High-Frequency Resonance of a Weak Ferromagnet: $MnCO_3$

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The high-frequency resonance of $MnCO_3$ in the canted state was found at 95.7 Gc/sec in zero field at 20.4°K which corresponds to a uniaxial anisotropy energy of 31.4×10^{-3} cm^{-1}. The frequency dependence of the resonance for magnetic fields parallel to the [111] direction and the angular dependence of the resonance for constant frequency were measured. The latter was found to be different from that of a pure antiferromagnet due to the anisotropic spin-spin interaction. At absolute zero we estimated the zero-field splitting to occur at approximately 132 Gc/sec. When the magnetic field was applied in the (111) plane, the resonance could not be observed due to broadening effects. The broadening effects were also large in magnetic fields smaller than 7 kG. $MnCO_3$ is the first weak ferromagnet with anisotropic spin-spin interaction where the high-frequency branch has been found.

1. INTRODUCTION

BELOW 32.4°K, $MnCO_3$ (rhombohedral crystal structure) becomes an antiferromagnet with a weak ferromagnetic component perpendicular to the [111] direction. This component is due to the anisotropic spin-spin interaction[1,2] and gives rise to two frequency branches for the $k=0$ mode. The low-frequency branch corresponds essentially to an oscillation of the ferromagnetic component around its equilibrium position and the high-frequency branch is similar to the resonance of a pure antiferromagnet but modified by the Dzialoshinskii-Moriya field H_{DM}. This field originates from the anisotropic spin-spin interaction which gives rise to a term $\sum_{i>k}\mathbf{d}_{ik}\cdot(\mathbf{S}_i\times\mathbf{S}_k)$ in the Hamiltonian. The low-frequency branch has been found by Date,[3] and we have discovered and investigated the high-frequency branch of $MnCO_3$.

2. THEORY

Turov and Gusseinov[4] (see also reference 2, Pincus,[5] and Borovik-Romanov[6]) calculated the resonance frequencies for rhombohedral weak ferromagnetic crystals of the α-Fe_2O_3 type based on Dzialoshinskii's theory. We can apply their results to $MnCO_3$. They obtained for the high-frequency branch[7]:

$$(\omega/\gamma)^2=(1/2M)^2[2Ba+q(q+h\sin\theta)+h^2\cos^2\theta], \quad (1)$$

where B is related to the molecular field coefficient, a is the uniaxial anisotropy energy, q is the anisotropic spin-spin energy, h is the magnetic field energy, and θ is the angle between the [111] direction and the magnetic field. One can substitute $2B/(2M)^2=1/\chi_\perp$, $q/2M=H_{DM}$, $h/2M=H$, where M is the saturation magnetization of one sublattice which is a function of temperature. $\chi_\perp$ corresponds to the susceptibility of a pure antiferromagnet perpendicular to the spins and H_{DM} is the effective field due to the anisotropic spin-spin interaction which for $MnCO_3$ is directed perpendicular to the [111] direction. We then obtain

$$(\omega/\gamma)^2=2H_EH_A+H_{DM}^2+H(H_{DM}\sin\theta+H\cos^2\theta), \quad (1a)$$

where the term $a/\chi_\perp$ was further reduced to $2H_EH_A$ by substituting for $a/2M$ the anisotropy field, H_A, along the [111] direction and for $M/\chi_\perp$ the exchange field, H_E. In Eqs. (1) and (1a) the anisotropy in the (111) plane was neglected. This anisotropy can be neglected as long as $H\gg H^*$. H^* is defined by

$$H^*=2H_EH_A'/H_{DM}, \quad (1b)$$

where H_A' is the anisotropy field in the (111) plane and is approximately 2G at 20.4°K.[8]

At constant frequency the resonance field is a function of orientation of the magnetic field with respect to the crystallographic axes. When the applied magnetic field is rotated in a plane perpendicular to the (111) plane while the frequency is kept constant, the resonance field can be described by

$$H^2\cos^2\theta+HH_{DM}\sin\theta=H_0^2, \quad (2)$$

where H_0 is determined by

$$H_0^2=(\omega/\gamma)^2-(2H_EH_A+H_{DM}^2). \quad (3)$$

Equation (2) was normalized by dividing it by H_{DM}^2 and it is plotted in Fig. 1 for various values of H_0, where H_0 is the magnetic field of the resonance when $\theta=0$. For $H_0/H_{DM}\gg1$ there appears a minimum close to the [111] direction. The minimum shifts towards $\theta=\pi/2$ for decreasing values of H_0/H_{DM} and it coincides with $\theta=\pi/2$ for $H_0/H_{DM}=1/\sqrt{2}$. This minimum is characteristic of a weak ferromagnet with anisotropic spin-spin interaction and its position is simply related to H_{DM}. For $H_0/H_{DM}>1$ the resonance field perpendicular to the [111] direction is always larger than that

