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Spontaneous non-reciprocal reflection of light from antiferromagnetic Cr_2O_3

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Abstract. The reflection of light from a medium with ordered spin structure characterized by the breakdown of time-reversal and parity symmetry is expected to be non-reciprocal even if the net magnetic moment of the medium equals zero. We report on the first experimental observation of spontaneous non-reciprocal rotation and circular dichroism in spin magnetoelectric Cr_2O_3. Non-reciprocal effects were observed below the antiferromagnetic transition temperature $T_N = 307$ K and their temperature behaviour roughly corresponds to that of the order parameter. Observed values of $(1-4)\times 10^{-4}$ for the magnetoelectric susceptibility in the optical range are several orders of magnitude higher than predicted earlier. This increase of the susceptibility is presumably attributable to electronic dipole transitions in the optical range.

1. Introduction

Among different optical phenomena in crystals a particular type of effect may be assigned to the so-called non-reciprocal (NR) effects. They are characterized by different phase velocities and/or attenuations for light waves travelling via the same optical path but in opposite directions. The most typical examples of these effects are the Faraday rotation observed in transmission and the Kerr effect observed in reflection (see e.g. [1]). As far as we know, up until now non-reciprocal optical effects were observed exclusively in media possessing a magnetic moment. This moment can be induced by a magnetic field in dia- and paramagnets or can arise spontaneously, as in ferro- or ferrimagnets. A magnetic moment induced by an electric current may also give rise to non-reciprocal phenomena [2]. In all these cases the time-reversal symmetry ($1'$) is broken; that is, the crystal may be in two different states converted into one another by the operation $1'$.

There exists a special class of magnetically ordered materials in which below the magnetic transition temperature T_N there is no net magnetic moment, but in addition to the time-reversal symmetry breaking the parity symmetry ($\bar{1}$) is also broken. At the same time the combined symmetry operation $\bar{1}'$ is retained. Magnetoelectrics (ME) are the most well known and widely studied materials [3–6] belonging to this class. Soon after the discovery of ME, theoretical analysis of light propagation in magnetoelectric antiferromagnets showed [7–10] that new optical phenomena should be found, when the spatial dispersion is taken into account. These phenomena, though being in some manifestations similar to those observed in media with a net magnetic moment, may exhibit some important differences. Some of these effects have been observed recently in transmission in Cr_2O_3 [11]. Since these new phenomena are related to the spatial dispersion they have smaller values as compared with corresponding NR effects in ferromagnets. Microscopical calculations showed that non-reciprocal rotation in reflection should be of the order of 10^{-8} rad [9]. Such a small value was not very encouraging for an experimental search and that is probably one reason for the absence of any experimental observation so far.

In the present paper we report results of theoretical and experimental studies of non-reciprocal reflection of light from the magnetoelectric spin antiferromagnet Cr_2O_3. This study is a part of our program on optical phenomena in magnetoelectric materials [11–14], but to a certain extent it was also stimulated by the confused state of the search for non-reciprocal optical phenomena in high-T_c superconductors (HTSC). During the last two to three years different groups reported contradicting data [15–20] in attempts to find evidence of the time-reversal symmetry breaking in HTSC predicted by anyon model theories [21–23]. Recently Dzyaloshinskii pointed out [24] that contradicting data of different groups could be reconciled, at least in principle, if anyons in adjacent planes of HTSC order antiferromagnetically in such a way that the crystal may be regarded as being magnetoelectric. Thus at a phenomenological level non-reciprocal effects in spin and anyon magnetoelectrics may be analysed in a similar way, though obviously microscopical mechanisms of light interaction with these two groups of crystals should be very different because of their different electronic structures. Nevertheless we believe that any reliable experimental result in one group of crystals might help in understanding similar phenomena in another group.

In section 2 of the present paper we give the symmetry analysis of non-reciprocal reflection of light from antiferromagnetic Cr_2O_3. Experimental details are given in section 3 and the data are presented in section 4 and discussed in section 5.

2. Symmetry analysis

We give here a phenomenological analysis of the reflection from a medium in which both time-reversal and three-dimensional parity symmetries are broken, but the combined symmetry ($\bar{1}'$) is preserved. Besides magnetoelectrics, this class includes materials with zero ME tensor (see below). For symmetry reasons these materials may also give rise to NR effects in reflection.

