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Magnetic Properties of $KMnF_3$. III. Nuclear and Electron Spin Resonance*

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Direct NMR experiments on Mn^{55} nuclei in $KMnF_3$ have confirmed that $KMnF_3$ is a weak ferromagnet. The strong field and temperature dependence of the NMR frequency is a result of the intermixing of the electron and nuclear excitation spectra. A four-sublattice model for the electronic magnetization has been used to analyze the angular dependence of the NMR frequency. This four-sublattice model employs two canting fields, an "overt" canting field H_2 and a "hidden" canting field H_5. The overt canting field introduces a term into the expression for the AFR frequency that is linear in the applied dc magnetic field; this linear dependence is verified by experiment. With $H_2=310\pm20$ Oe and $H_5=200\pm30$ Oe. the hidden canting angle between $\mathbf{M}_1$ and $\mathbf{M}_3$ is approximately 100°. The resonance frequency in the nuclear hyperfine field was found to be 676 ± 3 Mc/sec; when compared with the paramagnetic resonance results of Ogawa, this would suggest a 1.6% zero-point spin-wave reduction in $\langle S\rangle$.

INTRODUCTION

The magnetic systems $X\mathrm{MnF}_3$, where X is K, Cs, or Rb, have been the subjects of a large number of magnetic experiments.[1–9] There are three reasons for the great interest in the nuclear-resonance properties of these systems: the first is that the nucleus of the magnetic ion has a large hyperfine interaction with the magnetic electrons; the second is that the Mn^{55} nucleus is 100% abundant; and finally, the excitation spectrum of the magnetic electrons below the Neél temperature is characterized by the presence of one or two low-lying antiferromagnetic-resonance (AFR) modes. As a consequence of these properties, the nuclear system and the electron system are tightly coupled.

A calculation for the resonance modes of a coupled nuclear-electron system shows that the AFR frequency is increased by a term proportional to the thermally averaged nuclear magnetization and that the nuclear-magnetic-resonance (NMR) frequency is less than the expected hyperfine-field value. The theory of NMR in magnetic materials developed by de Gennes *et al.*[10] has been very successful in explaining the resonance frequencies in all of these systems. The NMR frequency for these systems is very strongly dependent on the temperature and the applied static magnetic field for temperatures well below the transition temperature; the dependence is an indirect one, resulting from a shift in the AFR frequency.

$KMnF_3$ has the cubic perovskite structure at room temperature; below $T=184$°K the structure changes to an orthorhombic phase with a space group $Pb_{nm}(D_{2h}{}^{16})$; as the temperature is further decreased, the crystal becomes a simple uniaxial antiferromagnet at $T_N=88.3$°K with $c/a<1$.[11] Below the temperature $T=81.5$°K the crystal transforms from its simple antiferromagnetic configuration to a canted antiferromagnet.[1] The presence of the weak moment was observed in the torsion measurements of Heeger *et al.*[1] The fluorine octahedra surrounding the Mn^{+2} ions are slightly distorted from their configuration in the paramagnetic state. If δ is the displacement of an ion from its position in the perovskite structure and a is the lattice constant, δ/a is typically of order 0.05.[11,12] F^{19} nuclear resonance studies in the canted state indicate that the distortion of the fluorine octahedra can be regarded as first a rotation of the octahedra in the paramagnetic state about the ⟨001⟩ pseudocubic direction followed by a tilting of the octahedra toward a ⟨110⟩ pseudocubic direction. (See Fig. 1.)

The neutron diffraction experiments of Scattarin *et al.*[13] have established that the magnetic structure of $KMnF_3$ is one in which each Mn^{+2} spin is surrounded by six antiparallel nearest-neighbor spins. The magnetic unit cell is twice the size of the chemical unit cell. It was not possible to detect the presence of the weak moment because the overt canting angle for the sublattice magnetizations is only of the order of 0.003°.

