Introduction to the Structure and Chemistry of Superconducting Materials

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The copper oxide superconductors are the latest and in some ways the most exotic of the series of new superconducting materials discovered during many decades of scientific research in the materials aspects of superconductivity. This tutorial lecture, summarized in part in the following, was designed to place the cuprate superconductors, for the non-expert, within the context of the superconducting materials which came before and bring all up to date on the latest developments in cuprates, where even after a decade of intensive research, new materials are being discovered which challenge our understanding.

1. INTERMETALLIC SUPERCONDUCTORS

It was no doubt the contrast between the chemistry of high temperature superconductors and the best superconducting materials which came before which was one of the stunning aspects of their discovery. These earlier materials were primarily intermetallic compounds, which in themselves of course followed a path since the discovery of superconductivity in Hg in 1911 toward increasing complexity, increasing T_c and improved superconducting properties. In one sense, the best of these from a practical point of view are based on the superconductivity in elemental Nb. As a chemist looking back on the way they developed between the 1940s and the 1970s, they would have been the result of relatively simple additions of elements to Nb to see what happened to the properties, resulting in the stabilization of the β tungsten structure for certain combinations of Nb with metalloid elements in what is the famous and very important A15 family of very high T_c and high critical field intermetallic superconductors of formula Nb_3X.

The crystal structure of this family of compounds is shown in figure 1.: It is based on the simple body-centered packing of the metalloid element (X) with Nb-Nb pairs on all the faces of the cube. Superconductors are found for Nb, Ta and V based compounds with T_cs generally between 15 and 20 K, the highest reported for the compound Nb_3Ge which can apparently only be prepared with a T_c of

23.2K as a sputtered film. This fact illustrates one of the important relations between the chemical stability and transition temperatures of superconducting materials - as the forces which give rise to superconductivity increase and the T_cs rise, the same forces tend to make the crystal structures unstable, a reasonable general rule which describes the materials which are superconducting due to electron phonon coupling (as the electron-phonon coupling increases, then structural distortions such as charge density wave behavior become more stable) Although electron-phonon coupling is not responsible for superconductivity in the cuprates, the same arguments have been made by many in their case as well - the Hg
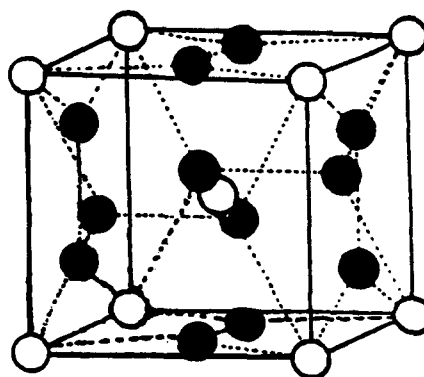

Fig 1. The A15 Crystal Structure, Nb_3X. Nb closed circles, X open circles.

cuprates for example, seem so much less thermodynamically stable than do low T_c materials such as La_2CuO_4.

The concept of charge counting is critical to the understanding of the behavior of the copper oxide superconductors - the doping away from the Cu2+ state, to an average copper valence of 2.2+ is one of the important empirical rules chemists need to design new superconducting materials and one of the important characteristics of the materials which must be successfully explained by any successful microscopic theory for the superconducting mechanism. The idea of charge counting, however, is a very old one in superconductivity, harking back to the earliest days of trying to understand the behavior of simple binary solid solutions of metals. The A15 structure superconductors are a particularly dramatic illustration of that principle in intermetallic superconductors, shown here in figure 2. The T_cs peak dramatically near 4.5 and 6.5 electrons per metal. In intermetallics this kind of behavior reflects the peaks in the electronic densities of states at those values of band filling - probably not happening for the same reason in the cuprates, but still reflecting an important characteristic of all superconducting materials regardless of the underlying superconducting mechanism.

Of course, with more and more research on intermetallic superconductors over the years, a dramatic variation in chemistry, and structure
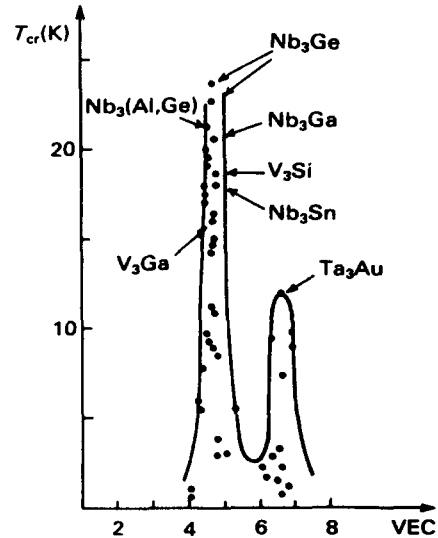

Fig. 2 The variation in T_c with electron count in A15 superconductors.

type was found, and materials of widely varying chemical and structural complexity and superconducting properties are known. Some examples which illustrate this point are shown in table 1, selected from the hundreds of intermetallic and complex compounds now known to be superconducting.

