

Effects of fluctuations in the orientational order parameter in the cyanobiphenyl (n CB) homologous series

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(Received 23 July 1999; revised manuscript received 7 September 1999)

Photopyroelectric measurements of the anisotropy in the thermal conductivity Δk vs temperature in the n CB ($n=5, \dots, 9$) series are reported. The data have been used to deduce the behavior of the orientational order parameter Q close to the nematic-isotropic ($N-I$) and smectic A -nematic ($A-N$) phase transitions, respectively. It has been shown that near the $N-I$ transition the data for 5CB and 6CB are consistent with the so-called "tricritical hypothesis," which predicts $\beta=0.25$. This is not true for 7CB and 8CB in which the order parameter exhibits a behavior that could be caused by the presence of fluctuations that become increasingly important when the transition temperature is approached. A very simple model, which takes into account the contribution of fluctuations to the orientational order, has been developed close to the $A-N$ transition and it has been shown that it is in good agreement with the experimental results. A semiquantitative explanation for the observed behavior in compounds with different nematic range has been also given.

PACS number(s): 61.30.-v, 64.70.Md, 66.60.+a

I. INTRODUCTION

The relevance of the order parameter in the study of phase transitions is well known. Its dimensionality is a key parameter in the identification of the universality class to which the transition belongs, while its behavior at the transition temperature T_c can be used to establish the order of the transition itself. If it is discontinuous (continuous) at T_c , then the transition is of the first (second) order.

Despite all this, the experimental results up to now available in the literature seem, at least in the case of liquid crystals (LC), less useful than the ones obtained from the measurements of other quantities for testing theoretical predictions [1]. They are usually affected by large uncertainties and poor reproducibility and this is mainly related to some experimental difficulties. The order parameter can be determined from the measurement of the anisotropy of some macroscopic quantities, such as, for example, the diamagnetic susceptibility [2], dielectric constant [3], and optical anisotropy [4] and it is assumed to be proportional to them.

In the case of the nematic-isotropic phase transition, order parameter data have been described in terms of the mean field (MF) model and there is still some debate on the consistency of the observed behaviors with the so-called "tricritical hypothesis" (TCH). This hypothesis [5,6], which was originally based on the analysis of the available experimental results, is supported by calculation based on high-resolution specific-heat measurements that showed that the third and fourth term coefficients in the Landau-de Gennes free energy expansion can be very small [1]. On the other hand, the specific-heat data did also show some inconsistency between the observed background discontinuity and the expected one, this being, among others, one of the reasons why the TCH is far from being considered fully satisfactory in the description of the $N-I$ transition [1].

At the smectic A -nematic phase transition a more rapid increase of the orientational order parameter below T_{AN} with

decreasing temperature has been obtained from the measurement of different quantities such as the anisotropy in the dielectric constant ($\Delta\epsilon$) [7], refractive index (Δn) [4], and more recently in the thermal conductivity (Δk) vs temperature data for 8CB and 9CB [8]. This effect depends on the width of the nematic range and it is more pronounced in 9CB, which has $T_{A-N}/T_{N-I}=0.994$, less evident in 8CB, where $T_{A-N}/T_{N-I}=0.977$ and practically absent in 8S5, where $T_{A-N}/T_{N-I}=0.936$ [8]. From the microscopic point of view this means that as T_{A-N} moves away from T_{N-I} , the orientational order tends to saturate with decreasing temperature and it is not substantially altered by the appearance of the smectic phase. A qualitative explanation for this observation has been given in terms of the coupling between the nematic (Q) and the smectic (ψ) order parameters on the basis of simple MF arguments [8]. A quantitative analysis of this effect should, however, consider the possible effect of fluctuation on the order parameter behavior close to T_{A-N} . In fact, it is well known that the $A-N$ transition is fluctuation dominated and its description in terms of the MF model is not appropriate.

