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Excitons and magnons in CoCO₃

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Experimental and theoretical investigations were made of the spectrum of the lowest exciton and magnon excitations in an antiferromagnetic CoCO₃ crystal. The Raman scattering method revealed two low-frequency lines at 35 and 57 cm⁻¹. These lines were attributed to one-magnon (corresponding to the high-frequency branch of the spin-wave spectrum) and two-magnon (corresponding to energies at the boundary of the Brillouin zone) scattering of light. A study was made of the influence of external magnetic field on the spectrum of the lowest exciton states and doublet splitting of lines at 178 cm⁻¹ was observed. A comparison of the results of a self-consistent molecular field theory with the experimental data made it possible to interpret the Raman spectrum and to reconstruct the dispersion dependence of the lowest excitations in the CoCO₃ crystal.

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INTRODUCTION

The magnetic properties of CoCO₃ crystals have been investigated relatively long time ago. A. S. Borovik-Romanov and the present authors[1,2] demonstrated that CoCO₃ goes over to the antiferromagnetic state at $T_N = 18.1 °K$ and that the magnetic moments do not become completely compensated after this transition but add up to a net ferromagnetic moment oriented in the basal plane (this moment in CoCO₃ is fairly large: $\sigma_D = 0.258\ \mu_B/$mole at $T \ll T_N$). The antiferromagnetism of CoCO₃ was confirmed by neutron-diffraction measurements.[3] It is important to note that the magnetic unit cell is identical with the crystallochemical cell: both consist of two formula units (CoCO₃ has the rhombohedral structure of the calcite type and its space group is D_{3d}^6). Recent measurements[4] demonstrated that the direction of the antiferromagnetic vector is the same as of the weak ferromagnetic moment: both are perpendicular to the trigonal axis.

The application of the phenomenological theory of spin waves to easy-plane antiferromagnets shows[5,6] that the spin-wave spectrum of such antiferromagnets has two branches: 1) a ferromagnetic (acoustic) branch, which—in the first approximation—does not have a gap at the center of the Brillouin zone in the absence of an external magnetic field; 2) an antiferromagnetic (optical) branch with a gap whose magnitude is governed by the exchange interaction and uniaxial anisotropy constants. The low-frequency branch of CoCO₃ was investigated in detail by resonance methods.[7] This investigation made it possible to determine the effective magnetic fields of the exchange interaction $H_E = 160$ kOe and of the Dzyaloshinskiĭ interaction $H_D = 51.5$ kOe (the magnetic measurements[2] give $H_D = 27$ kOe). The transverse component of the g factor was found to be in the range 3.3–4.0.[7] The high-frequency branch of the antiferromagnetic resonance in CoCO₃ has not yet been observed.

We shall report the results of a detailed investigation of the low-frequency spectrum of the Raman scattering of light in a CoCO₃ crystal, revealing one- and two-magnon scattering lines and making it possible to reconstruct completely the spin-wave spectrum of this compound. The experimental results and discussion are preceded by a theoretical analysis of the lowest excitations of the Co²⁺ ion in CoCO₃. The orbital nature of the ground state of Co²⁺ in this crystal makes it impossible to apply the usual spin-wave approximation and magnons are not pure spin excitations. The ground state of Co²⁺ in a cubic crystal field is the twelvefold-degenerate term $^4T_{1g}(^4F)$. The exact solution of the problem is impossible even within the $^4T_{1g}$ term allowing for the orthorhombic distortion, spin–orbit and exchange interactions, and collective nature of the excitations; therefore, we shall consider only the four lowest states. We

shall show that the calculation describes well the main experimental results.

THEORY

Electron states of the Co^{2+} *ion.* The ground state of the free Co^{2+} ion ($3d^7$ configuration) is the multiplet ^4F and the nearest excited term ^4P is separated by 14 000 cm^{-1}. The remaining states of the same configuration are doublets and the states of the other configurations are separated from the ground state by more than 40 000 cm^{-1}.[8]

We shall now consider the behavior of the energy levels of the Co^{2+} ion employing the single-ion approximation and the weak-coupling scheme. In a $CoCO_3$ crystal the Co^{2+} cation is surrounded by an octahedron of CO_3^{2-} anions. The distortion is trigonal along the c_3 axis. A cubic crystal field splits ^4F into $^4T_{1g} + ^4T_{2g} + ^4A_{2g}$ and the term ^4P behaves as $^4T_{1g}$. The ground state is $^4T_{1g}(^4F)$ and the cubic field adds a small admixture of a state of the same symmetry $^4T_{1g}(^4P)$. The result of this admixture is a reduction in the matrix elements of the orbital angular momentum L compared with those obtained using pure wave functions of the $^4T_{1g}(^4F)$ term. Moreover, a similar reduction occurs because of the covalent binding which distorts the pure d orbits. The two effects can be allowed for by replacing L with kL in the matrix elements calculated using the functions of the ground $^4T_{1g}$ state, where k is smaller than, but of the order of, unity.[9]

