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Symmetries and relationships between elements of the Mueller matrix spectra of the cuticle of the beetle *Cotinis mutabilis*

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**ABSTRACT**

The optical properties of light reflected from the cuticle of the scarab beetle *Cotinis mutabilis* are studied using variable angle Mueller matrix spectroscopic ellipsometry. Reflection of left-handed polarized light is demonstrated. Large amplitude interference oscillations in the elements of the normalized Mueller matrix ($\mathbf{M}$) reveal highly transparent materials comprising the beetle cuticle. Off-diagonal elements in $\mathbf{M}$ obey simple symmetry relationships due to the constraint in the cross-polarized reflection coefficients between $p$ and $s$ polarizations of chiral systems. $r_{ps} = -r_{sp}$. Based on the latter constraint and further interrelationships experimentally investigated, the number of independent elements in $\mathbf{M}$ resulted in only six. Reciprocity is probed from measurements performed in opposite sample orientations and the effects on $\mathbf{M}$ due to sample rotation by 90° are discussed. The results suggest relatively large areas in the cuticle of *C. mutabilis* with a helicoidal structure comprised of fibrils with a well-defined orientation.

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1. Introduction

Some birds, butterflies, insects and other creatures exhibit brilliant colors as a result of diverse optical phenomena produced by micro- and nanostructures [1]. Particularly, the shiny metallic colors reflected by the exoskeleton (the so-called cuticle) of some beetles show elliptical polarization properties [2]. Such color and polarization properties have been related to a Bragg-like reflection of the incident light produced from a twisted plywood or Bouligand structure [2,3]. This structure is comprised of the clustering of chitin nanofibrils wrapped by proteins in a planar woven-like structure [2]. This Bouligand structure resembles that of cholesteric (chiral) liquid crystals. That is, the nanofibrils in beetles’ cuticle have the same role as the molecules in the liquid phase. Some decades ago, the optical analogy between these structures was established [3]. In recent years, the advent of more sophisticated instrumental and analysis techniques have provided important insights into the polarization properties of beetle cuticles [4–11]. Thus, polygonal structures sized between 10 and 15 μm have been identified as responsible for selective reflection of left-handed polarized light [4,5]. Near to normal incidence reflectance of circularly polarized light [6,7], ellipsometry [8], and Mueller-matrix ellipsometry [9,10] have been used. More recently, much richer information on the chirality-induced polarization effects in the cuticle of several beetles has been provided by variable angle Mueller matrix spectroscopic ellipsometry [11]. Particularly, detailed information regarding beetles showing both left- and right-handed near-circular polarization was shown [11].

Although the Mueller matrices of the cuticles of several species of beetles have been reported, they represent a small number among the existing ones and, the investigation of other species will provide a more complete map of their polarization properties. Also, many details need further analysis for a better understanding of the fundamental properties of Mueller matrices determined from beetle cuticles. Thus, the investigation of the number of independent elements in the Mueller matrix as well as properties like reciprocity, symmetries, and depolarizance, are of importance for a reliable modeling of the experimental data.

In this work, we investigate the properties of the Mueller matrix of the cuticle of the scarab beetle *Cotinis mutabilis* (Gory and Percheron 1833). By using variable angle Mueller matrix spectroscopic ellipsometry, the interrelationships among the elements are investigated directly on the evidence provided by the experimental data. Also, based on a general Mueller matrix of a non-depolarizing chiral system, further relations are investigated as well as symmetries resulting from sample rotation. A short discussion on the interference oscillations observed in the elements of the Mueller matrix is also provided.

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2. Experimental details

The scarab beetle *C. mutabilis* is a species found in Mexico and the southwestern part of the United States [12]. As can be seen in the insert of Fig. 1, *C. mutabilis* shows a shiny metallic-like color on its abdominal side, which is comprised of a segmented structure. The color among specimens varies largely [12]. In this work, we study a specimen whose color strongly depends on the viewing angle; it looks red at normal incidence but turns green for grazing angles. For the study, samples of the cuticle were cut from the segments as small pieces (2 × 2 mm$^2$) using a sharp knife and tweezers. The selected areas were as flat and smooth as possible. In order to determine the polarization properties of the specimen, Mueller-matrix spectra were acquired using a dual rotating compensator ellipsometer (J. A. Woollam Co., Inc.). For that, the samples were mounted on glass slides with double-sided tape. Focusing probes with numerical aperture 0.045 for both the incident beam and the optical plane of incidence was parallel to the longitudinal side of the specimens, Mueller-matrix spectra were acquired using a dual rotating compensator ellipsometer (J. A. Woollam Co., Inc.). For that, the measurements were performed in the wavelength range of 1000 nm at angles of incidence between 20 and 75° in steps of 5°.

