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Mechanisms for the Effect of Electric and Magnetic Fields on Biological Systems

By

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Introduction

Work on the influence of electric and magnetic fields on the structure of cholesteric liquid crystals continued during this period. This report consists of preprints of several investigations submitted for publication in the Journal of Chemical Physics:

(1) "Electric Field Effects on the Dielectric Properties and Molecular Arrangements of Cholesteric Liquid Crystals", H. Baessler and M. M. Labes.

(2) "Electric Field Effects on the Optical Rotatory Power of a Compensated Cholesteric Liquid Crystal", H. Baessler, T. M. Laronge and M. M. Labes.

(3) "Magnetic Field Effects on a Compensated Cholesteric Liquid Crystal", T. M. Laronge, H. Baessler and M. M. Labes.

Electric Field Effects on the Dielectric Properties and Molecular Arrangements of Cholesteric Liquid Crystals

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Abstract

Measurements of dielectric constants of a cholesteryl chloride-cholesteryl myristate mixture having a strongly temperature dependent helical pitch have been performed in the presence and absence of an applied dc electric field. An analysis of the molecular arrangement in samples oriented by wall effects is presented, as well as the perturbations in this arrangement which occur both thermally and by the application of an electric field. Elastic moduli of bending and torsional strain are estimated from the threshold electric fields observed to (a) induce helical perturbation and (b) destroy the helical structure in the transition to a nematic phase.

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Introduction

The close relationship of nematic and cholesteric liquid crystals was first demonstrated by Friedel in 1922,[1] who was able to produce a nematic mesophase by mixing two cholesteric compounds of opposite optical rotatory power. Cholesteric-nematic phase transitions can be induced in such compensated mixtures thermally or by application of electric[2,3] and magnetic fields.[4] In each case that phase is stable for which the total free energy of the system is a minimum. A theory for the electric and magnetic field induced phase transitions has been proposed independently by Meyer[5] and deGennes,[6] and experimental corroboration has appeared of the predicted inverse dependence of the pitch of the helical structure on the electric field strength required to cause a transition from the cholesteric to nematic phase.[3]

Several studies have been made on a 1.75:1 mixture of cholesteryl chloride(C) and cholesteryl myristate(M), which has a strongly temperature dependent helical pitch at temperatures $\lesseqgtr 43°$, and is nematic at 43°.[7] An electric field acts on the system by interacting with the large electric dipole moments of the components. For C, the dipole moment approximately coincides with the long axis of the molecule, whereas for M, the dipole moment is at a pronounced angle to this long axis. Since the dielectric constant ε of a polar material depends on the average orientation of its permanent dipoles, following ε during a phase transition is a convenient probe for

studying changes in molecular arrangement. Furthermore, ε measurements in ordered phases yield data for the dielectric anisotropy which are necessary to estimate elastic constants of bending and torsional strain from the experimental values for the transition field.[5,6]

In this paper measurements of dielectric constants in the presence of dc electric fields are studied. In a subsequent paper, the effect of a magnetic field on the dielectric constant will be examined.

Experimental

Measurements of the dielectric constants were performed with pure C and M and with a 1.75:1.00 weight mixture(CM). (The molar mixture ratio is 2.57:1.0). The compounds were obtained from Steraloids, Inc. and used without further purification. The conductivity of the mixture was about $10^{-12}\ \Omega^{-1}\ cm^{-1}$ at 43°. Since the critical field for inducing a nematic phase varied inversely with the pitch of the helix,[3] in corroboration of the theory,[5,6] the influence of ionic impurity conduction on the observed phenomena can only be a second order effect.

The material was placed between silica discs partially covered with SnO_2 electrodes. Teflon or mylar films in the thickness range 4...127μ were used as electrode spacers. Care had to be taken to avoid bubbles between the electrodes, especially with thin samples. The samples were mounted in an optical cell which could be heated by a controlled temperature nitrogen stream. The cell could be placed between the poles of a special Varian 6" magnet with H either parallel

or perpendicular to the electrodes. All ε data reported herein are taken with a General Radio Impedance Bridge Type 1608A at a frequency of 1kc. No frequency dependence of ε was observed in the range $0.5 < f < 10$kc. During the measurements, a dc-bias of up to 200 volts could be applied to the sample. The dc-field was always parallel to the ac-field. The ac-voltage across the sample was usually less than 1 volt, and was insufficient to cause a phase transition. The uncertainty of the capacitance measurements is less than 0.5%.

Results

Dielectric constants of C, M and of CM mixtures at various electrode spacings d are plotted vs 1/T in Fig. 1. All curves are taken during cooling and display discontinuities at the isotropic liquid-cholesteric transition temperature. (The $T_{is \rightarrow chol}$ values are 80° for C, 75° for M and 62±1° for CM). A remarkable dip in the $\varepsilon(1/T)$ curve of CM occurs at $T_{nem} = 43 \pm 3°$.[7] Its position varies slightly from sample to sample indicating that T_{nem} is very sensitive to minor changes in the molecular ratio of the constituting compounds. The temperature range of this dip in ε increases with decreasing sample thickness d, and is approximately equal to the temperature range in which $Z_o \geqq 2d$ (Z_o = pitch of the helix) indicating a disturbance of the helical structure.[8] This is a confirmation of Sackmann et al's[7] values for the pitch obtained from optical diffraction studies. For $d > 25\mu$ the structure in the $\varepsilon(1/T)$ curve is smoothed out. Both the dip

at T_{nem} and the rise at $T = T_{is \rightarrow chol}$ disappear. In thin samples the ordering influence of the walls is obviously strong enough to establish helical alignment throughout the bulk - with the helical axis perpendicular to the walls - whereas in thick samples the direction of the helical axis varies as one proceeds into the bulk. As a result ε approaches the value of the isotropic liquid with increasing d. Under the microscope, thin samples of CM display a plane texture over a large homogeneous area indicative of an ordered helical structure.

Upon application of a dc-field to CM, a cholesteric-nematic transition can be induced if the condition $F > F_u = \text{const.} \frac{2\pi}{Z_o}$ is fulfilled.[5] The observed values for the critical field F_u are in good agreement with the reported phase diagram if one corrects for small shifts in T_{nem} with different samples.[3] Only with 4μ and 6μ samples are slightly higher F_u values observed. This is to be expected, since with thin samples the relative contribution of the surface energy to the total free energy of the system is more important. Fig. 2 shows the influence of a dc-field on ε. The fact that $\varepsilon(T=T_{nem})$ increases with F until at about 20 $KVcm^{-1}$ a saturation value is reached (Fig. 3) can be attributed to a field-induced alignment of the nematic phase. It may be noted that ε of pure C and M is insensitive to dc-fields up to $10^5 Vcm^{-1}$.

In addition to the increase of ε associated with the induced transitions from cholesteric to nematic, it is possible to observe changes in the dielectric constant of the undestroyed upper and lower

cholesteric phases. At a temperature where $F < F_u[Z_o(T)]$, ε increases with field. Basically this can be the result of two different processes: (1) Orientation of the helix axis under the influence of the field; (2) Reorientation of the molecules constituting the helical structure. In order to distinguish between these possibilities, several $\varepsilon(F)$-curves were taken at various temperatures with a 12.7μ sample for which $[\varepsilon(1/T)]_{F=o}$ had been determined. A typical curve is plotted in Fig. 4. If the sample is cooled down slowly from the isotropic state to the upper cholesteric, the $\varepsilon_{F=o}$ values of Fig. 1 are measured which refer to a well oriented helix. Application of a dc-field yields a completely reversible $\varepsilon(F)_{T=const}$ curve. The time constant for establishment of stable $\varepsilon(F)$ values is too short to be determined by steady state methods suggesting that a process operating on a molecular basis is involved, i.e. process 2 rather than 1. This is confirmed by the optical observation that the plane texture of the sample was unaffected by F indicating the absence of a macroscopic helical realigning process.

A different behavior is observed if the cholesteric phase is formed during a relatively rapid cooling process. In this case $\varepsilon_{F=o}$ is close to the extrapolated isotropic liquid-value indicating that the orientation of the helix is less perfect. At increasing F the $\varepsilon(F)$ curve shows an increase at lower fields and finally matches the former curve (see dashed curve in Fig. 2). Upon going back to F=o, ε approaches the value characteristic for the "ordered" cholesteric

phase. Obviously helical ordering throughout the sample took place at moderate fields. Three observations confirm this hypothesis: (1) The corresponding time constant for establishment of equilibrium was in the order of minutes suggesting involvement of a microscopic aligning process; (2) the optical reflectivity of the sample increased slightly, indicating elimination of previously existing helical perburbations;[9] (3) the plane texture is established.

With "thick" samples ($d > 25\mu$) both the orientation of the helix axis at moderate fields and the distortion of the cholesteric structure at higher fields are observed.

Discussion

To interpret the experimental data in terms of molecular arrangement, it is necessary to estimate dipole moments from ε measurements. In undiluted liquids consisting of molecules carrying a permanent dipole moment $\vec{\mu}$, the Onsager formula relates ε to the dipolar component of the dielectric polarizability. Maier and Meier[10] have extended the Onsager theory to ordered nematic phases, but their treatment requires knowledge of the anisotropy of the optical polarizabilities. Since at present no data are available for CM, the original formula applying to isotropic media will be used:[11]

$$\varepsilon_s - \varepsilon_\infty = \frac{3\varepsilon_s}{2\varepsilon_s + \varepsilon_\infty} \cdot \left(\frac{\varepsilon_s + 2}{3}\right)^2 4\pi N\alpha \qquad (1)$$

in which ε_s = static dielectric constant, ε_∞ = high frequency dielectric

constant, N = molecular density, α = dipolar part of the polarizability. This simplification does not introduce a serious error, since conclusions will be based on the relative changes of the components of the dipole moments parallel to the direction of the field rather than to absolute quantities.

α depends on the molecular arrangement. For an isotropic liquid the Langevin treatment yields $\alpha = \frac{\mu^2}{3kT}$. For partially ordered phases, it is more convenient to analyze the dipole component in the direction of the field $\vec{\mu}_{\parallel}$. Two structural possibilities must then be considered: $\vec{\mu}_{\parallel}$ is either parallel or antiparallel to $\vec{F}$, then $\alpha = \frac{\mu_{\parallel}^2}{kT}$ (bistable arrangement). When $\vec{\mu}_{\parallel}$ takes any position around an axis $\perp \vec{F}$, then $\alpha = \frac{\mu_{\parallel}^2}{2kT}$ (cylindrical arrangement). An example of the latter case would be a cholesteric structure with a helix axis $\parallel \vec{F}$ composed of molecules having a dipole moment forming an angle with the long molecular axis and capable of rotating around their long axis.

Dielectric Constant Measurements in the Absence of an Applied DC Field

From the ε values of the isotropic phase, the following ratio of the dipole moments can be calculated using eq. (1): $|\vec{\mu}_C|:|\vec{\mu}_M|:|\vec{\mu}_{CM}|$ = 1.00:1.17:1.00 (error 1%)[12], where the absolute value for μ_C is 1.66± 0.16D. ε_∞ was calculated from $\varepsilon_\infty \approx n^2 + 0.1n^2$ taking into account that usually for polar organic molecules the ionic polarizability is about 10% of the electronic polarizability.[13] The experimental value for the refractive index of isotropic CM is n = 1.500 at T = 72°.

In the cholesteric phases of C and M the long molecular

axes characterized by unit vectors $\vec{L}_C$ and $\vec{L}_M$ are assumed to be perpendicular to the helix axis ($\vec{h}$) which tends to be perpendicular to the walls. The dipole moment $\vec{\mu}_C$ of C molecules is due to the polar C-Cl bond at the 3-position of the steroid ring system. The conformation in the β-3 position is such that a very small angle (less than 10°) is formed by substituents with the average molecular plane, as can be clearly seen from Dreiding models. This means that $\vec{\mu}_C$ is approximately parallel to the long molecular axis. The pronounced drop of ε when C goes from the isotropic to the cholesteric phase means that the dipole component $\vec{\mu}_{\parallel}$ in the ac-field direction is greatly reduced. This is indicative of formation of a helical structure with a helix axis $\vec{h} \parallel \vec{F}$ where $\vec{L}_C \perp \vec{h}$. The fact that ε_C does not drop to $\varepsilon_\infty = 2.5$ can be attributed to (1) incomplete helix alignment in the bulk (for d = 25.4μ it holds $Z_{0\ C} \ll d$) and (2) a residual component of the dipole moment $\perp \vec{L}_C$.

In M molecules the dipole moment is a sum of the bond moments of the carbonyl group and the ester bond. The resulting dipole moment forms an angle of about 60° with the direction $\vec{L}_M$ of the long molecular axis. Therefore in a cholesteric phase of M with a helix axis $\vec{h} \parallel \vec{F}$ and $\vec{L}_M \perp \vec{h}$, $\vec{\mu}_{\parallel}$ should be higher than in the isotropic phase. This explains the observed increase of ε_M when passing $T_{is \rightarrow chol}$.

From the texture of thin samples of CM it follows that the helix axis is perpendicular to the electrode and therefore $\parallel \vec{F}$. If $\vec{L}_C \perp \vec{h}$ and $\vec{L}_M \perp \vec{h}$, it should be possible to calculate the dipolar part of ε_{CM} from the ε values of the cholesteric phases of pure C and

M. Fig. 1 shows the result (dashed line). The discrepancy between the calculated and the measured ε_{CM} values shows that in CM the dipole component parallel to the helix direction must be increased. This can be explained assuming that the long molecular axes $\vec{L}_C$ and $\vec{L}_M$ are no longer $\perp \vec{h}$ but rotated by an angle δ_o from a position $\perp \vec{h}$ towards the helix axis. The angle between $\vec{L}_C$ and $\vec{h}$ is therefore $\frac{\pi}{2} - \delta_o$. δ_o can be calculated from the increment $\varepsilon_{CM\ exp} - \varepsilon_{CM\ calc}$ using a graphical solution of eq. (1) with $\alpha = \frac{(\mu_C \cdot \sin\delta_o)^2}{kT}$. δ_o decreases from 25° to 20° as the temperature changes from 60° to 25°. It is often assumed that in a cholesteric phase the long molecular axes lie within the planes $\perp \vec{h}$. The present results indicate that this need not be the case.

The dip in the $\varepsilon(1/T)$ curve near $T = T_{nem}$ which is observed with thin samples must be due to a decrease of δ_o as a result of the aligning forces of the walls. The wall influence becomes stronger, i.e. the thickness of the boundary layer increases, with increasing pitch which corresponds to a decrease of the "internal" cholesteric binding energy.

