TODAY

SCHEDULE

	Date		Topic
1.	Wed	01.03.	Lec-1: Introduction
2.	Mon	06.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon	06.03.	EXERCISE 1
4.	Wed	08.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri	10.03.	Lec-4: Symmetry & Point Groups
6.	Mon	13.03.	EXERCISE 2
7.	Wed	15.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri	17.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon	20.03.	EXERCISE 3 (Linda)
10.	Fri	31.03.	Lec-7: Rietveld (Linda)
11.	Mon	03.04	EXERCISE 4: Rietveld (Linda)
12.	Wed	12.04.	Lec-8: ND & GI-XRD
13.	Fri	14.04.	Lec-9: XRR (Topias)
14.	Mon	17.04.	EXERCISE 5: XRR (Topias)
15.	Wed	19.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
16.	Fri	21.04.	Mössbauer
17.	Fri	21.04.	EXERCISE 6
18.	Thu	27.04.	Seminars: XPS, FTIR, Raman
19.	Fri	28.04.	Seminars: ED, HRTEM, SEM, AFM

EXAM

LINDA'S LECTURES & EXERCISES

- 15.03. WEDNESDAY: 14.15 – 16 (Ke3)
- 17.03. FRIDAY: 8.30 – 10 (Ke4)
- 20.03. MONDAY: 14.15 – 16 (Ke4)
- 31.03. FRIDAY: 8.30 – 10 (Ke4)
- 03.04. MONDAY: 10 – 13 (Ke3)
    - Two groups, 10-11.30 & 11.30-13

SEMINARS

- IR Fasiha Israr & Lisa Riedlsperger
- Raman Zonghang Song & Xueran Tao
- XPS Umaid Lone
- SEM Trang Pham & Erkka Koskenniemi
- AFM Joakim Kattelus & Matilda Antila
- HRTEM Luiza Souza & Henrik Stenbrink
- ED Christer Söderholm & Shadab Ishtiaq
- EELS Aleksi Rantanen & Jasmin Sonphasit

INSTRUCTIONS for SEMINAR PRESENTATIONS

- Topics: **IR, Raman, XPS, SEM, AFM, HRTEM, ED, EELS**
- Seminar presentation is mandatory
- Presentation slides will be put up in MyCourses afterwards
- **Seminars are part of the course content and it is likely that there will be questions in the exam related to these seminars**
- Given in a group of two students
- Evaluated in the scale: 10 ~ 20 points
- Presentation: 25+5 minutes
- Rough content of the presentation:
  - principle of the technique(s)
  - type of information gained
  - interpretation of the measured data
  - pros & cons
  - **two to four research examples**
    (you will be given some relevant research papers for an example)

INTRO

LECTURE 5: CRYSTALLOGRAPHY BASICS

- **From ”point-like” molecules to 3D crystals**
- **Translation in 3D crystals →**
  NEW SYMMETRY OPERATIONS (glide planes & screw axes)
- **From *Point groups* to *Space groups***
- **Crystal lattice, lattice points & unit cell**
- **International Tables of Crystallography**

Symmetry elements (Schönflies / Hermann-Mauguin)

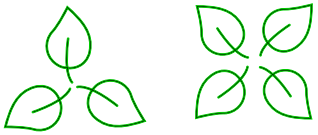
RECALL FROM PREVIOUS LECTURE:

Point / Molecular symmetry ⇨ One point remains unchanged

Identity ***E***

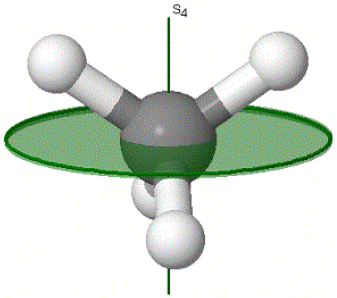
Symmetry/inversion center ***i*** **/** $\bar{1}$

Rotation axis C_n **/ 1, 2, 3, …**



Reflection/mirror plane σ **/** ***m***

Improper rotation axis S_n **/** $(\bar{1}, \bar{2}), \bar{3}, \bar{4}, \bar{6}$



NOTE:
- Improper rotation axis $\bar{1}$ and inversion center $\bar{1}$ are equivalent
- Mirror plane *m* and improper rotation axis $\bar{2}$ are equivalent

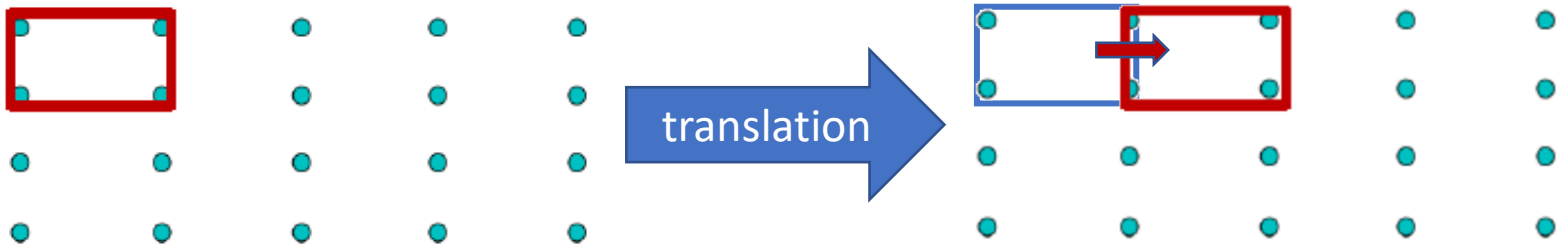
CRYSTAL 2D

FROM MOLECULES TO CRYSTALS

There are two things which make macroscopic (infinite) crystals different from discrete molecules in terms of symmetry: Translation & Space-filling

Translation in crystals

- Translation: move from one point to another (the entire object)
- This does not exist in molecules, but is the essence of macroscopic crystals exhibiting long-range order



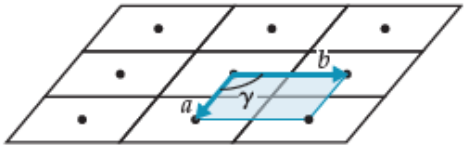
- Crystal lattice: regular, infinite pattern

FROM MOLECULES TO CRYSTALS

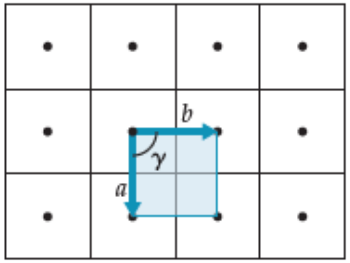
There are two things which make macroscopic (infinite) crystals different from discrete molecules in terms of symmetry: Translation & Space-filling

Space-filling → 5 lattices

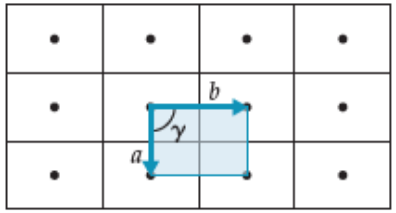
- Macroscopic crystals need to continuosly fill the space
- For molecules 5-fold rotation is possible, but not for crystals
  - *Quasicrystals can have 5-fold rotation: 2-component lattice*



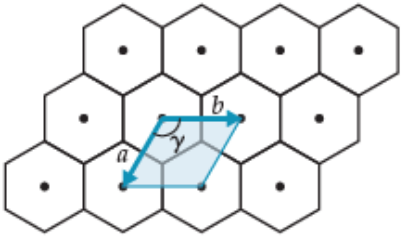
Oblique lattice ($a \neq b, \gamma =$ arbitrary)



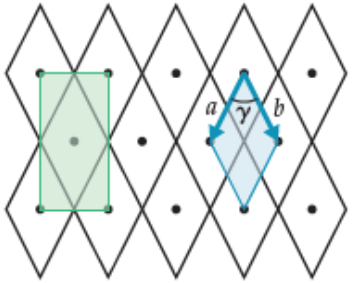
Square lattice ($a = b, \gamma = 90°$)



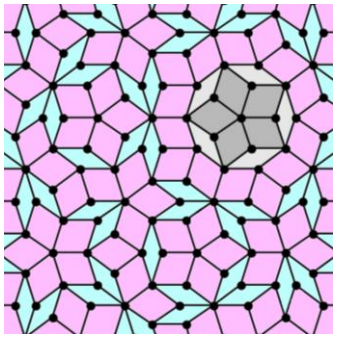
Rectangular lattice ($a \neq b, \gamma = 90°$)



Hexagonal lattice ($a = b, \gamma = 120°$)



Rhombic lattice ($a = b, \gamma =$ arbitrary)
Centered rectangular lattice



Quasicrystal

FROM MOLECULES TO CRYSTALS

The crystal lattice is the geometrical ’drawing board’, which is then filled with constituents that build a pattern: lattice points, basis, and unit cell

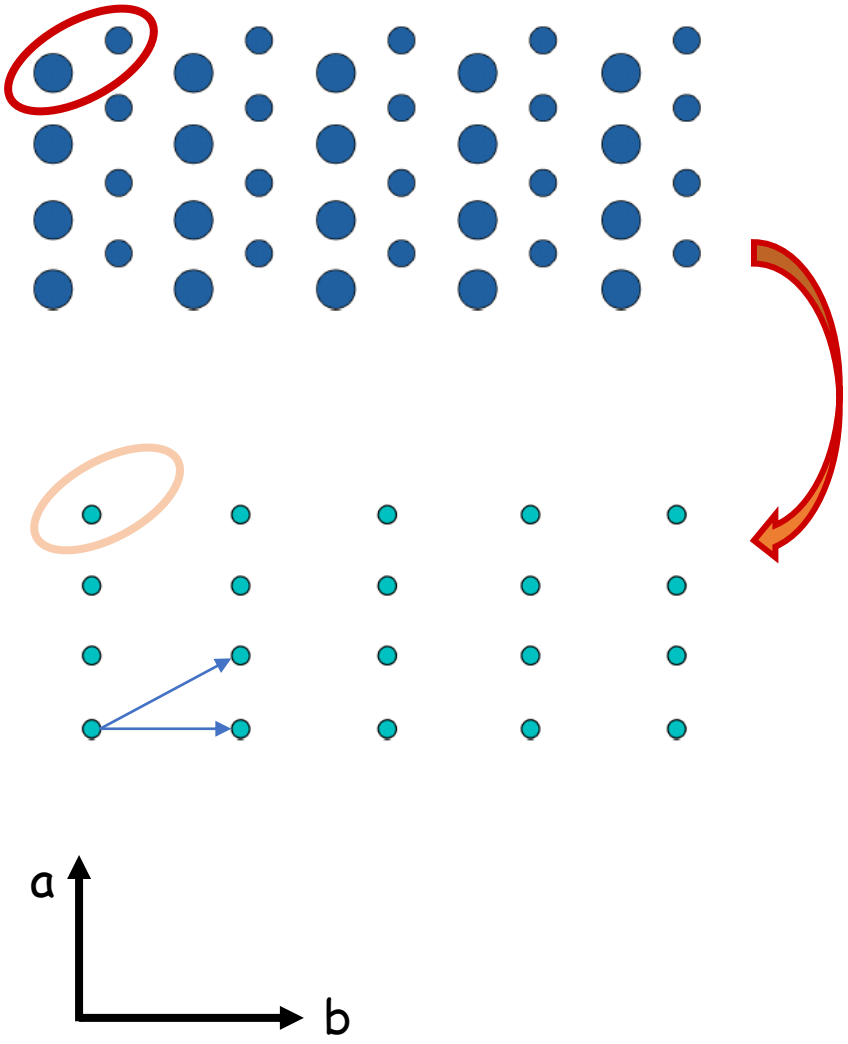
Basis:

- The atom (atom group) that is repeated

Lattice points

- The positions filled by the basis as a function of the symmetry operations for the lattice
- Each lattice point has identical environment + symmetry properties

  (=point group)

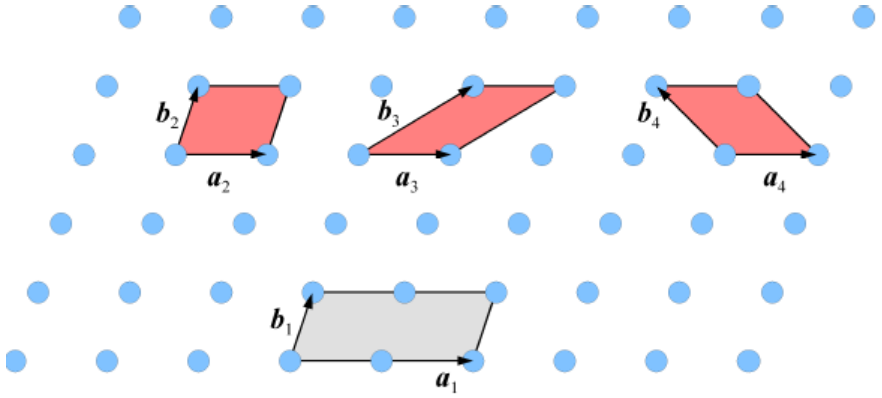


FROM MOLECULES TO CRYSTALS

The crystal lattice is the geometrical ’drawing board’, which is then filled with constituents that build a pattern: lattice points, basis, and unit cell

