

presumably a pseudotetragonal to true tetragonal transformation occurs near 329°C. It is interesting to observe the change of the transformation temperature in these layer compounds: If we represent these compounds by $(1-x)\text{Bi}_4\text{Ti}_3\text{O}_{12} + x\text{BaTiO}_3$, the transformation temperature is almost a linear function of the composition concentration x (Fig. 4). The tetragonal cubic transformation temperature of 120°C is used for $x=1$ (BaTiO_3).

In conclusion, we have reported a new ferroelectric compound with a layer structure. This compound represents a layer structure with a largest number of layers reported to date. In fact, one of us (P.H.F.) in collaboration with R. S. Roth, has prepared materials with a composition such that if they form single phase, these compounds would have still larger number of

layers, such as the cases $m=6, 7$, and 9 . Preliminary results show that all these materials have two phases: one is the phase of $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, and the other one is a cubic perovskite phase. Therefore, we conclude for the present that, at least in the system which consists of BaO , Bi_2O_3 , and TiO_2 , prepared in the ordinary atmosphere, the largest possible number of layers is 5.

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Moriya Interaction and the Problem of the Spin Arrangements in βMnS^\dagger

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A study is made of the nature of the anisotropic superexchange interaction of the form $\mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j$ recently proposed by Moriya. This interaction is permitted in βMnS , with symmetry requiring that \mathbf{D}_{ij} be normal to the plane defined by i, j , and the single intervening anion. It is conjectured that this interaction leads to a screw spin arrangement, with a 90° screw angle; in crystals considered heretofore the Moriya energy produces only a slight canting. The observed powder neutron diffraction pattern has been interpreted as indicating ordering of the third kind with spins normal to the ordering axis; this arrangement, however, does not have minimum dipolar energy. The present proposed arrangement leads to the same diffraction pattern, and the Moriya energy probably overbalances the dipolar.

I. THE NATURE OF THE MORIYA INTERACTION

IT has been demonstrated by Moriya¹ that, under certain restricted symmetry conditions, the combination of spin-orbit and superexchange interactions can produce an effective coupling between neighbor spins \mathbf{S}_i and \mathbf{S}_j of the form

$$(E_M)_{ij} = \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j. \quad (1)$$

Here $\mathbf{D}_{ij} = -\mathbf{D}_{ji}$ is an axial vector, the precise form of which is derived in Moriya's paper and also below in Eq. (11).

It is illuminating to obtain the Moriya coupling from elementary configuration interaction. Let the ground-state configuration G involving neighbor spins \mathbf{S}_i and \mathbf{S}_j already contain whatever configuration mixing is required to produce an energy of the form

$$E_G = C_0 - 2J_0 \mathbf{S}_i \cdot \mathbf{S}_j, \quad (2)$$

where J_0 arises from direct exchange and/or superexchange, and C_0 is independent of spin directions. Thus it is assumed that the various configurations entering into the usual theory of superexchange² already have been incorporated into G . The theory is now extended to include a group of intermediate configurations I_n , I_m in which either atom i is raised to its n th excited state or atom j is raised to its m th excited state. The matrix element connecting G and a given configuration I_n will be of the form

$$\langle I_n | H | G \rangle = \lambda_n \mathbf{l}_{nG} \cdot \mathbf{S}_i - 2J_n \mathbf{S}_i \cdot \mathbf{S}_j + C_n, \quad (3)$$

and similarly for $\langle I_m | H | G \rangle$. Here J_n arises from direct and/or superexchange between configurations G and I_n , as will presently be discussed; C_n is independent of spin or orbit operators; and \mathbf{l}_{nG} is the appropriate orbital matrix element connecting the basis functions of G and I_n .

The basis functions of G and I_n , in this method, are to be taken as single products of one-electron orbitals,

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¹ T. Moriya, Phys. Rev. 120, 91 (1960).

² See, for example, F. Keffer and T. Oguchi, Phys. Rev. 115, 1428 (1959).

and not as Slater determinants. Thus the orbital matrix element appears explicitly in (3), whereas the spin is left in operator form. This is the Dirac-Van Vleck permutation operator expansion,² $\sum_P H_P P$, extended to include spin-orbit coupling terms in the direct integral H_{PI} , where P_I is the identity permutation.