The full polarization properties of a sample are contained in the $4 \times 4$ Mueller matrix ($\mathbf{M}$), which for oblique incidence relates the Stokes vectors of the incident ($\mathbf{S}_i$) and reflected ($\mathbf{S}_r$) light beams according to [13].

$$\mathbf{S}_r = \mathbf{MS}_i = \begin{bmatrix} m_{11} & m_{12} & m_{13} & m_{14} \\ m_{21} & m_{22} & m_{23} & m_{24} \\ m_{31} & m_{32} & m_{33} & m_{34} \\ m_{41} & m_{42} & m_{43} & m_{44} \end{bmatrix} \mathbf{S}_i.$$  

(1)

In this work, we use normalized elements and $m_{11} = 1$. The Stokes vectors have the components,

$$\mathbf{S} = \begin{bmatrix} I \\ Q \\ U \\ V \end{bmatrix} = \begin{bmatrix} I_p + I_s \\ I_p - I_s \\ I_c \sin(2\psi) - I_s \cos(2\psi) \\ I_s \sin(2\psi) \cos(2\psi) \end{bmatrix}.$$  

(2)

where $I_p, I_s, I_c$, and $I - 45$ are, respectively, the irradiances of polarized light components parallel ($p$), perpendicular ($s$), at +45° and at −45° with respect to the plane of incidence; $I_p$ and $I_s$ are the intensities of right- and left-handed circularly polarized light.

3. Results and discussion

3.1. Cuticle microstructure

The helicoidal plywood structure associated to the Bragg-like reflection from the cuticle of beetles is schematically shown in Fig. 1(a). The structure is comprised of lamellae where in each lamella the chitin-protein nanofibrils are oriented in a specific direction which is defined by a unitary vector, the so-called director. The director is continuously twisted between adjacent lamellae by a small angle. The “pitch” ($\Lambda$) of the structure is the distance separating two lamellae after a full rotation of 360°. Fig. 1(b) shows a scanning electron microscopy cross-section image of the cuticle of *C. mutabilis*. At the top is located the epicuticle and observed as a thin layer of about ~100 nm. Below lies the exocuticle showing a multilayered structure. Depending on the thickness of the layers, two regions can be distinguished in the exocuticle, the outer exocuticle and the inner exocuticle with thicknesses 7.2 and 4.1 µm, respectively, for this specimen. At larger magnifications the fibril structure can be partially resolved.

