SOVIET PHYSICS JETP VOLUME 18, NUMBER 1 JANUARY, 1964

ANTIFERROMAGNETIC RESONANCE IN $MnCO_3$

A. S. BOROVIK-ROMANOV, N. M. KREĬNES, and L. A. PROZOROVA

Institute of Physical Problems, Academy of Sciences, U.S.S.R.

Submitted to JETP editor February 21, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) **45**, 64-70 (August, 1963)

A detailed study was made of the low-frequency branch of antiferromagnetic resonance in $MnCO_3$ in the range 4.5 to 15 Gc/sec. The results are described by Eq. (3) with $H_D = 4.4$ kOe, in good agreement with the static data. The effective field H_A responsible for the gap $H_{\Delta 1} = (2H_AH_E)^{1/2}$ in the energy spectrum is not due to crystallographic anisotropy but to hyperfine interaction with the nuclear moments that are becoming ordered. This is confirmed by the strong temperature dependence of $H_{\Delta 1}$ (the resonance field is shifted by 400 Oe when the temperature is decreased from 4.2 to 1.5° K). The sublattice magnetization is determined from this temperature dependence.

1. INTRODUCTION

IN rhombohedral antiferromagnets like $MnCO_3$ and α-Fe_2O_3, which have weak ferromagnetism, the sublattice magnetization is directed perpendicular to the principal axis. The antiferromagnetic resonance spectrum of such antiferromagnets has unusual properties. As has already been shown,[1-3] unlike ordinary antiferromagnets, these have a low-frequency branch, the frequency of which varies with the external field in the following fashion:

$$(\nu/\gamma)^2 = H_{\rm res}(H_{\rm res} + H_D) + H_\Delta^2 \cos 6\varphi, \qquad (1)$$

where $H_{\rm res}$ is the external field applied in the basal plane of the crystal, H_D is the Dzyaloshinskiĭ field which gives rise to the weak ferromagnetism, and γ is the gyromagnetic ratio. The second term in Eq. (1) arises from anisotropy in the basal plane, and the quantity H_Δ is expressed in terms of the effective anisotropy field.

The magnitude of the field H_D can be obtained independently of static measurements, since

$$H_D = \sigma/\chi_\perp, \qquad (2)$$

where σ is the spontaneous ferromagnetic moment and $\chi_\perp$ is the susceptibility in the basal plane. Hence, antiferromagnetic resonance studies on these compounds permit the verification of Eq. (1) not only qualitatively but quantitatively. Low-frequency antiferromagnetic resonance in α-Fe_2O_3 and $MnCO_3$ has been reported in a number of papers.[4-6] However, the crystals used in these experiments were not good enough. The line width turned out to be too large to permit reliable quantitative treatment of the data obtained. We had at our disposal crystals of $MnCO_3$ of high purity, in which the resonance line width was less than 100 Oe.

Preliminary investigation of the antiferromagnetic resonance of these crystals at one frequency (9.4 Gc/sec) showed a quantitative discrepancy from Eq. (1).[7] Hence, a wider study of the frequency and temperature dependence of the resonance line positions was undertaken. A discussion of the results of this work is the purpose of the present paper.

2. THE SAMPLES AND THE EXPERIMENTAL METHOD

The monocrystals of $MnCO_3$ that we used were prepared by Ikornikova of the Crystallographic Institute of the Academy of Sciences by the hydrothermal method.[8] 1) The majority of the crystals were in the shape of relatively thin platelets in which the trigonal axis was perpendicular to the plane of the platelet. They were perfectly transparent and most of them had good natural faces on the (001) planes; the lateral boundaries of the crystals were less perfect. The thickness of the platelets varied from 0.1 to 1 mm, and they were about 1 to 2 mm across. Some of the samples were made into flat disks about 1 mm in diameter.

The antiferromagnetic resonance investigations were carried out with a magnetic spectrometer with low-frequency field modulation. A set of

---

1) The authors sincerely thank N. Yu. Ikornikova for the crystals.

klystrons spanning the interval from 4.5 to 15 Gc/sec were used as microwave sources. The klystron frequency was automatically locked to the cavity resonant frequency. Rectangular cavities in H_{01n} modes were used; measurements at 4.5 Gc/sec were carried out in a coaxial cavity. The magnetic field was modulated at 30 c/sec. The low-frequency signal from the detector, which was proportional to the derivative of the absorption line, was amplified by a tuned amplifier and, after rectification by a phase detector, was recorded by an electronic XY recorder.

3. PARAMAGNETIC RESONANCE

The paramagnetic resonance of $MnCO_3$ was observed at room temperature on several crystals at different orientations of the magnetic field relative to the crystallographic axes. Unlike Date,[6] we did not find any anisotropy of the line width.[2)] As an example, we show in Fig. 1 the trace of a line obtained for $H \parallel Oz$ and $h_{rf} \perp Oz$. Identical curves were obtained at the other orientations. For all orientations and in all crystals we obtained $\Delta H = 250 \pm 20$ Oe, which is about one-tenth the width observed by Date. Date's high value for ΔH is probably attributable to the imperfection of the crystals he used. The line position corresponds to an isotropic g factor equal to 2.00 ± 0.01. The observed width is about one-tenth of the calculated dipole width (from 1.7 kOe for $H \parallel Oz$ to 3.0 kOe for $H \perp Oz$[6]). This narrowing is caused by the strong exchange interaction present in $MnCO_3$.

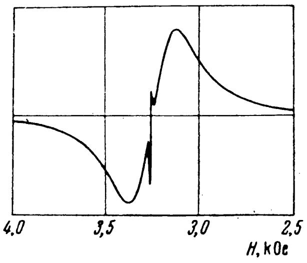

FIG. 1. Paramagnetic resonance line of $MnCO_3$ at room temperature ($\nu = 9.4$ Gc/sec, $H \parallel Oz$, $H_1 \perp Oz$). DPPH marker in center.

4. ANTIFERROMAGNETIC RESONANCE

$MnCO_3$ makes a transition to the antiferromagnetic state at 32.5° K.[1] All antiferromagnetic resonance experiments were conducted at temperatures below 4.2° K, i.e., well below T_N. The resonance was always observed with the static and rf fields mutually perpendicular. The lowest value of the resonance field was observed when it was directed in the basal plane. At 9.4 Gc/sec it was verified that, in accordance with [6,3], the resonance field in a direction at an angle φ with the basal plane varies as $H = H_0/\cos\varphi$, where H_0 is the resonance field in the basal plane. The line width has a corresponding variation. All the results quoted in this paper were obtained in experiments in which the static field was in the basal plane. We made a thorough study of the width and structure of the resonance line and the dependence of the resonance field on frequency and temperature. The results are presented and discussed below.

A. Width and structure of the line. A rather large number of crystals (more than ten) were examined at 4.2° K and 9.4 Gc/sec, and it was found that the line width differed strongly from sample to sample. In the worst cases it amounted to 250 Oe, in the best about 40 Oe. As a rule, the widest lines were found in the largest crystals. The narrowest line was observed in thin (about 0.1 mm) platelets. For one of these the line width was about 10 Oe. It must be emphasized that all of these crystals gave the same paramagnetic resonance line width.

In the majority of crystals the line was observed to consist of many components (see, for example, Fig. 2). These components were so close together that we could not determine their number or positions. The width of the individual components was apparently about 10 Oe. The splitting pattern of the line differed strongly from crystal to crystal. Moreover, the splitting pattern also changed when the crystal was rotated relative to the external field. In this the principal change was in the relative intensities of the components, which strongly affected the general shape of the line and shifted its maximum somewhat. However, these changes did not have a periodicity corresponding to the

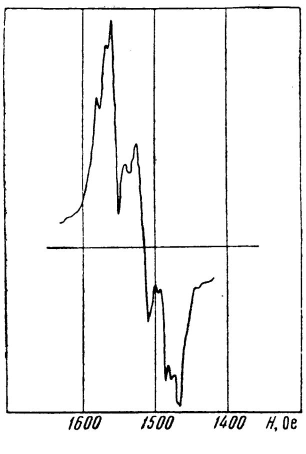

FIG. 2. Structure of the antiferromagnetic resonance line of $MnCO_3$ at 4.2°K ($\nu = 9.4$ Gc/sec). Sample in the form of a rectangular plate $1 \times 0.6 \times 0.1$ mm.

[2)] As the width of the line ΔH we take the distance between the maximum and minimum of the derivative of the absorption line.

symmetry of the crystal. We were also able to establish, to within ± 10 Oe at least, that the position of the maximum did not vary with a 60° period. The structure of the line did not change when the rf field was rotated out of the basal plane into the direction of the trigonal axis. It was also practically independent of the frequency at which resonance was observed. This was proved in experiments in which the crystal was placed on the bottom of the cavity, which was then excited in different H_{01n} modes. In doing this, the position of the crystal relative to the static and rf fields remained unchanged.

Upon lowering the temperature to 1.5° K the total line width was practically unchanged. However, the number of resolved fine-structure components increased, indicating that their widths decreased.

In summing up these results on line width, we must say that it is difficult at present to draw any conclusions about the true width of the main homogeneous resonance in $MnCO_3$. The observed complex line structure can be caused by various factors: crystal inhomogeneities, excitation of magnetostatic modes of non-uniform precession, and also perhaps excitation of spin waves by macroscopic surface inhomogeneities. We are presently studying this question more thoroughly and defer its discussion until the completion of these investigations.

An important result is our discovery that there is no anisotropy in the position of the line when the external field is rotated in the basal plane. From this it follows that the quantity H_{Δ}^2 in Eq. (1) is practically zero. From our data we obtain 0.1 kOe^2 as an upper limit for H_{Δ}^2. From this one can estimate that the limiting value of the anisotropy energy in the basal plane is $K_3 \leq 100$ erg. This result does not contradict the results of the enormously more sensitive static measurements,[9] which give $K_3 \leq 1$ erg.

B. Dependence of the resonance field on the frequency. A thorough check of Eq. (1) was made on two samples. The line width for these samples was about 80 Oe. In view of what was said above, we estimate the error in determining the value of the field corresponding to the main resonance to be ± 20 Oe, although the position of the maximum was reproducible in repeated experiments within ± 5 Oe. The results obtained are presented in Fig. 3. These results fit well an equation similar to Eq. (1), but without the factor cos 6φ that accounts for crystallographic anisotropy:

$$(\nu/\gamma)^2 = H_{\text{res}}(H_{\text{res}} + H_D) + H_{\Delta 1}^2. \qquad (3)$$

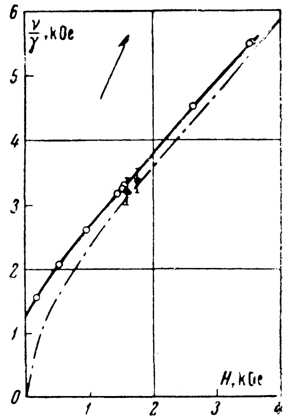

FIG. 3. Dependence of the reduced resonance frequency on the external field applied in the basal plane: ○ – this work, ● – results of Date.[6] The dashed curve was calculated from Eq. (1) with H_D = 4.4 kOe and $H_{\Delta}^2 = 0$. Continuous curve, from Eq. (3).

On the basis of 14 pairs of experimental measurements of ν and H_{res}, we found by a least-squares analysis the following values for the constants in Eq. (3):

$$H_D = 4.4 \pm 0.1 \text{ kOe}, \qquad H_{\Delta 1}^2 = 1.6 \pm 0.3 \text{ kOe}^2.$$

The curve constructed from Eq. (3) with these values for the constants (continuous line in Fig. 3) does not deviate from the experimental points by more than 1—2%. The points obtained by Date[6] lie systematically below ours (see Fig. 3). However, with a line width of 1 kOe as obtained by Date, the errors in determining the position of the maximum can exceed the observed discrepancy.

Our value for H_D is in excellent agreement with the value H_D = 4.4 kOe calculated from Eq. (2) from the data of static measurements of the spontaneous moment σ_0 and the susceptibility $\chi_{\perp}^0$.[1] However, the gap ($\mu H_{\Delta 1}$) turns out to have an order of magnitude greater than expected from our results on anisotropy. For comparison, the curve corresponding to H_D = 4.4 kOe and $H_{\Delta}^2 = 0$ is shown in Fig. 3 (dashed curve). The experimental values for H_{res} for a given frequency lie lower by 100—300 Oe than the corresponding points on the dashed curve, i.e., far outside the limits of experimental error. Thus, it is necessary to postulate the existence of another cause for the energy gap in $MnCO_3$ besides crystalline anisotropy. We shall consider this below.

C. Temperature dependence of the line position. The position of the line was observed to undergo a large shift when the temperature was lowered. Figure 4 shows resonance-line derivatives obtained for four temperatures. When the temperature is lowered from 4.2 to 1.5° K, the resonance field is lowered by about 400 Oe. Analysis of the data obtained at 1.5° K at different frequencies showed that they fit Eq. (3) well with the same value of H_D as used above, but with a different value for $H_{\Delta 1}^2$. Thus the temperature dependence

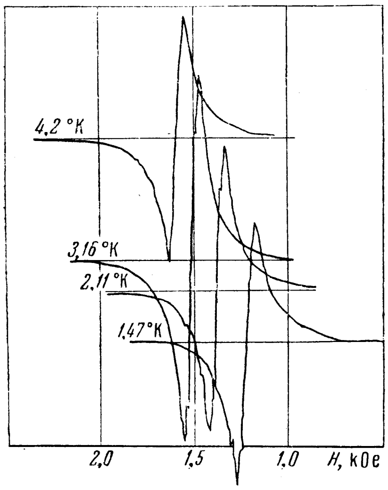

FIG. 4. Shift of the position of the antiferromagnetic resonance line as the temperature is lowered.

of the line position is determined by the temperature dependence of $H^2_{\Delta 1}$. In order to determine the latter dependence, the results obtained on the resonance-field shift with temperature for different frequencies were recalculated according to Eq. (3). It can be seen from Fig. 5 that if the values of $H^2_{\Delta 1}$ are plotted as a function of 1/T, then all the experimental points lie, within the limits of error, on a straight line. In view of what was said above about the uncertainty in the position of the main resonance, the line so obtained can be shifted in parallel fashion by an amount $\delta H^2_{\Delta 1} = \pm 0.3$ kOe^2. Hence we cannot say for certain whether the actual line goes through the origin or not. However, this circumstance ought not, in first approximation, affect the error in the magnitude of the slope. Our final conclusion is that there exists a gap $\epsilon_0 = h\gamma H_{\Delta 1}$ in the energy spectrum of MnCO$_3$, the magnitude of which is strongly temperature dependent, so that

$$H^2_{\Delta 1} = H^2_{\Delta 0} + a/T, \quad H^2_{\Delta 0} = 0.3 \pm 0.3 \text{ kOe}^2,$$

$$a = 5.8 \pm 0.5 \text{ kOe}^2 \cdot \text{deg}.$$

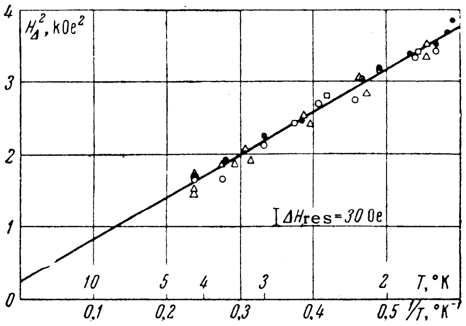

FIG. 5. Temperature dependence of $H^2_{\Delta 1}$: ○ – ν = 15.1 × 10^9 c/sec; △ – ν = 9.1 × 10^9 c/sec; ■ – ν = 7.3 × 10^9 c/sec; ● – ν = 5.8 × 10^9 c/sec. The indicated variation in $H^2_{\Delta 1}$ corresponds to a shift in line position of 30 Oe.

It should be mentioned that when the cavity was filled with liquid helium no change in line position was observed when the rf power was increased by 20 dB. But when cooling was effected by means of an exchange gas there was an observable shift in the line position; this was apparently caused by the large (up to one degree) superheating of the sample when the power incident on the cavity was increased.

5. EFFECT OF NUCLEAR ORDERING ON ANTIFERROMAGNETIC RESONANCE

The relatively large energy gap cannot be attributed to crystalline anisotropy. On the other hand, the strong temperature dependence suggests that it is connected with the degree of ordering of the nuclear moments—the only parameter that can change significantly in the temperature region under consideration. A similar effect was found in an investigation of the antiferromagnetic resonance of KMnF$_3$.[10] In that paper a theoretical analysis was given of the effect of ordering of the nuclear system on the antiferromagnetic resonance.

If, as usual, we represent the hyperfine interaction energy in the form

$$W = A\mathbf{SI}, \tag{4}$$

then at low temperatures, when the electron spins in antiferromagnets are completely ordered ($\langle \mathbf{S} \rangle = S$, where S is the spin quantum number), a strong effective field $H^{\text{eff}}_S = AS/h\gamma_n$ acts on the nuclear spins. This field brings about noticeable incipient ordering of the nuclear moments even at helium temperatures, which is confirmed by the heat capacity measurements on MnCO$_3$,[11] in which a significant contribution from nuclear ordering of the form $c_n = bT^{-2}$ has been observed below 2° K. The hfs constant can be determined from the value b = 2.7 × 10^5 erg-deg/mole obtained from the measurements $(A/K) = \sqrt{(b/R)(48/875)} = 0.013°$ K. In an antiferromagnet the ordered nuclei form sublattices corresponding to the sublattices of the electron spins. In accordance with Eq. (4), we can introduce in each of these sublattices an effective field produced at the electrons by the ordered nuclei:

$$H^{\text{eff}}_I = \frac{kI(I+1)S}{3g\beta}\left(\frac{A}{K}\right)^2\frac{1}{T}, \tag{5}$$

where I = $^5/_2$, the nuclear spin of Mn^{55}, and β is the Bohr magneton. It must be emphasized that the direction of this field coincides with the direction of magnetization of the sublattices. However, during antiferromagnetic resonance in MnCO$_3$ the magnetization vectors of the sublattices execute in the centimeter region vibrations with a frequency $\nu_{\text{res}} \sim 10^{10}$ c/sec relative to their static equilibrium position. This frequency is several times larger than the characteristic frequency of the nuclear system in the effective field of the hfs interaction $\nu_n = \gamma_n H_S^{\text{eff}} = AS/h = 690$ Mc/sec. Therefore during antiferromagnetic resonance the nuclear system will not oscillate together with the electron spins, and the field H_I^{eff} will act as an effective anisotropy field, always directed along the direction of magnetization of the sublattices. This field should produce in the spectrum[12] an energy gap equal to

$$H^2_{\Delta 1} = 2H_E H_I^{\text{eff}} = \frac{19\cdot 10^{-3} H_E}{T} \quad [\text{kOe}^2], \qquad (6)$$

where H_E is the effective field of the exchange interaction between sublattices. The experimental temperature dependence of $H^2_{\Delta 1}$ confirms Eq. (6) and offers convincing evidence of the validity of this mechanism for creation of the gap. It should be emphasized that a strong shift of the resonance line under the action of the field of the ordered nuclei is a special property of antiferromagnets in which a weak anisotropy field is multiplied by a large exchange field. From our data for the magnitude of the coefficient $a = 19 \times 10^{-3} H_E$ we found the magnitude of the effective exchange field to be $H_E = 300$ kOe. Since the magnetization of the sublattices in the ground state $M_0 = \chi_\perp H_E$, we obtain $M_0 = 13 \times 10^3$ G. This is in good agreement with the value $M_0 = \frac{1}{2} Ng\beta S = 14 \times 10^3$ G obtained under the assumption of complete saturation of the spin moments. Unfortunately, at the present time the error in our value for M_0, which is caused principally by the error in determining the hfs constant, amounts to approximately 15%. Hence for the time being we can state that the magnetization of the sublattices in the ground state of antiferromagnetic $MnCO_3$ differs from the nominal value by not more than 25%. However, it should not be too difficult to increase the accuracy of the hfs constant, and it seems to us that the method set forth is an important one for the study of the ground state of an antiferromagnet.

The authors sincerely thank P. L. Kapitza for his constant interest in the work, and M. S. Khaĭkin and S. P. Kapitza for valuable advice in the development of the apparatus.

---

[1] A. S. Borovik-Romanov, JETP **36**, 766 (1959), Soviet Phys. JETP **9**, 539 (1959).

[2] E. A. Turov, JETP **36**, 1254 (1959), Soviet Phys. JETP **9**, 890 (1959).

[3] E. A. Turov and N. G. Guseĭnov, JETP **38**, 1326 (1960), Soviet Phys. JETP **11**, 955 (1960).

[4] Anderson, Merrit, Remeika, and Jager, Phys. Rev. **93**, 717 (1954).

[5] Kumagai, Abe, Ono, Hayashi, Shimada, and Iwanaga, Phys. Rev. **99**, 1116 (1955).

[6] M. Date, J. Phys. Soc. Japan **15**, 2251 (1960).

[7] A. S. Borovik-Romanov, Int. Confer. on Magnetism and Crystallography, Kyoto, Japan, 1961.

[8] N. Yu. Ikornikova, Kristallografiya **6**, 745 (1961), Soviet Phys. Cryst. **6**, 594 (1962).

[9] Jan Kacer and N. M. Kreĭnes, JETP **41**, 1691 (1961), Soviet Phys. JETP **14**, 1202 (1962).

[10] Heeger, Portis, Teaney, and Witt, Phys. Rev. Letters **7**, 307 (1961).

[11] A. S. Borovik-Romanov and I. N. Kalinkina, JETP **41**, 1694 (1961), Soviet Phys. JETP **14**, 1205 (1962).

[12] P. Pincus, Phys. Rev. Letters **5**, 13 (1960).

Translated by L. M. Matarrese
13