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Photopyroelectric Determination of the Order of Liquid Crystal Phase Transitions[1]

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The photopyroelectric technique has been used to measure simultaneously the specific heat, the thermal conductivity, and the thermal diffusivity of 9CB liquid crystal in the temperature range 35 to 60°C, where the sample undergoes a weakly first-order phase transition and a second-order one. Measurements of the anisotropy of the thermal conductivity have also been performed, and the data have been used to establish the order of the above-mentioned phase transitions. Pretransitional effects in the isotropic phase in the thermal diffusivity have been found, and they have been associated with similar effects reported for the specific heat.

KEY WORDS: liquid crystals; phase transitions; photopyroelectric technique; thermal conductivity.

1. INTRODUCTION

It is possible to establish whether a phase transition has a first-order character just by detecting the latent heat associated with the transition itself. AC calorimetric techniques, however, which are based on the detection of temperature oscillation in the sample generated by a periodic heating, cannot detect the latent heat and it is generally believed that they are not suitable to discriminate between a first- and a second-order phase transition. In this paper, we show that if an AC calorimetric technique is sensitive to the anisotropy in thermal parameters, it can be used to perform high-resolution measurements devoted to the determination of the order of a phase transition. The photopyroelectric technique [1] has been used to

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measure simultaneously the specific heat (c), the thermal conductivity (k), and the thermal diffusivity (D) of 9CB liquid crystal in the temperature range 35 to 60°C, where it undergoes the smectic A–nematic (AN) and the weakly first-order nematic–isotropic (NI) phase transition. Though there are many data in the literature, especially specific heat data, showing that the AN transition is a second-order one [2], some doubts still remain [3]. Measurements of the anisotropy in k and D have been performed, and they have been associated with the order parameter. A discontinuity in this quantity at the transition temperature is the signature of a first-order phase transition, while a continuous order parameter means a second-order transition. We have found a clear discontinuity at the NI transition, while high-resolution measurements at the AN one do not show any discontinuity. Some features observed in the order parameter close to the AN transition are discussed, and finally, pretransitional effects in the isotropic phase close to the NI transition are reported.

2. MEASUREMENTS

In Fig. 1 the photopyroelectric setup used for the measurements is sketched. The sample was contained in a 30-μm cell and the temperature oscillation introduced by periodic heating was detected by a $LiTaO_3$ pyroelectric transducer which was the cover of one of the cell sides. Heating on the opposite side was produced via the absorption of a He–Ne laser

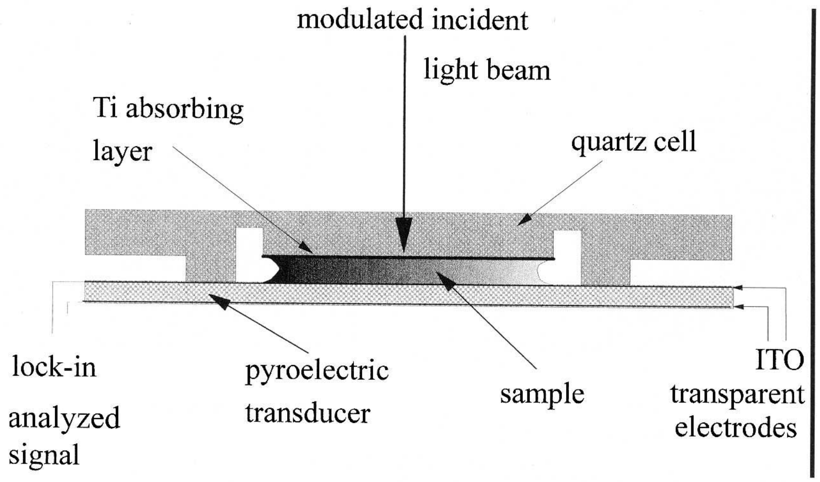

Fig. 1. Photopyroelectric setup.

light modulated at 26 Hz by a very thin (~200-nm) optically opaque and thermally transparent Ti layer in contact with the sample.

