Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Theoretical Reasons for the Thermodynamic Stability of a Blue Phase of Trigonal Symmetry

R. Ellinghaus [a b] & W. Muschik [a]
[a] Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergsfr. 36, 1000, Berlin 12, Germany
[b] Also Firma LOGIPLAN GmbH, Alt-Moabit 91b, 1000, Berlin 21, Germany
Version of record first published: 24 Sep 2006.

To cite this article: R. Ellinghaus & W. Muschik (1991): Theoretical Reasons for the Thermodynamic Stability of a Blue Phase of Trigonal Symmetry, Molecular Crystals and Liquid Crystals, 198:1, 73-78

To link to this article: http://dx.doi.org/10.1080/00268949108033384

Mol. Cryst. Liq. Cryst., 1991, Vol. 198, pp. 73–78
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Theoretical Reasons for the Thermodynamic Stability of a Blue Phase of Trigonal Symmetry

R. ELLINGHAUS[1] and W. MUSCHIK

Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 1000 Berlin 12, Germany

(Received July 25, 1990)

Starting out with a special trigonal ansatz for the alignment tensor field of a cholesteric liquid crystal we prove by using LANDAU theory, that this ansatz has a lower free-energy density than the cholesteric phase and the O^5-phase, discussed by Grebel *et al.* [1], in a certain region of the reduced temperature–chirality–plane. In this domain the trigonal phase ($C\frac{1}{2}$phase) may be the thermodynamical stable one. Using an extension of this ansatz we get an implicit equation for the interplanar spacing of certain lattice planes as a function of an external electric field. Therefore we are able to discuss electrostrictive effects of this trigonal phase.

Keywords: blue phase, trigonal symmetry, theory

1. INTRODUCTION

Using a free-energy density of DE GENNES-type and introducing different alignment tensor fields into this expression we get the thermodynamical most stable field by selecting the one with lowest resulting average free-energy. We discuss an alignment tensor field of trigonal symmetry and compare the corresponding free-energy to the isotropic, cholesteric, and O^5 phase.

This alignment tensor field exhibits an extension describing the influence of a constant homogeneous electric field. The modified tensor field depends on an appropriate parameter, describing the distorted spatial symmetry. Minimizing the corresponding free-energy for given electric field determines the equilibrium value of this parameter. We state the result in the limit of small electric fields.

[1] Also Firma LOGIPLAN GmbH, Alt-Moabit 91b, 1000 Berlin 21, Germany.

2. FREE-ENERGY AND ALIGNMENT TENSOR FIELD

As usual, we choose the free-energy density

$$F = \frac{1}{2}\left(aA_{ij}^2 + c_1 A_{ij,l}^2 + c_2 A_{ij,i}A_{kj,k} - 2d\epsilon_{ijk}A_{in}A_{jn,k}\right) - \beta A_{ij}A_{jk}A_{ki} + \gamma(A_{ij}^2)^2 - \frac{\chi}{2}E_i A_{ij}E_j \,, \tag{1}$$

with the alignment tensor field (A_{ij}), the electric field (E_i), and the totally antisymmetric third order tensor (ϵ_{ijk}). Our ansatz for the alignment tensor field reads

$$(A_{ij}) := \alpha \begin{pmatrix} \cos^2(q_z y) + \sin^2(q_z z) - 1 & \sin(q_z z)\cos(q_z z) & \cdots \\ \sin(q_z z)\cos(q_z z) & \cos^2(q_z z) + \sin^2(q_z x) - 1 & \cdots \\ \sin(q_z y)\cos(q_z y) & \sin(q_z x)\cos(q_z x) & \\ & \sin(q_z y)\cos(q_z y) & \\ \cdots & \sin(q_z x)\cos(q_z x) & \\ & \cos^2(q_z x) + \sin^2(q_z y) - 1 & \end{pmatrix} \tag{2}$$

