Experimental Studies on the Relationship between Order and Physical Properties in Liquid Crystals

by

Geetha Basappa

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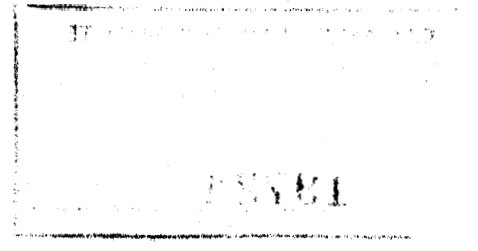
Doctor of Philosophy



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August, 1997

DECLARATION

I hereby declare that this thesis was composed by me independently and that it has not formed the basis for the award of any Degree, Diploma, Associateship, Fellowship or other similar title,

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CERTIFICATE

I certify that this thesis was composed by Ms. Geetha Basappa based on the investigations carried out by her at the Liquid Crystal Laboratory, Raman Research Institute, Bangalore, under my supervision. The subject matter of this thesis has not previously formed the basis of any Degree, Diploma, Associateship, Fellowship or other similar title.

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Contents

PREFACE

Liquid crystals are anisotropic fluids [1, 2]. They possess orientational order and/or one or two dimensional translational order. They consist of molecules with shape anisotropy which can be either rod-like or disk-like. In this thesis we will present experimental studies on liquid crystalline materials consisting of rod like molecules.

The nematic (N) liquid crystal is an orientationally ordered fluid. The smectic A (S_A) phase is an orientationally ordered fluid with an additional 1-dimensional translational order. In the nematic phase the molecules tend to be parallel to some common axis labelled by a unit vector called the director A. The orientational order is reflected in all the macroscopic tensor properties of the medium. Even though the molecules in the medium are usually polar there are as many dipoles which point 'up' as there are pointing 'down'. Hence the nematic phase is not ferroelectric and the states A and −A are indistinguishable.

In this thesis we have mainly studied the effect of strong electric fields (~ 500 esu) on some physical properties of nematic and smectic A liquid crystals.

In Chapter 1 we give a general introduction to the subject with particular reference to the phenomena relevant to the work reported in the remaining chapters.

In Chapter 2 we describe a new experimental technique to quantitatively study the effect of strong electric fields on liquid crystals. When an electric field is applied to a nematic liquid crystal, the field couples to the director through the dielectric anisotropy and tends to align the molecules parallel or perpendicular to the field depending on the sign of the anisotropy. The field dependent free energy density is given by

$$F^E = -\frac{1}{8\pi}\epsilon_{\parallel}E^2\cos^2\theta - \frac{1}{8\pi}\epsilon_{\perp}E^2\sin^2\theta \qquad (1)$$

where E is the electric field and $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the principal dielectric constants. If $\epsilon_{\parallel} > \epsilon_{\perp}$ then the director, A, aligns parallel to E. When the electric field is applied along the director, relating $\epsilon_{\parallel}$ to the orientational order parameter S [3] we obtain

$$F^E = -\frac{1}{12\pi}\Delta\epsilon_o S E^2 \qquad (2)$$

where $\Delta\epsilon_o$ is the dielectric anisotropy of the fully aligned state (S = 1). It can be seen from the above equation that the energy can be lowered if S takes a higher value in the presence of a field.

Compounds with the highly polar cyano end group have a large ϵ_a(~ 8 − 20) thus making the electric field effects quite pronounced. On the other hand, as the anisotropy in magnetic susceptibility is quite small ($\chi_a \sim 10^{-7}$ cgs units), the effect of even rather high magnetic fields on the order parameter and the transition temperature is also small [4]. However due to the finite resistance of the sample, when strong electric fields are applied it gets heated thus making quantitative measurements difficult. Recently, Lelidis et al [5-8] have designed an experimental technique in which they can overcome this problem by using short electric pulses with large equilibration times. They have quantitatively measured the electric field phase diagram in a few systems.

We have taken a different experimental approach to this problem. We have developed a technique in which we measure the *local* temperature of the sample under a strong electric field. This has been achieved by using a nickel resistance thermometer with a large resistance (~ 300 Ω) etched in a nickel coated glass plate using a photolithographic

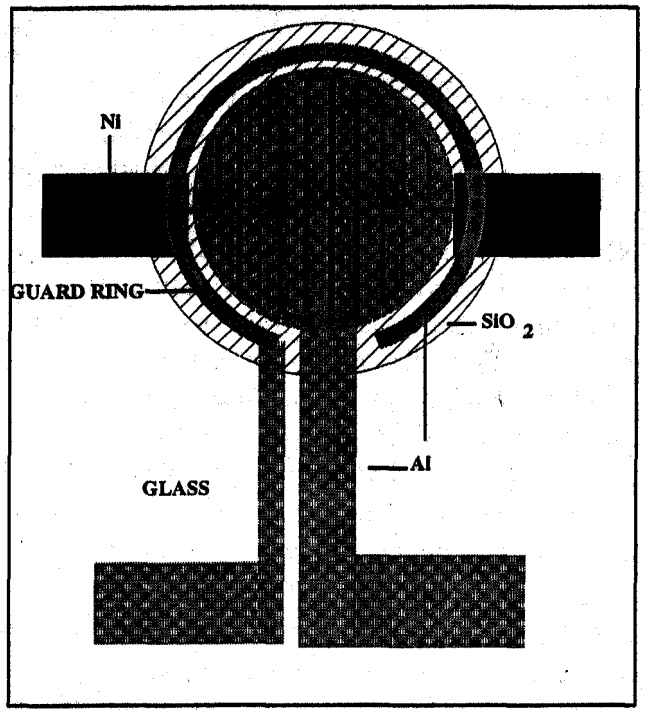

Figure 1: Schematic diagram indicating the geometric disposition of the nickel thermometer, SiO_2 insulator and the aluminium electrode on the lower plate of the cell. It includes a guard ring.

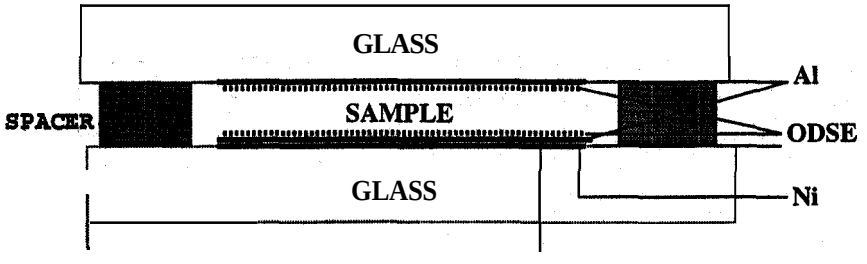

Figure 2: A side view of the constructed cell.

technique (see Figure 1). Above this film first an insulating layer of SiO_2 and subsequently an aluminium electrode are vacuum coated. This constitutes the bottom plate of the cell. The top plate is either an aluminium coated electrode or an electrode etched in an ITO coated plate. The side view of the cell is shown in Figure 2.

We use an impedance analysis of the cell to measure the dielectric constant ($\epsilon_{\|}$) and the resistance (R,) of the sample which give information on both the long range and short range order in the medium. We have also conducted light scattering measurements and optical transmission studies with a microscope which can be used in the reflection mode. Figure 3 shows the overall experimental setup.

In Chapter 3 we present the experimental results on the effect of a strong electric field on the nematic-isotropic phase transition in some compounds. When a field is applied to the isotropic phase it induces an orientational order in the medium. This leads to a weak induced anisotropy in all the physical properties, for eg to birefringence (Kerr effect). In

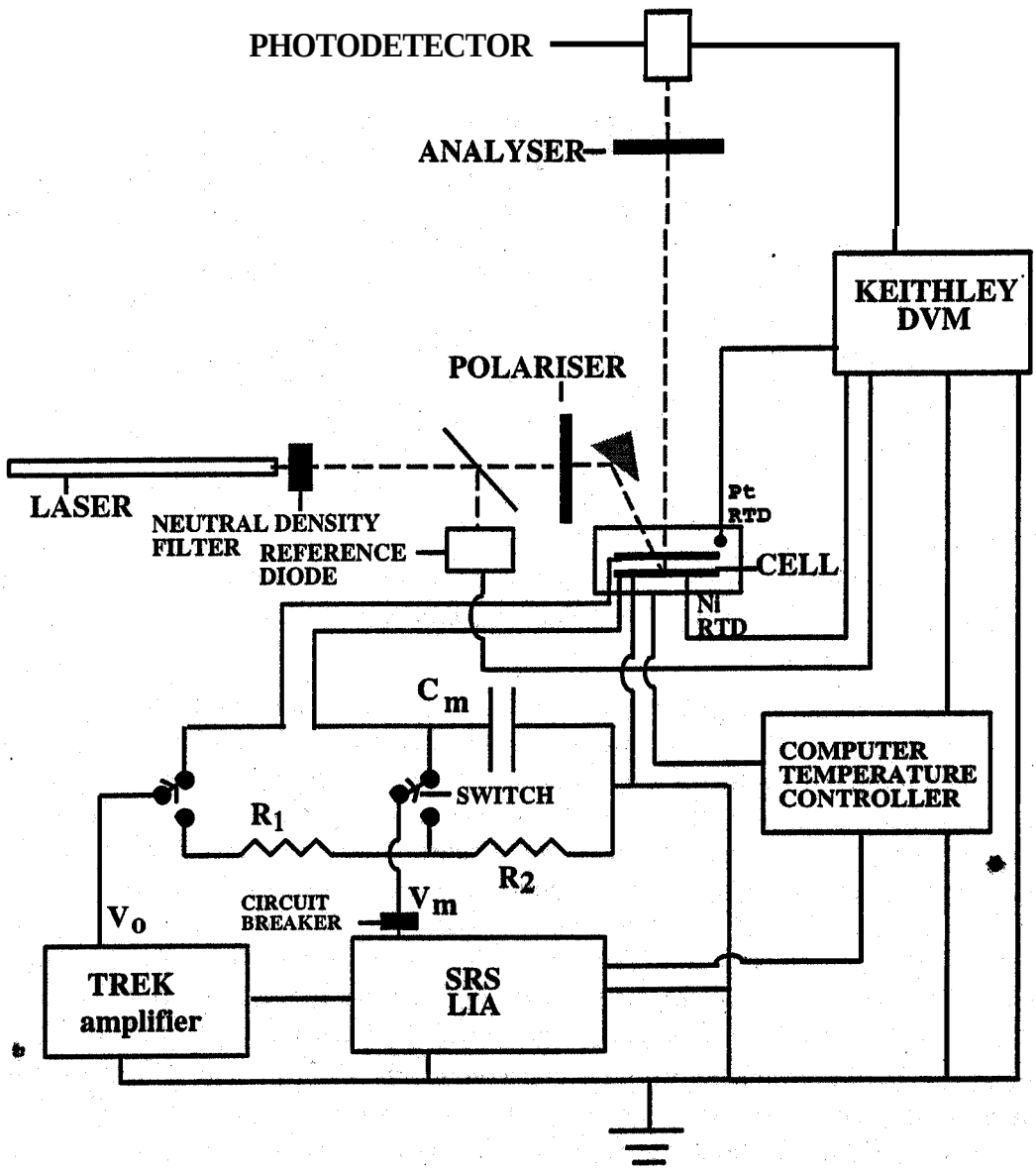

Figure 3: The block diagram of the overall experimental setup.

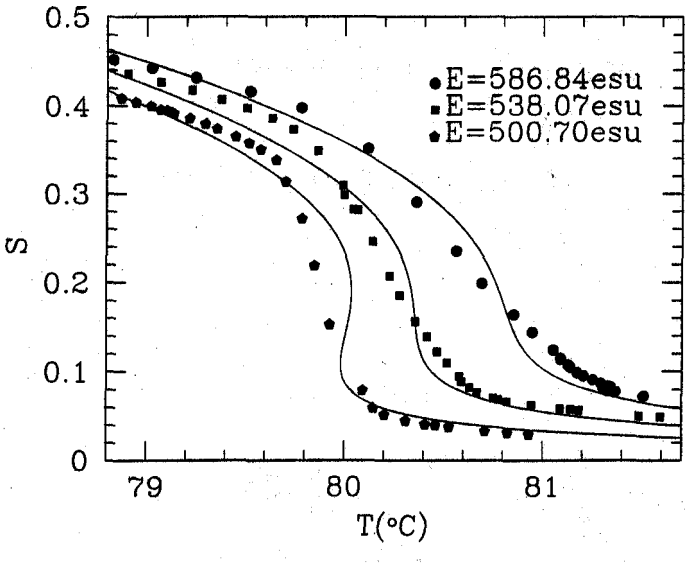

Figure 4: Variation of the order parameter as a function of temperature and field in an **80CB** sample across the N-I transition. The lines are fitted according to a Landau theory.

this paranematic phase the field induced order is uniaxial. Thus the higher temperature paranematic phase and the lower temperature nematic phase have the same symmetry, hence ruling out the possibility of a second order phase transition between them. As such, there can be either a jump in the order parameter at the transition point in a first order transition or a continuous evolution of the order parameter. It is expected that the jump in the order parameter at the traqsition point decreases as the field is increased, and goes to zero at the critical field. This phenomenon is similar to the classic liquid-gas transition under the application of pressure. There have been a number of theoretical calculations on the detailed phase diagrams in the presence of a field in the framework of the Landau theory [9-11]. There are also some molecular models that discuss this problem [12-14].

Using the $\epsilon_{\|}$ measurements we have constructed the electric field phase diagram for two compounds with positive dielectric anisotropy i.e. pentyl cyanobiphenyl and octyloxy cyanobiphenyl (8OCB). In both the cases we can reach the critical field. We fit the data to a Landau model. Figure 4 shows the variation of the order parameter of **80CB** as a function of temperature at different fields with the corresponding theoretical variations based on the Landau theory. It can be seen that the theoretical variation is somewhat more rapid than that of the experimental data. This is to be expected as it is known that even in the field free case the Landau theory predicts a much steeper variation of the order parameter as a function of temperature than is experimentally observed.

We have also used optical studies in the reflection mode to measure the influence of a strong electric field on the orientational order and the transition temperature in a material with negative dielectric anisotropy (4-methoxyphenyl-trans-4-pentylcyclohexyl-carboxylate). Here we see a small increase in the transition temperature as the field is

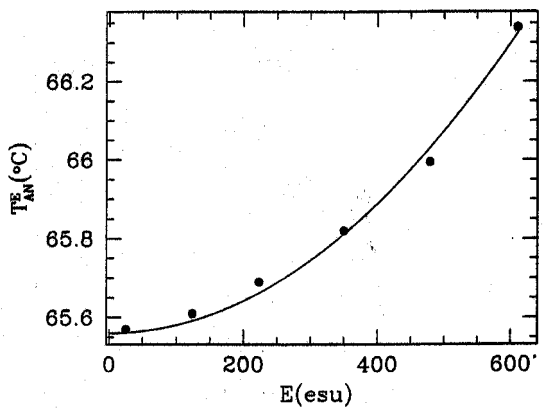

Figure 5: T^E_{AN} as a function of applied electric field in 8OCB. The symbols are experimental data. The calculated variation corresponds to the prediction of the Landau theory that the shift in transition temperature is proportional to E^2.

increased.

In Chapter 4 we present experimental results on the effect of a strong electric field on the N-S_A and S_A-N_R (reentrant nematic) phase transitions in a couple of systems. In the S_A phase the translational order couples with the orientational order and the S_A-N transition temperature depends on the field. We have used the resistance of the sample to detect the N-S_A phase transition in 80CB (T^E_{AN}) as a function of the applied electric field. We see that as the field is increased the transition temperature also increases (Figure 5). We have used an appropriate Landau theory to obtain the theoretical fit shown in the figure.

In view of the lower symmetry of the S_A phase, it usually occurs at lower temperatures compared to the N phase. However, it is now well established that in compounds whose molecules have strongly polar cyano or nitro end groups, the nematic phase can reenter, as the S_A liquid crystal is cooled to a low enough temperature [1, 2, 15]. It is also established that the S_A phase which occurs between the higher temperature N phase and the lower temperature reentrant nematic (N_R) phase is characterised by a layer spacing d which is somewhat longer than the molecular length. This S_A phase with such a 'partial bilayer' structure is called the A_d phase and arises due to an antiparallel orientation between neighbouring polar molecules [16, 17] such that the aromatic cores overlap.

High pressure studies on such reentrant systems show that the N-A_d transition temperature usually decreases with pressure and the A_d-N_R transition temperature increases with pressure ultimately making the A_d phase bounded above [18]. We have studied the electric field effect on a mixture of 8OCB-6OCB to look for a similar phase diagram. As we found it difficult to detect the transition temperatures using the dielectric constant and resistance of the sample at all the applied electric fields we have also used a simple light scattering technique for this purpose.

Both the A_d-N_R and A_d-N transition temperatures increase with field though the variation of the former is much stronger than that of the latter. We have applied fields up

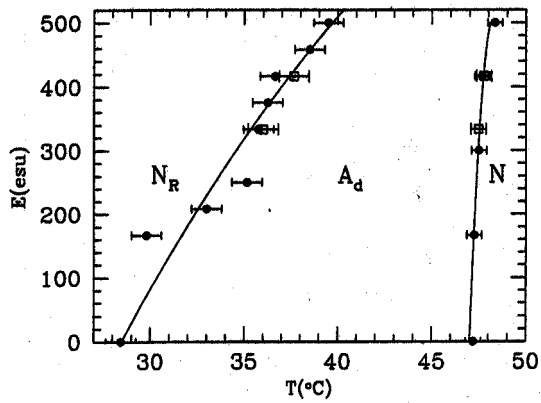

Figure 6: The electric field phase diagram for the 60CB - 8OCB mixture. Circles are data obtained from light scattering measurements and open squares are those obtained from the electrical impedance measurements. The solid lines are guides to the eye. Note that the data on the N_R-A_d transition are consistent with a change of slope around 200 esu.

to 500 esu (at 4111 Hz) on a sample with thickness $\sim 20\,\mu$m to construct the phase diagram shown in Figure 6. Though we have shown the field dependence of the A_d-N_R transition temperature by a smooth line as a guide to the eye note that the data is consistent with a change of slope around $\sim$ 200 esu.

We discuss this electric field phase diagram in the framework of an extended Landau-de Gennes theory. Finally we will summarise the predictions of a molecular model developed by our coworkers, extended to include the electric field effect on the phase transitions in a system exhibiting a reentrant phase [19-21] which broadly agree with the experimental results.

