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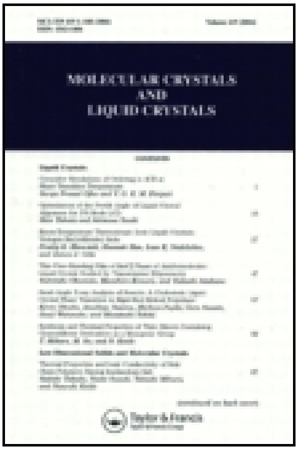

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Technical Aspects of Measurement of Elastic Constants and Diamagnetic Anisotropy of Nematic Liquid Crystals

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TECHNICAL ASPECTS OF MEASUREMENT OF ELASTIC CONSTANTS AND DIAMAGNETIC ANISOTROPY OF NEMATIC LIQUID CRYSTALS

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ABSTRACT We have measured the critical values of electric E_c and magnetic H_c fields in different types of Freedericksz transitions for 4-trans-n-hexyl-cyclohexyl- isothiocyanatobenzene (6CHBT). Capacitive and optical methods have been employed to detect these transitions. In the case of twist-type deformation we have proposed a new interference method for threshold fields determination. On the basis of these measurements diamagnetic anisotropy $\Delta\chi$ splay K_{11}, twist K_{22} and bend K_{33} elastic constants have been calculated for cells of various thickness, coated with different polyimides.

INTRODUCTION

Elastic constants must be known for description of phenomena occurring during interaction between ordered liquid crystal layer and electric and/or magnetic ieIds. At present works are under way throughout the world on increasing operational rate of liquid crystal displays. This involves first of all a search for mixtures with proper relation between electric and elastic properties. For this reason K_{ii} elastic constants measurements are a practical value. The classic method of elastic constants determination is based on investigations of Freedericksz transitions of various types. This term refers to deformations of nematic layer with homogeneous orientation that result from applying outer field (electric, magnetic or both). Elastic constants K_{ii} are calculated from the formula [1] (1)

$$K_{ii} = \frac{1}{\pi^2} F_i^{\alpha} \qquad (1)$$

where $F_i^m = \Delta\chi\mu_o(H_{ic}d)^2$ for deformation induced by magnetic field

$F_i^e = \Delta\varepsilon\varepsilon_o U_{ic}^2$ for deformation induced by electric field

d - is the sample thickness, $\Delta\varepsilon = \varepsilon_{//} - \varepsilon_{\perp}$ -is the dielectric anisotropy,

$\Delta\chi$ -is the magnetic susceptibility anisotropy

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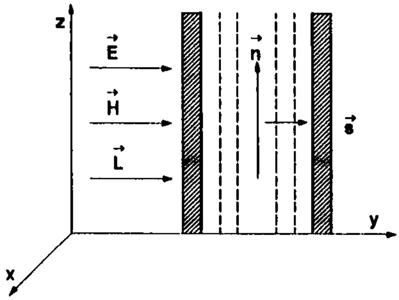

Figure 1. Geometrical layout used for threshold field determination of K_{11} : n - director, s - vector perpendicular to cell walls , L-vector indicating the direction of sample illumination. K_{11} constant is derived from data for Freedericksz transition homogeneous orientation ⇒ homeotropic orientation. Detection of Freedericksz transition is capacitive or optical.

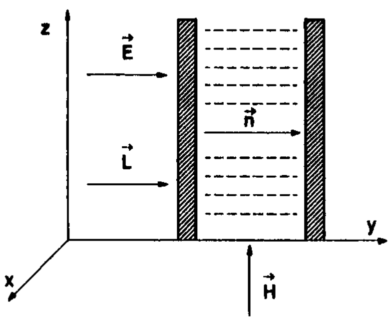

Figure 2. Geometrical layout for threshold field determination for K_{33} . K_{33} constant is derived form data for Freedericksz transition homeotropic orientation ⇒ homogeneous orientation. Detection of Freedericksz transition is optical or capacitive.

Measurement of threshold field intensity is the most straightforward method to determine the values of elastic constants K_{ii}. Freedericksz transitions can be detected with several methods. Determination of any anisotropic physical quantity that characterizes nematic liquid crystals as a function of $F^{\alpha}{}_{i}$

field allows for K_{ii} determination. Deformation is usually detected with optical or capacitive method (Fig.1,2,3).

