Nuclear Frequency Pulling in a Dzialoshinskii-Moriya-Type Weak Ferromagnet: MnCO₃†

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When $MnCO_3$ is in the canted state, it may be treated as consisting of two electron and two nuclear sublattices. For the above crystal we have calculated four eigenfrequencies; two correspond to electron modes, the other two to nuclear modes. From the temperature dependence of the low-frequency electron resonance we have determined the anisotropy field in the (111) plane, which consists of an approximate temperature-independent term of 0.98 ± 0.04 G and a temperature-dependent term of $(8.6\pm0.3)/T_n$ G, where T_n is the nuclear spin temperature. We have observed the nuclear resonance indirectly by measuring its effect on the electron resonance at 6 Gc/sec. For intermediate rf power levels two electron resonance lines were observed at $4.2°K$ between 538 and 638 Mc/sec. One of the lines corresponds to the unshifted resonance line; the other was dependent on the frequency only. This shift is due to partial saturation of the nuclear spin system, which saturates at 640 Mc/sec. The lowest observed nuclear frequency was 538 Mc/sec, which is 102 Mc/sec lower than the frequency we would expect if the nuclear and electron systems are decoupled. Direct Mn NMR, observed recently, is in good agreement with the above results.

I. INTRODUCTION AND THEORY

BELOW $32.4°K$,[1] $MnCO_3$ becomes a weak ferromagnet due to the anisotropic spin-spin interaction.[2] The crystal belongs to the space group D_{3d}^6. The electron resonance of $MnCO_3$ has two frequency branches. The low-frequency branch[3] corresponds essentially to an oscillation of the ferromagnetic component in the (111) plane (soft plane) and it is ferromagnetic in character, and the high-frequency branch[4] is similar to that of the antiferromagnetic resonance but modified by the anisotropic spin-spin interaction. We assume that the crystal is in Dzialoshinskii's state II[5] with the spins in the (111) plane and the ferromagnetic component along the $\langle 10\bar{1}\rangle$ directions when no external magnetic field is applied.

The Mn nuclei form essentially two antiferromagnetic sublattices, which are coupled antiferromagnetically to the electron sublattices (Fig. 1), and are coupled between themselves due to the indirect interaction between the nuclei,[6,7] via the hyperfine interaction.[8] The nuclear sublattices will become of importance at very low temperatures because the average nuclear polarization increases inversely to the nuclear temperature. One would expect that the above system has four eigenfrequencies because there are four sublattices. The

eigenfrequencies ω_+ and ω_- of the low- and high-frequency branch, respectively, as well as the nuclear frequency ω_n will be shifted, due to the coupling between the nuclear and the electron sublattices. This shift is calculated from the free energy which can be written as:

$$E=\tfrac{1}{2}N\hbar\gamma_e\langle S\rangle[H_E\mathbf{S}_1\cdot\mathbf{S}_2+H_{DM}\mathbf{k}\cdot\mathbf{S}_1\times\mathbf{S}_2$$
$$+\tfrac{1}{2}H_A(S_{1z}{}^2+S_{2z}{}^2)+(A\langle I\rangle/\hbar\gamma_e)(\boldsymbol{\sigma}_1\cdot\mathbf{S}_1+\boldsymbol{\sigma}_2\cdot\mathbf{S}_2)$$
$$-\mathbf{H}\cdot(\mathbf{S}_1+\mathbf{S}_2+\Gamma\{\boldsymbol{\sigma}_1+\boldsymbol{\sigma}_2\})-H_A{}'(S_{1y}-S_{2y})],\quad(1)$$

