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Semiconductor ⇄ Metal Phase Transitions

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Existing experimental data pertaining to the semiconductor ⇄ metal phase transitions found in some of the lower oxides of Ti and V are collated and summarized and the theoretical implications of the insulating ground states of these and other solid compounds of transition elements (e.g., NiO) discussed. In particular, the effect of dynamical Coulomb correlations on the validity of the Bloch–Wilson band theory is examined with special reference to the establishment of the "Mott-insulating" state.

Various models exhibiting thermally induced semiconductor ⇄ metal phase transitions are qualitatively described and their relevance to V_2O_3, VO_2, and Ti_2O_3 investigated.

Introduction

"Considerable surprise was expressed by several speakers that in crystals such as NiO in which the *d*-bands of the metal atoms were incomplete, the potential barrier between the atoms should be high enough to reduce the conductivity by such an enormous factor as 10^{10}."

This quotation taken from a discussion, edited by Mott (*1*), on a paper presented by de Boer and Verwey (*2*) at a conference entitled "The Conduction of Electricity in Solids" which was held in Bristol in 1937 seems to have been the first general realization that the then quite new Bloch–Wilson band theory of solids (*3*, *4*) was apparently incapable of describing, in a realistic way, the electrical properties of certain solid compounds of transition elements[1]—in particular at that time: MnO, Fe_2O_3, CoO, and NiO. For according to naive band theory concepts the incompletely filled *d*-shells of the metal ions (cations) in these compounds should lead to incompletely filled *d*-bands capable of supporting a metallic conductivity—which, in the present context, will be defined in terms of an electrical conductivity $\sigma(= ne\mu)$ in which the number density n of carriers is independent of temperature T, the T-dependence of σ deriving solely from that of the mobility μ, which decreases with increasing T.

By 1957 the only oxide of the first transition series containing an integral number of (< 10) *d*-electrons per cation which had been found to be metallic at all temperatures was TiO (*5*); it has been found, more recently, that this oxide becomes superconducting at 0.68°K (*6*).

Two years later, however, Morin (*7*) discovered that between these two limits lay single crystals of certain oxides of V and Ti—namely, VO, V_2O_3, VO_2, and Ti_2O_3 (containing, respectively, 3, 2, 1 and 1 *d*-electrons per cation)—which, while being certainly metallic at high temperatures (though admittedly with very low mobility) suddenly became semiconducting on cooling through a critical temperature T_t, respectively equal to 114°K, 153°K, 340°K and about 450°K. At these temperatures the electrical conductivity was observed to drop almost discontinuously[2] (except in the case of Ti_2O_3 in which the change was spread over about 100°, centred on 450°K) by a factor ranging from 10^2 for Ti_2O_3 and VO_2 to 10^6 for V_2O_3 and VO; the effect was further found to be reversible and, in the case of the V-oxides, to exhibit hysteresis ($\sim 12°$), reflecting the existence of metastable states. It appears then—at least from a naive point of view—that the validity of the band

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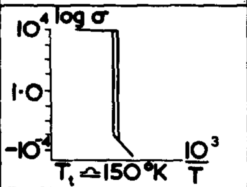
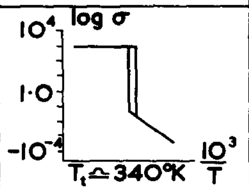
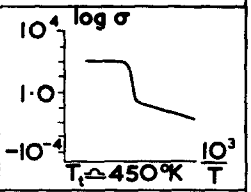
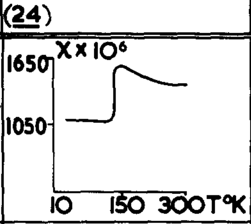
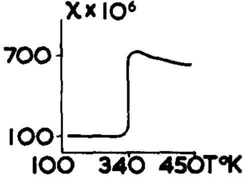
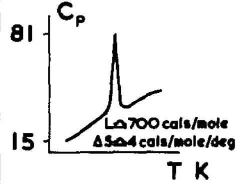
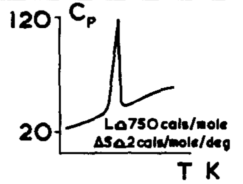
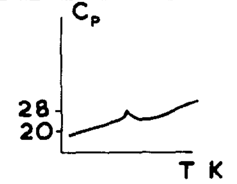
[1] It is of interest to remark that the reverse situation—namely, the existence of metallic conductivity despite an apparently filled band—had already (at that time) been encountered in the case of the alkaline earth metals. In the case of Mg, for example, the enigma could be solved immediately, however, simply by assuming that the (filled) 3*s* band be overlapped by the (empty) 3*p* band (*4*).

[2] This phenomenon seems to have been first observed in powder (polycrystalline) samples of V_2O_3 by Foëx (*8*) in 1946.

TABLE I

	V_2O_3; $(3d)^2$	VO_2; $(3d)^1$	Ti_2O_3; $(3d)^1$
Electrical Conductivity σ (σ ohm^{-1}cm^{-1})			
References	(7)(16)*(17-21)(22-23)*(24)	(7)(25-27)(28)*(29-30)(22)(31-33)*,(34)	(7),(35-37)
Magnetic Susceptibility χ (χ in c.g.s. mole^{-1})			
References	(12) (38)*,(39-41)	(12)(42-43)(26)(31)(22)(41)(44)*	(13-14),(38)*,(45)
Specific Heat C_p (C_p in cals. mole^{-1} deg^{-1})			
References	(46)	(46-48),(26),(22)	(49-50)
Crystal Structures	Monoclinic ↔ Corundum	Monoclinic ⟷ Rutile	Corundum ↔ Corundum
References	(51-54),(36)	(55-58),(54),(59)	(14),(60)
Volume Discontinuity at T_t, ΔV	0·6% to 3·5%	0·2%	0
References	(61),(51),(54),(62)	(54),(63)	(14),(64)
dT_t/dp (in deg/kbar)	−3·1 to −4·1	−0·1 to −0·46	?
References	(65),(54),(23),(62)	(54),(25)	
Order of Transition	1st	1st	2nd

a) The references are in chronological order.

b) Asterisks denote data on oriented single crystals

model for[1] V_2O_3, VO_2, and Ti_2O_3 depends sensitively on external conditions—in particular, temperature.

