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Liquid-crystal phase transitions of thin layers: A photothermal analysis

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A numerical analysis of the photothermal probe-beam signal generated at first- and second-order phase transitions in 4-*n*-octyl-4′-cyanobiphenyl (8CB) is proposed. A criterion for photothermal signal sensitivity in detection of phase transitions is given. The influences of probe-beam transverse offset and modulation frequency, as well as thermal parameters of the probed medium, on this sensitivity are investigated experimentally and theoretically. It is shown that the photothermal signal may be insensitive to the phase transitions for certain values of the modulation frequency and the probe-beam transverse offset, while a maximum of sensitivity is obtained for a range of values of these parameters. It is also shown that this sensitivity is improved if we use a probed medium with an effusivity smaller than the sample effusivity. A comparison of some of the results of the theory with experimental results is given.

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I. INTRODUCTION

The photothermal beam-deflection technique has proved to be a powerful tool for the study of optical and thermal materials properties [1,2]. This technique has been used for optical spectroscopy, imaging, and scanning microscopy in solids [3–5]. In a previous paper [6], we have shown that the photothermal probe-beam deflection has the ability to detect phase transitions in thermotropic liquid crystals. This technique involves an intensity-modulated heating beam focused to a small-diameter spot on the surface of the sample. Optical absorption in the sample produces a temperature-gradient field and an index gradient in both the sample and the adjacent material close to the sample surface. An optical probe beam directed through the heated region of the adjacent material is deflected by the mirage effect. The index gradient depends on the temperature distribution in the sample and consequently the probe-beam deflection is sensitive to the change in thermal properties of the sample.

Two experimental configurations can be used. In the first one (front configuration), both the probe beam and the heating beam are propagated in the front medium, while in the second configuration (rear configuration) the probe beam lies in the rear medium (Fig. 1). This last configuration requires the sample thermal-diffusion length to be larger than the sample thickness.

Using this technique, we have previously measured [7] the anisotropic thermal diffusivity in a discotic liquid crystal. This paper is concerned with the photothermal analysis of first- and second-order phase transitions in thin layers.

A three-dimensional calculation of the normal deflection angle shows the theoretical dependence of the photothermal signal sensitivity on the main physical parameters. Since the front configuration is, in all cases, less sensitive than the rear configuration, we have only studied this latter configuration. We make a comparison between the theoretical and experimental results obtained on a compound exhibiting first- and second-order phase transitions: the 4-*n*-octyl-4′-cyanobiphenyl (8CB).

II. THEORY

A. Photothermal beam deflection

The geometry used is shown in Fig. 1. The sample holder has a plane surface π. The sample is illuminated by a laser beam modulated with a frequency $f=\omega/2\pi$, perpendicular to this plane. The origin O of the Cartesian coordinates is located within π at the center of the heated spot. The y axis is parallel to the probe beam and the x axis parallel to π. The probe beam crosses the point $M(x,z)$. Cylindrical coordinates O, r, and z are also used.

We assume that the media surrounding the sample are optically nonabsorbing for the incident light. The absorbed radiation in the sample produces heat flow causing a temporal and spatial variation of the temperature $\Theta_s(r,z,t)$ in the sample $\Theta_f(r,z,t)$ in the front medium,

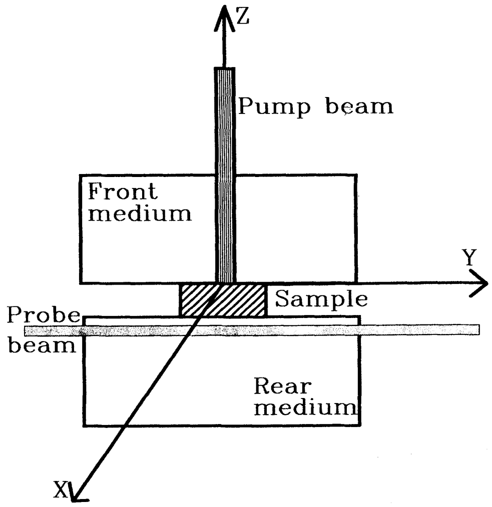

FIG. 1. Geometry of the optical beam-deflection experiment.

