

Electronic Properties of Some Chain and Layer Compounds

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Solids having chain- or layer-like structures may in certain circumstances approximate to 'one-' or 'two-dimensional' solids. The chains or layers can be separated by relatively large distances, of the order of the van der Waals atomic radii, and this results in extreme anisotropy in the electronic, vibrational, and mechanical properties. These properties to a large extent correspond to those appropriate for single chains or layers, and the interaction between the chains or layers can be treated as a perturbation. The materials are of considerable interest at present and their physical and chemical properties are being intensively studied in many laboratories throughout the world. The results obtained with the metallic members are particularly exciting and sometimes very puzzling.

It was a theoretical paper by Little¹ in 1964 that caused renewed interest in the so-called 'one-dimensional conductors'. This paper was concerned with the possibility of high-temperature superconductivity, particularly in long-chain organic molecules. The theory was based on electron-phonon (vibrational) interactions, and it was greeted with some criticism and scepticism. In 1973, Heeger and his colleagues at the University of Pennsylvania published some spectacular results on the electrical conductivity found in a few of their crystals of the organic charge-transfer complex TTF-TCNQ (1,4,5,8-tetrathiafulvalene-tetracyanoquinodimethane).² These crystals, which are extremely anisotropic in their physical properties, behave as metals at room temperature when the conductivity is measured along the stacks of molecules. At low temperatures, however, there is a change in behaviour, and the variation in conductivity with temperature corresponds to a small band gap semiconductor. There was some talk of super-conducting fluctuations in the crystals, and there is little doubt that the publicity associated with these experimental findings stimulated the wide interest and excitement in this class of materials. Chain-like solids have been studied for some time now, and the 'Krogmann type' solids³ such as the mixed-valency planar complexes of platinum have received attention from a number of groups, including that associated with Zeller at the Brown Boveri laboratories in Switzerland.⁴ A typical solid is $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$, sometimes abbreviated as KCP(Br), and here we have linear chains of platinum atoms in the crystal. The

¹ W. A. Little, *Phys. Rev. (A)*, 1964, **134**, 1416.

² L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Comm.*, 1973, **12**, 1125.

³ K. Krogman, *Angew. Chem. Internat. Edn.*, 1969, **8**, 35.

⁴ H. R. Zeller, in 'Festkörper Probleme', ed. H. J. Queisser, Pergamon, Oxford, 1973, Vol. 13, p. 31.

most important result, however, was reported in 1975 when a group working in the I.B.M. laboratories in California on the sulphur-nitrogen polymer (SN)_x announced that they had found superconducting behaviour.⁵ The transition temperature was quite low, in the region of a quarter of a degree Kelvin, but this is the first polymer and also the first pseudo 'one-dimensional' solid to behave in this way. It is not intended in this review to give an exhaustive account of all this work since this can be found in books and published articles.⁶ The subject is developing at an astonishing rate where many of the ideas are controversial to say the least, and it is possible only to give trends, and to mention some of the phenomena encountered.

Turning to the layer-type solids, there are many distinct classes and we should mention graphite and its compounds;⁷ the metal halides such as PbI₂, CoCl₂;⁸ the arsenic and antimony chalcogenides such as As₂Se₃, Sb₂S₃; the gallium chalcogenides GaS, GaSe;⁹ the 'inverse structure' silver subfluoride Ag₂F; and the transition-metal dichalcogenides based on MoS₂. The physical and chemical properties of many of these solids have been discussed in reviews.¹⁰ The last group consists of the sulphides, selenides, and tellurides of metals such as Ti, Zr, Hf, V, Nb, Ta, Mo, and W. Some of these layer materials are wide band gap semiconductors, *e.g.* HfS₂; some such as NbSe₂ are metals and superconductors; while others such as MoTe₂ are relatively small band gap semiconductors. The most interesting features of these materials are associated with the width and occupation of relatively narrow 'd' bands. The physical topics which have been studied in these layer materials include electron transport in narrow 'd' bands; excitons, including anisotropy effects, thickness effects, and screening by free carriers; metal-non-metal transformations; superlattice formation including Peierls distortions, Kohn anomalies, and charge-density waves; superconductivity and possible 'two-dimensional' superconductivity associated with a single layer or sandwich; and intercalation studies with a variety of metals and organic molecules. An extension of this work to ternary compounds such as Pb_xMo_yS_z has recently been made. These solids are related to the transition-metal chalc-

⁵ R. L. Greene, G. B. Street, and L. J. Suter, *Phys. Rev. Letters*, 1975, **34**, 577.

⁶ (a) 'Low-Dimensional Cooperative Phenomena', ed. H. J. Keller, Plenum Press, New York, 1975; (b) 'One Dimensional Conductors', ed. H. G. Schuster, Springer, Berlin, 1975.

⁷ See, for example, A. R. Ubbelhode, *Proc. Roy. Soc.*, 1972, **A327**, 289, and references therein; J. E. Fischer, T. E. Thompson, and F. L. Vogel, *Phys. Rev. Letters*, 1976, in press; M. E. Vol'pin, *et al.*, *J. Amer. Chem. Soc.*, 1975, **97**, 3366; E. L. Evans and J. M. Thomas, *J. Solid State Chem.*, 1975, **14**, 99.

⁸ See, for example, M. R. Tubbs, *Phys. Stat. Solidi (B)*, 1972, **49**, 11; 1975, **67**, 11; G. Harbeke and E. Tosatti, *R.C.A. Rev.*, 1975, **36**, 40.

⁹ See, for example, E. Mooser, I. Ch. Schlüter, and M. Schlüter, *J. Phys. and Chem. Solids*, 1974, **35**, 1269.

¹⁰ J. A. Wilson and A. D. Yoffe, *Adv. Phys.*, 1969, **18**, 193; A. D. Yoffe, in 'Festkörper Probleme', ed. H. Queisser, Pergamon, Oxford, Vol. 13, p. 1; *Ann. Rev. Mater. Sci.*, 1973, **3**, 147; 'Proceedings of the 12th International Conference on the Physics of Semiconductors', ed. M. H. Pilkuhn, Teubner, Stuttgart, 1974, p. 611. There will also be a book series called 'Physics and Chemistry of Materials with Layered Structures', managing editor E. Mooser, Reidel Publishing Co., to appear shortly, and a review by J. A. Wilson to appear in *Rev. Mod. Phys.*; V. L. Kalikhman and Ya. S. Umanski, *Soviet Phys. Uspekhi*, 1973, **15**, 728.

genides but are not layer materials. They have relatively high superconducting transition temperatures, but more important the highest superconducting critical fields yet determined. We can in fact expect a good deal of activity in all these areas.

1 Chain Compounds: Pseudo One-dimensional Systems

A variety of solids fall into this category and the reader is referred to reviews by Thomas and Underhill, Krogman and Day.⁶ In addition, the A15 or β -tungsten-type solids¹¹ such as Nb₃Sn, V₃Si, and Nb₃Ge, which are high-temperature superconductors having transition temperatures of 18, 17, and 23 K, respectively, may also be considered in this category, since the structure shows three interpenetrating orthogonal arrays of parallel chains of metal atoms. In this review we concentrate mainly on the conducting solids which are built up from metal-like strands or chains separated by relatively large distances, and there can be extreme anisotropy in many of the transport properties parallel and perpendicular to the chains. For some materials the anisotropy can reach values of the order of 10⁴—10⁵ at room temperature. Table 1 lists the electrical conductivity of some selected materials.¹² It is apparent from the values for the room-temperature conductivity that these materials are good conductors. Further, if the effective conductivity per strand is considered, then the values are similar to those for typical metals such as copper ($\sigma \sim 10^6 \Omega^{-1} \text{cm}^{-1}$).

Simple structures for TTF-TCNQ, KCP(Br), and (SN)_x are shown in Figures 1—4. In TTF-TCNQ negative charge is transferred from the TTF molecule to the TCNQ molecule. The planar TCNQ⁻ ions are stacked face to face as linear chains and in Figure 1 the chains would emerge out of the paper. The TCNQ⁻ chains are separated by similar chains of TTF⁺ cations. The highest electrical conductivity is along the chain direction, *i.e.* along the *b*-axis. Recent work suggests that the charge transfer is not complete and values quoted lie in the range 0.5—0.8 electrons per TTF molecule.¹³ The sketches in Figures 1—4 are idealized drawings and in the real structures there are subtle deviations which can influence the physical properties. Thus in KCP(Br) the successive atoms are not in equivalent positions and the CN groups are not planar. For (SN)_x polymer two models of the structure are at present available.¹⁴ The helical chain structure proposed by Boudeulle is given in Figure 3 but this differs in many respects from that of the Pennsylvania group, and further work, probably involving neutron diffraction or soft X-ray absorption, is needed to resolve this point.

A. Conductivity Measurements.—The electrical conductivity along the chain direction in crystals of TTF-TCNQ increases markedly on cooling, and some results are given in Figure 5. For a very few crystals the effect was more spec-

¹¹ See, for example, J. Ranninger, *J. Phys. (F)*, 1975, 5, 1083, and references therein.

¹² See, for example, J. S. Miller, *J. Amer. Chem. Soc.*, 1974, 96, 7131, and references therein.

¹³ P. Coppens, *Phys. Rev. Letters*, 1975, 35, 98.

¹⁴ M. Boudeulle, 1974, PhD. Thesis, Lyon; M. Boudeulle and P. Michel, *Acta Cryst.*, 1972, A28, S199; A. G. MacDiarmid, C. M. Mikulski, P. J. Russo, M. S. Saran, A. F. Garito, and A. J. Heeger, *Bull. Amer. Phys. Soc.*, 1975, 20, 360; *J.C.S. Chem. Comm.*, 1975, 476.

