

# Modulated antiferroelectric smectic phases with orthogonal and tilted structures

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The discovery of the ferroelectric nematic phase has brought with it a plethora of new polar liquid crystalline (LC) phases. One in particular is the antiferroelectric smectic A ( $\text{SmA}_{\text{AF}}$ ) phase. In this article, we show via observation and analysis of satellite peaks in the x-ray scattering pattern that the structure of the  $\text{SmA}_{\text{AF}}$  phase involves a one-dimensional density modulation of  $\approx 10\text{--}20$  nm lateral to the smectic layer normal. Further, we demonstrate a previously undiscovered phase where the antiferroelectric order is maintained into a tilted smectic phase demonstrating the robustness of the underlying frustration that leads to the modulated structure. We suggest that the modulations are only in a single dimension and appear parallel to the tilt plane. This new phase also shows a significantly different and complex response to an electric field from other discovered polar LC phases due to the ability to modulate both tilt and polarization direction.

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## I. INTRODUCTION

The discovery of the ferroelectric nematic phase ( $\text{N}_{\text{F}}$ ) in 2017 [1–4] has been accompanied by the subsequent discovery of a flurry of associated phases, including positionally ordered orthogonal [5,6] and tilted [7–9] ferroelectric and antiferroelectric phases [4,10–13]. The antiferroelectric splay nematic ( $\text{N}_{\text{S}}$ ) phase (sometimes referred to as the  $\text{SmZ}_{\text{A}}$  phase) exhibits nematic orientational order of the constituent molecules with an average director and either a one-dimensional (1D) [11,14,15] or two-dimensional (2D) [16–18] density modulation perpendicular to the director. The modulations consist of alternating domains of polarization splay separated by Ising walls. Across the domains, the density modulates, probably sinusoidally [11], such that it is maximized at the center of the splay domains and minimized at the domain walls that consist of apolar nematic regions with reduced mass density [14], which can result in weak but observable Bragg scattering peak [11]. Other modulated nematic phases where the polarization splay but does not change polarity between the domains have also been observed [19]. These modulated structures appear due to competition between flexoelectric effects and electrostatics [17].

The smectic equivalent of the  $\text{N}_{\text{S}}$  phase is the antiferroelectric smectic A ( $\text{SmA}_{\text{AF}}$ ). This phase has been observed in

single-component materials [12] as well as mixtures [13,20] and has been the subject of theoretical analysis [21] but has so far been assumed to be the smectic analog of the  $\text{N}_{\text{S}}$  phase, i.e., alternating splay domains but with the additional component of positional order in the form of smectic layers with their planes normal to the director. However, there has been no experimental verification of this and there are also significant open questions such as whether the phase exhibits 1D or 2D splay modulation [16,17]. Full experimental details can be found in the Supplemental Material [22].

In this article, we demonstrate conclusively that the  $\text{SmA}_{\text{AF}}$  phase exhibits an additional density modulation perpendicular to the layer planes due to the 1D splay domains. We also show that these modulations continue to exist even when molecules begin to tilt away from the layer normal in the form of a newly discovered antiferroelectric smectic C ( $\text{SmC}_{\text{AF}}$ ) phase that also exhibits 1D splay.

## II. EXPERIMENTAL

### A. Optical microscopy

Polarized light optical microscopy (POM) was performed using a Leica DM2700P polarized light microscope. A Linkam TMS 92 heating stage was used for temperature control. Images were recorded using a Nikon D3500 digital camera, using DigiCamControl software. Samples were studied sandwiched between two untreated glass coverslips or in cells purchased from Military University of Technology, Poland. The cells used here were assembled from parallel planes of glass coated in indium tin oxide (ITO) to allow for electric field application. For POM measurements, the ITO-coated substrates were coated with a polyimide layer that has

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been mechanically rubbed parallel and in the same direction (syn-parallel). For electrical measurements, this polyimide layer was omitted entirely. Details about the specifics of the cell are included with the relevant data.

The pitch was measured by illumination of the sample from the bottom via a 405 nm laser. Since the pitch axis of the bulk will fall along the director, the planar aligned cells were used to measure the pitch via light diffraction. The angle of diffraction was measured on a flat screen set away from the sample.

### B. Current response measurements

Current response measurements were undertaken using the current reversal technique. Triangular waveform ac voltages were applied to the sample cells with an Agilent 33220A signal generator (Keysight Technologies), and the resulting current outflow was passed through a current-to-voltage amplifier and recorded on a RIGOL DHO4204 high-resolution oscilloscope (Telonic Instruments Ltd, UK). Heating and cooling of the samples during these measurements was achieved with an Instec HCS402 hot stage controlled to 10 mK stability by an Instec mK1000 temperature controller. The liquid crystal (LC) samples were held in 5- $\mu\text{m}$ -thick cells with no alignment layer, supplied by AWAT. The measurements consist of cooling the sample at a rate of 1 K/min and applying a set voltage at a frequency of 10 Hz to the sample every 1 K. The voltage was set such that it would saturate the measured  $P_S$  and was determined before final data collection.

There are three contributions to the measured current trace: accumulation of charge in the cell ( $I_c$ ), ion flow ( $I_i$ ), and the current flow due to polarization reversal ( $I_p$ ). To obtain a  $P_{\text{Sat}}$  value, we extract the last one, which manifests as one or multiple peaks in the current flow, and integrate as

$$P_{\text{Sat}} = \int \frac{I_p}{2A} dt, \quad (1)$$

where  $A$  is the active electrode area of the sample cell.