[1] I. E. Dzialoshinskii, Zh. Eksperim. i Teor. Fiz. **33**, 1454 (1957) [translation: Soviet Phys.—JETP **6**, 1120 (1958)].
[2] T. Moriya, Phys. Rev. **117**, 635 (1960); (to be published).
[3] M. Date, J. Phys. Soc. Japan **15**, 2251 (1960).
[4] E. A. Turov and N. G. Gusseinov, Zh. Eksperim. i Teor. Fiz. **38**, 1326 (1960) [translation: Soviet Phys.—JETP **11**, 955 (1960)].
[5] P. Pincus. Phys. Rev. Letters **5**, 13 (1960).
[6] A. S. Borovik-Romanov, Zh. Eksperim. i Teor. Fiz. **36**, 766 (1959) [translation: Soviet Phys.—JETP **9**, 539 (1959)].
[7] In reference 4 a factor of 2 is missing in the first term on the right-hand side.
[8] H. J. Fink, Phys. Rev. **130**, 177 (1963).

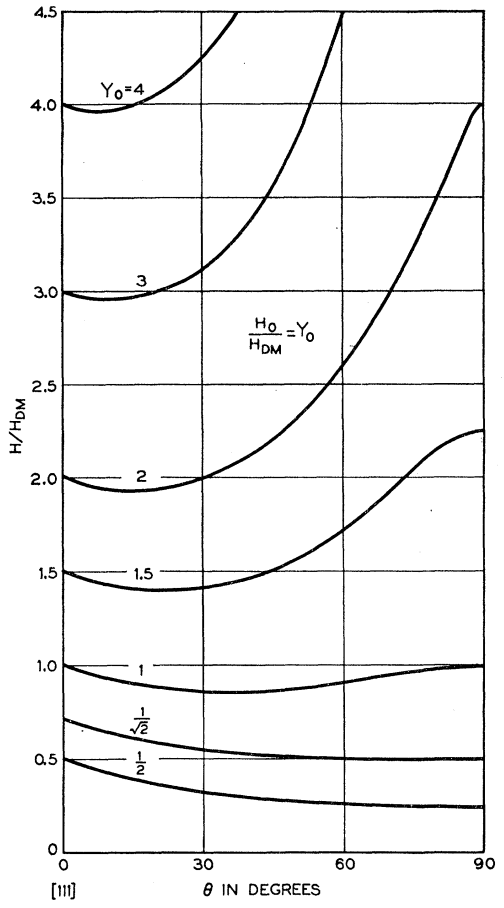

FIG. 1. The normalized angular dependence of the resonance for various constant values of H_0/H_{DM} as calculated from Eq. (2). $\theta=0°\equiv[111]$. The anisotropy in the (111) plane was neglected.

parallel to it and the opposite is true for $H_0/H_{DM}<1$, provided the frequency is kept constant. These results are contrasted to the low-frequency branch where the minimum field for constant frequency is always in the (111) plane and H follows a $1/\sin\theta$ law.[3]

3. EXPERIMENTAL RESULTS AND DISCUSSION

The spectrometer used in this experiment has been described previously.[9] It is a broad frequency band transmission type spectrometer and was used between 46 and 125 Gc/sec with a variable magnetic field up to 28 kG. The signal power was obtained from backward wave oscillators and the frequency was measured by beating it with the harmonics of an X-band signal generator. The magnetic field was measured with a rotating coil magnetometer and recorded by an x–y recorder. The spectrometer measures usually an admixture of absorption and dispersion. Two methods of detecting the resonance were used. For strong signals the output of the crystal detector was amplified by a dc amplifier and the relative absorption of $MnCO_3$ was plotted directly on an $x-y$ recorder as a function of the applied-magnetic field. For small signals the magnetic field was modulated by 400 cps and the signal was amplified and detected by a phase-sensitive detector and then recorded as a function of the applied field. A natural single crystal of $MnCO_3$ was placed into the waveguide and orientated with the help of a microscope. A plane which contained the [111] direction was aligned such that this plane was parallel to the plane in which the applied-magnetic field was rotated. The alignment of the crystal was checked by measuring first the $1/\sin\theta$ dependence of the low-frequency branch[3] at 47 Gc/sec. Five natural single crystals were used, the diameters of which varied between 1 and 2 mm and the shapes of which were approximately cubic.

