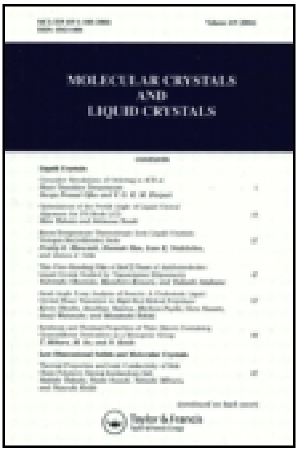

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Electrooptic Effect in the S_C Phase of TB10A

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ELECTROOPTIC EFFECT IN THE S_C PHASE OF TB10A

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Abstract The electrooptic response of the planar samples of TB10A in book-shelf and chevron geometries has been measured in the frequency range 1 Hz - 100 kHz. In order to have a linear response 4% of ferroelectric liquid crystal DOBA1MPC has been admixed to the non-chiral TB10A to create ferroelectricity in the mixture. In the S_C phase two low frequency relaxation processes have been found. The lower relaxation found in the region of several Hz corresponds to the deformation of the smectic layers, the higher one with the relaxation frequency of a few hundreds Hz corresponds to the azimuthal mode. These two relaxations give both positive resp. one positive and one negative contributions to the electrooptic response for the book-shelf resp. the chevron structures.

INTRODUCTION

The hexatic liquid crystal TB10A ($C_{10}H_{21}$-⌬-N=CH-⌬-CH=N-⌬-$C_{10}H_{21}$) is a very interesting material[1-4] exhibiting a rich polymorphism: Cr, S_G, S_F, S_I, S_C, S_A, Is. This substance, as well as the others from the same family (TBnA), atracts the attention of many authors especially due to the existence of three hexatic phases S_I, S_F, and S_G, which have been intensively studied by X-ray diffraction[4-7].

Here we want to study low frequency relaxation processes in the S_C phase of TB10A connected with collective vibrations of molecules. As the material is non-chiral, these processes cannot be detected neither in dielectric nor in electrooptic responses. When even a small amount of a chiral compound is admixed to TB10A, the local symetry is changed. Two-fold axis perpendicular to the long molecular axis becomes polar and along it the local spontaneous polarization appears[8,9]. As it was discussed in Ref. 10 the mixture is weakly ferroelectric but it does not differ very much from the non-chiral pure substance. On the other hand the ferroelectric properties of the mixture allow us to use experimental methods which are used for investigations of ferroelectric liquid crystals.

With the mixture the relaxation processes contribute to both dielectric and electrooptic responses, but the contributions will be small. For this reason it is necessary to choose a sensitive technique. The requirements better comply with the measurement of the electrooptic response because of the vanishing high frequency response. It enables to increase the sensitivity of the signal detection and to detect very weak contributions. In the dielectric permittivity measurements, on the contrary, there is always a high frequency background given by high frequency relaxations and electron polarization contributions, which can be higher than the contributions of the studied modes.

The other advantage of the optical method against the dielectric studies is that the D.C. conductivity does not influence the measured response. This becomes very important when the studied relaxation occurs at very low frequencies. The disadvantages of the optical methods remain the demand of a very good sample alignment and difficulties with a quantitative analysis of the measured responses.

EXPERIMENTAL TECHNIQUE

For the electrooptic response measurements the clasical setup has been used[11]. The planar sample of TB10A has been placed between crossed polarizers. When the liquid crystal alignment is homogeneous along the sample plane normal, the intensity of a transmitted light can be expressed as

$$I = I_o \sin^2 2\alpha \ \sin^2 \frac{\pi d \Delta n}{\lambda}, \qquad (1)$$

where I_0 is the intensity of the incident light, α is the angle between the optical indicatrix axes and the crossed polarizers, d is the sample thickness, Δn is the birefringence and λ is the light wave length. The change of this intensity under the A.C. electric field applied perpendicularly to the sample reads

$$\frac{\mathrm{d}I}{\mathrm{d}E} = 2I_o \sin^2 \frac{\pi d \Delta n}{\lambda} \sin 4\alpha \ \frac{\mathrm{d}\alpha}{\mathrm{d}E} + I_o \frac{\pi d}{\lambda} \ \sin^2 2\alpha \sin \ \frac{2\pi d \Delta n}{\lambda} \ \frac{\mathrm{d}\Delta n}{\mathrm{d}E}. \qquad (2)$$

The derivative of the intensity is detected by a photodiode connected to a lock-in nanovoltmeter.

In the S_A phase the applied electric field induces a tilt of molecules $\Theta = e(T) \cdot E$ in the plane perpendicular to the field[12]. As the mean orientation of molecule long axes is connected with the optical axis the angle α can be expressed as $\alpha = \alpha_0 + e(T) \cdot E$. In the S_A phase the second term in (2) can be neglected because under the electric field the optical indicatrix section in the sample plane does not change, therefore Δn remains constant. It is only the first term which gives contribution to the electrooptic response being maximum for $\alpha_0 = 22.5°$. In the $S_C{}^*$ phase the second term in Eq. 2 becomes also important because the optical indicatrix section changes under the field due to the vibration of the azimuthal angle.

To induce the ferroelectricity in the non-chiral TB10A 4 mol% of ferrolectric liquid crystal DOBA1MPC[13] have been admixed. All measurements of the electrooptic response of the planar sample of that mixture have been caried out in the red monochromatic light.

SAMPLE PREPARATION

The mixture of TB10A and DOBA1MPC has been sandwiched between two glass plates covered by transparent ITO electrodes. To achieve the planar geometry the sample in the S_A phase has been exposed to the A.C. electric field of 10 - 20 Hz for about one hour. For the electrooptic response measurements we have used two planar samples:

sample A: 12 μm thick with "weak planar surface anchoring" - which exhibits **book-shelf structure** in the S_C phase,

sample B: 7.5 μm thick with "strong planar surface anchoring" - which exhibits **chevron structure** in the S_C phase.

The weak anchoring was achieved by rubbing the glass plates on the velvet, for the strong anchoring the glasses were covered by a polyimide layer before the rubbing. It should be emphasized that in all studied samples the structure was helix-free unwound by the boundary conditions.

Sample A

As the ferroelectricity of the mixture is weak the polar interaction of the molecules with the surface is also weak. It results in the anchoring of molecules similar to that in non-chiral smectics, i.e. the anchorings with polarization "down" and "up" have the same energy and both are equally probable. The orientations of the molecules for these two anchorings differ by the angle 2Θ.

The direct consequence of these two possible anchorings on each glass surface is the existence of four different domains in the S_C* phase. Two of them are homogeneous (with polarization "down" or "up") and two twisted (twist along the sample thickness from the state "down" to "up" or from "up" to "down"). These four domains were found to be stable in the S_C* phase at vanishing electric field[10]. For the electrooptic experiment in the S_C* phase we have been able to choose either homogeneous or twisted domain.

As it is known from X-ray diffraction measurement[4] the layer spacing exhibits a strong temperature dependence in the S_C phase of TB10A, which is the consequence of the temperature dependence of the tilt angle Θ varying from 0° to 35° (see Ref. 10). The temperature dependence of the layer thickness causses a difficulty to keep the good alignement when the sample is cooled from the S_A to the S_C phase. At cooling focal conics appear, which causes the smectic layers become bent along the sample thickness.

Sample B

With this sample the strong anchoring conditions on the glass plates causes the smectic layers in the S_C* phase are arranged in chevrons created during cooling from S_A to S_C* phase. The presence of the chevrons is proved by the presence of zig-zag defects[14,15].

In the S_C* phase we were able to find an extinction between crossed polarizers. When the D.C. electric field was applied the extinction have been lost for any orientation of the polarizers. This behaviour can be explain by the model of the chevron structure proposed in Refs. 16, 17. This model is called a "triangulár director profile" (TDP) and consists in the linear director twist from the azimuthal angle ϕ_s at the upper surface to the angle ϕ_m at the chevron interface in the midle of the sample and again back to the angle ϕ_s at the lower surface.

EXPERIMENTAL RESULTS

We have carried out two types of measurements on both samples. First we have fixed the frequency of the applied electric field and measured the electrooptic response as a function of temperature varied from the S_A to the S_F phase in a rate of 0.5° K/min. The second type of the experiment was the measurement of the optical response in the frequency range from 1Hz to 100kHz at a stabilized temperature.

Sample A

In Fig. 1 the temperature dependence of the amplitude of the optical response is plotted for the sample A (d = 12 μm). The extinction have been found in the S_A phase, then the sample has been turned by the angle 22.5° with respect to the crossed polarizers. The measurement has been done on cooling without further change of the sample orientation. As it was verified during cooling the measurement was carried out in the homogeneous domain. Due to the weak ferroelectricity of the mixture, the electroclinic effect in the S_A phase is negligible. From the measured curve all the phase transitions can be identified. In the S_I phase the signal is much lower than that in the S_C phase and fluctuates. It is accompanied by the remarkable change of the texture in this phase. In the S_F phase the viscosity enormly increases, i.e. the electrooptic response is zero even for the low frequency used.

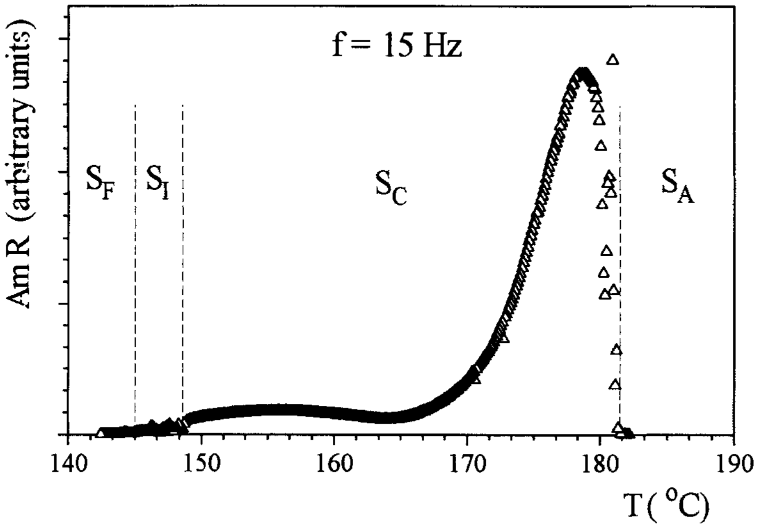


FIGURE 1 The temperature dependence of the amplitude of the electrooptic response for the sample A 12 μm thick. First the extinction was determined in the S_A phase, then the sample has been turned by 22.5° from the extinction position. The measurement has been caried out on cooling without changing the orientation of the sample.

For stabilized temperatures we have scanned the frequency in both the homogeneous and twisted domains. Fig. 2 shows the Cole-Cole diagrams, i.e. the imaginary part versus the real part of the electrooptic response for both the studied domains of the sample A. In all cases the extinction has been found, for the homogeneous domain between crossed polarizers, for the twisted domain for the angle $90°-2\Theta$ between the polarizer and the analyzer. In the twisted domain the adiabatic propagation of the light takes place, i.e. the plane of the polarized light follows the twist of the molecules. Then the sample has been turned by 22.5° from the extinction position.

In both domains we have found two relaxation processes. The detected electrooptic response can be written in the simplest form as a sum of two independent Debye relaxators with the relaxations frequencies f_1 and f_2 as

$$\frac{\mathrm{d}I}{\mathrm{d}E} = \frac{A}{1 - i\frac{f}{f_2}} + \frac{B}{1 - i\frac{f}{f_1}}, \tag{3}$$

where A, B are the amplitudes of respective contributions at zero frequency. The

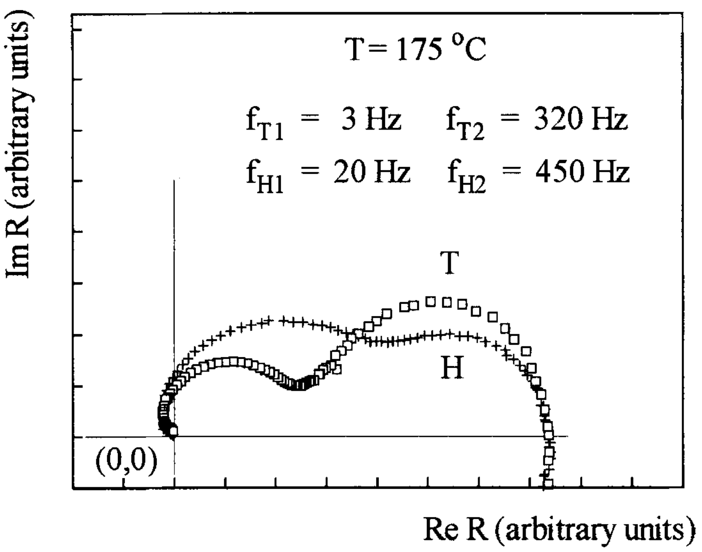


FIGURE 2 The Cole-Cole diagram, i.e. the imaginary part versus the real part of the electrooptic response for the homogeneous (H) and twisted (T) domains of the sample A (d = 12 μm). In both cases we have found two relaxation processes.

relaxation frequencies f_1 and f_2 have been determined by fitting the experimental data on the imaginary part of expression (3) as a function of the frequency. The temperature dependence of these frequencies for the homogeneous domain of the sample A are shown in Fig. 3.

In Fig. 4 typical examples of the frequency dependence of the amplitude of the

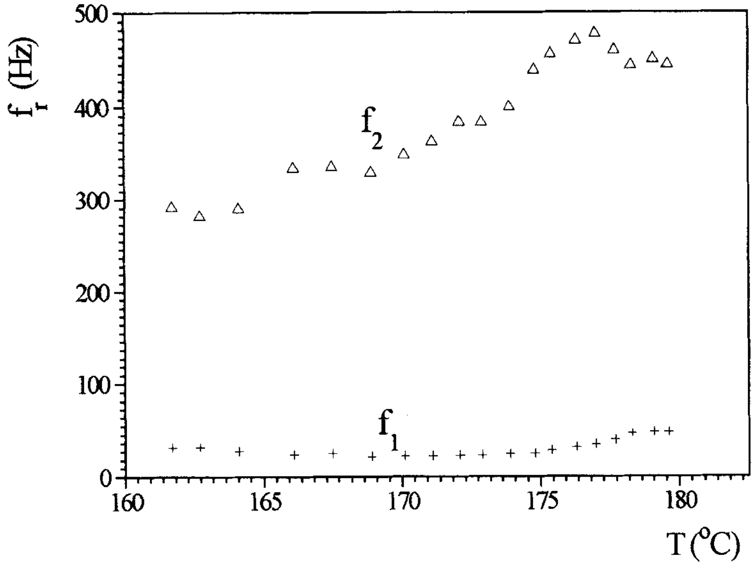


FIGURE 3 The temperature dependence of two relaxation frequencies found for the homogeneous domain of the sample A.

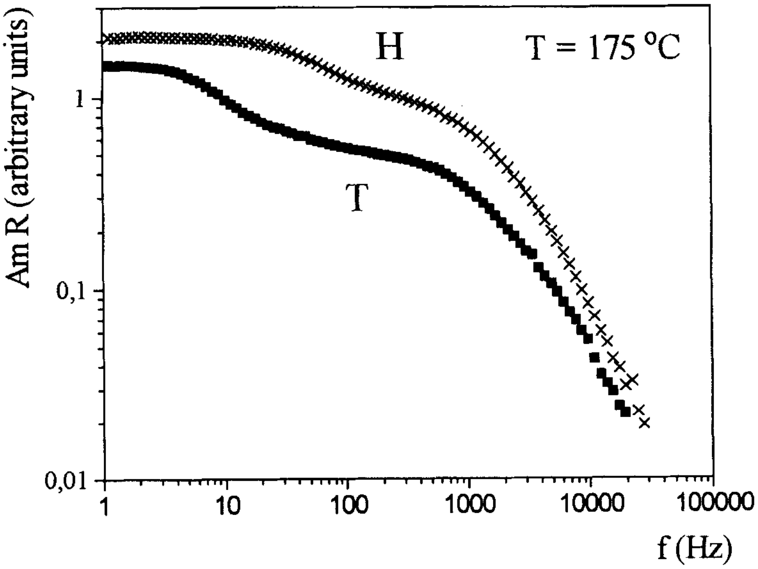


FIGURE 4 The frequency dependence of the amplitude of the electrooptic response for the planar sample A for the homogeneous and twisted domains. For both domains the sample has been turned by 22.5° from the extinction position.

electrooptic response for the homogeneous and twisted domains of the sample A are shown. For high frequencies the amplitude behaves as $1/f$ in all cases, which shows that two processes giving the contributions to the electroptical responce are independent and added as we suggested in Eq. 3.

Sample B

With the sample B the temperature dependence of the electrooptic amplitude has been similar to that for the sample A. For the sample B having the chevron structure we were able to find extinction between crossed polarizers without the electric field only. For the measurements of the electrooptic response we have also turned the sample by 22.5° from the extinction position as in the case of the sample A.

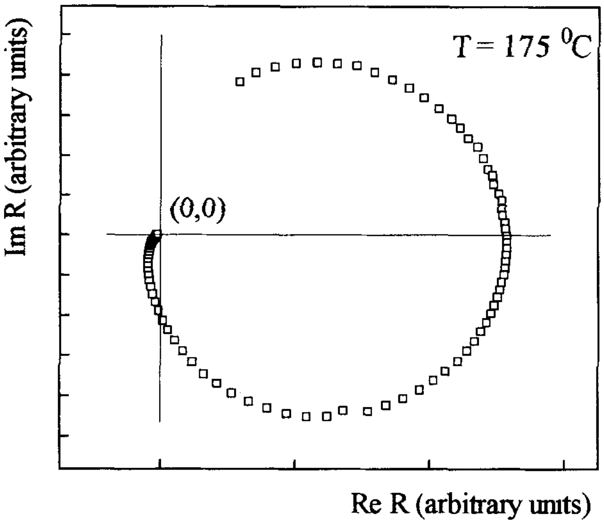
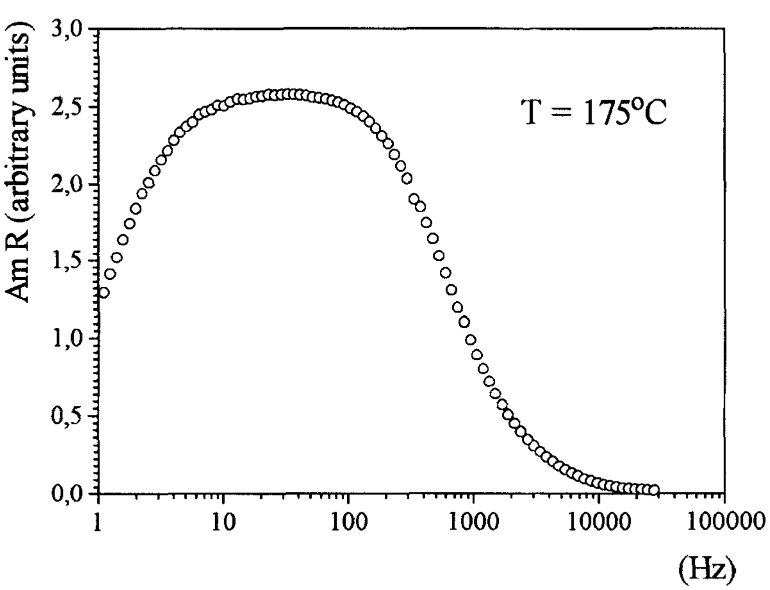


FIGURE 5 The Cole-Cole diagram of the electrooptic response for the sample B having the chevron structure. Two relaxation processes with the relaxation frequencies f_1 = 2 Hz and f_2 = 380 Hz have been found.

The frequency dependence of the detected signal for the sample B was found different from that for the sample A (see Figs. 5 and 6). To explain this difference it is necessary to consider opposite signs of two contributions to the electrooptic response. Equation 3 is then rewritten as

$$1 - i\frac{f}{f_2} \quad 1 - i\frac{f}{f_1}$$

By fitting the experimental data to the formula (4) we have found two relaxation frequencies whose values are in the same order as for the sample A. Also the contributions of these two modes are comparable (the constants *A* and *B* exhibit the similar values) as for the sample A (see Fig. 2).



DISCUSSION AND CONCLUSIONS

The electrooptic response has been measured for f = 15 Hz as a function of the temperature in both samples A and B. As the mixture of TB10A with DOBA1MPC is a weak ferroelectrics we did not find a measurable contribution from the soft mode (electroclinic effect) in the S_A phase. Similarly in the $S_C{}^*$ phase the electroclinic contribution should be also negligible.

We suggest the electrooptic response in the S_C* phase is given by another two relaxation mechanisms, found in the frequency dispersions (see Figs. 2, 6). These two modes are independent and their amplitudes at zero frequency (the constants A, B in Eqs. 3, 4) are comparable.

One of the modes with the relaxation frequency around hundreds Hz can be connected with the azimuthal angle fluctuations of the molecular orientation, keeping the constant tilt angle. This mode (denoted here as an azimuthal mode) is similar to the Goldstone mode in the helicoidal S_C* structure. It is necessary to note that in a homogeneous domain, when the smectic layers are strictly planar and perpendicular to the surfaces, the local polarization is either parallel or antiparallel to the applied field. Then a small electric field does not interact with the orientation of molecules and therefore the electrooptic response is equal to zero. This is not the case of our experiment, where we have either the chevron structure or the smectic layers are bent due to the existence of focal conics created during cooling from the S_A phase.

The other mode with the relaxation frequency in the range of several Hz can be connected with the deformation (redressing) of smectic layers, which results also in a change of polarization and therefore it interacts with the electric field. We suppose the layers are deformed easily under the field.

The non-monotoneous temperature dependence of the electrooptic response in the S_C* phase can be explain on the basis of analysis of Eq. 2. As the contribution to the electrooptic response is mainly given by the first term in Eq. 2, the sensitivity of the optical signal measurement is maximal in the S_A phase for $\alpha = 22.5°$. This condition is violated in the S_C* phase because the apparent tilt angle Θ increases on cooling, which results in the sensitivity decrease. At the same time the spontaneous polarization P_S increses as a consequence of the proportionality between P_S and Θ. In such a way one can explain the maximum of electrooptic response in the S_C* phase. Moreover, on cooling the continuous change of the texture occurs, which complicates the complete analysis.

To explain why the contributions to the electrooptic response from two modes are both positive or they have opposite signs, we need a model of the molecular structure within the sample. It will be discussed elsewhere.

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