The above spin-orbit expression is in the form most appropriate for a single electron and becomes more complicated if \mathbf{S}_i is the resultant spin of several electrons. The following paper by Pearson³ considers in detail the problem of Mn^{++} (spin $S=\frac{5}{2}$) in a tetrahedral environment; fortunately the complex results are not significantly different from those of the simple theory.

Moriya¹ has shown how J_n (his $b_{nn'}b_{m'n}$) arises in Anderson's⁴ new theory of superexchange. In general, however, in any theory of superexchange there will be Coulomb matrix elements, or combinations of matrix elements, and also overlap integrals, contributing to $\mathbf{S}_i \cdot \mathbf{S}_j$ dependent coupling between configurations G and I_n . Examples are given by Pearson.³ For both J_0 and J_n to be appreciable there must exist sizeable intra-atomic coupling to both the ground and excited orbitals of atom i . These orbitals are orthogonal; therefore if J_0 has its origin in σ -like bonding, J_n must arise from π -like bonding. Further details on the form of the multi-electron superexchange coupling are given in Pearson's paper.

The matrix elements \mathbf{l}_{nG} are imaginary, and therefore

$$\mathbf{l}_{nG} = -\mathbf{l}_{Gn}. \quad (4)$$

If the energy separation between ground and excited states of atom i or atom j is Δ_n or Δ_m , respectively, the perturbed ground-configuration energy is, in second order,

$$\begin{aligned} E_G^{(2)} &= E_G - \sum_n \Delta_n^{-1} \langle G | H | I_n \rangle \langle I_n | H | G \rangle \\ &\quad - \sum_m \Delta_m^{-1} \langle G | H | I_m \rangle \langle I_m | H | G \rangle \\ &= C - 2J\mathbf{S}_i \cdot \mathbf{S}_j - [\mathbf{A}_i \cdot \mathbf{S}_i, \mathbf{S}_i] \cdot \mathbf{S}_j \\ &\quad - [\mathbf{A}_j \cdot \mathbf{S}_j, \mathbf{S}_j] \cdot \mathbf{S}_i, \end{aligned} \quad (5)$$

where

$$\mathbf{A}_i \equiv 2 \sum_n \Delta_n^{-1} \lambda_n J_n \mathbf{l}_{nG}, \quad (6a)$$

$$\mathbf{A}_j \equiv 2 \sum_m \Delta_m^{-1} \lambda_m J_m \mathbf{l}_{mG}. \quad (6b)$$

Here C and J are very nearly equal to C_0 and J_0 , respectively, but include small contributions from the $C_n J_n$ and $(J_n)^2$ perturbation terms. The brackets represent negative commutators and equal $-i\mathbf{A}_i \times \mathbf{S}_i$ and $-i\mathbf{A}_j \times \mathbf{S}_j$, respectively. The spin-orbit coupling, in effect, modifies the exchange $\mathbf{S}_i \cdot \mathbf{S}_j$ so as to bring into play the additional components $\mathbf{A} \times \mathbf{S}$. One may think of each spin vector as having undergone the canonical transformation

$$\mathbf{S}' = T^{-1} \mathbf{S} T, \quad (7)$$

with T of the form

$$T = 1 + J_0^{-1} \mathbf{A} \cdot \mathbf{S}, \quad (8)$$

which brings the spin energy back into the simple expression

$$E_G^{(2)} = C_0 - 2J_0 \mathbf{S}'_i \cdot \mathbf{S}'_j. \quad (9)$$

Thus the configuration mixing transforms the problem into the exchange coupling of the twisted fictitious spins \mathbf{S}' .

Unless some asymmetry is present, the sums (6) will vanish, and this twisting effect will disappear. The geometry must distinguish between positive and negative scalar components of \mathbf{l}_{nG} along some direction. This direction cannot be simply defined by the polar vector \mathbf{r}_{ij} connecting atoms i and j , because \mathbf{A}_i and \mathbf{A}_j are axial vectors. Consequently there can be no Moriya-type coupling between two isolated atoms experiencing direct exchange, even if the atoms are nonidentical. There must exist indirect exchange through some third atom (or group of atoms) separated from i by the vector \mathbf{r}_{i3} ; and then the net \mathbf{A}_i will be along the axial vector defined by the cross product $\mathbf{r}_{i3} \times \mathbf{r}_{ij}$. Furthermore, some asymmetry must exist; the twisting will vanish, for example, if the indirect exchange involves two identical atoms at $|\mathbf{r}_{i3}| = |\mathbf{r}_{i4}|$ unless $(\mathbf{r}_{i3} + \mathbf{r}_{i4}) \times \mathbf{r}_{ij} \neq 0$.

