_2\)Cu\(_3\)O\(_x\). Arrows are added to mark the oxygen content of the samples assuming \(x = 7\) within twin domains and various numbers (j) of oxygen depleted layers at twin boundaries. Within these layers \(x\) is assumed to be 6. (Reprinted by permission from Nature Vol. 332 pp. 58. Copyright (c) 1988 Macmillan Magazines Ltd.)
Fig. A.1. Flux lines of the low density \(\text{YBa}_2\text{Cu}_3\text{O}_{7.5}\) at 800 G are decorated with cobalt. Partial flux lattice were found in the bulk, along the grain boundaries and in the large pores. The average spacing of flux lines is slightly larger than 1 \(\mu\)m. .............................................................. 68

Fig. A.2. Higher magnification of the "root" of the decorated flux lines gives a roughly estimated penetration depth of less than 2000 Å. .............................................................. 69

Fig. A.3. Decorated flux lines of the higher density YBCO at 800 G. Flux lines are pinned at tiny pores mostly. Self-adjustment of flux locations gives an average spacing of about 1.2 \(\mu\)m. .............................................................. 70

Fig. A.4. Same material as in Fig. A.3 at 150 G. Average spacing of the partial flux lattice is 3.8 \(\pm\) 0.2 \(\mu\)m. Again, most flux lines are pinned at tiny pores in this higher density material. .............................................................. 71
TABLES

Table 2.1. Calculated and experimental values of $x$ in $\text{YBa}_2\text{Cu}_3\text{O}_x$ with various number, $j$, of oxygen depleted layers at the coherent twin boundaries. .................................................. 16

Table 3.1. Stacking sequence of layers in unit cell. .................................................................................. 28

Table 3.2. $T_c$ of TCB and BCS systems with various number of CuO$_2$ layers. ........................................ 34

Table 3.3. $T_c$ and tentatively assigned coupling strength of boundary layer(s) of various systems. ....... 38
INTRODUCTION

Since the discovery of the La-Ba-Cu-O (LBCO) system of high-Tc oxide superconductors with \( T_c \approx 28^\circ \text{K} \) 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 \( T_c = 93^\circ \text{K} \) 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 \( T_c = 110^\circ \text{K} \) and 125° K respectively. Also, a perovskite-related Ba-K-Bi-O (BKBO) system\(^5\) with \( T_c \approx 30^\circ \text{K} \) became the first known high-Tc 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 \( \text{Cu}-\text{O} \) 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 \( \text{CuO}_2 \) layers that were common to all known high-\( T_c \) copper oxide superconductors. All these oxides except BKBO share a common pseudo-two-dimensional structure with \( \text{CuO}_2 \) planes sandwiched between metallic layers. This structure appears to play a critical role in the observed superconductivity. However, \( \text{CuO}_2 \) layer(s) by itself is not sufficient to make the oxides superconductors, e.g., tetragonal YBCO also has \( \text{CuO}_2 \) layers but does not show superconductivity.

In this work, a systematic comparison among all known high-\( T_c \) oxides has been done. Common features in addition to \( \text{CuO}_2 \) layers are pointed out. An imperfect macro-resonance-cell (MRC) description based on these common features, and an extensive study of published experimental work is proposed which could explain why orthorhombic YBCO is a superconductor and tetragonal is not. The YBCO, BCS and TCB systems all become superconductors when sufficient oxygen, as a dopant, is absorbed but \( T_c \) varies in a wide range. The imperfect MRC description proposed here also provides a qualitative explanation of these differences in \( T_c \). Based on the imperfect MRC description, the effect on \( T_c \) of the substitution of other elements in the YBCO system is also discussed.

The YBCO system with its tetragonal to orthorhombic transformation is particularly interesting because of the close structural similarity between the tetragonal phase which is not superconducting and the orthorhombic phase which is. A micro-twinned morphology is caused by this phase transformation. However, the mechanism involved has not been clarified in the literature. Based on the existing neutron
diffraction data and TEM observations in the literature, an ordering parameter is found and a detailed nucleation-and-growth mechanism is proposed which could explain the correlation between the oxygen uptake rate and the structural transformation as well as the results of in-situ TEM observations.

The superconducting orthorhombic YBCO is non-stoichiometric, i.e., oxygen-deficient. The amount$^6$ and the distribution of oxygen significantly alters the superconducting properties, e.g., non-superconducting tetragonal phase has oxygen content ranging between 6.0 and 6.5 with oxygen vacancies randomly distributed on the basal plane; the superconducting orthorhombic phase has oxygen content ranging between 6.5 and 7.0 with oxygen ordered on the basal plane and $T_c \leq 93$ K. It is essential to determine where the oxygen vacancies locate especially for an understanding of the variations in $T_c$. In the literature, it has been assumed that oxygen vacancies are randomly distributed within the twin domains. However, this configuration would leave the twin boundaries with unfavorably high energy since oxygen ions on the opposite sides of the twin boundaries would exert strong Coulomb repulsion force to each other due to their near neighbor positions. An oxygen-depleted twin boundary model is proposed here that could explain the observed difficulty of reaching the stoichiometric, YBa$_2$Cu$_3$O$_y$, in orthorhombic YBCO, avoid the high energy state at twin boundaries, preserve the coherency at twin boundaries and serve as fast diffusion paths for oxygen consistent with the nucleation-and-growth kinetics.

Twin formation in the YBCO system is discussed in Chapter 1. Chapter 2 is dedicated to a discussion of the amount and the distribution of oxygen vacancies in superconducting YBCO. In Chapter 3, the imperfect MRC description is proposed and the effect on $T_c$ of oxygen vacancies and doping substitutions is discussed for all the known high $T_c$ oxides. In Chapter 4, the expected effects of oxygen-depleted twin boundaries on superconducting properties in the YBCO system is discussed.
REFERENCES


CHAPTER 1. FORMATION OF COHERENT TWINS IN
YBa$_2$Cu$_3$O$_{7-\delta}$ SUPERCONDUCTORS

The 1-2-3 structure of the YBa$_2$Cu$_3$O$_{7-\delta}$ system, $6 \leq x \leq 7$, has a unique property; it acts like an "oxygen sponge," i.e., when cooling from the sintering temperature, $T_s$, usually around 950°C, the oxygen content increases monotonically (Fig. 1.1a) and when heating up, the oxygen content decreases. The oxygen disorder-order induced phase transition from the semiconducting tetragonal structure to the superconducting orthorhombic structure is accompanied by the formation of coherent twins at temperature $T_p$ and oxygen content $O_{x,p}$. Below $T_p$, the structure is orthorhombic with oxygen content $O_x > O_{x,p}$ when cooled slowly in an oxygen-rich ambient from the sintering temperature, $T_s$. Above $T_p$, the structure is tetragonal with $O_x < O_{x,p}$. The rate of oxygen uptake increases sharply at $T_p$ as shown in Fig. 1.1b which has the characteristic "$\lambda$" shape of a second order phase transition. Below 650°C it drops back to about the same rate as just before $T_p$, and with further cooling decreases gradually until by about 300°C no further oxygen uptake occurs. Both $T_p$ and $O_{x,p}$ are a function of the oxygen partial pressure, $P_{O_2}$ in the ambient under equilibrium conditions, e.g., for $P_{O_2} = 1$ atm (in 100% pure oxygen ambient), $T_p = 700^\circ$C, for $P_{O_2} = 0.2$ atm (in air or 20% $O_2$-80% Ar ambient), $T_p = 670^\circ$C, and for $P_{O_2} = 0.02$ atm (in vacuum or 2% $O_2$-98% Ar), $T_p = 620^\circ$C, and $O_{x,p}$ in this partial pressure range is about 6.5 - 6.6;[1] when $P_{O_2}$ decreases both $T_p$ and $O_{x,p}$ decrease.

Based on this information and in-situ transmission electron microscope (TEM) observations,[2-5] a model describing the mechanism of formation of coherent twins is presented which can help to explain some of the observed experimental results. In the slow cooling step, which is essential for good quality high $T_c$ material, the cooling rate, $dT/dt$, is small and usually constant. The changing oxygen content $dO_x/dt$ can thus also be considered as $dO_x/dT$. Although the diffusivity of oxygen in the material also changes as temperature decreases, for slow cooling rates and in not too low a temperature range it can be assumed that equilibrium is approached at least in porous or thin specimens. As seen in Fig. 1.1b, $dO_x/dT = dO_x/dt$ is the order parameter for this phase transition.
1.1. Nucleation

As revealed by in-situ neutron powder diffraction [8], at temperatures just above \( T_p \), i.e., the tetragonal structure, \( O(4) \) and \( O(5) \) sites are randomly occupied by equal amounts of oxygen with an average occupancy of each site about \( 1/4 \). The \( O(1) \) sites on the \( BaO \) layer, \( O(2) \) and \( O(3) \) sites on the \( CuO_2 \) layer are all fully occupied. At \( T_p \), the occupancy of the \((0, 1/2, 0)\), \( O(4) \), b-chain sites on the \( CuO \) basal plane layer starts increasing at a faster rate than the decrease of occupancy on the \((1/2, 0, 0)\), \( O(5) \), sites on the same layer. This suggests that the increased uptake of oxygen from the ambient goes primarily to the b-chain sites and an oxygen ordering process is in progress. The overall oxygen content increases at a rate much larger than just above \( T_p \) (Fig. 1.1b) indicating incorporation of oxygen from the ambient into the material is facilitated by the structural transformation. It is suggested here that this sudden increase of oxygen absorption rate is associated with a nucleation process, the formation of embryos of the orthorhombic phase.

Since the oxygen-ordered orthorhombic phase contains the linear chain structure on the basal plane, these embryos are assumed to consist of clusters of short parallel b-chains, i.e., \( Cu(1)-O(4)-Cu(1) \). They should first appear at the heterogeneous sites located at grain surfaces, i.e., grain boundaries and pore surfaces, since the internal stress due to the localized distortion associated with b-chain growth in the tetragonal matrix can be at least partially relaxed (Fig. 1.2). The formation of b-chain embryos at grain boundaries probably first develops by consuming oxygen in the \( O(4)-O(5) \) basal plane which would soon become depleted near the grain boundaries. Further growth of the orthorhombic ordered phase then would require a supply of oxygen from the ambient through the pore-grain boundary network (Fig. 1.2). Clusters of b-chains with b directions orthogonal to each other are equally probable because of the symmetry of the parent tetragonal structure. Furthermore, for stress compensation nucleation of an embryo with one b-chain direction tends to induce the nucleation of another with an orthogonal b-chain direction. Below \( T_p \), the oxygen-ordered configuration on \( O(4)-O(5) \) basal plane has a lower free energy than that of the oxygen-disordered configuration.\[^{[6]}\] Once initiated at a grain surface the extension of b-chains should be rapid. An elongated embryo with an oxygen-depleted zone around it is expected.

In powder-sintered materials, depending on the pressing process and the sizes and kinds of powders, there are many voids and open channels among grains. For high porosity material, the total internal pore
surface area may be larger than the total area of the grain boundaries. This free surface area may play a significant role in determining the physical properties of such a material. Grain boundaries also permit faster diffusion than that possible through a grain because of the "looser" structure. Significant diffusion of oxygen within a grain along the c-axis direction is unlikely to happen at temperatures below $T_p$ since the full occupancy of O(1), O(2) and O(3) sites at temperatures above $T_p$ suggest that these sites are more stable than O(4)-O(5) sites on the basal plane. Oxygen from the environment and from pore surfaces is likely to be distributed to the grains deep inside the sample primarily through this pore-grain boundary network. To diffuse into the grain, oxygen probably has to find a basal plane edge. Hence, grain boundary diffusion would often be required for supplying oxygen from the ambient to parts of the grains.