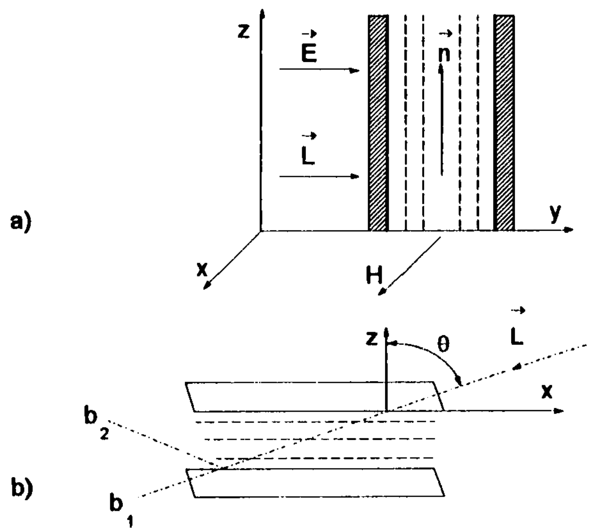

Figure 3. Geometrical layout for threshold field determination of K_{22}. K_{22} constant is derived from data for Freedericksz transition homogeneous orientation ⇒ twisted orientation. Detection of transition is optical: a) modification of P.Gerber and M.Schadt's method [1], b_1) Karat and Madhusudany's method [14] ,b_2) modification of Freedericksz and Tsvetkov's method [15]

Methods of threshold field detection have already been described and thoroughly analysed. Their advantages and disadvantages are well known [2-10] . In this paper we intend to present a consistent technique that we apply for fast (and sufficiently accurate, from the point of view of technical applications) determination of K_{ii} values, based on threshold methods. We would like to draw special attention to K_{22} elastic constant determination.

EXPERIMENT

Elastic constants K_{11} , K_{22} , K_{33} were determined for 6CHBT (4-trans-n-hexyl-cyclohexyl-isothiocyanatobenzene) with various methods employed.

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Freedericksz transitions were induced by electric or magnetic fields. Capacitive or optical method or both were used to detect these transitions. Block diagram of the system for critical Freedericksz fields H_{lc} and E_{lc} determination is shown in Fig. 4. Liquid crystal measurement cells were from 20 μm to 200 μm in thickness. Homeotropic orientation was obtained by applying lecithin.

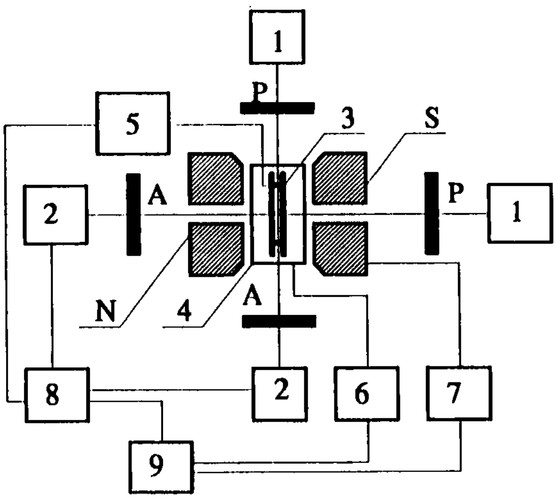

Figure 4. Block diagram of the system for critical Freedericksz fields H_{lc} and E_{lc} determination. 1 - He-Ne laser, 2 - photo detector, 3 - liquid crystal cell, 4 - thermostatic measuring chamber, 5 - RLC bridge, 6 - thermostabilizing system, 7 - electromagnet power supply control device with magnetic field intensity measurement, 8 - X-Y recorder, 9 - computer system for recording results , A - analyzer, P - polarizer.

Perpendicularity (orthogonality) between the optical axis and the cell walls was controlled by means of conoscopic observation. The conoscopic cross never shifted more than 0.02 mm from the microscope optical axis. This means that the angle between the line normal (perpendicular) to the cell wall and the director is lower than 0.005 (see photo. 1.). Homogeneous orientation was

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obtained by coating cell plate surfaces with various polyimides. Some cells were coated with ITO layer. Tilt bias angle (TBA) in measured cells was determined by interference method [11-13] and conoscopic observation (see photo 2 and 3). For the cells we used, this angle was below 0.012. Measurement time ranged from 10 to 100 minutes. During measurements the temperature was stabilised and changed from 20^{0} C to 26^{0} C. These changes of temperature are the result of methods employed for optical detection of Freedericksz transitions. Techniques employed to determine critical field intensities in our experiments are shown in Figs. 1 to 4. Standard technique was employed to determine elastic constants K_{11} and K_{33}[2, 6, 8, 9].

