Space Group - 2

Read

Ott Chapter 10 (exclude 10.1)

Hammond Chapter 4.6~4.7

Krawitz Chapter 1.6~1.8

Sherwood & Cooper Chapter 3.8

Hammond Chapter 2.1 ~ 2.5; 3.1 ~ 3.3; 4.1 ~ 4.5; 5.1 ~ 5.6

Krawitz Chapter 1.1 ~ 1.8

Space groups

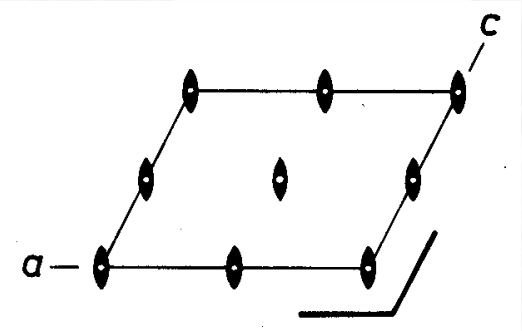
- Bravais lattice + point group → 230 space groups
  + screw axis
  + glide plane

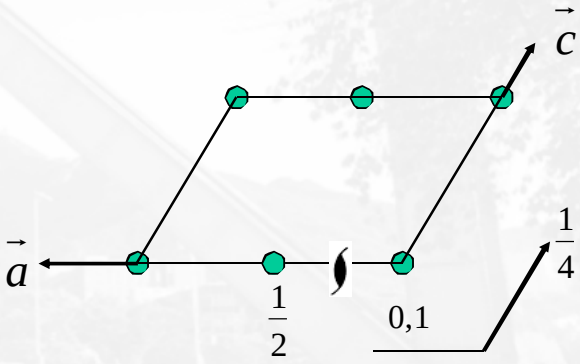
- Bravais lattice + point group= 73
- Bravais lattice + screw axis = 41
- Bravais lattice + glide plane = 116

- monoclinic system

$P\frac{2}{m}$, $C\frac{2}{m}$ (a-glide at $x, \frac{1}{4}, z$, $x, \frac{3}{4}, z$

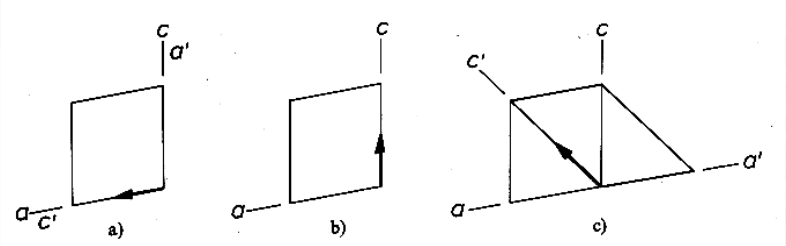
2_1 screw axis at $\frac{1}{4}, y, 0$, $\frac{1}{4}, y, \frac{1}{2}$, $\frac{3}{4}, y, 0$, $\frac{3}{4}, y, \frac{1}{2}$)





$-\frac{2}{m}$ subgroup 2, m

$2_1 \rightarrow 2$, c-glide $\rightarrow$ m



glide planes parallel to (010)

a-glide & n-glide can be converted to c-glide

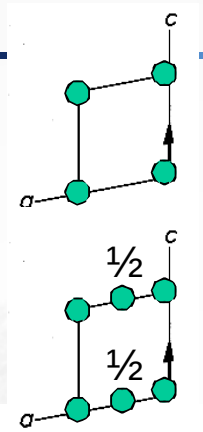
13 monoclinic space groups

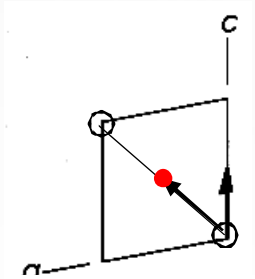
Point groups	Space groups	
2/m	P2/m $P2_1/m$ P2/c $P2_1/c$	C2/m –[a] C2/c –[b]
m	Pm Pc	Cm Cc
2	P2 $P2_1$	C2 –[c]

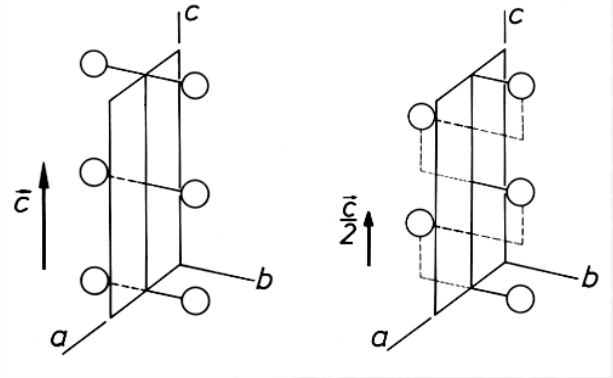
[a] $C2_1/m \equiv C2/m$, [b] $C2_1/c \equiv C2/c$, [c] $C2_1 \equiv C2$

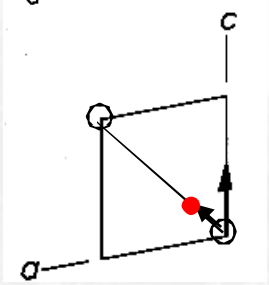
Why no d-glide in Monoclinic?

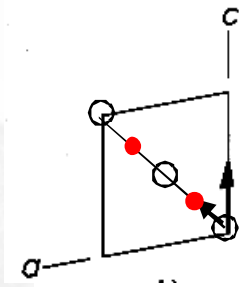
Skip

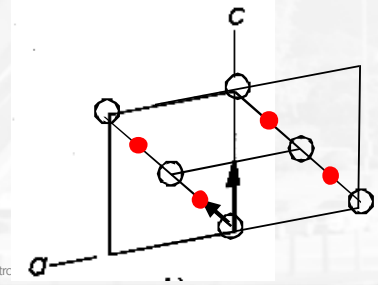








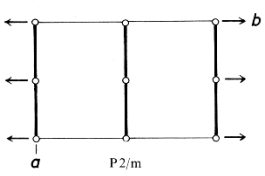


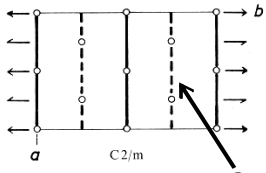


Space groups with d-glide

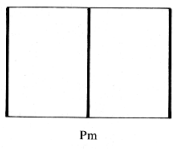
F d d d	I 4_1 m d
I 4_1 c d	I 4bar 2 d
I 4_1/a c d	F d 3bar
I 4bar 3 d	F d 3bar m
F d 3bar c	I a 3bar d

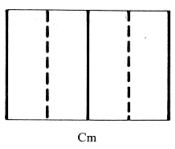
Space groups – Monoclinic; x,y,0 projection



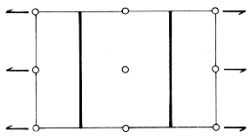


a-glide

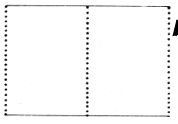


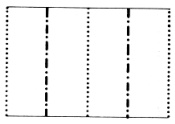


c-glide



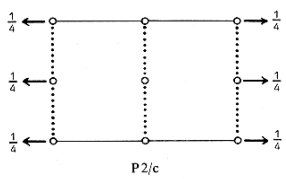
C2₁/m = C2/m

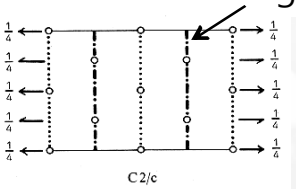


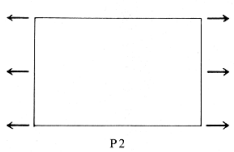


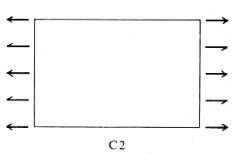
n-glide

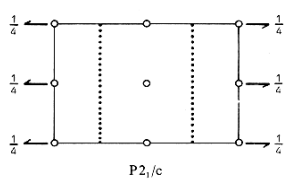
b Space groups of point group m



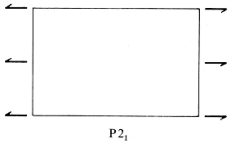






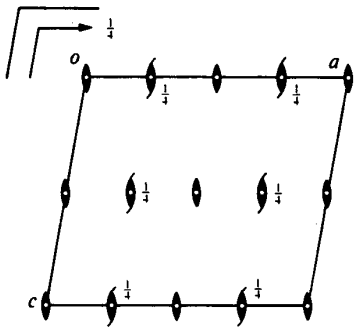


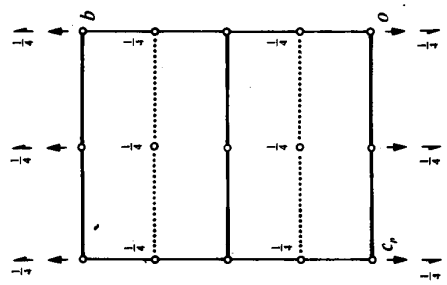
C2₁/c = C2/c

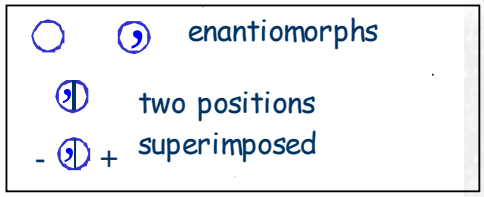


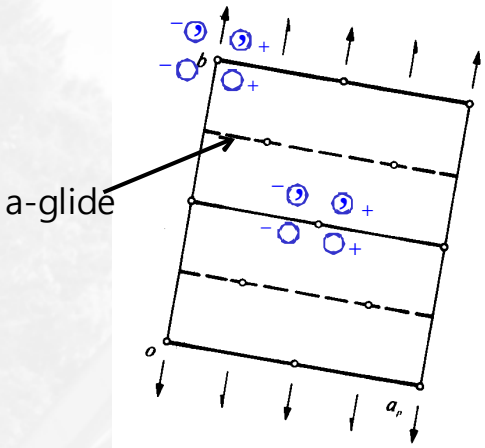
C2₁ = C2

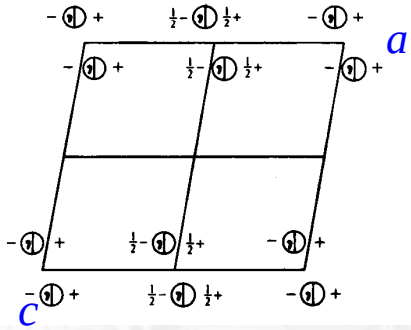
$C\frac{2}{m}$











International Tables for X-ray Crystallography

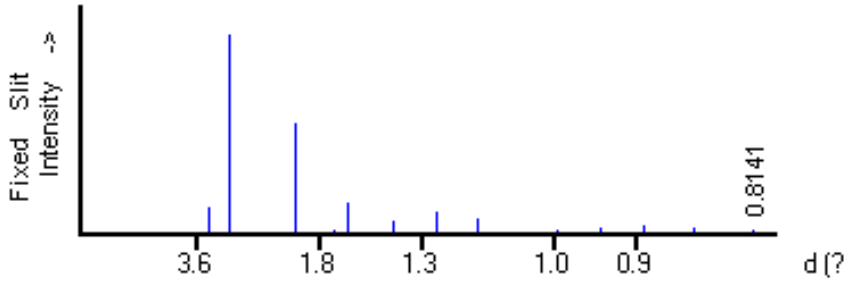
Powder Diffraction File (PDF)

CAS; chemical abstracts service registry number

PDF # 050628, Wavelength = 1.5405 (A)

05-0628	Quality: *
CAS Number:	7647-14-5
Molecular Weight:	58.44
Volume[CD]:	179.43
Dx: 2.163	Dm: 2.168
Sys: Cubic	
Lattice: Face-centered	
S.G.: Fm3m (225)	
Cell Parameters:	
a 5.640 b	c
α β	γ
SS/FOM: F17=93(.0108, 17)	
I/Icor: 4.40	
Rad: CuKa1	
Lambda: 1.5405	
Filter: Ni	
d-sp:	
Mineral Name:	
Halite syn	

Na Cl
Sodium Chloride
Ref: Swanson, Fuyat, Natl. Bur. Stand. (U.S.), Circ. 539, II, 41 (1953)



d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l
3.2600	13	1	1	1	1.2940	1	3	3	1	.94010	3	6	0	0
2.8210	100	2	0	0	1.2610	11	4	2	0	.89170	4	6	2	0
1.9940	55	2	2	0	1.1515	7	4	2	2	.86010	1	5	3	3
1.7010	2	3	1	1	1.0855	1	5	1	1	.85030	3	6	2	2
1.6280	15	2	2	2	.99690	2	4	4	0	.81410	2	4	4	4
1.4100	6	4	0	0	.95330	1	5	3	1					

