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VALENCY OF COPPER AND OXYGEN IN THE $YBa_2Cu_3O_{6.5+x}$ CERAMIC SUPERCONDUCTOR

A Thesis
Presented to
The Faculty of the Department of Chemistry
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In Partial Fulfillment for the Degree
Master of Science

By
Tuyen L. Vo
May, 1994

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ABSTRACT

Valency of Copper and Oxygen in the $YBa_2Cu_3O_{6.5+x}$ Ceramic Superconductor

by Tuyen L. Vo

The charge distribution of copper and oxygen in the $Y_1Ba_2Cu_3O_{6.5+x}$ superconductor is studied by wet chemical analysis. Samples of 0.1 g $Y_1Ba_2Cu_3O_{6.5+x}$ superconductor were dissolved in HCl solution and analyzed by redox titration with Ce^{4+}, Fe^{2+}, and H_2O_2, and by colorimetry with $Fe(o\text{-phenanthroline})_3{}^{2+}$. The results suggest that x is 0.48 ± 0.03 and that holes may exist as a $[Cu\text{-}O]^+$ rather than the formal charges Cu^{3+} or O^-.

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INTRODUCTION

In 1986 Bednorz and Muller discovered a copper oxide superconducting compound containing Lanthanum, Barium, Copper, and oxygen that made a major impact in this field.[1] Only months after this work was published, their results were duplicated for confirmation.[2-4] Before the first anniversary of the discovery, almost 100 papers were submitted for publication, and the breakthroughs achieved during this period surpassed the results in the whole 75 years since the discovery of the superconducting phenomenon in 1911 by Kramelingh Onnes.[6] This original La-Ba-Cu-O compound was the first example of the Copper Oxide Class of superconductors that has grown to more than 20 derivatives with Rare earth and Alkaline earth substitution (Table 1). The transition temperature (T_c), the criterion that indicates the level of performance, increased by 55°K in less than a year compared to an increase of about 17°K in the previous 75 years. The physical behavior of this new class of compounds has surpassed the properties predicted by the BCS theory,[6] the superconductivity theory that was awarded the Nobel Prize and was still widely accepted (circa 1986) by the scientific community. In the following years, there were conferences solely devoted to this topic, and the articles submitted at each conference approached one thousand.[7] Many termed 1986 the start of superconductor fever. In order to fully understand the impact of this discovery, it is appropriate to discuss further the phenomenon of superconductivity, the importance of its applications, and the reasons why the recently discovered materials receive world wide attention.

1. Superconductivity[8]

Superconductivity is defined by the remarkable electrical and magnetic properties of certain types of materials at quite low temperature (presently less than 135K). It had long been thought that the resistance of a pure metal dropped smoothly and became zero (i.e., a perfect conductor) as the temperature approached absolute zero. However, in 1911, Kamerlingh Onnes[9] discovered the remarkably sharp disappearance of electrical resistance from a thin rod of mercury in liquid helium (Figure 1). It was realized later that mercury had passed into a different electrical phase: the superconducting phase. This superconducting state is created by cooling the superconductors below a certain temperature, which is called the critical temperature. Above this temperature, superconductivity disappears and the materials return to their normal state. Each superconductor has its own critical temperature value. All superconductors, in their superconducting state, have zero resistivity and strong diamagnetic properties. The abrupt change from a conductor to a superconductor occurs at a thermodynamic transition state, depending on the temperature and the magnetic field strength at the surface of the materials. There are three important parameters in defining superconductors: the critical applied field strength (H_c), the critical current (J_c), and the critical temperature (T_c). These parameters, when exceeded, will destroy the superconducting capability. In its superconducting state, the material is shielded since it appears to be diamagnetic and thus exerts an opposing force to an externally applied magnetic field. This phenomenon is known as the Meissner effect (Figure 3). Based on this phenomenon, two types of superconductors can be identified.

Materials of the first type (Type I) expel an external magnetic field until this field exceeds the critical field value H_c; then they lose their superconductivity. Most of the materials of this type are pure metals. The second type (Type II) has two critical field values. After the first critical field is exceeded, the materials are not completely shielded from the external field but still exhibit the property of zero resistance. When the second critical field value is exceeded, the materials are fully penetrated by the external field and the superconductivity is destroyed. Most of the materials of this type are metallic and intermetallic alloys, and recently, ceramic oxides. Each superconductor has its own critical current density. If excess electrical current passes through the superconductor, the materials will breakdown and return to their normal state. A few terms and phenomena are briefly explained for clarification in the following sections.

BCS Theory: Developed by J. Bardeen, L. Cooper, and J. Schrieffer in 1957,[10] the theory successfully explained many superconducting properties in those materials discovered prior to 1986. The BCS theory states that in the superconducting state, lattice vibrations (phonons) pair up with mobile electrons and allow these electrons to move in particular trails to avoid random collisions. As a result, zero resistance is achieved. For this to happen, the materials should be at low temperature (near 0 K) to reduce the atomic (lattice) vibrations.

Meissner Effect: Materials in their superconducting state have the ability to expel an applied external magnetic field. This effect was discovered by Walther Meissner in 1933.[11] This property has been the key test to any superconductor discovered thereafter.

Josephson Effect : When a thin oxide layer is placed between two superconductor films, the two superconducting films are coupled together to allow current to flow through. As the system is exposed to various magnetic fields and radiation, the current changes because some electrons tunnel through the barrier. This phenomenon, which is termed the Josephson Effect,[12] is used to detect small magnetic changes.

Cooper Pair: When electrons moved through the lattice in the superconductor, they are paired up via phonon (lattice vibration) mediation. These special electron pairs are termed Cooper pairs.[13]

Isotopic Effect:[14-15] The T_c of superconductors changes as the samples are enriched with a particular isotope. This isotopic mass effect is due to the change in lattice vibrational energy, i.e. phonon frequency, which is essential for the formation of Cooper pairs.

2. The importance of superconductors[16]

Superconductivity is a very useful property. In addition to the use in the Superconducting Super Collider, scientists have suggested many other ingenious applications such as high field inductors (generators, energy storage, levitated trains,...), low power electronics (SQUID magnetometers, computer chips,...), and magnetic shields. These applications can be categorized into three areas: applications based on the zero resistance, applications based on the Meissner effect, and applications based on the quantum mechanical properties. A few examples of these applications are given here.

2.1. Perfect conductance

Because there is no energy lost through resistivity effects, superconductors could become an economical means of electrical transmission. They would also be viable in high power applications since they are potentially very efficient and require no heat dissipation. In the absence of current quenching, these applications include: electric generation, magnetohydrodynamics; magnetic energy storage (superconducting ring); power distribution networks; superconducting motors, electromagnetic thrust propulsion; magnets for energy research and NMR/MRI; magnets for levitated trains (MagLev); magnets used in separators for minerals and other particulates; and interconnections for integrated circuits.

2.2. Meissner effect

Although the Meissner effect is the defining property of a superconductor, few applications can be developed based on this phenomenon. The most significant applications are frictionless mechanical bearings, and magnetically shielded containers and sheets.

2.3. Quantum electronic behavior

Many applications can be found using Josephson junctions. Most of these applications are in the areas of electronics, basic science, and medicine. They are: superconductive transistors based on Josephson junction switching (switches 100 times faster than the semiconductor transistor employed in the 80486 chip! and consumes 1000 times less energy); picosecond chips such as the PSP-1000 (Picosecond Signal Processor) from HYPRES, Inc., of Elmsford, NY; and SQUID magnetometer (SQUID, Superconducting Quantum Interference Device, comprised of two Josephson junctions coupled together in a ring) for weak magnetic field detection. This equipment is used in geological surveys (sensitive up to 6 miles underground), in monitoring biomedical magnetism, and in other scientific research such as probing novel superconductors in heterogeneous samples.

3. The importance of the newly discovered materials

Until recently, materials could only be made superconducting at very low temperature (the highest T_c achieved prior to 1986 was with Niobium / Germanium: 23.3° K).[17-18] These materials are mostly metallic and intermetallic alloys, with the exception of a very few organic ($T_c < 3°K$) and ceramic ($T_c < 14°K$) superconductors. However, these organic and ceramic compounds were not only very rare but also were of little use due to their low

T_c, and low superconducting current density. In the 13 years period 1973-1986, most work had concentrated on increasing T_c by synthesizing new metallic and intermetallic alloys. The results were rather discouraging. Two discoveries prior to 1975 with a different class of compounds have proven to be very significant to subsequent research in the field of high T_c superconductivity. The first one was the discovery of the metallic oxide superconductor ($SrTiO_3$) in 1966.[19] The second one was the discovery of a perovskite superconducting metallic oxide with mixed valency ($BaPb_{1-x}Bi_xO_3$) in 1975.[20] These materials and the unsuccessful effort of seeking a better superconducting alloy had triggered the group at IBM Zurich to investigate the nickel oxide system and later the copper oxide system that eventually led in 1986 to the remarkable discovery[6] of a new family of ceramic oxide superconductors. This resulted in an explosion of research in the field of copper oxide superconductors. The result was that a copper oxide ceramic could have zero electrical resistance and that there was a possibility of making this family of materials superconducting at even higher temperature. The T_c record has since been broken with materials of the same elements (52^o K at 1 GPa),[21] with the Y-Ba-Cu-O system (>77^o K at atmospheric pressure)[22], the Bi-Sr-Ca-Cu-O system (up to 110^o K),[23-24] and most recently the Tl-Ba-Ca-Cu-O system (up to 125^o K).[25-26] The discovery made by Bednorz and Mullers and the subsequent work on these high T_c superconductors has gained worldwide attention that resulted in major ongoing research efforts in two aspects: novel high critical temperature (T_c) materials, and novel mechanism(s) of superconductivity.

3.1. Research for better superconductors

The main goals of superconductor research are an increase T_c, inexpensive compositions, and reduced cost of fabrication. As discussed earlier, superconductors that were known prior to 1986 only lost their electrical resistance at very low temperatures. This was achieved by cooling the materials with liquid helium. It has been impractical to design non-laboratory applications because the required use of liquid helium is very costly. As a result, superconductors were of limited use, although they were of considerable technological importance. These materials are also difficult to fabricate. It is worth noting that superconductors are not even practical in many laboratories and universities because many institutions do not have the resources to investigate or utilize these materials in most applications. With the discovery of this new class of materials, superconductors can operate at temperatures at or above 77 K, which allows the use of a much cheaper cryogen. They are also composed of more abundant elements and easy to fabricate. Utilization cost has been dramatically reduced. More applications can now become a reality. As a result, almost any institution can do research on these materials. However, using liquid nitrogen is still hazardous and cumbersome. Scientists have worked hard to make new cuprate materials that can superconduct at ambient temperature, a goal that has still not been realized.

3.2. Research for better theoretical models

An unprecedented world-wide effort in superconductivity research has taken place over the past four years (1986-1990). An enormous amount of experimental data as well as theoretical speculation has contributed to the understanding of these copper oxide-type materials that exhibit superconductivity above the boiling point of liquid nitrogen. The BCS theory appears to be obsolete in explaining the situation. It does not explain why phonon coupling (Cooper pairs) exist at such a high temperature; it does not explain why this new class of materials does not follow the isotopic effect predicted; it does not explain why they have higher critical current densities than predicted. The mechanism of high T_c superconductivity is currently being sought. Superconducting electron transport models via exciton, plasmon, magnon, and many more mechanisms were introduced. There have been many different theories developed, yet none has been fully supported.[27] Experiments to confirm these theories have been performed. Some have shed new light on the understanding of these materials and reshaped theoretical models to a more realistic representation.[28] When more experimental data become available, the best suited theory will become apparent. Higher T_c materials may then be synthesized and better applications of these materials may then be realized.