Dielectric Constant Measured with an Applied DC Field

Upon application of a dc-field to a cholesteric CM structure ordered by wall effects, the field produces a torque $|\vec{M}| = |\vec{\mu}_C \times \vec{F}| = |\mu_C| \cdot F \sin(\frac{\pi}{2} - \delta_o)$ acting to cause rotation of C molecules with their long axes towards the field direction. As a result $\vec{\mu}_{\parallel}$ and hence ε must

increase. Elastic forces counteract this rotation. The field dependence of ε of a cholesteric CM mixture can therefore be used to gain information concerning field induced molecular motion.

Microscopic observation shows that the cholesteric structure is preserved until the field reaches the critical value $F_u[Z_o(T)]$ at which a phase transition occurs. Two possibilities can be considered to explain the rotation of L_C towards the field direction: (1) the dc field tends to rotate the helix by an angle $\delta(F)$ so that in the bulk $\vec{h}$ is no longer parallel to $\vec{F}_{dc}$. In this case the contribution of the C molecules to the dipolar part of the polarizability is $\alpha_{(1)} = \frac{\mu_C^2 . \sin^2[\delta_o+\delta(F)]}{2kT}$ since $|\vec{\mu}_{C\parallel}| = |\vec{\mu}_C| . \sin(\delta_o+\delta)$ is subject to a "cylindrical" arrangement; (2) the dc field tends to rotate each individual C molecule by an angle $\delta(F)$ towards the field and $\vec{h} \parallel \vec{F}$ remains valid. Again $|\vec{\mu}_{C\parallel}| = |\vec{\mu}_C| \sin[\delta_o+\delta(F)]$ but since in this case the planes $\perp \vec{h}$ are also $\perp \vec{F}$ the situation can be described by the bistable model with $\alpha_{(2)} = \frac{\mu_{C\parallel}^2}{kT}$. The gain in electrostatic energy associated with both helical or molecular rotation is given by $\Delta g_F = \frac{1}{8\pi} \cdot F^2 \frac{\partial \varepsilon_s}{\partial \delta} \cdot \Delta\delta$. Since ε_s is approximately proportional to α, one can see that $\Delta E_{(2)} \approx 2\Delta E_{(1)}$ for the same bending angle $\delta(F)$. Furthermore helix rotation by a small angle δ would introduce additional splay energy whereas molecular rotation only increases bending and torsional energy. Therefore it can be concluded that (1) would lead to energetically unstable configurations. The reverse process however, i.e. field induced alignment of a disaligned helix, is

energetically favorable and is observed (see preceding section).

Molecular rotation within the helical structure gives rise to a conical perturbation of the helix. Meyer[5] has pointed out that this conical structure involves both bending and torsional strains, and is only stable if the corresponding elastic moduli k_{33} and k_{22} satisfy the inequality $k_{22} > k_{33}$.

The angle $\delta(F)$ was inferred from the field induced dielectric increment $\varepsilon_{chol}(F) - \varepsilon_{chol}(F=0) = \Delta\varepsilon_{chol}(F)$ using a graphical solution of eq. (1). The data are plotted in Fig. 5. Several conclusions can be drawn from these results: (1) There is a well defined threshold field F_ℓ for the onset of helical perturbation. For $F < F_\ell$ no perturbation occurs. For $F > F_u$ the helical structure is destroyed. This is in corroboration of Meyer's theory. For $F_\ell < F < F_u$, $\delta \sim F^2$.

(2) According to Meyer the following relationship must hold:

$$F_\ell = F_c\left(\frac{k_{33}}{k_{22}}\right)^{1/2} \quad . \quad F_u = F_c\left(\frac{k_{22}}{k_{33}}\right)^{1/2} \quad , \text{ i.e. } \frac{F_u}{F_\ell} = \frac{k_{22}}{k_{33}} \quad \text{and}$$

$$F_c = \frac{2\pi}{Z_o} \cdot \left(\frac{k_{22}}{\Delta\chi}\right)^{1/2} \qquad (2)$$

$\Delta\chi$ being the anisotropy of the dielectric susceptibility. Knowledge of F_ℓ and F_u therefore enables us to determine the ratio k_{22}/k_{33}. Table I summarizes the results for different temperatures, i.e. different values of the pitch. The average value is 4.1 ± 0.5, independent of temperature.

Table I

Ratios of Elastic Moduli as a Function of Temperature and Helical Pitch

d[μ]	T°C	Z_o[μ][6]	$F_\ell(\frac{kv}{cm})$	$F_u(\frac{kv}{cm})$	$\frac{k_{22}}{k_{33}}$	$\varepsilon_\parallel - \varepsilon_\perp$
12.7	58.2	2.4	5.5	22.0	4.0	1.50
4.1	57.0	2.56	9.9	38.0	3.95	1.52
10.0	55.0	3.10	7.5	27.0	3.63	1.60
12.7	51.0	4.90	2.8	12.0	4.29	1.68
12.7	50.2	5.35	2.95	13.0	4.4	1.70
12.7	41.0	20.0	0.85	4.1	4.8	1.87
6.0	35.0	5.7	6.0	22.0	3.7	1.96
6.0	27.0	3.2	10.7	44.0	4.1	2.13

Taking the approximate values for the pitch from Sackmann et al's data[7] and the values herein determined for $\Delta\chi$ allows calculation of k_{22} from $k_{22} = F_\ell F_u \, \Delta\chi \cdot (\frac{Z_o}{2\pi})^2$.

The anisotropy of the dielectric susceptibility is given by:

$$\Delta\chi = \frac{\varepsilon_{\parallel} - \varepsilon_{\perp}}{4\pi}$$

where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ refer to the situation where the long molecule axis is either parallel or perpendicular to the field. Assuming that $\varepsilon_{\parallel} = \lim_{F\to\infty} \varepsilon_{nem}(F)$ and that $\varepsilon_{\perp}$ is the value calculated for the case that both C and M molecules are perpendicular to the helix (see Fig. 1), one obtains the k_{22} values plotted in Fig. 6. k_{22} is strongly temperature dependent according to $k_{22}^{-1} = k_{22_o}^{-1} \cdot \exp(-\frac{E}{kT})$ with an activation energy $E = 0.60 \pm 0.05$ eV.

(3) The functional dependence of the bending angle δ on the applied field can be qualitatively explained on the basis of an energy consideration. Since one is dealing with bending and torsional strain induced by an electric field one must consider the energy terms $\Delta g_b(\delta)$, $\Delta g_t(\delta)$ and $\Delta g_F(\delta)$. The energy density of the electric field is given by:

$$g_F = \frac{1}{8\pi} F^2[\varepsilon_{\parallel}\sin^2\delta_o + \varepsilon_{\perp}\cos^2\delta_o] \qquad (3)$$

The variation with small changes in δ, i.e. $\delta \ll \delta_o$ is given by

$$\Delta g_F(\delta) = \frac{1}{4\pi} (\varepsilon_{\parallel} - \varepsilon_{\perp})F^2 \cdot \delta \sin\delta_o \cos\delta_o$$

Using Frank's notation the bending energy is:

$$g_b = 1/2\ k_{33}\ [b_1^2 + b_2^2]$$

For a right handed cartesian coordinate system with $z \parallel \vec{h}, \vec{F}$:

$$b_1^2 + b_2^2 = \left(\frac{\partial L_z}{\partial x}\right)^2 + \left(\frac{\partial L_z}{\partial y}\right)^2$$

Assume that for F = 0 bending forces can be neglected, the rotation

of L by a small angle δ towards the z-axis causes an increase in the mechanical energy

$$\Delta g_b(\delta) = k_{33} \left[\frac{\partial L_z}{\partial x} + \frac{\partial L_z}{\partial y}\right] \left[\frac{\partial^2 L_z}{\partial x \partial \delta} + \frac{\partial^2 L_z}{\partial y \partial \delta}\right] \cdot \delta \qquad (4)$$

For small δ we can approximate $\frac{\partial L_z}{\partial x}$, $\frac{\partial L_z}{\partial y} \sim \delta$

and eq. (4) becomes

$$\Delta g_b(\delta) = \text{const}_b \cdot k_{33}\, \delta^2 \qquad (5)$$

The energy associated with torsional strain is given by

$$g_t = 1/2 \cdot k_{22} \left[t_1 + t_2 + \frac{2\pi}{Z}\right]^2$$

t denoting the twist $[t_1 + t_2 = \frac{\partial L_x}{\partial y} + \frac{\partial L_y}{\partial x}]$. Assuming that $t_1 + t_2 \sim \delta$, and that the pitch is a linear function of δ as predicted in ref. 5 one arrives at

$$\Delta g_t(\delta) = \text{const}_t \cdot k_{22}\, \delta^2 \qquad (6)$$

Minimizing the total energy variation $\Delta g(\delta) = -\Delta g_F(\delta) + \Delta g_b(\delta) + \Delta g_t(\delta)$ with respect to δ yields the functional dependence $\delta(F)$:

$$\delta(F) = \frac{1/4\pi(\varepsilon_{\parallel} - \varepsilon_{\perp}) \sin \delta_o \cos \delta_o}{2\, \text{const}_b \cdot k_{33} + 2\, \text{const}_t \cdot k_{22}} \cdot F^2 = \text{const} \cdot F^2 \qquad (7)$$

This agrees with the experimental result that for $F_\ell < F < F_u$ δ follows the relation

$$\delta/\delta_c = \left(\frac{F}{F_u}\right)^{2.0 \pm 0.1}$$

Here δ_c denotes the limiting bending angle which is compatible with the preservation of the cholesteric structure. The experiment yields $\delta_c = 4.0 \pm 0.3°$, independent of temperature except near T_{nem}.

(4) For $F > F_u$ δ becomes $>\delta_c$ and the helix is destroyed. The induced nematic phase is ordered by the dc field. From the preceding discussion it is clear that the alignment is achieved by further rotation of C molecules towards F so that $\vec{L}_C$ tends to become parallel to $\vec{F}$. Alignment of $\vec{L}_C$ will certainly also cause alignment of the M molecules with their long molecular axes parallel to the field. Since $\sphericalangle$ $(\vec{L}_M, \vec{\mu}_M)$ is about 60° this reduces the contribution of the M molecules to $\vec{\mu}_{\parallel}$. However, with C : M = 0.72 : 0.28 molar ratio, the increase in the free energy due to an alignment $\vec{L}_M \parallel \vec{F}$ is overcompensated by a decrease of the free energy due to L_C alignment. Therefore the fact that a cholesteric-nematic phase transition can be induced in CM is essentially due to the presence of C molecules; M molecules are necessary to increase the pitch of the cholesteric structure and hence decrease the elastic forces counteracting molecular rotation.

Ordering of nematic phases by electric fields has been the subject of several investigations.[16] Therefore only a rough estimate of the degree of order S of the field induced nematic phase as defined by Maier and Saupe[17] will be given here. To a first approximation, the ratio of the slopes $d\varepsilon/d(1/T)$ for the isotropic and the nematic phase of an ordering degree S can be derived from eq. (1).

$$\frac{d\varepsilon/d(1/T)_{nem}}{d\varepsilon/d(1/T)_{is}} = \frac{f(\varepsilon_{nem})}{f(\varepsilon_{is})} \cdot \frac{1/3(2S+1)\left\{N_c\mu_c^2 + \frac{N_M}{2}[\mu_M \cos(\sphericalangle \vec{\mu}_M, \vec{F})]^2\right\}}{1/3[N_c\mu_c^2 + N_M\mu_M^2]}$$

where $$f(\varepsilon) = \frac{3\varepsilon_s}{2\varepsilon_s+\varepsilon_\infty} \cdot \left(\frac{\varepsilon_s+2}{3}\right)^2$$

Inserting the experimental values gives $S \approx 0.4$. This seems to be a reasonable value for a two component system in which the directions of the molecular dipoles are different with respect to the long molecular axes. Alignment of both $\vec{L}_C$ and $\vec{L}_M \parallel F$ leads to non-vanishing field induced torque in the ordered nematic phase, since $\vec{\mu}_M$ is not parallel to $\vec{L}_M$. It is therefore likely that the statistical deviation of the direction of the long molecular axes from the field imposed preferred direction is quite large.

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12. If in CM, interaction between $\vec{\mu}_M$ and $\vec{\mu}_C$ could be neglected, one should expect $|\vec{\mu}_C| : |\vec{\mu}_M| : |\vec{\mu}_{CM}| = 1.00:1.17:1.05$. The lower value for the average dipole moment in isotropic CM therefore indicates that clusters between C and M molecules are present in which the dipole moments form a certain angle with each other.

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14. It is not possible to draw conclusions regarding the orientation of the M molecules from the present ε measurements, since rotation of $\vec{L}_M$ towards $\vec{h}$ by a small angle does not change ε significantly.

It might, however, be expected from steric considerations that in the cholesteric phase of CM $\vec{L}_C$ is parallel to $\vec{L}_M$.

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Figure Captions

Fig. 1: Dielectric Constant Versus Reciprocal Temperature. 1: cholesteryl chloride; 2: cholesteryl myristate; 3-5: cholesteryl chloride-myristate mixtures at sample thicknesses d = 10μ (curve 3); d = 25.4μ (curve 4); d = 127μ (curve 5); dashed curve: ε calculated for the case that in cholesteric CM the long molecular axes of both C and M molecules are parallel to the electrodes.

Fig. 2: Dielectric Constant of CM Versus Reciprocal Temperature at Various DC Fields. Sample thickness: 127μ.

Fig. 3: Increase of the Dielectric Constant of CM with an Applied DC Field at $T = T_{nem} = 43°$. Sample thickness: 127μ.

Fig. 4: Dielectric Constant of Cholesteric CM Versus Applied DC Field Strength at T = 51°. Sample thickness: 12.7μ. Application of field to a sample with disordered helical structure yields the lower curve. After increasing F to F_u, the upper curve is observed which does not show a hysteresis effect. The upper curve is also observed upon application of field to a sample with wall oriented helical structure.

Fig. 5: Dependence of the Bending Angle δ on the DC Field at Different Temperatures. F_ℓ and F_u are the lower and upper limit of the field range in which the conical helical structure is stable.

Fig. 6: Temperature Dependence of the Elastic Modulus for Torsional Strain in CM. Open circles refer to data taken with a 12.7μ sample; closed circles refer to a 6μ sample.

