MEASUREMENTS OF THE ELASTIC CONSTANTS OF A LIQUID CRYSTAL

by

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Abstract

The bend and splay elastic constants of the nematic liquid crystal octylcyanobiphenyl (8CB) are measured as a function of temperature using an electric-field-induced deformation.

The capacitance and birefringence of a sample cell, temperature controlled to 0.1mK, were simultaneously measured as a function of applied voltage. The splay constant is determined from the critical voltage at the onset of the deformation (the Freedericksz transition). The bend constant is found by fitting the data above the critical voltage to the theory of Deuling, which is derived in full. The data is also analysed in the high- and low-field limits of the theory.

The bend elastic constant displays a pretransitional divergence near the nematic-smectic A phase transition due to smectic fluctuation effects. The divergent part is fit by a power law with a critical exponent of $1.0 \pm 0.1$.

The Deuling theory, which is based on the assumption of linear elasticity, shows systematic deviation from the data at high voltages at all temperatures, with the disagreement increasing rapidly as the smectic phase is approached.

This result suggests that the linear elastic theory of Deuling fails for large deformations and where smectic fluctuations contribute significantly to the bend elasticity. The failure near the smectic transition may be explainable by the quenching of smectic fluctuations by the deformation.
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I. INTRODUCTION

...things that seem to us hard and stiff must be composed of deeply indented and hooked atoms and held firm by their intertangling branches... Liquids, on the other hand, must owe their fluid consistency to component atoms that are smooth and round. For poppy seed can be poured as easily as if it were water...

Lucretius

1.1 The Liquid Crystalline State

Liquid crystals are indeed liquid in the sense that they flow and do not support shear stresses. However, unlike familiar liquids they have anisotropic optical and mechanical properties reminiscent of some crystalline solids. Liquid crystalline phases occur at temperatures intermediate between a high temperature normal liquid phase and a low temperature solid phase.

The source of the symmetry-breaking order present in liquid crystals is the asymmetry of the molecules. The material used in this study was 4,4'-n-octylcyanobiphenyl which has the structure shown in Fig. 1.

![Structure of 4,4'-n-octylcyanobiphenyl](image)

Figure 1 - The structure of 4,4'-n-octylcyanobiphenyl
This material, which we will hereafter refer to as 8CB, is typical of a large class of materials which show liquid crystalline phases. The essential characteristics of these materials are that they are composed of large organic molecules which are long compared to their width and relatively inflexible. We will concentrate on the macroscopic properties of the liquid crystal, and not attempt to solve the difficult problem of how the molecular structure conspires to produce them. For our purposes, one may picture the molecule as a hard rod.

The observed phases of 8CB are shown schematically in Fig. 2. The structure of these phases has been determined by X-ray and light scattering experiments, by their optical properties and by the nature of the defects visible under a microscope.

![Diagram of phases of 8CB](image)

**Figure 2 - Schematic diagram of the phases of 8CB**
At temperatures greater than 40.5°C 8CB is a normal liquid. This is the "isotropic" phase. The isotropic liquid is clear and slightly viscous, like a very fine machine oil. At 40.5°C there occurs a liquid-liquid phase transition to the "nematic" phase. This liquid is noticeably more viscous than the isotropic phase and often has a cloudy, turbid appearance. In this phase the long molecules tend to point in one direction on the average. The centres of mass of the molecules are still positionally disordered as in a normal liquid. This, the simplest liquid crystal phase, is the main subject of this study and is described at greater length in a later section. Of particular interest is the phase transition between this and the "smectic A" phase.

The smectic A phase is the simplest of the "layered" phases which are called, not surprisingly, smectic A, B, C etc. Many of these phases are known, although not enough to exhaust the alphabet. Some materials go directly into a smectic phase from the isotropic while others show several different smectic phases as the temperature is lowered.

The smectic A phase has a layer structure with the normal to the layers parallel to the long molecular axes on the average. The thickness of these layers in 8CB is 49 Å which is about twice the length of the 8CB molecule. 8CB is therefore called a "bilayer smectic". In appearance smectics A are less turbid-looking than nematics but are more viscous.

In the smectic A phase there is still no positional order within the layers. The "higher" smectics, B, C, etc. are
progressively more ordered within the layers. These phases will not concern us any further. In any event there are no higher smectic phases in 8CB, as it freezes to a waxy solid from the smectic A phase at 21.5°C.

Modern work in liquid crystals is motivated mainly by theoretical interest in their many phase transitions and by their widespread application as low-power electronic display devices. Liquid crystals have, however, been known and systematically studied since the middle of the 19th century. A historical review of the work before 1945 has been given by Kelker.

The modern field of liquid crystals has been the subject of several books, notably those of de Gennes and Chandrasekhar. The emphasis of the de Gennes book makes it particularly useful for understanding the nematic phase. Blinov discusses the various responses of liquid crystals to electric and magnetic fields and the device applications of nematics. An excellent review of experimental results has been given in the book by de Jeu.

We now turn to the specifics of the nematic and smectic A phases and the phase transition between them.
1.2 The Nematic Phase

In this section we give a brief review of the nematic phase.

The axis along which the long molecules tend to point in the nematic phase is a special direction in the liquid. Properties of the bulk liquid such as dielectric constant or index of refraction are different along this axis than in the plane perpendicular to it. The liquid is rotationally symmetric only about this special direction. It is convenient to define a unit vector, called the "director" which points along this symmetry axis of the crystal. The director, which we denote by $\hat{n}$, is in general a function of position. Of course, the concept of a spatially varying director is only useful on scales which are large compared to the molecular size.

The crystal described by $\hat{n}$ is identical to that described by $-\hat{n}$. That is, we require that all the physical quantities be invariant under the transformation $\hat{n} \rightarrow -\hat{n}$. This expresses the fact that in a nematic the long range molecular orientational order does not distinguish between one end of the molecule and the other. The liquid has this symmetry even if the molecules do not. Thus any correlation of the molecules that depends on their end-for-end orientations extends only to distances on the order of a molecular length. In the smectic A phase, where the concept of the director is still useful, it is probably these short range correlations that lead to the "bilayer" structure of the smectic layers in 8CB.

In the nematic phase the molecules are not all perfectly
aligned with the director. There is in general some distribution of orientations. As a first approximation, we may suppose that this distribution only depends on the polar angle \( \Theta \) between the long axis of the molecule and the director and not on the azimuthal angle. This is equivalent to assuming that the molecules are uncorrelated with respect to rotations about their long axes. In this approximation a measure of the degree of nematic order, a so-called "order parameter", is given by

\[ S = \frac{1}{2} \langle 3 \cos^2 \Theta - 1 \rangle \]

where \( \langle \rangle \) denotes an average over the distribution of orientations. Note that the equivalence of \( \hat{n} \) and \( -\hat{n} \) makes \( \langle \cos \Theta \rangle \) zero. Perfect alignment, all \( \Theta = 0 \) or \( \pi \), gives \( S = 1 \), while if \( \Theta \) is randomly distributed \( S = 0 \). A simple mean-field theory, the Maier-Saupe theory, of the nematic phase can be constructed by assuming that a particular molecule, labelled by \( i \), has an orientational energy proportional to

\[ -\frac{1}{2} (3 \cos^2 \Theta_i - 1) S \]

In the simplest version of this theory the proportionality constant is temperature independent. This theory correctly predicts that the isotropic-nematic transition is first order, that is, that \( S \) jumps discontinuously to a nonzero value at the transition temperature \( T_{NI} \). It also gives a qualitatively correct temperature dependence of \( S \) below \( T_{NI} \). More on this
theory can be found in the general references\textsuperscript{2,3,4,5}

The effect of walls or free surfaces on the nematic director is of some importance in liquid crystal experiments and applications. The interactions between a liquid crystal and the surface of a material are very sensitive to the chemical and physical state of the surface. This long studied problem is the subject of a recent monograph\textsuperscript{7}. The most desirable sort of surface is one which constrains the director to one given direction ("strong anchoring") which is experimentally known and is controllable by surface preparation. Suitably prepared surfaces produce well known boundary conditions on the director field and make the preparation of oriented single crystals possible.

The general continuum equations for the flow and deformation of nematics ("nematodynamics") are quite complex but the static case is remarkably simple. "Deformation" of the crystal simply means a spatially varying director field. As long as the scale of these static deformations is large compared to a molecular length we can consider the order parameter as if it was undisturbed by them. The "continuum limit" is

\begin{equation}
\alpha |\nabla \hat{n}| \ll 1
\end{equation}

where "\( \alpha \)" is a molecular length.

The crystal resists such deformations because to produce them one must do work against the intermolecular forces that tend to align the molecules. One can construct a linear elastic
theory of the director field by considering only lowest order
gradients of $\hat{n}$. A remarkable fact is that the symmetry of the
director field allows only three independent deformations and
consequently only three elastic constants. These deformations
are illustrated in Fig. 3.

The elastic free energy per unit volume associated with
these deformations is given by

$$f_N = \frac{1}{2} K_{11} (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_{22} (\hat{n} \cdot \nabla \times \hat{n})^2 + \frac{1}{2} K_{33} (\hat{n} \times \nabla \times \hat{n})^2$$

(4)

The three elastic constants are given the picturesque names
"splay", "twist" and "bend" and are known as the "Frank-Oseen
constants" after their originators $B$.

It is of interest to estimate the magnitude of the elastic
constants. Since $\hat{n}$ is dimensionless and $f_N$ has units
energy/volume the elastic constants must have units of force.
The elastic constants should be of order $U/a$ where $U$ is a
characteristic energy of the nematic ordering interaction and $a$
is the molecular length. For $U$ we may take $k_B T_{NI}$, where $T_{NI}$
is the nematic-isotropic transition temperature and $k_B$ is
Boltzmann's constant, since this transition occurs when the
temperature is such that the thermal energy $k_B T_{NI}$ per molecule
is comparable to the interaction energy which drives the nematic
order. In these materials $T_{NI} \approx 300K$ and $a \approx 50\AA$, $k_B \approx 10^{-24} \text{JK}^{-1}$
so $K \sim k_B T_{NI} / a \sim 10^{-12}$ Newton. As we will see later the elastic
constants are indeed of this order except at temperatures close
to the nematic-smectic A transition.
Figure 3 - The three independent deformations of a nematic and their associated elastic constants

Splay $K_{11}$

Twist $K_{22}$

Bend $K_{33}$
The task of the experiment to be described is to improve on this estimate.

Electric and magnetic fields have interesting and useful effects on nematics and almost all experiments and applications involve them. We will consider the electric field case since it is relevant to our experiment. The magnetic case is generally simpler however, since liquid crystals have very small magnetic susceptibilities.

The electric contribution to the free energy density is given by

$$f_E = -\frac{1}{2} \varepsilon_0 E \cdot \varepsilon(\hat{n}) \cdot E$$

where $E$ is the electric field, $\varepsilon_0$ is the permittivity of free space and $\varepsilon(\hat{n})$ is the dielectric constant tensor. Since the nematic is anisotropic the dielectric properties must be expressed as second rank tensors and the electric displacement vector $D = \varepsilon \cdot E$ is not, in general, parallel to $E$. We have written this tensor as a function of $\hat{n}$ since clearly its principal axes follow the crystal axes which are represented by $\hat{n}$. In the principal axis frame we have

$$\varepsilon = \begin{pmatrix}
\varepsilon_\perp & 0 & 0 \\
0 & \varepsilon_\parallel & 0 \\
0 & 0 & \varepsilon_\perp
\end{pmatrix}$$

where $\varepsilon_\parallel$ is the dielectric constant for fields parallel to $\hat{n}$ and $\varepsilon_\perp$ the constant for fields perpendicular to $\hat{n}$. Both $\varepsilon_\parallel$ and $\varepsilon_\perp$ depend on the degree of nematic order and hence on temperature.
In 8CB the dielectric anisotropy $\Delta \varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$ is positive.

The electric displacement in terms of the director field is

$$
\mathbf{D} = \varepsilon_0 \varepsilon_{\perp} \mathbf{E} + \varepsilon_0 \Delta \varepsilon (\mathbf{E} \cdot \mathbf{\hat{n}}) \mathbf{\hat{n}}
$$

so that equation (5) reduces to

$$
f_E = -\frac{1}{2} \varepsilon_0 \left( \varepsilon_{\perp} E^2 + \Delta \varepsilon (\mathbf{E} \cdot \mathbf{\hat{n}})^2 \right)
$$

Only the second term depends on $\mathbf{\hat{n}}$. In materials with positive $\Delta \varepsilon$ equation (8) implies that the free energy is minimized for $\mathbf{\hat{n}}$ parallel to $\mathbf{E}$. If $\mathbf{\hat{n}}$ is not aligned with $\mathbf{E}$ the crystal will feel a torque $\mathbf{T}$ per unit volume given by

$$
\mathbf{T} = \mathbf{D} \times \mathbf{E}
$$

$$
= \varepsilon_0 \Delta \varepsilon (\mathbf{E} \cdot \mathbf{\hat{n}}) (\mathbf{\hat{n}} \times \mathbf{E})
$$

This torque will reorient the crystal subject to a generalized form of viscous drag, the elastic stresses, given by equation (4), and the boundary conditions on $\mathbf{\hat{n}}$.

We will describe in the next chapter how we will measure the elastic constants by measuring the deformation of the director field when the elastic forces are balanced against known electric fields and surface boundary conditions.
1.3 The Smectic A Phase

In this section we give a more quantitative description of the layered structure of smectics and introduce the de Gennes model of the smectic A phase.

It has been found by X-ray scattering that to a good approximation the "layers" of a smectic may be described as a one-fourier-component mass density wave of the form

\[ \rho(r) = \rho_0 \left( 1 + \Re \left( \frac{\Psi}{\psi} \right) e^{i q_0 z} \right) \]

where \( \rho_0 \) is a background density and \( q_0 = \frac{2\pi}{d} \) where \( d \) is the layer spacing. \( \Re \) means "take the real part". The coordinates are such that the layers lie in the xy plane and \( \hat{n} \) is parallel to the z axis.

The complex amplitude \( \Psi \) is given by

\[ \Psi = \Psi e^{i q_0 u(r)} \]

where the real valued function \( u(r) \) gives the displacement of the layers and \( \Psi \), a real number, gives their amplitude. \( \Psi \) is the order parameter for the smectic A phase in the de Gennes model.

In order to get some idea of how the elastic properties of the smectic A phase differ from the nematic phase we consider a line integral
For a defect-free smectic this integral, no matter what its path, simply counts the number of layers between points A and B. Hence for a closed contour

\[ \frac{1}{d} \oint_{A}^{B} \hat{n} \cdot dl = 0 \]

from which we deduce that \( \nabla \times \hat{n} = 0 \) by Stokes theorem. We conclude that in a defect-free smectic "twist" or "bend" deformations, which involve \( \nabla \times \hat{n} \) by equation (4), are not allowed. This is equivalent to saying that the elastic constants \( K_{22} \) and \( K_{33} \) are infinite in a smectic.

The de Gennes model was inspired by an analogy between smectics A and superconductors. This model has stimulated most of the recent work on smectics and the nematic-smectic A phase transition. It is not a coincidence that de Gennes has also written a book on superconductors.

The connection between smectics A and superconductors can be made because both have an order parameter which is a complex number \( \Psi \). In the superconductor \( \Psi \) is the wavefunction of the Cooper pairs. In the smectic \( \Psi \) describes the magnitude and phase of the mass density wave. The free energy density in the de Gennes model is a generalization of the phenomenological Landau - Ginzburg expansion for a superconductor in powers of \( \Psi \).
and its gradients

\[ f_s = \alpha |\Psi|^2 + \frac{\beta}{2} |\Psi|^4 + \ldots \]

(14)

\[ + \frac{1}{2M_v} \left| \frac{\partial \Psi}{\partial z} \right|^2 + \frac{1}{2M_T} \left| (\nabla_T - i q_0 (\delta \hat{n}) ) \Psi \right|^2 + f_N + \ldots \]

where \( \alpha \) changes sign at \( T_{NA} \)

(15)

\[ \alpha = \alpha' (T - T_{NA}) \]

as usual for a Landau theory of a second order phase transition. \( \nabla_T \) is the gradient operator in the xy plane, transverse to the director. The gradient terms contain phenomenological "anisotropic masses" \( M_v \) and \( M_T \), which are equal for a superconductor, and the transverse gradient term contains a coupling to small variations in the director resulting from variations of \( u(r) \) in the plane of the layers. To the lowest order they are

(16)

\[ \delta \hat{n} = - \nabla_T u(r) \]

\( f_N \) is the nematic contribution to the free energy, equation (4), which now only contains the splay term.
Equation (14) has the same form as the Landau-Ginzburg free energy of a superconductor if we identify $\hat{n}$ with the vector potential $A$, and allow anisotropic Cooper pair masses. The quantity $q_o$ replaces $2e/c$ for the superconductor, where $2e$ is the charge of a Cooper pair and $c$ is the velocity of light.

We now recognize our earlier result, $\nabla \times \hat{n} = 0$, as the analog of the expulsion of a magnetic field $B = \nabla \times A$ by a superconductor (the well known Meissner effect).

Let us consider a simple case of equation (14), when $|\Psi|$ is spatially uniform. Then

\[<|\Psi|> = \sqrt{-\frac{\alpha}{\beta}} = \psi_0\]

and the transverse gradient terms drop out. This leaves

\[f_S = -\frac{\alpha^2}{2\beta} + \frac{B}{2} \left( \frac{\partial u}{\partial z} \right)^2 + \frac{K_{\|}}{2} (\nabla \cdot \hat{n})^2\]

where the new elastic constant $B$ is given by $B = \frac{\psi_0^2 q_o^2}{MV}$. The $B$ elastic constant is associated with displacements of the layers parallel to $\hat{n}$ while the nematic splay constant $K_{\|}$ is associated with the bending of the layers. $B$ can be measured by X-ray $^{12}$ and light $^{13}$ scattering.

We can form a characteristic length
\[ \lambda = \sqrt{\frac{K_{ij}}{B}} \]

which is the analog of the magnetic penetration depth in superconductors. In the smectic, \( \lambda \) measures the penetration depth of bend and twist deformations imposed as boundary conditions. Note that \( \lambda \) diverges as we approach \( T_{NA} \) from below. A similar effect occurs in the superconducting case.

There is a second length scale in the problem, namely the coherence length

\[ \xi = \sqrt{2M\alpha} \]

where we have ignored the anisotropy of \( M \). The coherence length measures the range over which a local perturbation of \( \Psi \) extends. The ratio of \( \lambda \) and \( \xi \) is the so-called "Landau Ginzburg parameter"

\[ k = \frac{\lambda}{\xi} \]

If \( k < \sqrt{2} \) a superconductor is said to be "type I" and the application of a magnetic field will lower the normal-superconducting transition temperature and make it first order. If \( k > \sqrt{2} \) the material is a "Type II" superconductor and the magnetic field first produces an intermediate "Shubnikov" phase where normal and superconducting areas coexist.
before the conductivity is driven completely normal at higher fields.

Smectic liquid crystals with second order nematic-smectic A transitions appear to be analogous to type I superconductors. The depression of $T_{NA}$ with the application of twist predicted by de Gennes was recently observed experimentally.

With any analogy, there is a point where the similarity ends. Several features of the smectic are quite unlike the superconductor and it is these features which make the smectic phase interesting. Because of the presence of the splay term in equation (19) the thermal fluctuations of $u(r)$ destroy the long range order of the smectic layers. One finds that the displacement $u(r)$ diverges logarithmically

$$\left< u^2(r) \right> \sim \log(q_0 L)$$

where $L$ is the sample dimension. Scattering X-rays from this "quasi-long range order" produces sharp power-law singularities in the intensity rather than the $\delta$-function like Bragg spots of true long range order. These have been observed by sensitive X-ray experiments. This divergence is a consequence of the linear elastic theory. To understand quasi-long range order one must turn to an anharmonic theory. This has been carried out by Grinstein and Pelcovits.

Another point of dissimilarity, again due to the splay term, is that $n$ does not have the gauge symmetry of $A$. This makes the theories of the nematic to smectic A phase transition
more complicated than those of the superconducting transition.

1.4 The Nematic - Smectic A Phase Transition

In this section we consider the effect of pretransitional smectic fluctuations on the nematic.

In the nematic phase the expectation value of the smectic A order parameter is zero but thermodynamic fluctuations of smectic-like order can have a large effect on the bulk nematic. Very near a second order nematic smectic A transition the nematic has "islands" of local smectic A-like order with dimensions given by a correlation length. Roughly speaking these islands strongly resist twist and bend deformations like a bulk smectic. As a result the overall twist and bend elastic constants of the nematic are increased.

The de Gennes model provides us with an analogous process in a superconductor, the pretransitional increase in diamagnetic susceptibility. The result of a calculation by Schmid translated into liquid crystalline terms gives

\[ K_{22} = K_{22}^0 + \frac{k_B T \mathbf{q}_0^2}{24 \pi} \frac{\chi_{\perp}^2}{\chi_{\parallel}} \]
where $\xi_{||}$ and $\xi_{\perp}$ are the correlation lengths parallel and perpendicular to $\hat{n}$ and $K_{ii}^0$ denotes a background nematic contribution. From the general theory of critical phenomena we expect the correlation lengths to diverge according to a power law

\begin{equation}
\xi_{||} = \xi_{||}^0 t^{-\nu_{||}} \quad \xi_{\perp} = \xi_{\perp}^0 t^{-\nu_{\perp}}
\end{equation}

where the reduced temperature $t$ is given by

\begin{equation}
t = \frac{T}{T_N} - 1
\end{equation}

Furthermore, according to the standard dogma of renormalization group theories we expect this phase transition to be in the same "universality class" as the three dimensional $XY$ spin model since this is a three dimensional crystal whose order parameter is the complex number $\Psi$. Thus the predicted correlation length exponents are
A number of experiments have measured these exponents by a variety of techniques and the consensus is now that the nematic smectic A transition fails to fit the standard picture outlined above. This failure has stimulated a large theoretical and experimental effort which is still ongoing.

