

tions" involving secondary electrons from the target, since this effect—if present at all—can be easily quenched by a uniform electric field.

and from Compton scattering from one detecting crystal to another (see Pond's thesis, p. 55).

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### Anisotropy Energy in $\text{MnF}_2$ at Low Temperatures\*

TAKEHIKO OGUCHI†

*Sarah Mellon Scaife Radiation Laboratory, University of Pittsburgh, Pittsburgh, Pennsylvania*

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The anisotropy energy in  $\text{MnF}_2$  is calculated by a spin-wave method. The magnetic dipole interactions and the interactions of individual ions with their surrounding crystalline fields give the anisotropy energy of  $-4.9 \times 10^6$  erg/cc at  $0^\circ\text{K}$ . The experimental value extrapolated to  $0^\circ\text{K}$  by Foner is  $-5.0 \times 10^6$  erg/cc. The temperature dependence of the anisotropy energy is obtained as  $E_{\text{an}}(T)/E_{\text{an}}(0) = [M(T)/M(0)]^{2.9}$ , where  $E_{\text{an}}(T)$ ,  $M(T)$  are the anisotropy energy and the magnetization of the sublattice at  $T^\circ\text{K}$ , respectively, and  $E_{\text{an}}(0)$ ,  $M(0)$  are the corresponding values at  $0^\circ\text{K}$ .

#### I. INTRODUCTION

**T**HEORETICAL studies of the temperature dependence of ferromagnetic anisotropy energy in a cubic crystal have been given by Van Vleck,<sup>1</sup> Zener,<sup>2</sup> Keffer,<sup>3</sup> and Kasuya.<sup>4</sup> Keffer, especially, explains the relationship between the nearest-neighbor quadrupole-quadrupole coupling theory of Van Vleck and that of Zener by means of the spin-wave approximation.

In an antiferromagnetic substance, the situation is similar to that of ferromagnetic substances in the classical theory. But in the quantum-mechanical treatment, there is some difference between ferromagnetism and antiferromagnetism. This makes the temperature dependence of the antiferromagnetic anisotropy energy differ from that of the ferromagnetic anisotropy energy. Recently the anisotropy energy has been observed in several antiferromagnetic substances. In this paper, the anisotropy energy at  $0^\circ\text{K}$  will be calculated and the temperature dependence of the anisotropy energy in  $\text{MnF}_2$  will be discussed by the spin-wave method.

#### II. ANISOTROPY ENERGY IN $\text{MnF}_2$

$\text{MnF}_2$  is a typical antiferromagnetic substance with a Néel temperature of  $68^\circ\text{K}$ . The magnetic anisotropy energy in  $\text{MnF}_2$  is evaluated from measurements of the magnetic susceptibility<sup>5</sup> and the antiferromagnetic

resonance.<sup>6,7</sup> According to Keffer,<sup>8</sup> the major part of the measured anisotropy in the susceptibility above the Néel point in  $\text{MnF}_2$  can be accounted for by magnetic dipole interactions, and the remainder is possibly due to the interactions of individual paramagnetic ions with their surrounding crystalline fields. Further, Keffer suggests that the temperature dependence of the anisotropy energy in  $\text{MnF}_2$  is proportional to the square of the sublattice magnetization below the Néel point. His theory is based on molecular field theory; on the other hand, we shall consider the temperature dependence of the anisotropy energy in  $\text{MnF}_2$  by means of the spin-wave approximation.

The crystal structure of  $\text{MnF}_2$  is of the rutile type. The unit cell of  $\text{Mn}^{++}$  ions may conveniently be pictured as a body-centered cube compressed along the  $z$  (or  $c$ ) axis. Lattice parameters, as determined from x-ray diffraction, are  $c = 3.3103$  Å and  $a = 4.8734$  Å.<sup>9</sup> Below the Néel point the spins at the corners of the compressed cube are all pointing one way along the  $z$  axis, while the spins at the centers are pointing the opposite way.<sup>10</sup>

A strong antiferromagnetic exchange interaction exists between a center spin and a corner spin, and there may be a weak antiferromagnetic exchange interaction between two nearest neighbor center spins (or corner spins); but, for the sake of simplicity, we shall neglect the latter.