In what follows, we shall be concerned with $KMnF_3$ in

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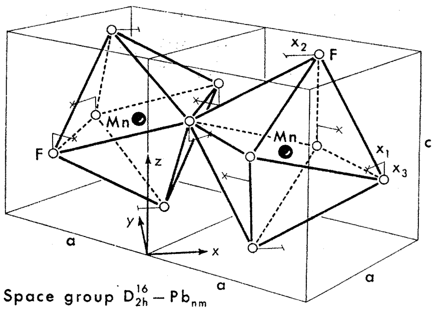

FIG. 1. Positions of the F⁻ ions in the distorted octahedra of $KMnF_3$ at $T=4.2$°K.

its canted configuration. Further, since the experiments were performed in the liquid-helium temperature range of 2–4°K, we assume the electronic sublattice magnetizations and anisotropy constants to be saturated.

THEORY

$KMnF_3$ in its orthorhombic state is isomorphic to the class of magnetic materials known as the orthoferrites. From the group-theoretical arguments, one can write a general expression for the magnetic energy of the system that is invariant under the magnetic group. In the case at hand, we can be more specific. Fortunately, x-ray analysis and F^{19} resonance experiments[12] have been performed on $KMnF_3$; from the positions of the fluorine ions surrounding a Mn^{+2} site, one can decide what anisotropy constants will be most important.

Expanding the potential energy for the distorted fluorine octahedra around the origin and keeping terms to second order in fluorine distortion, one has for the potential energy of a Mn_2 site (see Fig. 1):

$$V=(2x_3^2-x_1^2-\psi)z^2-2(\sqrt{2}x_3-x_2)zx-2\sqrt{2}x_1x_3zy+x_2^2x^2, \quad (1)$$

where distances are in units of a and $\psi=1-(a/c)^3$. Constant multipliers of the potential have been neglected since we are interested in only the symmetry of the potential. With $x_1\cong0.05$, $x_2\cong0.06$, $x_3\cong0.04$,[12] the zx and zy terms are of the same order of magnitude. The term second order in distortions (zy) is of the same order of magnitude as the zx term because the zx term is the result of the difference of two nearly equal distortions. Taking care of the signs of the distortions, similar expressions can be constructed from Eq. (1) for the remaining three sites. Since the single-ion magnetic energy has the symmetry of the potential, we let $\mathbf{R}_i\rightarrow\mathbf{M}_i$ ($i=1, 2, 3, 4$) and take as the magnetic energy of the electron system in the presence of an external field $\mathbf{H}_0$:

$$\begin{aligned}U=\lambda(\mathbf{M}_1+\mathbf{M}_3)\cdot(\mathbf{M}_2+\mathbf{M}_4)+\sum_{i=1}^{4}((K_3/M_0^2)M_{ix}^2-(K_1/M_0^2)M_{iz}^2-\mathbf{H}_0\cdot\mathbf{M}_1)\\-(K_2/M_0^2)(M_{1z}M_{1x}-M_{2z}M_{2x}+M_{3z}M_{3x}-M_{4z}M_{4x})-(K_5/M_0^2)(M_{1z}M_{1y}-M_{2z}M_{2y}-M_{3z}M_{3y}+M_{4z}M_{4y})\\+\frac{K_4}{M_0^4}\sum_{i=1}^{4}(M_{1z}^4+(M_{ix}+M_{iy})^4/4+(M_{ix}-M_{iy})^4/4), \quad (2)\end{aligned}$$

where the $\mathbf{M}_i$'s are the sublattice magnetizations. We assume there is only one antiferromagnetic exchange constant λ; further, we introduce a cubic anisotropy K_4 since the distortion from cubic symmetry is small. In the pseudocubic coordinate system, the cubic anisotropy has the form

