CHAPTER V

ELECTROCLINIC RESPONSE OF SOME FERROELECTRIC LIQUID CRYSTALS: Part I

5.1 Introduction

The electrooptic properties of ferroelectric liquid crystals are being studied extensively as these materials have considerable advantages over nematic liquid crystals in display applications. Meyer et al., (1975) who discovered ferroelectric liquid crystals, later found the electroclinic effect in the smectic A phase occurring at temperatures above the range of stability of the smectic C* phase (Garoff and Meyer, 1977, 1979).

The symmetry of smectic C phase composed of chiral molecules (i.e., C*) allows it to be ferroelectric. As we discussed in Chapter I, the symmetry elements of an achiral smectic C phase are a two-fold rotation axis C_2 perpendicular to the director and lying in the plane of the smectic layers, a mirror plane normal to the two-fold rotation axis and consequently an inversion centre i. The range of possible director orientations in the smectic C phase (at an angle θ with respect to tlie layer normal) lies on a cone as shown in figure 5.1.

When the srnectic C phase is composed of cliiral molecules, i.e., in the smectic

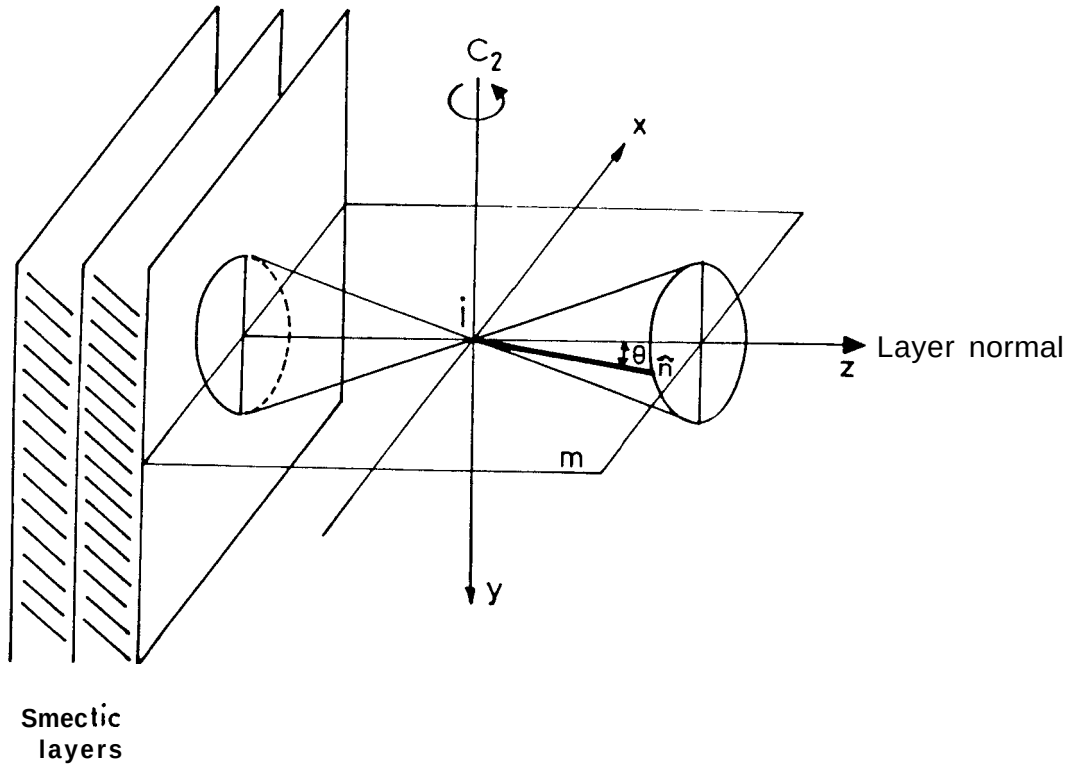


Figure 5.1. Symmetry elements in the smectic C phase.

C* phase, the mirror plane and thus the inversion ccntrc do not exist any longer. The remaining two-fold axis allows the existence of a permanent electric polarisation parallel to the C_2 axis. Thus, if a dipole perpendicular to the long axis of the molecule, i.e., a transverse dipole is present in the close vicinity of the chiral centre, each smcctic layer possesses a spontaneous electric polarisation. So an aligned sample can sustain a polarisation parallel to the C_2-axis.

A symmetry argument which is similar to that predicting ferroelectricity in a chiral smcctic C can be given to explain the origin of electroclinic effect in a smectic A phase composed of chiral molecules (Garoff and Meyer, 1979). An electric field E applied parallel to the smectic layers couples to the transverse component of the molecule's permanent electric dipole (p). This biases the free rotation of the molecules about their long axes since p tends to bc parallel to the applied field. The system has a two-fold axis along the electric field. The plane containing the layer normal and p is a mirror plane in a non-chiral system. But in the chiral system the rnirror symmetry of the plane containing the transverse polarisation caused by the electric field and the layer normal no longer exists. A molecular tilt can then be induced with respect to the layer normal in the orthogonal plane. This phenomenon of inducing tilt by tlic application of an electric field is called the electroclinic effect. This tilt is a linear function of the field (for small fields). A change in the director orientation produces a change in the direction of the optic axis. Hence the electrooptic response in this case is linear. The fluid nature of the layers allows an easy reorientation of the molecules in the direction of the applied field. The electroclinic effect resembles piezoelectricity in crystalline phases in some aspects. However the fluid nature of tlic liquid crystalline phase docs not allow any static shear strains which are associated with piezoelectricity in solid crystals.

Garoff and Meyer (1979) made a detailed study of the electroclinic (EC) coefficient in the well known ferroelectric compound *p*-decyloxybenzylidene-*p*'-amino-2-methylbutyl cinnamate (DOBAMBC) with an emphasis on the critical behaviour of the EC coefficient as the smectic A to smectic C* transition point is approached. They made the measurements on a sample whose geometry is shown in figure 5.2. Using copper wires as electrodes as well as spacers they applied an AC electric field (in tlie range 7-40 KHz) parallel to the plates of a homeotropically aligned liquid crystal sample of DOBAMBC, kept between crossed polarisers. By the application of an electric field parallel to the smectic layers, a tilt is induced in the plane normal to the field. A laser beam was allowed to fall on the sample at an angle of 45° in this plane. They monitored the change in the birefringence of the sample as the EC effect causes a tilt of the molecules. They studied the critical behaviour of the electroclinic effect near the second order smectic A - srnectic C* phase transition, and discussed the results in the framework of the Landau theory of A-C* transition. Their experimental data clearly showed a divergent behaviour for the EC response as transition from A to C* was approached. This behaviour was described by a single critical exponent y. For the material DOBAMBC this exponent y was found to be 1.11 $\pm$ 0.06 for the tilt susceptibility. This value is inconsistent with the mean field value of y=1 as well as the three dimensional XY value of γ=1.32.

In the ferroelectric C* phase, there are two possible modes for changes in the direction of orientation of $\hat{n}$ (Fig.5.3)

1. θ being fixed, only ϕ varies;
2. ϕ being fixed, only θ varies.

The former is known as the Goldstone mode, spin mode or cone mode. The latter, the variation in the tilt angle which is the primary order parameter in the A

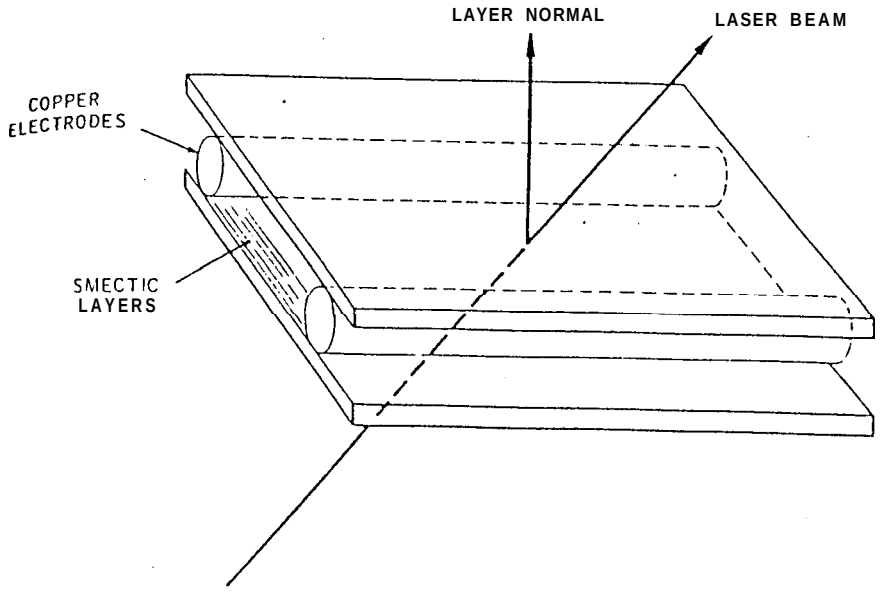


Figure 5.2. Experimental geometry used by Garoff and Meyer (1979).

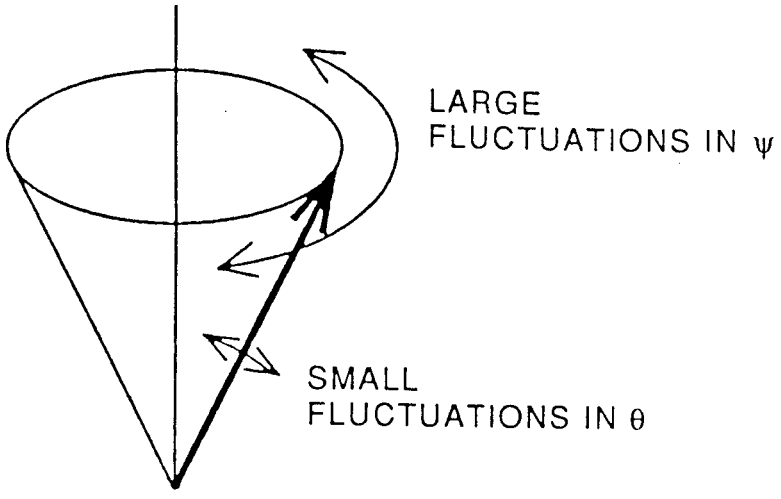


Figure 5.3. Schematic representation of ϕ and θ oscillations of the director.

to C* transition is known as the soft mode.

In the C* phase, θ variations are due to relatively small fluctuations around its thermodynamically determined value. The changes in θ are connected with the changes in layer thickness itself, thus requiring considerable elastic energy and hence the soft mode amplitude is relatively small. In the smectic C* phase, the azimuthal angle of the tilted layers and hence that of the polarisation can very easily change under the action of the external field. Hence there is very large contribution from tlie Goldstone mode which suppresses the soft mode.

On the other hand, in the A phase in which the director is parallel to the layer normal, the tilt angle is induced by using an electric field due to the electroclinic coupling between the induced polarisation and tilt. The tilt fluctuations are connected with local polarisation fluctuations along tlie layers and transverse to tlie tilt. Hence the soft mode is directly accessed in this phase. In the past few years, tliere have been a number of studies on tlie electroclinic cffcct. We will briefly rcvicw them in the following.

Beresnev *et* al. (1988) investigated the dynamics of tlie tilt angle near the C*-A transition in DOBAMBC by two different techniques, namely, using the pyroelectric technique in tlie C* phase and the electroclinic effect in tlie A phase. They measured the critical increase in the relaxation time for the electroclinic effect and their value of the critical exponent $\gamma \simeq 1.1$ is in agreement with the results of Garoff and Meyer. In their opinion, the disagreement with the mean field theory lies in the optical teclinique used for measuring the electroclinic response. The dipolar parts of the molecules which are located near their flexible chiral tails are responsible for the electric susceptibility. But the optical response is mainly due to the easily polarisable rigid skeletons of the molecules. According to them, there is no rigid

and temperature independent coupling between the two moieties. So the value of γ has to be corrected to take this temperature dependence into account.