### C. SHG microscopy

Second harmonic generation (SHG) investigations were performed using EHC D-type 5- $\mu\text{m}$ - and 10- $\mu\text{m}$ -thick parallel rubbed cells. SHG microscopy imaging was performed using a custom-built sample-scanning microscope. A detailed description of the setup can be found in Ref. [23]. The laser source was an erbium-doped fiber laser (C-Fiber A 780, MenloSystems) generating 785 nm, 95 fs pulses at a 100 MHz repetition rate. A combination of galvo mirrors and a long working distance objective (Nikon CFI T Plan SLWD, NA 0.3) was used to scan the focused beam in the sample plane. The scanning frequencies were much higher (a few hundred hertz) than the imaging frame rate (a few hertz). A long working distance 20 $\times$  objective (Nikon CFI T Plan SLWD, NA 0.3) collected the light coming from the sample. A set of 700 nm short-pass and 400 nm bandpass filters eliminated the fundamental IR light and any possible fluorescence signal. The images were finally acquired using a high-performance CMOS (complementary metal-oxide semiconductor) camera (Grasshopper 3, Teledyne Flir) with a typical integration time of 250 ms, dimensions of 1920  $\times$  1200 pixels, 12-bit depth,

and 0.285  $\mu\text{m}/\text{pixel}$ . A motorized half-wave plate for 800 nm rotated the polarization of the fundamental IR beam in the plane and, jointly with the analyzer in front of the camera, enabled us to perform polarization-resolved SHG. In the case of SHG-M images, the analyzer was removed to account for all contributions. Temperature dependence measurements were performed at a 1 K/min heating rate by imaging a small area of the sample. Intensity was computed as the mean intensity of a subregion. Upon heating from the  $\text{SmC}_P^H$  phase, the SHG intensity strongly decreased. A weak signal still present in the  $\text{SmC}_{AF}$  and  $\text{SmA}_{AF}$  completely disappeared in the  $\text{SmA}$  phase. The SHG signal in the  $\text{SmC}_{AF}$  and  $\text{SmA}_{AF}$  phases was more than 5 orders of magnitude smaller than that in the  $\text{SmC}_P^H$  phase. The SHG image in  $\text{SmC}_{AF}$  phase was acquired at a lower scanning speed, using pixel binning (16 $\times$ ), higher camera gain, and increased pump laser power. The polarization of the incoming beam was selected along the cells' rubbing direction after confirmation that the maximum SHG signal is obtained in that case.

### D. X-ray scattering

X-ray scattering measurements, both small angle (SAXS) and wide angle (WAXS), were recorded using an Anton Paar SAXSpoint 5.0. This was equipped with a primux 100 Cu x-ray source with a 2D EIGER2 R detector with a variable sample-detector distance. The x-rays had a wavelength of 0.154 nm. Samples were either filled into thin-walled quartz capillaries or held between Kapton tape. Temperature was controlled using an Anton Paar heated sampler with a range of 20–300  $^\circ\text{C}$  and the samples held in a chamber with an atmospheric pressure of  $>1$  mbar.

Background scattering patterns were recorded, scaled according to the sample transmission, and then subtracted from the samples' obtained 2D SAXS pattern. 1D patterns were obtained by radially integrating the 2D SAXS patterns. Peak positions and FWHM were recorded and then converted into  $d$  spacing following Bragg's law. In tilted smectic phases, the tilt was obtained from

$$\frac{d_c}{d_A} = \cos \theta, \quad (2)$$

where  $d_c$  is the layer spacing in the tilted smectic phase,  $d_A$  is the extrapolated spacing from the nontilted preceding phase, extrapolated to account for the weak temperature dependence of the preceding phases due to shifts in conformation and order, and  $\theta$  is the structural tilt angle.

For the modulated structures here, the  $d_{hk}$  spacing of each of the satellite peaks,  $[h,k]$ , can be calculated from

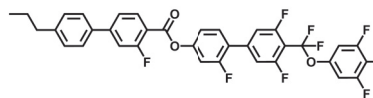
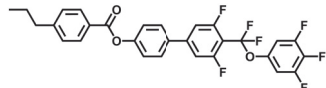
$$\frac{1}{d_{hk}^2} = \frac{h^2}{d_{10}^2} + \frac{k^2}{d_{01}^2}, \quad (3)$$

while the azimuthal angular position,  $\phi_{hk}$ , of a satellite peak is thus

$$\phi_{hk} = \tan^{-1} \left( \frac{k d_{10}}{h d_{01}} \right); \quad (4)$$

i.e.,  $d_{10}$  is at 90 $^\circ$  and  $d_{01}$  is at 0 $^\circ$ . In reality the  $[1,0]$  peak is not observed, so the index of each satellite was systematically guessed until they produced consistent predictions for the

TABLE I. Transition temperatures ( $T$ ) and associated enthalpies of transition ( $\Delta H$ ) for compounds 1 and 2 determined by differential scanning calorimetry (DSC) on cooling at a rate of 10 °C/min.  $A^m$  indicates determination via POM observations. Both materials exhibit signs of slight degradation in their DSC obtained transition temperatures, which combined with the different measurement geometries means that these are consistently 1–3 °C lower than when measured by other transition techniques.

| No. |                                                                                   | Melt        | SmC <sub>P</sub> <sup>H</sup> -SmC <sub>AF</sub> | SmC <sub>AF</sub> -SmA <sub>AF</sub> | SmA <sub>AF</sub> -SmA | SmA-N | N-Iso            |
|-----|-----------------------------------------------------------------------------------|-------------|--------------------------------------------------|--------------------------------------|------------------------|-------|------------------|
| 1   |  | T (°C)      | 117.9                                            | 120.6                                | 122.7                  | 133.8 | 228 <sup>m</sup> |
|     |                                                                                   | ΔH (kJ/mol) | 23.6                                             | 0.3                                  | 0.6                    | 0.05  |                  |
|     |                                                                                   |             |                                                  |                                      |                        |       |                  |
| 2   |  | T (°C)      | 92.3                                             |                                      | 86.6                   | 98.2  | 127.7            |
|     |                                                                                   | ΔH (kJ/mol) | 21.7                                             |                                      | 0.08                   | 0.04  | 0.3              |
|     |                                                                                   |             |                                                  |                                      |                        |       |                  |

[1,0] peak position. The position of the [1,0] peak was taken as the average of the predicted positions.

