Surface magneto-optical effects in cubic antiferromagnets

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Time-odd optical effects of electric quadrupole-magnetic dipole order, which are due to the spatial symmetry of a (001) surface layer, are predicted in reflection and transmission for certain classes of cubic antiferromagnet which do not exhibit bulk effects of the same multipole order. Reflection and transmission matrices for normal incidence at the vacuum-crystal interface are derived by taking the boundary conditions in relativistically covariant form, so ensuring that the requirements of reciprocity (time-reversal symmetry) are satisfied. These matrices show that the reflected and transmitted light should be rotated due to the properties of the surface layer. The possibility is discussed of observing this rotation in those classes of cubic antiferromagnet which do not display additional surface effects such as specular optical activity of surface origin or the surface Faraday effect.

I. INTRODUCTION

When electromagnetic radiation interacts with matter the oscillating electric and magnetic fields of the light wave may induce optical phenomena in a medium that are related to its bulk properties,[1–4] as well as surface effects that may be described in terms of properties that are permitted by the spatial symmetry of a surface layer.[5–8] However, on account of their relatively smaller magnitudes, surface effects are generally observed only in the absence of the corresponding bulk effect.

Many classes of uniaxial and cubic antiferromagnetic crystal may exhibit optical effects of magnetic origin both in transmission[4,9,10] and in reflection.[11–13] Theoretical considerations have shown[4,9] that such effects first arise at the level of induced electric quadrupoles and magnetic dipoles and that they may be described in terms of components of the time-odd property tensors, $G_{\alpha\beta}$ and $a'_{\alpha\beta\gamma}$, that are, respectively, second-rank axial and third-rank polar. There are, however, certain classes of cubic antiferromagnet, namely

$$m3,\ 432,\ \underline{\bar{4}}3\underline{m},\ m3m,\ m3\underline{m},\ \underline{m}3\underline{m},$$

which, to the order of electric quadrupole and magnetic dipole, may not display time-odd optical effects due to their bulk magnetic properties.[12] Such crystals would be suitable for the observation of surface effects.

In this paper we identify the classes of cubic antiferromagnet that may exhibit effects in transmission and in reflection due to components of the tensors $G_{\alpha\beta}$ and $a'_{\alpha\beta\gamma}$ that are allowed by the symmetry of the surface when the light path is along the normal to a cube face. This is a particularly favorable geometry for examining surface phenomena in reflection, as bulk effects of chiral[14] and magnetic[13] origin are absent in this arrangement for the full range of magnetic point-group symmetries of the cubic system. For simplicity, details are presented only for the magnetic point group $\underline{m}3\underline{m}$. An important aspect of our theory is the use of relativistically covariant forms for the boundary conditions[15] to determine the reflection and transmission matrices at the vacuum-crystal interface. Relativistic covariance is an essential requirement if both spatial and temporal symmetry constraints[16,17] are to be satisfied. This is discussed in Sec. II where the relevant electromagnetic theory is also summarized before being applied to a crystal of $\underline{m}3\underline{m}$ symmetry in Sec. III. In Sec. IV we discuss the possible coexistence of other surface effects.[7,8] Our conclusions follow in Sec. V.

II. ELECTROMAGNETIC THEORY

We consider reflection and transmission at the surface of a source-free, homogeneous, anisotropic, magnetic crystal in a vacuum. The xy plane of the laboratory system of Cartesian axes $O(x,y,z)$ is taken to lie in the interface with the vacuum in the half-space $z<0$ and the crystal in the half-space $z>0$. A monochromatic plane light wave with an electric field of the form

$$\mathbf{E}=\mathbf{E}^{(0)}\exp\{i\omega(n\boldsymbol{\sigma}\cdot\mathbf{r}/c-t)\} \tag{1}$$

is incident normally on the surface of the crystal from the vacuum side. In Eq. (1), ω is the angular frequency of the light wave, $\mathbf{E}^{(0)}$ is the complex amplitude for the refractive index n when propagation is in the direction of the unit wave-normal $\boldsymbol{\sigma}$, and c is the speed of light in a vacuum.

