Interface properties and refraction of light in twin-layered organic semiconductors

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Abstract. Polytypism associated with periodic twinning with mirror-like orientation of the unit cell in successive layers is often found in crystals of conjugated molecules. The negative and total refraction of light at the interface between the twinned layers is discussed in the case of monoclinic molecular solids of quaterthiophene.

1. Introduction

In recent years, much attention has been devoted to organic semiconductors and oligothiophenes (nT) are often considered as representative of these materials [1]. Moreover, there has been considerable interest in novel meta-materials exhibiting various phenomena associated with negative refraction [2]. Most examples of these peculiar phenomena have been demonstrated in the microwave region but are also feasible at optical frequencies using periodic photonic structures [3]. Negative refraction has also been demonstrated to occur at the interface between a normal medium and a uniaxial medium with one of the components of the electric and magnetic permittivity tensors being negative [4]. Another example has been demonstrated using twinned crystals of a III-IV semiconductor alloy [5]. Due to the match of the refractive index at the interface, the authors showed that there is no reflection and negative refraction occurs over a range of angles of incidence. By analogy we demonstrate that such a homo-junction and such phenomena can occur in twin crystals of conjugated molecules.

Many solids of conjugated molecules form monoclinic crystals with two or four molecules per unit cell and the first singlet molecular electronic state gives rise to two accessible exciton levels, the \( a_u \) and \( b_u \) Davydov components [6,7]. The former is polarized along the monoclinic \( b \) axis, while the transition moment (usually indicated by the \( L \) axis) to the \( b_u \) level is in the \( ac \) plane, in the case of 4T at about 27° to the normal \( c^* \) to the \( ab \) accessible face [8]. The latter transition can be detected by selecting \( ac \) as plane of incidence and \( p \) polarized light, a configuration which corresponds to mixed transverse/longitudinal propagation of light [9-13]. For the understanding of the 4T optical properties, the study of the crystal growth mode has been fundamental [14] and it has also revealed several
aspects which are interesting for a further optical investigation. The recognition of specific patterns on
the crystal surface lead to the discovery of polytypism associated with periodic polysynthetic twinning
with mirror-like orientation of the unit cell in successive layers with respect to the \( ab \) plane [15,16].
These twinned structures are often found and represent readily available interfaces between the layers.
Their optical properties are here discussed. In particular, we focus attention on the refraction and
reflection of light at the interface between two twin crystals.

2. Results and discussion

Crystals of the low-temperature polymorph of 4T [17] were grown by the floating drop technique
[14]. Figure 1 shows two scanning electron microscopy (SEM) images of the edge of a 4T crystal as
taken with 3 kV acceleration voltage of the electron beam. The typical layered structure is observed
with the most developed face along the \( ab \) plane. As discussed elsewhere [15,16], from the analysis of
the surface properties one deduces that an anomalous stacking of macro-layers is often found. The
rotation about \( c^* \) of each macro-layer with respect to the next ones generates alternating layers of
molecules tilted to the right or to the left with respect to the surface normal (inset of Fig. 1). This
appearance of periodic polysynthetic twinning in alternate A/B lamellar systems is attributed to
heterogeneous nucleation on the face of nuclei with different orientations [15,16].

![Figure 1. SEM images of a 4T crystal. Inset: sketch of the crystal’s lamellar structure [15,16].](image)