The temperature variation induced in the transducer generates a periodic electrical signal whose amplitude |V| and phase ϕ depend on the thermal properties of the sample. Under particular experimental conditions the theory predicts [1, 4] the following expressions:

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

$$\phi \propto -\sqrt{\pi f/D_s L_s} \tag{2}$$

Here f is the modulation frequency; Ls, D_s, $e_s=\sqrt{\rho_s c_s k_s}$, and ρ_s are the thickness, the thermal diffusivity, the thermal effusivity, and the density of the sample, respectively; f_e is the transducer plus detection cutoff 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, also knowing ρ_s, it is possible to determine $c_s=e_s/\rho_s\sqrt{D_s}$ and $k_s=e_s\sqrt{D_s}$.

The liquid crystal molecules can be roughly described as rigid rods, and it has been shown that the thermal conductivity is larger along the long molecular axis than along the short axis ($k_{\|}>k_{\perp}$) [5–7]. The anisotropy in the thermal conductivity, and therefore in the thermal diffusivity, can be investigated aligning the molecules in given directions. In our case the molecules have been aligned with the long axis parallel (homeotropic alignment) and perpendicular (planar alignment) to the hear flow direction. In the first case, we have measured $k_{\|}$, while in the second case $k_{\perp}$ was obtained. The homeotropic alignment has been achieved treating the cell walls with a trimethylcethylammonium bromide solution, while the planar one has been obtained sputtering a thin layer of quartz at an angle of about 60° (for details on orientation procedures see, e.g., Ref. [8]). It is worthwhile to note that the pyroelectric crystal slab as well as its ITO (indium thin oxide) electrodes are transparent to the visible radiation so that the alignment could be checked using a polarizing microscope. Two different heating rates have been used for the measurement over a wide temperature range and the high-resolution ones performed close to the transition temperature: in the first case the heating rate was $0.5\,\mathrm{mK \cdot min^{-1}}$, while in the second case it was $20\,\mathrm{mK \cdot min^{-1}}$.

RESULTS

Figure 2 shows the specific heat in the temperature range 35 to 60°C for the homeotropic and planar samples. As expected, the two curves

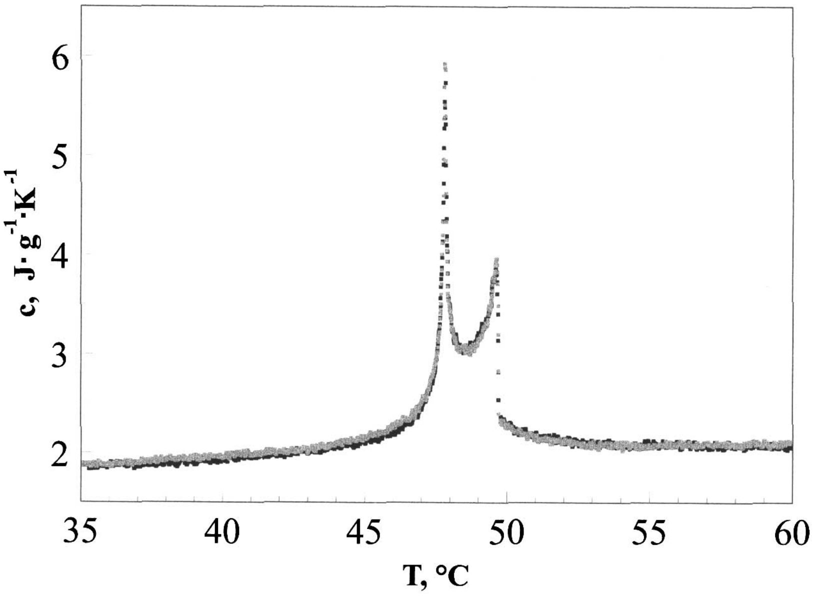

Fig. 2. Temperature dependence of the specific heat for the homeotropic and planar 9CB samples.

superimpose quite well, showing no remarkable differences in the two cases. The two peaks correspond to the AN transition at 47.8°C and to the NI transition at 49.7°C.

