Magnetic birefringence of light in the antiferromagnetic MnCO₃, CoCO₃, and CsMnF₃

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The temperature dependence of the birefringence of light was investigated in the rhombohedral MnCO₃, CoCO₃, and in the hexagonal CsMnF₃. It was observed that the difference $\Delta n = n_{\parallel} - n_{\perp}$ in these compounds experiences a strong change in the region of the corresponding Neel points. The MnCO₃ and CsMnF₃ remain optically uniaxial crystals, regardless of the orientation of the antiferromagnetism vector $\mathbf{1}$ in the basal plane. A dependence of the refractive-index difference on the direction of $\mathbf{1}$ is observed in CoCO₃, and this crystal becomes optically biaxial in the single-domain state. The results are discussed on the basis of the phenomenological expression for the tensor $\varepsilon_{ij}$ of the compounds in question.

INTRODUCTION

In earlier papers[1,2] we reported investigations of the influence of magnetic ordering on the birefringence of light in the antiferromagnetic crystals MnF₂, CoF₂, and NiF₂. In the present paper we report similar investigations on antiferromagnets with a different magnetic structure, MnCO₃, CoCO₃, and CsMnF₃.

The study of birefringence of a number of magnetically-ordered crystals (iron garnets[3-5] and antiferromagnets[6-8,1,2]) shows that the transition to the ordered state is accompanied by an abrupt change in the difference between the refractive indices of the crystals. We have shown[1,2] that the sign and magnitude of this effect in MnF₂, CoF₂, and NiF₂ cannot be attributed to the change produced by spontaneous strain in the lattice constants of the crystal. It appears that there is another not so trivial mechanism whereby the magnetically ordered state influences the birefringence.

This magnetic contribution $\Delta n_{\text{mag}}$ can be separated from the experimentally-measured difference between the refractive indices, as is done in[2], if the temperature dependence of the crystal lattice constants is known at sufficiently wide temperature intervals.

A study of the dependence of $\Delta n_{\text{mag}}$ on the magnetic structure of matter shows that in MnF₂ and NiF₂ the value of $\Delta n_{\text{mag}}$ is independent of the direction of the antiferromagnetism vector $\mathbf{1}$ relative to the crystallographic axes and the direction of the propagation of the light. In CoF₂, in addition to this isotropic $\Delta n_{\text{mag}}$, there is observed an anisotropic increment of $\Delta n_{\text{mag}}$, which depends on the components $\varepsilon_{ij}$. We note that by measuring the refractive-index differences it is possible to observe the isotropic effect only in crystals with symmetries lower than cubic.

The study of birefringence in MnCO₃, CoCO₃, and CsMnF₃ is of interest, in particular, because they are easy-plane antiferromagnets, unlike the uniaxial MnC₂, CoC₂, and NiF₂, in which the anisotropy in the plane is appreciable.

SAMPLES AND PROCEDURE

In the paramagnetic state, MnCO₃, CoCO₃, and CsMnF₃ are optically uniaxial crystals. The crystallographic symmetry of the isomorphic MnCO₃ and CoCO₃ is described by the symmetry group $D_{3d}$, while the symmetry of CsMnF₃ is described by $D_{6h}$. The unit cell of MnCO₃ or CoCO₃ contains two magnetic ions[9], while that of CsMnF₃ contains six Mn⁺ ions occupying two non-equivalent positions[10]. When the temperature is lowered, these compounds go over into an ordered antiferromagnetic state of the easy-plane type. The magnetic vectors of the sublattices in MnCO₃ and CoCO₃ are then canted and form a spontaneous magnetic vector $\mathbf{m}$, which lies in the basal plane and is perpendicular to the antiferromagnetic vector $\mathbf{1}$. The value of $\mathbf{m}$ is approximately 0.2% in MnCO₃ and approximately 5% of the nominal value of the sublattice magnetization in CoCO₃. According to the data of Alikhanov[11], in the absence of an external magnetic field the vector $\mathbf{1}$ in CoCO₃ lies in the vertical symmetry plane at an angle $\sim 45^\circ$ to the threefold axis $C₃$. The compound CsMnF₃ is a pure antiferromagnet[12].

In the basal plane, the crystallographic anisotropy of all three compounds is low, and therefore in a magnetic field (0.5-2 kOe), regardless of the field direction, the vector $\mathbf{1}$ always remains perpendicular to the field in this plane, and the vector $\mathbf{m}$, if it exists, is oriented along the field.

