

present results on phosphorescence so that it may well represent the true situation.

The examination of anisotropic phosphorescence indicates that there is certainly a center other than the V_1 center present in KCl x-rayed at 77°K which has an axis of symmetry along [011]. Moreover, this center can absorb light at 3650 Å and can be bleached anisotropically. Its absorption properties are therefore anisotropic even though this could not be observed directly in x-rayed KCl but is implied by the phosphorescent behavior. Further, the anisotropic phosphorescence disappears in the same temperature region as the V_1 center so that the center responsible for the phosphorescence may also disappear in this region. Thus, this center would have thermal-bleaching properties very similar to the V_1 center.

The results on electron-bombarded crystals are in agreement with the above findings. The same anisotropic phosphorescence is found and in this case the small induced dichroism indicated the presence of an anisotropic center. The fact that dichroism could be observed directly in electron-bombarded crystals is

probably due to the higher coloration obtained which makes the experimental observation simpler.

The results of KCl(Tl) are rather suggestive. It was noted that for KCl(Tl)⁵ one observes an x-ray induced resonance signal quite like that reported by Känzig. It is much more intense than in pure KCl for the same amount of x-raying. Our results show that one can easily find induced dichroism and anisotropic phosphorescence in this case. Thus, it is possible that the center in KCl(Tl) which shows noncubic symmetry in resonance is also manifested in the observed dichroism and anisotropic phosphorescence. It should be noted that phosphorescence in KCl(Tl) is shifted in wavelength from that found in pure KCl. This indicates that the centers involved are not identical.

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Problem of Spin Arrangements in MnO and Similar Antiferromagnets*

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The magnetic dipolar energy is computed for ordering of the second kind with the four antiferromagnetic sublattices of a face-centered cube making arbitrary spin directions with respect to one another, and this energy is shown to be of the same form in the sublattice direction cosines as is the calculated powder neutron-diffraction pattern. (The dipolar energy is also calculated for ordering of the third kind and shown to lead to a spin arrangement in disagreement with powder neutron-diffraction results on β MnS.) The observed neutron patterns in MnO and α MnS agree with minimum dipolar energy, but many spin arrangements can satisfy this and the spins are constrained only to certain regions. Other sources of anisotropy in Mn^{++} salts are shown to be much weaker. A model is introduced in which the spins are constrained by dipolar

and exchange forces to point parallel to (111) planes and constrained by the weaker anisotropy to a threefold set of easy axes within these planes. Nagamiya's small-field approximation for the field dependence of the powder susceptibility of a uniaxial antiferromagnet is extended to all values of the applied field, and a similar calculation is made for the powder susceptibility of our MnO model. Comparison with experimental data indicates that the weak within-plane anisotropy is $\sim 3 \times 10^4$ ergs/cm³ which is to be contrasted with the theoretical out-of-plane dipolar anisotropy of 10^7 ergs/cm³. A rough theory of antiferromagnetic resonance for our model seems to explain the partial paramagnetic-like absorption observed below the Néel point.

I. INTRODUCTION

THE problem of the arrangement of spins in antiferromagnetic MnO, and in the similar crystals α MnS and α MnSe, is not simple, and it will most likely remain somewhat unsettled until good single crystals are available for experimental study.

Neutron diffraction experiments give unquestioned evidence that the ordering in MnO is of the second kind,

that is, coordination of next-nearest neighbors.^{1,2} However, the problem of the direction in which the spins point (or multidirections, since the system can be divided into many sublattices) remains entirely open. The original neutron evidence¹ suggested an arrangement in which all spins pointed along [100] directions. Subsequently Kaplan³ showed that in ordering of the

¹ Shull, Strauser, and Wollan, *Phys. Rev.* **83**, 333 (1951).

² For an excellent review of antiferromagnetism, which we shall quote throughout this paper, see Nagamiya, Yosida, and Kubo, in *Advances in Physics* (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 1.

³ J. I. Kaplan, *J. Chem. Phys.* **22**, 1709 (1954).

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second kind the magnetic dipolar interactions should in theory align the spins parallel to (111) planes.

In MnO, in which the ionic configuration $Mn^{+2}O^{--2}$ should at least predominate, the Mn ions are for the most part in S states, and it is difficult to find any source of anisotropy that can compete with the magnetic dipolar interactions. Fortunately some recent Brookhaven neutron diffraction experiments on MnO, NiO, and α MnS suggest a (111)-plane arrangement, although Roth has pointed out that multi-spin axes will also fit the powder data and are perhaps to be preferred for the single-crystal data available only in NiO.^{4,5}

Kaplan showed that the dipolar energy constraining spins to (111) planes (for his single spin-axis model) should be of the order of 10^7 ergs/cm³. This large anisotropy disagrees with a much smaller anisotropy ($\sim 10^6$ ergs/cm³) estimated by Nagamiya⁶ from the field dependence of the powder susceptibility of MnO, as observed by Bizette, Squire, and Tsai.⁷

In this paper we reconcile Nagamiya's calculation and the large dipolar anisotropy by introducing a model in which, in addition to Kaplan's (111)-plane constraint, a much weaker anisotropy selects preferred directions in those planes.

But first we derive the dipolar anisotropy for a multi-spin axis arrangement in both ordering of the second kind and ordering of the third kind. We then estimate the magnitude of other sources of anisotropy from rather general considerations. After a discussion of the relation of the powder neutron-diffraction problem to the dipolar problems, we introduce our model in some detail. In the last two sections we apply this model to calculations of the powder susceptibility and antiferromagnetic resonance.