The Hamiltonian of the exchange interaction is

$$H_{\text{ex}} = |J| \sum (jk) \mathbf{S}_j \cdot \mathbf{S}_k, \quad (1)$$

<sup>6</sup> F. M. Johnson and A. H. Nethercot, Jr., Phys. Rev. **104**, 874 (1956).

<sup>7</sup> S. Foner, Phys. Rev. **107**, 683 (1957).

<sup>8</sup> F. Keffer, Phys. Rev. **87**, 608 (1952).

<sup>9</sup> M. Griffel and J. W. Stout, J. Am. Chem. Soc. **72**, 4351 (1950).

<sup>10</sup> R. A. Erickson, Phys. Rev. **90**, 779 (1953).

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† On leave from Tokyo University of Education, Tokyo, Japan.

<sup>1</sup> J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937).

<sup>2</sup> C. Zener, Phys. Rev. **96**, 1335 (1954).

<sup>3</sup> F. Keffer, Phys. Rev. **100**, 1692 (1955).

<sup>4</sup> T. Kasuya, J. Phys. Soc. Japan **11**, 944 (1956).

<sup>5</sup> J. W. Stout and M. Griffel, J. Chem. Phys. **18**, 1455 (1950); J. W. Stout and L. M. Matarrese, Revs. Modern Phys. **25**, 338 (1953).

where  $J/2$  is the exchange integral,  $\mathbf{S}$  is the spin operator, and  $\sum_{\langle j,k \rangle}$  is taken over pairs between a spin  $j$  on one sublattice and its nearest neighbors  $k$  on the other sublattice.

The second part of the Hamiltonian is the dipole-dipole interaction. This is written as

$$H_{\text{dip}} = \sum_{j,k} 4\mu^2 R_{jk}^{-5} (R_{jk}^2 \mathbf{S}_j \cdot \mathbf{S}_k - 3\mathbf{S}_j \cdot \mathbf{R}_{jk} \mathbf{S}_k \cdot \mathbf{R}_{jk}) \\ + \sum_{j,j'} 2\mu^2 R_{jj'}^{-5} (R_{jj'}^2 \mathbf{S}_j \cdot \mathbf{S}_{j'} - 3\mathbf{S}_j \cdot \mathbf{R}_{jj'} \mathbf{S}_{j'} \cdot \mathbf{R}_{jj'}) \\ + \sum_{k,k'} 2\mu^2 R_{kk'}^{-5} (R_{kk'}^2 \mathbf{S}_k \cdot \mathbf{S}_{k'} \\ - 3\mathbf{S}_k \cdot \mathbf{R}_{kk'} \mathbf{S}_{k'} \cdot \mathbf{R}_{kk'}), \quad (2)$$

where  $\mu$  is the Bohr magneton,  $R_{jk}$  is the distance between spins  $j$  and  $k$ , and  $\sum_{j,j'}$  (or  $\sum_{k,k'}$ ) are taken over pairs between a spin  $j$  (or  $k$ ) and its neighbors  $j'$  (or  $k'$ ) on the same sublattice, and  $\sum_{j,k}$  is taken over pairs to neighbors  $k$  on the other sublattice.

Although the orbital angular momentum is quenched in the  $\text{Mn}^{++}$  ion, Abragam and Pryce<sup>11</sup> derive an anisotropy energy due to coupling of the  $(3d)^5 {}^6S$  ground state with the  $(3d)^4(4s) {}^6D$  state via the combined action of the crystalline potential and the magnetic spin-spin interaction between pairs of electrons in an ion. The Hamiltonian of this type of the anisotropy energy can be written as<sup>12</sup>

$$H_c = D \sum_j (S_j^z)^2 + D \sum_k (S_k^z)^2, \quad (3)$$

where  $D$  is a constant and its numerical value is approximately  $-0.012 \text{ cm}^{-1}$  as estimated by Keffer.<sup>8</sup> Recently it has been reported<sup>13</sup> that the  $\text{Mn}^{++}$  ion is not completely quenched because of a partial electron transfer to the  $\text{Mn}^{++}$  ions from nearest  $F^-$  ions. The contribution to the anisotropy energy from this effect is not known, but it is a possibility that (3) contains it, because the numerical value of  $D$  was obtained semi-empirically.

