

Electronic Properties of Binary Compounds of the First-row Transition Metals

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1 Introduction: Binary Compounds

The first-row transition metals, by combining with non-metal atoms (particularly those of Group VI), form solid binary compounds which now number more than one hundred and are listed in the Table. Despite the similarities of the composition and structure of these compounds, a quite remarkable range of electronic properties is displayed. Their electronic conductivities, even for the stoicheiometric compounds, range from metallic through semiconducting to insulating; their magnetic behaviour includes examples of Pauli paramagnetism and ferro-, antiferro-, and ferri-magnetism.

Many of these compounds are the products of tarnishing of the parent metals and their conducting properties influence the progress of these reactions and have been basic to their theoretical explanation.¹

Likewise, the compounds appear very commonly as heterogeneous catalysts and again their electronic properties are involved in the basic chemisorptive steps that underlie their catalytic activity. Indeed, for a considerable period the conducting properties, or often the models that were thought to apply to them, determined the direction of much catalytic research.^{2,3} In the last few years, after some disillusionment with the results of this approach,⁴ interest has turned to the relation between activity and other electronic properties such as spectra^{5,6} and magnetic behaviour.⁷ Besides their involvement in these chemical processes, the compounds (or modifications of them formed by doping, non-stoicheiometry, or combination as in the ferrites) are of increasing interest in the applied areas of solid-state physics and electronics.

Notwithstanding the significance of these compounds, inorganic chemistry has tended to neglect them in favour of more complex co-ordination compounds of these metals. Essentially this is because the *d* electron properties of the latter compounds are similar in solution and in the solid state, whereas in the simple

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¹ K. Hauffe, *Progr. Metal Physics*, 1953, **4**, 71.

² G. Parravano and M. Boudart, *Adv. Catalysis*, 1955, **7**, 47.

³ K. Hauffe, *Adv. Catalysis*, 1955, **7**, 213.

⁴ (a) J. D. Cotton and P. J. Fensham, *Trans. Faraday Soc.*, 1963, **59**, 1444; (b) H. B. Charman, R. M. Dell, and S. S. Teale, *Trans. Faraday Soc.*, 1963, **59**, 453.

⁵ D. A. Dowden and D. Wells, *Actes du Deuxième Congr. Int. de Catalyse*, Technip, Paris, 1961, p. 1499.

⁶ J. Haber and F. S. Stone, *Trans. Faraday Soc.*, 1963, **59**, 192.

⁷ K. S. De, M. J. Rossiter, and F. S. Stone, *Proc. 3rd Internat. Congr. Catalysis*, North Holland, Amsterdam, 1965, p. 520.

binary compounds, co-operative electronic properties exist as a special feature of the solid compounds. Nevertheless, an understanding of the features of these compounds will be increasingly important as interest turns to metal-cluster compounds⁸ and such chain systems as copper bromide.⁹

As these compounds exhibit remarkable transitions in properties while retaining structural simplicity, they appear to offer a unique theoretical opportunity for the elucidation of these various phenomena. Although the data and the theoretical models are still somewhat limited, they do warrant overall presentation and assessment.

2 The 3d Electrons and Theoretical Models

In general, the electronic properties are a consequence of two facts: the 3d shells of the transition-metal ions are incompletely filled, and there is some measure of overlap of 3d orbitals with the surrounding anion and cation orbitals.

A consideration of electronic levels indicates that, upon compound formation, the 4s electrons from the metal atoms will transfer to fill the p orbitals of the anionic atoms, thus leaving the partially filled 3d orbitals outermost. The degeneracy of such 3d orbitals is lifted by interaction with the negatively charged anion ligands in the crystal.¹⁰ Figure 1 shows a cation octahedrally surrounded by anions as in the case of the NaCl structure exhibited by the oxides TiO–NiO, where the d electrons have lower energy if they face between the anions (t_{2g} orbitals) and higher energy if they face towards them (e_g orbitals). However, unlike the co-ordination compounds of these transition metals, the binary compounds have interionic distances which may permit extended overlap amongst these cation orbitals, and also favour overlap between the orbitals of the anions.

Accordingly, two theoretical models have been used in discussing their electronic properties. When appreciable overlap occurs between orbitals, band theory describes the delocalised electrons in terms of wave functions (Bloch functions) which extend throughout the solid and have equal amplitudes at equivalent lattice sites. On the other hand, the Heitler-London approach describes localised orbitals, which only overlap to a very small extent, in terms of a collection of wave functions each of which is centred on one particular ion in the lattice.¹¹

The example of TiO (d^2 , if the above electron transfer is assumed to be complete) best illustrates the effect of delocalisation on the electronic properties. The observed metallic conductivity and temperature-independent susceptibility (Pauli paramagnetism)¹² are characteristic of extensively delocalised electrons which result from the overlap of the partially filled t_{2g} orbitals on one cation

⁸ F. A. Cotton, *Quart. Rev.*, 1966, **20**, 389.

⁹ C. G. Barraclough and C. F. Ng, *Trans. Faraday Soc.*, 1964, **60**, 836.

¹⁰ D. E. O'Reilly, *J. Chem. Educ.*, 1961, **38**, 312.

¹¹ J. B. Goodenough, 'Magnetism and the Chemical Bond', ed. F. A. Cotton, Interscience, New York, 1963, ch. 1.

¹² (a) S. P. Denker, *J. Appl. Phys.*, 1966, **37**, 142; (b) A. A. Samokhvalov, A. G. Rustamov, *Soviet Phys. Solid State*, 1963, **5**, 877; (c) F. J. Morin, *Phys. Rev. Letters*, 1959, **3**, 34.

