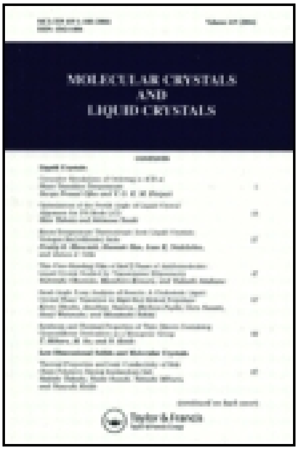

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DIELECTRIC METHOD FOR THE DETERMINATION OF TWIST ELASTIC CONSTANTS IN TILTED SMECTIC LIQUID CRYSTALS

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Abstract A simple and experimentally convenient method for determination of the twist elastic constants of the c-director in tilted smectic phases is proposed. The method consists in measurement of changes in electrical permittivity at high frequencies (about 1 MHz) caused by a DC electric field applied in the direction parallel to the smectic layers. A sensitive method for detection of changes in electric permittivity has been developed. The computer controlled apparatus performing the whole experiment is described. The results of measurement of an effective twist elastic constant in a ferroelectric liquid crystal are presented.

INTRODUCTION

Experimental data on elastic properties of smectic liquid crystals are rather scarce. The main reason for this is the fact, that the elastic properties of smectics are much more complex than that of nematic liquid crystals. In case of nematics, the elastic free energy density F depends on three elastic constants K_1, K_2, K_3 describing the splay, twist and bend deformation of the nematic director **n**.[1] They can be determined e.g. from different kinds of Freederics transition.

The corresponding description of elastic properties of smectic liquid crystals is much more complicated for two reasons. First, there exists more or less pronounced positional order in all smectic phases. In the simplest case of the smectic A phase (Sm A) it is a unidimensional positional order of molecular centers of gravity which demonstrates itself as a layered structure. Second, appearance of the layer structure is often accomplished by lowering of the symmetry of the considered liquid-crystalline phase. For both mentioned reasons the description of elastic properties of a smectic liquid crystal is quite complex.

ELASTIC ENERGY OF THE SMECTIC C PHASE

There are several models describing elastic properties of the smectic C (Sm C) phase.[2-5] We used here the description introduced first by the Orsay Group.[1,2] In this description the elastic free energy density is split into four parts:

$$F = F_s + F_c + F_{cs} + F_{ch} \tag{1}$$

F_s describes the deformation of smectic layers:

$$F_s = \frac{1}{2} A_{11} \Omega_{xx}^2 + \frac{1}{2} A_{12} \Omega_{yx}^2 + \frac{1}{2} A_{21} \Omega_{xy}^2 + \frac{1}{2} \overline{B} \cdot \gamma \tag{2}$$

where $\Omega_{ij} = \partial\Omega_i/\partial j$ (i,j=x,y,z) and Ω is the rotation vector. F_c is attributed to the energy of deformation of the **c** director, (i.e. the unit vector in the projection direction of the mean long molecular axis position onto the smectic layers plane):

$$F_c = \frac{1}{2} B_1 \Omega_{zx}^2 + \frac{1}{2} B_2 \Omega_{zy}^2 + \frac{1}{2} B_3 \Omega_{zz}^2 + B_{13} \Omega_{zx} \Omega_{zz} \tag{3}$$

F_{cs} describes the coupling between the c-director deformation and the layers deformation

$$F_{cs} = C_1 \Omega_{xx} \Omega_{zx} + C_2 \Omega_{xy} \Omega_{zy} \tag{4}$$

The last term, F_{ch}, is non-vanishing in chiral smectics C (Sm C^*) only:

$$F_{ch} = D_1 \Omega_{zx} + D_2 \Omega_{xx} + D \Omega_{zz} \tag{5}$$

All together, there appear 13 elastic coefficients in the Orsay[2] description.