As b-chain clusters at grain boundaries grow, embryos probably also develop homogeneously or heterogeneously inside the grain by local oxygen ordering. They are probably formed somewhat later than those at grain surfaces, since the internal stress developed by the b-chain ordering can not be partially relaxed as at grain surfaces and the incorporation of the limited available oxygen is competitive among embryos in the central region of the grain. The available oxygen would be quickly consumed by the formation of such nuclei. Oxygen-depleted zones would be formed around these nuclei setting up a concentration gradient between center and surface of the grains, causing more oxygen to diffuse into the grain. These b-chain clusters have locally the orthorhombic lattice structure with the lattice constants, $a$ and $b$ on the basal plane, smaller and larger, respectively, than $a_c$ of the parent tetragonal lattice. The tetragonal matrix surrounding the elongated nucleus experiences contraction at the ends of the b-chains and expansion at the sides parallel to the b-chains. When two clusters with orthogonal b-chain directions approach each other, the oxygen depleted zones and the strain fields overlap causing a reduction of the stress along one $<110>$ direction and enhancement along the orthogonal $<110>$ direction; impingement of the two domains along the latter $<110>$ direction eventually results in formation of a coherent twin boundary. The equilibrium width of the twin boundary zone is assumed in this model to be determined by a balance between the coulomb repulsion force of oxygen ions at opposite sides of the boundary and the chemical potential favoring extension of the b-chains. A "twin nucleus" within the grain with a narrow oxygen-depleted zone remaining at the twin boundary is expected (Fig. 1.2, left lower corner).
Either <110> direction on the basal plane can lie parallel to a twin boundary, i.e., the twin nuclei have two equally probable twin boundary orientations perpendicular to one another. These nuclei have been observed by in-situ TEM as randomly distributed and inter-penetrated orthogonal sets, a tweed-like structure (Fig. 1.3). Other combinations of b-chain nuclei, quartet, etc., are also possible, but with smaller probability than the doublet. When two b-chain clusters with the same b-chain direction approach each other, coalescence takes place resulting in a larger b-chain cluster.

Since oxygen content \( (O_x) \) is about 6.5 at \( T_p \), only half of the available b-chain sites of the orthorhombic phase in the grain are occupied by oxygen, i.e., the total volume of the orthorhombic twin nuclei is only about half the total volume of the grain. This leaves a relatively open structure for oxygen diffusion. Further transformation requires oxygen diffusion into the grain, the driving force being the tendency for further extension of b-chains, resulting in the observed sudden rise in rate of oxygen uptake at \( T_p \) as shown in Fig. 1.1b.

### 1.2. Growth

The b-chain clusters nucleated at grain surfaces grow most rapidly by incorporating oxygen readily supplied from the ambient. When the transformation is complete at grain surfaces, the diffusion of oxygen into the grain becomes more restricted, i.e., oxygen-depleted twin boundary zones. This can explain the sharp decrease of the rate of oxygen uptake below \( T_p \) (see Fig. 1.1b). The growth front of the twinned orthorhombic structure nucleated at grain surfaces gradually extends deeper into the grain by adding new b-chains at the growth front with oxygen being supplied from the ambient via the pore-grain boundary twin boundary network and by incorporating twin nuclei that have already formed inside the grain.

### 1.3. Coarsening

During the last stage of twin formation, coarsening takes place eliminating some of the twin boundaries, and thus decreasing total free energy. Small domains included within larger domains tend to disappear by localized oxygen diffusion within the boundary. As long as the temperature is still high enough to permit oxygen diffusion, this climbing process continues to coarsen the twin domains until the widths of the twins are several hundred Å. Rapid cooling severely inhibits this coarsening process; the resulting
structure contains more numerous fine twins. When cooling rate is very rapid, e.g., quenching from temperature above $T_p$, the tetragonal structure is partially preserved with oxygen content less than 6.5. There is insufficient time for oxygen absorption and thus insufficient oxygen to complete the growth of the b-chain orthorhombic structure. Quenching from temperature between $-350^\circ$C and $T_p$ yields intermediate $T_c$ with oxygen contents between 6.8 and 6.6. Sintered polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-a}$ is usually given a low temperature annealing step to enhance its superconducting properties. The annealing temperature is typically chosen below $T_p$ but above 400$^\circ$C in an oxygen-rich environment to permit further coarsening, stress relaxation and oxygen uptake.

In summary, a qualitative description for the formation of the twinned structure in $\text{YBa}_2\text{Cu}_3\text{O}_{7-a}$ is proposed. This model assumes oxygen-depleted twin boundary zones which serve as the primary oxygen diffusion paths from grain surfaces toward the interior of the grains and thus control the growth rate of the twins in the grain centers. These twin boundaries are formed during the growth of the b-chain embryos which are first nucleated heterogeneously at grain surfaces. The width of the oxygen-depleted twin boundary zones should be determined by the balance of the chemical potential energy at the ends of the b-chains at the edges of the twin domains and the coulomb repulsion energy between oxygen ions on the opposite sides of the twin boundaries. Under the ordinary processing condition, this is equivalent to the case $j = 3$ in this model. The rapid rate increase of oxygen uptake at $T_p$ is attributed to a high oxygen vacancy concentration in the grain during early stages of the tetragonal to orthorhombic transformation caused by the formation of embryos which quickly consume a large fraction of the oxygen in the grain at $T_p$. Completion of the transformation by growth of twins occurs most rapidly at the grain surfaces by absorbing oxygen from the ambient and more slowly in grain interiors. Coarsening of the twin domains then occurs by elimination of small domains included within larger domains by localized transfer of oxygen atoms across the twin boundaries. This coarsening process takes place during annealing, resulting in residual stress relaxation and reduction of residual oxygen vacancies within the twin domains. The observed oxygen deficiency remaining after long time annealing in oxygen can be explained if it is assumed that the equilibrium structure of coherent twin boundaries contains one or more layers of oxygen vacancies as proposed in this model.
REFERENCES


FIGURE CAPTIONS

Fig. 1.1. (a) Total oxygen content, \( x \), in \( \text{YBa}_2\text{Cu}_3\text{O}_x \) increases monotonically when cooled slowly from sintering temperature in 1 atm \( \text{O}_2 \) ambient. Note there is a kink at the structure transition temperature \( T_p \). Data deduced from Ref. 1. Scale of \( O_x \) is for (a) only. (b) The differentiation of the curve in (a) reveals a peak at \( T_p \) forming the characteristic ‘‘\( \lambda \)’’ curve of a second order phase transformation. Oxygen ordering on the basal plane is in progress starting at \( T_p \).

Fig. 1.2. Proposed nucleation of ordered oxygen clusters starts at grain surfaces, i.e., grain boundaries or pore surfaces, where the stress due to structural transformation can be partially relaxed. When two neighboring clusters with orthogonal b-chain directions meet, coherent twin boundaries with an oxygen-depleted zone are formed. Twin nuclei (insert at lower left corner) are formed later in the interior of the grain. They consume most of the available oxygen content in the grain at \( T_p \) forming a heavily interpenetrated tweed structure (Fig. 1.3a). An oxygen concentration gradient between the grain surface and the grain interior is set up. Further growth of the twin laths in the grain is limited by diffusion of oxygen into the grain center. The twin nuclei at the grain surfaces can grow faster with the oxygen supplied directly from ambient via the pore-grain boundary network and the oxygen-depleted twin boundaries. During the growth, twin laths in the grain interior are incorporated at the growth front.

Fig. 1.3. (a) Interpenetrated twin laths leave the untransformed matrix oxygen-depleted inside the grain. (b) A fully grown tweed structure would form a two-dimensional mutually-modulated regular pattern, possibly observed in some in-situ transmission electron microscopy observations during cooling from high temperature. The electron diffraction pattern of this structure may reveal an effective unit cell with \( \sqrt{2} a \times \sqrt{2} a \times -3a \). However, the structure contains both twin boundaries and high energy 90°-rotation boundaries, therefore it would be a metastable intermediate product.
Figure 1.1
(a) Heavily inter-penetrated twin-nuclei laths

(b) Regular tweed structure

Twin boundaries

90° Twist boundaries

Figure 1.3
CHAPTER 2. MODELS AND SIMULATIONS OF OXYGEN-DEPLETED TWIN BOUNDARIES

A model of twin boundaries in YBa$_2$Cu$_3$O$_{7-\delta}$ superconductors is proposed. Oxygen vacancies at twin boundaries are assumed to exist. These vacancies might also serve as fast diffusion paths for oxygen. The model can explain why the optimized oxygen stoichiometry is less than seven. Simulations of HREM lattice images based on the model are found to be consistent with observed lattice images which often show that the boundary affected zone is several atomic layers thick.

Since the discovery of the Y-Ba-Cu-O quaternary system superconductor,[1] the superconducting phase has been identified to be YBa$_2$Cu$_3$O$_7$[2] and its structure is an orthorhombic, defected trilayer perovskite with metal atoms ordered and having a deficiency of oxygen.[3,4] Oxygen has been shown to play an important role in determining $T_c$. The oxygen order-disorder transition has been studied by D. de Fontaine et al.[5] in the two dimensional system. The equilibrium value, $x$, of oxygen content in YBa$_2$Cu$_3$O$_x$ is determined by the processing temperature and oxygen partial pressure in the ambient as experimentally demonstrated by Gallagher et al.[6] Transition temperature as a function of oxygen content $x$ has been determined by Cava et al. with a gettered annealing technique.[7] The effects of fabrication process variables on optimization of $T_c$ have been extensively investigated. The achievable oxygen content under normal pressure, 1 atm O$_2$ or air, has consistently been found to be less than 7. Another interesting feature of the superconducting orthorhombic low temperature phase is the formation of a high density of coherent twins, during or after the structural transition from tetragonal to orthorhombic. Presumably this is a mechanism for the relaxation of transformation induced stresses. An extended annealing seems to enhance the superconducting properties.[8] A high density of twin boundaries should not only help relieve the internal stress but may also help increase $J_c$[9] and $T_c$.[10] A commonly used model[11] for the coherent twin boundaries involves near neighbor oxygen ions which would exert strong Coulomb repulsion and thus increase the twin boundary energy.

2.1. Models of Oxygen-Depleted Twin Boundaries

The oxygen vacant twin boundary model proposed here (Fig. 2.1) avoids this high energy state and preserves coherency at the boundaries. The model adopts the usual coherent boundary configuration,
except that oxygen sites on Cu-O basal planes between two neighboring Ba-O basal planes are not occupied. The number of oxygen vacant layers is assumed to vary depending on the processing conditions. With higher oxygen partial pressure, slower cooling rate or longer annealing duration, the expected number of vacant oxygen layers should become smaller. Since rapid oxygen diffusion in this material would not be expected to occur along the c axis direction, oxygen vacant twin boundaries may play a role in the diffusion of oxygen into or out of the structure. As pointed out by K-N. Tu et al.[12] the rate limiting step for oxygen flux leaving a specimen is the interfacial reaction rather than the diffusion within the specimen. If twin boundaries increase the rate of internal diffusion, this result becomes more understandable. It is interesting to note that the activation energy, 1.7 ± 0.1 eV, is just half of the oxygen site energy 3.41 eV, determined by Freitas et al.[13] The tetragonal to orthorhombic transformation could be diffusionless (Martensite-like)[14] or diffusion-controlled.[11] However, twins do not appear to form suddenly at the transition temperature.[11] This is an indication that the transformation is a diffusion-controlled nucleation-and-growth process as discussed in Chapter 1. At the transition temperature, nuclei of the orthorhombic phase apparently form in the tetragonal grains at grain boundaries or surfaces with two perpendicular directions of the b-chain. They probably grow by consuming near-by oxygen atoms and later by incorporating additional oxygen supplied from surfaces in contact with the atmosphere i.e., directional growth from grain boundaries or surfaces. When neighboring nuclei have the same b-chain directions, they coalesce during growth to form larger domains. Where domains with perpendicular b-chain directions meet, oxygen vacant twin boundaries are formed. Depending on the processing conditions, further absorption of oxygen from the external environment probably narrows the width of oxygen-vacant twin boundaries.