Table 1 Some representative 'metal-like' chain solids

Compound	Colour	Metal-metal separation along chain/Å	Effective radius of metal atom in chain/Å	Room temperature conductivity, $\sigma/\Omega^{-1}\text{cm}^{-1}$	Calculated ^a conductivity, $\sigma^*/\Omega^{-1}\text{cm}^{-1}$
<i>Organic charge-transfer complexes</i>					
TTF-TCNQ	black	—	—	$\sim 10^3$	2×10^3
HMTSF-TCNQ				$\sim 2 \times 10^3$	
(TTF) ₁₁ I ₈				$\sim 4 \times 10^2$	
<i>Planar complex systems</i>					
K ₂ Pt(CN) ₄ Br _{0.3} ·3H ₂ O	polished copper	~2.89	1.31	3×10^2	5.5×10^3
<i>parent compounds</i>					
K ₂ Pt(CN) ₄ ·3H ₂ O	—	3.5	1.31	5×10^{-7}	10^{-5}
Pt	—	2.77	1.39	9.4×10^4	9.4×10^4
<i>Sulphur-nitrogen polymer</i>					
(SN) _x polymer	brass	—	1.05	$\sim 1.7 \times 10^3$	
Hg _{2.86} AsF ₆	Alchemists' gold	2.84	1.5	8×10^3	
Ni _{0.25} Pt ₃ O ₄	—	2.80	1.31	3×10^3	1.8×10^4
Ir(CO) _{2.98} Cl _{1.07}	—	2.85	1.33	0.2	1.87

^a σ^* calculated for a single strand.

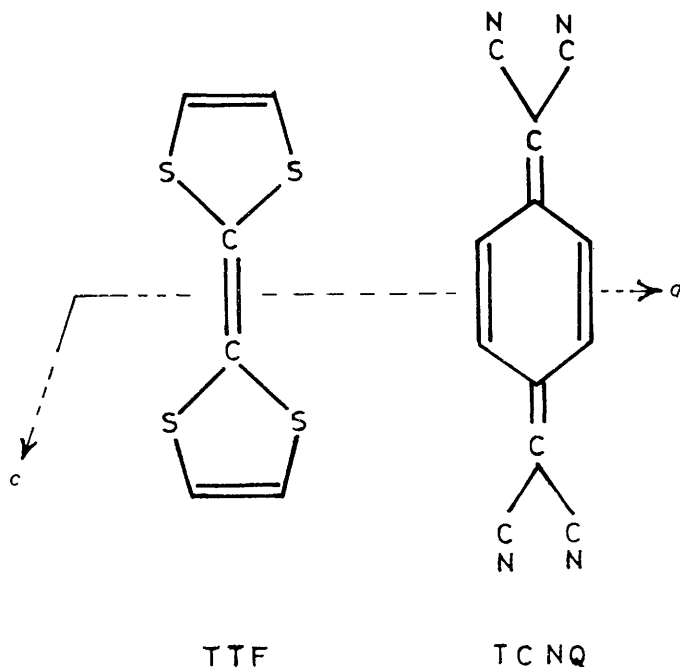


Figure 1 Simplified sketch of TTF and TCNQ molecules arranged according to the position of their ions in the crystal lattice. The planar TCNQ⁻ ions are stacked face to face in linear chains (emerging out of plane of the paper along the *c*-axis) separated by similar chains of TTF⁻ ions

tacular and the conductivity above 60 K seemed to approach values of the order of $10^6 \Omega^{-1} \text{cm}^{-1}$, comparable with copper at room temperature. This result caused quite a stir in the scientific community. Below 60 K, however, the conductivity decreases and the solid behaves as a semiconductor. We shall return to this point later. In the case of KCP(Br) there is a change in the slope of the conductivity curve at 120 K. The sulphur-nitrogen polymer on the other hand remains metallic below liquid helium temperatures and becomes superconducting at 0.33 K. This material is the first linear or polymeric system to be shown to be a superconductor, and it is certain that this result will have important consequences. The superconducting transition temperature does increase with pressure and has nearly doubled (0.54 K) in value by *ca.* 9 kbar.¹⁵

B. Optical Properties.—Further evidence for metallic behaviour along the chains comes from experiments on optical reflectivity and from n.m.r. spectroscopy, including measurements of Knight shifts, magnetic susceptibilities, and specific

¹⁵ W. D. Gill, R. L. Greene, G. B. Street, and W. A. Little, *Phys. Rev. Letters*, 1975, **35**, 1732.

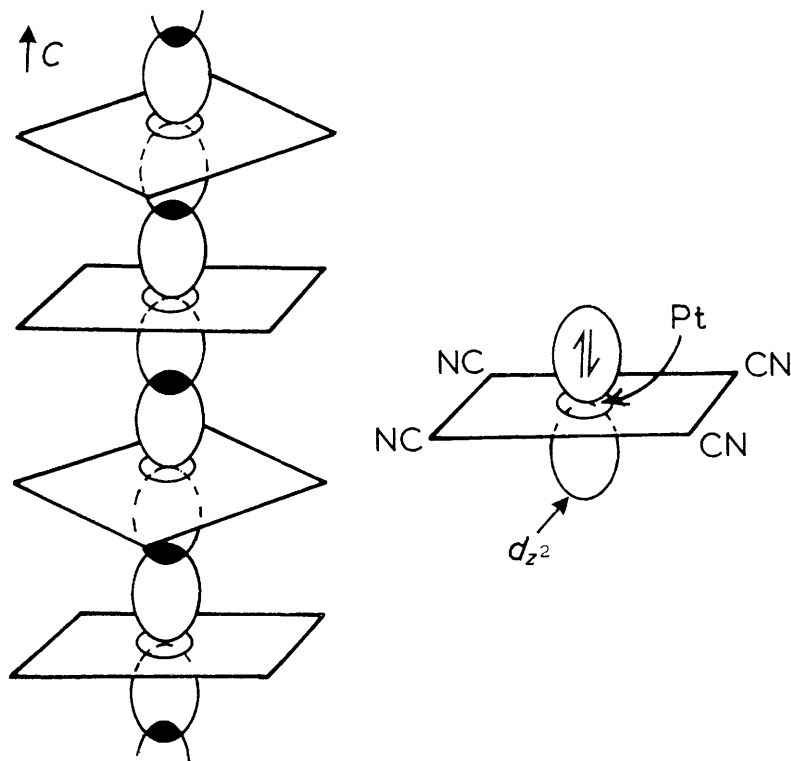


Figure 2 Idealized sketches of a $\text{Pt}(\text{CN})_4^{2-}$ group, and of the stacking of $\text{Pt}(\text{CN})_4^{2-}$ groups in a $\text{KCP}(\text{Br})$ crystal, showing the overlap of the d_z^2 atomic orbitals based on the Pt atoms. The CN groups are staggered to reduce Coulomb repulsion

heats. Figure 6 gives reflectivity spectra using polarized light.¹⁶ In all cases when the electric vector of the incident light is parallel to the chain direction, we find typical metallic (free carrier) reflection which can be described by the Drude theory, and from these results it is possible to obtain the dielectric constant, the electron relaxation time, and the plasma frequency. Perpendicular to the chains the solids behave as transparent dielectrics or semiconductors.

C. Peierls Distortions.—We have to ask why the conductivity of TTF-TCNQ, and less obviously KCP(Br), decreases at low temperatures (Figure 5), since the reverse is expected for metals. Many ideas have been put forward but the simplest is that we are concerned with a Peierls distortion of the lattice. The original idea of Peierls was simply that a one-dimensional solid with, for example,

¹⁶ For TTF-TCNQ see A. A. Bright, A. F. Garito, and A. J. Heeger, *Solid State Comm.*, 1973, 13, 943; for KCP(Br) see H. R. Zeller, ref. 6(a), p. 215; for $(\text{SN})_x$ see P. M. Grant, R. L. Greene, and G. B. Street, *Phys. Rev. Letters*, 1975, 35, 1743.

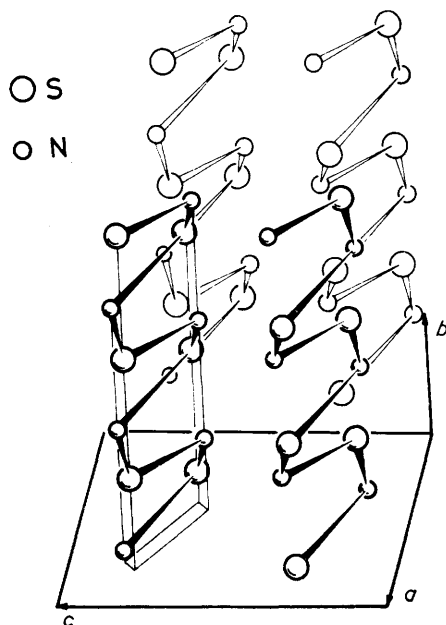


Figure 3 The structure of $(SN)_x$ showing parallel arrangement of the helical polymer strands (after Boudeulle¹⁴)

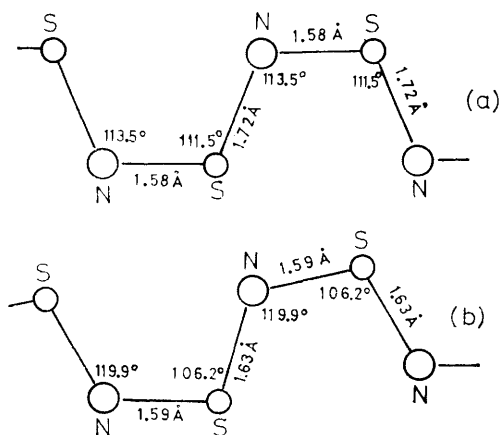


Figure 4 Representations of the two structures at present available for $(SN)_x$ showing bond lengths and bond angles [(a) after Boudeulle,¹⁴ (b) after MacDiarmid *et al.*¹⁴]

