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THERMAL CONDUCTIVITY OF P,P' AZOXYANISOLE

by

Mark Timothy Longley-Cook

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I hereby recommend that this dissertation prepared under my direction by Mark Timothy Longley-Cook entitled Thermal Conductivity of p,p' Azoxyanisole be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy

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Sept 27, 1971  
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## ABSTRACT

Measurements were made of the anisotropic thermal conductivity of the classic nematic liquid crystal, p,p' azoxyanisole ( $\text{CH}_3\text{OC}_6\text{H}_4\text{N}:\text{N}(\text{O})\text{C}_6\text{H}_4\text{OCH}_3$ ). This study was the first in which the longitudinal and perpendicular components of the conductivity tensor were measured independently of one another. Magnetic fields were used to align the liquid crystal. It was found that the thermal conductivity along the field direction was about 1.5 times that perpendicular to the field. The latter conductivity was  $3.53 \times 10^{-4}$  cal/sec-cm-deg at 120 °C. Both components of conductivity decreased as the temperature was increased. With the magnetic field parallel to the heat flux, the conductivity was constant below about 50 G, then rose and saturated at about 2 kG. The conductivity perpendicular to the field had a minimum at about 300 G and a maximum at about 3 kG before it finally saturated at high fields. The variation of the conductivity with magnetic field applied parallel to the heat flow was some two orders of magnitude greater than when the field was perpendicular. This fact permitted the inference that, without an applied

field, the 0.5 mm thick sample was fully aligned parallel to the copper interfaces. A zero field hysteresis was observed, the branch which the sample followed being determined by the direction of the previous alignment. The thermal conductivity measurements were performed with an apparatus specifically designed and built for this study. A parallel plate geometry was used. In anticipation of high heat leakage around the sample, procedures based on network theory were developed for analyzing the data. Relative variations in conductivity with magnetic field could be measured to 0.3%.

## CHAPTER 1

### LIQUID CRYSTALS

Some organic compounds with an elongated molecular structure have one or more ordered, fluid phases intermediate between their solid and isotropic liquid states. These anomalous phases, known as liquid crystals or mesomorphs, have a high degree of order with respect to the orientation of the molecules. The range of this order is typically a thousand times that of ordinary liquids. Detailed discussions of liquid crystals have appeared elsewhere (Brown and Shaw 1957, Gray 1962, Chistyakov 1967, Saupe 1958) so only those aspects relevant to this study will be considered here.

Of the three types of liquid crystals distinguishable under an optical microscope (Friedel 1922), only the nematic type was considered in the present investigation, in particular *p,p'* azoxyanisole (PAA). In a nematic mesophase, the molecules tend to align parallel to one another. The local direction of orientation, as characterized by the preferred direction of the long molecular axis, is constant over volumes containing some  $10^8$  molecules (Gray 1962, p. 78) if

there are no external aligning influences. The size of these aligned regions varies considerably with their method of measurement.

The orientation of the preferred axis is influenced by surfaces separating the liquid crystal and any solid material and also by applied fields. The orientation within the boundary layer, or pellicle, is determined by the nature and preparation of the surface.

Chatelain (1943) has shown that if a glass surface is thoroughly cleaned, the molecules in the pellicle align perpendicular to the surface. He has also shown that if the surface is rubbed in a particular direction the molecules align parallel to that direction.

Zwetkoff (1942) introduced a bulk order parameter

$$\varphi(T) = 1 - \frac{3}{2} \int_0^{\pi/2} f(\theta, T) 2\pi \sin^3 \theta \, d\theta$$

to describe the degree of order with respect to a preferred direction. Here  $T$  is the temperature and

$$f(\theta, T) 2\pi \sin \theta$$

is the probability density for local alignment at an angle  $\theta$  to the above preferred direction. A value of 1 for  $\varphi(T)$  corresponds to a perfectly aligned material (for example, crystalline solid PAA) and a value of 0 to an isotropic liquid. Chatelain (1955) obtained

orientation and ordering information from light scattering studies. For nematic PAA he observed a range for  $\phi(T)$  of 0.577 at 117°C to 0.445 at 132°C. Further studies of the order parameter are referenced in Saupe (1968). The direction of alignment at metal-mesomorph interphases is not as well known. Carr (1962) in dielectric constant studies on PAA and the present experiment give strong evidence for parallel alignment at metal surfaces.

It is well known that the preferred orientational directions can be aligned by electromagnetic fields. The rigidity of the intermolecular orientation allows a comparatively small magnetic field (1 kG) to align the liquid crystal. Moll and Ornstein (1917) have observed changes in the transparency of PAA under the application of a magnetic field. This and other optical studies (Naggiar 1939, Friedel 1922) indicate that the molecules throughout a sample of PAA are preferentially aligned parallel to the magnetic field. This has been confirmed more recently by others, in particular by Vainshtein, Chistyakov, Kosterin and Chaikovskii (1969) using x-rays. The last study also investigated alignment by electric fields.

Application of a shear force causes alignment parallel to the direction of shear as evidenced by

experiments of Marinin and Zwetkoff (1939) and others. There is also evidence for alignment perpendicular to a temperature gradient. This last phenomenon will be discussed in detail later.

Upon alignment of a nematic those macroscopic properties that can be nonscalar become anisotropic. Dielectric constants, refractive indices, magnetic susceptibilities, elastic constants and others are anisotropic when an alignment mechanism is applied. Transport properties such as electrical conductivity, viscosity, diffusion and thermal conductivity also show anisotropies.

Various observers have noted a temperature change when a magnetic field was applied to a liquid crystal, usually PAA (Moll and Ornstein 1919, Miesowicz and Jezewski 1935, Yun and Fredrickson 1970a). An explanation for this anomalous heat generation has been proposed (Longley-Cook and Kessler 1971) based on changes in the thermal conductance between the oven used to heat the liquid crystal and the temperature sensing device immersed in the liquid crystal. The probe lead, acting as a heat path to the laboratory, would cause a temperature gradient to exist between the oven and the probe. It was hypothesized that, as the anisotropic sample was aligned by a magnetic field, the conductance

of the mesomorph changed sufficiently to account for the observed temperature change.

Previous measurements of thermal conductivity, to be discussed presently, were inconsistent and were not sufficiently accurate to confirm this explanation. No direct measurements had been made of the conductivity along the long molecular direction. In addition all means of alignment had been either not variable by the experimenter (wall alignment) or subject to coupling with other fluxes (shear and electric field alignment). It was therefore desirable to accurately measure the components of the thermal conductivity tensor for PAA using a magnetic field for alignment.

## CHAPTER 2

### PREVIOUS CONDUCTIVITY MEASUREMENTS

Several investigators have made measurements of the thermal conductivity of liquid crystals. Their results for PAA are summarized in Table 1. In the discussion below,  $k_{\parallel}$  is the conductivity in the direction of the long molecular axis;  $k_{\perp}$ , perpendicular to the long molecular axis;  $k_0$ , of the nonaligned liquid crystal; and  $k_i$ , of the isotropic liquid. Throughout the paper, it will be assumed the two directions perpendicular to the long molecular axis are identical. All conductivity values in this paper have units of  $10^{-4}$  cal/sec-cm-deg. Unless specifically noted otherwise, all studies were performed on PAA.

The first explicit reference to the thermal conductivity of liquid crystals was made by Bereskin and Stewart (1941). In an incompletely reported experiment, they report that

if the molecules in liquid crystalline [PAA] are oriented by a magnetic field [of unspecified direction], the coefficient of heat conduction is thereby increased by (roughly) twenty-five per cent [sic].... The flow of heat [by orienting the molecules perpendicular to the temperature gradient] decreases the coefficient of heat conduction.

Table 1. Thermal conductivities reported for PAA

Mean Temperature (°C)	Thermal Conductivity (10 <sup>-4</sup> cal/sec-cm-deg)					Source
	k <sub>  </sub>	k <sub>o</sub>	k <sub>⊥</sub>	Orien- tation not stated	k <sub>i</sub>	
-	1.25k <sub>o</sub>					Bereskin and Stewart 1941; Stewart, Holland and Reynolds 1940
116.0				3.46		McCoy and Kowalczyk 1960
125.0				3.28		"
131.0				3.20		"
139.0					3.76	"
151.0					3.71	"
124.9		3.23		3.60 <sup>a</sup>		Picot 1966
145.0				3.84 <sup>a</sup>	3.39	"
127.2				3.48		"
125.0		3.2				Picot and Fredrickson 1968
123.	2.82 <sup>c,d</sup>	3.22 <sup>d</sup>	3.41 <sup>b,d</sup>			Fisher and Fredrickson 1969
126.		3.14	4.94 <sup>e</sup>			Rajan and Picot 1971
126.		3.24 <sup>d</sup>	3.60 <sup>d,e</sup>			"

<sup>a</sup>in the vicinity of the wire<sup>d</sup>purified sample<sup>b</sup>shear alignment<sup>e</sup>wall alignment<sup>c</sup>computed from  $k_o = (2k_{\perp} + k_{||})/3$

From the above quotation it can be inferred that  $k_{\parallel}$  is about 1.25  $k_0$ .

McCoy and Kowalczyk (1960), using a hot wire technique (Tsederberg 1965, pp. 40-50), investigated the thermal conductivity of three mesomorphic compounds in both the liquid crystalline and isotropic liquid states. The materials studied were p-hexyloxybenzoic acid, p-heptyloxybenzoic acid and PAA. No alignment process is mentioned.

Picot (1966) made a detailed study of the heat conductivity of several liquids using heat pulses and the hot wire technique. The conductivity of nonmesomorphic compounds were found to be influenced by the presence of the metal-liquid interface  $1\mu$  away. Similar changes in conductivity in the vicinity of the wire were observed for PAA. When the heat input, and hence the temperature gradient, was doubled, no change in the conductivity was observed, indicating that heat flow alignment did not take place. Measurements with an electric field applied parallel to the heat flow were inconclusive. A later paper (Picot and Fredrickson 1968) reviews some of the results.

Fisher (1969) and Fisher and Fredrickson (1969) have investigated the conductivity of purified PAA using the concentric cylinder technique (Tsederberg

1965, pp. 34-40). Wall alignment was believed not to contribute to the conductivity of the 0.5 mm thick sample. Rotation of the outer cylinder increased the apparent conductivity of the sample. Above a shear rate of  $100 \text{ sec}^{-1}$ , the conductivity appeared to saturate at 3.41. This value was ascribed to  $k_{\perp}$ . Using a swarm model developed by Sullivan (1966), Fisher (1969, pp. 39,49) derived the relationship

$$k_o = \frac{2 k_{\perp} + k_{\parallel}}{3}$$

Thus, a determination of  $k_{\parallel}$  was claimed from the conductivity measurements under sheared and unsheared conditions. The thermal conductivity was found to increase, but not saturate, when an electric field was applied parallel to the direction of heat flow.

Patharkar, Rajan and Picot (1971) have measured the thermal conductivity of PAA using a parallel plate geometry (Tsederberg 1965, pp. 24-34) with a variable sample thickness. Both commercial and purified grades were considered. The conductivity was observed to decrease with increased temperature gradient, in agreement with Bereskin and Stewart (1941). In another paper, Rajan and Picot (1971) studied the conductivity extrapolated to zero temperature gradient as a function

of sample thickness. An alternative explanation is discussed later in this paper.