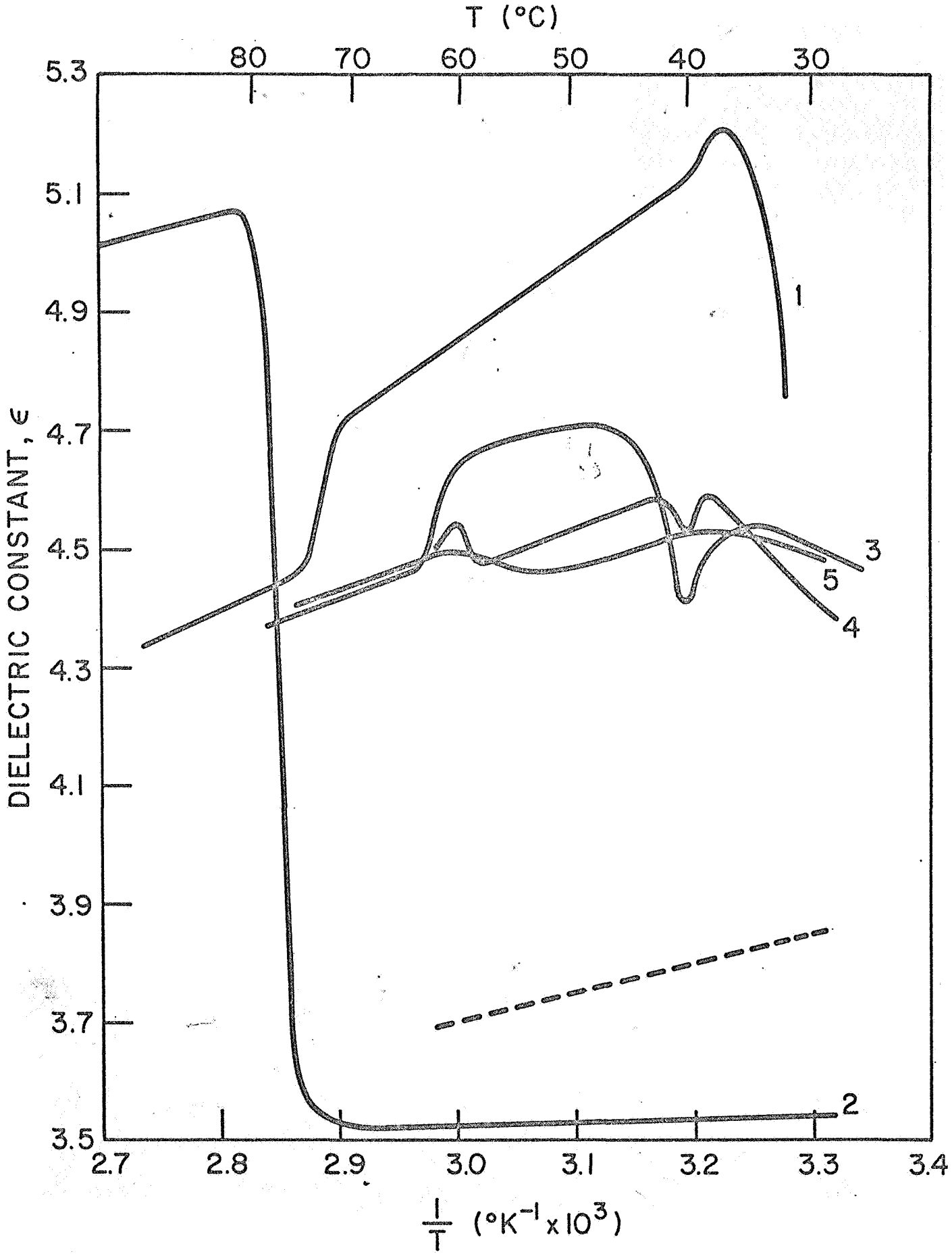


Fig. 1 Baerlocher & Labes

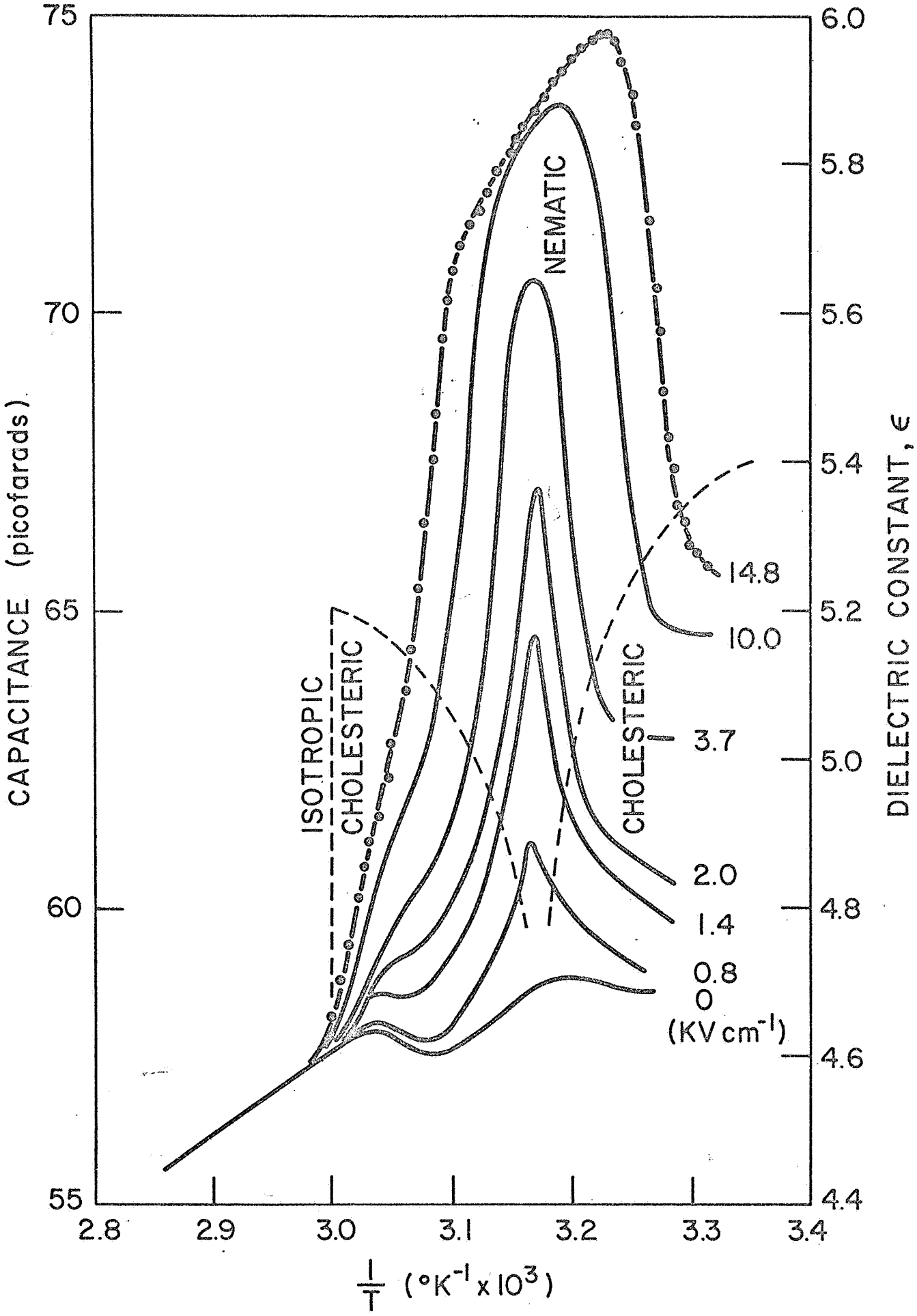


Fig. 2 Bauscher + Labes

Fig. 3 - Brinkman Valve

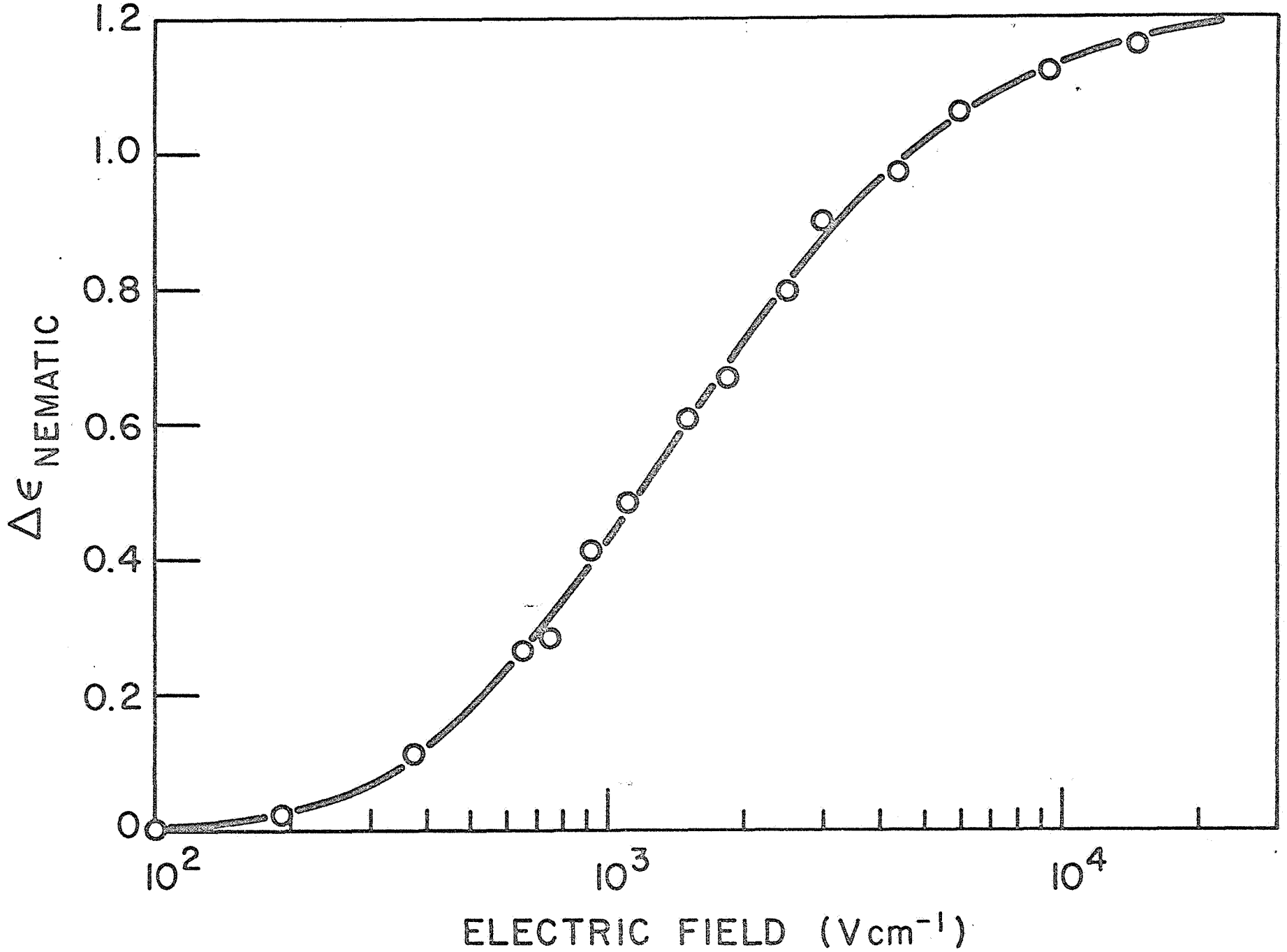
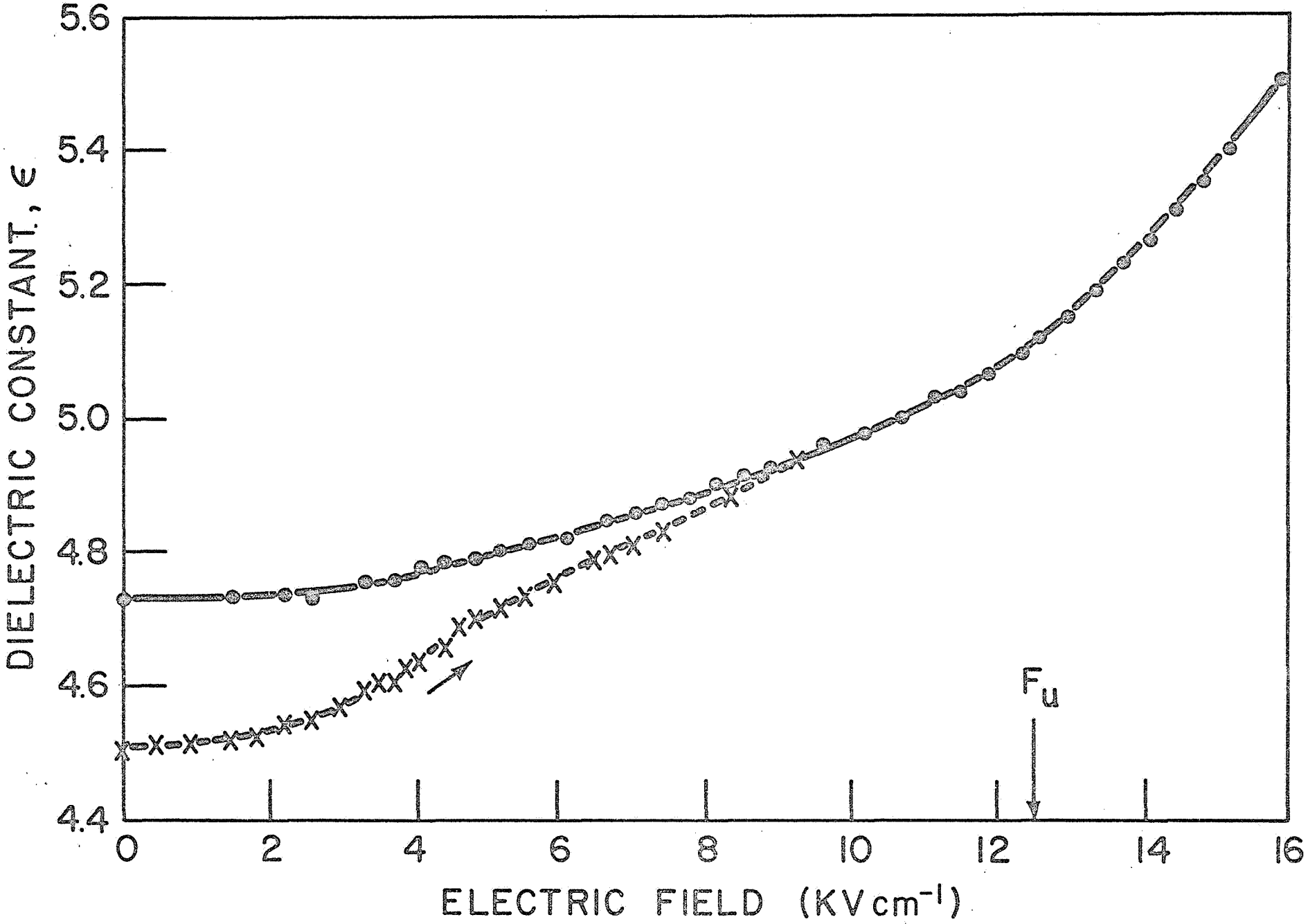


