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I. Abdulhalim, Ludovic Benguigui, R. Weil. Light transmission measurements in the liquid crystal SmC* phase of DOBAMBC at normal incidence. *Journal de Physique*, 1985, 46 (8), pp.1429-1433. 10.1051/jphys:019850046080142900 . jpa-00210087

HAL Id: jpa-00210087

<https://hal.science/jpa-00210087>

Submitted on 1 Jan 1985

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Classification
Physics Abstracts
61.30E — 78.30C

Light transmission measurements in the liquid crystal SmC* phase of DOBAMBC at normal incidence

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(Reçu le 21 décembre 1984, révisé le 19 mars 1985, accepté le 26 mars 1985)

Résumé. — Nous présentons des mesures de transmission de lumière dans des échantillons homéotropes smectiques C* de DOBAMBC sous incidence normale pour différentes épaisseurs dans tout le domaine spectral où la réflexion sélective se produit. Supposant que la baisse de transmission résulte d'une réflexion de Bragg, nous obtenons la dépendance en température du pas de l'hélice. Le calcul du spectre de réflexion/transmission utilisant la matrice caractéristique 4×4 montre un accord satisfaisant entre quantités mesurées et calculées.

Abstract. — We present measurements of the light transmission of homeotropic smectic C* samples (DOBAMBC) at normal incidence as a function of temperature for different thicknesses in the whole spectral region where selective reflection occurs. Assuming that the transmission dip is a result of Bragg reflection, we obtain the temperature dependence of the pitch. The calculations of the reflection and transmission spectra using the 4×4 characteristic matrix showed good agreement between measured and calculated quantities.

1. Introduction.

Some results of transmission and reflection measurements of single domain homeotropically aligned sample of the ferroelectric mesophase SmC* have been published by several authors [1-4].

The object of some of these studies [1, 2] was to determine the temperature dependence of the helicoidal pitch which has particular importance in the determination of the ferroelectric properties and their different possible applications. The measurements of Takezoe [1] *et al.* of the transmission at normal incidence on DOBAMBC cover only a small part (2.2μ – 2.8μ) of the interesting spectral region (2.1μ – 4.3μ). More precise results of the pitch measurements were reported recently by Rozanski [2], using four different optical techniques. One of them was by measuring the temperature dependence of the selective reflection at oblique incidence. However, his published data contains only one spectrum as a function of wavelength.

The object of the work of Hori [3, 4] was to reveal the characteristic features of selective reflection of SmC*. His measurements were done on a different material (CE3) which has a pitch comparable to wavelengths in the visible region. The agreement with computed spectra of Berreman [5] was only qualitative.

This paper deals with transmission measurements on DOBAMBC as a function of temperature and wavelength for different thicknesses in the whole spectral and thermal regions which exhibit selective reflection. Quantitative comparison with the calculations based on the 4×4 characteristic matrix method [6] shows very good agreement.

2. Experiment.

We used the well known material 2-methylbutyl p-(p-n-decyl-oxybenzylideneamino) cinnamate (DOBAMBC) which has a pitch comparable to wavelengths in the near infrared region. It was sandwiched between two quartz plates (4×12 mm) and aluminium foils were used as spacers to determine the sample thickness. The homeotropic alignment was achieved by coating the quartz plates with HTAB aqueous solution using the technique reported by Proust [7] *et al.* The molarity of the solution was 5×10^{-5} mole/l and the rate of withdrawal of the slides out of the solution was 0.1 cm/h. The area of the sample was circular with radius of 2 mm. The sample was heated in a small oven and a copper constantan thermocouple was used to measure the temperature within an accuracy of ± 0.25 °C.

The alignment of the sample was checked by observing birefringence colours appearing through a micro-

scope with magnification up to 500, between two polarizers. In passing through SmA to SmC* the sample colour changes from black to blue between crossed polarizers. This colour changes with decreasing temperature to violet and then to yellow. We also observed that, when the transmitted light is blue, a change in the relative angle of the analyser to the polarizer also causes the light to change to violet and then yellow. For the $144\ \mu$ thick sample we observed also green, but it was difficult to keep this sample aligned.