$$U_4=(K_4/M_0^4)(M_x^4+M_y^4+M_z^4). \quad (3)$$

If the cubic term is neglected, Eq. (2) becomes a special case of the more general energy expression given by Hermann,[14] which he derived from group theoretical considerations. We exclude the antisymmetric exchange interaction $\mathbf{D}\cdot\mathbf{M}_i\times\mathbf{M}_j$ of Dzialoshinski[15] and assume that single-ion anisotropy is repsonsible for the canting in this material. To solve Eq. (2) for its eigenfrequencies, transform to a polar coordinate system in which the polar axis is a pseudocubic ⟨001⟩ axis and the azimuthal angles are measured from the x axis which is a ⟨110⟩ type axis. (See Fig. 2.)

We are led to consider the spin configuration in which the spins are essentially along the ⟨001⟩ direction for the following three reasons: The first is the F^{19} resonance experiments of Sandle[2] which require that the spins lie in the xz plane (the F^{19} NMR frequency is determined largely by the applied static magnetic field and the dipolar interaction between the F^{19} nucleus and the electronic spins on the surrounding Mn^{+2} ions); the second reason is that our experiments show that a ⟨110⟩ direction is a symmetry direction for the NMR frequency; and third, from the configuration of the applied dc magnetic field and radio-frequency (rf) magnetic field used in our experiments, this configuration for the electron spins leads to a large enhancement factor for resonance absorption. If the substitution $\theta_i=\theta_{i0}+\delta\theta_i$ and $\phi_i=\phi_{i0}+\delta\phi_i$ is made in Eq. (2) in its polar coordinate form, one can expand to second order in small quantities and use the equations of motion for $\delta\theta_i$ and $\delta\phi_i$ to construct the resonance matrix. As expected, the

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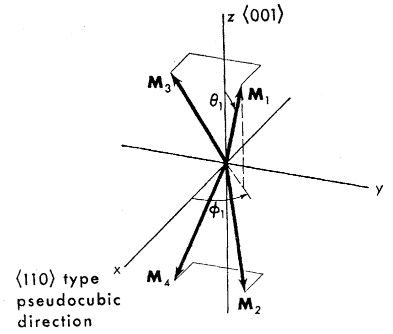

FIG. 2. The equilibrium positions of the sublattice magnetizations in the canted state for KMnF₃.

system has four AFR modes: two modes are exchange modes, and the remaining two modes are similar to the two low-lying modes one would have if KMnF$_3$ were treated as a two-sublattice system.[3]

To include the effect of the hyperfine interaction of the electrons with the Mn^{+2} nuclei, we add $4\lambda M\alpha m$ to the expression for the AFR frequencies[5] where α is proportional to the hyperfine coupling constant and m is the thermally averaged nuclear sublattice magnetization. The result of the calculation is that the resonance frequencies for $\mathbf{H}_0 \| \langle 110\rangle$ are given by[16]

$$\begin{aligned}(\omega_{\mathrm{I}}/\Gamma)^2 &= 4H_e[H_N+2H_1-4H_4] \\ &\quad +8H_5^2+H_2(H_0+H_2)\,, \\ (\omega_{\mathrm{II}}/\Gamma)^2 &\cong (\omega_{\mathrm{III}}/\Gamma)^2 \cong 4H_e^2\,, \qquad (4)\\ (\omega_{\mathrm{IV}}/\Gamma)^2 &= 4H_e[H_N+2H_1-4H_4+2H_3] \\ &\quad +2H_5^2+H_0^2+5H_0H_2+4H_2^2\,,\end{aligned}$$