Fig. 4 - Barnaby & Lane



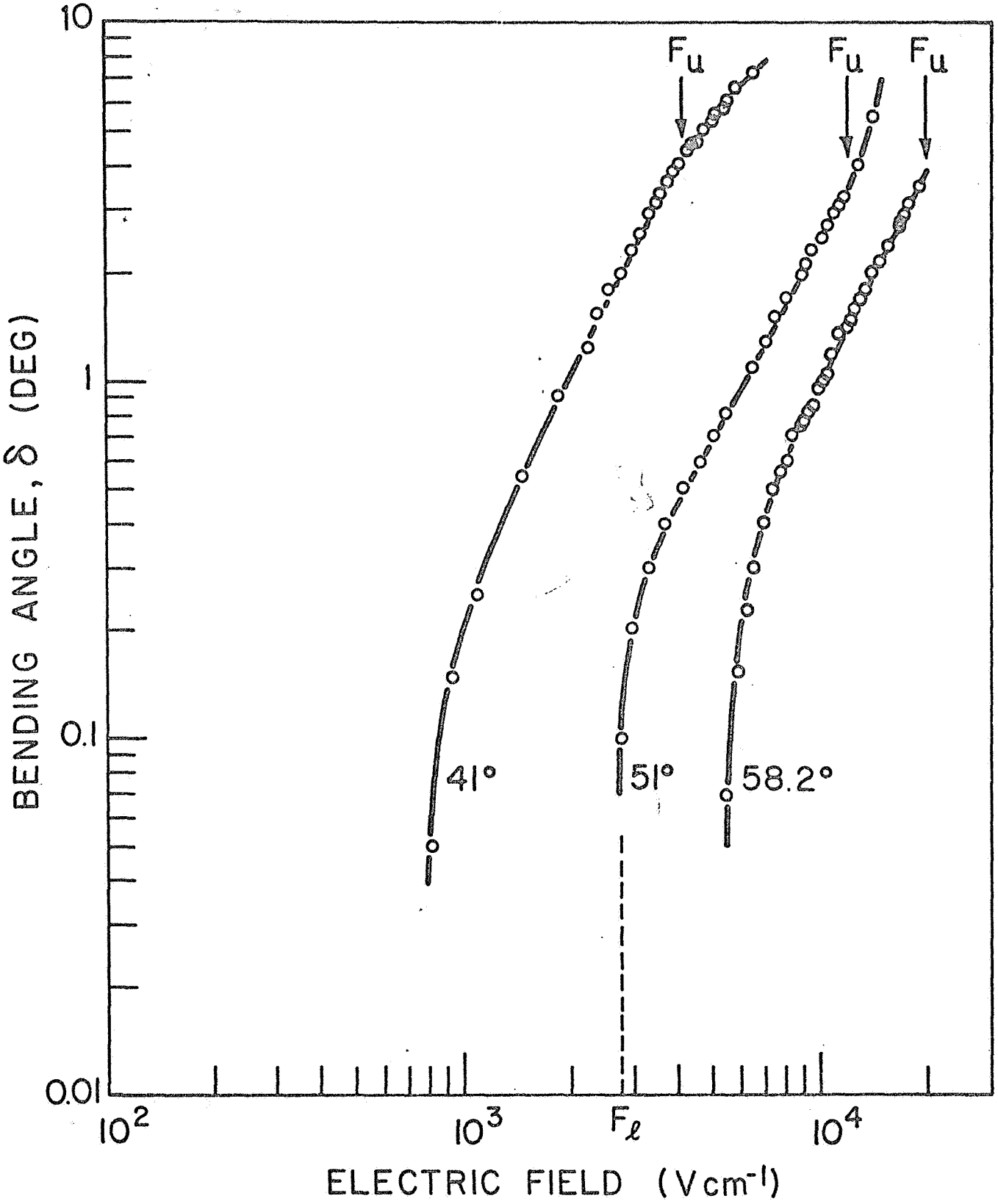


Fig. 5 - Bassler & Lahee

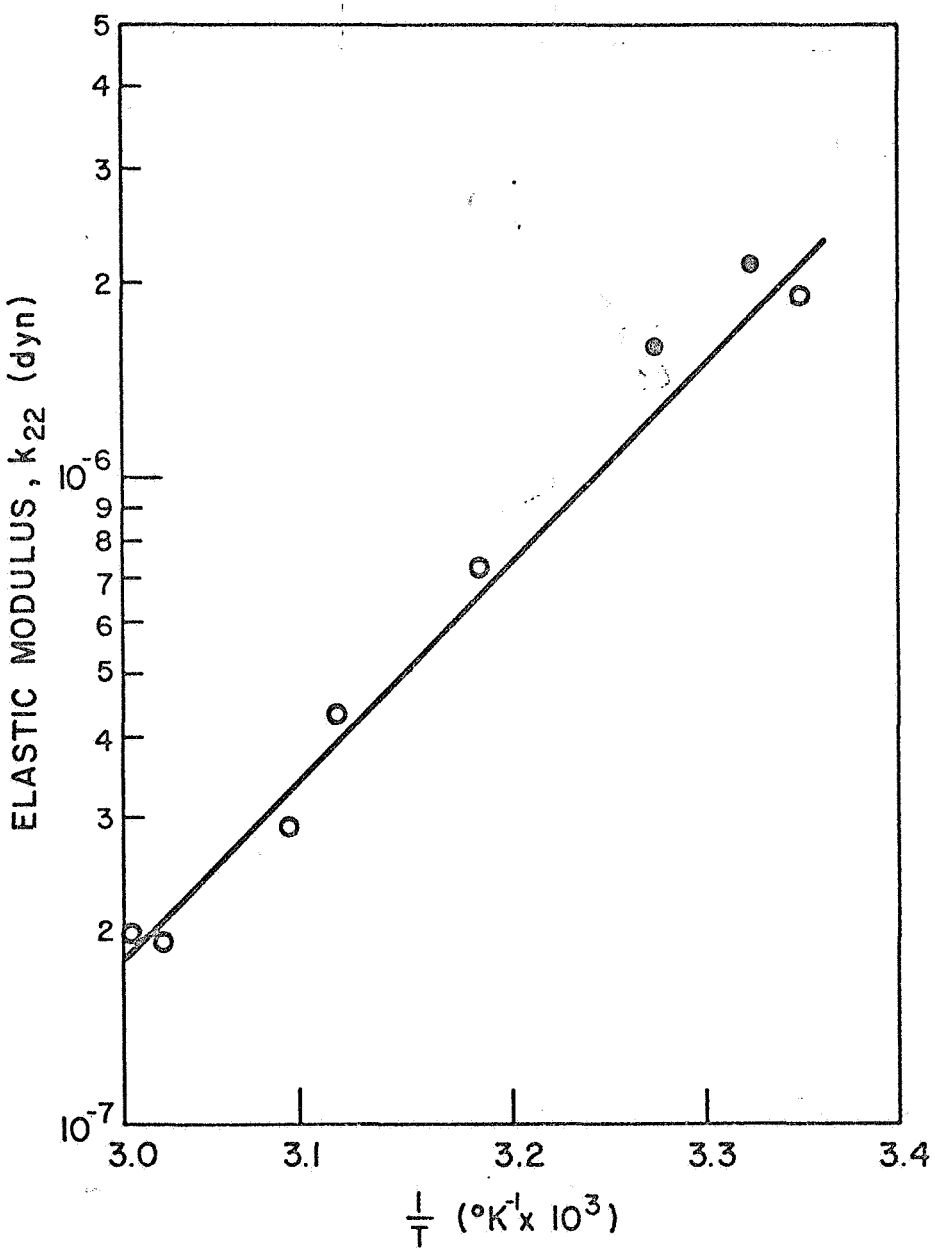


Fig 6 - Bracewell & Fabes

Electric Field Effects on the Optical Rotatory Power of a Compensated Cholesteric Liquid Crystal*

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By studying the optical rotatory power (OR) of a compensated cholesteric helical structure, it is possible to observe both thermally induced helical inversion and electric field perturbations of the helix. For a cholesteryl chloride-cholesteryl myristate 1.75:1 mixture, the OR changes sign at $T = T_{nematic} = 42°$ increasing to infinity prior to the inversion. Upon application of a dc electric field parallel to the helix axis, the OR decreases continuously and reversibly by a factor of four in the field range $0.25\ F_u < F < F_u$ where F_u denotes the critical field required to induce a nematic transition. This effect cannot be explained as a macroscopic reordering of the material, but is rather due to a decrease in pitch accompanying a conical helical perturbation. This perturbation arises from bending forces tending to align the dipole moments of cholesteryl chloride in the field direction. When a dc field is applied perpendicular to the helix axis, the pitch diverges logarithmically to infinity as F approaches the critical value for inducing a transition.

Introduction

Recently it has been established both theoretically[1,2] and experimentally[3-6] that the cholesteric structure of certain liquid crystals can be converted to nematic by application of electric or magnetic fields. An electric field-induced phase transition may occur when the molecular dipole moment is parallel to the long molecular axis, as is the case for the cholesteryl halides. An electric field tends to align the long molecular axes parallel to the field by applying a torque to those molecules which are at a certain angle with the field direction.[7] The equivalent condition for a magnetically induced cholesteric-nematic phase transition is that the anisotropy of the diamagnetic susceptibility $\chi_{\parallel} - \chi_{\perp}$ is positive, i.e. the long molecular axis again tends to align parallel to the field. Usually, this condition is only fulfilled with molecules containing aromatic rings, i.e. not with most derivatives of cholesterol.

In previous papers[4,7] we have studied electric field induced cholesteric-nematic phase transitions in a 1.75:1 weight mixture of cholesteryl chloride and cholesteryl myristate (CM). The advantage of this system is that it goes through a nematic state at a temperature $T_{nem} = 42...43°$ as Sackmann et al[8] have found. This implies that the pitch of the helix can be varied between about 2μ and ∞ by changing temperature. The experimentally determined values of the transition fields for an electric field parallel to the helix axis were in good agreement with theory.[7] Furthermore, it was found that the elastic

moduli for torsional (k_{22}) and bending strain (k_{33}) fulfill the inequality $k_{22} > k_{33}$ which gives rise to a conical perturbation of the helix before complete helix breakdown occurs. According to Meyer's theory, this perturbation should be accompanied by a tightening of the helix according to $Z_o/Z_u = k_{22}/k_{33}$ where Z_o and Z_u denote the pitch in the absence of a field and immediately before phase destruction occurs. Since it was found that $k_{22}/k_{33} \approx 4$, the pitch should decrease by the same factor. On the other hand, Z is predicted to approach infinity logarithmically as a cholesteric-nematic phase transition is induced by a field perpendicular to the helix axis. In the case of a magnetic field, this has been recently verified.[5,6]

The main purpose of the present investigation was to measure the electric field induced change in the pitch of the cholesteric structure of CM. The conventional technique of inferring Z from the distance of the Grandjean lines in a wedge-type sample could not be applied, since it is impossible to achieve homogeneous electric fields over a sufficiently large area. Therefore the optical rotatory power was measured, which is linearily related to the pitch as de Vries[9] and Cano and Chatelain[10] have shown. Furthermore, this technique promised to give some information concerning the "compensated" structure of the CM mixture. In particular the "inversion" of the helical structure at a temperature T_{nem} should manifest itself as a change in sign of the optical rotation.

Experimental

All measurements were done with a 1.75:1.00 weight mixture of cholesteryl chloride and cholesteryl myristate. The materials were obtained from Steraloids and used without further purification. The liquid crystal was placed between polished flat silica discs separated by a mylar spacer of 3, 6, 10 or 12.7μ thickness. In order to apply an electric field perpendicular to the supporting surfaces, the discs were partially covered with a conductive tin oxide layer. A field parallel to the surface could be applied between gold strips evaporated on the bottom and top disc. In this latter case, the electrode spacing was 0.2 cm. The sample was heated in an oven by a stream of temperature controlled N_2 or air.

The sample oven was inserted into a modified tube of a Rudolph polarimeter, which allowed determination of the optical rotation. It was provided with a photoelectric detection unit and a sodium lamp as a light source. The accuracy of the instrument was ±0.01°. The actual uncertaintity of the measurements, however, was usually higher and of the order ±3% but not less than 0.05°. This was mainly due to the turbidity of the liquid crystalline material. It caused scattering depolarization of the incident linear polarized light beam, thus increasing the minimum current of the photomultiplier by one to two orders of magnitude as compared with isotropic phases. The oven containing the sample could also be placed under a polarizing microscope. This allowed examination of the texture of the liquid

crystalline phase.

Results and Discussion

I. Optical Rotation in CM Without an Applied Field

A rigorous theoretical treatment of the optical rotatory power of cholesteric liquid crystals has been given by de Vries.[9] It is based on assuming that the cholesteric structure consists of a pile of optically anisotropic monomolecular layers. Subsequent layers are twisted by an angle $\psi = 360 \frac{a}{Z}$, where a is the thickness of the individual layer and Z the pitch of the resulting helical structure. The optical axis of the helical structure is identical with the helix axis $\vec{h}$, whereas the optical axis of the individual layers, each representing an uniaxial crystal, is perpendicular to the helix axis. The electric vector of a light beam propagating in the $\vec{h}$ direction of a cholesteric liquid crystal therefore encounters a pile of optically positive uniaxial crystal layers. This means that a linear polarized beam will experience refraction when passing from one layer to the next. One result is a rotation of the polarization plane. De Vries found that the specific rotation can be expressed by

$$r = \frac{360}{Z} \cdot \frac{\alpha^2}{8\lambda'^2(1-\lambda'^2)} \qquad (\text{deg cm}^{-1}) \qquad (1)$$

α is the relative birefringence of the single layers: $\alpha = \frac{\Delta n}{n}$ where n denotes the mean refractive index: $\lambda' = \lambda/\lambda_o$ where λ_o is the wavelength of maximum reflection. Using $\lambda_o = nZ$, eq(1) can be rewritten for a high pitch cholesteric structure,[11] i.e. $\lambda' << 1$:

$$r = \frac{360}{8\lambda^2} \cdot Z(\alpha n)^2 \qquad (2)$$

Eq(2) predicts that the optical rotation changes sign as the sense of the helical screw, i.e. the sign of Z, is changed. $r > 0$ refers to a right handed helix ($Z > 0$). An inversion of the helical structure, i.e. a change in the sense of structural rotation, necessarily means that the pitch goes through infinity. If inversion is temperature induced, the function $Z(T)$ should have a pole for $T = T_{inv} = T_{nem}$. Eq(2) predicts that in this case also the OR should go to infinity. Since the high rotatory power of cholesteric liquid crystals is related to the screwlike molecular arrangement rather than the specific rotation of the individual molecules, this is a somewhat surprising result and deserves some comment.

