

EXCITON AND EXCITON-MAGNON ABSORPTION IN ANTIFERROMAGNETIC  $\text{CsMnF}_3$ 

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The absorption spectrum of antiferromagnetic  $\text{CsMnF}_3$  is studied in detail in the C-group band region of the  $\text{Mn}^{2+}$  ion shifted from the inversion center. The temperature was varied in the range 1.2–60° K, and the external magnetic field from 0 to 25 kOe. Identification of the spectrum is made within the framework of group-theory analysis. It is shown that  $\text{CsMnF}_3$  is an unusual crystal among antiferromagnetic substances. For the  $\text{Mn}^{2+}$  ion in it, pure exciton transitions are allowed in the electric dipole approximation. The main properties of pure exciton and exciton-magnon absorption bands are obtained in accord with the Loudon scheme.<sup>[2]</sup> "Hot" and "cold" magnon satellites and also two-magnon satellites of pure exciton absorption bands have been observed in the absorption spectrum and investigated. The maximum magnon frequency at the boundary of the Brillouin zone is determined,  $\Delta_2 = 38 \text{ cm}^{-1}$ . The distortion of this quantity as a result of exciton-magnon interaction is discussed for processes induced by excitation of one or two magnons together with the exciton.

A new type of electric dipole optical transition called exciton-magnon has been observed in recent years in the majority of antiferromagnetic crystals studied. A number of papers<sup>[1-3]</sup> have been devoted to a review of the experimental and theoretical investigations of this problem.

It is characteristic that all exciton-magnon transitions are observed in crystals that are centrally symmetric relative to the ion absorbing the light. Pure electronic transitions for this case are forbidden in the limits of an unfilled  $3d^n$  electron configuration in the electric-dipole approximation, and only weak magnetic dipole transitions have been observed. The role of the magnon in the exciton-magnon process, which disturbs the inversion symmetry, is analogous to the role of a non-symmetric phonon in the electron-phonon mechanism of light absorption.

The theory of exciton light absorption as the most realistic approximation for the description of the exciton states of a magnetically ordered crystal was established by Loudon.<sup>[2]</sup> The basic results of this theory reduce to the following.

1. Elementary excitations of an antiferromagnetic crystal are collective Frenkel excitons. Spin waves are a special case of Frenkel excitons, in which the excited state differs from the ground state by a unit change in the spin projection on the magnetic axis.

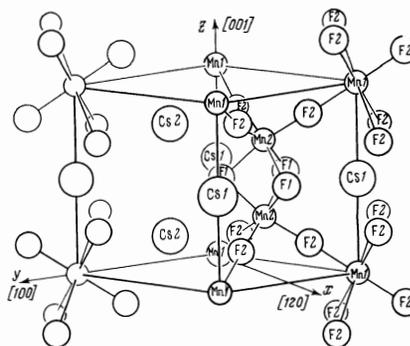
2. Exciton-magnon satellites arise as a result of the interaction between magnetic ions and represent a complicated two-particle excitation. If the simple Frenkel excitons are superpositions of single ion excitations, then the exciton-magnon state is a state of superposition of pair excitations.

In connection with the fact that the optical photon has zero momentum, according to the law of conservation, pure exciton lines correspond to creation of excitons with  $\mathbf{k} \approx 0$ . For exciton-magnon bands in absorption, two processes are of interest. In light absorption there can be produced either an exciton with wave vector  $\mathbf{k}$  and a magnon ( $-\mathbf{k}$ ), or only an exciton ( $\mathbf{k}$ ) with simultaneous absorption of a magnon ( $\mathbf{k}$ ). In the latter case,

there appears in the absorption spectrum a "hot" exciton-magnon band, the intensity of which depends on the thermal filling of the magnon states in the crystal. Experimentally, such a band has been observed in the spectrum of  $\text{MnF}_2$ .<sup>[4]</sup>

In the present paper, results are given of the investigation of the absorption spectrum of antiferromagnetic  $\text{CsMnF}_3$ . The optical absorption spectrum of this crystal was previously investigated experimentally by Stevenson.<sup>[5]</sup> However, the absolute similarity of the received spectrum with the previously investigated  $\text{MnF}_2$  spectrum, and also a private communication from the author to the effect that the studied samples were not pure, allow us to assume that data are lacking at the present time on the optical absorption spectrum of  $\text{CsMnF}_3$ . At the same time, this compound is of great interest in connection with the presence of two types of places for the  $\text{Mn}^{2+}$  ion in its elementary cell: centrally symmetric  $\text{Mn1}$  and  $\text{Mn2}$ , which is shifted from the inversion center by 0.21 Å.<sup>[6]</sup>

In the paramagnetic state,  $\text{CsMnF}_3$  has a hexagonal cell and the space group  $P6_3/mmc$  (Fig. 1). One third of the  $\text{Mn}^{2+}$  ions ( $\text{Mn1}$ ) occupy the center of the octahedral formed by the fluorine atoms, the angles of which are common with other octahedra, similar to the structure of perovskite. The local symmetry of  $\text{Mn1}$  is  $D_{3d}$ , its

FIG. 1. Half of an elementary cell of  $\text{CsMnF}_3$  [6].

closest magnetic neighbors are six Mn2 ions. The remaining two thirds of the  $Mn^{2+}$  ions—Mn2—are surrounded by a distorted octahedron of fluorine which has a common boundary and three corners with other octahedra. The symmetry of Mn2 is  $C_3$ ; its nearest neighbors are Mn1 ions and one Mn2 ion.