which is simply the additive superposition of three (well known) alignment tensor fields of the uniaxial cholesteric helix, each propagating along one of the three axes of a cartesian frame. The idea behind this ansatz is simple: The so called double twist condition $d_{i,j} = q\epsilon_{ijk}d_k$ [2] for the director field (d_i), which mathematically formulates the fact that each direction in space for the blue phase should "look" like a cholesteric helix, cannot be valid in the three dimensional EUKLIDEAN space for normed vector fields. Therefore we try this superposition of three orthogonal helices which in fact exhibitis the up to now experimentally unobserved trigonal (C_3^1) symmetry. In reduced quantities, defined by the relations

$$\mathcal{F} = 36F\frac{\gamma^3}{\beta^4} \,, \quad \alpha = s\mu \,, \quad s = \frac{\beta}{\sqrt{6}\gamma} \,, \quad t = 12a\frac{\gamma}{\beta^2} \,, \quad \xi_R^2 = 12c_1\frac{\gamma}{\beta^2} \,,$$

$$q_c = \frac{d}{c_1} \,, \quad \kappa = q_c\xi_R \quad \text{and} \quad \chi_r = 3\sqrt{6}\frac{\gamma^2}{\beta^3}\chi \tag{3}$$

this ansatz results in the mean free-energy density (for vanishing electric field $E = 0$)

$$\overline{\mathcal{F}}_{C_3^1} := \frac{\int_V \mathcal{F}_{C_3^1}\mathrm{d}x\mathrm{d}y\mathrm{d}z}{V} = \frac{1}{16}\left[\left(24(q_z/q_c)^2 + 24(q_z/q_c)\right)\mu^2\kappa^2 + 6\mu^2 t + 39\mu^4\right] \,. \tag{4}$$

The integration has to be performed over an arbitray volume V of spatial periodicity of the alignment tensor field. This expression is minimized by

$$q_z = -\frac{q_c}{2} \quad \text{and} \quad \mu = \sqrt{\frac{\kappa^2 - t}{13}} \,, \tag{5}$$

consequently we get

$$\overline{\mathcal{F}}_{C_3^1} = -\frac{3(t-\kappa)^2}{208} \ , \ \kappa^2 > t \ . \tag{6}$$

The free-energy density for the O^5-phase is [1]

$$\overline{\mathcal{F}}_{O^5} = \mathcal{F}_{O^5} = \frac{1}{4}\left(t-\kappa^2\right)\mu^2 - (23\sqrt{2}/32)\mu^2 + (499/384)\mu^4 \ , \tag{7}$$

which is minimized by

$$\mu = \frac{\sqrt{47904(\kappa^2-t)+42849}+207}{499\sqrt{2}} \ . \tag{8}$$

Introducing (8) into (7) and using (6) we get

$$\begin{aligned}\overline{\mathcal{F}}_{C_3^1} - \overline{\mathcal{F}}_{O^5} \ &= \ -\frac{249}{103792}\Phi^2 + \frac{69}{996004}\Phi\left(2\sqrt{47904\Phi+42849}+621\right) + \\ &+ \frac{985527}{7952095936}\left(\sqrt{47904\Phi+42849}+207\right) \ ,\end{aligned} \tag{9}$$

where $\Phi := \kappa^2 - t$. By numerical computation we get from (9)

$$\Phi > 196.31 \quad \Rightarrow \quad \overline{\mathcal{F}}_{C_3^1} < \overline{\mathcal{F}}_{O^5} \ . \tag{10}$$

In the framework of LANDAU theory the phase boundary for the isotropic – cholesteric transition is given by [3]

$$t_{IC} = \frac{3}{4}\kappa^2 + 1 \ . \tag{11}$$

Therefore the alignment tensor field (2) results in a smaller free-energy than the alignment tensors for the O^5 or the cholesteric phase [1], at least in the region

$$t > \frac{3}{4}\kappa^2 + 1 \qquad \wedge \qquad \kappa^2 > 196.31 + t \ . \tag{12}$$