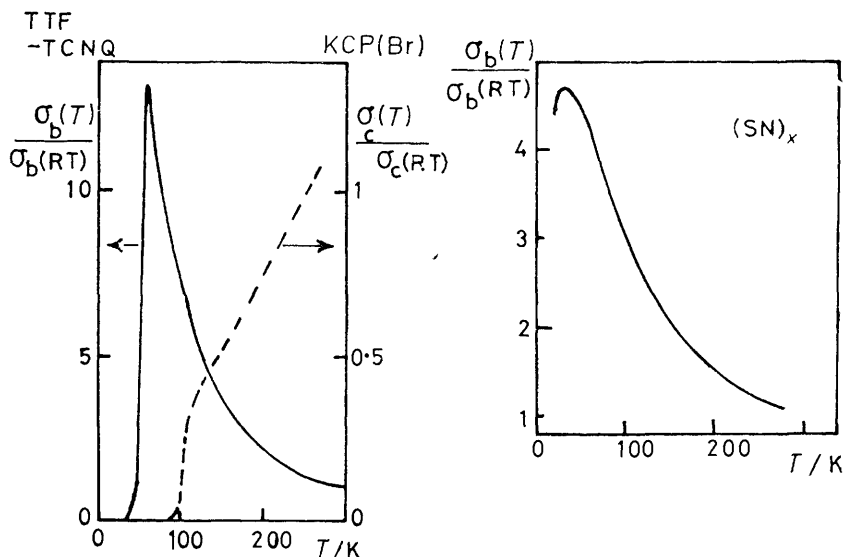


Figure 5 Temperature dependence of the electrical conductivity for single crystals, normalized to room temperature (RT). (Left) TTF-TCNQ, after Heeger and co-workers;⁶ and KCP(Br) after Zeller and co-workers.⁶ The change from metallic to semiconducting behaviour around the maximum on the curve is clearly seen for TTF-TCNQ. (Right) $(SN)_x$. This curve is for one of the better crystals, where $\sigma_{RT} = 1730 \Omega^{-1} \text{cm}^{-1}$. The crystal is metallic at all temperatures; (after V. V. Walatka, M. M. Labes, and J. H. Perlstein, *Phys. Rev. Letters*, 1973, **31**, 1139. See also G. B. Street, H. Arnal, W. D. Gill, P. M. Grant, and R. L. Greene, *Mater. Res. Bull.*, 1975, **10**, 877)

a half-filled energy band (*i.e.* a metal) would spontaneously undergo a transition to an insulator. The 'one-dimensional' solids are particularly prone to this kind of distortion. For a linear chain of equally spaced 'one-electron' atoms (*e.g.* H, Na, *etc.*) separated by a distance a , the simple energy band structure is as shown in Figure 7(a). We have a half-filled band and metallic behaviour. It is energetically favourable for the lattice to distort, for example in the manner shown in Figure 7(b), so that the unit cell doubles. This is equivalent to halving the Brillouin zone, and an energy gap is opened at the edge of the new zone for wave number $k = \pm\pi/2a$ in the manner discussed in elementary texts on solid-state physics and chemistry. All the occupied electron states are then in the lower energy band, while the upper band of higher energy contains only empty states. In this way there is a lowering of the kinetic energy of the electrons, but this must be set against an increase in elastic energy due to the structural distortion. It turns out that the balancing favours the opening up of a gap for quasi one-dimensional metallic systems and is probably still favourable for two-dimensional (layer-type) metals, but not for three-dimensional (normal) metals. In the discussion above the distortion leads to formation of a superlattice.

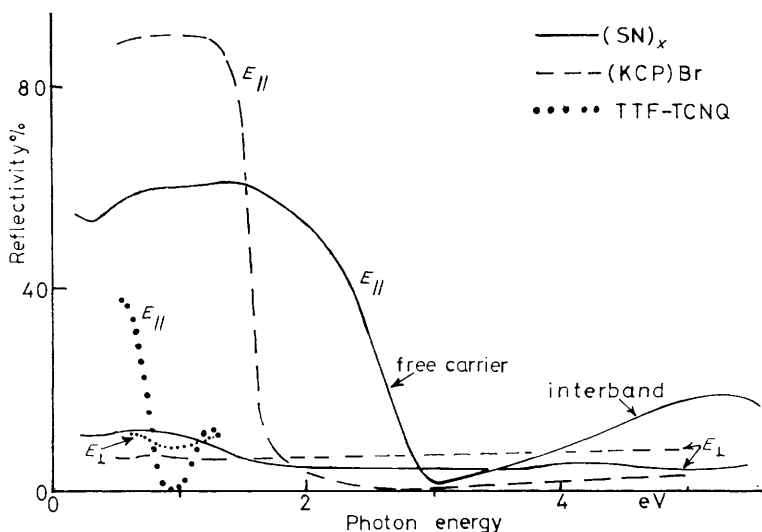


Figure 6 Reflectivity spectra from single crystals of TTF-TCNQ, KCP(Br), and $(\text{SN})_x$, using polarized light.¹⁶ When the electric vector of the incident light is parallel to the chains in the crystal ($E_{||}$) we see typical metallic free carrier reflection and interband transition regimes. For the other plane of polarization (E_{\perp}), the free carrier region is absent in this range of photon energies

When an energy gap opens up at the zone boundary, we have a small band gap semiconductor and a metal-semiconductor transition. The Peierls theorem suggests then that at the absolute zero a truly one-dimensional system will not be metallic. In Figure 7(c), which is another way of illustrating the Peierls distortion, we can see that the Brillouin zone boundary of the distorted insulating phase coincides with the wave vector k_F at the Fermi level of the undistorted metallic structure. In other words the new period in reciprocal space is now $2k_F$ along the chain direction. The new superlattice period is now $2\pi/2k_F$. This is also the wave vector where the Kohn type of anomaly¹⁷ involving soft phonon (vibrational) modes is expected.* In a sense the Kohn anomaly is a precursor of the Peierls distortion, since the phonons of wave vector $2k_F$ become increasingly soft as the temperature is lowered, until the static distortion or superlattice prevails. The experimental approach then is to look for a decrease or softening in the phonon frequency on cooling to temperatures where the Peierls distortion or metal-semiconductor transformation takes place. Many experiments on

*The 'Kohn anomaly' may be described theoretically as a singularity in the dielectric screening function and is observed experimentally as a softening (frequency $\omega \rightarrow 0$) of certain phonon modes q in a metal whose Fermi surface is just spanned by the wave vector q . See for example H. Rietschel, *Solid State Comm.*, 1973, 13, 1859.

¹⁷ See, for example, treatment by J. M. Ziman, in 'Principles of the Theory of Solids', 1965, Cambridge University Press, p. 129; also ref. 6(b).

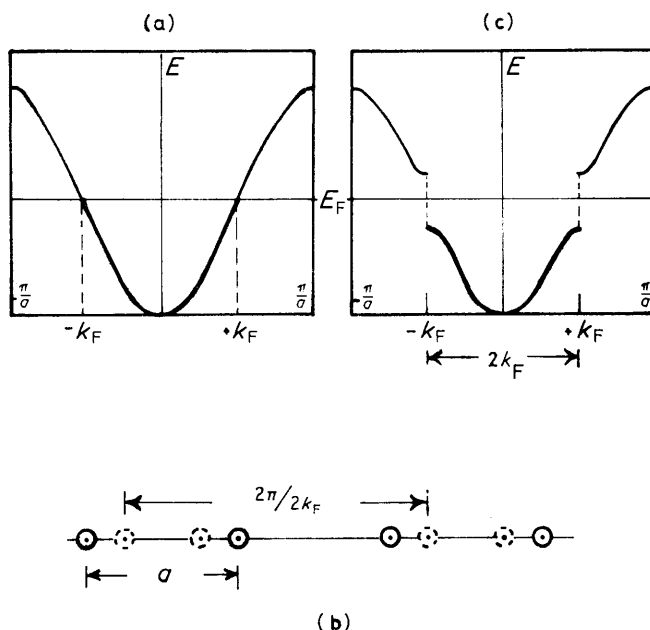


Figure 7 Energy (E) wave vector (k) diagrams for a linear chain of one-electron atoms separated by a distance ' a '. Figure 7(a) is for an undistorted chain resulting in a half-filled band, and the Fermi energy E_F is marked. When the lattice is distorted as shown in Figure 7(b) from the old, \circ , to the new \odot , positions, the unit cell now has a periodicity $2'a$ and a 'Peierls' gap opens up at $\pm k_F$, resulting in a small band gap semiconductor, Figure 4(c). The energy band for occupied states has been drawn as a thick line in both Figure 7(a) and Figure 7(c)

diffuse X-ray scattering and inelastic neutron scattering have shown that this does occur with KCP(Br), and that this material does go through a Peierls transition. On the other hand the evidence in the case of TTF-TCNQ is not conclusive.

Since KCP(Br) appears to be a good example of a solid in which a structural distortion leads to a small energy gap of the order of 0.2 eV, we look a little further into the electron energy scheme for this solid. This treatment is very qualitative, and in Figure 8 the energy bands are set out.¹⁸ The general ordering of the energy bands is surprisingly simple. In the simple $[\text{Pt}(\text{CN})_4]^{2+}$ system the crystal-field splitting of the d bands is such that the upper valence band is a full d band formed by the overlap of essentially d_{z^2} orbitals on the Pt atoms (d^2 configuration) along the chain direction, and this has been confirmed by e.p.r. measurements. The conduction band, which is empty, is thought to come from the overlap of metal p_z orbitals. The introduction of Br atoms to give KCP(Br),

¹⁸ M. J. Minot and J. H. Perlstein, *Phys. Rev. Letters*, 1971, **26**, 371.

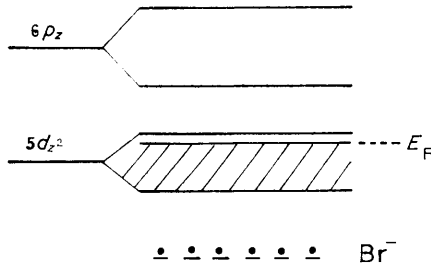


Figure 8 Simplified sketch of energy bands near the Fermi level E_F for KCP(Br). The relevant metal (Pt) atomic orbitals forming the bands are shown on the left. The Br^- energy lies below the d_z^2 band. As a result of the removal of electrons the d_z^2 band is roughly $5/6$ full, giving a 'hole' type metal

with one Br atom for every three Pt atoms, results in the removal of electrons from the ' d_z^2 ' band so that it is now only $5/6$ full (assuming 1.7 electrons per Pt atom). Since the band is now only partly filled, the solid is now a metal. The Fermi wave vector k_F now is $k_F = 0.85 \pi/c$, and the Peierls theorem suggests that an energy gap should open up at this wave vector and a superlattice should be formed. Experiments have shown that the energy gap $2\Delta \simeq 0.2$ eV and that the lattice distortion has a periodicity of 6–7 Pt atoms as predicted. The band scheme outlined in Figure 8 is very diagrammatic and elementary and there have been attempts to map out reliable band structures for KCP(Br).¹⁹ There are, however, problems associated with the structure of KCP(Br) and it would appear that this is not as simple as was originally supposed.

