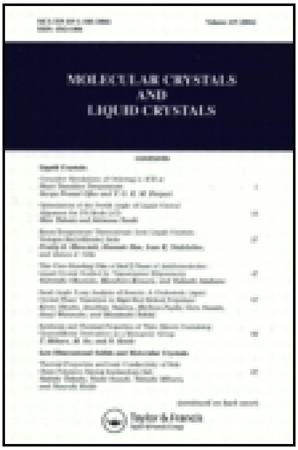

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Antiferroelectric Properties Induced by External Electric Field

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A theoretical possibility of the re-entrancy of the antiferroelectric properties in antiferroelectric liquid crystals under the influence of the high external electric field is discussed.

Keywords: antiferroelectric properties; dielectric coupling; ferrielectric structure

INTRODUCTION

Antiferroelectric liquid crystals were discovered more than two decades ago although unfortunately they were not reported as such [1]. In 1989 the first report where antiferroelectric liquid crystalline properties were recognized was published [2]. Since than, an extensive experimental and theoretical study based on the synthesis of a number of new materials that posses antiferroelectric properties in at least one of the numerous phases that appear in these systems has been occupying scientists [3].

The most indicative experiment to prove antiferroelectric properties of the material is the polarization of the sample in an external electric field. In chiral tilted smectics the reorientation of average molecular polarization results in the reorientation of the average molecular tilt in smectic layers. Consequently, optical properties of the system are influenced by the electric field. The direction of eigenvectors of optical indicatrix is changed and also the uniaxial optical properties of initially helicoidally modulated antiferroelectric phase transforms to the unwound biaxial antiferroelectric structure and with increasing electric field to the almost uniaxial unwound ferroelectric structure.

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Although theoretical studies of the phase diagram that present transitions from the modulated to the homogeneous structure and from unwound antiferroelectric to the unwound ferroelectric structures were reported [4], the behaviour of the system at a large external electric field was not studied.

In this report, a surprising effect is theoretically predicted. Since elongated molecules due to dielectric coupling tend to align the average long molecular axes parallel to the electric field, the increasing external electric field gives rise to a competition between the linear coupling with the piezoelectrically induced polarization and dielectric coupling with anisotropic dielectric properties of the system. With increasing field, the re-entrant structural transition to the system with ferrielectric properties is predicted. Counter intuitively, with increasing external electric field antiferroelectric properties of the structure become more pronounced.

THEORY

The aim of this report is the study of the transitions between different homogeneous (unwound) structures that are stable when an external electric field is applied. Chiral properties of the system are reflected only in the chiral piezoelectric coupling that results in polarization of tilted smectic layers. No chiral interlayer van der Waals interactions and achiral flexoelectric interlayer couplings that cause helicoidal modulations are considered [5].

The average tilt of the elongated molecules in the j-th layer is given by a tilt order parameter $\vec{\xi}_j = \theta\{\cos\varphi_j, \sin\varphi_j\}$, where θ is the magnitude of the tilt, which is constant in all layers, and φ_j gives the direction of the tilt vector with respect to the x axis. Polarization is perpendicular to the tilt and proportional to the tilt magnitude $\vec{P}_j = P_0\{-\sin\varphi_j, \cos\varphi_j\}$. Free energy is expressed in the tilt and the polarization as

$$f = \sum_j \frac{1}{2}a_{0,\xi}\vec{\xi}_j^2 + \frac{1}{4}b_{0,\xi}\vec{\xi}_j^4 + \frac{1}{2}a_{0,P}\vec{P}_j^2 - C_p\left(\vec{\xi}_j \times P_j\right)_z + \frac{1}{2}a_1\left(\vec{\xi}_j \cdot \vec{\xi}_{j+1}\right) - P_j \cdot \vec{E} - \frac{1}{2}\varepsilon_0(\varepsilon_e - \varepsilon_o)\left(\vec{\xi}_j \cdot \vec{E}\right)^2 \tag{1}$$

In Eq. (1) first two terms give van der Waals, steric and entropic intralayer part of the free energy. The parameter $a_{0,\xi} = a(T - T_0)$ becomes negative at the temperature T_0 where an isolated smectic layer would become tilted. Next two terms, $a_{0,P}$ and C_p give intralayer dipolar electrostatic contribution and chiral piezoelectric coupling of the tilt and polarization.

Parameter a_1 resumes interlayer steric and van der Waals interactions and is in studied systems always positive favouring anticlinic order. Last two terms give interactions of the polarly ordered layer with an external electric field. The novelty is that both, linear and quadratic dielectric coupling, is considered.

