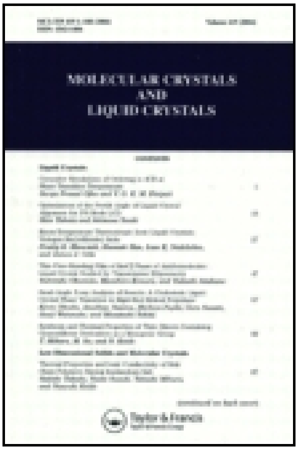

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Phase Transitions: Photoacoustic Detection

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Version of record first published: 28 Mar 2007.

To cite this article: F. Scudieri , M. Marinelli , S. Martellucci & U. Zammit (1987): Phase Transitions: Photoacoustic Detection, Molecular Crystals and Liquid Crystals, 143:1, 123-129

To link to this article: http://dx.doi.org/10.1080/15421408708084617

Mol. Cryst. Liq. Cryst., 1987, Vol. 143, pp. 123-129
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Printed in the United States of America

PHASE TRANSITIONS: PHOTOACOUSTIC DETECTION

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Abstract First and near second order phase transitions have been detected in 8CB liquid crystal by gas cell and microphone photoacoustic technique. A relaxation process in the smectic A phase has been observed. Magnetic field effect in the nematic phase on the photoacoustic signal is reported. Microcalorimetric analysis of the technique may be obtained.

INTRODUCTION

The gas cell and microphone photoacoustic (PA) technique consists of heating a sample in an air tight volume by a modulated laser or lamp source and analyzing the signal detected by a microphone due to overpressure in the gas cell.[1] The microphone signal is characterized by an amplitude and phase which are detected by a lock-in amplifier. This technique has been applied to solids for thermal parameters evaluation,[2,3] and a model for PA signal behaviour at phase transition in materials, developed by Korpiun et al.,[4,5] can be applied to liquid crystals for micro-calorimetric purposes. The PA signal behaviour at phase transitions in 8CB liquid crystal is reported in this paper. A relaxation phenomenon in the smectic A phase,when it is obtained through melting of the crystalline phase has been detected. The effect on the PA signal of an externally applied magnetic field in the nematic phase is shown. The present results are compared with the ones obtained by Louis et al.[6]

EXPERIMENTAL

The experimental set up is the standard gas cell microphone lock-in detection configuration.[7] An Ar^+ laser operating at 514.5 nm, mechanically chopped at a frequency of 30 Hz was used as the heating source. The beam was spread over the whole sample surface, on its free surface side, in order to avoid the effects due to horizontal thermal gradients. The 8CB liquid crystal, which exhibits cristalline(K), smectic A (S_A), nematic (N) and isotropic (I) mesophases, was placed in a volume 8x4x2 mm^3 and some methyl red was added to it to increase its absorption coefficient to about 300 cm^{-1} at the laser wavelength . In order to check whether the dye had substantially changed the L.C. thermal properties some calorimetric measurements were performed on the pure and dyed material and the results are shown in table 1.

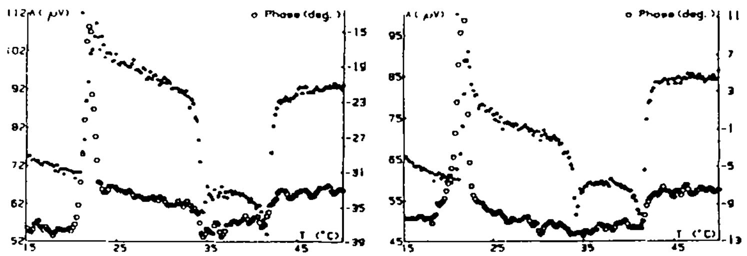
		$K-S_A$	S_A-N	N-I
pure	T(°C)	20.9	33.4	40.2
	Δ H(J/g)	88.13	0.31	3.32
dyed	T(°C)	20.8	33.0	40.1
	Δ H(J/g)	86.28	0.32	2.84

TABLE I Phase transition temperature and specific enthalpy changes for pure and dyed 8CB L.C.

Only the specific enthalpy change of the N-I transition has varied by about 15%, while all the other quantities, have not changed significantly. The temperature of the sample was varied by electrical heating and the temperature change rate, which was computer controlled, was set at a value of 0.1 - 0.2 °C/min, in order to avoid a continously rising signal background which is detected when the rate was set too high. The laser energy per pulse was about 5 μJ.Both PA signal A and phase Ø were detected as a function of temperature.