The energy (5) may be expressed in the form

$$E_G^{(2)} = C - 2J\mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j, \quad (10)$$

with

$$\mathbf{D}_{ij} \equiv i(\mathbf{A}_i - \mathbf{A}_j). \quad (11)$$

The direction of \mathbf{D} (but not the sense) will be determined by whatever axial vector, or resultant of axial vectors, is implicit in the geometry of the atomic arrangements.⁵ A simple example will be given in the next section.

Third order perturbation connects configurations $G - I_n - I_m - G$ resulting in a coupling containing terms of the form

$$\sum_{n,m} (\lambda/\Delta)_n (\lambda/\Delta)_m K_{nm} (\mathbf{S}_i \cdot \mathbf{l}_{nG}) (\mathbf{l}_{mG} \cdot \mathbf{S}_j),$$

where K_{nm} is the combination of Coulomb matrix elements connecting the basis functions of I_n and I_m . The sums over n and m are here correlated via K_{nm} , and no special asymmetry is required for nonvanishing of the dyadic $\sum_{n,m} (\lambda/\Delta)_n (\lambda/\Delta)_m K_{nm} \mathbf{l}_{nG} \mathbf{l}_{mG}$. In fact, this dyadic has the same transformation properties as $C_{ij} \mathbf{r}_{ij} \mathbf{r}_{ij}$, and hence this interaction is a source of the Van Vleck pseudodipolar coupling.⁶ Moriya¹ gives an expression for the dyadic in the language of Anderson's new theory of superexchange.

We are here principally concerned, however, with the interaction of Eq. (1). This was introduced by Moriya to account for the weak ferromagnetism exhibited by some predominantly antiferromagnetic crystals, such as $\alpha\text{Fe}_2\text{O}_3$. Dzialoshinski⁷ had shown previously by a crystal magnetic symmetry argument that

⁵ We are indebted to Prof. M. Tinkham for pointing out to us this simple and extremely useful method of locating the direction of \mathbf{D} .

⁶ J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937).

⁷ I. Dzialoshinski, J. Phys. Chem. Solids **4**, 241 (1958).

³ J. J. Pearson, following paper [Phys. Rev. **126**, 901 (1962)].

⁴ P. W. Anderson, Phys. Rev. **115**, 2 (1959).

weak ferromagnetism can be an intrinsic magnetic property of certain crystals, and that it arises from a slight canting of the antiferromagnetic sublattices. According to Dzialoshinski's phenomenological theory, the canting is allowed provided the canted sublattice arrangement contains precisely the same symmetry elements (full magnetic group, involving the combination of crystal symmetry and time-reversal) as does the uncanted arrangement. This is possible only for certain—generally low—crystal symmetries. Moriya's interaction provides the mechanism for Dzialoshinski's possibility; the symmetry conditions required for the existence of nonzero \mathbf{D} are equivalent to those required for canting.

Moriya extended the theory to $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, a crystal which does not exhibit weak ferromagnetism. Instead, according to Moriya, it breaks up into *four* sublattices, arranged in such a double canting pattern that the total magnetic moment is zero.

Let θ_{ij} be a possible angle of cant between the sublattices containing \mathbf{S}_i and \mathbf{S}_j , respectively. In all crystals considered hitherto, including $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, the Moriya energy (proportional to $\sin\theta_{ij}$ and hence to θ_{ij} for small canting) opposes a large ferromagnetic or antiferromagnetic energy (proportional to $\cos\theta_{ij}$ and hence to $1 - \frac{1}{2}\theta_{ij}^2$). Thus as the sublattices bend away from alignment the lowering of Moriya energy outweighs the gain of exchange energy until an equilibrium angle of cant is reached, usually a small angle.

In the next section we discuss the situation in βMnS , where the Moriya energy is not conflicting with exchange energy, and the canting angles between some of the four sublattices may well be a full 90° .

