Exciton-magnon absorption of light in antiferromagnetic siderite

V. V. Eremenko, Yu. G. Litvinenko, A. A. Motornaya, V. I. Myatlik, and V. V. Shapiro

Physico-technical Institute of Low Temperatures, Ukrainian Academy of Sciences
(Submitted April 16, 1973)
Zh. Eksp. Teor. Fiz. **65**, 1227–1236 (September 1973)

The absorption spectrum of linearly polarized light is measured in single crystals of antiferromagnetic iron carbonate in the 25 100–25 600-cm^{-1} frequency range and at temperatures between 4.2 and 100 °K ($T_N = 41.5$ °K). It is shown that the peculiarity of the exciton-magnon band shape is due to intersection of the magnon and phonon branches of the spectrum. The temperature dependence of the exciton and exciton-magnon absorption bands is analyzed by the correlation function method. The singularities of this dependence are ascribed to strong magnetic anisotropy of FeCO$_3$ caused by the properties of the Fe^{2+} ion.

INTRODUCTION

Siderite (iron carbonate FeCO$_3$) belongs to the D$_{3d}$ rhombohedral system and has a space symmetry group R$\bar{3}$c with two Fe^{2+} ions per unit cell. In the antiferromagnetic state the spins of the Fe^{2+} ions are oriented along the C$_3$ axis. The translation vectors are a = 5.76 Å long and the angle between them is $\alpha = 47°25'$.[1] In the antiferromagnetic state this crystal exhibits certain characteristic properties: 1) the behavior in strong magnetic fields is unusual for transition-metal carbonates;[2,3] 2) the temperature dependences of the magnetic susceptibilities $\chi_\parallel$ and $\chi_\perp$ are also unusual;[4] 3) the frequencies of the lowest magnetic excitations are very high.[5,6]

It seemed of interest to study the spectrum of the absorption of light in antiferromagnetic siderite and to investigate the influence of temperature on this absorption in the widest possible range. Previous investigations[7] have established that the absorption transitions involve not only the high-energy exciton states but also the low-frequency excitations and the discovery of the magnetic "bleaching" of siderite, i.e., the disappearance of the electric-dipole absorption bands in strong magnetic fields capable of inducing a fully magnetized state,[8] has established clearly the exciton-magnon nature of these bands. Therefore, there is every reason to expect that a study of the frequencies, intensities, and profiles of the electric-dipole absorption bands of FeCO$_3$ and of their temperature dependences would give information on the nature of the low-frequency magnetic excitations in this crystal and on the parameters that govern the magnetic properties of FeCO$_3$.

EXPERIMENTAL METHOD

Single crystals of FeCO$_3$ were cleaved from natural siderite minerals. Mechanical polishing produced plates 0.1–1.5 mm thick, which were fairly transparent to visible light. The Néel temperature of the investigated samples was deduced from the maximum of the temperature dependence of the longitudinal magnetic susceptibility $\chi_\parallel$: the value of this temperature ranged from 41.5 to 41.8° K.[1]

The investigation was carried out using a DFS-13 spectrograph with a linear dispersion of 4 Å/mm. The spectrum was recorded on a photographic film and then analyzed by the standard photometric method. The temperature of a sample was varied from 4.2 to 100° K: this was done in a cryostat using boiling helium vapor and an electric heater. The temperature was measured with a copper-constantan thermocouple to within 0.5°K.

EXPERIMENTAL RESULTS

The absorption spectrum of FeCO$_3$ consists of two groups of strong bands with frequencies in the range 24 500 cm^{-1} and 25 200 cm^{-1}. The transitions corresponding to these bands have not yet been determined precisely. However, it is known that the ground state of the Fe^{2+} ion in FeCO$_3$ is the term ^{5}D and all the excited states have spins S < 2. Consequently, the pure exciton bands should not be of the electric-dipole nature. A possible identification of one of the transitions is given in[7]. By analogy with the spectrum of FeF$_2$, the group of bands in the region of 25 200 cm^{-1} is attributed in[7] to the transition ^{5}T$_2$ → ^{3}T$_2$. The general appearance of the absorption spectrum in this region is shown in Fig. 1.