In the present paper we report on the quantitative analysis of the orientational order parameter data obtained from high resolution photopyroelectric measurements of Δk in the n CB homologous series, the thermal conductivity data being the ones we have already reported in Ref. [9]. It is shown that, while in 5CB and 6CB the results are consistent with the TCH, the β exponent of the orientational order parameter is larger in 7CB and 8CB than the 0.25 value predicted by the TCH. A possible explanation for such a behavior could be the increasing importance of smectic fluctuations in these two compounds when T_{N-I} is approached. A quantitative analysis of the Δk data close to the $A-N$ transition in 8CB and 9CB is also reported. The effect of fluctuations on the order parameter has been estimated assuming a proportionality between the smectic contribution to the orientational order δQ and the entropy δS_{A-N} . This leads to an expression

for Q that contains the specific-heat critical exponent α . Following this approach, and using the specific-heat data that, for each sample, have been obtained simultaneously to the thermal conductivity one to calculate α , we have found an excellent agreement between theory and experiment.

II. EXPERIMENT

The photopyroelectric setup used for the thermal conductivity measurements has been already described in Ref. [10]. Data have been obtained from a homeotropically (k_{\parallel}) and planarly (k_{\perp}) aligned samples contained in a 30- μm -thick cell. The alignment has been obtained treating the cell walls with a trimethylcetylammonium bromide solution in chloroform and a grazing angle sputtering of quartz, respectively. The sample plus transducer assembly was contained in a oven and the temperature rate change was 30 mK/min. In the case of high-resolution measurements at the A - N transition in 8CB and 9CB the temperature rate change was 0.3 mK/min.

It is well known [11] that a microscopic order parameter can be assumed to be proportional to the anisotropic part of a macroscopic tensorial quantity. Strictly speaking this is true only in the case of the magnetic susceptibility, where the intermolecular magnetic interactions are small if compared to the external field, while in all the other cases, arbitrary assumptions are required if the above mentioned proportionality will be preserved [11]. In LC, the thermal conductivity is a tensorial quantity and its value strongly depends on the sample orientational order. In the following, we will assume that $\Delta k = k_{\parallel} - k_{\perp} \propto Q$, a detailed discussion on the validity of this assumption being reported in Ref. [8].

Apart from the above mentioned assumption and as stated earlier, there are other aspects that in the past have made the order parameter behavior not very attractive for testing theoretical predictions. Such a test can be performed through the comparison between the theoretical and experimental value of the β exponent or through the determination of $Q^*(T^*)$ and $Q^{**}(T^{**})$, the lower and higher values of the order parameter (temperature) for which the isotropic and nematic phases are stable in the nematic and isotropic phases, respectively. In both cases, however, these quantities are obtained from fits and they are usually affected with relatively large statistical uncertainties. This is essentially due to the experimental determination of the order parameter that, in most cases, is affected by large errors, poor reproducibility, and a temperature resolution that is much lower than the resolution of our measurements. It must be said, however, that due to the very complicated connection between the thermal conductivity and the microscopic processes of the heat transport, the major drawback of the technique is that it does not give Q values but only a quantity proportional to it.

III. N - I TRANSITION

In the following we will describe our experimental results on 5CB, 6CB, 7CB, and 8CB on the basis of the TCH. Generally speaking, if one considers a Landau-de Gennes free energy expansion in powers of the order parameter up to the fourth order, a tricritical point occurs if $B = C = 0$, where B and C are the coefficients of the third- and fourth-order

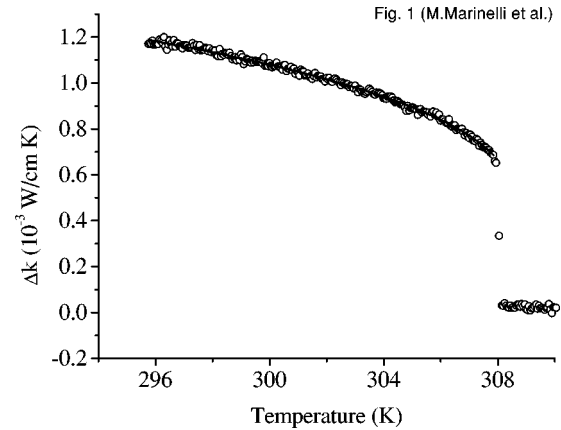


FIG. 1. Thermal conductivity anisotropy vs temperature for 5CB. Solid line corresponds to fit I in Table I.

terms. This makes essential the introduction of a sixth-order term in the expansion, whose role is crucial in the description of the critical behavior. The approximation seems to be supported by some calculations based on experimental results [1], but, as said before, is far from being fully satisfactory and more experimental and theoretical work needs to be done.

