Polarization periodicity in the B_1 columnar phase determined by resonant x-ray scattering

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We report structural results that evidence the polarization distribution of the blocks in the columnar phase of an achiral bent-core liquid crystal. The study was performed using resonant x-ray diffraction at the sulfur K edge on oriented samples aligned on substrates. The extra periodicity is revealed through the violation of the systematic extinction rule of the structural symmetry group along the experimentally accessible diffraction direction. Further data obtained from the polarization analysis of a resonant reflection give information concerning the transition mechanism between B_1 and B_2 phases.

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Liquid crystals are an intermediate state of matter with the fluidity of liquids and some of the essential properties of solid crystals, such as macroscopic anisotropy. In many cases they also have a microscopic periodicity represented by a low-dimensional translation lattice. Smectic phases are periodic in one dimension, i.e., the molecules segregate in layers (smectic layers), and within each layer molecules are arranged randomly. Consequently, the diffraction vector $\mathbf{Q}$ is perpendicular to the layers and only partial information concerning molecular orientation can be obtained using conventional x-ray diffraction. This can be easily understood since the contribution to the structure factor of an atom with form factor f positioned at $\mathbf{r}$ is $f \exp(i \mathbf{Q} \cdot \mathbf{r})$, i.e., it does not depend on the atom's position in the direction normal to $\mathbf{Q}$. Therefore, the diffraction diagram is sensitive only to the layer periodicity. For example, no information can be obtained for the molecular azimuth angle in tilted smectic phases. The situation is different with resonant x-ray scattering, where the x-ray energy is tuned to the K absorption edge of a given probe atom in the molecule. In this case, an inner-shell electron is excited to an outer-shell empty quantum state whose symmetry depends on the arrangement of the atomic neighborhood. Consequently, the atomic response contains an anisotropic contribution that, within a phenomenological framework, can be described by a second-order susceptibility tensor χ , relating the incident and diffracted fields for that particular atom [1]. Then the structure factor becomes anisotropic, i.e., it depends not only on the position of the atom along $\mathbf{Q}$ but also on its orientation in the structure, providing information about further periodicities related to the molecular azimuth.

Using the resonant diffraction technique, smectic phases of chiral rodlike liquid crystals with ferroelectric, antiferroelectric, and incommensurate periodicities were elucidated for the first time by Mach *et al.* [2]. A detailed study of the problem and key features of the technique were presented in [3]. The method allowed for the experimental determination of a number of different chiral smectic structures (see, for example [4–6]), solving definitively a controversy that had remained open for more than one decade.

In this work we extend the application of resonant x-ray scattering to two-dimensional (2D) periodic systems. In particular we study a columnar bent-core liquid crystal, but the analysis presented here can be applied to other materials containing periodic structures of low dimensionality. This class of materials is rather broad. In addition to bent-core liquid crystals [7–10], there are the structures that appear in the self-assembly process of some phospholipids (the ripple phase) [11], the arrangement of some dendritic dipeptides that organize in columnar periodic arrays [12], and the structure of some 1D electrical conductors composed of disk-shaped molecules [13].

Bent-core liquid crystals have attracted a lot of attention especially due to their peculiar characteristics regarding polarity and chirality. The unique packing of bent-core molecules in layers yields these properties. Figure 1(a) shows the molecular structure of the NG126 molecule used in this study. If we consider it as a bow, two different directors can be defined, the arrow (short director) and the string of the bow (long director). The bent shape hinders the rotation about the long axis, giving rise to polarization parallel to the short directors. Escape from this polarization leads to new molecular arrangements. Apart from pure smectic phases (e.g., B_2 or polar tilted smectic phase Sm-CP) there are structures with a 2D translation lattice where the layers are undulated, or even completely frustrated, conforming columnar phases (B_1). Up to now the structural analysis of bent-core liquid crystals using resonant x-ray scattering has been restricted to the B_2 phase. These studies have demonstrated unambiguously the two-layer polar periodicity of the antiferroelectric lamellar phase [14] as predicted by Link *et al.* [7], and elucidated the molecular orientational ordering (synclitic or anticlinic) from the polarization analysis of the diffracted beam [15]. In contrast, despite their evident interest, the columnar phases of bent-core mesogens have never been investigated under resonant conditions to our knowledge. In most columnar structures, conventional x-ray diffraction can only give partial information because the reciprocal lattice is reduced to a plane perpendicular to the columns, so the scalar structure factor is not sensitive to the components

