around themselves primarily for protection from predators. Shells are mainly made up of aragonite and small amounts of other minerals found in the molluscs' environment.

Shells have again a layered structure that is very similar to the pearls and thus exhibit almost all the optical features that we find in pearls. The important structural difference between a pearl and a shell is that the layers of a shell do not close upon themselves as in a perfect pearl. They always meet the external surface of the shell. As a result the shell surface is locally corrugated on a fine scale. Hence, we always get surface diffraction accompanying multilayer reflection. The reflection results in a metallic sheen of the shell and the diffraction orders are well separated from the specular reflections (Figure 2).

As in pearls, here also we find diffusion haloes. While in pearls they are seen in the reflection mode, in shells since they are thin, we can see them in the transmission mode. The halo arises from the diffraction of light by the crystallites of aragonite present in the different layers. Further all the optical properties exhibit marked polarization features.

Diffraction in heterogeneous liquid crystals

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We review briefly optical diffraction exhibited by periodically and non-periodically heterogeneous liquid crystals. Some of the novel features of the diffraction phenomena have been highlighted. We also discuss non-linear optics in such media. Attention has been paid to the present status in this area.

LIQUID crystals are states of matter with a molecular order between that of crystals and liquids. Many of them are optically heterogeneous. The heterogeneity arises from the fact that the index tensor varies from point to point inside the medium. For example, in the cholesterics, chiral smectic C and the twist grain boundary smectics (TGB), the index tensor periodically varies along the twist axis and remains a constant in an orthogonal direction. On the other hand, in the cubic blue phases, the index tensor is a three-dimensional periodic function of space. Further, in polymer dispersed liquid crystals (PDLC), it randomly varies in space. It is therefore to be expected that in all these media, light undergoes scattering, diffraction or both. In this article we briefly review diffraction from such liquid crystals.

Periodic liquid crystals

Cholesterics

The cholesteric liquid crystals (cholesterics) are made up of molecules that are locally aligned preferentially in a particular direction represented by the director, which twists uniformly about an orthogonal direction. This results in a helical structure of a definite pitch. We consider a plane wavefront of linearly polarized light incident along a direction normal to the twist axis. When its electric vector is parallel to the twist axis it emerges as a plane wavefront while for the electric vector in the orthogonal state it emerges as a periodically corrugated wavefront. The latter case leads to diffraction of light as in a phase grating[1]. In general, it is seen[2] that the various diffraction orders are mainly polarized with the electric vector perpendicular to the twist axis whereas the central or the zeroth order is mainly polarized with the electric vector parallel to the twist axis. Further, intensities of the different orders can be such that higher orders are more intense than the lower orders. The intensities are also a sensitive function of sample thickness. These are characteristic features of a phase grating.

Raman and Nath (RN) were the first to solve an equivalent optical problem[3] in the context of ultrasonic diffraction of light in isotropic liquids. In the RN theory, the diffraction pattern is obtained by Fourier transforming the corrugated wave front emerging from the medium. That is, the amplitude $F(q)$ of the diffracted light is given by:

$$F(q) = \int_{-\infty}^{\infty} U(y)\exp(-iqy)\mathrm{d}y,$$

where q is the scattering vector and $U(y)$ represents the corrugated wavefront described by:

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$$U(y) = A_0 \exp[i2\pi n(y)d/\lambda].$$

Here, A_0 is the amplitude of the incident plane wavefront, d is the thickness of the sample, λ is the wavelength of the incident light, y is the direction of phase variation and $n(y)$ the local refractive index of the medium.

In cholesterics, the diffraction pattern can be analysed in an analogous manner[4,5]. However, RN theory ignores the internal diffraction of light in the medium. Therefore, it is valid only for samples where the phase fluctuations inside the medium are very weak. Rokushima and Yamakita[6] have worked out a theory of phase gratings incorporating internal diffractions. In this approach, the sample is divided into thin sections, each contributing to the diffraction pattern. When a plane wavefront encounters the first section of the sample, the diffraction is similar to that described by the RN theory. Here each diffracted beam represents a plane wavefront. When these diffracted beams encounter the next section, they again get diffracted individually according to the RN theory. This process continues for each section throughout the sample resulting in a cascade of diffractions. This leads to a coupled wave theory[7,8] of diffraction. It may be mentioned that in absorbing heterogeneous media the RY theory in its present form is not applicable.