4. The chemistry of the copper oxide superconductors

High Temperature superconductivity has generated an overwhelming research effort in the past few years. Due to their easy preparation, a large number of copper oxide based compositions have been investigated. Most of them have been somewhat heterogeneous in nature since their purity depended on the method of synthesis. As discussed earlier, there is still little theoretical understanding about these materials. What is certain is that the critical temperatures of these materials are strongly dependent on their oxygen content. For example, it has been reported[29-32] that as the oxygen content decreased, $YBa_2Cu_3O_{6.5+x}$ changed from a superconductor with a T_c of 90°K to that with a lesser T_c, and finally, an insulator. These copper oxide superconductors have more oxygen than necessary to balance the collective cation charges in their respected formula, assuming Cu^{2+}, RE^{3+}, and AE^{2+} (RE= Rare Earth elements, Y, Bi, or Tl; AE=alkaline Earth elements). These extra oxygen atoms have been referred to as excess oxygen or oxygen defects. To explain this anomaly, it has been suggested[33-34] that Cu occurs in mixed oxidation states of 2+ and 3+, implying that oxygen occurs at a fixed oxidation state of 2-. In $LaCuO_3$, with uniform trivalent copper and no ground state electronic degeneration, the material is a conductor. It was thought that a mixed oxidation of Cu^{2+}/Cu^{3+} or Cu^{3+}/Cu^{4+} would play the key role in the exhibition of superconductivity.[6] With reference to $LaSrCuO_4$, an insulator where all coppers are trivalent, and to the ceramic superconductor $La_{2-x}Sr_xCuO_{4-y}$, Mullers[6] believed that a mixed Cu^{2+}/Cu^{3+} valence state was crucial for the occurrence of delocalization in the framework leading to semimetallic, metallic or superconducting properties. There is much X-ray valence band data that support this suggestion.[35-37] Thus, there is a widespread belief that the copper 3d-3d interaction is the important factor for superconductivity in the newly discovered materials.[6] Although Cu is widely considered as the site of oxidation, electronic band structure calculations[38-40] indicated that the valence band in these ceramic superconductors had considerable oxygen character. Furthermore, there is evidence of deviation from the 2- oxidation state in oxygen core electron spectra.[41-44] Electron-Energy-Loss-Spectroscopy (EELS) data revealed no significant deviation from Cu^{2+} in these compounds, including the n-doped superconductors; but there is considerable O^- character.[45-46] Much effort has been devoted to the theoretical and experimental study of these materials related to their structure and valency. Wherever possible, the simple designation "hole" or $[Cu\text{-}O]^+$ is used to represent the terms Cu^{3+}, O^-, or oxygen defect, which are yet to be determined.

4.1. Structure

X-ray diffraction measurements[47-48] indicate that these compounds have imperfect perovskite structures. All of them are characterized by having a planar copper-oxygen framework (Figure 2). This framework is often termed the copper sheet. These CuO_2 planar structures are sandwiched in between the remaining cations. These layers are known to be responsible for the superconductivity.[27] There are two unusual features in these compounds[49]: their ability to combine the perovskite structure AMO_3

and the rock salt structure AO forming intergrowth $(AMO_3)_m(AO)_n$, where A and B represent divalent and trivalent cations, respectively, and the property of copper(II) or copper(III) ions to be four- (square planar) and even five-coordinate in some crystal structures, that favor the sheet formation. The number m denotes the perovskite slabs or copper-oxygen layers. The number n determines rock salt type slabs that lie at the boundary of the perovskite units. For example, the family of m=1 oxides includes the famous $La_{2-x}Sr_xCuO_{4-y}$ compound discovered by Bednorz and Muller (n=1), and the family of m=3 contains the compound $Tl_2Ba_2Ca_2Cu_3O_{10}$ (n=3) with the present record T_c=125 K .

4.2. Valency

There was a necessity to determine the oxidation state of each component in the new superconductors in order to understand their material characteristics and develop theoretical superconductive models. The techniques most often employed for such determinations were solid state X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Spectroscopy (XAS), and X-ray Emission Spectroscopy (XES) analysis. However, there were strong controversies in XAS, XES, and XPS as to whether Copper existed in the 1+, 2+ or 3+ oxidation states.[33-37,41-46] Many groups supported the picture of copper mixed valences, while others argued that the hole could be a ligand hole (i.e., oxygen can be in the 1- state). The picture was further clouded when Fowler[50] pointed out that, regardless of the method of preparation, these surface analytical data represented both the superconducting features and the interfering contaminants associated with its surface. In addition, it was extremely hard to avoid measuring surface contamination without altering the information pertaining to the superconducting features. High energy transmission measurements seemed more appropriate. In a transmission mode EELS experiment, Nucker[45] found the O 1s binding energy line position which often is interpreted as characteristic of a ligand hole, or possible peroxide species, in $La_{2-x}Sr_xCuO_{4-y}$ and $YBa_2Cu_3O_{6.5+x}$. Further investigation showed similar results in $Bi_2Sr_2CaCu_2O_8$, $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$, and more importantly, the n-doped $Nd_{2-x}Ce_xCuO_{4-y}$.[46] There were criticisms and counter claims in other experiments. At this point, Schrieffer[51] concluded that there was no reliable information available on the true nature of the copper-oxygen charge distribution.

4.3 Wet chemical analysis

The most studied material was $YBa_2Cu_3O_{6.5+x}$. This is due to its stability, higher excess oxygen content than the originally discovered $La_{2-x}Sr_xCuO_{4-y}$ compound, simple fabrication, and easy testing for superconductivity (employing liquid nitrogen). Excess oxygen in this structure would either oxidize copper to Cu^{3+} or O^{2-} to O^-. If O^- existed, it would be hydrolyzed to hydrogen peroxide, when exposed to an acidic solution. Likewise, if copper existed as Cu^{3+}, upon dissolution, it would oxidize water to molecular oxygen:

$$4Cu^{3+} + 2H_2O \text{--->} 4Cu^{2+} + 4H^+ + O_2$$

Most of the subsequent analytical reactions are designed to occur during dissolution to capture the important species. If the medium was ^{18}O enriched water, the evolved oxygen would be heavy oxygen. It was shown in an isotopic oxygen experiment[52] that there was no Cu^{3+}, which led to the interpretation of O^- as a possible oxidation state for oxygen. However, using potassium permanganate as the titrant, Harris[53] has observed no peroxide in these compounds but rather a species which consumed H_2O_2 (possibly: Cu^{3+}). It was reported that the occasional formation of MnO_2 as a stable intermediate product was a sizable source of error.[53] Tang[54] had showed that there was no Cu^+ and that the excess oxygen evolved stoichiometrically as a gas upon dissolution. Applelman,[55] by measuring the evolved gas upon dissolution in HCl, observed no solvent oxidation due to these holes, which implied the absence of Cu^{3+}. From the results of these experiments, it was unclear whether the excess oxygen oxidized Cu^{2+} or O^{2-} in the solid matrix, and that whether this oxidized species behaved like Cu^{3+} or O^- upon dissolution. There is not yet experimental evidence to discern among these possibilities.

5. The goal of this research

To synthesize higher Tc cuprate superconductors requires an in-depth knowledge of these materials. It is essential to understand what makes them superconducting (the mechanism for superconductivity), and how they behave (the physical and chemical properties). In order to understand the materials' properties and superconducting mechanism better, it is necessary to elucidate the basic chemistry of these compounds, the oxidation states of individual ionic species in the lattice. It is known that a ceramic oxide, calcium aluminate, contains excess oxygen in its solid state structure. This calcium aluminate and the new copper oxide superconductors have remarkably similar behavior toward oxygen upon heating and cooling. Excess oxygen in calcium aluminate exists as peroxide. Because of the similarities of the two materials, it is speculated that excess oxygen in this oxide would, perhaps, also exist as O^- or peroxide. In this work, the possibility is further investigated that besides its usual oxidation state of 2-, oxygen in $YBa_2Cu_3O_{6.5+x}$ superconducting oxide also occurs in the 1- oxidation state. Driven by the controversies in solid state measurements, this investigation was designed to measure the behavior of excess charge sites of the $YBa_2Cu_3O_{6.5+x}$ superconductor upon dissolution by redox titration and colorimetry, and compare them to the results of known chemical species (BaO_2, $NaCuO_2$, etc.). It is assumed that similar chemical properties upon dissolution would mean a similar electronic arrangement in the former solid states.

EXPERIMENTAL

1. Chemicals and reagents

All dilutions were made with deionized water. Concentrated sulfuric acid was obtained from VWR Scientific. Concentrated hydrochloric acid was purchased from Chempure. Hydrogen peroxide (30% solution), barium(II) peroxide, copper(I) chloride, and copper(II) oxide were supplied by Spectrum Company. Iron(II) chloride was from Bryant Chemicals. Iron(III) chloride (hydrated) and cerium(IV) diammonium nitrate (hydrated) were purchased from Malinkrodt. Cerium(IV) sulfate (hydrated) was obtained from Fisher. Ortho-phenanthroline monohydrate was supplied by Aldrich. Sodium oxalate was from J.T. Baker. All these chemicals were obtained in the highest purity available. The $YBa_2Cu_3O_{6.5+x}$ superconductor was obtained from the IBM Almaden Research Center (batches III-206 and IV-116).

2. Apparatus

All standard solution preparations were done in 1000 mL volumetric flasks, except the sodium oxalate standard, which was prepared in a 100 mL volumetric flask. Transfer of the sodium oxalate standard was made with a 10 mL volumetric pipet. Transfers of other standard solutions were done with

25 mL (0.1 mL increment) Teflon stopcock burrets. Transfers of the remaining solutions were done by pipeting with volumetric pipets. Samples were analyzed in 50 mL beakers. Absorption measurements were made on a Hewlett-Packard 8451A Diode Array Spectrophotometer.

3. Standard solutions

A $2x10^{-2}$ M Ce^{4+} (in H_2SO_4) standard was prepared by adding 12g of $Ce(SO_4)_2$.n H_2O to 300 mL of 6 M H_2SO_4 solution in an Erlenmeyer flask. This solution was constantly stirred until all particles were dissolved. After all the solid was dissolved, 1 M H_2SO_4 was added until the appropriate concentration was achieved. The solution was filtered through a medium fritted glass funnel. This Ce^{4+} solution was standardized daily against 10 mL aliquots of freshly prepared $8x10^{-3}$ N $Na_2C_2O_4$ in 0.1 M H_2SO_4. The Fe^{2+} and H_2O_2 standard solutions were prepared by adding the appropriate amount of $FeCl_2$ and H_2O_2 to 3 M HCl and 0.5 M HCl solutions respectively. The Fe^{2+} solution was filtered through the medium fritted glass funnel for removal of possible undissolved particles. These two solutions were standardized against the Ce^{4+} standard by a procedure similar to the one used for analyzing the superconducting samples. A Ce^{4+} (in HCl) standard solution was made by dissolving $1x10^{-2}$ moles $Ce(NH_4)_2(NO_3)_6$.n H_2O in 500 mL of 3 M HCl solution. An additional amount of $Ce(NH_4)_2(NO_3)_6$.n H_2O was added as necessary to reach the desired concentration ($2x10^{-2}$ M). Due to its instability, this solution was standardized against the Fe^{2+} and Ce^{4+} standard solutions right before and after a sample analysis was made. To be consistent with the superconducting sample analysis (see later discussion), first the solution was converted to an ice slush by stirring in an external liquid nitrogen bath, stirred for 20 minutes, and then an excess amount of Fe^{2+} standard solution was added before back-titrating with the Ce^{4+} standard. If there was any difference, the average value of the standardization prior and after the sample analysis was employed in sample calculations. All standardization of Fe^{2+} and H_2O_2 solutions were done daily. Ferroin indicator (Fe(II)-ortho-phenanthroline complex) was prepared by dissolving $1x10^{-3}$ moles of $FeCl_2$ and $3x10^{-2}$ moles of ortho-phenanthroline.n H_2O in 500 mL of water and 2 mL of concentrated HCl.

