Nonreciprocal optical effects in antiferromagnetic Cr_2O_3 subjected to electric and magnetic fields

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A study was made of the temperature and field dependences of nonreciprocal rotation of the plane of polarization of light ($\lambda = 1.15 \mu m$) in an antiferromagnetic Cr_2O_3 crystal subjected to electric (E) or magnetic (H) fields in the $k \| c \| E \| H$ geometry. The nonreciprocal rotation NR(H) induced by a field H in Cr_2O_3 was attributed to competition between two contributions one of which was positive diamagnetic V_{dia} and the other was negative paramagnetic V_{para}, reflecting the behavior of the magnetic susceptibility $\chi_\|$. The temperature dependence NR(E) was qualitatively different from the temperature dependence of the magnetoelectric susceptibility $\alpha_\|$, indicating that they were different. The temperature dependences of NR(E) were explained by postulating a ferromagnetic contribution proportional to the magnetization **m** and an antiferromagnetic one proportional to the antiferromagnetic vector **l**. Separation of the NR into the ferromagnetic and antiferromagnetic contributions was made by two methods: 1) using the temperature dependences of NR(E) and $l(T)$; 2) using the value of V_{para} and the temperature dependence $\alpha_\|$ (T). A model describing the ferromagnetic and antiferromagnetic contributions to the NR in the specific case of the $^4A_{2g} \rightarrow {}^4T_{2u}$ transition was developed. The expressions obtained indicated that, in contrast to the ferromagnetic contribution of magnitude governed primarily by the spin–orbit interaction, the antiferromagnetic contribution was related to the pseudo-Stark splitting of the Cr_2O_3 levels.

1. INTRODUCTION

If a crystal is subjected to a magnetic field H or if it has a spontaneous magnetization **m**, it can exhibit nonreciprocal optical effects,[1] the best known of which is the Faraday effect. Lowering the symmetry of a crystal by eliminating the time reversal operation 1' alters the properties of material tensors,[2] giving rise in particular to imaginary antisymmetric corrections to the permittivity tensor ε_{ij}^a describing the Faraday effect:

$$\varepsilon_{ij}^a = s_{ijk}H_k + p_{ijk}m_k, \qquad (1)$$

where s_{ijk} and p_{ijk} are axial i tensors.[3,4] Equation (1) is valid in the case of diamagnetic or paramagnetic crystals subjected to a magnetic field or in the case of single-sublattice ferromagnets. The presence of several magnetic sublattices of specific crystal symmetry may give rise to new optical effects such as the nonreciprocal rotation (NR) of the plane of polarization induced by an electric field E (Ref. 3). Since the symmetry of the electric field E (polar i vector) differs from the symmetry of the magnetic field H or the magnetization **m** (axial c vectors), this effect is described by tensors which obey transformation properties quite different from those of the tensors s_{ijk} and p_{ijk}, demonstrating that the nonreciprocal rotation effect is fundamentally different from the Faraday effect. In general[1], the terms describing such effects can be written as follows[4,5]:

$$\varepsilon_{ij}^a = \gamma_{ijk}E_k + \nu_{ijkl}E_kE_l, \qquad (2)$$

where γ_{ijk} and ν_{ijkl} are polar c tensors.

Nonzero components of the tensors γ_{ijk} and ν_{ijkl} are determined by the actual magnetic symmetry of a crystal. In particular, the γ_{ijk} tensor is a property of crystals exhibiting a linear magnetoelectric effect, such as that found in the classical magnetoelectric Cr_2O_3 (Ref. 6). Clearly, the appear-ance of the magnetization **m**(E) induced by an electric field should, in accordance with Eq. (1), give rise to the Faraday effect (i.e., the nonreciprocal rotation), so that from the symmetry point of view the conditions for the appearance of the magnetoelectric and NR effects are identical. However, we must bear in mind that, in contrast to the magnetoelectric effect, the Faraday effect is governed by the properties not only of the ground state responsible for the magnetic phenomena, but also to a large extent by excited electron states. This circumstance opens up the possibility of the appearance of new magnetoelectric interaction mechanisms in the optical range and gives rise to a situation in which Eq. (2) cannot be derived from Eq. (1) allowing for the dependence **m**(E).

The purpose of our investigation was to determine experimentally and theoretically the nonreciprocal rotation NR due to an electric field in Cr_2O_3. Moreover, we investigated NR in Cr_2O_3 in a magnetic field, i.e., we studied the Faraday effect. A comparison of the results made it possible to distinguish clearly the microscopic mechanisms of these two different phenomena. To the best of our knowledge, such investigations had not been carried out before.