ICDD

PDF

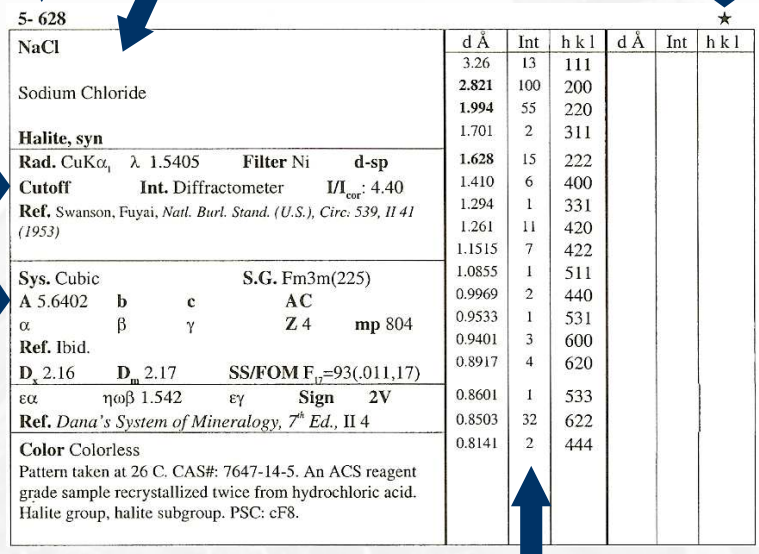
Quality mark
* Highest quality
i reasonable quality
o low quality
blank quality lower than o
c calculated data
r d's from Rietveld refinement

Set number
Add 1950 → year

Chemical formula
Chemical name
Mineral name

Experimental info
Types of X-ray
Wavelength
Monochromator/filter
Method of d measurement
Max measurable d-spacing
Method of I measurement
I/I(corundum)
Literature source

Physical data
Xtal system
International tables space group symbol
Axial lengths
Axial ratios
Interaxial angles
Number of chemical formulas in unit cell
Melting point
Literature source
X-ray density
Measured density
Figure of Merit



5- 628 ★

NaCl

Sodium Chloride

Halite, syn

Rad. CuKα$_1$ λ 1.5405 **Filter** Ni **d-sp**
Cutoff **Int.** Diffractometer **I/I$_{cor}$**: 4.40
Ref. Swanson, Fuyai, *Natl. Burl. Stand. (U.S.), Circ. 539, II 41 (1953)*

Sys. Cubic **S.G.** Fm3m(225)
A 5.6402 **b** **c** **AC**
α β γ **Z** 4 **mp** 804
Ref. Ibid.
D$_x$ 2.16 **D$_m$** 2.17 **SS/FOM F$_{17}$**=93(.011,17)
εα ηωβ 1.542 εγ **Sign** **2V**
Ref. *Dana's System of Mineralogy, 7th Ed.*, II 4

Color Colorless
Pattern taken at 26 C. CAS#: 7647-14-5. An ACS reagent grade sample recrystallized twice from hydrochloric acid. Halite group, halite subgroup. PSC: cF8.

d Å	Int	h k l	d Å	Int	h k l
3.26	13	111			
2.821	100	200			
1.994	55	220			
1.701	2	311			
1.628	15	222			
1.410	6	400			
1.294	1	331			
1.261	11	420			
1.1515	7	422			
1.0855	1	511			
0.9969	2	440			
0.9533	1	531			
0.9401	3	600			
0.8917	4	620			
0.8601	1	533			
0.8503	32	622			
0.8141	2	444			

General comments

D's, I's and Miller indices

ICDD

Quality mark

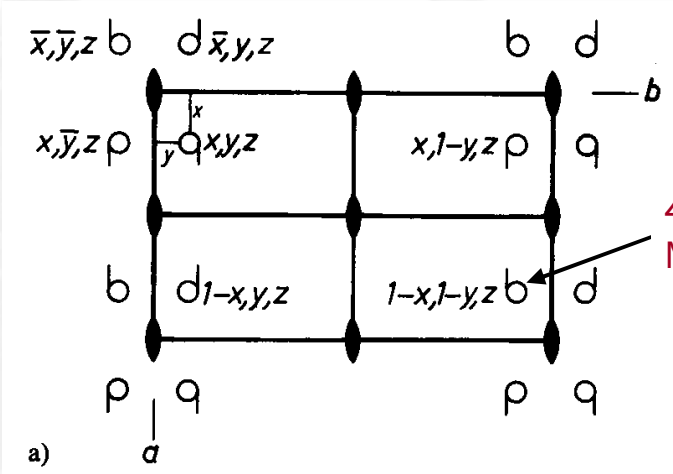
- * Highest quality
  - ✓ average Δ2θ < 0.03 degree, all lines were indexed, I measured quantitatively
- i reasonable quality
  - ✓ average Δ2θ < 0.06 degree, indexed with no more than two lines being unaccounted for, I measured quantitatively
- o low quality
  - ✓ low precision, poorly characterized, no unit cell data
- blank quality lower than o
- c calculated data
- r d's from Rietveld refinement

Space group - Pmm2

- for a point x, y, z (general point),

  symmetry element generates $\bar{x}, y, z;\ x, \bar{y}, z;\ \bar{x}, \bar{y}, z$

$x, y, z;\ \bar{x}, y, z;\ x, \bar{y}, z;\ \bar{x}, \bar{y}, z$ are equivalent (multiplicity of 4)



4-fold general position
Multiplicity of 4

Space group - Pmm2

- move the point x, y, z to mirror plane at $\frac{1}{2}, y, z$

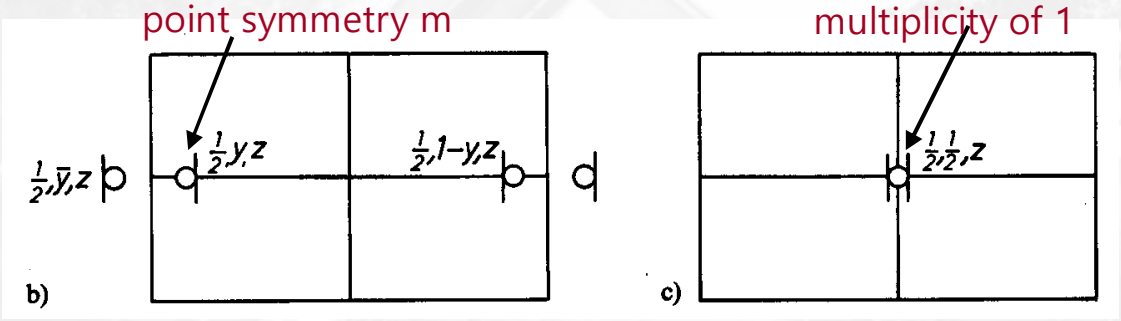
  x, y, z and $1-x, y, z$ coalesce to $\frac{1}{2}, y, z$

  $x, 1-y, z$ and $1-x, 1-y, z$ coalesce to $\frac{1}{2}, 1-y, z$

- multiplicity of 2
  - ✓ as long as the point remains on the mirror plane, its multiplicity is unchanged - degree of freedom 2

2-fold special position
point symmetry m

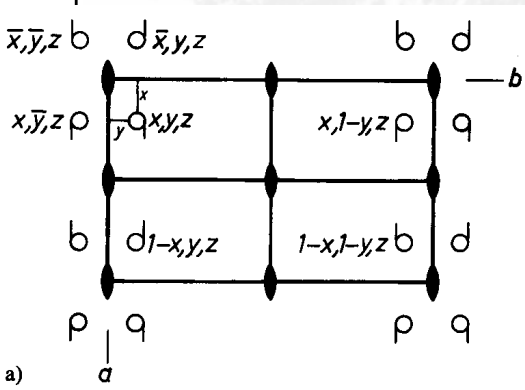
point symmetry mm2
multiplicity of 1



A special point arises from the merging of equivalent positions

Pmm2

Position	Degrees of freedom	Multi-plicity	Site symmetry	Coordinates of equivalent points
general	3	4	1	x,y,z; $\bar{x},\bar{y},z$; x,$\bar{y}$,z; $\bar{x}$,y,z
special	2	2	m	$\frac{1}{2}$,y,z; $\frac{1}{2}$,$\bar{y}$,z
		2	m	0,y,z; 0,$\bar{y}$,z
		2	m	x,$\frac{1}{2}$,z; $\bar{x}$,$\frac{1}{2}$,z
		2	m	x,0,z; $\bar{x}$,0,z
	1	1	mm2	$\frac{1}{2}$,$\frac{1}{2}$,z
		1	mm2	$\frac{1}{2}$,0,z
		1	mm2	0,$\frac{1}{2}$,z
		1	mm2	0, 0, z



Ott Chap 10

Space groups - multiplicity

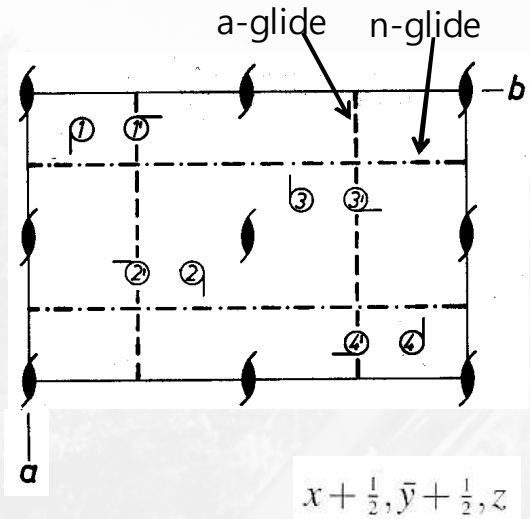
- screw axis and glide plane do not alter the multiplicity of a point

- $Pna2_1$: orthorhombic

n-glide normal to a-axis

a-glide normal to b-axis

2_1 screw axis along c-axis



General position – multiplicity of 4

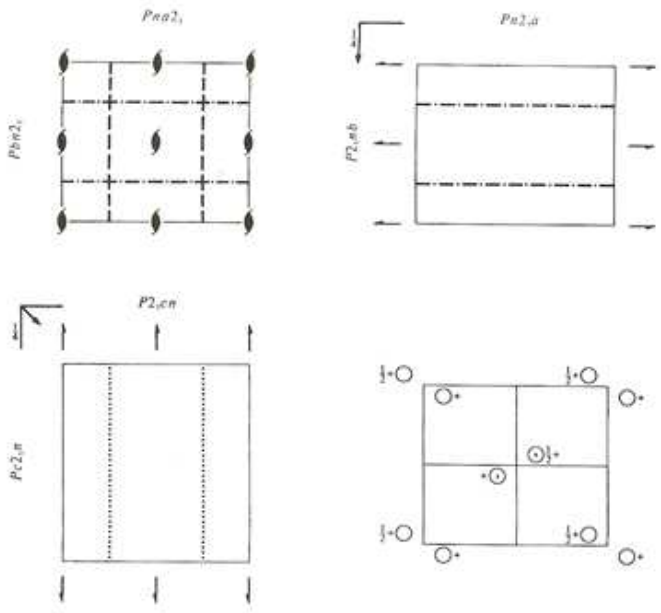
No special positions in $Pna2_1$

	$x+\frac{1}{2},\bar{y}+\frac{1}{2},z$	$\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$	$\bar{x},\bar{y},z+\frac{1}{2}$
① x,y,z,	② $\frac{1}{2}+x,\frac{1}{2}-y,z$,	③ $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$,	④ $1-x,1-y,\frac{1}{2}+z$
①′ $x,\frac{1}{4},z$,	②′ $\frac{1}{2}+x,\frac{1}{4},z$,	③′ $\frac{1}{2}-x,\frac{3}{4},\frac{1}{2}+z$,	④′ $1-x,\frac{3}{4},\frac{1}{2}+z$

$Pna2_1$

$Pna2_1$ C_{2v} $mm2$ Orthorhomb

No. 33 $Pna2_1$ Patterson symmetry Pmm



Origin on 112_1

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

Symmetry operations

(1) 1 (2) $2(0,0,\frac{1}{2})$ $0,0,z$ (3) a $x,\frac{1}{4},z$ (4) $n(0,\frac{1}{2},\frac{1}{2})$ $\frac{1}{4},y,z$

$Pna2_1$

CONTINUED No. 33 $Pna2_1$

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

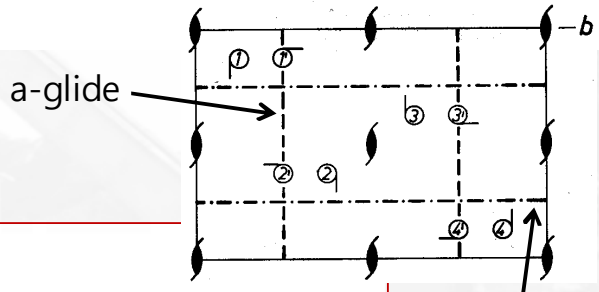
Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates			Reflection conditions
		④	②	③	General:
4 a 1	(1) x,y,z	(2) $\bar{x},\bar{y},z+\frac{1}{2}$	(3) $x+\frac{1}{2},\bar{y}+\frac{1}{2},z$	(4) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$	$0kl$: $k+l=2n$ $h0l$: $h=2n$ $h00$: $h=2n$ $0k0$: $k=2n$ $00l$: $l=2n$

