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Antiferromagnetism in Spinel-Like Compounds*

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A theoretical study on antiferromagnetism in certain "normal" spinels (cubic or tetragonally distorted), where the A cations are diamagnetic and B paramagnetic, has been made using the molecular field approximation. It is found that the most stable arrangement is one in which each <110> and <1$\bar{1}$0> row is antiferromagnetically ordered with the spin vectors pointing along these directions.

This arrangement predicts temperature independent magnetic susceptibility below the transition temperature for all fields. Reference is made to experimental confirmation of this in certain spinels.

Introduction

In this paper we discuss the antiferromagnetism of certain spinels (cubic or tetragonally distorted) where the A (tetrahedral) sites are occupied by diamagnetic cations and the B (octahedral) sites are occupied by paramagnetic cations such as Fe^{3+}, Mn^{3+} and Cr^{3+}. These are "normal" spinels, examples are $ZnFe_2O_4$, $CdFe_2O_4$, $ZnMn_2O_4$, $CdMn_2O_4$ etc. The two manganites are tetragonally distorted[1].

Owing to the occupation of the A sites by diamagnetic ions, we have to consider the spin ordering only in terms of B-B interactions. Antiferromagnetism of zinc ferrite has been discussed by Tachiki and Yosida[2] by assuming a magnetic superstructure of tetragonal symmetry with + and − spins alternating in (001) planes. Although this calculation is a step in the right direction, certain other spin super-structures in the presence of tetragonal distortion (e.g. in $ZnMn_2O_4$) may turn out to be more stable. In what follows, we explain these possibilities on the basis of molecular field approximation[3,4].

Molecular Field Formulation

Following Yaffet and Kittel[4], we subdivide the B lattice into four sub-lattices namely B_1, B_2, B_3 and B_4. If we consider one cation from each sub-lattice, they form a tetrahedral unit in the case of cubic spinels and tetragonal sphenoids for tetragonally distorted spinels. In the latter case the mutual distances are as follows: $R_{12}=R_{34}\neq R_{13}=R_{24}=R_{23}=R_{14}$.

We denote the molecular field coupling constants for the interaction between the sub-lattice i and j by the symbol b_{ij}. These are assumed to be negative. The molecular field acting on the i th lattice is given by

$$\boldsymbol{H}_i=\sum_{j=1}^{4} b_{ij}\boldsymbol{M}_j \qquad \begin{matrix} i=1,2,3,4 \\ j=1,2,3,4\,. \end{matrix} \tag{1}$$

The four equations typified by (1) contain sixteen interaction constants. From symmetry considerations we have only three independent constants namely $b_{11}(=b_{22}=b_{33}=b_{44})$; $b_{12}(=b_{21}=b_{34}=b_{43})$ and $b_{13}(=b_{31}=b_{14}=b_{41}=b_{24}=b_{42}=b_{23}=b_{32})$. Thus, we can write the four equations in the following explicit forms:

$$\begin{aligned} \boldsymbol{H}_1&=b_{11}\boldsymbol{M}_1+b_{12}\boldsymbol{M}_2+b_{13}\boldsymbol{M}_3+b_{13}\boldsymbol{M}_4 \\ \boldsymbol{H}_2&=b_{12}\boldsymbol{M}_1+b_{11}\boldsymbol{M}_2+b_{13}\boldsymbol{M}_3+b_{13}\boldsymbol{M}_4 \\ \boldsymbol{H}_3&=b_{13}\boldsymbol{M}_1+b_{13}\boldsymbol{M}_2+b_{11}\boldsymbol{M}_3+b_{12}\boldsymbol{M}_4 \\ \boldsymbol{H}_4&=b_{13}\boldsymbol{M}_1+b_{13}\boldsymbol{M}_2+b_{12}\boldsymbol{M}_3+b_{11}\boldsymbol{M}_4 \end{aligned} \tag{2}$$

The energy in the absence of an external magnetic field is

$$E=-\frac{1}{2}\sum \boldsymbol{H}_i\cdot\boldsymbol{M}_i\,. \tag{3}$$

Obviously, the magnitudes of the vectors $\boldsymbol{M}_i$ are identical. Hence,

$$\begin{aligned} E=&-[2b_{11}M^2+b_{12}(\boldsymbol{M}_1\cdot\boldsymbol{M}_2+\boldsymbol{M}_3\cdot\boldsymbol{M}_4) \\ &+b_{13}(\boldsymbol{M}_1+\boldsymbol{M}_2)\cdot(\boldsymbol{M}_3+\boldsymbol{M}_4)] \qquad (4) \\ =&-M^2\{2b_{11}+b_{12}[\cos(\pi-2\phi)+\cos(\pi-2\varphi)] \\ &+2b_{13}(1-\cos 2\phi)^{1/2}(1-\cos 2\varphi)^{1/2}\cos\theta\}\,, \qquad (5) \end{aligned}$$