Results and discussion

Figures 1, 2, 3, and 4 show the Δk vs T data for 5CB, 6CB, 7CB, and 8CB, respectively. The data have been fitted with a nonlinear fitting routine with the following expression:

$$\Delta k = k_0 + k_1(T^{**} - T)^\beta. \quad (1)$$

The choice of Eq. (1) comes from the assumption $\Delta k \propto Q$ and therefore the β exponent is equal to the order parameter one. k_0 , k_1 , T^{**} , and β are the adjustable parameters with the statistical uncertainties given by $\sigma_i = \sqrt{C_{i,j}\chi^2}$, where $C_{i,j}$ is the diagonal element of the variance-covariance matrix. The fit results are reported in Table I. The β values obtained from 5CB and 6CB data are, in all cases, consistent, within the uncertainties, with the tricritical value 0.25. No significant differences in the fit quality have been found for both compounds if β was fixed to

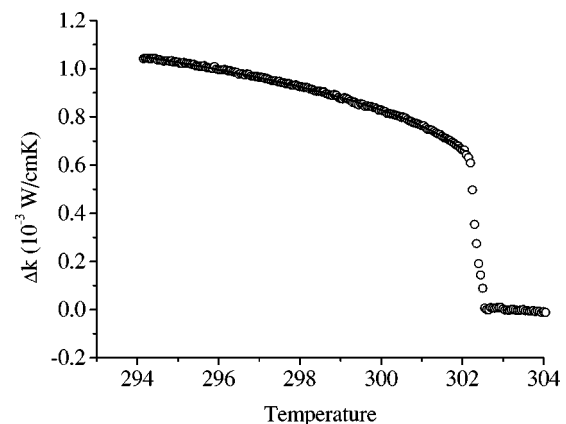


FIG. 2. Thermal conductivity anisotropy vs temperature for 6CB. Solid line corresponds to fit III in Table I.

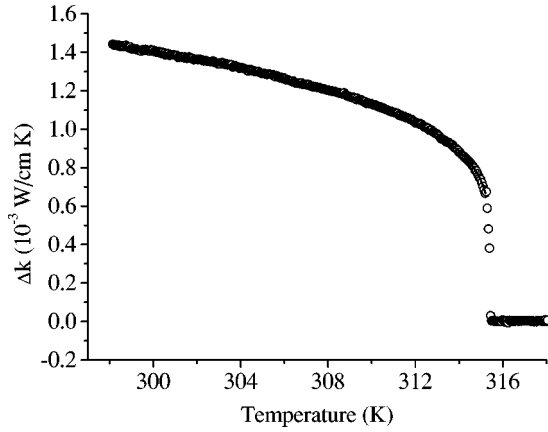


FIG. 3. Thermal conductivity anisotropy vs temperature for 7CB. Solid line corresponds to fit V in Table I.

0.25 (fits II and IV). In 5CB, fixing β (fit II), an increase of k_1 but also a decrease of k_0 with respect to fit I to an apparently unphysical negative value, which, however, has a large uncertainty, has been found, while in 6CB (fit IV) the variation of k_1 and k_0 with respect to fit III are within the statistical uncertainties. This leads to the conclusion that fit I and fit III are almost identical to fit II and IV, respectively.

The best fit for 7CB (fit V) gives $\beta = 0.31 \pm 0.01$, a value that differs significantly from the tricritical one. If we fix $\beta = 0.25$ (fit VI), the quality of the fit decreases, as shown by the increase of the χ^2 value, therefore suggesting that the data are not consistent with the TCH. Such a contradiction appears to be relevant if we consider that the 7CB data are less noisy than the 5CB and 6CB data and this is reflected in the statistical uncertainties that are, for all the parameters, smaller than the ones associated with these two compounds.

Fit VII corresponds to 8CB and it has been obtained considering data in a temperature range of 5.6 K below T_{N-I} . We have not included in the fit data points in the nematic phase below 308.1 K, since, as can be seen from Fig. 4 and discussed in more detail later on, they are affected by fluctuations associated to the $A-N$ transition. The obtained β value is larger than the one predicted by TCH but also larger than the 7CB one. Also in this case we have tried to fix $\beta = 0.25$ but this produces an increase of the χ^2 value as shown in fit VIII.

