Mn^{55} Nuclear Magnetic Resonance in MnF_2— The Suhl-Nakamura Interaction

H. YASUOKA,*† TIN NGWE,†‡ AND V. JACCARINO†
Department of Physics, University of California, Santa Barbara, California 93106

AND

H. J. GUGGENHEIM
Bell Telephone Laboratories, Murray Hill, New Jersey 07971

(Received 9 September 1968)

The NMR of Mn^{55} in antiferromagnetic MnF_2 has been reexamined, using both superregenerative and pulsed NMR techniques, in the temperature region 1.3–20°K. Instead of the single resonance originally reported, five distinct quadrupolar-split transitions are observed, whose separation yields a value of $e^2qQ/\hbar = 11.7\pm0.3$ MHz. The frequency of the central $(\frac{1}{2}\leftrightarrow-\frac{1}{2})$ transition extrapolates to 670.38 ± 0.05 MHz at 0°K. Were there no changes in the hyperfine interaction in going from ZnF_2:Mn to MnF_2, this would imply $\langle S_z\rangle_0/S = (99.41\pm0.03)\%$ in the antiferromagnetic ground state. The magnitude and m dependence of the linewidths of the individual transitions are reasonably consistent with the predictions of the Suhl-Nakamura theory (i.e., the indirect nuclear spin-spin interaction via virtual spin-wave excitations). The failure to observe a transient signal is attributed to the very short $T_2(<1\ \mu\text{sec})$ resulting from the latter interaction.

I. INTRODUCTION

NUCLEAR magnetic resonance (NMR) studies in antiferromagnets provide detailed information about the static and dynamic properties of the ordered spin system.[1] MnF_2 has proved to be a particularly fruitful example with the F^{19} and Mn^{55} nuclei ideally amenable to resonance investigations. From both the viewpoint of spin-wave theory and hyperfine interactions the fact that $Mn^{2+}(3d^6)$ is an S-state ion is additionally attractive since all orbital effects will be entirely negligible.

A few years ago a *single* Mn^{55} resonance was observed[2] in MnF_2 at low temperatures with a linewidth $\Delta\nu\simeq1.3$ MHz. Superregenerative detection techniques were employed and the 0°K resonance frequency was extrapolated to be 671.4 ± 0.2 MHz. The relatively large linewidth was interpreted as primarily arising from the indirect nuclear spin-spin interaction via the virtual excitation of spin waves—the so-called Suhl-Nakamura (SN) interaction.[3,4] The experimental result appeared to be not unreasonable since a homogeneously broadened line with this order of magnitude width had been predicted.[4]

However, two facets of this experiment prompted us to undertake the present investigation. First, there are a number of cases where the linewidth, as observed in a steady-state continuous wave (cw) experiment, has been shown to reflect inhomogeneous broadening.[5] This has been discerned from subsequent transient experiments (spin-echo studies) where invariably it was found that not only was the *homogeneous* linewidth much less than the cw width but less than the calculated spin-spin linewidths. Second, the fact that the Mn ion occupies a site of less than cubic point symmetry and the Mn^{55} nucleus $(I=\frac{5}{2})$ has a quadrupole moment $Q\simeq0.5\times10^{-24}$ cm^2 would suggest the possibility of a multiplet structure to the observed resonance such as was observed in the Co^{59} $(I=\frac{7}{2})$ resonance in antiferromagnetic CoF_2.[6] Indeed, a simple point charge calculation of the electric field gradient predicts an equally spaced five line spectrum, with adjacent components separated by approximately 1.8 MHz, rather than the *single* resonance previously observed. With these two aspects in mind we have repeated the cw experiments and have attempted transient measurements as well. Our experimental results are given in Sec. II followed by a theoretical interpretation in Sec. III.

II. EXPERIMENTAL PROCEDURE AND RESULTS

A. Experimental Methods

The steady-state Mn^{55} NMR signal was observed using a superregenerative oscillator spectrometer of a design similar to that used by Jefferts and Jones.[7] However, by a suitably modified quenching system, the quench rate and amplitude could be externally controlled and over a large range of rf levels. Frequency modulation was achieved with a silicon variable-capacitor diode (Varicap) instead of the more conventional mechanical vibrator. The dynamic quench rate range and the maximum frequency modulation amplitude were 100 kHz–2 MHz and about 5 MHz, respectively.