3.2. Mueller-matrix spectra of *Cotinis mutabilis*

Fig. 2 shows the experimental Mueller-matrix spectra of *C. mutabilis* in a contour map representation as a function of the angle of incidence ($\theta$) and wavelength ($\lambda$). The contours of positive values are limited with lines whereas the negative ones are only color-coded. Although some details are lost with this representation, it allows the identification of global features in $\mathbf{M}$. Details are discussed with specific spectra in sections below. In Fig. 2 it can be observed that for most angles of incidence and wavelengths $\mathbf{M}$ is block-diagonal. This structure of $\mathbf{M}$ resembles that of an isotropic sample (or pseudo-isotropic for uniaxial samples with the optic axis normal to the surface), where additionally $m_{22} = 1, m_{12} = m_{21} = -N, m_{33} = m_{44} = C$, and $m_{34} = -m_{43} = S$. The parameters $N, S, C$ and $C$ are defined in terms of the ellipsometric angles $\Psi$ and $\Delta$ according to $N = \cos(2\Psi), C = \sin(2\Psi)\cos(\Delta), S = \sin(2\Psi)\sin(\Delta)$. For instance, at the angle of incidence $\theta = 20°$ the isotropic-like structure of $\mathbf{M}$ is found for $\lambda/\Delta[500,750]$ nm, whereas at $\theta = 75°$ it is true for $\lambda/\Delta[450,550]$ nm. Furthermore, for dielectric materials $\Psi = 0$ at the Brewster angle ($\theta_B$), which leads to $m_{12} = m_{21} = -1, m_{33} = m_{44} \approx 0$, and $m_{34} = m_{43} \approx 0$. The latter conditions are fulfilled at $55° < \theta_B < 60°$ envisaging a dielectric character of the materials comprising the beetle cuticle with an effective refractive index $n_{eff} \approx 1.5$. Please cite this article as: E. Muñoz-Pineda, et al., Thin Solid Films (2013), http://dx.doi.org/10.1016/j.tsf.2013.11.144
Fig. 2. Contour maps of the experimental Mueller-matrix spectra of *C. mutabilis* at angles of incidence between 20° and 75°. The contours of positive values are limited with lines whereas the negative ones are only color-graded. White areas correspond to values between −0.1 and 0.1. Notice the block-diagonal structure except for a narrow spectral range within the visible range (400–700 nm) where the Bragg-like reflection takes place. A Brewster angle (θB) can be obtained where m_{12} = m_{21} = −1, m_{33} = m_{44} ≈ 0, and m_{34} = m_{43} ≈ 0. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In Fig. 2 it can be noticed that $\mathbf{M}$ deviates from the (pseudo-) isotropic case in a rather narrow spectral range depending on the angle of incidence, e.g. λ (nm) & θ = 20°. Of particular interest is when the cuticle of the beetle is illuminated with unpolarized light $\mathbf{S}_i = [1,0,0,0]^T$ (T denotes transpose). In this case and according to Eq. (1), the Stokes vector of the reflected beam is determined from the elements in the first column of the Mueller-matrix $\mathbf{S}_r = [m_{21},m_{31},m_{41}]^T$, the so-called polarizance of the sample. It can be noticed that $m_{41} < 0$ indicating that the incident light is reflected with left-handed polarization; the most negative values of $m_{41}$ are found at low angles of incidence and shift to shorter wavelengths for grazing incidence. This shift is visually detectable directly from the cuticle of the specimen which looks red at normal incidence but the color changes to green when the viewing angle increases. The ellipticity and azimuth of the polarization ellipse as well as the degree of polarization, can be calculated with relationships between the $m_{ij}$ elements providing a full description of the polarization state of light reflected from the cuticle of the beetle for incident unpolarized light [11].

On the other hand, an average measure of the depolarization produced by a system for all incident pure states is given by the depolarizance ($D$),

$$D = 1 - P(4) = 1 - \left[ \frac{1}{3} \left( \frac{\text{tr}(\mathbf{M}^T\mathbf{M})}{m_{21}^2} - 1 \right) \right]^{1/2}$$

where $P(4)$ is the degree of polarimetric purity [14]. Fig. 3 shows the dependence of $D$ with angle of incidence and wavelength for beetle’s cuticle in a polar contour graph. It can be observed the relatively low values of $D$ for most of wavelengths for the measurements at all angles of incidence. Additionally, the spectral decomposition (not shown) leads to one eigenvalue for wavelengths where $D > 0.02$ whereas the remaining eigenvalues smaller than 0.05. In the complementary spectral range where $D < 0.02$, two eigenvalues were found indicating that $\mathbf{M}$ can be sum decomposed in two matrices, presumably a mirror and a circular polarizer.

3.3. Symmetries and interrelationships of Mueller matrix elements

The relatively large values of the elements in the off-diagonal blocks of the Muller-matrix of *C. mutabilis* in Fig. 2 allow for an investigation of their interrelationships. A careful inspection provides the following relationships for all angles of incidence: $m_{12} = m_{21}, m_{31} = -m_{31}, m_{14} = m_{41}, m_{23} = -m_{32}, m_{24} = m_{42}$, and $m_{34} = -m_{43}$ leading to 9

Fig. 3. Polar contour map of the depolarizance produced by the cuticle of *C. mutabilis* calculated with Eq. (3) from the data in Fig. 2.
independent elements. This specific symmetry between has earlier been reported for isotropic and homogeneous chiral systems from a first order analysis in the chiral parameter [15]. In that work, the principal impact of chirality was expressed through the cross-polarized reflection coefficients $r_{ps} = -r_{sp}$ of the $2 \times 2$ Jones matrix ($\mathbf{J}$), which relates the $p$- and $s$- components of the incident ($E_i$) and reflected ($E_r$) electric field of the electromagnetic waves [13].

$$\begin{bmatrix} E_{tp} \\ E_{ts} \end{bmatrix} = \begin{bmatrix} r_{tp} & r_{ps} \\ r_{sp} & r_{ss} \end{bmatrix} \begin{bmatrix} E_{ip} \\ E_{is} \end{bmatrix}. \quad (4)$$

