



# *Randomized Grain Boundary Phase Showing Macroscopic Chiral Domains*

Dong Chen<sup>a</sup>, Haitao Wang<sup>b</sup>, Min Li<sup>b</sup>, Joseph MacLennan<sup>a</sup>, Matthew Glaser<sup>a</sup>,  
Noel Clark<sup>a\*</sup>

*<sup>a</sup>Department of Physics and Liquid Crystal Materials Research  
Center,  
University of Colorado, Boulder, CO 80309-0390.*

*<sup>b</sup>Key Laboratory of Automobile Materials (MOE) & College of  
Materials Science and Engineering, Jilin University, Changchun  
130012, China.*

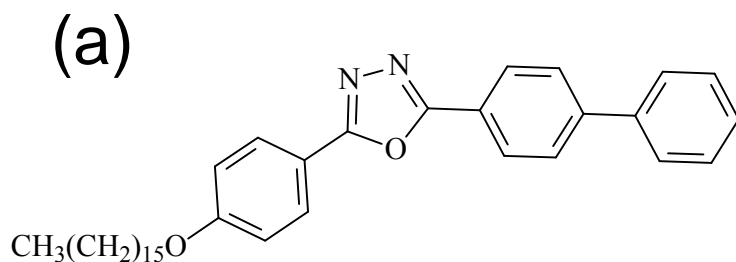


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ILCC 2012, Mainz, Germany

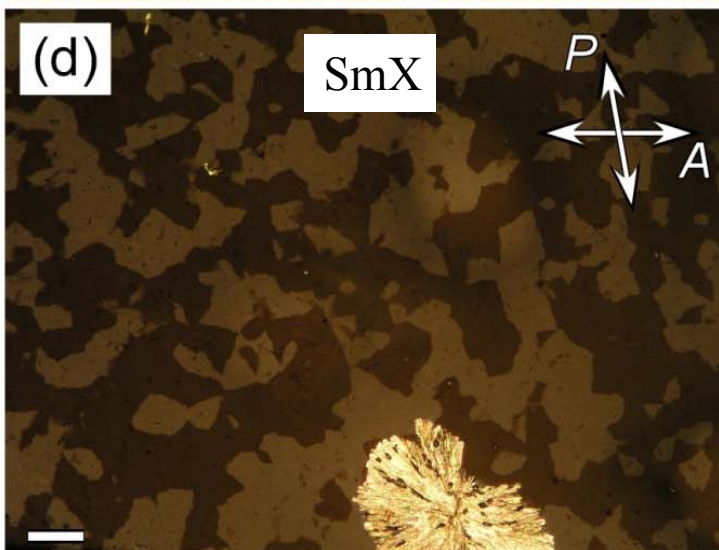
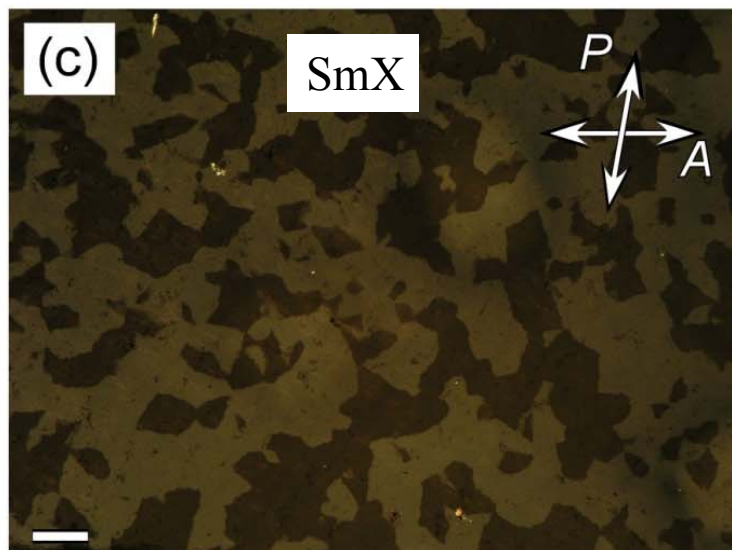
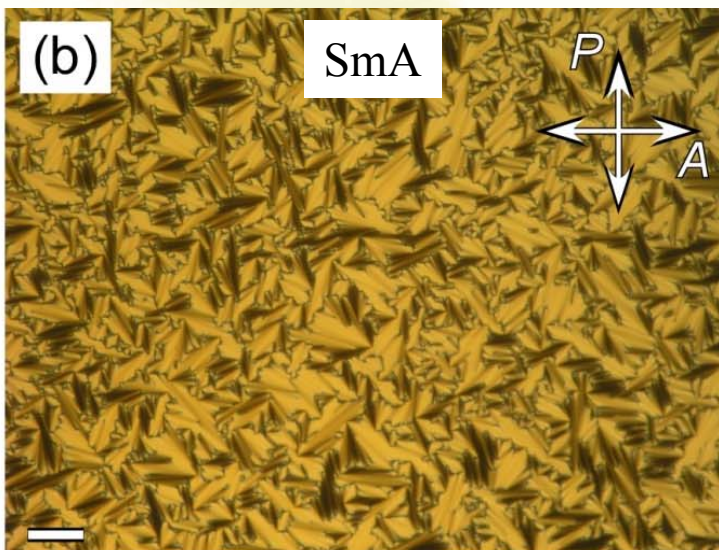


# *COBOXD and its DTLM images*



COBOXD

Iso (110°C) SmA (100°C) SmX (95°C) Cry

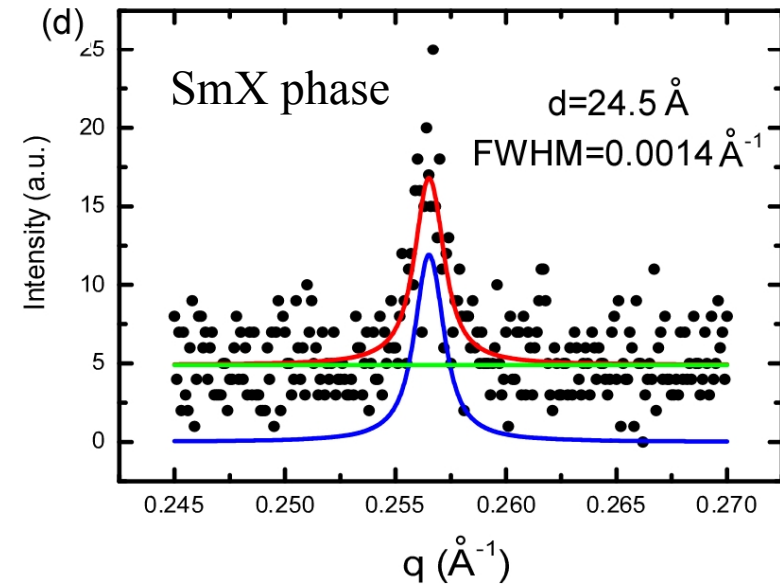
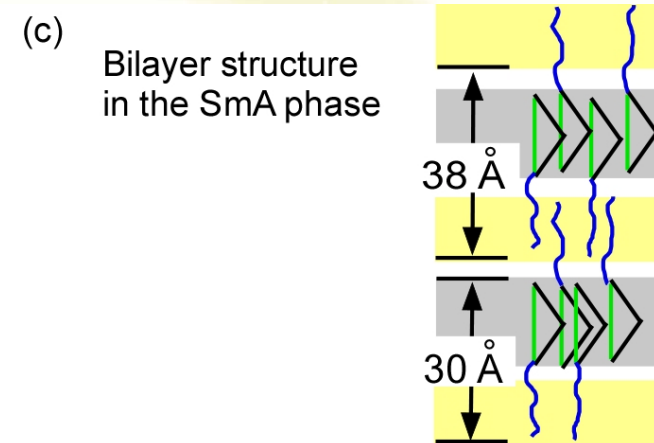
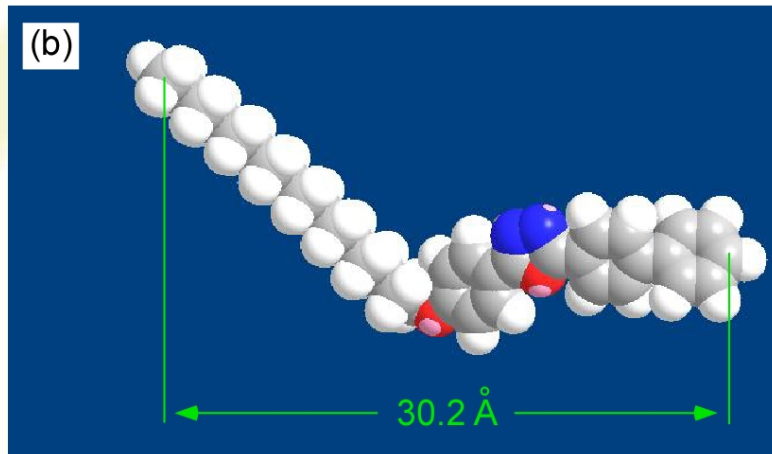
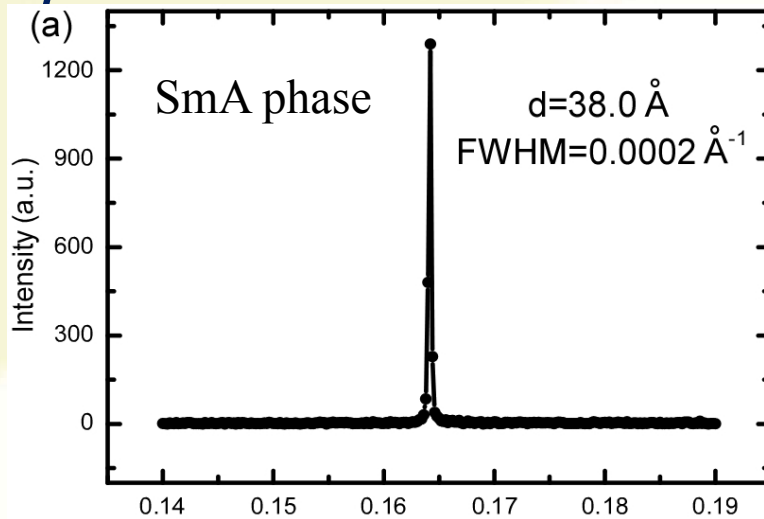