RESULTS AND DISCUSSION

Fig.1 shows the results for the PA signal A and Ø vs increasing temperature in three different cases.



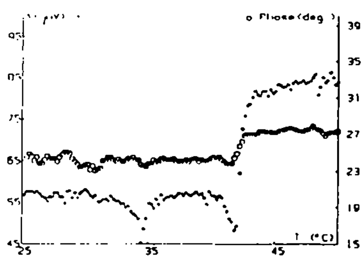


FIGURE 1. PA signal vs increasing temperature in 8CB L.C. in three different cases. See text.

In fig. 1b the temperature change rate was set at half the rate as in fig. 1a. In fig. 1c the PA signal is shown after having let the sample thermalize in the S_A phase for 24 hours at room temperature. The same result had been obtained in the case of decreasing temperature, starting from the I phase. All transitions are clearly detectable, even the S_A-N one, which is nearly second order. A microcalorimetric application of this technique according to the model by Korpiun et al. can therefore be expected. The signal A and Ø levels in the S_A phase, relative to the ones in the I phase are progressively lower in fig. 1b and 1c than in fig. 1a. This suggests that a relaxation process as a function of time was taking place in the S_A phase. The time evolution of the signal A was therefore studied, once the temperature had been set at 24.5 °C, the S_A phase having been reached from the K phase. The result is shown in fig. 2.

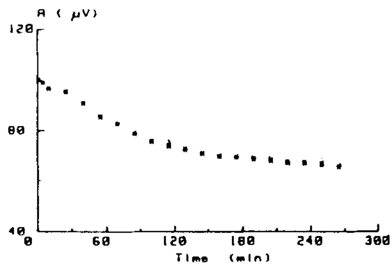


FIGURE 2. PA signal amplitude vs time in the S_A phase in 8CB L.C. at 24.5 °C.

A decrease of the signal A over a time range of several hours is evident. No relaxation phenomenon was observed when the S_A phase had been reached from the N phase. The observed relaxation phenomenon could be associated with defects rearrangement in the material.

Since the PA technique has proved to be very sensitive to the sample structure characteristics, some measurements were also carried out in aligned samples. Fig 3 shows

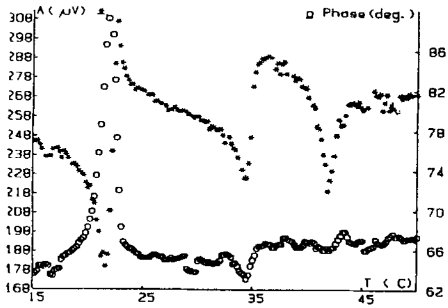


FIGURE 3. PA signal A and Ø vs temperature with an applied external magnetic field of 9 KG in 8CB LC.

result obtained for increasing temperature with an external applied field of 9 KG. The N phase signal A and Ø relative to the ones in the I phase are higher than in the situation with no field. Fig.4 shows the signal amplitude vs applied

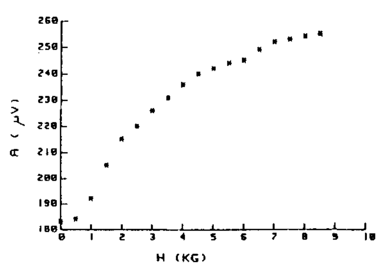


FIGURE 4. PA signal amplitude vs applied magnetic field in 8CB L.C.

magnetic field. The amplitude tends to saturate at a field of about 9 KG. The change in the PA signal A is due to the anisotropic thermal and optical properties of the liquid crystal.

The results of the present work can be compared with those obtained by Louis et al. On the contrary of what stated in such a paper, all phase transitions are detectable in both signal amplitude and phase even for sample front sample illumination. Moreover the PA signal vs temperature result reported in that paper shows a continously rising background which, as pointed out earlier, may be due to a too high temperature change rate.

CONCLUSIONS

Photoacoustic detection of first and near second order phase transition in 8CB liquid crystal has been reported. A relaxation phonomenon has been observed in the S_A phase when obtained through melting of the K phase. The effects of alignement in the N phase due to an external applied magnetic field are also detected.

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