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Simultaneous photoacoustic measurements of specific heat and thermal conductivity critical behaviour at a smectic A–nematic phase transition

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Simultaneous measurements of the thermal conductivity and specific heat at the smectic A–nematic phase transition in 4-*n*-octyl-4′-cyanobiphenyl (8CB) have been carried out with the photoacoustic technique. A critical increase in the thermal conductivity is reported. A critical decrease in the thermal diffusivity data confirms that the transition in 8CB is fluctuation dominated as also shown by the critical behaviour of the specific heat.

1. Introduction

The critical behaviour of the thermal transport properties in the vicinity of phase transitions has recently been reported for liquid crystal compounds. In particular simultaneous measurements of the specific heat, C_p, and thermal conductivity, k, have been carried out near the hexactic B–smectic A (S_B–S_A) transition in 4-*n*-hexyl-4′-*n*-pentyloxybiphenyl-4-carboxylate (650BC) [1] and near the smectic C–smectic A (S_C–S_A) transition in *n*-(4-*n*-heptyloxybenzylidene)-4′-*n*-butylaniline (70·4) [2]. The S_B–S_A transition had been shown to be fluctuation dominated with the specific heat showing critical behaviour with a large critical exponent ($\alpha = 0{\cdot}6$) [3]. Although the S_C–S_A transition had been placed by de Gennes [4] in the universality class of the *XY*-like transitions, the specific heat data have been shown to be well described by an extended mean field theory model [5]. A dip in the thermal diffusivity ($D = k/C_p\varrho$ where ϱ is the density) data in the vicinity of both phase transitions was observed thus showing that in both cases the behaviour of the thermal diffusivity was fluctuation dominated. The possibility of a crossover from mean field like to fluctuation dominated behaviour in the specific heat near the S_C–S_A transition was therefore suggested though rounding off in the data in the vicinity of the transition may have prevented it from being observed.

In this paper we report the results of simultaneous measurements of C_p, k and therefore D, in the vicinity of another *XY*-like phase transition, namely the smectic A–nematic ($S_{A\text{–}N}$), using the photoacoustic technique. The investigation was performed on 4-*n*-octyl-4′-cyanobiphenyl (8CB) and the critical behaviour of its thermal transport coefficients is reported for the first time. Though, in fact, the critical behaviour of the specific heat at this transition has been extensively studied for 8CB and other compounds, no experimental results have been as yet reported on the behaviour of the thermal conductivity and the thermal diffusivity at such a transition. The transition had been predicted [6] to be second order provided the ratio T_{AN}/T_{NI} is less than 0·87, where T_{AN} and T_{NI} are the S_A–N and N–I transition temperatures respectively. The

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existence of a tricritical point is therefore predicted. In the context of the experimental results, it was shown [7], with investigations carried out on the mixtures of compounds of the nCB series, that the value of the critical exponent of the specific heat lies in the range between $-0{\cdot}03$, which is very close to the value predicted by the three dimensional XY model ($-0{\cdot}02$), and the mean field tricritical value of 0·5 as T_{AN}/T_{NI} is increased. The tricritical point is found for $T_{AN}/T_{NI} = 0{\cdot}994$ which is greater than the theoretical value. On the basis of such calorimetric results the T_{AN}/T_{NI} dependence of the α values may be considered to be caused by a crossover between a tricritical and XY critical behaviour.

We have shown [8] that the photoacoustic technique may be used for simultaneous measurements of C_p, k and D in liquid crystals. Moreover since an adequate signal to noise ratio in the photoacoustic signal may be obtained by introducing very small temperature oscillations ($\Delta T \leqslant 4$ mK rms) and therefore small temperature gradients in the sample, the technique looks attractive to study the behaviour of thermal parameters near phase transitions. With respect to the technique developed by Huang *et al.* [9], which also allows simultaneous determination of C_p and k as a function of temperature performing however a frequency scan at each temperature value, photoacoustics provides the same results but by working at only one value of the modulation frequency.