The energy separating the ground triplet $^4T_{1g}$ from the higher levels is large compared with the splitting of this level by the trigonal field and by the spin–orbit interaction, so that we shall consider only the lowest orbital triplet of $^4T_{1g}(^4F)$. The Hamiltonian of the perturbation in an external magnetic field can be written in the following effective form[9]:

$$\mathcal{H}_{jo} = -\tfrac{3}{2}k\lambda LS - \delta(L_z^2 - \tfrac{2}{3}) - \mu_B H(-\tfrac{3}{2}kL + 2S), \tag{1}$$

where λ is the spin–orbit coupling constant, amounting to 180 cm^{-1} for the free ion; δ is the trigonal field parameter; μ_B is the Bohr magneton. The secular twelfth-order matrix splits into two identical sixth-order matrices which are quasidiagonal and consist of three blocks of the third, second, and first orders:

	$\lvert -1, \tfrac{3}{2}\rangle$	$\lvert 0, \tfrac{1}{2}\rangle$	$\lvert 1, -\tfrac{1}{2}\rangle$	$\lvert 0, \tfrac{3}{2}\rangle$	$\lvert 1, \tfrac{1}{2}\rangle$	$\lvert 1, \tfrac{3}{2}\rangle$
$\langle -1, \tfrac{3}{2}\rvert$	$-\tfrac{1}{3}\delta + \tfrac{9}{4}\lambda'$	$-\tfrac{9}{2\sqrt{6}}\lambda'$	0			
$\langle 0, \tfrac{1}{2}\rvert$	$-\tfrac{9}{2\sqrt{6}}\lambda'$	$\tfrac{2}{3}\delta$	$-\tfrac{3}{\sqrt{2}}\lambda'$	0		0
$\langle 1, -\tfrac{1}{2}\rvert$	0	$-\tfrac{3}{\sqrt{2}}\lambda'$	$-\tfrac{1}{3}\delta + \tfrac{3}{4}\lambda'$			
$\langle 0, \tfrac{3}{2}\rvert$		0		$\tfrac{2}{3}\delta$	$-\tfrac{9}{2\sqrt{6}}\lambda'$	0
$\langle 1, \tfrac{1}{2}\rvert$				$-\tfrac{9}{2\sqrt{6}}\lambda'$	$-\tfrac{1}{3}\delta - \tfrac{3}{4}\lambda'$	
$\langle 1, \tfrac{3}{2}\rvert$		0		0		$-\tfrac{1}{3}\delta - \tfrac{9}{4}\lambda'$

where $\lambda' = k\lambda$. Consequently, the state $^4F_{1g}(^4F)$ splits into six Kramers doublets. We shall confine ourselves to the two lowest doublets and we shall give their wave functions. The lowest doublet for all the values of δ/λ' is obtained from a cubic equation and has the wave functions

$$\begin{aligned}
\varphi_1 &= c_1\lvert -1, \tfrac{3}{2}\rangle + c_2\lvert 0, \tfrac{1}{2}\rangle + c_3\lvert 1, -\tfrac{1}{2}\rangle, \\
\varphi_2 &= c_1\lvert 1, -\tfrac{3}{2}\rangle + c_2\lvert 0, -\tfrac{1}{2}\rangle + c_3\lvert -1, \tfrac{1}{2}\rangle;
\end{aligned} \tag{2}$$

the next doublet is obtained from a quadratic equation and has the wave functions

$$\begin{aligned}
\varphi_3 &= c_4\lvert 0, \tfrac{3}{2}\rangle + c_5\lvert 1, \tfrac{1}{2}\rangle, \\
\varphi_4 &= c_4\lvert 0, -\tfrac{3}{2}\rangle + c_5\lvert -1, -\tfrac{1}{2}\rangle .
\end{aligned} \tag{3}$$

The expressions for the g factors of the lowest doublet are

$$\begin{aligned}
g_\parallel &= (6+3k)c_1^2 + 2c_2^2 - (3k+2)c_3^2, \\
g_\perp &= 4c_2^2 + 4\sqrt{3}c_1c_3 - \tfrac{3}{2}\sqrt{2}kc_2c_3
\end{aligned} \tag{4}$$

and for the first excited doublet:

$$g_\parallel' = (2-3k)c_5^2 + 6c_4^2, \quad g_\perp' = 0. \tag{5}$$

The values of λ' and δ were determined earlier[10] from a comparison of calculations with the experimental results of an investigation of the Raman scattering of light by electronic excitations in $Co\,CO_3$. The following values were obtained: $\lambda' = 136$ cm^{-1}, $\delta = 544$ cm^{-1}, $k = 0.75$. Use of these values yielded the following coefficients $c_1 - c_5$ in the wave functions (2) and (3): $c_1 = 0.428$, $c_2 = -0.834$, $c_3 = 0.349$, $c_4 = 0.946$, and $c_5 = -0.323$. Hence, the g factors were found to be: $g_\parallel = 2.87$, $g_\perp = 4.28$, $g_\parallel' = 5.34$, and $g_\perp' = 0$.

