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TWIST GRAIN BOUNDARY PHASES IN BINARY MIXTURES

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Abstract Two twist grain boundary phases (TGB-A and TGB-C*) have been observed in binary mixtures exhibiting a NAC multicritical point. The observed TGB phases are of very high thermal stability – for some concentrations the temperature range of their existence was as large as 40 K. Optical properties and textures has been investigated. Cano lines in the whole region of the TGB-A phase were observed. The pitch of the helix along with the rotation of polarization plane of light has been measured. A distinct influence of surface interactions on the stability of the twisted smectic A phase has been found.

INTRODUCTION

The recently discovered twisted smectic A phase[1] the existence of which has been theoretically predicted a short time earlier[2] awoke a large interest. Since the discovery a lot of papers has appeared confirming the existence of this twist grain boundary - smectic A (TGB-A) phase in many materials (see e.g. Ref.3-9). Recently, the twist grain boundary smectic C phase (TGB-C) was also observed.[4] In all known cases the thermal stability of TGB phases is quite small – the temperature range of existence rarely exceeds 1 K. The theory of Renn and Lubensky[10] predicts that the TGB-A phase should always appear if the molecular chirality is introduced near the NAC multicritical point in the phase diagram (i.e., where the nematic, smectic A and smectic C phases meet). Similar behaviour could be expected at the IsoNA-point where the isotropic, nematic and smectic A - phases meet[10]. According to Lubensky and Renn[10], the temperature span ΔT of the TGB-A-phase should increase with increasing chirality of the system ($\Delta T \sim p^{-2/3}$, p is the pitch of the helix in the chiral nematic (N^*) phase). Recently Renn[11] predicted the existence of the TGB-C^* phase close to the NAC-point

which is composed of twisted stacks of helical smectic C^* phase. This phase, however, has not been observed up to date.

In all experiments performed hitherto the multicritical points NAC or IsoNA has been realized in homologous series of chiral mesogenic substances with variable number of carbon atoms in alkyl end-chains of the molecule[3,9]. The TGB-A phase was also observed in mixtures of two chiral mesogenic components, each of them possessing the TGB-A-phase in its pure state[7].

EXPERIMENTAL

According to the Lubensky and Renn predictions[10,11] TGB-phases should exist in the vicinity of a N*AC point. To verify this prediction we have investigated many chiral two-component systems exhibiting a N*AC-point in the phase diagram. We used combinations of chiral and non-chiral substances possessing various sequences of phase transitions: SmC-Nematic, SmC-SmA-Nematic, SmC-SmA, SmA-Nematic, Nematic-Isotropic. For preparing of each binary mixture we always applied one chiral and one non-chiral material. The materials has been combined in the way giving binary phase diagrams with multicritical points. Different multicritical points has been obtained: IsoNA, NAC and ACG (the letters used denote various smectic phases, except N and Iso which stay for nematic and isotropic phase, respectively). The substances used in our investigations are listed in Table I. The phase sequences are also given in the table. Blue phases, existing in chiral materials, are omitted. Asterisks denote helical phases.

RESULTS

In two of the investigated binary systems we indeed observed TGB-phases near the NAC-point although none of the components used exhibits such a phase. One of the components of the mixture (di-heptyloxyazoxybenzene, HOAB) is non-chiral and exhibits a nematic and a smectic C phase. The second component is chiral (cholesteryl benzoate, ChB or cholesteryl myristate, ChM in our investigations) and forms a cholesteric (chiral nematic) and a smectic A phase. (The SmA phase is hidden or induced in the case of ChB). Such a choice of mixture components causes that both

TABLE I Substances used for preparing of binary mixtures.

