

Exchange Anisotropy in MnF_2

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It is found that the exchange anisotropy in MnF_2 is due to the mixing of the excited quartets into the ground state of Mn^{2+} by the spin-orbit coupling in the presence of a tetragonal crystalline field. Numerical estimate for the ratio of the anisotropic exchange field to the isotropic exchange field is in good agreement with the value deduced from the g-shift. Implications of our results are discussed.

I. INTRODUCTION

MnF_2 is a body-centered tetragonal crystal with Néel temperature equal to 66.5 K. The Mn^{2+} ions form an easy axis two-sublattice uniaxial antiferromagnet. The ground state of Mn^{2+} is 6S , an orbitally nondegenerate state. It was shown by Keffer⁽¹⁾ that the major contribution to the anisotropy energy in MnF_2 arises from the inter-ion point dipolar interactions in this noncubic crystal. The single-ion anisotropy was estimated to be roughly an order of magnitude less than the dipolar term. In addition to the dipolar and single-ion anisotropy energies, anisotropic exchange coupling between two Mn^{2+} spins \mathbf{S}_a and \mathbf{S}_b of the form, $-JS_a \cdot \mathbf{S}_b - J_a S_{a_z} S_{b_z}$, is also allowed in MnF_2 from symmetry considerations. The purpose of this paper is to examine the origin of the anisotropic exchange in MnF_2 and to estimate its magnitude. Our motivation of investigating this problem is explained in the following.

The strength of the anisotropic exchange coupling can be deduced from various experimental information. Using the measurements⁽²⁻⁴⁾ on the perpendicular susceptibility χ_{\perp} and the field H_c (i.e., the magnetic field for which the down-going antiferromagnetic resonance branch has zero frequency) together with the calculated point-charge dipolar fields⁽⁵⁾, Barak *et al.*⁽⁶⁾ determined the anisotropic exchange field $H_{AE} = (-0.91 \pm 0.03)\text{KOe}$ and the isotropic exchange field $H_E = (528.1 \pm 1.0)\text{KOe}$. A somewhat different approach of deducing H_{AE} can be carried out by using the value $H_E = (526.2 \pm 3.5)\text{KOe}$ from the neutron scattering experiments⁽⁶⁾, the measured H_c , and the calculated point-charge dipolar fields. Doing this, Barak *et al.*⁽⁶⁾ found $H_{AE} = (-0.88 \pm 0.09)\text{KOe}$. Both analyses lead to $H_{AE}/H_E \approx 2 \times 10^{-3}$. On the other hand, the order of magnitude of this ratio

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(4) M. Tinkham, Proc. Roy. Soc. (London) A236, 535 (1956).

(5) J. Barak, V. Jaccarino, and S. M. Rezende, J. Magnetism and Magnetic Materials, 9, 323 (1978).

(6) O. Nikotin, P. A. Lindgard, and O. W. Dietrich, J. Phys. C2, 1168 (1969).

can be estimated directly from the measured g -shift⁽⁷⁾ without introducing the calculated dipolar fields. This yields $H_{AE}/H_E < 10^{-6}$ (or equivalently, $H_{AE} < 0.50e$), which is three orders of magnitude less than that deduced from the other analyses.

To resolve the significant difference in the estimated values of H_{AE}/H_E , Barak *et al.*⁽⁸⁾ proposed that, instead of using the point-charge approximation, covalency and overlap effects between the Mn^{2+} and F^- ions should be included in calculating the dipolar fields. As a simple correction to their estimated point-charge dipolar fields, Barak *et al.* allowed for a decrease in the magnetic moment at the site of a Mn^{2+} ion by the amount corresponding to the net spin density at the surrounding F^- sites. In this manner they obtained an 8% reduction in the dipolar fields. Taking this reduction into consideration, the estimated value for H_{AE} becomes -0.24 KOe . However, the magnitude of this value is still much too large compared with that estimated from the g -shift.

