

INVESTIGATION OF THE EFFECT OF Mn^{2+} AND Fe^{2+} IMPURITIES ON THE ANTIFERRO-
MAGNETIC RESONANCE SPECTRUM IN $CoCO_3$

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Submitted January 27, 1971

Zh. Eksp. Teor. Fiz. 61, 320-331 (July, 1971)

The low-frequency branch of the antiferromagnetic resonance has been investigated both in pure $CoCO_3$ and in specimens of $CoCO_3$ containing Mn^{2+} and Fe^{2+} impurities in an amount $\leq 1.2\%$. Measurements were made over the frequency range from 23 to 60 GHz and over the temperature range from 1.2 to $12^\circ K$. It was found that in specimens with iron impurity, the low-frequency branch of the AFMR spectrum corresponds to pure $CoCO_3$. At frequency 45 GHz, however ($T = 4.2^\circ K$), splitting of the spectrum is observed. The temperature dependence and angular dependence of the position and magnitude of the splitting were studied in detail. A theoretical analysis was made of the observed phenomenon. The experimental results are described well by the results of the calculation. A study of specimens containing manganese impurity showed that this additive leads to a decrease of the magnitude of the Dzyaloshinskiĭ field H_D from 52 to 34 kOe. In this case no splitting of the spectrum was observed.

1. INTRODUCTION

THERE have recently been appearing an ever increasing number of papers, both theoretical and experimental, devoted to investigation of the effect of magnetic impurities on the behavior of magnetically ordered systems. This interest has arisen primarily because a small concentration of impurity, $\sim 1\%$, leads to a significant change of the properties of these systems. In the case of static measurements, the effect of the impurity manifests itself in a change of the susceptibility^[1], the magnetization, and the ordering temperature^[2]. In resonance measurements, the disturbances introduced by the impurities reduce to two cases: a) there is a change in the constants in the resonance-spectrum formulas, although the form of the formulas is retained^[3,4]; and b) additional absorption lines appear, corresponding to the so-called impurity modes^[4-7].

A qualitative picture of the impurity spin states in one-dimensional magnetically ordered systems has been described most completely, physically, by Weber^[8]. The frequency of the impurity modes is found to be, in first approximation, of the order of magnitude of the exchange interaction between the spins of the basic system and the impurity spin. When the frequencies of the excitations caused by the impurity lie outside the spin-wave band of the unperturbed system, these excitations are localized. In this case the amplitude of the spin precession falls off exponentially with distance from the position of the impurity. Local modes whose frequencies lie above the spin-wave band are called optical. These modes have been repeatedly observed in antiferromagnets of the "easy axis" type: in MnF_2 doped with cobalt^[9-11], iron^[11-14], and nickel^[14-16] impurity, and in $KMnF_3$ and $RbMnF_3$ with nickel^[16] and europium^[17] impurity.

When there is a gap in the spin-wave spectrum, localized "gap" modes can occur, whose frequencies lie below the spin-wave band. They have been observed

in the uniaxial antiferromagnets $FeCl_2$ with impurity Fe^{3+} and Mn^{2+} ,^[5] $CoCl_2 \cdot 2H_2O + Mn^{2+}$,^[6] $RbMnF_3 + Co^{2+}$,^[4] and $MnF_2 + Er^{2+}$.^[7]

Excitations caused by impurities have a nonlocal character if they lie inside the spin-wave band. The amplitude of the spin precession does not attenuate exponentially, as in the case of the localized modes, but remains finite for all spins of the lattice. We know of two experimental results that corroborate the existence of these states. Introduction of diamagnetic zinc into MnF_2 ^[18] leads to a resonance excitation caused by a change in the state of the Mn^{2+} ions surrounding the zinc. An isolated frequency occurs also in the system $Tb + Ho$ ^[19].

The present paper presents the results of resonance measurements in the low-frequency branch of the spectrum in an antiferromagnet of the "easy plane" type, $CoCO_3$. In an earlier investigation^[20] of antiferromagnetic resonance (AFMR) in $CoCO_3$, a splitting of the spectrum was observed at a frequency ~ 45 GHz. It was not possible at that time to determine the causes of the observed phenomenon. In the present paper, it is shown that this splitting is caused by the presence of iron impurity in the specimens. A parallel study was made of specimens of $CoCO_3$ into which manganese impurity had been introduced.

The crystallographic symmetry of $CoCO_3$ is described by space group D_{3d}^5 . At temperatures below $T_N = 18.1^\circ K$, there occurs antiferromagnetic ordering of the spins^[21], which lie in the basal plane, perpendicular to the axis C_3 . The presence of a Dzyaloshinskiĭ interaction leads to a canting of the spins, in consequence of which there is a weak ferromagnetic moment. An external magnetic field always orients the magnetic moment along the projection of the magnetic field on the basal plane.

