PHYSICAL REVIEW E **74**, 041707 (2006)

Strain effects at the hexatic-*B*–smectic-*A* transition in the 65OBC liquid crystal

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(Received 29 July 2005; revised manuscript received 18 July 2006; published 23 October 2006)

We have studied the hexatic-*B*–smectic-*A* (Hex*B*-Sm*A*) transition in *n*-hexyl-4′-*n*-pentyloxybiphenyl-4-carboxylate (65OBC) by means of a high-resolution ac photopyroelectric (PPE) calorimetric technique. A procedure for the interpretation of the PPE data, which allows the detection of an internal heating source due to strain annealing and/or latent heat, has been applied. We have found that the strain present in the sample depends on the kinetics of formation of the smectic phase once the sample is cooled from the isotropic one. The strain field keeps memory of this kinetics and can be only partially annealed on decreasing the temperature or cycling it around the Hex-Sm*A* transition. A reversible ordering-disordering process has been found at T_c and has been explained in terms of the competition between the order parameter variation with temperature and the constraints imposed by the disorder. The results confirm that the transition has a weakly first-order character with a specific heat critical exponent that disagrees with the available theoretical predictions. Our data show the importance of the disorder in 65OBC and we tried to clarify what would be the consequence of this result in theoretical modeling devoted to solving the puzzle of the Hex*B*-Sm*A* transition in this compound.

DOI: 10.1103/PhysRevE.74.041707 PACS number(s): 64.70.Md, 61.30.Eb

I. INTRODUCTION

Smectic (Sm) liquid crystals (LCs) can be represented as a three-dimensional (3D) stack of weakly interacting 2D layers having a liquidlike structure, due to the short range of the in-plane positional order of the molecules.

When a smectic is cooled, it happens, in some particular compounds, that a phase still having short-range plane positional order, but with long-range bond orientational order with sixfold symmetry, becomes stable. This is the hexatic phase (Hex) and it was found for the first time in *n*-hexyl-4′-*n*-pentyloxybiphenyl-4-carboxylate (65OBC) [1]. In the hexatic and smectic phases of this compound the molecule long axis is, on average, perpendicular to the layers and the phases are therefore called Hex*B* and Sm*A*, respectively.

The universality class of the Hex*B*-Sm*A* transition is still an open question. The hexatic order parameter is usually represented as $\Psi=|\Psi|\exp(i6\psi)$ and the transition should therefore belong to the 3D *XY* class, but experimental results, in particular high-resolution specific heat measurements, do not support this hypothesis. A review of the results available in literature is given in Ref. [2] and a range of experimental values for the critical exponent α between 0.48 and 0.65 is reported.

The first-order nature for the Hex*B*-Sm*A* transition was later predicted by considering the effect of the coupling between the hexatic order and the short-range molecular herringbone correlation via thermal fluctuation [3]. An improved version of this model has been recently proposed [4], but it is believed that, at least in the case of the specific heat in LCs, the phase ψ of the bond orientational order parameter does not play a significant role [2,5].

More recently it has been experimentally shown [5–7], in particular in 65OBC, that the transition is indeed weakly first order. Moreover, quasitricriticality due to the coupling of Ψ with the density or with the in-plane strain has been put forward [5]. Following, in fact, the analogy with the prediction for a compressible Ising model developed by Bergman and Halperin [8], in which the fluctuations in the strain are driven by the ones in the spin order parameter, it has been suggested that such a coupling could be responsible for a small latent heat in a section of a transition line which, without the coupling, is second order. The authors, however, did find a specific heat critical exponent ($\alpha=0.65$) that does not conform to the tricritical value ($\alpha=0.5$).

The importance of the structural disorder at the Hex*B*-Sm*A* transition of 65OBC has been emphasized in Ref. [6]. In particular, it has been found that disorder dramatically influences the behavior of the thermal transport parameters (i.e., thermal conductivity and thermal diffusivity) over the phase transition and it depends on the thermal history of the sample. Such a disorder can be reduced if the sample is slowly cooled from the isotropic phase (*I*) in a cell whose surfaces are treated with a surfactant, so as to increase the mean grain size of the focal conics in the initial Sm*A* phase. Even in the case of a sample in which the disorder was kept at a minimum; however, a critical exponent $\alpha=0.671\pm0.009$ has been obtained, in agreement with the ones reported in literature, but far from any possible theoretical prediction.

