Chapter 5

Phase Diagram Involving the Twist Grain Boundary Phase in the Vicinity of a Virtual Cholesteric-Srnectic A-Smectic C* Point

5.1 Introduction

Tlie nature of tlie nematic - smectic A - smectic C (NAC) meeting point has been tlie subject of extensive experimental studies[1,2]. These studies have been made all the more interesting by the recent predictions[3,4,5] of the cliiral version of tlie Chen-Lubensky(CL) model[6]. Depending on the strength of chirality, this theory expects different topologies for the meeting point,. When the chirality is zero one gets tlie usual NAC ~nulticriticalpoint,. In tlie presence of a cliiral field tlie theory proposes two alternatives depending on whether tlie system behaves like a type I or type II superconductor. In tlie case of the former, tlie cliiral nematic (cholesteric or Ch), smectic A (A) and cliiral smectic C (C*) phases meet at a critical end point. In type II systems tlie meeting point is preempted by the appearance of a new type of phase, namely, tlie *Twist Grain Boundary* (TGB) phase[3] which is the liquid crystal analogue of the Abrikosov flux lattice in superconductors[7]. On the experimental side, tlie zero chirality case - tlie NAC multicritical point - is well established[1,2,8]. For the chiral version, two different types of meeting point, viz., a triple point[9] and a multicritical point[10] have been reporled. However, the TGB phase, recognised to be identical[11] to tlie A* pliase discovered by Goodby et al[12], has not been found near the Cli-A-C* meeting point. This chapter describes tlie observation of a pliase diagram in which tlie TGB pliase appears, as expected by the theory, near a virtual Ch-A-C* meeting point.

5.1.1 Analogy between the Normal-Superconductor and the N-A transitions

Tlie basis of tlie analogy between the normal-superconducting transition in metals and tlie nematic-smectic A (N-A) transition in liquid crystals is that the ordered phases of both smectic A and superconductors are cliaracterised by a lion-vanishing complex order parameter ψ [13]. For a superconductor tlie order parameter is the wave function whereas for tlie smectic A pliase it is the mass density wave. The coupling between the smectic order parameter and tlie director fluctuation 611 is similar to that between the superconductor order parameter and tlie vector potential A. Furthermore, tlie spatial average of tlie twist n. (V $\times$ n) corresponds to the magnetic induction B. The field h conjugate to the twist, corresponds to the magnetic intensity H. Thus, tlie cholesteric phase is tlie analogue of a normal metal in an external magnetic field. Tlie expulsion of twist occurring at tlie cliolesteric to smectic A transition is then tlie liquid crystal analogue of tlie Meissner effect.

Renn and Lubensky extended[3] tliese arguments to find tlie analogue of tlie Abrikosov flux lattice phase in liquid crystals containing cliiral molecules. Supercoiiductors have been classified into type I and type II depending upon tlie value of the Ginzburg parameter $k \equiv \lambda/\xi$, where λ is tlie penetration depth (tlie thickness over which a deformation, for e.g., a weak magnetic field, penetrates tlie surface of the normal metal) and ξ is the coherence length (tlie distance over wliicli the local perturbation affects tlie amplitude of ψ). For type I superconductors, $k < \frac{1}{\sqrt{2}}$ and for type II, $k > \frac{1}{\sqrt{2}}$. If tlie material is a type

I superconductor then below the critical temperature the field lines of the applied magnetic field are completely expelled. This is the Meissner effect. On the otlier hand a type II superconductor exliibits a phase intermediate between tlie normal and superconducting phases, in which the magnetic field lines form a triangular array of vortices. The lattice of vortices is known as tlie Abrikosov flux lattice[7]. Tlie triangular lattices of vortices and tlie structure of a vortex line is shown in Figure 5.1. In type-I systems, fluctuations drive tlie second order mean-field normal to superconducting transition first order[14]. If the N-A transition behaves like a type I transition then it would always be first order and there would be no flux lattice analogue. In type II systems fluctuations are believed to lead to a second order transition characterised by the inverted XY model behaviour[15]. Although tlieoretical studies indicated that N-A transition belongs to an inverted XY class, experiments have shown XY class behaviour for a number of materials[16]. As such one can expect lo observe tlie liquid crystal analogue of the Abrikosov phase.

Renn and Lubensky have argued that tliis phase can be realised when the chiral molecules are present in tlie system and would consist of a regular array of parallel twist grain boundaries composed of regularly spaced parallel twist dislocations with axes that rotate from one grain boundary to the next and termed it as tlie ***Twist*** *Grain Boundary* (TGB) state. Tlie schematic representation of the cholesteric(Ch) pliase and tlie TGB pliase witli its pitch axis parallel to the X axis are shown in Figure 5.2. In tlie case of Ch phase the director $\hat{n}$ lies tlie YZ plane and rotates in a helical fashion as the coordinate X along the pitch axis increases. Tlre average configuration of tlie director in TGB pliase is very

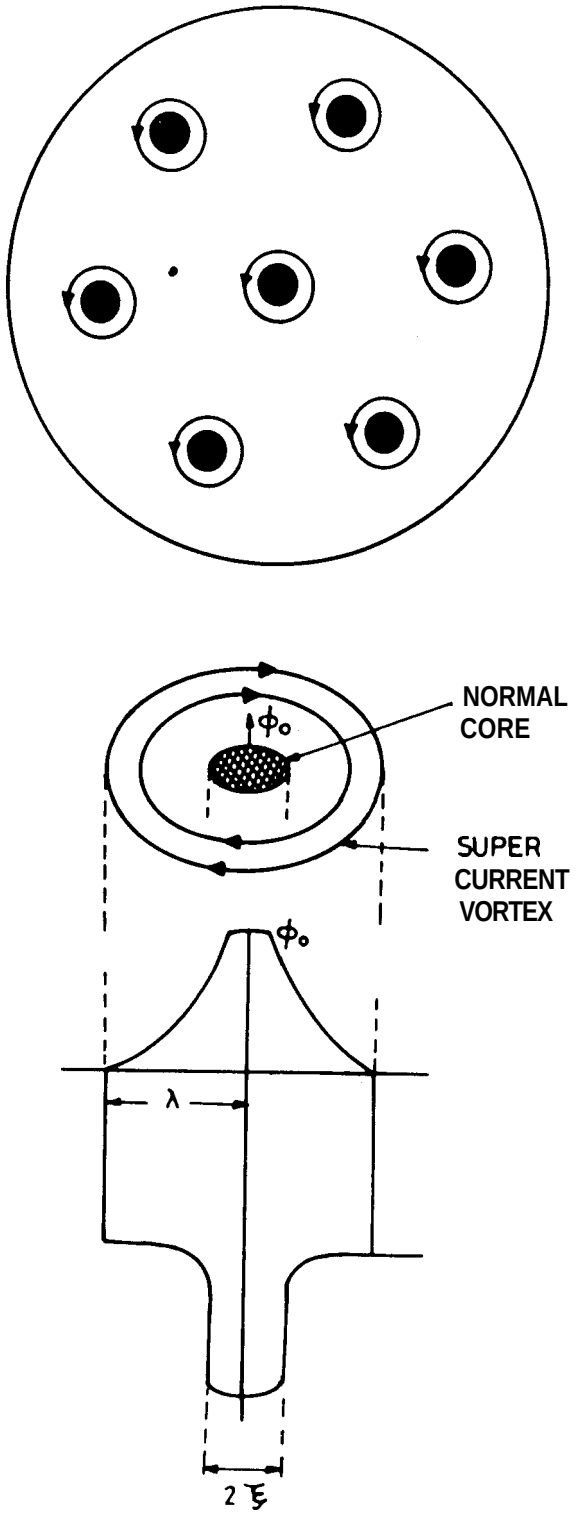


Figure 5.1: (a)The triangular lattices of vortices. (b) Structure of a vortex line.(From A.V.Narliker and S.N.Ekbote, *Superconductivity and superconducting materials*, p.43 *(1983))*.