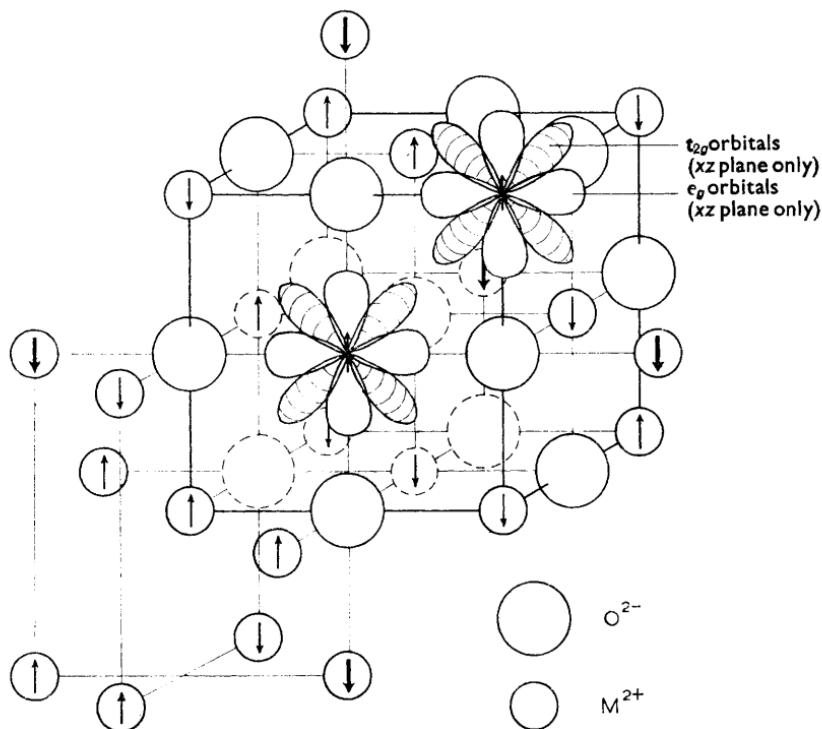


Fig. 1 The NaCl lattice, showing some of the orbitals present in the transition-metal oxides TiO to NiO . The t_{2g} orbitals, which lie between the anions, are favourably oriented for cation-cation overlap, such as is found in TiO . When the e_g orbitals are occupied, overlap with the p orbitals of oxygen causes an antiferromagnetic coupling of each cation spin dipole with those of the next-nearest-neighbour cations, as found in NiO , and indicated on the diagram

with those on the twelve adjacent cations. The overlap is sufficient to enable delocalisation analogous to that found for the $3s$ electrons in metallic sodium. Band theory predicts that for such a collection of electrons moving in the periodic potential of the cation lattice, the energy levels, which are specified by a linear momentum quantum number k , will be very closely spaced up to the number of levels necessary to accommodate two $3s$ electrons from each atom present. Beyond these levels, which are referred to as the ground state or valence band, a forbidden region exists until another series of levels, termed the excited-state band, begins.¹³

Figure 2 shows the energy of the electrons plotted against k (drawn as if k were continuous), together with a representation of the half-filled band of sodium. Under the influence of an external electric field, high electronic conduction is possible owing to the presence of empty levels in the band. In the alkaline-earth

¹³ C. Kittel, 'Introduction to Solid State Physics', 3rd edn., Wiley, New York, 1966, ch. 9.

metals, this band is filled by two *s* electrons from each atom, but conduction is still possible because other empty bands in fact overlap the filled band.

When two types of atom constitute the lattice, a more complex situation exists. For covalent non-transition-metal compounds such as InAs, which are also described by the band model, the valence electrons lose their *s* or *p* character and form one filled band delocalised over both the indium and arsenic cores, as represented in Figure 2c.¹⁴

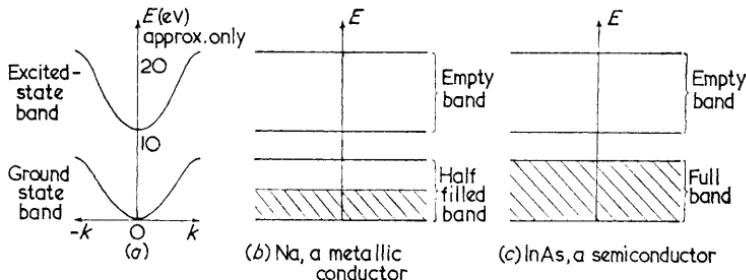


Fig. 2 Plot of energy (*E*) against wave vector (*k*), and schematic energy levels in band-type compounds

In the transition-metal compound considered here, the valence electrons (*s* and *p*) again form a band, but in the oxides, which are predominantly ionic, the band has a high density of states around the anions, which could be described as a purely anion band of overlapping filled *2p* orbitals. The *d* electron levels lie between this and the excited-state band, which now has a very high energy.

The extent of overlap of the *d* levels control magnetic and conductivity characteristics, as is evident from the example of TiO, the electronic structure of which is indicated in Figure 3.

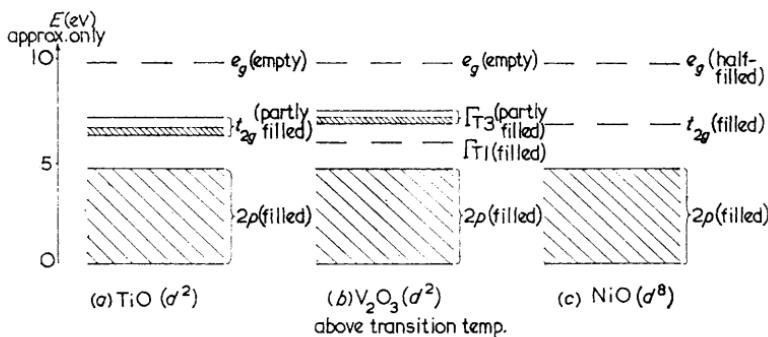


Fig. 3 Schematic energy levels showing the narrow, partly filled *d* bands present in TiO and V_2O_3 (above transition temperature), and the discrete *d* levels in NiO. The empty excited-state bands lie above the e_g levels

¹⁴ O. Madelung, 'Physics of III-V Compounds', Wiley, New York, 1964, ch. 2.

As will be seen in Section 7, NiO shows markedly different conductivity characteristics from TiO owing to localisation of both the e_g and t_{2g} electrons, which are best described by the Heitler-London approach. Morin¹⁵ has attributed this reduction in overlap of the t_{2g} orbitals to the contraction of the orbitals onto the cation sites as the nuclear charge increases across the series, resulting in a narrowing of the t_{2g} band-width until discrete levels are present (Figure 3c). Conductivity will now occur by jumps of electrons from one discrete level to another unoccupied one.

3 Magnetic Properties

The known magnetic properties of these compounds, shown in the Table and derived primarily from Goodenough's tabulations,¹⁶ fall into two main groups: those without and with spontaneous magnetic moments. Except for VO, which has Curie-Weiss paramagnetism,¹⁷ the first group consists of those with Pauli paramagnetism such as TiO, TiN, TiC, TiSe, and TiTe. The absence of a magnetic moment, except in an applied field, is due to the absence of magnetic interactions between electrons in an extensively delocalised band. Many of this group are superconductors below 10°K¹⁸ and all are metallic conductors above it. The second group, the remainder of the compounds, exhibit their spontaneous magnetisation as antiferro-, ferro-, or ferri-magnetism owing to the strong magnetic interactions which can arise either between electrons which are not as delocalised as in the first group while still permitting metallic conduction (the chalcogenides), or between localised electrons (most of the oxides). Indeed for the whole of the second group it is not possible to deduce, *a priori*, the extent of orbital overlap from the occurrence of spontaneous magnetisation.

In the oxide series MnO to NiO, magnetic interactions occur first between the 3d electrons on each cation to produce a high spin configuration (Hund's rule), and secondly between these localised dipoles to give a periodic antiparallel alignment throughout the lattice. The origin of both these effects lies in the quantum mechanical exchange energy which is due to the change in the Coulomb energy resulting from different spatial distributions of charge for different spin states. For alignment of the cation dipoles, the energy is given by $-2J\sum S_i \cdot S_j$ where S_i and S_j are the electron spins and J is the exchange integral which is negative for antiferromagnetism and positive for ferromagnetism (parallel coupling).¹⁹ Ferrimagnetism results from a non-equivalent antiparallel coupling.