III. RESULTS AND DISCUSSION

Compound 1 exhibits five mesophases with the phase order of N-SmA-SmA<sub>AF</sub>-SmC<sub>AF</sub>-SmC<sub>P</sub><sup>H</sup>, with the transition temperatures shown in Table I. The transition from the SmA-SmA<sub>AF</sub> phase generally shows very little textural change [12],

with the observations here consistent with that observation. In planar aligned cells (likely bookshelf arrangement of the layers), the SmA phase exhibits parabolic focal conics [Fig. 1(a)] [24,25], which are more prominent in thicker cells (Fig. S2 of the Supplemental Material [22]). These defects are retained upon cooling into the SmA<sub>AF</sub> phase, albeit they become significantly more visible [Fig 1(b)]. Upon further cooling into the SmC<sub>AF</sub> phase, the defect segment within the parabola splits down the middle into a darker and a light side [Fig 1(c)].

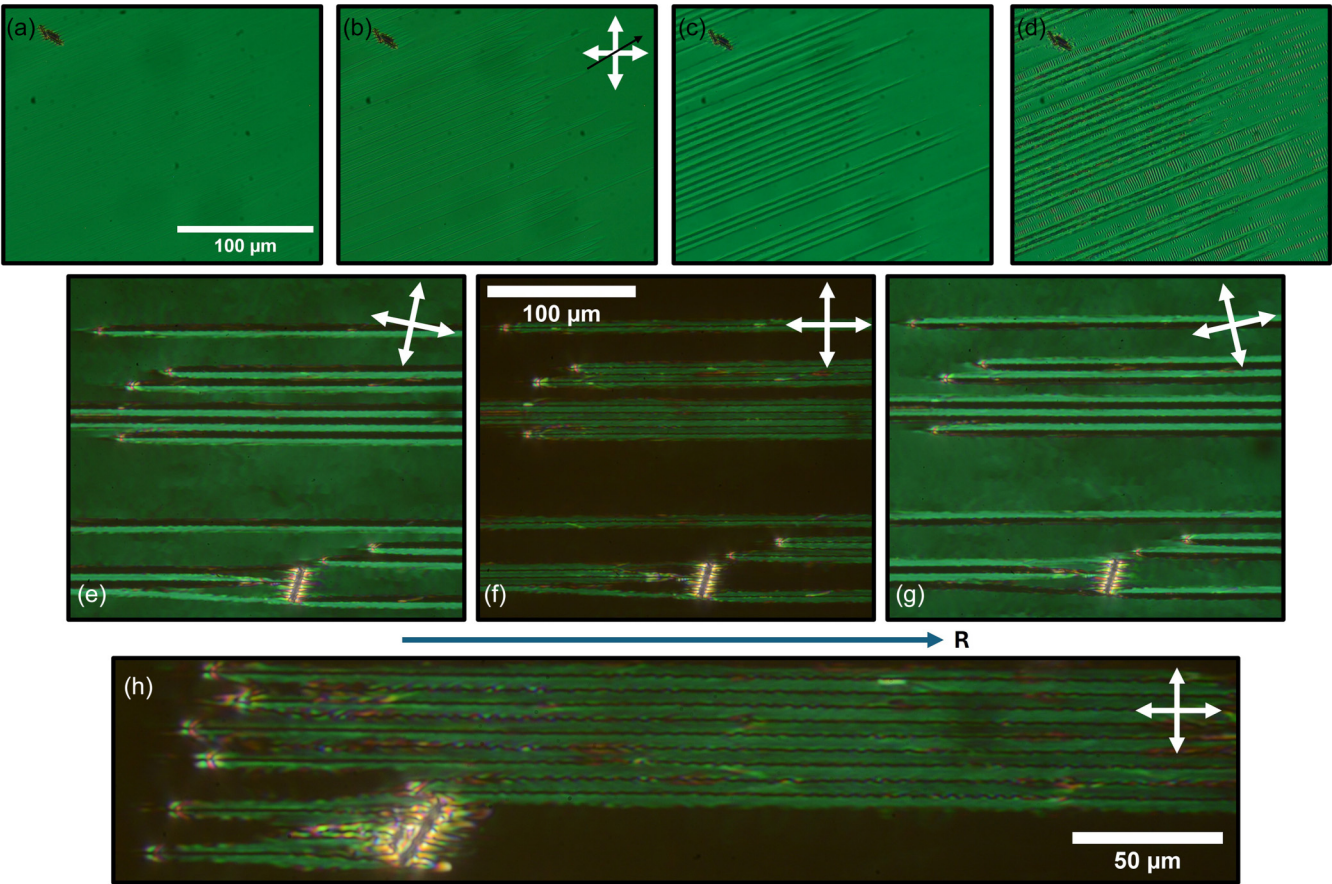


FIG. 1. POM images of compound 1 in (a) the SmA, (b)SmA<sub>AF</sub>, (c) SmC<sub>AF</sub>, and (d) SmC<sub>P</sub><sup>H</sup> phases. POM images were taken in a 5-5-μm cell with syn-parallel rubbed planar aligned substrates. White arrows indicate polarizer and analyzer orientations, and black arrow indicates the rubbing direction. (e)–(g) POM textures of the defects found in the SmC<sub>AF</sub> phase. Blue arrow indicates the rubbing direction. These defects are the evolution of the parabolic focal conic defects of the SmA phase. The sample can be rotated to bring each half of the defect’s subdomains into extinction, indicating that each domain has a different director orientation from themselves and the bulk uniform areas. (h) Each subdomain of the parabolic focal conic domain is joined by a discrimination line that appears to corkscrew.

