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Metallic and Nonmetallic Behavior in Transition Metal Oxides

Electron correlation effects in narrow *d* bands and polarons are discussed.

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For many crystalline solids our description of the conduction electrons is based on the Bloch-Wilson band theory of solids introduced in the early 1930's (*1*). The electrons are assumed to move freely and independently through the lattice, each with a well-defined wavelength and a long mean free path. This model breaks down for many 3*d* transition metal oxides, primarily because it neglects Coulomb interactions between the *d* electrons, and these are important when the energy bands are narrow. This was first recognized from the pioneering work of de Boer and Verwey on nickel oxide (NiO), cobaltous oxide (CoO), and ferric oxide (Fe_2O_3) in 1937 (*2*). The transition metal oxides show very diverse electrical behavior. They can be metals like titanium monoxide (TiO) or insulators like manganese monoxide (MnO), although the Wilson theory predicts metallic behavior in both cases for the partly filled 3*d* shells. Others, such as vanadium dioxide (VO_2), undergo a transition from metal to insulator at a critical temperature. The conduction electrons move in bands formed primarily from the *d* orbitals of the transition metal ions, and these are narrow because the ions are relatively far apart. The Wilson theory fails for such bands because it neglects electrostatic repulsion between the electrons, as Mott first pointed out in 1949 (*3*). This interaction leads to a localization of the *d* electrons and a nonconducting state. It also has a crucial effect on the nature of the transition from metal to insulator; this is a many-body effect, and there is as yet no generally recognized theory of what happens at the transition point (*4*).

A conduction electron moving through an ionic crystal will polarize and distort the lattice in its vicinity. This process is known as polaron formation (*5*), and the concept is especially important when we consider the semiconducting properties of these oxides. For wide-band conductors, like the alkali halide crystals, this electron-lattice interaction leads to a fairly small increase in the effective mass of the carrier. But in narrow-band materials entirely new effects can arise. The interaction with the lattice is much stronger because the electron moves slowly, thus giving the heavy ions time to respond more fully. The potential well produced by the deformation of the lattice may be sufficient to trap the electron on a particular ion, thus forming a "small polaron." At high temperatures the carrier then moves from site to site by a thermally activated hopping process with a rather low mobility of the order of 0.1 square centimeter per volt per second or less. The observed mobilities in many 3*d* transition metal oxides are of this order, and a controversial question at the present time is whether small polarons are formed. The evidence has recently been reviewed by Bogomolov *et al.* (*6*), Adler (*7*), and Austin and Mott (*8*). Many of the present uncertainties can only be resolved with better experimental data, and a major problem is the preparation of good crystals.

In this paper we shall confine ourselves mainly to the 3*d* oxides with the simplest structures. These are typical of a wide range of more complex systems which include ferrites, garnets, titanates, perovskites, and glasses.

Energy States of 3d Ions

First let us consider briefly the predictions of simple crystal field and band theory, neglecting any electron correlation effects. We assume, for simplicity, that the binding forces in the crystalline oxides are purely ionic. Although the measured covalency parameters are small (*9*) (~ 3 percent), they are important in a determination of the effective width of any *d* bands.

On this view the O^{2-} ions form closed shells, and the cations have the electron configurations $3d^n\ 4s^0$, where *n* has values from 0 (titanium dioxide, TiO_2) up to 9 (cupric oxide, CuO). The oxygen ions form a close-packed array with the relatively small 3*d* ions occupying sites of octahedral or lower symmetry. In the solid the filled 2*p* oxygen orbitals and the empty 4*s* levels broaden and interact to form bonding and antibonding states. Theory and experiment show that these are separated by about 5 electron volts in these oxides; the 3*d* states that we are concerned with lie within this forbidden gap (Fig. 1).

In a free transition metal ion there are five orbitally degenerate 3*d* states, each having a twofold spin degeneracy. In the oxide these are split by the intense electric field set up by the O^{2-} ions. Let us consider CoO as an example. The lattice has the cubic structure of rock salt, and the 3*d* cations are in an octahedral crystal field. This resolves the degeneracy of the ground state to give two upper (e_g) levels and three lower (t_{2g}) levels. The splitting

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(Δ in Fig. 1) is about 1 electron volt. Kramers' theorem (*7*) shows that the spin degeneracy of the orbitals is not removed, even in lower symmetries or by spin-orbit coupling. In CoO five of the seven *d* electrons occupy t_{2g} orbitals and the remaining two occupy upper e_g levels.

According to the Wilson band model, a crystalline array of *N* monovalent atoms, with *r* atoms per unit cell, will form an energy band with 2 *Nr* states. Thus if $r = 1$, the band is half-filled and metallic behavior is predicted regardless of the bandwidth—that is, a nonvanishing conductivity as the temperature *T* (in degrees Kelvin) approaches zero. On this basis the t_{2g} electrons in CoO should form a metallic band by overlap between the 3*d* ions, since $r = 1$. But in fact CoO is an insulator. This argument is strictly valid only above the Néel temperature (*7*); below 300°K CoO is antiferromagnetic and the lattice is slightly distorted (tetragonal).