II. DIPOLAR ANISOTROPY FOR FACE-CENTERED CUBE

A. Ordering of the Second Kind

We compute the dipolar anisotropy for the general case of ordering of the second kind when the four cubic sublattices are allowed to take arbitrary directions with respect to each other. Let the direction of the i th sublattice be given by the direction cosines α_i , β_i , γ_i . Following Luttinger and Tisza,⁸ we may denote each sublattice by

$$\alpha_i \mathbf{X}_8 + \beta_i \mathbf{Y}_8 + \gamma_i \mathbf{Z}_8,$$

where, for example, \mathbf{Z}_8 means a cubic antiferromagnetic array aligned in the z direction. It proves convenient to take as origins of the arrays the four points

$$(0, 0, 1) \quad (\frac{1}{2}, \frac{1}{2}, 0), \quad (0, \frac{1}{2}, \frac{1}{2}), \quad (\frac{1}{2}, 0, \frac{1}{2}).$$

⁴ Corliss, Elliott, and Hastings, *Phys. Rev.* **104**, 924 (1956).

⁵ W. L. Roth, *Bull. Am. Phys. Soc. Ser. II*, **2**, 119 (1957).

⁶ T. Nagamiya, *Progr. Theoret. Phys. Japan* **4**, 342 (1951).

⁷ Bizette, Squire, and Tsai, *Compt. rend.* **207**, 449 (1938). Their data is reproduced as Fig. 7 of reference 2. The units for the susceptibility, omitted in the figure, are g^{-1} .

⁸ J. M. Luttinger and L. Tisza, *Phys. Rev.* **70**, 954 (1946); **72**, 257(E) (1947).

Luttinger and Tisza have shown that the field at our second array resulting from our first array is given by

$$\frac{1}{4} N \mu (-\alpha_1 \mathbf{Y}_8 - \beta_1 \mathbf{X}_8) h_4,$$

where $\frac{1}{4} N$ is the number of dipoles per unit volume on an array, μ is the moment of each dipole, and

$$h_4 = 14.461. \quad (1)$$

Hence the interaction energy between arrays 1 and 2 will be given by

$$\begin{aligned} U_{12} &= (\frac{1}{4} N \mu)^2 (\alpha_1 \mathbf{Y}_8 + \beta_1 \mathbf{X}_8) \cdot (\alpha_2 \mathbf{X}_8 + \beta_2 \mathbf{Y}_8 + \gamma_2 \mathbf{Z}_8) \\ &= (\frac{1}{4} N \mu)^2 (\alpha_1 \beta_2 + \beta_1 \alpha_2) h_4. \end{aligned}$$

Similarly

$$\begin{aligned} U_{13} &= (\frac{1}{4} N \mu)^2 (\beta_1 \gamma_3 + \gamma_1 \beta_3) h_4, \\ U_{14} &= (\frac{1}{4} N \mu)^2 (\alpha_1 \gamma_4 + \gamma_1 \alpha_4) h_4, \\ U_{23} &= (\frac{1}{4} N \mu)^2 (\alpha_2 \gamma_3 + \gamma_2 \alpha_3) h_4, \\ U_{24} &= (\frac{1}{4} N \mu)^2 (\beta_2 \gamma_4 + \gamma_2 \beta_4) h_4, \\ U_{34} &= (\frac{1}{4} N \mu)^2 (\alpha_3 \beta_4 + \beta_3 \alpha_4) h_4, \\ U_{ii} &= 0, \quad i=1, 2, 3, 4. \end{aligned}$$

The total dipolar interaction energy will be the sum of the above energies, which may be written as

$$U = \frac{1}{2} (\frac{1}{4} N \mu)^2 h_4 [(\alpha_1 + \beta_2 + \gamma_4)^2 + (\alpha_2 + \beta_1 + \gamma_3)^2 + (\alpha_3 + \beta_4 + \gamma_2)^2 + (\alpha_4 + \beta_3 + \gamma_1)^2 - 4]. \quad (2)$$

This energy is obviously a minimum if

$$\begin{aligned} \alpha_1 + \beta_2 + \gamma_4 &= 0, \\ \alpha_2 + \beta_1 + \gamma_3 &= 0, \\ \alpha_3 + \beta_4 + \gamma_2 &= 0, \\ \alpha_4 + \beta_3 + \gamma_1 &= 0, \end{aligned} \quad (3)$$

and the minimum energy is given by

$$\begin{aligned} U_{\min} &= -2h_4 (\frac{1}{4} N \mu)^2 \\ &= -1.807 (N \mu)^2. \end{aligned} \quad (4)$$

We note that in the special case that all four arrays are in the same direction, Eq. (2) reduces to

$$U' = 3.615 (N \mu)^2 (\alpha\beta + \beta\gamma + \gamma\alpha). \quad (5)$$

This result was first obtained by Kaplan,⁹ his numerical constant being 3.588. In this special case, as noted by Kaplan, the minimum condition on direction is

$$\alpha_i + \beta_i + \gamma_i = 0, \quad (6)$$

and hence all dipoles point parallel to (111) planes.

We have so chosen our origins of the four arrays that for the above case the dipoles in any (111) plane all point in the same sense, an arrangement which Li⁹ calls ordering of the second kind, type A . It is possible to have all dipoles parallel without having a unique sense on any set of {111} planes, or what Li calls ordering of

⁹ Y-Y Li, *Phys. Rev.* **100**, 627 (1955).

the second kind, type *B*. In this case

$$\begin{aligned}\alpha_2 &= \alpha_3 = \alpha_4 = -\alpha_1, \\ \beta_2 &= \beta_3 = \beta_4 = -\beta_1, \\ \gamma_2 &= \gamma_3 = \gamma_4 = -\gamma_1,\end{aligned}$$

and Eq. (2) gives $U=0$, regardless of direction. This complete absence of dipolar anisotropy for type-*B* ordering has been noted by Li.