In Chapter 5 we describe the results of various experiments using a strong electric field on p-cyanophenyl p-n heptylbenzoate (CP7B) which has a larger dielectric anisotropy than those of the cyanobiphenyl compounds studied in the previous chapters. We argue that these experimental results indicate the presence of short range ***polar*** order in the medium. The new results obtained in this study are

- Electric field phase diagram of the paranematic-nematic phase transition.
- Field induced enhancement of the order parameter. Figures 7 shows $\epsilon_{\|}$ as a function of temperature at different applied electric fields. We have related the variation of $\epsilon_{\|}$ to the order parameter and discussed the enhancement of the order parameter in terms of the microscopic Kerr effect and the quenching of macroscopic thermal fluctuations.
- Conductivity measurements in particular near the electric field induced nematic-paranematic critical point. Figure 8 shows the variation of R_s as functions of temperature and field. The conductivity measurement shows the usual effects of a weak electrolyte, viz, a reduction in the conductivity at higher fields deep in the nematic

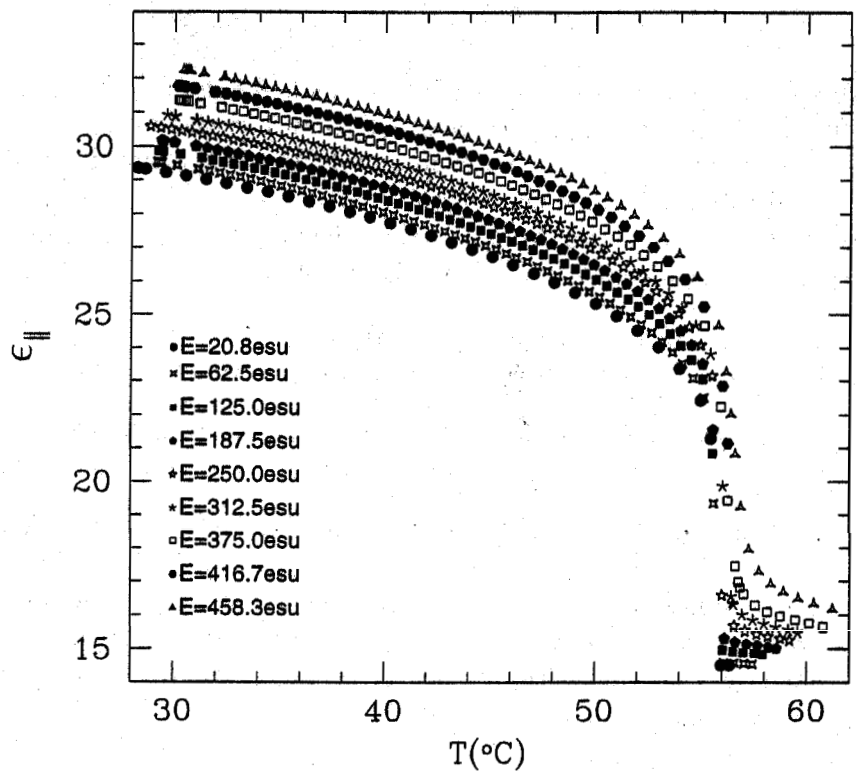

Figure 7: Variation of $\epsilon_{\|}$ as a function of temperature in nematic range of CP7B at different fields d=16 μm, f=4111Hz

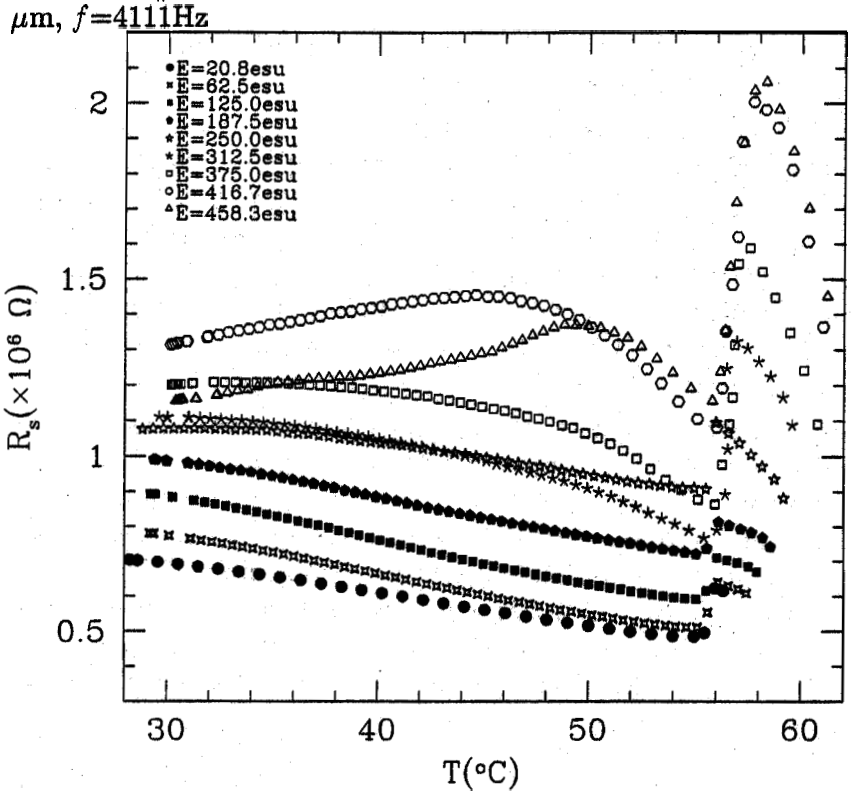

Figure 8: Temperature variations of the resistance of a 16 μm thick sample of CP7B at various values of the applied electric fields.