$CsMnF_3$  is a four-sublattice collinear antiferromagnet.<sup>[7,8]</sup> The magnetic elementary cell is identical with the crystallographic one. The strong negative anisotropies along the hexagonal axis determines the orientation of the electron spins in the basal plane with the axis of easy magnetization,  $[120]$ . The reversing field in the basis plane is  $H_c \approx 900$  Oe.

In the present work we investigated a single crystal of  $CsMnF_3$  of thickness 2.23 mm, grown by the Bridgman method in a helium atmosphere ( $T_m = 747 \pm 10^\circ C$ ). X-ray studies have shown that its structure is hexagonal and its lattice parameters  $a = 6.215 \pm 0.004 \text{ \AA}$  and  $c = 15.07 \pm 0.004 \text{ \AA}$  are in excellent agreement with the results of Zalkin, Lee and Templeton.<sup>[6]</sup>

The absorption spectrum in the C-group band region ( $24,900\text{--}26,000 \text{ cm}^{-1}$ )<sup>1)</sup> was photographed with a DFS-8 diffraction spectrograph with linear dispersion  $3 \text{ \AA/mm}$ . The sample temperature was varied in the range  $1.2\text{--}60^\circ K$ . By use of an SP-47 electromagnet, the magnetic field was changed from 0 to 25 kOe in the basal plane of the sample. An Ahrens polarizer was used to polarize the light.

## 1. FEATURES OF THE FINE STRUCTURE OF THE C-GROUP BAND IN THE ABSORPTION SPECTRUM OF $CsMnF_3$

Figure 2 shows the absorption spectrum of  $CsMnF_3$  in the C-group band region for  $T = 4.2^\circ K$  at various directions of propagation and polarization of the light. A comparison with the spectra of  $MnF_2$ ,  $KMnF_3$ ,  $RbMnF_3$ , previously obtained in this region,<sup>[9,10]</sup> shows that the spectrum for  $CsMnF_3$  is much more complicated. It is divided into three subgroup bands in Fig. 2.

The shortest-wave subgroup III (not completely shown in the figure) is similar to what has previously been observed in practically all crystals containing  $Mn^{2+}$ , and is connected with electron-phonon processes. This part of the spectrum consists of weak bands whose interpretation is complicated by the lack of data on the vibrational spectrum of  $CsMnF_3$ .

Subgroup II consists of three intense bands ( $C_{11}\text{--}C_{13}$ ) and is characteristic for crystals containing centrally symmetric  $Mn^{2+}$  ions of the Mn1 type. This part of the spectrum will be studied in a separate work using a thinner sample.

The subgroup band I, with a strongly developed fine structure, has not been previously observed in any of the studied crystals, and is apparently connected with the Mn2 center, which is characteristic of  $CsMnF_3$  crystals exclusively. This very subgroup is studied in

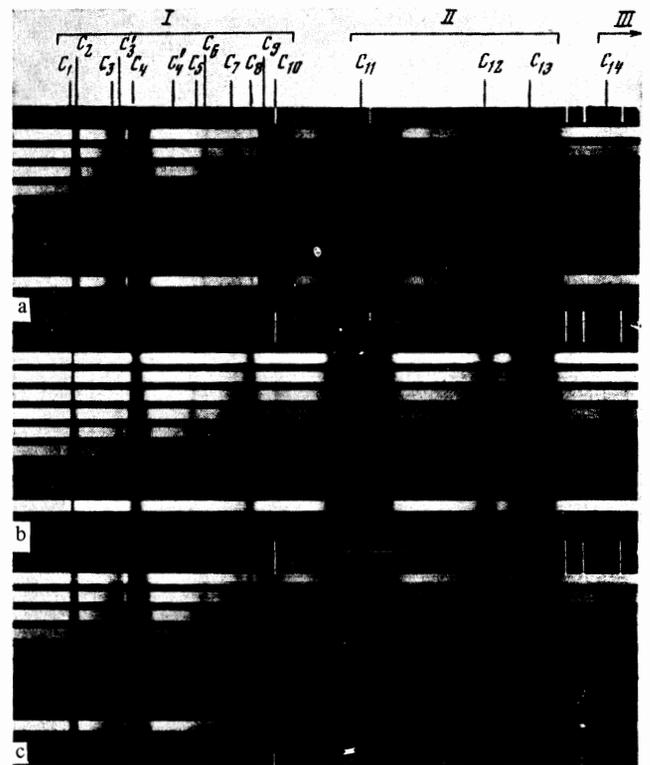


FIG. 2. Absorption spectrum of  $CsMnF_3$  in the region of the C-group bands for different directions of propagation and polarization of light: a —  $k \parallel C_6$ ,  $E \perp C_6$ ,  $h_p \perp C_6$ ; b —  $k \perp C_6$ ,  $E \parallel C_6$ ,  $h_p \perp C_6$ ; c —  $k \perp C_6$ ,  $E \perp C_6$ ,  $h_p \parallel C_6$ . Here  $k$  is the wave vector of the incident light,  $E$  and  $h_p$  its electric and magnetic vectors,  $C_6$  the crystallographic  $[001]$  axis;  $T = 4.2^\circ K$ .

detail in the present paper. It consists of a  $C_1\text{--}C_{10}$  band much less intense than the bands of subgroup II. A comparison of the four spectra of Fig. 2 supports the idea that only a change in the orientation of the electric vector  $E$  of the incident light affects the structure of the spectrum; no significant effect of the orientation of the magnetic vector has been observed. This fact indicates that all the bands in this part of the spectrum are of the electric dipole type.

