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ON THE CIRCULAR DICHROISM AND ROTATORY DISPERSION IN CHOLESTERIC LIQUID CRYSTALS WITH A PITCH GRADIENT

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Résumé. — On étudie théoriquement, sur la base d'un modèle physique simple, le dichroïsme circulaire et la dispersion rotatoire de la lumière dans un cristal liquide cholestérique avec un gradient de pas, pour plusieurs gradients et plusieurs épaisseurs. Tous les résultats obtenus sont interprétés à partir de considérations physiques simples.

Abstract. — The circular dichroism and rotatory dispersion of a cholesteric liquid crystal with a pitch gradient have been theoretically investigated, by using a simple model, for several values of the gradient and of the cholesteric thickness. All the obtained results have been interpreted by simple physical considerations.

1. **Introduction.** — It is well known that cholesteric liquid crystals exhibit peculiar optical properties. The modifications induced by a pitch gradient in some of these optical properties, namely in the light reflecting power dispersion, were theoretically investigated in reference [1]. This paper reports the results of an investigation concerning the modifications induced by a pitch gradient in the circular dichroism and rotatory dispersion of cholesteric liquid crystals. We will first of all consider the main optical properties of cholesterics related to the present work. Then the light transmission properties of cholesteric liquid crystals with a pitch gradient (CPG) will be treated by further development of the CPG model utilized in reference [1]. Finally we will show and discuss the modifications induced by a pitch gradient in the circular dichroism and rotatory dispersion of cholesterics. Cholesterics with a pitch gradient can be obtained experimentally by introducing a temperature gradient in specimens like cholesteryl nonanoate (CN), which shows a divergence of the cholesteric pitch near the smectic-A phase transition [2].

A relative variation of the pitch $\Delta P/P \simeq 80\%$ was observed. Furthermore a gradient of composition of

a mixture of two cholesterics of different pitch would probably induce a pitch gradient. A helicoidal structure with a pitch gradient, which is analogous to that investigated in this paper, was observed in crustacean and insect cuticles by Bouligand [3].

2. **Circular dichroism and rotatory dispersion in perfect cholesteric liquid crystals.** — The main optical properties of cholesterics were explained by De Vries [4]. By assuming that the helicoidal structure of the cholesteric is right-handed, the light at normal incidence is decomposed in two circularly polarized waves. Right circularly polarized light is reflected according to the Bragg law

$$\lambda_0 = \mu_d P \quad (1)$$

where μ_d is the refractive index for this kind of light, λ_0 the wavelength of the reflected light and P the cholesteric pitch. Left circularly polarized light passes through the cholesteric without suffering Bragg reflection. We will consider below only normal incidence. Chandrasekhar and Shashidhara Prasad [5], by an approach similar to the dynamical theory of X-ray or neutron diffraction, did develop a theory for light

reflecting power dispersion of a cholesteric. They used, for a non-absorbing cholesteric of finite thickness t_0 , a model which consists of a set of parallel planes spaced P apart. Each plane was supposed to have a reflection coefficient $-iQ$ for right circularly polarized light. The reflectivity of this kind of light as a function of the light wavelength λ is [3]

$$R = \frac{Q^2}{\varepsilon^2 + (Q^2 - \varepsilon^2) \coth^2 \left[\frac{t_0}{P} \sqrt{Q^2 - \varepsilon^2} \right]} \quad (2)$$

where

$$\varepsilon = 2\pi \frac{\lambda_0 - \lambda}{\lambda} \quad (3)$$

with λ_0 defined by eq. (1).