Following Kubo,<sup>14</sup> we define

$$S_j^+ = (2S)^{\frac{1}{2}} f_j a_j, \quad S_k^+ = (2S)^{\frac{1}{2}} b_k^* f_k, \\ S_j^- = (2S)^{\frac{1}{2}} a_j^* f_j, \quad S_k^- = (2S)^{\frac{1}{2}} f_k b_k, \\ S_j^z = S - a_j^* a_j, \quad S_k^z = -S + b_k^* b_k, \\ f_j = (1 - a_j^* a_j / 2S)^{\frac{1}{2}}, \quad f_k = (1 - b_k^* b_k / 2S)^{\frac{1}{2}}, \quad (4)$$

where  $a_j^*$  and  $b_k^*$  are creation operators and  $a_j$  and  $b_k$  are destruction operators of spin deviations. We substitute (4) into (1), (2), and (3) and then expand in descending powers of  $S$ ; and, at first, we consider all terms to order  $S$ . This is equivalent to neglecting the terms of third order or higher in the spin deviation operators,  $a_j$ ,  $a_j^*$ ,  $b_k$ , and  $b_k^*$ .<sup>15</sup> Although we could

obtain the eigenvalue of  $H_{\text{ex}} + H_{\text{dip}}$  in the spin-wave representation as Ziman<sup>16</sup> did, we shall neglect some terms in (2) which vanish by crystalline symmetry as far as the zero-wave-number spin waves are concerned and as a result do not contribute to the anisotropy energy in the approximation which we will use later. We introduce the Fourier transforms of  $a_j$ ,  $a_j^*$  and  $b_k$ ,  $b_k^*$ :

$$a_j = (2/N)^{\frac{1}{2}} \sum_{\lambda} a_{\lambda} e^{-i\lambda j}, \quad b_k = (2/N)^{\frac{1}{2}} \sum_{\lambda} b_{\lambda} e^{i\lambda k}, \\ a_j^* = (2/N)^{\frac{1}{2}} \sum_{\lambda} a_{\lambda}^* e^{i\lambda j}, \quad b_k^* = (2/N)^{\frac{1}{2}} \sum_{\lambda} b_{\lambda}^* e^{-i\lambda k}, \quad (5)$$

where  $\lambda$  is the wave number which refers to the reciprocal lattice of the sublattice, so that  $\lambda_x$  and  $\lambda_y$  take  $(N/2)^{\frac{1}{2}}$  values from  $-\pi/a$  to  $\pi/a$ , respectively, and  $\lambda_z$  also takes  $(N/2)^{\frac{1}{2}}$  values from  $-\pi/c$  to  $\pi/c$ .

In order to eliminate the interactions between  $\lambda$  and  $-\lambda$ , we define the new operators as follows:

$$a_{\pm\lambda} = (1/\sqrt{2})(a_{\lambda} \pm a_{-\lambda}), \\ b_{\pm\lambda} = (1/\sqrt{2})(b_{\lambda} \mp b_{-\lambda}), \quad (6)$$

and similarly for  $a_{\pm\lambda}^*$  and  $b_{\pm\lambda}^*$ . For  $\lambda=0$ , we must define  $a_0 = \alpha_0$  and  $b_0 = \beta_0$ . These transformations are defined only for the positive half-space of  $\lambda$ , i.e.,  $-\pi/a < \lambda_x \leq \pi/a$ ,  $-\pi/a < \lambda_y \leq \pi/a$ ,  $0 \leq \lambda_z \leq \pi/c$ . Furthermore, we introduce real operators as follows,

$$\alpha_{\lambda} = \frac{1}{2}[q_{\lambda} + r_{\lambda} + i(p_{\lambda} + s_{\lambda})], \\ \alpha_{\lambda}^* = \frac{1}{2}[q_{\lambda} + r_{\lambda} - i(p_{\lambda} + s_{\lambda})], \\ \beta_{\lambda} = \frac{1}{2}[q_{\lambda} - r_{\lambda} + i(p_{\lambda} - s_{\lambda})], \\ \beta_{\lambda}^* = \frac{1}{2}[q_{\lambda} - r_{\lambda} - i(p_{\lambda} - s_{\lambda})]. \quad (7)$$