FIG. 1. (Color online) (a) Molecular structure of the NG126 compound. The principal axes (u, v, w) of the susceptibility tensor χ of one sulfur atom are shown. A schematic representation of the bent-core molecules (P is the polarization direction) is displayed. (b) Model for the B_1 structure proposed in Ref. [14] showing its orientation with respect to the glass substrate. (c) Structure of the B_1 phase deduced from nonresonant scattering. (d) Resonant diffraction diagram for the structure in (b). The set of solid circles is the nonresonant diagram and the open circles are the reflections of resonant nature. The sizes of the dots indicate the relative intensities and the dashed line the experimentally accessible region. (e) Geometry of the diffraction experiment.

of the atomic positions along the columns. In addition, a glide plane relates columns with opposite polarity in antiferroelectric columnar phases, since usually these structures are synclitic. However, the systematic extinction rule that corresponds to this nonsymmorphic symmetry element prevents the appearance of the only reflections capable of differentiating between the columns. In contrast, forbidden reflections arise at the resonant wavelength [1] due to the tensor character of the structure factor. To illustrate the situation, Figs. 1(b) and 1(c) schematize an example of a bent-core columnar phase observed under resonant and nonresonant x rays, respectively. The color code (grayscale) in Fig. 1(b) denotes the different polarization direction along b , which can be observed under resonant x rays. In contrast, this information is not accessible out of resonance, so all the blocks are equivalent [gray color in Fig. 1(c)]. In this Rapid Communication, we report a structural study using resonant scattering of an antiferroelectric columnar phase. We will present experimental evidence of the polarization periodicity of the columns, and compare the results with other models proposed in the literature [16–18].

The NG126 liquid crystal studied in this work [Fig. 1(a)] exhibits the following phase sequence: Isotropic (157 °C)–columnar B_1 (100 °C)– B_2 (83 °C)–crystal, as obtained from previous x-ray measurements on cooling. The molecule contains sulfur atoms, which are the probe atoms for resonant scattering. Its synthesis and optical, dielectric, and structural properties have been previously reported [17–20]. The sample was prepared by spreading the material in the B_2 phase on a glass substrate treated with hexadecyl trimethyl ammonium bromide. By rubbing in a given direction, a specimen whose smectic layers are parallel to the substrate is obtained [14,15]. Since the rubbing process promotes a preferred direction for the molecular tilt, we can define a triad of axes X, Y, Z , with

Z along the glass plate normal and X along the rubbing direction [Fig. 1(e)]. Due to geometrical constraints (e.g., those imposed by the windows of the sample chamber), the region of accessible reciprocal space for the experimental setup did not extend to resonant reflections except along the Q_Z axis. The measurements were carried out at beamline X-19A of the National Synchrotron Light Source. A complete description of the three-circle goniometer including the polarimeter assembly was published previously [4]. The sample was mounted on a rotation platform of axis Z inside a two-stage oven allowing for a 20 mK resolution in temperature. The beam dimensions were set to 0.2 mm vertical by 0.5 mm horizontal using the adjustable slit assembly at the input arm. The vertical resolution ΔQ_Z was estimated to be $1.5 \times 10^{-3} \text{ \AA}^{-1}$.

Prior to any further study, it is essential to check if the sample remains aligned when it is heated to the B_1 phase and which is the orientation of the structure respect to the X, Y, Z triad. For this purpose, after tuning the beam energy to the sulfur K edge (2.473 keV) we optimized the alignment of the goniometer using the first- and second-order Bragg reflections from the layer structure observed in the B_2 phase. Then the material was heated up and Q_Z scans were carried out. Both peaks remained when the sample was heated and only their positions changed slightly and continuously over the whole temperature range. This means that the alignment of the sample is preserved at the transition to the B_1 phase. The observed peaks correspond, according to a previous work [17], to the reflections (002) and (004) in Fig. 1(d). Therefore, the structure is oriented with respect to the substrate as depicted in Fig. 1(b) or 1(c). When the sample is cooled down through the B_1 – B_2 transition temperature, the smectic layers of the B_2 phase are formed from the blocks belonging to the (001) planes of the B_1 structure. This quasicontinuous mechanism is in agreement with the small transition enthalpy (0.5 kJ/mol) reported in [18]. In the B_2 phase, the reciprocal space reduces to the dashed line in Fig. 1(d).