* Present address: Department of Metal Science and Technology, Kyoto University, Kyoto, Japan.
† Supported in part by the National Science Foundation.
‡ Present address: Department of Physics, University of California, Riverside, Calif.
[1] For a review of the NMR in antiferromagnets see V. Jaccarino, in *Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. 2A, Chap. 5.
[2] E. D. Jones and K. B. Jefferts, Phys. Rev. **135**, A1277 (1964).
[3] H. Suhl, Phys. Rev. **109**, 606 (1958).
[4] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **20**, 542 (1958).
[5] N. Kaplan, P. Pincus, and V. Jaccarino, J. Appl. Phys. **37**, 1239 (1966).
[6] V. Jaccarino, Phys. Rev. Letters **2**, 163 (1959).
[7] K. B. Jefferts and E. P. Jones, Rev. Sci. Instr. **36**, 983 (1965).

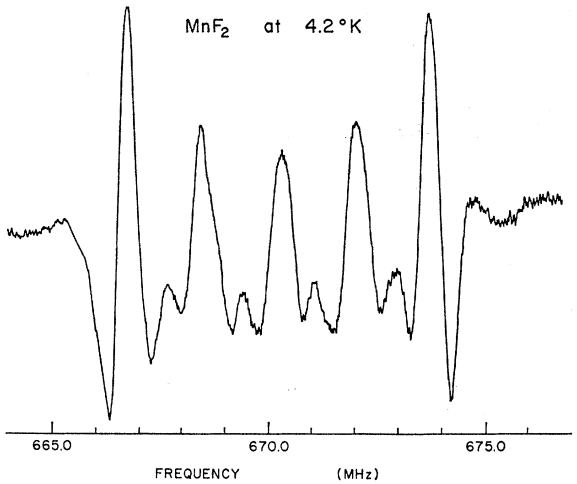

FIG. 1. A recording trace of the absorption signal of the Mn^{55} NMR in MnF_2 at 4.2°K as phase-sensitively detected at the fundamental modulation frequency. (Modulation frequency, $\nu_M=40$ Hz, depth of modulation, $\Delta\nu_M=150$ kHz, and a quench rate for the superregenerative detector, $\nu_Q=200$ kHz.) An interesting feature of the resonance structure is immediately apparent from the relative size of the peak amplitudes. If each line was *equally* broadened then the relative intensities would be 5:8:9:8:5. Had the outer resonances been broadened more than the central resonance—as would be the case for a quadrupolar induced transverse relaxation mechanism—then we would expect the relative intensities to be even more strongly peaked about the center value. However, just the opposite is observed. The central line is smaller in amplitude than the outer lines unambiguously pointing to a mechanism which requires that the central resonance be broadened more than the outer ones. The SN interaction as manifest in the expression for the second moment (Eq. 19) provides just such a mechanism.

In order to study the transient signal, a uhf spin-echo system was constructed. An applied microwave laboratory model PH20K pulsed oscillator was used as the transmitter-exciter. The design of the receiving system was similar to that previously utilized in uhf spin-echo experiments.[8] The helium Dewar tip which contained the MnF_2 sample was inserted in the tunable coaxial cavity.[9] This cavity was coupled to both exciter and receiver by a low impedance coupling. The excitation condition and the receiving sensitivity were optimized by direct observation of the I^{127} pure quadrupole resonance (NQR) in iodine whose frequency is approximately 640 MHz at room temperature.

B. Experimental Results

Steady state. Five equally spaced Mn^{55} NMR signals were observed in a single crystal of MnF_2 in the temperature range of 1.3–20°K using a frequency modulated superregenerative detector. A recording trace of the absorption signal as phase-sensitive detected at the fundamental modulation frequency (40 Hz) at 4.2°K is shown in Fig. 1. When an external magnetic field was applied along the easy axis [001], every line split into two components, one increasing and one decreasing in frequency with increasing magnetic field, as a consequence of the removal of the spatial degeneracy associated with the antiferromagnetic ordering. This behavior is similar to that reported for the Co^{59} NMR in CoF_2.[6] The frequency of the central resonance at elevated temperatures and the fractional frequency shifts with respect to the extrapolated 0°K frequency, 670.38±0.05 MHz, are given in Table I. They are compared with the corresponding F^{19} NMR data in MnF_2 taken from earlier studies.[10] Within experimental error, the observed temperature dependence of the fractional changes in the two resonances appear to agree signifying that either one gives a good measure of the temperature dependence of the sublattice magnetization. (Although the actual values of the Mn^{55} NMR frequency differ appreciably from those previously reported,[2] the same temperature dependence to the *fractional* change remains.)

TABLE I. Temperature dependence of Mn^{55} NMR frequency in MnF_2. Mn^{55} NMR frequencies for elevated temperatures are given in the first column. The second and third columns give the fractional decrease of the Mn^{55} and F^{19} NMR frequencies with respect to their 0°K values.