where $\tfrac{1}{2}N$ is the number of spins per sublattice; γ_e is the electron gyromagnetic ratio; $\langle S\rangle$ the thermal average of the electron spin; H_E the exchange field; $\mathbf{S}_1$ and $\mathbf{S}_2$ are unit vectors parallel to the electron sublattices; H_{DM} the canting field due to the anisotropic spin-spin interactions; H_A the anisotropy field parallel to the [111] direction[4]; A is the hyperfine interaction constant; $\langle I\rangle$ the average nuclear spin which is $I(I+1)A\langle S\rangle/3kT_n$; T_n is the nuclear spin temperature; $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ are unit vectors parallel to the nuclear sublattices which are aligned antiparallel to the electron sublattices when no external magnetic field is applied; $\mathbf{H}$ is the external magnetic field parallel to the [10$\bar{1}$] direction which we call the x direction. $\mathbf{H}$ is
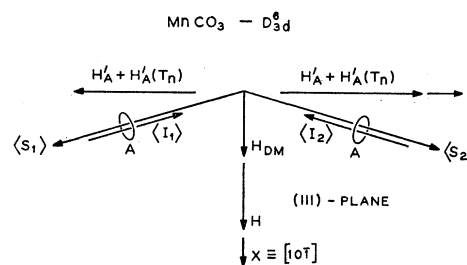
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† A preliminary account of the present paper was given at the 1963 Edmonton Physical Society Meeting [D. Shaltiel and H. J. Fink, Bull. Am. Phys. Soc. **8**, 464 (1963)] and at the 1963 Magnetism Conference [D. Shaltiel and H. J. Fink, J. Appl. Phys. **35**, 848 (1964)].
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[4] H. J. Fink and D. Shaltiel, Phys. Rev. **130**, 627 (1963).
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MnCO₃ — D³₃d

FIG. 1. The orientation of the electron and nuclear sublattices of $MnCO_3$ in the (111) plane when the external field is applied parallel to the [10$\bar{1}$] direction. $H_A{}'$ is the temperature-independent anisotropy field and $H_A{}'(T_n)$ is the anisotropy field which arise from the nuclear polarization.

assumed to be strong enough to order the magnetic domains such that the crystal forms a single domain; Γ is by definition $\langle I \rangle \gamma_n / \langle S \rangle \gamma_e$; γ_n is the nuclear gyromagnetic ratio; H_A' is an effective anisotropy field which is almost parallel to the electron sublattice magnetizations, and it is assumed to be parallel and antiparallel to the y direction. H_A' does not include any contribution from the nuclei. Because the anisotropy field H_A' in the (111) plane is very small, the last term on the right-hand side of Eq. (1) was written approximately. It should contain a sixfold symmetry in the (111) plane which was neglected because we have assumed above that the magnetic field is applied parallel to the x direction and that we are dealing with a single domain.

The effective magnetic fields on the ith electron and nuclear sublattices are calculated from $\mathbf{H}_i = \partial E / \partial \mathbf{M}_i$. When the equations of motion $d\mathbf{M}_i/dt = \gamma_i \mathbf{M}_i \times \mathbf{H}_i$ are solved, one obtains a secular determinant of eight order. The latter can be reduced to two four-by-four determinants. One matrix couples the low-frequency resonance ω_{p+} to the nuclear resonance ω_{np+}, and the other couples the high-frequency resonance ω_{p-} to the nuclear resonance ω_{np-}. The four-by-four determinants can be solved, and when we neglect higher order terms one obtains for the eigenfrequencies:

$$\omega_{p+} = \omega_+ [1 + \beta(T_n) \omega_n^3 \omega_E / \omega_+^4], \qquad (2)$$

$$\omega_{np+} = \omega_n [1 - 2\beta(T_n) \omega_n \omega_E / \omega_+^2]^{1/2}, \qquad (2a)$$

and

$$\omega_{p-} = \omega_- [1 - \tfrac{1}{2}(\omega_n/\omega_-)^2], \qquad (3)$$

$$\omega_{np-} = \omega_n [1 - \beta(T_n) \omega_n \omega_E / \omega_-^2], \qquad (3a)$$

where p stands for pulled frequency and $\omega_E = \gamma_e H_E$ is the exchange frequency.