where all terms small in comparison with $4H_e^2$ have been neglected in modes II and III. To identify the AFR mode that was used in our experiments to excite the nuclear resonance, we must solve for the enhancement factors for resonance absorption. We are interested in the rf susceptibility of the sublattice magnetization as a function of the driving rf field. Introduce $U_{\mathrm{rf}} = -\sum_{i=1}^{4} \mathbf{h}_0 \cdot \mathbf{M}_i e^{i\omega t}$ in Eq. (2) and solve for $\delta\theta_i$ and $\delta\phi_i$. The result of the calculation is that mode I is active for $\mathbf{h}_0=\mathbf{h}_x$ while mode IV is active for $\mathbf{h}_0=\mathbf{h}_z$ or $\mathbf{h}_0=\mathbf{h}_y$. We neglect modes II and III since their resonance frequencies are of order 1.4×10^{13} sec^{-1}. The enhancement factors η for sin $\phi_i \sim 0$ are given by

$$\begin{aligned}\eta_1 &= (\Gamma^2/\gamma)(\omega_0/\omega_{\mathrm{IV}}^2)(H_0^2+2H_0H_2+H_2^2+4H_5^2)^{1/2}\,, \\ &\qquad \mathbf{h}_0=\mathbf{H}_z \qquad (5)\\ \eta_2 &= (\Gamma/\gamma)\omega_0\omega/\omega_{\mathrm{IV}}^2\,, \qquad \mathbf{h}_0=\mathbf{h}_y\end{aligned}$$

for mode IV, and

$$\eta_3 = (\Gamma/\gamma)\omega_0\omega/\omega_{\mathrm{I}}^2\,, \qquad \mathbf{h}_0=\mathbf{h}_x \qquad (6)$$

for mode I. Where γ and Γ are the gyromagnetic ratios for the Mn^{55} nucleus and magnetic electrons, respectively, ω is the driving rf frequency, ω_0 is the hyperfine frequency of the nuclei, $H_2=K_2/M$ and $H_5=K_5/M$. Since the rf driving frequency $\omega/2\pi$ is approximately 600 Mc/sec, the approximation $\omega_{\mathrm{I,II}}^2-\omega^2 \cong \omega_{\mathrm{I,II}}^2$ has been used to derive Eqs. (5) and (6).

The NMR frequency is dependent not only on the magnitude of the applied dc magnetic field, but also on the direction of the magnetic field with respect to the crystallographic axes. The calculation of the AFR modes of Eq. (2) for $\mathbf{H}_0$ in the $\langle 001\rangle$ plane is in general very lengthy since the symmetry relation $\phi_1=-\phi_3$ is no longer valid. However, for $\mathbf{H}_0$ near the $\langle 110\rangle$ symmetry direction, the general 8×8 resonance matrix can be reduced to two 2×2 matrices. The AFR frequency of mode IV for $\mathbf{H}_0$ near the x axis is given by[16]

$$\begin{aligned}(\omega_{\mathrm{IV}/\Gamma})^2 &= 4H_e[H_N+2H_1-4H_4]+[4H_eH_3+H_5^2] \\ &\quad \times[1+\cos(\phi_1+\phi_3)]+3H_2(H_0\cos\phi+H_2) \\ &\quad +2H_5^2(\cos^2\phi_1+\cos^2\phi_3)/\sin^2\tfrac{1}{2}(\phi_1-\phi_3)\,, \qquad (7)\end{aligned}$$

where ϕ is the angle between $\mathbf{H}_0$ and the $\langle 110\rangle$ crystal direction. The equilibrium positions of the sublattice magnetization $\mathbf{M}_1$ and $\mathbf{M}_3$ are given by

$$\tan\phi_i = (H_0\sin\phi \pm 2H_5)/(H_0\cos\phi+H_2)\,, \quad i=1, 3\,, \qquad (8)$$

where the plus sign is used for $i=1$. Equation (7) reduces to the expression given for mode IV in Eqs. (4) with $\phi=0$ and $\phi_1=-\phi_3$ where ϕ_1 is given by Eq. (8).

