MaThCryst

IUCr

Introduction to Geminography

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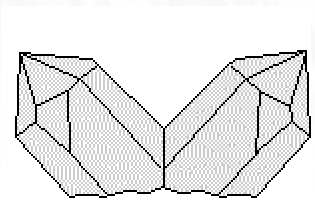
What is a twin?

With space group

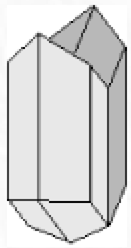
No space group

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.

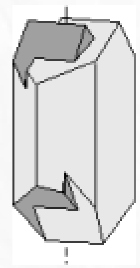
Mapping of individuals in twins



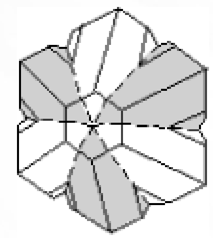
Reflection in {11$\bar{2}$2}



Reflection in (100)



Rotation about [001]



Reflection in {031} (cyclic twin)

Why a *reticular* theory?

- 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

Twin operation, twin element, twin law

- **Twin operation**: the transformation mapping the orientation of one individual onto the orientation of another individual.
- **Twin element**: the geometrical element in *direct lattice* (plane, axis, centre) 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, 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]

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

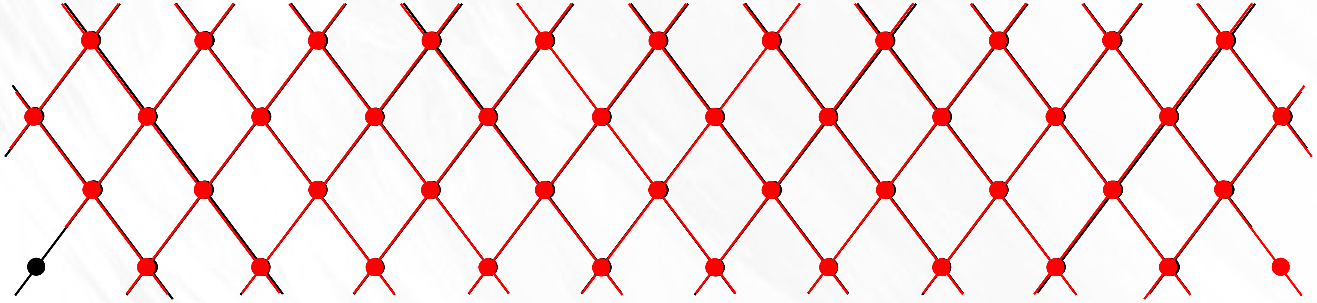
Two twin laws: the two cosets $\{3^{+}_{[001]}, 2_{[110]}\}$ and $\{3^{-}_{[001]}, 2_{[100]}\}$

Four twin operations – the four operations in the two cosets

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

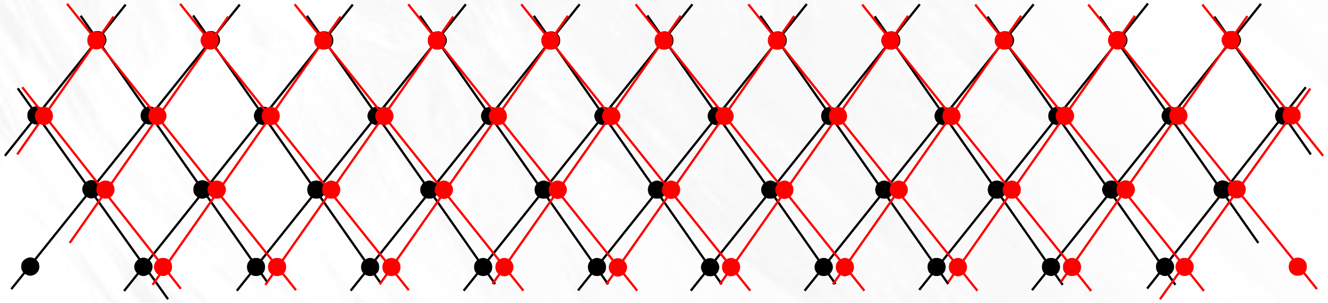
Symmetry of the twin expressed by a trichromatic point group (twin point group): $(3^{(3)}2^{(2,1)})^{(3)}$

