[9.9] of less than one part in 10^4 at $K=1$ and less than half a percent for $K=2$ at which point the value is 95% of the asymptotic value. Loss of calculational accuracy in the 20th coefficient prevents us from using the [10,10] where only about three places remain in the solution. When the standard Padé (one-point) approximant method is used, we may estimate E for $K=\infty$ to about 10% by averaging the twenty percent amplitude oscillation at $K=\infty$. The oscillation occurs because $K=\infty$ is an essential singularity. For $K<\infty$ agreement is rapidly obtained with the two-point method. It should be noted that the signs of the energy series are periodic with period 7, a rather long period. Consequently, a fairly large number of terms are required to obtain accurate results. The radius of convergence of the power series is about 0.5, the nearest singularities being located at about $-0.11\pm0.47i$, the same place as for the reduced susceptibility. Unfortunately, the antiferromagnetic case is quite similar to the function $c(x)$ discussed in Sec. 2. There is again a cut which crosses the negative real axis in the neighborhood of

-2. We do, however, obtain the value at $K=-1$ to better than 3% accuracy and it is again about 95% of the asymptotic value for $K=-\infty$. In Fig. 4 we have plotted our results for the energy as a function of K.

We have compared our results with those obtained by Katsura and Inawashiro[13] on the basis of an expansion through second order in J_{11} with $J_\perp$ summed to all orders. The agreement for the antiferromagnetic energy is good. There is a deviation reaching about 6% in the range $K=0.2$ to 0.5. For the ferromagnetic energy the agreement is good for $K=0$ to 0.3 but starting around $K=0.3$ there is a large kink in their results which causes them to be off by about 20% near $K=1$ although their error drops to only 3% at $K=\infty$. Their ferromagnetic susceptibility agrees nicely with ours for $K=0$ to about 0.5 where theirs falls below ours due to the finiteness implicit in their approximation. In Fig. 5 we have plotted the specific heat at zero magnetic field as far as we believed our results to be reliable.

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[13] S. Katsura and S. Inawashiro (private communication).

Zero-Field Manganese Nuclear Magnetic Resonance in Antiferromagnetic Manganese Fluoride

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The zero-field NMR of Mn^{55} has been observed directly in the antiferromagnetic state of MnF_2. A single resonance, with linewidth $\Delta\nu^{55}\simeq1.3$ Mc/sec, was observed in the frequency range of 650–675 Mc/sec and the temperature range of 1.3–20.5°K. The extrapolated Mn^{55} NMR frequency at 0°K is found to be ν_0^{55} $=671.4\pm0.2$ Mc/sec. Combining the 0°K Mn^{55} NMR frequency together with the dipolar field H_{dip} $=+5.770$ kOe and the hyperfine coupling constant $A^{55}=-(90.78\pm0.3)\times10^{-4}$ cm^{-1}, measured for Mn^{2+} in ZnF_2, gives a value for the zero-point spin deviation of $1-\langle S\rangle/S=(0.43\pm0.34)\%$. This value is to be compared with the value predicted by spin-wave theory of 2.37%. The observed temperature dependence of the Mn^{55} NMR frequency agrees, within experimental error, with the temperature dependence of the F^{19} zero-field NMR in antiferromagnetic MnF_2. Upper and lower limits of 1300 kc/sec and 600 kc/sec are placed on the contribution to the Mn^{55} NMR linewidth in antiferromagnetic MnF_2 by the Suhl-Nakamura interaction.

I. INTRODUCTION

NUCLEAR magnetic resonance (NMR) techniques in antiferromagnetic media provide a convenient method for obtaining information about the thermodynamic properties of these ordered spin systems. In particular, information concerning the zero-point spin-deviation, temperature dependence of the sublattice magnetization, and indirect nuclear spin interactions are readily obtained from NMR measurements.[1] MnF_2 is a particularly well-suited crystal for

studying the properties of antiferromagnetic spin systems since the Mn^{2+} ion is an S-state ion ($S=5/2$) and therefore the anisotropy field results mainly from the dipolar interaction. MnF_2 has the rutile structure with tetragonal symmetry and in the antiferromagnetic state the Mn^{2+} ions are ordered such as to consist of two interpenetrating sublattices with oppositely ordered spins.