If the arrays are allowed to take various directions with respect to each other, there are many possible solutions to Eq. (3) besides the conditions represented by Eq. (6).

We note that Eq. (3) defines only a general region of minimum anisotropy, not a single direction. Thus, under dipolar anisotropy alone, the spins will always have considerable freedom of movement. In the next section we discuss possible restrictions on this freedom which may arise from other sources of anisotropy.

B. Ordering of the Third Kind

In ordering of the third kind, or "improved ordering of the first kind," each of the four basic arrays building the face-centered cube has alternate planes (which we take as *yz* planes) of up and down dipoles. The arrays may not take arbitrary directions with respect to each other, however, as each site of the face-centered cube must be surrounded by 8 antiparallel and 4 parallel dipoles (nearest-neighbor correlation). In the Luttinger and Tisza notation, the arrays are of the form

$$\alpha_i \mathbf{X}_2 + \beta_i \mathbf{Y}_3 + \gamma_i \mathbf{Z}_3,$$

with

$$\begin{aligned}(\alpha_1, \beta_1, \gamma_1) &= -(\alpha_3, \beta_3, \gamma_3), \\ (\alpha_2, \beta_2, \gamma_2) &= -(\alpha_4, \beta_4, \gamma_4).\end{aligned}\quad (7)$$

We have taken origin points as in Sec. II A, above.

Using the Luttinger-Tisza field factors, we find

$$U_{13} = (\frac{1}{4}N\mu)^2(2\alpha_1\alpha_3 - \beta_1\beta_3 - \gamma_1\gamma_3)h_2,$$

$$U_{24} = (\frac{1}{4}N\mu)^2(2\alpha_2\alpha_4 - \beta_2\beta_4 - \gamma_2\gamma_4)h_2,$$

$$U_{12} = U_{14} = U_{34} = 0,$$

$$U_{ii} = -\frac{1}{2}(\frac{1}{4}N\mu)^2[f_3 + \alpha_i^2(f_2 - f_3)], \quad i = 1, 2, 3, 4,$$

where

$$h_2 = 7.992; \quad f_2 = -9.687; \quad f_3 = 4.844. \quad (8)$$

The total dipolar interaction energy is the sum of the above, and on invoking Eq. (7) we find

$$U = (\frac{1}{4}N\mu)^2[6.296 - 9.445(\alpha_1^2 + \alpha_2^2)]. \quad (9)$$

This is a minimum when $\alpha_1^2 = \alpha_2^2 = 1$, or when all dipoles are parallel to the *x* axis.

Corliss, Elliott and Hastings⁴ have studied the ordering of β MnS (zinc-blende structure) by using neutron diffraction. They find ordering of the third kind with, however, spins *perpendicular* to the *x* axis. We do not understand the source of an anisotropy large enough to

overcome the energy represented by Eq. (9). Spin-orbit coupling effects should be small in MnS. However, since the antiferromagnetic pattern has a unique direction in ordering of the third kind, it is possible that the superexchange mechanism itself may lead to nonisotropic terms.

III. OTHER SOURCES OF ANISOTROPY

A. Dipolar Anisotropy from Lattice Distortion

It is known that the face-centered cubic antiferromagnetic manganese salts distort along a [111] direction below the Néel point, that is, they undergo structural transitions to rhombohedral symmetry.¹⁰ This distortion, which is of the order of magnitude of a fraction of 1%, will perturb the dipolar anisotropy.

It is generally assumed that for ordering of type *A* the distortion is perpendicular to that set of (111) planes characterizing the order.¹¹ In this case the perturbed anisotropy energy must be of the form

$$\text{constant}(\alpha\beta + \beta\gamma + \gamma\alpha).$$

This is because dipole-dipole interactions can lead at most to an energy expression quadratic in the direction cosines (unless, as we discuss below, higher-order quantum-mechanical effects are considered), and the dipole array has threefold symmetry about the axis of distortion and symmetry for inversion of all dipoles. We have verified this by a rather lengthy perturbation calculation and find that Eq. (5) becomes

$$U' = [3.615 + 8.8\Delta](N\mu)^2(\alpha\beta + \beta\gamma + \gamma\alpha), \quad (10)$$

where Δ is the fractional increase in cube diagonal. We have assumed an accompanying decrease in dimensions perpendicular to this diagonal such that the density is unchanged.

B. Speculations on the Cause of Lattice Distortions

Smart and Greenwald¹¹ have argued that antiferromagnets with ordering of the second kind, type *A*, will distort perpendicular to the ordered (111) planes so as to minimize the exchange energy. It is claimed that such a distortion, since it uniformly changes the distance between sheets of up-spins and neighbor sheets of down-spins, will sufficiently lower the exchange energy to make type-*A* order distinctly preferable to type *B*, where no such alternate sheets of up and down spins exist.

Li,⁹ on the other hand, has argued that the distortion is probably due to anisotropic forces. We wish to point out that there are good theoretical reasons for doubting if anything other than exchange forces could cause a distortion approaching the magnitude of that observed. The change to rhombohedral symmetry may be thought

¹⁰ N. C. Tombs and H. P. Rooksby, *Nature* **165**, 442 (1950).

¹¹ J. S. Smart and S. Greenwald, *Phys. Rev.* **82**, 113 (1951).

of as a shear through an angle of a few thousandths of a radian. The energy involved, per cm^3 , will be of the order of this angle multiplied by the shear modulus. Taking as a conservative estimate a modulus of 10^{11} dynes/cm², we arrive at an energy of 10^7 to 10^8 ergs/cm³. In the absence of large spin-orbit coupling only the exchange energy can decrease, under a small distortion, by this order of magnitude.