The most important result here is the vanishing of $g_\perp'$ for the first excited state of the Co^{2+} ion. According to the ESR data, the g factors of the ground state of the Co^{2+} ion in crystals with the calcite structure are: $g_\parallel = 3.41$ and $g_\perp = 4.82$ for $CaCO_3$[11] and $g_\parallel = 3.06$ and $g_\perp = 4.94$ for $CdCO_3$,[12] which are close to the values obtained above and confirm the correct order of the quantities λ' and δ.

Self-consistent solution for the Co^{2+} *ion in a molecular field.* Since the Co^{2+} ion has a magnetic moment with orbital and spin contributions, the average magnetic moments (effective spins) and wave functions of the ground state of the ion in a molecular field have to be determined self-consistently as functions of the exchange constants; then, we can introduce local operators of the deviation from the ground state and next the exciton operators for the determination of the exciton states of the crystal. A similar calculation method has been used successfully in a determination of the energy levels of the Co^{2+} ion in a CoF_2 crystal.[3]

The exchange interaction between the neighboring Co^{2+} ions is complex and there are many exchange parameters which are difficult to determine theoretically or experimentally. We shall adopt the simplest approximation: we shall assume the exchange interaction to be isotropic and we shall allow only for the interaction between the nearest neighbors in different sublattices because this exchange is the strongest. The Hamiltonian of the whole crystal is then

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$$\hat{\mathcal{H}} = \sum_j \mathcal{H}_{j0} + \sum_l \mathcal{H}_{l0} + J\sum_{j>l} (S_j, S_l), \qquad (6)$$

where the indices j and l denote the two sublattices, $\mathcal{H}_{j0}$ is the single-ion Hamiltonian of the j-th ion of Eq. (1), J is the exchange constant, and the summation is carried out over the pairs of the nearest ions in different sublattices.

In the calculations dealing with the ground state and the effective magnetic moment of the Co^{2+} ion we shall confine ourselves to the two lowest doublets (2) and (3), separated from the others by ~ 600 cm^{-1}. [10] We shall assume that the moments of the ions are oriented in the basal plane along the x axis; then, the Hamiltonian of the j-th ion in the molecular field of the neighboring Co^{2+} ions is

$$\hat{\mathcal{H}}_j = \hat{\mathcal{H}}_{j0} + \hat{S}_{jx} F_j, \qquad (7)$$

where $F_j = JzS_l$, S_l is the average value of the moment of the ion in the l-th sublattice in the ground state, and $z = 6$ is the number of the nearest antiferromagnetic neighbors. The matrix form of the operator (7) in the space of the functions (2) and (3) is

$$\mathcal{H}_j = \begin{vmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \varepsilon' & 0 \\ 0 & 0 & 0 & \varepsilon' \end{vmatrix} - JzS \begin{vmatrix} 0 & a & b & 0 \\ a & 0 & 0 & b \\ b & 0 & 0 & 0 \\ 0 & b & 0 & 0 \end{vmatrix}; \qquad (8)$$

here, ε' is the energy of the second doublet at $T > T_N$, amounting to 164 cm^{-1}, [10] $a = \sqrt{3}c_1c_3 + c_2^2 = 0.954$, $b = \frac{1}{2}\sqrt{3}c_2c_4 + c_3c_5 = -0.796$. Diagonalization of Eq. (8) gives the energy levels E_{0-3} of the ion in the molecular field:

$$\left. \begin{aligned} E_0 &= 6JS\left\{ \frac{\varepsilon-a}{2} - \left[\left(\frac{\varepsilon+a}{2}\right)^2 + b^2\right]^{1/2} \right\}, \\ E_1 &= 6JS\left\{ \frac{\varepsilon+a}{2} - \left[\left(\frac{\varepsilon-a}{2}\right)^2 + b^2\right]^{1/2} \right\}, \\ E_2 &= 6JS\left\{ \frac{\varepsilon-a}{2} + \left[\left(\frac{\varepsilon+a}{2}\right)^2 + b^2\right]^{1/2} \right\}, \\ E_3 &= 6JS\left\{ \frac{\varepsilon+a}{2} + \left[\left(\frac{\varepsilon-a}{2}\right)^2 + b^2\right]^{1/2} \right\}, \end{aligned} \right\} \qquad (9)$$

which are given in increasing order of their energies. Here, $\varepsilon = 164/F_j$.