DETERMINATION OF ELASTIC CONSTANTS

Generally, in order to determine an elastic constant, one has to introduce a tension (a torque stress in case of liquid crystals) and measure the deformation (curvature strain) caused by this stress. Both tasks (introducing the stress and detection of strain) are quite difficult to solve. First of all, the sample must be suitably oriented. The meaning of this statement is more complex in case of smectic C phase than in case of nematics - the orientation must be in a way two-dimensional: besides the orientation of the smectic layers, also the tilt direction should be ordered. Secondly, the introducing of deformation is more difficult as compared with nematics. Smectic liquid crystals are more "hard" and in most cases one has to apply fields of very high strength.[6] This is not always possible. Thirdly, the deformation is more difficult to measure and the interpretation of results of measurements is somehow complicated because of low symmetry of smectic phases.

The problem of introducing deformation can be relatively easy solved in case of ferroelectric liquid crystals. These crystals can be easily deformed using electric field. Due to the presence of spontaneous polarization the deformation is detectable at electric fields strengths as small as 10^3 V/m. The coupling between the spontaneous polarization and the external electric field causes the torque

$$\vec{M}=\vec{P}_s\times\vec{E} \tag{6}$$

acting on unit volume of each smectic layer. This torque affects the distribution of the smectic **c** director. The deformation introduced in this way can be used for determination of the helix controlling elastic constants, i.e. the constant B_3 from eq.(3) and the constant D from eq.(5). The ratio of these constants determines the helical pitch p:

$$p=-2\pi\cdot\frac{B_3}{D}\ . \tag{7}$$

B_3 describes the tendency of the smectic C structure to align **c** directors in adjacent smectic layers in the same direction, whereas the D constant describes the tendency to built up the helical structure. In the present paper only these two elastic constants will be considered.

DETECTION OF DEFORMATION

The detection of deformation must be performed in two steps:

a) measurement of a macroscopic physical quantity. Usually, measurements of optical or dielectric properties are performed.

b) a model, connecting the macroscopic properties of a liquid crystal sample with changes in molecular structure on the microscopic level must be developed.

In this work we used a dielectric method for detection of deformation. The tensor of the electric permittivity of the smectic C phase has the following components[7]:

$$\begin{gathered}
\overline{\varepsilon_{11}}=\varepsilon'\overline{\cos^2\varphi}+\varepsilon_2\overline{\sin^2\varphi}\\
\overline{\varepsilon_{12}}=\overline{\varepsilon_{21}}=0\\
\overline{\varepsilon_{13}}=\overline{\varepsilon_{31}}=\frac{1}{2}(\varepsilon_3-\varepsilon_1)\sin 2\theta\ \overline{\cos\varphi}\\
\overline{\varepsilon_{22}}=\varepsilon'\overline{\sin^2\varphi}+\varepsilon_2\overline{\cos^2\varphi}\\
\overline{\varepsilon_{33}}=\varepsilon_1+\varepsilon_3-\varepsilon'
\end{gathered} \tag{8}$$

where $\epsilon'=\epsilon_1\cos^2\Theta+\epsilon_3\sin^2\Theta$. The main values of the local dielectric tensor (in the coordinate system connected with the average molecule orientation) are denoted ϵ_1, ϵ_2, ϵ_3. The azimuthal angle between the c-director and an arbitrary chosen x-axis is denoted φ, and Θ stands for the average tilt angle of molecules with respect to the smectic layers normal.

Equations (8) are valid for all periodic distributions of the smectic **c** director. The mean values of the trigonometric functions appearing in (8) can be calculated, if the distribution function of the **c** director $\varphi(z)$ is known. For instance in case of an undisturbed helix $\varphi(z)=q\cdot z$ ($q=2\pi/p$ is the wavevector of the helix) whereas for a helix-free structure (i.e. a usual, non-helical smectic C) $\varphi(z)=\pi/2$. After applying an electric field parallel to the smectic layers, the ideal helical distribution is distorted. This leads to changes in the electric permittivity measured in the same direction. We proposed to use these changes as a measure of the helix deformation, which in turn should enable us to determine the B_3 and D elastic constants. The relative change in the electric permittivity is a very convenient quantity, which can be used for this purpose. This quantity is defined as:

$$\frac{\delta\varepsilon}{\Delta\varepsilon}=\frac{\overline{\varepsilon_{22}}-\varepsilon_{22}^{H}}{\varepsilon_{22}^{C}-\varepsilon_{22}^{H}}\ . \tag{9}$$