Twinning by merohedry



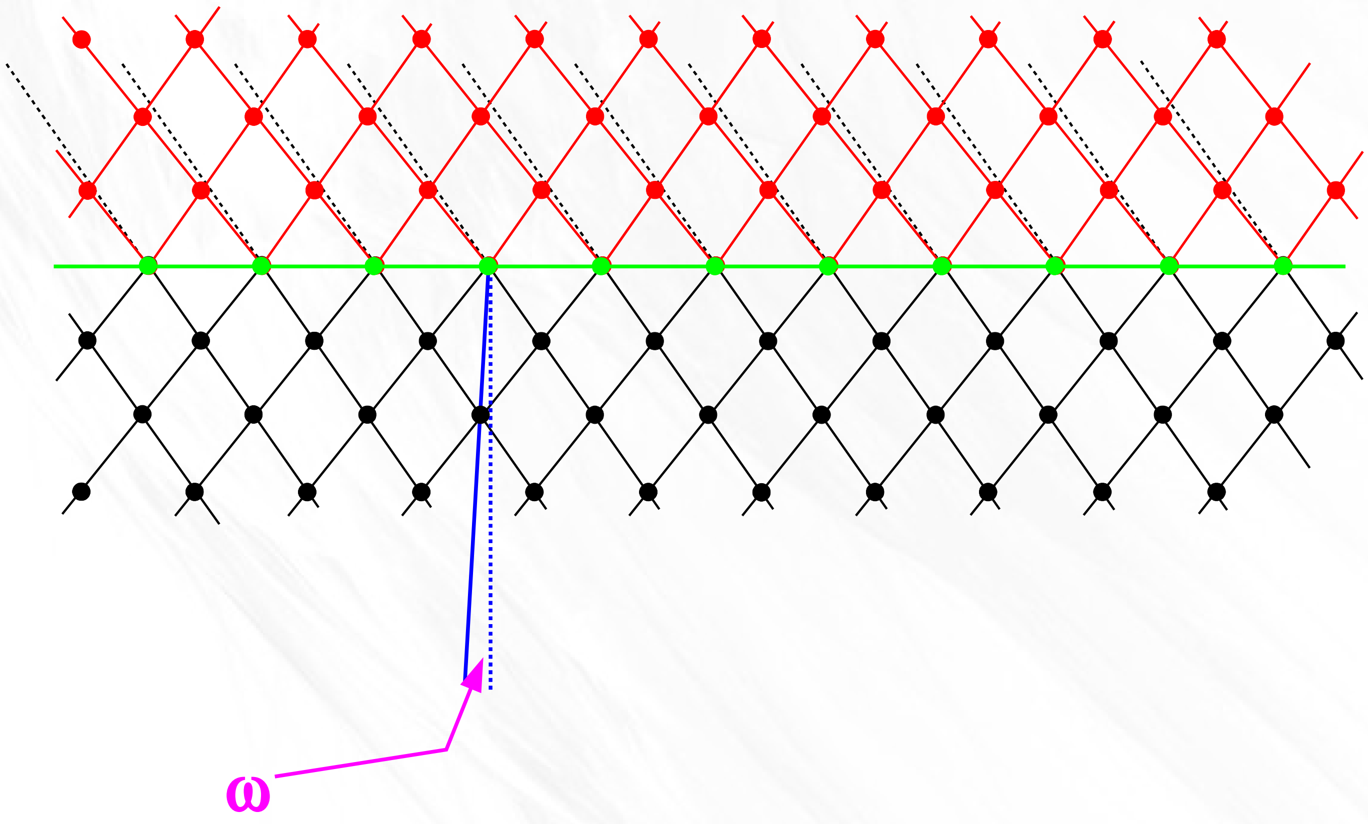
All nodes are restored by the twin operation: we say that **the twin index is *n* = 1**