and $\Theta_r(r,z,t)$ in the rear medium. When the pump beam is radially symmetric with a Gaussian profile, the small variation of the temperature in the rear material can be written in the form [8]

$$\Theta_r(r,z,t)=\sum_{m=0}^{\infty} A_m S_m J_0(\tau_m r) \times \exp[-\sigma_{rm}(l_s-z)]\exp(-j\omega t) , \quad (1)$$

where J_0 is the zero-order Bessel function. The sample thickness l_s is chosen to be less than the thermal-diffusion length $\mu_s=(\alpha_s/\pi f)^{1/2}$, where α_s is the sample thermal diffusivity. The different τ_m are given by the zeros of the first-order Bessel function $J_1(\tau_m r_c)=0$, where r_c is the sample radius. The term σ_{rm} is given by

$$\sigma_{rm}^2=\tau_m^2+j\omega\rho_r c_r/K_r , \quad (2)$$

where K_r, ρ_r, and c_r are, respectively, the thermal conductivity, the mass density, and the heat capacity of the rear medium. The term S_m is related to the heat source, which we assume to be a Gaussian excitation beam of intensity I_0 and radius r_g:

$$S_m=\frac{I_0 r_g^2}{2r_c^2 J_0^2(\tau_m r_c)}\exp(-\tau_m^2 r_g^2/8) ,$$

while A_m contains the thermal response of the sample to the excitation and is dependent on the thermal sample parameters c_s and K_s.

The vector deflection of the mirage-probe beam is given by the equation

$$\Phi=-\int_P \frac{1}{n}\frac{dn}{dT}\nabla\Theta_r\times d\mathbf{l} , \quad (3)$$

where n is the refractive index for the probed medium, P is the probe-beam path, and $d\mathbf{l}$ is an incremental distance along P. The deflection Φ can be decomposed into two components, one Φ_n normal to the sample surface π and one Φ_t parallel to π. If the sample radius r_c is much greater than the transverse offset x_0 i.e., the distance between the probe-beam axis and the pump beam, the resulting expression [8] for the normal component of the probe-beam deflection is

$$\Phi_n(x_0,z,t)=-\frac{2}{n}\frac{dn}{dT}\left[A_0 S_0(r_c^2-x_0^2)^{1/2}\sigma_{ro}\exp[-\sigma_{ro}(l_s-z)]+\sum_{m=1}^{\infty} A_m S_m \frac{\cos(\tau_m x_0)}{\tau_m}\sigma_{rm}\exp[-\sigma_{rm}(l_s-z)]\right] . \quad (4)$$

If we call the amplitude of the normal components oscillating $a_n(x_0,z)$ and the phase compared to the modulation of the pump beam $\phi_n(x_0,z)$, then

$$\Phi_n(x_0,z,t)=a_n(x_0,z)\exp[-j(\omega t+\phi_n)] . \quad (5)$$

B. Photothermal signal sensitivity for the detection of phase transitions

The deflection is related to the sample thermal conductivity K_s and the sample heat capacity c_s by the term A_m in Eq. (1). Since K_s and c_s depend on the average mean temperature, we can write $a_n=a_n(T)$ and $\Phi_n=\Phi_n(T)$. In order to study the normal deflection-angle response versus the bath temperature T near the phase-transition temperature T_c, we have used the asymptotic behavior [9] of the heat capacity $c_s(T)$ near T_c, namely

$$c_s(T)=\begin{cases}(A/\delta)\epsilon^{-\delta}+B & \text{with } \epsilon=(T-T_c/T_c) \text{ for } T>T_c \\ (A'/\delta')\epsilon'^{-\delta'}+B' & \text{with } \epsilon'=(T_c-T/T_c) \text{ for } T<T_c .\end{cases}$$

Values of A, B, A', B', δ and δ' are available for the smetic-A–nematic and nematic-liquid phase transitions of 8CB [9]. We have neglected the change in the thermal conductivity at the smetic-A–nematic transition.