II. PROPOSED SPIN ARRANGEMENT IN βMnS

The structure of βMnS -cubic is that of zinc blende. The lattice is composed of an fcc array of manganese atoms interpenetrating an fcc of sulphur atoms in such a way that every atom of one kind is surrounded tetrahedrally by atoms of the other kind. There exists no inversion symmetry, and in particular in $\{110\}$ planes the disposition of neighbors is that of Fig. 1. A single S^{--} ion lies off the line of cation centers. Thus, although the total crystal symmetry is high, the arrangement of neighbors allows a Moriya coupling. It is helpful to recall that if a unit cubic cell of zinc blende is divided into eight smaller cubes, only four of these have atoms at the center; if the other four contained center atoms there would be a balancing S^{--} below the line of cation

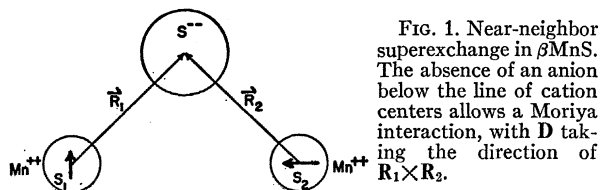


FIG. 1. Near-neighbor superexchange in βMnS . The absence of an anion below the line of cation centers allows a Moriya interaction, with \mathbf{D} taking the direction of $\mathbf{R}_1 \times \mathbf{R}_2$.

centers of Fig. 1, and no Moriya interaction would be possible.

The geometry of Fig. 1 defines an axial vector in the direction of $\mathbf{R}_1 \times \mathbf{R}_2$, i.e., normal to the plane of the figure; and, from the argument of Sec. I, it is clear that \mathbf{D}_{12} must lie in this direction. The Moriya energy of Eq. (1) will be a minimum when \mathbf{S}_1 and \mathbf{S}_2 are orthogonal, as shown in the figure. We have arbitrarily taken the *sense* of \mathbf{D}_{12} as opposite to that of $\mathbf{R}_1 \times \mathbf{R}_2$, i.e., as into the plane, and we shall maintain the convention throughout the lattice. If the actual sense, which cannot be determined from symmetry arguments, is out of the plane, the direction of $\mathbf{S}_1 \times \mathbf{S}_2$ must be reversed. This will have no significant effect on our conclusions, merely causing the proposed spin array to thread around in the opposite sense.

Let us now consider the four Mn^{++} neighbors surrounding a given S^{--} , such as is shown in the lower left of Fig. 2. Let \mathbf{r}_i be a unit vector in the direction of \mathbf{R}_i and note that all $\mathbf{r}_i \times \mathbf{r}_j$ are of magnitude $(8/9)^{1/2}$. Then the Moriya energy of the tetrahedron is

$$(E_M)_{\text{tet}} = (9/8)^{1/2} |\mathbf{D}| \sum_{i>j} (\mathbf{r}_i \times \mathbf{r}_j) \cdot (\mathbf{S}_i \times \mathbf{S}_j). \quad (12)$$

Since all Mn^{++} pairs are subject to the same isotropic superexchange, the exchange energy may be written

$$(E_E)_{\text{tet}} = -2J \sum_{i>j} \mathbf{S}_i \cdot \mathbf{S}_j \\ = -J[(\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4)^2 - 4S(S+1)]. \quad (13)$$

For negative J (antiferromagnetism) this energy will be a minimum if

$$\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4 = 0, \quad (14)$$

which condition can be achieved in a variety of ways.

The problem is to find the spin arrangement which minimizes $E_M + E_E$ for the entire lattice. It is not sufficient to consider a single tetrahedron, since neighbor tetrahedra overlap, i.e., have Mn^{++} ions in common. The variational problem is exceedingly complex, and we have not been able to find a rigorous solution.

By trial and error, however, we have arrived at a spin pattern which very likely has lowest energy. It is shown in Fig. 2 and, more clearly, in Fig. 3. The arrangement singles out a cube axis, which shall be called x . The spins then lie parallel to $\{100\}$ planes, with each plane containing an antiferromagnetic array. The spin direction of these arrays turns by 90° from plane to plane, the x axis being a sort of screw axis.

The arrangement obviously satisfies (14) and hence minimizes the dominant nearest-neighbor exchange energy. The much smaller Moriya energy is very low. Of the six spin-pairs summed over in Eq. (12), four make large noncancelling contributions and two yield zero, and the spin array is just such that E_M is the same for every tetrahedron in the lattice. One can easily find arrangements yielding lower $(E_M)_{\text{tet}}$ in a particular tetrahedron, but all such that we have considered yield a higher total E_M for all tetrahedra.