Certain magnetic and optical characteristics of the investigated substance are listed in the table. We know of no data whatever concerning the refractive indices of CsMnF₃.

The MnCO₃ and CoCO₃ crystals were grown at the Crystallography Institute of the USSR Academy of Sciences. The CsMnF₃ was grown by S. V. Petrov of our Institute[13]. The selected crystals were x-ray oriented and cut in the form of rectangular parallelepipeds. The edges of the MnCO₃ and CoCO₃ parallelepipeds coincided with the directions of $C₃$ (the $z$ axis) and $C₃$ (the $x$ axis), with $y \perp x \perp z$; in CsMnF₃ they coincided with the directions of $C₃$ (the $z$ axis) and $C₃$ (the $x$ axis), with $y \perp x \perp z$.

We measured the dependences of the refractive-

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_N$, °K</th>
<th>$H_p$, kOe</th>
<th>$H_d$, kOe</th>
<th>$x_{195}$ cm⁻¹/molecule</th>
<th>$\Delta n_{\text{mag}}$, °</th>
<th>$\varepsilon_{12}$</th>
<th>$\varepsilon_{23}$</th>
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<tbody>
<tr>
<td>MnCO₃</td>
<td>29.0</td>
<td>30.1</td>
<td>339</td>
<td>4.0</td>
<td>1.816</td>
<td>1.967</td>
<td>1.60</td>
</tr>
<tr>
<td>CoCO₃</td>
<td>17.0</td>
<td>18.1</td>
<td>169</td>
<td>4.1</td>
<td>1.855</td>
<td>1.855</td>
<td>1.60</td>
</tr>
<tr>
<td>CsMnF₃</td>
<td>53.5</td>
<td>53.5</td>
<td>339</td>
<td>3.6</td>
<td>1.967</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*The values of $T_N$ marked by an asterisk were obtained from magnetic measurements, and those without an asterisk were obtained by Kalinkina[14] from the measurements of the specific heat $C_p$ of MnCO₃ and CoCO₃.
The magnetic field was measured with apparatus described in [2] by a method with direct compensation for the path difference. The accuracy with which $\Delta n$ was measured depended on the quality of the crystal and ranged from $5 \times 10^{-5}$ to $2 \times 10^{-4}$. The sample was placed in an evacuated cell in an optical cryostat. The sample temperature was measured with a ZLZh-99-chromel thermocouple. The relative temperature-measurement accuracy was ±0.05°, and the absolute accuracy was ±0.3°. In a number of experiments, if no magnetic field was required, the single vacuum cell was replaced by a double cell constructed to resemble a Dewar. The jacket of this cell was evacuated to $10^{-3}$ mm Hg, and the internal part was filled with helium gas (~1 mm Hg). This construction improved the thermal contact between the sample and the cold junction of the thermocouple and kept the sample from sticking.

The magnetic field was produced with a superconducting solenoid and reached ~50 kOe.

**EXPERIMENTAL RESULTS**

**MnCO$_3$**

Just as in [2], the difference of the refractive indices was measured at two experimental configurations. In the first configuration light propagated in MnCO$_3$ along the $y$ axis, and the polarization plane made an angle 45° to the $x$ and $z$ axes. In this geometry we determined the temperature dependence of the refractive-index difference for light waves polarized along the $x$ and $z$ axes. A plot of $\Delta n_{xz}(T) = (n_x - n_z)T = (n_x - n_z)N_0/T$ is shown in Fig. 1. We see that in the region of 30 K there is an abrupt decrease of $\Delta n_{xz}(T)$. The whole curve resembles the analogous plot for MnF$_2$. The Néel point was determined from the maximum of the derivative $d\Delta n_{xz}/dT$ and amounted to 32°K. No kink could be observed on the $\Delta n_{xz}(T)$ curve at the point $T_N$, apparently because of the insufficient measurement accuracy. The value $T_N = 32°K$ differs from the value $T_N = 29.5°K$ obtained in measurements of the temperature dependence of the specific heat $c_p$ in MnCO$_3$ [17], but agrees quite well with magnetic-measurement data [13] ($T_N = 32.4°K$). According to the latter, turning on a magnetic field in the basal plane orients the magnetic domains in this plane. In our experiments, the field was directed along the $x$ axis, and consequently the vector 1 oriented itself along the $y$ axis. Within the limits of the experimental accuracy, we observed no change of $\Delta n_{xy}(T)$ whatever at any temperature and in magnetic fields up to 50 kOe.

