

## THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY ANISOTROPY IN A LIQUID CRYSTAL

*F. Mercuri, M. Marinelli, U. Zammit and F. Scudieri*

Dipartimento di Ingegneria Meccanica, II Università di Roma 'Tor Vergata' Via O. Raimondo 00173 Roma, Italy

### Abstract

Thermal conductivity ( $k$ ) and thermal diffusivity ( $D$ ) of the 9CB liquid crystal have been simultaneously determined by a photopyroelectric (PPE) technique in the temperature range from 308 K to 332 K where two different phase transitions occur. The measurements have been performed on oriented samples and the  $k$  and  $D$  anisotropy has been studied. The behaviour of the macroscopic order parameter vs. temperature has been determined and the order of the phase transitions checked.

**Keywords:** liquid crystals, photopyroelectric method, thermal anisotropy

### Introduction

Thermal transport is anisotropic in a liquid crystal (LC) when molecules are aligned along a given direction. It is known that the anisotropy in the thermal transport properties is related to the molecular shape anisotropy. In liquid crystals with rod-like molecules for instance, it has been shown that the thermal conductivity ( $k$ ) and the thermal diffusivity ( $D$ ) values have a maximum (minimum) when the heat flow direction is parallel (perpendicular) to the long molecular axis [2]. However, many aspects related to the mechanisms governing the thermal transport and its anisotropy in LC are still unclear. Nevertheless, due to the difficulty to perform thermal conductivity and thermal diffusivity measurements on aligned liquid crystal samples, only very few experimental data are available in literature. Moreover the rather poor temperature resolution of the measurements has not permitted a detailed investigation of the  $k$  and  $D$  behaviour close to the phase transitions.

In the present work a photopyroelectric a.c. technique (PPE) [1, 3-5] has been employed to simultaneously determine in a 9CB LC sample  $k$  and  $D$  (as well as the specific heat  $c$  which is not reported in this paper) as a function of temperature. In the investigated temperature range 9CB shows three different phases: the isotropic one with the LC molecules randomly oriented and other two phases, the smectic-A and the nematic one, in which the molecules align parallel. The mea-

measurements have been performed on a sample aligned with the molecules long axis parallel ( $\parallel$ ) and perpendicular ( $\perp$ ) to the heat flow direction respectively. From the thermal conductivity data the macroscopic (orientational) order parameter  $k_{\parallel}-k_{\perp}$  has been determined. High resolution measurements have been performed close to the smectic-A/nematic phase transition. The order of the two transitions has been also detected.

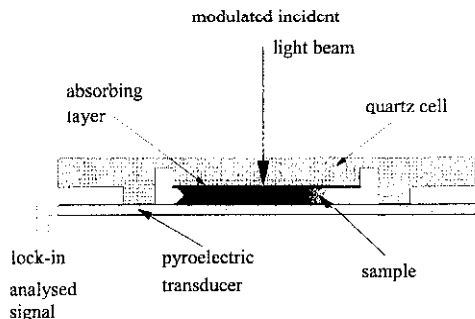


Fig. 1 Liquid samples cell

## Technique and theory

Photopyroelectric technique is an a.c. photothermal technique that allows high temperature resolution simultaneous measurements of static and dynamic thermal parameters on both liquid and solid samples. Moreover it has been proved to be more sensitive than other photothermal techniques as, for instance, the photoacoustic one [1]. In Fig. 1 a cell for liquid samples is sketched in its most common configuration. A  $30\ \mu\text{m}$  thick sample layer is confined between two parallel surfaces. A modulated incident light beam is absorbed at one of the surfaces inducing a temperature oscillation that propagates through the sample thickness to the opposite surface which is one of the two surfaces of a pyroelectric transducer consisting in a  $\text{LiTaO}_3$  crystal slab. The temperature variation induced in the transducer generates a periodic electrical signal whose amplitude  $|V|$  and phase  $\phi$  analysed by a lock-in amplifier, depend on the thermal properties of the sample. Under particular experimental conditions the theory predicts [3–5] the following expressions:

$$|V| \propto \frac{1}{\sqrt{1 + (f/f_c)^2}} \frac{e_p e^{(-\sqrt{\pi f/D_s} L_s)}}{(e_s + e_g)(e_p/e_s + 1)} \quad (1)$$

$$\phi \propto -\sqrt{\pi f/D_s} L_s \quad (2)$$

Here  $f$  is the modulation frequency,  $L_s$ ,  $D_s$ ,  $e_s = \sqrt{\rho_s c_s k_s}$  and  $\rho_s$  are the thickness, the thermal diffusivity, the thermal effusivity and the density of the sample,  $f_c$  is the

transducer plus detection cut-off frequency and  $e_p$  and  $e_g$  are the thermal effusivity of the pyroelectric and front medium, respectively. From Eqs (1 and 2) it can be noted how, once  $L_s$ ,  $f$ ,  $e_p$  and  $e_g$  are known, one can calculate  $D_s$  and  $e_s$ . Then, knowing also  $\rho_s$ , it is possible to determine  $c_s = e_s / \rho_s \sqrt{D_s}$  and  $k_s = e_s \sqrt{D_s}$ .