In order to get theoretical predictions for the NR reflection effects it is necessary to solve Maxwell's equations with appropriate boundary conditions. The latter can be derived in a standard way (see e.g. [25]) if the linear optical response of the inhomogeneous (because of a reflecting surface) medium is known. Extending the Onsager symmetry principle to an inhomogeneous medium with broken time-reversal symmetry, the constitutive relationship between the displacement vector $\boldsymbol{D}(\boldsymbol{r},\omega)$ and the electric field vector $\boldsymbol{E}(\boldsymbol{r},\omega)$ can be written as [26]

$$D_i(\boldsymbol{r},\omega) = \epsilon_{ik}(\boldsymbol{r},\omega)E_k(\boldsymbol{r},\omega) + \beta_{ikl}(\boldsymbol{r},\omega)\,\partial E_k(\boldsymbol{r},\omega)/\partial r_l + (\partial/\partial r_l)(\beta_{kil}(\boldsymbol{r},\omega)E_k(\boldsymbol{r},\omega)) \tag{1}$$

where $\epsilon_{ik}(\boldsymbol{r},\omega)$ is the symmetrical i-tensor of rank two and $\beta_{ikl}(\boldsymbol{r},\omega)$ is the c-tensor of rank three. The i-tensor remains invariant while the c-tensor changes its sign under the time reversal. In (1) we retain the terms only up to the first order in the spatial derivatives because we are interested in the optical effects originating in the broken parity symmetry.

The relative magnitude of these effects is in general of the order of a/λ, where λ is the wavelength of light and a is an interatomic spacing.

In a homogeneous ME medium, equation (1) simplifies to

$$D_i(\boldsymbol{r},\omega) = \epsilon_{ik}(\omega)E_k(\boldsymbol{r},\omega) + \gamma_{ikl}(\omega)\,\partial E_k(\boldsymbol{r},\omega)/\partial r_l \qquad (2)$$

where $\gamma_{ikl} = \beta_{ikl} + \beta_{kil}$ is the odd-parity c-tensor of rank three, symmetrical in the permutation of indices i and k. The second term in (2) is a key feature of the optical response of a medium with broken both time-reversal and parity symmetries and manifests itself in the linear spatial dispersion, i.e. in a linear dependence of an optical dielectric tensor on a wavevector of a light wave. As is seen from (2), all transmission NR optical effects in a homogeneous medium depend on γ_{ikl} (and also on ϵ_{ik} of course). Unlike the tensor γ_{ikl} which is symmetric under the permutations of the indices i and k, the tensor β_{ikl} does not possess such symmetry.

To derive boundary conditions for the electric and magnetic fields of the light wave we have to know how ϵ_{ik} and β_{ikl} vary with $\boldsymbol{r}$ near the medium boundary. This can be found only in microscopic theory [27]. This well-known difficulty, which one faces in considering the effects of the spatial dispersion in reflection of light, results in practice in a non-uniqueness of the boundary conditions. When analysing the reflection of light from the ME medium a certain type of boundary condition was postulated [9, 24] but its validity remains unproved.

In order to avoid these difficulties in deriving exact equations valid for analysing the experimental data, we shall take a different approach, based only on the space–time symmetry of the problem [28]. We shall analyse the reflection polarization 2×2 matrix R_{ik}, which relates Cartesian components of the amplitudes of the incident ($\boldsymbol{E}^{\mathrm{i}}$) and reflected ($\boldsymbol{E}^{\mathrm{r}}$) electric fields via $E_i^{\mathrm{r}} = R_{ik}E_k^{\mathrm{i}}$ in the case of the normal-incidence reflection of light. The components R_{ik} fulfil the following conditions:

$$R_{ik}(\psi) = R_{ki}(\psi') \qquad (3)$$

$$R_{ik}(\psi) = \pm R_{ki}(\sigma_v\psi') \qquad (4)$$

where ψ denotes symbolically a state of reflecting crystal, ψ' is obtained from ψ by the time-reversal operation and σ_v is a mirror reflection in a plane perpendicular to the reflection plane. If, for example, light propagates along the x-axis perpendicularly to the reflection surface, then σ_v acts as $y \to -y(\sigma_y)$ or $z \to -z(\sigma_z)$. In practice only a certain choice of orientation of y and z axes and, consequently, σ_v is convenient when (4) is applied to reflection of light from an anisotropic medium. The plus and minus signs in (4) refer to the diagonal and off-diagonal elements, respectively. The relation (3) represents the principle of reciprocity and is based on microscopic time-reversal symmetry. Equation (4) is derived from the reciprocity principle (3) in combination with σ_v transformation. If, in addition to the σ_v transformation, we take a 180° rotation around the normal to the boundary, C_2, we get a relation similar to (4), where σ_v is replaced by C_2 and plus signs for all matrix elements have to be taken. For further details see [28].

Relations (3) and (4) allow one to draw some conclusions about the possibility of observing the NR optical effects in reflection. By its definition the optical non-reciprocity means that the time reversal of state ψ leads to some changes of the intensity or polarization of the reflected light. As seen from (3), only the off-diagonal elements of the R-matrix may change under the time reversal, i.e. the NR effects are related to these elements. Hence, an odd-power dependence of R_{ik} on β_{ikl} will mean that NR effects in reflection may be observed. It follows also from (3) and (4) that if σ_v is the sample symmetry operation, i.e. $\sigma_v\psi = \psi$, then the NR effects at normal incidence are absent.