$\epsilon_{22}{}^{H}$ denotes here the component of electric permittivity perpendicular to the unperturbed helical axis and $\epsilon_{22}{}^{C}$ is the same component in the helix - free sample in the direction of spontaneous polarization. The $\delta\epsilon/\Delta\epsilon$ ratio can be obtained from eq. (8):

$$\frac{\delta\varepsilon}{\Delta\varepsilon}=2\overline{\cos^2\varphi}-1\ . \tag{10}$$

Thus, the only problem which remains is the calculation of the average value of $\cos^2\varphi$. The distribution of the **c**-director throughout the sample can be determined by solving the equation of motion[1]

$$-B_3\frac{\partial^2\varphi}{\partial z^2}+\gamma\frac{\partial\varphi}{\partial t}=|\vec{P}_s\times\vec{E}|\ . \tag{11}$$

The solution of eq.(11) in case of small deformation reads[8]:

$$\varphi=qz+\Phi_o\sin qz\cdot\cos(\omega t+\beta) \tag{12}$$

where β is the phase shift between field and deformation and

$$\Phi_o=\frac{P_sE_o}{B_3q^2\sqrt{1+\omega^2\tau^2}}\ . \tag{13}$$

Hence we are interested in the elastic constants only, we may limit ourselves to consider the stationary condition. In this case, i.e. in the low frequency limit the equations (12) and (13) become simpler. It can be shown, that in case of small deformations the average value of $\cos^2\varphi$ reads:

$$\overline{\cos^2\varphi} = \frac{1}{2} + \frac{1}{4}\phi_o^2 \, . \tag{14}$$

Finally,

$$\frac{\delta\varepsilon}{\Delta\varepsilon} = \frac{P_s^2 E^2}{2B_3^2 q^4} \tag{15}$$

From this equation the product B_3q^2 can be determined. This product has the meaning of an effective elastic constant B_{eff}. To measure it, only two parameters have to be known: the spontaneous polarization P_s and the relative change of dielectric permittivity $\delta\epsilon/\Delta\epsilon$. For small $\delta\epsilon$, this change should be a square function of the external field strength E. Since many standard methods for determining P_s have been developed we describe here only the method for determination of $\delta\epsilon/\Delta\epsilon$ ratio.

EXPERIMENTAL

It follows from eq.(15) that for determination of B_{eff} only two parameters have to be known: the spontaneous polarization P_s and the relative change in the electric permittivity $\delta\epsilon/\Delta\epsilon$.For determination of the spontaneous polarization we used the bridge method.[9] The changes in electric permittivity ϵ were determined with a sensitive resonance method (Fig.1).The sample

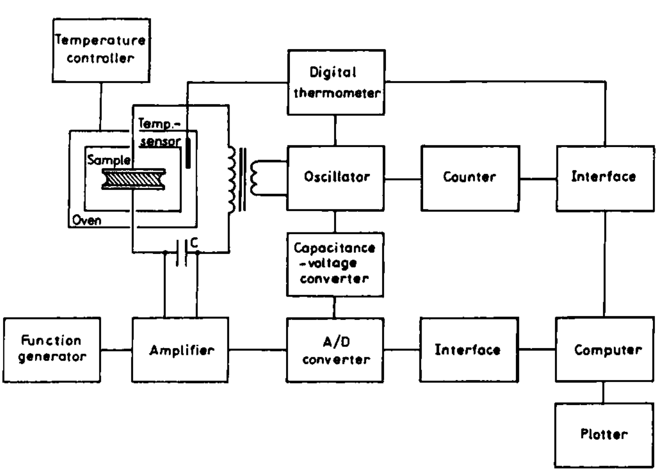

FIGURE 1 Experimental setup.

was a component of a resonant circuit. Its capacitance determined the oscillation frequency of an oscillator. In this way the electric permittivity changes were transformed into the changes of frequency. As the frequency changes δf are (for small δf) proportional to the permittivity changes δε, δf can be used as a measure of δε. Simultaneously, the capacitance was transformed into voltage using a specially constructed converter. Both the frequency and the output signal from the converter could be registered and stored by a personal computer. The temperature of the sample (stabilized with an accuracy of ± 0.01 K) and the DC voltage applied to the sample could be registered in a similar way. Using this apparatus relative changes $\delta\epsilon/\epsilon$ less than 10^{-5} could be detected at $f \approx 1.3$ MHz. This quite high sensitivity enabled the measurements of the helix deformation to be performed even close to the Sm C* - Sm A transition. The sample capacitor was constructed from two glass plates, covered with aluminium, separated by 100 μm thick teflon spacers. The voltage U, supplied by a function generator has the form of rectangular pulses of 5 Hz frequency and amplitude varying from -40 V to +40 V. This voltage was applied to the sample through the coil of the resonant circuit. The measurements were performed in the smectic C* phase of 4-octyloxy 4-[(2-methylbutyloxy)-carbonyl]-phenylbenzoate. This material has a phase transition from the smectic C* phase to smectic A phase at about 31 °C.

RESULTS

A typical dependence of the oscillator frequency on the DC voltage applied to the sample is shown in Figure 2. It can be inferred from the Figure, that the electric permittivity changes under the influence of DC voltage U and reaches a saturation value at high voltages. This

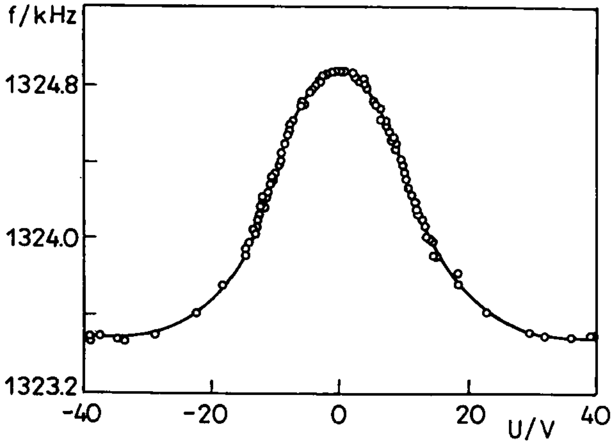

FIGURE 2 Resonant frequency as function of the DC voltage.

saturation value corresponds to $\epsilon_{22}{}^{C}$ defined in eq. (11) and the maximum frequency to $\epsilon_{22}{}^{H}$ from the same equation. It follows from eq. (15) that δf (which is proportional to $\delta\epsilon$) should be a square function of U. This is proved in Fig.3.

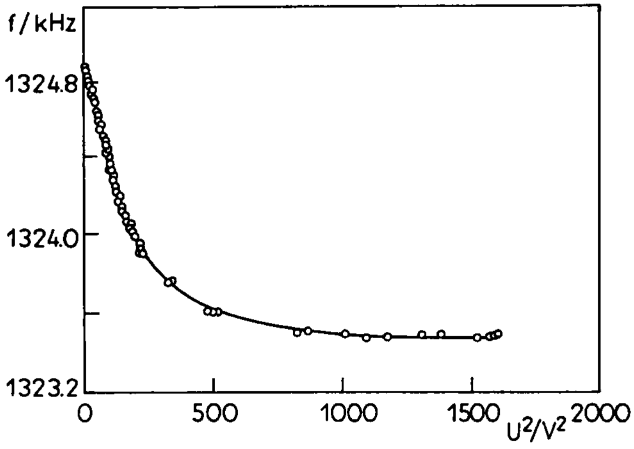

FIGURE 3 Resonant frequency as function of the square of the DC voltage.

