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Band Structures of Face-Sharing Octahedral MX_3^{n-} Chains

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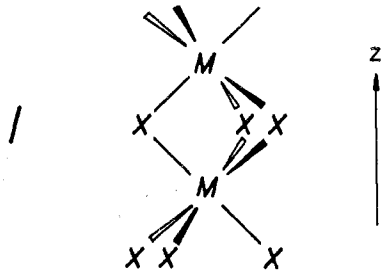
A number of ternary sulfides and chlorides of transition-metal ions consist of face-sharing octahedral MX_3^{n-} chains. The electrical and magnetic properties of some ternary compounds were examined employing the one-electron band structures of their MX_3^{n-} chains. The relative stabilities of the metallic and magnetic insulating states that arise from the d-block bands of the MX_3^{n-} chains were analyzed by taking electron–electron repulsion into consideration, and rough estimates for the lower bounds of the on-site repulsions of MX_3^{n-} chains were obtained. The antiferromagnetic contributions to the magnetic exchange parameters J of the MCl_3^- chains were also evaluated on the basis of the magnetic insulating states of their d-block bands.

A number of ternary sulfides[2] and chlorides[3] of transition-metal ions consist of face-sharing octahedral chains of the structural formula MX_3^{n-} (M = transition-metal element; X = S, Cl), **1**. It has been an important structural problem to determine whether or not and to what extent MX_3^{n-} chains deviate from an ideal face-sharing octahedral chain.[4] These materials are easily made nonstoichiometric and easily substituted with ions of varying size and charge,[2c-g,5] so that the associated structural disorder problems make it difficult to interpret the experimental data. Ternary sulfides of the stoichiometry $BaMS_3$ (M = Ti, V, Ta) contain MS_3^{2-} chains of formal M^{4+} ions, and ternary chlorides of the stoichiometry $AMCl_3$ (M = V, Cr, Mn, Fe, Co, Ni, Cu; A = Cs, Rb, N-$(CH_3)_4$) contain MCl_3^- chains of formal M^{2+} ions. In contrast to their structural similarity, these sulfides and halides exhibit rather different physical properties. For example, the sulfides are either metals or semiconductors at room temperature, while the chlorides are magnetic insulators. Such a difference in the physical properties is caused by a number of factors related to the overlap between the metal and ligand ion orbitals.[6a] Small overlap between them makes the resulting band narrow and the electron–electron repulsion on a metal ion (i.e., the on-site repulsion) poorly screened. A material with a partially filled band becomes a magnetic insulator rather than a nonmagnetic metal if the bandwidth is narrow compared with the on-site repulsion.[6,7]



Under the assumption that the physical properties of stoichiometric ternary compounds are primarily governed by the electronic structures of a single MX_3^{n-} chain, the electrical and magnetic properties of some ternary sulfides and chlorides are examined in the present work in terms of the one-electron band structures of the MS_3^{2-} and MCl_3^- chains, respectively. The major concern of our work is the relative stability of the metallic and magnetic insulating states arising from the partially filled d-block bands of the MX_3^{n-} chains. In our previous work[7] the role of electron–electron repulsion was analyzed from the viewpoint of band orbital occupancy, and a magnetic insulating state was identified as a band electronic configuration that has all the levels of one or several bands singly occupied. This simple band description is justified under the assumption that the magnetic (strictly speaking, ferromagnetic) insulating state predicted from band theory is a reasonable approximation for the appropriate Ising–HF configuration of the local moment Hartree–Fock theory.[6a] In the

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Table I. Atomic Parameters[a,b]

μ	ζ_μ	ζ_μ'	$H_{\mu\mu}$, eV
Ti 4s	1.075		−8.9
Ti 4p	0.675		−6.5
Ti 3d	4.55 (0.4206)	1.40 (0.7839)	−11.1
V 4s	1.30		−8.8
V 4p	0.90		−5.8
V 3d	4.75 (0.4755)	1.70 (0.7052)	−11.1
Mn 4s	1.80		−9.8
Mn 4p	1.80		−5.9
Mn 3d	5.15 (0.5311)	1.90 (0.6479)	−11.7
Ni 4s	2.10		−11.0
Ni 4p	2.10		−6.3
Ni 3d	5.75 (0.5733)	2.30 (0.5827)	−14.2
S 3s	1.817		−20.0
S 3p	1.817		−13.3
Cl 3s	2.033		−30.0
Cl 3p	2.033		−15.0

[a] The d orbitals are given as a linear combination of two Slater type functions, and each is followed in parentheses by the weighting coefficient.[12a,e] [b] A modified Wolfsberg-Helmholz formula was used to calculate $H_{\mu\nu}$.[22]

following we first examine the general features of the d-block bands common to the various MX_3^{n-} chains and, as a result, obtain the tight-binding expressions[8] of these bands. Subsequently, use is made of these expressions to simplify our analysis of the relative stabilities of the metallic and magnetic insulating states resulting from the d-block bands.