phase due to the sweeping of the ions by the field. As the field is increased to large values, the conductivity again increases due to an increase in the order parameter. Close to the critical point T_c, the conductivity shows an unusually large increase exhibiting a peak at a temperature slightly lower than T_c. We interpret the conductivity peak near T_c as arising from a critical slowing down of macroscopic polarised domains of molecules which have a parallel orientation.

- Divergence of the order parameter susceptibility near the electric field induced nematic-paranematic critical point using the third harmonic electrical signal.
- Generation of a second harmonic response in the electrical signal at T_c which implies the presence of polarised domains that do not reorient with the field.
- Deep in the nematic phase, at $\sim 33^oC$ we find that there is a large increase in the scattered intensity when a field of ~ 600 esu is applied, which implies that there is a field induced phase transition. We have ascertained that the lower temperature phase is neither biaxial nor a smectic phase. We tentatively interpret this to be a nematic-nematic phase transition which takes place due to a change in the short range order in the medium.

We may also note that there is a considerable body of theoretical work on the possibility of a ***polar*** nematic phase when the molecules carry a large dipole moment (see for example [22]). To our knowledge such a phase has not yet been discovered. Our observation of a strong ***polar short range order*** may indicate one possible route to the realisation of a polar nematic liquid crystal.

In Chapter 6 we present experimental results on the electrooptic response of some nematic liquid crystals with positive dielectric anisotropy to a low frequency square wave electric field (see Figure 9). As it can be seen from Figure 9 the optical response shows a peak at a specific field. We have also measured the current through the sample which saturates at some value of the field (Figure 10). We interpret the electrooptic response to arise from the flexoelectric coupling of the medium with the strong field gradient prevalent near the electrodes implied by the saturation of the current. The possible role of electrohydrodynamic instability is also discussed.

In Chapter 7 we present magnetic susceptibility measurements on a few mesogens. It is a convenient technique for measuring the order parameter of nematic liquid crystals. We use a standard Faraday balance technique using aluminium cups as the sample containers. The measurements have been made on the following compounds : p-cyanophenyl p-n heptylbenzoate (CP7B), octyloxy cyanobiphenyl(8OCB) 5-n-heptyl-2(4 cyanophenyl)-pyrimidine (RO CP7037) and 4-methoxy phenyl-trans-4- pentylcyclohexyl-carboxylate. Figure 11 shows the order parameter variation as a function of temperature for the above the compounds. These values are used in interpreting the $\epsilon_{\|}$ values in the appropriate chapters.

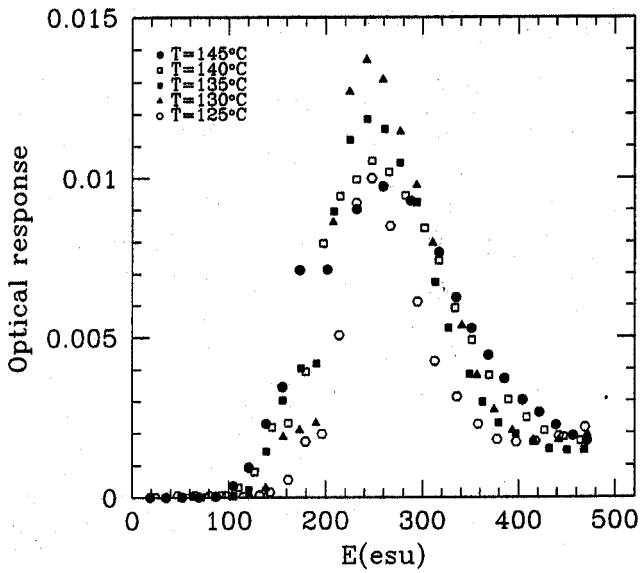

Figure 9: Optical response of pentyl cyanoterphenyl (5CT) as a function of field at different temperatures.

