TECHNISCHE UNIVERSITÄT WIEN

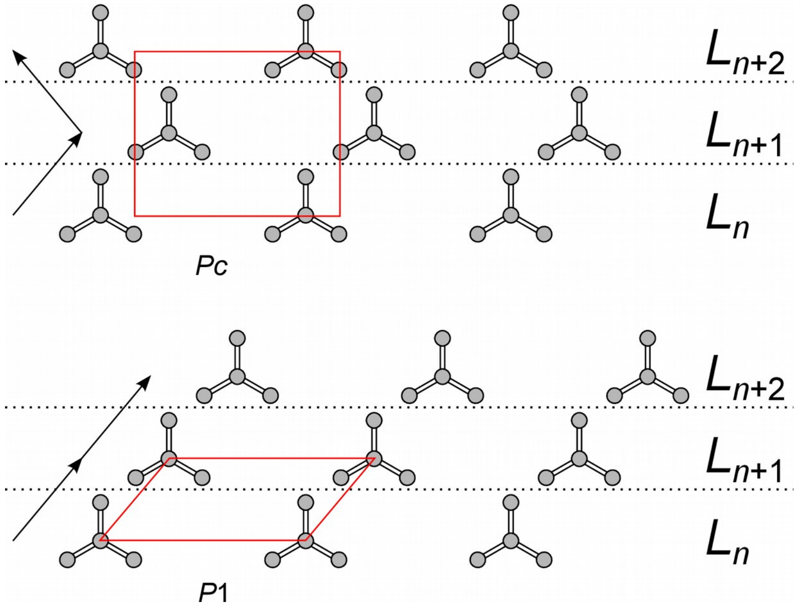
ECM MaThCryst satellite 2019

A short introduction to the OD theory

Berthold Stöger

Polytypism

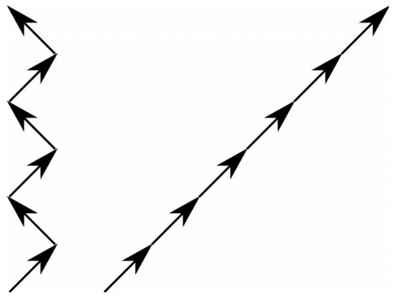
- Definition: Polytypes are (periodic) structures that are composed of (virtually) identical layers (rods), but differ in the stacking arrangement.
- Ubiquitous in all classes of compounds (minerals, inorganic, metal organic, organic, bio macromolecules).

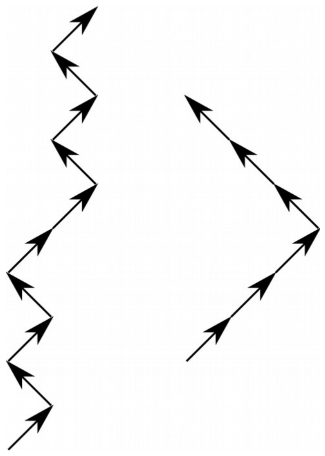


A. Guinier, *et al*. Nomenclature of polytype structures. *Acta. Cryst.* A**40**, 399–404, 1984.

Polytypism: consequences (1)

- Ordered polytypes:
  - Wurtzite vs. sphalerite
  - SiC
  - …
- Sporadic stacking faults:
  - Twinning
    - Overlap of two or more diffraction patterns.
  - Antiphase domains
    - Not easily accessible by diffraction.
    - Elongation of peaks in stacking direction.





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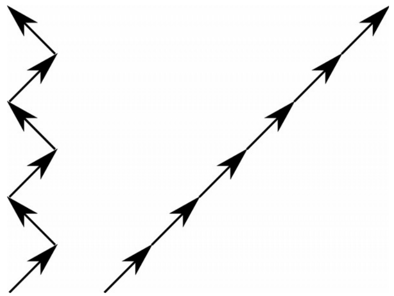
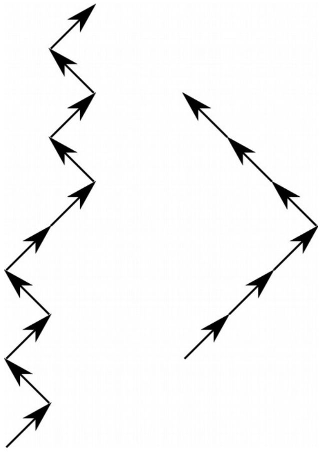
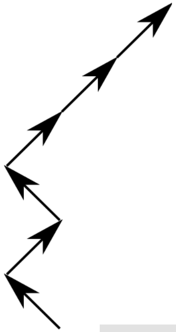


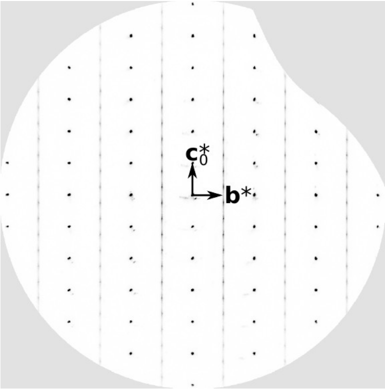


Polytypism: consequences (2)

- Mixing of ordered polytypes
  - Allotwins



- Disordered stackings
  - Streaks in stacking direction



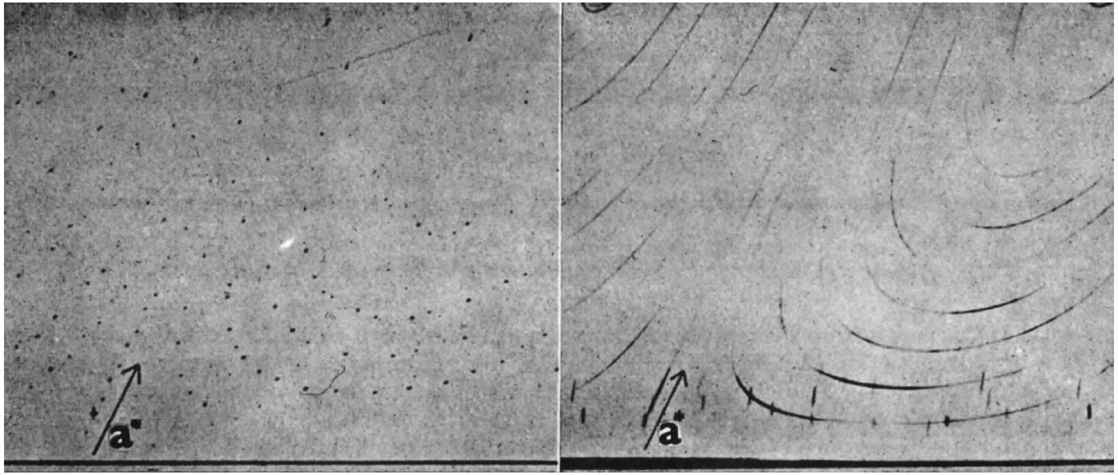
- Combination of the above!

Order/Disorder (OD) theory

- Explanation of the common occurrence of polytypism.
- Prediction of polytypism and twinning.
- Generalization of crystallinity to families of *locally equivalent* structures.
  - Interatomic interactions are local.
- Symmetry theory of families of *locally equivalent* structures.
- Very general.
  - Applies to an astounding number of polytypic materials.
- OD structures are special kind of polytypes:
  - All OD structures are polytypic (though sometimes disordered).
  - Not all polytypes are OD structures (but experience shows that most are!).

OD theory: a short history

- 1953: Diffraction pattern of wollastonite ($CaSiO_3$) by J. W. Jeffery
  - Sharp spots (order) and streaks (disorder) in the same diffraction pattern.
  - Recognition of ‘virtual’ symmetry in the structure.
- 1955: Reason of disorder of wollastonite and Madrell’s salt ($NaPO_3$) by K. Dornberger-Schiff
  - Non-space group symmetry operations of distinct layers lead to local equivalence.



Weissenberg photographs of wollastonite

J. W. Jeffery, *Acta. Cryst.* **6**, 821–404, 1953.
K. Dornberger-Schiff et al., *Acta Cryst.* **8**, 752–754, 1955.

OD theory: a short history

- 1956: Coinage of the term “Order-Disorder (OD) structures”.
  - Seminal paper.
  - Gives numerous examples of OD structures: Sphere packing, SiC, graphite, $B(OH)_3$, decaborane, chlorites.
  - Explains diffraction effects of disordered OD structures.
- 1961: Fundamentals of the OD theory
  - Partial operations (POs), OD groupoids, OD groupoid families.

K. Dornberger-Schiff, *Acta. Cryst.* **9**, 593–601, 1956.
K. Dornberger-Schiff & H. Grell-Niemann, *Acta Cryst.* **14**, 752–754, 1961.

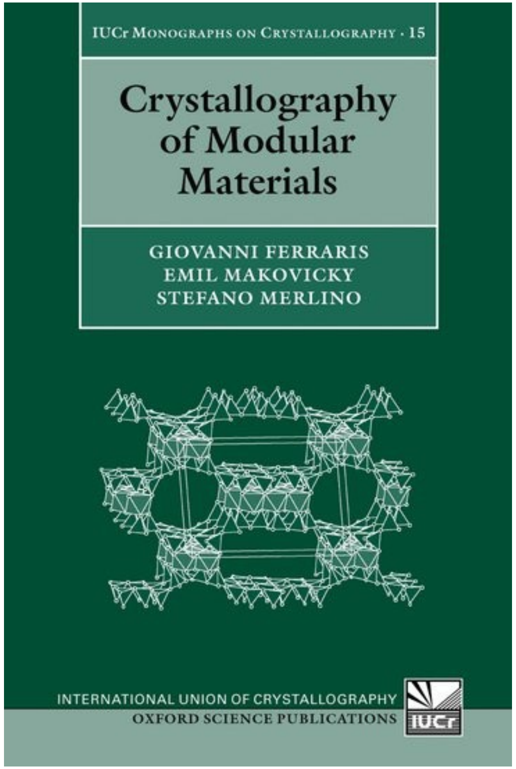
OD theory: a short history

- 1960ies and 1970ies: heyday of the OD school in the GDR (East Berlin).
  - Development of a symmetry theory of locally equivalent structures.
  - Notation for OD groupoid families of one kind of layers.
  - Derivation of the 400 types of (simple) OD groupoid families.
- 1980ies: Generalizations of the theory
  - Notation for OD groupoid families of more that one kind of layers.
  - MDO (maximum degree of order) polytypes
- Late 1980ies: Dying out of the OD school in the GDR.

OD theory: problems

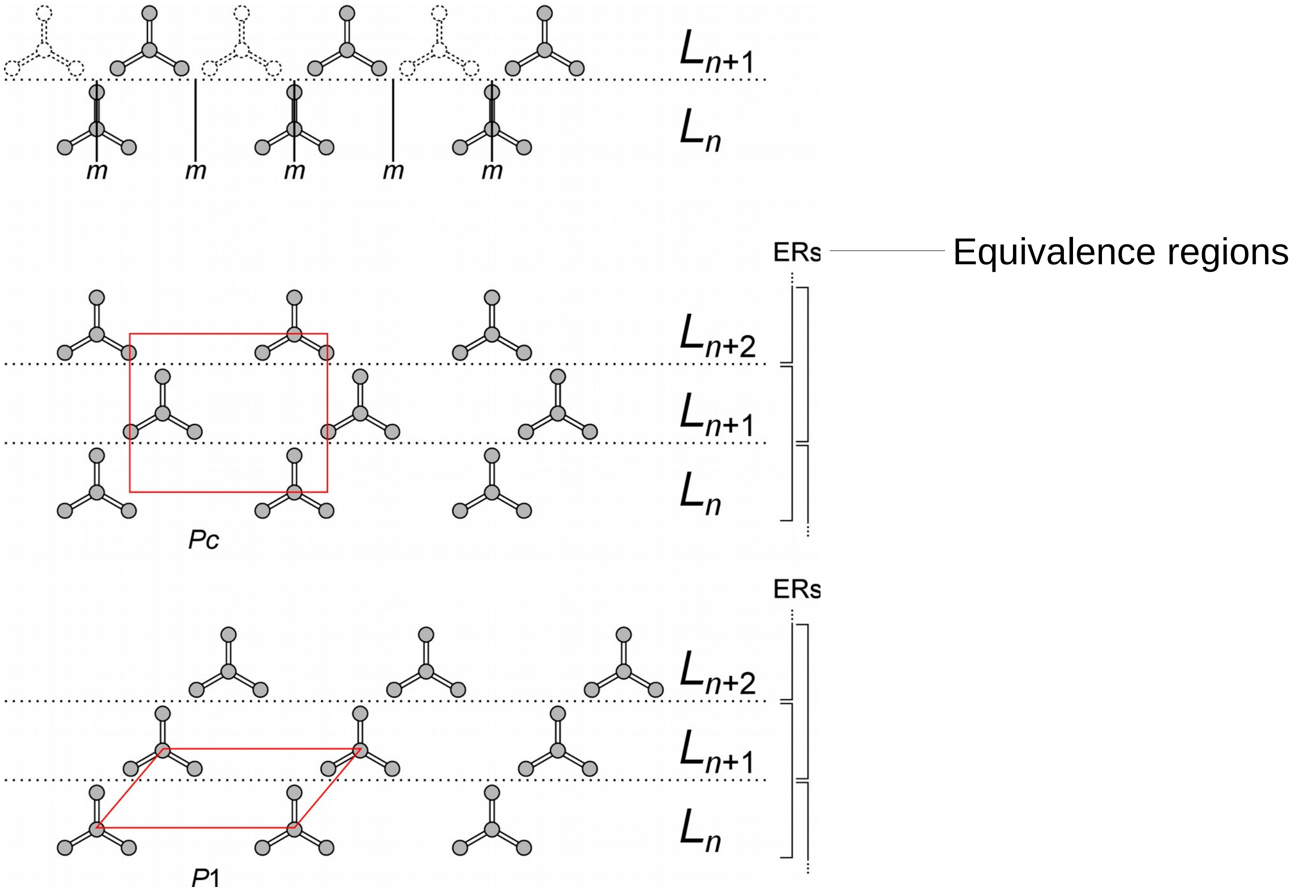
- Developed in isolation.
  - Literature written in German.
  - Literature written in an often impenetrable style.
- Idiosyncratic notations.
  - Looks more complicated than it is.
- Inconsistent use of the notations in the literature.
  - No standardization effort.
- Name clash with order/disorder phase transitions.
- Sudden disappearing of the OD school.
- OD descriptions are not unique.
  - Distinct descriptions leading to the same possible stacking arrangements.
- Theory not yet fully fleshed out.
  - Surprisingly many open questions.

OD Theory: recommended literature



G. Ferraris, E. Makovicky & S. Merlino. “Crystallography of Modular Materials”. *IUCr Monographs on Crystallography.* **15**, Oxford University Press, Oxford.

Introductory fictitious example



The vicinity condition (VC)

- Basic idea:
  - Interatomic interaction is only local.
  - There is one preferred way of connecting layers / objects.
- A structure fulfills the *vicinity condition* (VC) if
  - (*VCα*) it is composed *two-dimensionally periodic* layers belonging the a finite number *M* of equivalence classes.
  - (*VCβ*) adjacent layers possess a *common two-dimensional lattice*.
  - (*VCγ*) equivalent sides of equivalent layers contact to adjacent layers such that the resulting pairs are equivalent.
- A structure fulfilling the VC is not necessarily periodic!
  - See example from previous slide.
- Ambiguous stacking: *proper* OD structure
  - All polytypes are locally equivalent up to at least one layer width
- Unambiguous stacking: *fully ordered* structure.
- Attention: Usually, there is some deviation from *VCα* and *VCγ* because some operations are not valid for the whole crystal
  - An OD description is an *idealization*!

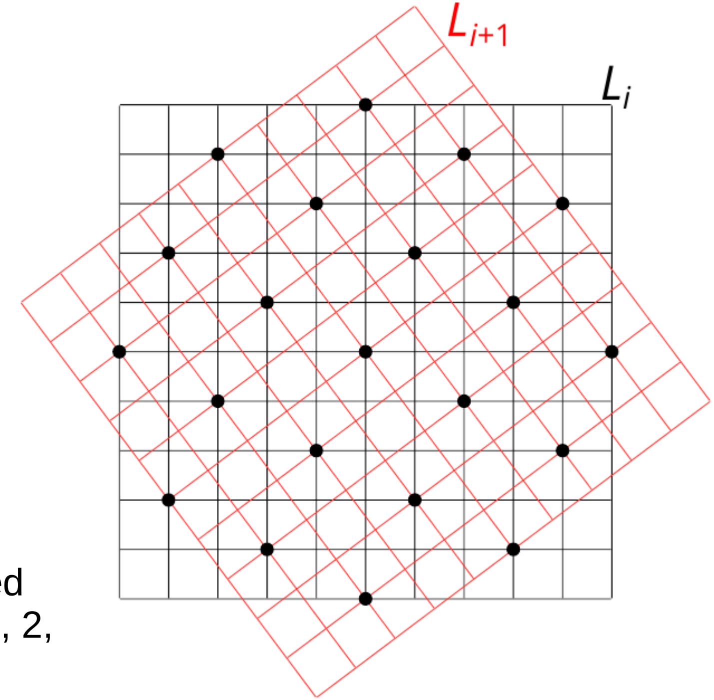
Vicinity condition: variants

- Application of the VC is inconsistently used in the literature.
- (*VCα*) it is composed two-dimensionally periodic layers belonging the a finite number *M* of equivalence classes.
  - (*VCα*’) M=1 kinds of layers → too strict.
  - (*VCα*’’) M=∞ kinds of layers → violates the idea of well defined building rule.
- (*VCβ*) neighbouring layers possess a common two-dimensional lattice.
  - (*VCβ*’) neighbouring layers possess the same lattice → too strict.
  - (*VCβ*’’) all polytypes possess a common two-dimensional layer lattice.

    → violates the idea of only local interactions.

Example of aperiodic polytypes

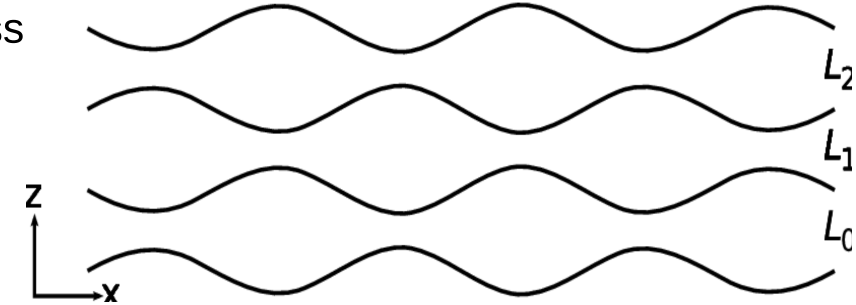
- Rotation of adjacent layers by $\pm\tan^{-1}(3/4)$
  - Equivalent pairs of layers.
  - Two layers have a common two-dimensional lattice.
  - Structure fulfills the VCβ.
- Periodic polytype:
  - Alternating rotation by $+\tan^{-1}(3/4)$ and $-\tan^{-1}(3/4)$.
- Non-periodic polytype:
  - Continuous rotation by $+\tan^{-1}(3/4)$.
- OD is a *bottom-up* approach:
  - We look at local interaction and construct stackings from there.
  - Despite starting with crystallographic layer symmetry, the stackings need not be crystallographic (i.e. can feature operations of other order than 1, 2, 3, 4 or 6).



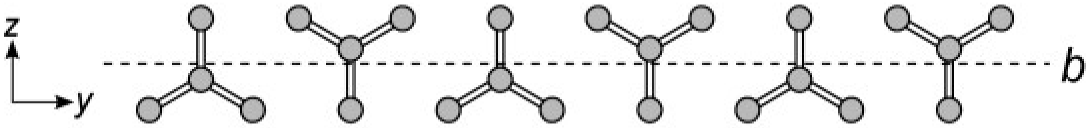
Lattices of two adjacent layers.
Dots: common lattice nodes.

OD layers

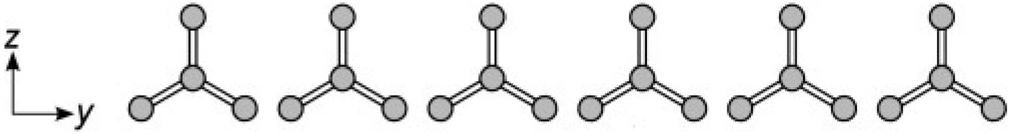
- OD layers are *two-dimensionally periodic* of finite thickness
  - No holes (simply connected).
  - No interactions over more than one layer width.
  - The layer interfaces need *not* be planar.

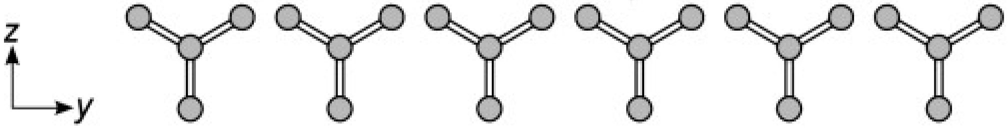


- OD layers follow purely *geometrical* considerations.
  - OD layer do not necessarily correspond to chemical layers.
- There are two types of OD layers:
  - Non-polar layers: the two sides of the layers are related by layer symmetry.



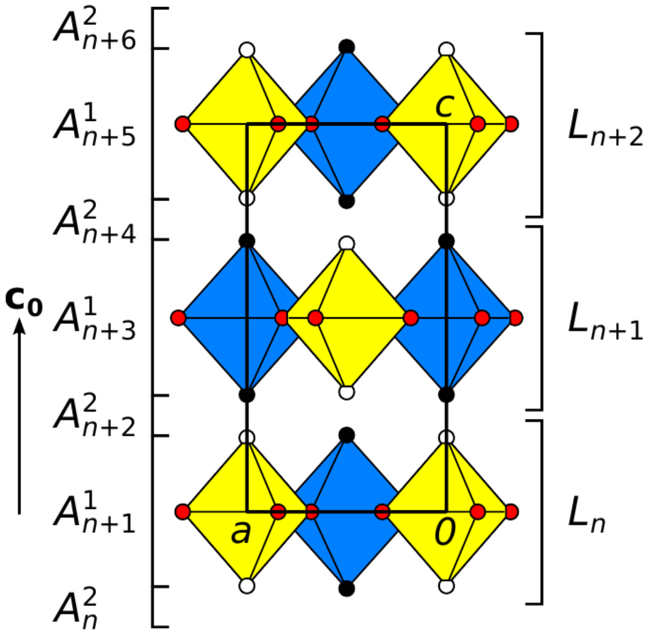
  - Polar layers: no symmetry relating the two sides of the layer. The layers possess two non-equivalent sides.
    - Polar layers may appear in two orientations with respect to the stacking direction.





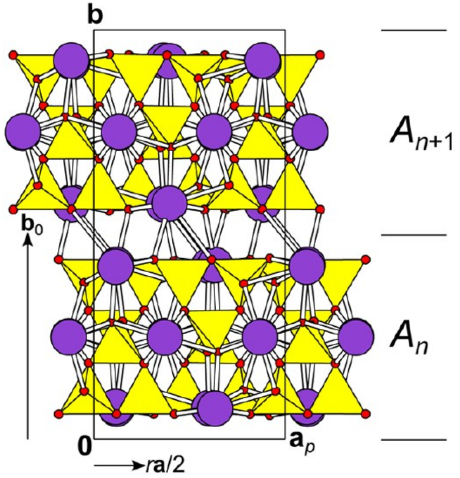
OD layers: coordinate systems

- The coordinate system is chosen such that two basis vectors span the layer lattice.
  - Typically **a** and **b**, but there may be reasons for different choices (e.g. existing structures, monoclinic direction in stacking direction, etc.)
- The third basis vector (stacking vector) is called $\mathbf{a}_0$, $\mathbf{b}_0$ or $\mathbf{c}_0$.
  - It is usually chosen perpendicular to the layer plane and of the length of one layer packet (smallest *n*-tuple of adjacent layers containing all types of layers).
  - In certain cases the stacking vector is chosen non-perpendicular to the layer plane (see later).

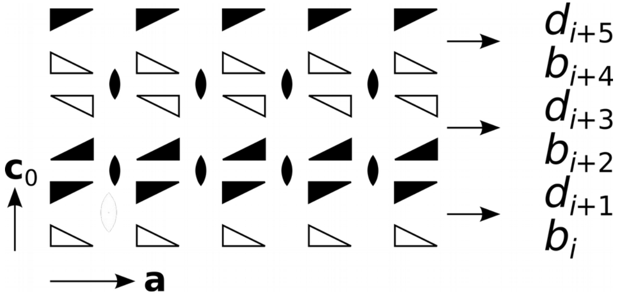


OD layers: symbols

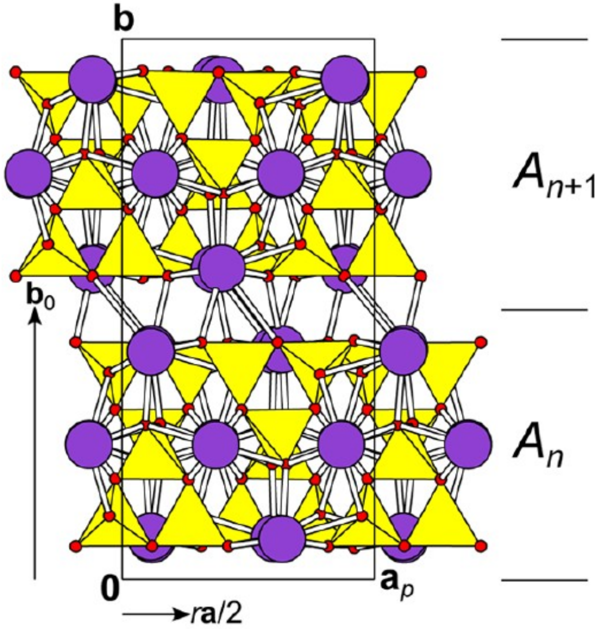
- A general layer is designated as L.
- Layers indexed by a sequential number:
  - L_i connects to L_{i+1} and L_{i-1}.
- If there are M>1 kinds of layers, the type of layer may be indicated in the superscript:
  - L^0, L^1, L^2, …
- Non-polar layers are written as A_i
  - Note the reflection plane of the "A" letter.
- Polar layers are written as b_i and d_i depending on their orientation with respect to the stacking direction.
  - Note that the letters "*b*" and "*d*" are related by reflection



β-$KAsO_3$



OD layers: symbols



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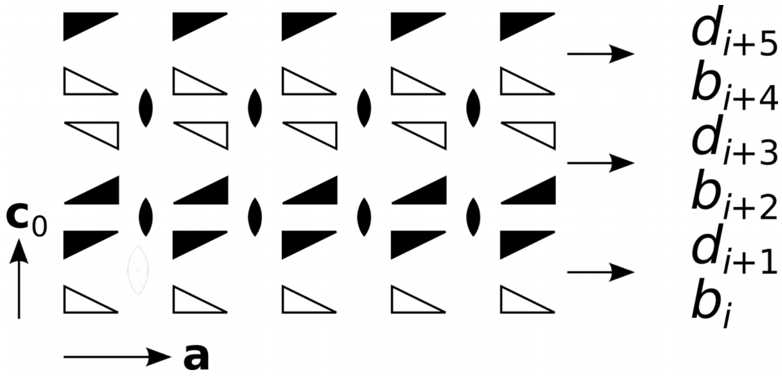
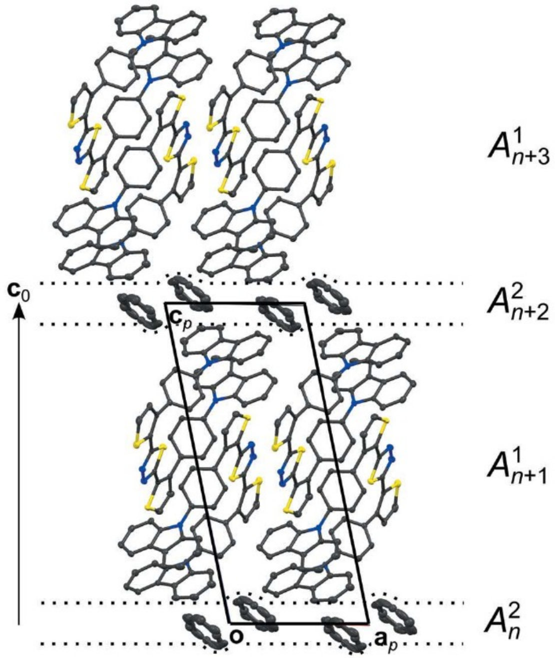


Fictitious example
(triangles black on one and white on the other side)



Organic solvate

Layer groups

- The symmetry of a two-dimensionally periodic layer belongs to one of 80 layer group *types*.
- Polar layers:
  - One of 17 types of layer groups.
  - Isomorphic to *plane groups*.
- Non-polar layers:
  - One of 63 layer group types with operations inverting the stacking direction.

crystal system lattice system	triclinic oblique	monoclinic oblique	monoclinic rectangular	orthorhombic rectangular	tetragonal square	trigonal hexagonal	hexagonal hexagonal
polar	$P11(1)$	$P11(2)$	$Pm1(1)$ $Pb1(1)$ $Cm1(1)$	$Pmm(2)$ $Pma(2)$ $Pba(2)$ $Cmm(2)$	$P(4)$ $P(4)mm$ $P(4)bm$	$P(3)$ $P(3)m1$ $P(3)1m$	$P(6)$ $P(6)mm$
non-polar	$P11(\bar{1})$	$P11(m)$ $P11(a)$ $P11(2/m)$ $P11(2/a)$	$P21(1)$ $P2_11(1)$ $C21(1)$ $P2/m1(1)$ $P2_1/m1(1)$ $P2/b1(1)$ $P2_1/b1(1)$ $C2/m1(1)$	$P22(2)$ $P2_12(2)$ $P2_12_2(2)$ $C22(2)$ $Pm2(m)$ $Pm2_1(b)$ $Pb2_1(m)$ $Pb2(b)$ $Pm2(a)$ $Pm2_1(n)$ $Pb2_1(a)$ $Pb2(n)$ $Cm2(m)$ $Cm2(e)$ $Pmm(m)$ $Pma(a)$ $Pba(n)$ $Pma(m)$ $Pmm(a)$ $Pma(n)$ $Pba(a)$ $Pba(m)$ $Pbm(a)$ $Pmm(n)$ $Cmm(m)$ $Cmm(e)$	$P(\bar{4})$ $P(4/m)$ $P(4/n)$ $P(4)22$ $P(4)2_12$ $P(\bar{4})2m$ $P(\bar{4})2_1m$ $P(\bar{4})m2$ $P(\bar{4})b2$ $P(4/m)mm$ $P(4/n)bm$ $P(4/m)bm$ $P(4/n)mm$	$P(\bar{3})$ $P(3)12$ $P(3)21$ $P(\bar{3})1m$ $P(\bar{3})m1$	$P(\bar{6})$ $P(6/m)$ $P(6)22$ $P(\bar{6})m2$ $P(\bar{6})2m$ $P(\bar{6}/mmm)$

Layer group symbols

- International Tables: $pm2m$, p_ancm

Lower case Bravais symbol: two-dimensional lattice

Direction of missing translation given in subscript of Bravais symbol

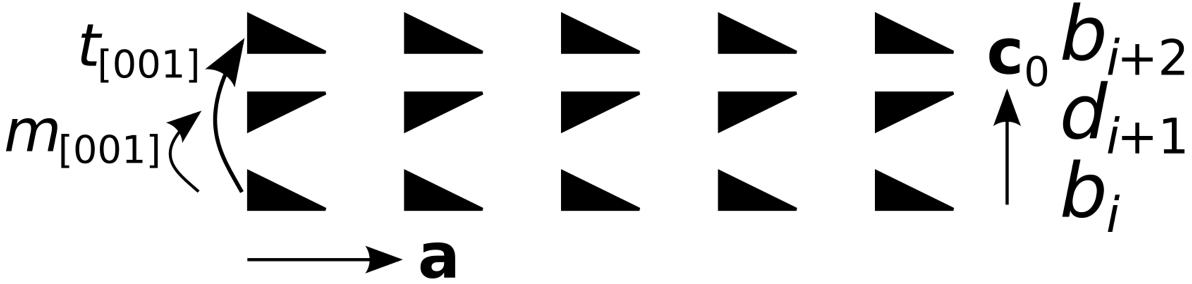
- OD-school: $Pm2(m)$, $P(n)cm$

Upper case Bravais symbol: three-dimensional object.

Direction of missing translation indicated by parenthesis.

Partial Operations (POs)

- Two layers of the same kind are mapped by *partial operations* (POs).
- A PO is based on a motion of Euclidean space $\mathbb{E}$.
  - Identity, inversion, rotation, reflection, higher roto-inversion, screw rotations and glide reflections can all form POs.
- A PO has a *source* and a *target* layer.
  - In the OD literature, POs are often written as ${}_{i,j}a$, ${}_{i,j}b$, where *i* and *j* are the source and target layers.
  - Note that i and j are reversed with respect to the notation of the last session.
- A PO can be seen as the restriction of a motion to the space occupied by the source layer.
  - → A partial function from the space occupied be the source into the space occupied by the target layer.
- For each layer L_i there is the identity PO ${}_{i,i}1$
- For each PO ${}_{i,j}a$ exists the inverse PO ${}_{j,i}a^{-1}$
- Two layers are always mapped by an infinity of POs, whereby we can choose one representative
  - See previous session.



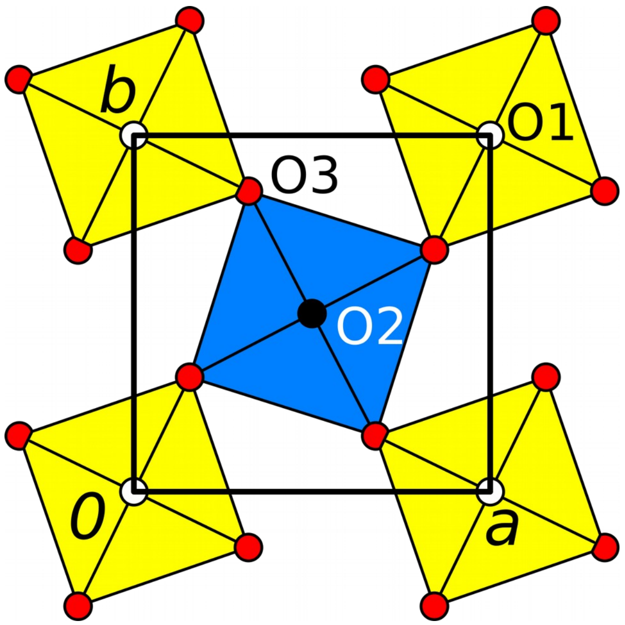
Identifying OD layers

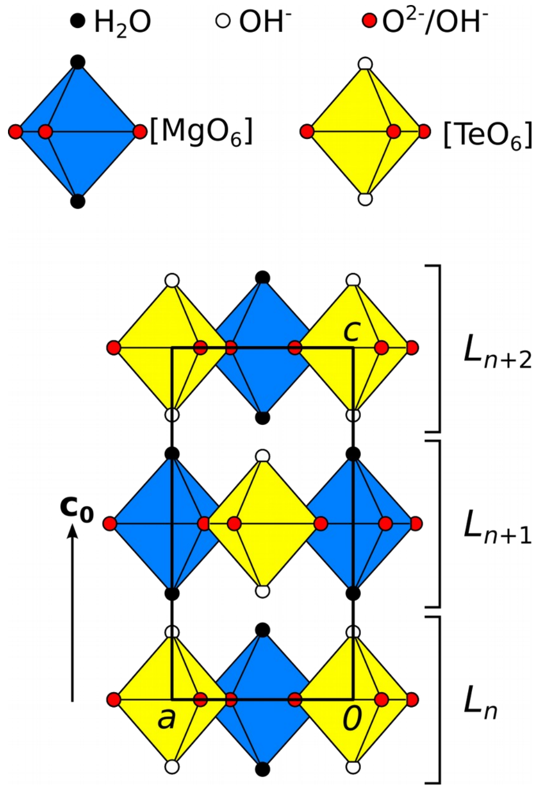
- Search for POs that explain the observed disorder phenomenon:
  - Twinning: POs with same linear part as twin operation.
  - Phantom atoms: POs that map heavy atoms on the ghost atoms.
- The POs may map a layer onto itself or relate adjacent layers.
- The layer interfaces need not be planar.
- Atoms may be located on the layer interfaces.
  - These atoms belong to both adjacent layers.
- The layer choice is not necessarily unique.
  - The chosen description should be as clear as possible.
- Aim for the *simplest* layer choice that explains all the observed effects.

H. Grell: “How to choose OD layers”, *Acta Cryst.* A**40**, 95–99 (1984).

OD vs. non-OD: $MgTeO_8H_8$

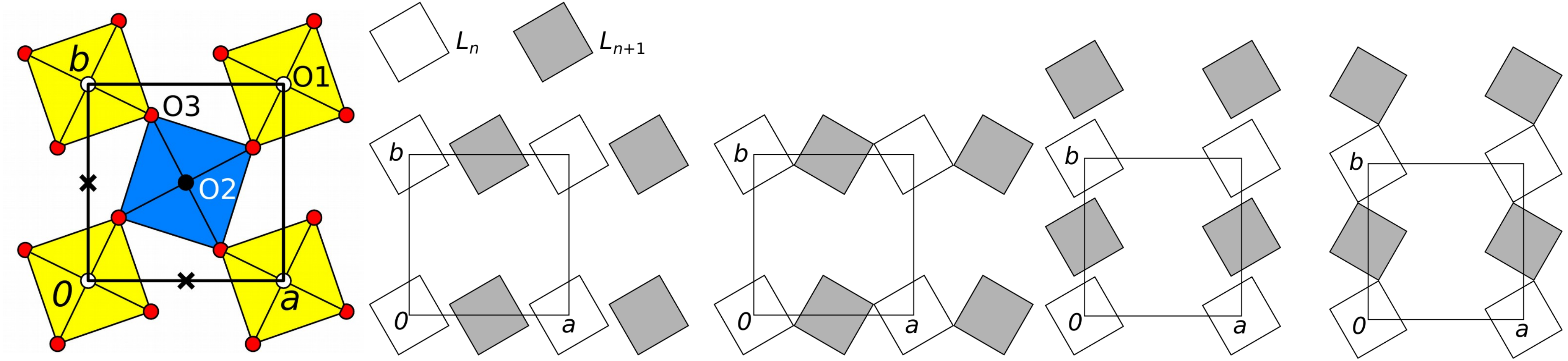
- Tetragonal [$P(4/m)$] layers with composition $Mg(H_2O)_2[TeO_2(OH)_4]$.
- H atoms predicted by bond-valence-sums.





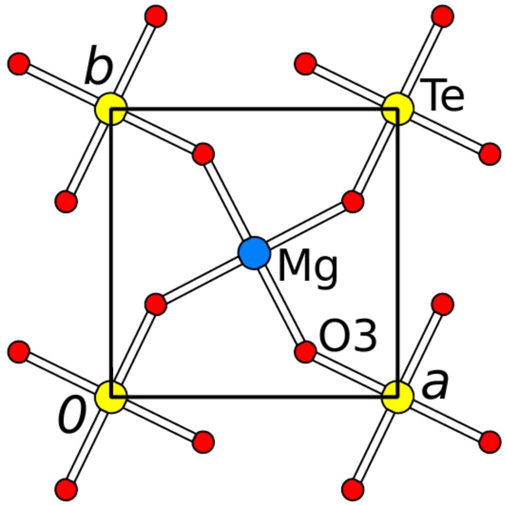
OD vs. non-OD: $MgTeO_8H_8$

- From one layer to the next:
- Two ways of placing origin → Mg/Te exchange.
- Two ways of octahedron orientation → Orientation inversion.
- Non-OD, since pairs of adjacent layers are non-equivalent.

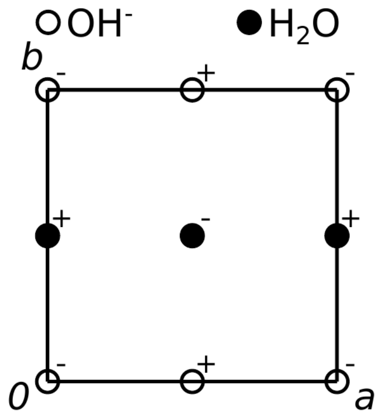


OD vs. non-OD: $MgTeO_8H_8$

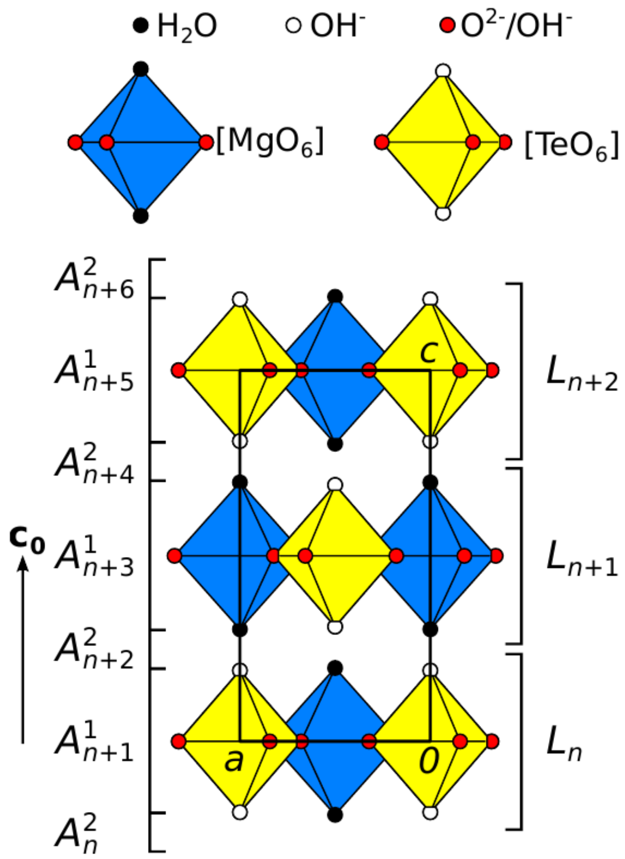
- Two kinds of layers → OD
- OD interpretation splits the observed disorder in two components:
  - Disorder owing to the hydrogen-bonding
  - Disorder owing to the symmetry of the octahedra
- OD is a *empirical* approach



A^1: $P(4/m)$

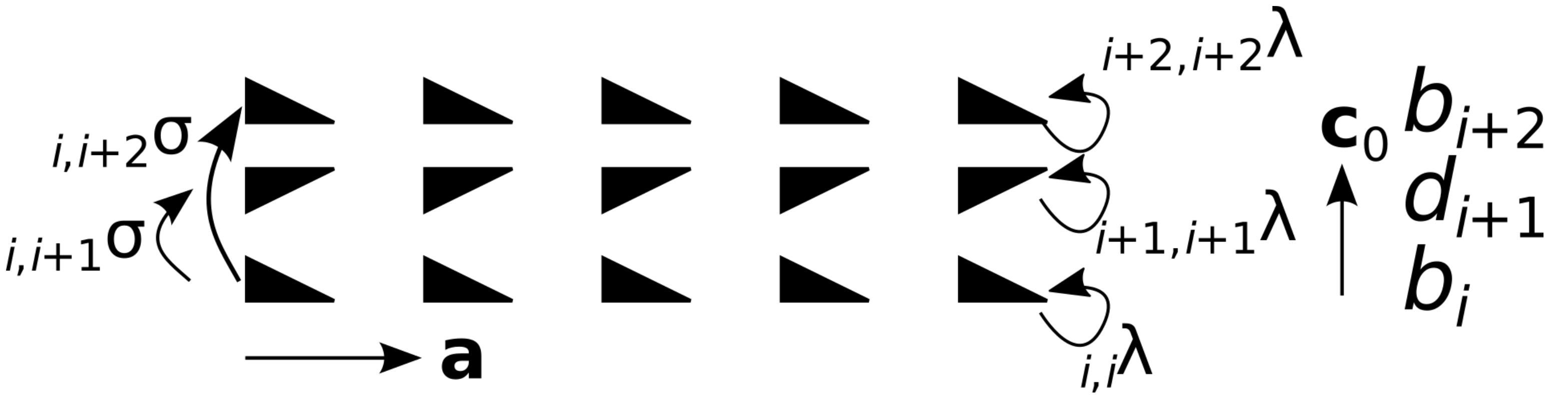


A^2: $Pmm(b)$



Classification of POs

- λ-POs (λ stands for "layer")
  - POs that map a layer L_i onto itself:
  - Also written as ${}_{i,i}\lambda$
  - Correspond to *local operations* in the last session.
  - The λ-POs of a given layer form a *group* that is *isomorphic* to the layer group.
    - From now on we will not differentiate between layer groups and groups of λ-POs.
- σ-POs (σ stands for "space")
  - POs that map a layer L_i onto a different layer L_j, $i \neq j$
  - Also written as ${}_{i,j}\sigma$



Classification of POs

- τ-POs
  - Keep the orientation with respect to the stacking direction.
  - For example stacking direction [001]:
    - The matrix representation of the linear part must have the form:

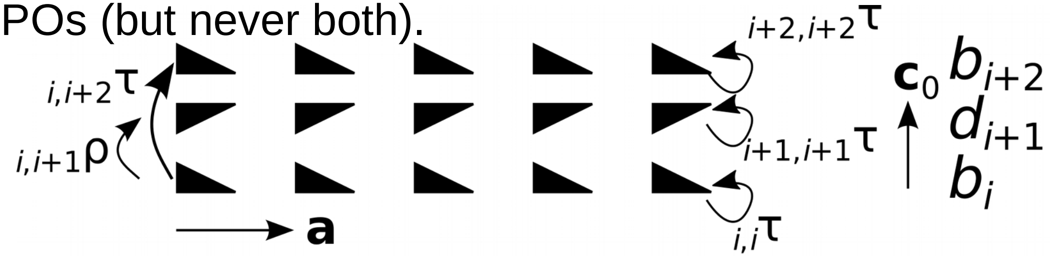
$$\begin{pmatrix} w_{11} & w_{12} & 0 \\ w_{21} & w_{22} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

- ρ-POs (ρ stands for “reverse”)
  - Invert the orientation with respect to the stacking direction
  - For example stacking direction [001]:
    - The matrix representation of the linear part must have the form:

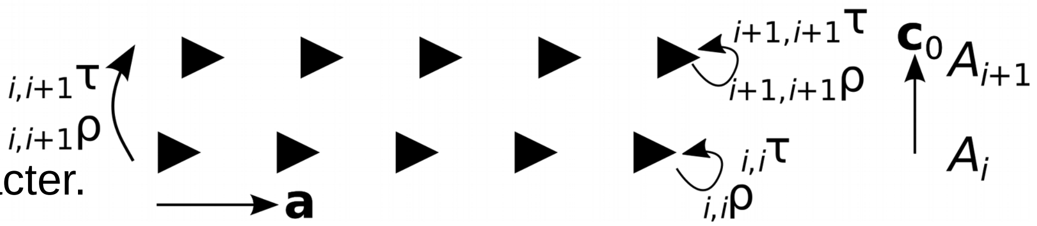
$$\begin{pmatrix} w_{11} & w_{12} & 0 \\ w_{21} & w_{22} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$$

Classification of POs

- Equivalent non-polar layers are always related by τ *and* ρ-POs.
  - The λ-POs of a non-polar layer comprise λ-τ-POs and λ-ρ-POs.
- Equivalent polar layers are related by τ *or* ρ-POs (but never both).
  - There are only λ-τ-POs in polar layers.
- Composition of τ and ρ-POs



$\circ$	τ	ρ
τ	τ	ρ
ρ	ρ	τ



- Inversion of an operation retains τ- and ρ-character.
- Conjugation (with other POs) retains τ- and ρ-character.

Notation for λ-POs

- λ-POs can only be operations that appear in layer groups.
- Therefore, we can use standard Hermann-Mauguin notation.
- Intrinsic translation of glides reflections and screw rotations only parallel to the layer plane.
- Direction of the operation only parallel or perpendicular to layer plane.
- Higher order (*n*>2) operations only with direction perpendicular to layer plane.

	λ-τ-POs	λ-ρ-POs
no direction	1, t	$\overline{1}$
direction in layer	m, a, b, c	2, 2_1
stacking direction	2, 3, 4, 6	m, a, b, c, n, $\overline{3}$, $\overline{4}$, $\overline{6}$

Notation for σ-POs

- In POs relating different layers, non-spacegroup intrinsic translations can appear for screw rotations and glide reflections.
- Generalization of the Hermann-Mauguin symbols.
- Unfortunately, rather idiosyncratic and inconsistent:
  - 2_r, 2_s: twofold rotation with intrinsic translation $r/2$, $s/2$ of the shortest lattice vector.
  - 2_2, 2_4, 2_6, …: twofold screw rotation mapping layer L_i onto L_{i+1}, L_{i+2}, L_{i+3}, …
  - 3_3, 3_6, 3_9, …: threefold screw rotation mapping layer L_i onto L_{i+1}, L_{i+2}, L_{i+3}, …
  - 4_4, 4_8, 4_{12}, …: fourfold screw rotation mapping layer L_i onto L_{i+1}, L_{i+2}, L_{i+3}, …
  - 6_6, 6_{12}, 6_{18}, …: threefold screw rotation mapping layer L_i onto L_{i+1}, L_{i+2}, L_{i+3}, …
  - $n_{r,s}$: glide reflection with intrinsic translation
    - Direction [100]: $r\mathbf{b}/2+r\mathbf{c}/2$
    - Direction [010]: $r\mathbf{c}/2+r\mathbf{a}/2$
    - Direction [001]: $r\mathbf{a}/2+r\mathbf{b}/2$
    - Except for hexagonal layers, of course.
  - a_r, b_r, c_r: shorthand for $n_{0,s}$ or $\mathrm{n}_{\mathrm{r},0}$ with intrinsic translation only in [100], [010] or [001] direction.
  - c_2, c_4, c_6, …: glide reflection mapping L_i onto L_{i+1}, L_{i+2}, L_{i+3}, … without intrinsic translation in the layer plane.
  - a_2, a_4, a_6, …: glide reflection mapping L_i onto L_{i+1}, L_{i+2}, L_{i+3}, … without intrinsic translation in the layer plane.
  - b_2, b_4, b_6, …: glide reflection mapping L_i onto L_{i+1}, L_{i+2}, L_{i+3}, … without intrinsic translation in the layer plane.

Notation for σ-POs

	σ-τ-POs	σ-ρ-POs
no direction	t	$\overline{1}$
direction in layer	$n_{r,2}$, c_2, etc.	2, 2_r
stacking direction	2_2, 3_3, 4_4, 6_6, etc.	m, $n_{r,s}$, $\overline{3}$, $\overline{4}$, $\overline{6}$

Continuation

- Two POs ${}_{i,j}a$ and ${}_{k,l}b$ are said to be a continuation if they are based on the same motion.
- In symbols: ${}_{i,j}a \leftrightarrow {}_{k,l}b$
- Extreme case: a motion has continuations for all layers

  → the motion is a *total operation* of the OD structure.
- *Reverse continuations* are continuations of POs that map L_i on L_j and L_j on L_i ($i \neq j$):
  - ${}_{i,j}a \leftrightarrow {}_{j,i}b$
  - A reverse continuation must be a σ-ρ-PO.
  - A reverse continuation represents a *symmetry operation* of the (L_i,L_j) *pair* of layers.
  - Pairs of layers that do not have a reverse continuation are polar.
    - These pairs can appear in two orientations with respect to the stacking direction.

NFZ Relationship

- To determine the number of stacking possibilities, we use the *NFZ relationship*.
- It is based on one known (L_i, L_{i+1}) pair of layers and gives the number of ways of placing L_{i+1} such that geometrically equivalent pairs of layers are obtained.
- *Coset decompostion* of the group of λ-τ-POs valid for both layers in the group of λ-τ-POs of L_i.

Group of λ-τ-POs of L_i
(extended to global operations)

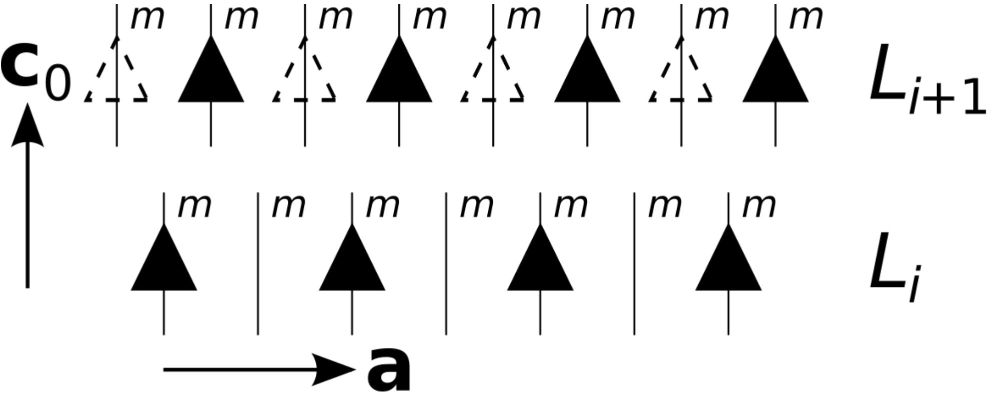
Common translation group of L_i and L

$$Z = N/F = [\mathcal{G}_i : \mathcal{G}_i \cap \mathcal{G}_{i+1}] = |\mathcal{G}_i/\mathcal{T}|/|(\mathcal{G}_i \cap \mathcal{G}_{i+1})/\mathcal{T}|$$

Number of positions of L_{i+1}
given the position of L_i

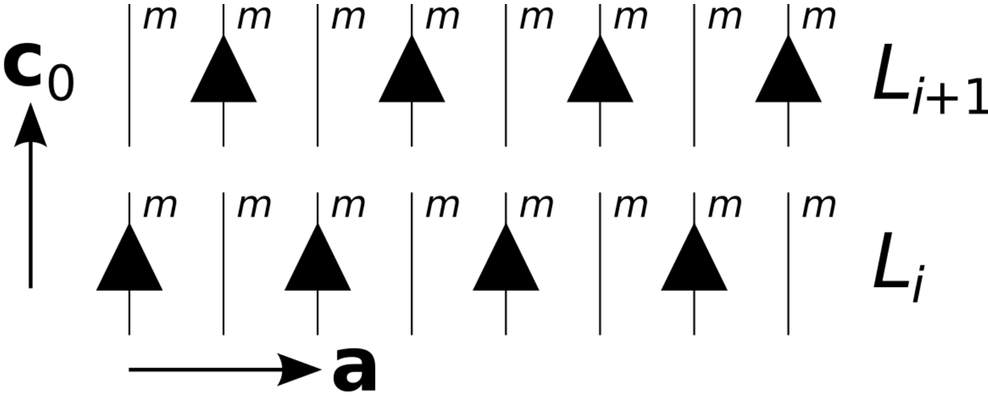
Group of λ-τ-POs of L_i that
have continuations in L_{i+1}
(extended to global operations)

NFZ Relationship



$\mathcal{G}_i = Pm1(1) \qquad \mathcal{G}_i \cap \mathcal{G}_{i+1} = P11(1)$

$Z = N/F = [m:1] = 2/1 = 2$

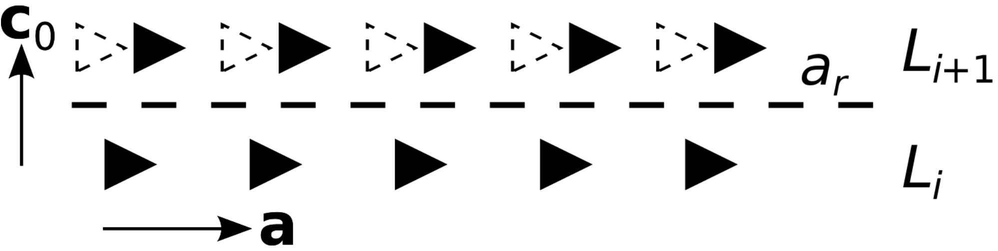


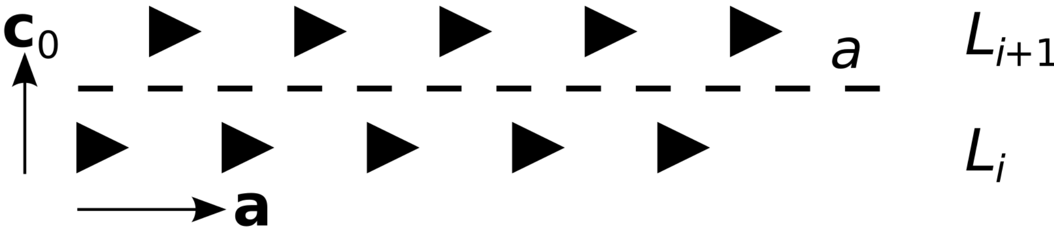
$\mathcal{G}_i = Pm1(1) \qquad \mathcal{G}_i \cap \mathcal{G}_{i+1} = Pm1(1)$

$Z = N/F = [m:m] = 2/2 = 1$

NFZ relationship

- One exception:
  - If there are σ-ρ-POs *and* no reverse continuations.
  - Application of the inverse of a σ-ρ-POs leads to a new lair pair with same L_i.
    - The two orientations of L_{i+1} are derived by double application of the motion of the inverse of a σ-ρ-PO
  - The number of stacking possibilities is doubled.
  - The NFZ relationship then reads as $Z=2N/F$.





$$\mathcal{G}_i = P11(1) \qquad \mathcal{G}_i \cap \mathcal{G}_{i+1} = P11(1)$$
$$Z = 2N/F = 2[1:1] = 2 \cdot 1/1 = 2$$

$$\mathcal{G}_i = P11(1) \qquad \mathcal{G}_i \cap \mathcal{G}_{i+1} = P11(1)$$
$$Z = N/F = [1:1] = 1/1 = 1$$

OD family

- Given an OD structure, all alternative stacking arrangements with equivalent pairs of layers form an *OD family* of structures.
- Examples:
  - Graphite ordered polytypes, twins, disordered stackings...
  - SiC ordered polytypes, twins, disordered stackings...

Category of an OD family

- Owing to the (VCγ), for an OD family of layers of M kinds, only certain successions of τ- and ρ-POs are possible.
- These define the category of an OD family.
- There are a finite number of categories, which simplifies the analysis of OD families in general, as there are only a finite number of cases to consider.
- For *M*=1 layers, there are 3 categories:
  - Category I:
    - …AAAA…
    - Layers are non-polar, σ-τ- and σ-ρ-POs.
  - Category II:
    - …bbbb…
    - Layers are polar, only σ-τ-POs.
  - Category III:
    - …bdbd…
    - Layers are polar, only σ-τ- and σ-ρ-POs.
    - Two kinds of layer contacts!

	No. non-polar	No. polar	σ-ρ-POs	Types of contacts
Category I	1	0	✓	1
Category II	0	1	×	1
Category III	0	1	✓	2

Category of an OD family

- For $M>1$ layers there are four categories
- E.g. for layers of $M=4$ kinds:
- Category I:
  - …$A^1b^2b^3b^4d^4d^3d^2A^1b^2b^3b^4d^4d^3d^2$…
- Category II:
  - …$b^1b^2b^3b^4b^1b^2b^3b^4$…
- Category III:
  - …$b^1b^2b^3b^4d^4d^3d^2d^1b^1b^2b^3b^4d^4d^3d^2d^1$…
- Category IV:
  - …$A^1b^2b^3A^4d^3d^2A^1b^2b^3A^4d^3d^2$…

	No. non-polar	No. polar	σ-ρ-POs	Types of contacts
Category I	1	$M-1$	✓	M
Category II	0	M	×	M
Category III	0	M	✓	$M+1$
Category IV	2	$M-2$	✓	$M-1$

Composition of POs

- The composition of two POs is defined if and only if the target of the first is the source of the second.
- The resulting PO has the source of the first and the target of the second PO:
  - ${}_{i,k}c = {}_{j,k}b \circ {}_{i,j}a$
- Composition of POs can be conveniently written using diagrams:

$$ {}_{k,l}c \circ {}_{j,k}b \circ {}_{i,j}a \quad \Longrightarrow \quad i \xrightarrow{a} j \xrightarrow{b} k \xrightarrow{c} l $$

- A diagram is said to *commute* if all paths between the same nodes are equal

$$ {}_{j,l}b \circ {}_{i,j}a = {}_{k,l}d \circ {}_{i,k}c = {}_{l,i}e \quad \Longrightarrow \quad \begin{tikzcd} i \arrow[r, "a"] \arrow[d, "c"'] \arrow[dr, "e"] & j \arrow[d, "b"] \\ k \arrow[r, "d"'] & l \end{tikzcd} $$

Groupoids

- A groupoid **G** is composed of
  - A set of objects obj(**G**) (=Layers)
  - A set or morphisms mor(**G**) (=POs)
  - Two mappings src,trg: mor(**G**) → obj(**G**)
  - A composition ◦ defined for a,b∈ob(**G**) if and only if src(b)=trg(a)

Groupoid axioms

Associativity	$({}_{i,k}c \circ {}_{j,k}b) \circ {}_{i,j}a = {}_{i,k}c \circ ({}_{j,k}b \circ {}_{i,j}a)$
Neutral element	${}_{j,j}1 \circ {}_{i,j}a = {}_{i,j}a \circ {}_{i,i}1 = {}_{i,j}a$
Inverse	${}_{j,i}a^{-1} \circ {}_{i,j}a = {}_{i,i}1$
	${}_{i,j}a \circ {}_{j,i}a^{-1} = {}_{j,j}1$

H. Brandt. “Über eine Verallgemeinerung des Gruppenbegriffes”. *Math. Ann.* **96**, 360–366 (1927).
C. Ehresmann. “Gattungen von Lokalen Strukturen”. *Jahresber. Deutsch. Math.-Verein.*, **60**, 49–77 (1957).

OD groupoids

- The composition of the POs of an OD structure forms an *OD groupoid*.
- Proof of groupoid properties are left as an exercise.
- Every polytype, twin, disordered stacking, etc. has its unique OD groupoid.
- An OD groupoid is composed of *M connected components*, where *M* corresponds to the number of types of layers.

OD groupoid families

- The infinity of space groups are categorized into 230 crystallographic *types* of space groups.
  - Space groups abstract from:
    - Orientation
    - Metrics
- In analogy: the OD groupoids are categorized into *OD groupoid families*.
  - OD groupoid families abstract from:
    - Orientation
    - Metrics
    - Stacking
  - All OD groupoids that are built according to the same *symmetry principle* belong to the same OD groupoid family.
  - There is an infinity of OD groupoid families.
  - For layers of one kind with all the same lattice, there are 400 OD groupoid families.
- All OD groupoids of the same OD groupoid family are of the same category.
- An OD groupoid family has a *point group*:
  - The group generated by the linear parts of all POs.
  - Need not be a crystallographic point group (see $\tan^{-1}$¾ example)!

OD groupoid family symbols

- Depends on the number *M* of kinds of layers and the category of the OD groupoid family.
- *M*=1, Category I (…AAA…)

$$\begin{array}{cccccc} P & m & a & (m) & \\ \{ & 2_{-1+r}/n_{s,2} & 2_s/n_{2,-1+r} & (2_2/n_{r,s}) & \} \end{array}$$

Layer group of non-polar layer.

One set of σ-POs relating adjacent layers. Usually contains σ-τ-POs and σ-ρ-POs.

- *M*=2, Category II (…bbb…)

$$\begin{array}{cccccc} P & m & m & (2) & \\ \{ & n_{s,2} & n_{2,r} & (2_2) & \} \end{array}$$

Layer group of polar layer.

One set of σ-POs relating adjacent layers. Only σ-τ-POs.

- *M*=3, Category III (…bdbdbd…)

$$\begin{array}{cccccc} P & b & a & (2) & \\ \{ & 2_r & 2_s & (n_{r+1,s+1}) & \} \\ \{ & 2_{r'} & 2_{s'} & (n_{r'+1,s'+1}) & \} \end{array}$$

Layer group of polar layer.

Two sets of σ-POs relating adjacent layers. Only σ-ρ-POs.

OD groupoid family symbols

- For layers of *M*>1 kinds:
  - Origin-relation of layers of different kind given by pair of parameters [*r*,*s*]
  - Corresponds to a shift in the layer plane of *r***a**+*s***b,** *r***b**+*s***c** or *r***c**+*s***a**.

Category I *M*=2 (…$A^1b^2d^2A^1b^2d^2$…):

$$\begin{array}{cccc} P & m & m & (m) \end{array} \quad [r', s'] \quad \begin{array}{ccccc} & P & m & m & (2) \\ \{ & 2_r & 2_s & (n_{r,s}) & \} \end{array}$$

Category II *M*=2 (…$b^1b^2b^1b^2$…):

$$op \quad \begin{array}{ccccc} & P & 1 & 1 & (2) \\ \{ & n_{2s+2s',4} & n_{4,2r+2r'} & (-) & \} \end{array} \quad [r, s] \quad \begin{array}{cccc} P & 1 & 1 & (2) \end{array} \quad [r', s']$$

OD groupoid family symbols

- For layers of M>1 kinds:
  - Origin-relation of layers of different kind given by pair of parameters [r,s]
  - Corresponds to a shift in the layer plane of r**a**+s**b,** r**b**+s**c** or r**c**+s**a**.

Category III M=2 (…$b^1b^2d^2d^1b^1b^2d^2d^1$…):

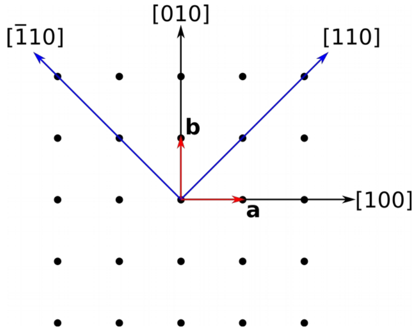
$$\begin{matrix} P & m & m & (2) \\ \{ & 2_r & 2_s & (n_{r,s}) & \} \end{matrix} \quad [r'', s''] \quad \begin{matrix} P & 1 & 1 & (2) \\ \{ & 2_{r'} & 2_{s'} & (-) & \} \end{matrix}$$

Category IV M=3 (…$A^1b^2A^1d^2A^1b^2A^1d^m$…):

$$\begin{matrix} P & m & m & (m) \end{matrix} \quad [r, s] \quad \begin{matrix} P & m & m & (2) \end{matrix} \quad [r', s'] \quad \begin{matrix} P & 2 & 2 & (2) \end{matrix}$$

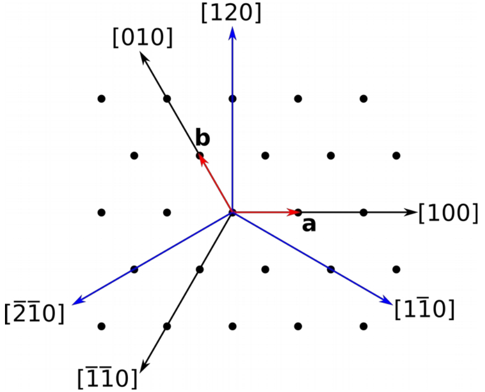
OD groupoid family symbols

- For tetragonal, trigonal and hexagonal OD families, five- or seven-placed symbols may be necessary.
- Reason: Directions that are equivalent in space groups e.g. <100> may not be equivalent.
- Tetragonal: symbols given in [100], [010], [001], [110], [$\bar{1}$10] direction.



$$
\begin{array}{cccccc}
P & 2_1/b & 1 & (1) & 1 & 1 \\
\left\{ \quad \right. & - & - & \begin{pmatrix} 4^+_4 \\ \bar{4}^+ \end{pmatrix} & \begin{array}{c} 2_{r+s} \\ n_{1+r-s,2} \end{array} & - \quad \left. \right\}
\end{array}
$$

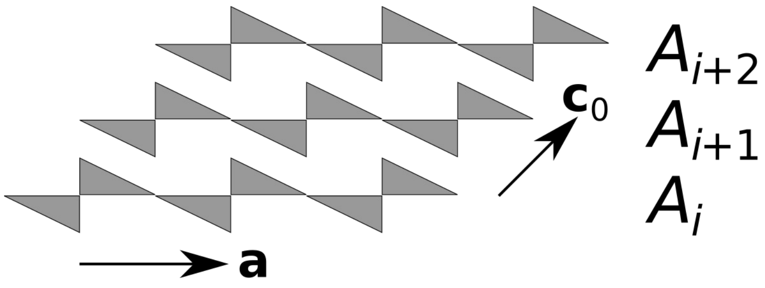
- Hexagonal: symbols given in [100], [010], [$\bar{1}\bar{1}$0], [001], [120], [$\bar{2}\bar{1}$0], [1$\bar{1}$0] directions.



$$
\begin{array}{cccccccc}
P & 1 & m & 1 & (m) & 1 & m & 1 \\
\left\{ \quad \right. & \begin{array}{c} 2_{r-s} \\ n_{s,2} \end{array} & - & - & \begin{pmatrix} 3^+_3 \\ \bar{3}^+ \\ 6^-_6 \\ \bar{6}^- \end{pmatrix} & \begin{array}{c} 2_s \\ n_{r-s,2} \end{array} & - & - \quad \left. \right\}
\end{array}
$$

Metric parameters

- Metric parameters of OD groupoids:
  - Lattice metrics of one layer (*a*, *b*, *γ*).
  - Layer widths.
  - Metric parameters of σ-POs (*r*, *s*).
  - Origin shifts of adjacent layers (*r*, *s*).
- Parameters *r*, *s* may be fixed by atoms located at the layer interface.
- In triclinic and monoclinic/rectangular OD groupoids:
  - For convenience, stacking vectors $\mathbf{a}_0$, $\mathbf{b}_0$ or $\mathbf{c}_0$ may be chosen not perpendicular to the layer planes.
  - Some metric parameters of σ-POs become 0. In return, angle of the stacking vector to the layer plane must be specified.



$$\begin{array}{cccccc} P & 1 & 2/m & (1) & \\ \{ & \bar{1} & 2_r/n_{2,s} & (\bar{1}) & \} \end{array} \quad \Rightarrow \quad \begin{array}{cccccc} P & 1 & 2/m & (1) & \\ \{ & \bar{1} & 2_r/c_2 & (\bar{1}) & \} \end{array}$$

Metric parameters

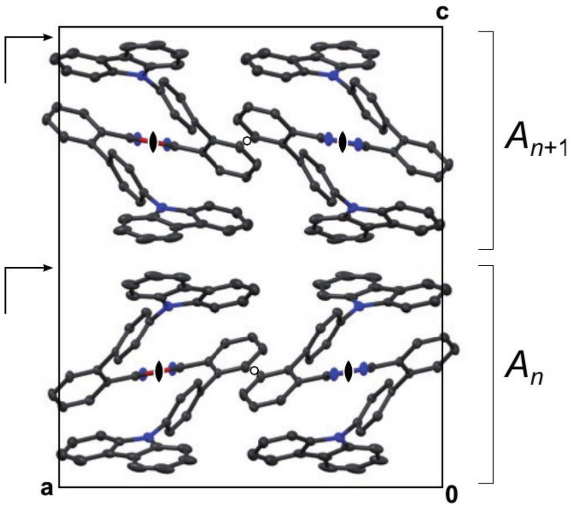
- OD groupoids can adopt special metric parameters for which the number of stacking possibilities change:

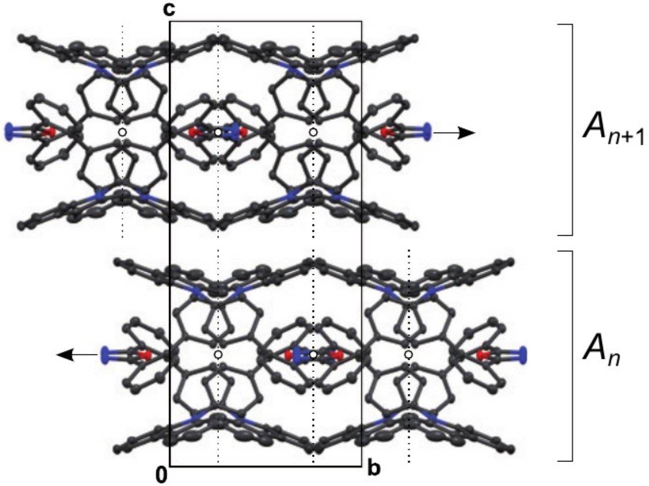
$$\begin{array}{ccccc} P & m & a & (m) & \\ \{ & 2_{-1+r}/n_{s,2} & 2_s/n_{2,-1+r} & (2_2/n_{r,s}) & \} \end{array}$$

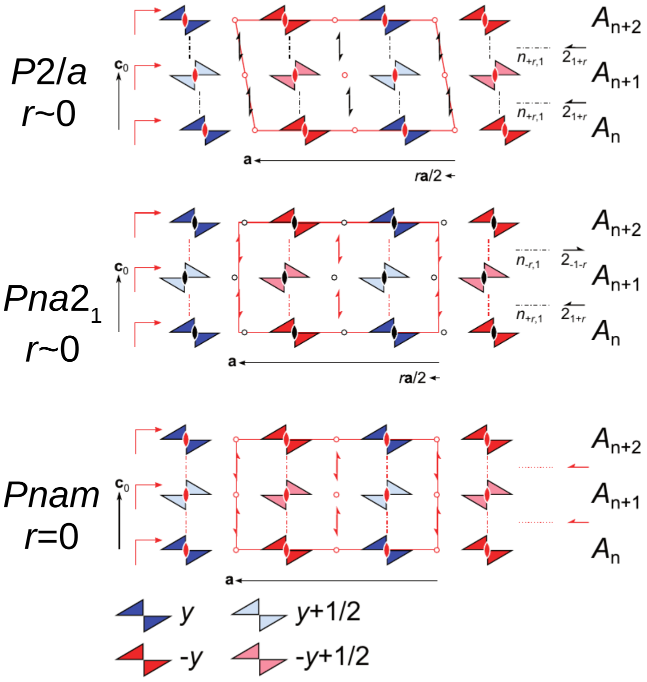
1. *general*: $Z = [Pma(2) : P11(1)] = 4$
2. $r \in \mathbb{Z}$: $Z = [Pma(2) : Pm1(1)] = 2$
3. $s \in \mathbb{Z}$: $Z = [Pma(2) : P1a(1)] = 2$
4. $r, s \in \mathbb{Z}$: $Z = [Pma(2) : Pma(2)] = 1$

Metric parameters

- The metric parameters can act as a measure of deviation from symmetry.
- Example:
  - Organic molecule
  - *s*=1, *r*~0.
  - For *r*=0: fully ordered, *Pnam*
  - Actual structure: $Pna2_1$



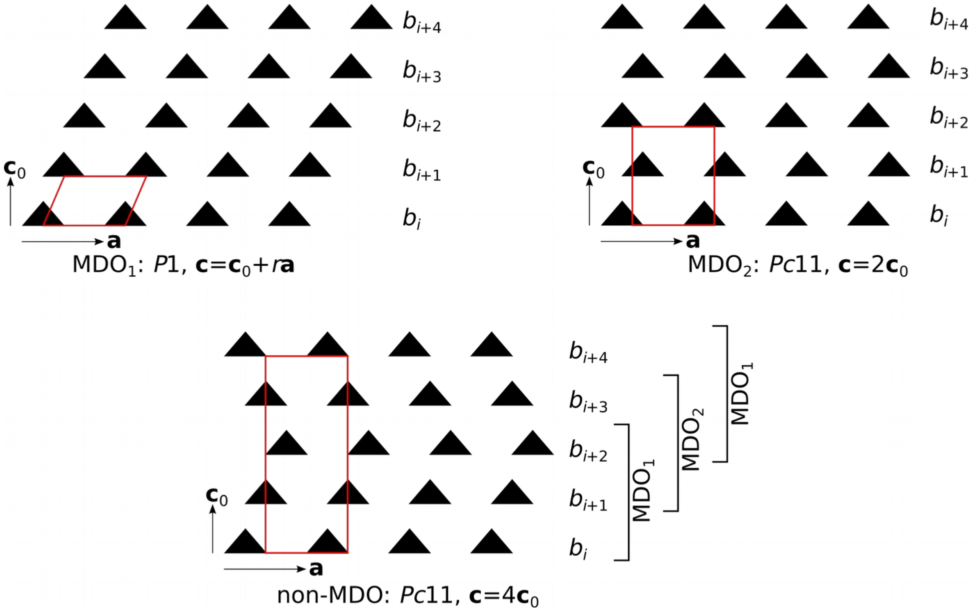




$$
\begin{array}{cccccc}
P & 1 & 2/a & & (1) & \\
\{ & 2_{r-1}/n_{s,2} & & - & (2_2/n_{r,s}) & \}
\end{array}
$$

MDO polytypes

- Polytypes that can not be decomposed into simpler polytype are said to be of a *maximum degree of order* (MDO).
- *Usually* in an MDO polytype not only all pairs, but also triples, quadruples, *n*-tuples of consecutive layers are equivalent.
- For any OD family, there is a finite number of MDO polytypes.
  - The symmetry of the MDO polytypes depends on the OD groupoid family and the metric parameters.



K. Dornbeger-Schiff. Geometrical Properties of MDO Polytypes and Procedures for their Derivation. *Acta. Cryst.* **A**38, 483-491, 1982.

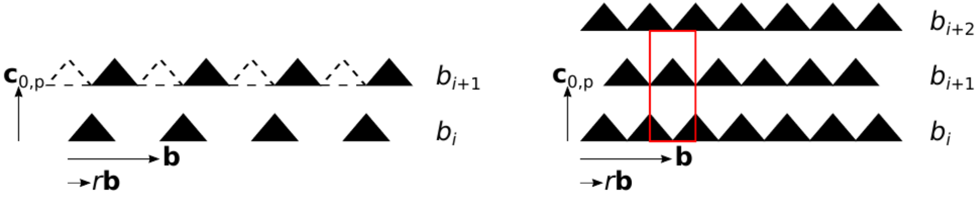
MDO polytypes

- All stackings can be decomposed into fragments of MDO polytypes:
  - A non-MDO polytype is a ordered succession of MDO fragments.
  - A twin can be an MDO polytype with fragments of other MDO polytypes at the twin boundary.
  - A disordered stacking can be described as an (weighted) overlay of MDO polytypes.
  - …
- The MDO polytypes can be considered as the “alphabet” of an OD family.
- In many cases if a $L_iL_{i+1}L_{i+2}$ triple is preferred during crystal growth, an MDO polytype is formed
  - In most cases (though not all) ordered bulk polytypes are of the MDO kind!

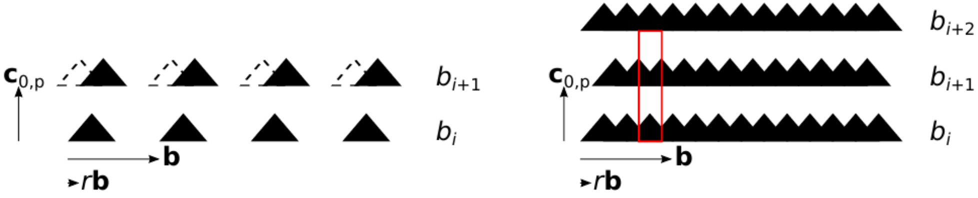
K. Dornbeger-Schiff. Geometrical Properties of MDO Polytypes and Procedures for their Derivation. *Acta. Cryst.* **A**38, 483-491, 1982.

Family structure

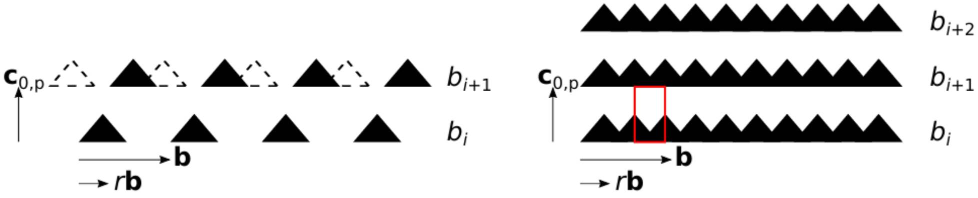
- The family structure is an equal overlap of all stacking possibilities.
- The symmetry of the family structure is obtained by extending all POs of a member to global operations and using these as group generator.
- The symmetry depends on the metric parameters *r*,*s*.
  - For irrational *r* or *s*, the symmetry is *not* a spacegroup!



(a) $r = \frac{1}{4}$, Am



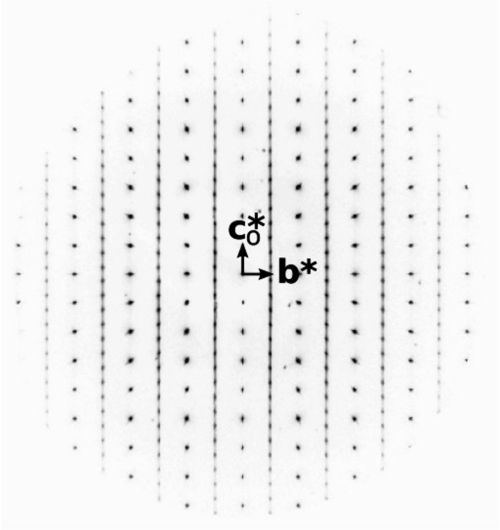
(b) $r = \frac{1}{8}$, Am



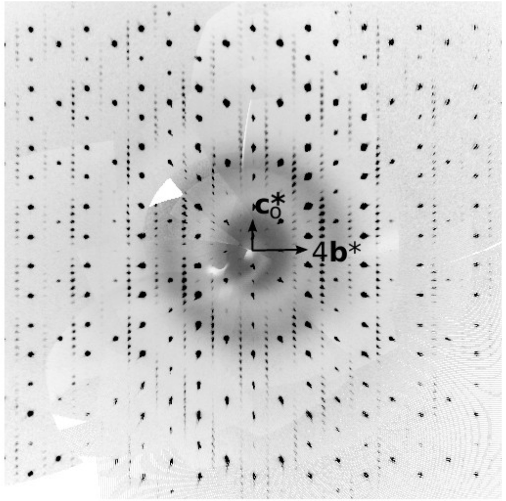
(c) $r = \frac{1}{3}$, Pm

Family structure

- Reflections corresponding the family structure (=family reflections) are always sharp.
  - These are realized for the whole stacking.
- Reflections of individual polytypes (=characteristic reflections) are sharp or diffuse.
  - Depends on the degree of order of the polytype.
  - Hence the name “order-disorder”.



$MgTeO_8H_8$: disordered polytypes



$KOH{\cdot}2H_2O$: ordered polytypes

Family structure

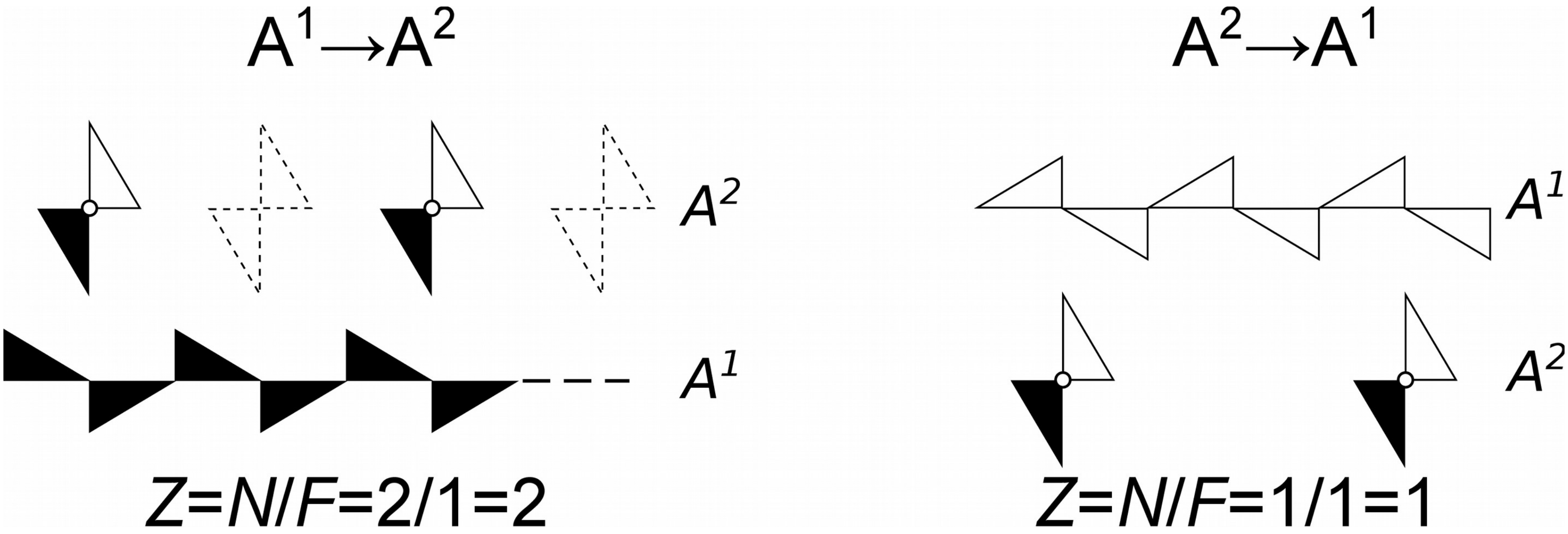
- Coset decomposition of point group of polytype in point group of family structure
  - Possible orientation domain states (twin individuals).
- Coset decomposition of space group of polytype in space group of family structure
  - Possible orientation and translation domain states (twin individuals and antiphase domains).

Maximum equivalence regions

- By definition (VC) pairs L_iL_{i+1} of adjacent layers are equivalent in all members of an OD family.
- In some OD families also $L_iL_{i+1}L_{i+2}$ triples are geometrically equivalent in all members of the OD family.
- The largest n-tuples $L_iL_{i+1}...L_{i+n-1}$ of consecutive layers layers that are geometrically equivalent in all members of an OD family are called maximum equivalence regions (MERs).
- If parts of an OD structure are part of more than 2 MERs, the choice of OD layers is ambiguous.

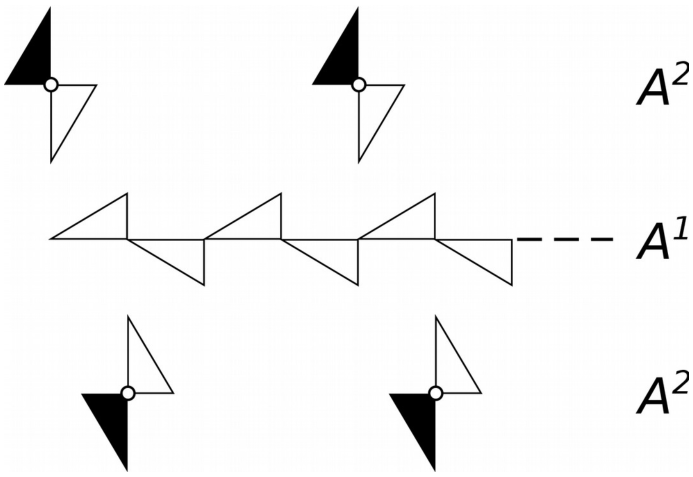
H. Grell: “How to choose OD layers”, *Acta Cryst.* A**40**, 95–99 (1984).

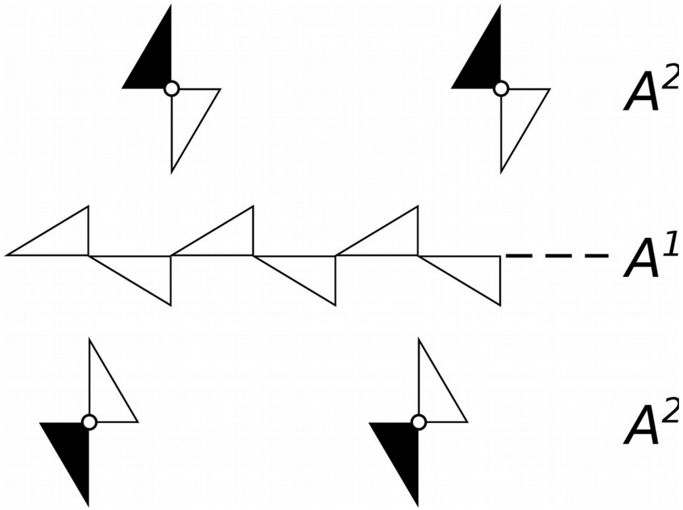
$K_2HAsO_4 \cdot 2,5H_2O$: layer pairs



$K_2HAsO_4 \cdot 2{,}5H_2O$: triples, etc.

- one kind of $A^1A^2A^1$ triple (follows directly from NFZ)
- one kind of $A^2A^1A^2$ triple
- one kind of $A^1A^2A^1A^2A^1$ quintupel
- two kinds of hexuples



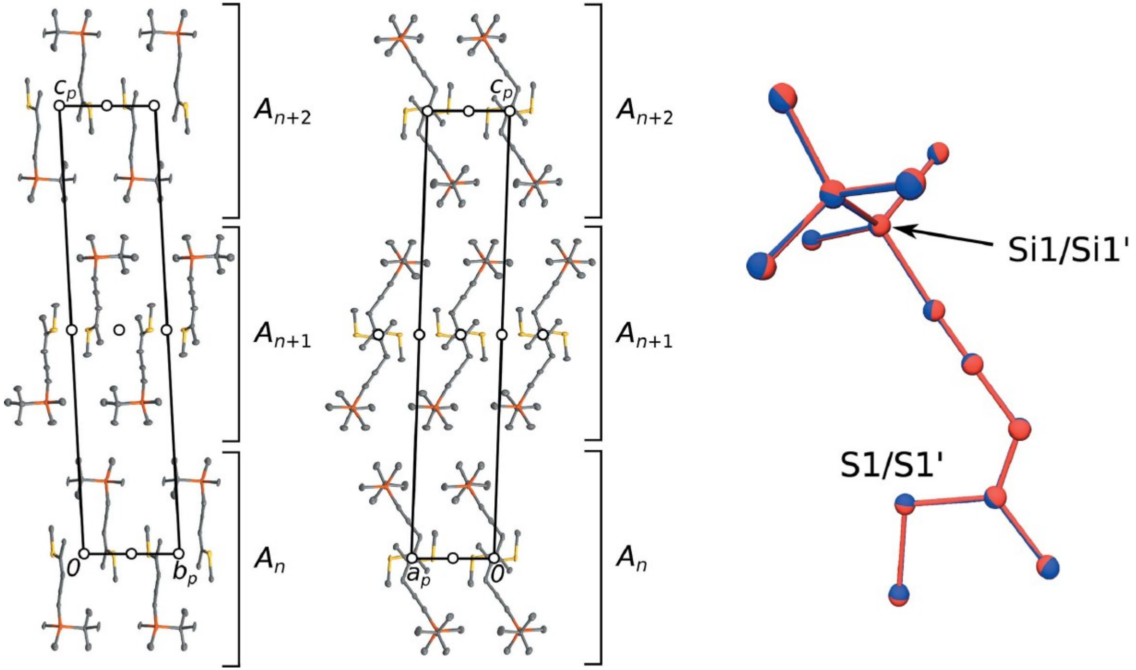


Desymmetrization

- An OD description is usually an *idealized* description.
- In actual polytypes, some POs will only be realized approximately.
- Deviation from ideal symmetry: *desymmetrization*.
- Seemingly paradox:
  - Disorder → higher symmetry (extreme: family structure)
  - Order → lower symmetry.
- Desymmetrization is one way of growing ordered polytypes:
  - The polytypes are not perfectly locally equivalent.
- For an OD description to be valid, desymmetrization should be reasonably small.
  - Excessive desymmetrization: These are not (OD) polytypes anymore.

Desymmetrization

- TBDMS-capped (3Z)-4-(methylthio)-3-penten-1-yne
  - OD structure with negligible desymmetrization



Desymmetrization

- TIPS-capped (3Z)-4-(methylthio)-3-penten-1-yne
  - OD structure with strong desymmetrization if described as composed of one kind of layer
  - Decompose into two layers and the desymmetrization vanishes