Thus the Hamiltonian can be written as

$$H = -\frac{1}{2}Nz|J|S(S+1)(1 + \Theta + \Phi^z) + \frac{1}{2}z|J|S \\ \times \sum_{\lambda} \{ [1 \pm \gamma_{\lambda} + \Theta + \Phi^z + \Psi_{\lambda}^{\pm z} \pm (\Psi_{\lambda}^{\pm y} - \Psi_{\lambda}^{\pm x})] q_{\lambda}^2 \\ + [1 \mp \gamma_{\lambda} + \Theta + \Phi^z + \Psi_{\lambda}^{\mp z} \mp (\Psi_{\lambda}^{\mp y} - \Psi_{\lambda}^{\mp x})] p_{\lambda}^2 \\ + [1 \mp \gamma_{\lambda} + \Theta + \Phi^z + \Psi_{\lambda}^{\mp z} \pm (\Psi_{\lambda}^{\mp y} - \Psi_{\lambda}^{\mp x})] r_{\lambda}^2 \\ + [1 \pm \gamma_{\lambda} + \Theta + \Phi^z + \Psi_{\lambda}^{\pm z} \mp (\Psi_{\lambda}^{\pm y} - \Psi_{\lambda}^{\pm x})] s_{\lambda}^2 \}, \quad (8)$$

where  $z$  is the number of the nearest neighbors and

$$\Phi^z = -(4\mu^2/z|J|) [\sum_{j'} R_{jj'}^{-5} (R_{jj'}^2 - 3Z_{jj'}^2) \\ - \sum_k R_{jk}^{-5} (R_{jk}^2 - 3Z_{jk}^2)], \\ \Psi_{\lambda}^{\pm z} = -(2\mu^2/z|J|) [\sum_{j'} R_{jj'}^{-5} (R_{jj'}^2 - 3Z_{jj'}^2) e^{i\lambda R_{jj'}} \\ \pm \sum_k R_{jk}^{-5} (R_{jk}^2 - 3Z_{jk}^2) e^{i\lambda R_{jk}}], \quad (9) \\ \Theta = -(2D)/(z|J|), \\ \gamma_{\lambda} = \cos \frac{1}{2} a \lambda_x \cos \frac{1}{2} a \lambda_y \cos \frac{1}{2} c \lambda_z,$$

and similarly for  $\Phi^y$ ,  $\Phi^x$ ,  $\Psi_{\lambda}^{\pm x}$ , and  $\Psi_{\lambda}^{\pm y}$ . The  $\pm$  or  $\mp$  signs in (8) mean that the upper signs are used for the positive half-space of  $\lambda$  and the lower signs are used for the negative half-space of  $\lambda$ .

Finally we introduce the following operators,  $A_{\lambda}$ ,  $A_{\lambda}^*$ ,

<sup>16</sup> J. M. Ziman, Proc. Roy. Soc. (London) **65**, 540 (1952).

<sup>11</sup> A. Abragam and M. H. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

<sup>12</sup> K. Yosida, Progr. Theoret. Phys. (Kyoto) **6**, 691 (1951).

<sup>13</sup> R. G. Shulman and V. Jaccarino, Phys. Rev. **103**, 1126 (1956).

<sup>14</sup> R. Kubo, Phys. Rev. **87**, 568 (1952).

<sup>15</sup> Since  $S$  is equal to  $\frac{5}{2}$ , this expansion is a good approximation.

$B_\lambda$ , and  $B_\lambda^*$ , defined by:

$$\begin{aligned} q_\lambda &= \frac{1}{\sqrt{2}} \left[ \frac{1 \mp \gamma_\lambda + \Theta + \Phi^z + \Psi_\lambda^{\mp z} \mp \Psi_\lambda^{\mp xy}}{1 \pm \gamma_\lambda + \Theta + \Phi^z + \Psi_\lambda^{\pm z} \pm \Psi_\lambda^{\pm xy}} \right]^{\frac{1}{2}} (A_\lambda + A_\lambda^*), \\ ip_\lambda &= \frac{1}{\sqrt{2}} \left[ \frac{1 \pm \gamma_\lambda + \Theta + \Phi^z + \Psi_\lambda^{\pm z} \pm \Psi_\lambda^{\pm xy}}{1 \mp \gamma_\lambda + \Theta + \Phi^z + \Psi_\lambda^{\mp z} \mp \Psi_\lambda^{\mp xy}} \right]^{\frac{1}{2}} (A_\lambda - A_\lambda^*), \\ r_\lambda &= \frac{1}{\sqrt{2}} \left[ \frac{1 \pm \gamma_\lambda + \Theta + \Phi^z + \Psi_\lambda^{\pm z} \mp \Psi_\lambda^{\pm xy}}{1 \mp \gamma_\lambda + \Theta + \Phi^z + \Psi_\lambda^{\mp z} \pm \Psi_\lambda^{\mp xy}} \right]^{\frac{1}{2}} (B_\lambda + B_\lambda^*), \\ is_\lambda &= \frac{1}{\sqrt{2}} \left[ \frac{1 \mp \gamma_\lambda + \Theta + \Phi^z + \Psi_\lambda^{\mp z} \pm \Psi_\lambda^{\mp xy}}{1 \pm \gamma_\lambda + \Theta + \Phi^z + \Psi_\lambda^{\pm z} \mp \Psi_\lambda^{\pm xy}} \right]^{\frac{1}{2}} (B_\lambda - B_\lambda^*), \end{aligned} \quad (10)$$

where

$$\Psi_\lambda^{\pm xy} = \Psi_\lambda^{\pm y} - \Psi_\lambda^{\pm x}, \quad (11)$$

and has the property that  $\lim_{\lambda \rightarrow 0} \Psi_\lambda^{\pm xy} = 0$  by the crystalline symmetry. The diagonalization leads to the eigenvalues

$$\begin{aligned} E &= -\frac{1}{2} N z |J| S(S+1) (1 + \Theta + \Phi^z) + \frac{1}{2} z |J| S \\ &\quad \times \sum_\lambda \{ [1 - \gamma_\lambda^2 + 2\Theta + 2\Phi^z + (\Psi_\lambda^{+z} + \Psi_\lambda^{-z}) \\ &\quad + (\Psi_\lambda^{+xy} - \Psi_\lambda^{-xy}) + \gamma_\lambda (\Psi_\lambda^{-z} - \Psi_\lambda^{+z}) \\ &\quad - \gamma_\lambda (\Psi_\lambda^{+xy} + \Psi_\lambda^{-xy}) ]^{\frac{1}{2}} (2n_\lambda + 1) + [1 - \gamma_\lambda^2 + 2\Theta \\ &\quad + 2\Phi^z + (\Psi_\lambda^{+z} + \Psi_\lambda^{-z}) - (\Psi_\lambda^{+xy} - \Psi_\lambda^{-xy}) \\ &\quad + \gamma_\lambda (\Psi_\lambda^{-z} - \Psi_\lambda^{+z}) + \gamma_\lambda (\Psi_\lambda^{+xy} + \Psi_\lambda^{-xy}) ]^{\frac{1}{2}} \\ &\quad \times (2n_\lambda' + 1) \}, \quad (12) \end{aligned}$$

where  $n_\lambda = A_\lambda^* A_\lambda$  and  $n_\lambda' = B_\lambda^* B_\lambda$  are the number of antiferromagnetic spin waves.

From (2) and (3), the part of the Hamiltonian which contains only the anisotropy energy is written as

$$H_{\text{an}} = H_{\text{an}}^{(0)} + H_{\text{an}}^{(1)} + H_{\text{an}}^{(2)}, \quad (13)$$

where  $H_{\text{an}}^{(0)}$  does not contain the operators (10) (the terms of order  $S^2$ ), while  $H_{\text{an}}^{(1)}$  contains the quadratic terms of the operators (10) (the terms of order  $S$ ). In the spin wave representation the diagonal terms of  $H_{\text{an}}^{(0)}$

$$1 - E_{\text{an}}(T)/E_{\text{an}}(0) = \frac{\{2v_0[S + \frac{1}{2} - N^{-1} \sum_\lambda (1 - \gamma_\lambda^2)^{-\frac{1}{2}}] - A\} [1 - M(T)/M(0)]}{(S+1)(\Theta + \Phi^z - \Phi^x) - 2\langle v_\lambda \rangle N^{-1} \sum_\lambda (1 - \gamma_\lambda^2)^{-\frac{1}{2}}}, \quad (21)$$

where the term  $A$  is of the order of  $S^0$  and is composed of many terms which come from  $E_{\text{an}}^{(2)}$ . Equation (21) gives the dependence of the anisotropy energy on the magnetization and should be valid at low temperatures.

