

Chapter 1

Structure-Property in the PAL30 Homologous Series of Molecules

Now that the existance of the $\text{Sm}(\text{CP})_\alpha$ and $\text{SmC}_\text{A}\text{P}_\text{A}$ phase have been put on a firm footing, we can extend this study to a broad category of molecules that share the same core, but have variations in the tail length. Our previous study focussed on PAL30, with a tail length of $n=14$ carbons. Inspired by previous studies by the Dublin group[?, ?, ?], where the n_{16} and n_{18} compounds were studied and a helical phase was tentatively determined based on periodicities of around $5n$ seen in atomic force microscopy images.

With the ability to directly probe the periodicity of these compounds with carbon K-edge resonant X-ray, we have the ability to provide direct evidence for helical phases in these molecules. The high-resolution provided by RSoXS additionally allows for a rich study of structure-property relationships, where the nature of the helical phase can be connected to the tail-length.

Interest in the PAL30 series of molecules is not confined to the discovery of helicity. The additional discovery of a bent-core de Vries like phase is also a motivating interest for

study of this series.

This chapter is organized under discussion of these two phases. First the helical, smectic Sm(CP) _{α} is presented and discussed for the n12, n14, and n16 molecules. Then the bent-core de Vries phase is presented and discussed for this series.

1.1 The Sm(CP) _{α} Phase: Smectic Chirality Beyond the B2 Phase

1.2 The bent-core de Vries phase

The evidence for a bent-core de Vries phase in PAL30 will be briefly reviewed. It is worth noting that the question of “what is a de Vries phase” is not settled, even for the simpler phases of rod-shaped molecules, see Jan Lagerwall’s thesis[?] for an excellent history and discussion of de Vries phases in the calamitic paradigm. For the purposes of this thesis, we take the broadest view of a de Vries: it is a tilted phase with no long-range order present in the tilt order parameter.

Even this broad definition is not free from ambiguity— what entails long-range order, and does it matter how the escape from long-range order is achieved? We will also see in this Chapter that the de Vries phase can be suppressed quite easily by a strong-alignment layer.

To satisfy our definition, we must prove two things about the phase under investigation to say it is a de Vries bent-core phase. First, it must be tilted. Second, it must have no long-range order present. Both of these facts are very difficult to establish in a positive manner, as there is no ‘smoking-gun’ evidence for either.

We claim that PAL30 is tilted for the following reasons: the smectic layer spacing is significantly less than the extended molecular length; the lower temperature phases are proven to be chiral (therefore tilted), and there is no observed smectic layer-contraction observed on

cooling, which would be expected for an orthogonal → tilted phase transition; and there is no measured change in the birefringence which would be predicted from an orthogonal phase to the helical $\text{Sm}(\text{CP})_\alpha$ (confirmed from RSoXS). Though individually, none of these facts are conclusive evidence for tilt, all of them in aggregate suggest that the highest temperature smectic phase of PAL30 is tilted. To see that there is no long-range order in the tilt order parameter, we can look at the textures of this phase and observe that they look orthogonal—they have the clean lines of a focal conic SmA phase. This is necessary but not sufficient, as other phase—such as the $\text{SmC}_\text{A}P_\text{A}$ phase—can also appear to be orthogonal, yet have a definite anti-clinic long range order. This anti-clinic order (and other, more exotic long helical ordering of the tilt order parameter) would however, show up in resonant x-ray scattering. The fact that the resonant x-ray scattering shown in ?? reveals zero periodic structure for PAL30 confirms that the tilt order in the Sm1 phase has no long-range order.

The actual way that this long-range order is escaped is still ambiguous. The simplest model, where the molecules are rotating freely around a cone whose opening angle is set by the molecular tilt seems unlikely from simple enthalpic space-filling arguments which would seem to exclude a model where neighboring molecules can be pointing in completely opposite directions with no energy cost. On the surface, this seems to be false, but close observation of the c-director fluctuations that occur in freely-suspended-films shows that at the molecular level the c-director can easily be fluctuating with π -rotations measured against neighboring molecules, so we cannot rule out this type of behaviour purely on enthalpic concerns. This is fluid-like model, where the molecules are actively rotating with no regard for their neighbors space.