The range of total reflection is defined by the condition $-Q < \varepsilon < Q$, which, taking into account eq. (3), becomes

$$\frac{2\pi\lambda_0}{2\pi + Q} < \lambda < \frac{2\pi\lambda_0}{2\pi - Q} \quad (4)$$

The width of this range is therefore

$$W_0 \approx \frac{Q\lambda_0}{\pi} \quad (5)$$

Eq. (2) shows that the light reflectivity depends on the physical parameters of the cholesteric, as the thickness t_0 , the pitch P and the reflection coefficient per pitch given by

$$Q \approx \frac{2\Delta\mu}{\mu} \quad (6)$$

where

$$\mu = \frac{1}{2} (\mu_1 + \mu_2) \quad (7)$$

and

$$\Delta\mu = \mu_1 - \mu_2 \quad (8)$$

μ_1 and μ_2 being the principal refractive indices of a nematic layer,

The different reflectivity of right and left circularly polarized light give rise to the phenomenon of circular dichroism, which is defined by

$$D = \frac{I_l - I_r}{I_l + I_r} \quad (9)$$

where I_l and I_r are the intensities of the transmitted left and right circularly polarized light, respectively. Eq. (9) can also assume the form

$$D = \frac{R}{2 - R} \quad (10)$$

Concerning the rotatory dispersion, it is known that well outside of the reflection band, the dispersion presents a normal behavior and the rotatory power, in radians per cm, is

$$\rho = -\frac{\pi(\Delta\mu)^2 P}{4\lambda^2} \quad (11)$$

Near the region of total Bragg reflection the rotatory dispersion becomes anomalous and is given by

$$\rho = -\frac{\pi(\Delta\mu)^2 P}{4\lambda^2} + \frac{\psi - \varepsilon}{2P} \quad (12)$$

where

$$\tan \left[\frac{t_0}{P} \psi \right] = \frac{\varepsilon}{\sqrt{Q^2 - \varepsilon^2}} \tanh \left[\frac{t_0}{P} \sqrt{Q^2 - \varepsilon^2} \right] \quad (13)$$

The first term of eq. (12) represents the normal part of rotatory dispersion, whereas the second term represents the anomalous part and depends strongly on the cholesteric thickness.

3. Circular dichroism in cholesteric liquid crystals with a pitch gradient (CPG). — Let consider a cholesteric with a constant pitch gradient along the helix axis Z , defined by

$$\text{grad } P = \frac{dP}{dZ} \quad (14)$$

In reference [1] it was shown that the width of the total light reflection range increases progressively by increasing the value of the gradient, until a critical gradient is reached.

The value of the critical gradient depends on the birefringence properties of the cholesteric according to the expression

$$\text{grad}_{\text{crit}} P = \frac{Q^2}{2\pi} = \frac{2}{\pi} \left(\frac{\Delta\mu}{\mu} \right)^2 \quad (15)$$

For gradient values lower than the critical gradient the width W of the total reflection range is given by

$$W(\text{grad } P, t_0) = W_0 + \mu_d \cdot \text{grad } P \cdot t_0 \quad (16)$$

For gradient values higher than the critical gradient eq. (16) represents the width of the reflection range, but total reflection is no longer achieved. In any case the width of the reflection range is defined by the values

$$\lambda_1 = \frac{2\pi\lambda_0}{2\pi + Q} \quad (17)$$

$$\lambda_2 = \frac{2\pi\lambda_{t_0}}{2\pi - Q} \quad (18)$$

where $\lambda_0 = \mu_d P_0$ and $\lambda_{t_0} = \mu_d P_{t_0}$ with P_0 being the pitch value on one face of the crystal and

$$P_{t_0} = P_0 + (\text{grad } P) \cdot t_0 \quad (19)$$

the pitch value on the other face.

In order to evaluate the light reflectivity of a cholesteric with a pitch gradient (CPG) as a function of the light wavelength λ , we will use a simplified model of the CPG on the line of the models adopted in references [1] and [6].

Three cases will be considered : $\lambda_1 < \lambda < \lambda_2$, $\lambda < \lambda_1, \lambda > \lambda_2$, with λ_1 and λ_2 being defined by eq. (17) and (18). When $\lambda_1 < \lambda < \lambda_2$ the CPG is divided in three parts, as suggested in figure 1, where the Z axis coincides with the helix axis of the cholesteric. The region II represented in figure 1 is defined by

$$P_\lambda - (\Delta P)_\lambda < P < P_\lambda + (\Delta P)_\lambda,$$

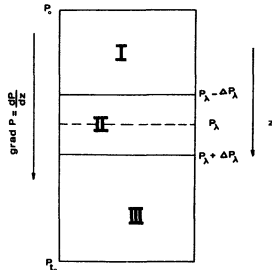


FIG. 1. — Schematic representation of the model for the cholesteric liquid crystal with a pitch gradient (CPG).

