Table IV. Comparison between the Calculated J_{AF} and the Experimental J Values of MCl_3^- Chains[a]

chain	J_{AF}(calcd) Charlot et al.[b]	J_{AF}(calcd) present work	J(exptl)
$CsVCl_3$	−64.0	−130	−160[c]
$N(CH_3)_4MnCl_3$	−13.1	−56	−8.7[d]
$CsNiCl_3$	−36.6	−84	−18.1,[e] −15.3,[f] −19.7[g]

[a] All the numbers are in cm^{-1} units. [b] Reference 11. [c] Reference 3e. [d] Reference 3g. [e] Reference 3o. [f] Reference 3p. [g] Reference 3q.

the sum of the ferromagnetic contribution J_F and the antiferromagnetic contribution J_{AF}, with expression 19a for J_{AF}

$$J_{AF} = -(1/n^2)\sum_{\mu=1}^{n} W_\mu S_{\mu\mu} \tag{19a}$$

where n is the number of unpaired d electrons in a metal ion, $S_{\mu\mu}$ is the overlap between two magnetic orbitals χ_μ centered on the nearest-neighbor ions, and W_μ is the width of the band built from χ_μ. In the present work, μ corresponds to a band all the levels of which are singly occupied, i.e., μ = 1a, 1e, or 2e. According to Charlot, Girerd, and Kahn[11] and eq 6, $S_{\mu\mu}$ may be approximated by eq 19b where ϵ_μ is the mean band

$$S_{\mu\mu} \simeq -W_\mu/[4(K-1)\epsilon_\mu] \tag{19b}$$

energy per unit cell of the band μ, and $K = 1.75$ (the constant in the Wolfsberg–Helmholz approximation).[9,11] From eq 19a,b

$$J_{AF} \simeq (1/n^2)\sum_{\mu=1}^{n} (W_\mu^2/3\epsilon_\mu) \tag{20}$$

Due to the approximation for the overlap introduced in eq 19b, J_{AF} is made origin-dependent (i.e., dependent on ϵ_μ) in eq 20. This is conceptually unsatisfactory but reasonable within the framework of the extended Hückel method.

Table IV lists the calculated J_{AF} values using eq 20, those of Charlot, Girerd, and Kahn[11] obtained from their calculations of $\{Cl_3(MCl_3)_m\}^{(m+3)-}$ (m = 1–6), and the experimental J values. The magnitudes of the present J_{AF} values are somewhat greater than those of Charlot, Girerd, and Kahn, but both sets exhibit the same trend that the magnitudes of the J_{AF} values vary as $VCl_3^- > NiCl_3^- > MnCl_3^-$. A proper treatment of J_F values, which may not be constant if not negligible, remains to be a problem.[11]

Summary and Concluding Remarks

A number of ternary sulfides and chlorides are made up of face-sharing octahedral MX_3^{n-} chains. The electrical and magnetic properties of some ternary compounds were discussed on the basis of the one-electron band structures of their MX_3^{n-} chains. The metallic and magnetic insulating states of the MX_3^{n-} chains were constructed from their d-block bands with appropriate assignment of band orbital occupancies, and the relative stabilities of these states were analyzed taking electron–electron repulsion into consideration. This analysis led to rough estimates for the lower bounds of the on-site repulsions of MX_3^{n-} chains. The antiferromagnetic contributions to the magnetic exchange parameters J were also examined for the MCl_3^- chains based upon the magnetic insulating states of their d-block bands. Our study suggests that one-electron band structures can be of use for the qualitative discussion of magnetic insulating states once the effect of electron–electron repulsion on band orbital occupancy is properly accounted for.

Acknowledgment. The work at North Carolina State University was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Faculty Research and Professional Development Fund through Grant TF-09223. The work at Cornell was generously supported by the National Science Foundation through Grant CHE 76-06099. M.-H.W. is grateful to Professors T. C. Caves and M. A. Klenin for helpful comments during the initial development of this paper, to Triangle Universities Computer Center for generous computer time, and most deeply to Dr. Baird H. Brandow for his critical and invaluable comments on the previous and present versions of this paper. The authors wish to thank Professor Galen D. Stucky for private communication of results prior to publication.

Registry No. $BaVS_3$, 12430-74-9; $CsVCl_3$, 20959-74-4; $N(CH_3)_4MnCl_3$, 18616-15-4; $CsNiCl_3$, 15455-69-3.

