



Optical spectra and dielectric function of quinquethiophene single crystals

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Abstract

The dielectric function of quinquethiophene crystals are calculated in the framework of macroscopic theory using Lorentz oscillators to fit the measured reflectance, absorption, and ellipsometry spectra assuming a simple uniaxial model with only electronic transitions. These dielectric function are compared with those obtained from the reflectance spectra via a Kramers-Kronig transformation.

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1. Introduction

Over recent years, many papers have been published that deal with the optical properties and the electronic states of conjugated molecular crystals. In particular, oligothiophenes (nT), which crystallize in the monoclinic crystallographic system, are frequently considered since they have gained

importance in technologies that exploit their characteristics in polymer and thin film form [1–3]. However, there is still no comprehensive theory of their opto-electronic properties, largely due to the lack of supporting experimental data hindered by practical limitations in that crystals are usually thin, plate-like and with only one developed face. The Frenkel–Davydov exciton model describes how the first non-degenerate singlet molecular states resonantly split in the crystal into a number of bands equal to the number of molecules in the unit cell [4]. For example, in oligothiophenes with four molecules per unit cell, the lowest energy

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molecular state gives rise to four bands, only two of which are optically accessible with different polarizations, the upper transition possessing a high oscillator strength [2–5]. A lot of data are reported in the literature, but detecting this transition in transmission is often complicated by saturation and crystal quality [3,5–14]. Recently reported spectra from thin crystals without the usual saturation problems reveal a strong polarized peak, which is generally attributed to the upper Davydov component, but its position is strongly affected by the polarization field generated by the oscillating dipoles and depends on the angle of the propagating wave with respect to the dipole direction. Indeed, in these media, two types of propagating wave are possible: purely transverse ordinary waves and mixed transverse and longitudinal polarization extraordinary waves. The mixed nature of the wave depending on the direction of the wave vector gives rise to the directional dispersion of the extraordinary polarization [15,16], which has been experimentally observed [9,11,12,14,16]. Few attempts to determine the dielectric tensor of oligothiophenes have recently been reported in the literature. For example, a deep analysis of the reflectance data has been recently carried out for 6T single crystals and the optical function deduced from the Kramers-Kronig (KK) relations and interpreted in terms of the electronic band structure of the material [16].

Here we report polarized reflectance, absorbance, and ellipsometry spectra of 5T single crystals over a wide spectral range. All these data and a simple Lorentz model for the different transitions allowed deducing the dielectric tensor of 5T in the framework of macroscopic dielectric theory assuming an uniaxial model. The results are compared with those obtained from reflectivity and the KK relations.

2. Experimental

Single crystals of 5T were grown as thin flakes about 1 mm^2 in size with thickness ranging from few hundreds of nm to few tens of μm . The 5T crystallographic structure is monoclinic with $a = 39\text{ \AA}$, $b = 7.77\text{ \AA}$, $c = 6\text{ \AA}$, $\beta = 97.7^\circ$ [17]. The

crystal face accessible for optical measurements corresponds to the bc lattice plane.

Polarized absorbance measurements were performed at room temperature with resolution down to 10 meV, using a spectrometer Perkin-Elmer Lambda 900, equipped with Glan-Taylor calcite polarizers. Prior to optical measurements, single crystals were selected by homogeneously extinguishing light under crossed polarizers. Near-normal incidence reflectance measurements were performed with the same apparatus equipped with a home-made accessory, the absolute reflectance values being obtained by correcting the measured data for the instrumental spectral response. The latter was in turn deduced by comparing the measured reflectance spectrum of an Al mirror with the absolute reflectivity spectrum of the same mirror collected with a PELA-1029 VW accessory for the spectrometer. Non-normal incidence reflectance was measured using an accessory for the same spectrophotometer. A collimated spectroscopic ellipsometer Sopra model ES4g was used to determine the used parameters $\tan(\psi)$ and $\cos(\Delta)$. The analyzer angle was either fix or follows the ψ value previously measured (tracking).

