Translational symmetry, point and space groups in solids

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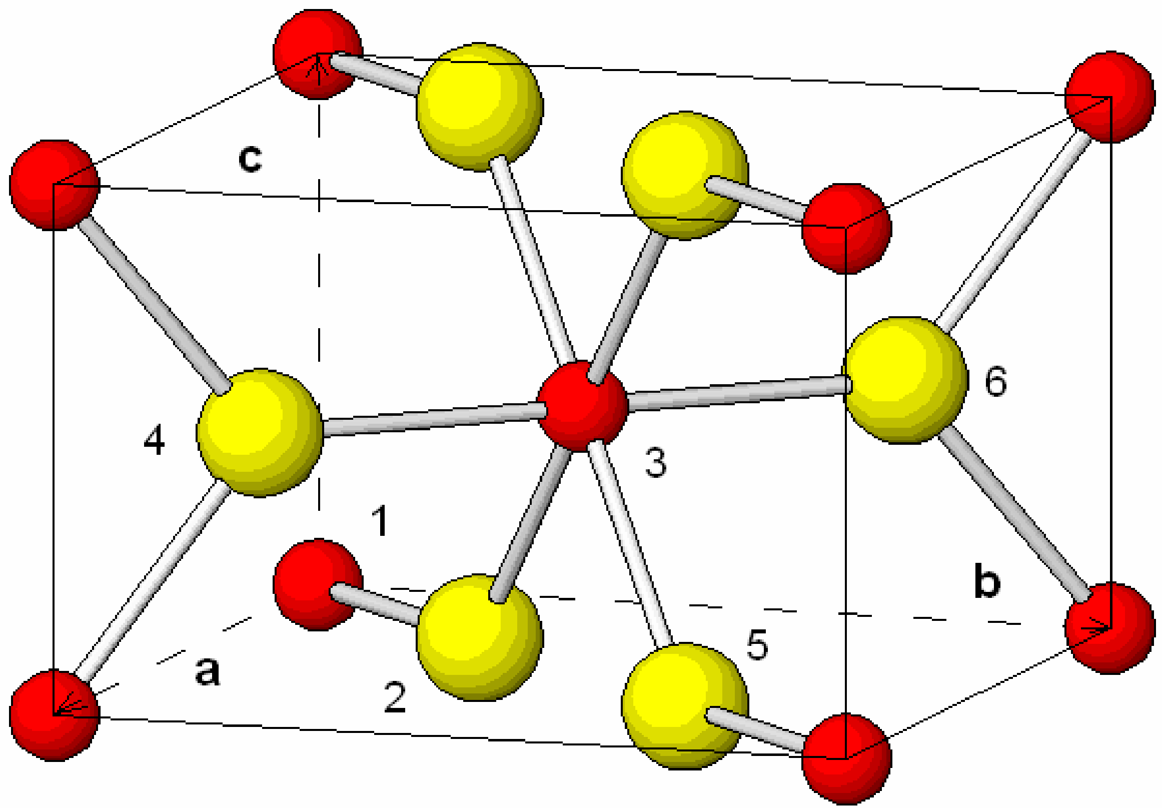
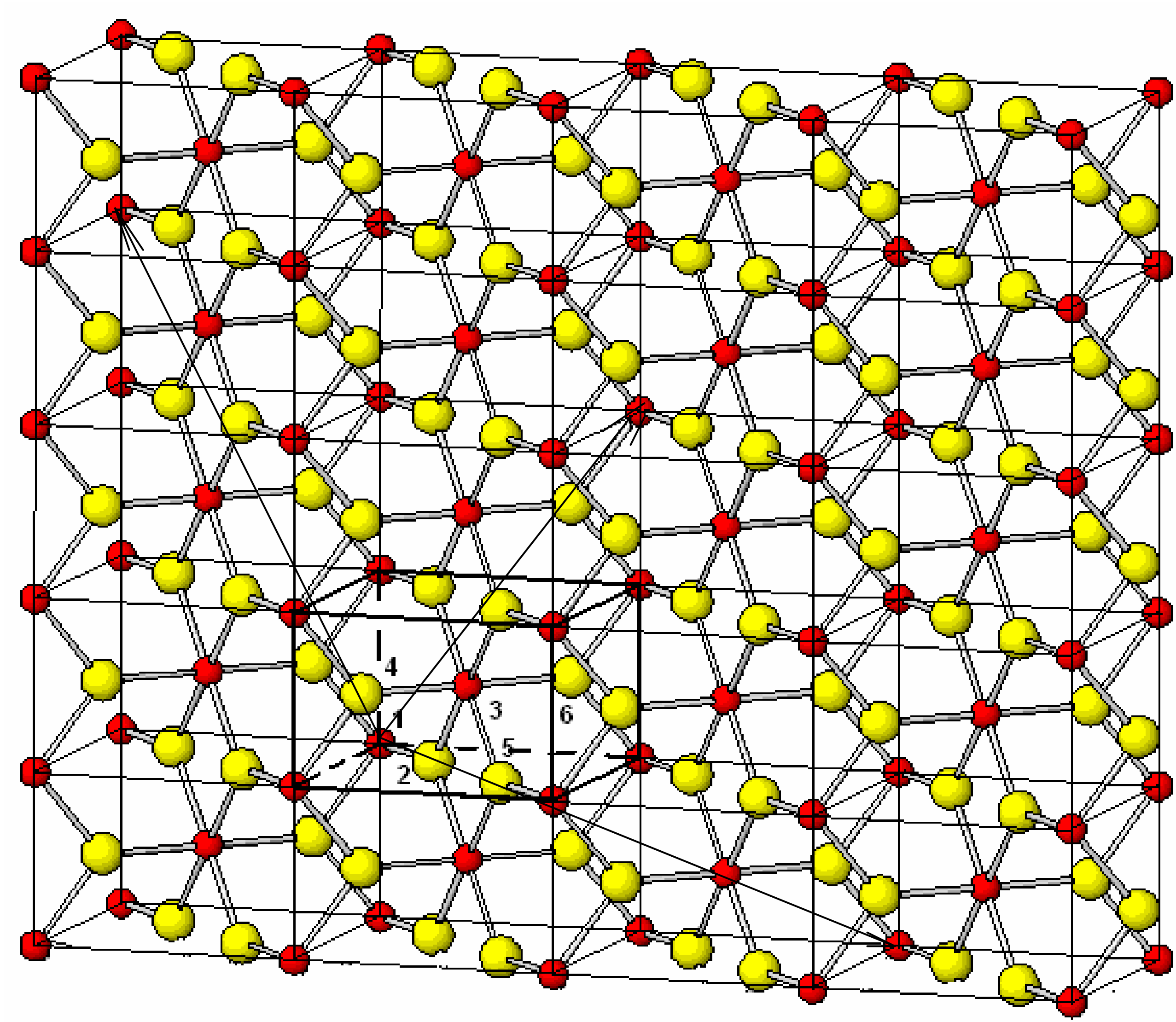
TiO_2