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Effect of Electron–Electron Repulsion on the Band Orbital Occupancy of a Partially Filled Degenerate Band

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Within the framework of Hartree–Fock band theory, the relative stabilities of the metallic and magnetic insulating states of a partially filled degenerate band were examined in terms of bandwidths, mean band energies per unit cell, and on-site repulsions. The insulating nature of magnetic insulators was rationalized in terms of unusual band orbital occupancy brought about by electron–electron repulsion when bandwidth is small.

In one-electron band theory the total energy per unit cell is simply given by the sum of all the occupied band orbital energies, thereby leading to the prediction that a crystalline material with partially filled band is a metal, while that with completely filled band is an insulator. A metal is converted into an insulator by unit cell doubling mechanisms such as spatial distortion of the lattice (i.e., Peierls distortion)[1] and introduction of an antiferromagnetic sublattice (i.e., Slater antiferromagnetism).[2] A crucial factor causing the Slater

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[1] R. E. Peierls, "Quantum Theory of Solids", Oxford University Press, London, 1955, pp 108–12.

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antiferromagnetism is electron–electron repulsion,[3a] which is generally responsible for a class of materials with partially filled bands to have insulating properties.[3] Typical examples are magnetic (Mott)[4] insulators which, upon increasing temperature, do not become metals but undergo a disordering of local magnetic moments.

One-electron band theory neglects electron–electron repulsion and assumes the existence of long-range spin order in crystalline materials. Consequently, magnetic insulators are not properly described by one-electron band theory. A number of theoretical studies[3] have dealt with the role of electron–electron repulsion in magnetic insulators and the question how to justify the existence of a Heisenberg-like spin Hamiltonian commonly used for the proper treatment of their spin dynamics. In the local moment Hartree–Fock theory[3a] the conceptual basis for the Hartree–Fock description of magnetic insulators is provided by Ising–HF configurations built upon spin-order dependent Wannier orbitals, and the main features of magnetic insulating states are explained by unusual solutions of the usual Hartree–Fock approximations.

Recently, the effect of electron–electron repulsion on band orbital occupancy was studied[5] for a half-filled nondegenerate band by using the Hartree–Fock band theory.[6] An insulating state of a half-filled nondegenerate band occurs when all the band levels are singly occupied. This kind of magnetic insulating state is unusual from the viewpoint of one-electron band theory, but minimizes electron–electron repulsion by virtue of avoiding double occupancy of band orbitals. Of course, such a band theory[5] does not explain either antiferromagnetism or spin disorder of magnetic insulators but provides a stability condition for the magnetic (strictly speaking, ferromagnetic) insulating state that is consistent with the conclusion derived from the many-body theoretical treatment.[3b]

In the present work the relative stabilities of metallic and magnetic insulating states of partially filled degenerate bands will be examined by using the Hartree–Fock band theory, so as to derive simple stability conditions for magnetic insulating states that are suitable for the qualitative rationalization of magnetic insulators based upon their one-electron band structures. Qualitative description of magnetic insulators by the band theory may be justified if the ferromagnetic insulating states predicted from it are fair approximations for the appropriate Ising–HF configurations of the local moment Hartree–Fock theory, which appears reasonable since a spin-order dependent Wannier orbital retains the one-site localized nature despite orbital rearrangement resulting from its local spin environment.[3a]

Theoretical Considerations

For the purpose of simplicity, we will consider a crystalline chain of repeat distance a. The band orbitals $\phi_{\mathrm{n}k}$, for bands n at wave vectors k, of such a chain are assumed to be the eigenfunctions of H (i.e., the operator for the kinetic plus the nuclear–electron attraction energies)[6a] with the band orbital energies $\epsilon_{\mathrm{n}k}$ (see eq 1). Further the band orbital energies $\epsilon_{\mathrm{n}k}$

$$\epsilon_{\mathrm{n}k} = \langle \phi_{\mathrm{n}k} | H | \phi_{\mathrm{n}k} \rangle \tag{1}$$

are assumed to behave as a tight-binding band, where ϵ_{n} is the mean band energy per unit cell and W_{n} is the bandwidth (see eq 2). For such a tight-binding band, the ratio of the available

$$\epsilon_{\mathrm{n}k} = \epsilon_{\mathrm{n}} - (W_{\mathrm{n}}/2) \cos (ak) \quad (-\pi/a \le k \le \pi/a) \tag{2}$$

band levels in a region $-k_1 \le k \le k_1$ to that of the total band levels in the first Brillouin zone $-K \le k \le K$ ($K = \pi/a$) is given by k_1/K.