We defer until the last chapter a review of the relevant experimental results of other authors. The general disagreements are two. First, the parallel and perpendicular correlation length exponents are not found to be equal. This is incomprehensible in any model which obeys "isotropic scaling". A renormalization group theory with "anisotropic scaling" was developed by Lubensky to account for this result. It predicts

\[ \gamma_{||} = 2 \gamma_{\perp} \]

The observed exponent ratio is smaller than this. The second major disagreement is that the exponents \( \gamma_{||} \) and \( \gamma_{\perp} \) are not found to be universal for different materials. This has led to the suggestion that these materials, which have second order nematic - smectic A transitions, lie close to a tricritical point where the transition becomes first order. Near such a point the critical exponents would be expected to exhibit "crossover" to tricritical values.
It is the objective of this experiment to measure the nematic elastic constants $K_{ll}$ and $K_{33}$ throughout the nematic range and particularly near the nematic to smectic A transition with sufficient accuracy to determine the critical exponent $\gamma_{ll}$. 
II. THEORY OF THE FREEDERICKSZ TRANSITION

It is a capital mistake to theorize before one has data.

Sir Arthur Conan Doyle
Scandal in Bohemia

2.1 The Director

In this chapter we will describe a particular electric field induced deformation of the nematic and outline how it can be used to determine two of the elastic constants.

This deformation is one of several similar electric and magnetic effects known collectively as "Freedericksz transitions" after their discoverer who first observed them in 1927. They are called "transitions" because, as we shall see, the onset of the deformation is formally a field-induced second order phase transition. Discussions of the Freedericksz transition can be found in the general references and thorough review papers have been written by Deuling and Chigrinov.

Consider the experimental set up shown in Fig. 4. A nematic sample is enclosed between the plates of a parallel plate capacitor. We assume that the two plates have been surface treated so that the director is rigidly anchored in the plane of the plate parallel to the x axis. The capacitor is formed by the planes z=0 and z=L. If the applied voltage is zero the surface treatment will suffice to produce a defect-free
Figure 4 - Schematic diagram of the Freedericksz transition

![Diagram](image)

\begin{align*}
V < V_c & \quad V \sim V_c & \quad V \gg V_c \\
\end{align*}

nematic crystal with \( n \) parallel to \( x \) everywhere.

Now consider what happens when the voltage across the capacitor is slowly increased, starting from zero. Initially nothing happens. The equilibrium director configuration for small voltages is uniform (Fig. 4a). Then at a "critical voltage" \( V_c \) the director begins to deform (Fig. 4b). The deformation increases from zero until at voltages much larger than \( V_c \) the director is nearly aligned with \( E \) except in thin regions near the walls (Fig. 4c).

The existence of a critical voltage below which there is no deformation can be explained qualitatively as follows. A deformed region with length scale \( l \) has an elastic energy density of order \( K/l^2 \) where \( K \) is the magnitude of the elastic constants (recall that \( K \) has units of force). If this deformation is just balanced by the electric energy of the same region, the electric energy density is of order \( \varepsilon_0 \Delta \varepsilon E^2 \) and
we find a characteristic length

\[ l \sim \frac{1}{E} \sqrt{\frac{K}{\varepsilon_0 \Delta \varepsilon}} \]  

(30)

Setting \( l = L \), the cell thickness and using \( V = E L \), we find a characteristic voltage for the balance of electric and elastic energy

\[ V \sim \sqrt{\frac{K}{\varepsilon_0 \Delta \varepsilon}} \]  

(31)

In due course we will see that the actual critical voltage is given by

\[ V_c = \pi \sqrt{\frac{K_{11}}{\varepsilon_0 \Delta \varepsilon}} \]  

(32)

For voltages less than \( V_c \) the elastic energy dominates, above \( V_c \) the electric energy is dominant. We now consider in detail the full solution for the equilibrium deformation for voltages above \( V_c \).

The solution of this problem is due to Deuling. The relevant equations are the free energy per unit volume, equations (4) and (5)

\[ f = \frac{1}{2} K_{11} (\nabla \cdot \nabla) + \frac{1}{2} K_{22} (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_{33} (\hat{n} \times \nabla \hat{n})^2 - \frac{1}{2} \varepsilon_0 D \cdot E \]  

(33)

with Maxwell's equations in the medium
(34) \[ \nabla \cdot \mathbf{D} = 0 \quad , \quad \nabla \times \mathbf{E} = 0 \]

(we assume the crystal is nonconducting) and the constituent equation

\[ \mathbf{D} = \varepsilon \cdot \mathbf{E} \]

\[ = \varepsilon_0 (\varepsilon_1 \mathbf{E} + \Delta \varepsilon (\mathbf{E} \cdot \mathbf{\hat{n}}) \mathbf{\hat{n}}) \]

subject to the rigid boundary conditions on the walls.

It is clear from symmetry that none of the vector quantities will have \( y \) components. The director field will be given by

\[ \mathbf{\hat{n}} = (\cos \phi, 0, \sin \phi) \]

where \( \phi \) is the angle between \( \mathbf{\hat{n}} \) and the \( x \) axis. Symmetry dictates that \( \phi \) and all other scalar quantities can be functions of \( z \) only. The free energy per unit area is then

\[ F = \frac{1}{2} \int_0^L \{ (K_{11} \cos^2 \phi + K_{33} \sin^2 \phi) \left( \frac{d\phi}{dz} \right)^2 - \mathbf{D} \cdot \mathbf{E} \} \, dz \]

Note that this deformation is independent of \( K_{22} \).

Consider the electric term first. From \( \nabla \times \mathbf{E} = 0 \) we deduce that \( \mathbf{E} \) is the gradient of a potential which, by symmetry can only depend on \( z \). Therefore \( \mathbf{E} = (0, 0, E_z) \). Similarly from \( \nabla \cdot \mathbf{D} = 0 \) we deduce that the \( z \) component of \( \mathbf{D} \) is independent of
z. From equation (35) it is

$$D_z = \varepsilon_0 \varepsilon_{\perp} (E_z + \Delta \varepsilon E_z \sin^2 \phi)$$

(38)

$$= \varepsilon_0 E_z (\varepsilon_{\parallel} \sin^2 \phi + \varepsilon_{\perp} \cos^2 \phi)$$

We now introduce the voltage \( V \)

$$V = \int_0^L E_z \, dz = \frac{D_z}{\varepsilon_0} \int_0^L (\varepsilon_{\parallel} \sin^2 \phi + \varepsilon_{\perp} \cos^2 \phi)^{-1} \, dz$$

(39)

thus we find that

$$D_z = \varepsilon_0 V \left\{ \int_0^L (\varepsilon_{\parallel} \sin^2 \phi + \varepsilon_{\perp} \cos^2 \phi)^{-1} \, dz \right\}^{-1}$$

(40)

Note that, while \( D_z \) is independent of \( z \) explicitly it is still a "functional" of \( \phi(z) \).

The electric term of equation (37) can now be integrated as

$$-\frac{1}{2} \int_0^L D \cdot E \, dz = -\frac{1}{2} V D_z$$

(41)

The free energy as a functional of \( \phi(z) \) using equations (37) and (40) is

$$F = \frac{1}{2} \int_0^L (K_{\parallel} \cos^2 \phi + K_{33} \sin^2 \phi) (\phi')^2 \, dz$$

(42)

$$- \frac{\varepsilon_0 V^2}{2} \left\{ \int_0^L (\varepsilon_{\parallel} \sin^2 \phi + \varepsilon_{\perp} \cos^2 \phi)^{-1} \, dz \right\}^{-1}$$

Hereafter we use primes to denote \( \frac{d}{dz} \).
Our task is to find $\phi(z)$ which minimizes $F$. To do this we make $\delta F$ (the first variation of $F$) zero subject to the conditions

\begin{equation}
\phi(0) = 0 \quad \phi(L/2) = \phi_m
\end{equation}

where $\phi_m$ denotes the maximum angle at the centre of the cell.

We find for $\delta F$

\begin{equation}
\delta F = \int_0^L \left\{ (K_{33} - K_{11}) \cos \phi \sin \phi (\phi')^2 (\delta \phi) + (K_{11} \cos^2 \phi + K_{33} \sin^2 \phi) \phi' (\delta \phi') + \frac{D_z^2}{\epsilon_0} \frac{(\epsilon_\perp - \epsilon_{11}) \cos \phi \sin \phi (\delta \phi)}{(\epsilon_\perp \cos^2 \phi + \epsilon_{11} \sin^2 \phi)^2} \right\} dz
\end{equation}

We then integrate the $\delta \phi'$ term by parts and are left with an integrand where $\delta \phi$ is a factor. Since $\delta \phi$ was arbitrary (the standard argument goes) the other factor in the integrand must be zero. This gives the nonlinear differential equation:

\begin{equation}
(K_{11} \cos^2 \phi + K_{33} \sin^2 \phi) \phi'' + (K_{33} - K_{11}) \sin \phi \cos \phi (\phi')^2 + \frac{D_z^2}{\epsilon_0} \frac{(\epsilon_\perp - \epsilon_{11}) \sin \phi \cos \phi}{(\epsilon_{11} \sin^2 \phi + \epsilon_\perp \cos^2 \phi)^2} = 0
\end{equation}

Multiplication of this equation by $2 \phi'$ and using $2 \phi'' \phi' = ((\phi')^2)'$ results in an equation which, when integrated over $z$ is
\[\int \left\{ (K_{11} \cos^2 \phi + K_{33} \sin^2 \phi) ((\phi')^2)' + 2(K_{33} - K_{11}) \sin \phi \cos \phi (\phi')^3 + 2 \frac{D^2(\varepsilon \phi - \varepsilon_{\perp}) \sin \phi \cos \phi \phi'}{\varepsilon_0 (\varepsilon_{\parallel} \sin^2 \phi + \varepsilon_{\perp} \cos^2 \phi)^2} \right\} \, dz = 0\]

The first and third terms can be integrated by parts. The second term then cancels out leaving

\[(K_{11} \cos^2 \phi + K_{33} \sin^2 \phi)(\phi')^2 = C + \frac{D^2 z}{\varepsilon_0 (\varepsilon_{\parallel} \sin^2 \phi + \varepsilon_{\perp} \cos^2 \phi)}\]

where \(C\) is the constant of integration. We use the boundary conditions from equation (43) with the additional condition that \(\phi'(L/2) = 0\) (which can be deduced by symmetry) to determine \(C\).

\[C = \frac{-D^2}{\varepsilon_0 (\varepsilon_{\parallel} \sin^2 \phi_m + \varepsilon_{\perp} \cos^2 \phi_m)}\]

The final solution will be in parametric form with \(\phi_m\) as the parameter.

Putting \(C\) into equation (47) and introducing reduced quantities

\[\gamma = \frac{\varepsilon_{\parallel}}{\varepsilon_{\perp}} - 1 \quad \kappa = \frac{K_{33}}{K_{11}} - 1\]

we get, after some rearrangement, a simple differential equation for \(\phi\).
\begin{equation}
\phi' = D_z \sqrt{\frac{\gamma}{\varepsilon_0 \varepsilon_\perp K_{\|}}} \left\{ \frac{\sin^2 \phi_m - \sin^2 \phi}{(1 + \kappa \sin^2 \phi)(1 + \gamma \sin^2 \phi)(1 + \gamma \sin^2 \phi_m)} \right\}
\end{equation}

Note that this equation admits the solution $\phi(z) = 0$ for all voltages.

We can now relate the voltage to the parameter. Rewriting equation (39) slightly

\begin{equation}
V = \frac{2 D_z}{\varepsilon_0 \varepsilon_\perp} \int_0^{L/2} \frac{dz}{(1 + \gamma \sin^2 \phi)}
\end{equation}

One can now use equation (50) for $d\phi/dz$ to change the variable of integration to $\phi$. $D_z$ drops out giving

\begin{equation}
V = 2 \sqrt{\frac{K_{\|}}{\varepsilon_0 \varepsilon_\perp \gamma}} \sqrt{1 + \gamma \sin^2 \phi_m} \int_0^{\phi_m} \left( \frac{1 + \kappa \sin^2 \phi}{(1 + \gamma \sin^2 \phi)(\sin^2 \phi_m - \sin^2 \phi)} \right) d\phi
\end{equation}

Using equation (52) we can determine $\phi_m$ for any given values of the voltage, the dielectric constants and elastic constants.

Returning to equation (50) we find that the variables are separated. Integration of the inverse of equation (50) gives

\begin{equation}
z = \frac{1}{D_z} \sqrt{\frac{\varepsilon_0 \varepsilon_\perp K_{\|}}{\gamma}} \sqrt{1 + \gamma \sin^2 \phi_m} \int_0^{\phi_m} \left( \frac{(1 + \kappa \sin^2 \phi)(1 + \gamma \sin^2 \phi)}{\sin^2 \phi_m - \sin^2 \phi} \right)^{1/2} d\phi
\end{equation}

A special case of this equation is $z=L/2$ and $\phi = \phi_m$. This
determines $D_z$.

\begin{equation}
(54) \quad D_z = \frac{(2/\nu)}{\gamma} \left[ \frac{\varepsilon_0 \varepsilon_1 K_{11}}{\varepsilon_\infty} \right] \sqrt{1 + \gamma \sin^2 \phi} \left\{ \frac{\phi_m}{\sin^2 \phi_m - \sin^2 \phi} \right\}^{1/2} \int_0^{\phi} \left\{ \frac{(1 + \kappa \sin^2 \phi)(1 + \gamma \sin^2 \phi)}{\sin^2 \phi_m - \sin^2 \phi} \right\} d\phi
\end{equation}

Using this expression for $D_z$ in equation (53), gives

\begin{equation}
(55) \quad Z = \left( \frac{L}{2} \right) \frac{\phi_m}{\phi_m} \left\{ \frac{(1 + \kappa \sin^2 \phi)(1 + \gamma \sin^2 \phi)}{\sin^2 \phi_m - \sin^2 \phi} \right\}^{1/2} \int_0^{\phi} \left\{ \frac{(1 + \kappa \sin^2 \phi)(1 + \gamma \sin^2 \phi)}{\sin^2 \phi_m - \sin^2 \phi} \right\} d\phi
\end{equation}

The parameter $\phi_m$ appears in both the integrand and the limits of these two integrals. It is a useful simplification to define a new parameter $\eta$ and change variables to $\psi$ where

\begin{equation}
(56) \quad \eta = \sin^2 \phi_m \\
\sin \phi = \sin \phi_m \sin \psi
\end{equation}

Then equation (52) becomes

\begin{equation}
(57) \quad V = 2 \sqrt{\frac{K_{11}}{\varepsilon_0 \varepsilon_1 \gamma}} \sqrt{1 + \gamma \eta} \left\{ \frac{1 + \kappa \eta \sin^2 \psi}{(1 + \gamma \sin^2 \psi)(1 - \eta \sin^2 \psi)} \right\}^{1/2} \int_0^{\pi/2} d\psi
\end{equation}

from which we can see that in the limit $\eta = 0$ (the limit of no deformation) we have
V is the critical voltage at which the deformation begins, as we foreshadowed in equation (32). Below $V_C$ the zero solution $\phi(z)=0$ is the global minimum of $F$ and there is no deformation.

It will be convenient to define a reduced voltage $v$ by

$$v = \frac{V}{V_C} - 1$$

We also define the integrals $A$ and $B$

$$A = \int_0^{\pi/2} \left\{ \frac{1 + \eta^2 \sin^2 \psi}{(1 + \eta \sin^2 \psi)(1 - \eta \sin^2 \psi)} \right\}^{1/2} d\psi$$

$$B = \int_0^{\pi/2} \left\{ \frac{(1 + \eta \sin^2 \psi)(1 + \eta \sin^2 \psi)}{1 - \eta \sin^2 \psi} \right\}^{1/2} d\psi$$

These integrals are related to complete elliptic integrals of the first kind, a fact we make use of later. We may define an "incomplete" version of $B$ as $B(\psi)$ which is the same as $B$ except that the upper limit of integration is $\psi$ instead of $\pi/2$.

In this notation the solution for the equilibrium deformation is
\[ v = \frac{2}{\pi} \sqrt{1 + s' \eta} A - 1 \]

\[ z = \left( \frac{1}{2} \right) B i \left( \sin^{-1} \left( \frac{\sin \phi}{\sqrt{\eta}} \right) \right) / B \]

The procedure to describe a particular deformation is the following. Given the material constants \( K \) and \( \delta \), solve equation (62) for the parameter \( \eta \) for a given reduced voltage \( v \). Then equation (63) defines the function \( \phi(z) \) implicitly.

In this notation \( dz/d\phi \) is given by

\[ \frac{dz}{d\phi} = \frac{L}{2B} \left\{ \frac{(1 + \kappa \sin^2 \phi)(1 + \delta \sin^2 \phi)}{\sin^2 \phi_m - \sin^2 \phi} \right\}^{1/2} \]

We will make use of this in later sections.

Fig. 5 shows how \( \phi \) varies with \( z \) for the choice of parameters \( \ell = 2, \delta = 1.4, K = 1 \) and various reduced voltages. Note that at higher voltages \( \phi \) approaches \( \pi/2 \) except in thin "boundary layers" near the walls. The thickness of these layers is the order of the length scale given in equation (30) and is inversely proportional to the voltage applied.
Figure 5 - Graph of director angle versus position in the cell, for $\gamma = 1.4 \ K = 1.$ and various reduced voltages
2.2 The Capacitance

In the last section we developed a theory for the deformation of a director field subject to certain boundary conditions by an electric field. Unfortunately we have no experimental probe which can measure the orientation of the director at a point inside the sample. We must consider the integrated effect of the deformation on the externally measurable properties of the cell. The two properties we measured were the capacitance and the birefringence (optical phase difference). These two integrated properties, along with thermal and electrical conductivity, are discussed by the Deuling review \(34\). The capacitance of the cell is the simplest of the two so we treat it first.

Reconsider equation (38)

\[
D_z = \varepsilon_0 E_z (\varepsilon_{\parallel} \sin^2 \phi + \varepsilon_{\perp} \cos^2 \phi)
\]

(65)

\[
= \varepsilon_0 E_z \varepsilon(z)
\]

Evidently \(\varepsilon(z)\) is an "effective" dielectric constant. If the cell was composed of infinitesimal series capacitors of capacitance \(dC\), thickness \(dz\) and area \(A\), then

\[
dC = \frac{A \varepsilon_0 \varepsilon(z)}{dz}
\]

(66)

The total capacitance is then \(C\) where
using equation (64) for $dz/d\phi$ to change the variable of integration to $\phi$

\[
\frac{1}{C} = \int \frac{1}{dC} = \int \frac{dz}{A \varepsilon_0 \varepsilon_r(z)} = \frac{2}{A \varepsilon_0 \varepsilon_r} \int_0^{L/2} \frac{dz}{(1 + \gamma \sin^2 \phi)}
\]

Note that at zero voltage the capacitance is

\[
C_0 = \frac{A \varepsilon_0 \varepsilon_r}{L}
\]

so in the notation of the last section

\[
c = \frac{B}{A} - 1
\]

where we have introduced the reduced capacitance $c$ by

\[
c = \frac{C}{C_0} - 1
\]

Fig. 6 shows a plot of reduced capacitance vs reduced voltage for $\gamma = 1.4$ and various values of $K$. 
Figure 6 - Graph of reduced capacitance versus reduced voltage, for $\gamma = 1.4$ and various $\kappa$ values.
Note that at large $\kappa$ values an inflection point appears near the origin. This was first noticed by Schad et al. 37.

To use this theory to extract $K_{11}$ and $K_{33}$ from C-V data the procedure is as follows. Suppose $\gamma$, which contains $\epsilon_{11}$ and $\epsilon_{\perp}$, is known, perhaps from a separate experiment. From measured capacitances and voltages one must extract $V_C$ and $C_0$ from data near the 'kink' in the C-V curve which marks the Freederickz transition. Then one produces reduced data according to equations (59) and (71). $V_C$, $\epsilon_{\perp}$ and $\gamma$ combine to give $K_{11}$ via equation (58). Note that $\epsilon_{\perp}$ can be obtained from $C_0$ and the area to thickness ratio $A/L$. Then a nonlinear fit of reduced data to equations (62) and (70) with $\kappa$ as a fitted parameter, $\gamma$ fixed, gives one the best-fit value of $\kappa$. The bend constant is then

$$K_{33} = K_{11}(1 + \kappa)$$

We refer to this procedure as the full nonlinear fit.

Obviously the inflection point which appears at high values of $\kappa$ makes determination of $V_C$ difficult, since it is hard to tell when the deformation has started. An error in $V_C$ affects the rest of the data via the reduction formula. Also note that the shape of the C-V curve depends as much on $\gamma$ as on $\kappa$. Thus accurate values of $\gamma$ are needed and $\gamma$ is a potential source of systematic error.

Multiparameter nonlinear fitting to both $\kappa$ and $\gamma$ is difficult because the integrals in question are poorly
conditioned. False and/or shallow minima abound. These pitfalls have been explored by Maze\cite{38}.

Because of the complexity of nonlinear fitting and the integrals involved, many authors have resorted to the limiting cases of high and low voltage\cite{39,40}.

The low voltage limit, valid just above $V_c$ is the case $\eta \sim 0$. It is straightforward to expand the integrands for small $\eta$ and integrate. For the voltage, equation (62), we get to lowest order in $\eta$

\begin{equation}
\nu = \frac{1}{4}(\kappa+\gamma+1)\eta
\end{equation}

Similarly for equation (70)

\begin{equation}
c = \frac{\gamma}{2} \eta
\end{equation}

whence we find that the reduced C-V data curve linearized near $\nu=0$ is

\begin{equation}
c = \frac{2\gamma}{\kappa+\gamma+1} \nu = S_{LFC} \nu
\end{equation}

With this we can extract a low field kappa

\begin{equation}
K_{LFC} = \gamma \left( \frac{2}{S_{LFC}} - 1 \right) - 1
\end{equation}

This seems like a simple way to get $K_{33}$. However the range of validity of the linearization is not easy to decide\cite{41}. This
approach may give erroneous results if there is an inflection point in the curve near $V_c$.

The high field limit is more difficult to arrive at because the integrals diverge in the $\eta = 1$ limit. This problem can be circumvented in the following way. We can rearrange the integrand of $B$ to get

$$B = (1 + \chi) A - \chi \int_0^{\pi/2} \left\{ \frac{(1 + \chi \eta \sin^2 \psi)}{(1 + \chi \eta \sin^2 \psi)(1 - \eta \sin^2 \psi)} \right\}^{1/2} \cos^2 \psi \, d\psi$$

Now using (62)

$$A = \frac{\pi \sqrt{V}}{2V_c \sqrt{1 + \chi \eta}}$$

We can express (70) as

$$\frac{C}{C_0} = (1 + \chi) - \frac{2 \chi V_c \sqrt{1 + \chi \eta}}{\pi \sqrt{V}} \int_0^{\pi/2} \left\{ \frac{1 + \chi \eta \sin^2 \psi}{(1 + \chi \eta \sin^2 \psi)(1 - \eta \sin^2 \psi)} \right\}^{1/2} \cos^2 \psi \, d\psi$$

in which we can safely put $\eta = 1$. So that

$$C = C_\infty + S_{\text{HFC}} \left( \frac{1}{\sqrt{V}} \right)$$

$$C_\infty = C_0 (1 + \chi)$$

$$S_{\text{HFC}} = \frac{2}{\pi} V_c \sqrt{1 + \chi \eta} C_0 \int_0^1 \sqrt{\frac{1 + \chi x^2}{1 + \chi x^2}} \, dx$$

Our notation differs somewhat from that of Uchida. One can use a linear fit to high field data to get $S_{\text{HFC}}$ and $C_\infty$. From
C_0 and C_oo we can extract \( \mathcal{E} \). Solving (81) numerically with this \( \mathcal{E} \), gives \( \kappa \) and hence \( k_{33} \). We call the reduced elastic constant arrived at in this way \( \kappa_{HFC} \). To see the limitations of this method consider how weakly the slope \( S_\text{HFC} \) depends on \( \kappa \). This is made clear in a plot of \( S_\text{HFC}/V_c C_o \) for various \( \mathcal{E} \) shown in Fig. 7. Thus a small error in \( S_\text{HFC} \) translates to a large error in \( \kappa_{HFC} \). Also, note that \( V_c \) and \( C_o \) are still needed to use this method so an inflection point may still be a problem. However this extrapolation is very useful to get \( \mathcal{E} \).

We have analyzed our capacitance data all three ways, low field, high field and full nonlinear fit using \( \mathcal{E} \) from the high field intercept.
Figure 7 - Graph showing the weak dependence of high field slope on the high field reduced elastic constant $\gamma$. The graph plots the slope $S_{HFC}/C_{0, V_c}$ against the high field kappa $K_{HFC}$ for different values of $\gamma$.
2.3 The Optical Phase Difference

Light polarized parallel to the director samples material with index of refraction $n_{||}$. Perpendicular to this the index is $n_{\perp}$. We define the birefringence $\Delta n$ by $\Delta n = n_{||} - n_{\perp}$. One would call $n_{\perp}$ the "ordinary index" $n_0$, and $n_{||}$ the "extraordinary index" $n_e$ in more customary notation. In 8CB $\Delta n > 0$.

Consider a capacitor with transparent electrodes, like the one shown in Fig. 4. Light polarized along the y direction encounters index $n_{\perp}$ whatever the voltage because $\hat{n}$ is always perpendicular to the y axis. Light polarized along x samples a variety of indices through the cell. If the two beams enter the cell in phase they emerge with an optical phase difference given by

$$d = \frac{2\pi}{\lambda} \int_0^L (n(z) - n_{\perp}) dz$$  \hspace{1cm} (82)$$

where $\lambda$ is the wavelength and $n(z)$ is the effective index sampled by the beam polarized along x. Note that our notation is different than that of Deuling. At zero voltage the phase difference is

$$d_0 = \frac{2\pi L}{\lambda} \Delta n$$  \hspace{1cm} (83)$$

and the capacitor acts like a waveplate with its "fast axis" along y. Clearly at infinite voltage both beams sample $n_{\perp}$ and $d = 0$. In practice we use one beam plane polarized at $45^\circ$ to
the x axis which has equal in-phase components along x and y.

From elementary crystal optics, the effective index $n(z)$ is given by

$$n(z) = \sqrt{\frac{n_{||} n_{\perp}}{n_{||}^2 \sin^2 \phi + n_{\perp}^2 \cos^2 \phi}}$$  \(84\)

As before we change the variable of integration in (82) using equation 64 for $dz/d\phi$. After some algebra we arrive at

$$1 - \frac{d}{d_0} = \frac{n_{||}}{\Delta n} \left( 1 - \frac{C}{B} \right)$$  \(85\)

where the new integral is

$$C = \int_0^{\pi/2} \left\{ \frac{(1 + \gamma n_{||}^2 \psi)(1 + \gamma n_{\perp}^2 \psi)}{(1 + \gamma n_{||}^2 \psi)(1 - n_{\perp}^2 \psi)} \right\}^{1/2} d\psi$$  \(86\)

with the reduced index of refraction as a new parameter

$$\gamma = \frac{n_{||}^2}{n_{\perp}^2} - 1$$  \(87\)

We define a quantity $\delta$ as the reduced phase

$$\delta = 1 - \frac{d}{d_0}$$  \(88\)

where we have chosen the signs to make $\delta$ positive. Note that $n_{||} / \Delta n$ can be related to $\gamma$ by
and that at infinite voltage $\delta$ approaches 1 because $d \rightarrow 0$. Graphs of $\delta$ versus $v$ are shown in Fig. 8. They have the same general shape as the c-v graphs shown in Fig. 6 but they have a somewhat different dependence on $\gamma$.

For large $K$ the problem caused by inflection point problem is also present in the optical case. Also, a nonlinear fit to $\delta$ vs $v$ involves knowing an additional material parameter $\gamma$ not needed in the capacitance case. Three integrals ($A$, $B$, and now $C$) must be calculated instead of two.

When the two beams emerge from the crystal the beam polarized along the x-axis has an additional phase $d$ over the phase of the beam polarized along the y-axis. Assuming no losses, the superposition of the two beams is an elliptically polarized beam with the same intensity as the ingoing linearly polarized beam. It would be possible to measure $d$ directly using, for example, a variable compensator. However, to simplify the data acquisition it was thought best to measure an intensity. Thus we placed the liquid crystal between crossed polarizers and measured the transmitted intensity. The elliptically polarized light emerging from the liquid crystal passed through a second polarizer (the "analyser") which is aligned at $90^\circ$ to the first. In this arrangement the measured intensity is

\[
\frac{h_m}{\Delta n} = \frac{\sqrt{1 + \gamma}}{\sqrt{1 + \gamma} - 1}
\]
Figure 8 - Graph of reduced phase versus reduced voltage, for $\kappa=1$, $\gamma=0.2$, and various values of $\gamma$. 
where $I_0$ is the ingoing intensity. As $d$ changes from $d_0$ to zero with increasing voltage the transmitted intensity oscillates forming a series of interference fringes. The number of these fringes $N$ is the number of wavelengths $\lambda$ in the zero voltage optical path length difference

\begin{equation}
N = \frac{d_0}{2\pi} = \frac{L}{\lambda} \Delta n
\end{equation}

(91)

to extract $d$ we must "deconvolve" the fringes by

\begin{equation}
d = \cos^{-1}(1 - \frac{2I}{I_0})
\end{equation}

(92)

Some care must be taken with the principal values of the inverse cosine to get the correct variation of $d$.

Once the fringes have been deconvolved to get the phase difference $d$ one can extract $d_0$ and $V_c$. Then the reduced phase data can be fit to the full nonlinear theory given earlier for $\delta$ and $\nu$. Considerations similar to the capacitance case apply to this full fit.

Once again we can consider the high and low field limits. Expanding equation (86) for small $\gamma$ we find

\begin{equation}
(90) \quad I = \frac{I_0}{2} \left(1 - \cos(d)\right)
\end{equation}
Using (73) the low field limit is

$$\delta = \frac{n_{\text{II}}}{\Delta n} \frac{\gamma}{4} \eta$$

The low field slope is $S_{\text{LFO}}$, so that the low field reduced elastic constant in this case is

$$\kappa_{\text{LFO}} = \left( \frac{n_{\text{II}}}{\Delta n} \frac{\gamma}{S_{\text{LFO}}} \right) - (\gamma + 1)$$

The high field expression is harder to arrive at than in the capacitance case. One finds that for $\eta \to 1$

$$\frac{V}{V_c} = \frac{-2 d_0}{\pi (\sqrt{1+\eta^2}-1)\sqrt{1+\gamma}} \left( \frac{1}{d} \right) \int_0^1 \frac{\sqrt{(1+\kappa x^2)(1+\gamma x^2)}}{1-x^2} \left[ 1 - \sqrt{\frac{1 + \nu^2}{1 + \nu x^2}} \right] dx$$

$$+ \frac{2 \gamma}{\pi \sqrt{1+\gamma}} \int_0^1 \sqrt{\frac{1 + \kappa x^2}{1 + \gamma x^2}} dx$$

$$V = S_{\text{HFO}} (1/d) + I_{\text{HFO}}$$

This is quite different from the high field capacitance result which gave $C$ linear in $1/V$. In principle one can get $\kappa$ from both the slope and the intercept. However the intercept $I_{\text{HFO}}$ is actually the infinite phase difference limit of equation (96) which occurs at small voltages far outside the range of validity.
of \( n \rightarrow 1 \). To determine the small value \( I_{\text{HF}} \) requires a rather long extrapolation from the data, and so it is subject to considerable error. \( I_{\text{HF}} \) actually contains the same integral as the capacitance high field slope, equation (81), and so suffers from the same weak \( K \) dependence. To use \( S_{\text{HF}} \) to get \( K_{33} \) requires \( V_c, d_0, \gamma \) and \( \gamma \). Once again the dependence on \( K \) is rather weak.

An important difference between the optical case and the capacitance case is that there is not enough information in the optical data to determine all the parameters. There is no information on \( \epsilon_L \) or \( \gamma \). However we have \( d_0 = 2\pi L \Delta n/\lambda \) which allows us to deduce \( \Delta n \) given \( L/\lambda \). The fit strategy will be fully explained in chapter 4.

We have analyzed our optical phase data in both the high and low field regions, and by the full nonlinear fit.

2.4 Problems With The Theory

In this section we critically examine the assumptions and limitations of the theory.

We will deal with a purely computational problem first. The three integrals we have derived, \( A, B \) and \( C \), must all be computed accurately and efficiently many times to carry out the nonlinear fits. They are all of the form
with various well-behaved functions $f$. For voltages much greater than $V_c$ one finds that $\eta$ becomes very nearly equal to 1 because $\phi_m$ is close to $\pi/2$ and $\eta = \sin^2 \phi_m$. Since $f(\pi/2)$ is nonzero, this means that the largest contribution to the integral comes from very near $\psi = \pi/2$. This makes $\Pi$ difficult to compute with standard numerical integration routines. Furthermore, $\eta$ eventually becomes computationally indistinguishable from 1, even using double precision arithmetic. These numerical problems can be dealt with by noting that

$$\int_0^{\pi/2} \frac{d\psi}{\sqrt{1 - \eta \sin^2 \psi}} = K(\eta)$$

where $K(\eta)$ is the complete elliptic integral of the first kind. It turns out that $44$ for $\eta \to 1$

$$K(\eta) \approx \log \left( \frac{1}{1 - \eta} \right)$$

and efficient algorithms exist for calculating $K(1-x)$ to high precision. Equation (101) suggests a more natural parameter is $\alpha$, where
\begin{equation}
\eta = 1 - e^{-\alpha}
\end{equation}

For high voltages, \( \eta \) rises approximately linearly with voltage.

\begin{equation}
\Pi = e^{\alpha/2} \int_0^{\pi/2} \frac{(f(\psi) - f(\pi/2)) d\psi}{\sqrt{1 + (e^{\alpha-1}) \cos^2 \psi}} + f(\pi/2) K(\eta)
\end{equation}

The integral is now well behaved and can be done by a standard routine with high precision. The places which were numerically difficult with \( \eta \) have been re-expressed with \( \alpha \). In practice, for \( V = 20V_c \) and actual values of \( \kappa, \gamma \) and \( \psi \) we found \( \alpha \) could be as high as fifty.

We now turn our attention to the limitations of the theory. The theory described is only valid for the equilibrium state of the director. If we sweep the voltage anything but quasi-statically there will be dynamic effects involving viscosities. In particular, the time constant for the director field to achieve equilibrium after a step change in voltage is infinite at \( V_c \). For particularly large steps one may actually produce fluid flow as well as reorientation. In practice it suffices to sweep very slowly through \( V_c \) and somewhat faster at higher voltages.

We assumed that we could produce surfaces where \( \hat{n} \) was completely fixed parallel to the surface. On a real surface this assumption may fail in two ways. \( \hat{n} \) may not be parallel and it may not be rigid. Motoooka and Fukuhara have considered
the theory with these assumptions relaxed. In the case of nonrigid alignment, so called "weak anchoring", one still finds a sharp critical voltage below which there is no deformation but its value is smaller than in the strongly anchored case. In the case when \( \mathbf{n} \) is not precisely perpendicular to \( \mathbf{E} \) at the walls, which may be caused by a "tilted" alignment by the surface treatment one finds some deformation occurs at all voltages with a large increase near \( V_c \) for the untilted case. The onset of the deformation is no longer abrupt. One could mistake the inflection points discussed earlier for this effect.

The difficulty with trying to quantitatively account for these effects is that new and undetermined parameters must be introduced to describe the surface. We tried to avoid this problem by selecting the best surface treatment known and assuming strong anchoring.

Let us turn now to problems arising from effects in the bulk liquid. The liquid has a small but finite electrical conductivity due to impurities. Generally speaking conductivity is only important in DC and low frequency AC experiments. At sufficiently high frequency (a kHz or so) the liquid crystal reacts as if the field had its RMS value, and conductivity effects are minimized. An insidious effect for experiments with accurate temperature control is ohmic heating. The conductivity of our material was sufficiently low that this was insignificant (\( R_{\text{cell}} > 20 \text{M}\Omega \)).

A more interesting space-charge effect is due to
"flexoelectricity". This is the liquid analog of piezoelectricity whereby a deformed nematic acquires an electrical polarization. The effect of this on the shape of the deformation above the Freedericksz transition has been included in the theory by Deuling. However this is really a dynamic effect in disguise because any space-charge will, with enough time, decay due to conduction. Furthermore we expect this to be a small effect in 8CB since it is most pronounced in pear or banana shaped molecules (8CB is more like a cucumber).

Next we consider the possible effects of the field and the deformation on the nematic itself. Recall that our treatment of the deformation was predicated on the assumption that \( |\nabla \hat{n}| \ll 1 \) where \( \alpha \approx 50 \). It is a simple matter to show that this assumption is not violated until very large fields for reasonable values of \( \kappa \) and \( \gamma \).

\[
(103) \quad a |\nabla \hat{n}| = \frac{2aB(\eta - sin^2\phi)^{1/2} cos\phi}{L\sqrt{1 + \kappa sin^2\phi}^{1/2}(1 + \gamma sin^2\phi)^{1/2}} \sim B \frac{a}{L}
\]

By equation (101) \( B \sim \alpha \) for large voltages. Similarly \( V \sim A \alpha \). Hence we must reach reduced voltages of order \( L/a \) for \( |\nabla \hat{n}| \ll 1 \). For this experiment \( L \approx 50 \mu \) so \( L/a \approx 10^4 \). The highest reduced voltage achieved was about 25. By this argument the deformation is not great enough to affect the molecular order parameter \( S \) directly. In principle the electric field can increase \( S \) directly but this is also a small effect at the fields we used.

Although the deformation and the field are not great enough
to affect the molecular order parameter, they can have an important effect on the orientational fluctuations of the director field. This effect is somewhat complicated because of the presence of smectic fluctuations near $T_{NA}$ which cause an increased $K_{33}$. This also has a director fluctuation-quenching effect. Inasmuch as bulk material properties are averages over the fluctuations of $\hat{n}$ they may be altered if the spectrum of fluctuations is changed. Actually, the distinction between director fluctuations and nematic order parameter fluctuations is an artifact of our continuum model.

The most interesting and complicated effect not contained in our continuum theory is the effect of $|\nabla \times \hat{n}|$ on the smectic order, which in turn effects $K_{33}$, which in turn effects the director, down our chain of models. We find

$$|\nabla \times \hat{n}| = \frac{2B(\eta - \sin^2 \phi)^{1/2} \sin \phi}{L(1 + K \sin^2 \phi)^{1/2}(1 + \gamma \sin^2 \phi)^{1/2}}$$

This is plotted in Fig. 9 for $K=1 \gamma=1.4$ and a sequence of reduced voltages.
Figure 9 - Graph of $\nabla x^n$ versus position in the cell, for the same conditions as in Fig. 5
For large voltages the effect is concentrated near the walls. Thus the centre of the cell has a higher effective $T_{NA}$ than regions near the walls. Madhusudana and Srikanta have carried out experiments on this effect. It must be pointed out that there are important differences between an experiment where the liquid is deformed at temperatures far from $T_{NA}^0$, the undeformed transition temperature, and then cooled through $T_{NA}$ and one in which these operations are reversed.

Having described the theoretical foundation of the experiment we next take up its realization.
III. THE EXPERIMENT

...our progress in natural philosophy is chiefly retarded by the want of proper experiments...

Hume

3.1 The Cell

Our experiment centered around a sample cell which held about six cubic millimeters of 8CB liquid crystal. It was a circular parallel plate capacitor with transparent electrodes whose inside surfaces were treated to produce the orientation effects discussed in the last chapter. This surface treatment is described below.

The sample of 8CB we used was kindly provided by Dr. David Dunmur. It was manufactured by BDH chemicals and was used without further purification.

The cell and its parts are shown in Fig. 10. The plates of the capacitor were formed by thin coatings of indium tin-oxide (ITO), a transparent conductor, on glass blocks. The glass blocks, coated and cut to size, were manufactured commercially. The ITO coating was a standard one used in display devices.

We masked the electrode pattern with Scotch tape and etched off the surrounding ITO with a strong HCl solution and zinc powder. The resulting plates were 0.5 inch across with a tab .125 inch wide for making electrical contact, which extended to
Figure 10 - The construction of the sample cell

COPPER CELL BODY

ALIGNMENT TABS

MACHINE SCREW TO MAKE ELECTRICAL CONTACT TO ITO.

SAMPLE VOLUME

LASER BEAM

MYLAR GASKET

GLASS

FINISHED CELL
the edge of the glass. The glass blocks had dimensions 1 inch by 1.25 inch and were .250 inches thick.

After masking and etching, the plates were surface treated to produce director alignment. This was done by evaporating silicon monoxide obliquely onto the surface. We used a film thickness of about 400 Å. The angle between the surface and the beam of SiO was 30°. This procedure produces alignment with the director in the plane of the surface with a direction perpendicular to the beam direction. This treatment is thought to produce the strongest anchoring with the least tilt angle of any treatment known.

The two glass blocks were separated by a thin mylar gasket. This gasket was cut from 0.001 inch thick Mylar of the sort used with overhead projectors. It had a circular hole cut in it which was slightly larger than the capacitor plates, so that the plates did not enclose any gasket material. The resulting thin cylindrical volume was the sample space. A narrow gap in the gasket led from the interior of the cell to the outside. This was included to allow for the slight thermal expansion of the liquid.

The blocks of glass were squeezed together by two halves of a copper cell body as shown in Fig. 10. Holes in the cell body allowed a laser beam to pass through the transparent capacitor. The glass was overlapped so that the two ITO contact tabs were accessible. We put small blobs of indium metal onto these tabs to make soft seats for two machine screws which came through nylon insulated holes in the cell body. The two halves of the
cell body were tightly screwed together by six cap screws. The finished cell fit inside the temperature control system which is described in the next section.

The thickness of the filled cell was measured using an interferometric apparatus which is shown in Fig. 11. The cell was wrapped with plastic pipe and enclosed in a foam block. Temperature controlled water was circulated through the pipe so that the cell could be held at 45°C. At this temperature the 8CB is isotropic with a nearly temperature independent index of refraction of 1.5670±0.0002. We measured the index with a refractometer which was temperature controlled using the same circulating water.