where the angles between the vectors $\boldsymbol{M}_1$ and $\boldsymbol{M}_2$ is $(\pi-2\phi)$, and between $\boldsymbol{M}_3$ and $\boldsymbol{M}_4$ is $(\pi-2\varphi)$. Likewise θ is the angle between $(\boldsymbol{M}_1+\boldsymbol{M}_2)$ and $(\boldsymbol{M}_3+\boldsymbol{M}_4)$. In order to get a physically meaningful result it is necessary

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to invoke the symmetry of the unit for minimizing the energy with respect to angles. Accordingly, we put $2\phi=2\psi$. Thus the values of 2ϕ and θ which minimize the energy are

$$\text{(i)}\ \ 2\phi=0,\qquad \text{(ii)}\ \ 2\phi=\pi,\ \ \theta=\pi,$$

$$\text{(iii)}\ \ 2\phi=\pi,\ \ \theta=0\,.$$

The corresponding energies are given by

$$E_1=-2M^2[|b_{12}|-|b_{11}|] \qquad (6)$$

$$E_2=-2M^2[2|b_{13}|-|b_{12}|-|b_{11}|] \qquad (7)$$

$$E_3=2M^2[|b_{11}|+|b_{12}|+|b_{13}|]\,. \qquad (8)$$

It is to be noted that $|b_{11}|$ is, of course, much less than $|b_{12}|$ or $|b_{13}|$. Hence the most stable state will be governed by the relative magnitudes of b_{12} and b_{13}. In our case, we have considered the case where $R_{13}>R_{12}$ (for tetragonally elongated spinels). This is true for zinc and cadmium manganites; however, even for zinc ferrite a similar elongation may exist at low temperatures as suggested by Tachiki and Yosida[2)]. In the present case the strength of the indirect exchange interaction can be taken to depend on the nearest neighbour distance. The role of oxygen orbital is different in spinel as compared to rock salt type lattice. For cubic spinels the nearest neighbour interaction will take place through the orbital $(1/\sqrt{3})(p_x+p_y+p_z)$ which overlaps equally with the three octahedral magnetic ions (For details see Sinha[5)]). We, therefore, assume that $|b_{12}|>|b_{13}|$. The lowest energy is thus E_1 with E_2 being higher than this. E_3 has a positive value and hence is unstable. We now consider the various spin configurations associated with these spin super-structures.

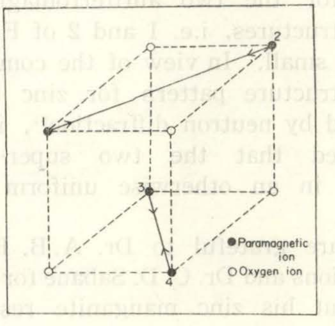

Fig. 1a.

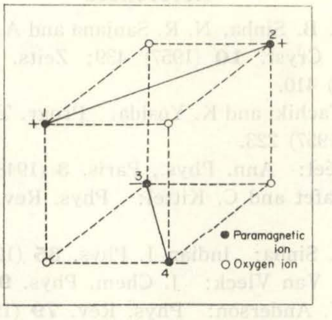

Fig. 1b.

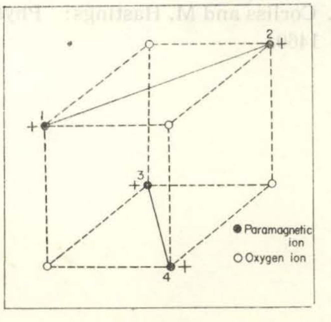

Fig. 1c.

The first case represents an antiferromagnetic super-structure, with the net magnetic moment in each $\langle 110\rangle$ and $\langle 1\bar{1}0\rangle$ row being independently zero. As far as the directions of the spin vectors associated with each sublattice are concerned, there are various possibilities. For a picture consistent with the symmetry of the unit, we choose the direction of the spin vectors along $\langle 110\rangle$ and $\langle 1\bar{1}0\rangle$ axes. The arrangement of the spin vectors is shown in Fig. 1a.

The second case (i.e., for E_2) corresponds to an ordering of + and − spins in alternate (001) planes. This is the same super-structure as considered by Tachiki and Yosida.

The third represents a purely ferromagnetic arrangement and, from energetic consideration, we have seen that it is the least likely. The latter two configurations are also shown in Fig. 1.