The static and dynamic properties of $CoCO_3$ have been studied in considerable detail^[21-24]. For the low-frequency branch of the AFMR spectrum, which was studied in the present paper, the dependence of reso-

nance frequency on magnetic field, without allowance for anisotropy in the basal plane, has the form^[25]

$$\left(\frac{\omega_{01}}{\gamma_1}\right)^2 = \frac{\chi_{\perp}}{\chi_{\parallel}}(H \sin \theta + H_D)H \sin \theta, \quad (1)$$

where γ_1 is the gyromagnetic ratio, corresponding to $g = 2.7$; $\chi_{\perp} = 1.85 \cdot 10^{-3}$, $\chi_{\parallel} = 1.21 \cdot 10^{-3}$ are the static susceptibilities in the basal plane and along C_3 ^[21]; $H_D = 52$ kOe is the Dzyaloshinskii field; and θ is the angle between the external magnetic field H and the axis C_3 of the crystal.

2. SPECIMENS AND METHOD OF MEASUREMENT

The $CoCO_3$ crystals were obtained by the method of hydrothermal synthesis. This method, for carbonates of the transition elements, was developed in detail in the papers of Ikornikova^[26-28]. In separate experiments, free carbon dioxide (in the form of "dry ice") was replaced by ammonium carbonate, $(NH_4)_2CO_3$, whose concentration was ~ 1.4 moles per liter of solvent. The solvent, the temperature, and the pressure corresponded to those indicated in^[26-28].

We discovered that the $CoCO_3$ specimens investigated in^[20] contained iron impurity from 0.2 to 2%. For synthesis of these crystals, $CoCO_3 \cdot Co(OH)_2 \cdot nH_2O$ powder, brand ChDA (analysis grade), was used, in which the iron content amounted to $\sim 0.002\%$. A possible reason for the occurrence of a larger iron content in the grown specimens is contact of the solution with the body of the autoclave. Therefore we paid special attention to the method of isolating the solution from the body of the autoclave.

Previously, in autoclaves lined with platinum or titanium, a cap made of the same material was tightened with an obturator. Apparently the obturator became loosened by the internal pressure and the solution made contact with the body of the autoclave, which led to an increase of iron content in the solution.

Figure 1 pictures the seal to the autoclave, which is lined with titanium. The base of the obturator is made of titanium. A teflon ring is the sealing element of this seal. A conical titanium ring restrains the teflon from slipping into the working space. The teflon is restrained from slipping upward by a copper ring. With its lower part, the teflon ring pushes against the titanium ring and the base of the obturator. Thus the solution is completely isolated from the body of the autoclave. In such an autoclave, $CoCO_3$ crystals were obtained that contained no iron impurity and that had a line width $\Delta H = 30$ Oe. As a source of carbon dioxide in these experiments, ammonium carbonate was used.

$CoCO_3$ crystals synthesized in a floating titanium bushing also contained no iron impurity. This method

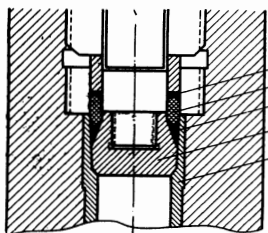


FIG. 1. Schematic drawing of the autoclave seal: 1—titanium lining; 2—titanium base of the obturator; 3—titanium ring; 4—teflon ring; 5—copper ring.

of isolating the solution was good only because the pressure inside the bushing exceeds the pressure between the wall of the autoclave and the bushing. Therefore the solution can only go out from the bushing. In regions isolated by this method, $CoCO_3$ crystals were obtained that contained manganese in the amount of 1 to 2%, which was specially introduced in the form of a charge of $MnCO_3$ in the proportion 1:100.

The iron and manganese impurity content in the specimens was determined after the resonance measurements were made. The analysis was made with the aid of an x-ray microanalyzer MS-46¹⁾. The absolute accuracy of the impurity determination was 0.2%, and the relative accuracy 0.1%.

The $CoCO_3$ monocrystals had the form of plates of irregular shape, with transverse dimension 0.5 to 1.5 mm and thickness 0.1 to 1 mm. The plane of the plates always coincided with the basal plane of the crystal, which was checked by x-ray investigations. To obtain minimum AFMR linewidth, all specimens were made into the form of disks^[23].

The measurements were made on a direct-amplification spectrometer over the frequency range from 23 to 60 GHz. The specimens were placed in the end of a shorted waveguide, which permitted easy change of the spectrometer frequency. In studying the angular dependence, the specimen was placed on the narrow wall of the waveguide at a distance of 1.5 mm from the shorted end. The amplified signal of change of intensity of reflected microwave power as a function of external magnetic field was registered on an x-y recorder. Stabilization and measurement of the temperature in the interval from 4.2 to 12°K were accomplished with the aid of a (Au-Fe) + Cu thermocouple, with an accuracy of 0.1°.