In order to determine K_{11} the values of C = f(U), C = f(H), T = f(U) and T = f(H) were measured. "C" and "T" are electric capacitance of liquid crystal cell and intensity of light passing through this cell respectively. Sinusoidal voltage was applied to cell electrodes with the value $U \in (0, 5V)$ and frequency f = 1.5 kHz induction B of magnetic field in which the cell was placed could be varied linearly within the range of 0 to 1 Tesla.

In order to determine K_{33} elastic constant the functions of C = f(H) and T = f(H) were measured. Optical detection of Freedericksz transitions in the measurements of K_{11} and K_{33} from the T = f(H) or T = f(E) functions involved determination of $\Delta\Phi$ = f(H) or $\Delta\Phi$ = f(U) functions. H_c and U_c values may be determined by means of analysis of the curves mentioned above. The $\Delta\Phi$ = f(U) and $\Delta\Phi$ = f(H) characteristics determine the change of phase difference between extraordinary and ordinary rays (which appears during transition of light through the liquid crystal sample) as a function of deformed magnetic field intensity H.

From the practical point of view the K_{22} elastic constant is the most important one (Fig.3.). Unfortunately, the capacitive method is of no use for twist type deformation, as this deformation does not result in any change of J. measurement cell capacitance. For this reason we must rely on optical methods. Several such methods for optical detection of Freedericksz J. transition for K_{22} elastic constant determination have been described[1, 10, 14]. Their concept is given in Fig.3.

Method 1

It is possible to determine threshold field by tracking b_1 beam intensity as a function of applied field intensity H. This method in a slightly different form was suggested by N.V.Madhusudana, N.Karat and S.Chandrasekhar in[14]. (see Fig.3).

Method 2.

If an experiment is performed with geometry as in Fig.3 we can use b_2 beam, i.e. the one reflected from one of the liquid crystal cell walls. By monitoring its intensity as a function of field intensity B it is possible to determine H_c for K_{22}. The phenomenon of total internal reflection was for the first time employed to determine magnetic thresholds by Freedericksz and W.Tsvetkov[15]. They used a lens and prism assembly.

Method 3

This is a conoscopic method, suggested by P.E.Cladis in 1972. All methods from 1 to 3 have several shortcomings. Methods 2 and 3 demand construction of special cell with properly polished sides (proper tilt of transverse cell edges). Method 3 is difficult (or even very difficult) from the technical point of view.

Method 4

If a twist type deformation is applied to a planar cell (see Fig.3), we may roughly approximate the light propagation as conforming to adiabatic propagation rule. Adiabatically guided light is the case for electromagnetic waves that satisfy the Mauguin condition, i.e.$\lambda \ll (n_e - n_o)P$, where P is the twisted texture spiral pitch. With the cell thick enough ($d \geq 10\ \mu m$) the Manguin condition is satisfied for all wavelengths from the visible range.

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P.R.Gerber and M.Schadt have shown in[1] that, if the approximation better than adiabatically guided light is employed, it is possible to monitor twist-type Freedericksz transition with light beam perpendicular to the cell surface.

For the layout as shown in Fig.3 the following is satisfied:

$$E_{y,o}(\frac{d}{2}) = iE_{z,o}\frac{n_e}{n_o}A\frac{4d}{\pi}\frac{W\cos\pi W}{1-4W^2} \quad (2a)$$

$$W = \frac{dP_o}{2\pi}(n_e - n_o) \quad (2b)$$

where:

$E_{y,o}$ and $E_{z,o}$ -are the vector amplitudes E of electromagnetic waves parallel to y and z axes respectively,

n_o and n_e -are the refractive index values for ordinary and extraordinary rays respectively,

$P_o = \omega / c$ (ω = angular frequency of electromagnetic wave),

A -is the constant,

d - is the liquid crystal cell thickness.

This means that large optical variations of transmission in the liquid crystal layer being a subject to the twist-type deformation occur in the vicinity of (2a) function maximum. This, in turn, occur for the values of W = 1, 2, 3..... Ultimately this results in linear rise of the intensity of light passing through the cell, as a function of ($H - H_c$). Linear rise of the transmission T is the case for the light beam which, having passed through the cell, has linear polarization along the y axis.

In order to satisfy the W = 1, 2, 3... condition, with W given by (2b), we may proceed in two ways:

1. change the ω value, or
2. change the $\Delta n = n_e - n_o$ value.

