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An interpretation for the optical activity in incommensurately modulated $[N(CH_3)_4]_2ZnCl_4$ using Jones calculus

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Abstract. Within the framework of Jones calculus a model is presented for the optics in incommensurately modulated structures. The results are compared with measurements of the birefringence $\Delta n(0,0,1)$ and of the optical activity coefficient $G(0,0,1)$ for $[N(CH_3)_4]_2ZnCl_4$. The model describes the spatial dispersion of the modulated dielectric tensor to vary along the modulation wave direction (parallel to the c axis) in the plane perpendicular to this direction (the (a,b) plane). The model shows that despite the fact that the average structure is centrosymmetric optical activity can occur due to the incommensurate modulation. The experimental values can be explained as the consequence of the periodic spatial dispersion of the dielectric tensor, together with appropriate boundary surfaces of the finite crystal, which represent a spontaneous breaking of the inversion symmetry of the modulated structure.

1. Introduction

The development, in recent years, of accurate equipment to determine the gyration tensor (which describes the optical activity) and the birefringence in crystals, has opened new fields of investigation. The high-accuracy universal polarimeter (HAUP), developed by Kobayashi *et al* (1986), has been used to determine the optical activity in the incommensurate (INC) phases of different materials (Saito *et al* 1987, Meekes and Janner 1988, Dijkstra and Janner 1990). The presence of a gyrational effect is remarkable, because both the space group of the average structure and the superspace group of these INC phases are centrosymmetric and should therefore not allow optical activity.

The optical activity is understood to originate from the spatial dispersion in the dielectrical properties of the crystal. Several authors have discussed the effects of this dispersion on the birefringence (Golovko and Levanyuk 1979, Fousek and Kroupa 1986, Meekes and Janner 1988), but a description of the optical activity turned out to be cumbersome. Meekes and Janner showed that there are some Fourier components of the gyration tensor which are allowed by the superspace group symmetry. Their approach predicts the directions of light propagation for which optical activity may occur, without specifying the corresponding fields.

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With a HAUP apparatus built in our laboratory we determined the gyration coefficient $G(0,0,1)$ and the birefringence $\Delta n(0,0,1)$ for $[N(CH_3)_4]_2ZnCl_4$ (tetramethylammonium tetrachlorozincate (TMAZC)). Below $T_i = 297$ K the INC phase of TMAZC can be described by the superspace group $Pcmn(00\gamma)(1s\bar{1})$, the modulation wavevector being $q = \gamma c^*$ (Madariaga *et al* 1987). At the lock-in phase transition temperature $T_c = 280$ K the modulation becomes commensurate: $q = 2/5c^*$. The polarization of the modulation is along the b axis, which in the lock-in phase gives a spontaneous polarization P_s along the same direction. Although Saito *et al* (1987) reported $G(0,0,1)$ to be zero in the INC phase, we find it to be non-vanishing. The gyration effect has been determined along both extinction directions (parallel to the a and b axes), giving different results.

In this paper a phenomenological model will be presented. It describes the gyration and birefringence, taking into account that the spatial dispersion due to the modulation causes the dielectric tensor to 'wiggle' in the (a,b) plane on going along the c direction, parallel to the modulation wave. It will be described in terms of Jones matrix calculus.

In section 2 we discuss the influence of the spatial dispersion due to the modulation on the dielectric properties. Section 3 deals with the representation and transformation by an optical medium, of polarized light. It is an introduction to section 4, in which the square-wave model will be described. Its implications are summarised in section 5. In section 6 the measurements on the birefringence and optical activity of TMAZC are given, and these are interpreted within the framework of the models in section 7. We draw conclusions in section 8.

2. Spatial dispersion in crystal optics

The electromagnetic properties of a medium are characterised by the (plane) monochromatic waves that can propagate through it. For a given frequency ω and direction of the wavevector k, different plane waves can exist, these being characterised by their polarizations and refractive indices.

