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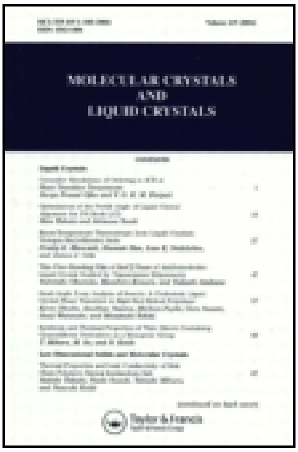

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Photopyroelectric Calorimetry Study of the Smectic A-Hexatic B Transition in Single Homeotropic Domain 65OBC Liquid Crystal Samples

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The work deals with the investigations of the smecticA-hexaticB phase transition in n-hexyl-4′-n-pentyloxybiphenyl-4-carboxylate liquid crystal compound in a single domain homeotropic sample and in a nonaligned sample. The specific heat, the thermal diffusivity, and the enthalpy exchange were monitored over the transition and, at the same time, polarization microscopy observations could be carried out. The transition during the first cooling run was found to be accompanied by a considerably larger defect annealing in the non aligned sample than in the homeotropic one.

Keywords Phase transitions; photopyroelectric calorimetry; specific heat; thermal diffusivity

Introduction

Photopyroelectric (PPE) calorimetry is a high-resolution ac technique which has been proved to be very useful in the study of phase transitions in liquid crystals (LC) [1,2]. In fact, it allows the simultaneous measurements of the specific heat, c, the thermal conductivity, k, and the thermal diffusivity, $D = k/\rho c$ (ρ is the density), and therefore, allows to study static as well as dynamic critical behavior associated with thermal parameters [1,3]. Moreover, in an upgraded setup, it also allows additional polarization microscopy observations and optical scattering measurements [4,5] thanks to the optical access to the sample necessary for the optically induced ac heating, necessary for the calorimetric measurements.

In this work, we focus, in particular, on the study of the smectic A-hexatic B (AB) transition where the determination of the universality class is still an open question. The transition should belong to the three-dimensional XY universality class [6], but experimental results, in particular, high-resolution specific heat measurements, do not support this hypothesis. A range of experimental values for the critical exponent α of the specific heat between 0.48 and 0.65 has in fact been reported [7], significantly different from the value $\alpha_{XY} = -0.02$. It was suggested that, in fact, the AB transition could have a first-order character because of the effect of the coupling between the hexatic order and the short-range molecular herringbone correlation via thermal fluctuation [8,9]. Indeed, it has been experimentally shown [3,10,11], in particular in n-hexyl-4′-n-pentyloxybiphenyl-4-carboxylate (65OBC),

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*Address correspondence to S. Paoloni, Dipartimento di Ingegneria Industriale, Università di Roma "Tor Vergata", Roma, Italy. E-mail: stefano.paoloni@uniroma2.it that the transition is weakly first order. Moreover, the hypothesis of quasitricriticality has been suggested [10], due to the coupling of the order parameter with the density or with the in-plane strain. However, a value $\alpha = 0.65$ of the critical exponent of the specific heat was further reported, that does not conform to the tricritical value of $\alpha = 0.5$. The influence of the structural disorder on the behavior of the thermal parameters over the *AB* transition of 65OBC has been emphasized in Ref. 3. However, even in the case of a sample in which the disorder was kept at minimum, a critical exponent of $\alpha = 0.67$ had been obtained, in agreement with earlier reports, but distant from any theoretical predicted values. The effect of disorder and strain over the *AB* transition was later also monitored by detecting enthalpy release associated to possible strain annealing as the more ordered hexatic *B* phase was entered during the cooling from the smectic *A* phase. It was found that the disorder present in the smectic *A* phase, whose extent depended on the way the sample had been cooled from the *I* phase, is largely annealed during the first cooling run over the *AB* transition [12].

Since it had been shown that the disorder present in the initial smectic *A* phase obtained after cooling of the sample from the isotropic phase may be related to the defects which form at the boundaries of the focal conics domains of different orientation, in this work, we study the *AB* transition in a single-domain homeotropic sample where the disorder level may be expected to be minimum. Upon cooling from the isotropic phase, 65OBC nucleates directly into the smectic *A* one, with no intermediate nematic phase, so permanent homeotropic alignment cannot be obtained by appropriate treatment of the sample cell walls or electric field. In this work, we report the results on a sample which we show can be aligned homeotropically in the smectic *A* phase by inducing a strain field within the sample volume which tends to align the molecules all toward a common homeotropic direction, thus favoring, in the whole sample volume, the formation of smectic planes with a common orientation.