The other symbols are

$$(\omega_+/\gamma_e)^2 = 2H_E(H_A' + H_A'(T_n)) + H(H + H_{DM}), \qquad (4)$$

$$(\omega_-/\gamma_e)^2 = 2H_E(H_A + H_A' + H_A'(T_n)) + H_{DM}(H_{DM} + H), \qquad (5)$$

$$\omega_n = A\langle S \rangle / \hbar, \qquad (6)$$

$$\beta(T_n) = \tfrac{1}{3}[I(I+1)](A/kT_n), \qquad (7)$$

$$H_A'(T_n) = I(I+1)A^2\langle S \rangle / 3k\hbar\gamma_e T_n. \qquad (8)$$

Similar expressions were found by DeGennes et al.[8] for an antiferromagnet and by Portis et al.[9] for KMnF₃ and CsMnF₃.[10] Equations (2) and (2a) and also (3) and (3a) are dependent upon each other via the parameter T_n which is the nuclear spin temperature. For MnCO₃ the second terms on the right-hand side of Eqs. (2) and (3) are small compared to unity and can be neglected to first approximation. When the nuclear

[9] A. M. Portis, G. L. Witt, and A. J. Heeger, J. Appl. Phys. 34, 1052 (1963).
[10] Kenneth Lee, A. M. Portis, and G. L. Witt, Phys. Rev. 132, 144 (1963).

temperature is eliminated by substituting Eqs. (2) into (2a) and (3) into (3a), one obtains for the pulled nuclear frequencies as a function of the magnetic field at which the electron resonance occurs

$$\omega_{np+}[= \omega_n/(\omega_+/\gamma_e)][2H_E H_A' + H(H + H_{DM})]^{1/2}, \qquad (2b)$$

and

$$\omega_{np-}[= \omega_n/(\omega_-/\gamma_e)^2] \times [2H_E(H_A + H_A') + H_{DM}(H_{DM} + H)]. \qquad (3b)$$

In this double-resonance experiment, we investigated the behavior of the electron low-frequency resonance as a function of temperature and also a function of nuclear frequency and nuclear power.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The spectrometer consisted of a quarter wavelength coaxial cavity which resonated around 6 Gc/sec in the TM_{01} mode, and whose resonance frequency could be changed by insertion of a dielectric plunger concentric to the center conductor of the cavity. The microwave power was transferred into and taken out of the cavity via 50-Ω coaxial transmission lines. At the end of the cavity, where the microwave magnetic field is a maximum, there was a small hole through which another 50-Ω coaxial line was inserted and which ended in a loop through which the rf power (450 to 900 Mc/sec) was transferred to the MnCO₃ crystal. The rf magnetic field was always perpendicular to the magnetic component of the microwave field and also to the static magnetic field. A line stretcher was inserted between the rf generator and the loop to ensure optimum power transfer to the crystal. The maximum power output of the signal generator was 200 mW. The absorption of the low-frequency resonance of MnCO₃ was measured directly as a function of the static magnetic field. The magnetic field was measured with a rotating coil magnetometer and recorded together with the absorption by an x-y recorder. The MnCO₃ crystals were grown hydrothermally and cut parallel to the (111) plane. The latter plane was parallel to the static magnetic field.

The best experimental accuracy of the position of the line was about 20 G when the static field was perpendicular to the microwave field due to the large linewidth. For other positions of the magnetic field the accuracy decreased due to loss of sensitivity.

Figure 2 shows the temperature dependence of the low-frequency electron resonance when no nuclear power was applied. The microwave frequency was kept constant at 6.15 Gc/sec and the static magnetic field was applied in the (111) plane. The experimental points were plotted by assuming that H_{DM} is temperature-dependent. The temperature dependence of the ferromagnetic component $\sigma = \chi_\perp H_{DM}$ is known from Borovik-Romanov's experiments.[1] We obtain a good fit to his

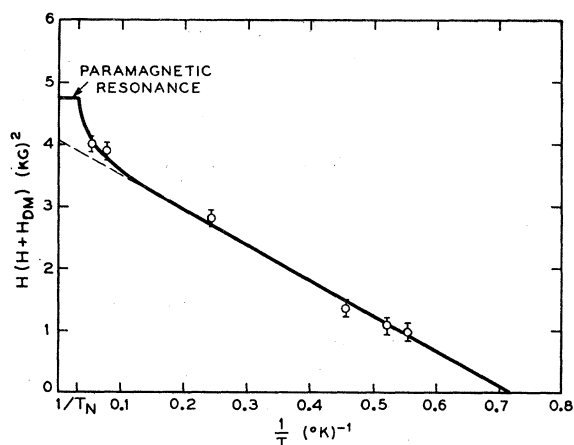FIG. 2. The temperature dependence of the electron low-frequency resonance field of MnCO₃. For detail see the text.