The treatment of the results associated with the Peierls distortion has also been simplified. There are in fact a number of associated phenomena connected with the regime where the semiconductor–metal transformation takes place, and where the transport properties as a function of temperature are anomalous. These phenomena include Kohn anomalies, charge-density waves of the kind postulated by Overhauser in 1968²⁰ involving dynamic lattice distortions which are connected with a divergence in the static dielectric functions of the electronic system at some wave vector, and Fröhlich-type superconductivity²¹ where because of strong electron–phonon interaction an ideal one-dimensional system can become superconducting in the Peierls distorted condition. In this situation superconductivity is thought to be due to travelling lattice waves (electrons + phonons) rather than electron pairs as in the normal Bardeen–Cooper–Schrieffer (BCS) theory. These topics, however, would require lengthy treatment and this is not possible in this review. Another factor which is important is the presence

¹⁹ D. M. Whitmore, *Phys. Letters (A)*, 1974, **50**, 55; L. Fritsche and M. Rafat-Mehr, ref. 6(b), p. 97; K. P. Messmer and D. R. Salahub, *Phys. Rev. Letters*, 1975, **35**, 533.

²⁰ A. W. Overhauser, *Phys. Rev.*, 1968, **167**, 691; *Phys. Rev. (B)*, 1971, **3**, 3173.

²¹ H. Fröhlich, *Proc. Roy. Soc.*, 1954, **A223**, 296; C. Mavroyannis, *J. Low Temp. Phys.*, 1975, **20**, 285.

of defects, for example interrupted strands in the crystal, which can introduce the problem of disorder into the system.

There is fairly good evidence for a Peierls-type distortion in KCP(Br). The situation for TTF-TCNQ is somewhat confused, and there is no clear evidence from structural work for such a distortion. It has been argued that a two-chain model is appropriate for this material. There are two separate potentially conducting chains and it is thought that above 60 K the TTF⁺ chains are metallic but the TCNQ⁻ chains remain insulating in some kind of Peierls state. Below 60 K where the transition from a metal to a semiconductor takes place there is strong interchain coupling and as a result of this interaction the solid will behave more as a three-dimensional system with a small energy gap developing. These conclusions are, however, speculative and reliable band structures are required. Some progress has been made in this direction.²² The electron energy bands which arise from the overlap of π -electron wavefunctions of nearest neighbours in the stacks of anion and cation radicals give a conduction band which can be thought of as a π -electron-type system with a bandwidth of 0.5 eV.

One interesting development in the synthesis of organic charge-transfer complexes has been the preparation of HMTSF-TCNQ (see Table 1; HMTSF = hexamethylene-1,4,5,8-tetraselenafulvalene) by Bloch *et al.*²³ This solid remains metallic even below 1 K, although superconductivity has not yet been found. It shows, however, that it is possible to synthesize organic solids which are pseudo one-dimensional but which resist Peierls-type distortions. The possibility remains that an organic solid will be synthesized which is a superconductor in the spirit of the Little theory.

D. Band Structure of (SN)_x Polymer.—It is fortunate that (SN)_x polymer crystals are metals even at low temperatures and do become superconducting at *ca.* 0.3 K. On the application of hydrostatic pressure in the region of 9 kbar the transition temperature is doubled. There have been speculations as to why this material does not undergo a Peierls distortion. No less than six band structures are now available.²⁴ Broadly speaking these can be classified into two groups. One of these considers a single chain of the (SN)_x polymer as a metal. From the helical structure and stacking of the SN groups in the unit cell it is shown that *two overlapping bands* cross the Fermi level. Perturbation theory can then be used to derive a three-dimensional band structure, since the chains are thought to be weakly coupled in the sense that they are linked by van der Waals' forces. Observation of crystals of (SN)_x in a high-resolution scanning electron micro-

²² I. P. Batra, B. I. Bennett, and F. Herman, *Phys. Rev. (B)*, 1975, **11**, 4927; G. Stollhoff, ref. 6(b), p. 257.

²³ A. N. Bloch, D. O. Cowan, K. Bechgaard, R. E. Pyle, R. H. Banks, and T. O. Poehler, *Phys. Rev. Letters*, 1975, **34**, 1561.

²⁴ (a) D. M. Parry and J. M. Thomas, *J. Phys. (C)*, 1975, **8**, L45; (b) W. I. Friesen, A. J. Berlinsky, B. Bergerson, L. Weiler, and T. M. Rice, *J. Phys. (C)*, 1975, **8**, 3549; (c) V. T. Rajan and L. M. Falicov, *Phys. Rev. (B)*, 1975, **12**, 1240; (d) H. Kamimura, A. M. Glazer, A. J. Grant, Y. Natsume, M. Schreiber, and A. D. Yoffe, *J. Phys. (C)*, 1976, **9**, 291; (e) M. Schlüter, J. R. Chelikowsky, and M. L. Cohen, *Phys. Rev. Letters*, 1975, **35**, 869; W. E. Rudge and P. M. Grant, *Phys. Rev. Letters*, 1975, **35**, 1799.

scope clearly shows the fibre-like character of the crystals and the fibres are readily separated. The dispersion of the energy levels in a direction perpendicular to the chains is therefore small. One such band structure and a sketch of one of the Fermi surfaces are shown in Figure 9. In the one-dimensional model there are two values for the Fermi wave vector k_F which are not a simple fraction of π/b , although $k_{F_1} + k_{F_2} = \pi/b$ and it is suggested that this is a possible reason for the absence of a Peierls distortion. There are of course other possible explanations. This band structure is consistent with the pronounced anisotropy in the electrical, optical, and mechanical properties.

In the second approach the proposed band structure for a single chain shows a degeneracy at the edge of the Brillouin zone in the manner well known for graphite, and the solid should be a semi-metal. However, for a single chain the system would undergo a Peierls distortion which would lift this degeneracy to form a semiconductor. It is argued that this does not happen because of the strong three-dimensional character of the solid. Essentially the difference between the two models is the degree of s - p mixing. Small s - p mixing gives two overlapping conduction bands. Strong s - p mixing results in the complete separation of the two bands giving the single conduction band of the second model. Only time will tell which of these two approaches is correct.

E. Conclusion.—The most important development in the work on metallic chain-like solids has been the synthesis of materials which do not undergo Peierls distortions at low temperatures. These include the organic charge-transfer solids such as HMTSF-TCNQ and the inorganic polymer $(\text{SN})_x$, which is a superconductor. There are other possibilities including the use of odd alternant hydrocarbons,²⁵ and the synthesis of new organic and inorganic polymers. For example, it should be possible to replace sulphur and nitrogen by different atoms in $(\text{SN})_x$ polymer. The electrical conductivity of $(\text{SN})_x$ can also be modified by the addition of electron donors and acceptors to give intercalates.²⁶ It is already known that acceptors such as the halogens (Cl_2 , Br_2 , I_2) increase the electrical conductivity in a temporary fashion. What is clear is that a good deal of interesting and important physics and chemistry is coming out of this work, and many challenging problems remain to be solved. Some of these are concerned with the anisotropy of the crystals, with the mechanism of electron conduction and superconductivity along and normal to the chains, and with the metal-non-metal transformation often seen at low temperatures.

2 Layer Compounds: Pseudo Two-dimensional Systems

It is impossible in a review of this length to discuss all layer-type solids, and in this section we will concentrate on the transition-metal dichalcogenides having the general formula MX_2 . However, many of the phenomena to be discussed are common to the other layer materials as well. We also restrict the discussion to compounds formed from the metals M belonging to the Groups IV, V, and

²⁵ R. C. Haddon, *Nature*, 1975, **256**, 394.

²⁶ F. Levy, 1975, unpublished results, Cambridge.

