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Theory of the Magnetic Anisotropy in $KMnF_3$†

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A theoretical calculation is made of the magnetic anisotropy in the cubic perovskite structure of $KMnF_3$ at room temperature and in its distorted structures at lower temperatures. These distortions are of two types: first, a small tetragonal distortion of the entire crystal; and then, below the antiferromagnetic Néel point, a distortion of the octahedron of fluorine atoms surrounding each manganese. The cubic anisotropy is obtained from a general spin-wave calculation of the zero-point dipole-dipole energy in a cubic antiferromagnet. The result is found to be the same as that for the ferromagnetic case. The anisotropy from the tetragonal distortion is obtained from the change in the classical Lorentz factors. In calculating the effect of the fluorine distortion, a generalization is introduced of Kondo's method for obtaining the anisotropic effective spin Hamiltonian produced by overlap and electron transfer between an Mn^{++} ion and its nonmagnetic neighbors. In its present form the method permits the ready calculation of this anisotropy for any symmetry and number of neighbors. Comparison with the microwave resonance and torque measurements of Portis, Teaney, and Heeger, reveals the last effect to be the most important and confirms the form of the spin Hamiltonian found here and its approximate magnitude.

I. INTRODUCTION

RECENT magnetic resonance experiments by Portis, Teaney, and Heeger[1] on antiferromagnetic $KMnF_3$, and torque measurements by Heeger on the same crystal have revealed the presence of important anisotropy fields acting on the manganese spins. It is the purpose of this paper to examine the sources of these fields and predict their magnitude.

The most important source of anisotropy is found to be a distortion, at temperatures below the Néel point, of the octahedron of fluorine atoms surrounding each manganese. In order to calculate the effective spin Hamiltonian produced by this distortion, a generalization is introduced of a method due to Kondo[2] for estimating, in lowest order perturbation theory, the anisotropic effect of overlap and electron transfer between a manganese ion and its nonmagnetic nearest neighbors. In its present form the method permits the calculation of this effect for any number of neighbors and any symmetry with very little additional work.

Keffer, Oguchi, O'Sullivan, and Yamashita[3] have shown that the spin-dependent interaction between an Mn^{++} ion and an F^- ion can be thought of in terms of an antibonding orbital of the type

$$\Phi'=(1+\tfrac{1}{2}S^2-\tfrac{1}{2}\lambda^2)\Phi-(S+\lambda)\Theta, \qquad (1)$$

where Φ represents a manganese $3d$ function and Θ a fluorine s or p function; S is the overlap between Φ and Θ, and λ the coefficient of electron transfer. Since the problem under consideration in that paper concerned nuclear magnetic resonance of the fluorine nucleus, the Φ part of that function was negligible and a hyperfine interaction proportional to $(S+\lambda)^2$ was obtained. Here, the concern is with the manganese $3d$ electron spins, so the Φ term should be the important one; and indeed the method used here shows that, to second order in S and λ, the spin Hamiltonian does depend on those quantities in the combination $S^2-\lambda^2$. In principle, then, it should be possible, when more accurate experimental values for the electron-spin-Hamiltonian constant and the exact positions of the fluorine are known, to combine this information with fluorine nuclear resonance results and obtain values for $(S+\lambda)^2$, $S^2-\lambda^2$, and hence S and λ individually.

At room temperature the $KMnF_3$ crystal has the cubic perovskite structure, with a manganese atom at the body center, fluorines at the face centers, and potassiums at the cube corners. Thus the magnetic symmetry is simple cubic, and each manganese is surrounded by an octahedron of fluorine nearest neighbors. The cubic anisotropy effects are discussed in Sec. II. As the temperature is lowered, the first effect is a contraction of the lattice constant from its value of 4.186 A at room temperature, and then a tetragonal distortion of the entire crystal occurs, as shown in Fig. 1. The anisotropy resulting from this tegragonal distortion is considered in Sec. III. Finally, below the Néel point a distortion of the fluorine octahedron is observed. This is dealt with in Sec. IV.

II. ZERO-POINT ANISOTROPY IN A CUBIC ANTIFERROMAGNET

The first anisotropy to be considered is the cubic. Van Vleck[4] has shown (and the calculation in Sec. IV confirms) that a cubic array of ordered dipoles can produce no anisotropy in first order perturbation theory, so no cubic contribution from the overlap and transfer effects is to be expected in lowest order. In

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[1] A. M. Portis, D. T. Teaney, and A. J. Heeger (to be published).

[2] J. Kondo, Progr. Theoret. Phys. (Kyoto) 23, 106 (1960).

[3] F. Keffer, T. Oguchi, W. O'Sullivan, and J. Yamashita, Phys. Rev. 115, 1553 (1959).

[4] J. H. Van Vleck, Phys. Rev. 52, 1178 (1937).

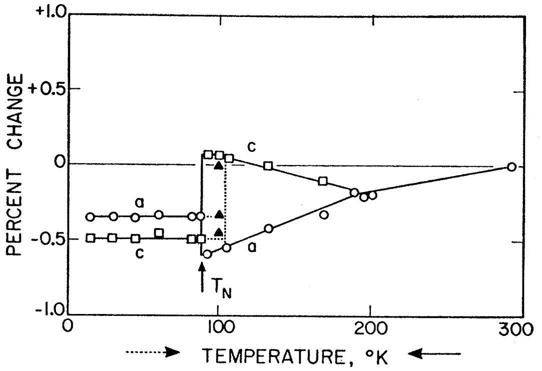

FIG. 1. Volume contraction and tetragonal distortion of the KMnF$_3$ crystal with temperature. *c*, *a*, and *a* are the tetragonal lattice constants. [After O. Beckman and K. Knox, Phys. Rev. **121**, 376 (1961).]

second-order, however, cubic anisotropy can be obtained, and that arising from the dipolar or pseudodipolar interaction of the manganese ions was calculated. This calculation was performed using second-order perturbation theory. The unperturbed Hamiltonian, H_0, was taken to be the exchange Hamiltonian,

$$H_0=J\sum_{i\neq j}\mathbf{S}_i\cdot\mathbf{S}_j, \tag{2}$$

where *i* and *j* were taken to run only over nearest neighbors, and *J* was taken to be a positive constant. The cubic lattice was broken up into two interlaced face-centered cubic sublattices, such that one sublattice contained all the nearest neighbors of any site in the other. Thus in H_0, *i* and *j* can be taken to run over different sublattices. Following Kubo,[5] the ground state of H_0 was assumed to be that in which all the spins on one sublattice were completely quantized in the positive direction along some arbitrary axis, and those on the other sublattice in the opposite direction along that axis; and it was assumed that for any states to be considered, the deviations from this ground state were small.

