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Fundamental Problems in the Electronic Structure of Transition-Metal Oxides*†

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The evolution of the electronic structure of a solid as it is formed from large interatomic separations to its equilibrium lattice configuration is analyzed. The importance of electronic correlations in the narrow-band regime is emphasized, particularly with regard to transport behavior. First, the case of a monovalent solid, such as Na, is analyzed in detail, and an effective one-electron representation, exact in the atomic limit, is introduced. It is shown that the ordinary band approximation fails miserably in this limit. Next, the more realistic case of a transition-metal oxide is considered. In the limit of strong correlations, it is emphasized that information deduced from optical experiments should not be used to analyze transport data within the band approximation, since the effective electronic density-of-states diagram can differ significantly from that derived from optical results. Finally, some fundamental difficulties in our present understanding are discussed.

I. Introduction

Transition-metal oxides, being fundamental components of many minerals, ores, ceramics, and glasses have been known and studied for as long as any other class of materials; however, they still remain among the most poorly understood solids in several fundamental respects (*1–3*). Initial interest in transition-metal oxides stemmed from the fact that they seemed to be ideal materials in which to study *d*-band electrons. In this respect, they are superior to the transition metals, in which the *d*-band is overlapped by the next higher *s* band, and thus a great deal of *s*–*d* hybridization is always present. A sketch of the $3d$ and $4s$ states in a typical iron-group transition metal as a function of inverse interatomic spacing is shown in Fig. 1(a). In such plots, the atomic limit (i.e., infinite separation) is the discrete spectrum on the extreme left; the sketch represents the spreading of the atomic levels into bands as the atoms are brought closer together. Since the $4s$ wave functions extend farther from the nuclei than the $3d$ functions (both because of the higher principal quantum number and the greater number of radial nodes), the $4s$ band spreads more quickly with decreasing interatomic separation. In the solid at the equilibrium separation, a_0, the $3d$ band lies entirely within the $4s$ band, and there is a net transfer of about one electron from the $4s$ band to the $3d$ relative to the ground-state atomic configuration (usually $4s^2 3d^n$). The cohesive energy of the solid, as in most metals, arises almost entirely from the partially filled nature of the $4s$ and $3d$ bands; although the $3d$ band is narrow, the fact that there are a large number of states (10 per atom) in the band results in a significant $3d$ contribution to the cohesive energy.

Figure 1(b) shows the analogous plot for a typical transition-metal oxide. An immediate difference between the two sketches is the order of the atomic energy levels of the metallic ion—the $3d$ states are below the $4s$ states in the oxide. The reason for this apparent discrepancy

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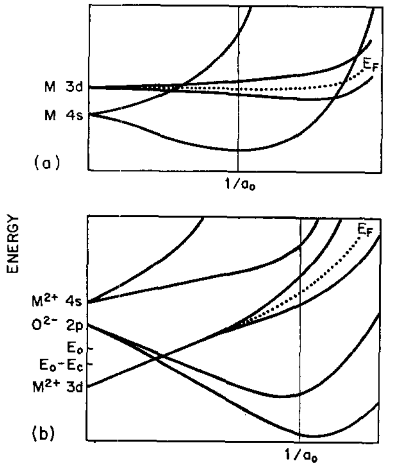

FIG. 1. Sketch of the energy-band structure near the Fermi energy E_F, as a function of the average inverse interatomic spacing for (a) a transition metal, M, and (b) a transition-metal oxide, MO. E_0 represents the average electronic energy in the ground state of the isolated ions; $(E_0 - E_c)$ represents the average ground-state energy of an electron at the equilibrium interatomic separation, a_0 (i.e., the minimum electronic energy).

is that for the oxide we must consider the atomic limit of infinitely separated *ions*, M^{2+} and O^{2-}, rather than neutral atoms. For the cation, M^{2+}, the two electrons that have been transferred are the 4*s* electrons, and the ground-state configuration is just $3d^n$. This effect can be understood by recalling that the reduction in energy of the *s* states relative to the *p*, *d*, *f*, ... states in any given electronic shell is due to their deeper penetration of the core; *s* electrons come relatively closer to the nucleus, and thus take better advantage of the greater positive charge density within the core. However, when the atom is ionized, the outer electrons are no longer present, and the effect of penetration is reduced; this in turn reduces the *s–p* energy difference, thus increasing the energy of the 4*s* levels relative to the 3*d* levels.

