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X-Ray Studies of Bond Orientational Order in Liquid-Crystalline Orthogonal Hexatic-B Phase.

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Abstract. – X-ray scattering measurements have been carried out for free-standing, thick monodomain films of the orthogonal hexatic-B phase. From Fourier analysis of Χ-scans, 6n-fold-symmetry order parameters were determined and proved to fulfill the scaling relation $C_{6n} = C_6^{n+\ln(n-1)}$. The temperature behavior of $C_6$ and $\lambda$ was found nonuniversal when comparing homologues, PIR5 and PIR7, differing in their range of the hexatic phase. The hexatic order parameter varies with the critical exponents 0.25, 0.20 (±0.03), respectively. For comparison results for compound RFL6, of other homologue series, are presented.

Introduction. – Some years ago it has been realized that liquid crystals are excellent systems [1, 2] to study 2D melting phenomena [3-5]. Hexatic smectic phases can be thought as a stack of 2D molecular layers, in which weak interlayer interactions stabilize quasi-long-range bond orientational order (BOO) found in two dimensions [5]. In such systems a local BOO can be described by the set of parameters $\Psi_{6n}(r) = \exp[i6\phi(r)]$, where $\phi$ is the angle between the bond direction and the reference axis. The symmetry of the basic order parameter, $\Psi_{6}$, locates the hexatic-liquid phase transition within the $XY$ universality class. Such a transition should be observed in an ideal form in case when fluctuations of other order parameters, e.g. arising from lower-temperature crystalline phase, become negligible. Theory predicts that for the hexatic phase the harmonics $C_{6n} = \text{Re}(\Psi_{6n})$ should scale as $C_{6n} = C_6^{\sigma(n)}$ where the exponents $\sigma(n)$ describe the multicritical crossover from $XY$ behavior (for $n = 1$) to uniaxial one (n = 2), to three-state Potts model (n = 3), to cubic one (n = 4) [6], etc. Asymptotically close to the phase transition, a simple relation between the exponents

\[ \sigma(n) = n + \lambda(T) n(n-1) \]  

is expected, where $\lambda(T)$ is the amplitude of the correction term to the mean-field result. Far from the phase transition, $\lambda$ in eq. (1) can be considered as an effective amplitude.

The scaling relation between harmonics in 3D systems has been tested and well established only for tilted smectic phases, Sm-F and Sm-I [7,8]. The reason is that in these systems monodomain samples, which are necessary to investigate the BOO by X-ray
methods, can be relatively easily obtained through the interaction with a magnetic field. However, the interpretation of the data for tilted systems is rather complex [9] because the coupling between the tilt and the BO order breaks the hexagonal symmetry of the system and influences the phase transition. Contrary to the tilted smectic phases, the interpretation of experimental results for untilted systems is more straightforward, but only very few X-ray studies have been performed for such systems [10,11]. The reason is that the untilted hexatic phase, Hex-B, was found in a limited number of compounds [12-14]. Moreover, there is no known general, efficient procedure in which a BOO monodomain sample can be prepared and the production of large domains is to some extent accidental. So far quantitative results regarding BOO in orthogonal hexatic phase are available, basing on electron scattering measurements, only for the systems with dimensionality close to the 2D limit [15,16]. X-ray scattering studies for the Hex-B phase in bulk were performed only on polydomain samples, thus while the existence of the long-range BO order was unambiguously proved [10,11], no quantitative results on the hexatic order parameter, C₈, were obtained.

In this communication, we report X-ray scattering measurements of the BOO in thick monodomain films, undertaken in order to study the thermal behavior of order parameters and test their multicritical scaling in the 3D untilted hexatic-B phase. In addition, the role of the molecular chain length as a factor influencing the hexatic-liquid phase transition was examined.

**Experimental.** Measurements were performed using a Siemens X-1000 system equipped with a two-dimensional position-sensitive area detector, a 2.0 kW sealed-tube X-ray generator and a 3-axis goniometer. The pyrrolic graphite monochromator providing a resolution in the azimuthal angle (equivalent to the rotation of the film around layer the normal) Δχ = 1.5° (FWHM) and a 0.5 mm collimator were used in the measuring set-up. All the experiments were done in the transmission mode for samples whose temperature was controlled within 0.02 K. The General Area Detector Diffraction Software (GADDS) was applied for data acquisition and processing. For each scattering pattern data were recorded after accumulation of ca. 30 MB counts.