The difference between the β values obtained for 7CB and 8CB is within the statistical uncertainties that in the

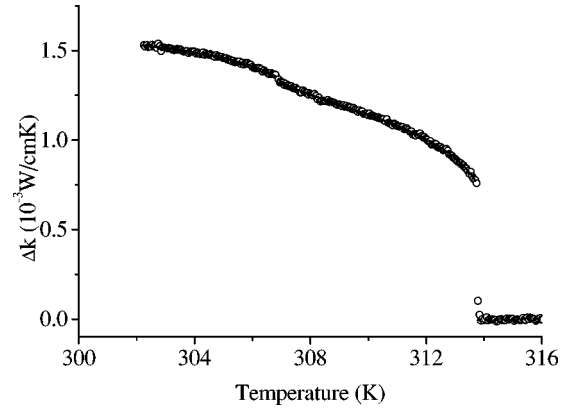


FIG. 4. Thermal conductivity anisotropy vs temperature for 8CB. Solid line corresponds to fit XII in Table II.

latter is much larger than in the former. This is mainly due to the much narrower temperature range used in fit VII and not to the quality of experimental data as can be seen from Figs. 3 and 4. We have then tried to apply a three-point adjacent smoothing to 7CB and 8CB data sets and fit them again. While in the case of 7CB no appreciable variation has been obtained in the parameters, small changes have been found in 8CB and the results correspond to fit IX. The χ^2 value of this fit and the statistical uncertainties are obviously smaller and this makes, in this case, the difference between the β values in fit V (7CB) and IX (8CB) statistically relevant.

There are several possible reasons that could explain the behavior we have found in 7CB and 8CB. One could be the presence of nematic fluctuations. It is, however, quite unlikely that the latter can produce such an effect in 7CB and 8CB and are practically negligible in 5CB and 6CB, where a β exponent consistent with the TCH has been found. Another possible explanation could be the presence of smectic fluctuations and their possible coupling to the nematic ones. 7CB has no thermodynamically stable smectic phase but it could not be excluded, at least in principle, that transient smectic order can appear locally in the nematic phase close to T_{N-I} . If this is the case, we expect that this effect becomes increasingly important in 8CB and 9CB with a subsequent increase of the β exponent. Fluctuations, in fact, can be regarded as a disturbance to the orientational order and can therefore produce a more rapid decrease of Δk close to the transition temperature that results in a larger β value. While nothing can be said on 9CB because of its very narrow nem-

TABLE I. Fit obtained using Eq. (1). For 8CB, only data 5.6 K below the $N-I$ transition have been considered. Fit IX has been obtained after a three-point adjacent smoothing of the experimental data set.

Fit	k_0	k_1	T^{**}	β	χ^2
I (5CB)	$(2.6 \pm 2.4)10^{-4}$	$(4.1 \pm 1.8)10^{-4}$	309.01 ± 0.54	0.32 ± 0.08	0.92
II (5CB)	$(-1 \pm 2)10^{-5}$	$(6.2 \pm 0.1)10^{-4}$	309.45 ± 0.12	0.25	1.45
III (6CB)	$(1.8 \pm 1.4)10^{-4}$	$(4.8 \pm 1.2)10^{-4}$	303.01 ± 0.66	0.27 ± 0.04	1.02
IV (6CB)	$(10.0 \pm 0.8)10^{-5}$	$(5.5 \pm 4.5)10^{-4}$	303.10 ± 0.75	0.25	1.02
V (7CB)	$(4.1 \pm 0.2)10^{-4}$	$(4.3 \pm 0.2)10^{-4}$	315.39 ± 0.26	0.31 ± 0.01	1.01
VI (7CB)	$(21.0 \pm 0.3)10^{-5}$	$(60.0 \pm 0.2)10^{-5}$	314.59 ± 0.26	0.25	1.6
VII (8CB)	$(5.2 \pm 1.3)10^{-4}$	$(3.7 \pm 1.0)10^{-4}$	314.07 ± 0.21	0.37 ± 0.06	1.1
VIII (8CB)	$(1.4 \pm 0.2)10^{-4}$	$(6.9 \pm 0.1)10^{-4}$	314.42 ± 0.05	0.25	1.4
IX (8CB)	$(5.4 \pm 0.8)10^{-4}$	$(3.5 \pm 0.6)10^{-4}$	314.04 ± 0.13	0.38 ± 0.01	0.5

