

## Structure of Four Families of Layered Copper-oxide High $T_c$ Superconductors\*

Peter Norman

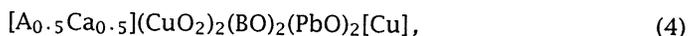
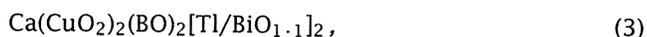
Faculty of Technology, Chisholm Institute of Technology,  
Box 197, Caulfield East, Vic. 3145, Australia.

### Abstract

Four major families of copper-oxide based high  $T_c$  superconductors have been identified by the following research groups: Bednorz and Muller (1986), Cava *et al.* (1988), Hor *et al.* (1987), Maeda *et al.* (1988), Sheng and Herman (1988) and Wu *et al.* (1987). It is now well established that the superconductivity is associated with the layers of copper-oxide and that some of the remaining structural building blocks in each primitive cell act as electron acceptors which induce the holes in the copper-oxide layers necessary for superconductivity.

### 1. Introduction

In order to illustrate the concept of local charge distribution, the formulae of the four families of high  $T_c$  superconductors may be written as

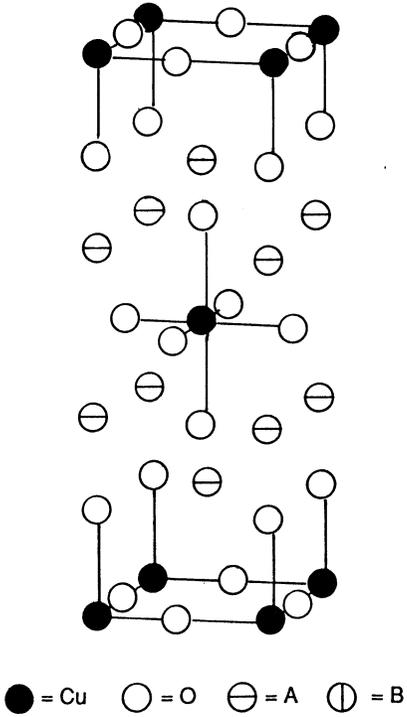


where A is a rare earth and B is an alkaline earth. The structural components in square brackets act as reservoirs which control the charge on the superconducting planes. It appears from the ensuing simple calculations that superconduction occurs when the concentration of holes in the oxygen  $pT$  bands is about one hole per twelve oxygen atoms in the copper-oxide planes, of the members of each of the four families. This concentration corresponds to an average charge of about  $-1.9$  per oxygen atom in the planes.

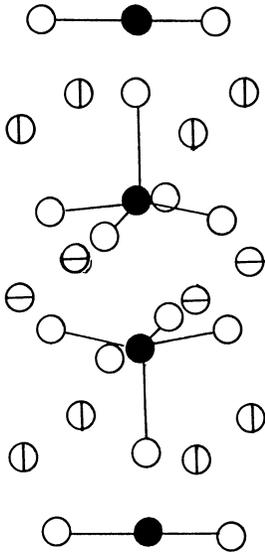
### 2. First Family

In 1986 Bednorz and Muller announced the discovery of the first high  $T_c$  superconductor. Subsequent research has shown that it is a member of a family which may be represented by the general formula (1). For comparative

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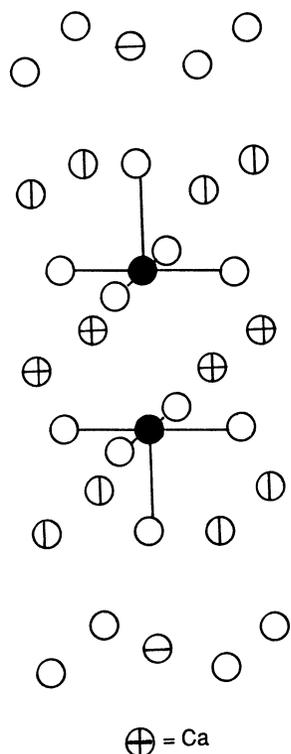


**Fig. 1.** Double primitive cell of member of the first family of high  $T_c$  superconductors.



**Fig. 2.** Primitive cell of member of the second family of high  $T_c$  superconductors. (Symbols are the same as in Fig. 1.)

purposes, the structure of two primitive cells of these compounds are shown in Fig. 1. The approximate dimensions of this double cell are  $a=3.8 \text{ \AA}$ ,  $b=3.8 \text{ \AA}$  and  $c=13.2 \text{ \AA}$ . Chen and Goddard (1988) have shown that the oxidation state of each copper atom in the copper-oxide planes is  $\text{Cu}^{\text{II}}(\text{d}^9)$ . If we assume that the nominal charges of the atoms in the charge reservoirs are  $\text{A}^{3+}$ ,  $\text{B}^{2+}$  and  $\text{O}^{2-}$  then the nominal charge of each oxygen atom in the superconducting copper-oxide layers is  $-1.9$ . Chen and Goddard (1988) have shown that this charge is due to the presence of holes in the oxygen  $p\pi$  bands. Each of these holes may be represented simply as  $\text{O}^+$  and their concentration, in order for superconductivity to occur, is about one hole per twelve oxygen atoms. When an oxygen  $p\pi$  electron moves into one of these holes it repolarises nearby copper  $d$  spins into local ferromagnetic order. As this conduction electron moves along it leaves behind a wake of ferromagnetically paired copper  $d$  spins in the form of a spin wave or magnon which attracts a second conduction electron. The net result is the attractive interaction between pairs of conduction electrons which Chen and Goddard (1988) call the magnon pairing mechanism of superconductivity in cuprate ceramics.