EXPERIMENTAL RESULTS

The nuclear resonance was observed in a cylindrical single crystal of KMnF$_3$. The cylinder was 8 mm in diameter and 20 mm in length. The single crystal of KMnF$_3$ was obtained from Semi-Elements Inc.[17] A marginal oscillator was used to detect the resonance; the oscillating element of the oscillator was a shorted

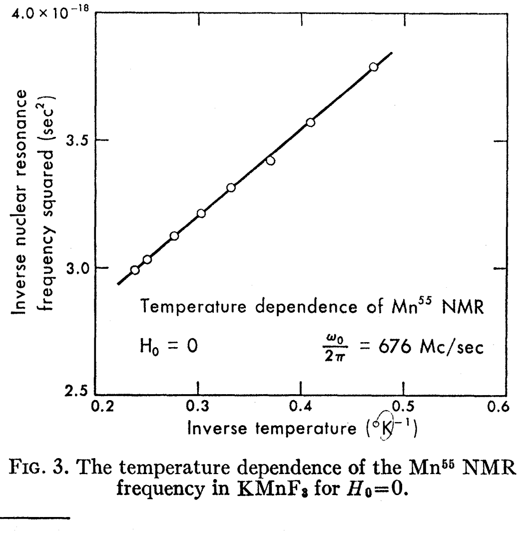

FIG. 3. The temperature dependence of the Mn^{55} NMR frequency in KMnF$_3$ for $H_0=0$.

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section of a parallel transmission line. The rf magnetic field was directed along a ⟨100⟩-type pseudocubic direction while the applied dc magnetic field was in the plane perpendicular to the rf field and along a ⟨110⟩-type axis. The NMR frequency is symmetrical about the ⟨110⟩ axis. Since mode I is active for $\mathbf{h}_0$ parallel to $\mathbf{H}_0$, we identify mode IV as the electron mode used to excite the nuclear resonance. The mode pattern for IV is one in which the weak moment oscillates along the ⟨001⟩ direction. The NMR frequency is then given by[10]

$$\omega_n^2=\omega_0^2(1-\Omega_0^2/\omega_{\mathrm{IV}}^2)\,, \tag{9}$$

where $\Omega_0^2=\Gamma^2 4H_eH_n$. Since H_n should have a T^{-1} dependence for temperatures in the range 2–4°K, ω_n^{-2} should be linearly dependent on T^{-1} for a constant dc magnetic field. A plot of $(2\pi/\omega_n)^2$ versus T^{-1} for $\mathbf{H}_0=0$ is given in Fig. 3. From Eqs. (4) and (9),

$$q(H_0)=4H_e[2H_1-4H_4+2H_3]+2H_5^2+4H_2^2+5H_0H_2\,, \tag{10}$$

where

$$q(H_0)=(4H_eH_N)/(\omega_0^2/\omega_n^2-1)-H_0^2\,.$$

A plot of $q(H_0)$ versus H_0 for $T=4.2$°K is given in Fig. 4; from the linear dependence of $q(H_0)$ on H_0 we have $H_2=310\pm20$ Oe. The field dependence of the NMR frequency is given in Fig. 4; the theoretical curve was determined with Eqs. (4) and (9) with $\omega_0/2\pi=676\pm3$ Mc/sec, $H_e=4.34\times10^5$ Oe, $H_2=310\pm20$ Oe, and $\alpha m=9.28/T$. The value of H_e is one-half the value used by Witt and Portis[18] since the magnitude of the sublattice magnetizations differ by a factor of 2. The factor of 2 enters because each sublattice magnetization in the model used by Witt and Portis is decomposed into two different sublattices in this four-sublattice model. We did not include demagnetization effects in the resonance expressions for the AFR modes since the shift in the AFR frequency by demagnetization effects is only important for antiferromagnets with small exchange fields.[19] It is likely that our experiments at low temperatures were not performed on a "magnetic" single crystal, since twinning effects are important for KMnF$_3$.[1] We assume that the nuclear resonance we observe originates in those crystallites with the spin configuration given in Fig. 2. "Field annealing" had no noticeable effect on the intensity or position of the nuclear resonance. The angular dependence of the NMR frequency is given in Fig. 6; the theoretical curve was

