The dielectric tensor in incommensurately modulated crystal phases

1992 J. Phys.: Condens. Matter 4 693

(http://iopscience.iop.org/0953-8984/4/3/010)

J. Phys.: Condens. Matter 4 (1992) 693–713. Printed in the UK

The dielectric tensor in incommensurately modulated crystal phases

E Dijkstra†, A Janner‡ and H Meekes†

† Research Institute for Materials, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

‡ Institute for Theoretical Physics, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Received 2 April 1991, in final form 16 July 1991

Abstract. A characterization of the dielectric properties in incommensurately modulated phases is presented. First a microscopic description is adopted. It takes into account the structural restrictions imposed on a microscopic scale by the superspace group. The macroscopic optical properties are derived from it. The optical activity as observed in the incommensurate phases of several compounds cannot be explained within a plain microscopic approximation. Therefore, a mesoscopic level is considered, implying averaging distances large with respect to the basic unit cell parameters or even the modulation wavelength, but small with respect to the size of the finite crystal. The phenomenological approach presented is compatible both with the microscopic description based on a superspace group symmetry, as well as with the macroscopic one involving the point group of the average structure. In the case considered here (one-dimensional incommensurate modulation) the optical properties of the dielectric medium are analysed in terms of subperiodic groups, periodic along the direction of the modulation wave and homogeneous along the other two directions. It is shown that the optical properties are affected by the incommensurability and that small changes in symmetry related to boundary conditions can lead to macroscopic effects. To interpret the experimental data more quantitatively a Jones model is applied, which describes the mesoscopic spatial dispersion of the modulated dielectric tensor to vary periodically along the modulation and being constant in the plane perpendicular to it. This model is compared with the experimental results for the ellipticity angle χ of $(N(CH_3)_4)_2ZnCl_4$ obtained for light propagating along the modulation.

1. Introduction

The determination of the optical birefringence is an important tool in the investigation of structural phase transitions. The behaviour of the birefringence provides information about the change of the crystallographic phase, temperature dependence and fluctuations of the order parameter. Optical activity is very sensitive to the presence or absence of certain symmetry properties of the crystals. The introduction by Kobayashi and Uesu (1983) and Kobayashi *et al* (1986) of a new type of polarimeter, the high-accuracy universal polarimeter (HAUP), opened the way to more reliable measurements of the optical birefringence and activity without being restricted to measurements along particular directions of the crystals. Moxon and Renshaw (1990) showed how the HAUP can also be used to determine linear and circular dichroism.

0953-8984/92/030693+21$03.50

Several members of the large family of A_2BX_4 dielectrics, which show a variety of different modulated phases, have been subjected to measurements of the birefringence and optical activity. One striking phenomenon is the fact that in the incommensurately modulated phases the optical activity is not equal to zero. Several structures of these phases can be described by centrosymmetric superspace groups and also their average structures are centrosymmetric. The optical activity is a third-rank tensorial property and one should therefore expect it to be zero in these phases.

To describe the optical properties of crystals one has to consider the spatial dispersion, this is the dependence on the wavevector of the dielectric permeability. The effect of spatial dispersion can be characterized by the parameter $a/\lambda = an/\lambda_0$, where a is some *characteristic dimension* having the same order of magnitude as the dimensions that are relevant for the polarizibilities, n is the refractive index for this wave, λ the wavelength of the light in the medium and λ_0 the wavelength of the light in vacuum. In a non-modulated crystal a can be taken equal to the (largest) lattice constant. Then, except in the neighbourhood of resonances (where n is large), the spatial dispersion is a weak effect: a constant dielectric tensor $\varepsilon^{\omega,k}$, with ω the frequency of the light and k its wavevector, can be used for the macroscopic electrodynamics. Due to the smallness of the parameter an/λ_0 the spatial dispersion can be expressed in terms of a power series expansion in ak ($k = |k|$).

In commensurately modulated crystal phases the characteristic dimension is in the order of the length of the unit cell of the superstructure, which is larger than that of the corresponding non-modulated crystal. Accordingly, the spatial dispersion can become more important than in the non-modulated case, but usually the same macroscopic crystal optics can be applied. In the next section this theory is summarized.

In incommensurately modulated crystals there is no three-dimensional lattice periodicity, so that, in principle, the unit cell is infinitely large (as large as the whole crystal) and the assumptions made above are no longer necessarily true. Spatial dispersion can become large due to the fact that a/λ can become much larger than in a non-modulated crystal, therefore the optical properties cannot be described merely by a constant $\varepsilon^{\omega,k}$ (although it may turn out to be a good approximation).

A theory of the optical properties of incommensurate (INC) crystal phases has to take into account the structural restrictions imposed on a microscopic scale by the superspace group. This is understood to be the $(3+d)$-dimensional space group, where d is the dimension of the modulation, that characterizes the symmetry properties of the INC phase (Janssen and Janner 1987). We will develop our considerations on the basis of the superspace group $Pcmn(00\gamma)(1s\bar{1})$ (de Wolff *et al* 1981) which is equivalent to $Pcmn(00\gamma')(ss\bar{1})$, where $\gamma' = 1 - \gamma$. This is the symmetry group for many members of the A_2BX_4 group mentioned above (Hogervorst 1986) and is in particular applicable to $(N(CH_3)_4)_2ZnCl_4$ (tetramethylammonium tetrachlorozincate, TMAZC) as shown by Dam and Janner (1986) and Madariaga *et al* (1987) and to Rb_2ZnBr_4 (Iizumi and Gesi 1983, Hogervorst and Helmholdt 1988, Meekes and Janner 1988). This $d = 1$ superspace group is centrosymmetric. This implies the presence of a four-dimensional centre of inversion in each unit cell of the structure that one gets by embedding the crystal in the superspace. One can avoid a superspace description and consider only the Fourier components of the crystal density. Then the superspace symmetry corresponds to symmetry conditions for these Fourier components 'up to a phase factor'. Accordingly, in the three-dimensional crystal there is, at most, one lattice plane (as $d = 1$) where inversion centres can occur. In the particular

case considered, for which the incommensurate modulation is along the c-axis such a plane is parallel to (a,b). The presence of one more point of inversion symmetry, not within that plane, would imply lattice translational symmetry, in contradiction with the incommensurability of the crystal. One can argue that the deviation from centrosymmetry has to be small and that on average the structure is centrosymmetric. Nevertheless, as morphological investigations have clearly shown (Janner *et al* 1980, Dam and Janner 1986) for an INC crystal structure the relevant symmetry is that of the superspace group, even for macroscopic properties.

The implications of the incommensurability for the theory are discussed in section 3, where the dielectric properties of INC crystal phases with $Pcmn(00\gamma)(1s\bar{1})$ as superspace group are considered. In the last part of section 3 it is shown that all the implications of the incommensurability for the optical properties can be understood on a mesoscopic scale, which allows consideration on that level of the symmetry breaking effects due to the finiteness of the INC crystal. Although the symmetry breaking is very subtle this does not imply smallness of the effects caused by such a change of symmetry. A well-known example is the sometimes large rotation of the principal axes of the indicatrix from the orthorhombic axes in the case of a very small monoclinic deviation. In section 4 a model is presented that takes into account, for appropriate experimental conditions, the local symmetry compatible both with the superspace group and with the global space group symmetry of the average structure. The symmetry breaking effects are then related to a choice in boundary conditions.

In sections 5 and 6 the optical activity in the INC phase of TMAZC is discussed on the basis of the present approach. The main features of the optical characterization reflect the results that can be obtained on a microscopic level as well. No complete microscopic derivation is given, so that the present interpretation of the data still remains a phenomenological one.

2. Spatial dispersion in non-modulated crystals

In this section we will treat a crystal as an unbounded, time independent, linear, spatial inhomogeneous optical medium. The dependence of the displacement field $\boldsymbol{D}(\omega,\boldsymbol{r})$ on the electric field $\boldsymbol{E}(\omega,\boldsymbol{r})$ with frequency ω is given by the material equation

$$\boldsymbol{D}(\omega,\boldsymbol{r}) = \int \boldsymbol{\varepsilon}^{\omega}(\boldsymbol{r},\boldsymbol{r}') \cdot \boldsymbol{E}(\omega,\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}'. \tag{1}$$

Agranovich and Ginzburg (1984) have shown that, due to the translational symmetry, we obtain from (1) in reciprocal space the convolution

$$\boldsymbol{D}(\omega,\boldsymbol{k}) = \sum_{\boldsymbol{h}\in\Lambda^*} \hat{\boldsymbol{\varepsilon}}^{\omega,\boldsymbol{k}}(\boldsymbol{h}) \cdot \boldsymbol{E}(\omega,\boldsymbol{k}-\boldsymbol{h}) \tag{2}$$

where $\boldsymbol{D}(\omega,\boldsymbol{k})$ is the macroscopic dielectric field with wavevector $\boldsymbol{k}$ and frequency ω, $\boldsymbol{E}(\omega,\boldsymbol{k}-\boldsymbol{h})$ and $\hat{\boldsymbol{\varepsilon}}^{\omega,\boldsymbol{k}}(\boldsymbol{h})$ are the Fourier components of the electric field and the dielectric tensor, respectively. The wavevectors $\boldsymbol{h}$ are elements of the reciprocal lattice Λ^* of the crystal.