In the Hartree–Fock band theory, the total electronic energy per unit cell is the sum of all the occupied band orbital energies plus that of all the Coulomb and exchange repulsions between the occupied band orbitals. As the total number of unit cells N of a chain increases, summations over k are replaced by integrations over k.[7]

$$\sum_{k} \rightarrow (N/2K) \int \mathrm{d}k \tag{3}$$

From eq 2 and 3

$$\sum_{-k_{\mathrm{n}} \le k \le k_{\mathrm{n}}} \epsilon_{\mathrm{n}k} = (N/2K) \int_{-k_{\mathrm{n}}}^{k_{\mathrm{n}}} \epsilon_{\mathrm{n}k} \, \mathrm{d}k = N[f_{\mathrm{n}}\epsilon_{\mathrm{n}} - (\sin (f_{\mathrm{n}}\pi)/2\pi) W_{\mathrm{n}}] \tag{4}$$

where f_{n} is the fractional occupancy of the band n, namely, $f_{\mathrm{n}} = k_{\mathrm{n}}/K$.

The band orbitals $\phi_{\mathrm{n}k}$ can be expressed in terms of the Wannier orbitals (orthogonal localized orbitals) $\psi_{\mathrm{n}j}$;[8] see eq 5, where $R_j = ja$ and $\psi_{\mathrm{n}j} = \psi_{\mathrm{n}}(r - R_j)$, i.e., the Wannier orbital

$$\phi_{\mathrm{n}k} = (1/\sqrt{N}) \sum_{j} [(\exp(ikR_j))\psi_{\mathrm{n}j}] \tag{5}$$

of the band n located in the unit cell j. With use of eq 5, summations of the Coulomb repulsions $J_{\mathrm{n}k\mathrm{n}'k'}$ and the exchange repulsions $K_{\mathrm{n}k\mathrm{n}'k'}$ (between the band orbitals $\phi_{\mathrm{n}k}$ and $\phi_{\mathrm{n}'k'}$) may be approximated by neglecting all but the on-site repulsions.[3a–c] Thus

$$\sum_{-k_{\mathrm{n}} \le k \le k_{\mathrm{n}}} \; \sum_{-k_{\mathrm{n}'} \le k' \le k_{\mathrm{n}'}} J_{\mathrm{n}k\mathrm{n}'k'} = (N/2K)^2 \int_{-k_{\mathrm{n}}}^{k_{\mathrm{n}}} \mathrm{d}k \int_{-k_{\mathrm{n}'}}^{k_{\mathrm{n}'}} \mathrm{d}k' (\phi_{\mathrm{n}k}\phi_{\mathrm{n}k} | \phi_{\mathrm{n}'k'}\phi_{\mathrm{n}'k'}) = N f_{\mathrm{n}} f_{\mathrm{n}'} (\psi_{\mathrm{n}j}\psi_{\mathrm{n}j} | \psi_{\mathrm{n}'j}\psi_{\mathrm{n}'j}) = N f_{\mathrm{n}} f_{\mathrm{n}'} U_{\mathrm{nn}'} \tag{6a}$$

and

$$\sum_{-k_{\mathrm{n}} \le k \le k_{\mathrm{n}}} \; \sum_{-k_{\mathrm{n}'} \le k' \le k_{\mathrm{n}'}} K_{\mathrm{n}k\mathrm{n}'k'} = (N/2K)^2 \int_{-k_{\mathrm{n}}}^{k_{\mathrm{n}}} \mathrm{d}k \int_{-k_{\mathrm{n}'}}^{k_{\mathrm{n}'}} \mathrm{d}k' (\phi_{\mathrm{n}k}\phi_{\mathrm{n}'k'} | \phi_{\mathrm{n}k}\phi_{\mathrm{n}'k'}) = N f_{\mathrm{n}} f_{\mathrm{n}'} (\psi_{\mathrm{n}j}\psi_{\mathrm{n}'j} | \psi_{\mathrm{n}j}\psi_{\mathrm{n}'j}) = N f_{\mathrm{n}} f_{\mathrm{n}'} J_{\mathrm{nn}'} \tag{6b}$$

Following the work of Kanamori[3c] and Brandow,[3a] the on-site repulsions $U_{\mathrm{nn}'}$ and $J_{\mathrm{nn}'}$ may be approximated by eq 7.