![Diagram](image)

**Figure 11 - Optical system used to measure thickness of filled cell**
A laser beam (\( \lambda = 6328 \text{ nm} \)), expanded and spatially filtered, was passed through a long focal length lens and reflected off the cell at an angle \( \Theta \) before it came to focus. At the focus a line of three closely spaced spots were produced. The outside two, which contained most of the intensity, were due to reflections from the outside air-glass surfaces of the cell. The central dim spot was the superposition of the two beams reflecting from the front and back surfaces of the sample volume. It was dim because the index of the liquid is not very different from that of the glass. The outside spots were masked by a slit which allowed the central spot to be projected onto a screen. On the screen one could clearly observe the angles \( \Theta \) at which the front and back reflections interfered to produce a dark fringe. This occurs at angles given by

\[
m \left( \frac{\lambda}{2L} \right) = \sqrt{n_{lc}^2 - \sin^2 \Theta}
\]

where \( m \) is an integer, \( n_{lc} \) is the liquid index and \( L \) is the sample thickness. Our turntable had an angular resolution of 0.01°. We observed five fringes which were reproducible to 0.03°. A fit to the data gave a thickness \( L \) of 39.5\( \mu \) ± 2 at the centre of the cell. The thickness uniformity of the cell was checked by observing the fringe pattern with a beam expanded to the area of the cell. We found that the cell was slightly lens shaped with the variation of thickness about two fringes, or about 1.5\( \mu \) to the outer edge, outside the plates. All our measurements were carried out on the same cell.
3.2 The Temperature Control

The "nematic range", $T_{N1} - T_{NA}$, of 8CB is 7°C. The pretransitional effects we wish to observe occur within about 1°C of $T_{NA}$. Thus good temperature measurement and control are essential to the experiment. Our temperature control system had two stages. The innermost was a feedback controlled copper cylinder (the "block") which enclosed the cell described earlier. The block was surrounded by foam insulation and enclosed in a cylindrical "can" wound with pipes through which temperature controlled water was pumped. The can, pipes and circulating water system were themselves insulated from the room. The complete thermostat is shown in Fig. 12. The inner block was a copper cylinder four inches long and four inches in diameter. It had a thermal capacity of about 2.7 kJ/K. A threaded axial hole with two keyways accepts the cell which was held in place by two plugs which were screwed in from each end. The keyways served to fix the cell orientation and provide electrical access. Optical access was provided by a smaller axial hole through the plugs. The outside surface of the cylinder block was threaded and wound noninductively with a heater wire which was varnished down for good thermal contact.

Into the end faces of the cylinder were installed three Fenwal thermistors epoxied inside copper bolts, as well as the sensor probe of a Hewlett Packard model 2804A quartz thermometer. The inner temperature control electronics are shown in Fig. 13. The control thermistor was balanced against a General Radio decade resistor in a Wheatstone bridge.
Figure 12 - The construction of the thermostat
Figure 13 - The temperature control circuit
The decade resistor had a minimum step of 0.01\(\Omega\). The bridge was driven by a 1.35 volt mercury battery. The error signal was amplified by a Hewlett Packard model 419A DC nullmeter which was used simply as a high gain amplifier with gain about 300 000. The DC nullmeter was "chopper stabilized" and had excellent noise rejection. The output of the nullmeter was given to a Kepco OPS-7-2 programmable power supply with the feedback shown. This feedback produces a combination proportional and integral control which drives the block heater. This feedback network has been used by Balzarini\(^5\) and some theoretical justification for it has been given by Forgan\(^5\).

A second thermistor, Wheatstone bridge and DC nullmeter were used to monitor shifts of the temperature on a chart recorder. This monitor bridge could be accurately nulled with a second General Radio decade resistor also with 0.01\(\Omega\) minimum step. Using this system and a gain of 100 000 one could easily observe changes as small as 50\(\mu\)K in the temperature.

The quartz thermometer was used to measure the absolute temperature of the block. It was calibrated to a Jarrett water triple-point cell and is believed to be absolutely accurate to 0.1mK over the course of the experiment. Far from \(T_{NR}\) in runs when the quartz thermometer was on another experiment we used the resistance of the remaining block thermistor measured by a Keithley 177 digital multimeter to get the absolute temperature. This thermistor was calibrated against the quartz thermometer previously.

The foam that surrounds the block was about two inches
thick. A temperature difference between the block and the outer can relaxed exponentially with a time constant of 17 hours. The outer can was brass and was completely wrapped with copper pipe which was soldered in place. The circulating water was provided by a large refrigerated bath which circulated its 35 litres of water about once an hour. The water bath is temperature controlled by switching between a refrigerator and a heater. We replaced the crude temperature control provided by the manufacturer with a circuit shown in Fig. 14. This circuit monitors the can temperature with a thermistor which is compared to a decade resistor in a bridge. The error signal from the bridge is used to determine the duty cycle of a square wave which switches between the heater and the fridge. This controller can hold the water temperature stable to better than 1mK. We maintained a constant temperature difference of a few degrees between the can and the block. Finally, to prevent room temperature shifts from affecting the electronics we enclosed them in a large insulated crate.

The control system just described could hold the temperature of the sample stable to 0.1 mK or better, with no drift over a period of days. We calibrated the monitor bridge decade resistor value at null against the absolute temperature measured by the quartz thermometer and the calibrated thermistor. The polynomial fit to this data which was used to get the temperature is incorporated into the data analysis programs reproduced in appendix A, as the function TEMP (R).
Figure 14 - The pulse-width modulation circuit used to control the bath temperature
3.3 The Electronic And Optical Systems

The experiment consisted of applying an AC voltage to the capacitor filled with nematic liquid crystal and measuring the capacitance and the intensity of light transmitted between crossed polarizers.

The applied voltage must be changed very slowly in order that the nematic orientation be in equilibrium in the field. During each of these sweeps the temperature must be held constant. The optical and electronic system to do this is shown in Fig. 15.

The experiment is controlled and the data collected by a Commodore PET minicomputer via an IEEE bus system. The voltage applied to the cell originates as a digital number written to a specific address in the PET memory. This number was converted to a DC level by an external 12 bit digital to analog converter which was connected to the memory expansion port provided inside the PET. The D/A provided a DC voltage variable between zero and ten volts in 4096 steps. This DC signal was delivered to the AM modulation input of a Hewlett-Packard model 3312 A signal generator via an op-amp circuit which converted the DC level from 0-10 volts to -2.7 - +2.7 volts. This voltage range allowed one to control the AC output level of the signal generator from zero to about 8 V_{RMS}. The op-amp circuit had built into it an RC network with a time constant of 30 seconds. This smooths the D/A steps so that no abrupt
Figure 15 - Block diagram of the electronic, optical and data acquisition system
jumps in voltage were presented to the cell. The output of the signal generator was amplified so that the final maximum voltage was about 20 $V_{\text{RMS}}$.

The PET computer's internal clock was used for timing the D/A step rate. The output voltage could be ramped as slowly as 0.05 mV/sec. The output voltage of the amplifier was measured by a Keithley 175 autoranging voltmeter controlled by the PET via the IEEE bus.

Most runs were done with a frequency of 1500 Hz and some earlier ones at 10kHz. The cell response was found to be independent of frequency in this range. The dielectric constant data of Dunmur, referred to later, was obtained at 1500 Hz.

The output of the amplifier was applied to the cell via a ratio transformer which forms part of a General Radio model 1615-A capacitance bridge. The bridge was used in a mode such that, when nulled, the transformer ratio was 1. The capacitance bridge was connected to the cell in the "shielded unknown" arrangement so that all the capacitance of the leads was excluded. We used coaxial leads all the way into the temperature controller so that all stray capacitances were excluded except those from the tabs inside the cell. The copper cell body completed the shielding.

The other arm of the capacitance bridge contains standard capacitors and taps onto the ratio transformer selectable by switches. The error signal of the bridge was fed to a Princeton Applied Research model 5204 lock-in amplifier which was used in vector mode. The reference signal for the lock-in was taken
from the signal generator. Nulling the bridge gave the cell capacitance from the position of the switches.

The procedure for collecting capacitance and voltage data was as follows. As the computer slowly increased the voltage, changes in cell capacitance were followed by manually nulling the bridge. Whenever a capacitance data point was desired, the D/A timing loop was manually interrupted and, after waiting for the voltage to stabilize, the measured capacitance was typed into the computer. The computer then read the voltage via the IEEE bus and recorded it and the capacitance on tape. The D/A stepping was then restarted. There were several problems with this. First, the bridge must be kept near null at all times or the voltage read by the Keithley 175 does not correspond to the actual cell voltage. The lock-in amplifier is so sensitive, however, that very small (\(< 100 \mu V\)) error signals could be maintained.

A second problem arose because the capacitance bridge controls which nulled the resistive part of the unknown impedance (the "dissipation factor") were damaged by a previous user. It was sometimes difficult to completely null the resistive part. Luckily, it was not a strong function of the voltage. We used the magnitude-phase option of the lock-in in order to observe when we had successfully nulled the capacitive part of the error signal, which occurs when the phase of the error signal is zero. Of course, we still had to null the resistive part well enough that the overall error signal was small.
Near the critical voltage we used ramp rates of about 0.05 mV/s. At larger voltages we could use larger ramp rates but the requirement of following the capacitance changes on the bridge meant that we had to use a slow ramp rate even far from $V_c$. It often took 12 hours to complete a capacitance run with several people nulling the bridge in shifts. Each set of capacitance data usually contained about 300 capacitance-voltage measurements at voltages from 0 to $20V_{RMS}$. The capacitance was in the range 200pf to 450pf and was measured to 0.01pf. On many runs the capacitance was not measured and the signal was applied to the cell directly from the amplifier and the bridge and lock-in not used.

The optical measurements were taken automatically simultaneously with the capacitance measurements. The light from a 10 mW helium-neon laser was attenuated and passed through the polarizers and the cell to fall on a phototransistor in the op-amp circuit shown in Fig. 15. The laser beam was not expanded so that it sampled only a small spot at the centre of the cell, where the thickness was measured previously. We attenuated the beam to about 0.5 $\mu$W. At these intensities the output of the phototransistor circuit shown is linear and the output voltage is about 1 volt. Since we only needed relative intensities the phototransistor circuit was uncalibrated. The output of this photometer was measured by a Keithley 177 voltmeter interfaced to the PET via the bus. The same program loop which timed the D/A steps periodically measured the intensity and the voltage and recorded them on the tape.
Because of the complex shape of the fringes it was necessary to record over a thousand data points at each temperature.

Progress of the experiment could be monitored by watching the fringes on an XY recorder which used the analog outputs of the voltage and photometer output voltmeters. On runs when capacitance was not measured the experiment could be run unattended under the control of the computer. Often this was done overnight.

The computer also periodically recorded the temperature on the tape either by reading the quartz thermometer or the calibrated thermistor via the Keithley ohmmeter. At the end of a run the data on the cassette tape was transferred to the main UBC computer via the bus and a serial fast line. All later analysis was done using the mainframe.

The next chapter concerns the analysis of the data.
IV. DATA ANALYSIS

Go, clear thy crystals!

Shakespeare, Henry V 2,iii,54

4.1 Fit Strategy And Deconvolution Of Fringes

In this chapter we fit the experimental data to the theory in the various ways described in chapter 2. We will extract several material parameters from the data, namely $\varepsilon_\parallel$, $\varepsilon_\perp$, $n_\parallel$, and $n_\perp$, in addition to the splay and bend elastic constants, $K_\parallel$ and $K_{33}$. Finally, we will examine the behaviour of the elastic constants and the other parameters near the nematic - smectic A phase transition.

Since the analysis is somewhat complex, we will outline it in this section. Fig. 16 shows some typical raw capacitance-voltage data. The inset shows the region near the critical voltage $V_c$. We generally found that the capacitance, for voltages between zero and the critical voltage, showed a slight positive slope. This may be due to edge effects or, more likely, to small regions of poor alignment. The Freedericksz transition itself showed only a very slight rounding, visible in the inset.

A flowchart for the capacitance data analysis is shown in Fig. 17. As was mentioned in chapter 2, one can extract from the capacitance data itself all the parameters needed for the
Figure 16 - An example of raw capacitance - voltage data
Figure 17 - Flowchart of capacitance data analysis

1. Raw C-V data
2. Fit to data near $V_c$, extract $C_0$, $V_c$ and $S_{LFC}$
3. Use fit to $C$ vs $1/V$ to get $C_\infty$ and $S_{HFC}$
4. Use $C_0$ and $A/L$ to get $\epsilon_{LFC}$
5. Use $C_\infty$ and $A/L$ to get $\epsilon_{HFC}$
6. Find $\delta$ parameter $\delta = (C_\infty/C_0)^{-1}$
7. Use $\delta$ and $\epsilon_{LFC}$ to get $\epsilon_{HFC}$
8. Use $\delta$ and $S_{HFC}$ to get $\kappa_{HFC}$
9. Use $\delta$ and $S_{LFC}$ to get $\kappa_{LFC}$
10. Reduce the capacitances $c = (C/C_0)^{-1}$
11. Use $\delta$ and $\epsilon_{LFC}$ to get $\kappa_{HFC}$
12. Use $\delta$ and $\epsilon_{LFC}$ to get $\kappa_{LFC}$
13. Reduce the voltages for 5 trial value of $V_c$
14. $v = (V/V_c)^{-1}$
15. Full nonlinear fit to $c, v$ gives $\kappa$, with $\delta$ fixed.
16. Use best $V_c$ and $\delta, \epsilon_{LFC}$ to get $\kappa_{HFC}$
17. $K_{33} = K_{HFC} (\kappa + 1)$
full nonlinear fit. Since our area to thickness ratio $A/L$ was not very well known, we chose it so that the values of $\varepsilon_L$ produced are in agreement with those of Dunmur \textsuperscript{53} for 8CB. Fig. 17 is essentially the flowchart of the program CF which carried out the capacitance data analysis. It is reproduced in appendix A.

The outcome of this analysis are values for the dielectric constants $\varepsilon_{//}$, $\varepsilon_{/\perp}$ and $\psi$, and the splay elastic constant $K_{//}$ as well as three values for the reduced elastic constant kappa $\kappa_{LFC}$, $\kappa_{HFC}$ and $\kappa$ from the full fit, all as a function of temperature. The next section concerns the results other than the elastic constants. The the elastic constant results are presented in the section following that.

The analysis of the optical data is somewhat more complicated than that of the capacitance data. A flowchart for this analysis is shown in Fig. 18. The deconvolution of the fringes to get the phase turned out to be more difficult than we anticipated. Fig. 19 shows some raw fringe data. Equation (91) which relates the transmitted light intensity to the optical phase difference assumes that there is no extinction or depolarization of the light. It is evident from the shape of the fringes in Fig. 19 that some loss occurred because the envelopes of the fringes are not constant with voltage. The effect is significant near $T_{NI}$ and becomes severe near $T_{NA}$.

We used the following scheme to deconvolve the fringes. A quadratic function was fit to data near each of the maxima and minima of the fringes and the extrema were found.
Figure 18 - Flowchart of optical data analysis

1. Raw fringe data
2. Deduce envelope from fits to peak positions and linear interpolation and extrapolation
3. Deconvolve fringes to get raw phase $d$
4. Fit near $V_c$ extract $d_0, V_c$ and $S_{LFO}$
5. Use $d_0$ to get $\Delta n$
6. Use $n$ from Dunmur data and $\Delta n$ to get $n_L, n_U, \gamma$
7. Use $S_{LFO}$ and fit to $\chi(T)$ to get $\kappa_{LFO}$
8. High field fit to $V$ vs $1/d$ use $\chi$ and $S_{HFO}$ to get $\kappa_{HFO}$
9. Reduce the phases $\delta = 1 - (d/d_0)$
10. Reduce the voltages for 5 trial values of $V_c$
   $V = (V/V_c) - 1$
11. Full nonlinear fit to $\delta, V$ to get $\kappa$ with $\chi, \gamma$ fixed
12. Use best $V_c$ and $\chi(T), E_{d1}(T)$ to get $\kappa_{II}$
13. $K_{33} = K_{II} (K + 1)$
Figure 19 - Examples of raw fringe data

\[ T = 36.169^\circ C \]

\[ T = 33.792^\circ C \]

\[ T = 33.557^\circ C \]

\[ T = 33.538^\circ C \]
An approximate upper envelope for the fringes was constructed by linearly interpolating between the positions of the maxima. For data at voltages below the first fringe we took the height of the first fringe to be the value of the upper envelope. Similarly we extrapolated the upper envelope to voltages above the last fringe. The same procedure was used to construct the lower envelope of the fringes. We could then normalize the data so that the fringes could be deconvolved to get the raw phases \( d \). This procedure worked well for fringes whose heights were nearly constant. Some typical raw phase data produced by this deconvolution is shown in Fig. 20. The extrapolation of the envelope below the first fringe allowed us to deconvolve the data in the region of the Freedericksz transition. Analysis proceeded according to the flow-chart in Fig. 18.

Unfortunately, some runs near \( T_{N\alpha} \) and near \( T_{N\beta} \) could not be deconvolved because the envelope was not well described by the linear interpolation used above. On these runs we fit the fringe maxima and minima to parabolae as before, then only deconvolved these extrema. This is the usual method used by other authors \(^5,4^2\). To get \( V_c \) for these cases we used fits to intensity data near the Freedericksz transition. In this method one cannot get \( d_0 \), except approximately by counting fringes and using equation \((92)\). We used a polynomial fit to \( d_0 \) values from data at other temperatures to interpolate to find the value \( d_0 \) needed to produce reduced phases to complete the fit. The analysis then proceeded as before.
Figure 20 - An example of raw optical phase data
The phase data analysis as in Fig. 18 was carried out by the program PF and its subroutines reproduced in appendix A. The deconvolution was done by a separate program. Note that in the optical case we make use of fits to the dielectric constant $\varepsilon_\perp$ and to $\varepsilon$ from the capacitance data. The parameter $\gamma$ was found by combining values of the birefringence $\Delta n$ obtained from $d_0$ and the thickness, and values of the average index $\bar{n} = (n_\parallel + 2n_\perp)/3$ from the measurements of Dunmur. $\bar{n}$ is nearly temperature independent.

As before we get three values of kappa, $\kappa_{\text{LFO}}$, $\kappa_{\text{HFO}}$ and the full fit $\kappa$ as well as $n_\parallel$, $n_\perp$ and $\gamma$, all as a function of temperature.

4.2 Dielectric And Refractive Index Results

This section concerns the extraction of material parameters other than the elastic constants, which are needed for the rest of the analysis.

Both optical and capacitance data near the Freedericksz transition were handled similarly. Two points were selected which straddled the critical voltage so that the small intermediate region of rounding was excluded. Then the data below the lower of these voltages were fit to a straight line. The zero voltage intercept of this line was taken to be the zero voltage capacitance ($C_0$) or optical phase difference ($d_0$), as the case may be.

The data above the upper voltage point were fit to a quadratic, up to a cut-off voltage of about $2V_c$. The
intersection of this quadratic and the linear fit below $V_c$ was taken to be the critical voltage. Later in the full fit this value was allowed to vary slightly to improve the fit.

The low field slope, $S_{LFc}$ or $S_{LFo}$, was found from the derivative of the quadratic fit at $V_c$. This procedure is carried out interactively in the routines PF and CF given in appendix A.

A graph of the critical voltage vs temperature is shown in Fig. 21. Away from $T_{NA}$, the critical voltage shows the gentle temperature dependence which is due to the variation in the degree of nematic order present. However, near $T_{NA}$ it shows an unexpected sharp increase. Our method of finding $V_c$ is susceptible to systematic error if the increase in $K_{33}$ near $T_{NA}$ is sufficiently large that the inflection point described in chapter 2 is present. This could lead to an overestimate of $V_c$ near $T_{NA}$. The increase shown in Fig. 21 is however much too large to be entirely due to this error. This increase in $V_c$ is due to a combination of the pretransitional behaviour of $K_{II}$, $\varepsilon_L$, and $\delta$. We will discuss the error in $V_c$ more fully in the next section when we consider the elastic constant $K_{II}$.

Fig. 22 shows a graph of the zero voltage capacitance, $C_0$ versus temperature. Notice that $C_0$, which is proportional to $\varepsilon_L$, also shows a small decrease near $T_{NA}$. We fit the $C_0$ data to a phenomenological temperature dependence, shown by the solid line in Fig. 22, in order to interpolate to get values of $\varepsilon_L$ needed for the phase data analysis. This phenomenological fit is the function CZFIT(T) in appendix A.
Figure 21 - Graph of the critical voltage versus temperature
Figure 22 - Graph of the zero voltage capacitance versus temperature
The high field analysis in the capacitance case is handled by the subroutine EXTRAP. A straight line was fitted to capacitance versus inverse voltage for voltages larger than a minimum voltage which was usually selected to be 17 volts. Fig. 23 shows some typical capacitance data plotted versus inverse voltage. The graph is quite straight even down to voltages only a few times $V_C$. This is because the approximation $\gamma = 1$ is a good one even at modest voltages. The slope $S_{HFC}$ was used to get the high field reduced elastic constant $\kappa_{HFC}$ which is discussed in the next section. The intercept $C_\infty$ is proportional to the dielectric constant $\epsilon_{||}$.

We used $C_0$ and $C_\infty$ to deduce $\epsilon_{||}$ and $\epsilon_\perp$ by adjusting the area to thickness ratio $A/L$ so that our results agreed with those of Dunmur $5^3$ for $\epsilon_\perp$. The dielectric constants we obtained are shown on the graph in Fig. 24. Note that the values we obtain from the extrapolation to infinite voltage are systematically larger than Dunmur's measurements. We return to this result in the next section when we discuss the determination of the reduced elastic constant $\kappa_{HFC}$ from $S_{HFC}$.

The dimensionless parameter $\delta$, which is independent of $A/L$, is shown in Fig. 25. Once again we fit a phenomenological temperature dependence to this data, the fit may be found in the function $GAM(T)$ given in appendix A.
Figure 23 - Graph of high field capacitance data plotted against inverse voltage
Figure 24 - Graph of the principal dielectric constants versus temperature
Figure 25 - Graph of the reduced dielectric constant $\varepsilon$ versus temperature.
Turning to the optical case, we now consider the results for the zero voltage phase difference $d_0$, which is proportional to $\Delta n$. This data is shown in Fig. 26 with a phenomenological fit given as the function DZFIT(T) in appendix A.