experimental results when we assume that $\chi_\perp$ is a constant below the Néel temperature and

$$\frac{\sigma(T)}{\sigma(0°K)}=\frac{H_{DM}(T)}{H_{DM}(0°K)}=\left[1-\left(\frac{T}{T_n}\right)^2\right]^{1/2}, \qquad (9)$$

where $H_{DM}(0°K)=4.61$ kG.

The solid line in Fig. 2 up to the Néel temperature was calculated from Eq. (4) with the following assumptions: $H_E=M/\chi_\perp$ has the same temperature dependence as shown in Eq. (9); $H_E(0°K)=334$ kG;
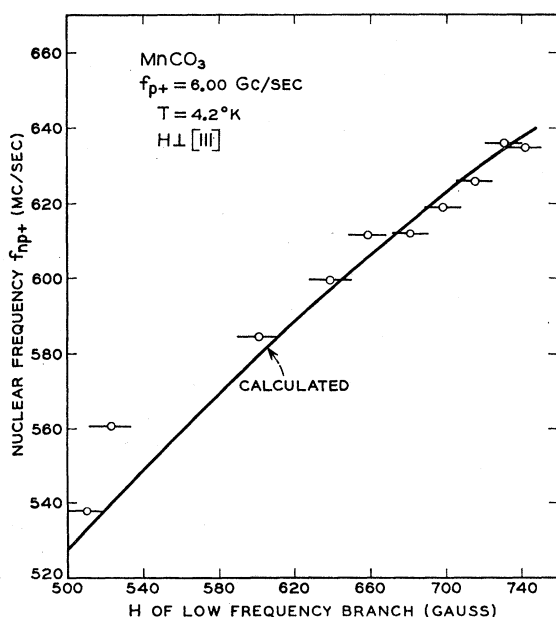

FIG. 3. The dependence of the resonance field of the electron low-frequency resonance of MnCO₃ on the nuclear frequency when the nuclear power was large enough to heat up the nuclear spin system.

$g=2.00$;[11] $T_n=T$; $H_{A}'=0.98$ G; $H_{A}'(T_n)=8.6/T_n$ G. The last two parameters were obtained from the extrapolation of the straight line in Fig. 2 (which was fitted to the low-temperature end, because there H_{DM} and H_E are insensitive to temperature changes) to very high temperatures and from the slope of the straight line. The resonance frequency of about 6 Gc/sec was chosen such that over the investigated temperature range we were able to observe a maximum variation in the resonance field without driving the resonance to zero field.

When, in addition to the microwave power, nuclear rf power was applied which was large enough to raise the nuclear spin temperature above that of the lattice, we obtained a shift of the position of the electron resonance line as shown in Fig. 3. Here the magnetic field at the maximum absorption of the electron resonance is plotted as a function of the nuclear frequency. The electron frequency f_{p+} was kept fixed at 6.00 Gc/sec, the temperature of the bath was 4.2°K, and the static magnetic field was applied in the (111) plane. For large nuclear power levels at 538 Mc/sec we just barely could observe a small shift. At 640 Mc/sec we obtained the largest shift of the electron resonance from about 510 to about 740 G. We were not able to shift the resonance to any higher field by applying higher nuclear frequencies. We make now the assumption that at 640 Mc/sec the nuclear spin temperature $T \rightarrow \infty$, and therefore we obtain from Eq. (2a) that $A\langle S\rangle/h=640$ Mc/sec.

The value of A for MnCO₃ may be obtained by making temperature and volume corrections to that obtained from electron paramagnetic resonance (EPR) experiments of Mn²⁺ in CaCO₃ for which $A=0.00878$ cm⁻¹ at 290°K.[12] As no other data on the Mn hyperfine constant in the carbonates are available we estimate these corrections from the EPR experiments in the oxide compounds with the NaCl structure, e.g., MgO and CaO where the local environment of the Mn²⁺ ions due to the oxygens is similar to that of MnCO₃.