3. EXPERIMENTAL RESULTS

A. Specimens of $CoCO_3$ and $CoCO_3 + Mn^{2+}$

In^[24], in an investigation of the low-frequency AFMR branch in $CoCO_3$ over the frequency range from 55 to 185 GHz at $T = 4.2^\circ K$, it was shown that when the magnetic field lies in the basal plane ($\theta = 90^\circ$), the frequency dependence of the spectrum is described by

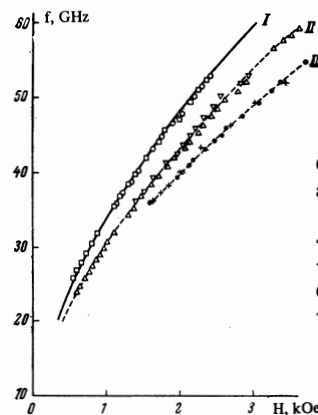


FIG. 2. AFMR spectra for various $CoCO_3$ specimens, taken at $T = 4.2^\circ K$ and with $H \perp C_3$; O and □—specimens 1 and 2; Δ and ∇—specimens 3M and 4M, containing manganese impurity $\sim 1.2\%$; + and ●—specimens 5M and 6M, containing manganese impurity $\sim 2.4\%$.

¹⁾The authors express their thanks to V. Matyskin for performing the impurity analysis.

Table I

CoCO ₃ Specimens	% Mn Impurity	H _D , kOe (g = 2.7)	ΔH, Oe
1M	<0.1	52	50
3M, 4M	1	42	100
5M, 6M	2.4	34	200

Note: Measurements at T = 4.2°K, H ⊥ C₃.

the expression (1). Curve I in Fig. 2 corresponds to this formula. It is seen that for CoCO₃ specimens in which no impurities were detected, the experimental points lie well on the extrapolated curve.

The same figure shows the results of measurements of the frequency dependence for CoCO₃ specimens with manganese concentrations ~1 and 2.4%. Addition of manganese leads to increase of the resonance field and broadening of the AMFR line-width (see Table I). The frequency dependence of the specimens investigated can be satisfactorily described by formula (1), but with different values of H_D (Table I). The experimental points fall well on curves II and III, which were constructed on the assumption that expression (1) is valid and that H_D is equal to 42 and to 34 kOe, respectively. Investigations of the angular dependence also supported the validity of formula (1) with values of H_D taken from Table I, both for the pure specimens and for the specimens doped with Mn²⁺.

B. Specimens of CoCO₃ + Fe²⁺

Our measurements showed that far away from the splitting, the frequency dependence of the resonance field for specimens of CoCO₃ containing iron impurity is described by expression (1), with a γ₁ and H_D corresponding to pure CoCO₃. At frequency γ ~ 45 GHz, however, a splitting of the spectrum is observed. The results of investigation of the frequency dependence in the region of splitting are shown in Fig. 3, where the solid curve corresponds to pure CoCO₃. The external magnetic field lies in the basal plane of the crystal; the temperature of the specimens is 4.2°K. It is seen that the frequency of the splitting is independent of the iron concentration and is the same for all the specimens, whereas the amount of splitting Δf²⁾, as well as the line-width ΔH, is determined by the amount of iron impurity (Table II).

At the same temperature, the angular dependence of the splitting was studied on one of the specimens (Fig. 4). When the magnetic field went out of the basal plane and the frequency f > 45 GHz, two absorption lines were observed. At small values of the angle θ between the external magnetic field and the axis C₃ of the crystal, the position of the line located at low fields was practically independent of this angle, and its dependence on the field for g = 2 can be described by the expression

$$(\omega/\gamma)^2 = (16 \text{ kOe})^2 + 11H^2 \cos^2 \theta. \quad (2)$$

But as can be seen from Fig. 5, the intensity of this line falls rapidly at small θ.

²⁾For the determination of Δf, see Fig. 9.

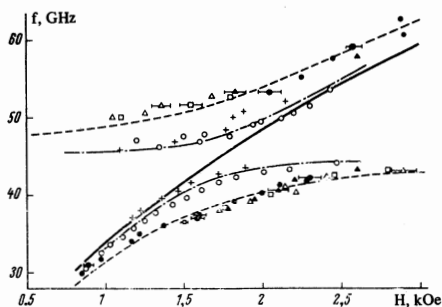


FIG. 3. AFMR spectra for various specimens of CoCO₃ containing iron impurity, at T = 4.2°K and with H ⊥ C₃: + and O—specimens 2I and 3I, containing iron impurity ~0.2%; ▲ and ●—specimens 4I and 5I, containing iron impurity ~1%; Δ and □—specimens 6I and 7I, containing iron impurity ~1.2%.

Table II

CoCO ₃ Specimens	% Mn Impurity	f ₀ , GHz	Δf, GHz	ΔH, μ
1I	0.1	45	—	30
2I, 3I	0.2	45	5	30
4I, 5I	1	45	14	150
6I, 7I	1.2	45	14	250

Note: Measurements at T = 4.2°K and H ⊥ C₃. Here f₀ is the frequency of splitting and ΔH is the AFMR line-width far away from the splitting, for f = 30 GHz.