4. Procedures

There were four distinct types of experiments performed in order to characterize the hole concentration and hole type. The first one involved a redox titration with ferrous solution to quantify the total hole concentration. The second test was a determination of hole reactivity toward hydrogen peroxide, which was crucial for the detection of the presence of Cu^{3+}. The third experiment was to determine the possible hydrogen peroxide formation upon dissolution by its reaction with ceric solution. The last part was to explore the reactivity of holes toward ferroin, a tris-ortho-phenanthroline iron(II) complex that does not react with peroxide species.

4.1. Hole quantization with Fe^{2+} solution

A known amount of ferrous standard was delivered to an HCl solution in a 50 mL beaker. This solution was made up with concentrated HCl until the desired acidity was reached. This aliquot was converted to an ice slush by continuously stirred with a glass rod or stirring bar while being cooled in an external liquid nitrogen bath. Then 0.1 g of $YBa_2Cu_3O_{6.5+x}$ was added and allowed to dissolve for 20 minutes while constantly being stirred. This solution was immediately titrated with the Ce^{4+} (in H_2SO_4) standard using the Ferroin indicator. To avoid possible interference by Cu^{1+} and Cu^{2+}, CuCl (0.02g) and CuO (0.03g) were tested with Fe^{2+} solution in a similar manner.

4.2. Hole characterization with H_2O_2 solution

To study the reaction of holes with hydrogen peroxide, a sample of H_2O_2 was placed in a 50 mL beaker and concentrated HCl was added to achieved the desired acid concentration. The aliquot was stirred and cooled to an ice slush with liquid nitrogen. Then 0.1g of the superconductor was added and stirred for 20 minutes as in the previous part. A stoichiometrically excess amount of Fe^{2+} with respect to the hydrogen peroxide content was added. The sample was back titrated with Ce^{4+} (in H_2SO_4) standard solution using ferroin indicator. To avoid interference due to copper catalytic oxidation of hydrogen peroxide, CuCl (0.02g) and CuO (0.03g) were analyzed in a similar manner for background subtraction. No significant interference was detected.

4.3. Hole characterization with Ce^{4+} solution

An additional test for the presence of peroxide was performed by cooling a known amount of Ce^{4+} (in HCl) standard with liquid nitrogen until becoming an ice slush. Then 0.1 g of $YBa_2Cu_3O_{6.5+x}$ was added and the mixture was stirred for 20 minutes until all oxide particles were dissolved. A stoichiometrically excess amount of Fe^{2+} standard (with respect to the quantity of Ce^{4+}) was immediately added to the solution. Then the solution was back-titrated with Ce^{4+} (in H_2SO_4) using Ferroin indicator.

4.4. Characterization with Ferous ortho-phenanthroline complex

To characterize the $YBa_2Cu_3O_{6.5+x}$ superconductor further, 5 mL of .04 N Fe^{2+} in 1 M HCl was added to 0.85 g of ortho-phenanthroline. The mixture was allowed to stand for 5 minutes for complete dissolution and complexation. Then 5 mL of 11 M HCl solution was added. The aliquot was stirred and cooled in liquid nitrogen until becoming an ice slush. A measured amount (between 0.025 g - 0.075g) of the $YBa_2Cu_3O_{6.5+x}$ superconducting material was added. The mixture was stirred for 20 minutes until all materials dissolved. Half (five mL) of the solution was removed for titration with Ceric standard (in H_2SO_4). The remaining part was appropriately diluted and the spectrophotometric absorption was measured at 510 nm. Peroxides from BaO2 powder, BaO_2 in HCl, and H_2O_2 were analyzed with Fe(o-phenanthroline)$_3^{2+}$ using similar procedures to serve as reference compounds for possible peroxide-ferroin interference. However, no significant interference was observed.

RESULTS AND DISCUSSION

1. Characterization of holes by Fe^{2+} solutions

Upon dissolution, $YBa_2Cu_3O_{6.5+x}$ superconductor oxidizes ferrous ion to ferric ion. This reaction can be employed to quantify the total number of holes present in the solid material. It was found that the reaction was affected by the temperature, the ferrous ion concentration, and the acid concentration.

1.1. Quantitative determination of total holes

The technique employed here was similar to that reported by Shafer.[56] This technique had been used for the analysis of holes in $La_{2-x}Sr_xCuO_{4-y}$. In this case, the $La_{2-x}Sr_xCuO_{4-y}$ superconducting sample was dissolved in H_2SO_4 solution and then was titrated with a standard ferrous solution. Whether holes exist as Cu^{3+}, O^- radical, or peroxide they oxidize ferrous ions to ferric ions. If the sample size is known, hole concentration per unit weight can be calculated. Since, in the solid state, each excess oxygen atom oxidizes two cupric ions or creates a peroxide unit, the number of moles of excess oxygen per mole of sample can be deduced. As a result, quantification of holes was feasible. In this experiment, however, the $YBa_2Cu_3O_{6.5+x}$ superconductor was dissolved in hydrochloric acid to avoid the interference of $BaSO_4$ precipitation. $YBa_2Cu_3O_{6.5+x}$ superconductor was highly reactive in HCl. It underwent an instantaneous redox reaction, and released molecular oxygen. Once the dissolution was completed, no hole was left to participate in the Fe^{2+}-hole titration. As a result, it was necessary to dissolve $YBa_2Cu_3O_{6.5+x}$ in an Fe^{2+}/HCl slush. From here on, the term pre-adding specifies the condition of an analyte present prior to the solution cooling process and the addition of the superconducting sample. Fe^{2+} was pre-added to maximize the reaction between Fe^{2+} and the existing holes in the lattice. Holes would not react completely with Fe^{2+} ions if they were not pre-added and pre-cooled. After the reaction was completed, the remaining Fe^{2+} was titrated with the Ce^{4+} (in H_2SO_4) standard. The results of $YBa_2Cu_3O_{6.5+x}$ reacting with the Fe^{2+} standard are shown in Table 2. The quantity of Fe^{2+} reacted was calculated (column 2), and normalized to a 1.000g sample size for statistical purposes (column 3).

Holes might exist in two forms: Cu^{3+} or O^-. A more convenient way is to consider these holes in the resonating form $[Cu\text{-}O]^+$. In this form, copper and oxygen alternatively have the oxidation states of 3+ and 1-, respectively. Regardless of whatever form the holes take, they can be reduced by Fe^{2+} according to the following half reactions:

$$Fe^{2+} + Cu^{3+} \longrightarrow Fe^{3+} + Cu^{2+}$$

$$Fe^{2+} + {}^{1}/_{2}\ O_2^{2-} \longrightarrow Fe^{3+} + O^{2-}$$

$$Fe^{2+} + [Cu\text{-}O]^+ \longrightarrow Fe^{3+} + Cu^{2+} + 0^{2-}$$

Consequently, Fe^{2+} is capable of determining the total quantity of holes present, regardless of the nature of their existence. Assuming that $YBa_2Cu_3O_{6.5}$ is the charge-neutral molecule, additional oxygen either oxidizes

O^{2-} to O^{-}, oxidizes copper to their +3 state, or creates a species such as $[Cu\text{-}O]^{+}$. Thus, each oxygen atom produces a peroxide unit, 2 Cu^{3+}, or 2 $[Cu\text{-}O]^{+}$. The number of moles of atoms of extra oxygen is equivalent to twice the amount of Fe^{2+} reacting with $YBa_2Cu_3O_{6.5+x}$. Since x is a dependent variable of the synthetic conditions, the exact formula weight of the $YBa_2Cu_3O_{6.5+x}$ superconductor is unknown. However, x in this compound can be determined by solving the following two equations simultaneously:

$$\text{FW} = \text{AtWt Ytrium} + 2\ \text{AtWt Barium} + 3\ \text{AtWt Copper} + (6.5+x)\ \text{AtWt Oxygen} \quad (1)$$

and:

$$X = \text{FW}/2\ .\ (\text{moles of } Fe^{+2} \text{ reacted per gram of } Y_1Ba_2Cu_3O_{6.5+x}) \quad (2)$$

where: FW is the formula eight of $YBa_2Cu_3O_{6.5+x}$, and AtWt indicates atomic weight.

Solving these equations yields the value of the excess oxygen in this compound. These results are shown in Column 4 of Table 2. The average value of x was 0.48 ± 0.03. The complete formula is $Y_1Ba_2Cu_3O_{6.98\pm0.03}$, which is in good agreement with the data reported for this batch by iodometric titration.[57] The inherent uncertainty of the technique, which was employed in this experiment, was small. Errors due to solution transfers, sample weighing, end point detection, etc. contributed less than 1% in the standardization process. However, the precision of the results was quite low. This might be due to the instability of holes upon dissolution. As previously noted, no hole was reduced by Fe^{2+} if the $YBa_2Cu_3O_{6.5+x}$ compound was dissolved prior to Fe^{2+} addition. It is reasonable to assume that Cu^{2+} and O^{2-} in the $YBa_2Cu_3O_{6.5+x}$ superconductor would not react with Fe^{2+}. In fact, the results were negative for the test of possible interference by analyzing CuO directly. It has been reported[54] that there was no Cu^+ in $YBa_2Cu_3O_{6.5+x}$ superconducting materials. Yet, as a precaution, CuCl, in which copper is in 1+ oxidation state, and an Fe^{2+} solution blank, which indicates the level of air oxidation, were also analyzed by the same procedures. There was no significant consumption of Fe^{2+} ions. There were even more ferrous ions (i.e., more Ce^{4+} titrant consumed) than expected in the CuCl analysis. This is explained by the oxidation process of cuprous by Ce^{4+}:

$$Cu^+ + Ce^{4+} \text{-->} Cu^{2+} + Ce^{3+}$$

Harris,[58] and later Nazzal,[59] employed iodometric titration techniques to quantify the total number of holes at room temperature. The reaction they based their methods on is:

$$\text{hole}_{(aq)} + 3\,I^- \text{--->} CuI + O^{2-} + I_2$$

Hole dissolution produces all or some of the following species: holes or $[Cu\text{-}O]^+_{(aq)}$, $Cu^{3+}_{(aq)}$, $O_2^{2-}{}_{(aq)}$, O_2, and Cl_2 (oxidation of Cl^- by Cu^{3+}). The first three can be considered as aqueous holes. The latter are by-products of the following reactions:

- If holes are a relatively strong oxidant:

$$\text{hole}_{(aq)} + Cl^- \text{--->} Cu^{2+} + O^{2-} + {}^1/_2 Cl_2$$

- If holes are trivalent copper:

$$4\ \text{hole}_{(aq)} + 2\,H_2O \dashrightarrow 4\,Cu^{2+} + 4\,O^{2-} + 4\,H^{+} + 0_2$$

- If holes undergo autoreduction:

$$\text{hole}_{(aq)} + \text{hole}_{(aq)} \dashrightarrow 2\,Cu^{2+} + O^{2-} + {}^{1}/_{2}O_2$$

Iodide ions reduce not only holes, but also chlorine[60] and oxygen[61-62] to yield I_2. Thus the amount of iodine formation is an indication of the number of holes present in the sample over any reasonable temperature range. However, in the experiment performed here, hole autoreduction was so fast that it was impossible to obtain a complete Fe^{2+}-hole reaction at room temperature. This disagreement with the iodometric procedures may be due to the fact that I^- (oxidation potential= -0.53 V) is a stronger reducing agent than Fe^{2+} (oxidation potential= -0.77 V). Indeed, air oxidation of Ferrous ions was a rather slow process with respect to the time scale employed in this experiment.