Figure 2 shows the square of the resonance frequency of the high-frequency branch plotted vs the square of the applied magnetic field for magnetic fields parallel to the [111] direction. The solid line in Fig. 2 is calculated from Eq. (1a) with $\theta=0$, $g=2.03$, and $2H_EH_A+H_{DM}^2=a/\chi_\perp+H_{DM}^2=1135$ kG^2. From the zero-field resonance, we were able to determine the uniaxial anisotropy energy at 20.4°K. $\chi_\perp$ was obtained directly from Borovik-Romanov's experiment and H_{DM} was calculated from the ferromagnetic component of the magnetization which is defined by[1]: $\sigma=H_{DM}\chi_\perp$. For simplicity we assume that $\chi_\perp$ is a constant below T_N of value 42×10^{-3} cgs units/mole (it varies by 5%). With[6] $\sigma(20.4°K)=152$ cgs units/mole we obtain for H_{DM} the value 3.62 kG and from this it follows that $a=47.2\times10^6$ ergs/mole at 20.4°K.

The anisotropy energy $K(T)$ is defined by $a(T)/2$

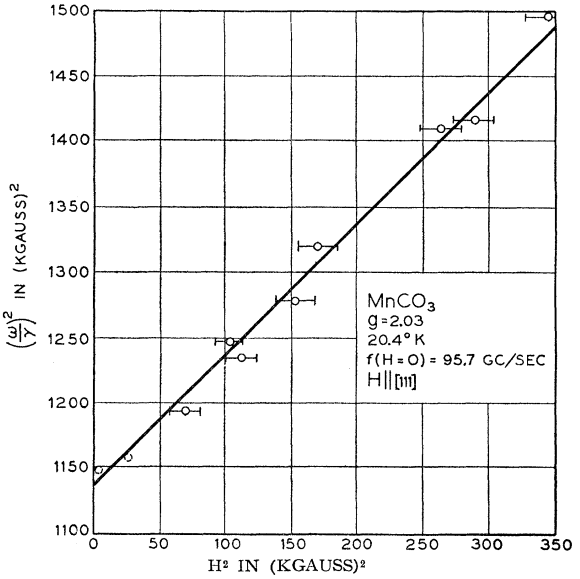

FIG. 2. The frequency dependence of the high-frequency resonance of $MnCO_3$ for magnetic fields parallel to the [111] direction. The solid line is calculated from Eq. (1a) with $\theta=0°$, $g=2.03$, and $H_{DM}=3.62$ kG.

[9] M. Peter, Phys. Rev. **113**, 801 (1959); J. B. Mock, Rev. Sci. Instr. **31**, 551 (1960).

$=NS^2K(T)$, where N is the total number of Mn ions and $S=5/2$. From this it follows that $K=31.4\times10^{-3}$ cm^{-1} per ion at 20.4°K. K consists of the sum of three contributions: the crystal field, K_1, the dipole-dipole interaction, K_2, and the pseudodipole interaction, K_3. The contribution from the crystal field is estimated approximately from the paramagnetic resonance experiments[10] of Mn^{2+} in $CaCO_3$, where $K_1=D=7.5\times10^{-3}$ cm^{-1}. K_3 is calculated from $(\Delta g/g)^2J$, where $J=12.8$ cm^{-1} is the effective superexchange coupling constant, which is estimated from $\chi_\perp$ and M. With $g\approx2.03$, K_3 becomes 2.9×10^{-3} cm^{-1}. Therefore, the contribution due to the dipole-dipole interaction is approximately 21×10^{-3} cm^{-1} at 20.4°K. With the above values one can estimate H^* [Eq. (1b)]. It has a value of approximately 300 G, and, therefore, for the fields we used in this experiment we were justified to neglect the anisotropy energy in the (111) plane. Figure 3 shows the angular dependence of the resonance for constant frequencies. The solid lines are calculated from Eq. (2)