Temperature (°K)	Mn^{55}NMR ν (MHz)	Mn^{55} NMR $10^2(\nu-\nu_0)/\nu_0$	F^{19} NMR $10^2(\nu-\nu_0)/\nu_0$
1.3	670.38±0.05	0	0
4.2	670.25±0.05	0.02±0.01	0.01
13.9	665.57±0.05	0.72±0.02	0.71
15.0	663.95±0.05	0.96±0.02	0.95
16.5	661.85±0.1	1.27±0.03	1.24
18.0	659.05±0.1	1.69±0.03	1.65

Accurate determinations of the linewidth and particularly the line shape are difficult to make using a superregenerative detector, because of the presence of side-band responses in the superregenerative spectrum. However, an estimate of the linewidth may be obtained from a study of the spectrum as the quench rate is varied. In our experiments the rate was varied from 100 kHz to 1 MHz at constant rf level. In the low end of this range, namely 100 –300 kHz, the observed spectrum does not change as a function of the quench rate. Restricting ourselves to this low quench rate the linewidth was measured as a function of temperature. A summary of the frequency and linewidth data taken at 4.2°K in zero applied field is given in Table II. Both the observed quadrupole splitting (1.75±0.05 MHz) and the linewidth were determined to be independent of temperature in the range of 1.3–18°K. It is to be noted that the linewidth for the transitions ($m=\pm\frac{5}{2}\leftrightarrow m'=\pm\frac{3}{2}$) appear to be narrower than the transition ($m=\frac{1}{2}\leftrightarrow m'=-\frac{1}{2}$) hence the observed peak intensity of the former is greater than the latter as can be seen in Fig. 1. The detailed relations between the nuclear electric quadrupole interaction and the nuclear spin-

[8] H. Yasuoka, J. Phys. Soc. (Japan) **19**, 1182 (1964).

[9] The cavity was actually designed and used by Dr. H. Suhl some 15 years ago.

[10] V. Jaccarino and L. R. Walker (unpublished).

TABLE II. A summary of the Mn^{55} NMR frequency and linewidth data in MnF_2 at 4.2°K. Lines A and B list the transitions. The second differences are defined in Eq. (11). The observed linewidths were obtained from a recording in which $\Delta\nu_M = 100$ kHz and $\nu_Q = 150$ kHz and not the trace shown in Fig. 1. The theoretical widths are calculated from the relation: Gaussian width $= 2(M_2)^{1/2}$ with M_2 given by Eq. (20). Although the error in the theoretical estimates may approach 10% the ratios of the widths are precisely $(57)^{1/2}$: $(117)^{1/2}$: $(145)^{1/2}$: $(117)^{1/2}$: $(57)^{1/2}$.

	A $+\frac{5}{2}\leftrightarrow+\frac{3}{2}$	$+\frac{3}{2}\leftrightarrow+\frac{1}{2}$	$+\frac{1}{2}\leftrightarrow-\frac{1}{2}$	$-\frac{1}{2}\leftrightarrow-\frac{3}{2}$	$-\frac{3}{2}\leftrightarrow-\frac{5}{2}$
	B $-\frac{5}{2}\leftrightarrow-\frac{3}{2}$	$-\frac{3}{2}\leftrightarrow-\frac{1}{2}$	$-\frac{1}{2}\leftrightarrow+\frac{1}{2}$	$+\frac{1}{2}\leftrightarrow+\frac{3}{2}$	$+\frac{3}{2}\leftrightarrow+\frac{5}{2}$
ν (MHz)	666.75±0.05	668.53±0.05	670.25±0.05	672.00±0.05	673.75±0.05
Second differences (MHz)	1.78	1.72	1.75	1.75	
Observed linewidths (Oe)	430±50	520±50	570±50	520±50	430±50
Theoretical linewidths $2(M_2)^{1/2}$	394	564	628	564	394

spin interaction and the effects they have on the linewidth are given in Sec. III.