2. APPARATUS

The NR induced by an electric field was measured using a modification of the polarimetric balance circuit[7,8] (Fig. 1). Light from a helium–neon laser of the LG-36A type ($\lambda = 1.15 \mu m$) passed through a polarizer, a crystal located in the gap of an electromagnet, a Faraday cell, and an analyzer before reaching the input of a differential photodetector representing two FD-10GA photodiodes connected to an amplifier so that the output electric signal was proportional to the difference between light intensities reaching the photodiodes. The electrical signal was passed on to a lock-detection circuit.
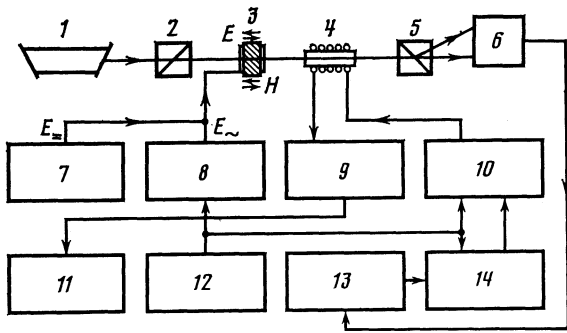
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FIG. 1. Schematic diagram of the apparatus used in the study of the non-reciprocal rotation in electric or magnetic fields: 1) laser; 2) polarizer; 3) sample; 4) Faraday cell; 5) analyzer; 6) photodetector; 7) voltage source; 8) voltage amplifier; 9) rectifier; 10) compensation circuit; 11) automatic plotter; 12) oscillator; 13) selective amplifier; 14) lock-in detector.
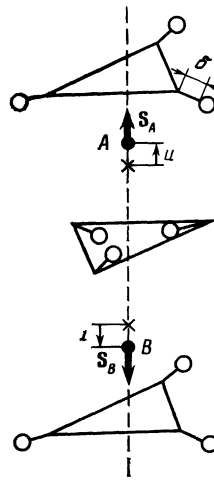

FIG. 2. Fragment of a unit cell of Cr_2O_3: ● denotes Cr^{3+}; O denotes O^{2-}

The rotation of the plane of polarization was measured by cancelling it out. The Faraday cell was subjected to a current of frequency, magnitude, and phase so as to compensate rotation of the plane of polarization induced by the NR. This method ensured the maximum sensitivity of the measurements irrespective of the magnitude of the signal and ensured that the recorded NR signal was independent of the laser radiation power. The current necessary for cancellation was determined automatically. The sensitivity of the measurements of the plane of rotation of the polarization was at least 0.05".

The field and temperature dependences of the Faraday effect were studied using a system for modulation of the polarization described in Ref. 8 in which a Faraday cell was used as a modulator and a compensator. In contrast to the preceding case, the compensating current through the Faraday cell was constant. The sensitivity of measurements of the rotation of the plane of polarization was ~0.5". A static magnetic field H up to $\pm$ 950 kA/m ($\pm$ 12 kOe) could also be applied to a crystal.

Crystals of Cr_2O_3 were cut to form plates of thickness ~600 μm at right-angles to the optic axis c to within ~0.2°. Semitransparent platinum electrodes were deposited on polished crystal faces. The transmission of a crystal together with the electrodes was ~50% at $\lambda = 1.15$ μm. A crystal could be subjected simultaneously to a static voltage (up to 1000 V) and an alternating voltage (up to 1200 V, 700 Hz) from suitable sources.

A crystal was placed in an optical cryostat in which measurements could be carried out in the temperature range 45–550 K. Determination of the NR in an electric field was made in the $k\|c\|E$ geometry whereas the NR in a magnetic field was measured in the $k\|c\|H$ geometry.

3. EXPERIMENTAL RESULTS

Chromium oxide Cr_2O_3 crystallizes in the corundum-type structure which has the space group D_{3d}^6 (Ref. 9). A unit cell, part of which is shown in Fig. 2, contains four Cr^{3+} ions occupying equivalent c positions (point symmetry 3) along the C_3 axis. The Cr^{3+} ions are shifted relative to the centers of octahedra in the direction of large triangles

formed by the O^{2-} oxygen ions. Below $T_N = 307$ K the compound Cr_2O_3 is an antiferromagnet with alternate directions of the spins oriented along the trigonal axis ($+$, $-$, $+$, $-$). The magnetic symmetry group is $\bar{3}'m'$. It was shown by Dzyaloshinskiĭ,[6] that the thermodynamic potential of this magnetic group contains terms of the type

$$W_{me} = \alpha_\| E_z H_z + \alpha_\perp (E_x H_x + E_y H_y), \qquad (3)$$

which are due to the existence of the magnetoelectric effect. The magnetoelectric effect was discovered experimentally by Astrov[10] and investigated in detail by several authors.[11,13] The optical properties of Cr_2O_3 were investigated[14-17] and, in particular, observations of the NR of the plane of polarization of light induced by an electric field in Cr_2O_3 were reported. A characteristic feature of the magnetoelectric and NR effects is the dependence of their signs on the type of antiferromagnetic domain, which makes it possible to use these effects in studies of the processes of switching of antiferromagnetic domains.[18]