Twinning by pseudo-merohedry

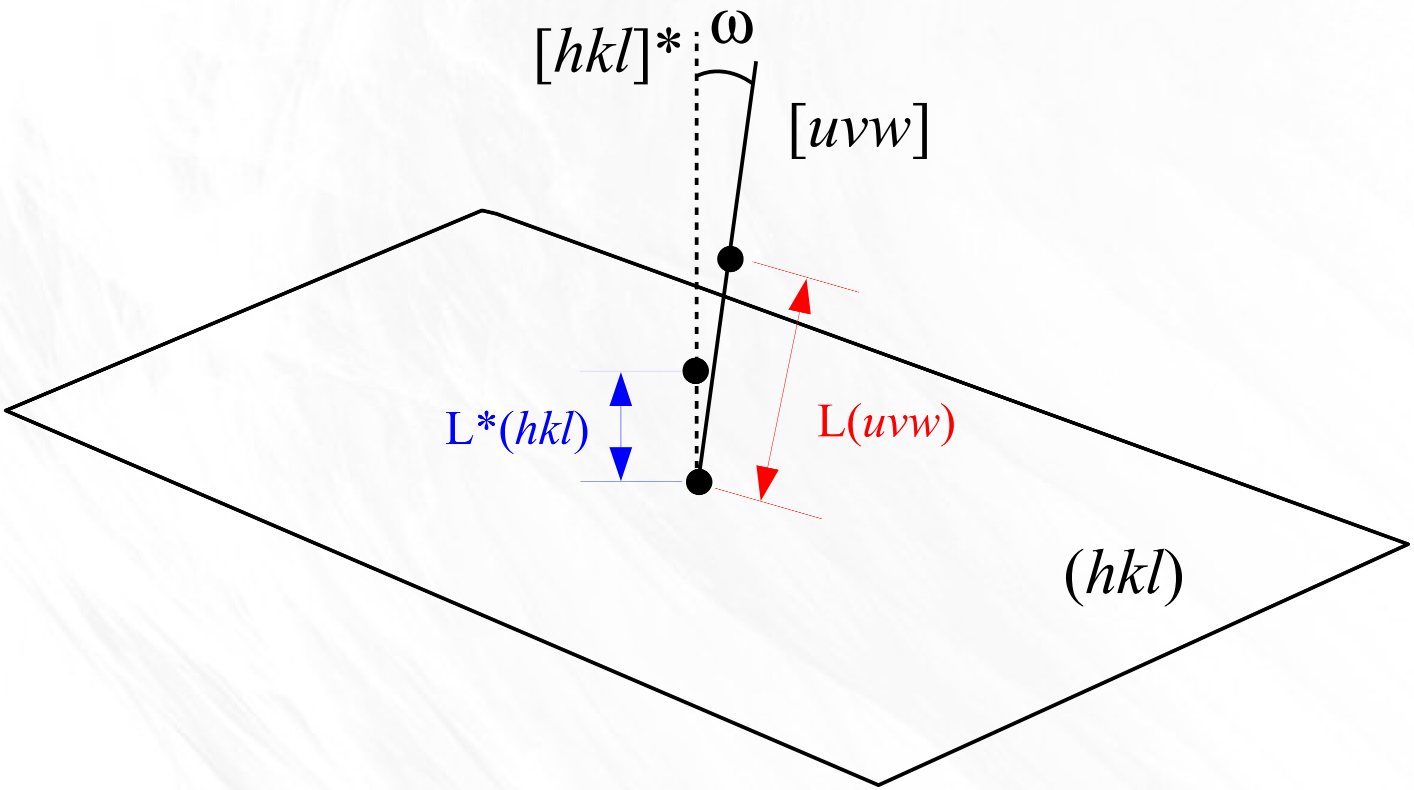


All nodes are *quasi*-restored by the twin operation:
we say that **the twin index is *n* = 1**