Unit cell

- Smallest possible part of the crystal lattice;
  - that repeats itself periodically;
  - to completely fills the lattice volume;
  - and is enough to describe the entire lattice perfectly



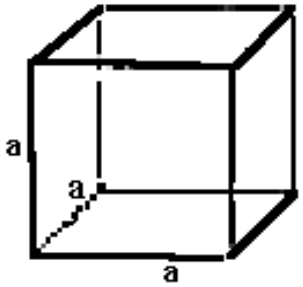
Choices of unit cell (in 2D)

- Choice of the unit cell not always unambiguous: several options

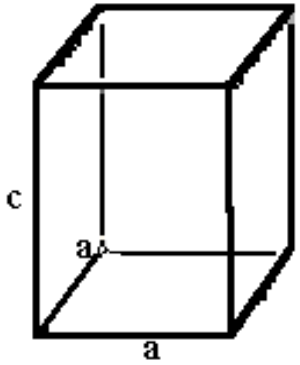
2D → 3D

LATTICES IN 3D: CRYSTAL SYSTEMS (7)

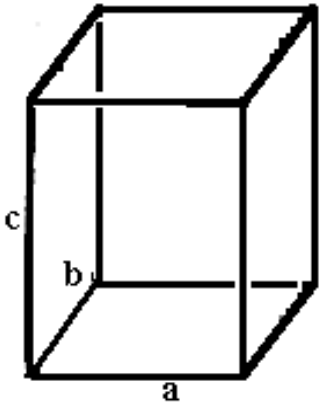
No information on the positions of atoms



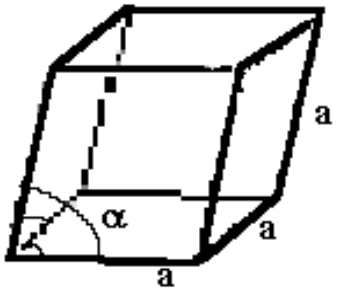
Cubic
a = b = c
α = β = γ = 90 º
NaCl, $MgAl_2O_4$



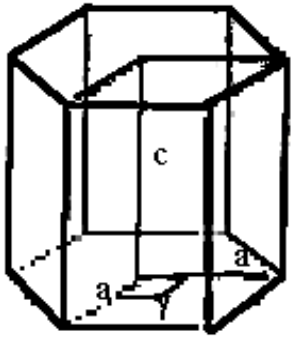
Tetragonal
a = b # c
α = β = γ = 90 º
TiO_2, K_2NiF_4



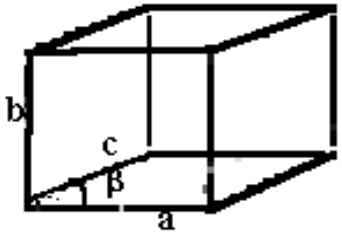
Orthorhombic
a # b # c
α = β = γ = 90 º
$YBa_2Cu_3O_7$



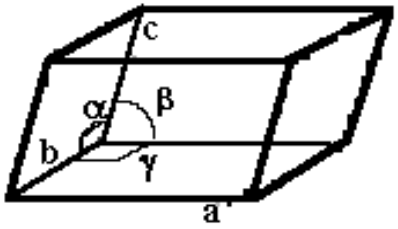
Rhombohedral
a = b = c
α = β = γ # 90 º
$BaTiO_3$ (low-T)



Hexagonal
a = b # c
α = β = 90, γ = 120 º
$LiNbO_3$

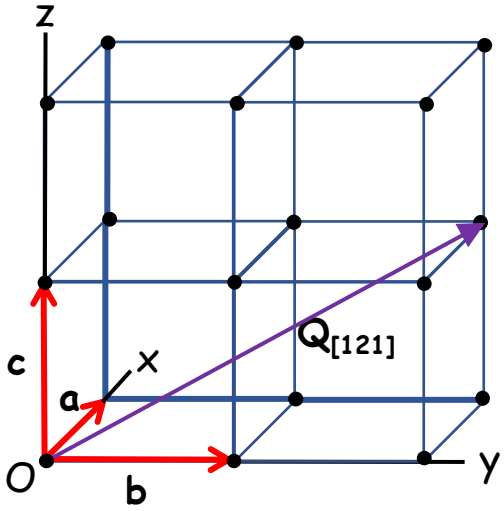


Monoclinic
a # b # c
α = γ = 90 º, β # 90 º
KH_2PO_4

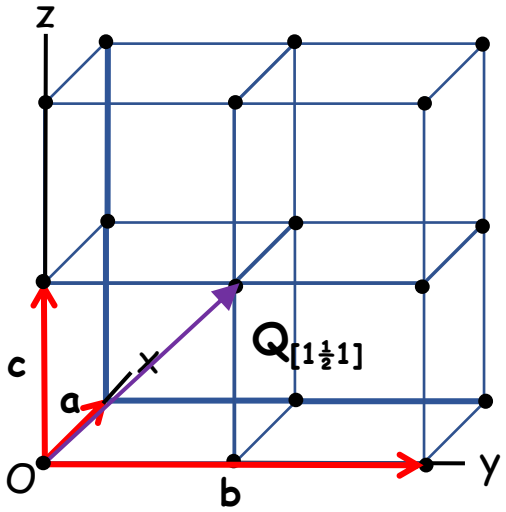


Triclinic
a # b # c
α # β # γ # 90 º

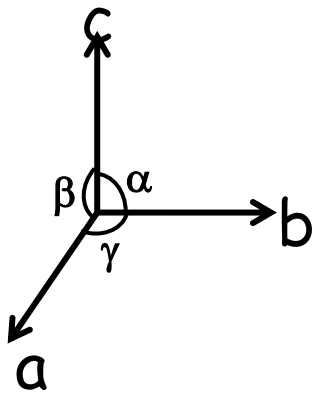
Each LATTICE POINT should be able to be described with the vector $Q_{[uvw]} = ua + vb + wc$, where *u*, *v* and *w* all are INTEGER values



Unit cell: YES



Unit cell: NO



Lattice points = unit cell corners

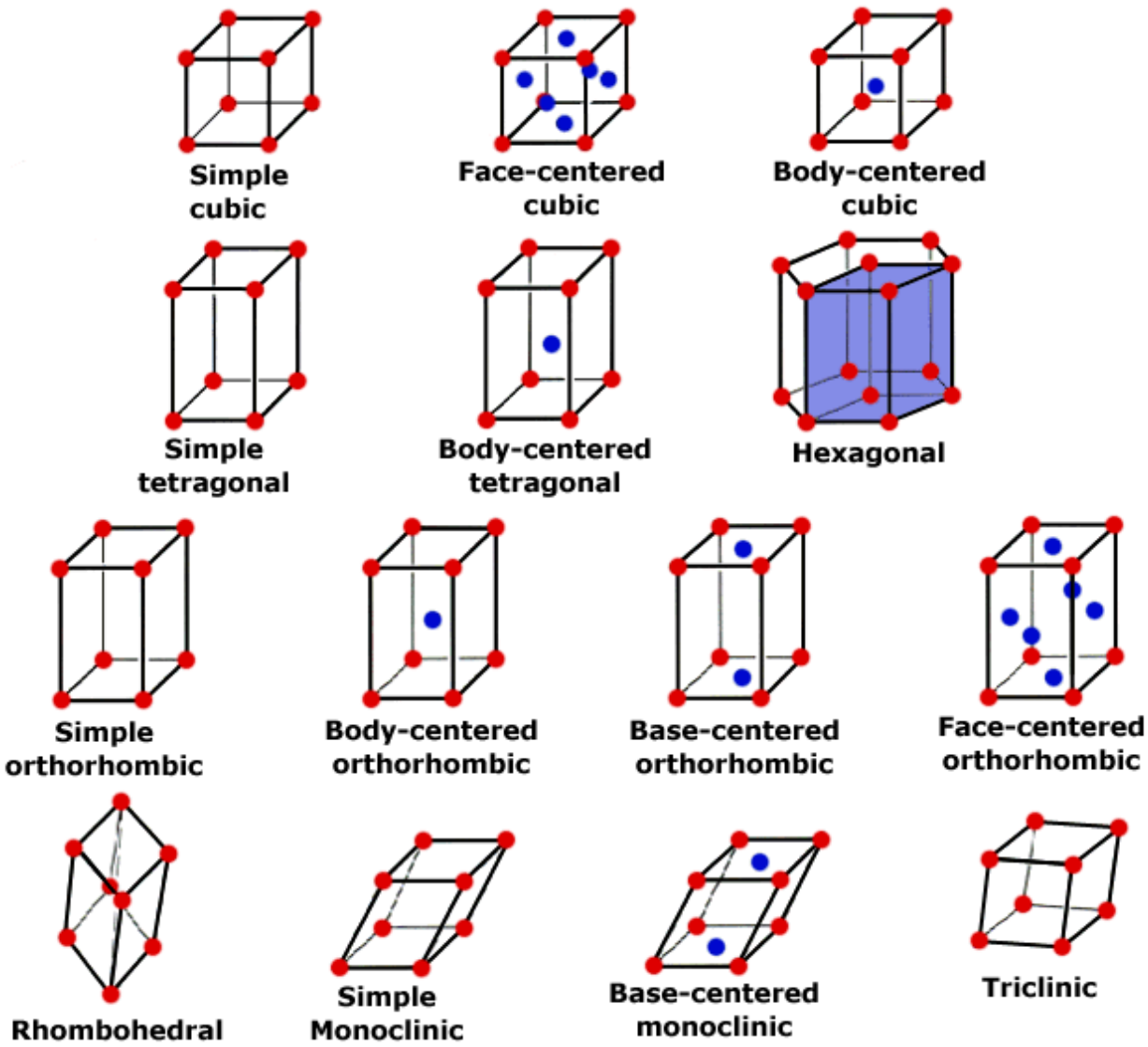
What we need to tell about the UNIT CELL

(basis)

- Shape & size of the unit cell *plus* the atomic positions in the unit cell
- Shape & size are given by:
  - Lattice parameters: ***a*, *b* ja *c***
  - Angles between the axes: **α, β ja γ**

LATTICES IN 3D: BRAVAIS LATTICES (14)

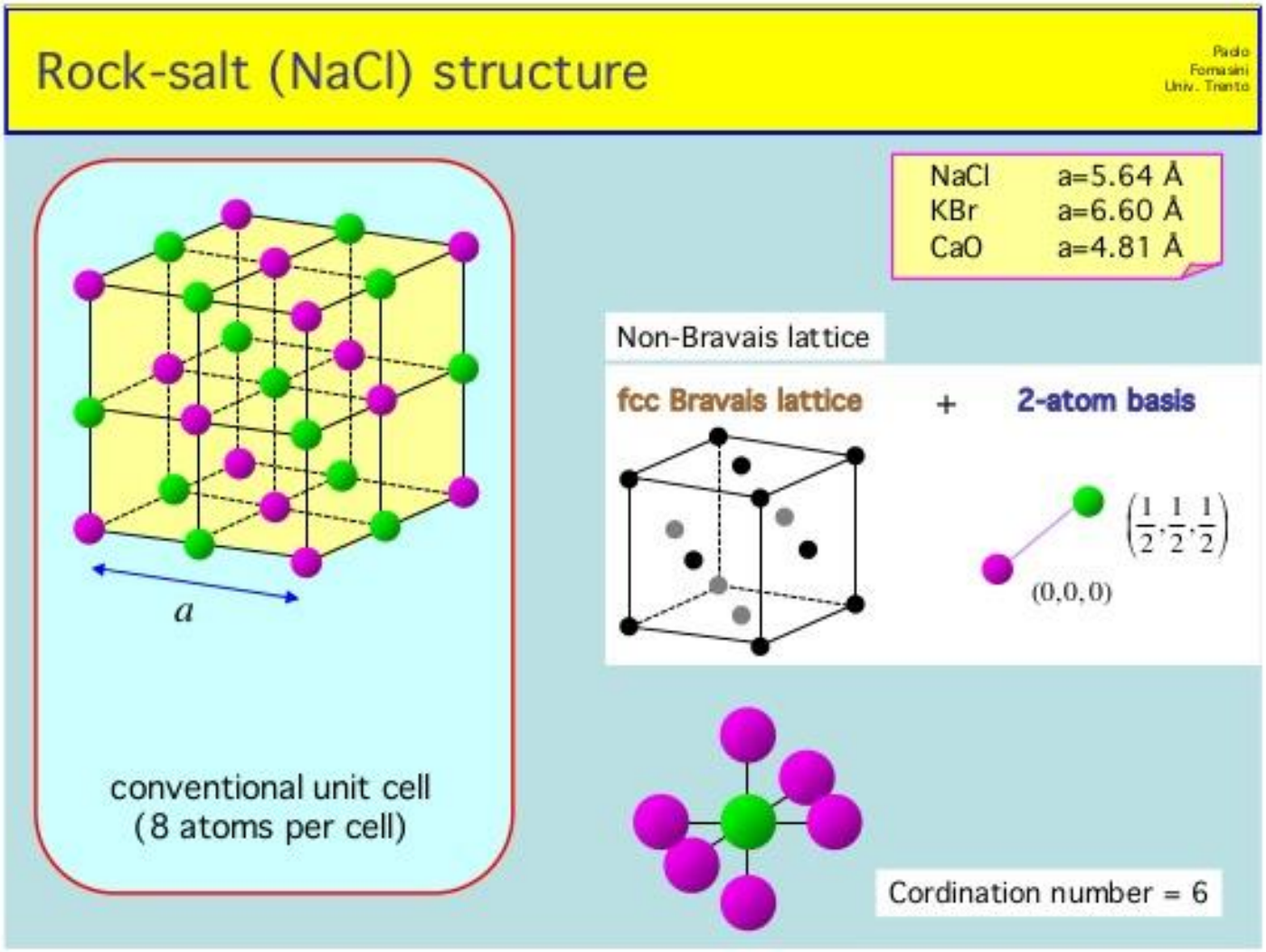
Basic stacking of lattice sites included (basis, not atoms)