A typical plot of voltage vs $1/d$ is shown in Fig. 27. Once again we find a straight line as expected from the high field theory. The slope and intercept, which give information about the reduced elastic constant, will be considered in the next section. This analysis was done by the subroutine HFLIN. Fits to the index data of Dunmur$^{53}$ were used to get the average index $\overline{n}$, given in the function ENBAR(T). Using the thickness measured before, we find the two indices of refraction $n_\parallel$ and $n_\perp$. These are shown in Fig. 28. Finally, the two indices were used to find the reduced quantity $\nu$ needed in the optical fits. This parameter is shown in Fig. 29. The temperature dependences of $d_0$, $\nu$ and $\gamma$ are very similar. All show pretransitional increases near $T_{NA}$.

All the data discussed in this section are tabulated in appendix B.
Figure 26 - Graph of the zero voltage phase difference $d_0$ versus temperature.
Figure 28 - Graph of the principal indices of refraction versus temperature
Figure 29 - Graph of reduced index of refraction $\nu$ versus temperature
4.3 Elastic Constant Results

The splay elastic constant \( K_{\|} \) is determined by the critical voltage \( V_c \) and the dielectric constants \( \varepsilon_\perp \) and \( \gamma \). The capacitance and optical phase difference at voltages above the Freedericksz transition depend on the dimensionless ratio \( 1+\kappa \) of the bend and splay constants and on the material constants \( \delta \) and \( \gamma \).

\[
K_{\|} = V_c^2 \varepsilon_0 \Delta \varepsilon / \pi^2
\]
\[
= V_c^2 \varepsilon_0 \varepsilon_\perp \gamma / \pi^2
\]

\[(106)\]

\[
K_{33} = K_{\|} (1 + \kappa)
\]

(107)

From the data shown in the last section we find the splay elastic constant shown in Fig. 30.

As the temperature is lowered the elastic constant increases. This is expected from mean field theory, which predicts that the elastic constants should be proportional to \( S^2 \), where \( S \) is the nematic order parameter. Near \( T_{NA} \) we find a sudden increase in \( K_{\|} \) not predicted by mean field theory. Recall that the de Gennes model predicts that \( K_{\|} \) is finite in the smectic phase. This does not preclude an increase in \( K_{\|} \), only that it should not diverge at \( T_{NA} \). In the next section we examine this and other pretransitional effects observed.
Figure 30 - Graph of the splay elastic constant versus temperature.
The largest source of uncertainty in $K_{II}$ is due to the uncertainty of the critical voltage $V_c$. It can be seen from Figs. 20, 21 and 24 that $V_c$ is more scattered than $\epsilon_1$ or $\gamma$. Also, $K_{II}$ depends on the square of $V_c$ and only linearly on $\epsilon_1$ and $\gamma$. The random error in $V_c$ was estimated from the behaviour of the full nonlinear fit, to be described later in this section.

Although the parameters $\epsilon_1$ and $\gamma$ have a small random error compared to $V_c$, they may contain significant systematic error as seen in the last section. The error bars shown in Fig. 30 were arrived at by neglecting the errors in $\epsilon_1$ and $\gamma$ compared to the error in $V_c$. It must be stressed that these are only estimates of the statistical error and do not reflect the possible systematic errors.

We now turn to the analysis required to obtain the reduced elastic constant kappa. The low field values of kappa, $K_{LFC}$ and $K_{LFO}$, were deduced from the slope of the data just above $V_c$ as described in the last section. In the capacitance case, the high field value of kappa $K_{HFC}$ was found from the slope $S_{HFC}$ by the subroutine HFC and the functions HFZ and HFARG given in appendix A. In the optical case we attempted to get $K_{HFO}$ from both the slope and the intercept. They were found by the subroutine HFO and the functions HFSZ, HFSARG, HFIZ and HFIARG.

The rest of the functions and subroutines in appendix A are concerned with the full nonlinear fit. The capacitance analysis program CF contains a loop which carries out the nonlinear fit for five trial values of $V_c$. On the first pass through the
loop the subroutine VFIND, which calls FAINT and uses the function VZ, fills arrays with values of $\eta$, $\alpha$ and the elliptic integral $K(\eta)$. FAINT and FBINT and functions FA and FB carry out the evaluation of $A$ and $B$. Subroutine REDCAP reduces the capacitance data. The actual fit routine is a simple one-dimensional version of parabolic extrapolation arranged to minimize calls to CHISQC, which evaluates the "goodness-of-fit" of the theory to the data. To reduce computation we re-use the values of $\alpha$, $\eta$, and the elliptic integral and linearly interpolate the theoretical function.

CHISQC calculates the sum of the squares of the perpendicular distances between a data point and the theory. This approach was motivated by the desire to ensure that the data was not systematically weighted by the use of only the capacitance residuals, as is customarily done in $\chi^2$ fits. The curve to be fit to has a steep rise and a long flat tail. If only "vertical" (capacitance) residuals were allowed to contribute to the goodness-of-fit criterion, the initial steep rise would be strongly weighted over the flat tail portion. Using "perpendicular" residuals removed this bias.

The optical phase program PF is similar to CF except in a few details. To reduce computation, the subroutine FEW replaces the large number of data points with about 250 averaged points. The data are reduced by REDPHS. The goodness-of-fit subroutine is CHISQP which uses the subroutine FCINT and FC to calculate the additional integral $C$. Upon exiting the main loop both PF and CF provide the best-fit values of and the curvature of
the goodness-of-fit function about the minimum. This provides a way of estimating the statistical errors in $V_c$ and $\kappa^{55}$. The subroutine PLTFIT can be used to produce plots of the theoretical fits and the residuals.

To test the programs we produced "simulated data" which obeyed the theory with known values of the parameters. Running our fit programs on the simulated data reproduced the correct input parameters in all cases, including the high and low field slope and intercepts. Thus we were confident that, in the happy event that the real data obeyed the theory, we would be able to extract the correct elastic constants.

The various results for the parameter kappa are collected together in Fig. 31. The general result is that kappa is near zero except within about 1°C of $T$ where the divergence of $K^{33}$ causes it to greatly increase.

The low field and full fit results are generally in agreement with one another for both the capacitance and optical cases, although the low field values have more scatter. The high field results show a large systematic disagreement, with the capacitance values larger than the full fit values and the optical values smaller.

In the optical case we have only plotted the high field results derived from the slope. The results for kappa from the intercept were scattered randomly. This was not unexpected given the long extrapolation to get the intercept.
Figure 31 - Graph of the reduced elastic constant $\kappa$ versus temperature
The systematic difference in kappa between the high field fit and the full fits can be attributed to bias introduced during the deconvolution of the fringes in the case of the optical data. Recall that we assumed that the envelope of the fringes was independent of voltage after the highest voltage fringe. The actual envelope probably increases with voltage. This approximation is particularly gross near $T_{NR}$ where the fringes are most affected by scattering and depolarization. The inexact deconvolution combined with the sensitivity of $K_{HF0}$ to small changes in the high field slope makes the elastic constants obtained from this data extremely unreliable.

The results from the high field analysis of the capacitance data are more significant. Here one cannot blame the larger kappa values on deconvolution. The linear fits to high field data unambiguously give systematically larger kappa values than low field fit. In the last section we saw that the values of $\epsilon_{||}$ obtained from the high field extrapolation were systematically larger than the measurements of Dunmur. This suggests that the high field approximation of Uchida and Takahashi is obeyed, but with "effective" parameters $\chi$ and $K$ which are larger than the low field values.

The full nonlinear fits to the Deuling theory were generally "eyeball" perfect. Often there was no visible deviation of theoretical fit from the data. Near $T_{NR}$ however the quality of the fit got progressively worse. Examples of direct comparisons between theoretical fits and reduced data are shown in Fig. 32 and Fig. 34. Systematic deviation between the
Figure 32 - Graph of theoretical fit to reduced phase data

T = 38.6113 °C

Data 1 in 10 points

Fit to theory
Residuals for data shown in Fig. 32

Perpendicular residual $\times 10^{-3}$

Reduced voltage
Figure 34 - Graph of theoretical fit to reduced capacitance data

$T = 33.8264 \, ^\circ\text{C}$

- Data
- Fit to theory

Reduced Capacitance vs. Reduced Voltage
Residuals for data shown in Fig. 34
data and the best fit can be seen on plots of the "perpendicular" residuals, which are the minimum distances between each reduced data point and the theoretical curve. These residuals would be randomly distributed if the theory fit the data to within errors. A plot of the residuals of the optical phase data shown in Fig. 32 is shown in Fig. 33. Note that for low voltages the residuals appear to be random, but at higher voltages they show a deviation from the theory which increases with voltage. In the case of the optical phase fits some of this deviation could be explained by the deconvolution error mentioned previously. We find, however, a similar trend in the residuals of the capacitance data which are shown in Fig. 35. In the capacitance case the residuals typically show systematic deviation at lower voltages than in the optical case. The same deviations from the theory have been previously observed by Maze.

The trend in the quality of the fits with temperature is interesting. We have calculated two quantities which measure the quality of the fits. The first is the standard deviation, which is the average magnitude of the perpendicular residuals such as those shown in Fig. 33. The standard deviation is obtained from the minimum value of the goodness-of-fit criterion, it is calculated by the subroutine PLTFIT in the appendix.
Figure 36 - The temperature variation of the standard deviation of the fits
Figure 37 - The temperature variation of the insensitivity of the fit to $k$
The second quantity is the curvature of the goodness-of-fit about the minimum, as a function of the parameter $K$. This is a measure of the sensitivity of the fit to the parameter $K$, the sharper the minimum the less the statistical error in $K$. Strictly speaking, this estimate of statistical error is only valid if the residuals are randomly distributed. The variation of the standard deviation and inverse curvature with temperature are shown in Figs. 36 and 37.

We found that the data showed a systematic deviation from the Deuling theory at high voltages. The failure of the theory was enhanced in the critical region close to $T_{NR}$.

Using the best fit values of kappa and the error estimated from the curvature we arrive at the results for $K_{33}$ shown in Fig. 38. As with $K_{ll}$, away from $T_{NR}$, $K_{33}$ shows a temperature dependence attributable to the classical increase of the nematic order parameter. Near $T_{NR}$, $K_{33}$ increases dramatically due to the smectic fluctuations. This is the subject of the next section.
Figure 38 - Graph of the bend elastic constant versus temperature
4.4 Results In The Critical Region

This section is concerned with phenomena observed at temperatures just above the nematic to smectic A phase transition.

Several effects made it difficult to get usable data close to $T_{NA}$. As previously mentioned, the fringes obtained from the optical measurements became distorted due to loss of intensity. Also, we observed that the time taken for the crystal to reorient in the field became so long that even very slow ramping of the voltage ($< 0.05 \text{V/sec}$) produced hysteresis. This slowness is presumably a consequence of the increase in the viscosity which opposes re-orientation. We were unable to collect useful data within about 20 mK of $T_{NA}$.

We could not directly determine $T_{NA}$. Indeed, the exact meaning of $T_{NA}$ is somewhat ambiguous in this experiment because of the depression of $T_{NA}$ by $N_x |^4$. Our results are derived from data taken at a range of fields, and hence deformations, so that the appropriate $T_{NA}$ is some average over the effective transition temperatures in various parts of the cell. An indirect determination of $T_{NA}$ will be described below.

Near $T_{NA}$ we observed small increases in $\Delta n$, $\chi$, and $K_{II}$. These may be due to changes in the short-range correlations of the molecules brought about by the smectic-like fluctuations. In mean field theory, $\Delta n$ is proportional to the order parameter $S$, given in equation (1). $\Delta n$ itself can be taken as the order parameter. We may view the pretransitional increase of $\Delta n$ as direct evidence that the nematic order
parameter is increased near the nematic-smectic A transition by non mean-field, that is, fluctuation effects.

The elastic constants are proportional to $S^2$ in mean field theory. Thus, to detect the effects of fluctuations, it is interesting to plot $K_{11}$ and $K_{33}$ versus $d_0^2$, which is proportional to $(\Delta n)^2$ and hence $S^2$. This is shown in Fig. 39 and 40.

We now fit the divergent part of $K_{33}$ to a power law and extract the critical exponent. Recall that the de Gennes model predicts

$$K_{33} = K_{33}^0 + C t^{-\gamma_{11}}$$

(108)

where $K_{33}^0$ is the "nondivergent" part, $t$ is the reduced temperature, $\gamma_{11}$ is a critical exponent and $C$ is a constant. We assume that the temperature dependence of $K_{33}^0$ is the continuation of the mean-field $K_{33}$ into the region near $T_{NA}$. The temperature dependence of $d_0$, away from the small increase near $T_{NA}$, is well described by

$$T = a + b d_0 + c d_0^2$$

(109)

Using this, and a fit to the linear part of the graph in Fig. 40, gives an expression for $K_{33}^0(T)$. 
Figure 39 - Graph of the splay elastic constant versus the square of the nematic order parameter.
Figure 40 - Graph of the bend elastic constant versus the square of the nematic order parameter
A graph of $\log \left( K_{33} - K_{33}^0(T) \right)$ versus $\log(t)$, for the correct value of $T_{NA}$, should be a straight line with slope $-\nu_1$ and intercept $\log(C)$. We therefore varied $T_{NA}$ to produce the best straight line fit, weighting the data points by their estimated error. We omitted the data above 36°C which was so close to the background that it contributed no information. The results of the fit were not strongly dependent on this upper cutoff. From the fit shown in Fig. 41 we find a critical exponent of 1.0 and a critical temperature of 33.507°C. The amplitude $C$ was $1.3 \times 10^{-14}$ newtons. From the curvature of $\chi^2$ with $T_{NA}$ near the minimum we estimate the statistical error in $T_{NA}$ to be 5 mK. The statistical error estimate for the exponent is only 0.02. Allowing for the sensitivity of the fit to choice of $K_{33}^0(T)$ and upper cutoff, a more reasonable error estimate is 0.1. It is difficult to see how our data could be consistent with an exponent lower than this. In particular our result is clearly inconsistent with the de Gennes prediction of 0.67 and with the light scattering and X-ray measurements by the MIT group, which give values near 0.7.
Figure 41 - Graph of the best fit of the divergent part of the bend elastic constant to a power law in the reduced temperature
It is interesting to fit the ratio of the elastic constants $K_{33}/K_{11} = \kappa+1$ to a power law. The error in kappa is smaller than that of either elastic constant and, since $K_{11}$ and $K_{33}$ have the same temperature dependence in mean field, the nondivergent part of $\kappa+1$ is expected to be temperature independent. Furthermore, the value of kappa far from $T_{NA}$ is essentially zero. Thus we may take the nondivergent part to be 1. Proceeding as before we find the fit shown in Fig. 42. We include all the data up to $T_{N1}$. This gives an exponent of 1.0 ± .1 and a critical temperature of 33.503°C ± .005, which is in agreement with the previous result.
Figure 42 - Graph of the best fit of the reduced elastic constant to a power law in the reduced temperature.
V. CONCLUSION

In reality we know nothing for truth lies in the abyss.

Democritus

We have measured the splay and bend elastic constants of 8CB using an electric field induced Freedericksz transition. The splay constant was determined from the critical voltage at the Freedericksz transition and the bend constant from the subsequent deformation of the director up to voltages about twenty times the critical voltage. We measured the deformation simultaneously from its effects on both the birefringence and capacitance of the sample. The principal dielectric constants and indices of refraction were deduced from the data, making use of the cell dimensions and published values of the average index \(^{53}\). As well as determining the various constants as a function of temperature, this method is also a strong test of the linear elastic theory of the deformation, particularly near the smectic A phase where the bend elasticity is dominated by smectic fluctuation effects. We also tested the internal consistency of the theory by examining the data in the high and low field limits.

It was found that the optical and capacitance results agreed with one another within errors, with the optical data having less uncertainty. In fits over the whole range of
voltages we found some deviation from the Deuling theory at all temperatures. A similar trend in the residuals was previously observed by Maze. Furthermore, elastic constant values determined from the high field capacitance data were systematically larger than the full and low field fits. The extrapolation of the capacitance to infinite voltage produced $\varepsilon_{ll}$ values which were larger than those measured by Dunmur. Near the nematic - smectic A phase transition we observed a deterioration in the quality of the fit to the Deuling theory. All these results suggest a breakdown of linear elasticity at large deformations and close to $T_{N\alpha}$. This breakdown could be due to the suppression of the smectic fluctuations, which are responsible for the large values of $K_{33}$, by deformations with nonzero $\nabla \times \mathbf{n}$. By this fluctuation-quenching mechanism, $K_{33}$ becomes strain dependent near $T_{N\alpha}$. A mean field theory of this nonlinear elasticity have been given by Chu and McMillan.

The validity of the linear elastic theory has been tested close to $T_{N\alpha}$ by Majoros et al. using magnetically produced deformations. They found no disagreement with the linear theory down to temperatures very close to $T_{N\alpha}$, where they observed the onset of a "stripe instability". This instability is observed when one cools a deformed nematic to just above the smectic transition. It is hypothesized that the instability signals the onset of nonlinear behaviour.

Our experiment has a somewhat different geometry than those discussed above and we used an electric, rather than magnetic, field. Direct comparisons with magnetic deformation experiments
are made difficult by the failure of the theory at high fields in the electric case, even far from $T_{NA}$. We did not observe a stripe instability above the smallest reduced temperature we reached, which was about $8 \times 10^{-5}$. Nevertheless, in contrast with Majoros et al., we did observe an increased deviation from the linear theory close to $T_{NA}$.

The critical exponent $\nu_{II}$ for the divergence of $K_{33}$ was found to be $1.0 \pm 0.1$. The critical temperature $T_{NA}$ was obtained from the fit and was found to be $33.507 \pm 0.004$. This error bar on $T_{NA}$ is probably too small, since we did not attempt to account for the drift due to sample degradation.

The critical exponent has been measured by many workers using a large variety of materials and techniques. Their published results are summarized in table 1. Our result is in agreement with some electrical Freedericksz transition experiments$^{25,30}$, although the experiments and analysis are different in many details. It is apparent from the table that there is wide disagreement about the value of this exponent. Some results are close to the de Gennes prediction of 0.67 but most are larger.

It seems unlikely that further experiments like the one described here will shed much light on the critical exponents of the nematic–smectic A transition until the deformation itself is better understood.
Table I – A Survey of the published values of the critical exponent $\gamma$.

