JOURNAL OF SOLID STATE CHEMISTRY 12, 349–354 (1975)

Low Temperature Conductivity of Transition-Metal Oxides*

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Received July 3, 1974

The usual models to study the conductivity properties of transition-metal oxides are examined critically. It is found that although the band structure picture explains many cases in a completely satisfactory way (e.g., ReO_3), it fails to explain the conductivity behavior of many crystals, e.g., transition-metal monoxides. Interpretation is given in terms of a model which involves itinerant metallic-s-electrons and oxygen-p-electrons, and localized highly correlated transition-metal d electrons. Such a model explains the good conductivity of TiO, the semiconducting properties of VO, and the good insulating character of MnO, FeO, CoO, and NiO. Extensions of the model to explain optical and magnetic properties are included.

The two opposing views of the electronic structure of a solid can be called the chemical view and the band-structure view. The first one essentially assumes that a solid is a collection of atoms, ions, or molecules, bound together by electrostatic forces, e.g., Coulombic, van der Waals, etc. These solids are by necessity insulating, and their optical and magnetic properties strongly resemble those of the constituent species. In particular, the optical absorption spectrum is strongly dominated by lines, i.e., narrow peaks.

The band picture, extremely successful in solid state physics in general, considers a solid as a collection of electrons which move more or less independently in a selfconsistent potential set by the ions and the other electrons. Well-known techniques have therefore been developed to study the spectrum (band structure and density-of-states) of such systems. If, when filled according to Fermi–Dirac statistics, the Fermi level falls in the middle of a region of allowed states, the resulting solid is a metal; if the Fermi level falls in the middle of a forbidden gap, the solid is an insulator or a semiconductor.

When applied to the transition-metal oxides, the band picture meets with varied fortunes: In some cases, it is remarkably successful as for instance in the determination of the electronic structure of ReO_3, where theory (*1*) and experiment (*2–4*) are in remarkably good agreement.

The situation is completely different in some other cases (*5*, *6*). This is most evident in the case of the transition-metal monoxides: TiO, VO, MnO, FeO, CoO, NiO.

The six transition-metal monoxides referred to above constitute an interesting family of solids. They all crystallize in rock-salt structure with similar lattice constants (ranging from 4.09 Å for VO to 4.43 Å for MnO) and with not too different melting points (from 1420°C for FeO to 1990°C for NiO). In other words, their structural and elastic properties are quite similar. Their conductivity properties are, however, completely different: TiO is a good metal, VO has semiconducting properties at low temperatures and probably exhibits a metal–insulator transition (*6*); the other four monoxides are excellent insulators. At room temperature TiO has a conductivity of 4.7 ×

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* Invited paper.

† Work supported in part by the National Science Foundation through Grant GH 34438.

‡ On an Organization of American States fellowship.

$10^3\ \Omega^{-1}\ \text{cm}^{-1}$; that of MnO is in the vicinity of $10^{-15}\ \Omega^{-1}\ \text{cm}^{-1}$ (*6*).

Their magnetic and optical properties are equally diverse (*6–14*). From them it emerges that there coexist localized (or narrow band) *d* states of the transition metal ions together with extended broad bands arising from the oxygen $2p$ and the metallic $4s$ states.

The theoretical situation is similarly mixed. The available band structure calculations (*15*, *16*) seem to describe the metallic oxides adequately, but fail to explain the properties of the insulators. Even if magnetic ordering is taken into account and antiferromagnetic band gaps are assumed to open up, band theory does not explain the properties of CoO or the insulating character of NiO above the Néel temperature.