$$\begin{aligned} U_{\mathrm{nn}} &= J_{\mathrm{nn}} = U \\ U_{\mathrm{nn}'} &= U', \quad \text{if n} \neq \text{n}' \\ J_{\mathrm{nn}'} &= J, \quad \text{if n} \neq \text{n}' \end{aligned} \tag{7}$$

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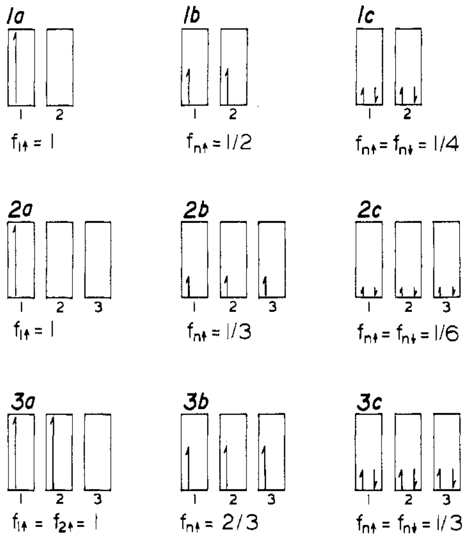


Figure 1. Schematic band representations of metallic and magnetic insulating states of partially filled degenerate bands.

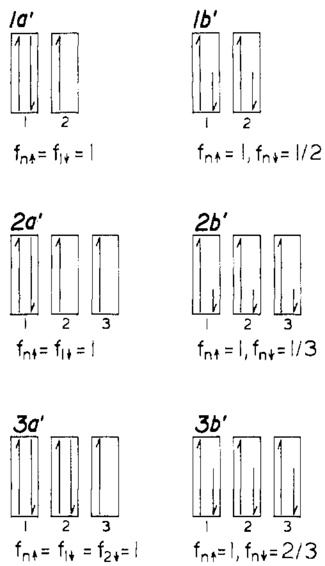


Figure 2. Schematic band representations of metallic and magnetic insulating states of partially filled degenerate bands.

Electron–Electron Repulsion and Band Orbital Occupancy

A. Insulating States and On-Site Repulsions. Figure 1 illustrates some metallic and insulating states of a partially filled degenerate band with mean band energy per unit cell ϵ and bandwidth W. Here **1a**, **2a**, and **3a** are magnetic insulating states, and **1c**, **2c**, and **3c** are nonmagnetic metallic states expected from one-electron band theory. The meaning of the metallic states **1b**, **2b**, and **3b** will become clear in our later discussion. The relative stabilities of these states may now be compared to examine the condition for the insulating states to be the most stable states in each case. Let us consider that there exists m electrons per unit cell to fill the degenerate band of degeneracy n ($m < n$) with mean band energy per unit cell ϵ and bandwidth W. The various states of Figure 1 belong to one of the cases in eq 8. With use of eq 4, 6, and 7, the

$$\begin{aligned}
&\mathbf{a}\text{:}\quad f_1\!\uparrow = f_2\!\uparrow = \ldots = f_m\!\uparrow = 1\\
&\mathbf{b}\text{:}\quad f_1\!\uparrow = f_2\!\uparrow = \ldots = f_n\!\uparrow = m/n \qquad (8)\\
&\mathbf{c}\text{:}\quad f_1\!\uparrow = \mathrm{f}_2\!\uparrow = \ldots = f_n\!\uparrow = m/2n\\
&\qquad f_1\!\downarrow = \mathrm{f}_2\!\downarrow = \ldots = f_n\!\downarrow = m/2n
\end{aligned}$$

total electronic energies per unit cell of the above states are written as in eq 9. Therefore the relative stabilities of the

$$\begin{aligned}
E(\mathbf{a}) &= m\epsilon + [m(m-1)/2](U'-J)\\
E(\mathbf{b}) &= m\epsilon - (n/2\pi)[\sin(m\pi/n)]W + (m/n)^2[n(n-1)/2](U'-J) \qquad (9)\\
E(\mathbf{c}) &= m\epsilon - (n/\pi)[\sin(m\pi/2n)]W + (\mathrm{m}/2n)^2[nU + 2n(n-1)U' - n(n-1)J]
\end{aligned}$$

various states of Figure 1 can be summarized as in eq 10.

$$\begin{aligned}
E(\mathbf{1a}) - E(\mathbf{1b}) &= W/\pi - (U'-J)/4\\
E(\mathbf{1a}) - E(\mathbf{1c}) &= \sqrt{2}W/\pi - (U + 2U' - J)/8
\end{aligned} \qquad (10\mathrm{a})$$

$$\begin{aligned}
E(\mathbf{2a}) - E(\mathbf{2b}) &= 3\sqrt{3}W/4\pi - (U'-J)/3\\
E(\mathbf{2a}) - E(\mathbf{2c}) &= 3W/2\pi - (U + 4U' - 2J)/12
\end{aligned} \qquad (10\mathrm{b})$$

$$\begin{aligned}
E(\mathbf{3a}) - E(\mathbf{3b}) &= 3\sqrt{3}W/4\pi - (U'-J)/3\\
E(\mathbf{3a}) - E(\mathbf{3c}) &= 3\sqrt{3}W/2\pi - (U + U' + J)/3
\end{aligned} \qquad (10\mathrm{c})$$

It turns out to be a difficult task to estimate the magnitudes of U, U', and J. For the magnetic insulator NiO, it has been estimated that $U \simeq 10$, $U' \simeq 8.4$, and $J \simeq 0.8$ eV.[3a] On the basis of this result, it may be assumed that

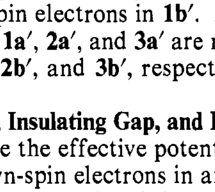
$$U' \simeq 0.84U \qquad J \simeq 0.08U \qquad (11)$$

in order to reduce our analysis from a three-parameter (U, U', and J) to a one-parameter (U) problem. From eq 10 and 11, it is found that the insulating states **1a**, **2a**, and **3a** are the most stable states of **1**, **2**, and **3**, respectively, when $W < {\sim}0.6U$.

Figure 2 shows the insulating and metallic states derived from the partially filled degenerate bands of Figure 1 when n more electrons are added. It can be easily shown that

$$\begin{aligned}
E(\mathbf{1a'}) - E(\mathbf{1b'}) &= E(\mathbf{1a}) - E(\mathbf{1b})\\
E(\mathbf{2a'}) - E(\mathbf{2b'}) &= E(\mathbf{2a}) - E(\mathbf{2b}) \qquad (12)\\
E(\mathbf{3a'}) - E(\mathbf{3b'}) &= E(\mathbf{3a}) - E(\mathbf{3b})
\end{aligned}$$

The metallic states **1b′**, **2b′**, and **3b′** simulate those expected from a spin-polarized local $\rho^{1/3}$ exchange approximation.[3a] For example, **1b′** is equivalent to the split band representation **1b″** shown below, where Δ_x refers to the exchange splitting. In



1b″

the present approximation $\Delta_x = (U + J)/2$, which is obtained, as will be discussed in the next section, by calculating the effective potentials per electron per unit cell exerted on the up-spin and down-spin electrons in **1b′**. According to eq 12, the insulating states **1a′**, **2a′**, and **3a′** are more stable than the metallic states **1b′**, **2b′**, and **3b′**, respectively, again if $W < {\sim}0.6U$.

B. Band Splitting, Insulating Gap, and Exciton. The on-site repulsions and hence the effective potentials experienced by the up-spin and down-spin electrons in an insulating state of a partially filled degenerate band depend upon the number of up-spin and down-spin electrons and also upon the presence of doubly and singly filled bands. This leads to band splitting, as examined in detail for MnO, CoO, and NiO by Brandow.[3a] As an example, the band splitting expected from **2a′** may now be considered. With use of the symbols d↑ and d↓ (s↑ and s↓) for the up-spin and down-spin electrons of the doubly (singly) occupied band, respectively, the effective potentials exerted

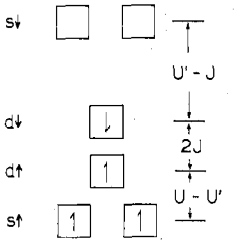


Figure 3. A split band representation of the magnetic insulating state **2a′**.

on the up-spin and down-spin electrons of **2a′** may be written as in eq 13a. If an extra electron were to be added into one

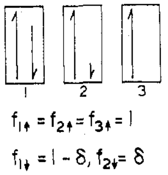
$$\begin{aligned} d\uparrow(\mathbf{2a'})&: \quad \epsilon + U + 2U' - 2J \\ d\downarrow(\mathbf{2a'})&: \quad \epsilon + U + 2U' \qquad (13a) \\ s\uparrow(\mathbf{2a'})&: \quad \epsilon + 3U' - 2J \end{aligned}$$

of the singly occupied bands of **2a′** this electron would feel the effective potential as shown in eq 13b. Thus the partially filled

$$s\downarrow(\mathbf{2a'}): \quad \epsilon + U + 3U' - J \qquad (13b)$$

degenerate band **2a′** will split as shown in Figure 3, which has the meaning of effective one-electron density of states (more precisely, the partial density of states for the Wannier orbitals located in a unit cell).[3a]