The Mn²⁺ hyperfine constant increased by 0.5 and 1% in[13] MgO and[14] CaO, respectively, when the temperature decreased from room temperature to very low temperatures. A difference of about 40% in volume between MgO and CaO hardly changed the value of the Mn²⁺ hyperfine constant in these compounds.[15] Measurements in MgO under hydrostatic pressure[16] show a large change of A with unit volume ($d \ln A/d \ln V$

[11] In Ref. 4 a g value of 2.03 was obtained by the best fit to the experimental results. We have measured the g value at 47.7 Gc/sec and 20.4°K and found $g=2.01\pm0.01$. The g value of 2.03 was probably too large.
[12] F. K. Hurd, M. Sachs, and W. D. Hershberger, Phys. Rev. 93, 373 (1954).
[13] W. M. Walsh, Jr., G. McKay, J. Jeener, and N. Bloembergen (to be published).
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[15] A. J. Shuskus, Phys. Rev. 127, 1529 (1962).
[16] W. M. Walsh, Jr., Phys. Rev. 122, 762 (1961).

$= -0.06$). Similar experiments on Mn^{2+} in[17] $CaCO_3$ show an even larger change in volume under hydrostatic pressure ($d \ln A/d \ln V = -0.12$). We therefore believe that the difference in volume of the unit cell does not very much effect the hyperfine constant of Mn and that the large change of A due to hydrostatic pressure is presumably due to an induced covalent bonding between the Mn and the oxygen ions. Neglecting any small correction due to the 19% larger unit cell of $CaCO_3$ compared with $MnCO_3$, and assuming $+0.5\%$ correction[13] due to the temperature change, the hyperfine constant of Mn^{2+} in $MnCO_3$ should be 88.2×10^{-4} cm^{-1}. With this value we obtain at absolute zero for $\langle S \rangle$ a value which is 2.1% smaller than $\frac{5}{2}$. This decrease in the value of the spin is due to the zero-point reduction of the electron spin which is consistent with the theory.[18,19] With the above value of A and $\langle S \rangle$ one calculates for $H_A'(T_n)$ a value of
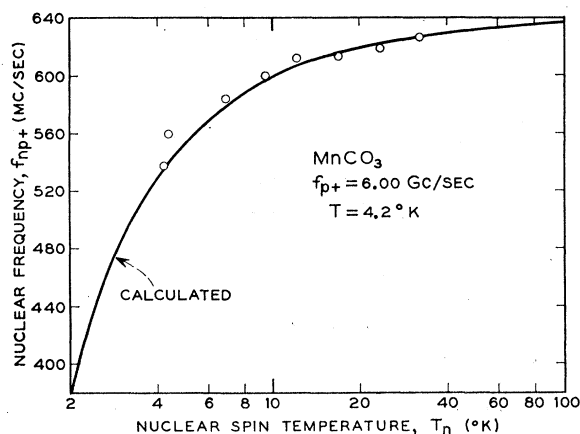

FIG. 4. The dependence of the nuclear spin temperature on the nuclear frequency of $MnCO_3$ for large nuclear power levels.

$8.46/T_n$ which is in good agreement with the experimental results obtained from Fig. 2.

From the experimental points of Fig. 3, the nuclear spin temperatures are calculated directly from Eq. (4) with the experimental value of $H_A'(T_n)$ obtained from Fig. 2, and they are shown in Fig. 4 as a function of nuclear frequency. The solid line in Fig. 4 is calculated from Eq. (2a) with $f_n = 640$ Mc/sec, $H_A'(T_n) = 8.6/T_n$ and $T = 4.2°$K. At the highest nuclear frequency (640 Mc/sec) the average nuclear magnetization is zero and the effective anisotropy field which arises from the nuclei is zero.