Centering	Lattice points /cell	Abbre-viation
Primitive	1	P
Base (A, B, or C) centered	2	A, B, C
Body centered	2	I
Hexagonal, rhombohedral	3	h / R
Face centered	4	F

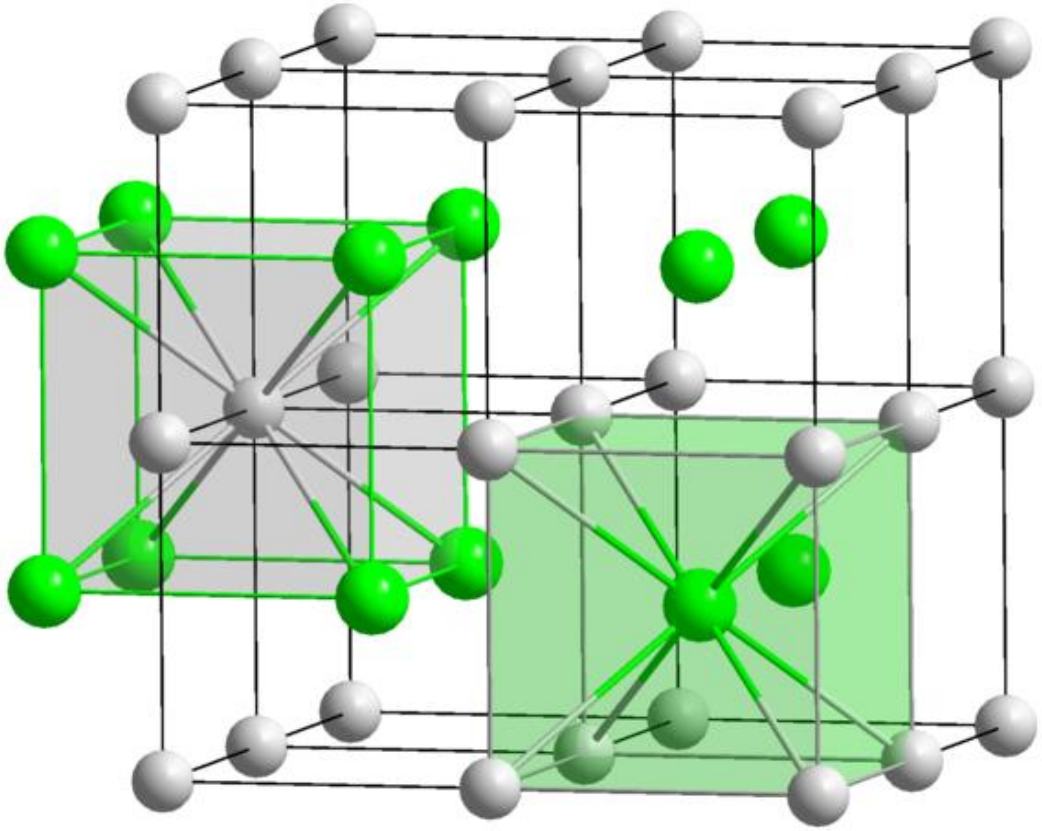
EXAMPLE

- **What is the Bravais lattice type of NaCl: Cubic F (basis: Na-Cl)**



Your EXERCISE question

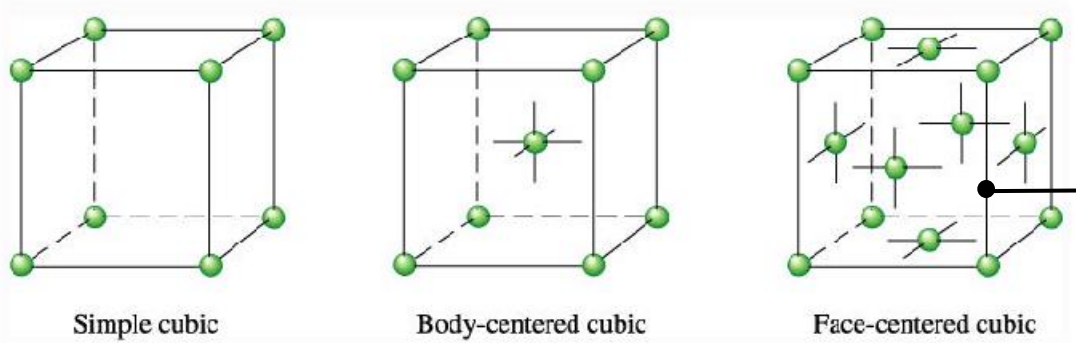
- What is the Bravais lattice type of CsCl

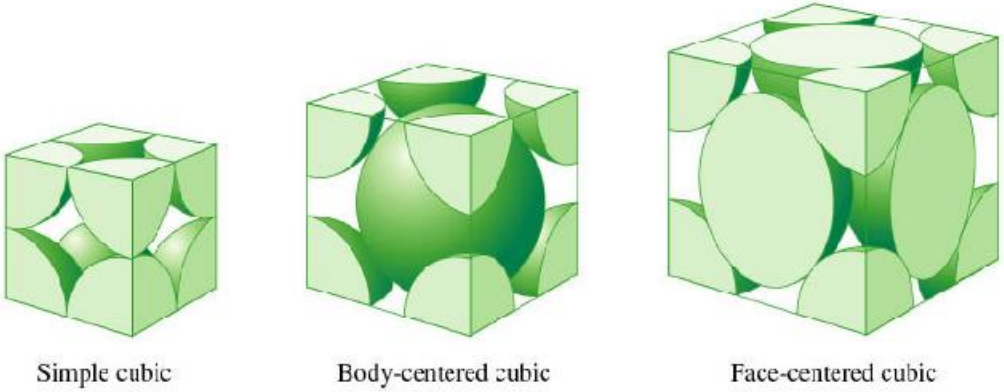


Counting atoms

NUMBER of FORMULA UNITS in UNIT CELL (Z)

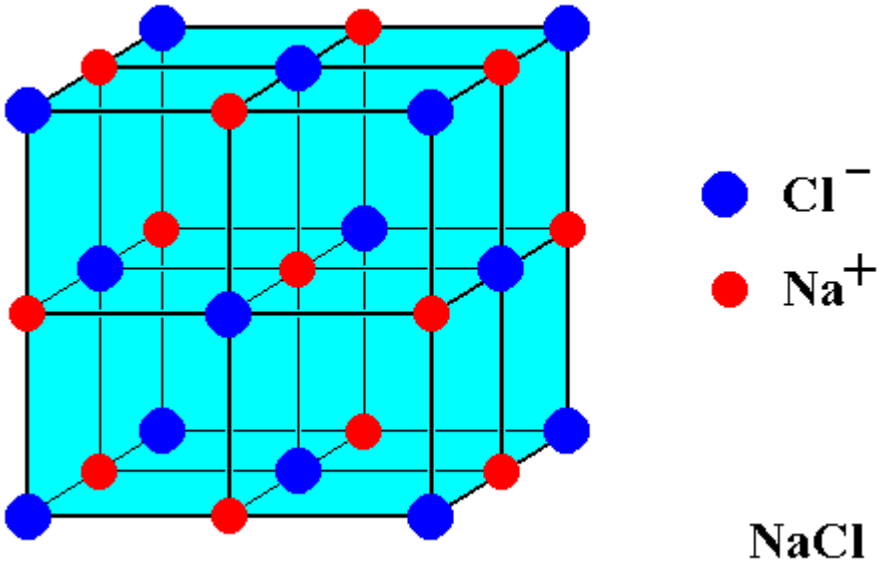
- typically 1 – 6, but can be tens or even hundreds
- atom inside unit cell: belongs only to one unit cell
- atom on unit cell face: belongs to two unit cells
- atom on unit cell edge: belongs to four unit cells
- atom on unit cell corner: belongs to eight unit cells





EXAMPLE

- **How many NaCl formula units in unit cell?**
- *answer…*



Lattice symmetry:

POINT GROUPS

The 2D point groups

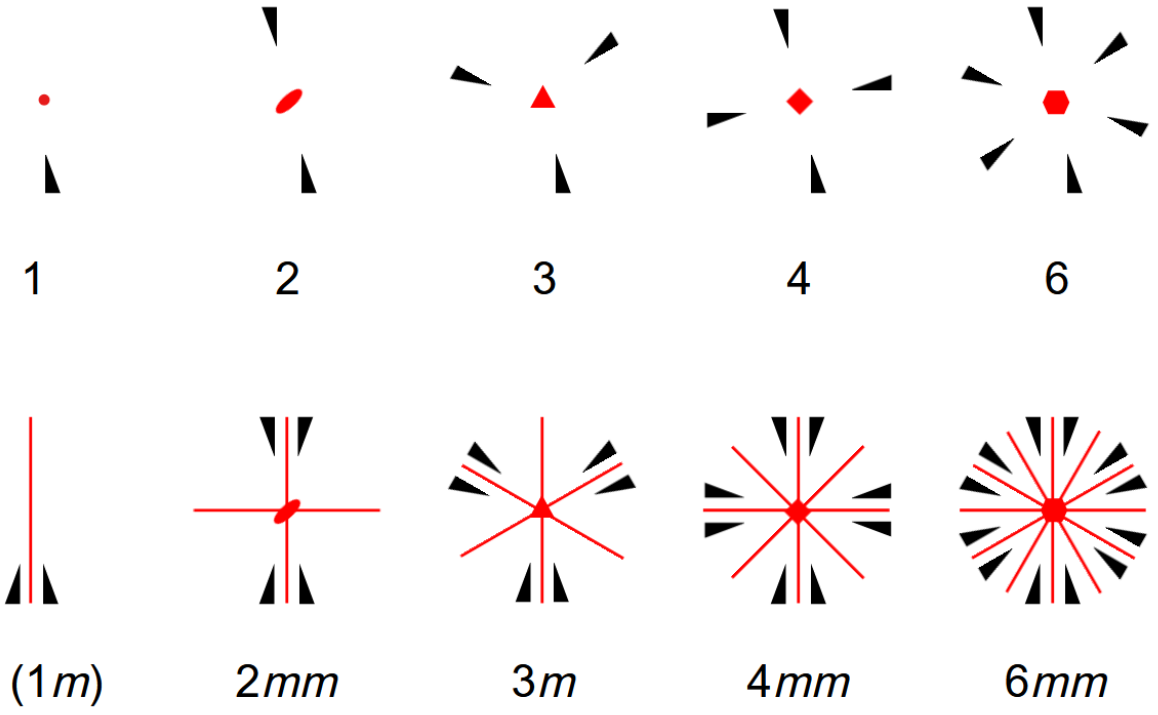
Crystallography fundamental rule of translation: units must stack without gaps!