Zili Li and Rosenblatt (1989) have made rnagnetoelectroclinic measurements in the smectic **A** phase of **DOBAMBC.** They took the sample between two plates treated for homeotropic alignment, as in the experiment of Garoff and Meyer. Further, they also applied a magnetic field at 45° to the director and lying in the plane in which the electroclinic tilting in the molecules occurs. In the smectic **A** phase, at a given temperature, they determined the ratio E/H^2 required to maintain molecular orientation normal to the layers, finding that this ratio had a weak temperature dependence. On the other hand, as $d\theta/dH^2$ was found to be $\propto (\mathrm{T} - T_{A-C\bullet})^{-1}$, they concluded that the anomalous electroclinic susceptibility exponent is due to a temperature-dependent optical-dipolar coupling coefficient.

Bahr and Heppke (1987) used in their experiments 4-(3-methyl-2-chlorohutanoyloxy)-4′-heptyloxybiphenyl with a high spontaneous polarisation. They used a planar oriented sample kept between crossed polarisers, applied a DC electric field parallel to the smectic layers and obtained values up to 10° for the induced tilt angle. In contrast to Beresnev et al., Bahr and Heppke found that the induced tilt to polarisation ratio in their rnatcrial is independent of temperature within tlic smectic **A** phase.

Qiu, Ho and Hark (1988) studied the critical behaviour of tlic electroclinic effect above the transition from smectic C* to smectic **A** using a surface-stabilized ferroelectric liquid crystal cell placed between crossed polarisers. They obtained a value of $\gamma = 1.04 \pm 0.05$ in a 1:1:1 mixture by weight of three ferroelectric liquid crystals which possess a phenyl benzoate core. The γ of this material is licnce consistent with the mean field value.

van Haaren and Rikken (1989 and 1991) measured the temporal behaviour of the electroclinic effect in a chiral smectic A liquid crystal by monitoring the optical response to a voltage pulse. They made the measurements on ZLI 4005, a commercial mixture at room temperature which is well above smectic C*-smectic A transition temperature. The electroclinic response time τ was found to decrease with increasing cell thickness d and electric field E, becoming constant for large d and E values. But such dependences were not observed in the equilibrium induced tilt angle on thick samples. They attributed the change in τ to a hindrance by the boundaries which affects the switching along the entire thickness of the cell.

Xue and Clark (1990) reported the surface EC effect in the smectic A phase of the commercial electroclinic mixture 7643. They used a total-internal-reflection technique to probe $\hat{n}$ near the liquid crystal-glass interface. They demonstrated that there is a small surface electroclinic effect induced by the polar interaction between a chiral liquid crystal and its bounding plate.

Nishiyama *et al.* (1987) observed a *giant* electroclinic effect in smectic A phase of the compounds 4′-(1-methylheptyloxy carbonyl)phenyl-4-octyloxybiphenyl-4-carboxylate and 1-methylpropyl p-[(p-decyloxybenzylidene)-amino]-cinnamate having a spontaneous polarisation of 250 $\mu C/m^2$ and 166 $\mu C/m^2$ respectively which are high when compared to the spontaneous polarisation of DOBAMBC having a value of 45 $\mu C/m^2$. The induced tilt angle increases linearly with the applied electric field and they found θ to saturate at about 16°. They observed the induced tilt angle of a few degrees even at a temperature which was 20" above T_{AC*}. Using several compounds, they found that the induced tilt angle is proportional to the spontaneous polarisation in the smectic C* phase. The response time was found to be less than 1 μs and, when normalised by the induced tilt angle, linearly depended on E.

Williams et al. (1991) reported the measurement of even a larger electroclinic effect which can be very important in applications. They used a recently synthesised material 4'-[3-nitro-4-(1-methyl heptyloxy)biphenyl]-4''-n-decyloxy benzoate (W317), and its polarisation was measured to be around 1300 $\mu C/m^2$. They measured electroclinic tilt angles of the order of 21°. Even at a temperature of 40°C above T_{C-A^*} they could measure a fairly large value of the electroclinic tilt angle.

Andersson et al. (1987) used the electroclinic effect for electrooptic modulation that can be detected through the full range of the A phase. The response is much faster than in the tilted C* phase. They made measurements of the induced tilt angle, the light modulation depth, and rise time.

Pavel and Glogarova (1991) studied the electroclinic effect in benzoic acid, 4-octyloxy 4|(2-methylbutyloxy) carbonyl|phenyl cstcr in tlie vicinity of the smectic A-smectic C* transition temperature. They showed that the relaxation frequency tended towards zero as the smectic A - smectic C* transition temperature was approached.

Sin-Doo Lee *et al.* (1991) found an anomalous behaviour of the electroclinic effect in the chiral compounds, S-2-methylbutyl-4'-n-hexyloxybiphenyl-4-carboxylate and S-2-methylbutyl-4°-n-heptyloxybiphenyl-4-carboxylate. They showed that the field-induced molecular tilt in the smectic A phase undergoes a sign inversion with respect to the layer normal as the temperature increases in both tlie compounds. The electroclinic response of the system disappeared at a particular temperature in the smectic A phase. They described this unusual behaviour in terms of a dynamically fluctuating mixture of at least two conformers that are separated by an energy barrier. They found that the energy barrier between these two conformers was comparable to the rotational barrier in normal hydrocarbons.

Due to the rapid optical response of the electroclinic effect and also because of its fundamental scientific interest, attempts are being made to study this effect in phases other than the smectic A phase. Zili Li *et al.* (1989) reported the observations of an electroclinic effect linear in transverse electric field in a surface-stabilized chiral nematic in SCE12 which is a commercial compound. They found the effect to increase very rapidly near the nematic-smectic A transition temperature from above. They argued that smectic layering may not be essential for the existence of the electroclinic effect. Later Zili Li *et al.* (1991a) have measured the temporal response of the nematic-electroclinic effect. They applied an AC electric field and measured both the in-phase and 90° out of phase optical responses. The apparent response time was found to depend on the driving frequency, especially close to the nematic-smectic A transition temperature. Such behaviour is indicative of multiple relaxation processes, each mechanism having its own characteristic response time. Far above T_{N-Sm_A}, they found the response time to be independcrit of frequency up to 100 KHz. In the same temperature region they observed response times of the order of 100 nS.

Zili Li *et al.* (1991b) have also measured the optical electroclinic relaxation time throughout the smectic A range in the multicomponent mixture SCE-12. They measured two dielectric processes in which the slower process corresponds to that observed usually over most of the smectic A range. Approximately 10 K above the smectic A-smectic C* transition temperature, however, the optical relaxation time begins to *increase* on increasing the temperature, in contrast to the behaviour of the slower dielectric peak. However the magnitude of the electroclinic coefficient decreased monotonically on approaching the srnectic A to nematic transition point.

Bahr and Heppke (1988) observed the electroclinic effect not only in the smectic

A phase without an underlying smectic C phase, but also in the more ordered, non-tilted smectic B and smectic E phases in the chiral compound 4-(4-methyl-2-chloropentanoyloxy)-4′-pentyloxybiphenyl. They showed that the electroclinic effect is a general property of orthogonal smectic phases containing chiral molecules. They found that the induced-tilt/applied field ratio in the smectic B phase is about twice as large as that in the smectic A phase while in the smectic E phase it is slightly smaller than that in the smectic B phase. They showed that the values of the electroclinic coupling constant increase at transitions to a more ordered phase and are nearly temperature independent within the ordered phases.

Komitov *et al.* (1991a) observed a sign reversal of the electroclinic coefficient in the smectic B* phase. They found the temperature where the coefficient vanished to be almost independent of the concentration of the chiral molecules. This is again attributed to conformational changes in the molecules with temperature.

Komitov et *al.* (1991b) described the electroclinic effect in the unwound state of the chiral nematic phase N*. They found the magnitude of the induced tilt typically to be one or two orders smaller than that in the A* phase.

Johno *et al.* (1991) used the X-ray technique to measure the layer thickness of smectic A phase under an electric field. They directly measured the tilt angle θ as a function of the field.

Dupont *et* al. (1991) have particularly emphasized the need to ensure working with relatively small applied electric fields near the A-C* transition point to be in the linear regime so that the comparison with the Landau theory is valid, which we will be referring to at a greater length in the next chapter.

Andersson et *al.* (1991) have pointed out that a tilt angle of 11.25 degrees in smectic A* materials is useful in the soft mode ferroelectric liquid crystal (SMFLC)

devices. Davey and Crossland (1991) have investigated the electroclinic effect from the point of view of its potential application in optical devices. They have also discussed the limitations of the electroclinic effect in device applications.

In earlier chapters we have discussed the electromechanical effect in cholesteric liquid crystals which arises from the chiral symmetry of the cholesteric phase and depends on the transport of ions through the helical medium. Our experiment to study this phenomenon in samples with fixed boundary conditions consisted of detecting the oscillations in the azimuthal angles of the director in a sample under an applied AC electric field. This set up is exactly similar to the one used for measurements of the EC coefficient. Further, several new ferroelectric compounds were synthesised in our chemistry laboratory (Shivkumar et al., 1991). Several properties of these materials like polarisation, the tilt angle, etc., have also been measured (Prasad et al., 1990). In this chapter, we present our measurements of the EC effect in several ferroelectric rnatcrials.

5.2 Theoretical Background

Following the Landau theory of Garoff and Meyer (1977), the mean field expression for the free energy density of a srnectic A liquid crystal consisting of chiral molecules can be written in the form,

$$F = F_o + \frac{1}{2} A(T)\theta^2 + \frac{1}{2}\chi_{\mathcal{P}}^{-1}\mathcal{P}^2 - \mathcal{P}\cdot E - \frac{\epsilon_\infty E^2}{2} - c\mathcal{P}\theta \qquad (5.1)$$

where F_o is the ground state free energy of the smectic A phase, $A(T)$ is the temperature-dependent Landau coefficient which goes to zero at the (non-chiral) A-C transition point, i.e., $A = a(T - T_c)$, θ is the induced tilt angie χ_P is a generalized susceptibility, $\mathcal{P}$ is the induced polarisation, E is the external electric field,

c is the electroclinic coefficient coupling $\mathcal{P}$ and 0, and ϵ_∞ is the high frequency dielectric constant.

The first two terms of equation (5.1) are the Landau expansion coefficients in the primary order parameter for the tilting orientation, i.e., 0. The electrostatic energy due to the polarisation is usually smaller than the thermal energy. The second and fourth terms in equation (5.1) describe the electrostatic free energy. The last term represents the lowest order coupling between $\mathcal{P}$ and θ. The polarisation $\mathcal{P}$ is the secondary order parameter of the $C^* - A$ transition as it makes only a relatively small contribution to the freeenergy density. Thus the susceptibility χ_P is taken essentially as temperature independent. $\mathcal{P}$ and θ are independent variables. By minirnising F with respect to 8 and $\mathcal{P}$ respectively we get,

$$a(T - T_c)\theta - c\mathcal{P} = 0 \tag{5.2}$$

$$\frac{\mathcal{P}}{\chi_{\mathcal{P}}} - c\theta - E = 0 \tag{5.3}$$

On simplifying,

$$\theta = \frac{Ec\chi_{\mathcal{P}}}{a(T - 3;) - c^2\chi_{\mathcal{P}}} \tag{5.4}$$

If T_c^* is the renormalised critical temperature

$$T_c^* = T_c + \frac{c^2\chi_{\mathcal{P}}}{a} \tag{5.5}$$

at which the electroclinic effect diverges, and with $\tilde{a} = aT_c^*$, we can write

$$\theta = \frac{c\chi_{\mathcal{P}}E}{\tilde{a}\left[\frac{T - T_c^*}{T_c^*}\right]} \tag{5.6}$$

Using equation (5.3), the polarisation $\mathcal{P}$ is given by

$$\mathcal{P} = \chi_{\mathcal{P}}(E + c\theta) \tag{5.7}$$

$$\text{or,} \quad \mathcal{P} = E\left[\frac{\chi}{\chi\mathcal{P}\ \mathbf{t}\ \frac{c^2\chi^2_{\mathcal{P}}}{\tilde{a}(\frac{T - T_c^*}{T_c^*})}}\right] \tag{5.8}$$

i.e., $\mathcal{P}$ also diverges as T_c^* is approached.