There are of course, several other differences between transition metals and their oxides. An additional complication in the oxides is the presence of anion energy levels. The highest occupied oxygen states are the 2*p* orbitals; their position above the cation 3*d* levels in the atomic limit of Fig. 1(b) reflects the fact that the ground state at infinite separation is *neutral* M and *neutral* oxygen, rather than M^{2+} and O^{2-}. However, as the interatomic spacing decreases, the electrostatic attraction between cation and anion sharply decreases the energy of the 2*p* states relative to that of the 3*d* and 4*s* states, thus favoring electronic transfer from metal atom to oxygen and stabilizing the ionic configuration. An important consequence of this is the fact that the cohesive energy of the solid primarily arises from the electrostatic attraction between cation and anion, rather than from any bandwidth effects. (Of course, in reality, there exists a resonance between ionic and covalent bonding which minimizes the energy and produces a ground state which is only partially ionized. The covalent bonding arises from 2*p*–4*s* hybridization. If the covalent contribution to the cohesive energy exceeds the ionic contribution, the lowest band in Fig. 1(b) should be more properly labelled as a 2*p*–4*s* bonding band, the highest as a 2*p*–4*s* antibonding band. In this case, the relative energy variation with interatomic spacing would then be much smaller. Some 2*p*–3*d* hybridization can also be present, as will be discussed subsequently.)

It is immediately evident from Fig. 1(b) that for transition-metal oxides with partially filled *d* subshells, the Fermi energy E_F lies within the *d* band. The band theory of conduction is then unambiguous—unless a splitting of the *d* band opens up along the entire Fermi surface, all such solids should be metallic. But given the symmetry of several important oxides, e.g., CoO, such a splitting cannot exist (*4*). The fact that CoO is an excellent insulator provides a major challenge to our understanding of the electronic properties of solids.

It has now been accepted that Mott's relatively early resolution of this problem is basically correct (*5*, *6*). Mott pointed out that for *narrow* energy bands the decrease in electronic energy due to band formation and subsequent delocalization, a quantity proportional to the bandwidth for any fixed configuration, can be quite small and might not overcome the increase in electrostatic repulsion brought about by the simultaneous appearance of two delocalized electrons on the same ion core. The latter energy, as we shall see in Section II, is essentially neglected in the usual band theory of solids. If this situation occurs, the ground state of the material is one in which the appropriate electrons are localized on their respective ion cores, and metallic conduction cannot occur. If no other electrons occupy partially filled bands, the material is called a Mott insulator. It is now evident that CoO is a Mott insulator, because of the extremely narrow 3*d* bandwidth.

It is relevant to ask why the 3*d* bands of many transition-metal oxides are sufficiently narrow to preclude delocalization, when the same is not true for the corresponding transition metals. (The latter, with the possible exception of Mn, all exhibit a 3*d* contribution to their cohesive energy, strong evidence for band formation.) The answer is once again evident from the sketches in Fig. 1. In the metals, the overlap of the 3*d* and 4*s* bands leads to strong hybridization, effectively widening the 3*d* band. On the other hand, in the oxides, the significant energy separations between the 3*d* bands and both the 2*p* and the 4*s* bands inhibit hybridization. For oxides in which the 3*d* band is close to or overlaps either the 4*s* band or the oxygen 2*p* band, delocalized 3*d* electrons become possible. Furthermore, particularly in the 4*d* and 5*d* transition-metal oxides, the *d* band itself could be sufficiently wide to support metallic conduction. Thus, the existence of good *d*-band metals such as ReO_3 (*7*) is not difficult to understand. The most fundamental problem remaining, however, is how to predict a priori which oxides are Mott insulators and which are well described by ordinary energy-band theory. It is this problem which is the major theme of this paper.