5 options for **rotational** symmetry

+

5 more options with **mirror** symmetry

= 10 point groups



Repetition on 2D symmetry groups: https://slideplayer.com/slide/4380042/

The 2D point groups

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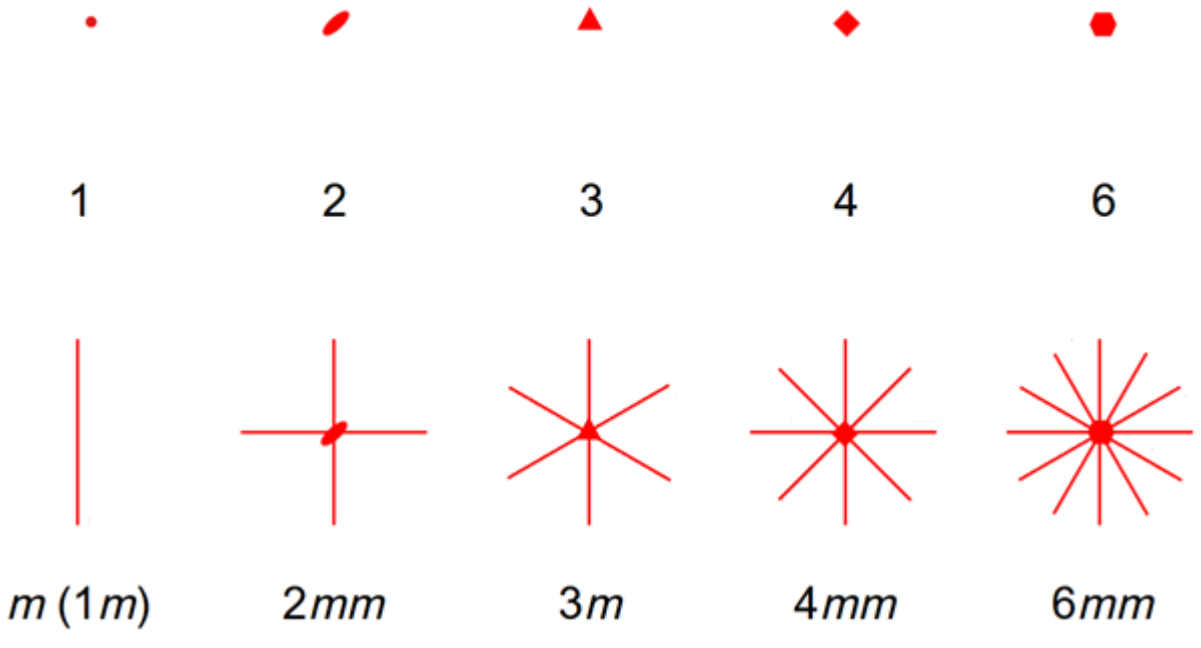


Point group graphical symbol shown in red

Repetition on 2D symmetry groups: https://slideplayer.com/slide/4380042/

New symmetry in 3D

Additional translation symmetry elements in INFINITE LATTICES

Combining translation with other symmetry operations/elements

→ new symmetry operations/elements: glide planes & screw axes

Screw axis

- Rotation plus translation

n_m (2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5)
For example: 2_1: rotation 180° and translation ½(*m*/*n*)

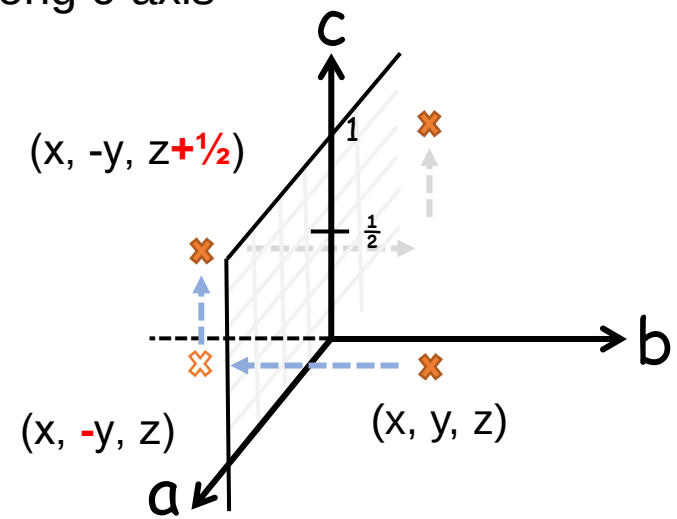
Glide plane

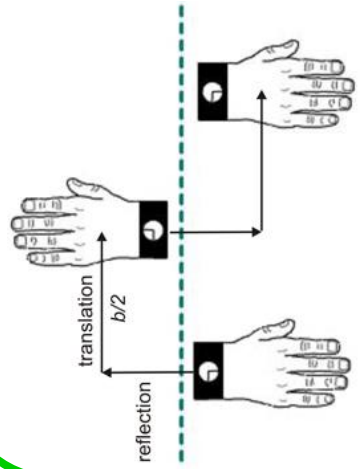
- Reflection against a mirror plane plus (half) translation parallel to the plane

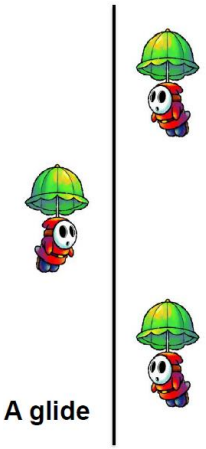
Axis glide plane: *a*, *b*, *c* (translations by ½*a*, ½*b*, ½*c* to each glide plane direction)
Diagonal glide plane: *n* [½(*a*+*b*), ½(*b*+*c*), ½(*c*+*a*)]
d [¼(*a*+*b*), ¼(*b*+*c*), ¼(*c*+*a*)] (so-called diamond glide plane)

GLIDE PLANE c (⊥ b)

Reflection (m) through ac-plane, followed by (half) translation (t) along c-axis

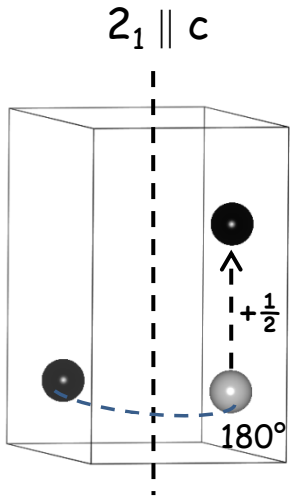




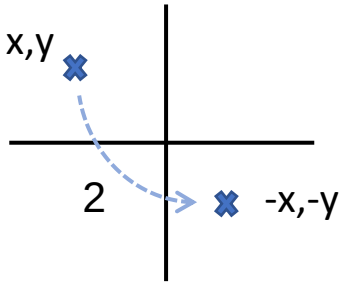


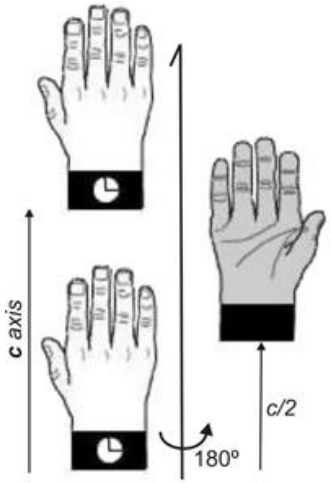
SCREW AXIS

Rotation (c) followed by translation (t)



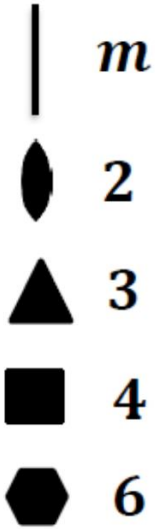
(x, y, z)
↓
(-x, -y, z)
↓
(-x, -y, z+½)





Symmetry elements in 3D

Element	What it does	Possible in crystal system
Identity (1)	-	All
Inversion ($\bar{1}$)	Inversion	All
Mirror plane (m)	Mirror	All but triclinic
2- fold rotation (2)	Rotate 180°	All but triclinic
3-fold rotation (3)	Rotate 120°	Trigonal, Hexagonal and Cubic
4-fold Rotation (4)	Rotate 90°	Tetragonal and Cubic
6-fold Rotation (6)	Rotate 60°	Hexagonal



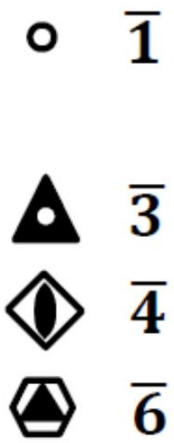
m *Mirror plane*

2 *2-fold rotation*

3 *3-fold rotation*

4 *4-fold rotation*

6 *6-fold rotation*



$\bar{1}$ *1-fold improper rotation = inversion point*

$\bar{3}$ *3-fold improper rotation*

$\bar{4}$ *4-fold improper rotation*

$\bar{6}$ *6-fold improper rotation*

POINT GROUPS

(from historical reasons)
DIFFERENT

SYMMETRY SYMBOLS

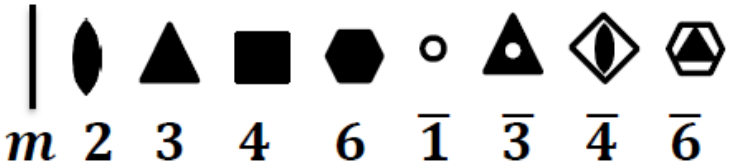
Schoenflies (S) symbols

- were developed first
- in molecular symmetry & spectroscopy

Hermann-Mauguin (H/M) symbols

- in crystallography
- long and short forms

Graphical symbols



3D point group graphical symbols

Table 1.1 Symmetry elements of crystal point groups.

System	Point group symmetry		Symmetry elements	Number of operations
	S	*H/M*		
Triclinic	C_1	1	$I = C_1$	1
	$C_i = S_2$	$\bar{1}$	$I, i(=S_2)$	2
Monoclinic	C_2	2	I, C_2	2
	$C_S = C_{1h} = C_{1v}$	m	I, σ	2
	C_{2h}	$2/m$	I, C_2, σ_h, i	4
Orthorhombic	C_{2v}	$mm2$	$I, C_2, 2\sigma$	4
	D_2	222	$I, 3C_2$	4
	D_{2h}	mmm	$I, 3C_2, 3\sigma, i$	8
Tetragonal	C_4	4	I, C_4	4
	S_4	$\bar{4}$	$I, S_4 (=C_2)$	4
	D_4	422	$I, C_4 (=C_2), 2C_2', 2C_2''$	8
	C_{4v}	$4mm$	$I, C_4, 2\sigma_v, 2\sigma_d$	8
	C_{4h}	$4/m$	$I, C_4 (=S_4), \sigma_h, i$	8
	D_{2d}	$\bar{4}2m$	$I, S_4 (=C_2), 2C_2', 2\sigma_d$	8
	D_{4h}	$4/mmm$	$I, C_4 (=S_4), 2C_2', 2C_2'', 2\sigma_v, 2\sigma_d, i$	16
Trigonal	C_3	3	I, C_3	3
	$C_{3i} = S_6$	$\bar{3}$	$I, S_6 (=C_3), i$	6
	D_3	32	$I, C_3, 3C_2$	6
	C_{3v}	$3m$	$I, C_3, 3\sigma_v$	6
	D_{3d}	$\bar{3}m$	$I, S_6 (=C_3), 3C_2, 3\sigma_d, i$	12
Hexagonal	C_6	6	I, C_6	6
	C_{3h}	$\bar{6}$	$I, S_3 (=C_3), \sigma_h$	6
	D_6	622	$I, C_6, 3C_2', 3C_2''$	12
	D_{3h}	$\bar{6}m2$	$I, C_3 (=S_3), 3C_2, 3\sigma_v, \sigma_h$	12
	C_{6h}	$6/m$	$I, C_6 (=S_6), \sigma_h, i$	12
	C_{6v}	$6mm$	$I, C_6, 3\sigma_v, 3\sigma_d$	12
	D_{6h}	$6/mmm$	$I, C_6 (=S_6), 3C_2', 3C_2'', 3\sigma_v, 3\sigma_d, \sigma_h, i$	24
Cubic	T	23	$I, 3C_2, 4C_3$	12
	T_h	$m3$	$I, 3C_2, 4C_3 (=S_6), 3\sigma_h, i$	24
	T_d	$\bar{4}3m$	$I, 3C_2 (=S_4), 4C_3, 6\sigma_d$	24
	O	432	$I, 3C_2, 4C_3, 3C_4$	24
	O_h	$m3m$	$I, 3C_2, 4C_3 (=S_6), 3C_4 (=S_4), 3\sigma_h, 6\sigma_d, i$	48

CRYSTAL CLASSES *i.e.* POINT GROUPS

(32)

The 32 Point Groups			
1	4	$\bar{3}$	6mm
$\bar{1}$	$\bar{4}$	32	$\bar{6}m2$
2	4/m	3m	6/mmm
m	422	$\bar{3}m$	23
2/m	4mm	6	$m\bar{3}$
222	$\bar{4}2m$	$\bar{6}$	432
mm2	4/mmm	6/m	$\bar{4}3m$
mmm	3	622	$m\bar{3}m$

The 32 Point Groups (Schoenflies)			
1 (C_1)	4 (C_4)	$\bar{3}$ (C_{3i})	6mm ($C_{6\sigma v}$)
$\bar{1}$ ($C_i = S_2$)	$\bar{4}$ (S_4)	32 (D_3)	$\bar{6}m2$ ($D_{3\sigma h}$)
2 (C_2)	4/m ($C_{4\sigma h}$)	3m ($C_{3\sigma v}$)	6/mmm ($D_{6\sigma h}$)
m (C_σ)	422 (D_4)	$\bar{3}m$ (D_{3d})	23 (T)
2/m ($C_{2\sigma h}$)	4mm ($C_{4\sigma v}$)	6 (C_6)	$m\bar{3}$ (T_h)
222 (D_2)	$\bar{4}2m$ (D_{2d})	$\bar{6}$ ($C_{3\sigma h}$)	432 (O)
2mm ($C_{2\sigma v}$)	4/mmm (D_{4h})	6/m ($C_{6\sigma h}$)	$\bar{4}3m$ (T_d)
mmm ($D_{2\sigma h}$)	3 (C_3)	622 (D_6)	$m\bar{3}m$ (O_h)

Which point groups are possible for each lattice type?