Measurements were made on 1-(4'-alkoxyphenylamino)-3-[5"-(2"-methylpyridyl)]-propen-1-one-3 compounds belonging to the PIR series described in ref. [12]. These compounds have three-ring mesogenic cores, with the center ring stabilized by the hydrogen bonding. They exhibit crystalline-B (Cry-B), hexatic-B (Hex-B) and smectic-A (Sm-A) phases upon heating from a crystal phase. Within a homologous series, the temperature range of the enantiotropic hexatic-B phase is controlled by the length of molecular terminal chains, in agreement with the generic phase diagram given by Aharony et al. [6]. For two examined homologues, PIR5 and PIR7, with 5 and 7 carbon atoms in the molecular tails, it is 4.8 K and 6.1 K, respectively. The results were compared with those obtained for a molecularly similar compound, RFL6, with 6-carbon tail, for which the range of the hexatic phase is 11.2 K [17]. Free-suspended (substrate-free) films of diameter ca. 5 mm, and thickness 20–50 µm were examined. In both Cry-B and Hex-B phases different probing areas of diameter 0.5 mm² gave the same X-ray diffraction patterns, with 6 spots of an almost perfect 6-fold symmetry (see fig. 1), thus all samples were single domains within the resolution of our X-ray machine. Single domains were grown in the course of several consecutive heating and cooling runs through the Hex-B–Cry-B phase transition. In the measurements, the temperature was changed with steps 0.1 K far from the Sm-A–Hex-B phase transition and close to the transition steps was reduced to 0.025 K. From the scattering patterns, scans along 2θ and along χ angles have been obtained by integration procedures performed on a 512 × 512 discrete map of intensities I(χ, 2θ). In order to reduce noise related to the quantization of the area detector, smoothing
integrations were performed in the range of 1° in the 2θ-angle around the peak position for the I(χ) profile. For I(2θ) profile integration over full azimuthal angle was performed.

Results and discussion. - The 2θ-scans reveal that the range of positional correlations in our samples did not exceed 150 A in the Hex-B phase, thus indeed only short-range in-plane translational order is present in this phase. Intensity profiles along the χ-angle were analyzed in details in order to determine the 6n-fold-symmetry order parameters. The degree of the BO order was determined by performing nonlinear least-square fit of χ-scan data to the Fourier cosine series [8]:

\[ I(χ) = \sum_{n=1}^{n_{max}} I_{6n} \cos 6n(χ - χ_0) + I' \],

where \( I_{6n} \) are modulation amplitudes of beams scattered on \( 6n \)-fold-symmetry structures, \( I' \) is an \( χ \)-angle-independent intensity and \( χ_0 \) is the reference peak position. Independently, we analyzed experimental data in terms of eq. (2) by applying two fitting procedures: i) a fit without any further restrictions for \( I_{6n} \); ii) a fit assuming the relation between \( I_{6n} \)

\[ I_{6n} = I_0 C_6^{σ(n)} + \lambda(n-1)n \],

which is equivalent to the scaling relation \( C_{6σ} = C_6^{σ(n)} \), with \( σ(n) \) given by eq. (1). In the second method \( λ \) was treated as an adjustable parameter and \( I' = \frac{I_0}{2} + I_{bg} \) was divided into two parts, one related to \( I_0 \)—the total scattering intensity from the hexatic structure—and the second \( I_{bg} \)—related to the background intensity. Both above fitting procedures, i) and ii),
provided essentially the same results; their chi-square tests coincided within 10% over the entire temperature range and calculated \( \chi \)-profiles are visually indistinguishable (see fig. 1). We also tried to fit the \( I(\chi) \) data using, in eq. (3), the value \( \lambda = 0.295 \), the estimation of the 3D-XY theoretical expression \( \lambda = 0.3 - 0.008n \) or equivalently \( \lambda = 0.3/(1 + 0.027n) \) [6]. However, deep in the hexatic phases this approximation gave unacceptable results (fig. 1).