When a DC electric field is applied to a liquid crystal cell, the ionic impurities present in the sample drift towards the electrodes forming electrical double layers. This leads to a partial screening of the applied field. Moreover, beyond a certain voltage, the charge injection from one or both the electrodes may result in a large field gradient across the sample (Blinov, 1983). To avoid these complications, it is preferable to apply an AC field rather than a DC field to liquid crystals. When an AC field is applied to a sample, θ oscillates at the frequency of the applied voltage. In this case, we have to take into account the dissipative contribution due to the viscosity of the sample. We can then write a phenomenological equation of motion :

$$\eta\dot{\theta} + \tilde{a}\left[\frac{T - T_c^*}{T_c^*}\right]\theta = c\chi_{\mathcal{P}}E \tag{5.9}$$

where η is an appropriate viscosity coefficient. If there is a sinusoidal variation of the applied field with time, i.e., $E = E_o\, e^{i\omega t}$, then the amplitude of the θ oscillations at the frequency ω can be written as

$$\theta_o = \frac{c\chi_{\mathcal{P}}E}{\left[\omega^2\eta^2 + \tilde{a}^2\left(\frac{T-T_c^*}{T_c^*}\right)^2\right]^{1/2}} \tag{5.10}$$

θ oscillates with rcspcct to the applied field with a phase angle given by

$$\delta = \tan^{-1}\left[-\frac{\omega\eta}{\tilde{a}\left(\frac{T-T_c^*}{T_c^*}\right)}\right] \tag{5.11}$$

It is clear from equation (5.10) that as T approaches T_c^*, the viscous term restricts the divergence of θ_o and thereby the amplitude tends to a saturation value. The relaxation time of the fluctuations of the order parameter θ, viz.,

$$\tau = \frac{\eta}{\tilde{a}\left[\frac{T-T_c^*}{T_c^*}\right]} \tag{5.12}$$

also diverges as T_c^* is approached.

These results have been obtained using the Landau mean field theory. In principle, fluctuations can modify the critical index for the divergence of the electroclinic coefficient. Hence, in general, the reduced temperature $\left[\frac{T-T_c^*}{T_c^*}\right]$ can be replaced by $\left[\frac{T-T_c^*}{T_c^*}\right]^{\gamma}$, where γ is the critical index in equations (5.10) to (5.12).

5.3 Experimental Set-up

Two conductive Indium-tin oxide coated glass plates were treated with polyimide and unidirectionally rubbed. A cell with a typical thickness of 7-10 μm was made using these plates as described in chapter II. We constructed a copper cell holder (Fig.5.4) to have a good thermal contact between the cell and the base of the INSTEC HSI-i microscope hot stage. Electrical contact was established between the ITO coating on the surface of the glass plates of the cell and the connecting wires using conductive silver paste. The sample was filled into the cell in the isotropic phase by capillary action. The cell was mounted in the cell holder and the temperature was controlled by INSTEC's mk1-i precision temperature controller. The microscope stage and substage were enclosed in a wooden box with thermocole lining to ensure a better thermal stability of the sample. The temperature of the sample could be controlled and measured to about 8 mK. We also recorded the temperature of the sample independently using a platinum resistance thermometer by fixing it by the side of the cell as shown in figure 5.4. The hot stage is in turn kept on the rotating stage of the Leitz polarising microscope. Starting from the isotropic phase, the sample was cooled slowly at the rate of 0.01 $^{\circ}C$ per min. to the cholesteric and then to the smectic A phase. The homogeneous alignment of the compounds for which we made measurements was reasonably good except for a few focal conic defects (Figures 5.5a and b). A schematic diagram of the planar

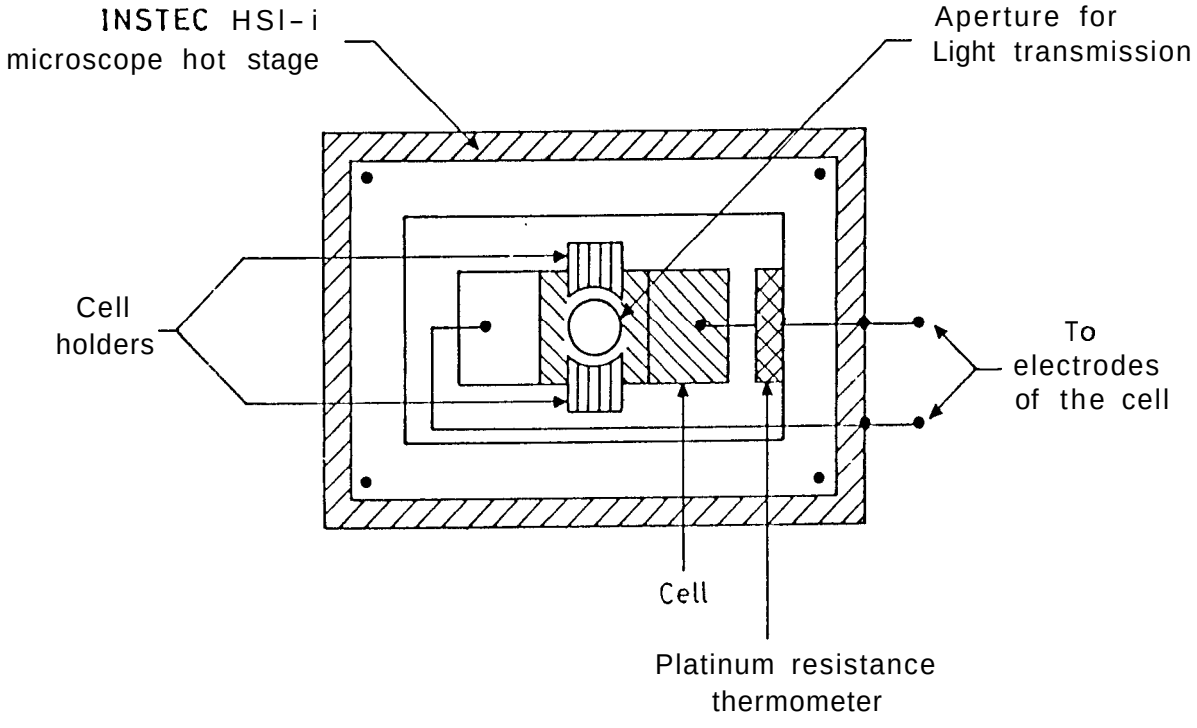


Figure 5.4. Schematic diagram of the cell holder used in the INSTEC microscope hot stage.

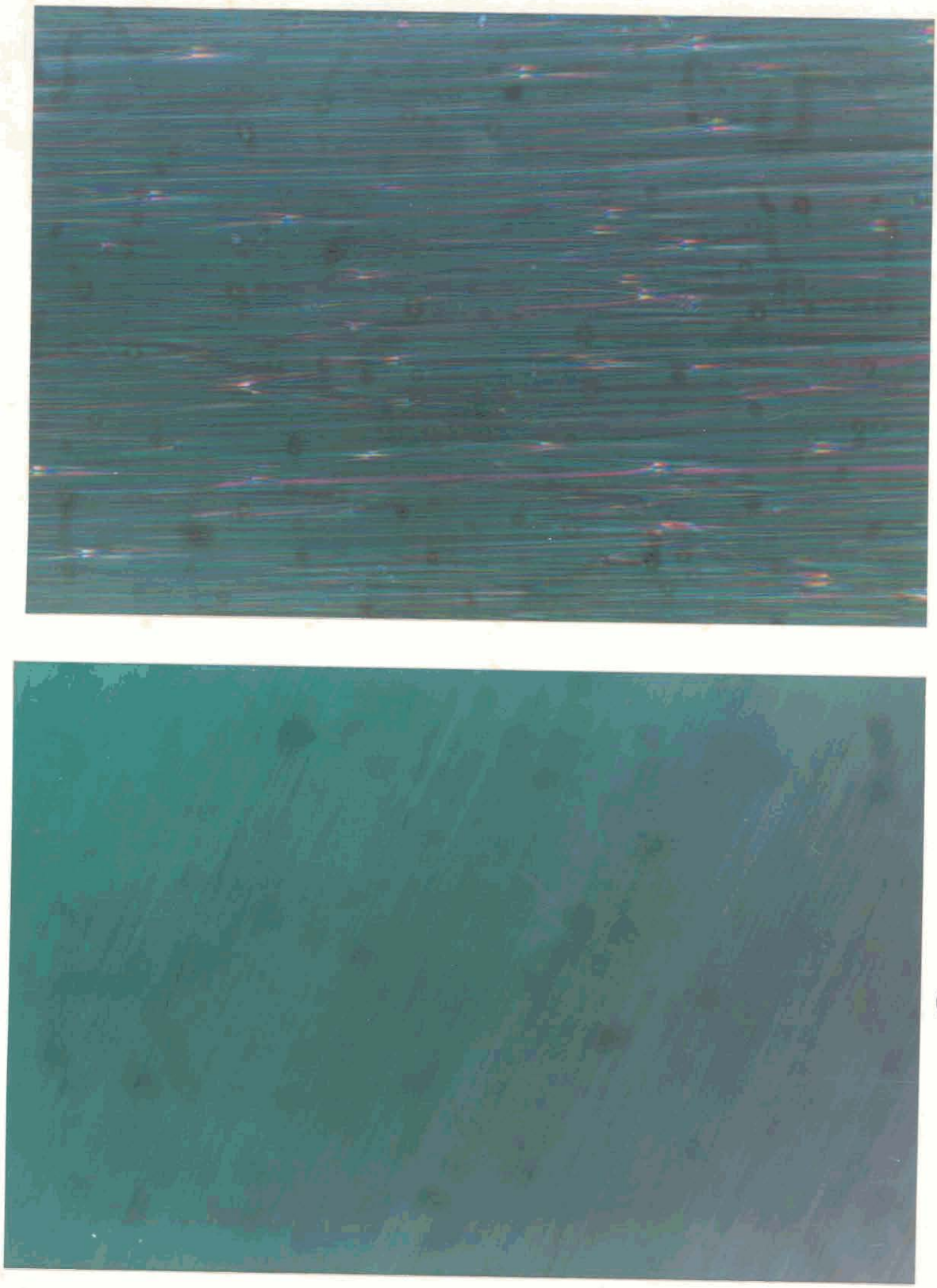


Figure 5.5. Photograph of a typical homeogeneously aligned ferroelectric sample (a) with the optic axis parallel to the polariser, (b) with the optic axis making an angle of 22.5° with the polariser.

sample with the smectic layers perpendicular to the surfaces of the cell is shown in figure 5.6. The experimental set up (Fig.5.7) is similar to that used for measuring the electromechanical effect of samples with fixed boundary conditions.

We made measurements on six systems, four of which belong to the homologous series [2S,3S]-4″-(2-chloro-3-methylpentanoyloxy) phenyl-trans-4''-n-alkoxy cinnamates synthesized in our chemistry laboratory [Shivkumar *et* al., 1991]. The general structural formula and the transition temperatures are shown in figure 5.8. The compounds have two chiral centres and a reasonably high value of polarisation in the ferroelectric phase (Prasad et al., 1990). We made the measurements on the 7th, 8th, 9th and 10th homologues all of which exhibit the phase sequence isotropic-cholesteric-smectic A-smectic C*. We also made measurements on two commercial samples, viz., SCE-5 and SCE-6 bought from BDH Ltd.