Instead of deducing H_{AE} indirectly from experimental results (this approach requires a precise knowledge of the dipolar fields), we investigate in this paper the origin of H_{AE} in MnF_2 and evaluate its magnitude. Since the ground state of Mn^{2+} has a spherical charge distribution, we propose that the pseudo-dipolar anisotropic exchange between two Mn^{2+} ions is caused by the mixing of the excited configurations of Mn^{2+} into its ground configuration 6S in a noncubic environment. The interaction responsible for this mixing is the spin-orbit coupling.

In the following section we derive the expressions for the isotropic exchange integral J and the anisotropic component J_z by calculating the effective exchange Hamiltonian between two Mn^{2+} ions. Our numerical estimate for $J_z/J (\equiv H_{AE}/H_E)$ has the same order of magnitude as that deduced from the g -shift. In the last section we discuss implications of our results.

II. CALCULATIONS

The low-lying states of a Mn^{2+} free ion, neglecting the spin-orbit coupling, are 6S , 4G , 4P , 4F , etc., as shown in Fig. 1a. In a cubic crystalline field, the excited states 4G , 4P , and 4F are combined linearly to form three three-fold orbitally degenerate ${}^4\Gamma_4$ states shown in Fig. 1b. These quartet states are^(8,9)

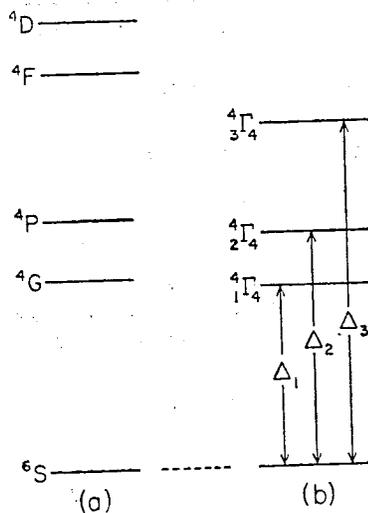


Fig. 1. a. The low-lying energy levels of a free Mn^{2+} ion in the absence of spin-orbit coupling.
b. The low-lying energy levels of Mn^{2+} in a cubic crystalline field in the absence of spin-orbit coupling.

(7) Unpublished result cited in reference 5.

(8) M. Blume and R. Orbach, *Phys. Rev.* **127**, 1587 (1962).

(9) R. R. Sharma, T. P. Das, and R. Orbach, *Phys. Rev.* **149**, 257 (1966).

$$\begin{aligned}
 |{}^4\Gamma_i, 1, M_i\rangle &= \left\{ \alpha_i |P, 1\rangle + \beta_i \left(\sqrt{\frac{3}{8}} |F, 1\rangle + \sqrt{\frac{5}{8}} |F, -3\rangle \right) \right. \\
 &\quad \left. - \gamma_i \left(\sqrt{\frac{7}{8}} |G, 1\rangle + \sqrt{\frac{1}{8}} |G, -3\rangle \right) \right\} |-\frac{3}{2}, M_i\rangle; \\
 |{}^4\Gamma_i, 0, M_i\rangle &= \left\{ \alpha_i |P, 0\rangle + \beta_i |F, 0\rangle + \gamma_i \left(-\sqrt{\frac{1}{2}} |G, 4\rangle + \sqrt{\frac{1}{2}} |G, -4\rangle \right) \right\} \\
 &\quad |-\frac{3}{2}, M_i\rangle; \\
 |{}^4\Gamma_i, -1, M_i\rangle &= \left\{ \alpha_i |P, -1\rangle + \beta_i \left(\sqrt{\frac{5}{8}} |F, 3\rangle + \sqrt{\frac{3}{8}} |F, -1\rangle \right) \right. \\
 &\quad \left. + \gamma_i \left(-\sqrt{\frac{1}{8}} |G, 3\rangle + \sqrt{\frac{7}{8}} |G, -1\rangle \right) \right\} |-\frac{3}{2}, M_i\rangle,
 \end{aligned} \tag{1}$$

where $i=1, 2$, and 3 . The coefficients α_i, β_i , and γ_i have been calculated by Blume and Orbach⁽⁸⁾ and also by Sharma, Das, and Orbach⁽⁹⁾. In Table I we list these coefficients together with Δ_i , the separation between ${}^4\Gamma_i$ and 6S , for different cubic field parameter $10Dq$. In the presence of a tetragonal distortion, such as the case in MnF_2 , ${}^4\Gamma_i$ splits into an orbital doublet $|{}^4\Gamma_i, \text{fl}, M_i\rangle$ and an orbital singlet $|{}^4\Gamma_i, 0, M_i\rangle$. Separation of the doublet and the singlet, from the ground state are denoted, respectively, by $\Delta_{i\perp}$ and Δ_{i0} .

