Thermal conductivity, diffusivity, and heat-capacity studies at the smectic-A–nematic transition in alkylcyanobiphenyl liquid crystals

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Thermal conductivity, diffusivity, and specific-heat studies were carried out simultaneously over the smectic-A–nematic transition in alkylcyanobiphenyl liquid crystals with different nematic ranges. The critical exponents of all the thermal parameters have been calculated and discussed in terms of the dynamic scaling law of the asymmetric planar magnet model, which applies to three-dimensional XY-like transitions.

The smectic-A to nematic (Sm-A–N) transition in liquid crystals has been a subject of extensive theoretical and experimental studies. The universality class of the transition has not, in fact, been definitely established and it has been shown that the transition can be both first and second order. On the basis of a mean-field molecular model, Kobayashi[1] and McMillan[2] have shown that the transition should be second order provided the ratio $T_{Sm\text{-}A\text{-}N}/T_{N\text{-}I}<0.87$, where $T_{Sm\text{-}N}$ and $T_{N\text{-}I}$ are the Sm-A–N and the nematic-isotropic (I) transition temperatures respectively, thus predicting the existence of a tricritical point (TCP) for $T_{Sm\text{-}A\text{-}N}/T_{N\text{-}I}=0.87$. Similar qualitative features were later obtained by de Gennes[3] and the order of the transition depended on the strength of the coupling between the smectic and nematic phases order parameter. Moreover, based on the analogy with the transition of a superconductor[3] and from the renormalization work by Lubensky and Chen,[4] the second order Sm-A–N transition was placed in the same universality class as a superfluid, namely, the class of the three-dimensional XY-like transitions.

Experimentally, the TCP in the Sm-A–N transition was observed in mixtures of 4-cyano-4′-n- alkylbiphenyl (nCB),[5] nOm [N(p alkoxy benzilidene) p-n-alky-anilines] homologous series compounds,[6] and heptyloxypentylthiolbenzoate (7S5) and octyloxycyanobiphenyl (80CB).[7] In particular, the calorimetric studies carried out on the nCB series showed that the critical exponent of the specific heat ranged between $\alpha=-0.03$, close to the XY value [-0.007 (Ref. 8)] for $T_{SM\text{-}A\text{-}N}/T_{N\text{-}I}=0.95$ and the mean-field tricritical value $\alpha=0.5$, in 9CB, for $T_{Sm\text{-}A\text{-}N}/T_{N\text{-}I}=0.994$. On the basis of such results it was suggested that the $T_{Sm\text{-}N}/T_{N\text{-}I}$ dependence of the α values could be caused by a crossover between tricritical and XY-like critical behavior. Such a crossover picture could not fit all the results. Furthermore it was found that even for compounds with larger nematic ranges (smaller values of $T_{Sm\text{-}A\text{-}N}/T_{N\text{-}I}$), whose α values tend to approach the XY-model one, the critical exponents of the susceptibility γ and correlation length ν were not consistent with the XY-model values.[9] The discrepancy persisted for compounds with α closer to the tricritical value.[10] There are other critical exponents, namely the ones of the thermal conductivity and thermal diffusivity, on which very little has as yet been reported, which can be determined and compared with the values and scaling laws predicted by the theory that applies to the superfluid transition to further investigate to what extent the XY model appropriately describes the critical behavior in the Sm-A–N transition.