An estimate of the zero-point spin deviation $\langle S\rangle/S$ for MnF_2 has been given by Clogston et al.[2] by making a comparison of the electron paramagnetic resonance (EPR) measurements of Mn^{2+} in ZnF_2 with the specific

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[1] For a review of NMR in antiferromagnetic media the reader is referred to the article by V. Jaccarino, in *Magnetism*, edited by H. Suhl and G. Rado (Academic Press Inc., New York, 1964).

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

heat data of Cooke and Edmonds.[3] The estimate of the zero point spin deviation given in Ref. 2 is $\langle S \rangle / S = (101 \pm 2)\%$ which is to be compared with the value predicted by spin-wave theory[4] of $\langle S \rangle / S = 97.63\%$. Lines,[5] also using spin-wave theory, but including anisotropy and next-nearest neighbor ferromagnetic interactions, calculates a value of $\langle S \rangle / S = 97.95\%$, while Walker,[6] using a perturbation theory technique, calculates $\langle S \rangle / S = 98.2\%$.

The temperature dependence of the sublattice magnetization, for antiferromagnetic MnF_2, has been measured by Jaccarino and Walker[7] using the F^{19} zero-field NMR. Heller and Benedek[8] have extended the F^{19} NMR measurements up to the Néel temperature of about $67°K$. Recently, Low[9] has been able to fit the F^{19} NMR data up to a temperature of about $\frac{3}{4} T_N$ using an interacting spin-wave model.

We wish to report in this paper, the results of the direct observation of the zero-field Mn^{55} NMR in the antiferromagnetic state of MnF_2. The zero-point spin deviation $\langle S \rangle / S$ is determined to higher accuracy than the estimate given in Ref. 2. Furthermore, it is found that within experimental error, the observed temperature dependence of the Mn^{55} NMR agrees with the temperature dependence of the F^{19} NMR reported by Jaccarino and Walker.[7] This result strengthens the validity of the measurement of the temperature dependence of the sublattice magnetization by NMR on the site of a nonmagnetic ion, such as F^{19} in MnF_2. The observed linewidth of the Mn^{55} NMR cannot be compared directly with the theoretical predictions of Suhl[10] and Nakamura[11] because of the experimental method which consisted of the use of super-regenerative oscillators for the detection of the Mn^{55} NMR. However, upper and lower limits can be placed on the Suhl-Nakamura interaction upon considering the effects of electric quadrupolar interactions on the Mn^{55} NMR spectrum.

II. EXPERIMENTAL

The zero-field Mn^{55} NMR was observed in a single crystal of MnF_2 in the frequency range of 650–675 Mc/sec and the temperature range of 1.3 to 20.5°K. The Mn^{55} NMR was also observed in polycrystalline samples of MnF_2 with a corresponding reduction of the signal-to-noise ratio of the resonance. The NMR spectrometer used to observe the Mn^{55} NMR was a loaded

half-wave line oscillator adjusted to oscillate in the self-quenching superregenerative mode. Attempts to observe the Mn^{55} NMR in MnF_2 with the NMR spectrometer oscillating in the cw mode have thus far proven unsuccessful. Detection of the Mn^{55} NMR signal was achieved by using frequency modulation and lock-in techniques. Because the length of a loaded half-wave line at 650 Mc/sec is of the order of inches, the line was placed outside the Dewar tip which contained the sample. In order to increase the filling factor, the Dewar did not have a nitrogen jacket around the tip.

The quench rate of the super-regenerative oscillator was adjustable with the maximum quench rate used being about 1.6 Mc/sec. The maximum frequency modulation amplitude was approximately 2 Mc/sec. As is the case with super-regenerative oscillators, a source of error can be the determination of the carrier frequency. We measured the frequency of the super-regenerative oscillator in the following manner: The frequency spectrum of the super-regenerative oscillator was displayed on an oscilloscope by using a panoramic spectrum analyzer. The quench rate was then modulated at 20 kc/sec with the result being that only the carrier frequency was unaffected by the modulation. The carrier frequency was then measured by zero beating a local oscillator with the NMR spectrometer and measuring the frequency of the local oscillator with a frequency counter. The frequency of the Mn^{55} NMR was determined from the symmetry of the resonance pattern which was displayed on a recorder. First harmonic detection was used whenever possible with second harmonic detection supplementing the measurements.