The theory in this paper is taken to the order of induced electric quadrupoles and magnetic dipoles. To this multipole order the $\mathbf{D}$ and $\mathbf{H}$ fields in matter are[18–20]

$$D_\alpha=\epsilon_0 E_\alpha+P_\alpha-\tfrac{1}{2}\nabla_\beta Q_{\alpha\beta}+\cdots, \tag{2}$$

$$H_\alpha=\mu_0^{-1}B_\alpha-M_\alpha+\cdots, \tag{3}$$

where P_α, $Q_{\alpha\beta}$, and M_α are, in Cartesian tensor notation, macroscopic volume densities of electric dipole moment, electric quadrupole moment, and magnetic dipole moment, respectively.

By means of the Maxwell equation $\boldsymbol{\nabla}\times\mathbf{E}=-\dot{\mathbf{B}}$, the space and time derivatives of the electric field $\mathbf{E}$ and the magnetic field $\mathbf{B}$ of a plane electromagnetic wave may all be expressed in terms of $\mathbf{E}$ when complex notation is used, such as that in Eq. (1). These space and time derivative fields are able to induce multipoles in matter, the moments of which are specified by their densities P_α, $Q_{\alpha\beta}$, M_α, ... Accordingly, these densities may all be expressed in terms of **E**, and so therefore may the response fields **D** and **H** in Eqs. (2) and (3). However, Post[21] has shown that, to be relativistically covariant, **D** and **H** for a linear and homogeneous dielectric must be a function of both **E** and **B** of the form

$$D_\alpha = A_{\alpha\beta}E_\beta + T_{\alpha\beta}B_\beta, \tag{4}$$

$$H_\alpha = U_{\alpha\beta}E_\beta + X_{\alpha\beta}B_\beta, \tag{5}$$

where for a medium of negligible absorption at the frequency of the wave

$$A_{\alpha\beta} = A^*_{\beta\alpha}, \quad X_{\alpha\beta} = X^*_{\beta\alpha}, \quad U_{\alpha\beta} = -T^*_{\beta\alpha}. \tag{6}$$

As an extension of Buckingham's notation for a nonmagnetic medium,[22] the induced multipole moment densities for a magnetic crystal have previously been taken, to the order of electric quadrupoles and magnetic dipoles, in the form[4]

$$P_\alpha = \alpha_{\alpha\beta}E_\beta + \omega^{-1}\alpha'_{\alpha\beta}\dot{E}_\beta + \tfrac{1}{2}a_{\alpha\beta\gamma}\nabla_\gamma E_\beta + \tfrac{1}{2}\omega^{-1}a'_{\alpha\beta\gamma}\nabla_\gamma \dot{E}_\beta + G_{\alpha\beta}B_\beta + \omega^{-1}G'_{\alpha\beta}\dot{B}_\beta, \tag{7}$$

$$Q_{\alpha\beta} = a_{\gamma\alpha\beta}E_\gamma + \omega^{-1}a'_{\gamma\alpha\beta}\dot{E}_\gamma, \tag{8}$$

$$M_\alpha = G_{\beta\alpha}E_\beta - \omega^{-1}G'_{\beta\alpha}\dot{E}_\beta. \tag{9}$$

The tensors in Eqs. (7)–(9) that describe the proportionality between the induced multipole moment densities and the field terms are macroscopic multipole polarizability densities of the medium. For instance, $\alpha_{\alpha\beta}$ is the familiar polarizability and $a_{\alpha\beta\gamma}$ is the quadrupole polarizability introduced by Buckingham[22] for molecules.

When Eqs. (7)–(9) are substituted into Eqs. (2) and (3), the expressions for **D** and **H** do not satisfy the covariant forms in Eqs. (4) and (5). We have shown,[23] however, that the covariance requirements of Post can be met only when the polarization densities in Eqs. (7)–(9) have the following forms:

$$P_\alpha = F_{\alpha\beta}E_\beta - \tfrac{1}{6}iS_{\alpha\beta\gamma}\nabla_\gamma E_\beta + (t_{\alpha\beta} - it'_{\alpha\beta})B_\beta + \cdots, \tag{10}$$

$$Q_{\alpha\beta} = \tfrac{1}{3}iS_{\alpha\beta\gamma}E_\gamma + \cdots, \tag{11}$$