The energy separation, $(U' - J - W)$, between the top of the d↓ band and the bottom of the s↓ band in Figure 3 is the insulating gap of **2a′** (i.e., the excitation energy required to produce a current-carrying state from **2a′**). In the Hartree–Fock theory, the unoccupied orbitals of an m-electron system reflect the potential created by m rather than $m - 1$ electrons,[9] and thus the position of the vacant s↓ band determined by eq 13b may be understood. However, it is of interest to obtain the insulating gap without introducing an extra electron. **2a″**



2a″

shows a metallic state resulting from the insulating state **2a′** by a slight change in the band orbital occupancy, where the magnitude of the change is measured by δ. The energy required per electron per unit cell for the insulator-to-metal transition **2a′** → **2a″** is

$$[E(\mathbf{2a''}) - E(\mathbf{2a'})]/\delta = (1 - \delta)(U' - J) - [\sin(\delta\pi)/\delta\pi]W = U' - J - W \quad (\text{as } \delta \to 0) \quad (14)$$

This is in agreement with the insulating gap obtained from eq 13 and Figure 3.

Our final topic of the present section is concerned with a band picture of crystal field excitons in magnetic insulators, which may be examined by considering hypothetical insulating states shown in Figure 4. The insulating state **4a** consists of the two bands 1 and 2 whose mean band energies per unit cell (bandwidths) are ϵ_1 and ϵ_2 (W_1 and W_2), respectively. When the down-spin electron of **4a** is promoted from the band 1 to the band 2 to produce another insulating state **4b**, the excitation energy is simply given by Δ ($=\epsilon_2 - \epsilon_1$) since the total on-site repulsions of **4a** and **4b** are the same. If the split band representation of **4a** (i.e., **4a′**) were to be used for the description of the above excitation, the excitation energy would be explained by the energy separation between the d↓ and s↓ bands, $(U' - J + \Delta)$, minus the particle-hole on-site interaction, $(U' - J)$.[3a] In any event, if $(U' - J)$ is large compared with $(W_1 + W_2)/2$, the excitation energy for **4a** → **4b** lies within the insulating gap, $[U' - J + \Delta - (W_1 + W_2)/2]$.

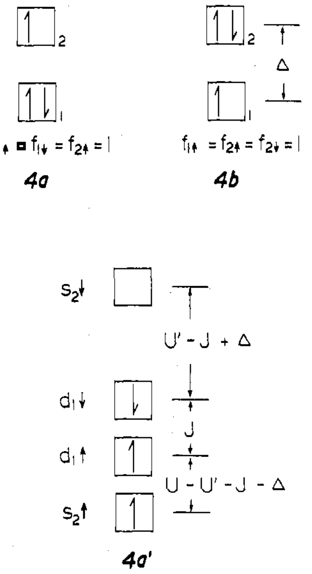


Figure 4. A schematic band representation of crystal field exciton. In **4a′**, it was assumed that $U > U' + J + \Delta$.

Discussion and Concluding Remarks

In essence the present work is a variation of the Stoner theory of band magnetism[6a] so that the magnetic insulating states predicted from this theory are ferromagnetic. Under the assumption that such insulating states are reasonable approximations for the appropriate Ising–HF configurations,[3a] the present band description of magnetic insulating states may be justified. In the present work electrons in magnetic insulating states have bandwidth by the very nature of the band theory, and the insulating feature of magnetic insulators is rationalized in terms of unusual band orbital occupancy brought about by electron–electron repulsion when bandwidth is small compared with on-site repulsion. Practically, these aspects are consistent with the results of the local moment Hartree–Fock theory.[3a]

An advantage of the present Hartree–Fock band description is that the relative stabilities of metallic and magnetic insulating states of a band can be readily estimated in terms of bandwidths and on-site repulsions. Orbitals obtained from SCF and one-electron methods exhibit qualitatively similar behavior in their crucial aspects,[10] i.e., relative orbital orderings and their variations with geometry distortion. Thus the band structures determined from one-electron band theory may be employed for the description of magnetic insulators with appropriate band orbital occupancy or conversely for the estimate of on-site repulsion with appropriate stability condition. These topics will be discussed in our subsequent paper.

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