Figure 3 reports the k data for the two alignments. The same values for $k_{\parallel}$ and $k_{\perp}$ have been obtained in the isotropic phase, while in the smectic and nematic mesophases, $k_{\parallel} > k_{\perp}$. A jump in both the cases is clearly visible at the NI transition and while $k_{\parallel}$ increases with decreasing temperature, $k_{\perp}$ slightly decreases in the nematic phase and then remains approximately constant in the smectic phase. Similar results have recently been obtained for 5CB [6] and 8CB [7]. In all cases there is a much slower temperature dependence of $k_{\perp}$ with respect to $k_{\parallel}$. Such a behavior can be understood if one considers the temperature dependence of the orientational order parameter, which accounts for the average orientation of the molecules along a given direction. This parameter increases with decreasing temperature, and therefore an increase in $k_{\parallel}$ and a decrease in $k_{\perp}$ should be expected. The different temperature dependence of the conductivity could be due to the different slopes of the k-vs-θ curve close to $\theta = 0$ and $\theta = \pi/2$, where θ is the angle between the molecule long axis and the direction of the heat flow. Assuming rod-like molecules, Rondelez et al. [5] have tried to explain the thermal conductivity behavior with the

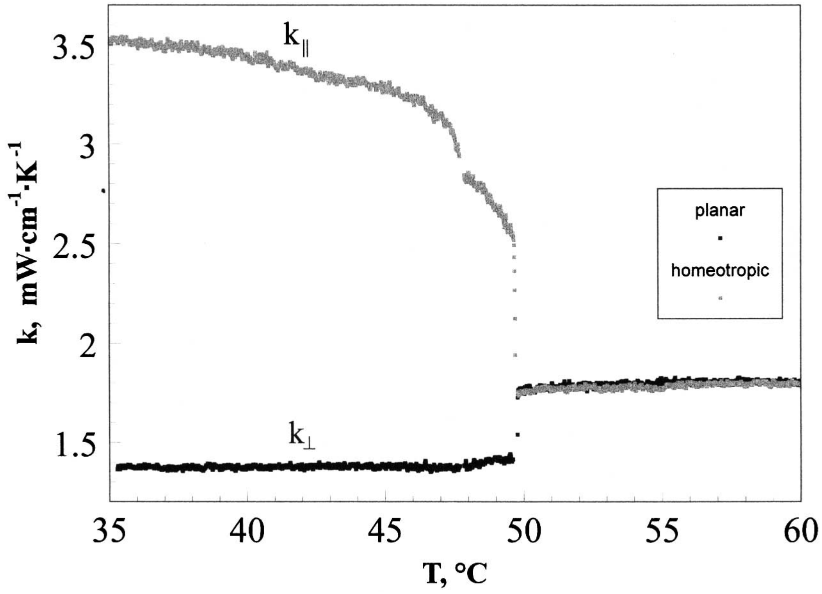

Fig. 3. Temperature dependence of $k_{\parallel}$ and $k_{\perp}$ in 9CB.

analogy between isolated liquid crystal molecules and individual crystalline grains in a polycrystalline material where the thermal conductivity depends on the grain size, which limits the mean free path of the thermal phonon. In this simple view, the elongated shape of the molecules can account for the larger k in the homeotropic case with respect to the planar one since the grain size along the heat flow direction in the homeotropic case is larger than the ones encountered in the planar case.

Another interesting feature which can be detected in Fig. 2 is the clear change in the temperature dependence of $k_{\parallel}$ close to the AN transition temperature: a steeper increase in $k_{\parallel}$ with decreasing temperature on the smectic side with respect to the nematic one is evident. On the other hand, minor changes appear in $k_{\perp}$ in the same temperature range. One possible hypothesis to explain such a behavior is related to the structure of the nematic and smectic A phases. In the first case the molecules are preferentially oriented along a given direction, which in the case of a homeotropic alignment, for example, is parallel to the heat flow direction. There is no correlation among the centers of mass of the molecules. The smectic A phase, on the other hand, can be regarded as a stack of planes in which all the molecules are preferentially oriented with the long axis perpendicular to the plane, with no in-plane correlation. A density modulation in the direction perpendicular to the plane appears below the AN transition temperature and major changes in the heat transport properties would therefore be expected only for heat propagation along this direction. Measurements in a liquid crystal having a smectic C phase [5], in which the molecular long axis is tilted with respect to the normal to the planes $\hat{z}$, however, show no particular features along $\hat{z}$, while a maximum in the conductivity has been found again along the long molecular axis. A more plausible explanation could be related to an increase in the orientational order in the smectic phase with respect to the nematic one due to the appearance of smectic layers. The effect shown in Fig. 4 is more evident in the present case than the one reported for 8CB [7]. This could be due to the width of the nematic range of 8CB, which is much larger (about 7K) than that one of 9CB. Since the orientational order increases with decreasing temperature in the nematic phase, it can approach more closely the smectic one in 8CB than in 9CB, where the AN transition is only a couple of degrees away from the NI one.

