

We thank Mr. J. Berkeley for making the infra-red measurements.

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CHEMISTRY

Covalent Super-Exchange in Solid State Physics

MAGNETIC coupling of next-to-nearest neighbours through a non-magnetic anion (super-exchange) has been explained by Anderson¹ by considering 'excited states' in which a single electron in a *p*-orbital of the anion is transferred to one of the neighbouring cations. Goodenough and Loeb² have emphasized correctly that such interactions are essentially covalent and have given the name 'semi-covalence' to Anderson's one-electron transfer. As stressed by Goodenough and Loeb, the increase in Curie or Néel temperatures in series such as MnO-FeO-CoO-NiO, or MnO-MnS-MnSe-MnTe, is evidence for the part played by covalence in magnetic coupling.

Anderson's theory leads to the prediction that super-exchange should be antiferromagnetic if the paramagnetic ion has its original *d*-shell half-full or more (manganese, iron, cobalt, nickel, copper) and ferromagnetic otherwise (titanium, vanadium, chromium). There are many exceptions to this rule, as shown in Table 1.

Table 1. FERROMAGNETIC AND ANTIFERROMAGNETIC COMPOUNDS OF ELEMENTS IN FIRST TRANSITION SERIES

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
MO	A(8)	A(8)		A(10)	A(10)	A(10)	A(10)	A
M ₂ O ₃	A(8)	A(8)	A(8 $\frac{1}{2}$)	A(10)	A(10)			
MO ₂		A(8 $\frac{1}{2}$)	F(9)	A(9 $\frac{1}{2}$)				
MS		A(8)	F(9)	A(10)	A(10)	A(10)	A(10)	A(10)
MS ₂ *				F(7)		F(7)	F(7)	
MSe		A(8)		A(10)				
MTe			F(9)	A(10)				
MAs				F(9)				
MSb			A(8)	F(9)				
MBi				F(9)				

A, Antiferromagnetic; F, ferromagnetic; (*n*), number of electrons in covalent structure.

* Only electrons in M-S bonds counted.

Numbers in parentheses in Table 1 refer to the number of electrons participating in covalent bonding; that is, the number of electrons in molecular orbitals surrounding an anion. Inspection of these numbers indicates that antiferromagnetism tends to occur when *n* is even, whereas ferromagnetic coupling occurs when *n* is odd.

To determine the number *n*, one must first consider the effect of crystal-field splitting on the 3*d*-levels of the paramagnetic cation. Let *n'* be the number of electrons in the upper level (for example, 2 for manganese ions, 1 for chromium ions (Cr²⁺), in an octahedral field). If *p* is the co-ordination number of

the cation and *q* that of the anion, $n = n' \frac{q}{p} + n''$,

where *n''* is the number of valence electrons of the anion. It makes no difference whether *n''* includes *s*-electrons or not, as the number of *s*-electrons is even. Thus for manganese sulphide, *p* = *q* = 6, *n'* = 2, *n''* = 8 (or 6), *n* = 10 (or 8) and is even. In chromium sulphide (CrS), *n'* = 1, *n* = 9 (or 7)

and is odd. Expressed in a different manner, *n'* is the number of 3*d*-electrons of the cation participating in the formation of hybrid orbitals, the nature of the latter being deduced from the symmetry of the anionic arrangement around a cation (for example, *d*²*sp*³ in octahedral manganese sulphide, *d*³*sp*³ in the distorted trigonal antiprism of α-Fe₂O₃).

Although no rigorous treatment can be carried out at this moment, a simple argument may suggest why the sign of super-exchange interaction depends on whether *n* is even or odd. Consider manganese sulphide, in which both cation and anion are in octahedral co-ordination. Both can use *d*²*sp*³ hybrid orbitals, and six bonding and six antibonding molecular orbitals can be formed around each sulphur. These orbitals contain 10 electrons, and so with respect to a fully covalent structure the compound is deficient in electrons. Four molecular orbitals will carry two electrons each; charge correlation requires that the two remaining electrons be as far apart as possible, that is, 180°. These will go into molecular orbitals on opposite sides of the anion, thus accounting for the large angle characteristic of super-exchange. These two molecular orbitals are not fully orthogonal because of overlap of the orbitals of the cation on either side of the central anion, and they may thus be considered to form two orthogonal three-centred orbitals of slightly different energies. The ground-state will be such that the two electrons in the bridge occupy the lowest of the 3-centre orbitals with spins antiparallel; these electrons in turn interact with the remaining *t*_{2g} electrons on the adjacent cations (as implied in ionic-covalent resonance), which will be coupled antiferromagnetically. The single electron in the 3-centre orbital of chromium sulphide must lead to ferromagnetic coupling.

A similar analysis can be carried out for other substances listed in Table 1. More complicated oxides (for example, ferrites) present an additional problem in that *n* is commonly not an integer (9.75 in Fe₃O₄). For fractional numbers between 9 and 10, one may hesitate to predict the sign of super-exchange; possibly in such cases a small amount of direct exchange between next neighbours is the determining factor. For example, chromium oxide (Cr₂O₃) is antiferromagnetic although it might be expected to be ferromagnetic (*n* = 8 $\frac{1}{2}$). Neutron diffraction reveals ferromagnetic coupling between cations at large distances and at large Cr-O-Cr angles; only interactions at shorter distances and through smaller angles (hence presumably not super-exchange) are antiferromagnetic. In dioxides with the rutile structure (vanadium, chromium, manganese dioxides), further complications arise from the possibility of extensive π-interaction between oxygen *p* (the oxygen is in trigonal planar hybridization) and metal *t*_{2g} orbitals. It is worth noting that the present arguments predict that a solid solution of vanadium oxide (VO₂) and manganese dioxide in the ratio 1 : 1 would have the same electron number as ferromagnetic chromium oxide, and should accordingly also be ferromagnetic, although the two end-members are both antiferromagnetic.

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