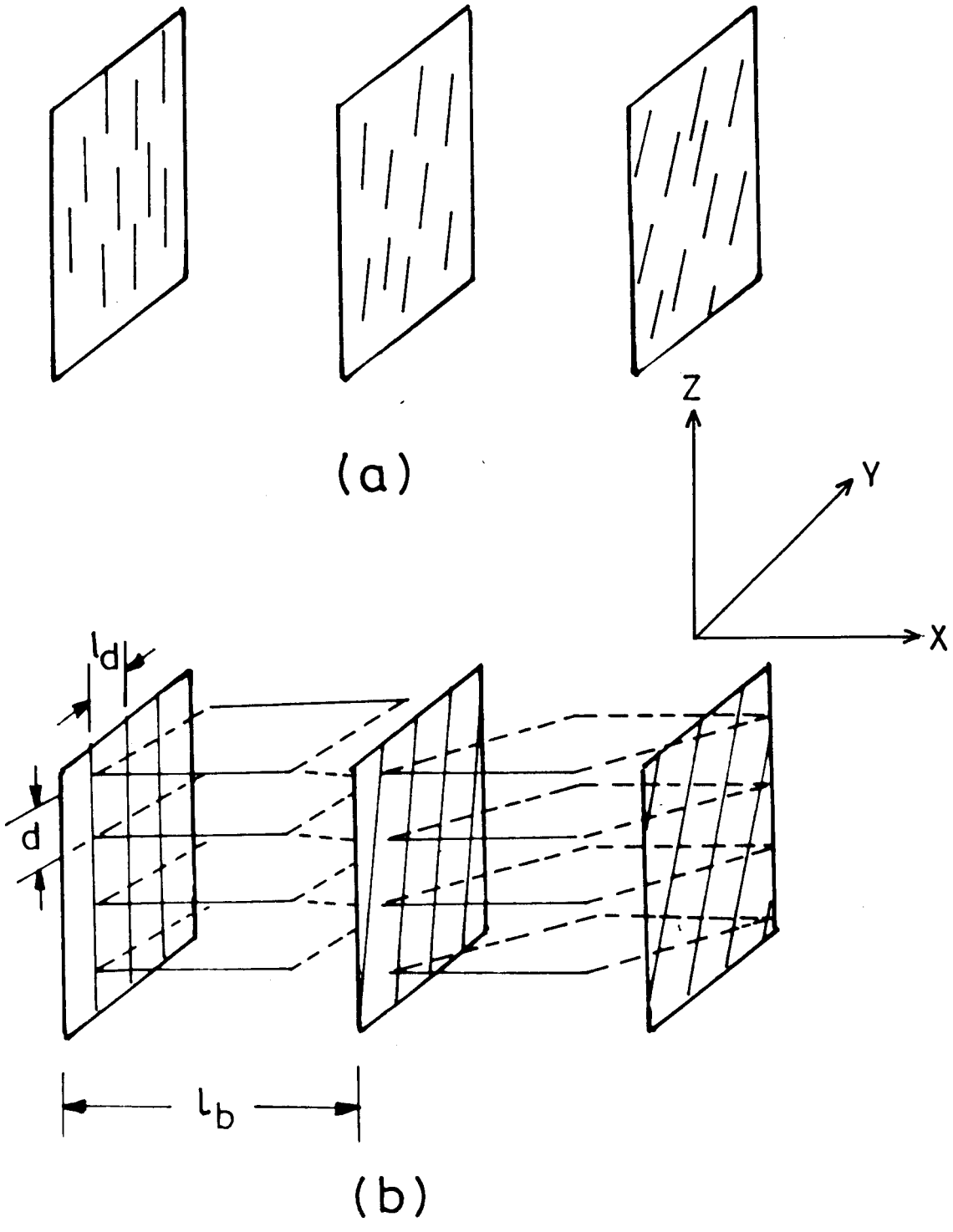


Figure 5.2: (a) Schematic representation of a cliolesteric(Ch) liquid crystal. (b) Schematic representation of the TGB state.(from Ref.[4])

similar to tliat of tlie Cli pliase. For tlie TGB state, there are regularly spaced twist grain boundaries separated by a distance l_b. Eacli grain boundary consists of regularly spaced screw dislocations separated by a distance l_d. Tlie configuration of molecules between tlie grain boundaries is essentially identical to tliat of tlie A pliase witli regularly spaced layers separated by a distance d.

5.1.2 Chiral Chen-Lubensky(CL) Model

A phenomenological model introduced by Chen and Lubensky[6] has been very successful in explaining experimental observations in tlie vicinity of the NAC multicritical point. Lubensky and Renn have generalised[4,5] this model to describe the effects of chirality on tlie NAC point and its immediate neighbourhood. One essential feature of these models is that the C phase is induced by the tilt of the nematic director relative to the layer normal. Tlie sign of the coefficient of tlie transverse gradient term $C_\perp$ decides wlietlier tlie ordered pliase is A or C phase. In the latter model in addition to tlie reduced temperature r $\sim$ T-T_{NA} (where T_{NA} is the N-A transition temperature) and the coefficient $C_\perp$ used in the NAC model, the chiral field li is introduced as one more variable. When h=0, tlie phase diagram in the $C_\perp$ - r plane, reduces to tlie original NAC diagram (Figure 5.3(a)). Notice tliat all tlie pliase boundaries NA, NC and AC are second order at tlie meeting point(P) and thus it is a multicritical point. When h$\neq$0 there are two possibilities depending upon wlietlier the system behaves like a type I or type II superconductor. If the material is type I tlie Cli-A and Ch-C* transitions would be first ostler whereas tlie A-C* transition is second order and terminates at a critical end point CEP(See Figure 5.3(b)). More in-