Neutron diffraction²⁰ reveals that, for these oxides, the exchange interaction is not between t_{2g} electrons on adjacent cations which are evidently too localised, but between the e_g electrons on next-nearest neighbours *via* the intervening oxide ion. Each cation thus has six next-nearest-neighbour dipoles aligned antiparallel

¹⁵ F. J. Morin, *Bell System Tech. J.*, 1958, **37**, 1047.

¹⁶ Ref. 11, p. 98.

¹⁷ S. Kawano, K. Kosuge, and S. Kachi, *J. Phys. Soc. Japan*, 1966, **21**, 2744.

¹⁸ B. T. Mathias, *Rev. Mod. Phys.*, 1963, **35**, 1.

¹⁹ A. H. Morrish, 'The Physical Principles of Magnetism', Wiley, New York, 1965, p. 275.

²⁰ C. G. Shull, W. A. Strauser, and E. O. Wollan, *Phys. Rev.*, 1951, **83**, 333.

Crystal structure and electronic properties of binary (and some ternary) transition-metal compounds

Structure	$\text{TiO}_{6-14+16}$	$\text{VO}_{6-78+26}$	VC	MnO	FeO	CoO	NiO
NaCl	TiN	TiC	VC	MnO	FeO	CoO	NiO
ZrN	ZrC	NbC					
HTN	HfC	TaC					
$\text{Ti}_3\text{O}_5\sharp$	V_2O_3	Cr_2O_3					
$\text{TiO}_{1.19-2+0}$	VO_2	Cr_2O_3					
Rutile	V_2O_5						
TiO_2							
Ti_3O_5							
TiO_3							
Ti_2O_5							
Ti_2O_7							
Ti_3O_8							
Ti_4O_7							
Ti_5O_9							
Ti_6O_{11}							
Ti_7O_{13}							
Ti_8O_{15}							
Ti_9O_{17}							
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Crystal structure:

exists only

Magnetic properties: $\mu_0 \mu_r = 1$
Conduction properties: $\kappa = 0$

metals to semiconductors;
metallic to semiconducting transition observed;
semiconductors

III. CONCLUSIONES.

Waddington in "Non-Stoichiometric Compounds," ed. L. Mandelcorn, Academic Press, New York, 1964, ch. 3.

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exist over a small composition range unless otherwise indicated (by a line joining the phase limits). The nominal formulae appear for the remaining compounds, of which only a selection are tabulated. The Magnesiates Ti_nO_{2n+1} ($n = 4$ to 8), have been omitted. The following are indicated by: d, diamagnetic; P, Curie-Weiss paramagnetic; PP, Pauli paramagnetic; f, ferromagnetic; af, antiferromagnetic; fi, ferrimagnetic.

here known, these are indicated by: underline —— metallic conductors;
 —— semiconducting transition observed:

exhibited (refer to Section 3 of text).
..... semiconductors.

Stoichiometric Compounds," ed. L. Mandelcorn, Academic Press, New York, 1964, ch. 3.

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as shown in Figure 1. Anderson²¹ has called this mechanism superexchange, and it arises from a small amount of overlap of the e_g orbitals and the neighbouring oxygen p orbitals, such that the spins of the two e_g orbitals are coupled owing to spin polarisation of the lobes of the oxygen orbital.

Particularly when the M–O–M angle is 180°, the exchange energy is considerable, as shown by the Néel points (T_N °K, temperature above which thermal vibrations destroy the magnetisation), which range from 122°K for MnO to 523°K for NiO. Calculations based on superexchange can give T_N within 10° for these oxides, which supports the use that Goodenough²² has made of the mechanism to explain insulating oxides in general. For compounds whose structures are more complicated than NaCl he has suggested that the exchange will be made up of a combination of M–O–M superexchange (either σ type overlap of e_g – p – e_g orbitals or π type overlap of t_{2g} – p – t_{2g} orbitals), direct cation–cation exchange of t_{2g} – t_{2g} orbitals, and indirect exchange through a mutually adjacent anion (M–O–M angle = 90°). Thus, in the corundum series, the anti-ferromagnetism of α -Cr₂O₃ is seen to arise from mainly cation–cation exchange linkages since there is no e_g electron, while that of α -Fe₂O₃, with half-filled e_g orbitals, is due to M–O–M super-exchange at 135°. Similarly, the same considerations are used to explain the behaviour of oxides with spinel (e.g., Fe₃O₄) and perovskite (e.g., NiO, Fe₂O₃) structures which, for the examples quoted, display ferromagnetism and ferrimagnetism respectively.

However, it is difficult to see what such exchanges mean in the complex NiAs structure, which is assumed by most of the simple chalcogenides like MnTe (antiferromagnetic), Cr₇Te₈ (ferromagnetic), and Fe₇S₈ (ferrimagnetic). Goodenough has recognised that greater delocalisation of 3d electrons exists in some of these compounds than is allowed in his exchange mechanism between essentially localised electrons, and has postulated that spontaneous magnetisation can also arise from exchange between electrons some of which are localised and some delocalised. This may be the beginnings of a theory which will explain the conducting and magnetic properties of such metallic antiferromagnets as Cr_{0.98}Te.²³ Some successful calculations have been done by Vonsovsky and Turov²⁴ for metallic iron with this model, involving direct exchange of cation–cation linkages as well as delocalised electronic levels. However, for metallic nickel,²⁵ a purely band approach involving interacting spin bands has proved more successful, and it must be concluded that the understanding of these magnetic interactions is still at a very elementary stage.

4 Conductivity: General Features

At present conductivity measurements provide the most direct information about the electronic structures of the compounds. The Table gives the type of conduction

²¹ P. W. Anderson, in 'Solid State Physics', vol. 14, ed. F. Seitz and D. Turnbull, Academic Press, New York, 1963.

²² (a) Ref. 11, ch. 3; (b) J. B. Goodenough, *Phys. Rev.*, 1960, **117**, 1442.

²³ F. Gronvold and E. F. Westrum, *Z. anorg. Chem.*, 1964, **328**, 272.

²⁴ S. V. Vonsovsky and E. A. Turov, *Soviet Physics*, 1953, **24**, 419.

²⁵ Ref. 19, p. 300.