Optical rotation is observed if the two circular polarized waves of opposite sense, into which an incident linear polarized wave can be split, have different velocities. In the cholesteric structure one circular - or, more generally, elliptically - polarized component is produced by the optical anisotropy of the monomolecular layers: a linear polarized wave with an electric vector E_ℓ vibrating in a plane containing the optical axis of a uniaxial crystal will emerge elliptically polarized unless E_ℓ is parallel or perpendicular to the optical axis (C_1). The second circular component (C_2) results from the rotation of the optical axes within the pile of uniaxial layers. To a first order approximation, both waves combine to give linear polarized light after leaving the liquid crystal. This, however, is

no longer possible, if the pitch approaches infinity. Both the angular velocity and the intensity of the component arising from the presence of a screwlike structure vanishes. Therefore, the emerging wave can no longer be plane polarized. At $T = T_{inv}$ the optical axes of the layers are parallel. If OR experiments are performed with relatively large beam cross section (in the present case about 0.25 cm^2), and if no ordering electric or magnetic field is applied, the preferential direction of the nematic liquid crystal varies within the sample area. The ordering influence of the wall only ensures that the molecular axes are parallel to the supporting surfaces. Thus the electric vector of an incident linear polarized beam has equal probability of making an angle between 0 and 90° with the local optical axis. This means that, on the average, the emerging wave will be approximately circular polarized. This simple model which in principle underlies de Vries' theory can qualitatively account for several facts: (1) with increasing pitch, the angular velocity of the C_2 but not of the C_1 wave decreases leading to an increase of the optical rotation; (2) if Z increases so that Z/2 becomes larger than the sample thickness, the amplitude of the C_2 wave decreases resulting in an increase of the ellipticity of the emerging wave; (3) for $Z \to \infty$, optical rotation can no longer be defined, and the emerging light should be circularily polarized. Formally this corresponds to infinite optical rotation.

From the foregoing arguments, it is clear that the OR of a cholesteric structure is a well defined property only if the sample is ordered so that the helix axis ($\vec{h}$) is parallel to the direction of the

incident light. This requires that the sample displays a plane texture. The focal conic structure does not fulfill this condition. Since it is known that the wavelength of maximum reflection decreases with increasing angle ϕ_i between $\vec{h}$ and the direction incident light,[12] a certain distribution of ϕ_i will lead to a distribution of λ' values with an average $\lambda' > \frac{\lambda}{nZ}$. Furthermore, if $\phi_i \neq 0$ the birefringence of the layers as seen by the incident wave decreases.

In contrast to most of the one component cholesteric systems, the CM mixture forms a plane texture when the isotropic melt is slowly cooled down between supporting quartz surfaces with a spacing of the order of 10μ. The isotropic-cholesteric transition temperature is 61.3 ± 0.5°. In the temperature range 61 to 55°, the plane texture appears to be less perfect than for T < 55°, where the texture consists of large homogeneous areas showing optical activity but no birefringence. Fig. 1 shows the specific optical rotation of CM at various temperatures and spacings of 10μ and 3μ. Data are taken on a cooling cycle; however, the same results are obtained on heating. The most remarkable result is the pole of the r(T) curve at T = 42.2°. For thin samples, r is greatly reduced in the temperature range where Z/2 is comparable with the sample thickness d. This is indicative of a disturbance of the cholesteric structure by wall influences similar to that leading to the formation of the Grandjean lines in wedge type samples.[13] For $d \geq 10\mu$ r is practically independent of d. Near the temperature T_{nem} where $r(T) \to \infty$, the "extinction" current of the photomultiplier, i.e. the minimum current which can be achieved when

polarizer and analyzer are in extinction position, displays a sharp increase (see Fig. 1).

From the experimental results, it follows that the pitch of cholesteric CM always fulfills the condition nZ > 5893Å. Therefore, the change in sign of the optical rotation must be due to an inversion of the helical structure at T_{nem} = 42.2°. Upon lowering the temperature from T > T_{nem} to T < T_{nem} one goes from a right handed to a left handed structure. This must be related to the fact that CM is a compensated structure of two components which separately form helices of opposite senses - a right handed cholesteryl chloride and a left handed cholesteryl myristate helix.[14] A helix inversion in a single component system (cholesteryl-2-(2 ethoxyethoxy)ethyl-carbonate) had been reported by Durand.[15] It can, however, be shown[16] that Durand actually dealt with a mixed system due to the presence of impurities.

Calculation of the pitch Z(T) from the experimental data using eq(2) requires knowledge of the birefringence α of the layers. Since no data are available for α the six Z-values reported by Sackmann et al[8] were used to evaluate α(T) using eq(2). α decreases approximately linearily from 4.75×10^{-2} at 25° to 3.4×10^{-2} at 60°. In a system composed of two kinds of molecules with different optical anisotropy, the resulting birefringence depends on the relative molecular orientation. The present results show that in CM the relative positions of C and M molecules change with temperature giving rise to an inversion of the helical structure. Therefore, it is to be expected that α also varies with temperature.

The empirical r(T) relationship was used to calculate the complete Z(T)-curve (Fig. 2). It is symmetric with respect to an axis through $T = T_{nem}$. Some deviation in the temperature range 61-55° is probably due to the imperfect plane texture, leading to lower r values. The angle between successive layers of the cholesteric structure can be derived from Z using the relation $\psi = 360 \cdot a/Z$ assuming a layer spacing a = 5Å. The curve (Fig. 3) illustrates that the displacement of successive layers is a linear process like thermal expansion. The empirical relation is $\psi = 4.4 \times 10^{-3} (T - T_{nem})$ (deg).

Upon passing the temperature $T = T_{nem}$, the polarimeter-multiplier current with polarizing and analyzing nicols in extinction position increases by nearly two orders of magnitude indicating a decrease in the degree of polarization of the emerging light. However, the turbidity and therefore the transparency of the sample for unpolarized light remains practically unchanged. Therefore, depolarization of linearily polarized light cannot be due to an increasing number of scattering centers. It can only be explained by an increase in ellipticity. The ellipticity is defined by e = arc tan (b/a) where a and b are the major and minor axes of the ellipse which the electric vector of the light is describing. The ratio b/a must be equal to the ratio of the multiplier current at extinction and transmission setting of the analyzer. Fig. 4 shows that e has a sharp peak at $T = T_{nem}$ as one would expect from theoretical reasons. The fact that e does not reach 90°, i.e. that the emerging light is not circularily polarized,

is probably due to the fact that the wall imposes some net preferential direction on the optical axis of the nematic phase.

II. Electric Field Effects on the Optical Rotatory Power

The results presented in the preceding section can be regarded as further experimental confirmation for the validity of de Vries' theory, and in particular, for the linear relationship between optical rotation and pitch of the helix. Therefore, the optical rotation can be used as a probe for field induced changes in the helical structure.

A. Electric Field Parallel to the Helix Axis

In a preceding paper,[7] we have reported on the influence of an electric field applied parallel to the helix axis of a cholesteric CM sample which was ordered by wall effects. As long as $d > Z_o/2$ the influence of the walls on the pitch of the cholesteric structure is negligible. However, for $F_\ell < F < F_u$ where F_u denotes the threshold field for inducing a cholesteric-nematic phase transition, there appeared to be a helical distortion which was not accompanied by a change in the plane texture of the material. From an analysis of the field induced change in the low frequency dielectric constant, it was concluded that in this field range the long axis of the molecules are bent by a small angle ($\lesssim 4°$) towards the helix axis. The driving force is the torque $\vec{m} = \vec{F} \times \vec{\mu}_c$ which the field exerts on the dipole moments $\vec{\mu}_c$ of the cholesteryl chloride molecules. The result is a conical perturbation of the helical structure with the helix axis and $\vec{F}$ still being parallel. According to Meyer's theory, the relationship $F_u/F_\ell = k_{22}/k_{33}$ should

be fulfilled. F_ℓ and F_u mark the lower and upper threshold field for helical perturbation without phase destruction. They are connected with the pitch and the dielectric anisotropy $\Delta\varepsilon_{\parallel}$ by $(F_\ell F_u)^{1/2} = 2\pi/Z_o \cdot \left(\frac{4\pi k_{22}}{\Delta\varepsilon_{\parallel}}\right)^{1/2}$ (3). k_{22} and k_{33} are the elastic constants for torsional and bending strain. It was also predicted that in the field range $F_\ell < F < F_u$

$$Z(F) = \frac{F_\ell}{F} \cdot Z_o \qquad (4)$$

The relative change in pitch occurring upon field variation between F_ℓ to F_u should therefore be $Z(F_\ell)/Z(F_u) = Z_o/Z_u = k_{22}/k_{33} = 4.1 \pm 0.5$.[7] This tightening up of the helix prior to the field induced cholesteric-nematic transition is surprising and required experimental verification.

The field dependence of the optical rotation in a CM sample was measured under the condition $\vec{F} \perp \vec{h}$ at several temperatures, i.e. several Z_o-values. $Z(F)$ is inferred from $r(F)_{T=const}$ by means of eq(2) using the empirically determined value for α. The transparency of the sample could be used as a probe for the occurrence of a phase transition. The nematic phase is aligned by the field and does not show remarkable light scattering. Therefore, the polarimeter photomultiplier current at the extinction position of analyzer and polarizer decreases sharply by about a factor of 50 for $F > F_u$. This allows determination of F_u. In the $r(F)$ curve (see Fig. 5) the phase transition manifests itself by a sudden drop to zero: the aligned nematic phase is optically positive with the optical axis $\parallel \vec{F}$. In parallel light propagating $\parallel \vec{F}$, the liquid crystal must therefore behave optically

isotropic and inactive. In the field range $F_\ell < F < F_u$, however, r(F) decreases monotonically, which indicates that the pitch actually decreases. Moreover, the condition $Z_o/Z_u = F_u/F_\ell$ is fulfilled (see Table I).

Table I

Relative Field Induced Change in the Helix Pitch

$Z_o(\mu)$	F_u/F_ℓ	Z_o/Z_u
2.3	4.7	4.0
2.9	3.8	2.9
4.3	3.9	4.5
5.8	3.3	3.6
6.8	4.3	4.9
8.0	3.7	4.3
13.7	3.7	4.3
average	3.9	4.1

The average numerical value agrees very well with the value 4.1 derived from capacitance measurements. The absolute values for F_ℓ and F_u fit eq(3) if the previously determined values for k_{22} and the dielectric anisotropy $\Delta\varepsilon_\parallel$ are inserted.[7]

The proposed functional dependence for Z(F) (see eq(4)) is not confirmed. This is not surprising, since eq(4) would imply a discontinuity of Z(F) at the beginning of the helical perturbation. There is, however, no physical reason for any discontinuity and a better approximation in the theoretical treatment would probably yield a

Z(F) relation which is closer to the experimental curve. Empirically the relation

$$Z(F) = Z_o[1 - (F/F_u)^n]$$

with n = 3.0±0.2 is fulfilled in the field range $1.2F_\ell < F < 0.8\ F_u$ (see Fig. 5).

It is necessary to comment on a process which could lead to a field dependent decrease of the optical rotation without involvement of a change in the helical pitch. If the field tends to break up the cholesteric plane texture and form small cholesteric domains in which the helix axis has a tendency to align perpendicular to the field, r would decrease because the light beam is then no longer parallel to $\vec{h}$ and the wavelength of maximum reflection is $\lambda_o < nZ_o$, i.e. $\lambda' > \lambda_o/nZ_o$ (see eq.1). Using Fergason's calculation of the dependence of λ_o on the angle ϕ_i between $\vec{h}$ and the direction of the incident light[12] one finds that ϕ_i must be about 45° to account for a decrease of λ'^2 (and therefore r) by a factor of 1.5. This rough estimate shows that the "cholesteric" domains would have to be rotated by an angle >45° in order to explain a reduction of r by a factor of 4. This could be possible only if their dimensions are smaller than the sample thickness, which is about 10μ in the present case. Microscopic observation, however, shows that the plane texture of CM consists of homogeneously ordered regions of an area of the order $10^4\mu^2$ which are essentially preserved upon application of a field $F < F_u$. Furthermore, the transparency of the sample does not change significantly for $F < F_u$ indicating the absence of formation of new scattering centers. Since the ordering

effect imposed by the walls on the cholesteric structure depends on the pitch, any field induced macroscopic ordering should depend on Z_o, whereas the observed ratio of Z_o/Z_u is independent of Z_o (see Table I). Therefore the influence of the dc electric field on the cholesteric phase of CM must take place on a microscopic level, involving bending of the individual molecules towards the field direction and tightening the helix. This microscopic effect should not be confused with previous reports on the influence of electric fields on the cholesteric phase which dealt with field induced re-orientation of the helix axis.[17]

B. Electric Field Perpendicular to the Helix Axis

Application of a magnetic field perpendicular to the helix axis should result in a destruction of the cholesteric phase and formation of a nematic phase if the anisotropy of the diamagnetic susceptibility $\Delta\chi > 0$. This process has been treated theoretically by De Gennes.[1] He found that the critical magnetic field H_c for which the pitch diverges logarithmically is $H_c = \frac{\pi^2}{2Z_o} \left(\frac{k_{22}}{\Delta\chi} \right)^{1/2}$ (5). The theory has been confirmed independently by Durand et al[5] and Meyer.[6] If the dielectric anisotropy $\Delta\varepsilon_\perp$ is positive - as it is with the CM system, since the major electric dipole component is that of the halide bond which is nearly parallel to the long molecular axis of C molecules - the same relationship should hold for CM upon application of a dc electric field $\perp \vec{h}$.[18]

Therefore, the optical rotatory power r(F) of cholesteric CM was measured under the condition $\vec{F} \perp \vec{h}$. r(F) increases with increasing

F. The field dependence of the pitch calculated from eq(2) is plotted in Fig. 6. The increase with F is in good agreement with De Gennes' theory. The critical field values F_c for phase transition are listed in Table II together with the calculated $k_{22}/\Delta\varepsilon_\perp$-values.

Table II

Critical Electric Field Values for Phase Transitions

When $\vec{F} \perp \vec{h}$

T(°C)	$Z_o(\mu)$	$F_c(KVcm^{-1})$	$k_{22}/\Delta\varepsilon_\perp$ [dyn]
56	2.8	13.0	4.8×10^{-7}
47.5	8.3	5.7	8.0×10^{-7}
40.0	18.0	3.5	14.0×10^{-7}
31.3	5.1	17.0	27.0×10^{-7}

The temperature dependence of $(k_{22}/\Delta\varepsilon)^{-1}$ fits an Arrhenius plot with an activation energy of 0.6±0.05 eV. The same activation energy had been measured for the absolute values of k_{22}^{-1}.