The temperatures T_t coincided with the temperatures at which it was already known (from existing data on powder samples) that the magnetic susceptibility χ of these oxides increased sharply from a constant (for $T < T_t$) to a temperature dependent value (*12*, *13*), reflecting a change in their magnetic structure.[2] In the case of the two V-oxides these

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[1] The experimental evidence as to whether VO undergoes such a change in electrical conductivity is, at present, contradictory (*7*, *9*, vs *10*, *11*) and in view of the general lack of data on this oxide it will not be discussed further.

[2] Only much later (post 1966) was the actual nature of these changes elucidated through the use of Mössbauer effect, nmr and neutron diffraction.

TABLE 2

Class 1

Metallic Compounds

3*d*-compounds: TiO, CrO_2, TiS, CoS_2, CuS_2
4*d*-compounds: NbO, RuO_2
5*d*-compounds: ReO_3

Class 2

Semiconducting Compounds

3*d*-compounds: NiO, CoO, MnO, FeO, Fe_2O_3, Cr_2O_3, MnS, MnS_2, FeS_2

Class 3

Transitional Compounds

3*d*-compounds: VO, V_2O_3, VO_2, V_3O_5, V_4O_7, V_6O_{13}, Ti_2O_3, Ti_3O_5, Fe_2O_4, NiS, CrS, FeS
4*d*-compounds: NbO_2.

superimposed electrical and magnetic changes are accompanied by a latent heat and also by a (martensitic) reduction in crystal symmetry with an associated discontinuous volume expansion ΔV on cooling through T_t; although the lattice parameters of Ti_2O_3 vary quite rapidly in the vicinity of T_t (*14*, *15*) there is no change in symmetry and no discontinuity in volume.

These facts, together with specific heat $C_p(T)$ data and measurements of the pressure dependence of $T_t(dT_t/dp)$, suggest that T_t is to be identified with the temperature of a *Semiconductor ⇄ Metal Phase Transition* which is of first order for V_2O_3 and VO_2 and of second order for Ti_2O_3 (Ehrenfest's 1932 classification).

Table 1 summarizes these experimental findings[1] with reference to which it should be mentioned that with the advent of purer and more stoichiometric single crystals the temperature range over which the transition occurs has been greatly reduced and the magnitude of the discontinuity in electrical conductivity increased (up to the present) by a factor of 10^3.

Oxides of the first (3*d*) transition series can thus be classified according as they are metallic at all temperatures, Class 1 (e.g., TiO); semiconducting at all temperatures, Class 2 (e.g., NiO); or undergo a semiconductor ⇄ metal phase transition on heating through a critical temperature T_t, Class 3 (e.g., V_2O_3). To date, membership of the three classes is augmented by sulphides of 3*d*-transition metals and by oxides of the 4*d*- and 5*d*-transition metals; a representative selection (cited by Adler (*66*)) is given in Table 2.

These experimental findings thus pose two questions:

"What is responsible for the existence of insulating ground states in the compounds of Classes 2 and 3, and can such states be in any way compatible with the band theory of solids?"

"In the case of Class 3 compounds, what is responsible for the establishment of a metallic state on heating through T_t?"

Before attempting to answer these questions it must be pointed out that all the considerations of this paper will involve the assumption that the bonding of the compounds in question is purely ionic.[2] The anions are, accordingly, considered to have closed 2*p*-shells and the characteristic behaviour of these materials attributed to the electrons originating from the *d*-subshells of the cations whose energies lie within the relatively wide gap (of the order 10 eV) between the bonding and antibonding *sp* bands (*68*); see Refs. (*69*) and (*70*) for supporting experimental evidence.

The present review paper is based on one given at the Third International Conference on Solid Compounds of Transition Elements[3] and it is my continued intention that it serve the dual purpose of directing the attention of solid state chemists to the field of semiconductor ⇄ metal phase transitions (with the hope that a more coherent interaction between physicists and chemists will result) and of forming a comprehensible yet comprehensive introduction to the evergrowing literature[4] on this subject, reviewed recently by Adler (*66*, *72*) and by Mott (*73*, *74*).

The Insulating Ground States of Class 2 Compounds, Coulomb Correlations and the Band Model

It turns out that the insulating ground states of all the Class 2 compounds quoted in Table 2 can, with the exception of MnO, CoO, and NiO, be

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[1] For an exhaustive survey of pre 1951 and 1967 data on the physico-chemical properties of Ti_2O_3 and the V-oxides "Gmellins Handbuch der Anorganishen Chemie," Vol. 41 (Ti, pp. 221–224) and Vol. 48 (V, Teil B, Lieferung 1, pp. 32–61), respectively, should be consulted.

[2] A more realistic treatment must, of course, include consideration of the effects of the covalency which is undoubtably present to some degree in these materials, especially ReO_3 (*67*) and VO_2 (*68*) for example, in which there exists the possibility of π-bonding between anion and cation orbitals.

[3] This conference was held in Oslo, Norway, 16–20 June 1969 under the auspices of the Norwegian Chemical and the Norwegian Physical Societies.

[4] See Ref. (*71*).

understood within the framework of the band theory of solids simply by taking into account the internal electric field originating from the doubly negative anions. For this field splits the original tenfold degenerate *d*-band[1] into subbands—the number and degeneracy of which is determined by the point symmetry of a cation with respect to the octahedrally coordinating anions and by Kramers' theorem—the highest completely filled one of which can, for every one of the compounds in question, be shown to be separated by a gap from the next higher lying completely empty subband; a necessary condition for the realization of this possibility is, of course, that there be an even number of *d*-electrons per primitive cell.