Band Structures

In this section the shapes and orbital components of the d-block bands of the MX_3^{n-} chains are examined in some detail so as to find their tight-binding expressions that are appropriate for a single metal ion. In the present work the band structures of the MX_3^{n-} chains were obtained from the tight-binding scheme[9] based upon the extended Hückel method.[10] From a set of atomic orbitals $\{\chi_\mu\}$ of a unit cell, a set of Bloch orbitals $\{b_\mu(k)\}$ is formed as eq 1 where k is the wave vector, $R_j = ja$,

$$b_\mu(k) = N^{-1/2}\sum_j e^{ikR_j}\chi_\mu(r - R_j) \quad (1)$$

and a is the repeat distance of the chain. With the Bloch orbitals, LCAO crystal orbitals $\psi_n(k)$ are expressed as eq 2.

$$\psi_n(k) = \sum_\mu C_{n\mu}(k)b_\mu(k) \quad (2)$$

The orbital energies $\epsilon_n(k)$ and the coefficients $C_{n\mu}(k)$ are obtained from the eigenvalue equation

$$\mathbf{H}(k)\mathbf{C}(k) = \mathbf{S}(k)\mathbf{C}(k)\epsilon(k) \quad (3)$$

where $H_{\mu\nu}(k) = \langle b_\mu(k)|H^{\text{eff}}|b_\nu(k)\rangle$ and $S_{\mu\nu}(k) = \langle b_\mu(k)|b_\nu(k)\rangle$. Band structures are determined by repeating the above calculation at various values of k. The atomic parameters of the extended Hückel calculations are detailed in Table I, and the lattice sums (i.e., the summation over j in eq 1) were carried out to third-nearest neighbors.

A. d-Block Bands. Figure 1 shows the d-block bands of a typical MX_3^{n-} chain that has the twofold screw rotation symmetry and the unit cell $(MX_3^{n-})_2$. The essential features of the d-block bands are identical with those of MCl_3^- chains (M = V, Mn, Ni) reported by Charlot, Girerd, and Kahn[11] who also worked out symmetry analysis of the d-block bands. Specifically, the space group is isomorphic with D_{6h} at the zone

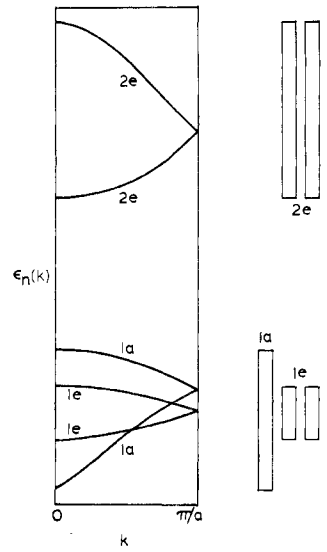

Figure 1. Two schematic representations of the d-block bands of a face-sharing octahedral MX_3^{n-} chain: (a) the variation of the band orbital energy as a function of wave vector (left) and (b) the block diagram (right).

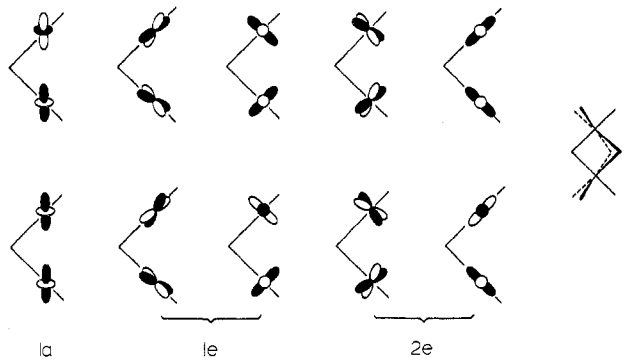

Figure 2. The nodal properties of the d-block bands at the zone center. The lower and upper diagrams refer to the bottom and top of each band, respectively.