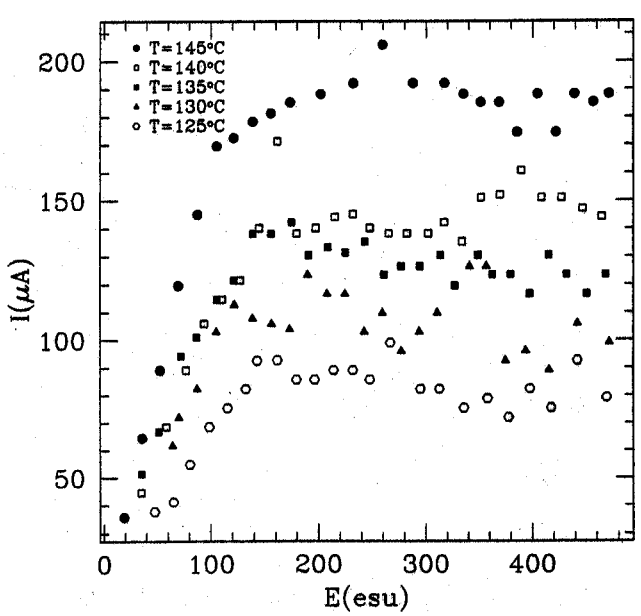

Figure 10: Current measured in a 5CT sample cell as a function of field at different temperatures.

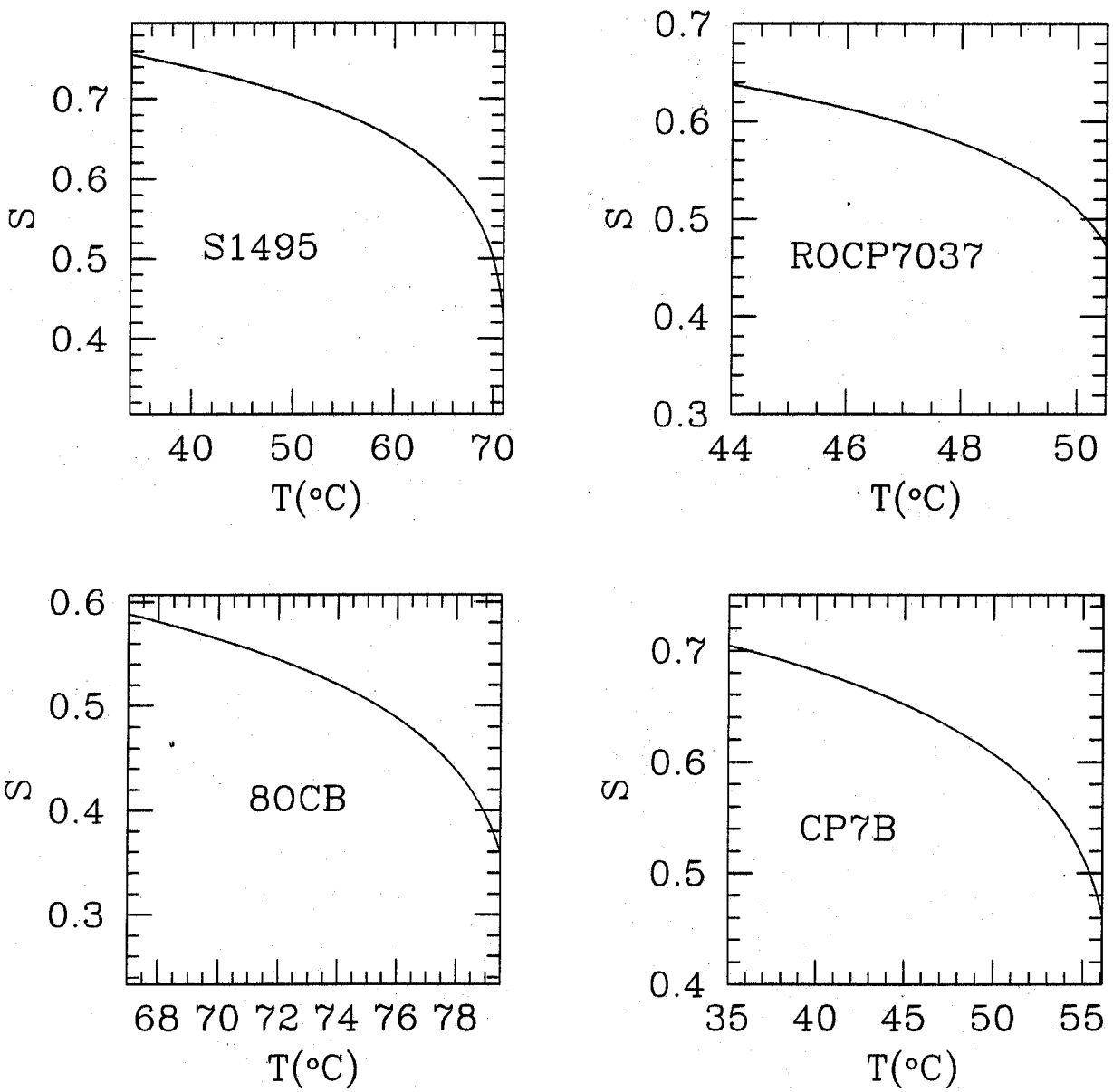

Figure 11: Order parameter measured using the magnetic susceptibility data as a function of temperature.