In this paper the results of the critical exponents of the thermal diffusivity D, thermal conductivity k, as well as that of the heat capacity c, are reported at the Sm-A–N transition in compounds and mixtures of the nCB series having different $T_{SM\text{-}A\text{-}N}/T_{N\text{-}I}$ values. The results are compared with the ones predicted by the theory of dynamic critical phenomena for an asymmetric planar magnet,[11] a model which is applicable to superfluid ^{4}He transition. The measurements were performed by using the photoacoustic (PA) technique in the gas microphone configuration, which has been shown to be well suited to study simultaneously the critical behavior of k, c, and D over phase transitions.[12] The photoacoustic technique is based on the effect of the periodic heating of a sample by a modulated lamp or laser source. In the gas microphone configuration, the heated sample is contained in a gas tight volume and induces in the volume gas a periodic overpressure which is detected by a microphone in a lock-in detection configuration. When the sample is optically and thermally thick[12] the PA signal phase depends on the sample thermal diffusivity $D=k/\rho c$ (ρ is the density), while the signal amplitude also depends on the sample thermal effusivity $e=(k\rho c)^{1/2}$. D, k, and c can thus be simultaneously worked out. The investigations were carried out on samples of 9CB, 8CB, and a 0.76 8CB mole fraction mixture of 8CB and 7CB. The values of $T_{Sm\text{-}A\text{-}N}/T_{N\text{-}I}$ were 0.994, 0.967, and 0.962, respectively. The results of c, D, and k are reported for each sample in Figs. 1, 2, and 3, respectively. In all the investigated samples the heat capacity and the thermal conductivity show peaks over the transition region. The thermal diffusivity data show a dip with a small-peak structure in the vicinity of the transition temperature. The peak is due to a sharper rise in the thermal conductivity than in the heat capacity in the region right next to the transition temperature. The slower rise in c can be due to rounding

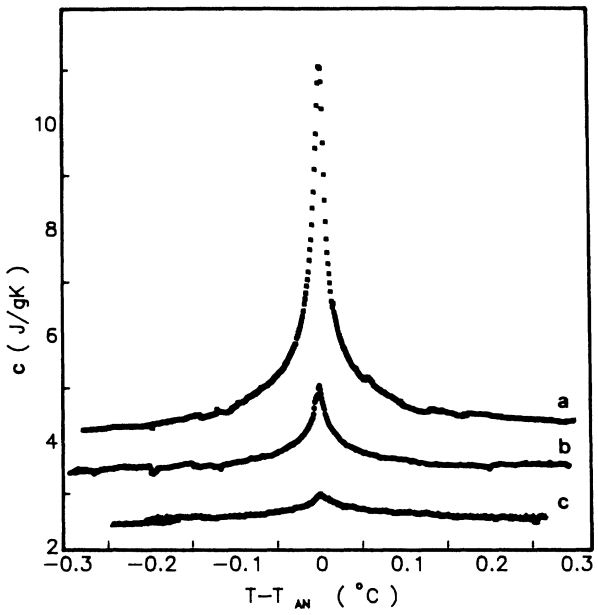

FIG. 1. Heat-capacity behavior for (a) 9CB, (b) 8CB, and (c) 7CB and 8CB mixture. One and two units were added to data sets (b) and (a), respectively.

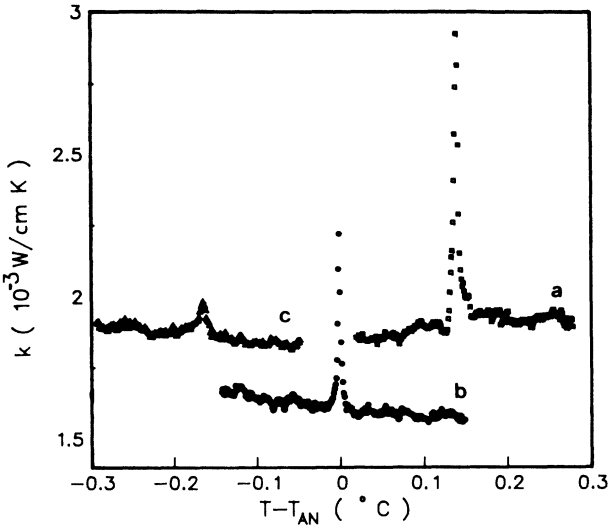

FIG. 3. Thermal conductivity critical behavior for (a) 9CB, (b) 8CB, and (c) 7CB and 8CB mixture. One unit was subtracted from data set (b) while data sets (a) and (c) were shifted by 1.5 °C on either side of the transition temperature.

of the data near the peak, as shown in the double-log plot of the singular term contribution to the c data, Δc, versus t (Fig. 4), which may affect the heat capacity more than the thermal conductivity. Δc has been obtained by fitting the c data with the power-law expression $c = A|t|^{-\alpha} + B + Et$ and then subtracting from the data the constant and linear terms $\Delta c = c - (Et + B)$. $t = T/T_{\text{Sm-}A\text{-}N}$ is the reduced temperature. In order to determine the critical exponents of the thermal parameters, since the k data were calculated off the c and D data, a fit was first performed on the latter two quantities values, on either side of the transition temperature, using the above mentioned expression for c and the power-law expression $D = R|t|^{-b} + S + Ut$ for D.