In the case of the nematic-liquid transition the thermal-conductivity behavior [10] is given by

$$K_s=\begin{cases}0.17\ \mathrm{W\,m^{-1}\,K^{-1}} & \text{for} T<T_c \\ 0.134\ \mathrm{W\,m^{-1}\,K^{-1}} & \text{for} T>T_c .\end{cases}$$

After substitution of $c_s(T)$ and K_s in Eq. (1), we present a typical variation of the calculated amplitude

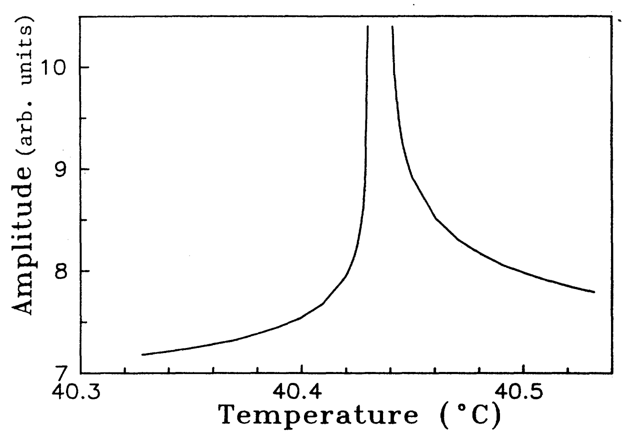

FIG. 2. Theoretical dependence of the amplitude a_n of the normal defelction of the probe beam vs the average mean temperature T at $f=1$ Hz.

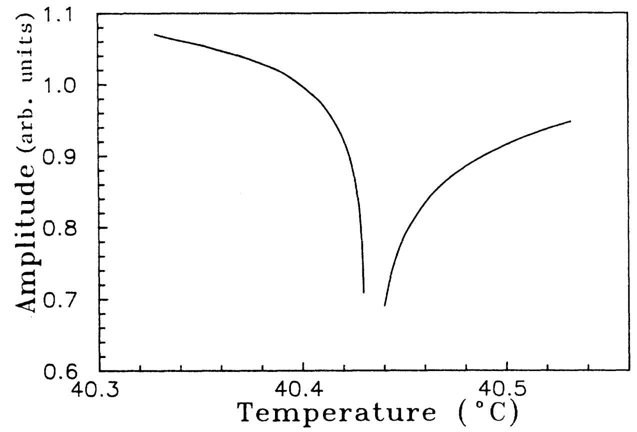

FIG. 4. Theoretical dependence of the amplitude a_n of the normal deflection of the probe beam vs the average mean temperature T at $f=20$ Hz.

$a_n(T)$ and phase $\phi_n(T)$ of the normal deflection probe beam near the nematic-liquid transition temperature T_c (Figs. 2 and 3). Thus we can observe that both the amplitude and phase of the photothermal signal are sensitive to the change in the sample heat capacity c_s and the sample thermal conductivity K_s. The behavior of $a_n(T)$ and $\Phi_n(T)$ near T_c is influenced by the modulation frequency. For $T<T_c$, the derivative da_n/dT is positive at $f=1$ Hz (Fig. 2), while it is negative at $f=20$ Hz (Fig. 4).

In order to quantify the sensitivity of the amplitude a_n in the detection of phase transitions, we introduce the relative variation S_a of a_n between two values of T below the transition temperature T_c: T_1 far from T_c and T_2 close to T_c. We write

$$S_a=\frac{a_n(T_2)-a_n(T_1)}{a_n(T_1)}\ , \qquad (6)$$

where $T_1=33.70\,°C$, $T_2=33.76\,°C$, and $T_c=33.77\,°C$ for the smetic-A–nematic transition, and $T_1=40.30\,°C$, $T_2=40.42\,°C$, and $T_c=40.43\,°C$ for the nematic-liquid transition [9].

The sensitivity of the signal phase S_ϕ is defined as an angle measuring the variation of the phase shift near the temperature transition:

$$S_\phi=\phi(T_2)-\phi(T_1)\ . \qquad (7)$$

Here, we note that the value $S_a=\pm 1$ corresponds to a maximum of magnitude sensitivity, while $S_a=0$ and $S_\phi=0$ indicate, respectively, that the signal magnitude and the signal phase do not detect the phase transition. The sensitivities S_a and S_ϕ depend parametrically on the transverse offset $x_{0'}$, on the modulation frequency f, and on thermal parameters of the probed medium.

