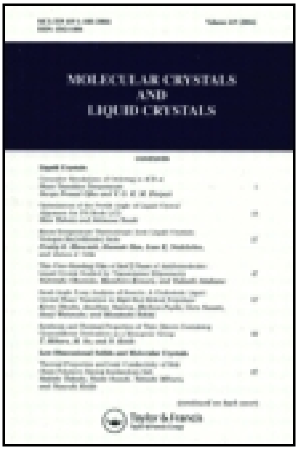

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Local Channeled Spectrum Analysis as a Measure of the Local Birefringence and Molecular Orientation in Liquid Crystals

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A new experimental technique is described for the measurement of local birefringence and molecular orientation in liquid crystals. This technique consists in analyzing the local channeled spectra obtained by optical polarising microscopy.

Keywords: Channeled spectrum, molecular orientation, local birefringence, grooves spectrum

1. INTRODUCTION

The average birefringence of an anisotropic uniaxial medium is defined by: $\Delta n = n_e' - n_o$ (BORN, 1933) where n_e' and n_o are respectively the extraordinary and ordinary refraction indices. The value of the n_e' depends on the orientation of optical axis, and is comprised between n_o and a maximal value n_e (i.e., the principal extraordinary index).

Calamitic liquid crystals constitute a standard example of uniaxial medium, as the molecules forming such systems possess an elongated form and display a free rotation around their director $\vec{k}$. Accordingly, the corresponding birefringence is equal to the difference of path between the average longitudinal and transverse vibrations created by an optical wave polarized linearly.

In liquid crystals the anisotopic medium is generally strongly heterogeneous as the molecular orientation varies across the sample. Moreover, as we deal with a quasi-liquid state, the position of the molecules depends on the mechanical stresses which are applied to the sample and on the anchoring of the molecules on their substrate. Thus, the birefringence measured by the current methods, namely by light extinction using a compensator, provide only an average in specific volumes, which are not indicative of the actual value of the local birefringence.

In this paper we propose a new optical method, which allows measurement of the local birefringence and provides also precise informations about the local molecular orientation in a given sample. In § 2 the principle of the method and description of the experimental technique are given. § 3 contains a number of illustrative examples of measurements of the local birefringence and molecular orientation in some liquid crystal phases.

2. PRINCIPLE OF THE METHOD AND DESCRIPTION OF THE EXPERIMENTAL TECHNIQUE

When natural light falls upon an homogeneous crystalline plane-parallel plate, inserted between polarizer P and analyzer A, whose optic axis is parallel to the surfaces of the plate, the emerged light intensity is equal to the square of the amplitude of the optical vibrations parallel to the A direction.

Let us note $S = S_o \cos \omega t$ the time dependent vibration which emerges from the polarizer (Figure 1). For a plate thickness e, the projections of the vibration along the x and y directions are:

$$x = S_o \cos\alpha \cos\omega t, \; y = S_o \sin\alpha \cos(\omega t - \phi) \qquad (1)$$

where α is the angle between the polarizer and the x direction, $\phi = 2\Pi\delta/\lambda$, with $\delta = (n_e - n_o)\, e$, and λ is the incidental light wave-length. After going through the analyzer, the sum of the components (2) becomes:

$$S' = x' + y' = S_o\,(\cos\alpha \cos\beta \cos\omega t + \sin\alpha \sin\beta \cos(\omega t - \phi)) \qquad (2)$$

where β is the angle between the direction x and the analyzer (Figure 1). Accordingly the vibration intensity will be:

$$I = I_o\,(\cos^2(\alpha - \beta) - \sin2\alpha \sin2\beta \sin^2(\phi/2)) \qquad (3)$$

where $I_o = S_o^2$.

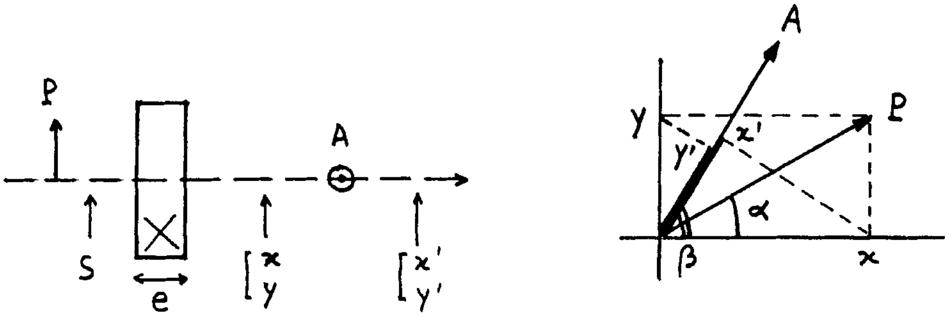


FIGURE 1 Classical scheme for measuring an optical path difference.