Next we take into account the spin-orbit coupling $\zeta \sum_j l_j \cdot s_j$. This coupling, to first order, mixes the three ${}^4\Gamma_i$ states into the ground state. The resulting perturbed ground state eigenfunctions are^(8,9)

$$\begin{aligned}
 |\Psi_{M_i}\rangle &= |{}^6S, M_i\rangle - \sum_{i=1}^3 \alpha_i \zeta \{ [a(M_i) |{}^4\Gamma_i, 1, M_i-1\rangle \\
 &\quad + b(M_i) |{}^4\Gamma_i, -1, M_i+1\rangle] / \Delta_{i\perp} + c(M_i) |{}^4\Gamma_i, 0, M_i\rangle / \Delta_{i0} \},
 \end{aligned} \tag{2}$$

where $a(M_i), b(M_i)$, and $c(M_i)$ are constants related to the matrix elements of the spin-orbit coupling between the ground state and the 4P term in ${}^4\Gamma_i$ states. (The other terms in ${}^4\Gamma_i$ are not linked to 6S by the spin-orbit coupling.) Explicitly, we have

$$\begin{aligned}
 a(M_i) &= \frac{1}{2} \langle {}^4P, 1, M_i-1 | \sum_j l_j^+ s_j^- | {}^6S, M_i \rangle; \\
 b(M_i) &= \frac{1}{2} \langle {}^4P, -1, M_i+1 | \sum_j l_j^- s_j^+ | {}^6S, M_i \rangle; \\
 c(M_i) &= \langle {}^4P, 0, M_i | \sum_j l_{jz} s_{jz} | {}^6S, M_i \rangle.
 \end{aligned} \tag{3}$$

Table I. Coefficients α_i, β_i , and γ_i in Eq. (1) and Δ_i (in cm^{-1}) measured from 6S for various values of $10Dq$ calculated in reference 9

i	α_i	β_i	γ_i	Δ_i
$10Dq=9000\text{cm}^{-1}$				
1	0.633	-0.127	0.763	19,501
2	0.761	0.285	-0.583	35,380
3	0.143	-0.950	-0.277	44,805
$10Dq=10000\text{cm}^{-1}$				
1	0.637	-0.135	0.759	18,546
2	0.751	0.334	-0.570	36,001
3	0.176	-0.933	-0.314	45,138
$10Dq=11000\text{cm}^{-1}$				
1	0.640	-0.143	0.755	17,588
2	0.739	0.355	-0.553	36,569
3	0.212	-0.912	-0.352	45,529

Table II. Values of $a(M_s)$, $b(M_s)$, and $c(M_s)$ defined by Eq. (3)

M_s	5/2	3/2	1/2	-1/2	-3/2	-5/2
$a(M_s)$	$+\sqrt{5}$	$+\sqrt{3}$	$+(1/2)\sqrt{6}$	$+(1/2)\sqrt{2}$	0	0
$b(M_s)$	0	0	$+(1/2)\sqrt{2}$	$+(1/2)\sqrt{6}$	$+\sqrt{3}$	$+\sqrt{5}$
$c(M_s)$	0	$-\sqrt{2}$	$+\sqrt{3}$	$+\sqrt{3}$	$+\sqrt{2}$	0

Numerical values⁽¹⁰⁾ for $a(M_s)$, $b(M_s)$, and $c(M_s)$ are listed in Table II.