Equation (1) can be approximated by considering the local dependence of the displacement field $\boldsymbol{D}(\omega,\boldsymbol{r})$ on the electric field $\boldsymbol{E}(\omega,\boldsymbol{r})$ and taking into account the

contribution due to the gradient of the electric field. Note that this is not a Taylor expansions approximation, because that would involve more terms. Then equation (1) reduces to

$$\boldsymbol{D}(\omega,\boldsymbol{r}) = (\varepsilon^{\omega}(\boldsymbol{r}) + \gamma^{\omega}(\boldsymbol{r}) \cdot \nabla_{\boldsymbol{r}}) \cdot \boldsymbol{E}(\omega,\boldsymbol{r}). \tag{3}$$

The *local dependence* of $\boldsymbol{D}(\omega,\boldsymbol{r})$ on $\boldsymbol{E}(\omega,\boldsymbol{r})$ is given by the symmetric second-rank dielectric tensor $\varepsilon^{\omega}(\boldsymbol{r})$, the *infinitesimal-non-local dependence* by the third-rank gyration tensor γ^{ω}, which is antisymmetric in its first two indices. In reciprocal space (3) leads to

$$\boldsymbol{D}(\omega,\boldsymbol{k}) = \sum_{\boldsymbol{h}\in\Lambda^*} \hat{\varepsilon}^{\omega}(\boldsymbol{h}) \cdot \boldsymbol{E}(\omega,\boldsymbol{k}-\boldsymbol{h}) + i \sum_{\boldsymbol{h}\in\Lambda^*} (\hat{\gamma}^{\omega}(\boldsymbol{h}) \cdot \boldsymbol{k}) \cdot \boldsymbol{E}(\omega,\boldsymbol{k}-\boldsymbol{h}) \tag{4}$$

where for $\hat{\varepsilon}^{\omega}(\boldsymbol{h})$ and $\hat{\gamma}^{\omega}(\boldsymbol{h})$ higher order terms in $\boldsymbol{k}$ are either neglected or implicit. Note that, comparing (2) with (4), the infinitesimal-non-local approximation is legitimate if we may approximate

$$\hat{\varepsilon}^{\omega,\boldsymbol{k}}(\boldsymbol{h}) = \hat{\varepsilon}^{\omega}(\boldsymbol{h}) + i\hat{\gamma}^{\omega}(\boldsymbol{h}) \cdot \boldsymbol{k}. \tag{5}$$

This is valid if the wavelength of the macroscopic field $\boldsymbol{E}(\boldsymbol{k})$ is long with respect to the microscopic fields $\boldsymbol{E}(\boldsymbol{k}-\boldsymbol{h})$ with $\boldsymbol{h} \neq 0$. For visible light this is, almost always, the case.

2.1. *Local approximation*

Let us investigate the material equation in the local approximation

$$\boldsymbol{D}(\omega,\boldsymbol{r}) = \varepsilon^{\omega}(\boldsymbol{r}) \cdot \boldsymbol{E}(\omega,\boldsymbol{r}). \tag{6}$$

This microscopic dielectric tensor is invariant for the space group symmetry of the crystal, in particular for the translations of the lattice Λ. Therefore, we write instead of (4), dropping the explicit notation for the dependence on ω

$$\boldsymbol{D}(\boldsymbol{k}+\boldsymbol{h}) = \hat{\varepsilon}(\boldsymbol{h}) \cdot \boldsymbol{E}(\boldsymbol{k}) + \sum_{\boldsymbol{h}'\in\Lambda^*,\boldsymbol{h}'\neq 0} \hat{\varepsilon}(\boldsymbol{h}-\boldsymbol{h}') \cdot \boldsymbol{E}(\boldsymbol{k}+\boldsymbol{h}'). \tag{7}$$

We assume that the medium possesses no external charges and no external currents with short-wavelength Fourier components. Then, we derive from the Maxwell equations for the short-wavelength Fourier components

$$|\boldsymbol{k}+\boldsymbol{h}|^2\, \boldsymbol{E}(\boldsymbol{k}+\boldsymbol{h}) - (\boldsymbol{k}+\boldsymbol{h})((\boldsymbol{k}+\boldsymbol{h}) \cdot \boldsymbol{E}(\boldsymbol{k}+\boldsymbol{h})) = \frac{\omega^2}{c^2}\boldsymbol{D}(\boldsymbol{k}+\boldsymbol{h}) \tag{8}$$

where c is the velocity of light in vacuum. Restricting to the transverse component $\boldsymbol{E}_{\perp}(\boldsymbol{k}+\boldsymbol{h})$ of $\boldsymbol{E}(\boldsymbol{k}+\boldsymbol{h})$, we get

$$\begin{aligned} \boldsymbol{E}_{\perp}(\boldsymbol{k}+\boldsymbol{h}) &= \frac{\omega^2}{c^2\,|\boldsymbol{k}+\boldsymbol{h}|^2}\boldsymbol{D}(\boldsymbol{k}+\boldsymbol{h}) \\ &\propto \frac{\omega^2 a^2}{4\pi^2 c^2}\hat{\varepsilon}(\boldsymbol{h}) \cdot \boldsymbol{E}(\boldsymbol{k}) = \frac{a^2}{4\pi^2\lambda_0^2}\hat{\varepsilon}(\boldsymbol{h}) \cdot \boldsymbol{E}(\boldsymbol{k}) \end{aligned} \tag{9}$$

where

$$|\boldsymbol{k}+\boldsymbol{h}| \approx |\boldsymbol{h}| > 2\pi/a \gg |\boldsymbol{k}| \tag{10}$$

is assumed, with a a characteristic length in the order of the lattice periodicity and $\lambda_0 = 2\pi c/\omega$ the wavelength in vacuum of the incident light. We can conclude that the transverse microscopic electric fields $\boldsymbol{E}_\perp(\boldsymbol{k}+\boldsymbol{h})$ for $\boldsymbol{h} \neq 0$ are small compared to the macroscopic field $\boldsymbol{E}(\boldsymbol{k})$, because $a^2/\lambda_0^2 \leqslant 10^{-6}$ (except for resonances in ω, where $\varepsilon(\boldsymbol{h})$ can become large).

The assumption of no external fields with short-wavelength Fourier components implies that the divergences of the short-wavelength displacements fields are zero. Using (7), this yields

$$(\widehat{\boldsymbol{k}+\boldsymbol{h}}) \cdot \hat{\varepsilon}(\boldsymbol{h}) \cdot \boldsymbol{E}(\boldsymbol{k}) + \sum_{\boldsymbol{h}' \in \Lambda^*, \boldsymbol{h}' \neq 0} (\widehat{\boldsymbol{k}+\boldsymbol{h}}) \cdot \hat{\varepsilon}(\boldsymbol{h}-\boldsymbol{h}') \cdot (\widehat{\boldsymbol{k}+\boldsymbol{h}'}) \boldsymbol{E}_\parallel(\boldsymbol{k}+\boldsymbol{h}') = 0 \tag{11}$$

where $(\widehat{\boldsymbol{k}+\boldsymbol{h}})$ and $(\widehat{\boldsymbol{k}+\boldsymbol{h}'})$ are unit vectors along $\boldsymbol{k}+\boldsymbol{h}$ and $\boldsymbol{k}+\boldsymbol{h}'$, respectively. We have neglected the fields $\boldsymbol{E}_\perp(\boldsymbol{k}+\boldsymbol{h})$ for $\boldsymbol{h} \neq 0$ and we obtain a set of equations (one equation for each $\boldsymbol{h} \neq 0$) that relates all parallel electric field components $\boldsymbol{E}_\parallel(\boldsymbol{k}+\boldsymbol{h})$ for $\boldsymbol{h} \neq 0$ to the macroscopic field components $\boldsymbol{E}(\boldsymbol{k})$. This set is formally infinite, but it can be truncated since for larger reciprocal wavevectors $\boldsymbol{h}$ the corresponding dielectric Fourier components $\hat{\varepsilon}(\boldsymbol{h})$ become very small. The truncated set leads to a unique solution only if the determinant of the homogeneous part is unequal to zero; if it is zero additional electromagnetic excitations are possible in the crystal, but we will not consider these here. Substituting the relations for $\boldsymbol{E}_\parallel(\boldsymbol{k}+\boldsymbol{h})$ into (7), we find a relation between $\boldsymbol{D}(\boldsymbol{k})$ and $\boldsymbol{E}(\boldsymbol{k})$

$$\boldsymbol{D}(\boldsymbol{k}) = \hat{\varepsilon}(0) \cdot \boldsymbol{E}(\boldsymbol{k}) + \sum_{\boldsymbol{h} \in \Lambda^*, \boldsymbol{h} \neq 0} \hat{\varepsilon}(-\boldsymbol{h}) \cdot \boldsymbol{E}_\parallel(\boldsymbol{k}+\boldsymbol{h}) \stackrel{\text{def}}{=} \varepsilon^{\boldsymbol{k}} \cdot \boldsymbol{E}(\boldsymbol{k}). \tag{12}$$

If we restrict the summation over Λ^* in this equation to the truncated set, we obtain an expression for $\varepsilon^{\boldsymbol{k}}$. It gives the dielectric response of the crystal to an incident field with wavevector $\boldsymbol{k}$ and the corresponding dielectric tensor is invariant for any transformation R of the point group K of the crystal

$$\varepsilon^{\boldsymbol{k}} = R \otimes R\varepsilon^{R\boldsymbol{k}}. \tag{13}$$

Normally speaking, as $\boldsymbol{k}$ is small, so also the $\boldsymbol{k}$-dependent part of $\varepsilon^{\boldsymbol{k}}$ is, and then this equation reduces in good approximation to the usual invariance condition (Nye 1985)

$$\varepsilon = R \otimes R\varepsilon. \tag{14}$$

2.2. *Infinitesimal-non-local approximation*

The phenomenon optical activity is understood to be caused by the non-local dependence of $\boldsymbol{D}(\boldsymbol{r})$ on $\boldsymbol{E}(\boldsymbol{r})$. For light waves in the optical region in insulators this is only a small effect and can therefore be described by (3)

$$\boldsymbol{D}(\boldsymbol{r}) = (\varepsilon(\boldsymbol{r}) + \gamma(\boldsymbol{r}) \cdot \nabla_{\boldsymbol{r}}) \cdot \boldsymbol{E}(\boldsymbol{r}). \tag{15}$$

For most of the (non-modulated) insulating materials it is enough to consider a single plane wave

$$D(k) = (\varepsilon^k + i\gamma^k \cdot k) \cdot E(k) \tag{16}$$

where ε^k is the symmetric second rank dielectric tensor from (15) and γ^k is a third rank tensor, which is antisymmetric in the first two indices ($\gamma_{ijl} = -\gamma_{jil}$), that describes the gyrotropy (optical activity) of the crystal (see Sommerfeld 1959 or Born 1933). This tensor is invariant for the point group symmetry. This means that one has

$$\gamma^k = R \otimes R \otimes R\gamma^{Rk} \tag{17}$$

for all orthogonal transformations R of the point group K of the crystal. The k-dependence of γ^k is very small and is therefore usually neglected. Then (17) reduces to

$$\gamma = R \otimes R \otimes R\gamma. \tag{18}$$

In summary, we can state that, within the assumptions of the description presented, the optical properties are governed by the point group symmetry of the crystal. One can also use the concept of the inverse dielectric function to come to the same conclusion (see Pick 1970, 1990).