Crystals are spatially inhomogeneous bodies on a microscopic scale. In general, the dielectric tensor, which describes the optical characteristics of the crystal, will have a k-dependence due to this spatial dispersion. Agranovich and Ginzburg (1984) derive the optics of a crystal in the presence of spatial dispersion. In classical crystal optics, this dispersion can, in most cases, be simplified rigorously. The effect of spatial dispersion on the optical properties is characterised by the parameter $a/\lambda = an/\lambda_0$, where a is the *characteristic dimension*, λ the wavelength of the plane wave in the medium, n the refractive index of this wave and λ_0 the wavelength in vacuuo. In a non-modulated crystal the characteristic dimension a may be taken to be of the order of the side of crystallographic unit cell, due to the lattice translational symmetry. Then, away from resonances in frequency (i.e. n not too large) spatial dispersion is weak. Under these conditions the crystal can be described as a homogeneous medium with a macroscopic dielectric tensor

$$\varepsilon(\omega, k) = \varepsilon(\omega) + i\gamma(\omega) \cdot k \tag{1}$$

where $\varepsilon(\omega)$ is the second-rank tensor describing the dielectric properties without taking spatial dispersion into account, and $\gamma(\omega)$ is the third-rank gyration tensor, which is zero in centrosymmetric materials.

If a crystal is modulated the optics become more complicated. Consider an electromagnetic wave propagating through a modulated crystal. Suppose the modulation is incommensurate, so there is no three-dimensional lattice translational symmetry. On propagating the wave will 'sense' a changing surrounding due to the presence of the modulation. As a result the wave itself will change while travelling. The characteristic dimension can become much larger than in a non-modulated crystal, and the optical properties can no longer be described by the tensors $\varepsilon(\omega)$ and $\gamma(\omega)$. In fact, in a real, incommensurate crystal the unit cell is, in principle, infinitely large and even for optical phenomena the effective unit cell is much larger than in the non-modulated case. This implies that spatial dispersion of ε and γ has to be taken into account. To interpret the experimental results we do not need to consider $\gamma(\omega, \boldsymbol{r})$. We will be able to describe the birefringence and optical activity observed by the use of a model of a spatially dependent dielectric tensor $\varepsilon(\omega, \boldsymbol{r})$. The origin of this optical activity is thus different in principle from that due to a non-zero $\gamma(\omega)$ in equation (1) for a non-modulated crystal.

One has to distinguish between local effects due to the displacive modulation and global (or long-range order) effects due to the incommensurability of that modulation. Locally, the modulation gives rise to a structure which deviates from the orthorhombic one allowing for non-diagonal terms in the dielectric tensor with respect to the orthorhombic axes. Those terms cannot be taken as constant over the whole structure, because that would be in contradiction with the orthorhombic symmetry of the average structure. This requirement can be realised by a periodic variation of the local effects, this being in harmony both with the long-range character of the incommensurability and its periodic nature. To conclude, the effective dielectric medium is described by local optical axes, periodically deviating from the orthorhombic ones of the average structure. This is compatible with a description based on the crystallographic structure giving rise to a microscopic space-dependent dielectric tensor having in its Fourier decomposition non-zero terms allowed by the superspace group symmetry in a manner described by Meekes and Janner (1988). The difference here is that a mesoscopic scale is considered and no imaginary antisymmetric dielectric tensor components are required. Indeed, our local dielectric tensor is both real and symmetric.

For the Jones calculation we will restrict ourselves to a rather simple description of the deviation angles; we will refer to it as the *square waveform*. The square wave is well applicable to the discommensuration regime (in the vicinity of the lock-in temperature T_c), but can also be viewed as the 'split approximation' of a sinusoidal modulation wave.

Suppose that the unmodulated crystal is described by a dielectric tensor compatible with the point group symmetry of the average crystal, which in the present case is orthorhombic (dropping the notation for the ω-dependence):

$$\varepsilon^0 = \begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix}. \tag{2}$$

We assume the crystal to be transversely modulated with wavevector along the $\boldsymbol{c}$ direction. We will only look at the influence of the square-wave modulation in the $(\boldsymbol{a}, \boldsymbol{b})$ plane. This causes the dielectric tensor to *wiggle* in this plane, meaning that the modulation gives rise to periodic off-diagonal elements, so that two of the axes

diagonalizing $\varepsilon(r)$ oscillate in the plane (a, b) as one moves along the c direction. We approximate the modulated dielectric tensor by homogeneous platelets parallel to the (a, b) plane, ensuring average orthorhombic behaviour. Taking into account the symmetry restrictions imposed by the superspace group for an appropriate modulation wavevector as derived by Meekes and Janner (1988), we can write for the contribution due to the modulation in platelet j

$$\varepsilon_{\text{mod}}(j) = \begin{pmatrix} 0 & (-)^j 2\varepsilon_5 & 0 \\ (-)^j 2\varepsilon_5 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{3}$$