On these assumptions, creation and annihilation operators for spin deviations from maximum alignment were introduced, and terms of third or higher order in these deviations were ignored. Thus,

$$\begin{aligned}S_i^+&\equiv S_i^x+iS_i^y\approx(2S)^{\frac{1}{2}}a_i,\\ S_i^-&\equiv S_i^x-iS_i^y\approx(2S)^{\frac{1}{2}}a_i^*,\\ S_i^z&=S-a_i^*a_i,\end{aligned}\tag{3}$$

for one sublattice, and

$$\begin{aligned}S_j^+&\equiv S_j^x+iS_j^y\approx(2S)^{\frac{1}{2}}b_j^*,\\ S_j^-&\equiv S_j^x-iS_j^y\approx(2S)^{\frac{1}{2}}b_j,\\ -S_j^z&=S-b_j^*b_j\end{aligned}\tag{4}$$

for the other. Here S is the spin quantum number of an atom, and the creation and annihilation operators satisfy the commutation relations:

$$\begin{gathered}[a_i,a_{i'}^*]=\delta_{i,i'},\quad [b_j,b_{j'}^*]=\delta_{j,j'},\\ [a_i,b_j]=[a_i^*,b_j]=[a_i^*,b_j^*]=[a_i,b_j^*]=0.\end{gathered}\tag{5}$$

In terms of these operators,

$$\begin{aligned}H_0=-\tfrac{1}{2}JS^2Nz+JS\sum_{i\neq j}[a_ib_j+a_i^*b_j^*]&\\ +JSz[\textstyle\sum_i a_i^*a_i+\sum_j b_j^*b_j],&\end{aligned}\tag{6}$$

where N is the number of magnetic atoms in the crystal and z is the number of magnetic nearest neighbors of one atom.

Introducing spin waves in the form:

$$\begin{aligned}a_i&=(2/N)^{\frac{1}{2}}\textstyle\sum_\lambda a_\lambda\exp(-i\mathbf{k}_\lambda\cdot\mathbf{R}_i),\\ b_j&=(2/N)^{\frac{1}{2}}\textstyle\sum_\lambda b_\lambda\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_j),\\ a_i^*&=(2/N)^{\frac{1}{2}}\textstyle\sum_\lambda a_\lambda^*\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_i),\\ b_j^*&=(2/N)^{\frac{1}{2}}\textstyle\sum_\lambda b_\lambda^*\exp(-i\mathbf{k}_\lambda\cdot\mathbf{R}_j),\end{aligned}\tag{7}$$

where λ runs over all $\mathbf{k}$ vectors in the first Brillouin zone for the sublattice under consideration, and using the fact that

$$\textstyle\sum_i\exp[i(\mathbf{k}_\lambda-\mathbf{k}_{\lambda'})\cdot\mathbf{R}_i]=\delta_{\lambda,\lambda'}\tag{8}$$

one obtains for the Hamiltonian,

$$\begin{aligned}H_0=K_0+\textstyle\sum_\lambda[K_{1\lambda}(a_\lambda b_\lambda+a_\lambda^*b_\lambda^*)&\\ +K_2(a_\lambda^*a_\lambda+b_\lambda^*b_\lambda)],&\end{aligned}\tag{9}$$

where

$$\begin{gathered}K_0=-\tfrac{1}{2}JS^2Nz,\\ K_{1\lambda}=K_1(-\lambda)=JS\textstyle\sum_h\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)\equiv JSz\gamma_\lambda,\end{gathered}\tag{10}$$

($\mathbf{R}_h$ equals $\mathbf{R}_i-\mathbf{R}_j$ and is independent of $\mathbf{R}_i$), and

$$K_2=SJz.\tag{11}$$

The a_λ's and b_λ's satisfy commutation rules:

$$\begin{gathered}[a_\lambda,a_{\lambda'}^*]=[b_\lambda,b_{\lambda'}^*]=\delta_{\lambda,\lambda'}\\ \text{and}\\ [a_\lambda,b_{\lambda'}]=[a_\lambda^*,b_{\lambda'}^*]=[a_\lambda,b_{\lambda'}^*]=[a_\lambda^*,b_{\lambda'}]=0.\end{gathered}\tag{12}$$

Finally, the following three successive transformations, similar to those introduced by Oguchi[6]:

$$a_{\pm\lambda}=(1/\sqrt{2})(A_\lambda\pm iA_{-\lambda}),\quad b_{\pm\lambda}=(1/\sqrt{2})(B_\lambda\mp iB_{-\lambda});\tag{13}$$

(defined only over the halfspace, $k_{\lambda z}>0$),

$$\begin{aligned}A_\lambda&=\tfrac{1}{2}[q_\lambda+r_\lambda+i(p_\lambda+s_\lambda)],\\ A_\lambda^*&=\tfrac{1}{2}[q_\lambda+r_\lambda-i(p_\lambda+s_\lambda)],\\ B_\lambda&=\tfrac{1}{2}[q_\lambda-r_\lambda+i(p_\lambda-s_\lambda)],\\ B_\lambda^*&=\tfrac{1}{2}[q_\lambda-r_\lambda-i(p_\lambda-s_\lambda)];\end{aligned}\tag{14}$$

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[5] R. Kubo, Phys. Rev. **87**, 568 (1952).

[6] T. Oguchi, Phys. Rev. **111**, 1063 (**1958**).

and

$$
\begin{aligned}
q_\lambda &= (1/\sqrt{2})\left(\frac{1-\gamma_\lambda}{1+\gamma_\lambda}\right)^{\frac14}(c_\lambda+c_\lambda^*),\\
ip_\lambda &= (1/\sqrt{2})\left(\frac{1+\gamma_\lambda}{1-\gamma_\lambda}\right)^{\frac14}(c_\lambda-c_\lambda^*),\\
r_\lambda &= (1/\sqrt{2})\left(\frac{1+\gamma_\lambda}{1-\gamma_\lambda}\right)^{\frac14}(d_\lambda+d_\lambda^*),\\
is_\lambda &= (1/\sqrt{2})\left(\frac{1-\gamma_\lambda}{1+\gamma_\lambda}\right)^{\frac14}(d_\lambda-d_\lambda^*),
\end{aligned}
\tag{15}
$$

reduce the Hamiltonian to the form:

$$
\begin{aligned}
H_0 = JSz[-(N/2)(S+1)+\textstyle\sum_\lambda(1-\gamma_\lambda^2)^{\frac12}]&\\
+JSz\textstyle\sum_\lambda(1-\gamma_\lambda^2)^{\frac12}(d_\lambda^*d_\lambda+c_\lambda^*c_\lambda),&
\end{aligned}
\tag{16}
$$

with c and d satisfying

$$
\begin{aligned}
[c_\lambda,c_{\lambda'}^*]=[d_\lambda,d_{\lambda'}^*]=\delta_{\lambda,\lambda'},&\\
[c_\lambda,d_{\lambda'}]=[c_\lambda^*,d_{\lambda'}^*]=[c_\lambda,d_{\lambda'}^*]=[c_\lambda^*,d_{\lambda'}]=0.&
\end{aligned}
\tag{17}
$$