2.2. Calculations and Experimental Values

During the tetragonal to orthorhombic structural transformation, twins are formed to minimize the distortion energy and to accommodate the volume change. The resulting twin width, when not in equilibrium, can vary from several hundred Å to a thousand Å. The average twin width (Wt) assuming equilibrium being achieved has been estimated as[15] \( W_t = \frac{ab}{(b-a)} \) and the twin boundary width, \( W_b(j) = \frac{2jab}{(a^2 + b^2)^{1/2}} \) as illustrated in Fig. 2.1. Assuming a perfect stoichiometric YBa2Cu3O7 within the twin domains and YBa2Cu3O6 at twin boundaries, then the average oxygen content, \( x \), in YBa2Cu3Ox, which is experimentally measured, would be
Applying $a = 3.822 \text{ Å}$, $b = 3.891 \text{ Å}$ from the work of Cava et al., the calculated values of $x(j)$ match the experimentally measured oxygen content very well (Table 2.1) suggesting that in their samples, near perfect stoichiometric YBa$_2$Cu$_3$O$_y$ may form within the twin domains but various layers of oxygen vacancies exist at twin boundaries. The oxygen deficiency study seems to indicate that under normal pressure processing, i.e., 1 atm O$_2$ or air, the ultimate oxygen stoichiometry is about 6.93 or equivalent to the case $j = 3$. Therefore it is believed that the effective range within which Coulomb repulsion force dominates is about equivalent to $j = 3$. However, it should be noted that there are always some vacancies dispersing within the twin domains at random or in an ordered structure. For oxygen concentration smaller than 6.93, most of the excess vacancies could disperse in the twin domains. Thus the number of oxygen vacant layers at twin boundaries may be smaller than the calculated $j$ which assumes all vacancies are condensed at twin boundaries.

Table 2.1. Calculated and experimental values of $x$ in YBa$_2$Cu$_3$O$_y$ with various number, $j$, of oxygen depleted layers at the coherent twin boundaries.

<table>
<thead>
<tr>
<th>$j$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{exp}$</td>
<td>6.975$^7$</td>
<td>6.94$^{16}$</td>
<td>6.92 ± 0.01$^{18}$</td>
<td>(6.9)</td>
<td>6.87</td>
<td>6.85</td>
<td>6.82</td>
<td>6.80</td>
<td>6.78</td>
</tr>
<tr>
<td>Ref.</td>
<td>7,16</td>
<td>17</td>
<td>16,18,19</td>
<td>20</td>
<td>21</td>
<td>22–24</td>
<td>25</td>
<td>16,23</td>
<td>7</td>
</tr>
<tr>
<td>$T_c$ ($^\circ$K)</td>
<td>90$^7$</td>
<td>89</td>
<td>95$^{19}$</td>
<td>87</td>
<td>90</td>
<td>91$^{22}$</td>
<td>91</td>
<td>NA</td>
<td>83</td>
</tr>
</tbody>
</table>

2.3. Simulations

Simulated high resolution electron microscope (HREM) images of twin boundaries with various $j$ values, different defocussing conditions and different sample thicknesses assuming uniform thickness across twin boundaries are shown in Fig. 2.2a-c respectively. The simulated images of the twin boundaries assuming no oxygen vacancies [(Fig. 2.2a) top] show no contrast across the twin boundaries regardless of the objective lens defocus and sample thickness. However, when a few layers of oxygen at twin boundaries are taken away, contrast across twin boundaries appears. The width of the contrast band increases in
proportion to $j$ as shown in Fig. 2.2a. Contrast at the twin boundaries also varies markedly with defocussing conditions as shown in Fig. 2.2b. Note that the apparent boundary widths also vary slightly. Contrast at twin boundaries due to sample thickness variation, as shown in Fig. 2.2c, is equally dramatic. It can vary from almost no contrast to strong contrast. Various band widths and different contrast at twin boundaries in real HREM images are commonly observed, e.g., Fig. 2.3,[14,27-30] in agreement with the model proposed here. However, it should be emphasized here that similar contrast variation could arise from local thickness change,[31] presumably due to preferential etch during sample preparation. It has been shown that in HREM in-situ heating and cooling experiments, the orthorhombic, superconducting phase with twin boundaries can transform to the tetragonal phase.[29,32,33] This process can be reversible, but twin boundaries normally reappear at different positions.[29] However, if a significant amount of oxygen evaporates from the sample due to heating by the electron beam, the process becomes irreversible.[34] Also, twin boundaries exposed to a focused beam for a short time, e.g., 1 minute, show a decrease in contrast.[14] Oxygen atoms in twin domains close to the twin boundaries may gain energy through electron bombardment to jump into the twin boundary vacancies. Thus, the contrast might be expected to smear out as illustrated by the simulated images in Fig. 2.2d. Hence, precautions should be taken when using HREM to image the twin boundaries. Furthermore, the change of internal stress due to thermal cycling or beam heating may cause twin refining process (Fig. 2.4). A highly refined twin structure is believed to lose its long range correlation along c-axis direction and yield a tweed structure.

In polycrystalline materials, grain boundaries without obstacles, e.g., second phase or segregations, are known to be fast diffusion paths. However, the total surface area perpendicular to the c-axis of the grain boundaries, compared to the total area of the twin boundaries in the grain, is small. Although there may be oxygen deficiency at grain boundaries, a correction of oxygen stoichiometry due to grain boundaries can be neglected. Nevertheless, if the tunneling mechanism is assumed, grain boundaries may still play an important role.

To apply the model of oxygen vacant twin boundaries to the real system, accurate determination of oxygen content as well as microstructure parameters, e.g. lattice constants, twin boundary width and average twin width, is essential. However, the uniformity of the oxygen content in polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_x$ has been reported to vary from grain to grain.[14,34] An extended annealing of the polycrystalline material
is needed to achieve thermal equilibrium. A single crystal specimen eliminating the grain boundary effect would be preferable.

2.4. Discussion

A study by Chen et al.[35] shows that the ordered vacancies within the body of the twin domains accounts for only 3% of the total volume in a YBa$_2$Cu$_3$O$_{6.72}$ sample. This discrepancy could be explained by the oxygen-depleted twin boundary model with $j = 3$. The high resolution image shown in Fig. 2.3 also matches the simulated images using the model proposed here with $j = 3$.

Since the equilibrium width of the oxygen-depleted zone at a twin boundary is determined by the balance of the Coulomb repulsion force and the chemical potential, the resulting optimized configuration may have at least one layer of oxygen vacancies condensed at the twin boundary ($j = 1$ case) where the repulsion energy is the highest. For $j \geq 2$, the repulsion energy decreases inversely proportional to the oxygen ion distance resulting in increasingly diffuse oxygen-depleted layers, i.e., oxygen-vacancy segregation at these layers is probably incomplete. For simplicity, however, this diffuse atmosphere of oxygen vacancies has been described as a number of layers of oxygen vacancies, $j$. 
REFERENCES


FIGURE CAPTIONS

Fig. 2.1. Oxygen vacant twin boundary models for (a) 1 vacant layer (j=1), (b) 3 vacant layers (j=2), and (c) 5 vacant layers (j=3). Note: The angle at twin boundaries and the length difference between the lattice constants (a) and (b) are exaggerated. For simplicity, only oxygen atoms (black dots) are shown.

Fig. 2.2. Simulated HREM [001] images of twin boundaries. Simulation parameters are chosen to correspond to the operating conditions in the JEOL 4000 FX electron microscope. Sample thickness is 100Å and objective lens defocus is -800Å unless specified otherwise. (a) Changes with respect to j from j = 0 (no oxygen depleted layer, top) to j = 3 (bottom). (b) Variation with respect to objective lens defocus; -400Å (top) to -1600Å (bottom) in increments of -400Å, j = 3. (c) Variation with respect to sample thickness; 50Å (top) to 200Å (bottom) in increments of 50Å, j = 3. (d) Total oxygen atom number fixed, but abrupt concentration changes at twin boundaries are gradually relaxed (j = 3).

Fig. 2.3. High resolution electron micrograph of a twin boundary in YBa$_2$Cu$_3$O$_x$ material reveals significant contrast across the twin boundary. (Photo courtesy of Dr. K. Hiraga.)

Fig. 2.4. A proposed twin-refining mechanism during a short pulse of electron beam heating. (a) Originally, twin boundary (TB) has oxygen depleted with oxygen content of stoichiometric O$_x$ and twin domains, α and β, with oxygen content O$_{7-8}$. (b) Electron beam bombards the specimen activating the diffusion of oxygen in b-chain near twin boundary and causing an oxygen-disordered zone, i.e., tetragonal structure (T). (c) The counterparts of the remaining twin domains are nucleated at the thin edge of the specimen where cooling is more efficient after beam is removed. (d) New twin boundaries and domains are formed. Twin refining always occurs at twin boundaries and appears as pairs as observed in TEM.
Figure 2.4

(a) Grain surface

(b) Oxygen depleted zone

(c) Oxygen disordered zone

(d) Tetragonal structure
CHAPTER 3. A HYPOTHESIZED MACRO-RESONANCE-CELL DESCRIPTION
FOR HIGH-Tc OXIDE SUPERCONDUCTORS

YBa$_2$Cu$_3$O$_{7.4}$ has the unique heavily twinned microstructure due to the tetragonal to orthorhombic phase transformation which does not occur in any of the other high-T$_c$ oxides including the three classes of pseudo two-dimensional copper oxide, i.e., Tl-Ca-Ba-Cu-O(TCB) system, Bi-Ca-Sr-Cu-O(BCS) system, and La-Sr-Cu-O(LSCO) system, and two kinds of three-dimensional isotropic bismuth oxide, i.e., Ba-Pb-Bi-O(BPBO) system and Ba-K-Bi-O(BKBO) system. Orthorhombic YBa$_2$Cu$_3$O$_{7.4}$ with oxygen content ranging from about 6.5 to 7.0 has poor metallic properties at temperature higher than T$_c$ and becomes superconducting at T$_c$. On the contrary, the higher symmetry parent structure, tetragonal YBa$_2$Cu$_3$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, which are absent in the nonsuperconducting tetragonal 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 YBa$_2$Cu$_3$O$_{7.4}$ is a superconductor and tetragonal YBa$_2$Cu$_3$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 absent in closely related nonsuperconducting phases such as tetragonal YBa$_2$Cu$_3$O$_x$.

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

All known high-T$_c$ oxide superconductors except BKBO share a common pseudo-two-dimensional structure with CuO$_2$ planes 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 bad 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., Cu^{II}O in YBa_{2}Cu_{3}O_{7-\delta}, Bi^{III}O_{2} in BCS and Tl^{III}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 according to the oxidation states found in the natural compound. These charge states represent cations in different environments of oxygen bonding,[1] 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 Ba(Pb_{0.7}Bi_{0.3})O_{3-\delta} [2] and the perovskite-related 2-1-4 structure of (La_{2-x}A_x)CuO_{4-\delta} with A = Ba, Sr, or Ca. Other variations of the oxygen breathing mode include the CuO_4 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_{2}Cu_{3}O_{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[3] 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 3.1). 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 3.1. Stacking sequence of layers in unit cell.

