Band Gaps and Electronic Structure of Transition-Metal Compounds

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A new theory is presented for describing band gaps and electronic structures of transition-metal compounds. A theoretical phase diagram is presented in which both the metallic sulfides and insulating oxides and halides occur in a quite natural manner.

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The origin of band gaps and characters of the valence and conduction electron states in $3d$ transition-metal compounds have been controversial topics for the last forty years.[1-3] Band-structure calculations in which exchange and correlation effects are replaced by effective one-particle potentials often predict metallic ground states or gaps which are an order of magnitude smaller than experimentally observed.[2,3] In the Mott-Hubbard theory[1] it is proposed that charge fluctuations of the type $d_i^n d_j^n \leftrightarrow d_i^{n-1} d_j^{n+1}$ (where i and j label transition-metal sites) which involve the d-d Coulomb and exchange interactions (U) are strongly suppressed because of the high energies involved (7–10 eV for the late transition metals[2] and also for the high-spin Mn^{2+} and Fe^{3+} compounds because of the exchange[4]). This idea forms the basis for an understanding of the low-energy-scale properties of the magnetic insulators in terms of spin-only Hamiltonians, the success of which confirms that charge fluctuations must be high-energy-scale properties. This separation into low (spin only) and high (charge fluctuation) energy scales also forms the basis for the very successful Anderson theory of superexchange[5] as well as the Goodenough-Kanamori rules.[6]

There are, however, several problems with the Mott-Hubbard theory in its simplest form. First it implies that the band gap is a d-d gap which is correct for Ti and V compounds. For the Co, Ni, and Cu compounds, however, the gap seems to be directly related to the electronegativity of the anion and therefore probably is of a charge-transfer type.[7,8] Also, it is difficult to understand that NiS, CuS, and CoS[9] are metallic since that would require a reduction of U from 7–10 eV in the oxides[2] to 1–2 eV in the sulfides. As already indicated, there is another charge-fluctuation energy which does not involve U, namely the charge transfer (Δ) $d_i^n \rightarrow d_i^{n+1}\underline{L}$, where $\underline{L}$ denotes a hole in the anion valence band. Δ is directly related to the electronegativity of the anion and the Madelung potential, both of which tend to stabilize an ionic ground state and an inert-gas valence configuration of the anion. The model Hamiltonian that incorporates both Δ and U is the Anderson Hamiltonian commonly used to describe rare-earth materials, but not commonly used for transition-metal compounds. Another charge fluctuation frequency proposed in the past[10] involves the $d^n \rightarrow d^{n-1}4s$ excitation. New information, however, shows that this is relatively unimportant especially for late-transition-metal compounds because of the high energy of the d^{n-1} state.[2] We will therefore neglect this, upon which the Anderson impurity problem becomes exactly solvable for insulators.

In this paper we describe the dependence of the conductivity gap and the nature of electron and hole states on U and Δ for transition-metal compounds. We show that the gap can be of either d-d or charge-transfer character depending on the relative size of U and Δ and that the gap can go to zero even if U is large. The model described solves all of the qualitative problems mentioned above.

A frequently used approximation for the insulating transition-metal compounds is to treat a central cation plus its nearest-neighbor anions as a cluster with as *Ansatz* the purely ionic configuration.[2,11] Hybridization and covalency as well as the d-d Coulomb interactions are then taken into account by a configuration-interaction approach considering configurations of the type d^n, $d^{n+1}\underline{L}$, $d^{n+2}\underline{L}$, etc. A better approximation is to include the anion valence-band width and to treat the transition metal as an impurity in the same way as the cluster; but now the $\underline{L}$ can delocalize and gets a band-wave-vector label which must be summed over.[12] In the limit of zero bandwidth or if the gap is large our theory converges to the cluster-theory result. An "exact" calculation would include also the translational symmetry of the transition-metal ions; but since the d-band dispersional widths are usually very small (< 0.5 eV even in single-particle calculations[3,13]), we expect that the neglect of this will only cause small errors in calculated band gaps and will not change the physics unless perhaps if the band gaps also turn out to be very small. The theory presented is therefore based on the assumption that a broken translational symmetry calculation is, as far as the transition-metal ions

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are concerned, a good approximation for transition-metal compounds.[14] In this limit the problem reduces to that of an Anderson impurity which we solve using recently developed many-body theory.[15]

The procedure is as follows. We first calculate the ground-state energy (E_G^n) of a transition-metal (d^n) impurity hybridizing with the anion valence band. This involves an n-electron or $(10-n)$-hole calculation, taking into account the d-d Coulomb and exchange interactions. In this way we assure charge neutrality of the system without making assumptions concerning the actual nature of the electrons and holes in the ground state. To find the true ground state this many-body calculation must be done for every irreducible representation of the point group spanned by n d electrons.[16] The full calculation then also yields the full excitation spectrum of the system including the ligand and crystal-field splittings. We then repeat the procedure for the states with one electron removed (ionized states) and obtain again the lowest-energy ionized state (E_I^{n-1}) of the $(n-1)$-electron system and also for the electron-affinity states containing $n+1$ electrons of which the lowest energy is E_A^{n+1}. The conductivity gap is given by the energy required for creation of an excitation in the solid in which the electron and hole are spatially well separated and therefore uncorrelated.[17] In terms of the above this is equivalent to

$$E_{\text{gap}} = E_I^{n-1} + E_A^{n+1} - 2E_G^n. \tag{1}$$

Note that the excitonic states are included in the n-electron calculation.

In Fig. 1 we show the energy-level diagram to demonstrate the principle of the calculations and to define the parameters used.[18] Hybridization together with correlation causes a rather complex picture consisting of bound states and band states for each of the configurations, and so we show only the hybridization shifts of the lowest-energy states which determine the band gap. The rather complicated total eigenvalue spectrum of the $(n-1)$- and the $(n+1)$-particle states, together with the fractional parentages of the ground state, determine the photoemission (UPS) and inverse-photoemission spectra, which have been calculated but will be presented elsewhere.[19]

The parameters of the calculation are the charge-transfer energy (Δ), the d-d Coulomb interaction (U) which includes exchange,[4] the anion valence band which was approximated by a semiellipse with a width (W) equal to 3 eV typical for halides,[13] and the hybridization interaction (T) which was assumed to be k independent ($1 \leq T \leq 2$ for the compounds of interest[2,11,20]). In the calculation, care was taken to include the degeneracies of the various states in the spirit of a $1/N_f$ calculation.[21] We calculated the n-electron or $(10-n)$-hole, the $(n-1)$-electron, and the

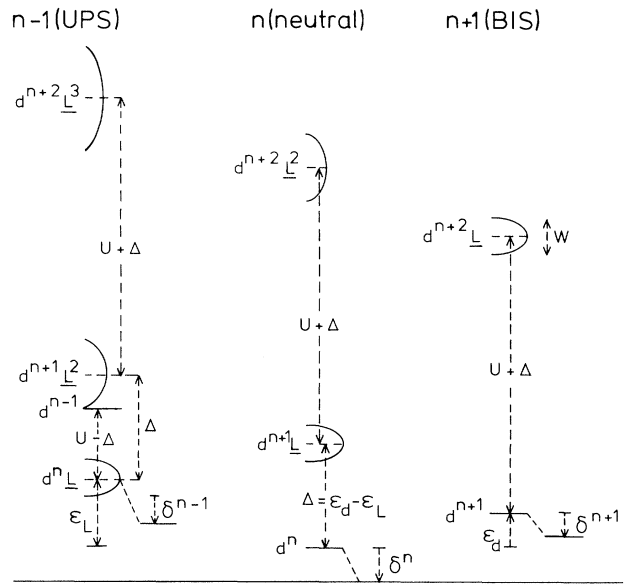

FIG. 1. Diagram showing the various states and parameters used in the theory.