The dielectric anisotropy $\Delta\varepsilon_\perp$ is defined as the difference between the $\varepsilon_\perp$ value perpendicular to the helix axis of the cholesteric structure and the ε_{nem} value of the nematic phase aligned parallel to F. Because of the low capacitance of the sandwich cell arrangement, it is not possible to measure $\Delta\varepsilon_\perp$ directly. Since, however, k_{22} is known, it can be inferred from the experimental value of $k_{22}/\Delta\varepsilon_\perp$ that $\Delta\varepsilon_\perp = 0.45 \pm 0.1$. There is a second way to calculate $\Delta\varepsilon_\perp$. It can be assumed that in the aligned nematic phase ε_{nem} is independent of whether F has been applied parallel or perpendicular to helix axis.

Therefore ε_{nem} can be taken from previous measurement[7] in which F was parallel to $\vec{h}$. $\varepsilon_{\perp}$ of the cholesteric phase forming a plane texture can be calculated from the individual dipole moments.[7] Application of Onsager's theory[19] yields $\varepsilon_{\perp} = 5.4 \pm 0.1$ at 45°. Since $\varepsilon_{nem} = 5.8$ at 45°, one gets $\Delta\varepsilon_{\perp} = 0.4 \pm 0.1$ at 45° in agreement with the experimental value.

With the parameters $\Delta\varepsilon_{\parallel}$, $\Delta\varepsilon_{\perp}$, k_{22} and k_{33}, the ratio of the critical fields parallel (F_u) and perpendicular (F_c) to the helix axis necessary to destroy the cholesteric structure can be determined. Combining eqs(3) and (5) yields

$$F_u/F_c = \frac{4}{\pi}\left(\frac{\Delta\varepsilon_{\perp}}{\Delta\varepsilon_{\parallel}}\right)^{1/2} \cdot (k_{22}/k_{33})^{1/2}$$

Inserting $\Delta\varepsilon_{\perp}/\Delta\varepsilon_{\parallel} = 0.25$ and $k_{22}/k_{33} = 4.1$ gives $F_u = 1.3\ F_c$. This means that rotation of the molecules within a plane perpendicular to the helix axis requires less energy than tending to align them parallel to the helix axis. In a bulk sample, where the wall influence on the local direction of the helix axis is negligible, it therefore is likely that an electric field tends to align the helix perpendicular to the field followed by helical breakdown.

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18. The critical electric field should be

$$F_c = \frac{\pi^2}{2Z_o}\left(\frac{4\pi k_{22}}{\Delta\varepsilon_\perp}\right)^{1/2}$$

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Figure Captions

Figure 1: Specific optical rotation of a 1.75:1.00 mixture of cholesteryl chloride and cholesteryl myristate. (1) 10μ sample; (2) 3μ sample - - -: photomultiplier current at extinction position of polarizer and analyzer.

Figure 2: Temperature dependence of the helix pitch of CM. The curve has been fitted to Sackmann et al's[8] data (x).

Figure 3: Temperature dependence of the angle between successive layers of the cholesteric structure of CM.

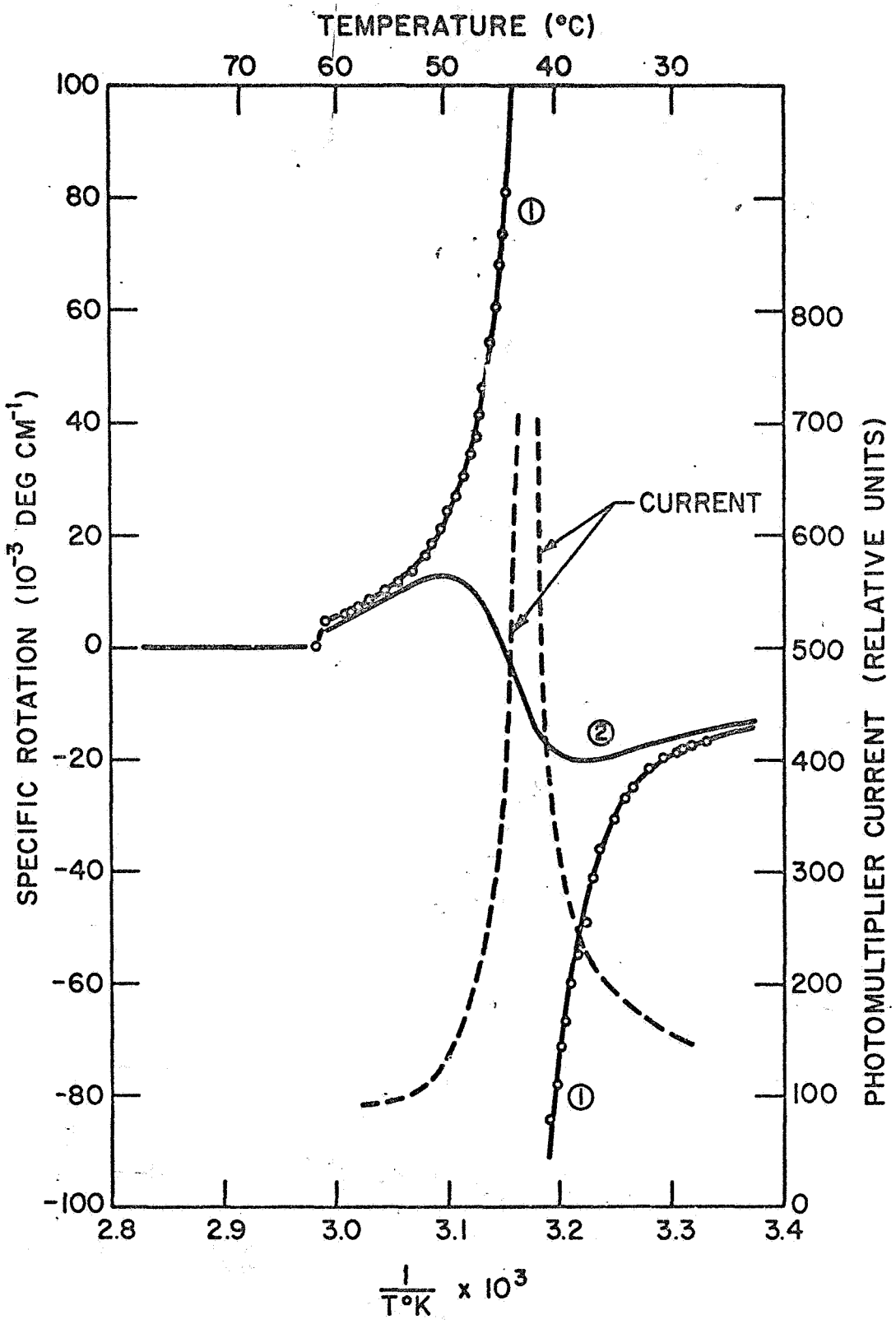
Figure 4: Temperature dependence of the ellipticity of light emerging from a cholesteric CM sample which is irradiated with plane-polarized light.

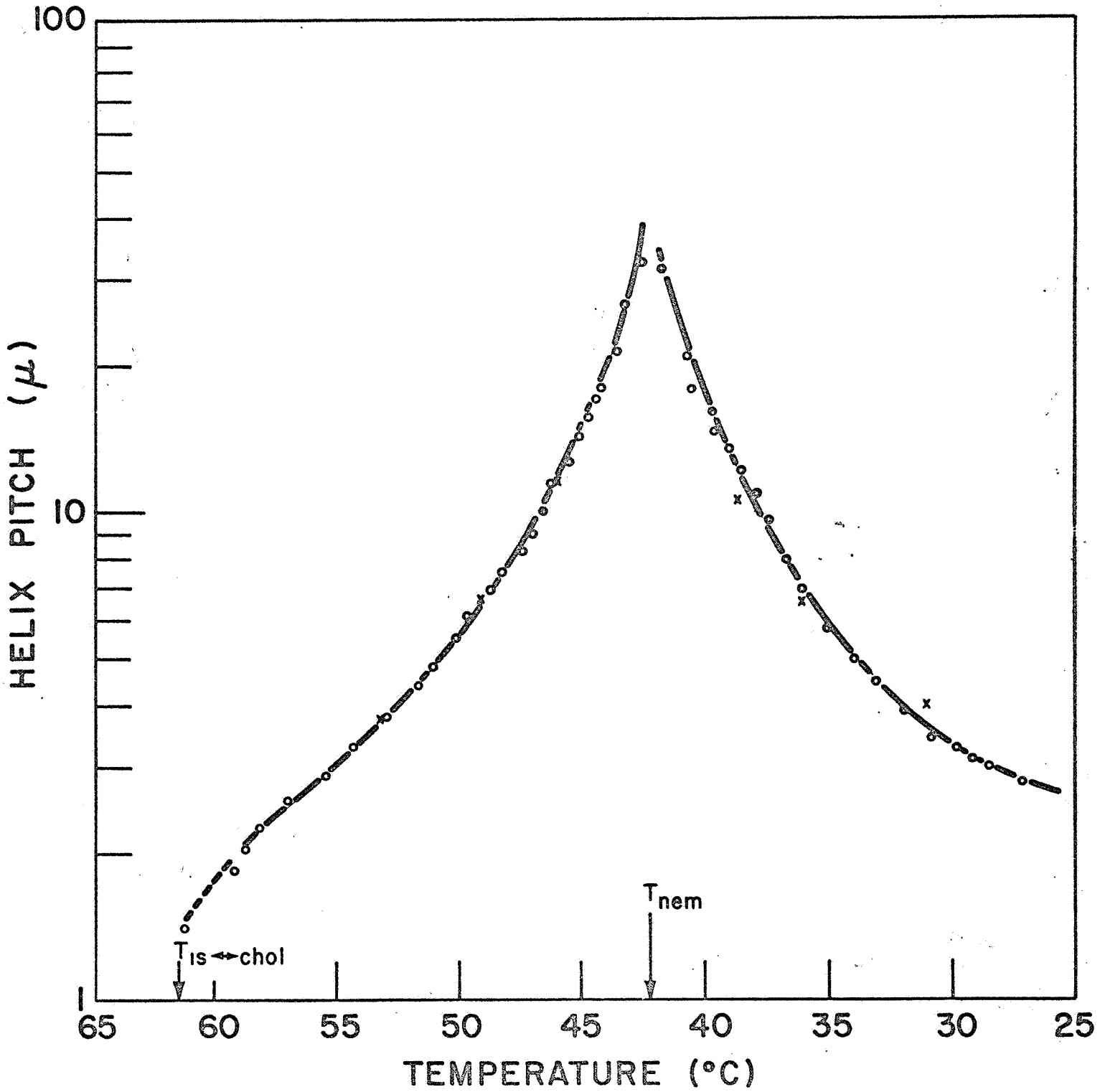
Figure 5: Dependence of the helix pitch of CM on an electric field applied parallel to the helix. Z(F) is only defined for $F < F_u$. The abrupt drop of Z(F) at $F = F_u$ is due to the sample being converted to a state showing no optical activity.

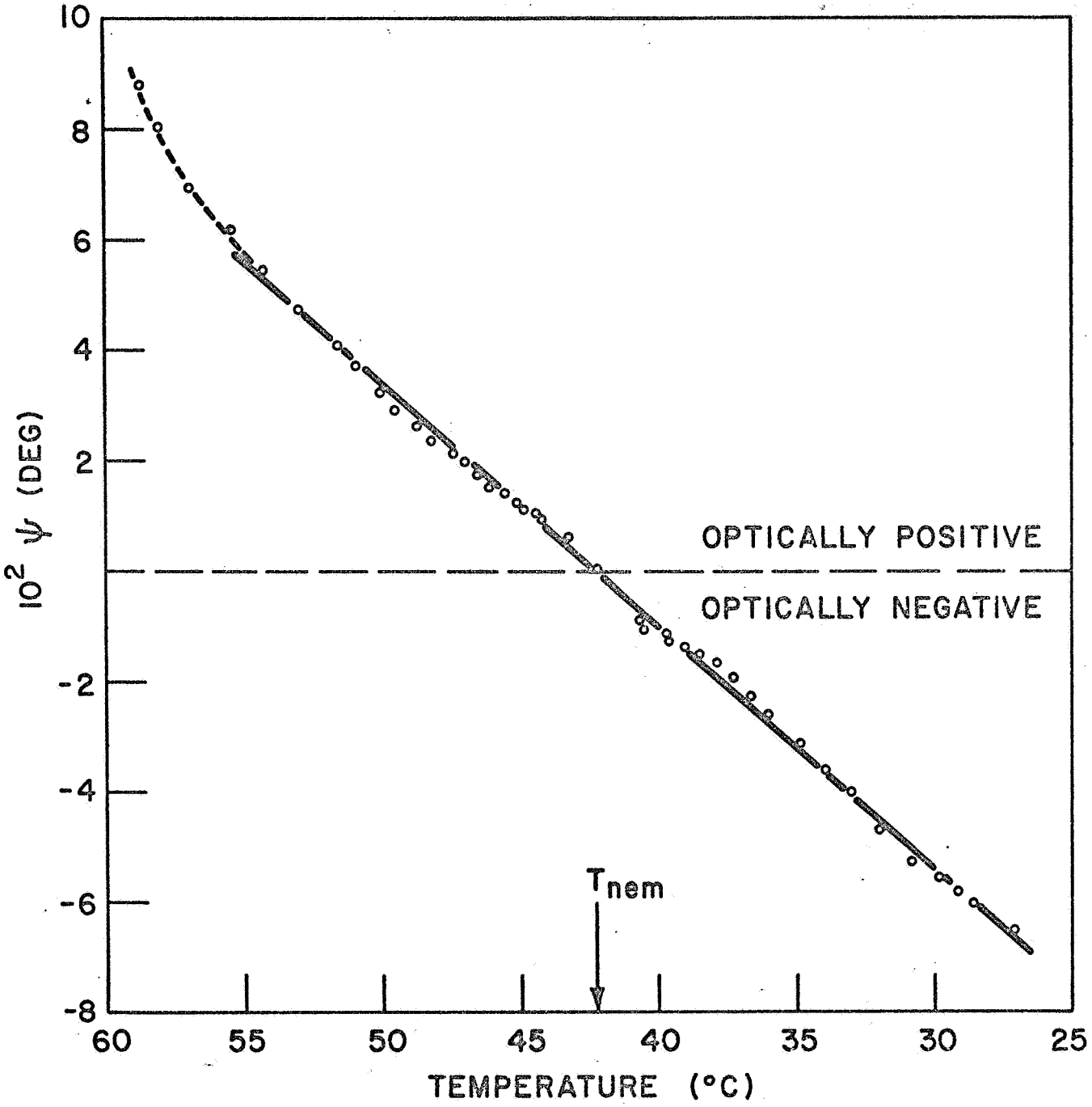
- - -: Theoretical curve[2] Z(F) for $F_\ell < F < F_u$.