Chiral smectic C

The chiral smectic C (Sc*) liquid crystalline phase is essentially similar to cholesterics excepting that the director precesses about the twist axis at a constant angle which is between zero and $\pi/2$. Further, the structure is locally biaxial. Here also, for propagation of light perpendicular to the twist axis, the medium acts as a phase grating resulting in diffraction. A typical diffraction pattern obtained in such a structure is shown in Figure 1. In view of the local biaxiality, a Sc* behaves very differently from a cholesteric. For example, in Sc*, the medium diffracts light for any azimuth of the linearly polarized incident light. The diffraction experiments in Sc* are usually carried out to determine the structural pitch and there have not been many studies on the optical features of the diffraction pattern. Recent experiments[9], on a particular Sc* liquid crystal, have led to the elucidation of some very interesting features associated with the diffraction pattern. Some of these have been depicted in Figure 2. Here, one finds that irrespective of the state of polarization of the incident light, the diffracted light in the different orders are nearly linearly polarized parallel to the twist axis. However, in thick samples, the polarization features of the diffraction pattern are sensitive to the temperature dependent optical parameters. Further, in all the samples studied, the zeroth order has nearly the same state of polarization as that of the incident light.

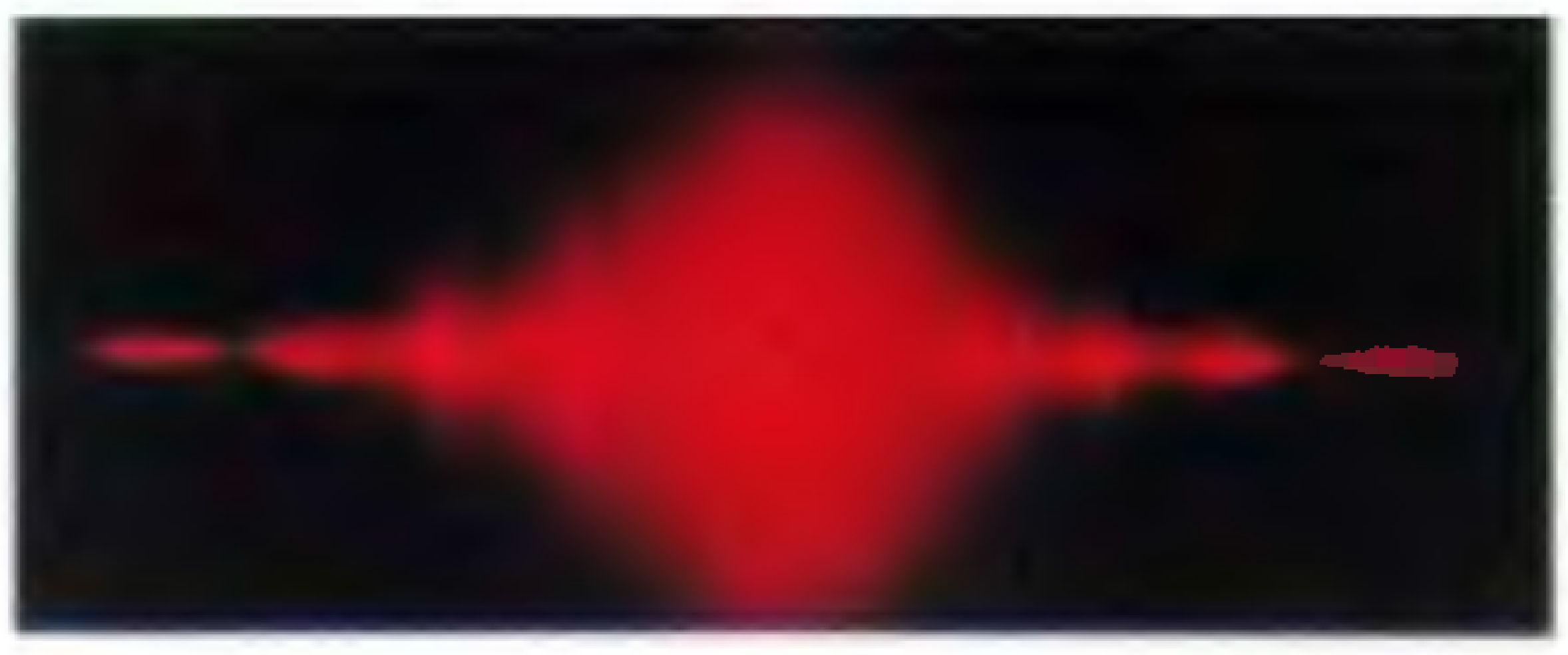

Figure 1. The diffraction pattern in a Sc* sample for a laser beam (He–Ne, λ = 633 nm). One can clearly see five orders of diffraction.