It should be noted that Stevenson<sup>[5]</sup> observed only subgroups II and III. Here the frequencies of the most intense absorption bands do not agree with those of the present work, but are equal, with an accuracy up to the experimental error, to the band frequencies of the previously studied  $MnF_2$  spectrum.

## 2. TEMPERATURE DEPENDENCE OF THE SPECTRUM. EFFECT OF THE EXTERNAL MAGNETIC FIELD

The temperature dependence of the absorption spectrum in the region of the subgroup band I is shown in Fig. 3. The fine structure of the spectrum practically disappears at  $T = 40^\circ K$ , i.e., long before the magnetic structure is disordered ( $T = 53.5^\circ K$ ). It is easy to see that with increase in temperature the bands are shifted to the long-wave part in different manners. For example, the bands  $C_3$ ,  $C_4$ ,  $C_9$ ,  $C_{10}$  are shifted at a greater rate than the others. In practice, a band shift begins at  $T > 20^\circ K$ . In this connection, the  $CsMnF_3$  spectrum

<sup>1)</sup>The C-group band in crystals that are centrally symmetric relative to the  $Mn^{2+}$  ion has been connected with the transition  $\Gamma_1(^6S) \rightarrow \Gamma_1$ ,  $\Gamma_3(^4G)$ . In this case, the levels of the ion with which the transition is connected are determined in first approximation by means of the irreducible representation group  $O_h$ ; the state of the free ion from which the state of the ion in the crystal comes is shown in brackets.

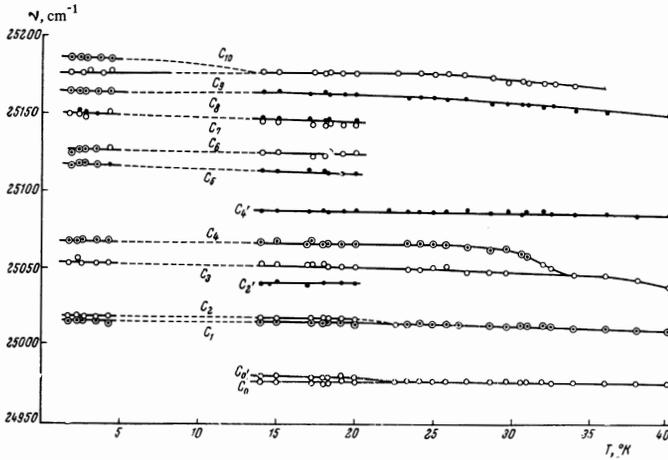


FIG. 3. Temperature dependence of the frequencies of the  $\text{CsMnF}_3$  absorption bands in the vicinity of the C-group bands (subgroup I). ● —  $E \parallel [001]$ , ○ —  $E \perp [001]$ .

differs from that previously studied in  $\text{MnF}_2$ ,  $\text{KMnF}_3$ ,  $\text{RbMnF}_3$ , where significant changes appeared in the frequencies of the bands even at  $T \sim 20^\circ\text{K}$ , while the graphs of the dependence of the band frequencies on temperature duplicated the curves of the temperature dependence of the short-range order parameter.<sup>[11]</sup> The bands  $C_0$ ,  $C'_0$  and  $C'_4$  do not exist at  $T < 13^\circ\text{K}$ . The difference in the rates of shift with temperature indicates the different nature of the observed bands.

In the analysis of the fine structure, intervals that are close to the maximum magnon frequency are reliably distinguished on the boundary of the Brillouin zone.<sup>[5]</sup>

$$\begin{aligned} \Delta_1(C_3 - C_1) &= 34 \text{ cm}^{-1} & \Delta_1(C'_3 - C_2) &= 34 \text{ cm}^{-1} & \Delta_1(C_7 - C_5) &= 34 \text{ cm}^{-1} \\ \Delta_2(C_8 - C_6) &= 38 \text{ cm}^{-1} & \Delta_2(C_1 - C_0) &= 38.3 \text{ cm}^{-1} & \Delta_2(C_2 - C'_0) &= 38.4 \text{ cm}^{-1} \\ & & \Delta_2(C_6 - C'_4) &= 38.3 \text{ cm}^{-1} & & \end{aligned}$$

Figures 4 and 5 show the absorption spectrum as a function of the external magnetic field at a temperature of  $4.2\text{--}20.4^\circ\text{K}$  for two different field orientations in the basal plane of the crystal.<sup>2)</sup>