The existence of such filled (and hence diamagnetic) subbands would, however, be incompatible with the magnetic nature of these materials which are known to be antiferromagnets at low temperatures ($T < T_N$) and Curie–Weiss paramagnets for $T > T_N$. Accordingly a breakdown of the band model must be admitted not only for MnO, CoO, and NiO but also for the remaining compounds in Class 2.

That band theory fails to give a realistic description of these materials is due to its inadequate treatment of the Coulomb interaction,[2] an inadequacy which, as first pointed out by Peierls (*75*), can be expected to have serious repercussions in the case of narrow bands, i.e., in the limit of large cation separations, "*a*." For in this limit the itinerant kinetic energy of the Bloch electrons—the magnitude of which is reflected in that of the bandwidth W (a decreasing function of "*a*"—can no longer dominate the potential energy associated with the repulsive Coulomb interaction between two electrons which band theory, by its neglect of dynamical correlations, allows to approach arbitrarily close[3] and, in particular, to occupy (momentarily) the same cation—that is, the occurrence of such "polar fluctuations" entails an increase in energy greater than the range of energies available, in this limit, to the electrons within the band in question. The band model is then said to have broken down since the conductivity (itinerancy) which it predicts can no longer be maintained without an overall increase in the energy of the system. The dominant contribution to this increase arises from double occupancy of the same orbital on the same cation—the intracationic Coulomb energy U; a significant factor influencing the magnitude of U is the polarization by the anomalous charge of such a double occupancy of its anionic environment (*76*).

That the breakdown is due to the *many*-electron aspect of the problem was already evident from the work of de Boer and Verwey. For it was known experimentally that if by some means (for example, by the introduction of small deviations from stoichiometry or purity) the number of electrons per cation could be made nonintegral then the conductivity would increase enormously; apparently then its absence in the pure, stoichiometric state could not solely be due to the intercation distance being too great to allow tunnelling. Inclusion of these dynamical (Coulomb) correlations (which can, in principle, be effected by taking, in place of the single Slater determinant envisaged in band theory, a linear combination of such determinants—the method of "configuration mixing") would lead, however, in the limit of large "*a*" (narrow bands), to a complete suppression of the polar fluctuations and hence to a quenching of the electrical conductivity; a finite energy (of order $U - W$) is then required to create a pair of free carriers.

The nature of this nonconducting state—in which an equal number of "would-be" conduction electrons are localized at each cation—is, it will be appreciated, very different from that of the insulating state contemplated in the Bloch–Wilson band theory and is rather described *exactly* in terms of another model[4]—that due to Heitler and London (*77*); see also Refs. (*78*, *79*). The theoretical implications of Peierls' 1937 remarks were not persued until 1949 when Mott (*80*) reopened the question with the first of a series of papers; accordingly, such nonconducting states have since become known as "Mott-insulators."[5]

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[1] The structure of these bands is determined by the space group of the crystal concerned and by the number of cations per primitive cell.

[2] Band theory is but a one-electron approximation to the actual many-electron problem.

[3] A statistical correlation between Bloch electrons of parallel spin is, of course, naturally effected through the Pauli principle which *is* taken into account in band theory through the use of a determinantal many-electron wave function—a Slater determinant—built up from one-electron Bloch functions.

[4] Even in this model a given electron is not permanently localized on the same cation since electron exchange between cations can occur; it is clear, however, that such exchanges cannot lead to a current.

[5] While in the presence of an (external) electric field neither a Bloch–Wilson nor a Mott insulator can support an electric current, their response to a magnetic field is very different; the filled bands of the former yield a diamagnetic susceptibility whereas the incomplete cation shells of the latter can give rise to localized moments which may or may not participate in a long-range magnetic order.

Using the intercation distance "a" as a parameter Mott predicted that a first-order phase transition into the metallic state (band model valid) should occur as "a" is reduced through a critical value "a_c", characteristic of the material in question. For as "a" is reduced the overlap of the wave functions of the localized electrons increases, screening the interaction of the resident electrons with their centres, until at $a = a_c$ the bound states (electrons with their respective centres) can no longer be maintained and each and every electron is simultaneously delocalized and a metallic state established.[1]

This zero temperature insulator $\rightleftarrows$ metal phase transition—a Mott tansition—has, in recent years, been subject to intense mathematical investigation. The majority of these investigations (*83–94*)—the work of Kohn (*95*) constituting an exception—have been based on a model due originally to Gutzwiller (*96*) and to Hubbard (*97*) in which electrons of antiparallel spin (moving in a half-filled s-band) are assumed to interact only when, in the course of their band motion, they encounter each other at the same cation. Of particular interest in connection with these many-body calculations is the exact solution of Bari and Lange (*98*) showing that such a system is nonconducting for W/U less than a certain upper bound—a result which holds independent of the number of dimensions of the system. Shortly after the appearance of Mott's revolutionary (at the time) 1949 paper Slater (*99*) suggested that the insulating nature of even MnO, CoO, and NiO could be understood within the framework of band theory simply by acknowledging their antiferromagnetic structure. For the intercationic exchange field associated with such a long-range ordering of the cation spins would give rise to a splitting of an otherwise half-filled (metallic) band into two subbands separated by a gap of the order of kT_N (*100*), where T_N is the Néel temperature; this splitting can be considered as deriving, from the establishment of a "magnetic primitive unit cell" containing twice the number of cations, one associated with each of the two sublattices on to which electrons of opposite spin are segregated by their exchange interaction. While such a mechanism certainly provides a qualitative[2] explanation of the nonmetallic nature of these oxides for $T < T_N$ it necessarily fails for $T > T_N$ owing to the vanishing at T_N of the long-range order.

Accordingly then, nonmetallic materials containing an odd number of electrons per primitive cell (e.g., MnO) and those materials containing an even number of electrons per primitive cell the nonmetallic nature of which either continues, even after the anion field splittings have been taken into account, to defy explanation in terms of conventional Bloch–Wilson band theory (e.g., NiO), or could be explained in this way were it not for their magnetic properties (e.g., FeO) are to be classified as Mott-insulators, lying on the insulating side of a Mott-transition.

