INDIRECT SPIN COUPLING IN NiAS TYPE MAGNETIC COMPOUNDS*

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ABSTRACT. A theoretical study of the spin coupling in the magnetic compounds crystallizing with NiAs structure is made following the spin polarization mechanism developed earlier. For this purpose, a seven centre unit of the crystal. i.e , a trigonal prism with the six magnetic ions at the corners and the anion at the centre, is chosen Since this mechanism operates through the empty orbitals of the system, crystal field calculations for the empty orbitals on the central ion (excitation model) and empty orbitals on the metal ions (charge transfer model), are carried out. A semi-quantitative estimate of the A–O–B, A–O–C and A–O–D interactions (where A, B, C, D represent the magnetic ions at the various corners of the trigonal prism and O stands for the anion at the centre) on this mechanism gives results in general agreement with the observed magnetic behaviour of the systems.

INTRODUCTION

Magnetic compounds crystallizing with NiAs structure present a difficult system for theoretical studies of magnetic indirect exchange interaction (Kramers 1934) While some compounds are antiferromagnetic (e.g. CrS, CrSe, MnTe, CrSb, etc) others exhibit ferromagnetic ordering (e.g CrTe, MnAs, MnSb) (Lotgering and Gorter 1957) The previous predictions (Anderson 1950) that cations having less than half filled d shells will couple ferromagnetically via the anion do not fit with the above systems (e.g. CrS and CrTe assuming that in both Cr has d^4 configuration). Similar difficulties are encountered when one attempts to rationalize such systems with the help of some recent suggestions (Anderson 1959, Wollen 1960.).

In what follows, we study the spin coupling in these systems on the basis of mechanisms recently developed by one of the authors and co-workers (Koide and Sinha 1959, Koide, Sinha and Tanabe 1959) and applied to different types of structures (Sinha and Koide 1960, Sinha 1961, Sinha and Sinha 1962). In essence, the mechanism takes into account the spin polarization of the anion electrons and the delocalization of the cation electrons operating through the agency of an ortho-normalized set of empty orbitals for the unit chosen with respect to the occupied anion and cation orbitals. For actual calculations, however, only a few

excited low lying orbitals are considered in that others will not be important because of large energy denominators.

CHOICE OF THEORETICAL MODEL

For this purpose, first a brief description of NiAs type structure is in order. The structure is hexagonal ($P6_3/mmc$ or D^4_{6h}) with each type of atom surrounded by six of the other. The anion or metalloid (e.g S, Te or As) is surrounded by six metal ions (e.g Cr^{2+} or Mn^{2+}) at apices of a trigonal prism. The metal ion, on the other hand, is surrounded octahedrally by six anions which are the immediate neighbours with two metal ions which are relatively closer than other metal ions.

The appropriate unit for describing the cation-cation and cation-anion-cation interactions for this system seems to be one trigonal prism with the metal ions at the corners and the anion at the centre. The unit chosen is shown in Fig. 1. The point symmetry group of this unit is D_{3h}. Likewise for the cation, the point symmetry group is a superposition of octahedral (due to six anions octahedrally co-ordinated) and the axial symmetry (owing to the presence of two cations one above and the other below lying on the $<III>$ axis of the octahedron defined by the anions). In classifying the atomic orbitals of the anion and cations we shall make use of the crystal field pertaining to the appropriate point symmetry groups as described above (Fig. 2 for cation surrounding)
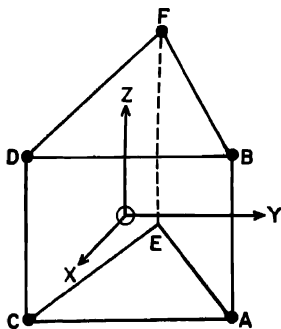

Fig. 1. Geometry of the model chosen. Open circle represents anion or metalloid and full circle a metal ion.
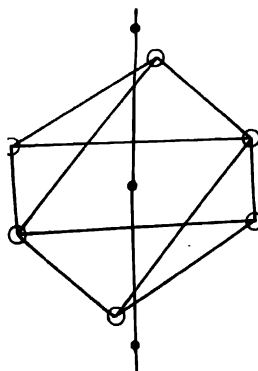
Fig. 2. Disposition of the anion octahedron and the two nearest neighbour metal ions around the central ion.