It should be noted that the fine structure of the spectrum does not change with increase in the intensity of the external magnetic field. The basic effect reduces to the change of the polarization properties of the individual bands. Here the polarization properties of the doublet  $C_1/C_2$  do not depend on the temperature but are essentially different for different directions of the external magnetic field. In the case in which  $H \parallel [120]$  (Fig. 4), for the range of fields 0.7–12 kOe, practically complete polarization of the components of the doublet is observed, while polarization for the case  $H \parallel [100]$  is absent at any orientation of the vector  $E$  relative to the field  $H$ . So far as the doublets  $C_0/C'_0$  and  $C_3/C'_3$  are concerned, no change of direction of the magnetic field is seen in them. Thus investigations in the external magnetic field do not contradict the conclusion as to the different nature of the doublet  $C_1/C_2$  on the one hand

<sup>2)</sup> The only bands of the C group (subgroup I) shown in the drawing are those which exhibit the effect of the external magnetic field. No noticeable effect of the field on the remaining bands of the considered subgroup was observed, a fact connected to a considerable extent with its lesser intensity and the great difficulties in its investigation.

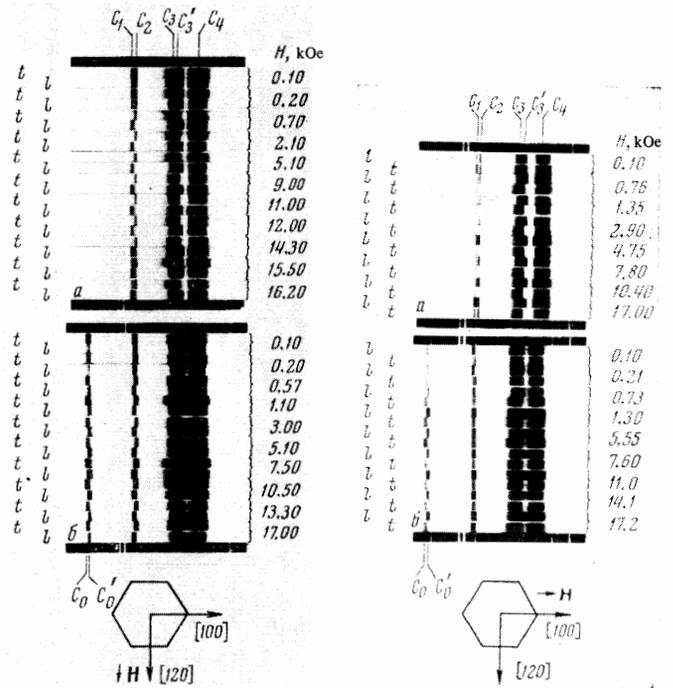


FIG. 4

FIG. 5

FIG. 4. Field dependence of the absorption spectrum of  $\text{CsMnF}_3$  in the region of the C-group bands (subgroup I): a — for  $T = 4.2^\circ\text{K}$  and b — for  $T = 20.4^\circ\text{K}$ , when the external magnetic field  $H \parallel [120]$  and the electric vector of the light wave  $E \parallel H$  in case  $l$  and  $E \perp H$  in case  $t$ .

FIG. 5. Field dependences of the absorption spectrum of  $\text{CsMnF}_3$  in the region of the C-group bands (subgroup I): a — for  $T = 4.2^\circ\text{K}$  and b — for  $T = 20.4^\circ\text{K}$ , with external magnetic field  $H \parallel [100]$  and the electric vector of the light wave  $E \parallel H$  in case  $l$  and  $E \perp H$  in case  $t$ .

and the doublets  $C_0/C'_0$ ,  $C_3/C'_3$  on the other, deduced on the basis of temperature studies.

### 3. DISCUSSION OF THE EXPERIMENTAL RESULTS

The experimental results were analyzed under the assumption that the studied band I subgroup is connected with the excitation of Mn2 ions. Knowing the local group symmetry of the absorbing light of the ion and the factor group of the magnetically ordered crystal, we can, by the Loudon scheme,<sup>[2]</sup> obtain the basic properties of pure exciton and exciton-magnon absorption bands.<sup>3)</sup>

The local group of the Mn2 ion (4 ions) for the case in which the magnetic moments are parallel to  $[100]$  is  $C_5$ , and the factor group of the crystal is  $D_{2h}$ . The wave functions of the Mn2 ion are transformed like the  $\Gamma_3$  and  $\Gamma_4$  representations of the  $C_5$  group. If the wave functions of the ion of one sublattice are transformed as  $\Gamma_3$  ( $\Gamma_4$ ), the corresponding wave functions of the ion of the other sublattice transform as  $\Gamma_4$  ( $\Gamma_3$ ). Figure 6 shows a

<sup>3)</sup> In [12] a complete group-theory analysis for the cases of exciton and exciton-magnon processes is given for a number of antiferromagnets, including  $\text{CsMnF}_3$ . The space groups of the crystal and the local groups of Mn1 and Mn2 ions are given for the cases in which the spins are oriented parallel to the  $[100]$  and  $[120]$  faces in the basal plane. Types of exciton and exciton-magnon transitions are determined, and also the selection rule for their observation at all critical points of the Brillouin zone.