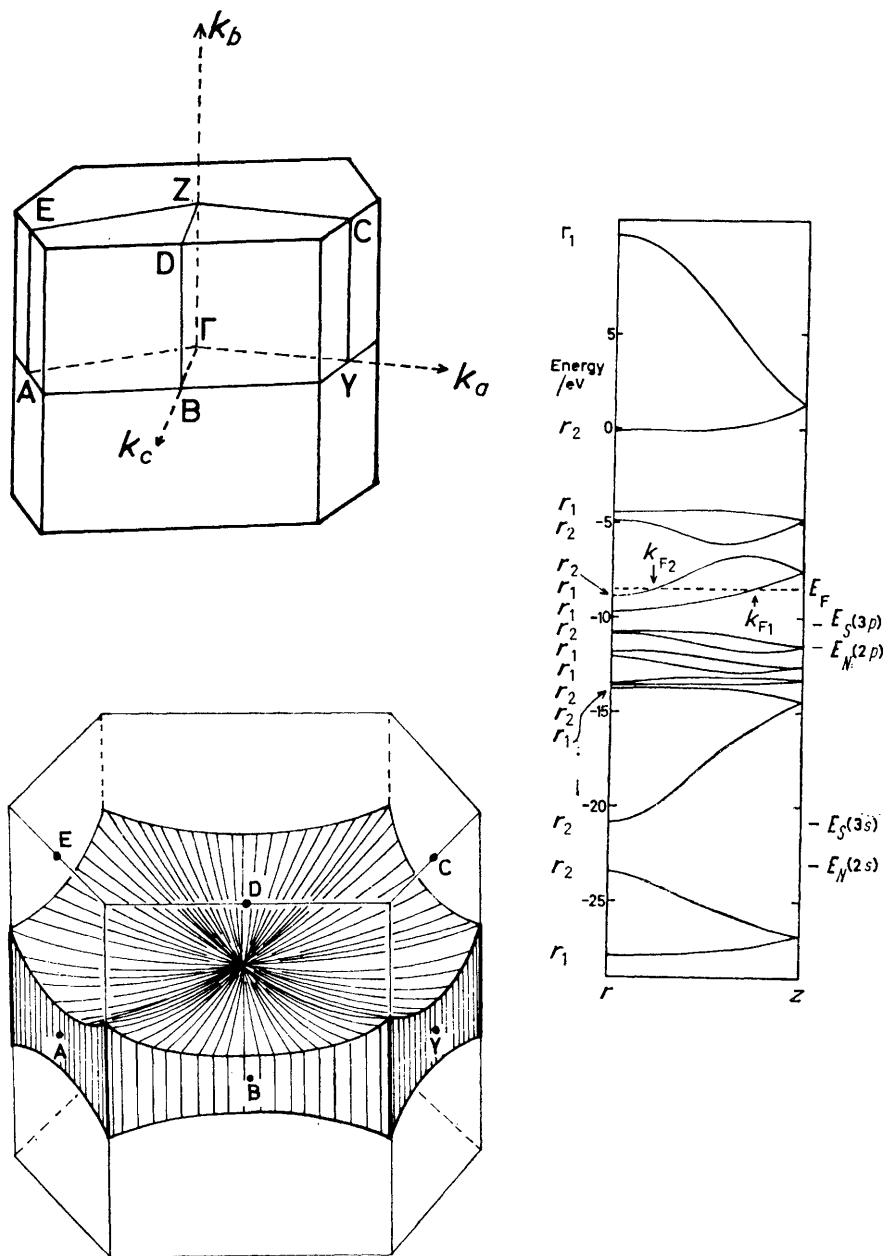


Figure 9 (Above left) The Brillouin zone of $(SN)_x$ polymer corresponding to the primitive monoclinic Bravais lattice. (Right) The calculated energy band scheme for a single chain of SN polymer, showing the two Fermi wave vectors k_{F1} and k_{F2} for the two conduction bands. This model predicts metallic behaviour for a single chain at all temperatures. (Below left) A possible three-dimensional Fermi surface for the upper conduction band of $(SN)_x$ for a three-dimensional band structure. The shape is biconcave. This model assumes weak interaction between chains in the three-dimensional band structure calculations

VI elements Ti, Zr, Hf; (V) Nb, Ta; (Cr) Mo, W; and with X = S, Se, or Te. Typical materials would then be ZrS_2 , $NbSe_2$, and MoS_2 . The dichalcogenides formed from other transition metals often form distorted structures within the layers and their properties can be more complicated.

It turns out that the most interesting features of these materials are associated with the 'd' bands, and to determine the electron energy levels it is necessary to make measurements on the various optical and electrical properties.

A material such as MoS_2 with a layer structure can be cleaved to give very thin crystals and it is relatively easy to obtain crystals several hundred Ångströms thick over quite large areas. Frindt has in fact made measurements on crystals a unit cell thick which is of the order of 12 Å and this corresponds to two layers.²⁷ Cleavage of the crystals along the layers takes place between sheets of sulphur atoms which are held together only by weak van der Waals' forces, and the structure for MoS_2 is based on the trigonal-prism configuration as shown in Figure 10. The other configuration frequently met is octahedral, for example with the Group IV compounds ZrS_2 and HfS_2 and with some members of the Group V compounds such as 1T-TaS₂.

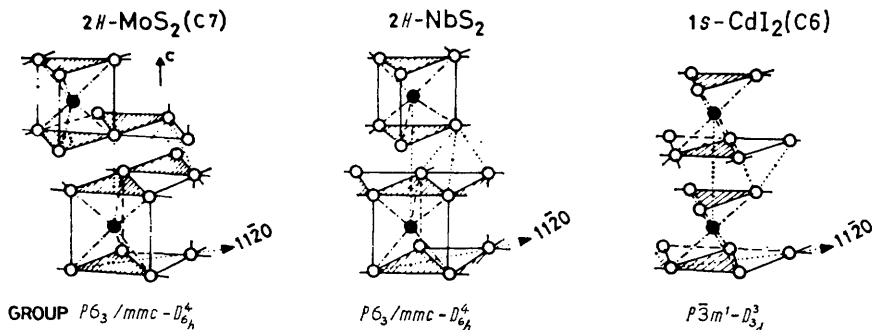


Figure 10 Stacking arrangement for 2H- MoS_2 , 2H- NbS_2 , and CdI_2 (equivalent to ZrS_2 and 1T-TaS₂) layer polytypes

A. Optical Properties and Band Structure.—The apparatus used to measure optical absorption in transmission is fairly straightforward. It is also possible to work in reflection, and the various polarization dependences are shown in Figure 11. The kind of optical absorption spectrum obtained for MoS_2 at helium temperatures in the visible and ultraviolet when the electric vector of the incident light is parallel to the layers ($E \perp c$) is shown in Figure 12. There is a good deal of structure here and this is used to build up a model of the electron energy levels. Peaks A and B are ground-state exciton peaks, and on careful examination of the spectra it is possible to see the higher-order excitons as well.*

*Excitons in solids are excited states which result from the Coulomb interaction between electrons and holes, analogous to a hydrogen atom. The excitation can be produced by the absorption in the solid of a photon of appropriate energy, usually just less than the band gap.

²⁷ R. F. Frindt, *J. Appl. Phys.*, 1966, 37, 1928.

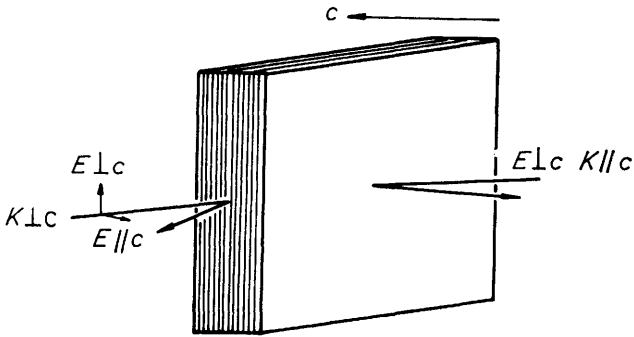


Figure 11 Schematic diagram showing the three possible configurations of polarization and incident directions for normal incident reflectivity of light

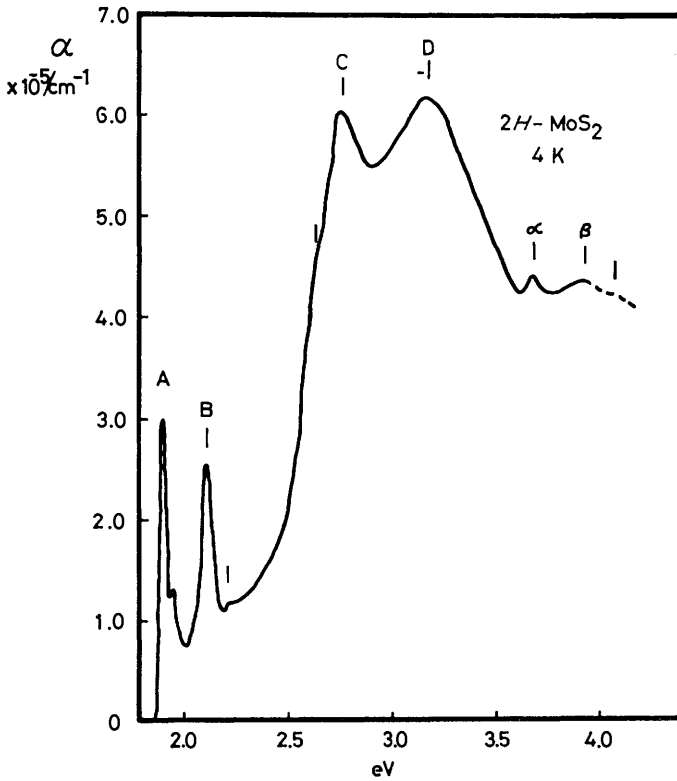


Figure 12 Transmission spectrum of $2H-MoS_2$ at 4 K showing the strong exciton peaks A and B

These are seen more clearly in modulation experiments. The excitons are delocalized or Mott-Wannier-type excitons with a binding energy for the ground state of the order of 0.05 eV. The effective Bohr radius of the ground-state exciton ($n = 1$) is of the order of 30 Å, while for $n = 2$ it is in the region of 120 Å. This is quite large and can become comparable with the thickness of some of the crystals used, and as will be shown later this can have some interesting effects.

There is now detailed information available from a wide variety of optical and electrical measurements. These include the use of synchrotron radiation, photoemission (both u.v. and X-ray photoelectron spectroscopy and angular-dependent photoelectron spectroscopy), and electron energy loss measurements. Using these results it is possible to propose an electron energy band scheme for the Group IV, V, and VI compounds and this is shown in Figure 13.

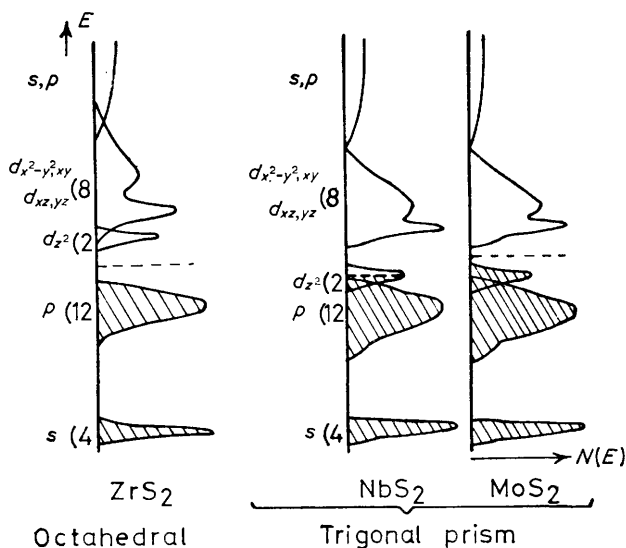


Figure 13 Suggested schemes for the electron energy (E) versus density of states $N(E)$, for the Group VI (MoS_2), Group V (NbS_2), and Group IV (ZrS_2) transition-metal dichalcogenides. The atomic orbitals involved in the bands are listed, and the number of electron states per band is given. Undistorted $1T\text{-TaS}_2$ would have a scheme similar to ZrS_2 but with the d_{z^2} band half filled, but the presence of superlattices causes minor changes to the energy bands and the Fermi surface

For the Group VI compounds we have a full d_{z^2} band formed by the overlap of essentially d_{z^2} orbitals based on the Mo atoms within the layers, and we obtain a semiconductor with a band gap of the order of 1 eV. Moving down to the Group V compounds with a d^1 configuration on the metal atom, the d_{z^2} band is now half filled, giving a metal and a superconductor. For NbSe_2 the transition temperature for superconductivity is 7.3 K. There are similarities

between these systems and the chain compound KCP(Br) since in both the conduction band is based on the d_{z^2} orbitals. For the Group IV compounds with a d^0 configuration on the metal atoms, the d_{z^2} band is now empty and we again have semiconductors or insulators with many interesting electrical properties. Because the co-ordination is octahedral for the Group IV dichalcogenides the crystal-field splittings will be somewhat different from those of the Group V and VI compounds with trigonal-prism co-ordination.