Now we have to establish when an odd-power dependence of R_{ik} on the components β_{ikl} takes place. To this end we use relations (3) and (4) and identify the state symbol ψ with the components β_{ikl}, i.e. we set $\psi = (\beta_{ikl})$. Since the tensor β_{ikl} describes the effects of the spatial dispersion, which are usually rather small, it is sufficient to consider only a dependence of the R-matrix up to the first order in β_{ikl}. Because the β_{ikl} depend on $\boldsymbol{r}$, the elements of the R-matrix must be regarded as functionals of $\beta_{ikl}(\boldsymbol{r})$. Being incomplete in general, this specification of ψ allows us, nevertheless, to take into account all the NR effects which are due to β_{ikl}. We should remember that the R-matrix depends also on the dielectric tensor $\epsilon_{ik}(\omega)$. This dependence is unknown in general and does not interest us here. For this reason we have excluded $\epsilon_{ik}(\omega)$ from the set of parameters $\{\psi\}$ and now relation (4) holds only if ϵ_{ik} is invariant under σ_v transformation.

Now we should like to refine the meaning of the approximation we made. The point is that relations (3) and (4) do not allow one to distinguish the first-order from, say, the third-order spatial dispersion effects. That is, the tensors $\hat{\alpha}$ and $\hat{s}$ may originate in part in the higher-order spatial dispersion. This does not lead to any mistakes until we go beyond the framework of the purely symmetry approach.

After the general relations (3) and (4) are adapted to our case we can get the symmetry-allowed form of the R-matrix. The crucial point here is the spatial symmetry of the tensor β_{ikl}; therefore we divide all the components β_{ikl} into two sets. The first set contains all those β_{ikl} which are invariant under all operations of a crystal point group. The remaining β_{ikl} remain unchanged only under those crystal point group symmetry operations that leave invariant a semi-infinite crystal, i.e. a reflecting sample. The latter set of β_{ikl} determines a reflection by a thin surface layer. This reflection is smaller by a factor a/λ than the reflection which is due to β_{ikl} from the first set. Hence, in the following we shall not consider reflection effects that are due to the components β_{ikl} from the second set.

There is some complication related to the coordinate dependence of β_{ikl} in a thin surface layer. This dependence may lead to an appreciable effect and reflect the modification of the optical response near the boundary. However, in the purely phenomenological approach such surface effects are indistinguishable from true bulk effects (see below). For this reason we shall neglect coordinate dependence of β_{ikl}. However, β_{ikl} defined in this way should be considered to be effective.

The tensor β_{ikl} may be represented quite generally in the form

$$\beta_{ikl} = \mathrm{i}(c/\omega)[\tfrac{1}{2}(e_{iln}\alpha_{kn} + e_{kln}\alpha_{in}) + e_{ikn}g_{nl}] + s_{ikl} \tag{5}$$

where e_{iln} is the unit antisymmetric tensor of rank three, the tensors α_{kn} and g_{kn} have the same symmetry properties as the ME tensor, and s_{ikl} is the symmetrical tensor in the permutation of all three indices i, k and l. The tensor γ_{ikl} in (2) does not depend on g_{kn}. Consequently, this tensor cannot be measured in transmission experiments. It contains information about the influence of the surface on the optical response and appears in boundary conditions for the electric ($\boldsymbol{E}$) and magnetic ($\boldsymbol{H}$) fields of a light wave. The 'natural' boundary conditions that are usually chosen [9, 24] have the tangential components of $\boldsymbol{E}$ and $\boldsymbol{H} = \boldsymbol{B} + \hat{\alpha}\boldsymbol{E}$, where $\boldsymbol{B}$ is the magnetic induction, and is continuous across the boundary. Such boundary conditions can be derived by using (5) if we neglect s_{ikl} and set $g_{nl} = (-\alpha_{nl} + \delta_{nl}\mathrm{Tr}\hat{\alpha})$. For this form of g_{nl} we get from (5)

$$\beta_{ikl} = \mathrm{i}(c/\omega)e_{iln}\alpha_{kn} + s_{ikl}. \tag{6}$$

The only additional quantity introduced in this approximation by the presence of the boundary is $\mathrm{Tr}\hat{g} = 2\mathrm{Tr}\hat{\alpha}$. However, there is no physical basis for such a choice of g_{nl} and, therefore, the above mentioned boundary conditions are questionable.

In the symmetry approach we do not need to take into consideration both tensors $\hat{\alpha}$ and $\hat{g}$ because of their identical symmetry properties. For this reason we may set $\psi = (\hat{\alpha}, \hat{s})$. Now the tensor $\hat{\alpha}$ effectively represents both $\hat{\alpha}$ and $\hat{g}$ in relation (5). This clearly demonstrates that notions of the bulk and surface contributions to the effects considered cannot be unambiguously defined within a purely symmetry approach.