III. NMR OF Mn^{55} IN ANTIFERROMAGNETIC MnF_2

The zero-field time-independent Hamiltonian for a given Mn^{55} nucleus in antiferromagnetic MnF_2 can be written[12] as

$$\mathcal{H} = A_z{}^{55}\langle S_z \rangle I_z + \gamma^{55} \hbar I_z \sum_i^N D_z{}^i \langle S_z{}^i \rangle + \sum_m Q_2{}^m (\nabla E)_2{}^{-m}, \quad (1)$$

where $\langle S_z \rangle$ is the time average spin polarization per Mn^{2+} ion, A^{55} the magnetic hyperfine interaction constant, I the nuclear spin, and γ^{55} the Mn^{55} nuclear gyromagnetic ratio. The second term in Eq. (1) is the magnetic interaction between the Mn^{55} nuclear moment with the dipolar field due to the neighboring electronic spins, $H_{dip} = \sum_i D_z{}^i \langle S_z{}^i \rangle$, where i is summed over all lattice points. The components of the D tensor have been calculated elsewhere[13] with the result $H_{dip} = +5.770$ kOe for $\langle S \rangle = 5/2$. The third term in Eq. (1) represents the electric quadrupole interaction of the

[3] A. H. Cooke and D. T. Edmonds, Proc. Phys. Soc. (London) **17**, 517 (1958).
[4] R. Kubo, Phys. Rev. **87**, 568 (1952); H. L. Davis, Phys. Chem. Solids **23**, 1349 (1962).
[5] M. E. Lines (private communication).
[6] L. R. Walker (to be published).
[7] V. Jaccarino and L. R. Walker, J. Phys. Radium **20**, 341 (1959).
[8] P. Heller and G. Benedek, Phys. Rev. Letters **8**, 428 (1962).
[9] G. G. Low, Proc. Phys. Soc. (London) **82**, 992 (1963).
[10] H. Suhl, Phys. Rev. **109**, 606 (1958); J. Phys. Radium **20**, 333 (1959).
[11] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **20**, 333 (1959).

[12] T. Moriya, Progr. Theoret. Phys. (Kyoto) **16**, 641 (1956).
[13] V. Jaccarino and L. R. Walker (to be published).

Mn^{55} nucleus with field gradients which exist since the manganese atom sits at a site of less than cubic symmetry.

An estimate of the relative strength of the Mn^{55} quadrupolar interaction compared to the hyperfine interaction can be made by considering the results obtained by Jaccarino on CoF_2.[14] Jaccarino[14] observed the Co^{59} zero-field NMR in antiferromagnetic CoF_2 which is isomorphic with MnF_2. The Co^{59} zero-field NMR spectrum consisted of seven lines separated by about 5 Mc/sec. The ground state of the Co^{2+} free ion is $(3d^7)$ ^4F and it is this electronic configuration which gives the main contribution to the electric field gradient at the cobalt site. Since Mn^{2+} in MnF_2 is an S-state ion, the d-electron contribution to the quadrupolar interaction present for the Co^{2+} ion in CoF_2 will be absent for Mn^{2+}. Thus it is concluded that the quadrupolar interaction energy given in Eq. (1) is small compared to the hyperfine interaction energy. Therefore, the second-order quadrupolar shift to the Mn^{55} NMR frequency is considered negligible.

The value of the hyperfine coupling constant A^{55} has been determined[2] by EPR measurements for Mn^{2+} in ZnF_2 to be $A^{55} = -(90.78 \pm 0.3) \times 10^{-4}$ cm^{-1}. Volume effect corrections to the hyperfine coupling constant are not considered to be important since the hyperfine coupling constant for Mn^{2+} in the same chemical ligand coordination is essentially independent of the dimensions of the host lattice.[15] For example, the variation of the hyperfine coupling constant for Mn^{2+} in MgO and CaO is of the order 0.5% for a lattice parameter variation of 11%. Furthermore, the various transferred hyperfine coupling constants for the F^{19} nucleus in Mn^{2+}:ZnF_2 agree,[2] within experimental error, with the values obtained from the F^{19} NMR in MnF_2.[16] This result tends to support the belief that the local environment of a Mn^{2+} ion in ZnF_2 more closely resembles that of MnF_2 rather than that of the ZnF_2 host lattice since the hyperfine field at the fluorine site should be strongly dependent upon dimensional changes. Therefore, it is felt that any variation of the hyperfine coupling constant A^{55} in going from the dilute to the concentrated crystal will be less than the experimental error given for A^{55}. Hence, the value of the hyperfine coupling constant A^{55} for Mn^{2+} is taken to be the value as determined by EPR for Mn^{2+} in ZnF_2.