Transient studies. The observation of a transient signal (free induction and/or spin echo) of Mn^{55} NMR in MnF_2 has also been attempted a number of times at various temperatures and applied magnetic fields. Unfortunately, however, we were unable to observe any signals. In order to check the conditions for excitation and the sensitivity of the receiver of the pulsed uhf NMR apparatus iodine NQR and Mn^{55} NMR in other materials (e.g., $RbMnF_3$ and Mn_3O_4) have been examined. With these transient signals one can estimate the limiting sensitivity of the apparatus in the following manner. First, the excitation condition can be checked using the iodine NQR signal, since in this instance there is no enhancement of the applied rf field. Using a coaxial-type sample cavity with $Q\approx 300$, the free induction signal associated with the $(\pm\frac{5}{2}\leftrightarrow\pm\frac{3}{2})$ transition is easily observed at 646 MHz at room temperature. The transverse rotating rf field (H_1) was determined to be of the order of 60 Oe by finding a 90° pulse condition for the free induction signal, $\gamma_n\alpha H_1 t_w = \pi/2$ where $\alpha=[I(I+1)-m(m-1)]^{1/2}$. With an H_1 of this magnitude the corresponding 90° pulse condition for the Mn^{55} NMR in antiferromagnetic MnF_2 would be obtained using a $3\sim4$ μsec rf pulse width (t_w). Second, the sensitivity of the receiver may also be checked using the I^{127} NQR signal in iodine. The signal-to-noise ratio of the latter is approximately 100 at room temperature so that even if the linewidth of the Mn^{55} NMR in MnF_2 were 10 times larger than the I^{127} NQR, it should be easily detectable at low temperatures in the antiferromagnetic state, providing T_2 is not too short. One other important factor to be considered is the recovery time of the receiving system. We have attempted to minimize this parameter but found that, at best, the detection system does not recover for approximately 5 μsec after applying a 3-μsec rf pulse width, with $H_1\simeq 60$ Oe. Using Mn^{55} spin-echo signals in $RbMnF_3$ and Mn_3O_4, the shortest T_2 that could be observed in the present apparatus is estimated to be about 2 μsec. Transcribed into units of magnetic field this implies that, if the *homogeneous* part of the Mn^{55} NMR linewidth in MnF_2 is more than 100 Oe, there is no possibility of observing transient signals with the present apparatus.

Combining these considerations with the observation that, within the experimental error, the newly measured linewidths qualitatively agree with the theoretical estimate (as we shall see in Sec. III), we conclude that the observed steady-state resonances are *homogeneously* broadened. This conjecture is also in keeping with the fact that the local field at the Mn^{55} nucleus associated with Mn^{2+} ion in MnF_2 is very insensitive to impurities or other kinds of lattice defects. The reason for this is simply that the hyperfine field has its origin in intra-atomic core polarization by the $3d$ electrons of a given ion. This situation is to be contrasted with the F^{19} NMR in MnF_2 where the local field is of overlap or transfer origin with the three neighboring Mn ions and is therefore extremely sensitive to strains, impurities, etc. We have examined the linewidth of the Mn^{55} NMR in various deliberately doped samples of MnF_2 (e.g., 1% Zn, V, Co, or Ni substituted for the Mn) and found no appreciable broadening of the resonance. Again, by way of contrast, the F^{19} NMR is broadened at least tenfold by such substitutions relative to the resonance in the impurity-free crystal.[11]

III. INTERPRETATION

A. Interaction Hamiltonian

An individual nuclear spin of a particular magnetic ion is coupled to its atomic electrons through the magnetic hyperfine interaction and to the other magnetic ions and their nuclei through dipolar interactions.[11] The nuclei are also coupled to each other by the indirect nuclear spin-spin interaction via virtual spin-wave excitations.[3,4] If the ion occupies a lattice site of less than cubic point group symmetry a nuclear electric quadrupole interaction is allowed and its effect on the observed spectra must be considered.[12]

Below the Néel temperature the Mn^{2+} spins in the body-centered tetragonal MnF_2 structure order with their moments colinear with the unique or c axis—[001]; see Fig. 2. This fortunate circumstance simplifies the description of the nuclear magnetic dipole and electric quadrupole interactions at the Mn^{2+} ion sites. Despite the low point symmetry (orthorhombic) both

[11] M. Butler, N. Kaplan, V. Jaccarino, and H. J. Guggenheim (unpublished).
[12] T. Moriya, Progr. Theoret. Phys. (Kyoto) **16**, 641 (1956).

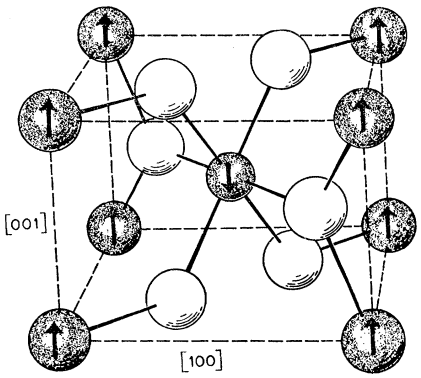

FIG. 2. The crystal and magnetic structure of MnF_2. The shaded balls represent Mn^{2+} ions, with the heavy arrows indicating the direction of the electronic spin magnetization, and the remaining ones are the intervening F^- ions.

