LECTURE 4: CRYSTALLOGRAPHY BASICS

- From 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

FROM MOLECULES TO CRYSTALS

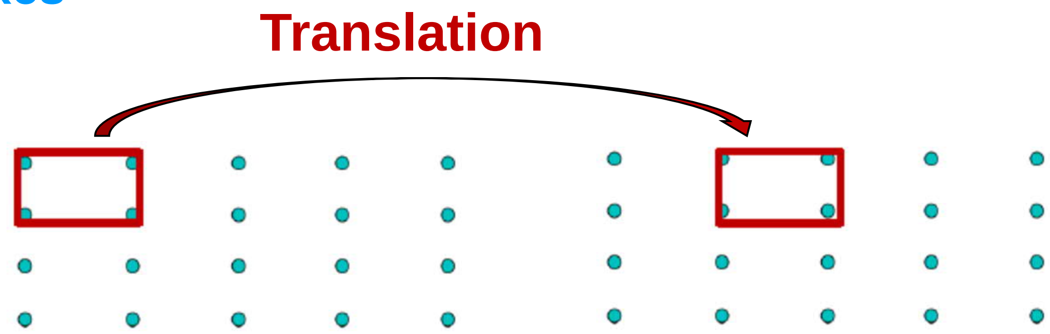
There are two things which make macroscopic (infinite) crystals different from discrete molecules in terms of symmetry: Space-filling & Translation

Space-filling

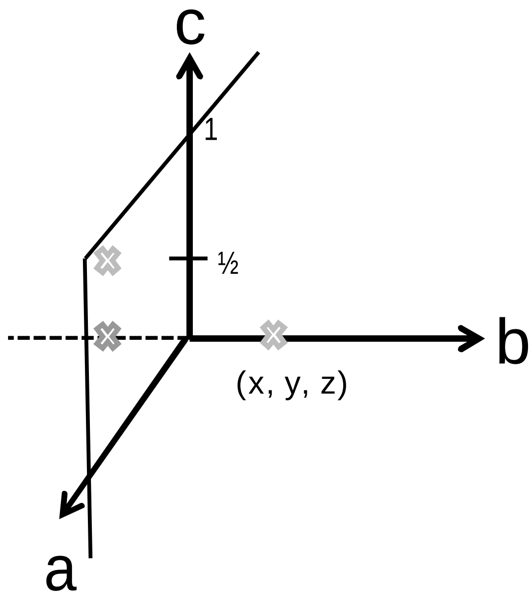
- **Macroscopic crystals need to cntinuosly fill the space → 5-cubes can not satisfy this (except in quasicrystals)**
- **For molecules 5-fold rotation is possible, but not for crystals**

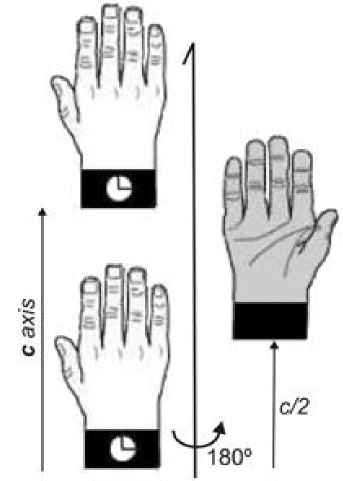
Translation in crystals

- **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**
- **Combining translation with other symmetry operations/elements → new symmetry operations/elements (not included in point groups): glide planes & screw axes**



GLIDE PLANE c (⊥ b)

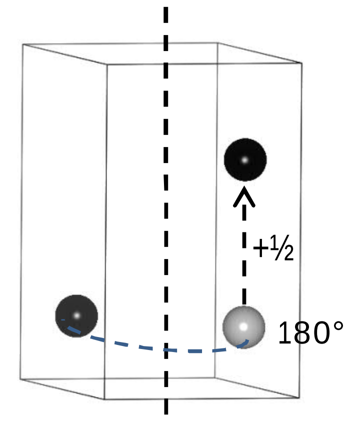




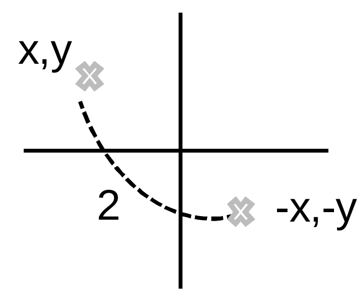
Rotation (c) followed by translation (t)