The δf on U^2 dependence is indeed linear for small δf. This is a strong argument supporting the model presented above. The linear dependence is well fulfilled for $\delta f/\Delta f < 0.5$ (Δf denotes the saturation value of δf). From the slope of the straight line in Fig.3 the value $\delta\epsilon/\Delta\epsilon \cdot 1/U^2$ can be extracted. From this data and polarization data obtained with the bridge method the effective elastic constant $B_{eff} = B_3 q^2$ can be obtained using eq.(15). The results are shown in Fig.4. The

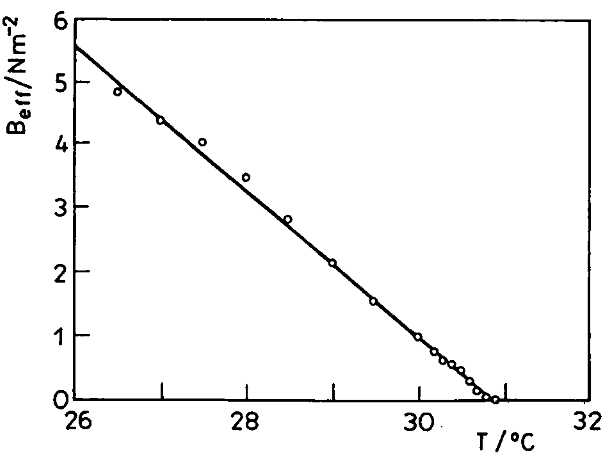

FIGURE 4 Temperature dependence of the effective twist elastic constant of the c director.

dependence of B_{eff} on temperature is linear in a broad temperature range and B_{eff}, as expected, reaches zero at the phase transition Sm C* - Sm A.

CONCLUSIONS

In the proposed method, the twist elastic constant of the c-director is measured in the presence of small deformations. In our opinion this is the proper way to investigate the elastic properties of liquid crystals - in contradiction to methods exploiting strong deformations (e.g. the method of helix unwinding).

The described method seems to be quite complex. It is, however, the simplest among the methods used so far.[10-13] Practically, only two measurements have to be performed: the measurement of the spontaneous polarization and of the relative change of electric permittivity caused by external electric field. The knowledge of the tilt angle is superfluous. If the pitch of the helical structure is known, not only the effective elastic constant B_{eff} but also the coefficients B_3 and D defined in eqs. (3) and (5) can be determined. We believe that the described method can be useful in investigations of elastic properties of various tilted smectic phases.

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REFERENCES

1. P. G. de Gennes, The Physics of Liquid Crystals, Clarendon Press, Oxford, 1974.
2. Orsay Group on Liquid Crystals, Solid State Comm. 9, 653, 1971.
3. I. Dahl and S. T. Lagerwall, Ferroelectrics, 58, 215, 1984.
4. F. M. Leslie, I. W. Stewart and M. Nakagawa, Mol.Cryst.Liq.Cryst. 198, 443, 1991.
5. T. Carlsson, I. W. Stewart and F. M. Lesie, J.Phys.A: Math.Gen. 25, 2371, 1992.
6. G. Pelzl, P. Kolbe, U. Preukschas, S. Diele and D. Demus, Mol.Cryst.Liq.Cryst. 53, 167, 1979.
7. J. Hoffmann, W. Kuczyński, J. Małecki and J. Pavel, Ferroelectrics, 76, 61, 1987.
8. P. Pierański, E. Guyon, P. Keller, L. Liebert, W. Kuczyński and P.Pierański, Mol.Cryst.Liq.Cryst.38, 275, 1977.
9. H. Diamant, K. Drenck and R. Pepinsky, Rev.Sci.Instr. 28, 30, 1957.
10. W. Kuczyński, Ber.Bunsenges.Phys.Chem. 85, 234, 1981.
11. W. Kuczyński, S. T. Lagerwall and B. Stebler, Proc. 11-th International Liquid Cryst.Conf., Θ-035-FE, Berkeley, USA, 1986.
12. F. Gouda, K. Skarp, G. Andersson, H. Kresse and S. T. Lagerwall, Jpn.J.Appl.Phys. 28 (10), 1887, 1989.
13. A. Levstik, Z. Kutnjak, I. Levstik and B. Žekš, Ferroelectrics, 109, 267, 1990.