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PREFACE

The discovery in 1986 of high temperature superconductivity has produced a flood of experimental and theoretical publications, approximately 10,000 of them. This book maps out some of the main currents in an ocean of papers. We concentrate on the experimentally determined physical properties of these materials, and compare these properties with the predictions of theoretical models.

It was not easy to choose the topics for this book, which is necessarily limited in size. Chapters which would have been desirable include nuclear magnetic and quadrupole resonance, magnetic ordering, microstructure, electron tunneling, photoemission, and thermoelectric properties in the mixed state. We expect this book to be the first in a series of volumes to be published by World Scientific on the physical properties of high temperature superconductors. Later volumes will incorporate some of the missing subjects, as well as further developments in some of the topics which are covered here.

The authors of this book have made a significant sacrifice, taking time from their own research during a period of very great activity. They have done a job which is extremely difficult because of the deluge of preprints and articles. There is no way the authors could be aware of all the worthy manuscripts which have been written, and certainly it has been impossible for them to include references to all the literature in the field. Indeed, only by leaving out a great deal could they give each chapter a form which can be readily grasped. We ask you, the reader, to be understanding of these problems if you discover that some of your own work has gone unmentioned.

Donald M. Ginsberg
Urbana, Illinois
Nov. 1, 1988

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INTRODUCTION, HISTORY, AND OVERVIEW OF HIGH TEMPERATURE SUPERCONDUCTIVITY

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In this introductory chapter we relate the historical background of high temperature superconductivity and indicate the main new phenomena which have been observed and some of the most important fundamental questions raised by them. The later chapters of this book describe some of these phenomena and questions in more detail, and give more references.

The history of high temperature superconductivity is briefly reviewed in Section I. The crystal structures are described in Section II. In Sections III and IV, we call attention to related compounds and background references, respectively. Section V presents some fundamental experimental results, and an attempt is made to determine whether the high temperature superconductors are fundamentally different from the classic superconductors (sometimes called the conventional superconductors). Section VI is a discussion of three of the most unusual properties of the high temperature superconductors: high superconducting transition temperature T_c, short coherence lengths, and large anisotropy. In Section VII, we consider some important fundamental questions to be investigated and list some of the experimental methods that may help answer those questions. Finally, Section VIII contains a summary, along with a few words of caution on the need for good sample quality and thorough sample characterization.

I. A BRIEF HISTORY OF THE FIELD

Materials have recently been discovered that exhibit superconductivity up to much higher temperatures than anyone had dared to hope. Since 1911, when Kamerlingh Onnes discovered superconductivity in mercury at 4.2K, the highest observed values of T_c gradually moved upward, thanks to the work of people such as B. T. Matthias, J. K. Hulm, J. E. Kunzler, and T. H. Geballe.[1,2] Finally, in 1973, J. R. Gavaler observed that sputtered films of Nb_3Ge began to become superconducting at 22.3K,[3] and this was soon pushed up to 23.2K by L. R. Testardi et al. by altering the sputtering conditions slightly.[4] In spite of great efforts to increase this limit further, it stood as the record until 1986. In that year, J. G. Bednorz and K. A. Müller[5] observed that a lanthanum barium copper oxide began its superconducting transition as it was cooled below 35K. For this discovery, which opened the way for all of the subsequent work on high temperature superconductors, Bednorz and Müller received the Nobel Prize in Physics in 1987.[6]

The work of Bednorz and Müller was at first greeted with some skepticism. People were aware that observations on other compounds of possible superconductivity at elevated temperatures had not been fruitful. For example, large diamagnetic anomalies had been reported[7] for CuCl at temperatures as high as 250K; this excited much interest, although the investigators who discovered the effect felt that a claim of superconductivity would have been "speculative". In fact, perfect diamagnetism and zero resistance were never obtained in CuCl, so its superconductivity has never been decisively proven. Another source of skepticism concerning the significance of Bednorz and Müller's data was the failure of the electrical resistance of their La-Ba-Cu-O compound to reach zero until the temperature had been reduced to approximately 11K.

