

## Coordination and materials properties

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**Abstract** - The importance of coordination in the materials properties is emphasized in general and the particular case of high temperature superconductors is dealt with in more detail. The coordination of copper to the neighbouring oxygen atoms and the mixed valence character of the transition metal are discussed.

All materials properties are primarily determined by their electronic structure, which is built from the chemical bonds of atoms or molecules in the crystalline or amorphous structure as the case may be.

One of the dreams of the materials scientist is to be able to design materials with specified properties. This dream is almost attained in some cases. Synthetic molecular metals, conducting polymers, polymer electrolytes, etc., can now be designed, in principle, from the knowledge of the interrelation between crystalline and electronic structures and physical properties. New fields of science and technology are appearing in which molecular size electronic or optical circuits are envisaged and the first steps in hardware learning neural networks are being taken. In all these new "molecular engineering" the role of chemistry and particularly coordination chemistry is clearly of prime importance.

The contribution of coordination chemistry to materials science does not restrain to materials synthesis and processing. It gives clear insights to the understanding of the physical properties. The present understanding of the solid state properties of silicon, for example, owes many basic ideas to coordination chemistry. It was the realization that each silicon atom is tetrahedrally coordinated to its 4 neighbours, through its  $sp^3$  hybrid orbitals, that gave a clear picture of the existence and meaning of the gap in the band structure. In opposition to this strong covalent bond system, typical of the so called covalent semiconductors, lie the very weak chemical bonds found, for example, in polymer electrolytes, in which, heteroatoms in a polymer chain, coordinate to metal ions as if the polymer would be an imobile solvent.

But, perhaps the hottest subject, at present, in the interface of chemistry-materials science is found in the high transition temperature superconductors, where the coordination of copper to the neighbouring oxygen atoms appears to be the essence of high temperature superconductivity. Due to its importance, this particular aspect will be dealt with in more detail below.

All this new subject started with the search for superconductivity in oxide perovskites which led Alex Müller and Georg Bednorz to the discovery of the first so called high temperature superconductor ( $T_c \approx 35$  K) - a new phase of a lanthanum-barium-copper oxide, with copper in a mixed valence state, earlier described by Bernard Raveau (ref.1). Since this discovery, the increase in superconducting transition temperatures does not seem to stop, the present well established record being held by the compound  $Tl_2Ca_2Ba_2Cu_3O_{10}$  with  $T_c \approx 125$  K (ref.2).

It was soon realized that the spectacular behaviour of these materials is apparently linked to the mixed-valence of copper and to the low dimensionality of the structure.

The 40 K superconductor,  $La_{2-x}M_xCuO_{4-y}$  ( $M = Ca, Sr, Ba$ ), (ref.3) has the  $K_2NiF_4$  perovskite structure, with MO layers intergrown with distorted  $CuO_6$  octahedron oxygen deficient layers.

The 95 K superconductor,  $YBa_2Cu_3O_{7-\delta}$  ( $0 \leq \delta < 0.5$ ), (ref.4) has an orthorhombic, oxygen deficient, perovskite structure with triple  $(Cu_3O_{7-\delta})_\infty$  layers kept together by yttrium ions. Each of these layers has two  $(CuO_{2.5})_\infty$  layers of corner sharing pyramids connected through  $(CuO_2)_\infty$  rows along the b axis.

The remarkable common feature of these structures is the two-dimensional Cu-O square lattice in the ab plane with Cu-O distances of the order of 1.94 Å as in copper oxide (Cu(II)). The oxygen atom along the c axis which completes the octahedra in the first case or the pyramid, in the second, is 2.3 Å away from the basal copper atom.

In the Y-Ba-Cu-O superconductor, there is, in addition, a one-dimensional Cu-O chain along the b axis, with a Cu-O distance of 1.94 Å. The copper atom in the chain is, however, only 1.86 Å apart from the oxygen on top of the neighbouring pyramid, this distance being similar to that in NaCuO<sub>2</sub> (Cu(III)).

The 80-110 K superconductors, of the Bi-Ca-Sr-Cu-O family, have similar structures with the Cu-O chains replaced by BiO layers.

Finally, the various phases of the more recent thallium superconductors, Tl<sub>2</sub>Ba<sub>2</sub>CuO<sub>6</sub> (T<sub>c</sub> ≈ 80 K), Tl<sub>2</sub>CaBa<sub>2</sub>Cu<sub>2</sub>O<sub>8</sub> (T<sub>c</sub> ≈ 105 K) and Tl<sub>2</sub>Ca<sub>2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> (T<sub>c</sub> ≈ 125 K), have structures which are similar to those of the Bi materials with the Bi-O layers replaced by depleted TlO layers. Tl<sub>2</sub>Ca<sub>2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> keeps the Cu-O chains as well.

