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A. Hadj-sahraoui[ab]; G. Louis[a]; B. Mangeot[b]; P. Peretti[ab]; J. Billard[c]
[a] DRP (UA 71 CNRS), Universiteé Pierre et Marie Curie, Paris Cedex 05, France [b] Laboratoire de Physique des Phases Condensées, Université René Descartes, Paris Cedex 06, France [c] LPMC (UA 542 CNRS), Collège de France, Paris Cedex 05, France

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Analysis of phase transitions by photothermal probe beam deflection

by A. HADJ-SAHRAOUI†‡, G. LOUIS†, B. MANGEOT‡, P. PERETTI†‡ and J. BILLARD§

†DRP (UA 71 CNRS), Université Pierre et Marie Curie, Place Jussieu 75252, Paris Cedex 05, France

‡Laboratoire de Physique des Phases Condensées, Université René Descartes, 75270 Paris Cedex 06, France

§LPMC (UA 542 CNRS), Collège de France, 75232 Paris Cedex 05, France

A recent photothermal technique has been used to study the smectic A–nematic and nematic–isotropic phase transitions in 4-*n*-octyl-4′-cyanobiphenyl and in binary mixtures of 4-*n*-octyl- and 4-*n*-octyloxy-4′-cyanobiphenyl. A numerical analysis shows that both amplitude and phase of the photothermal signal are sensitive to the change of certain thermal parameters for the sample.

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1. Introduction

A variety of techniques has been employed to measure the thermal parameters of mesophases. In recent years [1] the photoacoustic technique, using a gas microphone for detection, has shown that it can be a powerful tool to detect first or second order phase transitions on small amounts of thermotropic liquid crystals.

The photothermal probe beam deflection (the mirage effect), developed initially by Boccara *et al.* [2] is playing an increasing role in the study of thermal and optical properties of materials. In this technique a monochromatic modulated incident beam (pump beam), is focused to a small diameter spot on the surface of the sample. The absorption of optical energy produces heat flow which induces a refractive index gradient in the adjacent material close to the surface of the sample. A second laser beam (the probe beam) runs parallel to the surface, through the periodically heated air, at a distance x_0 away from the pump beam and a height z_0 above the surface. The refractive index gradient of the air depends on the temperature distribution in the sample and so the probe beam deflection in the air is sensitive to the modification of certain thermal properties of the sample.

Our objective in this present study is to show that the mirage effect is a useful tool with which to study phase transitions. In the following we first present a theoretical investigation of the deflection dependence on the thermal parameters in the phase change. The conclusions are tested on well known examples: 4-*n*-octyl-4′-cyanobiphenyl (8CB) and binary mixtures of 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) and (8CB).

2. Theoretical analysis

The experimental geometry used in this paper is shown in figure 1. The heated sample surface lies in the xy plane and we assume that the probe beam is parallel to the y axis and passes through the point $M(x, z)$. The heated spot is taken to be the origin.

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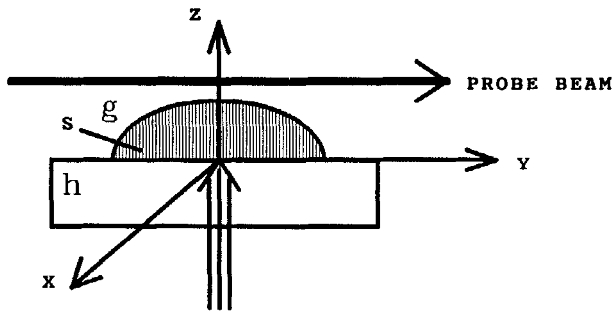

Figure 1. Geometry for the optical beam deflection experiments. The pump beam is normal to and the probe beam parallel to the sample surface. There is a transverse offset ($x_0 = 0{\cdot}3$ mm) between the probe beam and the heated spot. The sample droplet (s) lies on the fluoride holder (h): the probed medium is behind the air (g).