A similar lack of change in the refractive indices when the domains become oriented by the field was observed also in the second experimental configurations, when the light propagated along the $z$ axis. The difference $\Delta n_{xy}(T) = n_x - n_y$ turns out to be zero at all temperatures and fields. It follows from the results of the experiments with the magnetic field that the magnetic birefringence in MnCO$_3$ just as in MnF$_2$, does not depend on the direction of the vector 1 relative to the crystallographic axes.

**CoCO$_3$**

The experiments with CoCO$_3$ were performed on two different samples, since the poor quality and small dimensions of the crystals at our disposal did not make it possible to prepare a sample that was sufficiently transparent simultaneously in two perpendicular directions. In the field experiment the light was directed along the $z$ axis and we measured the refractive-index difference for waves polarized along the $x$ and $y$ axes. In the absence of a magnetic field, the difference $\Delta n_{xy} = n_y - n_x$ is not single-valued and does not exceed $10^{-5}$. In magnetic fields corresponding to orientation of the magnetic domains, the difference $\Delta n_{xy}$ increases sharply—see Fig. 2 (the curve in Fig. 2 was obtained at a sample temperature 3.0°K). This change of $\Delta n_{xy}$ in the course of magnetization of the sample was first observed in CoCO$_3$ by Kharchenko et al. [12] by the method of conoscopic figures. As follows from Fig. 2, the difference $\Delta n_{xy}$ continues to increase in magnetic fields greatly exceeding the value at which the domains become oriented in the crystal.

The temperature dependence of $\Delta n_{xy}$ at certain values of the magnetic field is shown in Fig. 3. The same figure shows for comparison data from [12], and also the temperature dependence of the square of the weak ferromagnetic vector $m$ [13]. The $m^2(T)$ curve can be successfully aligned with the $\Delta n_{xy}(T)$ curves obtained in strong magnetic fields. Our measurements of $\Delta n_{xy}(T)$ in weak fields yield a transition temperature $T_N = 17.0°K$, which agrees with the measurements of the specific heat $c_p$ of CoCO$_3$ [16]. Magnetic measurements yield $T_N = 18.1°K$. When the magnetic field is increased, the different $\Delta n_{xy}$ does not vanish at 17°K. This dragging of the curves at high temperatures seems to be
The temperature dependence of the refractive-index difference $\Delta n_{x}(T)$ in CoCO$_3$, obtained in various magnetic fields: $\bullet - H = 1.8$ kOe, $\times - H = 18.5$ kOe, $\Delta - H = 37$ kOe, $\circ - H = 46$ kOe, $\square$ - data of [15]. The dashed curves show the temperature of the square of the weak ferromagnetic vector $\sigma^2(T)$, connected with the antiferromagnetism induced by the magnetic field [13].

In the other experimental geometry, the light was directed along the $y$ axis and the temperature dependence of the refractive-index difference was measured for light waves polarized along the $x$ and $z$ axes

$$\Delta n_{x}(T) = \langle n_x - n_y \rangle - \langle n_x - n_y \rangle_{\text{at} \, k}.$$ 

Without the external magnetic field, the change $\Delta n_{x}(T)$ as a result of the magnetic ordering is small, about $0.3 \times 10^{-4}$. In Fig. 1, the plot of $\Delta n_{x}(T)$ below $T_N$ is shown dashed.

Just as in the preceding experimental configuration, the orientation of the domains by the magnetic field causes an abrupt change of $\Delta n_{x}(T)$ below the transition point (see Fig. 1). A field $\sim 2$ kOe was applied in this experiment along the $x$ axis, and the vector 1, as is well known, oriented itself in a plane perpendicular to the field.

A kink is observed on the $\Delta n_{x}(T)$ curves plotted without and with a field. Its position at $17^\circ$K coincides with the value obtained in the first experiment with this compound (see Fig. 3). The maximum change of $\Delta n_{x}(T)$ following application of a magnetic field ($\sim 2$ kOe) is

$$\Delta n_{x}(T) = \langle n_x - n_y \rangle - \langle n_x - n_y \rangle_{\text{at} \, k} = 1.3 \times 10^{-4}.$$ 

Unlike the preceding configuration, this quantity remained constant, within the limits of experimental accuracy, when the field was increased to $\sim 50$ kOe. Thus, the birefringence in CoCO$_3$, as in CoF$_2$, turns out to depend on the orientation of the vector 1 relative to the crystallographic axes.