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made in China

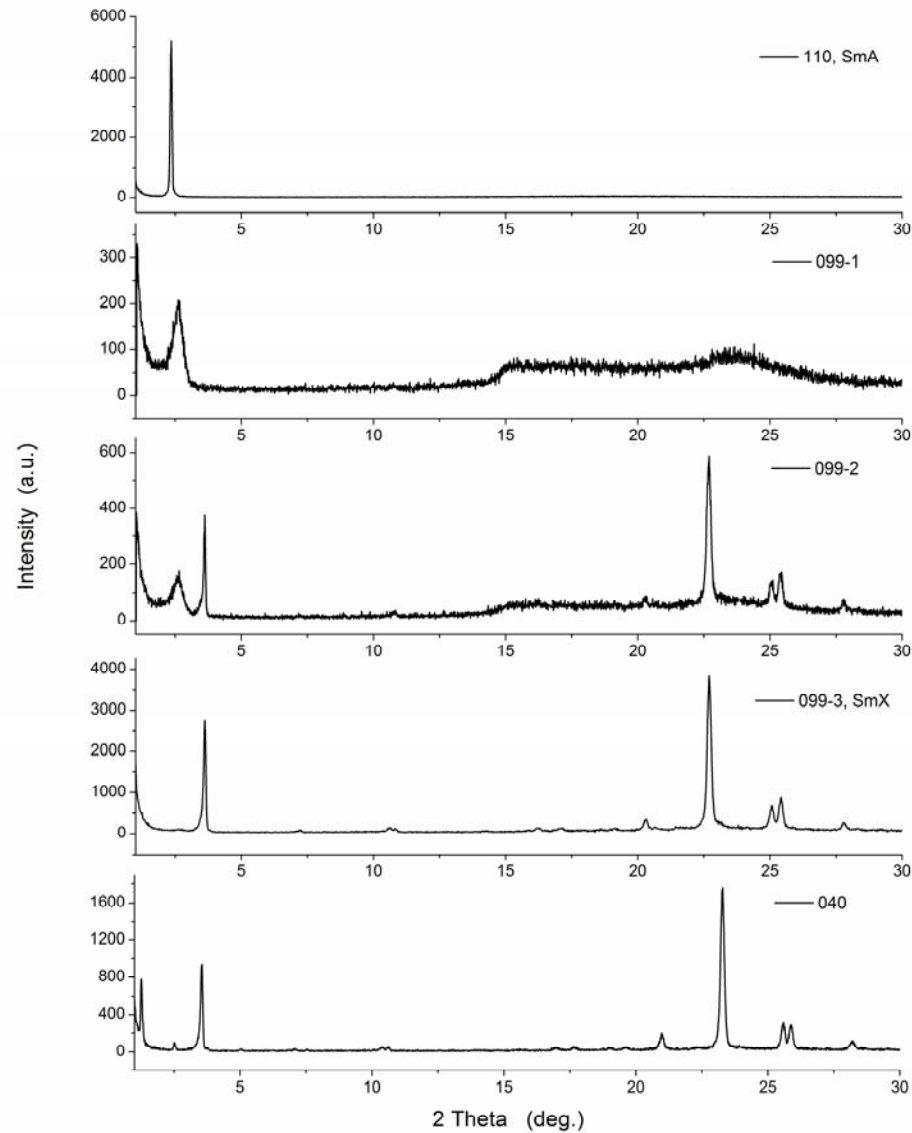


# X-ray diffraction of the SmA and SmX phases





# *X-ray diffraction on cooling*



SmA Phase

SmX phase

SmX phase transition to  
crystal phase

Crystal Phase

Crystal Phase

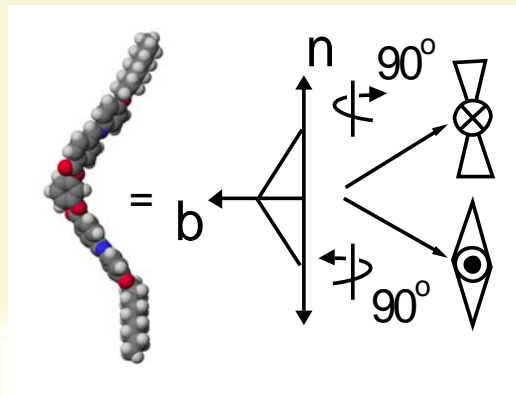


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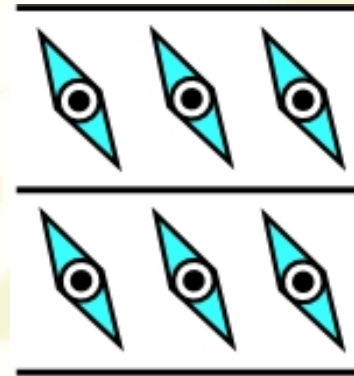




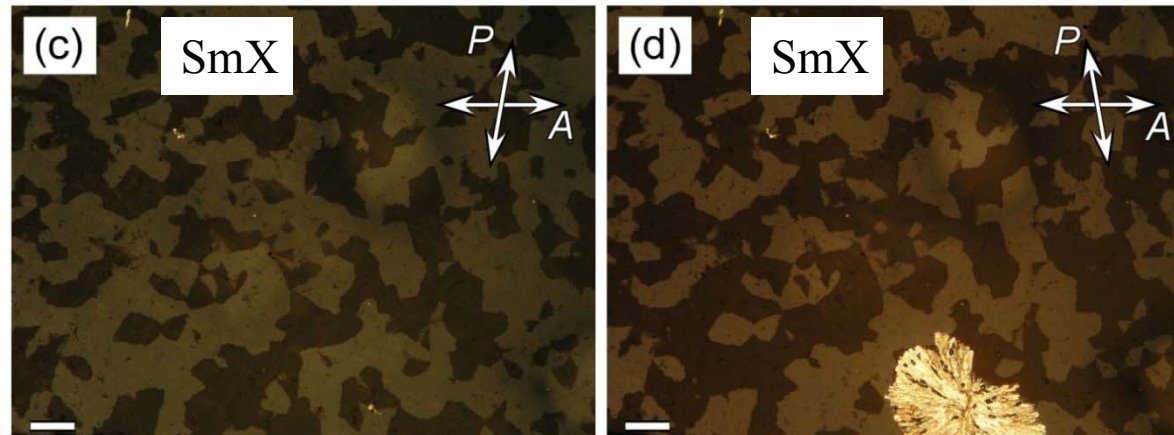
# Chiral layers: Interplay of bent core, molecular tilt and polarization