1.2. Behavior of holes with temperature, Fe^{2+} ions and HCl concentrations

It was found that more of the holes in $YBa_2Cu_3O_{6.5+x}$ superconductor reacted with Fe^{2+} at low temperature than at room temperature and there was no hole reaction if Fe^{2+} was not pre-added. This means that holes were very unstable upon dissolution in HCl. This does not happen in the case of BaO_2, with oxygen in the 1- oxidation state, or in the calcium aluminate case as discussed later in section 2.1. Samples also reacted more readily when there was more Fe^{2+} present. However, at each HCl concentration, there was a threshold concentration of Fe^{2+} that results in the amount of Fe^{2+} reacted becoming constant. At the same concentration of Fe^{2+}, the amount of reacted material increased as HCl increased.

1.2.1. Dependence of hole reactivity on Fe^{2+} concentration

The $YBa_2Cu_3O_{6.5+x}$ superconductor samples were analyzed with the same procedures for the determination of total holes. However, the Fe^{2+} concentration was varied from 0.01N to 0.15N at two different acid concentrations. There were two sets of data taken (Figure 3). The first set was at 6 M HCl and the solution was pre-cooled to an ice slush as previously described. The remaining set was taken at 3 M HCl. Due to the complete crystallization of the liquid at low temperature, the solutions were chilled only to 0°C prior to adding superconductor. Both curves show a similar behavior of the holes toward Fe^{2+}. As the concentration of Fe^{2+} increases, there were more Fe^{2+} reduced holes. After certain threshold concentrations, the amount of materials reacted approached a constant value. This can be explained by the fact that as the Fe^{2+} concentration initially increased, it caused more collisions between holes and Fe^{2+}, thus increasing Fe^{2+}-hole reaction and diminishing the autoreduction of holes. After reaching a certain Fe^{2+} concentration value, most holes have reacted. Increasing the

Fe^{2+} concentration further no longer has any effect. The interference due to air oxidation of ferrous ions was insignificant. The oxidation reaction of Fe^{2+} by oxygen is:

$$2\,Fe^{2+} + {}^{1}/_{2}O_2 \longrightarrow 2\,Fe^{3+} + O^{2-}$$

This reaction was rather slow in this experimental time frame. For a blank, it was determined that there was no loss of Fe^{2+} due to air oxidation for a period 45 minutes - three times as long as that required for an analysis. Thus, it is possible to detect all the added Fe^{2+}. In this system, there are two competing reactions involving holes:

- Autoreduction:

$$hole_{(aq)} + hole_{(aq)} \longrightarrow 2\,Cu^{2+} + O^{2-} + {}^{1}/_{2}O_2$$

- Fe^{2+} reduction:

$$hole_{(aq)} + Fe^{2+} \longrightarrow Cu^{2+} + O^{2-} + Fe^{3+}$$

If the autoreduction of holes is very fast, Fe^{2+} would not be able to reduce the holes. All the Fe^{2+} added to the solution would be detected. On the other hand, if holes react very slowly with one another, then there would be a complete oxidation of Fe^{2+} (all holes oxidized Fe^{2+}) that is independent of Fe^{2+} concentration, providing there is stoichiometrically enough Fe^{2+} for the redox reaction. The data showed that if Fe^{2+} was pre-added, some would be oxidized (at least, at ambient temperature or below). It suggests that the autoreduction of holes is slightly slower than the Fe^{2+} -hole reaction. Dissolved holes are closer to one another (more concentrated) than to Fe^{2+}. This is especially true in the vicinity of the solid-liquid interface layer and the diffusion layer. More collisions occur between holes; therefore, all holes will undergo autoreduction if the hole-hole reaction is fast. Not all holes are self-destroyed. In fact, all holes react with Fe^{2+} at -24°C. Consequently, the hole-Fe^{2+} reaction seemed to be faster. The following plausible reaction sequence can be deduced:

$$\text{Hole}_{(solid)} \text{ ---> } \text{Hole}_{(aq)} \quad [1]$$

$$\text{Hole}_{(aq)} + \text{Hole}_{(aq)} \text{ ---> } 2\,Cu^{2+} + 0^{2-} + {}^{1}/_{2}O_2 \quad [2]$$

$$\text{Hole}_{(aq)} + Fe^{2+} \text{ ---> } Cu^{2+} + O^{2-} + Fe^{3+} \quad [3]$$

It is likely that reaction [2] is slow whereas reaction [3] is fast.

1.2.2. Dependence of hole reactivity on acid concentration

The procedures employed was similar to the one used in the determination of total hole concentration, but the acid concentration was varied from 1 to 10 M at a constant Fe^{2+} concentration of 0.02N. The results are plotted in Figure 4. At low acid concentration, little Fe^{2+} was oxidized by holes. As the acid concentration increased, more Fe^{2+} reacted. This behavior supports the reaction steps proposed. Under the given procedures, reactions

[2] & [3] are faster than could be detected. However, it is possible to indirectly control [2] & [3] by controlling the rate of reaction [1]. As little as 10 mL of 0.6 M HCl solution yielded a fast, complete dissolution and showed no trace of post precipitation for 0.1 g $YBa_2Cu_3O_{6.5+x}$ samples. Increasing the acid concentration (thus ionic strength) would not accelerate but rather hinder the process. This deceleration caused the instantaneous hole concentration to be smaller. It is presumed that reaction [2] (two holes involved) is kinetically one order higher in hole concentration than that of reaction [3] (only one hole involved). The slow dissolution facilitates the Fe^{2+} -$hole_{(aq)}$reaction (reaction [3]). For a fixed Fe^{2+} concentration, Fe^{2+} will be more likely to attack the holes at higher acid concentration. On an equivalent time scale, an increase in HCl concentration corresponds to an increase in the time allowed for the Fe^{2+} -$hole_{(aq)}$ reaction.

1.2.3. Dependence of hole reactivity on temperature

$YBa_2Cu_3O_{6.5+x}$ superconductor samples were analyzed with solutions of 0.02 N Fe^{2+} , 6 M HCl pre-cooled at different temperatures (-24°, 0°, and 24°C). As shown in Figure 5, at higher temperature, there is a lower probability for the Fe^{2+}-hole reaction. At a higher temperature, the rate of dissolution increased, which increased the instantaneous hole $_{(aq)}$ concentration. An increase in aqueous hole concentration accelerated the $hole_{(aq)}$-$hole_{(aq)}$ reaction, since it was more dependent on the $hole_{(aq)}$ concentration than Fe^{2+} -hole process as discussed earlier. The rate increase in the reaction [2] was more profound. Fewer holes remained for reaction [3]. Consequently, fewer holes were detected by Fe^{2+}. The results of hole reactivity presented a qualitative scheme of hole behavior in HCl solution. Under the given procedures, reactions [2] and [3] were too fast to be studied directly. Only the consequence (Fe^{2+} consumed) was measured and extrapolated to the activity during dissolution. New experimental design is necessary to determine the reaction rates involved.

2. Determination of the distribution of hole types

2.1. With H_2O_2

Table 3 shows the results of reacting H_2O_2 with the $YBa_2Cu_3O_{6.5+x}$ superconductor. As in the case of Fe^{2+} above, H_2O_2 was pre-added and pre-cooled to ensure maximum H_2O_2-hole reaction. The amount of H_2O_2 remaining was determined by adding a stoichiometric excess of Fe^{2+}, then titrating against the Ce^{4+} (in H_2SO_4). The quantity of holes reacting with H_2O_2 was determined from the equivalents of H_2O_2 reacted (column 2), and normalized to 1.000 g of reactant (column 3). The mole ratio of holes reacted with H_2O_2 to total holes present, which was determined by the Fe^{2+} solution mentioned in section 1.1, is shown in column 4.

The peroxy anion (i.e., O_2^{2-} or O^-) in a particular ceramic material, calcium aluminate ($Ca_{12}Al_{14}O_{33+x}$), which has a striking similarity to the high T_c superconducting ceramic oxide in terms of its behavior toward oxygen, has recently been studied.[60] Stoichiometrically excess oxygen in calcium aluminate ceramics ($Ca_{12}Al_{14}O_{33+x}$) was first reported by Imlach.[63] Brisi[64] observed that the excess oxygen content varied with changes in quenching rate, and with oxygen partial pressures. Lower quenching rates and higher oxygen partial pressure yielded higher excess oxygen. The highest oxygen content was obtained with samples heated and slowly cooled (-3°C/min) to room temperature in a stream of pure oxygen. Engler[29] studied the effect of quenching rate in the $(RE)_1(Ba)_2Cu_3O_x$ ceramic superconductors and observed a similar behavior. Gallagher[30] reported that x is 7.0 if prepared in oxygen, and is 6.9 if prepared in air. When the compound is prepared in a stream of argon or helium, $Ca_{12}Al_{14}O_{33+x}$ loses excess oxygen[64-65] and changes its structure.[66-68] This behavior has been thoroughly described by Tarascon[31] and Schuller[32] in ceramic superconductors. Calcium aluminate is a charge neutral species. The oxygen gained is chemisorbed. This can only happen if excess oxygen oxidizes calcium to Ca^{3+} and aluminum to Al^{4+}, or if O^{2-} in the ionic matrix forms monovalent oxygen. Excess oxygen in calcium aluminate ceramics can oxidize the cations as proposed in the ceramic superconductors. This only happens if calcium and aluminum ions overcome the enormous ionization potential barrier to form Ca^{3+} or Al^{4+}. The alternative is that excess oxygen oxidizes O^{2-} in the lattice to form monovalent oxygen. It is clear that the latter is more favorable than the former. Indeed, excess oxygen in calcium aluminate form monovalent oxygen, and upon dissolution in acid, form hydrogen peroxide. The amount of peroxide formation is equal to the excess oxygen content.[64] In the solid state, the ceramic superconductors behave in the same way that the calcium aluminate does with respect to oxygen. Therefore, it is proposed that monovalent oxygen also results from the absorption of excess oxygen in the

$YBa_2Cu_3O_{6.5+x}$ structure, and hydrogen peroxide will form when dissolving in acid. If all holes in the $YBa_2Cu_3O_{6.5+x}$ exist as Cu^{3+}(reduction potential= 1.8 V),[69-70] then the amount of H_2O_2 (oxidation potential= -0.68V) reacted is equal to the total number of holes determined by Fe^{2+}. If O^- coexists with Cu^{3+}, then less H_2O_2 would react. If all of the excess oxygen exist as O^-, then one would find an excess of H_2O_2 which is stoichiometrically equal to the number of holes determined previously. The correlation of % of holes existing as O^- or Cu^{3+} and the amount of H_2O_2 detected is illustrated in Figure 6. The vertical axis represents the ratio of H_2O_2 detected to the total number of holes determined by Fe^{2+}-hole reaction. The dotted lines are the contributions of the individual species (Cu^{3+} and O^-) that may exist in the holes. Cu^{3+} reacts with H_2O_2, resulting in a decrease in the ratio. If 100% of the holes exist as Cu^{3+}, the ratio is -1. In contrast, the existence of O^- would result in an increase in the amount of H_2O_2 detected. This O^- makes the ratio increase, approaching 1 as the % of holes existing as O^- approaches 100. This graph is best described by the following equation:

$$X = Y/0.02 + 50$$

where: $X = \%$ of O^- in holes,

and: $Y =$ that ratio of H_2O_2 detected to the total number of holes determined by Fe^{2+} -hole reaction.