The cylindrical pump beam is modulated at a low frequency ω. Neglecting the anisotropy of the thermal properties of the sample, the three dimensional heat diffusion equation applied to the present case, gives the relationship

$$-\kappa_i \Delta\theta_i + j\omega\varrho_i c_i \theta_i = \beta_i I(r) \exp(\beta_i z),$$

for the sample surface temperature θ_i, where κ_i, ϱ_i and c_i are, respectively, the thermal conductivity, the mass density and the heat capacity of the medium i. The index i is taken to refer to the air (i = g), the sample material (i = s) or the holder (i = h); β_i is the optical absorption coefficient of the medium i ($\beta_i = 0$ for i = g or h). Lepoutre *et al.* [3] have shown that a solution of the diffusion equation can be given for the case of rear excitation, as a series expansion of the temperature modulation θ_i, namely

$$\theta_i(r, z) = \sum_{m=0}^{\infty} A_m S_m J_0(\gamma_m r) \exp[-\sigma_{gm}(l_s - z)].$$

Here J_0 is the zero order Bessel function, the sample thickness l_s is chosen to be less than the thermal diffusion length, the different γ_m are given by the zeros of the first order Bessel function $J_1(\gamma_m r_c) = 0$, where r_c is the sample radius and σ_{gm} is given by

$$\sigma_{gm}^2 = \gamma_m^2 + \frac{j\omega\varrho_g c_g}{\kappa_g}.$$

The two terms S_m and A_m are given in [3]; S_m describes the source distribution while A_m contains the thermal response of the sample to the excitation and is dependent on thermal parameters c_s and κ_s.

The magnitude and direction of the probe beam deflection $\mathbf{\Phi}$ are determined by the periodic gradient of the temperature in the air and are given, in vector notation, by the line integral:

$$\mathbf{\Phi} = -\int_P \frac{1}{n}\frac{dn}{dT} \nabla\theta \times d\mathbf{l}$$

where n is the refractive index for the gas, P is the probe beam path and $d\mathbf{l}$ is an incremental distance along P. The normal component Φ_z can be calculated analytically

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[3] if the sample radius r_c is much greater than the transverse offset x_0, when

$$\Phi_z(x_0, z) = -\frac{2}{n}\frac{dn}{dT}\left(A_0 S_0 (r_c^2 - x_0^2)^{1/2}\sigma_g \exp(-\sigma_g z) + \sum_{m=1}^{\infty} A_m S_m \frac{\cos(\gamma_m x_0)}{\gamma_m}\sigma_{gm}\exp(-\sigma_{gm} z)\right).$$

To determine the deflection angle response versus the sample temperature near a transition from phase 1 to phase 2, we use the asymptotic behaviour [4] of the heat capacity c_s near the transition temperature T_{12}, namely

$$c_s(T) = \frac{A}{\alpha}\varepsilon^{-\alpha} + B, \quad \text{with} \quad \varepsilon = (T - T_{12})/T_{12} \quad \text{for } T > T_{12},$$

$$c_s(T) = \frac{A'}{\alpha'}\varepsilon^{-\alpha'} + B', \quad \text{with} \quad \varepsilon' = (T_{12} - T)/T_{12} \quad \text{for } T < T_{12}.$$

Values of A, B, A', B', α and α' are available for the smectic A and nematic phases of 8CB [4] and our calculation used the values:

$$f(\equiv \omega/2\pi) = 10\,\text{Hz};\ r_c = 1\,\text{mm},\ x_0 = 0{\cdot}3\,\text{mm},\ l_s = 30\,\mu\text{m},$$

$$\kappa_s = 9 \times 10^{-2}\,\text{W m}^{-1}\,\text{K}^{-1},\ |\varepsilon| = 2 \times 10^{-3}.$$

We have neglected the change in the thermal conductivity at the smectic A–nematic transition. We present in figure 2 a typical variation of the calculated amplitude $|\Phi_z|$ of the normal deflection probe beam near the transition temperature $T_{S_A N}$. Thus, we can see that the mirage effect may be an interesting method which allows us to detect phase transitions in thermotropic compounds.

