Theory of Gyrotropic Birefringence*

R. M. HORNREICH† AND S. SHTRIKMAN
Department of Electronics, Weizman Institute of Science, Rehovoth, Israel
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A theoretical treatment of the optical effect known as gyrotropic or nonreciprocal birefringence is presented. By suitably renormalizing the electric dipole moment tensor, it is shown, for the case of lossless media, that 10 of the 18 independent quantities in the gyrotropic-birefringence tensor have their origin in electric quadrupole effects. The other eight are shown to be related to the magnetoelectric effect. The general results are applied to the materials Cr_2O_3 and $MnTiO_3$. The propagation of a plane wave along one of the crystalline axes of Cr_2O_3 is then considered. It is shown that the gyrotropic birefringence exhibits itself as a rotation of the principal optic axes, together with a change in the velocity of propagation of the wave in the medium. Next, the modified boundary conditions corresponding to the renormalized field vectors are given, and the case of a plane wave normally incident on a gyrotropically birefringent medium is discussed. It is noted that the field relations at a boundary will be modified even when the quadrupole contribution vanishes and the magnetoelectric tensor is isotropic, a case in which there is no gyrotropic birefringence in the medium itself. Foinally, a quantum-mechanical calculation of the gyrotropic-birefringence tensor at 0°K is given. The expressin obtained is applied to the case of Cr_2O_3, and the electric quadrupole and magnetoelectric contributions are separated. It is roughly estimated that, at optical frequencies, the electric-quadrupole-induced rotation of the principal optic axes of Cr_2O_3 is of the order of 10^{-6} rad, and the magnetoelectric-induced shift is two orders of magnitude less.

I. INTRODUCTION

THE possible existence of an additional optical effect, called gyrotropic or nonreciprocal birefringence, was first pointed out by Brown *et al.*[1] They showed that such an effect would appear in the form of a polar *c* tensor[2] (i.e., one that reverses sign under both space and time inversion) of rank 3. For the case of a lossless medium, this tensor also possesses intrinsic symmetry in that it is symmetric upon permutation of its first two indices. Property tensors having these properties may be found in 56 of the magnetic crystal classes.[2,3]

In Sec. II, we present a phenomenological theory of gryotropic birefringence. Since the magnetic classes in which gyrotropic birefringence is allowed are among those in which the magnetoelectric effect may occur,[4] the constitutative relations between the complex amplitudes of the fields are written so as to incorporate both these effects simultaneously. This is most conveniently done by combining all induced effects in a suitably renormalized electric dipole moment.[5] For the case of lossless media, it is shown that the gyrotropic birefringence property tensor has 18 linearly independent components before crystalline symmetry considerations are introduced. We then show that a physical basis for these 18 independent quantities may be found in electric quadrupole and magnetoelectric effects, with the former contributing 10 independent quantities and the latter eight. In particular, we consider the materials Cr_2O_3 and $MnTiO_3$, in which an experimental observation of gyrotropic birefringence may be possible.[1] Finally, the closely related effect of natural optical activity[6] is discussed and correlated with the point of view presented here.

In Sec. III, we briefly consider wave propagation in a medium exhibiting gyrotropic birefringence. The propagation of plane waves along one of the crystalline axes of Cr_2O_3 is analyzed and it is shown that the gyrotropic birefringence appears as a shift in the principal optic axes, together with a change in the velocity of propagation.

In Sec. IV, the boundary conditions on the renormalized field vectors of Sec. II are derived. We then go on to consider a plane wave normally incident on a gyrotropically birefringent medium such as Cr_2O_3. It is noted that the field relations at a boundary will be modified even in the case of an isotropic magnetoelectric tensor, a case wherein the tensor does not lead to any gyrotropic birefringence in the medium itself.

In Sec. V, we present a quantum-mechanical derivation of the gyrotropic birefringence tensor at 0°K. This is done by applying an electromagnetic wave to the crystal and calculating the expectation value of the current-density operator. The term linear in the wave vector is extracted and a transformation to localized (Wannier) functions is carried out. The general expression obtained is applied to the case of Cr_2O_3 and the electric quadrupole and magnetoelectric contributions discussed in Sec. II are separated. A rough estimate

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† Present address: Applied Research Laboratory, Sylvania Electronic Systems, 40 Sylvan Road, Waltham, Mass. 02154

[1] W. F. Brown, Jr., S. Shtrikman, and D. Treves, J. Appl. Phys. **34**, 1233 (1963).

[2] R. R. Birss, Rept. Progr. Phys. **26**, 307 (1963).

[3] J. Tenenbaum, Proc. Indian Acad. Sci., Sec. A **64**, 74 (1966).

[4] G. T. Rado and V. J. Folen, J. Appl. Phys. **33**, 1126 (1962), and references therein.

[5] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1960).

[6] E. U. Condon, Rev. Mod. Phys. **9**, 432 (1937).

of the shift in the principal optic axes in Cr_2O_3 at optical wavelengths due to gyrotropic birefringence is given.

In Sec. VI, we discuss and summarize our results for gyrotropic or nonreciprocal birefringence.

II. PHENOMENOLOGICAL THEORY, SYMMETRY CONSIDERATIONS, AND CONNECTION WITH MAGNETOELECTRIC EFFECT

The usual description of the optical properties of materials is obtained by using Maxwell's equations and taking the constitutive relations between the complex amplitudes of the fields in the form[5,7]

$$D_i=\bar{\epsilon}_{ij}(\omega,\mathbf{k})E_j\,, \tag{1a}$$

$$B_i=H_i\,, \tag{1b}$$

where E_i, D_i, H_i, and B_i are the electric field, electric displacement, magnetic field, and magnetic induction, respectively. The indices refer to Cartesian coordinates and summation over repeated indices is understood. The natural optical activity γ_{ijl} is then found by expanding $\bar{\epsilon}_{ij}(\omega,\mathbf{k})$ to first order in $\mathbf{k}$; thus

$$\bar{\epsilon}_{ij}(\omega,\mathbf{k})=\epsilon_{ij}(\omega)+i\gamma_{ijl}(\omega)k_l+\cdots. \tag{2}$$

Equation (1) is usually derived for the case of a nonmagnetic homogeneous material.[7] The excitation is assumed to be weak; thus the response function is taken as linear in the excitation. That is,

$$D_i(\mathbf{r},t)=\int_{-\infty}^{t}dt'\int d\mathbf{r}'\;\bar{\epsilon}_{ij}(t,\mathbf{r};\,t',\mathbf{r}')E_j(\mathbf{r}',t')\,, \tag{3a}$$

$$B_i=H_i. \tag{3b}$$

That the t' integration runs only from $-\infty$ to t follows from the causality principle. Also, because the properties of the material are time-invariant, the kernel can depend only on the time difference $\tau=t-t'$. For the case of a spatially homogeneous medium the kernel can in addition, depend only the difference $\boldsymbol{\varrho}=\mathbf{r}-\mathbf{r}'$. Taking $E_j(\mathbf{r}',t')=E_j\exp[i(\mathbf{k}\cdot\mathbf{r}'-\omega t')]$ and $D_i(\mathbf{r},t)=D_i\times\exp[i(\mathbf{k}\cdot\mathbf{r}-\omega t)]$, Eq. (1) follows directly, with

$$\bar{\epsilon}_{ij}(\omega,\mathbf{k})=\int_0^{\infty}d\tau\int d\boldsymbol{\varrho}\bar{\epsilon}_{ij}(\tau,\boldsymbol{\varrho})\exp(\mathbf{k}\cdot\boldsymbol{\varrho}-\omega\tau)\,. \tag{4}$$

We now wish to extend the above formulation to the case of magnetic materials and, in particular, to ordered magnetic solids, i.e., crystals. The outstanding characteristic or crystalline structures is that they are not spatially homogeneous, but are invariant only under a group of finite translation vectors. For this case transforming Eq. (3a) yields[7]

$$D_i(\omega,\mathbf{k})=\sum_{\mathbf{K}}\bar{\epsilon}_{ij}(\omega,\mathbf{k},\mathbf{K})E_j(\omega,\,\mathbf{k}+2\pi\mathbf{K})\,, \tag{5}$$

where $\mathbf{K}$ is an arbitrary reciprocal-lattice vector. To arrive at Eq. (1a), it is necessary to neglect all terms in the $\mathbf{K}$ summation except the term $\mathbf{K}=0$. At optical frequencies or lower, where $\mathbf{k}\ll\mathbf{K}$, such a procedure is justified[7] and we shall thus ignore all $\mathbf{K}\neq0$ terms in Eq. (5).

We now wish to take account of the fact that the crystals under consideration are magnetic, that is, that they are not invariant with respect to the operation of time reversal. For this case, and again neglecting all terms except the one in which $\mathbf{K}=0$, Eq. (1) is generalized to

$$D_i=\epsilon_{ij}(\omega,\mathbf{k})E_j+\alpha_{ij}(\omega,\mathbf{k})H_j\,, \tag{6a}$$

$$B_i=\beta_{ij}(\omega,\mathbf{k})E_j+\mu_{ij}(\omega,\mathbf{k})H_j\,. \tag{6b}$$

It should be noted that the ϵ_{ij} of Eq. (6) is *not* the same as the $\bar{\epsilon}_{ij}$ of Eq. (1). This point has been discussed by Condon[6] and we shall touch upon it briefly at the end of this section.

It will be useful to derive the transformation properties of the property tensors in Eq. (6) for later reference. This may be done by considering the physical fields, which are given by

$$e_i=\tfrac{1}{2}\{E_j\exp[i(\mathbf{k}\cdot\mathbf{r}+\omega t)]+E_j^*\exp[-i(\mathbf{k}\cdot\mathbf{r}+\omega t)]\}\,, \tag{7}$$

and similarly for d_i, h_j, and b_i. Under the operations of time reversal T and space inversion I we must have[2]

$$Te_j=e_j\,,\qquad Ie_j=-e_j\,, \tag{8a}$$

$$Td_i=d_i\,,\qquad Id_i=-d_i\,, \tag{8b}$$

$$Th_j=-h_j\,,\quad Ih_j=h_j\,, \tag{8c}$$

$$Tb_j=-b_j\,,\quad Ib_j=b_j\,. \tag{8d}$$

Inspection of Eq. (7) shows that the time-reversal operator, which takes t into $-t$, takes E_j into E_j^* and $\mathbf{k}$ into $-\mathbf{k}$ in the transformed system. Similarly, the space-inversion operator, which takes $\mathbf{r}$ into $-\mathbf{r}$, takes E_j into $-E_j$ and $\mathbf{k}$ into $-\mathbf{k}$ in the transformed system. Similar considerations apply to the other field vectors. Looking at Eq. (6), we see that we must have

$$T\epsilon_{ij}(\omega,\mathbf{k})=\epsilon_{ij}^*(\omega,-\mathbf{k}),\qquad I\epsilon_{ij}(\omega,\mathbf{k})=\epsilon_{ij}(\omega,-\mathbf{k}), \tag{9a}$$

$$T\alpha_{ij}(\omega,\mathbf{k})=-\alpha_{ij}^*(\omega,-\mathbf{k}),\ I\alpha_{ij}(\omega,\mathbf{k})=-\alpha_{ij}(\omega,-\mathbf{k}), \tag{9b}$$

$$T\beta_{ij}(\omega,\mathbf{k})=-\beta_{ij}^*(\omega,-\mathbf{k}),\ I\beta_{ij}(\omega,\mathbf{k})=-\beta_{ij}(\omega,-\mathbf{k}), \tag{9c}$$

$$T\mu_{ij}(\omega,\mathbf{k})=\mu_{ij}^*(\omega,-\mathbf{k}),\qquad I\mu_{ij}(\omega,\mathbf{k})=\mu_{ij}(\omega,-\mathbf{k})\,. \tag{9d}$$

For the case of insulating materials, Maxwell's equations may be written as

$$c\epsilon_{ilm}E_lk_m=-\omega B_i\,, \tag{10a}$$

$$c\epsilon_{ilm}H_lk_m=\omega D_i\,, \tag{10b}$$

where c is the velocity of light and ϵ_{ilm} is the unit antisymmetric tensor of rank three.

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[7] V. M. Agranovich and V. L. Ginzburg, Usp. Fiz. Nauk **76**, 643 (1962) [English transl.: Soviet Phys.—Uspekhi **5**, 323 (1962)]; V. L. Ginzburg, A. A. Rukhadze, and V. P. Silin, J. Phys. Chem. Solids **23**, 85 (1962).

It is now convenient to combine all induced effects in the material in a renormalized electric dipole moment P_i'. That is, instead of separating the induced currents into two parts, P_i and $c\epsilon_{ilm}M_lk_m$, where

$$P_i=(D_i-E_i)/4\pi\,, \tag{11a}$$

$$M_i=(B_i-H_i)/4\pi\,, \tag{11b}$$

we combine them by suitably renormalizing P_i. The required relation is[5,7]

$$P_i'=P_i+(c/\omega)\epsilon_{ilm}M_lk_m\,. \tag{12}$$

A renormalization such as that of Eq. (12) is always possible in a continuous medium. It does, however, lead to changes in the conditions on the field vectors at boundaries between continuous media. We shall defer the question of boundary effects to Sec. IV.

Using Eqs. (11) and (12), Maxwell's equations, (10a) and (10b), become

$$c\epsilon_{ilm}E_lk_m=-\omega B_i\,, \tag{13a}$$

$$c\epsilon_{ilm}H_l'k_m=\omega D_i'\,, \tag{13b}$$

where

$$D_i'=E_i+4\pi P_i'\,, \tag{14a}$$

$$B_i=H_i'. \tag{14b}$$

Thus, in renormalized form, Eq. (6a) becomes

$$D_i'=[\epsilon_{ij}-\alpha_{ik}\rho_{kl}\beta_{lj}+(c/\omega)(\alpha_{ik}\epsilon_{jlm}+\beta_{lj}\epsilon_{ikm})\rho_{kl}k_m -(c/\omega)^2(\delta_{sl}-\rho_{sl})\epsilon_{isk}\epsilon_{ljm}k_kk_m]E_j=A_{ij}E_j. \tag{15}$$

Here $\rho_{ij}=(\mu^{-1})_{ij}$ and δ_{ij} is the Kroneker delta.

We shall restrict our attention to media that are lossless in the frequency ranges of interest (these will be low frequencies and those in the optical range). For this case, we require that[1,5]

$$A_{ij}=A_{ji}^*\,, \tag{16}$$

from which it follows that

$$\epsilon_{ij}=\epsilon_{ji}^*\,, \tag{17a}$$

$$\rho_{ij}=\rho_{ji}^*\,, \tag{17b}$$

$$\alpha_{ij}=\beta_{ji}^*. \tag{17c}$$

Equations (17a) and (17b) express well-known restrictions[5] on the elements of the permitivity and permeability tensors in lossless media while Eq. (17c) connects the two generalized magnetoelectric-effect tensors of Eq. (6). Replacing β_{ij} by α_{ij}^* in Eq. (6b), we see that the real part of α_{ij} is the usual magnetoelectric tensor.[4] The meaning of the imaginary part of α_{ij} will be made clear further on when the ordinary optical activity is discussed.

Let us now examine the tensor A_{ij} in more detail. Since the effect of interest, gyrotropic or nonreciprocal birefringence, will be expressed by terms in A_{ij} that are linear in $\mathbf{k}$, the term in A_{ij} with the explicit quadratic $\mathbf{k}$ dependence is not of interest. Let us put

$$\tilde{\epsilon}_{ij}=\epsilon_{ij}-\alpha_{ik}\rho_{kl}\alpha_{jl}^*. \tag{18}$$

Inspection of Eq. (6) shows that the only difference between the tensors ϵ_{ij} and $\tilde{\epsilon}_{ij}$ is that they relate $\mathbf{D}$ to $\mathbf{E}$ when $\mathbf{H}=0$ or $\mathbf{B}=0$, respectively. We expand $\tilde{\epsilon}_{ij}(\omega,\mathbf{k})$ to first order in $\mathbf{k}$ as in Eq. (2) and now wish to find that part of $\mathbf{D}'$ that is linearly proportional to $\mathbf{k}$. Writing the part of $\mathbf{D}'$ linear in $\mathbf{k}$ as $\sigma_{ijm}k_m$, we have

$$\sigma_{ijm}=\gamma_{ijm}+(c/i\omega)(\epsilon_{ikm}\alpha_{jl}^*+\epsilon_{jlm}\alpha_{ik})\rho_{kl}\,, \tag{19}$$

where the property tensors in Eq. (19) and henceforth are dependent only on ω. We now separate σ_{ijm} into its real and imaginary parts, obtaining

$$\sigma'_{ijm}=\gamma'_{ijm}-(c/\omega)[(\epsilon_{ikm}\alpha''_{jl}-\epsilon_{jlm}\alpha''_{ik})\rho'_{kl} -(\epsilon_{ikm}\alpha'_{jl}+\epsilon_{jlm}\alpha'_{ik})\rho''_{kl}]\,, \tag{20a}$$

$$\sigma''_{ijm}=\gamma''_{ijm}-(c/\omega)[(\epsilon_{ikm}\alpha'_{jl}+\epsilon_{jlm}\alpha'_{ik})\rho'_{kl} +(\epsilon_{ikm}\alpha''_{jl}-\epsilon_{jlm}\alpha''_{ik})\rho''_{kl}]\,, \tag{20b}$$

where $\sigma_{ijm}=\sigma'_{ijm}+i\sigma''_{ijm}$, etc. It is Eq. (20b) that is of principal interest. Consulting Eqs. (2) and (9), we see that the property tensor σ''_{ijm} is a polar c tensor; that is, it is transformed into its negative when acted upon by either the time reversal or space-inversion operator.

It is thus the nonreciprocal or gyrotropic birefringence tensor of the medium.[1] Using Eq. (17b), we may rewrite Eq. (20b) as

$$\sigma''_{ijm}=\gamma''_{ijm}-(c/\omega)(\epsilon_{ilm}\tilde{\alpha}'_{jl}+\epsilon_{jlm}\tilde{\alpha}'_{il})\,, \tag{21}$$

where

$$\tilde{\alpha}'_{ij}=\alpha'_{ik}\rho'_{kj}-\alpha''_{ik}\rho''_{kj}. \tag{22}$$

From Eq. (9), we see, in the notation of Birss,[2] that α'_{ik} is an axial c tensor, α''_{ik} is an axial i tensor, ρ'_{kj} is a polar i tensor and ρ''_{kj} is a polar c tensor. Thus $\tilde{\alpha}'_{ij}$ is an axial c tensor.

From Eq. (17) it follows that

$$\sigma''_{ijm}=\sigma''_{jim}. \tag{23}$$

Thus the maximum number of independent components of σ''_{ijm} is reduced from 27 to 18. The property tensor incorporating the magnetoelectric effect, $\tilde{\alpha}'_{ij}$, is not restricted by Eqs. (17c) and (22) and thus has nine independent components, which are combined in the tensor

$$\delta_{ijm}=\epsilon_{ilm}\tilde{\alpha}'_{jl}+\epsilon_{jlm}\tilde{\alpha}'_{il} \tag{24}$$

in such a way as to form only eight linearly independent quantities; that is, Eq. (24) introduces the additional restraint that

$$\epsilon_{ijm}\delta_{ijm}=0. \tag{25}$$

We must now examine the property tensor γ''_{ijk} in order to determine the number of independent components it contains. Since, in Eq. (6), we have written separately the contributions to $\mathbf{D}$ and $\mathbf{B}$ from $\mathbf{E}$ and $\mathbf{H}$, respectively, we can consider there the case $\mathbf{B}=0$, $\mathbf{E}\neq 0$. Note that once we renormalize Eq. (6) using Maxwell's equation, this is no longer possible. For the case $\mathbf{B}=0$, we find that the tensor $\tilde{\epsilon}_{ij}$ relates $\mathbf{D}$ to $\mathbf{E}$ and is thus the true permitivity tensor of the medium. Upon expanding $\tilde{\epsilon}_{ij}$ in $\mathbf{k}$, we obtain successively the dipole, quadrupole, etc., contributions to the electric polarization of the medium. We thus conclude that γ''_{ijk} is an electric quadrupole tensor and, from this and Eq. (17), it follows that it has an intrinsic symmetry

$$P\gamma''_{ijk}=\gamma''_{ijk}, \tag{26}$$

where P is any permutation of the indices i, j, k. Thus intrinsic symmetry reduces the number of independent components of γ''_{ijk} from 27 to 10.

Now, using Eqs. (21) and (26), we have

$$\begin{aligned}
&\sigma''_{111}=\gamma''_{111}, \quad \sigma''_{222}=\gamma''_{222}, \quad \sigma''_{333}=\gamma''_{333},\\
&\sigma''_{121}=\sigma''_{211}=\gamma''_{112}-\bar{\lambda}_0\tilde{\alpha}'_{13}, \quad \sigma''_{112}=\gamma''_{112}+2\bar{\lambda}_0\tilde{\alpha}'_{13},\\
&\sigma''_{131}=\sigma''_{311}=\gamma''_{113}+\bar{\lambda}_0\tilde{\alpha}'_{12}, \quad \sigma''_{113}=\gamma''_{113}-2\bar{\lambda}_0\tilde{\alpha}'_{12},\\
&\sigma''_{122}=\sigma''_{212}=\gamma''_{221}+\bar{\lambda}_0\tilde{\alpha}'_{23}, \quad \sigma''_{221}=\gamma''_{221}-2\bar{\lambda}_0\tilde{\alpha}'_{23},\\
&\sigma''_{133}=\sigma''_{313}=\gamma''_{331}-\bar{\lambda}_0\tilde{\alpha}'_{32}, \quad \sigma''_{331}=\gamma''_{331}+2\bar{\lambda}_0\tilde{\alpha}'_{32},\\
&\sigma''_{232}=\sigma''_{322}=\gamma''_{223}-\bar{\lambda}_0\tilde{\alpha}'_{21}, \quad \sigma''_{223}=\gamma''_{223}+2\bar{\lambda}_0\tilde{\alpha}'_{21},\\
&\sigma''_{233}=\sigma''_{323}=\gamma''_{332}+\bar{\lambda}_0\tilde{\alpha}'_{31}, \quad \sigma''_{332}=\gamma''_{332}-2\bar{\lambda}_0\tilde{\alpha}'_{31},\\
&\qquad \sigma''_{123}=\sigma''_{213}=\gamma''_{123}+\bar{\lambda}_0(\tilde{\alpha}'_{11}-\tilde{\alpha}'_{22}),\\
&\qquad \sigma''_{132}=\sigma''_{312}=\gamma''_{123}+\bar{\lambda}_0(\tilde{\alpha}'_{33}-\tilde{\alpha}'_{11}),\\
&\qquad \sigma''_{231}=\sigma''_{321}=\gamma''_{123}+\bar{\lambda}_0(\tilde{\alpha}'_{22}-\tilde{\alpha}'_{33}),
\end{aligned} \tag{27}$$

where $\bar{\lambda}_0=\lambda_0/2\pi=c/\omega$. Thus a physical basis for the 18 independent quantities in the general gyrotropic birefringence tensor may be found in electric quadrupole and magnetoelectric effects, with the former contributing 10 independent quantities and the latter eight. The close connection between gyrotropic birefringence and the magnetoelectric effect has been recognized by Birss and Shrubsall.[8]

It is now of some interest to consider some materials in which an experimental observation of gyrotropic birefringence may be practical. For example, let us first consider Cr_2O_3 which has the magnetic point group $\bar{3}'m'$.[1,9] The symmetry of this point group reduces the number of independent elements of σ''_{ijm} from 18 to two.[3] Additionally, we find that the only nonzero elements of the electric quadrupole tensor are $\gamma''_{111}=-\gamma''_{122}$ and its permutations, while the only nonzero elements of the magnetoelectric tensor are $\alpha'_{11}=\alpha'_{22}$ and α'_{33}. Both α''_{ij} and ρ''_{ij} are null tensors for this crystal class. We thus know from Eq. (27) that the nonzero elements of the nonreciprocal birefringence tensor are given by

$$\begin{aligned}
&\sigma''_{111}=-\sigma''_{122}=-\sigma''_{212}=-\sigma''_{221}=\gamma''_{111},\\
&\sigma''_{132}=\sigma''_{312}=-\sigma''_{231}=-\sigma''_{321}\\
&\qquad\qquad =\bar{\lambda}_0(\alpha'_{33}/\mu'_{33}-\alpha'_{11}/\mu'_{11}).
\end{aligned} \tag{28}$$

[8] R. R. Birss and R. G. Shrubsall, Phil. Mag. **15**, 687 (1967).
[9] I. Dzyaloshinski, J. Phys. Chem. Solids 4, 241 (1958).

Thus one of the two independent σ''_{ijm} elements may be ascribed entirely to electric quadrupole interactions and the second to causes related to those of the magnetoelectric effect.

A second interesting material is $MnTiO_3$, which belongs to the magnetic point group $\bar{3}'$.[1] For this case, the number of independent elements of σ''_{ijm} is reduced from 18 to six.[3] The electric quadrupole tensor will have four independent elements and the magnetoelectric tensor will have three. As in the case of $\bar{3}'m'$, both α''_{ij} and μ''_{ij} are null tensors for the $\bar{3}'$ crystal class. The nonzero nonreciprocal birefringence components are now given by

$$\begin{aligned}
&\sigma''_{111}=-\sigma''_{122}=-\sigma''_{212}=-\sigma''_{221}=\gamma''_{111},\\
&\sigma''_{222}=-\sigma''_{121}=-\sigma''_{211}=-\sigma''_{112}=\gamma''_{222},\\
&\sigma''_{333}=\gamma''_{333},\\
&\sigma''_{132}=\sigma''_{312}=-\sigma''_{231}=-\sigma''_{321}\\
&\qquad\qquad =\bar{\lambda}_0(\alpha'_{33}/\mu'_{33}-\alpha'_{11}/\mu'_{11}),\\
&\sigma''_{131}=\sigma''_{311}=\sigma''_{232}=\sigma''_{322}=\gamma''_{113}-\bar{\lambda}_0\alpha'_{12}/\mu'_{11},\\
&\sigma''_{113}=\sigma''_{223}=\gamma''_{113}+2\bar{\lambda}_0\alpha'_{12}/\mu'_{11}.
\end{aligned} \tag{29}$$

Of the six independent nonreciprocal birefringence tensor components, three may be ascribed entirely to electric quadrupole interactions, one entirely to the magnetoelectric effect, and two to linear combinations of electric quadrupole and magnetoelectric effects.

Although we have concentrated our attention on gyrotropic birefringence in this section, it is useful to note that the closely related natural optical activity[6] may also be found by the procedure presented here. That this is so can be seen by considering Eq. (20a). It follows from Eqs. (2) and (9) that the σ'_{ijm} tensor given by Eq. (20a) is a polar i tensor and is thus the optical-activity tensor.[1] We use Eq. (17) to rewrite (20a) as

$$\sigma'_{ijm}=\gamma'_{ijm}-(c/\omega)(\epsilon_{ilm}\tilde{\alpha}''_{jl}-\epsilon_{jlm}\tilde{\alpha}''_{il}), \tag{30}$$

where

$$\tilde{\alpha}''_{ij}=\alpha''_{ik}\rho'_{kj}+\alpha'_{ik}\rho''_{kj}. \tag{31}$$

From Eq. (9) and the discussion following Eq. (22), it follows that $\tilde{\alpha}''_{ij}$ is an axial i tensor.

From Eq. (17), it follows that

$$\sigma'_{ijm}=-\sigma'_{jim}. \tag{32}$$

Thus the maximum number of independent components of σ'_{ijm} is reduced from 27 to nine. This is a well-known result.[5] The tensor $\tilde{\alpha}''_{ij}$ is not restricted by Eqs. (17c) and (31) and thus has nine independent components. On the other hand, the electric quadrupole tensor γ'_{ijk} is required to be antisymmetric under permutation of the indices i and j and symmetric under permutation of the indices j and k. It is therefore a null tensor and does not contribute to the optical activity tensor.[6] We thus find that the entire optical activity tensor comes from $\tilde{\alpha}''_{ij}$.

Let us compare this result with the usual one derived for the case of nonmagnetic materials having natural optical activity. The optical activity as usually written is[5]

$$\sigma'_{ijm} = (c/\omega)\epsilon_{ijl}g_{lm}. \tag{33}$$

We thus have

$$\epsilon_{ijl}g_{lm} = -(\epsilon_{ilm}\tilde{\alpha}''_{jl} - \epsilon_{jlm}\tilde{\alpha}''_{il}), \tag{34}$$

which yields

$$\tilde{\alpha}''_{ij} = g_{ij}, \quad i \neq j \tag{35a}$$

$$\tilde{\alpha}''_{ii} = g_{ii} - \tfrac{1}{2}\,\mathrm{Tr}\mathbf{g}, \tag{35b}$$

where by $\mathrm{Tr}\mathbf{g}$ we mean the sum of its main diagonal elements.

Let us now briefly return to the question of the difference between $\bar{\epsilon}_{ij}$ of Eq. (1) and ϵ_{ij} of Eq. (6). It is clear that $\bar{\epsilon}_{ij}$ cannot be the true permitivity tensor since, if it were, its quadrupole component would necessarily be zero and natural optical activity could not exist. In fact, $\bar{\epsilon}_{ij}$ is a renormalized tensor and thus incorporates within itself the $\tilde{\alpha}''_{ij}$ or g_{ij} tensor as well as the true permitivity. The essential point is that Maxwell's equations, (10a) and (10b), linearly relate the various electric and magnetic fields. Thus, in the constitutive relations of Eq. (6), it is always possible to replace any field vector by a linear combination of field vectors. This reshuffling of a set of linear equations will not, of course, change any physical results. However, once we rewrite our constitutive relations so as to relate new linear combinations of fields to each other, it is no longer possible to consider the property tensors appearing in these *renormalized* equations as purely electric or magnetic in origin.[6]

III. WAVE PROPAGATION

In this section we shall briefly consider the propagation of a plane wave in a medium exhibiting gyroscopic birefringence. In order not to lose sight of the physical results in a morass of algebra, we shall consider only the case of Cr_2O_3. Thus the tensors $\boldsymbol{\epsilon}$, $\boldsymbol{\mu}$, and $\boldsymbol{\alpha}$ are all real and diagonal, with their xx and yy components equal.

We restrict our attention to waves travelling in the x direction. In this case, Eq. (15) becomes

$$D_x' = (\tilde{\epsilon}'_{xx} - \gamma''_{xxx}k_x)E_x, \tag{36a}$$

$$D_y' = [\tilde{\epsilon}'_{xx} - \gamma''_{yyx}k_x + (c/\omega)^2k_x^2(1-\rho'_{zz})]E_y + (c/\omega)k_x(\tilde{\alpha}'_{zz} - \tilde{\alpha}'_{xx})E_z, \tag{36b}$$

$$D_z' = (c/\omega)k_x(\tilde{\alpha}'_{zz} - \tilde{\alpha}'_{xx})E_y + [\tilde{\epsilon}'_{zz} + (c/\omega)^2k_x^2(1-\rho'_{xx})]E_z. \tag{36c}$$

Combining Eqs. (13) and (14b) gives

$$D_x' = 0, \tag{37a}$$

$$D_y' = (c/\omega)^2k_x^2E_y, \tag{37b}$$

$$D_z' = (c/\omega)^2k_x^2E_z. \tag{37c}$$

In the case of Cr_2O_3, $\gamma''_{xxx} = -\gamma''_{yyx} = (c/\omega)\rho_{zz}\gamma$. Combining Eqs. (36) and (37), we find that

$$(\tilde{\epsilon}_{xx} - \rho_{zz}\gamma/v)E_x = 0, \tag{38a}$$

$$[\tilde{\epsilon}_{xx} + \rho_{zz}\gamma/v - \rho_{zz}/v^2]E_y + [(\tilde{\alpha}_{zz} - \tilde{\alpha}_{xx})/v]E_z = 0, \tag{38b}$$

$$[(\tilde{\alpha}_{zz} - \tilde{\alpha}_{xx})/v]E_y + [\tilde{\epsilon}_{zz} - \rho_{xx}/v^2]E_z = 0, \tag{38c}$$

where $v = \omega/ck_x$.

One nontrivial solution of Eq. (38) is, of course, $\rho_{zz}\gamma/v = \tilde{\epsilon}_{xx}$, with $E_y = E_z = 0$. This solution is, however, of no physical interest because our initial assumption in expanding $\boldsymbol{\epsilon}$ in a power series in $\mathbf{k}$ was that $\rho_{zz}\gamma/v \ll \tilde{\epsilon}_{xx}$ in the frequency ranges of interest. We therefore take $E_x = 0$ and restrict our attention to transverse waves. In order to obtain nontrivial solutions of Eq. (38), it is necessary that v satisfy

$$n_x^2n_z^2v^4 + n_z^2\gamma v^3 - [n_x^2 + n_z^2 + \mu_x\mu_z\Delta\alpha^2]v^2 - \gamma v + 1 = 0. \tag{39}$$

Here $n_x^2 = \tilde{\epsilon}_{xx}\mu_{zz}$, $n_z^2 = \tilde{\epsilon}_{zz}\mu_{xx}$, $\Delta\alpha = \tilde{\alpha}_{zz} - \tilde{\alpha}_{xx}$, and the redundent index on μ_{xx} and μ_{zz} has been dropped. To first order in γ and $\Delta\alpha^2$, the solutions of Eq. (39) are

$$v_{1,3} = \pm[1 + \tfrac{1}{2}\mu_x\mu_z\Delta\alpha^2/(n_z^2 - n_x^2) \mp \tfrac{1}{2}\gamma/n_x]/n_x, \tag{40}$$

$$v_{2,4} = \pm[1 + \tfrac{1}{2}\mu_x\mu_z\Delta\alpha^2/(n_z^2 - n_x^2)]/n_z. \tag{41}$$

One interesting point follows immediately from Eq. (40); the magnitude of the velocity of propagation in a gyrotropically birefringence medium changes when the direction of propagation is reversed. This result may be compared to that of Fuchs[10] in his study of wave propagation in a magnetoelectric medium.

We now restrict our attention to waves traveling in the $+x$ direction and resolve the electric fields E_y and E_z into components traveling at v_1 and v_2. Equations (38), (40), and (41) then require that

$$E_z^1/E_y^1 = -\Delta\alpha[\mu_x n_x/(n_z^2 - n_x^2)], \tag{42a}$$

$$E_y^2/E_z^2 = \Delta\alpha[\mu_z n_z/(n_z^2 - n_x^2)], \tag{42b}$$

From Eq. (42), we see as expected that the gyrotropic birefringence leads to a tilting of the principal optic axes in the yz plane. Note that when the wave is propagating in the x direction, the shift of the principal optic axes is due entirely to $\Delta\alpha$. This can be seen clearly if we set $\Delta\alpha = 0$ in Eq. (38). We then find that while the wave velocity v_1 is affected by γ, $E_z^1 = E_y^2 = 0$. Thus no shift of the principal optic axes occurs in this case. In order for γ to also lead to a shift in the principal optic axes, the direction of wave propagation must have a component in the xy plane that is not along the x or y axes.

