ANISOTROPY OF THE ZEEMAN EFFECT IN CUBIC ANTIFERROMAGNETIC $RbMnF_3$

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Doublet splitting of the narrow 25 143.5 cm^{-1} line from the $^6A_1(^6S_{5/2}) \rightarrow {}^4A_1, {}^4E({}^4G)$ transition is observed at low temperatures ($T \ll T_N = 82^\circ K$). Polarization investigations indicate that the observed transition is magnetic dipole in character. The line splitting is uniquely related to changes in the magnetic structure of the antiferromagnetic crystal $RbMnF_3$ in an external magnetic field $H > H_{cr} = (2H_AH_E)^{1/2} \approx 3$ kOe and is due to anisotropy of the g factor in the excited state of the Mn^{2+} ion. Measurement of the Zeeman effect in a strong magnetic field ($H_{cr} \ll H < H_E$; $H \leq 2 \times 10^5$ Oe) permits one to estimate the effective field of exchange interaction between the excited Mn^{2+} ion and unexcited ions, $H_{eff} \approx 140$ kOe. This value is much smaller than that for the exchange interaction in the ground state, which is $H_E = 890$ kOe.

PREVIOUS magnetooptical investigations of the antiferromagnetic crystal MnF_2[1,2] have shown that the absorption spectrum depends strongly on the magnetic symmetry of the crystal. This has been attributed to anisotropy of the exchange interaction in the excited states of the Mn^{2+} ion. However, it has not been possible to carry out a detailed study of MnF_2, which is tetragonal and has a collinear magnetic structure, since its symmetry changes abruptly at the spin-flop field ($H_{cr} = 95$ kOe).

The antiferromagnetic crystal $RbMnF_3$, because of its cubic structure, has a small anisotropy field, which permits a change in the direction of the magnetic moment of its sublattices by means of a relatively weak applied magnetic field ($H \sim 3$ to 5 kOe). In its optical spectrum $RbMnF_3$ has, besides broad and intense absorption bands, extremely narrow lines, which are convenient for magnetooptical investigations. This peculiarity of $RbMnF_3$ indeed led to its choice for the present investigation—the study of the effect of magnetic symmetry on the fine structure of the optical absorption spectrum.

Experimental method. In the experiments we studied the longitudinal ($\mathbf{k} \parallel \mathbf{H}$) and transverse ($\mathbf{k} \perp \mathbf{H}$) Zeeman effects (here $\mathbf{k}$ is the wave vector of the light, and $\mathbf{H}$ is the external magnetic field). In the first case the magnetic field, of intensity up to 200 kOe, was produced in a cooled solenoid, and the pulse method of magnetooptical investigation was employed. The transverse Zeeman effect (in fields up to 25 kOe) was studied with an SP-47[G] electromagnet. Comparison of the results in static and pulsed fields showed that the pulsed character of the method did not introduce any additional features of any kind.

Our spectral instrument was a DFS-13 diffraction spectrograph with a linear dispersion of 2 Å/mm. The investigations were carried out in polarized light at the temperatures 1.3, 4.2 K in a special optical cryostat with transparent quartz windows. An Ahrens prism served as the polarizer. The samples[1)] of $RbMnF_3$ were oriented by x rays and then cut along the principal crystallographic directions [100], [110], and [111].

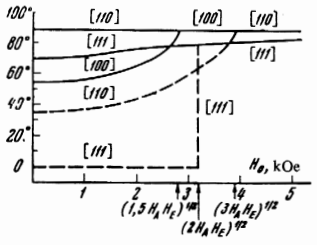

FIG. 1. Dependence of the angle between the directions of the antiferromagnetism vector and of the external magnetic field for different orientations of the latter (indicated on the curves). The dashed curves are cases that are not realized. The values $H_E = 8.9 \times 10^5$ Oe[3] and $H_A = 5.8$ Oe were used in the calculation.

