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OXIDE SUPERCONDUCTORS

ARTHUR W. SLEIGHT

Department of Chemistry, Oregon State University, Gilbert 153, Corvallis, OR 97331-4003 (U.S.A.)

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ABSTRACT

An overview of the structure, synthesis and stability, and properties of superconducting oxides is presented. Current theories regarding the underlying mechanism are briefly summarized.

INTRODUCTION

Superconductivity has been known in oxides since the early 1960s (Table 1). Throughout this short history of superconductors, the perovskite structure has been prominent: $SrTiO_{3-x}$, the W–Mo–Re bronzes, the (Ba, K)(Bi, Pb)O_3 phases and finally the perovskite related copper oxide superconductors. One notable exception is the $(Li, Ti)_3O_4$ spinel with a T_c of about 14 K. The highest T_c (zero resistance) is currently 122 K, and is found for a variety of phases containing Tl, Cu, Ca and O. The T_c of oxide superconductors not containing copper has also been rising. A T_c of 13 K was found for Ba(Bi, Pb)O_3 perovskites in 1975 [7]. Later in the (Ba, K)BiO_3 system, T_c was pushed up to 29 K and finally to 34 K [14]. More recently, a T_c of 37 K was reported in the (Ba, K, Rb)BiO_3 system [15]. Thus we now have superconductivity in noncopper systems at temperatures higher than that originally reported by Bednorz and Müller for the La/Ba/Cu/O system [8].

STRUCTURE

Although the structures of both the bismuth and copper-oxide-based superconductors may be related to the perovskite structure, the dominant theme of the copper oxide superconductors is the CuO_2 sheet. It is convenient to describe the various superconducting copper oxides in terms of the number of sheets that stack consecutively on top of one another. Thus, the

TABLE 1

History of oxide superconductors

Compound	T_c (K)	Date discovered	Ref.
TiO, NbO	1	1964	1
$SrTiO_{3-x}$	0.7	1964	2
Bronzes			
A_xWO_3	6	1965	3
A_xMoO_3	4	1969	4
A_xReO_3	4	1969	4
Ag_7O_8X	1	1966	5
$LiTi_2O_4$	13	1974	6
Ba(Pb, Bi)O_3	13	1975	7
(La, Ba)$_2CuO_4$	35	1986	8
$YBa_2Cu_3O_7$	95	1987	9
Bi/Sr/Cu/O	10	1987	10
Bi/Sr/Ca/Cu/O	90	1987	11
Tl/Ba/Ca/Cu/O	122	1988	12
K/Ba/Bi/O	29	1988	13

structures of La_2CuO_4, Nd_2CuO_4 and $Bi_2Sr_2CuO_8$ are one-layer structures. Two-layer structures are, for example, $Tl_2Sr_2CaCu_2O_{10}$ and $YBa_2Cu_3O_7$. (The third copper in $YBa_2Cu_3O_7$ is in the Cu–O chains rather than the CuO_2 sheets.)

A large family of superconductors exists with the ideal formulae $(A'O)_mA_2Ca_{n-1}Cu_nO_{2n+2}$, where A′ may be Tl or Bi and partially Pb, A is Ba or Sr, and m may be one or two (only two when A′ is exclusively Bi) [16]. The number of consecutively stacked CuO_2 sheets is indicated by n, which can range from one up to about five. Synthesis becomes increasingly difficult as the value of n increases. However, the n equal to infinity (e.g., no A′ or A cations with their associated oxygen) actually exists in the (Ca, Sr)CuO_2 system [17]. Attempts to dope the n equal to infinity structure to be conducting or superconducting have not been successful.

The CuO_2 sheets are nearly flat, but in fact are almost always slightly distorted from a purely planar arrangement. There are three different distortions of these CuO_2 sheets. One has all copper atoms in one plane and all oxygen atoms in a second plane slightly displaced from the copper plane. The CuO_2 sheets of $YBa_2Cu_3O_{6+x}$ have this distortion irrespective of oxygen content. This distortion is found in the outer CuO_2 sheets whenever two or more CuO_2 sheets are stacked consecutively.

Another common distortion of the CuO_2 sheet again has all copper atoms in one plane but now the oxygens are in two planes displaced in opposite directions from the copper plane. This is found in the one-layer compounds such as La_2CuO_4 and $Bi_2Sr_2CuO_8$. Both of the distortions of the CuO_2 sheets just described bend the Cu–O–Cu bond angles slightly away from

180°. Metal–oxygen–metal bond angles are generally observed to bend away from 180° whenever the *d* shell is filled (or nearly so), and the reasons for this have been discussed elsewhere [18]. The CuO_2 sheets may, however, be perfectly flat, as they are in tetragonal Nd_2CuO_4, $Tl_2Ba_2CuO_8$ and La_2CuO_4.