One may ask, at this point, if a study of the effects of the structural disorder on the transition can help in validating existing theoretical models for the Hex*B*-Sm*A* transition based on the Ψ strain coupling or suggests a new direction for future developments.

In the attempt to address this important issue, we have investigated, in detail, the origin and the evolution of the disorder that sets in 65OBC when it is cooled from the *I* phase. To achieve this, we have developed a data analysis procedure that enhances the capability of high-resolution ac photopyroelectric (PPE) calorimetry and qualitatively enables the detection of latent heat and/or energy released due to disorder annealing, which influences the behavior of the signal amplitude and phase.

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It has been found that the disorder present in the Sm*A* phase, which depends on the way the sample has been cooled from the *I* phase, is annealed during the first cooling run at the Hex*B*-Sm*A* transition. A fraction of it, however, is reintroduced in the sample as it is heated back to the Sm*A* phase. Annealing, in fact, takes place in every cooling run following the first one.

Upon heating, the analysis of the PPE data suggests that a small amount of latent heat is present and that the transition, therefore, has a weakly first-order nature. Latent heat is obviously present also upon cooling but it is overshadowed by the annealing process. We have also calculated the specific heat critical exponent, which is in excellent agreement with previously published data, but significantly different from any theoretical prediction.

The results reported above highlight the role of the macroscopic, surface-induced, disorder at the Hex*B*-Sm*A* transition. It is our opinion that the coupling between the hexatic order parameter and the strain field due to the disorder could represent a hint for further theoretical developments in the theory.

II. EXPERIMENT

The experimental setup we have used is described in Ref. [9]. It combines the capabilities of high-resolution ac calorimeter with those of polarizing microscopy. We can, in fact, monitor the structural evolution, via a sample texture analysis, and the thermal parameters during the same run.

The sample was contained in a 30-μm-thick cell and it was periodically heated by an acousto-optically modulated He-Ne. The laser power was decreased as much as possible to reduce the effect of thermal gradients. The heating laser modulation frequency was 38 Hz. The sample was first taken to the isotropic phase and then cooled into the Sm*A* phase with a temperature rate change of 300 mK/min. At 72 °C the rate was reduced to approximately 5 mK/min and kept constant. The sample temperature was then cycled around the transition one for three cooling runs and the corresponding following heating runs. We could not proceed further because of the sample degradation which in our setup is much faster than that reported in literature because of the very large surface-to-volume ratio.

III. RESULTS

The results reported in Figs. 1(a) and 1(b) show the data relative to the amplitude (A) and the phase (ϕ) of the PPE signal in the subsequent heating and cooling runs. Sample degradation resulted in a downshift of the transition temperature T_c, which was 20 mK per heating-cooling cycle, so the different data sets were shifted horizontally so as to align the T_c values for better comparison of the results. The A data basically coincide in the investigated temperature range while a pronounced difference in the temperature behavior of ϕ vs temperature is observed in the vicinity of the phase transition. A peak structure, with two minima on either side, is obtained for the first cooling run, a feature which becomes less evident in the second cooling run and eventually disappears on the third one. This feature is never observed in either of the heating runs which follow the cooling ones.