Patharkar (1971) found similar results in the thermal conductivity of another nematic, anisylidene p-amino phenyl acetate. Guyon, Pieranski and Brochard (1971) have studied the room temperature liquid crystal n-(p-methoxybenzylidene)-p-butylaniline (MBBA). They obtained (Guyon 1971)

$$.69 < \frac{k_{\perp}}{k_{\parallel}} < .70$$

at 29°C and a value of 15 for  $k_{\perp}$ . This latter value is exceptionally high for an organic liquid and may be in error (Guyon 1971). Lastly Yun (1970) has found the thermal conductivity perpendicular to a magnetic field to be smaller than the no-field value. The material Yun studied was decycloxybenzoic acid (DBA), a nematic that was claimed to exhibit anomalous heat generation similar to PAA (Yun and Fredrickson 1970a).

## CHAPTER 3

### THE EXPERIMENT

It was necessary that the direction of alignment be easily changed and that the alignment mechanism be passive so it would not contribute to heat transfer through convection or flux coupling. It was desirable that each conductivity tensor component be measured independently of the others. A rotatable magnet and a parallel plate geometry were therefore indicated.

The gap of the available magnet restricted the size of the conductivity cell to such an extent that guard heaters could not be used to control the heat flow. In anticipation of the resultant high heat leakage around the sample, procedures based on network theory were developed for optimizing design dimensions and analysis of the data. The apparatus is discussed below.

#### The Experimental Apparatus

The entire conductivity apparatus (Figure 1) was in a silvered-evacuated vessel to improve the temperature stability and to reduce non-linearities in the heat transfer arising from reradiation and

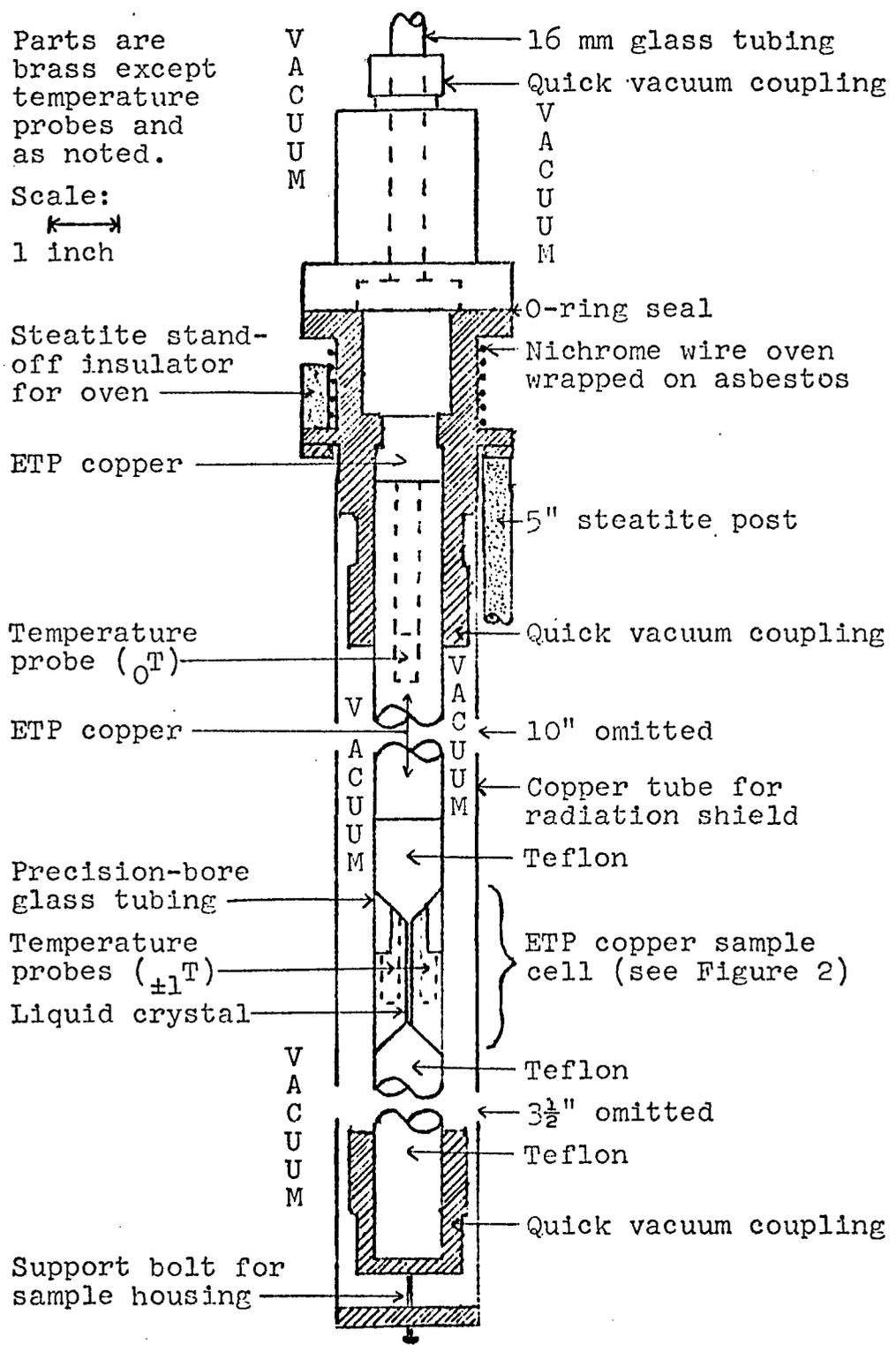


Figure 1. Thermal conductivity apparatus

convection. The pressure was less than  $10^{-4}$  torr. The only material connections across the vacuum were the following: a six-inch piece of 16 mm glass tubing which contained the 10 mm glass filling tube, temperature probe leads, and heating wires for the sample cell; three five-inch-by-one-half-inch-diameter steatite posts for support; and heater wires for a shielded, nichrome-wire oven. This oven, which was wrapped on asbestos and was used to heat the apparatus to the desired ambient temperature, was heated by a highly stable Kepco power supply, model JQE 25-4M-T. Long term temperature fluctuations were  $0.1^{\circ}\text{C}$ . Temperature differences across the sample were stable to  $3 \times 10^{-4}^{\circ}\text{C}$  over extended periods. To reduce the influence of drafts, the outside of the vessel was wrapped in asbestos paper and the equipment was enclosed in a cloth curtain.

A silvered copper tube served as both a radiation shield for the sample cell and a physical support for the sample chamber housing. Silvered, precision-bore glass tubing was used to isolate the sample from the vacuum. Machined copper parts were made of electrolytic tough-pitch (ETP) copper because of its high thermal conductivity (Parker 1967, p. 93). Within the upper 15 inches of the precision-bore glass was an ETP

copper rod that had been split down its center. The coaxial probe leads for the two thermometers in the sample cell were positioned in slots in this flat surface so they were surrounded by copper. Room was also allowed for the filling tube and wires for the heaters in the sample cell. In addition, a temperature probe ( $_0T$ ) was located three inches from the top of the split copper rod.

The ETP sample cell (Figure 2) occupied the bottom portion of the precision tubing. Teflon separated it from other metal parts of the apparatus. Each side (designated  $-1$  and  $+1$ ) of the cell contained a temperature probe ( $_{-1}T$  and  $_{+1}T$ ) and six 10-ohm resistors (International Resistance Company, "Termacoat") in series for creating a temperature gradient. These resistors were accurate to 1% and had a temperature coefficient of less than 25 ppm/ $^{\circ}C$ . In addition, they could be operated at half their maximum power at 240 $^{\circ}C$ .

Two methods of alignment were operative. Alignment of the preferred axis was achieved by a magnetic field. In the course of the experiment it became apparent that the copper walls produced alignment parallel to themselves throughout the sample in the absence of a magnetic field. No attempt was made to prepare the copper surfaces other than cleaning with acetone. The

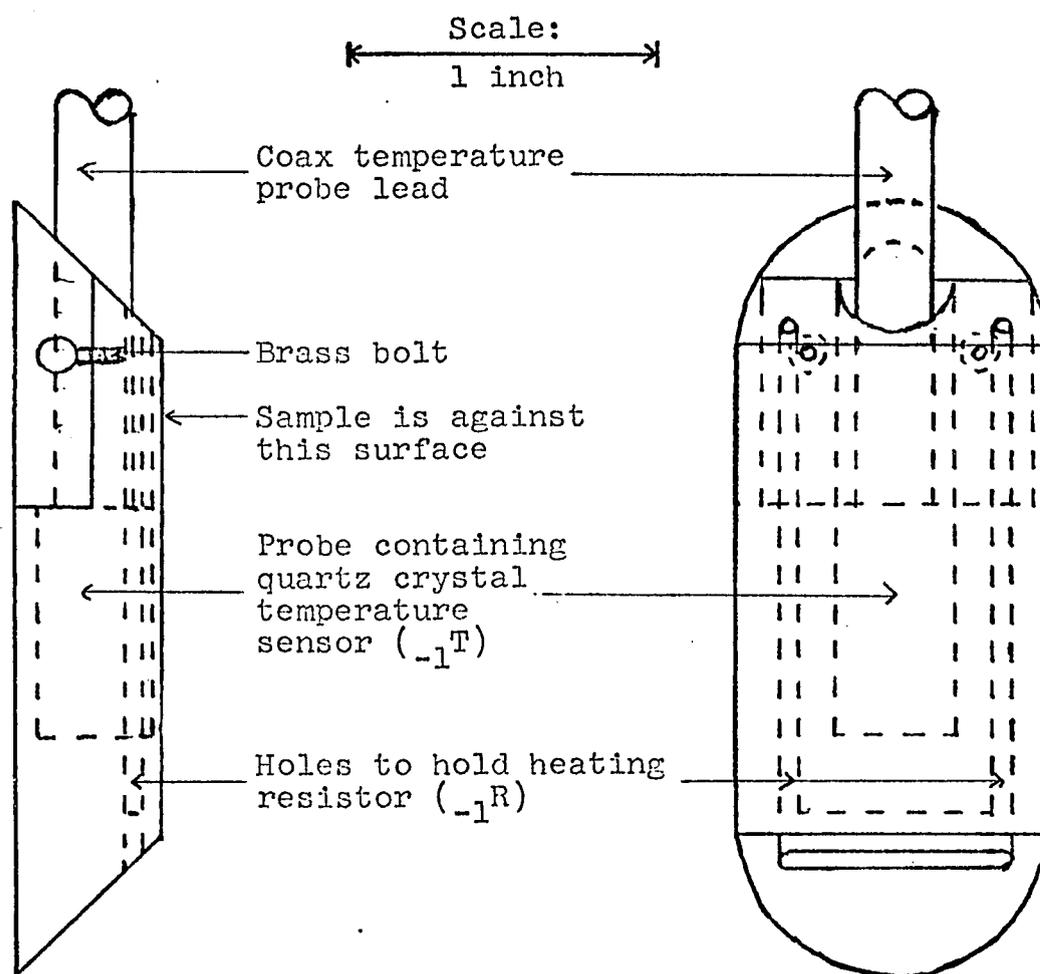


Figure 2. ETP copper conductivity cell, side -1

magnetic field (0 - 14 kG) could be applied parallel or perpendicular to the temperature gradient (which was always perpendicular to the copper sides of the cell) by a rotatable Magnion magnet, model L-128A. The magnet produced a field of homogeneity 10 ppm over the sample cell. A bucking coil was needed to remove the 30 G residual field of the magnet. A Bell gaussmeter equipped with a temperature-compensated probe was used to measure the magnetic field.