1. Dependence of S_a and S_Φ on transverse offset x_0

For a pump beam with a Gaussian profile the normal deflection is maximum for $x_0=0$ and decreases as x_0 increases. We have calculated the variation of the signal sensitivities S_a and S_ϕ versus the transverse offset. Figures 5 and 6 show, in the case of the nematic-liquid

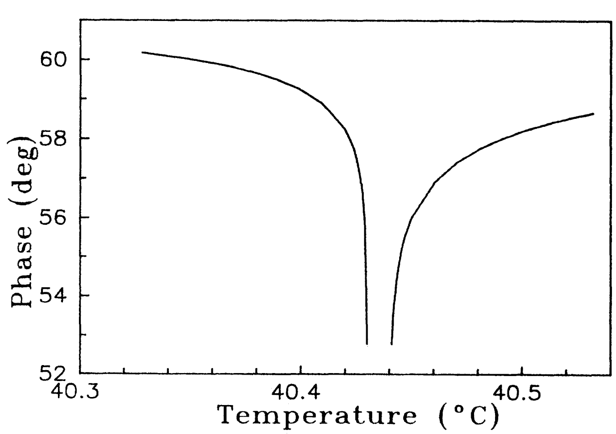

FIG. 3. Theoretical dependence of the phase ϕ_n of the normal deflection of the probe beam vs the average mean temperature T at $f=1$ Hz.

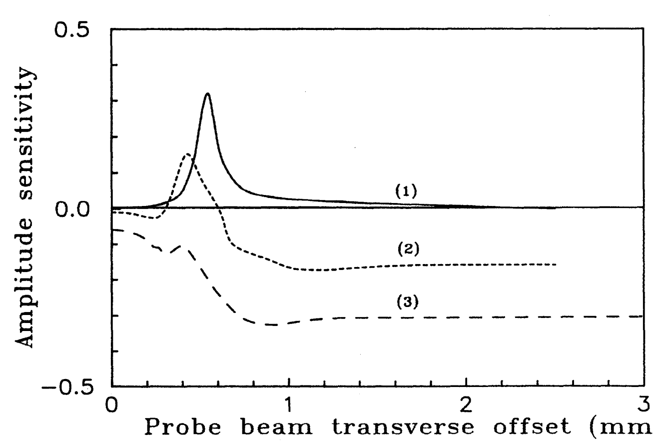

FIG. 5. Theoretical dependence of the amplitude sensitivity S_a on the probe-beam transverse offset x_0 at different frequencies. (1) $f=1$ Hz, (2) $f=20$ Hz, and (3) $f=30$ Hz.

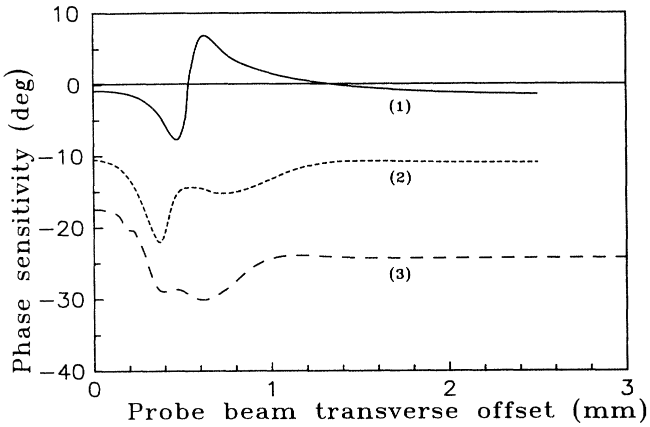

FIG. 6. Theoretical dependence of the phase sensitivity S_ϕ on the probe-beam transverse offset x_0 different frequencies. (1) $f=1$ Hz, (2) $f=20$ Hz, and (3) $f=30$ Hz.