symmetry  $C_{2d}$



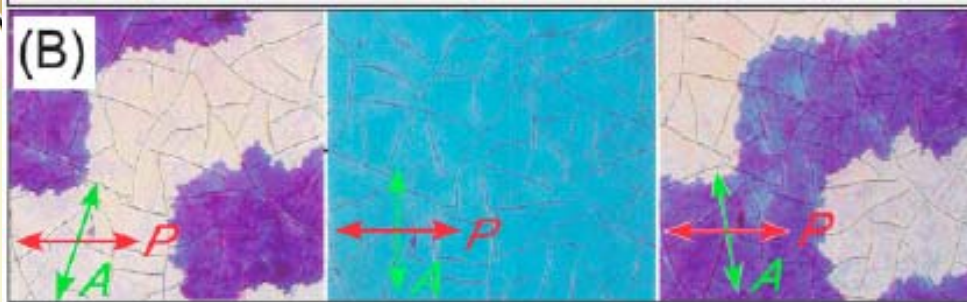
symmetry  $C_2$



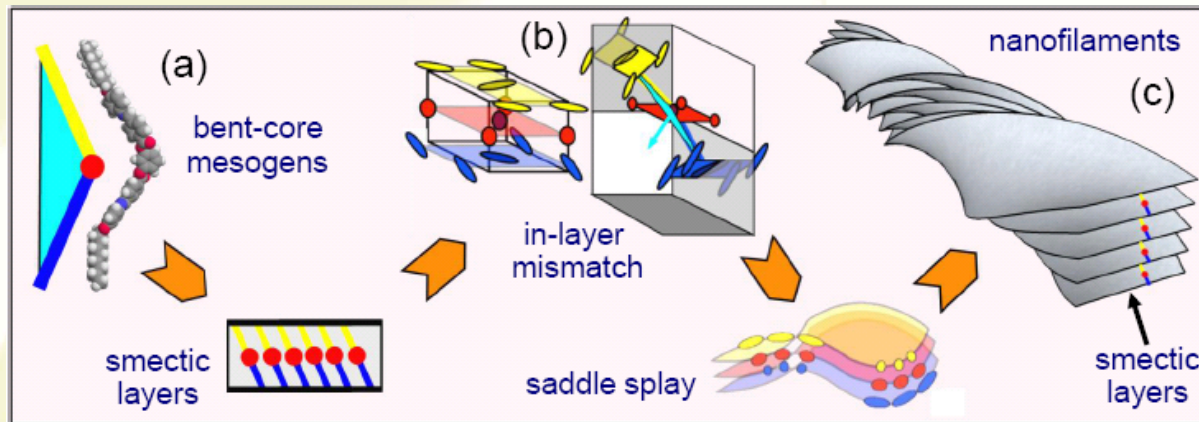
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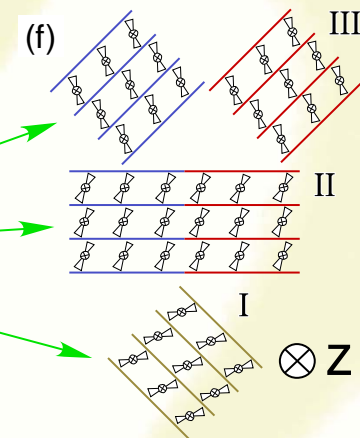
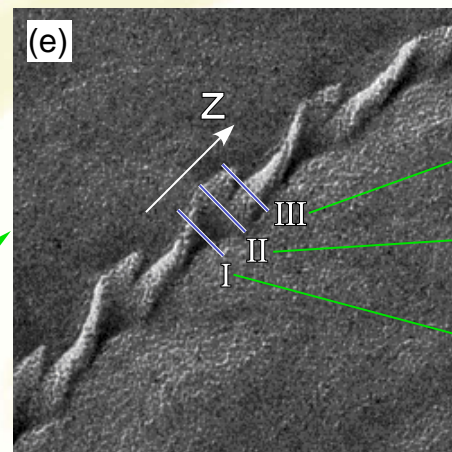
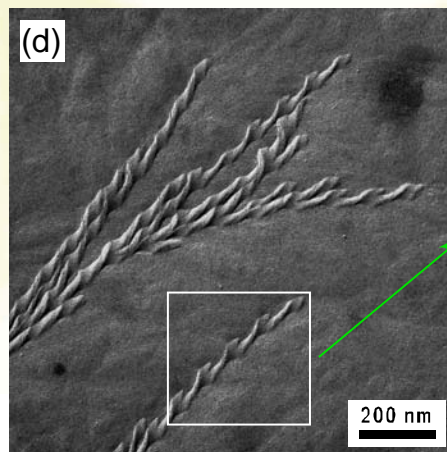
# The B4 Phase: Helical Nanofilaments



optical texture



self-assembly of the nanofilament phase

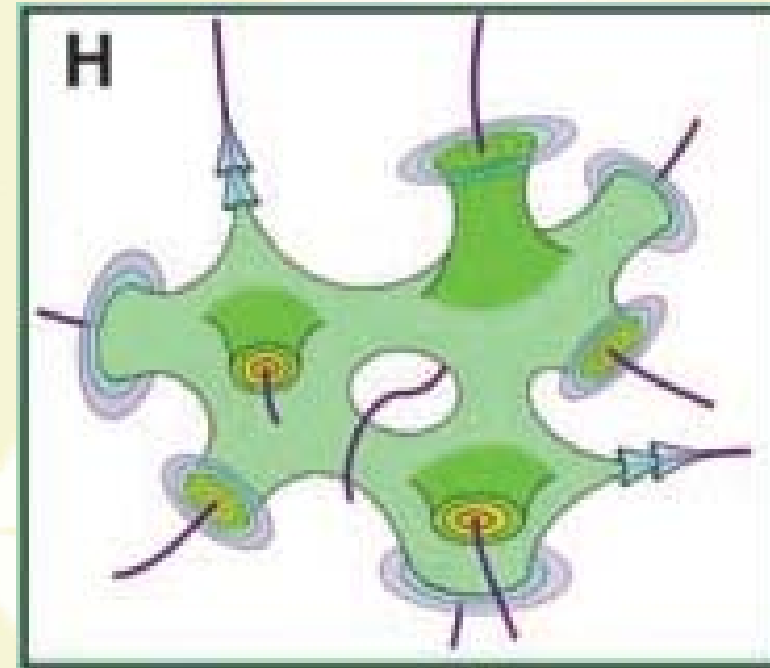


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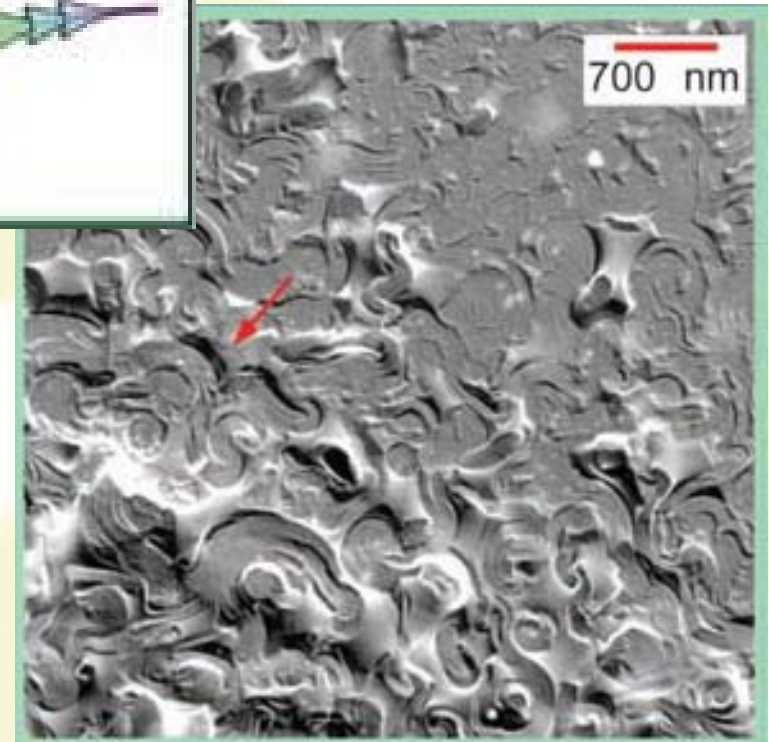
L. E. Hough et al., Science, 2009, 325



# *The DC phase: disordered focal conics*



self-assembly of disordered focal conics



optical texture



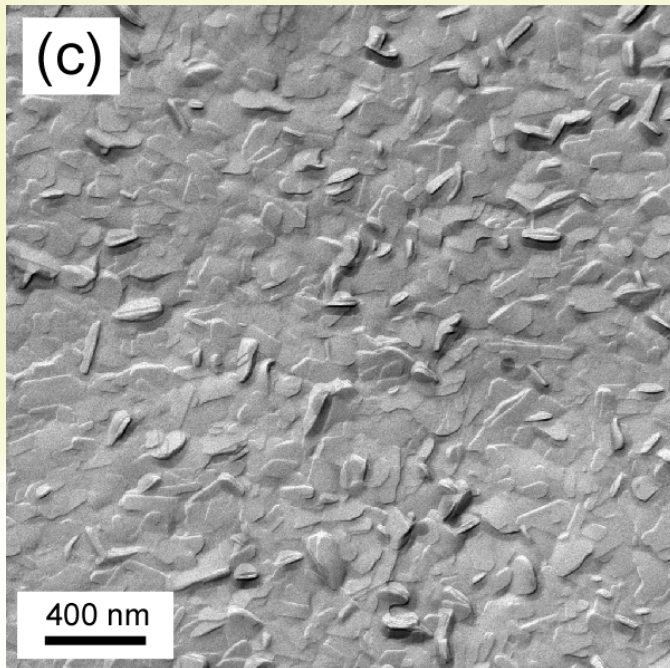
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L. E. Hough et al., Science, 2009, 325