$$M_\alpha = (t_{\beta\alpha} + it'_{\beta\alpha})E_\beta + \cdots, \tag{12}$$

where

$$F_{\alpha\beta} = \alpha_{\alpha\beta} - i[\alpha'_{\alpha\beta}], \tag{13}$$

$$S_{\alpha\beta\gamma} = [a'_{\alpha\beta\gamma} + a'_{\beta\gamma\alpha} + a'_{\gamma\alpha\beta}], \tag{14}$$

$$t_{\alpha\beta} = [G_{\alpha\beta} - \tfrac{1}{3}\delta_{\alpha\beta}G_{\gamma\gamma} - \tfrac{1}{6}\omega\epsilon_{\beta\gamma\delta}a'_{\gamma\delta\alpha}], \tag{15}$$

$$t'_{\alpha\beta} = G'_{\alpha\beta} - \tfrac{1}{2}\omega\epsilon_{\beta\gamma\delta}a_{\gamma\delta\alpha}. \tag{16}$$

In Eqs. (15) and (16), $\delta_{\alpha\beta}$ is the Kronecker delta and $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor.

To illustrate the need for covariant forms for **D** and **H**, we consider the Maxwell boundary condition on **H** at a vacuum-dielectric interface. In the absence of free current the tangential component of **H** is continuous. In the vacuum $\mathbf{H} = \mathbf{B}/\mu_0$, in which **H** is well-defined and unique because **B** has this property, as follows from the Lorentz force. By contrast, **H** in the dielectric is not uniquely defined by the Maxwell equation

$$\nabla \times \mathbf{H} = \dot{\mathbf{D}} + \mathbf{J}, \tag{17}$$

in which it first appears in physics, because specifying the curl of a vector does not fix the vector unambiguously. The difficulty is overcome by using the covariant form for **H**. A similar argument applies to **D**. The covariant multipole forms for these fields have, in addition, been shown to be translationally invariant in that they are independent of the arbitrary origin to which the multipole moments are referred.[15,23]

Of the polarizability tensors in Eqs. (13)–(16) $\alpha_{\alpha\beta}$, $\alpha'_{\alpha\beta}$, $a_{\alpha\beta\gamma}$, and $a'_{\alpha\beta\gamma}$ are polar, while $G_{\alpha\beta}$ and $G'_{\alpha\beta}$ are axial. Time-odd tensors have been placed in square brackets. Such tensors may exist only for magnetic media.[24] Quantum-mechanical expressions for the polarizability tensors in Eqs. (13)–(16) show that[23]

$$\alpha_{\alpha\beta} = \alpha_{\beta\alpha}, \quad \alpha'_{\alpha\beta} = -\alpha'_{\beta\alpha}, \tag{18}$$

$$a_{\alpha\beta\gamma} = a_{\alpha\gamma\beta}, \quad a'_{\alpha\beta\gamma} = a'_{\alpha\gamma\beta}. \tag{19}$$

The polarizabilities in Eqs. (13)–(16) may also be associated with distinct optical properties. Briefly, $\alpha_{\alpha\beta}$ accounts for double refraction in uniaxial and biaxial crystals,[25] $\alpha'_{\alpha\beta}$ describes the intrinsic Faraday effect in ferromagnets,[26] $G'_{\alpha\beta}$ and $a_{\alpha\beta\gamma}$ together give rise to optical activity,[1,2] and $G_{\alpha\beta}$ and $a'_{\alpha\beta\gamma}$ are responsible for gyrotropic and nonreciprocal birefringences in antiferromagnetic crystals.[4,9]