P.R.Gerber and M.Schadt have varied the wavelength of light beam illuminating the sample. As the double refraction $\Delta n = n_e - n_o$ is a function ofsample temperature, we may satisfy the W = 1, 2, 3... condition by varying this temperature. This means that for the proper temperature the rise of magnetic

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field intensity H (for $H > H_C$) will result in linear rise of the intensity of light passing through the cell.

In our experiment we proceeded as follows:

Liquid crystal cell with planar alignment was placed in thermostatic measuring chamber. Cell location was as shown in Fig. 3. Measurement began with H = 0. Assume that measurement began in room temperature T_0 . After switching the laser on we detected a certain value of radiation transmitted through the cell. Next, the sample temperature was raised very slowly (quasi statically). Transmission changed with the temperature. The temperature was raised until minimum sample transmission was achieved (theoretically this should be zero). Having attained this, the temperature was no longer raised. From this moment on, it was kept constant during relevant measurement. Assume that this values T_1 = const. Next, with fixed temperature T_1 , magnetic field was applied, increasing linearly. Until threshold value H_{2c} was attained, transmission did not change. From that moment, there was a marked increase of cell transmision. This phenomenon is of threshold nature (see Fig. 5). The only disadvantage of this method of threshold field determination is the fact that we have no influence on the measurement temperature. This temperature is unequivocally determined by liquid crystal birefringence, cell thickness and wavelength of applied light beam. Having determined critical field H_{2c} (and thus K_{22} elastic constant) values for temperatures e. g. T_1, T_2,...., T_n, we can easily, by means of interpolation, determine them for temperatures T_k, T_l, ...T_m, which one of interest for us.

It should be noted that Gerber and Schadt have "sensitised" Their measuring system by changing light wavelength, with temperature kept constant. On the other hand, we have "tuned up" to maximum sensitively by changing temperature with constant light wavelength. During the latter phase of the experiment (determination of H_{2c} in given temperature) the temperature was fixed and did not change.

In other words , both variants of described method of Freedericksz transition detection (in this geometrical layout) involve the "start" with minimum light transmission through liquid crystal sample.

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It should be noted that, in order to determine the "starting point" it is not necessary to know either wavelength of applied light beam or liquid crystal birefringence.

The fundamental advantage of this method is the fact that for K_{22} elastic constant determination we may use the same cell that is used for K_{11} elastic constant determination. Only geometrical layout of the experiment is different, but easy from the technical point of view.

RESULTS AND CONCLUSION

Fig. shows the intensity of light passing through the cell as a function of magnetic field intensity. We may discuss the possibility of producing such a plot with a step threshold; the answer, however, is simple. The step threshold is due to appear when the phase difference between ordinary and extraordinary rays is approximately equal to an odd multiple of half wavelength value.

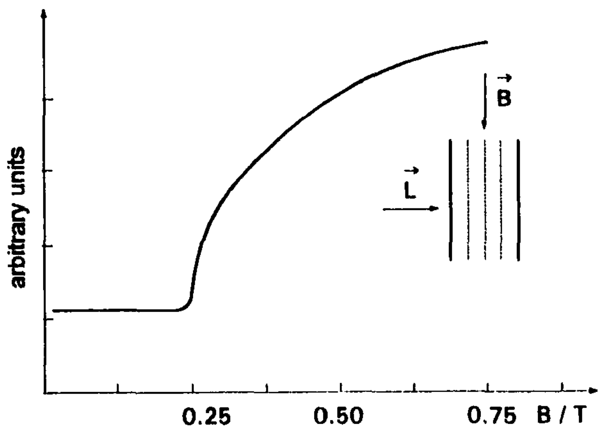

Figure 5 Transmitted light intensity plotted against magnetic field intensity; layout employed for twist-type deformation threshold field determination in cells with parallel alignment. This method, with laser beam perpendicular to cell walls, allows for precise threshold determination. Polariser and analyser crossed, with parallel or perpendicular alignment to nematic director at the surfaces.

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Threshold fields that characterise various types of Freedericksz transition given by (1) have been defined with two assumptions:

1 Perfect ordering of molecules on cell boundary surfaces (TBA = 0) i.e.$\Theta(-d/2) = \Theta(+d/2) = 0$

2 Infinitely great energy of binding between molecules and boundary surfaces (i.e. strong anchoring limit).

In practice these conditions are satisfied only approximately. The cells that we have used for K_{22} and K_{11} constants determination had the TBA value of less than 0.012 and λ = 0.0015. λ means here the reduced surface-coupling parameter and is given by $\lambda = \pi K / W_S d$, where K is the elastic constant, d is the cell thickness and W_S is the anchoring energy[11]. Anchoring energy has been determined by means of high field method [16] and has had the value of about 1.6×10^{-5} J / m^2

In order to determine elastic constants by means of ordered liquid crystal sample deformation with magnetic field, it is necessary to know diamagnetic susceptibility anisotropy $\Delta\chi$. Previously[17] we determined $\Delta\chi = 44\times10^{-8}$.