The critical exponent a for the thermal conductivity, which may also be described by a singular and background terms with an expression similar to the ones used or c and D, was then determined from the α and b values. The points closest to the transition temperature considered in the fit procedure were those for which $|t| > 1.2 \times 10^{-5}$. To within experimental error the critical exponents calculated for $T > T_{\text{Sm-}A\text{-}N}$ and $T < T_{\text{Sm-}A\text{-}N}$ were equal and the values are reported in Table I together with the samples respective $T_{\text{Sm-}A\text{-}N}/T_{N\text{-}I}$ values. The absolute values of the critical exponents of each thermal parameter progressively increase as $T_{\text{Sm-}A\text{-}N}/T_{N\text{-}I}$ increases. Regarding the heat

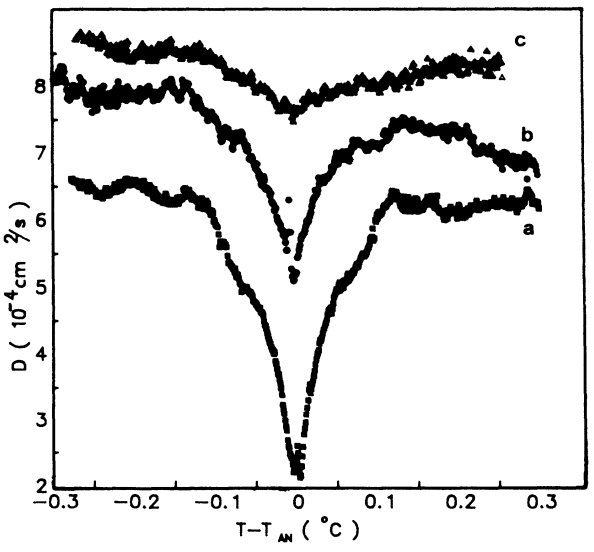

FIG. 2. Thermal diffusivity critical behavior for (a) 9CB, (b) 8CB, and (c) 7CB and 8CB mixture. One unit was respectively added to and subtracted from data sets (c) and (a).

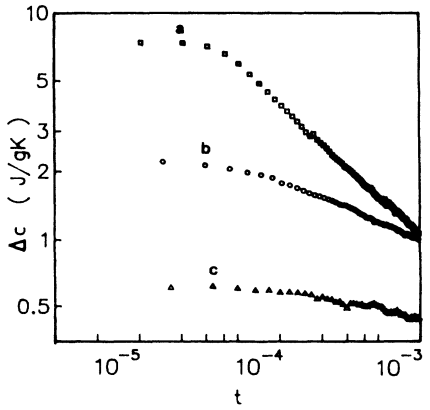

FIG. 4. Double-logarithmic plot of Δc vs t (see text) for (a) 9CB, (b) 8CB, and (c) 7CB and 8CB mixture.

TABLE I. Smectic-A–nematic-isotropic transition temperature ratios and critical exponents of heat capacity α, thermal diffusivity b, and thermal conductivity a of the investigated samples.

