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Peculiar properties of crystal optics in real modulated phases

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Abstract. Using Jones calculus, a model is developed for interpretation of the optical properties of an inhomogeneous medium with spatially modulated complex dielectric tensor. The parameters characterizing the optical activity, linear birefringence and also the indicatrix rotation are derived. Distortions of the modulation wave due to defects present are shown to affect strongly the optical properties of a crystal. The relevant physical phenomena responsible for that are discussed. It is revealed that the optical activity can originate from a semimacroscopic inhomogeneity of the structure and its local imperfections, as well as its polarization. The conclusions drawn should be valid irrespective of the modulation shape. The temperature evolution of the parameters involved in the model is considered for the case of incommensurately modulated material. The results are compared with the experimental data available for $[N(CH_3)_4]_2ZnCl_4$ and other incommensurate crystals.

1. Introduction

In recent years much attention has been paid to a controversial problem of the optical activity in incommensurate (INC) dielectric materials (Meekes and Janner 1988, Kobayashi 1991, Ortega *et al* 1992). Description of the optical phenomena in a non-absorbing uniform dielectric medium is given by a material equation with a complex dielectric tensor, which accounts for a first-order spatial dispersion (Agranovich and Ginzburg 1979):

$$\epsilon_{ij}(\omega, q) = \epsilon_{ij}^{(0)}(\omega) + \mathrm{i}e_{ijk}g_{kl}(\omega)q_l^{(\mathrm{u})} \tag{1}$$

where the real symmetric tensor $\epsilon_{ij}^{(0)}$ describes a purely birefringent medium, e_{ijk} denotes the unit pseudotensor antisymmetric in all its indices, g_{kl} the gyration pseudotensor, ω the frequency and q the wavevector of light, and $q^{(\mathrm{u})}$ the unit vector along q. In a centrosymmetric INC material, within an average structure approximation, g_{kl} is forbidden by symmetry, and more refined approaches are required for the application of (1) to incommensurately modulated structures. Namely, one has to consider properly the inhomogeneity of the INC crystal, i.e. the spatial inhomogeneity of $\epsilon_{ij}^{(0)}$ and g_{kl}, and how to get a semimacroscopic description from a microscopic one. Of particular note is a study by Meekes and Janner (1988) in which they have shown, without specifying the quantitative details, that the superspace symmetry of the INC phase allows for some microscopic gyration components. Stasyuk *et al* (1989) have suggested a visual model describing the INC crystal as a sequence of enantiomorphous layers with the opposite signs of gyration parameter. However, the model turned out to be non-gyrotropic as demonstrated by Vlokh *et al* (1991). A similar approach used by Dijkstra (1991a) made it possible to reveal that the structure with the modulated off-diagonal $\epsilon_{ij}^{(0)}$ components manifested an optical activity, in accordance with the appropriate symmetry considerations (Dijkstra *et al* 1992a).

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We believe that the theoretical studies available in the literature do not exhaust the problem. Regarding the quantitative estimations, the results of Dijkstra (1991a) are mainly concentrated on the $[N(CH_3)_4]_2ZnCl_4$ compound. There exist difficulties (Ortega *et al* 1992) in the explanation of the magnitude of the optical activity measured in some experiments. This has led Ortega *et al* to the conclusion that the optical activity in the INC compounds must be symmetry restricted to a value inaccessible for investigation. All the mentioned *theories deduce the optical activity from the ideal modulated structure.* So, Dijkstra *et al* (1992a) suppose that the averaging processes 'mix' different Fourier wavevectors of the INC modulation and cause a perfectly periodic variation of the dielectric parameters along the modulation direction. On the other hand, it would be of interest to consider contributions to the optical activity arising from distortions and polarization of a perfect INC structure, the more so that the latter does not show gyration in the average structure approximation. A well known fact is that the INC phases, owing to pinning, are particularly sensitive to the present defects, and this can be observed clearly in the linear birefringence (Jamet 1988, Mogeon *et al* 1989). We can expect the optical activity to be affected also by the interaction of the INC structure with defects (see Kushnir *et al* 1993), although the understanding of the origin of this is still lacking. It is noteworthy that the experimental results (Vlokh *et al* 1985, 1987) on the optical activity along the optical axes in K_2ZnCl_4 and Rb_2ZnCl_4, being in some contradiction with the HAUP data, point to the essential role of structural unipolarities and perfection of the samples (see also Arutyunyan *et al* 1982, Sanctuary *et al* 1985).

The problem must be looked at in the following way: which are the optical properties of the real inhomogeneous modulated materials, particularly the INC and the multidomain ferroelectric or ferroelastic ones? The purpose of this paper is just to study these points, considering the modulation of both real and imaginary parts of the dielectric tensor. We disregard below the symmetry aspects and the structural crystal incommensurability at the microscopic level and take those into account only on a phenomenological (physical) level. Section 2 is devoted to analysis of a number of typical modulated structures using Jones calculus. In section 3 we discuss the physical mechanisms for the influence of structural imperfections on the optical properties, consider the behaviour of the developed model with temperature, and give a comparison with the experimental results available. Finally, conclusions are drawn in section 4.

2. Jones model for a modulated dielectric medium

2.1. Perfect structure with modulated gyration component

Let us consider a crystal medium that has a gyration component modulated along one direction. With a view towards analytical simplicity we will restrict analysis to a square waveform of the modulation (see Dijkstra 1991a). Then the finite crystal can be treated as an optical layered structure (OLS) that consists of many optical layers (figure 1(*a*)) characterized by alternating gyration parameters $+G$ and $-G$ (Stasyuk *et al* 1989). The model can be used for an approximate description of the INC crystal. Another example is a multidomain ferroelectric phase, which occurs after the phase transition with a loss of the inversion centre.

Each layer is assumed to be a homogeneous elliptic phase retardation plate (Shurcliff 1965), with the thickness l equal to half the period of the modulation. Note that l is large enough to allow for an interpretation in terms of macroscopic parameters, but much smaller than the crystal dimensions. The two enantiomorphous layers form a unit modulation cell.