Figure 3 shows the results of an investigation of the process of magnetoelectric annealing of Cr_2O_3 obtained using the NR data. In these measurements a crystal was heated to about 5 K above the temperature $T_N = 307$ K and was
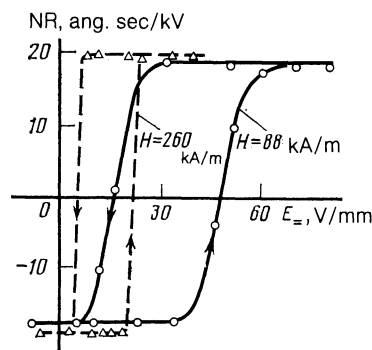

FIG. 3. Dependence of the specific nonreciprocal rotation in Cr_2O_3 on the field $E_=$ at $T = 301.5$ K after magnetoelectric annealing of a crystal in fields $E_=$ and H.

then cooled to $T = 301.5$ K in the presence of static magnetic (H) and electric $(E_=)$ fields. The field $E_=$ was then switched off and the crystal was subjected to an oscillating electric field $E = 1.2$ kV/mm; measurements were then made of NR(E) at the first harmonic ω of the electric field. Since the NR(E) effects due to different antiferromagnetic domains were subtracted, the dependences plotted in Fig. 3 represented effectively the dependences of the average antiferromagnetic moment of a crystal $\langle l \rangle$ on the electric field $E_=$ during annealing. An increase in the magnetic field H in which the annealing took place reduced the width of the hysteresis loop shown in Fig. 3 and shifted its center toward lower electric fields $E_=$. This behavior was clearly due to the presence of various defects which ensured the existence of preferred antiferromagnetic domains formed in the process of magnetoelectric annealing in a field $E_= = 0$. In qualitative descriptions of the observed dependences one should allow for the fact that the volume of a crystal dV occupied by a specific antiferromagnetic domain corresponds in the presence of the fields $E_=$ and H to a magnetoelectric energy

$$dW = \mathbf{m}_{me} H dV = \alpha_\| E_= H dV, \qquad (4)$$

which depends linearly on $E_=$ and H. Hence, it follows that in order to overcome an energy W_s needed to switch the volume dV, we require a field $E_=$ which decreases as a function of H. The shift of the center of the loop from the value $E_= = 0$ and the change of this shift with the field H point to the existence of a certain energy W_u responsible for the unipolarity of a sample and indicate that there is a certain average internal effective electric field $E_= \approx 15$ V/mm. It is clear from Fig. 3 that complete conversion of a sample to the single-domain state in a field $H = 340$ kA/m required a relatively weak electric field $E_= = 30$ V/mm.

Figure 4 shows the temperature dependence of the NR(E) exhibited by Cr_2O_3, measured at the first harmonic of the electric field applied to a sample converted to the single-domain state. The temperature and field dependences of the NR were practically independent of the polarization of light incident on a crystal. Hence, the possible influence of the birefringence of Cr_2O_3 on the results of the NR measurements, which could have been important because the condition $\mathbf{k}\|\mathbf{c}$ was not satisfied exactly, was negligible. The value of NR(E) depended linearly on the electric field E_- and was independent of the magnetic field, i.e., the effect was de-

scribed by the tensor γ_{ijk} in Eq. (2). It should be pointed out that the temperature dependence of the NR differed considerably from the temperature dependence of the magnetization, which appeared because of the magnetoelectric effect. The latter was characterized by a maximum at $T \approx 250$ K, disappearance of the effect at $T \approx 80$ K, and a negative sign at lower temperatures.[10-13] The NR was large when the magnetoelectric effect disappeared, indicating that the NR was not associated with the appearance of the magnetization $\mathbf{m}$. At this point the situation was unique and the NR was observed in a crystal without any macroscopic magnetic moment and in the absence of a magnetic field. The NR effects of the electric and magnetic fields were compared by investigating the field and temperature dependences of the NR in Cr_2O_3 under the action of a magnetic field $\mathbf{H}$.

Figure 5 shows the temperature dependence of the NR in Cr_2O_3 due to the application of a magnetic field H to a sample in the $\mathbf{k}\|\mathbf{c}\|\mathbf{H}$ (Faraday effect) geometry. Clearly, in a wide range of temperatures the Faraday rotation was positive and only in a narrow temperature interval near T_N the sign of the Faraday effect became negative. Near T_N the Faraday effect in Cr_2O_3 was relatively weak $V \approx -42''/$kA. Figure 5 includes also the results of measurements of the magnetic susceptibility $\chi_\|$ of Cr_2O_3 taken from Refs. 10, 19, and 20. Clearly, the temperature dependences of the Faraday effect in Cr_2O_3 are similar, except that in the range of temperatures investigated the sign of the Faraday effect was reversed twice. This behavior of the Faraday effect in Cr_2O_3 could be due to competition between two contributions: a positive temperature-independent diamagnetic contribution and a negative paramagnetic contribution with the temperature dependence reflecting the behavior of the magnetic susceptibility. Since at low temperatures the susceptibility $\chi_\|$ tended to zero, we could estimate the diamagnetic contribution to the Faraday effect $V_{dia} \approx 200''/$kA. For comparison, we determined the Verdet coefficients of isostructural crystals of sapphire Al_2O_3 and ruby $Al_2O_3:Cr^{3+}$ ($x \approx 0.02$–0.05%). Both crystals exhibited diamagnetic rotation $V_{dia} = 450''/$kA which was slightly greater than the diamagne-
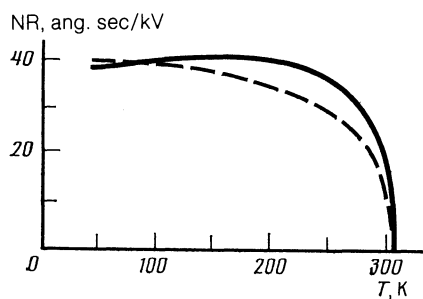

FIG. 4. Temperature dependence of the specific nonreciprocal rotation in Cr_2O_3 (continuous curve). The dashed curve is the antiferromagnetic contribution to the nonreciprocal rotation, representing the temperature dependence of the antiferromagnetic vector l.
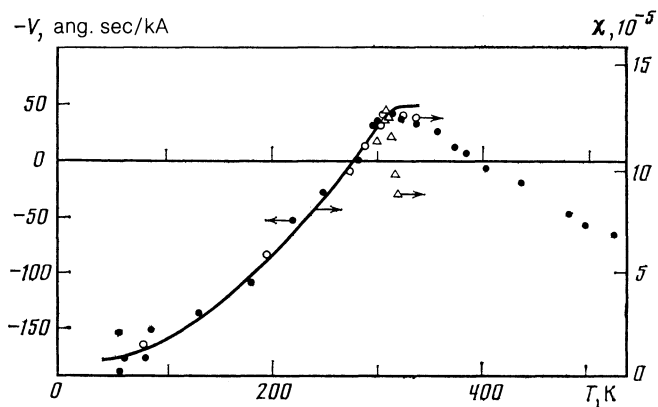

FIG. 5. Temperature dependence of the specific nonreciprocal rotation due to a magnetic field (Verdet coefficient) applied to Cr_2O_3 (●). This figure includes also the dependences of the magnetic susceptibility $\chi_\|$ of Cr_2O_3 taken from Ref. 10 (△), from Ref. 19 (continuous curve), and from Ref. 20 (○).

TABLE I. Transformations of vector components $\mathbf{E}_z$, $\mathbf{l}_z$, and $\mathbf{m}_z$ under the influence of independent symmetry elements of the D_{3d}^6 group

Operation	Changes in vector components due to transpositions of sublattices			Changes in vector components without allowance for transpositions of sublattices			Final results		
1	E_z	l_z	m_z	E_z	l_z	m_z	E_z	l_z	m_z
S_6	E_z	$-l_z$	m_z	$-E_z$	l_z	m_z	$-E_z$	$-l_z$	m_z
u_2	E_z	$-l_z$	m_z	$-E_z$	$-l_z$	$-m_z$	$-E_z$	l_z	$-m_z$

tic contribution in the case of Cr_2O_3. The paramagnetic rotation in Cr_2O_3 had a maximum in the vicinity of T_N and the Verdet coefficient was $V_{para} = -240''/kA$. It should be pointed out that the sign of the NR, corresponding to a given direction of the magnetization $\mathbf{m}$ created by a field $\mathbf{E}$ because of the magnetoelectric effect, was the same as the sign of the paramagnetic NR corresponding to the same direction of $\mathbf{m}$ but induced by the magnetic field $\mathbf{H}$.

4. THEORETICAL ANALYSIS

We shall now consider possible mechanisms of the NR in Cr_2O_3. From the phenomenological point of view the appearance of the magnetization $\mathbf{m}$ in a crystal should give rise to nondiagonal antisymmetric components of the permittivity tensor $\varepsilon_{xy}^a = ipm_z$ describing the NR or the Faraday effect. We call this the ferromagnetic contribution to the Faraday effect. Since it is not possible to describe the observed NR by this contribution alone, we shall consider how the vectors $\mathbf{E}$, $\mathbf{l} = \mathbf{S}_1 - \mathbf{S}_2 + \mathbf{S}_3 - \mathbf{S}_4$, and $\mathbf{m} = \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4$ transform in the D_{3d}^6 group. It follows from the transformation properties of these vectors (Table I) that the product $l_z E_z$ transforms exactly as m_z, so that in the tensor ε_{ij} we have to include terms of the $\varepsilon_{ij}^a = iql_z E_z$ type, describing the additional antiferromagnetic contribution to the NR. The antiferromagnetic term of the Faraday effect has been used to describe magnetooptic properties of weak ferromagnets[3] and to interpret the field dependence of the Faraday effect in $YFeO_3$ (Ref. 21). In the case of Cr_2O_3 the antiferromagnetic contribution to the NR can be regarded as the antiferromagnetic Faraday effect induced by an electric field, because in the presence of an electric field we can regard Cr_2O_3 as a longitudinal weak ferro-

magnet. The temperature dependences of the two contributions to the NR should be different. The ferromagnetic contribution should reflect the behavior of the magnetoelectric behavior of the susceptibility $\alpha_\parallel$, whereas the antiferromagnetic contribution should be governed by the sublattice magnetization. Since the ferromagnetic contribution disappears at $T \approx 80$ K (because $\alpha_\parallel = 0$), we can use the known dependence $m_i(T)$ (Ref. 22) to separate the antiferromagnetic contribution to the NR (Fig. 6). The difference between the observed NR and the antiferromagnetic contribution is practically identical with the temperature dependence of $\alpha_\parallel$ (Ref. 10). Note that the antiferromagnetic contribution to Cr_2O_3 is much greater than the ferromagnetic contribution. At $T \approx 250$ K the ferromagnetic contribution is maximal and the antiferromagnetic contribution is four times greater than the ferromagnetic one.