Thus, by analogy with the harmonic oscillator Hamiltonian, the eigenvalues of H_0 are

$$
\begin{aligned}
E^0(n_{c\lambda},n_{d\lambda}) = JSz[-\tfrac12 N(S+1)+\textstyle\sum_\lambda(1-\gamma_\lambda^2)^{\frac12}&\\
+\textstyle\sum_\lambda(1-\gamma_\lambda^2)^{\frac12}(n_{c\lambda}+n_{d\lambda})],&
\end{aligned}
\tag{18}
$$

where $n_{c\lambda}$ and $n_{d\lambda}$ take arbitrary non-negative integral values.

The perturbation, H_1, was taken in the form:

$$H_1 = D\sum_{i,j}[\mathbf{S}_i\cdot\mathbf{S}_j-3(\mathbf{S}_i\cdot\mathbf{R}_{ij})(\mathbf{S}_j\cdot\mathbf{R}_{ij})/|R_{ij}|^2], \tag{19}$$

where $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$ is the vector from lattice point i to nearest neighbor lattice point j. In terms of the direction cosines, α_h, β_h, and γ_h of $\mathbf{R}_{ij}$ with respect to Cartesian axes in which the z axis is the direction of quantization of the spins:

$$
\begin{aligned}
H_1 = DH_0/J-3D\sum_{i,j}(S_{ix}\alpha_h+S_{iy}\beta_h+S_{iz}\gamma_h)&\\
\times(S_{jx}\alpha_h+S_{jy}\beta_h+S_{jz}\gamma_h).&
\end{aligned}
\tag{20}
$$

Expressing H_1 in terms of c_λ and d_λ, and noting that sums of the form $\sum_h\alpha_h\gamma_h$ vanish by the crystal symmetry, one obtains

$$
\begin{aligned}
H_1 = A_0+\textstyle\sum_\lambda[A_{1\lambda}c_\lambda^*c_\lambda+A_{2\lambda}d_\lambda^*d_\lambda&\\
+A_{3\lambda}(c_\lambda^2+c_\lambda^{*2})+A_{4\lambda}(d_\lambda^2+d_\lambda^{*2})&\\
+A_{5\lambda}(c_\lambda d_\lambda-c_\lambda^*d_\lambda^*)+A_{6\lambda}(c_\lambda^*d_\lambda^*-c_\lambda d_\lambda^*)],&
\end{aligned}
\tag{21}
$$

where

$$
\begin{aligned}
A_0 = \tfrac32 SD\sum_h\Bigg\{N(S+1)\gamma_h^2&\\
-\tfrac12\sum_\lambda\Bigg[[2\gamma_h^2+(\alpha_h^2+\beta_h^2)\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)]&\\
\times\left(\frac{1-\gamma_\lambda}{1+\gamma_\lambda}\right)^{\frac12}+[2\gamma_h^2-(\alpha_h^2+\beta_h^2)\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)]&\\
\times\left(\frac{1+\gamma_\lambda}{1-\gamma_\lambda}\right)^{\frac12}\Bigg]\Bigg\},&
\end{aligned}
$$

$$
\begin{aligned}
A_{1\lambda} &= -\tfrac32 SD\sum_h\Bigg[[\gamma_h^2+\alpha_h^2\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)]\left(\frac{1-\gamma_\lambda}{1+\gamma_\lambda}\right)^{\frac12}\\
&\qquad+[\gamma_h^2-\beta_h^2\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)]\left(\frac{1+\gamma_\lambda}{1-\gamma_\lambda}\right)^{\frac12}\Bigg],\\
A_{2\lambda} &= -\tfrac32 SD\sum_h\Bigg[[\gamma_h^2+\beta_h^2\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)]\left(\frac{1-\gamma_\lambda}{1+\gamma_\lambda}\right)^{\frac12}\\
&\qquad+[\gamma_h^2-\alpha_h^2\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)]\left(\frac{1+\gamma_\lambda}{1-\gamma_\lambda}\right)^{\frac12}\Bigg],\\
A_{3\lambda} &= -\tfrac34 SD\sum_h\Bigg[[\gamma_h^2+\alpha_h^2\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)]\left(\frac{1-\gamma_\lambda}{1+\gamma_\lambda}\right)^{\frac12}\\
&\qquad-[\gamma_h^2-\beta_h^2\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)]\left(\frac{1+\gamma_\lambda}{1-\gamma_\lambda}\right)^{\frac12}\Bigg],\\
A_{4\lambda} &= -\tfrac34 SD\sum_h\Bigg[[\gamma_h^2-\alpha_h^2\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)]\left(\frac{1+\gamma_\lambda}{1-\gamma_\lambda}\right)^{\frac12}\\
&\qquad-[\gamma_h^2+\beta_h^2\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)]\left(\frac{1+\gamma_\lambda}{1-\gamma_\lambda}\right)^{\frac12}\Bigg],\\
A_{5\lambda} &= \tfrac12 iS\left[\left(\frac{1+\gamma_\lambda}{1-\gamma_\lambda}\right)^{\frac12}+\left(\frac{1-\gamma_\lambda}{1+\gamma_\lambda}\right)^{\frac12}\right]\sum_h\alpha_h\beta_h\\
&\qquad\times\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h),\\
A_{6\lambda} &= \tfrac12 iS\left[\left(\frac{1+\gamma_\lambda}{1-\gamma_\lambda}\right)^{\frac12}+\left(\frac{1-\gamma_\lambda}{1+\gamma_\lambda}\right)^{\frac12}\right]\sum_h\alpha_h\beta_h\\
&\qquad\times\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h).
\end{aligned}
\tag{22}
$$

Since in a cubic crystal the lowest powers of the direction cosines which can give anisotropy are fourth order, H_1 can first give anisotropic contributions to the energy in second order perturbation theory. Thus, only terms of H_1 which have matrix elements between the ground state and some excited state are of concern. These terms are

$$
\begin{aligned}
H_{1A} = \textstyle\sum_\lambda[A_{3\lambda}(c_\lambda^2+c_\lambda^{*2})+A_{4\lambda}(d_\lambda^2+d_\lambda^{*2})&\\
+A_{5\lambda}(c_\lambda d_\lambda-c_\lambda^*d_\lambda^*)].&
\end{aligned}
\tag{23}
$$

