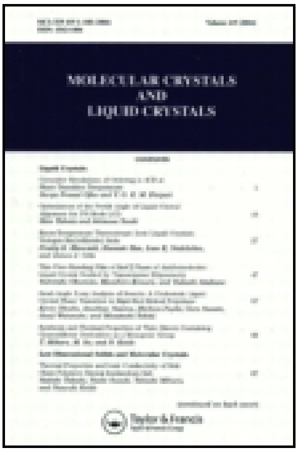

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Liquid Crystals Refractive Indices Behavior Versus Wavelength and Temperature

M. Warenghem [a] [b] & G. Joly [a] [b]

[a] Laboratoire de Dynamique et Structure des Matériaux Moléculaires C.N.R.S., U.R.A. 801

[b] Université des Sciences et Techniques de Lille, 59655, Villeneuve d'Ascq Cedex, FRANCE

Version of record first published: 24 Sep 2006.

To cite this article: M. Warenghem & G. Joly (1991): Liquid Crystals Refractive Indices Behavior Versus Wavelength and Temperature, Molecular Crystals and Liquid Crystals, 207:1, 205-218

To link to this article: http://dx.doi.org/10.1080/10587259108032100

Mol. Cryst. Liq. Cryst., 1991, Vol. 207, pp. 205–218
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

LIQUID CRYSTALS REFRACTIVE INDICES BEHAVIOR VERSUS WAVELENGTH AND TEMPERATURE.

M. WARENGHEM, G. JOLY
Laboratoire de Dynamique et Structure des Matériaux
Moléculaires
C.N.R.S., U.R.A. 801
Université des Sciences et Techniques de Lille
59655 Villeneuve d'Ascq Cedex - FRANCE

ABSTRACT A new refractometer designed in our laboratory is described : it allows a 3d diagram - refractive index versus wavelength and temperature - to be experimentally obtained for any transparent material. It consists in analyzing a channelled spectrum observed in the focal plane of a spectroscope illuminated with a white light source and where the sample under study is properly inserted. The spectrum acquisition is made by means of a linear array of photosensors. The fast response time of such technology allows measurements under unstable or gently varying conditions. This opportunity has been used to measure the dispersion curve of both ordinary and extraordinary indices versus temperature for several nematic liquid crystals. Numerical processing of the data is also considered.

INTRODUCTION

Numerous early studies on liquid crystals have been devoted to refractive index measurements[1-8]. But, given that in most applications the birefringence is the pertinent data to be known, measuring absolute values for indices held only few people attention. Now, with the new applications, especially in the field of non linear optics, polymer dispersed liquid crystals technology and possibly high power laser beam monitoring[9], such a measurement will be getting more and more interest. Usually the wavelength dependence of the index - the dispersion curve - is obtained from several independent index measurements, each additionnal point on the curve requiring an extra measurement. The temperature dependence of the index is obtained in the same way, increasing the number of experiments to be done.

Recently a refractometer has been proposed that allows the whole dispersion curve to be obtained in one experiment[10]. Any transparent material can be studied: liquid or solid, isotropic or anisotropic. The method consists in acquiring and analyzing a channelled spectrum. The acquistion time being quite large (≈ 12 hours), the sample had have to be well stabilized especially in temperature. In this paper, we present a new version of the refractometer with an acquisition time lower than one second, allowing gentle variations of the index to be measured. This set-up is used to measure both wavelength and temperature dependence of both ordinary and extraordinary index of liquid crystals, the whole data set being obtained in one hour experiment.

The principle of the refractometer is reminded in the first section. The new acquisition technique, the accuracy of the set-up and the sample requirement is discussed in the second section. The ability of such a set-up to measure gentle variation of the index is considered in the section three. The section four is devoted to the using of the data set in numerical processing. Finally, an application of this refractometer is proposed in the section five : the temperature dependence of liquid crystals indices is studied.