a = b = 4.594 Å; c=2.959 Å   Space group $P4_2/mnm$

Aperiodic unit (unit-cell content): two Ti (1,3) and four O (2,4,5,6)
Asymmetric unit: one Ti (1) and one O (2)



Translational symmetry: set of lattice points or lattice vectors **l**



Translational symmetry $\rightarrow$ direct lattice $\rightarrow$ set of lattice vectors $\mathbf{l}$

$$\mathbf{l} = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3 = \sum_{i=1}^{3} l_i\,\mathbf{a}_i\,; \qquad (l_1, l_2, l_3 \ : \ \text{integer numbers})$$

$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ $(\mathbf{a}, \mathbf{b}, \mathbf{c})$: unit-cell basis vectors

$$V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1) = \mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2) =$$
$$abc\,(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}$$

$$\mathbf{x}_s = \sum_i x_{s,i}\,\mathbf{a}_i$$

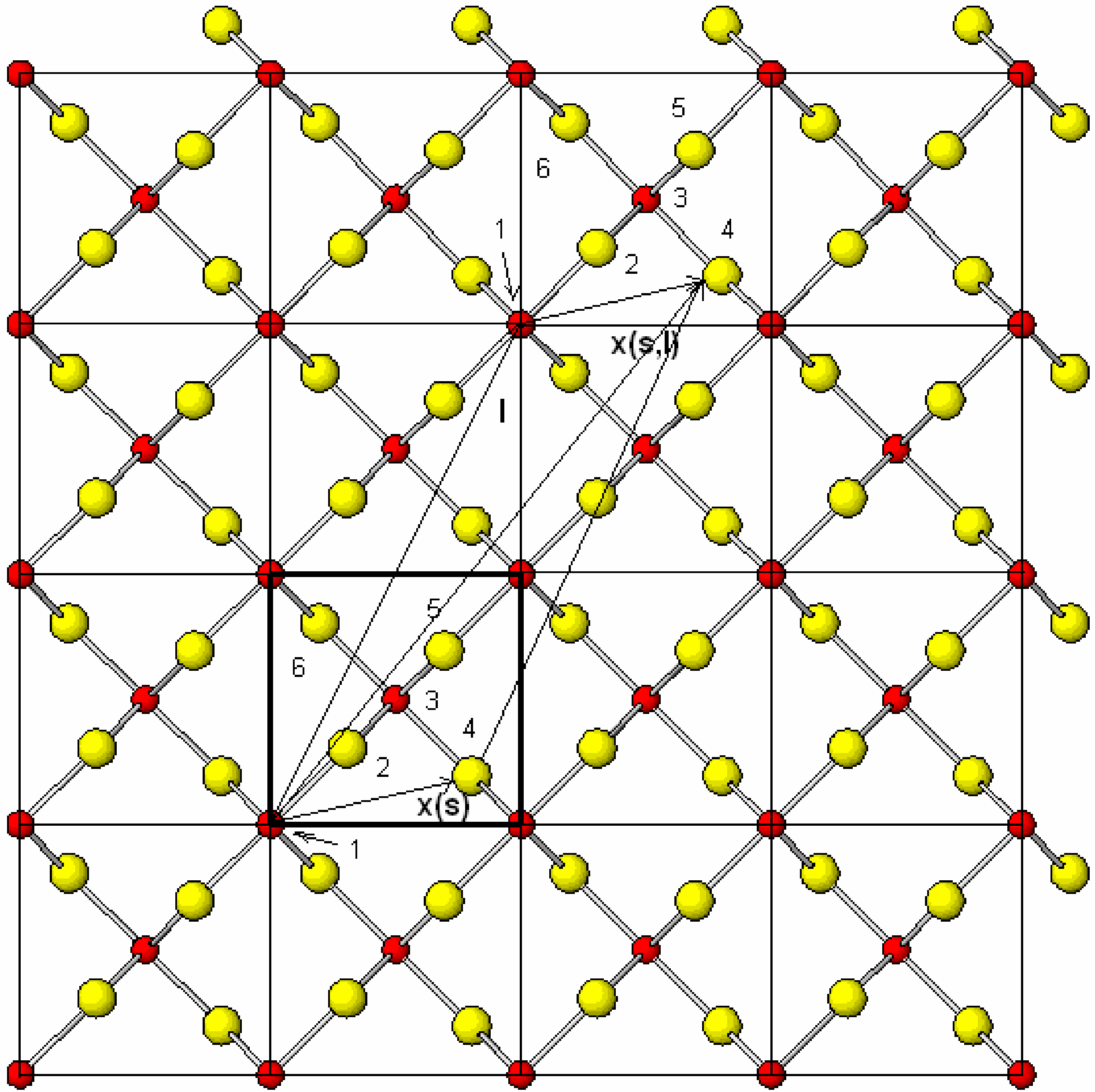
$x_{s,1}, x_{s,2}, x_{s,3}$ (x_s, y_s, z_s): atomic fractional coordinates (real numbers)

$$\boxed{\mathbf{x}_{s,\mathbf{l}} = \mathbf{x}_s + \mathbf{l}}$$

$\mathbf{x}_s$: position vector of s-th atom in the reference unit-cell

$\mathbf{x}_{s,\mathbf{l}}$: position vector of s-th atom in the $\mathbf{l}$-th unit-cell

$$\mathbf{x}_{s,\mathbf{l}} = \mathbf{x}_s + \mathbf{l} \qquad s=4, \quad \mathbf{l} = [1\ 2\ 0]$$