center ($k = 0$) but C_{6v} at any other wave vector k other than the zone center and the edge ($k = \pi/a$ or $-\pi/a$). Because of the twofold screw rotation symmetry, all the bands pair up at the zone edge. For simplicity, we may label the d-block bands as 1a, 1e, and 2e, of which the latter two are doubly degenerate as indicated in Figure 1b. Here 1a corresponds to a_1 and a_2, 1e to the lower e_1 and e_2, and 2e to the upper e_1 and e_2 in the notations of Charlot, Girerd, and Kahn.[11]

From the sulfide and chloride chains examined in our work, it is found that the 1a and 1e bands overlap while the 2e band is separated from them. This three-below-two splitting reflects the octahedral site symmetry of MX_3^{n-} chains. The widths of the 1a, 1e, and 2e bands vary depending upon the nature of the metal and ligand atoms, but the 1e band is narrow compared with 1a and 2e bands. It is noted that the 1a and 1e bands, respectively, correspond to the d_σ and d_π bands of MX_3^{n-} chains discussed by Stucky, Schultz, and Williams.[4] Although it is not shown in Figure 1, there is a substantial band gap between the d-block bands and others lying below.

B. Band Orbitals. The d-block bands at the zone center are schematically shown in Figure 2. The ligand orbitals (largely p orbitals of proper symmetry) combine out-of-phase with the d orbitals of Figure 2, but their contributions are small and hence are not shown. The shape and energy ordering of these orbitals are determined by the octahedral site symmetry of the individual metal atom. Superimposed onto this are the interactions offered by the ligands and direct metal–metal

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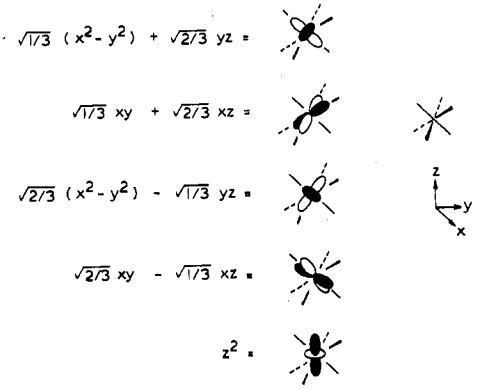
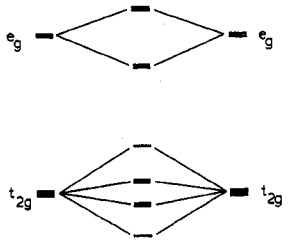
overlap.[12] The most common octahedral coordinate system has the Cartesian axes along three ligands. However, it is not a natural coordinate system for MX_3^{n-} chains, where z axis is most conveniently chosen along the threefold axis as in **1**. The d-block orbitals at a single metal center in this coordinate system are shown in **2**.[13]

2



The unit cell $(MX_3^{n-})_2$ contains two metal atoms and hence ten d-block orbitals. These are essentially the in- and out-of-phase combinations of the five d orbitals of each metal atom, as shown schematically in **3**. The splitting pattern in **3** applies

3



qualitatively to all such complexes, but the details of the pattern and magnitudes of the energy gaps are a sensitive function of the metal and the M–X–M bridging angle.[12e,14] The classic series that illustrates this trend is that of the discrete $M_2X_9^{3-}$ dimers (M = Cr, Co, W), in which the M–X–M angles decrease sharply from Cr to W.[15]

If direct metal–metal interactions are all important, the bottom of any band would be metal–metal bonding and the top metal–metal antibonding. As may be seen from Figure 2, this is so for the 1a band, but just the opposite obtains for the 1e and 2e bands. The effect has been analyzed in detail for a dimer elsewhere[12e]—it is a consequence of an indirect interaction or through-bond coupling.[16] To summarize the argument briefly, symmetry-adapted ligand orbitals interact either with the in-phase or with the out-of-phase metal combinations. Since the in-phase metal combinations turn out to overlap better with those ligand orbitals which lie below, the in-phase metal combinations rise to the top of the band. This effect may be overcome when the direct metal–metal interaction becomes strong either by virtue of a short metal–metal distance or by a proper orbital alignment as in the d_{z^2} orbitals of the 1a band. Thus the width and composition of the d-block bands is a function of the metal and the separation between the metal atoms. The d orbitals of the 1e band in Figure 2 are pointed away from the metal–ligand bond axis and also from the chain axis. These d orbitals are therefore weakly affected either by the ligands or by the direct metal–metal overlap, leading to a narrow bandwidth.