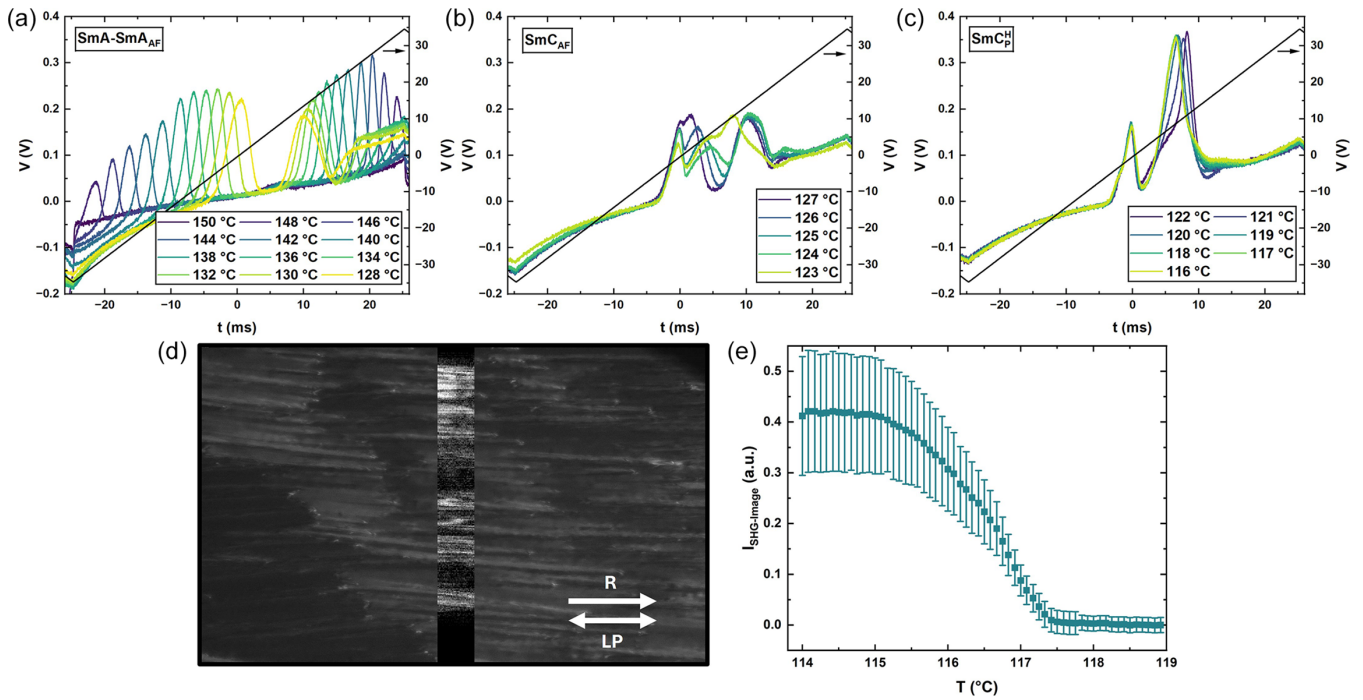


FIG. 2. Current response measurements for compound **1** in a 5- $\mu\text{m}$  cell with no alignment layer taken with a 10 Hz, 20  $V_{\text{RMS}}$  triangular voltage profile over (a) the SmA-SmA<sub>AF</sub> phases, (b) the SmC<sub>AF</sub> phase, and (c) the SmC<sub>P</sub><sup>H</sup> phase. (d) POM and SHG microscopy images of the SmC<sub>AF</sub> phase of compound **1** at 122 °C in a 5- $\mu\text{m}$ -thick syn-parallel rubbed planar aligned cell showing the inhomogeneity of the very weak signal found there. R denotes rubbing direction, while LP denotes the pump laser polarization. (e) Average SHG image intensity for compound **1** in a 10- $\mu\text{m}$ -thick syn-parallel rubbed planar aligned cell on heating from the SmC<sub>P</sub><sup>H</sup> phase. Error bars denote the standard deviation.

In the SmC<sub>P</sub><sup>H</sup>, periodic stripes appear perpendicular to the rubbing direction [Fig. 1(d)]. The periodicity of these stripes depends only weakly on temperature, with a slight reduction in periodicity with reducing temperature, but is independent of cell thickness. Light diffraction measurements reveal a periodicity of 2  $\mu\text{m}$  at 116 °C (Fig. S4 of the Supplemental Material [22]). Diffraction measurements above this temperature did not show a clear signal, preventing measurement of the exact temperature dependence of the periodicity.