A calculation of the ferromagnetic contribution can be made independently on the assumption that the magnetization $\mathbf{m}$ appears because of the same Faraday effect irrespective of how (by the field $\mathbf{E}$ or $\mathbf{H}$) it is created. In this case the ferromagnetic contribution NR_f is readily calculated from

$$HB_{para}/E = \alpha_\parallel V_{para}/\chi.$$

Figure 6 shows the temperature dependence of the ferromagnetic contribution obtained using the following parameters: $\chi_{T_N} = 1.3 \times 10^{-4}$ (Ref. 15), $V_{para}(T_N) = -240''/kA$, and $\mu_0 c \alpha_\parallel^{max} = 1.3 \times 10^{-3}$. The value of $\alpha_\parallel^{max}$ in Fig. 6 is selected to ensure the best agreement with the experimental results. It is in good agreement with the experimental values which are reported to range from 1.1×10^{-3} (Ref. 13) to 1.5×10^{-3} (Ref. 23).

We shall now consider the microscopic mechanisms which cause the antiferromagnetic contribution in Cr_2O_3 to appear in the specific case of a transition of the $^4A_{2g} \rightarrow ^4T_{2u}$ type (Fig. 7). We shall use the results of a theoretical analysis of the spontaneous Faraday effect, carried out in Ref. 24 in the case of $CrBr_3$, $CrCl_3$, and CrI_3 crystals in which the Cr^{3+} ion is found, as in Cr_2O_3, in a triagonal field. We can allow for the influence of the electric field using the results of Ref. 25, which analyzes the optical spectra of the Cr^{3+} ions in ruby. The Hamiltonian describing the positions of the Cr^{3+} levels in Cr_2O_3 can be written as follows:

$$H = H_0 + V_{cub} + V_{so} + V_{tr}^e + V_{tr}^o + V_{exch} + V_\varepsilon, \qquad (5)$$

where H_0 is the Hamiltonian describing a free ion; V_{cub} is the cubic part of the crystal field; V_{tr}^e and V_{tr}^o are the even and odd parts of the trigonal crystal field; V_{so} is the spin–orbit interaction; V_{exch} is the exchange interaction; $V_{tr}^o = A_1^0 T_{10}$, $V_{tr}^e = A_2^0 T_{20}$ (Ref. 25); V_ε is the energy of the interaction of a $3d$ electron with the electric field $\mathbf{E}$.
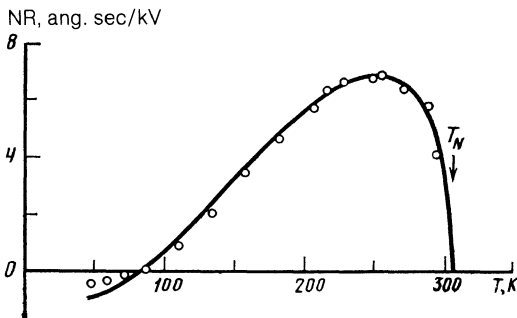
NR, ang. sec/kV

FIG. 6. Results of separation of the ferromagnetic contribution to the NR: the continuous curve is the difference between NR^{exp} and NR^{afm} (Fig. 4); the circles ($\bigcirc$) are the results of calculations of $\alpha_\parallel$ (Ref. 10) using the values of V_{para} and $\chi_\parallel$.

A Hamiltonian of the type described by Eq. (5) but without V_ε was used in Ref. 24 to account for the Faraday effect and the Hamiltonian without V_{exch} was used in Ref. 26 to deal with the pseudo-Stark splitting of the Cr^{3+} lines. According to the theory developed in Ref. 24, strong electric dipole transitions responsible for the high value of the Faraday effect occur from the ground state $^4A_2$ of the Cr^{3+} ion to excited states of the $^4T_2$ type. Splitting of the $^4A_2$ and $^4T_2$ levels yields $V_{tr}^{e,o}$, V_{so}, and V_{exch}^2 is shown in Fig. 7. The ground state $^4A_2$ of the Cr^{3+} ion hardly splits if we do not allow for V_{exch} and the exchange interaction is responsible for the splitting of the $^4A_2$ states into four sublevels ($m = 3/2, 1/2, -1/2, -3/2$). The state $^4T_2$ splits under the influence of $V_{tr}^{e,o}$ and V_{so} into six Kramers doublets and further splitting of these doublets is due to the exchange interaction V_{exch} between the ground and excited states. At $T = 0$, the optical transitions are possible the state $^4A_2$ ($m = 3/2$) to the state $C(m = 5/2)$ with the σ^+ polarization and to three states $^4A_i(m = 1/2)$ with the σ^- polarization. The expression for the specific rotation without allowance for the damping associated with the Cr^{3+} ion at, for example, the position A then becomes[24]