The Mueller matrix of a non-depolarizing optical system represented by the Jones matrix in Eq. (4) can be calculated with the standard procedure $\mathbf{M}_j = (\mathbf{J} \otimes \mathbf{J}^T)^{-1}$ where $\otimes$ denotes the Kronecker product, the asterisk means complex conjugation, and $\mathbf{T}$ is the matrix relating the Stokes and coherency vectors [13]. The components of the coherency vector are the elements of the coherency matrix in the Jones representation. For the present case, $\mathbf{M}_j$ was calculated with the additional constraint $r_{ps} = -r_{sp}$ leading to,

$$\mathbf{M}_j = \begin{bmatrix} (R_{pp} + R_{ss} + 2R_{ps})/2 \\ (R_{pp} - R_{ss} - 2R_{ps})/2 \\ -R_{sp} + R_{ps} \\ \text{Im} \left( (R_{sp} + R_{ps})/2 \right) \end{bmatrix},$$

$$R_{ps} = \left| r_{ps} \right|^2. \quad (5)$$

where $R_{ps}$ appears in the diagonal elements of Eq. (5) are absent in the first order analysis previously reported for isotropic and homogenous chiral systems [15]. It is clear that $\mathbf{M}_j$ in Eq. (5) displays the same symmetries as those found in Fig. 2 and, therefore, it represents a starting point to investigate a non-depolarizing estimate of the experimentally determined (depolarizing) Mueller matrix. In fact, in previous works [5-9] the optical properties of light reflected from beetle cuticles have been analyzed by numerically computing the Jones matrix in Eq. (4) using the Berreman method [16]. This method was originally developed for the analysis of the reflectance and transmittance spectra of cholesteric liquid crystals. Continuing with the analysis of the experimental data, it was found that $m_{31} = m_{44}$ in the experimental Mueller matrix as well as a scaling relationship of $m_{31}$ and $m_{44}$ with $m_{23}$ as is shown in Fig. 4 for selected angles of incidence. The two former elements show decreasing values with $\theta$ whereas $m_{23}$ increases at grazing incidence. This behavior with the angle of incidence was previously noted from a first order analysis in the chiral parameter [17]. The results shown in Fig. 4 reduce the number of independent elements to seven in the normalized Mueller matrix. For a homogeneous depolarizing medium with uniformly distributed optical properties and with motion-reversal symmetry, the number of independent parameters is ten [18].

With respect to the diagonal elements, $\mathbf{M}_j$ in Eq. (5) suggests two independent ways to estimate the normalized (indicated with superscript $n$) cross-polarized reflectance ($R_{ps}^n$) from the experimental Mueller matrix,

$$\left\langle R_{ps}^n \right\rangle = (1 - m_{23})/2, \quad (6)$$

and,

$$\left\langle R_{ps}^n \right\rangle = (m_{44} - m_{31})/2. \quad (7)$$

Fig. 5 shows the spectra calculated from Eqs. (6) and (7) for selected values of $\theta$. It is clear that the two calculations of $\left\langle R_{ps}^n \right\rangle$ are nearly identical. This result decreases the number of independent elements in the experimental Mueller matrix from seven to six. Also, in Fig. 5 the corresponding $m_{44}$ values are shown indicating a correlation with $\left\langle R_{ps}^n \right\rangle$. It can be observed that for low angles of incidence, $m_{44} < 0$ (characteristic of left-handed polarization) in a well defined spectral region. However, as the angle of incidence increases some sharp maxima appear in the...
short-wavelength region. These maxima correlate well with peaks in \( \langle R_{ps} \rangle \); more evidence is given below.

3.4. Muller-matrix symmetry effects of sample rotation

According to the helicoidal plywood structural model of the beetle cuticle shown in Fig. 1(a), it is structurally invariant under a rotation of \( \phi = 180^\circ \) around the z-axis. Therefore, invariance is expected for measurements performed at two such orientations. This result was experimentally confirmed for *C. mutabilis* and is illustrated in Fig. 6 with the spectra of \( m_{21}, m_{31}, \) and \( m_{41} \) for the lowest and highest measured angles of incidence \( (\theta = 20^\circ \text{ and } 75^\circ) \). From this symmetry it can be concluded that the cuticle of *C. mutabilis* is a reciprocal medium.