For the defects in the SmC<sub>AF</sub> phase, each subdomain of the defect can be brought into optical extinction by rotating the sample past the analyzer or polarizer direction [Figs. 1(e) and 1(g)]. This indicates a change in director orientation within each subdomain of the defect. The bulk uniform areas are brought into good extinction with the director fully parallel to the polarizer orientation suggesting that the SmC<sub>AF</sub> phase is optically uniaxial in the bulk or with the tilt plane perpendicular to the cell surfaces.

Current response measurements demonstrate the polar nature of the various mesophases. The SmA<sub>AF</sub> phase shows double peaks in the current response, indicating the presence of the two antiferroelectric sublattice domains [Fig. 2(a)]. The double peaks are also observed in the preceding SmA phase due to a high-temperature critical end point [26]. As the temperature is reduced, the peaks move closer to  $t = 0$  s. At the transition to the SmC<sub>AF</sub> phase, a third peak emerges [Fig. 2(b)], moving out of the negative polarity peak and to longer timescales with a similar temperature dependence as for the negative polarity peak in the preceding SmA<sub>AF</sub> phase. Eventually, the peak merges with the positive polarity peak

at the transition to the SmC<sub>P</sub><sup>H</sup> phase. In the SmC<sub>P</sub><sup>H</sup> phase [Fig. 2(c)], the familiar small peak before voltage polarity reversal corresponds to tilt reformation and the larger peak is due to simultaneous (or close to) tilt removal and polarization reversal [27]. Measurements in a cell with in-plane electrode (IPS) type electrodes show comparable results (Fig. S7 of the Supplemental Material [22]).

SHG measurements show only a very weak signal in the SmA<sub>AF</sub> and SmC<sub>AF</sub> phases, and SHG microscopy [Fig. 2(d)] shows that the origin of this signal is nonuniform and generally localized to defects. To observe an SHG signal in an antiferroelectric phase, the periodicity of the polarization reversal must be larger than  $\approx 100$  nm (such as for RM734 in the N<sub>S</sub> phase [17]) or the domains of opposite polarization will cancel the SHG signal. For small periodicities, a source can still be defects in the layer structure. In a 2D system, the periodicity is small enough that there will exist enough defects to cancel out the signal entirely. For a 1D modulation, although thin, the layer threads can be large, resulting in an excess of polarization domains for a particular orientation in a nonuniform manner causing a weak SHG signal as is seen here for the SmA<sub>AF</sub> and SmC<sub>AF</sub>. We thus take these SHG data as supportive of our phase assignment of a 1D modulation. The SmC<sub>P</sub><sup>H</sup> phase exhibits an SHG signal more than 5 orders of magnitude larger than the SmC<sub>AF</sub> phase [Fig. 2(e)], consistent with the suggested structure and previous measurements [12].

X-ray scattering measurements in the SmA phase show a single Bragg peak resulting from the smectic layers. Upon transition to the SmA<sub>AF</sub> phase, an additional scattering peak emerges at higher  $Q$  spacing than the layer spacing peak.

