Nuclear Magnetic Resonance Modes in Magnetic Materials. II. Experiment*

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As shown theoretically in a previous paper, the indirect coupling of nuclei through spin waves in ordered magnetic materials can give rise to a mixing of the nuclear-electronic resonance modes. The results of an experimental investigation of this effect in antiferromagnetic $KMnF_3$ are described. The mixing of modes permits Mn^{55} nuclear magnetic resonance absorption to be detected indirectly by monitoring the antiferromagnetic resonance. Such nuclear absorption has been observed for a range of frequencies between 570 and 685 Mc/sec at 4.2°K.

1. INTRODUCTION

During the course of experiments on antiferromagnetic $KMnF_3$,[1,2] an unexpected shift of the field for antifierromagnetic resonance (AFR) to lower values of field was noticed for decreasing temperatures in the liquid-helium range. This was the first indication of the strong interaction between the electronic and nuclear magnetizations in this material.[3–6] This interaction may be represented by

$$\mathcal{H}=\alpha\mathbf{M}\cdot\mathbf{m}, \tag{1}$$

where α is the hyperfine coupling constant, m and M are the nuclear and electronic magnetizations, respectively. Because of this coupling the AFR mode is sensitive to the nuclear polarization, particularly at low temperatures.

This enabled the Mn^{55} nuclear magnetic resonance (NMR) absorption to be observed indirectly by monitoring the AFR field while supplying energy at the appropriate nuclear frequencies. An interesting feature of these results is the marked depression of the NMR frequency from the value $\gamma\alpha M$, where γ is the nuclear gyromagnetic ratio.

This behavior is explained in a previous paper by the theory of de Gennes *et al.*,[7] who have examined the nuclear and electronic resonance modes in a magnetic material in the presence of strong coupling. The shift of the NMR frequency arises from the coupling of nuclear spins via the Suhl-Nakamura indirect interaction.[8]

Also implied by the measurements is a smaller zero-point reduction of the electronic spins than expected from the spin-wave theory.

2. THEORY

The crystal structure of $KMnF_3$ is the cubic perovskite type. Experiments of various kinds on this material have been reported including crystallographic[9] and neutron diffraction studies,[10] magnetic susceptibility and torsion measurements,[11] low-temperature specific heat,[12] and F^{19} NMR in both the paramagnetic[13] and antiferromagnetic[14] regions. Currently underway are experiments involving the direct observation of Mn^{55} NMR in the antiferromagnetic state.[15] The crystal orders antiferromagnetically at 88.3°K and undergoes a second transition at 81.5°K to a state in which a distortion of the fluorine octahedron surrounding each manganese ion causes a slight canting of the sublattice magnetization vectors. For an external magnetic field along the $\langle 001\rangle$ direction, the magnetic vectors lie along the $\langle 110\rangle$ and $\langle \bar{1}\bar{1}0\rangle$ directions, canted slightly towards the applied field.[11] The two AFR modes for this case are given by

$$(\Omega_1/\Gamma)^2=2\lambda M\alpha m+2\lambda(K_1-K_4)+(H_0+K_2/M)(H_0+4K_2/M), \tag{2}$$

and

$$(\Omega_2/\Gamma)^2=2\lambda M\alpha m+4\lambda K_4+(H_0+K_2/M)K_2/M. \tag{3}$$

Here M and m are the electronic and nuclear magnetizations, λ is the exchange coupling constant, and Γ is the electronic gyromagnetic ratio. The terms K_1, K_2, and K_4 represent the axial, orthorhombic, and cubic

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anisotropy constants, respectively. The term K_2 is responsible for the canting in this material.[16] The exchange field is λM while αm is the effective field seen by the electrons due to the nuclei. Note that the effect of this latter field is identical to that of an anisotropy field—it enters the resonance expression multiplied by twice the exchange field.

In the mode Ω_1, the weak moment essentially rocks back and forth in the canting plane while the weak moment in Ω_2 oscillates along the applied field. Thus, Ω_1 is excited by a field perpendicular to H_0 while Ω_2 is excited by a field parallel to this direction.

From the theoretical work of de Gennes and his co-workers,[7] the associated NMR modes are

$$\omega_1^2=\omega_0^2[1-\Omega_0^2/\Omega_1^2], \tag{4}$$

and

$$\omega_2^2=\omega_0^2[1-\Omega_0^2/\Omega_2^2]. \tag{5}$$

The term $\omega_0=\gamma\alpha M$ is the NMR frequency as given by Eq. (1) for the case of no mixing of the nuclear and electronic resonance modes. In the additional term, $\Omega_0^2/\Gamma^2=2\lambda M\alpha m$ and is the square of the AFR frequency in the presence of the hyperfine anisotropy field alone. It can be seen that the two electronic modes, Ω_1 and Ω_2, result in a splitting of the nuclear modes.