In this context, we are interested in the peculiarities of crystal optics at the interface between twin
layers. The optical properties can be described by the complex dielectric tensor \( \varepsilon \) [18] which for 4T
has recently been reported [8] and is diagonal with respect to principal axes taken along the \( b \) axis and
in the \( ac \) plane, along and perpendicular to \( L \). Refraction at the interface between two lamellas with
different orientations (A and B) has been studied by solving Fresnel’s equation in both media and
applying the usual boundary conditions on the tangential part of the fields. The direction of a light
beam propagating inside the two lamellas is given by the time averaged Poynting vector
\[ S = [c \cdot \text{Re}(\mathbf{E} \cdot \mathbf{H}^*)/(4\pi)] \]. In our calculations we take \( ac \) as the plane of incidence and assume that in the
first medium the \( L \) axis is tilted by a positive angle \( \alpha \) to the surface normal, while in the second
medium it is tilted by \( -\alpha \). The case of \( s \) polarization is trivial since the \( b \) polarized ordinary waves are
totally refracted without deviation. In the case of \( p \) polarization, on the other hand, the waves are in
general extraordinary and it is possible to have negative total refraction. Figure 2 shows the computed
angle of refraction as a function of the angle of incidence. In the range of energies we investigate,
there is always a region of negative refraction, where the incidence and refraction angles have opposite
sign. We also note that the curve obtained at energy \( h\omega = 2 \) eV, when absorption is weak, is nearly a
straight line, while at higher energies the curve bends and some incidence angles are forbidden. The
explanation is that as energy gets closer to the main excitonic transition, light propagating in a
direction perpendicular to \( L \) is increasingly absorbed and become evanescent (we consider evanescent
those waves for which \( \text{Im}[k_n] > \text{Re}[k_n] \)). Reflectivity of the same interface has been calculated, and it
vanishes for every angle of incidence and photon energy value. This phenomenon is known as total
refraction and it is due to the matching of the dielectric functions.
Taking into consideration the previous results, we underline that the quality of the samples is often probed under an optical microscope with crossed polarizer and analyzer. Indeed, if \( ac \) is taken as plane of incidence and the incident light is either \( p \) or \( s \) linearly polarized, the transmitted or reflected light by a crystal maintains its polarization since \( b \) is a principal axis of the dielectric tensor and \( a \) lies in the \( ac \) principal plane. However, this does not allow to distinguish between single crystals and twinned crystals as those discussed here. For this purpose, absorption measurements at oblique incidence with parallel polarizer and analyzer are required [8,12,19].

![Figure 2](Image)

**Figure 2.** Angle of refraction as a function of the angle of incidence at the interface between twinned A and B domains, for \( \hbar \omega = 2 \text{ eV} \) (solid line), 2.5 eV (dashed line), 3.0 eV (dotted line) and 3.2 eV (dash-dotted line). We considered \( ac \) as the plane of incidence and \( p \) polarization, so that the waves are extraordinary in both media. *Inset:* orientation of 4T unit cell in A and B domains with respect to the direction of the incident light beam.

In Fig. 3 we report the calculated absorption spectra of both a single crystal and a twinned crystal of the same total thickness, made of two equally thick domains. The spectra have been calculated by applying a 4x4 transfer matrix method [20]. We notice that the absorption of the single crystal strongly depends on the sign of the angle of incidence and vanishes at 50° because the refracted light propagates along the \( L \) axis. On the contrary, in a twinned crystal absorbance never vanishes since the contributions from the two layers vanish for different angles of incidence. In Fig. 3(b), the absorption minimum is at normal incidence because the two domains have equal thickness.

In Fig. 4, we report the experimental absorption spectra of a twinned crystal as measured at room temperature with \( ac \) as plane of incidence and \( p \) polarized light, using a Perkin-Elmer Lambda 900 spectrometer equipped with Glan-Taylor calcite polarizers. The absorption peak reaches its minimum intensity at 20° angle of incidence. We also report the simulated spectra obtained for a sample made of two twinned layers of thickness 0.15 \( \mu \text{m} \) and 0.07 \( \mu \text{m} \), where the thickest one is assumed to have its \( L \) axis positively oriented to the surface normal. Since the reflectivity between the layers is zero, the absorbance spectra of a multi-layered sample with alternating A and B layers is the same as those in
Fig. 4, provided that the total thickness of layers A and B are 0.15 μm and 0.07 μm, respectively. The numerical data compare very well with the experimental data, thus confirming the usefulness of oblique incidence absorption to obtain morphological information on the sample.

**Figure 3.** Absorption spectra of a 0.3 μm thick single crystal (a) and a crystal made of two twinned domains of thickness 0.15 μm each (b) calculated at different angles of incidence with ac as the plane of incidence and p polarization.

3. Conclusions

Conjugated molecules form crystals whose patterns, in some cases, reveal the presence of periodic polysynthetic twins which are symmetrically oriented with respect to the ab plane and which represent readily available interfaces between the layers with a peculiar property: they enable refraction of light without any reflection. Moreover, for a range of angles of incidence, negative refraction is predicted. This phenomenon, which has also been reported in the literature for twin structures of yttrium vanadate [5], is discussed in this work in the case of monoclinic 4T crystals, whose optical spectra in the UV-VIS region are given. This material is taken as representative of the wide class of molecular solids which, in the transparency region, can be used for steering light without reflection losses, in contrast to the inevitable loss when refraction is obtained by refractive index mismatch.

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Figure 4. Experimental absorption spectra for a crystal with twinned domains as measured at –20° (lower triangles), 0° (squares), 20° (circles) and 40° (upper triangles) angle of incidence. We also report in solid lines the absorption spectra calculated for a crystal made of two twinned domains of thickness 0.15 μm and 0.07 μm. As in the previous figure the plane of incidence is ac and the polarization is p.

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