Using the wavefunctions given by Eq. (2), we now calculate the exchange anisotropy. The anisotropic exchange interaction between the Mn^{2+} ions \mathbf{a} and \mathbf{b} .

$$\mathcal{H} = -JS_{\mathbf{a}} \cdot S_{\mathbf{b}} - J_{\perp} S_{\mathbf{a}z} S_{\mathbf{b}z} \quad (4)$$

can also be written as

$$\begin{aligned} \mathcal{H} &= -\frac{J}{2} (S_{\mathbf{a}}^+ S_{\mathbf{b}}^- + S_{\mathbf{a}}^- S_{\mathbf{b}}^+) - (J + J_{\perp}) S_{\mathbf{a}z} S_{\mathbf{b}z} \\ &\equiv -\frac{J_{\perp}}{2} (S_{\mathbf{a}}^+ S_{\mathbf{b}}^- + S_{\mathbf{a}}^- S_{\mathbf{b}}^+) - J_{\parallel} S_{\mathbf{a}z} S_{\mathbf{b}z}. \end{aligned} \quad (5)$$

Following Barak *et al.*⁽⁵⁾, we define the isotropic and the anisotropic exchange field by

$$\begin{aligned} H_E &= -zJS/g\mu_B; \\ H_{AE} &= -zJ_{\perp}S/g\mu_B, \end{aligned}$$

where z is the number of nearest neighbors, S is the magnitude of Mn^{2+} spin, and μ_B is the Bohr magneton. The ratio H_{AE}/H_E is simply

$$H_{AE}/H_E = (J_{\parallel} - J_{\perp})/J_{\perp}. \quad (6)$$

We note that the exchange Hamiltonian given by Eq. (4) or Eq. (5) is expressed in terms of the total spin of a Mn^{2+} ion. On the other hand, we can also express this Hamiltonian in terms of coupling between an individual $3d$ electron of ion \mathbf{a} and an individual $3d$ electron of ion \mathbf{b} :

$$\mathcal{H} = -\sum_{i,j=1}^5 J_{ij} \mathbf{s}_{i\mathbf{a}} \cdot \mathbf{s}_{j\mathbf{b}}, \quad (7)$$

where the summation is over the five $3d$ electrons of each ion, $\mathbf{s}_{i\mathbf{a}}$ and $\mathbf{s}_{j\mathbf{b}}$ represent, respectively, the i -th d -electron of ion \mathbf{a} and the j -th d -electron of ion \mathbf{b} , and J_{ij} is the exchange integral between these two electrons. We now calculate J_{\parallel} and J_{\perp} in terms of J_{ij} by equating the matrix elements of Eq. (5) to those of Eq. (7) evaluated between the perturbed ground states,

$$\langle \Psi_{M_s^a}^a \Psi_{M_s^b}^b | \frac{J_{\perp}}{2} (S_{\mathbf{a}}^+ S_{\mathbf{b}}^- + S_{\mathbf{a}}^- S_{\mathbf{b}}^+) + J_{\parallel} S_{\mathbf{a}z} S_{\mathbf{b}z} | \Psi_{M_s^a}^a \Psi_{M_s^b}^b \rangle = \langle \Psi_{M_s^a}^a \Psi_{M_s^b}^b | \sum_{i,j=1}^5 J_{ij} \mathbf{s}_{i\mathbf{a}} \cdot \mathbf{s}_{j\mathbf{b}} | \Psi_{M_s^a}^a \Psi_{M_s^b}^b \rangle. \quad (8)$$

As an illustrative example we take $M_s = M_s' = M_s'' = M_s''' = 3/2$. The left-hand side of the above equation, which operates in an $S=5/2$ manifold for each ion, then simply equals to $9J_{\parallel}/4$. Evaluation of the right-hand side of Eq. (8) is straightforward but laborious. In this case since we are dealing with couplings between individual spins, we need to know the many-electron wavefunctions of 6S (which is trivial), $|{}^4P, M_L\rangle$, $|{}^4F, M_L\rangle$, and $|{}^4G, M_L\rangle$ terms involved in Eqs. (1) and (2). These wavefunctions are in the form of linear combination of Slater determinants and can be derived in a standard manner⁽¹⁰⁾. Evaluating the matrix elements of $\sum_{i,j} J_{ij} \mathbf{s}_{i\mathbf{a}} \cdot \mathbf{s}_{j\mathbf{b}}$ between appropriate Slater determinants, we obtain