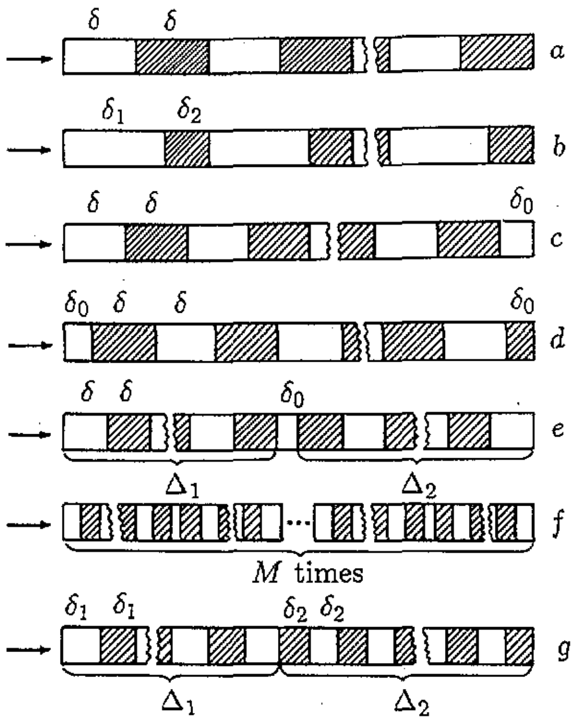

Figure 1. Typical OLSs representing schematically dielectric material with the square waveform of modulation. Unshaded and shaded regions have opposite signs of modulation parameters (see text). δ, δ_0, δ_1, δ_2 and Δ_1, Δ_2 denote the phase retardations in the optical layers and constituent substructures, respectively. Arrows display the light propagation direction.

The spatial average of such an OLS has inversion symmetry. Here we deal with a perfect modulation as the sample contains an integer number N of complete identical unit cells.

The Jones matrix of the layers for light propagation directions different from the optical axes may be written as (Vlokh *et al* 1991)

$$\mathbf{T}_{\pm} = \begin{pmatrix} \exp(-\mathrm{i}\delta/2) & \mp 2k\sin(\delta/2) \\ \pm 2k\sin(\delta/2) & \exp(\mathrm{i}\delta/2) \end{pmatrix} \tag{2}$$

where δ denotes the phase retardation in the layer and k the small eigenwave ellipticity. To a good approximation

$$k = G/(2\bar{n}\Delta n) \tag{3}$$

with $\bar{n}$ the mean refractive index and Δn the linear birefringence. One can study with Jones calculus (see Azzam and Bashara 1981) the optical properties of the OLS. Its Jones matrix is

$$\mathbf{T}_{2N} = [\mathbf{T}_{-}(\delta)\mathbf{T}_{+}(\delta)]^{N}. \tag{4}$$

An approximation linear in k will usually be used in this paper. This reduces (4) to

$$\mathbf{T}_{2N} = \begin{pmatrix} \exp(-\mathrm{i}\Delta/2) & 2\mathrm{i}k\tan(\delta/2)\sin(\Delta/2) \\ 2\mathrm{i}k\tan(\delta/2)\sin(\Delta/2) & \exp(\mathrm{i}\Delta/2) \end{pmatrix} \tag{5}$$

where $\Delta = 2N\delta$. The observed phase retardation of the OLS is determined from

$$\Delta_{2N}^{\text{ob}} = \arg V_{e1} - \arg V_{e2} = 2\tan^{-1}\{\tan(\Delta/2)[1 + 4k^2\tan^2(\delta/2)]^{1/2}\} + 2\pi m \qquad (6)$$

where $V_{e1,2}$ are the eigenvalues of $\mathbf{T}_{2N}$ and m is an integer. In (6) the term proportional to k^2 is the only result of inhomogeneity of the OLS imposed by the modulation. Taking small δ (see subsection 3.2), this term can be neglected, and we obtain $\Delta_{2N}^{\text{ob}} \simeq \Delta$. That holds for all OLSs considered further.

Next we have to check the eigenwaves of $\mathbf{T}_{2N}$ (Vlokh *et al* 1991). The eigenwave ellipticity K of the entire OLS found by standard methods (Azzam and Bashara 1981) becomes zero, unlike that of the constituent layers. This testifies that the gyration is absent, being in disagreement with the result derived by Stasyuk *et al* (1989). In terms of the description made by Shurcliff (1965), zero optical activity means that the OLS represents a transcendental composite phase retardation plate. Another example of such plates is given by Dijkstra (1991a), who has found that a certain sequence of purely birefringent optical layers can form a gyrotropic structure.

A unique feature of the model is that the reference coordinate system of the linear eigenwaves of the OLS is oriented over the angle

$$\Delta\theta_{2N} = -k\tan(\delta/2) \qquad (7)$$

with respect to that of the layers. The latter coincides with the crystallographic system of the high-temperature phase in both ferroelectric and INC crystals. In other words, the OLS exhibits a specific optical indicatrix rotation, which is the result of a perfect modulation. It is called a quasigyrotropic rotation (Vlokh *et al* 1991, 1992a) because of the origin from the gyrotropy in the optical layers. The optical activity is thus not the only consequence of the spatial modulation of the dielectric function, contrary to the usual belief, and can be accompanied by additional indicatrix rotation. From this viewpoint the models developed here and in the studies by Dijkstra (1991a) are complementary.

The indicatrix rotation in the INC crystal with the average symmetry *mmm* can be understood within the mesoscopic approach (Dijkstra *et al* 1992a). Namely, it is caused by a symmetry breaking owing to the fact that the surface boundaries of the OLS are located at equivalent position with symmetry $2/m$. Below, we will elucidate this subject more.

2.2. *Optical layered structure with extended unipolarity*

In this subsection we consider the optical properties of the OLS shown in figure 1(*b*). It is unipolar because the total volumes of the opposite layers are not equal ($\delta_1 \neq \delta_2$). The unipolar modulation cell reiterates periodically along the modulation direction. Such unipolarity we will refer to as 'regular' or 'extended'. The model seems to be realistic for polarized multidomain ferroelectric phases, or the discommensuration region in INC crystals at temperatures close to the lock-in one. The Jones matrix of the OLS becomes

$$\mathbf{T}_{\Delta\delta} = [\mathbf{T}_-(\delta_2)\mathbf{T}_+(\delta_1)]^N$$
$$= \begin{pmatrix} \exp\left(-\frac{i\Delta}{2}\right) & -\frac{2k\sin(\Delta/2)}{\sin[(\delta_1+\delta_2)/2]}\left[\sin\left(\frac{\delta_1-\delta_2}{2}\right) - 2i\sin\left(\frac{\delta_1}{2}\right)\sin\left(\frac{\delta_2}{2}\right)\right] \\ \frac{2k\sin(\Delta/2)}{\sin[(\delta_1+\delta_2)/2]}\left[\sin\left(\frac{\delta_1-\delta_2}{2}\right) + 2i\sin\left(\frac{\delta_1}{2}\right)\sin\left(\frac{\delta_2}{2}\right)\right] & \exp\left(\frac{i\Delta}{2}\right) \end{pmatrix} \qquad (8)$$