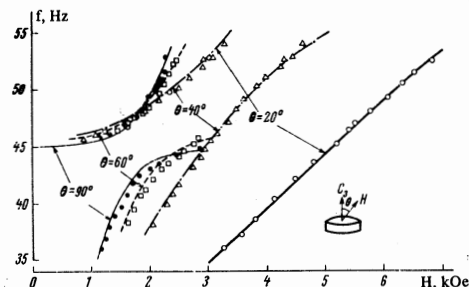


FIG. 4. Frequency dependence of AFMR spectrum for specimen 2I for various values of the angle θ, and at T = 4.2°K: O—θ = 20°; Δ—θ = 40°; ●—θ = 90°. Curves calculated by formula (13) for various θ's (indicated on the curves).

It was shown earlier^[20] that the amount of the splitting depends strongly on temperature. We made more careful temperature measurements. For this purpose, at each temperature the whole AFMR spectrum was taken, over the range from 36 to 53 GHz. This made possible a direct judgment of the magnitude and location of the splitting. The magnetic field in this case was always directed perpendicular to the axis C₃. Investigations were made on specimens containing different quantities of Fe²⁺ impurity. The results of the measurements for one of the specimens are shown in Fig. 6.

With rise of temperature, the frequency and amount of the splitting decrease. In specimens with different impurity content, the splitting disappears at different temperatures. On further increase of temperature,

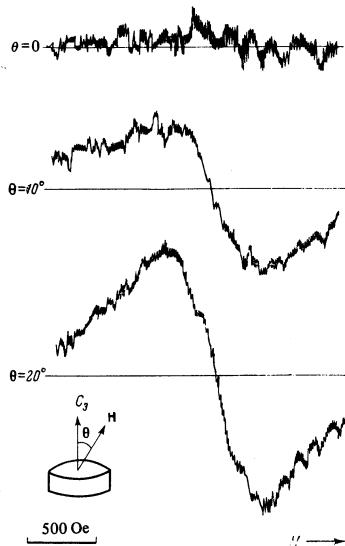


FIG. 5. Absorption-line record for various angles θ for specimen 2I; $f = 52.8$ GHz, $T = 4.2^\circ\text{K}$.

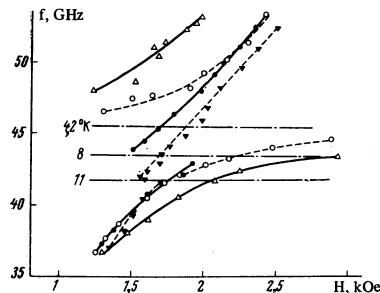


FIG. 6. AMR spectrum for specimen 2I at various temperatures ($H \perp C_3$): Δ — 1.2°K ; \circ — 4.2°K ; \bullet — 8°K ; \blacktriangledown — 11°K . The horizontal dotted lines correspond to the frequency of splitting.

there remains the effect of broadening of the AFMR line at the frequency of intersection of the branches (Fig. 7). This permitted a quite accurate determination of the frequency of interest. Thus was determined the temperature dependence of the splitting frequency, shown in Fig. 8. The agreement of the results for specimens with a different amount of splitting shows that the splitting frequency is independent of the impurity concentration.

We succeeded in determining the temperature dependence of the amount of splitting Δf (Fig. 9). It was found that the amount of splitting is not approximated by a power law, but changes with temperature according to the law $\Delta f/f_0 = k \log(T/T_N)$, where $T_N = 18^\circ\text{K}$.

4. THEORETICAL TREATMENT

We shall use a simple model. In one of the sublattices of the CoCO_3 antiferromagnet, impurity atoms replace Co atoms. This supposition does not decrease the generality of the results obtained, since within the framework of our discussions the impurity atoms located on the different sublattices are equivalent. The concentration of impurity atoms is so small that interaction of their magnetic moments with each other can

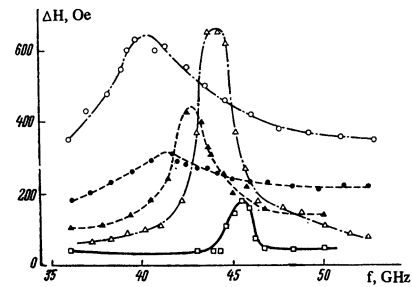


FIG. 7. Frequency dependence of AFMR line-width for various specimens at various temperatures ($H \perp C_3$): \square —specimen 1I, $T = 1.2^\circ\text{K}$; Δ , \blacktriangle , \bullet —specimen 2I at temperatures Δ — 7°K , \blacktriangle — 9°K , \bullet — 11°K ; \circ —specimen 4I, $T = 12^\circ\text{K}$.

be neglected. We shall also not take account of the fact that introduction of an impurity changes the state of the ions surrounding it. Starting with these assumptions, we shall try to determine the possible spectrum, of such a system.