Definition of obliquity



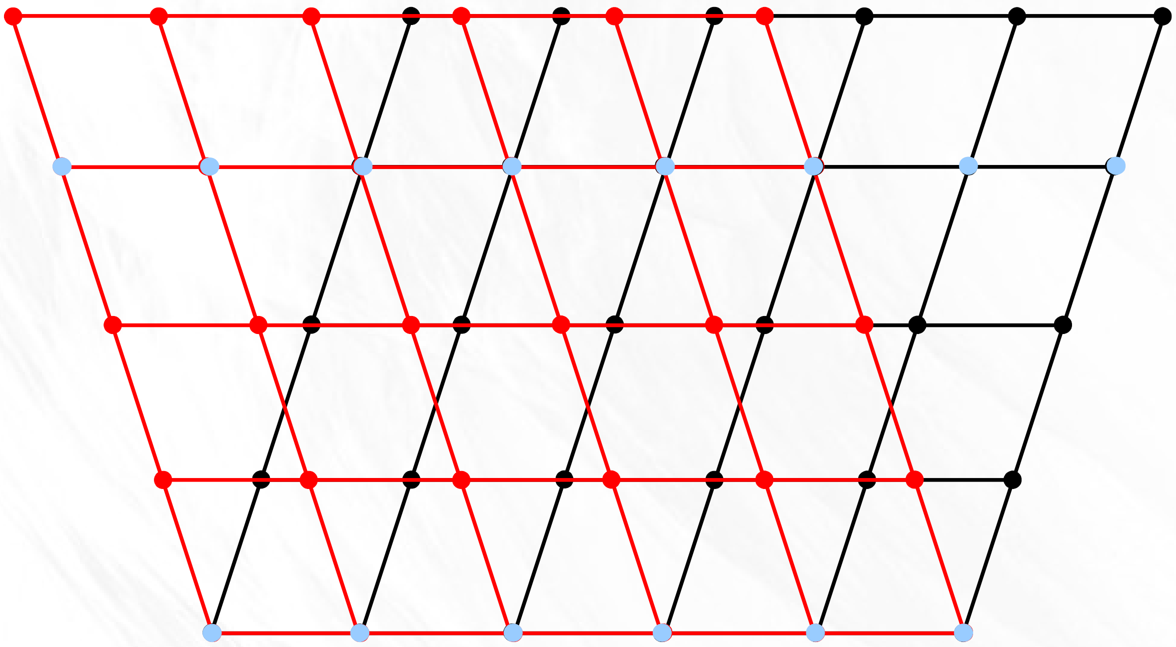
Computation of the obliquity



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

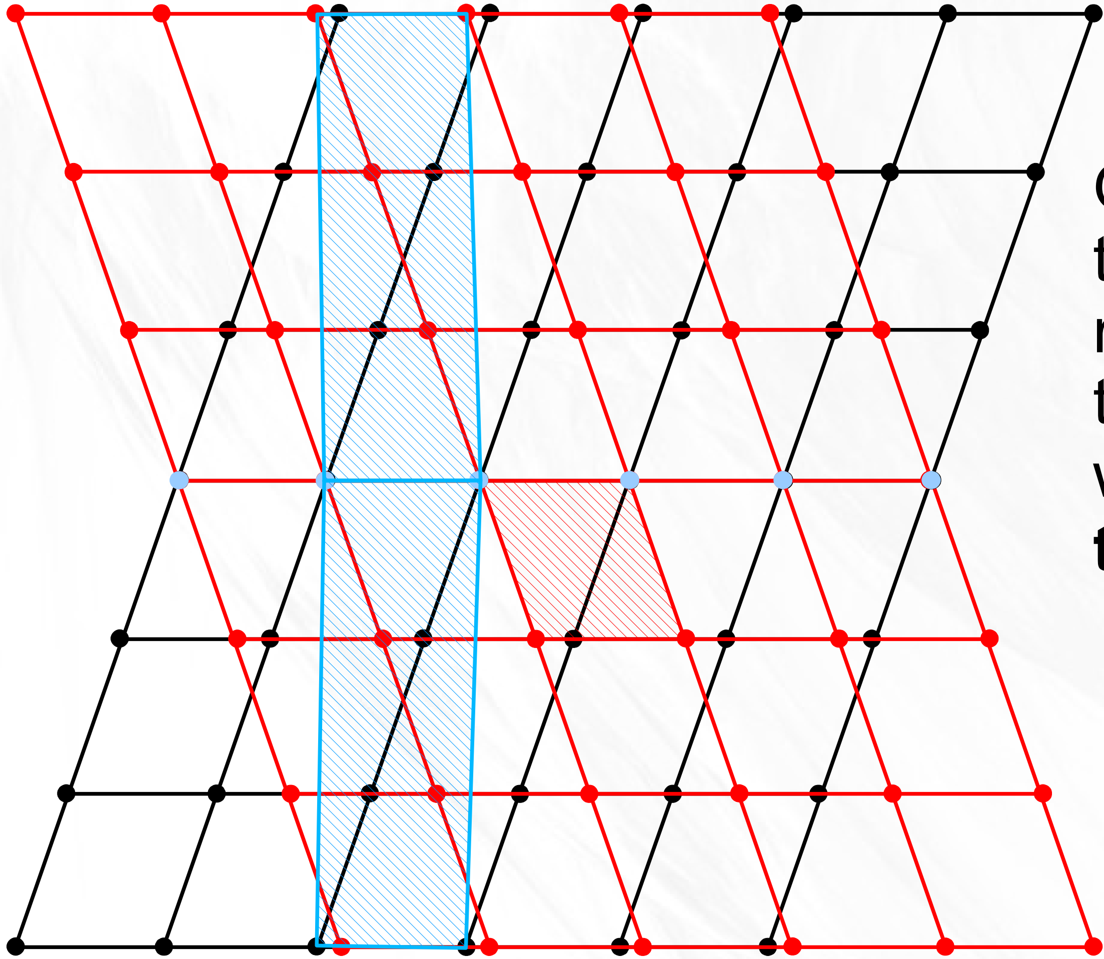
$$\omega = \cos^{-1}|hu+kv+lw|/L^*(hkl)L(uvw)$$

Twinning by reticular merohedry



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

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**

Computation of the twin index for twofold twins

N = number of lattice planes of the family (hkl) between two successive lattice nodes along [uvw]

$X = |hu + kv + wl|$

n = twin index

Primitive cell

Conditions on *h,k,l*	**Conditions on *u,v,w***	***N***	***n***
none	none	X	if X is odd: $n = X$
			if X is even: $n = X/2$

C-centered cell

Conditions on *h,k,l*	**Conditions on *u,v,w***	***N***	***n***
$h+k$ odd	$u+v$ and w not both even	$2X$	$n = X$
	$u+v$ and w both even	X	$n = X$
$h+k$ even	$u+v$ and w not both even	X	X odd: $n = X$
			X even: $n = X/2$
	$u+v$ and w both even	$X/2$	$X/2$ odd: $n = X/2$
			$X/2$ even: $n = X/4$

B-centered cell

Conditions on *h,k,l*	**Conditions on *u,v,w***	***N***	***n***
$h+l$ odd	$u+w$ and v not both even	$2X$	$n = X$
	$u+w$ and v both even	X	$n = X$
$h+l$ even	$u+w$ and v not both even	X	X odd: $n = X$
			X even: $n = X/2$
	$u+w$ and v both even	$X/2$	$X/2$ odd: $n = X/2$
			$X/2$ even: $n = X/4$

A-centered cell

Conditions on *h,k,l*	**Conditions on *u,v,w***	***N***	***n***
$k+l$ odd	$v+w$ and u not both even	$2X$	$n = X$
	$v+w$ and u both even	X	$n = X$
$k+l$ even	$v+w$ and u not both even	X	X odd: $n = X$
			X even: $n = X/2$
	$v+w$ and u both even	$X/2$	$X/2$ odd: $n = X/2$
			$X/2$ even: $n = X/4$

I-centered cell

Conditions on ***h,k,l***	Conditions on ***u,v,w***	***N***	***n***
$h+k+l$ odd	u, v, w not all odd	$2X$	$n = X$
	u, v, w all odd	X	$n = X$
$h+k+l$ even	u, v, w not all odd	X	X odd: $n = X$
			X even: $n = X/2$
	u, v, w all odd	$X/2$	$X/2$ odd: $n = X/2$
			$X/2$ even: $n = X/4$