Their results were, nevertheless, confirmed late in 1986 at the University of Tokyo[8] and at the University of Houston.[9] Early in 1987, groups at the University of Tokyo,[10] Bell Communications Research (Bellcore)[11] and AT&T Bell Laboratories[12] found that substitution of Sr for Ba in the La-Ba-Cu-O compound raises T_c to approximately 40K. Subsequent efforts to raise T_c, carried out mainly in China, Japan, and the United States, were successful, culminating in the announcement by M.-K. Wu and his group at the University of Alabama at Huntsville and C. W. Chu at the University of Houston,[13] of the first material capable of becoming superconducting in liquid nitrogen; it turned out to be $YBa_2Cu_3O_{7-\delta}$, with T_c a few degrees above 90K. The discovery was soon verified at Bellcore.[14]

The exact value of T_c depends on the method of heat treatment and oxidation. It should be noted that some people report the "onset temperature", where the resistance begins to fall steeply, but others report the temperature where the resistance becomes immeasurably small. Previously, people had usually reported $T_{1/2}$, where the resistance fell to half of its value at the onset temperature. The values given here refer to the onset temperature, although it is not always possible to determine this parameter precisely. In well made samples, it does not differ very much from $T_{1/2}$.

Following the discovery of these extraordinarily high superconducting transition temperatures, two families of compounds were discovered with even higher values of T_c. First came the announcement, by H. Maeda et al.[15] at the Tsukuba Laboratories in Japan, of superconductivity in a Bi-Sr-Ca-Cu-O compound with an onset at 120K in the resistance transition and at 110K in the transition toward perfect diamagnetism[16] which is also characteristic of superconductors. This was soon followed by a similar announcement by A. M. Hermann and Z. Z. Sheng at the University of Arkansas of a Tl-Ba-Ca-Cu-O compound with an onset temperature near 140K in the resistive transition and of 118K in the diamagnetic transition.[17,18]

II. STRUCTURE

While the La, Bi, and Tl compounds contain planes of Cu and O atoms, the Y compounds[19,20] have both planes and chains of Cu and O. (See Figure 1.) A great deal of work has focussed on the roles of these planes and chains in the yttrium compounds. It is now known that the planes play the major role in generating superconductivity, while the chains act as electron reservoirs which can be filled or emptied either by changing the oxygen stoichiometry or by other types of doping.[21-25] If the number of oxygen atoms per formula unit is reduced to 6.5 or 6.7 (the exact value is in question), the yttrium compound's T_c falls to 55 or 60K.[26-28] There is a tendency for the oxygen atom vacancies to occupy a single chain, and the $YBa_2Cu_3O_{7-\delta}$ compounds with $0 < \delta < 1$ tend to have ordered arrays of completely oxygen-depleted chains.[28-31] (When $\delta = 1$, there are no chains.)

It is possible to obtain a series of Bi or Tl compounds with varying stoichiometry, reflecting the possibility of inserting a varying number of Cu-O planes into the crystal structure's unit cell. For each new Cu-O plane, an adjacent Ca-O plane is also introduced. The general

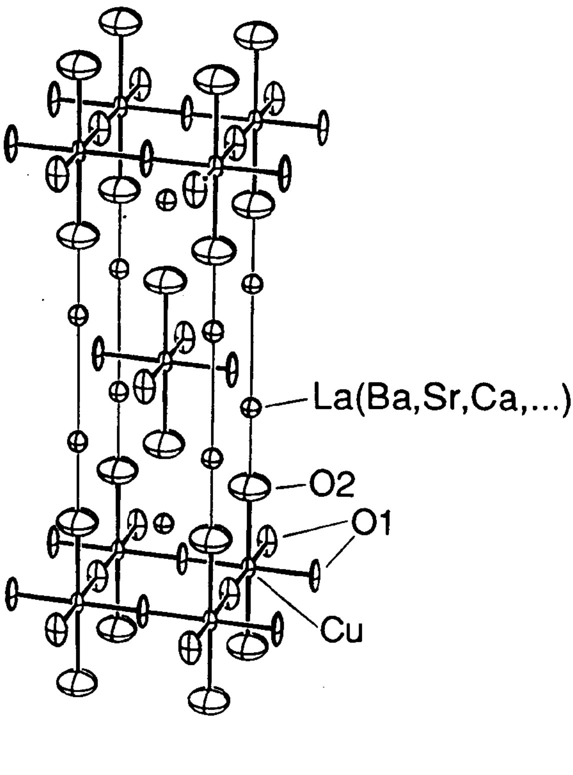


Figure 1a. The structure of $La_{2-x}A_xCuO_4$, where A = Ba, Sr, Ca,... Figure supplied by J. D. Jorgensen.