<table>
<thead>
<tr>
<th>YBa$_2$Cu$_3$O$_7$ (n=2)</th>
<th>Ba</th>
<th>O</th>
<th>Y</th>
<th>O$_2$</th>
<th>Ba</th>
<th>← center</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
<td>Cu</td>
<td></td>
<td>Cu</td>
<td>O</td>
<td>← edge</td>
</tr>
<tr>
<td></td>
<td>← corner</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bi$_2$CaSr$_2$Cu$_2$O$_8$ (n=2)</th>
<th>O</th>
<th>Sr</th>
<th>Ca</th>
<th>O$_2$</th>
<th>O$_1$</th>
<th>O</th>
<th>Bi</th>
<th>O</th>
<th>Cu</th>
<th>Cu</th>
<th>O</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bi</td>
<td>O</td>
<td>Cu</td>
<td>Cu</td>
<td>O</td>
<td>Bi</td>
<td>O</td>
<td>Sr</td>
<td>Ca</td>
<td>Sr</td>
<td>O</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tl$_2$CaBa$_2$Cu$_2$O$_8$ (n=2)</th>
<th>O</th>
<th>Ba</th>
<th>Ca</th>
<th>O$_2$</th>
<th>O$_1$</th>
<th>O</th>
<th>Ba</th>
<th>O</th>
<th>Tl</th>
<th>O</th>
<th>Cu</th>
<th>Cu</th>
<th>O</th>
<th>Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tl</td>
<td>O</td>
<td>Cu</td>
<td>Cu</td>
<td>O</td>
<td>Tl</td>
<td>O</td>
<td>Ba</td>
<td>Ca</td>
<td>Ba</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>La$_2$CuO$_4$ (n=1)</th>
<th>O</th>
<th>Cu</th>
<th>O</th>
<th>La</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O$_1$</td>
<td>O</td>
<td>O$_1$</td>
<td>La</td>
<td>Cu</td>
</tr>
</tbody>
</table>

| boundary | ← → | layer(s) |
A consideration of charge balance in stoichiometric YBa$_2$Cu$_3$O$_7$ shows Cu$_3$ should have a total charge of +7 which can be reasonably distributed as Cu$^{+2}$, Cu$^{+2}$ and Cu$^{+3}$, or in layer-stacking sequence:

$$\text{YBa}_2\text{Cu}_3\text{O}_7 \rightarrow \text{Cu}^{+3}\text{O} - \text{BaO} - \text{Cu}^{+2}\text{O}_2 - \text{Y} - \text{Cu}^{+2}\text{O}_2 - \text{BaO}$$  \hspace{1cm} (3.1)$$

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 Cu$^{+3} \rightarrow$ Cu$^{+1} + 2h$ with the electronic holes (h) located at the overlapped orbitals of O : 2p$_x$ and Cu : 3d$_{3s}$ along the c-axis direction or O : 2p$_y$ and Cu : 3d$_{3x}$ 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 YBa$_2$Cu$_3$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. 3.1a). Note the oxidation states of neighboring Cu1 atoms on the same b-chain would be oscillating out-of-phase and Cu cation on the basal plane of tetragonal YBa$_2$Cu$_3$O$_6$ has the fundamental oxidation state, Cu$^{+}$, hence could not oscillate harmonically. Similarly, the Cu$^{+2}$O$_2$ plane could be presented as shown in Fig. 3.1b with Cu$^{+2} \rightarrow$ Cu$^{+1} + h$ and holes are assumed to resonate between two lobes of the O : p orbitals on opposite sides of oxygen based on Pauling's resonating bond idea.$^{[1]}$ 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 CuO$_2$ plane would then be oscillating 180° out-of-phase. The central four oxygens at corners of the shaded square in Fig. 3.1b 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$^{[4]}$ necessary for the stabilization of superconducting pairs.

The Cu cations in the YBa$_2$Cu$_3$O$_{7-\delta}$ 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 x 2b x 2c) with double periods along the c-axis direction as in 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 CuO2 plane yielding a macro resonance of the whole crystal lattice. However, the Cu2-O1 distance is too long for strong coupling, the coupling (Fig. 3.2) is possibly assisted by a soft mode of lattice vibration as evidenced by electron energy loss spectroscopy[5] (EELS) and electron diffraction at low temperature.[6] The YBa2Cu3O6 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 description of holes by the dissociation of copper in the higher oxidation state into the lowest (fundamental) one, i.e., Cu+3 → Cu1+ + 2h in the CuO boundary layer and Cu+2 → Cu+1 + h in the CuO2 layers, would provide an antiferromagnetic correlated background necessary for the coupling of the superconducting pairs.[7] The calculated hole counts[8] for the superconducting phase YBa2Cu3O6 with x = 7.0 - 6.3 follows the same trend as Tc as a function of x[9] in the same range of oxygen content suggesting that hole pairs indeed relate to the superconductivity more directly. Experimentally, a strong electronic transition in the visible-near-uv optical spectra of nonsuperconducting, tetragonal YBa2Cu3O6 with 6.0 ≤ x < 6.33 is associated with the existence of a highly localized Cu+1 complex[10] as expected in the description: Cu+3 → Cu+1 + 2h and Cu+2 → Cu+1 + h, and is coincident with the antiferromagnetic phase in the same range of oxygen content.[11] 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.[12] A similar enhanced breathing-mode peak is observed in superconducting (La1.45Sr0.55)CuO4+δ over nonsuperconducting La2CuO4.[11] 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 La2CuO4, and yield a strong attractive force acting on the pair (Fig. 3.2).[12] 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[12] as all these observations suggest. These pre-existing free pairs could condense into coherent superconducting pairs when the temperature drops to Tc.[13]
3.2. Pseudogap, Delocalization and Mott’s I-M Transition

All the 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. According to Anderson's RVB theory, a perfect resonance lattice would lead to an insulator, e.g., $\text{La}_2\text{CuO}_4$ and $\text{BaBi}_3\text{O}_6$ ($\text{Ba}_2\text{Bi}^{III}\text{Bi}^{V}\text{O}_6$), instead of a superconductor. Friedel and Noguera 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 bad 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, these oxides would become superconductors as soon as they are doped to become metallized, 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 $\text{La(Ni}_{1-x}\text{B}_x\text{O}_3$ with $B = \text{Ti}^{+3}, \text{V}^{+3}, \text{Cr}^{+3}, \text{Mn}^{+3}, \text{Fe}^{+3}, \text{Co}^{+3}$ and $\text{Ni}^{+3}$. 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 $\text{K}^+$ in three-dimensional 1-1-3 perovskite-related ($\text{Ba}_{64}\text{K}_{20}\text{Bi}^{III}\text{V}_0\text{O}_{2-\delta}$; undoped $\text{BaBi}_3\text{O}_6$ ($\text{Ba}_2\text{Bi}^{III}\text{Bi}^{V}\text{O}_6$) is an insulator, or by doping elements, $\text{A}^{II}$, in quasi-two-dimensional 2-1-4 perovskite-related ($\text{La}_{1-x}\text{A}_{x}\text{Cu}^{III}\text{O}_{4-\delta}$ with $A = \text{Ba, Sr or Ca}$ where $\text{La}_2\text{Cu}^{III}\text{O}_6$ is an insulator; or (II) by creating disorder through changing the exchange potential with B-site substitutional dopant having the same (average) charge but different 3$d^a$, e.g., Bi in Ba ($\text{Pb}^{IV}_{0.7}\text{Bi}^{III}_{0.3}$) $\text{O}_{3.5}$ where $\text{BaPbO}_3$ 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 boundary layer to become superconducting orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. These oxygens acting as hole donors would 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., Cu$I$, Tl$I$, to a higher (nominal) oxidation state, e.g., Cu$^{II}$, Tl$^{III}$, which in turn can dissociate into a lower oxidation state, provides holes as charge carriers and oscillating about the average oxidation state II. In YBCO and 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 could be randomly distributed on capping layer(s). In both systems, oxygen could be absorbed to promote most of the cations on the capping layer(s). In the BCS system, however, fully oxidized boundary layers would have oxidation state Bi$^{III}$, which is the fundamental oxidation state of Bi and could not provide charge carriers. Further promotion to Bi$^V$ is probably accomplished by removing some of the oxygen, or by less absorption via fast cooling, so that the neighboring Bi-O-Sr bending configuration, due to the incommensurate bond of BiO to CuO and O$^{2-}$--O$^{2-}$ repulsion, could be straightened in turn reducing the bond length of Bi-O and promoting Bi$^{III}$ to Bi$^V$. 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 be also formed due to the requirement of charge balance. Once the critical doping level is exceeded, the charge carrier could be delocalized and the material would become metallic.

It is interesting to note that 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 in all the high-$T_c$ oxide superconductors. 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 have their oxidation state oscillating about the average. Also, each pair of copper ions, Cu$^{+2}$, in the square lattice of CuO$_2$ plane could contribute a pair of holes by 2Cu$^{+2}$ → 2Cu$^{+1}$ + 2h. These holes as determined by Hall measurement 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.
3.3. 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,$^{14}$ i.e., the total $N(E_F)$ can be dissociated into the sum of the partial $\Delta N(E_F)$ due to individual CuO$_2$ layers, the capping boundary layers and a correction term representing the coupling between CuO$_2$ layers and the capping layers:

$$N(E_F) = n_{CuO_2} \cdot \Delta N^{\text{CuO}_2} (E_F) + n_{\text{cap}} \cdot \Delta N^{\text{cap}} (E_F) + \Delta N_{\text{coupling}} (E_F)$$

where $n_{CuO_2}$ is the number of CuO$_2$ layers and $n_{\text{cap}}$ is the effective number of capping layers. When an energy band in $E(k)$ diagram does not intersect the zone $E_F \pm \Delta$, this branch will not contribute to the $N(E_F)$, i.e., $\Delta N(E_F) = 0$. When there are double boundary layers, the number of energy band related to these boundary layers is doubled but the contribution due to each band is not exactly the same. Thus $n_{\text{cap}}$ represents this effect. The same effect also exists in CuO$_2$ layers but much less significantly, since $E(k)$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 $N(E_F)^{19}$ 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 $E(k)$ 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:

$$\Delta N(E_F) = \int_{E_F - \Delta}^{E_F + \Delta} \text{DOS}(E) \, dE = \int B \, \left( \frac{dE}{dE(k)} \right)_{k_F - m' \Delta k}^{k_F + m' \Delta k} = \int B' \Delta k = B'(m' + m'') \Delta k = B'm \Delta k$$

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

$$\Delta k = \frac{\pi b}{N_A} = \frac{\pi}{V_o} a c$$

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 $T_c = A(\omega) \exp(-1/N(E_F)V)$ with constant $A$ and interaction parameter $V$, then

$$\ln T_c = A' + \ln \langle \omega \rangle - \frac{1}{N(E_F)V}$$

$$= A' + \ln \langle \omega \rangle - \frac{V_0}{B'naV} \left( \frac{1}{n_{CuO_2} m_{CuO_2}^e \cdot c_{CuO_2} + n_{cap} m_{cap}^e \cdot c_{cap} + \text{coupling term}} \right)$$

(3.5)

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, $T_c$ increases consistent with the trend in Table 3.2. When $n_{CuO_2} \to \infty$, 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., $Ca_{0.8}Sr_{0.14}CuO_2$, with infinite stacking sequence, has strong electron correlation effects to result in localized spin, antiferromagnetic exchange and semiconducting behavior.\(^{[20]}\)

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 3.2).

