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Impact of Surface Symmetry on Growth-Induced Properties

Claire Gervais and Jürg Hulliger*

Department of Chemistry and Biochemistry, University of Berne, Freiestrasse 3, 3014 Berne, Switzerland

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ABSTRACT: The influence of surface symmetries on growth-induced physical properties is studied. Three processes for which this impact is particularly significant are reviewed: (i) adsorption of chiral molecules on solid substrates, (ii) symmetry reduction due to adsorption of impurities during growth, and (iii) self-poisoning during growth. It is shown that surface symmetries may propagate to the entire growth sector, leading in case of (ii) and (iii) to a crystal composed of domains with different chemical compositions and physical properties. As an example, growth-induced pyroelectricity due to self-poisoning is systematically studied for the most representative faces of the 32 point groups. It shows that the knowledge of surface symmetries may help in the control and design of growth-induced properties. Finally, necessary steps toward the qualitative and quantitative prediction of growth-induced properties are proposed.

C'est la dissymétrie qui crée le phénomène.¹

Pierre Curie, 1894

1. Introduction

Although the term symmetry was already employed before the 19th century to designate something elegant and well-proportioned,^{2,3} its modern definition (a recurrence of the same pattern by a mathematical operation) was first used by Haüy in 1815 to analyze and classify crystals according to their geometry.⁴ In the 1830s, the idea that crystal symmetry influences the symmetry of the physical properties found its concrete expression in Neumann's principle, which states that *the symmetry elements of any physical property of a crystal must include all the symmetry elements of the point group of the crystal*. This statement, further generalized by Curie, is at the basis of every investigation of physical properties of crystals.^{5–7}

A few decades ago, the design of molecular materials with specific physical properties, also known as crystal or supramolecular engineering, became a subject of predilection for chemists.⁸ In particular, attention focused on the search for structures with polar or chiral properties because of evident applications in optics and pharmaceuticals.^{9,10} Several directions of research developed for that purpose: (i) modifying chemically the molecular building blocks in the hope they will pack in the desired architecture,¹¹ (ii) using tailor-made additives,¹² (iii) epitaxial growth of molecular systems on metal or inorganic surfaces.¹³ While (i) is devoted to the design of new architectures

exhibiting intended properties, (ii) and (iii) aim mainly at modifying the structure by acting during nucleation and growth at the surface of a crystal. In this respect, processes and phenomena taking place at the interface between a crystal and its environment are decisive. Consequently, symmetry-breaking at the surface and growth sectoring are often claimed to explain the appearance or the modification of bulk properties. For comprehensive reviews, see refs 12–14. However, almost no literature deals with a systematic study of the possible expressions of physical properties according to surface symmetry.

In this paper, we show that many aspects of surface phenomena can be understood by adopting a crystallographic point of view. In section 2, we review the literature dealing with the various ways surfaces play a role in growth-induced properties. Three main topics are addressed: deposition of chiral molecules on solid substrates, inclusion of impurities on crystal surfaces, and self-poisoning during crystal growth. In particular, we will address the question whether surface symmetry may be at the origin of growth-induced properties. In Section 3, this issue is further investigated by a case study, namely, growth-induced polarity formation: It has been observed that crystals of dipolar molecules, although determined as being centric by X-ray diffraction, showed significant nonlinear optical or pyroelectric effects.¹⁵ This phenomenon seems to be in contradiction with Neumann's principle (polar properties do not exist for a centric crystal). However, this paradox vanishes if considering symmetry on the surface.^{16,17} After a short paragraph dedicated to the relationship between surface and bulk symmetry, typical examples of the influence of symmetry on polarity formation will be presented. In Section 4, we generalize findings obtained for polarity to other growth-induced properties. It is

* To whom correspondence should be addressed. E-mail: publication.hulliger@iac.unibe.ch.

Table 1. Examples of Growth-Induced Properties^a

type	phenomenon	property	refs
A	heterogeneous catalysis	chirality	28–31, 76–90, review 13
		chirality	42, 91
	biomineralization	piezoelectricity	92, 93
		morphology	23, 94–96
B	inclusion of impurities, tailor-made additives, solid solution	optical anomalies	35, 53, 75, review 14, 19, 97
		chirality	35, 40–42, 55, 56, review 24
		cleavage	98
		morphology	18, 43, 52, 99–102
		polarity	44
		magnetism	46
		(polymorphism) ^b	47–50
C	orientational disorder, self-poisoning	morphology	60–64
		polarity	15, 25, 65, 74
		(polymorphism) ^b	26

^a For the classification in types A, B, C (see text). ^b The adsorption of an impurity during nucleation or self-poisoning leading to the crystallization of another polymorphic form are beyond the scope of this paper. They are noted here for information only.

shown that surface symmetry does not always reflect the symmetry of a growth sector. However, its study allows us to get a preliminary idea about the potentiality of a given growth sector to generate physical properties that are not allowed by an attributed symmetry of the bulk. A comprehensive understanding of mechanisms leading to growth-induced properties requires the elucidation of complex processes taking place during crystal growth, such as intrasectoral zoning.^{18,19} Finally, possible steps toward a prediction of growth-induced properties are proposed. In particular, the calculation of binding energies and their use in a stochastic growth model may be a feasible approach toward a quantitative prediction.

2. Growth-Induced Properties

2.1. Definition. By growth-induced properties, we understand “those arising from crystal growth”. One might argue that every physical property given by the crystal packing should be considered as growth-induced. Some exceptions may however be mentioned: If thermal bulk equilibration is effective enough, the thermalized crystal may exhibit physical properties independent of growth conditions. Typical examples are dislocations producing a stress. Growth-induced stress can result in a pseudo-piezoelectric effect, which may relax by thermal treatment. Similarly, growth-induced magnetism or optical birefringence vanished when annealing crystals.^{20–22}

Table 1 presents typical examples of growth-induced properties found in the literature. According to the number of chemical components involved or the type of growth (epitaxy or bulk growth), they may be ordered into three main classes.

A. Epitaxial Growth. Understanding the epitaxial growth of molecules on substrates is a subject of interest for research involving heterogeneous catalysis. Recognition of chirality by a substrate is of particular interest because of potential applications in the synthesis of enantiomerically pure compounds.¹³ In biomineralization, molecular recognition at the interface between inorganic materials and macromolecules is responsible for the shape of bones and shells.²³

B. Inclusion of Impurities. Inclusion of impurities in the lattice and formation of solid solutions are responsible for the modification of many growth-induced properties. Sometimes consciously employed for designing a specific property, impurity inclusion is an excellent way to generate physical phenomena during crystal growth.^{14,24}

C. Self-Poisoning. Properties may also be modified by the main component itself. Defects are created by misorientation of molecules or by conformational modifications. It leads sometimes to drastic changes such as the recurrent appearance

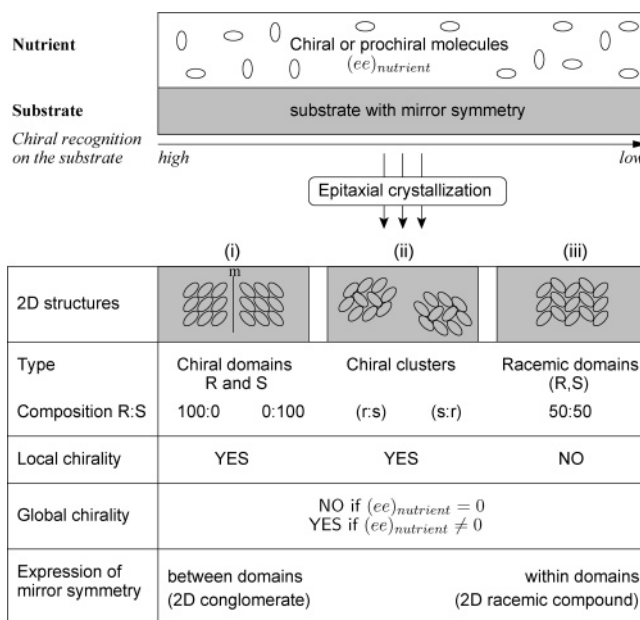


Figure 1. Two-dimensional structures (i–iii) formed by the adsorption of molecules on a substrate with mirror symmetry. $(ee)_{\text{nutrient}}$: enantiomeric excess of the nutrient. Depending on the chiral recognition ability of the substrate, local chirality may be observed in the adlayers. However, the mirror symmetry of the substrate prevents any enantioselectivity, that is, global chirality may arise only from a nutrient itself enantiomerically enriched.

of a metastable phase or the appearance of properties, which are not symmetry-allowed in a perfect crystal.^{25,26}

Hereafter, we focus on three representative examples of types A, B, and C, for which surface symmetry plays a significant role in the modification or appearance of growth-induced properties.

2.2. Deposition of Chiral Molecules on Crystalline Substrates. Literature shows a flourishing number of different cases, which is worth summarizing schematically: Figure 1, partially inspired from the comprehensive review of Barlow and Raval on metal surfaces,¹³ has been modified for our purposes, i.e., to highlight the influence of a mirror-symmetry on the expression of chirality at the surface. Here, mirror-surfaces designate surfaces possessing a mirror symmetry; surfaces without a mirror are said to be chiral.

The adsorption of chiral molecules (provided as a racemic mixture) on a mirror-surface may lead to three different assemblies (i–iii).^{27,28} Their occurrence depends on the chiral

recognition of the surface, i.e., the ability of local parts at the surface to recognize enantiomers R and S as distinct molecules (Note: hereafter, we use R and S for denoting enantiomers, but (D, L), and (d, l) pairs of enantiomers are evidently also concerned): (i) A high chiral recognition may give rise to the nucleation of R and S separately, leading to mirror-related chiral domains (local chirality). The mirror symmetry of the substrate has as a consequence the same amount of R and S nucleation sites randomly distributed across the surface, so that if the nutrient shows no enantiomeric excess ($ee_{\text{nutrient}} = 0$), global chirality remains zero. This is the most frequently observed type.¹³ (ii) Punctual assemblies composed of a constant ratio (r:s) of R and S molecules may form on the substrate. Clusters are enantiomerically enriched in one enantiomer giving rise to local chirality. However, if $ee_{\text{nutrient}} = 0$, an equal amount of clusters with reverse chirality (ratios (r:s) and (s:r), see Figure 1) are formed and global chirality is zero. For instance, the adsorption of the prochiral molecule nitronaphtalene on the face (111) of gold leads to randomly distributed chiral clusters composed of a constant ratio 8:2 or 2:8 of "R" and "S" surface-molecule complexes.²⁸ (iii) In case of a poor chiral recognition of the substrate, two-dimensional (2D) racemic domains may form. Here, the two enantiomers are related molecule-wise by a mirror symmetry, so that neither local nor global chirality can be expressed.²⁹

In summary, a mirror-surface may be locally enantioselective (e.g., the presence of pro-chiral *Re* and *Si* kinks), allowing the formation of chiral assemblies. However, the mirror symmetry at the surface prevents a general enantioselectivity, so that global chirality may appear at the surface only if the nutrient is already enantiomerically enriched (i.e., $ee_{\text{nutrient}} \neq 0$). In that case, it is likely that several patterns concomitantly develop at the surface,²⁷ to accommodate the unequal amount of both enantiomers. The extreme case of the adsorption of a pure enantiomer ($ee_{\text{nutrient}} = 1$) leads obviously to global chirality because the mirror symmetry cannot be expressed anymore by the chiral layer.

Aside from symmetry considerations, the reasons for the preferential appearance of one type of assembly or another remain poorly understood and need certainly a thorough investigation of the "anatomy" of the surface. Sholl³⁰ and Ahmadi³¹ performed density functional theory (DFT) calculations of binding energies between chiral molecules and chiral surfaces of platinum. They suggested that enantioselectivity is dependent on the number of interactions between the molecule and the kink sites present at the surface.³² As such, the density of kinks at the surface and the size of the adsorbed molecules are probably determinant for the enantioselectivity of the chiral substrates, as well as for the chiral recognition of mirror-surfaces discussed here.

Another interesting issue worth noting here is the relationships between the three types (i–iii) discussed above in two dimensions and the three-dimensional (3D) condensed phases observed in binary systems of enantiomers.³³ Namely, (i) corresponds to a 2D conglomerate, (ii) may be related to the formation of an intermediate compound between the two enantiomers, while (iii) is a 2D racemic compound. It is interesting to notice that contrary to the 3D space in which racemic mixtures crystallize preferentially as racemic compounds, the reverse is found in two-dimensions: In most of known examples, chiral molecules show a strong tendency to adsorb on a surface in a conglomerate way. The reduced set of symmetry elements available to achieve compact 2D packings compared to 3D could explain this behavior.³⁴

Although not the subject of this paper, reviews focusing on these two themes (i.e., topology of the surface and comparison

of symmetry elements available for 2D and 3D systems) would certainly be beneficial to the scientific community interested in chirality and chiral recognition.

2.3. Selective Inclusion of Impurities on Crystal Surfaces.

The observation that impurities adsorb preferentially on certain faces and modify the crystal habit is not new (see refs 35 and 36 and the comprehensive historical review on dye inclusion in ref 14). However, the question of how impurities may affect crystal growth processes has seen a revival in the last few decades, where the conjoint application of sophisticated microscopic and X-ray diffraction methods assisted by molecular modeling tools allows further inspection of mechanisms of impurity adsorption. The modification of growth-induced properties by impurities is an issue that is seen to be decisive in a multitude of different research fields, such as the interpretation of the growth history of minerals,^{18,37–39} the understanding of the origin of chirality in biological materials,^{24,40–42} and the design of materials with desired properties.^{12,43,44}

The basic explanation for a modification of properties is the reduction of crystal symmetry engendered by the anisotropic inclusion of impurities on different faces.¹² The terms growth dissymmetrization, tangential selectivity, and growth ordering of atoms are also employed, particularly for atomic solid solutions.^{19,45,46} It is worth emphasizing here that symmetry which is relating two sites might be broken either by a fundamental change of the geometry of the sites (i.e., coordinates of molecules are not related anymore by the symmetry operator) or by a difference of chemical composition between the two sites. Compositional variation may induce a change in the topology of sites, although it is not always the case. Think for instance about the replacement of a chlorinated component by its bromine relative: In this case, we would state that symmetry is conserved in a crystal domain if the *average* composition and the geometry of the sites over this domain are preserved. Most of the cases presented here deal with a variation of chemical composition, whereas the geometry of the sites remains more or less the same. Severe structural modifications induced by the adsorption of impurities (stabilization of polymorphic forms^{26,47,48} or formation of solid solutions showing a different crystal packing^{49,50}) are included in Table 1 for information but are not discussed in detail.

Heterogeneity in chemical composition is mainly encountered at two levels: among the growth sectors and among the different sites present at the surface of a growth sector.

A. Growth Sectoring. During the growth of a crystal, guest molecules present in the nutrient are confronted with growing faces, each possessing a different surface topology. As such, the affinity between the impurity molecule and the surface varies with the face. This can lead to a heterogeneous distribution of guests in the different growth sectors. Figure 2 exemplifies this experimentally well-known effect for a crystal in point group $2/m$, with a habit composed of the two families of faces $\{100\}$ and $\{011\}$. Growth sectors $\{100\}$ and $\{011\}$ may present drastic differences in their host:guest composition. However, within a family of faces, the different growth sectors are still related by the point group symmetries of the crystal and thus should in principle show on average identical compositions.

B. Anisotropic Adsorption within a Growth Sector. The second type of heterogeneity takes place at the surface of a growth sector and is responsible for the observed reduction of the growth sector internal symmetry. In that case, symmetry of the surface plays a preponderant role. Figure 3 shows a surface with no symmetry (i.e., symmetry 1) of a growing sector belonging to a crystal in point group $2/m$. Here, the four sites

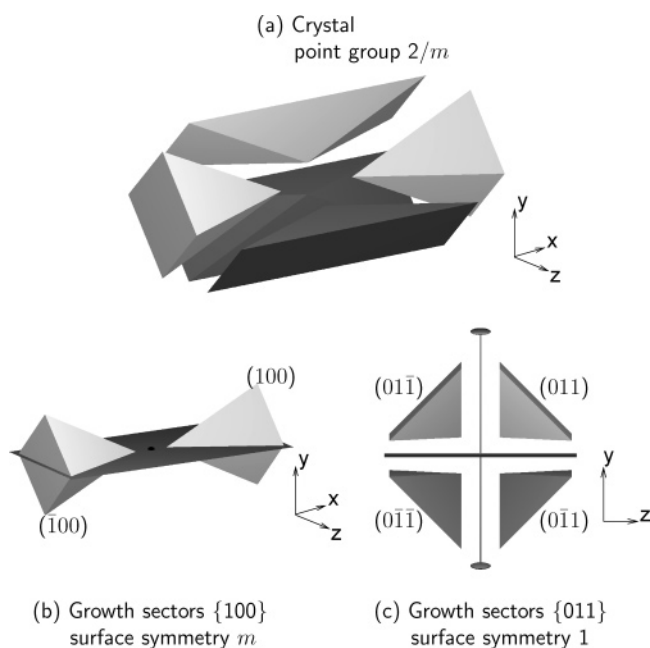


Figure 2. (a) Decomposition of a crystal with point group $2/m$ in growth sectors developing faces $\{100\}$ and $\{011\}$ (for clarity, the growth sector (011) on top is not shown here). (b) Growth sectors (100) and $(\bar{1}00)$ are related by a center of symmetry and are showing a mirror-surface. (c) The four growth sectors $\{011\}$ are related by the two-fold axis, the mirror and the center of symmetry. These sectors present no symmetry at their surfaces. As a result of this, a $2/m$ crystal presents two totally different faces to molecules which might be included in different amounts with respect to sectors $\{100\}$ and $\{011\}$.

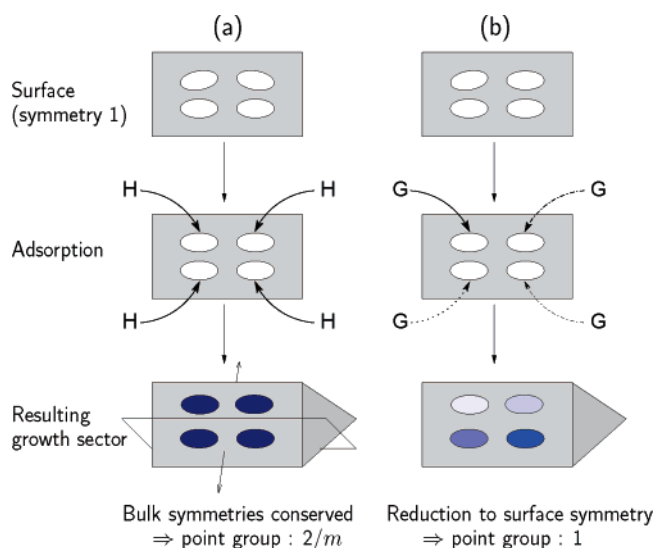


Figure 3. General principle of symmetry reduction. The surface of the growth sector has symmetry 1. The crystal is in point group $2/m$. Four independent sites assumed at the surface are described by ellipsoids. H: host molecule, G: guest molecule. Probabilities of adsorption of molecules are indicated by arrows (identical arrows denote identical probabilities). For resulting growth sectors, different blue colors indicate different chemical compositions. (a) Growth of a chemically pure crystal. (b) General case of the growth of an impure crystal or a solid solution.

symmetry-related in the bulk by the two-fold screw axis, the glide plane, and the center of symmetry, respectively, are symmetry-independent at the surface. In the absence of an impurity (Figure 3a), only host molecules H adsorb on the four independent sites. While the adsorption rate may be different, the final compositions of the four sites are obviously the same.

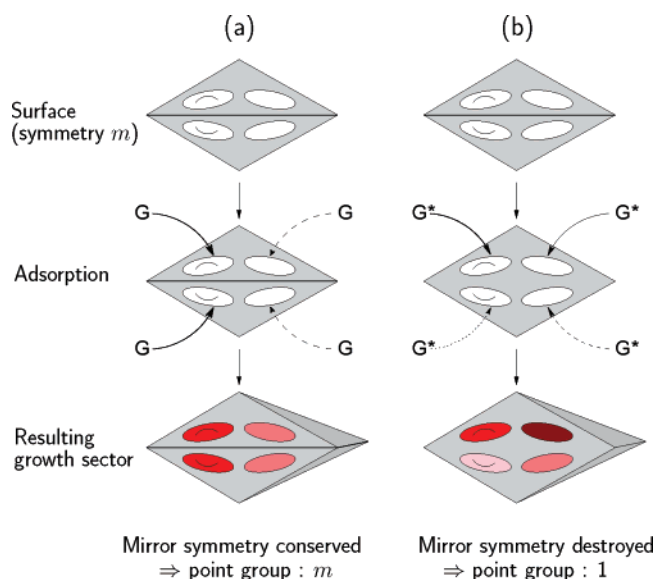


Figure 4. The symmetry of the growth sector may be lower than that of the surface. The surface of the growth sector has symmetry m . The crystal is in point group $2/m$. Two independent pairs of sites assumed at the surface are described by ellipsoids with or without a symbol inside. Within each pair, sites are related by a mirror symmetry. Probabilities of adsorption of guest molecules are indicated by arrows (identical arrows denote identical probabilities). For resulting growth sectors, different red colors indicate different chemical compositions. (a) Adsorption of an achiral guest molecule G or a racemic mixture of two enantiomers. (b) Symmetry reduction due to the adsorption of the pure enantiomer of a chiral guest molecule G^* . In that case, a further symmetry lowering is observed because improper symmetries are destroyed.

This leads to a conservation of the point group symmetries in the sector. However, for an adsorbing impurity G, there are four different possibilities of binding, each with a probability directly related to the affinity between the guest and the site (Figure 3b). As such, the four sites may accommodate a different amount of guest molecules, leading to an inhomogeneous composition for the bulk of the grown sector. In that case, the symmetry of the resulting growth sector reflects the symmetry of its surface. [Note: partial symmetry reduction may arise if the sites present similar binding energies. For instance, consider in Figure 3b that the guest molecules adsorb identically on the two left and right sites, respectively. In that case, the left (respectively, right) composition ratios are closely equivalent. The symmetry relating left and right (two-fold axis) is destroyed, but the mirror plane is conserved for the growth sector. However, it should be stressed that partial symmetry reduction is likely to be fortuitous, as it would require similar binding energies on sites presenting different topologies.]

The present example has shown that symmetry of a growth sector can be reduced to the symmetry of the surface. We may ask: Can symmetry be lower as that found on the surface of the growth sector? This question is illustrated in Figure 4, where a mirror-surface is considered. Two independent pairs of sites (white ellipsoids with or without a symbol inside) coexist at the surface. Each pair is composed of two sites related by a mirror symmetry. While the type, number, and strength of interactions taking place between a guest and the surface is equivalent at two mirror-related sites, their topological arrangement is mirror-reversed. In other words, even though not chiral themselves, the sites have a pro-chiral character. Consequently, the adsorption of an enantiomorphous guest may lead to the disappearance of the mirror symmetry (Figure 4b). More

generally, improper symmetries of the surface are destroyed, and the resulting growth sector belongs to an enantiomorphous subgroup of the surface point group. However, this further symmetry reduction is not possible for non-chiral guest molecules (Figure 4a) or when the racemic mixture of a chiral impurity is adsorbed.

Experimental evidence for symmetry reduction in growth sectors has been reported many times: (i) The modification of growth-induced properties which are determined by symmetry of the crystal may be a clue for symmetry reduction in growth sectors. Such properties are for instance chirality (enantiomeric distribution of (R,S) additives in a centrosymmetric crystal⁵¹), nonlinear optical effects (second harmonic generation (SHG) in centrosymmetric crystals⁴⁴), or optical properties (anomalous birefringence in cubic crystals^{52,53}). (ii) A direct confirmation of symmetry reduction consists of measuring the space group of each individual growth sectors by X-ray or neutron diffraction.^{52,54–56} However, the appropriate space group may be difficult to assign, especially when the deviation from the original point group symmetry is small. In such a case, optical microscopy may be more adequate because it is more sensitive to symmetry reduction.^{45,57–59}

2.4. Self-Poisoning and Orientational Disorder on Crystal Surfaces. If we take the definition for an impurity in its broader sense, i.e., “a contamination of a pure crystal”, then one can imagine that the crystallizing component itself may act as an impurity, when docking at the surface with a different conformation or orientation. Earliest examples of self-poisoning concerned low-weight polymer crystals.^{60–62} According to the temperature and concentration, long-chain molecules adsorbing on a growing face adopt several folding structures, which perturb the crystallization process. This conformational flexibility during docking is deemed to be responsible for the unusual crystallization rate and the morphology disparity found in *n*-alkane systems. In the same vein, the modification of morphology induced by a self-poisoning phenomenon is found for a broad range of compounds, going from proteins⁶³ to small organic molecules.⁶⁴ The mechanism involves the docking of improperly oriented molecules. Like any other impurity, they may act as growth inhibitors, inducing pronounced variations in the morphology. In extreme cases, self-poisoning impurities may inhibit the nucleation and the growth of one polymorphic form, favoring the crystallization of another one.²⁶

Self-poisoning may also affect properties other than morphology: Crystals of long-prolate dipolar molecules were found to show polar properties even though X-ray diffraction assigned a centric structure.¹⁶ On a growing face, a non-negligible probability that molecules dock with a 180° misorientation leads to ratios of good vs misoriented molecules that vary with the docking site (Figure 5). The main consequence is a disappearance of the center of symmetry and the appearance of polar effects in the growth sector.²⁵

It is important to stress here that the obtained polar structure is metastable; the equilibrium phase is allowed to be centric. Indeed, if molecules are allowed to relax in the bulk, then the final structure contains disorder but equally distributed among the sites. This bulk disorder should not be confused with the growth-induced disorder. However, the transition from the metastable state to the centric relaxed structure requires the 180° flipping of the molecules in the bulk. For long-prolate dipolar molecules as those experimentally investigated, this process needs a considerable amount of energy so that crystal equilibration and thus disappearance of growth-induced polarity is likely to be extremely slow.

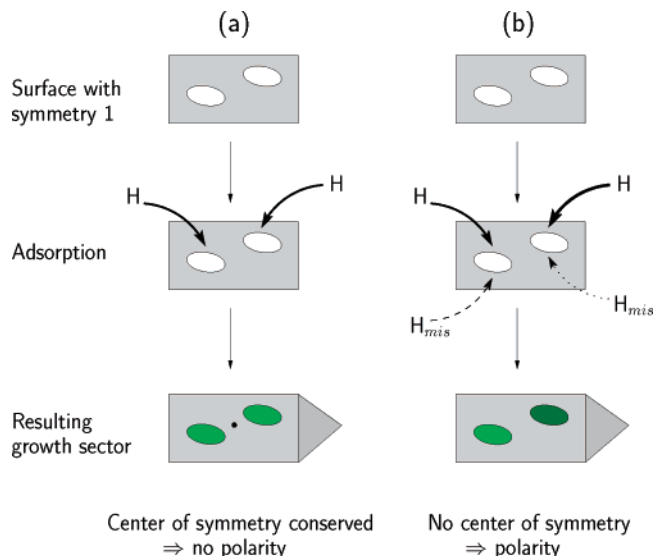


Figure 5. Principle of symmetry reduction applied to a special case of self-poisoning. The surface of the growth sector has symmetry 1. The seed crystal is in point group $\bar{1}$. Two independent sites assumed at the surface are described by ellipsoids. H: host polar molecule, H_{mis} : host molecule misoriented. Probabilities of adsorption of molecules are indicated by arrows (identical arrows denote identical probabilities). For the resulting growth sectors, different green colors indicate different compositions of well-oriented and misoriented host molecules. (a) Growth of a perfect crystal, no orientational disorder. (b) Growth of a real crystal, with a certain amount of orientational disorder varying with the site.

This mechanism leading to growth-induced polarity formation was demonstrated for an Ising-like model subjected to layer-by-layer growth.^{17,25} This growth model is roughly depicted in Figure 6 (for more details, see ref 17). The amount of polarity was assumed to be proportional to the difference between the total molar fractions of molecules in state down and up, $X_{net} = X(\downarrow) - X(\uparrow)$, once the system has reached its asymptotic state. The value of X_{net} depends on the temperature at which the crystal is grown, the set of interaction energies occurring at the surface, and the states of the previously docked molecules. The sine qua non condition for polarity formation ($X_{net} \neq 0$) in such a centric system is a difference between the two faulty orientations, i.e., between the interaction energies $E(tt)$ and $E(bb)$; see Figure 6. However, growth-induced polarity arises only if the probability of orientational disorder is non-negligible, i.e., the difference between good and faulty orientations (i.e., between $E(th)$ and $E(tt)$, $E(bb)$, respectively) is significant.

This growth model has been shown to be useful in estimating the amount of polarity occurring in real systems. For estimating X_{net} , a three-step procedure was developed: (i) calculation of interaction energies between a reference molecule and the first-sphere neighborhood; (ii) selection of relevant neighbors for each face (*hkl*) of the crystal; (iii) calculation of $X_{net}(hkl)$ by using a variant of the growth model adapted to the crystal structure investigated. The predicted repartition of polarity in the crystal was compared successfully to observed experimental SHG effects and pyroelectric measurements.⁶⁵ New developments were performed in the last few years to further understand this particular case of self-poisoning. (See, for example, the influence of a nonpolar impurity on polarity formation, investigated at both a theoretical^{66–68} and a predictive level.⁶⁹)

It is worth noting that the model shown in Figure 6 could be adapted to investigate phenomena other than polarity. For instance, the same kind of approach (i.e., the three-step procedure (i–iii) and the use of a simple growth model) could

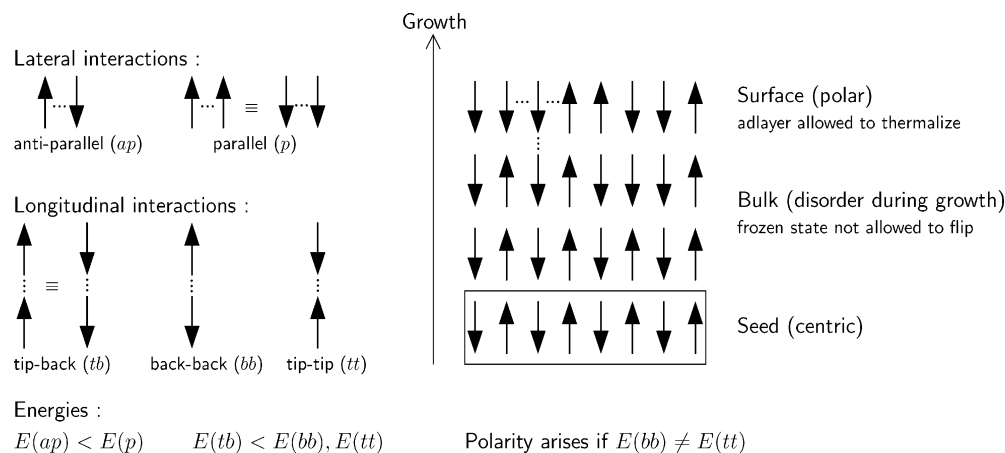


Figure 6. Model proposed to investigate growth-induced polarity formation. Molecules are represented by their dipole moment (black arrow), which is either in an up or down state. We assume the following growth model (right): in a square lattice, a molecule at the surface interacts with four lateral neighbors and one longitudinal neighbor (dashed lines). The state of its dipole (up or down) depends on the set of interaction energies with the five neighbors (left). Growth is performed layer-by-layer. Dipoles of the adlayer (only) are allowed to thermalize until equilibration. Once in the bulk, dipoles are not allowed to flip anymore (we assume a high-energy barrier, which is common sense when considering long-prolate molecules). For further details, see ref 25.

be employed to estimate the chemical composition of the growth sectors in the case of inclusion of impurities. Also, it might be appropriate for investigating growth phenomena of chiral compounds such as lamellar epitaxy encountered for 5-ethyl-5-methyl-hydantoin⁷⁰ or the epitaxy between the racemic compound and the enantiomer structure of alanine.⁷¹

3. Growth-Induced Properties and Surface Symmetry

3.1. Deduction of Surface Symmetry from the Crystal Point Group. As previously shown, the knowledge of symmetries expressed at the surface may help in the understanding and the prediction of growth-induced properties. Now that structure visualization tools are readily available, surface symmetry may be obtained by building the face and looking at the symmetries relating molecules at the surface. More rigorously, the same information may also be found in ref 72 (see Table 10.2.2, pp 756–771). This table gives face symmetries for the 32 point groups, i.e., the group of symmetry operations that transforms a face onto itself. (See also ref 19 (section 3.2.2) in which group theory is applied to determine possible crystal systems of growth sectors of alum mixed crystals, the result being used to conclude about the difference between observed and optical indicatrices.)

Here, we propose to rewrite the mathematical process leading to face symmetries, in order to adapt it for our purposes and to clearly show the relationships between surface symmetry and point group of the crystal. Moreover, we investigate in the next section the impact of face symmetries on physical properties, and we need to work with symmetry operators \hat{R} . The access to this information is not straightforward in ref 72. Finally, we find it appropriate to start our approach without any prior knowledge other than the point group of the crystal, so that even a reader not familiar with crystallography may follow the procedure.

We consider the symmetry elements $S[uvw]$ of the point group of a crystal. Hereafter, $S[uvw]$ denotes either a rotation axis with S the order and $[uvw]$ the direction of the axis, a mirror plane with $S = m$ and $[uvw]$ the normal to the plane, or any kind of symmetry operator (i.e., including symmetries 1 and $\bar{1}$) when generalization is required. The symmetry operators corresponding to $S[uvw]$ are represented by 3×3 matrices and are noted $\hat{R}_{S[uvw]}$. Their expression is available online on the

Bilbao Crystallographic Server.⁷³ The associated transposed matrices are denoted $\hat{T}_{S[uvw]}$. The face (hkl) is represented by the vector $v(hkl)$ running in the direction $[hkl]$. A symmetry element $S[uvw]$ is expressed at the surface if it respects the following equation:

$$\hat{T}_{S[uvw]}v(hkl) = v(hkl) \quad (1)$$

that is, if the vector $v(hkl)$ is an eigenvector of the transposed matrix $\hat{T}_{S[uvw]}$. The ensemble of symmetry elements of the point group satisfying eq 1 represents the set of symmetries present at the surface. This set, defined hereafter as the surface point group, can be either the point group of the crystal or one of its subgroups.

As an example, we consider a crystal in point group $2/m$, and we want to find the surface point group of the face (100). The four symmetry elements in the bulk are the identity (1), a two-fold axis running along b ($2[010]$), a mirror plane normal to b ($m[010]$) and a center of symmetry ($\bar{1}$). Applying eq 1 to the vector $v(100)$, for each of the four symmetry elements gives the following:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad \text{for } 1 \quad (2a)$$

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix} \quad \text{for } 2[010] \quad (2b)$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad \text{for } m[010] \quad (2c)$$

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix} \quad \text{for } \bar{1} \quad (2d)$$

According to eqs 2, only the mirror symmetry (and obviously symmetry 1) is conserved. Therefore, the surface point group of face (100) is m .

with $\hat{R}_{S[uvw]}$ the symmetry operator corresponding to $S[uvw]$ (see ref 73 for the matrix expressions of $\hat{R}_{S[uvw]}$). Equation 3 restricts the components p_i ($i = x, y, z$) of \mathbf{p} to certain values. The ultimate restriction is given by the center of symmetry, which imposes a vector null. However, considering a particular growth sector, the expression of \mathbf{p} must fulfill eq 3 only for the set of symmetries expressed in this growth sector. Assuming symmetry reduction, the symmetry of the growth sector is reduced to that of the surface. This allows pyroelectricity to occur in this growth sector (at least in some directions) despite a centric seed.

For example, we take a crystal in the centric point group $m\bar{3}$. Because of the center of symmetry, this crystal cannot be pyroelectric. However, let us consider the anisotropic adsorption of impurities on the growth sectors $\{100\}$ leading to a symmetry for the sectors reduced to that of their surface. As shown in Table 2, surfaces $\{100\}$ exhibit a symmetry $2mm$. The symmetry elements are identity (1), a two-fold axis ($2[100]$) and two mirrors ($m[010]$ and $m[001]$) (see Supporting Information). The application of eq 3 on a pyroelectric vector \mathbf{p} (p_x, p_y, p_z) for these four symmetry elements gives the following restrictions on \mathbf{p} :

$$\hat{R}_1 \mathbf{p} = \mathbf{p} \rightarrow \mathbf{p} \text{ free in all directions} \quad (4a)$$

$$\hat{R}_{2[100]} \mathbf{p} = \mathbf{p} \rightarrow \mathbf{p} \text{ forbidden in } y \text{ and } z \text{ directions} \quad (4b)$$

$$\hat{R}_{m[010]} \mathbf{p} = \mathbf{p} \rightarrow \mathbf{p} \text{ forbidden in } y \text{ direction} \quad (4c)$$

$$\hat{R}_{m[001]} \mathbf{p} = \mathbf{p} \rightarrow \mathbf{p} \text{ forbidden in } z \text{ direction} \quad (4d)$$

The set of eqs 4 and particularly the two-fold symmetry (eq 4b) prevents pyroelectricity to appear in the y and z directions. The pyroelectric vector is thus restricted to the form $\mathbf{p}(p_x, 0, 0)$. Therefore, if symmetry reduction occurs in growth sectors $\{100\}$, the component p_x of \mathbf{p} may be not zero. As such, pyroelectricity may be observed, providing that the direction of measurement of the electrical field has a component x , and that p_x is sufficiently large to be detected. Applying the same procedure to other faces of a crystal $m\bar{3}$, we find that pyroelectricity may be expressed in x and y directions for the growth sectors $\{110\}$ and $\{hkl\}$. It may also be observed in sectors $\{111\}$, in that case its three coordinates being equal ($p_x = p_y = p_z$).

In Table 2, we summarize for each of the 32 point groups what the non-zero coordinates of the pyroelectric vector would be if the growth sector exhibited the symmetry of the corresponding surface.

We illustrate Table 2 by an experimental case study, namely, growth-induced polarity observed in crystals of 4-chloro-4'-nitrostilbene.⁷⁴ Although these dipolar molecules crystallize in the centric point group $2/m$, pyroelectric effects were observed in sectors $\{011\}$. This may be explained by the formation of 180° orientational disorder during growth, which reduces the symmetry of these sectors to that of their surface (in that case, symmetry 1). There is no more symmetry restriction on \mathbf{p} , so that resulting pyroelectricity may be observed within growth sectors $\{011\}$. On the same crystals of 4-chloro-4'-nitrostilbene, pyroelectricity along the y direction could not be observed in growth sectors $\{100\}$, an experimental result consistent with the symmetry reduction preventing a pyroelectric effect to appear in this direction. Moreover, even though growth-induced pyroelectricity might geometrically appear in the x and z

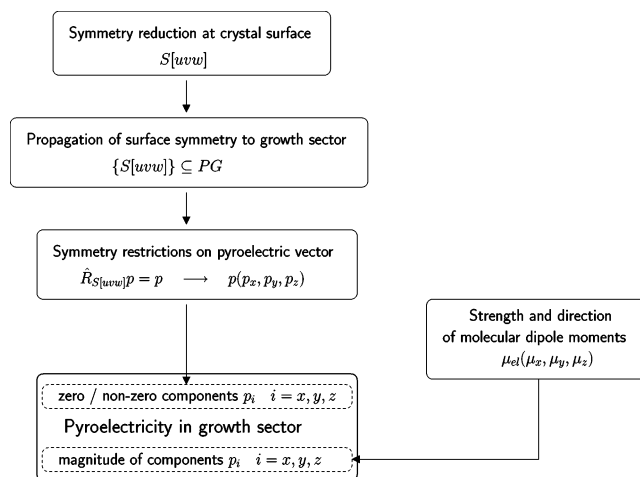


Figure 7. Methodology to evaluate growth-induced properties (here, pyroelectricity). Surface symmetry may give indications of the possibility to observe the property in the growth sector. However, only the analysis of the molecular packing (here, arrangement of dipoles in the structure) allows a quantitative prediction.

directions (see Table 2), an effect is unlikely to be observed because of the small magnitude of the components of the molecular dipole moments along these directions. Indeed, the long-prolate stilbene molecules are all almost parallel to the y -axis (angle of $\sim 18^\circ$), so that any pyroelectric effect in a direction other than y is very small and thus difficult to observe. Similar arguments hold here for the nonlinear optical effect: In sectors $\{011\}$, a significant second-harmonic generation (SHG) response was found along y , while no SHG effect was observed for a polarization of the fundamental wave along the x direction.⁷⁴

In summary, the appearance of a growth-induced pyroelectric vector \mathbf{p} due to symmetry reduction will depend on the growth sector investigated and on the symmetries present on the corresponding faces $\{hkl\}$ (Figure 7). Experimentally, growth-induced pyroelectricity may be observed only if the components of \mathbf{p} are sufficiently large in the direction of measurement of the electrical field, a magnitude determined by the Euler angles of the molecular dipole moments in relation to the crystal axes. It is worth noting that the procedure applied here for a vectorial property holds also for tensorial properties with rank > 1 which are particularly sensitive to symmetry. For instance, optical anomalies (rank 2) found in cubic crystals⁵² could be investigated by this approach.

4. Discussion

As shown in the preceding sections, when symmetry reduction occurs, the symmetry of the growth sector is reduced to that of the surface. However, some nuance must be added to this statement. Indeed, symmetry reduction may be partial when the probabilities of bindings on independent surface sites are equal (e.g., impurities do not dock at all on some sites). Conversely, the growth sector may have a symmetry lower than that of the surface, especially when the adsorbed impurity is chiral (see Figure 4b). Even if these cases are likely to be unexpected, the difference in chemical composition of the crystallographic sites may be so subtle that symmetry reduction remains unnoticed experimentally.

A method to definitely apprehend these cases consists of calculating the interaction energies of host and guest molecules (or of misoriented host molecules in case of self-poisoning) when they bind on each of the independent sites of the surface.

The symmetry relating the total set of binding energies is a good way to have direct access to the symmetry of the growth sectors (see, for instance, refs 69 and 65). These calculations may however be difficult to apply in case of, for example, a dominant dispersive part or interactions energies out to be dependent on the next-nearest neighbors, etc. Nevertheless, it allows us to get an accurate qualitative prediction of growth-induced properties by answering clearly the question of whether the growth process plays a role in the symmetry of physical properties of the sector investigated.

Calculating energies at the surface is also a necessary step toward a quantitative prediction of growth-induced properties. The host:guest ratios (or the amount of self-poisoning) in the different growth sectors may be roughly estimated by setting up a growth model that takes into account important factors, such as the availability of the different components at the crystal–nutrient interface or the influence of the molecules previously attached in the neighborhood. As shown previously, binding energies on several faces of a 4-chloro-4'-nitrostilbene crystal were calculated and used in a stochastic growth-model adapted to the structure.⁶⁹ It allowed the researchers to explain and to quantify growth-induced polarity arising in some growth sectors. Naturally, various bottlenecks habitually found in computational chemistry as well as the various assumptions and approximations of the growth models (e.g., simplified topology of the surface, no diffusion at the surface, surface relaxation neglected, docking molecules assumed to be rigid) prevent an exact quantitative prediction.

Therefore, it is clear that the investigation of surface symmetries represents only a very first step toward the prediction and the understanding of growth-induced properties. It allows us nevertheless to recognize the sensitivity of physical properties to the growth process. In particular, information as given in Table 2 for pyroelectricity provides the following:

(i) Help in detecting symmetry reduction. When a discrepancy between symmetry of the point group and that of the observed properties is detected, one should think about a possible symmetry reduction due to adsorption of impurities or to self-poisoning. The agreement between symmetries of the growth sectors given in Table 2 and observations represents in that case a further indication of symmetry reduction.

(ii) A potential aid for the design of physical properties. Knowing the crystal point group as well as the representative faces of the crystal morphology, one may get a general overview on properties that can appear in the different growth sectors. As such, efforts may be driven toward the use of tailor-made additives especially chosen to dock on the “interesting” faces.

Finally, another point that requires attention is the dissymmetrization arising at the subsector level. So far, our argument was based on the assumption of faces growing in a flat manner, that is, layer-by-layer. However, when growth arises via a dislocation-spiral mechanism, the docking of new molecules takes place along steps, further decomposing the growth sector into subsectors. This phenomenon is sometimes described in the literature as tangential selectivity¹⁹ (versus normal selectivity for layer-by-layer growth) and may give rise to the presence of hillocks on the growth surface.¹⁸ As growth sectors are related by the symmetry elements of the point group of the crystal, the subsectors defined by the hillocks are related by the symmetry elements of the growth sector. As such, they may upon growth lead to a further dissymmetrization of the crystal, by exhibiting different chemical compositions.^{37,75} In that case, the variation may be minute and its possible consequences on growth-induced properties are rather complex and difficult to apprehend. For

instance, it was observed that optical anomalies are particularly sensitive to dissymmetrization. While the observed optical indicatrix is often consistent with surface symmetry, it is less obvious that the optical subsector zoning reflects the symmetry of the hillocks.¹⁹ Rather, they often average to reflect the symmetry of the face, a phenomenon for which exact causes are still not fully understood.

5. Conclusion

The influence of point group symmetries on physical properties is well understood. However, the many examples given in this paper demonstrate that considering bulk symmetry only is sometimes not appropriate and may lead to puzzling differences between the theoretical prediction and the observation of physical properties. The phenomenon of symmetry reduction due to the insertion of impurities in the lattice or to self-poisoning reminds us that a crystal has a growth history and that properties may be influenced by the growth process. In this paper, we specifically focused on two points: (i) the symmetry of the surface may be easily derived from the point group of the crystal, and (ii) considering surface symmetry may give a good appreciation of growth-induced properties observed in the growth sectors. As an example, the systematic study of growth-induced pyroelectricity for various representative faces in the 32 crystallographic point groups was performed. It was shown for instance that a centric crystal may give rise to pyroelectricity in some growth sectors, provided that symmetry reduction took place and that the pyroelectric effects are strong enough to be observed.

The various considerations about surface symmetry discussed in this paper shed new light on the relationship between symmetries of the structure and symmetries of its physical properties. For growth-induced properties, Neumann's principle could be restated as follows: *The symmetry elements of any physical property of a growth sector of a crystal include all the symmetry elements of the point group of the growth sector.* In general, the principle remains valid for any domain of a crystal, provided that this domain has a homogeneous crystal structure.

Altogether, the phenomenon of symmetry reduction in growth sectors, as well as the further decomposition of these growth sectors in hillocks-subsectors, strikes the fundamental concept of homogeneity of a crystal: Does it still make sense to speak about an individual crystal when this one is composed of various domains with different chemical compositions, symmetries, and physical properties? It demonstrates clearly that any attempt of tentative classification or generalization is always subjected to limiting cases. Here, the crystallographic description of the structure fails to take into account sectoring due to growth dissymmetrization. If there is a final goal to this paper, it is to remind us that the description of a crystal structure by a set of symmetries and crystallographic atomic positions is an average of the reality and as such should be contemplated as not more than this.

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Supporting Information Available: Tables of surface symmetries and surface point groups for representative faces of the 32 point groups. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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