System	Minimum Requirements
Cubic	Four 3-fold rotation axis
Tetragonal	One 4-fold rotation (or RI) axis
Orthorhombic	Three perpendicular 2-fold axis
Rhombohedral	One 3-fold rotation (or RI) axis
Hexagonal	One 6 fold rotation (or RI) axis
Monoclinic	One 2 fold rotation axis or mirror plane
Triclinic	none

System	Point groups
Cubic	23, $m\bar{3}$, 432, $\bar{4}3m$, $m\bar{3}m$
Tetragonal	4, $\bar{4}$, 4/m, 422, 4mm, $\bar{4}2m$, 4/mmm
Orthorhombic	222, 2mm, mmm
Trigonal	3, $\bar{3}$, 32, 3m, $\bar{3}m$
Hexagonal	6, $\bar{6}$, 6/m, 622, 6mm, $\bar{6}m2$, 6/mmm
Monoclinic	2, m, 2/m
Triclinic	1, $\bar{1}$

The building blocks of 3D

7 Crystal systems

= geometrical bodies (unit cells) that can stack in 3D

& 14 Bravais lattices

= basic atomic arrangements within a unit cell

& 32 Point groups

= geometrical symmetry operation systems within the unit cell

→ 230 Space groups

= possible combinations of lattices and symmetry elements (impossible systems and doublets excluded)

→ SPACE GROUPS (230)

Triclinic

(For the enlarged unit cells, click here)

1. P 1 2. P -1

Monoclinic

(For a fuller list with alternative unique axes, origins, or enlarged unit cells click here)

3. P 1 2 1 4. P 1 2_1 1 5. C 1 2 1 6. P 1 m 1 7. P 1 c 1
8. C 1 m 1 9. C 1 c 1 10. P 1 2 / m 1 11. P 1 2_1 / m 1 12. C 1 2 / m 1
13. P 1 2 / c 1 14. P 1 2_1 / c 1 15. C 1 2 / c 1

Orthorhombic

(For a fuller list with alternative axes and origins click here)

16. P 2 2 2 17. P 2 2 2_1 18. P 2_1 2_1 2 19. P 2_1 2_1 2_1 20. C 2 2 2_1
21. C 2 2 2 22. F 2 2 2 23. I 2 2 2 24. I 2_1 2_1 2_1 25. P m m 2
26. P m c 2_1 27. P c c 2 28. P m a 2 29. P c a 2_1 30. P n c 2
31. P m n 2_1 32. P b a 2 33. P n a 2_1 34. P n n 2 35. C m m 2
36. C m c 2_1 37. C c c 2 38. A m m 2 39. A b m 2 40. A m a 2
41. A b a 2 42. F m m 2 43. F d d 2 44. I m m 2 45. I b a 2
46. I m a 2 47. P m m m 48. P n n n 49. P c c m 50. P b a n
51. P m m a 52. P n n a 53. P m n a 54. P c c a 55. P b a m
56. P c c n 57. P b c m 58. P n n m 59. P m m n 60. P b c n
61. P b c a 62. P n m a 63. C m c m 64. C m c a 65. C m m m
66. C c c m 67. C m m a 68. C c c a 69. F m m m 70. F d d d
71. I m m m 72. I b a m 73. I b c a 74. I m m a

Tetragonal

(For the enlarged C- and F-centred unit cells, click here)

75. P 4 76. $P 4_1$ 77. $P 4_2$ 78. $P 4_3$ 79. I 4
80. $I 4_1$ 81. P -4 82. I -4 83. P 4 / m 84. $P 4_2$ / m
85. P 4 / n 86. $P 4_2$ / n 87. I 4 / m 88. $I 4_1$ / a 89. P 4 2 2
90. P 4 2_1 2 91. P 4_1 2 2 92. P 4_1 2_1 2 93. P 4_2 2 2 94. P 4_2 2_1 2
95. P 4_3 2 2 96. P 4_3 2_1 2 97. I 4 2 2 98. I 4_1 2 2 99. P 4 m m
100. P 4 b m 101. $P 4_2$ c m 102. $P 4_2$ n m 103. P 4 c c 104. P 4 n c
105. $P 4_2$ m c 106. $P 4_2$ b c 107. I 4 m m 108. I 4 c m 109. $I 4_1$ m d
110. $I 4_1$ c d 111. P -4 2 m 112. P -4 2 c 113. P -4 2_1 m 114. P -4 2_1 c
115. P -4 m 2 116. P -4 c 2 117. P -4 b 2 118. P -4 n 2 119. I -4 m 2
120. I -4 c 2 121. I -4 2 m 122. I -4 2 d 123. P 4 / m m m 124. P 4 / m c c
125. P 4 / n b m 126. P 4 / n n c 127. P 4 / m b m 128. P 4 / m n c 129. P 4 / n m m
130. P 4 / n c c 131. $P 4_2$ / m m c 132. $P 4_2$ / m c m 133. $P 4_2$ / n b c 134. $P 4_2$ / n n m
135. $P 4_2$ / m b c 136. $P 4_2$ / n n m 137. $P 4_2$ / n m c 138. $P 4_2$ / n c m 139. I 4 / m m m
140. I 4 / m c m 141. $I 4_1$ / a m d 142. $I 4_1$ / a c d

Trigonal

(For the R-centred cells with hexagonal axes and the larger H-centred trigonal cells, click here)

143. P 3 144. $P 3_1$ 145. $P 3_2$ 146. R 3 147. P -3
148. R -3 149. P 3 1 2 150. P 3 2 1 151. $P 3_1$ 1 2 152. $P 3_1$ 2 1
153. $P 3_2$ 1 2 154. $P 3_2$ 2 1 155. R 3 2 156. P 3 m 1 157. P 3 1 m
158. P 3 c 1 159. P 3 1 c 160. R 3 m 161. R 3 c 162. P -3 1 m
163. P -3 1 c 164. P -3 m 1 165. P -3 c 1 166. R -3 m 167. R -3 c

Hexagonal

168. P 6 169. $P 6_1$ 170. $P 6_5$ 171. $P 6_2$ 172. $P 6_4$
173. $P 6_3$ 174. P -6 175. P 6 / m 176. $P 6_3$ / m 177. P 6 2 2
178. P 6_1 2 2 179. P 6_5 2 2 180. P 6_2 2 2 181. P 6_4 2 2 182. P 6_3 2 2
183. P 6 m m 184. P 6 c c 185. P 6_3 c m 186. P 6_3 m c 187. P -6 m 2
188. P -6 c 2 189. P -6 2 m 190. P -6 2 c 191. P 6 / m m m 192. P 6 / m c c
193. P 6_3 / m c m 194. P 6_3 / m m c

Cubic

195. P 2 3 196. F 2 3 197. I 2 3 198. P 2_1 3 199. I 2_1 3
200. P m -3 201. P n -3 202. F m -3 203. F d -3 204. I m -3
205. P a -3 206. I a -3 207. P 4 3 2 208. P 4_2 3 2 209. F 4 3 2
210. F 4_1 3 2 211. I 4 3 2 212. P 4_3 3 2 213. P 4_1 3 2 214. I 4_1 3 2
215. P -4 3 m 216. F -4 3 m 217. I -4 3 m 218. P -4 3 n 219. F -4 3 c
220. I -4 3 d 221. P m -3 m 222. P n -3 n 223. P m -3 n 224. P n -3 m
225. F m -3 m 226. F m -3 c 227. F d -3 m 228. F d -3 c 229. I m -3 m
230. I a -3 d

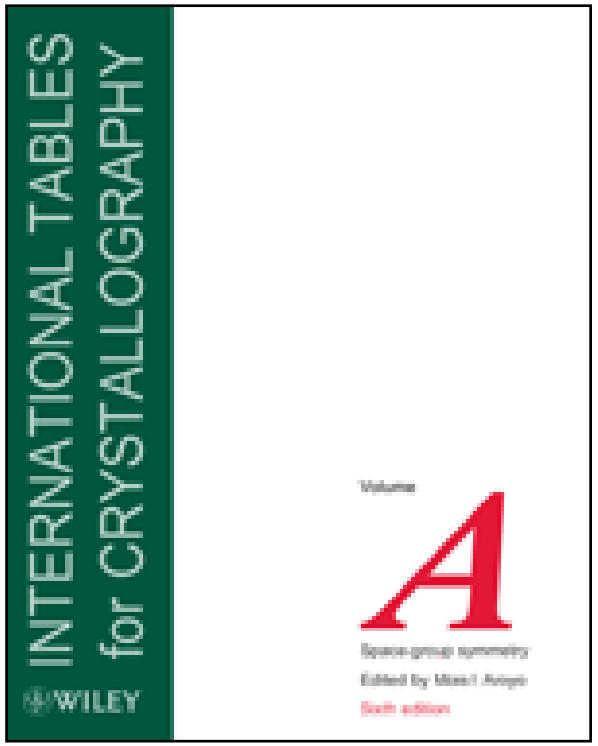
From: http://img.chem.ucl.ac.uk/sgp/large/sgp.htm

All space group diagrams and tables online:
http://img.chem.ucl.ac.uk/sgp/large/sgp.htm

BIBLE OF CRYSTALLOGRAPHY

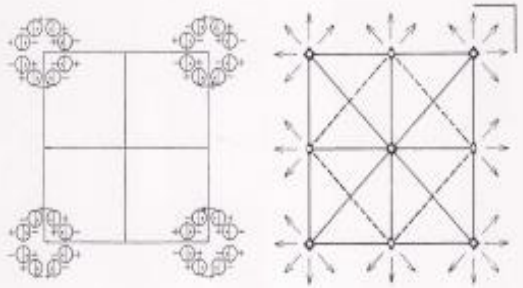
- **Space groups (and the characteristic information in 2 pages) are listed in International Tables for Crystallography**
- **Next-next slide: Space Group P4/mmm as an example**

https://it.iucr.org/



$P\,4/m\,m\,m$ D_{4h}^{1} $4/m\,m\,m$ Tetragonal

No. 123 $P\,4/m\,2/m\,2/m$ Patterson symmetry $P\,4/m\,m\,m$



Origin at centre $(4/m\,m\,m)$

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

Symmetry operations

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

Maximal non-isomorphic subgroups

I	$[2]P\,4\,2\,2$	1; 2; 3; 4; 5; 6; 7; 8
	$[2]P\,4/m\,1\,1\,(P\,4/m)$	1; 2; 3; 4; 9; 10; 11; 12
	$[2]P\,4\,m\,m$	1; 2; 3; 4; 13; 14; 15; 16
	$[2]P\,\bar{4}\,2\,m$	1; 2; 5; 6; 11; 12; 15; 16
	$[2]P\,\bar{4}\,m\,2$	1; 2; 7; 8; 11; 12; 13; 14
	$[2]P\,2/m\,2/m\,1\,(P\,m\,m\,m)$	1; 2; 5; 6; 9; 10; 13; 14
	$[2]P\,2/m\,1\,2/m\,(C\,m\,m\,m)$	1; 2; 7; 8; 9; 10; 15; 16

IIa none

IIb $[2]P\,4/m\,c\,c\,(c'=2c)$; $[2]P\,4_2/m\,m\,c\,(c'=2c)$; $[2]P\,4_2/m\,c\,m\,(c'=2c)$; $[2]C\,4/a\,m\,d\,(a'=2a, b'=2b)(P\,4/n\,b\,m)$; $[2]C\,4/m\,m\,d\,(a'=2a, b'=2b)(P\,4/m\,b\,m)$; $[2]C\,4/a\,m\,m\,(a'=2a, b'=2b)(P\,4/n\,m\,m)$; $[2]F\,4/m\,m\,m\,(a'=2a, b'=2b, c'=2c)(I\,4/m\,m\,m)$; $[2]F\,4/m\,m\,c\,(a'=2a, b'=2b, c'=2c)(I\,4/m\,c\,m)$