Scalar product of vectors in the oblique lattice reference:

$$\mathbf{l}^{(1)} \cdot \mathbf{l}^{(2)} = (\sum_i l_i^{(1)} \mathbf{a}_i) \cdot (\sum_j l_j^{(2)} \mathbf{a}_j) = \sum_{ij} l_i^{(1)} l_j^{(2)} \mathbf{a}_i \cdot \mathbf{a}_j$$

$\mathbf{a}_i \cdot \mathbf{a}_j = a_i\, a_j \cos(\mathbf{a}_i, \mathbf{a}_j) = G_{ij} = G_{ji}$; metric matrix component

$$l^2 = \mathbf{l} \cdot \mathbf{l} = \sum_{ij} l_i\, l_j\, \mathbf{a}_i \cdot \mathbf{a}_j =$$

$$= l_1^2 a^2 + l_2^2 b^2 + l_3^2 c^2 + 2 l_1 l_2 ab\cos\gamma + 2 l_1 l_3 ac\cos\beta + 2 l_2 l_3 bc\cos\alpha =$$

$= \sum_{ij} l_i\, l_j\, G_{ij} = \underline{l}^{T}\, \underline{G}\, \underline{l}$; squared length of a lattice vector

Reciprocal lattice

$$\mathbf{h} = h_1\mathbf{a}_1^* + h_2\mathbf{a}_2^* + h_3\mathbf{a}_3^* = \sum_{1}^{3}{}_i\, h_i\, \mathbf{a}_i^*; \quad (h1, h2, h3 \ : \ \text{integer numbers})$$

$\mathbf{h}$: reciprocal lattice vector

$\mathbf{a}_1^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$ ($\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$) : reciprocal unit-cell basis vectors

$$\begin{aligned} \mathbf{a}_1^* &= (1/V)\, \mathbf{a}_2 \times \mathbf{a}_3 \\ \mathbf{a}_2^* &= (1/V)\, \mathbf{a}_3 \times \mathbf{a}_1 \qquad \Rightarrow \qquad \mathbf{a}_i^* \cdot \mathbf{a}_j = \delta_{ij} \\ \mathbf{a}_3^* &= (1/V)\, \mathbf{a}_1 \times \mathbf{a}_2 \end{aligned}$$

Wave vector space

$$\mathbf{K} = \sum_i K_i\, (2\pi\, \mathbf{a}_i^*) = \sum_i K_i\, \mathbf{b}_i; \qquad K_1, K_2, K_3 \ : \ \text{real numbers}$$

$G_{ij}^* = \mathbf{a}_i^* \cdot \mathbf{a}_j^* = a_i^*\, a_j^* \cos(\mathbf{a}_i^*, \mathbf{a}_j^*)$; reciprocal metric matrix component

$$\underline{G}^* = \underline{G}^{-1} \qquad V^* = 1/V$$

$$h^2 = \mathbf{h} \cdot \mathbf{h} = \sum_{ij} h_i\, h_j\, \mathbf{a}_i^* \cdot \mathbf{a}_j^* = \sum_{ij} h_i\, h_j\, G_{ij}^* =$$

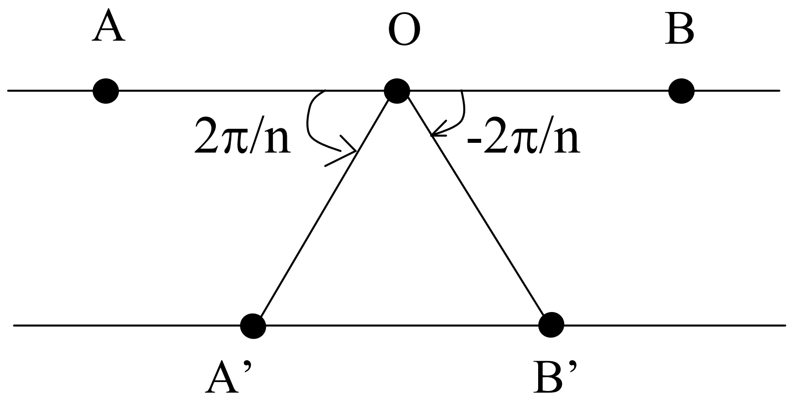
$$= h_1^2 a^{*2} + h_2^2 b^{*2} + h_3^2 c^{*2} + 2h_1h_2a^*b^*\cos\gamma^* + 2h_1h_3a^*c^*\cos\beta^* + 2h_2h_3b^*c^*\cos\alpha^*$$

The scalar product of a direct and a reciprocal lattice vector is an integer number

$$\mathbf{l} \cdot \mathbf{h} = \left(\sum_i l_i\, \mathbf{a}_i\right) \cdot \left(\sum_j h_j\, \mathbf{a}_j^*\right) = \sum_{ij} l_i\, h_j\, \mathbf{a}_i \cdot \mathbf{a}_j^* =$$

$$= \sum_{ij} l_i\, h_j\, \delta_{ij} = \sum_i l_i\, h_i = l_1h_1 + l_2h_2 + l_3h_3$$

Rotation axes consistent with translational symmetry



$\underline{A'B'} = m\,\underline{OA} = m\,\underline{OB}$;