II. Effects of Electronic Correlations in Narrow Energy Bands

The best starting point for attempting to understand the influence of electronic correlations on the electronic structure of solids is once again the atomic limit, $1/a = 0$. This limit can be completely analyzed (assuming that the energy-level structure of all the relevant atoms and ions is known) and easily points up the source of the failure of ordinary band theory in Mott insulators. In addition, the 3*d* band of several transition-metal oxides appears to be much more appropriately described by the atomic limit than by the band limit in which correlations are completely neglected.

As a simple example, let us consider the problem of N sodium atoms in a body-centered cubic array. Let a be the nearest-neighbor separation. We should be able to sketch the energy-band structure as a function of $1/a$, analogous to Fig. 1. However, an analysis of the atomic limit ($a \to \infty$) immediately shows the qualitatively incorrect features of such an approach in the narrow-band regime.

Sodium consists of an ion core of the Ne configuration ($1s^2 2s^2 2p^6$) plus an outer 3*s* electron. Since it costs at least 47 eV to remove an electron from a Na^+ core, we need consider only the 3*s* and higher levels in an analysis of the low-energy electronic structure of Na. Let us set the energy of a Na^+ core in its ground state as the zero of energy. If we restrict ourselves to only 3*s* outer orbitals, four many-body states are then possible for each atom, as indicated in Fig. 2(a). Highest in energy is an unoccupied Na^+ ion at $E = 0$; this state is nondegenerate. Next is a Na^+ core occupied by a single 3*s* electron, i.e., a Na atom in its ground state; since the 3*s* electron can have its spin either up or down, the state is doubly degenerate. The energy of this state is known exactly, since it is below the energy of the Na^+ core by the ionization potential of Na, 5.1 eV. In general, we set this state at E_0, where E_0 is the negative of the ionization potential. Finally, since we can at most doubly occupy the 3*s* level, there is a nondegenerate state representing a Na^- ion in its ground state. Both 3*s* electrons are attracted to the Na^+ core with an energy E_0, but since two electrons on the same atom must also repel each other, the total energy of the Na^- state is not $2E_0$ but somewhat higher. If we call the repulsive energy between the two 3*s* electrons on the same ion core U, then the Na^- state is at $2E_0 + U$. It is easily seen that since the energy of the negative ion is less than that of the atom by the electron affinity, the U for any atom is just

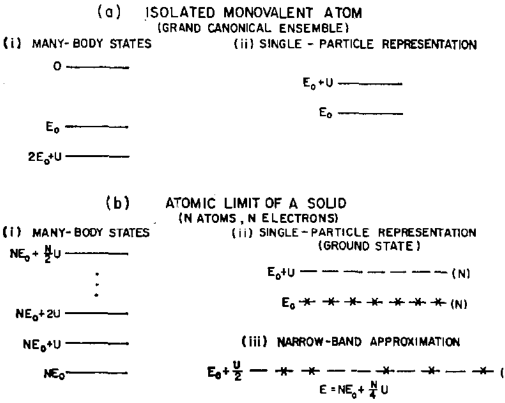

FIG. 2. Energy level diagram for a monovalent solid (e.g., Na) in the atomic limit (large interatomic separation). The energy of a singly ionized atom is taken as the zero of energy. (a) Single atom levels: (i) Many-body energy values; (ii) effective single-particle representation; the level at $E_0 + U$ falls to E_0 if the level at E_0 is unoccupied. (b) N-atom solid: (i) Many-body energy values; (ii) effective single-particle energy levels for the ground-state configuration (iii) ordinary band approximation.

the difference between its ionization potential and its electron affinity. For Na, the electron affinity is 0.5 eV, and this $U = 4.6$ eV.