Models Exhibiting a Thermally Induced Semiconductor $\rightleftarrows$ Metal Phase Transition

Before proceeding to discuss the mechanisms which are, in the light of present data, likely to be responsible for the transitions observed in Class 3 compounds it will be instructive to firstly review qualitatively the various models which have been presented in recent years which are, at least in principle, capable of exhibiting a thermally induced semiconductor $\rightleftarrows$ metal phase transition. Such models can be classified according as they attribute the electrical transition to

(i) the onset of an antiferromagnetic state on cooling through T_t,
(ii) a reduction in crystal symmetry on cooling through T_t, and
(iii) Coulomb correlations between the carriers.

Antiferromagnetic Models

If it is known that the ground state of a given nonmetallic material be antiferromagnetic—but which material should, according to band theory, be metallic—then the exchange field associated with the long-range magnetic order can be invoked to

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[1] It is of interest to remark that this possibility was actually pointed out long ago by Herzfeld (*81*) in 1927 in connection with dielectric instabilities; recent work in this direction (*82*) shows that the onset of the metallic phase may be preceded by an (electronic) ferro-, antiferroelectric phase.

[2] Quantitatively, however, there are difficulties; kT_N is an order of magnitude smaller than the activation energy for intrinsic (band) semiconduction. It is possible, however, for materials with more than one d-electron per cation that the magnitude of this latter energy finds origin in terms of an intracationic exchange (Hund rule) splitting (*101*); it has been suggested (*72*) that the persistence of semiconductivity for $T > T_N$ is connected with the persistence at these temperatures (at which no long-range order remains) of this highly local (intracationic) ordering. For further discussion, see J. C. Slater, *J. Appl. Phys.* **39**, 761 (1967).

split the half-filled (metallic) band into a filled and empty subband separated by a gap.[1]

It will be recalled that this mechanism had to be rejected for class 2 compounds simply because they did not become metallic for $T > T_N$, as the model implied they should. As first pointed out by Morin (*7*) in 1959, this objection no longer holds in the case of the antiferromagnetic compounds of Class 3, however, provided T_t be identified with T_N; the transition to the metallic state is here thus attributed to the vanishing at T_N of the (intercationic) exchange splitting.[2]

In the same year des Cloizeaux (*105*), by assuming that the exchange gap decreased (because of the decrease in sublattice magnetization) with excitation of electrons across it, obtained a second order antiferromagnetic (semiconductor) $\rightleftarrows$ itinerant paramagnetic (metal) phase transition. The same result has, more recently, been obtained on the basis of a one-electron model by Adler and Brooks (*106*) in the limit where the width of the paramagnetic (metallic) band is much less than the magnitude of the exchange gap—corresponding, for $T < T_N$, to magnetic saturation; the opposite limit also has been discussed by Adler (*107*).

A necessary condition for the feasibility of such models, when the antiferromagnetism is based on a simple 2-sublattice structure, is, of course, that the metallic band be exactly half filled; a generalization which procures a transition starting from a partially filled band has been effected (in the limit where the band is narrow compared to the magnitude of the low temperature gap) by De Graaf and Luzzi (*108*) in terms of Overhauser's static spin density waves (*109*)—a state in which the number density of electrons of a given spin varies periodically throughout the material in antiphase with that of the opposite spin electrons.

Distortion Models

The crystallographic changes which were known to accompany the electrical transitions in V_2O_3, VO_2, and Ti_2O_3 led Goodenough (*110*) to suggest (at a time when the existence or not of a magnetic ordering for $T < T_t$ had yet to be established) that the nonmetallic nature of these oxides for $T < T_t$ is to be attributed to the existence of homopolar bonds between the *d*-electrons on neighbouring cation pairs; it was considered that these cations would thereby get displaced from the positions they occupied for $T > T_t$. According as the displacements resulted in a reduction in crystal symmetry or not, the transitions were classified as "cooperative"—occurring sharply at a given temperature (e.g., V_2O_3 and VO_2)—or, as "non-cooperative"—the transition extending over an interval of temperature (e.g., Ti_2O_3); the energetics of the cooperative type of transition were subsequently discussed by Kawakubo (*111*) on the basis of a simple one-dimensional model.

From the point of view of band theory such cooperative transitions can be interpreted as a splitting (associated with the increase in the number of cations per primitive cell on entering the displaced, lower symmetry phase[3]) of a partially filled (metallic) band into two subbands separated by a gap; the lower, completely filled subband is then to be regarded as the bonding band and the upper, completely empty (at 0°K) subband the antibonding band originating from the bonding and anti-bonding levels within the primitive cells, each of which contains a Goodenough bond.

More generally, if band theory—together with a consideration of the anion field splittings and of the disposition of cations within the crystal structure—predicts an insulating ground state in terms of a filled subband[4] which can be interpreted as a bonding band, and if the material, which in its ground state is diamagnetic, undergoes at a finite temperature T_t a transformation to a structure of higher symmetry with a concommitant collapse of the bonding-antibonding gap then the low temperature ($T < T_t$)

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[1] In the case of materials containing an even number of electrons per primitive cell it is possible, after consideration of the anion field splittings, that the band model predict an insulating ground state in terms of a filled subband; the existence of such a filled (diamagnetic) subband would, however, be incompatible with the assumed antiferromagnetic nature of the material. In this event it is only necessary to assume that the anion field splittings are insufficient to ensure a gap in the density of states of the system whence a metallic (or semimetallic) state obtains; at this stage an exchange splitting can then be invoked. This possibility cannot, of course, be entertained in the case of similar materials which do not become metallic for $T > T_N$—for example, FeO, which must be classified as a Mott-insulator for $T \gtrless T_N$.