The next step was to investigate the polarization periodicity in our material by means of resonant diffraction. We first show that, in fact, Fig. 1(d) is the expected diffraction diagram under resonance for the structure in Fig. 1(b). Following [1], the systematic extinction rule for a nonsymmorphic symmetry operation $\{R|t\}$ is deduced from $F(h0l) = RF(h0l)R^{-1}\exp(iQ \cdot t)$. In our case, R is the reflection operation on the a – c plane, and $t = c/2$. Thus, for an $(h0l)$ reflection we have $F(h0l) = RF(h0l)R^{-1}\exp(i\pi l)$, i.e., if the structure factor is a second-rank tensor, we can have $F(h0l) \neq 0$. This happens irrespective of l , i.e., $(h0l)$ reflections are allowed even for $l = 2n + 1$ in resonant conditions (open circles). On the other hand, out of resonance $F(h0l)$ is isotropic (the second-rank tensor becomes now proportional to the identity matrix), and is non-null only if $l = 2n$ (full circles). All $(00l)$ reflections remain in the low-temperature bilayer B_2 structure, for which the whole diagram is reduced to just that line. It must be stressed that the model in Fig. 1(b) is, in practice, the only one that predicts the existence of resonant reflections in the dashed line of Fig. 1(d). Figures 2(a) and 2(b) represent two other possible structures. For each of the structures the expected diffraction diagram resulting from its symmetry group is schematized.

FIG. 2. (Color online) (a), (b) Proposed models for the polarization periodicity in a columnar structure together with their resonant diffraction diagrams. The dashed line indicates the experimentally accessible region. The orange dot represents the origin of the reciprocal lattice. (c) Alternative model for which resonant reflections should be observed on the dashed line.

Szydlowska *et al.* [16] proposed the B_1 reversed structure as shown in Fig. 2(a). Figure 2(b) shows the oblique version of the structure proposed by Folcia *et al.* [18]. As can be seen, for both models, there are no resonant peaks in the region of the reciprocal space that is accessible in our experiment (dashed line). This fact can be easily understood according to the following argument: (00 l) reflections are generated by the planes parallel to the substrate (represented by horizontal lines in Figs. 1 and 2). All the planes in Figs. 2(a) and 2(b) contain the same sequence of colors: blue-yellow-blue-yellow... for Fig. 2(a) and blue-blue-yellow-yellow... for Fig. 2(b), so they are equivalent regarding (00 l) reflections [a shift perpendicular to the (00 l) line is irrelevant] [21]. Thus in resonant conditions the real periodicity is d , contrarily to the structure in Fig. 1(b), whose periodicity is $2d$, originating the extra reflections. This means that, if the real structure of the material were one of those represented in Fig. 2(a) or 2(b), the resonant reflections observed at the B_2 phase should disappear on heating up the sample to the B_1 phase.

Therefore, according to the previous analysis, the existence of the resonant reflections (001), (003), etc. would indicate that the structure of our material in the B_1 phase is that represented in Fig. 1(b). Thus, the reciprocal space was scanned in the region between the observed nonresonant reflections (002) and (004) in the B_2 phase. A clear non-resolution-limited peak was observed just at the position $Q = (3/2)Q(002)$, i.e., the (003) reflection [see Fig. 3(a)]. The energy of the beam was then optimized using the intensity of the resonant peak and its evolution was followed on heating to the B_1 phase. The resonant peak was observed in the whole temperature range of the B_1 phase. The results demonstrate that the model given in Fig. 1(b) is the correct one. These measurements were performed using different samples, yielding the same results.