In all these superconductors, the mean valence of copper is always greater than 2, implying a mixed-valence state, which involves a partial oxidation of Cu(II) into Cu(III). This feature appears to be essential to superconductivity. It should be pointed out that such a mixed-valence is needed in order to have metallic or semimetallic conductivity. It should also be noted that the mixed valence (Cu(II) - Cu(III)) does not correspond to the existence of Cu<sup>2+</sup> or Cu<sup>3+</sup> ions but to a delocalization of holes over the Cu-O lattice. A configuration 3d<sup>9</sup>  $\bar{L}$  ( $\bar{L}$  = ligand hole) has indeed been observed by many authors using several different techniques and it is clear that in all these materials, oxygen non-stoichiometry has a prominent influence upon superconductivity. That influence is well illustrated in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> , for which T<sub>c</sub> decreases from 95 K for  $\delta \approx 0$  to 22 K for  $\delta \approx 0.6$  and materials with  $\delta > 0.6$  are not superconductors. The mean valence of copper is 2.3 for  $\delta = 0$ , 2 for  $\delta = 0.5$  and 1.67 for  $\delta = 1$  corresponding to the absence of mixed-valence Cu(II) - Cu(III) for  $\delta > 0.5$ . It is well known that Cu(II) and Cu(III) can only have coordination numbers larger than 3 and Cu(I) can only be linear, with twofold coordination. On the other hand the introduction of oxygen vacancies,  $\delta$ , occurs along the one-dimensional Cu-O chains. Based on these facts Raveau (ref.5) proposes the formulation YBa<sub>2</sub>[Cu<sub>2</sub><sup>II</sup> Cu<sup>III</sup>O<sub>7</sub>]<sub>1- $\delta$</sub>  [Cu<sub>2</sub><sup>II</sup>Cu<sup>I</sup>O<sub>6</sub>] <sub>$\delta$</sub>  for this material. He has further shown that T<sub>c</sub> varies almost linearly with the ratio Cu(III)/Cu<sub>TOTAL</sub>, for both YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  and La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4-y</sub>.

The transport properties data, in the normal state (T > T<sub>c</sub>), are reasonably well understood from the above features. In ceramic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> , the resistivity increases with  $\delta$  from a metallic-like behaviour for  $\delta = 0$  to a semiconductor type, for larger  $\delta$ . In single crystals ( $\delta = 0$ ), the resistivity in the ab plane is metallic-like but it is semiconductor type near T<sub>c</sub>, along the c axis (ref.6). This is in agreement with the dimensionality of the structure, featuring conducting paths on the Cu-O planes and chains and semiconducting (insulating) paths in the perpendicular direction.

The thermoelectric power (ref.7), which is positive, shows that the charge carriers are indeed holes. Its value increases with  $\delta$  and its temperature dependence is typical of a highly correlated hole system. The same type of behaviour is found for the new thallium compounds (ref.8).

Substitution of trivalent rare earths (Nd, Sm, Eu, Gd, Ho, Er, Lu) and lanthanum for yttrium does not significantly affect the superconducting properties (ref.9) but the replacement of copper by Ni, Fe or Zn has drastic effects on T<sub>c</sub>, suppressing superconductivity even for low levels of substitution (ref.10).

A very interesting case is the replacement of yttrium by praseodymium (ref.11). In ceramic Y<sub>1-x</sub>Pr<sub>x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> , T<sub>c</sub> decreases drastically as x increases from 0 to 0.5 and superconductivity is suppressed for x > 0.5. It was, at first, assumed that praseodymium would have valence 4, in the material, disrupting the electronic and probably the crystal structure, but it is now clear from neutron diffraction and soft-X-ray absorption spectroscopy data (ref.12), that it has valence 3 (same as Y) and that the crystal structure remains essentially the same, even for complete substitution. The drastic effect of this substitution, on the superconductivity can only be accounted for, to be due to drastic changes in the electronic structure, probably originating from the overlap of the praseodymium 4f and the copper 3d orbitals.

In conclusion, the Cu-O<sub>2</sub> planes appear to be the crucial feature of high temperature superconductivity, which occur through the pairing of holes. The one-dimensional Cu-O chains do not seem to play a role in superconductivity but rather act as charge reservoirs. The hole density is very low and their motion is strongly correlated. The true mechanism of pairing remains, however, a mystery.

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