These model band structures are idealized representations. There will be mixing of the orbitals forming the bands, and layer-layer interactions are important. Fairly reliable band structures are now available for many of the transition-metal dichalcogenides,²⁸ and in the case of the metals such as NbSe₂ and TaS₂ the shape of the Fermi surface has been calculated (see Figure 14).

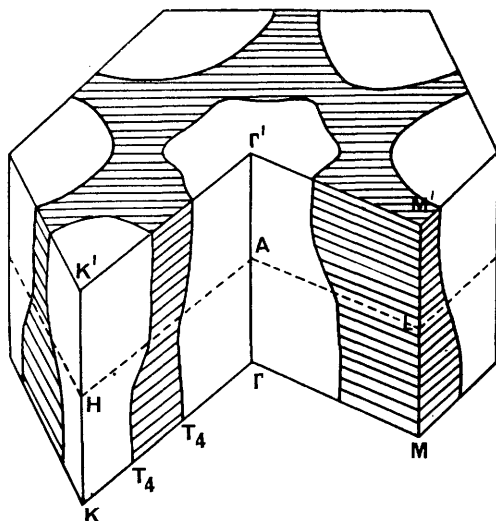


Figure 14 Schematic representation of the Fermi surface of $2H\text{-NbSe}_2$ unfolded into the double Brillouin zone. The shaded sections are electron-occupied states. A hole 'barrel shaped' Fermi surface is apparent along the centre of the zone $\Gamma A \Gamma'$. The narrow necking regions are also important for considering possible Kohn anomalies, Peierls distortions, and charge density waves (after Wexler and Wooley²⁸)

It turns out, however, that the overall ordering of the energy bands is not very different from those shown in Figure 13, and for the purposes of this review these model band structures will be sufficient.

B. Excitons and Screening.—Both experimental and theoretical work has been carried out concerning the anisotropy of the excitons (orbits, dielectric constants,

²⁸ See, for example, L. F. Mattheiss, *Phys. Rev. (B)*, 1973, **8**, 3719; G. Wexler and A. M. Wooley, *J. Phys. (C)*, 1976, in press.

and effective masses) and whether the excitons should be considered as two- or three-dimensional excitations. The effect of crystal thickness on exciton energies has also been considered. Using a particle-in-the-box idea it can be argued that the energy of the excitons should increase as the thickness is decreased, and this dependence should go as the inverse of the square of the crystal thickness. In addition, as the crystal thickness is reduced, scattering of the excitons at the surface should result in the disappearance of the higher-order excitons. Both these effects have been observed. Figure 15 shows results obtained by Frindt

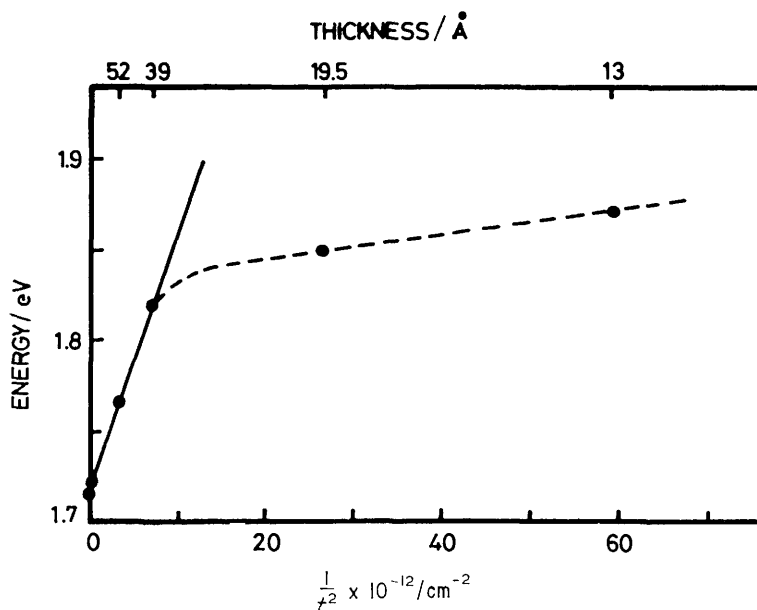


Figure 15 Variation in the energy of the ground-state exciton with crystal thickness (t) for WSe_2 (after Consadori and Frindt²⁹)

for WS_2 where the relation is linear down to a thickness in the region of 40 Å. Below this there is an unsurprising departure from a straight line.²⁹

It is also possible to observe and follow experimentally the screening of excitons by free carriers. If a semiconductor such as WS_2 which has sharp exciton features at low temperatures similar to those shown in Figure 12 contains impurity atoms of Nb or Na, then free carriers (holes or electrons) are present and these screen out the electron-hole interactions which normally give rise to excitons. This is an example of Thomas-Fermi screening. As a result the excitons are no longer stable and the sharp features in the spectra disappear. This phenomenon is associated with the metal-insulator transition.

²⁹ F. Consadori and R. F. Frindt, *Phys. Rev. (B)*, 1970, 2, 4893.

C. Metal–Non-metal Transformation in $1T$ -TaS₂.—A Group V metal dichalcogenide such as TaS₂ is a metal and a superconductor when the structure is based on the trigonal-prism configuration (see Figure 10). It is also possible to prepare crystals of TaS₂ with the octahedral co-ordination, $1T$ -TaS₂, and in the undistorted structure this compound should also be a metal, having a half-filled 'd' band. The electrical measurements on $1T$ -TaS₂, however, show very unusual behaviour when the temperature³⁰ or pressure is varied. A resistance–temperature plot is shown in Figure 16. Above 350 K (region $1T_1$) we have the

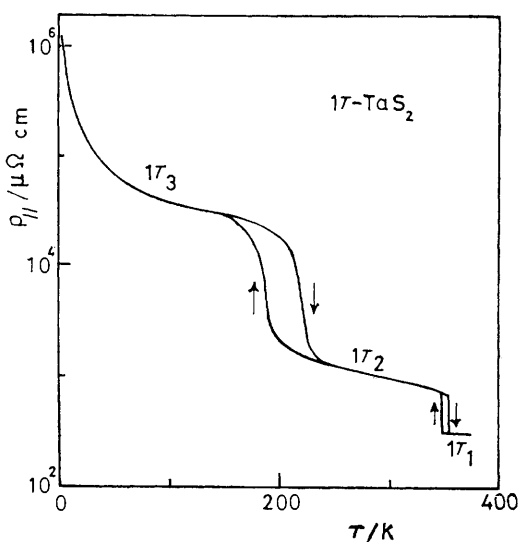


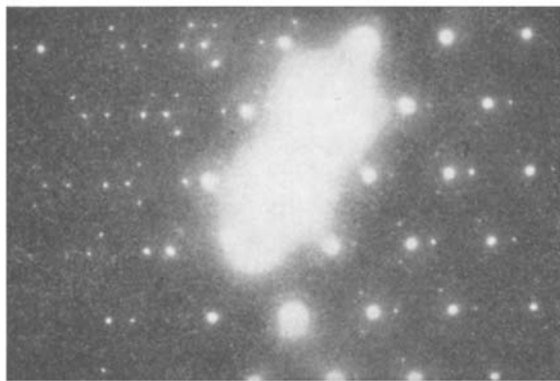
Figure 16 Resistivity versus temperature plot for $1T$ -TaS₂, showing the three regimes, $1T_1$, $1T_2$, and $1T_3$ (after Tidman and Frindt³⁰)

lowest resistivity (apparent metallic behaviour) with a discontinuous 50% increase at 350 K to the $1T_2$ region. Here the resistivity–temperature slope resembles that for a semiconductor, but the magnitude of the conductivity corresponds to a semi-metal or a poor metal. On further cooling to 190 K another discontinuity (with hysteresis) to the semiconducting $1T_3$ form can be seen. Careful electron diffraction (Figure 17),³¹ X-ray diffraction, and neutron diffraction measurements³² on this material as a function of temperature have led to a possible interpretation of these results in terms of charge-density waves.

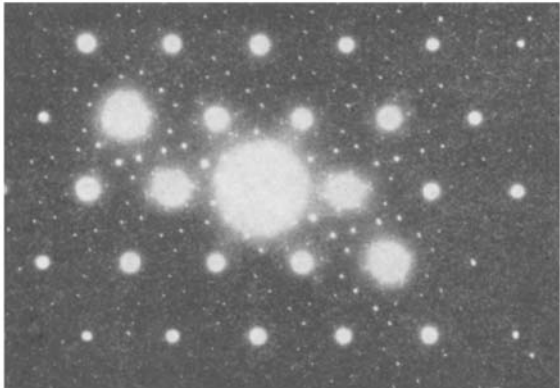
³⁰ A. H. Thompson, F. R. Gamble, and J. F. Revelli, *Solid State Comm.*, 1971, 9, 981; J. P. Tidman and R. F. Frindt, 1975, to be published.

³¹ J. A. Wilson, F. J. Di Salvo, and S. Mahajan, *Adv. Phys.*, 1975, 24, 117; P. M. Williams, G. S. Parry, and C. B. Scruby, *Phil. Mag.*, 1974, 29, 695; 1975, 31, 255.

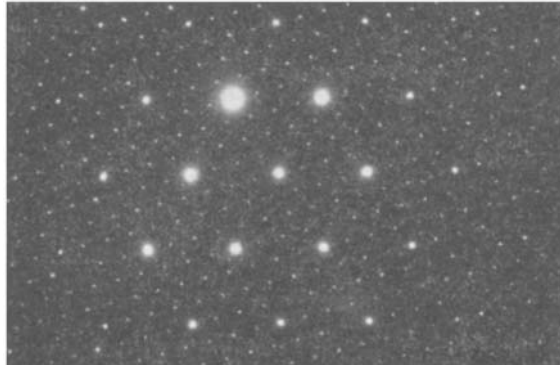
³² See analogous experiments by D. E. Moncton, J. D. Axe, and F. J. Di Salvo, *Phys. Rev. Letters*, 1975, 34, 734, and unpublished work.