Figure 5 shows the absorption of the electron resonance as a function of the applied field at 4.2°K for various nuclear power levels when the microwave frequency was kept constant at 6.00 Gc/sec and the nuclear frequency was kept constant at 619 Mc/sec.
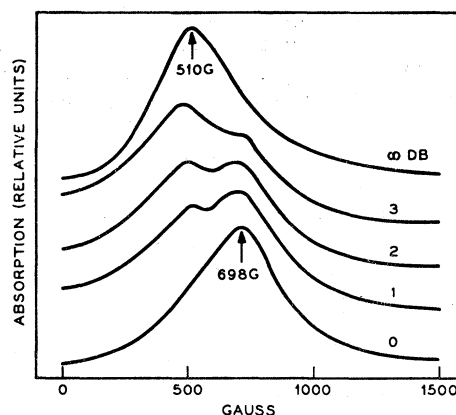
[17] D. F. Wait, Phys. Rev. 132, 601 (1963).
[18] P. W. Anderson, Phys. Rev. 86, 694 (1952).
[19] R. Kubo, Phys. Rev. 87, 568 (1952).

FIG. 5. The microwave absorption curves of the low-frequency branch of $MnCO_3$ as a function of applied magnetic field for various nuclear power levels at $f_{p+} = 6.00$ Gc/sec, $f_{np+} = 619$ Mc/sec, and $T = 4.2°$K. At zero dB attenuation the output power of the signal generator was about 200 mW.

The output power of the signal generator was about 200 mW at zero dB attenuation. For intermediate nuclear power levels, we observe two electron resonance lines. The position of one of the absorption lines corresponds to the unshifted line, the position of the other absorption line depends on the nuclear frequency only. A similar effect was observed by Heeger et al.[20] on $KMnF_3$ and Lee et al.[10] on $CsMnF_3$. The sum of the integrated intensities of the two resonance lines are constant within $\pm 10\%$ regardless of the nuclear power level. It therefore seems that for a given intermediate nuclear power level part of the crystal resonates at the low field and the rest of the crystal at a higher field.

Double-resonance experiments were also performed at an electron frequency of 9 Gc/sec. Measurements at 9 Gc/sec were less favorable than at 6 Gc/sec due to a smaller shift in the magnetic field of the electron resonance line when the nuclear spin system was saturated and also due to structure observed on the electron resonance line.[21,22] The shape of the structure changed when rf power at the nuclear frequency was applied. These effects have prevented the exact determination of the position of the line as well as the shift produced by the rf power level. No quantitative measurements were therefore obtained at 9 Gc/sec. Qualitative double-resonance experiments at 9 Gc/sec have shown that the electron resonance behaves as predicted by Eq. 2(b). A change in the intensity of the electron resonance line was also observed between 710 and 730 Mc/sec at 1.4°K, a temperature which was not reached at the 6-Gc/sec experiment. The change in the intensity of the electron resonance lines at frequencies which are 11

[20] A. J. Heeger, A. M. Portis, and Gerald Witt, Magnetic and Electric Resonance and Relaxation (North-Holland Publishing Company, Amsterdam, 1963), p. 694.
[21] A. C. Borovik-Romanov, N. M. Kreines, and L. A. Prozorova, Zh. Eksperim. i Teor. Fiz. 45, 64 (1963) [English transl.: Soviet Phys.—JETP 18, 46 (1964)].
[22] D. Shaltiel and H. J. Fink (to be published).

to 15% above the unpulled nuclear frequency is not understood. Lee et al.[10] have also observed a similar effect in $CsMnF_3$ at frequencies about 1.5% higher than the unpulled nuclear frequency. Further investigations of these resonances are in progress.

We also measured the angular dependence of the low-frequency branch in the (111) plane between 2.2 and 20.4°K when no nuclear power was applied. We found that the over-all variation of the magnetic field with angle was less than 50 G and that there was an approximate sixfold symmetry in the (111) plane. If one replaces in Eq. (4) H_A' by $H_A' \cos 6\varphi$ consistent with the crystal symmetry,[5] then one would expect that the maximum variation of the magnetic field is about 230 G in the (111) plane. The above discrepancy is attributed to a contribution of the anisotropy out of the (111) plane. The latter anisotropy goes into the equations of motion to a higher order of approximation. It is, however, larger by more than three orders of magnitude[4] than the anisotropy in the (111) plane.

