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One-dimensional conductors

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Abstract. A brief review of one-dimensional conductors with emphasis on the synthetic criterion, the model systems of radical ion salts, charge transfer complexes, metal chain systems, polymeric conductors and A_3B compounds is given.

Introduction

The interest in one-dimensional conductors arose out of the work of Little in 1964, who proposed that in certain organo-metallic structures high temperature superconductivity should in principle be possible. The conventional superconductivity based on the electron–phonon–electron interaction occurs at temperatures much lower than about one-tenth the Debye temperature of the solid, i.e. less than about 40 K. Little proposed that one can consider a polyene chain to which is attached a suitable polarisable substituent *R* such as a cyanine dye (figure 1). The polyene chain plays the role of a one-dimensional metal and the ' free ' electrons moving close to the substituents polarise it in such a way that a positive charge is induced. This charge attracts another electron of the core so that there is an effective electron–electron attraction. If this is greater than the coulomb repulsion between the conducting electrons, then a superconducting transition is likely.

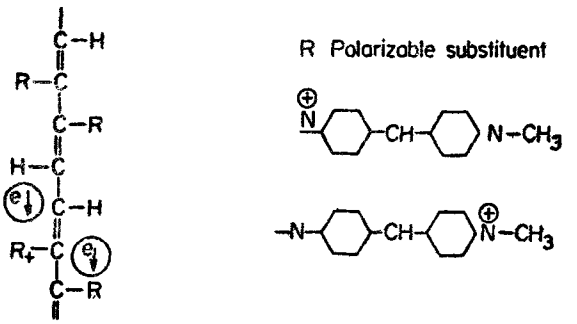

Figure 1. Little's model of a polyene chain.

While Little's idea of such a high temperature superconductor is theoretically feasible, the synthesis of a system conforming to these specifications has not been possible so far because of three objections.

(i) A one-dimensional metallic system can be shown to be unstable to changes in the crystal lattice period. This results in splitting of a partially filled band into a completely filled and an empty band. The band gap opens at twice the Fermi momentum, resulting in a dimerisation of the lattice and an insulator behaviour at lower temperatures. This is the Peierls transition.

(ii) The coulomb repulsive interaction itself should cause a Mott transition to an insulator state at lower temperatures.

(iii) One electron states are generally localised and cannot result in metallic state.

These objections can be partly overcome in quasi-one-dimensional systems (for example in helical systems with weakly interacting side chains). Instead of discussing the theoretical instabilities of such one-dimensional systems, let us examine some promising systems.

2. One-dimensional systems

There are four such one-dimensional systems which have been widely studied and these form the basis of four different types of one-dimensional conductors.

2·1. *Charge transfer complexes and radical ion salts*

Heeger and his colleagues from the University of Pennsylvania reported in 1973 that unusually high conductivity, closely resembling superconductivity were observed over short temperature intervals in an organic charge transfer salt TTF–TCNQ (tetrathiofulvalene-tetracyanoquinodimethane) around 58 K. The black crystalline complex TTF–TCNQ is a highly anisotropic conductor. Along the principal conducting axis which is the crystallographic *b*-axis, the conductivity is nearly $10^3\ \Omega^{-1}\,cm^{-1}$ and the anisotropy is about 500 to 1000 at room temperature. The anisotropy increases to at least 10^4 at about 60 K and the high conductivity fluctuations resembled almost superconductivity (figure 2). It was speculated that a structural instability prevents the stabilisation of superconducting state. The peak in conductivity gets diminished in defective crystals. In addition it was found that the TTF–TCNQ could be crystallised to form small black needles with fairly good metallic shining surface. The structural investigation revealed a parallel chain structure. Along the *c* and *a* direction, the conductivity is *via* the process $DA \rightarrow D^+A^-$ and hence activated. Along the *b* chain, there is a significant charge transfer (0·7 e) and conductivity is large. The role of TTF and TCNQ chains in such a system is far from clear. While both of them show fairly good semiconductivity independently, it is thought that above 60 K, the TTF^+ chains are metallic but the $TCNQ^-$ chains remain insulating because of some kind of Peierls state. Below 60 K a strong interchain coupling makes it more three-dimensional with small energy gap developing. There has been very interesting theoretical developments in these studies.