#### Temperature Measurement

All three temperatures ( $0^{\circ}\text{T}$ ,  $\pm 1^{\circ}\text{T}$ ) were measured using a Hewlett-Packard quartz thermometer which had a sensitivity of  $0.0001^{\circ}\text{C}$ . The ability of the thermometer to measure differential temperatures allowed conductivity measurements to be made to 0.3% with ease. The sensor is a piezoelectric quartz crystal oscillator. The crystal is cut so that it has an almost linear frequency-temperature curve. Calibration corrections for nonlinearity, supplied by the manufacturer, were applied to all measured temperatures. With an applied magnetic field, a very small effect on the measurement of the temperature difference across the isotropic sample was noted. Since this effect was reproducible and independent of the direction of the temperature gradient,

temperature measurements were corrected for it as appropriate. Further corrections such as hysteresis, drift, and offset did not contribute significantly to the results (Hewlett-Packard 1966, 1968). Thermal hysteresis did not contribute because the probes were cycled over small temperature changes. Long term drift did not contribute because the measurements were performed over a short period of time. Zero offset did not contribute because only temperature changes were considered. The temperature differences across the sample indicated a reproducibility of  $0.0002^{\circ}\text{C}$  existed throughout a single run.

#### Convection

The problem of convective heat transfer in liquids contained between vertical plates has been studied in detail by Kraussold (1934). He introduces an effective heat conductivity,  $k'$ , which includes both free convection and the true thermal conductivity,  $k$ . Kraussold found that the following empirical formula gave an excellent fit for liquids of widely varying characteristics:

$$\frac{k'}{k} = 0.11 R_2'^{0.29} \quad (3.8 < \log_{10} R_2' < 6.0)$$

where  $R_2'$  is the second Rayleigh number, or the product of the dimensionless Grashof and Prandtl numbers:

$$R_2' = \frac{g \rho^2 \beta}{\eta^2} t^4 \nabla T \times \frac{\eta c}{k}$$

Here  $g$  is the acceleration of gravity,  $\rho$  is the density,  $\beta$  is the coefficient of volumetric expansion,  $\eta$  is the dynamic viscosity,  $c$  is the heat capacity at constant pressure,  $t$  is the thickness of the sample, and  $\nabla T$  is the temperature gradient.

If the above formula could be extrapolated to  $k' = k$ , convection would cease at  $R_2' = 2000$ . The actual value of  $R_2'$  where convection starts is about 1000 (Kraussold 1934 and Ziebland 1969, p. 83), and, to be conservative, Tsederberg (1965, p. 22) recommends that  $R_2'$  be less than about 700 or 800.

The necessary physical constants for PAA can be found in papers by Porter and Johnson (1963) and Picot and Fredrickson (1968). Even incorporating the anisotropic viscosity (Miesowicz 1946),  $R_2'$  does not exceed  $(t^4 \nabla T) \times 10^5 \text{ cm}^{-3} \text{ deg}^{-1}$  outside a fraction of a degree of the transition temperatures (where  $\beta$  has singularities). For a sample thickness of 0.05 cm and a temperature gradient of 5 °C/cm (nominal values for the apparatus),  $R_2' = 3$ . Convection, therefore, can be completely ignored.

### Temperature Gradient Alignment

Stewart (1936) reported evidence from x-ray diffraction for the existence of an alignment mechanism associated with heat flow. The preferred direction of molecular orientation was perpendicular to the temperature gradient. Further data were presented by Stewart, Holland, and Reynolds (1940). The latter paper states that the alignment saturated at 1 °C/cm gradient and was strongly enhanced (at smaller temperature gradients) by rotation of the sample at 5 rpm about a vertical axis. The temperature gradients in the above experiments were vertical, a fact that may be important in a future explanation. Since the nominal temperature gradient of the current apparatus is 5 °C/cm, it is necessary to consider these observations in detail.

The x-ray results were significantly different depending on whether the temperature gradient was up or down. There is evidence (not fully selfconsistent) for this in both the papers mentioned above. This suggests either inaccurate temperature measurement (an unlikely possibility) or a gravity-dependent effect. Although ruled out by the authors, convection currents would be virtually impossible to eliminate. It should also be noted that shear fields do not exist when the sample is rotated at constant speed, as claimed.

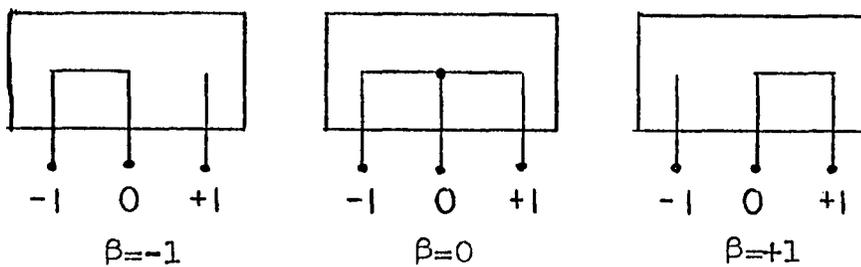
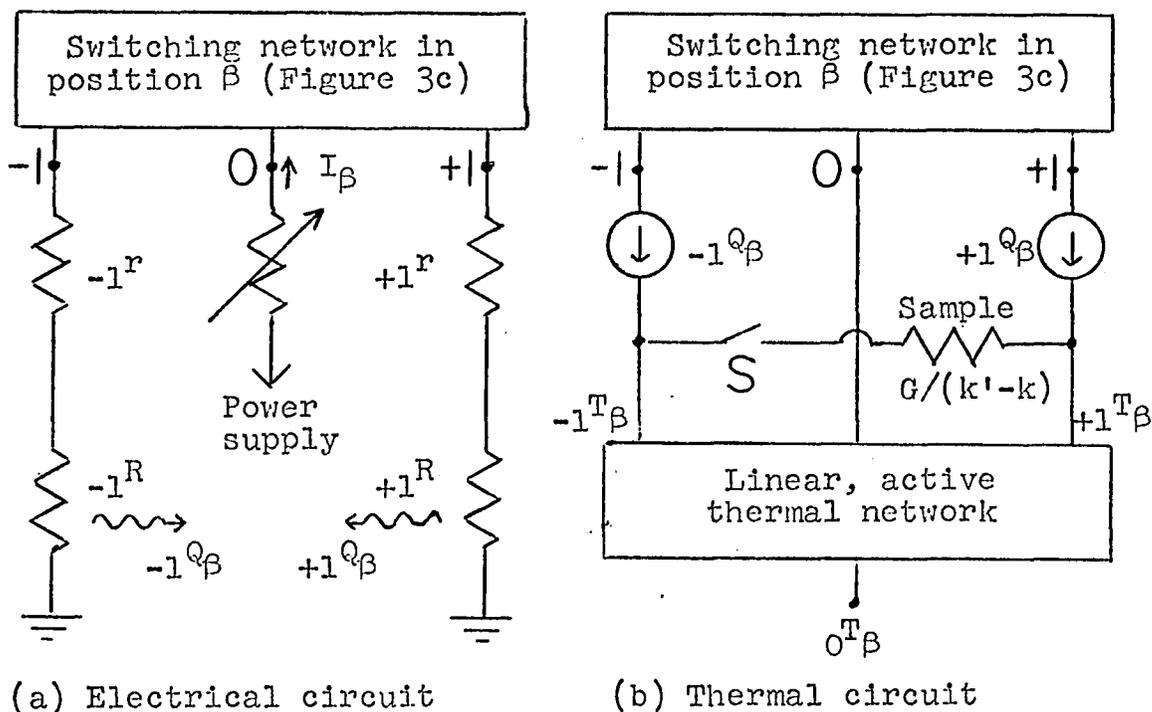
It is surprising that these papers have gone almost unnoticed in the literature (except for thermal conductivity studies after 1966), this in spite of four later notes by Stewart and his coworkers. The doctoral work of Picot (1966; Picot and Fredrickson 1968) showed there was no alignment change on doubling the (horizontal) heat flux. Similarly Fisher (1969; Fisher and Fredrickson 1969) found no change in thermal conductivity when the (horizontal) temperature gradient was varied between 12 and 36 °C/cm. On the other hand, Patharkar et al. (1971) observed temperature gradient effects in the range from 10 to 200 °C/cm. An increase in the temperature gradient was found to cause a decrease in conductivity. Their results below 10 °C/cm were inconclusive, but indicated that the heat flow did not influence the conductivity. This last experiment was performed in a convection-free parallel plate cell with the top plate heated.

It is noted that the temperature gradient alignment has been noticed if and only if the gradient was vertical. Although the evidence favors a null effect of heat flow on molecular alignment, a run was made to investigate this point. A temperature gradient of .5 °C/cm (a tenth the nominal gradient) did not change the conductivity (either with or without magnetic field).

The sensitivity, of course, decreased by a factor of ten. This run at lower temperature gradient verified that heat flow alignment as well as convection could be ignored.

#### Data Reduction Formulas

The present section will discuss the procedures used to obtain the thermal conductivity values from the raw data. Designate the two sides of the sample cell as  $-1$  and  $+1$ . Let the resistances imbedded in the copper blocks of the cell (Figure 2) be designated  $_{-1}R$  and  $_{+1}R$ , respectively, and let these resistors be in parallel with lead resistances  $_{-1}r$  and  $_{+1}r$  (Figure 3a). Let  $I_{\beta}$  be the total current flowing into the sample cell producing power  $_{\pm 1}Q_{\beta}$  by joule heating resistor  $_{\pm 1}R$ . Here  $\beta$  designates how the current is switched. If  $\beta$  is  $\pm 1$ , only resistor  $_{\pm 1}R$  is heated; if  $\beta$  is 0, both resistors are heated. The output impedance of the power supply is adjusted so the total power input to the sample cell is approximately independent of how the current is routed. In this manner, the sample's mean temperature remains constant and no extra delays are incurred while the thermally massive upper portion of the apparatus reaches equilibrium. Circuit analysis of Figure 3a gives, for  $\alpha = \pm 1$ ,



(c) Electrical or thermal switching network

Figure 3. Circuits used for the reduction of data

$$\alpha^Q \alpha = I_\alpha^2 \alpha^R$$

$$\alpha^Q_{-\alpha} = 0$$

$$\alpha^Q_0 = \left[ \frac{I_0 (-\alpha^R + -\alpha^r)}{\sum_{\beta} (\beta^R + \beta^r)} \right]^2 \alpha^R$$