$(n+1)$-electron Green's functions and determined the energy and character of the lowest-energy states.[22]

From Fig. 1 we see that the band gap is given by

$$E_{\text{gap}} = \Delta + 2\delta^n - \delta^{n-1} - \delta^{n+1}, \tag{2}$$

where δ^x are the hybridization shifts which, because of correlation, depend on x. These hybridization shifts, although exactly solvable in the Anderson impurity problem for this model, require solution of rather lengthy transcendental equations which will be described elsewhere.[19] To see how W, T, Δ, and U enter the problem we reproduce an analytical equation for δ^n with $n=8$ as in NiO, which is a good approximation to the exact numerical result:

$$\delta^n = 2\int_{-W/2}^{W/2} \frac{T^2\rho(\epsilon)\,d\epsilon}{\delta^n - \Delta - \epsilon - 2\Gamma(\delta^n - 2\Delta - U - \epsilon)},$$

where $\rho(\epsilon)$ is the ligand hole density of states, $T = \langle d^8|H|d^9\underline{L}\rangle$, and

$$\Gamma(z) = \int_{-W/2}^{W/2} \frac{T^2\rho(\epsilon)\,d\epsilon'}{z-\epsilon'}.$$

This and similar relations for δ^{n-1} and δ^{n+1} can be obtained by procedures described by Gunnarson and Schonhammer.[15] We note that Fig. 1 is drawn for $U > \Delta$. For $U < \Delta$ the lowest-energy state of the $(n-1)$-electron system would be d^{n-1} rather than $d^n\underline{L}$, so that Δ should be replaced by U in Eq. (2), from which we can already see that different band-gap characters are expected for $U > \Delta$ and $U < \Delta$.

We have done the above calculations for $n=9$, 8, 7, 1, 2, and 3 corresponding to Cu^{2+}, Ni^{2+}, Co^{2+},

Ti^{3+}, V^{3+}, and Cr^{3+}, respectively. Although the details depend weakly on n the general trend and basic physics is independent of n.

In Fig. 2 we show the calculated band gap as a function of Δ for various values of U. The actual calculation is for $n=8$ corresponding to Ni^{2+} as in NiO, NiS, and Ni dihalides. We see that for $U<\Delta$ (right-hand side) the band gap is proportional to U and we are in a Mott-Hubbard region. On the other hand, for $U>\Delta$ (converging lines) the gap is proportional to Δ and is of a charge-transfer nature. Also we see that for $U=0$, or equivalently if correlation and exchange is treated as an effective *one*-particle potential as in band theory,[3] $E_{gap}=0$ for all Δ and the system is metallic. Also for U large but $\Delta < W/2$ we obtain a metallic ground state.

In Fig. 3 we have summarized the above in a kind of phase diagram. The heavy solid line is where the band gap is $0.5T$. To the left and below this line the translation symmetry of the cations which we neglected will be important and if so the system may be metallic.[23] The dashed line is where $E_{gap}=0$ in our calculation.

We now discuss briefly the various regions marked in Fig. 3.

(A) *Mott-Hubbard insulators:* $E_{gap} \propto U$; both holes and electrons move in d bands and are heavy. Examples are V_2O_3, Ti_2O_3, Cr_2O_3 and their halides.

(B) *Charge-transfer semiconductors:* $E_{gap} \propto \Delta$ (and proportional to the electronegativity of the anion); holes are light (anion valence band) and electrons are heavy (d bands). Examples are $CuCl_2$, $CuBr_2$, CuO, $NiCl_2$, $NiBr_2$, and NiI_2.

(AB) *Intermediate region* bounded by two curves which show the appearance of bound states determining the lowest-energy $(n-1)$-electron states. Holes of intermediate mass, heavy electrons. Examples are NiO, NiF_2, CuF_2.

(C) *d-band metals:* Both holes and electrons are heavy. Examples are the high-temperature phases of V_2O_3, Ti_2O_3, TiO, and CrO_2.

(D) *"p"-type metals:* Holes in the anion valence band (light holes). Examples are CuS, CuSe, and NiSe. The pyrites (NiS_2, etc.) would belong to this class but the holes in the anion valence bands are accommodated in antibonding orbitals of sulfur pairs, forming a band gap.[24] Also CuI_2, if it existed, would belong here but apparently the material would rather form CuI and I than have holes in the iodine $5p$ band.[11]

(CD+C'D) *Intermediate region* in which there are strong fluctuations between the states d^n, $d^{n+1}\underline{L}$, $d^n\underline{L}$, and d^{n+1} since all have considerable weight close to the Fermi level. For U large this could describe NiS and for U small it describes semimetallic TiS_2 and $TiSe_2$. In the region C'D the calculated gap is unphysically negative although small ($<0.1T$). The negative sign may indicate that a nonuniform ground-state charge distribution has a lower energy than the assumed uniform charge density although, as remarked above, the neglect of transition-metal translational symmetry makes the theory questionable in this region.