The only nonzero matrix elements with the ground state are

$$
\begin{aligned}
\langle n_{c\lambda}=2|(c_\lambda^2+c_\lambda^{*2})|0\rangle &= \sqrt{2},\\
\langle n_{d\lambda}=2|(d_\lambda^2+d_\lambda^{*2})|0\rangle &= \sqrt{2},\\
\langle n_{c\lambda}=1,\ n_{d\lambda}=1|(c_\lambda d_\lambda-c_\lambda^*d_\lambda^*)|0\rangle &= 1.
\end{aligned}
\tag{24}
$$

Then the second order correction to the ground state given by H_{1A} is

$$E_{1A} = -2\textstyle\sum_\lambda(|A_{3\lambda}|^2+|A_{4\lambda}|^2+\tfrac12|A_{5\lambda}|^2)/\Delta_\lambda, \tag{25}$$

where

$$\Delta_\lambda \equiv E^0(n_{c\lambda}=1,\ n_{d\lambda}=1)-E^0(0) = 2JS_z(1-\gamma_\lambda^2)^{\frac12}. \tag{26}$$

Inserting these expressions and simplifying, one obtains

$$E_{1A}=-[9SD^2/(16Jz)]\sum_{\lambda,h,h'}\{[8\gamma_\lambda^2\gamma_h^2\gamma_{h'}^2$$
$$-8z\gamma_\lambda\gamma_h^2(1-\gamma_{h'}^2)\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)$$
$$+2((1-\gamma_h^2)(1-\gamma_{h'}^2)+\gamma_\lambda^2(\alpha_h^+)^2(\alpha_h^-)^2)$$
$$\times\exp(i\mathbf{k}_\lambda\cdot(\mathbf{R}_h-\mathbf{R}_{h'}))]/(1-\gamma_\lambda^2)^{\frac{3}{2}}\},\quad(27)$$

where

$$\alpha_h^+=\alpha_h+i\beta_h\quad\text{and}\quad\alpha_h^-=\alpha_h-i\beta_h.\quad(28)$$

When α_h^+, α_h^-, and γ_h have been expressed in terms of the direction cosines, α_1, α_2, α_3, of the axis of quantization with respect to the crystal axes, the result is

$$E_A=-[9D^2S/(4Jz)]\sum_\lambda\left[\frac{(1+\gamma_\lambda^2)}{(1-\gamma_\lambda^2)}\right]^{\frac{3}{2}}$$
$$\times[4\exp(i\mathbf{k}_\lambda\cdot(\mathbf{R}_x-\mathbf{R}_y))$$
$$-\exp(2i(\mathbf{k}_\lambda\cdot\mathbf{R}_x))-1]\Gamma,\quad(29)$$

where

$$\Gamma\equiv\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2.\quad(30)$$

Here the sum over h has been restricted to nearest neighbors, and $\mathbf{R}_x$ and $\mathbf{R}_y$ represent the vectors from the origin to two of these neighbors in perpendicular directions.

Since the major contribution to the anisotropy comes from large k's, it is sometimes desirable for simplicity to replace γ_λ by a constant equal to its average value over the surface of a sphere of the same volume as the first Brillouin zone. The volume of this zone in the k space corresponding to a sublattice is $4\pi^3/a^3$, where a is the interatomic spacing of the simple cube. The radius of the equivalent sphere is then given by

$$k=(3\pi^2)^{\frac{1}{3}}/a.\quad(31)$$

Then

$$\gamma_\lambda\equiv(1/z)\textstyle\sum_h\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_h)\approx(1/4\pi)\displaystyle\int d\Omega_k\exp(ika)$$
$$=(1/4\pi)\int_0^{2\pi}\int_{-1}^{1}\exp(ika\cos\theta_k)d(\cos\theta_k)d\phi_k$$
$$=\tfrac{1}{2}[\exp(ika)-\exp(-ika)]/ika$$
$$=(\sin ka)/ka=[\sin(3\pi^2)^{\frac{1}{3}}]/(3\pi^2)^{\frac{1}{3}}\approx0.\quad(32)$$

In this approximation:

$$E_A=[(9D^2SN)/(8Jz)]\Gamma,\quad(33)$$

since

$$\textstyle\sum_\lambda\exp[i\mathbf{k}_\lambda\cdot(\mathbf{R}_x-\mathbf{R}_y)]=\frac{1}{2}N\delta(\mathbf{R}_x-\mathbf{R}_y)=0$$

and (34)

$$\textstyle\sum_\lambda\exp(2i\mathbf{k}_\lambda\cdot\mathbf{R}_x)=\delta(\mathbf{R}_x)=0.$$

It is interesting to note that this result is just equal to that obtained in the ferromagnetic case. The approximations made in the preceding paragraph are not necessary, but the work of Charap and Weiss[7] seems to indicate that the corrections to this result are relatively unimportant.

The fact that g is so close to 2 in $KMnF_3$ indicates that the effect of spin-orbit coupling in this crystal is small, and that the dipolar interaction exceeds the pseudodipolar by nearly a factor of 100. Of course, the dipolar interaction, as contrasted with the pseudodipolar, is a long-range effect. Since its second-order energy decreases with neighbor distance as r_h^{-6}, however, the above nearest-neighbor formula should give an indication of its magnitude. An estimate of E_{anis} in this case can thus be obtained using

$$D=(g^2\beta^2)/r_h^3\quad\text{and}\quad J=10°\text{K}.$$

The result is

$$E_A=7\times10^{-21}\Gamma\text{ erg}$$

for the anisotropy energy at 0°K. Pincus[8] has shown that this anisotropy can be expected to decrease as the tenth power of the sublattice magnetization. It is too small to have any effect except at very low temperatures.

III. CLASSICAL ANISOTROPY FROM TETRAGONAL DISTORTION

The anisotropy produced by the tetragonal distortion of the manganese sublattices can be estimated using the results given by Mueller[9] for the departure of the Lorentz factors from $4\pi/3$ in a distorted NaCl structure. He gives for these factors:

$$\begin{aligned}L_{11}^z&=4\pi(\tfrac{1}{3}-0.06\epsilon_z),\quad L_{11}^x=4\pi(\tfrac{1}{3}+0.03\epsilon_z),\\L_{12}^z&=4\pi(\tfrac{1}{3}-1.94\epsilon_z),\quad L_{12}^x=4\pi(\tfrac{1}{3}+0.97\epsilon_z),\end{aligned}\quad(35)$$

where

$$\epsilon_z=c/a-1.\quad(36)$$

The dominant anisotropy energy is that due to the interaction of the two sublattices. Keffer[10] has shown it to have the form:

$$f_A'''=K_3(\alpha_1\alpha_2+\beta_1\beta_2),\quad(37)$$

where the α's and β's are direction cosines of the sublattice magnetizations and

$$K_3=M^2(L_{12}^z-L_{12}^x)\quad\text{at}\quad0°\text{K}.\quad(38)$$

If for ϵ_z the value obtained from Fig. 1 at 0°K is taken, K_3 has the value 8×10^{-19} erg. It would be expected to decrease as the cube of the magnetization. This anisotropy is more than an order of magnitude smaller than the second-order term obtained in the next section from the distortion of the fluorine octahedron.