[2] In retrospect the application of this model by Morin to VO, V_2O_3, VO_2, and Ti_2O_3 seems to have been rather forced since although it was known at the time (via the temperature dependence of the magnetic susceptibility) that a magnetic transition of some kind occurred at T_t, the existence of a long-range antiferromagnetic order in these oxides for $T < T_t$ had not been established; it is now known that only V_2O_3 is antiferromagnetic—see Refs. (*102–104*).

[3] In the case of ionic compounds a change in cation point symmetry can also lead to a gap through the presence for $T < T_t$ of a lower symmetry component in the anion field.

[4] This is only possible provided the number of electrons per primitive cell is even.

phase can be regarded as a distorted form of the high temperature ($T > T_t$) phase.

The stability of the "distorted" phase requires the decrease in electronic energy on entering this phase to dominate the strain energy which is quadratic in the distortion. Adler and Brooks (*105*) find that this is possible only when the width of the metallic band is much less than the magnitude of the bonding-antibonding gap; in this case the system then behaves for ($T < T_t$) as an intrinsic semiconductor with an energy gap which is due entirely to the distortion.[1]

Since the excited (semiconducting) electrons can no longer contribute to the homopolar bonding the magnitude of the gap must decrease with increasing temperature. Taking the gap to be linear in the distortion a first-order phase transition into the metallic state results (*106*) at a temperature T_t determined solely by the magnitudes of the gap and distortion at 0°K.

Still treating the distortion phenomenologically de Graaf and Luzzi (*112*) have pointed out, within the Hartree–Fock approximation, the renormalization of the distortion gap which is effected through the inclusion of the Coulomb interaction between electrons. The inclusion of this interaction leads to the possibility of an antiferromagnetically ordered ground state, the description of which, in the absence of an initial crystallographic distortion, becomes identical to that given by des Cloizeaux.

Nonphenomenologically, the distortion (lattice instability) must be derived starting from the coupled electron-lattice system; in the case of a polar lattice this has been done by Hanamura (*113*) by considering the interaction between the electrons (treated as Bloch electrons) and the transverse optical phonons. Very recently, an extension which includes also the interaction of the electrons amongst themselves has been presented by Aronov and Kudinov (*114*).

In connection with both antiferromagnetic and distortion models it should be appreciated that the band splittings envisaged therein can lead to an insulating ground state only provided the splitting be of sufficient magnitude to ensure that a gap opens up in *every* direction in momentum space and hence in the density of states of the system.

Correlation Models

It is characteristic of the two classes of models so far discussed that they are phenomenological in the sense that they rely for an explanation of the electrical transition on some other concommitant effect—either the onset of antiferromagnetism or a reduction in crystal symmetry; in this way the band model was retained for both the metallic and nonmetallic phases. It is quite possible, however, that a semiconductor $\rightleftarrows$ metal phase transition in some materials be unaccompanied by such effects; there are then open two possible interpretations of the nonmetallic ground states, both of which are intimately related to Coulomb correlations—namely, a Mott-insulating state or an excitonic insulating state. The question then arises as to whether such insulators can, with increasing temperature, undergo phase transitions into a metallic or semimetallic state.

A. *Mott-Insulator $\rightleftarrows$ Metal Phase Transition.* The possibility of such a phase transition of first order has been demonstrated by Fröhlich (*115*) on the basis of a simple model (with one electron per primitive cell) in which Coulomb correlations play a dominant role throughout. As $T \to T_t$ from below, the same correlations as were initially (at $T = 0^\circ$K) responsible for the establishment of the Mott-insulating ground state are considered to turn the thermal ionization of the localized electrons into delocalized band states (i.e., the creation of independent electron-hole pairs) into a cooperative process. For through screening effects the ionization energy[2] I becomes dependent on the existing degree of ionization x, i.e., the gap between the localized many-electron states and the conductive continuum of band states (*116*) decreases with excitation across it. As $T \to T_t$ the gap decrease avalanches until at $T = T_t$ the screening provided by the already ionized electrons reduces[3] the potential energy associated with the intracationic Coulomb repulsion U to a value comparable with the magnitude of the one-electron bandwidth W, whence I vanishes (or becomes exceedingly small) and the population of the band states increases catastrophically, leading to a first-order phase transition into the metallic state.

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[1] In this connection see also, J. B. Goodenough, *Czech. J. Phys.* **317**, 304 (1967) and Colloque Internationaux du C.N.R.S. No. 157 (1965) Editions du C.N.R.S. 1967.

[2] I is the energy required to ionize one cation and place the electron on a *distant*, already occupied cation where it experiences a repulsive Coulomb energy U. Since transitions (via tunnelling) to neighbouring occupied cations entails no further increase in energy the positive ion (the hole) and the negative ion (the electron) move in bands of widths W_h and W_e respectively; the existence of the hole band obviously relies on the existence of localized electrons, i.e., requires $x \ll 1$. The minimum energy I_0 required to create the first pair of free carriers is thus given by $I_0 = U - \frac{1}{2}(W_h + W_e)$.

[3] Even in the absence of such screening a reduction in the value of U is already effected through lattice polarization, which in the case of ionic crystals can be large (*76*).

An important feature of this model is that the a priori electronic transition between localized and delocalized states implies the existence at T_t of a magnetic transition and also the possibility of a crystallographic change. For in the low temperature phase ($T < T_t$) each cation has a localized moment (which may or may not couple to give rise to a long range magnetic order—energetically an antiferromagnetic ordering would appear in general to be the most favourable configuration) while for $T > T_t$ these moments are delocalized and move in a narrow band, whence a temperature-dependent spin paramagnetism, which at zero temperature reduces to Pauli paramagnetism, is anticipated. The possibility of a structural change arises in view of the difference in bonding in the two phases; in the case of ionic compounds the localization at T_t of the conduction electrons, which for $T > T_t$ provide both a contribution to the bonding via metallic cohesion and a screening of the cation–anion interaction, leads to a change in cation valency and to a change in the cation–anion interaction.