The bands in the 25 200 cm^{-1} group differ considerably from one another: there are two weak bands at 25 166 and 25 207 cm^{-1}, two relatively narrow but strong bands at 25 259 and 25 303 cm^{-1}, and four wide strong bands at 25 364, 25 396, 25 432, and 25 471 cm^{-1}. The behavior of the 25 166 and 25 259 cm^{-1} bands in magnetic fields[7,8] allows us to identify the 25 166 cm^{-1} as a pure exciton band and the 25 259 cm^{-1} band as its magnon satellite. The 25 207 and 25 303 cm^{-1} bands are a similar pair. The intervals between the bands in both pairs are similar and amount to ~95 cm^{-1}. The other bands in this group are formed with the assistance of optical phonons and are phonon replicas of the exciton-magnon transitions.

Figure 2 shows the profile of the exciton-magnon band at 25 259 cm^{-1}. We can see from Fig. 2 that the polarization of this band is only partial. The other bands of the same group are also partially polarized. Nevertheless, we may conclude that the 25 259 cm^{-1} band is of the electric-dipole nature. Moreover, there is no red asymmetry in the profile of this band, although such
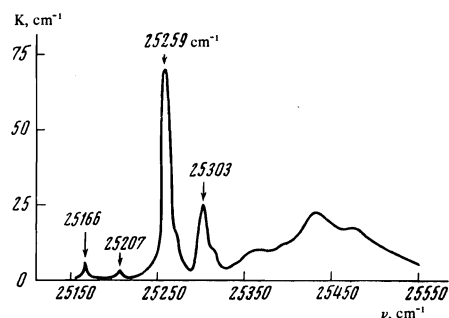

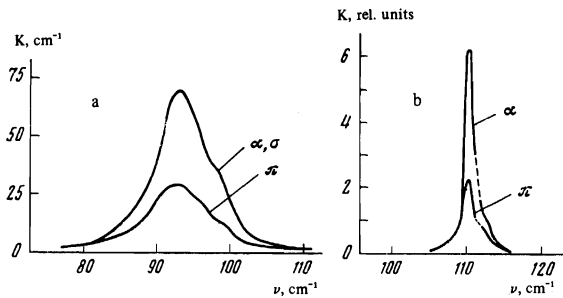FIG. 1. Absorption spectrum of FeCO$_3$ in the frequency range 25 100 – 25 600 cm^{-1}.

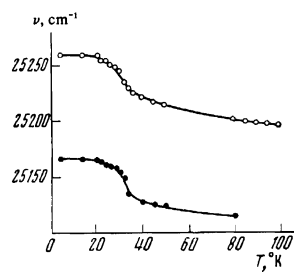FIG. 2. Profiles of the exciton-magnon absorption bands of $FeCO_3$; a) experimental profile; b) theoretical profile.

FIG. 3. Temperature dependences of the absorption frequencies of $FeCO_3$: (●) $\nu = 25\ 166\ cm^{-1}$ (pure exciton band); (○) $\nu = 25\ 259\ cm^{-1}$ (exciton-magnon band).
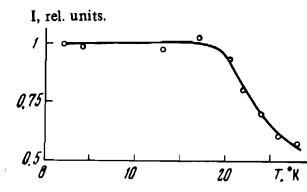
FIG. 4. Temperature dependence of the integrated intensity of the $\nu = 25\ 259\ cm^{-1}$ exciton-magnon band of $FeCO_3$.

asymmetry is typical of the exciton-magnon bands. Additionally, the temperature dependence of the frequency of the maximum of this band (Fig. 3) is unusual: a considerable low-frequency shift occurs not only on approach to the phase transition point (Néel temperature) but also at temperatures much above this point. Thus, whereas between 4.2°K and T_N the band shift is 35 cm^{-1}, between T_N and 100°K the band shifts a further 25 cm^{-1}. A temperature dependence of the frequency of a similar nature is also observed for the pure exciton band at 25 166 cm^{-1} so that the interval between these two bands remains practically constant throughout the temperature range 4.2—80°K.

As in the case of the 25 166—25 259 cm^{-1} band pair discussed above, the frequencies in the pair of the weaker bands at 25 207 and 25 303 cm^{-1} decrease linearly in the temperature range 4.2—20.4°K and then begin to fall more rapidly. At temperatures close to the Néel point, all the bands in this group begin to broaden rapidly. Therefore, it is not possible to study the positions of the maxima of the weak 25 207 and 25 303 cm^{-1} bands in a wide range of temperatures and this applies even more strongly to the wide exciton-magnon-phonon bands.