Summation over  $\beta = \pm 1$  (but not 0) is represented by  $\sum_{\beta}$ . The  $I_\alpha$  are not independent, and it can be shown that the last equation above can be rewritten in the following form

$$\alpha^Q_0 = I_0^2 \alpha^R \left[ 1 + \sqrt{\frac{I_{-\alpha} (I_0 - I_\alpha)}{I_\alpha (I_0 - I_{-\alpha})}} \right]^{-2}$$

It will be noted that the determination of the power generation does not require knowledge of the power supply voltage nor output resistance. Neither is it necessary to know the lead resistances. The currents were measured with a Honeywell potentiometer, model L2745. For the analysis below, it is convenient to define

$$0^Q \beta = 0$$

Figure 4 is a schematic diagram with the major heat flow paths indicated. Heat from the main oven has been ignored because it does not contribute to the analysis and, if included, would mask the significant heat flows. In terms of the parameters defined in the figure,

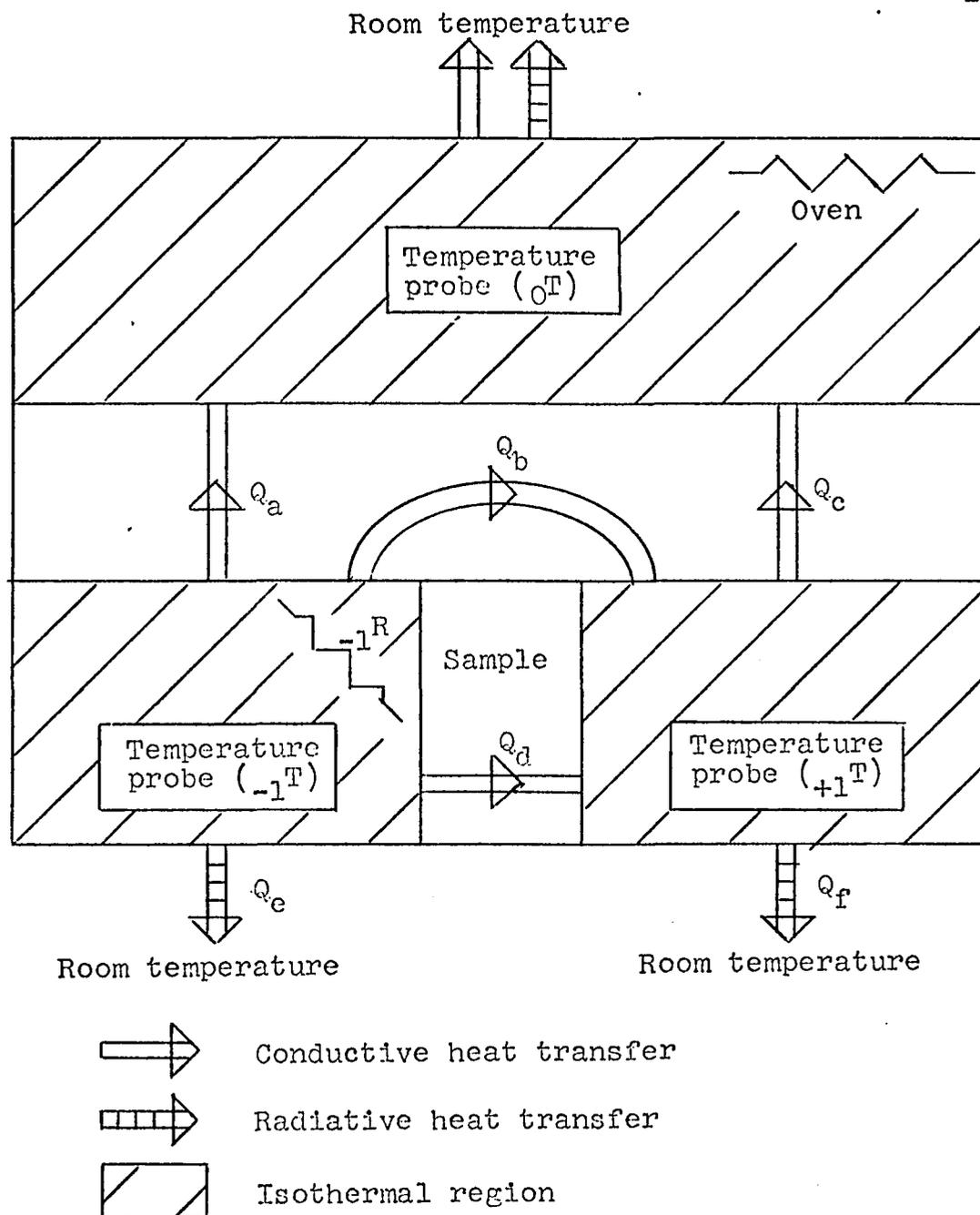


Figure 4. Schematic diagram of major heat flow paths

Schematic diagram of major heat flow paths resulting from the switching network (Figure 3c) being in position  $\beta=-1$ . The heat flow paths from the oven are ignored.

$$\begin{aligned}
 Q_a + Q_b + Q_d + Q_e &\approx -1^{Q-1} \\
 -Q_b + Q_c - Q_d + Q_f &\approx 0 = -1^{Q+1}
 \end{aligned}$$

Let the equilibrium temperatures be  $\alpha T_\beta$ . Here,  $\alpha$  designates the location of the temperature probe. If  $\alpha$  is  $\pm 1$ , the temperature is that of the copper block containing resistor  $\pm 1 R$ ; if  $\alpha$  is 0, then the temperature is measured at the top probe (Figure 1). The meaning of  $\beta$  is the same as in  $I_\beta$ . Because of the identical form of Ohm's law for electrical conduction and Fourier's law for thermal conduction, there exists an analogous electrical circuit for any thermal circuit (Roots 1969, pp. 1-13), and the results of network theory can be applied to the latter with temperature replacing voltage and heat flux replacing current density. In this duality, thermal and electrical resistivities are analogous. Heat and electrical capacitances are also related, and at equilibrium they can be replaced by open circuits. The thermal network used in this analysis is illustrated in Figure 3b. It will be noted that a change of conductivity in the sample from  $k$  to  $k'$  is accomplished by closing switch  $S$  in Figure 3b.  $G$  is a geometrical factor equal to the sample thickness divided by the cross-sectional area. Unless stated otherwise, switch  $S$  is open.

It is possible to define constants  $\alpha_{,\beta}^Z$  equivalent to the z-parameter matrix of network theory (Chirlian 1969, p. 470) such that

$$\alpha_{\beta}^T - 0_{\beta}^T = \alpha_{0}^T - 0_{0}^T + \sum_{\gamma} \alpha_{,\gamma}^Z (\gamma_{\beta}^Q - \gamma_{0}^Q)$$

The reciprocity theorem (Chirlian 1969, pp. 530-534) requires

$$\alpha_{,\gamma}^Z = \gamma_{,\alpha}^Z$$

Care must be exercised in the solution of these equations, because, in the analogous matrix equation, the heat and, thus, temperature matrices are almost singular if

$$\alpha_{\alpha}^Q \approx 2 \beta_{0}^Q$$

The above equations can be rewritten as ( $\beta = 0, \pm 1$ )

$$2 \sum_{\alpha} (\alpha_{\beta}^T - \alpha_{0}^T) - 4(0_{\beta}^T - 0_{0}^T) = \\ A \sum_{\alpha} (\alpha_{\beta}^Q - \alpha_{0}^Q) + B \sum_{\alpha} \alpha (\alpha_{\beta}^Q - \alpha_{0}^Q)$$

$$2 \sum_{\alpha} \alpha (\alpha_{\beta}^T - \alpha_{0}^T) = \\ B \sum_{\alpha} (\alpha_{\beta}^Q - \alpha_{0}^Q) + C \sum_{\alpha} \alpha (\alpha_{\beta}^Q - \alpha_{0}^Q)$$

where

$$A = \sum_{\alpha,\gamma} \alpha_{,\gamma}^Z \\ B = \sum_{\alpha} \alpha_{,\alpha}^Z \\ C = \sum_{\alpha,\gamma} \alpha \gamma_{,\alpha}^Z$$

Considering the right hand side of the second equation, each factor of the first term is much smaller than the corresponding factor of the second term. Specifically, if

$$\alpha^Q \alpha = 2 \beta^Q \beta = 1/x$$

then

$$C = 2 \beta x \sum_{\alpha} \alpha (\alpha^T \beta - \alpha^T \beta_0)$$

If switch S (Figure 3b) is now closed, all the above formulas can be rewritten with primes appended to all variables. It can be shown (Chirlian 1969, pp. 498-500) that

$$\begin{bmatrix} -1, -1^{Z'} & -1, 1^{Z'} \\ 1, -1^{Z'} & 1, 1^{Z'} \end{bmatrix} = \left[ \left[ \frac{(k-k')}{G} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} + \begin{bmatrix} -1, -1^Z & -1, 1^Z \\ 1, -1^Z & 1, 1^Z \end{bmatrix}^{-1} \right]^{-1} \right]$$

Thus

$$C' = C [1 - C(k-k')/G]^{-1}$$

or

$$k' = k - G/C + G/C'$$

Furthermore, it is possible to measure conductivity changes by only measuring the highly-stable temperature differences across the sample as a function

of, say, magnetic field. If

$$x' = x$$

it follows that

$$\alpha^{T'0} \approx \alpha^{T0}$$

Hence

$$k' = k + \frac{G}{C} \left[ \frac{\sum_{\alpha} \alpha (\alpha^{T\beta} - \alpha^{T0})}{\sum_{\alpha} \alpha (\alpha^{T'\beta} - \alpha^{T0})} - 1 \right]$$

The evaluation of G will be discussed next.

#### The Geometrical Factor

To determine the geometrical factor G, which is needed to reduce conductance values to thermal conductivity, it was necessary to calibrate the author's cell against another measurement of the conductivity of PAA. The results of Patharkar, Rajan and Picot (1971) were used for calibration because they used a parallel plate geometry and their results were available in sufficient quantity for analysis. The actual data used were those given in a later paper by Rajan and Picot (1971). These data differ slightly from those in the first paper, apparently as a result of recalibration of their apparatus. Their data for commercial grade PAA at 126°C extrapolated to zero temperature gradient are given in Table 1. The interpretation of the variation in

observed conductivity given in the latter paper was not considered valid by this author because of the strong wall-alignment forces observed in the current experiments. Instead it was believed that the micrometer screw used to adjust their plate separation was subject to backlash or the cell surfaces were not parallel. If the sample thickness is assumed to be  $d - \delta$ , rather than  $d$ ,

$$k_{\text{corrected}} = \left(1 - \frac{\delta}{d}\right) k_{\text{reported}}$$

If the left hand side is plotted against  $\delta$  for the small plate separations, a set of straight lines are obtained. These intersect at  $\delta = 1.65\mu$  and  $k_{\text{corrected}} = 3.35 \pm 1\%$ . This is the value of conductivity for PAA used in the calibration.