interaction tensors—which in general will have less than axial symmetry—do have the [001] direction as a common principal axis. If we restrict ourselves to the application of an external magnetic field H_0 parallel to the [001], or $\pm z$ direction, we may write the total nuclear Hamiltonian as[12]

$$\mathcal{H}=\mathcal{H}_M+\mathcal{H}_Q+\mathcal{H}_{SN} \tag{1}$$

with the Zeeman part

$$\mathcal{H}_M=[A_z^{55}\langle S_z\rangle_T-\gamma^{55}\hbar(H_0+\sum_i^N \mathfrak{D}_z{}^i\langle S_z\rangle_T)]I_z \equiv M(H_0,T)I_z, \tag{2}$$

the quadrupolar part

$$\mathcal{H}_Q=\tfrac{1}{2}P[3I_z^2-I(I+1)+\tfrac{1}{2}\eta(I_+^2+I_-^2)], \tag{3}$$

and the indirect spin-spin portion as

$$\mathcal{H}_{SN}=-\tfrac{1}{2}\sum_{i>j}^N B_{ij}[I_i^+I_j^-+I_i^-I_j^+]+\tfrac{1}{2}D\sum_i^N I_{zi}^2. \tag{4}$$

The quantities that appear in Eqs. (2), (3), and (4) are defined as follows: $A_z{}^{55}$ and γ^{55} are the z component of the magnetic hyperfine interaction tensor and gyromagnetic ratio, respectively, $\mathfrak{D}_z{}^i\langle S_z\rangle_T$ the electronic dipolar field generated by the ith Mn^{2+} spin as sensed by the reference spin, and $\langle S_z\rangle_T$ indicates the thermal average of the electron spin moment. The quadrupolar constants are defined as usual:

$$P=\frac{eQ^{55}}{2I(2I-1)}\frac{\partial E_z}{\partial z} \tag{5}$$

and the asymmetry parameter

$$\eta=\left(\frac{\partial E_x}{\partial x}-\frac{\partial E_y}{\partial y}\right)\Big/\frac{\partial E_z}{\partial z} \tag{6}$$

with $\mathbf{E}$ the electric field and x, y, and z the principal axes. Finally the coupling constants B_{ij} and D of Eq. (4) are given[4] by

$$B_{ij}=\frac{A^2}{2\gamma_0 J}f(r_{ij}) \quad \text{and} \quad D=\frac{A^2}{2\gamma_0 J}f(0) \tag{7}$$

with γ_0 the number of opposite sublattice nearest neighbors with which there is an exchange interaction J and the range $f(r_{ij})$ of the indirect spin-spin interaction as given by the spin-wave sum[13]

$$f(r_{ij})=\frac{1}{N}\sum_\lambda \frac{\cos\lambda r_{ij}}{[1-(\gamma_\lambda/\gamma_0)^2-\Delta^2]}. \tag{8}$$

From *a priori* estimates of the constants involved we know that $\mathcal{H}_M\gg\mathcal{H}_Q\approx\mathcal{H}_{SN}$; hence we may regard both $\mathcal{H}_Q$ and $\mathcal{H}_{SN}$ as small perturbations. First, let us neglect the terms containing the B_{ij} double summation term in Eq. (4). Then the eigenvalues of $\mathcal{H}$ to second order in $\mathcal{H}_Q$ are, neglecting the constant terms,

$$E_m=(M(H_0,T))m+(3P+\tfrac{1}{2}D)m^2 +\frac{\eta^2P^2}{M(H_0,T)}\left[-m^3+\frac{33}{4}m\right]. \tag{9}$$

B. Quadrupolar Constants

In zero external field we find the difference in frequency $\nu_{m\leftrightarrow m-1}{}^0(T)$ between adjacent Zeeman levels E_m and E_{m-1}, *to first order in* P, to be

$$\nu_{m\leftrightarrow m-1}{}^0(T)=\left\{\frac{A_z{}^{55}}{h}+\frac{\gamma^{55}}{2\pi}\sum_{i=1}^N \mathfrak{D}_z{}^i\right\}\langle S_z\rangle_T +\frac{2m-1}{h}(3P+\tfrac{1}{2}D), \tag{10}$$

and the second differences

$$\delta\nu\equiv\nu_{m\leftrightarrow m-1}(T)-\nu_{m'\leftrightarrow(m'-1)}(T)$$

with $m=m'+1$ are

$$\delta\nu=(1/h)(3P+\tfrac{1}{2}D), \tag{11}$$

independent of T and m. Since the observed second differences were found to be independent of m and m' we may use Eqs. (5), (7), and (11) to evaluate e^2qQ/h. The quantity $D/2h$ is calculated to be 0.15 MHz; combining this with the observed $\delta\nu=1.75\pm0.05$ MHz we find

$$e^2qQ/h=11.7\pm0.3 \text{ MHz}, \quad \text{observed} \tag{12}$$

[13] The notation is that of Ref. 4. Here, for simplicity, the hyperfine constant A is taken to be isotropic. (It is really the transverse component of A that enters into the SN interaction.) The quantity γ_λ is defined by

$$\gamma_\lambda=\sum_\rho \exp(i\lambda\rho)$$

with ρ a lattice vector connecting the spin in question with its nearest neighbor on the opposite sublattice; $\Delta^2=K/\gamma_0 J$, where K is the anisotropy energy constant.