It has been shown from Maxwell's equations and Eqs. (1)–(3) and (10)–(16) that in the electric quadrupole-magnetic dipole approximation the equation that describes wave propagation in a medium is[4]

$$[n^2(\sigma_\alpha\sigma_\beta - \delta_{\alpha\beta}) + \epsilon_0^{-1}\epsilon_{\alpha\beta}]E_\beta = 0, \tag{20}$$

where

$$\epsilon_{\alpha\beta} = \epsilon_0\delta_{\alpha\beta} + \alpha_{\alpha\beta} - i\alpha'_{\alpha\beta} + nc^{-1}\sigma_\gamma(A_{\alpha\beta\gamma} - iA'_{\alpha\beta\gamma}) \tag{21}$$

and

$$A_{\alpha\beta\gamma} = -\epsilon_{\beta\gamma\delta}G_{\alpha\delta} - \epsilon_{\alpha\gamma\delta}G_{\beta\delta} + \tfrac{1}{2}\omega(a'_{\alpha\beta\gamma} + a'_{\beta\alpha\gamma}), \tag{22}$$

$$A'_{\alpha\beta\gamma} = -\epsilon_{\beta\gamma\delta}G'_{\alpha\delta} + \epsilon_{\alpha\gamma\delta}G'_{\beta\delta} - \tfrac{1}{2}\omega(a_{\alpha\beta\gamma} - a_{\beta\alpha\gamma}). \tag{23}$$

For normal incidence the boundary conditions on the tangential components of the electric and magnetic fields, **E** and **B**, at the vacuum-crystal interface are[15]

$$E_x - E_{vx} = 0, \tag{24}$$

$$E_y - E_{vy} = 0, \tag{25}$$

$$B_x - B_{vx} = \mu_0(K_y - K_z\epsilon_{yz}/\epsilon_{zz}), \tag{26}$$

$$B_y - B_{vy} = -\mu_0(K_x - K_z\epsilon_{xz}/\epsilon_{zz}), \tag{27}$$

where quantities in the vacuum are denoted by the subscript v, $\mathbf{K}$ is the macroscopic surface current density of bound charge, and $\epsilon_{\alpha\beta}$ is defined in Eq. (21). It follows from the multipole expansion of the vector potential[15,20] that

$$K_\alpha = -n_\beta\left(\tfrac{1}{2} i\omega Q_{\alpha\beta} + \epsilon_{\alpha\beta\gamma} M_\gamma\right), \tag{28}$$

where $\mathbf{n} = -\hat{\mathbf{z}}$ is the outward unit normal to the crystal. To ensure that the boundary conditions in Eqs. (26) and (27) satisfy covariance requirements, it is necessary to use the covariant forms for $Q_{\alpha\beta}$ and M_α in Eqs. (11) and (12), respectively, in $\mathbf{K}$.

Since the electric field in the vacuum $\mathbf{E}_v$ comprises the electric fields $\mathbf{E}_i$ and $\mathbf{E}_r$ of the incident and reflected waves, respectively, the replacement

$$\mathbf{E}_v = \mathbf{E}_i + \mathbf{E}_r \tag{29}$$

may be made in Eqs. (24) and (25). Similarly, $\mathbf{B}_v$ in Eqs. (26) and (27) may be replaced by $\mathbf{B}_i + \mathbf{B}_r$. Equations (24)–(27) may then be rewritten in matrix form as[27]

$$(E_r)_j = R_{jk}(E_i)_k, \tag{30}$$

where R_{jk} is the 2×2 reflection matrix that relates the Cartesian components of the electric field of the incident wave to those of the reflected wave. It follows from time-reversal symmetry (reciprocity) that the reflection matrices for a sample in two time-conjugated equilibrium states (t) and ($-t$) must satisfy[16]

$$R_{jk}(t) = R_{kj}(-t). \tag{31}$$

A similar constraint is imposed on the transmission matrix T_{jk}, which may also be determined from Eqs. (24)–(27),[27] and which relates the Cartesian components of the electric field of the incident wave to those of the transmitted wave at the interface.

Because covariance embodies both spatial and temporal invariance, it is the key to obtaining reflection and transmission matrices with the correct symmetry properties.

III. THE MAGNETIC POINT GROUP $\underline{m}3\underline{m}$

We now apply the theory in Sec. II to a cubic antiferromagnet with magnetic point-group symmetry $\underline{m}3\underline{m}$ for normal incidence on a cube face. The crystal properties are described relative to Cartesian crystallographic axes $0(1,2,3)$ which are parallel to the cube edges.[24] We take the crystallographic three axis to be parallel to the z axis of the laboratory reference frame $0(x,y,z)$ and let the crystallographic 1 and 2 axes be rotated by an angle θ with respect to the x and y axes in the reflecting surface.