The integrated intensity of the exciton-magnon bands falls somewhat when the temperature is raised. The temperature dependence of the intensity of the 25 259 cm^{-1} band is plotted in Fig. 4. Above 30°K these bands begin to overlap and it is not possible to separate the contribution of each to the absorption spectrum. The general intensity of the whole group remains constant within the limits of the experimental error ($\pm 10\%$).

DISCUSSION

As mentioned earlier, there are grounds for assuming that the electric-dipole absorption bands of $FeCO_3$ are of the exciton-magnon nature. If we suppose that the magnon spectrum is not deformed by the excitation of excitons (i.e., if we ignore the exciton-magnon interaction), we find that the intensities of the electric-dipole bands corresponding to an exciton-magnon transition are[9]

$$I^{\xi}(\nu) = \frac{1}{N}\sum_{k,\mu}|\Pi^{\xi}(k)|^2|u_\mu(k)|^2\,\delta(h\nu - E_\mu^{mag}(k) - E^{exc}(k)). \quad (1)$$

In Eq. (1) the index ξ represents the direction of the electric vector of the incident light wave; ν is the frequency of light; k is the wave vector; $\Pi^{\xi}(k)$ is the projection, on the ξ axis, of the Fourier transformation of the electric-dipole moment vector $\Pi_{n\alpha,\ m\beta}$ of a pair of ions located at sites n and m, where the indices α and β identify the sublattices, i.e., the numbers of mag-

netic ions in a unit cell (α, β = I, II), and the index μ identifies the number of the magnon branch. The summation over k is limited to the first Brillouin zone (Fig. 5).

We shall assume, as is usual for antiferromagnets, that the exciton energy E^{exc} experiences practically no dispersion. In the case of the magnon energy $E_\mu^{mag}(k)$ we must determine first which of the lowest excitations participates in the optical transitions under consideration.

A calculation of the spectrum of the Fe^{2+} ions in a crystal field of rhombohedral symmetry subject to the spin-orbit interaction ($\lambda = -100\ cm^{-1}$) shows that the lowest electron excitations should correspond to transitions from the ground $\Psi_1|2\rangle$ to the excited $\Psi_2|-2\rangle$ and $\Psi_1|1\rangle$ states. Here,

$$\Psi_1 = \sqrt{2/3}\,Y_2{}^2 - \sqrt{1/3}\,Y_2{}^{-1}, \quad \Psi_2 = \sqrt{2/3}\,Y_2{}^{-2} + \sqrt{1/3}\,Y_2{}^1,$$

where the quantization axis z is selected along C_3. A study of the absorption in the far infrared[10] has shown that the transition to the state $\Psi_2|-2\rangle$ corresponds to the frequency $\nu_a = 25\ cm^{-1}$ and the transition to $\Psi_1|1\rangle$ corresponds to $\nu_b = 111\ cm^{-1}$. Since the interval between the exciton band and its strong satellite (95 cm^{-1}) is close to ν_b, we shall assume that this magnetic excitation participates in the optical transition in question. Although this excitation is not the lowest on the energy scale, we shall attribute it to a magnon because this corresponds simply to a change in the spin projection M_S by unity, whereas the orbital wave function is not affected.

An investigation of the inelastic scattering of neutrons[6] has demonstrated that a magnon branch exhibiting a weak dispersion intersects and interacts with a transverse acoustic phonon branch and this gives rise to new magnon-phonon branches whose dispersion is

$$E_\mu^{mag}(k) = \frac{1}{2}\{[\varepsilon_m + \varepsilon_f(k)] + (-1)^\mu[[\varepsilon_m - \varepsilon_f(k)]^2 + 4C_k{}^2]^{1/2}\};$$
$$\varepsilon_m = 111\ cm^{-1},\quad \varepsilon_f(k) = [S_\perp{}^2(k_x{}^2 + k_y{}^2) + S_\parallel{}^2 k_z{}^2]^{1/2}; \quad (2)$$
$$S_\parallel = 170\ A\ cm^{-1},\quad S_\perp = 215\ A\ cm^{-1},\quad C_{k\parallel} = 6.7\ cm^{-1},\quad C_{k\perp} = 5\ cm^{-1}.$$