For N atoms in the atomic limit, the possible many-body energy levels range from 0 to $2NE_0 + NU$, and the degeneracies are increased multifold. However, if we wish to represent the states of a real solid, we should require a fixed total number of 3s electrons, N. Thus, only a much smaller number of many-electron states are possible. Their energies can be represented by the expression,

$$E_n = NE_0 + nU, \tag{1}$$

where n is the number of doubly occupied (i.e., Na^-) ion cores; n can vary from 0 (all N atoms singly occupied) to $N/2$ (half of the atoms unoccupied Na^+ cores, the other half doubly occupied Na^- ions). The degeneracy of state n is

$$g_n = N!/(n!(N-n)!)\,2^{(N-2n)}, \tag{2}$$

since the $(N - 2n)$ singly occupied atoms can have either sign of spin. Thus, the ground state is 2^N-fold degenerate. The energy levels are shown in Fig. 2(b).

An important result of this analysis is that the exact many-body states in the atomic limit can be represented by an equivalent one-electron picture, provided the one-electron states are taken to be occupation-number dependent in a simple manner. This representation is also shown in Fig. 2 for both the single-atom and the N-atom situations. For a single atom, the choice of the energy of the Na^+ ion core as the zero of energy allows us to account for all the many-body states with just two one-electron levels, one for spin-up electrons and the other for spin-down electrons. If the ion core is unoccupied, both states are at E_0. However, as soon as either one of these states becomes occupied, the other rises to $E_0 + U$. Such a shift of states with occupation numbers is the price we must pay for a one-electron representation of a system in which correlations are important. It is easy to see that this representation recaptures the many-body states exactly: Either both levels are unoccupied ($E = 0$), one level is occupied by an electron of either spin ($E = E_0$), or both levels are occupied ($E = 2E_0 + U$). It is clear that the atomic limit of the N-atom problem also can be represented by one-electron states at either E_0 or $E_0 + U$, the latter state existing only if the corresponding atom is already occupied by an electron of the opposite spin. We can look at this effective one-electron picture as a "band" of $(N + n)$ states at E_0 and $(N - n)$ states at $E_0 + U$. Since $(N - n)$ of the former and n of the latter states are occupied, the total energy is $E = NE_0 + nU$, in agreement with Eq. (1).

For the ground state of the N-atom problem with one electron per atom, $n = 0$, the lower band is exactly filled and the upper band exactly empty, as is shown in Fig. 2(b)(ii). Since the energy gap between the bands is U, of the order of 5 eV, the state represents that of an insulator, an explicit demonstration of Mott's original suggestion. Note that the material is insulating despite the fact that the ground state is 2^N-fold degenerate; this degeneracy exists solely because of the freedom to flip a spin on any site, transitions which do not carry any current.

All of this might appear to be trivial, if no thought is given to the strikingly distinct results obtained using ordinary band theory. Band theory neglects electronic correlations, and the one-electron states do not then depend on occupation numbers. Thus, only a single 3*s* band exists for Na, having exactly $2N$ states at all times. In the atomic limit, $1/a = 0$, all $2N$ states are degenerate and located at the *average* energy $E_0 + U/2$. Note that this is not quite so bad as it first seems, since it is exact when an atom is unoccupied or doubly occupied. (Thus, it is a good approximation when the 3*s* band is nearly full or nearly empty.) But it always overestimates the energy of a singly or occupied atom; this is because neglect of correlations does not allow for two electrons to correlate their motions and avoid each other. But the critical difference between this approximation and the exact approach as far as the predicted electrical properties are concerned is that now the band is *half filled* for the case of one electron per atom. Thus, band theory predicts metallic conduction even in the atomic limit.