Maximal isomorphic subgroups of lowest index

IIc $[2]P\,4/m\,m\,m\,(c'=2c)$; $[2]C\,4/m\,m\,m\,(a'=2a, b'=2b)(P\,4/m\,m\,m)$

Minimal non-isomorphic supergroups

I $[3]Pm\bar{3}m$

II $[2]I\,4/m\,m\,m$

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	u 1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$	no conditions
		(5) $\bar{x},y,\bar{z}$	(6) $x,\bar{y},\bar{z}$	(7) $y,x,\bar{z}$	(8) $\bar{y},\bar{x},\bar{z}$	
		(9) $\bar{x},\bar{y},\bar{z}$	(10) $x,y,\bar{z}$	(11) $y,\bar{x},\bar{z}$	(12) $\bar{y},x,\bar{z}$	
		(13) $x,\bar{y},z$	(14) $\bar{x},y,z$	(15) $\bar{y},\bar{x},z$	(16) y,x,z	
						Special:
8	t .m.	$x,\frac{1}{2},z$	$\bar{x},\frac{1}{2},z$	$\frac{1}{2},x,z$	$\frac{1}{2},\bar{x},z$	no extra conditions
		$\bar{x},\frac{1}{2},\bar{z}$	$x,\frac{1}{2},\bar{z}$	$\frac{1}{2},x,\bar{z}$	$\frac{1}{2},\bar{x},\bar{z}$	
8	s .m.	$x,0,z$	$\bar{x},0,z$	$0,x,z$	$0,\bar{x},z$	no extra conditions
		$\bar{x},0,\bar{z}$	$x,0,\bar{z}$	$0,x,\bar{z}$	$0,\bar{x},\bar{z}$	
8	r ..m	x,x,z	$\bar{x},\bar{x},z$	$\bar{x},x,z$	$x,\bar{x},z$	no extra conditions
		$\bar{x},x,\bar{z}$	$x,\bar{x},\bar{z}$	$x,x,\bar{z}$	$\bar{x},\bar{x},\bar{z}$	
8	q m..	$x,y,\frac{1}{2}$	$\bar{x},\bar{y},\frac{1}{2}$	$\bar{y},x,\frac{1}{2}$	$y,\bar{x},\frac{1}{2}$	no extra conditions
		$\bar{x},y,\frac{1}{2}$	$x,\bar{y},\frac{1}{2}$	$y,x,\frac{1}{2}$	$\bar{y},\bar{x},\frac{1}{2}$	
8	p m..	$x,y,0$	$\bar{x},\bar{y},0$	$\bar{y},x,0$	$y,\bar{x},0$	no extra conditions
		$\bar{x},y,0$	$x,\bar{y},0$	$y,x,0$	$\bar{y},\bar{x},0$	
4	o m 2m.	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	no extra conditions
4	n m 2m.	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	no extra conditions
4	m m 2m.	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	no extra conditions
4	l m 2m.	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	no extra conditions
4	k m .2m	$x,x,\frac{1}{2}$	$\bar{x},\bar{x},\frac{1}{2}$	$\bar{x},x,\frac{1}{2}$	$x,\bar{x},\frac{1}{2}$	no extra conditions
4	j m .2m	$x,x,0$	$\bar{x},\bar{x},0$	$\bar{x},x,0$	$x,\bar{x},0$	no extra conditions
4	i 2mm.	$0,\frac{1}{2},z$	$\frac{1}{2},0,z$	$0,\frac{1}{2},\bar{z}$	$\frac{1}{2},0,\bar{z}$	hkl : $h+k=2n$
2	h 4mm	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			no extra conditions
2	g 4mm	$0,0,z$	$0,0,\bar{z}$			no extra conditions
2	f mmm.	$0,\frac{1}{2},0$	$\frac{1}{2},0,0$			hkl : $h+k=2n$
2	e mmm.	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$			hkl : $h+k=2n$
1	d $4/mmm$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$				no extra conditions
1	c $4/mmm$	$\frac{1}{2},\frac{1}{2},0$				no extra conditions
1	b $4/mmm$	$0,0,\frac{1}{2}$				no extra conditions
1	a $4/mmm$	$0,0,0$				no extra conditions

Symmetry of special projections

Along [001] $p\,4m\,m$
$a'=a$ $b'=b$
Origin at $0,0,z$

Along [100] $p\,2m\,m$
$a'=b$ $b'=c$
Origin at $x,0,0$

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

(Continued on preceding page)

EXAMPLES of INFORMATION

- **Space group number: 123**
- **Name: P4/mmm**
- **Complete name: *P* 4/*m* 2/*m* 2/*m* ; showing the symmetry elements (4-fold rotation axis, mirror planes)**
- **Crystal system: tetragonal**
- **Lattice type: P (primitive)**
- **Site symmetry of the highest-symmetry site: D_{4h}**
- **Asymmetric unit (basis): smallest closed part of space the entire space is filled by applying all symmetry operations**

On the second page:

- List of possible sites for the atoms
- These are indicated/named by: multiplicity, Wyckoff letter & site symmetry
- Not all sites are actually occupied by an atom
- On the top: general site (16u)
- At the bottom: the highest symmetry site (1a)
- Multiplicity: number of identical sites

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	*u*	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$	no conditions
			(5) $\bar{x},y,\bar{z}$	(6) $x,\bar{y},\bar{z}$	(7) $y,x,\bar{z}$	(8) $\bar{y},\bar{x},\bar{z}$	
			(9) $\bar{x},\bar{y},\bar{z}$	(10) $x,y,\bar{z}$	(11) $y,\bar{x},\bar{z}$	(12) $\bar{y},x,\bar{z}$	
			(13) $x,\bar{y},z$	(14) $\bar{x},y,z$	(15) $\bar{y},\bar{x},z$	(16) y,x,z	
							Special:
8	*t*	.*m*.	$x,\frac{1}{2},z$	$\bar{x},\frac{1}{2},z$	$\frac{1}{2},x,z$	$\frac{1}{2},\bar{x},z$	no extra conditions
			$\bar{x},\frac{1}{2},\bar{z}$	$x,\frac{1}{2},\bar{z}$	$\frac{1}{2},x,\bar{z}$	$\frac{1}{2},\bar{x},\bar{z}$	
8	*s*	.*m*.	$x,0,z$	$\bar{x},0,z$	$0,x,z$	$0,\bar{x},z$	no extra conditions
			$\bar{x},0,\bar{z}$	$x,0,\bar{z}$	$0,x,\bar{z}$	$0,\bar{x},\bar{z}$	
8	*r*	..*m*	x,x,z	$\bar{x},\bar{x},z$	$\bar{x},x,z$	$x,\bar{x},z$	no extra conditions
			$\bar{x},x,\bar{z}$	$x,\bar{x},\bar{z}$	$x,x,\bar{z}$	$\bar{x},\bar{x},\bar{z}$	
8	*q*	*m*..	$x,y,\frac{1}{2}$	$\bar{x},\bar{y},\frac{1}{2}$	$\bar{y},x,\frac{1}{2}$	$y,\bar{x},\frac{1}{2}$	no extra conditions
			$\bar{x},y,\frac{1}{2}$	$x,\bar{y},\frac{1}{2}$	$y,x,\frac{1}{2}$	$\bar{y},\bar{x},\frac{1}{2}$	
8	*p*	*m*..	$x,y,0$	$\bar{x},\bar{y},0$	$\bar{y},x,0$	$y,\bar{x},0$	no extra conditions
			$\bar{x},y,0$	$x,\bar{y},0$	$y,x,0$	$\bar{y},\bar{x},0$	
4	*o*	*m* 2*m*.	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	no extra conditions
4	*n*	*m* 2*m*.	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	no extra conditions
4	*m*	*m* 2*m*.	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	no extra conditions
4	*l*	*m* 2*m*.	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	no extra conditions
4	*k*	*m*.2*m*	$x,x,\frac{1}{2}$	$\bar{x},\bar{x},\frac{1}{2}$	$\bar{x},x,\frac{1}{2}$	$x,\bar{x},\frac{1}{2}$	no extra conditions
4	*j*	*m*.2*m*	$x,x,0$	$\bar{x},\bar{x},0$	$\bar{x},x,0$	$x,\bar{x},0$	no extra conditions
4	*i*	2*mm*.	$0,\frac{1}{2},z$	$\frac{1}{2},0,z$	$0,\frac{1}{2},\bar{z}$	$\frac{1}{2},0,\bar{z}$	*hkl* : $h+k=2n$
2	*h*	4*mm*	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			no extra conditions
2	*g*	4*mm*	$0,0,z$	$0,0,\bar{z}$			no extra conditions
2	*f*	*mmm*.	$0,\frac{1}{2},0$	$\frac{1}{2},0,0$			*hkl* : $h+k=2n$
2	*e*	*mmm*.	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$			*hkl* : $h+k=2n$
1	*d*	$4/mmm$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$				no extra conditions
1	*c*	$4/mmm$	$\frac{1}{2},\frac{1}{2},0$				no extra conditions
1	*b*	$4/mmm$	$0,0,\frac{1}{2}$				no extra conditions
1	*a*	$4/mmm$	$0,0,0$				no extra conditions

Symmetry of special projections

Along [001] $p\,4mm$
$\boldsymbol{a}'=\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$
Origin at $0,0,z$

Along [100] $p\,2mm$
$\boldsymbol{a}'=\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,0,0$

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

(*Continued on preceding page*)

EXAMPLE: Potassium tetrachloroplatinate(II): K_2PtCl_4

Space group: *P*4/*mmm* (No. 123)

Lattice parameters: $a = b = 7.023$ Å, $c = 4.1486$ Å

Atomic positions:

Pt	1*a*:	0,0,0
K	2*e*:	0,½,½
Cl	4*j*:	*x*,*x*,0 ; *x* = 0.23247

(a) Draw the unit cell with the atoms.

(b) Draw the projection of the unit cell in *c*-axis direction.

(c) Theoretical density is 3.37 g/cm^3. Calculate Z?
($N_A = 6.022 \times 10^{23}$; atomic weights: K 39.098; Pt 195.22; Cl 35.453)

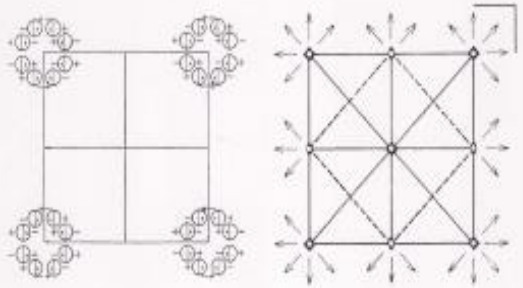
(d) Calculate the distances: Pt-Pt, Pt-K, Pt-Cl.

(e) What is the coordination number of platinum ?

(f) What is the site symmetry of platinum ?

$P\,4/m\,m\,m$ D_{4h}^{1} $4/m\,m\,m$ Tetragonal

No. 123 $P\,4/m\,2/m\,2/m$ Patterson symmetry $P\,4/m\,m\,m$



Origin at centre $(4/m\,m\,m)$

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

Symmetry operations

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

Maximal non-isomorphic subgroups

I	$[2]P\,4\,2\,2$	1; 2; 3; 4; 5; 6; 7; 8
	$[2]P\,4/m\,1\,1\,(P\,4/m)$	1; 2; 3; 4; 9; 10; 11; 12
	$[2]P\,4\,m\,m$	1; 2; 3; 4; 13; 14; 15; 16
	$[2]P\,\bar{4}\,2\,m$	1; 2; 5; 6; 11; 12; 15; 16
	$[2]P\,\bar{4}\,m\,2$	1; 2; 7; 8; 11; 12; 13; 14
	$[2]P\,2/m\,2/m\,1\,(P\,m\,m\,m)$	1; 2; 5; 6; 9; 10; 13; 14
	$[2]P\,2/m\,1\,2/m\,(C\,m\,m\,m)$	1; 2; 7; 8; 9; 10; 15; 16

IIa none

IIb $[2]P\,4/m\,c\,c\,(c'=2c)$; $[2]P\,4_2/m\,m\,c\,(c'=2c)$; $[2]P\,4_2/m\,c\,m\,(c'=2c)$; $[2]C\,4/a\,m\,d\,(a'=2a, b'=2b)(P\,4/n\,b\,m)$; $[2]C\,4/m\,m\,d\,(a'=2a, b'=2b)(P\,4/m\,b\,m)$; $[2]C\,4/a\,m\,m\,(a'=2a, b'=2b)(P\,4/n\,m\,m)$; $[2]F\,4/m\,m\,m\,(a'=2a, b'=2b, c'=2c)(I\,4/m\,m\,m)$; $[2]F\,4/m\,m\,c\,(a'=2a, b'=2b, c'=2c)(I\,4/m\,c\,m)$

Maximal isomorphic subgroups of lowest index

IIc $[2]P\,4/m\,m\,m\,(c'=2c)$; $[2]C\,4/m\,m\,m\,(a'=2a, b'=2b)(P\,4/m\,m\,m)$

Minimal non-isomorphic supergroups

I $[3]Pm\bar{3}m$

II $[2]I\,4/m\,m\,m$

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	u 1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$	no conditions
		(5) $\bar{x},y,\bar{z}$	(6) $x,\bar{y},\bar{z}$	(7) $y,x,\bar{z}$	(8) $\bar{y},\bar{x},\bar{z}$	
		(9) $\bar{x},\bar{y},\bar{z}$	(10) $x,y,\bar{z}$	(11) $y,\bar{x},\bar{z}$	(12) $\bar{y},x,\bar{z}$	
		(13) $x,\bar{y},z$	(14) $\bar{x},y,z$	(15) $\bar{y},\bar{x},z$	(16) y,x,z	
						Special:
8	t .m.	$x,\frac{1}{2},z$	$\bar{x},\frac{1}{2},z$	$\frac{1}{2},x,z$	$\frac{1}{2},\bar{x},z$	no extra conditions
		$\bar{x},\frac{1}{2},\bar{z}$	$x,\frac{1}{2},\bar{z}$	$\frac{1}{2},x,\bar{z}$	$\frac{1}{2},\bar{x},\bar{z}$	
8	s .m.	$x,0,z$	$\bar{x},0,z$	$0,x,z$	$0,\bar{x},z$	no extra conditions
		$\bar{x},0,\bar{z}$	$x,0,\bar{z}$	$0,x,\bar{z}$	$0,\bar{x},\bar{z}$	
8	r ..m	x,x,z	$\bar{x},\bar{x},z$	$\bar{x},x,z$	$x,\bar{x},z$	no extra conditions
		$\bar{x},x,\bar{z}$	$x,\bar{x},\bar{z}$	$x,x,\bar{z}$	$\bar{x},\bar{x},\bar{z}$	
8	q m..	$x,y,\frac{1}{2}$	$\bar{x},\bar{y},\frac{1}{2}$	$\bar{y},x,\frac{1}{2}$	$y,\bar{x},\frac{1}{2}$	no extra conditions
		$\bar{x},y,\frac{1}{2}$	$x,\bar{y},\frac{1}{2}$	$y,x,\frac{1}{2}$	$\bar{y},\bar{x},\frac{1}{2}$	
8	p m..	$x,y,0$	$\bar{x},\bar{y},0$	$\bar{y},x,0$	$y,\bar{x},0$	no extra conditions
		$\bar{x},y,0$	$x,\bar{y},0$	$y,x,0$	$\bar{y},\bar{x},0$	
4	o m 2m.	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	no extra conditions
4	n m 2m.	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	no extra conditions
4	m m 2m.	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	no extra conditions
4	l m 2m.	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	no extra conditions
4	k m .2m	$x,x,\frac{1}{2}$	$\bar{x},\bar{x},\frac{1}{2}$	$\bar{x},x,\frac{1}{2}$	$x,\bar{x},\frac{1}{2}$	no extra conditions
4	j m .2m	$x,x,0$	$\bar{x},\bar{x},0$	$\bar{x},x,0$	$x,\bar{x},0$	no extra conditions
4	i 2mm.	$0,\frac{1}{2},z$	$\frac{1}{2},0,z$	$0,\frac{1}{2},\bar{z}$	$\frac{1}{2},0,\bar{z}$	hkl : $h+k=2n$
2	h 4mm	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			no extra conditions
2	g 4mm	$0,0,z$	$0,0,\bar{z}$			no extra conditions
2	f mmm.	$0,\frac{1}{2},0$	$\frac{1}{2},0,0$			hkl : $h+k=2n$
2	e mmm.	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$			hkl : $h+k=2n$
1	d $4/mmm$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$				no extra conditions
1	c $4/mmm$	$\frac{1}{2},\frac{1}{2},0$				no extra conditions
1	b $4/mmm$	$0,0,\frac{1}{2}$				no extra conditions
1	a $4/mmm$	$0,0,0$				no extra conditions