where P_λ is obtained by the Bragg law (1) corresponding to the given λ and $(\Delta P)_\lambda$ is obtained by

$$(\Delta P)_\lambda = \frac{W_\lambda}{2 \mu_d} \tag{20}$$

with W_λ obtained from eq. (5) for λ replacing λ_0 . In other words the $(\Delta P)_\lambda$ corresponds to the half-width $W_\lambda/2$ of total reflection of a perfect cholesteric with a constant pitch P_λ . In this way the deviations from the Bragg law due to the pitch gradient are contained, in region II, inside the total reflection range. This allows us to assume, in analogy with the models of references [1] and [6], that the region II is equivalent, concerning the reflection properties, to a perfect cholesteric with the same thickness and with constant pitch P_λ . By using eq. (14) the thickness t_{II} of the region II is easily derived to be

$$t_{II} = \frac{2(\Delta P)_\lambda}{\text{grad } P} \approx \frac{QP_\lambda}{\pi \cdot \text{grad } P} \tag{21}$$

Once having defined the region II, the regions I and III are implicitly defined. As the regions I and III are outside of the total reflection range corresponding to the given λ , their reflectivity will be in general low (at least for crystals not too thick). Therefore the approximation can be introduced that the pitch is constant inside these regions and equal to

$$\frac{P_0 + P_\lambda - (\Delta P)_\lambda}{2} \quad \text{and} \quad \frac{P_\lambda + (\Delta P)_\lambda + P_{t_0}}{2},$$

respectively.

The thickness of region I is

$$t_I = \frac{P_\lambda - (\Delta P)_\lambda - P_0}{\text{grad } P} \tag{22}$$

and that of region III is

$$t_{III} = \frac{P_{t_0} - P_\lambda - (\Delta P)_\lambda}{\text{grad } P} \tag{23}$$

According to this model the total reflectivity of the crystal is

$$R = 1 - (1 - R_I)(1 - R_{II})(1 - R_{III}) \tag{24}$$

where R_I, R_{II}, R_{III} are the reflectivities of regions I, II, III, respectively. If $\lambda < \lambda_1$ the crystal reduces to the region III alone, but if $\lambda > \lambda_2$ the crystal reduces to the region I alone : in both cases it is assumed that the crystal has a constant pitch equal to

$$\bar{P} = \frac{P_0 + P_{t_0}}{2} \tag{25}$$

It has to be emphasized that if the CPG gradient is lower than the critical gradient the thickness of region II is bigger than the extinction length defined in reference [1]. In this case its reflectivity is equal to 1 and the intensity of transmitted light equal to zero. On the other hand, if the CPG gradient is higher than the critical gradient the thickness of region II is smaller than the extinction length and its reflectivity is smaller than one.

In any case the reflectivities R_I, R_{II}, R_{III} are calculated by using eq. (2) and then are inserted in eq. (24). The diffraction pattern for a given gradient value and a given thickness is obtained by performing the calculations at different λ 's.

Figure 2 shows the reflection patterns obtained for a CPG thickness equal to the extinction length and

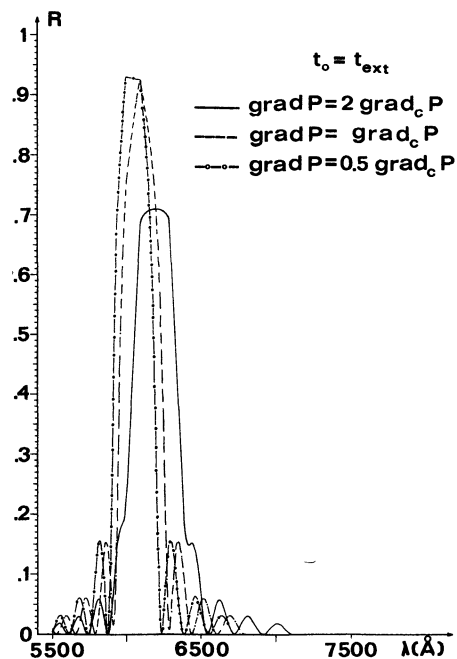


FIG. 2. — Light reflection patterns by a cholesteric liquid crystal with a pitch gradient (CPG) having a thickness equal to the extinction length for several gradient values.