Experimental

A standard PPE setup [13,3] has been used to perform the measurements. The sample was sandwiched between a 300-μm-thick *Z*-cut $LiTaO_3$ pyroelectric transducer and a glass plate whose surface, in contact with the LC, was coated with a 300-nm-thick optically opaque metallic layer. The thickness of the sample was 30 μm. Light from a modulated laser diode was absorbed by the metallic coating in contact with one of the LC sample side, and the temperature oscillations introduced in the sample were detected on the opposite side by the transducer. The modulation frequency was 38 Hz. A two-phase lock-in amplifier measured the signal amplitude and phase from which c, k, and D could be simultaneously retrieved from the appropriate theoretical expressions [13,14]. Moreover, the enthalpy exchange over the *AB* transition could also be detected thanks to an upgraded model for the signal amplitude and phase [13]. The power density and the temperature rate change were decreased as much as possible to minimize the influence of thermal gradients which induce smearing of the *V*s temperature profiles of the observed quantities. Following the successful single domain alignment of LC samples in the nematic phase induced by the strain fields resulting from the flow of the sample with respect of the cell walls [15], we have succeeded in obtaining single domain homeotropically aligned samples of LC in their *smectic A phase*, by inducing strain fields in the sample volume produced by displacement of LC sample cell cover, in our case the pyroelectric transducer, as reported in details elsewhere [16]. The achievement of the homeotropic alignment was verified both by the polarization microscopy imaging, performed at the same time as the calorimetric evaluations, and by monitoring the changes in the thermal diffusivity and conductivity which show larger values for homeotropic samples than for non aligned focal conics ones. This is because the thermal transport parameters are largest when measured with the heat flow parallel to the molecular long axis [17].

Results and Discussion

Figure 1 reports the thermal diffusivity behavior obtained over the *AB* and smectic *A*-isotropic (*AI)* transitions when heating a sample of 65OBC LC which presented focal conics textures and a single-domain homeotropic sample of the same compound, obtained by the previously mentioned strain induced effect. The homeotropic state was confirmed by polarization microscopy observations obtained between crossed polarizers (not reported), carried out together with the thermal evaluations, and where the uniform image was dark because of the lack of birefringence in the homeotropic sample. Both the *AB* and the *AI* transitions are clearly detectable in the thermal diffusivity profiles of both samples, and, in particular, the minimum over the *AB* transition is related to the strong divergence shown by the specific heat, with the thermal conductivity showing a smooth behavior [17,18]. The considerably larger thermal diffusivity values in the smectic *A* and hexatic *B* phases for the aligned sample is a further indication of the achievement of a good degree of homeotropic alignment. Figure 2 shows the high-resolution specific heat data over the *AB* transition obtained for the focal conics and homeotropic samples during the *first* cooling run, where the samples nucleated in the smectic *A* phase from the isotropic one, and during the subsequent heating run. Figure 3 reports the corresponding enthalpy release data. It must be remarked that the present enthalpy exchange detection method does not provide absolute values of the quantity but only relative values, at each temperature, as a function of the conditions of the sample or of the measurement [14]. The data sets relative to the homeotropic sample were horizontally shifted at larger temperatures for a clearer representation. It is clear that the specific heat behaviors over the transition for the two kind of samples, both for the heating and cooling runs, are extremely similar, indicating that the critical behavior is the same in all the reported cases. What is very different is the amount of enthalpy release occurring over the transitions in the various cases, indicating different extent of defect annealing, as previously suggested [12]. In particular, in the focal conics sample

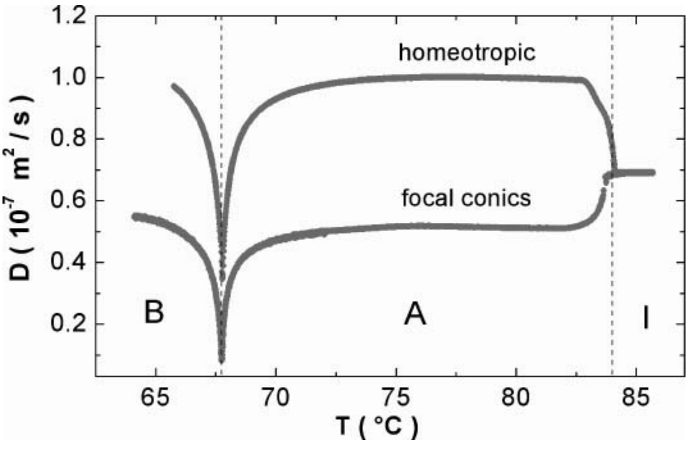

Figure 1. Thermal diffusivity profile over the hexatic B (B)-smectic A (A) and smectic A-isotropic (I) phase transitions for the focal conics and single-domain homeotropic 65OBC samples.