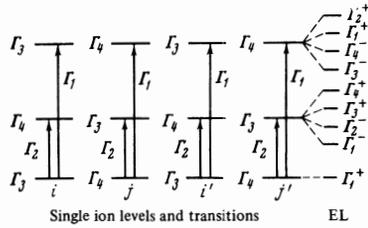


FIG. 6. Schematic representation of the process of exciton formation (EL = exciton level for  $k = 0$ ) from single ion excitations for four Mn2 ions (the magnetic moments are parallel to the [100] axis).

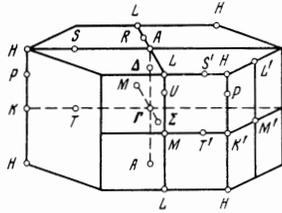


FIG. 7. Brillouin zone for the CsMnF<sub>3</sub> single crystal.

schematic representation of the process of exciton formation from single-ion excitation for the four Mn2 ions at the point  $\Gamma(0, 0, 0)$  of the Brillouin zone ( $k = 0$ , see Fig. 7). Since in our case none of the representations of the factor group  $D_{2h}$  has an additional degeneracy that is connected with the operation of time reversal, all the excitons are non-degenerate and appear as components of the Davydov splitting.<sup>4)</sup>

In connection with the fact that the ground state has the symmetry of the  $\Gamma_1^+$  factor group, the excitons active in light absorption are those transformed in the same way as the corresponding components of the dipole operator. The selection rules for excitons are given in Table I. Excitons of symmetry  $\Gamma_1^+$  and  $\Gamma_2^+$  are permitted in the absorption process.

Thus, CsMnF<sub>3</sub> is unusual among the antiferromagnetic crystals in that, owing to the natural distortion of the crystalline structure in the vicinity of Mn2 ions, pure exciton transitions are permitted in the electric dipole approximation. They can be realized without the creation of additional excitations (phonons, magnons). The additional exclusion according to spin in magnetically ordered crystals in the presence of exchange interaction is not rigorous. This question was discussed earlier by Ferguson et al.<sup>[13]</sup> The exchange mechanism of allowance of transitions in the electric dipole approximation is shown to be more important for transitions between states with identical symmetries of the orbital wave functions. Therefore, it should be expected that in the case of CsMnF<sub>3</sub> bands, similar to the transition  $\Gamma_1(^6S) \rightarrow \Gamma_1(^4G)$  in centrally symmetric crystals, will be more intense than the analog of the transition  $\Gamma_1(^6S) \rightarrow \Gamma_3(^4G)$ .

Table II gives the irreducible representations of the excitons for the critical points of the Brillouin zone,

<sup>4)</sup>The local group of the Mn2 ion, for the case in which the magnetic moments are parallel to the [120] axis, reduces to an identity transformation and the group-theory analysis does not yield unique results on the polarization of the exciton transitions. The absorption bands  $C_1/C_2$  in this case should be unpolarized, as is observed experimentally (Fig. 5).

Table I. Selection rule for excitons

Polarization	Active state	Polarization	Active state
Magnetic dipole process			
$h_\nu \parallel [100] (\sigma)$	$\Gamma_2^+$	Electric dipole process	
$h_\nu \parallel [001] (\pi)$	$\Gamma_3^+$		
$h_\nu \parallel [120] (\sigma)$	$\Gamma_4^+$		

Table II. Irreducible representations of excitons for critical points of the Brillouin zone, consistent with the corresponding representations at the point  $\Gamma(0, 0, 0)$

$\Gamma$	$\Gamma_1^+$	$\Gamma_2^+$	$\Gamma_3^+$	$\Gamma_4^+$	$\Gamma_1^-$	$\Gamma_2^-$	$\Gamma_3^-$	$\Gamma_4^-$
$M$	$M_1^+$	$M_2^+$	$M_3^+$	$M_4^+$	$M_1^-$	$M_2^-$	$M_3^-$	$M_4^-$
$M'$	$M_1^+$	$M_2^+$	$M_3^-$	$M_4^-$	$M_1^-$	$M_2^-$	$M_3^+$	$M_4^+$
$K$	$K_1$	$K_2$	$K_3$	$K_4$	$K_1$	$K_2$	$K_3$	$K_4$
$L$		$2L_1$				$2L_2$		
$L'$		$2L_1'$				$2L_2'$		
$A$		$2A_1$				$2A_2$		
$H$		$2H$				$2H$		

compatible with the corresponding representations at the point  $\Gamma(0, 0, 0)$ . A selection rule was obtained by the method of Lax and Hopfield<sup>[14]</sup> for double transitions, in which excitations at points with wave vectors  $k$  and  $-k$  participate simultaneously on the boundary of the Brillouin zone (Table III).

Identification of the bands  $C_0 - C_{10}$ , performed on the basis of the experimental data and considerations of group theory analysis, is given in Table IV.

The intense doublet  $C_1/C_2$  and the less intense  $C_5/C_6$ , which do not shift with increase in temperature (Fig. 3), can be connected with the pure exciton transitions allowed in the electric dipole approximation, to which the bands associated with the transitions  $\Gamma_1(^6S) \rightarrow \Gamma_1(^4G)$  and  $\Gamma_1(^6S) \rightarrow \Gamma_3(^4G)$  are analogous in centrally symme-

Table III

Product of the point representations on the boundary of the Brillouin zone with the wave vectors $k$ and $-k$	Expansion in representations of the factor-group $D_{2h}$ *
$M_i^\pm \cdot M_i^\pm (i = 1, 2, 3, 4)$	$\Gamma_1^+$
$M_i^+ \cdot M_i^- (i = 1, 2, 3, 4)$	$\Gamma_1^-$
$M_1^\pm \cdot M_2^\pm = M_3^\pm \cdot M_4^\pm$	$\Gamma_2^+$
$M_1^\pm \cdot M_3^\pm = M_2^\pm \cdot M_4^\pm$	$\Gamma_3^+$
$M_1^\pm \cdot M_4^\pm = M_2^\pm \cdot M_3^\pm$	$\Gamma_4^+$
$M_1^\pm \cdot M_2^\mp = M_3^\pm \cdot M_4^\mp$	$\Gamma_2^-$
$M_1^\pm \cdot M_3^\mp = M_2^\pm \cdot M_4^\mp$	$\Gamma_3^-$
$M_1^\pm \cdot M_4^\mp = M_2^\pm \cdot M_3^\mp$	$\Gamma_4^-$
$M_i^\pm \cdot M_i^\pm (i = 1, 2)$	$\Gamma_1^+ + \Gamma_3^+$
$M_1^\pm \cdot M_2^\pm$	$\Gamma_2^+ + \Gamma_4^+$
$M_1^+ \cdot M_1^- (i \neq 1, 2)$	$\Gamma_1^+ + \Gamma_3^-$
$M_1^\pm \cdot M_2^\mp$	$\Gamma_2^+ + \Gamma_4^-$
$K_1 \cdot K_1 (i = 1, 2, 3, 4)$	$\Gamma_1^+$
$K_1 \cdot K_3 = K_2 \cdot K_4$	$\Gamma_3^+ + \Gamma_4^-$
$K_1 \cdot K_4 = K_2 \cdot K_3$	$\Gamma_4^+ + \Gamma_3^-$
$K_1 \cdot K_2 = K_3 \cdot K_4$	$\Gamma_2^+ + \Gamma_1^-$
$L_1 \cdot L_1 \neq A_1 \cdot A_1 (i = 1, 2)$	$\Gamma_1^+ + \Gamma_2^+ + \Gamma_4^-$
$L_1 \cdot L_2 = A_1 \cdot A_2$	$\Gamma_3^+ + \Gamma_4^+ + \Gamma_1^- + \Gamma_2^-$
$L' \cdot L'$	$\Gamma_1^+ + \Gamma_2^+ + \Gamma_3^+ + \Gamma_4^+ + \Gamma_2^- + \Gamma_4^-$
$H \cdot H$	$\Gamma_1^+ + \Gamma_2^+ + \Gamma_4^+ + \Gamma_4^-$

\*The polarization of the twin transitions can be obtained by means of Table I.

Table IV. Identification of the  $C_0$ – $C_{10}$  absorption bands for the Mn<sup>2+</sup> ion in CsMnF<sub>3</sub>

Band	Polarization*	$\nu$ , cm <sup>-1</sup> $T = 15^\circ\text{K}$	Identification**	Active exciton	Point of the Brillouin zone
$C_0$	E    [100]	24977,7	$\nu_1 - \Delta_1$	$\Gamma_3^-$	$M, K, L, A$
$C_0'$	E    [120]	24980,7	$\nu_2 - \Delta_2$	$\Gamma_4^-$	$M, K, L, A$
$C_1$	{ E    [100] E    [120]	25016	$\nu_1$	$\Gamma_3^- + \Gamma_4^-$	$\Gamma$
$C_2$	E    [100]	25019	$\nu_2$	$\Gamma_2^-$	$\Gamma$
$C_3$	E    [100]	25050	$\nu_1 + \Delta_1$	$\Gamma_3^-$	$M, K, L, A$
$C_3'$	E    [120]	25053	$\nu_2 + \Delta_1$	$\Gamma_4^-$	$M, K, L, A$
$C_4$	UP	25068,3	$\nu_{1,2} + 2\Delta_1 - \text{EMI}$	$\Gamma_3^- + \Gamma_3^- + \Gamma_4^-$	—
$C_4'$	E    [001]	25089	$\nu_6 - \Delta_1$	$\Gamma_3^-$	$L, L', A, H$
$C_5$	E    [001]	25115,8	$\nu_5$	$\Gamma_3^- + \Gamma_4^-$	$\Gamma$
$C_6$	E ⊥ [001]	25127,3	$\nu_6$	$\Gamma_3^-$	$\Gamma$
$C_7$	UP	25149,8	$\nu_5 + \Delta_1$	$\Gamma_3^- + \Gamma_3^- + \Gamma_4^-$	$H, L'$
$C_8$	E    [001]	25165,3	$\nu_6 + \Delta_2$	$\Gamma_3^-$	$L, L', A, H$
$C_9$	E ⊥ [001]	25179,3	$\nu_5 + 2\Delta_1 - \text{EMI}$	$\Gamma_3^-$ or $\Gamma_4^-$	—
$C_{10}$	E ⊥ [001]	25187	$\nu_6 + 2\Delta_1 - \text{EMI}$	$\Gamma_3^-$ or $\Gamma_4^-$	—

\*UP – unpolarized.