The data were taken while cooling the samples. Equations (5.6) and (5.10) show that the electroclinic tilt angle increases with the applied field. As discussed by Dupont et al. (1991) the electroclinic response becomes a non-linear function of E if the applied field is too large. The linear regime shrinks as the response diverges when the temperature is reduced towards T_c^*. This is illustrated in figure 5.9 in which the voltage-dependence of the electroclinic response is shown at various temperatures. We appropriately reduced the applied voltage as we approached the A – C* transition temperature to be well within the linear regime.

As discussed in chapter IV, the intensity of the transmitted light beam which propagates orthogonal to the optic axis of a uniaxial medium between crossed polarisers is given by

$$T_1 = \frac{\sin^2 2\psi}{2}(1 - \cos \Delta\Phi) \tag{5.13}$$

where $\Delta\Phi$ is the optical phase difference and ψ is the azimuthal angle made by

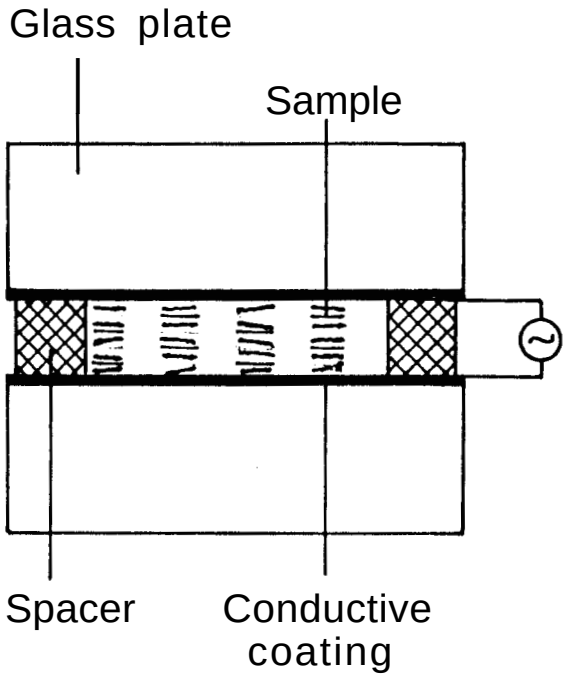


Figure 5.6. A schematic diagram of the planar sample with the smectic layers perpendicular to the surfaces of the cell.

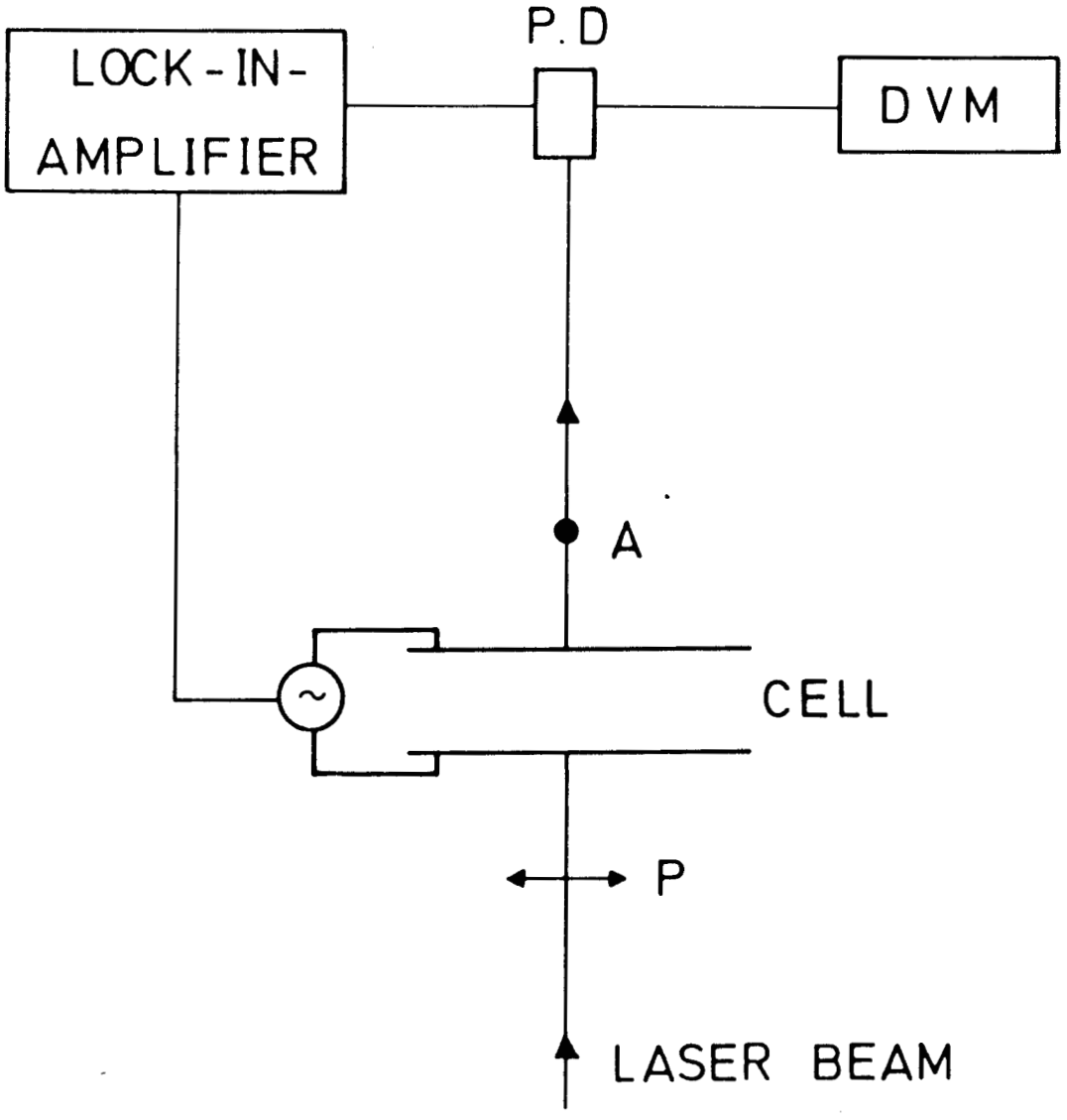
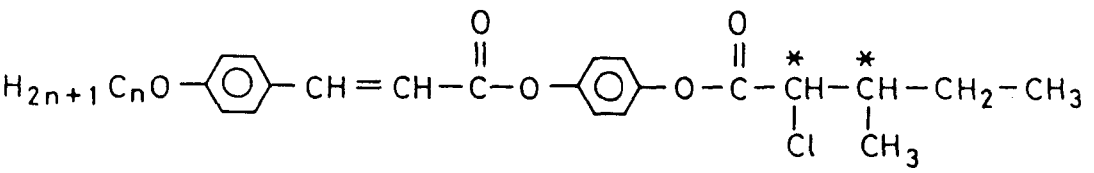


Figure 5.7. Block diagram of the experimental set-up to measure the electroclinic coefficient.



Compound number	n	C	S_{C^*}	S_A	N*	I
D7	7	. 61.5 .	68.5 .	88.0 .	95.0 .	
D8	8	. 61.0 .	73.0 .	93.0 .	96.5 .	
D9	9	. 69.0 .	78.0 .	95.0 .	97.0 .	
D10	10	. 56.0 .	80.0 .	98.5 .	99.0 .	

Figure 5.8. The general structural formula and transition temperatures of [2S,3S]-4′-(2-chloro-3-methyl pentanoyloxy) phenyl *trans*-4″-n-alkoxy cinnamates of the homologous series used in our experiments.

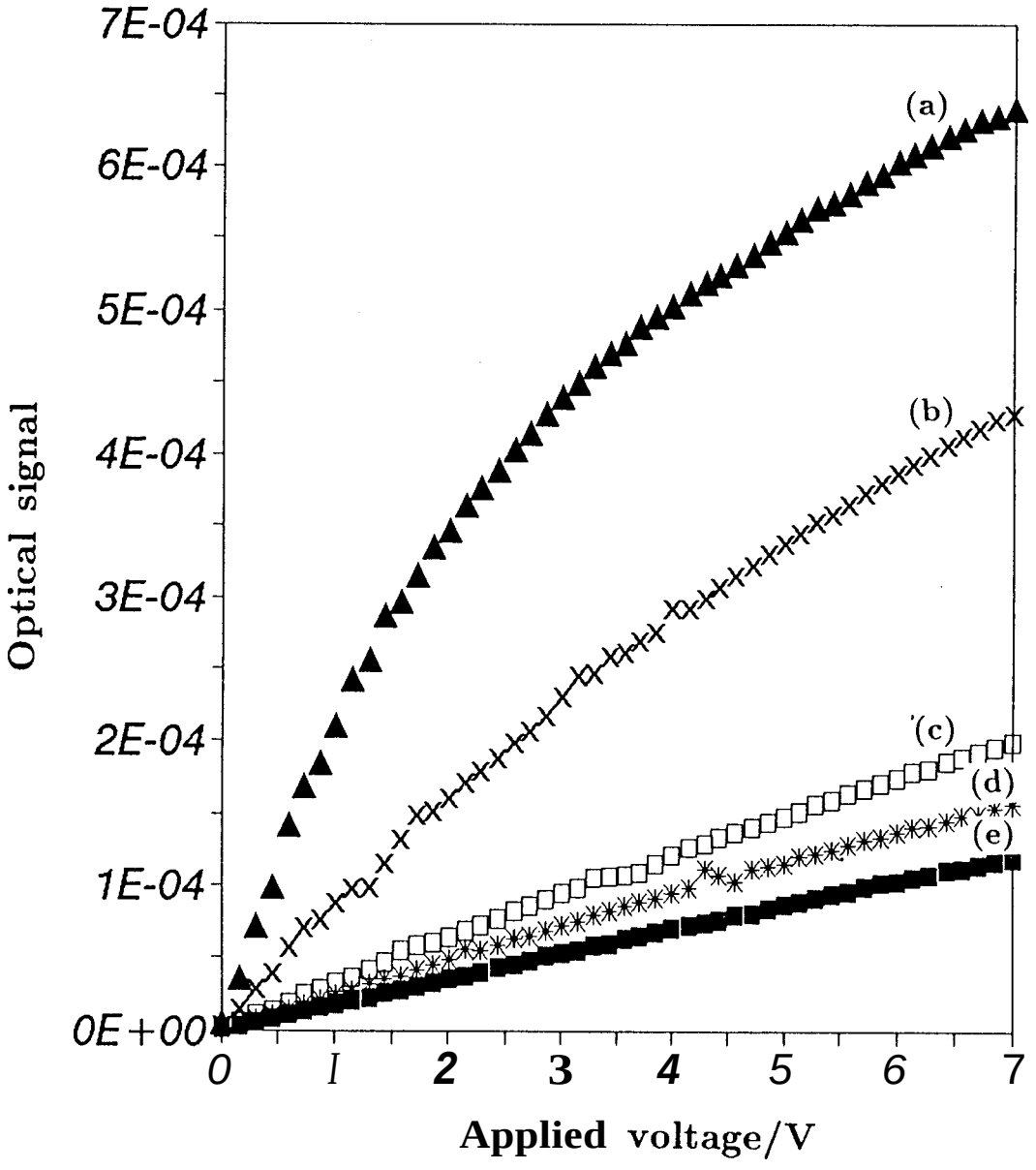


Figure 5.9. Plot of the optical response vs. applied voltage for the compound SCE-6 at the frequency of 1960 Hz for (a) (T_c + 0.7) K, (b) (T_c + 1.1) K, (c) (T_c + 1.9) K, (d) (T_c + **2.3)** K, (e) (T_c + 3.1) K.

the optic axis with the plane of polarisation of the incident beam. If the difference between the DC signals measured at $\psi = \pi/8$ radians and that measured at zero azimuthal angle is **I,,** using equation (5.13) we get

$$\mathbf{I,} = \frac{1}{4}(1 - \cos \Delta\Phi) . \tag{5.14}$$

When an AC field is applied, the induced tilt angle θ oscillates at the frequency of the applied field. A small change in the transmitted intensity I_f due to these oscillations is given by

$$I_f = \sin 4\psi(1 - \cos \Delta\Phi)\,\delta\psi .$$

In the present case $\psi = \pi/8$ and $\delta\psi = 0$ the induced tilt angle. Hence

$$I_f = (1 - \cos \Delta\Phi)\theta . \tag{5.15}$$

Dividing equation (5.15) by equation (5.14) we get,

$$\theta = \frac{I_f}{4I_o} . \tag{5.16}$$

The electroclinic coefficient is calculated using the equation e $= (\theta/E_o)$, where E_o is the amplitude of the applied electric field.