By including these enthalpic considerations we can build model where short-range order persists, but the size of these ordered domains is small, and they are randomly distributed such that an ensemble average of the tilt is zero. This is more of a disordered-crystal model, where short-range order persists, but is distributed in such a way that the macroscopic order parameter is still zero—much like the example of a cooled Ising model developing local

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ferroelectric ordering of spins, even though the total magnetization remains zero.

Regardless of how this long-range tilt order is broken, because these are polar molecules, we also have to consider the polar-ordering present in any phase. The way that the polar and tilt interact in the high-temperature de Vries SmA of PAL30 is unique to bent-cores.

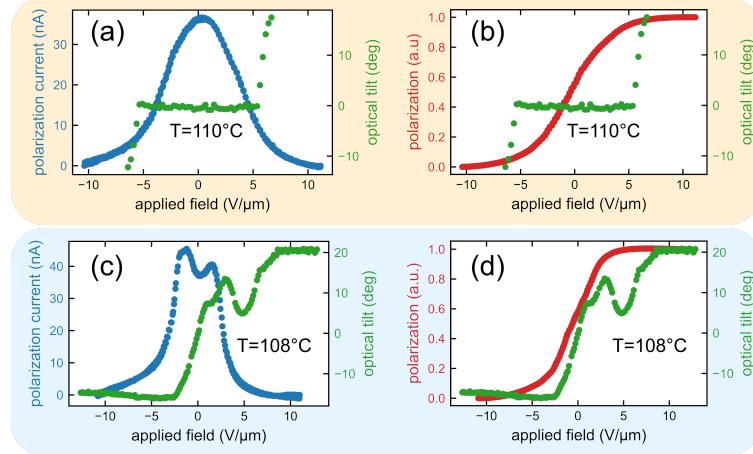


Figure 1.1: The polarization current and the optical tilt plotted as a function of applied field strength for both the Sm1 (de Vries SmA) (a,b) and the Sm2 ($\text{Sm}(\text{CP})_\alpha$) (c-d). The polarization current has additionally been integrated to calculate the time-dependant net polarization. The threshold electric field (E_{th}) required to manifest the tiger-stripes can be directly read from the green curve denoting the optical tilt (for $T=110^\circ\text{C}$, $E_{\text{th}} \approx 5 \text{ V}/\mu\text{m}$), and the saturation electric field where the net polarization is no longer changing (E_{sat}) can be directly read from the red curve, which denotes the net polarization, (for $T=110^\circ\text{C}$, $E_{\text{sat}} \approx 5 \text{ V}/\mu\text{m}$). Both E_{th} and E_{sat} are plotted in as the inset of ??.

The polarization current has been integrated to give the net polarization, which is a direct measure of the ensemble average of the molecular orientation with an applied electric field. The optical tilt measurements were done by analyzing the contrast between adjacent stripes. In the ground state, where there is no long-range order present in tilt, the contrast is zero. At a field whose strength is over some threshold value (E_{th}), the state transitions into a tilted (therefore chiral) state. The handedness of the domain sets the tilt direction. This tilt can be directly measured as it is proportional to the contrast between different handed domains:

$$\text{contrast} \propto \sin(4\theta) \quad (1.1)$$

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. Barring pathological examples, *any* alignment, orientation, or movement of the molecular long axis will show up as the observable separation of the texture into chiral domains.

With some unique exceptions[?] most bent-core systems have the tilt and polarity strongly coupled: where one moves, the other follows. Through symmetry, this can be expressed as the condition that rotations around the molecular long axis are forbidden: to transition to different states, the molecule must rotate around the smectic layer normal, confined to the tilt-cone. ?? clearly shows that for the Sm1 phase of PAL30, this is no longer the case. The movement of the polar director is completely decoupled from the movement of the c-director, which can only occur if the PAL30 molecules are rotating around the long axis, allowing their polarization to change while the optical tilt stays fixed. It is only after the polarization saturates and is completely aligned before there is any detectable movement of the tilt-director. The previous examples of this occurring in bent-cores required pulse-engineering the applied voltage, where a very large, fast voltage needed to be applied to see rotations around the long axis of the molecule. PAL30 is the first molecule where the polar and tilt order are decoupled enough to allow these long-axis rotations naturally.