So the dielectric tensor in platelet j is

$$\varepsilon(j) = \varepsilon^0 + \varepsilon_{\text{mod}}(j). \tag{4}$$

The eigenvalues of the corresponding matrix $\varepsilon(j)$ are

$$\lambda_\pm = \tfrac{1}{2}(\varepsilon_1 + \varepsilon_2) \pm \tfrac{1}{2}\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 16\varepsilon_5^2} \tag{5}$$

and for the two eigenvectors $(e_1^\pm, e_2^\pm)$, we find the azimuthal angles $\rho_\pm$, which reflect the deviation of the principal axes of $\varepsilon(j)$ from the orthorhombic axes, namely

$$\tan\rho_\pm = \frac{e_2^\pm}{e_1^\pm} = (-)^j \frac{(\varepsilon_2 - \varepsilon_1) \pm \sqrt{(\varepsilon_2 - \varepsilon_1)^2 + 16\varepsilon_5^2}}{4\varepsilon_5}. \tag{6}$$

The key point now is that due to the modulation there are no longer unique principal axes of the dielectric tensor for the whole crystal but a succession of locally twisted ones. The implications of such a situation are worked out in the following section.

3. Representation of polarized plane waves

Omitting the information about amplitude and absolute phase, the state of polarization of a totally polarized plane light wave can be represented by the *azimuthal angle* $\psi \in [0, \pi)$, the angle between the major axis of the ellipse of vibration and the positive direction of the x axis, and the *ellipticity angle* $\chi \in [-\pi/4, \pi/4]$, the arctangent of the ratio of the semi-minor axis to the length of its semi-major axis. This state can be represented by a Jones vector, which is two dimensional and has complex components. The polarization-modifying properties of an optical system which is non-depolarizing, frequency conserving and linear, can be described by a two dimensional *Jones matrix*, which transforms a given (initial) Jones vector into another (final) one. The matrices of the systems we will discuss are all elements of the group of special unitary transformations SU(2). For a complete description of Jones calculus see Jones (1941, 1948) and Azzam and Bashara (1988).

We will discuss three different basic cases.

3.1. Birefringent medium

The two eigenmodes are linear polarization states ($\chi = 0$). The propagation of an electromagnetic wave can be described by the superposition of the two linearly polarized waves with same frequencies and different propagation velocities. The difference in velocities, due to the birefringence Δn gives a *phase retardation*

$$\Delta_{\Delta n} = \frac{2\pi L}{\lambda_0}\Delta n \tag{7}$$

where L is the thickness of the sample and λ_0 the wave length of the light in vacuuo.

3.2. Gyrotropic non-birefringent medium

The two eigenmodes are circular polarization states ($\chi = \pm\pi/4$). The propagation of an electromagnetic wave in this medium can be described by the superposition of two circularly polarized waves with opposite sense of rotation and different velocities. These different velocities are determined by the two different refractive indices n

$$n^2 = n_0^2 \pm G\,.$$

Here n_0 is the refractive index without optical activity and G the gyration coefficient. The phase retardation is

$$\Delta_G = \frac{2\pi L}{\lambda_0}\frac{G}{n_0}\,. \tag{8}$$

3.3. Gyrotropic birefringent medium

In a rotating birefringent medium the determination of the solutions of the Fresnel equations are fairly complicated. Only for special directions of $\boldsymbol{k}$ can the solutions be easily found. The general case can often be simplified by neglecting the influence of the birefringence on the gyration. This means, in fact, that the total phenomenon is treated as a superposition of the two separate effects. In this approximation the solutions of the Fresnel equations give rise to two elliptically polarized waves with the main axes perpendicular, equal ellipticities and opposite sense of rotation. The velocities of propagation of the two waves are different and (omitting the notation for the implicit dependence of G on the birefringence) determined by corresponding refractive indices (Born 1933)

$$n_\pm^2 = \tfrac{1}{2}\left(n_0'^2 + n_0''^2 \pm \sqrt{(n_0'^2 - n_0''^2)^2 + 4G^2}\right) \tag{9}$$

with n_0' and n_0'' the refractive indices in absence of the gyrotropy and G the gyration coefficient.