Abbreviation	Phase sequence	Name	Remarks
Nonchiral substances			
POAB	N Iso	di-pentyloxyazoxybenzene	
HOAB	C N Iso	di-heptyloxyazoxybenzene	
6OCB	N Iso	hexyloxycyanobiphenyl	
8O07	C N Iso	4-n-heptyloxyphenyl-4′-n-octyloxy benzoate	
NCB-84	C A N Iso	Trade name NCB-84	Merck
Chiral substances			
Ch B	(A)N^* Iso	Cholesteryl benzoate	hidden SmA
Ch L	A N^* Iso	Cholesteryl laurate	
Ch M	A N^* Iso	Cholesteryl myristate	
CE 3	C^* N^* Iso	Trade name CE 3	BDH
CE 8	I C^* A N^* Iso	Trade name CE 8	BDH
ZLI 4421	C^* A Iso	Trade name ZLI 4421	Merck

competing factors, determining the occurrence of a TGB-phase, i.e. chirality and the tendency of creating smectic layers, increase simultaneously with the concentration of the chiral component. This joint action leads to an enormous enhancement of the TGB-phase stability. In some mixtures we observed TGB-phases in the temperature interval larger than 40 K. The phase diagram of the two-component system HOAB/ChB is shown in Fig.1. The phase diagram of the system HOAB/ChM is very similar.

As Fig. 1 shows, the temperature region of existence of the TGB-A-phase increases with the concentration of the chiral component ChB. Simultaneously, the smectic A phase becomes more stable. The last statement is proved by the appearance of the induced (or hidden) smectic A phase at high concentrations of ChB. At molar

fractions of ChB larger than 0.1 another TGB phase appears, presumably the TGB-C* phase. The phase diagram shown in Fig. 1 was constructed on the basis of microscope observation performed for pure substances, several mixtures of defined concentrations and contact preparations. Several optical methods (selective reflexion, optical activity, refractometry) were also used for identification of phases and detection of phase transitions. Phase transitions were also detected by dielectric and calorimetric measurements.

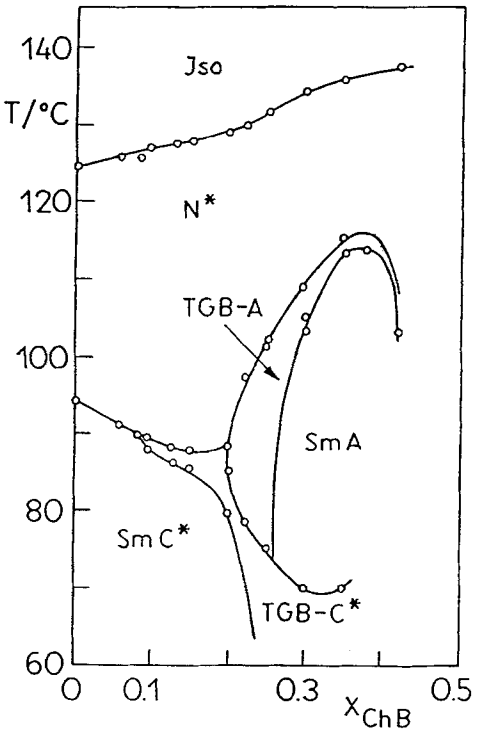


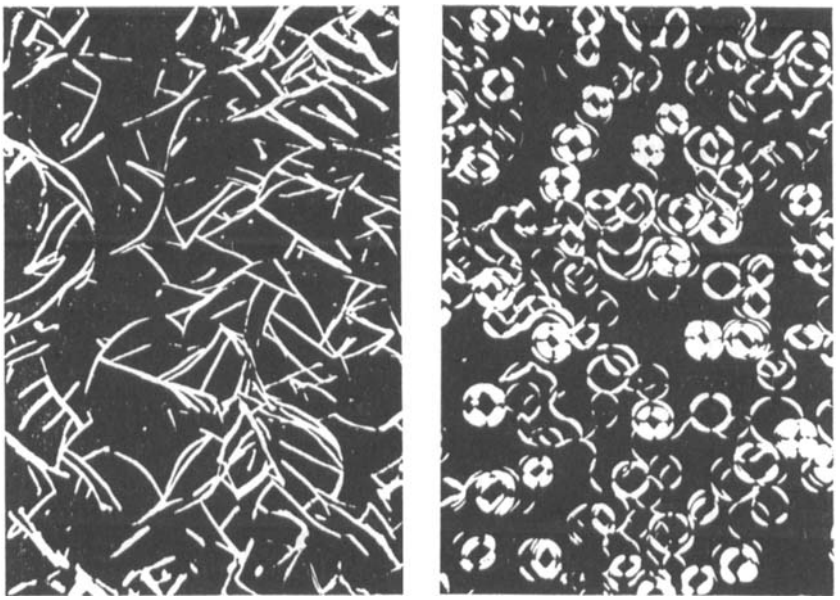
FIGURE 1 Phase diagram the system HOAB/Cholesteryl benzoate.