For the classification of anion orbitals (e.g. Te, Se, S) in the appropriate surrounding the outermost shell is taken into consideration i.e. $ns^2 \, np^6$ (the orbitals in $(n-1)$ shells downwards will be treated as constituting the ion core). The

$s^2 p^6$ description is not convenient for the present unit and hence we have to take into account the hybridisation of sp orbitals. If we consider the z axis as the line passing through the anion 0 and normal to the planes defined by the three cations above and below, then the following choice of orbitals seems appropriate : p_z and the three trigonal orbitals $\sigma_1, \sigma_2, \sigma_3$, given by,

$$\sigma_1 = \sqrt{\tfrac{1}{3}}\, s + \sqrt{\tfrac{2}{3}}\, p_x \qquad \qquad \ldots \quad (1)$$

$$\sigma_2 = \sqrt{\tfrac{1}{3}}\, s - \sqrt{\tfrac{1}{6}}\, p_x + \sqrt{\tfrac{1}{2}}\, p_y \qquad \qquad \ldots \quad (2)$$

$$\sigma_3 = \sqrt{\tfrac{1}{3}}\, s - \sqrt{\tfrac{1}{6}}\, p_x - \sqrt{\tfrac{1}{2}}\, p_y \qquad \qquad \ldots \quad (3)$$

The advantage of the above choice is that each of the σ's points mid-way towards the two cations lying on the vertical edges of the trigonal prism (e.g. AB) with p_z passing through the principal axis of symmetry. Thus the outer electronic configuration considered here amounts to $p_z{}^2 \sigma_1{}^2 \sigma_2{}^2 \sigma_3{}^2$. In view of the equivalence of σ_1, σ_2 and σ_3, we shall choose only one of these orbitals along with p_z i.e. the configuration $np_z{}^2\ n\sigma_i{}^2$ for describing the spin coupling in the subsequent calculations.

We now consider excited orbitals for an electron centred on the anion and moving in its field as well as the field of the cations at the corners of the trigonal prism. For this purpose, one electron of the anion is assumed to be promoted to excited orbitals, the energies of the various orbitals being calculated as in an atom under the influence of the crystal field. To fix ideas, let us first consider the possible excited orbital configurations for the ions S^{2-}, Se^{2-} and Te^{2-}. For S^{2-} the occupied outer shell configuration is $3s^2\,3p^6$ and hence the low lying excited orbitals to be considered on this ion are $4s$ and $3d$. Likewise, for Se^{2-}, with outermost filled shell structure $4s^2\,4p^6$ the possible empty orbitals are $5s$ and $4d$. On the other hand, for Te^{2-} with $5s^2\,5p^6$ the possible excited empty orbitals will be $6s$, $4f$. Of these, the d and f orbitals will undergo splitting under the influence of the trigonal crystal field. A rough estimate of this will be given now.

For the point group D_{3h}, the expression of the crystal filed is given by (Low 1960)

$$V_{D_{3h}} = A^0{}_0\ Y^0 + A_2{}^0 Y_2{}^0 + A_4{}^0 Y_4{}^0 + A_6{}^0 Y_6{}^0 + B_6(Y_6{}^6 + Y_6{}^{-6}) + \ldots \quad \ldots \quad (4)$$

where A's and B's are the coefficients and Y's are the normalized spherical harmonics. The coefficients for each system were determined by evaluating the expression given by Low (1960), the cations at the corners being treated as positive point charges. The effect of the first term in (4) is to give a constant shift of all the orbital levels. The other terms do not effect the s orbitals. The orbitals which

are most effected are the d and f. The splitting of empty d orbitals for S^{2-} and Se^{2-} is shown in Fig. 3. A similar calculation for $4f$ empty orbitals on Te^{2-} yields the level scheme as shown in Fig. 4.
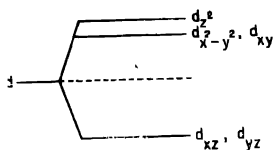

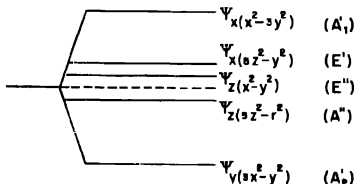Fig. 3   Level scheme for a $3d$ electron in crystal field with D_{3h} symmetry.

Fig. 4. Level scheme for an f electron in V_{D3h}.

