CHAPTER II
DISCOVERY OF SUPERCONDUCTIVITY AT 93 K IN Y-Ba-Cu-O

A. Overview

The study of cuprate superconductors at the University of Alabama in Huntsville (UAH) began on 14 December 1986 in response to the discovery of superconductivity above 30 K in the La-Ba-Cu-O system by Bednorz and Müller (see Chapter 1). During the six weeks prior to 29 January 1987, 130 AC resistivity and susceptibility tests were performed. All of the samples tested during that period contained lanthanum and none contained yttrium. Of the 122 tests on samples incorporating alkali earths, 102 were on samples containing strontium, twelve on samples containing calcium, and only eight on samples containing barium. Only samples with strontium were found to have transitions as high as 40 K, while the calcium and barium samples had consistently broader and slightly lower transitions. All but ten of the total 130 tests were on samples where the fractional substitution x for lanthanum was no greater than 0.175, since the transition rapidly broadened and decreased as x exceeded 0.1. In the superconducting compounds. Of these 120, 105 were on samples with compositions of the form $(La_{1-x}A')_2CuO_{4-y}$, eight on $(La_{1-x}(A',A'')_x)_{2}CuO_{4-y}$, six on $(La_{1-x}Sr)_2(Cu',M')O_{4-y}$, and one on $La_0.9Sr_{0.1}CuO_{3-y}$. The remaining ten tests on samples with x over 0.175 were all of other than "2-1-4" stoichiometry, none of which showed any indications of superconductivity. All but one of the ten were performed before 23 December during the first week of research.

Just two days after the detection on 26 January of a stable resistive transition indicative of superconductivity near 40 K in a sample containing mercury substituted for the alkali earths, efforts with this new material were immediately abandoned for a replacement of lanthanum by yttrium. Simultaneously, strontium, which had dominated

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the work of the previous six weeks, was replaced by the little-used barium as the doping ion, and the fractional substitution, which had never exceeded 0.175 in samples with "2-1-4" stoichiometry, was increased to 0.4. On 29 January 1987, all eight resistivity tests on four different samples from three separate batches of the new \((Y_{0.4}Ba_{0.6})_2CuO_{4-y}\) material displayed transitions with onsets between 89 K and 93 K.

This chapter will address the question of the motivation which led to the discontinuous leap in compositions from the 40 K superconductor \((La_{0.9}Sr_{0.1})_2CuO_{4-y}\) to the 90 K superconductor \((Y_{0.6}Ba_{0.4})_2CuO_{4-y}\). The ideas discussed were conceived and developed by the author during the two weeks prior to 17 January as a diversion to research on \((La, Sr)_2CuO_{4-y}\). The language used in this chapter will not reflect the later refinements in the terminology used to describe some of the features of the high-\(T_c\) materials. For example, the term "trivalent copper" has now been replaced with the more appropriate concept of a copper-oxygen \([Cu-O]^+\) complex.²

B. Motivation for the \((Y_{0.6}Ba_{0.4})_2CuO_{4-y}\) Composition

By early January 1987, three isostructural \(K_2NiF_4\)-type high temperature superconductors of nominal compositions \((La_{0.9}Ba_{0.1})_2CuO_{4-y}\), \((La_{0.9}Sr_{0.1})_2CuO_{4-y}\), and \((La_{0.9}Ca_{0.1})_2CuO_{4-y}\), with superconducting transition temperatures of approximately 35, 40, and 20 K, respectively, were known to exist.³⁴⁵ Given one independent variable, the doping ion, and one dependent variable, the transition temperature \((T_c)\), it was therefore reasonable to seek some simple characteristic of the doping ion (mass, electronegativity, etc.) having a direct correlation with the \(T_c\). No such property of possible significance was found, since most properties of the alkali earth ions, as with many other groups of elements, vary monotonically as one moves vertically along the periodic table.

However, in the course of the search, it was noticed that the ionic radius of the Sr$^{2+}$ ion (1.13 Å) most closely matched that of the La$^{3+}$ ion (1.15 Å). The conclusion was that the similar ionic radius of the Sr$^{2+}$ ion minimized the degree of the lattice distortions associated with the random presence of the doping ions, resulting in a characteristically higher and sharper transition. The particular reference proved fortunate since other sources were later found to list the ionic radius of La$^{3+}$ as 1.016 Å, designating Ca$^{2+}$ (0.99 Å) as the closest match.