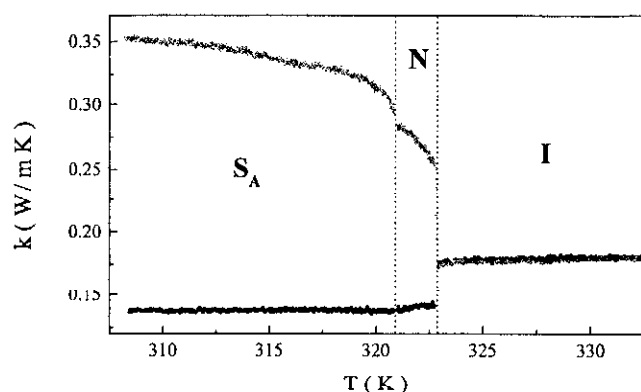


Fig. 2 9CB thermal conductivity data vs. temperature. The black squares are relative to planar alignment ( $k_{\perp}$ ). The light grey squares are relative to homeotropic alignment ( $k_{\parallel}$ )

As already mentioned, one of the features of the PPE technique is that it allows measurements on oriented samples [6]. It is worth noticing that in the smectic-A and the nematic mesophases, the molecules align spontaneously along one direction over sample regions called macrodomain. However, in order to investigate the thermal transport anisotropy, it is necessary to have a homogeneous alignment in the sample that is to say a single monodomain extended over the sample volume. This can be obtained in the photopyroelectric measurements with a suitable treatment of the cell walls. For a I.C sample to be aligned with the molecule long axis along the heat flow direction (homeotropic alignment), the cell wall must be previously treated with a solution of a trimethylcetylammonium bromide. On the other hand, to make the molecules align perpendicularly (planar alignment) to the heat flow direction a 300 Å thick  $\text{SiO}_2$  layer has been deposited on both the cell walls at an angle of about  $60^\circ$  with the normal to the walls themselves.

## Results and conclusions

In Fig. 2 is reported the 9CB  $k$  behaviour for both homeotropic and planar alignment. As expected the two measurements superimpose in the isotropic phase where the molecules are randomly oriented. Going into the  $N$  phase the  $k$  values reaches different levels for the two different alignment: the  $k_{\parallel}$  value shows an increase of about 30% while  $k_{\perp}$  goes to a lower level. Decreasing the temperature throughout the  $N$  phase  $k_{\parallel}$  and  $k_{\perp}$  values show a slight variation. At the ne-

matic/smectic-A (AN) phase transition  $k_{\perp}$  seems not to change appreciably differently from  $k_{\parallel}$  whose value shows a rapid rise just below the transition temperature.

The above results can be used to give a macroscopic description of the orientational ordering in our sample taking the  $k$  anisotropy  $k_{\parallel}$   $k_{\perp}$  as the macroscopic (nematic) order parameter [7]. In Fig. 3 the  $k_{\parallel}$ - $k_{\perp}$  behaviour is reported vs. temperature. The lack of orientational ordering in the isotropic phase obviously to a zero value of  $k_{\parallel}$ - $k_{\perp}$ . In the  $N$  phase the molecules align along one direction and  $k_{\parallel}$ - $k_{\perp}$  gets a positive value. Finally, just below the AN temperature transition the  $k_{\parallel}$ - $k_{\perp}$  behaviour shows an enhance of the orientational ordering due to the onset of the  $S_A$  phase.