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[7] S. H. Charap and P. R. Weiss, Phys. Rev. **116**, 1372 (1959); F. Keffer and T. Oguchi, Phys. Rev. **117**, 718 (1960).

[8] P. Pincus, Phys. Rev. **113**, 769 (1959).

[9] H. Mueller, Phys. Rev. **47**, 947 (1935).

[10] F. Keffer, Phys. Rev. **87**, 608 (1952).

IV. ANISOTROPY IN THE ANTIBONDING ORBITALS

The form of the distortion in the octahedron of fluorine atoms surrounding each manganese revealed by the x-ray measurements below the Néel point is shown in Fig. 2. In order to determine the symmetry of the effective spin Hamiltonian resulting from this distortion, the departure from cubic symmetry of the crystal field at the manganese due to the six neighboring fluorines was calculated on the assumption of a completely ionic crystal. In this calculation, the effect of moving an F^- ion from its undistorted octahedral site was approximated by adding to the octahedral field the field due to six point dipoles at the octahedral sites with moments equal to the F^- charge times the displacement of each fluorine ion under distortion. The field of these dipoles near the manganese atom was expanded in a Taylor series with the manganese site as origin, and only the second-order terms were kept. The result was a field with symmetry $(x+y)z$, where z is measured along the c axis and x and y along the two perpendicular a axes of the crystal. This indicated a spin Hamiltonian of the form

$$H=A[(S_x+S_y)S_z+S_z(S_x+S_y)] \tag{39}$$

produced by the fluorine distortion.

In order to obtain an experimental check, it was desirable to estimate the magnitude of the constant A, taking into account the overlap of the fluorine and manganese wave functions and the presence of some covalent bonding. This was accomplished by means of a method proposed by Löwdin[11] and applied by Kondo,[2] here generalized to apply to any symmetry. Basically, the method consists of taking the expectation value of the electron dipole-dipole and spin-orbit Hamiltonian in a state consisting of a Slater determinant of one-particle molecular orbitals, chosen to include the electron transfer effects. From the anisotropic energy, W, thus calculated, the spin Hamiltonian can then be computed. More specifically, the Hamiltonian considered was

$$H=H_1+H_2=\tfrac{1}{2}\sum_{i\neq j}[r_{ij}^2\mathbf{s}_i\cdot\mathbf{s}_j-3(\mathbf{s}_i\cdot\mathbf{r}_{ij})(\mathbf{s}_j\cdot\mathbf{r}_{ij})]/r_{ij}^5 +\textstyle\sum_i \xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i. \tag{40}$$

Actually, for the case of inversion symmetry, which was the one of interest here, H_2 has zero expectation value, so the energy, W_2, of H_2 was used. Then the anisotropic energy W is

$$W=\langle 0|H_1|0\rangle-\textstyle\sum_i[\langle 0|H_2|i\rangle\langle i|H_2|0\rangle]/(E_i-E_0). \tag{41}$$

The ground state, $|0\rangle$, was a Slater determinant of the following types of normalized one-electron orbitals:

Manganese $3d$ functions,

$$\Phi_1\alpha=R(r)[(3z^2-r^2)/\sqrt{3}]\alpha,\quad \Phi_3\alpha=2R(r)xy\alpha,$$
$$\Phi_2\alpha=R(r)(x^2-y^2)\alpha,\quad \Phi_4\alpha=2R(r)xz\alpha,$$
$$\Phi_5\alpha=2R(r)yz\alpha.$$

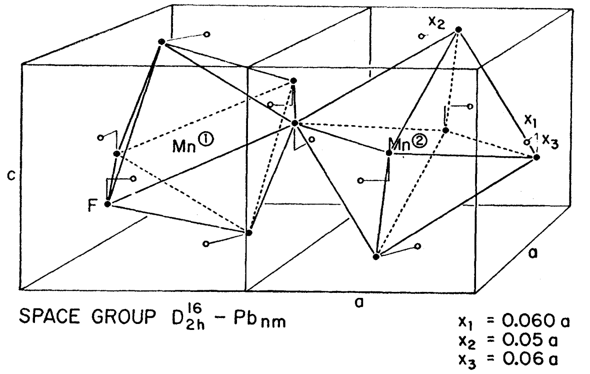

FIG. 2. Distortion of the fluorine sites in KMnF$_3$ at 65°K. The open circles represent the undistorted positions of the fluorines. (After Beckman and Knox.)

Nearest neighbor (fluorine) functions,

$$\Theta_1\alpha\cdots\Theta_i\alpha\cdots\Theta_N\alpha.$$

"Mixed" orbitals,

$$\chi_1\beta\cdots\chi_i\beta\cdots\chi_N\beta.$$

The number N depends on the number of nearest neighbors (six for KMnF$_3$) and on the number of orbitals considered for each neighbor (in the calculation for KMnF$_3$, one s and three p functions for a total of four). The manganese $3d$ functions above are expressed in terms of the crystal axes, and each of the Θ_i's is quantized along the line joining the site of that particular neighbor with the manganese site. The direction of spin quantization implied by the spin functions α and β is an arbitrary one having direction cosines l, m, and n with the crystal (x,y,z) axes. The mixed functions, χ_i, have the form:

$$\chi_i=\Theta_i+\lambda_i\psi_i,\quad \psi_i=\textstyle\sum_j a_{ij}\Phi_j. \tag{42}$$

The particular combination, ψ_i, chosen for each i forms that one of a complete set of manganese $3d$ functions quantized along the same axis as Θ_i which has a nonzero overlap with Θ_i. This overlap is denoted by S_i. All of the Θ_i functions are assumed to be orthogonal to one another. The parameters λ_i measure the amount of electron transfer.

In principle one could orthogonalize these orbitals, obtaining functions of the type given in Eq. (1), and calculate straightforwardly the matrix elements for their Slater determinant. However, a theorem proved by Löwdin facilitates the calculation of matrix elements of the type needed here between Slater determinants of large numbers of nonorthogonal orbitals. He defines the function $\rho(\mathbf{x},\mathbf{y})$ by

$$\rho(\mathbf{x},\mathbf{y})=\textstyle\sum_{ij} d_{ij}^{-1}u_i^*(\mathbf{x})u_j(\mathbf{y}), \tag{43}$$

where $u_i(\mathbf{x})$ are the one-electron orbitals (including spin) and d_{ij} is the "overlap matrix,"

$$d_{ij}\equiv\int u_i^*(\mathbf{x})u_j(\mathbf{x})d\mathbf{x}. \tag{44}$$

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[11] P. O. Löwdin, Phys. Rev. 97, 1474 (1955).