The conductivity of air was also needed. Tsederberg (1955, p. 143) gives 0.810 for 126°C. The geometrical factor  $G$  can be found by noting that

$$k - \frac{G}{C}$$

is invariant as shown in the previous section.  $G$  was found to be  $51 \times 10^{-4} \text{ cm}^{-1}$ . The primary source of error is the possibility of variation in the purity of the author's sample of PAA and the sample of Patharkar, Rajan and Picot. Although the absolute values of conductivity might be in error up to 5% for the above

reason, the relative values of conductivity are believed to be accurate to 0.3%, and were reproducible to that accuracy. The relative temperature coefficient of G, a result of differential thermal expansion, is  $-8 \times 10^{-4} \text{ deg}^{-1}$ .

## CHAPTER 4

### RESULTS AND THEIR INTERPRETATION

Measurements of the thermal conductivity of PAA, both with and without an aligning magnetic field, are presented in Figures 5-7. These results will be discussed in detail below. Figure 8 includes two supplementary graphs: a run at a tenth the nominal temperature gradient, for reasons discussed in the section "temperature gradient alignment", and an example of a run with magnetic field perpendicular to the temperature gradient on a different sample. A run with the field parallel to the temperature gradient produced similar results, the conductivity being equal to that of the first sample to within about 1%. The only major difference between samples was a change in the field necessary to remove the hysteresis, a reasonable effect in view of the lack of special surface preparation.

#### Zero and Saturating Magnetic Fields

The thermal conductivity as a function of temperature is graphed in Figure 5. On the scale of this figure, the no-field conductivity can be considered to be equivalent to  $k_1$ . Results, as a function of

Figure 5. The thermal conductivity of PAA as a function of temperature

First sample	Second sample	
□	■	$k_{\parallel}$
△	▲	$k_{\perp}$
○		No previous alignment
+		Isotropic liquid

All conductivities are in units of  $10^{-4}$  cal/sec-cm-deg. The variations of conductivity with a magnetic field applied perpendicular to the heat flux are too small to be significant on this graph. The point used to evaluate the geometrical factor is marked with a +.

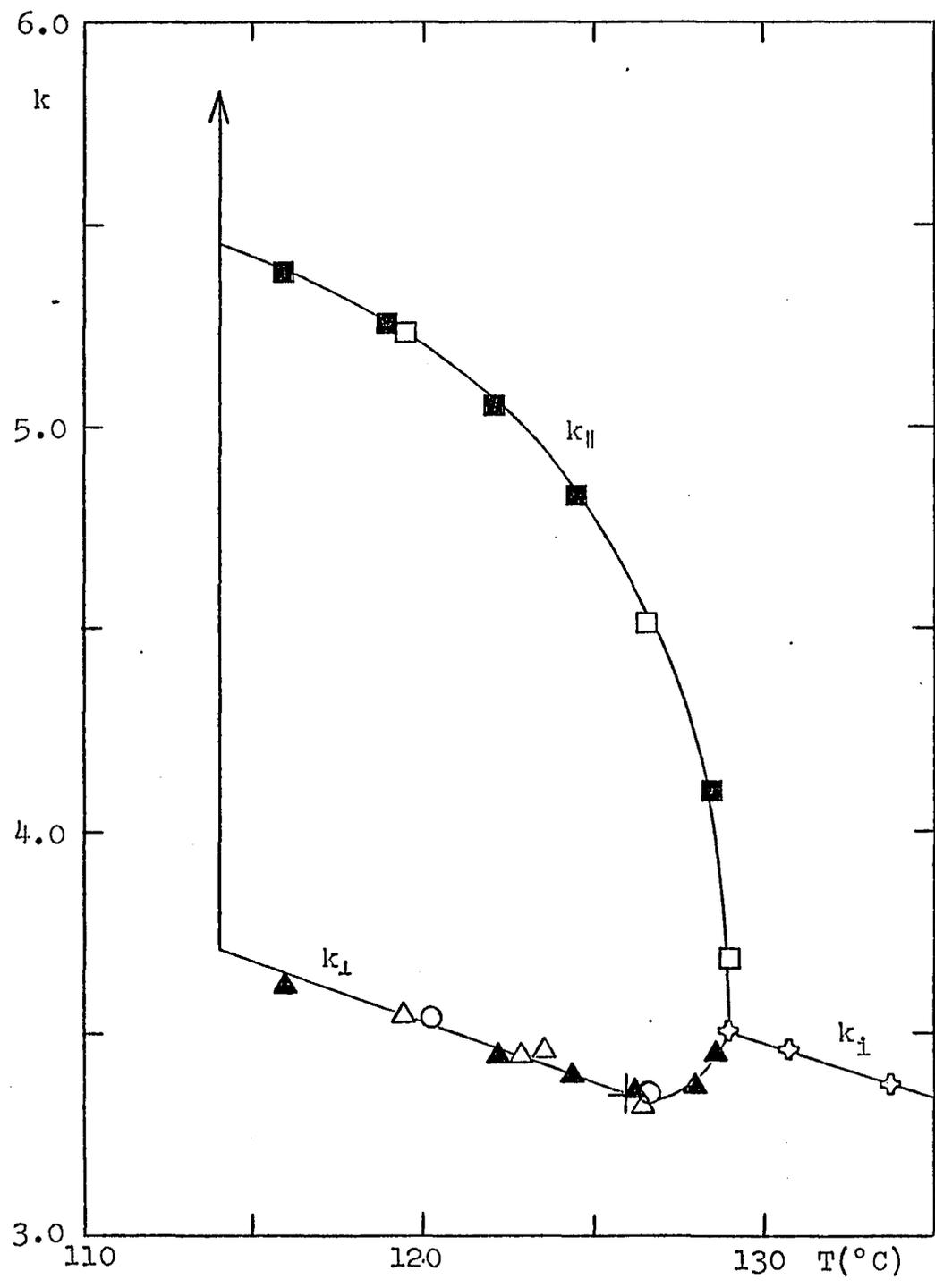


Figure 5: The thermal conductivity of PAA as a function of temperature

Figure 6. The thermal conductivity of PAA parallel to molecular orientation as a function of magnetic field at selected temperatures

○	$k^* \equiv k(H) - k' + 0.2$	119.5 °C
△	$k^* \equiv k(H) - k' + 0.8$	126.5 °C
▽	$k^* \equiv k(H) - k' + 2.0$	129.0 °C

All conductivities are in units of  $10^{-4}$  cal/sec-cm-deg and are measured relative to the conductivity  $k'$  at zero magnetic field with the previous field having been applied perpendicular to the direction of heat flow. Each curve has been further offset by different amounts in order to maintain legibility.

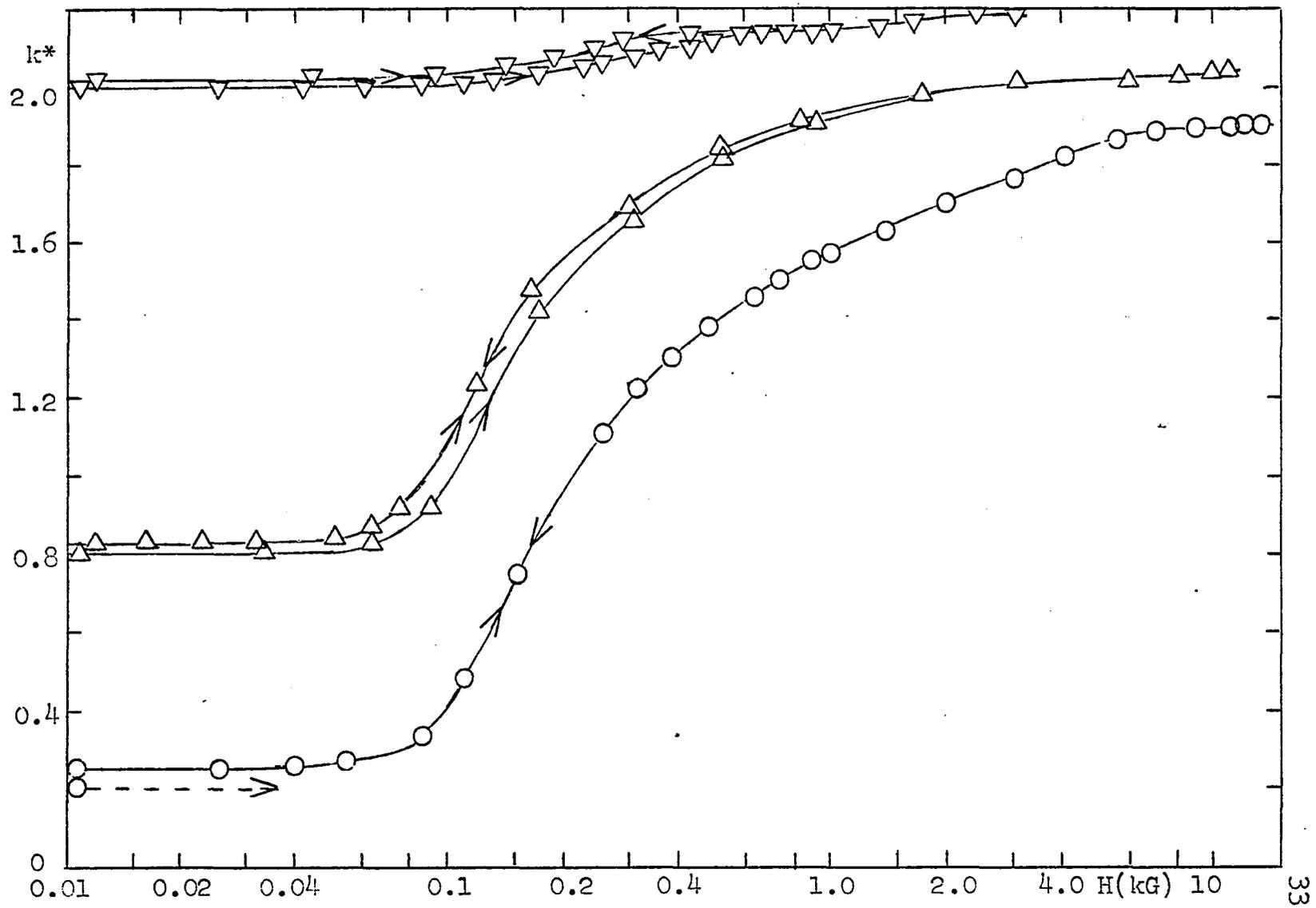


Figure 6. Thermal conductivity parallel to molecular orientation

Figure 7. The thermal conductivity of PAA perpendicular to molecular orientation as a function of magnetic field at selected temperatures

○	$k^* \equiv k(H) - k' + 0.03$	119.5 °C
△	$k^* \equiv k(H) - k' + 0.05$	126.5 °C
▽	$k^* \equiv k(H) - k' + 0.01$	129.0 °C

All conductivities are in units of  $10^{-4}$  cal/sec-cm-deg and are measured relative to the conductivity  $k'$  at zero magnetic field with the previous field having been applied perpendicular to the direction of heat flow. Each curve has been further offset by different amounts in order to maintain legibility.

