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Thermal Diffusivity Measurements in Nematic and Smectic Phases by Forced Rayleigh Light Scattering

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The forced Rayleigh light scattering technique has been applied to measurements of thermal diffusivity in liquid crystalline phases. In the nematic phase of *p*-methoxy benzylidene *p*-*n*-butyl aniline (MBBA), our results are in good agreement with the data obtained by classical methods. The thermal diffusivity anisotropy in smectic A and B phases has been measured here for the first time in *p*-butoxy benzylidene *p*-*n*-butyl aniline (BBOA). As in the nematic phase, the thermal diffusivity parallel to the long molecular axis is greater than perpendicular to it, i.e. $D_{\parallel} > D_{\perp}$. It is particularly striking that the thermal properties do not change significantly at the nematic to smectic phase transition. This suggests that the thermal diffusivity does not depend on the long range order properties of the various mesophases in a crucial manner, contrary to other transport properties such as the electrical conductivity. A tentative description of the thermal transport in terms of high frequency phonons seems adequate to explain our observations.

I INTRODUCTION

Thermal conductivity has been much less studied than other transport properties such as self diffusion or electrical conductivity. This is partly due to the absence of a microscopic theory to describe thermal transport in liquid crystalline materials. But the lack of an adequate method has also hampered the experimental efforts even in the comparatively simpler nematic phases. Early experiments by Yun et al.¹ and Fisher and Fredrickson² gave very contradictory results on the sign of the thermal anisotropy, because of difficulties in controlling the homogeneous molecular orientation throughout

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the cell.³ More recently, Longley-Cook and Kessler⁴ and Vilanove *et al.*⁵ using a heat flux method on well oriented samples have succeeded to assess that, in the nematic phase, the thermal conductivity is maximum parallel to the long molecular axis. However the necessity of growing large monodomains (several cm²) has prevented the extension of the method to the smectic phases. Thermal measurements by high speed holography⁶ and thermal lens blooming⁷ techniques have also been demonstrated in the isotropic phase of various liquid crystals, but not in the mesomorphic phases. In any case, the data analysis seems extremely complex and not readily applicable to the anisotropic nematic and smectic phases.

In this paper, we present thermal diffusivity measurements in the isotropic and liquid crystalline phases of *p*-methoxy benzylidene *p*-*n*-butyl aniline (the well-known MBBA) and *p*-butoxy benzylidene *p*-*n*-octyl aniline (BBOA). We have used here the forced Rayleigh scattering technique originally proposed by Eichler, Salje and Stahl⁸ for ordinary fluids. When extended to liquid crystals, this technique overpasses all the problems of the other methods. The experimental set up is described in Section III after a brief recall of the theoretical background (Section II). The results obtained in the various phases of MBBA and BBOA are presented in Section IV and discussed in Section V.

II THEORY

The forced Rayleigh light scattering is an extension of the well-known quasi elastic Rayleigh light scattering technique.⁹ In both cases, thermal diffusivity measurements are performed by analysing the time dependence of the light scattered by the thermal fluctuations inside the sample. In the classical technique these thermal fluctuations are produced by non-propagating entropy fluctuations, the amplitude of which are small and can be calculated from statistical mechanics.¹⁰ In the forced Rayleigh, a spatially periodic temperature distribution is generated by means of two laser beams intersecting under the angle θ and slightly absorbed by the sample (laser wavelength λ_0). The amplitude of the temperature variation is proportionnal to the absorbed light intensity and can be made much larger than with the spontaneous fluctuations. The resulting thermal phase grating is intense enough to strongly diffract a probing, low-power, beam of different wavelength λ_1 . After a heating pulse, the induced temperature variations throughout the sample are smeared out by thermal diffusion and the diffraction pattern disappears with a finite life time τ_1 .

Let us assume that the periodicity i of the temperature distribution (for small θ , $i \simeq \lambda_0/\theta$) is small compared to the sample thickness L and that L is

smaller than the light absorption length α^{-1} . The problem can thus be considered as one-dimensional and the heat conduction equation describing the induced temperature distribution writes

$$\rho C_p \frac{\partial T}{\partial t} - K \frac{\partial^2 T}{\partial x^2} = I_e(x) \quad (1)$$

K is the thermal conductivity in the x -direction for anisotropic materials, C_p is the heat capacity at constant pressure and ρ the density. $I_e(x)$ is the light intensity absorbed into the sample. For a sinusoidal fringe pattern and if I_0 is the light intensity of the heating laser beam, $I_e(x)$ writes

$$I_e(x) \propto \alpha L I_0 \sin^2\left(\frac{qx}{2}\right) \quad (2)$$

with $q = 2\pi/i$.