It should be pointed out that the spin directions of Figs. 2 and 3 have been drawn arbitrarily along the y and z axes. The pattern can be rotated by any angle about x without change of energy.

The Moriya energy automatically sets antiparallel the next-neighbor Mn^{++} ions along the x axis. Our arrangement has the same total near-neighbor plus next-neighbor exchange energy as does Anderson's⁸ "improved ordering of the first kind" (now called ordering of the third kind⁹). In fact, Anderson's pattern can be achieved if in Fig. 3 one rotates all spins which point along $\pm y$ so that they point along $\pm z$ (i.e., so that all spins lie parallel or antiparallel to a single axis), a process that obviously does not alter condition (14), although it reduces the Moriya energy to zero.

The observed powder neutron diffraction pattern of βMnS -cubic has been interpreted as indicating ordering of the third kind.¹⁰ However, the arrangement of Fig. 3 yields the same powder pattern, since the structure-factor cross terms between the set of z -directed spins and the set of y -directed spins average to zero in a powder. All that can be determined is that each of these sets of alternate $\{100\}$ planes has spins oriented normal to x . Single-crystal neutron diffraction can distinguish between our arrangement and uniaxial ordering of the third kind; however single crystals of βMnS -cubic would be exceedingly difficult to prepare. The αMnS is the stable form, and furthermore βMnS -cubic usually contains a high percentage of βMnS -hexagonal and also stacking faults.

We have not discussed βMnS -hexagonal, which has a powder pattern indicating a spin arrangement very similar to that of βMnS -cubic, differing in fact only in the stacking requirements of hexagonal and cubic close-packing.¹⁰ It is probable that the Moriya interaction also produces a screw arrangement in the hexagonal crystal.

It is unlikely that next-neighbor superexchange is very large in βMnS , since it must be routed through two intervening S^{--} ions. Therefore it is gratifying that the Moriya interaction of itself can cause the observed antiparallel orientation of those Mn^{++} ions which are next neighbors along x .

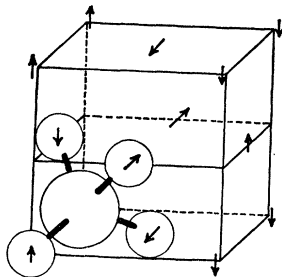


FIG. 2. Cubic cell of βMnS . Only the sulphur in the lowest left front corner is shown. The proposed arrangement of manganese spins is indicated by the arrows. (Also see Fig. 3.)

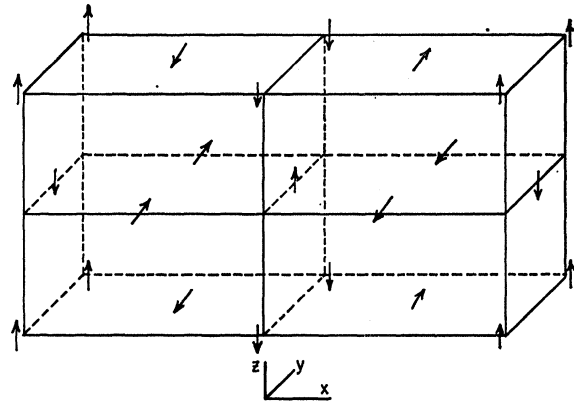


FIG. 3. Proposed spin arrangement in βMnS -cubic.

III. MORIYA ENERGY VERSUS DIPOLAR ENERGY

Because Mn^{++} is in the state ${}^6S_{5/2}$, there is probably very little anisotropy present in MnS other than the Moriya coupling and the magnetic dipole. As Moriya points out, anisotropy of the form (1) is first order in (λ/Δ) whereas single-ion and also pseudo-dipolar anisotropies are of order $(\lambda/\Delta)^2$. Since the fractional shift of the spectroscopic splitting factor g is also of order (λ/Δ) , Moriya estimates that

$$|\mathbf{D}| \sim |(g-2)/g|J. \quad (15)$$

This should be multiplied by a geometric factor related to the amount of asymmetry present, since (cf. Fig. 1) the S^{--} ion is far from the line of centers, the geometric factor will be close to unity.

In all forms of MnS , $(g-2)$ is very small. The value of the Curie-Weiss constant is not a reliable key to the value of g ; nevertheless it gives a rough indication of the order of magnitude of $(g-2)$. From the Curie constants given by Corliss, Elliott, and Hastings,¹⁰ we estimate

$$g \sim 1.97, 2.02, 2.07 \quad (16)$$

for α , β -cubic, and β -hexagonal MnS , respectively.