Now we consider Cr_2O_3. Below $T_N = 307$ K where tensors $\hat{\alpha}$ and $\hat{s}$ are non-zero, Cr_2O_3 has magnetic point group $\bar{3}'m'$ with spins of the Cr^{3+} ions pointing along the three fold axis C_3 in an alternating manner. As we have explained above we take the tensors $\hat{\alpha}$ and $\hat{s}$, which are compatible with the bulk symmetry of Cr_2O_3. If we choose a coordinate system such that $x \| U_2$ (two fold axis) and $z \| C_3$ then the only non-zero components of $\hat{\alpha}$ and $\hat{s}$ are [9]: $\alpha_{xx} = \alpha_{yy}$, α_{zz} and $s_{xxx} = -s_{xyy}$ (and their permutations). Now we may use relations (3) and (4) with $\psi = \{\hat{\alpha}, \hat{s}\}$ taking σ_y or σ_z as σ_v. It is easy to see that $\hat{s}$ remains invariant and $\hat{\alpha}$ changes sign under these operations. For the wavevector of light along x or z axes we get from (3) and (4)

$$R_{ik}(\hat{\alpha}, \hat{s}) = R_{ki}(-\hat{\alpha}, -\hat{s}) \tag{7}$$

$$R_{ik}(\hat{\alpha}, \hat{s}) = \pm R_{ki}(\hat{\alpha}, -\hat{s}) \tag{8}$$

where $i, k = y, z$ for $\boldsymbol{k} \| \boldsymbol{x}$ and $i, k = x, y$ for $\boldsymbol{k} \| \boldsymbol{z}$. In deriving (8) from (4) the transformations σ_z and σ_y have been used for the wavevectors $\boldsymbol{k} \| \boldsymbol{x}$ and $\boldsymbol{k} \| \boldsymbol{z}$, respectively. Recall that the invariance of the tensor $\hat{\epsilon}(\omega)$, on which the R-matrix depends in an unknown manner, under both the time reversal and the mirror reflections, is essential for validity of (7) and (8).

From (7) and (8) to the first order in $\hat{\alpha}$ and $\hat{s}$ we obtain

$$R = \begin{pmatrix} (1-\tilde{n}_y)/(1+\tilde{n}_y) & a_{xzz}\alpha_{zz} + a_{xyy}\alpha_{yy} \\ -a_{xzz}\alpha_{zz} - a_{xyy}\alpha_{yy} & (1-\tilde{n}_z)/(1+\tilde{n}_z) \end{pmatrix} \tag{9}$$

for $\boldsymbol{k} \| \boldsymbol{x}$, and

$$R = \begin{pmatrix} (1-\tilde{n}_x)/(1+\tilde{n}_x) & 2a_{xxx}\alpha_{xx} + a_{zzz}\alpha_{zz} \\ -2a_{zxx}\alpha_{xx} - a_{zzz}\alpha_{zz} & (1-\tilde{n}_x)/(1+\tilde{n}_x) \end{pmatrix} \tag{10}$$

for $\boldsymbol{k} \| \boldsymbol{z}$. Here $\tilde{n}_i = n_i + \mathrm{i}k_i$ is the complex index of refraction. Coefficients a_{ikl} cannot be obtained from the symmetry approach and should be derived from some model calculations. The elements R_{ii} are independent of $\hat{\alpha}$ or $\hat{s}$ in the linear approximation and are given by the usual Fresnel's formulae. Due to the high symmetry of the problem discussed, i.e. due to the normal incidence of the light travelling along the x or z axis, the R-matrix does not contain any components of s_{ikl} in the linear approximation. In other cases, e.g. at oblique incidence, relations (7) and (8) do not hold and the R-matrix will also depend on s_{ikl}.

It is interesting to compare the R-matrices (9) and (10) with the results obtained in [9] by solving Maxwell's equations together with the postulated boundary conditions. In both cases the reflection coefficients do not depend on the components s_{ikl}. However, in [9] the role of the tensor $\hat{s}(\omega)$ was not discussed at all when considering the reflection. The only difference lies in the fact that in the approach used in [9] the NR reflection for $\boldsymbol{k} \| \boldsymbol{z}$, i.e. when light propagates along C_3 axis, does not depend on the component α_{zz} of the

ME tensor, i.e. $a_{zzz} = 0$. This difference gives us an opportunity to illustrate an important role of the surface and, as a consequence, of the boundary conditions when effects of the spatial dispersion are investigated in reflection. The appearance of α_{zz} in (10) may be qualitatively interpreted as originating from a surface weak ferromagnetism which is allowed by symmetry in magnetoelectrics. Indeed, a surface normal $\boldsymbol{n}$ is a polar vector like an electric field vector and formally we may always consider the value $\alpha^{st}_{ik} n_k$, where α^{st}_{ik} is a static ME tensor, as being proportional to the m_i component of the surface magnetic moment density. In other words, we may say that the surface electric polarization due to the spatial inhomogeneity induces the surface magnetic moment in magnetoelectrics. This magnetic moment can give rise to the NR optical reflection effects which are analogous in their experimental manifestation to the Kerr effects in a ferromagnet. If the tensor α^{st}_{ik} is antisymmetric, then $\boldsymbol{m}$ is always parallel to the surface. Consequently, in this case the NR reflection effects cannot be observed at normal incidence if the symmetry of a reflecting sample is too high. In our case $\boldsymbol{n} \| \boldsymbol{z}$ and the only component of the surface magnetic moment is $m_z \sim \alpha_{zz}$. This is why α_{zz} appeared in (10). The simple boundary conditions in [9] do not take into account such an effect properly. Analogously, for $\boldsymbol{k} \| \boldsymbol{x}$, R_{yz} is dependent on α_{xx}. This is effectively included in (9) because $\alpha_{xx} = \alpha_{yy}$.