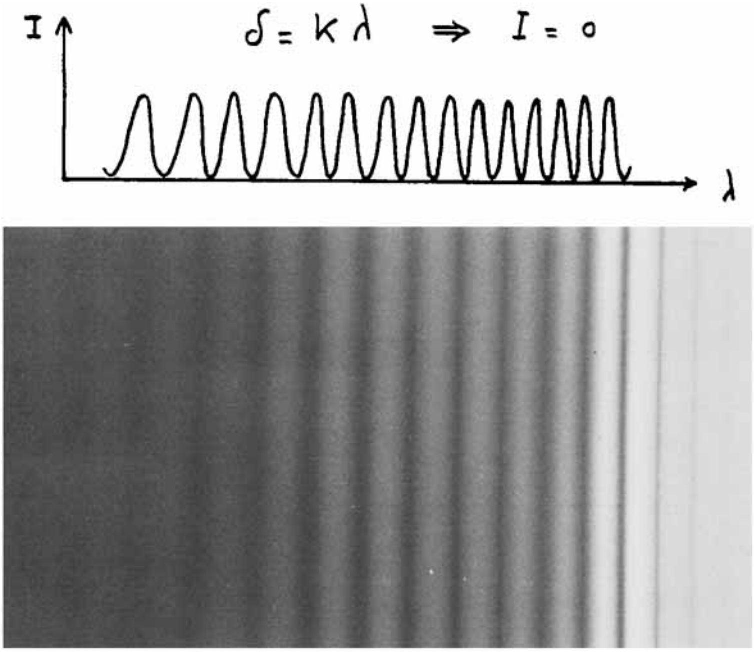


FIGURE 2 Channeled spectrum for an homogeneous medium. See Color Plate XVII.

When the polarizer and analyzer are perpendicular and form an angle of 45° with respect to the neutral lines of the plate x and y, (4) becomes:

$$I = I_o \sin^2 \Pi \, \delta/\lambda. \tag{4}$$

In order to verify the preceding sinusoidal dispersion lay, one uses classically a spectrometer, which provides sequence of extinctions for the successive values $\delta = k\lambda$. One gets black grooves parallel to the spectrometer slit, which are presented in Figure 2. The corresponding channeled spectrum is formed by parallel lines under the condition that δ has a constant value all across the sample.

However, the picture represented in Figure 2 holds only when dealing with a birefringent homogeneous plate (e.g., a quartz plate). By contrast, for an heterogeneous liquid crystal plate, one obtains a shifting of the channeled spectrum, the corresponding displacement being proportional to the variation of path induced by the heterogeneities of the sample. This consideration is the basis for the experimental device used in our new birefringence measurement method, which will now be described.

The principle scheme of our experiment is given in Figure 3. One can see in this figure that the light emerging from the microscope is separated in two distinct beams, one of which forms the image of the sample, and the other is used to form the channeled spectrum of the sample. This spectrum is the result of the path difference induced by a quartz plate Q and of the path difference provoked locally by the heterogeneous liquid crystal sample.

The camera is located in such a manner that it allows to visualize the superposition