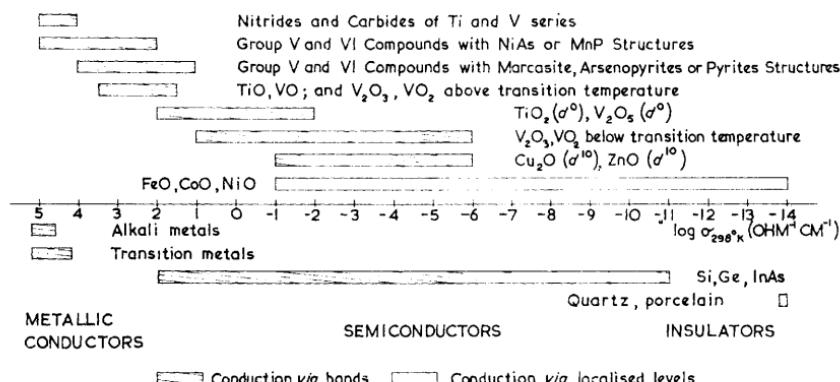


Fig. 4 Room-temperature conductivity of pure substances, and those for which the conductivity has been increased by the solid solution of impurity ions (up to 10% in some cases), or by the presence of non-stoicheiometric defects.^a Transition-metal compounds appear above the scale

^aFor a treatment of this topic see F. A. Kroger, 'The Chemistry of Imperfect Crystals', North Holland, Amsterdam, 1964

tivity exhibited and Figure 4 shows the observed conductivities at 298 K (σ_{298} K) of the salts both when pure and when doped, either by the solid solution of impurity ions (up to 10% in some systems), or by non-stoicheiometric defects. The temperature-dependence of these values shows certain marked characteristics, the significance of which is discussed below. If the conductivities could be measured near 0 K, the compounds would fall into two groups. Those referred to as metallic conductors would have a conductivity greater than their room-temperature value, while all other compounds would be insulators. As the temperature is raised, the conductivity of the group labelled semi-conductors increases owing to thermal excitation of electrons from trapping centres or from the normal ground state into current-carrying levels. At high temperatures, or with heavily doped samples, the conductivity may approach that of the metals, and it is this wide range of possible conductivities which characterises the semi-conductors from the metallic conductors and insulators, as can be seen in Figure 5 for TiO and NiO.

At any temperature,

$$\sigma = n |e| \mu \quad (1)$$

where n is the number of charge carriers present, e is the electronic charge, and μ , the mobility, is the rate at which they move under unit field gradient. n can be determined from measurements of the potential (V_H) induced across a conductor carrying a current, I , by the application of a magnetic field, H . This potential is known as the Hall voltage and its magnitude is given by

$$V_H = R_H I \times H \quad (2)$$

where the Hall constant

$$R_H = \frac{1}{\pm n |e| \mu} \quad (3)$$

where c is the velocity of light, and the + and - signs correspond to electrons or positive holes as the current carriers.²⁶

The combination of σ and V_H also enables μ_H , the Hall mobility, to be calculated, and it is from n and μ and their temperature-dependence that the electronic structure is inferred. Metallic conductors have values of n which are independent of temperature and equal to the number of electrons in the partially filled band, while semiconductors have n values which increase exponentially with temperature, from zero at 0°K, as thermal excitation of the electrons produces current carriers.

In discussing the significance of the mobilities two models of transport have to be considered: movement through bands, and jumps between discrete electronic levels. Transport in metallic conductors can only be explained by the band model, but in semiconductors both can apply. In the following sections the conductivities and mobilities will be interpreted in terms of the electronic structure described by these models.

5 Conductivity in Metallic Conductors

Of the many metallic conductors in the Table, the series TiO, TiN, and TiC has received most attention.²⁷ They are referred to as refractory hard metals, because in addition to their conductivity and magnetism they have physical similarities to the parent metals,²⁸ for example, TiC and TiN, like titanium, melt at above 1800°K. However, they are not to be regarded as metallic alloys because the bonding involves distinct ionic and covalent character. In the band model of conduction, which applies to metallic conductors such as these, the acceleration of the electrons through the energy levels of the crystal is described by the concept of the effective mass ratio m^*/m_0 which relates the acceleration possible in the periodic potential of the lattice to that of a free electron. A large effective mass ratio is associated with a small acceleration, as found in narrow bands where the interaction of the electrons with the periodic potential is appreciable.²⁹

The other concept used to characterise these band conductors is the relaxation time, τ , which refers to the frequency of interruption of the electronic acceleration by scattering. Mobility, relaxation time, and effective mass are then related by

$$\mu = \frac{e\tau}{m^*} \quad (4)$$

Finally, the product of the velocity and τ specifies the mean free path, λ , of the current carriers.

In general, two main scattering processes occur in metallic conductors. At low temperatures (usually not greater than 20°K for metals) μ is proportional to T^2 owing to scattering by impurities in the lattice. At higher temperatures the

²⁶ P. N. Shive, 'Semiconductor Devices', Van Nostrand, New York, 1959, ch. 24.

²⁷ (a) T. Tsuchida, Y. Nakamura, M. Mekata, J. Sakurai, and H. Takaki, *J. Phys. Soc. Japan*, 1961, **16**, 2453; (b) W. S. Williams, *Phys. Rev.*, 1964, **135**, A, 505.

²⁸ E. Dempsey, *Phil. Mag.*, 1963, **8**, 285.

²⁹ Ref. 26, ch. 15.

electrons are scattered by the aperiodicity caused by the thermal vibrations of the lattice atoms (lattice scattering), and in most of these conductors this type of scattering predominates, leading to a decrease in mobility with temperature according to $\mu \propto T^{-n}$, where n lies between 0.5 and 5.

However, TiO , TiN , and TiC all show wide ranges of non-stoichiometry as well as having very defective structures (for $\text{TiO}_{1.00}$, 15% anion and cation vacancies exist),³⁰ and impurity scattering is still effective at 300°K, so that the mobility of $\text{TiO}_{1.00}$ only decreases slightly with temperature, while that of $\text{TiO}_{1.22}$ increases slightly as reflected in the conductivity shown in Figure 5.

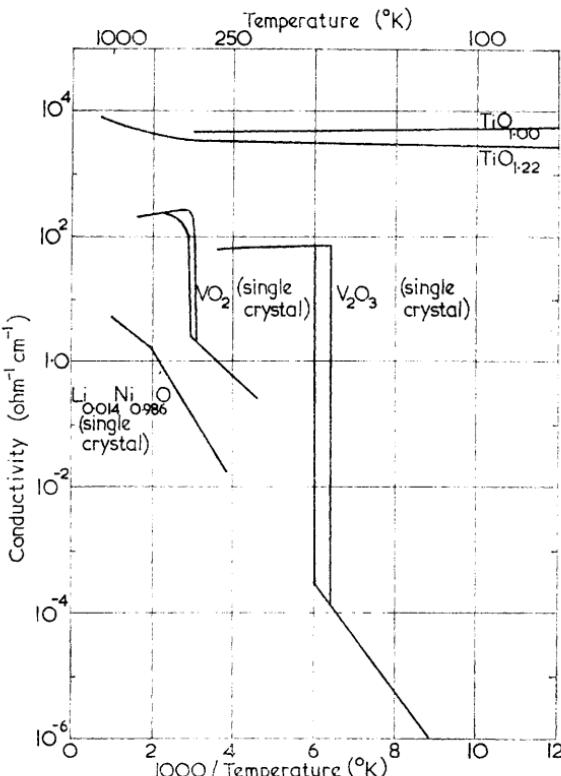


Fig. 5 Electronic conductivity as a function of temperature for various oxides [From the data of S. P. Denker (TiO);^{12a} F. J. Morin (VO_2 , V_2O_3);^{12c} and S. Koide, *J. Phys. Soc. Japan*, 1965, **20**, 123 (doped NiO)]

When it is assumed that the relaxation time of the conduction electrons in TiO is the same as for the metals, an effective mass ratio of 10 is deduced from the calculated Hall mobility of $1.0 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$,³¹ which supports transport in

³⁰ S. P. Denker, *J. Phys. and Chem. Solids*, 1964, **25**, 1397.