In this experiment, the amount of H_2O_2 consumed per total number of holes was 0.018± 0.068, which indicates that there is no hole-H_2O_2 reaction detectable under these conditions. Curve fitting the H_2O_2 data to the plot results in (50.9 ± 7.3)% of O^-, implies that 50.0% of the holes may exist as O^- and the other 50% as Cu^{3+}. There is a large uncertainty in this result because holes are unstable in the HCl solution, as previously mentioned, and the detection limit has been reached. It should be pointed out that some degree of peroxide-hole interaction has been observed in the perchlorate system.[53]

2.2. With Ce^{4+} (HCl based)

Table 4 shows the result of the reaction between the Ce^{4+}(in HCl) standard and $YBa_2Cu_3O_{6.5+x}$. The residual Ce^{4+} was determined by adding a stoichiometrically excess amount of Fe^{2+} and then back titrating with the Ce^{4+} (in H_2SO_4) standard. The amount of Ce^{4+} (in HCl) standard reacted (column 2) is thus equal to the equivalents of Fe^{2+} subtracted from the equivalents of Ce^{4+} (in H_2SO_4) standard. In contrast to the H_2O_2 case, more Cu^{3+} means less Ce^{4+} reacted, and more O^- means more Ce^{4+} reacted, since:

$$Cu^{3+} + Ce^{4+} \text{ ---> No reaction}$$

$$O_2^{2-} + 2\ Ce^{4+} \text{ ---> } O_2 + 2\ Ce^{3+}$$

The reaction of $YBa_2Cu_3O_{6.5+x}$ with hydrogen peroxide indicated that 50% of the holes existed as O^- and the remainder as Cu^{3+}. The Ce^{4+} experiment performed here serves as a check for any error due to the nature of the technique. Ce^{4+} (in HCl) solution was used to keep the properties of dissolved holes consistent (no solvent effect) with the hole-H_2O_2 analysis above. If $YBa_2Cu_3O_{6.5+x}$ is dissolved in a H_2SO_4 matrix, there would be precipitation of $BaSO_4$. Because Ce^{4+} is quite unstable in hydrochloric acid, the solution was standardized right before and after an analysis. The result, no loss of Ce^{4+} within the detection limit, strongly supports the data found in the H_2O_2 case. No loss of Ce^{4+} also implies that, perhaps H_2O_2 or other peroxide species do not exist. However, quantification of the remaining Ce^{4+} is carried out by Fe^{2+} redox titration and is subject to Cu^{3+} interference. There is no significant evidence to alter the conclusion that holes exist as 50% Cu^{3+}/50% O^-. In addition, since the size of $Ce(Cl)_6^{2-}$ complex is large, a steric effect may have prevented the reaction. As discussed in Section 1, the rate of hole autoreduction was significant. Since Ce^{4+} in HCl and Cu^{3+} are both unstable, quantitative determination of Cu^{3+} was impossible.

2.3. Reaction with Fe^{2+} masked with ortho-phenanthroline

Ferrous ions complexed with ortho-phenanthroline will not react in HCl with any peroxy anions which might form during hole dissolution. This made it possible for the acidic $Fe(\text{ortho-phenanthroline})_3^{2+}$ (0.02 M in 6 M HCl) solution to be used in the analysis of the reactivity of holes in various amounts of $YBa_2Cu_3O_{6.5+x}$ superconductor. Another set of samples of the same weights were analyzed with unmasked Fe^{2+} and, after the reaction was completed, ortho-phenanthroline was added to form the complex. Both sets of samples were measured for absorbance at 510 nm, where the molar absorptivity is 11,100.[71] The results are plotted in Figure 7. There are two factors to take into account: varying the weight of superconducting materials (0.025g-->0.075g) to eliminate the Fe^{2+} and HCl concentration effect, and dissolving the phenanthroline in 0.04 M Fe^{2+} and 0.5 M HCl prior to adding the required amount of HCl to eliminate the pH effect.[72] Although ortho-phenanthroline complexes very slowly with ferrous ions at pH<-0.3, the product (ferroin) would be stable even at very high acidity. In this application, a buffer solution can not be used since it is designed to keep the matrix constant. Ferrous ortho-phenanthroline (ferroin) has been widely used as an indicator in redox titration for its stability, including titration of H_2O_2 by Ce^{4+} solution. This indicates that when masked with ortho-phenanthroline, Fe^{2+} is not attacked by O_2^{2-}. Shapiro[73]has taken advantage of this behavior to analyze Fe^{2+} in the present of organic peroxides. If $Fe(o\text{-phenanthroline})_3^{2+}$ (oxidation potential = -1.14 V)[72] does not react with holes, then the holes are peroxy anions. Otherwise, if $Fe(ortho\text{-phenanthroline})_3^{2+}$ reacts, then the holes might possibly be Cu^{3+}. Indeed, 50% of the holes reacted. This is in good agreement with the results in section 2.1 and section 2.2: 50% of the holes behave like O^-, 50% behave like Cu^{3+}. To demonstrate that these sample analyses reflected the true concentration of Fe^{2+} unreacted by holes, the colorimetric samples were checked by redox titration. The results of the spectrophotometric and titrimetric determinations are plotted in Figure 8. There is good agreement between the two procedures. There is one possible error; not all of the Fe^{2+} complexes with the 1,10-phenanthroline. However, the formation of the complex was maximized in the presence of an acid at a favorable concentration (0.3 M HCl). In addition, after the complex was prepared, it was analyzed spectrophotometrically and titrated with Ce^{4+}

standard. The results showed that the absorption of Fe(ortho-phenanthroline)$_3^{2+}$ followed Beer's law, and that all Fe^{2+} complexed with ortho-phenanthroline. Walden[72] reported that in very highly acidic solution, although inhibiting the formation of the complex, neither decomposition nor oxidation occurred. Thus, it is reasonable to assume that Fe(ortho-phenanthroline)$_3^{2+}$ reactant will remain throughout the course of the $YBa_2Cu_3O_{6.5+x}$ superconductor analysis. In addition, the ratio of Fe(ortho-phenanthroline)$_3^{2+}$ complex reacted with holes is constant, and independent of the total amount of holes present (sample weight).

Figure 9 illustrates the behavior of holes and other peroxy species toward Fe(ortho-phenanthroline)$_3^{2+}$. To compare the behavior of holes toward other known substances, and to ensure that H_2O_2 would not react with Fe(ortho-phenanthroline)$_3^{2+}$ at the concentration investigated, the $YBa_2Cu_3O_{6.5+x}$ superconductor samples were replaced by 0.015 g of BaO_2 powder (assuming 80% are peroxide and the remainder are either oxide or hydroxide) which has at least 50% excess equivalents of peroxy than that of holes in the largest sample weight of $YBa_2Cu_3O_{6.5+x}$ superconductor employed. There was some evidence of Fe(ortho-phenanthroline)$_3^{2+}$ reacting, but at a very small amount (estimated at <10%) compared to that of an equivalent amount of holes in $YBa_2Cu_3O_{6.5+x}$ superconductor. Predissolved BaO_2 in 1 M HCl showed little sign of attacking Fe(ortho-phenanthroline)$_3^{2+}$. An amount of 0.020g of BaO_2 that was already dissolved in HCl solution was less reactive than 0.015 g of BaO_2 powder. Another test was performed with 1 mL of a 30% H_2O_2 solution. The result showed that Fe(ortho-phenanthroline)$_3^{2+}$ did not react. However, if Fe^{2+} was not masked with phenanthroline, it was completely oxidized by O_2^{2-} generated by the above species. This result suggests that at least 50% of the dissolved $YBa_2Cu_3O_{6.5+x}$ holes were stronger oxidants than peroxide.

3. Interpretation of Results:

The results can be interpreted as follows:

3.1. Holes do not exist as Cu^{3+} or O^-

At first, it seemed reasonable to argue that $[Cu\text{-}O]^+$ does not exist in this compound, otherwise O^- (i.e., $[Cu^{2+}\text{-}O^-]+$) and Cu^{3+} (i.e., $[Cu^{3+}\text{-}O^{2-}]^+$) would alternatively exist and when the surrounding matrix was either Ce^{4+} or H_2O_2, $[Cu\text{-}O]^+$ would react completely. Only 50% of holes react with $Fe(phen)_3{}^{2+}$ indicating that 50% are Cu^{3+} and the remaining half are O^-. This suggestion (Cu^{3+} and O^- coexist at a certain ratio) is also claimed in a recent publication.[61] However, a closer review of the situation may give a different perspective. Cu^{3+} in $NaCuO_4$ oxidizes water to yield molecular oxygen and protons:[62]

$$4Cu^{3+} + 2\,H_2O \longrightarrow 4\,Cu^{2+} + 4\,H^+ + O_2 \quad [4]$$

In HCl solution, a possible reaction is:

$$2\,Cu^{3+} + 2\,Cl^- \longrightarrow 2\,Cu^{2+} + Cl_2 \quad [5]$$

Reaction [4] would imply that any H_2O_2 present would also be preferentially oxidized. Moreover, H_2O_2 reacts with Cu^{3+} at about the same rate as bromide ion[63], which is chemically similar to I^-. As mentioned above, iodide reduction has been considered as a satisfactory method[71-72] for analyzing the hole concentration. Appelman[55] even observed (although another group claimed the reverse)[58] the reaction of Br^- with holes. If holes are Cu^{3+}, they would all react with H_2O_2. This did not happen in this experiment. In an isotopic experiment,[52] there was no sign of holes oxidizing water during its dissolution in HCl. Dissolved heavy oxygen $YBa_2Cu_3O_{6.5+x}$ superconductor in ordinary HCl aqueous solution yielded $^{18}0_2$ gas, and normal oxygen $YBa_2Cu_3O_{6.5+x}$ superconductor in ^{18}O HCl aqueous solution yielded $^{16}O_2$. This confirmed that reaction [4] did not occur, or more specifically, that formally charged Cu^{3+} was not present. Moreover, analysis of the evolved gases emitted during the dissolution process by a GC technique[48] yielded no chlorine. Tang[54] has used a NaOH trap to eliminate CO_2 (thus HCl or Cl_2 as well) and measured only 0_2 evolution from the $YBa_2Cu_3O_{6.5+x}$ superconductor dissolved in HCl. He found a direct relation between the hole concentration and the volume of gas produced. This means no chloride is oxidized, or again, no Cu^{3+} is present. It can be argued that only half of the holes were Cu^{3+}. If so, the following reactions should occur in the Ce^{4+} experiment:

- Peroxy type holes:

$$Ce^{4+} + hole_{(aq)} \dashrightarrow Ce^{3+} + Cu^{2+} + 1/2\, O_2$$

- Cu^{3+} type holes:

Ce^{4+} + $hole_{(aq)}$ ---> NR

Cl^- + $hole_{(aq)}$ ---> $^1/_2\ Cl_2$ + Cu^{2+} + 0^{2-}

$^1/_2\ H_2O$ + $hole_{(aq)}$ ---> $^1/_4\ O_2$ + H^+ + Cu^{2+} + O^{2-}

As a consequence, if a fraction of holes are O^-, there should be some Ce^{4+} consumed. The results showed no sign of Ce^{4+} consumed in this experiment indicating that neither Cu^{3+} nor O^- is present.