He then shows that for

$$H=H^{(1)}+H^{(2)}=\sum_i V_i+\tfrac{1}{2}\sum_{i\neq j} V_{ij}, \qquad (45)$$

the matrix element, $\langle 0|H|0\rangle$, of H in the Slater determinant state of the u's is given by

$$\langle 0|H|0\rangle=\int V_1\rho(\mathbf{x}_1',\mathbf{x}_1)d\mathbf{x}_1$$

$$+\frac{1}{2}\int V_{12}\begin{vmatrix}\rho(\mathbf{x}_1',\mathbf{x}_1) & \rho(\mathbf{x}_1',\mathbf{x}_2)\\ \rho(\mathbf{x}_2',\mathbf{x}_1) & \rho(\mathbf{x}_2',\mathbf{x}_2)\end{vmatrix}d\mathbf{x}_1d\mathbf{x}_2. \qquad (46)$$

Here V_i and V_{ij} are one- and two-particle operators, acting on the coordinates $\mathbf{x}_i'$ and $\mathbf{x}_j'$ of particles i and j. The convention is adopted that the V's operate only on the unprimed coordinates which are then set equal to the primed ones. The first term of Eq. (41) is immediately of the required form. The second term becomes of that form if the approximation introduced by Kondo, of replacing the energy denominator E_i-E_0 by an average value, $\langle\Delta E\rangle$, is used. That equation can then be written:

$$W=\langle 0|[\tfrac{1}{2}\sum_{i\neq j}[r_{ij}^2\mathbf{s}_i\cdot\mathbf{s}_j-3(\mathbf{s}_i\cdot\mathbf{r}_{ij})(\mathbf{s}_j\mathbf{r}_{ij})]/r_{ij}^5$$

$$-(1/\langle\Delta E\rangle)\sum_i \xi^2(r_i)(\mathbf{l}_i\cdot\mathbf{s}_i)^2$$

$$-[1/(2\langle\Delta E\rangle)]\sum_{i\neq j}2\xi(r_i)\xi(r_j)(\mathbf{l}_i\cdot\mathbf{s}_i)(\mathbf{l}_j\cdot\mathbf{s}_j)]|0\rangle. \qquad (47)$$

Only the first term will be dealt with in detail here, the others following in close analogy.

Since d, and consequently d^{-1}, have no elements connecting α and β spins, ρ has the form:

$$\rho=\rho_{\alpha\alpha}{}^{+}+\rho_{\beta\beta}{}^{-}. \qquad (48)$$

Substituting this into Eqs. (40) and (46) and performing the spin integration, one obtains

$$W_1=(g^2\beta^2/8)\int d\mathbf{r}_1d\mathbf{r}_2[(3\cos^2\theta-1)/r_{12}^3]$$

$$\times[\Delta\rho(\mathbf{r}_1,\mathbf{r}_1)\Delta\rho(\mathbf{r}_2,\mathbf{r}_2)-\Delta\rho(\mathbf{r}_2,\mathbf{r}_1)\Delta\rho(\mathbf{r}_1,\mathbf{r}_2)], \qquad (49)$$

where

$$\Delta\rho\equiv\rho^{+}-\rho^{-}, \qquad (50)$$

and θ is the angle between $\mathbf{r}_{12}$ and the direction of spin quantization. The overlap matrix d has the form:

$$\begin{array}{ccc}
\Phi_1\alpha\cdots\Phi_5\alpha & \Theta_1\alpha\cdots\Theta_N\alpha & \chi_1\beta\cdots\chi_N\beta\\
\hline
I & A & 0\\
\tilde{A} & I & 0\\
0 & 0 & I+B
\end{array}$$

where the row and column designations are listed across the top. The I's are unit matrices. The elements of submatrix A are

$$A_{ij}\equiv\int d\mathbf{r}\,\Phi_i(\mathbf{r})\Theta_j(\mathbf{r}). \qquad (51)$$

Expanding Φ_i in the set of five orthonormal manganese functions of which ψ_j is one, one obtains

$$A_{ij}=\left[\int d\mathbf{r}\psi_j(\mathbf{r})\Theta_j(\mathbf{r})\right]\left[\int d\mathbf{r}\Phi_i(\mathbf{r})\psi_j(\mathbf{r})\right]$$

$$=S_j\int d\mathbf{r}\Phi_i(\mathbf{r})\textstyle\sum_k a_{jk}\Phi_k(\mathbf{r})=S_ja_{ji}. \qquad (52)$$

Similarly for $I+B$:

$$\delta_{ij}+B_{ij}\equiv\int d\mathbf{r}\chi_i(\mathbf{r})\chi_j(\mathbf{r})$$

$$=\int d\mathbf{r}[\Theta_i(\mathbf{r})+\lambda_i\psi_i(\mathbf{r})][\Theta_j(\mathbf{r})+\lambda_j\psi_j(\mathbf{r})]$$

$$=\int d\mathbf{r}[\Theta_i(\mathbf{r})\Theta_j(\mathbf{r})+\lambda_i\psi_i(\mathbf{r})\Theta_j(\mathbf{r})$$

$$+\lambda_j\Theta_i(\mathbf{r})\psi_j(\mathbf{r})+\lambda_i\lambda_j\psi_i(\mathbf{r})\psi_j(\mathbf{r})]$$

$$=\delta_{ij}+(\lambda_iS_j+\lambda_jS_i+\lambda_i\lambda_j)\int\psi_i(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r}. \qquad (53)$$

Thus

$$B_{ij}=(\lambda_iS_j+\lambda_jS_i+\lambda_i\lambda_j)\textstyle\sum_k a_{ik}a_{jk}. \qquad (54)$$

At this point, two approximations were introduced. First, since the λ's and S's are small, quantities of higher than second order in them were neglected. Second, because of the fact that the Φ and Θ functions have different centers and because of the presence of the $1/r_{12}^3$ factor in the W integral, any term containing both Θ's and Φ's was assumed to be negligible. To second order in S and λ, d^{-1} is given by:

$$\begin{array}{ccc}
1+A\tilde{A} & -A & 0\\
-\tilde{A} & 1+\tilde{A}A & 0\ .\\
0 & 0 & I-B
\end{array}$$