Bearing in mind the actual crystal structure of $FeCO_3$, we can determine the electric-dipole moment vectors for each pair of the nearest ions with oppositely directed spin. We must bear in mind that a magnon of symmetry Γ_3^+ and excitons, whose possible symmetry is Γ_1^+, Γ_2^+, and Γ_3^+,[11] participate in the transition. The final results for the coefficients $\Pi^{\xi}_{n\alpha,\ m\beta}$ are listed in Table I. The Fourier transforms $\Pi^{\xi}(k)$ for the states Γ_1^+ and Γ_2^+ are given by the formulas

$$|\Pi^{\parallel}(k)|^2 = P^2(t_1{}^2 + t_2{}^2 + t_3{}^2 - t_1 t_2 - t_1 t_3 - t_2 t_3),$$
$$|\Pi^{\perp}(k)|^2 = \tfrac{1}{3}(3Q^2 + 5R^2 - 2\sqrt{3}QR)(t_1{}^2 + t_2{}^2 + t_3{}^2)$$
$$+ \tfrac{2}{3}(3Q^2 - R^2 - 2\sqrt{3}QR)(t_1 t_2 + t_1 t_3 + t_2 t_3)$$

and for the states Γ_3^+ they are given by the formulas

$$|\Pi^{\parallel}(k)|^2 = B^2(t_1 + t_2 + t_2)^2,$$
$$|\Pi^{\perp}(k)|^2 = \tfrac{2}{3}(E^2 + 3F^2)(t_1{}^2 + t_2{}^2 + t_3{}^2 - t_1 t_2 - t_1 t_3 - t_2 t_3).$$

The following notation is used in these formulas and in Table I:

$$\omega = e^{i\pi/3}, \quad t_1 = \sin\left[a(\tfrac{1}{2}k_z \cos\theta - k_y \sin\theta)\right],$$
$$t_2 = \sin\left[\tfrac{1}{2}a(k_z \cos\theta + k_y \sin\theta + \sqrt{3}k_x \sin\theta)\right],$$
$$t_3 = \sin\left[\tfrac{1}{2}a(k_z \cos\theta + k_y \sin\theta - \sqrt{3}k_x \sin\theta)\right],$$

where the coefficients P, Q, R, B, E, F are the phenomenological parameters, and $\theta = 28°$ is the angle between the translation vectors and the C_3 axis. The results obtained are in full agreement with the selection rules obtained for exciton-magnon transitions by a group-theoretic method in[11] and listed in Table II for some high-symmetry points of the Brillouin zone.

The quantities $|u_\mu(k)|^2$ in Eq. (1) represent the magnon contribution to the magnon-phonon branches and they can be represented in the form

$$|u_1(k)|^2 = \sin^2 \Phi_k,$$
$$|u_2(k)|^2 = \cos^2 \Phi_k,$$
$$\mathrm{tg}\, 2\Phi_k = \frac{2C_k}{\varepsilon_f(k) - \varepsilon_m}. \qquad (3)$$

Numerical calculations of the absorption band profile based on Eq. (1) for the exciton symmetry Γ_3^+ and of the density of magnon states

$$\rho(\nu) = \frac{1}{N}\sum_{k,\mu} |u_\mu(k)|^2 \delta[h\nu - E_\mu^{\mathrm{mag}}(k)] \qquad (4)$$

were carried out on a computer. The results are plotted in Figs. 2 and 6. It is evident from Fig. 2 that the calculated profile of the absorption curve is in qualitative agreement with the experimental observations: we find that the partial polarization of the band and the absence of the red asymmetry are correctly predicted by these
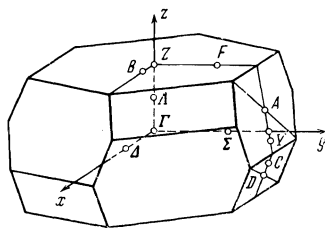

FIG. 5. Brillouin zone of a rhombohedral crystal.

TABLE I

	Exciton symmetry and polarization			
	Γ_1^+, Γ_3^+		Γ_3^+	
	$E_0 \parallel C_3$	$E_0 \perp C_3$	$E_0 \parallel C_3$	$E_0 \perp C_3$
Π_{01}^{ξ}	P	$Q - \sqrt{3}\,R$	B	$E + iF$
Π_{02}^{ξ}	$-P$	$-Q + \sqrt{3}\,R$	$-B$	$-E - iF$
Π_{03}^{ξ}	$\omega^2 P$	$Q + iR$	B	$-E + iF$
Π_{04}^{ξ}	$-\omega^2 P$	$-Q - iR$	$-B$	$E - iF$
Π_{05}^{ξ}	$-\omega P$	$Q - iR$	B	$-2iF$
Π_{06}^{ξ}	ωP	$-Q + iR$	$-B$	$2iF$

Here, E_0 is the electric vector of the incident light wave.