Sample	0.24 7CB+0.76 8CB mole fraction	8CB	9CB
$\frac{T_{\text{Sm-}A-N}}{T_{N-I}}$	0.962	0.967	0.994
α	0.14±0.03	0.28±0.03	0.52±0.04
b	−0.01±0.03	−0.04±0.03	−0.08±0.04
a	0.13±0.06	0.24±0.06	0.44±0.08

capacity data, the critical exponent values for 9CB and 8CB are in agreement with the ones reported by Thoen, Marynissen, and Van Dael (0.5 and 0.3, respectively).[5] As for the mixture value, Thoen, Marynissen, and Van Dael reported a value of $\alpha=0.1$ for $T_{\text{Sm-}A-N}/T_{N-I}=0.961$. In the present case the value of α is slightly larger, consistent with the trend of increasing values of α as $T_{\text{Sm-}A-N}/T_{N-I}$ increases. Employing the hyperscaling relation $d\nu=2-\alpha$ where $d=3$ dimensions, ν may be determined. Using the dynamic scaling law for an asymmetric planar magnet model $\alpha=\nu/2(\epsilon+\tilde{\alpha}/\nu)$, where $\epsilon=4-d$ and $\tilde{\alpha}=\max(\alpha,0)$, the predicted values of a in the case of a three-dimensional XY model can be obtained. The calculated values for 9CB, 8CB, and mixture are $a=0.5$, 0.43, and 0.38, respectively. Although the same trend as the one obtained experimentally of the a values as a function of $T_{\text{Sm-}A-N}/T_{N-I}$ is observed, the values predicted by the scaling laws are substantially larger than the experimental ones and they would lead, in all the three cases, to a stronger divergence in the thermal conductivity than in the heat capacity over the phase transition. This would cause a divergence of the thermal diffusivity as well, in contrast with the reported data. This behavior would also be found for a value of α consistent with the three-dimensional XY model as a would be 0.34. It is most surprising that the discrepancy between predicted and experimental values increases as the $T_{\text{Sm-}A-N}/T_{N-I}$ value progressively decreases and that is where the value of α tends to approach the α_{XY} value. The best agreement is in fact found at the TCP. A similar result had been obtained for the hexatic B–smectic-A transition in n-hexyl-4-n pentyloxybiphenyl-4-carboxylate (650BC),[13] another transition whose critical behavior had been predicted to be XY-like. There was a good agreement between the predicted and experimental values of a even though a value of $\alpha=0.6$, much larger than α_{XY}, had been obtained.

In conclusion, it has been shown that the critical exponents of the heat capacity, thermal conductivity, and thermal diffusivity obtained at the smectic-A–nematic transition in samples with different nematic ranges are inconsistent with the dynamic scaling law predicted by a model that applies to three-dimensional XY-like phase transitions. The discrepancy has been shown to increase the more the sample nematic range increases, even though the critical exponent of the heat capacity tends to approach α_{XY}. This is consistent with the picture that even in compounds with large nematic ranges, the critical exponents of the correlation length and susceptibility are also inconsistent with the ones predicted by the XY model.

[1]K. K. Kobayashi, Phys. Lett. **31** 125 (1970).
[2]L. McMillan, Phys. Rev. A **4**, 1238 (1971).
[3]P. G. de Gennes, Solid State Commun. **10**, 753 (1972).
[4]T. C. Lubensky and J. H. Chen, Phys. Rev. B **17**, 366 (1978).
[5]J. Thoen, H. Marynissen, and W. Van Dael, Phys. Rev. Lett. **52**, 204 (1984).
[6]K. J. Stine and C. W. Garland, Phys. Rev. A **39**, 3148 (1989).
[7]M. E. Huster, K. J. Stine, and C. W. Garland, Phys. Rev. A **36**, 2364 (1987).
[8]J. C. Le Guillou and J. Zinn-Justin, Phys. Rev. B **21**, 3976 (1980).
[9]C. W. Garland, M. Meichle, B. M. Ocko, A. R. Kortan, C. R. Safinye, L. J. Yu, J. D. Lister, and R. J. Birgeneau, Phys. Rev. A **27**, 3234 (1983), and references therein.
[10]B. Ocko, R. J. Birgeneau, J. D. Lister, and M. E. Neubert, Phys. Rev. Lett. **52**, 208 (1984).
[11]P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).
[12]U. Zammit, M. Marinelli, R. Pizzoferrato, F. Scudieri, and S. Martellucci, Liq. Cryst. **4**, 619 (1989).
[13]G. Nounesis, C. C. Huang, and J. W. Goodby, Phys. Rev. Lett. **56**, 1712 (1986).