\*\*EMI – Exciton-Magnon Interaction.

tric crystals. The doublets correspond to splitting in the field of local symmetry  $C_S$  of the levels  $\Gamma_1$  and  $\Gamma_3(^4G)$  of the cubic group  $O_h$  ( $\Gamma_1, \Gamma_3(^4G) \rightarrow \Gamma_3 + \Gamma_4$ ). The polarization properties of these bands (Figs. 2 and 4) permit us to connect them with the completely concrete excitons at the point  $\Gamma(0, 0, 0)$  of the Brillouin zone (Table IV). The absence of polarization of the bands in fields below 0.7 kOe—the turning field (when the magnetic moment is uniquely oriented along the [100] axis, perpendicular to the field; Fig. 4)—is evidently connected with the equally probable distribution of the magnetic moment along the three axes in the basal plane of the crystal, equivalent to the easy-magnetization axis [120]. Deterioration of the polarization of the bands in field  $H > 12$  kOe (Fig. 4) is due to distortion of the collective magnetic structure and the appearance of a component of the magnetic moment parallel to the [120] axis. Thus the bands  $C_1$  and  $C_5$  are connected with the transitions by exciton levels which are combinations of single-ion transitions  $\Gamma_1^+$  and  $C_2$  and  $C_6$  by combinations of single-ion transitions  $\Gamma_2^+$  (Fig. 6).

The absence of Davydov splitting, which would be expected for the bands  $C_1$  and  $C_5$  (Fig. 2), indicates that the interaction of the excited states of the Mn<sup>2+</sup> ion is insufficient for the resolution of the  $\Gamma_3^- + \Gamma_4^-$  components of this splitting. Quantitative estimates of the value of the Davydov splitting, carried out according to the formulas of<sup>[15]</sup> show that it should not exceed  $10^{-4}$  cm<sup>-1</sup>. For this reason, the band  $C_1$  in Fig. 2 is seen to be unpolarized, and  $C_5$  to be weakly polarized.

The bands  $C_0/C_0'$  and  $C_4'$ , which are lacking at low temperature, deserve special attention (Figs. 3–5). They are sharply polarized and their intensity increases with increasing temperature. These bands appear at  $T \sim 13^\circ\text{K}$  on the long-wave side of the pure exciton bands  $C_1, C_2$  and  $C_6$ , and are separated from them by an interval  $\Delta_2 = 38$  cm<sup>-1</sup>, which is close to the maximum frequency of the magnon on the boundary of the Brillouin zone.

The appearance of such a type of band is not characteristic of compounds containing Mn<sup>2+</sup>. The ground state of the Mn<sup>2+</sup> ion is an orbital singlet  $\Gamma_1(^6S)$ , and the nearest excitation is separated from the ground state by  $\sim 2 \times 10^4$  cm<sup>-1</sup>. There are no orbital states separated from the ground state by  $\sim 40$  cm<sup>-1</sup>; these can be populated with increasing temperature. In this connection,

the bands  $C_0, C_0'$  and  $C_4'$  can be regarded as “hot” exciton-magnon satellites of the pure exciton bands  $C_1, C_2$  and  $C_6$ .

The difference in principle between the “hot” and the well-known “cold” exciton-magnon bands is evident. The appearance of “cold” bands is connected with the excitation of exchange-coupled ion pairs: the transition of one ion to an excited orbital state (exciton) is accompanied by a reversal of the spin in the other ion (magnon). The energy of the resulting excitation is greater than the energy of a pure exciton transition. Therefore the “cold” exciton-magnon band appears on the shortwave side of the ground state.

The appearance of “hot” exciton-magnon bands is connected with a single-ion process. The absorption of the energy leads to a transition to the excited orbital state of the ion, which is already thermally excited (it has reversed spin). It is clear that such bands can be observed only at significantly higher temperatures and are located on the long-wave side of pure excitons. In the case of a “hot” magnon satellite, the situation is analogous to that discussed previously for luminescence,<sup>[16]</sup> when the orbital and spin excitations do not exist simultaneously and cannot interact with each other. Therefore, the interval  $\Delta_2 = 38$  cm<sup>-1</sup> corresponds to the maximum frequency of the magnon on the boundary of the Brillouin zone.

The bands  $C_3, C_3', C_7, C_8$ , which are removed from the corresponding pure exciton bands  $C_1, C_2, C_5, C_6$  by the interval  $\Delta_1 = 34$  cm<sup>-1</sup>, are close to the maximum magnon frequency, and are shifted upon increase in temperature to the side of the fundamental bands. These bands can be regarded as “cold” exciton-magnon bands. Their behavior is similar to the behavior of the exciton-magnon electric dipole bands  $C_1$  and  $C_4$  in KMnF<sub>3</sub> and RbMnF<sub>3</sub>.<sup>[10]</sup> The interval  $\Delta_1 = 34$  cm<sup>-1</sup> between “cold” exciton-magnon bands and pure exciton bands correspond to the maximum frequency of the magnon, which is distorted because of the presence of interaction between the exciton and magnon, which is simultaneously important in this case.<sup>[17]</sup>

Knowing the polarization, it is possible, by means of Tables II and III, to determine the points of the Brillouin zone, with the excitations of which the observed exciton-magnon transitions are connected (Table IV). It is characteristic that “hot” and “cold” satellites of one and the same exciton band are identically polarized and behave identically in an external magnetic field (Figs. 4, 5). However, the “hot” exciton-magnon band is much narrower than the “cold” one (Figs. 4 and 5). Evidently, this difference is due to the presence of an exciton-magnon interaction in the process of formation of the “cold” magnon satellite, which is absent in the process of formation of the “cold” magnon satellite, which is absent in the process of formation of the “hot” satellite.