3.2. Possible hole existence as $[Cu\text{-}O]^+$

As previously discussed, formal Cu^{3+} does not exist. Unfortunately, the data that led to the interpretation of a 50:50 O^-/Cu^{3+} distribution corresponds to the situation where holes are present as $[Cu^{(2+y)}\text{-}O^{(2-y)}]^+$. It is hard to distinguish whether the species would simply not react and allow autoreduction to occur, or whether all the oxidation can be accounted for by the reduction of the counter species. However, it is hard to imagine why the Cu^{3+} would not oxidize its neighboring O^- in an analogous reaction to that of Ce^{4+} and O_2^{2-}. The plausible alternative is the existence of holes as $[Cu\text{-}O]^+$. This species can be considered as: $[Cu^{(2+y)}\text{-}O^{3(2-y)}]^+$, where y denotes the weighed average of charges. Thus, this species would bear both the peroxy and the trivalent copper characteristic. Consequently, although BaO_2 or H_2O_2 would not react with the Fe(o-phenanthroline)$_3^{2+}$ (oxidation potential is 1.14 V), holes would still be able to do so. Because of the size of the complex (steric effect), hole-hole interaction is more efficient than hole-Fe(o-phenanthroline)$_3^{2+}$; therefore, fewer holes (50%) were detected. In the case of Ce^{4+} reaction (reduction potential is 1.4 V) holes have considerably more trivalent copper character than ordinary peroxide, and thus would not be oxidized by Ce^{4+} . The steric effect is also another factor. H_2O_2 is quite a strong oxidant. It will only be oxidized[75-78] (oxidation potential is 0.68 V) by other species having a very high reduction potential such as Ce^{4+} , MnO_4^-, or Cu^{3+}. Although holes have some Cu^{3+} behavior, it is not sufficient to make them a distinctively stronger oxidant than their counterpart O_2^{2-} . In addition H_2O_2 is a charge neutral species. Because it is difficult to induce the polarization required for the oxidation, the hole-H_2O_2 reaction does not take place. It is also worth mentioning that most reactions involving holes described thus far involved Fenton reagents, proceeding through a free radical intermediate,[79-81] and might undertake different reaction paths than that being proposed. However, an electrochemical experiment indicated that the existence of a diffusing intermediate is unlikely.[82]

3.3. Electronic arrangement of the $YBa_2Cu_3O_{6.5+x}$ superconductor in its solid state

It has been shown that the three representative compounds, $NaCuO_2$, $YBa_2Cu_3O_{6.5+x}$, and BaO_2 , exhibit different chemical reactivity upon dissolution. This may mean there are differences in the corresponding solids. The following discussions are based on one assumption; the chemical behavior upon dissolution is an indication of the former electronic arrangement in the solid state.

3.3.1. Absence of Cu^{3+} in the solid structure

The possibility of $[Cu\text{-}O]^{p+}$ existence during dissolution has been examined. The remaining problem is whether charges are distributed (by fluctuation or resonating) among the coppers in the structure or are localized at some places. $NaCuO_2$ is a well established Cu^{3+} compound. It has been reported that Cu in this compound can and will reduce water upon dissolution. If Cu^{3+} is present in the $YBa_2Cu_3O_{6.5+x}$, then it would reduce the water and the isotope of oxygen released would be that of water, not the sample. There is no such evidence.[52] It is clear that Cu^{3+} does not exist in the solid $YBa_2Cu_3O_{6.5+x}$ structure as in $NaCuO_2$.

3.3.2. Absence of O^- in the solid structure

If holes are O^- then samples should behave like BaO_2, a well- established peroxide solid. This would mean: **1)** there would be no reaction with $Fe(o\text{-phenanthroline})_3^{2+}$, and **2)** these peroxide holes would not perish upon dissolution even at room temperature (like BaO_2 and calcium aluminate). However, the holes were very unstable and did react with Fe(o-phenanthroline)$_3^{2+}$. Employing the same principles stated above, the solid state electronic arrangement would not be O^-.

3.3.3. Presence of $[Cu\text{-}O]^+$ with charge delocalization

If Cu^{3+} and O^- coexisted at a certain ratio, 50/50 as previously shown, it is hard to imagine why they would not undergo autoreduction unless they can not overcome the energy barrier, and thus must exist as charge localized species. It is worth mentioning that in the Fe^{2+} analysis above, holes can only be detected during and not after the dissolution. Furthermore, no intermediate species upon hole dissolution was found.[82] This means the reaction of this material occurs at the interface or in the solid state. If the ionic solid matrix stabilizes these ions, then at the solid liquid interface during dissolution, holes should react with the surrounding liquid. Since Cu^{3+} and O^- can not reduce the counter charged species in the solid due to matrix stabilization, they reduce the Ce^{4+} (only O^-) or water of Cl^- in the solution. The results in this experiment showed no Ce^{4+}-hole interaction (no O^- at any ratio). There was no evidence of liberated oxygen bearing the characteristic isotope of water,[52] and no chloride oxidation.[54,56] This may mean no Cu^{3+} at any ratio. Thus it is concluded that in their solid state, holes exist as $[Cu\text{-}O]^+$ rather than charge localized species.

CONCLUSION

The concentration and types of holes in $YBa_2Cu_3O_{6.5+x}$ (IBM batches III-206 and IV-116) in solution by redox titration with various reagents have been investigated. From the results of the hole-Fe^{2+} reaction, it was found that x=0.48±.03 yielding the formula $YBa_2Cu_3O_{6.98\pm.03}$. Holes are highly reactive. They undergo 100% autoreduction at room temperature. The reactivity of the holes is affected by the Fe^{2+} concentration, the acid concentration, and the reaction temperature. The results of hole-H_2O_2 and hole-Ce^{4+} were negative, implying that there might be coexistence of Cu^{3+}/O^-. However, 50% of the holes reacted with Fe(ortho-phenanthroline)$_3^{2+}$. From the results of hole-H_2O_2, hole-Ce^{4+}, and hole-Fe(ortho-phenanthroline)$_3^{2+}$ reactions, it is concluded that formal Cu^{3+} and O^- do not exist but rather a species with charge delocalization such as $[Cu^{(3-y)+}\text{-}O^{(2-y)-}]^+$. The results also confirmed the oxygen ligand hole characteristic previously reported. The results of this experiment would serve as an explanation for the discrepancies among core level spectra observed. Different experimental conditions would induce $[Cu^{(3-y)+}\text{-}O^{(2-y)-}]^+$ to different levels of cuprate or O^- character. This would result in either Cu^{3+} enriched (up to 100%) or O^- ligand band characteristic spectra. These results would partly explain why a copper-oxygen sandwich layer (copper sheets) is a necessity for superconductivity in this class of compounds. These results would also serve as a model for band structure electronic calculations.

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Table 1

High Tc Copper Oxide Superconductors

Chemical Formula	**T_c (°K)**	**Date of discovery**
$La_{2-x}M^{2+}_{x}CuO_{4-x}$ (M=Ca, Sr, Ba)	25-40	Apr. 1986
$Ba_2Ln^{3+}Cu_3O_{6.5+x}$ (Ln= Lanthanide)	90-95	Feb. 1987
$(Tl,Bi)_m(Ba,Sr)_2Ca_{1-n}Cu_nO_{m+2n+2}$	20-120	Feb. 1988
(m=1,2 n=1,2,3)	same	Mar. 1988
$Pb_2Sr_2Ln^{3+}_{0.5}Ca_{0.5}Cu_3O_8$	70	Nov. 1988
Ln-Tl-Ca-Sr-Cu-O	90	Dec. 1988
$Ln^{3+}_{2-x}Ce^{4+}CuO_{4-y}$ (Ln= Pr,Nd, Sm)	15-25*	Jan. 1989

(* n-type superconductor)

(After reference 49.)

Table 2

Determination of X in $YBa_2Cu_3O_{6.5+x}$ by Fe^{2+}

Sample Weight (g)	Fe^{2+} Reacted	Normalized to 1g sample	Calculated X value
.1065	1.533×10^{-3} M	1.439×10^{-2} M	.479
.1091	1.355×10^{-3} M	1.242×10^{-2} M	.414
.1103	1.476×10^{-3} M	1.338×10^{-2} M	.446
.1062	1.738×10^{-3} M	1.637×10^{-2} M	.505
.0984	1.534×10^{-3} M	1.559×10^{-2} M	.502
.1032	1.453×10^{-3} M	1.408×10^{-2} M	.468
	Averages:	**1.437×10^{-2} M**	**.475 ± .03**

Table 3

Determination of X in $YBa_2Cu_3O_{6.5+x}$ by H_2O_2

Weight of Sample (g)	H_2O_2 Reacted	Normalized to 1g sample	Mole Ratio H_2O_2/Fe^{2+}
.1005	1.231×10^{-5} M	1.225×10^{-4} M	.085
.1016	-0.950×10^{-5} M	$-.0940 \times 10^{-4}$ M	-.065
.1040	-1.273×10^{-5} M	-1.224×10^{-4} M	-.085
.1017	0.000×10^{-5} M	0.000×10^{-4} M	.000
.0987	1.167×10^{-5} M	1.180×10^{-4} M	.082
1.017	1.485×10^{-5} M	1.460×10^{-4} M	.102
.0988	0.102×10^{-5} M	0.107×10^{-4} M	.007
		Average:	**.018 ± .068**

Table 4

Determination of X in $YBa_2Cu_3O_{6.5+x}$ by Ce^{4+}

Weight of Sample (g)	Ce^{4+} Reacted	Ce^{4+} Normalized to 1g Sample	Mole Ratio Ce^{4+}/Fe^{2+}
0.1016	5.694×10^{-6} M	5.604×10^{-5} M	.037
.0997	2.001×10^{-5} M	2.007×10^{-5} M	.134
.1028	-1.823×10^{-6} M	-1.773×10^{-6} M	-.118
		Average:	0.018 ± .078

FIGURE CAPTIONS

Figure 1. The electrical resistance with respect to temperature of Mercury observed by Onnes. (after reference 9).

Figure 2. The solid state structures of the new copper oxide superconductors. The CuO_2 sheets are highlighted (after reference 49).

Figure 3. Quantity of holes in 0.1 g samples reduced by Fe^{2+} as a function of Fe^{2+} concentration in HCl solution. The % of holes reacted is plotted againts the Fe^{2+} concentration (moles/liter). **a)** at -24°C in 6 M HCl, **b)** is at 0°C in 3 M HCl.

Figure 4. Illustration of the effect of HCl concentration on hole-Fe^{2+} interaction. The % of holes reacted is plotted agains the HCl concentration. The reaction was carried out with a 0.1 g sample in 0.02 M. Fe^{2+} at -24°C.

