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Natural optical activity vs circular Bragg reflection studied by Mueller matrix ellipsometry

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ABSTRACT

This work compares the reflection optical response of a homogeneous sample with natural optical activity with the Bragg reflection from an inhomogeneous system consisting of a periodic helicoidal structure. Examples of periodic helicoidal systems are cholesteric liquid crystals and the cuticle of some beetles. For transmitted light natural optical activity and Bragg reflection essentially lead to the same type of optical response, but there are fundamental differences on how they reflect circularly polarized light. The Mueller matrix symmetries for the two types of media are theoretically deduced and experimentally verified with ellipsometry measurements.

1. Introduction

The vast majority of ellipsometry measurements in anisotropic non-magnetic materials involve media in which the only relevant constituent tensor is the dielectric tensor, $\boldsymbol{\varepsilon}$. The optical response of most solids is determined in terms of the principal elements of $\boldsymbol{\varepsilon}$, which define isotropic, uniaxial or biaxial optical properties, and the rotations that define their orientations. The constitutive equations in terms of $\boldsymbol{\varepsilon}$ and the permeability tensor $\boldsymbol{\mu}$ are:

$$\mathbf{D} = \boldsymbol{\varepsilon}\mathbf{E}, \tag{1a}$$

$$\mathbf{B} = \boldsymbol{\mu}\mathbf{H}. \tag{1b}$$

One interesting situation occurs when the direction of anisotropy varies periodically in space, in special when the dielectric tensor components exhibit a helical spatial variation along the thickness direction. Samples with these characteristics enter in a specific regime called the circular Bragg regime, in which their reflectance is high only if the handedness of the incident wave is the same as the structural helix. The most well-known samples exhibiting these characteristics are cholesteric liquid crystals [1], but similar responses are found in the solid cuticle of some beetles [2] and it has been artificially engineered in chiral sculptured thin films [3]. Materials with these characteristics are sometimes referred as Reusch piles. They were first described in 1869 [4] as mutilayer structures of an anisotropic dielectric material in which there is an incremental rotation from every layer to the next about the axis normal to the layers.

Circular Bragg reflection requires media characterized by a helicoid chiral structure but the constituent materials do not require to be chiral. Therefore, chirality arises at a macroscopic or mesoscopic level. A different situation occurs when a homogeneous material with natural optical activity is studied. In this case, chirality is caused by some handedness that is intrinsic to the atomic or molecular structure of the material. Natural optical activity also manifests as a distinctive response of the material with the handedness of circular polarization but, typically, it is only recognized for light transmitted through these materials with the circular dichroism and optical rotation effects. Much less well-known is the effect (or, more precisely, the absence of any effect) that natural optical activity has on the reflection of circular polarized light (CPL). This work explores the similarities and differences in the reflective optical response of homogeneous samples with natural optical activity and inhomogeneous structures that exhibit a circular Bragg regime.

2. Theory

2.1. Electromagnetic theory

A more complete formulation of anisotropy needs to incorporate additional constituent tensors, for example, in the so-called bianisotropic formulation:

$$\mathbf{D} = \boldsymbol{\varepsilon}\mathbf{E} + \boldsymbol{\rho}\mathbf{H}, \tag{2a}$$

$$\mathbf{B} = \boldsymbol{\mu}\mathbf{H} + \boldsymbol{\rho}'\mathbf{E}, \tag{2b}$$

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in which $\boldsymbol{\rho}$ and $\boldsymbol{\rho}'$ are two magnetoelectric tensors. In practice, most media that can be studied by spectroscopic ellipsometry are Lorentz reciprocal, which means that there exist a symmetry if the source and the detector of an optical signal are interchanged. This implies:

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}^T,\ \boldsymbol{\mu} = \boldsymbol{\mu}^T,\ \boldsymbol{\rho} = -\boldsymbol{\rho}'^T, \tag{3}$$

where the superscript T indicates transposition. In this case, the magnetoelectric tensors, that in general are written as $\boldsymbol{\rho} = \boldsymbol{\chi} - i\boldsymbol{\alpha}$ and $\boldsymbol{\rho}' = \boldsymbol{\chi}^T + i\boldsymbol{\alpha}^T$, must satisfy $\boldsymbol{\chi} = 0$ and $\boldsymbol{\alpha} \neq 0$. For this reciprocal case the constitutive equations for a bianisotropic reciprocal medium can be rewritten as:

$$\mathbf{D} = \boldsymbol{\varepsilon}\mathbf{E} - i\boldsymbol{\alpha}\mathbf{H}, \tag{4a}$$

$$\mathbf{B} = \boldsymbol{\mu}\mathbf{H} + i\boldsymbol{\alpha}^T\mathbf{E}. \tag{4b}$$

In absorbing media all the tensor constitutive equations, i.e. $\boldsymbol{\varepsilon}$, $\boldsymbol{\alpha}$ and $\boldsymbol{\mu}$, become complex.