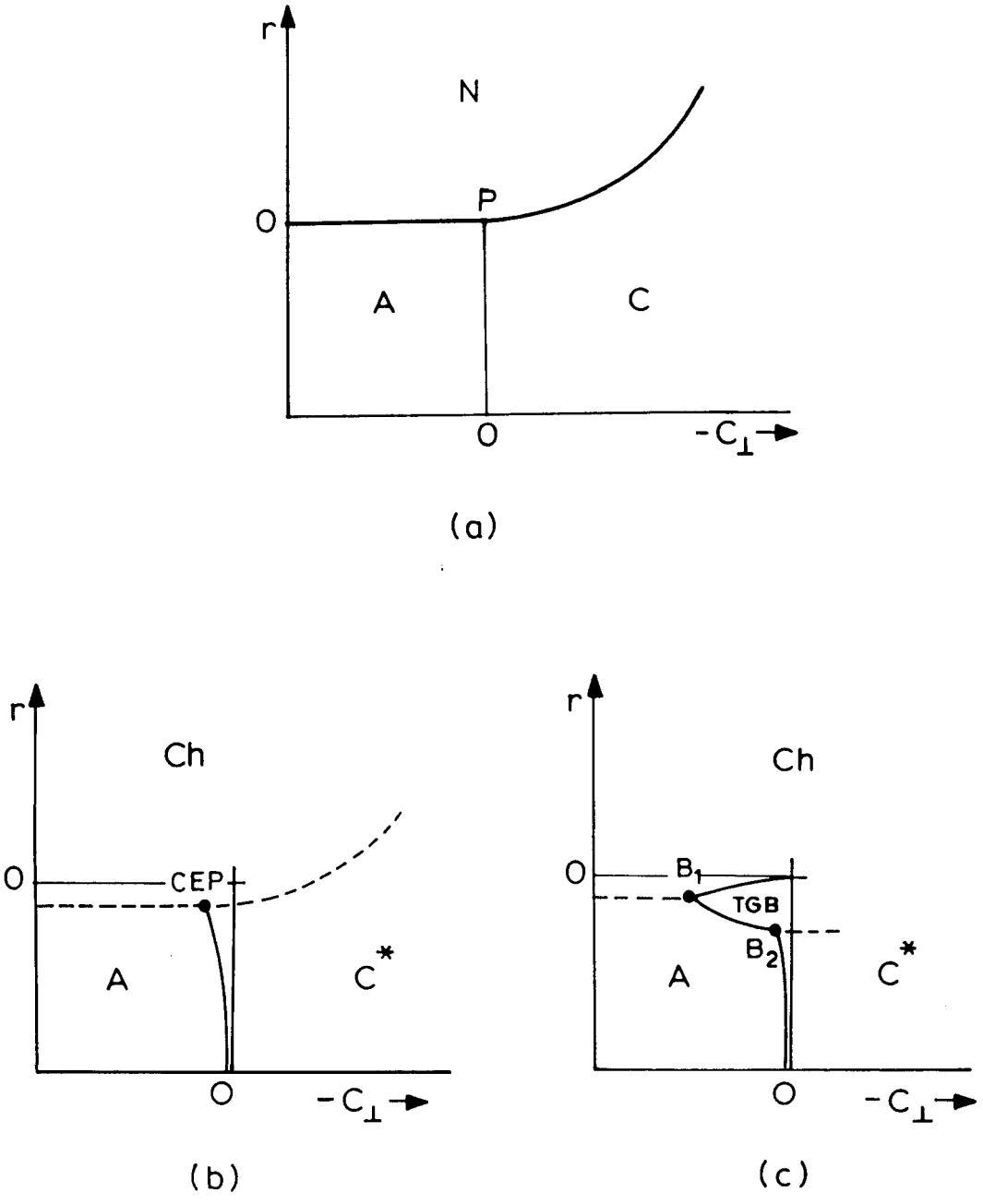


Figure 5.3: (a) Mean-field phase diagram for tlie Chiral CL model in the r-$C_\perp$ plane when h=0. P is tlie NAC multicritical point. (h) Mean-field pliase diagram for the chiral CL model when h≠0 for type I systems. Tlie dashed line is the first order boundary and the solid line second order. Tlie A-C* transition line terminates at a critical end point(CEP). *(c)* Mean-field phase diagram when h≠0 for type II systems. The TGB phase intervenes between tlie Ch and A phase. B_1 and B_2 are bicritical points.

teresting things happen when the system is type II. Tlie TGB pliase intervenes between Cli and A phases as shown in Figure 5.3(c). Both tlie Cli-TGB and TGB-A pliase boundaries are second order whereas Cli-A would remain first order. Thus tlie point B_1 at which Cli, A and TGB pliases meet is a bicritical point. Further analysis[5] of tliis model brought out more features in this pliase diagram viz., appearance of the tilted TGB pliase etc. We will not discuss them here.

5.1.3 Experimental background

At around tlie same time as tliat of tlie tlieoretical prediction[3] of tlie TGB phase, Goodby et al, reported[12] tlie discovery of a new liquid crystalline pliase, wliicli they termed as A* pliase, between the isotropic and the cliiral smectic C (C*) pliase in some members of tlie homologous series (S)-1-methylheptyl 4′-[(4″ -n -alkyloxyphenyl) propionoyloxy-biphenyl-4-carboxylate] (nP1M7). The experimental temperature-alkyl chain length phase diagram for the homologous series nP1M7 is shown in Figure 5.4. Tlie A* pliase has properties consistent with its being identified with the theoretically predicted TGB pliase. X-ray scattering intensities from unaligned samples of tlie A* pliase are similar to those of a powdered A phase. Experiments using aligned samples sliowed tliat the scattering intensity is intense on a cylinder with a symmetry axis coincident with the pitch axis[11] as predicted by tlie tlieory for tlie TGB pliase. Also, optical microscopic studies sliowed cliolesteric-like textures for tlie A* phase[12]. The pitch axis in the A* phase is rotated by 90^o with respect to tliat in the C* pliase suggesting that tlie pitch axis lies in the plane of tlie layers rather than

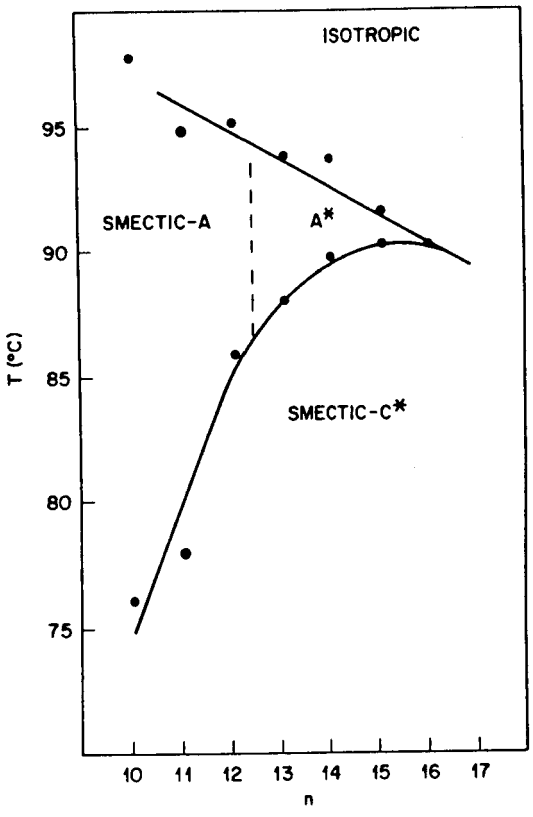


Figure 5.4: Experimental phase diagram for tlie homologous series nP1M7. (from Ref.12).

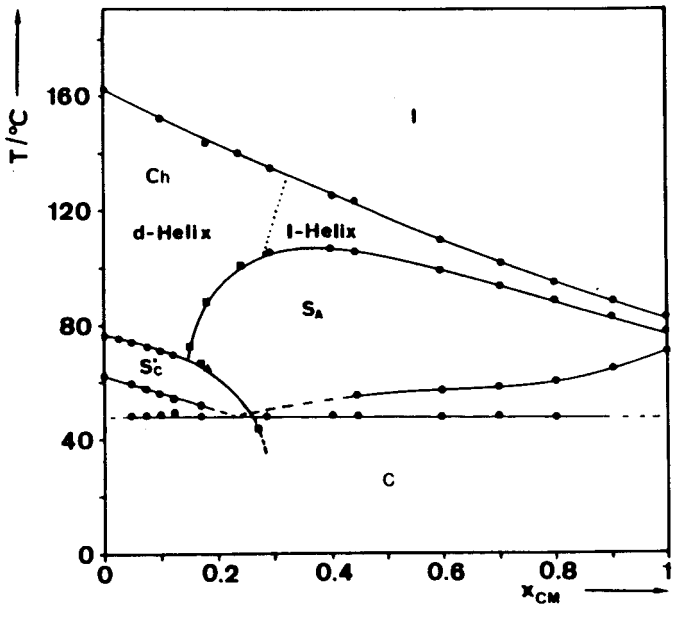


Figure 5.5: Temperature-concentration(T-X) phase diagram of the CE3/CM binary system. The dashed line is the helix inversion line (from Ref.10).

perpendicular to the layers, as in tlie C* phase. Tlie calorimetry showed clear anamolies[12,17] indicating that the A* and C* phases are indeed distinct tlier-modynamical phases. Lavrentovicli et al, observed in a binary liquid crystalline system, the TGB phase to occur between the Ch and the A phase[18]. Later, Slaney and Goodby found the Cli - A* - A phase sequence to occur in a single component system[19]. Pollmann and Schulte have reported an interesting phase diagram(See Figure 5.5) in wliicli tlie Cli, A and C* pliases meet at a multicritical point and no TGB phase was observed[10]. This could be perhaps due to the following reason. In tlie vicinity of the multicritical point tlie sign of tlie Ch pitcli changes giving rise to a helix inversion line (shown as a dashed line in the figure). The large pitch of tlie Ch phase near the meeting point would reduce the value of the chiral field, thus probably suppressing the TGB phase.

5.2 Experimental

5.2.1 Materials used

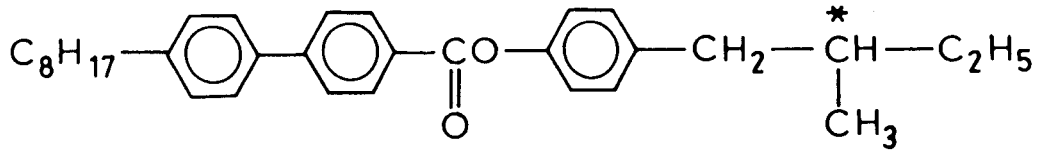
Experiments have been carried out on binary mixtures of 4-(2'-methyl butyl) phenyl 4'-n-octyl biphenyl -4-carboxylate(CE8-from BDH) and 4-n-dodecyloxy biphenyl-4'-(2'-me thyl butyl)benzoate (C12)[20]. Tlie structural formulae and the transition temperatures of tlie materials are given in Table 5.1.

5.2.2 Experimental techniques

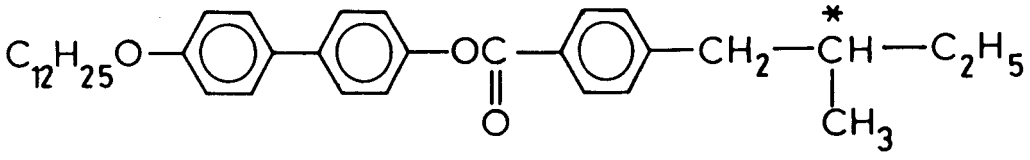
To establish the existence of the TGB phase, optical microscopy, DSC, X-ray diffraction and selective reflection techniques have been employed. Tlie DSC

Table 5.1: Structural formulae and transition temperatures (°C) of the materials used.

CE8



C12



Material	Iso		BP		Ch		A		C*
CE8	.	139.8	.	135.9	.	134.1	.	84.4	.
C12	.	137.7	.	135.45	.	–	.	117.6	.

Iso= isotropic phase, BP = Blue phase,

Cli = cliolesteric, A = smectic A,

C* = chiral smectic C.

and X-ray diffraction methods have been described in tlle previous chapters. Tlic details of the selective reflection method will be described in 55.3.4.

5.3 Results and Discussion

5.3.1 Optical microscopic studies

Tlic partial temperature concentration (T-X) phase diagram, obtained using a programmable hot stage(Mettler FP82) in conjunction with a polarising microscope, is shown in Figure 5.6. It is seen that for X < 0.32 (X is the weight fraction of C12 in CE8) tliere is a direct Ch-A transition. For X > 0.32, a new phase appears which grows at the expense of the A pliase and gets bounded near X = 0.7. Optical microscopic studies showed that on cooling, the Ch phase transforms into tlie A phase through an intermediate pliase.

Tlie microphotograph obtained for X = 0.6 at 118° C is shown in Figure 5.7. Tlie transition to the intermediate phase is signalled by tlie appearance of the filament texture, characteristic of the TGB phase[12,19]. As tlie temperature is lowered to the A pliase this pattern vanishes resulting in a homeotropic texture. On further cooling tlie A phase goes to a C* phase.

For X > 0.62, there is no A phase and for mixtures with 0.62 < X < 0.7 tlie sequence Ch-TGB-C* is seen. It is interesting to note that for any concentration the TGB phase occurs at temperatures above tlle A and/or the C* phase, a feature observed earlier[19] and also predicted by the theory.

Tlie plane texture (molecular director parallel to the substrate) of tlle TGB pliase shows that it has a lielical structure, and the helical axis lies in a direction