**CsMnF$_3$**

The temperature dependence of the refractive-index difference in CsMnF$_3$ duplicates qualitatively the results obtained earlier for MnF$_2$ and MnCO$_3$ and in the present study for MnCO$_3$. The crystal remains optically uniaxial at all temperatures and magnetic fields applied in the $xy$ plane. The quantity $\Delta n_{x}(T)$ changes abruptly in the region $T_N$ and does not depend on the applied field. The plot of $\Delta n_{x}(T) = \langle n_x - n_y \rangle - \langle n_x - n_y \rangle_{\text{at} \, k}$ is shown in Fig. 1. The obtained value $T_N = 52^\circ$K differs somewhat from the $53.5^\circ$K known from magnetic measurements.

To separate $\Delta n_{\text{mag}}$ for MnCO$_3$, CoCO$_3$ and CsMnF$_3$, as was done in [2] for MnF$_2$ and CoF$_2$, data are necessary on the temperature dependence of the lattice constants of the investigated compounds. Unfortunately, no such data are known to us.

**THE DIELECTRIC TENSORS $\varepsilon_{ij}$**

The dependence of the refractive indices of the components of the tensor $\varepsilon_{ij}$ on the magnetic state of the crystal can be described by starting from symmetry considerations, as was done in [2]. The components of the tensor $\varepsilon_{ij}$ are obtained from the expression for the density of the internal electromagnetic energy of light in a crystal, with allowance for the terms quadratic in the magnetic moments, which are responsible for the magnetic birefringence. We assume here that in antiferromagnets the magnetic birefringence is determined primarily by the vector 1, inasmuch as the value of the vector $m$ is always much lower.

For MnCO$_3$ and CoCO$_3$, taking into account the symmetry of the crystal (symmetry group D$_{3d}$), the expression for the electromagnetic-energy density is

$$\varepsilon = \varepsilon_0 + \frac{1}{8\pi} \left( \varepsilon_x E_x^2 + \varepsilon_y E_y^2 + \varepsilon_z E_z^2 \right) + \frac{1}{4\pi} \left( \varepsilon_{xx} E_x^2 E_y^2 + \varepsilon_{yy} E_y^2 E_z^2 + \varepsilon_{zz} E_z^2 E_x^2 \right) \dot{\varepsilon}_0 + \frac{1}{2\pi} \left( \varepsilon_{xy} E_x E_y + \varepsilon_{yz} E_y E_z + \varepsilon_{zx} E_z E_x \right) \dot{\varepsilon}_0 + \frac{1}{\pi} \left( \varepsilon_{xyz} E_x E_y E_z \right) \dot{\varepsilon}_0.$$ 

The second derivatives of $\varepsilon$ with respect to $E_x$ and $E_y$ are the components of the tensor $\varepsilon_{ij}$:

$$\varepsilon_{xx} = \varepsilon_0 + \frac{1}{8\pi} \left( 2\varepsilon_x E_x^2 + 2\varepsilon_y E_y^2 \right) \dot{\varepsilon}_0 + \frac{1}{4\pi} \left( \varepsilon_{xx} E_x^2 E_y^2 + \varepsilon_{yy} E_y^2 E_z^2 + \varepsilon_{zz} E_z^2 E_x^2 \right) \dot{\varepsilon}_0 + \frac{1}{2\pi} \left( \varepsilon_{xy} E_x E_y + \varepsilon_{yz} E_y E_z + \varepsilon_{zx} E_z E_x \right) \dot{\varepsilon}_0 + \frac{1}{\pi} \left( \varepsilon_{xyz} E_x E_y E_z \right) \dot{\varepsilon}_0.$$ 

Here $\varepsilon_0$ and $\dot{\varepsilon}_0$ are the diagonal elements of the tensor $\varepsilon_{ii}$ for the uniaxial crystals MnCO$_3$ and CoCO$_3$ in the paramagnetic state.