Interesting development in the synthesis of organic charge transfer complexes has been the recent preparation of (a) TSeF–TCNQ, (b) DSeDTF–TCNQ, (c) TTT–$TCNQ_2$, (d) $(TTT)_2I_3$, (e) $(TSeT)_2Cl$ which also show similar

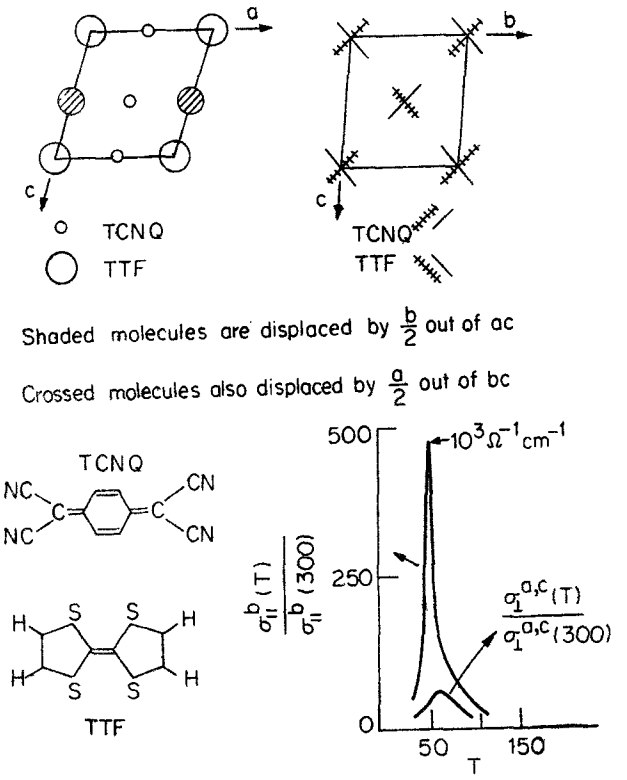

Figure 2. Crystal structure and conductivity of TTF–TCNQ.

conductivity peaks. Also a system like HMTSF–TCNQ has been crystallised which again is a one-dimensional metal and remains metallic down to about 0·03 K without undergoing any Peierls transition.

There have also been very detailed studies on the thermoelectric power, optical reflectivity spectra and other thermal and magnetic properties which further reconfirm the one-dimensional nature and the Peierls transition.

2·2 *Metal chain systems*

A number of metal chain systems also show very interesting one-dimensional conducting properties. The classic example is that of $K_2Pt(CN)_4Br_{0.3}\ 3H_2O$. Here a platinum atom and four CN groups form a planar structure. These planes build up to form a platinum chain (figure 3). Out of all the possible ligands, d_{z^2} is normal to the plane of the complex. The halogens (Br) attract some of the electrons from the d_{z^2} band and give rise to holes in it. Such a partial population of d_{z^2} band gives rise to its one-dimensional conductivity. The ESR spectra also confirm this. Whereas the Pt–Pt distance along the *C*-direction in $K_2Pt(CN)_4$ is 3·5 Å, it reduces to as low as 2·89 Å upon halogenation. This is quite close to 2·77 Å the Pt–Pt distance in Pt metal. Correspondingly the room temperature conductivity increases from $3{\cdot}5 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ in KCP to $3 \times 10^{2}\ \Omega^{-1}\ cm^{-1}$ in KCP–Br, a magnitude of 10^9 times. The temperature dependence of σ_{11}, of

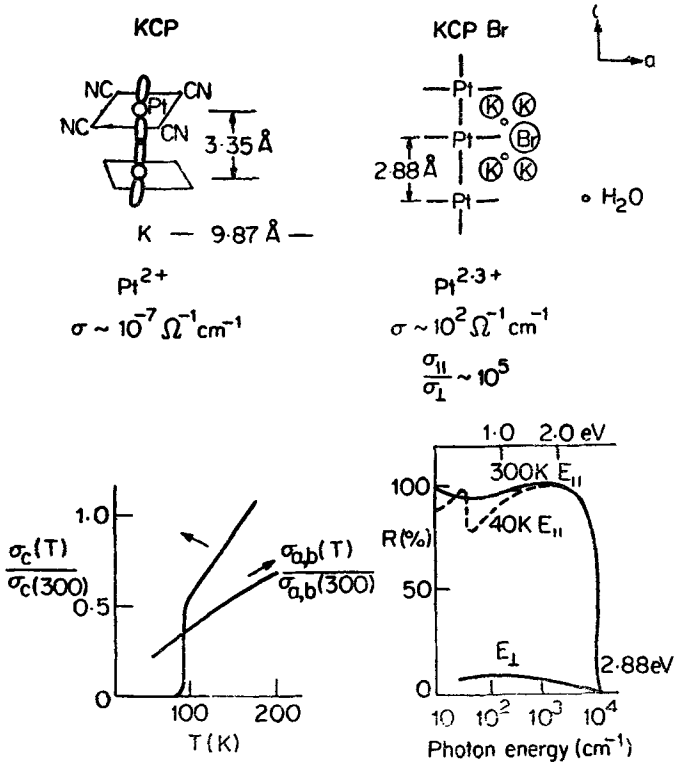

Figure 3 (a). The metal chain complex $K_2Pt(CN)_4$ and $K_2Pt(CN)_4Br_{0.3}$: crystal structure, conductivity and reflectivity data.