F-centered cell

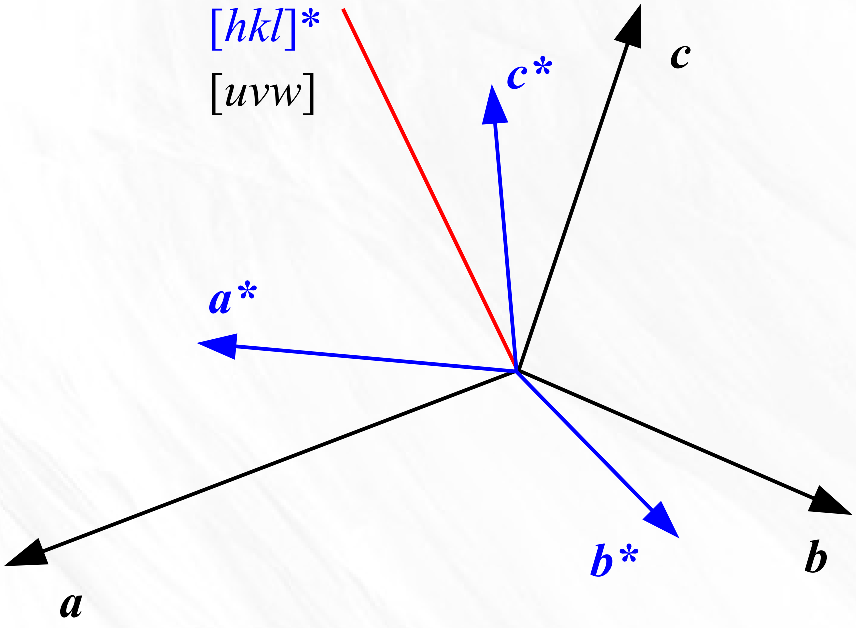
Conditions on ***h,k,l***	Conditions on ***u,v,w***	***N***	***n***
h, k, l not all odd	$u+v+w$ odd	$2X$	$n = X$
h, k, l all odd	u, v, w all odd	X	$n = X$
h, k, l not all odd	$u+v+w$ even	X	X odd: $n = X$
			X even: $n = X/2$
h, k, l all odd		$X/2$	$X/2$ odd: $n = X/2$
			$X/2$ even: $n = X/4$

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* $a = 8.359$Å, $b = 5.352$Å, $c = 6.866$Å,

Twinned on (210)

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

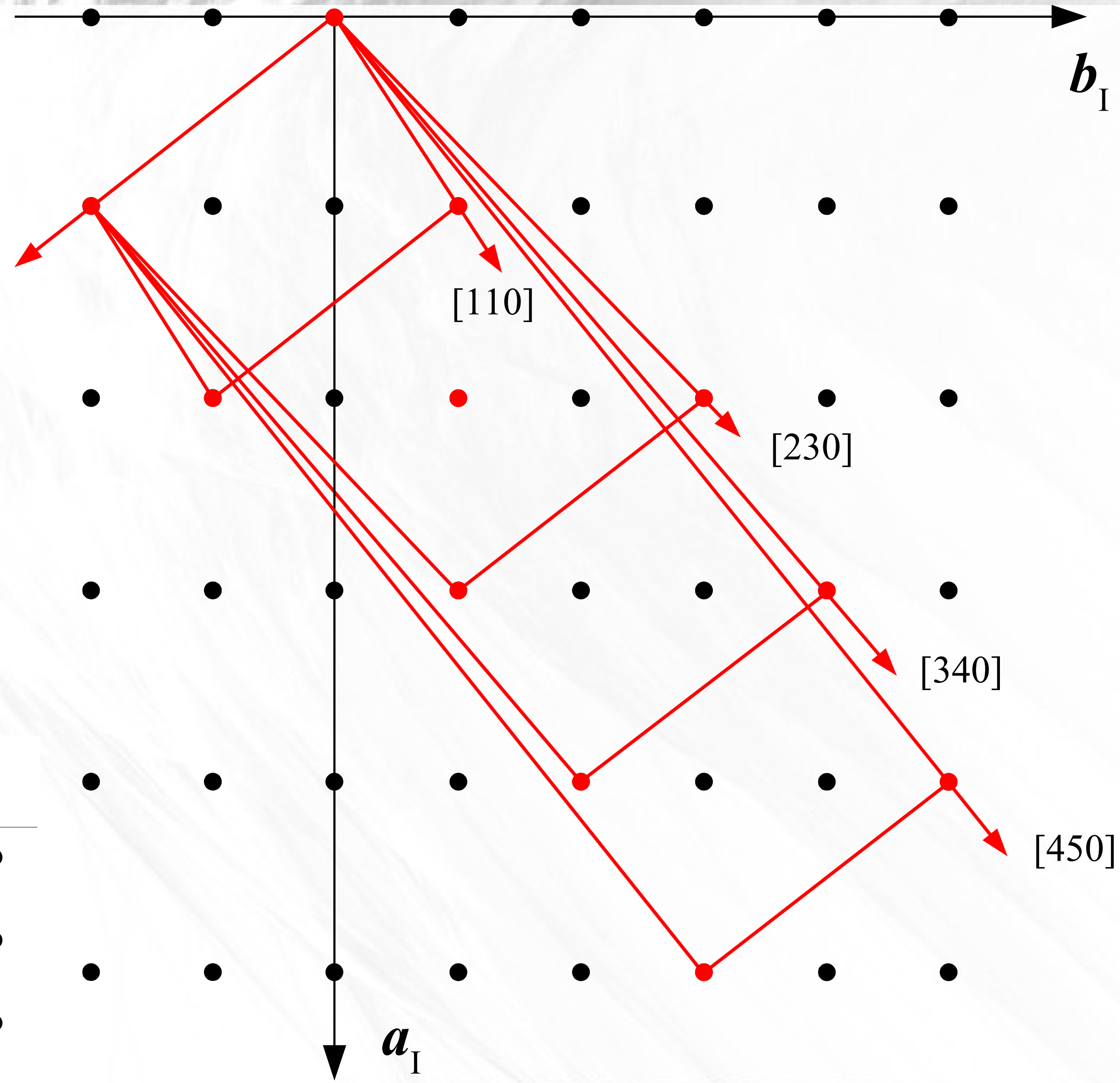
$$\langle 210| \begin{vmatrix} 1/a^2 & 0 & 0 \\ 0 & 1/b^2 & 0 \\ 0 & 0 & 1/c^2 \end{vmatrix} = \langle 0.02862 \quad 0.03491 \quad 0| \quad = \langle 1 \quad 1.220 \quad 0|$$