Thus, the molecular field lifts the Kramers degeneracy and the two doublets split into four nondegenerate states Ψ_i:

$$\left. \begin{aligned} |j,0\rangle &= a_0\left\{ \varphi_1 + \varphi_2 + \frac{b}{\varepsilon - E_0'}(\varphi_3 + \varphi_4) \right\}, \\ |j,1\rangle &= a_1\left\{ \varphi_1 - \varphi_2 + \frac{b}{\varepsilon - E_1'}(\varphi_3 - \varphi_4) \right\}, \\ |j,2\rangle &= a_2\left\{ \varphi_1 + \varphi_2 + \frac{b}{\varepsilon - E_2'}(\varphi_3 + \varphi_4) \right\}, \\ |j,3\rangle &= a_3\left\{ \varphi_1 - \varphi_2 + \frac{b}{\varepsilon - E_3'}(\varphi_3 - \varphi_4) \right\}, \end{aligned} \right\} \qquad (10)$$

where

$$E_m' = \frac{E_m}{6JS}, \quad a_m = \left\{ \frac{1/2}{1 + b^2/(\varepsilon - E_m')^2} \right\}^{1/2}, \quad m = 0, 1, 2, 3.$$

In fact, as shown below, the splitting of the excited term should be practically zero, which corresponds to the zero value of the corresponding factor g_1' [see Eq. (5)].

The self-consistency condition for the j-th ion in the limit $T \to 0$ gives

$$S_j = \partial E_0/\partial F_j = -S_l = -S. \qquad (11)$$

This equation yields the condition for the determination of the average moment in the ground state as a function of $J(F_j)$:

$$S = \frac{a}{2} + \left[\left(\frac{\varepsilon+a}{2}\right)^2 + b^2\right]^{1/2} - \varepsilon(\varepsilon+a) \Big/ 4\left[\left(\frac{\varepsilon+a}{2}\right)^2 + b^2\right]^{1/2}. \qquad (12)$$

The energies and the eigenfunctions are the same for the ions in the other sublattice.

Since $\varepsilon = 164/6JS$, Eq. (12) relates two unknown parameters J and S. A second equation can be obtained by taking any experimental value of the exciton (magnon) energy. However, one has to go over first to the exciton representation.

Excitons and magnons. We shall assume that the approximate ground state of an antiferromagnetic $CoCO_3$ crystal is

$$\Psi_g = \prod_j |j,0\rangle \prod_l |l,0\rangle, \qquad (13)$$

where $|j,0\rangle$ and $|l,0\rangle$ are the functions of the ground state of the ions in the molecular field. We shall introduce the local excitation creation and annihilation operators:

$$\eta_{mj}^+ = |j,m\rangle\langle j,0|, \quad \eta_{mj} = |j,0\rangle\langle j,m| \qquad (14)$$

and similar operators η_{ml}^* and η_{ml} for the ions in the other sublattice. When the Hamiltonian (6) is expressed in terms of these operators, we obtain

$$\mathcal{H} = \text{const} + \mathcal{H}^{(2)} + \mathcal{H}^{(3)} + \mathcal{H}^{(4)}, \qquad (15)$$

where

$$\begin{aligned} \mathcal{H}^{(2)} = &\sum_{m=1}^{3} \varepsilon_m \left(\sum_j \eta_{mj}^+ \eta_{mj} + \sum_l \eta_{ml}^+ \eta_{ml} \right) + J\{S_{01j}^y S_{01l}^y (\eta_{1j} - \eta_{1j}^+)(\eta_{1l} - \eta_{1l}^+) \\ &+ S_{01j}^x S_{01l}^x (\eta_{1j}^+ + \eta_{1j})(\eta_{1l}^+ + \eta_{1l}) + S_{02j}^x S_{01l}^x (\eta_{2j}^+ + \eta_{2j})(\eta_{1l}^+ + \eta_{1l}) \\ &+ S_{03j}^y S_{01l}^y (\eta_{3j} - \eta_{3j}^+)(\eta_{1l} - \eta_{1l}^+) + S_{03j}^x S_{01l}^x (\eta_{3j}^+ + \eta_{3j})(\eta_{1l}^+ + \eta_{1l}) \\ &+ S_{01j}^y S_{03l}^y (\eta_{1j} - \eta_{1j}^+)(\eta_{3l} - \eta_{3l}^+) + S_{03j}^y S_{03l}^y (\eta_{3j} - \eta_{3j}^+)(\eta_{1l} - \eta_{1l}^+) \\ &+ S_{01j}^x S_{03l}^x (\eta_{1j}^+ + \eta_{1j})(\eta_{3l}^+ + \eta_{3l}) + S_{03j}^x S_{01l}^x (\eta_{3j}^+ + \eta_{3j})(\eta_{1l}^+ + \eta_{1l})\}, \end{aligned} \qquad (16)$$