Using the proposed form of the tilt and polarization order parameters, after elimination of polarization, the free energy expressed in units of temperature has the following form

$$\frac{f}{a} = \sum_j \frac{1}{2}A\theta^2 + \frac{1}{4}B\theta^4 + \frac{1}{2}A_1\theta^2\cos(\varphi_{j+1} - \varphi_j) - \sigma\theta\cos\varphi_j - \frac{1}{2}\Delta\sigma^2\theta^2\sin^2\varphi_j \tag{2}$$

where new parameters are

$$A = (T - T_0) - \frac{C_p^2}{aa_{0,P}} \qquad B = \frac{b_{0,\xi}}{a} \qquad A_1 = \frac{a_1}{a}$$
$$\sigma = \frac{E}{E^*} \qquad E^* = \frac{aa_{0,P}}{C_p} \qquad \Delta = \frac{(\varepsilon_e - \varepsilon_o)aa_{0,P}^2}{C_p^2} \tag{3}$$

The symmetry of the problem requires that polarizations can have only two directions with respect to the external field which due to the perpendicular direction of the polarization to the tilt results also in the defined direction of the tilt (Fig. 1). Using the Ansatz

$$\begin{aligned}\vec{\xi}_{2j} &= \theta(\cos\alpha, \sin\alpha)\\ \vec{\xi}_{2j+1} &= \theta(\cos(-\alpha), \sin(-\alpha))\end{aligned} \tag{4}$$

and

$$\begin{aligned}\vec{P}_{2j} &= \theta\left(\cos\left(\alpha + \frac{\pi}{2}\right), \sin\left(\alpha + \frac{\pi}{2}\right)\right)\\ \vec{P}_{2j+1} &= \theta\left(\cos\left(-\alpha + \frac{\pi}{2}\right), \sin\left(-\alpha + \frac{\pi}{2}\right)\right)\end{aligned} \tag{5}$$

the average free energy of two layers gets the form

$$\frac{f}{a} = \sum_j \frac{1}{2}A\theta^2 + \frac{1}{4}B\theta^4 + \frac{1}{2}A_1\theta^2\cos(2\alpha) - \sigma\theta\cos\alpha - \frac{1}{2}\Delta\sigma^2\theta^2\sin^2\alpha. \tag{6}$$

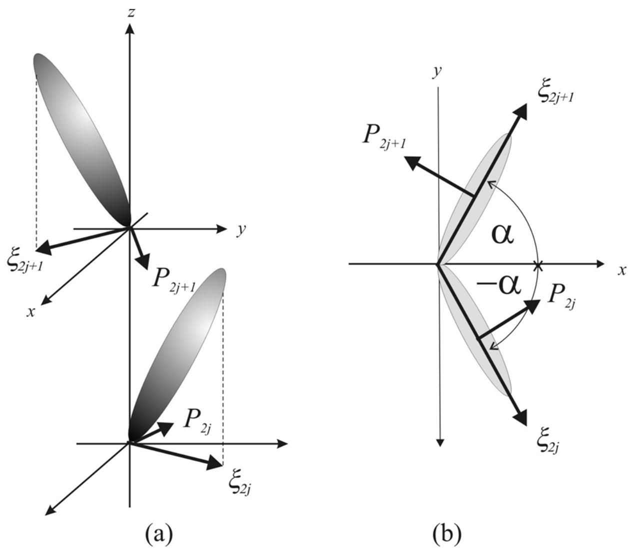

FIGURE 1 Molecular tilts in neighbouring layer. (a) 3D presentation, (b) projection of two neighbouring layers onto the interface between considered layers.

The miminization of the free energy with respect to ® gives three different homogeneous solutions.

Antiferroelectric Anticlinic Structure ($\alpha = \pi/2$)

The structure that presents the solution when chiral van der Waals interlayer interactions are neglected is stable only in the absence of the external electric field. Real chiral systems are almost always helicoidally modulated over a few hundred layers. Such a structure can be found only in some special systems at a temperature of the helix reversal. The experiments [6] have shown that the structure that is present when the antiferroelectric structure unwinds is very close to this approximation. Since helicoidal modulation and its behaviour is not the topic of this report, the analysis will be limited to the antiferroelectric structure at the helix reversal temperature.

Nonparallel Ferrielectric Structure ($0 < \alpha < \pi/2$)

Increasing the external electric field, long molecular axes start to rotate and the system becomes polarized. The magnitude of the α

decreases and the polarization becomes more and more parallel to the electric field (Fig. 1).

$$\cos\alpha = \frac{\sigma}{\theta(A_1 + \Delta\sigma^2)} \tag{7}$$

The structure has due to non-complete cancellation of polarization ferrielectric properties.