1) TALBOT-RAYLEIGH REFRACTOMETER: THE PRINCIPLE

This white light source refractometer is based upon a phenomenon first observed years ago by Talbot[11]. As a transparent phase plate is partially inserted in the field of an ordinary spectroscope illuminated with a white light source, dark bands appear in the diffraction orders in the same side of the plate, due to interferences between the upper and lower part of the beam, just as a Rayleigh interferometer do (fig.1). This order of diffraction looks like a channelled spectrum. The position of the bands in the spectrum is correlated with the phase retardation introduced by the plate, that means the position of the bands links the wavelength with the refractive index of the material the plate is made of. Therefrom the dispersion curve can be issued using a proper spectrum analysis.

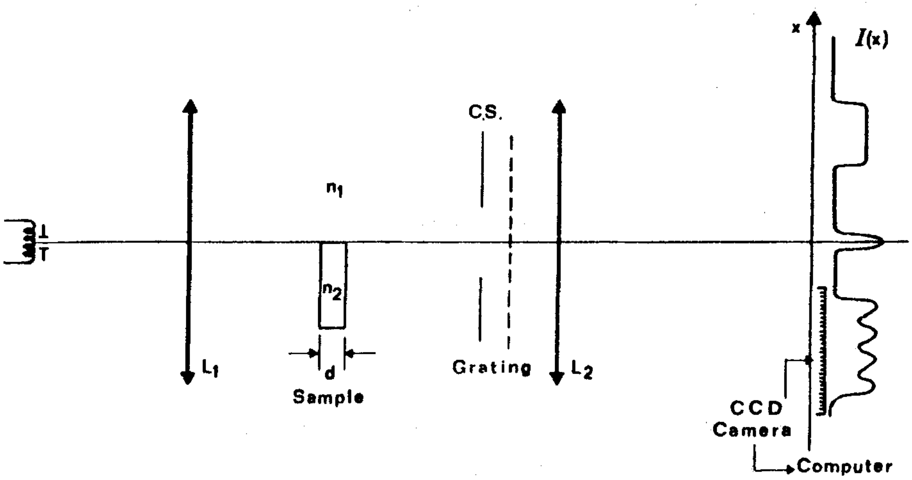

FIGURE 1 Basic set-up to observe the Talbot bands : a grating spectroscope illuminated with a white light source.

Whether or not Talbot have considered measuring dispersion curve using its observation, - and he likely did - he could not do it easily due to the sharpness of the image to be analyzed.

Schematically, the principle of the refractometer lies in two equations. That of the grating, linking the diffracted wavelength λ with the abscissa (angular θ or linear x) of the associated point in the focal plane (Fig.1) :

$$p \sin(\theta) = k\,\lambda$$
$$p\,(x - x_0) / \sqrt{(x - x_0)^2 + f^2} = k.\lambda \qquad (1)$$

where p, k, x_0, f are respectively the period of the grating, the diffraction order, the zero order abscissa in the focal plane and the focal length of the output lens. The second equation is that of a dark band existence, that is to say a destructive interference condition. Assuming m is an interference order defined as usual:

$$(n(\lambda) - 1)\, d = m.\lambda \qquad (2)$$

where n(λ) and d are respectively the index and the thickness of the phase plate, dark bands correspond to half integer values for m:

$$m = l + 1/2 \,;\, l : \text{integer} \qquad (3)$$

Experimentally speaking, a measurement consists in acquiring the spectrum and second in analyzing the data.

) EXPERIMENTAL SET UP

In the first version of the refractometer, the data acquisition consisted of a silicon photodetector mounted on a motorized translation stage and it took about 12 hours to complete the spectrum acquisition. Although very efficient, that clumsy technology has been replaced by a modern CCD camera. More precisely, it is a linear array of silicon photosensor that insures the data acquisition. Made of 3456 pixels, 10.7 micrometer wide each, this array covers 35 millimeters, allowing the whole spectrum to be stored in just one array scanning. Using that technology, the acquisition time now mainly depends on the array sensor sensitivity. With a sensitivity of 0.7 lux for an integration time of 20 millisecond and the adjunction in the set-up of a cylindrical lens, the whole channelled spectrum is stored within one second.