It should be emphasized that the screening effects leading to the reduction in I can be realized only provided that for $T < T_t$ the semiconducting electrons move in a band and not by phonon-induced hopping; this, of course, imposes, for the viability of the model, a limit on the strength of the electron—(optical) phonon interaction.

The special case where the Mott-insulating ground state is antiferromagnetically ordered has been considered by Bulaevskii and Khomskii (*117*). Movement of the semiconducting carriers is here restricted by the Pauli principle leading to a narrowing of the electron and hole bands or equivalently, to an increase in the gap; the magnitude of I now depends also on the value of the mean sublattice magnetization, s—itself a decreasing function of T in view both of the thermal disordering of the localized spins and of the decrease in their number due to the creation of carriers. Ignoring the x dependence of U and taking I to be a decreasing function of s a first-order transition into the metallic state is obtained provided $U < W$, a condition which, however, would appear to violate the initial assumption of a Mott-insulating ground state, requiring $U > W$.

B. *Excitonic Insulator $\rightleftarrows$ Semimetal Phase Transition.* If on cooling the lattice parameters of a semimetal vary in such a way as to reduce the band overlap then according to Bloch–Wilson band theory there should be a continuous transition from the semimetallic state to a conventional insulating state, reflected by a continuous decrease to zero in the electrical conductivity as the overlap decreases through zero.

In 1956 Mott suggested that for a very small number of electrons and holes (i.e., in the limit of small overlap) the screening provided by these carriers would be insufficient to prevent the formation of bound electron-hole pairs and the system would accordingly make a first-order phase transition into a nonconducting state with an associated discontinuous decrease to zero in the electrical conductivity. Some time later, however, Knox (*118*), considering the transition from the insulating end, pointed out that if the exciton binding energy exceeded the one-electron band-gap then the Bloch–Wilson insulating state would become unstable against the formation of excitons and a new intermediate phase—an excitonic insulating phase—would be established.

Thus in the excitation spectrum of a low-density semimetal there will appear at 0°K, in the presence of the Coulomb interaction a (many-electron) gap; at low T the system is then semiconductive. With increasing T excitation across the gap leads to a screening of the attractive electron-hole interaction and this in turn results in a decrease of the gap itself until at a critical temperature a second-order phase transition into the semimetallic state occurs. The reason for the change in order from that predicted originally by Mott is that the establishment of the excitonic phase (which was *not* contemplated by Mott) involves the creation of a charge density wave which couples to the lattice causing therein an instability and a resulting divergence in the static dielectric constant. These ideas conceived originally by Knox and by Kohn (*119*) have been developed by Jerome et al. (*120*) who demonstrate, in particular, the much less drastic (continuous) quenching of the electrical conductivity which is associated with this second-order phase transition.

As first pointed out by des Cloizeaux (*121*) the excitonic phase is characterized either by an antiferromagnetic order or, in the case of strong carrier-phonon coupling by a lattice distortion; the realization of this latter possibility can change the order of the transition from second to first (*122*). In similarity to the Fröhlich transition the magnetic and crystallographic changes are here likewise consequences of an a priori electronic (hole) transition driven by the Coulomb interaction.

Finally it is of interest to realize (*123*) that the excitonic insulating phase can be regarded as the analogue of the (electronic) antiferroelectric phase which Fröhlich (*82*) has conjectured should appear as an intermediate phase during the transition from a Mott-insulating state to a metallic state.

Theories of Class 3 Compounds

It now becomes pertinent to enquire which of the available models exhibiting a thermally induced semiconductor $\rightleftharpoons$ metal phase transition is relevant to any particular compound of Class 3. For only three compounds V_2O_3, VO_2, and Ti_2O_3 is there sufficient experimental evidence on the basis of which a decision can be made—which decision, in view of the ever increasing accumulation of data, can at present be regarded as only tentative. It happens that these three compounds are also the simplest materials—in the sense that each cation in a given compound has the same integral number of *d*-electrons and that the crystal structures concerned are relatively simple—to which the models can be expected to be (directly) applicable.

Since all three compounds contain an even number of electrons per primitive cell there exists the possibility (especially in view of the low symmetry of their ground states) that the insulating nature of their ground states can be understood within the framework of band theory. Further it seems probable owing to the smallness of the splittings effected by the lower symmetry components of the anion field that two or more partially *overlapping* *d*-subbands are involved in the conduction for $T > T_t$.

V_2O_3

The electrical transition in this oxide is accompanied by both magnetic [antiferromagnetic (*102–104*) $\rightleftharpoons$ itinerant electron paramagnet] and crystallographic [monoclinic $\rightleftharpoons$ rhombohedral] transitions. The philosophy of the phenomenological theories (*66*) is to attribute the low-temperature semiconductivity to the presence of a gap in the density of states caused by a combination of the crystallographic and magnetic distortions. To ensure an antiferromagnetic ground state characterized by a large local moment (1.2 μB—see Ref. *124*) it is necessary to assume that the splitting derives *initially* from the exchange field associated with the long-range magnetic order and that the magnitude of this splitting ($\sim kT_N$) exceeds the width of the high temperature ($T > T_t$) metallic band; kT_N is, however, an order of magnitude smaller than the activation energy for semiconduction. Accordingly, it is assumed by Adler (*66*) that the monoclinic distortion *then* acts in such a way as to stabilize the occupied antiferromagnetic subband, thereby increasing the gap; thermodynamically, the transition deriving from the distortion could dominate the second-order magnetic transition and a first-order antiferromagnetic semiconductor $\rightleftharpoons$ metal phase occur, in accordance with the experimental findings.

There are, however, a number of difficulties with this model:

(i) The Mössbauer data of Shinjo and Kosuge (*21*) reveal a discrepancy ($\sim 60°$) between T_t and T_N ($T_t < T_N$)—the latter being obtained by an extrapolation of the ($T < T_t$) internal field temperature dependence—implying that magnetic ordering is not the prime mover.