$\underline{A'B'} = 2\underline{OA'}\cos(2\pi/n) = 2\underline{OA}\cos(2\pi/n) = m\,\underline{OA}$

$$\Downarrow$$

$$2\cos(2\pi/n) = m \quad \text{(integer number)}$$

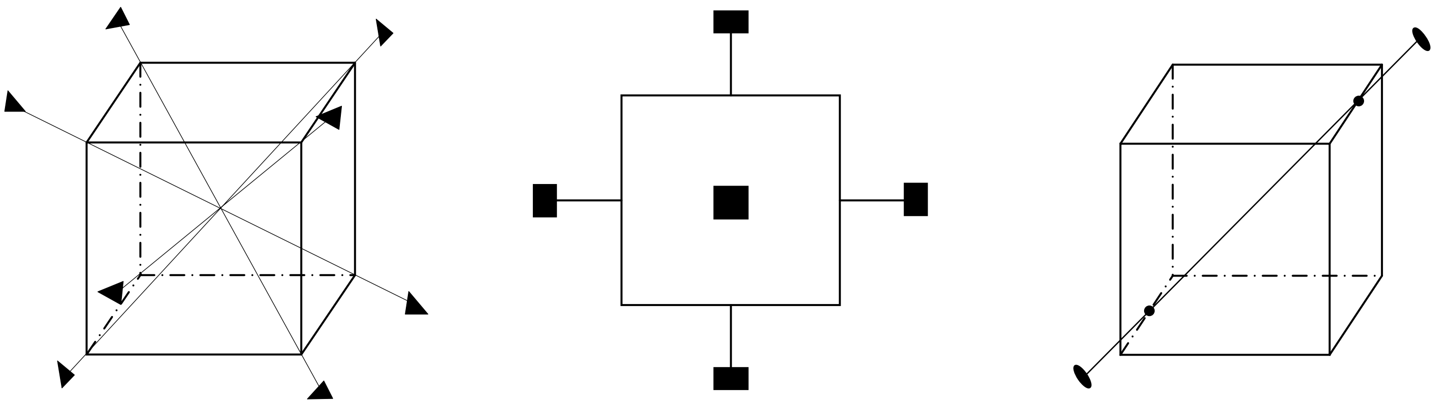
As $-1 \leq \cos(2\pi/n) \leq 1$, then $-2 \leq m \leq 2$, and $m = -2, -1, 0, 1, 2$.

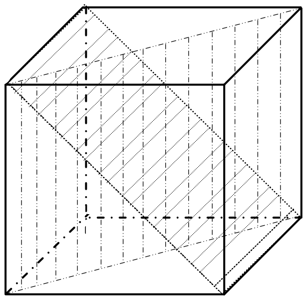
By solving for n, the solutions are $n = 1, 2, 3, 4, 6$

32 crystallographic point goups

Triclinic	Monoclinic	Orthorhombic	Trigonal	Tetragonal	Hexagonal	Cubic
1	2		3	4	6	
$\bar{1}$	$\bar{2}$ = m		$\bar{3}$	$\bar{4}$	$\bar{6}$	
	2/m			4/m	6/m	m $\bar{3}$
		mm2	3m	4mm	6mm	
		222	322	422	622	23 432
			$\bar{3}$m	$\bar{4}$2m	$\bar{6}$m2	$\bar{4}$3m
		mmm		4/mmm	6/mmm	m$\bar{3}$m

Cubic point groups:
symmetry axes and mirror planes





Symmetry operator $\boldsymbol{S}$: rotational $\boldsymbol{R}$ and translational $\boldsymbol{t}$ components

$$\Downarrow$$

$$\boldsymbol{S} = \{\boldsymbol{R}|\boldsymbol{t}\}$$

Matrix notation: $\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \underline{\underline{R}} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} + \underline{t}$

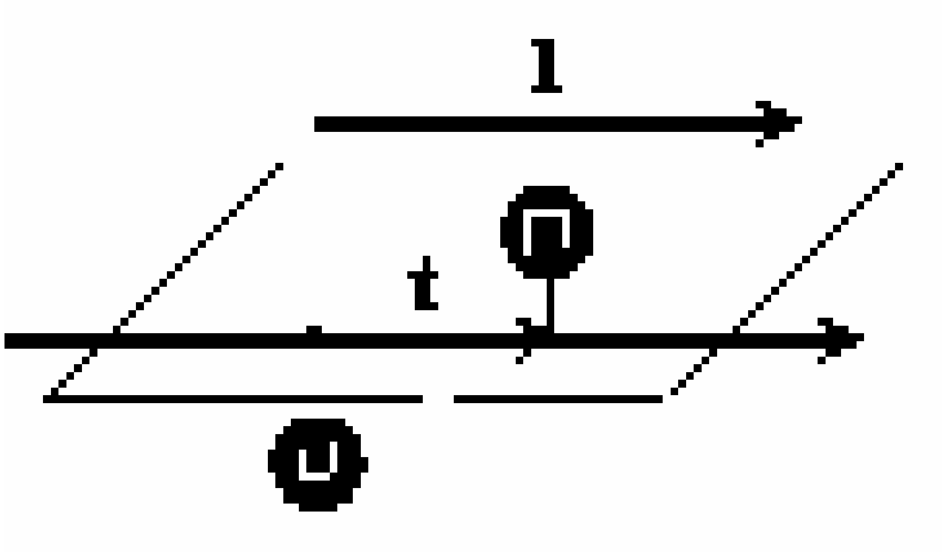
Example: twofold screw axis along y (2_1 // [010])

$$\underline{\underline{R}} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \underline{t} = \begin{bmatrix} 0 \\ 1/2 \\ 0 \end{bmatrix} \qquad \begin{cases} x' = -x \\ y' = y + \frac{1}{2} \\ z' = -z \end{cases}$$