<table>
<thead>
<tr>
<th>REFERENCE (no.)</th>
<th>Material</th>
<th>Method</th>
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<td>Sprunt et al (22)</td>
<td>8OCB</td>
<td>0.75\pm0.04</td>
</tr>
<tr>
<td></td>
<td>8CB</td>
<td>0.72\pm0.05</td>
</tr>
<tr>
<td></td>
<td>8S5</td>
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<td>Ocko et al (23)</td>
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<td>0.83\pm0.01</td>
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<tr>
<td></td>
<td>9S5</td>
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<tr>
<td></td>
<td>8CB</td>
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<tr>
<td></td>
<td>10S5</td>
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<tr>
<td></td>
<td>9CB</td>
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<tr>
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<tr>
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<td>BBOA</td>
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<td>Cheung et al (31)</td>
<td>BBMBA</td>
<td>1.0\pm0.1</td>
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APPENDIX A - COMPUTER PROGRAMS

A.1 Main Routine For Capacitance Analysis CF

Program CF for fitting Capacitance data

device 4 data file
device 11 output file for fit results

IMPLICIT REAL*8(A - H, O - Z)
LOGICAL FIRST

Arrays needed for plots

REAL*4 VPLOT(100), BLOT(100), ALOT(100), VAPLOT(100)
REAL*4 V(1000), C(1000)

Arrays to hold data and reduced data and results

DIMENSION VDATA(500), CDATA(500), VRED(500), CRED(500)
DIMENSION VCARAY(5), HFKRAY(5), FTKRAY(5), CHIFIN(5)
DIMENSION NRAY(5), CURV(5), VRAY(500,5), CRAY(500,5)
DIMENSION VTHRAY(500,5), CTHRAY(500,5), RCRAY(500,5)
DIMENSION VTHRAY(500,5), RESV(500), RESC(500),
1 VTH(500), CTH(500)

Arrays needed for BEFORE fit

DIMENSION CBFOR(200), VBFOR(200), YBFOR(200), WT(200)
DIMENSION YDBFOR(200), SBFOR(5), SIGBFR(5), ABFOR(5),
1 BBFOR(5)
DIMENSION PBFOR(2)

Arrays for AFTER fit

DIMENSION CAPT(500), VAFT(500), YFAFT(500)
DIMENSION YDAPT(500), SAFT(5), SIGAFT(5), AAFT(5),
1 BAFT(5)
DIMENSION PAFT(3)

DIMENSION ALFRAY(500), ETARAY(500), ELARAY(500)
COMMON AK, ANU, GAMMA, PIBY2, ALPHA, ETA
COMMON /PARAM/ ALFRAY, ETARAY, ELARAY
COMMON /SAVEK/ ELIP

PIBY2 = DARCOS(0.0D0)
PI = 2.D0 * PIBY2

Read code to tag output. FREAD is a free format READ.
WRITE (5,10)
10 FORMAT (1X, 'Capacitance fit for:')
WRITE (6,20)
20 FORMAT (1X, 'RUN NAME DATA.... 1 for JULY, 2 for AUG'
1 )
   CALL FREAD(6, 'I:', MONTH)
WRITE (6,30)
30 FORMAT (1X, 'Input number part of run name')
   CALL FREAD(6, 'R*8:', RNUM)
   IF (MONTH .EQ. 1) WRITE (5,40) RNUM
   IF (MONTH .GE. 2) WRITE (5,50) RNUM
40 FORMAT (1X, ' JULY', F10.5)
50 FORMAT (1X, ' AUG', F10.5)

C
C Read the Temperature
C
WRITE (6,60)
60 FORMAT (1X, 'What is the MBOX value (in ohms)?')
   CALL FREAD(6, 'R*8:', EMBOX)

C
C Read in capacitance file
C
   K = 1
70 CONTINUE
   READ (4,90,END=80) VDATA(K), CDATA(K)
   K = K + 1
   GO TO 70
80 CONTINUE
   NDATA = K - 1
90 FORMAT (2F30.15)
C
C Read in locations of transition
C
100 CONTINUE
   WRITE (6,110)
110 FORMAT (1X, 'Line # just before transition?')
1 )
   CALL FREAD(6, 'I:', NBFOR)
   WRITE (6,120)
120 FORMAT (1X, 'What line # just after?')
   CALL FREAD(6, 'I:', NAFTER)
C
C Fill array for BEFORE fit
C
   DO 130 J = 1, NBFOR
      CBFOR(J) = CDATA(J)
      VBFOR(J) = VDATA(J)
130 CONTINUE
   NB = NBFOR
C
C Deduce largest capacitance
C
   CMAX = 0.0D0
   DO 140 K = 1, NDATA
IF (CDATA(K) .GE. CMAX) CMAX = CDATA(K)
140 CONTINUE

C
Fill AFTER array up to fixed fraction of CMAX
C
WRITE (6,150)
150 FORMAT (1X, 'input a FRACT (used .625)')
CALL FREAD(6, 'R*8:', FRACT)
CF = FRACT * CMAX
J = NAFTER
K = 1
160 CONTINUE
CAFT(K) = CDATA(J)
VAFT(K) = VDATA(J)
J = J + 1
K = K + 1
IF (CDATA(J) .GE. CF) GO TO 170
GO TO 160
170 CONTINUE
NA = K - 1
NM = J - 1

C
Do the two fits before and after VCRIT.
DOLSF is a polynomial fit library subroutine.
C
CALL DOLSF(1, NB, VBFOR, CBFOR, YFBFOR, YDBFOR, WT, 0, 1
1 SBFOR, SIGBFR, ABFOR, BBFOR, SSBFOR, .TRUE., 2
2 PBFOR)
C
CALL DOLSF(2, NA, CAFT, VAFT, YFAFT, YDAFT, WT, 0, 1
1 SAFT, SIGAFT, AAFT, BAFT, SSAFT, .TRUE., PAFT)
C
ALGRAF is a library plotting routine.
C
DO 180 M = 1, NM
V(M) = VDATA(M)
C(M) = CDATA(M)
180 CONTINUE
CALL ALGRAF(V, C, NM, -1)
C
DO 190 J = 1, 50
VPD = DFLOAT(J) * VDATA(NM) / 5.D1
VPLT(J) = VPD
BPLT(J) = PBFOR(1) + PBFOR(2) * VPD
190 CONTINUE

DO 200 J = 1, 100
CPD = (DFLOAT(J)*(CMAX - PBFOR(1))/1.D2) + 9.D-1 *
1 PBFOR(1)
APLT(J) = CPD
VAPLT(J) = PAFT(1) + PAFT(2) * CPD + PAFT(3) * CPD
1 * CPD
DO 200 CONTINUE
C
CALL ALGRAF(VPLOT, BLOT, -100, 0)
CALL ALGRAF(VAPLOT, APLOT, -100, 0)
C
ALDONE is a library routine which initiates plots
CALL ALDONE
C
WRITE (6,210)
210 FORMAT (IX, 'You like this fit? 0.=YES...')
CALL FREAD(6, 'R*8:', YESNO)
IF (.NOT. (YESNO .EQ. 0.D0)) GO TO 100
C
CALL critical voltage VCRIT
C
AAA = PAFT(3) * PBFOR(2) * PBFOR(2)
BBB = 2.D0 * PBFOR(1) * PBFOR(2) * PAFT(3) + PAFT(2) * PBFOR(2) - 1.D0
CCC = PAFT(3) * PBFOR(1) * PBFOR(1) + PAFT(2) * PBFOR(1) + PAFT(1)
IF (PBFOR(2) .EQ. 0.0D0) GO TO 220
C
DISC = DSQRT(BBB*BBB - 4.D0*AAA*CCC)
VCRIT = (-1.D0/(2.D0*AAA)) * (DISC + BBB)
GO TO 230
C
220 CONTINUE
VCRIT = CCC
C
Find low field slope SLFC
C
230 CONTINUE
CEE = PBFOR(1) + PBFOR(2) * VCRIT
SLFC = 1.D0 / (2.D0*PAFT(3)*CEE + PAFT(2))
C
deduce GAMMA with extrapolation to infinite field
C
VMIN = 17.D0
C
CALL EXTRAP(NDATA, VDATA, CDATA, VMIN, NBFOR, VCRIT, 1.
CZERO, CINF, SHFC, SQR, GAMMA)
T = TEMP(EMBOX)
EPZERO = 8.85418782D0
CEMPTY = 3.524D0 * EPZERO
CEPSPRP = CZERO / CEMPTY
C
use initial slope as first guess of AK = kappa
C
AK = (GAMMA*(((2.0D0*CZERO)/(SLFC*VCRIT)) - 1.0D0)) - 1.1.D0
C
write out things so far
WRITE (5,240) EMBOX, T
WRITE (5,250) EPSPRP
240 FORMAT (1X, 'Mbox= ', F10.5, ' Temp= ', F10.6)
250 FORMAT (1X, 'Eperp = ')
WRITE (5,260) NBFOR, NAFTER, FRACT
WRITE (5,270)
WRITE (5,290) SSBFOR
WRITE (5,280)
WRITE (5,290) SSAFT
WRITE (5,300) CZERO
WRITE (5,310) CINF
WRITE (5,320) GAMMA
WRITE (5,330) SLFC
WRITE (5,340) VCRI
WRITE (5,350) AK
260 FORMAT (1X, 'Nbfor= ', I5, ' Nafter= ', I5, ' Fract= ', F10.5)
270 FORMAT (1X, 'Fit to capacitance before Vcrit:')
280 FORMAT (1X, 'Fit after Vcrit ( was quadratic in V)')
290 FORMAT (1X, 'Sum of squares= ', F30.15)
300 FORMAT (1X, 'CZERO= ', F30.15)
310 FORMAT (1X, 'CINF= ', F30.15)
320 FORMAT (1X, 'GAMMA= ', F30.15)
330 FORMAT (1X, 'initial SLFC= ', F30.15)
340 FORMAT (1X, 'VCRI= ', F30.15)
350 FORMAT (1X, 'estimated KAPPA= ', F30.15)

C Try a 5 values of VCRI
C
WRITE (6,360)
360 FORMAT (1X, 'Give me a range (+/-) around VCRI..')
CALL FREAD(6, 'R*8:', VCRAN)
VCORIG = VCRI
FIRST = .TRUE.
C
DO 620 NVC = 1, 5
C
VCRI = (VCORIG - VCRAN) + DFLOAT(NVC - 1) * (VCRAN/
1 2.0)
VCARAY(NVC) = VCRI
C
call high field subroutine
C
370 CONTINUE
AKHF = AK
CALL HFC(SHF, GAMMA, VCRI, CZERO, AKHF)
C
HFKRAY(NVC) = AKHF
WRITE (5,380) VCRI, CZERO
380 FORMAT (1X, 'High field fits for VCRI=', F16.8,
1 ' CZERO=', F16.8)
WRITE (5,390) AKHF, SHF, SQR
390  FORMAT (1X, 'Kappa high field=', F16.8, ' slope=',
1     F16.8, ' Sqr=', F16.8)

reduce the data

CALL REDCAP(NDATA, VDATA, CDATA, CZERO, VCRIT, NRED,
1     VRED, CRED)
NRAY(NVC) = NRED

fill ALFRAY,ETARAY and ELARAY which store alpha,eta and K(1-eta)

IF ( .NOT. FIRST) GO TO 410
ETA = 0.0D0
ALPHA = 0.0D0
DO 400 I = 1, NRED
VFIND finds the correct alpha for the given voltage
CALL VFIND(VRED(I))
ALFRAY(I) = ALPHA

DELIK is a library function which calculates the complete elliptic integral K(1-eta)
ELARAY(I) = DELIKM(DEXP(-1.0D0*ALPHA),IND)
ETARAY(I) = 1.0D0-DEXP(-1.0D0*ALPHA)
400  CONTINUE
FIRST = .FALSE.
410  CONTINUE

Do the fitting

ITMAX = 30
ITER = 0
DELK = 0.5D0
AK2 = AK
AK1 = AK2 - DELK
AK3 = AK2 + DELK
CALL CHISQC(NRED, CRED, VRED, AK1, F1, CTH, VTH,
1     RESC, RESV)
CALL CHISQC(NRED, CRED, VRED, AK2, F2, CTH, VTH,
1     RESC, RESV)
CALL CHISQC(NRED, CRED, VRED, AK3, F3, CTH, VTH,
1     RESC, RESV)
420  CONTINUE
WRITE (5,430)  ITER, DELK
430  FORMAT (1X, '####### iter=', I5, ' ###### delK='
1     , F20.15)
WRITE (5,440)
440  FORMAT (14X, 'kappa', 20X, 'chisqr')
WRITE (5,460) AK1, F1
WRITE (5,450)
WRITE (5,460) AK2, F2
WRITE (5,450)
WRITE (5,460) AK3, F3
450  FORMAT (1X, '------------------------')
460  FORMAT (1X, F30.15, F30.15)
C

A1 = (F1 + F3 - 2.0D0*F2) / (2.0D0*DELK*DELK)
IF (A1 .LE. 0.0D0) GO TO 500
B1 = (F2 - F1 + A1*(DELK*DELK - 2.0D0*AK2*DELK)) /
1 DELK
AKNEW = -1.0D0 * B1 / (2.0D0*A1)
CALL CHISQC(NRED, CRED, VRED, AKNEW, FNEW, CTH, VTH,
1 RESC, RESV)
DELK = DABS(AK2 - AKNEW)
C
this is the convergence criterion
CONV = 1.0D-4
C
IF (DELK .LE. CONV) GO TO 540
C
Iteration
C
ITER = ITER + 1
IF (ITER .GE. ITMAX) GO TO 520
IF (AKNEW .GT. AK3) GO TO 480
IF (AKNEW .LT. AK1) GO TO 490
IF (AKNEW .GT. AK2) GO TO 470
C
case that AK1<AKNEW<AK2
F3 = F2
AK3 = AK2
F2 = FNEW
AK2 = AKNEW
AK1 = AK2 - DELK
CALL CHISQC(NRED, CRED, VRED, AK1, F1, CTH, VTH,
1 RESC, RESV)
GO TO 420
470 CONTINUE
C
case that AK2<AKNEW<AK3
F1 = F2
AK1 = AK2
F2 = FNEW
AK2 = AKNEW
AK3 = AK2 + DELK
CALL CHISQC(NRED, CRED, VRED, AK3, F3, CTH, VTH,
1 RESC, RESV)
GO TO 420
480 CONTINUE
C
case that AK3<AKNEW
C
DELK=DABS(AK2-AK3)
F1 = F3
AK1 = AK3
F2 = FNEW
AK2 = AKNEW
AK3 = AK2 + DELK
CALL CHISQC(NRED, CRED, VRED, AK3, F3, CTH, VTH,
1 RESC, RESV)
GO TO 420
490 CONTINUE
C
case that AKNEW<AK1
C
DELK=DABS(AK2-AK1)
F3 = F1
AK3 = AK1
F2 = FNEW
AK2 = AKNEW
AK1 = AK2 - DELK
CALL CHISQC(NRED, CRED, VRED, AK1, F1, CTH, VTH, 1
RES, RESV)
GO TO 420

C
C
500 CONTINUE
WRITE (5,510)
510 FORMAT (1X, 'Parabolic fit curves wrong way!')
GO TO 620
C
C
520 CONTINUE
WRITE (5,530)
530 FORMAT (1X, 'Too many iterations!')
GO TO 620
C
C
540 CONTINUE
WRITE (5,550) CONV
550 FORMAT (1X, 'Fit has converged. CONV=', F20.10)
C
C
write out results of fit
AK = AKNEW
FTKRAY(NVC) = AKNEW
CHIFIN(NVC) = FNEW
CURV(NVC) = A1

DO 560 J = 1, NRED
   VTHRAY(J,NVC) = VTH(J)
   CTHRAY(J,NVC) = CTH(J)
   VRAY(J,NVC) = VRED(J)
   CRAY(J,NVC) = CRED(J)
   RVRAY(J,NVC) = RESV(J)
   RCRAY(J,NVC) = RESC(J)
560 CONTINUE

C

WRITE (5,570) AK
WRITE (5,580) A1
WRITE (5,590) CHIFIN(NVC)
WRITE (5,600) VCRIT
570 FORMAT (1X, 'KAPPA= ', F20.15)
580 FORMAT (1X, 'CURVATURE= ', F20.15)
590 FORMAT (1X, 'CHISQC= ', F20.15)
600 FORMAT (1X, 'VCRIT= ', F20.15)

C
C
C
plot

WRITE (6,610)
610 FORMAT (1X, 'Do you wanna plot? (0=NO)'
CALL FREAD(6, 'R*8:', YESNO)
IF (YESNO .EQ. 0.D0) GO TO 620

CALL PLTFIT(NRED, VRED, CRED, VTH, CTH, RESV, RESC, STD)

620 CONTINUE

WRITE (5,630)
630 FORMAT (1X, 'VCRIT,.HIGH FIELD K,.FIT K,.CHISQ'

JMIN = 1
CHIMIN = CHIFIN(1)
DO 650 J = 1, 5
   WRITE (5,660) VCARAY(J), HFKRAY(J), FTKRAY(J), CHIFIN(J)
   IF (CHIFIN(J) .LT. CHIMIN) GO TO 640
   GO TO 650
640 CONTINUE
   JMIN = J
   CHIMIN = CHIFIN(J)
650 CONTINUE
660 FORMAT (1X, 4F16.8)

best one now labelled by JMIN

WRITE (6,670) JMIN
670 FORMAT (1X, 'Best chisqr value is number', 16)
WRITE (6,680)
680 FORMAT (1X, 'Wanna look at plots?..0=NO')
CALL FREAD(6, 'R*8:', YESNO)
   IF (YESNO .EQ. 0.0D0) GO TO 700

NRED = NRAY(JMIN)
DO 690 J = 1, NRED
   VTH(J) = VTHRAY(J,JMIN)
   CTH(J) = CTHRAY(J,JMIN)
   VRED(J) = VRAY(J,JMIN)
   CRED(J) = CRAY(J,JMIN)
   RESV(J) = RVRAY(J,JMIN)
   RESC(J) = RCRAY(J,JMIN)
690 CONTINUE

CALL PLTFIT(NRED, VRED, CRED, VTH, CTH, RESV, RESC, STD)

700 CONTINUE

Write out relevant stuff on device 11

WRITE (11,710) MONTH, RNUM, T, FTKRAY(JMIN), CHIFIN(JMIN), CURV(JMIN), STD, VCARAY(JMIN), 2HFKRAY(JMIN), CZERO, CINF
A.2 Subroutine REDCAP

subroutine to produce reduced capacitance data

SUBROUTINE REDCAP(NDATA, VDATA, CDATA, CZERO, VCRIT, 1 NRED, VRED, CRED)
IMPLICIT REAL*8(A - H, O - Z)
DIMENSION VDATA(500), CDATA(500), VRED(500), CRED(500)
J = 1
DO 10 K = 1, NDATA
VR = (VDATA(K)/VCRIT) - 1.0D0
IF (VR .LE. 0.0D0) GO TO 10
VRED(J) = VR
CRED(J) = (CDATA(K)/CZERO) - 1.0D0
J = J + 1
10 CONTINUE
NRED = J - 1
RETURN
END

A.3 Subroutine CHISQC

Goodness of fit for capacitance data

SUBROUTINE CHISQC(NRED, CRED, VRED, TESTK, F, CTH, 1 VTH, RESC, RESV)
IMPLICIT REAL*8(A - H, O - Z)
DIMENSION CRED(500), VRED(500), VTH(500), CTH(500), 1 RESC(500)
DIMENSION ALFRAY(500), ETARAY(500), ELARAY(500), 1 RESV(500)
COMMON AK, ANU, GAMMA, PIBY2, ALPHA, ETA
COMMON /PARAM/ ALFRAY, ETARAY, ELARAY
COMMON /SAVEK/ ELIP

AK = TESTK
DO 10 J = 1, NRED
ALPHA = ALFRAY(J)
ETA = ETARAY(J)
ELIP = ELARAY(J)
CALL FAINT(A)
CALL FBINT(B)
VTH(J) = (((1.DO/PIBY2)*DSQRT(1.DO+GAMMA*ETA)*A) - 1.
1 0D0
CTH(J) = (B/A) - 1.0D0
10 CONTINUE

LV = 1
LC = 1
SUM = 0.0D0

DO 120 M = 1, NRED

deduce LC LV s.t.
VTH(LV)>VRED(M)>VTH(LV-1)
CTH(LC)>CRED(M)>CTH(LC-1)

NV = LV
IF (VRED(M) .GT. VTH(NRED)) GO TO 40
IF (VRED(M) .LE. VTH(1)) GO TO 50
20 CONTINUE
NV = NV + 1
IF (NV .EQ. NRED + 1) NV = 2
IF ((VRED(M) .LE. VTH(NV)) .AND. (VRED(M) .GT. VTH(NV - 1))) GO TO 30
GO TO 20
30 CONTINUE

LV = NV
SL = (CTH(LV) - CTH(LV - 1)) / (VTH(LV) - VTH(LV - 1))
CTHINT = CTH(LV - 1) + SL * (VRED(M) - VTH(LV - 1))
GO TO 60

40 CONTINUE
case VRED(M)>VTH(NRED)
SL = (CTH(NRED) - CTH(NRED - 1)) / (VTH(NRED) - VTH(NRED - 1))
CTHINT = CTH(NRED) + SL * (VRED(M) - VTH(NRED))
GO TO 60

50 CONTINUE
case VRED(M)<VTH(1)
SL = (CTH(2) - CTH(1)) / (VTH(2) - VTH(1))
CTHINT = CTH(1) - SL * (VTH(1) - VRED(M))
GO TO 60

60 CONTINUE

RESC(M) = CTHINT - CRED(M)
CRESQR = RESC(M) * RESC(M)


```
NC = LC
IF (CRED(M) .GT. CTH(NRED)) GO TO 90
IF (CRED(M) .LE. CTH(1)) GO TO 100

C 70 CONTINUE
NC = NC + 1
IF (NC .EQ. NRED + 1) NC = 2
IF (((CRED(M) .LE. CTH(NC)) .AND. (CRED(M) .GT. CTH(1)) .AND. (CRED(M) .GT. CTH(NC - 1))) GO TO 80
GO TO 70

C 80 CONTINUE
LC = NC
SL = (VTH(LC) - VTH(LC - 1)) / (CTH(LC) - CTH(LC - 1))
VTHINT = VTH(LC - 1) + SL * (CRED(M) - CTH(LC - 1))
GO TO 110

C 90 CONTINUE
    case CRED(M) > CTH(NRED)
SL = (VTH(NRED) - VTH(NRED - 1)) / (CTH(NRED) - CTH(NRED - 1))
VTHINT = VTH(NRED) + SL * (CRED(M) - CTH(NRED))
GO TO 110

C 100 CONTINUE
    case CRED(M) < CTH(1)
SL = (VTH(2) - VTH(1)) / (CTH(2) - CTH(1))
VTHINT = VTH(1) - SL * (CTH(1) - CRED(M))

C 110 CONTINUE
RESV(M) = VTHINT - VRED(M)
IF (RESV(M) .GT. 1.0D0) RESV(M) = 1.0D0
VRESQR = RESV(M) * RESV(M)
RESQR = 1.0D0 / ((1.0D0/VRESQR) + (1.0D0/CRESQR))
SUM = SUM + RESQR

120 CONTINUE

F = SUM
RETURN
END
```

A.4 Subroutine EXTRAP

C subroutine to do the high field analysis of cap data

SUBROUTINE EXTRAP(NDATA, VDATA, CDATA, VMIN, NBFOR, VCRIT, CZERO, CINF, SLOPE, SS, GAMMA)
IMPLICIT REAL*8(A - H, O - Z)
DIMENSION VDATA(500), CDATA(500), VFIT(500),
1 VIFIT(500)
DIMENSION CFIT1(300), CFIT2(300), YF(500), YD(500),
1 WT(500)
DIMENSION S(3), SIG(3), A(2), B(2), P(2)

C Get CZERO from fit
C
DO 10 J = 1, NBFOR
VFIT(J) = VDATA(J)
CFIT1(J) = CDATA(J)
10 CONTINUE

C DOLSF is a library polynomial fit routine
CALL DOLSF(1, NBFOR, VFIT, CFIT1, YF, YD, WT, 0, S,
1 SIG, A, B, SS, .TRUE., P)

C
CZERO = P(1)

C FIT INVERSE VOLTAGES V>VMIN

K = 1
DO 20 J = NBFOR, NDATA
IF (VDATA(J) .LT. VMIN) GO TO 20
VFIT(K) = 1.DO / VDATA(J)
CFIT2(K) = CDATA(J)
K = K + 1
20 CONTINUE

NFIT = K - 1

C DOLSF is a library polynomial fit routine
CALL DOLSF(1, NFIT, VFIT, CFIT2, YF, YD, WT, 0, S,
1 SIG, A, B, SS, .TRUE., P)