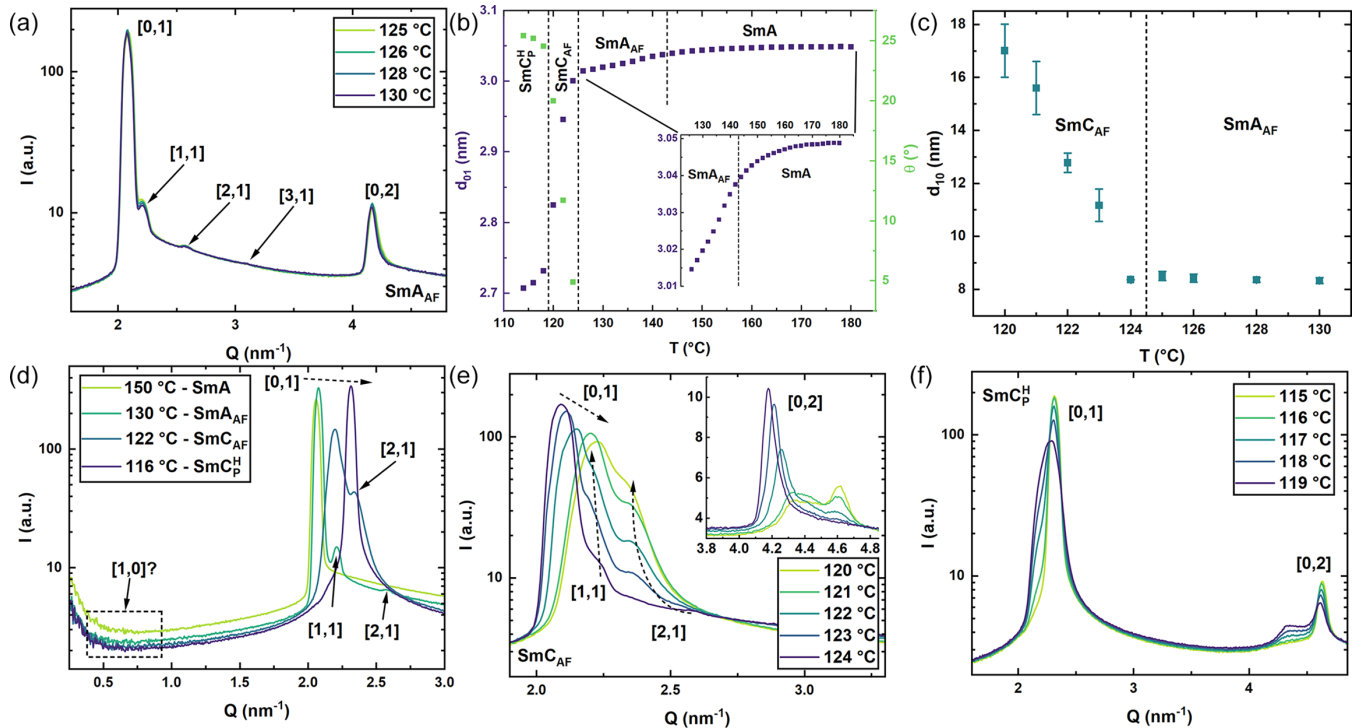


FIG. 3. (a) 1D x-ray scattering pattern for compound **1** in the  $\text{SmA}_{\text{AF}}$  phase. (b) Temperature dependence of the layer thickness with the inset showing an enlarged region of the  $\text{SmA}$  and  $\text{SmA}_{\text{AF}}$  phases. (c) Temperature dependence of the lateral density modulation thickness. (d) 1D x-ray scattering pattern with a different sample-detector distance showing the absence of a  $[1,0]$  peak for all phases. 1D x-ray scattering patterns for (e) the  $\text{SmC}_{\text{AF}}$  phase and (f) the  $\text{SmC}_{\text{P}}^{\text{H}}$  phase.

As the temperature is reduced, the intensity of the additional peak increases followed by the appearance of two further peaks at even higher  $Q$  spacing [Fig. 3(a)]. The x-ray scattering pattern can be well indexed by a 2D rectangular lattice where the layer peak is the  $[0,1]$  peak and the others are successive  $[h,1]$  peaks considering both their  $Q$ -space and azimuthal positions (Fig. S6 of the Supplemental Material [22]). A schematic of the scattering planes associated with these peaks can be found in Fig. S7 of the Supplemental Material [22]. While the  $d_{01}$  length scale (layer separation) is weakly temperature dependent, decreasing slightly as the temperature is reduced [Fig. 3(b)], the  $d_{10}$  distance implied by the indexing is temperature independent with a length scale of 8.4 nm [Fig. 3(c)]. For the data presented here, no peak in that region could be observed [Fig. 3(d)]. This is perhaps not surprising as all observations of the Bragg peak associated with this lateral density modulation for the  $\text{N}_{\text{S}}$  phase published so far [11,28,29] have been obtained using synchrotron radiation, while these data are collected using a laboratory-based scattering setup with around 5 orders of magnitude less flux. The Bragg peak in the  $\text{N}_{\text{S}}$  phase is extremely weak due to the low amplitude of the associated density modulation and this is consistent with the data presented here for the  $\text{SmA}_{\text{AF}}$  phase, although the presence of higher-order peaks may imply that the lateral density modulation has longer range than the smectic layers despite the lower amplitude of the modulation. For the  $\text{N}_{\text{S}}$  phase, satellite peaks have not been observed as the  $[0,1]$  peak is not Bragg-like (the phase is nematic) and is broader and less intense; thus, any satellite peaks would be

orders of magnitude weaker and hidden by the broad  $[0,1]$  peak.

The  $\text{SmC}_{\text{AF}}$  phase can be indexed using the same 2D rectangular lattice as the  $\text{SmA}_{\text{AF}}$  [Fig. 3(e)]. Nonorthogonal lattices such as 2D oblique or 3D monoclinic patterns would show peaks with negative indices at different  $Q$  values (e.g., both  $[1,1]$  and  $[-1,1]$ ) and these are not observed. The  $[0,1]$  peak moves to longer  $Q$  as the molecules in the layers tilt away from the layer normal leading to a reduction in the layer spacing,  $d_{01}$ . For most polar smectics, the tilt develops over 10–20 °C before saturating [7,8,27], but here it occurs rapidly, reaching  $\approx 20^\circ$  within 4 °C [Fig. 3(b)]. The  $[n,1]$  peaks move toward the  $[0,1]$  peak indicating an increase in the lateral density modulation,  $d_{10}$ . Upon transition to the  $\text{SmC}_{\text{P}}^{\text{H}}$  phase, the satellite peaks vanish and only a single  $[0,1]$  peak is left [Fig. 3(f)], indicating a melting of the lateral density modulation at the transition from the antiferroelectric  $\text{SmC}_{\text{AF}}$  phase to the ferroelectric  $\text{SmC}_{\text{P}}^{\text{H}}$  phase.

For the  $\text{N}_{\text{S}}$  phase, both 1D [11] and 2D [17,18] have been proposed and so we consider both options for the  $\text{SmA}_{\text{AF}}$  phase here. A 2D splayed  $\text{SmA}_{\text{AF}}$  should give additional scattering peaks (e.g., a  $[1,1,1]$  peak using a tetragonal lattice); however, these additional cross-scattering peaks are not observed, which strongly suggests 1D splay rather than 2D. Additionally, the very weak SHG signal measured in the  $\text{SmA}_{\text{AF}}$  and  $\text{SmC}_{\text{AF}}$  phases is supportive of 1D splay as the origin of the signal is likely irregularities and defects. In a 2D splayed system with modulation period in the 10 nm range, these would cancel out, but in 1D the cancellation might be