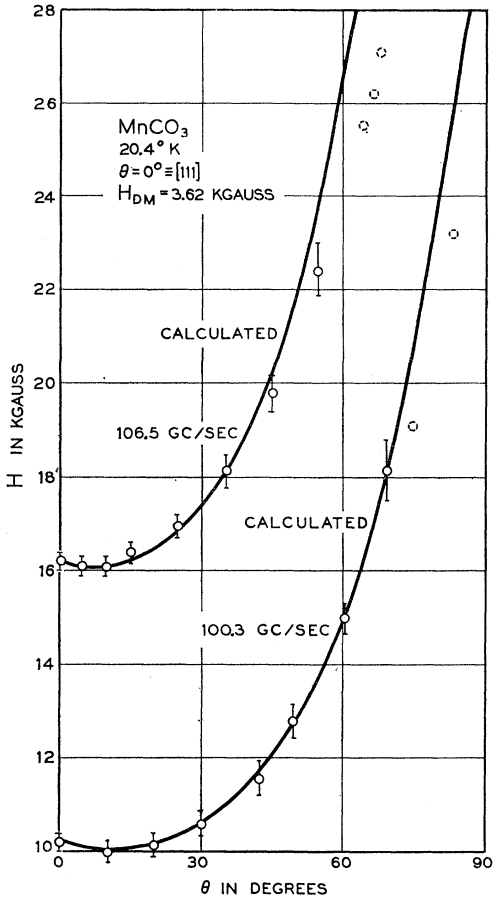

FIG. 3. The angular dependence of the high-frequency resonance of $MnCO_3$ for constant frequencies. $\theta=0°$ corresponds to the [111] direction. The solid lines are calculated from Eq. (2) with $H_{DM}=3.62$ kG.

[10] F. K. Hurd, M. Sachs, and W. D. Hershberger, Phys. Rev. **93**, 373 (1954).

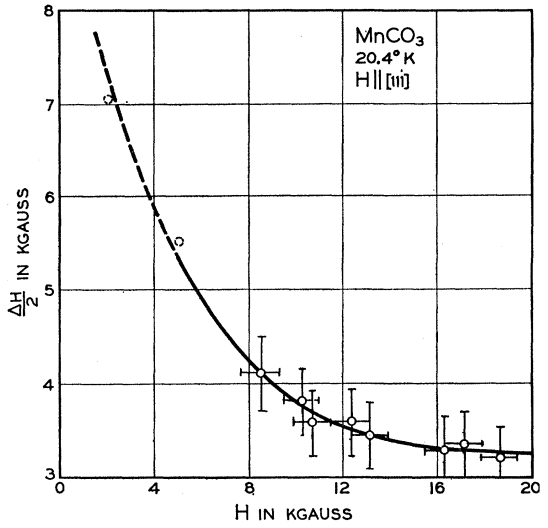

FIG. 4. The half-linewidth of the high-frequency resonance of $MnCO_3$ as a function of magnetic field when the magnetic field is applied parallel to the [111] direction.

with $H_{DM}=3.62$ kG and they are in good agreement with the experiment. The experimental points show that the minimum is not at the [111] direction.

The half-linewidth of the resonance for magnetic fields parallel to the [111] direction was 3 to 4 kG for fields larger than 9 kG and for smaller fields the absorption lines broadened appreciably (Fig. 4). Figure 5 shows the observed half-linewidth of the resonance when the applied-magnetic field is rotated in a plane perpendicular to the (111) plane and the frequency is kept constant. The linewidth increases when the magnetic field is rotated away from the [111] direction.

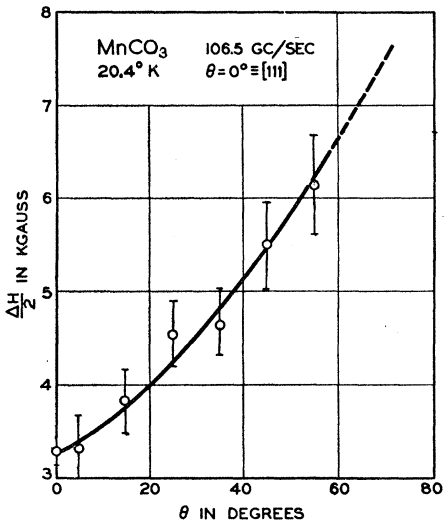

FIG. 5. The half-linewidth of the high-frequency resonance of $MnCO_3$ for constant frequency when the applied-magnetic field is rotated in a plane perpendicular to the (111) plane. $\theta=0°$ corresponds to the [111] direction.

When the magnetic field is applied perpendicular to the [111] direction, the line broadens so much (more than 15 kG) that it can no longer be observed.