Using such a fixed photosensor, only one diffraction order can be stored, contrary to the previous version where orders k = +1, 0, -1 were stored. As a result, the calibration of the spectroscope is no longer performed in the same way. The calibration is necessary to determine the actual values for the parameters that come into the relation (1), namely the focal length and the origin of the abscissas; the period of the grating being measured using an high accuracy goniometer. In the first version of the refractometer, these parameters have been determined from the abscissas in the focal plane of the Helium-Neon line (0.6328 µm) for k = -1 and k = +1. Now it is the Argon line (0.5145 µm) abscissas for k = +1 and k = +2 that are entered in the equation (1) to obtained the desired parameters.

The image analysis has not been modified in the principle. It consists of three steps : first the positions of every dark band in the spectrum is determined, second these positions are converted into wavelengths using the diffraction relationship (1) and third, the associated index values are calculated from the the destructive interference conditions (2) and (3). At last the dispersion curve is built up from as many data points as dark bands.

As previously said, the parameters that come into the relation (1) are obtained from calibration, but two more parameters appear in the interference condition: the thickness d and the order of interference l. Their actual values are obtained as in the first version of the refractometer, nevertheless let us remind it. The thickness is measured by means of a displacement sensor (accuracy : 0.5µm). The order of interference varies by one unity from a dark band to the next one, but we need a starting value. This value is derived from equation (2) using the measured thickness d and a pair of values for index and wavelength known from literature or measured in our lab.

$$m_{ref} = (n_{ref}(\lambda_{ref}) - 1)d/\lambda_{ref} \tag{4}$$

$$l_{ref} = \mathrm{INT}(m_{ref}) \tag{5}$$

This pair of values and the associated interference order will be refered afterwards as the reference point and the reference order. The latter must be known unambiguously and that brings us to discuss accuracy of such a set-up and how precisely the sample must be shaped.

Assuming that the reference point is known with a very good accuracy, the deviation for m_{ref} mainly depends on that of the thickness. The unambiguous determination of l_{ref} imposes the knowledge of the thickness within the range $\lambda/n-1$, that is to say about 1 micrometer. Moreover, the destructive interference condition must be written down as an optical path averaged over the studied sample area. Should the front wave be too distorded, the interference pattern disappears (Fig.2).

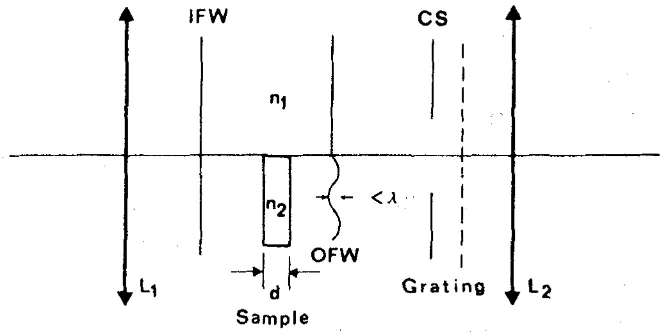

FIGURE 2 Front wave distorsion after travelling through the sample.
IFW: Input front wave; OFW: Output front wave.

That means the sample must be a well shaped plate with both index and thickness constant over the whole studied area. The front wave distorsion tolerance being one wavelength and assuming an homogeneous material with a constant index, the thickness must be kept within $\lambda/n\text{-}1 \approx 1\mu m$ over the studied area. It should be noted that this area can be much more smaller than the whole sample.

Assuming that requirement fulfilled, bands can be observed and dispersion curve issued with an accuracy mainly depending on that of the reference point. Suppose the reference index given with an accuracy of 1.10^{-5}, the whole curve will be given with an accuracy of the same order : $\approx 3.10^{-5}$. This set-up has been tested using a Schott glass plate in the range 0.4 - 0.9 µm. This range depends on the source spectrum and on the optical component transmittancies, the sensor array working in the range 0.3 - 1.1µm. As discussed in the first paper[10], the bands are only visible in a wavelength range correlated with both the the number of lines of the grating and the interference order, that is to say index and thickness of the sample : a collimating slit is inserted in the set-up to adjust properly the different parameters in order to enlarge that range. This slit also determine the studied area of the sample.