Solving Eq. (1) and keeping only the fluctuating terms, one obtains the temperature distribution within the sample at the end of the heating pulse, $t = t_p$ and for $t > t_p$

$$\delta T(t, x) = \delta T(t = t_p) e^{-t/\tau} \cos qx \quad (3)$$

where

$$\tau^{-1} = \frac{Kq^2}{\rho C_p} = Dq^2 \quad (4)$$

D is the thermal diffusivity along the Ox axis.

This periodic temperature distribution produces a spatial modulation of the refractive index n (through the volume thermal expansion, $\partial n/\partial T = \partial n/\partial \rho \cdot \partial \rho/\partial T$). The sample then acts as an optical phase grating¹¹ for the low power probing laser beam. The maximum phase variation is

$$\phi_M = \frac{2\pi}{\lambda_1} L \frac{\partial n}{\partial T} \delta T(t \geq t_p) \quad (5)$$

The intensity I_1 of the first-order diffracted beam is proportionnal to ϕ_M^2 . Therefore, the time dependence of $I_1(t)$ following the heating pulse is

$$I_1(t) \propto e^{-2t/\tau} \quad (6)$$

The intensity decreases exponentially with a time constant $\tau_1 = \tau/2 = Dq^2/2$ which is directly proportional to the thermal diffusivity to be measured.

III EXPERIMENTAL SET-UP

Our experimental set up is very similar to the arrangement originally used by Eichler *et al.*⁸ to study thermal diffusivity in ordinary liquids. It is based upon a simple two-beam interferometer to produce the periodic heating pattern. (Figure 1). The heating laser is an Argon laser $\lambda_0 = 5145 \text{ \AA}$ (Spectra Physics model 165) which is mechanically chopped to obtain $40 \mu\text{s}$ light pulses with an adjustable repetition rate from 20 ms to 33 minutes. The periodicity i of the optical grating is determined by the cross angle θ between the two beams issued from the power laser. Typical values for i are $10\text{--}100 \mu\text{m}$. As the optical grating is made of linear stripes, the measurement of the various components of the thermal diffusivity tensor in anisotropic materials such as liquid crystals is achieved by rotating, with a Dove prism, the fringe orientation in the sample plane. The diffracted beam of a 2 mW He-Ne laser is detected by a RTC-XP2230B phototube fitted with a $300 \mu\text{m}$ pin hole. The time dependence of the diffracted light intensity is then averaged over about 500 heat pulses in a multichannel analyzer, the output of which is fed into a HP 9825 calculator.

The sample is a thin slab of liquid crystal between 2 glass slides separated by $150 \mu\text{m}$ spacers. The deposition of SiO under oblique incidence¹² on the glass surfaces insures the homogeneous alignment of the various liquid crystalline phases. Large monodomains ($\sim 1 \text{ cm}^2$) are obtained with the molecules all aligned in a specific direction parallel to the glass surfaces (planar configuration). In the smectic A and B phases, the smectic planes are thus perpendicular to the glass surfaces.

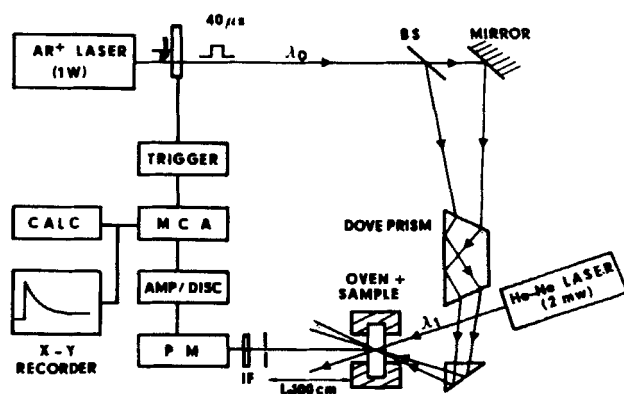


FIGURE 1 Experimental set-up. MCA: multichannel analyser (Intertechnique-BM 25), CALC: calculator (HP 9825), PM: phototube (RTC-XP2230 B) pin hole $\varnothing = 300 \mu\text{m}$. IF: narrow-band interference filter at 6328 \AA .