The transition temperature associated with these super-structures are determined immediately from the energy values. The one pertaining to the most stable state (i.e. E_1) is

$$T_{c1}=\frac{S(S+1)}{3k}g^2\beta^2[|b_{12}|-|b_{11}|] \qquad (9)$$

Similar expressions can be obtained for T_{c2} and T_{c3}.

Derivation of Susceptibility

In deriving the susceptibility below the

Neel temperature*, we follow the same procedure as adopted by Van Vleck[6)] and Anderson[7)]. The main difference, however, arises because of the presence of two negative exchange constants J_{12} and J_{13} in our model. The effective field on the sublattice one is

$$\boldsymbol{H}_1^{eff}=\boldsymbol{H}_0-a_{12}\boldsymbol{S}_2-a_{13}(\boldsymbol{S}_3+\boldsymbol{S}_4)\ , \tag{10}$$

where $a_{12}=2|J_{12}|z/g$ and $a_{13}=2|J_{13}|z/g$ with $z=2$ for the present model. We can write down the equivalent expressions for the other three sublattices easily. Let the applied field $\boldsymbol{H}_0$ be perpendicular to all the sublattice spin vectors. On the application of this field, we shall have $\boldsymbol{S}_1=\boldsymbol{S}_1{}^0+\delta\boldsymbol{S}_1$, where

$$|\delta\boldsymbol{S}_1|=|\boldsymbol{S}_1{}^0|\frac{|\boldsymbol{H}_0-a_{12}\delta\boldsymbol{S}_2-a_{13}(\delta\boldsymbol{S}_3+\delta\boldsymbol{S}_4)|}{|a_{12}\boldsymbol{S}_2{}^0+a_{13}(\boldsymbol{S}_3{}^0+\boldsymbol{S}_4{}^0)|} \tag{11}$$

Since $(\boldsymbol{S}_3{}^0+\boldsymbol{S}_4{}^0)=0$, this yields, assuming $|\delta\boldsymbol{S}_1|=|\delta\boldsymbol{S}_2|$ and $|\delta\boldsymbol{S}_3|=|\delta\boldsymbol{S}_4|$,

$$2a_{12}|\delta\boldsymbol{S}_1|+2a_{13}|\delta\boldsymbol{S}_3|=\boldsymbol{H}_0\ . \tag{12}$$

Finally summing over all the sublattices

$$2(a_{12}+a_{13})[|\delta\boldsymbol{S}_1|+|\delta\boldsymbol{S}_2|+|\delta\boldsymbol{S}_3|+|\delta\boldsymbol{S}_4|]=4\boldsymbol{H}_0\ . \tag{13}$$

The magnetization is given $\boldsymbol{M}=(1/4)Ng\beta\delta S$. Thus we get the susceptibility as

$$\chi_{\langle 001\rangle}=\frac{Ng\beta}{2(a_{12}+a_{13})}=\frac{Ng^2\beta^2}{4z(|J_{12}|+|J_{13}|)}\ , \tag{14}$$

which is independent of temperature. Proceeding in the same fashion, we have for field applied in $\langle 110\rangle$ or $\langle 1\bar{1}0\rangle$ direction.

$$\chi_{\langle 110\rangle}=\chi_{\langle \overline{11}0\rangle}=\chi_{\langle 001\rangle}\ . \tag{15}$$

Hence, it can be easily shown that the total susceptibility at $\chi_{(T<T_c)}=\chi_{(T_c)}$ is independent of temperature below T_c for powder or single crystals.

Following the standard procedure[7)] the susceptibility above the Curie temperature is

$$\chi_{(T>T_c)}=\frac{S(S+1)Ng^2\beta^2}{3k(T+\theta)} \tag{16}$$

with

$$\theta=2S(S+1)z[|J_{12}|+2|J_{13}|]/3k\ . \tag{17}$$

Discussion

The foregoing analysis shows that by taking the inherent anisotropy of tetragonally distorted spinels into account, it is possible to pin down a specific model of antiferromagnetic spin super-structure for such systems. Observations made on zinc manganite by Dr. Sabane[8)] of this Laboratory show a constant susceptibility below 300°K for field strength of the order of 4000 Oersteds.

For zinc ferrite, the difference between the interaction constants b_{12} and b_{13} is expected to be very small. Consequently the energy difference and the transition temperatures for the two antiferromagnetic spin super-structures, i.e. 1 and 2 of Fig. 1, will also be small. In view of the complexity of super-structure pattern for zinc ferrite as revealed by neutron diffraction[9)], it may be presumed that the two super-structures coexist in an otherwise uniform chemical system.

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* In the following, we confine our attention only to the super-structure which corresponds to E_1 and T_{c1}.