### III. NUMERICAL EVALUATION AND COMPARISON WITH THE EXPERIMENTS

In order to get the numerical value of the coefficient of  $[1 - M(T)/M(0)]$  on the right-hand side of (21),

and  $H_{\text{an}}^{(1)}$  can be written

$$E_{\text{an}}^{(0)} = -\frac{1}{2} N z |J| S(S+1) (\Theta + \Phi^z - \Phi^x), \quad (14)$$

$$E_{\text{an}}^{(1)} = z |J| S \langle v_\lambda \rangle \sum_\lambda (1 - \gamma_\lambda^2)^{-\frac{1}{2}} + 2z |J| S v_0 \sum_\lambda (1 - \gamma_\lambda^2 + 2u_0)^{-\frac{1}{2}} n_\lambda, \quad (15)$$

where by  $\langle v_\lambda \rangle$  we mean average over  $\lambda$ , and

$$\begin{aligned} 2u_\lambda &= 2\Theta + 2\Phi^z + (\Psi_\lambda^{+z} + \Psi_\lambda^{-z}) + \gamma_\lambda (\Psi_\lambda^{-z} - \Psi_\lambda^{+z}), \\ 2v_\lambda &= 2\Theta + 2\Phi^z - 2\Phi^x + \Psi_\lambda^{+z} + \Psi_\lambda^{-z} - \Psi_\lambda^{+x} - \Psi_\lambda^{-x} \\ &\quad - \gamma_\lambda (\Psi_\lambda^{+z} - \Psi_\lambda^{-z} - \Psi_\lambda^{+x} + \Psi_\lambda^{-x}). \quad (16) \end{aligned}$$

$E_{\text{an}}^{(2)}$  is the diagonal terms of order  $S^0$ , because they will be useful later,<sup>17</sup> but we do not write the detailed form. Since  $\Theta$ ,  $\Phi$ , and  $\Psi_\lambda^\pm$  are of the order of  $10^{-2}$  we neglected terms involving their squares in the derivation of (15); also in the first term of (15),  $2u_\lambda$  in the denominator was neglected and  $v_\lambda$  in the numerator was replaced by its average,  $\langle v_\lambda \rangle$ , since both of them are much smaller than 1 and the term  $\lambda=0$  does not contribute to the summation. In the second term,  $u_\lambda$  and  $v_\lambda$  were replaced by  $u_0$  and  $v_0$ , respectively, because this term contains  $n_\lambda$  so that the major contribution to the summation comes from  $\lambda \cong 0$ .

The magnetization of the sublattice is, in the same way,

$$M(T) = M(0) + \Delta M, \quad (17)$$

$$M(0) = N\mu(S + \frac{1}{2}) - \mu \sum_\lambda (1 - \gamma_\lambda^2)^{-\frac{1}{2}}, \quad (18)$$

$$\Delta M = -2\mu \sum_\lambda n_\lambda (1 - \gamma_\lambda^2 + 2u_0)^{-\frac{1}{2}}. \quad (19)$$

Equation (19) can also be written as,<sup>18</sup>

$$\begin{aligned} \Delta M &= -[4N\mu kT(2u_0)^{\frac{1}{2}}/\pi^2 z |J| S] \\ &\quad \times \sum_{n=1}^{\infty} K_1(nz |J| S(2u_0)^{\frac{1}{2}}/kT)/n, \quad (20) \end{aligned}$$

where  $K_1$  is a Hankel function. Using (14) to (19), we can eliminate the term  $\sum_\lambda n_\lambda (1 - \gamma_\lambda^2 + 2u_0)^{-\frac{1}{2}}$ , obtaining the following formula (in this formula, we include all terms of order  $S$  and  $S^0$ ):

we can replace the summation over the wave numbers in (21) by an integration over  $\lambda$ , namely,<sup>14</sup>

<sup>17</sup> In deriving  $E_{\text{an}}^{(2)}$ , we used the Taylor expansion

$$f = (1 - n/2S)^{\frac{1}{2}} = 1 - n/4S \dots$$

If we put<sup>14</sup>  $f = \sum_{k=0}^{\infty} c_k n^k$ , we obtain  $f = 1 - 0.146n + 0.093n^2 \dots$ . The difference between these two expansions is not of serious importance in our case.