To provide suitable light absorption at the 5145 Å Argon laser wavelength, we have doped the samples with a dye. Concentrations of about 5×10^{-4} (by weight) of methyl red were found to be sufficient and give absorption length $\alpha^{-1} \sim 300 \mu\text{m}$. Under these conditions, the 40 μs light pulses with a CW laser power of 1 W produce a maximum temperature increase of the sample of less than 10 m °K.

IV RESULTS

1 Calibration experiment

First experiments have been carried out in ethanol doped with methyl red. The value of the thermal conductivity K obtained from the experimental determination of the decay time $\tau/2$ (see Eq. (6)) is

$$K = 3.9 \pm 0.1 \text{ cal/}^\circ\text{K cm sec at } 22^\circ\text{C.}$$

The excellent agreement of this value with handbook data ascertains the validity of the method.

2 *p*-methoxy benzylidene *p*-*n*-butyl aniline (M.B.B.A.)

The measurements have been performed in both the nematic and isotropic phases of MBBA. Figure 2 shows a typical picture of the time dependence of the diffracted intensity after the heating pulse. The decrease looks qualitatively exponential and could in principle be analyzed with Eq. (6) as in the case of ethanol. However it is clear that the diffracted intensity does not decay back to zero as expected in the ideal case, at least at the time scale of the recording. This constant background is due to additional photochemical processes induced by the high power laser pulse. It will eventually decay by intramolecular relaxation of the photo excited species¹³ or by translational mass diffusion¹⁴ (after about one second for this particular case). The detailed understanding of this long-lived optical diffraction grating is not fundamental here. The important idea is that Eq. (6) has to be modified since the maximum phase variation of the grating ϕ_M is the sum of two terms

$$\phi_M = \phi_{\text{thermal}} + \phi_{\text{background}}$$

ϕ_{thermal} is the phase variation of the thermal grating and decays exponentially with a time constant τ .

$\phi_{\text{background}}$ is the phase variation of a second grating superimposed over the thermal grating and due to additional photo chemical processes. Its life time

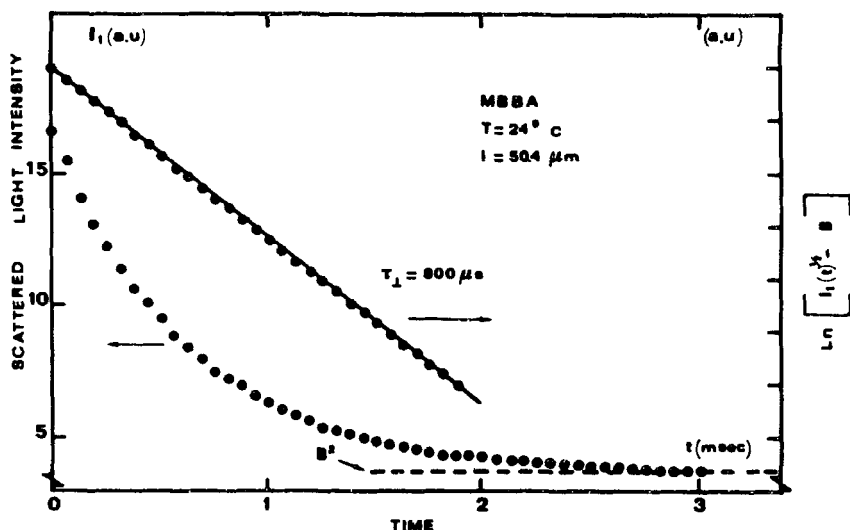


FIGURE 2 Raw data of the time dependence of the diffracted light intensity as displayed on the multichannel analyzer after a 500 pulses averaging. fringe spacing = 50.4 μm . fringes are oriented parallel to the long molecular axes. The slope of the semi-log plot yields the relaxation time τ_{\perp} of the thermal grating due to the thermal diffusivity D_{\perp} normal to the long molecular axes.

is several orders of magnitude longer than τ . Thus the diffracted intensity I_1 writes

$$\frac{I_1}{I_0} \propto \phi_M^2 = (Ae^{-t/\tau} + B)^2$$

where A and B are the amplitude factors for the thermal and photochemical gratings respectively.