Detailed considerations yield

$$\kappa > B \quad \Rightarrow \quad \mathcal{F}_{col} > \mathcal{F}_{O^5} \tag{13}$$

for some $B < 2.52$, therefore the free-energy of the C_3^1 phase is lower than the free-energies of the O^5, isotropic, and cholesteric phases in the domain

$$\kappa^2 > 196.31 + t \ , \ \ t > 0 \ . \tag{14}$$

The smallest chirality κ in this area equals 14.01. The resulting phase diagram is sketched in figure 1.

3. THE EXACT SOLUTION

Unfortunately, the field (2) is no solution of the EULER-LAGRANGE equations of the variational min-max problem for the free-energy density. Therefore, our ansatz only represents an approximation of the stable field. As motivated below the exact

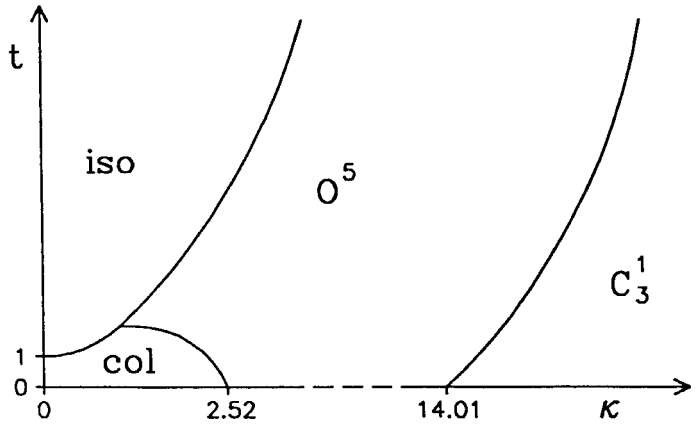

FIGURE 1

field exhibits also the trigonal symmetry and, of course, induces a lower free-energy density as (2), enlarging the stability region for this phase sketched in figure 1.

Let $\mu_{ij} := (\sqrt{6}\gamma/\beta)A_{ij}$ and assume $c_2 = 0$ then the EULER-LAGRANGE equations read [1]

$$0 = \frac{1}{2}\left(t\mu_{ij} - \xi_R^2\mu_{ij,ll} - 2\kappa\xi_R^2\epsilon_{ln(i}\mu_{j)l,n}\right) - 3\sqrt{6}\mu_{il}\mu_{lj} + 4(\mu_{ln})^2\mu_{ij} - \sqrt{6}(\mu_{ln})^2\delta_{ij} \ . \quad (15)$$

The equations (15) represent a set of five independent, second-order, quasi-linear PDEs, which can be solved numerically. The restriction of the field (2) and its first order derivatives to the surface of the cube

$$[0, 1/(2q_z)] \times [0, 1/(2q_z)] \times [0, 1/(2q_z)] \quad (16)$$

serve as boundary conditions for the problem. These restricted fields show also the C_3^1-symmetry (and no other one except translational symmetry) which implies that the solution must also exhibit this C_3^1-symmetry. The paper on this numerical solutions will be published elsewhere.

4. ELECTROSTRICTION

As motivated in [4], an appropriate ansatz for the field (A_{ij}) subjectet to an constant homogeneous electric field parallel to the z-axis is given by

$$(A_{ij}(E)) := \alpha \begin{pmatrix} \cos^2(\phi(y + g_E/4) - \pi/2)) + \sin^2(q_z z) - 1 & & \\ \sin(q_z z)\cos(q_z z) & & \cdots \\ \sin(\phi(y + g_E/4) - \pi/2))\cos(\phi(y + g_E/4) - \pi/2)) & & \end{pmatrix}$$

$$\begin{array}{ccc} & \sin(q_z z)\cos(q_z z) & \\ \cdots & \cos^2(q_z z)+\sin^2(\phi(z))-1 & \cdots \\ & \sin(\phi(x))\cos(\phi(x)) & \end{array}$$

$$\left.\begin{array}{ccc} & \sin(\phi(y+g_E/4)-\pi/2))\cos(\phi(y+g_E/4)-\pi/2)) & \\ \cdots & \sin(\phi(x))\cos(\phi(x)) & \\ & \sin^2(\phi(y+g_E/4)-\pi/2))+\cos^2(\phi(x))-1 & \end{array}\right) . \tag{17}$$

The function ϕ is a solution of the differential equation

$$\phi' = \pm w\sqrt{1-\frac{\mathcal{E}^2}{w^2}\sin^2(\phi)}\ ,\ w>0\ ,\ \mathcal{E}:=2E\sqrt{\frac{\chi_r}{\mu}}\ . \tag{18}$$

The up to now arbitrary parameter w has to be determined by minimizing the resulting mean free-energy. For symmetry reasons the implication

$$E=0 \implies \{\phi(x)=q_z x \ \wedge\ w=\pm q_z \ \wedge\ g_E=2\pi/q_z\} \tag{19}$$

is valid so that $A_{ij}(\mathrm{O}) = A_{ij}$ holds. Assuming that the volume of the unit cell is independent of the electric field [5,6] we get after some rather involved computations an implicit equation [4] for the change of the period of the spatial structure of the field (17). This equation can be solved in some special cases. One of this solutions yields an approximation for the electrostrictive effect in the limit of small electric fields [4]

$$g_{\|E} = \frac{4\pi}{q_c}\left(1-\frac{832\sqrt{13}E^4\chi_r^3}{3q_c^2\sqrt{(\kappa^2-t)^3}\kappa^2}\right)\ ,\ E\ll q_c\frac{(\kappa^2-t)^{\frac{1}{4}}}{\sqrt{\chi_r}} \tag{20}$$

where $g_{\|E}$ is the period of the spatial structure induced by the field (17) parallel to the electric field.

5. SUMMARY

Using an explicit ansatz we predict the possibility that an alignment tensor field of C_3^1 symmetry may be thermodynamically stable in a material characterized by sufficently high chirality. Although our ansatz only represents an approximation of the thermodynamical stable field, we show that the exact solution will have the same symmetry. The alignment tensor field is modified straight forward to incorporate electrostrictive effects. The result for weak electric fields is the occurence of electrostriction with a leading term in E^4.

6. ACKNOWLEDGEMENT

We appreciate the financial support by the DEUTSCHE FORSCHUNGSGEMEINSCHAFT "Sonderforschungsbereich Flüssigkristalle" and thank Christina Papenfuß for helpful comments.

References

1. H. Grebel, R. M. Hornreich, and S. Shtrikman, Landau theory of cholesteric blue phases. *Phys. Rev. A*, **28**:1114, 1983.
2. B. Pansu, R. Dandoloff and E. Dubois-Violette. The double twist connection and the S^3 blue phase. *J. Physique*, **48**:297, 1987.
3. R. M. Hornreich, M. Kugler, and S. Shtrikman. Localized instabilities and the order-disorder transition in cholesteric liquid crystals. *Phys. Rev. Let.*, **48**:1404, 1982.
4. R. Ellinghaus, Ch. Papenfuß, and W. Muschik. Electrostriction in liquid crystals. In *Proceedings of the 6. Conference of Continuum Models of Discrete Systems*, Longman Scientific, to appear.
5. G. Heppke, B. Jérôme, H.-S. Kitzerow, and P. Pieranski. Electrostriction of BPI and BPII for blue phase systems with negative dielectric anisotropy. *J. Phys. France*, **50**:549, 1989.
6. V. E. Dmitrienko. Electro-optic effects in blue phases. In *Proceedings of the 12. International Liquid Crystal Conference, Freiburg*, 1989.