In our sample, transition temperatures were $108\ ^\circ\text{C}$ from the isotropic to smectic A phase and $92\ ^\circ\text{C}$ from SmA to smectic C*. The spectrometers used were the Cary 14 in the spectral range $0.65\ \mu$ - $2.5\ \mu$ and Perkin Elmer 580B in the spectral range $2.5\ \mu$ - $40\ \mu$. The sample was mounted inside the small oven in the object beam perpendicular to the beam direction and an empty cell was placed in the reference beam path. The spectra were measured at the isotropic phase passing through SmA then at the SmC* phase with cooling rate of $1\ ^\circ\text{C}/\text{min}$. as a function of temperature at different wavelengths. The net transmission at SmC* is obtained relative to the isotropic phase. In doing this one cancels out the effect of the molecular absorption bands of the material, a problem which is difficult to overcome if one measures the transmission as a function of wavelength.

3. Results and discussion.

Some of the measured transmission spectra are given in figure 1. The pitch dependence on the temperature is obtained using the Bragg condition :

$$\lambda_{\min} = n_{av} \cdot P \quad (1)$$

where n_{av} is the average refractive index (see Appendix) and can be calculated from the knowledge of the tilt

angle θ which depends on the temperature according to the relationship.

$$\theta = \theta_0(T_c - T)^\beta \quad (2)$$

where $\theta_0 \simeq 9.5^\circ$ and $\beta \simeq 0.45$ according to the measurements of the Orsay group [8]. The pitch dependence on the temperature is shown in figure 2.

The agreement with previous results is very good [1, 2]. In the narrow thermal region close to the transition point it is difficult to measure the pitch using this method, since the dip minimum is very small. For the sample with thickness $L = 11.0\ \mu$ the pitch seems to be higher in the temperature region $4\ ^\circ\text{C} < T_c - T < 7\ ^\circ\text{C}$. This could be due to the surface effect which is greater than in thicker samples. Our measurements fit very well the relation :

$$P(T_c - T) = \frac{C}{(T_c - T)^{1/3}} \quad (3)$$

where C is found to be approximately $3.6\ [\mu] [^\circ\text{C}]^{1/3}$. The pitch does not diverge at T_c since the relation holds up till $1.5\ ^\circ\text{C}$ close to the transition point. According to previous results [1, 2], the pitch shows a sharp increase near $T_c - T = 1.5\ ^\circ\text{C}$, then it decreases toward T_c .

In some of the spectra in figure 1, one observes the existence of more than one minimum in the transmission curves. The explanation of this is given according to figure 3, which is the dip wavelength dependence on $(T_c - T)$ as calculated using relationships (1), (2) and (3). It is clear from this figure that there could exist one, two or three minima in the transmission spectra as a function of temperature at constant wavelength. However, in order to observe two or three distinct and clear dips one has to choose an appropriate wavelength, the correct rate of cooling and the thermal fluctuations must be smaller than the temperature difference between the dips, such that the temporal

Fig. 1. — Measured transmission spectra as a function of temperature at different wavelengths for two thicknesses $L = 44.0\ \mu$ (lower) and $L = 102.0\ \mu$ (upper).

Fig. 2. — Pitch (in microns) as a function of temperature for the four thicknesses as indicated. Some of the results of Takezoe *et al.* [1] and Rozanski [2] obtained using the selective reflection method are shown denoted by * and x, respectively.

Fig. 3. — Dependence on temperature of the dip wavelength, as computed using relations (1), (2), (3) and n_{av} .

interval used to cool the sample from one dip temperature to the next is greater than the response time of the spectrometer. The choice of the value for β in relation (2) does not affect strongly the shape of the curve in figure 3, as checked by us for $\beta = 0.4, 0.35, 0.3$ and 0.25 . The existence of more than one minimum in the curves of figure 1 seems not to be due to inhomogeneities in the sample, since it appears in the spectra for all the samples in the same place. The possibility of attributing the phenomenon to the temperature dependence of the absorption bands is also excluded, since this dependence is very small as we checked. Furthermore, in the neighbourhood of $\lambda = 2.3 \mu$ there exist no absorption bands and the phenomenon still exists.