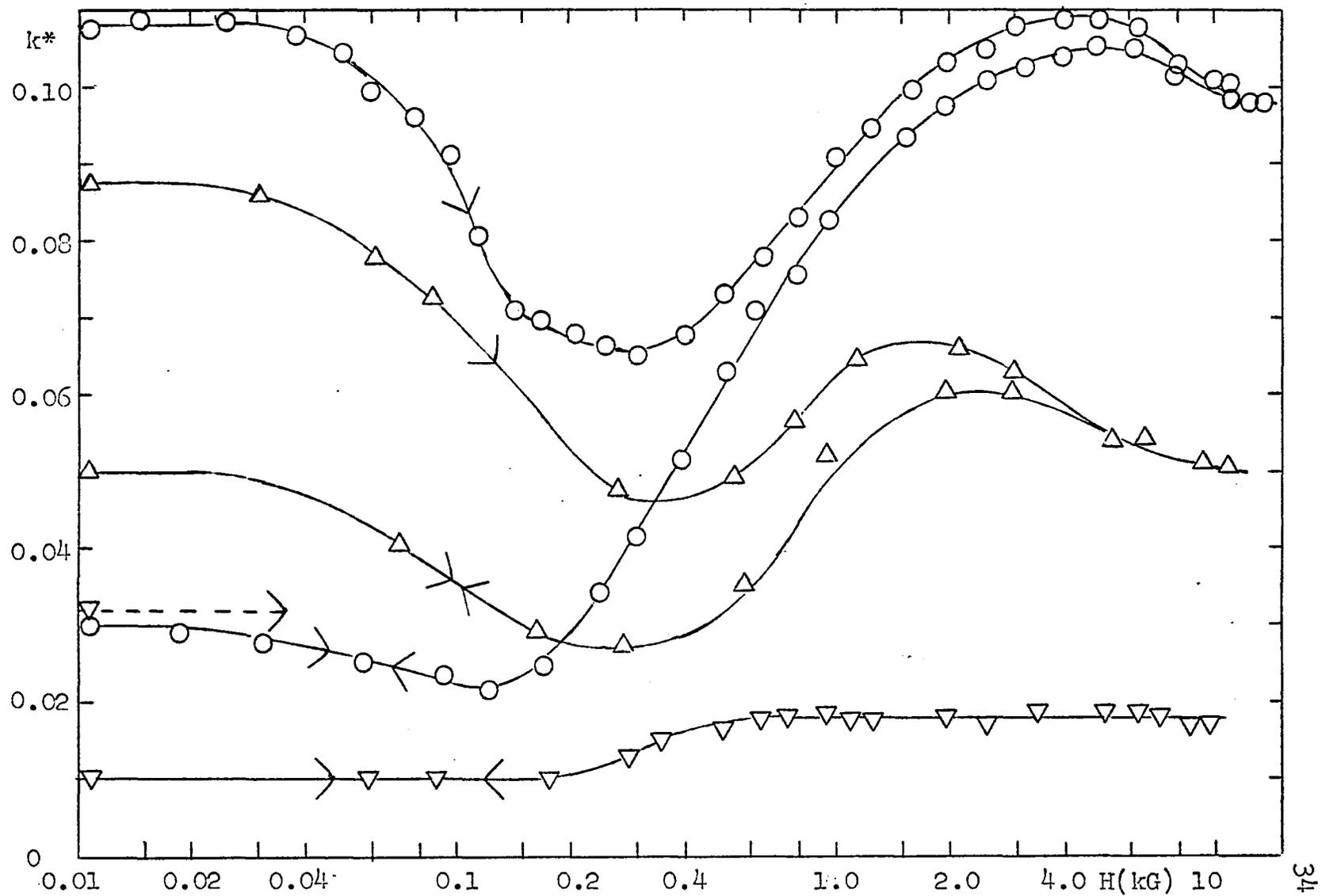


Figure 7. Thermal conductivity perpendicular to molecular orientation

Figure 8. Supplementary graphs of the thermal conductivity of PAA perpendicular to molecular orientation as a function of magnetic field

- △ First and second samples, respectively, at  $126\frac{1}{2}$  °C. The conductivities are recorded with respect to  $k_1$ .
- The conductivity at 0.5 °C/cm minus the conductivity at 5 °C/cm. Both have mean temperatures of  $119\frac{1}{2}$  °C.

All conductivities are in units of  $10^{-4}$  cal/sec-cm-deg.

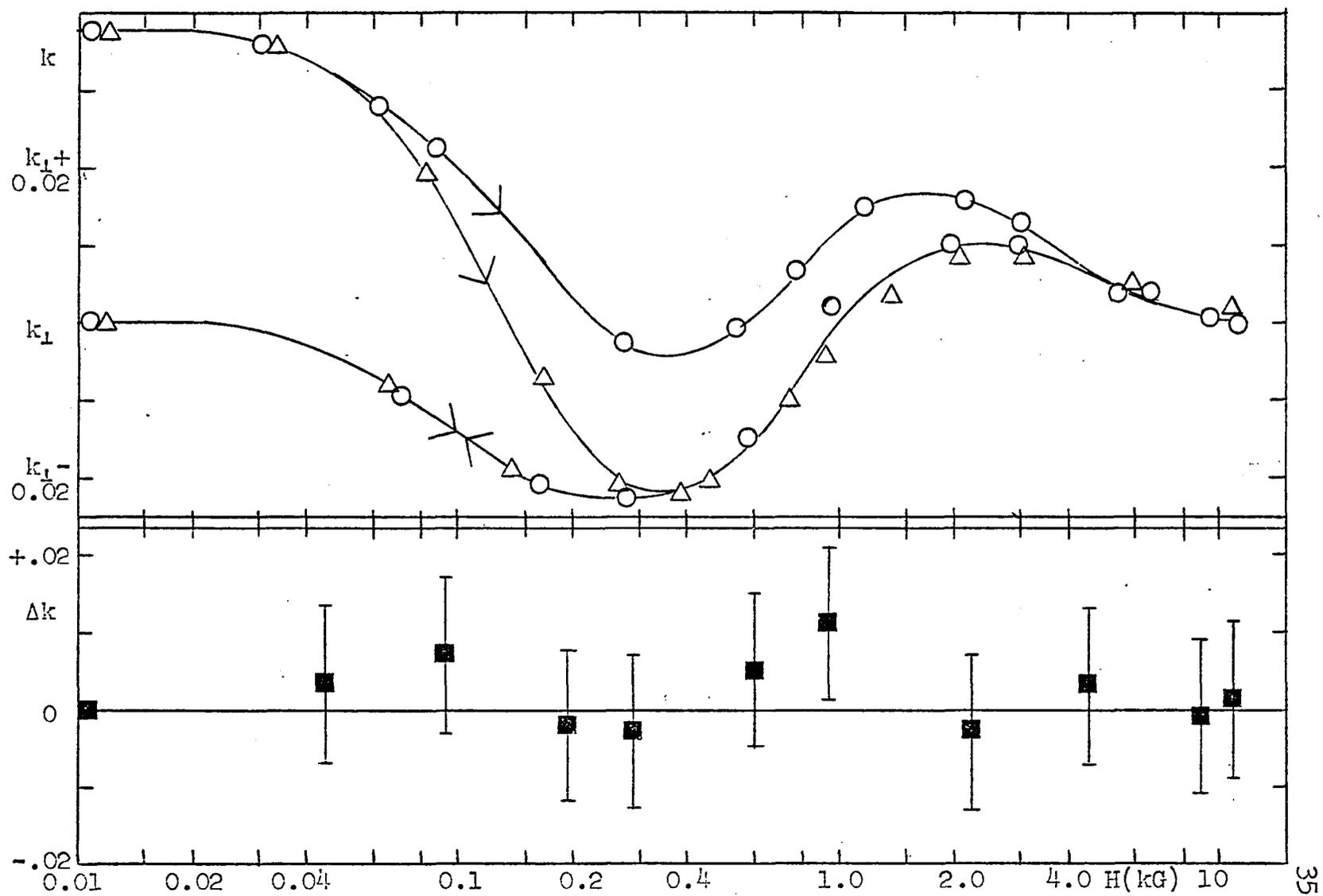


Figure 8. Supplementary graphs of conductivity perpendicular to orientation

temperature, for  $k_{\parallel}$  are also presented. The theory of liquids, especially molecular liquids, is far from complete. Empirical formulas have at least the same importance as theoretical ones. It is known that the thermal conductivity of liquids usually decreases linearly with temperature increase (McLaughlin 1964). A similar relationship has been suggested for liquid crystals (McCoy and Kowalczyk 1960), a hypothesis substantiated by this work for  $k_{\perp}$ .

It has been shown by Filippov (1954) and quoted by Tsederberg (1965, pp. 203-204) that for a given liquid, as a function of temperature,

$$k \propto \rho^{4/3}$$

where  $\rho$  is the density. The thermal coefficient of expansion

$$\beta = - \frac{1}{\rho} \frac{d\rho}{dT}$$

for PAA (Porter and Johnson 1963) is  $8.66 \times 10^{-4} \text{ deg}^{-1}$ . Thus the predicted logarithmic derivative of  $k$  with respect to  $T$  is  $-1.2 \times 10^{-3} \text{ deg}^{-1}$ . This last value is in poor agreement with the observed value of  $-8 \times 10^{-3} \text{ deg}^{-1}$ . Agreement with another empirical relationship that holds for most liquids (McLaughlin 1964)

$$\frac{d \ln k}{dT} = - 2.8 (\beta - \beta_0)$$

where

$$\beta_0 = 5 \times 10^{-4} \text{ deg}^{-1}$$

is no better.

The variation of the thermal conductivity with respect to magnetic field is some two orders of magnitude smaller when the magnetic field is applied parallel to the copper walls than when it is perpendicular. It is inferred that the molecular orientation at copper-mesomorph interfaces is parallel to the interface, and that in the absence of a magnetic field this alignment extends throughout the 0.5 mm sample. Similar long range order has been observed by Zocher and Ungar (1938), Carr (1962), Lord and Labes (1970) and Finlayson (1971). Such an orientational phenomenon (both in direction and strength) was assumed by Longley-Cook and Kessler (1971) to explain the anomalous magnetocaloric effect.

Measurements of thermal conductivity were made in the sequence liquid crystal, isotropic, and liquid crystal phases, respectively. No change was observed in the conductivity (either with or without magnetic field alignment) between the liquid crystal phase that had been obtained by heating the solid and one derived from cooling after 36 hours in the isotropic state.

Thus the history-dependent results of Yun and Fredrickson (1970a) appear to have been a result of sample decomposition at elevated temperatures.

No phenomenological theory of thermal conductivity has been developed for anisotropic liquids. Of the standard theories of heat transport in liquids that can be easily generalized to anisotropic media (Tsederberg 1965, pp. 188-198, and McLaughlin 1969, pp. 42-60) none can be successfully used to explain the observed anisotropy. These theories can be divided into two groups: those that do not include the intermolecular space as a parameter, and those that do.

As the sound velocity sometimes appears in the theoretical treatments, it is worthwhile to note here that the sound velocity is almost isotropic for MBBA (Lord and Labes 1970). In those theories that do not include the intermolecular volume, one obtains

$$\frac{k_{\parallel}}{k_{\perp}} = \left(\frac{d_{\parallel}}{d_{\perp}}\right)^n \approx 3^n$$

for PAA. Here  $d_{\parallel}$  and  $d_{\perp}$  are the length and diameter of the rod-like nematic molecules, and  $n$  is a positive, negative, or zero integer, depending on the theory. Clearly the theories do not adequately predict the observed ratio (1.4) of conductivities.