Equilibrium orientation of the magnetic sublattices and group-theoretical analysis of the spectrum. $RbMnF_3$, as already mentioned, has a cubic structure of the perovskite type and becomes antiferromagnetic below $T_N = 82^\circ K$ with the ordering direction along the body-diagonal of the cube—[111]. It is characterized by a strong exchange interaction ($H_E = 8.9 \times 10^5$ Oe) and a weak magnetic anisotropy ($H_A = 3.85$ Oe). The value of H_A varies slightly from sample to sample.[3] The critical field is not high: $H_{cr} = (2H_AH_E)^{1/2} \approx 3$ kOe.

Cole and Ince[3] made a detailed study of the magnetic structure of $RbMnF_3$ as a function of the intensity of an external magnetic field in various orientations. The results of importance to us are illustrated in Fig. 1.

The simplest case is $\mathbf{H} \parallel [100]$. As the magnetic field increases the spins smoothly turn from the [111] axis and when $H > (1.5H_AH_E)^{1/2}$, they become perpendicular to the field along the two-fold axis.

When $\mathbf{H} \parallel [110]$, two cases are possible—initially the sublattices are oriented at 35° in the same (100) plane, or they are perpendicular to the field in adjacent quadrants. In the latter case, which is the one realized, there occurs no change of magnetic symmetry of the crystal in relatively small fields ($H \ll H_E$).

The case $\mathbf{H} \parallel [111]$ is interesting. If in the initial state the spins are oriented along the same [111] axis, then in a field $H = (2H_AH_E)^{1/2}$ one should observe a flopping of the magnetic sublattices. However, special experiments[3] failed to disclose this effect. Evidently, even in small fields the spins line up along one of the

[1)]We take this opportunity to thank sincerely N. N. Mikhaĭlov and S. V. Petrov for making the single crystals of $RbMnF_3$ available to us.

three other three-fold axes at an angle of 70° to the field. As the field is increased, the spins smoothly turn and only in a rather high field (see Fig. 1) do they become perpendicular to it.

In strong magnetic fields ($H \gg H_{cr}$) there occurs a "canting" of the magnetic sublattices, and a moment appears along the external field. The angle of "cant" t in the fields investigated (up to 200 kOe) does not exceed 10° ($t \sim H/2H_E$ [3]).

Starting with these results, we shall carry out a group-theoretical analysis of the expected Zeeman effect. In doing this, it should be borne in mind that in an antiferromagnetic crystal the structure of the spectrum is determined, not by the external magnetic field, but by the exchange interaction. Hence, in seeking the symmetry of $RbMnF_3$, which is determined as the intersection of group of the crystal O_h and of the magnetic moment $C_{\infty h}$, it is necessary to consider the orientation of the magnetic moments of the sublattices M_1.

If the initial state $M_i \parallel [111]$, and the intersection of O_h and $C_{\infty h}$ gives the group C_{3i}. But if the magnetic moment is oriented along the four-fold or two-fold axes, then this intersection gives respectively the groups C_{4h} and C_{2h}. The inequivalent complex-conjugate representations $\{\Gamma_4, \Gamma_5\}$ in the group C_{3i} and $\{\Gamma_5, \Gamma_6\}$, $\{\Gamma_7, \Gamma_8\}$ in C_{4h} in the majority of cases are degenerate in pairs,[4] forming two-dimensional representations. In constructing the magnetic groups [5] an additional degeneracy does not appear,[6] but the degeneracy mentioned above is retained. In the group C_{2h} there are degenerate states.

Thus, one expects that an optical absorption line will be split upon changing of the magnetic symmetry of a cubic antiferromagnet by means of reorientation of the magnetic sublattices in an external magnetic field. In relatively weak magnetic fields ($H_{cr} < H \ll H_E$) splitting is possible with the magnetic field oriented along the [100] and [111] axes (symmetry changes from C_{3i} to C_{2h}). But in a strong field ($H \gg H_{cr}$) at these same orientations degeneracy should again arise, since the symmetry approximates respectively C_{4h} and C_{3i}, and the splitting should decrease with increasing field. On the other hand, with the field oriented along [110] the splitting can be expected only in strong magnetic field ($H_{cr} \ll H < H_E$), when the symmetry of the crystal approximates C_{2h}.