The propagation monochromatic plane wave with a angular frequency ω, such that the time dependence is given by $\exp(i\omega t)$, in bianisotropic homogeneous and some types of inhomogeneous media can be conveniently treated with the Berreman method [5]. Briefly, this method defines a differential propagation matrix or Berreman transfer matrix, $\boldsymbol{\Delta}$, that describes the transformation of the generalized field vector $\boldsymbol{\psi} = (E_x, H_y, E_y, -H_x)$ (being z the direction orthogonal to the medium boundaries) with the differential equation $\frac{\partial \boldsymbol{\psi}}{\partial z} = -ik_0\boldsymbol{\Delta}\boldsymbol{\psi}$ in which $k_0 = \omega/c$. The ψ vector and $\boldsymbol{\Delta}$ matrix used here should not be confused with the ellipsometric angles ψ, Δ typically used in ellipsometry measurements. From the eigenanalysis of $\boldsymbol{\Delta}$ one can deduce the polarization of the forward and backward propagating eigenmodes in the medium.

We can now consider the simple case of an isotropic optical active medium, in which $\boldsymbol{\varepsilon} = \mathrm{diag}(\varepsilon,\varepsilon,\varepsilon)$ and $\boldsymbol{\alpha} = \mathrm{diag}(\alpha,\alpha,\alpha)$. The Berreman transfer matrix is:

$$\boldsymbol{\Delta} = \begin{bmatrix} 0 & 1-\dfrac{\xi^2}{\varepsilon-\alpha^2} & \dfrac{\alpha\left(\xi^2-\alpha+\varepsilon\right)i}{\varepsilon-\alpha^2} & 0 \\ \varepsilon & 0 & 0 & \alpha i \\ -i\alpha & 0 & 0 & 1 \\ 0 & -\dfrac{\alpha\left(\xi^2-\alpha+\varepsilon\right)i}{\varepsilon-\alpha^2} & \varepsilon-\dfrac{\xi^2\varepsilon}{\varepsilon-\alpha^2} & 0 \end{bmatrix}, \tag{5}$$

where $\xi = n_0 \sin\theta$, θ is the angle of incidence and n_0 the refractive index of the incidence medium. For normal incidence ($\xi = 0$) the eigenanalysis of this matrix is very simple, with the two pairs of eigenvalues given by $\pm(\sqrt{\varepsilon}+\alpha)$ and $\pm(\sqrt{\varepsilon}-\alpha)$. The four eigenvectors, casted as matrix columns, are given by.

$$\boldsymbol{\psi} = \begin{bmatrix} i & i & -i & -i \\ i\sqrt{\varepsilon} & -i\sqrt{\varepsilon} & -i\sqrt{\varepsilon} & i\sqrt{\varepsilon} \\ \dfrac{1}{\sqrt{\varepsilon}} & \dfrac{-1}{\sqrt{\varepsilon}} & \dfrac{1}{\sqrt{\varepsilon}} & \dfrac{-1}{\sqrt{\varepsilon}} \end{bmatrix}, \tag{6}$$

where each column of the matrix is, respectively, the eigenvector corresponding to the eigenvalues $(\sqrt{\varepsilon}+\alpha)$, $-(\sqrt{\varepsilon}+\alpha)$, $(\sqrt{\varepsilon}-\alpha)$ and $-(\sqrt{\varepsilon}-\alpha)$. The ratio between eigenvector elements (e.g. $\psi_{00}/\psi_{20} = E_x/E_y = -i$) indicates that the eigenvectors always correspond to circular polarized waves. But, interestingly, the eigenvectors do not depend on α and only the eigenvalues contain information about the magnetoelectric properties of the medium. This means that optical activity only manifest as a bulk property but it has no effect on the interface reflection [6,7]. A sort of intuitive microscopic explanation for this phenomenon can be given with the Ewald-Oseen extinction model [8]. According to this model, the incident light does not only interact with the reflecting medium at the surface, but it has a certain penetration depth during which it is extinguished, inducing the atoms of the medium to radiate secondary waves that coherently superpose with the incident wave. In chiral media this coherent superposition can have a net chiral effect towards a certain handedness but, at normal incidence, there is a reversal of wave helicity upon mirror reflection that makes the two contributions of opposite handedness to cancel out within the penetration depth.