SCREW AXIS

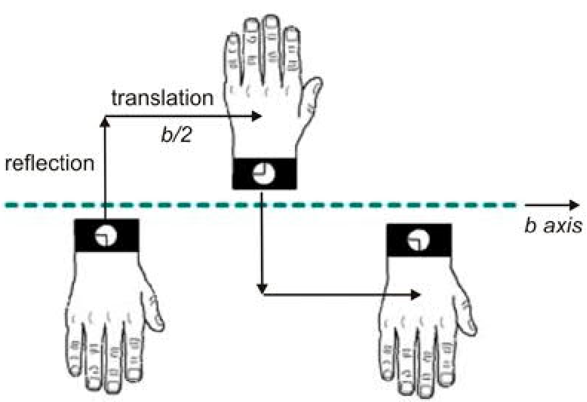
$2_1 \parallel c$

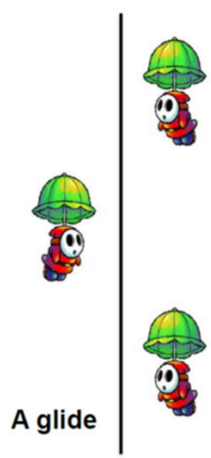


x,y,z -> -x, -y, z+½



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





In infinite lattice there are additional translation symmetry elements:

Translation

Translation (move) from one point to another point

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 180º 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* (siirrot ½*a*, ½*b*, ½*c* kuhunkin liukutason suuntaan)
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)

(from historical reasons)

DIFFERENT

SYMMETRY SYMBOLS

- **Schoenflies (S) symbols**
  - were developed first
  - in molecular symmetry & spectroscopy
- **Hermann-Mauguin (HM) symbols**
  - in crystallography
  - long and short forms
- **Graphical symbols**

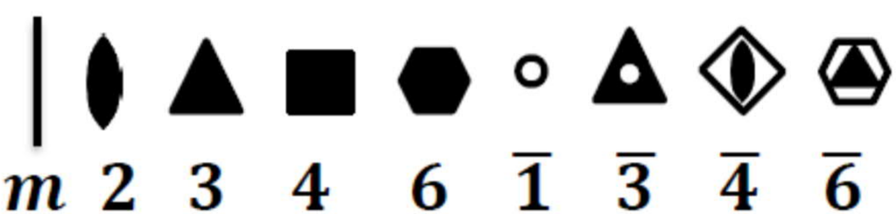


Table 1.1 Symmetry elements of crystal point groups.

System	Point group symmetry S	Point group symmetry H/M	Symmetry elements	Number of operations
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

Symmetry elements (Schönflies/Hermann-Mauguin)

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 / ($\bar{1}$, $\bar{2}$), $\bar{3}$, $\bar{4}$, $\bar{6}$