³¹ Ref. 12b.

a narrow band (cf. $m^*/m_0 = 0.98$, $\mu = 21 \text{ cm.}^2 \text{ v}^{-1} \text{ sec.}^{-1}$, for free electrons in the wide band of sodium).

6 Transition from Delocalised to Localised Electrons

As indicated in Section 3, the change from Pauli paramagnetism to spontaneously magnetised systems does not simply correspond to a transition from delocalised to localised electronic states. However, in this section it will be seen that such a correspondence can be established for the change from metallic to non-metallic conduction. Mott³² has predicted that, as the nuclear separation of a delocalised system is increased, a sharp transition to the localised state occurs with a consequent drop in conductivity. Two examples provide evidence for this relationship.

The first has already been implied in Section 2, namely, the transition from metallic conduction in TiO to semiconducting or insulating behaviour in NiO . Successive localisation occurs owing to the increase in interaction of the electrons with the nuclear charges across the series, and Morin³³ has shown that the metallic compounds, TiO and the high-temperature forms of VO , V_2O_3 , and VO_2 , have more $t_{2g}-t_{2g}$ and more π -type $t_{2g}-p$ overlap than the insulators MnO , FeO , and Cr_2O_3 .

Secondly, such delocalisation in V_2O_3 and VO_2 is abruptly destroyed at 160°K and 340°K respectively, as shown by a transition to semiconducting behaviour and a change in the magnetic state. Figures 5 and 6 summarise the experimental evidence. Goodenough³⁴ attributes this change to a crystallographic distortion involving the pairing of the cations, so that the electrons become trapped in metal-metal pair bonds.

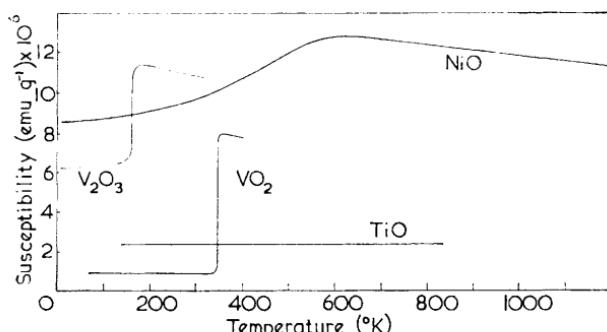


Fig. 6 Magnetic susceptibility as a function of temperature for various oxides [From the data of A. A. Samokhvalov and A. G. Rustamov (TiO);^{32b} K. Kosuge (VO_2);³⁶ P. H. Carr and S. Foner, *J. Appl. Phys. Suppl.*, 1960, 31, 344S (V_2O_3); and J. R. Singer, *Phys. Rev.*, 1956, 104, 929 (NiO)]

³² N. F. Mott, *Phil. Mag.*, 1961, 6, 287.

³³ F. J. Morin, *J. Appl. Phys. Suppl.*, 1961, 32, 2195.

³⁴ Ref. 11, p. 256.

In the corundum structure assumed by Ti_2O_3 as well as V_2O_3 , the trigonal ligand field splits the t_{2g} orbitals into those which lie in the basal planes of the cation octahedra (Γ_{1g}), and those which point above and below these planes in the direction of the c axis (Γ_{1u}), as shown in Figure 3. Pairing can occur in both these directions. In the case of Ti_2O_3 (d^1), the c -axis electrons are not delocalised even at high temperatures, and pairing, which occurs over a wide temperature range (500°K — 350°K), only alters the conductivity slightly. However, V_2O_3 (d^2), in addition to having one electron per cation in the localised c -axis bonds, has one electron per cation in the basal-plane orbitals. Hence c -axis pairing, which occurs between 500°K and 400°K , does not alter the conductivity, but the transition of electrons in the basal plane from delocalised to paired at 160°K causes the conductivity to drop by a factor of 10^6 within a degree, and the magnetic properties to change from paramagnetic to antiferromagnetic.

Before such detailed crystallographic data were available, the transition in conductivity was interpreted by Morin³⁵ as due to the onset of antiferromagnetism which split the partially occupied d bands into non-conducting spin or magnetic sub-bands. However, in the case of VO_2 (d^1), Kosuge³⁶ observed that the Mössbauer line of Fe, doped into VO_2 crystals, remained unsplit below the transition temperature (340°K), revealing that the magnetic transition is from paramagnetic to diamagnetic, rather than to antiferromagnetic. This supports the contention of Goodenough³⁴ and Adler and Feinleib³⁷ that cation pairing causes the transition in both magnetic and conductivity behaviour.

The characteristics of the semiconductivity, observed below the transition temperature in these oxides, provide a clue to the electronic structure of the nominally unoccupied higher-energy d levels. Owing to an excess of 1 part in 10^5 of vanadium in VO_2 , n -type semiconductivity occurs as determined from the negative sign of both the Hall³⁸ and the Seebeck coefficient.³⁹ It can be accounted for by the thermal promotion of electrons from their trapping centres into an unfilled band which Goodenough⁴⁰ attributes to π type overlap between $t_{2g}-p-t_{2g}$ orbitals in the plane perpendicular to the V-V pairs. The room-temperature mobility of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ indicates that this is a narrow band. For non-stoichiometric semiconductors electrons are said to be trapped when they are localised in the positive potential of a vacant anion site, or localised on an interstitial cation, forming V^{3+} in this case. The number of untrapped electrons available for current carrying is given by

$$n_{\text{mobile}} = n_{\text{total}} \exp(-E_D/kT)$$

where E_D is the trapping energy, given by the slope of the plot of $\log \sigma$ against $1/T$, the temperature-dependence of the mobility being assumed small compared

³⁵ F. J. Morin, *Phys. Rev. Letters*, 1959, **3**, 34.

³⁶ K. Kosuge, *J. Phys. Soc. Japan*, 1967, **22**, 551.

³⁷ D. Adler and J. Feinleib, *Phys. Rev. Letters*, 1964, **12**, 700.

³⁸ I. Kitahiro, T. Ohashi, and A. Watanabe, *J. Phys. Soc. Japan*, 1966, **21**, 2422.

³⁹ I. Kitahiro and A. Watanabe, *J. Phys. Soc. Japan*, 1966, **21**, 2423.

⁴⁰ J. B. Goodenough, *Bull. Soc. chim. France*, 1965, 1200.

with that of n_{mobile} .⁴¹ Figure 5 shows this plot to have the expected negative gradient for the semi-conducting regions of the oxides considered.

TiO_2 (d^0), rutile, does not show a crystallographic transition like that of VO_2 . When it is slightly oxygen-deficient, the n -type conductivity which occurs can be interpreted in terms of electron promotion from the traps, first to one, then to a still higher unfilled band.⁴² This is evidence of an electronic structure similar to that of VO_2 , where two such bands were indicated by transport in the metallic and semiconducting regions respectively.

Detailed information is not available for the Magneli series $\text{V}_n\text{O}_{2n-1}$ ($n = 4$ to 8), which exhibit semiconductivity without a transition to the metallic state.⁴³ An abrupt change in the magnetic susceptibility occurs in some cases.⁴⁴

Similar information regarding the electronic structure of already occupied d levels is obtained from p -type semiconduction which occurs in oxygen-excess structures where the valence of the cations can easily be increased. For example, Cu_2O (d^{10}), as distinct from those p -type oxides with localised d electrons discussed in the next section, exhibits p -type conduction in a band, as deduced from the positive sign of the Hall coefficient and the negative temperature-dependence of the mobility.⁴⁵ The current is carried by the positive holes (p) formed in the otherwise full d band by the absence of electrons, which, when trapped, can be represented as Cu^{2+} ions adjacent to cation vacancies.

7 Compounds with Localised $3d$ Electrons

Oxides having a $3d$ structure which cannot be described by the band model are best accounted for by the localised model. This group has been reviewed by Jonker and van Houten.⁴⁶ The presence of localised electrons is deduced from the absence of metallic conductivity.⁴⁷ A minimum conductivity of $10 \text{ ohm}^{-1} \text{ cm.}^{-1}$ would be expected if delocalised electrons were present. However, the series MnO to NiO , which have high-spin d -electron configurations (d^5 to d^8), shows a conductivity of the order of $10^{-14} \text{ ohm}^{-1} \text{ cm.}^{-1}$ when pure and stoichiometric. In addition, localised states have been inferred from the similarity of the visible and ultraviolet spectra of the oxides to those of the complexed species in solution.⁴⁸

When non-stoichiometric, the oxides MO_{1+x} are p -type semiconductors and this is ascribed to an exchange of electrons between M^{2+} ions and the M^{3+} ions present as chemical defects, as in p -type Cu_2O . The conductivity should indicate features of the electronic ground state if a suitable model for transport through localised energy levels were used. Two approaches have been adopted.

⁴¹ N. F. Mott, and R. W. Gurney, 'Electronic Processes in Ionic Crystals', Clarendon Press, Oxford, 2nd edn., 1948, ch. 5.

⁴² J. H. Becker and W. R. Hosler, *Phys. Rev.*, 1965, **137**, A, 1872.

⁴³ S. Kachi, T. Takada, and K. Kosuge, *J. Phys. Soc. Japan*, 1963, **18**, 1839.

⁴⁴ K. Kosuge, T. Takada, and S. Kachi, *J. Phys. Soc. Japan*, 1963, **18**, 318.

⁴⁵ M. O'Keefe, Y. Ebisuzaki, and W. J. Moore, *J. Phys. Soc. Japan, Suppl.*, 2, 1963, **18**, 131.

⁴⁶ G. H. Jonker and S. van Houten, 'Halbleiterprobleme VI', ed. F. Sauter, Friedr. Vieweg und Sohn, Braunschweig, 1961, p. 118.

⁴⁷ N. F. Mott, *Proc. Phys. Soc.*, 1949, **62**, A, 416.

⁴⁸ R. Newman and R. M. Chrenko, *Phys. Rev.*, 1959, **114**, 1507.

Heikes and Johnston⁴⁹ recognised that, when a Ni^{2+} – Ni^{3+} pair exchange an electron, the distortion of the surrounding anion charges alters so as always to be centred about the Ni^{3+} ions, and this contributes an activation energy to the electron jump. The mobility μ is then given by

$$\mu = \frac{a^2 e \nu_0}{kT} \exp(-q/kT)$$

where a is the closest cation–cation distance; ν_0 is the jump frequency, of the order 10^{13} sec.⁻¹, the frequency of lattice vibrations, suggesting that jumps occur when vibrations cause the mutual approach of the cations.

On the other hand, Holstein⁵⁰ has presented a formal treatment of a current carrier together with its accompanying lattice polarisation, and for this pair the name polaron is used. At temperatures greater than half the Debye temperature of the lattice, charge transport is predicted to be by activated jumps, and mobility to increase with temperature (as for Heikes and Johnston's approach). Lattice vibrations are such that polarisation effects are restricted to a few lattice spacings around the Ni^{3+} , and the polarons in such circumstances are described as small. However, at lower temperatures, the polarisation extends over a large distance, and the polarons interact with each other to form what is called a band of polaron states, so that charge transport now has a mobility which increases with decreasing temperature.

When attempts were made to use experimental evidence to distinguish these two approaches,⁵¹ difficulties arose. First, transport measurements on powdered oxides are difficult and not always reproducible, particularly when the conductivity is low. To minimise these difficulties, the conductivity, in compounds such as NiO , has been increased by high dope concentrations of Li_2O , added to form a solid solution of Li^+ and the complementary Ni^{3+} ions in the NiO lattice.⁵² However, the presence of Li^+ raises other uncertainties. In addition, the theoretical significance of the Hall voltage and the Seebeck effect in these jump-type and antiferromagnetic compounds has only recently been investigated, and is not as clearly understood as the band-type conductors.⁵³

Improved experimental methods and the use of single crystals of NiO with only low Li_2O concentrations have now led to results which can be reliably discussed.⁵⁴

Seebeck measurements above 100°K , together with conductivity data, have been interpreted by Heikes and Johnson to favour the simple jump process. After some approximations, the Seebeck coefficient is found to vary inversely as the number of charge carriers, and its constancy above 500°K , on this theory,

⁴⁹ R. R. Heikes and W. D. Johnston, *J. Chem. Phys.*, 1957, **26**, 582.

⁵⁰ T. Holstein, *Ann. Phys. New York*, 1959, **8**, 325, 343.

⁵¹ A. J. Bosman and C. Crevecoeur, *Phys. Rev.*, 1966, **144**, 763.

⁵² E. J. W. Verwey, 'Semiconducting Materials', Butterworths, London, 1951, p. 151.