The broadening of the lines at low magnetic fields (<2kG) is probably caused to a large extent by domain effects. For large magnetic fields the crystal appears to be a single domain.[8] When the magnetic field is decreased, the crystal divides itself into many magnetic domains and thereby the linewidth of the resonance for small fields is increased considerably due to disorder.

The low-field broadening together with that of the angular broadening explain why we could not observe reliably the angular dependence for magnetic fields smaller than 7 kG. Inhomogeneities in the crystals as they are likely to occur in natural crystals could be an additional cause for line broadening. This may partially explain the broad lines.

At 4.2°K we have searched for the resonance up to a frequency of 125 Gc/sec. We were not able to detect it, and it is unlikely that the resonance in finite fields is below 125 Gc/sec at 4.2°K. We, however, can estimate the zero-field splitting at absolute zero. From Zener's theory it follows that[11]

$$a(0)/a(T)=[M(0)/M(T)]^3, \tag{4}$$

where M is the sublattice magnetization. The ferromagnetic component can be written as

$$\sigma=\chi_\perp H_{\mathrm{DM}}=\chi_\perp|\mathbf{\Delta}|M, \tag{5}$$

where $\mathbf{\Delta}$ is a constant vector parallel to the [111] direction.[2] With the assumption that $\chi_\perp$ is independent of temperature, we obtain

$$a(0)=a(T)[\sigma(0)/\sigma(T)]^3. \tag{6}$$

The ratio $\sigma(0)/\sigma(T)$ is known from experiment[6] and a at 20.4°K was determined above. With $\sigma(0)/\sigma(T)=188/152$ and $H_{\mathrm{DM}}(0)=\sigma(0)/\chi_\perp=4.48$ kG, we obtain for the zero-field resonance at absolute zero 132 Gc/sec. The assumption that $\chi_\perp$ and $|\mathbf{\Delta}|$ are temperature independent includes implicitly the assumption that the canting angle is temperature independent. If we assume that $M(0)=(N/2)g\mu_B\langle S\rangle$ where $\langle S\rangle=5/2$ at 0°K, then it follows that the anisotropic spin-spin interaction constant $|\mathbf{\Delta}|=0.318$ Oe^2 mole/erg for $MnCO_3$. The anisotropy field parallel to the [111] direction is then approximately 2.1 kG at 20.4°K.

In order to check the consistency of the above assumptions and the experimental results, we have measured the change of the resonance field as a function of temperature between 16 and 20.4°K when the frequency was kept constant. At $f=106.5$ Gc/sec we obtained for $(\Delta H/\Delta T)$ at approximately 20.4°K the value 3.2 kG/°K. We checked this by calculating $(dH/dT)_{f,T}$. We obtain when substituting Eq. (6) into Eq. (1a) and differentiating:

$$\left(\frac{dH}{dT}\right)_{f,T}=-\frac{1}{2\chi_\perp H_{\mathrm{res}}(T)}\left[3\frac{a(T)}{\sigma(T)}+\frac{2\sigma(T)}{\chi_\perp}\right]\left(\frac{d\sigma}{dT}\right)_T. \tag{7}$$

$(d\sigma/dT)^{20.4°\mathrm{K}}=-4.52$ cgs units/mole °K which follows from Borovik-Romanov's experiments, and with the above-quoted values for $\chi_\perp$, M, a, and σ, we obtain $(dH/dT)_{f,T}=3.1$ kG/°K, for $f=106.5$ Gc/sec and $T=20.4$°K, which is in good agreement with the experimental value of 3.2 kG/°K. As mentioned previously, in the present experiment dispersion and absorption were measured simultaneously, in general. It was possible only for certain frequencies to determine the center of the resonance directly. This was when a pure absorption or dispersion signal was observed. For other frequencies we calculated the center of the resonance by assuming a Lorentzian line shape.[12] The uncertainty of the resonance field of the center of the line is due to the broad lines, and we believe this uncertainty to be less than 20% of the half-linewidth.

Because the dimensions of the samples were only slightly smaller than half the free-space wavelength of the signal, uncertainties in the center and width of the line are also possible due to size effects. Some of the samples investigated gave a zero-field resonance at 20.4°K which was by 2 to 3% larger than that shown in Fig. 1. This might be due to uncertainties in the center of the resonance and due to possible strain and impurities in the natural crystals which could give rise to a slightly larger anisotropy energy.

4. CONCLUSIONS

In the two sublattice model for $MnCO_3$, the free energy can be written approximately:

$$E=\tfrac{1}{2}NS^2[J\mathbf{S}_1\cdot\mathbf{S}_2+d\mathbf{k}\cdot(\mathbf{S}_1\times\mathbf{S}_2)+K(S_{1z}^2+S_{2z}^2)-\delta\mathbf{h}\cdot(\mathbf{S}_1+\mathbf{S}_2)]. \tag{8}$$

$\mathbf{S}_1$ and $\mathbf{S}_2$ are unit vectors parallel to the sublattice magnetizations; $\mathbf{k}$ is a unit vector parallel to the [111] direction; $\mathbf{h}$ is a unit vector parallel to the applied-magnetic field; J is the effective-exchange energy; d is the effective anisotropic spin-spin energy; K is the uniaxial anisotropy energy; δ is equal to $g\mu_BH/S$. In our experiment we have determined K from the high-frequency branch of the zero mode at 20.4°K. The resonance was found at 95.7 Gc/sec from which we calculated the value K of 31.4×10^{-3} cm^{-1}/ion; this corresponds to an anisotropy field of 2.1 kG parallel to the [111] direction. J and d were calculated from Borovik-Romanov's experiment and we obtained at 20.4°K, $J=12.8$ cm^{-1}, and $d=0.17$ cm^{-1}. For the largest magnetic fields used in this experiment the term δ was larger than d but smaller than J by approximately a factor of 10. All these data together give a

[11] C. Zener, Phys. Rev. **96**, 1335 (1954).

[12] M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. **126**, 1395 (1962).

fairly complete picture of the interactions in $MnCO_3$ represented by a two-sublattice model.

$MnCO_3$ is the first canted spin system with anisotropic spin-spin interaction of the Moriya type[2] where experimental evidence of the existence of both frequency branches has been established. The high-frequency resonance is similar in character to the resonance of a pure antiferromagnet but modified by the Dzialoshinskii-Moriya field H_{DM}. For constant frequency this resonance is anisotropic and a minimum occurs for $H_0 > H_{DM}/\sqrt{2}$ which coincides neither with the [111] direction nor is it perpendicular to the [111] direction. H_0 is the resonance field when H is parallel to the [111] direction. For large magnetic fields the minimum is close to the [111] direction. The position of the minimum is simply related to H_{DM}. The frequency dependence was found to agree with the existing theory.[4,6] The half-linewidth for magnetic fields larger than 9 kG is 3 to 4 kG for fields applied parallel to the [111] direction and increases with decreasing magnetic field; it also broadens considerably when the magnetic field is rotated away from the [111] direction. Due to the broadening of the resonance line perpendicular to the [111] direction, the resonance could not be observed in the (111) plane. In the (111) plane one would expect, however, the resonance to be isotropic for $H \gg 300$ Oe.

At 4.2°K we did not find the resonance up to a frequency of 125 Gc/sec. From Zener's theory[11] and the assumption that the anisotropic spin-spin interaction constant d is a temperature independent we expect the zero-field resonance at absolute zero to occur at approximately 132 Gc/sec. The consistency of our assumptions and our experimental results with those of Borovik-Romanov were checked by measuring the change of the resonance field for constant frequency (106.5 Gc/sec) between 16 and 20.4°K. We obtained from the experiment 3.2 kG/°K which compares favorably to the calculated value of 3.1 kOe/°K at 20.4°K. We may, therefore, conclude that the existing theories on weak ferromagnetism are in good agreement with the experimental results of $MnCO_3$. There is, however, no satisfactory theory which explains the linewidth of the resonance and its anisotropy.

Note added in proof. Based on a two sublattice model the line shape was calculated by solving the equations of motion with a damping term of the Landau and Lifshitz type. The frequency line shape is neither Gaussian nor Lorentzian; it reduces to a Lorentzian line for $\Delta\omega \ll \omega \cdot \Delta\omega = 2\alpha\omega_e$, where α is the damping constant and ω_e the exchange frequency. By differentiating Eq. (1a), Fig. 5 can be approximately explained by choosing an appropriate value for α. The increase in ΔH for decreasing magnetic fields (Fig. 4) agrees qualitatively with the above calculations, however, the numerical agreement is poor if α is kept constant and independent of frequency. The frequency linewidth is of more fundamental nature than ΔH. The above considerations agree also qualitatively with the low frequency branch. The authors are indebted to Dr. L. R. Walker for pointing out an error in our calculation.

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