several gradient values, by using the cholesteric characteristic quantities reported in reference [5], namely $Q = 0.1$, $P = 4\,000 \text{ \AA}$, $\lambda_0 = 6\,000 \text{ \AA}$ (or $\mu_d = 1.5$). The value of the extinction length is 8μ and the critical gradient is $15.9 \text{ \AA} \cdot \mu^{-1}$. All the reflection patterns show oscillations, which are recognized as Pendellosung fringes in reference [7]. It appears that for gradient values of $0.5 \text{ grad}_{\text{crit}} P$ and $1 \text{ grad}_{\text{crit}} P$ the maximum of the reflectivity is nearly one, as it is expected if the model is valid according to reference [1]. Furthermore the widths of these two reflection patterns are nearly the same and equal to roughly 1.7 times the width of the diffraction pattern of a perfect infinite non-absorbing crystal (Darwin curve). In the present case the width of the Darwin curve is 192 \AA . The obtained values are in satisfactory agreement with the predictions of eq. (16).

The reflection pattern corresponding to a gradient value of $2 \text{ grad}_{\text{crit}} P$ show a reduction to nearly 0.7 of the maximum reflectivity. The lack of total reflection in this case is due to the gradient being higher than the critical value.

The reflection width in this case is nearly twice the width of the Darwin curve, in satisfactory agreement with the prediction of eq. (16).

Figure 3 shows the reflection patterns obtained for the same gradient values of figure 2, but for a cholesteric thickness equal to twice the extinction length. It appears that the reflectivity maxima corresponding to the two lower gradient values are still nearer to one than the corresponding maxima of figure 2, whereas the reflectivity maximum corresponding to the gradient value $2 \text{ grad}_{\text{crit}} P$ remains essentially the same. These facts are quite compatible with

the CPG model. The widths of the three reflection patterns are also in this case in satisfactory agreement with eq. (16), which predicts a linear increase of W with the thickness.

Figures 4 and 5 show the reflection patterns obtained for the same gradients, but for the thicknesses $t_0 = 5 t_{\text{ext}}$ and $t_0 = 10 t_{\text{ext}}$, respectively, where t_{ext} represents the extinction length. Also in these cases

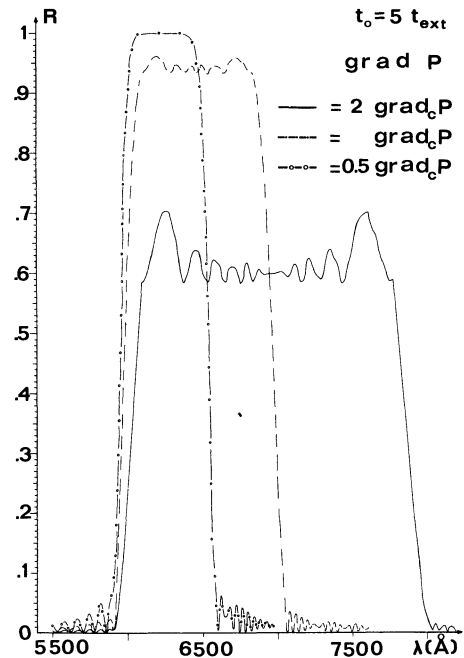


FIG. 4. — Light reflection patterns by a cholesteric liquid crystal with a pitch gradient (CPG) having a thickness equal to five times the extinction length, for several gradient values.