3) INDEX VARIATION MEASUREMENT

Keeping in mind that storing a spectrum and analyzing it are two different operations that can be done separately and the acquisition time is less than a second, a slow variation of the index can be studied. Spectra are periodically stored as the index varies under an external influence, i.e. temperature or electric field... The value of the external parameter P_{ext} being measured at every acquisition, the processing of the different spectrum will result in a 3d diagram $n(\lambda,P_{ext})$.

As the index varies, the bands shift in the spectrum and possibly the reference order will change as well. Therefore this has to be properly checked. Providing that the spectra are stored frequently enough to prevent the reference order from varying more than one unity from one spectrum to the next one, reference orders can be attributed to each spectrum unambiguously using only one reference point, namely that one of the first spectrum. These reference orders are determined step by step by visual inspection of the chart as shown on figure 3. Plotted on this chart are the positions of the bands on the x-axis and the value of the external parameter P_{ext} on the y-axis. Each horizontal line corresponds to one spectrum, also plotted on this chart is the reference wavelength λ_{ref}: the reference order does not change unless a band runs across the line. For instance, the reference order decreases one unity between the two spectra a and b as noted on figure 3.

Otherwise the spectrum analysis does not change. Finally, a comprehensive data set is obtained and a set of curves can be issued as it will be seen in the section 5 where the application to liquid crystals is demonstrated.

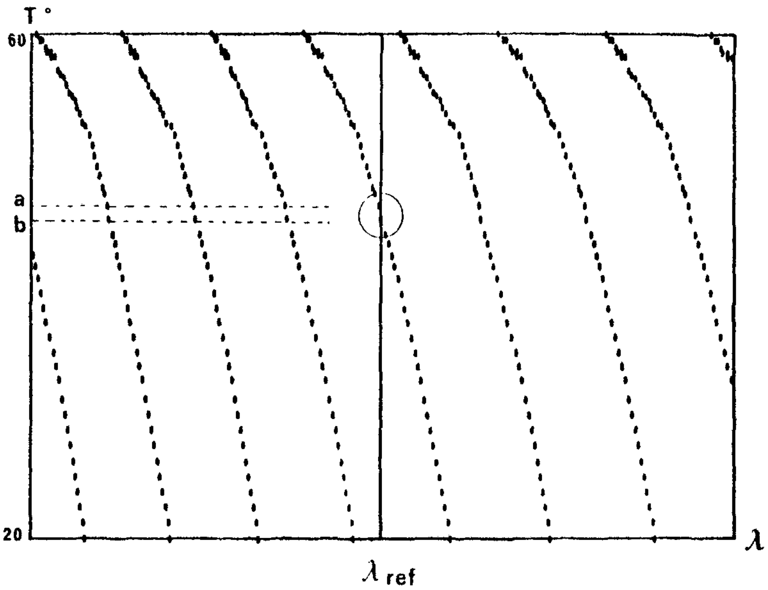

FIGURE 3. Dark bands positions in the spectrum (x-axis) for different values of an external parameter (y-axis), temperature in this case ; (immersion oil).

4) NUMERICAL PROCESSING

As the whole set of data are stored, numerical processing can be undertaken. According to the variable involved, there are mainly two different interesting processings: one expressing the wavelength dependence of the index and the other expressing the dependence of the index versus the external parameter such as temperature. Regarding the wavelength dependence, our image analysis automatically fits the experimental values with the expansion usually used by the glass manufacturers:

$$n^2(\lambda) = A_1 + A_2.\lambda^{+2} + A_3.\lambda^{-2} + A_4.\lambda^{-4} + A_5.\lambda^{-6} + A_6.\lambda^{-8} + \ldots \quad (6)$$

This expression is the first terms of a Cauchy-like formula, involving the absortion bands of the materials. In our case, the different parameters A_i now depend on the external parameter P_{ext}. Conversely, theories that involve and link polarizabilities and indices by means of Lorenz-Lorentz formulas and absorption bands[12,13], can be confronted with experimental results.