and $\varepsilon_m = E_m - E_0$; S_{mn}^α are the matrix elements of the spin operators (for the j and l sublattices) based on the functions (10) and given by

$$S_{02}^x = 2a_0 a_2 \varepsilon, \quad S_{01}^y = 2a_0 a_1 i\left(a + \frac{b^2}{\varepsilon - E_1'} - \frac{b^2}{\varepsilon - E_0'}\right), \qquad (17)$$

$$S_{03}^y = 2a_0 a_3 i\left(a + \frac{b^2}{\varepsilon - E_3'} - \frac{b^2}{\varepsilon - E_0'}\right), \quad S_{01}^x = 2a_0 a_1 \left(c + \frac{b^2 d}{(\varepsilon - E_0')(\varepsilon - E_1')}\right),$$

$$S_{03}^x = 2a_0 a_3 \left(c + \frac{b^2 d}{(\varepsilon - E_0')(\varepsilon - E_3')}\right).$$

The terms $\mathscr{H}^{(3)}$ and $\mathscr{H}^{(4)}$ are, respectively, of the third and fourth order in the operator η, and in solving the one-exciton problem these terms can be justifiably neglected.

Going over to the exciton operators η_{mq} and $\bar{\eta}_{mq}$, we shall carry out the Fourier transformation

$$\eta_{mj}=N^{-\frac{1}{2}}\sum_q \exp\{-iqR_j\}\eta_{mq}, \quad \eta_{ml}=N^{-\frac{1}{2}}\sum_q \exp\{iqR_l\}\bar{\eta}_{mq} \quad (18)$$

and apply similar procedures to the other operators. Then, the Hamiltonian (16) becomes

$$\mathscr{H}^{(2)}=\sum_{m=1}^{3}\varepsilon_m\sum_q (\eta_{mq}{}^+\eta_{mq}+\bar{\eta}_{mq}{}^+\bar{\eta}_{mq})+\sum_q \{a_1(\eta_{1q}{}^+\bar{\eta}_{1q}{}^++\eta_{1q}\bar{\eta}_{1q})$$
$$+b_1(\eta_{1q}{}^+\bar{\eta}_{1-q}+\eta_{1q}\bar{\eta}_{1-q}{}^+)+b_2(\eta_{2q}{}^+\bar{\eta}_{2q}{}^++\eta_{2q}\bar{\eta}_{2q}+\eta_{2q}\bar{\eta}_{2-q}{}^++\eta_{2q}{}^+\bar{\eta}_{2-q})$$
$$+a_3(\eta_{3q}{}^+\bar{\eta}_{3q}{}^++\eta_{3q}\bar{\eta}_{3q})+b_3(\eta_{3q}{}^+\bar{\eta}_{3-q}+\eta_{3q}\bar{\eta}_{3-q}{}^+)\} \quad (19)$$

together with the terms in which the operators η_{1q} and η_{3q} are mixed; these terms are omitted because their coefficients are small compared with $\varepsilon_3-\varepsilon_1$. The Hamiltonian (19) then splits into three independent parts. Separate diagonalization of each of these parts gives the exciton energies originating from the first, second, and third single-ion excited levels:

$$\hbar\omega_m{}^\pm=(\varepsilon_m{}^2+b_m{}^2-a_m{}^2\pm 2\varepsilon_m b_m)^{\frac{1}{2}}. \quad (20)$$

Here, $m=1, 2,$ or 3:

$$a_{1(3)}=J\gamma_q\{(S_{01(3)}{}^x)^2+(S_{01(3)}{}^y)^2\}, \quad a_2=b_2=-J\gamma_q(S_{02}{}^x)^2,$$
$$b_{1(3)}=J\gamma_q\{(S_{01(3)}{}^x)^2-(S_{01(3)}{}^y)^2\}; \quad (21)$$

$$\gamma_q=\exp\left(iq_z\frac{b}{2}\right)\left[\exp(iq_y a)+\exp\left(-iq_y\frac{a}{2}\right)2\cos\frac{a\sqrt{3}}{2}q_x\right]$$
$$+\exp\left(-iq_z\frac{b}{2}\right)\left[\exp(-iq_y a)+\exp\left(iq_y\frac{a}{2}\right)2\cos\frac{a\sqrt{3}}{2}q_x\right], \quad (22)$$

where a and b are the projections of the fundamental vector of the $CoCO_3$ unit cell onto a plane perpendicular to the trigonal axis and onto the axis itself. The expression (20) gives the second equation supplementing Eq. (12), as required in the determination of the unknown parameters J and S.