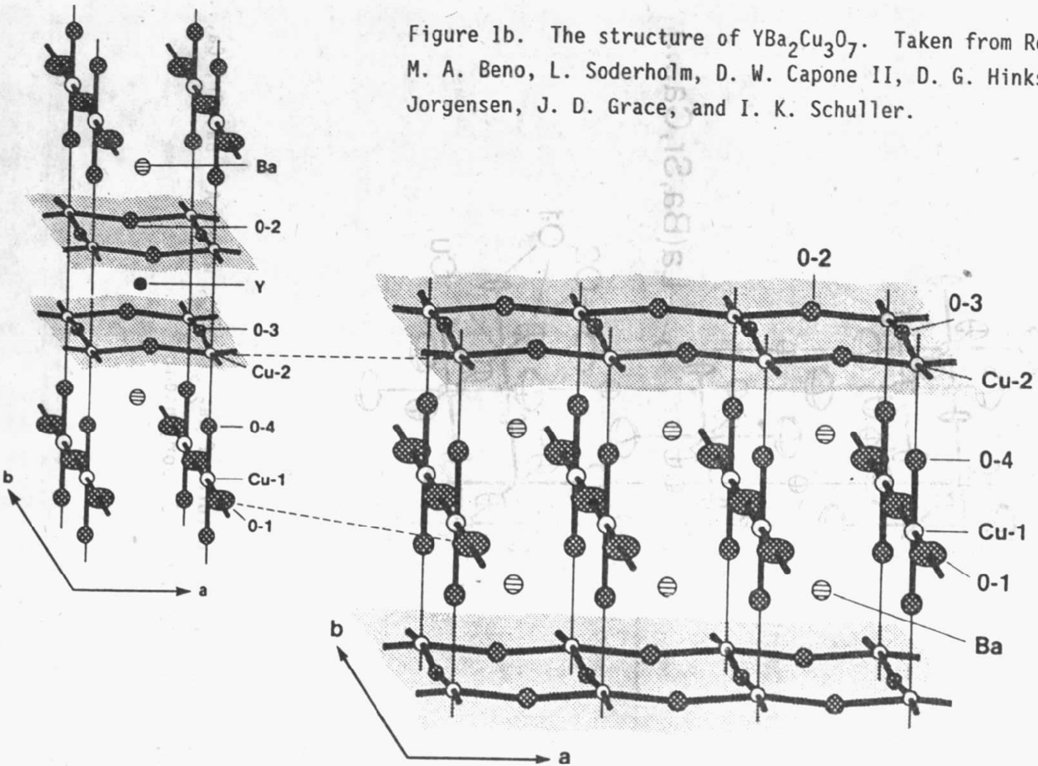
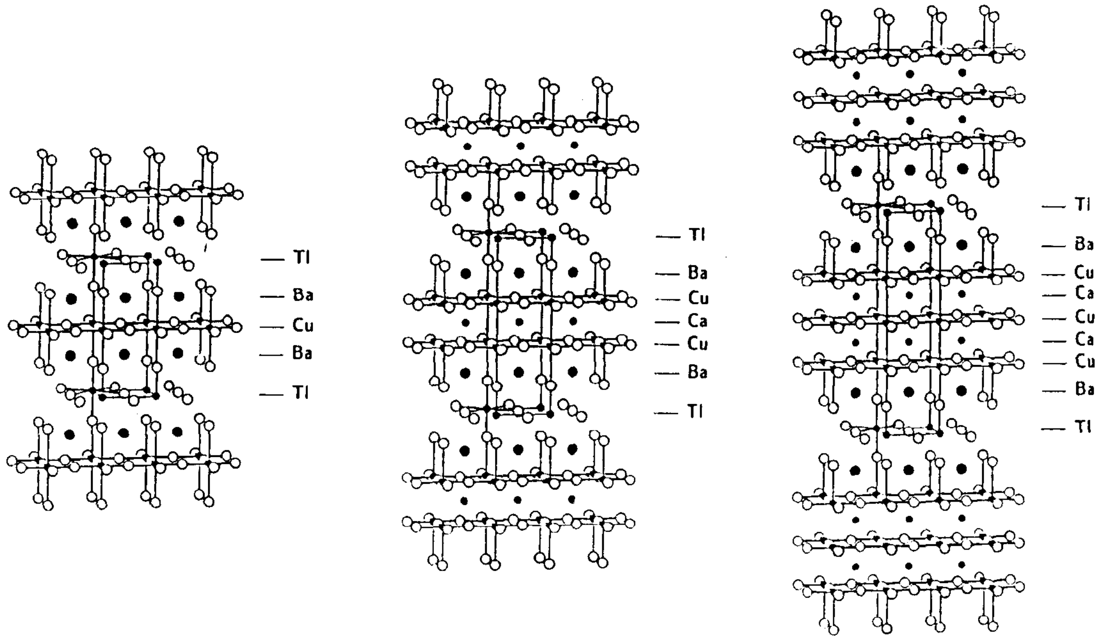
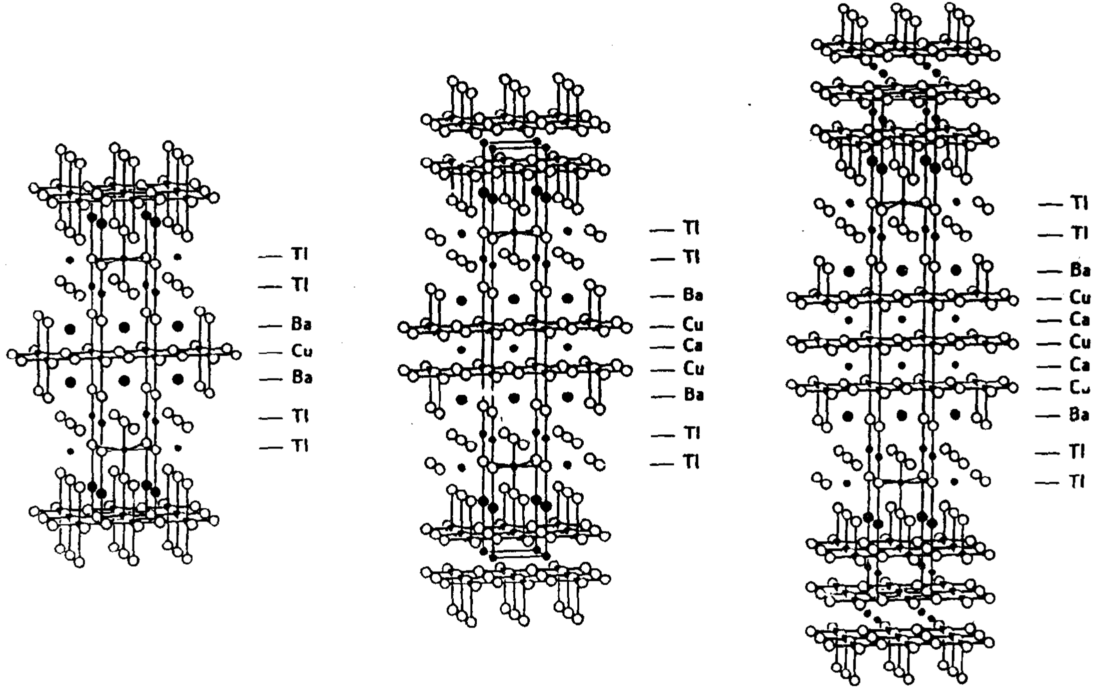