Thus the curve of Figure 2 can still be fitted with an exponential but one should take first the root square of the raw data and subtract the background term. A log-plot gives a straight line of slope τ^{-1} (instead of $\tau^{-0.5}$ as previously).

The accuracy on the τ -determination is about 1% and the reproducibility better than 3%. The dependence of τ_{\parallel} and τ_{\perp} versus the fringe spacing is plotted on Figure 3, where $\tau_{\parallel}(\tau_{\perp})$ is the decay time of the grating due to thermal conductivity parallel (perpendicular) to the long molecular axis. Both are proportional to q^{-2} as expected from Eq. (4). Values of D_{\perp} and D_{\parallel} , as obtained from the slope of τ vs q^{-2} , are

$$\begin{aligned} D_{\parallel} &= 1.51 \pm 0.01 \cdot 10^{-3} \text{ cm}^2/\text{s at } 22^{\circ}\text{C} \\ D_{\perp} &= 0.89 \pm 0.015 \cdot 10^{-3} \text{ cm}^2/\text{s} \end{aligned}$$

By convention, D_{\parallel} and D_{\perp} refer to measurements parallel and perpendicular to the local optical axis.

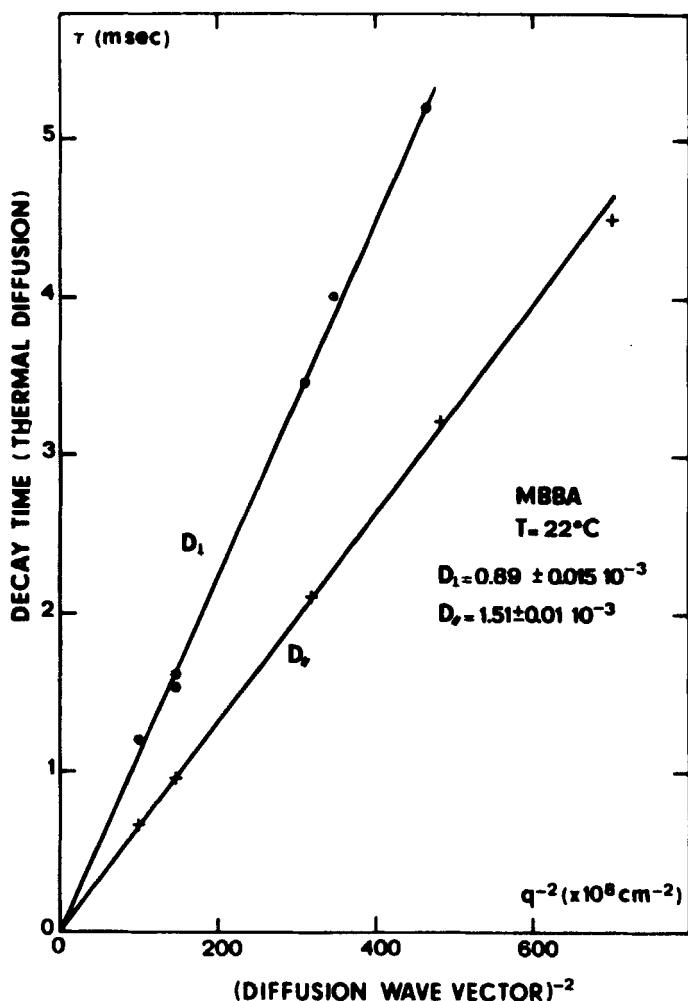


FIGURE 3 q^{-2} —dependence of τ_\parallel and τ_\perp for MBBA at 22°C . The fringe spacing was varied between 50 and $167 \mu\text{m}$. The slopes yield the thermal diffusivity coefficients D_\parallel and D_\perp parallel and perpendicular to the long molecular axis respectively.

Figures 4 and 5 show the temperature dependence of D_\parallel and D_\perp , and of K_\parallel and K_\perp respectively in the nematic and isotropic phases. The K values were calculated from the D values using $K = \rho C_p D$ and taking the literature data for ρ (Ref.15) and C_p (Ref.16). It is striking that D_\perp decreases at the nematic to isotropic phase transition while K_\perp increases. This is due to the strong increase of C_p which overcompensates the decrease of D_\perp .