with $\Delta = N(\delta_1 + \delta_2)$ the approximate total phase retardation. Note that the eigenwave ellipticity and the indicatrix rotation in the OLS may be derived easily (see appendix) from the appearance of its Jones matrix, simplifying the analysis. Further we will drop the expressions for Jones matrices of the OLSs, giving only K and $\Delta\theta$ values. In particular, for Jones matrix (8)

$$K_{\Delta\delta} = k\sin[(\delta_1 - \delta_2)/2]/\sin[(\delta_1 + \delta_2)/2] \tag{9}$$

$$\Delta\theta_{\Delta\delta} = -2k\sin(\delta_1/2)\sin(\delta_2/2)/\sin[(\delta_1 + \delta_2)/2]. \tag{10}$$

The ellipticity of only one of the orthogonal eigenmodes is represented in (9).

To clarify the significance of $\Delta\theta$, find the azimuth of the output light that may be qualified as a characteristic of the optical response of the OLS discussed. One gets (see appendix)

$$\chi_{\Delta\delta} = \frac{k}{\sin[(\delta_1 + \delta_2)/2]}\left[\sin\left(\frac{\delta_1 - \delta_2}{2}\right)\sin\Delta + 2\sin\left(\frac{\delta_1}{2}\right)\sin\left(\frac{\delta_2}{2}\right)(\cos\Delta - 1)\right] + \theta\cos\Delta. \tag{11}$$

Both $K_{\Delta\delta}$ and $\Delta\theta_{\Delta\delta}$ contribute to $\chi_{\Delta\delta}$, as seen from (11). However, the contributions differ from the standpoint of symmetry. If the symmetry operation of time inversion ($\boldsymbol{q} \to -\boldsymbol{q}$) is considered (Sirotin and Shaskolskaya 1979), the OLS should be replaced by its enantiomorph, with $k \to -k$ and $\delta_1 \rightleftarrows \delta_2$ in formula (8). This leads to alteration of the sign of $\Delta\theta_{\Delta\delta}$, whereas $K_{\Delta\delta}$ remains invariant. A pseudoscalar gyration parameter G for a given direction in the crystal is known to be characterized by

$$G = q_i^{(\mathrm{u})} g_{ij} q_j^{(\mathrm{u})}. \tag{12}$$

Accordingly, optical activity does not alter under the time inversion, contrary to the rotation angle of the indicatrix. Thus the mentioned contributions to the optical response (11) indeed originate from the optical activity and the indicatrix rotation.

The optical activity within the model is attributed to unipolarity of the OLS. In the case of small δ_1, δ_2

$$K_{\Delta\delta} \simeq k\eta \tag{13}$$

where η is the unipolarity coefficient:

$$\eta = (\delta_1 - \delta_2)/(\delta_1 + \delta_2). \tag{14}$$

When the crystal is not unipolar ($\delta_1 = \delta_2$), we have the results of subsection 2.1. For a single-domain structure ($\delta_1 = 0$ or $\delta_2 = 0$), $K = \mp k$ and $\Delta\theta = 0$, as for a homogeneous crystal.

2.3. Optical layered structure with local boundary imperfection

In the OLS displayed in figure 1(c), a perfect modulation is disturbed at one crystal boundary by the presence of a non-compensated optical layer with the phase retardation $\delta_0 \neq \delta$. Such a defect in a periodic structure we will refer to as 'local' or 'point' unipolarity. From energy considerations, the physical realization of the model is less possible than that of the model presented in subsection 2.1. Indeed, a non-unipolar multidomain structure of the ferroelectric phases provides minimum electrostatic energy in a system. Regarding the INC phases, the phase solitons are known to originate and annihilate in pairs. Dijkstra (1991a) and Dijkstra *et al* (1992a) also supposed that the phase of the INC modulation had to be zero at the sample surfaces, contrary to Stasyuk and Shvaika (1991). We illustrate here the effect of a local distortion of modulation wave on optical properties.

The OLS turns out to be an elliptic phase retardation plate, with

$$K_{\delta_0} = k\frac{\sin(\delta_0/2)}{\cos(\delta/2)}\left[\cos\left(\frac{\delta-\delta_0}{2}\right)\cot\left(\frac{\Delta}{2}\right) - \sin\left(\frac{\delta-\delta_0}{2}\right)\right] \tag{15}$$

$$\Delta\theta_{\delta_0} = k\frac{\sin[(\delta-\delta_0)/2]}{\cos(\delta/2)}\left[\sin\left(\frac{\delta_0}{2}\right)\cot\left(\frac{\Delta}{2}\right) - \cos\left(\frac{\delta_0}{2}\right)\right] \tag{16}$$

where Δ is the total phase retardation in the OLS.

The optical activity can be interpreted in terms of unipolarity, but its character is not trivial. Even if the optical activity of $2N$ layers is assumed to be cancelled, the optical activity of the OLS does not reduce to that of the non-compensated layer. Then, both K_{δ_0} and $\Delta\theta_{\delta_0}$ behave critically in the vicinity of $\Delta = 2\pi m$, where $m = \pm 1, \pm 2$, etc. This demonstrates an unexpected feature for the optical properties of real inhomogeneous systems: a dependence on the exact sample thickness concerned with the phase retardation. Naturally, equations (15) and (16) are valid unless K and $\Delta\theta$ become comparable with respect to unity. For small δ and δ_0, K_{δ_0} is determined mainly by the divergent term in (15), which is proportional to $k\delta_0$, while $\Delta\theta_{\delta_0}$ is determined by the almost constant term in (16) proportional to $k(\delta-\delta_0)$. The cases of $\Delta = 0$ and its vicinity need a special analysis (see subsections 2.9 and 3.2).

2.4. *Non-unipolar 'shifted' optical layered structure*

The OLS shown in figure 1(d) does not have any unipolarity. The phase of the modulation acquires the same non-zero values at the sample surfaces, since $\delta_0 \neq \delta$. This forms a structure 'shifted' with regard to the OLS of figure 1(a). The corresponding optical characteristics become

$$K_{\Delta\varphi} = 0 \tag{17}$$

$$\Delta\theta_{\Delta\varphi} = \frac{k}{\cos(\delta/2)}\left[-2\sin\left(\frac{\delta-\delta_0}{2}\right)\sin\left(\frac{\delta_0}{2}\right)\cot\left(\frac{\Delta}{2}\right) + \sin\left(\frac{\delta-2\delta_0}{2}\right)\right]. \tag{18}$$

The optical activity is zero as a consequence of the absence of unipolarity. The major part of the indicatrix rotation is associated with the second term in (18), similarly to (7). However, a small term appears in (18), proportional to $k\delta_0(\delta-\delta_0)$ and divergent at $\Delta = 2\pi m$. This is caused by the boundary conditions, which can be formulated in terms of local distortions of the modulation placed symmetrically at the boundary surfaces.

2.5. *Optical layered structure with local imperfection in the sample volume*

If local distortion of the modulation occurs inside the volume of the sample (see figure 1(e)), the optical parameters of the (unipolar) OLS are found to be

$$K_{\Delta_1\delta_0\Delta_2} = \frac{k}{\cos(\delta/2)}\left[\sin\left(\frac{\delta}{2}\right)\cot\left(\frac{\Delta}{2}\right) - \sin\left(\frac{\delta-\delta_0}{2}\right)\cos\left(\frac{\Delta_1-\Delta_2}{2}\right)\Big/\sin\left(\frac{\Delta}{2}\right)\right] \tag{19}$$

$$\Delta\theta_{\Delta_1\delta_0\Delta_1} = -\frac{k}{\cos(\delta/2)}\sin\left(\frac{\delta-\delta_0}{2}\right)\sin\left(\frac{\Delta_1-\Delta_2}{2}\right)\Big/\sin\left(\frac{\Delta}{2}\right). \tag{20}$$

The significance of the phase retardations Δ_1, Δ_2 and δ_0 is obvious from the figure. One can see that the optical activity and the indicatrix rotation have singularities of $\cot(\Delta/2)$ or $(\sin(\Delta/2))^{-1}$ type at $\Delta = 2\pi m$. The model becomes clearer when we take $\delta_0 = 0$. Then

$$K_{\Delta_1\Delta_2} = -2k\tan\left(\frac{\delta}{2}\right)\sin\left(\frac{\Delta_1}{2}\right)\sin\left(\frac{\Delta_2}{2}\right)\Big/\sin\left(\frac{\Delta}{2}\right) \tag{21}$$

$$\Delta\theta_{\Delta_1\Delta_2} = -k\tan\left(\frac{\delta}{2}\right)\sin\left(\frac{\Delta_1-\Delta_2}{2}\right)\Big/\sin\left(\frac{\Delta}{2}\right). \tag{22}$$

Here the optical activity is purely a result of local distortion of the perfectly periodic modulation wave, despite the lack of unipolarity (see Vlokh *et al* 1992a). Like the boundary imperfections, such distortion leads to enhancement of the optical activity and the indicatrix rotation in the vicinity of $\Delta = 2\pi m$. It is worth noting that the model dealing with the imperfections of modulation inside the sample volume, instead of the boundary ones, is more universal and realistic in practice.

2.6. Effect of many local imperfections

In this subsection we test the effect of many local imperfections of a periodic structure on the optical properties of the latter. Generally, the imperfections can be distributed randomly. We consider analytically the simplest case of a periodic distribution. Suppose the OLS discussed in the previous subsection to be repeated M times as depicted in figure 1(*f*). Simplifying the situation, this yields the OLS with $2M$ structural defects. Its optical activity and indicatrix rotation become

$$K_M = \frac{k}{\cos(\delta/2)}\left[\sin\left(\frac{\delta}{2}\right)\cot\left(\frac{\Delta}{2M}\right) - \sin\left(\frac{\delta-\delta_0}{2}\right)\cos\left(\frac{\Delta_1-\Delta_2}{2}\right)\Big/\sin\left(\frac{\Delta}{2M}\right)\right] \tag{23}$$

$$\Delta\theta_M = -\frac{k}{\cos(\delta/2)}\sin\left(\frac{\delta-\delta_0}{2}\right)\sin\left(\frac{\Delta_1-\Delta_2}{2}\right)\Big/\sin\left(\frac{\Delta}{2M}\right) \tag{24}$$

where Δ again denotes the phase retardation in the entire OLS. If we compare (23), (24) with (19), (20), we see that singularities at $\Delta = 2\pi m$ disappear for certain non-zero m. On the contrary, K_M and $\Delta\theta_M$ are enhanced M times when Δ is close to $\Delta = 0$. In fact, $\cot(\Delta/2M)$ behaves here as $\sim 2M/\Delta$, while $\cot(\Delta/2)$ behaves as $\sim 2/\Delta$. The effect of local imperfections thus turns out to be cumulative. Note that similar results can be derived for other composite OLSs. Moreover, we expect this to be true for a random imperfection distribution.

2.7. Optical layered structure with different periodicities

Let the structure be formed by joining the two OLSs of figure 1(*c*) when they have different periodicities $2l_1$ and $2l_2$ (phase retardations $2\delta_1$ and $2\delta_2$, respectively), and the non-compensated layers be characterized by $\delta_{01} = \delta_1$, $\delta_{02} = \delta_2$. We arrive at the OLS depicted in figure 1(*g*), for which

$$K_{\delta_1\delta_2} = k\sin\left(\frac{\delta_1-\delta_2}{2}\right)\cos\left(\frac{\Delta_1}{2}\right)\cos\left(\frac{\Delta_2}{2}\right)\Big/\left[\cos\left(\frac{\delta_1}{2}\right)\cos\left(\frac{\delta_2}{2}\right)\sin\left(\frac{\Delta}{2}\right)\right] \tag{25}$$

$$\Delta\theta_{\delta_1\delta_2} = \frac{k}{2\cos(\delta_1/2)\cos(\delta_2/2)} \times\left[\sin\left(\frac{\delta_1-\delta_2}{2}\right)\sin\left(\frac{\Delta_1-\Delta_2}{2}\right)\Big/\sin\left(\frac{\Delta}{2}\right) - \sin\left(\frac{\delta_1+\delta_2}{2}\right)\right] \tag{26}$$

where Δ_1 and Δ_2 are the phase retardations in the constituent OLSs. In the limit of $\delta_1 = \delta_2$ the optical activity vanishes since the structure transforms to the perfect OLS (figure 1(a)).

The expressions (25) and (26) do not have extra peculiarities besides the ones mentioned above. We therefore conclude that the existence of more than one periodicity in the modulated material does not introduce an appreciable effect, compared with the case of one periodicity $2l$ (cf Dijkstra *et al* 1992a). The two cases are hardly distinguishable also in a manner suggested by Dijkstra *et al* (1992a) because the phase retardation in the optical layers is, mainly, less significant than π.

2.8. *Optical layered structures with modulated off-diagonal component of symmetric dielectric tensor*

Dijkstra (1991a) and Dijkstra *et al* (1992a) suggested a model for an INC crystal in which the off-diagonal component $\epsilon_{12}^{(0)}$ of the real symmetric dielectric tensor is modulated along the z axis. This involves a spatial dependence of local position ρ of the optical indicatrix

$$\tan(2\rho) = 2\epsilon_{12}^{(0)}/(\epsilon_{11}^{(0)} - \epsilon_{22}^{(0)}). \tag{27}$$

Except in the narrow vicinity of $\Delta = 0$, the modulation depth is small, and (27) reduces to

$$\rho = \epsilon_{12}^{(0)}/(2\bar{n}\Delta n). \tag{28}$$

Supposing a simple square waveform of the modulation, we get the model of Dijkstra (1991a) with small ρ varying from $+\rho$ to $-\rho$ in the optical layers. Besides the INC phases, multidomain ferroelastic ones should be the relevant cases. The Jones matrix of the layers takes the form

$$\mathbf{T}_{\pm}^{\rho} = \begin{pmatrix} \exp(-\mathrm{i}\delta/2) & \mp 2\mathrm{i}\rho\sin(\delta/2) \\ \mp 2\mathrm{i}\rho\sin(\delta/2) & \exp(\mathrm{i}\delta/2) \end{pmatrix} \tag{29}$$

where δ is again the phase retardation in the layer. Calculations for the OLS with perfect modulation (figure 1(a) where ρ is now modulated, instead of k) give the following optical parameters:

$$K_{2N}^{\rho} = \rho\tan(\delta/2) \tag{30}$$

$$\Delta\theta_{2N}^{\rho} = 0 \tag{31}$$

while the overall phase retardation $\Delta_{2N}^{\mathrm{ob}} = 2N\delta$ remains practically unaffected. Expressions (30) and (31) reduce to those derived by Dijkstra (1991a). In other words, an ideal structure with modulated $\epsilon_{12}^{(0)}$ gives rise to optical activity.

Using (29), one can analyse other OLSs. So, we obtain

$$K_{\Delta\delta}^{\rho} = 2\rho\sin(\delta_1/2)\sin(\delta_2/2)/\sin[(\delta_1+\delta_2)/2] \tag{32}$$

$$\Delta\theta_{\Delta\delta}^{\rho} = \rho\sin[(\delta_1-\delta_2)/2]/\sin[(\delta_1+\delta_2)/2] \tag{33}$$

and

$$K_{\Delta\varphi}^{\rho} = \frac{\rho}{\cos(\delta/2)}\left[2\sin\left(\frac{\delta-\delta_0}{2}\right)\sin\left(\frac{\delta_0}{2}\right)\cot\left(\frac{\Delta}{2}\right) - \sin\left(\frac{\delta-2\delta_0}{2}\right)\right] \tag{34}$$

$$\Delta\theta_{\Delta\varphi}^{\rho} = 0 \tag{35}$$

for the OLSs shown in figures 1(b) and (d), respectively.

Comparing (30)–(35) with the relevant formulae from sections 2.1, 2.2 and 2.4, we see that the behaviour of indicatrix rotation within the OLS model for modulated g_{ij} coincides with the behaviour of optical activity within the model for modulated $\epsilon_{ij}^{(0)}$, and vice versa. One can easily substantiate this for arbitrary OLS. It is evident now that the phenomenon of indicatrix rotation can be looked at in a more general manner than has been done in section 2.1. Namely, we are able to point out the following reasons for both the optical activity and indicatrix rotation in a spatially modulated medium with average inversion symmetry:

(i) inhomogeneity of the (even perfect) structure on a semimacroscopic scale (see Meekes and Janner 1988, Dijkstra *et al* 1992a, Vlokh *et al* 1992a);

(ii) polarization of the structure inducing a general unipolarity; and

(iii) local distortions of the phase of the modulation wave, the effect of which can accumulate.

2.9. *Modulated structure in the absence of linear birefringence*

All the results derived above refer to essentially anisotropic ($\Delta n \gg G$) directions in crystals studied in HAUP-type experiments. On the other hand, it should be of interest to clarify the case of a weak anisotropy ($\Delta n = 0$). A relevant analysis for the optical properties of the crystal with modulated gyration parameter is then very simple. One must use a more general form for the basic Jones matrix (2) that transforms into the Jones matrix for an optical rotator (see Shurcliff 1965, Azzam and Bashara 1981) when $|k| = 1$. The resulting Jones matrix for each typical OLS is given by the product of Jones matrices of rotators.

As a result, the overall optical rotatory power ψ of a system becomes additive and differs from zero only when non-compensated layers occur. Especially for the OLS shown in figure 1(b),

$$\psi_{\Delta\delta} = \psi_0 \eta \tag{36}$$

where ψ_0 denotes the optical rotatory power for a 'single-domain' crystal with the same thickness. The optical activity is related to unipolarity of the sample, in accordance with the experimental results reported by Vlokh *et al* (1985, 1987) for the optical axis directions in INC materials. Naturally, indicatrix rotation vanishes within the model.

Regarding the model presented in the previous subsection, it describes an isotropic medium when $\Delta n = 0$, as the phase retardations in the layers become zero (cf Dijkstra 1991a). The model can give rise to neither optical activity nor indicatrix rotation.

Thus, we see that the origin of the optical activity in a modulated dielectric medium differs in the two alternative cases considered.

2.10. *Structure with traingularly modulated gyration component*

To simulate a sinusoidal modulation, consider a triangular shape of the modulation wave, instead of the square one. Let the structure be perfect with zero phase at the surface boundaries (cf the OLS in figure 1(a)). We assume the unit modulation cell representing one complete period to consist of $4N_0$ birefringent optically active layers. For the first half-period their eigenwave ellipticities are given successively by

$$0,\ k',\ 2k',\ \ldots,\ (N_0 - 1)k',\ N_0k',\ (N_0 - 1)k',\ \ldots,\ 2k',\ k'$$

where $k' = k/N_0$. The phase retardation per layer is $\delta/(2N_0)$ with δ the phase retardation in half the unit cell. Similarly for the second half-period, k' must be replaced by $-k'$, etc.

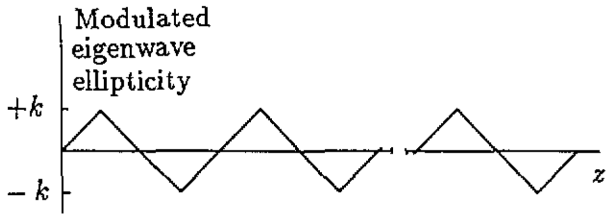

Figure 2. Schematic representation of a perfect triangular modulation wave.

Using the basic Jones matrix (2) of one layer and assuming the crystal to contain N unit cells, one can obtain in the continuous limit ($N_0 \to \infty$) the resulting Jones matrix of the triangularly modulated structure (figure 2).

The optical parameters of the latter can be written as

$$K^t_{2N} = 0 \tag{37}$$

$$\Delta\theta^t_{2N} = -2k[1 - \cos(\delta/2)]/[\delta\cos(\delta/2)]. \tag{38}$$

The peculiarities of the optical activity and the indicatrix rotation turn out to be analogous to those of the square-modulated structure studied in section 2.1. In particular, restriction to $\delta \ll 1$ yields $\Delta\theta^t_{2N} \simeq -k\delta/4$, while (7) reduces to $\Delta\theta_{2N} \simeq -k\delta/2$. Similar conclusions can be drawn by consideration of other typical modulated structures. As an example, we examine a 'shifted' structure that is an analogue of the OLS shown in figure 1(d). Appropriate Jones calculations result in

$$K^t_{\Delta\varphi} = 0 \tag{39}$$

$$\Delta\theta^t_{\Delta\varphi} = k[(c\cos\delta_0 + \sin\delta_0 - 1/\delta_0) + (\cos\delta_0 - c\sin\delta_0)\cot(\Delta/2)] \tag{40}$$

with

$$c = 1/\delta_0 + 2[1 - \cos(\delta/2)]/[\delta\cos(\delta/2)] \tag{41}$$

where Δ and δ_0 have the usual meaning, and $|\delta_0| < |\delta|$. Keeping the terms proportional to $k\delta$, $k\delta_0$ and $k\delta\delta_0$ for small δ and δ_0 in (40), one concludes that expressions (18) and (40) give just the same behaviour of the indicatrix rotation. The only difference in the models is a factor $\frac{1}{2}$ for triangular modulation.

The analysis performed proves the optical properties of a modulated medium to be independent of the exact modulation shape (see Dijkstra 1991b). We thus may confirm that the same mechanisms are responsible for the optical activity and the indicatrix rotation when a sinusoidal modulation takes place. Notice that numerous discrepancies are available between our results and those reported by Stasyuk and Shvaika (1991) for a sinusoidal regime. So, the 'shifted' structure with modulated gyration component manifests the optical activity (Stasyuk and Shvaika 1991), while we find the contrary.

3. Discussion of the model

3.1. Interaction of incommensurate structure with defects

In this subsection we elucidate the physical reasons for distortions of the modulated INC structure. It is a well known fact (Cummins 1990) that the assumption concerning the perfect periodicity of the modulation wave has a limited field of use. In practice, the discrete underlying lattice and particularly extrinsic defects (impurities, vacancies, etc) can cause pinning of the modulation wave. We refer to numerous theoretical works (e.g. Rice *et al* 1981, Errandonea 1986, Srolovitz *et al* 1987) for explanation of the interaction between the INC structure and defects. Here we consider the effect of the point defects related to the phase of the modulation. Then local distortions of the phase should be concerned with an excess energy due to the soliton–defect interaction. Within the phenomenological approach used in section 2 the effect of random structural defects on the optical activity is just simulated by the appearance of optical layers with phase retardation unequal to that of the rest.

Furthermore, we must emphasize the role of rigid or frozen-in defects with low mobility, as those impose maximum distortions in a regular soliton distribution, causing enhancement of the optical activity and indicatrix rotation. Structure–defect interaction is known (Srolovitz *et al* 1987) to become efficient when soliton velocity and defect diffusivity are comparable. In the case of fixed defects, this occurs when the temperature of the system is kept stable for a certain time. It is noteworthy that the HAUP-type experiments are performed under exactly the conditions mentioned (see Dijkstra *et al* 1991). As the optical activity in INC crystals depends on the efficiency of structure–defect interaction, we expect that different values of gyration can be observed for different rates of temperature variations in experiments (cf Mogeon *et al* 1989). Probably, the data of relatively 'quick' experiments for optical axis directions (Vlokh *et al* 1985, 1987) differ for that reason from those of the HAUP ones. Another reason is mentioned in section 2.9.

The recent study by Kushnir *et al* (1993) revealed that a notable part of the optical activity in the INC $[N(CH_3)_4]_2ZnCl_4$ had to be attributed to defect concentration in the sample. The indicatrix rotation detected in the experiment decreased with annealing. An important fact for understanding of the problem was the conspicuous effect of x-ray radiation damage on the optical properties of $[N(CH_3)_4]_2ZnCl_4$. X-ray defects are known (Bziouet *et al* 1987, Jamet 1988) to increase strongly the global thermal hysteresis of the modulation wavevector, but hardly influence the memory effect in the INC phases. They can therefore be referred preferably to fixed defects, that being consistent with our interpretation.

Pinning by the point defects strengthens with decreasing temperature of the INC crystal, as the pinning potential overcomes the interaction between more and more distant solitons. Immediately close to the lock-in temperature the long-range order of the structure is destroyed by defects, and the solitons can be distributed in a random way, forming a chaotic state (Jensen and Bak 1984, Prelovšek and Blinc 1984). This should be reflected in the optical characteristics.

Generally, we remark that a conspicuous spatial dispersion should be characteristic of the INC phases as analysed by Golovko and Levanyuk (1979). However, these phases are materialized in crystals with average inversion symmetry. Despite the latter, a gyration can exist (Dijkstra 1991a). Then, any disturbance of a regular structure or its polarization induce symmetry breaking and increase of the optical activity. It is a reasonable assumption that the major effects producing the optical activity occur in the bulk of the INC material rather than at its boundary surfaces as predicted by Dijkstra (1991a). Those effects originate from defects contained in the structure. Accordingly, the sign of the optical activity seems to be also determined by related phenomena.

3.2. Value and temperature variations of the optical activity and the indicatrix rotation

Let us concentrate on the behaviour of the optical parameters derived in section 2. This can be realized by considering the typical magnitudes and the temperature evolution for the parameters involved in the model (k, ρ, δ, δ_0, Δ, etc). The main peculiarity found is a small value of the predicted effects. Dropping the singular terms in expressions for K and $\Delta\theta$, which need special examination, we see that the optical parameters are proportional to $k\delta$ or $k\delta_0$. Otherwise, $K/k \sim \delta$ where k represents in fact the eigenwave ellipticity in uniform material without an inversion centre.

For the INC phases, it seems unlikely that there are grounds for believing the characteristic length $2l$ to exceed in order of magnitude the INC periodicity dimension. Then we can estimate $\delta \simeq 5 \times 10^{-5}$, 3×10^{-3} and 3×10^{-2} for $[N(CH_3)_4]_2ZnCl_4$, Rb_2ZnBr_4 and $[N(CH_3)_4]_2CuCl_4$, respectively, where data by Meekes and Janner (1988), Dijkstra (1991a) and Ortega *et al* (1992) are employed. One must take into account that such large difference in δ can be cancelled in the observed gyration by the corresponding difference in magnitudes of the linear birefringence.

We consider the optical activity data for the $[N(CH_3)_4]_2ZnCl_4$ compound ($K \simeq 10^{-3}$, $G \simeq 10^{-7}$) studied by several groups (Kobayashi *et al* 1986, Dijkstra *et al* 1992b, Kushnir *et al* 1993, among others) to be reliable enough. In order to make simple but very rough estimations, assume that the gyration parameters G_i of the crystals mentioned do not differ significantly in magnitude. Using expressions like (3), one can deduce the relation between the data for different INC materials:

$$K_i/K_j \simeq \Delta n_j/\Delta n_i. \qquad (42)$$

We should thus predict very small values $K \simeq 2 \times 10^{-5}$ in Rb_2ZnBr_4 and $K \simeq 2 \times 10^{-6}$ in $[N(CH_3)_4]_2CuCl_4$, which are outside the capacity of the experimenter. The work by Ortega *et al* (1992) proves that. Similar estimations for Rb_2ZnCl_4 yield $K \simeq 5 \times 10^{-5}$, while Kobayashi *et al* (1988) obtained the (average) value $K \simeq 5 \times 10^{-4}$. This can be understood only with the view that the gyration in Rb_2ZnCl_4 is an order of magnitude larger than in $[N(CH_3)_4]_2ZnCl_4$. On the other hand, defects and unipolarity in a crystal can enhance the optical activity, as observed by Kushnir *et al* (1993).

Other conditions occur in multidomain ferroelectric phases, where, for example, $l \simeq 10\ \mu m$. At sufficiently large linear birefringence we may expect an unusual behaviour of the optical activity and the indicatrix rotation (see Vlokh *et al* 1992a) in such inhomogeneous phases.

We now turn to temperature evolution of the parameters involved in the Jones model of the INC crystal. Both optical activity and indicatrix rotation depend on the modulation depth for ϵ_{ij} components, i.e. on k and ρ. The modulation depth has to be related to the order parameter amplitude. This is why the optical activity near the normal–INC phase transition temperature T_i can be interpreted (see Saito and Kobayashi 1991, Fousek 1991) according to a power law

$$G \simeq (T_i - T)^{\beta}. \qquad (43)$$

However, application of formula (43) is rather limited. A few different cases for the optical activity behaviour near T_i are found experimentally (see Kobayashi *et al* 1986, Meekes and

Janner 1988, Dijkstra *et al* 1992b, Kushnir *et al* 1993). The optical activity can follow (43), or become zero already below T_i, or exhibit a residual effect in the normal phase. This is explained by the influence of structural defects on the optical activity as shown in this paper.

Pinning by defects produces more pronounced effects when temperature lowers towards T_c, the lock-in–INC transition point. The structure can acquire some unipolarity (Sanctuary *et al* 1985), which depends on the prehistory of a sample and the presence of external fields. Furthermore, the soliton density n_s tends to zero on approaching T_c, and the modulation period $2l$ determining the size of the optical effects is related to n_s as $2l \sim n_s^{-1}$. All these factors should cause an increase of the optical activity. Note that similar phenomena are, to a certain extent, characteristic for temperatures below T_c.

Finally, we examine the behaviour of the model near a specific temperature T_0, where the linear birefringence passes through zero. The latter happens in $[N(CH_3)_4]_2ZnCl_4$. Close to T_0, the modulated parameters increase strongly: $k \to \pm 1$ and $\rho \to \pm\pi/4$. We assume that all the phase retardations depend linearly on temperature (Δ, δ, $\delta_0 \sim T - T_0$) in the vicinity of T_0, while $k, \rho \sim (T - T_0)^{-1}$ according to (3) and (28). Checking the perfect modulated structure gives $K^{\rho}_{2N} \sim \rho\delta \simeq$ const, which results in a zero gyration parameter observed near T_0 (see data reported by Kobayashi *et al* (1986) and Dijkstra *et al* (1992a, b)). The imperfect structure considered in section 2.5 manifests another behaviour:

$$K_{\Delta_1\delta_0\Delta_2} \sim k\delta/\Delta \sim \alpha(T - T_0)^{-1} \tag{44}$$

when we account for only the first term in (19). Relation $\Delta n \sim \gamma(T - T_0)$ causes gyration G to be non-zero in the vicinity of T_0:

$$G = 2K\bar{n}\Delta n \simeq 2\alpha\gamma\bar{n}. \tag{45}$$

The higher the defect concentration, the larger is the coefficient α, as shown in section 2.6. Relevant experimental data are reported by Kushnir *et al* (1993).

On the other hand, one can directly notice that the eigenwave ellipticity K is very sensitive near T_0: it becomes zero if the gyration is zero, and tends to ± 1 if the latter remains non-zero at T_0 owing to small unipolarity, etc. We observe again a link between the optical properties and a specific state of the sample, as is often the case for INC crystals. Unfortunately, it is difficult to clarify experimentally the exact temperature dependence of K in a narrow vicinity of T_0 because of the hard effects of the optical equipment imperfections (Moxon and Renshaw 1990).

4. Concluding remarks

In this paper a phenomenological model is presented that describes visually the crystal optics of a spatially modulated dielectric medium with average inversion symmetry. Several typical inhomogeneous structures are analysed with Jones calculus. The model explains the presence of optical activity in the INC material, as well as the effect of unipolarity and structural defects on the optical properties. The model is thus expected to contain the essential physical ingredients of the problem, although the link with the crystal symmetry is disregarded, which has been the main concern of the works by Meekes and Janner (1988) and Dijkstra *et al* (1992a). A further effect is shown to be possible: an indicatrix rotation, which can be detected in HAUP-type experiments. Within the present approach, the linear birefringence related to the phase retardation of a system is affected only in the approximation quadratic in modulated parameters k and ρ. The relevant phemomena turn out to be weak, except in the narrow vicinity of a specific temperature T_0 (see Dijkstra 1991a). It implies that other efficient mechanisms are responsible for the behaviour of the linear birefringence in the INC crystal (Fousek 1991).

In our view, the role of the boundary surfaces in crystal optics of modulated systems (Dijkstra 1991a) is exaggerated. The corresponding sensitivity of the optical parameters to the boundary conditions represents one of the remaining problems. Immediately, that points to a small value of the effects predicted. On the other hand, such a singularity may be a consequence of the oversimplified analytical description. In this paper we have shown schematically how the importance of the bulk crystal can increase within the model.

The soliton distribution in real INC systems can be much more complicated in comparison with that supposed by Dijkstra (1991a). This would arise from the influence of random defects on the modulation, the coexistence of more than one periodicity, etc. A good illustration is given by Pan and Unruh (1990) for a discommensuration pattern in the lock-in phase of K_2ZnCl_4. As a result, we should analyse a complex superposition of the modulated structures discussed in this paper. Of course, such a model has to be cumbersome, but includes some efficient integrating factors. We think that the latter would remove the critical behaviour of the model with respect to accidental conditions.

Finally, we stress that the model shows the smallness of the gyration effect in INC materials. Indeed, an approximation of the average structure gives zero optical activity in a centrosymmetric INC crystal, which is unfoundedly presumed to be uniform. In a more accurate approximation, considering the spatial inhomogeneity of the structure leads to optical activity. However, the spatial scale $2l$ of the inhomogeneity is small. Within the model presented in the paper, it is difficult to explain why the gyration is of an order of magnitude comparable with that of α-quartz.

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Appendix

Let us derive the optical parameters of a composite phase retardation plate whose Jones matrix has the following form in the coordinate system related to the principal axes of the constituent optical layers:

$$\mathbf{T}_S = \begin{pmatrix} \exp(-i\Delta/2) & k(a+ib) \\ k(-a+ib) & \exp(i\Delta/2) \end{pmatrix}. \tag{A1}$$

$\mathbf{T}_S$ is unimodular as $k \ll 1$ and $\mathbf{T}_{S,22} = \mathbf{T}_{S,11}$, $\mathbf{T}_{S,21} = -\mathbf{T}_{S,12}$. The Jones matrices discussed in the paper can be reduced to (A1), including $\mathbf{T}_\pm$. Suppose for simplicity that other optical components (polarizer, analyser, etc) are perfect, contrary to the works of Kobayashi *et al*

(1986) and Vlokh *et al* (1992b). Then the Jones vector of the light transmitted through a crystal is defined as follows:

$$\boldsymbol{E}_{SO} = \mathbf{T}_S \boldsymbol{E}_{SI} \tag{A2}$$

with $\boldsymbol{E}_{SI}$ representing the Jones vector of a linearly polarized light wave incident on the crystal:

$$\boldsymbol{E}_{SI} = \begin{pmatrix} 1 \\ \theta \end{pmatrix}. \tag{A3}$$

In (A3) θ is the small incident polarization azimuth. The azimuth χ and the ellipticity ϵ of the output light associated with $\boldsymbol{E}_{SO}$ are given by

$$\chi = \mathrm{Re}(E_{SO,y}/E_{SO,x}) \qquad \epsilon = \mathrm{Im}(E_{SO,y}/E_{SO,x}). \tag{A4}$$

The value θ_0 of the symmetry azimuth ($\chi_0 = \theta_0$) and the characteristic ellipticity ϵ_0 defined as the output ellipticity at $\theta = \theta_0$ (Vlokh *et al* 1992b) become

$$\theta_0 = K\cot(\Delta/2) + \Delta\theta \tag{A5}$$

$$\epsilon_0 = 2K \tag{A6}$$

respectively, where

$$\Delta\theta = -kb/[2\sin(\Delta/2)] \tag{A7}$$

$$K = -ka/[2\sin(\Delta/2)]. \tag{A8}$$

Note that θ_0 and ϵ_0 are the quantities measured experimentally within the polarimetric method of Vlokh *et al* (1992b).

Performing the analogous calculations for the Jones matrix $\mathbf{T}_+$ of a homogeneous birefringent optically active crystal yields

$$\theta_0 = k\cot(\delta/2) \tag{A9}$$

$$\epsilon_0 = 2k. \tag{A10}$$

We emphasize that the Jones matrices $\mathbf{T}_+$ and $\mathbf{T}_S$ are defined in the same coordinate system.

Comparing (A5), (A6) with (A9), (A10), one can see that K and $\Delta\theta$ imply the eigenwave ellipticity and the indicatrix rotation in an inhomogeneous OLS described by (A1). This conclusion can also be arrived at by examining the azimuthal angles and ellipticities of the eigenmodes of $\mathbf{T}_S$ in approximation linear in k. Thus, the optical activity and the indicatrix rotation are related in a simple way to the real and imaginary parts of the off-diagonal elements of $\mathbf{T}_S$. Moreover, K and $\Delta\theta$ can be immediately detected in polarimetric experiments (see Vlokh *et al* 1992a, Kushnir *et al* 1993). These values contribute also to the light intensity function employed in HAUP (Kobayashi *et al* 1986).

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