5.4 Results and Discussion

In the smectic A phase, the electroclinic relaxation time is very short, but it rapidly increases as the transition point is approached as given by equation (5.12). In figure 5.10 we have shown a typical frequency dependence of the electroclinic coefficient for the eighth homologue at $\sim T_c^* + 0.2°K$ when the relaxation time is quite long. We have taken detailed measurements of the temperature dependence of the electroclinic coefficients at a sufficiently high frequency ~2 KHz to avoid effects due to ionic

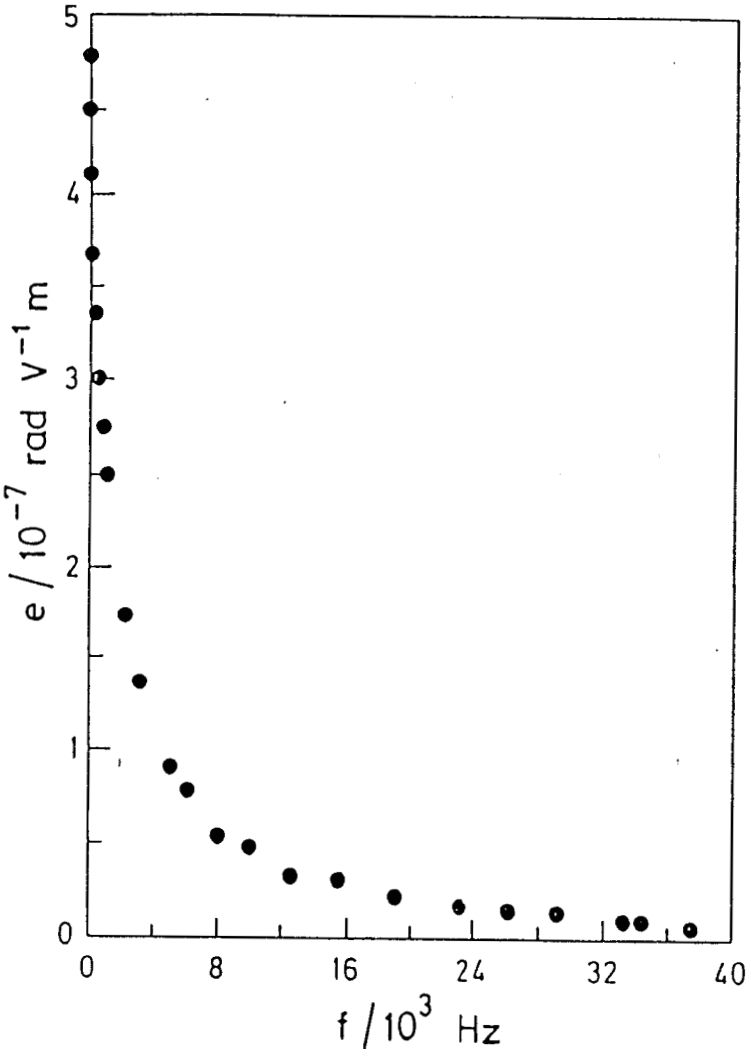


Figure 5.10. Frequency dependence of the electroclinic coefficient, e of the eighth homologue of the compound whose structural formula is shown in figure 5.3, at $(T_c^* + 0.2)$ K.

conductivity of the medium. We recorded both the amplitude and phase of the electroclinic signal in a temperature range up to about $\sim$ 1-2° above T_c^*. The electroclinic coefficient rapidly increases as the A-C* phase transition temperature is approached (see for example figure 5.11). The measured phase angle of the signal is slightly less than π radians at temperatures far above T_c^*, and decreases as the temperature is decreased, i.e., the actual phase delay of signal increases as T_c^* is approached. The rate of this variation grows as T_c^* is approached.

From equation (5.6), if the mean field theory is valid, the inverse electroclinic coefficient $e^{-1} = (E/\theta)$ should be a linear function of T. In figures 5.12 to 5.17, we have plotted the inverse electroclinic coefficient (e^{-1}) as a function of temperature for the six systems studied. As expected from the Landau theory the variation of e^{-1} is quite linear at temperatures not too close to T_c^*. As we approach T_c^* however, the relaxation time increases, the dissipative contribution becomes prominent and the electroclinic coefficient saturates (equation 5.10) as we have made the measurements at a few KHz. The slope of the linear variation depends on the ratio of the coefficient of the first term of the Landau expression, a, and the electroclinic coupling constant, *c* (equation 5.6). The slopes have the magnitudes 1.1×10^7, 1.55×10^7, 2.1×10^7 and 1.6×10^7 for the 7th, 8th, 9th and 10th homologues respectively. As the chemical nature and the smectic A range of all the four homologues are very similar, the slopes have the same order of magnitude. We can also point out here that the alignment of the 7th homologue was inferior to that in other samples. On the other hand, in the case of SCE-5 and SCE-6, the slope is an order of magnitude larger being 2×10^8 and 1.1×10^8 respectively. The $\mathcal{P}/\theta$ value of the 10th homologue of the pure compound is $\simeq 2.35 \times 10^{-3}$ C/m^2 in the ferroelectric phase, at $\sim T_c^* - T = 5°$ (Prasad *et* al., 1990). For SCE-6, this ratio is $\sim 1.3 \times 10^{-4}$ C/m^2 at a similar

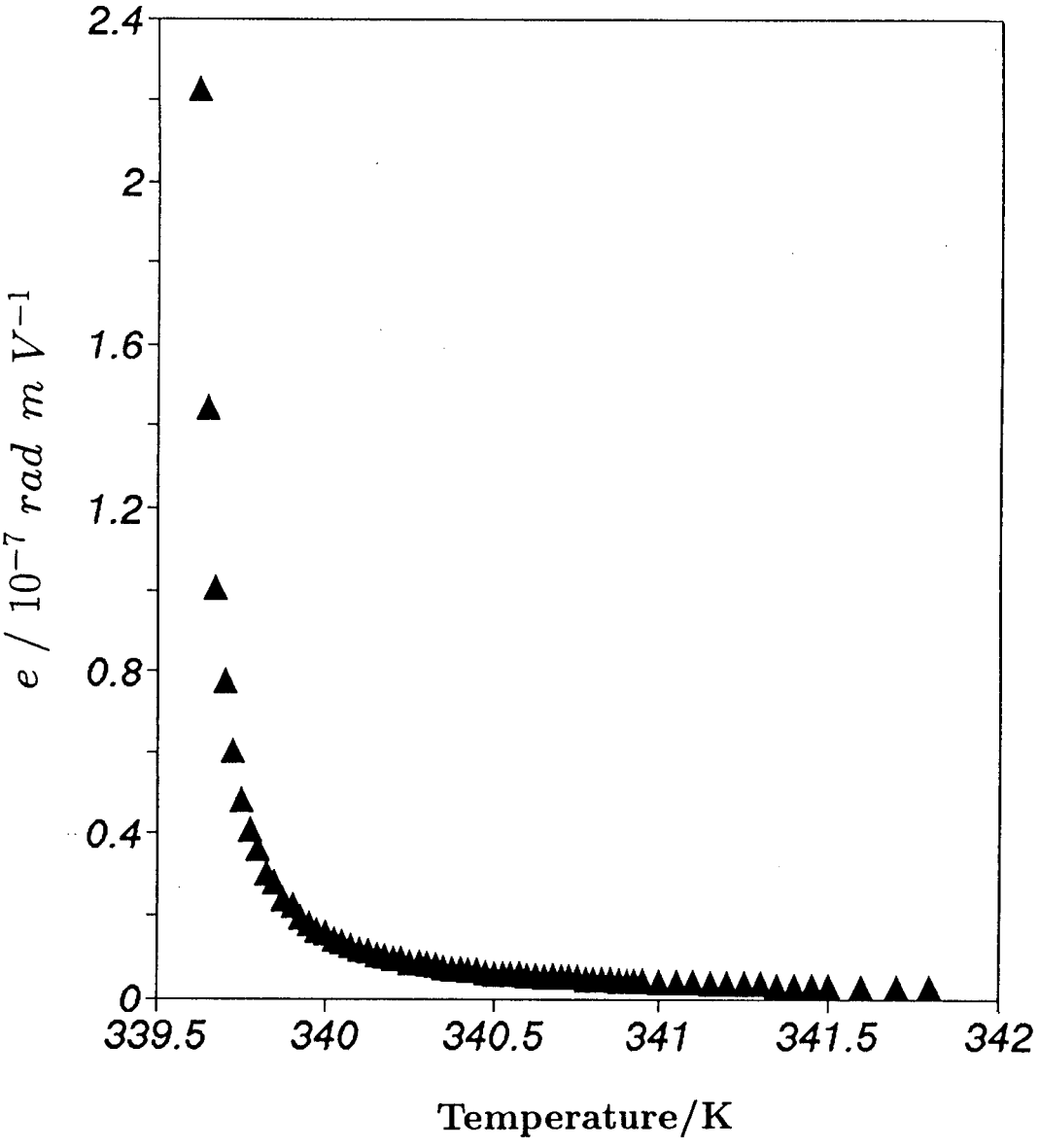


Figure 5.11. Temperature variation of e at 88 Hz for the compound SCE-5.