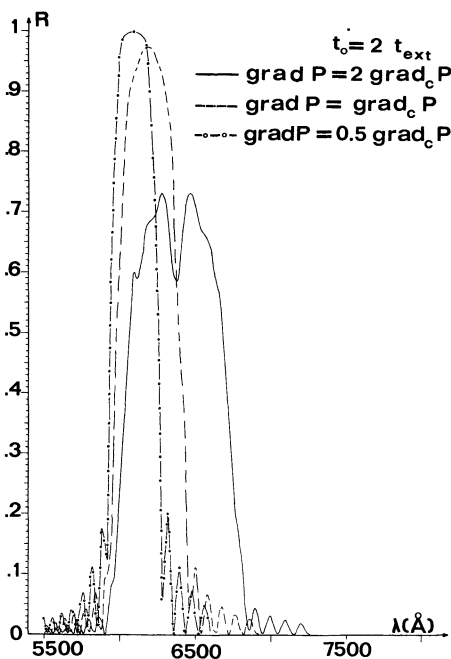


FIG. 3. — Light reflection patterns by a cholesteric liquid crystal with a pitch gradient (CPG) having a thickness equal to two times the extinction length, for several gradient values.

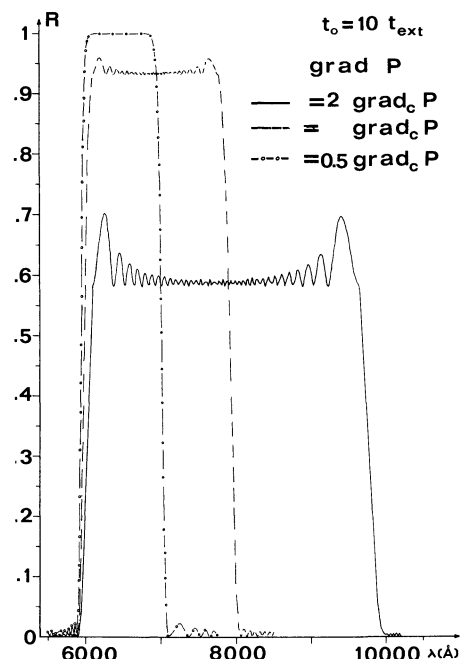


FIG. 5. — Light reflection patterns by a cholesteric liquid crystal with a pitch gradient (CPG) having a thickness equal to ten times the extinction length, for several gradient values.

the widths of all the curves are in quite good agreement with the predictions of eq. (16). From the reflection patterns so obtained it is quite easy to derive the circular dichroism by using eq. (10). As an example figure 6 shows the circular dichroism for a CPG having a thickness $t_0 = 5 t_{ext}$ and different gradient values.

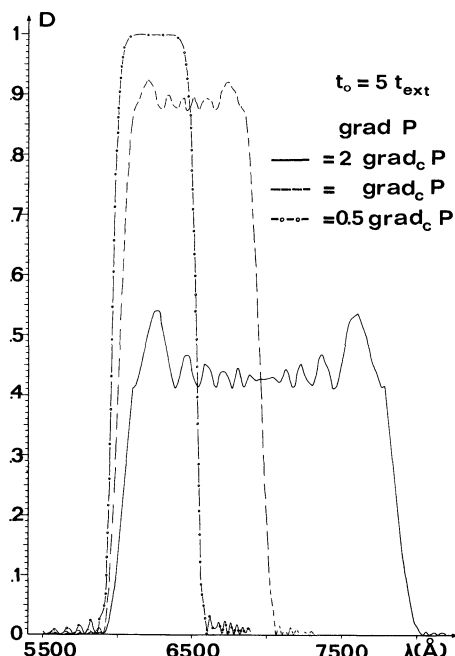


FIG. 6. — Circular dichroism of a cholesteric liquid crystal with a pitch gradient (CPG) having a thickness equal to five times the extinction length, for several gradient values.

4. Rotatory dispersion in CPG. — In order to evaluate the rotatory dispersion in a given CPG, the rotatory power of each of the three regions associated with our CPG model was calculated by using eq. (12) and (13). By knowing the thickness of the three regions, three rotation angles were easily calculated and added together. The result was divided by the total thickness of the considered CPG. The mean rotatory powers so obtained as a function of the light wavelength λ were plotted in figures 7, 8 and 9, for different CPG thicknesses and gradient values.