$$p_A(\omega) = \frac{2\pi\omega}{n\hbar c} p_\alpha^2 \left\{ \frac{1}{(\omega_{C(\alpha)g}^2 - \omega^2)} - \sum_{i=1}^{3} \frac{a_{A_i(\alpha)}}{(\omega_{A_i(\alpha)g}^2 - \omega^2)} \right\}$$

(6)

(all the notation is the same as in Ref. 24). Obviously, in the case of the ion with the opposite direction of the spin (at the position B) the Faraday effect has the same value but the opposite sign, so that in the absence of $\mathbf{E}$ and $\mathbf{H}$ there is no Faraday effect. If $T \ne 0$, we must naturally allow for transitions from other components of the $^4A_2$ ($m = 1/2, -1/2, -3/2$) level to the states A_i, B_i, and C, but if the frequency of light ω is sufficiently far from the absorption line that the difference ($\omega_{4T_2} = \omega$) is much greater than the values of all the other splittings, we can simply multiply Eq. (6) by the relative magnetization $m(T)/m(0)$.

The application of an electric field E does not result in additional splitting of the components of the ground and excited states of the Cr^{3+} ion. Inclusion of V_ε in the second order of perturbation theory shows that the terms of the type

$V_{tr}^o V_\varepsilon$ generally shift the levels proportionally to the electric field.[25] The energies of the ground and excited states then become

$$E_{^4A_2}(^3/_2) = E_{^4A_2}(^3/_2) - A_1^o \varkappa_0 E_z,$$

$$E_{^4T_2(C,A_i)} = E_{^4T_2(C,A_i)}^0 + A_1^o \varkappa_{(C,A_i)} E_z,$$

(7)

where $E_{^4A_2}^0$ and $E_{^4T_2}^0$ are the energies of the ground and excited states in the absence of an electric field; A_1^0 is the magnitude of the odd trigonal field [in the model of point charges we have $A_1^0 = 16e^2\delta(3\pi/2)^{1/2}/R_0$, as given in Ref. 25]; $\varkappa_0$ and $\varkappa_{C,A_i}$ are coefficients which are the same for ions at the A and B positions and which represent mixing of the wave functions of the states of opposite parity with the wave functions of the ground and excited (C, A_i) states by the odd trigonal field V_{tr}^o (the expression for $\varkappa_0$ is given in Ref. 25). Note that A_1^0 has opposite signs for the type A and B ions, which gives rise to a pseudo-Stark splitting of the Cr^{3+} lines in Cr_2O_3. The frequencies of the transitions to the states C and A_i for the type A and B ions deduced allowing for Eq. (7) are (see Fig. 7)

$$\omega_{C,A_i}^{A(B)} = \omega_{C,A_i} \pm |A_1^o|(\varkappa_0 + \varkappa_{C A_i})E_z.$$

(8)

Substituting Eq. (8) into Eq. (6) and summing over four ions in a unit cell, we obtain

$$\mathbf{g}_\alpha = 2p(\omega)(\mathbf{m}_A + \mathbf{m}_B) + 2q(\omega)(\mathbf{m}_A - \mathbf{m}_B) = p(\omega)\mathbf{m} + q(\omega)\mathbf{l},$$

(9)

where $\mathbf{g}_\alpha$ is the gyration vector and

$$q(\omega) = \frac{2\pi\omega}{n\hbar c} p_\alpha^2 \left\{ \frac{|A_1^o|(\varkappa_0 + \varkappa_C)E_z}{(\omega_{C(\alpha)g}^2 - \omega^2)^2} \right.$$

$$\left. - \sum_{i=1}^{3} \frac{a_{A_i}^2 |A_1^o|(x_0 + \varkappa_{A_i})E_z}{(\omega_{A_i(\alpha)g}^2 - \omega^2)^2} \right\}.$$

(10)

The expression (9) is written down for a transition to a single state α of the $^4T_2$ symmetry and one unit cell. We can obtain a general expression by summing Eq. (9) over other
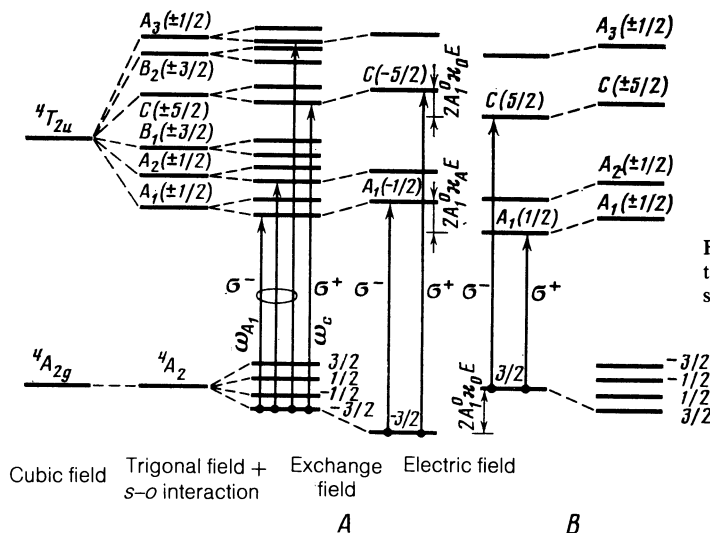