3. Spatial dispersion in incommensurately modulated crystals

3.1. Microscopic description

3.1.1. Local approximation. The optical properties in the INC modulated phase can be derived along the same lines as we did for the non-modulated crystals. We will assume the crystal to respond linearly and time-independently (i.e. far from resonances). The space-dependent dielectric tensor $\varepsilon^\omega(r)$ in (6) must now be invariant for the superspace group $Pcmn(00\gamma)(1s\bar{1})$ that describes the symmetry properties of the INC phase.

In the INC phase equation (6) remains valid within a local approximation. The wavevectors h can be characterized by four integral indices (h,k,l,m) according to $h = ha^* + kb^* + lc^* + mq$ and are therefore elements of M^*, which is a Z-module of rank 4 generated by a^*, b^*, c^* (spanning the reciprocal lattice Λ^* of the basic structure) and $q = \gamma c^*$ (the modulation wavevector) (see Janssen and Janner 1987). In the INC phase equation (7) takes the form

$$D(k+h) = \hat{\varepsilon}(h) \cdot E(k) + \sum_{h' \in M^*, h' \neq 0} \hat{\varepsilon}(h-h') \cdot E(k+h'). \tag{19}$$

The spatial dispersion in the INC phase can be characterized by a small number of Fourier components of the dielectric tensor that noticeably influence the optical properties. For $h = 0$ we have the macroscopic tensor $\hat{\varepsilon}(0)$, which is the dominant term if spatial dispersion is negligible. For $h \neq 0$ we only have to consider short wavevectors h_i ($|h_i|$ small). In the INC phase as above, wavevectors of the form $h =$

$(0,0,l,m)$ can have long wavelengths for suitable choices of l and m. However, for larger indices l and m, less structural information will be carried by the wavevector, and hence, the corresponding Fourier tensor component $\hat{\varepsilon}(\boldsymbol{h})$ represents only a minor contribution. Furthermore, the influence of a dielectric Fourier component $\hat{\varepsilon}(\boldsymbol{h})$ to $\boldsymbol{E}_\perp(\boldsymbol{k}+\boldsymbol{h})$ is in a first approximation proportional to the square of the corresponding wavelength (see equations (9) and (24)–(29)). Thus, the wavevectors with relatively long wavelengths and low indices are expected to dominate the optical properties.

For a given $\boldsymbol{h} = (h,k,l,m) \in M^*$ we can derive which tensor elements $\varepsilon_{ij}(\boldsymbol{h})$ of the corresponding tensorial Fourier component are allowed by the superspace group $G_S = Pcmn(00\gamma)(1s\bar{1})$. These elements can be embedded as associated to reciprocal lattice vectors $\boldsymbol{h}_S$ in the four-dimensional lattice Σ^*, with the same integral components (h,k,l,m). We can write $\boldsymbol{h}_S = (\boldsymbol{h}_E, \boldsymbol{h}_I)$, with $\boldsymbol{h}_E = (h,k,l)$ defined in the three-dimensional *external* subspace and with $\boldsymbol{h}_I = (m)$ defined in the one-dimensional *internal* subspace, perpendicular to the external one. The tensorial Fourier components are also embedded, according to $\hat{\varepsilon}(\boldsymbol{h}_S) = \hat{\varepsilon}(\boldsymbol{h})$. A general element $g_S \in G_S$ can be written as $\{R_E, R_I \mid t_S\}$, with R_E the three-dimensional orthogonal transformation and R_I the internal transformation of the four-dimensional superspace transformation R_S and $t_S = (t_E, t_I)$ the superspace translation (Janssen and Janner 1987). The invariance of $\hat{\varepsilon}(\boldsymbol{h})$ with respect to g_S is given by (Janner and van Beest 1983)

$$\hat{\varepsilon}(\boldsymbol{h}) = R_E \otimes R_E \hat{\varepsilon}(R_E \boldsymbol{h}) e^{(R_S \boldsymbol{h}_S)\cdot t_S}. \tag{20}$$

In table 1 we see that the different parity conditions for h, k, l and m lead to different scalar products $(R_S \boldsymbol{h}_S)\cdot t_S$, and so different choices of $\boldsymbol{h} = (0,0,l,m)$ give rise to different selection rules (20) for the corresponding elements $\hat{\varepsilon}_{ij}(\boldsymbol{h})$ of the dielectric tensor (see table 2). Note that the dielectric tensors are given in a coordinate system that coincides with the present orthorhombic crystallographic axes of the basic structure (the structure in the absence of the modulation). The contributions due to different $\hat{\varepsilon}(\boldsymbol{h})$ occur in (19) as a linear superposition. Therefore, it is possible to take for every group of wavevectors with the same parity one representative Fourier wave $\boldsymbol{h}$, find the contribution of each corresponding representative $\hat{\varepsilon}(\boldsymbol{h})$ and then sum over all their effects. The choice of these representatives depends on the modulation wavevector. We will do this explicitly for TMAZC in the next section.

Table 1. The scalar products $(R_S \boldsymbol{h}_S)\cdot t_S$ for the elements g_S of G_S.

g_S	$(R_S \boldsymbol{h}_S)\cdot t_S$	g_S	$(R_S \boldsymbol{h}_S)\cdot t_S$
$\{c_x, 1 \mid \frac{1}{2}0\frac{1}{2}0\}$	$(-h+l)\pi$	$\{2_x, \bar{1} \mid \frac{1}{2}0\frac{1}{2}0\}$	$(h-l)\pi$
$\{m_y, 1 \mid 0\frac{1}{2}0\frac{1}{2}\}$	$(-k+m)\pi$	$\{2_y, \bar{1} \mid 0\frac{1}{2}0\frac{1}{2}\}$	$(k-m)\pi$
$\{n_z, \bar{1} \mid \frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$	$(h+k-l-m)\pi$	$\{2_z, 1 \mid \frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$	$(-h-k+l+m)\pi$
$\{1, 1 \mid 0000\}$	0	$\{\bar{1}, \bar{1} \mid 0000\}$	0

Suppose we have the representative Fourier components with wavevectors $\boldsymbol{h}_i = (0,0,l,m)$ with l/m = odd/odd for $i = 1$, l/m = odd/even for $i = 2$ and l/m = even/odd for $i = 3$. Furthermore, we have the constant contribution with $\boldsymbol{h}_0 = 0$. In table 2 one finds the expressions for the corresponding dielectric tensors $\hat{\varepsilon}(\pm\boldsymbol{h}_i)$, $i = 0,1,2,3$, which are allowed by G_S. Fourier components with parity l/m =

Table 2. The form of the tensor $\varepsilon(h)$ depends on the l and m indices of $h = (h, k, l, m)$. The corresponding subperiodic groups G_i are given.

h_i	h_0	h_1	h_2	h_3	
h, k, l, m	e,e,e,e o,o,o,o	e,e,o,o o,o,e,e	e,e,o,e o,o,e,o	e,e,o,e o,o,e,o	other
$\hat{\varepsilon}(h_i)$	$\begin{pmatrix} \varepsilon_6 & 0 & 0 \\ 0 & \varepsilon_7 & 0 \\ 0 & 0 & \varepsilon_8 \end{pmatrix}$	$\begin{pmatrix} 0 & \varepsilon_5 & 0 \\ \varepsilon_5 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \varepsilon_9 \\ 0 & 0 & 0 \\ \varepsilon_9 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \varepsilon_4 \\ 0 & \varepsilon_4 & 0 \end{pmatrix}$	0
G_i	P_xmmm	P_xccm	P_xcmm	P_xmcm	

even/even will not be considered, because their effect is difficult to distinguish from the dominant part of $\hat{\varepsilon}(0)$. Note that $\hat{\varepsilon}(h) = \hat{\varepsilon}(-h)$ follows from $\varepsilon(r)$ being real in a lossless medium and because of the total inversion symmetry element of the superspace group. The seven wavevectors $\pm h_i$ with $i = 0,1,2,3$ are (by the described procedure) the smallest wavevectors with structural importance. To obtain the propagating fields, we will restrict from now on $h \in M^*$ to $h = \pm h_i$ with $i = 0,1,2,3$. Terms of the form $\hat{\varepsilon}(h_i - h_j)E(k + h_j)$ with $i, j \neq 0$, $i \neq j$ will be neglected, while they do not contribute directly to the macroscopic field $D(k)$. From (8) and (19) we derive the Fresnel equations

$$(\hat{\varepsilon}(0) - F(n \pm p_i)) \cdot E(k \pm h_i) + \hat{\varepsilon}(\pm h_i) \cdot E(k) = 0 \tag{21}$$

for $i = 1,2,3$, and for $h = 0$

$$(\hat{\varepsilon}(0) - F(n)) \cdot E(k) + \sum_{i=1,2,3} (\hat{\varepsilon}(-h_i) \cdot E(k + h_i) + \hat{\varepsilon}(h_i) \cdot E(k - h_i)) = 0 \tag{22}$$

where $n = ck/\omega$, $p_i = ch_i/\omega$ and

$$F(n \pm p_i) = |n \pm p_i|^2 \, 1 - (n \pm p_i) \otimes (n \pm p_i) \tag{23}$$

1 being the identity.