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	**ω**
110	5.36°
~~120~~	~~14.03°~~
230	5.86°
340	2.50°
450	0.69°



uvw	**ω**
110	5.36°
230	5.86°
340	2.50°
450	0.69°

Summary

uvw	ω	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

$$[u_{1,hkl}v_{1,hkl}w_{1,hkl}] = [001]$$
$$[u_{2,hkl}v_{2,hkl}w_{2,hkl}]\ [1\bar{2}0]$$
$$[u_{\perp}v_{\perp}w_{\perp}]=[340]$$

$$\mathbf{P} = \begin{vmatrix} 0 & 1 & 3 \\ 0 & \bar{2} & 4 \\ 1 & 0 & 0 \end{vmatrix} \qquad |\mathbf{P}| = 10 > 0$$

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

Cell parameters of the (210) twin in celestine

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

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

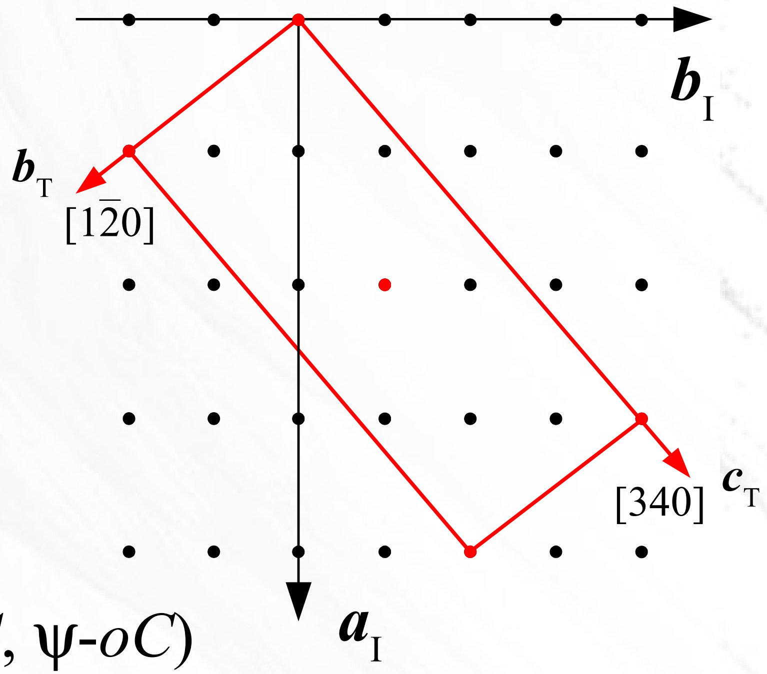
$$a_\mathrm{T} = c_\mathrm{I} = 6.866 \text{ Å} \qquad b_\mathrm{T} = 13.581 \text{ Å} \qquad c_\mathrm{T} = 32.972 \text{ Å}$$