2. Theory and experiment

The photoacoustic effect is based on the periodic heating of the sample induced by a modulated lamp or laser source. In the gas microphone configuration the heated sample is contained in a gas-tight volume (cell) and induces a periodic overpressure in the cell gas which is detected by the microphone and a lock- in amplifier. The theory for the photoacoustic effect has been developed by Rosencwaig *et al.* [10]. When the sample is optically and thermally thick, we have shown [11] that the amplitude Q and the phase ϕ of the period pressure oscillation

$$S = Q\exp(j\omega t + \phi - \tfrac{1}{4}\pi)$$

reduce to very simple expressions and are given by

$$Q = \frac{I_0 P_0 \gamma \mu_g p}{T_0 L_g (2)^{3/2} \omega^{1/2} (p^2 + 2p + 2)^{1/2} (1 + q) e_g}$$

and

$$\phi = \tan^{-1}\left(-1 - \frac{2}{p}\right),$$

where the subscripts s and g refer to the sample and cell gas respectively, $\mu = (2D/\omega)^{1/2}$ is the thermal diffusion length ω is the modulation frequency

$$p = \mu_s/\mu_\beta, \quad \mu_\beta = 1/\beta, \quad q = e_s/e_g, \quad e = (p\varrho C_p)^{1/2}.$$

In addition β is the optical absorption coefficient γ is the ratio of the gas specific heat at constant pressure and volume L_g is the cell gas thickness I_0, P_0, T_0, are the laser beam power density, the cell ambient pressure and the sample surface DC absolute temperature, respectively. From the phase data p, and therefore D, can be determined. From the amplitude data q can also be determined and C_p and k can be evaluated. Thus C_p, k and D can be measured from the photoacoustic signal amplitude and phase data obtained from only one value of the modulation frequency.

The sample of 8CB (BDH K24) was contained in a 1 cm diameter, 1 mm deep volume, obtained in a gold plated copper sample holder which was electrically heated.

The sample was illuminated with a He–Ne laser operating at $\lambda = 3{\cdot}39\,\mu m$ with a power density incident on the sample of $1\,mW/cm^2$. The value of the optical absorption coefficient at such wavelength was $\beta \approx 1500\,cm^{-1}$ [8]. The laser beam was mechanically chopped at 30 Hz. With such values of the absorption coefficient and modulation frequency, the conditions for an optically and a thermally thick sample are fulfilled. Since the sample is hygroscopic, it was placed in vacuum (10^{-4} mbar) for several hours in order to remove moisture and then sealed in the PA cell in a nitrogen atmosphere. The heating rate was 0·8 mK/min near the phase transition region where data were collected every mK.

3. Results and discussion

The temperature dependence of the photoacoustic signal amplitude and phase behaviour is reported in figures 1 (*a*) and 1 (*b*), respectively. The phase transition

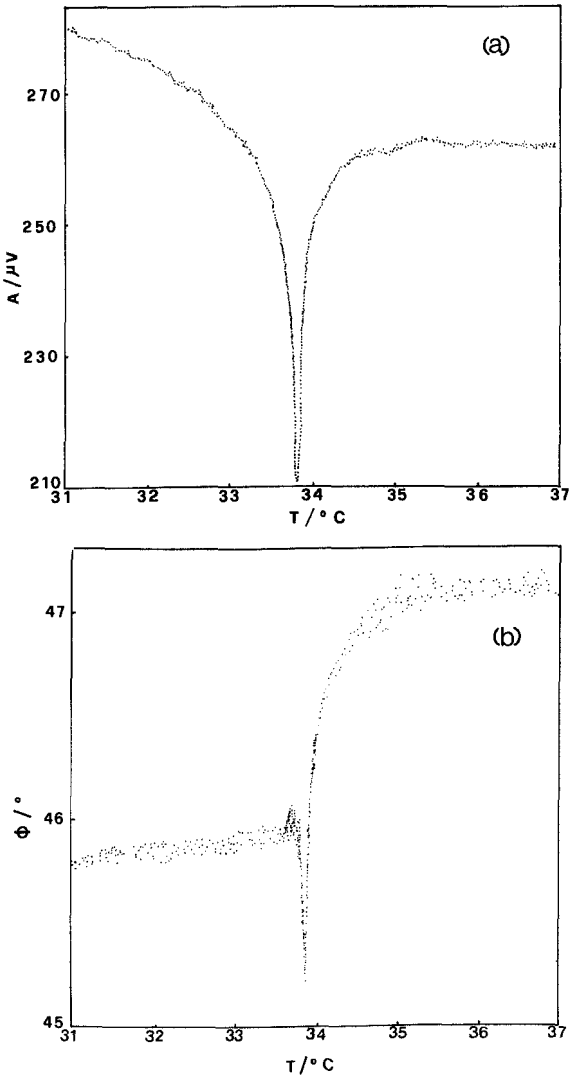


Figure 1. Photoacoustic signal amplitude (*a*) and phase (*b*) versus temperature for 8CB.