It would indeed be useful if a model existed which could interpolate between the atomic limit for large a and the band limit, which should be accurate for small a (including near the equilibrium interatomic separation for Na, a fact that follows from the known applicability of the band approximation for the alkali metals). Fortunately, such a model indeed exists. Hubbard (*8*) suggested the use of the Hamiltonian,

$$H = \sum_{k,\sigma} E(k) n_{k,\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} - (N/4)\, U, \tag{3}$$

where $E(k)$ are the one-electron energies as a function of the wave vector, k, $n_{k,\sigma}$ are the occupation numbers of the Bloch state of wave vector k and spin σ, and $n_{i\sigma}$ are the occupation numbers of electrons of spin σ localized on the ion core whose equilibrium position is the lattice vector R_i. The Hamiltonian (*3*) can be obtained from the appropriate many-body Hamiltonian for a solid by replacing the electronic Coulomb interaction by a short-range repulsion in which two electrons repel only when they are localized on the same ion core. The first term in Eq. (3) is the band approximation, including the electronic repulsion included on the average; the second term adds an energy U every time a spin-up and a spin-down electron are simultaneously present on an ion core; the third term is just a constant that subtracts off the average value of the intraionic electronic repulsions which otherwise would be counted twice (in both previous terms). The Hubbard Hamiltonian has the advantage that, as we shall show, it is exact in both the atomic and the band limits, and is thus a good model for interpolation between them. Provided the material is not ferromagnetic, the average value of the correlation term in Eq. (3) is just

$$\begin{aligned} U \sum_i n_{i\uparrow} \langle n_{i\downarrow} \rangle &= (1/2)\, U \sum_i n_{i\uparrow} \\ &= (N/4)\, U, \end{aligned} \tag{4}$$

since the average number of down-spin electrons is 1/2 and the total number of up-spin electrons is $N/2$. Thus, the one-electron approximation of the correlation term is just cancelled by the constant term, demonstrating that Eq. (3) reduces to the ordinary band approximation in the one-electron limit. On the other hand, in the atomic limit,

$$E(k) = E_0 + U/2,$$

as discussed previously. The sum in the first term of Eq. (3) then gives

$$N E_0 + (N/4)\, U. \tag{5}$$

This sum is nontrivial, since it would appear to give $N_0 E_0 + NU/2$, rather than Eq. (5); however, simply adding the one-electron energies to obtain the total energy is incorrect, since it counts the interaction terms twice. The correct answer, Eq. (5), is easily interpreted, however. In the atomic limit of the one-electron approximation, placing the N electrons in the $2N$ possible degenerate states (all at $E = E_0 + U/2$) must be done randomly, since all electrons but the one under consideration are treated on the average. Thus, $N/4$ ion cores are unoccupied, $N/2$ are singly occupied, and $N/4$ are doubly occupied. Since each of the doubly occupied ion cores contribute an additional repulsive energy U, the total energy in the one electron approximation is properly given by Eq. (5). Hence, in the atomic limit the Hubbard approximation gives

$$E = N_0 E_0 + nU, \tag{6}$$

where n is the number of doubly occupied ion cores. Since Eq. (6) agrees with the previous result, Eq. (1), the Hubbard Hamiltonian is also exact in the atomic limit.

As the interatomic spacing is reduced from large values, a sketch of the spreading of the two quasi one-electron levels at E_0 and $E_0 + U$ is shown in Fig. 3(a). The two bands spread with increasing $1/a$ and eventually overlap at a critical point for which the bandwidth is approximately equal to U (*3*, *9*). This point represents the critical density at which an insulator–metal transition, known as a Mott transition, occurs. The average energy per electron is indicated on the sketch, and is a minimum at the equilibrium spacing, a_0. Note that in the insulating region, no cohesive energy exists; the minimum of energy either occurs at metallic densities or else no solid forms. The reason for this is that for metallic bonding, the cohesive energy comes almost entirely from the partial occupancy of the band; if we assume a crystal structure appropriate to metallic bonding but do not have any band overlap, there is no cohesion. We might be tempted to conclude that no Mott insulators exist. However, this neglects the possibility of electrons other than the localized ones contributing the cohesion. In fact, a glance at Fig. 1(b) shows that the cohesive energy of a transition-metal oxide can arise solely from ionic binding, without the necessity of a partially filled band contribution. Similarly, the formation of a filled $2p$–$4s$ bonding band entirely from covalency effects is sufficient to yield cohesion without any additional metallic bonding. Thus, transition-metal oxides can be, and indeed often are, Mott insulators.