**Table 3.2.** $T_c$ of TCB and BCS systems with various number of $CuO_2$ layers.

<table>
<thead>
<tr>
<th>$n_{CuO_2}$</th>
<th>SBL</th>
<th>DBL</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCB System</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>80 K</td>
</tr>
<tr>
<td>2</td>
<td>90 K*</td>
<td>110 K</td>
</tr>
<tr>
<td>3</td>
<td>110 K</td>
<td>125 K</td>
</tr>
<tr>
<td>4</td>
<td>122 K</td>
<td>162 K</td>
</tr>
<tr>
<td>BCS System</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>25 K†</td>
<td>38 K</td>
</tr>
<tr>
<td>2</td>
<td>75 K</td>
<td>95 K</td>
</tr>
<tr>
<td>3</td>
<td>110 K</td>
<td></td>
</tr>
<tr>
<td>YBCO</td>
<td>2</td>
<td>93 K</td>
</tr>
</tbody>
</table>

\(^{[21]}\)Data from Ref. 21.

\(^{[20]}\)TiCa$_2$Ba$_2$Cu$_4$O$_{11-\delta}$ with $T_c = 162$ K is not confirmed. (High $T_c$ update.)

\(^{[22]}\)Data from Ref. 22.

\(^{[23]}\)Data from Ref. 23. Also an alternation of SBL and DBL ($Y_2BaCuO_{15-\delta}$) in sequence yield $T_c = 40$ K.\(^{[24]}\)

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. (3.5).
As shown in the calculated \( E(k) \) of the BCS system, a flat double layer arrangement of the boundary layers \( \text{Bi}_2\text{O}_2 \), i.e., \( \text{BiO-BiO} \), shows little contribution to the total \( N(E_F) \), but a puckered triple layer arrangement, i.e., \( \text{Bi}_2\text{O}_2-\text{Bi} \) which could exist momentarily assuming \( \text{O}_6-\text{Bi}^{V}-\text{O}_{\text{Bi}} \) chains, where \( \text{Bi}^{V} \rightarrow \text{Bi}^{III} + 2h \), are oscillating along c-axis direction, shows enhanced coupling between these capping layers and the \( \text{CuO}_2 \) layers yielding much higher total \( N(E_F) \) by bringing up more \( \text{CuO}_2 \) bands close to the \( E_F \) level and bringing down \( \text{Bi}_2\text{O}_2 \) bands to intersect with the \( E_F \pm \Delta \) zone. As a consequence, both \( m_{\text{CuO}_2} \) and \( m_{\text{BiO}_2} \), as well as the coupling term would be all increased. According to Eq. (3.5), this configuration could thus result in a higher \( T_c \) than that of the \( \text{BiO-BiO} \) flat double layer arrangement. The quasi-two-dimensional character of 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 \( \text{Bi}_2\text{O}_2 \) boundary layers in the BCS system shows dramatic coupling effect between these capping layers and \( \text{CuO}_2 \) layers. Similar coupling effect could exist in other copper oxide superconductors, e.g., \( \text{O}_{9\text{a}}-\text{Ti}^{III}-\text{O}_{\text{Biv}} \) chains, where \( \text{Ti}^{III} \rightarrow \text{Ti}^{I} + 2h \), oscillate along the c-axis direction.

Both \( \text{Bi-Ca-Sr-Cu-O} \) (BCS) and \( \text{Tl-Ca-Ba-Cu-O} \) (TCB) systems with double boundary layer have their stacking sequence of the cations shifts when crossing these double boundary layers (Table 3.1). However, the double-layered two-dimensional array of \( \text{O}-\text{Bi}^{V}-\text{O} \) and \( \text{O}-\text{Ti}^{III}-\text{O} \) along the c-axis direction in \( \text{Bi}^{V}\text{O}_6 \) and \( \text{Ti}^{III}\text{O}_6 \) octahedra in the double boundary layers of the BCS and TCB systems, respectively, apparently couple the resonance of the cation-lattice even better than the one-dimensional chain of \( \text{Cu}^{III}\text{O}_4 \) does in the single boundary layer of the YBCO system. This could be attributed to the dimensions of the octahedra network of \( \text{BiO}_6 \) and \( \text{TlO}_6 \), which matches that of the \( \text{CuO}_2 \) planes above and below better than the one-dimensional square chain does in \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) and 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 \( T_c \left(\sim 110 \text{ K}\right) \) in the 2-2-2-3 phase, than that \((\sim 125 \text{ K})\) of the TCB system in the same phase may be qualitatively understood on the basis of the model. The very weak bonding between two \( \text{BiO} \) boundary layers, i.e., the cleavage plane, the incommensurate bonding lengths between \( \text{Bi-O} \) and \( \text{Cu-O} \), and more importantly, the oxidation state of \( \text{Bi} \) at the boundary layers being the fundamental oxidation state III, i.e., only a small fraction of \( \text{Bi}^{III} \) is promoted to \( \text{Bi}^{V} \) by oxygen vacancies resulting in a smaller carrier concentration.
than in the TCB system, probably results in a MRS less stable, i.e., smaller $\Delta$, than that achieved in the TCB system according to Eq. (3.5) and that $\Delta$ is proportional to $T_c$.

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,$^{[25]}$ show that major features of the lower complex of valence and conduction bands near $E_p$ are mainly determined by the three $\text{Cu} : 3d^5$ orbitals and the six, seven, or eight sets, respectively, of $\text{O} : 2s^22p^6$ 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 $E_p$ evolve. One broad anisotropic band across $E_p$ sharply is due to the antibonding $\text{Cu} : 3d - \text{O} : 2s$ orbitals in one-dimensional $\text{O}_4-\text{Cu}_1-\text{O}_4$ b-chain and has little contribution to the total $\text{N}(E_p)$. The other narrow band across and staying close to $E_p$ is from the nonbonding $\text{Cu} : 3d - \text{O} : 2p$ orbitals in the same b-chain. This narrow band has a large portion intersecting the zone $E_p \pm \Delta$ which stabilizes or pins the $E_p$ position and contributes largely, together with the two-dimensional antibonding band from the CuO$_2$ planes, to the total $\text{N}(E_p)$.

Structures with double layers of the CuO plane in $\text{YBa}_2\text{Cu}_3\text{O}_x$ (1-2-4-8 structure) films have a lower $T_c = 80 \text{ K}$,$^{[22]}$ compared to $T_c = 93 \text{ K}$ 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 for the second CuO layer which acts as a damping boundary and phase shifter could pose difficulty on coupling the oscillation of the oxidation state of Cu1 in the second boundary layer to that in the first boundary layer. 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$_2$O$_2$ 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., $\Delta$ of 1-2-4-8 structure is smaller, than that of the 1-2-3-(7) structure and result in the observed lower $T_c$ than that of the 1-2-3-7 structure.

It is interesting to compare the case $n_{\text{CuO}} = 2$ (Table 3.3) of all three systems in Table 3.2. For single boundary layer (SBL), BCS system has $T_c = 75 \text{ K}$ 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 double boundary layers (DBL), TCB system has $T_c = 110 \text{ K}$, followed by BCS system with $T_c = 95 \text{ K}$ and then YBCO.
system with $T_c = 80$ K. It seems for the double layers of interwoven BiO$_6$ octahedra network more freedom, due to the weak bonding between two BiO layers, i.e., the cleavage plane, is allowed to rearrange those incommensurate Bi-O bonds, into a wavy configuration, than in the single boundary layer which is sandwiched by the rigid CuO$_2$ layers. Its coupling strength becomes stronger though it is still weaker than that of the Tl$_2$O$_2$ layers which match better to the CuO$_2$ layers. On the other hand, the double-layered linear chains in YBa$_2$Cu$_4$O$_8$ have shown a strong disadvantage due to the dimensional incompatibility to the two-dimensional CuO$_2$ plane. Its coupling strength is weaker than that of the single layer and $T_c$ drops.

Table 3.3 also shows a tentatively assigned coupling strength 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, (La$_{1.35}$Sr$_{0.15}$)CuO$_{4.6}$ (LSCO system, $n_{\text{CuO}_2} = 1$), (Ba$_{0.6}$K$_{0.4}$)BiO$_{3.3}$ (BKBO system) and Ba (Pb$_{0.7}$Bi$_{0.3}$) O$_{3.5}$ (BPBO system) without boundary layer (NBL) are also listed. It seems the boundary layer(s) in copper oxide with less overlapping, therefore less interference and more flexibility, and better coupling to the CuO$_2$ layers will 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 yields an irregular three-dimensional charge-network of cation 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 two-dimensional CuO$_2$ layers is well preserved. In addition, magnetic ordering on the copper sublattice, which is absent in the bismuth/lead sublattice,$^{26}$ 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 bismuth oxide family.
Table 3.3. $T_c$ and tentatively assigned coupling strength of boundary layer(s) of various systems.

<table>
<thead>
<tr>
<th></th>
<th>$n_{CuO_6} = 2$</th>
<th>NBL</th>
<th>SBL</th>
<th>DBL</th>
<th>(S+D) BL</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Quasi-twodimensional</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copper oxide</td>
<td>TCB System</td>
<td>medium</td>
<td>90 K</td>
<td>strong</td>
<td>110 K</td>
</tr>
<tr>
<td></td>
<td>BCS System</td>
<td>medium-weak</td>
<td>75 K</td>
<td>medium</td>
<td>strong</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(BiO-BiO)</td>
<td>(Bi-O$_2$-Bi)</td>
</tr>
<tr>
<td></td>
<td>YBCO System</td>
<td>medium</td>
<td>medium-weak</td>
<td>weak</td>
<td>40 K</td>
</tr>
<tr>
<td></td>
<td>LSCO System</td>
<td>weak (n=1)</td>
<td>93 K</td>
<td>80 K</td>
<td>38 K</td>
</tr>
<tr>
<td><strong>Isotropic three-dimensional</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bismuth oxide</td>
<td>BKBO System</td>
<td>weak</td>
<td>30 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BPBO System</td>
<td>very weak</td>
<td>13 K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4. Substitution, Doping and Isotope Effect

A well prepared pure 1-2-3 structured sample with full substitution of Y with the whole series of lanthanides, except Ce, Pr, Tb and Pm (artificial element) virtually shows the same $T_c$.[27,28] This could be understood by realizing that the bands related to the Y-site layer with +3 charge are far above $E_F$ level. On the other hand, the oxidation state of Ce, Pr, or Tb all could be III or IV. This tendency toward oxidation state IV could, according to the proposed MRC description, thus change the vibration frequency and unbalance the oxidation state of Cu2 in the CuO$_2$ plane yielding a less stable MRS. However, Eu$^{III}$ doped with Pr$^{III}$, e.g., $(Eu_{0.9}Pr_{0.1})Ba_2Cu_3O_7-\delta$, could partially balance the charge effect and still yields a $T_c = 80$ K.[29] Meanwhile, $(Y_{1-x}Pr_{x})Ba_2Cu_3O_7-\delta$ can not balance the charge poison of Pr$^{IV}$ and has $T_c$ dropped to zero for $x \geq 0.6$. [30] Replacing Y with elements in the same column of the periodic table could reveal the size effect of Y-site on $T_c$. Indeed, full replacement with Sc yields an insulator. Partial replacement up to $Y_{0.2}Sc_{0.8}$ still maintains $T_c = 60 - 75$ K.[31] On the other hand, pure LaBa$_2$Cu$_3$O$_{7-\delta}$ usually shows $T_c$ well below that of YBa$_2$Cu$_3$O$_{7-\delta}$.[27] However, $T_c = 90$ K[32] for LaBa$_2$Cu$_3$O$_{7-\delta}$ and $T_c = 82$ K[29] for $(Y_{0.5}La_{0.5})Ba_2Cu_3O_{7-\delta}$ have been reported. These results indicate that size effect of Y-site on $T_c$ is not as strong as the charge effect as long as a critical doping level which yields the lattice crash down is not exceeded. Also worth
notice is that the heavy mass and strong magnetic moment of lanthanides do not show any significant effect on \( T_c \). However, Er, Ho, and Dy 1-2-3 compounds all show reentry of antiferromagnetic properties at \( T < 1 \) K\(^{33,34}\) in magnetic susceptibility measurement indicating that the superconductivity mechanism taking over paramagnetism into (perfect) diamagnetism at \( T_c \) might have an antiferromagnetism running at background.