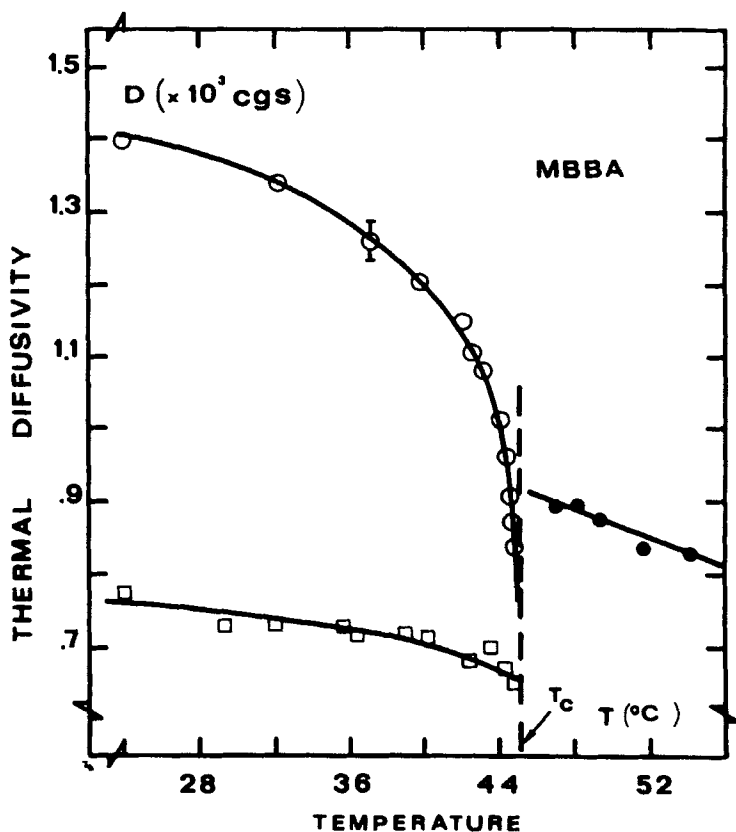
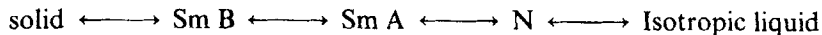


FIGURE 4 Temperature dependence of the thermal diffusivity coefficients of MBBA: D_{\parallel} and D_{\perp} in the nematic phase and D_0 in the isotropic phase.

3 *p*-butoxy benzylidene *p*-*n*-octyl aniline (BBOA)

BBOA is a higher homolog of MBBA. In addition to the nematic and isotropic phases, it exhibits two smectic phases A and B:



The samples have been prepared in the planar configuration as those of MBBA. However, in order to obtain sufficiently large monodomains in the smectic phases, it was necessary to cool very slowly ($<0.1^{\circ}\text{C}/\text{min}$) through the nematic to smectic A phase transition. In this way, the molecules are aligned uniformly parallel to the glass plates, the smectic planes being thus perpendicular.

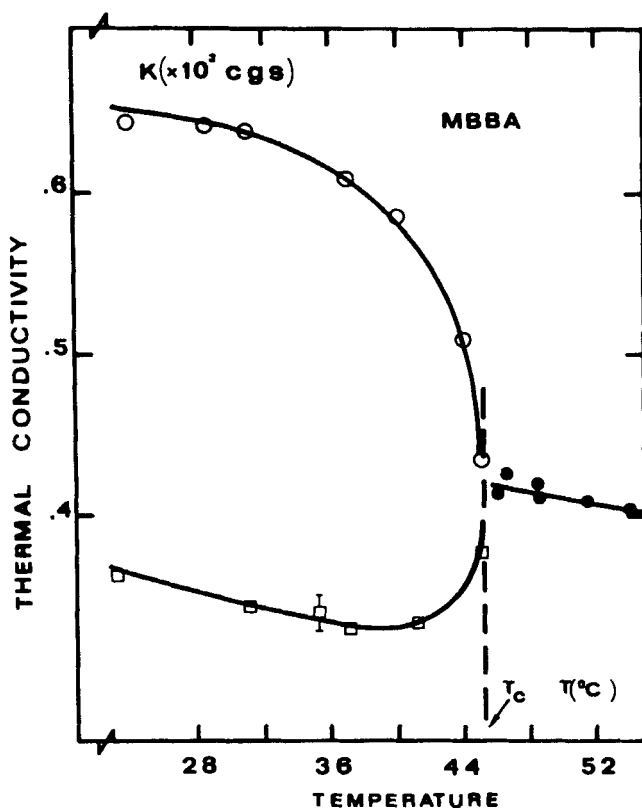


FIGURE 5 Temperature dependence of the thermal conductivity coefficients, K_{\parallel} , K_{\perp} and K_0 for MBBA as derived from the data of Figure 4 by $K = \rho C_p D$.