The textures observed in our mixtures were very similar to that described in the literature[1,4,7]. They also resembled the textures we have observed in other substances possessing TGB-A phase (for instance, in "standard" TGB-substance 14P1M7[1,3,5]). In what follows, the description of textures and other properties of the TGB-phases will be done using the example of mixture HOAB/ChB with 0.25 molar fraction of ChB (later, we call this mixture H25CB).

The observed textures are strongly influenced by the method of preparation of the surface of the cell. In case of planar boundary conditions (preferring the Grandjean-texture in the cholesteric phase) we observed a similar Grandjean-like texture in the TGB-A phase. In this case the transition point cholesteric-TGB-A was easily noticeable due to a distinct change in the appearance of characteristic defect lines, so called "oily streaks". In the low temperature phase these defects became more diffuse and gradually vanished after few transitions cholesteric – TGB-A forth and back. In wedge-shaped cells the Grandjean - Cano steps were observable if the orientation of the sample was

uniform.

In case of homeotropic boundary conditions (confining glass plates coated with a layer of cetyl-methyl-ammonium bromide, CTAB), the observed textures depended strongly on the thickness of the sample. During cooling of samples of about 20 μm thickness we observed at 100°C the appearance of light, thin lines (filaments). The density of filaments increased with decreasing temperature and they merged gradually giving finally a texture similar to the Grandjean-texture with many "oily streaks". This texture resembled that shown in Fig. 3 of Reference 8. The situation in thinner cells (10 μm and less) was different. In this case, at 100°C filaments appeared (Fig. 2a) which has been replaced at temperatures few degrees lower by regular, non-twisted structure of smectic A (homeotropic texture). Both textures, filament and homeotropic, were stable during some days at constant temperature.



a b

FIGURE 2 Textures of the TGB-A phase in the mixture HOAB + 0.25 mol ChB
a) close to the cholesteric phase (98°C)
b) close to the TGB-C* phase (78°C).

On further cooling of the sample the filaments reappeared at about 78°C. In this case, however, the appearance of filaments was different (Fig. 2b). The most striking

feature of this new kind of filaments is their spiral shape. The direction of spiraling was the same for all spirals - in our case all growing filaments were turning to the right (as viewed in the microscope).

At 75°C we observed a phase transition to a new phase which existed in a broad temperature region down to at least 60°C. This transition was also observed by dielectric and optical measurements (Fig. 3,4). We suppose that the phase below 75°C is the TGB-C* phase which exhibits not only the twisting of the smectic layers but also a twist of the tilt direction within the layers. This phase, the existence of which in the vicinity of N*AC point in chiral systems was predicted by Renn[11] has not been observed up to now. The assignment of the low temperature phase to a TGB-C* structure is based on three observations:

1° In thin samples, after fast cooling from the homeotropic texture existing below 95°C the obtained texture contains a small number of spiral filaments. The areas between the filaments exhibit a texture typical for regular twisted smectic C* phase (bluish colour of optical rotation usually observed in SmC* phases with a quite high tilt angle $\theta \sim 45°$).

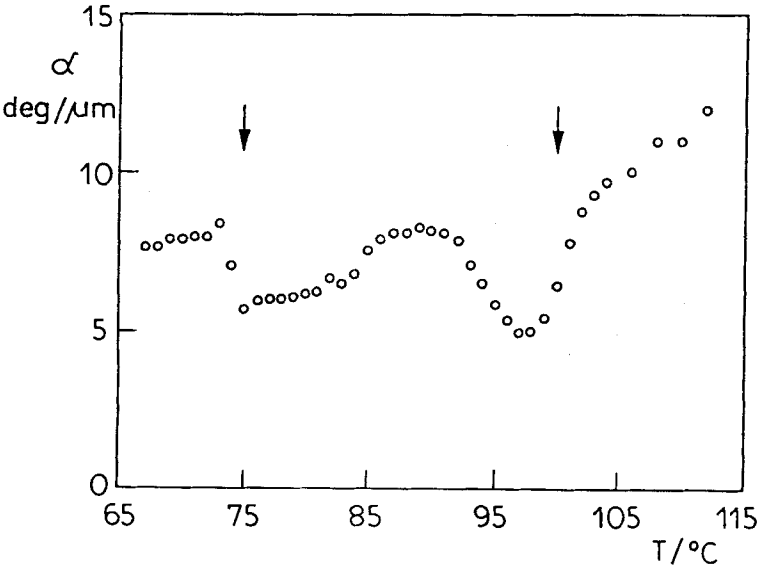


FIGURE 3 Rotation of the light polarization plane as function of temperature in the mixture HOAB/0.25 CB measured at wavelength 576 nm. Arrows indicate phase transition temperatures.