The other possible processing concerns the second external variable named P_{ext}. An interesting case is the temperature dependence of the refractive index: this is considered in the next section.

5) APPLICATION TO LIQUID CRYSTALS

As previously said[10], birefringent materials can be studied using this refractometer, providing that the sample is a monocrystal with a well known optical axis direction. In case of liquid crystals study, among several geometries10, the easiest way to obtain the ordinary and extraordinary indices is the planar texture between parallel polarizers (Fig.4). Extraordinary index is obtained for polarizers parallel to the optical axis and after a quarter turn of both polarizers, the ordinary index is measured.

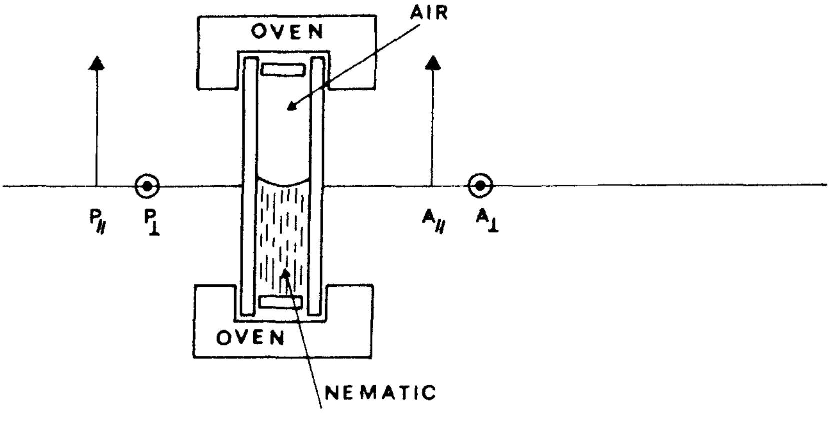

FIGURE 4. Sample geometry to study both temperature and wavelength dependence of liquid crystals indices.

The liquid crystal must be placed into a container : providing that the container covers the intervene in the channelled spectrum formation. The glass plates are strongly rubbed to insure the liquid crystal to be a monocrystal, that is controlled by viewing the sample through crossed polarisers, the thickness has been chosen quite low (≈75µm) ; as a result, the dispersion curve will be built up from about 50 data points instead of more than 100 in case of a 200µm thick sample and the wavelength range will be sligthly reduced as well (0.5µm - 0.9µm). The reference point has been measured in our lab using a total internal reflection set-up[14]. The sensitivity of this set-up is 2.10^{-4}, that is more than enough in the case of nematics where the thermal motion prevents from having a better accuracy. The external parameter involved in this application is the temperature, therefore the sample has been inserted in an oven. Allowed temperature rates are such as the resulting temperature change during one acquisition time(1s) is negligible: the 2°c/mn adopted temperature rate is well suited. The temperature is measured using a flat sensor sticked onto the sample wall very close to the studied area (3mm). The actual sample temperature and the measured one differ from each other less than .1°c, value controlled by clarification of known compounds in the range 30°c-100°c. Figures 5,6 show the complete set of curves obtained. The repeatability of such measurement is very good; however it is worth noticing that sometimes the Talbot bands pattern is totally distorded due to some defect travelling and relaxing in the sample during the heating process. Obviously such experiments are disregarded.

As it can be seen on these figures, the experiment can cover a temperature range that contains the nematic-isotropic temperature transition. By properly choosing the temperature range and the heating rate, it is possible to obtain the index values in the transition region and therefrom test the different theories correlating refractive indices, birefringence and order parameter[15].