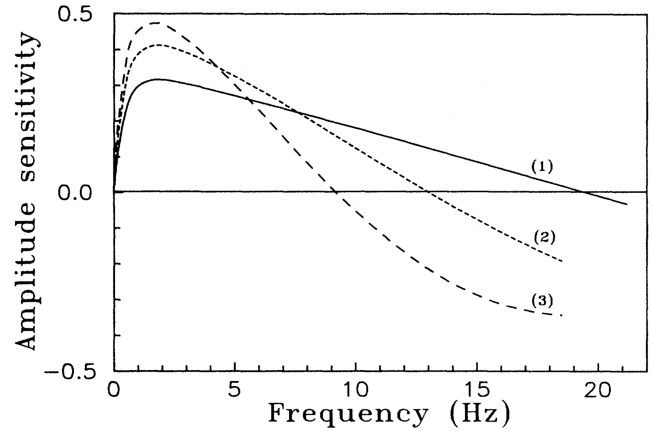

FIG. 7. Theoretical dependence of the amplitude sensitivity S_a on the modulation frequency for different values of the sample thickness l_s. (1) $l_s=10$ μm, (2) $l_s=15$ μm, and (3) $l_s=20$ μm.

phase transition, the theoretical dependence of S_a and S_ϕ on the probe-beam transverse offset at three modulation frequencies ($f=1$, 20, and 30 Hz). When $x_0=0$ the amplitude sensitivity approaches zero and the phase sensitivity is minimum; for $x_0>1$ mm both the amplitude sensitivity and the phase sensitivity remain constant. The optimal value of x_0 is chosen in an interval in order to agree with two requirements. The first is to obtain an appreciable signal in order to improve the signal-to-noise ratio. The second is to achieve a maximum of S_a and S_ϕ. It should be pointed out that positive S_a and S_ϕ correspond to an increase of the photothermal signal amplitude and phase during the phase transition, while negative S_a and S_ϕ correspond to a decrease of the photothermal signal amplitude and phase.

2. *Dependence of S_a and S_ϕ on modulation frequency*

We have calculated, using Eq. (4), the dependence of the magnitude sensitivity S_a and the phase sensitivity S_ϕ versus the modulation frequency for several thicknesses l_s of the sample. The range of frequencies has been chosen so that, for all frequencies, the sample thickness l_s remains smaller than the thermal-diffusion length μ_s.

Calculations have been made for opaque samples which are thermally thin, using the standard values $r_c=1$ cm, $z=60$ μm, $r_g=200$ μm, and $x_0=0.6$ mm. The probed medium is air ($\alpha_r=K_r/\rho_r c_r=2.15\times10^{-5}$ m^2/s; $K_r=0.026$ W m$^{-1}K^{-1}$) and the front medium is fluorite ($\alpha_f=K_f/\rho_f c_f=3.6\times10^{-6}$ m^2/s; $K_f=9.7$ W m$^{-1}K^{-1}$) (Table I).

Figure 7 shows the frequency dependence of S_a in the case of nematic-isotropic phase transition in 8CB. The frequency value f_c at which $S_a=0$ depends on the sample thickness l_s and decreases for higher values of l_s. When $f=f_c$ the signal magnitude is insensitive ($S_a=0$) to the changes in the sample thermal parameters near the phase transition. For the low-modulation frequency range ($f<f_c$), S_a is positive, and for the high frequencies ($f>f_c$) the sensitivity S_a is negative.

Figure 8 shows the frequency dependence of S_ϕ. The phase sensitivity increases with the frequency modulation and, for all values of the frequency, $S_\phi<0$ and the signal phase decreases near the phase transition.

3. *Dependence of S_a and S_ϕ on the thermal properties of the probed medium*

In order to study the effect of the nature of the probed medium in the detection of phase transition, we have calculated S_a and S_ϕ in the case of nematic-liquid transition versus frequency, using the thermal conductivity K_r and the heat capacity c_r of the probed medium as parameters. Calculations were made for three different probed media (Table I) in the rear pumping configuration with fluorite as the front medium.

TABLE I. Thermal parameters of different probed media.

	Air	CCl_4	Fluorite
Mass density (kg m^{-3})	1.2	1600	3180
Heat capacity[a] (J kg^{-1} K^{-1})	10^3	0.83×10^3	0.85×10^3
Conductivity[a] (W m^{-1} K^{-1})	0.026	0.103	9.7
Effusivity (J m^{-2} K^{-1} s$^{-1/2}$)	5.6	0.37×10^3	5.12×10^3

[a] Reference [11].