The above expressions show that sizeable nuclear "frequency pulling" requires low AFR frequencies (hence, small anisotropy fields), strong exchange fields, and large nuclear magnetizations.

3. EXPERIMENTAL RESULTS

For the nuclear magnetic double resonance studies, a rectangular reflection cavity resonating in the TE_{101} mode at 9.5 kMc/sec was used. A one loop coil of approximately 1.5 mm diam was introduced through a small hole in the cavity wall and fixed around the sample. Several different samples were used, all from the same batch,[17] roughly cubic in shape and about 1 mm on a side. To the coil was connected an rf oscillator capable of supplying 5 or more watts of power in the frequency range of 500–700 Mc/sec. This configuration resulted in the applied magnetic field, the microwave field and the rf field being mutually perpendicular. The large signals from these crystals permitted the absorption to be observed directly using dc detection. At a particular nuclear driving frequency and for low rf powers only the unshifted AFR line is observed. As the power is increased beyond a critical power level, a shifted line is noted at a higher value of field. The shifted field position is independent of the power level.[18]

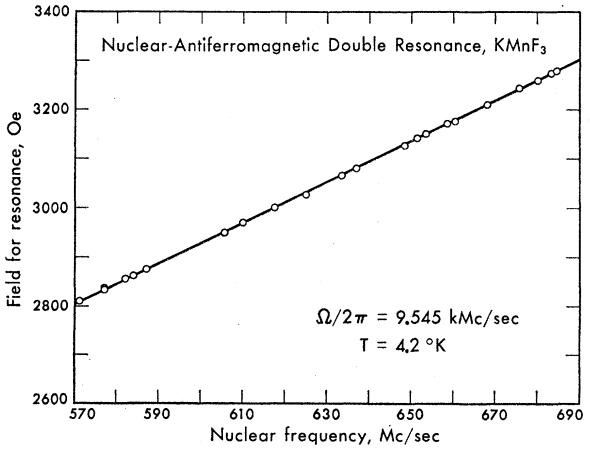

FIG. 1. The values of the shifted field for antiferromagnetic resonance at various nuclear driving frequencies.

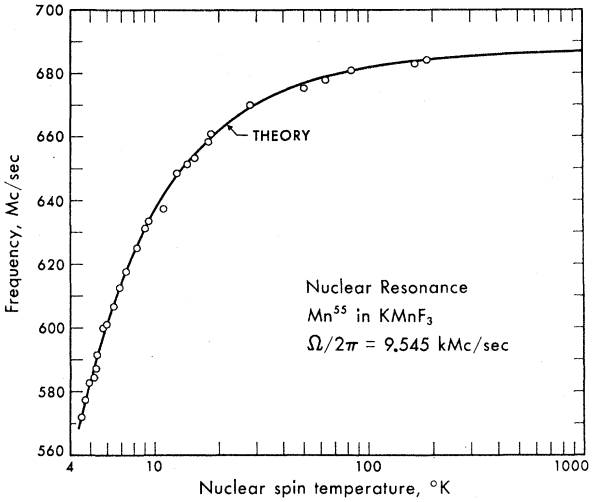

FIG. 2. The implied Mn^{55} nuclear magnetic resonance frequency as a function of the nuclear spin temperature.

As seen from Fig. 1 such NMR absorption was observed over a 110-Mc/sec range of driving frequencies at 4.2°K. For lower frequencies, the two field positions merged while, for frequencies near ω_0, shifts of over 450 Oe were obtained.

It can be seen from Eqs. (2) and (3) how the field for AFR at low temperatures serves as a measure of the nuclear spin temperature. (At liquid-helium temperatures the sublattice magnetization is within 0.1% of its saturation value and changes slowly with decreasing temperature.) Therefore, the double resonance data of Fig. 1 can be used to imply the dependence of the Mn^{55} NMR frequency on the nuclear spin temperature. This is shown in Fig. 2. The NMR frequency extrapolated to infinite spin temperature is 687 ± 2 Mc/sec. Below 10°K the resonance frequency falls rapidly to an

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[17] We wish to thank Dr. R. G. Shulman of Bell Telephone Labs for supplying the sphere of $KMnF_3$ from which these samples were cut.

[18] Measurements with a power variation of a factor of 10–15 show at most a difference in the shifted field of +3 Oe at highest powers. This corresponds to a change of the nuclear spin temperature of 0.2°K or less.

indicated value of about 565 Mc/sec at 4.2°K. It is important to bear in mind that the temperature variable here is that of the nuclear spins and that the electric spins have the value corresponding to the lattice temperature of 4.2°K for all the data on this graph.