while a simple point change calculation using an antishielding factor $(1-\gamma_\infty)\simeq 9$ and $Q=0.5\times 10^{-24}$ cm^2 yields

$$e^2qQ/h=11 \text{ MHz}, \quad \text{calculated}. \tag{13}$$

Although the agreement must surely be considered fortuitous it is nevertheless assuring to know that an interaction of this magnitude is expected and was found, contrary to the results of the earlier investigation.[2] (Note that the observation of constant second differences does not necessarily imply that $\eta\ll 1$ but only that $|P|\ll|M(0,T)|$; even if $\eta\simeq 1$ the term in η^2P^2 is much less than the experimental uncertainty in the measurement of $\delta\nu$.)

C. "Determination" of $\langle S_z\rangle_0$

By extrapolation of the resonance frequency of the transition $(m=+\frac{1}{2}\leftrightarrow m'=-\frac{1}{2})$ to 0°K we obtain, using Eq. (10),

$$\nu_{\frac{1}{2}\leftrightarrow-\frac{1}{2}}{}^0(0)=\left\{\frac{A_z{}^{55}}{h}+\frac{\gamma^{55}}{2\pi}\sum_{i=j}^{N}\mathfrak{D}_z{}^i\right\}\langle S_z\rangle_0. \tag{14}$$

Now $\sum_i{}^N\mathfrak{D}_z{}^i=2308$ Oe[10] so that $(\gamma^{55}/2\pi)\sum_i{}^N\mathfrak{D}_z{}^i$, $=2.423$ MHz. Until recently it has been common to obtain the desired value of A from EPR hyperfine studies of the single paramagnetic ion (Mn^{2+} in our instance) in diamagnetic but otherwise isomorphic environment. For example, diamagnetic ZnF_2 and MnF_2 have identical structures with nearly identical lattice parameters. When Mn^{2+} is studied as a dilute impurity in ZnF_2 it is found that $A_z{}^{55}=-272.15\pm 0.90$ MHz. If we combine these values with the observed $\nu^0{}_{\frac{1}{2}\leftrightarrow-\frac{1}{2}}(0)=670.38\pm 0.05$ MHz we find from Eq. (14) that $\langle S_z\rangle_0=2.485$ and $\langle S_z\rangle_0/\langle S\rangle=(99.41\pm 0.03)\%$.

However, it is generally agreed[14,15] that there are additional contributions to $A_z{}^{55}$ in MnF_2—that do not appear in $Mn{:}ZnF_2$—which result from cation-cation interactions in the magnetically dense crystals. These interactions are manifestations of electron transfer and orthogonality effects that are propagated through the strong overlap of cation and ligand wave functions. No detailed calculations have been attempted for MnF_2 but the sign and magnitude of the change in $A_z{}^{55}$ that is expected is such as is necessary to bring it into agreement with the theoretical values[16] for the zero point spin deviation; $\langle S_z\rangle_0/S=97.6\%$. Suffice it to say that the present experiment does *not* by itself give a value for $\langle S_z\rangle_0$.

D. Broadening of Quadrupolar Split Lines

The indirect nuclear spin-spin interaction is a primary source of line broadening in both ferromagnetic and antiferromagnetic crystals. Recently, Sherrington[17] has extended the original SN theory[3,4] to quadrupolar split lines such as is the case for the Co^{59} NMR in CoF_2 and the Mn^{55} NMR in MnF_2. His results were obtained using the Kubo-Tomita[18] correlation function method. Identical conclusions are reached using the moment expansion method of Pryce and Stevens.[19] We outline the latter calculation below. The SN interaction is a two-body interaction and it is sufficient to consider the unperturbed Hamiltonian as

$$\mathfrak{IC}_0=M(0,T)[I_{zi}+I_{zj}]+[2P+\tfrac{1}{2}D][I_{zi}{}^2+I_{zj}{}^2] \tag{15}$$

and the effective perturbing Hamiltonian as

$$\mathfrak{IC}_p=-\tfrac{1}{2}\sum_{i>j}B_{ij}(I_i{}^+I_j{}^-+I_i{}^-I_j{}^+). \tag{16}$$

