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CRYSTALLINE MATERIALS
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NEW HIGHLY CONDUCTING SYSTEMS

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INTRODUCTION

Crystalline inorganic and organic solids with the potential for high electrical conductivity in one or two dimensions are discussed in this section which includes all crystalline materials which have metal-like behaviour especially if they indicate the possibility of superconductivity. Not included are the typically amorphous conducting organic polymers, such as polypyrrole, polyaniline etc. which have excited wide-spread interest over the last few years, but which raise quite different chemical and physical questions.

The materials under discussion can roughly be divided into three classes:

- I. "Classical" Inorganics like metal oxides, sulfides, selenides or halides.
- II. Coordination compounds of metal ions with mainly organic ligands such as metal dithiolates, phthalocyaninates.
- III. Solids comprised of organic ions responsible for the conduction path and inorganic counterions.

I. "Classical" Inorganic Solids

(A) Oxides

The potentiality of classical inorganic solid-state chemistry for generating simple solids with only 3 or 4 different kinds of atoms has been demonstrated recently with the discovery of high temperature superconductivity in different classes of this type of compounds.

The first report of the onset of superconductivity at a high temperature ($\sim 30\text{K}$) in the Ba-La-Cu-O system by Bednorz and Mueller in mid 1986 led to a number of studies aimed at determining the identity and the structure of the superconducting phase. These intense efforts showed in late 1986 that the superconducting phase has the composition $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ (M = Sr or Ba; $x \sim 0.1-0.2$; $T_c \sim 30-40\text{K}$), the phase that has been known since 1979. In late 1986 Chu et al. found that the T_c of this Ba-La-Cu-O phase increases to a higher temperature, which suggested to them that La

166

should be replaced by Y so as to induce an internal pressure. This effort led to the discovery of the new superconducting Y-Ba-Cu-O system in early 1987 that shows superconductivity at $T_c > 90\text{K}$ (higher than liquid nitrogen temperature) under ambient pressure. Intense studies on this Y-Ba-Cu-O system showed that it has the composition $\text{Y Ba}_2 \text{Cu}_3 \text{O}_{7-y}$ ($y \approx 0.10-0.19$). The related phases of composition $\text{L Ba}_2 \text{Cu}_3 \text{O}_{7-y}$ ($\text{L} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}$ or Yb) are also found to exhibit high temperature superconductivity ($T_c \approx 90-100\text{K}$).

Another recent and promising advance to higher T_c has been made in the BaBiO_3 system. By partially substituting K in the place of Ba transition temperatures around 20K have been reached so far.

A number of studies on low-dimensional molybdenum bronzes have shown that the blue bronze $\text{K}_{0.3}\text{MoO}_3$, the purple bronze $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$, and the Magnelli phase Mo_4O_{11} show charge density wave phenomena, and that the purple bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ becomes a superconductor at 1.9 K.

These surprising new findings stimulated much new preparative chemical work. Many of the ternary and/or quaternary lanthanide/transition-metal/chalcogenide system should be explored in the future in order to find out whether the known superconducting phases are unique or whether a systematic path to higher transition temperatures can be found by chemical variations. At the moment it is very hard to predict in which direction these chemical efforts should be aimed. In this regard we should mention the frequent reports of materials with indications of superconducting behaviour at 240 K. Unfortunately the identity of these materials is unknown at the present time. It is clear that additional investigations of these materials will lead to exciting new results.

(B) Other Chalcogenides and Halides

There are many other simple classical inorganic solids with low-dimensional metal-like behaviour which have been studied in detail during the last decade because of their special physical properties. The metal di- and trichalcogenides need special mention in this respect. Highly conducting materials with layered structures have been found among metal disulfides while many triselenides show very interesting one-dimensional collective phenomena. Superconducting phases have even been found among the so-called Chevrel phases, which are transition metal sulfides. Some "linear" tetraselenides (Nb and Ta) with parallel spines of polyiodide chains have been added to these interesting solids recently. Though an overwhelming amount of work has been done in this area during the last two decades, this field still remains a fruitful area for further preparative efforts, e.g. by systematically changing the transition metals, their oxidation states, and their chalcogenide linkage in the lattice.

There have been various reports of high temperature ($>77\text{K}$) superconductivity in a number of other materials, but these have generally not been confirmed. An excellent example is provided by CuCl , for which giant diamagnetic anomalies have been observed in a number of laboratories. However, it has not been possible consistently to repeat the observations. Reports on the properties of CuCl samples are reminiscent of comments by Chu, for example, that the high T_c signals in $\text{YBa}_2\text{CuO}_{6+x}$ were elusive, initially, and difficult to stabilize. Perhaps CuCl and other such materials should be reinvestigated in view of the early observations on $\text{YBa}_2\text{CuO}_{6+x}$ and of the recent findings of high temperature superconductivity.

167

II. Coordination Compounds

We will divide this section into two groups of complexes.

- (A) Those with classical "hard" bases as ligands such as CN^- or NH_3 and
- (B) those with "soft" donor atoms in the ligands, especially with sulfur, selenium and phosphorus.