From equation (21) we can calculate the microscopic fields $E(k \pm h_i)$, and with these the electric fields $E^{\hat{k},\nu}(r)$ that can propagate along given direction $\hat{k} = |k|$ $(\nu = 1,2)$.

For $k \| \hat{x}$

$$E^{\hat{x},2}(r) = \begin{pmatrix} \dfrac{2(n^2 - \varepsilon_3)\varepsilon_5 \cos(h_1 \cdot r)}{(n^2 - \varepsilon_3)(p_1^2 - \varepsilon_1) - n^2 p_1^2} + \dfrac{2inp_3\varepsilon_4 \sin(h_3 \cdot r)}{(n^2 - \varepsilon_3)(p_3^2 - \varepsilon_1) - n^2 p_3^2} \\ 1 \\ \dfrac{2inp_1\varepsilon_5 \sin(h_1 \cdot r)}{(n^2 - \varepsilon_3)(p_1^2 - \varepsilon_1) - n^2 p_1^2} + \dfrac{2(p_3^2 - \varepsilon_1)\varepsilon_4 \cos(h_3 \cdot r)}{(n^2 - \varepsilon_3)(p_3^2 - \varepsilon_1) - n^2 p_3^2} \end{pmatrix} \cdot E_2^0 e^{ik \cdot r} + \text{CC} \tag{24}$$

with $n^2 = \varepsilon_{22}^{(100)}$ given by (32) and

$$E^{\hat{x},3}(r) = \begin{pmatrix} \dfrac{2(n^2 - \varepsilon_3)\varepsilon_9 \cos(h_2 \cdot r)}{(n^2 - \varepsilon_3)(p_2^2 - \varepsilon_1) - n^2 p_2^2} \\ \dfrac{2\varepsilon_4 \cos(h_3 \cdot r)}{p_3^2 + n^2 - \varepsilon_2} \\ 1 + \dfrac{2inp_2\varepsilon_9 \sin(h_2 \cdot r)}{(n^2 - \varepsilon_3)(p_2^2 - \varepsilon_1) - n^2 p_2^2} \end{pmatrix} \cdot E_3^0 e^{ik \cdot r} + \text{CC} \tag{25}$$

with $n^2 = \varepsilon_{33}^{(100)}$ given by (32).

For $\boldsymbol{k} \| \hat{\boldsymbol{y}}$

$$\boldsymbol{E}^{\hat{y},1}(\boldsymbol{r}) = \begin{pmatrix} 1 \\ \dfrac{2(n^2-\varepsilon_3)\varepsilon_5 \cos(\boldsymbol{h}_1\cdot\boldsymbol{r})}{(n^2-\varepsilon_3)(p_1^2-\varepsilon_2)-n^2p_1^2} + \dfrac{2inp_2\varepsilon_9 \sin(\boldsymbol{h}_2\cdot\boldsymbol{r})}{(n^2-\varepsilon_3)(p_2^2-\varepsilon_2)-n^2p_2^2} \\ \dfrac{2inp_1\varepsilon_5 \sin(\boldsymbol{h}_1\cdot\boldsymbol{r})}{(n^2-\varepsilon_3)(p_1^2-\varepsilon_2)-n^2p_1^2} + \dfrac{2(p_2^2-\varepsilon_2)\varepsilon_9 \cos(\boldsymbol{h}_2\cdot\boldsymbol{r})}{(n^2-\varepsilon_3)(p_2^2-\varepsilon_2)-n^2p_2^2} \end{pmatrix} \cdot E_1^0 \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} + \mathrm{cc} \tag{26}$$

with $n^2 = \varepsilon_{11}^{(010)}$ given by (33) and

$$\boldsymbol{E}^{\hat{y}3}(\boldsymbol{r}) = \begin{pmatrix} \dfrac{2\varepsilon_9 \cos(\boldsymbol{h}_2\cdot\boldsymbol{r})}{p_2^2+n^2-\varepsilon_1} \\ \dfrac{2(n^2-\varepsilon_3)\varepsilon_4 \cos(\boldsymbol{h}_3\cdot\boldsymbol{r})}{(n^2-\varepsilon_3)(p_3^2-\varepsilon_2)-n^2p_3^2} \\ 1 + \dfrac{2inp_3\varepsilon_4 \sin(\boldsymbol{h}_3\cdot\boldsymbol{r})}{(n^2-\varepsilon_3)(p_3^2-\varepsilon_2)-n^2p_3^2} \end{pmatrix} \cdot E_3^0 \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} + \mathrm{cc} \tag{27}$$

with $n^2 = \varepsilon_{33}^{(010)}$ given by (33).

And for $\boldsymbol{k} \| \hat{\boldsymbol{z}}$

$$\boldsymbol{E}^{\hat{z},1}(\boldsymbol{r}) = \begin{pmatrix} 1 \\ \dfrac{2\varepsilon_5(p_1^2+n^2-\varepsilon_2)\cos(\boldsymbol{h}_1\cdot\boldsymbol{r}) - 4inp_1\varepsilon_5 \sin(\boldsymbol{h}_1\cdot\boldsymbol{r})}{(n^2-p_1^2)^2+\varepsilon_2^2-\varepsilon_2(n^2+p_1^2)} \\ -2\dfrac{\varepsilon_9}{\varepsilon_3}\cos(\boldsymbol{h}_2\cdot\boldsymbol{r}) - 2i\dfrac{\varepsilon_9}{\varepsilon_3}\sin(\boldsymbol{h}_2\cdot\boldsymbol{r}) \end{pmatrix} \cdot E_1^0 \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} + \mathrm{cc} \tag{28}$$

with $n^2 = \varepsilon_{11}^{(001)}$ given by (34) and

$$\boldsymbol{E}^{\hat{z},2}(\boldsymbol{r}) = \begin{pmatrix} \dfrac{2\varepsilon_5(p_1^2+n^2-\varepsilon_1)\cos(\boldsymbol{h}_1\cdot\boldsymbol{r}) - 4inp_1\varepsilon_5 \sin(\boldsymbol{h}_1\cdot\boldsymbol{r})}{(n^2-p_1^2)^2+\varepsilon_1^2-\varepsilon_1(n^2+p_1^2)} \\ 1 \\ -2\dfrac{\varepsilon_4}{\varepsilon_3}\cos(\boldsymbol{h}_3\cdot\boldsymbol{r}) \end{pmatrix} \cdot E_2^0 \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} + \mathrm{cc} \tag{29}$$

with $n^2 = \varepsilon_{22}^{(001)}$ given by (34).

In the case that all p_i become large, and so $\boldsymbol{k}+\boldsymbol{h} \approx \boldsymbol{h} \parallel \hat{\boldsymbol{z}}$, the transversal components of the microscopic fields $\boldsymbol{E}_\perp(\boldsymbol{k}+\boldsymbol{h})$ go to zero as p_i^{-2} as prescribed by (9). The longitudinal microscopic fields $\boldsymbol{E}_\parallel(\boldsymbol{k}+\boldsymbol{h})$ go either to zero as p_i^{-1} or remain constant (independent of p_i).

3.1.2. Infinitesimal-non-local approximation. In the material equation

$$\boldsymbol{D}(\boldsymbol{r}) = (\varepsilon(\boldsymbol{r}) + \gamma(\boldsymbol{r})\cdot\nabla_{\boldsymbol{r}})\cdot\boldsymbol{E}(\boldsymbol{r}) \tag{30}$$

$\gamma(\boldsymbol{r})$ is also invariant under the superspace group symmetry. These symmetry restrictions are worked out for the Fourier tensor components $\gamma(\boldsymbol{h})$, with $\boldsymbol{h} \in M^*$, of the gyration tensor by Meekes and Janner (1988), for the different setting, however, $Pcmn(00\gamma)(ss\bar{1})$. The corresponding solutions of the Fresnel equation can be derived as above. These expressions have not yet been worked out and are not needed in the present analysis of the incommensurate crystal optics.