General position

Special position

Symmetry of special projections



Symmetry operations

(1) 1 (2) $2(0,0,\frac{1}{2})$ $0,0,z$ (3) a $x,\frac{1}{4},z$ (4) $n(0,\frac{1}{2},\frac{1}{2})$ $\frac{1}{4},y,z$

General position – multiplicity of 4
No special positions in $Pna2_1$

- The number of equivalent points in the unit cell = **multiplicity**
- A **general position** is a set of equivalent points with point symmetry (site symmetry) 1
- A **special position** is a set of equivalent points with point symmetry (site symmetry) higher than 1
- The asymmetric unit of a space group is the smallest part of the unit cell from which the whole cell may be filled by the operation of all the symmetry operations

- General form : Set of equivalent faces, each of which has symmetry 1
- Special form : Set of equivalent faces, each of which has symmetry higher than 1
- Limiting form : A special case of either a general or a special form. It has the same number of faces, each of which has the same face symmetry, but the faces are differently arranged.
- Asymmetric face unit : The smallest part of the surface of the sphere which, by the application of the symmetry operations, will generate the entire surface of the sphere

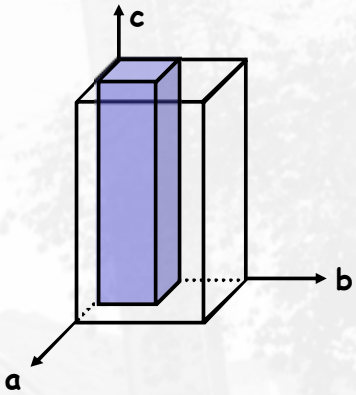
Space groups - asymmetric unit

- The asymmetric unit of a space group; the smallest part of the unit cell from which the whole cell may be filled by the operation of all the symmetry operations.

$$V_{\text{asymm.unit}} = \frac{V_{\text{unit cell}}}{\text{multiplicity of general position}}$$

- Asymmetric unit of Pmm2 ($a \neq b \neq c$, multiplicity of 4)

  $0 \le x \le \frac{1}{2}$, $0 \le y \le \frac{1}{2}$, $0 \le z \le 1$ $\quad V_{\text{asym.unit}} = V_{\text{unit cell}} / 4$



- Asymmetric unit contains all the information necessary for the complete description of a crystal structure

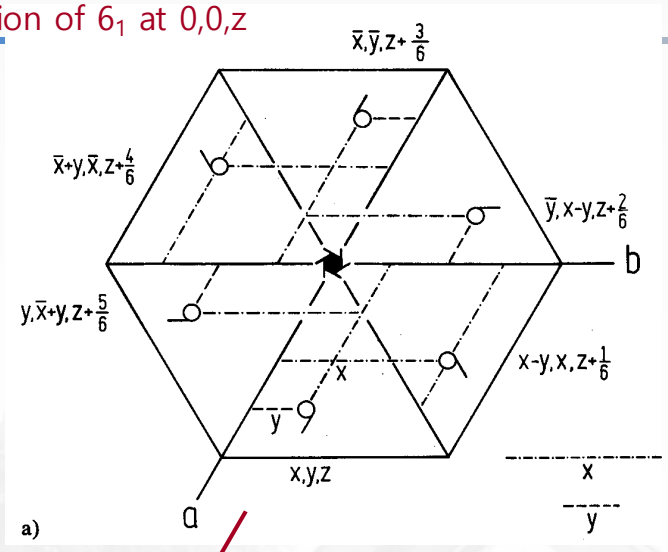
Unit cell

the smallest unit of volume that contains all of the structural and symmetry information and that can reproduce a pattern in all of space by translation.

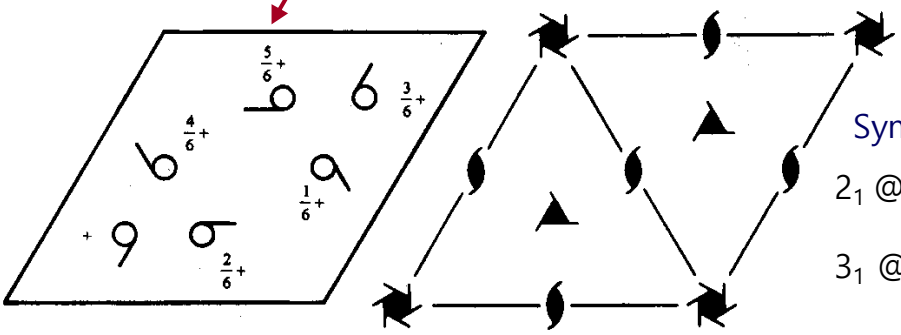
Look hard at the fig. 10.13 and table 10.4 (space group P2/m) of Ott

Space groups - $P6_1$

Operation of 6_1 at 0,0,z



Lattice translation

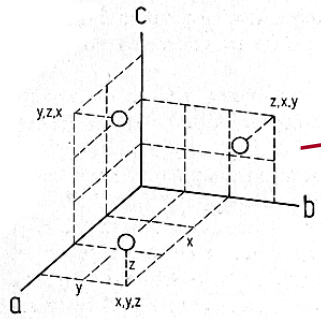


Symmetry elements of $P6_1$

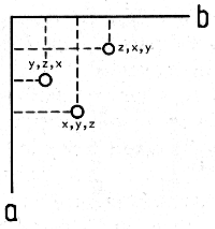
2_1 @ ½,½,z

3_1 @ 2/3,1/3,z & 1/3,2/3,z

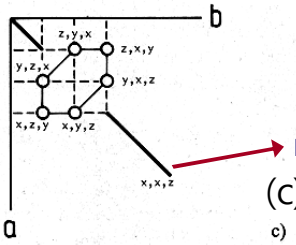
48-fold general position of space group $P\frac{4}{m}\bar{3}\frac{2}{m}$ (221)



(a) 3-fold rotation

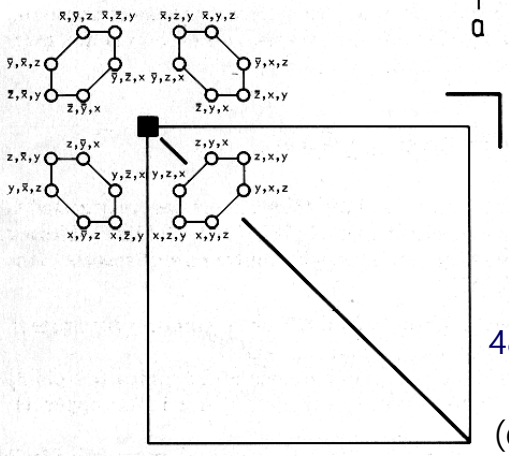


(b) projection on x,y,0 → 3



mirror plane @ x,x,z → 6

(c)



4-fold rotation @ 0,0,z

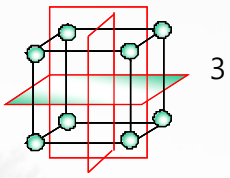
& mirror plane @ x,y,0 (planr of paper)

→ 6 x 4 x 2 = 48

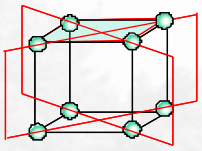
48 points can be generated by symmetry 4/m 3 m

(d)

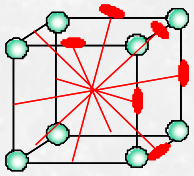
$\frac{4}{m}\bar{3}\frac{2}{m} (\equiv m\bar{3}m)$



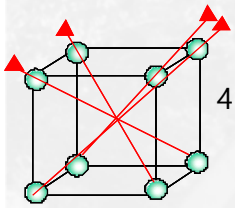
3



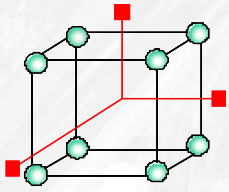
6



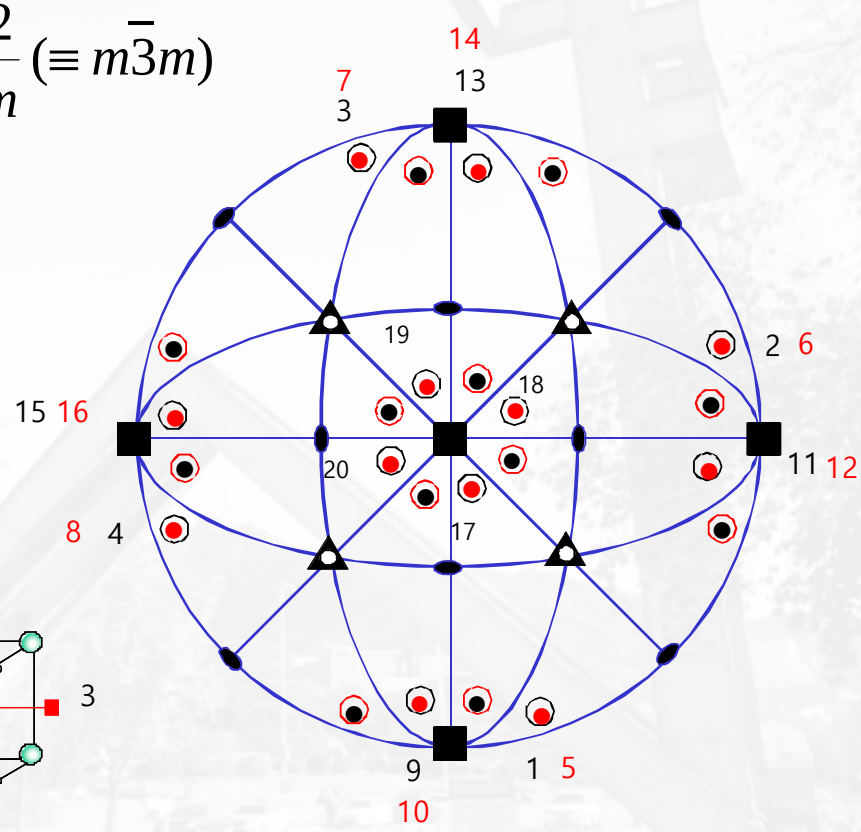
6



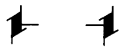
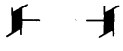
4



3



(e) Symmetry axes parallel to the plane of projection

Symmetry axis	Graphical symbol	Screw vector of a right-handed screw rotation in units of the shortest lattice translation vector parallel to the axis	Printed symbol
Twofold rotation axis		None	2
Twofold screw axis: '2 sub 1'		$\frac{1}{2}$	2_1
Fourfold rotation axis		None	4
Fourfold screw axis: '4 sub 1'		$\frac{1}{4}$	4_1
Fourfold screw axis: '4 sub 2'		$\frac{1}{2}$	4_2
Fourfold screw axis: '4 sub 3'		$\frac{3}{4}$	4_3
Inversion axis: '4 bar'		None	$\bar{4}$

(f) Symmetry axes inclined to the plane of projection (in cubic space groups only)

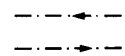
Symmetry axis	Graphical symbol	Screw vector of a right-handed screw rotation in units of the shortest lattice translation vector parallel to the axis	Printed symb
Twofold rotation axis		None	2
Twofold screw axis: '2 sub 1'		$\frac{1}{2}$	2_1
Threefold rotation axis		None	3
Threefold screw axis: '3 sub 1'		$\frac{1}{3}$	3_1
Threefold screw axis: '3 sub 2'		$\frac{2}{3}$	3_2
Inversion axis: '3 bar'		None	$\bar{3}$

OTT Chap 15.2

International Tables for X-ray Crystallography

1.4. Graphical symbols for symmetry elements in one, two, and three dimensions

(a) Symmetry planes normal to the plane of projection (three dimensions) and symmetry lines in the plane of the figure (two dimensions)

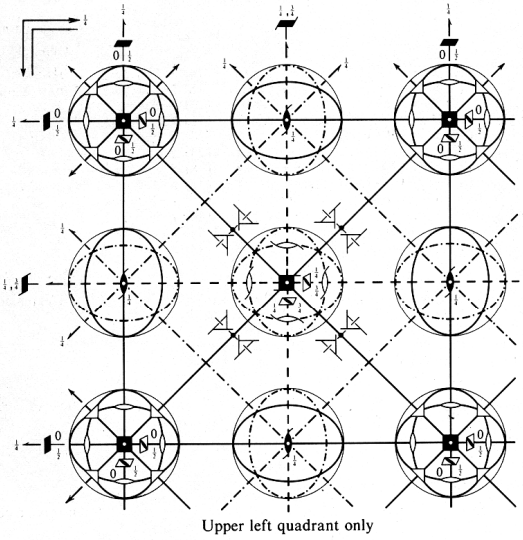
Symmetry plane or symmetry line	Graphical symbol	Glide vector in units of lattice translation vectors parallel and normal to the projection plane	Printed symbol
Reflection plane, mirror plane Reflection line, mirror line (two dimensions)		None	*m*
'Axial' glide plane Glide line (two dimensions)		$\frac{1}{2}$ along line parallel to projection plane $\frac{1}{2}$ along line in plane	*a*, *b* or *c* *g*
'Axial' glide plane		$\frac{1}{2}$ normal to projection plane	*a*, *b* or *c*
'Diagonal' glide plane		$\frac{1}{2}$ along line parallel to projection plane, combined with $\frac{1}{2}$ normal to projection plane	*n*
'Diamond' glide plane (pair of planes; in centred cells only)		$\frac{1}{4}$ along line parallel to projection plane, combined with $\frac{1}{4}$ normal to projection plane (arrow indicates direction parallel to the projection plane for which the normal component is positive)	*d*

OTT Chap 15.2

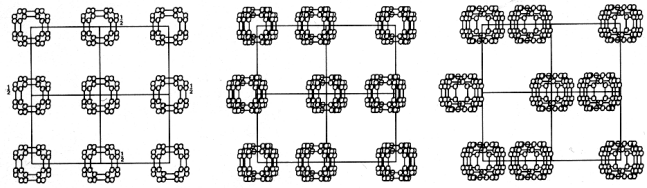
International Tables for X-ray Crystallography

$Fm\bar{3}m$ O_h^5 $m\bar{3}m$ Cubic

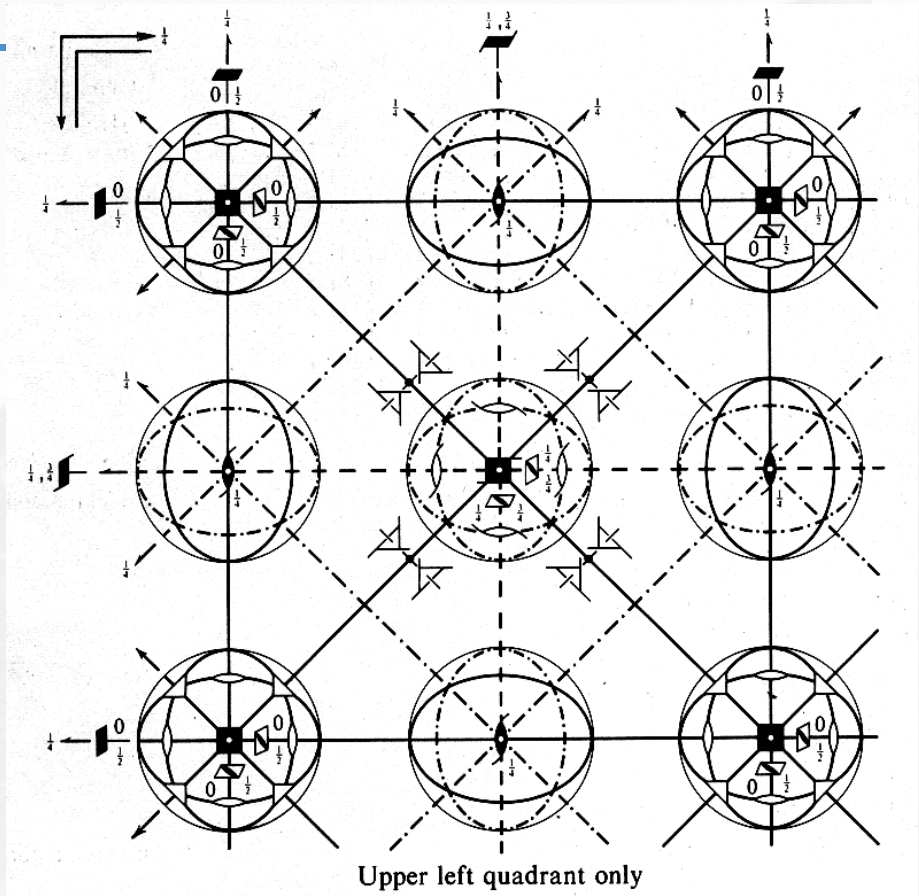
No. 225 $F4/m\bar{3}2/m$ Patterson symmetry $Fm\bar{3}m$



Upper left quadrant only



orthographic representation



Upper left quadrant only

International Tables for X-ray Crystallography

- International Tables for Crystallography, Brief teaching edition of Volume A: Space-group symmetry

  Edited by Theo Hahn

- International Tables for Crystallography, Volume A: Space-group symmetry

  Edited by Theo Hahn

International Tables for X-ray Crystallography

Short Hermann-Mauguin symbol

Schoenflies symbol

Point group

Crystal system symbol

Space group number

Full Hermann-Mauguin symbol

Patterson symmetry

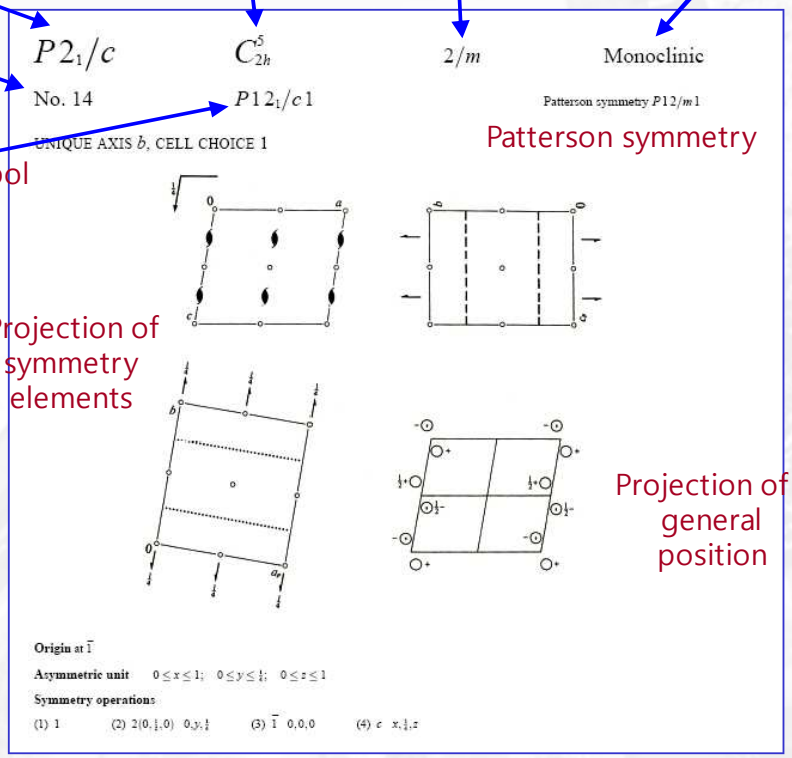
Projection of symmetry elements

Projection of a general position

Choice of origin

Asymmetric unit

Symmetry operations



General & special positions

CONTINUED No. 14 $P2_1/c$

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

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates				Reflection conditions
						General:
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l$: $l=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
				General position			Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			hkl : $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl : $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$
				Special position			

Symmetry of special projections

Along [001] $p2gm$
$\mathbf{a}' = \mathbf{a}_p$ $\mathbf{b}' = \mathbf{b}$
Origin at $0,0,z$

Along [100] $p2gg$
$\mathbf{a}' = \mathbf{b}$ $\mathbf{b}' = \mathbf{c}_p$
Origin at $x,0,0$

Along [010] $p2$
$\mathbf{a}' = \frac{1}{2}\mathbf{c}$ $\mathbf{b}' = \mathbf{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2] $P1c1$ (Pc, 7); 1; 4
[2] $P12_11$ ($P2_1$, 4); 1; 2
[2] $P\bar{1}$ (2); 1; 3

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [2] $P12_1/c1$ ($\mathbf{a}' = 2\mathbf{a}$ or $\mathbf{a}' = 2\mathbf{a}+\mathbf{c}$, $\mathbf{c}' = 2\mathbf{a}+\mathbf{c}$) ($P2_1/c$, 14); [3] $P12_1/c1$ ($\mathbf{b}' = 3\mathbf{b}$) ($P2_1/c$, 14)

Minimal non-isomorphic supergroups

I [2] $Pnna$ (52); [2] $Pmna$ (53); [2] $Pcca$ (54); [2] $Pbam$ (55); [2] $Pccn$ (56); [2] $Pbcm$ (57); [2] $Pnnm$ (58); [2] $Pbcn$ (60); [2] $Pbca$ (61); [2] $Pnma$ (62); [2] $Cmce$ (64)

II [2] $A12/m1$ ($C2/m$, 12); [2] $C12/c1$ ($C2/c$, 15); [2] $I12/c1$ ($C2/c$, 15); [2] $P12_1/m1$ ($\mathbf{c}' = \frac{1}{2}\mathbf{c}$) ($P2_1/m$, 11); [2] $P12/c1$ ($\mathbf{b}' = \frac{1}{2}\mathbf{b}$) ($P2/c$, 13)

- Asymmetric unit
  - ✓ a region of space which fills all space when all the symmetry operations of the space group are applied
  - ✓ smaller than a unit cell
- Unit cell
  - ✓ a region of space which fills all space when the translation operations are applied

Origin at $\bar{1}$

Asymmetric unit $0 \le x \le 1$; $0 \le y \le \frac{1}{4}$; $0 \le z \le 1$

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{4},0)$ $0,y,\frac{1}{4}$ (3) $\bar{1}$ $0,0,0$ (4) c $x,\frac{1}{4},z$

- Symmetry operations
  - ✓ (n) of the general equivalent position can be obtained from (1) x,y,z by symmetry operation number (n)
  - ✓ (3) –x,-y,-z ← 1bar with 0,0,0 as inversion point

4	*e*	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$

Origin at $\bar{1}$

Asymmetric unit $0 \le x \le 1;\quad 0 \le y \le \frac{1}{4};\quad 0 \le z \le 1$

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{2},0)$ $0,y,\frac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) *c* $x,\frac{1}{4},z$

Screw part — Screw axis — Location of inversion point

c glide, glide plane x,¼,z

- Symmetry operations

Origin at $\bar{1}$

Asymmetric unit $0 \le x \le 1;\quad 0 \le y \le \frac{1}{4};\quad 0 \le z \le 1$

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{2},0)$ $0,y,\frac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) *c* $x,\frac{1}{4},z$

Screw part — Screw axis — Location of inversion point

c glide, glide plane x,¼,z

2 0, 1/4 , z 2-fold rotation around the line 0, ¼, z

a x, y, ¼ glide reflection w/ glide component (1/2, 0, 0) thru the plane x, y, ¼ (plane // (001) at z = ¼)

2 (0,0,1/2) ¼, 0, z 2-fold screw rotation w/ screw part (0,0,1/2) for which the corresponding screw axis coincides w/ the line ¼,0,z (runs // to [001] thru the point ¼,0,0)

- Generators
  - ✓ Symmetry operations and their sequence, selected to generate all symmetrically equivalent points of the general position from a point x,y,z
  - ✓ Set of symmetry operators which when successfully multiplied yield ALL of the operators of the group
  - ✓ List of symmetry operations selected that can generate all of the symmetry operations of the space group

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

translations

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{4},0)$ $0,y,\frac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) c $x,\frac{1}{4},z$

- Positions
  - ✓ Multiplicity (rank); # equivalent points per unit cell
  - ✓ Wyckoff letter
  - ✓ Site symmetry (point symmetry of the position)
  - ✓ Coordinates of the equivalent positions

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$		
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$		
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$		
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$		

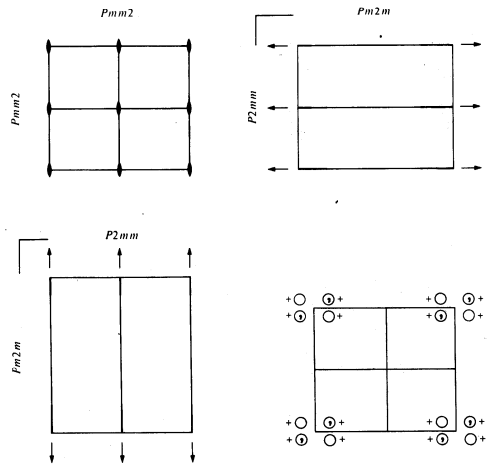
General position

Special position

Space group - Pmm2

$Pmm2$ C_{2v}^1 $mm2$ Orthorhombic

No. 25 $Pmm2$ Patterson symmetry $Pmmm$



Origin on $mm2$

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

Symmetry operations

(1) 1 (2) 2 0,0,z (3) m x,0,z (4) m 0,y,z

- short space group symbol
- Schoenflies symbol
- point group
- crystal system
- number of space group
- full space group symbol