IV. BOUNDARY CONDITIONS

In this section we shall consider the conditions imposed on the electromagnetic field at the boundary of a

[10] R. Fuchs, Phil. Mag. **11**, 647 (1965).

gyrotropically birefringence medium. We first discuss the changes in the usual boundary conditions caused by the field renormalization of Sec. II and then go on to consider the case of an incident plane wave.

Let us consider the conditions on the renormalized field $\mathbf{H}'$ at a boundary. In the case of a boundary between two media denoted by (1) and (2), the usual boundary condition is

$$c\mathbf{n}\times(\mathbf{H}_2-\mathbf{H}_1)=4\pi\boldsymbol{\kappa}\,, \tag{43}$$

where $\mathbf{n}$ is the positive normal to the boundary surface S, drawn from (1) into (2), and $\boldsymbol{\kappa}$ is the surface current density. Using Eqs. (11b) and (14b), Eq. (43) becomes

$$c\mathbf{n}\times(\mathbf{H}_2'-\mathbf{H}_1')=4\pi[\boldsymbol{\kappa}+c\mathbf{n}\times(\mathbf{M}_2-\mathbf{M}_1)]\,, \tag{44}$$

which is the required relation.

We now consider the condition on the renormalized field $\mathbf{D}'$ at a boundary. In this case the usual boundary condition is

$$\mathbf{n}\cdot(\mathbf{D}_2-\mathbf{D}_1)=\sigma\,, \tag{45}$$

where σ is the surface charge density. From Eqs. (11a), (12), and (14a),

$$\partial\mathbf{D}'/\partial t=\partial\mathbf{D}/\partial t+4\pi c\nabla\times\mathbf{M}\,. \tag{46}$$

Upon integration, Eq. (46) becomes

$$\mathbf{D}'=\mathbf{D}+4\pi c\int_{-\infty}^{t}(\nabla\times\mathbf{M})dt\,. \tag{47}$$

Combining Eqs. (45) and (47) gives

$$\mathbf{n}\cdot(\mathbf{D}_2'-\mathbf{D}_1')=\sigma+4\pi c\int_{-\infty}^{t}[\mathbf{n}\cdot\nabla\times(\mathbf{M}_2-\mathbf{M}_1)]dt\,. \tag{48}$$

Equations (44) and (48) express the boundary conditions on the renormalized field vectors $\mathbf{H}'$ and $\mathbf{D}'$. We see that, in the renormalized representation, there appears a surface current

$$\boldsymbol{\kappa}'=c\mathbf{n}\times(\mathbf{M}_2-\mathbf{M}_1)\,, \tag{49a}$$

and a surface charge

$$\sigma'=4\pi c\int_{-\infty}^{t}[\mathbf{n}\cdot\nabla\times(\mathbf{M}_2-\mathbf{M}_1)]dt\,. \tag{49b}$$

Note that $\boldsymbol{\kappa}'$ and σ' satisfy the continuity equation

$$4\pi\nabla\cdot\boldsymbol{\kappa}'+\partial\sigma'/\partial t=0; \tag{50}$$

thus charge conservation is maintained in the renormalized system.

Let us now consider specifically the boundary between a magnetoelectric medium and a lossless isotropic dielectric. We restrict ourselves to the case of plane waves, in which case the time dependence of the field vectors is given by $e^{-i\omega t}$. In order to include the boundary condition at $t=-\infty$ required by Eqs. (48) or (49b), we generalize this time dependence slightly to $e^{-(\delta+i\omega)t}$, with the understanding that in the limit $\delta\to-0$.

In the case of insulating materials, we set $\boldsymbol{\kappa}=\sigma=0$ and take medium 2 as the magnetoelectric one, dropping the 2 index. In the lossless dielectric, $\mathbf{D}_1'=\mathbf{D}_1$ and $\mathbf{H}_1'=\mathbf{H}_1$.

With the above discussion in mind, Eqs. (44) and (48) become

$$\mathbf{n}\times(\mathbf{H}'-\mathbf{H}_1)=4\pi\mathbf{n}\times\mathbf{M}\,, \tag{51a}$$

$$\mathbf{n}\cdot(\mathbf{D}'-\mathbf{D}_1)=\left[\frac{-4\pi c}{\delta+i\omega}\right]\mathbf{n}\cdot\nabla\times\mathbf{M}\,. \tag{51b}$$

These then are the conditions on the renormalized fields at the boundary between a gyrotropically birefringent medium and a lossless dielectric.

Let us now consider the effects occurring when a normally incident wave impinges on a gyrotropically birefringent medium. As in Sec. III, we restrict our attention to Cr_2O_3 and waves traveling in the x direction. We take the external dielectric to be the vacuum and denote the incident wave by ρ and the reflected wave by r. We then have, in the vacuum,

$$H_z^\rho=E_y^\rho\,,\qquad H_y^\rho=-E_z^\rho\,, \tag{52a}$$

$$H_z^r=-E_y^r\,,\quad H_y^r=E_z^r\,. \tag{52b}$$

We have already solved, in Sec. III, the wave propagation problem in Cr_2O_3. From Eqs. (13a) and (14b) we see that

$$E_z=-vH'_y\,,\quad E_y=vH'_z\,. \tag{53}$$

Using Eqs. (40)–(42) and (53), we find, to first order in $\Delta\alpha$, that

$$H'_y=-\Delta\alpha[\mu_xn_x/(n_z+n_x)]E_y-n_zE_z\,, \tag{54a}$$

$$H'_z=n_xE_y+\Delta\alpha[\mu_zn_z/(n_z+n_x)]E_z\,. \tag{54b}$$

Writing the magnetization $\mathbf{M}$ in Eq. (51a) in terms of $\mathbf{E}$ and $\mathbf{H}'$ and using Eq. (54), the pertinent boundary conditions become

$$E_y^\rho+E_y^r=\rho_zn_xE_y-\sigma E_z\,, \tag{55a}$$

$$E_z^\rho+E_z^r=\sigma E_y+\rho_xn_zE_z\,, \tag{55b}$$

$$E_y^\rho-E_y^r=E_y\,, \tag{55c}$$

$$E_z^\rho-E_z^r=E_z\,, \tag{55d}$$

with

$$\sigma=(\tilde{\alpha}_xn_z+\tilde{\alpha}_zn_x)/(n_z+n_x)\,. \tag{56}$$

One interesting solution of Eq. (55) is for the case $E_z^\rho=0$. We then find that E_z^r is given, to first order in $\tilde{\alpha}$, by

$$E_z^r=2\sigma/(1+\rho_xn_z)(1+\rho_zn_x)\,. \tag{57}$$

Thus even when $\tilde{\alpha}_x=\tilde{\alpha}_z$ and there is no gyrotropic birefringence, the isotropic magnetoelectric effect will show itself through E_z^r, the reflected component of the electric field.

V. QUANTUM-MECHANICAL TREATMENT AT 0°K

In this section we formally calculate the elements of the gryotropic birefringence tensor at 0°K. In general, we shall follow the procedure of Agranovich and Ginzburg[11] in their calculation of spatial dispersion. An alternate approach is that of Condon.[6]

Consider a perfect crystal acted upon by a monochromatic plane wave of frequency ω and wave vector $\mathbf{k}$. The electric field vector is taken as

$$\mathbf{e}=\tfrac{1}{2}[\mathbf{E}_0e^{i\mathbf{k}\cdot\mathbf{r}}e^{-i\omega t}+\mathbf{E}_0{}^*e^{-i\mathbf{k}\cdot\mathbf{r}}e^{i\omega t}], \tag{58}$$

and may be derived from the vector potential

$$\mathbf{A}=-(c/\omega)\ \mathrm{Re}[i\mathbf{E}_0e^{i\mathbf{k}\cdot\mathbf{r}}e^{-i\omega t}] \tag{59}$$

according to the relation

$$\mathbf{e}=-(1/c)\partial\mathbf{A}/\partial t. \tag{60}$$

The magnetic field associated with the plane wave is then given by

$$\mathbf{h}=\mathrm{curl}\mathbf{A}. \tag{61}$$

We take the field strengths to be such that only terms linear in $\mathbf{A}$ need be included in our Hamiltonian. Then in the presence of the plane wave we have

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1(t), \tag{62}$$

where $\mathcal{H}_0$ is the Hamiltonian of the unperturbed system and $\mathcal{H}_1(t)$ is given by

$$\mathcal{H}_1(t)=\sum_\gamma\left[-\frac{e}{2mc}[A_{\gamma i}\pi_{\gamma i}+\pi_{\gamma i}A_{\gamma i}]-\frac{ie}{mc}\epsilon_{ijk}A_{\gamma i}S_{\gamma i}k_k-(e/c)\xi_\gamma(r_\gamma)\epsilon_{ijk}A_{\gamma i}S_{\gamma j}r_{\gamma k}\right]. \tag{63}$$

The quantities in Eq. (63) are as follows; e and m are the electron charge and mass, respectively; $r_{\gamma i}$, $\pi_{\gamma i}$, and $S_{\gamma i}$ are, respectively, the ith Cartesian components of the position, mechanical momentum, and spin operators of the γth electron; $\xi_\gamma(r_\gamma)$ expresses the radial dependence of the spin-orbit term of the γth electron, ϵ_{ijk} is the antisymmetric unit tensor, and summation over repeated indices is understood. The γ summation indicates that the contributions of all electrons in the crystal must be included.