The splitting of the cation occupied and empty orbitals (e g. for Cr^{2+} or Mn^{2+}) are determined for an octahedral field due to six anions and an axial field due to two cations lying on $<111>$ axis (i.e. z) one above and the other below. The crystal field is expressed as

$$V = V_c + V_a \qquad \qquad \dots \ (5)$$

$$= A_0^0 Y_0^0 + A_2^0 Y_2^0 + A_4^0 Y_4^0 + D_4^0 \left[Y-_4^0 \sqrt{\frac{10}{7}} \left((Y_4^3 + Y_4^{-3}) \right) \right] + \qquad \dots \ (6)$$

For the case of d^4 type ions (e.g. Cr^{2+} or Mn^{3+}) one can calculate the splitting for a positive d electron hole in d^5 configuration. The level scheme calculated on this basis turns out to be as shown in Fig. 5.
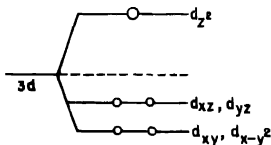

Fig. 5.   Level scheme for d election of a d^4 ion placed in the crystal field of symmetry of Fig. 2.

Thus for a weak field case the four electrons of d^4 type ion will be distributed in the low lying orbitals d_{xy} $d_{x^2-y^2}$, d_{xz}, d_{yz} and the hole will exist in the upper d_{z^2} orbital. For d^5 ion (i.e. Mn^{2+}), all the orbitals will be singly occupied.

Further among the low lying empty orbitals for d^5 (e.g. Mn^{2+}) ion i.e. $4s$ and $4p$, calculations based on the potential given by eq. (5) shows that the p_z orbital is depressed whereas p_x and p_y are pushed up, the s orbital being unaffected by the axial field.

As suggested before (Koide, Sinha and Tanabe 1959, Sinha 1961), the excited orbitals which are involved in the electron transition in the present mechanism

are selected both on the 'excitation model' as well as 'charge transfer model'. The orbitals on the anions which are made available as a result of crystal field depressions constitute the orbitals according to the excitation model.

In the charge transfer model, we take such linear combinations of the empty cation orbitals (e.g. d_z2, s, etc. on d^1 type ions and p_z, s etc. on d^6 type ions) which belong to the various irreducible representations of the point symmetry group of the unit chosen. For the bigger seven centre system (see Fig. 1) one has to classify such orbitals based on the point group D_{3h}. However, the calculations for a ten electron system for this unit (i.e. four electrons from the central ion and one each from the cations) will become unwieldy. We shall, therefore, study the interactions between the various ions separately, namely, A-B, A-C and A-D via the central ion (see Fig 1). We shall classify such orbitals for each dicationic unit according to the relevant symmetry element present.

In the case of systems such as CrS, CrSe, CrTe, the empty orbitals on the metal ions are of even symmetry namely, $3d_z2$ and will be denoted by d_k where k stands for $(a, b, c, d, \text{etc.})$. The appropriate molecular orbitals formed for each di-cationic unit will be orthogonalized with respect to the $p_0 (= p_c)$ and $\sigma_0 (-\sigma_c)$ orbitals of the central ion.

Thus for A-B unit we have

$$\phi_q(d) = (d_a + d_b - 2s_{ac}\sigma_0)/\sqrt{2(1 - 2s^2_{ac})} \qquad \ldots \quad (7)$$

$$\phi_u(d) = (d_a - d_b - 2s_{ap}p_0)/\sqrt{2(1 - 2s_{ap}^2)} \qquad \ldots \quad (8)$$

where the symmetry element is taken to be the reflection in the xy plane passing through the central ion; g and u stand for even and odd respectively and

$$S_a\sigma = <d_u | \sigma_0>, \quad S_{ap} = < (d_u | p_0 > \qquad \ldots \quad (9)$$

are the overlap integrals. Owing to overlap considerations, the role of σ_0 orbital is not expected to be important in the study of A-C and A-D interactions. These interactions will therefore be considered through the p_0 orbital of the central ion.

The molecular orbitals for other units can be expressed in the same manner.

In what follows, we first present the formal theory and then consider the specific cases in the subsequent sections.