(ii) The existence of a metallic band of width $< kT_t (\sim 10^{-2}$ eV) seems rather unlikely.

(iii) A recent X-ray analysis (*125*) of the V_2O_3 crystal structure in the vicinity of T_t has revealed that the pair-wise contraction of the basal plane cations—from which the aforementioned crystallographic splitting derives—does not in fact occur; the transformation to monoclinic symmetry involves only a tilting of the hexagonal *c* axis of the rhombohedral, high-temperature phase.

(iv) In order that the monoclinic distortion augment the exchange gap it is necessary (*66*) that the initial antiferromagentic ordering be Cr_2O_3 type; this is not borne out by the recent neutron diffraction work of Moon (*124*) which indicates that the antiferromagnetism in V_2O_3 involves a ferromagnetic coupling between *c* axis *V–V* pairs—that is, ferromagnetic (010) planes in the McWhan–Rice–Remeika monoclinic cell (*125*).

From (iii) it might be conjectured that the cystallographic distortion is of magnetostrictive (or exchange strictive) origin; the veracity of this conjecture could be immediately determined by investigating whether under the suppression of semiconductivity—as has been effected by McWhan and Rice (*126*) using a pressure of 25 kbars—the symmetry change still occurs at 154°K ($= T_t$ at atmospheric pressure).

That the conduction for $T > T_t$ takes place in two or more overlapping bands is strongly suggested by the experimental data of these workers on the temperature and pressure dependence of the pressure-sustained metallic state and is further endorsed by the transport data of Austin and Turner (*127*).[1]

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[1] The existence of partially overlapping subbands is certainly consistent with symmetry requirements as has been shown by Kleiner (*128*) and is further in fact necessary to prevent strong anisotropy in conductivity—see Refs. (*16*, *22*, *23*); the subbands concerned are the a_{1g} bonding band and the lowest $e_g(\pi)$ band.

The recent discovery by Moon [see Ref. (*124*)] *via* neutron diffraction of large local moments (~ 1.2 μB) in the antiferromagnetic phase would appear to vitiate, however, the interesting suggestion of McWhan and Rice that the transition is of excitonic origin. For the excitonic insulating phase is characterized by *either* an antiferromagnetic order *or* a crystallographic distortion; in the case of V_2O_3, in view of the strong electron-lattice interaction [implied by the low mobility (*24*)], it is assumed that the latter is realized whence a first-order transition becomes viable; for other condemnatory evidence see Ref. (*125*).

There remains the possibility that V_2O_3 is, in its ground state, a Mott-insulator which is antiferromagnetically ordered, the symmetry change being simply a consequence of the change in ionicity and screening at T_t. The transition to the metallic state would then follow as in Fröhlich's model, adapted to recognize the antiferromagnetic ground state; alternatively, see Mott (*74*).

VO_2

In this oxide the electrical transition is accompanied only by a crystallographic distortion from body-centred tetragonal ($T > T_t$) to monoclinic ($T < T_t$) symmetry; the reduction in symmetry derives from a noncolinear pairing up of cations which for $T > T_t$ are equally spaced along the tetragonal *c* axis. VO_2 is paramagnetic for $T \gtrless T_t$ (*22*, *129*), exhibiting for $T < T_t$ a temperature-independent susceptibility which increases at T_t to a temperature-dependent value deriving from itinerant (conduction) electrons of low mobility (*31*).

It would thus appear that this oxide is the ideal candidate for the distortion model provided the existence of a paramagnetic susceptibility for $T < T_t$ can be understood. In this connection there are two possibilities, namely Van Vleck (high frequency) paramagnetism deriving from (a) the component of electronic angular momentum perpendicular to the axis of the cation pairs, and (b) a departure in spherical symmetry of the anions due to possible covalency effects or to polarization by the cation field. The magnitudes of these contributions must, of course, be sufficient to dominate the diamagnetism of the system [see Ref. (*130*)].

It is possible, however, to understand the establishment of the homopolar bonds here envisaged between the cation pairs for $T < T_t$ in terms of the Fröhlich model, in the following way:

(i) On cooling through T_t Coulomb correlations cause a localization of the *d*-electrons (one per cation) on the body-centred tetragonal lattice.

(ii) A lowering in the energy of this localized state is then achieved by the electrons on successive *c*-axis cations adopting antiparallel spins—a pair-wise antiferromagnetic order.[1]

(iii) Owing to the change in cation valency and to the reduction in screening of the cation–anion interaction upon localization, the lattice undergoes a distortion which results in the formation of cation pairs.

(iv) The increase in overlap of the wave functions of the localized electrons resulting from these displacements leads to a pair-wise delocalization of the *d*-electrons (whose spins in the localized state were already antiparallel) into a homopolar bond.

Analysis of optical (*69*, *70*) and Hall effect (*31*) data as well as the band structure of Ref. (*68*) and the isotropy in conductivity found by Bongers (*28*) suggest that for $T > T_t$ VO_2 could be a semimetal with two or more overlapping *d*-subbands whence there exists the possibility, though not the necessity, that the transition be an excitonic phase change which in view of the strong electron-lattice interaction [implied by the low mobility (*31*, *132*)] is of first order.

Ti_2O_3

On cooling through T_t this oxide exhibits no change in crystal symmetry and does not order antiferromagnetically (*133*); there is, however, a sharp decrease in the *c*/*a* ratio.

It follows from a symmetry analysis by Kleiner (*128*) of the *d*-bands in the corundum structure that the insulating ground state of this oxide is quite consistent with probable band structure, the valence and conduction bands being, respectively, the a_{1g}- and the $e_g(\pi)$-subbands; for $T < T_t$ the material is thus an intrinsic semiconductor with a gap of about 0.06 eV (*35*, *37*).

Van Zandt et al. (*134*) have presented a phenomenological model for the semiconductor $\rightleftarrows$ metal phase transition which relies on the anomalous increase[2] in the *c*/*a* ratio on heating through T_t; this increase, they point out, has two possible consequences:

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[1] There can be no *long*-range antiferromagnetic order in such one-dimensional *c*-axis threads (*131*).

[2] It has been suggested by Brooks (*135*) and by Mott (*74*) that the increase in the *c*/*a* ratio is a consequence of the crystal adjusting itself so as to increase the entropy of the semiconducting electrons and thereby lower its free energy.

(i) It tends to equalize the spacing of the c-axis cation pairs, thereby increasing the width of the a_{1g} valence band,

(ii) It leads to a reduction in the spacing between basal plane cations, thereby increasing the width of the $e_g(\pi)$ conduction band.

Accordingly, there is a reduction in band gap with increasing temperature and an eventual overlapping leading to the establishment of a semimetallic state. Supporting evidence that two partially overlapping bands are involved in the conduction for $T > T_t$ comes from the temperature dependence of the magnetic susceptibility (*136*).

In connection with the viability of this model it should perhaps be pointed out that within the framework of existing theories of the excitonic insulating state it is difficult to see [in view of the small zero temperature (one-electron) band gap] how, upon inclusion of the Coulomb interaction between electrons and holes, the conventional insulating ground state can remain stable; it should be noted that neither a change in lattice symmetry nor the onset of an antiferromagnetic phase (both of which can be characteristic of the excitonic insulating state) are observed on cooling through T_t.

Epilogue

The principal impression to be gained from this article is that a satisfactory nonphenomenological understanding of the thermally induced semiconductor $\rightleftarrows$ metal phase transitions exhibited by Class 3 materials continues to constitute a challenging problem in theoretical solid state physics; the reason for this is, of course, the many-body nature of the problem. It is well-known that to deal with phase transitions in systems other than the ideal Bose gas and the two-dimensional Ising model (in zero magnetic field and including interactions only between nearest neighbours) it has proved necessary to develop various approximation methods, such as mean-field theories (in which some aspect of the statistical problem is ignored so as to permit solution in closed form) or series expansions of the thermodynamic functions near the transition point; it is a common feature of such methods, however, that they become least satisfactory in the immediate vicinity of the transition point. The reason for this is usually to be traced to their inadequate treatment of the correlations responsible for the occurrence of the transition; in the vicinity of the transition point these correlations become so dominant that even the most delicate approximations can have drastic consequences. Accordingly, it is possible that the nature of the transition predicted by such approximate treatments be dependent on the approximations used. All the models discussed above are open to such criticisms; thus they are, at their best, capable only of predicting the possibility of semiconductor $\rightleftarrows$ metal phase transitions.

While it was not the aim of this article to discuss the transport properties of solid compounds of transition elements there are two outstanding comments that warrant mention. Firstly, in both the semiconducting and metallic phases the electrons responsible for the characteristic behaviour of these materials move in narrow d-bands; accordingly, the usual formulae of band theory are likely to break down for the electrons are now spread over a range of energies comparable to the magnitude of the bandwidth ($W \gtrsim kT$). A simple example is provided by the electron specific heat, c_v, at high temperatures which in the case of a narrow band tends to zero as $1/T^2$ (*136*) rather than to the classical value of $3/2k$ which obtains in the case of a wide band. Secondly, it is often suggested [see, e.g., Refs. (*74*) and (*138*)] that the high-electronic effective masses found in these materials are to be attributed to polaron formation. The viability of this suggestion requires, however, the number density of the electron gas to be sufficiently low to ensure that the electron-lattice interaction responsible for the polaron formation be not inhibited by screening effects; in the case of semimetallic phases such densities can, of course, be realized. The existence of polaron bands imposes, however, a limit on the magnitude of the scattering of the polarons by (thermal) optical phonons, which magnitude is reflected in that of the mobility, μ. For should polaron formation reduce the static lattice (Bloch) bandwidth to a value $W < kT$ then the definition of polaron Bloch states requires $\mu \gtrsim 1$ cm^2/Vsec (*139*); for $\mu \lesssim 1$ cm^2/Vsec the polaron must be considered to move from cation to cation not in a band (i.e., by tunnelling) but by phonon-induced hopping (*140, 141*).

On the experimental side efforts should be made to prepare pure stoichiometric single crystals of these materials—especially those of Class 3, This will probably entail the development of new techniques. Once obtained, it is essential, for a meaningful correlation of data, that experiments be performed on the *same* crystal (or at least on samples cut from the same boule). It need hardly be stressed that our understanding of the electronic properties of these materials has been much retarded by the unavailability of good samples.

Finally, I should like to draw attention to the very definite poverty of information concerning the dielectric and the thermodynamic properties of Class 3 compounds. In connection with the former, frequency dependent measurements would be of particular interest; at present there exists data only on the temperature dependence of the dielectric constant of V_2O_3 at ultrahigh frequencies (*142*)[1] and of the high-frequency conductivity of VO_2 for $T < T_t$ (*145*). The majority of the existing thermodynamic data was, in general, obtained long ago on ill-defined samples and the integrity of the results obtained is, in some cases, rather questionable; an attempt (after the style of Westrum, Grønvold, and co-workers) should thus be made to rectify this situation.

It is thus to be concluded from this review that solid compounds of transition elements—in particular, oxides, and sulphides—provide striking examples of the breakdown of the band theory of electrons in solids due both to electron–electron (Mott-insulation) and electron–phonon (hopping polarons) interaction and it is my opinion that there is still much that could be learned from a closer collaboration between physicists and solid state chemists.

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[1] T. Kawakubo has informed me of his measurements of the temperature dependence of the dielectric constant ϵ' of VO_2 along the monoclinic a_m axis at 24 GHz. Between 100 and 330°K ϵ' increases monotonically from 22 to 26 and then attains a value of at least 60 within a few degrees of 340°K ($= T_t$). This behaviour could well be connected with a divergence in ϵ' reflecting the onset of an intermediate ferro-, anti-ferroelectric phase (*82*) possessing a distinct (triclinic) crystal structure (*143, 144*).

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