The behavior of the  $C_4, C_9, C_{10}$  bands, which shift toward pure exciton bands with increase in temperature more rapidly than the exciton-magnon bands, recalls the behavior of the  $C_2$  band in KMnF<sub>3</sub> and RbMnF<sub>3</sub>.<sup>[10]</sup> These bands are evidently two-magnon satellites of the corresponding pure exciton bands  $C_{1,2}, C_5$  and  $C_6$  (Table IV). The deviation of the interval between the bands  $C_4, C_5$  and  $C_{10}$  and the corresponding pure exciton bands from the value  $2\Delta_1 = 68$  cm<sup>-1</sup> ( $\Delta(C_{1,2} - C_4)$ )

$= 51 \text{ cm}^{-1}$ ,  $\Delta(C_9 - C_5) = 63.5 \text{ cm}^{-1}$ ,  $\Delta(C_{10} - C_8) = 60 \text{ cm}^{-1}$ ) indicates a still stronger exciton-magnon interaction in this complicated process in comparison with the previously considered process in which a single magnon was created. The latter assumption is supported by the sharply expressed "blue" asymmetries of the band  $C_4$  (Fig. 2) which, as a rule stronger the greater the exciton-magnon interaction.

The rapid fall-off in intensity of the observed bands with increase in temperature is not surprising in the case of the exciton-magnon bands. So far as the pure exciton bands are concerned, weakening of the intensity can be connected with an increase in amplitude of the oscillations of the ions with increase in the temperature and corresponding increase in the probability of the stay of the Mn<sup>2+</sup> ion in the inversion center.

The value  $\Delta_2 = 38 \text{ cm}^{-1}$  exceeds the estimate of Stevenson<sup>[5]</sup> for the maximum magnon frequency  $\nu_M = g\mu_B(H_E + H_A) = 33 \text{ cm}^{-1}$ . This can be connected with the error in the determination of the exchange field  $H_E$  and the anisotropy field  $H_A$  or with the width of the exciton zone. The latter, in any case, does not exceed several  $\text{cm}^{-1}$ .

<sup>1</sup>D. D. Sell, J. Appl. Phys. 39, 1030 (1968).

<sup>2</sup>R. Loudon, Adv. Phys. 17, 243 (1968).

<sup>3</sup>V. V. Erëmenko and A. I. Velyaeva, Usp. Fiz. Nauk 98, 27 (1969) [Sov. Phys.-Uspekhi 12, 320 (1969)].

<sup>4</sup>D. S. McClure, R. Meltzer, S. A. Reed, P. Russel and J. W. Stout, Optical Properties of Ions in Crystals, New York, 1967.

<sup>5</sup>R. Stevenson, Canad. J. Phys. 43, 1732 (1965); 44,

3269 (1966).

<sup>6</sup>A. Zalkin, K. Lee and D. H. Templeton, J. Chem. Phys. 37, 697 (1962).

<sup>7</sup>L. B. Welsh, Phys. Rev. 156, 370 (1967).

<sup>8</sup>K. Lee, A. M. Portis and G. L. Witt, Phys. Rev. 132, 144 (1963).

<sup>9</sup>V. V. Erëmenko and A. I. Belyaeva, Fiz. Tverd. Tela 5, 2877 (1963) [Sov. Phys.-Solid State 5, 2106 (1964)].

<sup>10</sup>A. V. Antonov, A. I. Belyaeva and V. V. Erëmenko, Fiz. Tverd. Tela 8, 3397 (1966) [Sov. Phys.-Solid State 8, 2718 (1967)].

<sup>11</sup>V. V. Erëmenko, Doctoral Dissertation, Physico-technical Institute of Low Temperatures, Acad. Sci. Ukrainian SSR, Khar'kov, 1967.

<sup>12</sup>N. A. Sergienko, V. V. Erëmenko and A. I. Belyaeva, Works (Trudy) Physico-technical Institute of Low Temperatures, Acad. Sci. Ukrainian SSR, No. 3, Khar'kov, 1969.

<sup>13</sup>J. Ferguson, H. J. Guggenheim and Y. Tanabe, J. Appl. Phys. 36, 1046 (1965); Phys. Rev. Lett. 14, 737 (1965).

<sup>14</sup>M. Lax and J. J. Hopfield, Phys. Rev. 124, 115 (1964).

<sup>15</sup>J. P. van der Ziel, Phys. Rev. 161, 483 (1967).

<sup>16</sup>A. I. Belyaeva, S. V. Petrov, V. I. Sileav, Ukr. Fiz. Zh. 13, 2052 (1968) [Ukr. Phys. J. 13, 1462 (1968)].

<sup>17</sup>R. J. Elliott, M. F. Thorpe, G. F. Imbusch, R. Loudon and J. B. Parkinson, Phys. Rev. Lett. 21, 147 (1968).

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