TABLE II

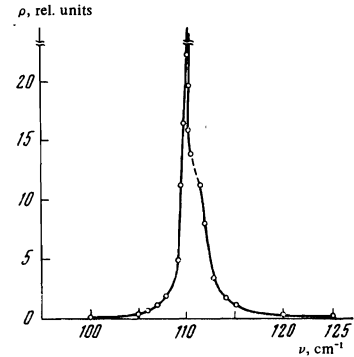| Point in Brillouin zone	Exciton symmetry	Polarization of electric-dipole transition
$Z\left(0, 0, \dfrac{\pi}{a\cos\theta}\right)$	Γ_1^+, Γ_2^+ Γ_3^+	$E_0 \perp C_3$ $E_0 \parallel C_3$
$A\left(0, \dfrac{2\pi}{3a\sin\theta}, \dfrac{\pi}{3a\cos\theta}\right)$	$\Gamma_1^-, \Gamma_2^+, \Gamma_3^+$	$E_0 \parallel C_3, \perp C_3$
$D\left(0, \dfrac{2\pi}{3a\sin\theta}, -\dfrac{2\pi}{3a\cos\theta}\right)$	$\Gamma_1^+, \Gamma_2^+, \Gamma_3^+$	—

FIG. 6. Density of magnon states in $FeCO_3$.

calculations. The absence of the red asymmetry in the profile of the exciton-magnon band is due to the fact that the dispersion of the magnon branch of $FeCO_3$ appears in practice only because of its intersection with the acoustic phonon branch, so that the density-of-states curve (Fig. 6) becomes almost symmetric, in contrast to most other cases when the density drops suddenly on the high-frequency side. The theoretical absorption curve is shifted toward higher frequencies compared with the experimental spectrum. The interval between the pure exciton and the exciton-magnon bands is not 93 cm^{-1} but 110 cm^{-1}. This difference is due to the fact that neither the exciton dispersion nor the exciton-magnon interaction is allowed for in the calculations. It is probable that this results in a considerable narrowing of the calculated absorption band, compared with the experimental profile.

The approximation of the magnon dispersion by the formula (2) is least appropriate in the region of contact between the branches and, therefore, this region is represented by dashed curves in Figs. 2 and 6.

We shall interpret the temperature dependence of the average frequency (the frequency of the center of gravity) of the exciton line and its magnon satellite, as well as the integrated intensity of this satellite, using the results of Fujiwara and Tanabe[12] who obtained expressions for the temperature dependences of the moments of these bands. In particular, the formula for the integrated intensity of the exciton-magnon band, i.e., for its zeroth moment, is

$$I^0 = \frac{1}{4}\sum_{m\beta,\, m'\beta'} (\Pi_{n\alpha,\, m\beta}^{\xi})^* \Pi_{n\alpha,\, m'\beta'}^{\xi} \left\{ \frac{1}{3}\langle S_{m\beta}^- S_{m'\beta'}^+\rangle + \frac{1}{2S}\langle S_{n\alpha}^z S_{m\beta}^- S_{m'\beta'}^+\rangle \right.$$
$$\left. + \frac{1}{6S(2S-1)}\langle [3(S_{n\alpha}^z)^2 - S(S+1)]S_{m\beta}^- S_{m'\beta'}^+\rangle \right\} \qquad (5)$$

$(\beta \neq \alpha)$. In order to find the temperature dependence of the average frequency $\langle \nu\rangle$, we must calculate the first moment, but it is much simpler to find this dependence by considering the shift of the levels of the excited and ground states in the molecular field approximation. As

shown in[12], there is little difference between the results obtained in these two ways.

Finally, the average frequency of the exciton-magnon band is

$$\langle \nu \rangle = \nu_1 + 2J(Z-1)\langle S_I{}^z \rangle \{(S-1)J'/J - (S+1)\}. \quad (6)$$

The temperature dependence of the frequency of the exciton line is

$$\nu_9 = \nu_2 + 2JS(Z-1)\langle S_I{}^z \rangle \{J'(S-1)/JS - 1\}. \quad (7)$$

In Eqs. (6) and (7) the frequencies ν_1 and ν_2 include the terms which are independent of temperature; J is the integral of the exchange between the unexcited nearest antiferromagnetic neighbors; J' is the integral of the exchange between the photoexcited and unexcited nearest antiferromagnetic neighbors. According to Eqs. (6) and (7), at low values of J the energy interval between the exciton and exciton-magnon bands should be almost constant, which is indeed observed experimentally (Fig. 3).