This decoupling results in an important distinction because, unlike their calamitic cousins, these bent-core molecules are not inherently chiral. They only develop chirality once they pack into phases. They require tilt and smectic ordering before the mirror-symmetry breaking required for chirality is achieved. They also require that the tilt and polar order are strongly coupled—free rotations around the long-axis result in a return of mirror-symmetry and the chirality of the phase is lost. In contrast to the calamitics, who merely have to ‘discover’ their own inherent chirality once a field is applied (for instance, in the electroclinic effect), the bent-cores must spontaneously create their own. This is not a new discovery, the B2 phases[?] have long been known to develop spontaneous chirality on cooling from an achiral phase. This is however the first discovery of field-activated chirality in a bent-core system, where chirality is induced at a certain voltage, but then returns to an achiral ground state when the voltage is removed.

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The closest thing to a developed model for this phase is the Landau-de Gennes model put forth by Eremin et al.[?] where they discovered an electro-clinic analog in a hockey-stick compound. Broadly, their model describes an orthogonal bent-core phase where the polar director is free to move. On application of an electric-field, the polarization of the molecules orients. An enthalpicphase transition is then driven by excluded-volume interactions, where the molecules can pack more efficiently by tilting.

This interaction is described by the following Landau-de Gennes free energy:

$$f(P, \theta, T, E) = \overbrace{(a_0(T - T_\theta)\theta^2 + b\theta^4 + c\theta^6)}^{f_\theta} + \underbrace{(\alpha_0(T - T_P)P^2 + \beta P^4 + \gamma P^6 - PE)}_{f_P} + \underbrace{(-\Gamma(P\theta)^2)}_{f_{\theta P}} \quad (1.2)$$

Though this model was originally formulated to describe the transition from an orthogonal phase to a tilted one, we can adapt it to our bent-core de Vries phase by changing the interpretation of θ from the molecular tilt to the optical tilt.

Though this model successfully captures the overall nature of the electrically-driven onset of chirality in the bent-core de Vries phase, where the molecules first orient their polar directors to the field, and on the achievement of total polar alignment, an optical tilt develops, it leaves much to be desired. Because this model does not demand details of the microscopic interactions that lead to the observed transition, there is an abundance of fitting parameters that will lead to overfitting and the model loses most of its predictive power.

Because of this, efforts must be undertaken to develop a microscopic model of this de Vries phase.

1.2.1 Textures of bent-code de Vries phase

1.2.2 Electro-optics of bent-core de Vries phase

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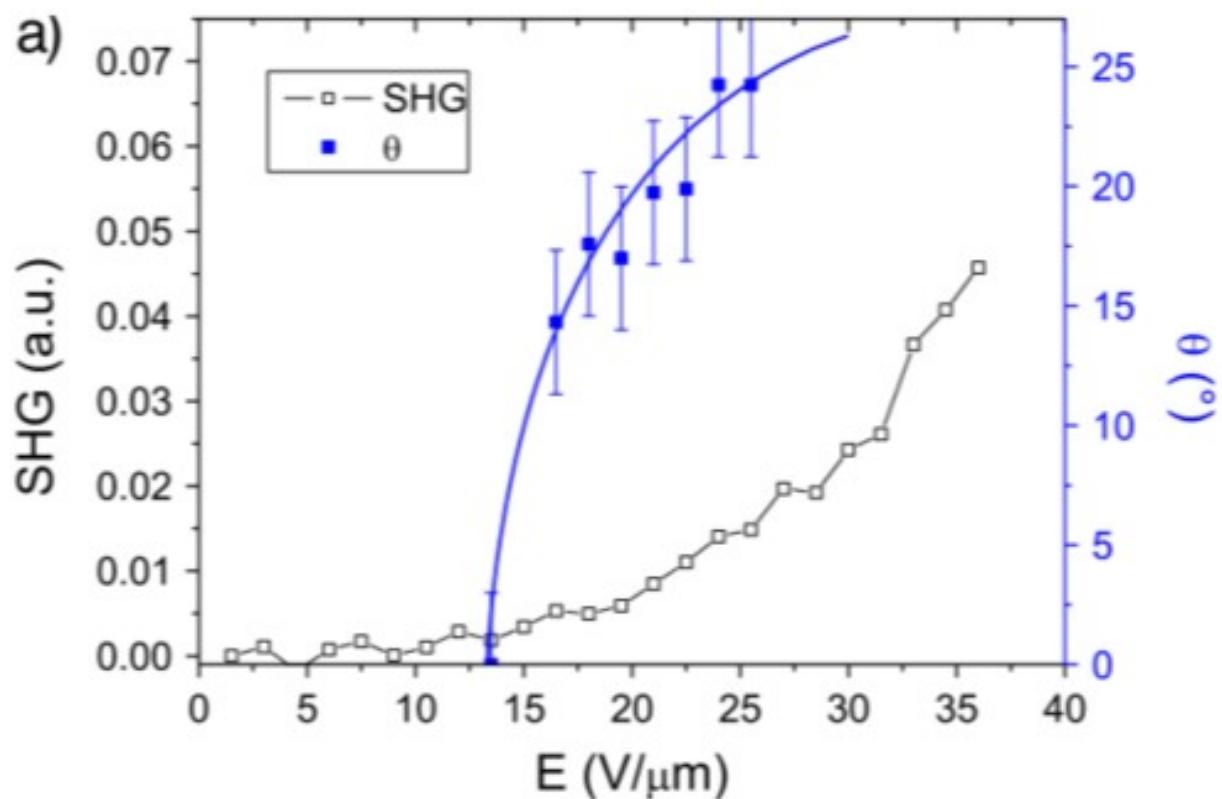