FORMULATION OF INTERACTION MECHANISM

For each type of interaction under study, we choose a "three centre and a six electron" system represented by M_1OM_2. Of these, four electrons belong to the central ion and are assumed to exist in the configuration $p^2_0\sigma^2_0$. Further, we consider one representative electron from each magnetic ion M_1 and M_2 and the respective orbitals are denoted by u_1 and u_2. The orbitals may be taken to be

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either $d_{x^2-y^2}$, d_{xy} or d_{yz}, d_{zx}.   Two possibilities might exist; under reflection in the plane bisecting normally the line joining the two metal ions or any appropriate rotation by $180°$ we may have

$$u_1 \overset{\mathrm{R}}{\longleftrightarrow} u_2, \text{ or } \quad u_1 \overset{\mathrm{R}}{\longleftrightarrow} -u_2 \qquad \dots \quad (10)$$

with R standing for the appropriate symmetry operation. The set of excited orbitals are formally denoted by ϕ_g, ϕ_u. With the above definition in mind, the wave functions of the total system which constitute the eigenstates of the S^2 operator are written below.

Ground State

Triplet :

$$|^3\psi_0>_{od} = {}^3\{3(u_1\,u_2)^1(p_0)^2\, {}^1(\sigma_0)^2\} \qquad \dots \quad (11)$$

Singlet :

$$|^1\psi_0> = {}^1\{{}^1(u_1\,u_2)^1(p_0)^2\, {}^1(\sigma_0)^2\} \qquad \dots \quad (12)$$

Excited States — involving one electron transition from p_0 orbital.

Triplets   •

$$|^3\psi_1(g,\,u)>_{od,\,\,ev} = {}^3\{{}^1(u_1\,u_2)\,{}^3(p_0\,\phi_g,\,u)\,{}^1(\sigma_0)^2\} \qquad \dots \quad (13)$$

$$|^3\psi_2(g,\,u)>_{ev,\,\,od} = {}^3\{3(u_1\,u_2)^3\,(p_0\,\phi_g,\,u)\,{}^1(\sigma_0)^2\} \qquad \dots \quad (14)$$

Singlets

$$|^1\psi_1(g,\,u)>_{ev,\,od} = {}^1\{{}^3(u_1\,u_2)\,{}^3(p_0\,\phi_g,\,u)\,{}^1(\sigma_0)^2\} \qquad \dots \quad (15)$$

For one electron transitions from the σ_0 orbital, we shall have similar expressions as above except that the role of p_0 and σ_0 is interchanged. The notations *ev*, *od* denote the symmetry of the total wave function under the appropriate symmetry operation.

The matrix elements of the Hamiltonian (in atomic units $e = \hbar = m = 1$)

$$H = \sum_i H_i + \sum_{i<j} \frac{1}{r_{ij}} \qquad \dots \quad (16)$$

within the manifold given above are easily obtained following the methods of earlier papers (Sinha *et al.* 1959 to 1962).

The energies of the ground triplet and singlet states are given respectively as

$$^3E_0 = E_0 - J(u_1\,u_2) \quad \text{and} \quad {}^1E_0 = E_0 + J(u_1 u_2)$$

their mean being E_0. Likewise, for the energies of the various excited triplet and singlet states we shall take a mean $Em = Q_{g,\,u}$ neglecting the relatively small

exchange integrals compared to coulomb and one electron terms contained $Q_{g,u}$. The singlet or triplet depressions, other than those due to direct exchange $J(u_1 u_2)$ can be expressed in the second order perturbation of the various zeroth order ground states as a result of interaction with the excited states (Sinha *et al*)

$$\delta E(2S+1) = \sum_m \frac{< S_{p,\sigma} = 0 \mid H \mid S_{p,\sigma} = 1 > \cdot S_{p,\sigma} = 1 \mid H \mid S_{p,\sigma} = 0 >}{E_m - E_0} \quad (17)$$

Thus the splitting of energies between the triplet and singlet can be expressed as

$$2J_{eff} - {}^3E - {}^1E$$

$$= \left\{ \sum_g 4 \mid \frac{< u_1 \phi_g \mid u_1 \phi_0 > \mid^2}{E_g - E_0} - \sum_u 4 \mid \frac{< u_1 \phi_u \mid u_1 p_0 > \mid^2}{E_u - E_0} \right\}$$

$$+ \left\{ \sum_g \frac{4 \mid < u_1 \phi_u \mid u_1 \sigma_0 > \mid^2}{E_u - E_0} - \sum_g \frac{4 \mid < u_1 \phi_g \mid u_1 \sigma_0 > \mid^2}{E_g - E_0} \right\}$$