atic range, the results reported in Table I, particularly fits V, VII, and IX, show that β increases from 7CB and 8CB and that this increase could be statistically relevant. It should be noted that the results obtained for 8CB do not agree with those reported in Ref. [7], where, from $\Delta\varepsilon$ measurement, a β value consistent with the TCH one has been obtained. Though we think that more accurate data, leading to a definite conclusion, are needed, it seems, however, on the basis of the fit results, that the influence of smectic fluctuations cannot be excluded.

Apart from the above mentioned hypothesis, the main conclusion that can be drawn from the results reported above is that the TCH, though it seems to be confirmed in several LC, is not generally applicable. We believe that it can provide a useful background for the development of more satisfactory theories that will include other effects as, for example, the above mentioned possible effect of fluctuations.

IV. A-N TRANSITION

In the following we will discuss Δk vs T data obtained for 8CB and 9CB. These two compounds exhibit a smectic A phase and we will analyze in detail the behavior of $\Delta k(\propto Q)$ close to the T_{A-N} transition temperature. For this purpose simple theoretical models will be introduced and contrasted with the experimental data.

A. Theory

The order of the A-N transition is still an open question: though most of the experimental results can be described in terms of a model developed for a second-order phase transition [12], some recent work seems to suggest that a very weak first-order contribution could be present [13]. In the following we will assume a purely second-order nature as we have already done in the analysis of the specific-heat data [8,10], obtained simultaneously with k .

If, after Landau, we approximate the free energy close to a phase transition as a series expansion and if only terms up to the second power are considered, we have

$$F - F_0 \approx \frac{1}{2} \chi_{N-I}^{-1} \delta Q^2 + \frac{1}{2} \chi_{A-N}^{-1} |\psi|^2 + \lambda |\psi|^2 \delta Q. \quad (2)$$

where χ_{N-I} and χ_{A-N} are the nematic and smectic susceptibility, respectively, λ is a negative constant, δQ is the contribution to the orientational order induced by the smectic layering, and $|\psi|^2$ is the amplitude of the density wave that represents the smectic order parameter. The expression simply comes out from the sum of the smectic and nematic contribution to the free energy with the addition of a coupling term between the two order parameters. Minimizing with respect to δQ we obtain

$$\delta Q = \lambda \chi_{N-I} |\psi|^2. \quad (3)$$

χ_{N-I} being a response function that increases approaching T_{N-I} , it turns out that δQ , close to T_{A-N} , decreases if T_{A-N} moves away from T_{N-I} . As already said, this is consistent with the experimental results reported in Ref. [8], for 8S5, 8CB, and 9CB, but, as pointed out in the same paper, gives only a qualitative description of the order parameter behav-

ior. If one wants to go into further details and use the same MF approach for a quantitative description of the orientational order parameter close to T_{A-N} , the temperature dependence of δQ must be considered. Assuming the MF values for the susceptibility and the order parameter exponent $\gamma = 1$ and $\beta = 1/2$, we get

$$\delta Q \propto |T - T_{A-N}| \quad (4)$$

and therefore for $T < T_{A-N}$

$$Q = Q_N + \delta Q = Q_0 + Q_1 |T - T^{**}|^{\beta} + Q_2 |T - T_{A-N}|, \quad (5)$$

where Q_N is the orientational order parameter in the nematic phase in the absence of smectic order and the usual power law description for the nematic orientational order parameter has been used, or

$$\Delta k = k_0 + k_1 |T - T^{**}|^{\beta} + B |T - T_{A-N}|. \quad (6)$$

It is well known, however, that the MF approach cannot be used for the description of the A-N transition that is fluctuation dominated. This means that, at least in the vicinity of T_{A-N} , the behavior of the orientational order could be different from that reported in Eq. (5) if one considers the fluctuation contribution to Q . Assuming a proportionality between Q and the entropy of the system S , this contribution can be easily obtained. δS_{A-N} can be calculated taking the integral of the singular part of the specific heat

$$c_s = A |T - T_{A-N}|^{-\alpha} (1 + D |T - T_{A-N}|^x) \quad (7)$$

including the correction to scaling term, which will give the crossover to the regular behavior. We therefore get

$$\begin{aligned} Q &= Q_N + \delta Q \\ &= Q_0 + Q_1 |T - T^{**}|^{\beta} \\ &\quad + Q_2 |T - T_{A-N}|^{1-\alpha} + Q_3 |T - T_{A-N}|^{1+x-\alpha} \end{aligned} \quad (8)$$

or

$$\begin{aligned} \Delta k &= k_0 + k_1 |T - T^{**}|^{\beta} \\ &\quad + k_2 |T - T_{A-N}|^{1-\alpha} + k_3 |T - T_{A-N}|^{1+x-\alpha}. \end{aligned} \quad (9)$$

Comparing Eq. (6) and Eq. (9), it turns out that the smectic order contribution is very different in the two cases. While in the MF approach we simply have a linear term that is added to the nematic background below T_{A-N} ; in Eq. (9) the contribution of the smectic layering has a different temperature dependence and it is also present on both sides of the transition temperature. It should be noted that δQ decreases if α decreases and that Eq. (9) tends to Eq. (6) when α goes to zero and the correction to scaling term is not included.

B. Results and discussion

Figures 4 and 5 report the Δk vs T data for 8CB and 9CB. The data have been fitted with the fitting routine mentioned above using Eqs. (6) and (9) and the results are reported in Table II. We have used Eqs. (6) and (9) both below and above T_{A-N} , thus implicitly $A/A' = D/D' = 1$ [14], where

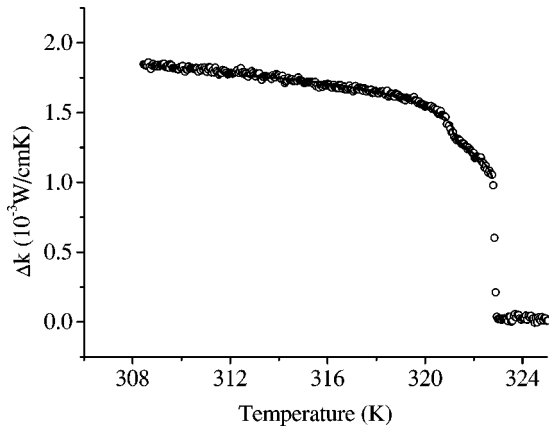


FIG. 5. Thermal conductivity anisotropy vs temperature for 9CB. Solid line corresponds to fit XIII in Table II.

primed coefficients refer to $T < T_{A-N}$. The value of the critical exponent α and T_{A-N} have been also fixed to the one resulting from the specific-heat data, which, as said before, have been obtained simultaneously with the thermal conductivity from the same experimental data set. The values are $\alpha_{8CB} = 0.32$ and $\alpha_{9CB} = 0.52$. The x exponent of the correction to scaling term has been fixed to 0.5, this values giving the best fit in the case of the specific heat.

Fit X in Table II has been obtained using Eq. (6) and fixing $\beta = 0.37$. As can be seen from the χ^2 value, the fit has a rather poor quality. This is also confirmed by the residue plot (not shown) that shows a systematic deviation, especially in the smectic region. The B value is very small and this clearly means that data can be only fitted if the MF term, which should account for smectic contribution, is practically zero. Fit XI corresponds to 9CB data fitted with Eq. (6). To compensate for the very narrow nematic range present in this compound and therefore for the small number of data points in this region, we have only considered data points in the smectic region down to 312.44 K. As shown by the χ^2 value, also in this case the quality of the fit is rather poor.

As expected, the results lead to the conclusion that the MF model does not succeed in giving a quantitative description of the order parameter behavior close to T_{A-N} . We can then conclude, as in the case of other thermodynamic quantities, that the observed behavior of the orientational order parameter in the vicinity of T_{A-N} , is affected by fluctuations. It should be noted once again that the arguments and the conclusions reported above could be reached because of the high sensitivity and temperature resolution of our measurements.