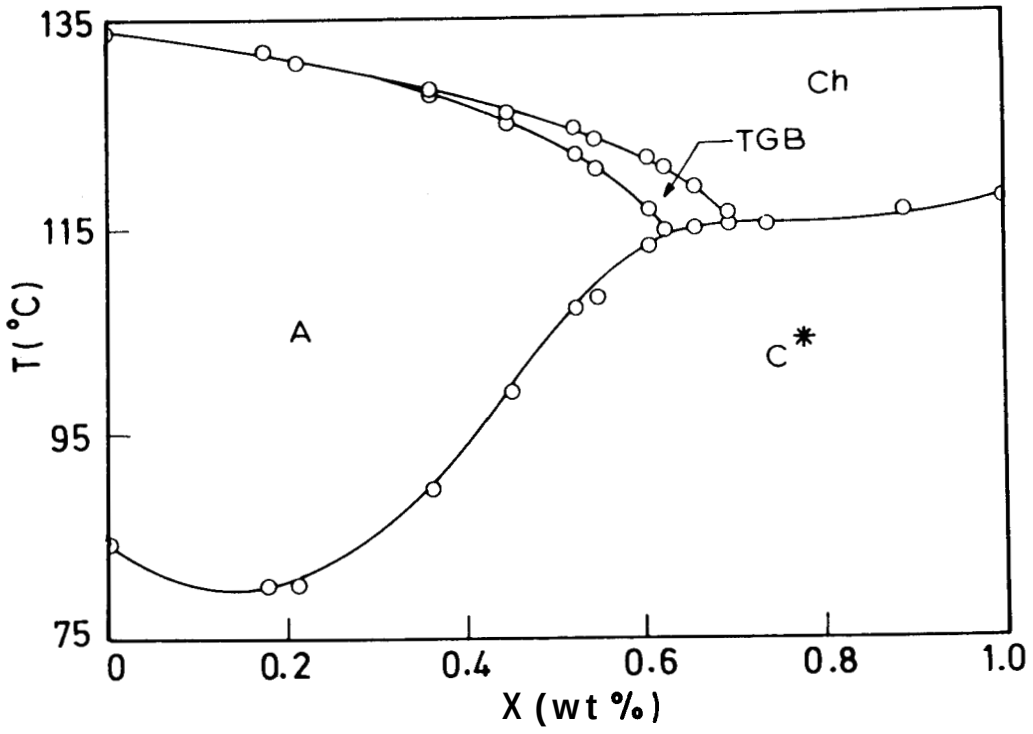


Figure 5.6: Partial temperature-concentration (T-S) diagram for CE8/C12 binary system. X = weight% of C12 in the mixture. The solid lines are meant to serve as a guide to the eye.

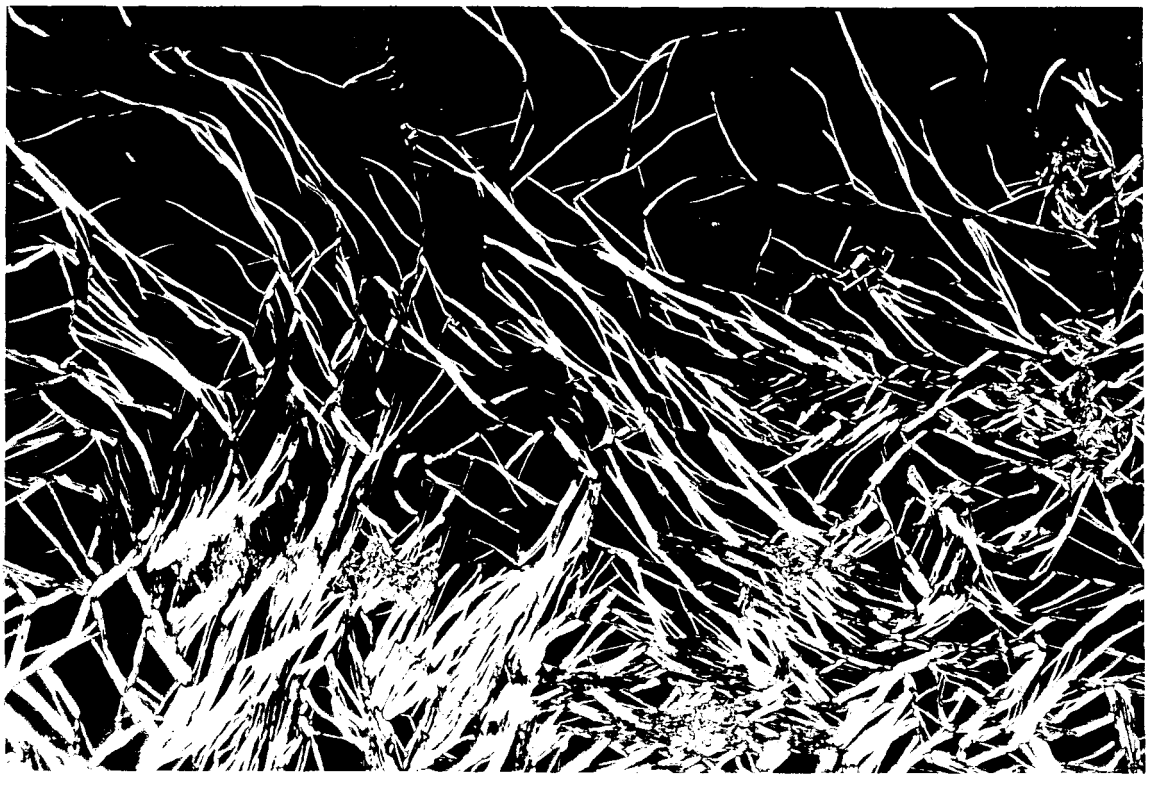


Figure 5.7: Tlie filament texture characterstic of the TGB phase as seen when tlie sample is cooled from the cholesteric phase. Tlie photograph was taken at **3.6** °C below the Cli–TGB transition point in X = 0.6 sample (Magnification: x 125)

parallel to the layers of tlie phase. Thus, the liquid crystal phase has a twisted layer structure. Selective reflection measurements confirming this structure will be described later.

5.3.2 Differential Scanning Calorimetric (DSC) studies

The differential scanning calorimeter scan for X = 0.6 and 0.66 are shown in Figures 5.8 and 5.9. It is observed that the Ch-TGB transition is quite strong but relatively broad[21]. In contrast, tlie TGB-A transition in X = 0.6, is extremely weak, nevertheless clear on an enlarged scale (see inset of Figure 5.8). Tlie A-C* transition is sharp and appears to be second order wliile the TGB-C* transition in X = 0.66, is quite strong. All these features are in good agreement with earlier observations[12,18,19].

5.3.3 X-ray diffraction studies

Layer spacing (d) measurements were carried out using samples filled in Lindemann glass capillaries and employing a computer controlled Guinier Xray diffractometer (Huber 644). The temperature dependence of d for X = 0.6 is shown in Figure 5.10. On increasing the temperature d increases continuously in the C* phase, saturates in tlie A phase at a relatively constant value and continues to be so in the TGB phase. For ;'; = 0.66 also (Figure 5.11), the d value increases with increasing temperature in the C* pliase and attains a constant value in tlie TGB pliase. The line profiles in the C*, A and TGB pliases were found to be comparable but increase in width on going to tlie Ch phase. In both