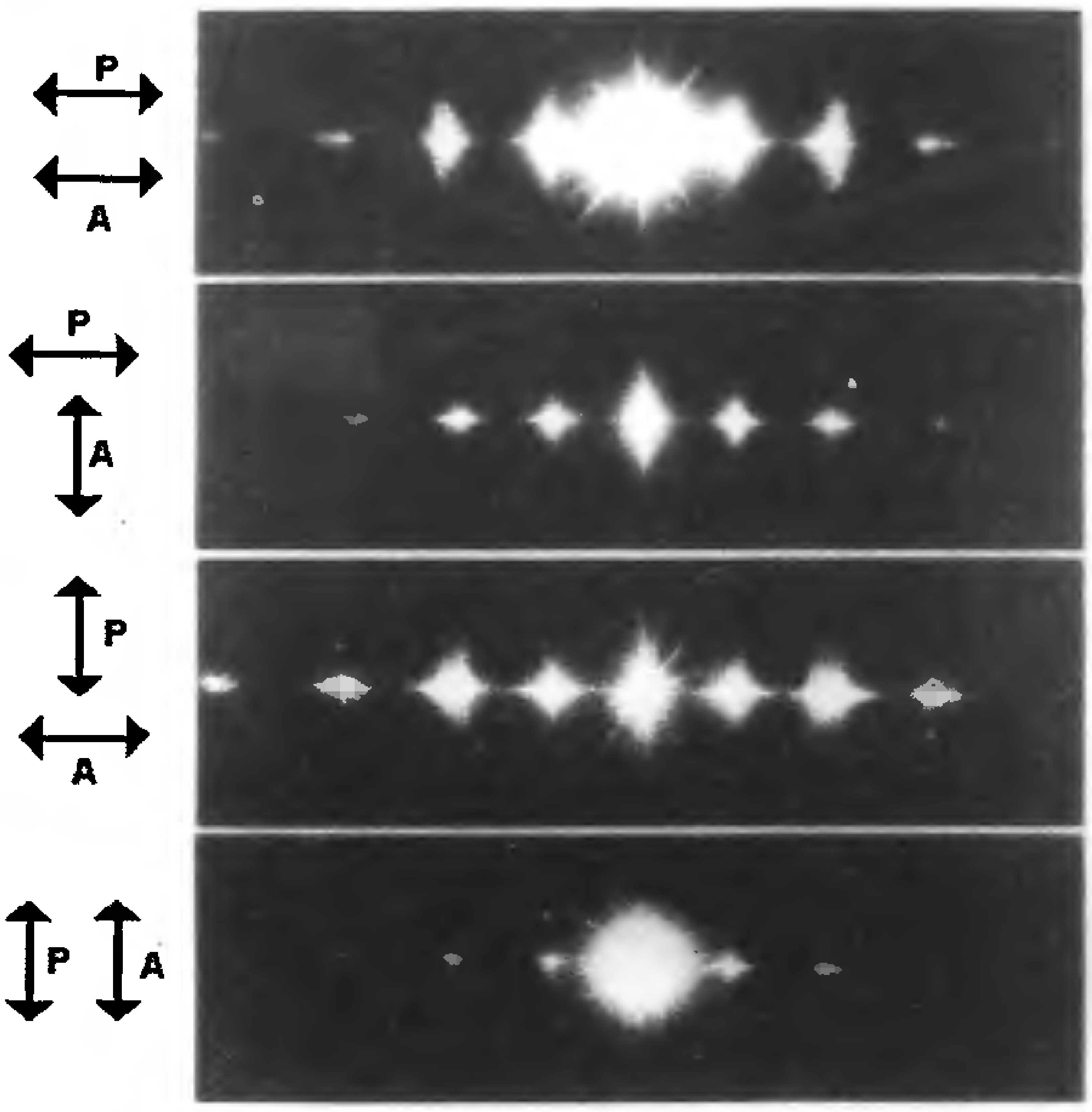

Figure 2. The diffraction patterns of a 50 µm Sc* sample at room temperature (≈ 25°). In each pattern, the first symbol denotes the setting of the polarizer P and the second symbol denotes the setting of the analyser A with respect to the twist axis of the Sc*.

The problem of optical diffraction in a Sc* can be solved either by a generalization of the RN theory of phase gratings[5] or by using the RY theory of anisotropic dielectric gratings[6,7]. Many of the observed features[9] can be accounted for by the RY theory.

Twist grain boundary smectics

The twist grain boundary smectic phases are endowed with many interesting optical properties. In this phase, thick smectic blocks are helically stacked with intermediate twist grain boundaries. The important feature of the structure is the possibility of incommensuration between the pitch of the helix and the thickness of the

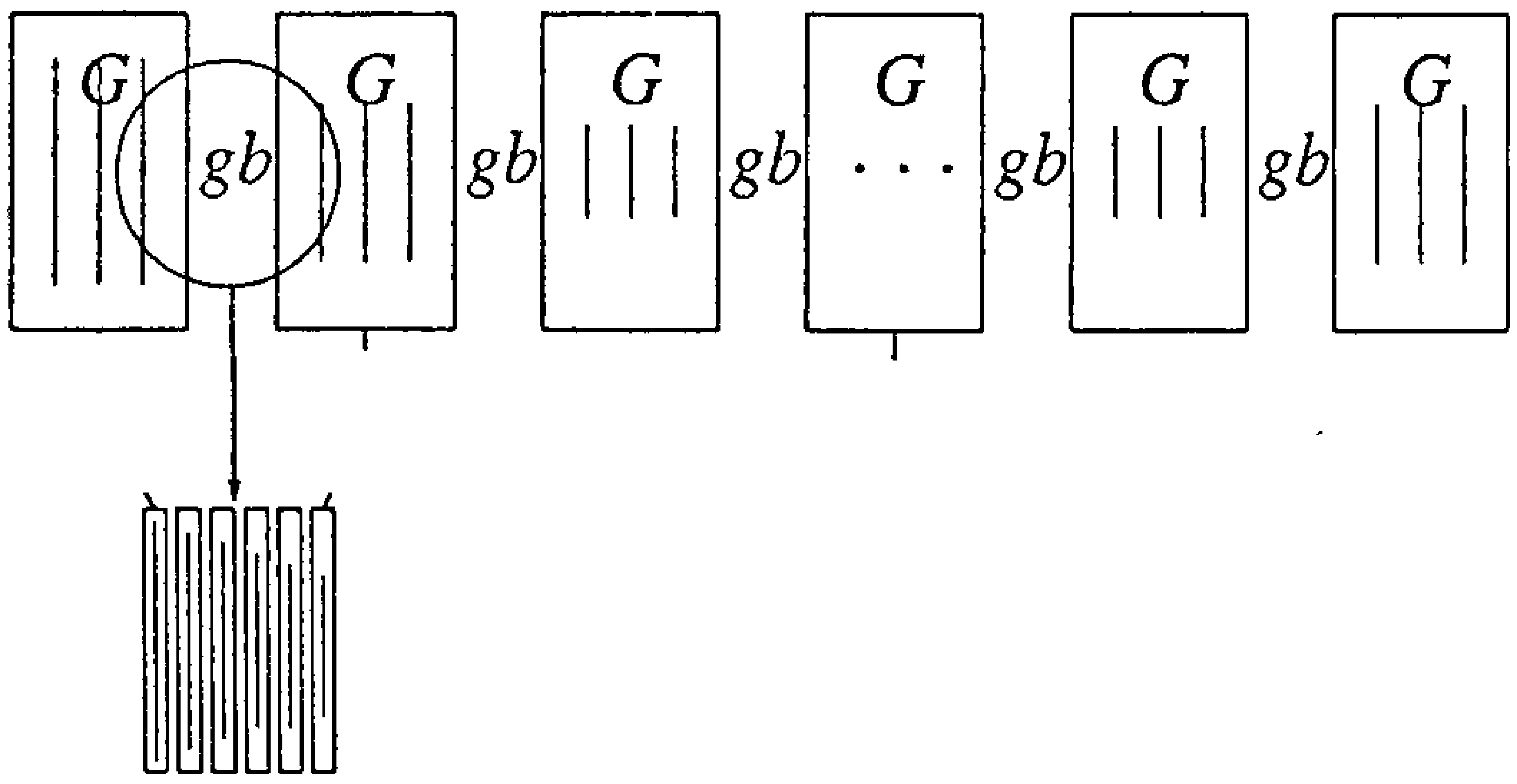

Figure 3. A model of TGB_A. G represents a smectic block and gb represents a grain boundary. The vertical line represents the projection of the local director.

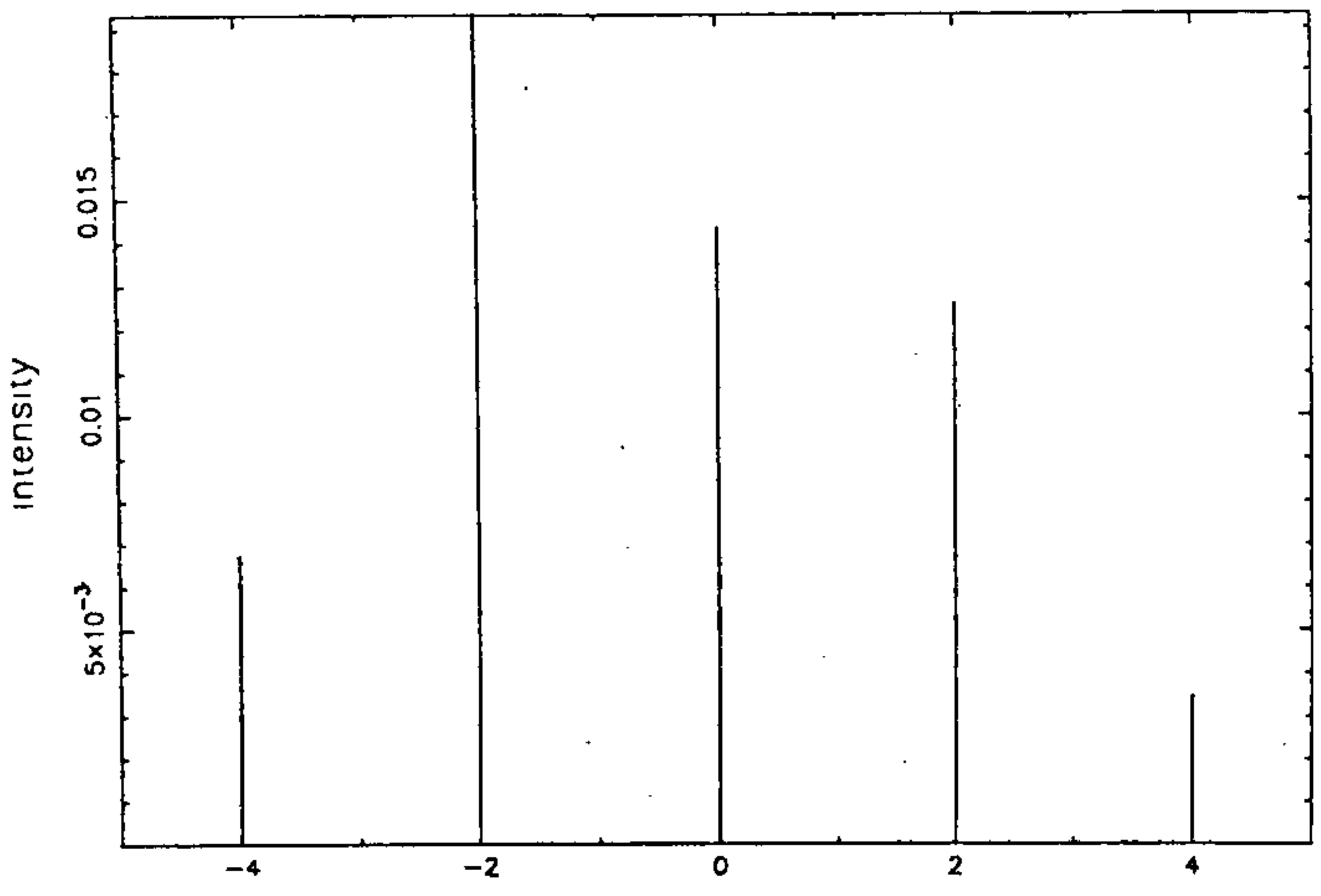

Figure 4. Computed diffraction pattern of an absorbing $TGB_{C_\parallel}$. The numbers on the abscissa represent the orders of diffraction.

smectic blocks. Optically, the smectic blocks can be thought of as thick birefringent plates. Similarly, one can consider a grain boundary as a helical stack of thin birefringent plates. These thin plates smoothly rotate and connect the adjacent smectic blocks (see Figure 3). The smectic blocks could be of either smectic A or smectic C structure. Then they are designated respectively as TGB_A and TGB_C. Also the diffraction features of TGB_C are in general sensitive to the orientation of the local 2-fold axis with respect to the twist axis. For example, it can have its 2-fold local axis either parallel ($TGB_{C_\parallel}$) or perpendicular ($TGB_{C_\perp}$) to the twist axis.

In the case of TGB_A or $TGB_{C_\parallel}$ the diffraction pattern is similar to that of cholesterics whereas for $TGB_{C_\perp}$ the diffraction pattern is rather similar to that of Sc*. From the diffraction pattern of TGB_A or $TGB_{C_\parallel}$ one can evaluate[10] the sizes of smectic blocks and the grain boundaries. In the absorbing case, the diffraction patterns of TGB_A and $TGB_{C_\perp}$, obtained using the RN theory, continue to be symmetric. However, interestingly, in absorbing $TGB_{C_\parallel}$ the pattern becomes asymmetric due to local biaxiality. This is obvious in the computed diffraction pattern shown in Figure 4.

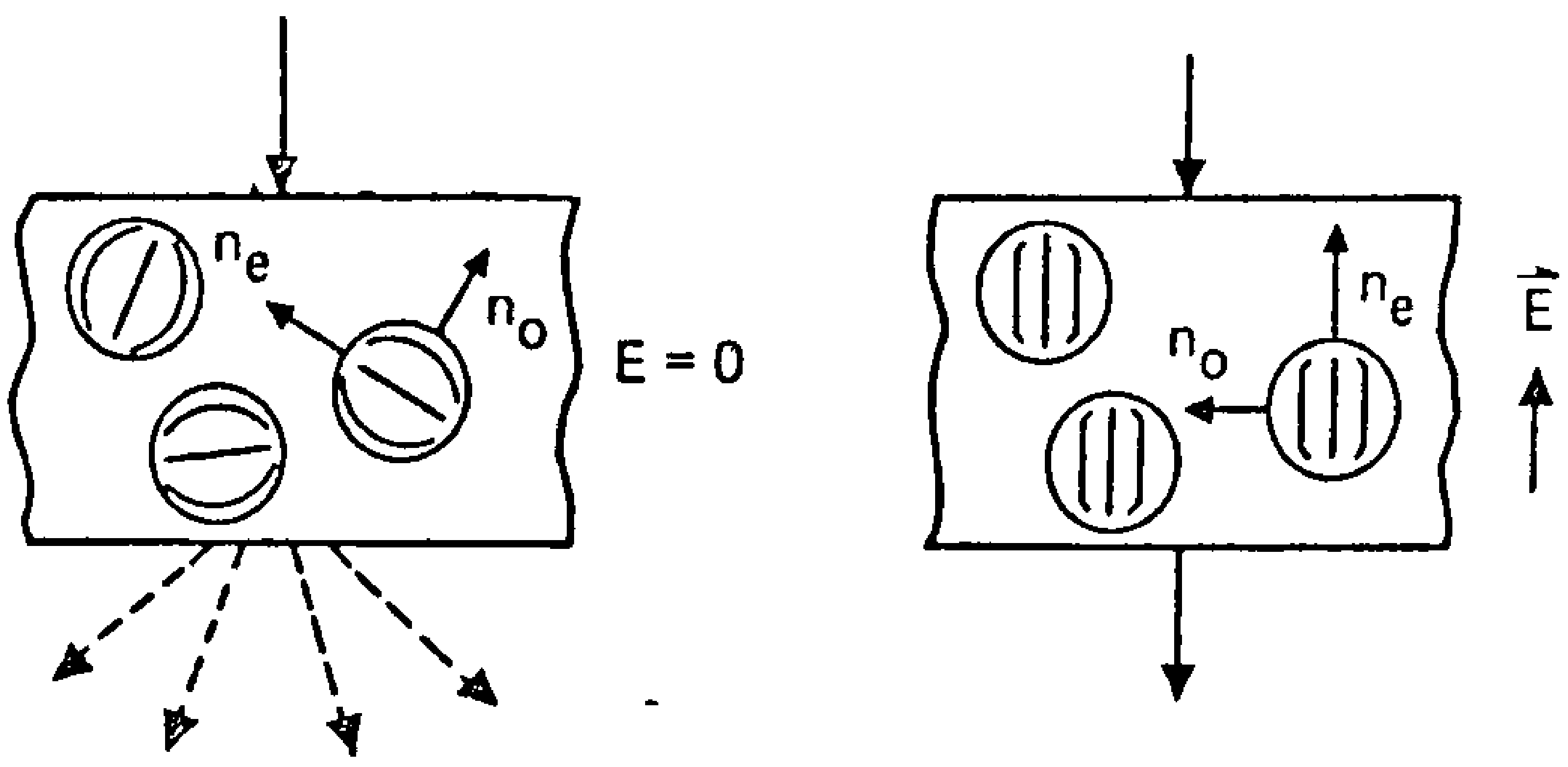

Figure 5. The director configuration in the nematic droplets of PDLC. In each droplet the director is tangential to the droplet surface. n_0 and n_e are the ordinary and the extraordinary refractive indices of the nematic. E represents the direction of the externally applied electric field.

Non-periodic liquid crystals

Quasi-periodic blue phases

The blue phases are optically isotropic. They appear in some cholesterics over a narrow range of temperatures close to the cholesteric–isotropic phase transition. In general, there are three blue phases, viz. BPI, BPII and BPIII. The phases BP1 and BPII have cubic symmetry. On the other hand, the structure of BP III is still not well-established. There are some indications that the BP III is a quasiperiodic structure[11]. As a consequence, the optical diffraction in one-dimensional quasi-periodic cholesteric[12] is of relevance to the analysis of optical diffraction in BPIII.

We consider one particular model of a quasi-periodic cholesteric. It is twisted in a particular direction according to a Fibonacci sequence[13], i.e. two incommensurate but uniformly twisted regions of thicknesses l_1 and l_2 occurring in a Fibonacci sequence. Within each unit there is a uniform helical stack of birefringent layers, with a total twist of 2π. Also $l_1 = (1 + h)l_2$ where $1/h = (\sqrt{5} + 1)/2$. Here, the dielectric tensor is locally uniaxial and gradually rotates along the twist axis but with two incommensurate periods. In the diffraction mode, for light incident with its electric vector perpendicular to the twist axis, the emergent wavefront has corrugations due to phase fluctuations. It may be mentioned that in a periodic cholesteric[5], in the same geometry, the diffraction peaks will occur at the wave vectors $q = 2\pi(N/l)$, N being an integer. However, the diffraction pattern of this quasi-periodic cholesteric has peaks at

$$q = \frac{2\pi}{l(1+h^2)}(r + hs),$$

where r and s are integers and h is an irrational number. Further, it is well known that in a quasi-periodic amplitude grating, the intense diffraction peaks occur when r and s are in the ratio of successive Fibonacci numbers[13]. Interestingly, in this quasi-periodic phase grating such a result is not found. The intensity in any given order is a function of the birefringence of the medium, sample thickness and wavelength. We may expect similar diffraction features in BPIII.

Inhomogeneous cholesterics

In cholesterics, one assumes that the director rotates uniformly in space giving raise to a uniform pitch in the medium. In practice, the sample is generally sandwiched between two substrates. The surface effects due to the substrates usually create inhomogeneities in the structure. We have investigated cholesterics with pitch distortion. We find that even a distortion of the order of two per cent can alter the diffraction features considerably[14]. For instance, each diffraction order becomes a broad top-hat intensity profile instead of being narrow and sharp.

Polymer dispersed liquid crystals

In recent times, polymer dispersed liquid crystals have attracted considerable attention since they have gained a lot of importance in display devices. Here, we highlight the interesting optical properties associated with such heterogeneous media. The simplest of the PDLCs are obtained in the two-phase region of a binary mixture of a nematic and a polymer. Here we have droplets of a nematic liquid crystal suspended in an optically isotropic polymer matrix. In a normal polymer matrix, the different droplets will have different orientations as shown in Figure 5. In the case of droplets that are very large compared to the wavelength of light, one is in the regime of geometrical optics. Even in this case, an incident beam of light gets scattered due to random phase corrugations of the incident plane wavefront. This results in a poor transmission. Surprisingly, the system can be brought to a near transmission state by the application of an electric field. Beyond a threshold electric field, the different droplets are brought into the same orientation with the director in each droplet aligned in the direction of the external field. Invariably the materials are so chosen that the refractive index of the isotropic polymer matches with the ordinary refractive index of the nematic liquid crystal. Then it is easy to see that for an incident light beam propagating along or opposite the direction of the external field there is a good transmission irrespective of the polarization state of light while for the orthogonal direction of propagation the ordinary wave is transmitted and the extraordinary wave is diffracted.

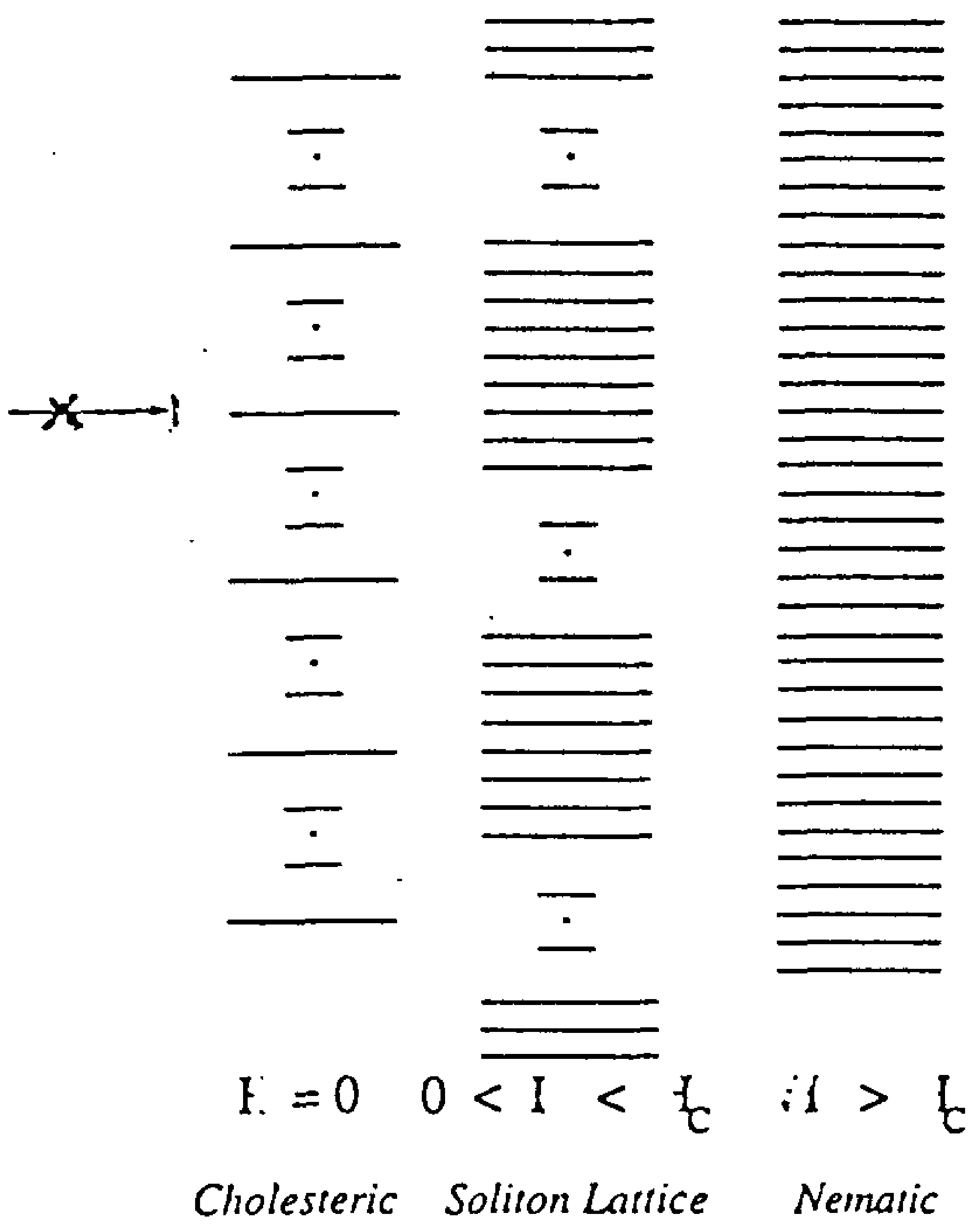

Figure 6. Transformations of a cholesteric structure due to the no linear optical effects in the phase grating mode. I_c represents t threshold intensity for the cholesteric to nematic transition.

Nonlinear optics in liquid crystals

Now we describe briefly nonlinear optics in heterogen ous liquid crystals. We consider a cholesteric in th phase grating mode. If the light intensity is high enoug then the electric field of the light wave couples to th director resulting in a mechanical torque on the directo This torque will distort the uniformly twisted choles teric. In fact, the effect of the light beam will be simil to that of an external electric or a magnetic field actin perpendicular to the twist axis. The uniform cholesteri will become non-uniform with walls of 180° twist sep rated by large, nearly untwisted regions. In other word this is akin to a soliton lattice. With increase of lig intensity, the width of the untwisted region increase and at a particular threshold intensity the structure ge completely unwound. The associated structural tran formations are depicted in Figure 6. The light beam wi also suffer diffraction in this mode. Hence, as the struc ture begins to unwind, the diffraction pattern continu ously gets altered and disappears altogether at th threshold intensity.

We now end with a brief note on the generation of second harmonic wave in PDLC's. Though both th polymer matrix and the suspended nematic droplets d not on their own exhibit second harmonic generation (SHG), the composite structure leads to a SHG. This arises at the interface of the droplets and the matrix. The effect has been experimentally established though indirectly. In this context, an interesting possibility of optical diffraction of SHG is worth mentioning. Even when all the droplets are aligned such that the ordinary wave emerges without diffraction, the second harmonic wave will suffer diffraction. Hence, we can expect the main beam of the fundamental to be surrounded by a diffraction halo of its second harmonic.

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