The sets of coefficients \( I_{6n} \) for few temperatures in the hexatic phase are presented in fig. 2. Deep in the hexatic phase \( I_{6n} \) with value \( n_{\text{max}} = 24 \) was found sufficient to describe the modulation of \( I(\chi) \), as higher components did not improve fits. Close to the Hex-B–Sm-A phase transition temperature, the number of harmonics, which significantly account in the fitting function, decreases because decreasing of \( 6n \)-fold–symmetry order parameters \( C_{6n} \) is followed by decreasing value of coefficients \( I_{6n} \). In fig. 2 is also presented a linearized plot of the experimental data pointing out directly that the scaling relation (3) is fulfilled. Consequently, the scaling relation between the \( C_{6n} \) components is well established and it allows us to determine the behavior of both \( C_{6} \) and \( \lambda \) across the hexatic phase, without studying any higher \( C_{6n} \) harmonics independently.

The temperature behavior of the correction parameter \( \lambda \) in compounds PIR5 and PIR7 is shown in fig. 3, together with data for the compound RFL6 presented for comparison. In all studied compounds, \( \lambda \) close to 0 was found deep in the Hex-B phase, in agreement with predictions of the mean-field theory [6]. As the Hex-B–Sm-A phase transition is approached, \( \lambda \) increases indicating that XY-type fluctuations arise and they become more pronounced the broader the Hex-B phase is. However, none of the examined systems fully crossed over to

\[ C_6 = A(1 - T/T_c)^3 \]

In the insert the log-log plot of \( C_6 \) vs. reduced temperature is presented for PIR5 \( (\beta = 0.25) \) and RFL6 \( (\beta = 0.15) \).
the XY critical region because the 3D-XY value of $\lambda = 0.3 - 0.008n$ has never been reached. A similar temperature dependence of $\lambda$ was previously observed in tilted hexatic Sm-F phase for some homologues of the TBA series [7].

Besides analysis of the $\lambda$-coefficient, additional information about the nature of the Hex-B–Sm-A phase transition results from the temperature behavior of the hexatic order parameter, $C_6$. As this phase transition is approached, the values of $C_6$ decreased critically (fig. 4) suggesting that the transition is rather close to continues. The relevant critical exponents and amplitudes are $\beta = 0.25 \pm 0.03$, $A = 2.4 \pm 0.2$ and $\beta = 0.20 \pm 0.03$, $A = 1.7 \pm 0.3$ for PIR5 ($\Delta T = 4.8$ K) and PIR7 ($\Delta T = 6.1$ K), respectively. However, amplitudes $A > 1$ of the order parameter might imply that the simple power law, $C_6 = A[1 - T/T_c]^\beta$, is not sufficient to describe the $C_6(T)$ variation across the short hexatic phase. It should be pointed out that for RFL6, a compound with much broader Hex-B phase ($\Delta T = 11.2$ K), an acceptable amplitude $A = 1.3 \pm 0.3$ was obtained and accompanied by the critical exponent $\beta = 0.15 \pm 0.03$. Thus, it can be suggested that the effective exponents $\beta$ are influenced by the range of the hexatic phase. For three examined compounds, the critical exponents are much higher than the value of $\beta = 0.08$ reported for the tilted hexatic phase [9]. Our data for the orthogonal hexatic phase, especially those relevant to a sufficiently broad phase, are markedly different from the value of $\beta = 0.35$, expected for 3D-XY model. On the other hand, they are similar to the experimental $\beta = 0.19$, deduced previously from the measurements of birefringence in the Hex-B phase [18] and seem to be closer to $\beta = 0.24$, which results from three-state 3D-Potts model [19]. However, the relation to this model is not clear, since in the examined systems, contrary to nmOBC compounds [11], there is no obvious X-ray evidence for the herringbone order, which would result in 3-state symmetry, inherent to the model.

Summarizing, we found that the scaling relation between BOO harmonics $C_{6n}$ is fulfilled in the orthogonal hexatic-B smectic phase. We also observed that the behavior of both the correction scaling parameter $\lambda$ near the hexatic-liquid phase transition and the critical exponent $\beta$ is dependent, in the homologue series, on the molecular chain length which controls the temperature range of the hexatic phase. These results might suggest that the Hex-B–Sm-A phase transition is strongly influenced by fluctuations of the crystalline order parameter arising from the neighboring low-temperature Cry-B phase.

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