One point remains unchanged

⇨ **Point/Molecular symmetry**

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

WHAT WE LIKE TO KNOW ABOUT THE CRYSTAL STRUCTURE

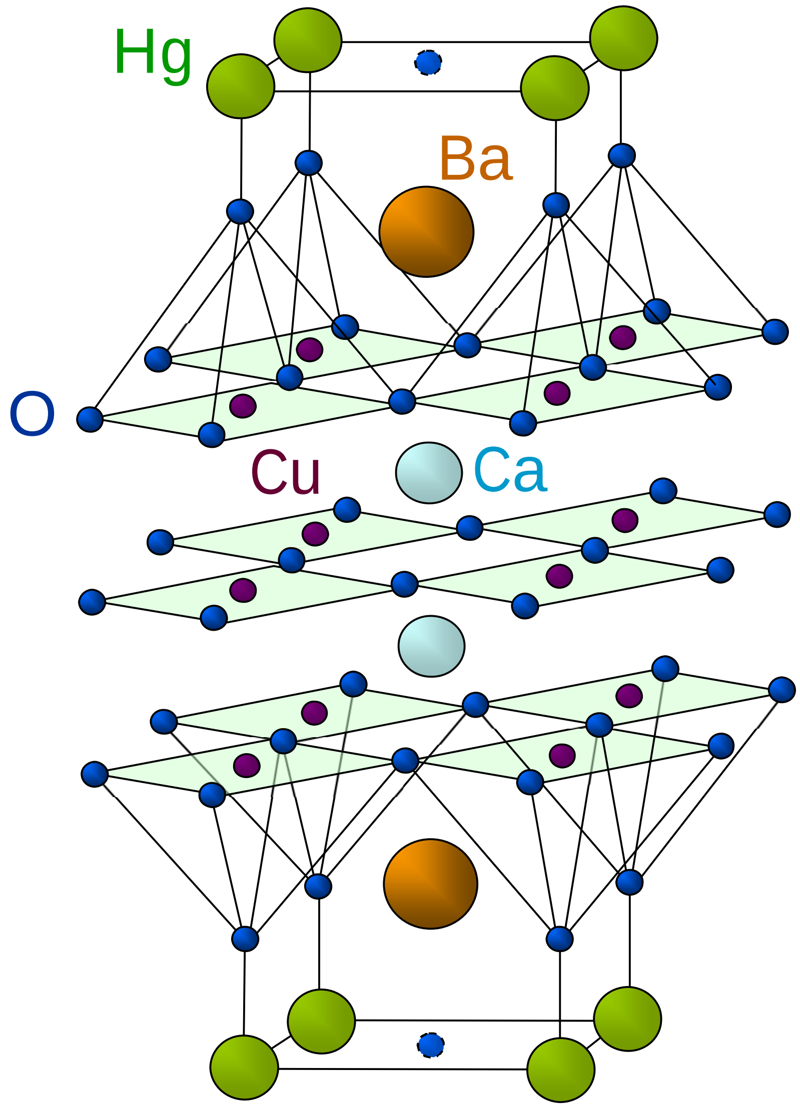
CRYSTALLOGRAPHY

- **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.**

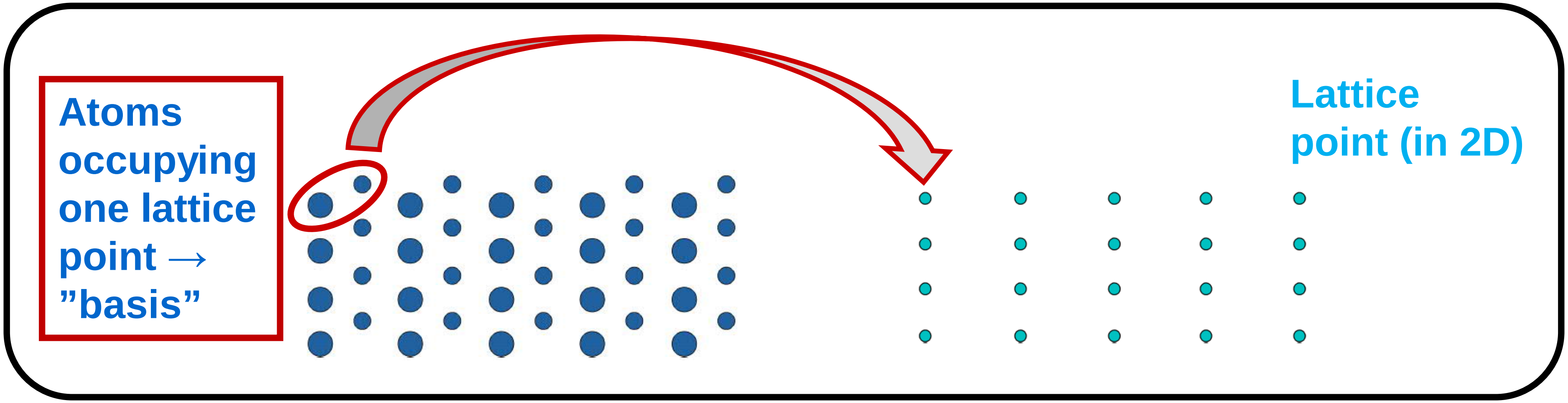
Discussed in Lecture 2!



