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NOTE ON "MACROSCOPIC DESCRIPTION OF COMPENSATED CHOLESTERIC AND CHIRAL SMECTIC LIQUID CRYSTALS"

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Abstract Investigating the symmetry properties of compensated chiral liquid crystals we point out that the macroscopic description suggested recently by Pleiner and Brand[1] can not be applied for these materials. We also discuss the hysteresis of the homeotropic to fingerprint texture transition in compensated cholesterics and its consequence on the measurement of the temperature dependence of the pitch.

INTRODUCTION

The truly hydrodynamic[2-4] (or "coarse grained"[5]) description regards chiral liquid crystals as layered systems having a layer thickness equal to the helical pitch. In order to describe variations within a pitch length a modified, local description has been proposed recently by Pleiner and Brand[1] for long pitch cholesterics or smectics C*. According to this theory compensated cholesterics or compensated smectics C* would require a special treatment[1] yielding a vanishing thermomechanical coupling constant (Leslie parameter[6] λ_3) and as a consequence the experiments on the thermomechanical coupling[7,8] ought to be reinterpreted.

The aim of the present note is to point out two mistakes in the paper of Pleiner and Brand[1]. First we will show that the symmetry properties of compensated chiral systems are different from that of achiral ones thus the starting point of the theory[1] can be queried. Secondly we will prove that contrary to the statement in Ref.1 our method of measuring the temperature dependence of the pitch yields

an upper limit for dq_o/dT.

SYMMETRY OF A COMPENSATED CHIRAL LIQUID CRYSTALLINE SYSTEM

The term "compensation" means that the helical pitch of a chiral substance (usually a mixture) becomes infinite at a specific temperature (and concentration). This phenomenon is accompanied by a helix inversion, i.e. the handedness of the helical structure below and above the compensation temperature is opposite.

There are four ways to realize a compensated chiral liquid crystalline system.

i. Mixing two different cholesteric compounds of opposite handedness (i.e. a right-handed (A^+) and a left-handed (B^-) one).[9] This method is working for chiral smectics C^* too.[10]

ii. Mixing two special left-handed cholesterics (A^- and B^-).[11] Compensation occurs at two different concentrations.

iii. Mixing a special right-handed cholesteric (A^+) with a nematic (B).[12]

iv. According to recent observations a helix inversion can occur even in a single chiral compound.[13] At a specific temperature this compound "compensates itself", i.e. its helical structure disappears.

In contrary to the statement of Pleiner and Brand in Ref.1 the above systems are chiral and do not possess the same symmetries as the corresponding achiral counterparts. Cholesterics or smectics C^* lack the mirror symmetry even at the compensation point. This fact follows from the structure of the individual molecules. In all the systems discussed above the disappearance of the helical structure is not a consequence of a change in symmetries but rather results "accidentally" from the complex nature of the intermolecular interactions. Hence there is no reason to suppose that all the coupling coefficients, which are connected to chirality have to vanish at the same temperature where $q_o=0$. Of course these parameters may depend

on q_0 and may be expanded into series, nevertheless it is not allowed to neglect the zeroth order term a priori. Consequently the chiral coupling coefficients including the Leslie parameter[6] λ_3 need not be zero at the compensation point.

As experimental evidences one can regard the measurement on the thermomechanical coupling[7,8] which still will be discussed later and the measurement of the pitch and spontaneous polarization of a compensated smectic C^* mixture.[10] Adopting the train of thoughts of Pleiner and Brand[1] one should expect that at the compensation point the spontaneous polarization disappears as well as the helical structrure. Experiments have shown instead that the compensation of the helix and the compensation of the polarization occurs at different concentrations and temperatures[10] so a compensated smectic C^* with infinite pitch has a nonzero spontaneous polarization.

The only way to create a centrosymmetric substance from chiral components is to mix the two antipodes of the same compound (A^+ and A^-) in a ratio 1:1. In these racemic mixtures which are exactly achiral independently of temperature in contrast to compensated systems the linear thermomechanical coupling is excluded by the mirror symmetry.

The series expansion against q_0 as proposed in Ref.1 may be useful to analyse the behaviour of possible biaxial parameters of cholesterics. According to theoretical predictions[14] cholesterics locally should have a biaxial symmetry which is due to the helical structure. At the compensation point this biaxiality vanishes with the helix thus compensated cholesterics are exactly uniaxial with vanishing biaxial parameters. (Chiral biaxial lyotropic nematics are out of our present scope.) However we would like to note that this biaxiality must be very small,[15] its existence has not been proved experimentally in thermotropic cholesterics and is usually neglected in continuum theories.[5,6,16] In this approximation there is no need for a special treatment of compensated chiral systems, instead one can simply use the local description with $q_0=0$.