Forestalling the report given below, we shall mention that the experimental energy of the high-frequency branch of the spin-wave spectrum is 35 cm^{-1} for $q=0$. Using this value, we obtain $J=1.9$ cm^{-1} and $S=1.03$. We can now calculate the energies of the required levels at any point in the Brillouin zone. The results of the calculations at the points Γ, Z, D, and A (Fig. 1) are given in Table I.
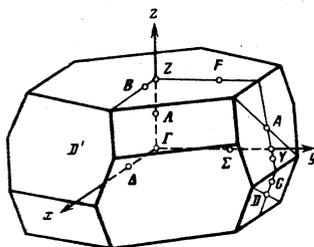
FIG. 1. Brillouin zone of the $CoCO_3$ crystal. The principal singular (high-symmetry) points are shown.

TABLE I. Calculated frequencies (cm^{-1}) of excitons and magnons in $CoCO_3$ ($S=1.03$, $J=1.9$ cm^{-1}).

m	$\Gamma(0,0,0)$, $\gamma=6$	$Z(0,0,\pi/c)$, $\gamma=0$	$A(0,2\pi/3a,\pi/3c)$, $\gamma=1.73$	$D(0,2\pi/3a,-2\pi/3c)$, $\gamma=-1$
1	4.63 35.7	22.28	18.1 26.2	19.9 24.6
2	169.5 182.3	176.17	174.3 178.0	175.1 177.2
3	182.35 169.91	176.24	178.1 174.4	177.3 175.2

EXPERIMENTAL METHOD

A block diagram of the apparatus used to investigate the Raman scattering spectra in an external magnetic field is shown in Fig. 2. The excitation sources were LG-36A He+Ne($\lambda=6328$ Å, output power about 80 mW) and LG-31 He+Cd($\lambda=4416$ Å, 15 mW) lasers. A laser beam was reflected by a rotatable mirror M_1 and passed through an iris diaphragm D, separating the plasma lines in the laser discharges; the beam was then focused by a lens L_1 on a sample located inside an optical helium cryostat with a superconducting solenoid. The light scattered at 90° was collected by a lens L_2 on the entry slit of a DFS-12 spectrograph. A prism P was placed in front of the slit: this prism rotated the image of the laser beam track in the sample parallel to the edges of the entry slit. Interchangeable diffraction gratings were used in the spectrometer: these gratings concentrated light in the second order in the blue-green (in the case of the He+Cd laser) or red (in the case of the He+Ne laser) parts of the spectrum. The instrumental function of this spectrometer was symmetric and its width did not exceed 1 cm^{-1}. The spectrometer was calibrated on the basis of the neon and mercury emission lines. The error in the measurement of the frequencies of the narrow spectral lines did not exceed ±1 cm^{-1}. The spectra were recorded with the aid of an FÉU-79 photomultiplier and a photon-counting circuit.

The superconducting solenoid in the cryostat had a working aperture 16 mm in diameter and it consisted of two series-connected coils with a common axis; these coils were made of Nb-60% Ti wire whose diameter was
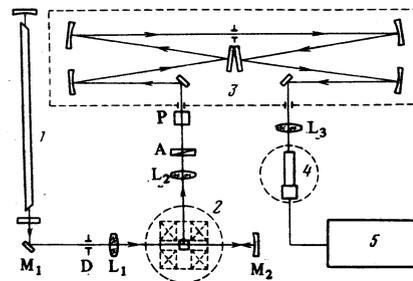
FIG. 2. Block diagram of the apparatus used to investigate the Raman spectra of crystals in an external magnetic field: 1) laser; 2) cryostat with superconducting solenoid and sample; 3) DFS-12 spectrometer; 4) cooled FÉU-79 photomultiplier; 5) photon-counting circuit; L_1–L_3 are focusing and projecting lenses; M_1 and M_2 are mirrors; D is an iris diaphragm; A is an analyzer; P is a rotatable prism.
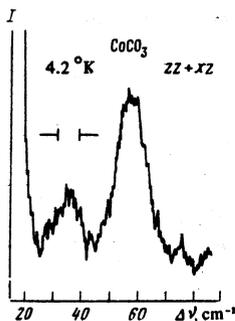
FIG. 3. Experimental record of the one- and two-magnon scattering spectrum of a $CoCO_3$ crystal obtained at $T = 4.2\,°K$. The incident light was directed along the x axis and polarized along the z axis; the scattered light was not polarized and it was directed along the y axis.

0.3 mm. The maximum field at the center between the coils was 49 kOe and its inhomogeneity did not exceed 1% over the whole length of the sample. The power supply source was a P-138 dc stabilizer, which made it possible to vary continuously the solenoid current in the range 0–30 A.

Our samples were synthetic $CoCO_3$ single crystals grown by the hydrothermal method.[14] These crystals were of good optical quality and had a good faceting. We cut samples parallel and perpendicular to the c_3 axis; their linear dimensions were $2 \times 3 \times 1$ mm and the faces were carefully polished.

