Long-wave IR spectrum of $CoCO_3$—high-frequency mode of antiferromagnetic resonance (AFMR) and two-magnon absorption

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For the first time ever, we have observed in $CoCO_3$ a high-frequency AFMR mode and two-magnon absorption, and we have measured the shift of the two-magnon absorption line in the magnetic field H. For a satisfactory description of the AFMR it is necessary to calculate the frequencies accurate to terms of second order in H.

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Cobalt carbonate $CoCO_3$ (symmetry group D_{3d}^6) below $T_N = 18.1$ K becomes a weak ferromagnetic with a total magnetic moment line in the basal plane.[1] The results of static magnetic measurements yielded the Dzyaloshinskiĭ field ($H_D = 27 \pm 1.5$ kOe) and the angle between the magnetic moments of the sublattices and the antiferromagnetism axis ($\delta \approx 7°$).[1] Resonance investigations were heretofore performed only for the low-frequency (LF) AFMR mode.[2] From the results of these investigations there were estimated the g factor ($g_\perp = 3.3 \pm 0.2$) and the Dzyaloshinskiĭ field ($H_D = 51.5 \pm 8$ kOe), the value of the latter being substantially different from that determined from static measurements.[1] It was of interest to observe the high-frequency (HF) AFMR mode and to determine the parameters of the theory from the obtained data. To investigate the HF AFMR mode and the two-magnon absorption, we investigated the absorption spectrum of $CoCO_3$ in the frequency range 12.5–150 cm^{-1}, using a diffraction spectrometer.

The investigations were performed on cobalt-carbonate single crystals containing as impurities iron (several tenths of a percent by weight), manganese, and nickel (several hundredths of a percent).[1)] The crystals were grown by hydrothermal synthesis and produced good conoscopic figures, thus attesting to the absence of a block structure. At 34.6 and 54.7 cm^{-1} (these frequencies are cited for $T \to 0$), absorption lines connected with magnetic ordering of the crystal were observed (Fig. 1). With increasing temperature, the lines broadened and their intensities decreased, and at $T \approx 14$ K they merged with the background but experienced a small shift (Fig. 2). As

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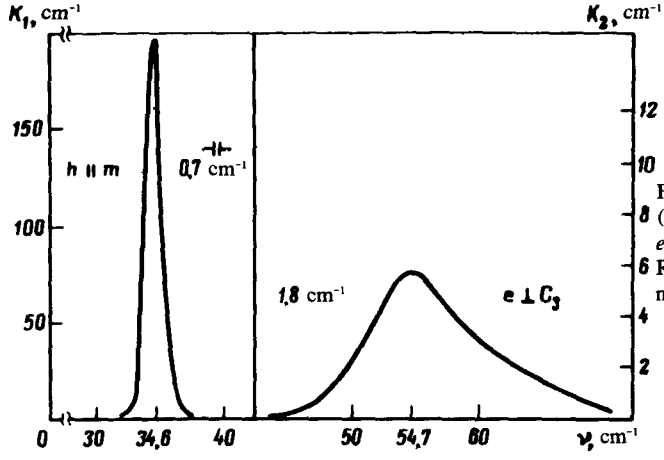

FIG. 1. Absorption spectra of $CoCO_3$ (observed contours), $T=5$ K: *e,h*—electric and magnetic vectors of RF field; *m*—weak ferromagnetic moment.

seen from Fig. 1 the 34.6-cm^{-1} magnetic-dipole line has approximately a Lorentz shape, and the 54.7-cm^{-1} electric-dipole line is asymmetrical. The line parameters are listed in Table I.

From calculations within the framework of the crystal-field theory[3] it follows that the first excited doublet in the cobalt carbonate is separated from the ground state by 163 cm^{-1}. Consequently, the observed lines cannot be connnected with electronic transitions. The 34.6- and 54.7-cm^{-1} lines are interpreted by us as the RF mode of AFMR and as two-magnon absorption. The behavior of the 54.7-cm^{-1} line in a magnetic field (Fig. 3) confirms this interpretation. If the two-magnon line were the results of the "intrinsic magnon + impurity magnon" process, then a shift would also be observed at $H \| C_3$, owing to the difference between the g factors of the impurity and

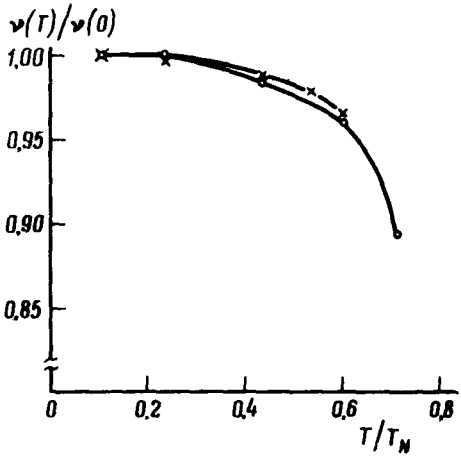

FIG. 2. Temperature dependence of the frequencies of two-magnon absorption (crosses) and of the RF AFMR mode (circles).