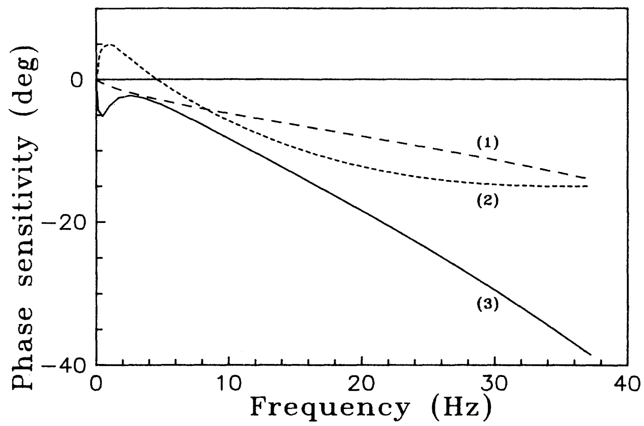

FIG. 8. Theoretical dependence of the phase sensitivity S_ϕ on the modulation frequency f for different values of the sample thickness l_s. (1) $l_s=10$ μm, (2) $l_s=15$ μm, and (3) $l_s=20$ μm.

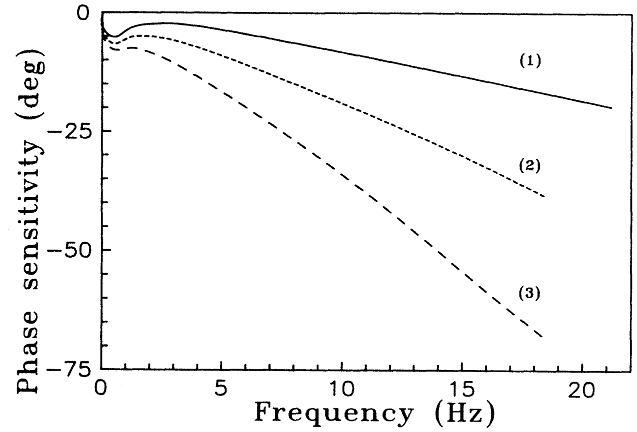

FIG. 10. Theoretical effect of the probed medium on the phase sensitivity S_ϕ. (1) Fluorite, (2) CCl_4, and (3) air.

Figures 9 and 10 show the theoretical frequency dependence of S_a and S_ϕ for three probed media. For a given frequency value, S_a and S_ϕ decrease from air to CCl_4 and from CCl_4 to fluorite. Thus an improved sensitivity is obtained when the probed medium has smaller effusivity (Table I).

In the detection of phase transitions we have to take into account the nature of the probed medium, which should have the following characteristics: a high value of dn/dT (typically 10^{-4}°C^{-1} for liquids and 10^{-5}°C^{-1} for solids), leading to an improvement of the photothermal signal magnitude, and an effusivity smaller or at the most equal to the sample effusivity in order to improve S_a and S_ϕ.

III. EXPERIMENT

A. Experimental setup

We used a modulated beam from a He-Ne near-infrared laser (3.39 μm) of 5 mW power for the heating. The probe beam (632.8 nm) was created by a He-Ne laser of 2 mW power. The deflection (no more than a few milliradians) was measured by a position sensor (a Centronic QD 50-5 silicon detector) placed at suitable distance (about 20 cm) from the illuminated sample surface. An electromechanical chopper was used as a light modulator in the frequency-modulation range 0.1–200 Hz. The output signal was detected by a lockin amplifier (PAR 5206). Both amplitude and phase data were collected by a microcomputer. Electrical heating, monitored by a microprocessor (Coreci MCF/RNZ), ensured that the average temperature T was scanned in the range 5–200 °C. The average temperature of the sample changes at a rate of 0.06 °C min^{-1}, and this temperature was measured using a platinum-resistance thermometer. The samples (the weight of which is about 0.05 mg) are 8CB (B.D.H. Chemicals, Ltd., without further purification). The fluorite and air were the front medium and the probed medium, respectively.