3.2. Macroscopic description

3.2.1. Local approximation. From equation (19) we derive the macroscopic displacement field

$$D(k) = \hat{\varepsilon}(0) \cdot E(k) + \sum_{i=1,2,3} (\hat{\varepsilon}(-h_i) \cdot E(k+h_i) + \hat{\varepsilon}(h_i) \cdot E(k-h_i)). \tag{31}$$

Substituting the previously obtained fields $E(k \pm h_i)$ into (31) gives the dependence of $D(k)$ on $E(k)$ for different k. This is described by a k-dependent constant macroscopic dielectric tensor $\varepsilon^k = \varepsilon^s$, with $s = (s_x, s_y, s_z)$ a unit vector along k, via $D(k) = \varepsilon^s E(k)$, the wavelength-dependence being implicit. We get diagonal tensors with elements

$$\varepsilon_{11}^{(100)} = \varepsilon_1 + \frac{2\varepsilon_5^2}{p_1^2 + n^2 - \varepsilon_2}$$

$$\varepsilon_{22}^{(100)} = \varepsilon_2 + \frac{2(n^2-\varepsilon_3)\varepsilon_5^2}{(n^2-\varepsilon_3)(p_1^2-\varepsilon_1) - n^2 p_1^2} + \frac{2(p_3^2-\varepsilon_1)\varepsilon_4^2}{(n^2-\varepsilon_3)(p_3^2-\varepsilon_1) - n^2 p_3^2} \tag{32}$$

$$\varepsilon_{33}^{(100)} = \varepsilon_3 + \frac{2\varepsilon_4^2}{p_3^2 + n^2 - \varepsilon_2} + \frac{2(n^2-\varepsilon_3)\varepsilon_9^2}{(n^2-\varepsilon_3)(p_2^2-\varepsilon_1) - n^2 p_2^2}$$

$$\varepsilon_{11}^{(010)} = \varepsilon_1 + \frac{2(n^2-\varepsilon_3)\varepsilon_5^2}{(n^2-\varepsilon_3)(p_1^2-\varepsilon_2) - n^2 p_1^2} + \frac{2(p_2^2-\varepsilon_2)\varepsilon_9^2}{(n^2-\varepsilon_3)(p_2^2-\varepsilon_2) - n^2 p_2^2} \tag{33}$$

$$\varepsilon_{22}^{(010)} = \varepsilon_2$$

$$\varepsilon_{33}^{(010)} = \varepsilon_3 + \frac{2(n^2-\varepsilon_3)\varepsilon_4^2}{(n^2-\varepsilon_3)(p_3^2-\varepsilon_2) - n^2 p_3^2} + \frac{2\varepsilon_9^2}{p_2^2 + n^2 - \varepsilon_1}$$

$$\varepsilon_{11}^{(001)} = \varepsilon_1 + \frac{\varepsilon_5^2}{(n+p_1)^2 - \varepsilon_2} + \frac{\varepsilon_5^2}{(n-p_1)^2 - \varepsilon_2} - \frac{2\varepsilon_9^2}{\varepsilon_3}$$

$$\varepsilon_{22}^{(001)} = \varepsilon_2 + \frac{\varepsilon_5^2}{(n+p_1)^2 - \varepsilon_1} + \frac{\varepsilon_5^2}{(n-p_1)^2 - \varepsilon_1} - \frac{2\varepsilon_4^2}{\varepsilon_3} \tag{34}$$

$$\varepsilon_{33}^{(001)} = \varepsilon_3 + \frac{\varepsilon_9^2}{(n+p_2)^2 - \varepsilon_1} + \frac{\varepsilon_9^2}{(n-p_2)^2 - \varepsilon_1} + \frac{\varepsilon_4^2}{(n+p_3)^2 - \varepsilon_2} + \frac{\varepsilon_4^2}{(n-p_3)^2 - \varepsilon_2}.$$

In general the additional fields $E(k \pm h)$ will have wavelengths that are short with respect to $E(k)$. Then, the refractive indices p_i are quite large with respect to n, $\sqrt{\varepsilon_1}$, $\sqrt{\varepsilon_2}$ and $\sqrt{\varepsilon_3}$. Only if the modulation wavevector is different from a rational approximant l/m with l, m small integers or if the modulation amplitude becomes negligible, the effective dielectric tensor becomes k-independent

$$\varepsilon = \begin{pmatrix} \varepsilon_1 - 2\varepsilon_9^2/\varepsilon_3 & 0 & 0 \\ 0 & \varepsilon_2 - 2\varepsilon_4^2/\varepsilon_3 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix}. \tag{35}$$

Fousek and Kroupa (1986), who consider a special case, obtain a correction in the refractive indices that is equivalent to $2\varepsilon_4^2/\varepsilon_3$ and a minor correction which in our description is given by $2\varepsilon_4^2/p_3^2$. This last term appears in (32)–(34) by assuming p_3 large and neglecting terms of order smaller than p_3^{-2}. The effect of both contributions is the same in our derivation and in that of Fousek and Kroupa.

In the case that ϵ is k-independent, the invariance relation (20) for the superspace group reduces to

$$\epsilon = R_E \otimes R_E \epsilon. \tag{36}$$

This means that ϵ is invariant for the external point group K_E, which is a subgroup of the three-dimensional point group K of the average structure (Janner and van Beest 1983). Otherwise we have

$$\epsilon^k = R_E \otimes R_E \epsilon^{R_E k}. \tag{37}$$

So we see that ϵ^k is invariant with respect to the group of k denoted by K_k, which is a subgroup of the three-dimensional point group K_E. The group K_E is not necessarily a *proper* subgroup of K and in most cases is simply K. In particular for TMAZC one has $K_E = K = mmm$.

3.2.2. Infinitesimal-non-local approximation. For the tensorial Fourier components of the position-dependent third-rank gyration tensor $\gamma(r)$ of (3), one can now derive in an analogous way, as for ϵ^k in the local approximation, that the resulting macroscopic, constant gyration tensor γ^k is also invariant for K_E

$$\gamma^k = R_E \otimes R_E \otimes R_E \gamma^{R_E k}. \tag{38}$$

This equation, as well as the corresponding previous ones, shows that the direction of k has a symmetry-reducing effect as compared to the k-independent tensor. For instance if we take on the non-modulated orthorhombic lattice of TMAZC $k = (k, 0, 0)$, then we must consider the group of k given by $K_k = 2mm$. For this point group we can derive from (38) that $\gamma^k \cdot k = 0$ and therefore it gives no effect (see (4)). Taking $k = (k_1, 0, k_3)$ we have correspondingly the point group $K_k = m_y$, which allows $\gamma^k_{131} = -\gamma^k_{311}$ to be unequal to zero. But, as shown by Meekes and Janner (1988) the optical activity parameter is given by

$$G = \tfrac{1}{2} s_i e_{ijl} \gamma_{jlm} k_m \tag{39}$$

with $e_{ijl} = 1$ for (ijl) an even permutation and $e_{ijl} = -1$ for an odd permutation, s the unit vector along k and implicit summation convention adopted. Therefore, the contribution of γ^k_{131} to the optical activity is, as given by (39), again zero. If we take general $k = (k_1, k_2, k_3)$ and thus $K_k = 1$, all components γ^k_{ijl} can differ from zero and can, in principle, give rise to optical activity. This effect is expected to be very small, because the first term unequal to zero in a power series expansion of γ^k in k is quadratic in k (as $K_E = mmm$). Nevertheless, for TMAZC optical activity has been detected even for directions like $k = (k, 0, 0)$ and $k = (k_1, 0, k_3)$ (Dijkstra *et al* 1992), so taking into account the spatial dispersion of γ^k does not really help.

In the next paragraph we will see that the boundary surfaces of the crystal will allow the appearance of a gyration effect, as already suggested by the symmetry breaking considerations made in the introduction.

3.3. Mesoscopic description

In both cases considered in the previous section the optical non-homogeneity of the sample giving rise to the spatial dispersion, is expressed in terms of two macroscopic tensors ε^k and γ^k, allowed by the superspace group $Pcmn(00\gamma)(1s\bar{1})$. Although we have taken into account the effects of the spatial dispersion due to the modulation, as already said, these macroscopic properties do not explain the presence of optical activity in the INC phase. For this reason we consider a finer description involving averaging over distances large with respect to the crystal parameters, but small with respect to the size of the finite crystal, and we will call that a mesoscopic scale. The symmetry of the resulting medium has of course to be compatible with the superspace group of the modulated structure as well as the point group of the medium in a macroscopic description. In that case the non-homogeneity can be reduced to a periodic place-dependent dielectric tensor, with components still compatible with the underlying superspace group conditions. Furthermore, both the finiteness of the crystal and the spontaneous symmetry breaking associated with a choice of the boundary conditions have to be considered. In this section and the next, we will discuss how to come to a consistent description. We will restrict to the case $k \parallel \hat{x}$.

3.3.1. Local approximation. Assumption (10), which states that $h \gg k$ for all relevant $h \in \Lambda^*$, is no longer valid in the INC phase (for all $h \in M^*$). Now let us investigate what will happen if we have a number of long-wavelength Fourier wavevectors $h_1, \ldots, h_\nu \in M^*$ for which this assumption does not hold. This implies that all these vectors are along the incommensurate direction (i.e. parallel to c^*). This set of wavevectors is such that for all h_i in this set there is a $h_j = -h_i$ within it. We rewrite (11) for all $h \in M^*$, $h \neq 0, h_1, \ldots, h_\nu$, taking for the mesoscopic fields $E(k + h_i)$ also the perpendicular field into account, as

$$\sum_{h' \in M^*}{}' S^k(h,h') E_\parallel(k+h') = -(\widehat{k+h}) \cdot \hat{\varepsilon}(h) \cdot E(k) - \sum_{i=1}^{\nu} (\widehat{k+h}) \cdot \hat{\varepsilon}(h-h_\nu) \cdot E(k+h_\nu) \quad (40)$$

where the prime denotes the restriction of the summation to elements $h' \neq 0, h_1, \ldots, h_\nu$ and

$$S^k(h,h') = (\widehat{k+h}) \cdot \hat{\varepsilon}(h-h') \cdot (\widehat{k+h'}). \quad (41)$$

Let us introduce N as the total number of reciprocal lattice vectors in M^* (which is in fact infinite for an infinite crystal). So we obtain $N - \nu - 1$ equations with $N - \nu - 1$ microscopic field components $E_\parallel(k + h')$. This means that we can write all $E_\parallel(k + h_j)$, $j = \nu + 1, \ldots, N$, as an expression containing only the macroscopic field $E(k)$ and the mesoscopic fields $E(k + h_i)$, with $i = 1, \ldots, \nu$. If we substitute these expressions in (19) we get the set of equations,with $i = 1, \ldots, \nu$

$$\begin{aligned} D(k+h_i) &= \varepsilon^k(h_i) \cdot E(k) + \sum_{j=1}^{\nu} \varepsilon^k(h_i - h_j) \cdot E(k+h_j) \\ D(k) &= \varepsilon^k(0) \cdot E(k) + \sum_{j=1}^{\nu} \varepsilon^k(-h_j) \cdot E(k+h_j) \end{aligned} \quad (42)$$

where the contributions of the microscopic fields are now implicit in the k-dependent mesoscopic dielectric tensors $\varepsilon^{k}(h_i)$. From the original set of N vector equations (19), $N-1-\nu$ have now been eliminated and $\nu+1$ equations remain, which represent the set of Fresnel equations for the present case (in an analogous way as occurs in the microscopic description of section 3.1). In these mesoscopic material equations the dielectric tensors $\varepsilon^{k}(0)$ and $\varepsilon^{k}(h_i)$ still have to be invariant with respect to the superspace group (taking properly into account the presence of the light wavevector k) because a correct averaging never decreases the symmetry.