IV. ZERO-POINT SPIN DEVIATION

Table I lists the measured Mn^{55} NMR frequency for several temperatures in antiferromagnetic MnF_2. The extrapolated Mn^{55} NMR frequency at 0°K is $\nu^{55}(0)$ = 671.4 ± 0.2 Mc/sec. An expression for the Mn^{55} NMR frequency ν^{55} is easily derived from the Hamil-

tonian given in Eq. (1) with the result

$$\nu^{55}(T) = \{ (\tfrac{5}{2})c \,|\, A^{55}| - (\gamma^{55}/2\pi)H_{\mathrm{dip}} \}\langle S\rangle/S, \qquad (2)$$

where c is the velocity of light, A^{55} is expressed in units of cm^{-1} and for the fully aligned state, $\langle S\rangle = S = \tfrac{5}{2}$. The temperature dependence of the Mn^{55} NMR frequency ν^{55} is contained in $\langle S\rangle$. The temperature dependence[17] of the hyperfine coupling constant A^{55} is negligible for the temperature range given in Table I.

Using the previously defined parameters and the 0°K Mn^{55} NMR frequency, Eq. (2) gives for the zero-point spin deviation

$$\langle S\rangle/S = (99.57 \pm 0.34)\%, \qquad (3)$$

or rewriting Eq. (3)

$$1 - \langle S\rangle/S = (0.43 \pm 0.34)\%. \qquad (4)$$

As can be seen from Eq. (3), the estimate of $\langle S\rangle/S$ = $(101 \pm 2)\%$ given in Ref. 2 is in agreement with our results obtained from the Mn^{55} zero-field NMR. Equation (3) also shows that the measured zero-point spin deviation, including experimental error is in disagreement with the theoretical predictions previously mentioned. The preceding analysis which led to the Mn^{55} NMR frequency given by Eq. (2), does not include any hyperfine interactions between a manganese nucleus and a neighboring electronic spin other than the dipolar interaction. At the present time there is no experimental evidence that any new hyperfine interactions should be included in Eq. (1). At this point it must be stressed that the results given in Eqs. (3) and (4) are based on the assumption that A^{55} in MnF_2 equals A^{55} in Mn^{2+}: ZnF_2. The analysis which led to this assumption has been discussed in Sec. III.

There is further evidence that theoretical predictions for other antiferromagnetic spin systems underestimate the zero-point spin deviation $\langle S\rangle/S$. Montgomery, Teaney, and Walsh[18] have reported a value for the zero-point spin deviation for antiferromagnetic $KMnF_3$ by combining the specific heat data for $KMnF_3$ together with the EPR measurement of A^{55} for Mn^{2+} in $KMgF_3$. Montgomery, Teaney and Walsh[18] give $\langle S\rangle/S$ = $(99.8 \pm 1.5)\%$, a value which is to be compared with the previously mentioned theoretical predictions. It is interesting to note that both the $KMnF_3$ experiment and our MnF_2 experiment suggest that the ground state for these antiferromagnetic spin systems is very close to the Néel state.

V. TEMPERATURE DEPENDENCE OF THE Mn⁵⁵ ZERO-FIELD NMR

Table I gives a comparison of the Mn^{55} NMR temperature dependence with the F^{19} NMR temperature dependence as measured by Jaccarino and

[14] V. Jaccarino, Phys. Rev. Letters **2**, 163 (1959).
[15] S. Geschwind (to be published).
[16] R. G. Shulman and V. Jaccarino, Phys. Rev. **103**, 1126 (1956); **108**, 1219 (1957).

[17] W. M. Walsh, Jr. (private communication).
[18] H. Montgomery, D. T. Teaney, and W. M. Walsh, Jr., Phys. Rev. **128**, 80 (1962).