It is straightforward to show that the spin-orbit term in Eq. (63) contributes only to the magnetoelectric-type terms in Eq. (19) and not to the electric quadrupole effect. Since it has been shown[12] that this contribution is negligible, we shall not consider it further here. We shall also, at this point, discard the Zeeman term in Eq. (63). The effect of this term will be reintroduced in Eq. (85) by the simple expedient of replacing the orbital angular momentum operator $\mathbf{l}$ by $\mathbf{l}+2\mathbf{s}$.

We will thus work with the perturbation

$$\mathcal{H}_1(t)=-\frac{e}{2mc}\sum_\gamma(A_{\gamma i}\pi_{\gamma i}+\pi_{\gamma i}A_{\gamma i}). \tag{64}$$

Let us write the complete set of eigenstates of the unperturbed Hamiltonian as $|\mathbf{q},n\rangle$. Since our system has translational symmetry, these eigenstates will be many-electron Bloch functions. The quantity $\mathbf{q}$ is the wave vector associated with the Bloch function, and n represents the other quantum numbers entering into the specification of the state, including that specifying the band to which the state belongs. The ground state of the system, i.e., the state occupied by the system at absolute zero, will be written $|0\rangle$ and will have $\mathbf{q}=0$.

Using time-dependent perturbation theory to second order, the expectation value of any operator $F(\mathbf{r})$ is found to be[13]

$$\langle F\rangle=\langle 0|F|0\rangle-\mathrm{Re}\left\{\sum_{\mathbf{q},n\neq 0}\langle 0|F|\mathbf{q},n\rangle\langle n,\mathbf{q}|\mathcal{H}_1{}^-|0\rangle\frac{e^{-i\omega t}}{\hbar(\omega_{n,\mathbf{q}}-\omega)}+\sum_{\mathbf{q},n\neq 0}\langle 0|F|\mathbf{q},n\rangle\langle n,\mathbf{q}|\mathcal{H}_1{}^+|0\rangle\frac{e^{i\omega t}}{\hbar(\omega_{n,\mathbf{q}}+\omega)}\right\}, \tag{65}$$

where we write

$$\mathcal{H}_1(t)=\tfrac{1}{2}[\mathcal{H}_1{}^-e^{-i\omega t}+\mathcal{H}_1{}^+e^{i\omega t}]. \tag{66}$$

In Eq. (65), $\hbar\omega_{n,\mathbf{q}}$ is the energy of the state $|\mathbf{q},n\rangle$ and we have fixed the zero of energy by taking $\langle 0|\mathcal{H}_0|0\rangle=0$.

Consider now the matrix element $\langle n,\mathbf{q}|\mathcal{H}_1{}^-|0\rangle$; we wish to know for which values of $\mathbf{q}$ this matrix element will be nonzero. These values may be found as follows: Let T_η be the operator that translates the lattice a distance $\boldsymbol{\eta}$ and let $\boldsymbol{\eta}$ be such a translation that $[T_\eta,\mathcal{H}_0]=0$. Then

$$T_\eta|n,\mathbf{q}\rangle=e^{i\eta\cdot\mathbf{q}}|n,\mathbf{q}\rangle. \tag{67}$$

We also have, from the form of $\mathcal{H}_1{}^-$,

$$T_\eta\mathcal{H}_1{}^-(T_\eta)^{-1}=e^{i\eta\cdot\mathbf{k}}\mathcal{H}_1{}^-. \tag{68}$$

It then follows that $\langle n,\mathbf{q}|\mathcal{H}_1{}^-|0\rangle\neq 0$ if and only if

$$\boldsymbol{\eta}\cdot[\mathbf{k}-\mathbf{q}]=2\pi l, \tag{69}$$

where l is an integer. This requires that

$$\mathbf{k}-\mathbf{q}=2\pi\mathbf{b}, \tag{70}$$

where $\mathbf{b}$ is any whole-number multiple of a reciprocal lattice vector. As was pointed out in Sec. II, it is generally possible to neglect those terms arising from nonzero values of $\mathbf{b}$. Thus, in conclusion, of the matrix elements $\langle n,\mathbf{q}|\mathcal{H}_1{}^-|0\rangle$, only the elements $\langle n,\mathbf{k}|\mathcal{H}_1{}^-|0\rangle$

[11] V. M. Agranovich and V. L. Ginzburg, Usp. Fiz. Nauk **77**, 663 (1962) [English transl.: Soviet Phys.—Uspekhi **5**, 675 (1963)].

[12] W. F. Brown, Jr., R. Hornreich and S. Shtrikman, Phys. Rev. **168**, 574 (1968).

[13] A. Messiah, *Quantum Mechanics* (North-Holland Publishing Co., Amsterdam, 1962).

need be considered. Similarly, it may be shown that, of the matrix elements $\langle n,\mathbf{q}|\mathcal{H}_1^+|0\rangle$, only the elements $\langle n,-\mathbf{k}|\mathcal{H}_1^+|0\rangle$ need be considered.

We now take as F the current operator $\mathbf{J}(\mathbf{r})$. To the same approximation as in Eq. (64), this operator may be written as[13]

$$\mathbf{J}(\mathbf{r})=\sum_\gamma \frac{e}{2m}[\boldsymbol{\pi}_\gamma\delta(\mathbf{r}-\mathbf{r}_\gamma)+\delta(\mathbf{r}-\mathbf{r}_\gamma)\boldsymbol{\pi}_\gamma], \tag{71}$$

where $\delta(\mathbf{u})$ is the Dirac delta function.

However, it will be more convenient to calculate $\langle\mathbf{J}(\boldsymbol{\kappa},\omega)\rangle$ than $\langle\mathbf{J}(\mathbf{r},\omega)\rangle$. We therefore Fourier transform Eq. (71), using

$$\delta(\mathbf{r}-\mathbf{r}_\gamma)=\frac{1}{(2\pi)^3}\int e^{i\boldsymbol{\kappa}\cdot(\mathbf{r}-\mathbf{r}_\gamma)}d\boldsymbol{\kappa}, \tag{72}$$

to obtain

$$\mathbf{J}(\boldsymbol{\kappa})=\sum_\gamma \frac{e}{2m}[\boldsymbol{\pi}_\gamma e^{i\boldsymbol{\kappa}\cdot\mathbf{r}_\gamma}+e^{i\boldsymbol{\kappa}\cdot\mathbf{r}_\gamma}\boldsymbol{\pi}_\gamma]. \tag{73}$$

Now, using Eqs. (65) and (73) and the relation

$$\langle J_i(\mathbf{k},\omega)\rangle-\langle J_i\rangle_0=\sigma_{ij}(E_0)_j, \tag{74}$$

where $\langle J_i\rangle_0$ is the current present in the absence of the plane wave (due to permanent electric and/or magnetic moments), we obtain for the complex conductivity tensor

$$\begin{aligned}\sigma_{ij}(\mathbf{k},\omega)=(ie^2N/m\omega)\delta_{ij}+\frac{ie^2}{4m^2\hbar\omega}\sum_{\gamma,\delta,n\neq0}\Bigg\{&\left(\frac{1}{\omega-\omega_{n,\mathbf{k}}}\right)\\ &\times\langle0|\pi_{\gamma i}e^{-i\mathbf{k}\cdot\mathbf{r}_\gamma}+e^{-i\mathbf{k}\cdot\mathbf{r}_\gamma}\pi_{\gamma i}|\mathbf{k},n\rangle\\ &\times\langle n,\mathbf{k}|\pi_{\delta j}e^{i\mathbf{k}\cdot\mathbf{r}_\delta}+e^{i\mathbf{k}\cdot\mathbf{r}_\delta}\pi_{\delta j}|0\rangle\\ &-\left(\frac{1}{\omega+\omega_{n,-\mathbf{k}}}\right)\langle n,-\mathbf{k}|\pi_{\gamma i}e^{-i\mathbf{k}\cdot\mathbf{r}_\gamma}+e^{-i\mathbf{k}\cdot\mathbf{r}_\gamma}\pi_{\gamma i}|0\rangle\\ &\times\langle0|\pi_{\delta j}e^{i\mathbf{k}\cdot\mathbf{r}_\delta}+e^{i\mathbf{k}\cdot\mathbf{r}_\delta}\pi_{\delta j}|-\mathbf{k},n\rangle\Bigg\},\end{aligned} \tag{75}$$

where N is the total number of electrons in the system and δ_{ij} is the Kroneker delta. The complex dielectric constant $\epsilon_{ij}(\mathbf{k},\omega)$ may be obtained directly from Eq. (75) by means of the relation

$$\epsilon_{ij}(\mathbf{k},\omega)=\delta_{ij}+(4\pi i/\omega)\sigma_{ij}(\mathbf{k},\omega). \tag{76}$$