6) CONCLUSION

In this paper, has been described a refractometer that allows the refractive index of a material to be measured versus both wavelength and a second external parameter, providing that the index variation

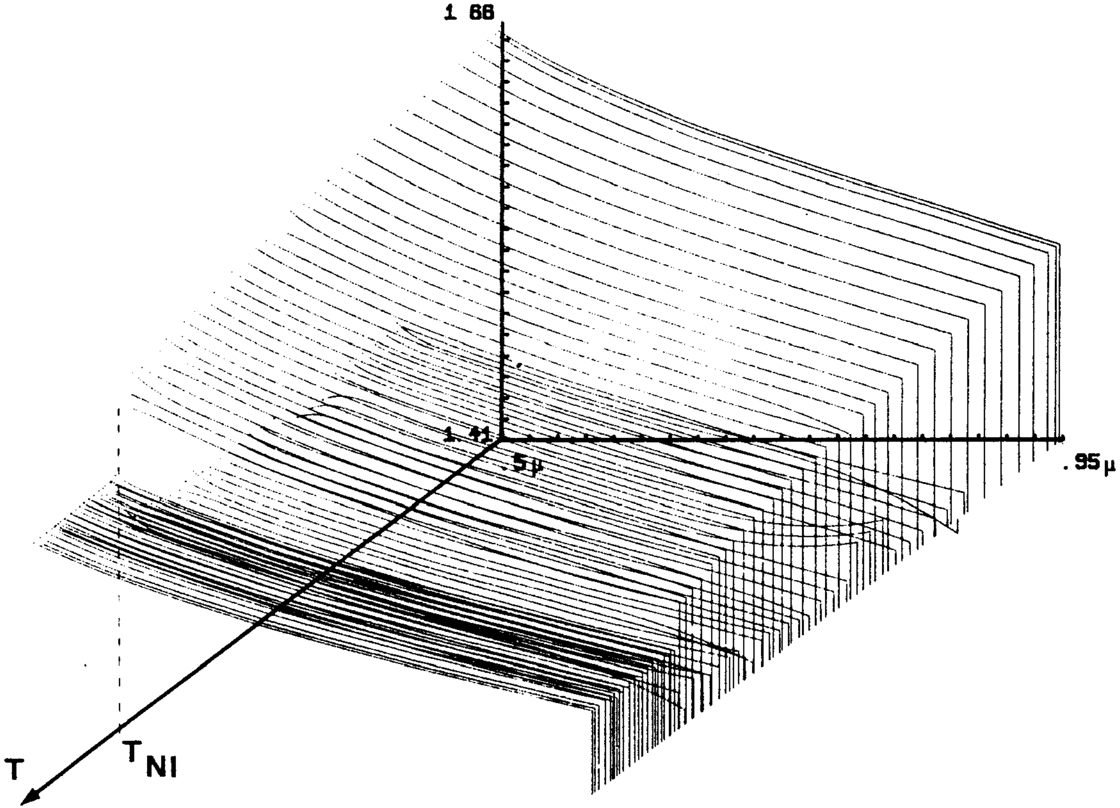

FIGURE 5 3d diagram n(λ,T) for the compound 1083 (BDH), extraordinary and ordinary indices are plotted. T_{NI} transition temperature, 49.2°.