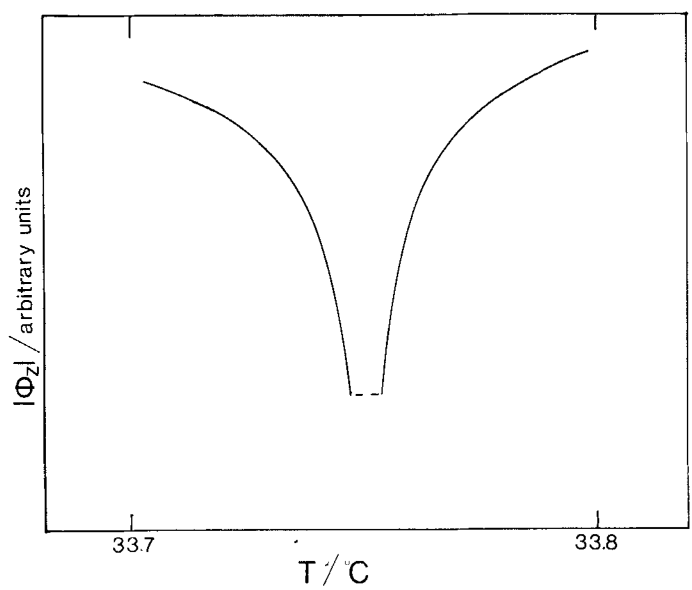

Figure 2. Theoretical dependence of the normal amplitude component $|\Phi_z|$ versus the average mean temperature.

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3. Experiment and results

The experimental set-up is shown in figure 3. We used a modulated He–Ne near-infrared laser (3·39 μm) of 5 mW power as the excitation source. A rear pumping configuration was chosen, the medium probed being air. The probe beam was a 632·8 nm He–Ne laser of 2 mW power. The deflection (no more than a few milliradians) was measured by a position sensor (silicon detector Centronic QD 50-5) placed at a suitable distance from the illuminated sample surface. The pump beam was modulated by a variable frequency light chopper in the frequency modulation range 10–200 Hz. The output signal was detected by a lock-in amplifier (PAR 5206). Both amplitude and phase data were collected by a microcomputer.

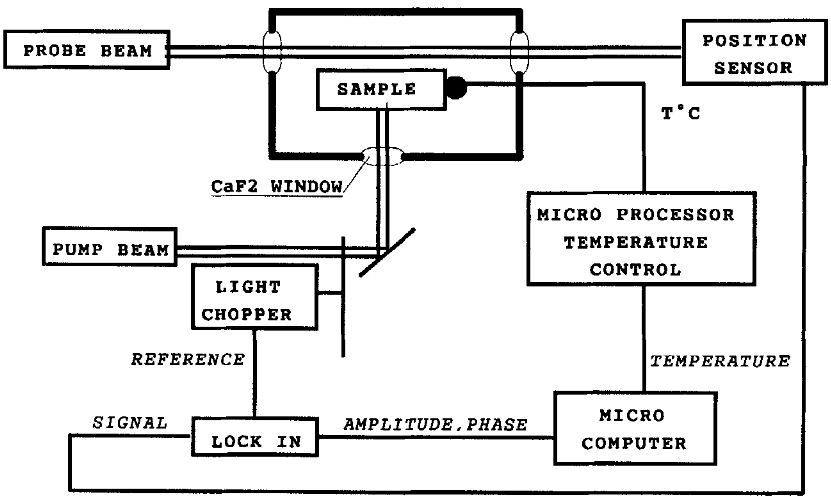

Figure 3. Block diagram of the experimental set-up.

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The liquid crystal droplet 0·05 mg in weight and 40 μm in thickness, was placed on a fluoride substrate which was transparent to the near-infrared excitation light. This sample holder was mounted on an *XYZ* microdisplacement platform, and enclosed in a thermally isolated box. Electrical heating, monitored by a microprocessor (Coreci MCF/RNZ), ensured that the average temperature was scanned in the range 5–200°C. The average temperature of the sample changes at a rate of 0·06°C^{l} min^{-1}, and this temperature was measured using a platinum resistance thermometer. The photothermal signal was measured at 1 atm, on 8CB and 8OCB samples (B.D.H. Chemicals Ltd, without further purification).

Figure 4 shows the normal deflecting signal Φ_z versus the average temperature of the sample surface for 8CB. All measurements were made for a beam offset of 300 μm. Both the phase and the amplitude of the photothermal signal show important variations near the phase transition. In the literature the values of molar transitional enthalpy changes are [5]: 0·125–0·305 kJ mol^{-1} for the smectic A–nematic transition and 0·8–1·232 kJ mol^{-1} for the smectic–isotropic transition. All transitions are clearly detectable, even the S_A–N, which is essentially a second order [6] phase transition. The experimental peak at the S_A–N transition temperature is broader than that predicted, presumably due to a modification of the crystal droplet dimensions during the phase transition, or to the presence of impurities in the sample.