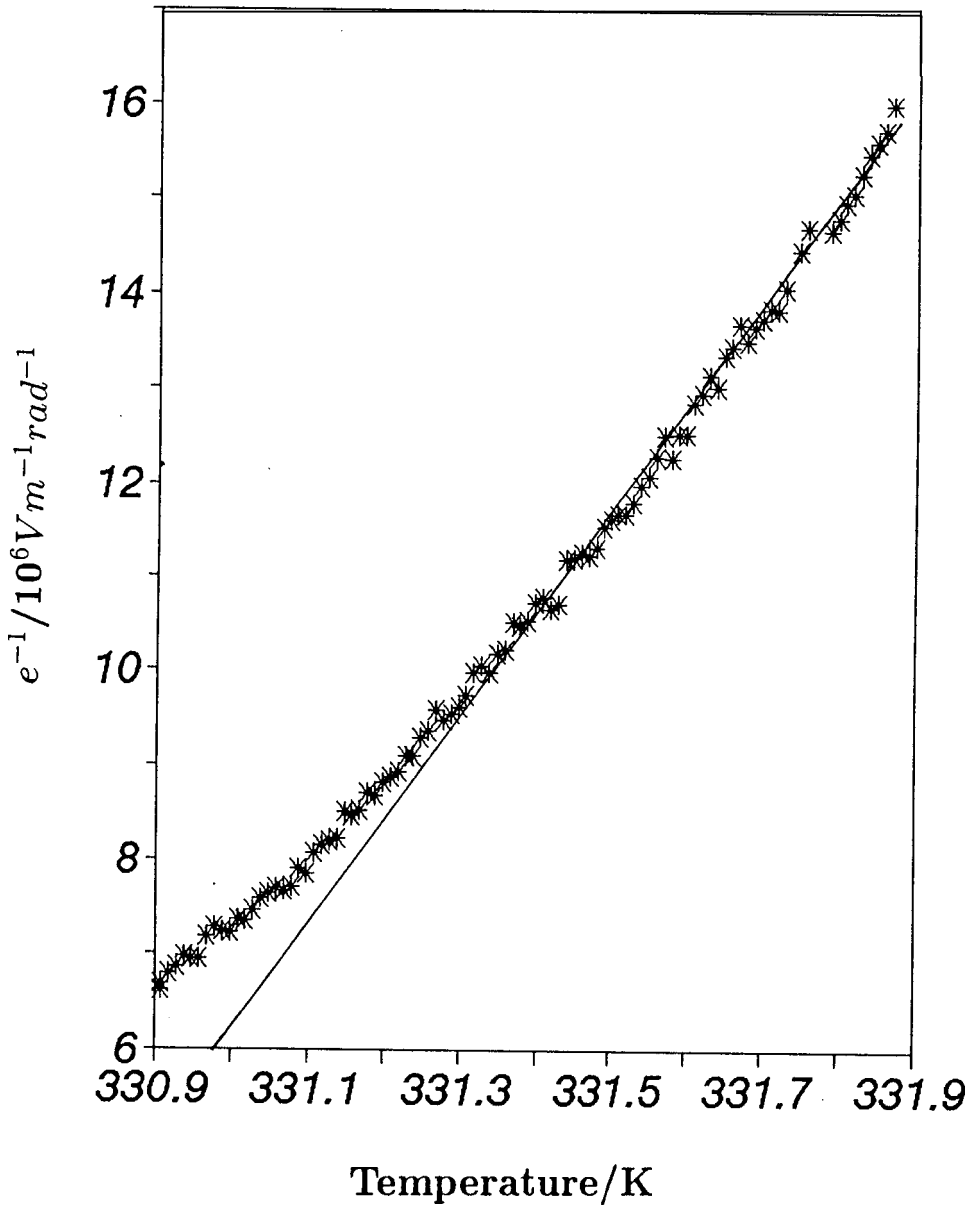


Figure 5.12. Temperature dependence of the inverse electroclinic coefficient, e^{-1} of the 7th homologue at 777 Hz.

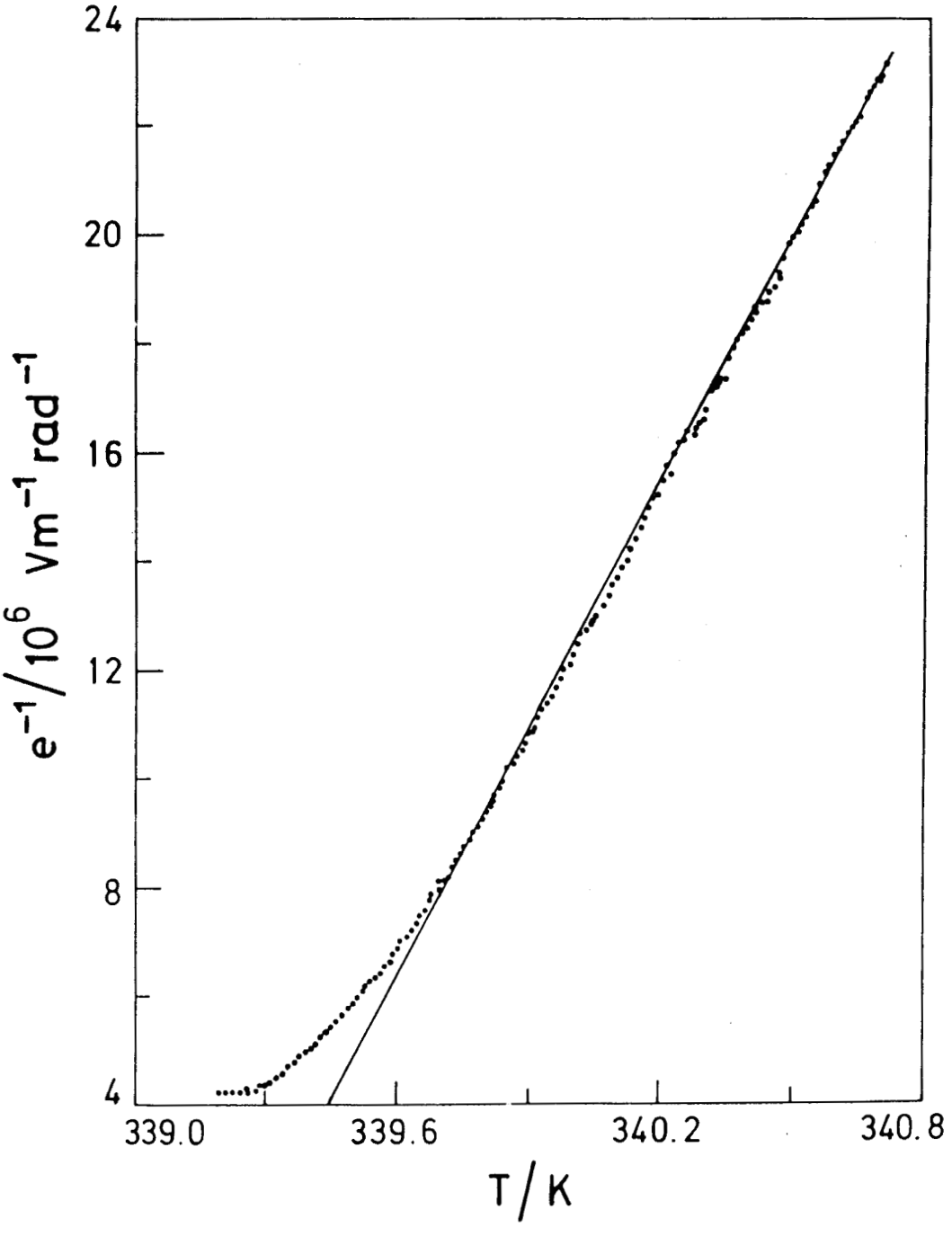


Figure **5.13.** Temperature dependence of the inverse electroclinic coefficient, e^{-1} of the 8th homologue at 1960 Hz.

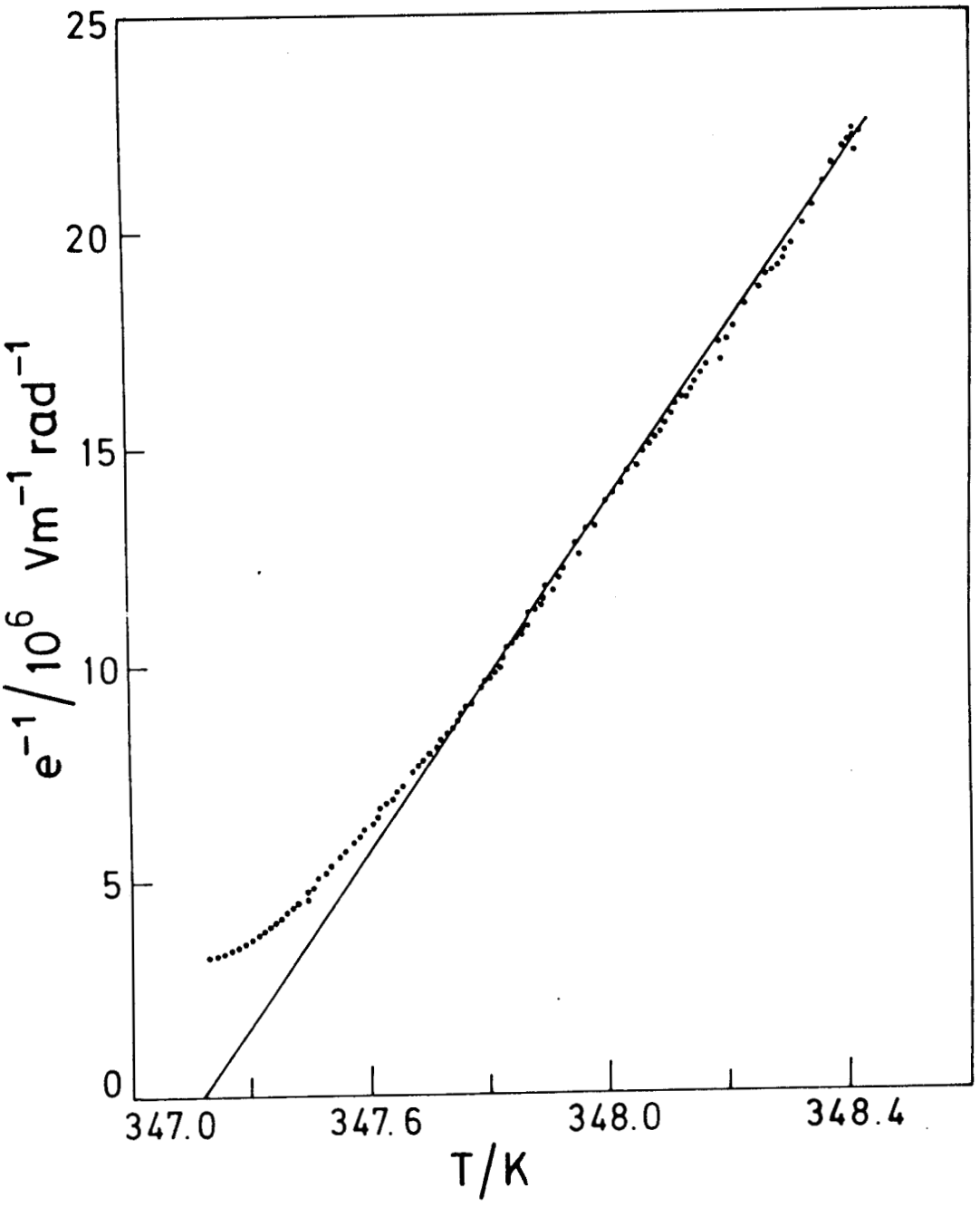


Figure 5.14. Temperature dependence of the inverse electroclinic coefficient, e^{-1} of the 9th homologue at 1960 Hz.

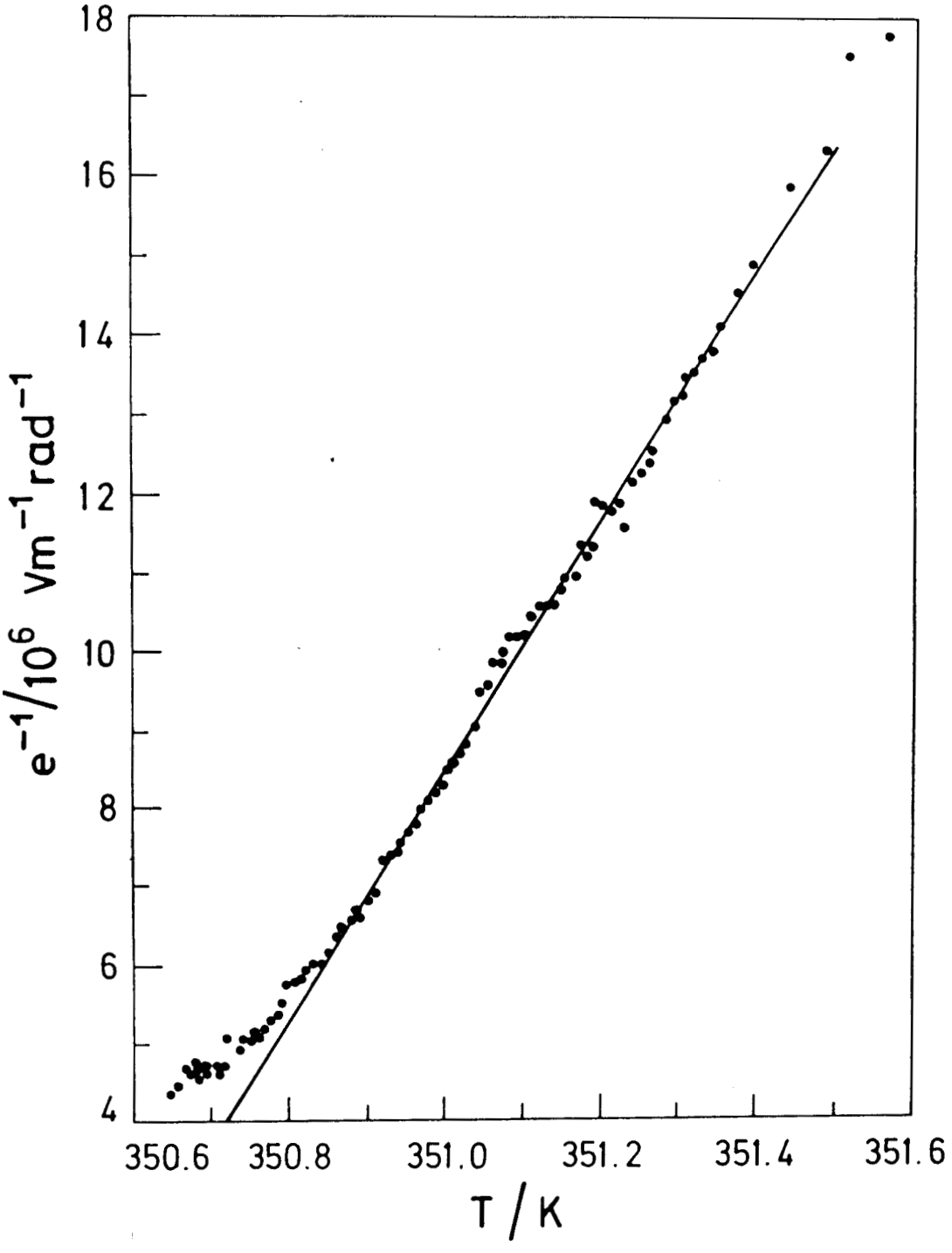


Figure 5.15. Temperature dependence of the inverse electroclinic coefficient, e^{-1} of the 10th homologue at 1960 Hz.