C. Remainder of the Anisotropy

In a discussion of the problem of MnF_2 , we have listed some other sources of anisotropy in antiferromagnets with predominately *S*-like magnetic ions.¹² The principle mechanism invoked for MnF_2 involved the interaction between excited states of Mn^{++} and the tetragonal crystalline field, and led to an anisotropy energy of the order of 5×10^5 ergs/cm³ (about 1/10 of the magnetic dipolar anisotropy).

Since the crystalline field in MnO , apart from the small effect of the distortion, has cubic symmetry, the anisotropic interaction with excited states of Mn^{++} will be a higher order perturbation than in MnF_2 , and will lead to an anisotropy energy considerably smaller in magnitude.

On the other hand, MnO is not as ionic as MnF_2 , and a considerable anisotropy may arise from spin-orbit coupling in the nonionic configurations. This sort of interaction would also affect the *g* factor, and since both susceptibility and microwave resonance measurements indicate a value of *g* very close to 2, we estimate that the anisotropy energy is $\sim 10^5$ ergs/cm³ or less. This rough estimate is based on the Kittel-Van Vleck approximation of anisotropic exchange coupling of order of magnitude $(g-2)^2$ times the exchange energy.¹³

The nonclassical part of the dipolar interaction will be a further source of anisotropy.¹⁴ This yields an energy of order $0.05(N^2\mu^2/S)$ or $\sim 10^5$ ergs/cm³, and it has a very complicated directional dependence.¹⁵

All of the above anisotropies will have terms of the form of Eq. (10). In addition, they will have terms of higher order in the direction cosines which should pin down the spins to certain preferred orientations within the (111) planes.

IV. POWDER NEUTRON-DIFFRACTION PATTERN

We calculate the powder neutron-diffraction pattern to be expected from ordering of the second kind with arbitrary orientation of the four dipolar arrays with respect to each other.

The structure factor for scattering from an (*hkl*) plane is¹⁶

$$S_{hkl} = \sum_i a_i \exp[2\pi i(hu_i + kv_i + lw_i)], \quad (11)$$

¹² F. Keffer, Phys. Rev. **87**, 608 (1952).

¹³ J. H. Van Vleck, J. phys. radium **12**, 262 (1951).

¹⁴ J. Tesson, Phys. Rev. **96**, 1192 (1954).

¹⁵ M. H. Cohen and F. Keffer, Phys. Rev. **99**, 1135 (1955). The calculation in this paper is for ferromagnetism, but antiferromagnetism should be very similar.

¹⁶ O. Halpern and M. H. Johnson, Phys. Rev. **55**, 898 (1939).

where a_i is the magnetic scattering amplitude from a dipole at (u_i, v_i, w_i) and is given by

$$a_i = \mathbf{e} \cdot \boldsymbol{\kappa}_i \mathbf{e} \cdot \mathbf{s} - \boldsymbol{\kappa}_i \cdot \mathbf{s}. \quad (12)$$

Here \mathbf{e} is a unit vector perpendicular to the scattering plane, $\boldsymbol{\kappa}_i$ is a unit vector in the spin direction of the *i*th dipole, and \mathbf{s} is the spin of the neutron.

The sum in Eq. (11) is over all dipoles of the unit magnetic cell. We have four basic arrays of the Luttinger-Tisza type \mathbf{Z}_8 (see Sec. IIA). The common part of the structure factor of all four arrays is

$$(1 - e^{\pi i h})(1 - e^{\pi i k})(1 - e^{\pi i l}),$$

which equals 8 if *h, k, l* are all odd, zero otherwise. Thus,

$$S_{hkl} = 8[a_1 e^{\pi i l} + a_2 e^{\frac{1}{2}\pi i(h+k)} + a_3 e^{\frac{3}{2}\pi i(k+l)} + a_4 e^{\frac{5}{2}\pi i(h+l)}], \quad [h, k, l \text{ all odd}] \quad (13)$$

where $a_1 \cdots a_4$ are scattering amplitudes characteristic of the origin points of the four basic arrays. (We choose origins as in Sec. IIA.)

For unpolarized neutrons we may average $|S_{hkl}|^2$ over all directions of \mathbf{s} . We use the relation

$$\langle 4a_i a_j \rangle_{\mathbf{s}} = \boldsymbol{\kappa}_i \boldsymbol{\kappa}_j - \mathbf{e} \cdot \boldsymbol{\kappa}_i \mathbf{e} \cdot \boldsymbol{\kappa}_j.$$

A further average is then taken over $\pm h, \pm k, \pm l$ and over permutations of *h, k, l* as is appropriate for a powder pattern. After a few algebraic manipulations, we obtain

$$\langle |S_{hkl}/8|^2 \rangle_{\mathbf{s}} = \frac{2}{3} + [(\alpha_1 + \beta_2 + \gamma_4)^2 + (\alpha_2 + \beta_1 + \gamma_3)^2 + (\alpha_3 + \beta_4 + \gamma_2)^2 + (\alpha_4 + \beta_3 + \gamma_1)^2 - 4] P_{hkl}, \quad [h, k, l \text{ all odd}] \quad (14)$$

where

$$P_{hkl} = (i^{h+k}hk + i^{k+l}kl + i^{h+l}hl) / [12(h^2 + k^2 + l^2)].$$

We note with astonishment that the expression in square brackets in (14) is identical to that in (2). If we assume any of the arrangements, given by Eq. (3), which lead to minimum dipolar anisotropy, we have a powder pattern independent of the precise nature of the multi-spin axis orientations.