Figure 5 shows the temperature dependence of the thermal diffusivity D and of the thermal conductivity k in the isotropic phase. It is clearly evident that D starts to decrease much farther away than k. Such a decrease can be related to pretransitional effects due to the presence in the isotropic phase of pseudo-nematic and pseudo-smectic domains which appear and disappear temporally and spatially [9]. The relaxation time of such a

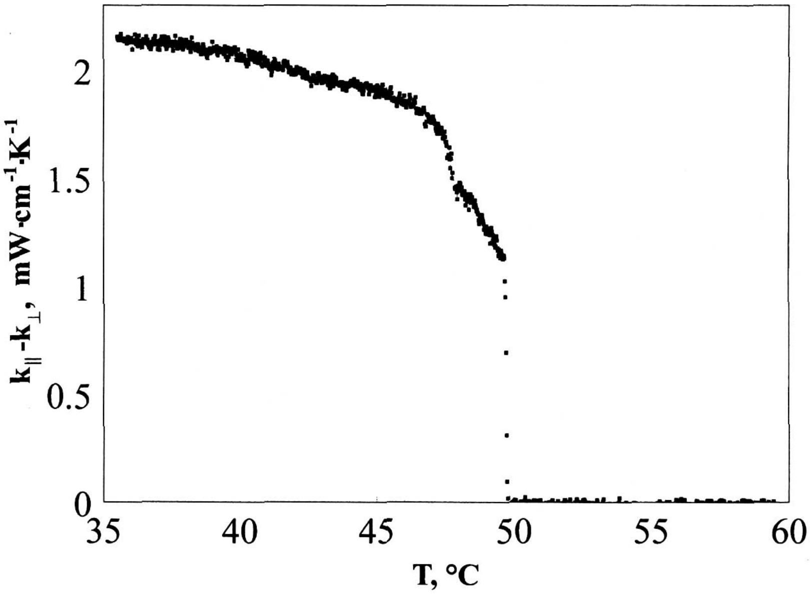

Fig. 4. Temperature dependence of $k_{\parallel}$-$k_{\perp}$ in 9CB.

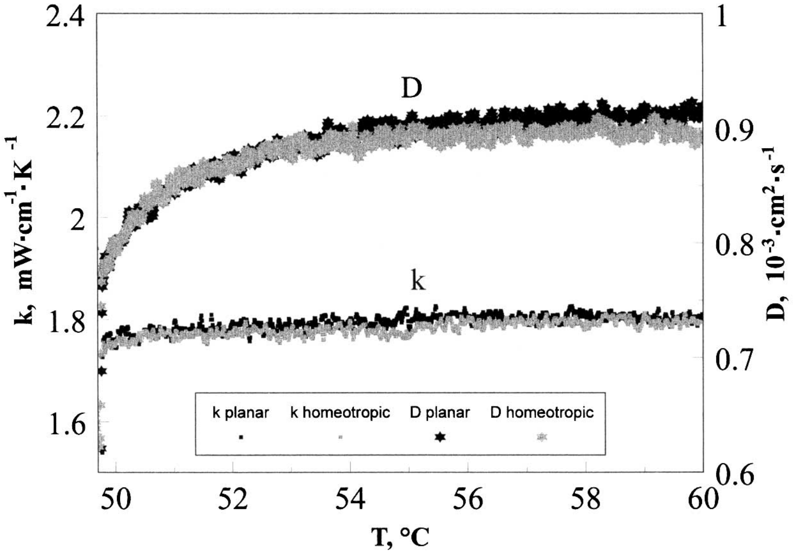

Fig. 5. Temperature dependence of *k* and *D* for homeotropic and planar 9CB samples.

domain increases when T_{AN} is approached [9], but this phenomenon affects only the thermal diffusivity, and not the thermal conductivity. Now, since $D = k/(\rho c)$, where ρ is the density, the observed pretransitonal effect in D must be correlated with a similar pretransitional effect in c, with ρ approximately constant in the temperature range in Fig. 5 [10].

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