The ellipticity angle, defined by

$$\tan 2\chi = \frac{\Delta_G}{\Delta_{\Delta n}} = \frac{G}{\bar{n}\Delta n} \tag{10}$$

where $\bar{n}$ is the mean refractive index. The phase retardation is

$$\Delta = \frac{2\pi L}{\lambda_0}(n_+ - n_-) \,. \tag{11}$$

From this equation and the expressions for the sum and product of the roots $n_\pm^2$ as in equation (9) we derive

$$\Delta^2 = \left(\frac{2\pi L}{\lambda_0}\right)^2 \{n_+^2 + n_-^2 - 2\sqrt{n_+^2 n_-^2}\} = \left(\frac{2\pi L}{\lambda_0}\right)^2 \{n_0'^2 + n_0''^2 - 2\sqrt{n_0'^2 n_0''^2 - G^2}\} \,. \tag{12}$$

For most cases we may assume $G \ll n_0'^2, n_0''^2$; so that using equations (7) and (8) we may write

$$\Delta^2 = \left(\frac{2\pi L}{\lambda_0}\right)^2 \left((n_0' - n_0'')^2 + \frac{G^2}{n_0' n_0''}\right) = \Delta_{\Delta n}^2 + \Delta_G^2 \,. \tag{13}$$

4. Square-wave model

As already explained, the transformation of a state of polarization by an optical device can be described by a 2×2 complex matrix, the Jones matrix. It gives the Jones vector of the outgoing polarization state for a given incoming polarization state. An optical system can be characterised completely, by its two eigenmodes (the eigenvectors of the Jones matrices) and the corresponding eigenvalues.

The Jones matrix of a birefringent platelet with its principal axes making an angle ψ with the reference axes, is given by

$$\mathbf{W} = \mathbf{R}(\psi)\mathbf{W}_0(\Gamma)\mathbf{R}(-\psi) \tag{14}$$

where $\mathbf{R}(\psi)$ is the rotation matrix and $\mathbf{W}_0$ is the Jones matrix for the retardation plate. These are given by

$$\mathbf{R}(\psi) = \begin{pmatrix} \cos\psi & -\sin\psi \\ \sin\psi & \cos\psi \end{pmatrix} \tag{15}$$

$$\mathbf{W}_0(\Gamma) = \begin{pmatrix} e^{-i\Gamma/2} & 0 \\ 0 & e^{i\Gamma/2} \end{pmatrix} \tag{16}$$

where Γ is the retardation of the platelet. The matrix $\mathbf{W}$ is unitary ($\mathbf{W}^\dagger\mathbf{W} = 1$).

Consider two identical birefringent platelets with thickness $\Lambda/2$ and retardation $\Gamma/2$ put together with different azimuthal angles: the first with $\phi(z) = \rho$ and the second with $\phi(z) = -\rho$ (see figure 1). The two platelets together form one unit cell of the modulation; a modulated finite crystal can be seen as a long sequence of these unit cells. Note that such a unit cell has no inversion symmetry, although its average has. We characterise this unit cell by a Jones matrix S_+. One can also consider a Jones matrix S_- describing the unit cell one obtains from the previous one by total inversion.

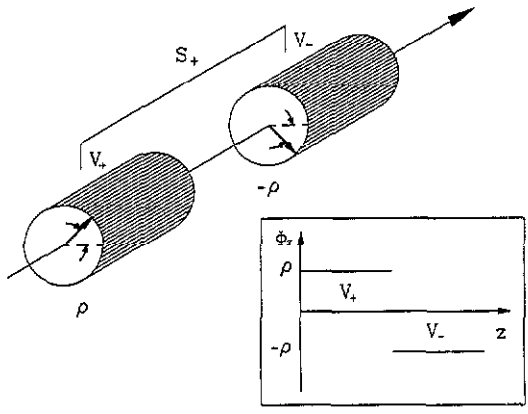

Figure 1. One unit cell for the square modulation wave (see text).