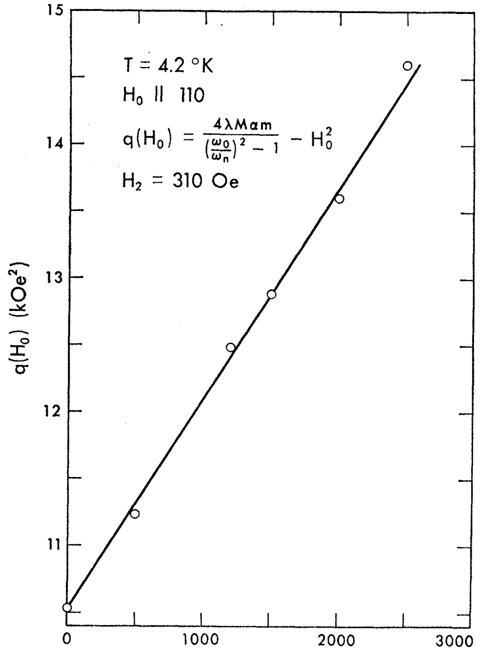

FIG. 4. Linear dependence of $q(H_0)$ on H_0. The linear dependence is a result of the overt canting in KMnF$_3$.

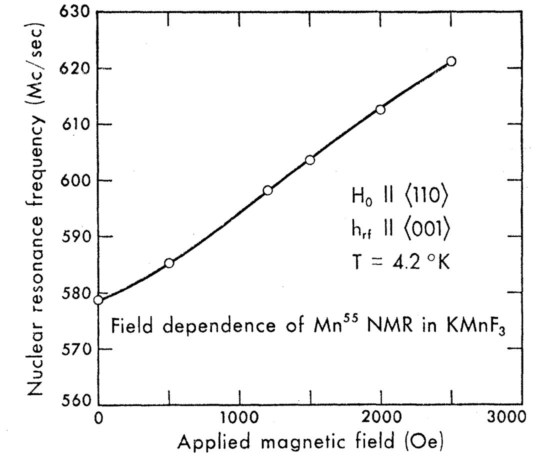

FIG. 5. The field dependence of the NMR frequency for H_0 parallel to a ⟨110⟩-type pseudocubic axis.

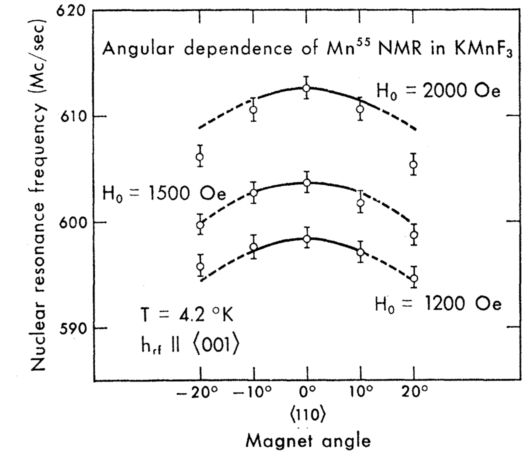

FIG. 6. The angular dependence of the Mn^{55} NMR frequency in KMnF$_3$ for H_0 near a ⟨110⟩-type pseudocubic crystal axis.

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determined by Eqs. (7), (8), and (9) with $H_5=200\pm30$ Oe. $H_3=3.02\pm0.4$ Oe and $H_1-2H_4=-0.12\pm0.05$ Oe.

DISCUSSION

The results of the direct Mn^{55} NMR experiments are in good agreement with the AFR mode whose resonance frequency is given by Eqs. (4) and (7). The enhancement of the resonance absorption is caused by the rocking of the sublattice magnetization at the driving frequency[20]; for mode IV, if $\mathbf{H}_0$ is parallel to the $\langle 001\rangle$ axis $\eta\cong85$ which gives signal-to-noise enhancement of $\sim7\times10^3$, while mode I would have a signal to noise enhancement of the order of 25 for $\mathbf{h}_0$ parallel to the $\langle 100\rangle$ or $\langle 010\rangle$ pseudocubic axis.