It is assumed that the coupling constant $|3P+\frac{1}{2}D|\gg|B_{ij}|$ for all nuclear spin pairs I_i and I_j; hence there are $2I$ distinct transitions for which $\Delta m=\pm 1$. Defining the particular state vectors α and β for the individual spins by the relations $I_z|\alpha\rangle=m|\alpha\rangle$ and $I_z|\beta\rangle=m+1|\beta\rangle$ the second moment of the line associated with the transition from m to $m+1$ is

$$\begin{aligned}\hbar^2\langle\Delta\omega^2\rangle_{m\to m+1}=&\frac{1}{(2I+1)N}\sum_i\sum_{i>j}[(\langle\alpha_i\alpha_j|\mathfrak{IC}_p|\alpha_i\alpha_j\rangle\\&-\langle\beta_i\alpha_j|\mathfrak{IC}_p|\beta_i\alpha_j\rangle-\langle\beta_i\alpha_j|\mathfrak{IC}_p|\alpha_i\beta_j\rangle)^2+(\langle\alpha_i\beta_j|\mathfrak{IC}_p|\alpha_i\beta_j\rangle\\&-\langle\beta_i\beta_j|\mathfrak{IC}_p|\beta_i\beta_j\rangle+\langle\beta_i\alpha_j|\mathfrak{IC}_p|\alpha_i\beta_j\rangle)^2\\&+\sum_{s\neq\beta,\alpha}^{(2I+1)}\{(\langle\alpha_is_j|\mathfrak{IC}_p|\alpha_is_j\rangle-\langle\beta_is_j|\mathfrak{IC}_p|\beta_is_j\rangle)^2\\&+(\langle\alpha_is_j|\mathfrak{IC}_p|s_i\alpha_j\rangle-\langle\beta_is_j|\mathfrak{IC}_p|s_i\beta_j\rangle)^2\}].\end{aligned} \tag{17}$$

Inserting $\mathfrak{IC}_p$ from Eq. (16) only a limited number of matrix elements survive, namely those which conserve the *total* energy of the system; thus

$$\begin{aligned}\hbar^2\langle\Delta\omega^2\rangle_{m\to m+1}=&\frac{1}{(2I+1)N}\\&\times\sum_i\sum_{i>j}[2(\langle\alpha_i\beta_j|(-\tfrac{1}{2}B_{ij})I_i{}^+I_j{}^-|\beta_i\alpha_j\rangle)^2\\&+(\langle\alpha_i(\alpha-1)_j|(-\tfrac{1}{2}B_{ij})I_i{}^+I_j{}^-|(\alpha-1)_i\alpha_j\rangle)^2\\&+(\langle\beta_i(\beta+1)_j|(-\tfrac{1}{2}B_{ij})I_i{}^-I_j{}^+|(\beta+1)_i\beta_j\rangle)^2].\end{aligned} \tag{18}$$

In any macroscopic size sample the rapid decrease of B_{ij} with increasing $\mathbf{r}_i-\mathbf{r}_j$ ensures the absolute con-

[14] J. Owen and D. R. Taylor, Phys. Rev. Letters **16**, 1164 (1966).
[15] Nai Li Huang, R. Orbach, and E. Simanek, Phys. Rev. Letters **17**, 134 (1966).
[16] L. R. Walker (private communication).
[17] D. Sherrington, J. Appl. Phys. **39**, 502 (1968). Dr. Sherrington first called to the authors' attention the incorrect expression for $\hbar^2\langle\Delta\omega^2\rangle_{m\to m+1}$ that is quoted in Ref. 1. He has also very kindly communicated his correct expression to us prior to publication. Unfortunately, through a typographical error, the $I_z=m$ dependence is not correct in his Eq. (8), but is given correctly in our Eq. (19). [See also D. Sherrington, J. Phys. C (Proc. Phys. Soc.) **1**, 748 (1968).]
[18] R. Kubo and K. Tomita, J. Phys. Soc. (Japan) **9**, 888 (1954).
[19] M. H. L. Pryce and K. W. H. Stevens, Proc. Phys. Soc. (London) **A63**, 36 (1951).

vergence of the double summation, hence we may neglect any surface effects and replace

$$\sum_{\substack{i\\ i>j}}\sum_{j}=\tfrac{1}{2}\sum_{\substack{i\\ i\neq j}}\sum_{j}$$

by the single sum $\frac{1}{2}N\sum_j$. Then using the well-known values of the matrix elements of the operator I^+ and I^- we find

$$\hbar^2\langle\Delta\omega^2\rangle_{m\to m+1}=[8(2I+1)]^{-1}\sum_j B_{ij}^2$$
$$\times\{2(I-m)^2(I+m+1)^2+(I+m)^2(I-m+1)^2$$
$$+(I-m-1)^2(I+m+2)^2\}. \quad (19)$$