More detailed symmetry arguments (*7*) show that for oxides with one cation per unit cell and an odd number of *d* electrons per cation, crystal field splitting alone can *never* give an insulating ground state. But for some oxides with a low symmetry and an even number of cations per unit cell, it could, at least in principle. For compounds like MnO, CoO, and NiO the Wilson band theory certainly fails.

Classification

It is convenient for us [following Adler (*7*)] to group the simple 3*d* oxides in three classes according to their observed electrical behavior. A representative selection is given in Table 1. The common crystal structures which occur are rock salt (as in NiO), rutile (as in VO_2), and corundum (as in chromic oxide, Cr_2O_3).

Compounds in class I are insulators when pure. Some have empty *d* bands (class Ia), and others have a partly filled *d* shell (class Ib); the latter are antiferromagnetic. All these materials become extrinsic semiconductors when suitably doped. Compounds in class II are metallic at all temperatures with resistivities between 10^{-1} and 10^{-6} ohm-centimeter. Some are superconducting (TiO), and others are ferromagnetic (chromium dioxide, CrO_2). Compounds in class III undergo a sharp transition to a highly conducting state at a critical temperature. This is illustrated in Fig. 2 for a few compounds; some dozen or so materials are now known which show similar but less striking changes. The transition is always accompanied by a small crystallographic change and sometimes by a change in magnetic ordering.

The semiconducting behavior of the compounds in class Ib was first studied by de Boer and Verwey in the 1930's; they introduced the concept of a semiconductor with a mixed valence state. For example, if Li^+ ions are substituted for Ni^{2+} ions in NiO, then Ni^{3+} ions are created to maintain charge neutrality. The Li^+-Ni^{3+} complex forms a dipole (Fig. 3). When the Ni^{3+} ion (or hole state) is thermally ionized from the Li^+ center, it moves through the crystal giving *p*-type conduction. This shows that the 3*d* orbitals of the nickel ions overlap sufficiently to allow some current to pass. Thus the absence of conductivity in *pure* NiO is not simply due to the large separation between the Ni^{2+} ions; it must be a many-body electron effect.

Electron Correlation

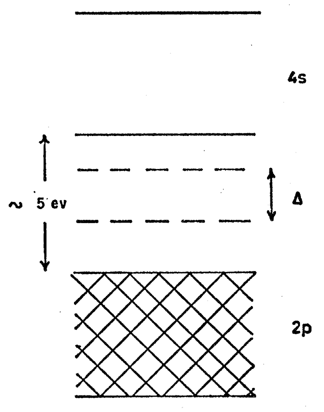
The conditions under which Coulomb interactions between the charge carriers in a crystalline lattice can lead to localization and nonconducting behavior were first investigated by Mott (*3, 10*) in 1949. He considered a simple cubic lattice of *N* one-electron (hydrogen) atoms with a periodicity *a* at $T = 0$°K.

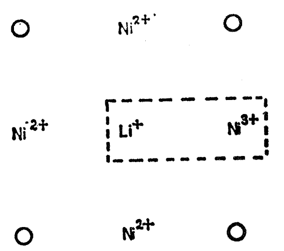
For an electron moving in such a lattice, there are, according to the band model, 2*N* Bloch wave functions of the form

$$\psi = \exp(ikx)U(x)$$

in the first band. In this equation *k* is the wave vector of the electron in the *x* direction, *U* is a periodic function of *x*, and *i* is $\sqrt{-1}$. This allows for the two spin directions. The antisymmetrical *N*-electron wave function for this model is usually written as a determinant in terms of the half of these wave functions with the lowest energy. This wave function neglects correlations between electrons of opposite spins in the same orbitals. It allows fluctuations in which two electrons with antiparallel spins appear on the *same* atom. Such "polar" fluctuations or ionic states are necessary for the metallic conduction predicted by this model. But because of the Coulomb repulsion energy between the electrons (e^2/r_{12}, where *e* is the electronic charge and r_{12} is the distance between electrons 1 and 2—we denote its mean over one atom by *I*), ionic states are energetically unfavorable. On the other hand, by spreading out or delocalizing to form a conduction band, the electrons have minimized their kinetic energy, and a measure of this is the bandwidth *W*.

In order for a metallic state to be stable, *W* must be larger than *I*. But if the overlap between the centers is





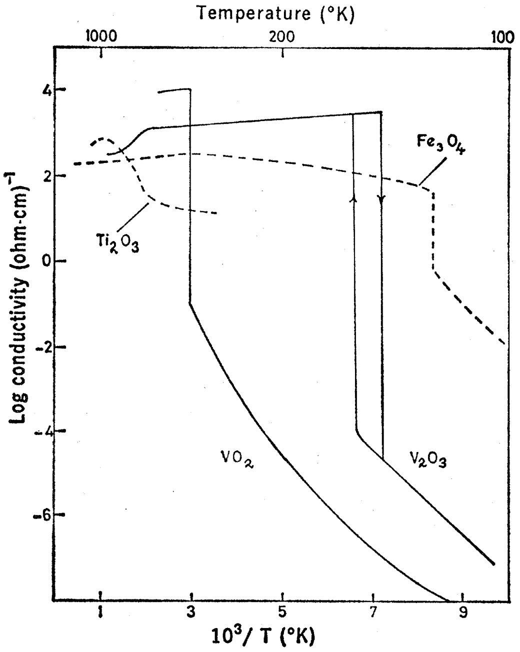


Fig. 1 (top left). Schematic energy levels in a 3*d* oxide. Fig. 2 (right). Transitions from metal to insulator. Fig. 3 (bottom left). The Ni^{3+} hole bound to a Li acceptor center.

small and W is less than I, then the Coulomb energy term is more significant and the electrons tend to stay far apart. Mott argued that in this case the Coulomb repulsive energy is minimized by placing exactly one electron on each center. More precisely, one electron is placed in each of the localized Wannier wave functions (Fig. 4) which can be formed from the Bloch states of the whole band. This gives a nonconducting state at $T = 0$ which is sometimes known as a Mott insulator. A formal proof of this nonconducting property for large values of a has been given by Kohn (*11*).