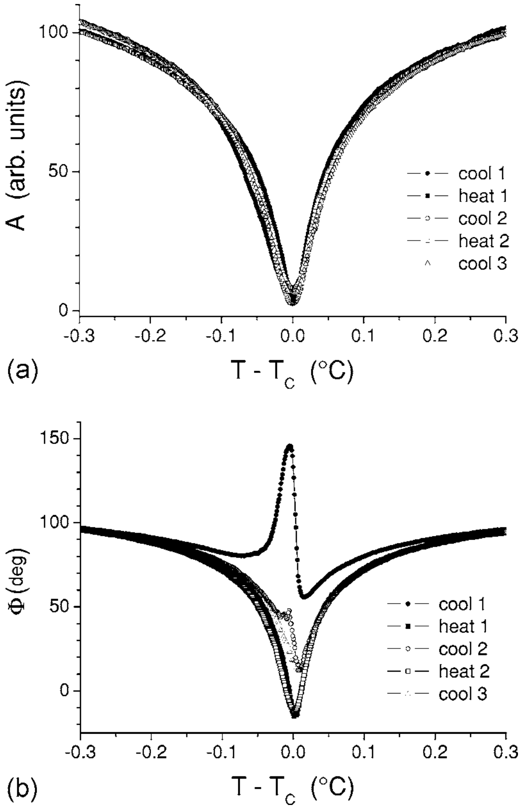

FIG. 1. Amplitude (a) and phase (b) of the PPE signal as a function of temperature in the various cooling and heating measurements.

A similar behavior was reported in Ref. [6], where it was shown that the temperature dependence of both the amplitude A and the phase ϕ of the PPE signal at the transition, depended on how fast the sample was initially cooled from the *I* phase. A large initial cooling rate at the *I*-Sm*A* transition, in fact, gave rise, during the first cooling run, to a peak structure similar to the one reported in Fig. 1(b), strictly connected to the disorder present in the sample. Such a structure almost disappeared if the sample initial cooling rate was lowered or some external ordering field was applied. When present during the first cooling run, the peak structure was suppressed after the sample was cooled to the Hex*B* phase for the first time and was no longer observable when the sample was subsequently cycled over the Hex*B*-Sm*A* transition.

The dependence of such features on the mean grain size in the Sm*A* phase initially obtained on the first cooling from the isotropic phase suggests a correlation with strain and disorder present in such a phase. In fact, a lower temperature side peak in the specific heat (c_p) measurement was reported in the literature [5,7], which also was attributed to nonequilibrium features in the system, namely, the presence of strained regions in the sample, depending not only on the sample thermal history, but also on the temperature scanning rate. Moreover, the fact that, in this work, the features are strongly reduced and eventually become suppressed for the runs fol-

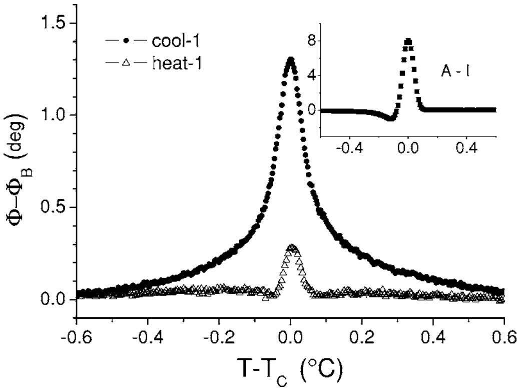

FIG. 2. Phase data relative to PPE front detection measurements (see text) over smectic-*A*–hexatic-*B* transition and smectic-*A*–isotropic transition (inset).

lowing the first time the sample enters the Hex*B* phase may suggest an annealing of such defects occurring during the transition to the more ordered Hex*B* phase. If that were the case, energy release would be expected during the annealing, constituting an "internal" ac heating source, which would add vectorially to the external one due to the laser heating. If we consider, in fact, a disordered sample volume which, at a given temperature, is about to anneal, the ac temperature oscillation produced by the external heating source would represent a small perturbation that could trigger the annealing process and therefore a delayed ac enthalpy release. The features observed in the phase signal over the initial Sm*A* -Hex*B* transition could then be the result of such enthalpy release.

In order to verify this scenario, we have repeated the measurements still using the PPE technique but in this case in the so-called front detection (FD) configuration [10–12]. In this configuration heat is generated by light absorption at the sample–pyroelectric transducer interface, unlike the previous measurements performed in the so-called back detection (BD) configuration where heat is generated on the sample side opposite the one in contact with the transducer. In the FD measurements, for adequate frequency values [10–12], the signal phase does not depend on the sample thermal parameter variation over the phase transition. It can therefore show changes only when latent heat or other heat exchange terms are involved or in the case of relaxing (phase lagged) specific heat, such as in glassy transitions [13].