3. Experimental results

The continuous curves in Figs. 1(a)–(c) show the normal incidence absorbance and near-normal incidence reflectance spectra of a 5T single crystal taken on the bc crystal face with the electric field of the incident light along the b - or c -axis. The c polarized spectra show a strong peak centred at about 3.6 eV in the case of absorption and 3.4 eV, with a minimum at about 3.7 eV in the case of reflection. This structure almost completely disappears in the case of b polarization, the weak structure at this energy in Fig. 1(b) being attributed to the quality of this sample. Indeed, in some cases, the thickest crystals contain few flakes slightly rotated with respect to each other around a^* . The lineshape of the spectra in Fig. 1(b) below about 2.5 eV and the detection of interference fringes are attributable to an enhancement of the measured reflectance due to the light reflected from the back of the sample, since at these energies

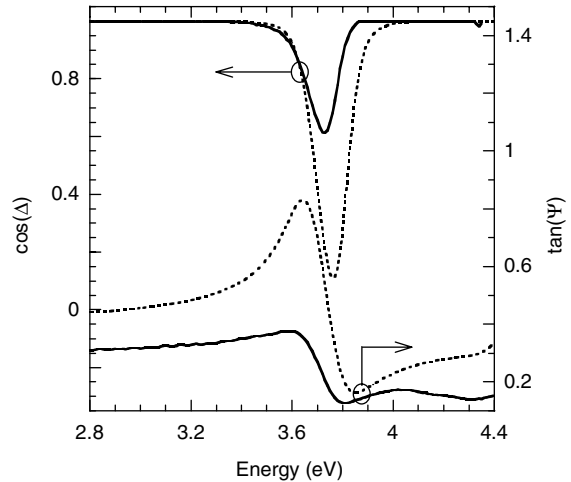
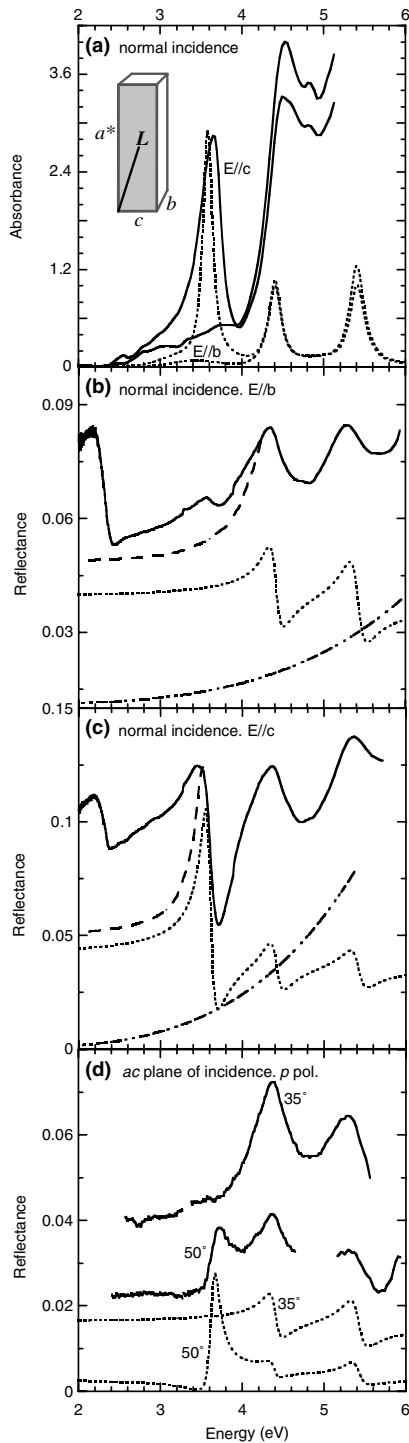


Fig. 2. Ellipsometry functions measured (continuous lines) at 70° angle of incidence on the bc 5T face with ac as plane of incidence and calculated using the Lorentz model (dotted lines).

the crystal is transparent (see Fig. 1(a)). For energies higher than 4 eV, the reflectance spectra show broad peaks centred at about 4.75 eV and 5.7 eV, whilst an absorbance peak is detected at 4.5 eV with a shoulder at 4.8 eV. The continuous lines in Fig. 1(d) show the reflectance spectra of the 5T single crystal taken at different angles of incidence on the bc crystal face with ac as plane of incidence and p polarization. In the high energy region, the position of the main bands does not substantially depend on the angle of incidence. On the contrary,