If a certain angle of incidence is considered ($\xi \neq 0$), then α contributes to the eigenmodes [9,6,7], but its effect is very minor because, in general, $\alpha \ll \varepsilon$. Due to this fact, spectroscopic ellipsometry studies in optically active materials (e.g. in inorganic crystals such as quartz, sodium chlorate, cinnabar, etc. or in common organic compounds such as tartaric acid, glucose, benzil, etc) do not need to consider the contribution of optical activity. The influence that their natural gyrotropy has in the Fresnel reflection coefficients is around 10^{-5} or smaller, so it tends to be below the experimental sensitivity. On the contrary, for transmission measurements in bulk samples the optical activity scales by the ratio of the optical pathlength to the wavelength providing factors of enhancement of around 10,000 and making the circular birefringence and circular dichroism transmission effects easily detectable.

Recently, we reported the first spectroscopic determination of natural optical activity in a semiconductor ($AgGaS_2$) above the bandgap using an ellipsometry measurement [7]. For that work we took advantage of the fact that this crystal belongs to the tetragonal point group $\bar{4}2m$ and, unlike for the isotropic case we have discussed, it has an anisotropic magnetoelectric tensor: $\boldsymbol{\alpha} = \mathrm{diag}(\alpha,-\alpha,0)$. In [7] we showed that reflection measurements (specially those at normal incidence) become sensitive to anisotropic forms of the magnetoelectric tensor. The natural optical activity of these materials changes as a function of the incoming polarization, and one remarkable consequence of this is that reflection optical activity effects are not invariant under a sample rotation.

Next, we can consider the case of a twisted medium following a periodic helical structure. The dielectric tensor can be expressed as [5,1]:

$$\boldsymbol{\varepsilon}(z) = \begin{bmatrix} \bar{\varepsilon}+\delta\cos 2\beta z & \beta\sin 2\beta z & 0 \\ \delta\sin 2\beta z & \bar{\varepsilon}-\delta\cos 2\beta z & 0 \\ 0 & 0 & \varepsilon_e \end{bmatrix}, \tag{7}$$

where $\bar{\varepsilon} = (\varepsilon_e+\varepsilon_o)/2$, $\delta = (\varepsilon_e - \varepsilon_o)/2$ and $\beta = 2\pi/P$, where P is the pitch of the helix and ε_e and ε_o are respectively the extraordinary and ordinary dielectric constants that define the in-plane birefringence (δ) at every layer. The Berreman propagation matrix of this inhomogeneous medium is given by

$$\boldsymbol{\Delta}(z) = \begin{bmatrix} 0 & 1-\dfrac{\xi^2}{\varepsilon_e} & 0 & 0 \\ \varepsilon+\delta\cos 2\beta z & 0 & \delta\sin 2\beta z & 0 \\ 0 & 0 & 0 & 1 \\ \delta\sin 2\beta z & 0 & \varepsilon-\xi^2-\delta\cos 2\beta z & 0 \end{bmatrix}. \tag{8}$$

This propagation matrix, or the dielectric tensor in Eq. (7), have the same symmetry that a monoclinic crystal with the monoclinic axis perpendicular to the crystal surface or that in an uniaxial crystal in which the optic axis lies parallel to the sample surface and not aligned with any of the axes of the reference frame. The difference with respect to these cases, is that here there is a z-dependence that cannot be obviated since the medium is inhomogeneous. Simple solutions (analytical for the case of normal incidence and numerical for the rest) have been provided [5,1,10] by considering a local rotating coordinate system along the helical axis. In the interval $n_oP < \lambda < n_eP$ the eigenvectors corresponding to the eigenvalues represent almost circularly polarized waves and the numerical calculation of the reflection and transmission coefficients reveals that circularly polarized light is reflected if it has the handedness of the cholesteric structure and transmitted if it has the opposite handedness.

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