Suppose in the INC crystal the existence of one distinguishable mesoscopic coherence length l_0; its nature will be described in the next section and further on. In M^* we can find Fourier wavevectors of the type h_i with $i=1,\ldots,\nu$ and of all different (l,m) parity conditions that correspond to periodicities in the crystal which are very close to l_0. So that after averaging this dense set of Fourier wavevectors, one arrives at three effective mesoscopic Fourier wave vectors 0 and $\pm h_0$ with $|h_0| = 2\pi/l_0$. For this description the microscopic indices h, k, l and m are no longer meaningful. Therefore, instead of (42), as the h_i are all parallel to the $\hat{z}$-axis, we can write in direct space a material equation (restricting to a sinusoidally modulated dielectric tensor)

$$D(x,y,z) = \varepsilon^{\text{meso}}(z)\cdot E(x,y,z) = \left[\varepsilon + \eta\cos\left(\frac{2\pi}{l_0}z+\phi\right)\right]\cdot E(x,y,z) \tag{43}$$

with ϕ a constant phase, l_0 no more small with respect to the wavelength of the light and

$$\eta = \eta_0+\eta_1+\eta_2+\eta_3 = \begin{pmatrix} \varepsilon_6 & \varepsilon_5 & \varepsilon_9 \\ \varepsilon_5 & \varepsilon_7 & \varepsilon_4 \\ \varepsilon_9 & \varepsilon_4 & \varepsilon_8 \end{pmatrix}. \tag{44}$$

The tensors η_i describe that part of η that corresponds to the tensor form in table 3 for the listed h_i, and their strengths depend on the choice of l_0 and the modulation. In the next section we will describe the optical properties on the basis of η. Equation (43) can be treated in formally the same way as we did for the microscopic description.

Table 3. The phases occurring in TMAZC. The phase transition temperatures, the modulation wavevector ($q = \gamma c^*$) and the space groups are given.

Phase	VI	V	IV	III	II	I
T (K)	< 161	< 181	< 276.5	< 280	< 297.6	> 297.6
γ	1/3	0	1/3	2/5	inc.	0
Symmetry	$P2_12_12_1$	$P2_1/c11$	$P112_1/n$	$Pc2_1n$	$Pcmn(00\gamma)(1s\bar{1})$	$Pcmn$

Kobayashi (1990) showed that in the INC phase a place-dependent, complex order parameter exists that gives rise to helical structures in the INC phase. From (43) one sees that this complex order parameter can be interpreted as being the fundamental Fourier component with wavevector h_0 of $\eta(z)$.

3.3.2. Infinitesimal-non-local approximation. We can treat the optical activity in the same way as we did with the dielectric tensor and obtain an equation that is similar to (43).We then need the same invariance properties as those derived by Meekes and Janner (1988). We will not do this here, because the inhomogeneity of the dielectric properties as described by (43) can already give rise to optical activity as we will see in the next section.

4. Modulated dielectric tensor optics

The modulated dielectric tensor $\epsilon^{meso}(z)$ that occurs in the mesoscopic material equation (43) is homogeneous with respect to translations in the (a,b) plane and inhomogeneous along c. Its spatial average $\overline{\epsilon^{meso}(z)}$ has the point group symmetry mmm. The Euclidean symmetry of $\epsilon^{meso}(z)$ is not given by a space group nor by a superspace group nor by a point group. Indeed it is periodic along c (with periodicity l_0) and is constant along a and b. The symmetry is that of a rank two tensor field invariant with respect to a subperiodic group. The subperiodic group has analogous properties as a space group (Opechowski 1986), but instead of a three-dimensional lattice it is characterized by continuous translational symmetry along two directions a and b and a discrete one along c. The anisotropy related to the orthorhombic symmetry in the (a,b) plane is still present. The further concepts of point group and non-primitive translations still apply. In the present case where the point group of $\overline{\epsilon^{meso}(z)}$ is mmm, one can show that there are four inequivalent subperiodic groups denoted as $P_z mmm$, $P_z ccm$, $P_z cmm$ and $P_z mcm$. The generators of $P_z mmm$ are then written on the basis $A = a$, $B = b$ and $C = l_0 c/|c|$

$$(t_1 00),\ (0 t_2 0),\ (001),\ m_x,\ m_y,\ m_z \tag{45}$$

for infinitesimal t_1 and t_2. For $P_z ccm$ instead of m_x one now has $c_x = \{m_x \mid 00\frac{1}{2}\}$ and instead of m_y one has $c_y = \{m_y \mid 00\frac{1}{2}\}$, and so on for the other two subperiodic groups.

Each tensor η_i $(i = 0, \ldots, 3)$ is invariant with respect to one of these subperiodic groups G_i as denoted in table 2. Therefore, every tensor η_i has a different symmetry reducing effect. To illustrate this we will work out the contribution of η_1.

The coordinates of equivalent positions of $P_z ccm$, modulo the one-dimensional lattice translations $(0,0,n)$, are (in a general position with point symmetry 1)

$$\begin{array}{llll} x,y,z & \bar{x},y,z+\frac{1}{2} & x,\bar{y},z+\frac{1}{2} & x,y,\bar{z} \\ \bar{x},\bar{y},\bar{z} & x,\bar{y},\bar{z}+\frac{1}{2} & \bar{x},y,\bar{z}+\frac{1}{2} & \bar{x},\bar{y},z. \end{array} \tag{46}$$

Special equivalent positions with maximal point symmetry are at

$$0,0,0 \qquad 0,0,\tfrac{1}{2} \qquad \text{with point symmetry } 2/m \tag{47}$$

and at

$$0,0,\tfrac{1}{4} \qquad 0,0,\tfrac{3}{4} \qquad \text{with point symmetry } 222. \tag{48}$$

This situation is analogous to that one finds in the space group $Pccm$ (Hahn 1983). The difference from the optical point of view is not so much due to the lattice

translations along a and b, but to the fact that positions with different point symmetry are for visible light at microscopic distance in the space group case ($|c| \ll \lambda$), whereas that is no more the case for the subperiodic group (l_0 is not small with respect to λ). For that reason the optical symmetry of the crystal, in a mesoscopic description, depends on the exact position of (001) boundary surfaces: at a general position, at $z = 0$ or at $z = 1/4$ (for an origin at $\bar{1}$). Only the last two cases are considered, because associated with a maximal point symmetry.

A rank-2 symmetric tensor field, invariant with respect to $P_z ccm$, is constant along $\hat{x}$ and $\hat{y}$, periodic along $\hat{z}$ and has with Fourier wavevectors $K = Lh_0 = (2\pi L/l_0)\hat{z}$, the Fourier components $\hat{\eta}(K)$ satisfying the symmetry condition

$$\hat{\eta}(K) = R \otimes R\hat{\eta}(RK)e^{i(RK)\cdot v(R)} \tag{49}$$

for elements $g = \{R \mid v(R)\}$ of $P_z ccm$. This gives for $\hat{\eta}$ the possible forms

$$\hat{\eta}(L) = \begin{pmatrix} \varepsilon_6 & 0 & 0 \\ 0 & \varepsilon_7 & 0 \\ 0 & 0 & \varepsilon_8 \end{pmatrix} \qquad \text{for } L \text{ even}$$

$$\hat{\eta}(L) = \begin{pmatrix} 0 & \varepsilon_5 & 0 \\ \varepsilon_5 & 0 & 0 \\ 0 & 0 & \varepsilon_8 \end{pmatrix} \qquad \text{for } L \text{ odd.} \tag{50}$$

The modulated dielectric tensor described by (51) is illustrated in figure 1.

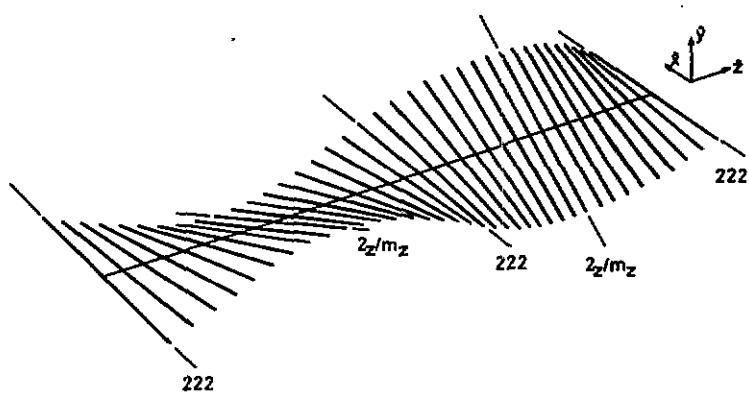

Figure 1. The variation in space of the modulated dielectric tensor $\varepsilon^{\text{mcso}}(z)$.

Several sorts of boundary surfaces can play a role in the optics of an incommensurate crystal. Let us assume these are nothing else than the faces with indices $(00lm)$ which are all parallel to (001) of a finite crystal, and that these faces are at equivalent positions. In that case the optical properties of the medium change with the exact positions of these (001) boundary surfaces. In a situation like this one also observes the case of a set of optical slabs. We will illustrate with a Jones model how a specific choice of boundary surfaces at equivalent positions with point symmetry 222 can give optical activity.