$$\langle \Psi_{5/2}^a \Psi_{5/2}^b | \sum_{i,j=1}^5 J_{ij} \mathbf{s}_{i\mathbf{a}} \cdot \mathbf{s}_{j\mathbf{b}} | \Psi_{5/2}^a \Psi_{5/2}^b \rangle = \frac{9}{100} \left[1 + 2 \sum_{i=1}^3 (c_{i\perp}^2 + 2c_{i\parallel}^2) \right] \sum_{i,j=1}^5 J_{ij}, \quad (9)$$

where $c_{1\perp} = \zeta \sum_{i=1}^3 \alpha_i / \Delta_{i\perp}$, $c_{2\perp} = \zeta \sum_{i=1}^3 \alpha_i \beta_i / \Delta_{i\perp}$, $c_{3\perp} = \zeta \sum_{i=1}^3 \alpha_i \gamma_i / \Delta_{i\perp}$, and $c_{i\parallel}$ is defined the same

(10) For example, J.S. Griffith, *The Theory of Transition-Metal Ions*, Cambridge University Press, 1964, Chapter 4.

as $c_{i\perp}$ except that $\Delta_{i\perp}$ is replaced by $\Delta_{i\parallel}$. Equating Eq. (9) to $9J_{\parallel}/4$ yields

$$J_{\parallel} = \frac{1}{25} \left[1 + 2 \sum_{i=1}^3 (c_{i\perp}^2 + 2c_{i\parallel}^2) \right] \sum_{i,j=1}^3 J_{ij}. \quad (10)$$

In a similar manner, we calculate J_{\perp} by choosing $M_i = M'_i = 3/2$ and $M'_i = M''_i = 1/2$ in Eq. (8). We find

$$J_{\perp} = \frac{1}{25} \left[1 + 3 \sum_{i=1}^3 (c_{i\perp}^2 + c_{i\parallel}^2) \right] \sum_{i,j=1}^3 J_{ij}. \quad (11)$$

In deriving J_{\parallel} and J_{\perp} we have ignored terms of the order of $(\zeta/\Delta_{i\perp})^4$ and $(\zeta/\Delta_{i\parallel})^4$ and higher order terms.

Substituting our expressions for J_{\parallel} and J_{\perp} into Eq. (6), the ratio H_{AE}/H_E can be readily estimated. Using the value $\zeta = 300 \text{ cm}^{-1(8)}$, $\Delta_{i\parallel} - \Delta_{i\perp} \approx 250 \text{ cm}^{-1(11)}$, and the information in Table I, we find $\sum_{i=1}^3 c_{i\perp}^2$ and $\sum_{i=1}^3 c_{i\parallel}^2$ are of the order of 10^{-4} . As a result we can write, to a good approximation,

$$\begin{aligned} H_{AE}/H_E &\approx \sum_{i=1}^3 (c_{i\parallel}^2 - c_{i\perp}^2) \\ &\approx 2\zeta^2 (\Delta_{\perp} - \Delta_{\parallel}) \left[\left(\sum_{i=1}^3 \frac{\alpha_i^2}{\Delta_i} \right) \left(\sum_{i=1}^3 \frac{\alpha_i^2}{\Delta_i^2} \right) + \left(\sum_{i=1}^3 \frac{\alpha_i \beta_i}{\Delta_i} \right) \left(\sum_{i=1}^3 \frac{\alpha_i \beta_i}{\Delta_i^2} \right) \right. \\ &\quad \left. + \left(\sum_{i=1}^3 \frac{\alpha_i \gamma_i}{\Delta_i} \right) \left(\sum_{i=1}^3 \frac{\alpha_i \gamma_i}{\Delta_i^2} \right) \right]. \end{aligned} \quad (12)$$