Binary mixtures of 8CB and 8OCB have also been investigated by the mirage effect. Small samples (100 mg) of the mixtures were prepared in the following way.

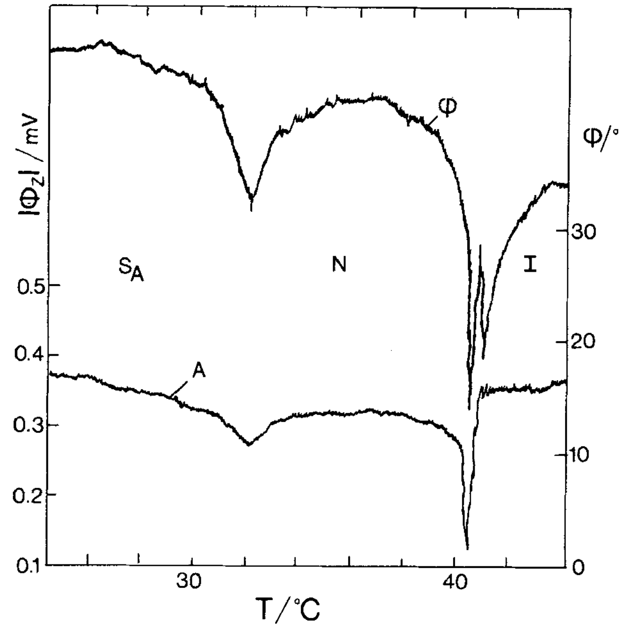

Figure 4. Experimental dependence of the amplitude $|\Phi_z|$ and the phase shift φ_z of the normal beam deflecting signal Φ_z, versus the average sample temperature.

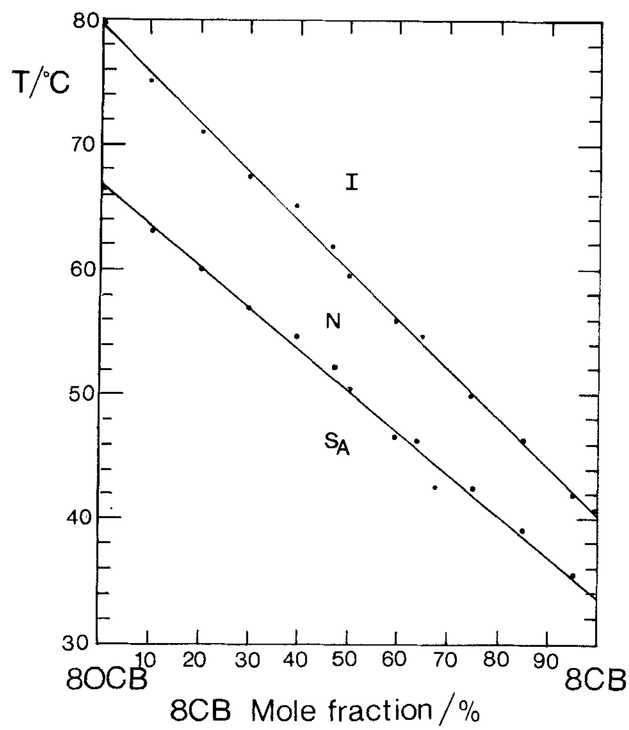

Figure 5. Experimental phase diagram for the binary 8CB–8OCB mixture.

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Each compound was weighed out with 1 per cent accuracy and placed in a small tube. The binary product was dissolved in ether and the solvent evaporated on an ultrasonic bath at 40°C. The observed S_A–N and N–I transition temperatures are plotted in the phase diagram shown in figure 5. The accuracy is not sufficient to detect the very narrow two phase regions. The phase diagram obtained is an accord with that determined from the observation of contact preparations [7] with an optical microscope.

4. Conclusion

The photothermal probe beam deflection technique has been shown to be an effective interesting tool with which to study phase transitions on very small amounts of sample (0·05 mg of pure material or binary mixtures). These preliminary results lead us to expect that anisotropic thermal transport properties, governed by the molecular orientation, could be studied with samples placed between two fluoride plates, properly coated and oriented. It is also possible to realize a contactless thermal imaging technique to study sample inhomogeneities.

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