Figure 6 shows the temperature dependence of D_{\parallel} and D_{\perp} in the various phases of BBOA.

It is observed that D_{\parallel} increases monotonously when T decreases. No drastic changes are detected at the smectic A to nematic or smectic A to smectic B phase transitions. The anisotropic ratio D_{\parallel}/D_{\perp} is ~ 2.10 at 70°C and ~ 2.28 at 48°C .

V DISCUSSION

The results obtained with ethanol are very close to the literature data and can be considered as a good test of the accuracy of the forced Rayleigh scattering technique for thermal diffusivity measurements.

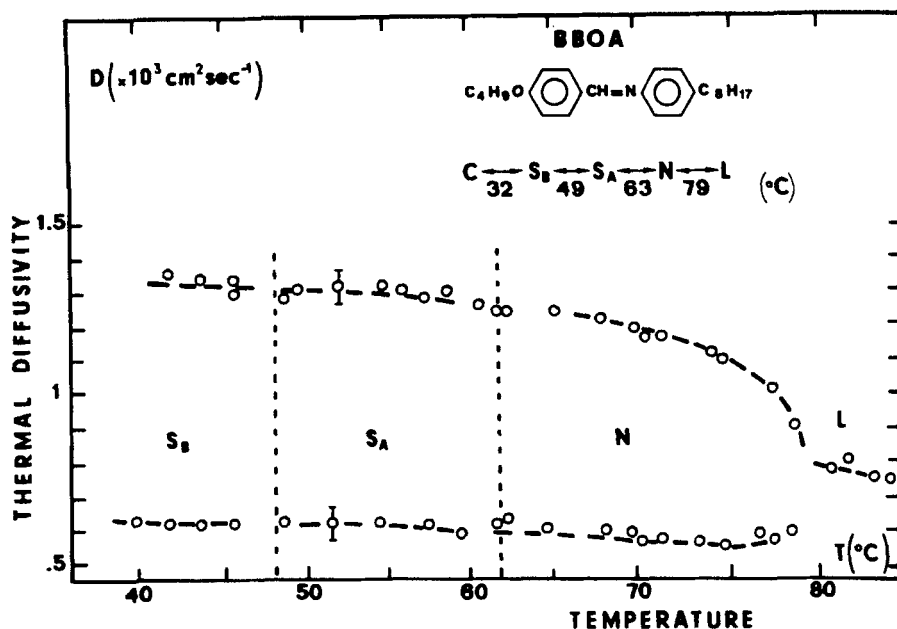


FIGURE 6 Temperature dependence of the thermal diffusivity coefficients in the various phases of BBOA: smectic B, smectic A, nematic and isotropic phases.

In the nematic and isotropic phases of MBBA, the present results are in fair agreement with the heat conductivity data obtained by Vilanova *et al.*⁵ using a heat flux method. The maximum discrepancy is less than 3% in the nematic phase and somewhat higher, ~20% in the isotropic phase. These differences may stem from experimental difficulties in controlling the heat losses in the large samples required by the heat flux method. It may also be due to the conversion factors between the thermal diffusivity D and the thermal conductivity K . There is indeed some scattering in the C_p data reported in the literature and the values measured recently by Koren,⁷ although in agreement with previous results by Janik,¹⁶ are at variance with those of Takako.¹⁷ Last, the heat flux method requires large temperature differences, typically 2 orders of magnitude higher than with the forced Rayleigh, and the temperature gradients are close to the threshold value for the onset of the Benard instability.¹⁸

By the thermal lens technique, Koren⁷ and Kuroda *et al.*⁶ using two slightly different experimental schemes, have also reported values for D in the isotropic phase of MBBA. However the large differences (by a factor of 10) between the absolute values of D in these two experiments and also the

difficulties in the data analysis as discussed by Koren⁷ make extremely difficult the comparison with the present results.