2° The shape of filaments and the way in which they are coming into existence suggests the lowering of the symmetry of the low-temperature phase.

3° The unusual light scattering-phenomenon which, at the first sight, could be interpreted as Bragg scattering at a three-dimensional lattice .

The twisted structure of all phases existing in the described mixture H25CB is clearly confirmed by optical measurements. In Fig. 3 the rotation of the polarization plane of light in various phases is shown. The results shown in Fig. 3 were obtained using a wedge-shaped sample. The thickness of the sample, needed for a rotation of the polarization plane by π or its multiple, was used for the calculation of the optical rotation.

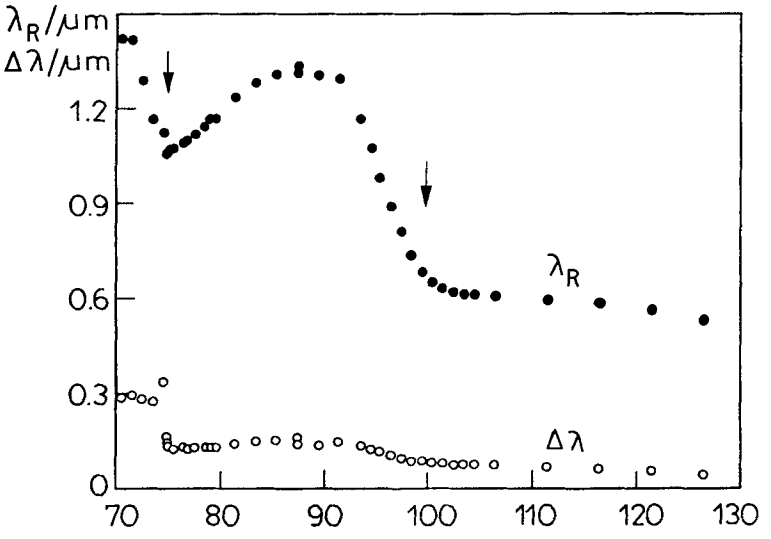


FIGURE 4 The wavelength of the selective reflexion in the mixture HOAB/0.25ChB as function of temperature. Phase transitions temperatures are indicated by arrows.

The selective reflexion was measured in a plane-parallel sample of 30 μm thickness using a Carry 19 spectrometer. The results of measurements are shown in Fig. 4. The optical measurements in the TGB-C*-phase could only be performed close (about 5 K) to the transition TGB-A → TGB-C*. At lower temperatures the homogeneity of the sample became worse and the selective reflection line broadened lowering the

measurement accuracy to the great extend. However, the TGB-C* phase was stable down to the crystallization temperature (below 60°C).

DISCUSSION

According to the prediction of Renn and Lubensky[10] we have found TGB phases at the chiral NAC-point. However, Renn and Lubensky expect that these phases should always exist close to the NAC-multicritical point if chirality is introduced . This is clearly not the case. Our investigations proved that the occurrence of TGB-phases is rather an exception than a rule. Among many binary systems we have investigated (c.f. Table I) only in mixtures of HOAB and some cholesteryl esters exhibiting a smectic A phase TGB-phases exist. Mixtures of cholesteryl esters with other non-chiral substances exhibiting SmC phase as well as those of HOAB with other chiral substances did not show TGB-phases. This observation seems to suggest that the existence of a multicritical point in the phase diagram is a necessary but not sufficient condition for the existence of a TGB-phase. We presume that some specific intermolecular interactions are also necessary for the stability of such a phase. The present experimental observations do not gives, however, a sufficient basis for any more detailed hypothesis.