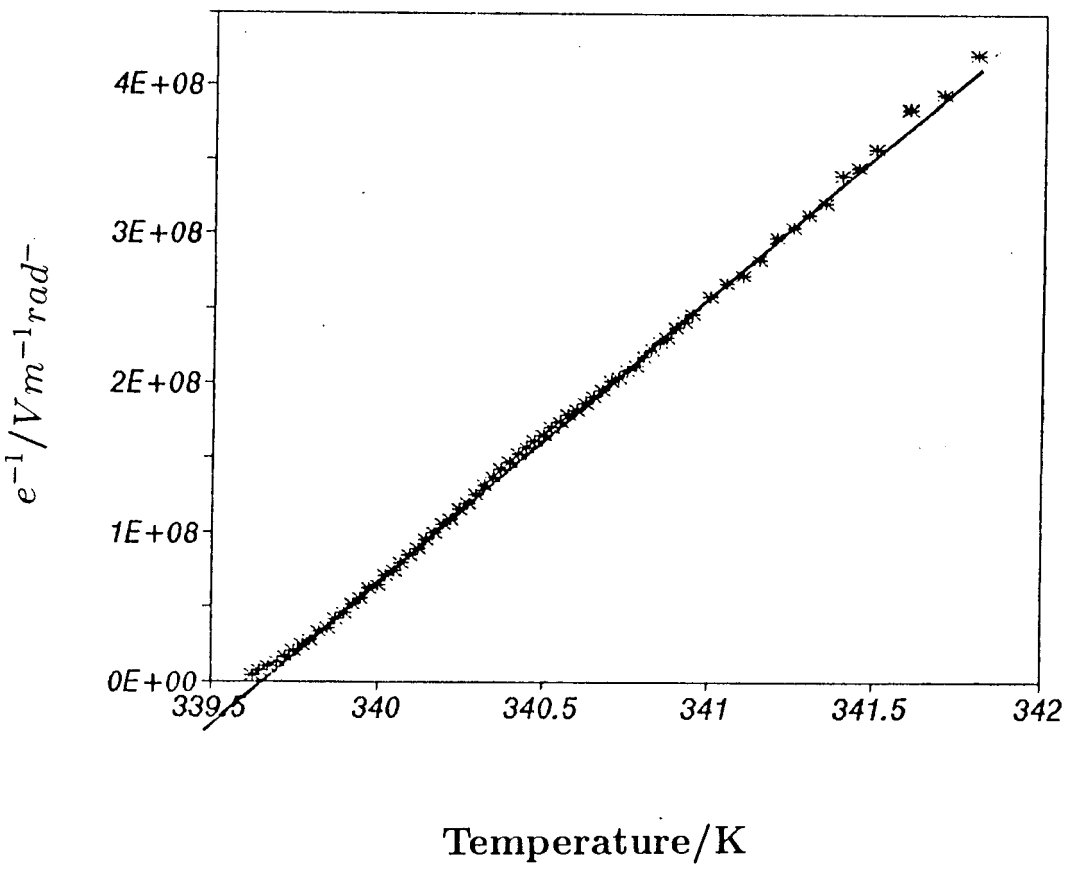


Figure 5.16. Temperature dependence of the inverse electroclinic coefficient, e^{-1} of SCE-5 at 88 Hz.

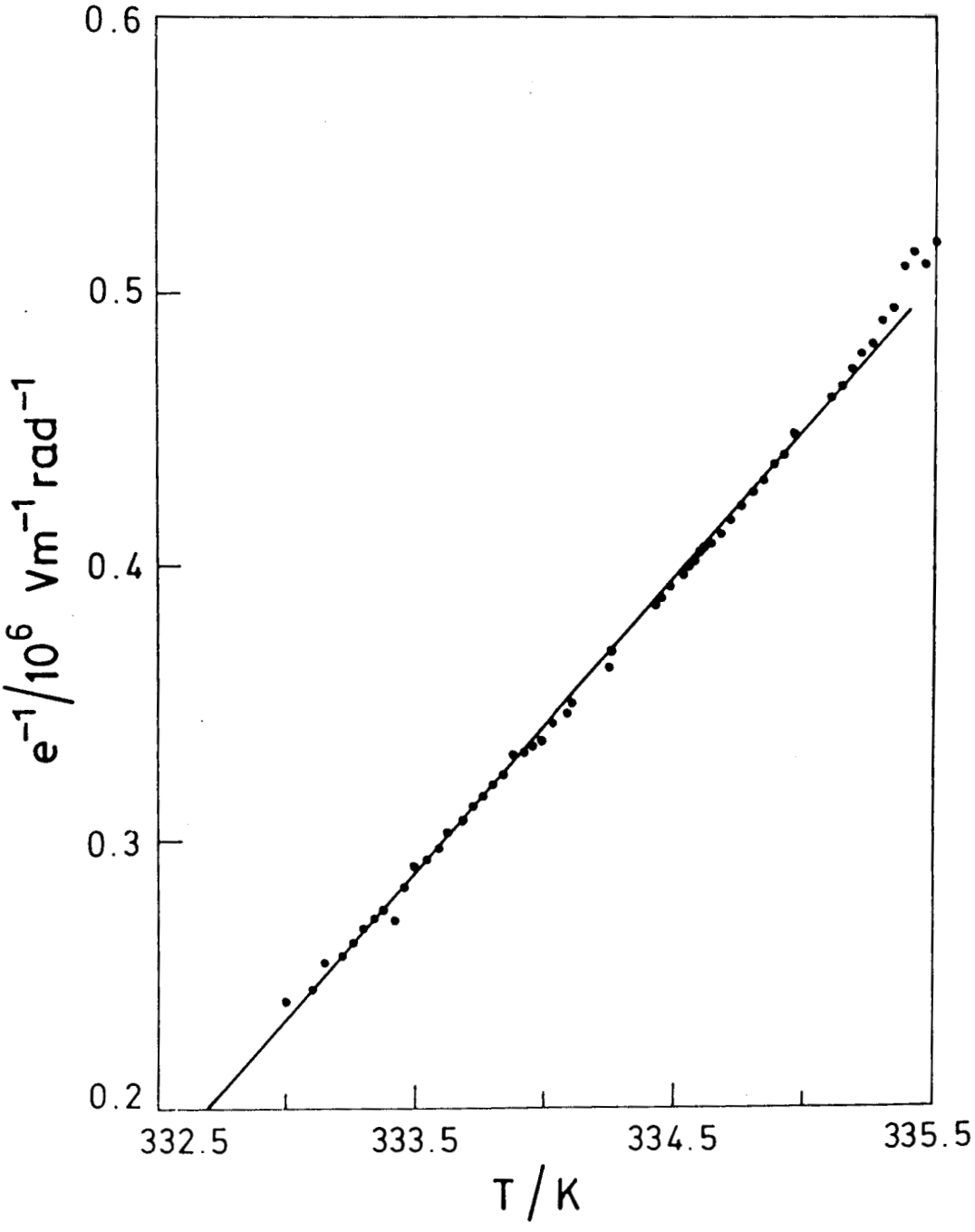


Figure 5.17. Temperature dependence of the inverse electroclinic coefficient, e^{-1} of SCE-6 at 1960 Hz.

relative temperature in the S_c^* phase (BDH catalogue). From equations (5.6) and (5.8), $\frac{P}{\theta} \sim c\chi_{\mathcal{P}}$, while the slope of e^{-1} vs. T plot is $\sim \frac{a}{c\chi_P}$ from equation (5.6). As $\mathcal{P}/\theta$ is an order of magnitude larger in the pure compounds compared to SCE-6, the slope is correspondingly smaller.

Though the results broadly agree with the Landau mean field model, we wanted to check this in a detailed manner using the phase angle measurements of the electrooptic signal. We have fitted our data on the amplitude and phase of the electroclinic signal of the eighth homologue to equations (5.10) and (5.11). Following Garoff and Meyer (1979), we use a temperature dependent viscosity

$$\eta = \eta_o e^{B/T} \tag{5.17}$$

where B is an activation energy in temperature units.

We adjusted the six parameters listed below to get an overall minimum in the χ^2 values for *both* the amplitude and the phase of the electroclinic signal: δ_b (the background phase angle far above T_c^*): 3.098 rad, B = 1971 K, T_c^* = 339.17 K, $\eta_o\omega/\tilde{a} = 2.475 \times 10^{-6}$, $c\chi_P/\tilde{a} = 2.135$ x 10^{10} and $\gamma = 1.0$. The results are shown in figures 5.18 and 5.19.

While the fit is not very good, as there are systematic deviations in both the parameters (Figures 5.18 and 5.19), it is clear that y cannot be significantly different from the mean field value. This is in agreement with other measurements on this index (Dupont et al., 1991). We should also note that our compound slowly deteriorated with time, and we have not taken into account this factor in the present calculations, as it appeared to be unimportant within one run.