On the other hand, no information of sufficient accuracy exists to determine the anisotropy of the separation of the molecules. X-ray results of Vainshtein et al. (1969) suggest the molecules are closely packed. Molecular volumes as determined from bond lengths and density measurements give the same conclusion. There is no more than a 0.1% change in density at the solid-nematic transition for PAA (Porter and Johnson 1963). (Neither is there a change in the thermal expansion coefficient at this transition.)

#### Field Parallel to Heat Flow

Thermal conductivity measurements were made with magnetic fields applied either parallel or perpendicular to the direction of heat flow. Figure 6 illustrates the results for the parallel case at three representative temperatures: just below the isotropic transition ( $129^{\circ}\text{C}$ ), well within the nematic range ( $126\frac{1}{2}^{\circ}\text{C}$ ), and just above the melting point ( $119\frac{1}{2}^{\circ}\text{C}$ ). The curves have been arbitrarily shifted on the ordinate axis to maintain legibility. Note that the abscissa is plotted on a logarithmic axis. Successive points were taken in an orderly progression of magnetic field as indicated by the arrowheads in the figure.

Because of the high sensitivity of the apparatus in relation to the scale of the graph, the (statistical) error is smaller than the plotted points. At low fields, the conductivity remained virtually constant until 40 to 100 G (depending on the temperature). To confirm that such constancy is not a result of the logarithmic abscissa (which would flatten any continuous curve near zero), one need only compare the low field conductivity with the curves A and B of Figure 9. These curves are

$$k = \alpha H + \beta$$

and

$$k = \alpha H^2 + \beta$$

respectively. The shapes of these curves are independent of  $\alpha$  and  $\beta$ . A change in either of these parameters merely shifts the curves along the abscissa or ordinate axes, respectively.

Hysteresis was observed in the thermal conductivity at zero field. The conductivity was higher if the sample had been previously aligned parallel to the heat flow than perpendicular. Although this hysteresis will be discussed in greater detail in the next section, it is worthwhile to point out here that the lower conductivity will be used for  $k_0$  and/or  $k_1$  in the following analyses.

Figure 9. Curves based on interpretations of the thermal conductivity of PAA parallel to molecular orientation as a function of magnetic field

Curve A	$k = \alpha H + \beta$
Curve B	$k = \alpha H^2 + \beta$
Curve C	$k = f(\alpha H)$ (Langevin analysis)
Curve D	Analysis of Guyon et al. (1971). Curve adapted from that paper using values for PAA at 120 °C.
○	Experimental values at 119½ °C from this study.

All conductivities are in units of  $10^{-4}$  cal/sec-cm-deg.

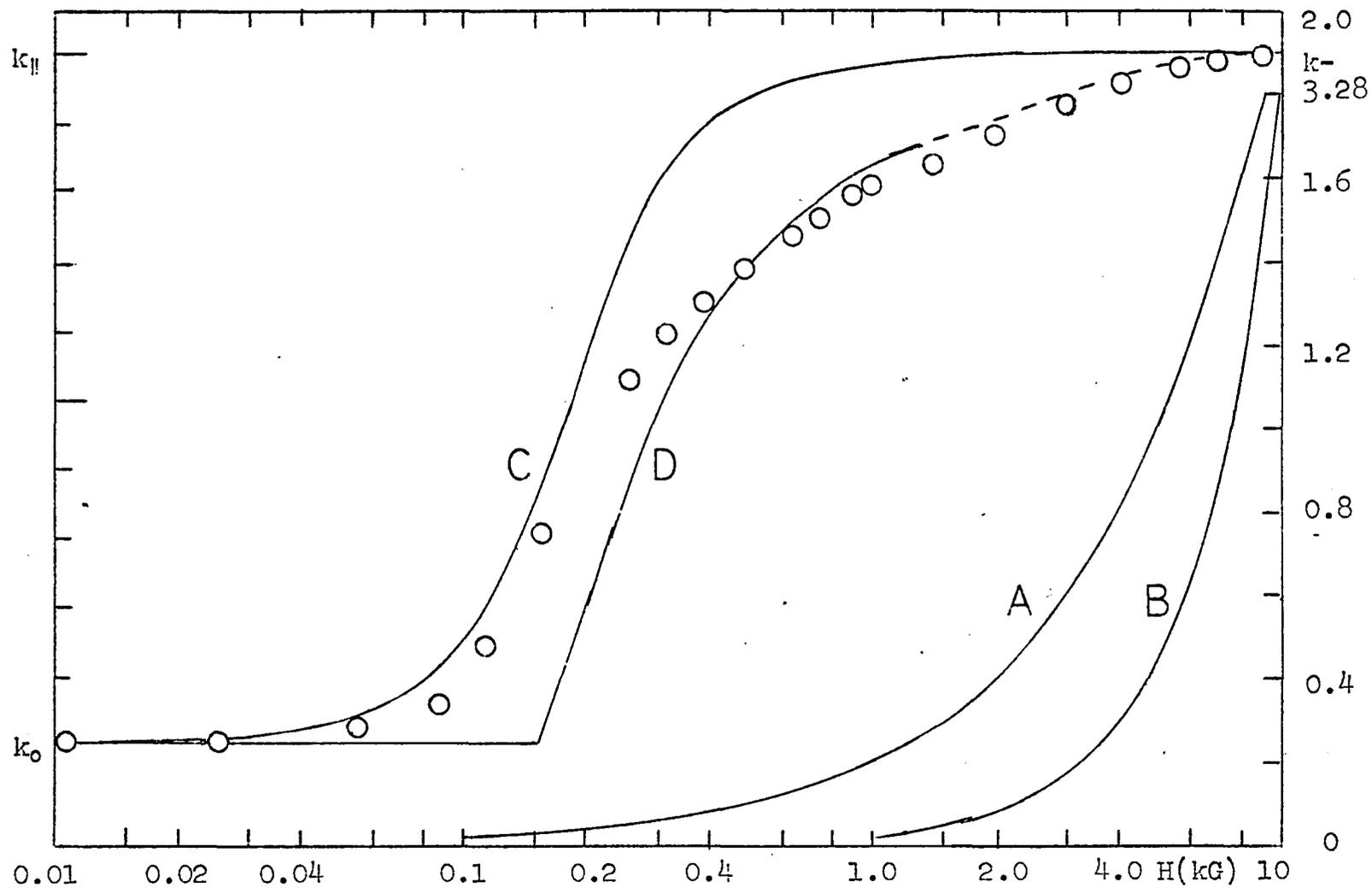


Figure 9. Curves based on interpretations of conductivity parallel to orientation <sup>17</sup>

It is instructive to compare the observed thermal conductivities with those predicted by an analysis similar to that used by Langevin to interpret polarization. Consider a volume,  $V$ , that is sufficiently far from the sample container walls so the walls do not influence the orientation. This (temperature dependent) volume is chosen small enough so that the preferential orientation within it is essentially constant throughout, yet not so small that the orientation of molecules outside is strongly affected by molecules in the middle of the volume. In other words,  $V$  is approximately the cube of the extent of the preferred molecular order. It will be assumed that  $V$  is independent of the magnetic field,  $H$ , and that each  $V$  can be treated independently by Boltzmann statistics. If such a volume aggregate is oriented at angle  $\theta$  with respect to  $H$ , its conductivity parallel to the field is

$$k_{\parallel}(\theta) = k_{\perp} + (k_{\parallel} - k_{\perp})\cos^2\theta$$

Designate this as

$$k_{\parallel}(\theta) = a + b \cos^2\theta$$

and let

$$c = \sqrt{\frac{\chi_a V \rho}{k_B T}}$$

where

$$\chi_a = \chi_{\parallel} - \chi_{\perp} > 0$$

is the anisotropic part of the diamagnetic susceptibility per unit mass,  $\rho$  is the density, and  $k_B$  is Boltzmann's constant. The conductivity is averaged over  $\theta$  while weighted by

$$W(\theta) = \exp(c^2 H^2 \cos^2 \theta) \sin \theta$$

Thus

$$k = \frac{\int (a + b \cos^2 \theta) W(\theta) d\theta}{\int W(\theta) d\theta}$$

where the limits of integration are 0 and  $\pi/2$ . Hence

$$k = a + \frac{b}{2cH} \left[ \frac{1}{F(cH)} - \frac{1}{cH} \right] \equiv f(cH)$$

where  $F(x)$  is Dawson's integral (Gautschi 1964, pp. 298, 319)

$$F(x) = e^{-x^2} \int_0^x e^{t^2} dt$$

It should be noted that an inherent error in this interpretation is that the true thermal conductivity is no more equal to the function presented here than to the reciprocal of the weighted mean of the resistivity. Fisher (1969, pp. 39, 49) neglected this point in his calculation of  $k_0$ . However the analysis here is an underestimate by, at worst, about

$$- \frac{1}{2} \left[ \frac{2k_{\perp}}{3} + \frac{k_{\parallel}}{3} - \frac{1}{2/(3k_{\perp}) + 1/(3k_{\parallel})} \right] \approx .02 k_{\perp}$$

This is half the difference between the mean conductivity and the reciprocal of the mean resistivity.

The conductivity has been plotted as curve C, Figure 9. Arbitrarily,  $c$  was chosen to be  $10 \text{ kg}^{-1}$ ; any other choice merely shifts the curve along the abscissa. The ordinate axis is linear and determined by  $k_{\parallel}$  and  $k_{\circ}$ . The fit with the experimental data is poor, especially at low temperatures. The experimental curves fail to show the near-symmetry about the point of inflection

$$cH \approx 1.9$$

that is evident in the theoretical curve, if plotted against a logarithmic abscissa.

The above model does not consider wall alignment. An elementary method to incorporate the influence of the walls is to consider

$$k = f(0) \quad (H \leq H_0)$$

$$k = f(cH - cH_0) \quad (H > H_0)$$

Here  $H_0$  is a field of about 200 G that is necessary to overcome the wall alignment. The fit with observed data is not improved. Fitting the data where the field begins to have an effect, say, leads to a curve that

rises too steeply and saturates too suddenly. Thus if the fit is improved in one region, it is worse in the two others.

Recently Guyon et al. (1971) have extended results of de Gennes (1969), Rapini, Papoular and Pincus (1968) and Leslie (1970) in a theoretical analysis of the thermal conductivity of a sample of nematic liquid crystal between two parallel surfaces distance  $d$  apart. A temperature gradient and a magnetic field are applied perpendicular to these surfaces. The alignment is specified by minimization of the free energy per unit area

$$F = \frac{1}{2} \int_{-\frac{1}{2}d}^{\frac{1}{2}d} dz [K_{11} \sin^2 \theta (d\theta/dz)^2 + K_{33} \cos^2 \theta (d\theta/dz)^2 - \chi_a H^2 \cos^2 \theta]$$

with respect to  $\theta(z)$ . The angle  $\theta$  has the same meaning it had in the Langevin analysis. The boundary conditions are

$$\theta(\pm \frac{1}{2}d) = \frac{1}{2}\pi$$

All molecules at distance  $z$  are assumed to be parallel to one another and alignment throughout the sample is assumed parallel to a specific plane that includes the field. The elastic moduli,  $K_{ii}$ , were defined by Frank (1958).