We note, to avoid confusion, that there are both qualitatively and quantitatively different surface effects, mentioned above, which are due to the components β_{ikl} allowed by the symmetry of a reflecting sample, but not by the bulk symmetry. We do not consider such effects here.

Of course, in order to get quantitative estimations of α_{ik} from experimental data, the usual procedure of solving Maxwell's equations with appropriate boundary conditions is needed for an estimation of unknown coefficients a_{ikl} in (9) and (10). At this stage we use the result of [9] and take $a_{xzz} = a_{zxx} = 1/(1 + \tilde{n}_x)^2$, $a_{xyy} = 1/(1 + \tilde{n}_z)^2$ and $a_{zzz} = 0$.

The rotation $\Delta\varphi$ of the polarization plane of the linearly polarized light and the circular dichroism $\Delta R/2R_0 = (R_+ - R_-)/(R_+ + R_-)$, where R_+ and R_- are the reflection coefficients for the right and left circularly polarized light, respectively, are given by the equations

$$\Delta\varphi = \mathrm{Re}[(R_{ii} - R_{kk}) \sin 2\varphi + 2R_{ik}]/(R_{ii} + R_{kk}) \tag{11}$$

$$\Delta R/2R_0 = 2\,\mathrm{Im}(R_{ii} + R_{kk}) R_{ik}/(|R_{ii}|^2 + |R_{kk}|^2) \tag{12}$$

where φ is the azimuth angle of the polarization plane of the incident light. The NR contributions to both effects are related to the c-tensor α_{ik}, which changes its sign under the time reversal.

Finally, we should like to draw attention to possible situations where the NR effects in reflection arise entirely due to the tensor $\hat{s}$ but not to $\hat{\alpha}$. An example is a tetragonal magnetoelectric with the magnetic point group $4'/m'mm'$ which has the only non-zero $\hat{\alpha}$- and $\hat{s}$-tensor components $\alpha_{xx} = -\alpha_{yy}$ and s_{xyz}. Such a magnetic point group is characteristic of antiferromagnetic rare-earth phosphates and vanadates and also of $CoCs_3Cl_5$ [6]. By using the above procedure it can easily be shown that the non-reciprocity for light normally incident along a four fold axis is due to s_{xyz} exclusively. The same component should produce the non-reciprocity in reflection from a cubic antiferromagnet with the magnetic point group $m'3m$. In this case $\hat{\alpha} = 0$ for symmetry reasons but time-reversal and parity symmetries are broken and s_{xyz} is non-zero.

3. Experiment

The rotation $\Delta\varphi$ of the reflected linearly polarized light was studied by the polarimetric technique. The light from a 633 nm helium–neon laser passed through a linear polarizer and a magneto-optical modulator, and was reflected back at a small angle, about 2°, by the sample. The reflected light passed through an analyser and was detected by a photodiode. The electric signal was monitored by the lock-in technique and the sensitivity was about $\Delta\varphi = 10^{-6}$ rad. A similar optical geometry was used for measurements of the reflection circular dichroism and the sensitivity was about 10^{-6} (more details were given in [18]).

Since the laser beam spot on the sample was about $d \simeq 0.5$ mm in diameter, and we did not attempt to resolve an antiferromagnetic domain pattern, the crucial point was to get a single-domain state of the sample. This was done by means of a magnetoelectric annealing procedure, where the crystal was cooled from the temperature 340–350 K through $T_N = 307$ K under DC electric field $E_z = 500$ V mm^{-1} and magnetic field $H_z = 10$ kOe. These values were sufficient [13] to obtain two distinguishable antiferromagnetic states l^+ ($E_z^+H_z^+$ or $E_z^-H_z^-$) and l^- ($E_z^-H_z^+$ or $E_z^+H_z^-$) connected by the time-reversal operation $1'$. Since there are no dipole fields in the antiferromagnet, the annealing fields were switched off after cooling the sample to a low temperature and the measurements were performed without any external fields, i.e. the spontaneous effects were measured.

The samples were cut from x-ray oriented Cr_2O_3 boules grown by the Verneuil method. Their faces were carefully polished using a diamond abrasive with grain size less than 0.5 μm. The high optical quality of sample surfaces was confirmed by the absence of any spurious signals above T_N and by a low depolarization level of the reflected light.