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

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

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; α_T = 92.50º

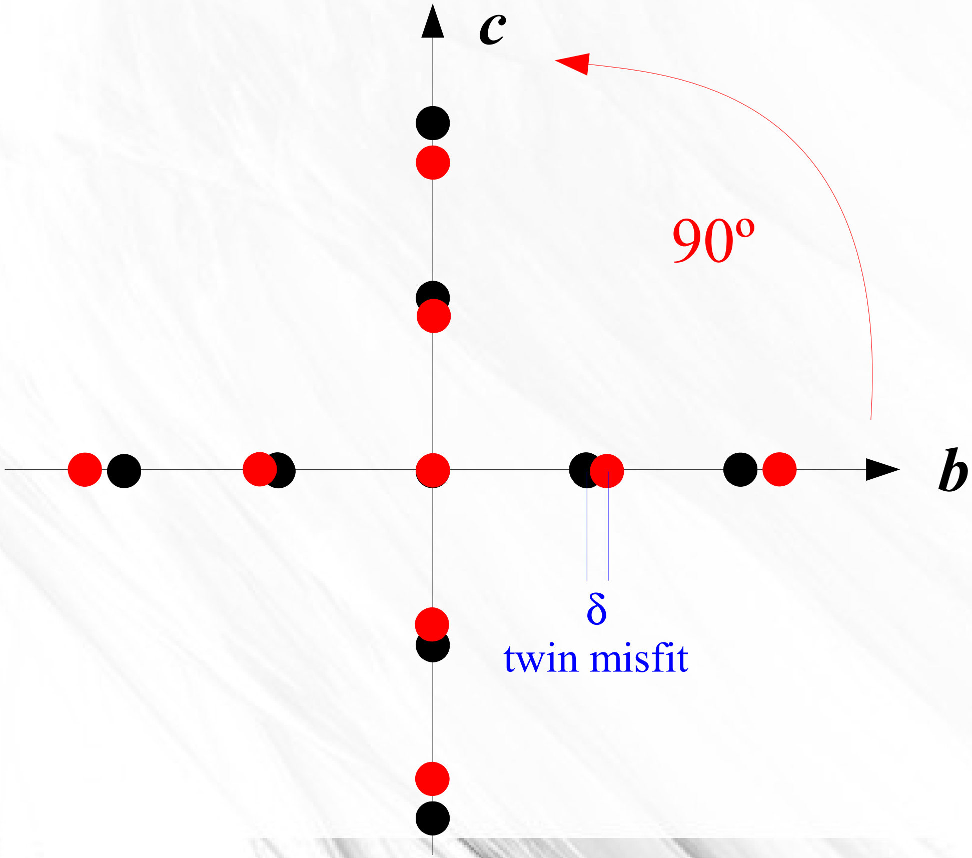


mA, ψ-oA (easily transformed to mC, ψ-oC)

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

Zero-obliquity (reticular) pseudo-merohedry

b ≈ ***c***



Limits of the reticular theory

Twins with the same twin index and obliquity do not occur with the same frequency – ex. albite (010) and pericline [010] twins in triclinic pseudo-monoclinic plagioclases
Twins with higher index / obliquity occur sometimes more frequently than twins with lower twin index / obliquity – contradicting the “necessary” condition

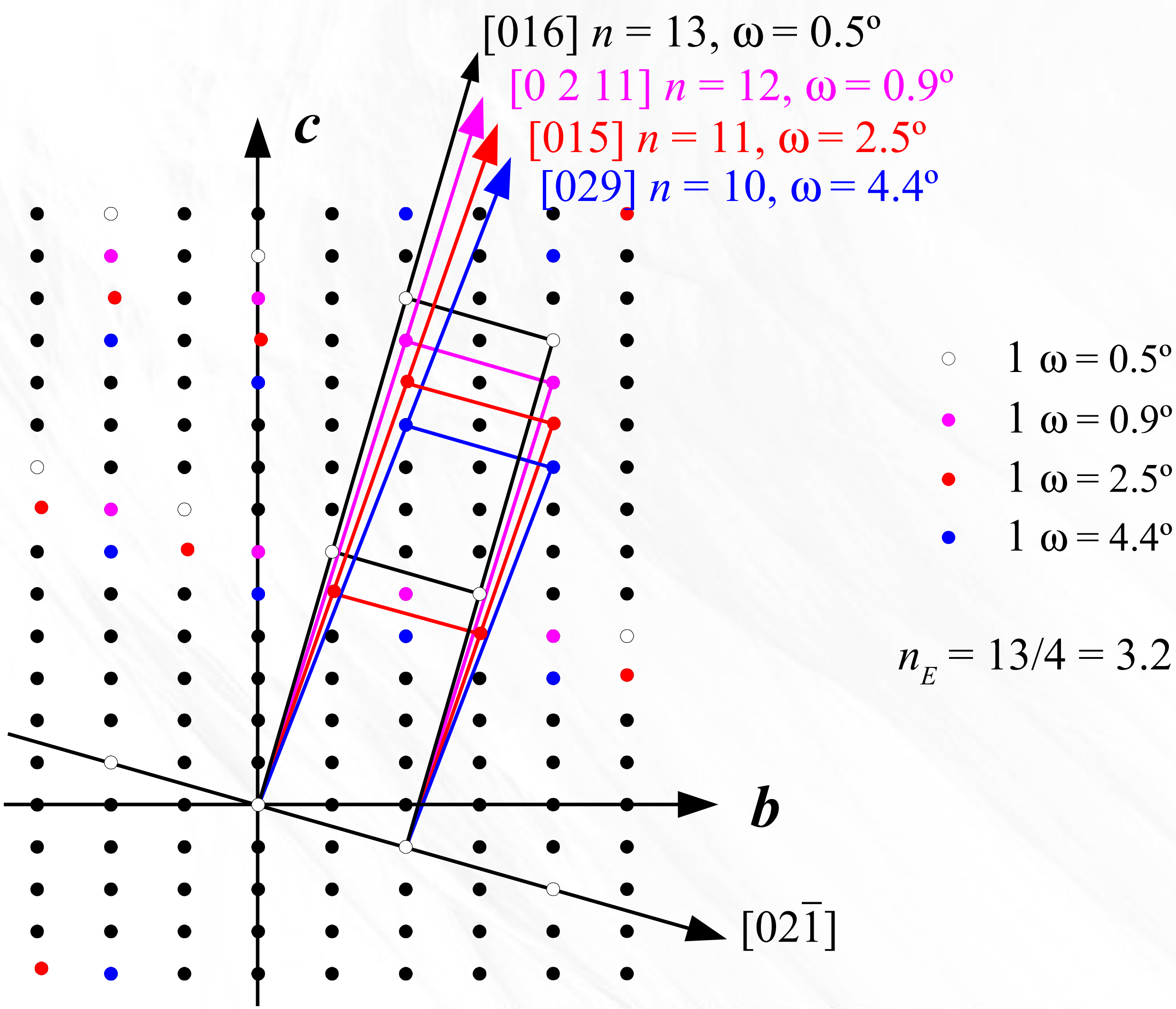
Hybrid twins

Somebody chooses one out of N
We take them all

Friedelian twins

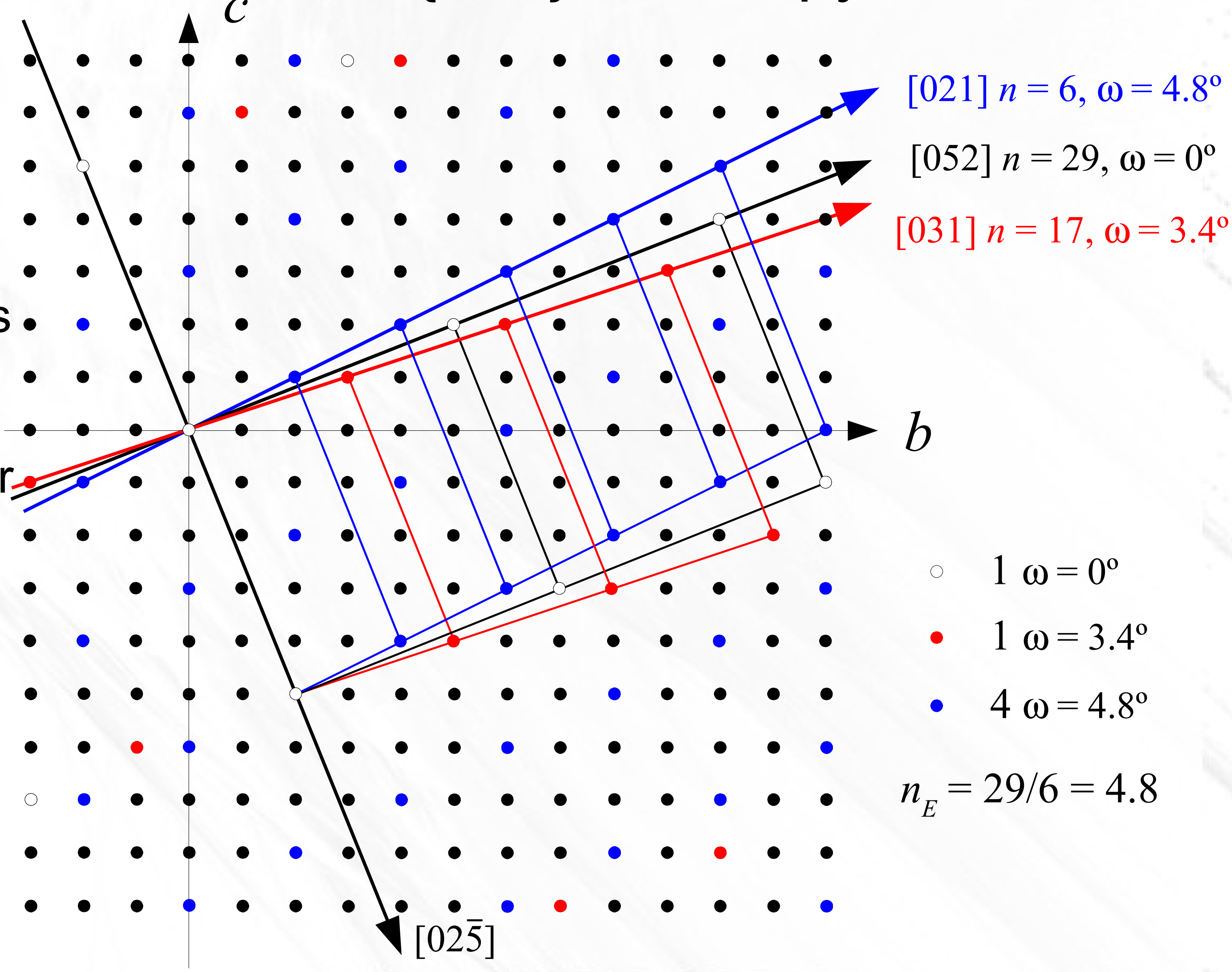
- The probability of occurrence on a twin is inversely proportional to the twin index and to the obliquity
- Friedel's empirical criterion: $n \leq 6$, $\omega \leq 6^{\circ}$
- Twins for which the above criterion is obeyed are termed “Friedelian twins”

{012} twin in forsterite *Pbnm*



{052} twin in pyrite $Pa\bar{3}$

In a cubic lattice, for each (*hkl*) plane there is a direction [*hkl*] exactly perpendicular



Some examples of calculation

The software “Geminography”