$$- 2J(u_1 u_2) \quad (18)$$

If we were to disregard the effect of the direct exchange for the time being, the coupling due to the spin polarization mechanism (i.e terms in the curly brackets) is dependent on the relative symmetry of ground and excited orbitals as well as their energy difference. Transitions between orbitals having the same symmetry stabilize the triplet state and those between orbitals of different symmetry stabilize the singlet state. When the excited orbitals $\phi_{g,u}$ are centred on the anion, they are automatically orthogonal to the ground state atomic orbitals p_0 or σ_0. However, for the molecular orbitals constituted as in (7) to (8) from the cation empty orbitals the overlap integrals such as S_{ap}, $S_{a\sigma}$ will be important. Thus for the choice of orbitals as in (7) and (8), the hybrid exchange integrals of the type $< u_1 w_{p,\sigma} \mid u_1 \phi_{gu} >$ take the following specific forms.

$$< u_1 \phi_g \mid u_1 p_0 > = \{ < u_1 d_a \mid u_1 p_0 > + < u_1 d_b \mid u_1 p_0 > - 2s_{a\sigma} < u_1 \sigma_0 \mid u_1 p_0 > \}/$$
$$\sqrt{2(1 - 2S^2_{a\sigma})} \quad \dots \quad (19)$$

$$< u_1 \phi_w \mid u_1 p_0 > = \{ < u_1 d_a \mid u_1 p_0 > - < u_1 d_b \mid u_1 p_0 > - 2s_{ap} < u_1 p_0 \mid u_1 p_0 > \}/$$
$$\sqrt{2(1 - 2S^2_{ap})} \quad \dots \quad (20)$$

$$< u_1 \phi_u \mid u_1 \sigma_0 > = \{ < u_1 d_a \mid u_1 \sigma_0 > - < u_1 d_b \mid u_1 \sigma_0 > - 2S_{ap} < u_1 p_0 \mid u_1 \sigma_0 > \}/$$
$$\sqrt{2(1 - 2S^2_{ap})} \quad \dots \quad (21)$$

$$< u_1 \phi_g \mid u_1 \sigma_0 > = \{ < u_1 d_a \mid u_1 \sigma_0 > + < u_1 d_b \mid u_1 \sigma_0 > - 2S_{a\sigma} < u_1 \sigma_0 \mid u_1 \sigma_0 > \}/$$
$$\sqrt{2(1 - 2S^2_{a\sigma})} \quad \dots \quad (22)$$

The integrals of the type $<ab/cd>$ represent the coulomb interaction $(1/r_{12})$ between the two charge densities $a^*(1)$ b(1) and $c^*(2)$ d(2). The magnitude of the integrals occurring on the left hand side of (19) to (22) will depend on the sign and magnitude of the various integrals on the right hand side. The integrals of the

type $<u_1 d_b / u_1 p_0>$, $<u_1 d_b | u_1 \sigma_0)$ and $S <u_1 \sigma_0 | u_1 p_0>$ are expected to be negligible owing to their disposition and overlap considerations.

We shall now discuss the specific interactions namely, AOB, AOC and AOD based on the concepts developed above.

APPLICATION TO SPECIFIC CASES

First, we consider the A-B interaction in the unit A-O-B. The symmetry element is reflection in the xy plane passing through 0 and bisecting normally the line AB. The anion orbitals σ_0 and p_0 (p_z) have already been described (cf. equations (1) to (3). For the singly occupied cation orbitals u_1 and u_2 in the case of CrS, CrSe, CrTe, we choose d_{yz} (d_{zx}) which has the maximum overlap with the anion orbitals. In the case of MnTe like systems, d_{z^2} type orbitals will be choosento represent u_1 and u_2.

The choice of empty orbitals on the anion and cations is guided by crystal field depressions of the next shell orbitals. For CrS, CrSe, the empty orbitals on the anion centre are taken to be d_{yz}, d_{zx} (cf Fig 3) both odd under the above operation and for CrTe, the lowest is $\psi_g(3x^2 - y^2)$ being an even orbital, the others lying appreciably higher up. For empty orbitals on cations, $3dz^2$ is taken for $Cr^{2+} X^{2-}$ system and $4p_z$ for $Mn^{2+} X^{2-}$ systems. These orbitals have been chosen both from energy as well as overlap considerations.
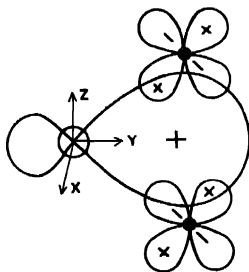

Fig 6   Schematic representation of the σ_0 and d_{yz} orbitals for AOB interaction.