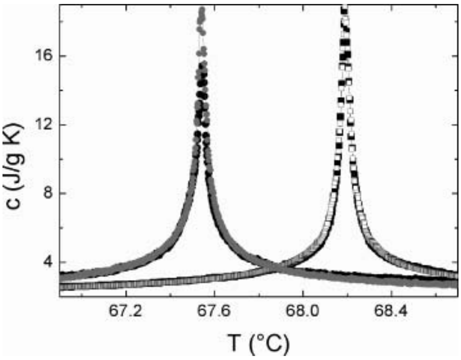

Figure 2. Specific heat profiles over the *AB* transition. Circles for focal conics sample; squares for homeotropic sample. Black symbols for cooling, gray symbols for heating. Homeotropic sample data were shifted to larger temperatures.

obtained by the nucleation of the smectic *A* phase from the isotropic one during the first cooling run, a very large release of enthalpy occurs over the *AB* transition, much larger both in peak value and in temperature range than that obtained during the subsequent heating over the transition. Therefore, a considerable amount of defect annealing occurs when the sample, from the initially formed smectic *A* phase, first enters the more ordered hexatic *B* phase, while a smaller amount of annealing occurs during the subsequent heating run. What is shown here is very similar to what observed by specific heat studies over the same transition in the same sample [19]. In fact, in that case, beside the main large peak over the transition, a small side peak was observed which progressively grew smaller until it eventually disappeared upon repeated cycling over the transition temperature. This was also presumed to be associated to annealing of defects occurring as the transition is repeatedly crossed. In our case, it is the initial smectic *A* phase which is very defective as it nucleates from the isotropic phase, with no intermediate nematic phase. Most of these defects anneal during the occurrence of the first *AB* transition, upon cooing the sample, and a smaller enthalpy release is detected during the subsequent sample heating. It was presumed in the

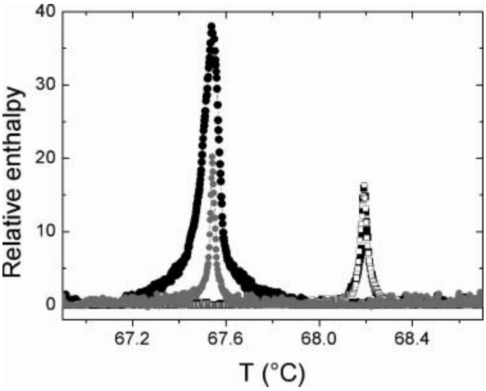

Figure 3. Relative enthalpy release (see text) profiles over the *AB* transition. Circles for focal conics sample; squares for homeotropic sample. Black symbols for cooling, gray symbols for heating. Homeotropic sample data were shifted to larger temperatures.

earlier study [12], that defects originated mainly from the boundaries of the differently oriented focal conics domains. In the case of the homeotropic sample, the behavior of both the specific heat and the enthalpy release appears completely reversible between the first cooling and subsequent heating runs, unlike what occurs in the focal conics sample. Moreover the extent of defect annealing, as probed by the enthalpy release, during the first cooling run is considerably smaller with respect to that found during the corresponding run in the focal conics sample. This has probably to do with the lack of "grain" boundaries in the homeotropic sample. Finally, the fact that the behavior of the specific heat over the *AB* transition in 65OBC LC is the same in samples with markedly different amounts of defects indicates that the critical behavior over the transition is little affected by the defects, at least to the extent of defect concentration contained in the present samples.

Conclusions

Photopyroelctric calorimetry was employed to simultaneously monitor the behavior of the specific heat, the thermal diffusivity, and the released enthalpy and also to perform polarization microscopy imaging over the *AB* phase transition of 65OBC LC compound in a single homeotropic domain sample and in a nonaligned focal conics sample. The homeotropic alignment in the smectic *A* phase*,* in samples which show no nematic phase, was obtained by inducing a strain field within the sample volume which tends to align the molecules all toward a common homeotropic direction, obtained by displacement of the cell cover. The transition during the first cooling run was found to be accompanied by a considerably larger defect annealing in the nonaligned sample than in the homeotropic one, presumably because of the "grain" boundaries in the former, where defects are expected to originate.

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