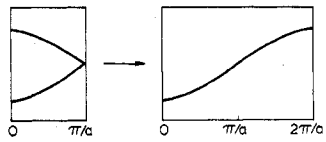
Table II. Band Structures of MX_3^{n-} Chains[a,b]

MX_3^{n-}	ϵ_t	ϵ_e	W_{1a}	W_{1e}	W_{2e}
VS_3^{2-}	−9.95	−5.20	3.24	0.44	5.55
VCl_3^-	−10.57	−7.24	2.13	0.20	4.05
$MnCl_3^-$	−11.50	−9.90	0.71	0.17	1.53
$NiCl_3^-$	−13.99	−12.63	0.41	0.27	0.89

[a] All the numbers are in eV units. [b] The geometrics of the VS_3^{2-}, VCl_3^-, $MnCl_3^-$, and $NiCl_3^-$ chains were taken from ref 2a, 3e, 3g, and 3n, respectively.

C. A Simplified Representation. To examine the effect of electron–electron repulsion on band orbital occupancy,[7] it is convenient to employ orthogonal localized orbitals (i.e., Wannier orbitals).[17] The unit cell $(MX_3^{n-})_2$ has two metal ions and thus ten d-block orbitals. In such a case (in general, for bands having cusps such as those in Figure 1 at the zone edge), the use of the single zone (i.e., $-\pi/a \le k \le \pi/a$) leads to poorly localized orbitals, while the use of the double zone (i.e., $-2\pi/a \le k \le 2\pi/a$) leads to nicely localized orbitals at half the previous spacing.[18] In other words, as far as the localized orbitals are concerned, the effective repeat distance is $a/2$ (or, the effective unit cell is MX_3^{n-}). This is expected since the localized orbitals of the d-block bands for instance should be similar in nature to the d orbitals of each metal ion. Therefore, the d-block bands of MX_3^{n-} chains obtained by using the real unit cell $(MX_3^{n-})_2$ may be interpreted as if they refer to the effective d-block bands for a single metal ion, which is schematically shown in **4** for the 1a band.

4



Consequently each of the 1a, 1e, and 2e bands may be approximated by the tight-binding band of the type

$$\epsilon_n(k) \simeq \epsilon_n - (W_n/2)\cos(bk) \qquad (4)$$

where n refers to 1a, 1e, or 2e, $b = a/2$, W_n is the width of the band n, and ϵ_n is the mean band energy per unit cell (see eq 5). The mean band energies per unit cell of the 1a and

$$\epsilon_n = (b/2\pi)\int_{-\pi/b}^{\pi/b} \epsilon_n(k)\,dk \qquad (5)$$

1e bands, ϵ_{1a} and ϵ_{1e}, are only slightly different from each other, so that it is convenient to choose a common centroid for the two bands by defining the weighted average $\epsilon_t = (\epsilon_{1a} + 2\epsilon_{1e})/3$. Thus the d-block bands can be written as in eq 6 where ϵ_e is

$$\begin{aligned} \epsilon_{1a}(k) &\simeq \epsilon_t - (W_{1a}/2)\cos(bk) \\ \epsilon_{1e}(k) &\simeq \epsilon_t - (W_{1e}/2)\cos(bk) \\ \epsilon_{2e}(k) &\simeq \epsilon_e - (W_{2e}/2)\cos(bk) \end{aligned} \qquad (6)$$

the mean band energy per unit cell of the 2e band. Table II

(12) For an analysis of the factors governing metal–metal interactions in dimers and oligomers, see: (a) R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 7240 (1976); (b) J. W. Lauher, M. Elian, R. H. Summerville and R. Hoffmann, *ibid.*, **98**, 3219 (1976); (c) A. Dedieu and R. Hoffmann, *ibid.*, **100**, 2074 (1978); (d) A. Dedieu, T. A. Albright, and R. Hoffmann, *ibid.*, **101**, 3141 (1979); (e) R. H. Summerville and R. Hoffmann, *ibid.*, **101**, 3821 (1979).

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(14) (a) R. Saillant and R. A. D. Wentworth, *J. Am. Chem. Soc.*, **91**, 2174 (1969); (b) D. V. Korolkov and V. N. Pak, *Zh. Strukt. Khim*, **11**, 834 (1970); (c) D. V. Korolkov and H. Miessner, *Teor. Eksp. Khim.*, **9**, 336 (1973).

(15) For an excellent review of the geometrical questions in these dimers see F. A. Cotton and D. A. Ucko, *Inorg. Chim. Acta*, **6**, 161 (1972).

(16) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971).

(17) (a) J. M. Ziman, "Principles of the Theory of Solids", Cambridge University Press, London, 1964, pp 148–51; (b) J. C. Slater, "Quantum Theory of Molecules and Solids", Vol. 2, McGraw-Hill, New York, 1965, pp 154–8.

(18) M. Lax, "Symmetry Principles in Solid State and Molecular Physics", Wiley, New York, 1974, p 219, and references therein.

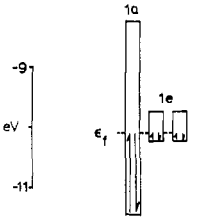

Figure 3. The metallic state of the VS_3^{2-} chain expected from the one-electron band picture.

lists the values of ϵ_t, ϵ_e, W_{1a}, W_{1e}, and W_{2e} for the VS_3^{2-}, VCl_3^-, $MnCl_3^-$, and $NiCl_3^-$ chains. It should be noticed that the number of d electrons to fill the d-block bands is that of a single metal ion in the effective unit cell MX_3^- and that the energy difference ($\epsilon_e - \epsilon_t$) represents the crystal field splitting Δ_{CF} of the d orbitals under the locally octahedral environment.

Electrical and Magnetic Properties

In a rationalization of the electrical and magnetic properties of MX_3^{n-} chains based on their d-block bands, the one-electron band picture leads to conceptual problems since it neglects electron–electron repulsion. In this section electron–electron repulsion is incorporated into our analysis in terms of the on-site repulsions[7] which we treat as phenomenological parameters. The metallic and magnetic insulating states of an MX_3^{n-} chain are constructed with appropriate assignment of the d-block band orbital occupancies, and consideration of their relative stabilities provides rough estimates for the magnitudes of the on-site repulsions. On the basis of the magnetic insulating states of the d-block bands, the antiferromagnetic contributions to the magnetic exchange parameters J[6,11] were calculated for the MCl_3^- (M = V, Mn, Ni) chains as well.

A. Electrical Properties. Let us consider the electrical properties of a few MX_3^- chains from the viewpoint of the one-electron band picture. $BaTiS_3$ is reported to be a semiconductor.[2h] Each TiS_3^{2-} unit of the TiS_3^{2-} chain has a formal Ti^{4+} (d^0) ion, and thus there is no electron to fill its d-block bands. Our calculation shows that the d-block bands of the TiS_3^{2-} chain are separated from the completely filled bands lying below by a band gap of $\sim$1.3 eV, in agreement with the nonmetallic behavior of $BaTiS_3$. Early work on $BaVS_3$ by Gardner, Vlasse, and Wold revealed[2a] that $BaVS_3$ is weakly metallic at room temperature. In the VS_3^{2-} chain each VS_3^{2-} unit contains a formal V^{4+} (d^1) ion so that there exists one electron per VS_3^{2-} to fill its d-block bands, thereby leading to the partially filled bands shown in Figure 3. The presence of such partially filled overlapping bands accounts for the metallic property of $BaVS_3$, but it is quite exceptional that, as a nearly one-dimensional material with one electron per site, $BaVS_3$ is not a Peierls insulator at room temperature.[4,19] A Peierls distortion likely to occur in the VS_3^{2-} chain is the pairing of V^{4+} ions along the chain axis shown in **5**, where δ

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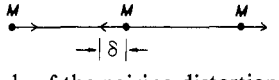

measures the magnitude of the pairing distortion. Each of the d-block bands splits into two bands by the distortion, as is shown in Figure 4 for the 1a and 1e bands. Note that the split bands overlap and hence provide a metallic state for the VS_3^{2-} chain if the pairing is not significant (i.e., when $\delta < \sim 0.09$ Å). Such an aspect was predicted to be crucial for the room-temperature metallic property of $BaVS_3$ by Stucky, Schultz, and Williams.[4]

The one-electron band description presented above appears to be satisfactory but cannot account for the recent experimental results on stoichiometric samples of $BaVS_3$.[2c-g] Upon lowering of the temperature, $BaVS_3$ undergoes a crystallographic transition from hexagonal to orthorhombic near 240 K. This structural transition makes each chain of V^{4+} ions slightly zigzagging but causes no drastic change in the electrical conductivity.[2c,d] A sharp decrease in the electrical conductivity occurs below 70 K, which is however not related to a structural transition such as the pairing distortion **5** but to a Slater antiferromagnetic transition.[2c,d,6a,20] Electron–electron repulsion is an important factor causing the antiferromagnetism[6a] and is generally responsible for magnetic insulators like $AMCl_3$ which, with increasing temperature, do not become metals but undergo a disordering of the local magnetic moments.[6a] Were the d-block bands of the MCl_3^- chains (M = V–Cu; $M^{2+} = d^3$–d^9) filled according to the one-electron band picture, all the MCl_3^- chains except for $FeCl_3^-$ would be incorrectly predicted to be metals. It is well established that consideration of electron–electron repulsion provides the key for understanding magnetic insulating states.[6] In the next section the relative stabilities of the metallic and magnetic insulating states of MX_3^{n-} chains are examined by taking electron–electron repulsion into consideration.

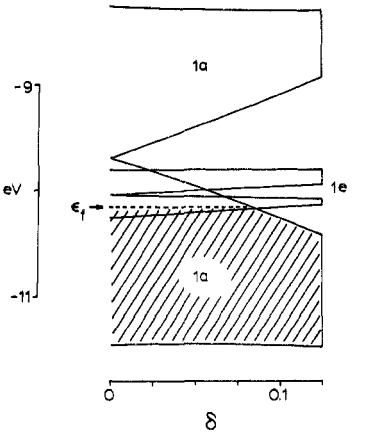

Figure 4. The widths of the two split bands resulting from each of the 1a and 1e bands of the VS_3^{2-} chain as a function of δ (A). The shaded area indicates that every band orbital is doubly occupied.

B. Estimates of On-Site Repulsions. In our previous work the total electronic energy of a band electronic state is given in terms of the mean band energies, bandwidths, and on-site repulsions.[7] The on-site repulsions U, U', and J are defined in eq 7[6a-b] where ψ_{nj} is the Wannier orbital of the band n

$$U = (\psi_{nj}\psi_{nj}|\psi_{nj}\psi_{nj})$$
$$U' = (\psi_{nj}\psi_{nj}|\psi_{n'j}\psi_{n'j}) \quad n \neq n' \tag{7}$$
$$J = (\psi_{nj}\psi_{n'j}|\psi_{nj}\psi_{n'j}) \quad n \neq n'$$

located on a site j. In our work the on-site repulsions are regarded as phenomenologocal parameters. To reduce our later analysis from a three-parameter (U, U', and J) to a one-parameter (U) problem, it is assumed that

$$U' \simeq 0.84U \qquad J \simeq 0.08U \tag{8}$$

which we adopt from the estimates on NiO that $U \simeq 10$, $U' \simeq 8.4$, and $J \simeq 0.8$ eV.[6a,7]

Schematically shown in Figure 5 are the metallic and magnetic insulating states of the VS_3^{2-}, VCl_3^-, $MnCl_3^-$ and $NiCl_3^-$ chains resulting from their partially filled d-block bands. In comparing the relative stabilities of these states, it is convenient to use the tight-binding expressions of the

(19) R. E. Peierls, "Quantum Theory of Solids", Oxford University Press, London, 1955, pp 108–12.

(20) (a) J. C. Slater, *Phys. Rev.*, **82**, 538 (1951); (b) T. Matsubara and T. Yokoda, *Proc. Int. Conf. Theor. Phys.*, 693 (1954); (c) J. des Cloizeaux, *J. Phys. Radium*, **20**, 606, 751 (1959).