Figure 1b. The structure of $YBa_2Cu_3O_7$. Taken from Ref. 20b, by M. A. Beno, L. Soderholm, D. W. Capone II, D. G. Hinks, J. D. Jorgensen, J. D. Grace, and I. K. Schuller.



n = 1 n = 2 n = 3

Figure 1c. The structure of $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$. The corresponding bismuth compound has the same structure, with Tl replaced by Bi. Figure supplied by A. W. Sleight and C. C. Torardi.



n = 1 n = 2 n = 3

Figure 1d. The structure of $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$. The corresponding bismuth compound has the same structure, with Tl replaced by Bi. Figure supplied by A. W. Sleight and C. C. Torardi.

chemical formula for the Bi and Tl compounds is $B_yA_2Ca_{n-1}Cu_nO_x$, where B is Bi or Tl, A is Sr for the Bi compound and Ba for the Tl compound, and n is the number of Cu-O layers per unit cell: n = 1, 2, 3, 4...[32] The subscript y is 1 or 2, denoting single or double (adjacent) layers of Tl-O; for the superconducting Bi compounds, y = 1. By increasing n, T_c is raised at least to 120K for a Bi compound[33-35] and to 125K for a Tl compound ($Tl_2Ba_2Ca_2Cu_3O_x$ holds the high-T_c record at this time[16]), and it might be possible to reach a T_c of 180K this way.[32] (A report of T_c = 162K in one of the Tl compounds is still unconfirmed, as are all other reports of T_c values greater than 125K in various compounds.)

It is proving difficult to produce single-phase samples of the Bi and Tl compounds. A mixture of phases is usually seen, each having its own number of Cu-O planes and Ca-O planes per unit cell. This "syntactic intergrowth" has made it difficult to do good physics experiments.

The first observations of superconductivity in the new materials have usually been made on polyphase samples. The stoichiometry and even the crystal structure of the superconducting components of these samples were determined with great rapidity, frequently by several laboratories, within one to three days after the initial observations. In each case, neutron diffraction measurements[36] are required to determine the position of the oxygen atoms with certainty, since x-ray diffraction data are insensitive to the position of atoms containing a small number of electrons. The La compounds have a tetragonal structure. The Y compounds with approximately 7 oxygen atoms per formula unit are orthorhombic, and almost always exhibit twinning. It was speculated that the twin planes in these $YBa_2Cu_3O_{7-\delta}$ samples are a source of high temperature superconductivity, but this idea has seemed less convincing since the discovery of even higher T_c values in the Bi and Tl compounds, which do not exhibit twin planes. Furthermore, Raman effect data on untwinned $YBa_2Cu_3O_{7-\delta}$ show the presence of superconductivity.[37]

On numerous experimental and theoretical grounds, it is believed that charge transport and superconductivity in the La, Y, Bi, and Tl compounds are dominated by holes on the oxygen sublattice in the Cu-O planes.[38-41]

III. RELATED COMPOUNDS

Investigations of superconducting oxides have been carried on for some time. Before 1986, the highest T_c for any oxide was announced by A. W. Sleight in 1975: $BaPb_{.73}Bi_{.27}O_3$ becomes superconducting at 13K.[42] It is probable that we should consider this compound as one of the high-temperature superconductors, since it shares with the other members of this group an abnormally high value of T_c, compared with the Sommerfeld constant γ, the coefficient of the linear term (the electronic part) of the normal-state specific heat.[43] Indeed, on a plot of T_c vs. γ, the high-temperature superconductors fall on a single curve.[44] It should be noted, however, that $BaPb_{.73}Bi_{.27}O_3$ does not have isolated planes or chains of Cu and O atoms. The discovery that compounds with chemical formulas $Ba_{1-x}K_xO_{3-y}$ are superconducting,[45] and that the onset T_c can be as high as 29.8K[46] has raised the question of whether they are similar to the other high-temperature superconductors, even though they have a cubic structure (at least, at room temperature), no Cu atoms, and display variable-range hopping (and therefore localized electronic states) in the normal state.[47] The work on various low-temperature superconducting oxides has recently been reviewed.[48]

Since the initial work by Bednorz and Müller, the search for new high-T_c superconductors has proceeded mostly by following a simple strategy: the substitution of a chemical element by another with similar chemical properties, as indicated by the periodic table of the elements. In choosing substitute elements, care must be given to the ionic radii[49] if one wants to keep the same crystal structure. These considerations have been useful in the development of perovskites in general and the new superconductors in particular. See Figure 2, in which some ionic radii are plotted. The Figure makes it evident, for example, why one would try doping with Ca atoms in place of Cu atoms, or Bi in place of Pb. The effect of pressure on T_c provides a suggestion about possible substitutions; if T_c increases with pressure, this suggests making an atomic substitution to decrease the size of the