It may be remarked that the cations are closest in AOB unit compared to other units. Further from overlap considerations the occupied orbital of the anion which partakes more strongly in the indirect exchange interaction is σ_0 rather than p_0 (See Fig. 6). The effective exchange integral for this unit can be written for CrS, CrSe (with d_{ε_i} standing for d_{yz} or d_{zxa} on anion and ϕ_g or ϕ_u as given by (7) and (8) d_a being d_{z^2}) as

$$2J_{eff} = \left\{ \sum_i \frac{4|<u_1 d_{\varepsilon_i} | u_1 \sigma_0>|^2}{\Delta E_{\varepsilon_i}} + \frac{4|<u_1 \phi_u | u_1 \sigma_0>|^2}{\Delta E_u} - \frac{4|<u_1 \phi_g | u_1 \sigma_0>|^2}{\Delta E_g} \right\}$$
$$- 2J(u_1 u_2) \qquad (23)$$

Since optical experiments on similar systems indicate that anions effectively shield the metal ions from one another (Casselman and Keffer 1960), the direct exchange is expected to be very feeble. We, therefore, neglect $J_7(u_1u_2)$. The terms in (23) owing to the excitation model i.e. $\Sigma_i 4 | < u_1d_{\varepsilon_i} | u_1\sigma_0 > |^2/\Delta E\varepsilon_i$ stabilize the singlet state. The terms due to charge transfer are better understood on expanding the integrals in atomic orbitals.

$$\frac{4 | <u_1\phi_u | u_1\sigma_0 > |^2}{\Delta E_u} \approx \frac{4 | < u_1d_u | u_1\sigma_0 > |^2}{\Delta E_u[2(1-2S_{u^2p})]} \qquad (24)$$

$$\frac{4 | < u_1\phi_g | u_1\sigma_0 > |^2}{\Delta E_g} \approx \frac{4 | \{ <u_1d_u | u_1\sigma_0 > \cdot 2S_{a_u} <u_1\sigma_0 | u_1\sigma_0 > \} |^2}{\Delta E_g[2(1-2S_{a_u}^2)]} \qquad \dots \quad (25)$$

Using Mulliken's approximation (Mulliken 1953), we can write

$$<u_1d_a | u_1\sigma_0 > = \tfrac{1}{2} S_{1\sigma} \{ <u_1d_a | u_1u_1) + <u_1d_a | \sigma_0\sigma_0 > \} \qquad \dots \quad (26)$$

where $S_{1\sigma} = <u_1 | \sigma>$. The integral of the type centred at one cation, will be zero unless the azimuthal quantum numbers of the orbitals satisfy (Condon and Shortley 1953)

$$m_l(u_1) + m_l(d_a) = m_l(u_1) + m_l(u_1) \qquad \dots \quad (27)$$

This will have finite value only when the orbitals involved are of the type $d_z 2$, p_z, etc. For the present case when u_1 is d_{yz} or d_{xy} and $d = d_z2$, this integral vanishes. Thus to a rough approximation

$$2J_{eff}(CrSe, CrS) \approx 4 \left\{ \sum_i \frac{| u_1d_{\varepsilon_i} | u_1\sigma_0 > |^2}{\Delta E_{\varepsilon_i}} - \frac{2S_{a^2_u} | < u_1\sigma_0 | u_1\sigma_0 > |^2}{\Delta E_g(1-2S_{a^2_u})} \right\} \qquad (28)$$

In view of the $S_{a_u}^2$ factor and the overlap of $u_1\sigma_0$ which is expected to be smaller when $u_1 = d_{yz}$ than when it is d_z2, the last term in (29) will be relatively small compared to first terms. Thus the singlet state is likely to be more stabilized and the coupling in CrSe, CrS will be antiferromagnetic. For CrTe where the excitation orbitals is $f_a = \psi_g (3x^2 - y^2)$ we get

$$2J_{eff} (CrTe) \approx 4 \left\{ - \frac{| <u_1f_a | u_1\sigma_0 > |^2}{\Delta E_a} - \frac{2S_{a_u}^2 | <u_1\sigma_0 | u_1\sigma_0 > |^2}{\Delta E_g(1-2S^2_{a_u})} \right\} \qquad \dots \quad (29)$$

