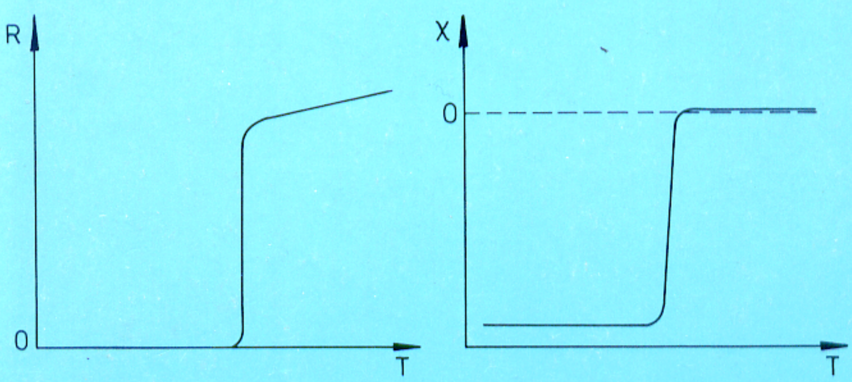
ISSN 0770 - 0520

PHYSICALIA MAGAZINE

Driemaandelijks 4 - 6 / 1989
Trimestriel Vol 11 n° 2

HIGH-Tc SUPERCONDUCTORS



Part I

IVAN K. SCHULLER

TRENDS IN THE PHENOMENOLOGY OF HIGH-Tc SUPERCONDUCTORS

Y. Bruynseraede and Ivan K. Schuller*

Interdisciplinary Center for Superconductivity
K.U.Leuven - IMEC v.z.w., B-3030 Leuven

ABSTRACT

In this introductory contribution we attempt to chronicle some developments and properties of the new superconducting oxides. Following an outline of the crystal structure, the influence of substitutions, the interplay between magnetism and superconductivity and the proximity effect and thin films, a number of the challenges facing the solid state community are described. Whether these superconducting ceramics will have a revolutionary impact remains to be seen, but their potential has set an unprecedented race in laboratories around the world.

INTRODUCTION

Why is it that superconductivity produces such a fascination? Some of it is certainly due to the potential applications, much of the motivation comes however from a purely basic interest. The microscopic theory took fifty years to be developed, a number of unusual quantum phenomena at the macroscopic level are observed, and principally it is the playground for the study of quantum many body phenomena in general. Moreover, the theory of superconductivity has also been extended to the field of liquid helium, nuclear physics and even cosmology.

* Visiting Professor at the K.U. Leuven.
Permanent address: Physics Department, University of California
San Diego, La Jolla, California 92093, USA

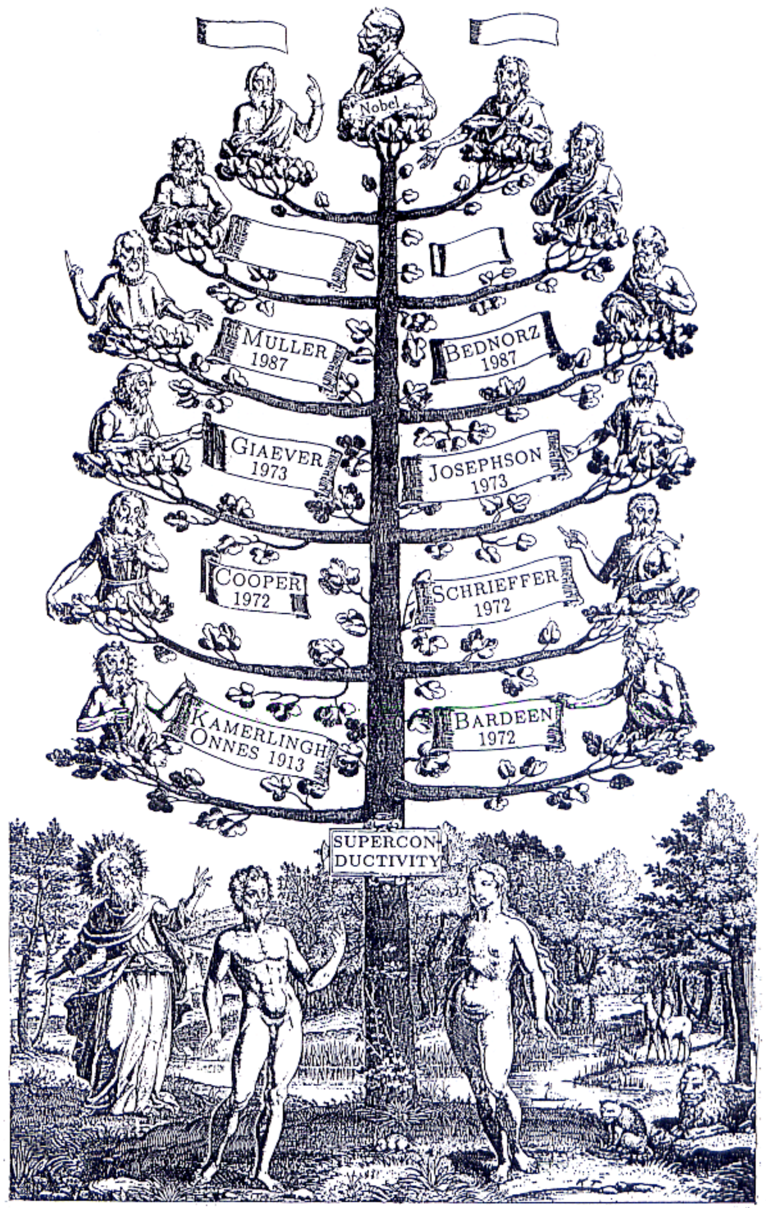
Superconductivity is also the field which produced a large number of Nobel Prizes in Physics, and caught the interest of experimentalists and theorists since its discovery in 1911 by Kamerlingh Onnes [1]. It is quite illustrative to look at the genealogical tree of superconductivity in order to understand the amount of discoveries and new ideas which have evolved from this field. All of the discoveries have been unexpected, met an initial skepticism and then eventually were rapidly followed by a series of confirmations. This is certainly true in all cases where a Nobel Prize was awarded ; the original discovery, the formulation of the Bardeen - Cooper - Schrieffer theory, the discovery of Giaever tunnelling and the Josephson effect and by the spectacular discovery of high temperature superconductivity in ceramic oxides.

Based on experimental information and (presumed!) theoretical understanding, the view prior to 1986 was that the maximum value of the superconducting transition temperature T_c of any material would not increase much above $\sim$ 23 K, the record held since 1973 by the A_{15} compound Nb_3Ge. In fact, between 1911 and 1986, T_c only increased at an average rate of $\sim$ 0.25 K per year.

However, in 1986 K. Alex Müller and J. Georg Bednorz of the IBM Zürich Research Laboratory discovered a material (Ba-La-Cu-O system) that was superconducting at higher temperatures ($\simeq$ 30 K) than had ever before been achieved. Since then other high temperature superconductors have been engineered and the maximum T_c value of the new copper oxide superconductors has risen at an average rate of $\sim$ 50 K per year to its present value of $\sim$ 125 K ! Thus superconductivity near room temperature no longer seems out of the question, as it did a few years ago. Exactly why these materials are superconducting remains however a mistery, but they are all structurally related to a crystallographic family of ceramics known as perovskites.

Perovskites are the earth's most abundant minerals and are fascinating from a technological point of view due to their vast array of electrical properties. Whereas a given crystal structure is usually associated with a specific electrical property, perovskites run the gamut from insulators to semiconductors, superionic conductors, metal - like conductors and now high - temperature superconductors. They form currently the basis of a \$ 20 - billion - per - year electroceramics industry, a figure that could be eclipsed by applications of the high - T_c ceramics.

What accounts for this extraordinary range of properties? The importance



Adapted by K. Temst from the original genealogical tree in "Livre contenant la généalogie et descente de ceux de la Maison de Croy" by Jacques de Bye (1610). Courtesy of the Central Library of the K.U. Leuven.

of structure and stoichiometry in the new superconductors suggests the answer: slight modifications of the ideal perovskite architecture often results in new electrical - or other - features.

One of the most striking aspects of all presently known high T_c superconductors with T_c 's greater than 30 K is that they are copper oxides with layered structures, all possessing CuO_2 planes. The series of $T_c \simeq 95$ K R-Ba-Cu-O superconductors, where R is a rare earth element, has a crystal structure which, in addition to CuO_2 planes, contains CuO chains which appear to play an important role in the superconductivity of these materials.

Further experimentation will surely yield new information concerning the mechanism responsible for the high T_c superconductivity in these materials, and progress in developing a theory can be anticipated. In the meantime, it will be most interesting to observe the advances in developing practical devices that are based on these new oxide materials.

CHRONOLOGY

Although the discovery by Bednorz and Müller was submitted to Zeitschrift für Physik in mid - April and appeared in September [2] it received little attention until the Materials Research Society meeting in Boston, December 1986. There, these findings were substantiated by a University of Houston group under Chu [3] and by a University of Tokyo group under Kitazawa and Tanaka [4]. By the turn of the year at least six groups, Argonne National Laboratory, University of Tokyo, The Institute of Physics in Bejing [5], ATT Bell Laboratories [6], Bell Communications Research [7] and IBM Zürich Laboratories [8] had demonstrated that by substituting strontium for barium the transition temperature T_c could be raised to 40 K. The University of Houston group then reported [9] that the application of high pressure shifted the onset of T_c up to an astonishing 52 K.

A dramatic breakthrough came when superconductivity was observed in polyphase materials at temperatures above that of liquid nitrogen. The first announcement in the USA was from the National Science Foundation on February 16th that Chu's group at the University of Houston had observed transition onset temperatures above 95 K [10]. By substituting the rare earth yttrium in place of the lanthanum in the La-Ba-Cu-O material they obtained a polyphase material with indications of a T_c in excess of 90 K - the liquid nitrogen barrier was finally broken.

Immediately groups from several laboratories identified, in a matter of days, that the superconducting phase was black and had a composition of $Y_1Ba_2Cu_3O_{7-\delta}$ which is commonly denoted as the "1-2-3" compound. The green, non-superconducting phase was later recognized as being one of the phases synthesized by Michel and Raveau [11] and having the composition $Y_2Ba_1Cu_1O_5$. Next the race was on to determine the crystal structure of the superconducting phase and how it depended on the processing of the material, in particular on the oxygen content. The structure of the 1-2-3 compound was determined by a rapid succession of experiments by different groups using X - ray powder, X - ray single - crystal and neutron diffraction [12]. The structure consists of two dimpled CuO_2 planes separated by an Y layer which contains no oxygen and intercalated with two BaO and one CuO layers (containing CuO - chains).

By the time of the 1987 March Meeting of the American Physical Society - a mere two weeks after the announcement of Chu's work - hundreds of papers from all over the world were presented at the Woodstock of Physics session on March 18th. The revolution was here, and many felt that this was one of the golden ages of physics.

The first report of a superconductor in the bismuth and thallium copper oxide family came from the laboratory of Raveau [13]. The system was Bi-Sr-Cu-O and did not attract much attention. Subsequently, the Bi-Sr-Ca-Cu-O system was studied in Germany, and higher T_c 's were obtained [14]. In January 1988, Maeda [15] announced high T_c in the Bi-Sr-Ca-Cu-O system and Hermann [16] announced high T_c in the Tl-Ba-Ca-Cu-O system.

It is now well established that there exists a large family of compounds of the type $(AO)_mM_2Ca_{n-1}Cu_nO_{2n+2}$. The A cation can be Tl, Pb, Bi or mixtures of these elements, with m=1 or 2. The M cation is Ba or Sr, and substitution of Ca by Sr is frequently observed. The number of stacked CuO_2 layers is given by n. The highest temperature at which zero resistivity was obtained in this family is $\sim$ 125 K.
($TlBa_2Ca_3Cu_4O_{11}$, $(Tl,Pb)Sr_2Ca_2Cu_3O_9$; $Tl_2Ba_2Ca_2Cu_3O_{10}$).

Recently, Cava et al. [17] found that the compound $Ba_{0.6}K_{0.4}BiO_3$ has a $T_c \sim 30$ K. This material is in stark contrast to the copper oxides for two reasons : (1) superconductivity occurs in a three dimensionally connected Bi-O array (and not a two dimensional array as in the Cu-O based compounds); (2) there are no magnetic fluctuations present.

fect measurements in single crystals are needed so that the sign of the charge carriers is determined. Some theoretical ideas depend heavily on the presence only of holes not electrons for the superconducting mechanism [31].

A large number of experiments have established by now that changes in the doping critically affect the superconductivity. For instance, in the Y-Ba-Cu-O compounds the change of oxygen stoichiometry from 7 to 6.5 decreases the transition temperature from 92 K to zero. The problem in establishing the exact role of the oxygen stoichiometry is that "everything is connected with everything else" as Engels said. The oxygen stoichiometry is correlated with changes in the oxygen ordering, with changes in lattice parameters and a variety of structural distances. Because of this it is very hard to sort out the phenomenology: i.e. which is the critical parameter. This has given rise to several conflicting viewpoints, which will only be settled if general trends are observed simultaneously in a large variety of systems. To quote P.W. Anderson "the story is not over until the fat lady sings".

SUBSTITUTIONS

One of the interesting questions that immediately arises is why these oxide superconductors are so special. Is it something peculiar to the structure of the materials or does the particular electronic structure of the elements play a role. This type of general questions can only be answered by tedious, exhaustive substitution experiments were one of the constituents is progressively substituted by another [32]. The system that has been studied most extensively as far as substitutions are concerned is the Y-Ba-Cu-O system. Substitutions that do not change the valency of the substituted elements do not affect the transition temperature very strongly. For instance, trivalent Y can be substituted by all the first row rare-earth elements with the exclusion of Pm, which has not been studied and Ce, Pr and Tb which sometimes are tetravalent or mixed valent. Substitutions of divalent Ca and Sr for divalent Ba in the original high T_c compound has only a minor effect on the transport properties. The general structural features between various compounds also indicate that the intercalant unit and the separator such as the Y and Ca do not seem to play a major role on the superconductivity but to keep the structure together and to provide the conduction holes or electrons. Detailed studies for varying substitutions of the divalent Sr for the trivalent La in the La_2CuO_4 are quite revealing [33]. The superconducting transition temperature versus effective hole concentration (obtained from Hall effect data and valency count) shows an n shaped behavior, with a maximum transition temperature at a hole concentration of 0.2 [34]. The situation in the Y-Ba-Cu-O type compounds is more confusing. In this case it has been claimed that the transition temperature shows an s shaped behavior as a function of hole concentration on the CuO_2 planes. However, in this case it is necessary to determine independently the exact distribution of holes in between the CuO_2 planes and CuO chains. These arguments have been based mostly on an ionic model which may be incorrect if applied to these metallic compounds. Other types of arguments regarding the location of the holes may change the shape of this curve considerably. Substitutions on the CuO_2 planes however are found to be quite detrimental for the superconductivity. Quite small amounts of substitutions depress the superconducting transition temperature considerably. A similar situation is also observed in the $BaBiO_3$ type compounds. Substitutions of K on the Ba site gives rise to a 30 K superconductor whereas substitutions on the Bi site with Pb only give rise to a 13 K superconductor [35]. The moral of all this is not to damage too much the conduction units.