Figure 2 shows the behavior of the FD excess signal phase, with respect to the background, for the first cooling run over the Sm*A*-Hex*B* phase transition, after the sample had initially been rapidly cooled down (0.3 °C/min) from the isotropic phase, and also for the subsequent heating run. The signal phase shows a single-peaked feature which is considerably reduced in peak value and temperature width for the heating run. So it could be that over the first cooling run the peak is associated mainly with the enthalpy release related to the defect annealing, with a small latent heat possibly due to a small first-order character of the transition, while it is essentially due to latent heat in the subsequent heating run. In fact, the shape of the peak in the heating run qualitatively resembles that observed over the Sm*A*-*I* transition, which is known to have a pronounced first-order character, and it can therefore be associated with the latent heat. The peaks, in such a case, do not show a gradual rise at either side of the transition temperature as in the first cooling run over the Sm*A*-Hex*B* transition, but they show abrupt changes over comparable and relatively small temperature intervals across the respective transition temperatures, presumably associated with the two-phase coexistence region for the two transitions. Also, the phase variation over the Sm*A*-Hex*B* transition is considerably smaller than the one observed over the Sm*A*-*I* transition, thus showing that the possible first-order character in the former case is much smaller than in the latter.

We have therefore tried to account for the effect of the internal heating source by including, in the model used to calculate the sample thermal parameters from the signal amplitude and phase in the BD configuration, the effect of a delayed source uniformly distributed in the sample volume, mimicking volume heat release. Such a source comes into play and sums up vectorially with the external source as the temperature is changed over the phase transition region. The experimental data for A and ϕ have been simultaneously fitted, the fitting parameters being, initially, the sample thermal parameters and the amplitude of the internal source I_{int}. Since, in agreement with what has been obtained in Ref. [6], the thermal conductivity derived from the fits remains fairly constant over the Sm*A*-Hex*B* transition, as in the case of the Sm*A*-nematic phase transition [14] we have decided to fix its value over the transition in order to reduce the number of free parameters, which are, therefore, c_p and I_{int}. We have found that, in all cases, this assumption reduces the scattering in the calculated values of the thermal parameters, without altering their overall profile.

Thanks to this additional heating source in the model, the A and ϕ data could be successfully fitted, even in the temperature region very close to $T_{\text{Hex}B\text{-Sm}A}$, with a continuous profile of the thermal conductivity. When the model without the internal source has previously adopted [6], it was possible to successfully fit both A and ϕ data only provided the thermal conductivity and, to a certain extent, the specific heat showed an unrealistic steep decrease in the temperature region of approximately 0.2 °C over T_c. So in such a temperature region the data could not be considered; also because the effect of rounding due to temperature gradients is particularly relevant in that range. One of the consequences of the present approach is that, with respect to the previous approach, the largest c_p values, obtained close to T_c, are in better agreement with the ones obtained with other techniques [5,7]. The thermal parameter values obtained with this model outside this temperature region are in good agreement with the ones obtained previously.

Considering now the results shown in Figs. 3(a) and 3(b), both c_p and I_{int} show single peaks over the transition despite the nonregular profile of the signal phase during the cooling run. In the case of the cooling run the I_{int} peak is slightly shifted to lower temperature with respect to the c_p one. Moreover, the I_{int} peak shows a larger peak value and temperature width with respect to the subsequent heating measurement. This latter feature is qualitatively similar to what was previously shown for the FD measurement phase signal

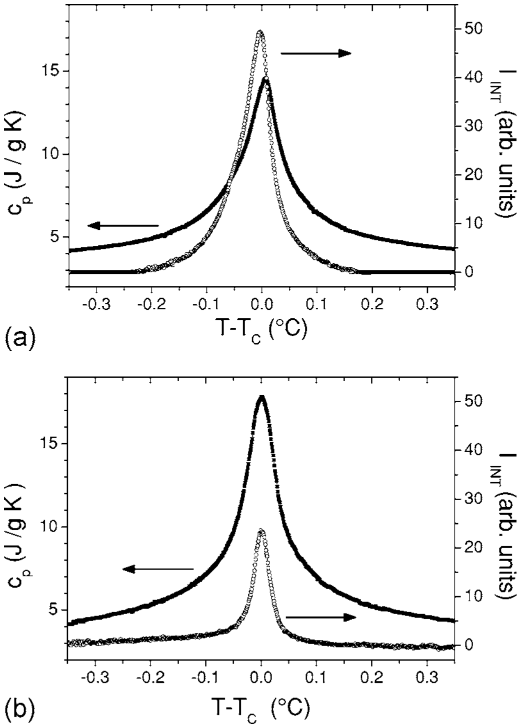

FIG. 3. Specific heat and internal source amplitude (see text) for first cooling run (a) and the subsequent heating run (b) over smectic-*A*–hexatic-*B* transition.

data. This then suggests that, for the first cooling run, I_{int} is mainly related to the presence of heat released during the annealing process, while it is reasonable to assume that the peak upon heating is mainly due to the latent heat associated with the possible weak first-order character of the transition. A latent heat value of 0.04±0.02 J/g, measured over this transition by adiabatic scanning calorimetry, has been reported in Ref. [7], though this value is stated to be close to the ultimate resolution of the employed technique. A small first-order character of this transition cannot, therefore, be ruled out. Latent heat could contribute also in the cooling run, but it is probably overshadowed by the annealing process which gives rise to larger and wider features. In this respect, it is reasonable to assume that the annealing process would progress as the ordered phase is entered and this can probably explain, for the first cooling run, the shift to lower temperature of the peak of I_{int} with respect to the one for c_p which provides an indication of T_c. Finally, since the introduction of an enthalpy release term in the model has been able to account for features in the PPE signal presumably related to the presence of defects, it may be that also other reported features, such as the lower-temperature secondary side peak in c_p measurements [5,7], also attributed to the presence of strained regions in the sample, could have been possibly accounted for by an equivalent enthalpy term in the model used to calculate c_p.

We have performed six successive cooling-heating cycles on the same sample, after its initial heating into the isotropic phase. The results for c_p and I_{int} are reported, respectively, in Figs. 4(a) and 4(b). The heating and cooling data show distinctive features. The c_p results for the heating runs show identical behavior with the largest obtained peak values. The results for the first cooling run show the smallest peak value and width, this being possibly due to smearing associated with strain, which should be maximum in this run. The values for the successive cooling runs then show a progressive tendency to approach the ones of the heating runs, apart from the peak region where contamination plays a significant role. As for I_{int}, the cooling curves are systematically larger in peak value and broader with respect to the heating ones, though their width and peak value tend to decrease in the cooling runs following the first. Moreover, the peak positions in the cooling runs are at slightly lower temperature with respect to the specific heat and the curves are broader on the lower-temperature side of the peaks. This is consistent with defect annealing taking place, which, as stated above, becomes more relevant as the Hex*B* phase is entered. Such an annealing is more pronounced during the first cooling run, when the defect density is supposedly largest, but seems to take place also in the following cooling runs. The fact that the temperature width of the peaks of I_{int} is larger for the cooling runs with respect to the heating ones should also point in the direction of I_{int} being substantially associated with defect annealing in the former case, since the annealing temperature of the various parts of the sample would depend on the local random distribution of strain. On the other hand, the width of the I_{int} peaks during the heating runs would be related only to the two-phase coexistence region, which remains unchanged during the subsequent heating runs. In fact,

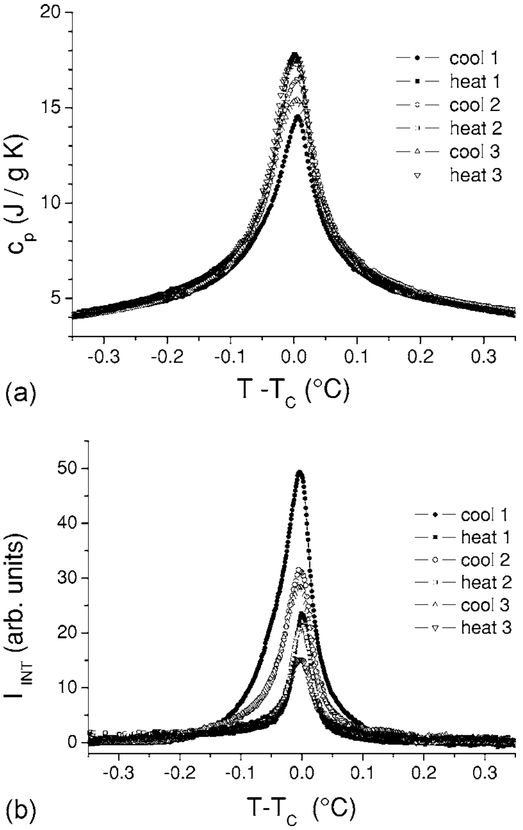

FIG. 4. Specific heat (a) and internal source amplitude (b) for the various cooling and heating runs over smectic-*A*–hexatic-*B* transition.

this width of I_{int} (70–80 mK) is similar to the one of the coexistence region (approx. 60 mK) reported in Ref. [5] and obtained by another ac technique, but is considerably larger than the one (14 mK) reported in Ref. [7] and obtained with a dc technique. We cannot provide a definite explanation for this discrepancy. The progressive decrease of the peak values of I_{int} for the subsequent heating runs is presumably due to contamination which, as stated above, takes place pretty rapidly in the present compound with the present measuring configuration.

It should be pointed out that, though ac techniques in general fail to provide quantitative information of latent heat over a first-order phase transitions, the BD PPE configuration proves to be able to qualitatively detect even small amounts of transition enthalpy.

The critical behavior of the specific heat has been analyzed by fitting the data in Fig. 4(a) with the expression

$$c_p = B_\pm + A_\pm |T - T_c|^{-\alpha}.$$

Adding to the expression a linear background term $E(T - T_c)$ and a correction to scaling one $(1 + D|T - T_c|^{-0.5})$, we obtained $E \approx D \approx 0$; therefore with no influence on the fit quality. Data points corresponding to the temperature range where $I_{int} \approx 0$ only were included in the fit. This implies that, for the heating runs, the data in a range of approximately 80 mK around T_c could not be considered for the fit. When the purpose of the analysis is to establish the universality class of the transition, the relatively large temperature range around T_c not considered in the fit represents a severe limitation on the possibility to reach such a goal. This is the only way, however, to unambiguously obtain information on the effect of pretransitional fluctuations on the specific heat, avoiding the complications arising from the presence of the two-phase coexistence region. Also in the case of Ref. [5], data points in a quite large temperature range around T_c ($\approx$60 mK) were not considered in the fit. Following this procedure, we have fitted the data coming from heating and cooling runs and we have obtained α (0.650 ± 0.003) and A_-/A_+ (1.100 ± 0.005) values that in all cases are approximately the same, within the statistical uncertainties.

It should be finally mentioned that the sample texture evolution during calorimetric measurements was continuously monitored. It has been found that a focal conic pattern forms as the sample is first cooled in the Sm*A* phase and that it does not change with decreasing temperature and at the Hex*B*-Sm*A* transition. Such a pattern, however, depends on the kinetics of the formation of the Sm*A* phase at the Sm*A*-*I* transition. Large temperature rate changes gave patterns with small focal conic domains, while slow cooling, combined with the application of external fields, resulted in a significant increase of the domains. Once formed at the Sm*A*-*I* transitions, these patterns were frozen in the sample.

IV. DISCUSSION

Let us try to summarize the main experimental results obtained in this work: (i) the focal conic texture in the Sm*A* and the behavior of c_p in the first cooling run depends on the way (temperature rate change, external fields, etc.) the sample is cooled from the *I* phase into the Sm*A* one and does not change with temperature in the ordered phases; (ii) there is an internal heating source, due to latent heat and strain annealing that is different from zero in a temperature region close to the Hex*B*-Sm*A* transition upon both cooling and heating the sample; (iii) the amplitude of this internal source is larger upon cooling the sample than on heating.

These results can be explained as follows. The formation of the focal conic pattern is strongly affected by the presence of some defects induced in the sample by the cell surfaces and by the necessity for the system to reduce the elastic energy, as the temperature is lowered. Due to the large surface-to-volume ratio in our experimental setup, the effect of such surface-induced defects is very important and can be reduced by treating the surfaces with a surfactant to induce sample alignment. Nevertheless, since 65OBC has no nematic phase, the ability of this surface treatment to align the sample is limited and the defects cannot be totally removed. The concentration of defects, as well as the final focal conic pattern, depend also, of course, on the temperature rate change at the Sm*A*-*I* transition: the faster the rate, the more disordered the sample. We have tried several different combinations of rates and surface treatments, and also with an external electric field applied to the sample, but we could only affect the size of the average dimension of the focal conic grains.

There is an important question, at this point, that deserves an appropriate answer: how can we explain the connection between the macroscopic disorder, also related to the features of the focal conic pattern, and the behavior of c_p over T_c? It is well known, in fact, that in the case of other LCs phase transitions, namely, the Sm*A*-nematic in 8CB, in which there is an increase of the correlation length of the fluctuations at T_c and the contribution to the singular term in c_p comes from a length scale of the order of a micrometer, the macroscopic disorder plays no evident role. No difference, is found, for instance, in 8CB [15], in the c_p critical behavior between nonaligned and monodomain samples, though some recent results on ferroelectric compounds have shown differences between nonaligned and aligned samples [16]. Why, on the contrary, in 65OBC does the macroscopic disorder, largely due, in our case, to surface effects, extend its influence to the microscopic length scale particularly in the first cooling run where the specific heat profile is strongly altered? The possible answer, in our opinion, comes from the "fragility" of the Hex*B* phase, witnessed by the relatively large value of dT_c/dp in this compound (30 K/kbar) [5], where p is the pressure.

It is our opinion that one of the distinctive feature of the Sm*A* phase in *n*OBCs, namely, the extremely well-defined layering which gives rise to unusual second and third harmonic peaks in the x-ray Bragg reflection [17], is disturbed by the amount of surface-induced layer distortion and that the effect of this disorder, because of the fragility mentioned above, can extend to the microscopic scale.

The annealing process that takes place upon cooling influences the microscopic scale disorder only, as suggested by the fact that the focal conic pattern does not change. This means that the curvature of the smectic layers, strongly affected, in our case, by defects pinned at the surface, remains approximately the same as observed within the resolution of our optical investigation system. Such pinned surface defects represent a constraint that generates disorder in the system, and they survive in the competition with the increase in plane sample ordering occurring when the sample enters the Hex*B* phase.

Once the sample is heated back to the Sm*A* phase, the presence of the constraints reproduces a structural configuration with microscopic scale distortions similar to the one present in the same phase during the first cooling. As a consequence, part of the microscopic disorder is reintroduced in the sample and annealing effects continue to take place in every cooling run following the first one. It is a kind of reversible ordering-disordering process driven by, respectively, the entry into the ordered Hex*B* phase and the elastic distortion induced by the surface defects in the Sm*A* phase. The induced disorder can eventually combine with the topological disorder initially introduced during the first cooling from the isotropic phase.

It is now widely accepted, as also shown by our results, that the Hex*B*-Sm*A* transition has a weak first-order character whose origin is still unclear. The major part of the recent theoretical research is based on the model proposed by Bruinsma and Aeppli (BA) [3], in which the first-order character of the transition originates from the sixfold hexatic and twofold herringbone order parameters coupling. Depending on the strength of this coupling, the transition can become a second-order one at a tricritical point.

The experimental results, however, do not support this theoretical prediction in 3D systems. Heat capacity measurements, in particular, have shown that in compounds in which there is no evidence of herringbone order, the α critical exponent remains unusually large and does not conform to the *XY* and/or BA behavior for a second-order phase transition. The same happens in mixtures in which the temperature range of the Hex*B* phase is very large. The contradiction, in this case, comes from the fact that the larger the temperature difference between the Hex*B*-Sm*A* and the Hex*B*-Cr*E* transitions, at which the herringbone order is established, the smaller should be the effect of the herringbone fluctuations at $T_{\text{Hex}B\text{-Sm}A}$.

This puzzling situation has recently motivated some refinements of the BA idea which are based on renormalization group [4] and Monte Carlo [18] calculations. In all cases, however, the attempt to reconcile theoretical and experimental results has failed.

The relevance of the herringbone order, at least in specific heat experiments, at the Hex*B*-Sm*A* transition has been questioned by Haga *et al.* [5]. It is their opinion, in fact, that c_p depends more on the average lateral distance between molecules than on bond angles. As an alternative, their tentative explanation of the weakly first-order nature of the transition comes from the in-plane Ψ density or Ψ strain coupling. The theoretical base of their approach stems from the analogy with the compressible Ising problem solution provided by Bergman and Halperin. In this scenario, the Ψ density or Ψ strain coupling derives from the fluctuations of the in-plane strain induced by the fluctuations of the hexatic order parameter and they induce a quasitricritical behavior for which $\alpha = 0.5$.

Although this value represents a significant improvement with respect to the previous theoretical predictions for an *XY*-like behavior ($\alpha_{XY} = -0.017$), it is still smaller than the experimental one, $\alpha \approx 0.65$. Moreover, a tricritical behavior implies that different compounds can have different α, depending on the distance of their transition from the tricritical point. This is in contrast with the almost constant α value found in several LCs and mixtures [19].

The results we have obtained in this work show the important role of defects in the Hex*B*-Sm*A* transition. One may argue that this is due to the peculiarity of our sample cell in which the rather large surface-to-volume ratio favors the formation of defects. This is certainly true, but the presence of effects also associated with defect and strain observed with other techniques suggests that the characteristic geometry of our setup cannot be the only explanation for what we have observed close to $T_{\text{Hex}B\text{-Sm}A}$.

What is probably strongly correlated with our setup is the phenomenon we have called "reversible annealing," in which disorder is reintroduced in the sample every time it is heated across the Hex*B*-Sm*A* transition. In Ref. [5], in fact, no difference, apart from the c_p low-temperature shoulder upon cooling, has been found between heating and cooling runs. Though this reversible process is a peculiarity of our experiment, nevertheless it can be seen as something enhancing the disorder always associated with the transition.

Let us now envisage the possible consequences of our results in the theoretical description of the Hex*B*-Sm*A* transition.

The effect of the disorder can be accounted for with an elastic coupling term, Ψ strain, in the Hamiltonian. In our view, the meaning of this term is substantially different from the one suggested in Ref. [5]. In that case, in fact, the strain that the authors refer to is the one due to the in-plane fluctuation of the hexatic order parameter. Molecules in the hexatic phase are seen as elastically coupled spins and their fluctuations generate strain. In our case, we speculate that the fluctuations of Ψ are affected by a macroscopic strain field generated by the disorder present in the sample. The study of the consequences of the presence of this coupling term on the α critical exponent and on the order of the transition is beyond the scope of this paper, but we hope that our results will stimulate further research.

V. CONCLUSIONS

The results we have reported in this paper confirm the weak first-order nature of the Hex*B*-Sm*A* transition in 65OBC and the unusually large value of the specific heat critical exponent that does not conform either to 3D *XY* predictions or to the tricritical ones, leaving unsolved the puzzle of the universality class of this transition.

On the other hand, we have demonstrated that the disorder present in the sample plays a major role at the transition. It is frozen in the sample at the Sm*A*-*I* transition, is partially annealed at the Hex*B*-Sm*A* one, and, in our case, is in part reintroduced once the sample is heated back to the Sm*A* phase. This kind of ordering-disordering process is generated by the competition between the in-plane order variation with temperature and the constraints imposed by the topological disorder. We speculate that these mechanisms can be included in the theoretical description of the transition by a coupling term between the hexatic order parameter and a macroscopic strain field, which should not simply smear the transition, but should extend its effect to a microscopic scale and is at the origin of the annealing process.

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