TABLE I. Zero-field Mn^{55} NMR frequencies in the antiferro-magnetic state for various temperatures are given in the first column. The second and third columns give the fractional frequency shifts of the Mn^{55} and F^{19} zero-field NMR with respect to the 0°K frequencies ν_0^{55} and ν_0^{19}.[a]

T(°K)	ν^{55}(Mc/sec)	$(\nu_0^{55}-\nu_T^{55})/\nu_0^{55}$	$(\nu_0^{19}-\nu_T^{19})/\nu_0^{19}$
1.3	671.4±0.2	0	...
3.25	...	...	0.002%
4.2	671.4±0.2	0	...
13.81	...	...	0.697%
13.9	668.8±0.3	(0.69±0.07)%	...
14.00	...	...	0.75%
20.2	...	...	2.363%
20.5	654.2±0.3	(2.56±0.07)%	...
20.82	...	...	2.59%
21.00	...	...	2.66%

[a] $\nu_0^{55} = 671.4 \pm 0.2$ Mc/sec; $\nu_0^{19} = 159.9784$ Mc/sec.

Walker.[7,13] A source of error in the Mn^{55} NMR data is the uncertainty in the temperature of the sample. This uncertainty results from not having a nitrogen jacket around the Dewar tip and thus providing a mechanism for heating the sample by radiation. At liquid-helium temperatures the variation of frequency with temperature is small and hence a temperature error is not a serious effect. However, at liquid-hydrogen temperatures the variation of the NMR frequency with temperature is starting to become important as evidenced by the F^{19} NMR data given in Table I. The temperature of the sample in this temperature region was determined by a carbon resistor.

As can be seen from Table I, the temperature dependence of the Mn^{55} NMR frequency agrees, within experimental error, with the F^{19} NMR data. Therefore it is concluded that the temperature dependence of the sublattice magnetization $(M \sim \langle S \rangle)$ as measured by Jaccarino and Walker[7,13] using the F^{19} NMR is a valid technique.

VI. Mn^{55} NMR LINEWIDTH IN ANTIFERRO-MAGNETIC MnF_2

An accurate determination of the Mn^{55} NMR line-width or lineshape cannot be made at the present time because of the use of a super-regenerative NMR spectrometer. An estimate of the Mn^{55} NMR linewidth can be made by noting that the sideband responses of the super-regenerative spectrum will be just resolved when the quench rate is of the order of the NMR line-width. The quench rate was adjusted to fulfill the afore-mentioned requirements with the result that the Mn^{55} NMR linewidth in antiferromagnetic MnF_2 is estimated to be of the order of 1.3 Mc/sec. This value for the linewidth was determined to be independent of temperature in the range of 1.5–20°K.

The theory of the indirect nuclear spin-spin interaction contribution to the Mn^{55} NMR linewidth in antiferromagnetic MnF_2 has been treated in the literature by Suhl[10] and Nakamura.[11] Nakamura estimates that $\delta\nu^{55} \simeq 700$ kc/sec. Neither Suhl nor Nakamura consider the possibility of broadening due to the splitting of the NMR line by electric quadrupole interactions. The electric quadrupole interaction for Mn^{55} in MnF_2 has been calculated by us using a point charge model together with an antishielding factor $(1-\gamma_\infty) \simeq 9$. The calculated quadrupolar interaction constant $e^2qQ/h \simeq 9$ Mc/sec and leads to a frequency splitting of 2.7 Mc/sec between the two outermost transitions. Since only a single resonance was observed, it is concluded that the quadrupolar interaction has been overestimated. The possibility that we are observing only the $\frac{1}{2} \to \frac{1}{2}$ transition is ruled out by Jaccarino's[14] results on CoF_2, where all of the cobalt quadrupolar transitions were observed and the effects of strains should be more pronounced than for MnF_2.

Upper and lower limits to the Suhl-Nakamura interaction can be estimated in the following manner. There are two extreme cases to consider: (1) The quadrupolar broadening is negligible and the entire linewidth is due to the Suhl-Nakamura interaction and (2) The splitting between the two outermost quadrupole transitions is of the order of the observed linewidth with the Suhl-Nakamura interaction broadening each transition to the extent that the NMR spectrum appears as a single line. The first case gives that the upper limit to the Suhl-Nakamura interaction for Mn^{2+} in MnF_2 is 1.3 Mc/sec and the second case gives that the lower limit is of the order of 600 kc/sec. Thus, it is estimated that the linewidth of the Suhl-Nakamura interaction lies between 600–1300 kc/sec.