- projection of symmetry elements
- projection of general position

CONTINUED No. 25 $Pmm2$

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

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			Reflection conditions
4	i	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $x,\bar{y},z$	(4) $\bar{x},y,z$	General: no conditions
2	h	m . .	$\frac{1}{2},y,z$	$\frac{1}{2},\bar{y},z$			Special: no extra conditions
2	g	m . .	$0,y,z$	$0,\bar{y},z$			
2	f	. m .	$x,\frac{1}{2},z$	$\bar{x},\frac{1}{2},z$			
2	e	. m .	$x,0,z$	$\bar{x},0,z$			
1	d	$mm2$	$\frac{1}{2},\frac{1}{2},z$				
1	c	$mm2$	$\frac{1}{2},0,z$				
1	b	$mm2$	$0,\frac{1}{2},z$				
1	a	$mm2$	$0,0,z$				

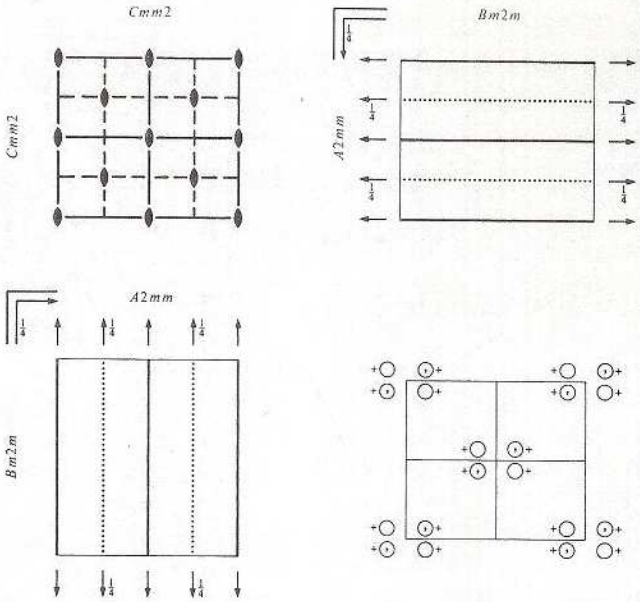
General position

Special position

Symmetry directions a, b, c

① $Cmm2$ C_{2v}^{11} $mm2$ Orthorhombic

② No. 35 $Cmm2$ Patterson symmetry $Cmmm$



④ **Origin** on $mm2$

⑤ **Asymmetric unit** $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{2}$; $0 \le z \le 1$

⑥ **Symmetry operations**

For $(0,0,0)+$ set

(1) 1 (2) 2 $0,0,z$ (3) m $x,0,z$ (4) m $0,y,z$

For $(\frac{1}{2},\frac{1}{2},0)+$ set

(1) $t(\frac{1}{2},\frac{1}{2},0)$ (2) 2 $\frac{1}{4},\frac{1}{4},z$ (3) a $x,\frac{1}{4},z$ (4) b $\frac{1}{4},y,z$

① *Headline*: Section 2.2.3.
Short Hermann–Mauguin symbol (Section 2.2.4 and Chapter 12.2) | Schoenflies symbol (Chapters 12.1 and 12.2) | Crystal class (Point group) (Section 10.1.1 and Chapter 12.1) | Crystal system (Section 2.1.2)

② Number of space group [Same as in *IT* (1952)] | Full Hermann–Mauguin symbol (Section 2.2.4 and Chapter 12.3) | Patterson symmetry (Section 2.2.5)

③ *Space-group diagrams*, consisting of one or several projections of the symmetry elements and one illustration of a set of equivalent points in general position. The numbers and types of the diagrams depend on the crystal system. The diagrams and their axes are described in Section 2.2.6; the graphical symbols of symmetry elements are listed in Chapter 1.4.
For monoclinic space groups see Section 2.2.16; for orthorhombic settings see Section 2.2.6.4.

④ *Origin* of the unit cell: Section 2.2.7. The site symmetry of the origin and its location with respect to the symmetry elements are given.

⑤ *Asymmetric unit*: Section 2.2.8. One choice of asymmetric unit is given.

⑥ *Symmetry operations*: Section 2.2.9 and Part 11. For each point $\bar{x}, \bar{y}, \bar{z}$ of the general position that symmetry operation is listed which transforms the initial point x, y, z into the point under consideration. The symbol describes the nature of the operation, its glide or screw component (given between parentheses), if present, and the location of the corresponding symmetry element.
The symmetry operations are numbered in the same way as the corresponding coordinate triplets of the general position. For centred space groups the same numbering is applied in each block, *e.g.* under 'For $(\frac{1}{2}, \frac{1}{2}, 0)+$ set'.

[*Continued on inside back cover*]

② **Generators selected** (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2},\frac{1}{2},0)$; (2); (3)

③ **Positions**

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
			$(0,0,0)+$	$(\frac{1}{2},\frac{1}{2},0)+$			General:
8	*f*	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $x,\bar{y},z$	(4) $\bar{x},y,z$	hkl : $h+k=2n$ $0kl$: $k=2n$ $h0l$: $h=2n$ $hk0$: $h+k=2n$ $h00$: $h=2n$ $0k0$: $k=2n$
4	*e*	m . .	$0,y,z$	$0,\bar{y},z$			Special: as above, plus no extra conditions
4	*d*	. m .	$x,0,z$	$\bar{x},0,z$			no extra conditions
4	*c*	. . 2	$\frac{1}{2},\frac{1}{4},z$	$\frac{1}{2},\frac{3}{4},z$			hkl : $h=2n$
2	*b*	$mm2$	$0,\frac{1}{2},z$				no extra conditions
2	*a*	$mm2$	$0,0,z$				no extra conditions

④ **Symmetry of special projections**

Along [001] $c2mm$
$\mathbf{a}' = \mathbf{a}$ $\mathbf{b}' = \mathbf{b}$
Origin at $0,0,z$

Along [100] $p1m1$
$\mathbf{a}' = \frac{1}{2}\mathbf{b}$ $\mathbf{b}' = \mathbf{c}$
Origin at $x,0,0$

Along [010] $p11m$
$\mathbf{a}' = \mathbf{c}$ $\mathbf{b}' = \frac{1}{2}\mathbf{a}$
Origin at $0,y,0$

⑤ **Maximal non-isomorphic subgroups**

I
[2] $C1m1$ (Cm, 8) (1; 3)+
[2] $Cm11$ (Cm, 8) (1; 4)+
[2] $C112$ ($P2$, 3) (1; 2)+

IIa
[2] $Pba2$ (32) 1; 2; (3; 4) + $(\frac{1}{2},\frac{1}{2},0)$
[2] $Pbm2$ ($Pma2$, 28) 1; 3; (2; 4) + $(\frac{1}{2},\frac{1}{2},0)$
[2] $Pma2$ (28) 1; 4; (2; 3) + $(\frac{1}{2},\frac{1}{2},0)$
[2] $Pmm2$ (25) 1; 2; 3; 4

IIb [2] $Ima2$ ($\mathbf{c}' = 2\mathbf{c}$) (46); [2] $Ibm2$ ($\mathbf{c}' = 2\mathbf{c}$) ($Ima2$, 46); [2] $Iba2$ ($\mathbf{c}' = 2\mathbf{c}$) (45); [2] $Imm2$ ($\mathbf{c}' = 2\mathbf{c}$) (44); [2] $Ccc2$ ($\mathbf{c}' = 2\mathbf{c}$) (37); [2] $Cmc2_1$ ($\mathbf{c}' = 2\mathbf{c}$) (36); [2] $Ccm2_1$ ($\mathbf{c}' = 2\mathbf{c}$) ($Cmc2_1$, 36)

⑥ **Maximal isomorphic subgroups of lowest index**

IIc [2] $Cmm2$ ($\mathbf{c}' = 2\mathbf{c}$) (35); [3] $Cmm2$ ($\mathbf{a}' = 3\mathbf{a}$ or $\mathbf{b}' = 3\mathbf{b}$) (35)

⑦ **Minimal non-isomorphic supergroups**

I [2] $Cmmm$ (65); [2] $Cmme$ (67); [2] $P4mm$ (99); [2] $P4bm$ (100); [2] $P4_2cm$ (101); [2] $P4_2nm$ (102); [2] $P\bar{4}2m$ (111); [2] $P\bar{4}2_1m$ (113); [3] $P6mm$ (183)

II [2] $Fmm2$ (42); [2] $Pmm2$ ($\mathbf{a}' = \frac{1}{2}\mathbf{a}, \mathbf{b}' = \frac{1}{2}\mathbf{b}$) (25)

① *Headline* in abbreviated form.

② *Generators selected*: Sections 2.2.10 and 8.3.5. A set of generators, as selected for these *Tables*, is listed in the form of translations and numbers of general-position coordinates. The generators determine the sequence of the coordinate triplets in the general position and of the corresponding symmetry operations.

③ *Positions*: Sections 2.2.11 and 8.3.2. The general Wyckoff position is given at the top, followed downwards by the various special Wyckoff positions with decreasing multiplicity and increasing site symmetry. For each general and special position its multiplicity, Wyckoff letter, oriented site-symmetry symbol, as well as the appropriate coordinate triplets and the reflection conditions, are listed. The coordinate triplets of the general position are numbered sequentially; *cf. Symmetry operations*.

Oriented site-symmetry symbol (third column): Section 2.2.12. The site symmetry at the points of a special position is given in oriented form.

Reflection conditions (right-most column): Section 2.2.13.

[*Lattice complexes* are described in Part 14; Tables 14.2.3.1 and 14.2.3.2 show the assignment of Wyckoff positions to Wyckoff sets and to lattice complexes.]

④ *Symmetry of special projections*: Section 2.2.14. For each space group, orthographic projections along three (symmetry) directions are listed. Given are the projection direction, the plane group of the projection, as well as the axes and the origin of the projected cell.

⑤ *Maximal non-isomorphic subgroups*: Sections 2.2.15 and 8.3.3.

Type **I**: *translationengleiche* or *t* subgroups;
Type **IIa**: *klassengleiche* or *k* subgroups, obtained by 'decentring' the conventional cell; applies only to space groups with centred cells;
Type **IIb**: *klassengleiche* or *k* subgroups, obtained by enlarging the conventional cell.

Given are:
For types **I** and **IIa**: Index [between brackets]; 'unconventional' Hermann–Mauguin symbol of the subgroup; 'conventional' Hermann–Mauguin symbol of the subgroup, if different (between parentheses); coordinate triplets retained in subgroup.
For type **IIb**: Index [between brackets]; 'unconventional' Hermann–Mauguin symbol of the subgroup; basis-vector relations between group and subgroup (between parentheses); 'conventional' Hermann–Mauguin symbol of the subgroup, if different (between parentheses).

⑥ *Maximal isomorphic subgroups of lowest index*: Sections 2.2.15, 8.3.3 and 13.1.2.

Type **IIc**: *klassengleiche* or *k* subgroups of lowest index which are of the same type as the group, *i.e.* have the same standard Hermann–Mauguin symbol. Data as for subgroups of type **IIb**.

⑦ *Minimal non-isomorphic supergroups*: Sections 2.2.15 and 8.3.3.
The list contains the reverse relations of the subgroup tables; only types **I** (*t* supergroups) and **II** (*k* supergroups) are distinguished. Data as for subgroups of type **IIb**.

Space groups - origin

- All centrosymmetric space groups are described with an inversion centers as origin. A 2nd description is given if a space group contains points of high site symmetry that do not coincide with a center of symmetry.

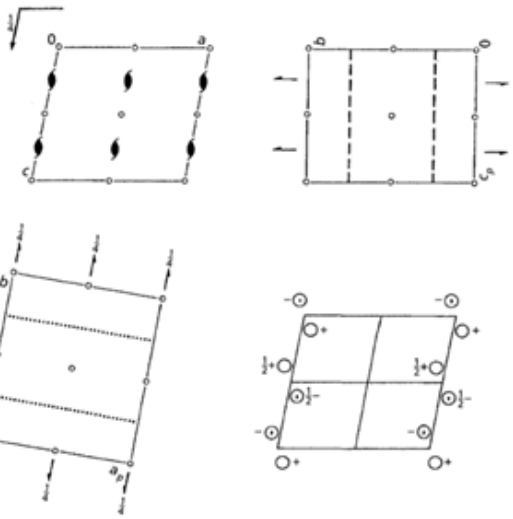
- For non-centrosymmetric space groups, the origin is at a point of highest site symmetry. If no site symmetry is higher than 1, the origin is placed on a screw axis or a glide plane, or at the intersection of several such symmetry elements.

$P2_1/c$ (14)

$P\,2_1/c$ C_{2h}^5 2/m Monoclinic

No. 14 $P\,1\,2_1/c\,1$ Patterson symmetry $P\,1\,2/m\,1$

UNIQUE AXIS *b*, CELL CHOICE 1



Origin at $\bar{1}$

Asymmetric unit $0\le x\le 1;\ 0\le y\le \frac{1}{4};\ 0\le z\le 1$

Symmetric operations

(1) 1 (2) $2(0,\frac{1}{4},0)$ $0,y,\frac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) c $x,\frac{1}{4},z$

2 choices for the unique axis b or c

3 choices of unit cell

Unique axis b, cell choice 1
Unique axis b, cell choice 2
Unique axis b, cell choice 3

Unique axis c, cell choice 1
Unique axis c, cell choice 2
Unique axis c, cell choice 3

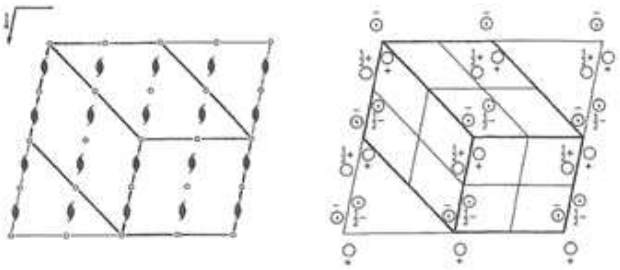
Total 8 pages

$P2_1/c$ (14) (continued)

(b) $P\,2_1/c$ C_{2h}^5 2/m Monoclinic

No. 14

UNIQUE AXIS *b*, DIFFERENT CELL CHOICES



$P\,12_1/c\,1$

UNIQUE AXIS *b*, CELL CHOICE 1

Origin at $\bar{1}$

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

Generators selected (1); t(1,0,0); t(0,1,0); t(0,0,1); (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates				Reflection conditions
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\frac{1}{2}+z$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\frac{1}{2}-y,\frac{1}{2}+z$	General: $h0l$: $l=2n$; $0k0$: $k=2n$; $00l$: $l=2n$
2	d	1	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			Special: as above, plus hkl: $k+l=2n$
2	c	1	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl: $k+l=2n$
2	b	1	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl: $k+l=2n$
2	a	1	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl: $k+l=2n$

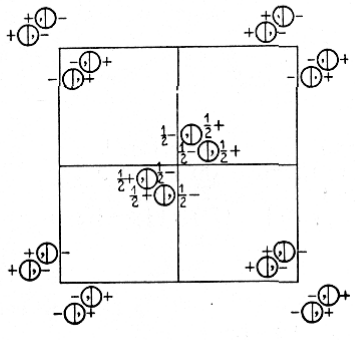
Hammond chap 4

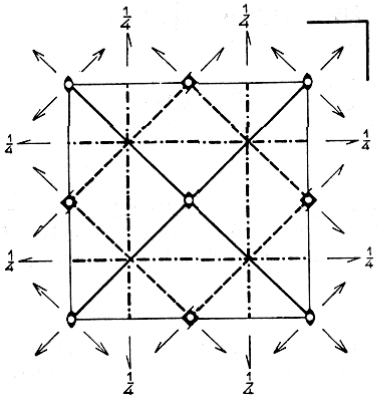
Fig. 4.13. Space group $P2_1/c$ (No. 14) (from the *International Tables for Crystallography*), (a) unique axis *b*, cell choice 1, (b) unique axis *b*, different cell choices.

Rutile, TiO_2

P* 4₂/*m n m D_{4h}^{14} 4/*m m m* Tetragonal

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





Ott Page 204

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

Asymmetric unit $0\le x\le \frac{1}{4};\ 0\le y\le \frac{1}{2};\ 0\le z\le \frac{1}{2};\ x\le y$

Symmetry operations

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

Rutile, TiO_2

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
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) $y+\frac{1}{2},\bar{x}+\frac{1}{2},z+\frac{1}{2}$	General:
			(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) $\bar{y},\bar{x},\bar{z}$	$0kl: k+l=2n$
			(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) $\bar{y}+\frac{1}{2},x+\frac{1}{2},\bar{z}+\frac{1}{2}$	$00l: l=2n$
			(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	$h00: h=2n$
8	j	..m	x,x,z $\bar{x}+\frac{1}{2},x+\frac{1}{2},\bar{z}+\frac{1}{2}$	$\bar{x},\bar{x},z$ $x+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2}$	$\bar{x}+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2}$ $x,x,\bar{z}$	$x+\frac{1}{2},\bar{x}+\frac{1}{2},z+\frac{1}{2}$ $\bar{x},\bar{x},\bar{z}$	Special: as above, plus no extra conditions
8	i	m..	$x,y,0$ $\bar{x}+\frac{1}{2},y+\frac{1}{2},\frac{1}{2}$	$\bar{x},\bar{y},0$ $x+\frac{1}{2},\bar{y}+\frac{1}{2},\frac{1}{2}$	$\bar{y}+\frac{1}{2},x+\frac{1}{2},\frac{1}{2}$ $y,x,0$	$y+\frac{1}{2},\bar{x}+\frac{1}{2},\frac{1}{2}$ $\bar{y},\bar{x},0$	no extra conditions
8	h	2..	$0,\frac{1}{2},z$ $0,\frac{1}{2},\bar{z}$	$0,\frac{1}{2},z+\frac{1}{2}$ $0,\frac{1}{2},\bar{z}+\frac{1}{2}$	$\frac{1}{2},0,\bar{z}+\frac{1}{2}$ $\frac{1}{2},0,z+\frac{1}{2}$	$\frac{1}{2},0,\bar{z}$ $\frac{1}{2},0,z$	$hkl: h+k,l=2n$
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	$0,0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			$hkl: h+k+l=2n$

General position

Special position

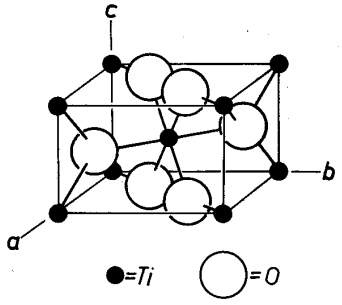
International Tables for X-ray Crystallography

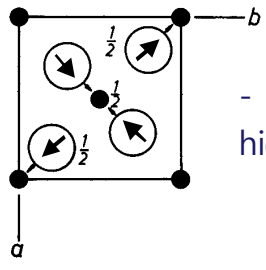
Rutile, TiO_2

Lattice + basis

Space group + positions of atoms (general or special)

A		B		
Lattice	**Basis**	**Space group**	**Positions of the atoms**	
tetragonal P	Ti: 0,0,0 $\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$P\,4_2/mnm$	a	Ti: 0,0,0 $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
$a_0=4.59$ Å $c_0=2.96$ Å	O: 0.3, 0.3, 0 0.8, 0.2, $\frac{1}{2}$ 0.2, 0.8, $\frac{1}{2}$ 0.7, 0.7, 0	$a_0=4.59$ Å $c_0=2.96$ Å	f	O: x,x,0 $\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2}$ $\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2}$ $\bar{x},\bar{x},0$ x=0.3





- B is simpler than A when positions of high multiplicity are involved.

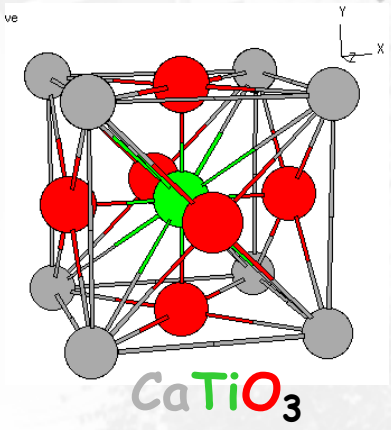
- B shows clearly which atoms are related to one another by the symmetry elements of the space group.

Table 11.2. Data for the three most important metal structure types, Cu, Mg and W, and for α-Po

	Cu ccp	Mg hcp	W bcc	α-Po sc
Lattice + basis	Cubic F 0,0,0	Hexagonal P 0,0,0; $\frac{2}{3},\frac{1}{3},\frac{1}{2}$	Cubic I 0,0,0	Cubic P 0,0,0
Space group + Positions occupied	F 4/m $\bar{3}$ 2/m (a) 0,0,0	P 6_3/m 2/m 2/c (c) 0,0,0; $\frac{2}{3},\frac{1}{3},\frac{1}{2}$	I 4/m $\bar{3}$ 2/m (a) 0,0,0	P 4/m $\bar{3}$ 2/m (a) 0,0,0
Coordination number	[12]		[8]	[6]
Atomic radii	$\frac{1}{4}a_0\sqrt{2}$	$\frac{1}{2}a_0$	$\frac{1}{4}a_0\sqrt{3}$	$\frac{1}{2}a_0$
Packing efficiency	0.74		0.68	0.52
Further examples	Ag, Au Ni, Al Pt, Ir Pb, Rh	Mg (1.62) Ni (1.63) Ti (1.59) Zr (1.59) Be (1.56) Zn (1.86)	Mo, V Ba, Na Zr, Fe	–

Perovskite, $CaTiO_3$

- Ca-corner
- O- face centered
- Ti- body centered
- high temperature – cubic, $Pm\bar{3}m$ (No.221)



$$Ca:\ 1a,\ m\bar{3}m,\ \ 0,0,0$$

$$Ti:\ 1b,\ m\bar{3}m,\ \ \frac{1}{2},\frac{1}{2},\frac{1}{2}$$

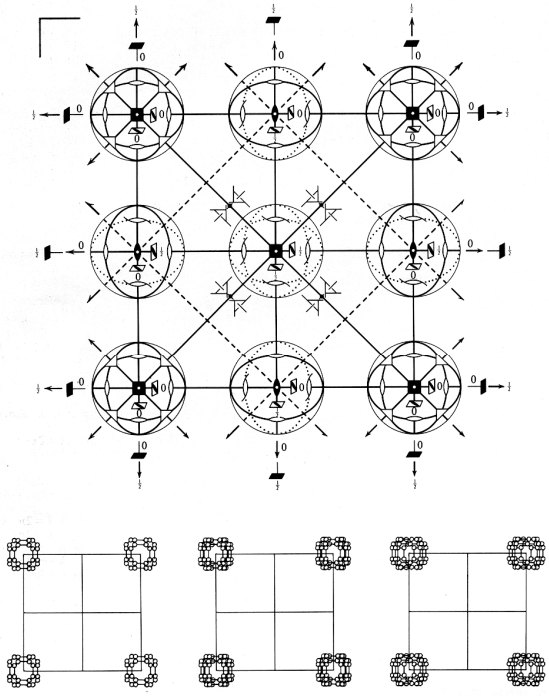
$$O:\ 3c,\ 4/mmm,\ \ 0,\frac{1}{2},\frac{1}{2}\ \ \frac{1}{2},0,\frac{1}{2}\ \ \frac{1}{2},\frac{1}{2},0$$

- Ti - 6O
- O - 4Ca + 2Ti
- Ca - 12O

3	*d*	4/*m m .m*	½,0,0	0,½,0	0,0,½
3	*c*	4/*m m .m*	0,½,½	½,0,½	½,½,0
1	*b*	*m* $\bar{3}$ *m*	½,½,½		
1	*a*	*m* $\bar{3}$ *m*	0,0,0		

$Pm\bar{3}m$ O_h^1 $m\bar{3}m$ Cubic

No. 221 $P4/m\bar{3}2/m$ Patterson symmetry $Pm\bar{3}m$



Origin at centre $(m\bar{3}m)$

Asymmetric unit $0\le x\le\frac{1}{4}$; $0\le y\le\frac{1}{4}$; $0\le z\le\frac{1}{4}$; $y\le x$; $z\le y$

Vertices 0,0,0 $\frac{1}{2}$,0,0 $\frac{1}{2},\frac{1}{2},0$ $\frac{1}{2},\frac{1}{2},\frac{1}{2}$

Symmetry operations
(*given on page* 664)

CONTINUED No. 221 $Pm\bar{3}m$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5); (13); (25)