FIG. 7. Splitting of the $^4A_{2g}$ and $^4T_{2u}$ states of the Cr^{3+} ions at the positions A and B under the influence of the cubic crystal field, trigonal field, spin-orbit interaction, exchange interaction, and electric field.

states of the same symmetry and over the number of unit cells in a crystal. The presence of two terms in Eq. (9) has a simple physical meaning. In general, the expression for g can be written in the form

$$\mathbf{g} = 2(p_A \mathbf{m}_A + p_B \mathbf{m}_B), \qquad (11)$$

where p_i represents the sublattice magnetooptic susceptibilities. In the absence of the fields $\mathbf{E}$ and $\mathbf{H}$, we have $\mathbf{g} = 0$ because $\mathbf{m} = 2(\mathbf{m}_A + \mathbf{m}_B) = 0$ and $p_A = p_B = p_0$ since the positions A and B are equivalent. The electric field $\mathbf{E}$ gives rise to $m_z = \alpha_{\parallel} E_z$ and, consequently, to a ferromagnetic contribution $p_0 \alpha_{\parallel} E_z$. Moreover, under the influence of the field $\mathbf{E}$ there are changes in the quantities p_i: $p_A = p_0 + qE_z$ and $p_B = p_0 - qE_z$, which gives rise to the antiferromagnetic contribution $ql_z E_z$.

It therefore follows that the antiferromagnetic distribution is related to the inequivalence of the positions of A and B of the Cr^{3+} ion in the presence of an electric field $\mathbf{E}$, manifested by pseudo-Stark splitting. It is clear from Eq. (9) that the application of an electric field $\mathbf{E}$ or of a magnetic field $\mathbf{H}$ gives rise also to a ferromagnetic contribution $p_0(\omega)m$, which is related to the disappearance of mutual compensation of the magnetic moments of the sublattices, i.e., it is associated with the appearance of $\mathbf{m}$. It is important to note that, in accordance with Eq. (10), the frequency dependences of the ferromagnetic and antiferromagnetic contributions are different and we can expect a faster increase in the antiferromagnetic contribution on approach to the resonance frequency.

We shall now estimate the value of $|A\,{}^{0}_{1}|(\varkappa_0 + \varkappa_c)$ subject to the following assumptions. 1) We shall assume that splitting of the ${}^4T_2$ level in the trigonal field is much greater than the spin–orbit splitting. It is then sufficient to include in Eq. (10) the transitions only to the states C and A $(a^2_{A_2} \approx a^2_{A_3} \approx 0)$. Such a situation occurs, for example, in chromium halides.[24] 2) We shall assume that $\varkappa_C \approx \varkappa_{A_1}$. We can then show easily that

$$p(\omega) = p_\alpha^2 \frac{2\Delta\omega}{(\omega^2_{C(\alpha)g} - \omega^2)^2},$$

$$q(\omega) = p_\alpha^2 |A_1^0| (\varkappa_0 + \varkappa_{C(\alpha)}) E_z \frac{4\omega_{C(\alpha)g}\Delta\omega}{(\omega^2_{C(\alpha)g} - \omega^2)^3},$$

$$\frac{q(\omega)}{p(\omega)} = \frac{|A_1^0|(\varkappa_0 + \varkappa_{C(\alpha)})E_z 4\omega_{C(\alpha)g}}{(\omega^2_{C(\alpha)g} - \omega^2)}. \qquad (12)$$

where $\Delta\omega = \omega_{A(\alpha)} - \omega_C$. Since the antiferromagnetic contribution in the case of Cr_2O_3 at $T = 250$ K is approximately four times greater than the ferromagnetic contribution $[p(\omega)m/q(\omega)l \approx 4]$, we obtain

$$|A_1^0|(\varkappa_0 + \varkappa_c)E_z \approx \frac{2m}{l} \frac{\omega_c^2 - \omega^2}{\omega_C}.$$

Substituting $\omega = 9800$ cm^{-1} and $m/l = 0.37 \times 10^{-5}$ at $T = 250$ K, together with $E = 10^5$ V/cm, we find that an increase in ω_C from 16 000 to 30 000 cm^{-1} increases the pseudo-Stark splitting from 1 to 2 cm^{-1}. Such a splitting is reported in Ref. 26 for the R lines of Cr^{3+} in ruby.