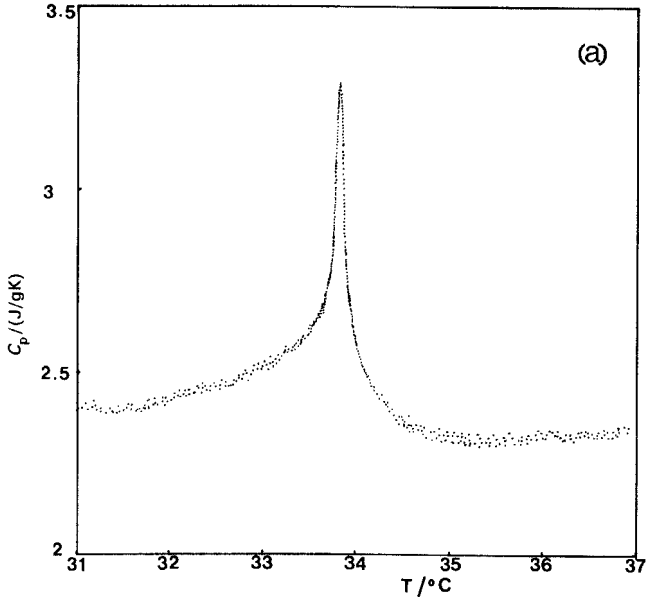
temperature T_{S_AN} is 33·82°C. The calculated values of C_p, k and D are reported in figures 2(*a*), (*b*) and (*c*), respectively. The specific heat data were fitted with the power law

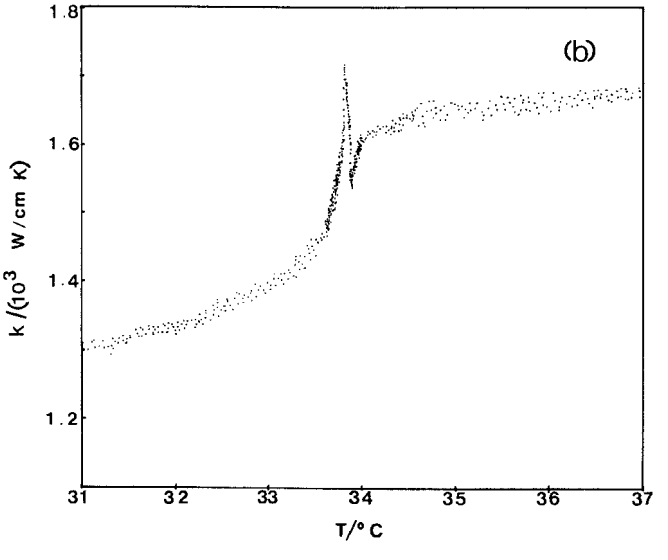
$$c = A + B|\varepsilon| + C|\varepsilon|^{-\alpha}(1 + D|\varepsilon|^{\Delta})$$

where

$$\varepsilon = \frac{T - T_{S_AN}}{T_{S_AN}}$$

is the reduced temperature, α is the critical exponent and the factor $(1 + D\|\varepsilon|^{\Delta}$ represents the scaling correction [12] with $\Delta = 0{\cdot}5$ [13]. The fit was carried out on points ranging between $|\varepsilon_{max}| = 3 \times 10^{-3}$ and $|\varepsilon_{min}| = 5 \times 10^{-5}$. The points corresponding to smaller values than $|\varepsilon_{min}|$ were not considered because they are affected by rounding.





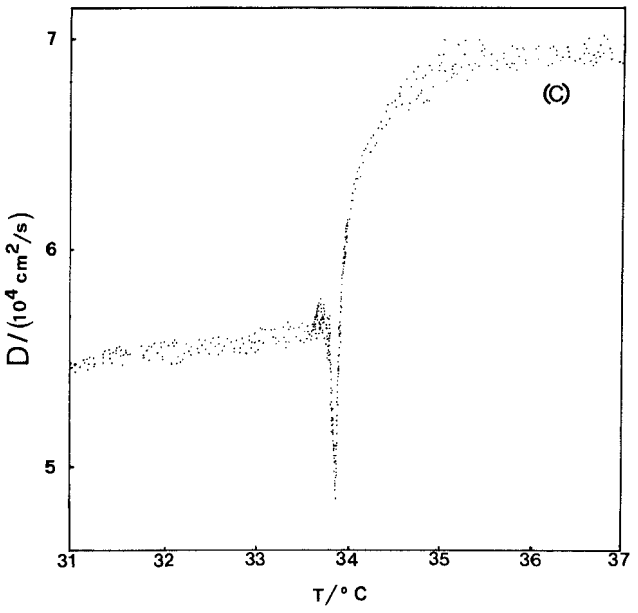


Figure 2. Specific heat (*a*), thermal conductivity (*b*) and thermal diffusivity (*c*) data versus temperature for 8CB.