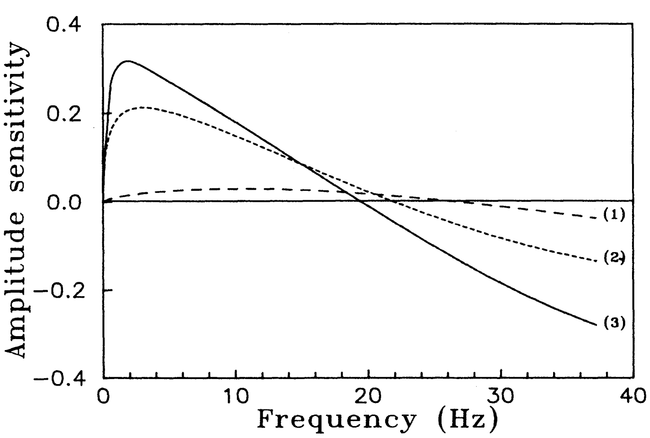

FIG. 9. Theoretical effect of the probed medium on the amplitude sensitivity S_a. (1) Fluorite, (2) CCl_4, and (3) air.

B. Results and discussion

Between 20 and 50 °C, the 8CB sample undergoes two phase transitions at 33.7° and 40.5 °C according to the following sequence: smetic-A–nematic-isotropic. Figures 11 and 12 show the direct experimental plot of the photothermal signal amplitude as a function of temperature along the nematic-isotropic phase transition, at two different modulation frequencies. As expected theoretically the signal magnitude increases during the phase transition at a low frequency ($f=1$ Hz), while it decreases at a higher frequency ($f=20$ Hz). A decrease of the phase signal can be observed during the phase transition at the two preceding frequencies (Figs. 13 and 14). In this experimental configuration, the smetic-A–nematic transition could also be detected.

When the probed medium is air, both the amplitude and the phase signal are sensitive to the changes in thermal parameters during the two phase transitions. When the probed medium is fluorite, the photothermal signal is less sensitive to these changes; consequently, the smetic-A–nematic transition is not detected. The variations of the magnitude and the phase decrease during the

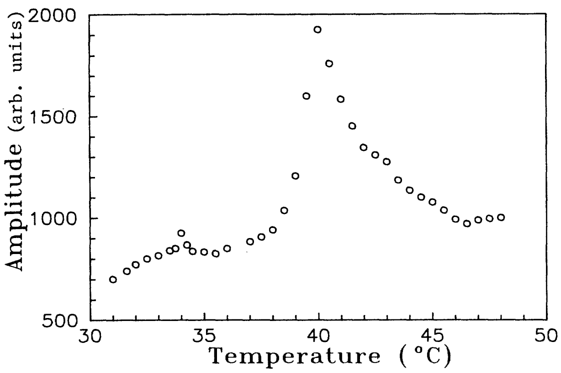

FIG. 11. Variation of the amplitude a_n of the probe-beam normal deflection vs the average sample temperature near the nematic-liquid transition of 8CB with a modulation frequency of the pump beam of $f=1$ Hz.

nematic-liquid transition.

The dependence of S_a and S_ϕ on the thermal properties of the probed medium may be understood by discussing the usual one-dimensional solution of the heat equation. In this case the rear-medium temperature Θ_r is obtained for $\tau_m=0$ in Eq. (1). Then the term A_m is given by

$$A_m=\frac{(1+R_f)(1+R_r)\exp(-\sigma_s l_s)}{1-R_f R_r \exp(-2\sigma_s l_s)}\frac{1}{K_s\sigma_s},$$

where R_r and R_f characterize, respectively, the thermal reflection sample-rear medium at $z=-l_s$ and the thermal reflection sample-front medium at $z=0$:

$$R_r=\frac{1-B}{1+B}, \quad R_f=\frac{1-G}{1+G}$$

$$\text{with } B=\frac{(K_r c_r \rho_r)^{1/2}}{(K_s c_s \rho_s)^{1/2}} \text{ and } G=\frac{(K_f c_f \rho_f)^{1/2}}{(K_s c_s \rho_s)^{1/2}},$$

and, $\sigma_s=(1+j)(\omega\rho_s c_d/K_s)^{1/2}$.