To estimate the size of $|\mathbf{D}|$ we shall take $(g-2)/g = 0.01$ and, from an analysis of Smart,¹¹ $J/k = 10.5^\circ\text{K}$. Then

$$|\mathbf{D}| \sim 1.5 \times 10^{-17} \text{ erg}. \quad (17)$$

Pearson's more detailed calculation³ yields a very rough result of about an order of magnitude smaller.

The strength of the Moriya interaction for the arrangement of Fig. 3 is, per atom and per cm^3 ,

$$\begin{aligned} E &= \frac{1}{2}(8)(0.707)\left(\frac{5}{2}\right)^2|\mathbf{D}| \\ &= 17.7|\mathbf{D}| \\ &\sim 25 \times 10^{-17} \text{ erg/atom} \\ &\sim 5.7 \times 10^6 \text{ erg/cm}^3, \end{aligned} \quad (18)$$

or perhaps an order of magnitude smaller (Pearson).

The only other anisotropy energy not dwarfed by

¹¹ J. S. Smart (to be published).

⁸ P. W. Anderson, Phys. Rev. **79**, 705 (1950).

⁹ J. S. Smart, Phys. Rev. **86**, 968 (1952).

¹⁰ L. Corliss, N. Elliott, and J. Hastings, Phys. Rev. **104**, 924 (1956).

this will be the magnetic dipole. Elsewhere¹² we have shown that the classical dipolar interaction energy of an array exhibiting uniaxial ordering of the third kind is given by

$$E_D = (\frac{1}{4}N\mu)^2[6.296 - 18.890\alpha^2], \quad (19)$$

where N is the number of dipoles per cm^3 , μ is the moment of each dipole, and α is the direction cosine between the common spin direction and the ordering axis (which we have taken along x). In βMnS -cubic this energy becomes

$$E = 4.36(1 - 3\alpha^2) \times 10^5 \text{ erg/cm}^3. \quad (20)$$

It was pointed out¹² that this sizeable energy is a minimum if the dipoles are parallel to x , whereas the neutron diffraction data¹⁰ give unequivocal evidence that the dipoles are perpendicular to x . We stated that we did not understand the source of an anisotropy large enough to overcome this dipolar energy.

We now propose that the Moriya energy twists the spins around into the arrangement of Fig. 3. The dipolar energy of this arrangement is given by Eq. (20), with $\alpha=0$. Thus the net dipolar energy to be overcome is

$$\Delta E_D = 1.3 \times 10^6 \text{ erg/cm}^3, \quad (21)$$

which is smaller than (18), but larger than Pearson's estimate. The situation is admittedly nip and tuck; but if E_M is not sufficient to bring the spins into a pattern consistent with the neutron diffraction results,

then we still don't understand this paradoxical situation. Surely any crystal-field type single-ion anisotropy would not prefer some direction in the yz plane, when from symmetry it could as well pick out an equivalent direction with $\alpha \neq 0$ and thus take advantage of the dipolar energy. And besides, as we have pointed out, such an anisotropy should be much smaller than E_M . Furthermore, large pseudodipolar anisotropy seems out of the question.

If E_M only slightly exceeds ΔE_D , the spin arrangement will be some compromise, which might be hard to distinguish by neutron diffraction. Furthermore, the temperature dependence of E_M will be different from that of E_D , and the ordering arrangement may bend with temperature.

It is interesting to consider the situation in MnS_2 . The pyrite structure has inversion symmetry through the center of the unit cube and also through any Mn site. This results in $E_M=0$ for the arrangement of Fig. 3. Perhaps other slightly canted arrangements are possible, with small E_M . There does exist an asymmetry, such as shown in Fig. 1, in the disposition of nearest neighbors. However, the next-neighbor superexchange should be large in this lattice; and an antiparallel next-neighbor ordering along x , together with the inversion, would make large total E_M impossible. It is therefore significant that the neutron diffraction experiment¹³ reveals ordering of the third kind with spins parallel to x , i.e., minimum dipolar energy.

¹² F. Keffer and W. O'Sullivan, Phys. Rev. **108**, 637 (1957).

¹³ J. Hastings, N. Elliott, and L. Corliss, Phys. Rev. **115**, 13 (1959).