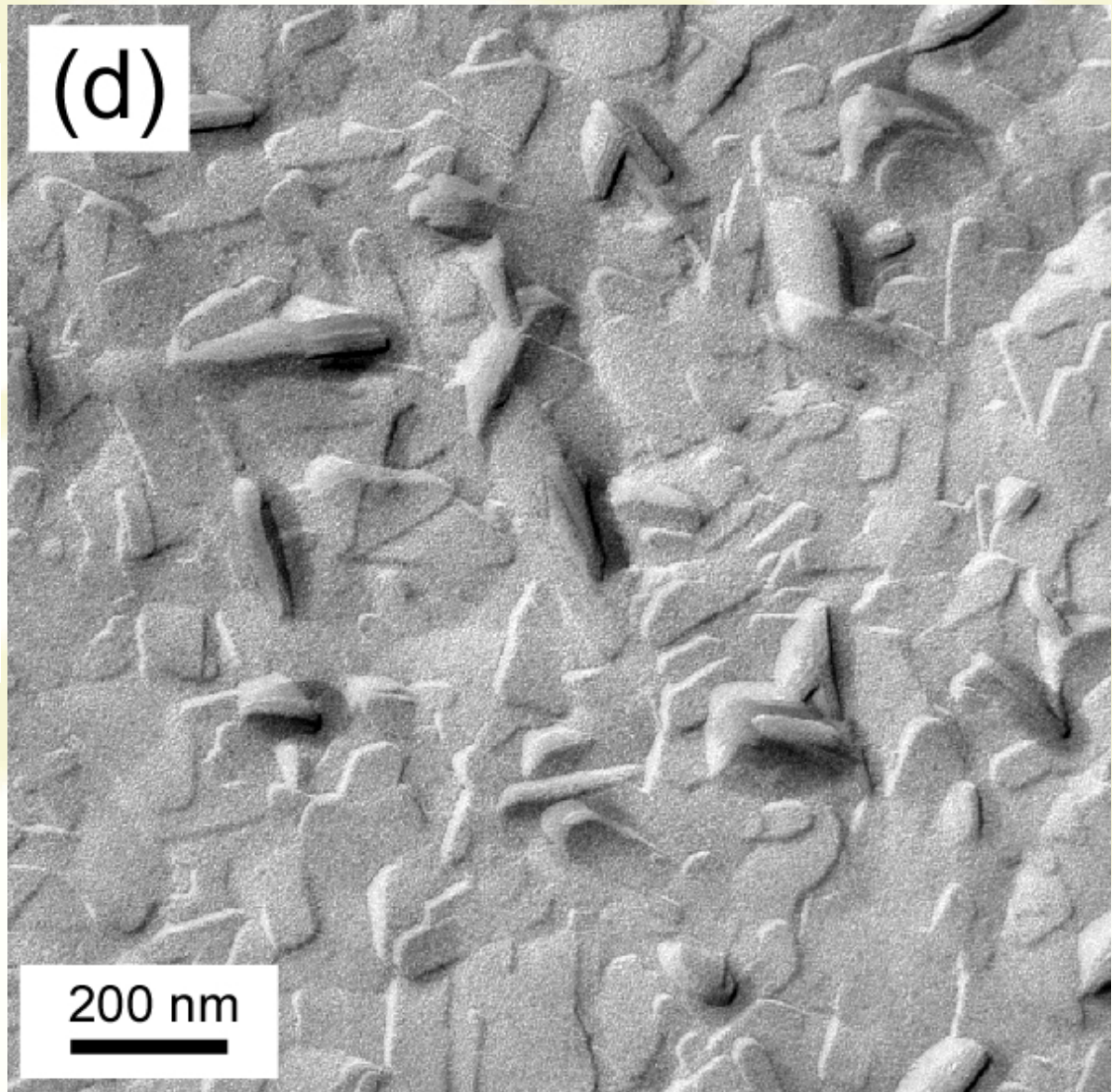




# *TEM images of the SmX phase at the air/liquid crystal interface*



Blocks of smectic layers are oriented at different directions.

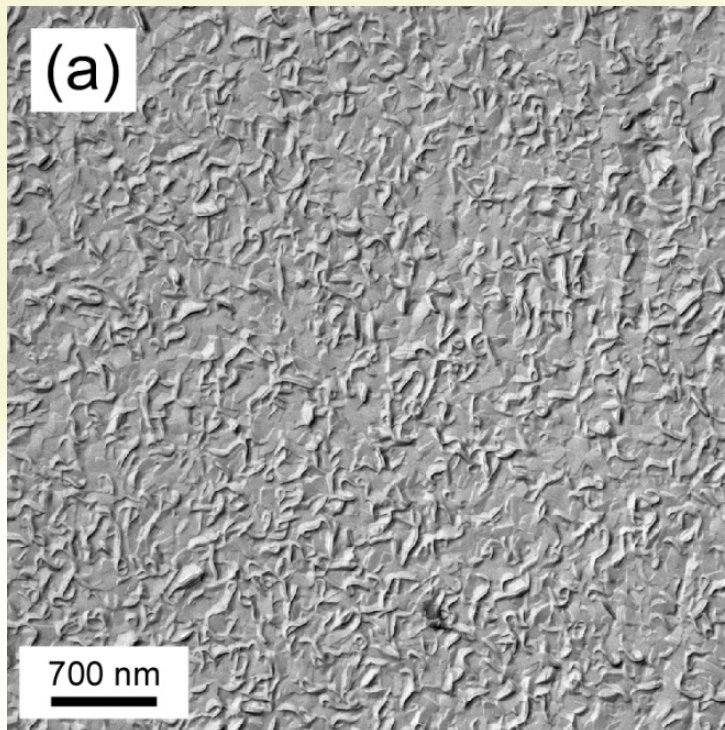


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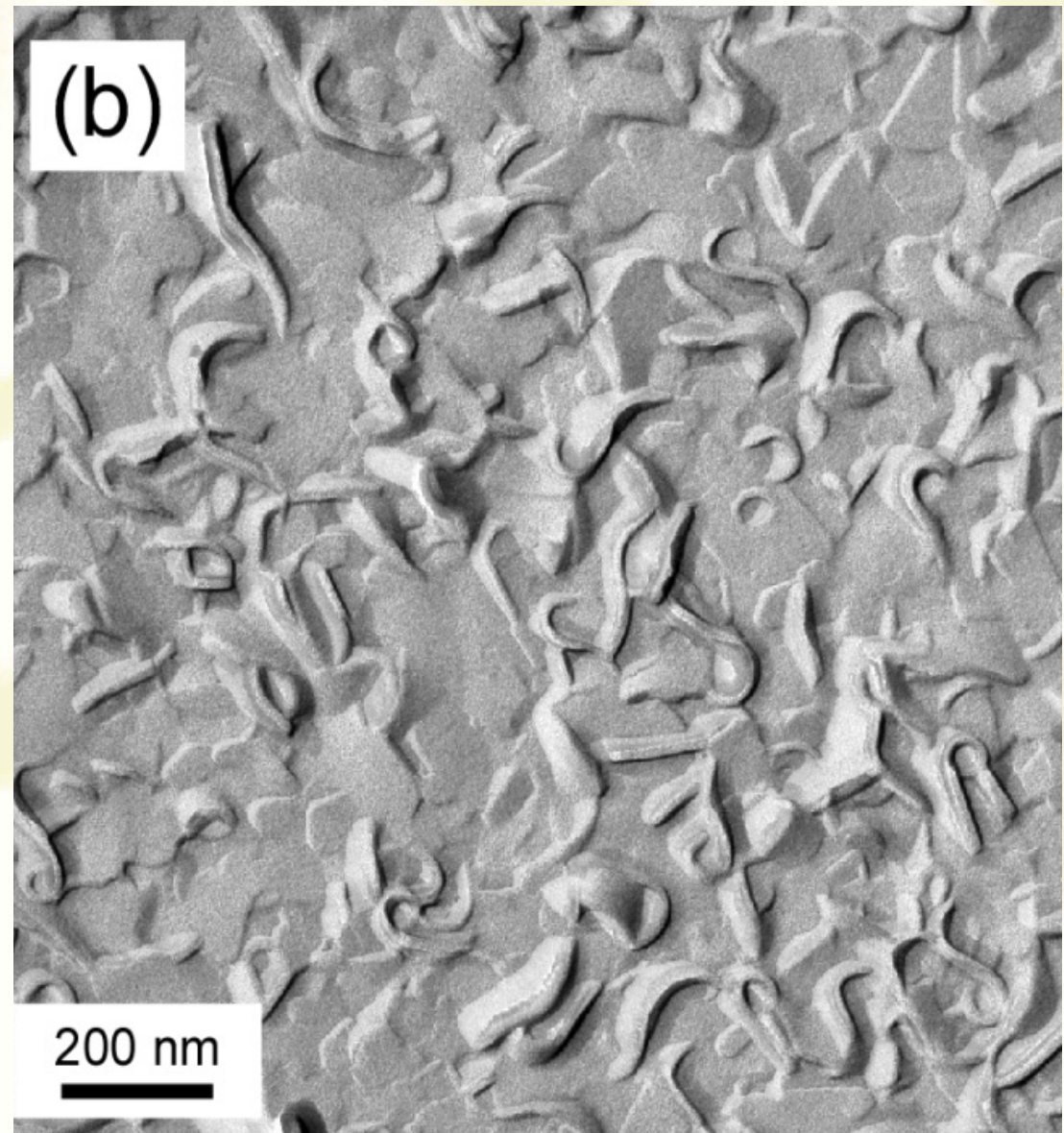