Fig. 1. (a) Absorbance spectra of a 5T single crystal as measured (—) at normal incidence with the electric field of the incident light either along the c - or b -axis and corresponding spectra (···) calculated for a 300 nm thick sample using the principal dielectric function obtained from the Lorentz model. Inset: sketch of the 5T unit cell and of the L -axis direction in the ac^* plane (the accessible face is along the bc plane). (b,c) Reflectance spectra of a 5T single crystal as measured (—) at near-normal incidence with the electric field of the incident light along either the b -axis (b) or the c -axis (c) and corresponding spectra (···) calculated using the Lorentz model. The low energy tails (---) and the scattering background (-·-·-) used when applying the KK transformations are also reported. (d) Reflectance spectra in arbitrary units of a 5T single crystal as measured (—) for different angles of incidence with ac as plane of incidence and p polarized light and corresponding spectra (···) calculated using the Lorentz model. At the energies where the instrument response is not known, the measured spectra are omitted.

the minimum at 3.7 eV clearly detected at normal incidence (see Fig. 1(c)) is not observed for $\theta = 35^\circ$ and a peak at about the same energy is found in the case $\theta = 50^\circ$. Finally, the continuous lines in Fig. 2 show the ellipsometry spectra taken at 70° angle of incidence on the *bc* 5T face with *ac* as plane of incidence.

4. Discussion

The response of a material to the electromagnetic radiation can be described in terms of the electric displacement vector $\mathbf{D} = \hat{\epsilon}\mathbf{E}$, \mathbf{E} being the driving photon field and $\hat{\epsilon}$ the dielectric function which can be expressed in the form of Lorentz oscillators

$$\hat{\epsilon} = \epsilon_\infty + \sum_j \frac{\omega_{Tj}^2 f_j}{\omega_{Tj}^2 - \omega^2 - i\gamma_j \omega} \quad (1)$$

where j indicates the different transitions with oscillator strength f_j and ϵ_∞ is a background contribution from higher energy transitions. The energy $\hbar\omega_{Tj}$ is the resonant energy corresponding to the transverse excitation, and γ_j is a generic damping term. In general, the dielectric function depends on the angular frequency ω (time dispersion) and on the magnitude of the wave vector (spatial dispersion) since the relation between \mathbf{D} and \mathbf{E} is not local (i.e. \mathbf{D} at a point is not determined solely by \mathbf{E} at that point). However, this latter aspect will be neglected in this context. Within these approximations and considering the monoclinic crystallographic structure of 5T, the dielectric tensor is given by

$$\hat{\epsilon} = \begin{vmatrix} \hat{\epsilon}_{xx} & 0 & \hat{\epsilon}_{xz} \\ 0 & \hat{\epsilon}_{yy} & 0 \\ \hat{\epsilon}_{zx} & 0 & \hat{\epsilon}_{zz} \end{vmatrix} \quad (2)$$

with respect to a Cartesian system with the y -axis directed along the monoclinic axis (b in the case of 5T). Although it can be brought into diagonal form for a convenient choice of principal axes, the two principal axes perpendicular to b also vary with frequency. Similarly as reported for other oligothiophenes in the energy region of the first transition (polarized along the long molecular

axis), we choose to neglect the axial dispersion towards the high frequency region because the upper resonances originate from several molecular transitions and we are unable to accurately take it into account. Hence, the diagonal form is defined by the b -axis and the vectorial sum L on the unit cell of the dipoles polarized along the long molecular axis, so that L is inclined at about $\alpha = 24^\circ$ with respect to the normal to the *bc* face (see the inset in Fig. 1(a)). The diagonal tensor reads

$$\epsilon = \begin{vmatrix} \hat{\epsilon}_{\perp L} & 0 & 0 \\ 0 & \hat{\epsilon}_b & 0 \\ 0 & 0 & \hat{\epsilon}_{\parallel L} \end{vmatrix} \quad (3)$$

where the components are related to those of tensor (2) by means of a rotation matrix [15].