Roth has shown that the observed powder pattern seems to be consistent with a value of -4 for the bracket in Eq. (14); and we note that this value corresponds to minimum dipolar anisotropy. Further information on the spin orientations awaits single-crystal diffraction measurements, although even here the analysis may be obscured by possible domain effects.¹⁷

V. PROPOSED SPIN MODEL

We have noted that various arrangements satisfy both minimum dipolar anisotropy and the powder neutron-diffraction pattern. However, only the arrangement of all spins parallel (type *A*) seems to explain the distortion below the Néel point. This distortion should

¹⁷ We wish to thank Dr. W. L. Roth for a most informative discussion of the neutron diffraction problem.

couple the four arrays to one another, inasmuch as it upsets the zero balance of nearest-neighbor exchange forces. And the coupling should compel all four arrays to point in the same direction. Therefore we shall assume a single spin axis and hence all spins constrained by the dipolar energy to be parallel to (111) planes.

We consider two types of anisotropy: (1) the large dipolar energy given by Eq. (10), and (2) a much smaller energy coming from sources discussed in Sec. III. This latter anisotropy will select special minimum directions within the (111) planes, and because of the threefold symmetry (and in addition the twofold up-down symmetry of antiferromagnetism) its leading term will be of the form

$$U'' = -\frac{1}{2}K_2 \cos 6\eta, \quad (15)$$

where η is the planar angle between the actual spin direction and a preferred direction. In addition this latter anisotropy will add a small correction to the numerical constant in Eq. (10), and we may write the out-of-plane anisotropy in the form

$$U' = K_1(\alpha\beta + \beta\gamma + \gamma\alpha). \quad (16)$$

Except for small corrections,

$$K_1 \approx 3.615(N\mu)^2. \quad (17)$$

For MnO, $\mu = 5\beta = 4.64 \times 10^{-20}$ erg/oersted, $N = 4.59 \times 10^{22}$ Mn atoms/cm³, and

$$K_1 \approx 1.64 \times 10^7 \text{ ergs/cm}^3, \quad (18)$$

a result first obtained by Kaplan.³ This applies, of course, only to a sample at 0°K, and K_1 should drop with the square of the sublattice magnetization as the temperature rises.

We expect K_2 to be very much smaller, of the order of 10^4 to 10^5 ergs/cm³.

Arrangements other than all dipoles parallel to (111) planes, but which satisfy minimum dipolar anisotropy, will also be expected to have a large energy constraining the spins to certain regions, and a much smaller energy picking out certain directions. Therefore, although such arrangements would modify the details of the calculations in the next sections, they should not affect the general nature of the results.

VI. FIELD DEPENDENCE OF POWDER SUSCEPTIBILITY: UNIAXIAL SYMMETRY

The problem of the field dependence of the powder susceptibility of an antiferromagnetic material with uniaxial symmetry has been solved for small applied fields by Nagamiya.⁶ Before considering our complex spin model of MnO, we wish to generalize his calculation to all field values. This is necessary since we assume K_2 to be so small that Nagamiya's approximations will no longer apply.

In the two-sublattice molecular-field approximation

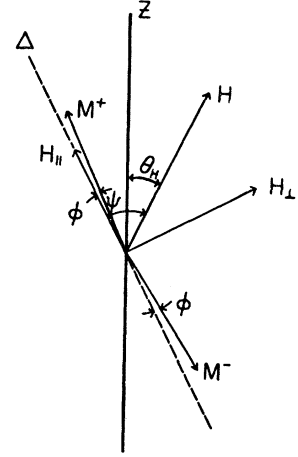


FIG. 1. Definition of angles used in Eq. (19).

the free energy of the system of spins is very nearly

$$F \approx -\frac{1}{2}H^2(\chi_{11} \cos^2\psi + \chi_{\perp} \sin^2\psi) - \frac{1}{2}K \cos[2(\psi - \theta_H)] + \text{const.} \quad (19)$$

Here the notation is that of reference 2. The angles are defined by Fig. 1, and we assume ϕ very small. This amounts to the usual assumption that the molecular field is very much larger than either the applied field H or the anisotropy "field" K/M .

We introduce the well-known "critical field"

$$H_c = [2K/(\chi_{\perp} - \chi_{11})]^{1/2}, \quad (20)$$

which is the value of the field H which, applied parallel to the preferred spin direction, causes the spins suddenly to flop to a position orthogonal to H . For convenience we measure H in units of H_c :

$$h = H/H_c. \quad (21)$$

The minimum condition on F with respect to ψ is

$$h^2 = \sin[2(\psi - \theta_H)]/\sin 2\psi. \quad (22)$$

The component of induced magnetization along the direction of the applied field is

$$M_H = \chi_{11}H + (\chi_{\perp} - \chi_{11})H \sin^2\psi, \quad (23)$$

and the powder susceptibility is given by a spherical average of M_H/H :

$$\chi_p = \chi_{11} + (\chi_{\perp} - \chi_{11}) \langle \sin^2\psi \rangle_{\text{av}}.$$

From (22) we have

$$\sin^2\psi = \frac{1}{2} + \frac{1}{2}(h^2 - \cos 2\theta_H)/(1 - 2h^2 \cos 2\theta_H + h^4)^{1/2}, \quad (24)$$

which must be averaged over all values of θ_H . The result is

$$\chi_p = \chi_{11} + (\chi_{\perp} - \chi_{11}) \left[\frac{1}{2} + \frac{h^2 - 1}{8h^2} + \frac{(h^2 + 1)(3h^2 - 1)}{16h^3} \sin^{-1} \left(\frac{2h}{h^2 + 1} \right) \right]. \quad (25)$$