For the purpose of estimating H_{AE}/H_E numerically, we have ignored in the last equation the small difference in tetragonal crystalline field splitting for different 4G_4 quartets, i.e., we have taken $\Delta_{i\parallel} - \Delta_{i\perp} = \Delta_{\parallel} - \Delta_{\perp}$. The value for Δ_i depends on the cubic field parameter $10Dq$ as indicated in Table I. For $10Dq = 9 \times 10^3 \text{ cm}^{-1}$, $10 \times 10^3 \text{ cm}^{-1}$, and $11 \times 10^3 \text{ cm}^{-1}$, we find H_{AE}/H_E equal to -3.9×10^{-6} , -4.5×10^{-6} , and -5.2×10^{-6} , respectively. These are in excellent agreement with the order of magnitude of H_{AE}/H_E estimated from the g-shift. Since the isotropic exchange field, H_E , is known to be 528 KOe, our calculations yield a value ≈ -2 Oe for the anisotropic exchange field, H_{AE} .

III. DISCUSSION AND CONCLUSION

In the above section we have shown that the isotropic exchange coupling in MnF_2 is a result of mixing of the excited 4G_4 states into the ground state of Mn^{2+} by the spin-orbit coupling in a tetragonal crystalline field. Obviously, in a cubic system we expect $J_{\parallel} = J_{\perp}$ and H_{AE} should vanish. Our expression for H_{AE}/H_E satisfies this criterion if we let $\Delta_{\perp} = \Delta_{\parallel}$ in Eq. (12).

Our numerical estimate of H_{AE}/H_E confirms the result expected from the g-shift, i. e., H_{AE}/H_E is of the order of -10^{-6} . Since H_{AE} is several orders of magnitude less than the other fields involved in the analysis ($H_E \sim 500 \text{ KOe}$, $H_C \sim 100 \text{ KOe}$, and dipolar fields $\sim (3-6) \text{ KOe}$), it is obvious that if we wish to deduce H_{AE} from χ_{\perp} , H'_C , and spin wave dispersion, we should use an extremely accurate value for the inter-ion magnetic dipolar fields. Barak *et al.*⁽¹²⁾ pointed out the necessity of including overlap and covalency effects between Mn^{2+} and F^- ion in estimating the dipolar fields. As we have stated in Section I, by introducing an 8% **reduction** in the magnetic moment of an M^{2+} ion, they obtained $H_{AE} = -0.24 \text{ KOe}$. This value is two orders of magnitude too large compared with our estimate from first principles. Hence a more complete calculation for the magnetic dipolar interaction is needed. Furthermore, it has been shown by Watson and Freeman¹³ that as a result of the overlap and covalency effect, the charge density at the site of the magnetic ion is actually **increased**. This is caused by a depletion of charge densities from the region in between the magnetic ion and the ligands. Therefore, in an accurate calculation of the magnetic dipolar interaction, one should use the complete molecular orbitals for the magnetic ions and their

(11) R.N. Figgis, *Introduction to Ligand Fields*, John Wiley and Sons, 1966.

(12) R. E. Watson and A. J. Freeman, Phys. Rev. 134, A1526 (1964).

surrounding ligands (which also carry a net spin density because of the overlap and covalency effects).

Finally, it should be pointed out that the wave functions, Eq. (2), which were used in deriving J_{\parallel} and J_{\perp} are correct only to the first order in spin-orbit coupling. Consequently, we found that our results for J_{\parallel} and J_{\perp} vary slightly for different choices of the M_i values used in Eq. (8). However, we found that our numerical estimates for H_{AE}/H_E are consistently of the order of $\sim 10^{-6}$. To obtain expressions for J_{\parallel} and J_{\perp} that are independent of the M_i values chosen in Eq. (8), we need to carry out perturbation of the wavefunctions to second order spin-orbit coupling⁽¹³⁾. We found that such refined calculations did not alter our conclusions; namely, the anisotropic exchange in MnF_2 is a result of the mixing of the excited states into the ground state of Mn^{2+} by the spin-orbit coupling and the ratio of anisotropic exchange field to isotropic exchange field is of the order of $\sim 10^{-6}$.

(13) From Eq. (10) and Eq. (11) we note that J_{\parallel} or J_{\perp} differs from the isotropic exchange integral ($= \sum_{i,j=1}^5 J_{ij}/25$) by a factor $\sim (\zeta/\Delta_i)^2$. Hence perturbation in wavefunctions to second order in spin-orbit coupling could be of some importance.