We made calculations of the reflection and transmission of light using our method [6] based on the 4×4 characteristic matrix. Since the incident light is unpolarized in our experiment, we calculate the average quantity $R = (R_{pp} + R_{ps} + R_{ss} + R_{sp})/2$. Since at normal incidence the incidence plane is not defined, the S and P indices represent the polarization along y and x axis respectively, when the propagation is along z axis. Then, R_{ps} (or R_{sp}) means the reflected spectra as measured by an analyser rotated along the y axis (or x axis) when the incident light is polarized parallel to the x axis (or y axis). And R_{pp} (or R_{ss}) is the reflected spectra when the analyser and polarizer are both parallel to the x axis (or to the y axis). The dielectric constants [1] of DOBAMBC are $\epsilon_1 = \epsilon_2 = 2.18$, $\epsilon_3 = 2.75$ and for the quartz plates $\epsilon_0 = 2.40$.

Calculated reflection peak heights for the thicknesses 11.0μ , 22.0μ , 44.0μ and 102.0μ are given in figure 4

Fig. 4. — Reflection peak height as a function of temperature difference at the minimum of the measured transmission dip for four samples as indicated, compared to the calculated curves (solid lines).

together with the experimental results (assuming $R = 1 - T$). The agreement is good confirming the validity of the model. The small disagreement could be a result of the neglect of absorption, dispersion and the temperature dependence of the principal dielectric constants. As T approaches T_c , the reflection is very small for the thin samples, and our measurements hold only until some temperature before T_c .

A saturation behaviour is observed as the departure from the transition point increases. The increase of the reflection peak height with $(T_c - T)$ is attributed to the decrease of the pitch, since it causes the number of periods $N = L/P$ to increase, and it saturates, because the pitch becomes nearly constant far from T_c . The saturation is achieved faster for thicker samples, because then N increases faster. The fact that the reflection peak height saturates at only 50 % for thick enough samples indicates that only one component of the incident light, which has the same helicity as the media, is reflected [9, 10]. However, the theoretical curves in figure 4 saturate in thick samples more fastly than in thin samples according to the above explanation, the experimental data shows saturation at $T_c - T \simeq 10^\circ\text{C}$ independently of the sample thickness. This is related to a feature seen in figures 1, 4, 5, which is the decrease of the transmission dip depth at wavelength around $\lambda = 2.4 \mu$ or at temperature $T_c - T = 11^\circ\text{C}$. We are not sure if this originates from experimental conditions or it is a property of the medium. If so, then some correction to the theory must be made, since it does not appear in the theoretical curves given in figure 4.

Another noticeable feature seen in all spectra in figure 1 is that the high temperature end of the spectra do not reach the same value as the low temperature end. This we refer to two possible reasons. One is that the sample is less aligned after passing the dip mini-

Fig. 5. — Transmission spectra as a function of wavelength at different temperatures for two thicknesses $L = 22.0 \mu$ (lower) and $L = 11.0 \mu$ (upper).

num, because of the relatively high cooling rate which could induce misalignment domains and thermal fluctuations. Second is the existence of absorption which according to the Borrmann effect [11] causes an increase of the transmitted intensity in the shorter wavelength side of the dip (or the lower temperature side in our spectra).

The difference between the two sides of the dip becomes larger as the temperature gets further from T_c . Hence, the sample should exhibit more misalignment or higher absorption, which is consistent with the possible explanation just mentioned.

The behaviour of the spectral width as a function of temperature (Fig. 6) is a result of the temperature dependence of the number of periods N , since the spectral width is narrower as N increases. The agreement with the theoretical curves is good, but it is not perfect and the measured values are usually in the higher side of the theoretical curves, probably because of imperfections and misalignments in the samples.

The thermal width decreases with the wavelength and the sample thickness (Fig. 1), a result which is also seen in the calculated spectra. In contrast to the simple expression for the spectral width as could be deduced from De Vries [9] or Chandrasekhar [10] *et al.* theories, the expression of the thermal width is more complicated, because the pitch and birefringence are strong functions of temperature, so that we cannot give a simple physical interpretation to that behaviour according to these theories.