In conclusion, we have presented a theory which describes a large variety of transition-metal compounds. We have shown that a large d-d Coulomb interaction is necessary but not sufficient to obtain a large band gap. We have also indicated why the replacement of exchange and correlation effects by an effective one-particle potential leads to anomalously small gaps or even metallic systems.

We have shown that for $U>\Delta$, as expected for the heavier transition metals, the gap is of charge-transfer

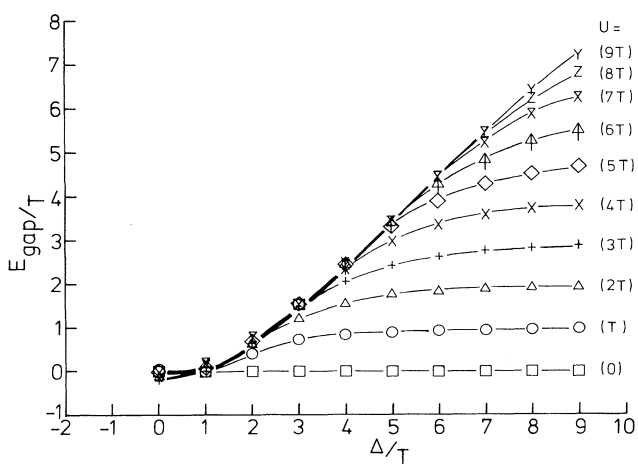

FIG. 2. The calculated band gap as a function of Δ for various values of U all in units of T. For the materials considered 1.0 eV $< T <$ 1.5 eV and $W=3T$.

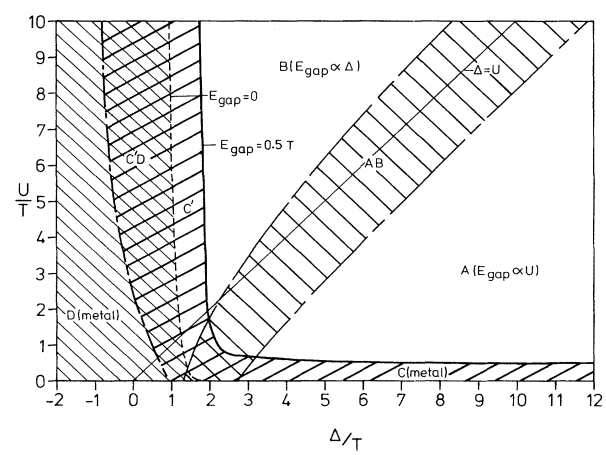

FIG. 3. A phase diagram exhibiting the various regions discussed in the text. The heavy solid line is the semiconductor-metal separation line.

type while for $U < \Delta$, as for the light-transition metals, the gap is of a d-d type. Since the electronegativity differences between cation and anion determine the charge-transfer energy, the band gap for large U is roughly proportional to the electronegativity of the anion. So it is quite natural to expect the gap to close for the sulfides of Ni and Cu even though the d-d Coulomb interactions remain large. In the limit of large band gaps ($E_{\text{gap}} > W/2$) our theory converges to the cluster-theory results.[2]

In future papers we will present the details of the theory and use it to describe the various forms of spectroscopy of transition-metal compounds. These experiments can be used to determine the parameters of the theory.

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[16]For each irreducible representation we obtain the lowest-energy state and the excitation spectrum. The full excitation spectrum then includes excitations between the ground-state irreducible representation and other states of the same or other irreducible representation.

[17]Compared to the excitation spectrum calculated by density functional theory an additional energy is therefore required to separate the electron from its exchange-correlation hole as present in the ground state.

[18]Note that this diagram represents the states used for only *one* of the many irreducible representations for each of the three problems.

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