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates				Reflection conditions
48 *n* 1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{x},y,\bar{z}$	(4) $x,\bar{y},\bar{z}$		*h,k,l* permutable
	(5) z,x,y	(6) $z,\bar{x},\bar{y}$	(7) $\bar{z},\bar{x},y$	(8) $\bar{z},x,\bar{y}$		General:
	(9) y,z,x	(10) $\bar{y},z,\bar{x}$	(11) $y,\bar{z},\bar{x}$	(12) $\bar{y},\bar{z},x$		no conditions
	(13) $y,x,\bar{z}$	(14) $\bar{y},\bar{x},\bar{z}$	(15) $y,\bar{x},z$	(16) $\bar{y},x,z$		
	(17) $x,z,\bar{y}$	(18) $\bar{x},z,y$	(19) $\bar{x},\bar{z},\bar{y}$	(20) $x,\bar{z},y$		
	(21) $z,y,\bar{x}$	(22) $z,\bar{y},x$	(23) $\bar{z},y,x$	(24) $\bar{z},\bar{y},\bar{x}$		
	(25) $\bar{x},\bar{y},\bar{z}$	(26) $x,y,\bar{z}$	(27) $x,\bar{y},z$	(28) $\bar{x},y,z$		
	(29) $\bar{z},\bar{x},\bar{y}$	(30) $\bar{z},x,y$	(31) $z,x,\bar{y}$	(32) $z,\bar{x},y$		
	(33) $\bar{y},\bar{z},\bar{x}$	(34) $y,\bar{z},x$	(35) $\bar{y},z,x$	(36) $y,z,\bar{x}$		
	(37) $\bar{y},\bar{x},z$	(38) y,x,z	(39) $\bar{y},x,\bar{z}$	(40) $y,\bar{x},\bar{z}$		
	(41) $\bar{x},\bar{z},y$	(42) $x,\bar{z},\bar{y}$	(43) x,z,y	(44) $\bar{x},z,\bar{y}$		
	(45) $\bar{z},\bar{y},x$	(46) $\bar{z},y,\bar{x}$	(47) $z,\bar{y},\bar{x}$	(48) z,y,x		
24 *m* . . *m*	x,x,z	$\bar{x},\bar{x},z$	$\bar{x},x,\bar{z}$	$x,\bar{x},\bar{z}$	z,x,x	$z,\bar{x},\bar{x}$
	$\bar{z},\bar{x},x$	$\bar{z},x,\bar{x}$	x,z,x	$\bar{x},z,\bar{x}$	$x,\bar{z},\bar{x}$	$\bar{x},\bar{z},x$
	$x,x,\bar{z}$	$\bar{x},\bar{x},\bar{z}$	$x,\bar{x},z$	$\bar{x},x,z$	$x,z,\bar{x}$	$\bar{x},z,x$
	$\bar{x},\bar{z},\bar{x}$	$x,\bar{z},x$	$z,x,\bar{x}$	$z,\bar{x},x$	$\bar{z},x,x$	$\bar{z},\bar{x},\bar{x}$
24 *l* *m* . .	$\frac{1}{2},y,z$	$\frac{1}{2},\bar{y},z$	$\frac{1}{2},y,\bar{z}$	$\frac{1}{2},\bar{y},\bar{z}$	$z,\frac{1}{2},y$	$z,\frac{1}{2},\bar{y}$
	$\bar{z},\frac{1}{2},y$	$\bar{z},\frac{1}{2},\bar{y}$	$y,z,\frac{1}{2}$	$\bar{y},z,\frac{1}{2}$	$y,\bar{z},\frac{1}{2}$	$\bar{y},\bar{z},\frac{1}{2}$
	$y,\frac{1}{2},\bar{z}$	$\bar{y},\frac{1}{2},\bar{z}$	$y,\frac{1}{2},z$	$\bar{y},\frac{1}{2},z$	$\frac{1}{2},z,\bar{y}$	$\frac{1}{2},z,y$
	$\frac{1}{2},\bar{z},\bar{y}$	$\frac{1}{2},\bar{z},y$	$z,y,\frac{1}{2}$	$z,\bar{y},\frac{1}{2}$	$\bar{z},y,\frac{1}{2}$	$\bar{z},\bar{y},\frac{1}{2}$
24 *k* *m* . .	$0,y,z$	$0,\bar{y},z$	$0,y,\bar{z}$	$0,\bar{y},\bar{z}$	$z,0,y$	$z,0,\bar{y}$
	$\bar{z},0,y$	$\bar{z},0,\bar{y}$	$y,z,0$	$\bar{y},z,0$	$y,\bar{z},0$	$\bar{y},\bar{z},0$
	$y,0,\bar{z}$	$\bar{y},0,\bar{z}$	$y,0,z$	$\bar{y},0,z$	$0,z,\bar{y}$	$0,z,y$
	$0,\bar{z},\bar{y}$	$0,\bar{z},y$	$z,y,0$	$z,\bar{y},0$	$\bar{z},y,0$	$\bar{z},\bar{y},0$
12 *j* *m* .*m* 2	$\frac{1}{2},y,y$	$\frac{1}{2},\bar{y},y$	$\frac{1}{2},y,\bar{y}$	$\frac{1}{2},\bar{y},\bar{y}$	$y,\frac{1}{2},y$	$y,\frac{1}{2},\bar{y}$
	$\bar{y},\frac{1}{2},y$	$\bar{y},\frac{1}{2},\bar{y}$	$y,y,\frac{1}{2}$	$\bar{y},y,\frac{1}{2}$	$y,\bar{y},\frac{1}{2}$	$\bar{y},\bar{y},\frac{1}{2}$
12 *i* *m* .*m* 2	$0,y,y$	$0,\bar{y},y$	$0,y,\bar{y}$	$0,\bar{y},\bar{y}$	$y,0,y$	$y,0,\bar{y}$
	$\bar{y},0,y$	$\bar{y},0,\bar{y}$	$y,y,0$	$\bar{y},y,0$	$y,\bar{y},0$	$\bar{y},\bar{y},0$
12 *h* *mm*2 . .	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$0,x,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	$\frac{1}{2},0,x$	$\frac{1}{2},0,\bar{x}$
	$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$	$0,\frac{1}{2},\bar{x}$	$0,\frac{1}{2},x$
8 *g* .3*m*	x,x,x	$\bar{x},\bar{x},x$	$\bar{x},x,\bar{x}$	$x,\bar{x},\bar{x}$		
	$x,x,\bar{x}$	$\bar{x},\bar{x},\bar{x}$	$x,\bar{x},x$	$\bar{x},x,x$		
6 *f* 4*m* .*m*	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},x$	$\frac{1}{2},\frac{1}{2},\bar{x}$
6 *e* 4*m* .*m*	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	$0,0,x$	$0,0,\bar{x}$
3 *d* 4/*m* *m* .*m*	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$0,0,\frac{1}{2}$			
3 *c* 4/*m* *m* .*m*	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			
1 *b* $m\bar{3}m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$					
1 *a* $m\bar{3}m$	$0,0,0$					

Special: no extra conditions

General position

Special position

3	*d*	4/*m* *m* .*m*	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$0,0,\frac{1}{2}$
3	*c*	4/*m* *m* .*m*	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$
1	*b*	$m\bar{3}m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$		
1	*a*	$m\bar{3}m$	$0,0,0$		

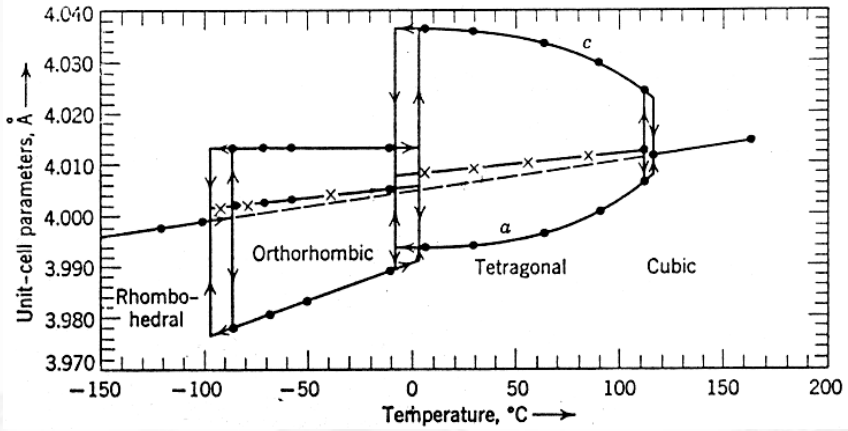
Symmetry of special projections

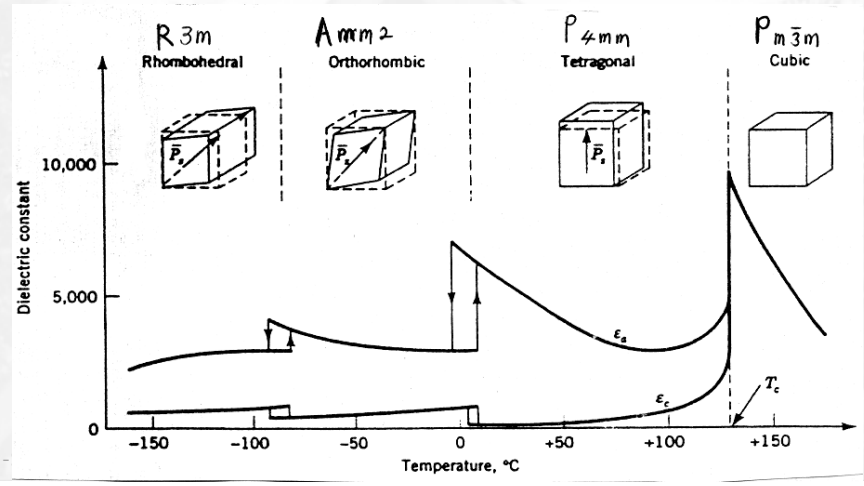
Along [001] $p4mm$
$\mathbf{a}'=\mathbf{a}$ $\mathbf{b}'=\mathbf{b}$
Origin at 0,0,*z*

Along [111] $p6mm$
$\mathbf{a}'=\frac{1}{3}(2\mathbf{a}-\mathbf{b}-\mathbf{c})$ $\mathbf{b}'=\frac{1}{3}(-\mathbf{a}+2\mathbf{b}-\mathbf{c})$
Origin at *x*,*x*,*x*

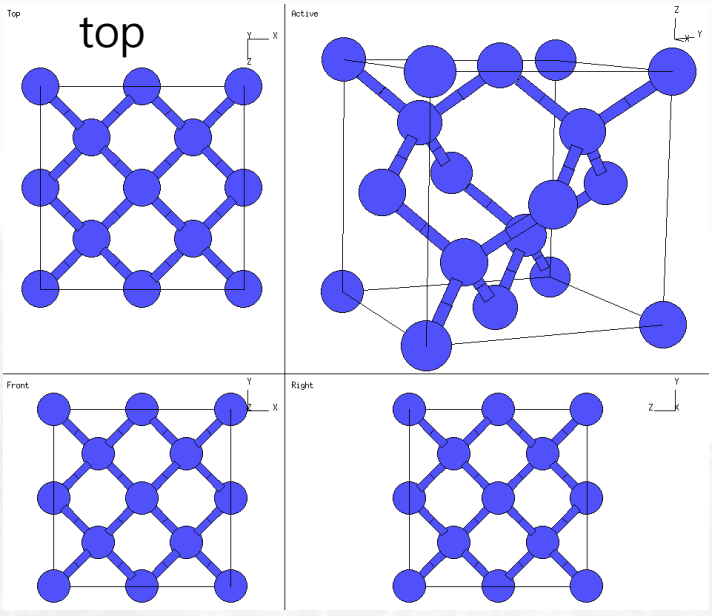
Along [110] $p2mm$
$\mathbf{a}'=\frac{1}{2}(-\mathbf{a}+\mathbf{b})$ $\mathbf{b}'=\mathbf{c}$
Origin at *x*,*x*,0

Perovskite, $BaTiO_3$





Diamond



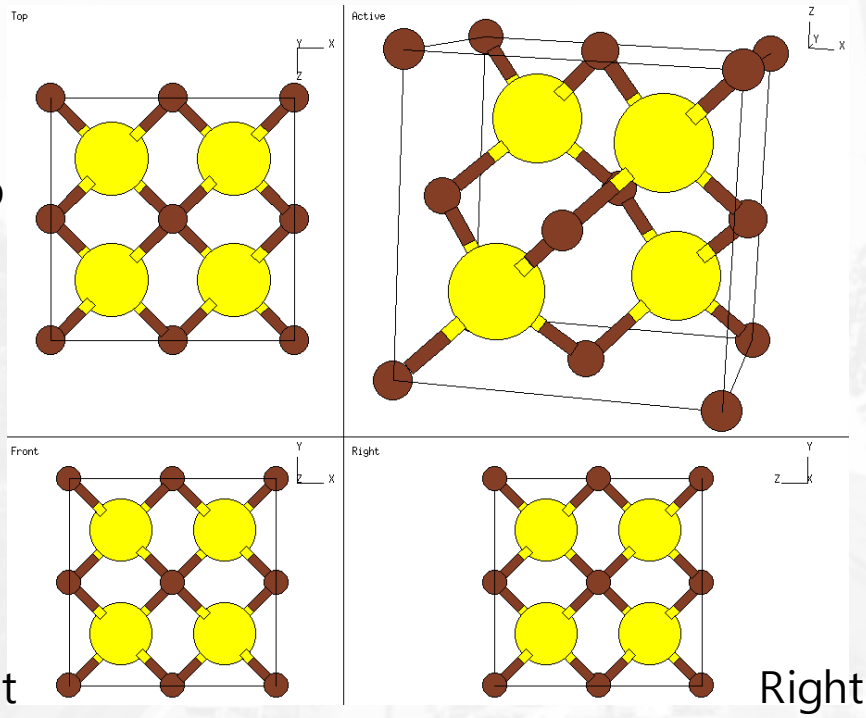
$F\,\frac{4}{d}\bar{3}\frac{2}{m}$ (No.227)

$Fd\bar{3}m$

Zinc blende, ZnS

$F\bar{4}3m$ (No.216)

Top



Front

Right

Zinc blende, ZnS

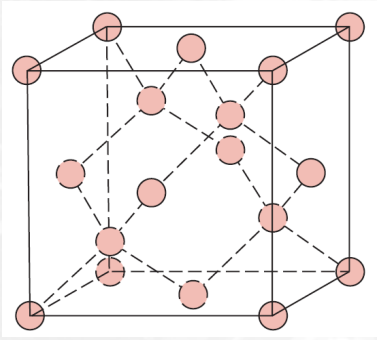
- diamond derivative structure
- Zn and S replace the C atoms in diamond
- Zn cubic close packing; S ½ tetrahedral site
- Zn and S cubic close packing displaced by $\frac{1}{4},\frac{1}{4},\frac{1}{4}$