C CINF = P(1)
SLOPE = P(2)
GAMMA = (CINF/CZERO) - 1.DO
RETURN
END

A.5 Subroutine HFC And Functions HFZ And HFARG

C Subroutine to calculate high field kappa
C
SUBROUTINE HFC(SHF, GAMMA, VCRIT, CZERO, AKHF)
IMPLICIT REAL*8(A - H, O - Z)
LOGICAL LZ
EXTERNAL HFZ
COMMON /HFCOM/ TK, G, ST
TK = AKHF
G = GAMMA
PI = 2.D0 * DARCOS(0.D0)
ST = (PI*SHF/(2.D0*G*ZERO*VCRIT*DSQRT(1.D0+G)))
HFERR = 1.D-8
AKMAX = 1.D3
AKZ = -1.D0

ZERO2 is a library root finding routine
CALL ZERO2(AKZ, AKMAX, HFZ, HFERR, LZ)
AKHF = AKZ
RETURN
END

FUNCTION HFZ(AKHF)
IMPLICIT REAL*8(A - H, O - Z)
COMMON /HFCOM/ TK, G, ST
EXTERNAL HFARG
TK = AKHF
HFZ = (DGAU16(0.0D0, 1.0D0, HFARG)) + ST
RETURN
END

FUNCTION HFARG(X)
IMPLICIT REAL*8(A - H, O - Z)
COMMON /HFCOM/ TK, G, ST
TOP = 1.D0 + TK * X * X
BOT = 1.D0 + G * X * X
HFARG = DSQRT(TOP/BOT)
RETURN
END

A.6 Main Routine For Phase Data Analysis PF

C Program PF for fitting phase data

C device 4 input phase data
device 11 output fit results

IMPLICIT REAL*8(A - H, O - Z)
LOGICAL FIRST

Arrays needed for plots

REAL*4 VPLOT(100), BPlot(100), APlot(100), VAPLOT(100)
REAL*4 V(5000), PH(5000)
Arrays to hold data and reduced data and results

DIMENSION VDATA(5000), PHDAT(5000), VRED(500)
   PHRED(500)
DIMENSION VCARAY(5), HFKSRA(5), HFKIRA(5), FTKRAY(5),
   CHIFIN(5)
DIMENSION NRAY(5), CURV(5), VRAY(300,5), PHRAY(300,5)
DIMENSION VTHRAY(300,5), PHTHRA(300,5), RPHRAY(300,5)
DIMENSION RVRAY(300,5), RESV(500), RESPH(500)
DIMENSION VTH(500), PTH(500)

Arrays needed for BEFORE fit

DIMENSION PHBFOR(500), VBFOR(500), YFBFOR(500),
   WT(500)
DIMENSION YDBFOR(500), SBFOR(5), SIGBFR(5), ABFOR(5),
   BBFOR(5)
DIMENSION PBFOR(2)

Arrays for AFTER fit

DIMENSION PHAFT(1000), VAFT(1000), YFAFT(1000)
DIMENSION YDAFT(1000), SAFT(5), SIGAFT(5), AAFT(5),
   BAFT(5)
DIMENSION PAFT(3)

DIMENSION ALFRAY(500), ETARAY(500), ELARAY(500)

COMMON AK, ANU, GAMMA, PIBY2, ALPHA, ETA
COMMON /PARAM/ ALFRAY, ETARAY, ELARAY
COMMON /SAVEK/ ELIP

PIBY2 = DARCOS(0.0D0)
PI = 2.0D0 * PIBY2

Read in a code to tag output with

WRITE (5,10)
10 FORMAT (1X, 'Phase fit for:')
WRITE (6,20)
20 FORMAT (1X, ' run name 1 = JULY  2 = AUG'
   1 )
   CALL FREAD(6, 'I:', MONTH)
WRITE (6,30)
30 FORMAT (1X, 'Input number part of run name')
   CALL FREAD(6, 'R*8:', RNUM)
   IF (MONTH .EQ. 1) WRITE (5,40) RNUM
   IF (MONTH .GE. 2) WRITE (5,50) RNUM
40 FORMAT (1X, ' JULY', F10.5)
50 FORMAT (1X, ' AUG', F10.5)

Read the Temperature
WRITE (6,60)
60 FORMAT (1X, 'What is the MBOX value (in ohms)?')
CALL FREAD(6, 'R*8:', EMBOX)

C
C Read in phase file
C
K = 1
70 CONTINUE
READ (4,100,END=80) VDATA(K), PHDAT(K)
K = K + 1
GO TO 70
80 CONTINUE
NDATA = K - 1
WRITE (5,90) NDATA
90 FORMAT (1X, 'There are ', I10, ' data points...')
100 FORMAT (2F30.15)

C
C Read in locations of transition
C
110 CONTINUE
WRITE (6,120)
120 FORMAT (1X, 'Line # just before transition?')
1 CALL FREAD(6, 'I:', NBFOR)
WRITE (6,130)
130 FORMAT (1X, 'What line # just after?')
CALL FREAD(6, 'I:', NAFTER)

C
Fill array for BEFORE fit
C
DO 140 J = 1, NBFOR
   PHBFOR(J) = PHDAT(J)
   VBFOR(J) = VDATA(J)
140 CONTINUE
NB = NBFOR

C Fill AFTER array down to fixed fraction of PHDAT(1)
C
WRITE (6,150)
150 FORMAT (1X, 'input a FRACT (used .625)')
CALL FREAD(6, 'R*8:', FRACT)
PHFIN = FRACT * PHDAT(1)
J = NAFTER
K = 1
160 CONTINUE
   PHAFT(K) = PHDAT(J)
   VAFT(K) = VDATA(J)
   J = J + 1
   K = K + 1
IF (PHDAT(J) .LE. PHFIN) GO TO 170
GO TO 160
170 CONTINUE
NA = K - 1
NFIN = J - 1
Do the fits to before and after $V_{CRIT}$

DOLSF is a library polynomial fit routine

```fortran
CALL DOLSF(1, NB, VBFOR, PHBFOR, YFBFOR, YDBFOR, WT, 0, SBFOR, SIGBFR, ABFOR, BBFOR, SSBFOR, .TRUE., PBFOR)
```

```fortran
CALL DOLSF(2, NA, PHAFT, VAFT, YPAFT, YDAFT, WT, 0, SAFT, SIGAFT, AAFRT, BAFRT, SSAFT, .TRUE., PAFT)
```

Do the plots

```fortran
DO 180 M = 1, NFIN
   V(M) = VDATA(M)
   PH(M) = PHDAT(M)
180 CONTINUE
CALL ALGRAF(V, PH, NFIN, -1)
```

```fortran
DO 190 J = 1, 5
   VPD = DFLOAT(J) * VDATA(NFIN) / 5.D0
   VPLOT(J) = VPD
   BPLOT(J) = PBFOR(1) + PBFOR(2) * VPD
190 CONTINUE
```

```fortran
DO 200 J = 1, 100
   PHD = (DFLOAT(J)*(1.2D0*PBFOR(1) - PHFIN)/1.D2) + PHFIN
   APLOT(J) = PHD
   VAPLOT(J) = PAFT(1) + PAFT(2) * PHD + PAFT(3) * PHD
200 CONTINUE
```

```fortran
CALL ALGRAF(VPLOT, BPLOT, -100, 0)
CALL ALGRAF(VAPLOT, APLOT, -100, 0)
CALL ALDONE
```

```fortran
WRITE (6,210)
210 FORMAT (1X, 'You like this fit? 0.=YES...')
CALL FREAD(6, 'R*8:', YESNO)
IF (.NOT. (YESNO .EQ. 0.D0)) GO TO 110
```

Calculate critical voltage

```fortran
AAA = PAFT(3) * PBFOR(2) * PBFOR(2)
BBB = 2.D0 * PBFOR(1) * PBFOR(2) * PAFT(3) + PAFT(2) * 
     1 PBFOR(2) - 1.D0
CCC = PAFT(3) * PBFOR(1) * PBFOR(1) + PAFT(2) * PBFOR( 
     11) + PAFT(1)
IF (PBFOR(2) .EQ. 0.0D0) GO TO 220
```
DISC = DSQRT(BBB*BBB - 4.D0*AAA*CCC)
VCRIT = (-1.D0/(2.D0*AAA)) * (DISC + BBB)
GO TO 230

220 CONTINUE
VCRIT = CCC

Calculate low field slope

230 CONTINUE
CEE = PBFOR(1) + PBFOR(2) * VCRIT
SLFO = 1.D0 / (2.D0*PAFT(3)*CEE + PAFT(2))
deduce GAMMA from fit to capacitance gammas

T = TEMP(EMBOX)
GAMMA = GAM(T)

Get deltaN and ANU from ENBAR and DZERO

DZERO = PBFOR(1)
THICK = 37.2D0 / 0.6328D0
DELN = DZERO / (2.D0*PI*THICK)
ENB = ENBAR(T)

ENPAR = ENB + (2.0D0/3.D0) * DELN
ENPERP = ENB - (1.0D0/3.D0) * DELN
ANU = ((ENPAR*ENPAR)/(ENPERP*ENPERP)) - 1.D0

Fit high voltage vs 1/phase to a line

WRITE (5,240) VDATA(NDATA)
240 FORMAT (1X, 'Give me VMIN......last voltage is', F10.5)
CALL FREAD(6, 'R*8:', VMIN)

CALL HFLIN(NDATA, VDATA, PHDAT, VMIN, SHF, YHF, SQR)
use initial slope as first guess of KAPPA

AK = ((-1.D0*ENPAR*ANU*DZERO)/(DELN*VCRIT*SLFO)) - (11.D0+GAMMA)

write out things so far

WRITE (5,250) EMBOX, T
WRITE (5,260) ENPAR, ENPERP
WRITE (5,270) GAMMA
270 FORMAT (1X, 'Gamma        = ') 
WRITE (5, 280) NBFOR, NAFTER, FRACT 
C 
WRITE (5, 502) 
WRITE (5, 310) SSBFOR 
WRITE (5, 300) 
WRITE (5, 310) SSAFT 
WRITE (5, 320) DZERO 
WRITE (5, 330) DELN 
WRITE (5, 340) ANU 
WRITE (5, 350) SLFO 
WRITE (5, 360) VCRIT 
WRITE (5, 370) AK 
280 FORMAT (1X, 'Nbfor= ', I5, ' Nafter= ', I5, 
1 ' Fract= ', F10.5) 
290 FORMAT (1X, 'Fit to capacitance before Vcrit:') 
300 FORMAT (1X, 'Fit after Vcrit ( was quadratic in V)') 
310 FORMAT (1X, 'Sum of squares= ', F30.15) 
320 FORMAT (1X, 'DZERO= ', F30.15) 
330 FORMAT (1X, 'DELN= ', F30.15) 
340 FORMAT (1X, 'NU= ', F30.15) 
350 FORMAT (1X, 'initial SLFO= ', F30.15) 
360 FORMAT (1X, 'VCRIT= ', F30.15) 
370 FORMAT (1X, 'estimated KAPPA= ', F30.15) 
C 
C Reduce the number of data points after Vcrit to 250 
C 
NFEW = 250 
CALL FEW(VDATA, PHDAT, NDATA, VCRIT, NFEW) 
C 
C Try a range of VCRIT 
C 
WRITE (6, 380) 
380 FORMAT (1X, 'Give me a range (+/-) around VCRIT..') 
CALL FREAD(6, 'R*8:', VCRAN) 
VCORIG = VCRIT 
FIRST = .TRUE. 
C 
DO 650 NVC = 1, 5 
C 
VCRIT = (VCORIG - VCRAN) + DFLOAT(NVC - 1) * (VCRAN/ 
1 2.DO) 
VCARAY(NVC) = VCRIT 
C call high field subroutine 
C 
390 CONTINUE 
AKHFS = AK 
AKHFI = AK 
CALL HFO(SHF, YHF, VCRIT, GAMMA, ANU, DZERO, AKHFS, 
1 AKHFI) 
C 
HFKSRA(NVC) = AKHFS 
HFKIRA(NVC) = AKHFI
WRITE (5, 400) VCRIT
WRITE (5, 410) SHF, YHF
WRITE (5, 420) AKHFS, AKHFI, SQR

400 FORMAT (1X, 'Vcrit= ', F16.8)
410 FORMAT (1X, 'HFslope= ', F16.8, ' HFIntercept= ', F16.8)
420 FORMAT (1X, 'Slope HFk=', F16.8, ' Intercept HFk= ', F16.8, ' SQR= ', F16.8)

C reduce the data
C
CALL REDPHS(NDATA, VDATA, PHDAT, DZERO, VCRIT, NRED, VRED, PHRED)
NRAY(NVC) = NRED

C fill ALFRAY, ETARAY and ELARAY
C
IF (.NOT. FIRST) GO TO 440
ETA = 0.0D0
ALPHA = 0.0D0
DO 430 I = 1, NRED
    CALL VFIND(VRED(I))
    ALFRAY(I) = ALPHA
C DELIKM is a library elliptic integral K(1-x)
    ELARAY(I) = DELIKM(DEXP(-1.0D0*ALPHA), IND)
    ETARAY(I) = 1.0D0 - DEXP(-1.0D0*ALPHA)
430 CONTINUE
FIRST = .FALSE.
440 CONTINUE

C Do the fitting
C
ITMAX = 30
ITER = 0
DELK = 0.5D0
AK2 = AK
AK1 = AK2 - DELK
AK3 = AK2 + DELK
CALL CHISQP(NRED, PHRED, VRED, AK1, F1, PHTH, VTH,
    RESPH, RESV)
CALL CHISQP(NRED, PHRED, VRED, AK2, F2, PHTH, VTH,
    RESPH, RESV)
CALL CHISQP(NRED, PHRED, VRED, AK3, F3, PHTH, VTH,
    RESPH, RESV)
450 CONTINUE
WRITE (5, 460) ITER, DELK
460 FORMAT (1X, '##### iter=', I5, ' ##### delK=', F20.15)
WRITE (5, 470).
470 FORMAT (14X, 'kappa', 20X, 'chisqr')
WRITE (5, 490) AK1, F1
WRITE (5, 480) AK2, F2
WRITE (5, 480)
WRITE (5,490) AK3, F3
480 FORMAT (1X, '---------------------')
490 FORMAT (1X, F30.15, F30.15)

C
A1 = (F1 + F3 - 2.0D0*F2) / (2.0D0*DELK*DELK)
IF (A1 .LE. 0.0D0) GO TO 530
B1 = (F2 - F1 + A1*(DELK*DELK - 2.0D0*AK2*DELK)) / DELK
AKNEW = -1.0D0 * B1 / (2.0D0*A1)
CALL CHISQP(NRED, PHRED, VRED, AKNEW, FNEW, PHTH, VTH, RESPH, RESV)
DELK = DABS(AK2 - AKNEW)

C
CONV = 2.0D-3
C
IF (DELK .LE. CONV) GO TO 570
C
C Next iteration
C
ITER = ITER + 1
IF (ITER .GE. ITMAX) GO TO 550
IF (AKNEW .GT. AK3) GO TO 510
IF (AKNEW .LT. AK1) GO TO 520
IF (AKNEW .GT. AK2) GO TO 500

C case that AK1<AKNEW<AK2
F3 = F2
AK3 = AK2
F2 = FNEW
AK2 = AKNEW
AK1 = AK2 - DELK
CALL CHISQP(NRED, PHRED, VRED, AK1, F1, PHTH, VTH, RESPH, RESV)
GO TO 450

500 CONTINUE
C case that AK2<AKNEW<AK3
F1 = F2
AK1 = AK2
F2 = FNEW
AK2 = AKNEW
AK3 = AK2 + DELK
CALL CHISQP(NRED, PHRED, VRED, AK3, F3, PHTH, VTH, RESPH, RESV)
GO TO 450

510 CONTINUE
C case that AK3<AKNEW
C DELK=DABS(AK2-AK3)
F1 = F3
AK1 = AK3
F2 = FNEW
AK2 = AKNEW
AK3 = AK2 + DELK
CALL CHISQP(NRED, PHRED, VRED, AK3, F3, PHTH, VTH, RESPH, RESV)
GO TO 450

CONTINUE

CASE THAT AKNEW<AK1

DELK = DABS(AK2 - AK1)

F3 = F1
AK3 = AK1
F2 = FNEW
AK2 = AKNEW
AK1 = AK2 - DELK

CALL CHISQP(NRED, PHRED, VRED, AK1, F1, PTH, VTH,
1
RESPH, RESV)

GO TO 450

CONTINUE

WRITE (5,540)

540 FORMAT (1X, 'Parabolic fit curves wrong way!')

GO TO 650

CONTINUE

WRITE (5,560)

560 FORMAT (1X, 'Too many iterations!')

GO TO 650

CONTINUE

WRITE (5,580) CONV

580 FORMAT (1X, 'Fit has converged. CONV=', 'F20.10)

WRITE (5,600) AK
WRITE (5,610) A1
WRITE (5,620) CHIFIN(NVC)
WRITE (5,630) VCRIT

600 FORMAT (1X, 'KAPPA= ', 'F20.15)
610 FORMAT (1X, 'CURVATURE= ', 'F20.15)
620 FORMAT (1X, 'CHISQP= ', 'F20.15)
630 FORMAT (1X, 'VCRIT= ', 'F20.15)

plot
WRITE (6, 640)
640 FORMAT (1X, 'Do you wanna plot? (0=NO)')
CALL FREAD(6, 'R*8:', YESNO)
IF (YESNO .EQ. 0.D0) GO TO 650
CALL PLTFIT(NRED, VRED, PHRED, VTH, PHTH, RESV, 1, RESPH, STD)
650 CONTINUE
WRITE (5, 660)
660 FORMAT (1X, 'VCRIT...Slope HFk...Intcpt HFk...FitK... 1 ...chisqr')
JMIN = 1
CHIMIN = CHIFIN(1)
DO 680 J = 1, 5
   WRITE (5, 690) VCARAY(J), HFKSRA(J), HFKIRA(J), 1 FTKRAY(J), CHIFIN(J)
   IF (CHIFIN(J) .LT. CHIMIN) GO TO 670
GO TO 680
670 CONTINUE
JMIN = J
CHIMIN = CHIFIN(J)
680 CONTINUE
690 FORMAT (1X, 5F14.7)
best one now labelled by JMIN
WRITE (6, 700) JMIN
700 FORMAT (1X, 'Best chisqr value is number', I6)
WRITE (6, 710)
710 FORMAT (1X, 'Type any number to go on to plots')
CALL FREAD(6, 'R*8:', YESNO)
NRED = NRAY(JMIN)
DO 720 J = 1, NRED
   VTH(J) = VTHRAY(J, JMIN)
   PTH(J) = PTHRA(J, JMIN)
   VRED(J) = VRAY(J, JMIN)
   PHRED(J) = PHRAY(J, JMIN)
   RESV(J) = RVRAY(J, JMIN)
   RESPH(J) = RPHRAY(J, JMIN)
720 CONTINUE
CALL PLTFIT(NRED, VRED, PHRED, VTH, PHTH, RESV, RESPH, 1, STD)
Write out relevant stuff on device 11
WRITE (11,730) MONTH, RNUM, T, FTKRAY(JMIN),
1CHIFIN(JMIN), CURV(JMIN), STD, VCARAY(JMIN),
2HFKSRA(JMIN), HFKIRA(JMIN), DZERO
730 FORMAT (16, F10.5, 9E20.10)
C
C
STOP
END

A.7 Subroutine REDPHS

C subroutine to produce reduced data
C
SUBROUTINE REDPHS(NDATA, VDATA, PHDAT, DZERO, VCRIT,
1 NRED, VRED, PHRED)
IMPLICIT REAL*8(A - H, O - Z)
DIMENSION VDATA(5000), PHDAT(5000), VRED(500),
1 PHRED(500)
J = 1
DO 10 K = 1, NDATA
 VR = (VDATA(K)/VCRIT) - 1.0D0
 IF (VR .LE. 0.0D0) GO TO 10
 VRED(J) = VR
 PHRED(J) = (1.0D0 - (PHDAT(K)/DZERO))
 J = J + 1
10 CONTINUE
NRED = J - 1
RETURN
END

A.8 Subroutine CHISQP

C Goodness of fit, Phase case
C
SUBROUTINE CHISQP(NRED, PHRED, VRED, TESTK, F, PHTH,
1 VTH, RESPH, RESV)
IMPLICIT REAL*8(A - H, O - Z)
DIMENSION PHRED(500), VRED(500), VTH(500), PHTH(500),
1 RESPH(500)
DIMENSION ALFRAY(500), ETARAY(500), ELARAY(500),
1 RESV(500)
COMMON AK, ANU, GAMMA, PIBY2, ALPHA, ETA
COMMON /PARAM/ ALFRAY, ETARAY, ELARAY
COMMON /SAVEK/ ELIP
C
AK = TESTK
FNU = (DSQRT(1.0D0+ANU)) / (DSQRT(1.0D0+ANU) - 1.0D0)
DO 10 J = 1, NRED