Since the matrix elements at equivalent lattice sites are equal, we need evaluate the matrix elements in Eq. (75) only at sites comprising one unit cell. For sites within this unit cell, we have $\mathbf{k}\cdot\mathbf{r}\ll1$ for $\mathbf{k}$ values of interest. We shall choose the unit cell containing the c.m. of our system; thus we also have $\mathbf{k}\cdot\mathbf{R}\ll1$, where $\mathbf{R}=N^{-1}\times\sum_\gamma\mathbf{r}_\gamma$. We now expand the operators and wave functions in Eq. (75) in $\mathbf{k}$, keeping only terms to first order in $\mathbf{k}$. To the same order of approximation we may replace $\omega_{n,\mathbf{k}}$ by $\omega_{n,0}=\omega_n$. We now expand as follows[14]:

$$e^{\pm i\mathbf{k}\cdot\mathbf{r}_\gamma}\simeq1\pm i\mathbf{k}\cdot\mathbf{r}_\gamma, \tag{77}$$

$$\begin{aligned}|\mathbf{k},n\rangle&\simeq e^{i\mathbf{k}\cdot\mathbf{R}}\left[|0,n\rangle+\frac{1}{mN}\sum_{n'\neq n}\frac{\langle n',0|\mathbf{k}\cdot\mathbf{\Pi}|0,n\rangle}{\omega_n-\omega_{n'}}|0,n'\rangle\right]\\ &\simeq(1+i\mathbf{k}\cdot\mathbf{R})|n\rangle+\frac{1}{mN}\sum_{n'\neq n}\frac{\langle n'|\mathbf{k}\cdot\mathbf{\Pi}|0\rangle}{\omega_n-\omega_{n'}}|n'\rangle,\end{aligned} \tag{78}$$

where $\mathbf{\Pi}=\sum_\gamma\boldsymbol{\pi}_\gamma$ and $|n\rangle=|0,n\rangle$. Considering one of the matrix elements in Eq. (75) as an example, and using Eqs. (77) and (78) gives

$$\begin{aligned}\langle0|\pi_{\gamma i}e^{-i\mathbf{k}\cdot\mathbf{r}_\gamma}+e^{-i\mathbf{k}\cdot\mathbf{r}_\gamma}\pi_{\gamma i}|\mathbf{k},n\rangle&\simeq2\langle0|\pi_{\gamma i}|n\rangle\\ &+\frac{2}{mN}\sum_{n'\neq n}\frac{k_j\langle n'|\Pi_j|n\rangle\langle0|\pi_{\gamma i}|n'\rangle}{\omega_{n'}-\omega_n}\\ &+2ik_j\langle0|\pi_{\gamma i}R_j|n\rangle-i\mathbf{k}\cdot\langle0|\pi_{\gamma i}\mathbf{r}_\gamma+\mathbf{r}_\gamma\pi_{\gamma i}|n\rangle.\end{aligned} \tag{79}$$

To simplify Eq. (79), we make use of the commutation relations between the operators appearing therein. As before, the spin-orbit interaction terms may be neglected. The following relations then hold:

$$\langle0|\pi_{\gamma i}|n\rangle=-im\omega_n\langle0|r_{\gamma i}|n\rangle, \tag{80a}$$

$$\langle0|\Pi_i|n\rangle=-imN\omega_n\langle0|R_i|n\rangle, \tag{80b}$$

and

$$\langle0|\pi_{\gamma i}r_{\gamma j}+r_{\gamma j}\pi_{\gamma i}|n\rangle=-im\omega_n\langle0|r_{\gamma i}r_{\gamma j}|n\rangle-\hbar\epsilon_{ijk}\langle0|l_{\gamma k}|n\rangle. \tag{81}$$

Using Eqs. (80) and (81) in Eq. (79) gives

$$\begin{aligned}\langle0|\pi_{\gamma i}e^{-i\mathbf{k}\cdot\mathbf{r}_\gamma}+e^{-i\mathbf{k}\cdot\mathbf{r}_\gamma}\pi_{\gamma i}|n\rangle=&-2im\omega_n\langle0|r_{\gamma i}|n\rangle\\ &-m\omega_nk_j\langle0|r_{\gamma i}r_{\gamma j}|n\rangle+i\hbar k_j\epsilon_{ijk}\langle0|l_{\gamma k}|n\rangle\\ &+2ik_j\langle0|\pi_{\gamma i}|n\rangle\langle n|R_j|n\rangle.\end{aligned} \tag{82}$$

We shall be particularly interested in the case of Cr_2O_3, where the symmetry element IT, where I is the space-inversion and T the time-reversal operator, will belong to the group of point operations that leave the system macroscopically invariant. For this case $\langle n|R_j|n\rangle=0$.

We now write out the expression for the part of $\epsilon_{ij}(\mathbf{k},\omega)$ that is linear in $\mathbf{k}$, i.e., the part proportional to $i\mathbf{k}$. Using Eqs. (75), (76), and (82), we obtain

$$\begin{aligned}\sigma_{ijl}=\left(\frac{2\pi ie^2N_1^2}{m\hbar\omega^2}\right)\sum_{\gamma,\delta,n\neq0}\Bigg\{&\frac{\omega_n}{\omega-\omega_n}[\langle0|r_{\gamma i}|n\rangle(im\omega_n\langle n|r_{\delta j}r_{\delta l}|0\rangle-\hbar\epsilon_{jlk}\langle n|l_{\delta k}|0\rangle)-(im\omega_n\langle0|r_{\gamma i}r_{\gamma l}|n\rangle+\hbar\epsilon_{ilk}\langle0|l_{\gamma k}|n\rangle)\\ &\times\langle n|r_{\delta j}|0\rangle]-[\omega_n/(\omega+\omega_n)][\langle n|r_{\gamma i}|0\rangle(\langle0|r_{\delta j}r_{\delta l}|n\rangle+\hbar\epsilon_{jlk}\langle0|l_{\delta\kappa}|n\rangle)\\ &-(im\omega_n\langle n|r_{\gamma i}r_{\gamma l}|0\rangle-\hbar\epsilon_{ilk}\langle n|l_{\gamma k}|0\rangle)\langle0|r_{\delta j}|n\rangle]\Bigg\}.\end{aligned} \tag{83}$$

[14] V. I. Cherepanov and V. S. Galishev, Fiz. Tverd. Tela 3, 1085 (1961) [English transl.: Soviet Phys.—Solid State 3, 790 (1961)].

Here N_1 is the number of unit cells in the crystal and the γ,δ sums in Eq. (83) are over the electrons in one unit cell. In fact, we may restrict these sums further to include only those electrons outside closed shells, i.e., only the magnetic electrons on the cations.

We now wish to transform the Bloch function $|n\rangle$ to linear sums of localized (Wannier) functions. These functions, for the case of electrical insulators, may be identified with a particular lattice site. We then have

$$|n\rangle=(N_0)^{-1/2}\sum_{\sigma}|n_\sigma\rangle\,, \tag{84}$$

where N_0 is the number of cation sites and the σ sum is over all such sites. The function $|n_\sigma\rangle$ is the true antisymmetric Wannier function at lattice site σ. Note that all lattice sites in a given unit cell are nonequivalent insofar as we consider only the translational symmetry of the lattice. Thus electrons excited at different sites within the unit cell belong to different bands. Of course, it may be that some of these bands will turn out to be degenerate once the rotational symmetry of the lattice is considered.

To the extent that we neglect contributions arising from cation-cation coupling (i.e., exchange), we may take the state $|n_\sigma\rangle$ as an antisymmetrized sum of products of single-electron functions wherein only eigenfunctions of electrons belonging to a particular cation site and its neighboring anions are included.

Since it appears[15] that there are no exchange contributions to at least the magnetoelectric effect in Cr_2O_3 at 0°K, this approximation does not seem unreasonable.