4. Results and discussion

Results for the rotation $\Delta\varphi = \varphi^r - \varphi^i$ for two principal orientations of the incident wavevector $\boldsymbol{k}\|\boldsymbol{x}$ and $\boldsymbol{k}\|\boldsymbol{z}$ are shown as a function of temperature around T_N in figure 1. All the data clearly show that just below T_N a rotation appears. The non-reciprocity of the rotation is proved by the fact that it is of opposite sign for the two different states l^+ and l^- connected by the time-reversal transformation. When $\boldsymbol{k}\|\boldsymbol{z}$, i.e. when the wavevector is oriented along the optical axis, the rotation does not depend on the polarization azimuth of the incident light. When $\boldsymbol{k}\|\boldsymbol{x}$ and $\boldsymbol{E}^i\|\boldsymbol{y}$ ($\varphi^i = 0$) or $\boldsymbol{E}^i\|\boldsymbol{z}$ ($\varphi^i = 90°$) there is no rotation above T_N, although there is below T_N with the sign opposite to that in the previous case. When $\varphi^i = 45°$, then in accordance with (11), a reciprocal rotation due to the crystallographic birefringence is also present and varies above and below T_N.

The results of the circular dichroism measurements $\Delta R/2R_0$ as a function of temperature are shown in figure 2. They also clearly point to the non-reciprocity in reflection and to the presence of two antiferromagnetic states l^+ and l^-.

Results for the ME susceptibility $(\alpha'_{xx}+\alpha'_{zz})$ in the case $\boldsymbol{k}\|\boldsymbol{x}$ ($\varphi^i = 0$) evaluated according to (9) and (11) in a wider temperature range are shown in figure 3. Also shown in this figure are the temperature variations of the static ME susceptibilities α_{ii}^{st} [4] and of the sublattice magnetization $\langle m\rangle$ [29]. The ME susceptibility at optical frequency varies approximately proportionally to $\langle m\rangle$ as it should from the symmetry requirements [30].

Thus the study of Cr_2O_3 unambiguously shows that the reflection of light from two magnetically ordered states l^+ and l^- is non-reciprocal for both rotation and the circular dichroism. Measured values of the rotation $\Delta\varphi$ and the dichroism $\Delta R/2R_0$ allow the ME

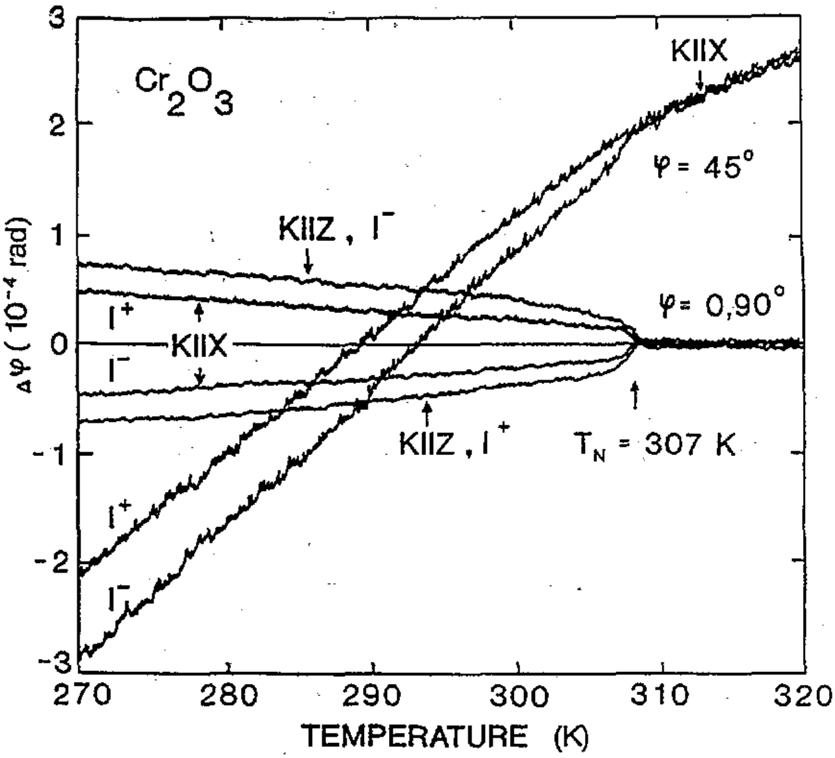

Figure 1. The NR rotation $\Delta\varphi$ versus temperature in two antiferromagnetic states l^+ and l^- and for two principal orientations of the wavevector k of the incident–reflected light wave.

susceptibilities in the optical range to be evaluated. Using (9)–(12) and taking $n_i \simeq 2.5$ at $T = 270$ K we get

$$\alpha'_{xx} = \alpha'_{yy} = -1.8 \times 10^{-4} \qquad \alpha'_{zz} = +4.3 \times 10^{-4} \tag{13}$$

$$\alpha''_{xx} = \alpha''_{yy} = -0.9 \times 10^{-4} \qquad \alpha'_{zz} = +2.2 \times 10^{-4}. \tag{14}$$

The values of α'_{ii} are of the same order of magnitude as the static ME values $\alpha^{st}_{xx} \simeq -1.0 \times 10^{-4}$ and $\alpha^{st}_{zz} \simeq 1.0$–$1.5 \times 10^{-3}$ (at $T = 260$ K) [6]. Arbitrarily we chose the positive sign for α'_{zz}, but in fact the sign may be changed when going from the static case to the optical range.

Recently a gyrotropic rotation $\Delta\theta$ of the optical indicatrix in Cr_2O_3 in the transmission was observed [11], which is also related to the tensor $\hat{\alpha}(\omega)$ and according to equation (42) from [9] varies as

$$\Delta\theta \simeq -(\alpha'_{zz} - \alpha'_{xx})/2\Delta n_{zx}. \tag{15}$$

According to our measurements $\Delta\alpha'_{zx} = 6.2 \times 10^{-4}$ and $\Delta n_{zx} = 5.8 \times 10^{-2}$, and therefore the expected rotation at 633 nm is $\Delta\theta \simeq 5 \times 10^{-3}$. Although this is of the same order of magnitude, the value is higher than $\Delta\theta \simeq 1.2 \times 10^{-3}$ observed at 1156 nm [11], but the difference is not too large and can be attributed to the difference of the wavelengths.

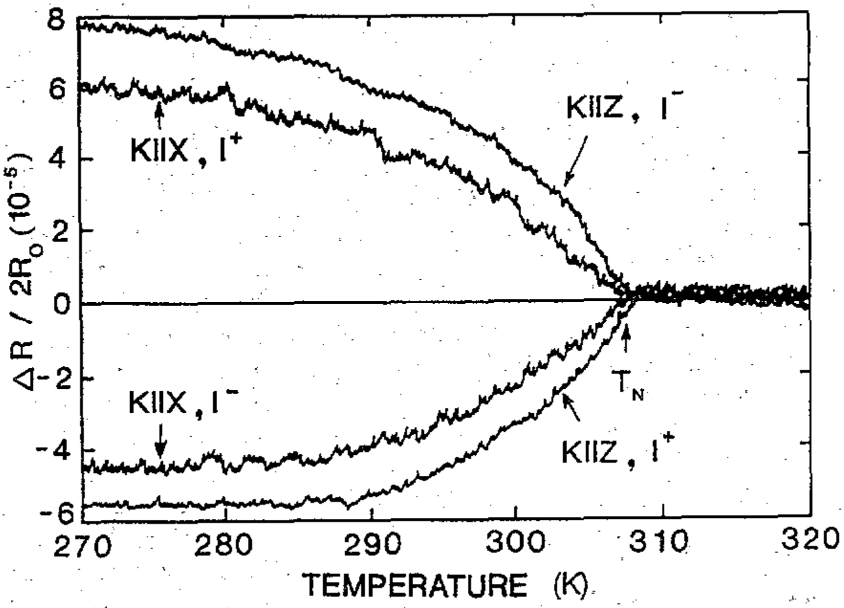

Figure 2. The reflection circular dichroism versus temperature.

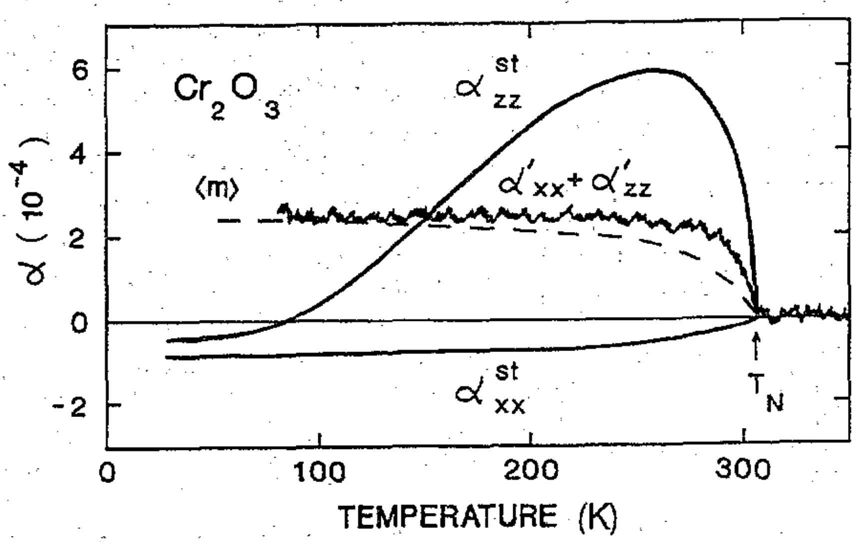

Figure 3. The optical ME susceptibility $(\alpha'_{xx}+\alpha'_{zz})$ as compared with the sublattice magnetization $\langle m \rangle$, dashed curve (see [29], in relative units), and with static ME values (see [4]).

