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Abstract

The properties of the dielectric tensor of a monoclinic crystal are reviewed and the nature of transverse excitations is pointed out. Reflection equations for normal incidence on the (010)-plane and (001)-plane are presented, by use of which full information on all tensor components may be obtained from reflection measurements and Kramers-Kronig analysis. A reflection equation for oblique incidence on faces $(h_1,0,h_3)$ with plane of incidence (010) and transverse magnetic polarization allows the comparison of reflectance spectra calculated from the dielectric tensor components with respective experimental spectra. Simple model calculations related to exciton structures in molecular crystals and quasi onedimensional materials are displayed.

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I. INTRODUCTION

The largest group of organic molecular crystals crystallizes in the monoclinic crystal system [1]. Since the large oscillator strength of singlet excitons makes absorption measurements in most cases difficult, optical investigation of such crystals are usually performed by reflection spectroscopy. In the last years, many reflection experiments have been done on different crystallographic faces of the same crystal, e.g. [2] - [6]. These spectra, however, where not compared to each other on the basis of an unifying macroscopic dielectric (or crystal-optics) theory.

On the other hand, the microscopic theory of exciton bands in molecular crystals was faced with the problem of the convergence of dipole interaction lattice sums. The longitudinal macroscopic fields were not always taken into account properly, as recently emphasized by Philpott and Lee [7]. The macroscopic fields may be easily understood from the point of the dielectric theory and are automatically included in calculations based on this theory [8].

It also appeared to the authors, that in some work the difference between the directional dispersion of the excitons arising from the longitudinal macroscopic fields and the spatial dispersion of exciton bands was not pointed out in a clear way. For these reasons it seems worthwhile to compile all the information on the dielectric properties and theory of monoclinic crystals, though everything except the formulation of the reflection equations, fitted for use by a computer, may be taken from the literature.

The reflection equations (9), (10), (11), (12) and (24), presented in Section IV, allow for the full evaluation of all components of the dielectric tensor. Once this tensor is known, the reflection equation (16) allows a comparison of calculated reflection spectra from the planes, containing the monoclinic axis, with experimental data. The application of the dielectric theory to the experimental analysis becomes simple, if the axial dispersion of the tensor axis is negligible (Section IV). Model calculations will be presented and some relations to the interesting reflection spectroscopy of quasi one-dimensional materials [9,10] will also be pointed out (Section VI).

II. THE DIELECTRIC TENSOR IN MONOCLINIC CRYSTALS

The relation between the macroscopic electric field [11] $\underline{E}(\omega,\underline{k})$ and the macroscopic dielectric displacement $D(\omega,\underline{k})$ may be expressed by a dielectric tensor $\varepsilon_{i,j}(\omega,\underline{k})$, as long as $2\pi/|\underline{k}|$ is small compared to the lattice constants [12]. The dependence of $\underline{\underline{\varepsilon}}$ on $\underline{k}$, the wave vector of the fields, is referred to as spatial dispersion.

In a monoclinic crystal, the form of this tensor is given in a cartesian system, where the y-axis is directed along the second order axis in class C_2 and C_{2h} or perpendicular to the symmetry plane in class C_s. Later we will fix the x- and z-axis tangential and normal to crystal faces, containing the <010> axis. In class C_{2h} one has

$$(1) \qquad \underline{\underline{\varepsilon}}\,(\omega,\underline{k}) = \begin{pmatrix} \varepsilon_{xx}(\omega,\underline{k}) & \varepsilon_{xy}(\omega,\underline{k}) & \varepsilon_{xz}(\omega,\underline{k}) \\ \varepsilon_{xy}(\omega,\underline{k}) & \varepsilon_{yy}(\omega,\underline{k}) & \varepsilon_{yz}(\omega,\underline{k}) \\ \varepsilon_{xz}(\omega,\underline{k}) & \varepsilon_{yz}(\omega,\underline{k}) & \varepsilon_{zz}(\omega,\underline{k}) \end{pmatrix}$$

and in classes C_2 and C_s

$$(2) \qquad \underline{\underline{\varepsilon}}\,(\omega,\underline{k}) = \begin{pmatrix} \varepsilon_{xx}(\omega,\underline{k}) & \varepsilon_{xy}(\omega,\underline{k}) & \varepsilon_{xz}(\omega,\underline{k}) \\ \varepsilon_{xy}(\omega,\underline{-k}) & \varepsilon_{yy}(\omega,\underline{k}) & \varepsilon_{yz}(\omega,\underline{k}) \\ \varepsilon_{xz}(\omega,\underline{-k}) & \varepsilon_{yz}(\omega,\underline{-k}) & \varepsilon_{zz}(\omega,\underline{k}) \end{pmatrix}$$

with all components usually complex.

For the development of $\underline{\underline{\varepsilon}}(\omega,\underline{k})$ in powers of $\underline{k}$ in the three classes the reader is referred to [12]. When spatial dispersion is neglected, the tensor $\underline{\underline{\varepsilon}}(\omega)$ has in all the classes of the monoclinic system the form

$$(3) \qquad \underline{\underline{\varepsilon}}(\omega) = \begin{pmatrix} \varepsilon_{xx}(\omega) & 0 & \varepsilon_{xz}(\omega) \\ 0 & \varepsilon_{yy}(\omega) & 0 \\ \varepsilon_{xz}(\omega) & 0 & \varepsilon_{zz}(\omega) \end{pmatrix}$$

In general, it will not be possible to bring this tensor into diagonal form, as the real part of $\underline{\underline{\varepsilon}}$ would become diagonal for a different cartesian system of axis x,z than the imaginary part of $\underline{\underline{\varepsilon}}$. The directions of the dielectric tensor axes perpendicular to y for both, the real and imaginary part, will in general depend on ω, a result known as axial dispersion.