4.1. The square-waveform Jones model

In a previous paper (Dijkstra 1991) a Jones model is presented that treats the η_1 part of the modulated dielectric tensor $\varepsilon^{\text{meso}}(z)$. It describes the crystal to consist of homogeneous slabs: each slab can be characterized by its two eigenpolarizations which are linearly polarized states oriented along directions deviating from the orthorhombic axes of the average structure by azimuths of ρ and $-\rho$ alternatingly. The polarization state of a plane wave with $k \| z$ after two subsequent slabs will be elliptically polarized. We will describe the model briefly here. We write for $\varepsilon^{\text{meso}}(z)$ only the transversal components and restrict to the η_1 contribution. We approximate the cosine dependence on z by a square waveform and then partition the medium in slabs, labeled by n, with thickness $l_0/2$. This gives

$$\varepsilon^{\text{meso}}(n) = \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix} + (-)^n \begin{pmatrix} 0 & \varepsilon_5 \\ \varepsilon_5 & 0 \end{pmatrix}. \tag{51}$$

The eigenmodes in slab n are linear polarization states with azimuths $\rho_\pm$, given by:

$$\tan \rho_\pm = (-)^n \frac{(\varepsilon_2 - \varepsilon_1) \pm \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4\varepsilon_5^2}}{2\varepsilon_5}. \tag{52}$$

The retardation Γ of one slab becomes:

$$\Gamma = \frac{\pi l_0}{\lambda_0} \Delta n = \frac{\pi l_0}{2\bar{n}\lambda_0} (\varepsilon_+ - \varepsilon_-) \tag{53}$$

where λ_0 is the wavelength of the incident light, $\Delta n = \sqrt{\varepsilon_+} - \sqrt{\varepsilon_-} \approx \frac{1}{2}(\varepsilon_+ - \varepsilon_-)/\bar{n}$ is the birefringence of the slab and ε_+ and ε_- are the eigenvalues of $\varepsilon^{\text{meso}}(n)$:

$$\varepsilon_\pm = \tfrac{1}{2}(\varepsilon_1 + \varepsilon_2) \pm \tfrac{1}{2}\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4\varepsilon_5^2}. \tag{54}$$

So we get:

$$\Gamma = \frac{\pi l_0}{2\bar{n}\lambda_0} \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4\varepsilon_5^2}. \tag{55}$$

The optical properties of such a system can be calculated by Jones matrix calculus. The whole crystal is built up out of the same pairs of two subsequent slabs: the optical unit cells. The retardation of one optical unit cell is (considering only the $\rho = \rho_+$ state and $\Gamma \ll 1$)

$$\Delta = 2\Gamma \cos 2\rho = \frac{\pi l_0}{\bar{n}\lambda_0} \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4\varepsilon_5^2} \cos 2\rho. \tag{56}$$

This gives the birefringence:

$$\Delta n = \frac{\lambda_0}{2\pi l_0} \Delta = \frac{1}{2\bar{n}} \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4\varepsilon_5^2} \cos 2\rho. \tag{57}$$

The crystal has the same eigenpolarizations as one optical unit cell. Those are elliptical eigenpolarizations (with the main axes along the a- and b-direction of the crystal), with ellipticity angle:

$$\chi = \frac{\Gamma}{4}\sin 2\rho = \frac{\pi l_0}{8\bar{n}\lambda_0}\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4\varepsilon_5^2}\sin 2\rho. \tag{58}$$

The optical properties of an optical unit cell are given by χ the ellipticity angle, for $k \parallel c$. This can also be described by a gyration vector $\gamma^{(k)}$ that points along the c-axis. The parameter of optical activity is given by

$$G = s \cdot \gamma^{(k)} = \bar{n}\Delta n(001)\tan 2\chi \tag{59}$$

where again s is the unit vector along k (see Dijkstra 1991 and Born 1933). In this case $\gamma_3^{(k)}$ becomes (see (39))

$$\gamma_3^{(k)} = \gamma_{123}k_3. \tag{60}$$

We can derive from (58) and (59), using $k_3 = 2\pi\bar{n}/\lambda_0$, $p_1 = \lambda_0/l_0$ and taking $\tan 2\chi = 2\chi$

$$\gamma_{123} = \frac{\lambda_0}{32\bar{n}^2 p_1}(\varepsilon_+ - \varepsilon_-)^2 \sin 4\rho. \tag{61}$$

Normally, the second-rank pseudo tensor g_{ij} is used to describe the optical activity. The optical activity discussed here is given by the tensor element:

$$g_{33} = \gamma_3^{(k)} s_3 = \gamma_{123} s_3 k_3 = \frac{\pi}{16\bar{n}p_1}(\varepsilon_+ - \varepsilon_-)^2 \sin 4\rho. \tag{62}$$

The gyration effect is constant for the whole crystal. In the model, the point group symmetry mmm is reduced to 222, which allows γ_{123} to be non-zero (see (38)). The symmetry breaking is caused by the fact that the surface boundaries of the crystal are located at equivalent Wyckoff positions with point symmetry 222. There is also another optical configuration possible: it is obtained by substituting $\rho \rightarrow -\rho$ in all optical unit cells. The crystal thus obtained is the enantiomorph for which χ, $\gamma_3^{(k)}$, γ_{123} and g_{33} change sign. In principle, the two configurations are equally probable. In a specific single crystal, however, only one of them will, in fact, occur due to a spontaneous breaking of symmetry associated to small accidental defects.

5. Application to TMAZC

In table 3 the different phases of TMAZC are listed. In figure 2 the temperature-dependence of the modulation wave vector $q = \gamma c^*$ in the phases II, III and IV is plotted. In the INC phase γ varies from 0.420 to 0.408 (Madariaga *et al* 1987) and then jumps at the lock-in phase transition temperature to 2/5.

In figure 3 the most dominant reciprocal lattice vectors are plotted. They have the lowest indices ($h = k = 0$ and l and m within the circle around the origin) and their ratios l/m are close to $-\gamma$ (within the slice around the γ-line in the figure). With these reciprocal lattice vectors long wavelength Fourier components of the dielectric tensor are connected. For different temperatures the orientation of the γ-line in figure 3 changes. For certain temperatures γ goes through rational values l/m with low indices l and m; for instance $\gamma = 5/12$ at $T \approx 290$ K. However, it is not possible to say which specific components will be responsible for certain optical phenomena observed; in our phenomenological approach that information follows from measurements.

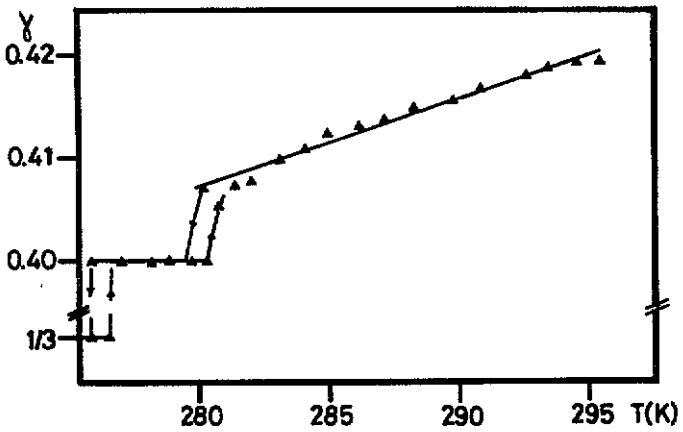

Figure 2. The value γ of the modulation wave vector $q = \gamma c^*$ in the incommensurate phase of TMAZC as a function of temperature (from Marion 1981). The plotted line is a linear fit. The value γ of the vector $q = \gamma c^*$ as a function of temperature (from Marion 1981).

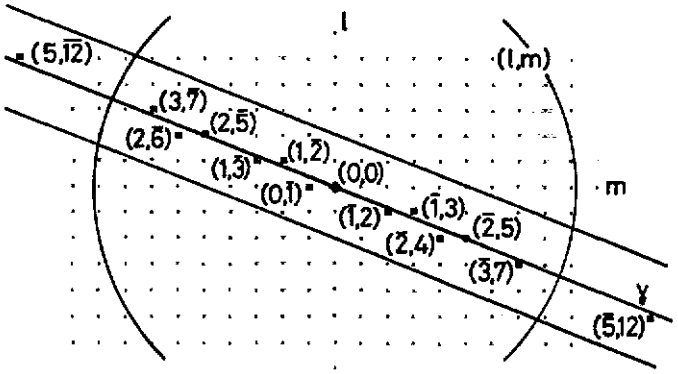

Figure 3. A $(0, 0, l, m)$ slice in the reciprocal space M^*. The most important reciprocal lattice vectors $h = (0, 0, l, m) \equiv (l, m) \in M^*$ are those with low indices l and m (i.e. inside a sphere around (0,0)) and that are close to the γ-line (the line $l = -\gamma m$) of TMAZC.

6. Optical activity of TMAZC

In figure 4 we find the ellipticity angle measured with the HAUP for a sample cut perpendicular to c. Dijkstra (1991) already reported these measurements, but in the fitting procedure the so-called δY-error was not eliminated properly. This δY-error is caused by the intrinsic eccentricities of the rotation stages on which the polarizers of the HAUP are mounted. The elimination of this error is performed now by the method described by Dijkstra *et al* (1991) and Moxon and Renshaw (1990). From Dijkstra (1991) we know that at $T_0 = 288$ K $\Delta n(001)$ becomes zero. In figure 4 we see that $\chi \approx 10^{-3}$ at this temperature. In (58) we see that $\Delta n(001) = 0$ implies that $\rho = \pi/4$, which gives with (53) that $4\varepsilon_5^2 \gg (\varepsilon_1 - \varepsilon_2)^2$. Then, from equation

(59) at T_0 (from figure 4) we derive

$$\varepsilon_5 \cdot \frac{l_0}{\lambda_0} \approx \frac{4\bar{n}\chi}{\pi} \approx 0.002. \tag{63}$$

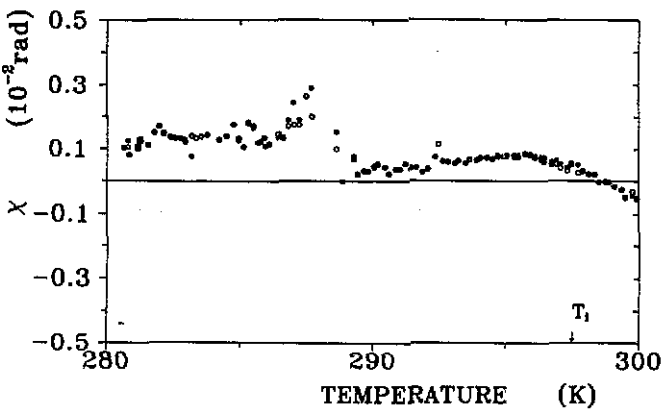

Figure 4. The ellipticity angle χ in phases I and II of TMAZC, measured along the (001)-direction. Open circles refer to the measurements with the electric field polarized along *a*, closed circles refer to those with the electric field polarized along *b*.

So we see that the influence of ε_5 can be quite significant and that l_0 is in the order of λ_0. Then, we can conclude that the major effect of the spatial dispersion due to the incommensurate modulation occurs in the optical activity, and is very difficult to recognize in measurements of the birefringence. The effect can also be described by a constant effective $\gamma^{\text{eff}} = \gamma_{123}$ (or equivalently by the element g_{33} of the second-rank pseudo tensor), which is allowed by the point group 222. This point group allows γ_{231} and γ_{312} to be non-zero too. These can give rise to optical activity along the *a*-axis and along the *b*-axis, respectively.

In the INC phase g_{33} goes to zero at T_c (Dijkstra *et al* 1992), but g_{13} remains unequal to zero (Kobayashi *et al* 1986, Dijkstra and Janner 1990) due to the presence of discommensurations in which the $Pc2_1n$ symmetry of the lock-in phase is already present. If we substitute some of the chlorine by bromine in TMAZC it locks in into a monoclinic phase with $q = c^*/3$ and $P112_1/n$ symmetry (see Colla *et al* 1984). Dijkstra and Janner (1990) have measured the optical activity along the (101) direction of such a solid solution (0.77 Br versus 3.23 Cl). The optical activity along this direction is given by:

$$G(101) = g_{11}\cos^2\phi + g_{33}\sin^2\phi + 2g_{13}\sin\phi\cos\phi = 0.36g_{11} + 0.64g_{33} + 0.96g_{13}$$

where $\phi = 53°$ is the angle between the (101) direction and the *a*-axis of the crystal. $G(101)$ is unequal to zero in the INC phase, but goes to zero rapidly on approaching the monoclinic lock-in phase, as should be expected because of the fact that the lock-in phase for this material is centrosymmetric and no discommensuration contribution to g_{13} can occur.

7. Final remarks

The presented description shows that the optical properties are affected by incommensurability and that small changes in symmetry related to boundary conditions can lead to macroscopic effects. This in itself is not strange. We can compare this situation with the ferromagnetism in iron at room temperature. For most of the properties, iron can be described as cubic. Only very small deviations from this cubic symmetry allow the very large ferromagnetic properties. Furthermore, we see that boundaries, defects and/or impurities determine the actual direction among the cubic equivalent ones of the magnetization of the iron. The situation for the optical symmetry of the INC crystal is comparable. A certain point symmetry of the boundary surfaces of the crystal will be more favourable. Then the crystal can still have more possible optical configurations with the same probability. On entering the INC phase small accidental effects will determine the optical medium observed. It is thus very well possible that measurements for the optical activity in the INC phase on different samples will give both signs for the gyration and that the size of the effect is related to the presence of defects.

We can imagine that a finite incommensurately modulated crystal is a dielectric medium of which the elementary excitations (i.e. the electromagnetic propagation modes for light waves) are resonant to the dimensions of the crystal. We can compare this situation with a finite string of which the vibration modes have wavelengths that fit into the length of the string. For the crystal this means that the coherence length l_0 fits into the length d of the crystal between its (001) surfaces or other structural relevant boundaries, and that the phase $(2\pi z/l_0)+\phi$ of $\varepsilon^{\text{meso}}(z)$ is always the same at these surfaces.

The description based on the complex, place-dependent order parameter of Kobayashi (1990) fits fairly well in the present views. We expect, however, that within that description symmetry breaking elements like boundary surfaces will also play a role.

The physical meaning of the occurrence of a specific boundary condition in an INC crystal as assumed in the mesoscopic model is not yet fully understood. The presented model, however, turns out to also be applicable to the multidomain monoclinic phase IV (see Dijkstra *et al* 1992). A further investigation of this phase can help in the understanding of the role of the boundaries for the optical properties in INC phases as well. Also, the nature of a mesoscopic length l_0 needs further analysis. It could be related to the fact that certain point symmetries at the boundary surfaces are more in favour. But we do not know whether there is one precisely defined l_0 or not. In the description presented in this paper, the presence of such a mesoscopic length is essential, but a specific value is not required: there may be more than one different periodicities all giving a contribution to the same effect, which is linear and in the present parameter range to a good approximation proportional to the thickness of the crystal (see Dijkstra 1991). However, it is of interest to search for specific dependences on the wavelength of the probing light. If there is only one sharply defined l_0, then the crystal can be viewed as a folded Solč filter, which has very specific transmission properties that can be detected (see Yariv and Yeh 1984). Dijkstra *et al* (1992) have verified the validity of some aspects of this mesoscopic description by measurements of the different components of the gyration tensor.

At present, the model only decribes the effect of g_{33}. We expect that the effect of symmetry reducing by the boundary surfaces is more generally applicable, implying

that very probably g_{11} and g_{22} can also be unequal to zero as allowed for by the point group 222.

Acknowledgments

The authors are much obliged to Dr T Janssen and Professor Dr R M Pick for discussions about this matter. We also would like to thank Professor Dr P Bennema for his valuable support and participation. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter).

References

Agranovich V M and Ginzburg V L 1984 *Crystal Optics with Spatial Dispersion, and Excitons (Springer Series in Solid State Sciences)* vol 42, ed H-J Queisser (Berlin: Springer)
Born M 1933 *Optik* (Berlin: Springer)
Colla E, Muralt P, Arend H, Perret R, Godefroy G and Dumas C 1984 *Solid State Commun.* **52** 1033
Dam B and Janner A 1986 *Acta Crystallogr.* A **42** 69
Dijkstra E 1991 *J. Phys.: Condens. Matter* **3** 141
Dijkstra E and Janner A 1990 *Ferroelectrics* **105** 113
Dijkstra E, Kremers M and Meekes H 1992 *J. Phys.: Condens. Matter* **4** 715
Dijkstra E, Meekes H and Kremers M 1991 *J. Phys. D: Appl. Phys.* **24** 1861
Fousek J and Kroupa J 1986 *Czech. J. Phys.* B **36** 1192
Hahn Th 1983 *Int. Tables Cryst. IUCr* vol A (Dordrecht: Reidel)
Hogervorst A C R 1986 *PhD Thesis* University of Delft
Hogervorst A C R and Helmholdt R B 1988 *Acta Crystallogr.* B **44** 120
Iizumi M and Gesi K 1983 *J. Phys. Soc. Japan* **52** 2526
Janner A and Beest B W van 1983 *Proc. 11th Int. Colloquium on Group Theoretical Methods in Physics (Istanbul, 1982) Springer Lectures Notes in Physics* vol 180, ed M Serdaroglu and E Inonu (Berlin: Springer) p 269
Janner A, Rasing Th, Bennema P and Linden W H van der 1980 *Phys. Rev. Lett.* **45** 1700
Janssen T and Janner A 1987 *Adv. Phys.* **36** 519
Kobayashi J 1990 *Phys. Rev.* B **42** 8332
Kobayashi J, Kumomi H and Saito K 1986 *J. Appl. Crystallogr.* **19** 377
Kobayashi J and Uesu Y 1983 *J. Appl. Crystallogr.* **16** 204
Madariaga G, Zuñiga F J, Pérez-Mato an Tello M J 1987 *Acta Crystallogr.* B **43** 356
Marion G 1981 *J. Physique* **42** 469
Meekes H and Janner A 1988 *Phys. Rev.* B **38** 8075
Moxon J R L and Renshaw A R 1990 *J. Phys.: Condens. Matter* **2** 6807
Nye J F 1985 *Physical Properties of Crystals* (Oxford: Oxford University Press) ch 14
Opechowski A 1986 *Crystallographic and Metacrystallographic Groups* (Amsterdam: North-Holland) ch 7 and further
Pick R M 1970 *Adv. Phys.* **19** 269
Pick R M 1989 *Proc. NATO-ARW Conf. on Common Problems of Quasicrystals, Liquid Crystals and Incommensurate Insulators: Geometry and Thermodynamics (Preveza)* (New York: Plenum)
Saito K, Kawabe T and Kobayashi J 1987 *Ferroelectrics* **75** 153
Sommerfeld A 1959 *Vorlesungen über Physik IV, Optik* (Leipzig: Geest and Portig) ch 4
Wolff P M de, Janssen T and Janner A 1981 *Acta Crystallogr.* A **37** 625
Yariv A and Yeh P 1984 *Optical waves in crystals* (New-York: Wiley) ch 4