The effect of the Coulomb terms e^2/r_{12} up to this point is intra-atomic; that is to say, it deals with the interaction of electrons within an atom. However, the Coulomb interaction is long-range, and this leads to some further considerations. Mott originally proposed that there ought to be a discontinuous change in the carrier density n at a critical spacing a_c, which depends on the material. The argument is as follows. If one free electron and hole were created in the insulator, they would attract each other by way of the Coulomb interaction

$$V = -e^2/\mathrm{K}r$$

(where K is the static dielectric constant) and form a bound state, or exciton pair. If many carriers were present, however, the Coulomb field is screened,

$$V = -(e^2/\mathrm{K}r)\exp(-\alpha r)$$

(where α is the screening constant) and bound states are not formed. Thus, as a decreases, a sharp transition occurs from a state with no free carriers (at $T = 0$) to a large metallic density (Fig. 5).

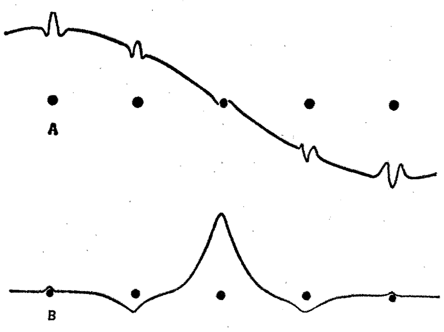


Fig. 4. (A) Bloch wave function which gives a conducting state. (B) Localized Wannier wave function which gives a nonconducting state. The filled circles represent atoms.

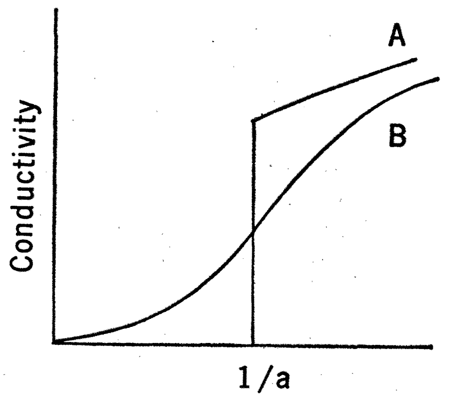


Fig. 5. (A) Mott transition. (B) Wilson metal, if we assume a finite mean free path for the electrons in the metallic phase; a is the interatomic distance.

Hubbard (*12*) has shown how the e^2/r_{12} term can produce a forbidden gap between occupied and nonoccupied states in the middle of an s-band (Fig. 6). In this model the Hubbard gap (ε in Fig. 6) drops continuously to zero as a decreases and does not vanish suddenly as predicted by Mott. But in Hubbard's approximation the *long-range* Coulomb interactions, which would give exciton pairs, are neglected. Mott now believes that, when a changes continuously, a discontinuous change in the number of charge carriers is *unlikely*, and that the model of Kohn (*13*), which predicts an infinite series of second-order changes leading up to the transition, is likely to be near the truth. The matter is by no means certain, but nonetheless it remains highly probable that a critical value of a still exists, on one side of which the material does not conduct when the temperature is zero and on the other side of which it behaves like a metal, but with no discontinuity in n.

We see that for an insulator like NiO, the Hubbard gap is the energy required to create a pair of $\mathrm{Ni^+}$–$\mathrm{Ni^{3+}}$ ions in pure material. This is probably about 1 to 5 electron volts. For the other compounds in class Ib the energy requirements are comparable, and we regard these compounds as Mott-Hubbard insulators with a large gap. We also note that a Mott-Hubbard insulator has localized magnetic moments, but the existence of the gap ε does not depend on any long-range magnetic ordering of these moments; NiO remains an insulator above the Néel point.

In oxides that are semiconducting as a result of impurities, the energy needed to create a free carrier is much less than that in the corresponding insulator—the ionization energy of a $\mathrm{Li^+}$–$\mathrm{Ni^{3+}}$ center is a few tenths of an electron volt. The motion of the free carrier ($\mathrm{Ni^{3+}}$ hole) through the lattice can be described as follows. The problem is like that of the hydrogen lattice for $a > a_c$, but with one electron missing. The hole, or defect electronic state, has a large number of equivalent lattice sites available to it. Since the motion of the hole does not require two electrons on one site at any time, the correlation term I described earlier does not arise. We expect, therefore, that the single hole will move with a definite wave number k, just like an electron in a band, and that the bandwidth will be narrow. However, this neglects any question of polaron formation, which we now discuss.

Table 1. Classification of transition metal oxides and nickel sulfide.

Class	Compounds
	Insulators
Ia	Sc_2O_3, TiO_2, V_2O_5 (empty d bands)
	Semiconductors
Ib	NiO, CoO, MnO, FeO, Fe_2O_3, Cr_2O_3 (antiferromagnetic)
	Metals
II	TiO (superconducting), CrO_2 (ferromagnetic), ReO_3 (*5d*)
	Transition from insulator to metal
III	VO_2, V_2O_3, Ti_2O_3, Fe_3O_4 (*3d*); NiS, NbO_2 (*4d*)

Polaron Models

The possibility that a slow-moving electron in an ionic crystal can be trapped by the polarization cloud around it was first investigated by Landau in 1933. If the electron remains for some time in the vicinity of a particular ion, the lattice will deform. Positive ions move toward the electron, and negative ions move away from it.

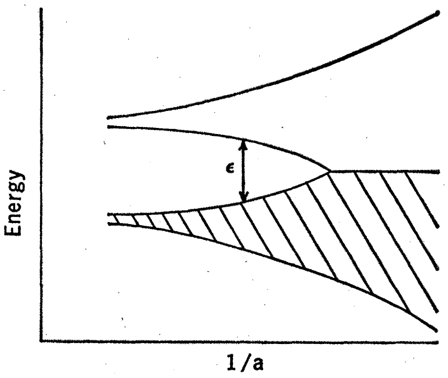
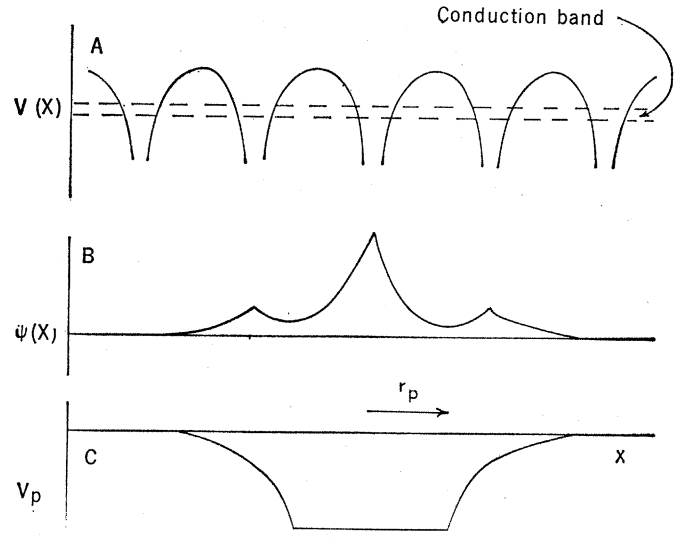


Fig. 6. Splitting of a narrow conduction band as envisaged by Hubbard. Shaded states are occupied.



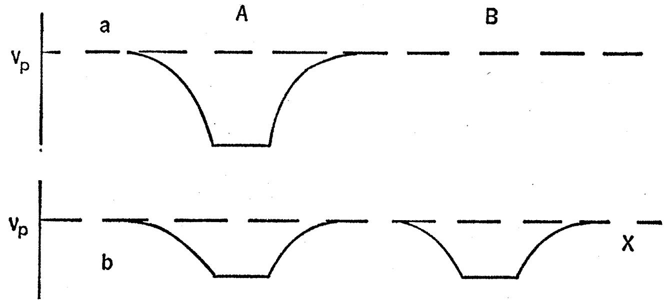


Fig. 7 (left). (A) Field of the electron in the undistorted lattice. (B) Wave function of the electron for a polaron of intermediate radius r_p. (C) Trapping potential; for $x > r_p$ this is given approximately by Eq. 1. For $x < r_p$ this equation does not apply because of the finite size of the electron, and we assume for simplicity that V_p is constant. Fig. 8 (above). Polarization wells before hopping. (a) Unexcited well (the electron is in well *A*). (b) Both wells are excited so that the electron can tunnel from *A* to *B*.

The electrostatic potential near the electron is then

$$-e/\mathrm{K}r$$

But if the ions did not move, the potential would be

$$-e/\mathrm{K}_\infty r$$

where K_∞ is the high-frequency dielectric constant. Thus the polarization of the lattice gives a potential well of the form

$$V_p = -e^2/\mathrm{K}_p r \qquad (1)$$

where

$$1/\mathrm{K}_p = 1/\mathrm{K}_\infty - 1/\mathrm{K}$$

This is illustrated in Fig. 7. The effective radius r_p of this well is determined by minimizing the total potential and kinetic energy. There are two limiting cases. (i) For large polarons the kinetic energy of the electron dominates, and r_p is much greater than the interatomic distance. The electron still moves in a band, but the mass is slightly enhanced. (ii) For small polarons r_p is less than the interatomic distance, and the electron is trapped on a single ion. Its kinetic energy is negligible, and the energy of the polaron is approximately

$$W_p = -e^2/\mathrm{K}_p\, r_p$$

An estimate of W_p may be obtained by various methods, the simplest of which treats the induced polarization on a continuum basis. Values of the order of 1 electron volt are found for these oxides (*8*).

The kind of polaron which is formed depends on the "rigid-lattice" bandwidth ($2J$) of the crystal. By this we mean the electronic bandwidth when the ions of the lattice are held rigidly in place, so that no polaron can be formed. The bandwidth $2J$ is a measure of the kinetic energy gained by the electron in spreading out to form a delocalized state. But W_p is the energy gained by the electron in forming a *localized* state; thus the condition for the formation of a small polaron is

$$W_p > 2J$$

The work of Holstein (*14*) and others has given us a detailed understanding of the way in which the small polaron can move through a crystal. At fairly high temperatures (of the order of $T > \frac{1}{2}\theta$, where θ is the Debye temperature), the polaron moves from site to site by thermally activated hopping. Thermal fluctuations momentarily give equivalent distortions of the lattice at neighboring sites (Fig. 8), and the electron tunnels across. If $2J$ is not too small compared with W_p (*15*), the probability of hopping is

$$P = \nu \exp(-W_H/kT) \qquad (2)$$

where ν is a lattice vibration frequency ($\sim 10^{13}$ cycles per second for the 3*d* oxides) and k is the Boltzmann constant; W_H is the hopping energy and is approximately

$$W_H = \tfrac{1}{2}W_p - J$$

Conduction is a random diffusion process, and the drift mobility μ *increases* with temperature as

$$\mu = \mu_0 \exp(-W_H/kT)$$

where

$$\mu_0 = e\,a^2\,\nu/kT \simeq 0.1\ \mathrm{cm^2\ volt^{-1}\ sec^{-1}}$$

and a is the hopping distance (a few angstroms).

We see that the hopping process gives a low mobility (< 1 square centimeter per volt per second) and, if J is comparable with $\frac{1}{2}W_p$, the hopping energy can be quite small. The electron remains on one site for an average time of P^{-1} second before hopping. Equation 2 shows that this trapping time is at least ν^{-1} or the time for one molecular vibration ($\sim 10^{-13}$ second).

Below a temperature of the order of $\frac{1}{2}\ \theta$, however, the small polaron behaves like a heavy particle moving by the band mechanism. The electron, qualitatively like the large polaron, tunnels through the crystal carrying its polarization cloud with it. The effective mass of the small polaron is

$$m_p = m^* \exp\gamma \qquad (3)$$

where

$$\gamma \sim W_H/(\tfrac{1}{2}\hbar\omega_0) \qquad (4)$$

and $\hbar$ is Planck's constant. Here m^* is the rigid-lattice effective mass of the electron and ω_0 is the frequency of an optical phonon. The polaron bandwidth is

$$2J_p = 2J\exp(-\gamma)$$

Thus a large decrease in bandwidth, and an increase in effective mass, can occur, since γ is $\gtrsim 3$. Here again the mobility is small (< 1 square centimeter per volt per second) and decreases with rising temperature. The transition from band to hopping conduction occurs *gradually* (Fig. 9) at a temperature T' which depends on the parameters. According to Holstein (*14*), T' is of the order of $\frac{1}{2}\ \theta$, but Lang and Firsov predict much lower values (*5*). Moreover, recent experimental work on MnO by de Wit and Crevecoeur (*16*) suggests that the transition temperature may be lower.

If γ is ~ 2, then W_H from Eq. 4 is $\sim \hbar\omega_0$ (say, 0.05 electron volt). Such a small hopping energy would be difficult to identify from experimental data, especially as μ varies as

$$T^{-1} \exp(- W_H/kT)$$

But the effective mass (Eq. 3) would still be appreciably enhanced, perhaps by a factor of 10. A polaron, then, depending on the temperature range and the magnitude of $2J/W_p$, can behave as a heavy particle moving in a band or it can move by hopping.

Rigid-lattice bandwidths are very difficult to estimate in the transition metal oxides. The $3d$ overlap is indirect, involving hybridization with the $2p$ orbitals; in addition, the d functions are very anisotropic. Overlap integrals from antiferromagnetic data indicate that J is $\sim$ 0.1 to 0.3 electron volt for NiO.

Before we turn to the experimental evidence on $3d$ oxides, it is worth noting that polaron hopping behavior has been observed by Gibbons and Spear (*17*) in molecular sulfur crystals. These authors find that J is $\sim$ 0.05 electron volt, $W_H = 0.18$ electron volt, and $W_p = 0.48$ electron volt for injected electrons. The drift mobility is very low ($< 10^{-3}$ square centimeter per volt per second), and the electron is trapped on one molecule during many molecular vibrations. In this case the trapping is due to distortion of the molecule and not to polarization of the surroundings. Similar behavior can occur in other molecular crystals.

Semiconducting Oxides

Titanium dioxide. Pure rutile has an empty d band and is an insulator. When Ti^{3+} (d^1) ions are introduced, by reduction or doping, rutile becomes an n-type semiconductor. On account of the large dielectric constant, the donor activation energies are very small and all the carriers are thermally ionized above about 20°K.

Table 2. Activation energies for Fe^{2+}–Fe^{3+} transport in various systems at 300°K.

System	Activation energy
FeO, Fe_2O_3, and Fe_3O_4 crystals	Narrow-band conduction, hopping (?) at high temperatures
Ferrites	0.2 to 0.3 ev
Iron phosphate glasses	0.7 to 1 ev

Recently, Bogomolov *et al.* (*6*) and others at Leningrad have carried out a variety of experiments on rutile, from which they obtained strong evidence of small polaron conduction with a hopping energy W_H of $\sim$ 0.13 electron volt. Figure 10 shows the drift mobility (μ) characteristic which they interpret as hopping conduction for temperatures greater than $\sim$ 300°K. Bogomolov and Mirlin (*18*) also observed a broad peak in the optical absorption centered at 0.8 electron volt. Such a peak is predicted for small polarons, where the photon energy $h\nu$ is $\sim 2\ W_p$, and is due to a Franck-Condon excitation of the electron out of its polarization well. Bogomolov *et al.* (*6*) estimate from their measurements that

$$W_p \sim 0.4 \text{ ev}$$

and that

$$\gamma = W_p/\hbar\omega_0 \sim 4$$

and

$$m_p = m^* \exp \gamma \sim 150\, m$$

(m is the rest mass of the electron in a vacuum). Thus, according to these authors, polaron formation leads to a very large enhancement of the effective mass.

Evidence that electrons bound to donor centers also form polarons has been found by Dominik and MacCrone (*19*) from dielectric loss at 4°K.

Nickel oxide. Lithium-doped NiO is a p-type semiconductor which has been very extensively studied. Early workers concluded from resistivity and thermoelectric power (thermopower) measurements that the mobility was very low ($\ll 10^{-2}$ square centimeter per volt per second), with W_H approximately equal to 0.1 electron volt or more at room temperature. Recent studies, based on samples free of grain boundary scattering, show much higher mobilities. Uncertainties in the analysis (*20*) lead to two possible mobility curves (Fig. 11) but there is no suggestion of a hopping energy at temperatures below $\sim$ 500°K.

Some idea of the bandwidth can be obtained by the following argument. In a band model the de Broglie wavelength of the charge carriers ($\hbar/m_p v$) (v is the thermal velocity of the carriers) cannot be less than the mean free path between collisions. An equivalent condition is that

$$\mu > e\hbar/(m_p v)^2$$

Thus, for NiO at 1000°K, the data in Fig. 11 imply that m_p is $> 10\ m$, or is $J < 0.03$ electron volt for band conduction.

Experimental evidence on m_p is conflicting. Bosman and van Daal (*21*) infer that $m_p = 6\ m$ from their thermopower studies at high temperatures. They suggest that the free carriers are large polarons and that there is no hopping conduction (curve 2, Fig. 11). Hall-effect data (*22*) indicate a larger effective mass. If m_p is larger than about 20 m, we believe (*8*) that hopping conduction is likely at high temperatures (curve 1, Fig. 11), because of small polaron formation or Anderson localization (see the section on $3d$ ions in glasses below). It is not clear from optical studies (*23*) whether the free holes form polarons, but there is strong evidence (*21, 23*) that bound holes form *small* polarons, which hop around the Li centers.

Below 525°K, NiO is antiferromag-

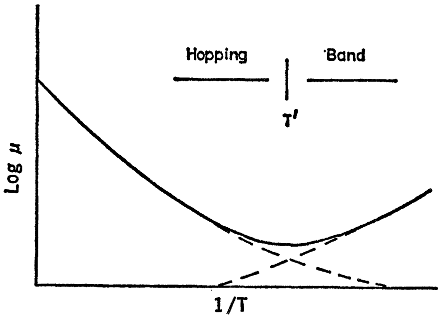


Fig. 9. Drift mobility of a small polaron predicted by Holstein (*14*).

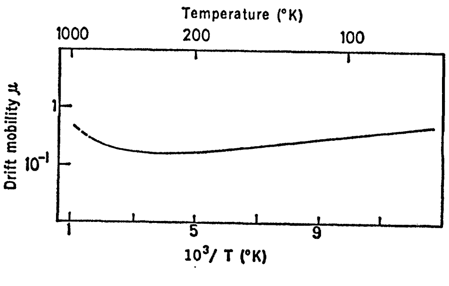


Fig. 10. Drift mobility of electrons in TiO_2 (*6*).

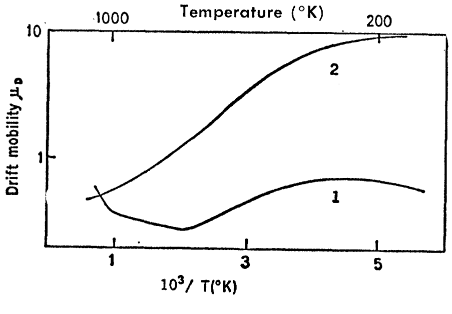


Fig. 11. Drift mobility of holes in NiO. After various authors cited in (*8*).

netic and the overlap of the *d* orbitals through oxygen ions couples nickel ions with antiparallel spins. A Ni^{3+} hole can only move from one magnetic sublattice to the other if thermal agitation produces a spin reversal at one site. Contrary to observation, this should lead to a drastic reduction in the mobility below the Néel temperature. One possibility we have discussed elsewhere (*8*) [see also Appel (*5*)] is that a spin polaron is formed, in which the spins near the carrier are canted so as to be parallel rather than antiparallel. The spin polaron, we assume, could move without activation energy.

Other crystalline oxides. Similar behavior is observed in doped CoO and α-Fe_2O_3. The drift mobilities are ~ 0.1 square centimeter per volt per second, and they are fairly insensitive to temperature from 200° to 1000°K. In contrast, de Wit and Crevecoeur (*16*) find an activated mobility in *p*-type MnO and suggest that small polarons are formed because of the strong Jahn-Teller lattice distortion in the d^4 state of the Mn^{3+} hole.

The drift mobilities of ferrites and garnets also show a hopping energy and are very small (*8*). Thus in doped cobalt ferrite ($CoFe_2O_4$), the mobility for electron transfer between Fe^{2+} and Fe^{3+} ions is ~ 10^{-4} square centimeter per volt per second, and the activation energy is ~ 0.2 electron volt. But for Fe^{2+}–Fe^{3+} transfer in natural magnetite (Fe_3O_4), a crystal with very similar structure, the mobility is ~ 0.1 square centimeter per volt per second and is not thermally activated. The reason for this difference is not clear (*8*).

Metallic Compounds

Titanium monoxide has the d^1 configuration and shows many properties of a normal metal. The resistivity is ~ 10^{-4} ohm-centimeter, and the metal becomes superconducting at 0.68°K. This shows that the *d* orbitals in these oxides can give good metallic conduction.

Chromium dioxide is ferromagnetic with a magnetic moment of 2 Bohr magnetons per metal ion. Mott has postulated (*24*) that this material is a semimetal with a small Hubbard gap, as is the case for vanadium trioxide (V_2O_3) (see below).

Transitions from Metal to Insulator

As we have already stated, some transition metal oxides and sulfides show a transition from semiconductor behavior, which is probably intrinsic, to "metallic" behavior at a critical temperature T_t (Fig. 2). These include VO_2, V_2O_3, titanium trioxide (Ti_2O_3), nickel sulfide (NiS), and Fe_3O_4, all materials in which there are electrons in the 3*d* band. By "metallic" behavior we mean a conductivity in the range 10^3 to 10^4 per ohm-centimeter which varies little with temperature.

The mechanism for the transition is certainly not the same for all these materials. Thus in Fe_3O_4 the octahedral sites contain a mixture of Fe^{2+} and Fe^{3+} ions, and at low temperatures the electrons take up positions so that the two kinds of ion form a superlattice. The transition occurs when this long-range order of electrons is destroyed. Nothing of this kind can occur in the other substances listed. There have been many theoretical attempts to explain their properties (see *7*, *24*), and there is as yet no certainty about the correct model. Some of the salient facts that have to be explained are as follows.

1) There is always some change of volume or of structure at the transition; thus in the high-temperature phase of VO_2 the vanadium ions are equally spaced along the *c*-axis but below T_t they pair up. In V_2O_3 there is a volume expansion of 3 percent below the transition; in Ti_2O_3 and NiS there is a change in the *c/a* ratio.

2) Nickel sulfide and V_2O_3 are antiferromagnetic with moments of about 2 and 1 Bohr magnetons, respectively (*25*), in the semiconducting phase; VO_2 and Ti_2O_3 are not antiferromagnetic, and none of these materials shows long-range antiferromagnetic order in the metallic phase.

3) The band gap in the semiconducting phase is small (< 0.5 electron volt). In those oxides which show antiferromagnetism (NiS and V_2O_3), it has been suggested that this is a small "Hubbard" gap of the same kind as in NiO, and that these materials are close to the critical lattice spacing for the insulator-to-metal transition. In other oxides the gap may be due to a crystal distortion or to lower symmetry (see the section on energy states above) with or without magnetic ordering.

4) Vanadium dioxide and V_2O_3 in the metallic phase show evidence of being semimetals (like bismuth), that is to say, of having a fairly small number (~ 0.2 per ion) of electrons and an equal number of holes. The main evidence comes from optical (*26*) and thermopower (*27*) measurements and high-pressure studies (*28*). This behavior may be due to bands which overlap slightly as a consequence of the crystal structure or overlapping Hubbard bands. Alternatively, if the Hub-

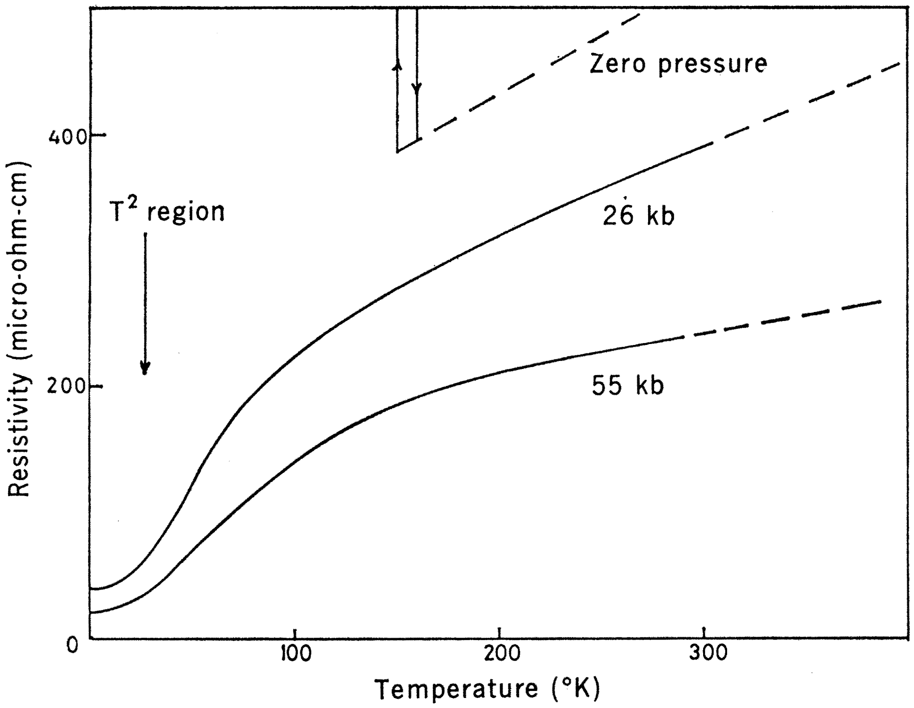


Fig. 12. Resistivity as a function of temperature in the metallic phase of V_2O_3. At pressures above 25 kilobars the metallic phase is stable down to 0°K. [After McWhan and Rice (*28*)].

bard gap (or band gap) is small and equal to less than half the binding energy of a polaron (W_p), the semimetal may consist of a gas of n- and p-type polarons (*24*). The carriers could lower their energy by forming polarons as long as the density is low and the polarization clouds do not overlap.

5) In most theories the thermodynamic "driving force" for the transition is thought to be the high entropy of the conduction electrons in the metallic state; there are, of course, other possibilities, such as a change in the magnetic or phonon entropy. The former hypothesis would imply a very large effective mass. Polaron formation has been suggested to account for this (*24*).

6) Adler and Brooks (*29*) have shown that a crystal with a narrow half-filled band will always be distorted at 0°K to give a band gap, if the decrease in electronic energy from distortion more than compensates for the strain energy, as in the Jahn-Teller effect. Their model also predicts a decrease and ultimate vanishing of the gap with rising temperature, due to excitation of carriers across it.

7) In the case of V_2O_3, which contracts by 3 percent in the metallic phase, McWhan and Rice (*28*) have shown that above a pressure of 25 kilobars the metallic phase is stable down to the lowest temperature. The resistance-temperature curves they obtain above these pressures are shown in Fig. 12. At low temperatures the resistivity is proportional to T^2. This behavior can be explained on the assumption that the material is a semimetal and the resistivity is due to collisions between electrons and holes. To account for the magnitude of the resistivity and the saturation at about 200°K, one must assume a very low degeneracy temperature (or almost classical electron gas) and thus an effective mass of $\sim 20\ m$. This is consistent with the high entropy needed to provide the driving force for the transition. Such a high effective mass in our view suggests polaron formation.

To summarize, then, this class of material has in the semiconducting phase a small intrinsic band gap, which may be due to structure or in some cases may be a Hubbard gap. Comparatively small changes of volume, structure, or c/a ratio cause a small amount of overlapping between the bands, so that carriers of both signs are present in the ground state. These have a high effective mass, probably due to polaron formation, and the entropy of the electron gas is such that at the critical temperature the metallic phase has the lower free energy.

The 3d Ions in Glasses

So far we have been concerned with crystalline substances. Many glasses can be prepared containing $3d$ transition metal ions with different valence states, for example, Fe^{2+} and Fe^{3+} ions in phosphate glasses. Such materials show electronic conduction (*8, 30*). A comparison with the crystalline $3d$ oxides is interesting because it throws light on another type of electron localization, namely, Anderson localization.

Anderson (*31*) has shown that for a narrow-band (tight-binding) situation all the states are localized if the mean disorder potential W_D between the ions is greater than ~ 5 times the total bandwidth. For the $3d$ glasses, polaron bands are unlikely, and the hopping probability between centers is proportional to

$$\exp\{-(W_H + \tfrac{1}{2}W_D)/kT\} \qquad (5)$$

Table 2 compares the activation energy for Fe^{2+}–Fe^{3+} exchange in a glass with that in the crystalline oxides. The difference between the glasses and ferrites is probably too large to be simply a W_D disorder term, but at present there is no direct evidence about the size of this term in either group of material. At low temperatures multiphonon hopping processes are frozen out, and W_H in formula 5 should vanish, leaving the W_D contribution. However, low-temperature data on vanadate glasses indicate that there is no W_D term, and the conduction activation energy tends to zero (*8*).

Impurity conduction in $3d$ oxide crystals is probably a similar process (*30*), and again there is no evidence of a disorder term of the expected magnitude. This behavior is not fully understood but it may mean that at low temperatures the electron hops preferentially a distance greater than that to the nearest neighbor (*8*), because it can thereby find a state for which W_D is lower.

Summary

Many of the striking properties of these materials arise from Coulomb interactions between the d electrons and a strong electron-lattice coupling. Disorder also has a marked influence, and this aspect is perhaps the least understood at the present time. All these effects lead to localized electron states and a failure of conventional band theory. The study of these materials should give a deeper understanding of low-mobility charge transfer in a wide range of systems and of the nature of metallic and nonmetallic states in solids.

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$$J < \hbar\omega_0 \quad (2J << W_p)$$

the hopping process is nonadiabatic, and the preexponential term (ν) in Eq. 2 is different. For recent work on both types of hopping, see reference *8*.

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