Of course, the first step was to try substituting stable divalent cations of the appropriate size in order to test the postulate. Because partial replacements of copper in (La,Sr)$_2$CuO$_4$ with various nonmagnetic ions had already shown mercury to be among the least detrimental to the superconductivity (17 January), it was assumed that the relatively large Hg$^{2+}$ ion (radius 1.10 Å) was actually occupying the lanthanum and strontium sites. However, given the low decomposition temperature of mercuric oxide (500 °C) and the extremely high vapor pressure of the metal above that temperature, the possibility that no mercury would remain in the samples after reaction was acknowledged. Nevertheless, considering its ionic size and stable divalent state, it was reluctantly chosen as the only element that could potentially rival strontium.

Since it was well established that perovskites and perovskite-related structures frequently stabilize uncommon valences (perhaps most notably in the existing superconducting perovskites, see Chapter 1), a search of the literature was conducted in an attempt to predict the most probable valence states and lattice sites of the candidate elements. The search quickly became redirected when a possible alternative course was
revealed in an extensive work on perovskites by Francis Galasso. Two small parts of that study were of immediate interest. The first concerned the ordering of multiple ions occupying equivalent sites in perovskite lattices. The second demonstrated the remarkably consistent connection between the possible existence of an \( \text{ABO}_3 \)-type perovskite structure in a given system, its symmetries, etc. and the ionic sizes of the A and B ions. One statement in particular was most vital:

The largest group of complex perovskite type compounds has the general formula \( \text{A(B'}_{0.5}\text{B''}_{0.5})\text{O}_3 \). When the structure of the compounds is ordered, and most of them are, they adopt the structure shown in Fig. 2.5. It was postulated by Galasso et al. that an ordered distribution of the B ions is most probable when a large difference existed in either their charges or ionic radii.

While the statement referred to ordering of ions in the smaller 6-coordination octahedral B site in the usual \( \text{ABO}_3 \)-type perovskites, the arguments were presumed applicable in varying degrees to many situations, including the larger 12-coordination A site and, in the "2-1-4" materials, the corresponding 9-coordination lanthanum site (hereinafter also referred to as the A site). G. Demazeau's work on \( \text{La}_2(\text{Li}_{0.5}\text{Cu}_{0.5})\text{O}_4-y \) in 1972 provided one such example of B-site ordering in the "2-1-4" compounds. Therefore, a new approach was apparent—instead of selecting similar ions to minimize the effects of random occupation of the A site, one should choose sufficiently different ions to maximize the probability of an ordered distribution. Another consideration inferred from Galasso's work was to utilize closer to a one-to-one ratio of the appropriate ions to reduce the minimum possible range of ordering and thereby improve the chances.

Two constraints on the selection were assumed necessary. First, the average

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valence of the A ions should remain between 2.5+ and 3+ and preferably close to 2.9+
as with (La\(_{0.9}\)Sr\(_{0.1}\))\(_2\)CuO\(_{4-y}\) in order to preserve the mixed valency of the copper essential
for conductivity. Second, in light of the extreme sensitivity of perovskites to the ionic
sizes of their component ions, the weighted average volume of the A ions (or simply
radius cubed, \(<r^3> = 1.51 \text{ Å}^3\) in the case of the A\(\prime = \text{Sr}^{2+}, x = 0.1\) compound) should be
preserved in order to support and preserve the structure. The arguments for average
volume as the appropriate constraint\(^\text{11}\) will be given elsewhere.

Since the sources consulted implied that even the largest quadravalent cations
(e.g., Ti\(^{4+}\), Zr\(^{4+}\), and Pb\(^{4+}\)) exclusively occupy the smaller B site in perovskites (as in the
former high-T\(_c\) record holder for perovskites-- Ba(Pb,Bi)O\(_3\)) and later tests on January
18 and 19 suggested that the monovalent alkali metal ions Na\(^+\) and K\(^+\) (with sizes
similar to Ca\(^{2+}\) and Ba\(^{2+}\), respectively) could not successfully substitute for strontium in
(La,Sr)\(_2\)CuO\(_{4-y}\),\(^\text{12}\) the possibility of increasing the difference in valence was eventually
ruled out. Restricted to divalent and trivalent cations, all of the constraints could not be
met concurrently. Since preservation of the structure was given highest priority, the
precedence was assigned beginning with average volume, followed by average valence,
and finally a near one-to-one ratio.

Because La\(^{3+}\) is the largest stable trivalent cation, a combination of a smaller
trivalent cation and a larger divalent cation was the only alternative. Since partial
substitutions of copper with the smaller nonmagnetic ions of Ga\(^{3+}\) (11 January) and Al\(^{3+}\)
(13 January) had already been found to suppress superconductivity in the (La,Sr)\(_2\)CuO\(_{4-y}\)

\(^\text{11}\) One example of a packing condition averaging radius instead of volume which was
originally and surprisingly overlooked is Galasso's definition of the tolerance factor for
the compounds he described in the previous excerpt. Galasso, op. cit., p.16. Originally
\(^\text{12}\) Superconductivity News 1(9), 4 (1988) reported that the University of California San
Diego and the DuPont Corporation "synthesized a new superconducting oxide based
upon alkali [metal] doping for lanthanum in La\(_2\)CuO\(_{4-y}\)." M. A. Subramian and
coworkers reported similar results. M. A. Subramian, J. Gopalaknshan, C. C. Torardi,
compound, the size of the Cu$^{3+}$ ion was assumed to represent an extreme lower bound on the size of the A ions. Thus, La$^{3+}$ yielded to the smaller Y$^{3+}$ ion (radius 0.93 Å) while the large Ba$^{2+}$ ion (radius 1.35 Å) regained its position over Sr$^{2+}$. Other possible trivalent cations were considered less promising because of unstable or high vapor pressure oxide forms, unpredictable valence states, large magnetic moments, and so forth, and some have since been proven suitable, or even superior, substitutes for yttrium, including thallium, bismuth, and most of the rare earth elements.\(^\text{13}\) The uncommon occurrence of perovskites with Y$^{3+}$ as the exclusive A ion suggested that materials too close to the composition Y$_2$CuO$_4$ were unlikely to be isostructural with the La$_2$CuO$_4$ compound. Binary oxides containing yttrium and a smaller metal ion tend to prefer structures such as spinels or garnets over perovskite or perovskite-like structures.

Restricted to an average ionic volume of the A ions dictated by 
\[ (\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4 \] and adjusting x in \((\text{Y}_{1-x}\text{Ba}_x)_2\text{CuO}_4\) to match it, the composition (Y$_{0.575}$Ba$_{0.425}$)$_2$CuO$_{4-y}$ was calculated and found to have a low but tolerable average valence of 2.575+ and a near one-to-one ratio of yttrium and barium. Since the composition approached the limit of the ability of the anticipated structure to maintain its stoichiometry through the formation of oxygen vacancies and trivalent copper\(^\text{14}\) and an ordered distribution of yttrium and barium ions would necessarily incorporate them in a ratio of small integers, the composition was later, and rather subjectively, rounded to the 3:2 ratio of (Y$_{0.6}$Ba$_{0.4}$)$_2$CuO$_{4-y}$. Little consideration was given to the possible exact nature of the ordering and its implications for the crystal symmetry.

Yttrium oxide was finally obtained on Friday, 23 January just as the first

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\(^{14}\) The analogous limiting compound considered at that time was (La$_{0.5}$Sr$_{0.5}$)$_2$CuO$_4$. However, it was later shown that oxygen vacancies begin to compensate Sr$^{2+}$ doping in such a way that the fraction of trivalent copper is limited to ~0.3 at 1 atm O$_2$ and ~0.45 in pressures as high as 100 atm. J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, S. S. P. Parkin, Phys. Rev. Lett. 61, 1127 (1988).
(La$_{1-x}$Hg$_x$)$_2$CuO$_{4+y}$ sample was being made. After 24 hours at 995 °C in air, it was removed from the furnace and tested the following Monday with some encouraging results-- a stable, reproducible resistance drop around 38 K (just as anticipated based upon the similar ionic sizes of Hg$^{2+}$ and Sr$^{2+}$), apparent evidence that at least some mercury had indeed been retained in the material. From 26 to 28 January, transitions were detected in all seven tests on four different samples (two with x=0.075 and two with x=0.125) with onsets ranging from 37.0 to 39.5 K. The importance of ionic size and its connection with T$_c$ seemed certain. Figure 1 shows one of these resistivity curves.

Figure 1. Resistivity vs. Temperature in LHe for "(La$_{0.925}$Hg$_{0.075}$)$_2$CuO$_{4+y}$," 28 January 1987.

However, it is most likely that the tests were deceptive and the interpretations erroneous. Decomposition of the mercuric oxide at 500 °C and subsequent evaporation of the metal would leave a significant fraction of A site vacancies in the samples,
assuming the structure could support them. In April 1987, Grant et al.\textsuperscript{15} demonstrated that pure La\textsubscript{2}CuO\textsubscript{4} will superconduct near 40 K when properly reacted. At first glance, this would appear to provide a \textit{fifth} data point connecting the ionic size of the A' ion (in this case, La\textsuperscript{3+} itself) to the $T_c$ in the "2-1-4" compounds. However, Fine \textit{et al.}\textsuperscript{16} later attributed the superconductivity to a lanthanum deficient phase with an optimal composition near (La\textsubscript{0.95}[$\text{La}_{0.05}$])\textsubscript{2}CuO\textsubscript{4}. This vacancy doping is assumed responsible for the copper mixed valency in the same manner as alkali earth doping and would therefore better explain the observed transition in the "mercury" samples, thereby eliminating both lanthanum and mercury from the ionic size-$T_c$ connection in the (La, A')\textsubscript{2}CuO\textsubscript{4-y} materials.

C. Early Results and Evaluation

Nevertheless, on 28 January, motivated by the latest results, yttrium oxide, barium carbonate, and copper oxide were mixed in the appropriate amounts to make (Y\textsubscript{0.6}Ba\textsubscript{0.4})\textsubscript{2}CuO\textsubscript{4-y}, thoroughly ground in a mortar and pestle, pressed into pellets, and placed in a furnace in air at 996±2°C for 24 hours, the same conditions previously used for most of the (La,A')\textsubscript{2}CuO\textsubscript{4-y} materials. The following day, the pellets were removed hot from the furnace and found to consist of black particles embedded in a green matrix. Despite the overall greenish color, they were not insulating. A small bar was cut, fitted with platinum leads, and lowered into a liquid helium dewar for testing (See Further Comments on Resistivity Tests in the following section). Just below 90 K, the resistivity began to drop rapidly, reaching zero (\textit{i.e.}, below the detectability threshold of the apparatus) near 50 K. The results of that first test are shown in Figure 2.


Figure 2. Resistivity vs. Temperature in LHe for \((Y_{0.6}\text{Ba}_{0.4})_2\text{CuO}_{4-y}\) Sample #1, 29 January 1987.

Fearing the possibility of false temperature readings, the same piece was quickly retested in liquid nitrogen, again with an onset near 90 K. As another batch went into the furnace, a second piece from the original batch was tested with similar results. Tests on samples from the second and third batches, impatiently removed from the furnace after two and four hours, respectively, were found to have even higher and sharper transitions. In all, eight tests on four samples from three separate batches were performed that day. All showed transitions with onsets ranging upwards from 89 K and averaging 93 K and midpoints nearing 93 K. The resistivity curves of sample #3 (one of the better samples) are depicted in Figure 3.

After adjustments of \(x\) in \((Y_{1-x}\text{Ba}_x)_2\text{CuO}_{4-y}\) resulted in inferior materials, superconductivity was confirmed in samples having the original composition.\(^{17}\) The major phases were later identified and the basic crystal structure of the superconducting

phase determined and confirmed by various groups.\textsuperscript{18,19} The basic crystal structure has come to be known as "123."

The composition \((Y_{0.6}Ba_{0.4})_{2}CuO_{4-y}\) had visibly failed to produce a single phase material. Instead, it had fallen serendipitously almost precisely on the tie line in the equilibrium phase diagram between the so-called Y123 superconducting phase \((YBa_{2}Cu_{3}O_{7-y})\) and the insulating "green phase" \((Y_{2}BaCuO_{5})\). This was fortunate since the presence of \(Y_{2}BaCuO_{5}\) significantly less detrimental to the connectivity of the superconducting grains in polycrystalline samples than the other phases adjacent to the Y123 phase having lower melting points, namely CuO and BaCuO\(_{2}\) (which combine to form a eutectic with \(T_{E} \sim 870\text{-}890^\circ C\)). The particular choice of \(x\) was coincidentally


within 0.02 of the center of a narrow window from 0.33 to 0.50 along the "2-1-4" stoichiometry cut in which the Y123 phase could exist at equilibrium (see Figure 4). Note that had other sources been used for the ionic radii values or had the weighted average radius of the A ions been preserved instead of volume, the original composition might have been barium-rich to the point that an equilibrium sample would have been completely devoid of the Y123 phase \((i.e., x > 0.5)\). Note also that a straight substitution of lanthanum with yttrium in the "2-1-4" materials yields compositions incapable of possessing any perovskite-like or superconducting phases at equilibrium.

![Figure 4. Early Equilibrium Phase Diagram of the YO\(_{1.5}\)-BaO-CuO Ternary System showing "2-1-4" cut.\(^{20}\)](image)

\((Y_{0.6}Ba_{0.4})_2CuO_4-y\) had also failed to preserve the "2-1-4" structure. However, the constraints imposed on the composition, in requiring a relatively large amount of barium, were sufficient to yield a perovskite related material, in this case an unusual variation on the basic ABO\(_3\)-type perovskite. This failure was probably most

responsible for the drastic increase in transition temperature. It is curious to note here that Bednorz and Müller were ironically seeking an oxygen-deficient ABO$_3$-type structure when they discovered superconductivity in mixed-phase samples containing the superconducting "2-1-4" phase.\textsuperscript{21} Equally ironic is the fact that if the average volume condition had been applied to the oxygen deficient ABO$_3$-type compound La$_3$Ba$_4$Cu$_9$O$_{14-y}$ (a known phase at that time), the composition Y$_{0.8}$Ba$_2$Cu$_3$O$_{7-y}$ would have been the result.

In support of the argument that relatively large amounts of barium were necessary to form a perovskite-type structure, Frase and coworkers later found two new phases in the YO$_{1.5}$-BaO-CuO phase diagram - the simple perovskite Ba$_3$YCu$_2$O$_x$ with yttrium sharing the B sites with copper and the oxygen deficient double perovskite Ba$_2$CuO$_3$.\textsuperscript{22} Coincidentally, both lie on the barium-rich end of the (Y$_{1-x}$Ba$_x$)$_2$CuO$_{4-y}$ cut. It should also be pointed out that lanthanum and all of the rare earth elements having stable trivalent states can form the 123 structure (although praseodymium has failed to produce a superconducting material).\textsuperscript{23} However, the largest of the group, La$^{3+}$, has a range of solid solubility between the 123 phase and the "3-3-6" compound mentioned above, making it among the more difficult to process as pure 123. The large rare earths, Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, and possibly Gd$^{3+}$ (in order of decreasing size), have decreasingly smaller ranges of solid solutions along the same line, appearing to attest to the validity of an average volume constraint and to the connection between size difference and ordering.\textsuperscript{24}

In one important aspect, (Y$_{0.6}$Ba$_{0.4}$)$_2$CuO$_{4-y}$ did succeed, albeit in a far different

manner than what was expected. The large difference in ionic sizes of the yttrium and barium ions was sufficient to designate them similar but nonetheless distinct, ordered sites in the new structure. However, the difference was so great that instead of ordered occupation of the 9-coordination A sites in the "2-1-4" structure, the new structure had located the smaller yttrium ions in 8-coordination sites and the larger barium ions in la-coordination sites, thus taking the concept of average ionic size one step further in its correspondence with coordination number. Furthermore, the existence of a doping ion with a continuously variable concentration was not eliminated but simply shifted, in a sense, from the divalent metal ions to the oxygen atoms and their corresponding vacancies. Perhaps most importantly, whereas the two-dimensional nature of the 40 K superconductors was inherent to the parent compound La$_2$CuO$_4$ independent of the presence of the divalent alkali earth ions, the layered structure of the Y123 material was a direct consequence of the ordered planes of yttrium and barium and therefore, in a small way, marked a new class of superconducting cuprates. The new 100 K+ superconductors similarly derive their structures from ordered planes of the large metal ions.

D. Further Comments on Resistivity Measurements

The resistivity measurements previously mentioned were made by a conventional 4-probe AC technique. Four annealed platinum leads were attached with dots of indium to samples cut into bars of dimensions roughly 1 x 1 x 3 mm$^3$. The samples were mounted adjacent to a non-standard alumel-chromel thermocouple (~2 mm separation) calibrated to an accuracy of ±0.1 K at 273.16 K (melting point of H$_2$O), ±0.3 K at 77.35 K (boiling point of LN$_2$), and ±5 K at 4.22 K (boiling point of LHe). Good thermal contact between the sample and thermocouple junction was accomplished by a small amount of thermal grease. RMS currents of approximately 1 mA (stable to ±0.1%) at 39.9 Hz were supplied by an EG&G PAR model 5301A lock-in amplifier.
Sample voltages were input to the lock-in differential preamplifier (model 5316) having an input impedance of 100 MΩ controlled dynamically by an RS232C interface to an IBM AT personal computer to continuously provide the optimum full scale sensitivity in steps of approximately one third of a decade. Sample temperature was controlled by manual lowering of the sample into a dewar containing LHe or LN2. Voltage and thermocouple data were acquired by the computer via 13-bit (12 plus sign) A/D (Industrial Computer Source IBM PC Data Acquisition System). Each data point in the figures represents an average of at least 40 readings taken over a 5 second period.