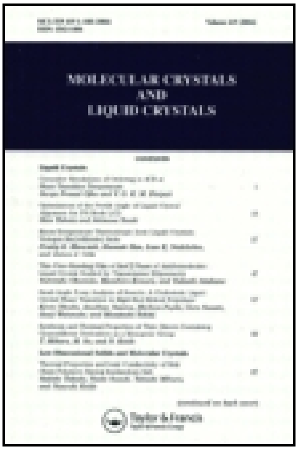

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Chirality, Chirality Transfer and the Chiroclinic Effect

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The overview of chiral levels and the chirality transfer between them. The phenomena associated with the chirality transfer found and/or theoretically predicted for achiral polar smectics are discussed. The chiroclinic effect is presented as an example in more details.

Keywords: chirality, chirality transfer, chiroclinic effect, polar smectics

1. INTRODUCTION

Chirality and chiral properties are the topic that has been attracted an attention of a number of scientists from various fields for more than a century [1–4]. However, the chiral symmetry of matter or shortly – the chirality – is still not completely understood. Besides the fundamental chirality in the subatomic level, the chiral properties can be found in the microscopic (molecular) level, mesoscopic (structural) level, and in the macroscopic (chiral objects) level. Chirality can be transferred within the same level or between the levels – from microscopic to macroscopic levels, and also vice versa – from macroscopic to microscopic levels. The phenomena share the same name – the chirality transfer, although they are very different in origin as well as in the consequences.

In this contribution the overview of the possible chirality transfers is presented, its relevance and application for polar smectics is discussed in more details and finally the prediction of the phenomenon which can be considered as an example of the chirality transfer within

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the microscopic level as well as to the mesoscopic level is described. If the nontilted but polarly ordered achiral smectic system is doped by chiral dopants, tilted structure should appear. The name *chiroclinic effect* was suggested for the phenomenon [5].

2. CHIRALITY AND CHIRALITY TRANSFER

The question of the chirality of life stimulated scientists for a long time. First definition of the chirality was given already in 1884 by lord Kelvin in his Baltimore lectures. He stated "I call any geometrical figure or group of points "chiral" and say it has "chirality", if its image in a plane mirror cannot be brought into coincidence with itself" [6].

If Kelvin's definition is applied to the molecules, than it is said that molecules are chiral. The simplest model chiral molecule is the carbon atom linked to four different groups (Fig. 1-below left). The model of such a molecule can be used as an educational tool for showing the essence of chirality [7]. When the model is placed in front of the mirror, it is clearly seen that there is no rotation of the model which would make the model seen exactly as the mirror image. Such a simple molecule can be considered as a rigid one and the model of the molecule is quite faithful. However, molecules which form liquid crystals are much larger and more complex. They appear in a number of different conformations which have exactly or almost exactly equal energies and therefore appear in the sample simultaneously. Most of these conformations are generally chiral. Even if material made of complex molecules is considered as achiral, a specific molecule is not achiral in a well defined moment in general. Conformations of opposite chiralities have equal probabilities and each molecule can adopt a number of different conformations within the time evolution. Considering the whole sample, the ensemble average is achiral as well as the time average for a single molecule is also achiral.

Organic crystals and liquid crystals form a huge variety of different complex structures. Although structures cannot be described in the same way as molecules, the chiral symmetry can be attributed to them. As the structure in liquid crystals is formed by many molecules, positions and orientations are described by the spatial variation of order parameters which are given as spatial dependent functions. The mirror tests for the chiral symmetries can be applied for these functions and the structure can be recognized as chiral or non-chiral and the sign of the structural chirality can be defined by definition. For example, helical arrangement (Fig. 1-above right) of the chiral nematic is obviously a chiral structure as it changes the handedness if the mirror symmetry operation is applied. The sign of the structural chirality is associated with the handedness of the helix and which handedness of the helix is considered as positive was a matter of definition.

Solid or liquid crystalline structures are formed due to interactions between molecules which are of van der Waals (attractive and steric), electrostatic, hydrogen bonding etc. origin. Each molecule can be described by the interacting field around itself and the field obviously reflects the symmetry of the molecule. Therefore interacting fields of chiral molecules also have chiral symmetry. When another chiral molecule is found in a chiral field, it often happens that it adopts the position and orientation which has chiral properties. In this way the chiral structure is formed of chiral molecules. It is called a chirality transfer from the molecular to the structural level and is very common in liquid crystals. Chiral molecules form helicoidally modulated chiral nematics, chiral blue phases, chiral TGB phases, helicoidally modulated phases in tilted polar smectics formed of rod-like molecules, tilted polar layers in bent-core systems and more. However, chiral molecules form also achiral structures like non-tilted SmA phase. Surprisingly, no predictions can be made in general from the chiral structure of the molecule to the chirality of the phase. There are many materials where the structural chirality even reverses handedness upon temperature changes and understanding of the origins of this behavior is still an open question [8,9].

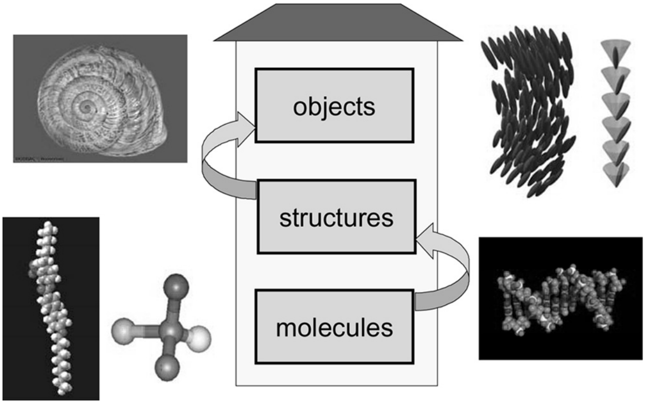

FIGURE 1 Chirality and the chirality transfer in the upward direction. Examples of molecular chirality and object chirality are given on the left and the structural chirality on the right (pictures are from various internet pages).

In the macroscopic world, objects of a natural origin are almost always chiral. Even "symmetric" smooth stones found in the river banks almost always reflect the rough asymmetric original shape. However, the chirality of the non-living nature is the property of the object and it appears without a preference for a single chirality. It is just the opposite for living species that are chiral in general. For example, slugs' houses are mostly of the same handedness (Fig. 1-above left). The spiral is mostly left handed. Exceptions are extremely rare and can be found in a few terrestrial slugs. The specimen which is a mirror image of normal specimens appears very rarely within the same sort. The slugs are only the most evident example due to the spiral shape of the house, however almost all the rest of living organisms are chiral, the man is chiral, the animals are chiral, many of plants are chiral . . . the mirror almost always shows the differences. The chirality associated with objects can be called macroscopic or object chirality.

When the structure which forms chiral objects is considered, it is very often chiral. Living species are formed by chiral DNA, which is hardly considered as a single molecule due to its size and complexity. The most evident chirality transfers from the structural to the object level are freeze fractures in liquid crystals. The fracture of the instantly frozen sample, which preserves the chiral structure of the sample is also chiral as an object.

Chirality transfer appears also within the same level. If complex achiral system is doped by chiral dopants, the chirality becomes often pronounced. The chiral dopant molecules and their chiral interaction field favor only one sort of chiral conformation of the complex host molecules and host molecules become chiral in temporal and ensemble average. The phenomenon is called intermolecular chirality transfer [10].

The chirality transfer within the structural level was found only recently [11,12]. If achiral molecules that have the ability to adopt chiral position and orientation are doped into the system with a chiral structure, they act like a chiral dopant.

Transfer within object can be observed everywhere. The simple example is the spiral staircase (Fig. 2-above right) which is obviously made by chiral stairs; another funny example is the water, which flows through the left or right handed fussili pasta [13] and the jet of water has an extended screw-like shape.

Chirality transfer is effective also in the opposite way, from the macroscopic level toward the microscopic one. When nematic liquid crystals with achiral structures are filled in special chiral cells they adopt the helicoidal modulation of the nematic structure with one sense only (Fig. 2-above left). Recent reports about doping of achiral

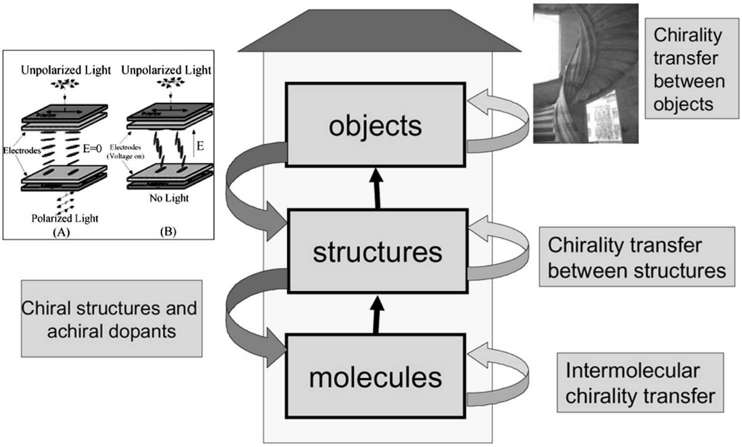

FIGURE 2 Chirality transfer within the level (right) and in the downward direction (left).

bent core molecules in chiral structures open the question if the effect of structure favors chiral conformations, which can be explained in chirality transfer from the structural to the molecular level [10].

There are many examples of the chirality and chirality transfers in the world around us. Materials that form polar smectic phases are extremely reach with respect to mentioned phenomena. Therefore, they are discussed in more details.

3. CHIRALITY IN POLAR SMECTICS

Tilted smectic liquid crystals of achiral rod-like molecules form achiral tilted structure. However, in 1974 Meyer predicted that tilted smectic liquid crystals made of chiral molecules should form polar layers. Synthesis and experimental results almost immediately confirmed his idea [14].

A closer look to the chiral tilted smectic structure shows that three vectors (layer normal, projection of the tilt onto the layer and polarization) form characteristic chiral structure of the layer. Although the polarity is the consequence of the tilt and molecular chirality, generally called piezoelectric effect, the structural chirality that can always be defined for three non-planar vectors, is also an essential property of chiral tilted smectic layers.

In addition, the tilt appears in chiral nontilted smectics when the electric field is applied. The polarization, which is induced by the electric field, induces also tilt. The phenomenon is called electroclinic effect.

However, polarization is a more general concept. The shape of the molecule can also reveal a geometric polarization, i. e. the shape which has the symmetry properties of the polarization. Some considerations have shown that even in non-polar molecules, the shape which reveals the geometric polarization is essential for the appearance of the tilt, making again a tilted smectic layer structurally chiral [15], although the chirality of the layer structure was recognized only later. Unfortunately the "geometric polar ordering" is hard to observe without a presence of the polarization, which has a component perpendicular to the tilt. But addition of such a dipole makes constituent molecules chiral.

Bent core polar smectics enable the formation of the polar layers without molecular chirality, which was a surprise, when these systems were reported for the first time [16]. Bent core molecules are a nice example of the geometric polarity, which is in addition associated with the polarization and enables the observation of the geometric dipole direction. The triad tilt, layer normal and polarization reveal structural chirality without a molecular chirality. As the molecular chirality is absent, domains are formed where both – left handed and right handed triad are present.

Finally, chirality transfer in tilted smectics is a basis for the control of the magnitude of the polarization and other chiral properties as the helicoidal modulations at mesoscopic level with consequent macroscopic properties like optical rotatory power or selective reflection. Chiral dopant is added to the achiral tilted smectic in very low concentrations. The intermolecular chirality transfer induces the imbalance in chiral conformations of host molecules which results in induced polarization and other consequences of molecular chirality to the mesoscopic structure. As the effect is linear for very low dopant concentrations, it allows for the fine tuning of desirable macroscopic properties [10].

4. CHIROCLINIC EFFECT

As mentioned in the previous section, the triad found in smectics layer normal, tilt (clinicity) and polarity reveals the chirality of the layer. Chirality transfer present in chiral molecular systems therefore assures two situations (Fig. 3):

chirality + clinicity → polarity *piezoelectric effect*
and
chirality + polarity → clinicity *electroclinic effect*.

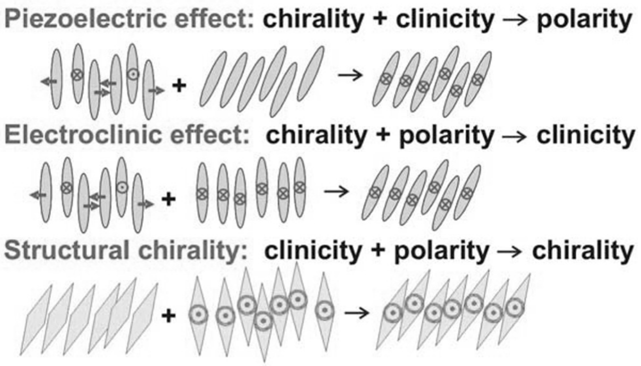

FIGURE 3 Schematic presentation of experimentally observed relations within the triad: polarity, clinicity and chirality.

In achiral bent core systems smectic layers where polarization and tilt appear simultaneously form chiral smectic layers. Therefore:

clinicity + polarity → chirality *structural chirality*.

The symmetry of the relation between the three properties allows for the prediction of another phenomenon. The bent core molecules can form polarly ordered but non-tilted structures. If to such a material chirality is added by a chiral dopant, the chirality transfer to the structural level should stimulate that polarly ordered smectic layers become tilted (Fig. 4). Because instead of the polarization induced by the electric field in chiral sample – the electroclinic effect – here the chirality is induced in polar sample by a chiral dopant chiral field – the phenomenon is called the *chiroclinic effect*. Three main phenomena could be observed

- For the anticlinically tilted achiral antiferroelectric structure where oppositely chiral domains exist, domains of a single chirality will prevail, if the system is doped. The same would be valid for the synclinically tilted ferroelectric structure, which are extremely rare.
- For the non-tilted but polarly ordered phase, the anticlinic antiferroelectric or synclinic ferroelectric (depending of the material) would be induced upon chiral doping
- In doped synclinic antiferroelectrically ordered or anticlinic ferroelectrically ordered structures or structures of the same symmetry that consist of chiral molecules, tilts and polarization in neighboring layers would differ.

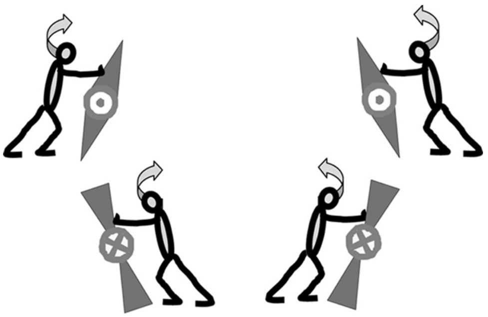

FIGURE 4 Chiral dopant molecules (left handed chiral daemons – left, and right handed – right) induce chiral structure of one handedness via chirality transfer form the molecular (dopant) to the structural level.

In order to estimate these phenomena, the free energy of a doped system has to be considered.

$$G = \sum_j \frac{1}{2}\, a_{0P}\, P_j^2 + \frac{1}{4}\, b_{0P}\, P_j^4 + \frac{1}{2}\, a_{0t}\, \xi_j^2 + \frac{1}{4}\, b_{0t}\, \xi_j^4 + \frac{1}{2}\, \Omega_0\, (\xi_j \times \bar{P}_j)_z^2 + \frac{1}{2} a_{1P} (\bar{P}_j \cdot \bar{P}_{j+1}) + \frac{1}{2}\, a_{1t}\, (\xi_j \cdot \xi_{j+1})_j + h_0 (\xi_j \times \bar{P}_j)_z \tag{1}$$

Here the first two terms with the temperature dependent a_{0P} give rise for the stabilization of the polarly ordered but nontilted phase. The parameter a_{1P} defines the relative orientation of polarizations in neighboring layers, antiferroelectric for the positive a_{1P} and ferroelectric for the negative a_{1P}. The second two terms in the first line of the equation (1) give rise for the stabilization of the tilt. For a typical bent core system that has only one stable phase, the temperature dependence of a_{0t} is not pronounced, but for systems where the tilt appears at higher temperatures than polarization, its temperature dependence is essential [17]. Similarly as for the relative polar ordering in neighboring layers, for positive a_{1t} anticlinic tilt order is stabilized and for negative a_{1P} synclinic tilt order is favored. The negative Ω_0 favors perpendicular orientation of the tilt with respect to the polarization and the polarization can have two opposite direction with respect to the tilt. The last term with h_0 is the consequence of the chiral field of chiral dopant molecules. It favors only one orientation of the polarization with respect to the tilt or vice versa. From the dopant molecular structure is not possible to account for the sign of h_0 at present. However, the oppositely handed dopant molecules favor opposite relative orientations of the polarization with respect to the tilt.

Minimization of the free energy leads to the theoretical confirmation of the three statements quoted before.

- The free energy of the oppositely tilted domains with respect to the polarizations differ energetically for approximately

$$2h_0\,\theta_0 P_0, \tag{2}$$

  where θ_0 is the magnitude of the tilt and P_0 the magnitude of the polarization in the non-doped sample.
- The magnitude of the induced tilt upon doping in the polarly ordered and non-tilted phase is proportional to the magnitude of the polarization and the chiral phenomenological field.

$$\delta\theta = h_0\,\frac{P_0}{a_{0t} - a_{1t} + \Omega_0\,P_0^2} \tag{3}$$

  Close to the transition temperature the approximation from the equation (3) is not valid anymore and minimization equations have to be solved simultaneously (Fig. 5).
- Magnitudes of the tilt and the polarization differ if the structural layer chirality alternates. Therefore in doped synclinic antiferroelectric and anticlinic ferroelectric structures the magnitudes of the tilt and the polarization are modulated.

$$\begin{aligned}\delta\theta &= \pm|h_0|\left(\frac{B}{AB - C^2}\right)P_0\\ \delta P &= \pm|h_0|\left(\frac{A}{AB - C^2}\right)\theta_0\end{aligned} \tag{4}$$

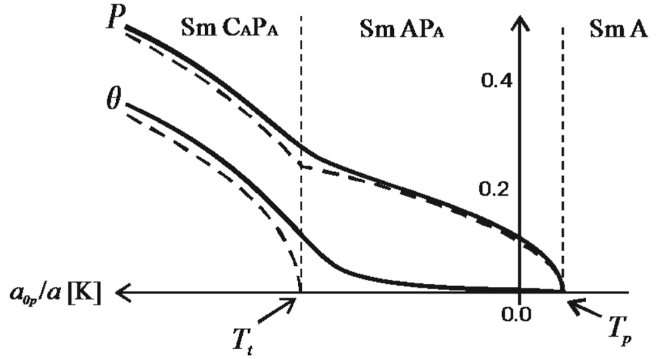

FIGURE 5 Theoretical prediction of the tilt and polarization temperature dependence in the non-doped sample (dashed line) and the doped sample (solid line).

where

$$\begin{aligned} A &= (a_{0p} - a_{1p}) + 3b_{0p}\, P_0^2 + \Omega_0\, \theta_0^2; \\ B &= (a_{0t} - a_{1t}) + 3b_{0t}\, \theta_0^2 + \Omega_0\, P_0^2; \\ C &= -h_0 + 2\Omega_0 P_0\, \theta_0. \end{aligned} \tag{5}$$

Unfortunately, except the first theoretical conclusion (2) which was experimentally observed almost immediately after discovery of bent core systems, for the pronounced effects materials which would enable observations do not exist yet. To observe the tilt induction, the material with a continuous transition from the non-tilted to the tilted polarly ordered phase would be necessary. However, to my best knowledge its observation was not reported yet. The precise observation of the tilt and amplitude modulation in the doped but still stable synclinic antiferroelectric phase by the x-ray measurements has not been performed yet.

5. CONCLUSIONS

The paper present an overview of the chirality with respect to levels of the chirality and the chirality transfer within levels and between levels. A special emphasis is given to the general concept of chirality levels and transfer typical for polar smectics. Finally, a recent example of the chirality transfer within the molecular level or from the molecular to the structural level is presented. The chiroclinic effect is the name where the smectic system with an existing polar order becomes tilted upon doping with a chiral dopant. The phenomenon is similar to the electroclinic effect; however the field which induces tilt is the chiral field of dopant molecules. The phenomenon is also used for a long known phenomenon, where the tilted smectic structure formed of achiral rod-like molecules becomes polar and helicoidally modulated upon doping with a chiral dopant. This old phenomenon can be in analogy with tilting effect called *chiropolar effect* [18].

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