As is known from the theory of weak solutions^[29], the thermodynamic potential, correct through terms linear in the concentration, can be written in the form

$$\Phi = \Phi_0 + c\Phi_1, \quad (3)$$

where Φ_0 is the thermodynamic potential of the pure substance, Φ_1 is the term due to the presence of the impurity, and c is the impurity concentration. In our case, as was shown by Dzyaloshinskii^[30], Φ_0 , correct through terms of second order in the magnetic moment, has the form

$$\begin{aligned} \Phi_0 = & \frac{1}{2}Bm^2 + \frac{1}{2}al_z^2 \\ & + \frac{1}{2}bm_x^2 + q(l_xm_y \\ & - l_y m_x) - mh. \end{aligned} \quad (4)$$

The z axis is directed along the axis C_3 of the crystal, the x axis along one of the second-order axes lying in the basal plane. Here the following symbols have been introduced: M_1 and M_2 are the magnetic moments of the sublattices per unit volume,

$$\begin{aligned} M_1^2 = M_2^2 = M_0^2, \\ m = \frac{M_1 + M_2}{2M_0}, \\ l = \frac{M_1 - M_2}{2M_0} \end{aligned}$$

and $h = 2M_0H$, where H is the external magnetic field. For the case $H_x \neq H_z \neq 0$, $H_y = 0$, we get from (4) for the ground state

$$\begin{aligned} m_y = l_x = l_z = 0, \quad l_y \approx 1; \\ 2M_0m_x = \chi_{\perp}(H_x + H_D), \quad H_D = \frac{q}{2M_0}, \quad \chi_{\perp} = \frac{4M_0^2}{B}, \\ 2M_0m_z = \chi_{\parallel}H_z, \quad \chi_{\parallel} = 4M_0^2/(B + b). \end{aligned} \quad (5)$$

From (4) is also obtained the expression (1), which describes the low-frequency branch of the AMFR.

The term Φ_1 , due to the presence of the impurity, we shall write in the form

$$\Phi_1 = -(H_E l \sigma + H_T m \sigma + \frac{1}{2}G \sigma^2 + \sigma H), \quad (6)$$

where σ is the magnetic moment of the impurity per unit volume. The values of H_E and of H_T are deter-

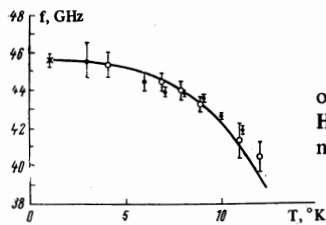


FIG. 8. Temperature dependence of the frequency of splitting with $H \perp C_3$: O—specimen 2I; O—specimen 4I; X—specimen 1I.

mined by the difference and the sum, respectively, of the exchange interactions of the impurity with the sublattices. In order to explain the angular dependence (2), it would be necessary to introduce a term $\frac{1}{2}G\sigma_Z^2$, describing the single-ion anisotropy. The negative sign of the anisotropy constant was chosen in accordance with the fact that for $T < T_N$, the spins in FeCO_3 are arranged along C_3 . In the expression (6) we shall omit the term proportional to $\mathbf{m} \cdot \boldsymbol{\sigma}$, since calculations have shown that the corrections introduced by this term are small.

First we shall determine the ground state of the impurity and its spectrum, considering oscillations of the magnetic moment of the impurity without allowance for the coupling with oscillations of the spins of the basic system. In angular variables, for $H_x \neq H_z \neq 0$ and $H_y = 0$, with use of (5), the expression (6) can be rewritten in the form

$$\Phi_1 = -\sigma(H_x \cos \varphi + H_z \sin \varphi) \sin \psi - \sigma H_x \cos \psi - \frac{1}{2}G\sigma^2 \cos^2 \psi, \quad (7)$$

where ψ and φ are the polar and azimuthal angles between the impurity magnetization σ and the axes z ($\parallel C_3$) and x ($\parallel C_2$). The equilibrium position of the impurity magnetization is determined by minimization of (7), which gives

$$\text{tg } \varphi = H_E/H_x, \quad H_A \sin \psi \cos \psi + H_z \sin \psi - H_x \cos \psi = 0, \quad (8)$$

where $H_A = G\sigma$ and $H_x^2 = H_x^2 + H_E^2$.

The resonance frequency for the impurity, in angular variables, is determined from the equation

$$\left(\frac{\omega_{02}}{\gamma_2}\right)^2 = \left[\frac{\partial^2 \Phi_1}{\partial \psi^2} \frac{\partial^2 \Phi_1}{\partial \varphi^2} - \left(\frac{\partial^2 \Phi_1}{\partial \psi \partial \varphi} \right)^2 \right] \frac{1}{(\sigma \sin \psi)^2}, \quad (9)$$

which in our case takes the form

$$\left(\frac{\omega_{02}}{\gamma_2}\right)^2 = H_x^2 + H_z H_x \text{ctg } \psi + H_A H_x \frac{\cos 2\psi}{\sin \psi}. \quad (10)$$