$HgBa_2Ca_2Cu_3O_{9-\delta}$

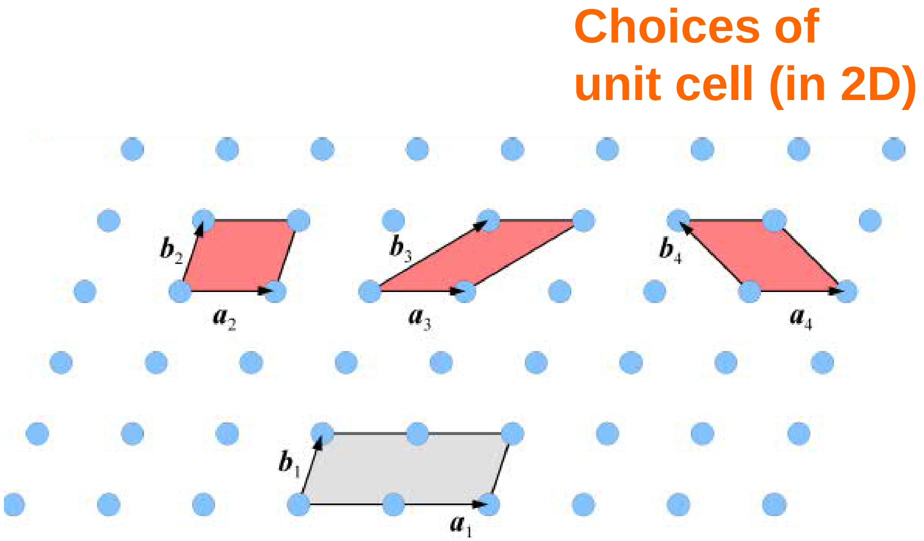
CRYSTAL LATTICE

- **Regular (infinite 3D) arrangement of lattice points**
- **Lattice point: consists of one or more atoms (= basis)**
- **Each lattice point has identical environment + symmetry properties (point group)**

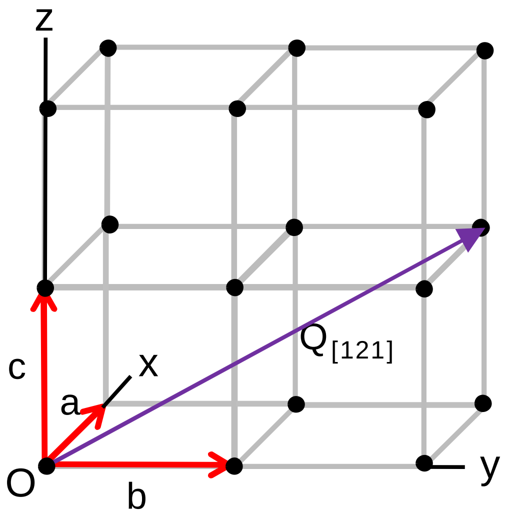


UNIT CELL

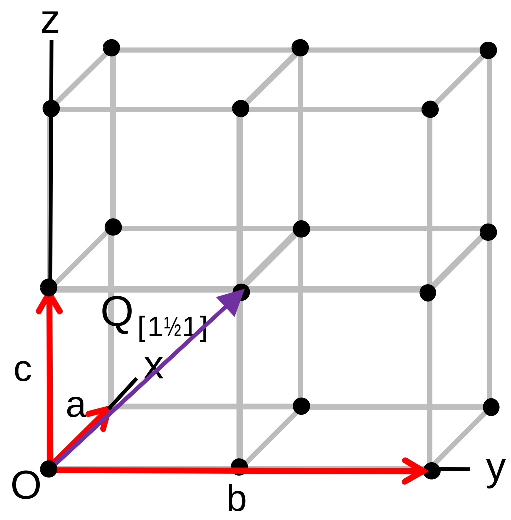
- Smallest possible microscopic 3D part of the crystal lattice that repeats itself periodically and completely fills the lattice volume, and is enough to describe the lattice perfectly
- Choice of the unit cell not always unambicious: several possible choices



Each lattice point should be able to be described with the vector $Q_{[uvw]} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, where u, v and w all are integer values