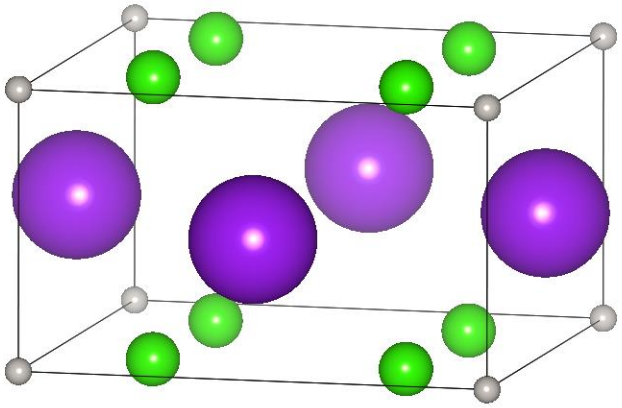
Symmetry of special projections

Along [001] $p\,4m\,m$
$a'=a$ $b'=b$
Origin at $0,0,z$

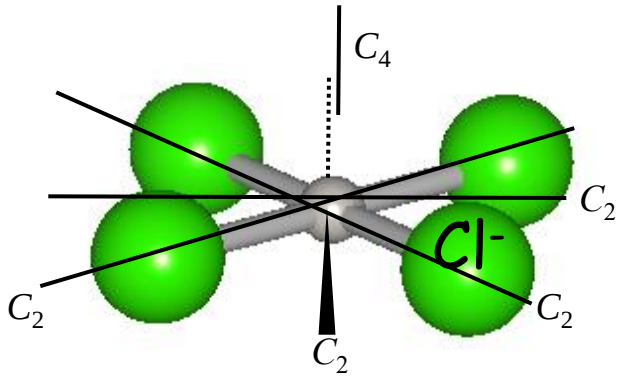
Along [100] $p\,2m\,m$
$a'=b$ $b'=c$
Origin at $x,0,0$

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

(Continued on preceding page)

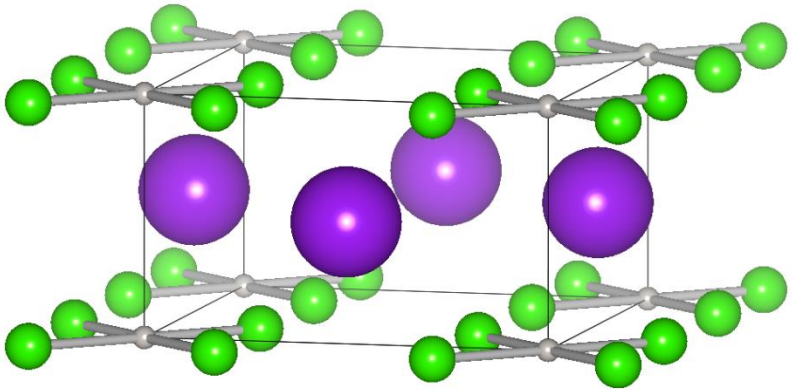


Pt: 1 atom in unit cell
K: 2 atoms in unit cell
Cl: 4 atoms in unit cell

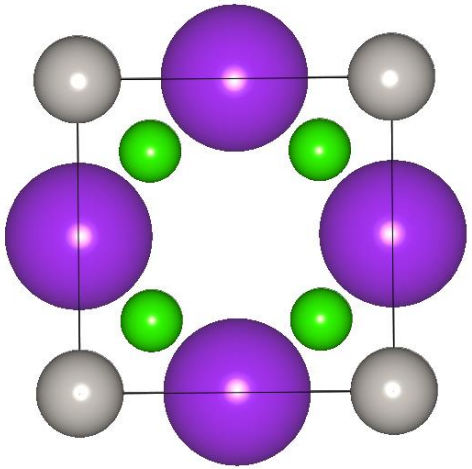


Site symmetry of Pt: D_{4h}

Bond lengths:
Pt-Pt: $(1\text{-}0)^2 \cdot 4.15$Å
Pt-K: $\sqrt{[(0.5\text{-}0)^2 \cdot 7.023Å + (0.5\text{-}0)^2 \cdot 4.149Å]} = 4.08$Å
Pt-Cl: $\sqrt{[(0.232\text{-}0)^2 \cdot 7.023Å + (0.232\text{-}0)^2 \cdot 7.023Å]} = 2.30$Å



ab-projectio
(seen from *c*-direction)



K_2PtCl_4

- $\rho = 3.37 \times 10^6$ g/m^3
- V = 7.023 Å x 7.023 Å x 4.1486 Å = 204.62×10^{-30} m^3
- M = (2 x 39.098 + 195.22 + 4 x 35.453) g/mol = 415.228 g/mol
- $Z = (V \times \rho \times N_A) / M = 1$
- Distances: Pt-Pt: 4.15 Å
  Pt-K: 4.08 Å
  Pt-Cl: 2.31 Å ($\rightarrow$ chemical bond)
- CN(Pt) = 4
- Pl site symmetry: D_{4h}

WHAT WE LIKE TO KNOW ABOUT THE CRYSTAL STRUCTURE

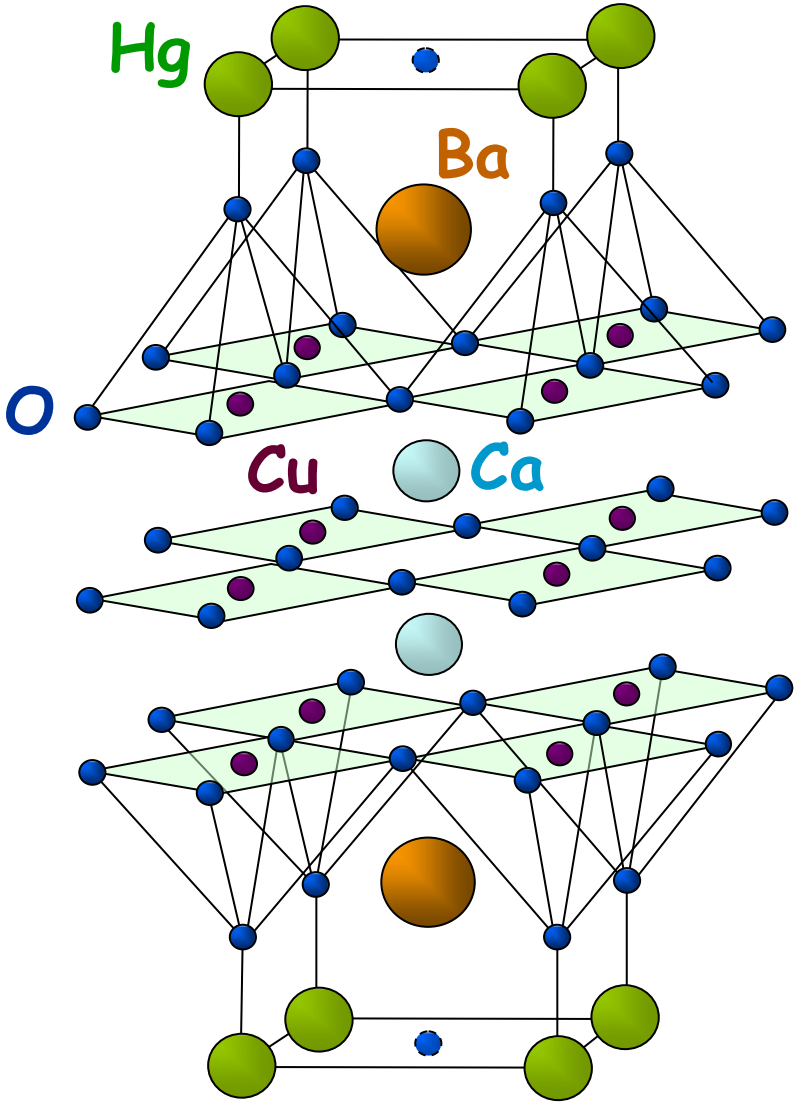
CRYSTALLOGRAPHY

- **symmetry**
- **unit cell**
- **lattice parameters**
- **number of formula units in unit cell**
- **space group**
- **etc.**

CRYSTAL CHEMISTRY

- **coordination numbers**
- **coordination polyhedra**
- **bond lengths/angles**
- **occupation factors**
- **etc.**

Discussed in Lecture 2!



$HgBa_2Ca_2Cu_3O_{9-\delta}$

EXAMPLE: Chromium oxychloride CrOCl

Space group *Pmmn* (No. 59)

Lattice parameters: a = 3.88 Å, b = 3.20 Å, c = 7.72 Å (Z = 2)

Atomic positions:

Cr	2*a*	z = 0.109
Cl	2*b*	z = 0.327
O	2*b*	z = 0.960

(a) Draw the unit cell.

(b) Give for chromium:

- bond lengths
- coordination numbers
- site symmetry

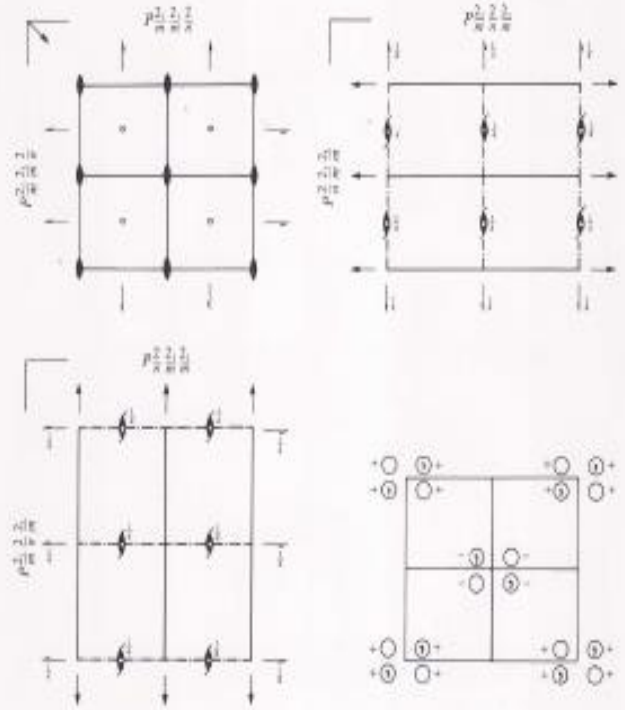
(c) Calculate BVS for chromium.