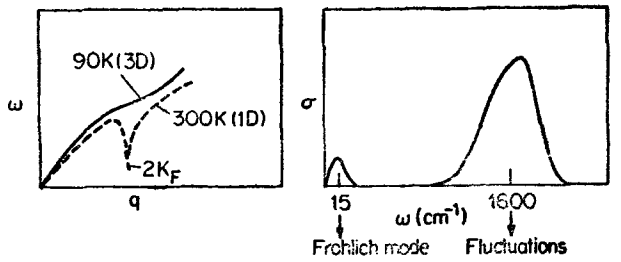

Figure 3 (b). The a.c. conductivity of $K_2Pt(CN)_4$ $Br_{0.3}$.

KCP-Br shows a semiconductor to insulator transition at about 100 K. However some high pressure experiments indicate that a transition to superconducting state at about 6 K with 60 kbar of pressure is likely. The optical properties show a typical plasma edge in the visible. At lower temperatures (< 40 K) a pinned-Frohlich mode is observed in the reflection spectrum. Below the Peierls transition temperature, the lattice distortion should cause a charge density wave along the linear Pt chains. Within the continuum model, the CDW should move freely along the chain carrying the electrons with it leading to a Frohlich superconductor. In

real systems the CDW may be pinned to the impurity, etc., and instead of superconductivity, a peak in a.c. conductivity only may be observed. In fact such a peak has been observed at 1600 cm^{-1}. There have also been interesting observations of the 2 k_F instability as a soft phonon mode.

As in charge transfer salts, a number of new interesting metal chain systems have been investigated recently (figure 4). (i) $Hg_{2\cdot86}AsF_6$ (Hg chain) Hg–Hg = 2·66 Å, incommensurate with the lattice, superconducting below 4·1 K– mercury extrudes out of the chain? (ii) $Ir(CO)_3Cl$ – Ir chain, Ir–Ir = 2·85 Å metallic, (iii) $(TTT)_{1\cdot2}$ $NiS_4C_4H_4$ – TTT chain, activated – 0·11 eV–mixed valence, (iv) Nickel pthalocyanine iodide, (v) Niobium tetraiodide – Nb chain activated 0·02 ev.

2·3. *Polymeric conductors*

A very interesting example of this is the polymer (SN) . The structural investigations show that the sulphur and nitrogen atoms are somewhat randomly distributed in a helical type (figure 4). It has a room temperature resistivity of $1\cdot7 \times 10^3$ Ω^{-1} cm^{-1}. The polymer does not show a metal insulator transition and remains metallic and in fact becomes a superconductor at 0·26 K. A field of 335 Oe lowers this transition temperature to about 0·1 K. The band structure calculations seem to indicate a weak three-dimensional nature. Attempts have been made to partially halogenise the polymer and also to replace a few of the S-atoms with Se.

2.4. *A_3B compounds*

The β-tungsten structure of the A_3B compounds is being reexamined to form mutually orthogonal *A* chains. This one-dimensional nature is considered to be responsible to the relatively high transition temperatures in these substances. The Fermi surface also correspondingly indicates three degenerate bands corresponding to the localised electrons.

In addition to these systems of polyiodide chains, metal ligand systems have been proposed for highly anisotropic conductivity. Whatever might be the system, if the one-dimensional metallic state has to be stabilised, certain basic conditions have to be satisfied. These are (i) the existence of unpaired electrons, (ii) a uniform crystal structure such that in the absence of electron–electron interactions, the unpaired electrons would delocalise into a single metallic band. Any distortion in the system will open up a forbidden band and leads to a semiconducting state. (iii) relatively weak electron-electron repulsive interaction—this can be achieved in practice by having highly polarisable substituents attached to the molecule. (iv) maximisation of the intermolecular transfer integral, this can be achieved either by an increase in the degree of overlap of the conducting molecular orbitals

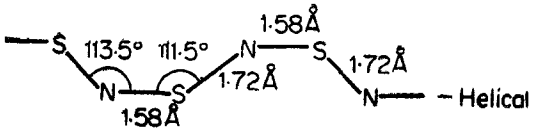

Figure 4. $(SN)_x$ polymer.

or by reducing the intermolecular spacing, (v) crystallisation techniques. Thus one can see that there is a wide variety of one-dimensional conducting systems which can be suitably modified so as to yield not only metallic conductivity but also superconductivity. Many new one-dimensional systems have been proposed by Little and others, and the field of one-dimensional conductors has become very exciting.

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