MAGNETISM AND SUPERCONDUCTIVITY

It is well known in traditional low temperature superconductivity that superconductivity and magnetism are mutually exclusive. In some cases if the superconducting electrons are spatially separated from the magnetic moments, superconductivity and magnetism can coexist. It was found quite surprisingly that the substitution of Y with for instance the magnetic ion Gd [36] does not change at all the transition temperature. Very soon after this discovery it was argued that the reason for this lack of interaction is the fact that the superconducting electrons reside on the CuO_2 planes and they do not "see" the magnetic ions, just like in the case of the old magnetic-superconductors. The presence of these magnetic ions is however manifest at very low temperature where an antiferromagnetic ordering of the Gd ions gives rise to a large specific heat peak [37]. The exact mechanism for this magnetic ordering has not been established uniquely. Arguments have been advanced which claim that the antiferromagnetic coupling occurs because of RKKY coupling of the conduction electrons, however measurements in the metallic and insulating phase indicate that the coupling is of a dipolar origin. The issue of this magnetic ordering is still a subject of investigation. Clearly it is important to establish if the antiferromagnetic coupling is through the conduction electrons in the CuO_2 layers, and if so what does this imply for the mechanism of superconductivity. A completely different antiferromagnetic coupling occurs at high temperature in the CuO_2 planes [38]. These have been established in a series of polarized neutron scattering measurements in the La_2CuO_4 powder and single crystal system and also in Y-Ba-Cu-O powder samples. The presence of antiferromagnetic order in the superconducting state is still controversial. It is possible that antiferromagnetic fluctuations are still present in the superconducting state although they are quite hard to detect. Detailed studies as a function of doping have established the magnetic phase diagram. As the antiferromagnetism disappears the superconductivity turns on, although the presence of antiferromagnetic fluctuations in the superconducting state may still be possible. This gives rise to a variety of theoretical models which are based on a magnetic type of mechanism . One extensively studied theoretical model of this type is the so called Resonating Valence Bond model [39].

PROXIMITY EFFECT AND THIN FILMS

Thin films have played a major role in the physics and application of low temperature superconductors. Much of the key physics such as the temperature dependence of the superconducting energy gap, the Josephson effect and so on has been obtained using thin films. In fact thin films and superconductivity are quite intimately linked. The superconductivity field has influenced the thin film field and vice versa. This was mostly due to the fortunate occurrence that the superconducting coherence length in conventional superconductors is much longer than any imperfections present in ordinary thin films. The situation in the high temperature superconducting field is quite different. The superconducting coherence length as obtained from critical field measurements is very short and of the order of the unit cell size. As a consequence small imperfections at the surfaces of thin films make them quite difficult to be used in devices which require perfection at the length scale of the coherence length. Since in many cases, thin films are prepared in vacuum, questions regarding the stoichiometry at the surface as compared to the bulk of the materials are also important. It is safe to state that to date thin films do not have a comparable impact in the field of high T_c superconductivity as compared to the low temperature superconductors. Of course the main driving force behind the development of thin films is the development of devices, which mostly will need to be in thin film form. This implies that in order to extract valuable information from thin films a much higher structural, stoichiometric and surface perfection is necessary which will keep many thin film physicists happy for years to come.

CONCLUSION

After the now famous "Woodstock of Physics", the all-night jamboree on the *new superconductors, Business Week and Time listed the wonders that the new materials might make possible* : high - powered electric cars, magnetically levitated trains, and new ways of transmitting and storing electrical energy with no loss of power. But after the initial hoopla, the excitement over the high - temperature superconductors is cooling down. It's going to be a long time before we can go to the hardware store and buy a spool of superconducting wire or a tiny superfast superconducting computer!

ACKNOWLEDGEMENTS

This work was supported by the Belgian Concerted Action (G.O.A.) and Interuniversity Attraction Poles (I.U.A.P.) Programs (at K.U. Leuven) and the U.S. National Science Foundation Grant N^o DMR-88/03185 and the Office of Naval Research N^o 00014-88K-0480 (at U.C.S.D.). International Travel was provided by NATO grant N^o 0005/89.

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