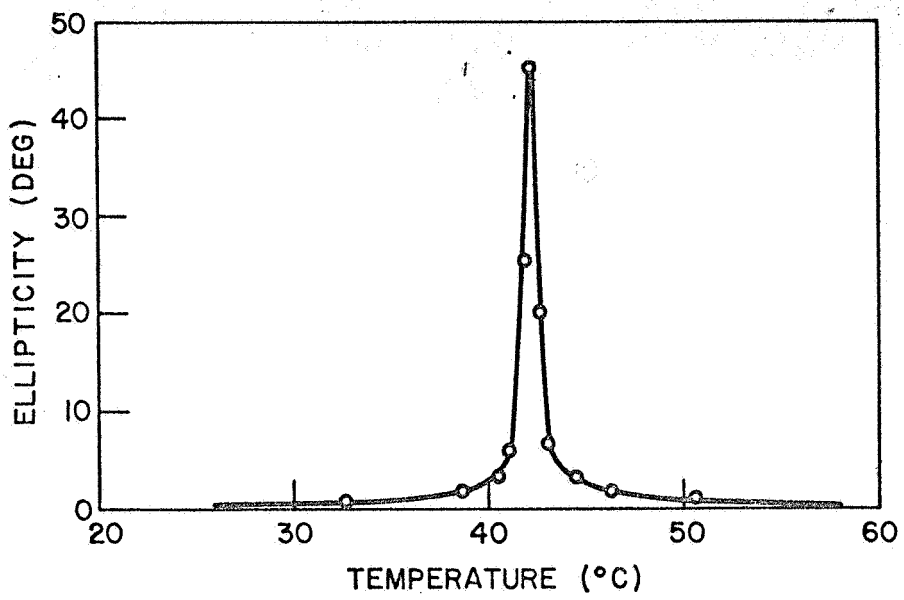
-·-·-: Field induced change in the helix pitch $[Z_o - Z(F)]$.

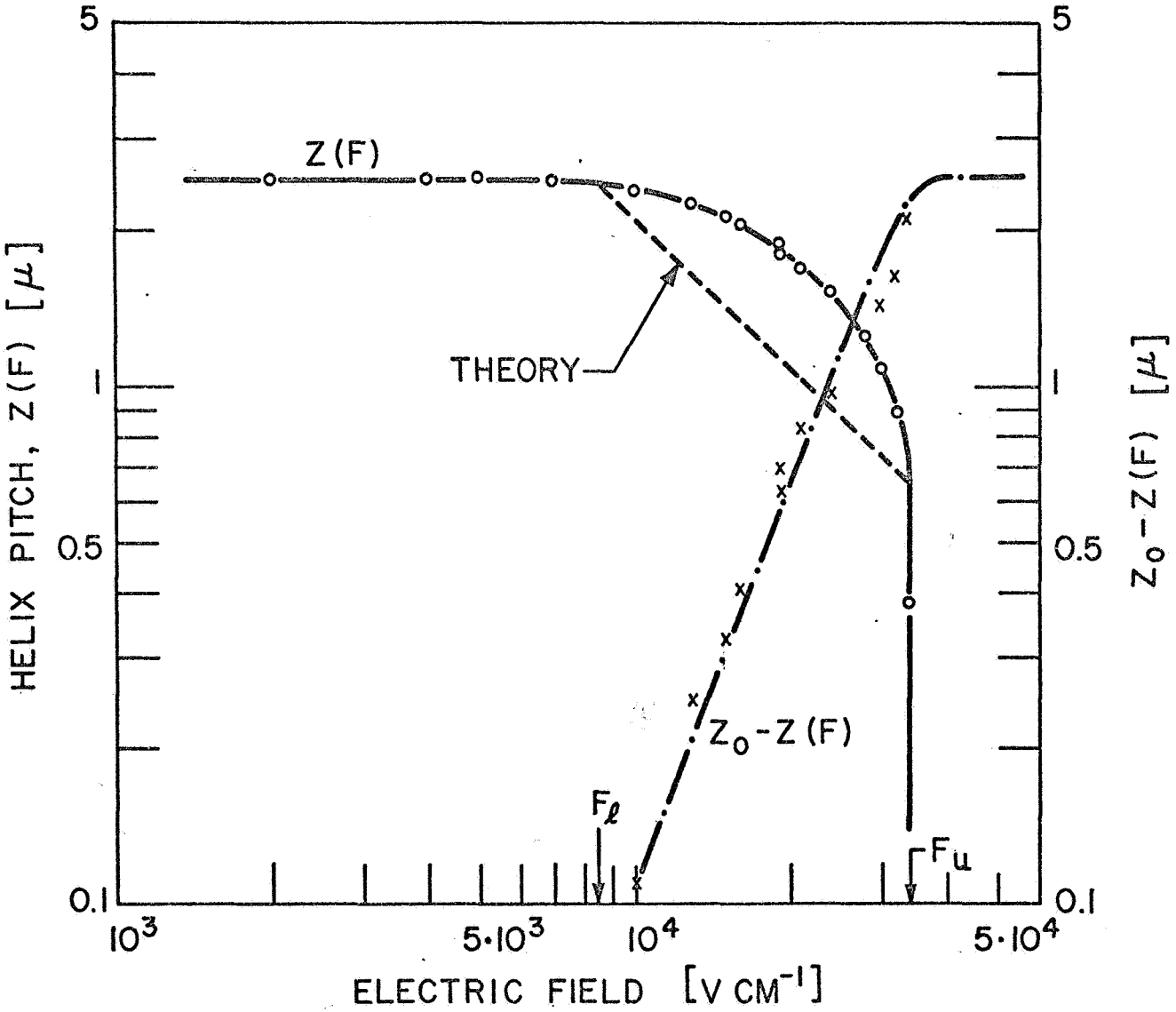
Figure 6: Helix pitch of CM versus electric field applied perpendicular to the helix axis. - - -: theoretical curve[1].

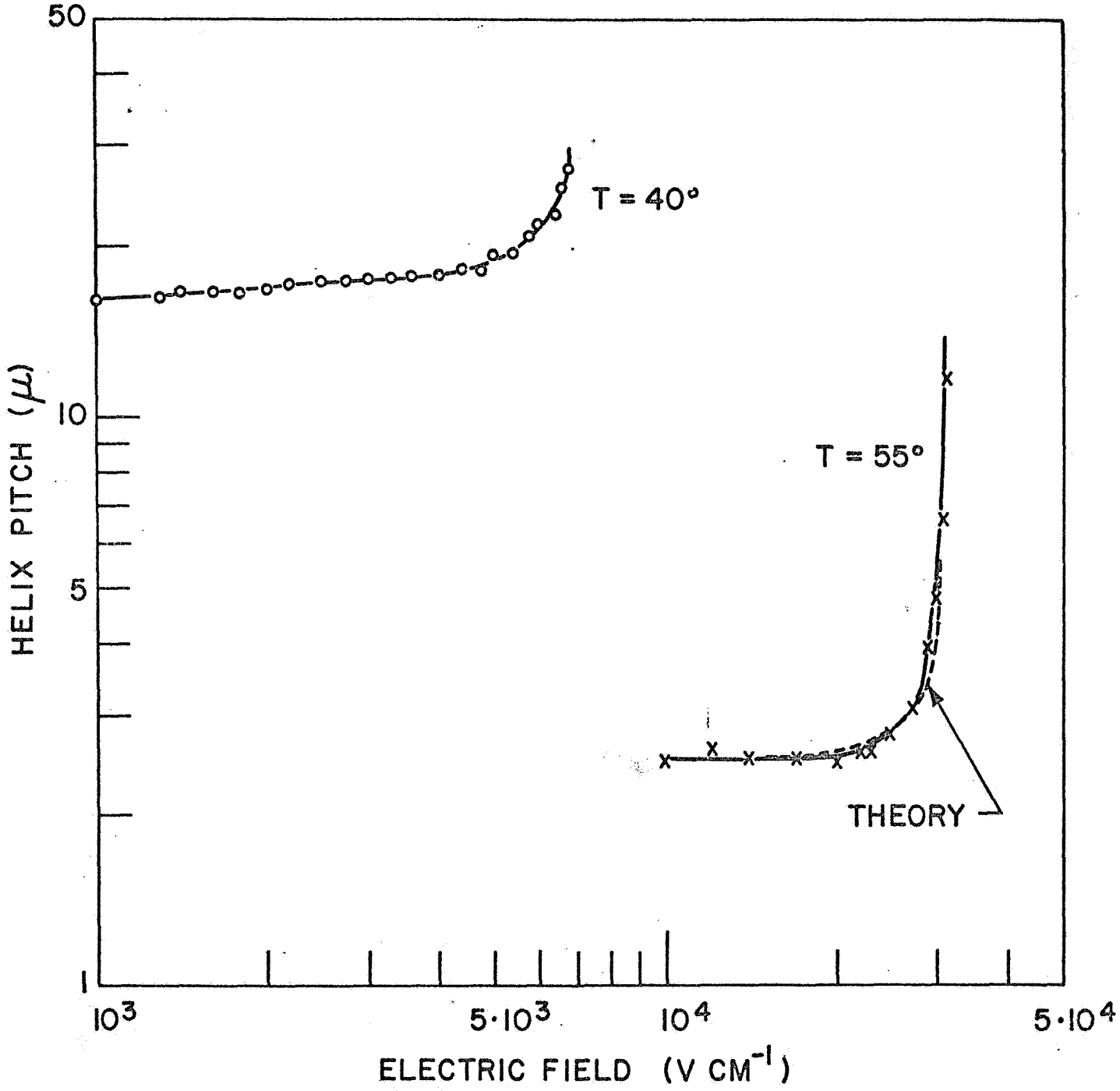

TEMPERATURE (°C)
70
60
50
40
30
100
80
60
40
20
0
-20
-40
-60
-80
-100
SPECIFIC ROTATION (10^{-3} DEG CM^{-1})
800
700
600
500
400
300
200
100
0
PHOTOMULTIPLIER CURRENT (RELATIVE UNITS)
CURRENT
①
②
①
2.8
2.9
3.0
3.1
3.2
3.3
3.4
$\frac{1}{T°K} \times 10^3$


100
10
1
HELIX PITCH (μ)
65
60
55
50
45
40
35
30
25
TEMPERATURE (°C)
T is ↔ chol
T nem


10
8
6
4
2
-2
-4
-6
-8
$10^2\ \psi$ (DEG)
OPTICALLY POSITIVE
OPTICALLY NEGATIVE
T_{nem}
60
55
50
45
40
35
30
25
TEMPERATURE (°C)


ELLIPTICITY (DEG)
50
40
30
20
10
0
20
30
40
50
60
TEMPERATURE (°C)


5
5
Z(F)
THEORY
1
1
0.5
0.5
0.1
0.1
HELIX PITCH, Z(F) [μ]
Z₀-Z(F) [μ]
Z₀-Z(F)
F_ℓ
F_u
10³
5·10³
10⁴
5·10⁴
ELECTRIC FIELD [V CM⁻¹]


50
10
5
1
HELIX PITCH (μ)
T = 40°
T = 55°
THEORY
10³
5·10³
10⁴
5·10⁴
ELECTRIC FIELD (V CM⁻¹)

Magnetic Field Effects on a Compensated Cholesteric Liquid Crystal

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By measuring changes in the dielectric constant of a 1.75:1 cholesteryl chloride-cholesteryl myristate (CM) mixture in the presence of magnetic fields H up to 10 KG, the orientation of the molecular and helical axes with respect to the field direction can be deduced, and the possibility of a dependence of the alignment process on the pitch Z of the helix is explored. When the sample thickness is much greater than Z, there is no preferred direction for the helix axis in the bulk, and applying H either $\perp$ or $\parallel$ to the sample causes the helix axis to align $\parallel$ H. This effect only occurs at $Z > 10\mu$, and only partial ordering occurs even at $T_{nematic}$. The angle δ between the long molecular axis of cholesteryl chloride and a plane $\perp$ to the helix axis is reduced by application of H. Since δ is determined by the internal mechanical energy of the cholesteric structure, the decrease in δ becomes more pronounced as Z approaches infinity. A comparison is also made of the effects of electric and magnetic fields on CM; an electric field of 500 V/cm counteracts a magnetic field of the order of 10 KG. The anisotropy of the diamagnetic susceptibility is deduced to be $\sim 10^{-9}$.

Introduction

Cholesteric structures display two types of behavior in a magnetic field which depend on the anisotropy of the diamagnetic susceptibility of the constituent molecules.[1-6] If we define two components of the magnetic susceptibility, $\chi_{\parallel}$ and $\chi_{\perp}$, parallel and perpendicular to the long molecular axes, the two cases can be described as follows:

(1) When $\chi_{\parallel} - \chi_{\perp} > 0$, then the long molecular axes tend to align parallel to an applied magnetic field producing an orientation of the helix axis perpendicular to the field. Above a critical magnetic field H_c, helical unwinding can occur. This effect has been observed by Durand et al[4] and by Meyer[5] for a cholesteric phase consisting of mixtures of p-azoxyanisole and cholesteryl esters.

(2) When $\chi_{\parallel} - \chi_{\perp} < 0$, then the long molecular axes tend to align perpendicular to the magnetic field producing an orientation of the helix axis parallel to the field, and no helix unwinding can occur because no field induced torque can act on the individual molecules in an aligned helix. Experimentally, this macroscopic reorientation of the helix axis was suggested by Sackmann et al[3] from MNR results on a study of benzene dissolved in a cholesteryl chloride-cholesteryl myristate (CM) mixture, and subsequently confirmed by observing a periodically varying refractive index in a 1.75:1 CM sample aligned in a magnetic field of 20 KG for several hours.[6]

The aim of the present investigation was to examine the possibility of a correlation between the pitch of the helical structure and the degree of orientation produced by a constant magnetic field. Since the dielectric constant ε of such a material depends on the average orientation of its permanent dipoles, monitoring changes of ε in the presence of an applied magnetic field can serve as a probe for molecular rearrangement.[7]

Experimental

1.75:1.00 CM mixtures (by weight) were prepared from compounds obtained from Steraloids, Inc., and melted between silica discs partially covered with tin oxide electrodes. The electrodes were separated by teflon or mylar spacers in the thickness range 12.7 to 254μ . The samples were mounted in an optical cell which could be heated with a controlled temperature nitrogen stream. The cell was mounted between the poles of a special 6" Varian magnet mounted on trunnions to allow rotation of the field direction with respect to the sample. Dielectric constant measurements were made with a General Radio 1608 A Impedance Bridge at a frequency of 1 Kc. The uncertainty of the capacitance values is less than 0.5%. DC electric fields were applied with a Keithley 241 power supply.