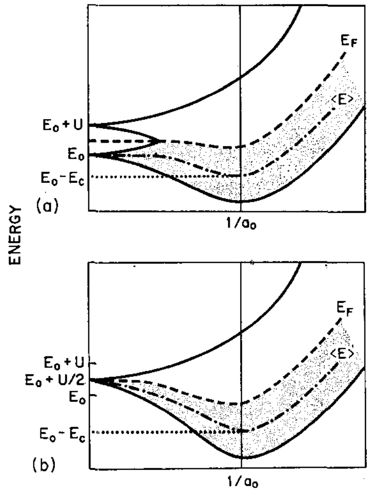

FIG. 3. (a) Sketch of the energy-band structure as a function of inverse interatomic separation for a monovalent solid in the Hubbard approximation. E_F indicates the Fermi energy and $\langle E\rangle$ the average ground-state electronic energy, $(E_0 - E_c)$ represents the minimum electronic energy. Shaded states are filled at $T = 0$. (b) Band approximation for the same physical problem. For the solid shown here, the equilibrium interatomic separation is well in the metallic region.

In Fig. 3(b), the band approximation analogous to Fig. 3(a) is sketched. It is terribly in error in the Mott-insulating region, but it approaches the more accurate Hubbard approximation long before densities appropriate to ordinary metals such as Na are reached. Unfortunately, the Hubbard approximation has proved difficult to analyze in the region near the Mott transition, and no calculation appropriate to any real material has even been attempted in this regime. However, as shall be discussed in Section III, for some Mott insulators, all relevant bands appear to be either near the band limit or the atomic limit, and the actual electronic structure can be approximated without the necessity for sophisticated computation.

III. Electronic Structure of Transition-Metal Oxides

It might be expected that the metallic oxides should be well approximated by ordinary band theory, and, in fact, there is strong evidence that such is the case for ReO_3. The band-structure calculation of Mattheiss (*10*) has had success in interpreting several experiments which measure the shape of the Fermi surface (*11*, *12*). On the other hand, some metallic oxides appear to be only borderline metals (*13*, *14*), and electronic correlations must be taken into account. It is, of course, not surprising that ordinary band calculations have not yet had much success at all in explaining the experimental data taken on Mott insultors (*15*).

Recently some progress has been made in understanding the electronic structure of the Mott-insulating transition-metal oxides. One particularly promising approach is the self-consistent-field $X\alpha$ cluster method by Slater and Johnson (*16*). In such calculations, the ground state of a cluster consisting of a central cation surrounded by its nearest-neighbor anions is self-consistently expressed in terms of one-electron molecular orbitals, characterized by their energies, occupation numbers, and electronic charge-density distributions. This method should be expected to give good results in predicting the energies of optical transitions involving localized electrons; thus it appears to be particularly suited to Mott insulators, which have a large density of localized states near the Fermi energy. Johnson et al. (*17*) have applied the method to NiO, and found good agreement with X-ray photoemission data (*15*). The $X\alpha$ calculations can be expected to be extremely useful for analysis of the optical spectra of all of the Mott insulators, but it is not yet clear whether they will be of use in either interpreting transport behavior or predicting if a given solid is insulating or metallic.

An entirely different approach has also been used to analyze both optical and transport properties of Mott insulators (*18*, *19*). This method begins with the atomic limit and adjusts the free-ion energy levels by accounting for the effects of the Madelung potential, screening, covalency, and crystalline-field splittings calculated at the actual equilibrium, configuration of the solid. These give the appropriate energy levels which should spread approximately symmetrically into bands, much as in Fig. 3(a). The bandwidths for the $2p$ and $4s$ bands can then be estimated from ordinary band calculations or from photoemission experiments. Good agreement with the optical spectrum of NiO, for example, is found if the $3d$ band of this Mott insulator is taken as less than 0.1 eV wide (*18*); this very narrow bandwidth is consistent with recent uv-photoemission results (*20*), although difficult to understand theoretically. Since correlations are explicitly taken into account in this approach, an ordinary band-structure diagram is inappropriate. However, an effective one-electron plot analogous to those discussed in Section II can be used (*21*), and such a diagram is shown in Fig. 4 for NiO. Ordinary bands are drawn to the left of the energy axis, localized states to the right. States shown as dashed lines represent possible optical transitions from occupied localized states only.