Birss's tables[24] show that the time-even tensors $G'_{\alpha\beta}$ and $a_{\alpha\beta\gamma}$ in Eq. (16) and the time-odd tensor $\alpha'_{\alpha\beta}$ in Eq. (13) may not exist for this crystal class, although components of the remaining property tensors in Eqs. (13)–(15), namely $\alpha_{\alpha\beta}$, $G_{\alpha\beta}$, and $a'_{\alpha\beta\gamma}$, may exist. However, those of $a'_{\alpha\beta\gamma}$ vanish because of the constraint in Eq. (19), and hence the bulk properties of the medium are described by the following tensor components:

$$\alpha_{11} = \alpha_{22} = \alpha_{33},$$

$$G_{11} = G_{22} = G_{33}. \tag{32}$$

The symmetry of the (001) surface layer differs from that of the bulk crystal and is determined by the subgroup of symmetry operations of the $\underline{m}3\underline{m}$ point group that leave a semi-infinite crystal (i.e., a reflecting sample) invariant.[8,11] It follows from group symmetry tables[28] that the appropriate surface symmetry is $4\,\underline{m}\,\underline{m}$. The nonvanishing components of the surface tensors $G^s_{\alpha\beta}$ and $a'^s_{\alpha\beta\gamma}$ that are consistent with this surface symmetry are readily identified as

$$G^s_{11} = G^s_{22}, \quad G^s_{33},$$

$$a'^s_{123} = -a'^s_{213} = a'^s_{132} = -a'^s_{231}, \tag{33}$$

where use has also been made of the intrinsic symmetry property in Eq. (19).

Tensor components in the laboratory frame $0(x,y,z)$ may be expressed in terms of those in the crystallographic system $0(1,2,3)$ by means of the transformation for a rotation

$$t_{\alpha\beta}\ldots = t_{ij}\ldots a^\alpha_i a^\beta_j \ldots, \tag{34}$$

where a^α_i is the direction cosine between the α axis in $0(x,y,z)$ and the i axis in $0(1,2,3)$. Application of Eq. (34) to the tensor components in Eqs. (32) and (33) yields

$$\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = \alpha_{11},$$

$$G_{xx} = G_{yy} = G_{zz} = G_{11},$$

$$G^s_{xx} = G^s_{yy} = G^s_{11}, \quad G^s_{zz} = G^s_{33},$$

$$a'^s_{xyz} = a'^s_{xzy} = -a'^s_{yxz} = -a'^s_{yzx} = a'^s_{123}. \tag{35}$$

For normal incidence $\boldsymbol{\sigma} = (0,0,1)$, and we then find from Eqs. (21)–(23) and Eq. (35) that the propagation equation (20) may be written in component form as

$$\begin{bmatrix} -n^2 + \epsilon_0^{-1}\epsilon_{xx} & 0 & 0 \\ 0 & -n^2 + \epsilon_0^{-1}\epsilon_{yy} & 0 \\ 0 & 0 & \epsilon_0^{-1}\epsilon_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = 0, \tag{36}$$

where

$$\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = (\epsilon_0 + \alpha_{11}). \tag{37}$$

It is interesting that the tensors $G_{\alpha\beta}$ and $a'_{\alpha\beta\gamma}$ do not contribute to Eq. (36) even though certain components, listed in Eq. (35), may exist. Equation (36) shows that the characteristic waves travelling along the z axis in the crystal are polarized parallel to the x and y axes and have the same refractive index, namely

$$n = (1 + \epsilon_0^{-1}\alpha_{11})^{1/2}. \tag{38}$$

The components of the electric and magnetic fields of the two waves in the crystal are thus

$$\mathbf{E}\|x\!: \mathbf{E} = E_x(1,0,0), \quad \mathbf{B} = E_x(0,n/c,0), \tag{39}$$

$$\mathbf{E}\|y\!: \mathbf{E} = E_y(0,1,0), \quad \mathbf{B} = E_y(-n/c,0,0), \tag{40}$$