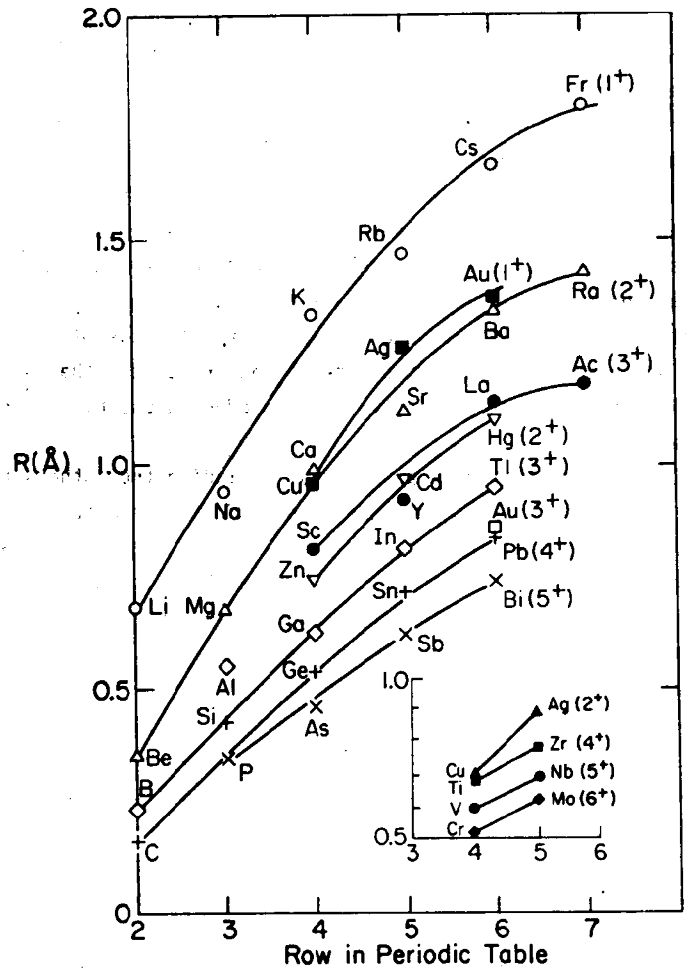


Figure 2. Ionic radii of some of the chemical elements. These data are useful in selecting atomic substitutions to attempt. Plotted from data given in Ref. 49; see that reference for the radii of other ions also. Graph provided by T. R. Lemberger.

structure's unit cell.

By means of chemical substitutions, a large number of compounds have been made having properties similar to those of the parent compounds which we have listed. For each possible combination of cations and their stoichiometry, however, a complete exploration of the possibility of high-temperature superconductivity requires a thorough testing of compounds with different amounts of oxygen, and with different methods of oxidation. In addition, the sequence of heat treatments of the ingredients may be critical, since some of the necessary intermediate products may be metastable, or may attack the crucible or other intermediate products. Because one can never try all possible heat treatments and oxidation procedures, one can never be sure that a cation stoichiometry already tried will not produce a useful superconductor some day.

It should be noted that many physicists, including the authors of this book, refer to a high temperature superconductor as a "ceramic" only if it is polycrystalline, whereas ceramists use the word "ceramic" to refer to any inorganic, nonmetallic solid, whether it is polycrystalline or a single crystal. The high temperature superconductors are indeed nonmetallic, in that they have normal-state resistivities that are very high (but not infinite), and in that they are brittle.

There have been reports of superconductivity at temperatures higher than 125K. Values up to room temperature and even beyond 500K have been claimed. These reports, however, have not passed the usual tests:

1. The material must show a decrease of the electrical resistance to a value too small to be measured with reasonably good equipment.
2. The material must show magnetic flux expulsion when it is cooled in a constant magnetic field (the Meissner effect).
3. The material must be stable.
4. The production of the material and the effects observed must be reproducible at different times and in different laboratories.