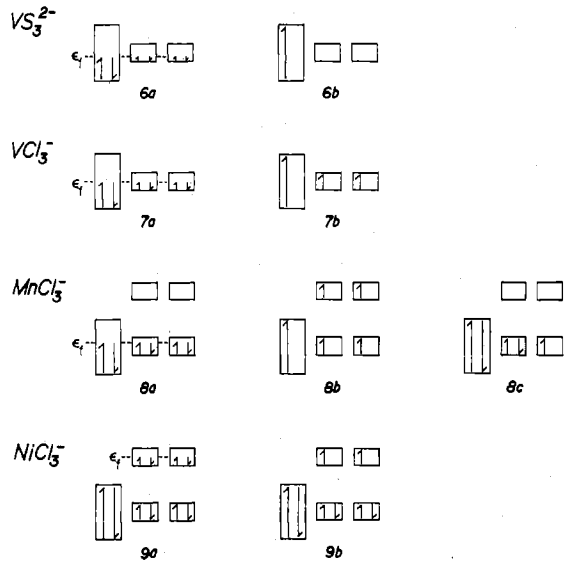

Figure 5. Schematic representations of the metallic and magnetic insulating states of the VS_3^{2-}, VCl_3^-, $MnCl_3^-$, and $NiCl_3^-$ chains.

d-block bands summarized in eq 6 and Table II. For the metallic state **6a** of the VS_3^{2-} chain, the total electronic energy per VS_3^{2-} is given by eq 9a[7] where the fractional band occu-

$$E(\mathbf{6a}) = \epsilon_t - (W_{1a} \sin (f_{1a}\pi) + 2W_{1e} \sin (f_{1e}\pi))/\pi + (f_{1a}^2 + 2f_{1e}^2)U + (4f_{1a}f_{1e} + 2f_{1e}^2)(2U' - J) \quad (9a)$$

pancies f_{1a} and f_{1e} (respectively of the 1a and 1e bands) are determined by two conditions: The Fermi levels ϵ_f of the 1a and 1e bands are the same (see eq 10a), and the sum of all

$$\epsilon_f = \epsilon_t - (W_{1a}/2) \cos (f_{1a}\pi) = \epsilon_t - (W_{1e}/2) \cos (f_{1e}\pi) \quad (10a)$$

the fractional band occupancies is equal to the number of d electrons per VS_3^{2-} unit (see eq 10b). From eq 10 and Table

$$2f_{1a} + 4f_{1e} = 1 \quad (10b)$$

I, we obtain eq 11.

$$f_{1a} \simeq 0.4567 \qquad f_{1e} \simeq 0.216 \quad (11)$$

The magnetic insulating state **6b** of the VS_3^{2-} chain has all the levels of the 1a band singly occupied. A similar magnetic insulating state can be constructed by having all the levels of one of the degenerate 1e bands singly occupied. However the total electronic energy per VS_3^{2-} of such a state is exactly the same as that of **6b** in the present approximation. That is

$$E(\mathbf{6b}) = \epsilon_t \quad (9b)$$

The band degeneracy problem just described is quite analogous to the CoO problem analyzed in detail by Brandow.[6a,7] From eq 9 and 11 and Table II, expression 12a is obtained. As

$$VS_3^{2-}: \quad E(\mathbf{6a}) - E(\mathbf{6b}) \simeq -1.04 + 0.27U \text{ (eV)} \quad (12a)$$

expected from one-electron band picture, eq 12a indicates that the metallic state **6a** is always more stable than the magnetic insulating state **6b** if the on-site repulsion U is neglected. From eq 12a, the condition for the magnetic insulating state **6b** to be more stable than the metallic state **6a** becomes

$$VS_3^{2-}: \quad E(\mathbf{6a}) - E(\mathbf{6b}) > 0, \quad \text{if } U > \sim 3.9 \text{ eV} \quad (12b)$$

The estimate of the on-site repulsion U just described is very crude at best and may only give a lower bound of U. In general the estimate of U is not a simple problem, and the magnitudes of U estimated for a number of compounds span a wide range of values—as low as less than 1 eV and as large as more than 10 eV.[6a] If we proceed in a manner similar to the above for the various states of the VCl_3^-, $MnCl_3^-$ and $NiCl_3^-$ chains, their total electronic energies are given as in Table III. Thus the results (13)–(15) are obtained from Tables II and III.