Table 1: Some interesting examples of Intermetallic or compound superconductors

Compound	Symmetry	Structure Type	Tc
Nb_3Ge	cubic	A15	23.2
BiNi	hexagonal	B-8$_1$	4.2
Au_5Ba	hexagonal	D-2	0.7
NbN	cubic	B-1	17.3
PdTe	trigonal	C-6	1.5
$PbMo_6S_8$	rhombohedral	Mo_3Se_4	15.2
$ScRu_4B_4$	tetragonal	$LuRu_4B_4$	7.2
$LaRh_3Si_5$	orthorhombic	$U_2Co_3Si_5$	4.4

2. "OLD" OXIDE SUPERCONDUCTORS

With the important exception of $BaPb_{.75}Bi_{.25}O_3$ (BPBO), described further in a subsequent section, all oxide superconductors discovered before 1986 appear to behave like conventional electron-phonon coupled superconductors, and have T_cs which do not stand out with respect to their intermetallic competitors of the same historical period. Their densities of states are often lower, as expected, but so are their T_cs. Inspection of their crystal structures and electronic properties suggests that the critical factor which was missing in these early oxide superconductors, with the exception of BPBO, is the extensive metal-oxygen covalency in the electronic band at the Fermi Energy found extensively in the cuprates.

The crystal structure of the highest T_c oxide superconductor which does not include Bi or Cu, $LiTi_2O_4$, is shown in figure 3. This (Spinel) structure is based on the cubic closest packing of oxygens in which one half of the available octahedrally coordinated interstitial sites are occupied by Ti and one eighth of the available tetrahedral sites are occupied by Li. The TiO_6 octahedra share edges to form infinite one-dimensional chains. The chains, however, intersect in three directions, making the structure fully three-dimensional. The Ti-Ti separation across the shared edges is short enough so that there is direct metal-metal bonding and the conduction band is of primarily Ti 3d character.
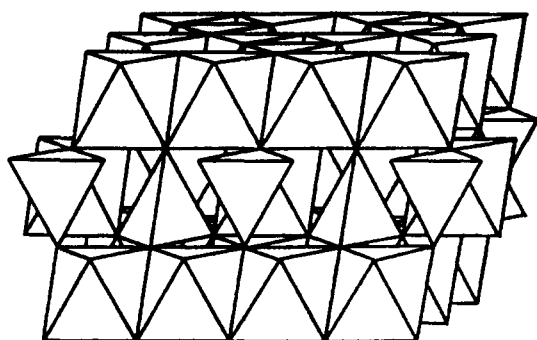

Fig 3: The spinel crystal structure of $LiTi_2O_4$. Shown are LiO_4 tetrahedra and TiO_6 octahedra.

Two other old oxide superconductors, NbO and TiO, with T_cs of 1K or below, also show clear, extensive metal-metal bonding. These can be considered as defective rock-salt structures, but are more easily seen as a network of MO_4 squares sharing corners, as shown in figure three. The metal-metal separation between the faces of some of the squares is very small and so a conduction band of metal d character is formed.
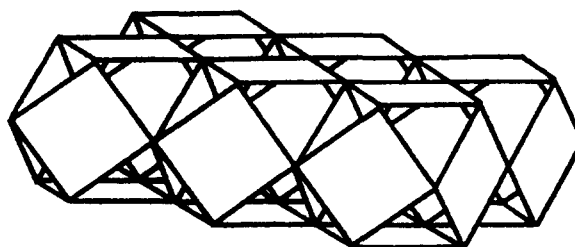

Fig 4: The crystal structure of NbO. The NbO_4 square coordination polyhedra are represented as simple squares: oxygens at the corners and Nb in the centers of the squares not shown for clarity.