There is still one more distortion of the CuO_2 sheets which is found only in the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ family. A wave develops in these structures perpendicular to the *c*-axis. This wave is apparently caused by complex bonding in the Bi–O sheets, but the wave propagates to the CuO_2 sheets as well. The periodicity of the wave is considerably larger than that of the ideal unit, and the wave is normally not commensurate with the ideal unit cell. For the $Bi_2Sr_{2-x}R_xCaCu_2O_{8+\delta}$ phases where R is a rare earth cation, the wave modulation can range from about 4 to about 5 times the *a* or *b* axis. The smaller value is for high x values [19], and the largest values are for small x and small δ [20]. Similar modulations are found for "$Bi_2Sr_2CuO_6$" which again vary with the actual composition.

Recently, several other structures based on CuO_2 sheets have been discovered. One of these is represented as $Pb_2Sr_2(Ca, Y)Cu_3O_8$ where T_cs range up to about 77 K [21]. Another new series [22] can be represented as $Bi_2Sr_2(R, Ce)_2Cu_2O_{10+\delta}$ and $Tl_2Ba_2(R, Ce)_2Cu_2O_{10+\delta}$ where R is a trivalent rare earth cation. In this case, T_cs range up to about 30 K.

SYNTHESIS AND STABILITY

The synthesis of the high T_c superconductors has been highly challenging. The general rule is that a fairly narrow temperature range exists for a successful synthesis of the basic structure. Frequently, a second treatment under controlled oxygen pressure is necessary to convert the basic structure to a composition which is superconducting. Such requirements for synthesis are highly unusual and suggest that the compounds being prepared are actually not thermodynamically stable. However, we may divide these metastable superconductors into two classifications. One class is stable at some temperature/pressure condition but not stable at room temperature and below. This is actually a common class of metastable materials if one considers solid solutions or doped systems. These are systems where the point defects dictate that the materials cannot be truly thermodynamically stable at the lowest temperatures. However, the usual situation is that an ideal composition exists which is stable at 0 K. There are only a few oxide systems where a compound stable at high temperature is not stable at low temperature. Such compounds are termed endothermic compounds or entropy stabilized compounds. Examples are mullite ($Al_6Si_2O_{13}$), $CuAl_2O_4$ and Fe_2TiO_5. In these cases, it has been established that the entropy stabilization is through point defects [23].

It also appears that the $(A'O)_mA_2Ca_{n-1}Cu_nO_{2n+2}$ compounds are also entropy stabilized compounds. Low temperature syntheses have uniformly failed for these materials which have the highest T_cs. In fact, these materials are only formed very close to their melting points. No exotherms of compound formation are detected when these phases are prepared from the binary oxides. Crystallographic studies always show a high concentration of point defects in these compounds. These phases possess significant ranges of composition and frequently the ideal composition does not fall within the phase field. Thus, we speak of superconducting $Bi_2Sr_2CaCu_2O_{10}$, but this composition has apparently not been prepared as a single phase [24].

The other route to metastability is illustrated by $YBa_2Cu_3O_{6+x}$. Although the optimum superconductivity is for $x = 1$, we always initially prepare a phase where x is significantly less than one. Thermodynamic stability for the $YBa_2Cu_3O_{6+x}$ phase appears highest for $x = 0$, but present evidence suggests that even this phase is not thermodynamically stable below about 600 °C. Nonetheless, one can easily prepare $YBa_2Cu_3O_7$ by first preparing $YBa_2Cu_3O_{6+x}$ where x is less than one and then oxidizing this phase to $YBa_2Cu_3O_7$. Attempts to prepare $YBa_2Cu_3O_7$ directly with high oxygen pressure fail [25], confirming that this phase is actually not thermodynamically stable at any temperature/pressure condition. This, of course, is also true of almost any compound prepared by an intercalation or ion exchange reaction. The n-type copper oxide superconductors [26] typified by $(Nd, Ce)_2CuO_{4-\delta}$ also require a two step synthesis in order to become superconducting. This suggests that these materials are also metastable at the oxygen content required for superconductivity. Of course, these phases are also metastable at low temperatures by virtue of the fact that they are doped systems, i.e., Ce^{IV} on Nd^{III} sites.

The metastability of the high T_c superconductors is also generally evident in crystallographic studies. For the $(A'O)_nA_2Ca_{n-1}Cu_nO_{2n+2}$ phases, point defects are observed everywhere except within the CuO_2 sheets themselves. Interstitials, vacancies and antisite disorder are rampant elsewhere, but especially in the (A'O) part of the structure. Furthermore, the A′ and O atoms in this part of the structure never rest on their ideal positions. In the $YBa_2Cu_3O_7$ structure, we see that the oxygen of the Cu–O chains is disordered so that locally these chains are presumed to be zig-zagged instead of linear. Thus, crystallographic studies confirm the metastability of these phases and they also point the part of the structure causing the metastability.