Table III. Total Electronic Energies per MCl_3^- Unit of the Metallic and Magnetic Insulating States of MCl_3^- Chains[a,b]

state	E, eV
7a	$3\epsilon_t + E_a$
7b	$3\epsilon_t + 3U' - 3J$
8a	$5\epsilon_t + E_a$
8b	$5\epsilon_t + 2\Delta_{CF} + 10U' - 10J$
8c	$5\epsilon_t + 2U + 8U' - 4J$
9a	$2\epsilon_e + E_b + E_c$
9b	$2\epsilon_e + U' - J + E_c$

[a] $E_a = -(W_{1a} \sin (f_{1a}\pi) + 2W_{1e} \sin (f_{1e}\pi))/\pi + (f_{1a}^2 + 2f_{1e}^2)U + (4f_{1a}f_{1e} + 2f_{1e}^2)(2U' - J)$, $E_b = -(2W_{2e} \sin (f_{2e}\pi))/\pi + 2f_{2e}^2(U + 2U' - J)$, $E_c = 6\epsilon_t + 3U + 18U' - 9J$, and $\Delta_{CF} = \epsilon_e - \epsilon_t$. [b] $f_{1a} = f_{1e} = 0.5$ in 7a; $f_{1a} \simeq 0.5764$ and $f_{1e} \simeq 0.9618$ in 8a; $f_{1a} = f_{1e} = 1$ and $f_{2e} = 0.5$ in 9a.

$$VCl_3^-: \quad E(\mathbf{7a}) - E(\mathbf{7b}) \simeq -0.81 + 0.87U \text{ (eV)} \quad (13)$$

$$MnCl_3^-: \quad E(\mathbf{8a}) - E(\mathbf{8b}) \simeq -3.43 + 1.09U \text{ (eV)} \quad (14a)$$

$$MnCl_3^-: \quad E(\mathbf{8c}) - E(\mathbf{8b}) \simeq -3.20 + 0.80U \text{ (eV)} \quad (14b)$$

$$NiCl_3^-: \quad E(\mathbf{9a}) - E(\mathbf{9b}) \simeq -0.57 + 0.54U \text{ (eV)} \quad (15)$$

Consequently the approximate values of U that would make the magnetic insulating states of the VCl_3^-, $MnCl_3^-$, and $NiCl_3^-$ chains more stable than their metallic states are found to be

$$VCl_3^-: \quad E(\mathbf{7a}) - E(\mathbf{7b}) > 0, \quad \text{if } U > \sim 0.9 \text{ eV} \quad (16)$$

$$MnCl_3^-: \quad E(\mathbf{8a}) - E(\mathbf{8b}) > 0, \quad \text{if } U > \sim 3.1 \text{ eV} \quad (17a)$$

$$NiCl_3^-: \quad E(\mathbf{9a}) - E(\mathbf{9b}) > 0, \quad \text{if } U > \sim 1.1 \text{ eV} \quad (18)$$

Further the condition that **8b** is more stable than **8c** in the $MnCl_3^-$ chain is

$$MnCl_3^-: \quad E(\mathbf{8c}) - E(\mathbf{8b}) > 0, \quad \text{if } U > \sim 4.0 \text{ eV} \quad (17b)$$

From eq 17a and 17b, it is estimated that $U > \sim 4.0$ eV in the $MnCl_3^-$ chain.

The band orbital occupancy of a magnetic insulating state is unusual from the viewpoint of the one-electron band picture but minimizes electron–electron repulsion by virtue of avoiding band orbital double occupancy.[7] The above discussion suggests that one-electron band structures can be of use for the discussion of magnetic insulating states if the effect of electron–electron repulsion on band orbital occupancy is properly accounted for. An additional example of the use of one-electron band structures is considered in the next section, where the magnetic insulating states of the MCl_3^- chains (M = V, Mn, Ni) are employed to calculate the antiferromagnetic contributions to their magnetic exchange parameters J.

C. Magnetic Properties of MCl_3^- (M = V, Mn, Ni) Chains. Exchange interactions in binuclear and one-dimensional magnetic materials are usually described by the Heisenberg-like spin Hamiltonian. The existence of such a Hamiltonian has been justified by a number of theoretical studies.[6] In predicting the signs of the magnetic exchange parameters J in magnetic insulators, the Goodenough–Kanamori rules for superexchange are found to be valuable.[6c] Recently Girerd, Charlot, and Kahn proposed a method[11,21] that allows the estimate of J for one-dimensional magnetic insulators based on band structures: The exchange parameter J is given by

(21) J.-J. Girerd, M.-F. Charlot and O. Kahn, *Mol. Phys.*, **34**, 1063 (1977).
(22) J. H. Ammeter, H.-B. Bürgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 3686 (1978).

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}

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

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

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

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

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

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.

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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

(1) R. E. Peierls, "Quantum Theory of Solids", Oxford University Press, London, 1955, pp 108-12.

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