where use has been made of Eq. (1) and the Maxwell equation

$$\nabla \times \mathbf{E} = -\dot{\mathbf{B}}. \tag{41}$$

Before applying the boundary conditions in Eqs. (24)–(27) it is necessary to determine the components of the surface current density **K** in Eq. (28) that are induced in the surface layer by the light wave fields in Eqs. (39) and (40). When Eqs. (11), (12), (14)–(16), and (35) are used in Eq. (28), the following results are obtained:

$$\mathbf{E}\|x: \quad \mathbf{K} = E_x(0,\gamma,0), \tag{42}$$

$$\mathbf{E}\|y: \quad \mathbf{K} = E_y(-\gamma,0,0,), \tag{43}$$

where

$$\gamma = \tfrac{1}{3}(G_{11}^{s} - G_{33}^{s}) + \tfrac{1}{6}\omega a_{123}'^{s}. \tag{44}$$

Then by substituting Eqs. (39), (40), (42), and (43) into the boundary conditions in Eqs. (24)–(27) and rewriting the four equations in the form of Eq. (30), it can be shown that the elements of the reflection matrix R_{jk} are

$$R_{xx} = R_{yy} = (1-n)/(1+n),$$

$$R_{xy} = -R_{yx} = 2\mu_0 c\gamma/(1+n)^2. \tag{45}$$

Because γ is time odd, as can be seen from Eq. (44), the reciprocity condition in Eq. (31) is satisfied.

Apart from the dependence of γ in Eq. (44) on surface tensor components rather than those of the bulk medium, the matrix elements in Eq. (45) are identical to the corresponding forms that have been derived in terms of bulk properties for Cr_2O_3 (symmetry $\underline{3}\,\underline{m}$) when the light path is parallel to the optic axis.[12] Thus the effects observed in reflection from Cr_2O_3,[11] namely nonreciprocal rotation and circular dichroism, should be exhibited by the crystal class $\underline{m}3\underline{m}$ due to the symmetry of the surface layer.

The components of the corresponding transmission matrix T_{jk} that follows from the boundary conditions in Eqs. (24)–(27) are

$$T_{xx} = T_{yy} = 2/(1+n),$$

$$T_{xy} = -T_{yx} = R_{xy} = 2\mu_0 c\gamma/(1+n)^2, \tag{46}$$

and hence the transmitted light (through the first interface) is also rotated.

As the components of $G_{\alpha\beta}^{s}$ and $a_{\alpha\beta\gamma}'^{s}$ in Eq. (44) can be shown to vanish for crystals which are invariant under reflection in a plane perpendicular to the surface or for which a C_4 rotation about the light path produces the time-reversed crystal form, it follows from tables[28] that the effects described by Eqs. (45) and (46) would be exhibited only by those cubic antiferromagnets which belong to the classes

$$23, \quad \underline{m}3, \quad 432, \quad \bar{\underline{4}}3\underline{m}, \quad \underline{m}3\underline{m}. \tag{47}$$

IV. OTHER SURFACE EFFECTS

Although the surface effects described by Eqs. (45) and (46) are the only ones for the chosen orientation that may be exhibited within the electric quadrupole-magnetic dipole approximation by a crystal with magnetic point group symmetry $\underline{m}3\underline{m}$, additional surface effects may exist for certain of the other point groups listed in Eq. (47). For example, Nelson and Ivanov[8] have shown that when a linearly polarized light beam is incident normally on a (001) surface of a nonmagnetic crystal belonging to the class $\bar{4}3m$, the reflected and transmitted beams undergo a rotation which may be described in terms of time-even surface tensors of electric quadrupole-magnetic dipole order, like $G_{\alpha\beta}'$ and $a_{\alpha\beta\gamma}$ in Eq. (16). Such effects have been observed in a GaAs crystal,[29–32] which has $\bar{4}3m$ symmetry, and should also occur in crystals belonging to the associated magnetic subgroups, namely $\bar{\underline{4}}3m$ and $\bar{4}3\underline{m}$. Furthermore, we find that the cubic class 23 should exhibit a similar effect. It can be shown from the theory in Sec. II that the time-even contributions to the elements of the reflection matrix R_{jk} in Eq. (30) are

$$R_{xx} = [1 - n^2 + i\mu_0 c(ng - p\sin 2\theta + q\cos 2\theta)]/D, \tag{48}$$

$$R_{yy} = [1 - n^2 + i\mu_0 c(ng + p\sin 2\theta - q\cos 2\theta)]/D, \tag{49}$$

$$R_{xy} = R_{yx} = -i\mu_0 c(p\cos 2\theta + q\sin 2\theta)/D, \tag{50}$$

where n is the refractive index defined in Eq. (38), g, p, and q are functions of the components of the surface tensors $G_{\alpha\beta}'^{s}$ and $a_{\alpha\beta\gamma}^{s}$, θ is the angle between the crystallographic and laboratory axes in the reflecting surface, and

$$D = (1+n)(1+n-i\mu_0 cg). \tag{51}$$

For the class 23

$$g = G_{12}'^{s} - G_{21}'^{s} + \tfrac{1}{2}\omega(a_{113}^{s} + a_{223}^{s} - a_{311}^{s} - a_{322}^{s}), \tag{52}$$

$$p = G_{11}'^{s} - G_{22}'^{s} - \omega[\tfrac{1}{2}(a_{123}^{s} + a_{213}^{s}) - a_{312}^{s}], \tag{53}$$

$$q = G_{12}'^{s} + G_{21}'^{s} + \tfrac{1}{2}\omega(a_{113}^{s} - a_{223}^{s} - a_{311}^{s} + a_{322}^{s}), \tag{54}$$

while for the class $\bar{4}3m$

$$g = 2G_{12}'^{s} + \omega(a_{113}^{s} - a_{311}^{s}), \tag{55}$$

$$p = 2G_{11}'^{s} - \omega(a_{123}^{s} - a_{312}^{s}), \tag{56}$$

$$q = 0. \tag{57}$$

The matrix elements in Eqs. (48)–(50) reduce to the forms that Nelson and Ivanov[8] derived for the class $\bar{4}3m$ using a different procedure to the one described here when, as they did, we set $g=0$ and neglect p in Eqs. (48) and (49).

Although components of $G_{\alpha\beta}'^{s}$ and $a_{\alpha\beta\gamma}^{s}$ may also exist for the class 432, there is no rotation at the (001) surface since $p=q=0$, while g has the form in Eq. (55).

It follows by inspection from the matrix elements in Eqs. (45), (46), and (48)–(50) that only the time-even effects of electric quadrupole-magnetic dipole order may depend on the crystal orientation θ.

In addition to surface phenomena of electric quadrupole-magnetic dipole order, effects may also arise at the electric dipole level due to components of the time-odd, antisymmetric, second-rank polar tensor $\alpha'^{s}_{\alpha\beta}$, which describes a surface Faraday effect.[7] It is readily shown from symmetry considerations[24,28] that this effect should occur at a (001) surface layer in cubic crystals belonging to the magnetic point groups 23, 432, and $\bar{4}3\underline{m}$, even though the bulk tensor $\alpha'_{\alpha\beta}$ is zero for all cubic crystals.[24]

Because electric dipole effects are very much larger than those of electric quadrupole-magnetic dipole order, it follows from Eq. (47) that the observation of the time-odd phenomena described by Eqs. (45) and (46) would be limited to the point groups $\underline{m}3\underline{m}$ and $\underline{m}3$. For the same reason the magnetic point group $\bar{4}3m$ would be the only one suited to the observation of the time-even effects derived from Eqs. (48)–(50). Similar difficulties do not, however, arise for the nonmagnetic point groups 23 and $\bar{4}3m$ since these may not possess components of the time-odd tensor $\alpha'_{\alpha\beta}$.[24]

V. CONCLUSION

The theory presented in this paper provides the basis for selecting crystals that would be suitable for the measurement of surface effects of different multipole order in the absence of the corresponding bulk effect. Such measurements would be of value in establishing the magnitudes of the different multipole orders of surface effect which, in turn, would be useful in assessing their relative importance compared with those of the bulk medium in reflection at an interface. It has been suggested[7] that the surface Faraday effect and the bulk magnetoelectric effect may have similar magnitudes in the optical region. This could be investigated by comparing the surface Faraday effect measurements on a crystal of magnetic point group symmetry 23, 432, or $\bar{4}3\underline{m}$ with the values that have been obtained experimentally for the magnetoelectric properties of Cr_2O_3.[10,11] As the observed rotation in reflection and transmission in a GaAs crystal[29–32] has been interpreted in terms of surface properties of electric quadrupole-magnetic dipole order,[8] it seems likely that other surface effects of the same multipole order that we describe in this paper should also be capable of measurement.