It now remains to calculate the correlation functions in the specific case of $FeCO_3$. We shall do this using the results of Lee and Liu,[13] but in the decoupling of a chain of the Green's functions we shall use (as, for example, in[12]) the random phase approximation. The Hamiltonian for $FeCO_3$ can be written in the form

$$\mathcal{H} = J \sum_{n,\alpha,\Delta} S_{R_{n\alpha}} S_{R_{n\alpha}+\Delta} - g\mu_B H_A \sum_n (S^z_{R_{nI}} - S^z_{R_{nII}}) \quad (8)$$

with summation in the first exchange term over the nearest antiferromagnetic neighbors; the exchange interaction between the ferromagnetic neighbors is weaker[14] and we shall ignore it. The second term of the Hamiltonian (8) corresponds to a uniaxial magnetic anisotropy. We shall assume that this anisotropy is due to the properties of a single ion.

Then, the correlation function can be represented in the form[13]

$$\langle S_{n\alpha}{}^- S_{m\beta}{}^+ \rangle = \frac{2\langle S_\beta{}^z \rangle}{N} \sum_k \varphi_{\beta\alpha}(k) \exp[-ik(R_{n\alpha} - R_{m\beta})], \quad (9)$$

where

$$\varphi_{11}(k) = \frac{1}{2}\left[-1 + \frac{A(0)+h_A}{\omega_k}\,\mathrm{cth}\,\frac{\omega_k}{2k_B T}\right],$$

$$\varphi_{22}(k) = -\frac{1}{2}\left[1 + \frac{A(0)+h_A}{\omega_k}\,\mathrm{cth}\,\frac{\omega_k}{2k_B T}\right], \quad (10)$$

$$\varphi_{21}(k) = -\varphi_{12}(k) = \frac{1}{2}\frac{A(k)}{\omega_k}\,\mathrm{cth}\,\frac{\omega_k}{2k_B T}.$$

The notation used in Eq. (10) is:

$$A(k) = A(0)\gamma_k, \quad A(0) = 2JZ\langle S_I{}^z \rangle,$$
$$h_A = g\mu_B H_A, \quad \omega_k = \{[A(0)+h_A]^2 - [A(k)]^2\}^{1/2}, \quad (11)$$

$$\gamma_k = \frac{1}{Z}\sum_\Delta e^{ik\Delta}$$

with summation over the nearest antiferromagnetic neighbors ($Z = 6$). It is worth mentioning specially that in calculating the temperature dependences we have allowed only for the excitation of the magnon states $\Psi_1|1\rangle$ and have ignored the excitation $\Psi_2|-2\rangle$. This may worsen considerably the quantitative agreement between the calculated and experimental results but can hardly affect the qualitative conclusions.

The average value of the magnetization of the sublattice α is given by the formula[13]

$$\langle S_\alpha{}^z \rangle = \frac{(S-\Phi_\alpha)(1+\Phi_\alpha)^{2S+1} + (S+1+\Phi_\alpha)\Phi_\alpha^{2S+1}}{(1+\Phi_\alpha)^{2S+1} - \Phi_\alpha^{2S+1}}, \quad (12)$$

where S is the spin of the ground state and

$$\Phi_\alpha = \frac{1}{N}\sum_k \varphi_{\alpha\alpha}(k). \quad (13)$$

As assumed, the magnetic anisotropy is basically of the single-ion nature and it does not disappear at high temperatures. Hence, we can estimate the average magnetization (12) subject to the condition $JZ \ll h_A \ll k_B T$:

$$\langle S_I{}^z \rangle / S \approx (S+1)h_A/3k_B T, \quad (14)$$

i.e., the sublattice magnetization varies slowly at temperatures above T_N. According to Eqs. (6) and (7), a similar temperature dependence is exhibited by the average frequencies of the exciton-magnon and exciton absorption bands, in agreement with the experimental results (Fig. 3).