<sup>18</sup> J. A. Eisele and F. Keffer, Phys. Rev. **96**, 929 (1954).

$$\begin{aligned}
& \sum (1 - \gamma_\lambda^2)^{-\frac{1}{2}} \\
&= (2\pi)^{-3} \int_{-\pi/\alpha}^{\pi/\alpha} \int_{-\pi/\alpha}^{\pi/\alpha} \int_{-\pi/c}^{\pi/c} \{1 - [\cos(a\lambda_z/2) \\
&\quad \times \cos(a\lambda_y/2) \cos(c\lambda_z/2)]^2\}^{-\frac{1}{2}} d\lambda_x d\lambda_y d\lambda_z \\
&= (2\pi)^{-3} \frac{N}{2} \int \int \int_{-\pi}^{\pi} \{1 - [\cos(\lambda_1/2) \\
&\quad \times \cos(\lambda_2/2) \cos(\lambda_3/2)]^2\}^{-\frac{1}{2}} d\lambda_1 d\lambda_2 d\lambda_3 \\
&= (N/2)1.15. \tag{22}
\end{aligned}$$

The exchange integral is evaluated as  $z|J| = 4.24 \times 10^{-15}$  erg from the perpendicular susceptibility  $\chi_1 = 24.4 \times 10^{-3}$  per mole.<sup>19</sup> The lattice sums in  $\Phi$  have been calculated by Keffer<sup>8</sup>:

$$\begin{aligned}
(6/N) \sum_k R_{jk}^{-5} (Z_{jk}^2 - X_{jk}^2) &= -4.85, \\
(6/N) \sum_{j'} R_{jj'}^{-5} (Z_{jj'}^2 - X_{jj'}^2) &= 9.25. \tag{23}
\end{aligned}$$

Thus we obtain the following values,

$$\begin{aligned}
\Phi^z - \Phi^x &= 1.45 \times 10^{-2}, \quad \langle v_\lambda \rangle = 1.61 \times 10^{-2}, \\
\Theta &= 0.11 \times 10^{-2}, \quad v_0 = 2.28 \times 10^{-2}, \\
A &= 0.64 \times 10^{-2}. \tag{24}
\end{aligned}$$

Substituting (22) and (24) into (21), we get

$$1 - E_{\text{an}}(T)/E_{\text{an}}(0) = 2.9[1 - M(T)/M(0)], \tag{25}$$

or approximately,

$$E_{\text{an}}(T)/E_{\text{an}}(0) = [M(T)/M(0)]^{2.9}. \tag{26}$$

If we tentatively assume that  $S$  is infinite and that the Hamiltonian of the anisotropy energy does not contain cross terms in the spin operator, as  $H_c$  in (3) does not, then the numerical value of the coefficient in (25) will be 2 instead of 2.9. This is the limiting classical case of no correlation between neighboring spins (molecular field approximation). On the other hand, if we assume that  $S$  is infinite and that the Hamiltonian of the anisotropy energy is only the dipole-dipole interaction  $H_{\text{dip}}$  in (2), then the numerical coefficient in (25) will be 3. This is the classical case of complete correlation between all spins, because the major contribution to the excitation energy comes from the spin wave of  $\lambda=0$ .

From (14) and (15), we can obtain the anisotropy energy at 0°K as follows:

$$\begin{aligned}
E_{\text{an}}(0) &= -(N/2)z|J|S(S+1)(\Theta + \Phi^z - \Phi^x) \\
&\quad + z|J|S\langle v_\lambda \rangle \sum_\lambda (1 - \gamma_\lambda^2)^{-\frac{1}{2}} \\
&= -4.9 \times 10^6 \text{ erg/cc.} \tag{27}
\end{aligned}$$

According to the molecular field theory,<sup>8</sup>  $E_{\text{an}}(0)$  is  $-5.2 \times 10^6$  erg/cc. The close agreement between the spin-wave theory and the classical theory is caused by the fact that the increase of the absolute value of the first term in (27) as compared with the classical theory is almost canceled by the second term which comes from the zero-point energy of the spin wave.