In its general form, $\underline{\underline{\varepsilon}}(\omega)$ contains eight unknown functions of ω. These are the four real and the four imaginary parts of ε_{xx}, ε_{xz}, ε_{yy} and ε_{zz}. When axial dispersion is neglected in a first order approximation, and the direction of the dielectric axes x and z are known, the six unknown functions ε_{xx}, ε_{yy} and ε_{zz} may be obtained from three suitable reflection spectra by Kramers-Kronig analysis, as is done in the following paper for anthrance [8].

More insight into a tensor of the form (3) can be obtained from a model where the polarizability tensors of several oscillators, polarized parallel to y and in different directions in the xz-plane sum up to the dielectric tensor [13].

III. PURE TRANSVERSE EXCITATIONS

If one extends the well known concepts of transverse and longitudinal plane waves in isotropic media to inhomogeneous plane waves in anisotropic media, a transverse wave, sometimes called solenoidal, is characterized by div $\underline{E} = 0$, $\underline{E} = \underline{E}_t$, a longitudinal wave, sometimes called irrotational, by curl $\underline{E} = 0$, $\underline{E} = \underline{E}_\ell$. The wave equation for waves propagating with wave vector $\underline{k}$ and transverse electric field $\underline{E}_t$ ($\underline{E}_t \cdot \hat{\underline{k}} = 0$) and longitudinal electric field $\underline{E}_\ell$ ($\underline{E}_\ell = E_\ell \hat{\underline{k}}$) with $\hat{\underline{k}} = \underline{k}/|\underline{k}|$ is

$$(4) \qquad \frac{\omega^2}{c^2}\, \underline{\underline{\varepsilon}}(\underline{E}_t + \underline{E}_\ell) = k^2 \underline{E}_t$$

For pure transverse excitations one has

$$\text{(4a)} \qquad \frac{\omega^2}{c^2}\ \underline{\underline{\varepsilon}}\ \ \underline{E}_t = k^2\ \underline{E}_t$$

This means, in pure transverse excitations $\underline{E}$ is an eigenvector of $\underline{\underline{\varepsilon}}$, and $\underline{k}$ is perpendicular to $\underline{E}$.
For monoclinic crystals, one eigenvector of $\underline{\underline{\varepsilon}}$ points in y-direction, the associated $\underline{k}$ vector has no component parallel to y, but may have any direction perpendicular to y. The wave is a homogeneous plane wave, it is linearly polarized and has the dispersion $\omega^2/c^2\ \ \varepsilon_{yy} = k^2$. These transverse waves may be excited by light striking on a crystal surface, containing the y axis (e.g. (001)), with plane of incidence (010) and the electric vector parallel to y (TE-polarization).
For the two eigenvectors perpendicular to y, the behaviour is more complicated. Because the tensor cannot in general be brought to diagonal form for both real and imaginary part, as mentioned in Section II, the eigenvectors $\underline{E}_t$ have a real and imaginary part, which will differ in direction. The $\underline{k}$ vector perpendicular to $\underline{E}_t$ will therefore also have different directions for the real and imaginary part, except when $\underline{k}$ is parallel to y.

Therefore, in general, one arrives at nonhomogeneous elliptically polarized plane waves. For $\underline{k}//y$ one has two homogeneous elliptically polarized plane waves with $\underline{k}$ vectors given by (5) and (6)

$$\text{(5)} \qquad \underline{k}_1=(0,k_1,0), \quad k_1 = \frac{\omega}{c}\ \frac{1}{\sqrt{2}}\left(\varepsilon_{xx}+\varepsilon_{zz}+\sqrt{(\varepsilon_{xx}-\varepsilon_{zz})^2+4\varepsilon_{xz}^2}\right)^{1/2}$$

$$\text{(6)} \qquad \underline{k}_2=(0,k_2,0), \quad k_2 = \frac{\omega}{c}\ \frac{1}{\sqrt{2}}\left(\varepsilon_{xx}+\varepsilon_{zz}-\sqrt{(\varepsilon_{xx}-\varepsilon_{zz})^2+4\varepsilon_{xz}^2}\right)^{1/2}$$

and electric fields given by (7) and (8) respectively

$$\text{(7)} \qquad \underline{E}_1 = E_1\ \frac{(\varepsilon_{xx}-\varepsilon_{zz} + \sqrt{(\varepsilon_{xx}-\varepsilon_{zz})^2 + 4\varepsilon_{xz}^2}, 0, 2\varepsilon_{xz})}{\left(2(\varepsilon_{xx}-\varepsilon_{zz})^2+2(\varepsilon_{xx}-\varepsilon_{zz})\sqrt{(\varepsilon_{xx}-\varepsilon_{zz})^2+4\varepsilon_{xz}^2}+8\varepsilon_{xz}^2\right)^{1/2}}$$

$$\text{(8)} \qquad \underline{E}_2 = E_2\ \frac{(2\varepsilon_{xz}, 0, \varepsilon_{zz} - \varepsilon_{xx} - \sqrt{(\varepsilon_{xx} - \varepsilon_{zz})^2 + 4\varepsilon_{xz}^2})}{\left(2(\varepsilon_{zz}-\varepsilon_{xx})^2 - 2(\varepsilon_{zz}-\varepsilon_{xx})\sqrt{(\varepsilon_{xx}-\varepsilon_{zz})^2 + 4\varepsilon_{xz}^2} + 8\varepsilon_{xz}^2\right)^{1/2}}$$