In principle, an objection can be raised that the detected peak could correspond to the tails of the (103) or (203) reflections in Fig. 2(b). Thus the structural model of that figure would not be completely excluded. In response to this idea we have two arguments. First, the rocking curves of the nonresonant peaks [see the inset of Fig. 3(a)] are very sharp

FIG. 3. (Color online) (a) Resonant reflections observed in the B_2 phase (full circles) and in the B_1 phase (open squares). In both cases the reflection is centered at $Q = (3/2)Q(002)$. The beam energy was 2.4728 keV. The inset shows a typical rocking curve of the (002) nonresonant reflection. (b) Azimuth of the scattered radiation for the resonant peak in the B_2 phase as a function of the sample orientation angle φ . The full circles are experimental results and the thick line is the best fit. Dashed line corresponds to the Sm- C_A P $_A$ phase. Thin line corresponds to a perfect monodomain Sm- C_S P $_A$ sample with $\alpha = 54^\circ$. The scheme represents a molecule within a B_2 layer, where the orientation of the eigenvectors u, v, w is not symmetry restricted as in Fig. 1(a).

[full width at half maximum (FWHM) of 0.03°] indicating a great uniformity of the homeotropic layer structure. Second, the lattice parameters in the B_1 phase are known to undergo large variation with temperature [17]. This would imply an important change of the detected resonant intensity, since the tails would come into the experimentally accessible region in different proportions at different temperatures. No such change was observed.

Another possible structure (in principle not excluded by the above data) is schematized in Fig. 2(c). Here, both families of planes have different color proportions, thus giving rise to resonant reflections on the dashed line. However, this type of structure is unlikely since the contrast between planes would be small (the ratio blue/yellow in every layer is more balanced) and, consequently, the magnitude of the resonant peak should appear greatly reduced in comparison with the reflection observed in the B_2 phase.

The model proposed for the mechanism of the phase transition from B_1 to B_2 [17] implies a synclinc configuration for the B_2 phase, i.e., a synclinc antiferroelectric Sm- C_S P $_A$ phase. In order to investigate the synclinc or anticlinc nature of the structure we performed an analysis of the polarization of the resonant peak in that phase. Due to the 2_1 screw axis of the Sm- C_A P $_A$ phase, the resonant scattered radiation is purely π polarized independently of the azimuthal orientation φ [dashed line in Fig. 3(b)] [1]. Furthermore, the π character of the polarization is kept even if the molecule does not have a mirror plane in the structure so that the principal directions u, v , and w of the anisotropic susceptibility of the resonant atom have an arbitrary orientation [see the scheme in Fig. 3(b)]. This polarization characteristic is very demanding and robust since, evidently, it also holds for multidomain samples with a distribution of azimuths for the tilt directions.

We carried out a polarization analysis of the resonant reflection in the B_2 phase, using the polarimeter assembly. Briefly, it consists of a pyrolytic graphite crystal mounted on the 2θ arm that can rotate about the direction of the diffracted beam. Its Bragg angle θ_p for our x-ray energy is close to

45° ($\theta_p = 48.3^\circ$ for 2.475 keV), so it works like an almost perfect optical analyzer. The full circles in Fig. 3 represent the values $\omega'(\varphi)$ of the analyzer position that maximize the detected intensity for different angles φ . The data were obtained after subtraction of the σ -polarized background. The results unambiguously discard the possibility of a Sm- $C_A P_A$ phase and consequently the B_2 phase must be synclinic. This confirms the model proposed for the B_1 - B_2 transition.

For the sake of completeness we present now an elementary study of the polarization in the case of a Sm- $C_5 P_A$ phase. The analysis is much more involved in this case although an important simplification arises if the molecule has a mirror plane so that $\mathbf{v}$ is perpendicular to that plane [as in Fig. 1(a)]. Under this condition, Fernandes *et al.* [15] have shown that for a σ incoming beam the resonant scattered radiation is linear, but there is a rotation ω of the polarization plane of the diffracted field $\mathbf{E}_d$ with respect to the incident field $\mathbf{E}_i$ [see Fig. 1(e)] given by

$$\tan \omega = \frac{\cos \alpha \cos \theta \cos \varphi - \sin \alpha \sin \theta \cos 2\varphi}{\sin \alpha \sin 2\varphi}, \quad (1)$$