Whenever necessary, we used narrow-band dielectric filters selecting the laser working wavelengths, a half-wave mica plate for rotating the plane of linear polarization of the He–Ne laser beam, and Polaroid films as an analyzer.

EXPERIMENTAL RESULTS AND DISCUSSION

The spectra of the Raman scattering of light by electron and phonon excitations in a $CoCO_3$ crystal were determined earlier[10] in a wide range of temperatures. In the present study we concentrated our attention on the low-frequency part of the spectrum with the aim of finding the magnon scattering lines. We also determined the influence of an external magnetic field on the lowest exciton states.

The $CoCO_3$ crystals were opaque in the yellow-green part of the spectrum but had narrow transmission "windows" in the red and blue parts.[14] This made it possible to determine the Raman spectra in transmitted lines using the 6328 Å He + Ne or 4416 Å He + Cd laser lines. When the latter laser was used, we found two new low-temperature lines with maxima at 35 and 57 cm^{-1} (Fig. 3), which we attributed to the one-magnon (corresponding to the high-frequency branch of the spin-wave spectrum) and two-magnon scattering of light.[1] The following experimental observations justified this identification. The most important was the spectral position of the lines. In this frequency range we did not expect any other transitions because all the phonon and exciton states were characterized by much higher frequencies.[10] Moreover, there were no such lines in the spectra of the isomorphous compounds $FeCO_3$ and $CaCO_3$, as checked by us under the same experimental conditions. Another factor was the influence of temperature on these lines:

the heating of a sample by just a few degrees above $4.2\,°K$ caused both lines to broaden rapidly and to merge with the background (their intensities were approximately two orders of magnitude lower than the intensities of the other exciton lines). On the other hand, cooling from 4.2 to $1.8\,°K$ sharpened the lines and the peak at 35 cm^{-1} became particularly clear.

Polarization measurements indicated that the high-frequency (35 cm^{-1}) line was mainly present in the spectra corresponding to the nondiagonal components of the scattering tensor and the high-frequency (57 cm^{-1}) line was approximately the same in all the polarizations. These results agreed with the selection rules for the one- and two-magnon scattering of light.[17] The very low intensities of these lines prevented us from investigating the influence of a magnetic field.

In the case of the low-frequency exciton lines the application of an external magnetic field of up to 46 kOe intensity, directed at right-angles to the trigonal axis, did not alter their spectral positions or intensities. When the field was parallel to the c_3 axis, we observed doublet splitting (linear in respect of the field) of the exciton line at 178 cm^{-1} whose g factor was $g'_{\parallel} = 3.7$ (Fig. 4). The components of this doublet were polarized: the low-frequency line was present mainly in the xz polarization and the high-frequency line in the xx polarization (the first index denotes the polarization of the incident light and the second that of the scattered light). Two other lines shown in Fig. 4 were associated with the second exciton transition (207 cm^{-1}) and with the E_g phonon (222 cm^{-1}). In this polarization the lowest-frequency E_g phonon had the lowest intensity.[10] No definite conclusions could be drawn about the influence of a magnetic field on these lines because of their low intensities and considerable half-widths. However, we found that in other polarizations there was a shift of the E_g phonon by ~2 cm^{-1} in the direction of lower frequencies when a field $H = 45$ kOe was applied (this result was obtained for any direction of the external field).

We shall now analyze the experimental results and compare them with the calculations. The calculated values of the frequencies at $q = 0$ (see Table I) are 4.63, 35.7, 169.8, and 182.3 cm^{-1}; the experimental values at $T = 4.2\,°K$ are ~0,[7] 35, 178, and 207 cm^{-1}. In view
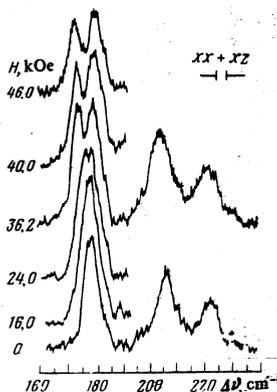
FIG. 4. Influence of an external magnetic field of $H \parallel c_3 \parallel z$ orientation on the low-frequency part of the exciton scattering spectrum of $CoCO_3$; $k \parallel z$, $E \parallel x$, $k' \parallel y$.

of the rough approximations made in the calculations [the Dzyaloshinskiĭ interaction is ignored, only the lowest states are considered, no allowance is made for the admixture of high-energy states, the third- and fourth-order terms in the Hamiltonian (15) are ignored, and so on], the agreement (particularly the qualitative one, namely the presence of just four frequencies in the spectrum) can be regarded as good. Thus, our values of the constant of the trigonal field $\delta = 544$ cm^{-1}, spin-orbit interaction $\lambda = 136$ cm^{-1}, and exchange interaction between the nearest antiferromagnetic coupled neighbors $J = 1.9$ cm^{-1} can be used as the starting points in more accurate calculations.

