

**substance: binary transition-metal oxides**  
**property: character of d electrons**

The character of an atomic outer electron, once the atom has been incorporated into a solid, depends upon the relative magnitudes of three competitive energies: the bandwidth  $W_b$  arising from interatomic interactions between like atoms on equivalent lattice sites in the crystal, the correlation energy  $U$  arising from intraatomic electrostatic interactions between electrons of the same manifold, and a stabilization of electronic energies  $\Delta_{el}$  arising from electron-phonon interactions that produce a local or a cooperative distortion of the structure.

**1. Bandwidth:** Interatomic interactions between  $N$  like atoms on a periodic array broaden the energy of an atomic state into a band of energies containing  $2N/\nu$  states, where the factor two is due to the spin degeneracy and  $\nu$  is the number of like atoms per primitive unit cell of the crystal structure. In the tight-binding approximation, the width of the band of  $2N$  energies in a Bravais lattice ( $\nu = 1$ ) is given by  $W_b \approx 2zb$ , where  $b$  is the transfer (resonance) integral for electron tunneling between like atoms on nearest-neighbour equivalent sites  $b_{ij} = (\psi_i, H' \psi_j) \approx \epsilon_{ij}(\psi_i, \psi_j)$ .  $H'$  is the perturbation of the potential at  $\mathbf{R}_j$  due to an atom at  $\mathbf{R}_i$ ,  $\epsilon_{ij}$  is a one-electron energy, and  $(\psi_i, \psi_j)$  is the wave function-overlap integral for degenerate, localized states at  $\mathbf{R}_i$  and  $\mathbf{R}_j$ . The wave functions  $\psi_i$  and  $\psi_j$  contain covalent admixtures of anion s and p wave functions, which makes M – X – M interactions competitive with M – M interactions.

**2. Electrostatic correlation energies:** The magnitude of the intraatomic electron-electron electrostatic energies is sensitive to the radial extension of the wave functions. On the free atom it is responsible for differences  $U$  in the successive ionization potentials associated with electrons from the same shell. For outer s and p electrons, the free-atom  $U$  is generally less than about 2 eV; for 4 f electrons it is generally greater than 10 eV. The d electrons at free atoms have intermediate energies  $U$ . In a solid, covalent mixing with nearest-neighbour anions extends the wave functions, reducing  $U$ . Moreover, covalent mixing raises the d-state energies; therefore, since covalency increases with the formal valence on the cation, the energy differences between successive valence states is further decreased in a solid. Finally, interactions between like atoms further decrease  $U$  through a screening parameter  $\xi(b)$  that increases with  $b$ : for example  $U = (|\psi_m(1)|^2, V|\psi_m(2)|^2)$ ,  $V = (e^2/r_{12})\exp(-\xi r_{12})$  for two electrons occupying the same atomic state with wave function  $\psi_m$ . In the absence of a bandwidth  $W_b$ , the energy  $U$  splits the energies of different formal valence states. If this splitting is larger than the bandwidth ( $U > W_b$ ), then a compound with a single formal valence state may be semiconducting whereas it is metallic if the bandwidth is larger ( $U < W_b$ ). Atomically localized electrons have  $W_b \ll U$ , itinerant electrons have  $W_b \gg U$ , and "intermediate" electrons have  $W_b \approx U$ . Localized and intermediate electrons may impart a spontaneous atomic moment; itinerant electrons do not. Unless  $U$  is augmented by crystal-field splittings or separates a high-spin  $d^5$  from a  $d^6$  configuration, its magnitude for d electrons in solids appears to be not greater than about 3 eV, which is why it is possible to stabilize several valence states with the same anion. For example, VO,  $V_2O_3$ ,  $VO_2$ , and  $V_2O_5$  all have a Fermi energy between the broad V:4s and  $O^{2-}:2p^6$  bands, which are not separated by more than about 6 eV. Thus an average correlation splitting  $U_{av} \leq 2$  eV is indicated for the vanadium oxides, and the intermediate condition at  $W_b \approx U$  is indeed encountered in  $V_2O_3$  and  $VO_2$ .

**3. Crystallographic phase changes and semiconductor-metal transitions:** The electron-phonon interactions, local or cooperative, that introduce an electronic stabilization  $\Delta_{el}$  of occupied relative to empty states may either increase an existing energy gap between valence and conduction bands or it may introduce one. The former case represents a semiconductor-semiconductor transition; the latter a semiconductor-metal transition. In general, a semiconductor-metal transition is caused by either the edge crossing of filled and empty bands (or level and a band) or the collapse of a band splitting. It is instructive for interpretation of the data in the following tables to consider the variety of ways that  $\Delta_{el}$  can influence the relative band (or level) energies.

**a) Mixed valence.** The spinels hausmannite ( $Mn_3O_4$ ) and magnetite ( $Fe_3O_4$ ) represent two different classes of mixed-valent compounds. Hausmannite,  $Mn^{2+}[Mn_2^{3+}]O_4$ , is a normal spinel with  $Mn^{2+}$  ions in tetrahedral sites and  $Mn^{3+}$  ions in octahedral sites. The d electrons are localized ( $W_b < U$ ), and the octahedral-site  $Mn^{2+}$  level lies discretely above the tetrahedral-site  $Mn^{2+}$  level as well as the octahedral-site  $Mn^{3+}$  level. Since valence transfer between ions on different sites is thus inhibited, the compound is an insulator. Magnetite, on the other hand, is an inverse spinel,  $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$ ; and in the cubic phase, stable at room temperature, the mixed valence occurs on crystallographically equivalent sites. Under these conditions, valence exchange may readily occur via electron tunneling from one equivalent site to its neighbour, and  $Fe_3O_4$  is a good conductor at room temperature. However, the tunneling time  $\tau \approx \hbar/2\pi z b$  may be long compared to a local optical-mode vibration period  $\tau_R \approx 10^{-12} \dots 10^{-13}$  s. In such a case ( $\tau > \tau_R$ ), the electron (or hole) becomes trapped in a local deformation, and thermal energies must then overcome an activation-energy barrier  $\epsilon_a$  before valence exchange via tunneling can occur. An electron (or hole) "dressed" in its local deformation is called a small polaron, and the mobility of a small polaron is described by diffusion theory as  $\mu = (eD_0/kT) \exp(-\epsilon_a/kT)$  rather than by the scattering theory used for itinerant electrons, which gives  $\mu = e\tau_s/m^*$  with  $\tau_s$  the mean free time between collisions and  $m^*$  the effective mass of the charge carrier. An activated mobility makes the temperature dependence of the conductivity,  $\sigma = ne\mu$ , typical of a semiconductor even though the density  $n$  of charge carriers does not change with temperature. As the concentration of small polarons increases, interactions between them tend not only to reduce  $\epsilon_a$ , but also to introduce a polaron ordering that creates distinguishable lattice positions for the two valence states. Long-range order is accompanied by a cooperative electron-phonon interaction, which replaces local and random deformations. In the case of  $Fe_3O_4$ , where the polaron concentration is a maximum, a complex long-range valency ordering occurs below the Verwey temperature  $T_v = 119$  K to render the compound semiconducting. At temperatures just above  $T_v$ , strong electron-phonon interactions are evident and the conductivity  $\sigma$  continues to increase with increasing temperature as if the abrupt transition at  $T_v$  were a semiconductor-semiconductor transition. However, the temperature dependence of  $\sigma$  decreases with increasing temperature, becoming essentially temperature-independent by room temperature. These data are consistent with short-range ordering between small polarons persisting above  $T_v$ , but with  $\epsilon_a$  vanishing as a result of polaron-polaron interactions in the totally disordered state.

A non integral number of itinerant electrons per transition-metal atom may give rise to the formation of charge-density waves. Some argue for this alternative in  $Fe_3O_4$ .

**b) Single valence.** In crystalline compounds containing transition-metal compounds in a single valence state, three situations need to be distinguished:  $W_b \leq \Delta_{el} \ll U$ ,  $W_b \approx U \leq \Delta_{el}$ , and  $U < W_b \leq \Delta_{el}$ .

**(i) Localized-electron manifolds ( $W_b \ll U$ ):** Semiconductor-semiconductor transitions may be induced by localized-electron stabilization. Important examples include:

**Low-spin to high-spin transitions** are induced by the greater entropy associated with the higher multiplicity of the high-spin configurations. Since such a transition requires a transfer of antibonding electrons from  $\pi$ -bonding to  $\sigma$ -bonding states, the effective radius of the high-spin configuration is larger, causing an enhanced thermal expansion of the lattice. Such a transition may be smooth with an order parameter defined as the fraction of configurations that are low-spin.

**Cooperative Jahn-Teller distortions** remove an accidental orbital degeneracy. Although the enthalpy of the localized-electron manifold is increased linearly with the atomic displacements of the distortion, the sign of the distortion is only determined – as are the elastic restoring forces – to order square of these displacements. Nevertheless, a cooperative, static distortion is commonly stabilized below a finite temperature  $T_{JT}$ . If the orbital angular momentum of the manifold is not quenched in the high-temperature phase, the internal magnetic fields generated by a collinear-spin configuration in a magnetically ordered state will stabilize a distortion that preserves the spin-orbit coupling unless  $T_{JT}$  occurs above the magnetic-ordering temperature. Such distortions

occurring below the antiferromagnetic Néel temperature  $T_N$  are illustrated by  $\text{Fe}_{1-\delta}\text{O}$  and  $\text{CoO}$ . In  $\text{Mn}_3\text{O}_4$ , the high-spin  ${}^5\text{E}_g(\text{d}^4)$  configuration at octahedral-site  $\text{Mn}^{3+}$  ions has its orbital angular momentum quenched by the crystalline fields, and  $T_{\text{tr}}$  for the tetragonal ( $c/a > 1$ ) to cubic transition is quite independent of the ferrimagnetic Curie temperature  $T_C$ .

**Exchange striction** below a magnetic-ordering temperature reflects changes in the interatomic bonding between magnetic atoms as a result of the long-range magnetic order. The distortion of  $\text{MnO}$  from cubic to rhombohedral symmetry below  $T_N$  provides a classic illustration.

**(ii) "Intermediate" electrons ( $W_b \approx U$ ):** Semiconductor-metal transitions may be induced by a change from strong to weak correlations with increasing temperature. Such a transition is also marked by a change from a magnetically ordered state to a phase containing no spontaneously magnetic atoms. These transitions may be understood from Fig. 1 to represent a change from at  $W_b < U$  to  $W_b > U$ . Such a transition is first-order, the phase containing strongly correlated itinerant electrons ( $W_b < U$ ) having the larger volume. Such a transition is illustrated by metastable  $\text{NiS}$  with B8 structure, which is stabilized at low temperatures by quenching. It is also illustrated in a more complex way by  $\text{V}_2\text{O}_3$ .

**(iii) Itinerant electrons with weak correlations ( $W_b > U$ ):** Semiconductor-metal transitions may also be induced by other mechanisms. Among these are:

**Band-edge crossing induced by axial-ratio changes:**  $\text{Ti}_2\text{O}_3$  exhibits a smooth semiconductor-metal transition with increasing temperature that is correlated with a remarkable increase in the  $c/a$  ratio. At low temperatures, electrons are trapped in molecular orbitals of  $c$ -axis  $\text{Ti} - \text{Ti}$  pairs; the  $a_1$  bands of  $t_{2g}$  parentage directed parallel to the  $c$ -axis are split in two by the  $\text{Ti} - \text{Ti}$  pairing along this axis in the corundum structure. The  $e_\pi$  bands formed by  $\text{Ti} - \text{Ti}$  interactions in the basal plane lie discretely above the lower, filled  $a_1$  band if  $c/a$  is small. For larger  $c/a$  ratios, the two bands overlap.

**Band splitting by cation clustering:** If partially filled bands are formed by  $\text{M} - \text{M}$  interactions, a change in translational periodicity of the metal atom  $\text{M}$  may split the band into filled and empty bands. Such changes are generally commensurate with the original crystalline array, as in the formation of cationic clusters or a commensurate charge-density wave with wave vector  $q = n\alpha$ ; but incommensurate charge-density waves with  $q = \lambda\alpha$ , where  $\lambda$  is non-integral, have also been reported. In a two-dimensional band, the energy gap opened up at the new Brillouin zone boundaries by a charge-density wave may not be large enough to make the crystal semiconducting; in this case a semimetal-metal transition is observed instead of a semiconductor-metal transition. Several of the layered chalcogenides exhibit the formation of two-dimensional charge-density waves at low temperatures.

The B8 structure of  $\text{FeS}$  exhibits a triangular-cluster formation below the temperature  $T_\alpha$ . This example is particularly interesting because the high-spin  $\text{Fe}^{2+}$  ions retain atomically localized majority-spin electrons at all temperatures; the single minority-spin electron per high-spin  $\text{Fe}^{2+}$  ion is itinerant for  $T > T_\alpha$ , but localized to triangular  $\text{Fe}_3$  cluster below  $T_\alpha$ . This observation emphasizes the fact that with magnetic atoms the majority-spin and minority-spin electrons see different potential energies. This difference is particularly important for high-spin  $\text{d}^6$  ions in which a large intraatomic-exchange stabilization is present for the majority-spin electrons, but absent for the minority-spin electron.

The presence of a magnetic moment on the cation also makes the transfer integrals  $b_{ij}$  no longer spin-independent, which is the basis of the exchange striction mentioned above. The spin dependence of the transfer integrals also introduces a spin-disorder scattering that is responsible for the maximum in the resistivity at  $T_N$  in the "metallic" phase of  $\text{FeS}$ ; in  $\text{CrO}_2$  it produces a sharp cusp in resistivity versus temperature at the ferromagnetic Curie temperature  $T_C$ . Where there are mixed valencies, but with a small concentration of charge carriers, this effect may produce magnetic polarons just above  $T_C$  that give rise to a giant magnetoresistance.

On lowering the temperature of  $\text{FeS}$ , the orientation of the magnetic moments changes from within the basal planes to parallel to the  $c$ -axis at a spin-flip temperature  $T_S \geq T_\alpha$ . With spins parallel to the  $c$ -axis, spin-orbit coupling orders the minority-spin electrons into the orbitally twofold degenerate  $d_\perp$  (or  $e_\pi$ ) minority-spin bands of  $t_{2g}$  parentage within the basal planes; these bands are then half-filled because the spin degeneracy is removed. Triangular-cluster formation below  $T_\alpha$  splits these bands in two to give a semiconductor-metal transition.

In  $\text{FeS}$ , spin reorientation and spin-orbit coupling removed a band overlap to make possible the formation of a semiconducting phase by a cluster formation (a commensurate charge-density wave) that splits a narrow, partially filled  $d$  band. In  $\text{VO}_2$ , ferroelectric-type displacements perform the same function. A cation

displacement from the center of symmetry of an octahedral interstice destabilizes two  $t_{2g}$  orbitals relative to the third if it is towards a terminal anion; it destabilizes all  $t_{2g}$  orbitals equally if toward an octahedral face. If the d shell is empty, as at a  $Ti^{4+}$  ion, displacements may occur to a terminal oxygen, an octahedral edge, or an octahedral face, as is illustrated by the three ferroelectric phases of  $BaTiO_3$ . Such displacements are common where the gain in energy of the binding states is larger than the elastic restoring force (both vary as the square of the atomic displacements, and static distortions are anticipated by a "softening" of specific optical-vibration modes). For the  $V^{4+}$  ion, with one outer d electron, displacement is toward a terminal oxygen to form a vanadyl complex ion  $(VO)^{2+}$ . If  $z$  is parallel to the axis of the complex, the single d electron is stabilized in the  $d_{xy}$  orbital. Above  $T_{tr} \approx 67^\circ C$ ,  $VO_2$  has the tetragonal rutile structure;  $V - V$  interactions form a  $d_{||}$  band within chains of edge-shared octahedra aligned parallel to the  $c$ -axis and  $V - O - V$  interactions between chains create an overlapping  $\pi^*$  band, so the metallic conductivity is nearly isotropic. Below  $T_{tr}$   $V^{4+}$ -ion displacements produce a semiconducting, monoclinic phase. The displacements have two components: a  $\langle 110 \rangle$  displacement within the basal planes toward a terminal oxygen, which stabilizes the  $d_{||}$  band relative to the  $\pi^*$  bands, and a  $V - V$  pairing within the  $c$ -axis chains to split the now half-filled  $d_{||}$  band in two. Small substitutions of Cr for V reveal the two-component character of the displacements; for a limited Cr concentration half the  $c$ -axis chains show only  $M - M$  pairing and half show only the zig-zag antiferroelectric displacements due to vanadyl-complex formation. Where pairing occurs, the  $V^{4+}$  ions are non-magnetic; where only vanadyl formation occurs, the  $V^{4+}$  ions carry a magnetic moment. Thus  $VO_2$  represents a situation where  $U \approx W_b \leq \Delta_{el}$ .

Although  $W_b > U$  clearly holds in the Magnéli shear phase  $Ti_4O_7$ , the situation is analogous. In this structure,  $TiO_2$  slabs  $4c$  thick are connected by "shear" planes across which Ti atoms of one slab are in interstitial positions relative to those in the other slab. Ferroelectric-type displacements allow for a strong relaxation that stabilizes condensation of  $O^{2-}$ -ion vacancies into the shear planes; but these displacements destabilize the d states at Ti atoms of a slab face relative to those in the bulk of the slabs. Thus within the bulk of the slabs the situation is analogous to  $VO_2$ , and at low temperatures Ti - Ti pairing within  $c$ -axis chains of the slab traps out the electrons to create a semiconducting phase as in low-temperature  $VO_2$ . However, just above  $T_{tr}$  in this case the Ti - Ti pairing becomes disordered and mobile. Such mobile homopolar bands have been named bipolarons as they represent two-electron species localized and dressed by a local lattice deformation; they migrate as a small polaron with an activated mobility.