# *FFTEM image of the SmX phase fractured in the bulk*



Blocks of smectic layers are oriented at different directions.



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# Chevron inclination, layer collapsing



Fig. 7.25. Defects mediating regions of opposite (vertical) chevron inclination are essentially of the bookshelf type.

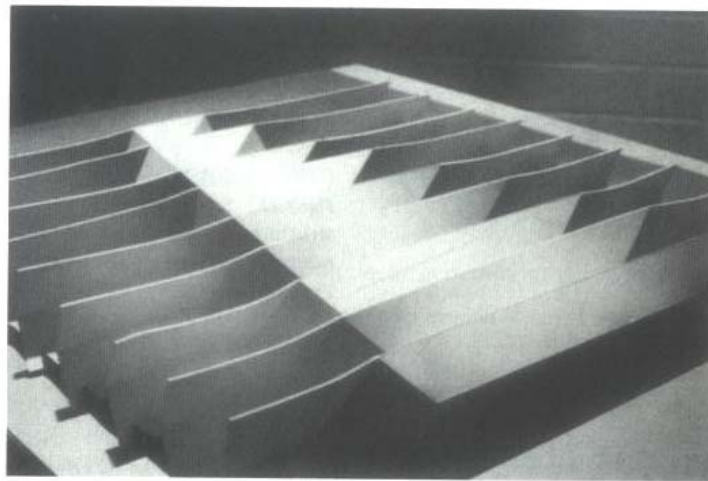
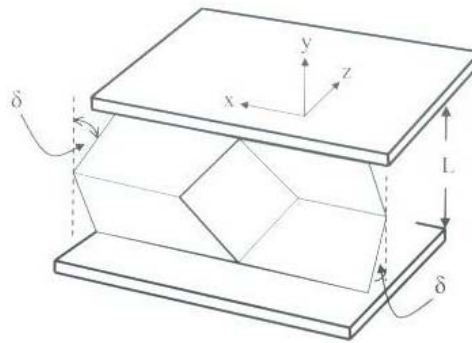
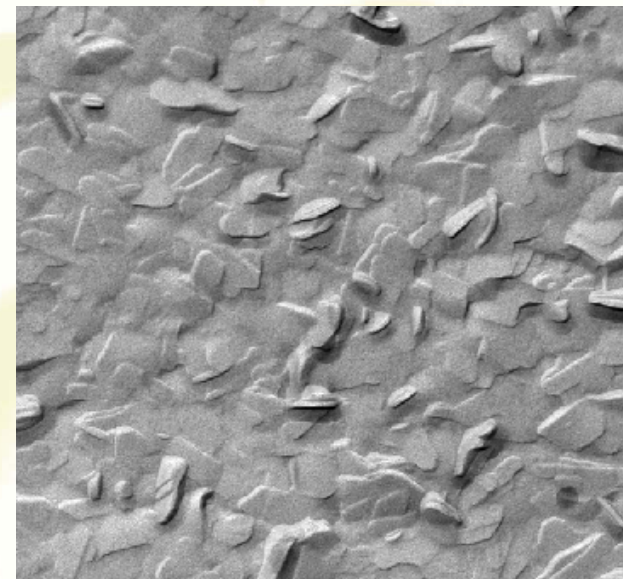
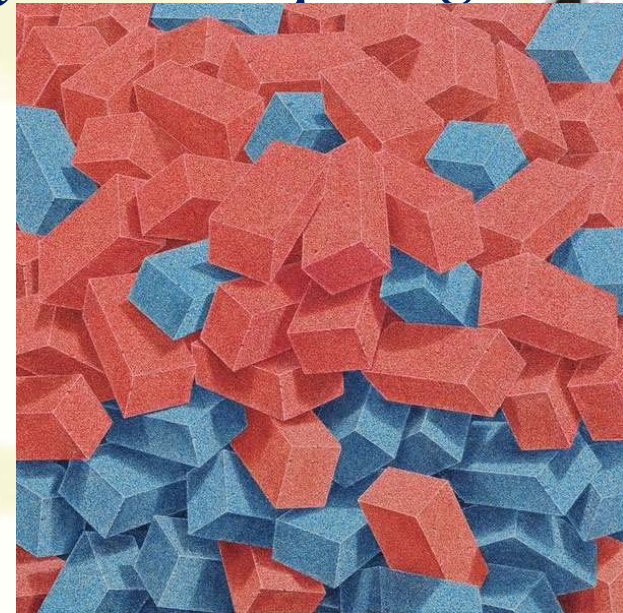


Fig. 7.26. Model of a pair of zigzag lines mediating two regions of opposite uniform (vertical) chevron inclination. Building a cardboard model of the respective structure gives an intuitive idea of why the mediating regions are oriented in bookshelf geometry, with the

normal to the layer plane being tilted with respect to the rubbing direction. (Reproduced by permission of Taylor & Francis, I. Dierking et al., *Liq. Cryst.*, **19**, (1995), 179 (<http://www.tandf.co.uk/journals>).)