Ferroelectric Synclinic Structure ($\alpha = 0$)

This structure where the tilt is homogeneously tilted perpendicularly to the electric field, has long been considered as the only structure stable at high electric fields. However, if dielectric coupling becomes important this is no more true. When the right side of the Eq. (7) becomes larger than 1, the nonparallel ferrielectric structure re-enters. Two critical fields exist – the lower critical field where the ferroelectric synclinic structure becomes stable

$$\sigma_{\mathrm{low}} = \frac{1 - \sqrt{1 - \Delta A_1 \theta^2}}{2\Delta\theta} \tag{8}$$

and, surprisingly, also the higher critical field, where dielectric coupling starts to orient molecules again towards the parallel or antiparallel direction to the external electric field and the ferrielectric structure becomes stable again.

$$\sigma_{\mathrm{high}} = \frac{1 + \sqrt{1 - \Delta A_1 \theta^2}}{2\Delta\theta} \tag{9}$$

Loosely speaking about ferrielectric properties as a combination of ferroelectric and antiferroelectric properties, the results are rather counterintuitive: further increase of electric field diminish ferroelectric properties of the system and enhances its antiferroelectric properties.

RESULTS AND CONCLUSIONS

To consider the phase diagram, i.e., structures in dependence of electric field and the temperature, also the minimization of the tilt magnitude is needed since the tilt also influences the critical field. The complete phase diagram is given on Figure 2. It is clearly seen that at high temperatures, where the non-tilted SmA phase would be stable in the absence of the electric field, the critical field is higher than in lower regions where molecules are already tilted. Electroclinically induced tilt is smaller and therefore the 3/4high should be much

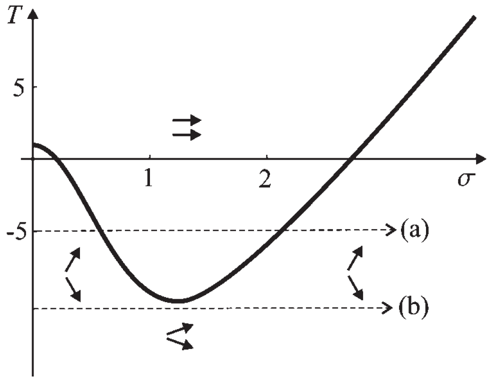

FIGURE 2 E–T dependent phase diagram. Structures are marked with arrows. (a) At higher temperatures two continuous transitions (to and from the synclinic phase exist), while at lower temperatures only nonmonotonous change of the phase difference 2α is expected.

higher. At lower temperatures the competition between both effects becomes important already at lower fields and consequently the critical field 3/4high is lower. In the phase diagram is clearly seen that at temperatures, where without an electric field the structure is already tilted, a re-entrant region of the ferrielectric structure exists. However, such a phase diagram should not be present in all systems. In materials, where antiferroelectric anticlinic nearest interlayer interaction is strong, and piezoelectric interaction is weak, the complete reorientation of the average molecular axes perpendicular to the electric field should not develop. The critical ratio of parameters, that gives nearest interlayer interactions, piezoelectric and dielectric couplings, where this is true, is:

$$A_{1,\mathrm{crit}} = \frac{1}{\Delta\theta^2} \tag{10}$$

In such systems instead of three different regions (Fig. 2 line a), only the nonmonotonous evolution of the tilt direction ® would be present (Fig. 2 line b). To my best knowledge experimental observations of such behaviour do not exist. Good candidates for such studies would be racemized mixtures of systems that also in a racemate have stable anticlinic phase.

To resume, a theoretical analysis of the behaviour of nonmodulated antiferroelectric anticlinic systems in an external electric is presented. In contrast to a common expectation, the re-entrancy of antiferroelectric properties was found at high electric fields. Two critical electric fields exist in some systems while in almost racemic mixtures only nonmonotonous behaviour of the tilt direction with respect to the direction of the electric field should be observed.

REFERENCES

[1] Levelut, A. M., Germain, C., Keller, P., Liebert, L., & Billard, J. (1983). *J. Phys.*, *44*, 623.

[2] Chandani, A. D. L., Gorecka, E., Ouchi, Y., Takezoe, H., & Fukuda, A. (1989). *Jap. Jou. Appl. Phys.*, *28*, L1265.

[3] Čepič, M., Gorecka, E., Pociecha, D., & Vaupotič, N. (2003). *Relaxation Phenomena*, Springer Verlag: Berlin, Heidelberg, chap. 5.4, 332.

[4] Boulbitch, A. A. & Toledano, P. (1998). *Euro. Phys. Jou. B6*, 355.

[5] Čepič, M. & Žekš, B. (2001). *Phys. Rev. Lett.*, *87*, 085501.

[6] Fukuda, A., Takanishi, Y., Ishikawa, K., & Takezoe, H. (1994). *J. Mat. Chem.*, *4*, 997.