TABLE I.

Frequency of maximum, cm^{-1}	Polarization	Intensity at maximum, cm^{-1}	Width at $K_{max}/2$ level, cm^{-1}	Integrated intensity, cm^{-2}
34.6 ± 0.3	$h \parallel m$	207	1.3	520
54.7 ± 1	$e \perp C_3$	6.7	10.6	104

matrix ions. The two-magnon absorption line shift in a weak ferromagnet was observed here for the first time, although it had been predicted theoretically long ago;[4] its observation was made possible by the rather large angle of inclination of the magnetic moments of the sublattices to the antiferromagnetism axis in $CoCO_3$.

The plot of the HF-mode frequency against H (Fig. 3) agrees qualitatively with the theoretical one. The quantitative agreement is poor, possibly for the following reasons: it is known[5] that the resonant frequency of the HF mode of a weak ferromagnet is given by the formulas

$$\omega_2 = \gamma_\perp [(2H_E H_A + H_D^2) + HH_D]^{1/2} \qquad H \perp C_3, \tag{1}$$

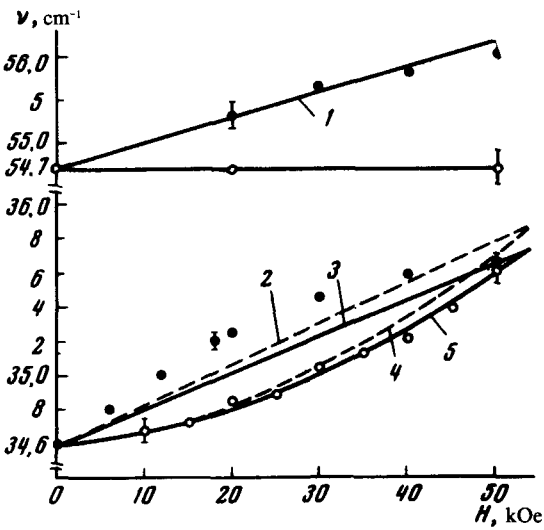

FIG. 3. Dependence of the frequencies of the absorption lines on external magnetic field, $T=2$ K: •, ○—experimental points for $H \perp C_3$ and $H \parallel C_3$, respectively; 1—calculation by formula,[4] $\Delta\nu = 2g\mu H \sin\delta$; 2,3—calculation by formulas (1) and (2) respectively for $g_z = 3.5$ and $H_D = 100$ kOe; 4,5—the same as 2 and 3, but for $g_z = 3.3$ and $H_D = 90$ kOe.

$$\omega_2 = \gamma_\perp [(2H_E H_A + H_D^2) + (g_z/g_\perp)^2 H^2]^{1/2} \qquad H \parallel C_3 , \tag{2}$$

where γ is the magnetomechanical ratio; H_E and H_A are the effective exchange and anisotropy fields. The experimentally obtained data have made it possible to use formulas (1) and (2) to calculate H_D and g_z. It is seen from Fig. 3, however, that experiment can be reconciled with theory only for $H \| C_3$ and moreover if $g_z > g_\perp$. On the other hand from static data[1] $(g_z/g_\perp) \approx (\chi_z/\chi_\perp)^{1/2} = 0.8$ and from EPR data[1] it follows that

The experimental data for $H \perp C_3$ cannot be described by formula (1) for any values of the parameters in this formula, as can be clearly seen from Fig. 3. For a satisfactory description it is necessary to have a term with H^2. A special analysis (to simplify the calculations, the g factor was assumed to be isotropic, an assumption that does not influence the character of the result) has shown that such a term with a minus sign does indeed appear in expression (1) if the expansion is not restricted to terms linear in H. The form of this term is $(H_A/2H_E)H^2$. In addition, in the terms linear in H there appear terms with coefficients of the type $H_A/2H_E$, $H_D/2H_E$, and $(H_D/2H_E)^2$. In the previously investigated crystals these coefficients could be neglected. In $CoCO_3$, the ratio $H_A/2H_E \approx 0.5$–0.7 (this rough estimate follows from the expression for the frequency in a zero field, $\omega^2 = \gamma_\perp (2H_E H_A + H_D^2)^{1/2}$, and $H_D/2H_E \approx (0.15$–$0.2)$, so that more accurate formulas must be used. This leads to a renormalization of the parameters obtained from the static and the dynamic experiments, and consequently makes it possible to reconcile them.

Observation of two-magnon absorption makes it possible to estimate the energy at the Brillouin-zone boundary, namely 27–37 cm^{-1}. This means that the HF branch does not disperse, or may even have a negative dispersion, possibly as a result of the appreciable anisotropy field. Strong anisotropy leads also to a weak dependence of the resonance frequencies on the temperature (Fig. 2). Attention is called to the unusual shape of the two-magnon absorption line. In contrast to the one previously observed,[4] the HF front is here less steep, and may point to an unusual spin-wave dispersion law and to a peculiar magnon interaction.

We note in conclusion that the HF mode of AFMR and the two-magnon process were observed simultaneously and independently with the aid of light scattering.[3]

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