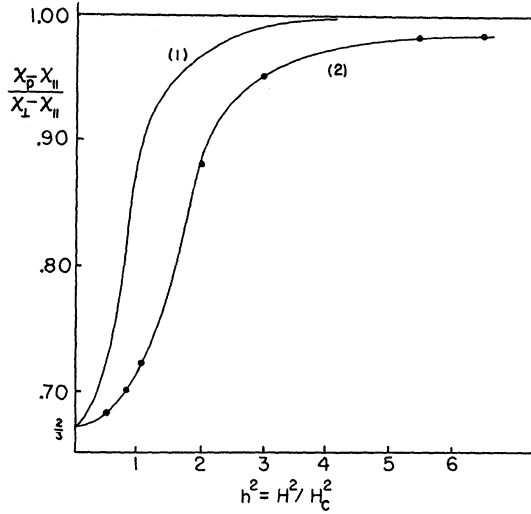


FIG. 2. Powder susceptibility as a function of applied field. Curve (1) for the case of uniaxial symmetry, Eq. (25), with H_c defined by Eq. (20). Curve (2) for the case of magnetization constrained to a plane of threefold symmetry, Eq. (31) numerically integrated, with H_c defined by Eq. (32).

Nagamiya's result follows from (25) with the assumption that $h^2 \ll 1$:

$$\chi_p \approx \chi_{11} + (\chi_1 - \chi_{11}) \left[\frac{2}{3} + (4/15)h^2 \right], \quad [h^2 \ll 1]. \quad (26a)$$

In addition we have

$$\chi_p \approx \chi_{11} + (\chi_1 - \chi_{11}) \left[\frac{1}{2} + (\pi/8) \right], \quad [h^2 = 1], \quad (26b)$$

and

$$\chi_p \approx \chi_{11} + (\chi_1 - \chi_{11}) \left[1 - (2/15)h^4 \right], \quad [h^2 \gg 1]. \quad (26c)$$

The general expression (25) is plotted as curve (1) in Fig. 2. The curve has an inflection point at $h^2 = 1$, which is the powder-susceptibility analog of the single-crystal flop.

VII. FIELD DEPENDENCE OF POWDER SUSCEPTIBILITY: MAGNETIZATION CONSTRAINED TO A PLANE

A. General Case

We now consider the case of a very large anisotropy constraining the magnetization to a plane of m -fold symmetry, and a much smaller anisotropy within the plane. (This is our model of MnO with $m=3$.)

We assume that the applied field H is small compared to the anisotropy "field" K_1/M for motion out of the plane, but not small compared to the within-plane "field" K_2/M . Under this condition the sublattice magnetization vectors will swing about within the plane. Let H make the angle θ_1 with the normal to the plane, and let the projection $H \sin \theta_1$ make the angle θ_2 with respect to the preferred axis. Then the free energy for motion within the plane will be given by

$$F \approx -\frac{1}{2}H^2 \sin^2 \theta_1 (\chi_{11} \cos^2 \psi + \chi_1 \sin^2 \psi) - \frac{1}{2}K_2 \cos[2m(\psi - \theta_2)] + \text{const.} \quad (27)$$

The critical field for the case $\theta_2=0$ can be found by expanding (27) about $\epsilon = (\psi - 0)$:

$$F \sim -\frac{1}{2}H^2 \sin^2 \theta_1 + [K_2 m^2 - \frac{1}{2}H^2 \sin^2 \theta_1 (\chi_1 - \chi_{11})] \epsilon^2 + \text{const.} \quad (28)$$

It is seen that the magnetization vectors will flop when $H \sin \theta_1$ reaches

$$H_c' = [2m^2 K_2 / (\chi_1 - \chi_{11})]^{1/2}. \quad [\theta_2 = 0]. \quad (29)$$

However, we show below that for other values of θ_2 the critical field for a flop may be smaller than (29).

The minimum within-plane direction will be given by the following analog of Eq. (22):

$$\frac{H^2 \sin^2 \theta_1}{[2mK_2 / (\chi_1 - \chi_{11})]} = \frac{\sin 2m(\psi - \theta_2)}{\sin 2\psi}; \quad (30)$$

and the powder susceptibility will be the following spherical average:

$$\chi_p = \langle (\chi_{11} \cos^2 \psi + \chi_1 \sin^2 \psi) \sin^2 \theta_1 + \chi_1 \cos^2 \theta_1 \rangle_{\text{AV}} = \frac{2}{3}\chi_{11} + \frac{1}{3}\chi_1 + (\chi_1 - \chi_{11}) \langle \sin^2 \psi \sin^2 \theta_1 \rangle_{\text{AV}}. \quad (31)$$

Before performing this spherical average one must of course solve Eq. (30) for $\sin^2 \psi$ as a function of θ_1 and θ_2 . For values of $m > 1$ the expression is very complicated and χ_p is most easily obtained by numerical integration.

For cases $m > 1$ hysteresis effects should appear if the applied field ever exceeds the critical field. That is, above H_c the magnetization direction snaps to easy axes more nearly perpendicular to H (and such axes will exist for $m > 1$); and therefore on lowering H a powder susceptibility should be observed that is much closer to χ_1 than is that of a randomly oriented sample.

B. Application to Our Model ($m=3$)

For our proposed (111)-plane constraint the value of m is 3, and Eq. (30) is cubic in $\cos^2(2\psi)$. Examination of the values of H and θ_2 for which the discriminant of this equation changes sign discloses that the smallest value of critical field for a flop is obtained at $\theta_2 = 30^\circ$ and for $H \sin \theta_1$ equal to

$$H_c = [2mK_2 / (\chi_1 - \chi_{11})]^{1/2}. \quad [m=3; \theta_2=30^\circ]. \quad (32)$$

To see this, note that for $\theta_2 = 30^\circ$, $m=3$, Eq. (30) becomes

$$\frac{H^2 \sin^2 \theta_1}{[2mK_2 / (\chi_1 - \chi_{11})]} = \frac{\sin(2\psi)[4 \sin^2(2\psi) - 3]}{\sin 2\psi}. \quad (33)$$

The solution to this equation which for $H=0$ starts at $\sin^2(2\psi) = \frac{3}{4}$ disappears abruptly when the critical field (32) is reached, and only the solution $\sin 2\psi = 0$ remains.