Then,

$$\begin{aligned}
\Delta\rho \approx & \sum_{i,j=1}^{5} (I+A\tilde{A})_{ij}\Phi_i\Phi_j + \sum_{i,j=1}^{N} (1+\tilde{A}A)_{ij}\Theta_i\Theta_j \\
& - \sum_{i,j=1}^{N} (I-B)_{ij}(\Theta_i+\lambda_i\psi_i)(\Theta_j+\lambda_j\psi_j) \\
= & \sum_{i,j=1}^{5} \Phi_i\Phi_j[\delta_{ij}+\sum_k S_k a_{ki} S_k a_{kj}] \\
& + \sum_{i,j=1}^{N} [\delta_{ij}+\sum_k S_i a_{ik} S_j a_{jk}]\Theta_i\Theta_j \\
& - \sum_{i,j=1}^{N} [\delta_{ij}-(\lambda_i S_j+\lambda_j S_i+\lambda_i\lambda_j)\sum_k a_{ik}a_{jk}]\Theta_j\Theta_i \\
& + \sum_{i,j=1}^{N} \delta_{ij}\lambda_i\lambda_j[\sum_k a_{ik}\Phi_k][\sum_l a_{jl}\Phi_l] \\
= & \sum_{i,j=1}^{5} [\delta_{ij}+\textstyle\sum_k (S_k^2-\lambda_k^2)a_{ki}a_{kj}]\Phi_i\Phi_j \\
& + \sum_{i,j=1}^{N} [\lambda_i S_j+\lambda_j S_i+\lambda_i\lambda_j+S_iS_j] \\
& \times[\textstyle\sum_k a_{ik}a_{jk}]\Theta_i\Theta_j. \qquad (55)
\end{aligned}$$

The last sum can be neglected, since in the products $\Delta\rho\Delta\rho$ which occur in W it contributes only terms of fourth order in λ and S, and terms which contain both Φ's and Θ's. Finally, then,

$$\begin{aligned}
\Delta\rho \approx & [\sum_{i=1}^{5} \Phi_i\Phi_i]+[\sum_{i,j=1}^{5}\sum_{k=1}^{N} a_{ki}a_{kj}(S_k^2-\lambda_k^2)\Phi_i\Phi_j] \\
\equiv & [\sum_{i=1}^{5} \Phi_i\Phi_i]+[\sum_{i,j=1}^{5} \Delta_{ij}\Phi_i\Phi_j] \equiv (\rho_0+\rho')RR. \qquad (56)
\end{aligned}$$

Each Φ_i can now be expanded in spherical harmonics in a system in which the spin direction is the z axis. This gives for ρ_0 and ρ':

$$\rho_0=\textstyle\sum_m Y_2^{m*}Y_2^m, \quad \rho'=\sum_{m',m''}\rho_{m',m''}'Y_2^{m'}Y_2^{m''}, \qquad (57)$$

and for W_1:

$$\begin{aligned}
W_1 = & -(g^2\beta^2/8)\int d\mathbf{r}_1 d\mathbf{r}_2 R^2(r_1)R^2(r_2) \\
& \times[(3\cos^2\theta-1)/r_{12}^3][\rho_0(\mathbf{r}_1,\mathbf{r}_1)\rho'(\mathbf{r}_2,\mathbf{r}_2) \\
& +\rho_0(\mathbf{r}_2,\mathbf{r}_2)\rho'(\mathbf{r}_1,\mathbf{r}_1)-2\rho_0(\mathbf{r}_1,\mathbf{r}_2)\rho'(\mathbf{r}_2,\mathbf{r}_1)]. \qquad (58)
\end{aligned}$$

Noting that, for $r_2>r_1$,

$$\begin{aligned}
(3\cos^2\theta-1)/r_{12}^3 = & \frac{\partial^2}{\partial z_1^2}(1/r_{12}) \\
= & \frac{\partial^2}{\partial z_1^2}\sum_{l=0}^{\infty}[4\pi/(2l+1)][r_1^l/r_2^{l+1}] \\
& \times\sum_{m=-l}^{l} Y_l^m(\theta_1,\phi_1)Y_l^{m*}(\theta_2,\phi_2) \\
= & \sum_{l=0}^{\infty}\sum_{m=-l}^{l}[4\pi/(2l+1)][r_1^{l-2}/r_2^{l+1}] \\
& \times Y_l^{m*}(\theta_2\phi_2)\biggl[-(2l-1)\sin\theta_1\cos\theta_1\frac{\partial}{\partial\theta_1} \\
& -l(2l-1)\sin^2\theta_1+l(l-1)+m^2\biggr]Y_l^m(\theta_1,\phi_1), \qquad (59)
\end{aligned}$$

one can write for W_1:

$$\begin{aligned}
W_1 = & -\tfrac{1}{2}g^2\beta^2\sum_{l=0}^{\infty}\sum_{m=-l}^{l}4\pi\left[\frac{[l^2-m^2][(l-1)^2-m^2]}{(2l+1)(2l-3)}\right]^{\frac{1}{2}} \\
& \times\left[\int_0^{\infty}dr_2\, P^2(r_2)r_2^{-l-1}\int_0^{r2} r_1^{l-2}P^2(r_1)dr_1\right] \\
& \times\biggl[\int d\Omega_1 d\Omega_2\, Y_l^{m*}(\Omega_2)Y_{l-2}^m(\Omega_1) \\
& \times\{(5/8\pi)[\rho'(\Omega_1,\Omega_1)+\rho'(\Omega_2,\Omega_2)] \\
& -\rho_0(\Omega_1,\Omega_2)\rho'(\Omega_2,\Omega_1)\}\biggr] \\
= & -2g^2\beta^2\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left[\frac{(l^2-m^2)[(l-1)^2-m^2]}{(2l+1)(2l-3)}\right]^{\frac{1}{2}}R_{l-2} \\
& \times\sum_{m',m'',m'''}\biggl[(5/8\pi)\delta_{m''',0}\int d\Omega_1\, Y_{l-2}^m(1) \\
& \times\int d\Omega_2\, Y_l^{m*}(2)Y_l^{m'}(2)Y_l^{m''}(2) \\
& -\int d\Omega_1\, Y_l^{m'''*}(1)Y_l^{m'}(1)Y_{l-2}^m(1) \\
& \times\int d\Omega_2\, Y_l^{m'''}(2)Y_l^{m*}(2)Y_l^{m''}(2)\biggr]\rho_{m'm''}, \qquad (60)
\end{aligned}$$

where

$$R_l\equiv\int_0^{\infty}dr_2\, P^2(r_2)r_2^{-l-3}\int_0^{r2}P^2(r_1)r_1^l dr_1. \qquad (61)$$