III. CONCLUSIONS

It has been shown experimentally, as predicted earlier,[8] that due to the Suhl[6]-Nakamura[7] interaction the Mn nuclei in $MnCO_3$ at low temperatures may be treated as forming two sublattices whose polarization is inversely proportional to the nuclear temperature. Due to the hyperfine interaction the nuclear sublattices are coupled to the electron sublattices. The electron sublattices resonate at a much higher frequency than the nuclear sublattices and therefore the nuclear sublattices cannot follow readily the microwave field when the electrons resonate. Therefore, the electrons see in addition to the usual anisotropy field (due to the crystalline electric field and due to the dipole-dipole interaction) an additional field which arises from the nuclear polarization and which is inversely proportional to the nuclear spin temperature. The nuclear contribution to the anisotropy energy can be destroyed by raising the nuclear spin temperature separately above that of the lattice by applying large nuclear power levels at the nuclear resonance frequency. This can be accomplished because of the long nuclear spin-lattice relaxation time.

The total magnetic spin system of $MnCO_3$ has four eigenfrequencies given by Eqs. (2) to (3a), because there are four coupled sublattices. Equations (2) and (3) correspond to the electron resonance modes and (2a) and (3a) to the nuclear resonance modes. Equations (2) and (2a) and also (3) and (3a) are dependent upon each other via the nuclear spin temperature which was a variable in this experiment when large nuclear power levels were applied. Formally, the nuclear resonance frequencies and the resonance field of the electron resonances are related by Eqs. (2b) and (3b) when the nuclear spin temperature is varied. Equations (2b) and (3b) do not explain the physical

mechanism which leads to this behavior. Portis et al.[9] make "pinning effects" of the electrons on lattice imperfections (dislocations, surfaces, etc.) responsible for the observed behavior (Figs. 3 and 4).

When the electron sublattices of $MnCO_3$ resonate we see in the (111) plane an anisotropy field of $H_A' = 0.98 \pm 0.04$ G which is temperature-independent within the experimental range and accuracy, and a temperature-dependent term of $H_A'(T_n) = (8.6 \pm 0.3)/T_n$ G, where T_n is the nuclear spin temperature. The latter term is in good agreement with that calculated from the hyperfine interaction constant and which is $8.34/T_n$ G at 4.2°K. In zero external field and for low nuclear power levels (when the nuclear spin temperature is that of the lattice), the nuclear magnetic resonance of Mn should occur at a frequency

$$\omega_{np+} = \omega_n [H_A'/(H_A' + H_A'(T_n))]^{1/2}, \qquad (2c)$$

which approaches zero for $T_n \to 0°K$.

For intermediate nuclear power levels we observed two electron resonance lines. One of the lines corresponds to a nuclear spin temperature equal to that of the lattice, the other has a nuclear spin temperature uniquely related to the nuclear frequency only and given by Eq. (2a). Part of the spins of the crystal resonate at the low field and the rest of the spins at a higher field. From the angular dependence of the electron resonance in the (111) plane we anticipate a contribution of the anisotropy out of the (111) plane to the low-frequency resonance. Additional double resonance signals were observed at frequencies above the unpulled nuclear frequency. The origin of the latter resonances is not understood.

Note added in proof. Recently one of the authors, D.S., (to be published) has observed directly the NMR of Mn in $MnCO_3$ as function of temperature and magnetic field. The nuclear signal was largely enhanced as is expected from the relatively low power needed to saturate the nuclear system in our experiments. He finds that the nuclear frequency depends strongly on field and temperature as predicted by Eq. (2a). Since the direct NMR ω_+ and consequently ω_{np+} in Eq. (2a) are varied simply by varying the external magnetic field he was able to observe at 1.4°K a shifted nuclear resonance frequency below 300 Mc/sec, less than half the unshifted resonance frequency ω_{n+}. Increase of ω_{np+} towards ω_n caused by partial and full saturation of the nuclear system was also observed. ω_{n+} measured both from high-field extrapolation and from saturation of the nuclear system was equal to 640.0 ± 0.2 Mc/sec at 4.2°K in excellent agreement with our double-resonance measurements.