The substitution of \( \text{Ba}_2 \) in \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) with \( \text{(BaSr)} \) or \( \text{(BaCa)} \) shows \( T_c = 82 \)\(^{35}\) and 77 K\(^{29}\) respectively, indicating that size effect of Ba-sites is slightly more significant than that at Y-site. This could be due to Ba layers, sandwiching the single boundary layer, CuO, could influence the coupling of CuO chain layer to the CuO\(_2\) planes. The charge effect of replacing Ba is expected to be as strong as that of replacing Y. Since the difference of charges at these two sites determines dominately the vibration frequency of Cu in CuO\(_2\) plane. However, chemistry does not allow such a substitution.

Doping of Cu with transition metals in the same row all shows \( T_c \) drops\(^{36}\) very quickly as expected from the model for the various oxidation states of these elements are not fully compatible with that of copper. Doping \( \text{Zn}^{II} \) at Cu2 site\(^{37}\) is especially bad for \( T_c \). Since there is no other oxidation state to oscillate (\( \text{Zn}^{II} \) is the fundamental oxidation state), \( T_c \) drops quickly to zero as Zn content increased to 13 at.\% in YBa\(_2\) (Cu\(_{1.4}\)Zn\(_{0.6}\))O\(_7\) or Y(BaO)\(_2\)(CuO)(((Cu\(_{0.8}\)Zn\(_{0.2}\))O\(_2\))\(_2\). Doping \( \text{Ga}^{III} \) at Cu1 site\(^{37}\) shows more tolerance of \( T_c \) toward the charge of Cu1 site in CuO basal plane. In Y (BaO)\(_2\)((Cu_{0.73}Ga_{0.27})O)(CuO\(_2\))\(_2\), \( T_c \) still maintains \(-67\) K, indicating that the contribution of CuO\(_2\) planes (2 layers per unit cell) to the total NE\(_p\) is more significant than that from the CuO chain (1 layer per unit cell). Surprisingly, substitution of same-column-element Ag at CuO chain site shows a dramatic \( T_c \) drop\(^{38}\) Y(BaO)\(_2\)((Cu_{0.93}Ag_{0.07})O)(CuO\(_2\))\(_2\) has \( T_c = 10\) K indicating that size effect on the Cu1-O1 bonding is very strong as also indicated by the fast increase of lattice parameter c, with a and b remaining almost unchanged. The reason for this could be attributed to the weaker bonding of Ag-O1, compared with Cu1-O1, as well as Ag having the fundamental oxidation state I. Thus even only small amount of Ag replacing Cu on b-chain site, MRS is destabilized rapidly.

Doping with F presumably replacing O4 site on basal plane\(^{39}\) reveals very small charge effect of O4 site on \( T_c \) in single phase sample YBa\(_2\)Cu\(_3\)\(_x\)F\(_x\)O\(_{6.5+\delta-0.5\delta} \) with \( x \) up to 0.066. For doping level in the range \( 1.65 \geq x \geq 0.165 \), BaF\(_2\), CuO and other unknown phases appear but \( T_c \) remains around 90 K.
intriguing report of $T_c = 155$ K in YBa$_2$Cu$_3$F$_2$O$_7$\(^{[40]}\) is not confirmed. F with $-1$ charge state, comparing with O$^{2-}$, seems should largely alter the charge balance of YBCO and the ordering of oxygen on basal plane since every F$^{-1}$ replacing O$^{2-}$ would yield one Cu$^{+3}$ in the boundary layer to Cu$^{+2}$ and reduce the charge carrier concentration. However, due to the very limited solubility, supersaturated YBCO(F) always dissociates into more stable BaF$_2$, CuO and other phases. Within solubility, a unit cell with Cu$^{2+}$F, instead of Cu$^{+3}$O, on the basal plane can still assist establishing MRS since Cu$^{+2}$ $\rightarrow$ Cu$^{+1}$ + h is not the fundamental oxidation state. Actually, due to the same charge state as that of Cu$^{+2}$O$_2$ layers, $T_c$ increases slightly before F concentration oversaturate, indicating that MRS charge carriers indeed are holes from Cu in oxidation state higher than the fundamental one.

On the other hand, when doped with S\(^{[41]}\) from the same column as O, YBa$_2$Cu$_3$O$_6$S or Y(BaO)$_2$(Cu$^{+2}$O$_2$)$_2$(Cu$^{+3}$S) shows the same $T_c$ as YBa$_2$Cu$_3$O$_6$, but with sharper phase transition, more complete Meissner effect, and larger unit cell. S has wide range of charge state, ±2, ±4, ±6, which could benefit the establishment of MRS at $T_c$ due to its multiple charge states and yields a sharper transition. Meanwhile, the larger lattice size of YBa$_2$Cu$_3$O$_6$S with $a = 3.855$ Å and $b = 3.919$ Å, comparing with $a = 3.822$ Å and $b = 3.891$ Å of YBa$_2$Cu$_3$O$_7$, will yield a slightly larger average twin width\(^{[42]}\) $W_t = ab/(b-a) = 236$ Å, comparing with 216 Å of YBa$_2$Cu$_3$O$_7$. The oxygen-depleted twin boundaries with stoichiometry YBa$_2$Cu$_3$O$_6$, are nonsuperconducting magnetic flux pinning sites. Larger twin width thus leads to less twin boundaries and hence fewer flux pinning and more complete Meissner effect.

Isotope exchange of $^{18}$O for $^{16}$O shows a small decrease of $T_c$\(^{[43-46]}\) which indicates that oxygen vibration is related to the superconductivity, but not very strongly. This small isotope effect gives $\alpha_{ox} \leq 0.05$ in the expression $T_c = \omega_{eff} = \Pi (M_i^{15})$ where $M_i$ is the atomic mass density of the ith specie in the material and $\omega_{eff}$ the effective Debye frequency. Comparing with $\alpha_{ox} = 0.16$ for layer-loosely-coupled (La$_{1-x}$Sr$_x$)$_2$CuO$_4$\(^{[47,48]}\) and $\alpha_{ox} = 0.2$ for three-dimensional bismuth-lead oxide Ba(Pb$_{1-x}$Bi$_x$)O$_3$\(^{[49]}\) YBCO system has very small isotope factor $\alpha_{ox}$. Since isotope effects of Cu\(^{50}\) and Ba\(^{51}\) are also insignificant, traditional weak-coupling electron-phonon interaction may not be the dominating superconducting mechanism. Instead, boundary layer coupling favored by the energy-lowering mechanisms, i.e., Peierl's deformation enhanced by lattice softening in LO mode and magnetic ordering on the cation sublattice, could be the main reason of high pair-condensation temperature in YBCO system.
In summary, the MRC description of the orthorhombic YBa$_2$Cu$_3$O$_{7-d}$ proposed here reveals many fascinating features when considering the correlations between the lattice structure and these physical properties. These features include various ways of lowering the energy of the system. For example, Jahn-Teller effect, or Peierl's deformation, which is equivalent to the breathing mode of oxygen vibration when considering different groups of oxygens, breaks the symmetry, lowers the energy, creates a gap at $E_F$ and forms an insulating phase in RVB state with localized singlet pairs. Oxygen vacancies, dispersing in the twin domains or condensing at twin boundaries, also reduce the internal strain energy and result in Mott-Hubbard insulator-metal transition with free (delocalized) hole pairs as the charge carriers providing the necessary background for the charge and magnetic moment variation of copper. The same Jahn-Teller effect may be enhanced by lattice softening at LO mode and magnetic ordering on copper sublattice yielding the strong coupling of CuO and CuO$_2$ layers, further reducing the system energy and condensing the free pairs into superconducting state. Since a system in resonance state has the lowest system energy, the MRC description with all these energy-lowering mechanisms provides a possible low energy state and a very rich background for discussing possible superconducting mechanisms. Each of these possible mechanisms, e.g., spin density wave (SDW), charge density wave (CDW), etc., may reveal just one of the many facets of the superconductivity in high-$T_c$ oxides. The MRC description proposed here contains several key elements of these mechanisms. With the aid of the MRC description, qualitatively the common and distinctive features of the current known oxide superconductors can be understood systematically. However, dealing with the superconductivity problem, the excitation involving holes and the kinetics of holes motion must be formulated in quantum-mechanical fashion. The resonance valence band (RVB) theory$^{[32]}$ may provide the tool for such a task.
REFERENCES


[49] B. Batlogg (private communication).


FIGURE CAPTIONS

Fig. 3.1 (a) Cu in CuO basal plane of YBa$_2$Cu$_3$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 O : 2$p_z$ and Cu : 3$d_{3z^2-r^2}$ along the c-axis direction or O : 2$p_y$ and Cu : 3$d_{3x^2-r^2}$ 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 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 $E_p$. 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. 3.2 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. 3.1b). (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:

\[ \text{Cu}^{+3} \rightarrow \text{Cu}^{+1} + 2h \]

Oxidation state III Oxidation state II Oxidation state I

Figure 3.1a
(b) Cu$^{+2}$O$_2$ plane:

\[
\begin{array}{c}
\text{Oxidation states} \\
\begin{array}{c}
\text{Oxidation states} \\
\text{Cu}^{+2} \rightarrow \text{Cu}^{+1} + h \\
\text{Oxidation states}
\end{array}
\end{array}
\]

Figure 3.1b
CHAPTER 4. EFFECTS OF OXYGEN-DEPLETED TWIN BOUNDARIES ON SUPERCONDUCTING PROPERTIES

An imperfect macro-resonance-cell (MRC) description for high-\(T_c\) oxide superconductors based on their common features and minimum energy principles suggests that copper in its high oxidation state may dissociate into the fundamental, i.e., the lowest, oxidation state and contribute hole(s) as charge carriers. In the normal conducting (NC) state of \(\text{YBa}_2\text{Cu}_3\text{O}_7\), each Cu on the CuO basal plane contributes two holes \((\text{Cu}^{+3} \rightarrow \text{Cu}^{+1} + 2\text{h})\) and Cu on the CuO\(_2\) planes contributes one hole \((\text{Cu}^{+2} \rightarrow \text{Cu}^{+1} + \text{h})\). These holes form charge carrier pairs and are delocalized. However, the coupling between CuO and CuO\(_2\) layers is weak in the NC state and the propagation directions of the holes are random except in the presence of an applied field. In the superconducting (SC) state, the oxidation states of copper may oscillate between I and III forming a three-dimensional resonating network and the coupling between CuO and CuO\(_2\) layers is strong. Free pairs of holes could condense into coherent superconducting pairs. In the static SC mode, i.e., no field applied, there is no net current. In the dynamic SC mode, hole pairs would be driven by the applied field resulting in a net current.