The linear dependence of $q(H_0)$ indicates that canting is important in this material; the NMR experiments supplement the torsion experiments of Heeger *et al.*,[1] which first showed that KMnF_3 was a canted antiferromagnet. *A priori*, one cannot neglect the Dzialoshinski canting mechanism; however, its contribution to the overt canting field should be small since the distortion of the fluorine octahedra from cubic symmetry is small and the shift in g value of a Mn^{+2} ion in KMnF_3 from the spin-only value is only of order of 10^{-3}. Furthermore, the calculation of the single-ion anisotropy energy of KMnF_3 by Pearson[21] shows that the distortion of the fluorine octahedra from their perovskite configuration could account for a canting field of the order of 300 Oe.

The value of the hyperfine NMR frequency given here differs by 1.6% from the value of 687 Mc/sec given by Witt and Portis[18] from double-resonance experiments. We have also performed direct NMR experiments using a magnetic-field configuration in which $\mathbf{H}_0$ is parallel to a $\langle 100\rangle$ type axis, while $\mathbf{h}_0$ is perpendicular to $\mathbf{H}_0$ and parallel to a $\langle 110\rangle$ pseudocubic axis. This configuration is very similar to the configuration used by Witt and Portis in the double-resonance experiments. We find that the field dependence of the nuclear resonance that would correspond to the resonance excited by Witt and Portis is very complicated for 3250 Oe$>H_0>$2500 Oe. A plot of the NMR frequency versus H_0 has a minimum for $H_0\sim2750$ Oe; we were unable to follow the nuclear resonance through the minimum because the resonance seemed to broaden as we approached the minimum. It is possible that Witt and Portis were able to obtain a shift in the field for AFR for rf frequencies above 676 Mc/sec because they were driving the nuclear system in the high-frequency wing of the nuclear resonance. This difference in the hyperfine-field frequency for KMnF_3 obtained by the direct NMR experiments and double-resonance experiments should be compared with the results of similar experiments performed on CsMnF_3. In the case of CsMnF_3,[22] the nuclear resonance has a linewidth of the order of 0.20 Mc/sec. The agreement between the two types of experiments for the hyperfine-field frequency for CsMnF_3 is very good. Davis's[23] calculation for the zero-point spin wave reduction in a simple cubic structure predicts a 2.97% reduction in $\langle S\rangle$. If a volume correction is made for the fluorine octahedra surrounding a Mn^{+2} site, Ogawa's[24] paramagnetic resonance studies of the Mn^{+2} ion in KMgF_3 would give 687 Mc/sec as the value of the hyperfine frequency. Our value of 676±3 Mc/sec would thus suggest a zero-point spin-wave reduction in $\langle S\rangle$ of 1.6%±0.04%.

There are two reasons why we have had to use a four sublattice model to interpret the results of the NMR experiments. The first reason is that in Eq. (1) for the expansion of the potential for a Mn_2 site the xz and zy terms are of the same order of magnitude. The introduction of a term with the symmetry zy into the energy expression results in a four-sublattice system. The second reason is that if $H_5=0$ in Eq. (4), the resulting energy expression can be solved for its eigenfrequencies for $\mathbf{H}_0$ in an arbitrary direction in the $\langle 001\rangle$ plane; it is not necessary to use a small-angle approximation to obtain reasonable expressions for the AFR frequencies. We found we could not fit the angular dependence of the NMR frequency with this two sublattice model (if $H_5=0$, $\mathbf{M}_1$ and $\mathbf{M}_3$ can be viewed as being on the same sublattice).

ACKNOWLEDGMENTS

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