MEASUREMENT OF THE TEMPERATURE DEPENDENCE OF THE HELICAL PITCH

It is well known that a cholesteric with a homeotropic surface treatment can have either a homeotropic or a fingerprint texture depending on the thickness to pitch ratio ($\alpha = |q_0| L = 2\pi L/|P_0|$). Using for instance a wedge-like sample one can determine a critical value α_{cr} which is the lower limit for the existence of the fingerprint texture.[17] On the other hand one can derive from the continuum theory[6] an instability criterium which yields that above $\alpha_{th} = \pi K_3/K_2$ the homeotropic texture can not exist.[7] The two threshold values do not coincide, $\alpha_{cr} < \alpha_{th}$, which allows for a hysteresis. In the intermediate region, $\alpha_{cr} < \alpha < \alpha_{th}$, a metastable homeotropic texture can exist due to the nucleation mechanism of the fingerprint texture.

Let the homeotropic texture be formed in a sample of a constant thickness and temperature maintaining $0 < \alpha < \alpha_{cr}$. Then increasing α slowly one can enter the metastable state $\alpha_{cr} < \alpha < \alpha_{th}$ preserving the homeotropic texture. Increasing α further at α_{th} a homogeneous deformation (a declination of the director) starts in the sample which is then immediately transformed into the fingerprint texture. If we now decrease α nothing happens until $\alpha = \alpha_{cr}$ where the fingerprint texture disappears. This type of hysteresis has been observed on compensated cholesterics.[7]

Around the compensation temperature T_{comp} q_0 and α read

$$q_0 = \frac{dq_0}{dT}(T - T_{comp}) \tag{1}$$

$$\alpha = |q_0| L = \left|\frac{dq_0}{dT}(T - T_{comp})\right| L = \left|\frac{dq_0}{dT}\right| |T - T_{comp}| L = \left|\frac{dq_0}{dT}\right| \Delta T\, L \tag{2}$$

It shows that changing the temperature we can change α as well. We can introduce the critical temperatures ΔT_{cr} and ΔT_{th} which correspond to α_{cr} and α_{th} respectively.

From the hysteresis we could determine the temperature ΔT_{exp}

where the homeotropic to fingerprint texture transition occurs. Though ΔT_{exp} and ΔT_{th} ought to coincide according to the above picture, we have to take into account that as it was pointed out in Ref.1 a real sample necessarily possesses thickness and temperature inhomogeneities, surface defects or dust particles. They all influence the quality of the homeotropic texture introducing local distortions of the director field. These defects can initiate the transition into the fingerprint texture without the need for an intermediate homogeneous deformation. Thus actually $\Delta T_{exp} \lesssim \Delta T_{th}$ can be observed.

Using Eq.(2) one gets

$$\left|\frac{dq_o}{dT}\right| = \frac{\alpha_{th}}{\Delta T_{th} L} = \frac{K_3 \pi}{K_2 L} \frac{1}{\Delta T_{th}} \tag{3}$$

Substituting ΔT_{th} for its measured value $\Delta T_{exp} < \Delta T_{th}$ in Eq.(3) we obtain the measured value $\left|dq_o/dT\right|_{exp}$ with the relation

$$\left|\frac{dq_o}{dT}\right|_{exp} > \left|\frac{dq_o}{dT}\right| \tag{4}$$

The pourer the quality of the homeotropic texture, the smaller ΔT_{exp} and the higher the value of $\left|dq_o/dT\right|_{exp}$.

Thus we can conclude that this method for measuring the temperature dependence of the pitch of compensated cholesterics yields an upper limit[7] for dq_o/dT instead of a lower limit as stated by Pleiner and Brand in Ref.1. Combining this with the fact that the Leslie parameter[6] λ_3 need not be zero at the compensation we can draw the conclusion that the experiments on the thermomechanical coupling[7,8] do not need a reinterpretation.

SUMMARY

We have shown that the symmetry of compensated chiral systems differ from that of their achiral counterparts. Consequently the treatment proposed by Pleiner and Brand[1] can not be applied to describe com-

pensated cholesterics or compensated smectics C^*.

The chiral coupling coefficients in cholesterics and smectics C^* (as e.g. the thermomechanical ones) are independent of the helix and do not vanish at the compensation point. Thus the starting point for the reinterpretation[1] of the experiments on thermomechanical coupling[7,8] is incorrect and leads to conclusions which are inconsistent with experimental findings.

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