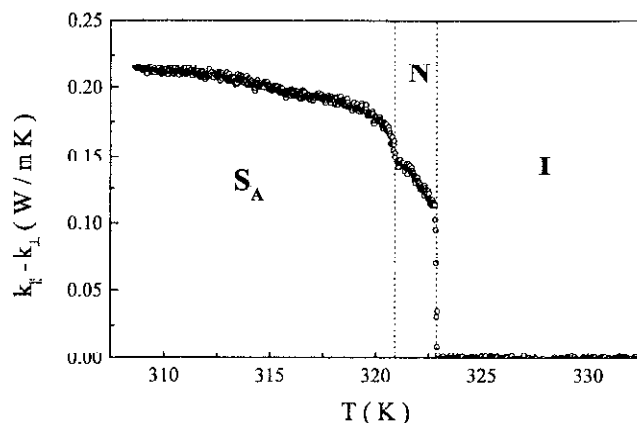


Fig. 3  $k_{\parallel}$ - $k_{\perp}$  behaviour vs. temperature

From the  $k_{\parallel}$   $k_{\perp}$  behaviour is also possible to check the phase transitions order. We have a first (second) order phase transition if the order parameter does (does not) show a discontinuity at the transition temperature. The plot of Fig. 3 clearly shows the first order nature of the NI transition. The situation is less clear at the AN transition where the resolution of the measurement does not enable us to establish the transition order. In order to do that, we have performed high resolution measurements in a small temperature range around the AN transition temperature  $T_{AN}$ . It is worth pointing out that improving the temperature resolution of the measurements corresponds to reducing the thermal gradients generated into the sample by the measurement technique as well as collecting points with a reduced temperature step. In fact, too large temperature inhomogeneities may lead to the collected signal averaged over a temperature interval comparable with the adopted temperature step. In our set-up this can be done by decreasing the incident light power and slowing down the sample rate. In Fig. 4 the  $k_{\parallel}$ - $k_{\perp}$  behaviour has been determined by measurements performed with heating rate of  $0.5 \times 10^{-3} \text{ K min}^{-1}$  and introducing temperature variations of fraction of  $10^{-3} \text{ K}$  in-

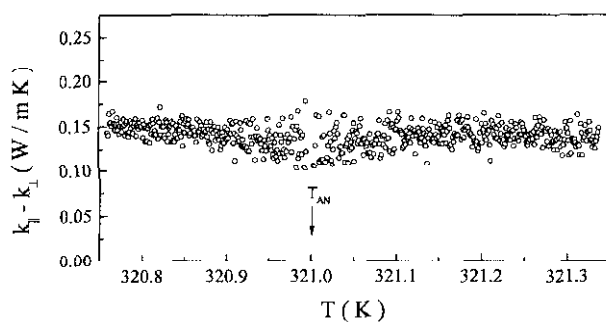


Fig. 4  $k_{\parallel} - k_{\perp}$  behaviour vs. temperature at the AN phase transition obtained by high temperature resolution measurements (see text)

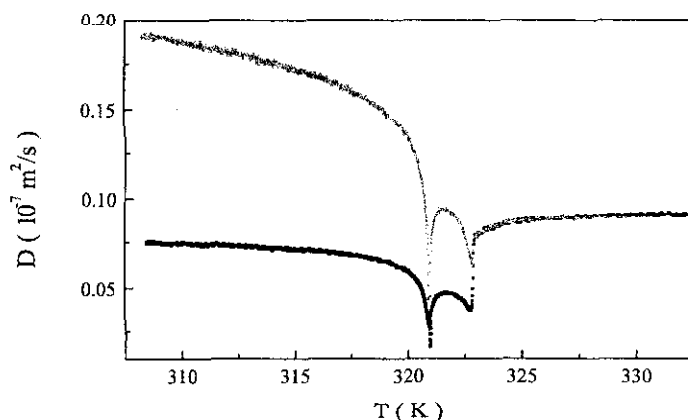


Fig. 5 9CB thermal diffusivity data vs. temperature. The black squares are relative to planar alignment ( $D_{\perp}$ ). The light grey squares are relative to homeotropic alignment ( $D_{\parallel}$ )

side the sample that enable us to collect data every  $10^{-3}$  K. (In the measurements of Fig. 3 the heating rate was  $20 \times 10^{-3} \text{ K min}^{-1}$  and the heating power ten times larger.) The reduction of the heating power causes a decrease of the signal to noise ratio and that is the reason for a larger data scattering with respect to that one of the Fig. 3. The result which comes out from Fig. 4 is that the  $k_{\parallel} - k_{\perp}$  behaviour shows no discontinuity. To explain the slightly larger dispersion of points close to  $T_{AN}$  it must be remind that the  $k$  value is determined by the pyroelectric signal phase and amplitude that has a minimum at  $T_{AN}$ . This corresponds to a minimum in the signal to noise ratio and consequently to a maximum in the dispersion of the data points. We must conclude that in the limit of our resolution the 9CB smectic-A/nematic phase transition is a second order one. It is important to notice how we have been able to detect the phase transition order even with an a.c. calorimetric technique as the PPE one which does not detect latent heat.

Finally Fig. 5 shows the plot of  $D_{\parallel}$  and  $D_{\perp}$  vs. temperature. The anisotropy in the  $D$  behaviour is evident. Furthermore at the transition temperatures  $D$ , unlike the thermal conductivity, clearly shows a critical behaviour. High resolution measurements were then performed in the  $T_{AN}$  region on both planar and homeotropic aligned samples in order to compare the two  $D$  critical behaviours. The collected data have been fitted with a usual expression including a singular term  $\propto |t|^{-b}$  where  $t=(T-T_{AN})/T_{AN}$ . The obtained values of the fitting parameters, and in particular those of the critical exponent  $b$ , coincide for the two different alignments. It follows that the  $D$  critical behaviour does not depend on absolute values of the thermal diffusivity. A detailed analysis of the 9CB critical behaviour at the smectic-A/nematic phase transition, as it is beyond the aim of this paper, will be reported elsewhere [8].

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