Simulation of the spectra in Figs. 1 and 2 can be based on a model where several Lorentz oscillators as in Eq. (1) and polarized in different directions sum up each component of the dielectric tensor (3). Table 1 shows the corresponding parameters adjusted to obtain the best description of all the experimental curves in Figs. 1 and 2. The lowest energy transition is L polarized and contributes only to the $\epsilon_{\parallel L}$ component, and an additional oscillator at 4.4 eV is taken into consideration originating from higher L polarized molecular transitions. The low energy resonance in the $\epsilon_{\parallel L}$ component corresponds, within the approximations of the model, to the transverse component of the b_u Frenkel exciton originating from the first molecular transition. The band in the spectra measured at normal incidence in Figs. 1(a) and (c) is shifted to higher energy with respect to the transverse component as a consequence of directional dispersion. When compared with the parameters

Table 1
Parameters used for calculating by Eq. (1) the function $\hat{\epsilon}_{\parallel L}$ ($j = 1, 2$), $\hat{\epsilon}_{\perp/L}$ ($j = 2, 3$) and $\hat{\epsilon}_b$ ($j = 2, 3$) shown in Fig. 3

j	1	2	3
$\hbar\omega_{Tj}$ (eV)	3.28	4.4	5.4
f_j	0.5	0.02	0.02
γ_j		0.04 $\hbar\omega_{Tj}$	
ϵ_∞		2.2	

reported in the literature for other oligothiophenes [10] a lower f_j value for the first L polarized transition is reported in Table 1, as a consequence of the higher energy of the transverse component. Higher molecular transitions at 4.4 eV and 5.4 eV and polarized along the short molecular axis M contribute to the two perpendicular dielectric components which are assumed equal (uniaxial approximation). The simulated spectra on the basis of this model are also reported in Figs. 1 and 2 (dotted lines) for comparison. Neglecting the contribution of light scattering which affects the measured reflectance, the lineshape of the calculated curves resembles the experimental ones. In particular, the reflectance band at lowest energy in Figs. 1(c) and (d) is strongly dependent on the angle of incidence: at normal incidence a minimum is observed at 3.7 eV, which is absent in the spectrum calculated for $\theta = 35^\circ$, whilst a peak is revealed for $\theta = 50^\circ$. We observe that the extinction of the main band for $\theta = 35^\circ$ where the refracted wave vector is directed along the L -axis indicates that in this spectral region the refractive index $n \approx \sqrt{\epsilon_b} \approx \sqrt{\epsilon_{\perp L}} \approx 1.4$ as deduced from Snell's law. By contrast, the upper transitions are not seen to shift so markedly due to their comparatively low oscillator strengths. The dotted lines in Fig. 3 summarizes the dielectric function obtained using Eq. (1) and the parameters in Table 1, which allow to calculate the different spectra in Figs. 1 and 2.

A general experimental method to determine the optical function of a solid is also measuring its reflectivity spectrum $R(\omega)$ and using the KK relations. Indeed, the Fresnel coefficient can be written in the form $r(\omega) = [R(\omega)]^{1/2} e^{i\phi(\omega)}$, where $[R(\omega)]^{1/2}$ represents the ratio of the amplitudes of the reflected and incident waves and $\phi(\omega)$ gives the phase shift. Since we only measure $R(\omega)$, the KK relations are required to calculate the phase shift given by [18]

$$\phi(\omega) = -\frac{1}{2\pi} \int_0^\infty \ln \left| \frac{\omega' + \omega}{\omega' - \omega} \right| \frac{d \ln R(\omega')}{d\omega'} d\omega' \quad (4)$$

In the case of monoclinic systems, with ac plane of incidence and s polarized light an ordinary transverse wave propagates. The reflectivity is given by $|\hat{r}_b|^2$, where the Fresnel coefficient \hat{r}_b is

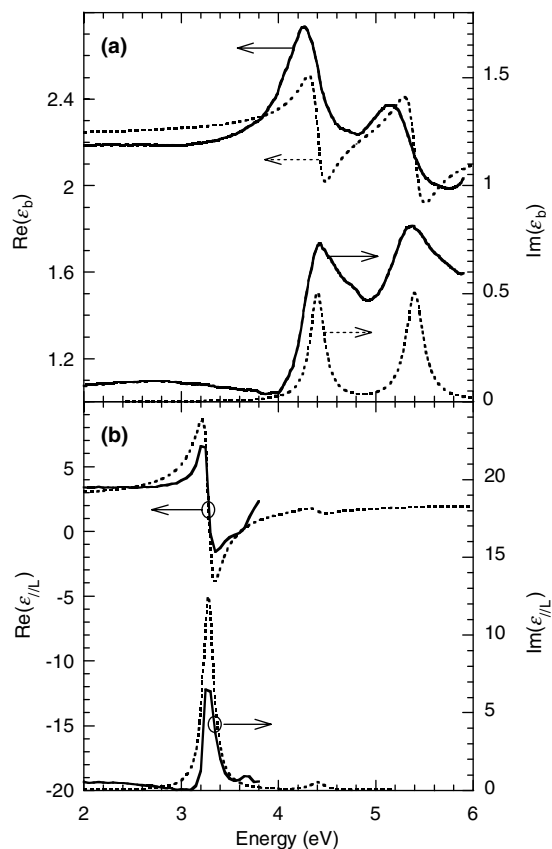


Fig. 3. Real and imaginary parts of the components of the dielectric tensor (3) obtained within the uniaxial approximation using either Eq. (1) and the parameters in Table 1 (---) or the KK relations (—).

$$\hat{r}_b = \frac{1 - \sqrt{\hat{\epsilon}_b}}{1 + \sqrt{\hat{\epsilon}_b}} \quad (5)$$

which allows $\hat{\epsilon}_b$ to be deduced. By contrast, in the case of p polarization an extraordinary wave propagates that is not completely transverse and the Fresnel coefficient depends on both the $\hat{\epsilon}_{\parallel L}$ and $\hat{\epsilon}_{\perp L}$ components. It is given by [15]

$$\hat{r}_p(\theta) = \frac{\cos \theta - \frac{[(\hat{\epsilon}_{\perp L} \cdot \sin^2 \alpha + \hat{\epsilon}_{\parallel L} \cdot \cos^2 \alpha) - \sin^2 \theta]^{1/2}}{[\hat{\epsilon}_{\parallel L} \cdot \hat{\epsilon}_{\perp L}]^{1/2}}}{\cos \theta + \frac{[(\hat{\epsilon}_{\perp L} \cdot \sin^2 \alpha + \hat{\epsilon}_{\parallel L} \cdot \cos^2 \alpha) - \sin^2 \theta]^{1/2}}{[\hat{\epsilon}_{\parallel L} \cdot \hat{\epsilon}_{\perp L}]^{1/2}}} \quad (6)$$

and the reflectivity is $|\hat{r}_p(\theta)|^2$.

Considering the spectra taken at normal incidence shown in Figs. 1(b) and (c), the contribution of scattered light has been assumed as indicated in the figures and subtracted from the measured curves. The reflectivity beyond the high energy cut-off at $\omega_{\max} = 6\text{eV}$ was extrapolated as $R(\omega) = R(\omega_{\max})(\omega_{\max}/\omega)^2$. The low frequency region was approximated by a gradually decreasing amount shown by the dashed lines, which gives reflectivity values at the lowest energies in agreement with the static dielectric constant reported in the literature [19]. This allowed to deduce the complex Fresnel coefficients \hat{r}_b and $\hat{r}_p(\theta = 0^\circ)$ from Eqs. (5) and (6) using the measured reflectance and the phase shift from Eq. (4). In turn, $\hat{\epsilon}_b$ was deduced from \hat{r}_b . Similarly, $\hat{\epsilon}_{\parallel L}$ was deduced from $\hat{r}_p(\theta = 0^\circ)$ with the added assumption that the other perpendicular principal dielectric component $\hat{\epsilon}_{\perp L}$ is equal to $\hat{\epsilon}_b$. In principle, both these components can be deduced from angle dependent measurements, but the accuracy of their absolute values here does not warrant such a determination. The results are compared in Fig. 3 with those calculated with the Lorentz model, at least in the low energy range, where a *L* polarized structure at about 3.2eV is detected. For higher energies, the dielectric function deduced from the KK relations are omitted, since they are strongly dependent on the lineshape of the scattering contribution; moreover, $R(\omega)$ should also be known over a wider frequency spectrum.

5. Conclusions

Absorbance, reflectance, and ellipsometry spectra of 5T single crystals enabled determination of the principal dielectric components of the 5T dielectric tensor using either the Lorentz model or the KK relations within an uniaxial approximation and a reasonable agreement is found. For the different experimental configurations, a marked shift of the lower resonance due to the macroscopic field is naturally apparent. Vibronic replica of the molecular transitions are not included, nor any coupling between different molecular transitions, and thus the assumption is that the pure electronic transitions are primarily

responsible for determining the dielectric function. Structure in the lowest resonance can only be simulated from more refined dipole theory, whilst the upper resonances seen in the spectra represent envelopes of several molecular transitions. Nevertheless, the overall representation is relatively consistent and reasonable description of all the experimental data is given.

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