Figure 5. Quantity of holes reduced at different temperatures. The data were taken with a 0.1 g sample in 0.02 M Fe^{2+}, 6 M HC1 solution. The % of holes reacted is plotted agains the temperature.

Figure 6. Hole-fraction reacted with H_2O_2 (the ratio of the quantity of holes reacted with H_2O_2 to the total number of holes reacted with Fe^{2+}) in relation to percentage of Cu3+. **a)** Contribution of O^- species, which causes an increase of H_2O_2. **b)** Contribution of Cu^{3+} species, which causes a decrease in H_2O_2. **c)** The sum of the two contributions which directly relates to the % of Cu^{3+} or O^- present.

Figure 7. Hole interaction with Fe^{2+} and $Fe(phen)_3^{2+}$ plotted against the sample weight. **a)** The number of moles of Fe^{2+} reacted. **b)** The number of moles of $Fe(phen)_3^{2+}$ reacted. **c)** The ratio of slope in a) over that in b).

Figure 8. Analysis of Fe^{2+}. **a)** By titration. **b)** Spectrophotometry.

Figure 9. Absorbance measurements of $Fe(phen)_3^{2+}$ reacted with different peroxy species. **a)** Reaction with 0.075 g $YBa_2Cu_3O_{6.5+x}$ powder. **b)** Reaction with 0.015 g BaO_2 powder. **c)** Reaction with 0.02 g BaO_2 predissolved in 1 M HCl. **d)** Reaction with 1ml H_2O_2 (30%). Hole equivalents in a) are less than 75% with respect to O_2^{2-} equivalents in b), c), and d).

Figure 1

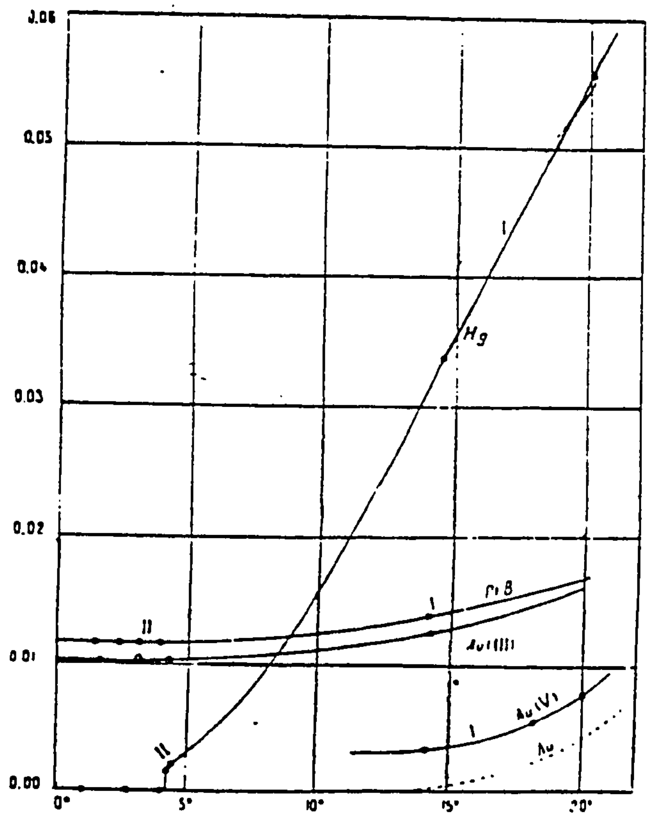
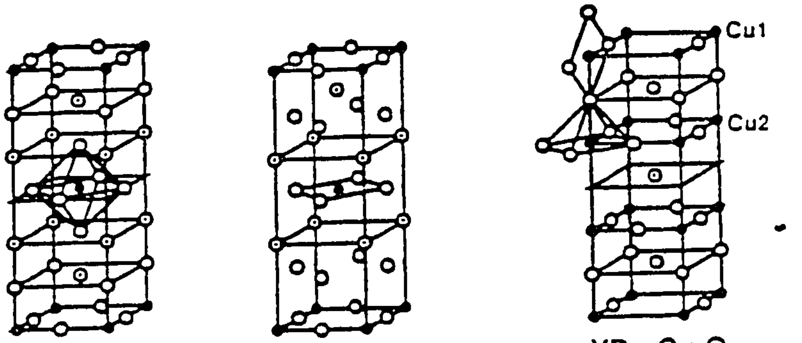

0.06
0.05
0.04
0.03
0.02
0.01
0.00
0°
5°
10°
15°
20°
I
Hg
Pt B
I
II
Au (III)
Au (V)
I
Au
II

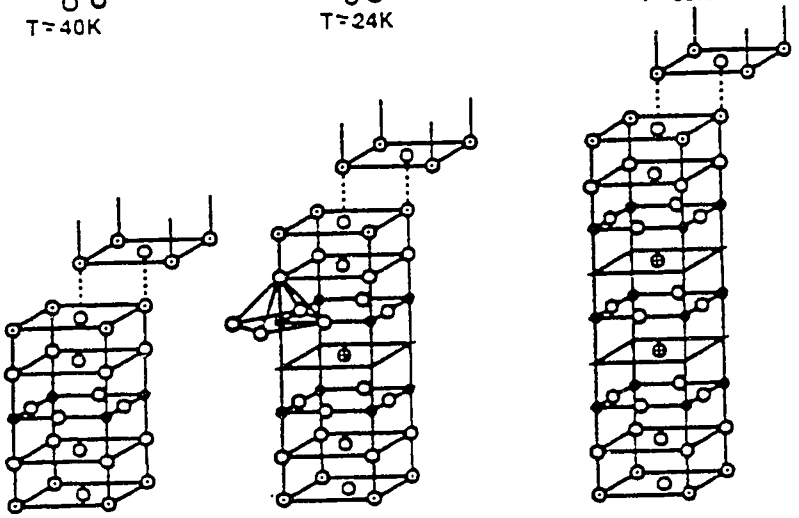
Figure 2



La$_2$CuO$_4$ (T)
La, Sr ⊙
Cu ●
O ○
T≈40K

Nd$_2$CuO$_4$ (T')
Nd, Ce ⊙
Cu ●
O ○
T≈24K

YBa$_2$Cu$_3$O$_7$
Y ⊙ Cu ●
Ba ○ O ○
T≈90K



Bi$_2$Sr$_2$Cu$_1$O$_{6+y}$
c≈24.6 Å
T$_c$~10K
Bi ⊙ Ca ⊕
Sr ○ Cu ●
O ○

Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+y}$
c≈30.7 Å
T$_c$≈85K
Bi ⊙ Ca ⊕
Sr ○ Cu ●
O ○

Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+y}$
c~37.1 Å
T$_c$≈110K
Bi ⊙ Ca ⊕
Sr ○ Cu ●
O ○