In conclusion : Light transmission measurements on samples of different thicknesses of the SmC* liquid crystalline mesophase (DOBAMBC) were performed. In assuming that the dip minimum is a result of Bragg reflection, we obtained the temperature dependence of

Fig. 6. — Measured spectral width as a function of temperature difference for two thicknesses $L = 11.0 \mu$ and $L = 22.0 \mu$ compared to the calculated curves (solid lines).

the helicoidal pitch. The agreement with previous results based on the same method is very good. The physical interpretation of the behaviour of the reflection peak height, depth and width is given in terms of the behaviour of pitch, number of periods inside the sample, and refractive index dependence on the temperature. In spite of small quantitative discrepancies arising from the inaccuracy of the parameters used in the calculations, neglect of absorption and dispersion, we found good agreement between calculated and measured results, confirming the validity of the theoretical model.

Acknowledgments.

We would like to thank Dr. Dan Igner for his advice concerning sample alignment. We wish to thank also Prof. M. Foleman for his permission to use the spectrometers, Prof. R. Blinc for supplying the DOBAMBC sample and Mr. P. Ron for his technical help.

Appendix.

CALCULATION OF AVERAGE REFRACTIVE INDEX AS A FUNCTION OF TILT ANGLE. — The dielectric tensor ellipsoid (Fig. 7) in the local frame of reference $\zeta\eta\chi$ have the equation

$$\frac{\zeta^2}{\varepsilon_1} + \frac{\eta^2}{\varepsilon_2} + \frac{\chi^2}{\varepsilon_3} = 1. \quad (1)$$

Since $\psi = 0$, then one goes from this frame to the xyz frame by two rotations, resulting in the relationship :

$$\begin{pmatrix} \zeta \\ \eta \\ \chi \end{pmatrix} = \begin{pmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \theta \cos \phi & \cos \theta \cos \phi & \sin \theta \\ \sin \theta \sin \phi & -\sin \theta \cos \phi & \cos \theta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (2)$$

Fig. 7. — Schematic showing principal axis of the local dielectric tensor ellipsoid in some SmC* molecular layer.

where

$$\phi = \frac{2\pi}{P} \cdot z.$$

Using this relation in equation (1), one obtains the dielectric ellipsoid equation in the xyz frame. Assuming a plane polarized wave exists in some molecular layer v where its polarization vector makes an angle α_v with the x axis, then a vector representing this polarization direction will be given by the equation $y = \tan \alpha_v \cdot x$.

The refractive index which such light feels in the layer is given by the intersection of the polarization vector with the dielectric ellipsoid [12]. Suppose that this intersection is given by the coordinates (x_v, y_v) , then the refractive index is given by $n_v = x_v / \cos \alpha_v$.

and after some algebra one obtains :

$$n_v = \frac{\tilde{n}_0}{\sqrt{1 - K^2 \sin^2 \gamma_v}},$$

where

$$\tilde{n}_0 = \sqrt{\epsilon_1}; \quad \tilde{n}_e = \left(\frac{\epsilon_2 \epsilon_3}{\epsilon_2 \sin^2 \theta + \epsilon_3 \cos^2 \theta} \right)^{1/2}$$

$$K^2 = \frac{\tilde{n}_e^2 - \tilde{n}_0^2}{\tilde{n}_e^2} \quad \text{and} \quad \gamma_v = \alpha_v - \phi_v.$$

The average refractive index may be taken as

$$n_{av} = \sqrt{\frac{\tilde{n}_0^2 + \tilde{n}_e^2}{2}}.$$

or it could be obtained using the averaging :

$$n_{av} = \frac{1}{\pi} \int_0^\pi n_v d\gamma_v$$

$$n_{av} = \tilde{n}_0 \left\{ 1 + \left(\frac{1}{2} \right)^2 K^2 + \left(\frac{1.3}{2.4} \right)^2 K^4 + \left(\frac{1.3.5}{2.4.6} \right)^2 \cdot K^6 + \dots \right\}$$

since $0 < K < 1$, then up to the 2nd order one gets

$$n_{av} = \tilde{n}_0 \left\{ 1 + \frac{1}{4} \cdot \frac{\tilde{n}_e^2 - \tilde{n}_0^2}{\tilde{n}_e^2} \right\}.$$

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