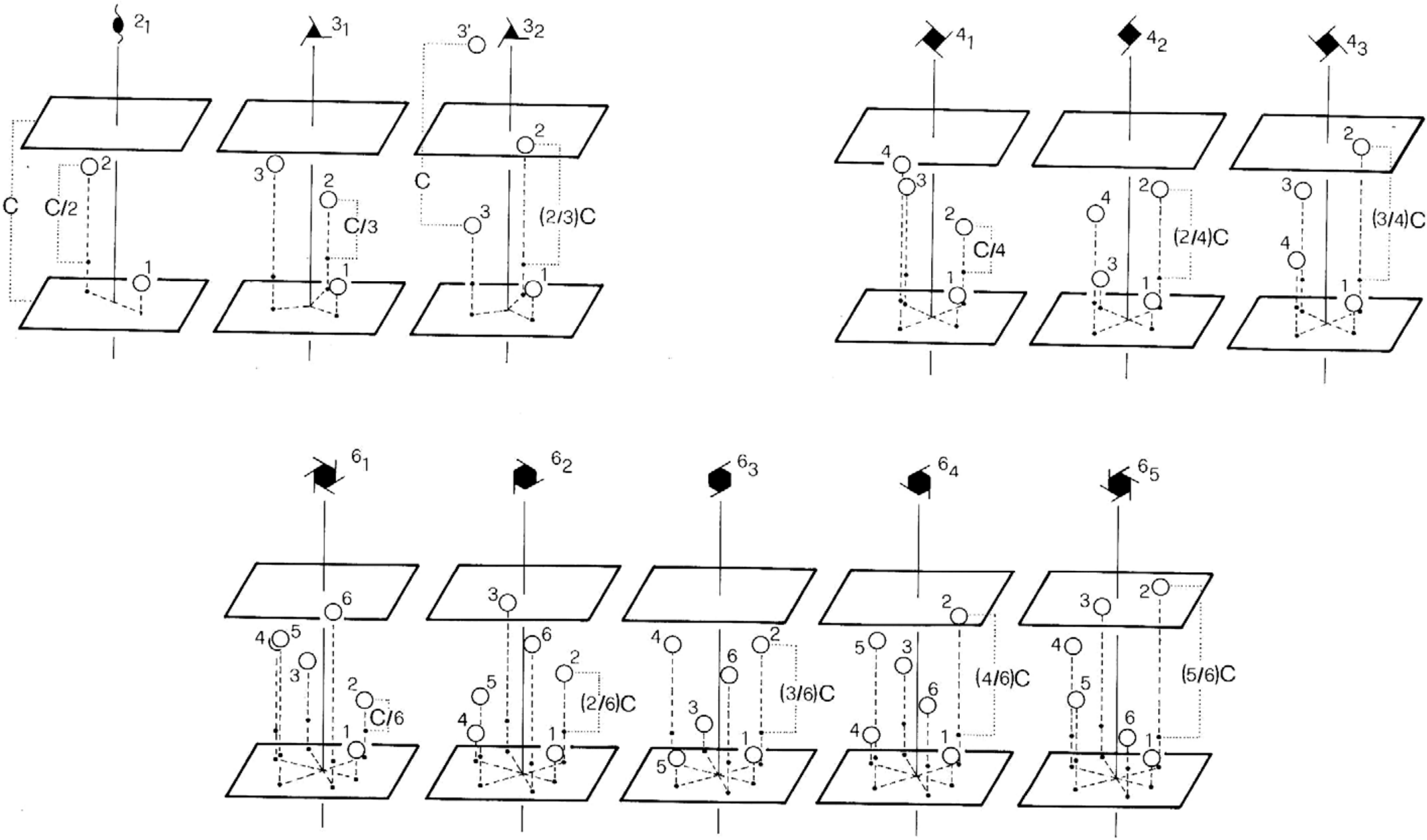
Glide planes: $\boldsymbol{R} = m \qquad \mathbf{t} = \mathbf{l}/2$

a: $\mathbf{t} = \mathbf{a}/2$; b: $\mathbf{t} = \mathbf{b}/2$; c: $\mathbf{t} = \mathbf{c}/2$;

n: $\mathbf{t} = (\mathbf{a}_i + \mathbf{a}_j)/2$



Screw axes



2_1
C
C/2
3_1
C/3
3'
3_2
C
(2/3)C
4_1
C/4
4_2
(2/4)C
4_3
(3/4)C
6_1
C/6
6_2
(2/6)C
6_3
(3/6)C
6_4
(4/6)C
6_5
(5/6)C

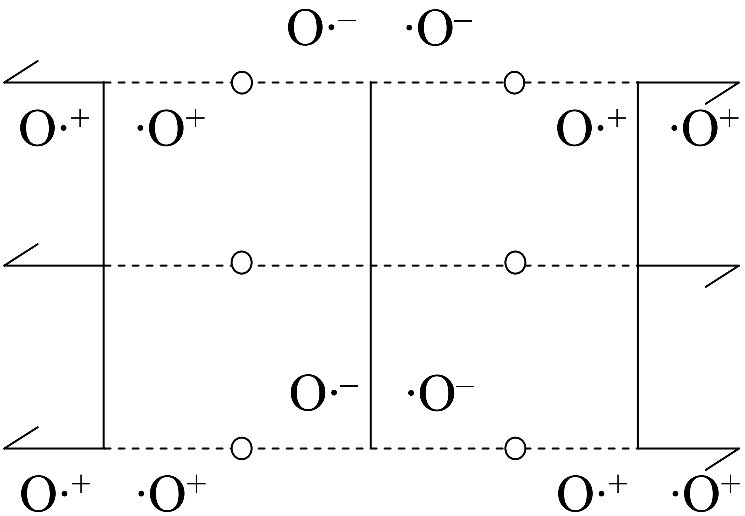
Fourfold screw axis 4_2 along z (4_2 // [001])

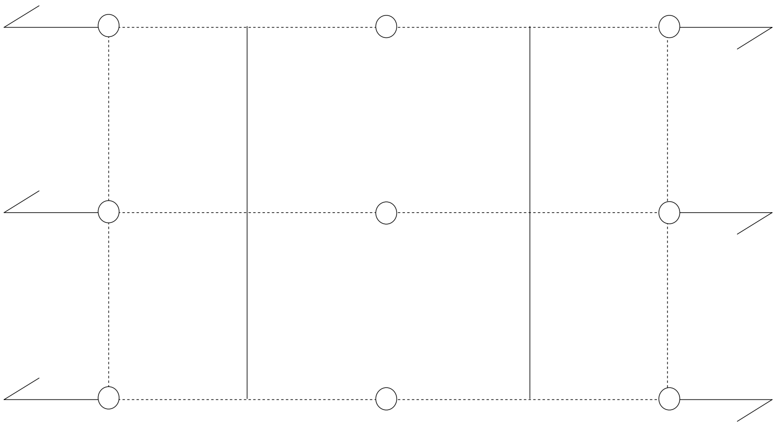
$$\underline{\underline{R}} = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \underline{t} = \begin{bmatrix} 0 \\ 0 \\ 1/2 \end{bmatrix} \qquad \begin{cases} x' = -y \\ y' = x \\ z' = z+1/2 \end{cases}$$