Unlike the two-sublattice antiferromagnets MnCO$_3$ and CoCO$_3$, the compound CsMnF$_3$ is a six-sublattice antiferromagnet and $\varepsilon$ should be resolved along the vectors [15]:

$$l_0 = \pm s_1, s_2, s_3; \quad m_0 = \pm s_1, s_2, s_3; \quad m_0 = \pm s_1, s_2, s_3; \quad m_0 = \pm s_1, s_2, s_3;$$

Here $s_1$ and $s_2$ are the magnetic moments of the Mn I ions occupying the crystallographic positions (0, 0, 0) and (0, 0, $\frac{1}{2}$); $s_3$ are the magnetic moments of the ions Mn II occupying the positions ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). However, inasmuch as the vectors $l_0, m_0, l_0,$ and $m_0$ are much smaller than $l_1$ and $l_2$, we confine ourselves in the expansion to terms quadratic in $l_1$ and $l_2$:

$$\varepsilon = \varepsilon_0 + \frac{1}{8\pi} \left( 2\varepsilon_x E_x^2 + 2\varepsilon_y E_y^2 \right) \dot{\varepsilon}_0 + \frac{1}{4\pi} \left( \varepsilon_{xx} E_x^2 E_y^2 + \varepsilon_{yy} E_y^2 E_z^2 + \varepsilon_{zz} E_z^2 E_x^2 \right) \dot{\varepsilon}_0 + \frac{1}{2\pi} \left( \varepsilon_{xy} E_x E_y + \varepsilon_{yz} E_y E_z + \varepsilon_{zx} E_z E_x \right) \dot{\varepsilon}_0 + \frac{1}{\pi} \left( \varepsilon_{xyz} E_x E_y E_z \right) \dot{\varepsilon}_0.$$ 

Here $\alpha_1, \beta_1, \gamma_1,$ and $\eta_1$ are the magnetooptical constants.

The components of the tensor $\varepsilon_{ij}$ for CsMnF$_3$ are given by

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Experiments have yielded for MnCO₃ and CsMnF₃, the following: a) $\Delta n_{xy}$ is equal to zero also in the magnetically-ordered region, both in a zero magnetic field and in fields up to ~50 kOe. In the basal plane, respectively. As shown by Bazhan, in the absence of an external magnetic field, lies in a vertical symmetry plane and makes angles ~22° and 45° with the basal plane, respectively. As shown by Bazhan, in Nicol, this angle is a function of the crystal temperature and of the field applied in the basal plane, and vanishes at a critical field value 14 kOe. If we assume a similar effect in CoCO₃, then the projections $l_2$ and $l_y$ vary with a field parallel to the x axis, and therefore the difference $\Delta n_{xz}$ should depend on the field also after the vanishing of the domain structure.

In conclusion, we thank P. L. Kapitza for interest in the work and E. Dzyaloshinski for useful discussions.

APPENDIX

In our earlier paper[14], errors crept into the expressions for the density of the internal electromagnetic energy $\mathcal{E}$ and the dielectric tensor $\epsilon_{ij}$ of the crystals MnF₂, CoF₂, and NiF₂. When suitably corrected, formulas (5)–(10) of[14] become respectively

$$\mathcal{E} = \varepsilon_0 \varepsilon_{ij} \frac{1}{2} \left( \frac{\lambda_i \lambda_j}{n_i n_j} + \frac{\lambda_i \lambda_j}{n_i n_j} \right) \varepsilon_{ij}$$

In Fig. 1, the plot of $\Delta n = n_2 - n_1$ is shown vertically. The change of $\Delta n_{xz}$ (T) as the domain structure vanishes is observed only in the antiferromagnetic region.

In conclusion, we thank P. L. Kapitza for interest in the work and E. Dzyaloshinski for useful discussions.

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In addition, the tensor $T_{ij}$ becomes diagonalized by rotation of the $x$ and $z$ axes through an angle $\alpha$:

$$\Delta n_x = -n_x - n_y = \frac{1}{2} \left( \frac{\lambda_1}{n_1^2} - \frac{\lambda_2}{n_2^2} \right) + \frac{1}{2} \left( \frac{\lambda_1}{n_1^2} - \frac{\lambda_3}{n_3^2} \right),$$

$$\Delta n_y = n_x - n_y = \frac{1}{2} \left( \frac{\lambda_2}{n_1^2} - \frac{\lambda_3}{n_2^2} \right) + \frac{1}{2} \left( \frac{\lambda_2}{n_1^2} - \frac{\lambda_3}{n_2^2} \right).$$

$$\Delta n_z = n_x - n_y = \frac{1}{2} \left( \frac{\lambda_3}{n_1^2} - \frac{\lambda_2}{n_2^2} \right) + \frac{1}{2} \left( \frac{\lambda_3}{n_1^2} - \frac{\lambda_2}{n_2^2} \right).$$

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