In calculating the temperature dependence of the integrated intensity of the exciton-magnon band, the correlation functions of the $\langle (S_{n\alpha}^z)^r S_{m\beta}^- S_{m'\beta'}^+ \rangle$ type are decoupled as follows:

$$\langle (S_{n\alpha}^z)^r S_{m\beta}^- S_{m'\beta'}^+ \rangle \to \langle (S_{n\alpha}^z)^r \rangle \langle S_{m\beta}^- S_{m'\beta'}^+ \rangle. \quad (15)$$

Using the approximation (15), we can represent Eq. (5) in the form

$$I^i = \frac{\langle S_I{}^z \rangle}{16NS(2S-1)}\{S(S-1)+(2S-1)\langle S_I{}^z \rangle + \langle (S_I{}^z)^2 \rangle\} \quad (16)$$

$$\times \sum_k |\Pi^i(k)|^2 \left(1 + \frac{h_A + A(0)}{\omega_k}\,\mathrm{cth}\,\frac{\omega_k}{2k_B T}\right).$$

The quantities $\langle (S_\alpha^z)^2 \rangle$ were calculated by Lee and Liu.[13]

It follows from Eq. (16) that the weakening of the integrated intensity of the exciton-magnon band of $FeCO_3$ in the temperature range $0-30°$ K is primarily due to a reduction in $\langle S_I^z \rangle$.

Thus the special features of the profiles of the electric-dipole absorption bands of antiferromagnetic $FeCO_3$ and the dichroism of these bands can be explained in a unified manner on the basis of the exciton-magnon absorption mechanism. The usual temperature dependences of the frequencies and intensities of the absorption bands are due to the strong single-ion magnetic anisotropy of $FeCO_3$.

¹ L. I. Mirkin, Spravochnik po rentgenostrukturnomu analizu polikristallov (Handbook on X-Ray Structure Analysis of Polycrystalline Materials), Fizmatgiz, M., 1961.

² I. S. Jacobs, J. Appl. Phys. **34**, 1106 (1963).

³ V. I. Ozhogin, Zh. Eksp. Teor. Fiz. **45**, 1687 (1963) [Sov. Phys.-JETP **18**, 1156 (1964)].

⁴ H. Bizette and B. Tsai, C. R. Acad. Sci. **238**, 1575 (1954).

⁵ G. A. Prinz and D. W. Forester, Proc. Seventeenth Ann. Conf. on Magnetism and Magnetic Materials, Chicago, USA, 1971 (AIP Conf. Proc. Vol. 5, Part 1),

publ. by American Institute of Physics, New York, 1971, p. 279.

[6] D. E. Wrege, S. Spooner, and H. A. Gersch, Proc. Seventeenth Ann. Conf. on Magnetism and Magnetic Materials, Chicago, USA, 1971 (AIP Conf. Proc. Vol. 5, Part 2), publ. by American Institute of Physics, New York, 1971, p. 1334.

[7] D. S. McLure, R. Meltzer, S. A. Reed, P. Russell, and J. W. Stout, Optical Properties of Ions in Crystals (Proc. Conf., John Hopkins University, Baltimore, Md., 1966), publ. by Interscience, New York, 1967, p. 257.

[8] V. V. Eremenko, Yu. G. Litvinenko, and V. I. Myatlik, ZhETF Pis. Red. 12, 66 (1970) [JETP Lett. 12, 47 (1970)].

[9] D. D. Sell, R. L. Greene, and R. M. White, Phys. Rev. 158, 489 (1967).

[10] V. M. Naumenko and S. G. Knyazev, Doklad na Mezhdunarodnoĭ konferentsii po magnetizmu, Moskva, 1973 (Paper presented at Intern. Conf. on Magnetism, Moscow, 1973).

[11] N. A. Sergienko, V. V. Eremenko, and A. I. Belyaeva, Fizika nizkikh temperatur (Physics of Low Temperatures) No. 17, FTINT AN UkrSSR, 1972, p. 98.

[12] T. Fujiwara and Y. Tanabe, J. Phys. Soc. Jap. 32, 912 (1972).

[13] K. H. Lee and S. H. Liu, Phys. Rev. 159, 390 (1967).

[14] R. F. Altman, S. Spooner, and D. P. Landau, Proc. Eighteenth Ann. Conf. on Magnetism and Magnetic Materials, Denver, Colorado, USA (1972).

Translated by A. Tybulewicz
124