The integrals of products of three spherical harmonics were evaluated using the tables given in Condon and Shortley.[12] In terms of the coefficients $c^k(l,m;l',m')$

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[12] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), Chap. 6, p. 178.

given there, W_1 becomes

$$W_1=-2g^2\beta^2\pi \sum_{l,m,m',m'',m'''} \left[\frac{[l^2-m^2][(l-1)^2-m^2]}{(2l+1)(2l-3)}\right]^{\frac{1}{2}}$$
$$\times R_{l-2}[(-1)^{m'}[5(2l+1)^{\frac{1}{2}}/8\pi]$$
$$\times c^2(2,m';2,0)\delta_{2,l}\delta_{0,m}\delta_{0,m'''}\delta_{m'',-m'}$$
$$-[(-1)^{m'}/4\pi][(2l+1)(2l-3)]^{\frac{1}{2}}$$
$$\times c^{l-2}(2,m''';2,m')c^l(2,m''';2,m')$$
$$\times\delta_{m,m'''-m'}\delta_{m'',-m'}]\rho_{m',m''}'. \quad (62)$$

Evaluation of these coefficients gives

$$W_1=-(3g^2\beta^2/7)(R_0-8R_2/7)(\rho_{0,0}'-\rho_{1,-1}'-\rho_{2,-2}'). \quad (63)$$

In terms of the Δ_{ij}'s previously defined (Eq. 56):

$$W_1=-(3g^2\beta^2/7)(R_0-8R_2/7)\sum_{i\leq j} C_{ij}\Delta_{ij}, \quad (64)$$

where C is the matrix:

$i \diagdown j$	1	2	3	4	5
1	$\frac{1}{2}(3n^2-1)$	$-\sqrt{3}(l^2-m^2)$	$-2\sqrt{3}lm$	$\sqrt{3}ln$	$\sqrt{3}mn$
2		$-\frac{1}{2}(3n^2-1)$	0	$3ln$	$-3mn$
3			$-\frac{1}{2}(3n^2-1)$	$3mn$	$3ln$
4				$\frac{1}{2}(1-3m^2)$	$3lm$
5					$\frac{1}{2}(1-3l^2)$

The evaluation of W_2, the spin-orbit term, proceeds along the same lines. After the spin integration has been performed and inversion symmetry invoked, the only anisotropic term remaining is:

$$W_2=(2\langle\Delta E\rangle)^{-1}\int \xi(r_1)\xi(r_2)l_1^z l_2^z \sum_{m,m',m''} \rho_{mm'}'$$
$$\times Y_2^m(1')Y_2^m(2')Y_2^{m''}(2)Y_2^{m'}(1)d\mathbf{r}_1 d\mathbf{r}_2$$
$$=-[\langle\xi\rangle^2/\langle\Delta E\rangle][\rho_{1,-1}'-4\rho_{2,-2}']$$
$$=-[\langle\xi\rangle^2/\langle\Delta E\rangle]\sum_{i\leq j} C_{ij}'\Delta_{ij}, \quad (65)$$

where

$$\langle\xi\rangle\equiv\int_0^\infty P^2(r)\xi(r)dr, \quad (66)$$

and C_{ij}' differs from C_{ij} only in its isotropic parts. For anisotropy calculations such as this, that difference can be ignored, and the total energy, W, written as:

$$W=W_1+W_2=-[(3g^2\beta^2/7)(R_0-8R_2/7)$$
$$+\langle\xi\rangle^2/\langle\Delta E\rangle]\sum_{i\leq j} C_{ij}\Delta_{ij}. \quad (67)$$

The anisotropy energy for any crystal symmetry and number of neighbors can now be obtained simply by calculating the appropriate Δ_{ij}'s and substituting them into this general formula. Note that to this order of perturbation theory no cubic terms occur, as mentioned earlier.

In the particular calculation for $KMnF_3$, Kondo's values were used for R_0, R_2, $\langle\xi\rangle$, and $\langle\Delta E\rangle$. They are:

$$R_0=3.06a_0^{-3}; \qquad R_2=0.54a_0^{-3};$$
$$\langle\xi\rangle=395 \text{ cm}^{-1}; \quad \langle\Delta E\rangle=29\,250 \text{ cm}^{-1}.$$

The following values of the S's and λ's were used:

$$S_s=0.05; \quad S_\sigma=S_\pi=0.07;$$
$$\lambda_s=0.02; \quad \lambda_\sigma=\lambda_\pi=0.15.$$

The S's are based on a calculation of Casselman and Keffer[13] with S_σ and S_π set equal for convenience. The λ's were estimated from nuclear resonance results of Shulman and Knox.[14] With these numbers and the symmetry pictured in Fig. 2, the Δ matrix is:

$$\begin{array}{ccccc}
-0.05 & 0 & +0.00008 & -0.002 & -0.002 \\
 & -0.05 & +0.003 & +0.0009 & -0.0005 \\
 & & -0.07 & -0.0008 & -0.0009 \\
 & & & -0.07 & -0.0001 \\
 & & & & -0.07
\end{array}$$

giving for W:

$$W\approx[2\times10^{-17}(l+m)n+2\times10^{-18}lm$$
$$-2\times10^{-18}(l-m)n] \text{ erg}. \quad (68)$$

Matrix element 3,3 does not rigorously cancel the contributions of 4,4 and 5,5, so it is possible that, if more significant figures were known, a term in W proportional to n^2 might be present. The spin Hamiltonian constant A of Eq. (39) was obtained by taking the expectation value of that equation in a state with spin component $\frac{5}{2}$ along (l,m,n) and equating this to W. The result was

$$A=2\times10^{-18} \text{ erg.}^{15}$$

V. COMPARISON WITH EXPERIMENT

Portis, Teaney, and Heeger's[1] resonance results and Heeger's torque measurements confirm that the dominant term in the spin Hamiltonian has the above form, and Heeger from his torque data estimates a value of A equal to 6×10^{-18} erg. Thus the results given here are in order-of-magnitude agreement with experiment.

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[13] T. N. Casselman and F. Keffer, Phys. Rev. Letters 4, 498 (1960).

[14] R. G. Shulman and K. Knox, Phys. Rev. Letters 4, 603 (1960); Phys. Rev. **119**, 94 (1960).

[15] *Note added in proof.* The values given by Kondo for R_0 and R_2 (which he obtained from an empirical estimate by Watanabe) may be too large. A calculation of these quantities using Watson's recent Hartree-Fock Mn^{++} functions[16] yields

$$R_0=0.490a_0^{-3} \quad R_2=0.268a_0^{-3}.$$

If these values are used in the above analysis, the theoretical value of A is reduced to $\approx1\times10^{-18}$ erg.

[16] R. E. Watson, Phys. Rev. **118**, 1036 (1960).