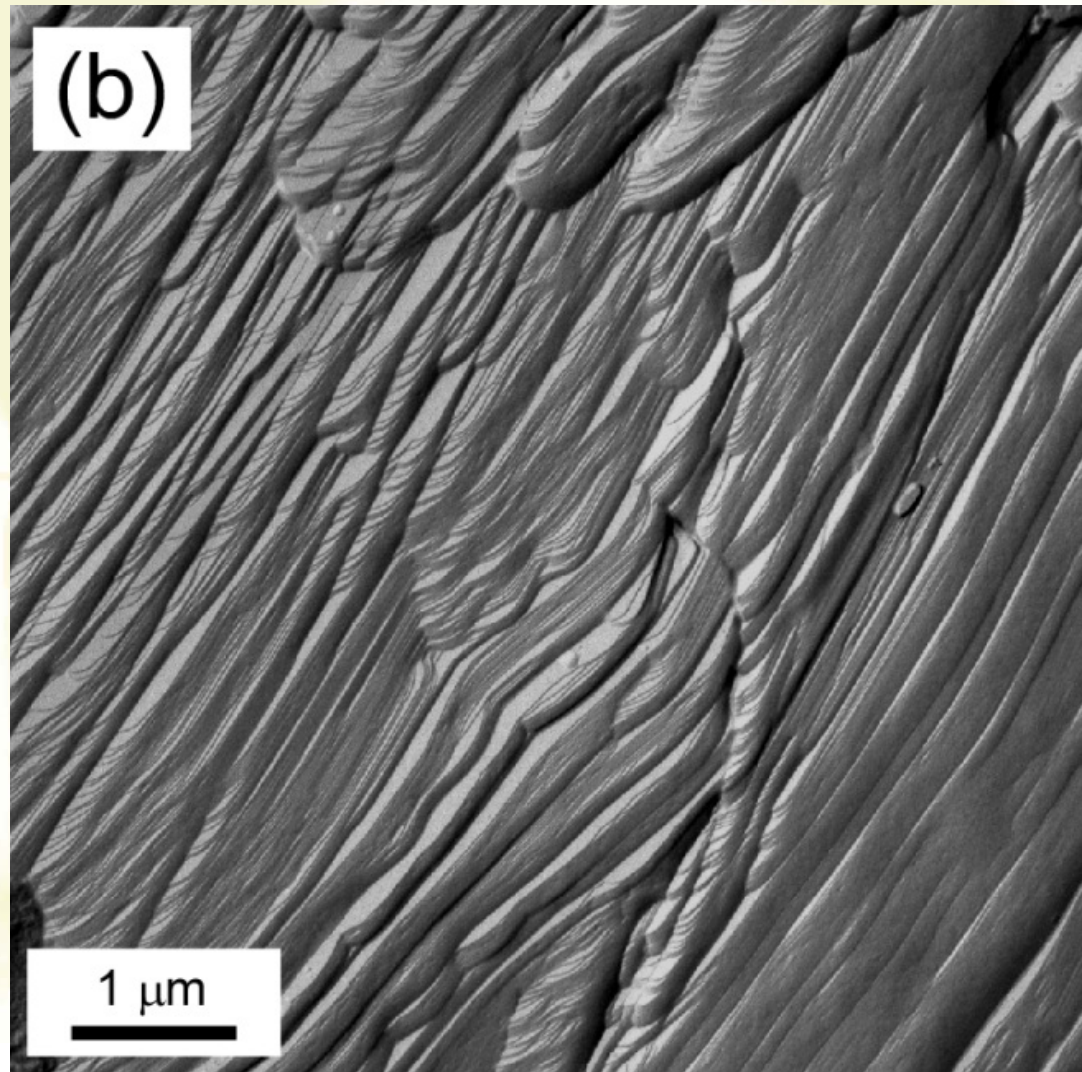


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from internet



## *TEM images of the crystal phase at the air/crystal interface*

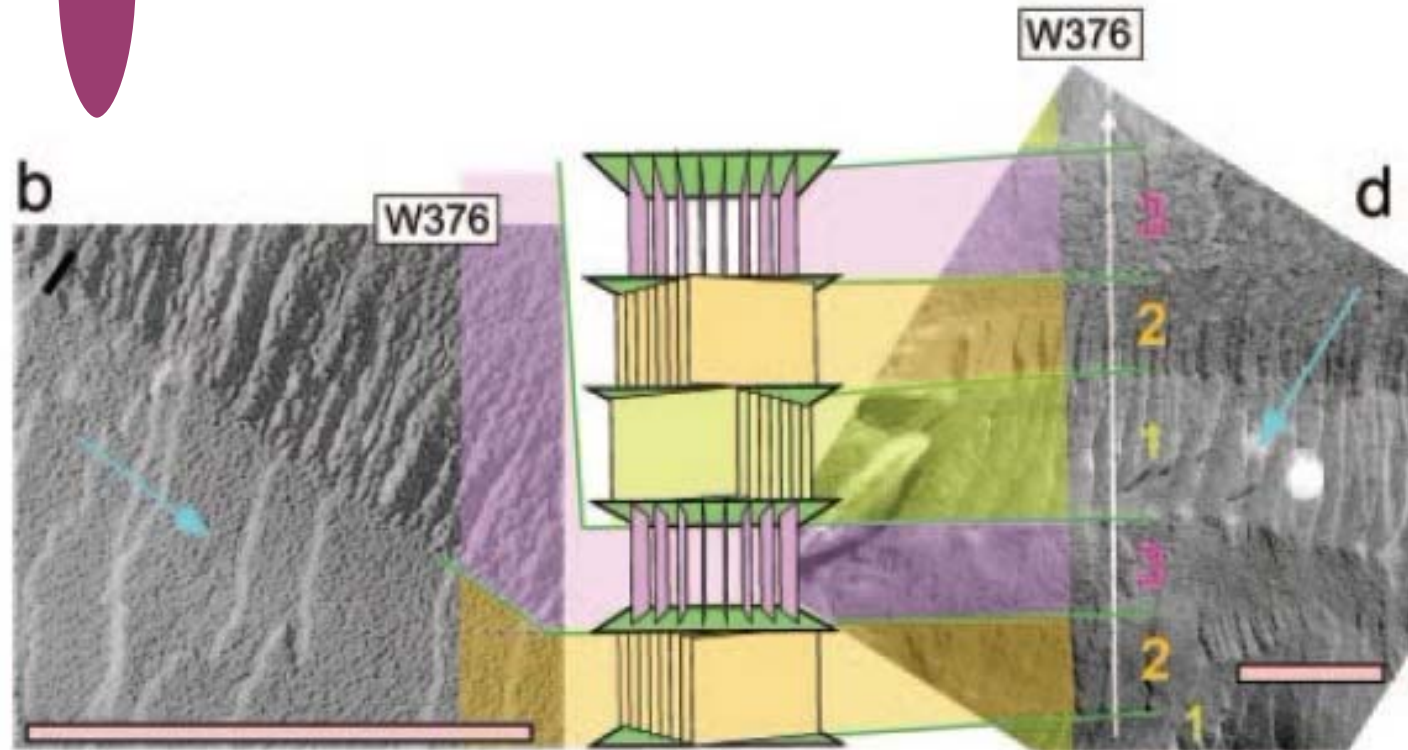


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## *Twist grain boundary phase*



## *Randomized grain boundary phase*

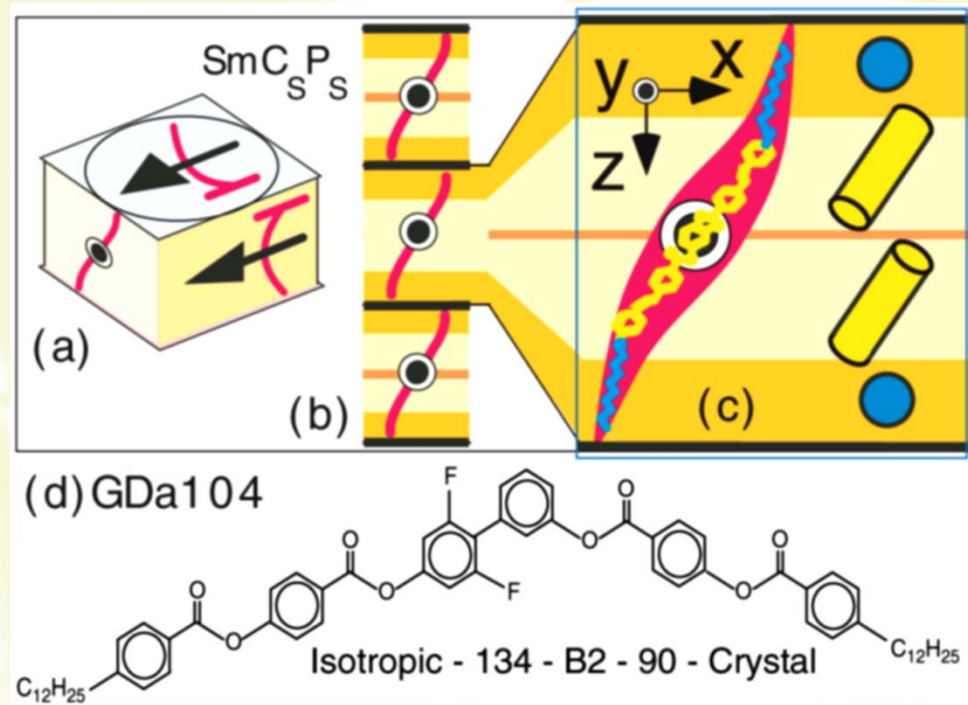


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J. Fernsler et al. PNAS, 2005, **102**