Figure 3

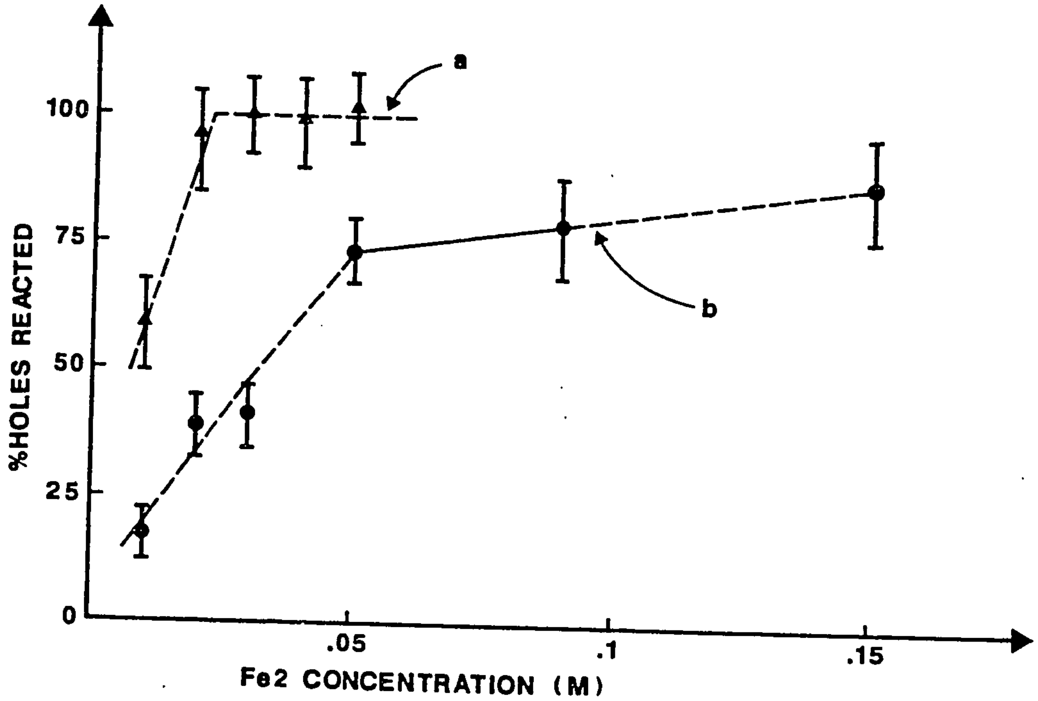


Figure 4

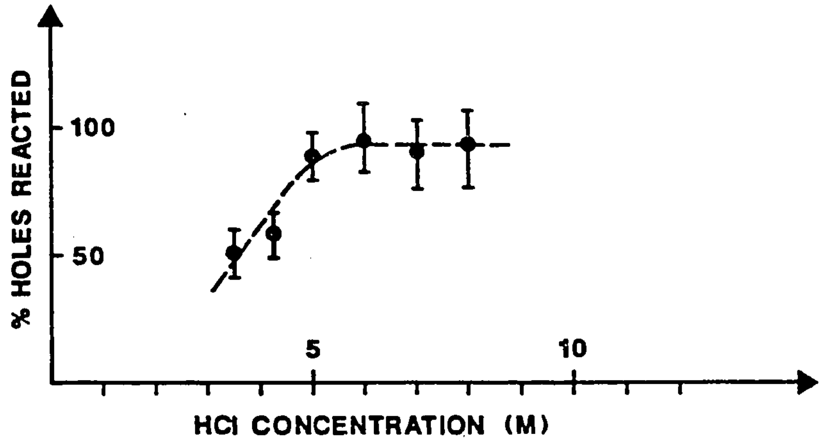


Figure 5

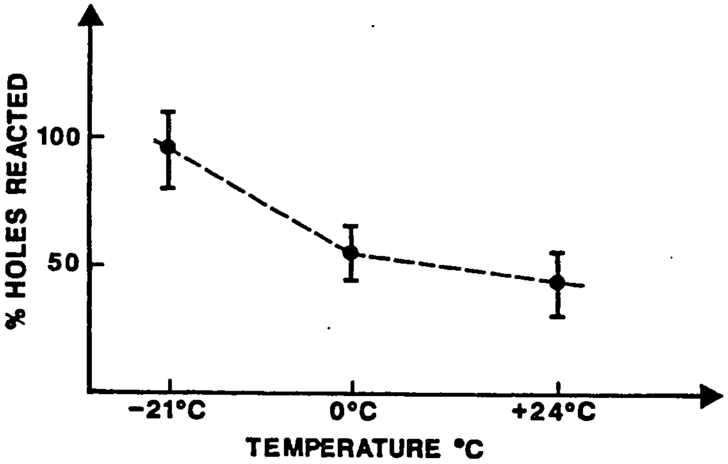
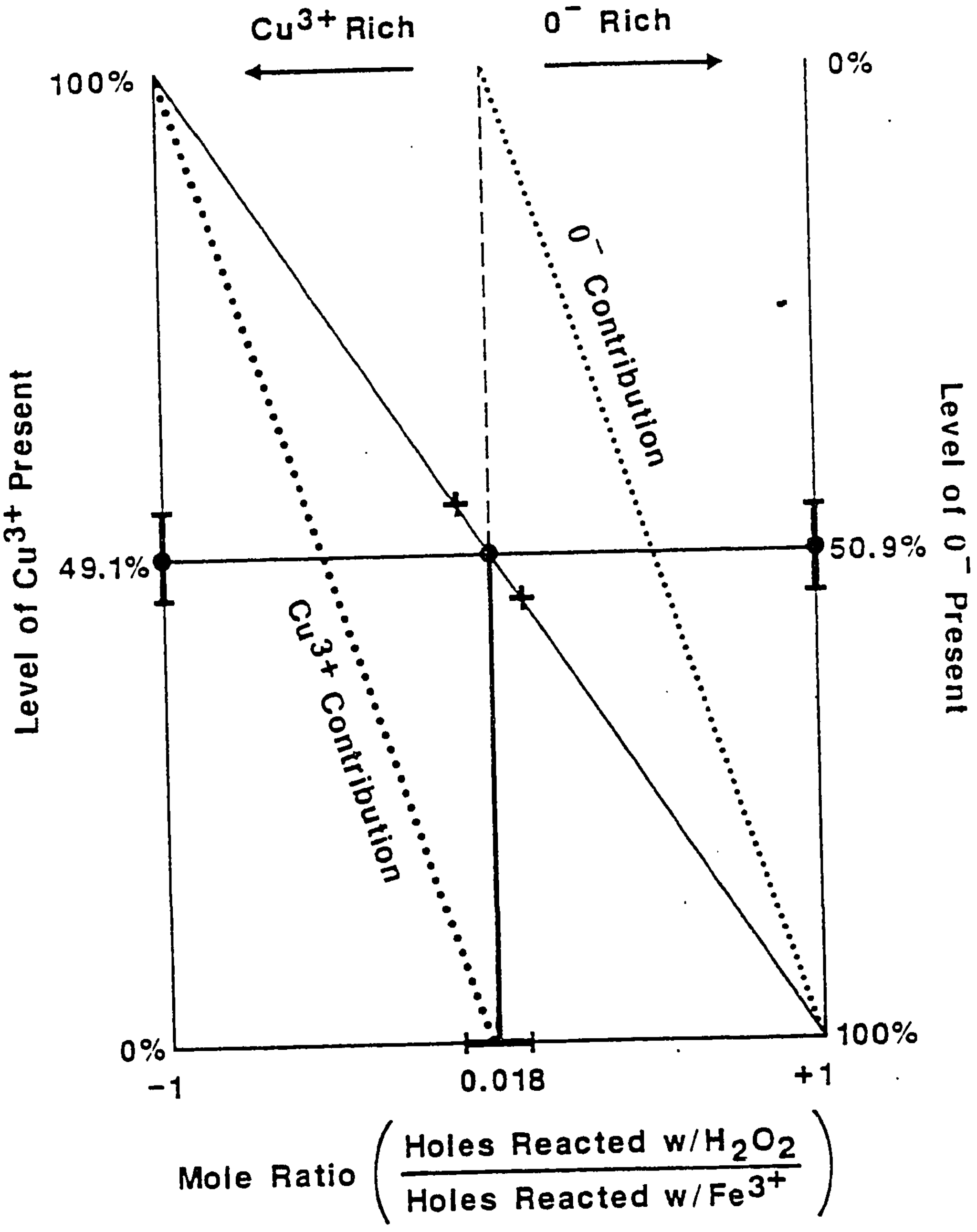


Figure 6



Cu^{3+} Rich
O^- Rich
100%
0%
O^- Contribution
Cu^{3+} Contribution
Level of Cu^{3+} Present
Level of O^- Present
49.1%
50.9%
0%
100%
-1
0.018
+1
Mole Ratio $\left(\frac{\text{Holes Reacted w/}H_2O_2}{\text{Holes Reacted w/}Fe^{3+}}\right)$

Figure 7

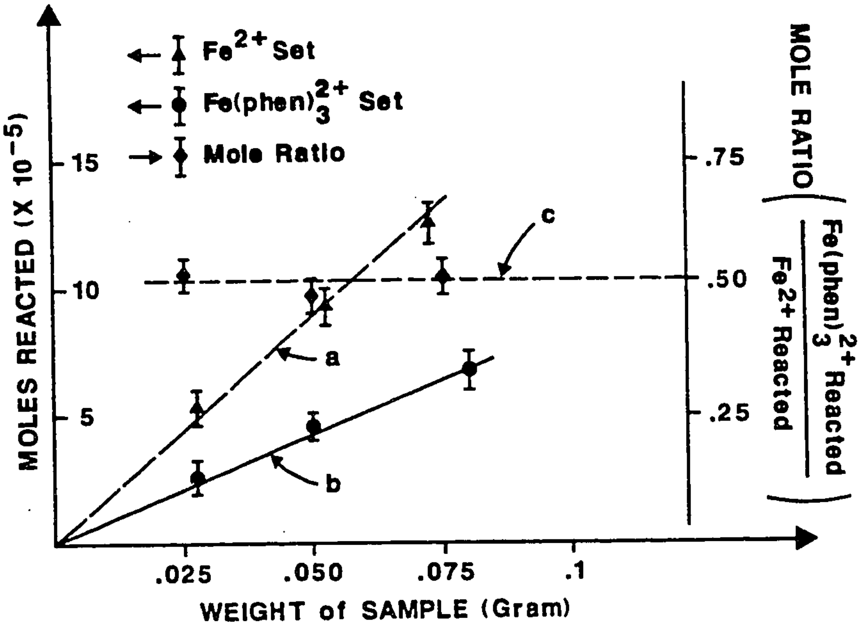

Fe^{2+} Set
Fe(phen)$_3^{2+}$ Set
Mole Ratio
MOLES REACTED (X 10^{-5})
15
10
5
.025
.050
.075
.1
WEIGHT of SAMPLE (Gram)
a
b
c
.75
.50
.25
MOLE RATIO $\left(\frac{\text{Fe(phen)}_3^{2+}\text{ Reacted}}{\text{Fe}^{2+}\text{ Reacted}}\right)$

Figure 8

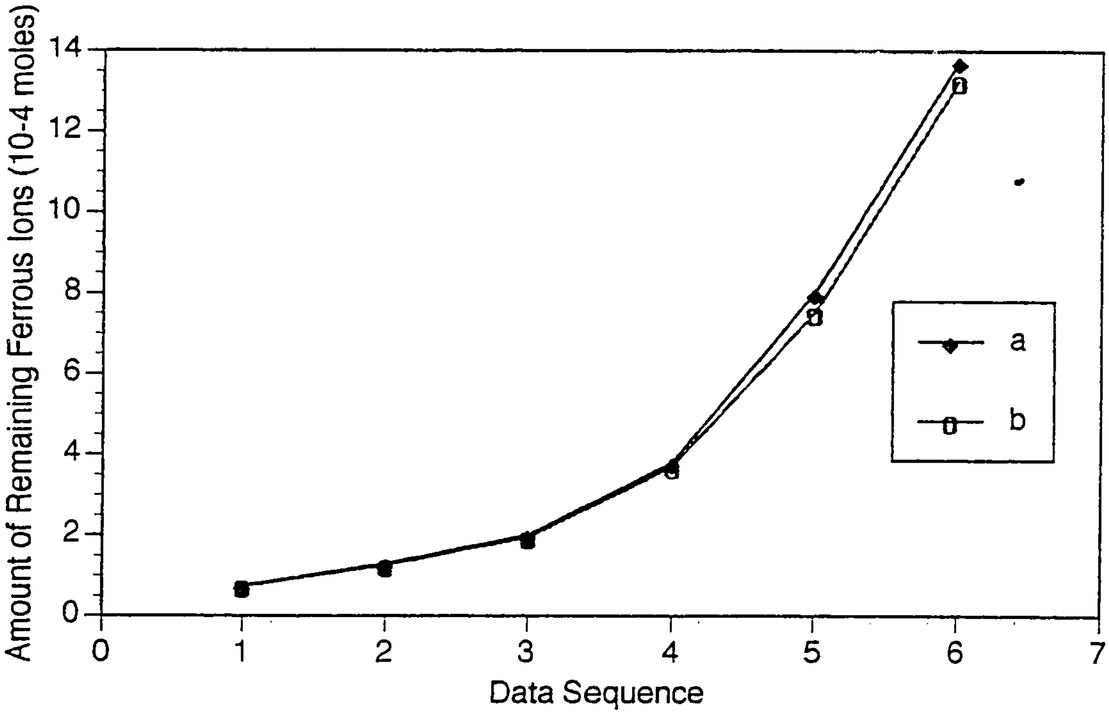
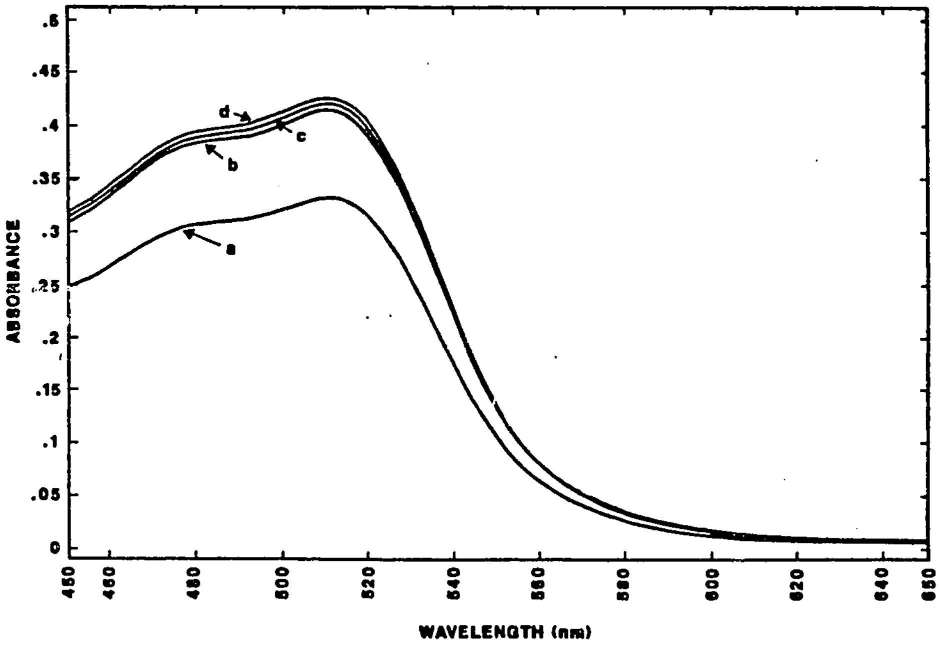

Amount of Remaining Ferrous Ions (10-4 moles)
14
12
10
8
6
4
2
0
0
1
2
3
4
5
6
7
Data Sequence
a
b

Figure 9


.5
.45
.4
.35
.3
.25
.2
.15
.1
.05
0
ABSORBANCE
450
460
480
500
520
540
560
580
600
620
640
650
WAVELENGTH (nm)
a
b
c
d