We shall report two analogies to the mechanism of the antiferromagnetic contribution to Cr_2O_3. 1) It is known that in the case of rare-earth iron garnets at the magnetic compensation point the disappearance of the magnetization $\mathbf{m}$ is not accompanied by vanishing of the Faraday effect because

of the inequivalence of the magnetic ions (and also because of the difference between the ions themselves) responsible for the Faraday effect. In principle, the occurrence of the Faraday effect at $T = T_{room}$ can be treated as the appearance of the antiferromagnetic Faraday effect. In contrast to this case, the inequivalence of the positions of the ions in Cr_2O_3 is manifested only in the presence of an electric field $\mathbf{E}$ and it gives rise to an antiferromagnetic contribution to the NR. 2) It is shown in Ref. 27 that in order to describe the temperature dependences of the magnetoelectric susceptibility $\alpha_{\parallel}$ we must include the influence of the electric field $\mathbf{E}$ on the exchange constant (two-ion mechanism) and on the g factors of the Cr^{3+} ions at different positions (g factor mechanism). The existence of the g factor mechanism is essential for explaining the reversal of the sign of $\alpha_{\parallel}$ at temperatures $T < 100$ K and the finite value of the effect at $T = 0$. In the two cases $E = 0$ and $E \neq 0$ we find that $\mathbf{m}$ can be described by expressions analogous to Eq. (11):

$$\mathbf{m} = \sum_i g_i \mathbf{S}_i = 0, \qquad E = 0, \qquad (13)$$

$$\mathbf{m} = \sum_i (g_i \Delta \mathbf{S}_i + \Delta g_i \mathbf{S}_i), \qquad E \neq 0, \qquad (14)$$

where ΔS_i and Δg_i are the changes in the spin and in the g factor under the influence of the field. Equation (14) includes two contributions which can be interpreted as the ferromagnetic contribution ($g\Delta S$), associated with the change in the population of the ground state, and the antiferromagnetic contribution, due to the change in the spin–orbit mixing of the ground and excited states in an electric field.

The existence of the antiferromagnetic contribution to the NR in Cr_2O_3 opens up certain possibilities for the solution of the interesting physical problem of determination of the absolute direction of $\mathbf{l}$ in a single-domain crystal. In fact, we can solve this problem only if we know the direction of the spin in one of the sublattices of Cr_2O_3 after magnetoelectric annealing in known fields. The answer can be obtained by investigating the magnetoelectric effect if we know in advance whether an increase or a reduction in the spin brings the Cr^{3+} ions closer to the oxygen ions in an electric field (Fig. 2). The existing theory does not answer this question. It is possible that we can obtain an answer more simply to another question: how the magnetooptic susceptibility Cr^{3+} is influenced by the approach toward or displacement away from the oxygen ions? The problem in fact consists of determination of the absolute sign of the expression for $(\varkappa_0 + \varkappa_c)$.

5. CONCLUSIONS

This investigation shows that in the case of a Cr_2O_3 antiferromagnet, in addition to the NR(H) induced by a magnetic field (Faraday effect), there is also NR(E), induced by an electric field. These two effects are completely different because the transformation properties of the vectors $\mathbf{H}$ (axial c) and $\mathbf{E}$ (polar i vector) are different. The magnetic field $\mathbf{H}$ can induce NR(H) in any crystal, whereas an electric field $\mathbf{E}$ can induce NR(E) linear with respect to the field only in crystals with a specific magnetic symmetry, particularly those which exhibit the symmetry operation $\bar{1}'$. This operation does apply to the Cr_2O_3 symmetry below $T_N = 307$ K and our investigation enabled us to reveal a new effect in the form of NR(E). In a wide range of temperatures

$T < 250$ K the NR(E) effect is characterized by a value of $\sim -40''/kV$, which can be detected reliably by the modern polarimetric methods. It should be pointed out that the paramagnetic effect NR(H) in Cr_2O_3 reaches values $\sim -240''/kA$, i.e., the specific values of NR in this crystal observed in electric and magnetic fields are comparable.

We found that NR(E) in Cr_2O_3 is due to two different mechanisms. The former is associated with the appearance of a magnetization **m** in an external electric field because of decompensation of the sublattice magnetization (ferromagnetic contribution), and its temperature dependence is analogous to the corresponding dependence in the case of the magnetoelectric susceptibility. The latter is due to disappearance of the crystallographic equivalence of the positions of the magnetic Cr^{3+} ions in an electric field and its temperature dependence is analogous to the corresponding dependence of the antiferromagnetic vector l (antiferromagnetic contribution).

A microscopic analysis of the $^4A_{2g} \rightarrow {}^4T_{2u}$ electron transition in the Cr^{3+} ion demonstrated that the ferromagnetic contribution is due to the exchange splitting of the ground state and the spin–orbit splitting of the excited state. In contrast, the antiferromagnetic contribution is associated with the pseudo-Stark splitting of the states of the Cr^{3+} ions in an electric field, creating opposite changes in the magnetooptic susceptibility of the chromium ions in different sublattices.

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