The above, of course, always stabilises the triplet state and the coupling will be ferromagnetic. While considering the case of MnTe, we recapitulate that $u_1 = d_z2$ and $d_a = p_z$ and hence the integral $<u_1d_a | u_1u_1>$ is quite appreciable. (Koide, Sinha and Tanabe 1959). Further the overlap density $u_1\sigma_0$ is expected to be quite appreciable. However, as shown before, the first and second terms in

(25) nearly cancel each other and accordingly the effective exchange integral for MnTe can be written as

$$2J_{eff}(MnTe) = 4 \left\{ \frac{|< u_1\phi_u | u_1\sigma_0 >|^2}{\Delta E_u} - \frac{|< u_1 f_a | u_1\sigma_0 >|^2}{\Delta E_a} \right\} \dots \quad (30)$$

In view of the large overlap of d_z2, p_z with σ_0 and smaller energy denomination it is expected that the charge transfer model will be more important in the present case and hence the second term in (30) will be of smaller magnitude. Therefore (30) would stabilize the singlet state.

For MnAs, MnSb also, the charge transfer model will be more important owing to a high degree of covalency but the choice of orbitals for u_1 and d_a is the same CrTe and accordingly the coupling is expected to be ferromagnetic. In the case of CrSb, the metal ion ground state configuration will be d^3, with d_z2, d_{yz}, $d_{z,x}$ being pushed down and d_{xy}, $d_{x^2-y^2}$ pushed up. For the excited orbital however, p_z is pushed down owing to crystal field effects. Thus the choice of u_1 and d_a is the same as MnTe and the charge transfer model would lead to a stabilization of the singlet state.

Study of A-C Interaction

As indicated before, the role of σ_0 orbital of the central ion will not be of importance for the present unit as compared to the p_0 orbitals. Further, using the criterion of maximum overlap (in Fig. 7), the choice of u_1 for d^4 ions is $d_{x^2-y^2}$, (d_{xy}). On the same basis it can be seen that the excited orbital such as d_{yz} (d_{zx}) on the excitation model on S, Se, Te, etc. will have lesser significance than the s orbital to a certain extent. Thus for A-C interaction, we discusse the charge transfer model and the s-orbital effect for the excitation model. Now $p_0(= p_z)$ is an even orbital under reflection in XZ plane. Hence for d^4 type ions (CrS, CrSe, CrTe, MnAs, MnSb) with $u_1 = d_x2_{-y}2$, $d_a = d_z2$ the effective interaction can be written as

$$2J_{eff} = -4 \left\{ \frac{2S^2_{ap}|< u_1 p_0 | u_1 p_0 >|^2}{\Delta E_u(1-2S^2_{aP})} - \frac{|< u_1 s | u_1 p_0 >|^2}{\Delta E_s} \right\} \quad \dots \quad (31)$$

which would always favour parallel coupling between A and C. The above is also true for CrSb except that $u_1 = d_z2$ and $d_a = d_x2_{-y}2$. In the case of systems such as MnTe, CrSb with $d_a = p_z$ and noting that S_{ap} is likely to be negative (See Fig. 7), we have

$$2J_{eff} = 2 \left\{ \frac{|< u_1 d_a | u_1 p_0 >|^2}{\Delta E_g} - \frac{|< u_1 d_a | u_1 p_0 > +2| S_{ap} |< u_1 p_0 | u_1 p_0 >|^2}{\Delta E_u(1-2S^2_{ap})} \right\}$$
$$\dots \quad (32)$$

which assuming that ΔE_g and $\Delta E_u (1-2S^2_{ap})$ are comparable would be negative in sign and hence the parallel case is again favoured. One can, therefore, conclude

that A-C interaction is ferromagnetic in all cases although the strength of the interaction will be weaker compared to A-B interaction.
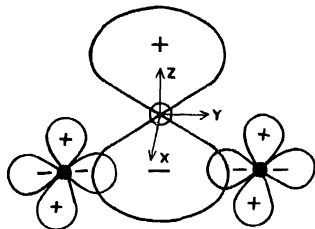

Fig 7 Schematic representation of the p_0 and   Fig. 8 Same as Fig. 7, for AOD interaction.
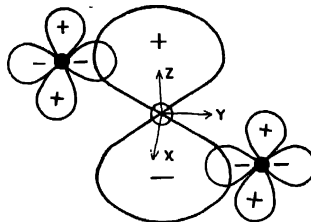$d_{x^2-y^2}$ orbitals for AOC interaction

Study of AOD Interaction .