At this point, we should emphasize the advantages of the forced Rayleigh scattering method for thermal measurements

- 1) the length scale of the thermal diffusion process can be measured with great accuracy ($\sim 1\%$)
- 2) the maximum temperature increase is kept small, $\sim 10\text{ m}^\circ\text{K}$, which minimizes convection instabilities and allows for measurements close to phase transitions,
- 3) anisotropic thermal diffusivities are measured by simply rotating the heating linear fringe pattern.
- 4) very small samples are required, typically less than 4 mm^2 over a thickness of $150\text{ }\mu\text{m}$.

Two limitations must be mentioned:

- 1) This is the thermal diffusivity D , and not the thermal conductivity K , which is actually measured. Should absolute K values be needed, additional determinations of ρ and C_p are necessary. On the contrary, if only anisotropic ratios are required, it is obvious that $D_{\parallel}/D_{\perp} = K_{\parallel}/K_{\perp}$.
- 2) whenever the pure sample lacks light-absorbing bands at the heating laser wavelengths, it is necessary to use a dye admixture.

Our experimental results in the nematic and smectic phases of MBBA and BBOA show clearly that the thermal diffusivity is anisotropic. It is greater parallel to the long molecular than normal to it, by about a factor 1.6 and 2.2 in the two examples studied here. This result, although challenged for some time,^{2,3} has been obtained by several authors^{1,4,5} and is now widely accepted. However the origin of this anisotropy has never been studied in details. The present study may cast some light on this problem, by allowing to compare results obtained in both smectic and nematic phases for the first time. It is particularly striking that the anisotropic ratio D_{\parallel}/D_{\perp} stays nearly the same in three mesomorphic phases with such different molecular arrangements as nematic, smectic A and smectic B phases. At the opposite, transport properties such as mass transport, and ionic conductivity are strongly affected by the appearance of the smectic order. The anisotropic ratio can cross the $D_{\parallel}/D_{\perp} = 1$ line in some cases,^{19,20} which proves that the mass transport is considerably slowed down in the direction normal to the smectic layers.

The two different behaviors for transport properties may look surprising. However one should recall that the thermal and mass transport are related to different modes of motion.

Mass transport is related to the low-frequency modes unlike thermal transport which is related to the cooperative, high frequency, phonon-like modes. These phonons have short wavelengths, of the order of a molecular (or atomic) spacing and lifetimes $\sim 10^{-12}$ sec. which corresponds to mean free paths $\sim 20 \text{ \AA}$.²¹ If one recalls that liquid crystal molecules have typical size of 20 \AA length $\times 7 \text{ \AA}$ width, it is therefore not surprising that the thermal conductivity is not sensitive to the long range molecular ordering, smectic or nematic, as experimentally observed.

This may also give some clue to the understanding of the thermal anisotropy in liquid crystals. We tentatively suggest that the thermal anisotropy is related to the molecular shape anisotropy. For elongated molecules, it is expected that the mean free path and also the number of phonon modes within a single molecule is anisotropic. This makes the thermal conductivity to be maximum along the long molecular axis.

This explanation is of course only qualitative. However it is in direct analogy with the well-known "box effect" observed by Biermasz and de Haas²² in solids around 5°K . At these low temperatures, the thermal conductivity is a function of the dimensions of the sample since the mean free path of the thermal phonons is ultimately limited by the sample size. Here, at room temperature, the mean free path is limited by the molecular size, and the thermal conductivity of liquid crystals will be a function of the molecular shape. Further experiments are currently under way to substantiate these points.

VI CONCLUSION

We have demonstrated that the forced Rayleigh scattering technique is well suited to the study of thermal diffusivity in anisotropic liquid crystalline phases. Its numerous advantages over the classical heat flux method has allowed to extend the measurements previously reported in the nematic and isotropic phases down into the smectic phases. Our results show unambiguously that

- 1) the thermal conductivity is anisotropic in the mesomorphic phases,
- 2) contrary to the case of the electrical conductivity, the thermal transport perpendicularly to the smectic planes is not affected by the existence of a quasi solid ordering.

Point 2) implies that the thermal processes in liquid crystals should not be explained primarily by the long range ordering of the molecules. We qualitatively suggest that they can be understood in the framework of intramolecular processes, e.g. the thermal anisotropy being a consequence of the molecular shape anisotropy.

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