The textures and apparent phase transitions observed in mixtures exhibiting TGB-phases are dependent on the sample thickness. In thin samples regular structures without layer twisting are preferred. The critical thickness, below which the TGB-A phase becomes unstable with respect to the SmA phase was about 10 μm in the H25CB mixture. This value exceeds many times the pitch of the helix in bulk samples (about 1 μm, see Fig. 4). Thus, we are not dealing in thin samples with the usual unwinding of the helix due to the surface interactions (well known in cholesteric and smectic C* phases) but rather with a stabilization of regular non twisted smectic phases. This effect of surfaces seems to demonstrate that the difference in free-energy density of a usual, regular smectic (SmA or SmC) and that of a twist grain boundary phase (TGB-A or TGB-C*) is small. This conclusion is supported by the observation that the transition enthalpy between mentioned phases is usually quite small[8,9]. In our calorimetric investigations performed for mixtures HOAB/ChB of various concentrations the transi-

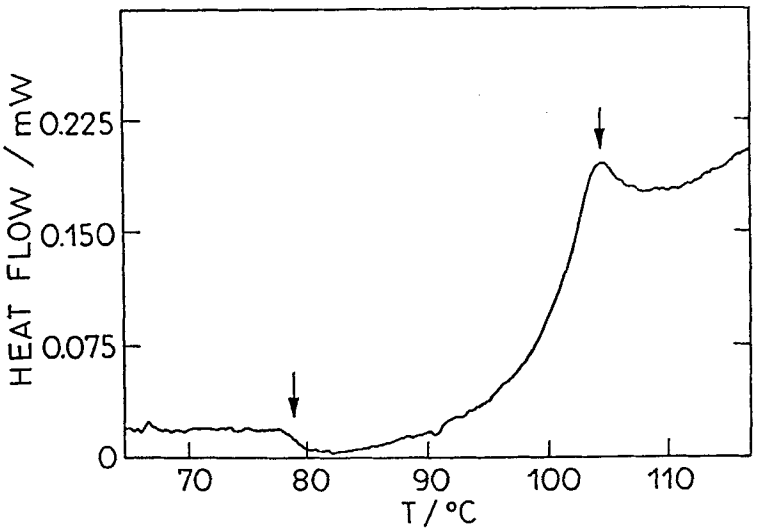


FIGURE 5 DSC-trace of the mixture HOAB/0.25 ChB obtained at heating rate 5 K/min. Arrows show phase transitions.

tions cholesteric→TGB-A and TGB-A→TGB-C* were hardly detectable as well (Fig. 5).

The effect of surfaces is also visible at the transition TGB-A → TGB-C* (at about 75°C in the mixture H25CB). In thin samples (below 14 μm) the regular, non-twisted structure of SmA exists above 78°C. At slightly lower temperature spiral filaments appear which are turning clockwise while growing. If the cooling rate is low (about 1 K/min) filaments are gradually filling the whole sample volume and another TGB-phase appears. The texture of this phase resembles diffuse texture of TGB-A. However, if the cooling is rapid the filaments hardly have time to develop at the phase transition and the sample assumes the texture of the usual, regular smectic C* without twisted layers (schlieren texture) divided by small number of filaments. This observation is a strong argument that the phase below 75°C is the TGB-C*-phase indeed.

CONCLUSIONS

In mixtures of HOAB and some cholesteryl esters (ChB,ChM) we discovered twist grain boundary phases TGB-A and TGB-C* of extraordinary high thermal stability with a large range of existence of the TGB phases up to 40 K. The TGB phases in these mixtures exist in the vicinity of the multicritical N*AC* point. This observation supports

the theory of Renn[11]. We observed a new kind of textures slightly above the phase transition TGB-A → TGB-C*. The most characteristic property of these textures are spiral filaments of constant handedness. We have performed measurements of helical pitch and of optical activity in both observed TGB-phases. Our observations demonstrated a strong dependence of the phase structure and phases sequence on the sample thickness. These observations seem to prove that the lowering of free energy of the TGB phase gained due to smectic layer twisting (forced by high chirality) is compensated by an increase of the elastic energy of array of defects (screw dislocations). The final outcome - creation of twist grain boundary phase or a regular, non-twisted smectic phase - is a result of the delicate interplay between elastic and chiral forces and can be easily inverted, e.g. by relatively weak surface interactions.

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