In this situation also the effective anion orbital would be p_0 which is odd under rotation by $180°$ around a-axis. With $u_1 = d_{x^2-y^2}$, $d_a = d_z2$ and excitation orbital s, the effective exchange integral for CrS, CrSe, where excitation model is more important is given by

$$2J_{eff} = |<u_1s|u_1p_0>|^2/\Delta E_s \qquad . \qquad (33)$$

and for the systems CrTe, MnAs, JnSb where the charge transfer mechanism is expected to be important (cf. ξ 6) it is

$$2J_{eff} = -2|<u_1d_a|u_1p_0>|^2/\Delta E_g \qquad ... \qquad (34)$$

The former (cf. eq. 33) favours antiferromagnetic stabilization and the latter (cf eq. 34) ferromagnetic. For the systems MnTe, CrSb, with $u_1 = d_z2$, $d_a = p_z$ the charge transfer process gives

$$2J_{eff} = 2|<u_1d_a|u_1p_0>|^2/\Delta E_g \qquad ... \qquad (35)$$

favouring antiferromagnetic coupling between A and D. It may be noted that the weaker AOD interaction is acting in the same direction as the A-B interaction for the said systems.

GENERAL CONCLUSIONS

The foregoing analysis shows that in the NiAs type magnetic compounds the spin-polarization mechanism provides a reasonable explanation of the observed spin coupling. It shows that the strongest interaction based on this mechanism is A-O-B i.e. between the closest magnetic ions via the σ_0 orbital of the anion. The A-O-C and A-O-D interactions are feeble, the former always giving rise to parallel alignment, the latter strengthening A.O.B interaction.

The details of these interactions can be classified under two headings, namely
(1) Coupling via excited orbitals belonging to the central ion (excitation model)
and (2) Coupling via excited cationic orbitals (charge transfer model).

In deciding as to which of the two models plays a dominant role in specific
cases, we are guided by a rough idea of the energy denominators as well
as the hybrid exchange integrals occurring in the numerators (c.f. eq.
(22)). Further, we now briefly assess the energy denominators. On the excita-
tion model, the foregoing analysis tacitly assumes that only those excited empty
orbitals on the central ion constitute a semilocalized bound state, which are
depressed owing to the crystal field perturbations. In addition to the constant
shift of all the levels, the splitting of p, d or f levels will be of the order
of 2 to 5 eV, as the estimate made here and in earlier work shows (Sinha
et al. 1962). Further the energy denominators occurring in equation (18)
can be taken to be equal to the excitation energy to the appropriate excited orbital
(atomic or molecular). For the orbitals on the excitation model we estimate this
from atomic energy states for the free ions (e.g. S) (Watson 1958) plus $2|e|$ well.
Thus S^{--} ion in a crystal would be approximately equivalent to argon atom
along with additional corrections due to crystal field splittings. For the charge
transfer model, we estimate the energy denominators as approximately equal
to the energy involved in transferring one electron from the anion to cation
which in turn is roughly derived from the appropriate ionization potential of
the metal ion and the electron affinity of the anions. (Koide, Sinha and Tanabe
1959). The tentative estimates are indicated below :

Substance	ΔE(excitation)	ΔE(charge transfer)
CrS, CrSe	10 ev.	>20 ev.
CrTe	~15 ev.	~15 ev.
MnTe	~15 ev.	<15 ev.

From the above, it appears that in compounds such as CrS, CrSe or generally
$M^{2+}X^{2-}$ (X being S and Se), the excitation model dominates and leads to antifer-
romagnetic coupling. For MX where X is Te, As, Sb it seems that, in general,
the charge transfer model will dominate the excitation mechanism. In CrTe,
both may be equally important but they act in the same direction. This is quite
consistent with the stronger covalency in MTe, MAs, MSb etc. We have already
discussed before as to which of the hybrid exchange integrals are likely to be
important. A numerical estimate for the various exchange and overlap integrals
is not attempted keeping in mind the hopelessly difficult job of having an accurate
knowledge of the various orbitals involved in such systems. No Hartree-Fock
calculations are available except for some free transition metal ions. It is hoped
that a better knowledge of electronic orbitals in crystals in future will render
it possible to make quantitative estimates.

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