where θ is the Bragg angle and α the molecular tilt. Equation (1) is represented by the thin line in Fig. 3(b). As can be seen, the experimental data are also incompatible with a perfectly aligned Sm- $C_5 P_A$ phase. However, some accordance is reached if a significant amount of angular spread of the tilt azimuths about the rubbing axis is permitted. If we propose a Gaussian distribution for the azimuth of the tilt directions,

$$P(\phi) = K/360 + C(1 - K)\exp[-\phi^2/2\delta^2], \quad (2)$$

a reasonable fit is obtained with $\alpha = 54^\circ$, $\delta = 60^\circ$, and $K = 0.02$ [thick line in Fig. 3(b)]. In Eq. (2) C is a normalization constant and $K \in [0,1]$ is the proportion of sample showing uniform ϕ distribution. The diffracted beam is an incoherent mixture of fields that are linearly polarized in different directions, each one emerging from a different domain in the sample [22]. As can be seen, a high δ value was obtained, which means that in this material the effectiveness of the rubbing process to fix the tilt azimuth is rather limited and a broad distribution of orientations occurs. On the other hand, $\alpha = 54^\circ$ is clearly above the value 45° of the optical tilt [19]. This may be simply explained by the position of the sulfur atom within the molecule. Unlike the case of Ref. [15], the resonant atom is not embedded in the rigid core but connected to the terminal flexible chain [Fig. 1(a)]. Consequently, the molecular mirror is lost in the environment of the sulfur element and the orientation of the local eigenaxes of the

polarizability tensor ($\mathbf{u}, \mathbf{v}, \mathbf{w}$) cannot be simply connected to the molecular tilt [scheme in Fig. 3(b)]. In this most general situation, the polarization of the scattered beam may be elliptical. The analysis of the ellipticity of the diffracted wave is beyond the scope of the present experiment. However, the fact that our data can be fitted to a model limited to linear polarization suggests that the ellipticity is weak, if nonzero.

Finally, it is interesting to point out an apparent discrepancy between the present results and previous reports [18,19] where the B_2 phase of this material was established to be Sm- $C_A P_A$. In those works the identification was carried out on the basis of textures by subjecting the material to ac electric fields. In fact, if the temperature is lowered from the B_1 phase in the absence of field, the resulting texture in the B_2 temperature range is inconclusive. Only after the application of an electric field (and switching it off) is the texture recognizable as Sm- $C_A P_A$. Thus, the conclusion is that the electric field produces deracemization of the sample and segregates it into two enantiomorphous homochiral domains. There are precedents for the occurrence of this phenomenon in both bent-core [23] and rodlike [24] liquid crystals.

In summary, the polarization periodicity was made explicit in the B_1 phase of a bent-core liquid crystal by means of resonant x-ray diffraction. Although the study was performed in a material that presents a B_2 phase on cooling, the result could, in principle, be extended to other columnar phases in the sense that they may be considered a special case of undulated structures originated from the frustration of a lamellar phase [9,10]. Finally, the synclinic arrangement of the B_2 phase was demonstrated through the polarization analysis of the resonant reflection. This result is compatible with a simple B_1 - B_2 transition mechanism in which the blocks in the (001) pseudolayers of the columnar structure stretch to conform to the smectic layers in the B_2 phase.

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- [21] Notice that in the structure of Fig. 2(b) adjacent blocks along the horizontal solid lines with the same color are not strictly equal since they are related by a two-fold axis (in fact, they “see” a different neighborhood). However, $(00l)$ planes are still equivalent. The color code does not represent the real symmetry of the structure in this case. It is just a simplification.
- [22] The important angular spread of tilt directions gives rise to $\omega'(\varphi)$ values that deviate considerably from the expected behavior for a monodomain sample. This is due to the low degree of polarization of the scattered radiation, which presents contributions of linear states with a broad azimuth distribution. For example, in our sample we found $\omega'(0) = \omega'(180^\circ) = 0$ both experimentally and theoretically, whereas Eq. (1) gives $\omega(0) = \omega(180^\circ) = 90^\circ$.
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