**Fig. 3.** Primitive cell of member of the third family of high  $T_c$  superconductors.

### 3. Second Family

In 1987 Hor *et al.* and Wu *et al.* reported another perovskite superconductor with an even higher  $T_c$ , given by the general formula (2). The primitive cell of this compound is shown in Fig. 2 with the cell dimensions  $a=3.8 \text{ \AA}$ ,  $b=3.9 \text{ \AA}$  and  $c=11.7 \text{ \AA}$ . Calculations by Chen and Goddard (1988) indicate that all copper atoms in this family are also  $\text{Cu}^{\text{II}}$ . If the other nominal charges

are  $A^{3+}$ ,  $B^{2+}$  and  $O^{2-}$  for the oxygen atoms in the (BO) layers, then the charge of the oxygen atoms in the  $(CuO_2)$  planes and the  $(CuO_{0.7})$  chains is  $-1.9$ . Once again this represents an average occurrence of about one hole per twelve oxygen atoms in the planes. Chen and Goddard (1988) suggested that members of this family of superconductors carry their supercurrents along both the chains and planes of copper oxide.

#### 4. Third Family

During 1988 Maeda *et al.* and Sheng and Herman demonstrated that another large family of high  $T_c$  superconductors can be made with the general formula  $A_2B_2Ca_{n-1}Cu_nO_{4+2n}$ , where A may be Tl or Bi, B is an alkaline earth and  $n = 1, 2$  or 3. For convenience only the case of  $n = 2$ , with  $T_c \sim 110$  K, will be considered here. The formula for the case  $n = 2$  may be written as  $Ca(CuO_2)_2(BO)_2[AO]_2$ . The general structure of these compounds is shown in Fig. 3 where  $a = 3.8 \text{ \AA}$ ,  $b = 3.8 \text{ \AA}$  and  $c = 15.4 \text{ \AA}$ . Actually this formula and Fig. 3 represent only half of the unique primitive cell which has  $c = 30.8 \text{ \AA}$ .

It should be noted that if the oxygen atoms in the copper-oxide layers of these compounds are in the state  $O^{1.9-}$  then some further oxidation mechanism

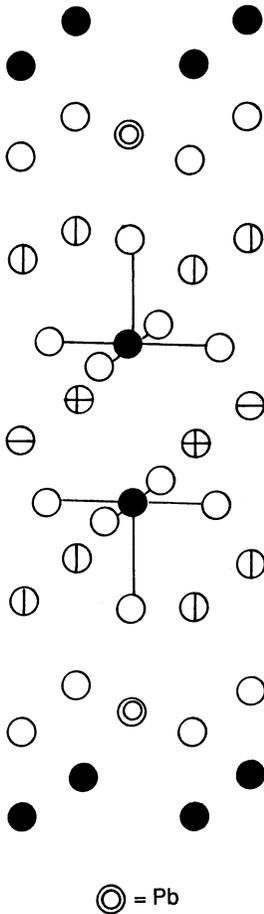


Fig. 4. Primitive cell of member of the fourth family of high  $T_c$  superconductors.

is required. One possibility is that additional oxygen atoms in the state  $O^{2-}$  may be squeezed into the AO layers until they reach the required concentration of  $AO_{1.1}$ .

Torardi *et al.* (1988) have suggested an alternative oxidation mechanism involving band overlap in the thallium atoms. A further mechanism proposed by Cheetham *et al.* (1988) is that up to 16% of the B atoms may be absent from the standard formula of the compound in order that superconduction may occur. As yet, Chen and Goddard (1988) have not published their findings regarding electron-magnon coupling in compounds of this third family.

## 5. Fourth Family

Recently Cava *et al.* (1988) have announced their production of a further group of superconductors with a general composition given by formula (4), where A is a rare earth and B is an alkaline earth. These compounds have a critical temperature  $\sim 70$  K and the dimensions of a typical primitive cell (see Fig. 4) are  $a = 3.8 \text{ \AA}$ ,  $b = 3.8 \text{ \AA}$  and  $c = 15.8 \text{ \AA}$ . In order for the oxygen atoms in the copper-oxide sheets of these compounds to have the critical concentration of about one oxygen  $p\Gamma$  hole for every twelve oxygen atoms, it appears that the oxidation states of the remaining atoms are  $A^{3+}$ ,  $Ca^{2+}$ ,  $Cu^{2+}$  (in the  $CuO_2$  sheets),  $B^{2+}$ ,  $O^{2-}$  (in the BO and PbO sheets) and  $Pb^{2+}$ ,  $Cu^{1+}$  in the outermost connecting layers. So far Chen and Goddard (1988) have not announced their calculations for these compounds but presumably their electron-magnon coupling mechanism would still be applicable.

## 6. Conclusions

From the analysis outlined here it seems likely that all members of the four high  $T_c$  superconducting families of layered copper-oxide compounds considered employ a common superconducting mechanism which depends on a critical concentration of oxygen  $p\Gamma$  holes in the copper-oxide layers. Presumably it is for this reason that these compounds will only superconduct at their maximum recorded temperatures provided the established stoichiometries and preparation techniques are adhered to. Calculations made by Chen and Goddard (1988) predict that the highest critical temperature for any of the copper-oxide superconductors now under development is likely to be around 225 K. Presumably time will tell.

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