# Formation of macroscopic chiral domains in a fluid smectic phase of achiral molecules



Theoretical calculation

$SmC_A P_A$  OR=0.1°/μm

$SmC_S P_F$  OR=0.05°/μm

Experiment

OR=0.04°/μm

For  $\lambda=650$  nm

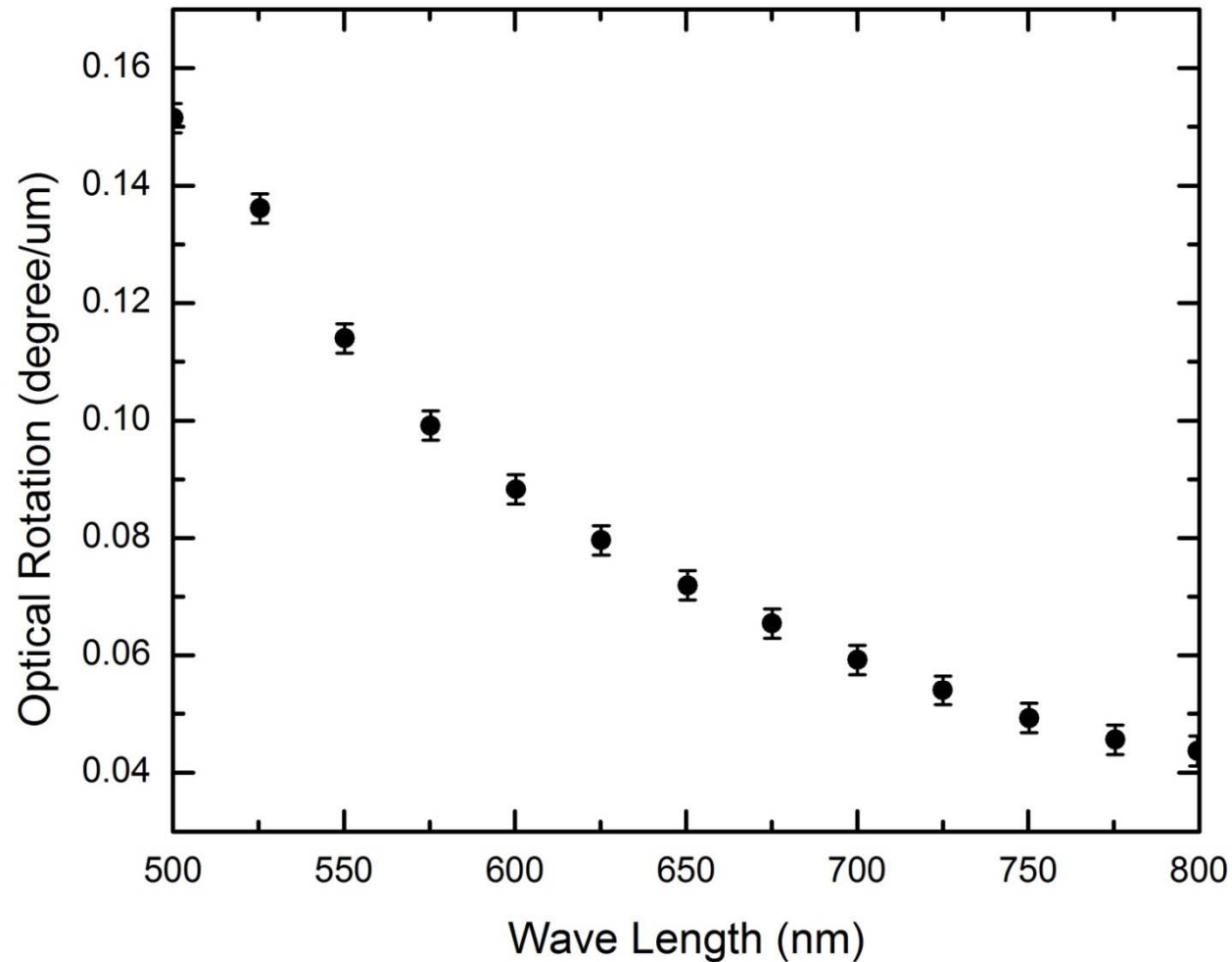


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L. E. Hough et al., PRL, 2005, **95**



## *Optical rotation due to layer chirality*



OR = 0.07°/ $\mu\text{m}$  For  $\lambda = 650$  nm

The optical rotation is attributed to the layer chirality.

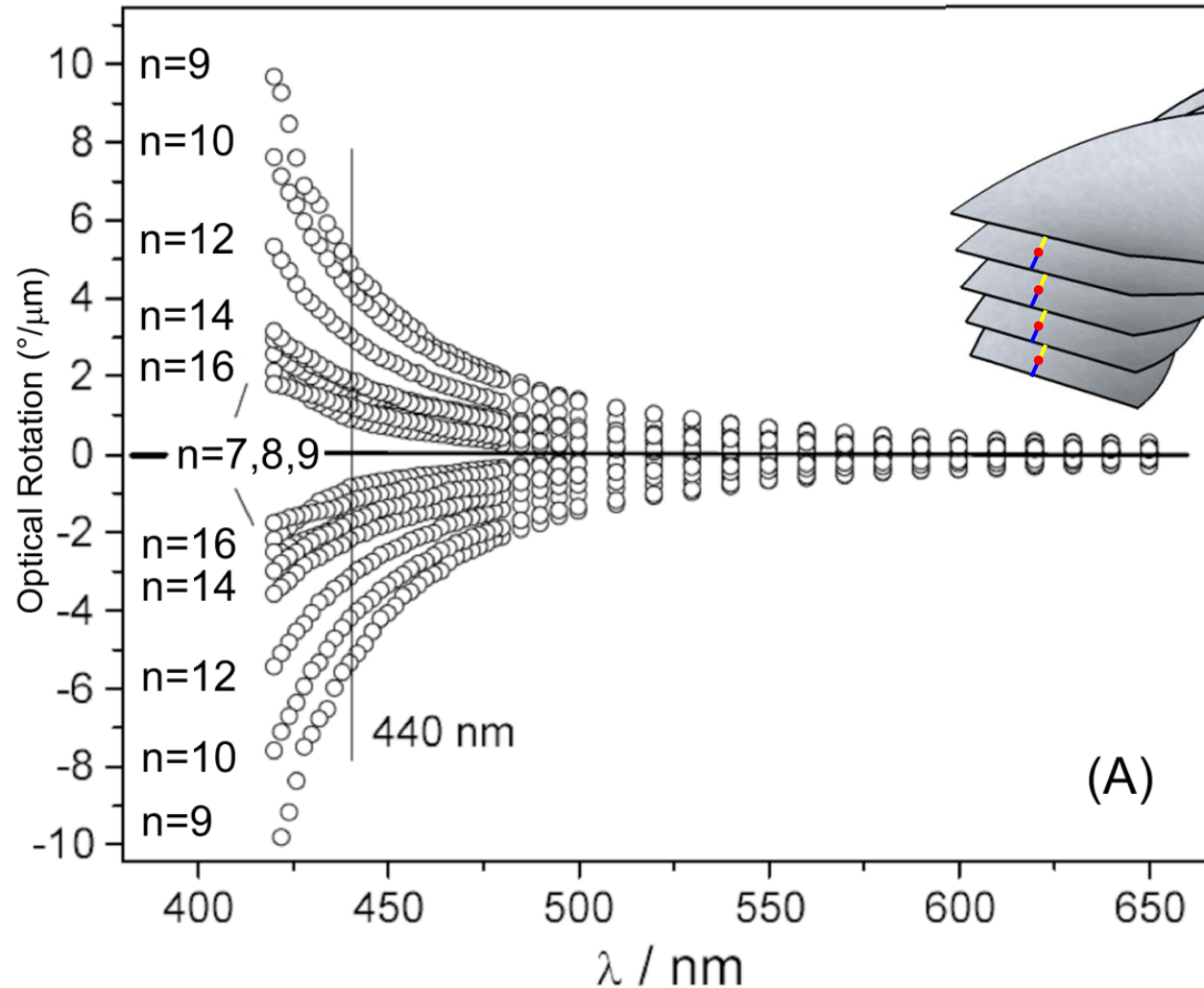


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# Optical rotation of helical nanofilaments



OR =  $0.5^{\circ}/\mu\text{m}$   
for  $\lambda=650$  nm

10 times higher  
than layer chirality

Optical Rotation of the B4 phase in the homolog series, P-n-OPIMB.



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L. E. Hough et al., Science, 2009, **325**



## *Summary*

- 1) Randomized Grain Boundary Phase of Achiral Hockey-Stick-Like Molecule
  - a) showing macroscopic chiral domains.
  - b) made of smectic blocks, randomly oriented.
  - c) optical rotation purely attributed to layer chirality, no helical structure.
  - d) layer collapsing plays an important role in forming this phase.
- 2) New molecular structure self-assembles into new microstructures.