It appears at first that the wavelength range of anomalous rotatory power depends on the cholesteric thickness, for a given gradient, and on the gradient for a given thickness. A quantitative comparison with the data of the preceding figures shows that in any case the width of this range is nearly equal to the corresponding width of the reflection range. This fact can be explained with our CPG model, by considering that a change in the light wavelength induces a displacement of region II inside the crystal. Until region II remains inside the crystal, Bragg reflection exists and therefore anomalous rotatory power exists as well. For a fixed gradient, an increase of the thickness induces an increase in the reflection width [see eq. (16)] and therefore in the range of anomalous

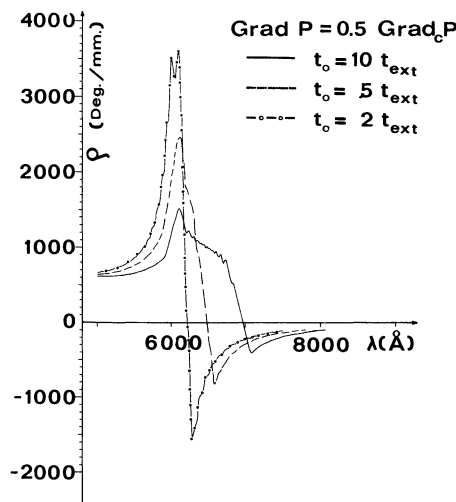


FIG. 7. — Rotatory dispersion of a cholesteric liquid crystal with a pitch gradient (CPG) having $grad P = 0.5 grad_{crit} P$, for several thicknesses.

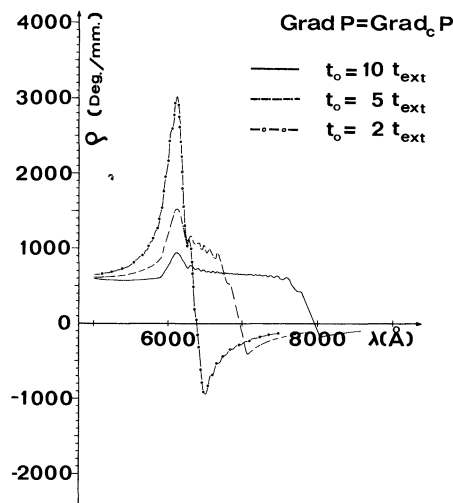


FIG. 8. — Rotatory dispersion of a cholesteric liquid crystal with a pitch gradient (CPG) having $grad P = 1 grad_{crit} P$, for several thicknesses.

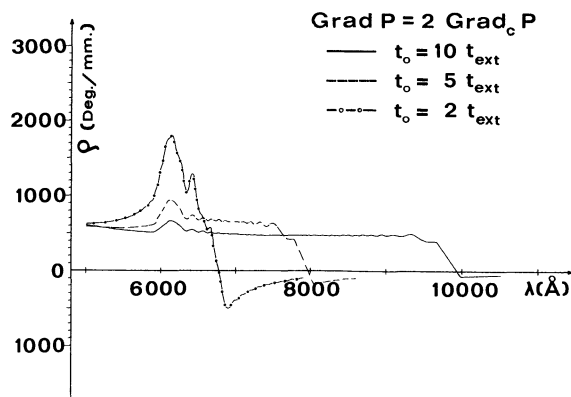


FIG. 9. — Rotatory dispersion of a cholesteric liquid crystal with a pitch gradient (CPG) having $grad P = 2 grad_{crit} P$, for several thicknesses.

rotatory power. Similarly, for a fixed thickness, an increase in the gradient induces an increase in the reflection width and therefore in the anomalous rotatory power range.

Secondly it appears that for a fixed thickness, an increase of the gradient implies a reduction of the magnitude of the anomalous effect. This might be explained by considering that an increase of the gradient reduces the intensity of the Bragg diffracted light and therefore the magnitude of the effect of anomalous rotatory power.

5. Conclusion. — The circular dichroism and the anomalous rotatory dispersion of a cholesteric liquid crystal with a pitch gradient were investigated as a function of the gradient and of the cholesteric thickness. The obtained results were compared with the optical properties of perfect cholesterics. The modifications of these properties induced for the different cholesteric thicknesses by the pitch gradient were interpreted on the basis of simple physical considerations.

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