In order to permit hole pairs propagation, absence of some holes on the CuO plane, yielding imperfect resonance locally, is essential. This may be realized in several ways, e.g., a small number of O4 jumping to O5 sites, residual oxygen vacancies located on O4 site, doping with elements with different charges, etc. All these defects can cause locally unsynchronized resonance delocalizing hole pairs and shifting the nonconducting (insulating) state into the conducting state.\(^{[1]}\) One type of site where oxygen is expected to be deficient is at the twin boundaries if oxygen is depleted on the CuO layer. The CuO\(_2\) layers, on the other hand, have empty overlapped-orbitals \((\text{Cu : } 3\text{d},\text{e}_{\gamma} \text{ and O : } 2\text{p})\) since \(\text{Cu}^{+2} \rightarrow \text{Cu}^{+1} + \text{h}\) contributes only one hole. CuO\(_2\) layers must be coupled to the CuO layer to maintain a macro resonance state of the whole lattice.

4.1. SIS Josephson Junction and Glassy States

Oxygen-depleted twin boundaries, with stoichiometric \(\text{YBa}_2\text{Cu}_3\text{O}_6\) have CuO\(_2\) planes but are missing the Cu-O chains. Cu at the twin boundaries is in the fundamental oxidation state, Cu\(^{+1}\). Thus the resonance of the Cu frame would not propagate across the twin boundaries, i.e., these twin boundaries are in a
nonsuperconducting state. Insulating twin boundaries together with the twin domains on both sides could be assumed to form a superconductor-insulator-superconductor (SIS) Josephson junction. (A similar situation could exist at some grain boundaries.) Inside a grain or crystal, the (110) and/or (1-1 0) twin boundaries together with the (001) 90°-rotation boundaries or grain boundaries would form a three dimensional network dividing the grain into many superconducting clusters weakly coupled by SIS Josephson junctions. Such a superconducting glassy state including intra- and inter-grain Josephson junctions, would be expected to result in a significant reduction of average current density in polycrystalline oxide superconductors especially when temperature is near $T_c$. \[2\]

Due to an extremely short coherence length in the YBCO system, $\xi_{\parallel} = 7 \text{ Å}, \xi_{\perp} = 34 \text{ Å}$,\[3\] the pair potentials at the interfaces, $\Delta_{\parallel}(0)$ and $\Delta_{\perp}(0)$, are considerably weakened.\[2\] Near $T_c$, the critical current $I_c$ is proportional to the product of the pair potential at both interfaces and can be expressed as

$$I_c \propto \Delta_{\parallel}(0)\Delta_{\perp}(0) \propto \Delta_0^2 \left( \frac{b}{\xi} \right)^2 \propto (T_c - T)^2 \quad (4.1)$$

where $b$ is the extrapolation length of the pairing potential into the insulating region.\[4\] The critical current has an anomalous temperature dependence and reduces dramatically when temperature approaches $T_c$. For $T < T_c$, $I_c \propto \Delta_0^2 \propto (T_c - T)$ having the same temperature dependence as in ordinary type-II superconductors with moderate coherent length.

For tunneling to occur, the thickness ($d$) of the insulating layer, i.e., the width ($W_{ab}$) of the oxygen-depleted zone at twin boundary or grain boundary, should be smaller than or at most near the coherence length of the oxide superconductor. Since $\xi_{\perp} = 34 \text{ Å} (T_{c\perp} = 77 \text{ K}) = 60.7 \text{ Å}[5]$ or about 42.9 Å across a twin boundary), the largest distance the superconducting current could tunnel through at liquid nitrogen temperature would be about eight layers (~ 43.6 Å) of insulating $\text{YBa}_2\text{Cu}_3\text{O}_x$. Experimentally, this expectation is supported by comparing various numbers ($j$) of oxygen-depleted layers at twin boundary to the $I_c(O_x)$ data (Fig. 4.1).\[6\] $I_c$ drops almost linearly with increasing thickness of the insulating layers and approaches zero when $O_x < 6.80$. This is consistent with Cava's\[7\] measurement of $T_c$ as a function of $O_x$. In Ref. [7], $T_c$ was almost constant for $O_x > 6.80$ and drops quickly when $O_x < 6.78$. For $O_x = 6.72$, patches of double cell structure\[8,9\] with stoichiometric $O_x = 6.50$ (homologous phase: 1/2 case) and other homologous phases, e.g., stoichiometric $O_x = 6.60$ (homologous phase: 3/5 case),\[9\] have been found with transmission
electron microscopy in the oxygen-heavily-depleted material. In these materials, oxygen vacancies at (0, \( \frac{1}{2} \), 0) sites in twin domains and at twin boundaries are reorganized into more stable homologous phases, especially the double cell structure, with smaller numbers (−3) of oxygen-depleted layers at twin boundaries which is believed to be the range over which Coulomb repulsion dominates. Presumably, this is also the cause of the peculiar behavior of resistivity in normal conduction.

The width of the twin boundary also should affect the magnitude of the phase shift (\( \phi \)) according to the Ferrell-Prange equation:

\[
\frac{\partial^2 \phi}{\partial y^2} = \frac{1}{\lambda_f^2} \sin \phi
\]

when superconducting wave tunnels through the boundary, where \( \lambda_f \) is the Josephson penetration depth and is given by \( \lambda_f^2 = \hbar/4\pi e I_c \mu (2\lambda + d) \).

4.2. Flux Pinning and Vortex State

When a magnetic field is applied to a YBCO superconductor, the nonsuperconducting areas, possibly at twin boundaries as well as some grain boundaries with stoichiometric \( \text{YBa}_2\text{Cu}_3\text{O}_6 \), are expected to provide the permeable local paths for magnetic flux lines. That these boundaries act as the pinning sites for flux lines has been successfully demonstrated by the decoration technique (see Appendix A). Because of the very fine twinning structure, numerous grain boundaries and voids, small grain size and high porosity, as well as the existence of other nonsuperconducting phases, e.g., \( \text{CuO, BaCuO}_2 \) and \( \text{Y}_2\text{BaCuO}_4 \), a regular flux lattice in the vortex state is difficult to obtain. Near liquid nitrogen temperature, only partial flux lattices have been observed. Also, in YBCO material, because the average width of the twin domains, \( w_{td} = 200 - 300 \text{ Å} \), is smaller than the penetration distance, \( \lambda_{pe} = 1250 \text{ Å} \), a regular flux lattice with all lattice sites pinned at the twin boundaries is unlikely since the vortex diameter is about \( 2\lambda \). However, the numerous twin boundaries acting as flux pinning sites should raise the lower critical field, \( H_{c1} \), above the intrinsic value of pure \( \text{YBa}_2\text{Cu}_3\text{O}_6 \) without twin boundaries.

It is well known that type-II superconductors have a negative surface energy between the normal conducting phase (NCP) and the superconducting phase (SCP). The "glassy" state due to the high density of twin boundaries thus provides a large favorable surface area for SCP nucleation when NCP is cooled.
from above \( T_c \) in zero field or when the field is reduced from above \( H_{c3} \) at \( T < T_c \). The resulting \( H_{c2} \) is therefore expected to be smaller than the intrinsic value for a perfect YBa\(_2\)Cu\(_3\)O\(_7\) domain.

The remanent magnetic moment in the hysteresis loop from the magnetization measurement can be attributed to the trapping of flux lines at these insulating boundaries as well. In addition, the flux pinned at twin boundaries can also explain the less than 100% Meissner effect or imperfect diamagnetism measured in field cooled (FC) YBCO crystals (without grain boundary) in which twin boundaries are the only strong pinning sites when flux exclusion progresses as temperature drops below \( T_c \). In zero field cooled (ZFC) specimens, time-dependent magnetization-relaxation phenomena have been reported by several groups.\(^{18,20}\) This could be due to the weak linking, i.e., the insulating boundaries, in this material. A stable magnetization configuration (state), which minimizes the energy of all the weak couplings, may not initially be achieved. As time passes, the system may transit from one metastable state to another metastable state having lower energy.

When a magnetic field is applied parallel to the junction plane of a SIS structure, a surface screen current perpendicular to the field is developed within the penetration depth, \( \lambda \), from the boundary of each superconducting domain. If the thickness, \( d \), of the insulating layer is too large, e.g., \( > 50 \) Å, and the transmission coefficient for tunneling current is too small, no tunneling current exists. However, if \( d \) is comparable or smaller than the coherence length, \( \xi \), the screen currents can tunnel through the insulating layers and form a complete loop. Depending on the strength of the applied field, discrete numbers of flux-oid, i.e., quantized flux lines with \( \Phi_0 = \hbar c / 2e = 2 \times 10^{-7} \) Gauss cm\(^2\), can penetrate the insulating layers with vortex currents surrounding each flux line. The higher the field applied, the more fluxons are pinned at the junctions. In the presence of a uniform magnetic field, \( H \), the current per junction width, \( J(x) \), can be expressed as

\[
J(x) = I_0 \sin \left( \pi \frac{H(2\lambda + d)x}{\Phi_0} + \phi(0) \right)
\]

The tunneling current density would be modulated along the junction producing \( J = 0 \) nodes where flux lines are pinned. When \( H = 0 \), the expression reduces to the fundamental dc equation \( J = I_0 \sin \phi \) where \( \phi \) is the phase difference between the pair waves in the superconductors on the two sides of a Josephson junction.
4.3. Superlattice, Band-folding and Minigaps

When calculating the energy band structure of YBa$_2$Cu$_3$O$_{7-\delta}$, a homogeneous matrix extending infinitely in all directions is presumed to exist. In the real material, however, a dense twin structure is estimated to have an average spacing ~ 216 Å between coherent twin boundaries. Their presence breaks the inversion symmetry of the presumed infinite matrix, introduces boundary mirror and glide symmetry operations into the crystal symmetry, and forms polarized boundaries. Since CuO$_2$ layers are not strongly affected by the presence of these oxygen-depleted twin boundaries, only energy bands related to the CuO b-chain plane are affected by the new symmetry operation.

Along the direction perpendicular to the twin boundary plane, the whole lattice is similar to a structure with a widely spaced superlattice, i.e., b-chains run zig-zag across twin boundaries with a repeating unit of about 156 b-chain units (assuming average $W_z = 216$ Å). This superlattice structure with glide symmetry thus requires the b-chain related bands folded into a $\pi/156$ b Brillouin zone in $\overline{k}_y$ direction yielding band degeneracy at zone boundary (Y) and subtle changes toward $\Gamma$-point. However, the CuO plane is coupled to the neighboring CuO$_2$ layers via Peierl's deformation of oxygen atoms creating a Jahn-Teller gap. A calculation employing a tight binding model with 75 b-chain unit reveals minigaps at zone boundary with scale as small as 200 Kelvin as expected, and unknown gaps at the $\Gamma$-point. These minigaps give rise to the semiconducting or semimetallic character of the CuO b-chain plane. Due to the splitting of degenerated points at zone boundaries, these densely packed, b-chain-plane-related bands are further flattened. However, $T_c$ should be only slightly enhanced by the twinning geometry.