The great advantage of this particular approach is its ability to also account for transport properties of both pure and doped Mott insulators. As in ordinary semiconductors, the results of nonstoichiometry or doping are donor- or acceptor-like states in the energy gap, and these states then dominate the electrical conductivity of the material. But in the case of strongly correlated states, the entire effective one-electron density-of-states must be recalculated (*18*), and unexpected results are often obtained. To illustrate the reason for this, consider Li-doped NiO. Li enters NiO substitutionally for Ni, but since it is monovalent, charge neutrality

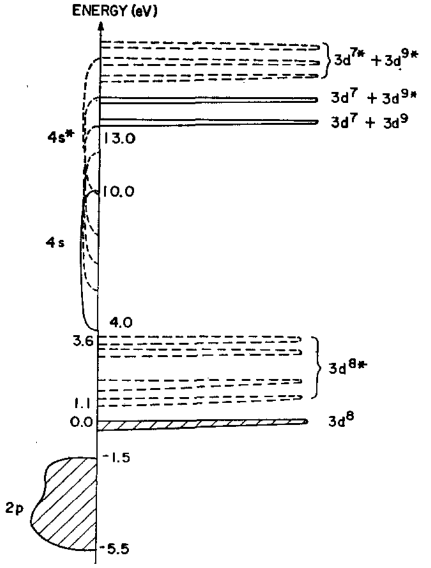

FIG. 4. Optical density-of-states sketch for NiO. Extended states are shown to the left, localized states to the right. States which are occupied at $T = 0$ are shaded. States enclosed by dashed lines are available for excitations only from filled localized states. An asterisk refers to excited crystalline-field-split states.

is maintained only by creation of Ni^{3+} ions. Ni^{3+} can be looked at as acceptor-like, since it represents an intrinsic Ni^{2+} ion with an extra hole. This hole can accept an electron either from the $3d$ band or the $2p$ band. A glance at the optical density-of-states diagram of Fig. 4 suggests that the latter process is unlikely to contribute much to the electrical conductivity, since the $2p$ band is 1.5 eV below the $3d$ band; despite the much higher mobility expected in the wider band, no observable hole density should be present below at least 1500 K. However, this is a faulty analysis. Note that the optical $2p$–$3d$ band separation follows from the difference in energies of the two atomic-limit transitions:

$$3d^8 \rightarrow 3d^7 4s \qquad (7)$$

$$2p^6 + 3d^8 \rightarrow 2p^5 + 3d^8 4s. \qquad (8)$$

The latter excitation is highly energetic due to the relatively high energy of the $3d^8 4s$ (Ni^+) configuration. On the other hand, when some Ni^{3+} ions are present, a hole in the $2p$ band can be obtained via the transition:

$$2p^6 + 3d^7 \rightarrow 2p^5 + 3d^8. \qquad (9)$$

This transition does not require the formation of a Ni^+ ion and requires much less relative energy than Eq. (8). Consequently, when Ni^{3+} ions are present, it does not require an additional 1.5 eV to excite a hole in the $2p$ band; in fact, the two electronic excitations occur at virtually the same energy (*18*). Once again, we must pay a price for treating a strongly-correlated system in an effective one-electron representation—the electrical density-of-states can be sharply different from the optical density-of-states. An estimate of the former for Li-doped NiO is shown in Fig. 5. This analysis helps to resolve a major problem for NiO—the apparently incompatibility of highly mobile transport in a very narrow band; the resolution is that the conductivity takes place predominantly in the relatively wide $2p$ band, some of whose states are made much more energetically accessible for transport by the presence of Ni^{3+} ions in the material.