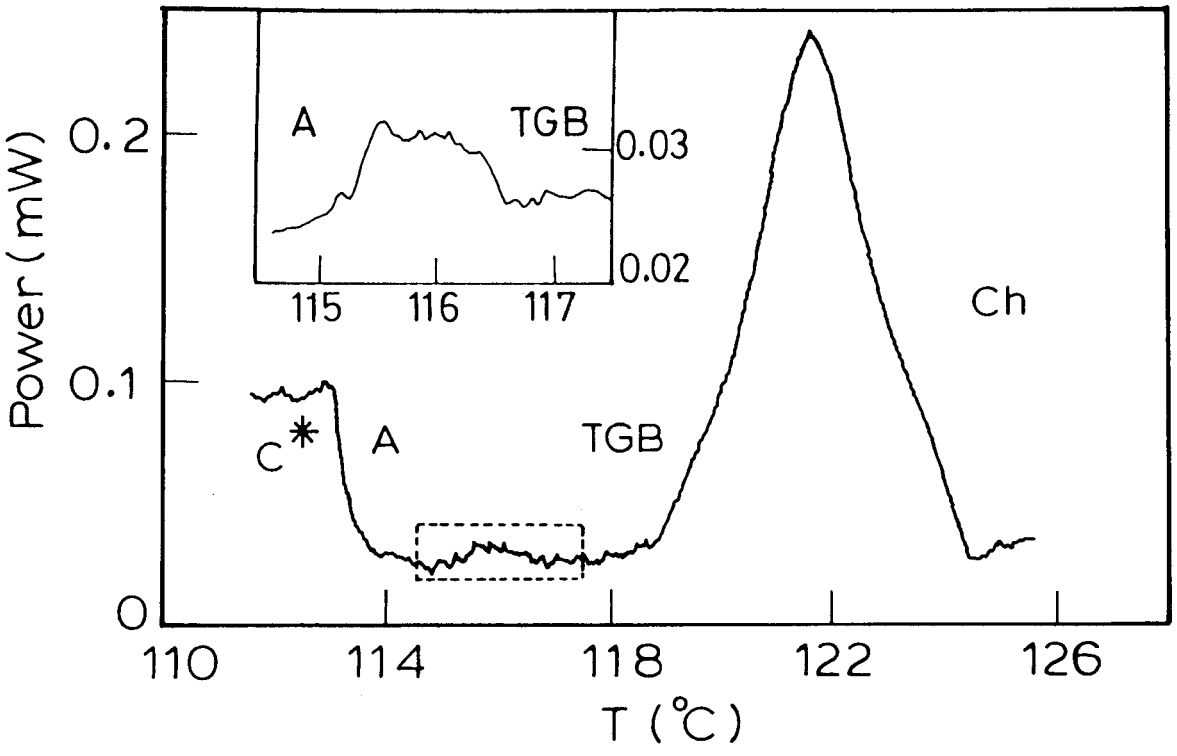


Figure 5.8: Differential scanning calorimeter scan obtained on heating (rate 5 °C/min) for X = 0.6. The region enclosed in dashed lines is shown on an enlarged scale as an inset.

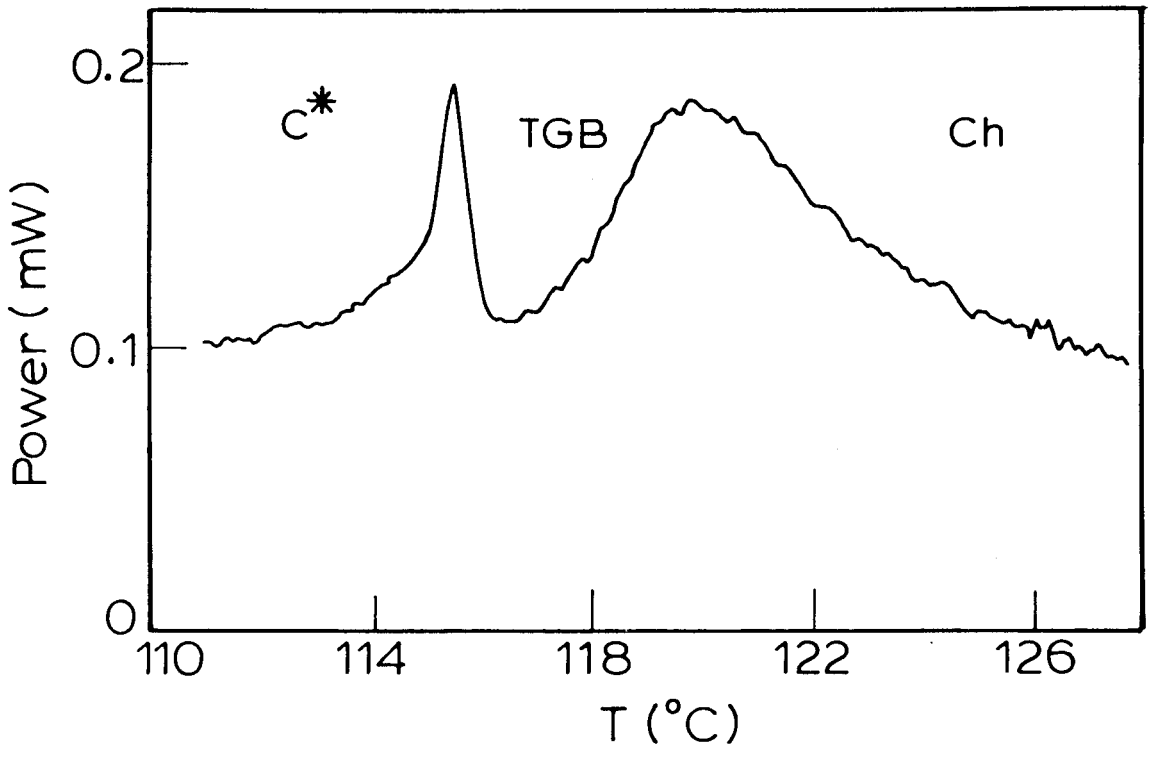


Figure 5.9: Differential scanning calorimeter scan obtained on heating (rate 5 °C/min) for X = 0.66.

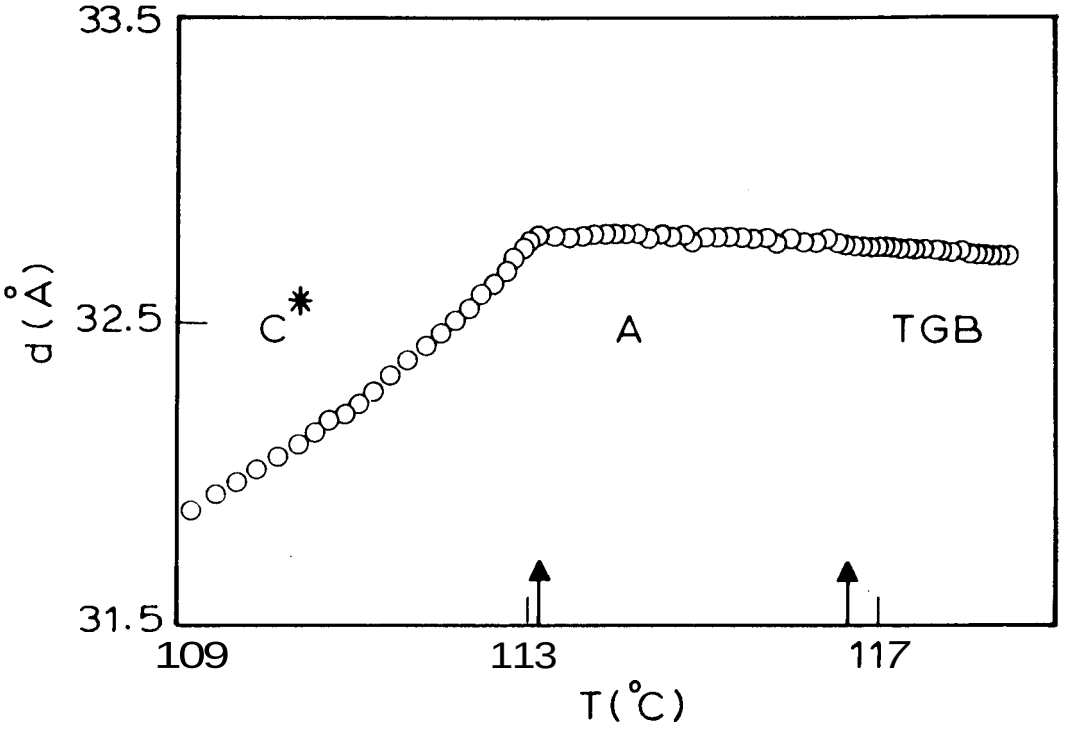


Figure 5.10: Temperature dependence of the smectic layer spacing for X = 0.6. The arrows indicate the C*-A and A-TGB transition temperatures.