The critical field (32) is smaller by a factor $\sqrt{3}$ than the critical field (29) for $\theta_2=0$. This has its origin in the fact that at $\theta_2=30^\circ$ the magnetization snaps to a perpendicular axis which is an easy axis, whereas at $\theta_2=0$

it snaps to a hard axis. (In either case it goes over an anisotropy hill and hysteresis effects should be observable.)

We now define h as H/H_c , using the smaller value, given by Eq. (32), for H_c .

The results of numerical integration are plotted as curve (2) in Fig. 2. It is apparent that the curve has an inflection point somewhere between $h=1$ and $h=3$, that is, between the two critical fields (32) and (29). Limiting solutions of the problem are

$$\chi_p \approx \chi_{11} + (\chi_1 - \chi_{11})[(2/3) + (1/45)h^2], \quad [h^2 \ll 1], \quad (34a)$$

$$\chi_p \approx \chi_{11} + (\chi_1 - \chi_{11})(1 - 0.36h^{-4}), \quad [h^2 \gg 1], \quad (34b)$$

which are to be compared with (26a) and (26c).

In attempting to apply curve (2), Fig. 2, to the case of MnO or α MnS we must be very careful. In the first place, our model may not be correct, and multi-spin axes may be present. This will affect the numerical results, but not seriously, since we believe that in any reasonable model the spins will be constrained by the dipolar anisotropy only to a region, and not a single direction.

In the second place, as H gets larger the spins can begin to move out of the constrained pane. Nagamiya¹⁸ has considered the powder susceptibility for the orthorhombic case, with different anisotropies in two perpendicular directions. This case somewhat resembles ours, in that we also have K_1 and K_2 for movement of the spins perpendicular to and parallel to the plane. In terms of $q = K_2/K_1$, Nagamiya finds

$$\chi_p \approx \frac{2}{3}\chi_1 + \frac{1}{3}\chi_{11}[(2/15)(1+q)h^2 - (2/35)qh^4 + (4/315)(1+q^2)h^6 + \dots]. \quad [h^2 \ll 1]. \quad (35)$$

We cannot use this formula for all values of h , and furthermore the symmetry conditions are different in Nagamiya's case and in our model. Nevertheless, we can see from Eq. (35) the general effect of two anisotropies. Since we expect $q \approx 10^{-3}$, the correction to our results should be negligible until H begins to approach the very large critical field for a flop out of the plane, given by Eq. (46) in Sec. IX.

VIII. ESTIMATE OF K_2 IN MnO FROM POWDER SUSCEPTIBILITY DATA

Bizette, Squire, and Tsai have measured χ_p of MnO down to 14°K and in fields of 5000 and 24 000 oersteds.⁷ We find that our curve (2) of Fig. 2 gives a reasonable fit to their data, extrapolated to 0°K, with

$$H_c \approx 2.1 \times 10^4 \text{ oe.} \quad (0^\circ\text{K}) \quad (36)$$

Here Eq. (32) is used to define H_c . The critical field will increase with increasing temperature.

(It should be mentioned that in order to fit both the 5000-oe and the 24 000-oe data with the same value of

¹⁸ T. Nagamiya, *Physica* **22**, 249 (1956).

H_c it was found necessary to use a value of $\chi_1 \approx 0.87 \times 10^{-4} \text{ g}^{-1}$ at 0°K, which is 3% larger than the value at the Néel point. This is in line with the spin-wave-theory prediction that χ_1 should rise slightly as temperature drops.)

From Eqs. (32) and (36) we now find

$$\begin{aligned} K_2 &\approx 6.4 \times 10^3 \text{ ergs/g} \\ &\approx 3.2 \times 10^4 \text{ ergs/cm}^3. \quad (0^\circ\text{K}) \end{aligned} \quad (37)$$

The values (36) and (37) are to be compared with estimates made by Nagamiya,¹⁹ using a uniaxial model and the approximation (26a):

$$H_c(\text{Nag.}) \approx 3.6 \times 10^4 \text{ oe,}$$

$$K(\text{Nag.}) \approx 5.7 \times 10^4 \text{ ergs/g.}$$

It is seen that our model leads to a smaller anisotropy. This is because it is more difficult to swing the spins around in a powder sample when they are confined to planes, and hence a smaller K is required to fit the same set of data.

The value of K_2 is reasonable, as has been discussed in Sec. III C.

At the end of Sec. VII A we pointed out that hysteresis effects should be observed whenever $H > H_c$. However, the full effect should not be felt until H exceeds the larger H_c , defined by Eq. (29), for $\theta_2 = 0$. This field, for MnO, we estimate as $\approx 3.6 \times 10^4$ oe. The largest field used by Bizette, Squire, and Tsai, 2.4×10^4 oe, fell too short of this larger H_c —although it slightly exceeded (36)—to produce much hysteresis. It would be interesting to apply a field of, say, 4×10^4 oe (or a larger field at higher temperature) to a powder sample of MnO. If the powder remained unshaken on removal of the field, the susceptibility in small fields should subsequently be dependent on direction. A sintered sample should show the same effect.

Néel²⁰ has discussed the effect that domain walls, if they exist, might have on the field dependence of powder susceptibility; and he has proposed a model which could explain the MnO data. Precise measurements of hysteresis effects might enable one to distinguish between his mechanism and ours.