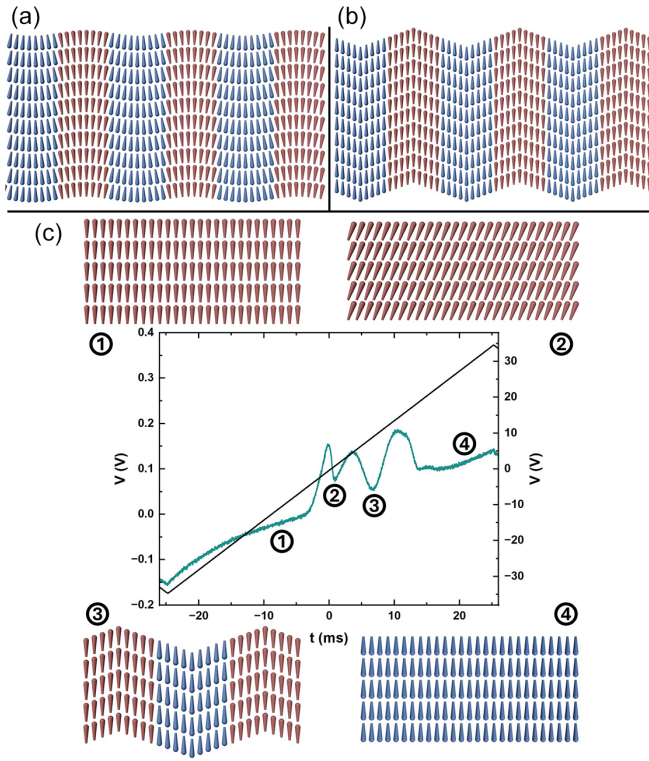


FIG. 4. Schematics of the proposed structure of (a) the  $\text{SmA}_{\text{AF}}$  and (b)  $\text{SmC}_{\text{AF}}$  phases. Regions of alternate polarization are separated by Ising walls, while in the  $\text{SmC}_{\text{AF}}$  splay is limited to the regions mediating change of tilt sign. While the  $\text{SmC}_{\text{AF}}$  schematic has been drawn fully chevron, in reality this structure is likely weaker and more sinusoidal. (c) Current response measurement for compound **1** in the  $\text{SmC}_{\text{AF}}$  phase in a 5- $\mu\text{m}$ -thick cell with no alignment layer. (1) and (4) show the saturated  $\text{SmA}_{\text{F}}$  state, (2) shows the  $\text{SmC}_{\text{P}}$  state, and (3) shows the ground-state  $\text{SmC}_{\text{AF}}$  phase.

lost around defects and a weak signal could be observed. The proposed  $\text{SmA}_{\text{AF}}$  structure is shown in Fig. 4(a).

For the  $\text{SmC}_{\text{AF}}$ , the possibilities are wider as 1D antiferroelectric modulations could be perpendicular, parallel, or at some angle to the tilt plane, while 2D modulations would be a combination of these possibilities. The x-ray is again only fitted using a 2D rectangular lattice suggesting 1D splay, while POM observations (Fig. S3 of the Supplemental Material [22]) strongly suggest that the structure must be optically uniaxial. From these two observations, we suggest that the structure of the  $\text{SmC}_{\text{AF}}$  phase presented here is of alternating polarization domains comprised of alternating positive and negative tilt subdomains. The alternating tilt subdomains of same polarization sign are joined by a region of splay, while the opposite polarization domains are joined by Ising walls. The proposed structure is shown in Fig. 4(b).

We note that there are similarities in the structures presented here and those observed for bent core LCs [30,31], particularly for the  $\text{SmA}_{\text{P}}$  phase where anticlinic layer order of the polarization vector along with the bent molecular shape mimics the proposed structure of the  $\text{SmC}_{\text{AF}}$  phase [32]. In bent cores, the polarization vector is perpendicular to the long molecular axis rather than parallel and so the preferred

flexoelectric deformation mode is bend rather than splay as for the molecules and phases presented here.

Having established the ground-state structure of the  $\text{SmC}_{\text{AF}}$  phase, the effects of electric field on the structure can be presented [Fig. 4(c)]. Since other longitudinally polar mesophases have shown the ability to undergo a field-induced phase transition to their orthogonal (nontilted) equivalent [8,9,27,33], a sufficiently high positive or negative voltage results in a field-induced phase transition to an  $\text{SmA}_{\text{F}}$  state [Fig. 4(c), (1)] as the saturated state of electric field application. Increasing the voltage toward 0 V allows the tilt to reform giving an  $\text{SmC}_{\text{P}}$  state [Fig. 4(c), (2)]. Further increase of the voltage toward 0 V and beyond results in the ground state of the  $\text{SmC}_{\text{AF}}$  phase [Fig. 4(c), (3)]. This happens past the 0 V position due to the viscosity and dynamics of the system, meaning that it lags behind the electric field switching. Increasing the voltage toward the saturation voltage results in a field-induced phase transition to an  $\text{SmA}_{\text{F}}$  with opposite polarization to the initial state [Fig. 4(c), (4)].