400K
1T₁



295K
1T₂
1T-TaS₂



140K
1T₃

Figure 17 Transmission electron diffraction patterns for the three different temperature regimes shown in Figure 16. The pattern in the 1T₃ regime corresponds to an incommensurate charge-density wave, but on passing to the 1T₂ regime there is a first-order transition and the period changes to being commensurate with the lattice (after Williams, Parry, and Scruby⁵¹)

This concept was developed in 1968 by Overhauser and we have already referred to it in the section on chain materials. A charge-density wave can be a lower energy state and is a sinusoidal variation in the electron density with a certain wave vector. This can result in a Coulomb attraction between the regions of electron concentration built up by the charge-density wave and the ions in the lattice, and a periodic structural distortion of the lattice is formed which has the same wave vector as the charge-density wave. This is a kind of superlattice. The periodicity of the charge-density wave, however, can be shown to be determined by the shape of the Fermi surface of the metal, and there does not need to be a simple relation between the distortion and the periodicity of the underlying lattice. It can be incommensurate with the lattice. Referring to Figure 6, for $1T$ -TaS₂ in the $1T_1$ phase the distortions are not seen at all and we have the most metallic-like state. As the crystal is cooled to the $1T_2$ phase, the incommensurate distortions appear, while in the $1T_3$ phase, the superlattice wave vector has become a commensurate multiple* of the reciprocal lattice vector, and the crystal then forms a commensurate superlattice. When a commensurate superlattice is formed small energy gaps open up in certain regions of the Fermi surface and these no longer contribute to metallic conductivity. In this way it is possible to interpret the curves shown in Figure 16 in terms of a decrease in the extent of the Fermi surface. This behaviour is not unlike that discussed under Peierls distortions in 'one-dimensional' systems where we considered metal-insulator transitions. Peierls distortions were originally used only in discussions of one-dimensional systems, and for commensurate superlattices. The arguments used were based on energetic grounds in terms of a lowering of the electron kinetic energy *versus* expenditure of strain energy. The other approach of Overhauser based on charge-density waves comes from electronic considerations in which a many-body formalism is developed. The periodic lattice distortion follows formation of the charge-density waves, but it is also necessary to have strong electron-phonon coupling. The theory can predict the nature of the superlattice whether incommensurate or commensurate, once the detailed shape of the Fermi surface for the undistorted lattice is known, and to some is the more satisfying approach. There is thus a strong inter-relation between charge-density waves (and spin-density waves), soft phonon modes, Kohn anomalies, and Peierls distortions.

These experiments have provided the strongest direct evidence of charge-density waves, and they have led to considerable interest in their possible role in other phenomena, for example in superconductivity.

D. Transport and Superconducting Properties.— $2H$ -NbSe₂ is a metal and a type 2 superconductor with a transition temperature T_c in the region of 7.3 K. Many

*The superlattice wave vectors for a commensurate superlattice in the case of the 'one-dimensional' solids are integral multiples of the reciprocal lattice vectors, for example a two-times superlattice. For 'two-dimensional' systems the situation is different. For $1T$ -TaS₂ at low temperatures the commensurate superlattice is $\sqrt{13}$ by $\sqrt{13}$ times the reciprocal lattice vector. For $2H$ -NbSe₂ it is nearly 3×3 . The reason for this is that in the layer-type solids the superlattice wave vector may be in a different direction than the reciprocal lattice vector.

experiments have been made to determine the effect of magnetic fields on T_c with the field perpendicular and parallel to the layers, and on the superconducting energy gaps by i.r. and tunnelling measurements. In the early work on $2H-NbSe_2$, $2H-TaS_2$, and $2H-TaSe_2$, the resistivity, magnetic susceptibility, and Hall constant behaved in an unusual way³³ as the crystal was cooled to temperatures approaching T_c (Figure 18). For example, on cooling, the Hall constant changed

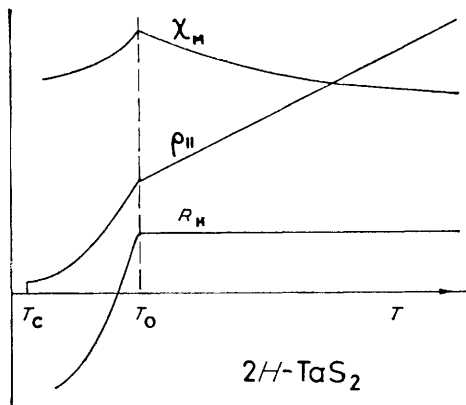


Figure 18 Idealized sketch of results analogous to those obtained by Lee et al.³³ for the Hall coefficient R_H , the resistivity ρ , and magnetic susceptibility χ , for crystals of $2H-TaS_2$. Anomalous behaviour takes place at temperatures below that shown by the dotted line. T_c is the superconducting transition temperature, T_0 is the onset temperature for the charge-density wave

sign from positive (hole conduction) to negative (electron conduction) and the conductivity deviated from linear behaviour. More recently it has been shown that in $2H-NbSe_2$ there are anomalies in the heat capacity³⁴ at the same temperature as the start of the Hall reversal and the departures from linear behaviour in resistivity with temperature, around 32 K. Again careful electron diffraction and neutron diffraction measurements show the formation of superlattice distortions for $NbSe_2$.³⁵ The superlattice is approximately 3×3 but is not quite commensurate with the lattice. A number of suggestions have been made to explain these results. One argument is that the anomalies in the transport and heat capacity measurements result from the stabilization of an incommensurate charge-density wave at around 35 K. When the charge-density wave is formed, however, it has only a minor effect on the shape of the Fermi surface and for this reason the anomalies in the electrical conductivity are of a minor character. The

³³ See H. W. S. Lee, M. Garcia, H. McKinzie, and A. Wold, *J. Solid State Chem.*, 1970, 1, 190.

³⁴ J. M. E. Harper, T. H. Gaballe, and F. J. Di Salvo, *Phys. Letters*, 1975, 54A, 27.

³⁵ P. M. Williams, C. B. Scruby, and G. Tatlock, *Solid State Comm.*, 1975, 17, 1197; also the chapter by P. M. Williams on charge-density waves in the series edited by E. Mooser (see ref. 10).

other argument is based simply on lattice contraction and the effect on the details of the 'd' band formation. There are similarities in the fluctuations seen in the transport properties of 2H-NbSe₂ and 2H-TaSe₂ and many of the chain-like solids already discussed.

Charge-density waves have also been shown to have an important bearing on the superconducting properties of NbSe₂ and NbS₂. In particular the magnitude of the pressure dependence of the superconducting transition temperature appears to be directly related to presence of a superlattice.³⁶ In NbSe₂, where a superlattice has been observed, the superconducting transition temperature increases with pressure from 7.3 to 9 K at ca. 30 kbar. It is thought that at this pressure the superlattice is no longer stable and the lattice reverts to the undistorted structure. At higher pressures the transition temperature does not vary appreciably with increase in pressure. Two important factors which can influence the superconducting transition temperature are the density of electron states at the Fermi level and the electron-phonon interaction. These pressure experiments suggest that the density of states is more important. The charge-density wave and the coupled superlattice will result in a reduction in the density of states at the Fermi level, in a manner analogous to that discussed for Peierls distortions. As the superlattice is eliminated by the application of pressure the density of states at the Fermi level will increase, resulting in an increase in T_c . These are speculations, however, and there is a need for experimental support for these ideas.

E. Intercalation with Organic and Inorganic Atoms and Molecules.—It has been known for some time that it is possible to introduce organic and inorganic molecules and atoms between the layers in a variety of layer-type solids. This is the process of intercalation. Perhaps the best documented are graphite³⁷ and the clays,³⁸ and more recently new materials have been synthesized by reaction of the constituent compounds following intercalation between the layers.³⁹ In the case of the transition-metal dichalcogenides, a number of research groups have been active in this field.⁴⁰ Essentially three different types of impurity have been studied in some detail. They can all be classified as electron donors, since there is no clear evidence that impurities which act as electron acceptors can be introduced in the van der Waals gap.

³⁶ P. Molinié, D. Jérôme, and A. J. Grant, *Phil. Mag.*, 1974, **30**, 1091; also J. Friedel, *J. de Phys.*, 1975, **36**, L279

³⁷ See, for example, W. Rüdorff and E. Schulze, *Z. anorg. Chem.*, 1954, **277**, 156; and also ref. 7.

³⁸ See, for example, R. E. Grimm, 'Clay Mineralogy', McGraw Hill, New York, 2nd edition, 1968; D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, and J. O. Williams, *J.C.S. Dalton*, 1974, **20**, 2207, 2211.

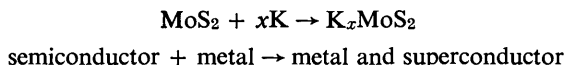
³⁹ See review by J. M. Thomas, *Phil. Trans. Roy. Soc.*, 1974, **277**, 751.

⁴⁰ See, for example, F. R. Gamble and T. H. Geballe, 'Solid State Chemistry Series', ed. N. B. Hannay, Plenum Press, New York, Vol. 3; R. Schöllhorn and A. Lurf, *J. Less Common Metals*, 1975, **42**, 89; J. V. Acrivos, *J. Phys. Chem.*, 1974, **78**, 2399; G. V. Subbarao, M. W. Shafer, and J. C. Tsang, *J. Phys. Chem.*, 1975, **79**, 553, 557; J. Cousseau, L. Trichet, and J. Rouxel, *Bull. Soc. chim. France*, 1973, 872.