Accuracy of elastic constants determination by threshold methods depends primarily on the accuracy oh threshold fields determination. This accuracy, according to our estimation based on repeatability of results obtained for various cells, is not better than 15 per cent.

Our results, averaged for 30 measured cells, are: $K_{11} = (7.5\pm1.2)\times10^{-12}$ N, $K_{22} = (3.5\pm0.6)\times10^{-12}$ N and $K_{33} = (9.5\pm1.2)\times10^{-12}$ N , at 298 K. These results are in a good agreement with those given in [17] for T = 298 K. 6CHBT (T_c = 316 K) from our laboratory has been tested by F.Hoffman-La Roche[13, 18]. They have obtained the following results: from[13] $K_{11} = 8.57\times10^{-12}$ N, $K_{22} = 3.70\times10^{-12}$ N and $K_{33} = 9.51\times10^{-12}$ N for T = 295 K.; from[18] K_{33}/K_{11}=1.10 for 306 K.

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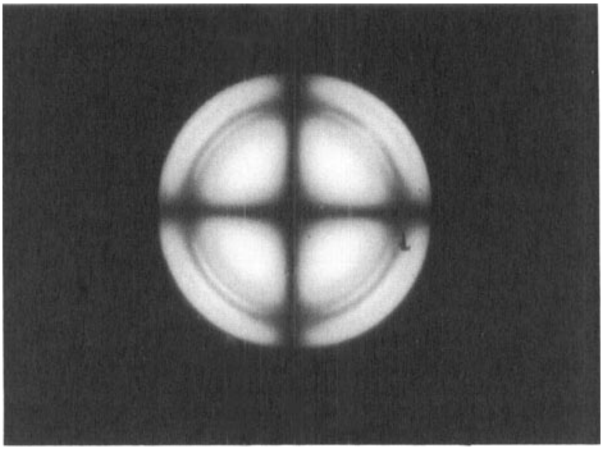

Photo 1. Conoscopic image of homeotropic texture in nematic phase of 6CHBT , ∠ (s , n) <0.005

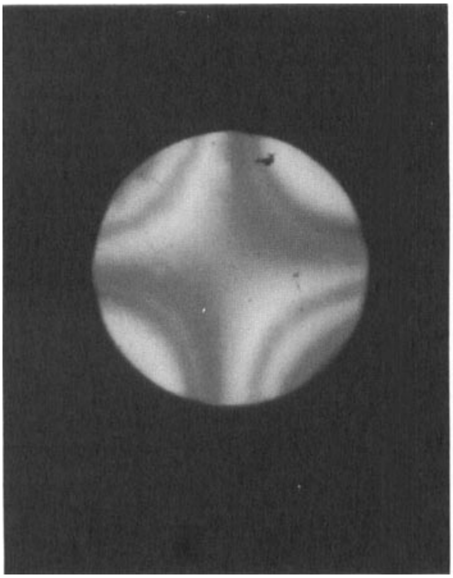

Photo 2.Conoscopic image of planar texture of 6CHBT ∠ (s , n) <1.567

See Color Plate I.

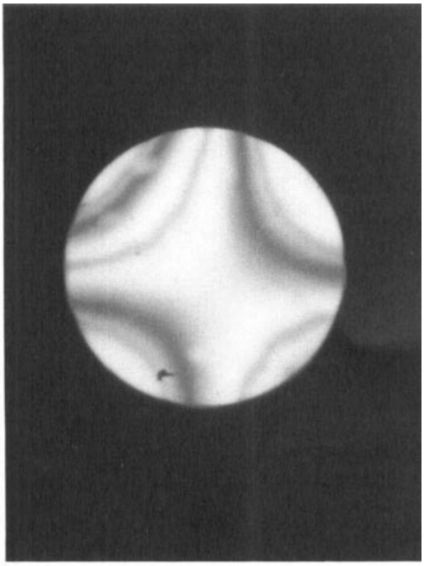

Photo 3 Conoscopic image of planar texture of 6CHBT ∠ (s , n) ≈ 1.543

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