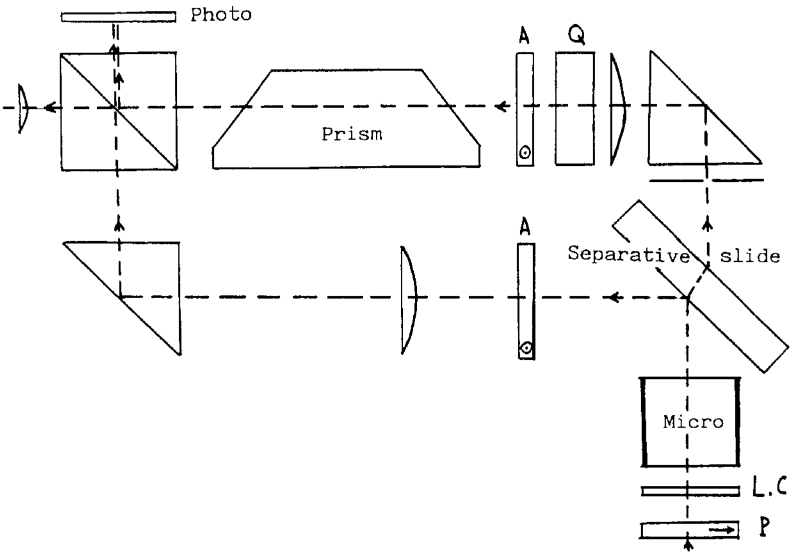


FIGURE 3 Principle scheme for the local channeled spectrum analysis.

of the two preceding images, and to analyze the obtained spectrum from which can be deduced the variation of the local birefringence from one point to another of the sample. On Figure 4 an illustrative spectrograph is shown, which contains the following informations: 1) the image of the sample; 2) the corresponding channeled spectrum measured along a given direction of the sample; 3) the reference channeled spectrum of the quartz plate; 4) an emission spectrum corresponding to a standard reference sample (here Zn-Ha-Cd) which allows to classify the channeled spectrum following the rank of the observed grooves.

We will now show in specific illustrative examples how one can deduce from the preceding method the local birefringence measurement, and the local molecular orientation of liquid crystal phases.

3. LOCAL BIREFRINGENCE AND LOCAL MOLECULAR ORIENTATION

The procedure used in order to work out the local birefringence in a given liquid crystal phase (here a sample of the nematic phase of the biphenyl K27) consists in three stages which are shown in Figure 5.

1) At first, the path difference resulting from the sole quartz sample is calculated. The quartz plate used in our experiment has two millimeters width. Its indices have the standard values $n_e = 1.553$ and $n_o = 1.544$. Accordingly the birefringence is $(n_e - n_o)q \simeq 0.01$ which yields a path difference between the ordinary and extraordinary vibrations of $\delta_q = (n_e - n_o)_q\, e_q \simeq 20$ μm. A more accurate measurement of δ_q can be obtained by comparing the channeled spectrum of quartz (Figure 5a) with the emission spectrum of the reference

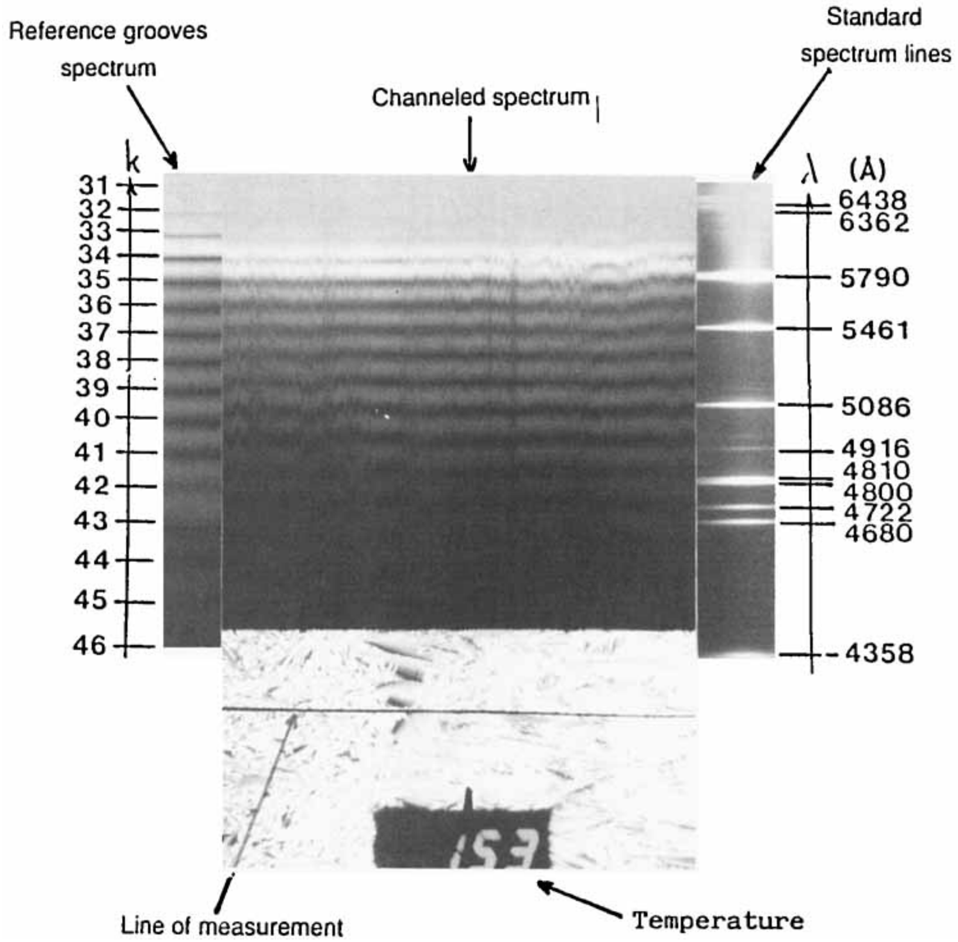


FIGURE 4 Spectrograph of the nematic phase of biphenyl K27. The image is described in the text. See Color Plate XVIII.

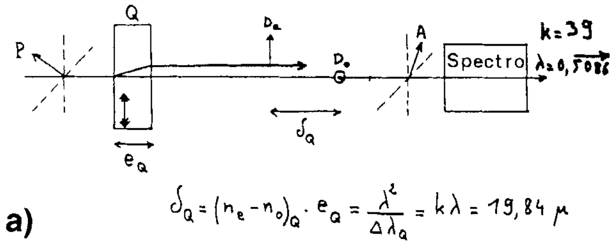
sample (Hg-Zn-Cd) where one can verifythat the blue emitted ray coincides with the groove of rank $k = 39$. Thus $\delta_q = k\lambda = 19.84\ \mu\text{m}$.

2) The second stage of our method consists in measuring the shifting of the various grooves due to the heterogeneity of the considered liquid crystal sample. This shifting which is shown in Figure 5b corresponds to the path difference: $\delta_s = \Delta n_s \cdot e_s$, where $\Delta n_s = (n_e - n_o)_s$ is the local birefringence of the sample at a given point. δ_s is generally small compared to δ_q. The total path difference $\delta_T = \delta_q + \delta_s$ induces a shift of the channeled spectrum towards the blue or the red as illustrated in Figure 5b. More precisely, one has:

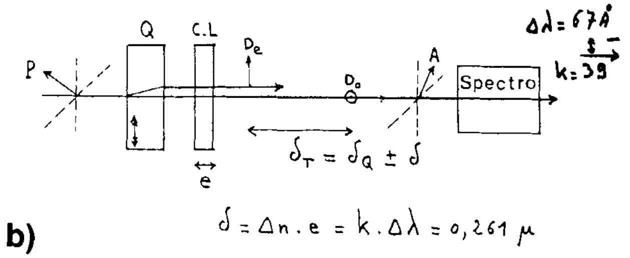
$$|\delta_T| = |\delta_q + \delta_s| = (n_e - n_o)_q\, e_q + \Delta n_s\, e_s = k\lambda + k\,\Delta\lambda \qquad (5)$$

3) One can see that the local birefringence of the sample at a given point Δn_s,

Homogeneous birefringent slide



Heterogeneous liquid crystal slide



Constant depth – Δn variable

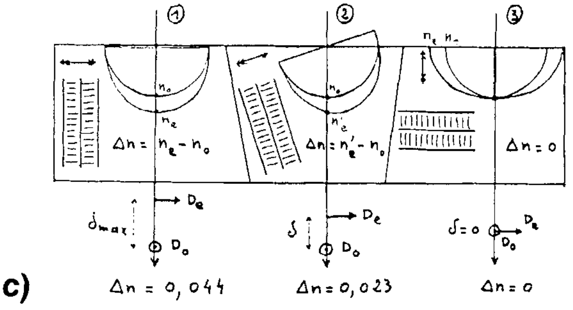


FIGURE 5 Illustrative example of the different stages of the method: a) channeled spectrum of an homoeneous plate; b) shifting of the grooves for an heterogeneous sample; c) shifting corresponding to a smectic A phase. See Color Plate XIX.

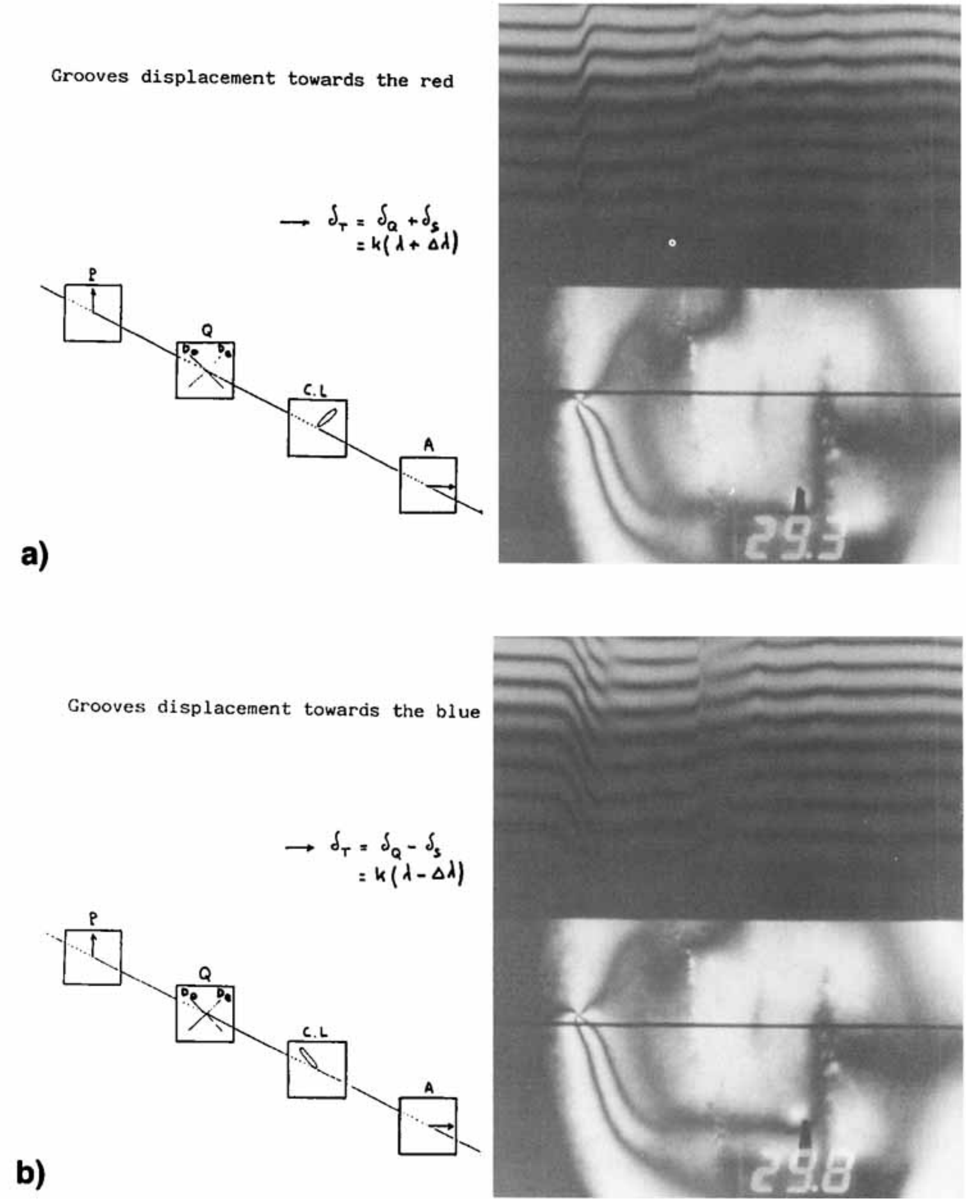


FIGURE 6 Principle of measurement of the local molecular orientation: a) shifting towards the red; b) shifting towards the blue. See Color Plate XX.

can be straightforwardly obtained from Equation (5), when using a sample of constant width e_s. One gets:

$$\Delta n_s = k\Delta\lambda / e_s \tag{6}$$

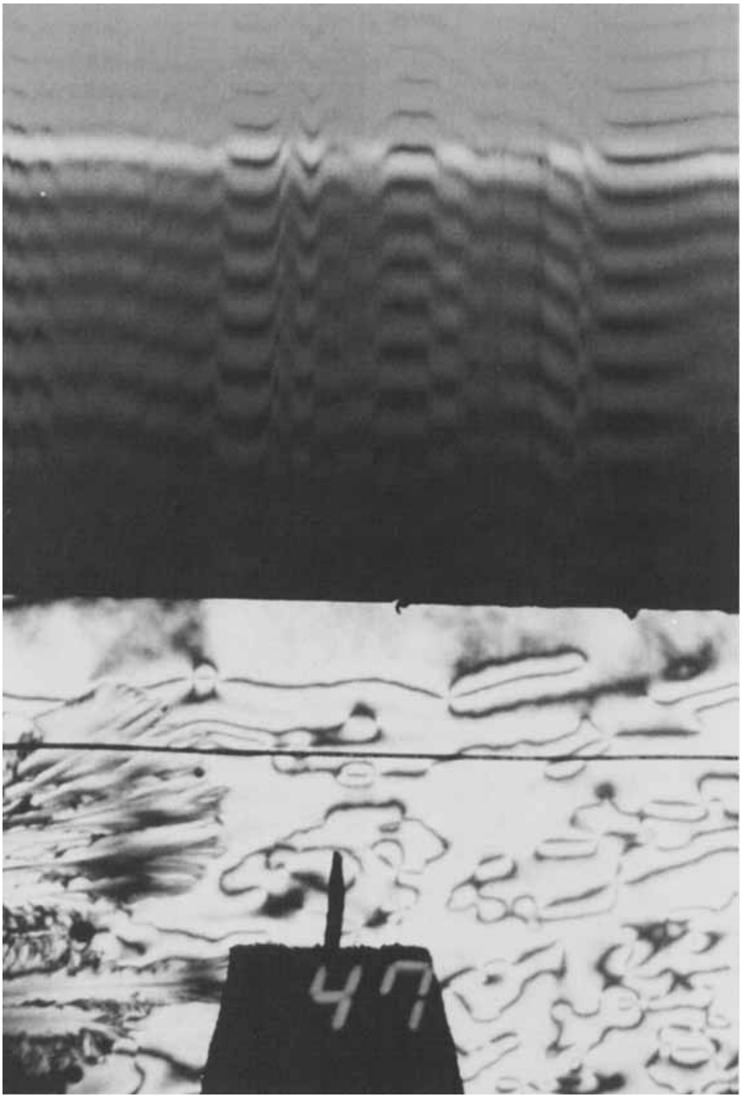


FIGURE 7 Continuous variation of the shifting for a nematic phase in which the molecular unit is tilted with respect to the optical axis from an angle Θ with $0 < \Theta < 90°$. See Color Plate XXI.

Figure 5c illustrates the application of Equation (6).

Depending of the shifting due the sample inhomogeneity takes place toward the red or the blue, one can deduce the relative orientation of the molecular unit with respect to the quartz optical axis. If the molecules are parallel to the preceding axis, the path difference will be added: (i.e., $\delta_T = \delta_q + \delta_s$), and the shift will be towards the larger wave lengths (Figure 6a), whereas when the path difference is $\delta_T = \delta_q - \delta_s$ one gets a shift towards the smaller wave-lengths (Figure 6b).

Besides the preceding extreme cases, one can visualize the intermediate situations where the molecular unit is tilted with respect to the quartz optical axis from an angle Θ with $0 < \Theta < 90°$. It leads to a wide variation of the shifts represented in Figure 7, which can be interpreted, accounting that the sample width is fixed, as a continuous variation of the molecular orientation along a given direction in the sample. In other words one has a map of the molecular orientation at each point of the sample along the preceding direction.

In summary, our method provides a clear cut measurement of the local birefringence and molecular orientation in all liquid crystal phases. This method is simple and fast. Its precision is limited by experimental measure of the observed shifts, which can be improved by using thin quartz plates and by replacing the optical determination of the grooves positions, by a densitometric measurement.

Reference

1. Born, M., Optik, Berlin (Springer 1933).