Glide plane c parallel to xz (c // (010))

$$\underline{\underline{R}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \underline{t} = \begin{bmatrix} 0 \\ 0 \\ 1/2 \end{bmatrix} \qquad \begin{cases} x' = x \\ y' = -y \\ z' = z+½ \end{cases}$$

Space group $P2_1/m$





Shift of the origin by **b**/4

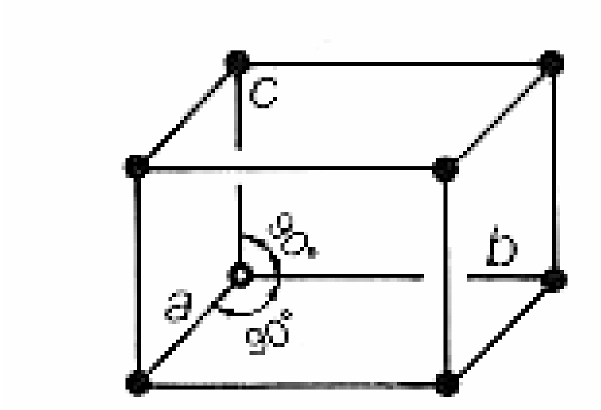
Space group $P2_1/m$:

derived from point group *2/m* by combination with the *P* monoclinic lattice, and replacement of the 2 axis by the 2_1 screw axis

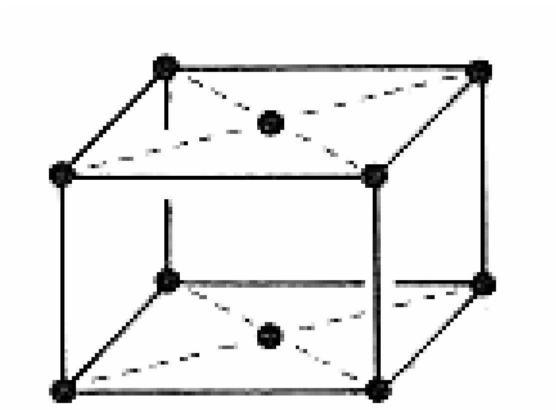
	Origin on the mirror plane	Origin on the symmetry centre
1.	x,y,z	x,y,z
2.	x,-y,z	x,½-y,z
3.	-x ,½+y,-z	-x ,½+y,-z
4.	-x ,½-y,-z	-x ,-y,-z