Note that the second moment of the transitions $\{-(m+1)\to -m\}$ and $(m\to m+1)$ are identical. For $I=\frac{5}{2}$ we may summarize the values of the second moments as follows: Using the notation

$$M_2(m\to m+1)\equiv\hbar^2\langle\Delta\omega^2\rangle_{m\to m+1},$$
$$M_2(\tfrac{1}{2}\to -\tfrac{1}{2})=\frac{145}{24}\sum_j B_{ij}^2;$$
$$M_2\begin{pmatrix}\frac{1}{2}\to & \frac{3}{2}\\ -\frac{3}{2}\to & -\frac{1}{2}\end{pmatrix}=\frac{117}{24}\sum_j B_{ij}^2; \quad (20)$$
$$M_2\begin{pmatrix}\frac{3}{2}\to & \frac{5}{2}\\ -\frac{5}{2}\to & -\frac{3}{2}\end{pmatrix}=\frac{57}{24}\sum_j B_{ij}^2.$$

These are to be compared with the value of M_2 for the unsplit line,

$$M_2(\text{unsplit})=\tfrac{1}{3}I(I+1)\sum_j B_{ij}^2=\frac{70}{24}\sum_j B_{ij}^2. \quad (21)$$

The quantity $\sum_j B_{ij}^2$, defined in Eq. (7), is obtained using the following values for the relevant parameters: A—The transverse component of the Mn^{55} hyperfine interaction has been measured[20] in the $ZnF_2:Mn^{2+}$ EPR experiments, $A_\perp=-98.8\pm0.5\,eG=1.83\times10^{-18}$ erg. $2\gamma_0 J$—Since the exchange interaction between the two nearest neighbors (nn) on the same sublattice is much smaller in magnitude than is the one between the eight *nnn* on the opposite sublattice we neglect the former and use the accurate measurements of $\chi_\perp$[21] to obtain $J_{nnn}=1.76°K=2.43\times10^{-16}$ ergs and therefore $2\gamma_0 J=3.89\times10^{-15}$ ergs. KS—The anisotropy energy KS may then be accurately determined from the electron antiferromagnetic resonance frequency[22]; $KS=1.06°K=1.46\times10^{-16}$ ergs. The quantity $\Delta=(KS/\gamma_0 JS)^{1/2}=0.1735$ which determines the range of the SN interaction and is used to compute $\sum_j[f(r_{ij})]^2=1.06$.[23] Finally we obtain $\sum_j B_{ij}^2=0.790\times10^{-42}$ erg^2. The observed and calculated linewidths are given in Table II. The values quoted are for the separation between maximum and minimum slope. For a Gaussian-shaped curve this is $2\times(M_2)^{1/2}$. It is difficult to estimate the combined errors in the calculated quantities used above but we feel the theoretical widths are probably accurate to better than 10%.

The predicted trend of linewidth increasing as one goes toward the central $(\frac{1}{2}\leftrightarrow-\frac{1}{2})$ transition is confirmed but the errors are such as to preclude a more quantitative comparison. In general, there may be some modulation broadening contribution to the linewidths as well as strain-induced quadrupolar broadening. Both of these effects would be most severe for the outer transitions and may explain the fact that these transitions are not proportionately as narrow as expected. The general agreement in magnitude is most satisfying and probably represents the only example to date where the SN theory and experiment have been put to a quantitative test.

ACKNOWLEDGMENTS

We are indebted to Professor D. Hone, Professor P. Pincus, and Dr. L. R. Walker for numerous discussions pertaining to this work and related studies on the SN interaction. We wish to express our appreciation to Dr. D. Sherrington for having presented us with his results on the SN broadening of the quadrupolar split lines prior to their publication.

[20] A. M. Clogston, J. P. Gordon, V. Jaccarino, M. Peter, and L. R. Walker, Phys. Rev. **117**, 1222 (1960).

[21] C. Trapp and J. W. Stout, Phys. Rev. Letters **10**, 157 (1963).

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

[23] We have used Table I in Ref. 4 to extrapolate a new value for $\sum_j[f(r_{ij})]^2$ using the more accurate value of Δ. However, the large difference between our value of 1.06 and Nakamura's value of 2.65 arises almost entirely from the fact that the latter author failed to subtract the self-energy term in his spin-wave sum. This makes his Mn^{55} M_2 estimate too large by approximately 2.5. The details of this are discussed by D. Hone, V. Jaccarino, Tin Ngwe, and P. Pincus (unpublished).