Perhaps the most extensively studied of the "old" oxide superconductors are those of the type A_xWO_3 which have the hexagonal tungsten bronze structure, shown in figure 5. The structure occurs most commonly for the large alkali A ions K, Rb, and Cs. The crystal structure consists of planes of WO_6 octahedra sharing corners in the three-fold pattern shown in the figure: this pattern of octahedra is repeated in all layers, stacked one directly on top of the next. The triangular pattern brings the metals closer to one another than in the perovskite structure, and the greatly extended orbitals of tungsten make these compounds have orbital character at the Fermi level dominated by the metal orbitals. Many materials are known to be superconducting in this family, with T_cs ranging from approximately 2K to 7K. A variable alkali ion content in the tunnel is possible, which allows the adjustment of the electron count to optimize T_c. In spite of the wide range of work done on these materials there remains in the literature considerable disagreement about the composition

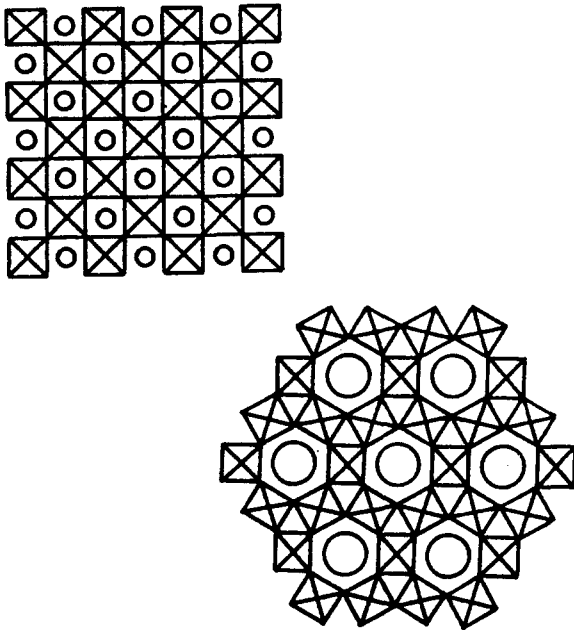dependence of their physical properties, which might be worth reconsideration.

Fig 5: The perovskite and hexagonal tungsten bronze structures. Shown is one elementary layer, made of MO_6 octahedra sharing corners, with the large ions in the cavities.

The most unusual of the oxide superconductors known before 1986 is $BaPb_{.75}Bi_{.25}O_3$, with a T_c of 12K. This material has the simple perovskite crystal structure (fig. 5), with a small tilting of the $(Pb/Bi)O_6$ octahedra, and Pb and Bi disordered among the octahedra. $BaPbO_3$ is a metal because covalent Pb-O bonding gives rise to a broad Pb 6s-O2p band which overlaps in energy with another more narrow band dominated by oxygen character. $BaBiO_3$, on the other hand, is an insulator with the perovskite structure. The insulating state forms due to the electronically driven charge disproportionation of Bi^{4+} to Bi^{3+} and Bi^{5+} (speaking for simplicity's sake from a "formal valence" point of view - the real situation is more complicated, involving holes on the oxygen p orbitals as well.) and localization of charge. The original experiments seeking superconductivity in the $BaPbO_3$ - $BaBiO_3$ solid solution were motivated by the prevailing views art the time that superconductivity might be induced in such s system exactly where one

passed from the conducting to insulating state, which turned out to be correct in this case, as it is in the cuprates. When Bi or Sb is added to $BaPbO_3$ their electrons are donated to the broad Pb-O band, and superconductivity is induced at partial substitutions of 25%, with T_cs of 12 and 3.5K respectively, near the composition induced metal-insulator transition. The scattering from the Bi and Sb cores is not sufficient to cause localization in the three-dimensional materials. Starting from $BaBiO_3$ itself, metallic conduction and superconductivity can be induced by doping with K on the Ba site, thus leaving the electronically active sites alone, resulting in a T_c of 30K. Ba has one more electron than K so the K substitution drives the electron count in the same direction as does Bi substitution when starting from $BaPbO_3$. The optimal T_cs are found at considerably different electron concentrations in the two cases, however, as shown in figure 6. The overriding opinion in the community at the present time is that these materials are conventional electron-phonon coupled superconductors, due to a body of evidence which includes significant oxygen isotope effect. I for one am not so convinced, remembering how easy it was in the beginning to dismiss the Tcs of cuprates as being "explainable" by conventional BCS when their T_cs were on the order of 30K. Layered materials such as Ba_2PbO_4, $Ba_3Pb_2O_7$ and $Ba_4Pb_3O_{10}$ are known in this family, but their electrical properties on doping seem to be dominated by the effects of scattering of the Bi on the Pb sites, as they all become more insulating on doping.
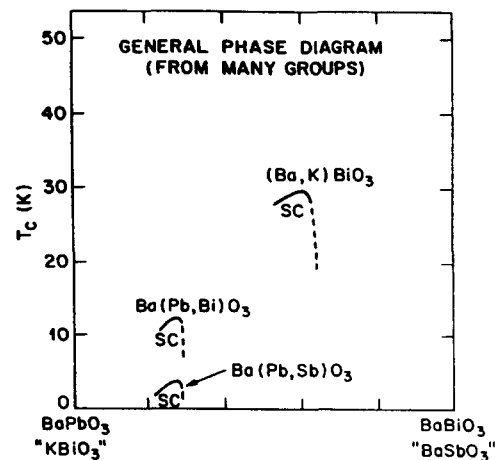

Fig 6: A composite Tc vs. Electron count/composition diagram for the $BaPbO_3$-$BaBiO_3$ based family of perovskite superconductors.