It should be noted that R_r and R_f must lie between

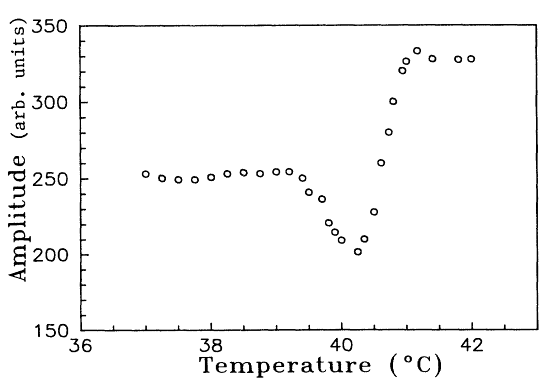

FIG. 12. Variation of the amplitude a_n vs the average sample temperature near the nematic-liquid transition of 8CB at $f=20$ Hz.

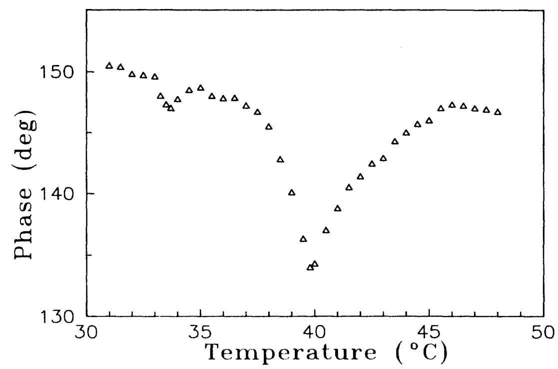

FIG. 13. Variation of the phase shift Φ_n vs the average sample temperature near the nematic-liquid transition of 8CB at $f=1$ Hz.

-1 and $+1$. When $K_r c_r \rho_r \gg K_s c_s \rho_s$, the thermal-reflection coefficient R equals -1, then $A_m \to 0$ and the rear-medium temperature Θ_r is independent of the sample thermal parameters.

In this case, both magnitude sensitivity and phase sensitivity approach zero. We obtain the result as mentioned above when $K_f c_f \rho_f \gg K_s c_s \rho_s$.

If $K_r c_r \rho_r \ll K_s c_s \rho_s$ and $K_f c_f \rho_f \ll K_s c_s \rho_s$ (i.e., $R_r=1$, $R_f=1$) the thermal response A_m becomes

$$A_m=\frac{4\exp(\sigma_s l_s)}{1-\exp(-2\sigma_s l_s)}\frac{1}{K_s\sigma_s}.$$

In this case, the rear-medium temperature Θ_r depends only on the sample thermal parameters. This results in a higher sensitivity of the photothermal signal towards the change in these parameters during the phase transition. The magnitude and phase sensitivity are close to the maximum. Other values of R_r and R_f correspond to various intermediate cases.

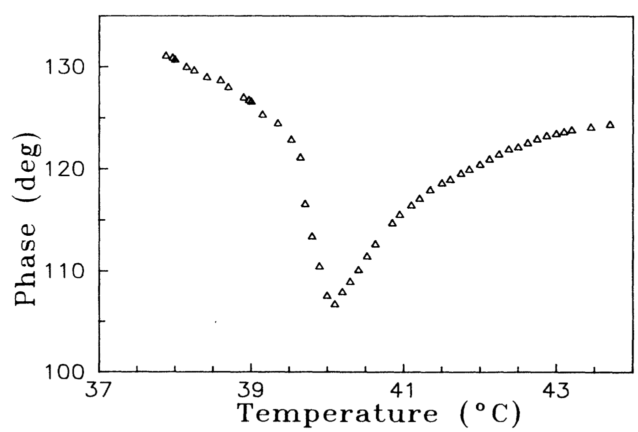

FIG. 14. Variation of the phase shift Φ_n vs the average sample temperature near the nematic-liquid transition of 8CB at $f=20$ Hz.

IV. CONCLUSIONS

We have shown by numerical analysis that the photothermal probe-beam technique, in the rear configuration, can detect first- and second-order phase transitions of very small amounts of a particular compound. It has been found that the sensitivities of the amplitude and phase of the photothermal signal can be improved by the choice of a probed medium and front medium with an effusivity smaller than the sample effusivity. A solid material that is optically nonabsorbing for the incident light and with a suitable effusivity can be used as probed medium. We have also found that detection sensitivity depends on the modulation frequency and the probe-beam transverse offset. In order to detect phase transitions, it would be necessary to first determine the appropriate values of the modulation frequency and the probe-beam transverse offset.

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