This may be due to residual impurities and to the presence of small temperature gradients in the sample, caused by the present heating stage configuration, which do not, however, seem to affect the values of the critical exponents and coefficients. They would also account for the lower peak value found with respect to other data reported in literature (4–4·5 J/g K) [14, 15]. The result of the theoretical fit is reported in figure 3.

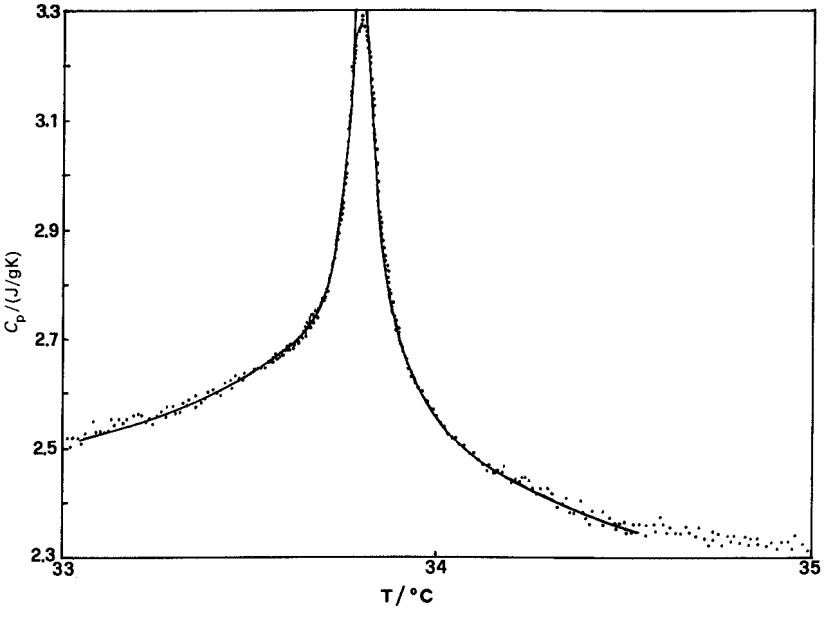


Figure 3. Specific heat data versus temperature together with the power law fit (solid line) for 8CB.

Values of $\alpha'(T < T_{S_AN}) = 0{\cdot}30 \pm 0{\cdot}03$ and $\alpha(T > T_{S_AN}) = 0{\cdot}29 \pm 0{\cdot}03$ and the ratio $C'/C = 1{\cdot}02 \pm 0{\cdot}07$ were obtained. The α values found in the literature range between $\alpha = \alpha' = 0{\cdot}25 \pm 0{\cdot}02$ [16] and $\alpha = \alpha' = 0{\cdot}31 \pm 0{\cdot}03$ [15] while those of C'/C range between $0{\cdot}83 \pm 0{\cdot}05$ [15] and 1·08 [14]. The results compare favourably therefore with those reported in the literature. The thermal diffusivity and conductivity show a sharp dip and peak respectively in the vicinity of the phase transition. This demonstrates that the conventional theory for critical slowing down is not applicable for this transition since it assumes that the transport coefficients vary smoothly through the transition temperature. This, on the other hand, is in agreement with the fact that the S_A–N transition is helium like and therefore a fluctuation dominated one, as shown by the critical behaviour of the specific heat. A similar behaviour in both k and D has been observed in the smectic C–smectic A transition is 704 [2] and in the hexactic–smectic A transition for 650BC [1] and also interpreted as being due to a critical slowing down of thermal fluctuations. In our data a dip just after the peak in k and a small peak just before the dip in D are present. No explanation for these secondary features is available at the moment. Furthermore, their presence make a fit of the data with a power law dependence rather difficult. For a clearer picture of the behaviour of the thermal transport properties, measurements on aligned samples should be attempted since for a polydomain sample it is very difficult to establish the modes which govern the thermal conduction process near the transition. In this way the anisotropy of k and D could also be investigated.

4. Conclusions

Photoacoustic thermal conductivity and thermal diffusivity measurements have been reported for the first time together with heat capacity data in the vicinity of the S_A–N transition in a liquid crystal (8CB). The critical exponent and the ratio of the coefficients of the critical term for the specific heat data are in agreement with those reported in the literature. A critical decrease in the thermal diffusivity and a critical increase in the thermal conductivity have been found and they confirm that the transition in 8CB is fluctuation dominated.

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