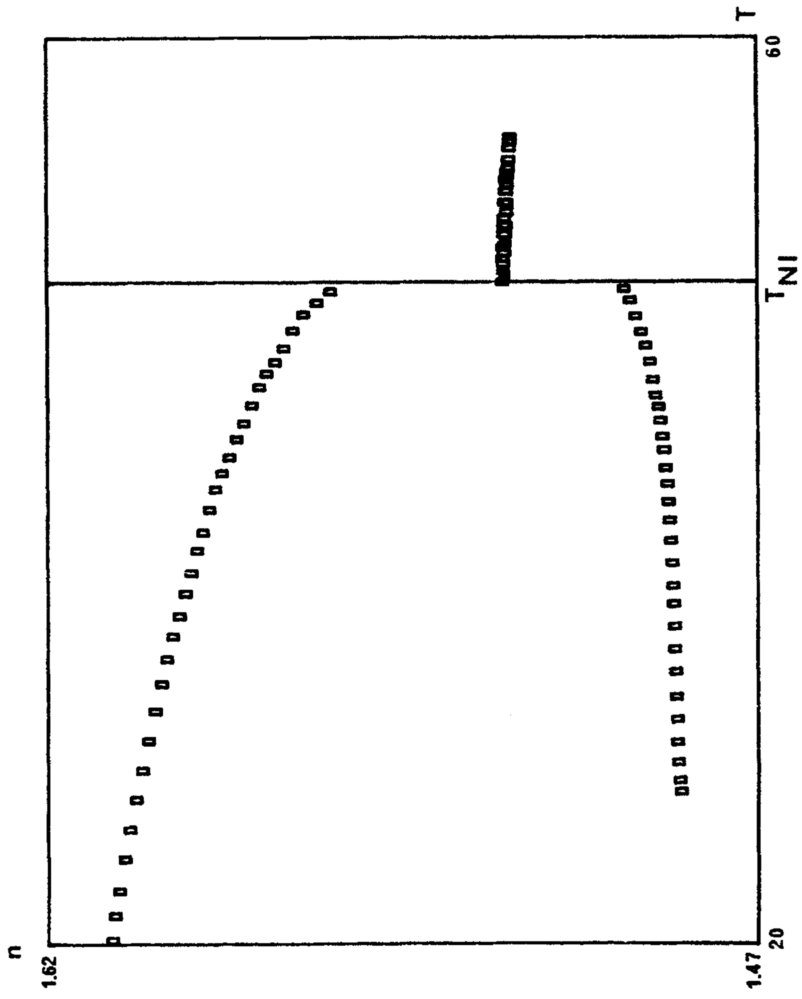

FIGURE 6 Ordinary and extraordinary indices versus temperature
λ = 0.6328 μm (1083 BDH)

due to the latter is slow compared to one second. Such a refractometer is an interesting new tool in three different points of view. In a technicological point of view since one obtain the whole set of data in one hour experiment with the help of only three initial values: the index, the associated wavelength and the value for the corresponding external parameter, temperature for instance. In an experimental point of view since one obtain absolute values for indices of any materials, and not only birefringence in the anisotropic material cases. And at last in a theoretical point of view in the sense that theories correlating refractive indices and molecular parameters can be tested or, in case of temperature dependence, phase transition regions can be explored quite finely.

REFERENCES

1. P. Chatelain and M. Germain, C.R.Acad.Sc.,t.259,p.127,(1964).
2. M. Brunet-Germain, C.R.Acad.Sc., B271, p.1075, (1970).
3. I. Haller, H.A. Huggins and M.J. Freiser, Mol.Crys.Liq. Crys., 16, p.53-59, (1972).
4. G. Labrunie and M. Bresse, C.R.Acad.Sc., B276, p.647, (1973).
5. G. Pelzl, R. Rettig and D. Demus, Z. phys. Chemie ,256, p.305-311, (1975).
6. E.G. Hanson and Y.R. Shen, Mol.Crys.Liq. Crys., 36, p.193, (1976).
7. W.H. de Jeu and P. Bordewijk, J. Chem. Phys., 68, p.109, (1978).
8. R.G. Horn, J. de Phys., 39, p.105, (1978).
9. A. Schmid, S. Papernov, Z.W. Li, K. Marshal, T.Gunderman, J.C.Lee, M. Guardalben, S. Jacob, This meeting.
10. M. Warenghem, C.P. Grover, Rev. Phys. Appl., 23, p.116, (1988).
11. H.F. Talbot, Philos. Mag., 1, p.364, (1837).
12. M.F. Vuks, Opt. Spektrosk., 20, p.644,(1966).
13. S.T.Wu, Phys. Rev., 33, p.1270, (1986).
14. M. Warenghem, Study of evanescent field.., 13th I.L.C.C., Vancouver, (1990).

15. For example, W.H. de Jeu, Physical properties of liquid crystalline materials, (Gordon and Breach, New York), (1980).