Compound **2** has previously been reported to exhibit  $\text{N-SmA-SmA}_{\text{AF-SmC}_{\text{P}}^{\text{H}}}$  phase behavior [12], although no satellite peaks were observed in the  $\text{SmA}_{\text{AF}}$  phase, so no verification of the structure was presented. However, if the data collection time is increased (here by a factor of 10), then weak peaks can be observed in both the  $\text{SmA}_{\text{AF}}$  and the reported  $\text{SmC}_{\text{P}}^{\text{H}}$  phase [Fig. 5(a)]. Neither the  $\text{SmA}_{\text{AF}}$  nor  $\text{SmC}_{\text{P}}^{\text{H}}$  phase exhibits any SHG signal [12] and so we conclude that the  $\text{SmC}_{\text{P}}^{\text{H}}$  phase reported for compound **2** previously is actually another example of the  $\text{SmC}_{\text{AF}}$  phase. When the two additional peaks observed in both the  $\text{SmA}_{\text{AF}}$  and  $\text{SmC}_{\text{AF}}$  phases are indexed, we find that the [1,1] peak is hidden by the intense [0,1] peak associated with the smectic layers, indicating a much longer pitch of the lateral modulation than for compound **1** [Fig. 5(a) and Fig. S6(c) of the Supplemental Material [22]]. The satellite peak indexing predicts a consistent position for the [1,0] peak although no peak is observed due to the apparent weakness of the density modulation amplitude. For compound **2**, the  $\text{SmA}_{\text{AF}}$  shows a reduction in the lateral density modulation periodicity throughout the phase before it then increases in the  $\text{SmC}_{\text{AF}}$  phase as for compound **1** [Fig. 5(b)]. The increased  $d_{01}$  of compound **2** versus compound **1** explains why these peaks were not observed previously as it shifts all the satellite peaks closer to the intense [0,1] peak hiding the most intense and most obvious peak in the main [0,1] peak. Once again we see that the transition between the  $\text{SmA}_{\text{AF}}$  and  $\text{SmC}_{\text{AF}}$  phases shows a continuation of the same lattice and we suggest that here again both materials show 1D modulations with the modulations parallel to the tilt plane in the  $\text{SmC}_{\text{AF}}$  phase.

In the polar nematic phases, the role of ferroelectricity is to allow formation of both 1D and 2D polarization-modulated structures [3,4,10]. Here, we expect a similar role of flexoelectricity, which drives the inclusion of splay in the structures and stabilizes antiferroelectric order resulting in  $\text{SmA}_{\text{AF}}$  and  $\text{SmC}_{\text{AF}}$ . Due to the layer stiffness, the amount of splay is lower than that for the nematic phase, as shown by birefringence measurements [20], as the layers will resist the splay. The proposed  $\text{SmC}_{\text{AF}}$  structure provides the opportunity to expel the splay from the bulk layers to the regions where the layer tilt changes sign, reducing the elastic cost of layer splay.

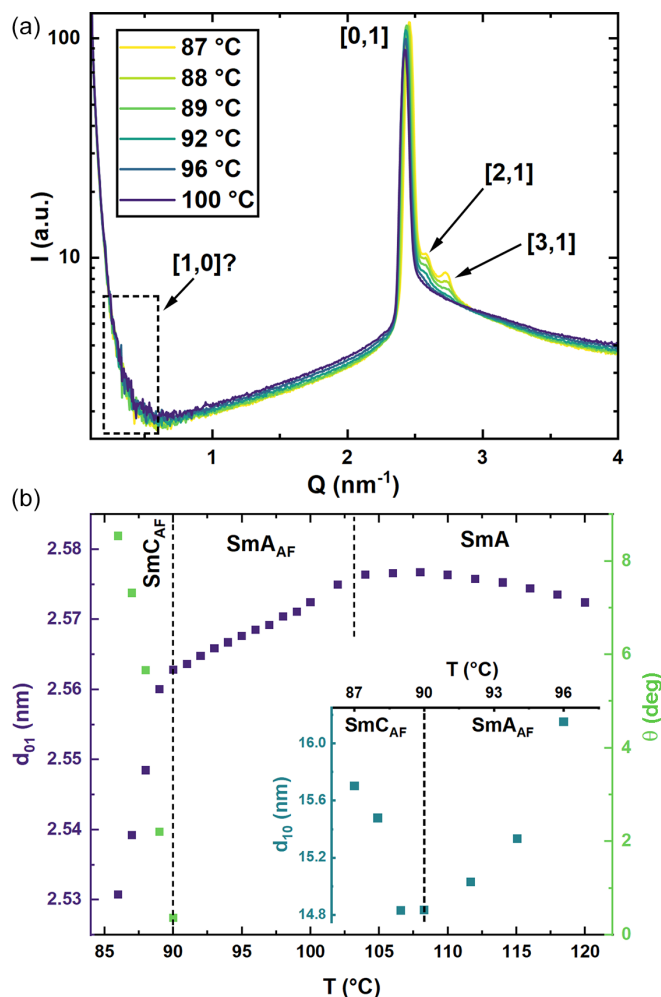


FIG. 5. (a) 1D x-ray scattering pattern for compound **2** throughout both the  $\text{SmA}_{\text{AF}}$  and  $\text{SmC}_{\text{AF}}$  phases with the transition between the two at 90 °C. (b) Temperature dependence of the smectic layer thickness,  $d_{01}$ , with the inset showing the dependence of the lateral density modulation,  $d_{10}$ .

The increasing relevance of bend flexoelectricity as the  $\text{SmC}_{\text{P}}^{\text{H}}$  is approached [34] also results in a preference for 1D splay as bend is an inherently biaxial deformation [35].

#### IV. CONCLUSIONS

In conclusion, it was shown that the  $\text{SmA}_{\text{AF}}$  phase is modulated and exhibits a 1D splay modulation rather than 2D as well as the discovery of a new polar liquid crystalline phase, the  $\text{SmC}_{\text{AF}}$  phase in compounds **1** and **2**, which exhibits a 1D chevron modulated structure parallel to the tilt plane. Additional references have been cited in the Supplemental Material [22].

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J.H. conducted POM, DSC, current response, and x-ray scattering data. C.J.G. and W.C.O. completed the chemical synthesis and structural characterization. P.M.R., N.O., N.S., and A.M. conducted SHG measurements. All authors contributed to interpretation of all data and the final manuscript.

The authors declare that they have no competing interests.

#### DATA AVAILABILITY

The data associated with this paper are openly available from the University of Leeds Data Repository [36].

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