The following papers contain some of the results described in this thesis.

1. Effect of strong electric fields on phase transitions in some liquid crystals.

Geetha Basappa and N.V. Madhusudana, Molecular Crystals and Liquid Crystals, 288, (1996) 161.

2. Effect of a strong electric field on the reentrant nematic to smectic A_d phase transition .

Geetha Basappa, A.S. Govind and N.V. Madhusudana (J. Phys. in press).

3. Effect of a strong electric field on a nematogen : Evidence for polar short range order.

Geetha Basappa and N.V. Madhusudana (submitted for publication).

Other Publications:

1. Unusual patterns in the growth of smectic liquid crystals. R. Prathibha, Geetha Basappa and N. V. Madhusudana, Key Engineering Materials, 103, (1995) 27.

2. Growth patterns of some smectic C liquid crystals in some binary mixtures. R. Prathibha, Geetha Basappa, N. V. Madhusudana and B. K. Sadashiva (submitted for publication).

References

[1] P. G. de Gennes and J. Prost, *The* Physics of Liquid Cystals, 2nd ed. (Clarendon Press Oxford, 1993).

[2] S. Chandrasekhar, Liquid Crystals, 2nd ed. (Cambridge University Press, 1992).

[3] Introduction to Liquid *Crystals*, E. B. Priestley, P. J. Wojtowicz, and P. Sheng, eds., (Plenum Press, 1975).

[4] C. Rosenblatt, "Magnetic field dependence of the nematic-isotropic transition temperature.," Phys. Rev. **A24,** 2236 (1981).

[5] I. Lelidis, M. Nobili, and G. Durand, "Electric-field-induced change of the order parameter in a nematic liquid crystal.," Phys. Rev. E 48, 3818 (1993).

[6] I. Lelidis and G. Durand, "Electric-field-inducedisotropic-nematic phase transition.," Phys. Rev. E 48, 3822 (1993).

[7] I. Lelidis and G. Durand, "Electrically induced **isotropic-nematic-smectic-A** phase transitions in thermotropic liquid crystals.," Phys. Rev. Lett. 73, 672 (1994).

[8] I. Lelidis and G. Durand, "Electrothermal effect in nematic liquid crystals.," Phys. Rev. Lett. **76,** 1868 (1996).

[9] Y. Poggi and J. C. Filippini, "Magnetic field dependence of the order parameter in a nematic single crystal.," Phys. Rev. Lett. 39, 150 (1977).

[10] C. Fan and M. J. Stephen, "Isotropic-nematic phase transition in liquid crystal.," Phys. Rev. Lett. 25, 500 (1970).

[11] R. M. Hornreich, "Landau theory of the isotropic-nematic critical point," Phys. Lett. **A109,** 232 (1985).

[12] J. Hanus, "Effect of the molecular interaction between anisotropic molecules on the optical Kerr effect. Field induced transition.," Phys. Rev. 178, 420 (1969).

[13] P. J. Wojtowicz and P. Sheng, "Critical point in the magnetic field-temperature phase diagram of nematic liquid crystals.," Phys. Lett. A48, 235 (1974).

[14] K. L. Savithramma and N. V. Madhusudana, "Effect of electric field on the nematic-isotropic phase transition of compounds with a strong longitudinal dipole moment.," Mol. Cryst. Liq. Cryst. 103, 99 (1983).

[15] P. E. Cladis, "New liquid-crystal phase diagram.," Phys. Rev. Lett. 35, 48 (1975).

[16] N. V. Madhusudana and S. Chandrasekhar, "The role of permanent dipoles in nematic order," Pramana Supplement 1, 57 (1973).

[17] A. J. Leadbetter, R. M. Richardson, and C. N. Colling, "The structure of a number of nematogens," J. Phys. 36, C1–37 (1975).

[18] A. N. Kalkura, R. Shashidhar, and N. S. R. Urs, "High pressure studies on reentrant nematagens," J. Phys. 44, 51 (1983).

[19] N. V. Madhusudana and J. Rajan, "A simple molecular theory of double reentrance exhibited by highly polar compounds.," Liq. Cryst 7, 31 (1990).

[20] A. S. Govind and N. V. Madhusudana., "A simple molecular theory of a nematic-nematic phase transition in highly polar compounds.," Liq. Cryst. 14, 1539 (1993).

[21] A. S. Govind and N. V. Madhusudana., Liq. Cryst. (in press).

[22] B. Groh and S. Dietrich, "Long-ranged orientational order in dipolar fluids.," Phys. Rev. Lett. 72, 2422 (1994).