3. COPPER OXIDE SUPERCONDUCTORS

The cuprate superconductors entered the public spotlight in November of 1986, with the historic report of superconductivity in La-Ba-Cu-O at 28K. Although strictly from a temperature point of view this was not astoundingly higher than the highest T_c known for intermetallic superconductors, the fact that it occurred in a ceramic material was truly remarkable. The discovery is a tribute to the creativity of George Bednorz and Alex Muller - they looked for superconductivity where no-one else expected to find it. With the discovery of superconductivity in Y-Ba-Cu-O at 90K, the "Holy Grail of Solid State Physics", in the laboratories of M.K. Wu and C.W. Paul Chu soon thereafter, the world of condensed matter physics was never the same.

Many reviews have been written about the structures and crystal chemistry of the layered copper oxide based compounds which give rise to high temperature superconductivity, and so I will not repeat that here. The structures, briefly, consist of layers of CuO_4 sharing corners in the familiar checkerboard geometry, alternating with what are now commonly called "charge reservoir layers" which the chemist uses to control the amount of hole-doping on the CuO_2 planes. The complexity of these materials has increased with time - as chemists adjust the sizes and chemical bonding in the charge reservoir and intermediary layers to synthesize compounds by design - to obtain members of structural families which they expect to exist but which had not been observed in simpler chemical combinations.

It would have been useful indeed in the early days of the field to have set up a "commission" to set some minimum standard of data quality and reproducibility for reporting new superconductors. An almost countless number of "false alarms" have been reported in the past decade, some truly spectacular. Koichi Kitazawa from the University of Tokyo coined these reports "USOs", for Unidentified Superconducting Objects, in a clever cross-cultural double entendre likening them to UFOs (Unidentified Flying Objects, which certainly are their equivalent in many ways) and to "lies" in the Japanese translation of USO. These have caused great excitement on occasion, but more often distress. It is important, however, to keep in mind what a report of

superconductivity at 130K in a ceramic material two decades ago might have looked like to rational people if it came out of the blue sky with no precedent. That having been said, it is true that all the reports of superconductivity in new materials which were later confirmed to be true did conform to some minimum standard of reproducibility and data quality. I have tried to keep up with which of the reports have turned out to be true and which haven't. There have been two common problems: 1. Experimental error- due, generally, to inexperienced investigators unfamiliar with measurement methods or what is required to show that a material is superconducting. This has become more rare as the field matures. And 2.: "New" superconductors are claimed in chemical systems already known to have superconductors containing some subset of the components. This is common even now, and can be difficult for even experienced researchers to avoid. The previously known superconductor is present in small proportions, sometimes in lower T_c form due to impurities added by the experimentalist trying to make a new compound. In a particularly nasty variation on this, sometimes extra components not intentionally added are present - such as Al from crucibles or CO_2 from exposure to air some time during the processing. I wish I had a dollar for every false report of superconductivity in a Nb containing oxide where the authors had unintentionally made NbN in small proportions.

Table 2 represents what I believe to be the structurally and chemically unique superconducting copper oxides discovered since 1986. If you know of any which I have missed, and which have confirmed superconductivity, please let me know (with references). Some are grouped together and counted as a single superconductor: for instance the 123 structure forms for Ba-Y-Cu but not for Sr-Y-Cu, where an additional element is required on the "chain" site for stabilization: about once every 6 months a "new" superconductor is reported with a different stabilizing ion present, I count them all together as one new superconductor.

Finally, I show in figure 7 the rate of new copper oxide superconductor discovery vs. time in the past decade. What might not be generally recognized by the non-expert is the fact that the discovery rate is dual peaked. The first peak represents the dramatic appearance in 1988 of the new Bismuth and Thallium

based families of superconductors. The second peak, somewhat unexpected after so much work had already been done, reflects the appearance in many laboratories around the world of high pressure synthetic apparatus - and the resulting discovery of many new materials. Included in the secondary peak are the mercury-based and carbonate based

intermediary layer materials, both of which benefited greatly from the high pressure synthetic techniques. This technique was critical in the discoveries of all the new superconductors found in 1996.

Table 2: Copper Oxide Superconductors Found Since 1986

$Ba_2YCu_3O_7$
$Ba_2YCu_4O_8$
$Ba_4Y_2Cu_7O_{15}$

"$Bi_2Sr_2CuO_6$"
$Bi_2Sr_2CaCu_2O_8$
$Bi_2Sr_2Ca_2Cu_3O_{10}$

$Tl_2(Ba,Ln)_2CuO_6$
$Tl_2Ba_2CaCu_2O_8$
$Tl_2Ba_2Ca_2Cu_3O_{10}$
$Tl(Ba,Ln)_2CuO_5$
$TlBa_2CaCu_2O_7$
$TlBa_2Ca_2Cu_3O_9$
+ (Tl,Pb)Sr equivalents

$Sr_{1-x}CuO_2$
$(Sr,Nd)CuO_2$

$(X,Cu)(Eu,Ce)_2(Eu,Sr)_2Cu_2O_8$ X=Pb,Ga

$Hg(Ba,La)_2CuO_{4+\delta}$
$HgBa_2CaCu_2O_{6+\delta}$
$HgBa_2Ca_2Cu_3O_{8+\delta}$
$Hg_2Ba_2CaCu_2O_{7+\delta}$
$(La,Ba)_2CuO_4$
$La_2CuO_{4+\delta}$
$(Nd,Ce)_2CuO_4$

$Nd_2CuO_{4-d}F_\delta$
$Sr_2CuO_3F_x$
$(Nd,Ce,Sr)_2CuO_4$
$(La,Sr)_2CaCu_2O_6$
$(Eu,Ce)_2(Eu,Sr)_2Cu_3O_9$

$Pb_2(Sr,Ln)_2Cu_2O_6$
$PbSr_2(Ln,Ca)Cu_3O_8$

$(Cu,X)Sr_2(Y,Ca)Cu_2O_7$
X= Pb, CO_2, SO_3, BO_3,
     Bi, Mo

$GaSr_2(Y,Ca)Cu_2O_7$
$NbSr_2(Nd,Ce)_2Cu_2O_{10}$

$(Cu,CO_2)(Ba,Sr)CuO_{3+\delta}$
$(Cu,CO_2)(Ba,Sr)CaCu_2O_{5+\delta}$
$(Cu,CO_2)(Ba,Sr)Ca_2Cu_3O_{7+\delta}$

$TlO_x(CO_3)_y(Sr,Ca)_{n+1}Cu_nO_z$

$Sr_{0.4}Ca_{13.6}Cu_{24}O_{41}$
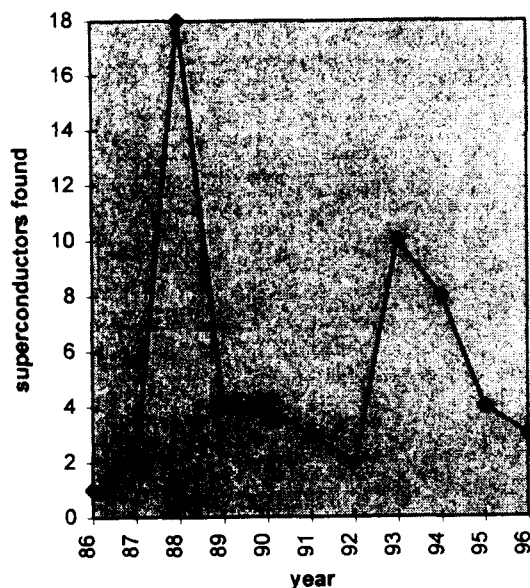
$(Sr,K)_2CuO_2Cl_2$
$(Sr,K)_3Cu_2O_4Cl_2$

Fig 7: The Rate of discovery of new Copper Oxide Superconductors

4. CONCLUSIONS

The most important of the materials discovered in 1996, if all is confirmed to be true as originally reported, is the $Ca_{13.6}Sr_{0.4}Cu_{24}O_{41}$ superconductor. This material does not have the CuO_2 plane in the same geometry as do all other cuprate superconductors, but rather a Cu_2O_3 plane with a "2-leg ladder" geometry. Discussion of this complex material is not possible in the remaining space for this article, and may be premature at this point, but it is certainly highly possible that it has opened the door to a new kind of cuprate superconductor which may prove to be the subject of many studies in the future and may have an important influence on the theoretical models for cuprate superconductivity. It is a sign, especially, that new materials still wait to be discovered, and, as in the whole history of this field, will help to guide the intellectual and technological directions which solid state physics will follow in the decades to come.

REFERENCES

There are many excellent general references on superconducting materials. Some of them used to prepare this review are:

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