This system consists of the same platelets, now the first platelet has $\phi(z) = -\rho$ and the second $\phi(z) = \rho$. Accordingly we have (cf Yariv and Yeh 1984)

$$\mathbf{S}_{\pm} = \mathbf{V}_{\mp}\mathbf{V}_{\pm} \tag{17}$$

where

$$\mathbf{V}_{\pm} = \mathbf{R}(\pm\rho)\mathbf{W}_0(\Gamma/2)\mathbf{R}(\mp\rho)\,. \tag{18}$$

Substituting equations (15) and (16) we obtain

$$\mathbf{V}_{\pm} = \begin{pmatrix} a+\mathrm{i}b & \pm\mathrm{i}c \\ \pm\mathrm{i}c & a-\mathrm{i}b \end{pmatrix} \qquad \mathbf{S}_{\pm} = \begin{pmatrix} A+\mathrm{i}B & \pm C \\ \mp C & A-\mathrm{i}B \end{pmatrix} \tag{19}$$

where

$$\begin{aligned} a &= \cos\Gamma/4 & A &= \cos^2\Gamma/4 - \cos 4\rho \sin^2\Gamma/4 \\ b &= -\cos 2\rho \sin\Gamma/4 & B &= -\cos 2\rho \sin\Gamma/2 \\ c &= -\sin 2\rho \sin\Gamma/4 & C &= -\sin 4\rho \sin^2\Gamma/4\,. \end{aligned}$$

The eigenmodes of $\mathbf{V}_{\pm}$ are linear polarization states with azimuthal angles $\psi^{\mathbf{V}\pm}_{\text{slow}}$ and $\psi^{\mathbf{V}\pm}_{\text{fast}}$, with

$$\begin{aligned} \psi^{\mathbf{V}\pm}_{\text{slow}} &= \pm\rho \\ \psi^{\mathbf{V}\pm}_{\text{fast}} &= \pi/2 \pm \rho \end{aligned} \tag{20}$$

and the retardation of half the unit cell is still

$$\Delta^{\mathbf{V}\pm} = \Gamma/2. \tag{21}$$

The eigenvalues of $\mathbf{S}_{\pm}$ are given by

$$\begin{aligned} \Lambda_{\text{slow}} &= A - \mathrm{i}\sqrt{B^2 + C^2} \\ \Lambda_{\text{fast}} &= A + \mathrm{i}\sqrt{B^2 + C^2}\,. \end{aligned}$$

So the retardation $\Delta^{\mathbf{S}\pm}$ of the unit cell becomes

$$\begin{aligned}\Delta^{\mathbf{S}\pm} &= \arg(\Lambda_{\text{fast}}) - \arg(\Lambda_{\text{slow}}) \\ &= 2\tan^{-1}\left(\frac{\sqrt{B^2+C^2}}{A}\right) \\ &= 2\tan^{-1}\left(\frac{\sqrt{4\cos^2 2\rho\cot^2\Gamma/4+\sin^2 4\rho}}{\cot^2\Gamma/4-\cos 4\rho}\right).\end{aligned} \tag{22}$$

The eigenmodes of $\mathbf{S}_\pm$ are elliptic eigenmodes oriented along the reference coordinate axes (the orthorhombic axes) with ellipticity angles $\chi^{\mathbf{S}\pm}_{\text{slow}}$ and $\chi^{\mathbf{S}\pm}_{\text{fast}}$, with

$$\begin{aligned}\tan\chi^{\mathbf{S}\pm}_{\text{slow}} &= \pm\frac{-\cot\Gamma/4+\sqrt{\cot^2\Gamma/4+\sin^2 2\rho}}{\sin 2\rho} \\ \tan\chi^{\mathbf{S}\pm}_{\text{fast}} &= \pm\frac{-\cot\Gamma/4-\sqrt{\cot^2\Gamma/4+\sin^2 2\rho}}{\sin 2\rho}.\end{aligned} \tag{23}$$

5. Interpretation of the model

The results derived in the previous section simplify significantly if we take $\Gamma \ll 1$. Considering from (17) merely the case $\mathbf{S}_+$ and the slow ray, we may write for the ellipticity angle, using equation (23)

$$\chi^{\mathbf{S}} \simeq \tfrac{1}{8}\Gamma\sin 2\rho \tag{24}$$

and for the retardation, with equation (22)

$$\Delta^{\mathbf{S}} \simeq \Gamma\cos 2\rho. \tag{25}$$

From these two equations one obtains the azimuthal angle

$$\tan 2\rho \simeq 8\chi^{\mathbf{S}}/\Delta^{\mathbf{S}} \tag{26}$$

and the retardation per semi-unit cell ($\mathbf{V}_\pm$)