With the above in mind, it is clear that the matrix elements $\langle 0_{\sigma'}|r_{\gamma i}|n_\sigma\rangle$, $\langle 0_{\sigma'}|l_{\gamma i}|n_\sigma\rangle$ or $\langle 0_{\sigma'}|r_{\gamma i}r_{\gamma j}|n_\sigma\rangle$ will be zero unless $\sigma=\sigma'$ and the γ electron is at the σ site. Now, using Eq. (84), Eq. (83) becomes

$$\begin{aligned}\sigma_{ijl}=\left(\frac{2\pi ie^2N_1^2}{m\hbar\omega^2N_0}\right)\sum_{\sigma,n\neq 0}\Bigg\{&\frac{\omega_n}{\omega-\omega_n}\Big[\langle 0_\sigma|R_{\sigma i}|n_\sigma\rangle(im\omega_n\langle n_\sigma|R_{\sigma j}R_{\sigma l}|0_\sigma\rangle-\hbar\epsilon_{jlk}\langle n_\sigma|L_{\sigma k}+2S_{\sigma k}|0_\sigma\rangle)\\&-(im\omega_n\langle 0_\sigma|R_{\sigma i}R_{\sigma l}|n_\sigma\rangle+\hbar\epsilon_{ilk}\langle 0_\sigma|L_{\sigma k}+2S_{\sigma k}|n_\sigma\rangle)\langle n_\sigma|R_{\sigma j}|0_\sigma\rangle\Big]-\big[\omega_n/(\omega+\omega_n)\big]\\&\times\Big[\langle n_\sigma|R_{\sigma i}|0_\sigma\rangle(im\omega_n\langle 0_\sigma|R_{\sigma j}R_{\sigma l}|n_\sigma\rangle+\hbar\epsilon_{jlk}\langle 0_\sigma|L_{\sigma k}+2S_{\sigma k}|n_\sigma\rangle)\\&-(im\omega_n\langle n_\sigma|R_{\sigma i}R_{\sigma l}|0_\sigma\rangle-\hbar\epsilon_{ilk}\langle n_\sigma|L_{\sigma k}+2S_{\sigma k}|0_\sigma\rangle)\langle 0_\sigma|R_{\sigma j}|n_\sigma\rangle\Big]\Bigg\}\,.\end{aligned} \tag{85}$$

Here the σ sum is over the cation sites within the one unit cell, and $R_{\sigma l}$, $L_{\sigma i}$, $S_{\sigma i}$, etc., are the sum of the single-electron operators at site σ. As discussed earlier, we have replaced **l** by **l**+2**s** in going from Eq. (83) to Eq. (85). The general expression for σ_{ijl} given by Eq. (85) may be compared with Eq. (19), in Sec. II, where the phenomenological treatment was given. Using Eqs. (21), (23), and (30), we find that the three tensors γ''_{ijl}, $\tilde{\alpha}'_{ij}$, and $\tilde{\alpha}''_{ij}$ are given by

$$\begin{aligned}\gamma''_{ijl}=\frac{4\pi e^2N_1^2}{\hbar\omega N_0}\sum_{\sigma,n\neq 0}\frac{\omega_n^2}{\omega_n^2-\omega^2}&\\\times\mathrm{Im}\big[\langle 0_\sigma|R_{\sigma i}|n_\sigma\rangle\langle n_\sigma|R_{\sigma j}R_{\sigma l}|0\rangle&\\+\langle 0_\sigma|R_{\sigma j}|n_\sigma\rangle\langle n_\sigma|R_{\sigma i}R_{\sigma l}|0\rangle\big]&,\end{aligned} \tag{86a}$$

$$\tilde{\alpha}'_{ij}=\frac{4\pi e^2N_1^2}{mcN_0}\sum_{\sigma,n\neq 0}\frac{\omega_n}{\omega_n^2-\omega^2}\times\mathrm{Re}\big[\langle 0_\sigma|L_{\sigma j}+2S_{\sigma j}|n_\sigma\rangle\langle n_\sigma|R_{\sigma i}|0\rangle\big], \tag{86b}$$

$$\tilde{\alpha}''_{ij}=\frac{4\pi e^2N_1^2}{mc\omega N_0}\sum_{\sigma,n\neq 0}\frac{\omega_n^2}{\omega_n^2-\omega^2}\times\mathrm{Im}\big[\langle 0_\sigma|L_{\sigma j}+2S_{\sigma j}|n_\sigma\rangle\langle n_\sigma|R_{\sigma i}|0\rangle\big]. \tag{86c}$$

We now consider specifically the case of Cr_2O_3. We first simplify Eq. (86) by introducing the point-group symmetry of the crystal. If, following Osmond,[16] we label the Cr^{+3} sites in the unit cell by the letters A through D, we find that the point-group operations $2_\perp$, $\bar{1}'$, and $\bar{2}'_\perp$ interchange B with C, D with C, and A with C, respectively. In addition, these operations leave the products of matrix elements appearing in Eq. (86) invariant. Thus, it is only necessary to calculate the matrix elements in Eq. (86) at one lattice site (say, site C) and to multiply the result by four.

From Eq. (86), we find that the magnetoelectric coefficients in Cr_2O_3 at 0°K are given by

$$\tilde{\alpha}_{ii}=\frac{\pi e^2N}{12mc}\sum_{n\neq 0}\left(\frac{\omega_n}{\omega_n^2-\omega^2}\right)\times\mathrm{Re}\big[\langle 0|L_i+2S_i|n\rangle\langle n|R_i|0\rangle\big], \tag{87}$$

where $i=x$, y, or z.

Similarly, the electric quadrupole contribution to the

[15] S. Alexander and S. Shtrikman, Solid State Commun. **4**, 115 (1966); R. Hornreich and S. Shtrikman, Phys. Rev. **161**, 506 (1967). [The following corrections should be made in the latter reference: Eq. (1), change $\pm$ to $\mp$ preceding the third term on the right; Eq. (4), multiply right side by β^2; Eq. (15), change $\pm$ to $+$ preceding the last term on the right; Table I, multiply given values for $|b_1'|$ by 2. In addition, Eqs. (16)–(22) make use of the fact that $g_\perp/g_\parallel\approx 1$ for Cr_2O_3. We are grateful to Dr. M. Mercier and J. Tenenbaum for calling these errors to our attention.]

[16] W. P. Osmond, Proc. Phys. Soc. (London) **79**, 394 (1962).

gyrotropic birefringence is

$$\gamma''_{111}=-\frac{\pi e^2 N}{6\hbar\omega}\sum_{n\neq 0}\left(\frac{\omega_n{}^2}{\omega_n{}^2-\omega^2}\right)\times\mathrm{Im}[\langle 0(R_1)^2|n\rangle\langle n|R_1|0\rangle]. \quad (88)$$

Calculation of the matrix elements appearing in Eqs. (87) and (88) is a difficult problem and will not be attempted by us here. The calculation is in many respects similar to those involved in studies of the electric-field-induced shift in the paramagnetic resonance frequencies of Cr^{3+} in ruby.[17–19]

We content ourselves here with a rough estimate of the gyrotropic birefringence in Cr_2O_3 at optical frequencies. We take the magnetic dipole strength of the order of an electric dipole times the fine-structure constant $e^2/\hbar c=1/137$ and the quadrupole strength to be an electric dipole times the ratio of the lattice spacing a to the wavelength λ of the field in the medium. Taking $\omega_n\simeq 250\ \mathrm{cm}^{-1}$ in Cr_2O_3.[20] we find that $\gamma''_{111}/(c/\omega)\Delta\alpha \simeq 10^2$ at a free-space wavelength of 5000 Å. Now from Eq. (87) we see that $\Delta\alpha(\omega)/\Delta\alpha(0)=\omega_n{}^2/\omega^2\simeq 10^{-4}$. Taking[21] $\Delta\alpha(0)=4\times 10^{-5}$, we thus find that $|\gamma''_{111}k| \simeq 4\times 10^{-7}$. We thus expect the optical gyrotropic birefringence in Cr_2O_3 to lead to a shift in its principal axes of roughly 10^{-6} rad when the effect is due to the electric quadrupole and roughly 10^{-8} rad when the effect is of magnetoelectric origin.

[17] J. O. Artman and J. C. Murphy, in *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963), p. 634.
[18] E. B. Royce and N. Bloembergen, Phys. Rev. **131**, 1912 (1963).
[19] J. O. Artman and J. C. Murphy, Phys. Rev. **135**, A1622 (1964).
[20] K. A. Wickersheim, J. Appl. Phys. 34, 1224 (1963).
[21] D. N. Astrov, Zh. Eksperim. i Teor. Fiz. **40**, 1035 (1961) [English transl.: Soviet Phys.—JETP **13**, 729 (1961)].

VI. SUMMARY

We have presented various aspects of the effect known as gyrotropic or nonreciprocal birefringence.[1] We first considered the effect phenomenologically and showed that its origins lie in electric quadrupole and magnetoelectric[4] effects. Of the maximum of 18 independent coefficients in the gyrotropic birefringence tensor in a lossless medium, we find that 10 are entirely quadrupolar in nature, with the rest being in general linear combinations of quadrupole and magnetoelectric contributions. We also show the close formal connection between natural optical activity[6] and the magnetoelectric effect.

We then briefly consider a plane wave propagating in a gyrotropically birefringent medium, limiting ourselves to the case of Cr_2O_3. The gyrotropic birefringence is shown to exhibit itself as a shift in the principal optic axes of the system.[1] The question of boundary effects between a gyrotropically birefringent medium and a lossless dielectric is then discussed.

Finally, a quantum-mechanical treatment of gyrotropic birefringence is given, using the method of Agranovich and Ginzburg.[11] The general results obtained are applied to Cr_2O_3 and expressions for the quadrupole and magnetoelectric contributions to the gyrotropic-birefringence tensor in this material are given. Using these expressions and published data,[20,21] it is roughly estimated that the electric-quadrupole-induced shift in the principal optic axes of Cr_2O_3 is of the order of 10^{-6} rad and the magnetoelectric-induced shift is two orders of magnitude less.

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