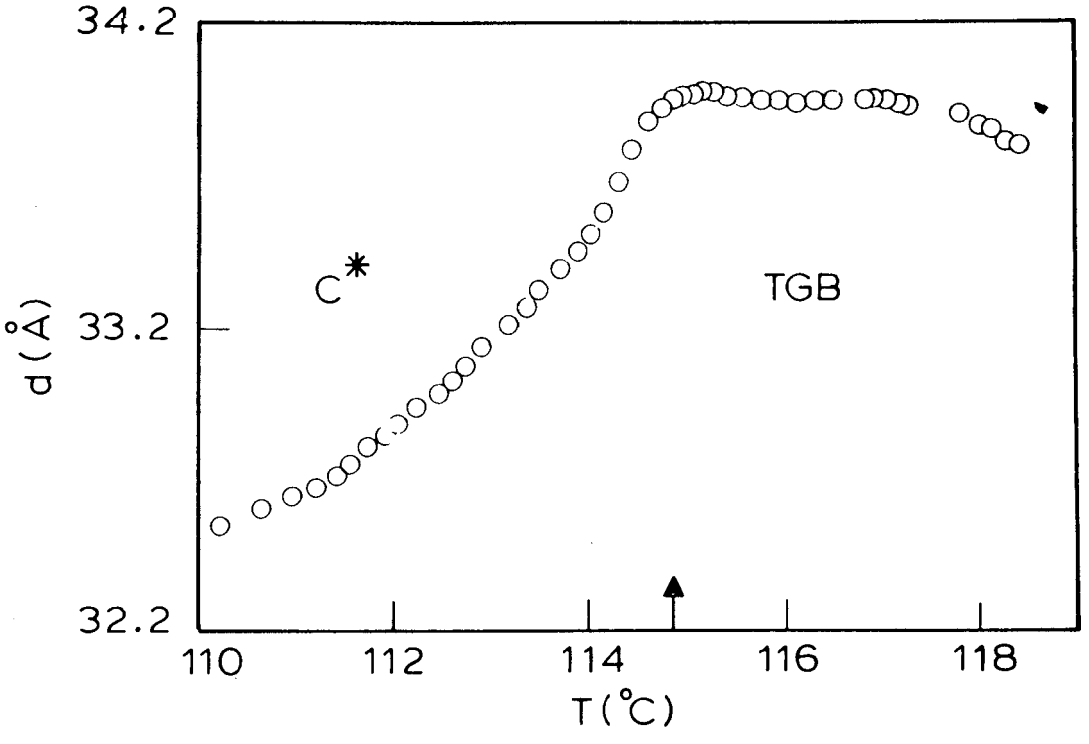


Figure 5.11: Temperature dependence of the smectic layer spacing for X = 0.66. The arrow indicates the C*-TGB transition temperature.

A and TGB phases tlie d/l ratio (1 =length of tlie niolecule) was found to be ~0.9, a value typical of a monolayer smectic A pliase.

5.3.4 Selective reflection studies

A necessary feature of tlie TGB pliase is tlie simultaneous existence of smectic layering as well as a macroscopic helical structure witli its axis parallel to tlie layer planes. In order to demonstrate that the intermediate phase is indeed TGB, we have carried out transmitted light intensity measurements as a function of the incident beam wavelength. Experiments were done using a VIS/IR spectrophotometer (Hitachi U3400, wavelength range 400-2400 nm)[22]. Samples (thickness $\sim 50\mu$ m) were contained between glass plates coated witli a polymer solution and unidirectionally buffed, a procedure which produces an alignment of tlie molecular director parallel to the plates. Tliis in turn aligns the helical axis of the TGB phase to be perpendicular to tlie glass surfaces. The sample cell was placed inside a calibrated hot stage whose temperature was regulated to a constancy of ± 25 mK during any scan. Optical transmission measurements were carried out at several temperatures in tlic Cli and TGB pliases. Tlie spectrum obtained for X = 0.6 at 1.1°C below tlie Ch–TGB transition is shown in Figure 5.12. The minimum observed at 2000 nm represents the wavelength λ_{min} of selective reflection from tlie TGB phase. Tlie thermal variation of λ_{min} for two concentrations X = 0.6 and 0.66 are shown in Figure 5.13 and Figure 5.14. Tlie trend observed (steady increase of λ_{min} as tlie temperature is lowered) and tlie value of the full width at half maximum of ilie spectra ($\sim 0.13\ \lambda_{min}$) are in good agreement with tlie observations of Srajer et al[11] for tlie TGB pliase of

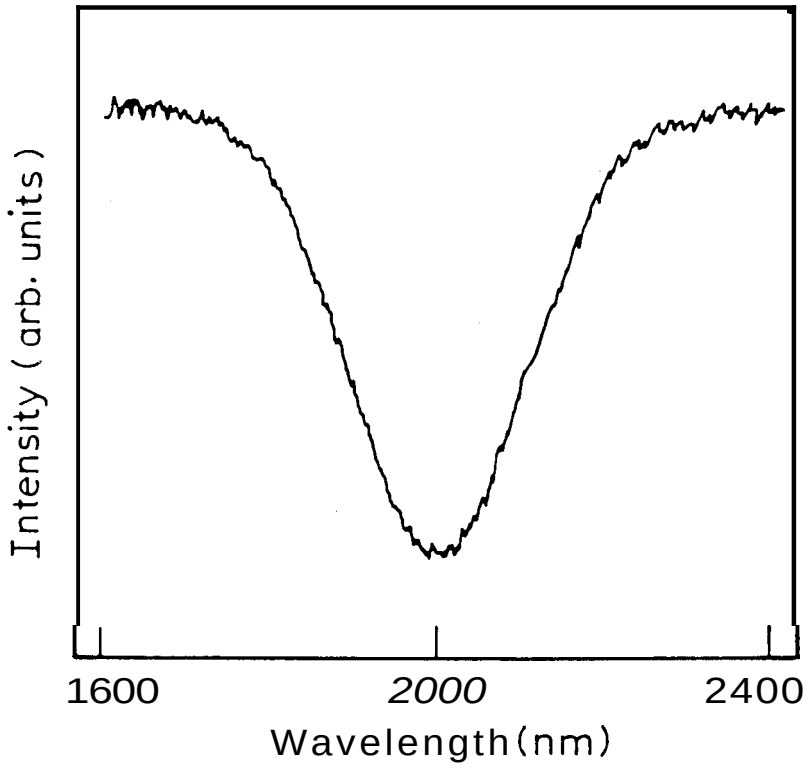


Figure 5.12: Typical optical transmission spectrum in the TGB pliase for X = 0.6. The wavelength (λ_{min}) corresponding to tlie minimum in the plot is related to the pitch of the lielical structure.