Figure 1.2: Experimental data for ‘hockey-stick’ compound studied by Eremin et al.[?] Note, the threshold for optical tilt. The lines guide the eye.

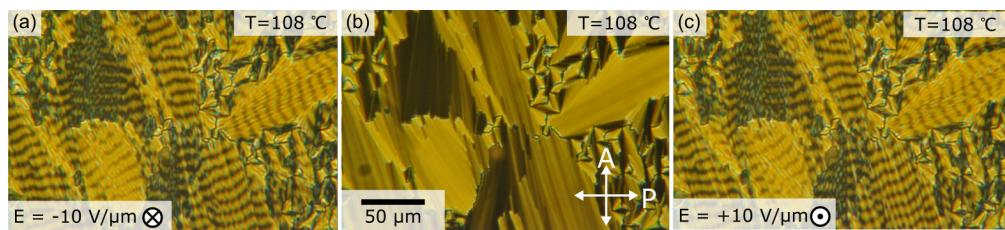


Figure 1.3:

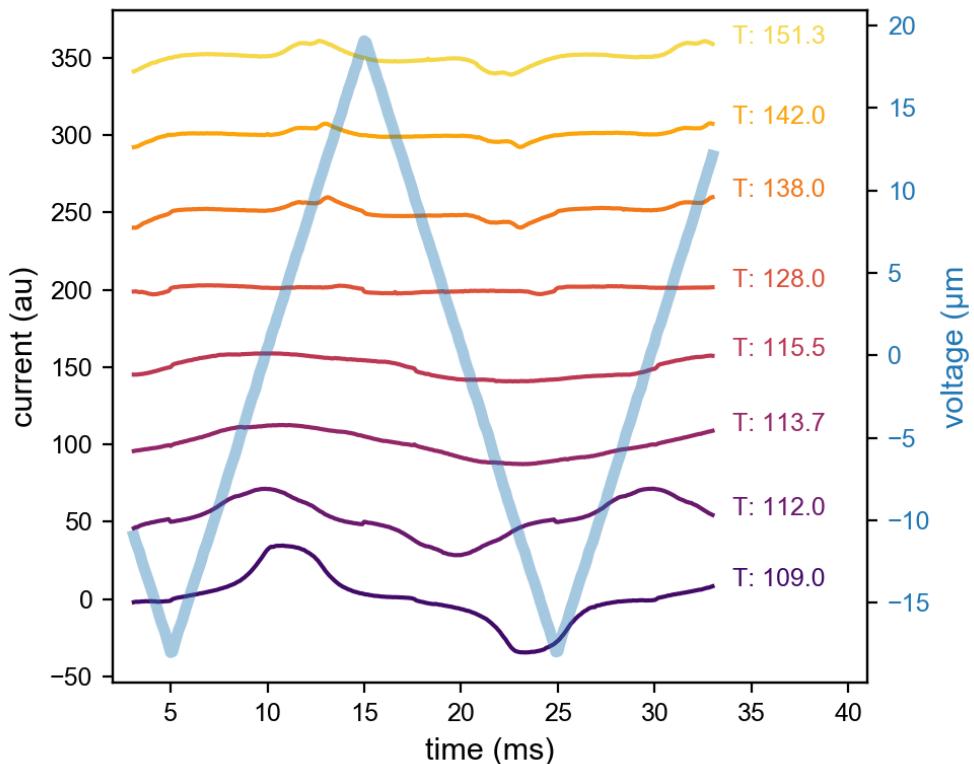


Figure 1.4:

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1.2.3 X-ray analysis of bent-core de Vries phase

1.3 Discussion for the bent-core de Vries phase

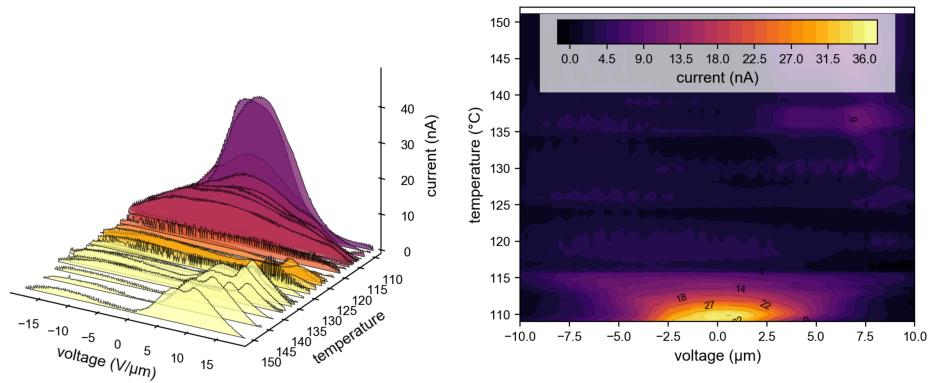


Figure 1.5:

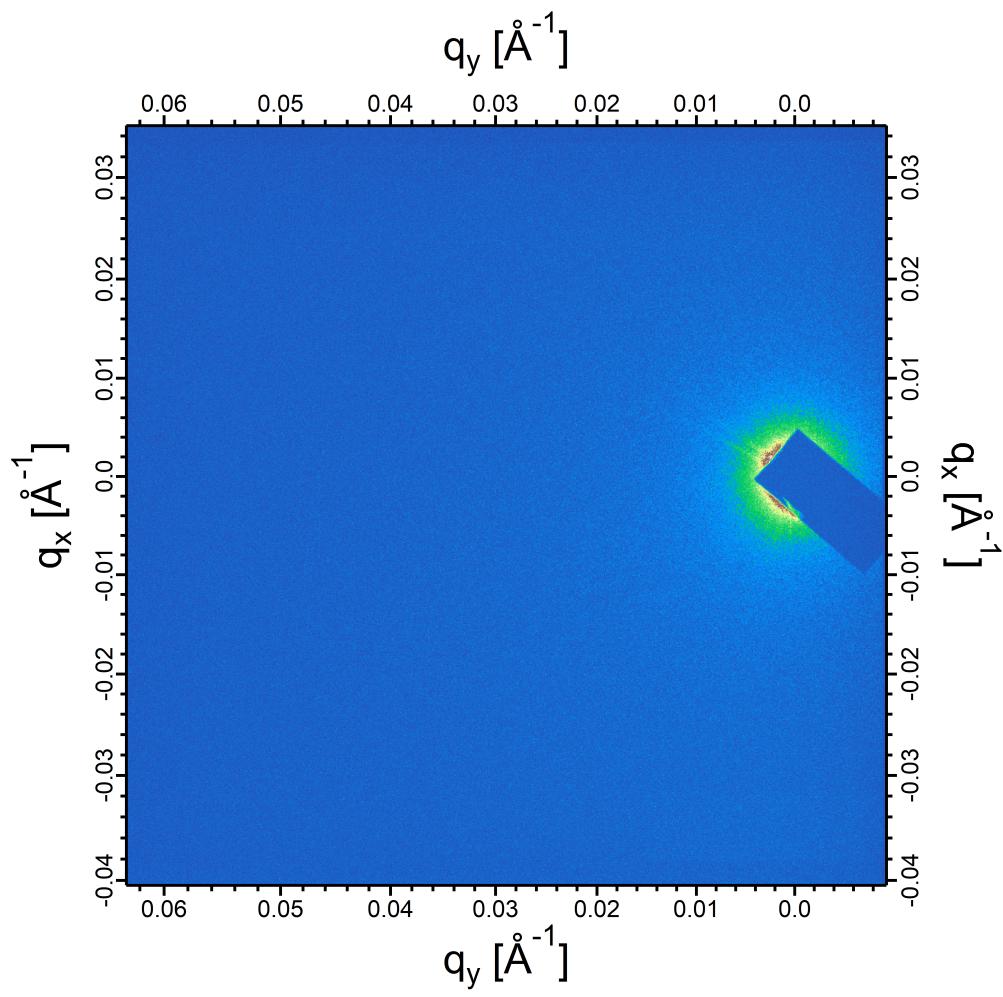


Figure 1.6:

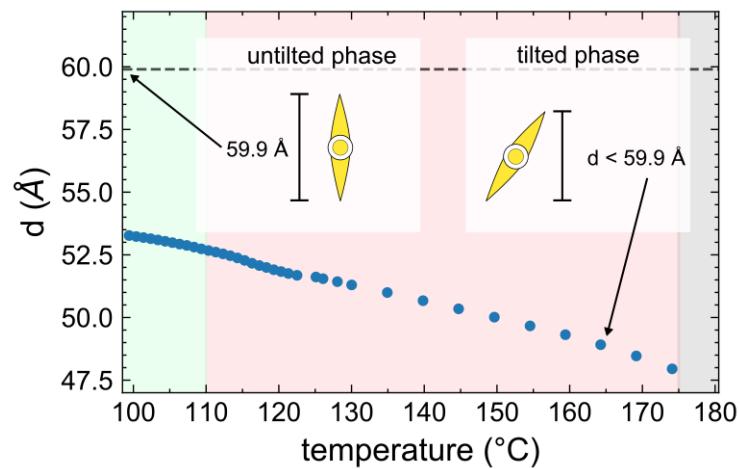


Figure 1.7:

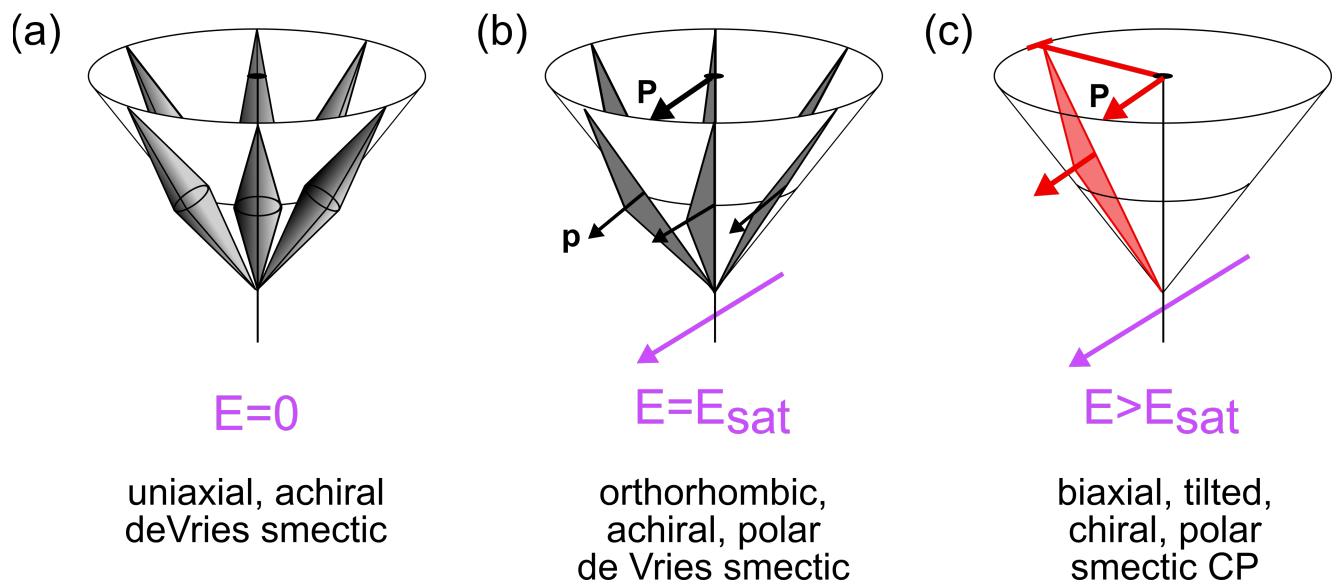


Figure 1.8: