International School on Fundamental Crystallography
Uberlândia, Brazil, 25 November - 3 December 2012

# Twinned crystals: definitions

Massimo Nespolo, Université de Lorraine, France
massimo.nespolo@crm2.uhp-nancy.fr

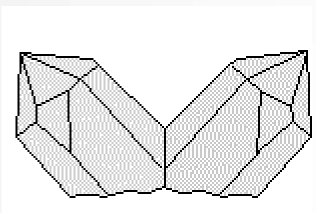
# What is a twin?

With space group

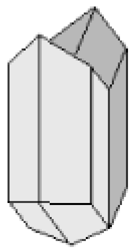
No space group

A twin is a heterogeneous edifice built by homogeneous crystals (individuals) of the same phase in different orientations, related by an operation (the twin operation) that does not belong to the point group of the individual.

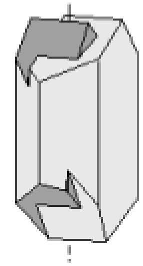
# Mapping of individuals in twins



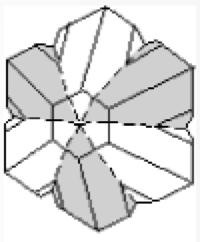
Reflection in $\{11\bar{2}2\}$



Reflection in (100)



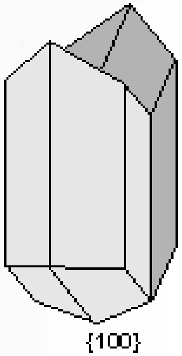
Rotation about [001]



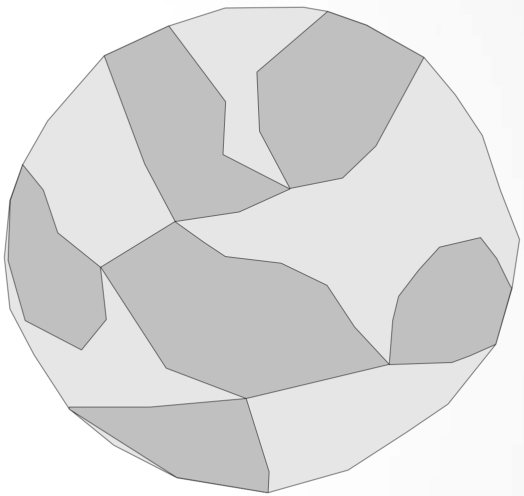
Reflection in {031} (cyclic twin)

**Twinning is a point-group phenomenon**

# Definition




Two individuals

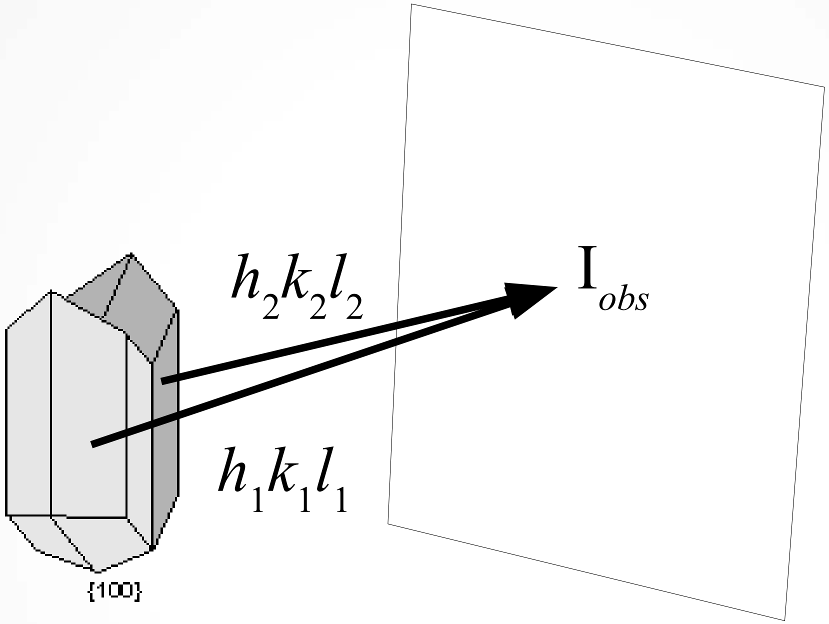


Two orientation domains (domain states, variants) with N domains

# Problems related to twins. I. Effects of twinning on the diffraction pattern.

- Because twinning is a point group phenomenon, intensities from twins do not interfere but simply sum up.
- This means that there is no phase relation between diffractions from different individuals.
- The measured intensities are the sum of the intensities from the individuals weighted by the volumes of the individuals.

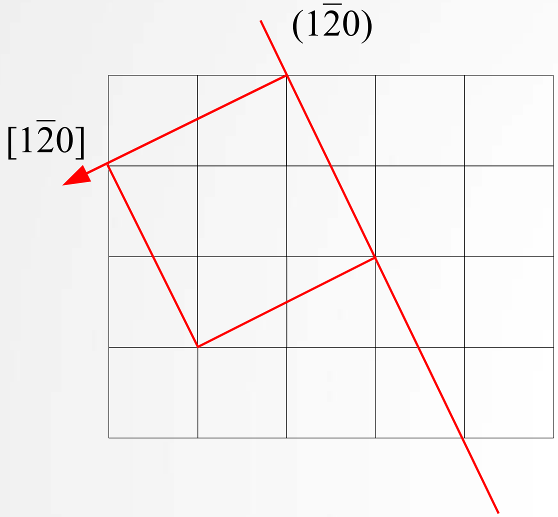
# Problems related to twins. I. Effects of twinning on the diffraction pattern.




$$I_{obs} = V_{I1}I(h_1k_1l_1)+(1\text{-}V_{I1})I(h_2k_2l_2)$$

For $n$ individuals: $I_{obs} = \Sigma_n V_{In} I(h_nk_nl_n)$

# $\{1\bar{2}0\}$ twin in melilite ($P\bar{4}2m$)




$$\langle \boldsymbol{abc}|_I \begin{bmatrix} 1 & 2 & 0 \\ \bar{2} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \langle \boldsymbol{abc}|_T$$

Miller indices are covariant

$$\langle hkl|_I \begin{bmatrix} 1 & 2 & 0 \\ \bar{2} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \langle hkl|_T$$

Representation of the twin operation in the twin basis

$$\begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

# Find non-equivalent reflections related by the twin operation

- Express the indices of the reflections in the basis of the twin.
- Apply the twin operation in the basis of the twin and get the indices of the reflection related by twinning.
- Transform back the indices of this new reflection in the basis of the individual.

# Effect of {1$\bar{2}$0} twinning on 3$\bar{1}$1 reflection

3$\bar{1}$1 Reflection from individual 1 in the setting of the twin

$$\langle 3\,\bar{1}\,1|_I \begin{bmatrix} 1 & 2 & 0 \\ \bar{2} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \langle 551|_T$$

Reflection from individual 2

$$\langle 551|_T \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \langle \bar{5}51|_T$$

Reflection from individual 2 in the setting of individual 1

$$\langle \bar{5}51|_T \begin{bmatrix} 1 & 2 & 0 \\ \bar{2} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}^{-1} = \langle \bar{5}51|_T \begin{bmatrix} 1/5 & \bar{2}/5 & 0 \\ 2/5 & 1/5 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \langle 131|_I$$

# $3\bar{1}1$ and 131 are not equivalent in $P\bar{4}2m$

$$\langle 3\,\bar{1}\,1| \begin{bmatrix} 0 & 1 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \langle 1\,3\,1|$$

Determinant = +1

Trace = +1

Symmetry operation = $4^{-}_{[001]}$

$$4_{[001]} \notin \bar{4}2m$$

# Effect of $\{1\bar{2}0\}$ twinning on 100 reflection

Reflection from individual 1

$$\langle 100|_I \begin{bmatrix} 1 & 2 & 0 \\ \bar{2} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \langle 120|_T$$

Reflection from individual 2

$$\langle 120|_I \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \langle \bar{1}20|_T$$

Reflection from individual 2 in the setting of individual 1

**Non integers!**

$$\langle \bar{1}20|_T \begin{bmatrix} 1 & 2 & 0 \\ \bar{2} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}^{-1} = \langle \bar{1}20|_T \begin{bmatrix} 1/5 & \bar{2}/5 & 0 \\ 2/5 & 1/5 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \left\langle \frac{3}{5}\,\frac{4}{5}\,0 \right|_I$$

# Effect of $\{1\bar{2}0\}$ twinning on 100 reflection

**Norm of the vectors in reciprocal space**

$$\sqrt{\langle 100| \begin{bmatrix} 1/a^2 & 0 & 0 \\ 0 & 1/a^2 & 0 \\ 0 & 0 & 1/c^2 \end{bmatrix} |100\rangle} = 1/a$$

$$\sqrt{\left\langle \frac{3}{5}\frac{4}{5}0 \right| \begin{bmatrix} 1/a^2 & 0 & 0 \\ 0 & 1/a^2 & 0 \\ 0 & 0 & 1/c^2 \end{bmatrix} \left| \frac{3}{5}\frac{4}{5}0 \right\rangle} = 1/a$$

# Effect of $\{1\bar{2}0\}$ twinning on 100 reflection

A reflection from individual **1** is repeated by the twin operation in a position where there is no reflection from the individual **2**.

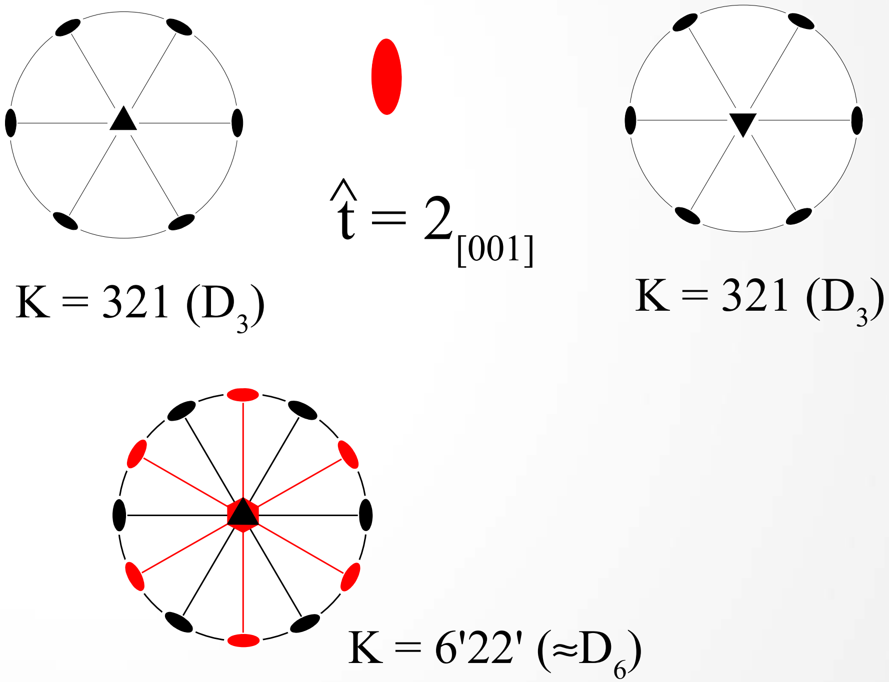
If the second position is not rational (non-integer indices) the software will not find the unit cell of the individual, but only that of the twin, without knowing it is a twin.

It the second position is rational but correspond to an absent reflection from individual 2, then the systematic absences are affected and you won't get the right space group.

In any case, you won't be able to refine the structure unless you into account the presence of twinning.

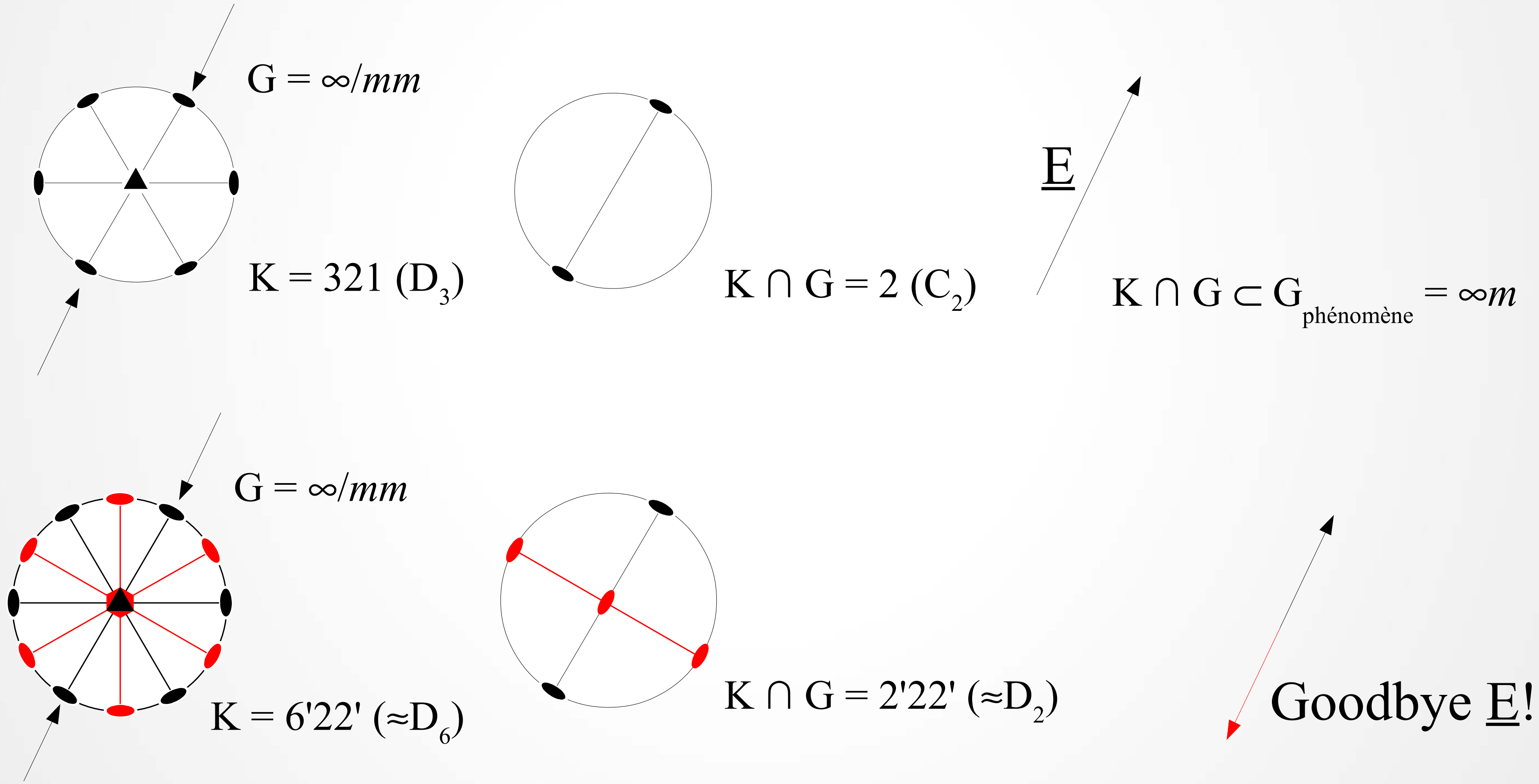
# Problems related to twins. II. Effects of twinning on physical properties.

## Swiss twin in α quartz



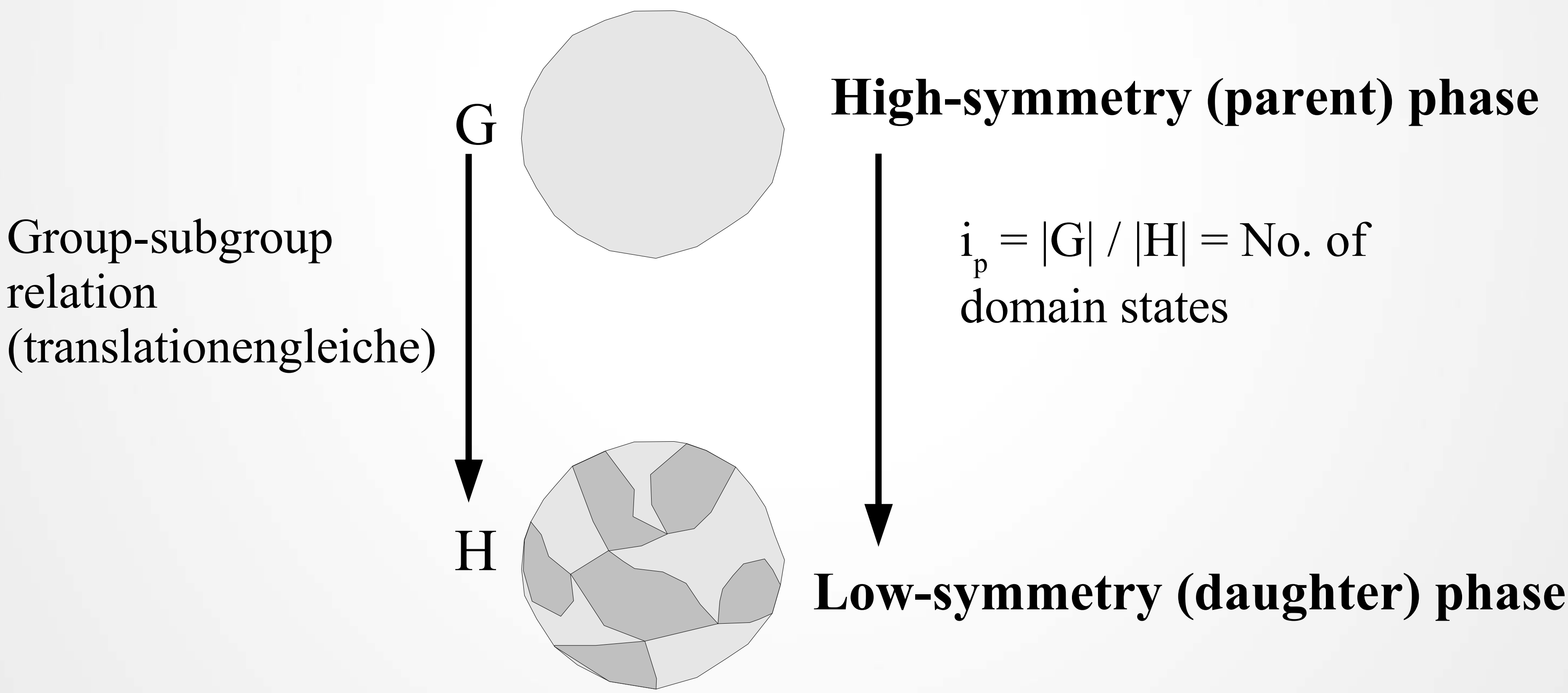

## Killing of piezoelectricity

# Interpretation of piezoelectricity in α quartz by Curie law



# Genetic classification of twins - 1

Transformation twins. Driving force: **symmetry change following a phase transition**



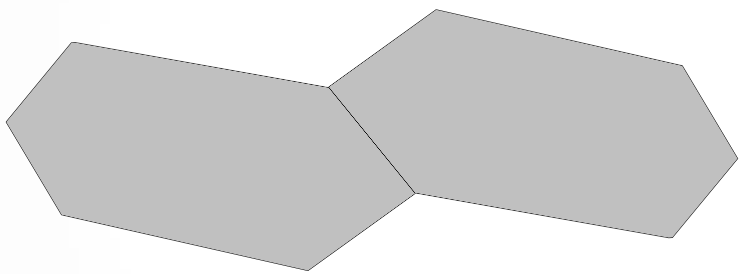
# Genetic classification of twins - 2

Mechanical twins. Driving force: the application of an **external force**

In general, no precise symmetry relation between the original crystal and the resulting twin.

# Genetic classification of twins - 3

Growth twins. Driving force: the "**randomness**" (errors in crystal growth or coalescence of nano or macrocrystals)



No symmetry relation between the original crystal and the resulting twin.

For the formation of the twin, the of the interface is important: a substructure must continue, precisely or approximately, across the interface.

# Symmetry of a twin

- $H_i$ is the point group of the i-th individual (same *type* for all the individuals)
- $H^*$ is the intersection group: $H^* = \cap_i H_i$.
- $\tilde{t}$ is a twin operation
- K is the (chromatic) point group obtained as extension of $H^*$ by $\tilde{t}$
- The coset decomposition of K in terms of $H^*$ gives $N = |K|/|H^*|$ cosets (twin laws), from each of which one coset representative (twin operation) is chosen.

|K| is the order of K

# Twin operation, twin element, twin law

- **Twin operation**: the isometry mapping the orientation of one individual onto the orientation of another individual.
- **Twin element**: the geometrical element in *direct space* (plane, axis, center) about which the twin operation is performed.
  - Correspondingly, twins are classified as reflection twins, rotation twins and inversion twins
- Twin law: the set of twin operations equivalent under the point group of the individual, obtained by coset decomposition.

# Example of twin law *vs.* twin operation & twin element

Crystal belonging to the geometric crystal class 2 (*b*-unique) twinned by 120º about [001]

$$\{1, 2_{[010]}\} \cup \{3^{+}_{[001]}, 2_{[110]}\} \cup \{3^{-}_{[001]}, 2_{[100]}\}$$

Two twin laws: the two cosets $\{3^{+}_{[001]}, 2_{[110]}\}$ and $\{3^{-}_{[001]}, 2_{[100]}\}$

Four twin operations – the four operations in the two cosets

Three twin elements: [001], [110] and [100]

Symmetry of the twin expressed by a trichromatic point group (twin point group): $(3^{(3)}2^{(2,1)})^{(3)}$

# Lattice restoration vs. structure restoration

- The lattice represents the periodicity of the crystal structure.
- A high degree of lattice restoration is a necessary, although not sufficient, condition for a good structural match across the interface.
- The lattice restoration is measured by the twin index $\boldsymbol{n}$ (inverse of the fraction of the lattice nodes restored by the twin operation) and by the obliquity $\boldsymbol{\omega}$ (deviation from perfect restoration).

# Twin lattice and twin index

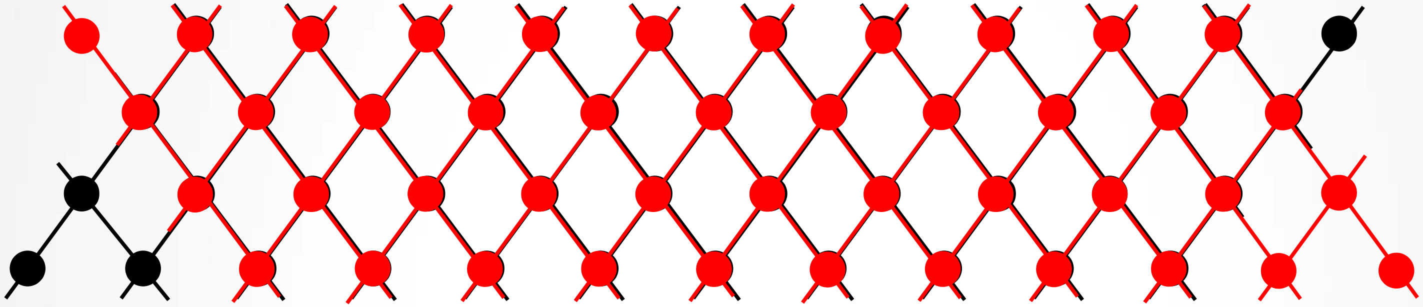
- The twin index is the number of lattice nodes restored or quasi-restored by the twin operation.
- The (quasi)-restored nodes define a lattice, the **twin lattice**.
- (Quasi)-restored nodes define the cell based on the pair of elements (plane/direction) defining the cell of the twin lattice.
- The twin lattice either coincides with the lattice of the individual (twinning by merohedry) or is a sublattice of it (twinning be reticular merohedry/polyholohedry).

# Reticular classification of twins

## Categories of twins: lattice quasi-restoration and symmetry of the twin lattice

**Hereafter K is the achromatic point group isomorphic to the chromatic twin point group**

# Twinning by merohedry



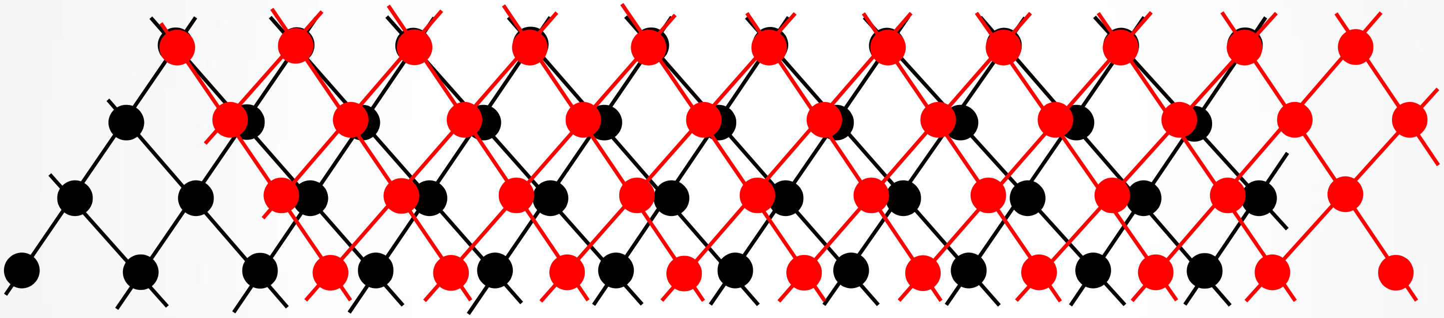
All nodes are restored by the twin operation: we say that **the twin index is *n* = 1**

$$H^* = H;\ K \supset H$$

# Subclassificaton of twinning by merohedry

- H = point group of the individual
- D = holohedral point group of the individual
- D($\mathbf{L}_{ind}$) = point group of the lattice of the individual
- D($\mathbf{L}_T$) = point group of the lattice of the twin
- If D($\mathbf{L}_{ind}$) > D the individual has a specialized metric
- If $\tilde{t} \in$ D, we speak of **syngonic merohedry**
- If $\tilde{t} \in$ D($\mathbf{L}_{ind}$) but $t \notin$ D, we speak of **metric merohedry**

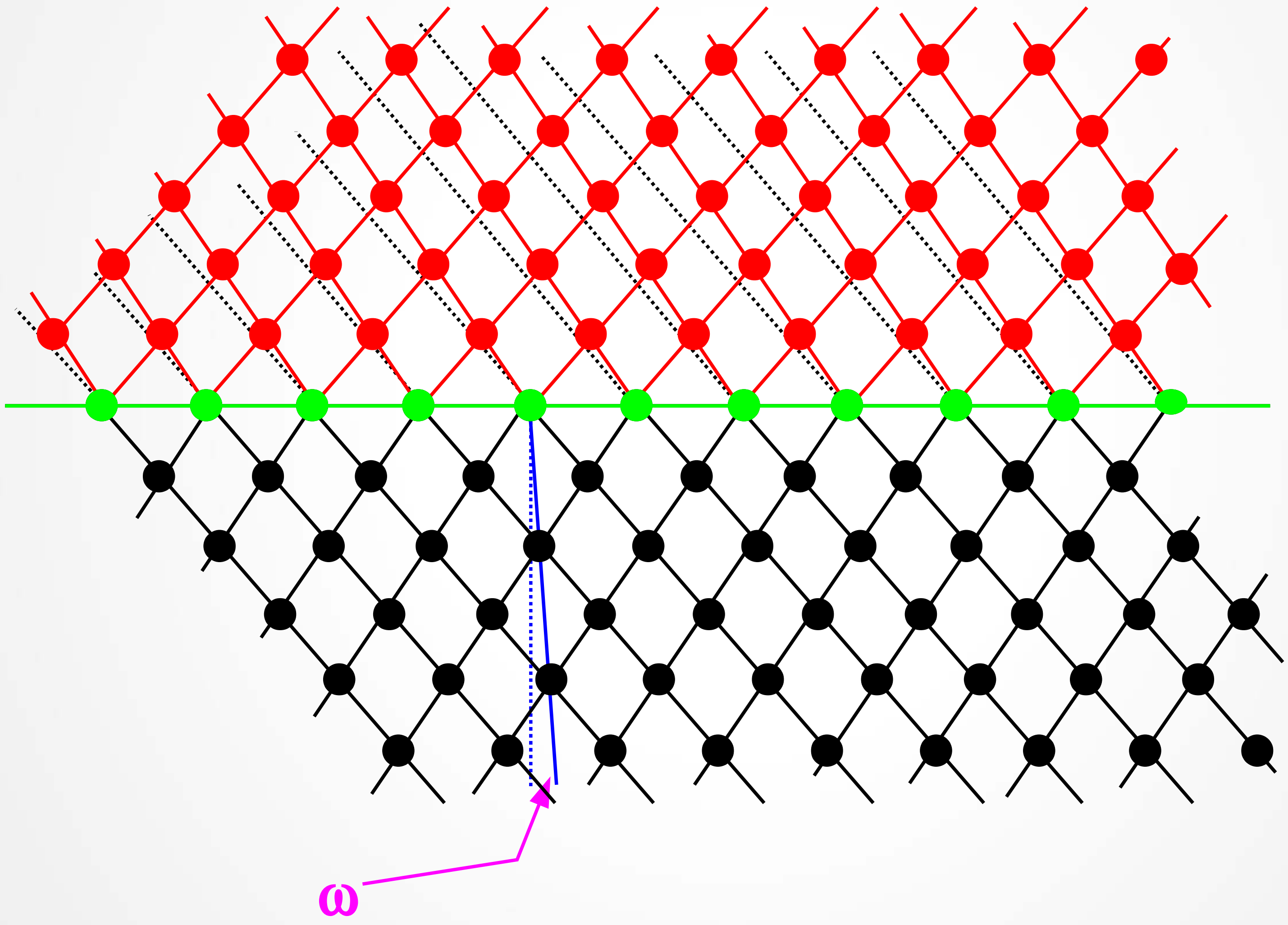
# Twinning by pseudo-merohedry



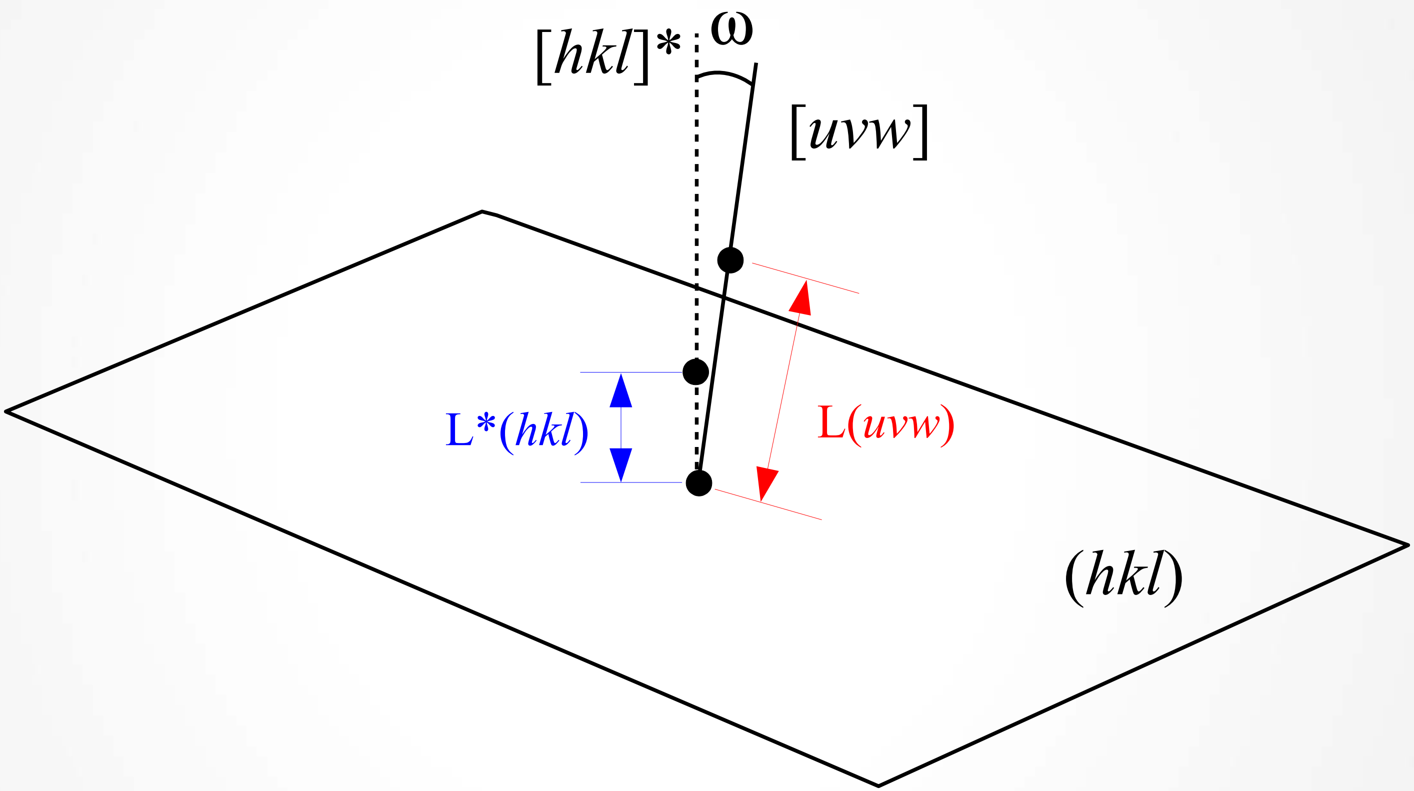
All nodes are *quasi*-restored by the twin operation: we say that **the twin index is *n* = 1**

$$H^* = H_{(\omega = 0)};\ K \supset H$$

# Definition of obliquity



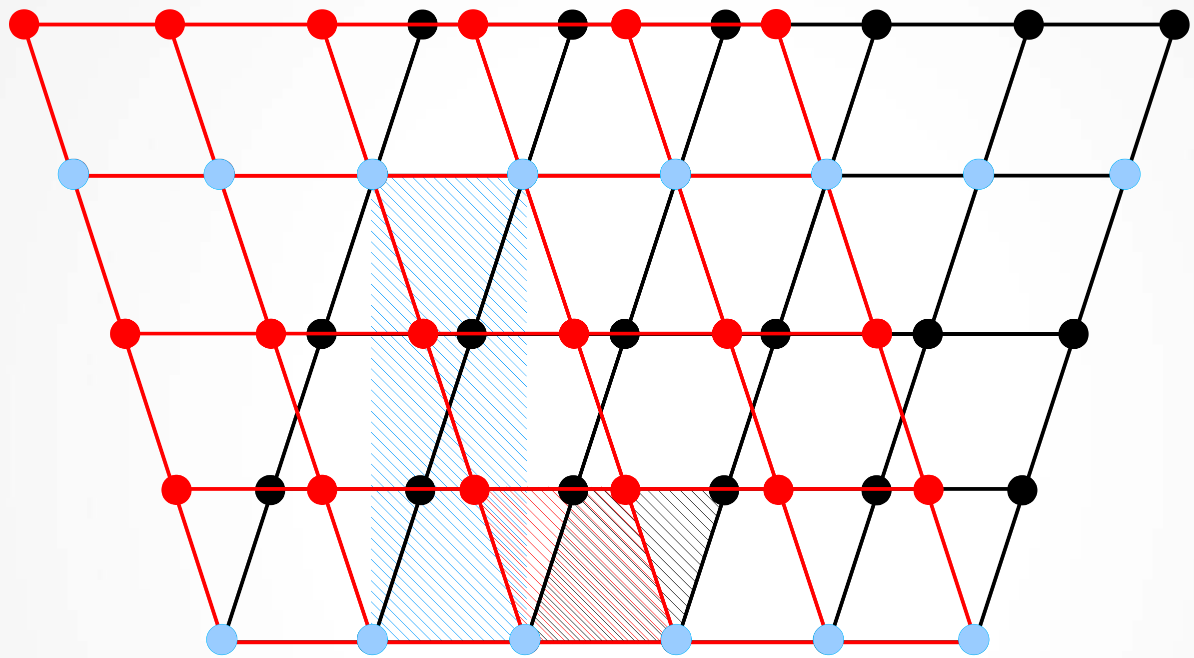
# Computation of the obliquity




$$L^*(hkl)L(uvw)\cos\omega = \langle hkl|\mathbf{a^*b^*c^*}\rangle\langle \mathbf{abc}|uvw\rangle = |hu+kv+lw|$$

$$\omega = \cos^{-1}|hu+kv+lw|/L^*(hkl)L(uvw)$$

# Twinning by reticular merohedry

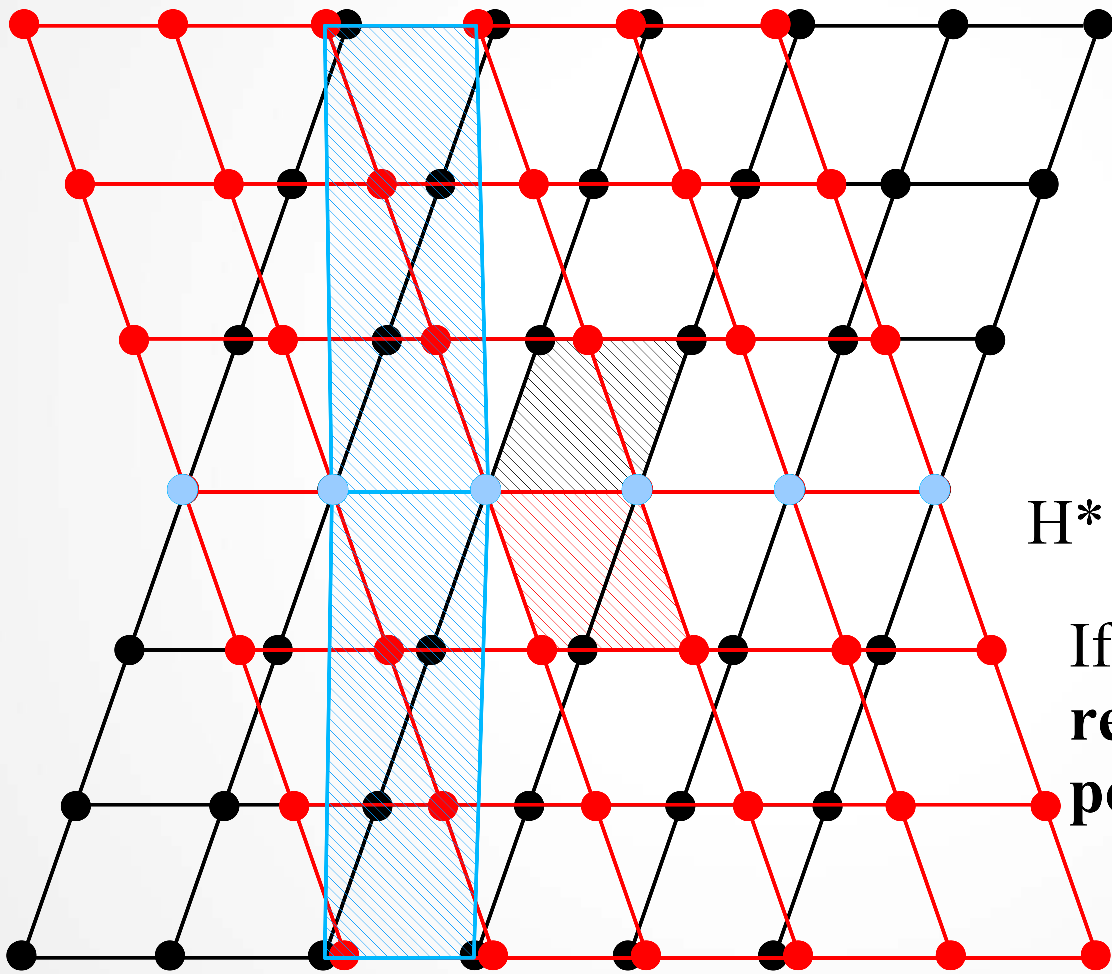


One node out of three is restored by the twin operation: we say that **the twin index is *n* = 3**

H* ≠ H; K ⊃ H*

If K = H we speak of **reticular polyholohedry**

# Twinning by reticular pseudo-merohedry



One node out of three is *quasi*-restored by the twin operation: we say that **the twin index is *n* = 3**

$H^* \neq H_{(\omega = 0)}$; $K \supset H^*$

If K = H we speak of **reticular pseudo-polyholohedry**

# Why a *reticular* theory of twinning?

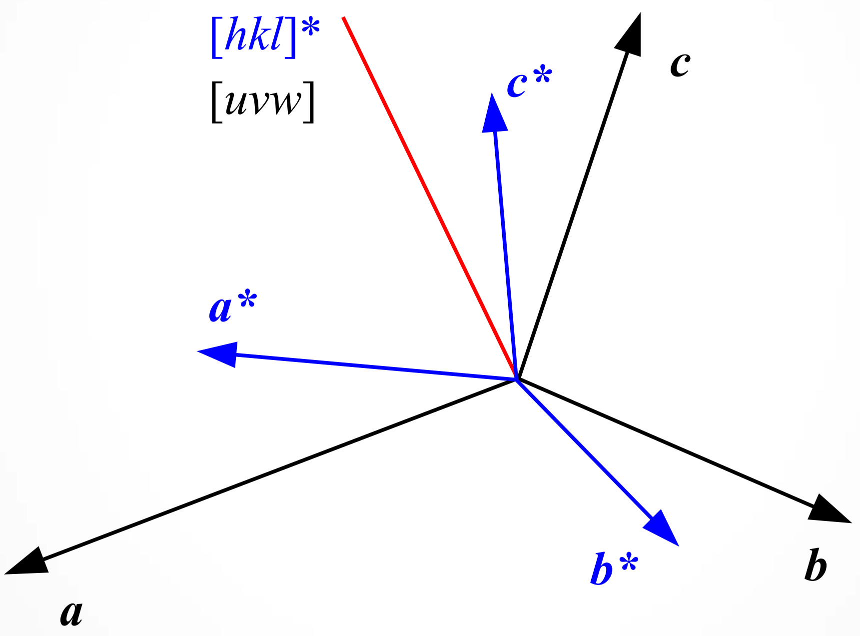
- Twinning is governed by the structural match at the interface of the individuals
- To study this structural match means to investigate twins *case by case*
- The reticular theory makes abstraction of the structure and concentrates on the lattice
- This approach is reasonable, although approximate, because the lattice represents the periodicity of the structure
- A good lattice match is a necessary, although not sufficient, condition for a good structural match

# Probability occurrence of twins in term of the reticular theory

- A twin is a “mistake” or a “compromise”
- A coherent or semi-coherent interface is necessary for a twin to form
- The better is the “atomic restoration” the higher is the probability that a twin occurs
- The analysis of the atomic restoration reduces the study of twins almost to a “case-by-case” investigation (but see what I have to say later...)
- The reticular theory allows a general approach in terms of lattice restoration as a necessary (not sufficient) condition
- The lower are the twin index and the obliquity, the higher is the probability that a twin occurs

# How to find the direction [*uvw*] quasi-perpendicular to (*hkl*)?

Easy! Find the irrational expression of [*hkl*]* in direct space




How?

# Easy!

Find $u,v,w$ (in general non-integer) satisfying:

$$\langle hkl|\boldsymbol{a}^*\boldsymbol{b}^*\boldsymbol{c}^*\rangle = \langle uvw|\boldsymbol{abc}\rangle$$

$$\langle hkl|\mathbf{I}|\boldsymbol{a}^*\boldsymbol{b}^*\boldsymbol{c}^*\rangle = \langle uvw|\boldsymbol{abc}\rangle$$

$$\langle hkl|\mathbf{G}^*\mathbf{G}|\boldsymbol{a}^*\boldsymbol{b}^*\boldsymbol{c}^*\rangle = \langle uvw|\boldsymbol{abc}\rangle$$

$$\langle hkl|\mathbf{G}^*|\boldsymbol{abc}\rangle\langle\boldsymbol{abc}|\boldsymbol{a}^*\boldsymbol{b}^*\boldsymbol{c}^*\rangle = \langle uvw|\boldsymbol{abc}\rangle$$

$$\langle hkl|\mathbf{G}^*|\boldsymbol{abc}\rangle 3 = \langle uvw|\boldsymbol{abc}\rangle$$

$$\langle hkl|\mathbf{G}^* = \langle uvw|$$

and of course... $\langle uvw|\mathbf{G} = \langle hkl|$

# Exercise

Celestine, $SrSO_4$, *Pbnm* $a = 8.359Å$, $b = 5.352Å$, $c = 6.866Å$,

Twinned on (210)

Find the directions quasi-perpendicular to (210) and CHOOSE ONE!

$$\langle 210| \begin{vmatrix} 1/a^2 & 0 & 0 \\ 0 & 1/b^2 & 0 \\ 0 & 0 & 1/c^2 \end{vmatrix} = \langle 0.02862 \quad 0.03491 \quad 0| = \langle 1 \quad 1.220 \quad 0|$$

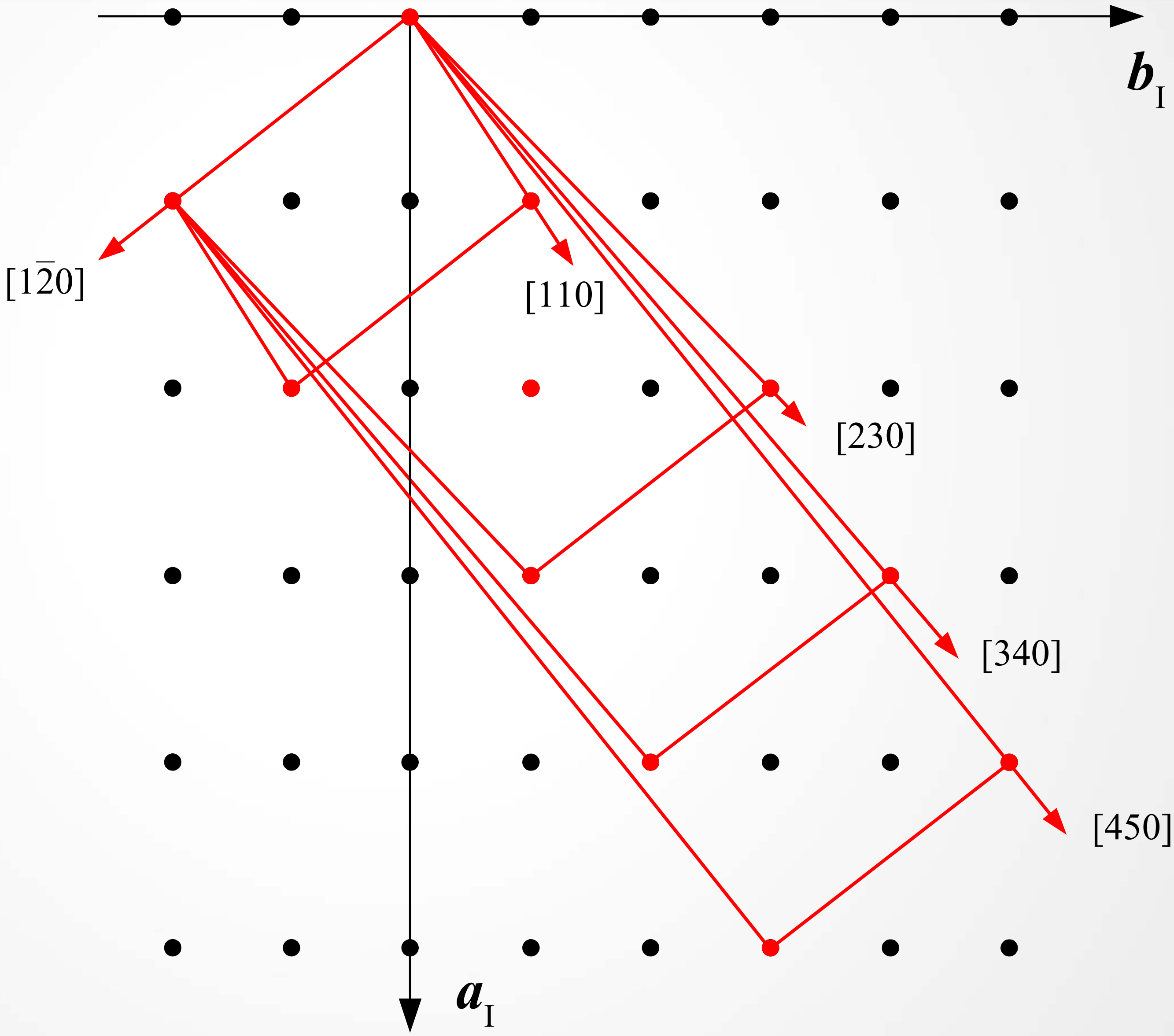
| ***u*** | ***v*** | ***v/u*** |
|---|---|---|
| 1 | 1 | 1 |
| 1 | 2 | 2 |
| 2 | 3 | 1.5 |
| 3 | 4 | 1.333 |
| 4 | 5 | 1.25 |

# Calculate the obliquity

$$\omega = \cos^{-1}|hu+kv+lw|/L^*(hkl)L(uvw) = \cos^{-1}\frac{\langle hkl|uvw\rangle}{\sqrt{\langle hkl|\mathbf{G}^*|hkl\rangle}\sqrt{\langle uhv|\mathbf{G}|uvw\rangle}}$$

| ***uvw*** | **$\omega$** |
|---|---|
| 110 | 5.36° |
| ~~120~~ | ~~14.03°~~ |
| 230 | 5.86° |
| 340 | 2.50° |
| 450 | 0.69° |

# Exercise: results




| *uvw* | ω |
|---|---|
| 110 | 5.36º |
| 230 | 5.86º |
| 340 | 2.50º |
| 450 | 0.69º |

# Summary

| *uvw* | $\omega$ | *n* |
|---|---|---|
| 110 | 5.36º | 3 |
| 230 | 5.86º | 7 |
| 340 | 2.50º | 5 |
| 450 | 0.69º | 13 |

# Cell parameters of the twin lattice

A matter of basis transformation....

$$\langle \mathbf{a} \quad \mathbf{b} \quad \mathbf{c} | \mathbf{P} = \langle \mathbf{a}' \quad \mathbf{b}' \quad \mathbf{c}' |$$

$$\mathbf{G}' = | \mathbf{a}' \quad \mathbf{b}' \quad \mathbf{c}' \rangle \langle \mathbf{a}' \quad \mathbf{b}' \quad \mathbf{c}' | =$$

$$= \mathbf{P}^t | \mathbf{a} \quad \mathbf{b} \quad \mathbf{c} \rangle \langle \mathbf{a} \quad \mathbf{b} \quad \mathbf{c} | \mathbf{P} = \mathbf{P}^t \mathbf{G} \mathbf{P}$$

$$\mathbf{P} = \begin{vmatrix} u_{1,hkl} & u_{2,hkl} & u_{\perp} \\ v_{1,hkl} & v_{2,hkl} & v_{\perp} \\ w_{1,hkl} & w_{2,hkl} & w_{\perp} \end{vmatrix}$$

**But check the determinant!**

$[u_{1,hkl} v_{1,hkl} w_{1,hkl}]$ and $[u_{2,hkl} v_{2,hkl} w_{2,hkl}]$ are contained in ($hkl$)
(choose the shortest!)

$[u_{\perp} v_{\perp} w_{\perp}]$ is the direction quasi-perpendicular to ($hkl$)

# Directions [*uvw*] contained in a plane (*hkl*)

A plane of the family (*hkl*) which passes through the origin is $hx+ky+lz = 0$.

A direction [*uvw*] passes through the origin and the node *uvw*.

The direction [*uvw*] is contained in the plane (*hkl*) if $hu+kv+lw = 0$.

Calculate the cell parameters of the (210) twin in celestine.

# Cell parameters of the (210) twin in celestine

$$[u_{1,hkl} v_{1,hkl} w_{1,hkl}] = [001]$$

$$[u_{2,hkl} v_{2,hkl} w_{2,hkl}]\ [1\bar{2}0]$$

$$[u_{\perp} v_{\perp} w_{\perp}]=[340]$$

$$\mathbf{P} = \begin{vmatrix} 0 & 1 & 3 \\ 0 & \bar{2} & 4 \\ 1 & 0 & 0 \end{vmatrix}$$

$$|\mathbf{P}| = 10 > 0$$

N.B. $n = 5$ but $|\mathbf{P}| = 10$. Why?

# Cell parameters of the (210) twin in celestine

$$\mathbf{P}^t\mathbf{G}\mathbf{P} = \begin{vmatrix} 0 & 0 & 1 \\ 1 & \bar{2} & 0 \\ 3 & 4 & 0 \end{vmatrix} \begin{vmatrix} a^2 & 0 & 0 \\ 0 & b^2 & 0 \\ 0 & 0 & c^2 \end{vmatrix} \begin{vmatrix} 0 & 1 & 3 \\ 0 & \bar{2} & 4 \\ 1 & 0 & 0 \end{vmatrix} =$$

$$= \begin{vmatrix} 0 & 0 & c^2 \\ a^2 & -2b^2 & 0 \\ 3a^2 & 4b^2 & 0 \end{vmatrix} \begin{vmatrix} 0 & 1 & 3 \\ 0 & \bar{2} & 4 \\ 1 & 0 & 0 \end{vmatrix} = \begin{vmatrix} c^2 & 0 & 0 \\ 0 & a^2 + 4b^2 & 3a^2 - 8b^2 \\ 0 & 3a^2 - 8b^2 & 9a^2 + 16b^2 \end{vmatrix}$$

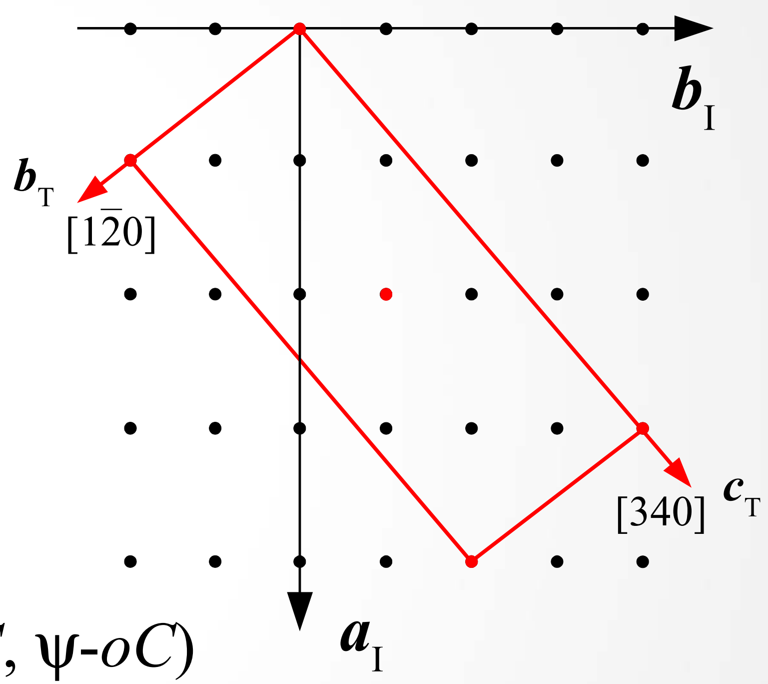
$$a_{\mathrm{T}} = c_{\mathrm{I}} = 6.866\ \text{Å} \qquad b_{\mathrm{T}} = 13.581\ \text{Å} \qquad c_{\mathrm{T}} = 32.972\ \text{Å}$$

$$\alpha_{\mathrm{T}} = \cos^{-1}\frac{3a^2 - 8b^2}{b_{\mathrm{T}}c_{\mathrm{T}}} = \cos^{-1}\frac{-19.533}{13.581 \cdot 32.972} =$$

$$= \cos^{-1}\left(-0.0436\right) = 92.50^{\circ}$$

# Twin lattice and pseudo-symmetry of (210) twin in celestine

$a_T$ 6.866 Å; $b_T$ = 13.581 Å:
$c_T$ = 32.972 Å; $\alpha_T$ = 92.50º




*mA*, ψ-*oA* (easily transformed to *mC*, ψ-*oC*)

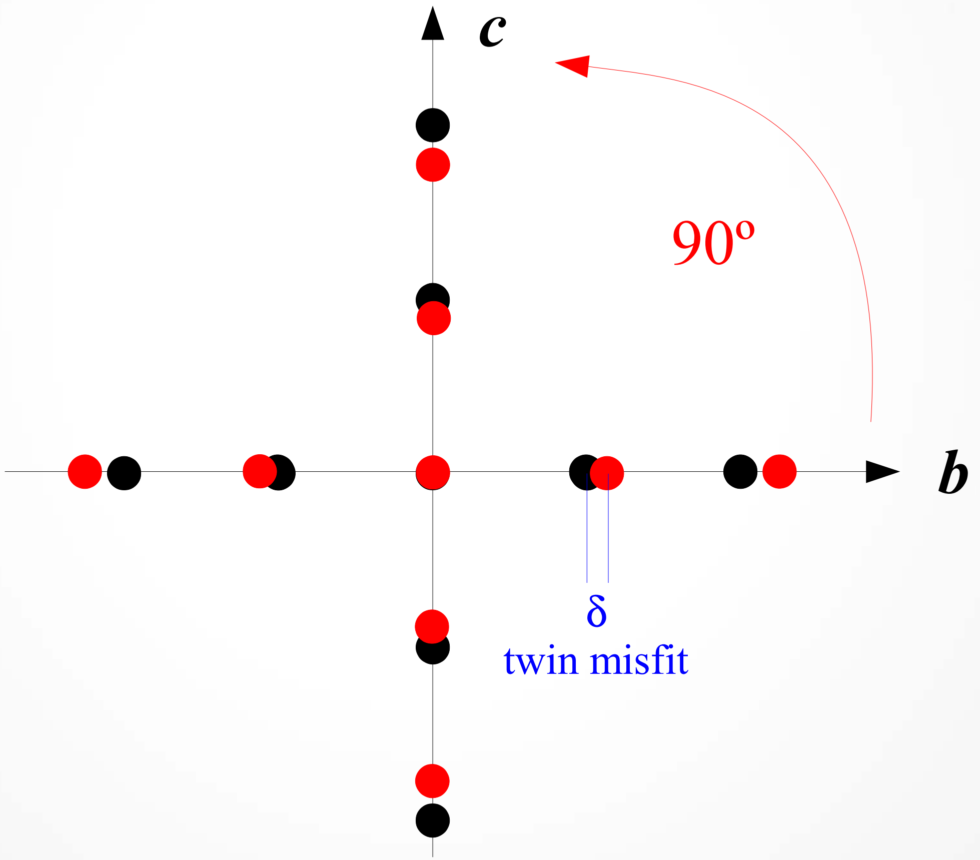
**In twinning, the pseudo-symmetry is often more important than the true symmetry**

# TLS vs TLQS twinning

- Twin Lattice Symmetry (TLS): the restoration of the lattice of the individual (total or partial) is perfect.
- Twin Lattice Quasi-Symmetry (TLS): the restoration of the lattice of the individual (total or partial) is imperfect.
- TLQS only occurs when $\omega \neq 0$ if the twin operation is twofold.
- When the twin operation is a (direct or inverse) rotation of order higher than 2, TLQS may occur also for $\omega = 0$.

# Zero-obliquity TLQS twinning

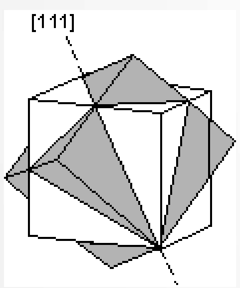
$b \approx c$



# i-TLS vs. e-TLS

**i**ntrinsic **T**win **L**attice **S**ymmetry: when the perpendicularity (*hkl*)/[*uvw*] does not depend on the metric

| **Lattice system** | **lattice plane** | **lattice direction** |
|---|---|---|
| triclinic | --- | --- |
| monoclinic (*b*-unique) | (010) | [010] |
| orthorhombic | (100)<br>(010)<br>(001) | [100]<br>[010]<br>[001] |
| tetragonal | (001)<br>(*hkl*) | [001]<br>[*hkl*] |
| rhombohedral and hexagonal (hexagonal axes) | (0001)<br>(*hki*) | [001]<br>[2*h*+*k*,*h*+2*k*,0] |
| Cubic | (*hkl*) | [*hkl*] |



Rotation about ⟨111⟩

# i-TLS vs. e-TLS

**e**xtrinsic **T**win **L**attice **S**ymmetry: when the perpendicularity (*hkl*)/[*uvw*] ***does*** depend on the metric

example: orthorhombic crystal with primitive lattice, pair (121)/[561]

| *a* | *b* | *c* | ω(°) | type of twinning |
|---|---|---|---|---|
| 4.00 | 5.000 | 8.00 | 2.85 | TLQS |
| 4.00 | 5.000 | 9.00 | 1.81 | TLQS |
| 4.00 | 5.200 | 9.00 | 0.36 | TLQS |
| 4.00 | 5.165 | 8.95 | 0 | e-TLS |