$$\Gamma \simeq 8\chi^{\mathbf{S}}/\sin 2\rho\,. \tag{27}$$

The model shows that a unit cell containing a complete period of the modulated tensor has elliptic eigenpolarizations the main axes of which coincide with the crystallographic (orthorhombic) axes. A sequence of identical unit cells will have the same eigenpolarizations (meaning the same ellipticity), so such a system will be birefringent and optically active. The retardation of a sequence of M identical unit cells will be M times the retardation of one unit cell. One remaining problem arises from the fact that the optical properties of such a crystal are very sensitive to its boundaries. If a sequence of M unit cells $\mathbf{S}_+$ is enlarged by a semi-unit cell on one side and one

on the other side (a $\mathbf{V}_-$ at the starting boundary and a $\mathbf{V}_+$ at the end), a sequence of $M+1$ $\mathbf{S}_-$ unit cells is obtained, with an opposite ellipticity. So we see that the crystals boundary surfaces select the eigenpolarizations; they cause the breaking of the symmetry. The electrostatic energies of the boundaries allow only some of the possible configurations, with minimal energies. However, if a given configuration is allowed, its enantiomorphic configuration is also allowed; which of the two will be realised depends on the surface effects.

In section 7 we will see that the temperature dependence of the birefringence and optical activity measured in the INC phase of TMAZC can be understood as a specific temperature behaviour of the azimuthal angle ρ, and we will relate this behaviour to the modulated dielectric tensor $\epsilon(j)$ of equation (4).

6. Optical measurements on TMAZC

In this section only some of the results of the measurements will be reported for illustrating the applicability of the approach presented in this paper for interpreting the optical activity observed. A more complete report will be published somewhat later.

A TMAZC crystal was grown from an aqueous solution as described by Arend *et al* (1986). A sample was sawn perpendicular to the **c** axis and polished to a thickness of 2.57±0.05 mm. With the HAUP the birefringence and gyration were determined for the para-electric phase I, the incommensurate phase II and the commensurate lock-in phase III. A red He–Ne laser ($\lambda_0 = 632.8$ nm) was used as light source. The measurements were performed for the two different extinction directions.

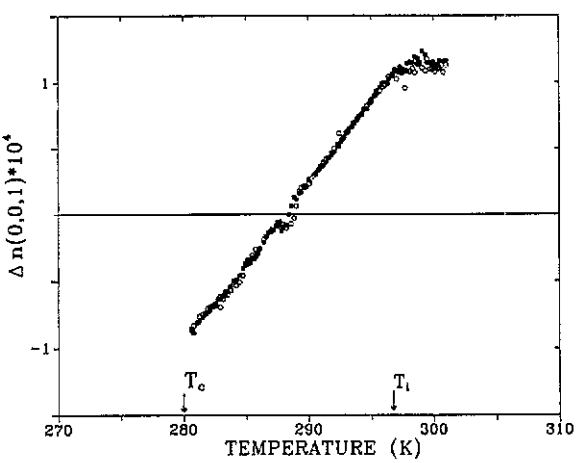

Figure 2. Birefringence along the **c** direction $\Delta n(0,0,1)$ of TMAZC. Open circles refer to the measurements with the incoming polarization along the *a* direction, the full circles refer to those along the *b* direction.

In figure 2 the results for the birefringence $\Delta n(0,0,1)$ are given. The INC phase extends from the normal–INC phase transition temperature $T_i = 297$ K to the lock-in temperature $T_c = 280$ K. At $T_0 = 288$ K the birefringence goes through zero.

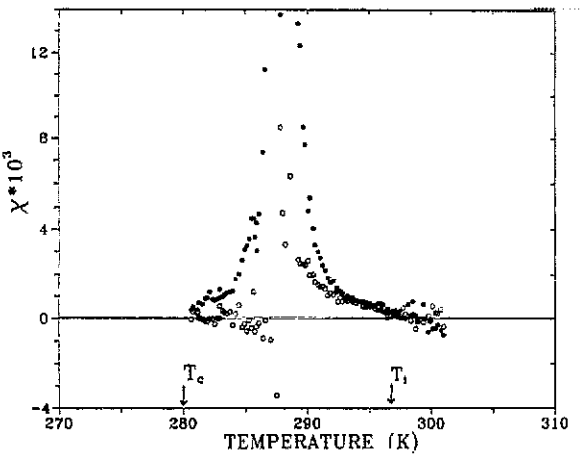

Figure 3. Ellipticity angle χ as found from the measurements with the polarization along the *a* direction (open circles) and along the *b* direction (full circles).

The results for χ are plotted in figure 3. Note that in the vicinity of T_0 the data for both extinction directions differ. The measurements close to T_0 are less accurate due to the fact that the precise extinction directions, in so far as they are present, are difficult to determine. The error in χ caused by this experimental problem is only present for temperatures that within 1 K of T_0, so the differences for χ for the different extinction directions have to be taken seriously and are certainly not due to this restriction of the experimental method. Their cause is subject for further study. In the lock-in phase the results for χ scatter very much due to the discommensurations (as explained in section 7), so the data below T_c are unfit for interpretation.

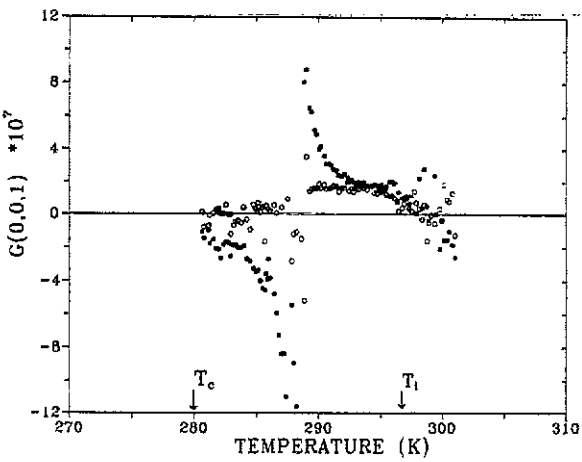

Figure 4. Gyration along the *c* direction $G(0,0,1)$ of TMAZC. Open circles refer to the measurements with the incoming polarization along the *a* direction, the full circles refer to those along the *b* direction.

To obtain the optical activity $G(0,0,1)$ from the HAUP data we measured with an Abbe refractometer and by the method of 'minimum deviation angle' the effective

refractive index to be $\bar{n} = 1.527 \pm 0.002$. In figure 4 the results for $G(0,0,1)$ are plotted. The differences in χ for different extinction directions are reflected very drastically in the gyration. The behaviour of the gyration for temperatures between 290 K and 297 K is easier to interpret, while the results for both a- and b-polarizations are the same. In this region $G(0,0,1)$ goes from zero at T_i to approximately 2×10^{-7} continuously.

7. Application of the model to TMAZC

To calculate from the model the birefringence and optical activity for a realistic material we need to estimate the length L for the unit cell used in the model. Meekes and Janner (1988) have shown that in the INC phase long-wavelength Fourier components $\boldsymbol{h} = (0,0,l,m) = l\boldsymbol{c}^* + m\boldsymbol{q}$ (where $\boldsymbol{q}$ is the modulation wavevector) are present. If one of these becomes dominant, then its wavelength will determine L. We will not go into the details of this, because we will see that even values for L that differ in two orders of magnitude do not give significantly different results. We will assume L to be larger than the modulation wavelength L_{mod} and smaller than the discommensuration distance L_{DISC}.

We have the modulation wave with wavevector $\boldsymbol{q} = \gamma\boldsymbol{c}^*$ on an orthorhombic basic lattice. At the lock-in phase transition temperature T_c, γ jumps from an incommensurate value $\gamma = (r+\delta)/s$, with r, s integers and δ a small (irrational) number, to a commensurate value $\gamma_c = r/s$. Due to this discontinuity the crystal will not lock-in homogeneously, but will do so in domains which are commensurate, but with different phases, separated by discommensurations in which the phase changes relatively rapidly. The distance between the discommensurations is given by

$$L_{\text{DISC}} = (r/\delta)c \tag{28}$$

with c the length of the orthorhombic unit cell in the c direction. L_{DISC} can become quite large (of the order of 100 nm).

For TMAZC the length of the modulation wavevector γ jumps at T_c from $\gamma = 0.405$ to $\gamma_c = \frac{2}{5}$ (Marion 1981). This gives an estimation for the discommensuration distance

$$L_{\text{DISC}} = 80c \simeq 100 \text{ nm} \tag{29}$$

where we have used $c = 12.28$ Å (Marion 1981). The modulation wavelength is

$$L_{\text{mod}} \simeq 0.4^{-1} \times c \simeq 3 \text{ nm}. \tag{30}$$

The wavelengths L_{FLW} of relevant Fourier long waves are of the order of 10 nm (Meekes and Janner 1988, Dijkstra *et al* 1991) are within the corresponding range. Accordingly, the length of the unit cell is estimated to be

$$L_{\text{mod}} \simeq 3 \text{ nm} < L < L_{\text{DISC}} \simeq 100 \text{ nm}. \tag{31}$$

Then the retardation of a unit cell becomes

$$3 \times 10^{-6} < \Delta = (2\pi L/\lambda_0)\Delta n(0,0,1) < 10^{-4} \tag{32}$$

where we have taken $\lambda_0 = 632.8$ nm and $\Delta n(0,0,1) \simeq 10^{-4}$.

Equation (6) shows that values for $\rho \simeq \pi/4$ can be obtained if $4\varepsilon_5 \gg \varepsilon_2 - \varepsilon_1 = 2\bar{n}\Delta n$, with Δn the birefringence for the non-modulated crystal. In this case the retardation of a unit cell Δ becomes much smaller than the retardation of a semi-unit cell $\Gamma/2$. This reflects the fact that the internal fields can be rather strong, but that due to averaging the resulting macroscopic fields are much smaller. Furthermore, we see from equation (24) that for $\rho \to 0$, $\chi \to 0$ very rapidly and Δ becomes equal to Γ (25), as one should expect for a non-modulated system.

One striking feature in the experimental results is that the ellipticity angle χ reach a maximum at T_0 where the birefringence, and so the retardation per unit cell Δ, is zero. This can be understood with equations (24) and (25) to be due to the fact that at T_0 $\rho = \pi/4$. In reality, more parameters are expected to be involved than are taken into account in this model. Our main goal, however, is here to find an explanation for the presence of optical activity in centrosymmetric INC phases. The question that must be answered now is: what hypotheses in the model cause the symmetry to be broken?

The Hamiltonian of the infinite, incommensurately modulated crystal has inversion symmetry, but the spontaneous realisation of the INC phase in a finite crystal breaks this symmetry. In the model we needed a definite starting and ending value, i.e. we considered a sequence of complete unit cells starting with a definite value for the azimuthal angle for the first semi-unit cell. Which one depends on accidental local perturbative effects, but then the last semi-unit cell is fixed by a periodicity requirement. This means physically that the phase of the modulation at one boundary of the crystal is related to the phase at the other boundary. The finite electrostatic energies of these boundaries could be the main cause for this.

8. Concluding remarks

The optical properties in the INC phase have to be treated very carefully. The presence of optical activity cannot be described by the average structure, which is homogeneous and centrosymmetric. The spatial dependence of the dielectric function due to the modulation has to be taken into account properly. Essential to a proper understanding is the interplay between local deviation from a centrosymmetric average structure and the global periodicity of the incommensurate modulation. In this paper an explanation is given for the presence of optical activity in the INC phase using Jones calculus to treat the spatial dispersion of the dielectric tensor. The model described gives elliptic eigenmodes for a sequence of full unit cells. Elliptic eigenmodes correspond to systems that are birefringent and optically active. The unit cells in the model are no longer centrosymmetric, but their spatial average is. The experimental results for $G(0,0,1)$ and $\Delta n(0,0,1)$ indicate that an additional dielectric tensor component ε_5, which describes the locally wiggling of the dielectric tensor in the $(\boldsymbol{a},\boldsymbol{b})$ plane, is quite large with respect to the effect of the birefringence $n\Delta n$, particularly at the temperature for which the birefringence is zero. The temperature behaviour of the birefringence and the optical activity can be described by a particular temperature dependence of the parameters involved. The differences that are found between the measurements with the incoming light polarized along the different extinction directions cannot be explained at present. The particular role of the $\boldsymbol{b}$ direction (being parallel to the polarization of the modulation) may be the relevant structural element in this.

The spontaneous realisation of an INC phase in a (finite) crystal causes the breaking of the inversion symmetry. The boundaries of the crystal are the cause of this. The electrostatic energies of the boundaries only allow some configurations, with minimal energies, to occur in reality. But given a certain allowed configuration the enantiomorphic configuration is also allowed. We therefore expect that for many experiments on different samples the gyration effects will show both signs.

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