$F\bar{4}3m$ (No.216)

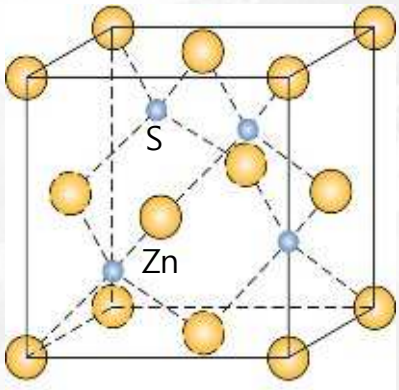
Zn: 4a, $\bar{4}3m$, $0,0,0$

Zn: 4c, $\bar{4}3m$, $\frac{1}{4},\frac{1}{4},\frac{1}{4}$

Diamond, Si, Ge



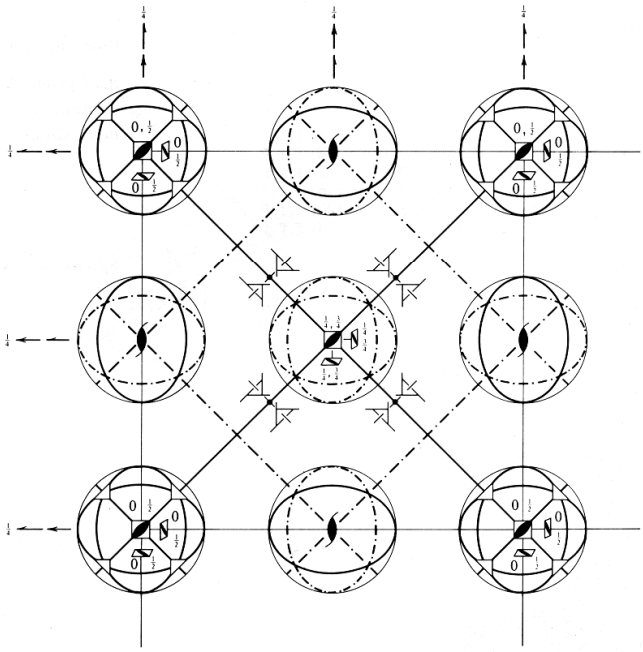
Zinc blende structure
ZnS, SiC



Zinc blende, ZnS

$F\bar{4}3m$ T_d^2 $\bar{4}3m$ Cubic

No. 216 $F\bar{4}3m$ Patterson symmetry $Fm\bar{3}m$



Upper left quadrant only

Zinc blende, ZnS

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(0,\frac{1}{2},\frac{1}{2})$; $t(\frac{1}{2},0,\frac{1}{2})$; (2); (3); (5); (13)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates (0,0,0)+	(0,½,½)+	(½,0,½)+	(½,½,0)+
96	*i*	1	(1) x,y,z (5) z,x,y (9) y,z,x (13) y,x,z (17) x,z,y (21) z,y,x	(2) $\bar{x},\bar{y},z$ (6) $z,\bar{x},\bar{y}$ (10) $\bar{y},z,\bar{x}$ (14) $\bar{y},\bar{x},z$ (18) $\bar{x},z,\bar{y}$ (22) $z,\bar{y},\bar{x}$	(3) $\bar{x},y,\bar{z}$ (7) $\bar{z},\bar{x},y$ (11) $y,\bar{z},\bar{x}$ (15) $y,\bar{x},\bar{z}$ (19) $\bar{x},\bar{z},y$ (23) $\bar{z},y,\bar{x}$	(4) $x,\bar{y},\bar{z}$ (8) $\bar{z},x,\bar{y}$ (12) $\bar{y},\bar{z},x$ (16) $\bar{y},x,\bar{z}$ (20) $x,\bar{z},\bar{y}$ (24) $\bar{z},\bar{y},x$

General position

48	*h*	. . *m*	x,x,z $\bar{z},\bar{x},x$	$\bar{x},\bar{x},z$ $\bar{z},x,\bar{x}$	$\bar{x},x,\bar{z}$ x,z,x	$x,\bar{x},\bar{z}$ $\bar{x},z,\bar{x}$	z,x,x $x,\bar{z},\bar{x}$	$z,\bar{x},\bar{x}$ $\bar{x},\bar{z},x$
24	*g*	2 . *m m*	$x,\frac{1}{4},\frac{1}{4}$	$\bar{x},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},x,\frac{1}{4}$	$\frac{1}{4},\bar{x},\frac{1}{4}$	$\frac{1}{4},\frac{1}{4},x$	$\frac{1}{4},\frac{1}{4},\bar{x}$
24	*f*	2 . *m m*	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	$0,0,x$	$0,0,\bar{x}$
16	*e*	. 3 *m*	x,x,x	$\bar{x},\bar{x},x$	$\bar{x},x,\bar{x}$	$x,\bar{x},\bar{x}$		
4	*d*	$\bar{4}3m$	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$					
4	*c*	$\bar{4}3m$	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$					
4	*b*	$\bar{4}3m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$					
4	*a*	$\bar{4}3m$	$0,0,0$					

Special position

Reflection conditions

h,k,l permutable

General:

hkl : $h+k, h+l, k+l = 2n$
$0kl$: $k, l = 2n$
hhl : $h+l = 2n$
$h00$: $h = 2n$

Special: no extra conditions

Point group vs. Space group

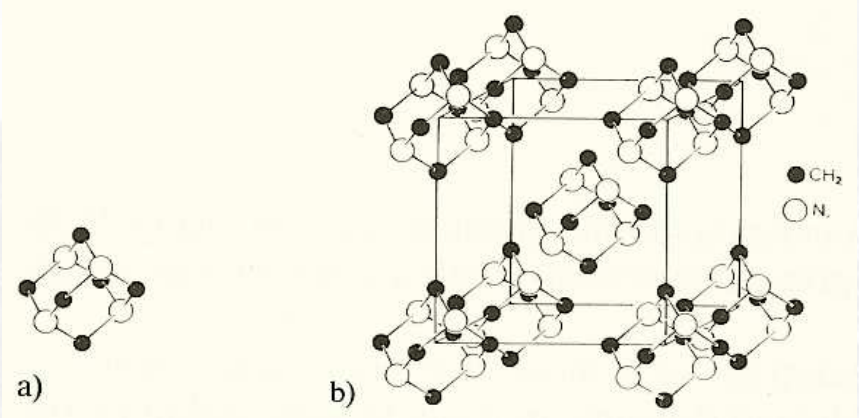
Point groups: A group of point symmetry operations, whose operation leaves at least one point unaltered. Any operation involving lattice translations is thus excluded	Space groups: A group of symmetry operations which include lattice translations
1 $\bar{1}$ 2 m 3 $\bar{3}$ 4 $\bar{4}$ 6 $\bar{6}$	1 $\bar{1}$ 2 m 2_1; a, b, c, n, e, d 3 $\bar{3}$ $3_1, 3_2$ 4 $\bar{4}$ $4_1, 4_2, 4_3$ 6 $\bar{6}$ $6_1, 6_2, 6_3, 6_4, 6_5$ lattice translations
a, b, c α, β, γ	a_0, b_0, c_0 α, β, γ
Order of the symmetry operations e.g. 4/m 2/m 2/m | | | c < a > < 110 >	Order of the symmetry operations e.g. $P4_2/m$ 2/m 2/m | | | c < a > < 110 >
General form: Set of equivalent faces each with face symmetry 1	General position: Set of equivalent points each with site symmetry 1
$f_{\text{asymmetric face unit}} = \frac{f_{\text{sphere}}}{\text{multiplicity of general form}}$	$V_{\text{asymmetric unit}} = \frac{V_{\text{unit cell}}}{\text{multiplicity of general point}}$
Multiplicity of general form of the point group	Multiplicity of the general position in all space groups with a P-lattice that are isomorphous with that point group
Special form: Set of equivalent faces each with face symmetry >1	Special position: Set of equivalent points each with site symmetry >1

Ott Chap 10

Molecular symmetry vs. Crystal symmetry

Point group of molecule — relation — Space group of crystal

Symmetry of hexa-methylene-tetramine ($C_6H_{12}N_4$)

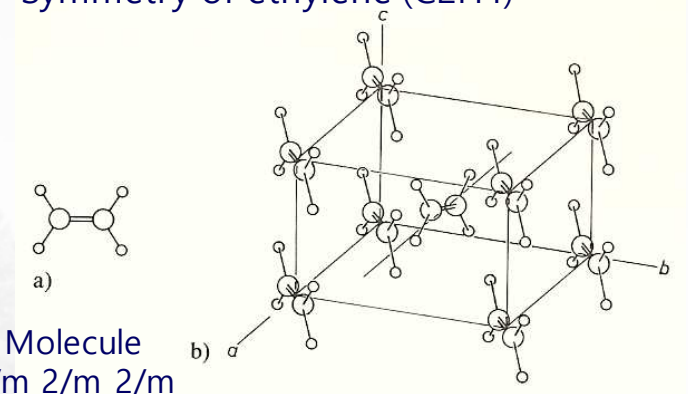


Molecule; $\bar{4}3m$ Crystal structure; $I\bar{4}3m$

Molecules occupy positions with site symmetry $\bar{4}3m$.
Not a general case

Molecular symmetry vs. Crystal symmetry

Symmetry of ethylene (C2H4)



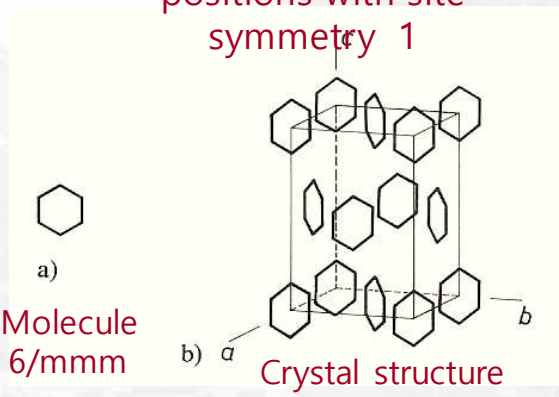
Molecule
2/m 2/m 2/m

Crystal structure
$P2_1/n\ 2_1/n\ 2/m$
(Pnnm)

Molecules occupy positions with site symmetry 2/m

Symmetry of Benzene (C6H6)

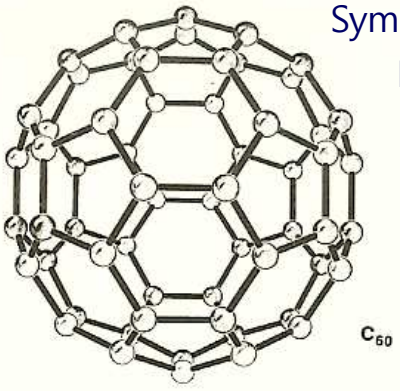
Molecules occupy positions with site symmetry $\bar{1}$



Molecule
6/mmm

Crystal structure
Pbca

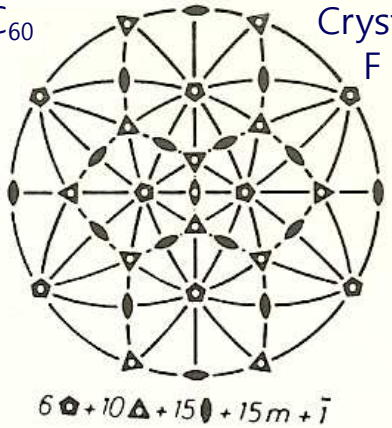
Molecular symmetry vs. Crystal symmetry



a)

Symmetry of C_{60}

Molecule
2/m $\bar{3}\,\bar{5}$



b)

Crystal structure of C_{60}
F 4/m $\bar{3}$ 2/m (ccp)

Ott page 147
The point groups of molecules are not limited to the 32 crystallographic groups. They may contain such symmetry elements as 5-fold axes which are incompatible with a crystal lattice. These non-crystallographic point groups are described in Sect.9.7.

No simple relationship between molecular symmetry & crystal symmetry

todos

- Read (Space Group 2)
  - ✓ Ott Chapter 10
  - ✓ Hammond Chapter 4.6~4.7
  - ✓ Krawitz Chapter 1.6~1.8
  - ✓ Sherwood & Cooper Chapter 3.8
  - ✓ Hammond Chapter 2.1 ~ 2.5; 3.1 ~ 3.3; 4.1 ~ 4.5; 5.1 ~ 5.6
  - ✓ Krawitz Chapter 1.1 ~ 1.8

- Space Group-2 HW (due in 1 week)
  - ✓ Ott chapter 10 --- 7, 9, 13, 14
  - ✓ Hammond chapter 4 --- 1, 2