If in an experiment one wants to excite pure transverse waves, where ε_{yy} is not involved, these two waves are the only possible ones, because their direction of propagation is fixed parallel to the y direction and does not change with frequency. In order to excite these pure transverse excitations light has to strike normal on the (010) face of the crystal [5], with any polarization direction. In general, both of the elliptically polarized "eigenwaves" will be excited. Only the intensity ratio of these two waves will vary with the polarization of the incident light beam.

IV. REFLECTIVITY

To the knowledge of the authors, the reflectivity from absorbing anisotropic crystals has first been calculated by Berek [14]. As his result cannot easily be used in a computer program, which should start from the dielectric tensor (3), we recalculated the normal incidence reflection from the (010) plane (Section IV.1) and the TH-reflectivity for the plane of incidence (010) and non normal incidence (Section IV.2).

IV.1 Normal incidence on the (010) plane

The reflectivity from the (010)-plane (equivalent to the xz plane) for normal incidence is given in terms of a reflectivity tensor $\underline{r}$, which connects the transverse electric field $\underline{E}^{inc} = (E_x^{inc}, 0, E_z^{inc})$ of the incident wave with the transverse electric field of the reflected wave $\underline{E}^{ref} = (E_x^{ref}, 0, E_z^{ref})$. In this way, we have the most general solution, which allows to calculate the absolute reflectivity and ellipticity of the reflected light for any polarization of the incident light.

$$(9) \qquad (E_x^{ref}, E_z^{ref}) = \begin{pmatrix} r_{xx} & r_{xz} \\ r_{zx} & r_{zz} \end{pmatrix} \qquad \begin{pmatrix} E_x^{inc} \\ E_z^{inc} \end{pmatrix}$$

The problem is solved for the four unknown variables E_x^{ref}, E_x^{ref} and E_1, E_2 (equations (7) and (8)) by making use of the four independent boundary conditions for the tangential electric and magnetic fields in the x and z direction.

The final result is

$$(10) \qquad r_{xx} = \frac{(\varepsilon_{xx}-\varepsilon_{zz})(B-A) - W(C-1)}{W(A+B+C+1)}$$

$$(11) \qquad r_{zz} = \frac{(\varepsilon_{zz}-\varepsilon_{xx})(B-A) - W(C-1)}{W(A+B+C+1)}$$

$$(12) \quad r_{xz}=r_{zx} = \frac{2\ \varepsilon_{xz}\ (B-A)}{W(A+B+C+1)}$$

with abbreviations

$$A = \frac{1}{\sqrt{2}}\ (\varepsilon_{xx} + \varepsilon_{zz} + W)^{1/2}$$

$$B = \frac{1}{\sqrt{2}}\ (\varepsilon_{xx} + \varepsilon_{zz} - W)^{1/2}$$

$$C = (\varepsilon_{xx}\varepsilon_{zz} - \varepsilon_{xz}^{2})^{1/2}$$

$$W = ((\varepsilon_{xx} - \varepsilon_{zz})^{2} + 4\varepsilon_{xz}^{2})^{1/2}$$

For the case that $\underline{\underline{\varepsilon}}$ may be diagonalized and the x and z axis are chosen parallel to the axes of the diagonalized tensor, (10), (11) and (12) reduce to

$$(13) \qquad r_{xx} = \frac{1-\ \varepsilon_{xx}^{1/2}}{1+\ \varepsilon_{xx}^{1/2}}$$

$$(14) \qquad r_{zz} = \frac{1-\ \varepsilon_{zz}^{1/2}}{1+\ \varepsilon_{zz}^{1/2}}$$

$$(15) \quad r_{xz}=r_{zx} = 0$$

IV.2 TH-reflectivity at non normal incidence with (010) as plane of incidence

The calculation for the TH-reflectivity for (010) as plane of incidence and non normal incidence is straightforward. It proceeds along the lines of the derivation for an uniaxial crystal and the reflection at a plane normal to the optical axis, the socalled basal plane, as given by Mosteller and Wooten [15].

With θ as the angle of incidence, the result is

$$(16)\qquad R_{TH(010)}(\theta) = \left| \frac{\cos\theta-(\varepsilon_{zz}-\sin^2\theta)^{1/2}/(\varepsilon_{xx}\varepsilon_{zz}-\varepsilon_{xz}^2)^{1/2}}{\cos\theta+(\varepsilon_{zz}-\sin^2\theta)^{1/2}/(\varepsilon_{xx}\varepsilon_{zz}-\varepsilon_{xz}^2)^{1/2}} \right|^2$$

Note, that the cartesian system x,y,z is fixed to the orientation of the surface, which is the xy plane. If reflectivities from a different face parallel to y are to be calculated, the tensor $\underline{\underline{\varepsilon}}(0)$ (3) has to be transformed like

$$(17)\qquad \underline{\underline{\varepsilon}}(\phi) = \underline{\underline{S}}(\phi)\ \underline{\underline{\varepsilon}}(0)\ S^{-1}(\phi)$$

with

$$(18)\qquad S(\phi) = \begin{pmatrix} \cos\phi & 0 & -\sin\phi \\ 0 & 1 & 0 \\ \sin\phi & 0 & \cos\phi \end{pmatrix}$$

ϕ is the angle of rotation of the plane, with respect to which $\underline{\underline{\varepsilon}}(0)$ is defined, into the new plane, for which R is to be calculated. ϕ is taken as positive for a right hand rotation around the y-axis.

For normal incidence and $\underline{E} \parallel \underline{x}_o$, $\underline{x}_o$ being the unit vector in x direction, (16) becomes

$$(19)\qquad R = \left| \frac{1 - \underline{x}_o\ \underline{\underline{\varepsilon}}^{-1}\ \underline{x}_o}{1 + \underline{x}_o\ \underline{\underline{\varepsilon}}^{-1}\ \underline{x}_o} \right|^2$$

For normal incidence on the (001)-plane ($\underline{ab}$-plane) of a monoclinic crystal and $\underline{E} \parallel \frac{\underline{a}}{|\underline{a}|}$ equation (19) has already been published in [16].

Although the tensor $\underline{\underline{\varepsilon}}$ is not symmetric with respect to a reflection at the yz-plane, ε_{xz} changes its sign, $R(\theta)$ is symmetric, as may be seen from (16), which yields the same result for $+\theta$ and $-\theta$.

Let us now assume, that $\underline{\underline{\varepsilon}}$ is diagonalized in an axis system, which is rotated with respect to the xyz-system by an angle $-\alpha$ around the y-axis, where it has the form

$$(20)\qquad \underline{\underline{\varepsilon}}\ (-\alpha) = \begin{pmatrix} \varepsilon_\perp & 0 & 0 \\ 0 & \varepsilon_b & 0 \\ 0 & 0 & \varepsilon_{\parallel} \end{pmatrix}$$

We then have via transformation (17) for the components of $\underline{\underline{\varepsilon}}(0)$

$$\text{(21)} \quad \begin{aligned} \varepsilon_{xx} &= \varepsilon_{\perp} \cos^2\alpha + \varepsilon_{||} \sin^2\alpha \\ \varepsilon_{yy} &= \varepsilon_b \\ \varepsilon_{zz} &= \varepsilon_{\perp} \sin^2\alpha + \varepsilon_{||} \cos^2\alpha \\ \varepsilon_{xz} &= 1/2 \sin 2\alpha \, (\varepsilon_{\perp} - \varepsilon_{||}) \end{aligned}$$

Using equation (21), equation (16) yields

$$\text{(22)} \quad R_{TH(010)}(\theta) = \left| \frac{\cos\theta - (\varepsilon_{zz} - \sin^2\theta)^{1/2} (\varepsilon_{||}\varepsilon_{\perp})^{-1/2}}{\cos\theta + (\varepsilon_{zz} - \sin^2\theta)^{1/2} (\varepsilon_{||}\varepsilon_{\perp})^{-1/2}} \right|^2$$

This is physically the same as the TH-reflection from an uniaxial crystal with the optical axis (extraordinary tensor component $\varepsilon_{||}$) at an angle $-\alpha$ from the normal of the reflecting plane, and the plane of incidence containing the optical axis. Therefore, for $\alpha=0$ (22) yields

$$\text{(23)} \quad R_{TH,\text{basal plane}}(\theta) = \left| \frac{\cos\theta - (\varepsilon_{||} - \sin^2\theta)^{1/2} (\varepsilon_{||}\varepsilon_{\perp})^{-1/2}}{\cos\theta + (\varepsilon_{||} - \sin^2\theta)^{1/2} (\varepsilon_{||}\varepsilon_{\perp})^{-1/2}} \right|^2$$

Equation (23) for the TH-reflection from the basal plane of an uniaxial crystal appears also in [15], [17]-[19] and [28]. Bulaevskii and Kukharenko [19] have also presented an equation valid for the geometry of equation (22). The reflection is however given in a more complicated way, from which it is not obvious that $R(\theta) = R(-\theta)$.

It should be noted, as follows from (22), that normal incidence reflection spectra measured from a plane with angle $-\alpha'$ between the normal and the dielectric axis are not equivalent to reflection spectra from a plane with angle $-\alpha''$ and an angle of incidence $\theta = (\alpha' - \alpha'')$, positive for right handed rotation around y. This is the reason why, for instance, the oblique incidence TH-polarized spectra from the (001) plane of anthracene with plane of incidence (010) cannot be compared directly with normal incidence spectra of artificially cut planes of anthracene cut parallel to the <010> axis and with $\underline{E} \perp$<010> as measured by Hymowitz and Clark [20].

The ε_{yy} component of the dielectric tensor may be obtained from a normal incidence reflection $|r_{yy}|^2$ spectrum from faces $(h_1,0,h_3)$ and $\underline{E} \parallel y$.

$$r_{yy} = \frac{1 - \varepsilon_{yy}^{1/2}}{1 + \varepsilon_{yy}^{1/2}} \tag{24}$$

If, in a reflection experiment at near normal incidence, one wants to avoid longitudinal excitations it is better to use TE- than TH-reflection [5], as the longitudinal field $\underline{E}_\ell$ will in general be smaller for TE-polarization, especially, if the electric vector of the incident radiation lies roughly in the direction of a dielectric tensor axis. In this approximation, we assume that the dielectric tensor can be diagonalized. For any other mode of excitation of the crystal longitudinal fields $\underline{E}_\ell$ are involved [5].

V. Kramers-Kronig relations and sum rules

The evaluation of the dielectric constants ε_{xx}, ε_{yy} and ε_{zz}, when equations (13), (14) and (24) are applicable, is a well known procedure.

In principle full information on ε_{xx}, ε_{zz} and ε_{xz} should be obtainable from equations (10), (11) and (12). When only absolute intensities of the reflectance $|r_{xx}|^2$, $|r_{xz}|^2 = |r_{zx}|^2$, $|r_{zz}|^2$ are measured (note, that this may be done in any x - z coordinate system perpendicular to y), the phases of r_{xx}, r_{xz} and r_{zz} must be evaluated from $|r_{xx}|$, $|r_{xz}|$ and $|r_{zz}|$ by a Kramers-Kronig analysis. This is possible, since r_{xx}, r_{xz} and r_{zz} describe linear and causal relationships between incident and reflected fields.

The problem of additional pole contributions in the Kramers-Kronig analysis, as it is well known for TH-polarized light at oblique incidence (e.g. [21], [22]) and the accuracy of the method needs further theoretical consideration.

The Kramers-Kronig relations for an anisotropic material are applicable for every component of the $\underline{\underline{\varepsilon}}(\omega,k)$ tensor separately [12], [23]. By use of the sum rules [23] (25) or, neglecting spatial dispersion (26), an $n_{eff,i}(\omega)$ may be defined by equation (27).

$$\int_0^\infty \left[\mathrm{Im}\ \varepsilon_{ij}(\omega',\underline{k}) + \mathrm{Im}\ \varepsilon_{ij}(\omega', -\underline{k})\right] \omega' d\omega' = \pi\omega_p^2\delta_{ij} \tag{25}$$

$$(26) \qquad \int_0^\infty \operatorname{Im} \boldsymbol{\varepsilon}_{ij}(\omega')\ \omega' d\omega' = \frac{\pi}{2}\ \omega_p^{\,2}\ \delta_{ij}$$

with $\omega_p^{\,2} = \frac{4\pi\ Nne^2}{m}$, where N is the density of molecules, n the number of electrons per molecule and e and m charge and mass of the free electron respectively:

$$(27) \qquad n_{\mathrm{eff},i}(\omega) = \frac{m}{2\pi\ Ne^2} \int_0^{\omega} \operatorname{Im} \varepsilon_{ii}(\omega')\ \omega'\ d\omega'$$

$n_{\mathrm{eff},i}(\omega)$ may be roughly interpreted as the number of electrons of one molecule, which can be transferred to higher energy states up to a frequency ω for the electric vector in the direction i.

For molecular crystals formed by hydrocarbons, where one has a significant energy separation between the H1s, C2s and C 2p electrons on the one hand and the C1s core electrons on the other hand $n_{\mathrm{eff},i}(\omega)$ should saturate between about $\hbar\omega$ = 50 to 100 eV at the number of H1s, C2s and C 2p electrons, independent of the direction i.

VI. REFLECTIVITIES FOR A SIMPLE DIELECTRIC MODEL

In order to illustrate the results obtained above, in particular equation (22) for the reflectivity, numerical calculations were performed. For the sake of simplicity a simple dielectric model was used:

$$(28) \qquad \begin{aligned} \varepsilon_{||}(\omega) &= A + \frac{B}{1-(\frac{\omega}{\omega_o})^2 - \frac{1}{\omega_o}\ \gamma} \\ \varepsilon_{\perp} &= \text{constant} \end{aligned}$$

with the following expression for ε_{zz} in equation (22)

$$\varepsilon_{zz} = \varepsilon_{\perp}\sin^2\alpha + \varepsilon_{||}\cos^2\alpha,$$

and $A = 1$, $B = 2$, $\gamma = 0.1$ and $\omega_o = 4.55$ eV.
The time dependence is taken to be $e^{-i\omega t}$.
Figure 1 shows the spectra for real and imaginary part of $\varepsilon_{||}$, as given by these equations.

We have chosen this particular model for various reasons. First, it is very simple and one might therefore hope to get a better insight in the complex reflectance behaviour of monoclinic crystals. Secondly the parameters are such that the model roughly represents the dielectric behaviour as observed experimentally for anthrance single crystals (see Fig. 4 of the following paper [8]). Anthrance seems to be a representative case since the electronic spectra of a number of organic molecules are dominated by one allowed $\pi-\pi^*$ transition with large oscillator strength, which in the crystal gives rise to a strong metallic like reflectance band for one particular crystal face and polarization.
Further in a rough approximation this model reflects the dielectric properties of quasi onedimensional solids, the optical properties of which have received considerable attention recently [9], [10], [18].

Reflectance spectra have been calculated by use of equation (22) for different angles α, where α is the angle between the transition moment of the oscillator described by (28) and the normal of the reflecting surface.The plane of incidence of the TH-polarized light contains these two directions as shown in the inserts of Fig. 2. In Fig. 2 the results for various angles α are displayed for normal incidence ($\Theta = 0$) keeping $\varepsilon_\perp = 2 + i$.
When the transition moment of the oscillator is parallel to the surface ($\alpha = 90^\circ$) one obtains the well known reflectance band between the transverse (ω_T) and longitudinal frequency (ω_L) of the oscillator. When it is perpendicular to the surface ($\alpha = 0$), the oscillator cannot be excited with light at normal incidence.

The shift of the reflectance band due to the change of α is clearly demonstrated in Fig. 2. Note that in our model the $\underline{k}$ dependence of $\underline{\underline{\varepsilon}}$ is completely neglected. The change of the reflectance band is entirely due to the anisotropy of the dielectric tensor. It is merely caused by the longitudinal fields as discussed in connection with equation (4). We refer to this effect as directional dispersion and do not want to call it spatial dispersion, as for instance done in Ref. [22].

The directional dispersion is equivalent to the nonanalytic behaviour of the exciton bands in the case $\underline{k} \to 0$ at the Γ point of the Brillouin zone as pointed out in [5] and calculated in the microscopic theory [7], [24], [25]. Including the dependence of $\underline{\underline{\varepsilon}}$ not only on ω but also on $\underline{k}$ (spatial dispersion) is equivalent to have the exciton frequency depend not only on the direction but also on the magnitude of $\underline{k}$. In this way exciton band structure calculations are related to the dielectric tensor model $\underline{\underline{\varepsilon}}(\omega,\underline{k})$. Such band structure calculations have been performed for instance for anthrance in Ref. [26], and [27].

In Fig. 3 we have displayed the results of our model calculations for $\alpha = 90^\circ$, 60°, 30° and 0° for various angles of incidence Θ. In addition to the directional dispersion discussed in connection with Fig. 2 ($\Theta = 0$ spectra) one observes shifts and intensity variations in the reflectance bands for a given α when the angle of incidence Θ is changed. From one set of reflectance bands with fixed α it is not easy to deduce the pure directional dispersion. This is because at non normal incidence the directions of the real- and imaginary part of the $\underline{k}$ vector are different and may not easily be compared to the direction of $\underline{k}$ in normal incidence measurements from a set of different reflecting faces (Fig. 2), where $\underline{k}$ is always normal to the surface.

One might suspect that for a given $\alpha \neq 0$ spectra at angles $+\Theta$ and $-\Theta$ should be different (e.g. Ref. [22], p. 273), since the directional dispersion of excitons in monoclinic crystals is not symmetric with respect to reflection on the yz-plane. It is clear from equation (22) and the above discussion that this is not the case, rather the reflectance is independent from the sign of Θ. This again demonstrates the difficulties of probing directional dispersion of exciton bands in monoclinic crystals in oblique angle of incidence experiments.

The spectra in Fig. 3 with $\alpha = 0$ represent the case where the oscillator is oriented perpendicular to the reflecting surface. The dependence of the reflectance on the angle of incidence Θ shows close similarities to the experimentally observed reflectance at non normal incidence with TH-polarized light from quasi onedimensional single crystals of $K_2[Pt(CN)_4]Br_{0.3} \times 3\,H_2O$ by Brüesch [18] for those crystal faces where the platinum chains are perpendicular to the reflecting surface. The model calculations of Brüesch starting from an equation equivalent to equation (23) describe his experimental results very well.

The possibility to apply a macroscopic dielectric or crystal optics theory to materials as different as molecular crystals [8] and quasi onedimensional solids shows the usefulness of this approach.

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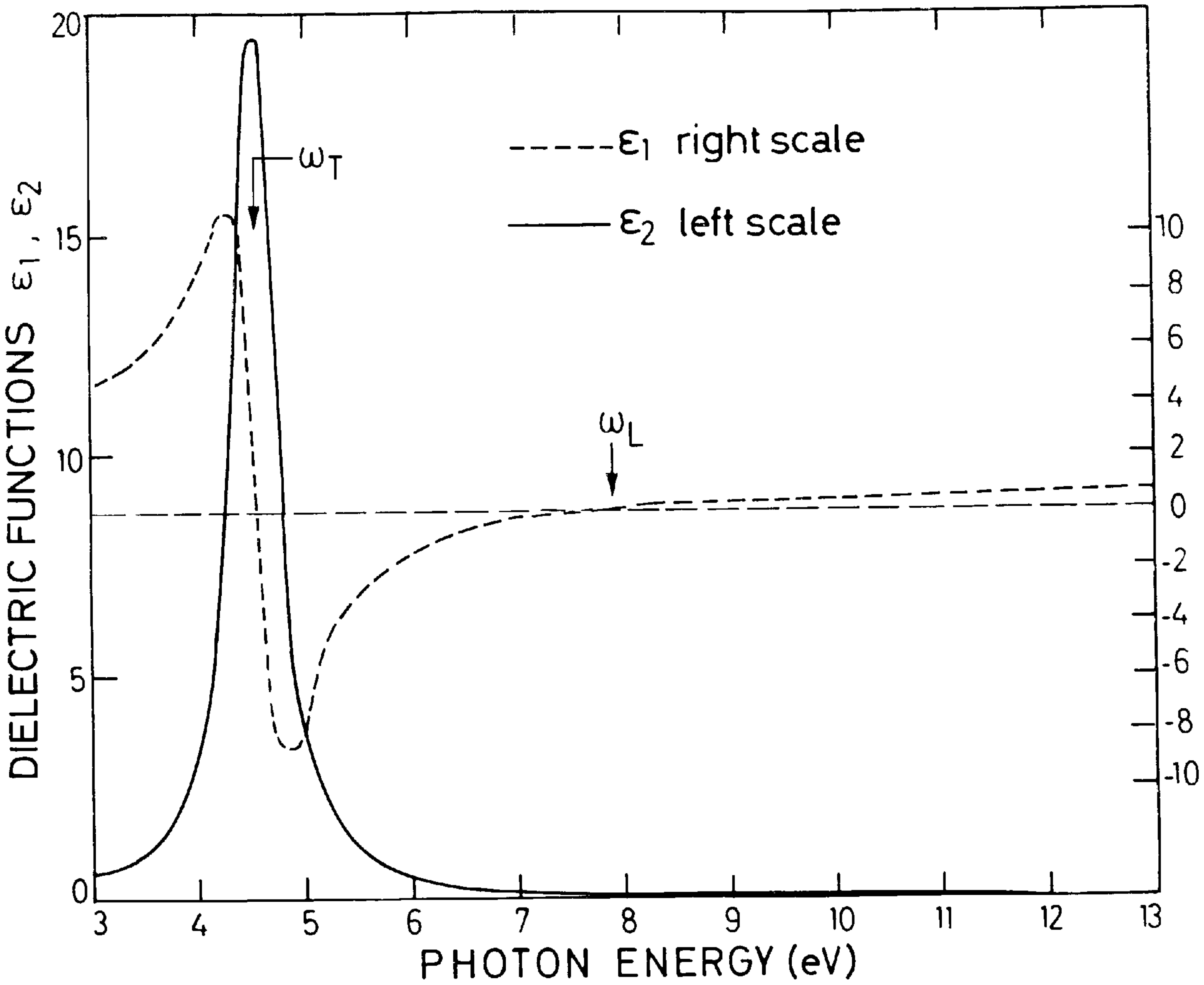
Figure Captions

Fig. 1 Real part (solid line, left scale) and imaginary part (dashed line, right scale) of the dielectric function $\varepsilon_{||}$ (equation (28)) used for the calculation of the reflectance.

Fig. 2 Normal incidence reflectance for various orientations α of the model oscillator (Fig. 1) and $\varepsilon_{\perp} = 2+i$ with respect to the reflecting surface calculated with equation (22).

Fig. 3 Reflectance spectra calculated according to equation (22) for the same orientations of the model oscillator as in Fig. 2. Additionally the angle of incidence θ of the TH-polarized light was varied.



DIELECTRIC FUNCTIONS ε_1, ε_2
PHOTON ENERGY (eV)
----- ε_1 right scale
—— ε_2 left scale
ω_T
ω_L
0
5
10
15
20
3
4
5
6
7
8
9
10
11
12
13
10
8
6
4
2
0
-2
-4
-6
-8
-10

Fig. 1

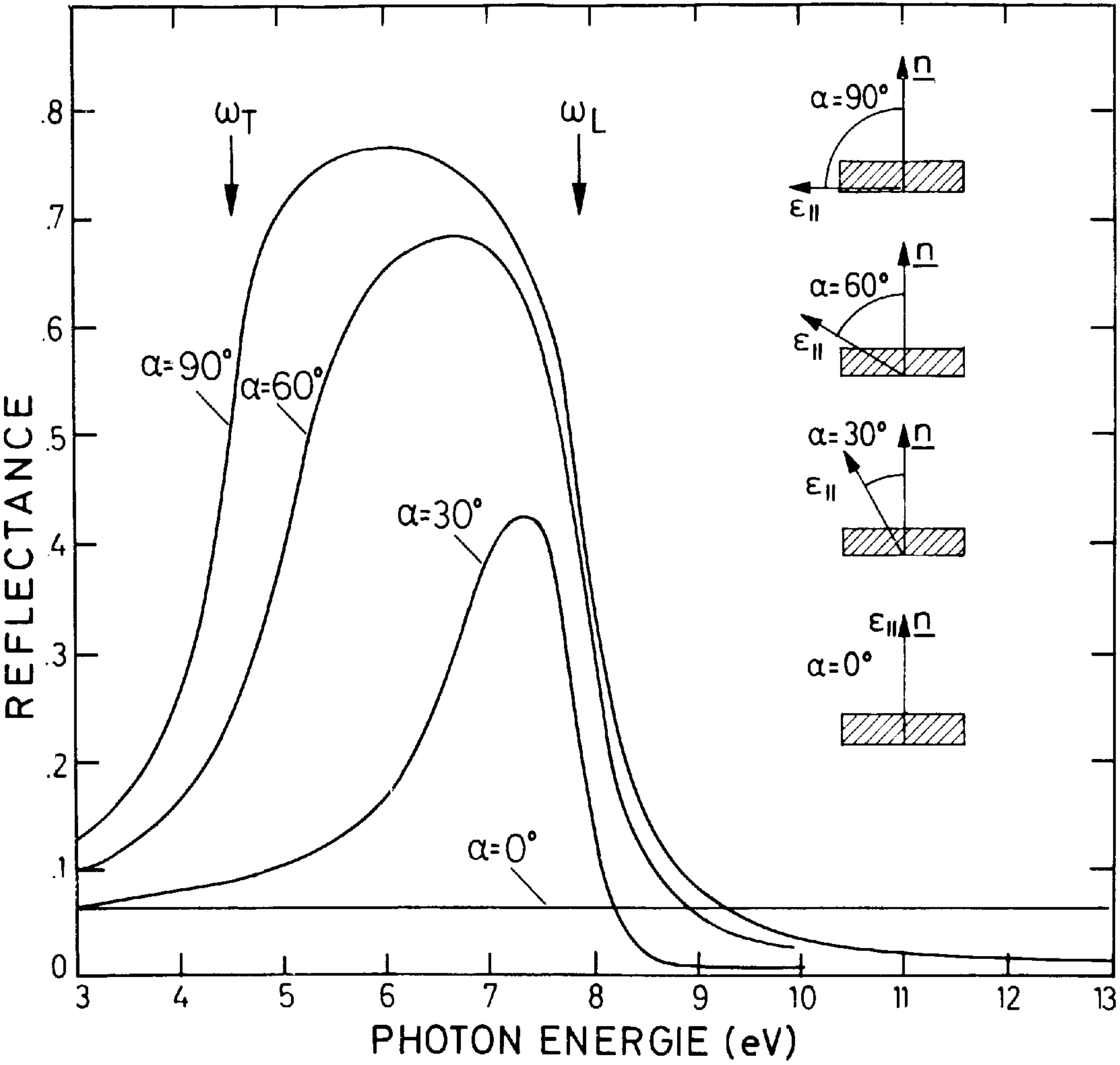

REFLECTANCE
.8
.7
.6
.5
.4
.3
.2
.1
0
3
4
5
6
7
8
9
10
11
12
13
PHOTON ENERGIE (eV)
ω_T
ω_L
α=90°
α=60°
α=30°
α=0°
n
ε_∥
α=90°
α=60°
α=30°
α=0°

Fig. 2

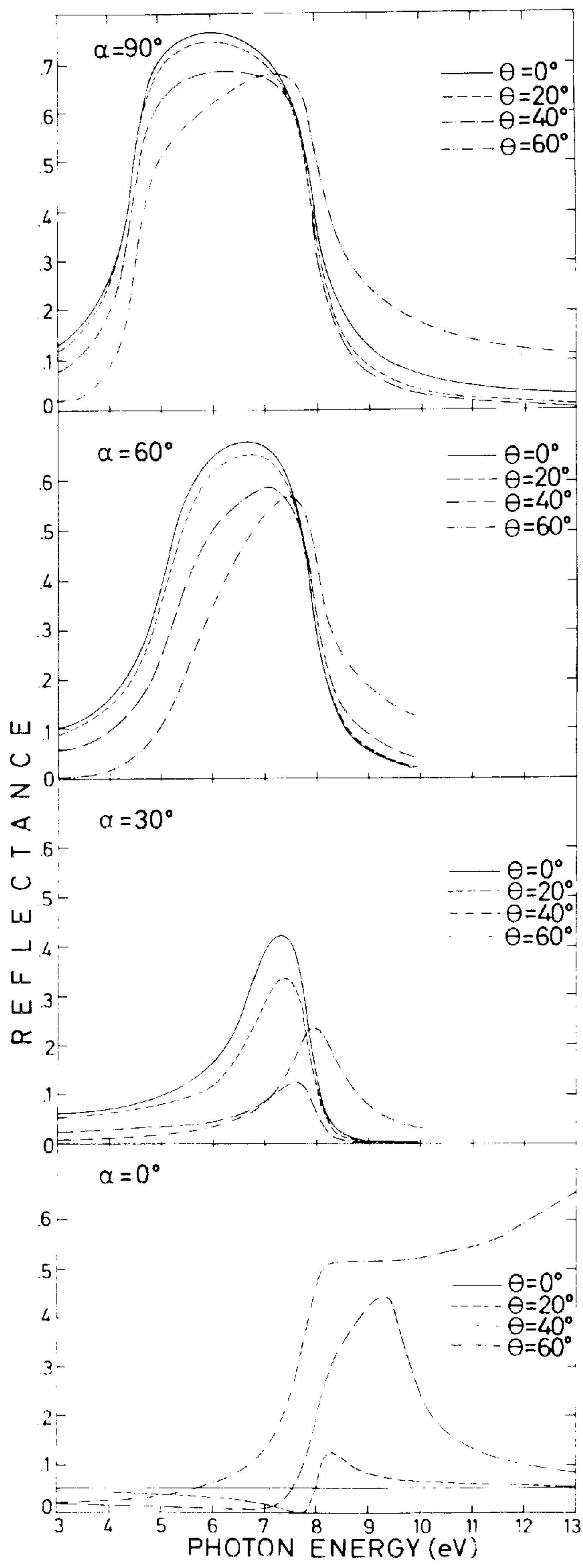

α=90°
θ=0°
θ=20°
θ=40°
θ=60°
α=60°
θ=0°
θ=20°
θ=40°
θ=60°
α=30°
θ=0°
θ=20°
θ=40°
θ=60°
α=0°
θ=0°
θ=20°
θ=40°
θ=60°
0
.1
.2
.3
.4
.5
.6
.7
REFLECTANCE
3
4
5
6
7
8
9
10
11
12
13
PHOTON ENERGY (eV)

Fig. 3