There exist two distinct regions of conductivity separated by a critical field

$$H_c = \frac{\pi \xi}{d}$$

where  $\xi$  is a coherence length defined by de Gennes (1969)

$$\xi = \frac{1}{H} \frac{K_{11}}{\chi_a}$$

This transition was observed by Fréedericksz and Zolina (1933) and is predicted to occur at 143 G (Helfrich 1969) in the present experiment. For

$$H \leq H_c$$

the conductivity is just  $k_{\perp}$  and for

$$H > H_c$$

the thermal resistivity

$$\frac{1}{k} = \frac{1}{d} \int_{-\frac{1}{2}d}^{\frac{1}{2}d} [k_{\perp} + (k_{\parallel} - k_{\perp}) \cos^2 \theta]^{-1} dz$$

is calculated by eliminating  $x$  from the two simultaneous integral equations

$$d = 2 \xi \int_0^{\frac{1}{2}\pi} g(u) du$$

$$d = 2 \xi k \int_0^{\frac{1}{2}\pi} g(u) [k_{\perp} + x (k_{\parallel} - k_{\perp}) \sin^2 u]^{-1} du$$

Here

$$g^2(u) = \frac{1 + x \left( \frac{K_{33}}{K_{11}} - 1 \right) \sin^2 u}{1 - x \sin^2 u}$$

The conductivity is continuous, but not smooth, at Fréedericksz' transition.

For the case where

$$\frac{K_{33}}{K_{11}} = 2.5$$

which is close to the value 2.43 given by Saupe (1960) for PAA at 120 °C, the conductivity, adapted from Guyon et al. (1971), has been plotted as curve D, Figure 9. The fit with the data for 119½ °C is good and reproduces all the qualitative points with the exception of the slight smoothing observed at Fréedericksz' transition. A supplementary numerical scale for the ordinate has been included.

#### Field Perpendicular to Heat Flow

The results for the magnetic field applied perpendicular to the temperature gradient are illustrated in Figure 7. The first paragraph of the above section applies equally here. Note, however, the change of the conductivity scale between Figures 6 and 7. Compared to the parallel case, the conductivity is almost independent of field. The sensitivity of the apparatus introduces an error of  $10^{-3}$  in k.

The Langevin-like analysis of the previous section can be developed for the case where the

temperature gradient is perpendicular to the magnetic field by merely changing the values of a and b. The easiest way to obtain the conductivity is to note that since the trace of a matrix is invariant under rotation of the axes

$$k_{\parallel}(\theta) + 2 k_{\perp}(\theta) = k_{\parallel} + 2 k_{\perp}$$

Thus

$$\begin{aligned} k_{\perp}(\theta) &= \frac{1}{2}(k_{\parallel} + k_{\perp}) - \frac{1}{2}(k_{\parallel} - k_{\perp}) \cos^2 \theta \\ &= a + b \cos^2 \theta \end{aligned}$$

With this new definition of a and b, the Langevin solution of the previous section is valid here. The monotonically varying result, however, clearly does not describe the conductivity. (At 129 °C, although the theoretical and experimental curves are similar, it would be necessary that

$$k_0 \approx k_{\perp} < k_{\parallel}$$

hold, in contradiction with the theory.)

De Gennes (1969) has made an analysis similar to that of Guyon et al. (1971) for the magnetic field perpendicular to a solid-mesomorph interface. However, since all molecules are assumed to lie parallel to the interface, it would be expected that

$$k = k_{\perp}$$

Because the above interpretations fail to describe the conductivity, a qualitative explanation will be sought. The small changes in the thermal conductivity above 3 kG can be interpreted as improving the degree of molecular order. For fields less than about 30 G, wall alignment extends to at least half the plate separation and the conductivity is independent of the field. At fields intermediate between these two values, the variation of conductivity with magnetic field is somewhat complex. It is not obvious how the conductivity could lie outside the range specified by  $k_{\perp}$  and  $k_{\parallel}$ .

Heat flow alignment has already been ruled out and alignment at the glass and teflon sides of the cell would produce a monotonically changing conductivity. It has been theoretically shown (Helfrich 1963) that alignment inversion walls similar to Bloch and Néel walls in ferromagnets are possible in nematic liquid crystals. However the thickness of such walls is too great to affect the conductivity at the fields under discussion. This is because the change in preferred orientation between adjacent molecules is too small to influence the conductivity.

One possible interpretation of the variation of the conductivity as a function of field strength

can be made using a generalized conductivity tensor. All theories of and experiments on liquid crystals have considered anisotropic physical properties to be identical along the directions of the two shorter molecular axes. It is not unreasonable to assume the diagonalized conductivity tensor has three unequal components. The transverse conductivity would then be related to those two components that have elsewhere in this dissertation been lumped together as  $k_{\perp}$ . The hypothesis that the transverse conductivities are decoupled is reasonable when one considers the non-cylindrical nature of PAA. The molecular axes are 3.5 Å, 6.2 Å and 18.0 Å. The electric dipole (presumably important for alignment near an electrically conducting surface) is at an angle to the major axis. Lastly, and most important, is x-ray evidence by Chistyakov and Chaikovskii (1968) that in a magnetic field, PAA molecules tend to align in such a way that their shortest molecular diameters are parallel to one another and perpendicular to the field. This means that for the present experiment, the magnetic field causes alignment in the direction of the temperature gradient. It is also possible that the principal axes of the conductivity tensor do not coincide with those of the susceptibility tensor.

Before concluding this chapter a qualitative interpretation for the hysteresis in the thermal conductivity at zero magnetic field will be given. The zero field conductivity was observed to be dependent on whether or not the previous field was parallel or perpendicular to the temperature gradient. It was believed that a field perpendicular to a surface could leave some molecules perpendicular to that surface when the field was removed. The situation would resemble a dome-like structure with all molecules pointing towards a point on the surface. This structure would be metastable, collapsing under a field parallel to the surface. The resulting alignment would be fully parallel to the wall. As the temperature is increased, the metastable structure is harder to create, and the hysteresis is diminished.

## CHAPTER 5

### CONCLUSION

It is worthwhile to reconsider some of the earlier thermal conductivity measurements on PAA. Only the first observation, that of Bereskin and Stewart (1941), indicated

$$k_{\parallel} > k_{\perp}$$

Picot (1966; Picot and Fredrickson 1968) using the hot-wire method obtained comparatively low values for thermal conductivity. This is believed to be partly a result of poor thermal contact between the highly ordered nematic and the high curvature of the wire's surface. Uniformity in the conductivity near the wire is critical for correct evaluation of results obtained by this method. Because of wall alignment, the measurements of Fisher (1969; Fisher and Fredrickson 1969) without shear alignment were almost certainly of  $k_{\perp}$  and not  $k_0$ . Regarding the conductivity under shear, Rajan and Picot (1971) report that further communications with A. G. Fredrickson and C. K. Yun "raise the possibility of convection due to secondary flows caused by eccentricity in Fisher's concentric annulus

cell." The measurements of Patharkar et al. (1971) have already been analyzed. The measurements of Guyon et al. (1971) on the anisotropic conductivity of MBBA and the observations of Yun (1970) on DBA are in qualitative agreement with the author's on PAA.

While on the subject of anisotropic thermal conductivities, a comparison might be made with polymers. Anderson (1966) reports that for thermoplastics and rubbers

$$k_{\perp} < k_o < k_{\parallel}$$

where alignment is obtained by stretching. The explanation is that "thermal energy is transported more easily along main chain valences than along secondary valences and van der Waals bindings."

Consider also the transport coefficients for PAA that have been reported in the literature. Let the anisotropy of property  $p$  be

$$\frac{p_{\parallel}}{p_{\perp}} - 1$$

The anisotropies in the transport coefficients are tabulated in Table 2. There is no strong relationship among the anisotropies other than that all transport is easiest when the molecules are aligned parallel to the gradient direction.

Table 2. Anisotropies of transport coefficients for PAA near 120°C

Property	Anisotropy	Reference
Mass diffusion	0.27	Yun and Fredrickson (1970b)
Electrical conductivity	0.5	Helfrich (1969)
Thermal conductivity	0.47	Present study
Viscosity <sup>a,b</sup>	2.83	Miesowicz (1946)
Viscosity <sup>a,c</sup>	1.70	Miesowicz (1946)

<sup>a</sup> $\eta_{||}$ : orientation parallel to velocity gradient

<sup>b</sup> $\eta_{\perp}$ : orientation parallel to velocity

<sup>c</sup> $\eta_{\perp}$ : orientation perpendicular to both velocity and its gradient.

In the first chapter, it was mentioned that the initial impetus for these measurements was the anomalous magnetocaloric effect. A brief calculation will now be made of the temperature rise that could be expected when a liquid crystal is aligned by a magnetic field. As the direction of the temperature change has already been discussed in the literature (Longley-Cook and Kessler 1971) and confirmed by the present measurements which show

$$k_{\parallel} > k_{\perp}$$

only the magnitude of the change will be considered here. The liquid crystal sample and temperature probe lead act as a heat path between the oven used to heat the sample and room temperature. Denote the thermal conductances (to the temperature sensor) as  $K_{1x}$  and  $K_p$ , respectively. If the oven temperature is  $T_o$  and room temperature  $T_r$ , the observed temperature will be

$$T = T_r + \frac{K_{1x}}{K_{1x} + K_p} (T_o - T_r)$$

so

$$T(^{\circ}\text{C}) \approx 125 - \frac{100 K_p}{K_{1x}}$$

where

$$K_{1x} \gg K_p$$

$$T_r = 25^{\circ}\text{C}$$

$$T_0 = 125 \text{ }^\circ\text{C}$$

Thus if the alignment (or realignment) changes the liquid crystal conductance by

$$\Delta K_{1x} \approx 0.2 K_{1x}$$

the change in the temperature of the probe will be

$$\Delta T = \frac{100 K_p}{K_{1x}^2} \Delta K_{1x} \approx .2 \text{ }^\circ\text{C}$$

Here

$$K_p \approx 3 \times 10^{-5} \text{ cal/sec-deg}$$

and

$$K_{1x} \approx 3 \times 10^{-3} \text{ cal/sec-deg}$$

The temperature change agrees with the changes reported in the literature.

#### Recommendations

There are several areas where further experimental work is needed in liquid crystals. Some of those areas which have been brought out in the present study follow. It was proposed that the conductivity tensor, and probably others, have two unequal components that have previously been classed as perpendicular. It is also possible that the principal axes of the various tensors are not coincident. Further study is needed to clarify this point. The effect of impurities on

heat conduction has only been qualitatively investigated (Patharkar et al. 1971). The possibility of temperature gradient alignment is far from settled. The thickness of the pellicle at metal-mesomorph interfaces when there is no other means of alignment has never been investigated.

Theoretical studies should be made of the conductivity of disordered or inhomogeneous media. This may be the only method for the determination of  $k_0$  because temperature fluctuations, wall alignment or convection appear to make an experimental determination impossible. Theoretical investigations of conductivity are needed for the general case where the molecules are not restricted a priori to lie parallel to a given plane.

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