4. DISCUSSION

The electronic mode excited in these experiments is given by Eq. (2). The temperature dependence of this mode is well described by the term αm which varies inversely with the temperature. Values for the quantities appearing in this expression are

$$\Omega/\Gamma=3410 \text{ Oe}; \quad \lambda M=8.68\times10^5 \text{ Oe}; \quad \alpha m=9.48/T \text{ Oe};$$
$$(K_1-K_4)/M=2.9 \text{ Oe}; \quad \text{and} \quad K_2/M=340 \text{ Oe}.$$

The numbers quoted here for K_2/M and λM are smaller than those previously reported. The present value for λM is in better agreement with measurements of the magnetic susceptibility of[19] $KMnF_3$ and with the values of λM obtained for $RbMnF_3$.[20,21] The larger value for K_2/M was obtained from torsion measurements of the weak ferromagnetic moment at 4.2°K.[11] As Heeger noted, the measured weak moment at 4.2°K was large in comparison with a similar measurement at 77°K. Pearson's calculation[16] of the single-ion anisotropy in $KMnF_3$ also suggests a smaller value.

Equation (4) is then used to describe the appropriate nuclear mode. This is to be expected due to two reasons. For one, the mode (4) is excited by an oscillating field at right angles to the static field as is mode (2). This corresponds to the experimental arrangement. The second reason lies in the difference of the enhancement factors for the two modes. As the electronic spins can follow at the relatively slow nuclear driving frequencies, an enhanced rf field at the nucleus results. Calculations for $KMnF_3$ shows the factor to be ≈ 200 for mode (4) and ≈ 1 for mode (5).

If the only effect of the nuclear electronic coupling (1) were the presence of the hyperfine anisotropy term in (2), then for nuclear driving frequencies near ω_0, a shift of the AFR to higher fields would be expected for increasing power at that frequency. However, as Eqs. (4) and (5) imply and as seen by the experimental results, the effect of nuclear saturation on the NMR must also be considered.

To explain how the value of AFR field shift is obtained for a given nuclear frequency the following may be said: To obtain resonance absorption for frequencies lying between the values $\omega(T)$ at the lattice temperature [Eq. (4)] and ω_0 (corresponding to infinite spin temperature), a certain degree of nuclear saturation is required. Corresponding to this change of nuclear polarization, a definite field shift is predicted by Eq. (2). To excite at nearly ω_0 the nuclear magnetization must be saturated and the largest field shift results. A mechanism to nucleate nuclear absorption over such a large span of frequencies is discussed in a following paper.[22]

Combining Eqs. (2) and (4) we have

$$\omega/2\pi=687[1-1.42/T]^{1/2}, \quad \text{Mc/sec}.$$

This expression is represented by the solid curve in Fig. 2 and agrees well with the experimentally derived data. The extrapolated frequency of (687 ± 2) Mc/sec is also in good agreement with the value of (687.3 ± 0.4) Mc/sec obtained from paramagnetic resonance of Mn^{++} in the isomorphic crystal $KMgF_3$.[12] This represents an experimental measure of $\langle S\rangle$ at 4.2°K and implies that the expectation value of the spin at this temperature is $\frac{5}{2}$ to within experimental error. From the spin-wave theory of antiferromagnets at low temperatures[23] and from calculations by Davis[24] reductions in $\langle S\rangle$ of 3.12 and 2.49%, respectively, are predicted for a NaCl-type structure. Low-temperature specific-heat measurements in[12] $KMnF_3$ give a value for $A\langle S\rangle$ in agreement with that found here.

Similar observations have been made in the hexagonal antiferromagnet[25] $CsMnF_3$ and in the canted antiferromagnet $MnCo_3$.[26] In both these cases, the Mn^{55} NMR was observed indirectly using the double-resonance technique. In the former case, a spin reduction of $(3\pm1)\%$ is mentioned. However, this result was based on comparisons with rather rough calculations of the hyperfine field as an independent measure of the hyperfine coupling constant was not available. In $MnCO_3$ a decrease of 1.5% was found. Direct observation of Mn^{55} NMR in the cubic antiferromagnet[21] $RbMnF_3$ implies a very small zero-point reduction.

[19] NMR studies of F^{19} in paramagnetic $KMnF_3$(Ref. 14) provide a measure of the electronic magnetization. The exchange constant is then implied from the relation $\lambda=1/\chi(T_N)$, where T_N is the Neèl temperature.

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