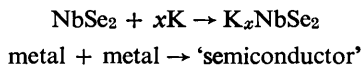
(i) *Organic molecules such as amines.* These are Lewis bases (electron donors) and include aniline, pyridine, cyclopropylamine, octadecylamine, and tetrathiofulvene. Some of this work has been reviewed by Gamble and Geballe. It is a relatively simple matter to intercalate a solid such as TaS₂ with an organic amine. The solid is introduced into the hot liquid or vapour, and the crystal can swell in a dramatic and spectacular way. The separation between the layers in some circumstances can reach values in the region of 60 Å, where the thickness of a single layer is only of the order of 6 Å. Figure 19 shows the probable orientation of some of the molecules with respect to the MX₂ layers and the position of the lone-electron pair on the nitrogen atom. There is, however, some controversy on this point.^{40a}

It is argued that some charge transfer takes place from the organic molecule to the host lattice although there is not complete agreement on this point. What is interesting is that these solids after intercalation remain superconductors, and it is tempting to argue that we are concerned here with superconductivity associated with the single layers themselves. There is some experimental support for this idea from experiments on superconductivity as a function of crystal thickness.⁴¹ However, a number of theoreticians are opposed to this view, and require that the superconductivity of the intercalated solid be truly three-dimensional.

(ii) *Alkali-metal and pseudo alkali-metal atoms.* Atoms such as Na, K, Rb, Cs, Ca, Sr, Ba, Ga, Ge, Cu, Ag, Sn, Pb, Hg (also Eu, Yb) can be introduced between the layers of solids such as MoS₂ or NbSe₂ from metal-ammonia solutions or by electrolysis. Another method is to use molten alkali halides. There is an increase in the 'c' spacing after intercalation and for the metal-ammonia solutions some ammonia also enters with the alkali-metal atoms. Ionization $K \rightarrow K^+ + e$ is more complete than for the organic molecules, and the intercalate K_xMoS₂ becomes metallic and a superconductor, with T_c for K_{0.4}MoS₂ being 6.5 K.⁴² In the system



we can follow the transformation from a semiconductor to a metal by optical⁴³ and electrical techniques. If we begin with 2H-NbSe₂, which is a metal, and intercalate with alkali-metal atoms then we find



to form a semiconductor. These findings can be readily explained if we look at the model given for the electron energy levels in Figure 13. Intercalation of

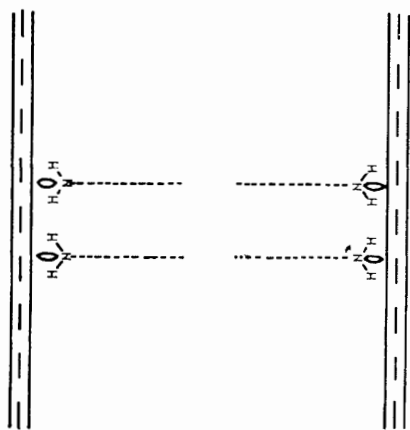
^{40a} F. R. Gamble and B. G. Silbernagel, *J. Chem. Phys.*, 1975, **53**, 2544.

⁴¹ R. F. Frindt, *Phys. Rev. Letters*, 1972, **28**, 299.

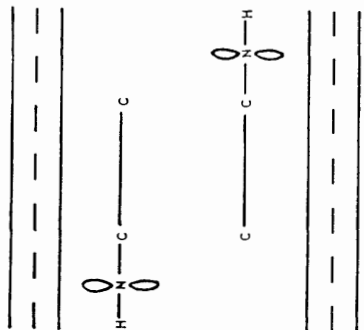
⁴² A. M. Hermann, R. Somoano, V. Hadek, and A. Rembaum, *Solid State Comm.*, 1973, **13**, 1065.

⁴³ J. V. Acrivos, W. Y. Liang, J. A. Wilson, and A. D. Yoffe, *J. Phys. (C)*, 1971, **4**, 418.

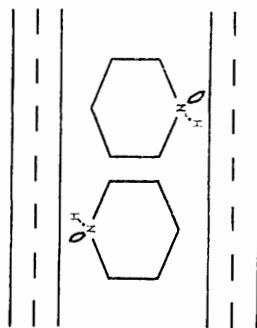
octadecylamine



aniline



piperidine



pyridine

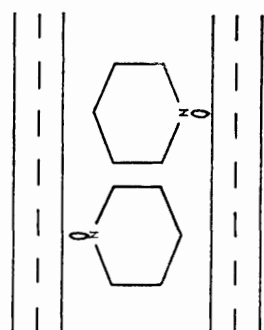


Figure 19 Probable orientation of organic molecules containing nitrogen with respect to the MX_2 layers after intercalation. The Figure also shows the position of the lone electron pair on the nitrogen atom

TaS₂ with hydrogen⁴⁴ gives H_xTaS₂ and with $x < 0.1$ T_c rises from 0.8 to 4.2 K. For the Group IV intercalate Li_{0.3}Ti_{1.1}S₂, T_c is fairly high in the region of 13 K.⁴⁵ Here T_c is the superconducting transition temperature.

New types of complex involve the use of the metallocenes of cobalt and chromium which appear to act as pseudo alkali metals,⁴⁶ and the orientation of the molecule between the layers is thought to be as shown in Figure 20. There

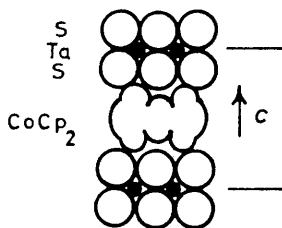


Figure 20 Sketch of an intercalation complex between a transition-metal dichalcogenide (e.g. TaS₂) and a metallocene (e.g. CoCp₂, where Cp is cyclopentadienyl).⁴⁶ The metallocene appears to act as a pseudo-alkali metal

have also been many studies on the complex molybdenum–sulphur systems⁴⁷ such as Pb_{0.5}Mo₃S₄, Pb_{1.0}Mo_{5.1}S₆, and SnPbMoS₅. These are not layer materials, but have very interesting properties. The superconducting transition temperatures are in the region of 13 K, but the critical fields $H_{C2}(0)$ can reach tremendous values in the region 500–700 kG, probably the highest yet attained. We can expect a good deal of activity on this topic.

(iii) *Transition-metal atoms.* Intercalates formed from the 3d transition-metal atoms Ti, V, Cr, Mn, Fe, Co, and Ni have many interesting magnetic properties. It has been shown by a number of investigators that compounds such as Mn_{1/3}NbSe₂ or Cr_{1/3}NbSe₂ are ferromagnetic at low temperatures.⁴⁸ The Mn and Cr sit in the van der Waals gap in specific sites, e.g. octahedral in the case of Cr_{1/3}NbSe₂. It is argued that the ferromagnetic coupling between the Cr³⁺ ions in the van der Waals gap is by superexchange through Cr–Se–Cr units, and by interaction with conduction electrons.

F. Conclusions.—The electronic properties of layer materials and their inter-

⁴⁴ D. W. Murphy, F. J. Di Salvo, G. W. Hull, J. W. Waszczak, S. F. Mayer, G. R. Stewart, S. Early, J. V. Acrivos, and T. H. Geballe, *J. Chem. Phys.*, 1975, **62**, 967.

⁴⁵ H. E. Burz, A. S. Cooper, E. Corenzwit, M. Marezio, B. T. Matthias, and P. H. Schmidt, *Science*, 1972, **175**, 884, 1465.

⁴⁶ M. B. Dines, *Science*, 1975, **188**, 1210.

⁴⁷ R. Odermatt, Q. Fischer, H. Jones, and G. Bongi, *J. Phys. (C)*, 1974, **7**, L13; S. Foner, E. J. McNiff, E. J. Alexander, *Phys. Letters*, 1974, **49A**, 269; B. T. Matthias, *I.E.E.E. Trans.*, 1975, **11** (magnetism volume), 154.

⁴⁸ See, for example, I. M. Verhoeve and R. C. Sherwood, *J. Phys. and Chem. Solids*, 1971, **32**, 167; J. Rouxel, A. Le Blanc, and C. A. Royer, *Bull. Soc. chim. France*, 1971, 2019.

calates are highly anisotropic, and in many circumstances the solid can be considered as a stack of quasi 'two-dimensional' layers. As we might expect, the layer materials exhibit a number of properties which lie between the 'one-' and 'three-' dimensional types of solid. To take one example, charge-density waves are most pronounced in 'one-dimensional' systems, weaker in 'two-dimensional' systems, and weakest in the 'three-dimensional' systems. The same is true of Kohn-type anomalies. Many important topics have of necessity been omitted from this discussion. These include phonon energies, angular-dependent photoemission experiments, the effects of pressure, and the mechanical properties. Because of space limitations we have also concentrated on the transition-metal dichalcogenides. There is, however, a great deal of interest in the other layer materials, and in particular graphite and the graphite intercalates are being studied in many laboratories throughout the world. The intercalates formed from graphite with the so-called super-acids $\text{HF} + \text{SbF}_5$, and possibly $2\text{HF} + \text{HfF}_4$, are highly conducting solids,⁴⁹ with a conductivity approaching that of copper.

On the practical side there are possible applications and some of these have already been mentioned. These include for example their use as catalysts, i.r. detectors, superconducting quantum interference detectors (SQUIDS) for the detection of small magnetic fields,⁵⁰ computer components, and as possible switching materials. They are also of course important lubricants. Systems such as $\text{TiS}_2 + \text{Li}$ are being used as model solids in the study of the 'super ionic' or 'fast ionic' conductors,⁵¹ and indeed some of the layer solids based on the transition-metal trichalcogenides coupled with alkali-metal atoms are themselves candidates for use in high current density batteries. They are also being studied as possible electronic switching materials. The related alloy systems such as lead-molybdenum-sulphur have important magnetic properties in the superconducting state. Solids such as PbI_2 have potential applications as holographic materials.⁵²

Many fundamental problems remain to be solved, and other systems such as the antistructures Hf_2S and Ag_2F need to be examined. These studies will require experimental and theoretical work of considerable skill and ingenuity.

⁴⁹ J. M. La Lancette and J. La Fontaine, *J.C.S. Chem. Comm.*, 1973, 815; S. Loughin, C. Y. Yang, and J. E. Fischer, *Appl. Optics*, 1976, in press; see also ref. 7.

⁵⁰ F. Consadori, A. A. Fife, R. F. Frindt, and S. Gyax, *Appl. Phys. Letters*, 1971, **18**, 233; commercial SQUIDS based on 2H-NbSe_2 are now available.

⁵¹ Unpublished work by Dr. B. C. H. Steele and his co-workers at Imperial College, London.

⁵² H. J. Tolle and R. Memming, *Appl. Phys. Letters*, 1975, **26**, 349.