[R^0 values: Cr^{III}-O^{-II}: 1.724, Cr^{III}-Cl^{-I}: 2.08]

P m m n D_{2h}^{13} *m m m* Orthorhombic

No. 59 $P\,2_1/m\,2_1/m\,2/n$ Patterson symmetry *P m m m*

ORIGIN CHOICE 1



Origin at $m\,m\,2/n$, at $\frac{1}{4},\frac{1}{4},0$ from $\bar{1}$

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

Symmetry operations

(1) 1 (2) 2 0,0,*z* (3) $2(0,\frac{1}{4},0)$ $\frac{1}{4},y,0$ (4) $2(\frac{1}{4},0,0)$ $x,\frac{1}{4},0$
(5) $\bar{1}$ $\frac{1}{4},\frac{1}{4},0$ (6) $n(\frac{1}{4},\frac{1}{4},0)$ $x,y,0$ (7) *m* $x,0,z$ (8) *m* $0,y,z$

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

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates				Reflection conditions
8	*g*	1	(1) x,y,z (5) $\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2},z$	(2) $\bar{x},\bar{y},z$ (6) $x+\frac{1}{2},y+\frac{1}{2},z$	(3) $\bar{x}+\frac{1}{2},y+\frac{1}{2},\bar{z}$ (7) $x,\bar{y},z$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$ (8) $\bar{x},y,z$	General: $hk0$: $h+k=2n$ $h00$: $h=2n$ $0k0$: $k=2n$
							Special: as above, plus
4	*f*	.*m*.	$x,0,z$	$\bar{x},0,z$	$x+\frac{1}{2},\frac{1}{2},\bar{z}$	$x+\frac{1}{2},\frac{1}{2},z$	no extra conditions
4	*e*	*m*..	$0,y,z$	$0,\bar{y},z$	$\frac{1}{2},y+\frac{1}{2},\bar{z}$	$\frac{1}{2},\bar{y}+\frac{1}{2},z$	no extra conditions
4	*d*	$\bar{1}$	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{3}{4},\frac{3}{4},\frac{1}{4}$	$\frac{3}{4},\frac{1}{4},\frac{3}{4}$	$\frac{1}{4},\frac{3}{4},\frac{3}{4}$	hkl : $h,k=2n$
4	*c*	$\bar{1}$	$\frac{1}{4},\frac{1}{4},0$	$\frac{3}{4},\frac{3}{4},0$	$\frac{3}{4},\frac{1}{4},0$	$\frac{1}{4},\frac{3}{4},0$	hkl : $h,k=2n$
2	*b*	*mm*2	$0,\frac{1}{2},z$	$\frac{1}{2},0,\bar{z}$			no extra conditions
2	*a*	*mm*2	$0,0,z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			no extra conditions

Symmetry of special projections

Along [001] *c* 2*m m*
$\boldsymbol{a}'=\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$
Origin at $0,0,z$

Along [100] *p* 2*m g*
$\boldsymbol{a}'=\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,\frac{1}{4},0$

Along [010] *p* 2*g m*
$\boldsymbol{a}'=\boldsymbol{c}$ $\boldsymbol{b}'=\boldsymbol{a}$
Origin at $\frac{1}{4},y,0$

Maximal non-isomorphic subgroups

I [2]$P\,2_1\,2\,2$ 1; 2; 3; 4
[2]$P\,1\,1\,2/n\,(P\,2/c)$ 1; 2; 5; 6
[2]$P\,1\,2_1/m\,1\,(P\,2_1/m)$ 1; 3; 5; 7
[2]$P\,2_1/m\,1\,1\,(P\,2_1/m)$ 1; 4; 5; 8
[2]$P\,m\,m\,2$ 1; 2; 7; 8
[2]$P\,m\,2_1\,a\,(P\,m\,n\,2_1)$ 1; 3; 6; 8
[2]$P\,2_1\,m\,n\,(P\,m\,n\,2_1)$ 1; 4; 6; 7

IIa none

IIb [2]$P\,c\,m\,n\,(c'=2c)(P\,n\,m\,a)$; [2]$P\,m\,c\,n\,(c'=2c)(P\,n\,m\,a)$; [2]$P\,c\,c\,n\,(c'=2c)$

Maximal isomorphic subgroups of lowest index

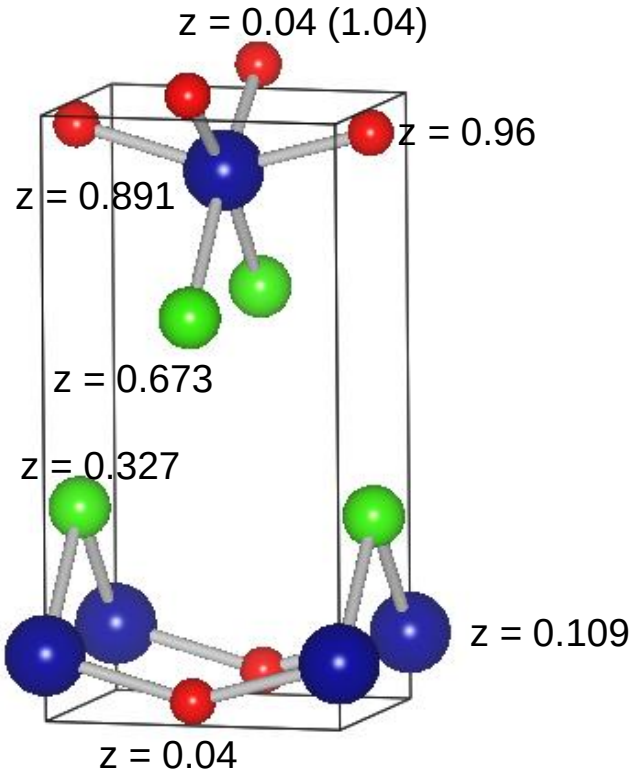
IIc [3]$P\,m\,m\,n\,(\boldsymbol{a}'=3\boldsymbol{a}$ or $\boldsymbol{b}'=3\boldsymbol{b})$; [2]$P\,m\,m\,n\,(c'=2c)$

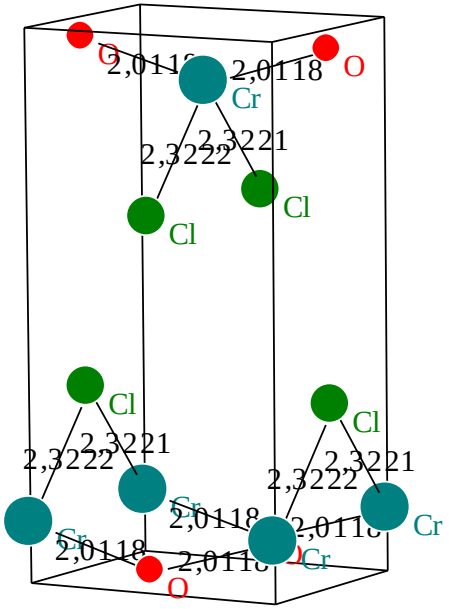
Minimal non-isomorphic supergroups

I [2]$P\,4/n\,m\,m$; [2]$P\,4_2/n\,m\,c$

II [2]$A\,n\,m\,a\,(C\,m\,c\,m)$; [2]$B\,m\,m\,b\,(C\,m\,c\,m)$; [2]$C\,m\,m\,m$; [2]$I\,m\,m\,m$; [2]$P\,m\,m\,b\,(2\boldsymbol{a}'=\boldsymbol{a})\,(P\,m\,m\,a)$; [2]$P\,m\,m\,a\,(2\boldsymbol{b}'=\boldsymbol{b})$

CrOCl





Chromium bonding

2 x Cr-Cl: $\sqrt{\{(0.891-0.673) \times 7.72\ \text{Å}\}^2 + \{0.5 \times 3.20\ \text{Å}\}^2} = 2.3222\ \text{Å}$

2 x Cr-O: $\sqrt{\{(0.960-0.891) \times 7.72\ \text{Å}\}^2 + \{0.5 \times 3.88\ \text{Å}\}^2} = 2.0118\ \text{Å}$

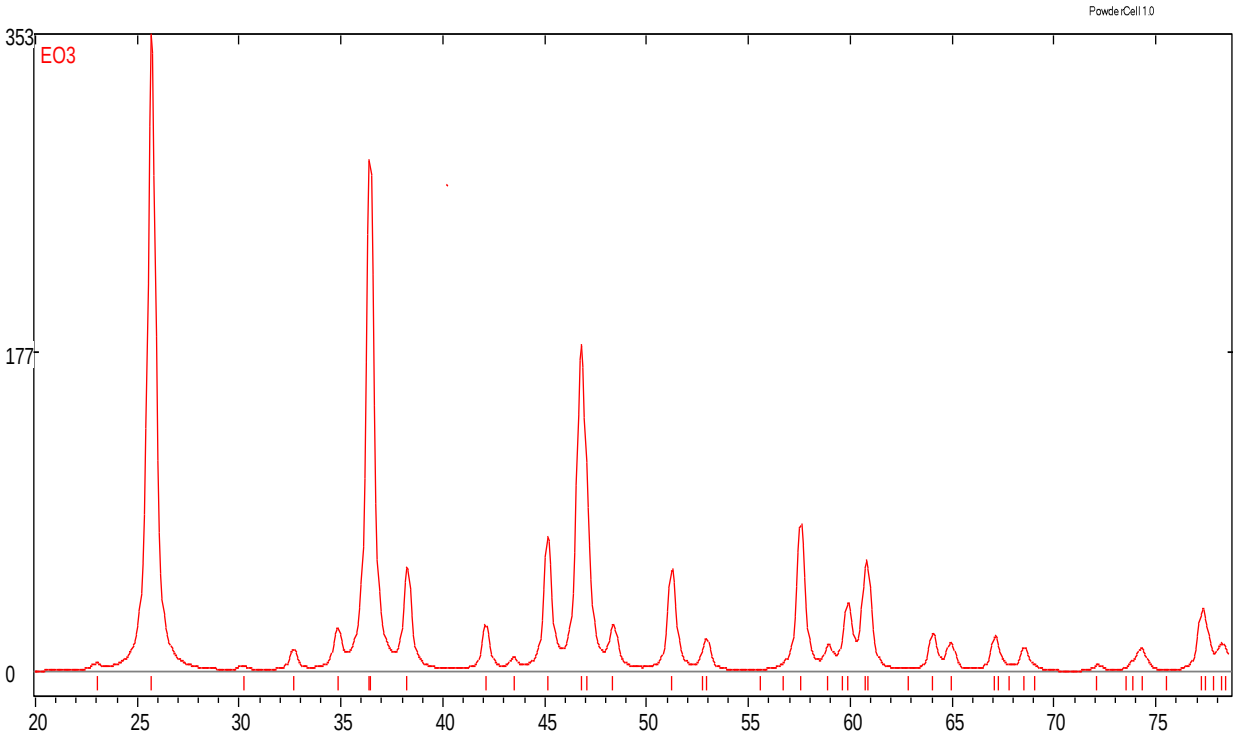
2 x Cr-O: $\sqrt{\{[(1-0.891)+0.04] \times 7.72\ \text{Å}\}^2 + \{0.5 \times 3.20\ \text{Å}\}^2} = 1.9706\ \text{Å}$

CN(Cr) = 6

Cr site symmetry: C_{2v}

BVS(Cr): +2.985

CrOCl: simulated XRD pattern based on the structure data



Your EXERCISE question

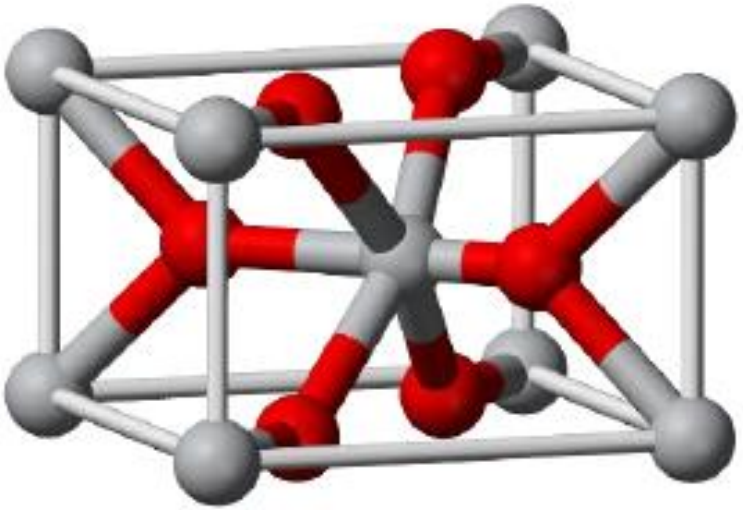
White balls are Ti atoms, red balls are oxygen atoms.

Unit cell parameters: a = b = 4.5937 Å, c = 2.9587 Å; all angles 90^{o}.

(a) What is the crystal system?

(b) What is the formula of the compound ?

(c) Please calculate the density.



Some extra slides...

CLASSIFICATIONS

- ”Macroscopic shape of the crystal”
  → ”Point group for the lattice” → **7 CRYSTAL SYSTEMS**
  (can fill the space without holes; no information of the lattice points/atoms)

CRYSTAL SYSTEM & LATTICE POINTS (historical importance)

- Combination of crystal system and lattice type → **14 Bravais lattices**
- **Lattice type:** positions of **lattice points** (≠ atoms) within the cell considered:
  primitive (P), body-centered (I), face-centered (F), base-centered (A/B/C), rhombohedral (R)

CRYSTAL SYSTEM & SYMMETRY (most important in crystallography)

- Possible combinations of point symmetry elements (which leave one point fixed)
  → **32 (geometric) cystal classes**
  → describe completely the symmetry of macroscopic crystals

  There are an infinite number of **three-dimensional point groups**, but the crystallographic restriction results in there being only 32 crystallographic point groups.
- Considering also the translational symmetry operations in 3D
  → **230 space groups**

Crystal System	# of Point Groups	# of Crystal Lattices
Cubic	**5**	**3**
Tetragonal	**7**	**2**
Orthorhombic	**3**	**4**
Monoclinic	**3**	**2**
Triclinic	**2**	**1**
Hexagonal	**7**	**1**
Trigonal	**5**	**1**
Totals	**32**	**14**

Supporting material

Mathematical descriptions of 2D point groups:

https://www.cryst.ehu.es/plane/get_point_genpos.html

https://en.wikipedia.org/wiki/Point_groups_in_two_dimensions