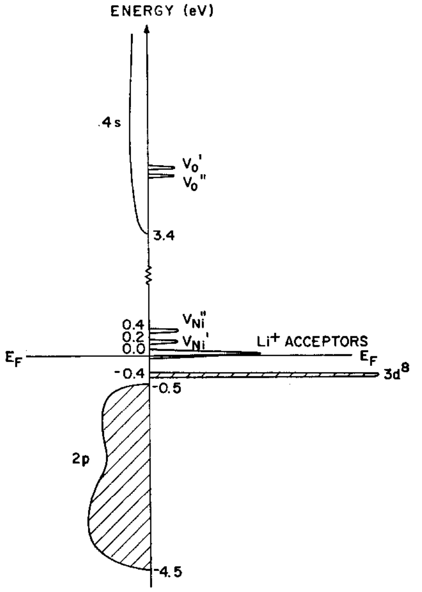

FIG. 5. Electrical density-of-states sketch for Li-doped NiO. Extended states are shown to the left, localized states to the right. States which are occupied at $T = 0$ are shaded. Partial self-compensation by means of oxygen vacancies is assumed, pinning the Fermi level in the lowest acceptor level at low temperatures. V_x' and V_x'' refer to singly and doubly ionized x vacancy levels, respectively.

The major disadvantages of this method are the empirical means used for estimating screening, covalency effects, and $3d$ bandwidth, the lack of a quantitative scheme for improving the approximations systematically, and the inability to predict a priori which materials are Mott insulators. Koiller and Falicov (*22*) have recently introduced another semi-empirical method of calculation which differs from the one described above in only a few details. However, a criterion for predicting which materials are Mott insulators is suggested—if the energy of the bottom of the $4s$ band is significantly greater than the ground state energy of the $3d^n$ configuration of the transition-metal ion, it is concluded that the material is a Mott insulator. This criterion appears to work for the iron-group monoxides, with the exception of VO and FeO. However, it is not yet clear whether or not it is more generally applicable, and it is certainly a risky means for prediction. Obviously, overlap of the $3d^n$ ground state with either the $4s$ or the $2p$ bands is *sufficient* for metallic behavior, but it may not be necessary. For example, the band calculation of Mattheiss (*10*) for ReO_3 indicates a $5d$ band well separated from the $2p$ and $6s$ bands, yet capable of highly mobile metallic conduction. Since a small, negative Knight shift is observed in ReO_3 (*23*), there is also experimental evidence against significant s–d hybridization in this material.

IV. Conclusions

The most fundamental unsolved problem in the transition-metal oxides is still as it was 40 years ago, a method for a priori prediction of which materials are metallic and which insulating. It is possible that this problem can be reduced, for example, to an analysis of the amount of d–s or p–d hybridization or, more likely, to a calculation of the relative magnitudes of the d bandwidth and the intra-ionic correlation energy, U. However, no such calculations have yet been accurately carried out for any real oxide, either Mott insulator or metal.

Although as discussed in Section III, a consistent explanation of the electrical and optical properties of one well-studied material, NiO, does exist, this analysis is far from unique (*24*) and suggests at least one additional problem—Why should the $3d$ bandwidth of NiO be more than an order of magnitude narrower than predicted by band calculations? This problem has ominous overtones, since the maximum band narrowing within the Hubbard model appears to be only a factor of two (*25*). However, there is direct experimental (*15*, *20*) as well as analytic (*18*) evidence for these very narrow bandwidths suggesting that even the Hubbard model may be inadequate for a material such as NiO, a conclusion that is particularly discouraging in view of the difficulties in applying this model to a real material.

In conclusion, it should be noted that many other fundamental problems, such as a consistent explanation for the diverse magnetic properties of these materials (*1*–*3*) or an understanding of the multitude of insulator–metal transitions (*4*), have not even been touched on in this discussion. Clearly, a great deal of work remains to be done. However, to end on an optimistic note, the hope now exists that the renewed interest in oxides arising from their potential applications will stimulate advances in resolving some of these difficulties before long.

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