On the other hand, at normal incidence the sample rotation of \( \phi = 90^\circ \) around the z-axis interchanges the p and s components and according to MJ in Eq. (4), a change of sign is expected in some elements. Since normal incidence measurements are not accessible with the current ellipsometric system, some insight on this symmetry is provided with the measurement at the lowest angle of incidence \( \theta = 20^\circ \). As can be observed in Fig. 7, the sample rotation of \( \phi = 90^\circ \) causes a clear inversion of \( m_{21} \) and \( m_{31} \) leaving invariant \( m_{41} \). Nevertheless, as the angle of incidence increases such symmetry is lost as shown for \( \theta = 75^\circ \). In particular, it is noteworthy the strong effect produced by this sample rotation on \( m_{41} \) showing peaks with positive and relatively high values (~0.4).

As was noted in paragraphs above, the sharp peaks appearing in \( m_{41} \) at large angles of incidence are correlated with the peaks in the normalized cross-polarized reflectance \( \langle R_{ps} \rangle \). The correlation is more clear in the spectra of Fig. 8 which correspond to the measurement after sample rotation of \( \phi = 90^\circ \). In the reflectance spectra of monodomain cholesteric liquid crystals, complex interference patterns appear due to the mixing of the optical eigen-modes propagating in the structure [19–22]. Similar phenomena might explain the sharp peaks observed in Fig. 8 at a grazing incidence in the short wavelengths spectral range.

![Fig. 6. Experimental spectra of Mueller-matrix elements of \( m_{21}, m_{31}, \) and \( m_{41} \) at sample orientations \( \phi = 0 \) and 180°. Left and right panels correspond to angles of incidence 20 and 75°, respectively. Notice the invariance of the spectra in the direct and reverse orientations.](image)

![Fig. 7. Same as in Fig. 6 but for sample orientations \( \phi = 0 \) and 90°. At angle of incidence \( \theta = 20^\circ \) this rotation changes the sign of \( m_{21} \) and \( m_{31} \) whereas \( m_{41} \) remains invariant. A more complex behavior results for \( \theta = 75^\circ \).](image)

![Fig. 8. Same as Fig. 5 but after 90° sample rotation. At larger angles of incidence, sharp peaks appearing in \( m_{41} \) at short wavelengths correlate well with those in \( \langle R_{ps} \rangle \).](image)
orientations of the director in different areas (polydomain structure), such sample rotations would produce only statistically equivalent \( m_{21} \) or \( m_{31} \) spectra.

3.5. Interference oscillations

In Figs. 4–8, the spectra of the Mueller matrix elements show clear interference oscillations. However, the dependence of the frequency of the oscillations with wavelength and angle of incidence is complex. Indeed, our ongoing investigation indicates that they are related to the propagating modes in the cuticle of \( C. \) mutabilis. A comprehensive analysis will be reported elsewhere. Nevertheless, they are indicative of highly transparent materials in the exocuticle and provide a mean to estimate the thickness of the layer responsible for the polarization properties. As is known, multiple reflections inside a film of thickness \( d \) will produce maxima or minima in the optical measurements when the phase factor \( \beta = \pi m \), where \( m \) is an integer number. Hence, an estimated value of the cuticle thickness can be determined according to the equation,

\[
\beta = \frac{4nD}{\lambda} \sqrt{N_{\text{eff}}^2 - \sin^2 \theta} = mn.
\]

Thus, from the spectra of \( m_{21} \) at \( \theta = 20^\circ \) and \( n_{\text{eff}} = 1.5 \), Eq. (8) gives \( d = 7.5 \mu m \) as the thickness of the region producing the Bragg-like reflection in agreement with the value determined from the image in Fig. 1(b).

4. Conclusions

The properties of the Mueller matrix of light reflected from the cuticle of the scarab beetle \( C. \) mutabilis have been investigated. The reflection of left-handed polarized light is demonstrated with a strong blue-shift as the angle of incidence increases. Highly transparent materials comprising the beetle cuticle were revealed. The Bragg-like reflection originates from a region estimated to be 7.5 \( \mu m \) thick. The off-diagonal elements of \( \mathbf{M} \) in the experimental data obey simple symmetry relationships resulting from the relation \( r_{ps} = -r_{sp} \) for the cross-polarized reflection coefficients between p- and s-polarizations of chiral systems. Further relationships between the elements of \( \mathbf{M} \) were experimentally investigated on the basis of a non-depolarizing Mueller matrix reducing the number of independent elements to six. Rotational symmetries evidence relatively large areas with a well-defined director of fibrils in the cuticle of the beetle \( C. \) mutabilis.

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