(A) "Classical" Complexes

The work in this area produced a number of 1d conductors and/or semiconductors which have been intensively investigated by physical methods during the last decades. The most famous examples are the mixed-valence compounds KCP, platinum-oxalates, $\text{Hg}_{3-x}\text{AsF}_6$ and metal porphyrins. The experiments in this field were motivated mainly by theoretical predictions. First of all there were the conjectures of Peierls, Kohn, Froehlich et al. predicting the behaviour of 1d metals and secondly there was the proposal of Little who suggested the detailed structure of an excitonic high temperature superconductor. Though the latter goal has not been achieved yet, the development in the field of 1d coordination compounds is a typical example of the fruitful collaboration between theoreticians and experimentalists in materials science.

(B) Sulfur, Selenium, Phosphorus, etc., as Ligands

Many transition metal compounds involving the above mentioned donor atoms, especially dithiolates, have been prepared recently with the aim of obtaining highly conducting materials. The efforts are twofold. It is planned,

- (i) to obtain solids with networks of higher dimensionality and
- (ii) to use the metal thiolate derivatives as anions in connection with other "stacking" organic cations such as the TTFs.

(i) Bis(dithiolato)metal complexes

Many conducting crystalline dithiolate metal complexes have been prepared recently and investigated with respect to their conductivity. The experiments in this field again are guided by theoretical predictions. For example Hofmann has provided guidelines for the selection of compounds - many of which are still unknown - which may be candidates for desirable highly conductive behaviour. Much further preparative work is needed before one is able to estimate the potential of these systems with respect to their conductive properties.

(ii) Dithiolate anions and donor cations

This latter aspect is connected with the "organic" materials. One can think of innumerable combinations between dithiolato-metal anions and planar organic radical cations crystallizing in very different lattice types: At this point we wish to call attention to superconductivity in $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ ($\text{H}_2\text{dmit} = 4,5\text{-dimercapto-1,3-dithiol-2-thione}$), the first molecular superconductor containing a transition metal complex; the conductivity pathway is not known.

III. Organics

At least three classes of solids can be discerned under this heading:

- (A) Crystals in which the conduction path is made up by stacks of negatively charged radical anions. Simple inorganic metal ions, classical complex cations or more "organic" ions such as ammonium or phosphonium cations act as counterions without contributing to the conduction directly. The TCNQ salts are a typical example.
- (B) Solids made up of stacks of planar organic cations and non conducting counter anions. $(TMTSF)_2X^-$, the Bechgaard Salts, are mentioned as example here.
- (C) Crystals containing segregated stacks of organic radical anions, counter-balanced by stacks of planar organic cation, one famous example being TTF-TCNQ.

(A) Radical Anion Chains

The age of organic conductors began with the discovery of TCNQ and the high electrical conductivity of some of its salts by the DuPont group in the early sixties. Since then many hundreds of solids containing TCNQ-anion stacks as the conducting unit have been investigated. No superconductors have been found under these materials so far.

Very recently a similar type of organic radical anions - obtained by chemical reduction of differently substituted N-dicyanobenzoquinonediimines - could be isolated as stacked materials. Some of them show much higher conductivities compared to those of most of the TCNQ salts especially at very low temperatures.

(B) Radical Cation Chains

The exploration of solids containing organic cation stacks counter-balanced by simple inorganic anions like perchlorate, triiodide, etc., resulted in the only organic superconductors so far known. Aromatic hydrocarbons, sulfur, oxygen, and selenium heterocycles have been used as donors in these substances. They are oxidized by different means - chemically or electrochemically - in the presence of different anions which results in the formation of highly conducting crystalline materials. Only a small number of anions have been used so far and it is suggested that the variation of these ions should be explored in a broad fashion. Some of these are layered compounds and the question of which kind of counterions fits best in this structure should be investigated. Very recently the range of anions built into these solids has been extended: Metal cluster anions and metaldithiolates have been introduced, the latter leading to another superconducting material.

Since so much work has been done on the chalcogenofulvalene donors chemists should be stimulated to provide other promising donor systems. To stimulate the development of new low-dimensional organic and inorganic based solids, to test concepts and observe anticipated phenomena theoretical insight described in such a way that enables the synthetic chemist to design and prepare new materials to test and extend the theories is necessary. Little's model was particularly good example of this, whereas, the Haldane conjecture was not.

168
(C) Segregated Stacks of Radical Cations and Radical Anions

The segregated "double" stack material TTF-TCNQ paved the way for the explosive development of organic conductors. It has been a fruitful area in the past. Though many combinations of different planar organic radical anions and radical cations have been isolated and investigated intensively none of them has turned out to be superconducting.

The only organic superconductors so far have been found in the group of hole conductors like $(\text{TMTSF})_2\text{X}$ but none of them in the huge class of organic electronic conductors like the TCNQ salts. Certainly the question arises: Why is this so? So far this question has not been answered. Therefore, theoretical work in this direction is recommended.

The above discussion of highly conducting materials has only been concerned with the preparation and investigation of this wide variety of solids in bulk, which means as single crystals. The so-obtained solid state properties certainly can be further varied by using specially prepared samples, like LB films, sputtered films or by the inclusion of these compounds into other matrices to enhance the overall conductivity. Only minor efforts in these directions have been undertaken up to the present time.

Since future developments in science are difficult to predict this contribution more or less gives a summary of the "chemical" status quo in low-dimensional highly conducting materials hinting only at some clearly open questions.