Fit XII has been obtained fixing $\beta = 0.37$, which is the value we have obtained from fit VII in Table I. k_0 , k , and T^{**} were adjustable parameters and it is interesting to note that the values we have obtained are consistent, within the statistical uncertainties, to the ones reported in Table I, fit VII. Moreover, the uncertainties associated with k_0 , k , and T^{**} are much smaller in fit XII than in fit VII and this confirms that in this last case they were essentially due to the reduced temperature range used in the fit. We have also tried to fit the data fixing their value to those obtained in fit VII and no appreciable variation in the fit quality was detected. The fit quality is excellent as can be seen from χ^2 and the solid line reported in Fig. 4 and it confirms the validity of the assumptions we have made in the derivation of Eq. (9).

In 9CB the effect of smectic layering on the orientational order below T_{A-N} is more evident than in 8CB as can be seen from Fig. 5 and as expected from Eq. (9), since $\alpha_{9CB} > \alpha_{8CB}$. The vicinity of T_{N-I} and T_{A-N} makes the data analysis more difficult, but, nevertheless, fit XIII, which has been obtained with Eq. (9) and fixing $\beta = 0.37$, is of a good quality as shown by the χ^2 value and by the solid line in Fig. 5. We have tried to fit the data with β as a free parameter but we got values with huge statistical uncertainties and fit quality that did not show any significant variation if β was fixed to different values around 0.37. This is obviously due to the very narrow nematic range of this compound.

Δk vs T data for $\bar{8}S5$ has been reported in Ref. [8] and nothing similar to what was found in 8CB and 9CB could be detected close to T_{A-N} . Obtaining $\alpha_{\bar{8}S5} = -0.02$, this is consistent with what we should expect from Eq. (9), where δQ must decrease with decreasing α and therefore the effect of smectic layering is less and less evident moving from 9CB to 8CB and $\bar{8}S5$.

V. CONCLUSIONS

The temperature dependence of the orientational order parameter Q has been derived from photopyroelectric measurements of the anisotropy in the thermal conductivity $\Delta k \propto Q$. The results obtained for 5CB, 6CB, and 7CB close to the $N-I$ phase transition have been contrasted to the theoretical prediction of the so-called ‘‘tricritical hypothesis.’’ While in the case of 5CB and 6CB we found a good agreement between the theory and the experiment; this was not possible for 7CB. Possible reasons for this disagreement have been discussed and it is suggested that the disagreement could be due to the presence of fluctuations in a temperature region close to T_{N-I} .

TABLE II. Fits X and XI have been obtained using Eq. (6), while fits XII and XIII have been obtained using Eq. (9).

Fit	k_0	k_1	T^{**}	$B (T < T_{A-N})$	χ^2	
X (8CB)	$(-8.1 \pm 1.3)10^{-4}$	$(12.3 \pm 0.5)10^{-4}$	317.19 ± 0.49	$(-0.2 \pm 1.2)10^{-6}$	10	
XI (9CB)	$(-2.6 \pm 6.2)10^{-3}$	$(1.3 \pm 0.3)10^{-3}$	323.75 ± 0.90	$(-5 \pm 1)10^{-5}$	5	
Fit	k_0	k_1	T^{**}	k_2	k_3	χ^2
XII (8CB)	$(3.7 \pm 0.4)10^{-4}$	$(4.7 \pm 0.2)10^{-4}$	314.27 ± 0.08	$(-6.0 \pm 0.1)10^{-5}$	$(3.00 \pm 0.2)10^{-5}$	1
XII (9CB)	$(10.8 \pm 0.7)10^{-4}$	$(2.4 \pm 0.5)10^{-4}$	322.77 ± 0.14	$(-14.0 \pm 0.8)10^{-5}$	$(3.0 \pm 0.8)10^{-5}$	1.4

A quantitative analysis of Δk vs T in the vicinity of the T_{A-N} has been also reported for 8CB and 9CB compounds. A model that takes into account the contribution of the fluctuations to the order parameter close to the $A-N$ transition has been developed and compared with the experimental results. We have found a good agreement between the theory and the experiments, the model being also able to account for the

different effect of fluctuations in Q reported close to T_{A-N} in compounds with different nematic ranges.

ACKNOWLEDGMENT

The authors would like to thank M. Anisimov for many useful discussions during the preparation of the manuscript.

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