There is in addition a puzzling inconsistency which within this framework is impossible to resolve. Mattheiss (*16*) in his calculation has taken ad hoc crystal potentials which are derived from *neutral-atom* Hartree–Fock–Slater charge densities (see Fig. 1). He thus obtains oxygen *p* bands (six states per unit cell) well below the transition metal *d* bands (10 states per cell). If the bands are filled according to Fermi statistics, the resulting state corresponds to O^{2-} and a doubly ionized transition metal. On the other hand Switendick (*17*), starting from a superposition of Ni^{2+} and O^{2-} ions, obtains a band picture of NiO (see Fig. 2) in which the narrow $3d$ band is below the $2p$ band; the final state then corresponds to neutral Ni and O atoms. Any intermediate approach would give overlapping oxygen *p* and transition-metal *d* bands, leading to an excellent conductor with probably peculiar magnetic properties and contrary to the experimental data.

In order to explain the narrowness of the observed *d* bands (*13*), a localized cluster approach has been proposed (*18*). This picture, although successful in some respects, fails to explain the metallic character of TiO, the properties of VO and some aspects of the optical properties of the other monoxides.

The hybrid model which we propose here is an extension of that of Adler and Feinleib (*8*). It is susceptible, however, to providing quantitative details, which previous treatments did not include.

Our model, although computationally

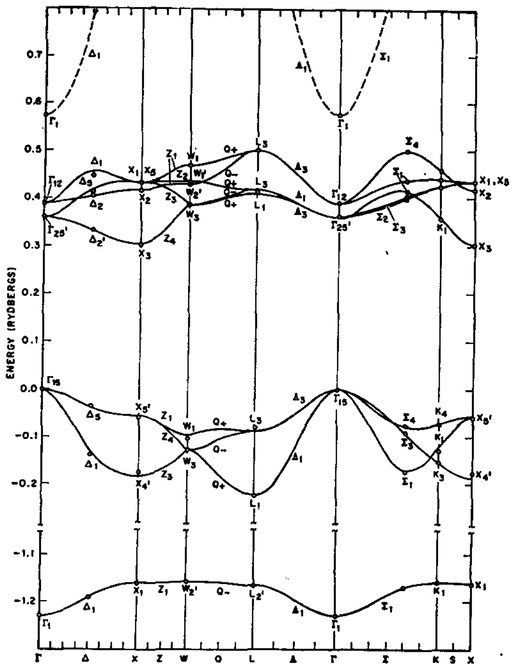

FIG. 1. The electronic band structure of NiO as calculated by Mattheiss (*16*).

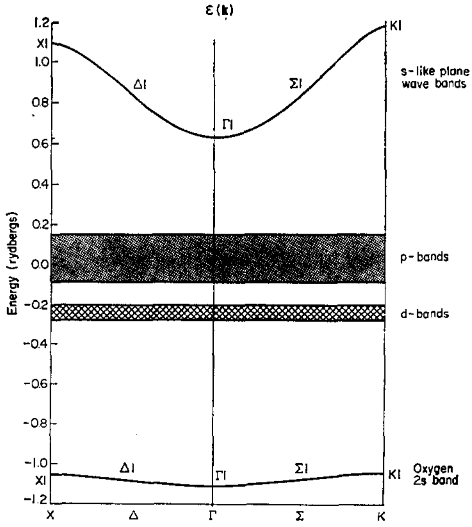

FIG. 2. The electronic band structure of NiO as calculated by Switendick (*17*).

simple, is conceptually rather complex and should be developed in successive steps. It is based for all cases in the following assumptions.

(i) The crystal potential is that arising from an ionic solid with doubly ionized metal M^{2+} and oxygen O^{2-} ions, as observed experimentally and consistent with the rocksalt structure.

(ii) The metal 4*s* and the oxygen 2*p* states are always described by a band picture. We have not repeated the band structure calculation for these states but rather have taken the pertinent information (*16*) from existing calculations (see Fig. 3). Some of the numbers quoted there need to be corrected by a Madelung-type contribution because of the assumed ad hoc neutral potential used in their determination. In particular the energy gap between 2*p* and 4*s* states must decrease due to this effect. It is interesting to remark that for NiO the experimental value coincides with the value obtained by Switendick who used the $Ni^{2+}O^{2-}$ potential. Similarly, for TiO, Ern and Switendick (*15*) who used an ionic $Ti^{2+}O^{2-}$ potential, obtained an energy gap in close agreement with experiment, and 3 eV smaller than the value given by Mattheiss (*16*).

(iii) The metal 3*d* electrons are to be considered either in a weakly correlated band picture for the metallic oxides or in a strongly correlated ionic picture for the insulating ones. In the second case, and also in building a criterion to choose one model, atomic data for the M^{2+}: $(3d)^n$ and M^{2+}: $(3d)^{n-1}(4s)$ configurations are necessary. These are obtained from experimental tables of atomic spectra (*19*, *20*).

Metallic vs Insulating Behavior: A Criterion

In order to decide whether the atomic or the band picture is valid for the 3*d* electrons, a clear-cut criterion should be developed. The crystal potential, acting on the one-electron orbitals, is responsible for four major effects: (i) the appearance of a very wide 4*s* band; (ii) the splitting of the five *d* states into a triplet Γ_5 and a doublet Γ_3; (iii) the hybridization of the 3*d* and 4*s* states at general points in the Brillouin zone; (iv) the spreading of the *d* levels into fairly narrow bands.

The effects (iii) and (iv) are closely related. It is evident from the published band structures that most of the *d*-band width is due to the *s*–*d* hybridization. As the 3*d* levels decrease in energy with respect to the 4*s* states and the hybridization gets consequently smaller, the width of the *d* bands decreases sharply.

While the crystal potential tends to spread the *d* states into bands, the intraatomic correlation between *d* electrons acts in the opposite direction. It favors crystal states in which the number of *d* electrons for each ion

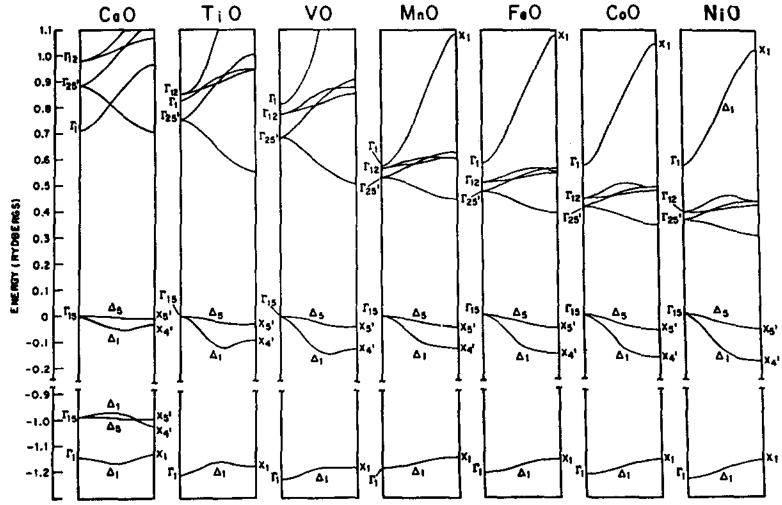

FIG. 3. The electronic band structure of the transition-metal monoxides as calculated by Mattheiss (*16*).

is constant: Fluctuations involve energies which are large, of the order of typical Coulomb energies (~10 eV).

If we assume that the tendency of the d electrons to form bands is dominated by the s–d hybridization effect, a quantitative comparison of the two opposing effects can be made. A crystal built out of M^{2+} ions in the $(3d)^n$ configuration, ground state term, would be in a perfectly insulating state, better pictured as a collection of independent ions. In each of these ions the electrons are strongly correlated. A crystal made of M^{2+} ions in the lowest term of the $(3d)^{n-1}$ $(4s)$ configuration should, on the other hand, attain its state of lowest energy by taking full advantage of the wide band properties of the $4s$ states; it goes accordingly into a metallic state. In the first approximation the $4s$ state will decouple from $(3d)^{n-1}$ core and spread into a band of width W_s. In higher order approximations the s–d hybridization and the d–d band effects should produce a band of $3d$ states in which electrons should still be at least partially though not very strongly correlated. In other words, the structure should become similar to that of a pure transition metal.

The energy difference in going from the $(3d)^n$ to the $(3d)^{n-1}$ $(4s)$ state is made out of two contributions:

$$\Delta E = \Delta E_p - \Delta E_b. \tag{1}$$

The first term is the promotion energy from the ground state term of the $(3d)^n$ configuration of the ion to the $(3d)^{n-1}$ $(4s)$ configuration. For the latter we take the weighted average value of the terms obtained from parallel-spin and antiparallel-spin coupling of the $4s$ electron to the ground state term of the $(3d)^{n-1}$ configuration. For example, in Ni^{2+}

$$\Delta E_p = \{\tfrac{5}{8}E[3d^7 4s(^5F)] + \tfrac{3}{8}E[3d^7 4s(^3F)]\} - E[3d^8(^3F)], \tag{2}$$

which amounts to 7.0 eV. The second term in Eq. (1) is the energy gained by an s electron in dropping from a localized level to the bottom of a wide band. During that spreading we assume that the center of gravity of the band remains unchanged in energy. Therefore, for a face-centered cubic s band, the tight-binding approximation would give

$$\Delta E_b = (3/4)W_s, \tag{3}$$

where W_s is the total bandwidth.

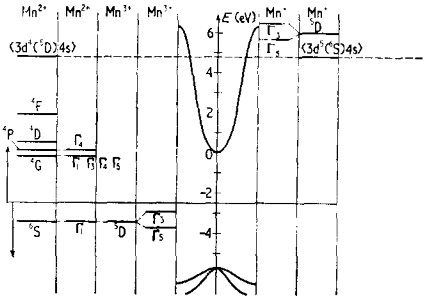

Fig. 5. Electronic structure of MnO.

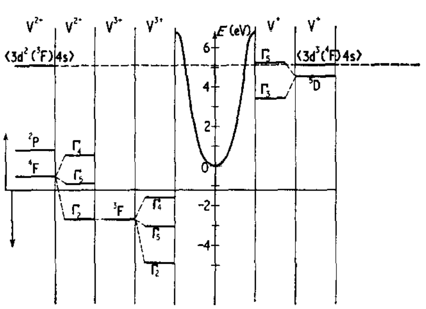

Fig. 4. Electronic structure of VO.

For NiO, $\Delta E_b = 4.4$ eV. Our criterion can now be clearly stated: If $\Delta E > 0$ the oxide will be metallic. In this latter case a band description is the most suitable starting point: such is the case for TiO ($\Delta E = -0.6$ eV). If E is positive and small, as in VO($\Delta E = +0.5$ eV), the material may exhibit a metal–insulator transition and neither the band nor

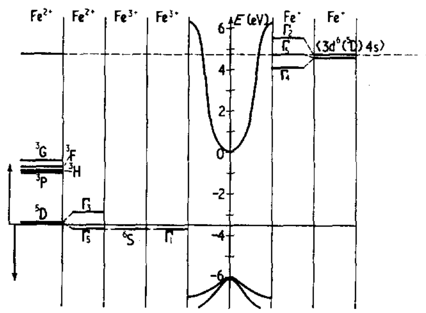

Fig. 6. Electronic structure of FeO.

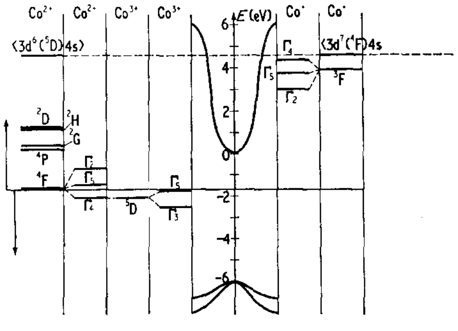

FIG. 7. Electronic structure of CoO.

Comparison with experiment—NiO

Theory: Bottom of 3d to 4s bands

Γ_4: 2·9 eV Γ_5: 3·6 eV Γ_2: 4·3 eV

Bottom of 2p to 3d bands

Γ_3: 8·9 eV Γ_5: 9·7 eV

Bottom of 2p to 4s bands

6·2 eV

Inter-ionic transitions

$\Gamma_4 \rightarrow \Gamma_3$: 5·7 eV

$\Gamma_5 \rightarrow \Gamma_3$: 6·3 eV

$\Gamma_4 \rightarrow \Gamma_5$: 6·5 eV

$\Gamma_5 \rightarrow \Gamma_5$: 7·1 eV

$\Gamma_2 \rightarrow \Gamma_3$: 7·1 eV

$\Gamma_2 \rightarrow \Gamma_5$: 7·9 eV

Experiment: Onset of bands: from 3 to 4·3 eV
Peaks at: 4·9 eV, 6·1 eV, 7·2 eV and 8·5 eV

FIG. 9.

the hybrid description is completely satisfactory. Finally, for the other four oxides, ΔE is positive and large (MnO: 3.4 eV; FeO: 3.4 eV; CoO: 1.6 eV; NiO: 2.6 eV) and the band picture definitely does not hold. For these cases (and for VO as well) we proceed to construct a hybrid model which can be better described by a multiple diagram. Specific examples of the five transition-metal monoxides are given in Figs. 4–8.

These hybrid models have been used successfully to explain optical properties (*21*) and the antiferromagnetic behavior of these insulating compounds (*22*). As an example of the agreement between theory and experiment we show in Fig. 9 the values of the optical features of the NiO structure as shown in Fig. 8. These structural features include: (a) transition from the 3*d* states to the 4*s* band

$$(3d)^n \rightarrow (3d)^{n-1} + (4s)_{\mathbf{k}}; \tag{4}$$

(b) transition from 2*p* to the 3*d* states

$$(3d)^n + (2p)_{\mathbf{k}} \rightarrow (3d)^{n+1}; \tag{5}$$

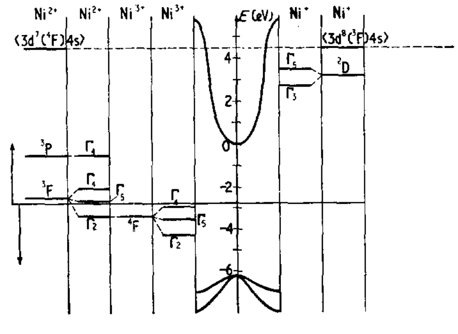

FIG. 8. Electronic structure of NiO.

(c) transition between 2*p* and 4*s* bands; and (d) interionic transitions between levels of different ions

$$(3d)^n + (3d)^n \rightarrow (3d)^{n+1} + (3d)^{n-1}. \tag{6}$$

The comparison with experimental data of Powell and Spicer (see Fig. 10) is quite satisfactory.

As a final remark, the model is also capable of describing well the magnetic properties of these solids. There is evidence that this should be so: The observed magnetic moments [6] are all in good agreement with those expected from the crystal-field-split ground state obtained from the ground term of the $(3d)^n$ configuration.

It has been possible now to include hybridization corrections in perturbation theory and thus calculate the effective exchange coupling between spins and therefore the

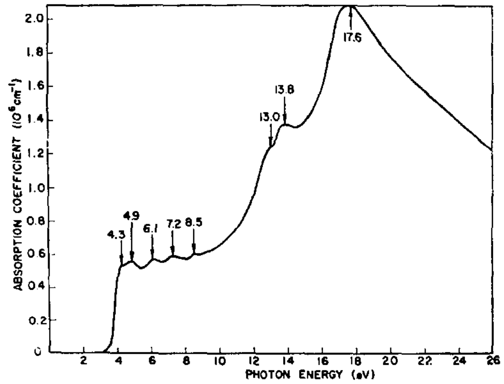

FIG. 10. The experimentally determined NiO absorption coefficient from the work of Powell and Spicer (*11*).

long-range magnetic properties. The agreement (*22*) is once again satisfactory.

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