For an oxygen-depleted YBa$_2$Cu$_3$O$_{7}$ sample with $O_x \geq 6.80$, $T_c$ is almost unchanged since the extrapolation length of the pair potential is about 37 Å. The width of the oxygen depleted region at a twin boundary would never be expected to be this large. For $O_x < 6.78$, the oxygen vacancies dispersed in the twin domains start rearranging into a series of homologous phases with the double cell structure as the most stable end phase in the series and $T_c$ drops rapidly to that of the secondary stable structure (~60° K).

In summary, these twin boundaries together with the 90°-rotation boundaries and grain boundaries divide the material into many superconducting clusters weakly coupled by SIS Josephson junctions, i.e., in a superconducting glassy state. Oxygen-depleted twin boundaries may provide hole-absent sites necessary
for yielding local imperfect resonance and delocalization of hole pairs. The critical current as expected from the model would decrease as the number of the oxygen-depleted layers increases causing a wider insulating thickness in the SIS Josephson junction structure. The same effect also would be reflected in the room-temperature resistivity which increases almost linearly with increasing numbers \((1 \leq j \leq 3)\) of oxygen-depleted layers at twin boundaries. Imperfect Meissner effect, remanent magnetization as well as the time-dependent magnetization-relaxation phenomena all can be qualitatively understood based on this model. Oxygen-depleted twin boundaries can provide not only the pinning sites for the magnetic flux but also the nucleation sites for the superconducting phase, yielding the measured \(H_{c1}\) and \(H_{c2}\) higher and lower than the intrinsic value respectively. Finally, the model is consistent with the fact that \(T_c\) is nearly constant for oxygen contents above 6.8 but drops quickly when oxygen content is less than 6.78 as oxygen vacancies become rearranged into a more stable secondary structure. Even though the model is only qualitative, it is consistent with a large number of experimental observations and may be helpful in further development of a fundamental understanding of superconductivity in this interesting material.
REFERENCES


Fig. 4.1 Critical current density as a function of oxygen content, $x$, in YBa$_2$Cu$_3$O$_y$. Arrows are added to mark the oxygen content of the samples assuming $x = 7$ within twin domains and various numbers ($j$) of oxygen depleted layers at twin boundaries. Within these layers $x$ is assumed to be 6. (Reprinted by permission from Nature Vol. 332 pp. 58. Copyright (c) 1988 Macmillan Magazines Ltd.)
Figure 4.1

Oxygen content ($O_x$)

$J_c$ (A cm$^{-2}$)

j = 7, j = 5, j = 3, j = 1
CONCLUSIONS

In this work, a detailed nucleation-and-growth mechanism (Chapter 1) for the formation of microtwins in the orthorhombic YBCO system is proposed. The following conclusions are based on the model proposed in Chapter 1:

1.1. The ordering parameter is suggested from neutron scattering data to be the oxygen uptake rate, \( \frac{dO_d}{dT} = \frac{dO_d}{dt} \).

1.2. The observed details of micro-twin formation associated with the tetragonal-orthorhombic structural transformation are explained by the proposed nucleation-and-growth mechanism.

1.3. The oxygen uptake rate during the structural phase transformation is consistent with the proposed nucleation-and-growth mechanism.

1.4. The intermediate structure observed during phase transformation in in-situ TEM experiments are probably composed of interpenetrated twin laths in the matrix of tetragonal \( \text{YBa}_2\text{Cu}_3\text{O}_6 \).

The twin boundary model proposed in Chapter 2 leads to the following conclusions.

2.1. The twin boundary structure generally assumed in the literature is energetically unfavorable because of too high Coulomb repulsion between neighboring oxygen ions at the boundary.

2.2. An oxygen-depleted zone at twin boundaries is proposed which preserves coherency and avoids close oxygen neighbors and could also serve as a fast diffusion path for oxygen during the tetragonal to orthorhombic phase transformation.

2.3. The observed difficulty of reaching the stoichiometric orthorhombic \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) could be explained by this model since at least one layer of oxygen is missing at the twin boundaries \( j = 1 \).

2.4. The observed oxygen content in orthorhombic YBCO under normal processing pressure, i.e., 1 atm air or \( \text{O}_2 \), might have several layers of depleted oxygen at twin boundaries \( j \leq 3 \).

In Chapter 3, an imperfect macro-resonance-cell description suggested by the common features in addition to \( \text{CuO}_2 \) layers of current known high-\( T_c \) oxide superconductor is proposed, which leads to the
following conclusions:

3.1. It is suggested by this 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.

3.2. 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.

3.3. Variations in $T_c$ corresponding to different numbers of CuO$_2$ layers in BCS and TCB systems can be rationalized.

3.4. 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).

3.5. $T_c$ 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.

3.6. Effects on $T_c$ due to the substitution of other element in the YBCO system can be qualitatively rationalized.

Finally, for the YBCO system based on the proposed nucleation-and-growth mechanism, the oxygen-depleted twin boundary model and the imperfect macro-resonance-cell description, the following qualitative conclusions can be made concerning some of the superconducting properties.

4.1. A high density of intra-grain SIS Josephson junctions would be expected to exist in the YBCO system because of the twin boundaries and the 90° twist boundaries which would form a three-dimensional network resulting in a "glassy state" of small superconducting domains separated by thin insulating layers in superconducting YBCO.

4.2. Critical current would be expected to have anomalous temperature dependence and reduce dramatically as temperature approaches $T_c$. 
4.3. Critical temperature may be slightly enhanced by the oxygen-depleted twin boundaries.

4.4 The measured $H_{c1}$ and $H_{c2}$ would be expected to be higher and lower than the intrinsic values respectively.
Flux pinning in the sintered high $T_c$ oxide superconductors, YBa$_2$Cu$_3$O$_{7-δ}$, in the vortex state has been demonstrated for the first time using the Bitter pattern technique and scanning electron microscopy. External magnetic fields of 150 Gauss (G) or 800 G perpendicular to the specimen surfaces were applied during the evaporation of cobalt after the specimens cooled with liquid nitrogen had reached a temperature below $T_c$. All specimens thus decorated with cobalt show non-uniformly distributed flux pinning positions as would be expected due to the porosity and multiphase character of the specimens as well as the relatively low field applied.

The direct observation of the flux-line arrangement in a type II metallic superconductor, Pb(6.33 at.%)-In, was clearly demonstrated by H. Träuble and U. Essmann$^{[1]}$ using liquid helium cooling, cobalt decoration and replica for transmission electron microscopy to study the effect of defects created by plastic deformation of the specimen on the flux-line arrangement. However, the new high $T_c$ superconductors, YBa$_2$Cu$_3$O$_{7-δ}$, are typically powder-sintered thus have a complicated morphology, e.g., pores and several phases coexisting, as well as a highly anisotropic crystal structure. Therefore, the flux pinning positions, and thus magnetization behavior, can be very different from the classical, homogeneous alloy superconductors. Because at $T_c \approx 95^\circ K$, we were able to use liquid nitrogen as coolant to perform the flux decoration experiment and to directly observe the inhomogeneous magnetization of the new high $T_c$ oxide superconductors with the scanning electron microscope.

The sintered YBCO material was first carefully polished from both sides down to about 1 mm thickness. A simple levitation test was then performed to assure that the polished material had not been fully degraded. It has been reported that at room temperature, surface degradation occurred in one week and that above 150$^\circ$C, rapid degradation occurred.$^{[2]}$ The sample was then loaded in a cryostat cooled with liquid nitrogen to achieve a temperature, typically 84$^\circ K$, below $T_c$ after pumping the system to $<10^{-6}$ torr and backfilling with helium to $10^{-1}$ torr range. The magnetic field from a solenoid was then applied and cobalt evaporated from a tungsten filament. After warming up to room temperature, the specimens were immediately transferred to the scanning electron microscope chamber and inspected.
Two kinds of specimens were used in these decoration experiments, a low density material (Figs. A.1 and A.2) in which sintering was very incomplete containing large angular pores and a higher density material (Figs. A.3 and A.4) having smaller, more rounded and more numerous pores.

Figure A.1 shows flux pinning at pores, grain boundaries and also in the bulk. Pinning positions within some of the grains indicate that a bulk superconducting mechanism does occur. However, decorations along the grain boundaries particularly at pores were more frequently observed. A fully decorated fluxsoid revealing the shape of the trapped external flux lines in 3-dimension is shown in Fig. A.2. These decorated flux lines were interwoven with the flux lines of nearby pinning fluxsoids and stayed standing after the magnetic field was turned off. On the contrast, a single isolated fluxsoid can’t maintain the decorated flux lines standing. A rough estimation from the diameter of the decorated fluxsoid in Fig. A.2 gives a value of <2000 Å for the penetration depth. The fields applied in both figures were 800 G.

Figures A.3 and A.4 show the effect of field strength, 800 G and 150 G, respectively, on the average spacing of flux pinning positions in the higher density material which contain numerous discrete tiny pores. In both cases all the pinning points are at pores, but for the low field the average spacing is about 3.8 micrometers whereas for the high field case the average spacing is about 1.2 micrometer.

The inhomogeneous decoration results observed in these samples raised the possibility that artifacts could have been responsible for the decoration. Therefore three experiments were carried out to check this possibility. Only one parameter was changed during each experiment. Cobalt was evaporated onto the specimen (1) at 279.5°K instead of 85°K, (2) no field applied, and (3) copper evaporation instead of ferromagnetic cobalt; all other conditions remained as before. All three of these experiments revealed uniform deposition consistent with the interpretation of inhomogeneous decoration as due to flux pinning. The observed inhomogeneous pinning may be attributed to the relatively low applied field, the porosity and the multiphase character of the sintered oxide material as well as the possibility of surface degradation and the anisotropic crystal structure of the superconducting phase.

These superconductors are a multiphase material which may contain CuO, BaCuO₂, Y₂BaCuO₅, YBa₂Cu₃O₇₋₅ (tetragonal) and YBa₂Cu₃O₇₋₅ (orthorhombic). Only the last one is a superconducting phase. The superconducting phase, YBa₂Cu₃O₇₋₅ (orthorhombic), is highly unstable and easily degraded in an ambient with moisture. In the vortex state, depending on the applied field and temperature, the
YBa$_2$Cu$_3$O$_{7-x}$ orthorhombic phase can be normal state rich or superconducting phase rich which further reduces the possible decorating area. Finally, the anisotropy of the crystal structure may preclude decoration if the applied field is not nearly parallel to the c-axis of the lattice.

Considering the size of the grains relative to the thickness of the specimen, the fluxoids have to penetrate many grain diameters to reach the other surface. Therefore the strong anisotropy and numerous pores of this material may play an important role in the location of pinning sites and thus local magnetization behavior. This technique also allows to directly distinguish the superconducting and normal conducting areas on a microscale. New experiments with single crystal and higher field for full development of a flux lattice are in progress.
REFERENCES


FIGURE CAPTIONS

Fig. A.1. Flux lines of the low density YBa$_2$Cu$_3$O$_{7-\delta}$ at 800 G are decorated with cobalt. Partial flux lattice were found in the bulk, along the grain boundaries and in the large pores. The average spacing of flux lines is slightly larger than 1 $\mu$m.

Fig. A.2. Higher magnification of the "root" of the decorated flux lines gives a roughly estimated penetration depth of less than 2000 Å.

Fig. A.3. Decorated flux lines of the higher density YBCO at 800 G. Flux lines are pinned at tiny pores mostly. Self-adjustment of flux locations gives an average spacing of about 1.2 $\mu$m.

Fig. A.4. Same material as in Fig. A.3 at 150 G. Average spacing of the partial flux lattice is $3.8 \pm 0.2$ $\mu$m. Again, most flux lines are pinned at tiny pores in this higher density material.
Figure A.2
Figure A.3