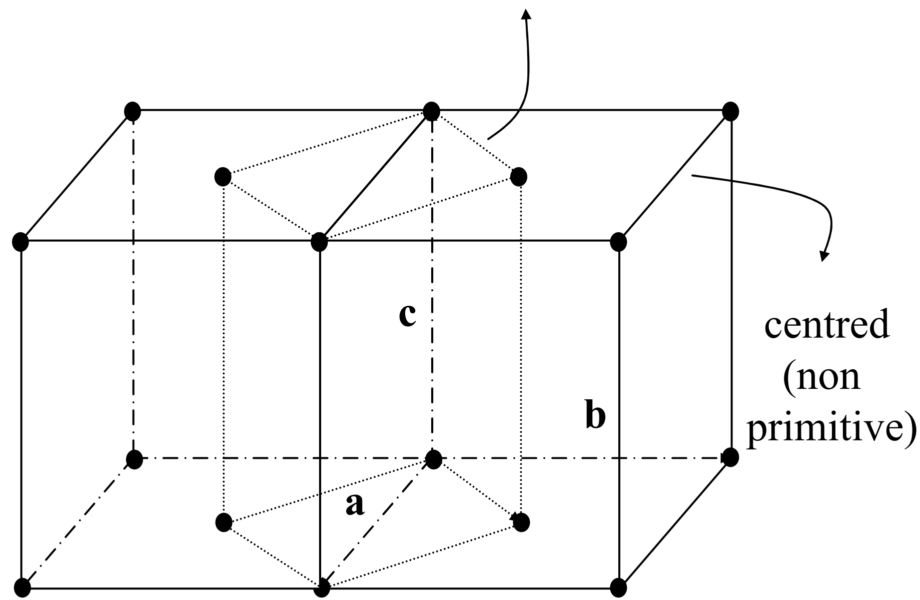
Monoclinic *P* and *C* Bravais lattices

P



C





14 Bravais lattices

Triclinic *P*

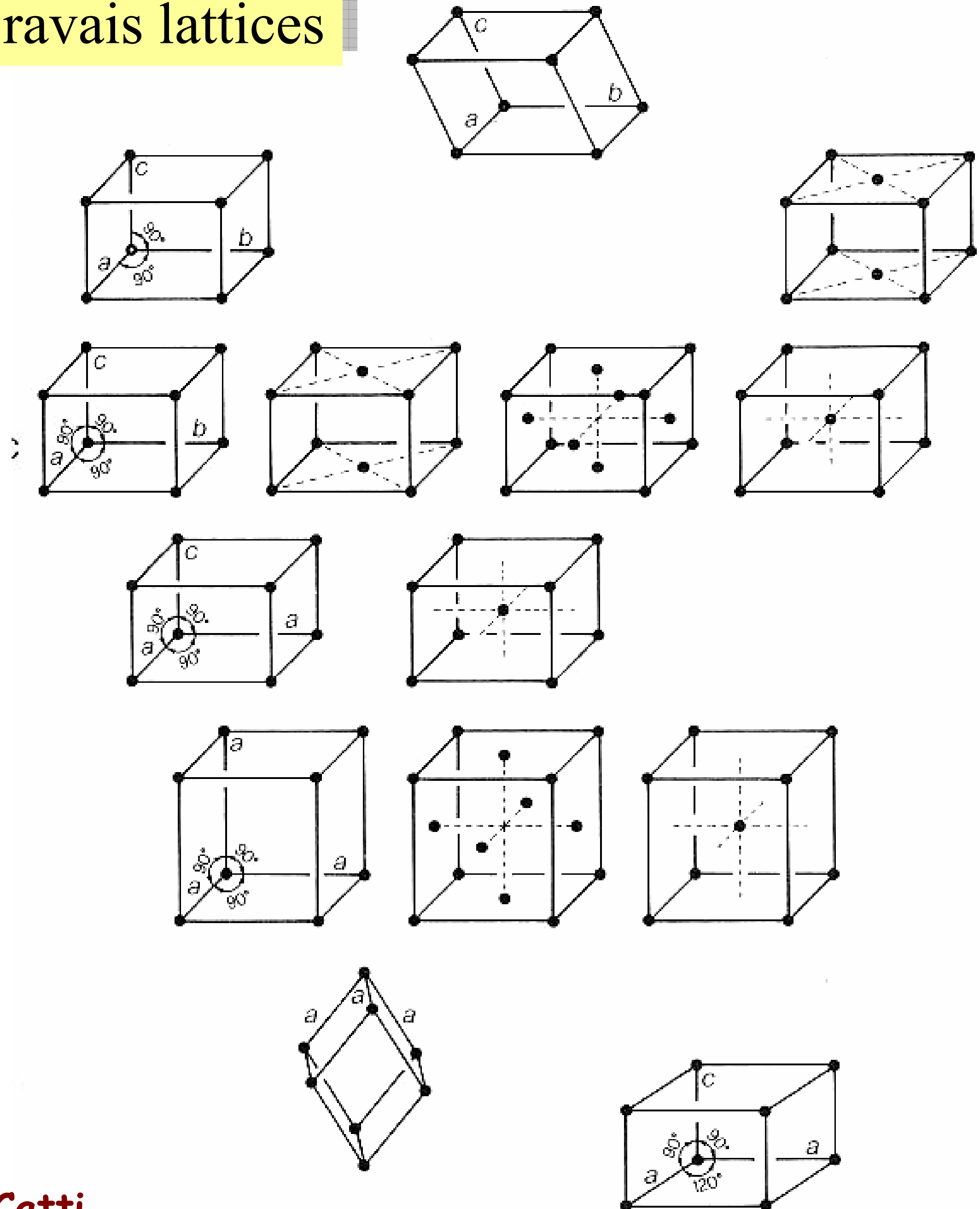
Monoclinic *P, C*

Orthorhombic *P, C, F, I*

Tetragonal *P, I*

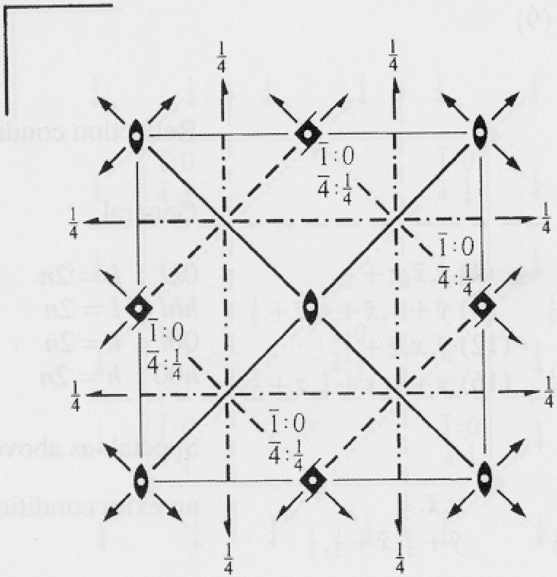
Cubic *P, F, I*

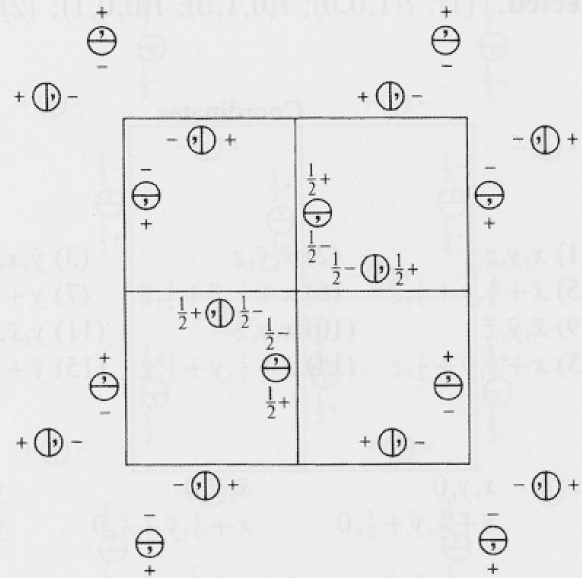
Rhombohedral *R*
Hexagonal *P*



$P4_2/mnm$ $\quad D_{4h}^{14}$ $\quad 4/mmm$ $\quad$ Tetragonal

No. 136 $\quad P\ 4_2/m\ 2_1/n\ 2/m$ $\quad$ Patterson symmetry $P4/mmm$





Origin at centre (mmm) at $2/m\,1\,2/m$

Asymmetric unit $\quad 0 \le x \le \frac{1}{2}; \quad 0 \le y \le \frac{1}{2}; \quad 0 \le z \le \frac{1}{2}; \quad x \le y$