Before we go on to a description of the experimental results, let us see whether there are any degenerate states for the Mn^{2+} transition of interest: $^6A_1(^6S_{5/2}) \rightarrow {}^4A_1, {}^4E(^4G)$. The decomposition of the representations of the group O_h according to the irreducible representations of the corresponding groups of the intersection of O_h and C_h are presented in the table. Complex conjugate representations are grouped in curly brackets; they form two-dimensional representations in the corresponding groups. This table shows that the transition $^6A_1(^6S_{5/2}) \rightarrow {}^4A_1, {}^4E(^4G)$ is a good one for observation of the Zeeman effect associated with a change of magnetic structure of the cubic antiferromagnet $RbMnF_3$.

State	Symmetry group: O_h Original	O_h With spin-orbit	C_{3i}	C_{4h}	C_{2h}
Ground	Γ_1	Γ_7 Γ_8	$\{\Gamma_4+\Gamma_5\}$ $\{\Gamma_4+\Gamma_5\}+2\Gamma_6$	$\{\Gamma_7+\Gamma_8\}$ $\{\Gamma_5+\Gamma_6\}+\{\Gamma_7+\Gamma_8\}$	$\Gamma_3+\Gamma_4$ $2\Gamma_3+2\Gamma_4$
Excited	Γ_1	Γ_8	$\{\Gamma_4+\Gamma_5\}+2\Gamma_6$	$\{\Gamma_5+\Gamma_6\}+\{\Gamma_7+\Gamma_8\}$	$2\Gamma_3+2\Gamma_4$
	Γ_3	Γ_6 Γ_7 Γ_8	$\{\Gamma_4+\Gamma_5\}$ $\{\Gamma_4+\Gamma_5\}$ $\{\Gamma_4+\Gamma_5\}+2\Gamma_6$	$\{\Gamma_5+\Gamma_6\}$ $\{\Gamma_7+\Gamma_8\}$ $\{\Gamma_5+\Gamma_6\}+\{\Gamma_7+\Gamma_8\}$	$\Gamma_3+\Gamma_4$ $\Gamma_3+\Gamma_4$ $2\Gamma_3+2\Gamma_4$

Experimental results and discussion. Measurements were made on the line with frequency $\nu_0 = 25\ 143.5\ cm^{-1}$, which has a half-width of about 2 cm^{-1}. It is situated on the long-wavelength side of the intense electric-dipole bands of the transition $^6A_1(^6S_{5/2}) \rightarrow {}^4A_1, {}^4E(^4G)$, which were studied earlier.[7]

The line ν_0 is split into a doublet when the orientation of the external magnetic field is along the four-fold [100] and three-fold [111] axes and does not respond to any magnetic field of intensity up to 25 kOe along the [110] axis (Fig. 2). In accordance with this, the angular dependences of the magnitude of the Zeeman splitting of the ν_0 line have the form of the rosettes shown in Fig. 3. When $H \parallel [111]$ the magnitude of the splitting gradually increases with increasing magnetic field, approaching the value 3.4 cm^{-1}, and when $H \parallel [100]$ the maximum splitting (3.3 cm^{-1}) is reached already in a field of 2.8 kOe. These results agree well with the character of the change of the direction of the magnetic moments of the sublattices in an external field and permit one to estimate the magnitude of the anisotropy field H_A. Assuming that the exchange field is $H_E = 8.9 \times 10^5$ Oe,[3] we obtain a value of 5.8 Oe for H_A. This value agrees satisfactorily with earlier estimates.[3]

The polarization of the components of the Zeeman splitting of the line $\nu_0 = 25\ 143.5\ cm^{-1}$ is determined by the orientation of the magnetic vector of the light wave h relative to the direction of the magnetic sublattices M_i (Fig. 2). This means, firstly, that the optical transition responsible for the appearance of the absorption line ν_0 (and, evidently, other narrow absorption lines) is magnetic-dipole, and, secondly, that the observed splitting is determined by the change in

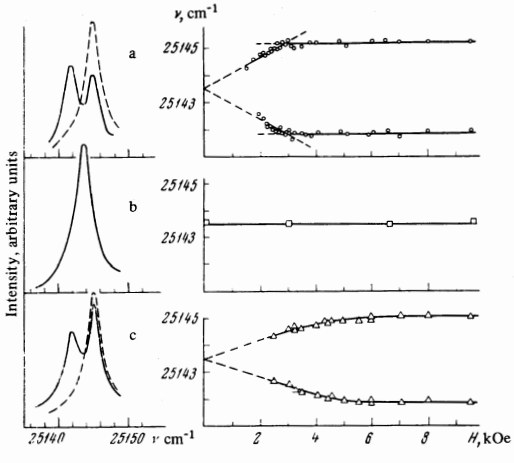

FIG. 2. Zeeman splitting of the line with frequency $\nu_0 = 25\ 143.5$ cm^{-1}, T = 4.2 K: a – $\mathbf{H} \parallel [100]$, $\mathbf{k} \parallel [001]$, H = 3250 Oe; b – $\mathbf{H} \parallel [110]$, $\mathbf{k} \parallel [1\bar{1}0]$ H = 3250 Oe; c – $\mathbf{H} \parallel [111]$, $\mathbf{k} \parallel [1\bar{1}0]$, H = 25 kOe. Dashed curve – $\mathbf{e} \perp \mathbf{H}$, $\mathbf{h} \parallel \mathbf{H}$, $\mathbf{h} \perp \mathbf{M}_i$; continuous curve – $\mathbf{e} \parallel \mathbf{H}$, $\mathbf{h} \perp \mathbf{H}$.

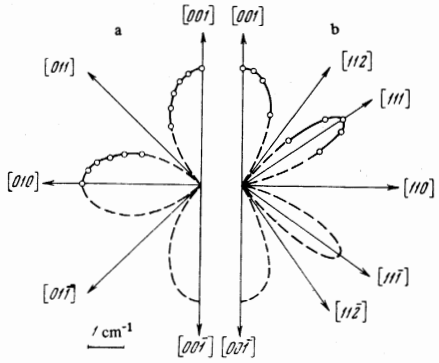

FIG. 3. Anisotropy of the Zeeman splitting: a – **H** in the (100) plane, b – **H** in the (110) plane; T = 1.3 K, H = 5 kOe

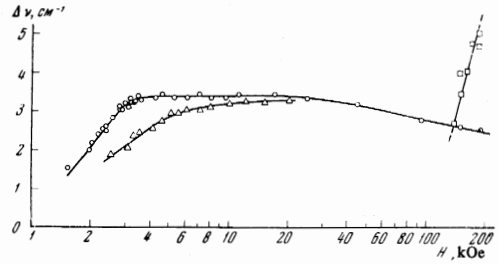

FIG. 4. Dependence of the magnitude of the splitting on the intensity of the magnetic field (T = 4.2 K): O = **H** || [100], Δ – **H** || [111], □ – **H** || [110].

magnetic structure (orientation of the sublattices) and not by the external field **H** itself. Evidence for this is the character of the dependence of the observed splitting on the direction and intensity of the external field. In fact, the results obtained are in good agreement with the above group-theoretical analysis of the splitting of optical absorption lines in a cubic antiferromagnet when the orientation of its magnetic sublattices $\mathbf{M}_i$ is varied by an external magnetic field **H**.

When the temperature was raised from 1.3 to 20.4°K only an insignificant broadening of the bands was observed, without any redistribution of intensity among the components. (The magnitude of the splitting in units of kT is about 5°K.) This suggests that the observed splitting is associated with the excited states of Mn^{2+}.

In strong magnetic fields (up to 200 kOe), the magnetic moment which appears along the field again changes the magnetic symmetry of the crystal. This leads to the appearance of a doublet splitting of the ν_0 band in a field **H** || [110], and for other orientations of the external magnetic field the magnitude of the splitting decreases (Fig. 4). This also agrees well with the scheme considered above.

It should be noted that the study of the polarization of magnetic-dipole optical absorption lines permits one to determine uniquely the direction of the magnetic moments of the sublattices in an antiferromagnetic crystal, since it is just these orientations (and not those of the external field) which determine the relative intensity of the Zeeman components.

In going on to a discussion of the nature of the Zeeman splitting observed in $RbMnF_3$, we first remark that this effect cannot be due to lifting of "sub-lattice degeneracy," which is invoked to explain the Zeeman effect in antiferromagnetic fluorides with the rutile structure.[1,2] In fact, in the latter case, as long as the intensity of the external field is less than the flopping field, the energy of the ions the spins of which are parallel to the applied field (**H** || C_4) are increased by $g\mu_B H$, whereas the energy of the ions of the second sublattice are decreased by $g\mu_B H$. As a result a splitting $\Delta\nu \approx 2g\mu_B H$ is observed. But when the field $H_{cr} = (2H_A H_E)^{1/2}$ (95 kOe in the case of MnF_2) is reached, the magnetic sublattices are flipped by 90° ($\mathbf{M}_i \perp \mathbf{H}$) and the Zeeman splitting disappears.

In the case of $RbMnF_3$, the rotation of the magnetic sublattices in an external field proceeds gradually, beginning at small intensities. The Zeeman splitting appearing when **H** || [111] and **H** || [110] does not disappear even in a field $H > H_{cr} \approx 3$ kOe, when the rotation of the magnetic sublattices is complete and their magnetic moments are aligned perpendicular to the external field ($\mathbf{M}_i \perp \mathbf{H}$), but, on the contrary, it attains its maximum value. In the latter case, the magnetic sublattices are equivalent relative to the external field, and hence any Zeeman effect due to lifting of "sublattice degeneracy" should disappear.

The Zeeman effect observed in $RbMnF_3$ is obviously due to other cases. The above group-theoretical analysis and its comparison with the observed anisotropy of the Zeeman effect is evidence that the latter is uniquely determined by the orientation of the magnetic moments of the sublattices $\mathbf{M}_i$ relative to the crystallographic axes. This suggests that the observed effect is due to anisotropy in the exchange splitting of the energy levels of excited states of Mn^{2+}. A similar effect has been observed in optical absorption lines in crystals of rare-earth garnet-ferrites[8] and has been theoretically interpreted as a result of anisotropy of the exchange splitting of the levels of the rare-earth ions in the calculation of the marked spin-orbit interaction.[9] The excited states of Mn^{2+}, unlike the ground ^6S state, have a non-zero orbital moment, hence for them, as in the case of the rare-earth ions,[8] the exchange splitting is described by an effective field which can significantly differ from the exchange field.

The observed anisotropy of the Zeeman splitting is evidently due to anisotropy of the g factor of the excited state of Mn^{2+}. If this is so, then Fig. 2 shows that the values of the g factor in the directions [100] and [111] are close to zero and only g[100] differs from zero. Thus, the Zeeman effect can be described by the following simple functions in fields less than $H_E = 8.9 \times 10^5$ Oe:

$$\Delta\nu = g_{[110]}\mu^* H_{\text{eff}} - g_{[110]}\frac{\mu^* H_{\text{eff}}}{2}\left(\frac{H}{2H_E}\right)^2 \quad \text{for } \mathbf{H} \parallel [100] \text{ or } [111],$$

$$\Delta\nu = g_{[110]}\mu^* H + g_{[110]}\mu^* H_{\text{eff}}\frac{H}{2H_E} \quad \text{for } \mathbf{H} \parallel [110] \qquad (1)$$

(here μ^* is the effective magnetic moment). The second term describes the contribution to the Zeeman effect due to "canting" of the magnetic moments of the sublattices in the external field. It is clear that in the two cases considered it will enter with different signs. By making use of the experimental values of $\Delta\nu$, it is easy to find the magnitude of H_{eff}, which turns out to be 140 kOe.

From Eq. (1) it is seen that the magnitude of the Zeeman splitting in the first case will decrease, and in a field $H = 2 \times 10^5$ Oe should amount to 2.6 cm^{-1}. In the second case ($H \parallel [110]$), on the other hand, one should observe a rapid rise in the magnitude of splitting in a strong field. Both these features are indeed seen experimentally (Fig. 4).

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