⁵³ (a) L. Friedman and T. Holstein, *Ann. Phys.*, 1963, **21**, 494; (b) L. Friedman, *Phys. Rev.*, 1963, **131**, 2445; (c) E. R. Heikes, in 'Informal Proceedings of the Buhl International Conference on Materials', Pittsburgh, 1963, ed. E. R. Schatz, Gordon and Breach, New York, 1966, p. 1.

⁵⁴ S. P. Mitoff, *J. Chem. Phys.*, 1961, **35**, 882.

means that any activation energy present in the conductivity (see Figure 5) must arise from the mobility term. A mobility of 10^{-4} $\text{cm}^2 \text{v}^{-1} \text{sec.}^{-1}$ with an activation energy, q , ranging from 0.1 to 0.5 ev was deduced. The jump process also finds support from the presence of high-frequency relaxation losses in NiO samples over the range 4° to 300°K,⁵⁵ although these results could be due to jump conduction involving impurity defects rather than the Ni^{2+} – Ni^{3+} exchange.

However, there is some experimental evidence that favours Holstein's polaron view, if the difficulty of interpreting Hall constants in such complex magnetic materials is set aside. For NiO, the temperature coefficient of the Hall mobility is negative between 200° and 500°K, which accords with movement in a polaron band.⁵⁶ There is a discontinuity in the Hall voltage through the Néel temperature and above T_N it takes on as yet unexplained negative values. The conductivity, on the other hand, shows only a slight change in slope at T_N and Heikes⁵⁷ accounts for this in terms of the magnetic effects on the jump mobility.

8 Chalcogenides and Pnictides

Of the chalcogenides and pnictides (Group V) of the transition metals, those having the NiAs and the closely related MnP structure (Table) have been most investigated.⁵⁸ All exhibit spontaneous magnetisation and their characteristically high room-temperature conductivity lies between 10^2 and $10^5 \text{ ohm}^{-1} \text{ cm.}^{-1}$ (Figure 4). These values indicate conduction in bands, since they can only be explained by assuming high mobilities (1 to 100 $\text{cm}^2 \text{v}^{-1} \text{sec.}^{-1}$) such as are only possible in the band scheme. As these compounds all possess a large natural deviation from stoichiometry (of the order of 1%), the conductivity may be high even though it may not be of the metallic type, so it is difficult to distinguish between metallic conduction and semiconduction in a band with a large number of current carriers. Hall measurements cannot, as yet, readily be interpreted to enable the number of charge carriers to be calculated, as there is an additional component to the Hall voltage in such magnetic compounds.⁵⁹ It has been inferred, however, that of compounds investigated, only Cr_3Te_4 ,⁶⁰ MnTe ,⁶¹ Fe_2Te_3 ,⁶² and Fe_7S_8 ⁶³ are semiconductors, while some sulphides⁶⁴ and selenides⁶⁵ of chromium exhibit a semiconducting to metallic transition (Table).

⁵⁵ (a) S. van Houten, *J. Phys. and Chem. Solids*, 1962, **23**, 1045; (b) S. van Houten and A. J. Bosman, Ref. 53c, p. 123.

⁵⁶ I. G. Austin, A. J. Springthorpe, and B. A. Smith, *Phys. Rev. Letters*, 1966, **21**, 20.

⁵⁷ Ref. 53c.

⁵⁸ (a) W. Albers and C. Haas, in 'Proceedings of the Seventh International Conference on the Physics of Semiconductors', Paris, 1964, Academic Press, New York, 1965, p. 1261; (b) S. Fujime, M. Murakami, and E. Hirahara, *J. Phys. Soc. Japan*, 1961, **16**, 183; (c) K. van Con and J. P. Suchet, *Compt. rend.*, 1963, **256**, 2823.

⁵⁹ (a) R. Karplus and J. M. Luttinger, *Phys. Rev.*, 1954, **95**, 1154; (b) M. Nogami, *Jap. J. Appl. Phys.*, 1966, **5**, 134.

⁶⁰ J. P. Suchet and P. Imbert, *Compt. rend.*, 1965, **260**, 5239.

⁶¹ (a) J. D. Wasscher, A. M. J. H. Seuter, and C. Haas, Ref. 58a, p. 1269; (b) H. Yakada, T. Harada, and E. Hirahara, *J. Phys. Soc. Japan*, 1962, **17**, 875.

⁶² F. Aramu and P. Manca, *Nuovo Cimento*, 1964, **33**, 1025.

⁶³ A. Theodosiou, *Phys. Rev.*, 1965, **137**, *A*, 1321.

⁶⁴ T. Kamigaichi, K. Masumoto, and T. Hihara, *J. Phys. Soc. Japan*, 1960, **15**, 1355.

⁶⁵ K. Masumoto, T. Hihara, and T. Kamigaichi, *J. Phys. Soc. Japan*, 1960, **15**, 1209.

The origin of the high mobility and metallic conductivity in most of the compounds is not yet well understood. The possibility exists of metallic conduction through bands formed by the overlap of the partially filled t_{2g} levels, which are split into two sub-levels, as in the corundum structure of V_2O_3 (Figure 3). Moreover, Goodenough⁶⁶ has shown that overlap is favoured when the cations are displaced slightly into the easily accessible tetrahedral sites, which may be occupied by up to 10% of the cations, resulting in a high conductivity. However, this explanation alone could not apply to the nickel salts, which have filled t_{2g} levels, and Suchet⁶⁷ and Albers and Haas⁶⁸ recognising the marked covalence of these compounds, postulate an overlapping of either the broad $4s$ cation or the broad p anion band with the narrow d bands. This leads to a redistribution of the electrons amongst the bands so that transport can occur with a greatly increased mobility.

Hulliger and Mooser⁶⁹ have studied the series formed from transition metals and anions such as S_2^{2-} , PS^{3-} , and P_2^{4-} , a selection of which is shown in the Table. From consideration of crystal-field splittings, they have been able to relate both the crystal structure and the conductivity to the number of d electrons present. These compounds, like the previous group, have very high conductivity, ranging from 1 to 10^4 $\text{ohm}^{-1} \text{cm.}^{-1}$ at room temperature, again indicative of movement in overlapping d - s or d - p bands. On the basis of the Seebeck coefficient and the temperature-dependence of conductivity, Hulliger and Mooser inferred that only the structures with the d^7 configuration are metallic. Here there are six non-conducting t_{2g} electrons above which lies an unfilled band containing the additional one electron per cation. Superconductivity is found amongst this group,¹⁸ which are expected to be Pauli-paramagnetic. Semiconductivity occurs in the remaining compounds, where metallic conductivity is prevented by the accommodation of the d electrons in exactly half-filled, high-spin bands as for MnS_2 (d^5 , pyrites structure) or in completely filled d sub-bands (d^4 , d^6 , marcasite structures, and d^5 , arsenopyrites structure). In the marcasite compounds, a diamagnetic state results from the large crystal-field splitting caused by the covalent anions. In the d^5 arsenopyrites structures additional cation-cation pairing exists. Both these and the $NiAs$ type compounds provide a fertile field for investigations towards a more definite description of their unique conductivity patterns.