Results and Discussion

Fig. 1 presents the changes in the dielectric constant $\Delta\varepsilon$ observed with magnetic fields applied to a 127μ thick sample as a

function of temperature. Fields applied parallel to the sample plane cause an increase in the dielectric constant at temperatures near $T_{nematic} = 42\text{-}43°$. Fields applied perpendicular to the sample plane produce a decrease in the dielectric constant at the same temperatures. This effect can only be observed on samples which are not strongly oriented throughout the bulk by wall effects; a 12.7 μ thick sample shows no change in ε with 7 KG fields perpendicular to the sample plane.

The latter result is plausible since microscopic observation shows that thin samples of CM display a plane texture. Hence, the helix axis is already oriented perpendicular to the sample plane by wall effects, thus satisfying the condition of minimal free energy with a magnetic field applied perpendicular to the sample plane.

The situation is different with thick samples. Usually it is assumed that the aligning influence of the walls extends over a surface layer of a thickness comparable with the pitch Z. Therefore for a sample thickness $d \gg Z$, there is no preferred direction for the helix axis in the bulk of the sample. If $\vec{H}_{\perp}$ is applied and the helix axis $\vec{h}$ aligns parallel to $\vec{H}$, the dielectric constant should approach the value observed with thin samples. This, however, is not the case: in the temperature range where Z is low,[8] the dielectric constant is equal or slightly below the zero field curve. Furthermore, the reproducibility of both these curves is poor (±0.1 ε-units), indicating that the field does not eliminate fluctuation in the volume

orientation pattern, and that the orientation effect exerted by a field of 10 KG on a cholesteric phase with a pitch < 10μ is very small.

Near $T = T_{nem}$, in a temperature range where $Z > 20\mu$, the dielectric constant with H perpendicular to the sample plane, drops below the zero field curve[7] both for thick and thin samples (neglecting wall effects on the zero field-curve for thin samples in a temperature range where $Z > 2d$) and the ε values are quite reproducible. This indicates that the cholesteryl chloride molecules, which have a dipole moment parallel to their long molecular axis and which have been shown to give the major contribution in the dielectric constant of CM,[7] are rotated so as to make their long axes ($\vec{L}_c$) parallel to the walls, i.e. $\vec{L}_c$ tends to align perpendicular to $\vec{H}$. In the cholesteric phase of CM, $\vec{L}_c$ makes an angle δ between 25° and 20° with any plane perpendicular to the helix axis.[7] The fact that $\delta > 0$ implies that in a thin sample with $\vec{h}$ perpendicular to the walls, the C molecules can contribute to ε. The reduction of ε observed with application of $H_\perp$ must therefore correspond to a reduction of δ. Since, however, δ is determined by the internal mechanical energy of the cholesteric structure, at constant field the decrease of δ becomes more pronounced as Z approaches infinity. The maximum H- induced drop of ε at $T = T_{nem}$ can be determined from a previous measurement of the dielectric increment $\Delta\varepsilon_1$ arising from the C molecules in the cholesteric phase.[7] If full alignment of $\vec{L} \perp \vec{H}$ had been achieved, the dipole moment $\vec{\mu}_c$ can no longer contribute to ε, as is the case when ε is measured at frequencies far above the dipole

relaxation frequency. The fact that $\Delta\varepsilon_1 = 0.8$, whereas the observed decrease of ε at $H_\perp = 10$ KG is only 0.3, shows that at H = 10 KG a saturation alignment of the nematic phase of CM has not yet been achieved.

The result that magnetic fields below 10 KG are insufficient to completely orient a cholesteric structure composed of nonaromatic molecules is more clearly demonstrated by the $\varepsilon(T)$-curve in the presence of a magnetic field parallel to the sample plane. When the helix axis is rotated $\parallel$ H one has cylindrical symmetry of the C dipole component $|\vec{\mu}_{c\parallel}| = |\vec{\mu}_c| \cos\delta \approx |\mu_c|$ around the helix axis which is perpendicular to the analyzing ac field direction. The resulting dipolar polarizability would be $\alpha_c = \mu_c^2/2kT$ instead of $\alpha_{is} = \mu_c^2/3kT$ for a macroscopically disordered structure. A calculation of the resulting ε from the Onsager formula, using previously determined values for the dipole moments of C and M molecules[7] yields $\varepsilon_{max}(H_\parallel) = 5.4$. When going from the isotropic melt to a cholesteric structure with $\vec{h} \parallel \vec{H}$ and $\vec{H} \perp \vec{F}_{ac}$, ε should increase by 0.9 ε-units. Experimentally, no such increase is observed except near $T = T_{nem}$, where again the nematic phase is partially ordered, as is demonstrated by the increase of ε by ≈ 0.3.

These results suggest that at moderate magnetic fields only those aliphatic cholesteric structures can be oriented which show helical compensation. One has first to achieve saturation alignment of the nematic phase. Upon subsequent temperature variation, the helical structure will rebuild in the sense giving a condition of minimum energy.

Fig. 2 compares the effect of an electric field and a magnetic field applied to CM. Both fields are applied perpendicular to the sample; the electric field tends to align C molecules perpendicular to the walls, the magnetic field tends to align C molecules parallel to the walls. An electric field of the order of 500 V/cm thus counteracts a magnetic field of the order of 10 KG.

The relationship between magnetic field effects and electric field effects has been examined for nematic materials by several workers.[9,10] Assuming that alignment depends on the anisotropies of dielectric constant and diamagnetic susceptibility, the following energy relationship should hold:

$$E^2 \quad \Delta\varepsilon/4\pi \quad = \quad H^2 \; \Delta\chi$$

This of course is only an approximation, as Carr has discussed,[9] and has to be modified if the anisotropy of the conductivity is significant. For p-azoxyanisole, the ratio E/H is $\sim$ 1, although Rowell et al[10] report E/H $\sim$ 2 for deuterated p-azoxyanisole as estimated from NMR measurements.

Clearly in the cholesteric system where E/H $\sim$ .05, $\Delta\chi$ must be much smaller than for the aromatic nematic system. Using the value for $\Delta\varepsilon/4\pi$ = 0.13 determined in our previous work,[7,11] $\Delta\chi$ must be of the order of 10^{-9}. No direct measurements of susceptibilities or their anisotropies are available for cholesteric liquid crystals; experiments are in progress to obtain these values.

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7. H. Baessler and M. M. Labes, J. Chem. Phys. (in press).

8. For CM the dependence of Z on the temperature can be expressed by the formula $Z(T) = 4.09 \times 10^{-3}/T-T_{nem}$ yielding minimum pitch values of about 2.5μ near the cholesteric-isotropic transition temperature (61°) and room temperature.

9. For both a current study and a discussion of earlier work see E. F. Carr, Advances in Chemistry Series 63, 76 (1967).

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Figure Captions

Figure 1: Change in the Dielectric Constant as a Function of Temperature for Magnetic Fields Applied Perpendicular and Parallel to the Plane of a 127μ Thick CM Sample.

Figure 2: Change in the Dielectric Constant as a Function of Electric Field for a CM Sample with and without an Applied Magnetic Field of 10 KG Perpendicular to the Plane of a 127μ Thick CM Sample at $T_{nematic} \pm 1°$.

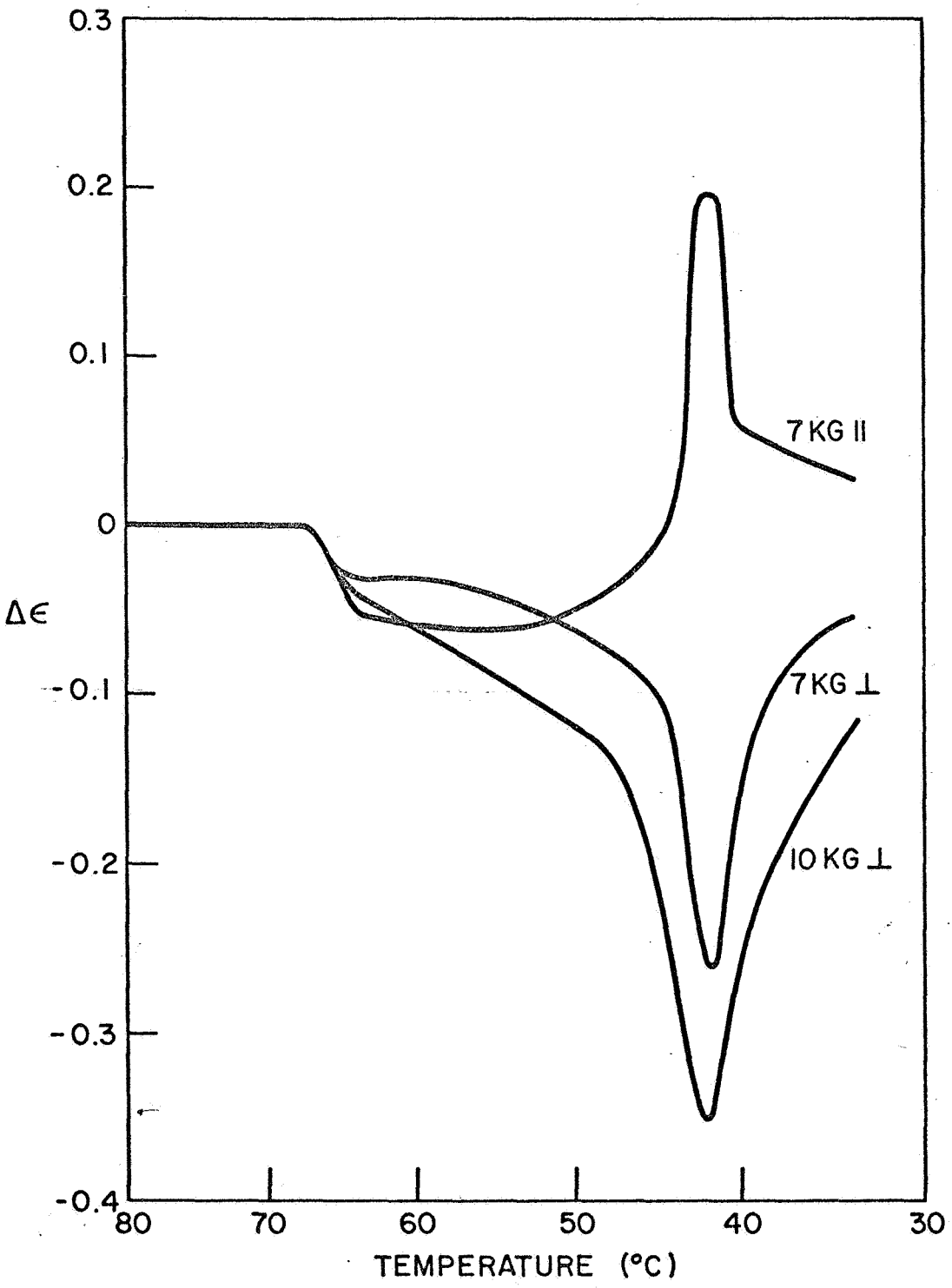

Fig. 1 Laurence Barretor. Labo

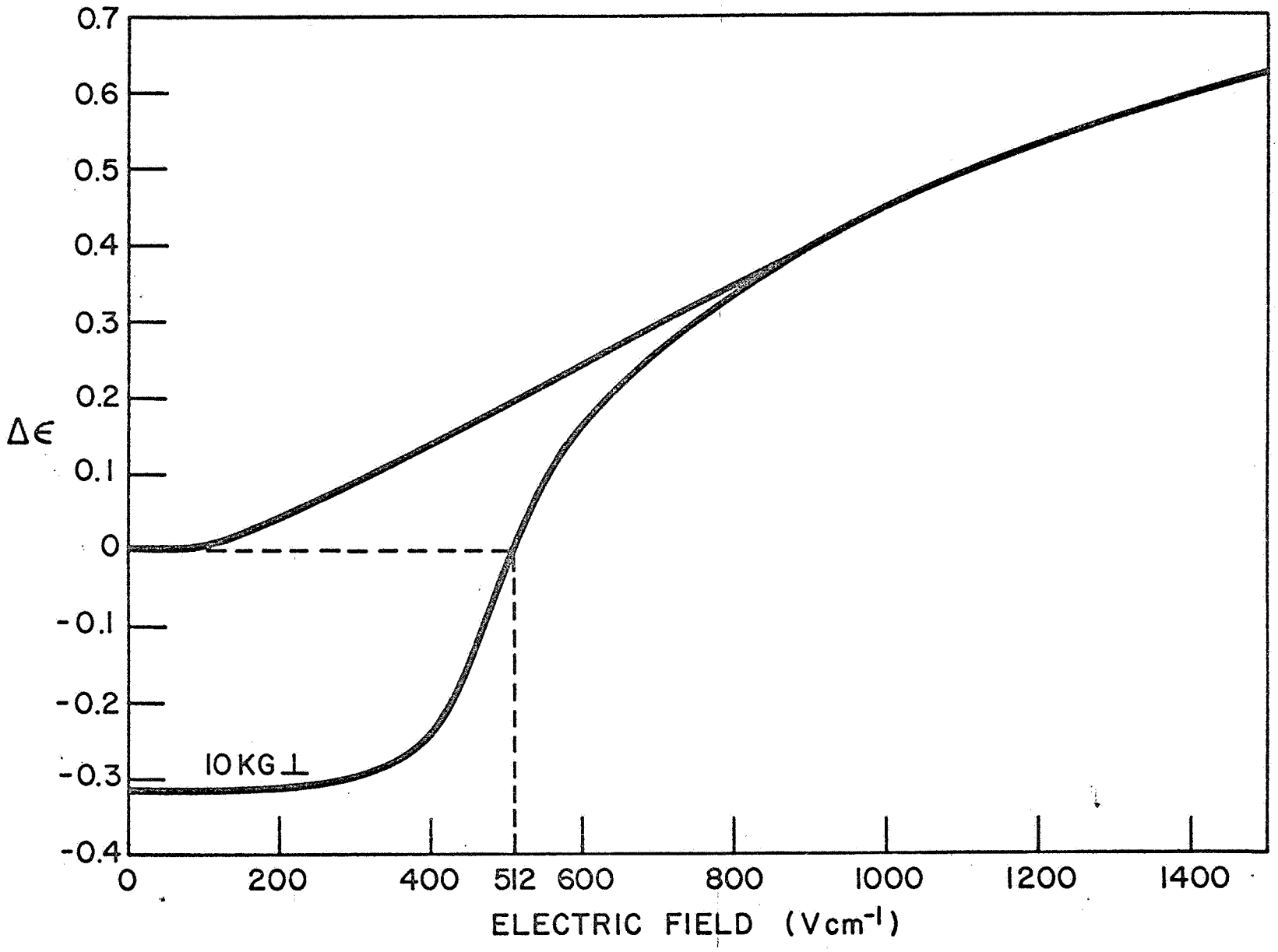

Fig. 2 Lawrence, Barnes, Kahan