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[1] A. D. Buckingham and M. B. Dunn, J. Chem. Soc. A **1971**, 1988.

[2] L. D. Barron, *Molecular Light Scattering and Optical Activity* (Cambridge University Press, Cambridge, 1982).

[3] E. B. Graham and R. E. Raab, Proc. R. Soc. London, Ser. A **430**, 593 (1990).

[4] E. B. Graham and R. E. Raab, Philos. Mag. B **66**, 269 (1992).

[5] N. Bloembergen and P. S. Pershan, Phys. Rev. **128**, 606 (1962).

[6] L. Hecht and L. D. Barron, Chem. Phys. Lett. **225**, 525 (1994).

[7] I. Dzyaloshinskii and E. V. Papamichail, Phys. Rev. Lett. **75**, 3004 (1995).

[8] D. F. Nelson and A. L. Ivanov, Opt. Lett. **23**, 86 (1998).

[9] R. M. Hornreich and S. Shtrikman, Phys. Rev. **171**, 1065 (1968).

[10] R. V. Pisarev, B. B. Krichevtsov, and V. V. Pavlov, Phase Transit. **37**, 63 (1991).

[11] B. B. Krichevtsov, V. V. Pavlov, R. V. Pisarev, and V. N. Gridnev, J. Phys.: Condens. Matter **5**, 8233 (1993).

[12] E. B. Graham and R. E. Raab, J. Phys.: Condens. Matter **9**, 1863 (1997).

[13] E. B. Graham and R. E. Raab, Phys. Rev. B **59**, 7058 (1999).

[14] M. P. Silverman and J. Badoz, J. Electromagn. Waves Appl. **6**, 587 (1992).

[15] E. B. Graham and R. E. Raab, Proc. R. Soc. London, Ser. A **456**, 1193 (2000).

[16] A. L. Shelankov and G. E. Pikus, Phys. Rev. B **46**, 3326 (1992).

[17] G. S. Canright and A. G. Rojo, Phys. Rev. B **46**, 14 078 (1992).

[18] L. Rosenfeld, *Theory of Electrons* (North-Holland, Amsterdam, 1962), Chap. 2.

[19] F. N. H. Robinson, *Macroscopic Electromagnetism* (Pergamon, Oxford, 1973), pp. 56–62.

[20] E. B. Graham, J. Pierrus, and R. E. Raab, J. Phys. B **25**, 4673 (1992).

[21] E. J. Post, *Formal Structure of Electromagnetics* (North-Holland, Amsterdam, 1962), p. 132.

[22] A. D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967).

[23] R. E. Raab and E. B. Graham, Ferroelectrics **204**, 157 (1997).

[24] R. R. Birss, Rep. Prog. Phys. **26**, 307 (1963).

[25] M. J. Gunning and R. E. Raab, J. Opt. Soc. Am. A **15**, 2199 (1998).

[26] E. B. Graham and R. E. Raab, J. Appl. Phys. **69**, 2549 (1991).

[27] R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1979), p. 353.

[28] S. Bhagavantam, *Crystal Symmetry and Physical Properties* (Academic, London, 1966), p. 53.

[29] A. R. Bungay, N. Kugler, and N. I. Zheludev, Phys. Lett. A **174**, 335 (1993).

[30] A. R. Bungay, S. V. Popov, Yu. P. Svirko, and N. I. Zheludev, Chem. Phys. Lett. **217**, 249 (1994).

[31] A. R. Bungay, Y. Pointel, and N. I. Zheludev, J. Lumin. **60–61**, 36 (1994).

[32] N. I. Zheludev, S. V. Popov, Yu. P. Svirko, A. Malinowski, and D. Yu. Paraschuk, Phys. Rev. B **50**, 11 508 (1994).