Later, we made some improvements in our experimental arrangement. The whole set-up was computer controlled. Further, to measure the coefficients of Landau

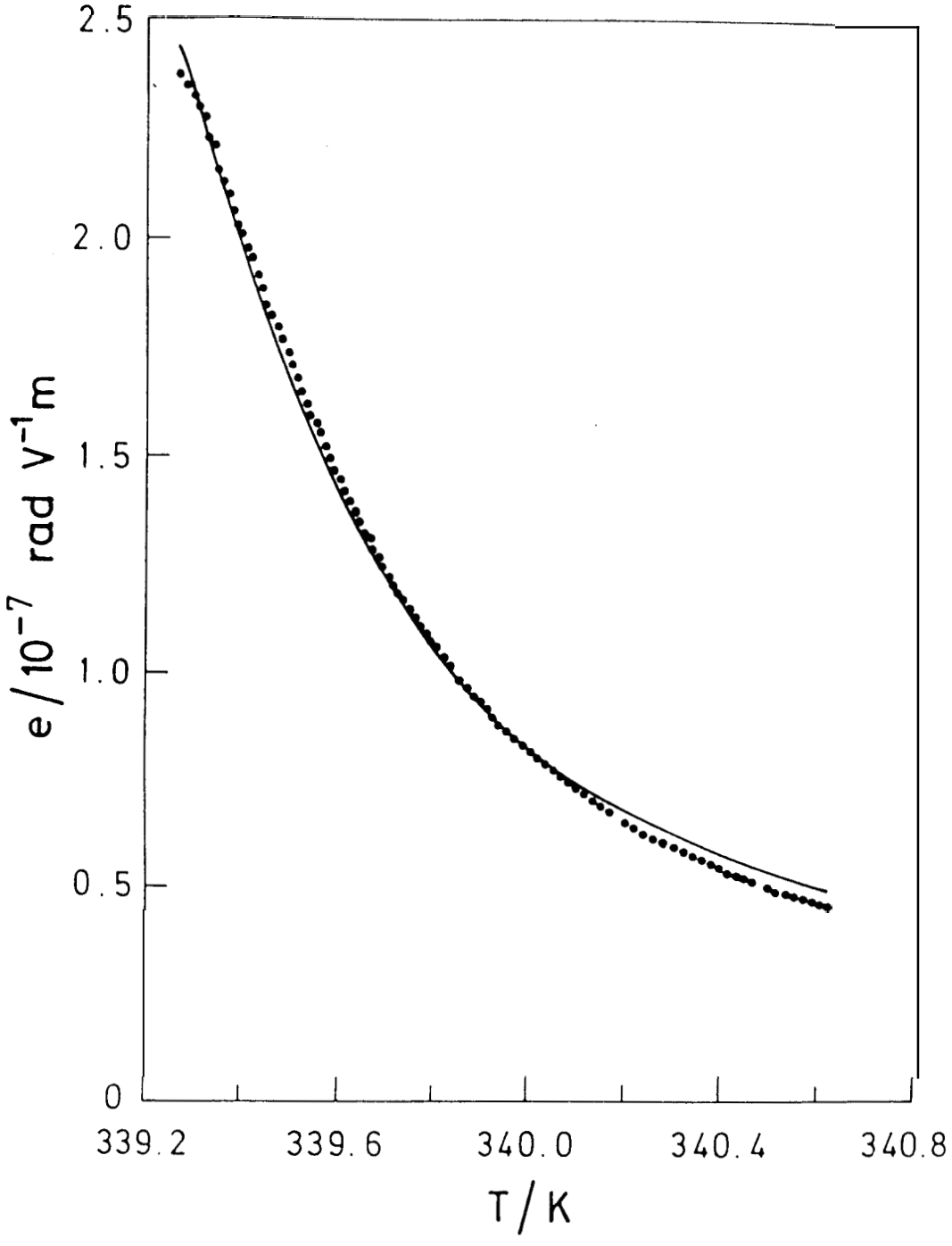


Figure 5.18. Divergence of e in the 8th homologue as T_c^* is approached. The continuous line is the theoretical variation given by equation (5.10).

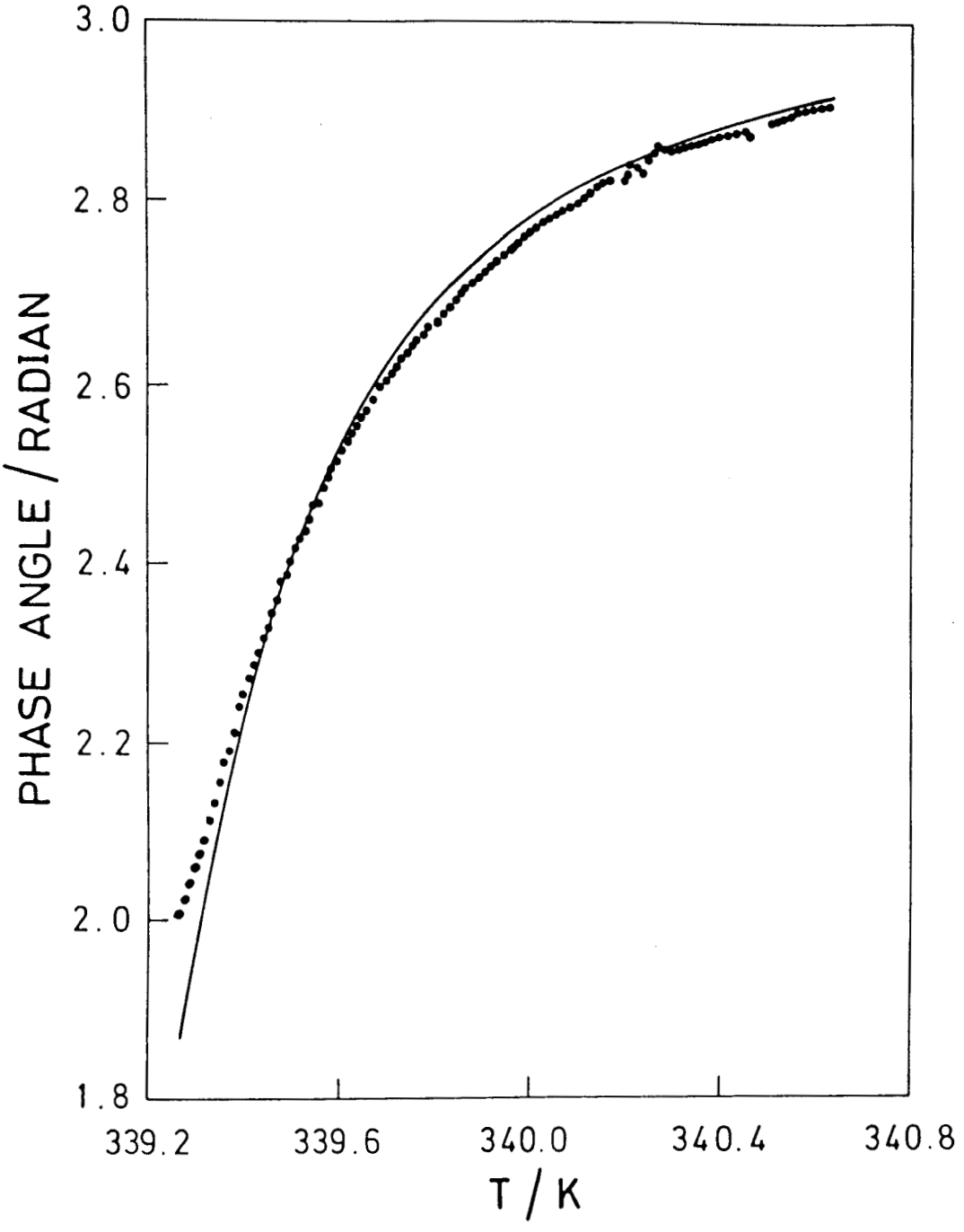


Figure 5.19. Temperature variation in the phase angle of the electroclinic signal in the 8th liomologue. The continuous line is the theoretical variation given by equation (5.11).

expansion like $\chi_{\mathcal{P}}$, it is necessary to make other measurements like that of the current through the sample. Further, in order to test the validity of equation (5.12), a measurement of the frequency dependence of e is necessary. In the next chapter, we describe experiments in which we have measured both optical and conductivity signals. We have used the data to calculate the coefficients of the Landau theory in two samples.

References

ANDERSSON,G., DAHL,I., KOMITOV,L., MATUSZCZYK,M., LAGERWALL,S.T., SKARP,K., STEBLER,B., COATES,D., CHAMBERS,M. and WALBA,D.M., 1991, *Ferroelectrics*, 114, 137.

ANDERSSON,G., DAHL,I., KELLER,P., KUCZYNSKI,W., LAGERWALL,S.T., SKARP,K. and STEBLER,B., 1987, Appl. Phys. Lett., 51, 640.

BAHR, Ch., and HEPPKE,G., 1987, Liquid Crystals, 2, 825.

BAHR,Ch. and HEPPKE,G., 1988, Phys. Rev. A., 37, 3179.

BERESNEV,L.A., BLINOV,L.M., OSIPOV,M.A. and PIKIN,S.M., 1988, *Mol. Cryst.* Liquid *Cryst.*, **158A**, 1.

BLINOV,L.M., 1983, *Electro-optical* and Magneto-optical Properties of Liquid Crystals, (John Wiley & Sons, Ltd.).

DAVEY,A.B. and CROSSLAND,W.A., 1991, Ferroelectric, 114, 101.

DUPONT,L., GLOGAROVA,M., MARCEROU,J.P., NGUYEN HU TINH, DESTRADE,C., and LEJCEK,L., 1991, J. Phys. 11, 1, 831.

GAROFF,S., and MEYER,R.B., 1977, Phys. Rev. Lett., 38, 848.

GAROFF,S., and MEYER,R.B., 1979, Phys. Rev. *A,* 19, 338.

GOODBY,J.W., BLINC,R., CLARK,N.A., LAGERWALL,S.T., OSIPOV,M.A., PIKIN,S.A., SAKURAI,T., YOSHINO,K., and ZEKS,B., 1991, Ferroelectric Liquid Crystals, (Gordon & Breach Science Publishers).

JOHNO,M., CHANDANI,A.D.L., TAKANISHI,Y., OUCHI,Y, TAKEZOE,H., and FUKUDA,A., 1991, Ferroelectrics, 114, 123.

KOMITOV,L., FLATISCHLER,K., ANDERSSON,G., LAGERWALL,S.T. and STEBLER, B., 1991a, Ferroelectrics, 114, 151.

KOMITOV,L., LAGERWALL,S.T., STEBLER,B., ANDERSSON,G. and FLATISCHLER,K., 1991b, Ferroelectrics, 114, 167.

LEGRAND,C., ISAERT,N., HMINE, J., BUISINE,J.M., PARNEIX,J.P., NGUYEN H.T. and DESTRADE,C., 1991, *Ferroelectrics*, 121, 21.

MEYER,R.B., LIEBERT,L., STRZELECKI,L., and KELLER,P., 1975, *J*. Phys. Lett. (Paris), 64, 307.

NISHIYAMA,S., OUCHI,Y., TAKEZOE,H., and FUKUDA,A., 1987, ***Jap. J. Appl.*** Phys., 26, L1787.

PAVEL,J. and GLOGAROVA,M., 1991, Ferroelectrics, 114, 131.

PRASAD,S.K., KHENED,S.M., CHANDRASEKHAR,S., SHIVKUMAR,B., and SADASHIVA,B.K., 1990, Mol. *Cryst.* Liquid *Cryst.,* **182B**, 313.

QIU,R., HO, J.T. and HARK,S.K., 1988, Phys. Rev. A., 38, 1653.

SHIVKUMAR,B., SADASHIVA,B.K., KRISHNA PRASAD,S., and KHENED,S.M., 1991, Ferroelectrics, 114, **273.**

SIN-DOO LEE, PATEL,J.S., and GOODBY,J.W., 1991, Phys. Rev. Lett., 66, 449.

SKARP,K. and HANDSCHY,M.A., 1988, Mol. *Cryst. Liquid Cryst.*, 165, 439.

VAN HAAREN,J.A.M.M. and RIKKEN,G.L.J.A., 1989, Phys. Rev. **A.,** 40, 5476.

VAN HAAREN,J.A.M.M. and RIKKEN,G.L.J.A., 1991, Ferroelectrics, 114, 113.

WILLIAMS,P.A., CLARK,N.A., BLANCAROS,M., WALBA,D.M. and WAND,M.D., 1991, Ferroelectrics, 121, 143.

XUE, J. and CLARK,N.A, 1990, Phys. Rev. *Lett.*, 64, 307.

ZILI LI, AKINS, R.B., DILI SI, G.A., ROSENBLATT,C. and PETSCHEK,R.G., 1991b, Phys. Rev. **A,** 43, 852.

ZILI LI, AMBIGAPATHY,R., PETSCHEK,R.G. and ROSENBLATT,C., 1991a, *Phys. Rev. A.*, 43, 7109.

ZILI LI, PETSCHEK,R.G. and ROSENBLATT,C., 1989, Phys. Rev. Lett., 62, 796.

ZILI LI and ROSENBLATT,C., 1989, Phys. **Rev.** *A.*, 39 1594.