PROPERTIES

When the copper of the CuO_2 sheets is exclusively in the divalent state, we have antiferromagnetic insulators. As these sheets are doped with either

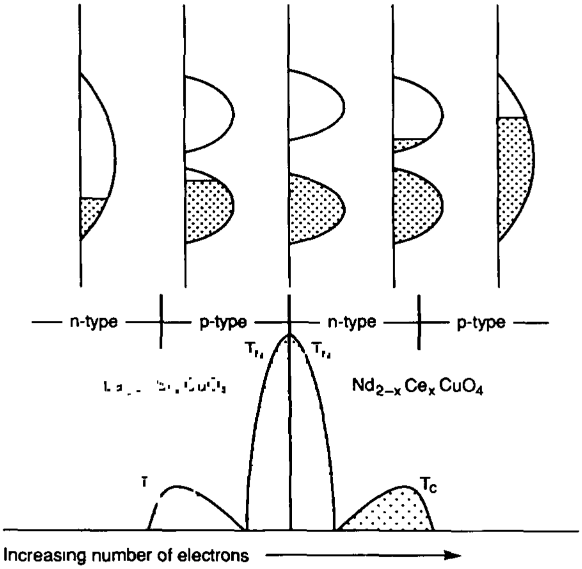

Fig. 1. Schematic phase diagram (lower) and schematic band structure (upper) for A_2CuO_4 phases, both n- and p-types. These diagrams are highly idealized. For example, the magnetic region is larger and the superconducting region is smaller on the n-type side than on the p-type side.

holes (Cu^{III}) or electrons (Cu^{I}), the antiferromagnetic insulating state is destroyed and superconductivity appears (Fig. 1). Initially, T_c increases with carrier concentration. However at the highest doping levels, superconductivity disappears and the materials appear to adopt rather normal metallic properties.

The copper of the CuO_2 sheets frequently has a fifth or a fifth and sixth oxygen atom coordinated to it. This Cu–O distance is always considerably longer than the Cu–O distance within the CuO_2 sheet. The structure which has given us our only example of an n-type copper oxide which becomes superconducting has copper coordinated only to the four oxygens of the CuO_2 sheet. Many attempts to dope this structure to give p-type copper oxide superconductors have failed [27]. Thus, it appears that p-type doping to give mobile holes requires a coordination number for copper of greater than four. This could then be the explanation for why the superconducting properties of the p-type copper oxides eventually degrade as the number of consecutively stacked CuO_2 sheets increases. The inner sheets have a copper coordination number of only four; thus, only the outer sheets are effective for mobile carriers of the holes produced by the p-type doping.

Relating T_c to the carrier concentration is difficult due partly to difficulties in actually determining the carrier concentration. However, there is another, more intrinsic, difficulty. Solid solutions and doped systems are necessarily inhomogeneous on a microscopic level. Owing to the short coherence lengths in these systems, the inhomogeneities are on a length scale that frequently causes the phases to be electronically inhomogeneous. This does not necessarily suggest that phase segregation is occurring or that the samples are poorly prepared. The natural statistics of solid solutions and doped systems dictate that microscopic regions must have different compositions. Although plots of T_c and Meissner fraction vs. carrier concentration frequently suggest some optimum composition, even this composition must necessarily be microscopically inhomogeneous in ways that could cause electronic inhomogeneity. It would seem hopeless to understand many properties of the high T_c superconductors unless we can also learn to model better the intrinsic inhomogeneities of these systems. There is no reason to be optimistic that we can somehow improve the homogeneity, and it would appear that all the high T_c superconductors may be significantly inhomogeneous.

SUMMARY

Of course, we would all like to know the nature of the electron–electron attractive force which has led to such a dramatic breakthrough in superconducting properties. At this time, there is no consensus on the actual mechanism, but there has been much progress. We do know that singlet electron pairs are involved just as in the well known superconductors with lower T_c. There is ample evidence for the classic electron–phonon interaction as long as the T_c is not above 40 K. Both doped La_2CuO_4 and $BaBiO_3$ give significant oxygen isotope effects [28,29].

Several theories were developed which were unique to the CuO chains or the twinning in $YBa_2Cu_3O_7$. Obviously, these theories are now discarded. Theories uniquely based on a π^* band or an oxygen p band may also now be discarded because of symmetry at the Fermi level demonstrated by the presence of high T_c superconductivity in both p-type and n-type copper oxides (Fig. 1). The nature of the magnetic interaction in the high T_c superconductors has been confused by the fact that the high T_c superconductors tend to be intrinsically inhomogeneous. We know that doping destroys the long range magnetic order in these systems, and this is consistent with the traditional view that magnetism and superconductivity tend to be mutually exclusive phenomena.

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