Antiferromagnetic resonance in  $\text{MnF}_2$  has been observed by Johnson and Nethercot<sup>6</sup> and by Foner,<sup>7</sup>

<sup>19</sup> H. Bizette and B. Tsai, *Compt. rend.* **238**, 1575 (1954).

TABLE I.

T°K	1 - M(T)/M(0)	
	Jaccarino-Shulman	Eisele-Keffer <sup>a</sup>
4.22	0.000063	0.00010
10.2	0.00216	0.00285
13.95	0.00735	0.0073
16.0	0.0107	0.0105
17.0	0.0122	0.0123
20.4	0.0243	0.0200

<sup>a</sup> Numerical values were calculated by F. Keffer (unpublished).

and the anisotropy energy at 0°K is given by Foner using the theory of Keffer and Kittel.<sup>20</sup> His experimental value is

$$E_{\text{an}}(0) = -5.0 \times 10^6 \text{ erg/cc.} \tag{28}$$

This lies midway between the values obtained by the spin-wave theory and the classical theory.

In addition, Foner<sup>7</sup> gives the temperature dependence of the anisotropy energy in the same experiment. The experimental values are in good agreement with the molecular field theory over a wide temperature region.<sup>21</sup> On the other hand, Jaccarino and Shulman<sup>22</sup> obtained the temperature dependence of the magnetization of the sublattice by observing the nuclear magnetic resonance of a fluorine ion. Their result is in reasonable (though not detailed) agreement with the result of the spin wave theory<sup>18</sup> at low temperatures, as shown in Table I.

Any attempt, at present, to get from experiment a value of the exponent in  $E_{\text{an}}(T)/E_{\text{an}}(0) = [M(T)/M(0)]^n$  is not too meaningful, because of the large random scattered values of  $E_{\text{an}}(T)$ . However, a value of  $n > 2$  seems required by Foner's data, because his observed values of  $\omega_{H=0}(T)/\omega_{H=0}(0)$ , which corresponds to  $\{E_{\text{an}}(T)/E_{\text{an}}(0)\}^{\frac{1}{2}}$  or to  $\{M(T)/M(0)\}^{n/2}$ , are smaller than  $M(T)/M(0)$  obtained by Jaccarino and Shulman. Until more accurate measurements of  $E_{\text{an}}(T)$  are available, we cannot get a correct value of  $n$  to be compared with the theoretical formula (26).

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<sup>20</sup> F. Keffer and C. Kittel, *Phys. Rev.* **85**, 329 (1952).

<sup>21</sup> According to molecular field theory,  $E_{\text{an}}(T)$  is proportional to  $[M_B(T)]^2$ ,  $[M_B(T)]$  is the magnetization obtained by using the Brillouin function, and  $\omega_{H=0}(T)$  (antiferromagnetic resonance frequency without external field) is proportional to  $[E_{\text{an}}(T)]^{\frac{1}{2}}$ ; the latter statement holds because, according to reference 20,  $\omega_{H=0}/\gamma = (2H_E H_A)^{\frac{1}{2}} = [2(\lambda M)(E_{\text{an}}/M)]^{\frac{1}{2}} = (2\lambda E_{\text{an}})^{\frac{1}{2}}$ , where  $\lambda$  is a constant. Foner observed that  $\omega_{H=0}$  is proportional to  $M_B(T)$ . This shows that the experimental values can be explained by molecular field theory under the assumption that  $M_B(T)$  is a good approximation for the magnetization. However, the  $M_B$  curve disagrees with the magnetization curve observed by Jaccarino and Shulman.<sup>22</sup> We do not know the reason why  $\omega_{H=0}(T)/\omega_{H=0}(0)$  is in good agreement with  $M_B(T)/M_B(0)$  over a wide temperature region.

<sup>22</sup> V. Jaccarino and R. G. Shulman, *Phys. Rev.* **107**, 1196 (1957).