Symmetry operations

(1) 1	(2) $2 \quad 0,0,z$	(3) $4^{+}(0,0,\frac{1}{2}) \quad 0,\frac{1}{2},z$	(4) $4^{-}(0,0,\frac{1}{2}) \quad \frac{1}{2},0,z$
(5) $2(0,\frac{1}{2},0) \quad \frac{1}{4},y,\frac{1}{4}$	(6) $2(\frac{1}{2},0,0) \quad x,\frac{1}{4},\frac{1}{4}$	(7) $2 \quad x,x,0$	(8) $2 \quad x,\bar{x},0$
(9) $\bar{1} \quad 0,0,0$	(10) $m \quad x,y,0$	(11) $\bar{4}^{+} \quad \frac{1}{2},0,z; \quad \frac{1}{2},0,\frac{1}{4}$	(12) $\bar{4}^{-} \quad 0,\frac{1}{2},z; \quad 0,\frac{1}{2},\frac{1}{4}$
(13) $n(\frac{1}{2},0,\frac{1}{2}) \quad x,\frac{1}{4},z$	(14) $n(0,\frac{1}{2},\frac{1}{2}) \quad \frac{1}{4},y,z$	(15) $m \quad x,\bar{x},z$	(16) $m \quad x,x,z$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5); (9)

Positions

Multiplicity	Wyckoff letter	Site symmetry	Coordinates				Reflection conditions
							General:
16	k	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y}+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2}$	(4) $y+\frac{1}{2},\bar{x}+\frac{1}{2},z+\frac{1}{2}$	$0kl$: $k+l=2n$
			(5) $\bar{x}+\frac{1}{2},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(6) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$	(7) $y,x,\bar{z}$	(8) $\bar{y},\bar{x},\bar{z}$	$00l$: $l=2n$
			(9) $\bar{x},\bar{y},\bar{z}$	(10) $x,y,\bar{z}$	(11) $y+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2}$	(12) $\bar{y}+\frac{1}{2},x+\frac{1}{2},\bar{z}+\frac{1}{2}$	$h00$: $h=2n$
			(13) $x+\frac{1}{2},\bar{y}+\frac{1}{2},z+\frac{1}{2}$	(14) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$	(15) $\bar{y},\bar{x},z$	(16) y,x,z	
							Special: as above, plus
8	j	$..m$	x,x,z	$\bar{x},\bar{x},z$	$\bar{x}+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2}$	$x+\frac{1}{2},\bar{x}+\frac{1}{2},z+\frac{1}{2}$	no extra conditions
			$\bar{x}+\frac{1}{2},x+\frac{1}{2},\bar{z}+\frac{1}{2}$	$x+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2}$	$x,x,\bar{z}$	$\bar{x},\bar{x},\bar{z}$	
8	i	$m..$	$x,y,0$	$\bar{x},\bar{y},0$	$\bar{y}+\frac{1}{2},x+\frac{1}{2},\frac{1}{2}$	$y+\frac{1}{2},\bar{x}+\frac{1}{2},\frac{1}{2}$	no extra conditions
			$\bar{x}+\frac{1}{2},y+\frac{1}{2},\frac{1}{2}$	$x+\frac{1}{2},\bar{y}+\frac{1}{2},\frac{1}{2}$	$y,x,0$	$\bar{y},\bar{x},0$	
8	h	$2..$	$0,\frac{1}{2},z$	$0,\frac{1}{2},z+\frac{1}{2}$	$\frac{1}{2},0,\bar{z}+\frac{1}{2}$	$\frac{1}{2},0,\bar{z}$	hkl : $h+k,l=2n$
			$0,\frac{1}{2},\bar{z}$	$0,\frac{1}{2},\bar{z}+\frac{1}{2}$	$\frac{1}{2},0,z+\frac{1}{2}$	$\frac{1}{2},0,z$	
4	g	$m.2m$	$x,\bar{x},0$	$\bar{x},x,0$	$x+\frac{1}{2},x+\frac{1}{2},\frac{1}{2}$	$\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2},\frac{1}{2}$	no extra conditions
4	f	$m.2m$	$x,x,0$	$\bar{x},\bar{x},0$	$\bar{x}+\frac{1}{2},x+\frac{1}{2},\frac{1}{2}$	$x+\frac{1}{2},\bar{x}+\frac{1}{2},\frac{1}{2}$	no extra conditions
4	e	$2.mm$	$0,0,z$	$\frac{1}{2},\frac{1}{2},z+\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\bar{z}+\frac{1}{2}$	$0,0,\bar{z}$	hkl : $h+k+l=2n$
4	d	$\bar{4}..$	$0,\frac{1}{2},\frac{1}{4}$	$0,\frac{1}{2},\frac{3}{4}$	$\frac{1}{2},0,\frac{1}{4}$	$\frac{1}{2},0,\frac{3}{4}$	hkl : $h+k,l=2n$
4	c	$2/m..$	$0,\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},0,0$	hkl : $h+k,l=2n$
2	b	$m.mm$	$0,0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			hkl : $h+k+l=2n$
2	a	$m.mm$	$0,0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $h+k+l=2n$

Symmetry of special projections

Along [001] $p4gm$
$\mathbf{a}'=\mathbf{a}$ $\mathbf{b}'=\mathbf{b}$

Along [100] $c2mm$
$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}$

Along [110] $p2mm$
$\mathbf{a}'=\frac{1}{2}(-\mathbf{a}+\mathbf{b})$ $\mathbf{b}'=\mathbf{c}$

- <u>General position:</u>

  set of symmetry-related points not lying on any purely rotational symmetry element; their number (multiplicity) is equal to the order of the symmetry group

$$\Downarrow$$

All symmetry operators act on the general position

- <u>Special position:</u>

  set of symmetry-related points lying on one or more purely rotational symmetry elements; the multiplicity is equal to the order of the symmetry group divided by the product of multiplicities of all symmetry elements on which each point lies

$$\Downarrow$$

The symmetry operators corresponding to symmetry elements on which the points lie do not act on the special position

TiO_2 - space group $P4_2/mnm$

		x	y	z
1 - Ti(1)	2*a*	0	0	0
3 - Ti(2)		½	½	½
2 - O(1)	4*f*	0.3048	0.3048	0
4 - O(2)		0.1952	0.8048	½
5 - O(3)		0.6952	0.6952	0
6 - O(4)		0.8048	0.1952	½