Solutions of equations (8) and (10), corresponding to the observed spectrum (2), are obtained if one sets $\psi = \frac{1}{2}\pi - \Delta$, where $\Delta \ll 1$. This is the case when $H_E > H_A$ and $H_z \ll H_E - H_A$. Then $\Delta = H_z/(H_E - H_A)$, and

$$\left(\frac{\omega_{02}}{\gamma_2}\right)^2 = H_x(H_E - H_A) + \left(1 - \frac{H_A}{2H_E}\right) H_x^2 + \frac{2H_E^2 + H_A H_E}{2(H_E - H_A)^2} H_x^2. \quad (11)$$

Agreement with the observed spectrum (2) is obtained with the values $H_A = 18$ kOe and $H_E = 27$ kOe. The coefficient of H_x^2 obtained is 15 times smaller than that of H_z^2 ; and experimentally, of course, we were not able to observe this dependence.

Now, with knowledge of the ground state of the impurity, it is possible, by starting with the thermodynamic potential (3), to obtain an expression for the resonance frequency of coupled oscillations of the impurity and the basic system. For simplicity we shall suppose that the external magnetic field lies in the

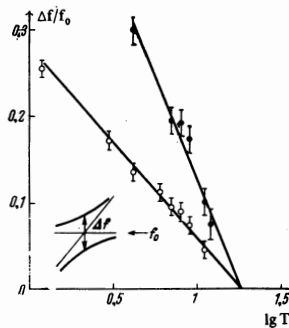


FIG. 9. Temperature dependence of the amount of splitting for two specimens with $H \perp C_3$: ●—2I; ○—4I.

basal plane and is directed along the x axis. In Cartesian coordinates, the equations of motion are written thus:

$$\begin{aligned} \frac{2M_0}{\gamma_1} \frac{d\mathbf{m}}{dt} &= \left[\mathbf{m} \frac{\partial \Phi}{\partial \mathbf{m}} \right] + \left[\mathbf{l} \frac{\partial \Phi}{\partial \mathbf{l}} \right], \\ \frac{2M_0}{\gamma_1} \frac{d\mathbf{l}}{dt} &= \left[\mathbf{m} \frac{\partial \Phi}{\partial \mathbf{l}} \right] + \left[\mathbf{l} \frac{\partial \Phi}{\partial \mathbf{m}} \right], \\ \frac{c}{\gamma_2} \frac{\partial \boldsymbol{\sigma}}{\partial t} &= \left[\boldsymbol{\sigma} \frac{\partial \Phi}{\partial \boldsymbol{\sigma}} \right]. \end{aligned} \quad (12)^*$$

The low-frequency branch of the AFMR in CoCO_3 is caused by oscillations of the components m_y , m_z , and l_x . By considering only these components and solving equations (12), we get

$$\omega^4 - (\omega_{01}^2 + \omega_{02}^2 + cQ^2)\omega^2 + \omega_{01}^2\omega_{02}^2 = 0, \quad (13)$$

where

$$Q^2 = \gamma_1 H_E \sigma / \chi_{ii}, \quad (14)$$

and where ω_{01} and ω_{02} are determined by equations (1) and (11) respectively ($H_z = 0$).

From (13) it is possible to find the amount of the splitting $\Delta\omega$, which corresponds to the condition $\omega_{01} = \omega_{02}$. We have as the result

$$\Delta\omega = \gamma c \bar{Q}. \quad (15)$$

5. DISCUSSION OF THE RESULTS OBTAINED, AND COMPARISON OF THEM WITH THEORY

We shall first discuss the results of the measurements on specimens with iron impurity. Figure 3 shows, dotted, the curves calculated by formula (13), where, in accordance with (15), $cQ^2 = (2\pi\Delta f)^2$. Our treatment was carried out for the case that the external magnetic field lay in the basal plane. The value of the field however does not enter into formula (14) for the magnitude of the coupling. Therefore, assuming the correctness of (13) for arbitrary orientation of the magnetic field, where ω_{01} is determined by (1) and ω_{02} by (11), we constructed the curves shown in Fig. 4. In this case also there is good agreement of the observed frequency dependence with the calculated, for various orientations of the external magnetic field.

From our discussions it is seen that the frequency of the impurity mode ω_{02} is proportional to the magnetization of the sublattices. The results of static measurements^[21] show that the magnetization of the sublattices decreases with temperature, as T^2 . The solid curve in Fig. 8, constructed thus, corroborates

* $\left[\mathbf{m} \frac{\partial \Phi}{\partial \mathbf{m}} \right] \equiv \mathbf{m} \times \partial \Phi / \partial \mathbf{m}$.

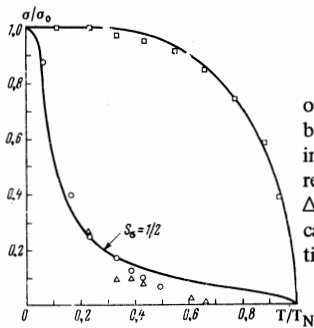


FIG. 10. Temperature dependence of the reduced magnetizations of the basic systems (upper curve) and of the impurity (lower curve, $S_G = 1/2$). \square —results of static measurements; points Δ (specimen 2I) and \circ (specimen 4I), calculated from the amount of splitting according to formula (16).

our result. The temperature dependence of the amount of splitting has a different character (Fig. 9). In the temperature range $T < 5^\circ K$, where the splitting frequency remains practically constant, a strong temperature dependence of the amount of splitting is observed. This fact can be explained in the following way.

In accordance with formulas (14) and (15), the amount of splitting can be written in the form

$$\Delta f = (c\gamma_i^2 H_E \sigma / 4\pi^2 \chi_{||})^{1/2}. \quad (16)$$

Because H_E and $\chi_{||} = 1.21 \times 10^{-3}$ [21] do not change in this temperature range, the whole temperature dependence of the amount of splitting, as follows from (16), is contained in the temperature dependence of the impurity magnetization. Within the framework of our discussions, the magnetic moment of the impurity is considered as purely paramagnetic, in an effective field that, in accordance with (11), is expressed as $H_{eff} = [H_E(H_E - H_A)]^{1/2} = 16$ kOe. Then the temperature dependence of the impurity magnetization can be determined by using the molecular-field model. For this purpose, we construct the Brillouin function $B_{S_G}(y)$ with

$$y = \frac{g\beta S_G H_r \sigma}{kT}, \quad H_r \sigma = H_{eff} \frac{M_T}{M_0} \quad (17)$$

where S_G is the impurity spin, and M_T and M_0 are the magnetizations of the sublattices of the basis system at $T \neq 0$ and $T = 0$, respectively.

In Fig. 10, a curve has been plotted that describes the change of magnetization of the sublattices of the basic system (upper curve). The experimental points are taken from [21]. The lower curve, calculated from (17), describes the temperature dependence of the impurity magnetization for $S_G = 1/2$. The experimental points on this curve were obtained from the temperature dependence of the amount of splitting according to formula (16). For this, the values used were $\sigma_0 = 600$ cgs emu/cm³ for $T = 0$, $c_1 = 0.1\%$ for specimen 2I, and $c_2 = 0.95$ for specimen 4I. The values obtained for the concentrations c_1 and c_2 agree in order of magnitude with the measured values (Table II).

In specimens of $CoCO_3$ containing manganese impurity, over the frequency range that we investigated, up to 80 GHz, the additional branch of the absorption was not observed. At the same time, the effective value of H_D decreased from 52 kOe for pure $CoCO_3$ to 34 kOe when the content of manganese impurity was $\sim 2.4\%$ (Table I). A similar effect was observed in hematite [3], which addition of Ti^{4+} of the order of 0.4% changed H_D from 22 to 16 kOe. It may be supposed that the interaction of manganese with cobalt is far

greater than in the case of iron. Then the frequency of the impurity mode should lie above the frequency range investigated by us. At the same time, the larger size of the interaction should lead to a larger change of the effective fields on introduction of manganese impurity.

6. CONCLUSION

Introduction of iron impurity into $CoCO_3$ leads to the appearance of an additional branch of the oscillations, whose frequency is independent of the impurity concentration and diminishes with increase of temperature in proportion to the sublattice magnetization ($\propto T^2$). The amount of the splitting increases with increase of impurity concentration and decreases with increase of temperature, as $\log(T/T_N)$. The experimentally observed angular dependence of the splitting (Fig. 4) can be described by assuming the presence, at the impurity, of a single-ion anisotropy field $H_A = 18$ kOe, directed along the axis C_3 , and of an exchange field $H_E = 27$ kOe. Far away from the splitting, the AFMR spectrum of $CoCO_3$ with iron impurity corresponds to the same value $H_D = 52$ kOe as for pure $CoCO_3$. It must be emphasized that in $FeCO_3$ the exchange field ~ 240 kOe, whereas in our case the field H_E acting on the Fe^{2+} impurity is orders of magnitude smaller.

In $CoCO_3$ there is observed a considerable difference in the values of H_D obtained earlier from static [21] ($H_D = 27$ kOe) and resonance [24] measurements ($H_D = 52$ kOe). It is therefore of interest to carry out static and resonance measurements on the same specimens, in order to establish whether this difference is connected with impurities.

In specimens of $CoCO_3$ with Mn^{2+} impurity, over the frequency range investigated by us, the additional branch of the absorption was not observed. However, the AFMR spectrum is described by other values of H_D , whose magnitudes are determined by the concentration of manganese impurity.

In conclusion, the authors express their deep thanks to P. L. Kapitza for constant interest in the research and are very thankful to A. S. Borovik-Romanov for valuable advice and for discussions of the results obtained. The authors are grateful to N. Yu. Ikornikova for growing the crystals and to V. A. Tulin, M. A. Savchenko, V. V. Tarasenko, and V. A. Kalganov for numerous and helpful discussions.

¹T. Miyashita, H. Kond, and S. Miyahara, *J. Phys. Soc. Japan* **27**, 256 (1969).

²Y. Kasai, S. Miyazima, and I. Syozi, *Progr. Theoret. Phys. (Kyoto)* **42**, 1 (1969).

³A. H. Morrish and C. W. Searle, *Proc. Intern. Conf. Magnetism, Nottingham, 1964* (London, 1965), p. 574.

⁴W. J. Ince, D. Gabbe, and A. Linz, *Phys. Rev.* **185**, 482 (1969).

⁵M. Motokawa and M. Date, *J. Phys. Soc. Japan* **23**, 1216 (1967).

⁶N. Fujii, M. Motokawa, and M. Date, *J. Phys. Soc. Japan* **25**, 700 (1968).

- ⁷L. L. Chase and H. J. Guggenheim, *Bull. Am. Phys. Soc.* **13**, 390 (1968).
- ⁸R. Weber, *Z. Physik* **223**, 299 (1969).
- ⁹T. M. Holden, R. A. Cowley, W. J. L. Buyers, and R. W. H. Stevenson, *Solid State Comm.* **6**, 145 (1968).
- ¹⁰T. M. Holden, W. J. L. Buyers, and R. W. H. Stevenson, *J. Appl. Phys.* **40**, 991 (1969).
- ¹¹R. Weber, *J. Appl. Phys.* **40**, 995 (1969).
- ¹²R. Weber, *Phys. Rev. Lett.* **21**, 1260 (1968).
- ¹³R. Blewitt and R. Weber, *J. Appl. Phys.* **41**, 884 (1970).
- ¹⁴A. Oseroff and P. S. Pershan, *Phys. Rev. Lett.* **21**, 1593 (1968).
- ¹⁵P. Moch, G. Parisot, R. E. Dietz, and H. J. Guggenheim, *Phys. Rev. Lett.* **21**, 1596 (1968).
- ¹⁶L. F. Johnson, R. E. Dietz, and H. J. Guggenheim, *Phys. Rev. Lett.* **17**, 13 (1966).
- ¹⁷S. Shionoya and M. Hirano, *Phys. Lett.* **26A**, 533 (1968).
- ¹⁸E. C. Svensson, T. M. Holden, W. J. L. Buyers, R. A. Cowley, and R. W. H. Stevenson, *Solid State Commun.* **7**, 1693 (1969).
- ¹⁹H. B. Møller, J. C. G. Houmann, and A. R. Mackintosh, *Phys. Rev. Lett.* **19**, 312 (1967).
- ²⁰A. S. Borovik-Romanov and V. F. Meshcheryakov, *ZhETF Pis. Red.* **8**, 425 (1968) [*JETP Lett.* **8**, 262 (1968)].
- ²¹A. S. Borovik-Romanov and V. I. Ozhogin, *Zh. Eksp. Teor. Fiz.* **39**, 27 (1960) [*Sov. Phys.-JETP* **12**, 18 (1961)].
- ²²E. G. Rudashevskii, *Zh. Eksp. Teor. Fiz.* **46**, 134 (1964) [*Sov. Phys.-JETP* **19**, 96 (1964)].
- ²³A. S. Borovik-Romanov and V. F. Meshcheryakov, *Zh. Eksp. Teor. Fiz.* **53**, 853 (1967) [*Sov. Phys.-JETP* **26**, 519 (1968)].
- ²⁴G. D. Bogomolov, Yu. F. Igonin, L. A. Prozorova, and F. S. Rusin, *Zh. Eksp. Teor. Fiz.* **54**, 1069 (1968) [*Sov. Phys.-JETP* **27**, 572 (1968)].
- ²⁵E. A. Turov and N. G. Guseinov, *Zh. Eksp. Teor. Fiz.* **38**, 1326 (1960) [*Sov. Phys.-JETP* **11**, 955 (1960)].
- ²⁶N. Yu. Ikornikova, *Kristallografiya* **6**, 745 (1961) [*Sov. Phys.-Crystallogr.* **6**, 594 (1962)].
- ²⁷N. Yu. Ikornikova, in the collection *Gidrotermal'nyi sintez kristallov (Hydrothermal Synthesis of Crystals)*, "Nauka", 1968, pp. 141-154.
- ²⁸N. Yu. Ikornikova, Doctoral dissertation, Institute of Crystallography, Academy of Sciences, USSR, 1970.
- ²⁹L. L. Landau and E. M. Lifshitz, *Statisticheskaya fizika (Statistical Physics)*, "Nauka", 1964, p. 330. (Translation, Pergamon Press and Addison-Wesley, 1969, Sec. 88).
- ³⁰I. E. Dzyaloshinskiĭ, *Zh. Eksp. Teor. Fiz.* **32**, 1547 (1957) [*Sov. Phys.-JETP* **5**, 1259 (1957)].

Translated by W. F. Brown, Jr.