A question arises as to what extent the ME susceptibilities α_{ii} derived from reflection experiments are due to the bulk properties and not to the boundary effects. The answer can be found only outside the framework of the phenomenological treatment, i.e. in microscopic theory. The rough estimates of the optical ME susceptibilities in Cr_2O_3 were given in [9].

The values of the order of 10^{-8}–10^{-9} were found, these being 4–5 orders of magnitude lower than our experimental values $\alpha_{ii} \simeq 10^{-4}$. This serious discrepancy may be due to the fact that estimates were made in a model which took into account only dipole transitions in the infrared region with $h\nu \simeq 250$ cm^{-1} [9]. But in the optical range the contributions to α_{ii} from magnetic transitions as well as from the polar lattice modes decrease to zero. The contribution from the electronic transitions should become dominant and resonance enhancement of the ME susceptibilities may occur. If we take the magnetic dipole strength in (87) from [9] to be of the order of an electric dipole times the fine-structure constant 1/137 and the electric dipole oscillator strength for the electronic transition centred at $h\nu_n \simeq 3$ eV to be of the order of 10^{-3}, we get $\alpha_{ii} \simeq 10^{-4}$, which is consistent with experiment. Thus, there is no strong evidence that surface effects play a large role as compared to bulk ones, but the question of surface and bulk relative contributions requires further investigation.

In its experimental manifestation, the NR rotation and circular dichroism in reflection from antiferromagnetic Cr_2O_3 resemble the well-known Kerr rotation and ellipticity intrinsic to ferro- and ferrimagnets [1]. Both these effects are non-reciprocal, spontaneous and the sign of the effects can be changed by switching the magnetic domains. Nevertheless, these two effects are different from the point of view of symmetry requirements. As pointed out in [31] there is an experimental test to distinguish ferromagnetic from magnetoelectric NR optical effects in reflection experiments. Here we give a simple physical explanation of the distinction between these two cases. Following [31] we consider the reflection of left- and right-incident light from a magnetoelectric slab to the left and right, respectively. As we have discussed in section 2, there is a magnetic moment density near the surfaces of the slab. The directions of the magnetic moments at the left and right surfaces are opposite to each other. In contrast, the direction of the magnetic moment density vector in the ferromagnetic slab does not change. The same conclusion can be drawn more formally if we notice that the last term in (1) containing the spatial derivative of β_{ikl} has opposite signs on the left and right surfaces of the slab. This distinction between the ME and ferromagnetic slabs provides a way of distinguishing between them by comparing the NR reflection effects for the left- and right-incident light in both cases. The rigorous proof of the experimental test for ME origin of the NR effects has been given in [31].

If Cr_2O_3 had possessed a net magnetic moment one should follow the prescription of [31] to separate ME non-reciprocal effects from ferromagnetic ones. However, this is not the case for Cr_2O_3 which has no experimentally detected macroscopic magnetic moment. This fact is reflected in its magnetic point group. Theoretically, a net magnetic moment may appear in Cr_2O_3 if, for example, we ignore the commonly accepted assumption on localization of the microscopic magnetic moment density on Cr^{3+} ions [32]. But such a magnetic moment, if it existed, would be of third order in the spin–orbit interaction, i.e. negligibly small.

Another possible source of the spontaneous macroscopic magnetic moment which exists in some antiferromagnets is the piezomagnetic effect [33]. This effect is absent in Cr_2O_3 for symmetry reasons, since the combined space–time inversion symmetry operation $\bar{1}'$ changes the sign of a piezomagnetic tensor. It therefore equals zero in Cr_2O_3.

Thus there can be no doubt that the ferromagnetic contribution to the NR effects is absent for Cr_2O_3. For this reason we measured reflection of light only from one side of the crystal. If, however, the magnetic structure of a crystal being investigated is not well known—as, for example, in the case of metallic states of high-T_c superconductors—then one should follow the full procedure suggested in [31].

5. Conclusion

In conclusion, we have observed experimentally the NR optical effects in reflection from the spin magnetoelectric Cr_2O_3. As far as we know this is the first observation of non-reciprocal effects in a medium with zero net magnetic moment and with broken time-reversal symmetry. The values of the ME susceptibilities in the optical range are of the same order of magnitude as the static ones and are many orders of magnitude higher than expected. The NR rotation in Cr_2O_3 is of the order of 10^{-4} rad. Though this value is lower than in magnetics with a magnetic moment, it is quite an appreciable effect.

Similar measurements of the rotation were performed by us on another spin antiferromagnet Nd_2CuO_4 ($T_N \simeq 250$ K) which is assumed to possess a ME structure [34]. The study with a comparable sensitivity gave null results.

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