9 Halides

Halides of the bi- and ter-valent transition metals have antiferromagnetic Néel temperatures below 100°K , and for some, such as MnF_2 , the magnetic structure has been extensively investigated.⁷⁰ However, very little has been reported on their electronic conductivity, so their electronic structure is unknown.

⁶⁶ Ref. 11, p. 276.

⁶⁷ J. P. Suchet, *Physica Status Solidi*, 1966, **15**, 639.

⁶⁸ W. Albers and C. Haas, *Phys. Rev. Letters*, 1964, **8**, 300.

⁶⁹ F. Hulliger and E. Mooser, *J. Phys. and Chem. Solids*, 1965, **26**, 429.

⁷⁰ H. Bizette and B. Tsai, *Compt. rend.*, 1954, **238**, 1575.

10 Limitations of Current Theoretical Models

Theories of electrical transport and magnetic exchange can qualitatively account for the general features of conductivity and magnetism of transition-metal compounds in terms of either the delocalised or localised model of the electronic structure. We must now see to what extent calculations of the energy levels can reproduce the electronic structure indicated by experiment.

For electrons known to be localised, the method of Heitler and London (Section 3), based on atom-centred functions, should enable reasonably accurate calculations to be performed, but they have only been successful in the case of the simple hydrogen molecule. When extended to a solid lattice of heavy atoms with localised electrons, such as NiO, the difficulty of including the large number of electron-electron and electron-nuclear interactions renders the calculations extremely difficult,⁷¹ and success is not yet in sight.

These difficulties, however, are not inherent in the band approach, where electrons are described as free and move in a periodic potential provided by all the ions in the lattice. Accurate calculations have been performed for the outer *s* electrons in sodium metal, where use of the band approach is justified by the fact that the experimentally determined effective mass ratio is close to unity ($m^*/m_0 = 0.98$, $\mu = 21 \text{ cm}^2 \text{ v}^{-1} \text{ sec.}^{-1}$, band-width *ca.* 9 ev).⁷²

For the chalcogenides and pnictides, where the mobility is likewise high, use of the band approach would also be valid, although the complications caused by the presence of many overlapping bands and intricate crystal forms have prevented calculations from being performed.

However, for metallic oxides, such as TiO, low mobilities of $0.1-1.0 \text{ cm}^2 \text{ v}^{-1} \text{ sec.}^{-1}$ and effective mass ratios of $10-100$ indicate a significant deviation from the free-electron model, as caused by an increased interaction of the electrons with the lattice potential. Although these situations can be described formally in terms of a narrow band (*ca.* 3 ev wide), the concept of a band breaks down when band theory is used to calculate the mean free path,⁷³ which comes to be between 0.3 and 3.0 Å. This is less than the lattice spacing in these compounds, and cannot be accounted for on the basis of known scattering processes.

Despite the apparent inapplicability of some band concepts to these compounds, the qualitative success of the theory in describing the conduction and magnetic properties has been responsible for the increasing use of band calculations, especially since no other approach is available by which even approximate calculations can be made for solid lattices. Bilz⁷⁴ replaced the Plane Wave Bloch functions used for sodium by a set of atomic functions modified by a periodic function (Tight Binding or Linear Combination of Atomic Orbitals approach⁷⁵), and after approximating for many of the parameters, obtained a crude representation for TiO, TiN, and TiC. Ern and Switendick⁷⁶ chose a function which

⁷¹ J. B. Goodenough, Ref. 53c, p. 65.

⁷² D. Pines, *Phys. Rev.*, 1954, **95**, 1090.

⁷³ A. F. Joffe, 'Physics of Semiconductors', Infosearch, London, 1960, p. 424.

⁷⁴ H. Bilz, *Z. Physik*, 1958, **153**, 338.

⁷⁵ J. Callaway, 'Energy Band Theory', Academic Press, New York, 1964, p. 102.

⁷⁶ V. Ern and A. C. Switendick, *Phys. Rev.*, 1965, **137**, A, 1927.

approximates to an atomic function within spheres around each ion, but which represents a Plane Wave function between the spheres (Augmented Plane Wave APW method⁷⁷). For TiO, TiN, and TiC these calculations indicated a 7–11 ev-wide t_{2g} band which, in the case of TiO, overlaps with the 4s band, and for TiN and TiC overlaps with the 2p anion band, permitting a redistribution of electrons between the bands. Although these calculations do not indicate a narrow d band, they explain the fractional number of conduction electrons per Ti atom found from the Hall coefficient and conductivity data.⁷⁸ The band structure of Cu₂O has also been estimated by this approach.⁷⁹

It would not be expected that band calculations could provide a description of NiO, and this has been confirmed by Yamashita⁸⁰ who performed a Tight Binding calculation which predicted metallic conductivity, at variance with the facts. In an attempt to include magnetic effects, Switendick⁸¹ performed a more detailed APW calculation on NiO, and incorporated antiferromagnetic interactions into the band structure using the concept of spin bands. Although this approach, in which the d band is split into two spin bands containing electrons of opposite spin, has had some usefulness for transition metals, it does not yield real predictions of magnetic properties. However, for NiO, these calculations predicted the observed insulating properties. Five electrons occupy one spin band, while the remaining three electrons of opposite spin occupy the other spin band, which, because it is split by the crystal field, has full t_{2g} levels, thus preventing conductivity. This argument is nevertheless unsatisfactory, since it cannot be applied to CoO, which has one less d electron, but also shows insulating properties.

It is clear that only very limited success has been achieved in predicting the observed electronic properties, and a more accurate description of the electronic structure may need new concepts. First, these must be more applicable to orbitals which do not overlap as much as in the metals and, secondly, these should enable magnetic interactions to be incorporated adequately. Goodenough⁸² has explored the possibility of using an extended Molecular Orbital scheme, with magnetic interactions between localised and delocalised electrons, while Hubbard⁸³ has suggested that a unified many-body approach may be possible by use of Green's functions.

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⁷⁷ Ref. 75, p. 95.

⁷⁸ Ref. 27b.

⁷⁹ J. P. Dahl and A. C. Switendick, *J. Phys. and Chem. Solids*, 1966, **27**, 931.

⁸⁰ J. Yamashita, *J. Phys. Soc. Japan*, 1963, **18**, 1010.

⁸¹ A. C. Switendick, Quarterly Progress Report No. 49, Solid-State and Molecular Theory Group, Massachusetts Inst. of Tech., 1963, p. 41.

⁸² Ref. 11, p. 158; Ref. 40.

⁸³ J. Hubbard, Ref. 53c, p. 99.