A comparison of the theory and experiment shows that the observed two lines in the region of the lowest exciton transition (178 and 207 cm^{-1}) are associated with the Davydov splitting, and the splitting in the molecular (exchange) field of each of these terms is close to zero (~ 0.1 cm^{-1}). Moreover, the absence of the influence of an external field directed at right-angles to the trigonal axis seems to be a natural result because $g_\perp' = 0$ for the excitons [see Eq. (5)]. The experimental value of $g_\parallel'$ for the line at 178 cm^{-1} is $g_\parallel' = 3.7$ and the calculations give $g_\parallel' = 5.34$. It is difficult to expect a quantitative agreement in this case because the calculated value is obtained for single-ion states.

The unexpected result of our study is the very low intensity of the peak representing the one-magnon scattering of light in CoCO$_3$. It should be noted that in all the antiferromagnetic compounds containing Co^{2+} investigated before—CoF$_2$,[18] RbCoF$_3$,[19] KCoF$_3$,[20] and TlCoF$_3$[21]—the intensities of the one-magnon scattering of light have been of the same order as those of the exciton lines.

We shall now consider the dispersion of the magnon branches. The experimental values of the frequencies for the one- and two-magnon scattering of light are 35 and 57 cm^{-1}. If we consider that the contribution of the interaction between magnons is small and that the density of the magnon states is highest at the boundary of the Brillouin zone, we find that the magnon energy corresponding to q_{max} is $\nu_{q_{max}} = 29$ cm^{-1} (the calculated value in Table I is 22 ± 4 cm^{-1}). This last estimate is confirmed by an analysis of an experimentally observed behavior of the low-frequency phonons in the Raman spectrum of CoCO$_3$:[10] the corresponding line becomes broader and is shifted anomalously by the antiferromagnetic ordering. As pointed out before,[10] this behavior may be associated with an additional phonon relaxation channel in the antiferromagnetic state of this compound: this relaxation involves dissociation of a phonon into an exciton and a magnon with energies on the boundary of the Brillouin zone (where the density of the corresponding states is highest). This process is shown schematically in Fig. 5. The contribution of the magnon states to the spectral position and frequency of the phonon line is supported by the observed (see above) influence of an external magnetic field. The phonon frequency at $T = 4.2$ °K is 222 cm^{-1}[10] and it is equal to the sum of the boundary frequencies of an exciton and a magnon. A calculation given above shows that the frequencies of
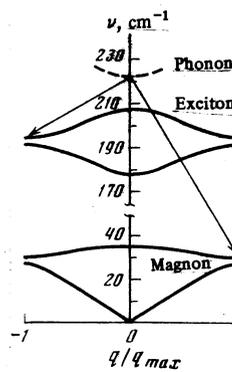
FIG. 5. Schematic representation of the spectrum of the lowest excitations of a CoCO$_3$ crystal in the antiferromagnetic state. The arrows represent dissociation of a photon into an exciton and a magnon.

both excitons on the boundary of the Brillouin zone are close to one another (the maximum splitting at the point A is less than 4 cm^{-1}) and the absolute values of these frequencies are of the order of the arithmetic mean of the frequencies at the point $q = 0$, i.e., it amounts to 193 cm^{-1} (on the basis of the experimental data). Therefore, the magnon energy at the boundary of the Brillouin zone is 29 cm^{-1}, which is in agreement with direct determinations of the two-magnon spectra (it readily follows from the symmetry considerations that the contributions to the phonon line frequency and width may come from all the singular points in the Brillouin zone; this is due to the low symmetry of the crystallomagnetic cell of CoCO$_3$ in the antiferromagnetic state).

We may conclude that our experimental results and their comparison with the proposed theory allow us to reconstruct completely the spectrum of the lowest excitations in a CoCO$_3$ crystal in the antiferromagnetic state. Such results are given in Fig. 5. The splitting of magnons and excitons at the boundary of the Brillouin zone is zero at the point Z, and it does not exceed ± 5 cm^{-1} for magnons and ± 3 cm^{-1} for excitons at other high-symmetry points (Table I). It should be noted that the magnon frequency $\nu_0 = 35$ cm^{-1} for $q = 0$ allows us to estimate the uniaxial magnetic anisotropy field in CoCO$_3$. The application of the usual phenomenological theory formulas $\nu_0 = g\mu_B\sqrt{2H_AH_E + H_A^2}$[6,22] with $H_E = 160$ kOe and $g_\perp = 3.3$[7] yields $H_A = 115$ kOe, i.e., the anisotropy field is comparable with the exchange field. This explains the weak dispersion of the high-frequency branch of the spin-wave spectrum.

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