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## *Acknowledgement*

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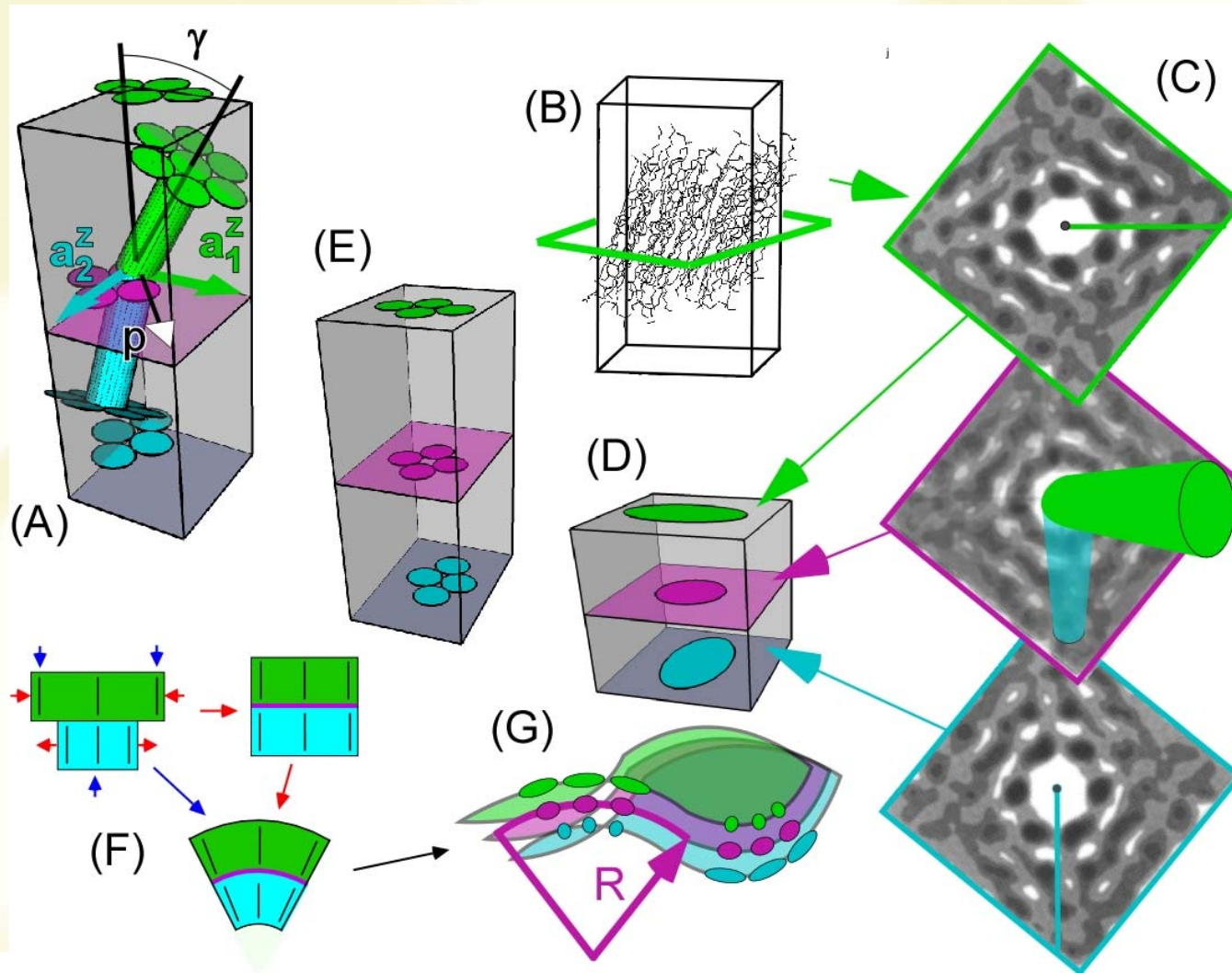


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# *Saddle-splay curvature: Driven by the intra-layer structural mismatch*





## specific rotation



$$[\alpha]_d^T = \alpha/lc$$

$\alpha$  = observed rotation in degrees.

$l$  = cell path length in decimeters. (1 decimeter = 1 dm = 10 cm.

A standard polarimeter tube is 1.00 dm in length.)

$c$  = concentration in g ml<sup>-1</sup> for a pure liquid compound  
(i.e., the liquid's density), or g 100 ml<sup>-1</sup> for a solution.

- Sucrose +66.47°
- Lactose +52.3°
- Cholesterol -31.5°
- Camphor +44.26°
- Penicillin V +223°
- Taxol -49°
- (S)-bromobutane +23.1°
- (R)-bromobutane -23.1°
- (+)-cavicularin +168.2°

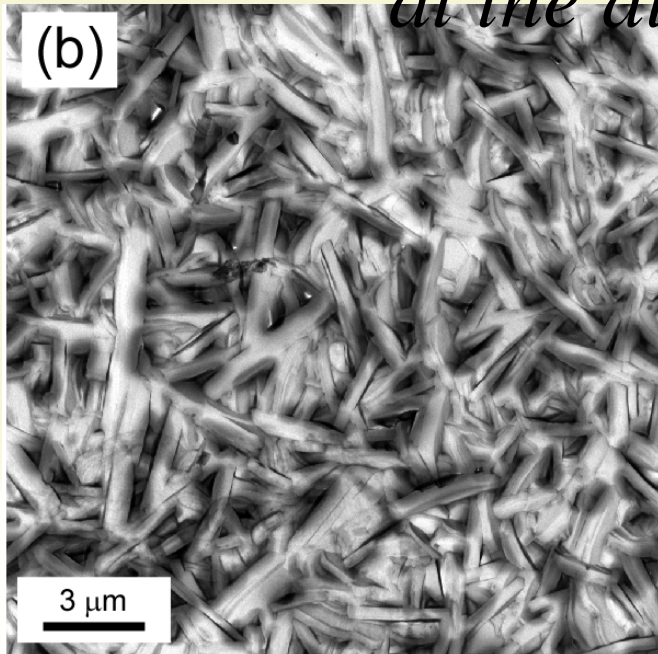




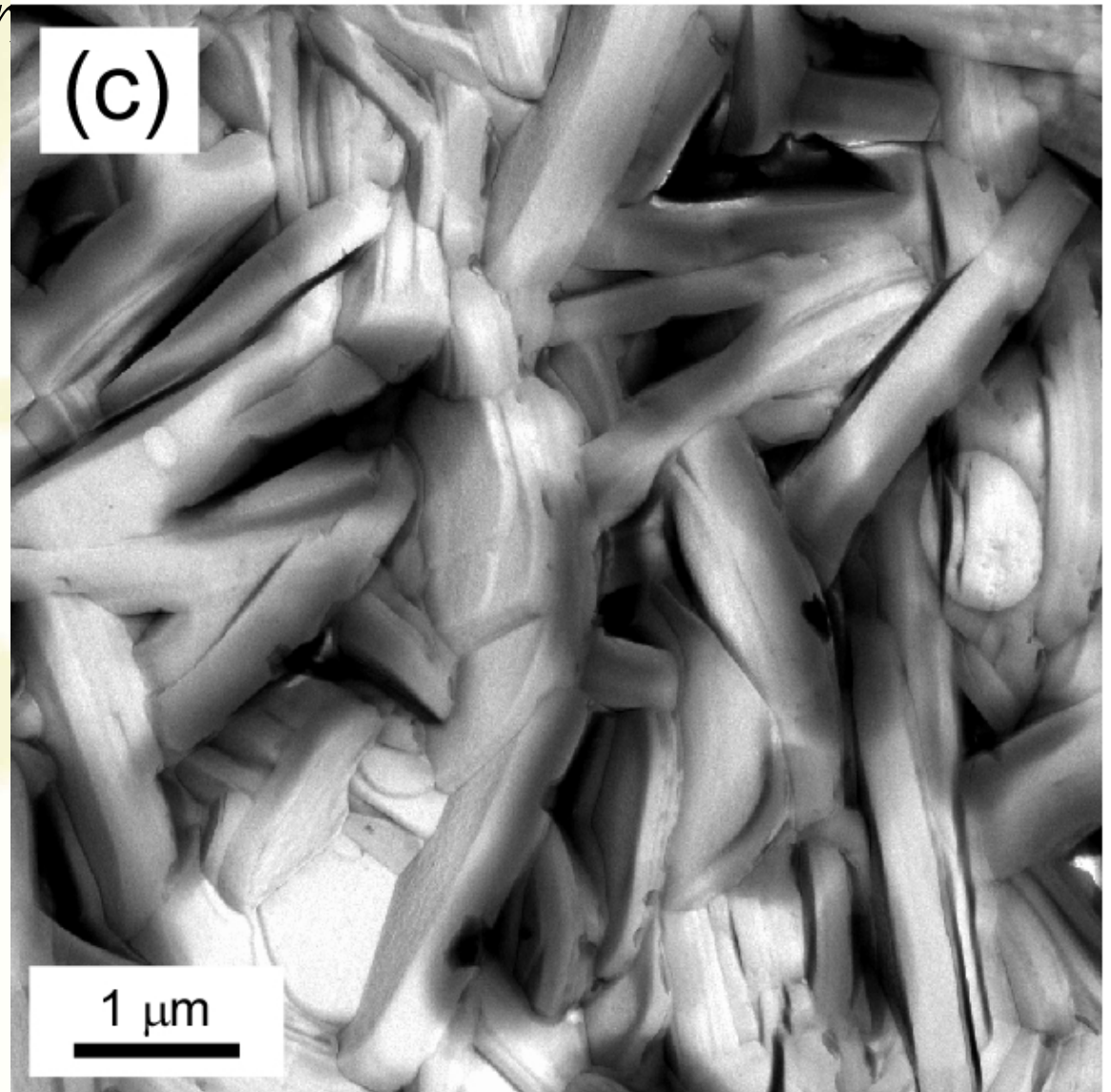
# *TEM images of the twist grain boundary phase*



*at the air*



Disordered blocks of smectic layer at the air interface.



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# *Outline*

## 1) Microstructure of the bent-core liquid crystal phases

- a) The DC phase: Disordered focal conics
- b) The B4 phase: Helical nanofilaments

## 2) The randomized grain boundary phase

- a) Optical texture: macroscopic chiral domain
- b) FFTEM: blocks of smectic layers
- c) Optical rotation: layer chirality
- d) XRD: layer collapsing



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