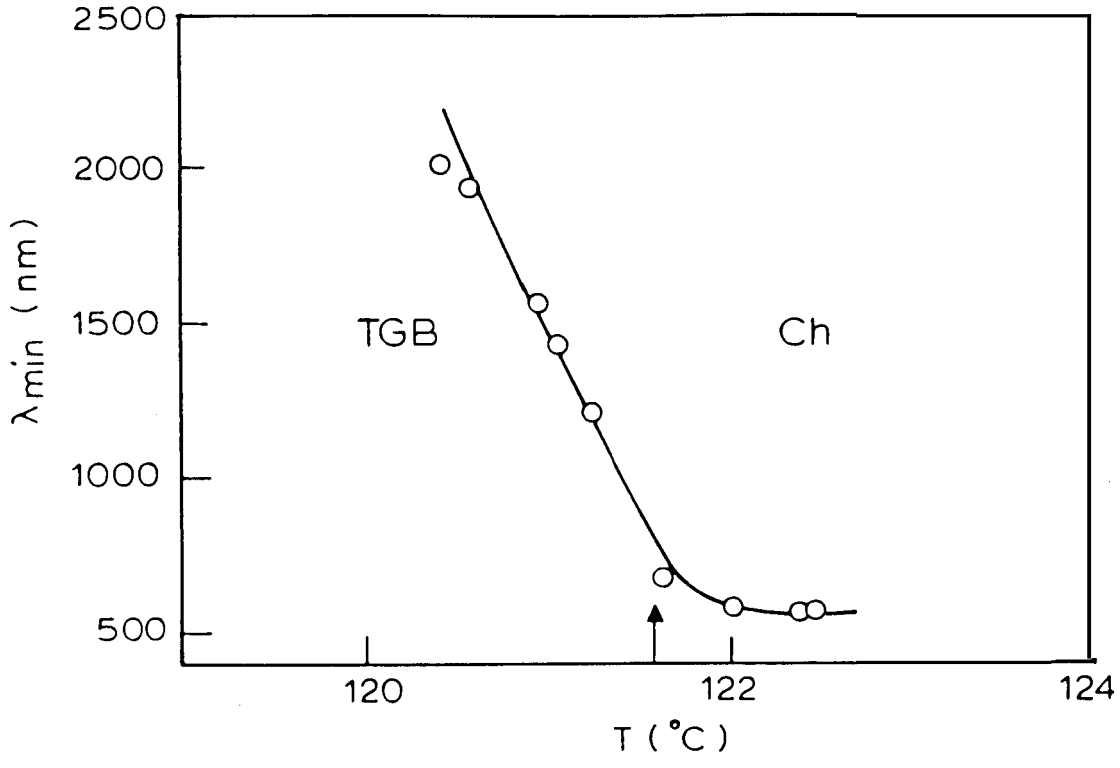


Figure 5.13: Temperature dependence of λ_{min} near the Ch-TGB transition for X = 0.6. The arrow indicates the transition temperature.

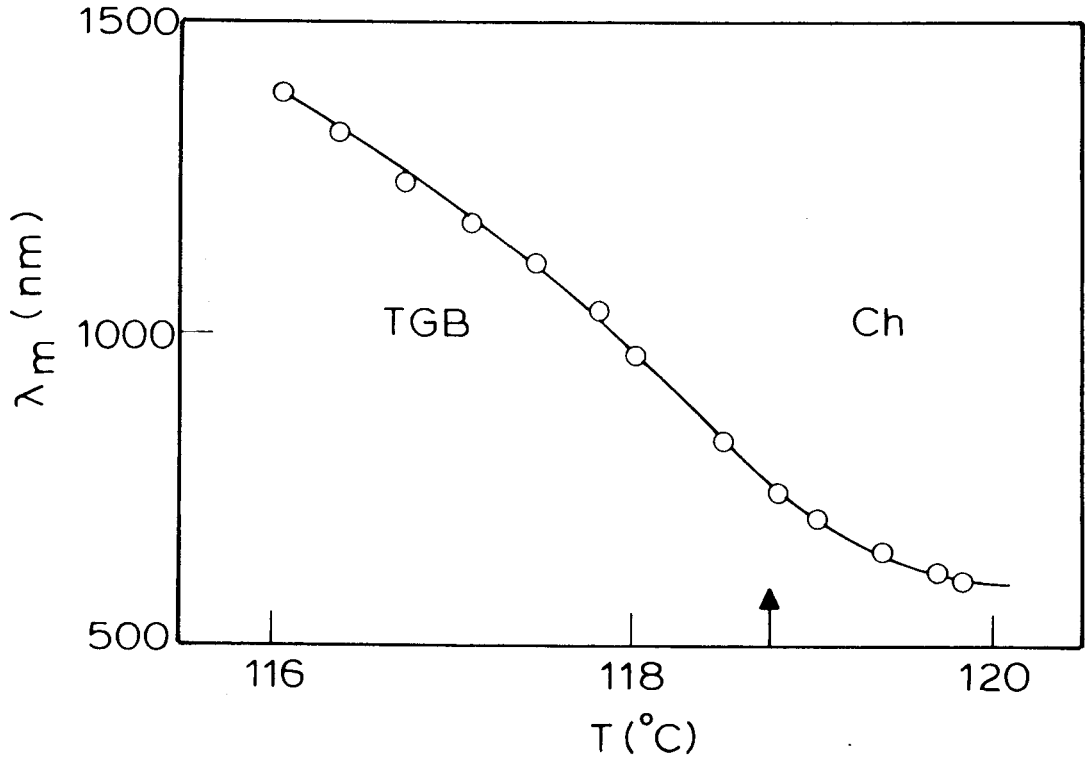


Figure 5.14: Temperature dependence of λ_{min} near the Ch-TGB transition for X = 0.66. The arrow indicates the transition temperature.

+14P1M7. Tliese results, together with tlie X-ray and optical data presented above, confirm that this phase is tlie twist grain boundary phase.

All these results establish the existence of the TGB phase near a virtual chiral NAC point in a binary phase diagram as predicted by tlie theory.

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[21] The transition temperatures for the TGB phase are often found to vary a little, particularly with respect to the method of examination. As tlie phase is essentially a frustrated phase it is possible that parameters like for example, surface pinning etc., can alter the transition temperatures and the actual temperature range of the phases involved.

[22] Tlie spectrometer was kindly provided by the Dept. of Inorganic and Physical Chemistry, I.I.Sc., Bangalore.