ALPHA = ALFRAY(J)
ETA = ETARAY(J)
ELIP = ELARAY(J)
CALL FAINT(A)
CALL FBINT(B)
CALL FCINT(C)
VTH(J) = (((1.D0/PIBY2)*DSQRT(1.D0+GAMMA*ETA)*A) - 1.
1 0D0
PHTH(J) = FNU * (1.D0-(C/B))
10 CONTINUE
C
C
LV = 1
LP = 1
SUM = 0.0D0
C
DO 120 M = 1, NRED
C
deduce LP LV s.t.
C VTH(LV)>VRED(M)>VTH(LV-1)
C PHTH(LP)>PHRED(M)>PHTH(LP-1)
C
NV = LV
IF (VRED(M) .GT. VTH(NRED)) GO TO 40
IF (VRED(M) .LE. VTH(1))  GO TO 50
20 CONTINUE
NV = NV + 1
IF (NV .EQ. NRED + 1) NV = 2
IF ((VRED(M) .LE. VTH(NV)) .AND. (VRED(M) .GT. VTH(1 NV - 1))) GO TO 30
GO TO 20
30 CONTINUE
C
LV = NV
SL = (PHTH(LV) - PHTH(LV - 1)) / (VTH(LV) - VTH(LV - 1))
PHINT = PHTH(LV - 1) + SL * (VRED(M) - VTH(LV - 1))
C
GO TO 60
C
40 CONTINUE
case VRED(M)>VTH(NRED)
SL = (PHTH(NRED) - PHTH(NRED - 1)) / (VTH(NRED) - VTH(NRED - 1))
PHINT = PHTH(NRED) + SL * (VRED(M) - VTH(NRED))
GO TO 60
C
50 CONTINUE
case VRED(M)<VTH(1)
SL = (PHTH(2) - PHTH(1)) / (VTH(2) - VTH(1))
PHINT = PHTH(1) - SL * (VTH(1) - VRED(M))
C
60 CONTINUE
C
RESPH(M) = PTHINT - PHRED(M)
PHRESQ = RESPH(M) * RESPH(M)

NC = LP
IF (PHRED(M) .GT. PHTH(NRED)) GO TO 90
IF (PHRED(M) .LE. PHTH(1)) GO TO 100

70 CONTINUE
NC = NC + 1
IF (NC .EQ. NRED + 1) NC = 2
IF ((PHRED(M) .LE. PHTH(NC)) .AND. (PHRED(M) .GT. PHTH(NC - 1))) GO TO 80
GO TO 70

80 CONTINUE
LP = NC
SL = (VTH(LP) - VTH(LP - 1)) / (PHTH(LP) - PHTH(LP - 1))
VTHINT = VTH(LP - 1) + SL * (PHRED(M) - PHTH(LP - 1))
GO TO 110

90 CONTINUE
C case PHRED(M)>PHTH(NRED)
SL = (VTH(NRED) - VTH(NRED - 1)) / (PHTH(NRED) - PHTH(NRED - 1))
VTHINT = VTH(NRED) + SL * (PHRED(M) - PHTH(NRED))
GO TO 110

100 CONTINUE
C case PHRED(M)<PHTH(1)
SL = (VTH(2) - VTH(1)) / (PHTH(2) - PHTH(1))
VTHINT = VTH(1) - SL * (PHTH(1) - PHRED(M))
GO TO 110

110 CONTINUE
RESV(M) = VTHINT - VRED(M)
IF (RESV(M) .GT. 1.D10) RESV(M) = 1.D10
VRESQR = RESV(M) * RESV(M)
RESQR = 1.0D0 / (((1.0D0/VRESQR) + (1.D0/PHRESQ))
SUM = SUM + RESQR
120 CONTINUE
F = SUM
RETURN
END
A.9 Subroutine HFLIN

C
C
SUBROUTINE HFLIN(NDATA, VDATA, PHDAT, VMIN, SHF, YHF, 1 SQR)
IMPLICIT REAL*8(A - H, O - Z)
DIMENSION VDATA(5000), PHDAT(5000), VFIT(2000)
DIMENSION S(3), SIG(3), A(2), B(2), P(2)

C
C FIT INVERSE VOLTAGES V>VMIN
C
K = 1
DO 10 J = 1, NDATA
  IF (VDATA(J) .LT. VMIN) GO TO 10
  VFIT(K) = VDATA(J)
  PIFIT(K) = 1.D0 / PHDAT(J)
  K = K + 1
10 CONTINUE
NFIT = K - 1

C DOLSF is a library polynomial fit routine
CALL DOLSF(1, NFIT, PIFIT, VFIT, YF, YD, WT, 0, S, 1 SIG, A, B, SS, .TRUE., P)

C
SHF = P(2)
YHF = P(1)
SQR = SS
RETURN
END

A.10 Subroutines HFO And FEW And Related Functions

C High field subroutine to get AKHFS and AKHFI
C
SUBROUTINE HFO(SHF, YHF, VCRIT, GAMMA, ANU, DZERO, 1 AKHFS, AKHFI)
IMPLICIT REAL*8(A - H, O - Z)
LOGICAL LZ1, LZ2
EXTERNAL HFSZ, HFIZ
COMMON /HFCOM/ TK, G, U, ST

TK = AKHFS
G = GAMMA
U = ANU
PI = 2.D0 * DARCOS(0.0D0)

C
DEN = 2.D0 * VCRIT * DZERO
ST = (-1.D0*SHF*PI*(DSQRT(1.D0+U) - 1.D0)DSQRT(1.1D0+G)) / DEN
ZERO2 is a library root finding routine
CALL ZERO2(AKZ1, AKMAX1, HFSZ, HFERR1, LZ1)
IF ( .NOT. LZ1) WRITE (5,10)
10 FORMAT (1X, ' NO ROOT FOUND in slope High Field fit...' )
AKHFS = AKZ1

ST = (PI*YHF*DSQRT(1.D0+G)) / (2.D0*G*VCRIT)

ZERO2 is a library root finding routine
CALL ZERO2(AKZ2, AKMAX2, HFIZ, HFERR2, LZ2)
IF ( .NOT. LZ2) WRITE (5,20)
20 FORMAT (1X, ' NO ROOT FOUND in intercept High Field fit...' )
AKHFI = AKZ2
RETURN
END

HFSZ is zero when slope HFK is found
DOUBLE PRECISION FUNCTION HFSZ(AKHFS)
IMPLICIT REAL*8(A - H, O - Z)
COMMON /HFCOM/ TK, G, U, ST
EXTERNAL HFSARG
TK = AKHFS
HFSZ = ST - DGAU16(0.0D0,1.0D0,HFSARG)
RETURN
END

DOUBLE PRECISION FUNCTION HFSARG(X)
IMPLICIT REAL*8(A - H, O - Z)
COMMON /HFCOM/ TK, G, U, ST
X2 = X * X
T = 1.D0-(DSQRT((1.D0+U)/(1.D0+X2*U)))
HFSARG = T * DSQRT((1.D0+TK*X2)*(1.D0+G*X2)) / (1.D0-X2)
RETURN
END

DOUBLE PRECISION FUNCTION HFIZ(AKHFI)
IMPLICIT REAL*8(A - H, O - Z)
COMMON /HFCOM/ TK, G, U, ST
EXTERNAL HFIARG
TK = AKHFI
HFIZ = ST - DGAU16(0.0D0, 1.0D0, HFIARG)
RETURN
END

C
DOUBLE PRECISION FUNCTION HFIARG(X)
IMPLICIT REAL*8(A - H, O - Z)
COMMON /HFCOM/ TK, G, U, ST
X2 = X * X
HFIARG = DSQRT((1.D0+TK*X2)/(1.D0+G*X2))
RETURN
END

C Subroutine to thin data after VCRIT to save $$

SUBROUTINE FEW(VDATA, PHDAT, NDATA, VCRIT, NFEW)
IMPLICIT REAL*8(A - H, O - Z)
DIMENSION VDATA(5000), PHDAT(5000), VFEW(500),
1 PHEW(500)
DIMENSION VBIN(50), PHBIN(50), YF(50), YD(50), WT(50),
1 S(50)
DIMENSION SIG(50), A(50), B(50), P(3)

J = 1
10 CONTINUE
IF (VDATA(J) .GE. VCRIT) GO TO 20
J = J + 1
GO TO 10
20 CONTINUE
NV = J

C Determine the bin size and print it out..

NBIN = (NDATA - J) / NFEW
IF (NBIN .LE. 3) NBIN = 4
WRITE (6,30) NV, NFEW, NBIN
30 FORMAT (1X, 'Number bfor Vc=', 16, ' chop to', 16,
1 ' bins=', 16)

DO 50 L = 1, NFEW

VSUM = 0.0D0

DO 40 M = 1, NBIN
VBIN(M) = VDATA(J)
PHBIN(M) = PHDAT(J)
VSUM = VSUM + VDATA(J)
J = J + 1
40 CONTINUE

VFEW(L) = VSUM / DFLOAT(NBIN)
DOLSF is a library polynomial fit routine
CALL DOLSF(2, NBIN, VBIN, PHBIN, YF, YD, WT, 0, S, 
   SIG, A, B, SQR, .TRUE., P)

PHEW(L) = P(1) + P(2) * VFEW(L) + P(3) * VFEW(L) * 
   VFEW(L)

50 CONTINUE

L = 1
NDATA = NV + NFEW - 1

DO 60 K = NV, NDATA
   VDATA(K) = VFEW(L)
   PHDAT(K) = PHEW(L)
   L = L + 1
60 CONTINUE

RETURN
END

A.11 Subroutine PLTFIT

Subroutine to plot results of fit

SUBROUTINE PLTFIT(NRED, VRED, CRED, VTH, CTH, RESV, 
   RESC, STD)
IMPLICIT REAL*8(A - H, 0 - Z)
REAL*4 V(500), C(500), VFIT(500), CFIT(500), RV(500), 
   RC(500)
REAL*4 PRES(500)
DIMENSION VRED(500), CRED(500), ALFRAY(500), 
   ETARAY(500)
DIMENSION ELARAY(500), VTH(500), CTH(500), RESV(500), 
   RESC(500)

SUMPR2 = 0.0D0

DO 10 J = 1, NRED
   VFIT(J) = VTH(J)
   CFIT(J) = CTH(J)
   RV(J) = RESV(J)
   RC(J) = RESC(J)
   PR2 = 1.D0 / ((1.D0/RESV(J))**2 + (1.D0/RESC(J))**2)
   SUMPR2 = SUMPR2 + PR2
   PRES(J) = DSQRT(PR2)
   V(J) = VRED(J)
   C(J) = CRED(J)
10 CONTINUE
STD = DSQRT(SUMPR2/NRED)
20 CONTINUE
WRITE (5,30) STD
30 FORMAT (1X, 'Standard deviation= ', F30.15)
WRITE (6,40)
40 FORMAT (1X, '0=Quit 1=fit graph 2=Vresid 3=Cresid 4=Pre')
CALL FREAD(6, 'R*8:', GRAPH)
IF (GRAPH .EQ. 0.0D0) RETURN
IF (GRAPH .EQ. 1.D0) GO TO 70
IF (GRAPH .EQ. 2.D0) GO TO 50
IF (GRAPH .EQ. 3.D0) GO TO 60
C
CALL ALGRAF(V, PRES, NRED, 0)
CALL ALDONE
GO TO 20
C
50 CONTINUE
C
CALL ALGRAF(V, RV, NRED, 0)
CALL ALDONE
GO TO 20
C
60 CONTINUE
C
CALL ALGRAF(V, RC, NRED, 0)
CALL ALDONE
GO TO 20
C
70 CONTINUE
CALL ALGRAF(V, C, NRED, -1)
CALL ALGRAF(VFIT, CFIT, -1*NRED, 0)
CALL ALDONE
GO TO 20
END

A.12 Function TEMP(R)

C Function to evaluate Temperature
C
DOUBLE PRECISION FUNCTION TEMP(R)
IMPLICIT REAL*8(A-H,O-Z)
A=91.356938270024003D0
B=-0.068776762624791D0
C=0.000027138365424D0
D=-0.00000004534137D0
C
TEMP=A+B*R+C*R*R+D*R*R*R
RETURN
END
A.13 Subroutine VFIND And Function VZ

C finds best alpha for a given voltage
C
SUBROUTINE VFIND(V)
IMPLICIT REAL*8(A - H, O - Z)
LOGICAL LZ
EXTERNAL VZ
COMMON AK, ANU, GAMMA, PIBY2, ALPHA, ETA
COMMON /VOLT/ VD
VD = V
VERROR = 1.0D-9
ALFMAX = 100.0D0
ALFMIN = 0.0D0
C ZERO2 is a library root finding routine
CALL ZERO2(ALFMIN, ALFMAX, VZ, VERROR, LZ)
ALPHA = ALFMIN
RETURN
END
C VZ=0 when correct ALPHA is found
C
DOUBLE PRECISION FUNCTION VZ(ALPHA)
IMPLICIT REAL*8(A - H, O - Z)
COMMON AK, ANU, GAMMA, PIBY2, ALFDUM, ETA
COMMON /SAVEK/ ELIP
COMMON /VOLT/ V
ALFDUM = ALPHA
ETA = 1.0D0-DEXP(-1.0D0*ALPHA)
C DELIKM is a library elliptic integral K(1-x)
ELIP = DELIKM(DEXP(-1.0D0*ALPHA),IND)
CALL FAINT(A)
VZ = (V + 1.0D0) - (1.0D0/PIBY2) * DSQRT(1.0D0+GAMMA*ETA) * A
RETURN
END

A.14 Subroutine FAINT, FBINT And FCINT And Related Functions

C
SUBROUTINE FAINT(A)
C
IMPLICIT REAL*8(A - H, O - Z)
COMMON AK, ANU, GAMMA, PIBY2, ALPHA, ETA
COMMON /SAVEK/ ELIP
EXTERNAL FA
T = DSQRT((1.0D0+AK*ETA)/(1.0D0+GAMMA*ETA))
EIP = T * ELIP
A = DEXP(ALPHA/2.0D0) * DGAU16(0.0D0,PIBY2,FA) + EIP
DOUBLE PRECISION FUNCTION FA(PHI)
IMPLICIT REAL*8(A - H,O - Z)
COMMON AK, ANU, GAMMA, PIBY2, ALPHA, ETA
ES2 = ETA * (DSIN(PHI)) ** 2
T1 = DSQRT((1.0D0+AK*ES2)/(1.0D0+GAMMA*ES2))
T2 = DSQRT((1.0D0+AK*ETA)/(1.0D0+GAMMA*ETA))
FA = (T1 - T2) / DSQRT(1.0D0+(DEXP(ALPHA) - 1.D0)*(
1DCOS(PHI))**2)
RETURN
END

SUBROUTINE FBINT(B)
IMPLICIT REAL*8(A - H,O - Z)
COMMON AK, ANU, GAMMA, PIBY2, ALPHA, ETA
COMMON /SAVEK/ ELIP
EXTERNAL FB
T = DSQRT((1.0D0+AK*ETA)*(1.0D0+GAMMA*ETA))
EIP = T * ELIP
B = DEXP(ALPHA/2.DO) * DGAU16(0.0D0,PIBY2,FB) + EIP
RETURN
END

DOUBLE PRECISION FUNCTION FB(PHI)
IMPLICIT REAL*8(A - H,O - Z)
COMMON AK, ANU, GAMMA, PIBY2, ALPHA, ETA
ES2 = ETA * (DSIN(PHI)) ** 2
T1 = DSQRT((1.0D0+AK*ES2)*(1.0D0+GAMMA*ES2))
T2 = DSQRT((1.0D0+AK*ETA)*(1.0D0+GAMMA*ETA))
FB = (T1 - T2) / DSQRT(1.0D0+(DEXP(ALPHA) - 1.D0)*(
1DCOS(PHI))**2)
RETURN
END

SUBROUTINE FCINT(C)
IMPLICIT REAL*8(A - H,O - Z)
COMMON AK, ANU, GAMMA, PIBY2, ALPHA, ETA
COMMON /SAVEK/ ELIP
EXTERNAL FC
T = DSQRT((1.DO+AK*ETA)*(1.DO+GAMMA*ETA)/(1.DO+ANU* ETA))
EIP = T * ELIP
C = DEXP(ALPHA/2.DO) * DGAU16(0.0D0,PIBY2,FC) + EIP
RETURN
END

DOUBLE PRECISION FUNCTION FC(PHI)
IMPLICIT REAL*8(A - H,O - Z)
COMMON AK, ANU, GAMMA, PIBY2, ALPHA, ETA
ES2 = ETA * (DSIN(PHI)) ** 2
\[
T_1 = \text{DSQRT}\left((1.0 + AK \times ES2)(1.0 + GAMMA \times ES2)/(1.0 + ANU \times 1ES2)\right)
\]
\[
T_2 = \text{DSQRT}\left((1.0 + AK \times ETA)(1.0 + GAMMA \times ETA)/(1.0 + ANU \times 1ETA)\right)
\]
\[
FC = \frac{(T_1 - T_2)}{\text{DSQRT}(1.0 + (\text{DEXP}(\text{ALPHA}) - 1.0) \times (1.0 \cos(\text{PHI}))^2)}
\]
RETURN
END

A.15 Function GAM(T)

Function fit to GAMMA from capacitance data

\[
\text{DOUBLE PRECISION FUNCTION GAM(T)}
\]
\[
\text{IMPLICIT REAL*8(A - H, O - Z)}
\]
\[
X = \text{DLOG}(2.0 - \text{DLOG}(T - 33.53D0))
\]
\[
A = -0.658253255683873D0
B = 0.597035483376152D0
C = 0.037285118112837D0
D = -0.001866105990918D0
E = -0.003583587750158D0
F = -0.000485871203777D0
G = 0.000526397253193D0
\]
\[
P = A + B \times X + C \times X \times X + D \times X \times X \times X + E \times X \times X \times X \times X + F \times X \times X \times X \times X \times X + G \times X \times X \times X \times X \times X \times X
\]
\[
\text{GAM} = 1.0 \div (P - 0.70D0 \times X + 1.36D0)
\]
RETURN
END

A.16 Function ENBAR(T)

Function for fit to Dunmur data to give average index

\[
\text{DOUBLE PRECISION FUNCTION ENBAR(T)}
\]
\[
\text{IMPLICIT REAL*8(A - H, O - Z)}
\]
\[
A = 0.742523521312106D0
B = 0.056009345076744D0
C = -0.000840433621095D0
D = -1.939980547157384D0
\]
E = 0.294319650826645D0
F = -0.008355771448850D0
G = 0.000079379753787D0

ENPAR = A + B*T + C*T*T
ENPERP = D + E*T + F*T*T + G*T*T*T

ENBAR = (2.0D0*ENPERP + ENPAR) / 3.0D0
RETURN
END

A.17 Function DZFIT(T)

Function to evaluate DZERO from fit to optical data

DOUBLE PRECISION FUNCTION DZFIT(T)
IMPLICIT REAL*8(A - H, O - Z)

X = DLOG(2.0D0 - DLOG(T - 33.53D0))

A = 50.476158877086664D0
B = 5.395037153990744D0
C = -1.025087215412876D0
D = -0.2410467372979D0
E = 0.051954473728999D0
F = 0.02330878762354D0

DZFIT = A + B*X + C*X*X + D*X*X*X + E*X
1*X*X*X + F*X*X*X*X*X
RETURN
END

A.18 Function CZFIT(T)

Function to deduce CZERO from fit to capacitance data

DOUBLE PRECISION FUNCTION CZFIT(T)
IMPLICIT REAL*8(A - H, O - Z)
X = DLOG(2.0D0 - DLOG(T - 33.53D0))

A = 0.005439002097344D0
B = 0.000366059220110D0
C = -0.00035032443337D0
D = -0.00021504535889D0
E = -0.00001795711260D0
F = 0.00001446343032D0
FX = A + B*X + C*X*X + D*X*X*X + E*X*X*X + F*X*X*X*X
CZFIT = 1.0D0 / FX
RETURN
END
APPENDIX B - DATA TABLES

Table II - Results of Capacitance Data Fits

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>K ± δK</th>
<th>Vc ± δVc</th>
<th>K_HFC</th>
<th>C_o</th>
<th>C_oo</th>
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<td>$d_0$ 0.0461</td>
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<td>-----------------</td>
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Table IV - Elastic Constant Results

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<th>type</th>
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<th>$K_{11}$ ± $\Delta K_{11}$</th>
<th>$K_{33}$ ± $\Delta K_{33}$</th>
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<td>°C</td>
<td>10$^{-12}$ N</td>
<td>10$^{-12}$ N</td>
</tr>
<tr>
<td>F</td>
<td>33.5334</td>
<td>14.014 ± 0.99</td>
<td>181.66 ± 16.89</td>
</tr>
<tr>
<td>F</td>
<td>33.5370</td>
<td>9.172 ± 0.50</td>
<td>180.48 ± 14.38</td>
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<tr>
<td>C</td>
<td>33.5370</td>
<td>9.619 ± 0.66</td>
<td>164.00 ± 14.55</td>
</tr>
<tr>
<td>F</td>
<td>33.5437</td>
<td>8.548 ± 0.49</td>
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<tr>
<td>F</td>
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<td>9.202 ± 0.50</td>
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</tr>
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<td>C</td>
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<td>8.211 ± 1.22</td>
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</tr>
<tr>
<td>F</td>
<td>33.5819</td>
<td>8.234 ± 1.92</td>
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</tr>
<tr>
<td>F</td>
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</tr>
<tr>
<td>C</td>
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<td>7.691 ± 0.80</td>
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<tr>
<td>F</td>
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<tr>
<td>F</td>
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<tr>
<td>F</td>
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<tr>
<td>F</td>
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<td>7.530 ± 1.01</td>
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<td>F</td>
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<td>7.596 ± 0.92</td>
<td>20.92 ± 4.10</td>
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<tr>
<td>F</td>
<td>33.8264</td>
<td>7.583 ± 1.05</td>
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</tr>
<tr>
<td>C</td>
<td>33.8264</td>
<td>7.493 ± 0.67</td>
<td>20.89 ± 2.65</td>
</tr>
<tr>
<td>F</td>
<td>34.1255</td>
<td>7.151 ± 0.63</td>
<td>13.63 ± 1.59</td>
</tr>
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REFERENCES