IX. ANTIFERROMAGNETIC RESONANCE

The problem of antiferromagnetic resonance in MnO is complicated by the presence of four pairs of up and down sublattices. Next-nearest-neighbor exchange forces couple the members of each pair to each other and nearest-neighbor exchange forces cross-couple the various pairs. The latter coupling is further complicated by the distortion, which increases the exchange between spins of neighbor (111) sheets. All of these interactions,

¹⁹ See reference 2, p. 40. The units for the value of K are incorrectly stated in this reference as ergs/cm³.

²⁰ L. Néel, in *Proceedings of the International Conference on Theoretical Physics, Tokyo and Kyoto, 1954* (Science Council of Japan, Tokyo, 1954).

taken together with a complicated anisotropy, will lead to a very involved equation of motion which will have a great number of normal-mode solutions. Without a detailed understanding of all the energies we cannot hope to set up, much less to solve, such an equation.

However, we can get a good picture of the general nature of the resonance from a simpler model. We will assume a single exchange energy coupling a single up sublattice to its down partner. Kaplan³ has shown that under this assumption the magnetic dipolar energy is given by

$$U' = \frac{1}{4}K_1[-1 + \frac{3}{2}(\gamma^2 + \gamma'^2) + \alpha\alpha' + \beta\beta' - 2\gamma\gamma']. \quad (38)$$

Here x and y axes are taken in the (111) plane, z axis normal to the plane, and the primed and unprimed direction cosines refer to the two sublattices. The constant K_1 is the same as that of Eq. (17).

We may subtract from (38) an isotropic term in $\alpha\alpha' + \beta\beta' + \gamma\gamma'$, since this only adds a small amount to the exchange-energy Hamiltonian. We are left with

$$U' = \text{const} + \frac{3}{4}K_1[\frac{1}{2}(\gamma^2 + \gamma'^2) - \gamma\gamma']. \quad (39)$$

To this we add a within-plane anisotropy energy of the form of Eq. (15), which for two sublattices may be written as

$$U'' = \text{const} + \frac{1}{2}K_2(\sin^2 3\eta + \sin^2 3\eta'). \quad (40)$$

For small displacements from the preferred axis, which we take as the x axis, Eq. (40) may be written as

$$U'' \approx \text{const} + (9/2)K_2(\beta^2 + \beta'^2). \quad (41)$$

We further add, for generality, an anisotropy of a form not considered in Sec. VII:

$$U''' \approx K_3\beta\beta'. \quad (42)$$

The total anisotropy energy is now of a form given by Eq. (39) of Keffer and Kittel²¹ for the orthorhombic case:

$$f_A = \frac{1}{2}K_1'(\gamma^2 + \gamma'^2) + \frac{1}{2}K_2'(\beta^2 + \beta'^2) + K_3'\gamma\gamma' + K_4'\beta\beta'. \quad (43)$$

where we now identify

$$K_1' = \frac{3}{4}K_1, \quad K_2' = 9K_2, \quad K_3' = -\frac{3}{4}K_1, \quad K_4' = K_3. \quad (44)$$

The antiferromagnetic resonance frequencies are discussed in Keffer and Kittel. There are in general two different modes, which now correspond to motion out of the plane and motion within the plane.

(1) *Motion out of the plane.*—Here, in the absence of an applied field, the resonance frequency at 0°K is

²¹ F. Keffer and C. Kittel, Phys. Rev. **85**, 329 (1952).

given by

$$\omega_3 = -\omega_4 = \gamma H_c'' \approx \gamma[6K_1\chi_\perp]^{1/2}, \quad (45)$$

where we have replaced the exchange field H_E by its equivalent $\lambda M = \chi_\perp^{-1}M$. It is seen that H_c'' is the critical field for a flop out of the plane. Using (18) for an estimate of K_1 we find

$$H_c'' \approx 5 \times 10^5 \text{ oe}. \quad (46)$$

This field is so very much larger than the critical field (36) for motion within the plane, and also so much larger than the fields used in powder susceptibility experiments, that we feel justified in our assumption of the previous sections that the magnetization vectors are actually constrained to the plane.

The resonance frequency (45) corresponds to wavelengths of the order of 0.2 mm.

(2) *Motion within the plane.*—Here, in the absence of an applied field, the resonance frequency at 0°K is given by

$$\omega_1 = -\omega_2 = \gamma H_c' \approx \gamma[(18K_2 - 2K_3)/\chi_\perp]^{1/2}. \quad (47)$$

In the absence of K_3 the critical field is identical to that of Eq. (29). Presumably some effects of K_3 were included in deducing the size of H_c' from experiment. Our estimate of 3.6×10^4 oe corresponds to wavelengths of the order of 3 mm.

It should be pointed out that although the critical field increases with temperature, the resonance frequency will in general decrease. This is shown in Keffer and Kittel, and it has been experimentally verified²² for MnF₂. Since K_2 is probably even more strongly temperature dependent than the dipolar-type anisotropy of MnF₂, it may well be that for a long way below the Néel point the in-plane resonance frequency is in the centimeter range. If so, this may account for the continuation of paramagnetic absorption seen below the Néel point in thin disk polycrystalline samples of MnO, MnS and MnSe,²³ and for the small residual absorption seen in powdered samples of MnO and MnS.²⁴

We wish to caution the reader that not only have we made here the drastic two-sublattice simplification discussed above, but also in the discussion of within-plane motion we have restricted ourselves to the small-angle approximation of Eq. (41). For applied fields of the order of H_c' the resonance frequencies will be much more complicated.

²² F. M. Johnson and A. H. Nethercot, Jr., Phys. Rev. **104**, 847 (1956).

²³ Okamura, Torizuka, and Kojima, Phys. Rev. **82**, 285 (1951).

²⁴ L. R. Maxwell and T. R. McGuire, Revs. Modern Phys. **25**, 279 (1953).