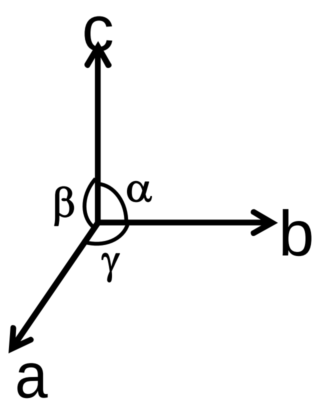
Unit cell: YES



Unit cell: NO

What we need to tell about the UNIT CELL

- 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**



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)

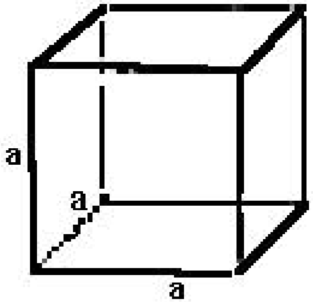
- Possible combinations of point symmetry elements (which leave one point fixed) → **32 (geometric) cystal classes** → describe completely the symmetry of macroscopic crystals

  There are an infinite number of **three**-dimensional point groups, but the crystallographic restriction results in there being only **32** crystallographic point groups.

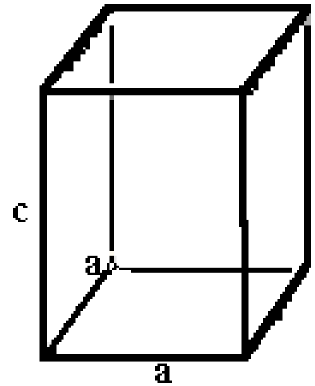
- Considering also the translational symmetry operations in 3D → **230 space groups**

CRYSTAL SYSTEMS (7)

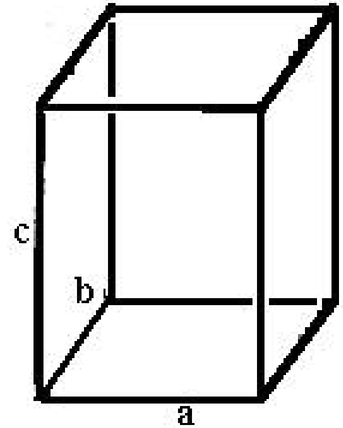
No information of the positions of atoms



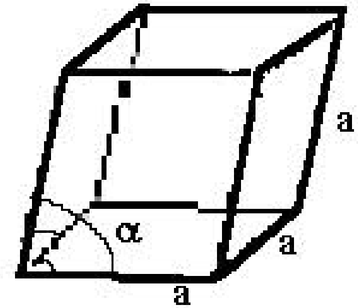
Cubic
a = b = c
$\alpha = \beta = \gamma = 90^{o}$
NaCl, $MgAl_2O_4$



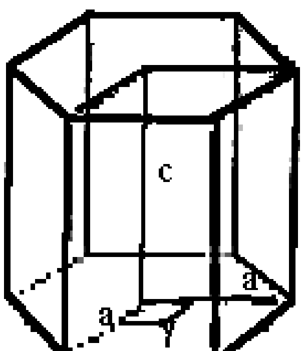
Tetragonal
a = b # c
$\alpha = \beta = \gamma = 90^{o}$
TiO_2, K_2NiF_4



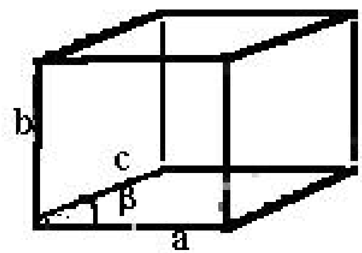
Orthorhombic
a # b # c
$\alpha = \beta = \gamma = 90^{o}$
$YBa_2Cu_3O_7$



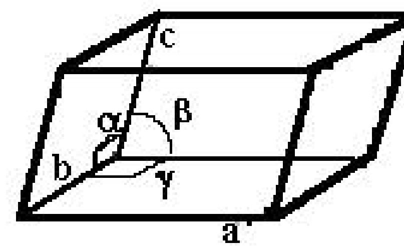
Rhombohedral
a = b = c
$\alpha = \beta = \gamma$ # 90^{o}
$BaTiO_3$ (low-T)



Hexagonal
a = b # c
$\alpha = \beta = 90, \gamma = 120^{o}$
$LiNbO_3$



Monoclinic
a # b # c
$\alpha = \gamma = 90^{o}$, β # 90^{o}
KH_2PO_4



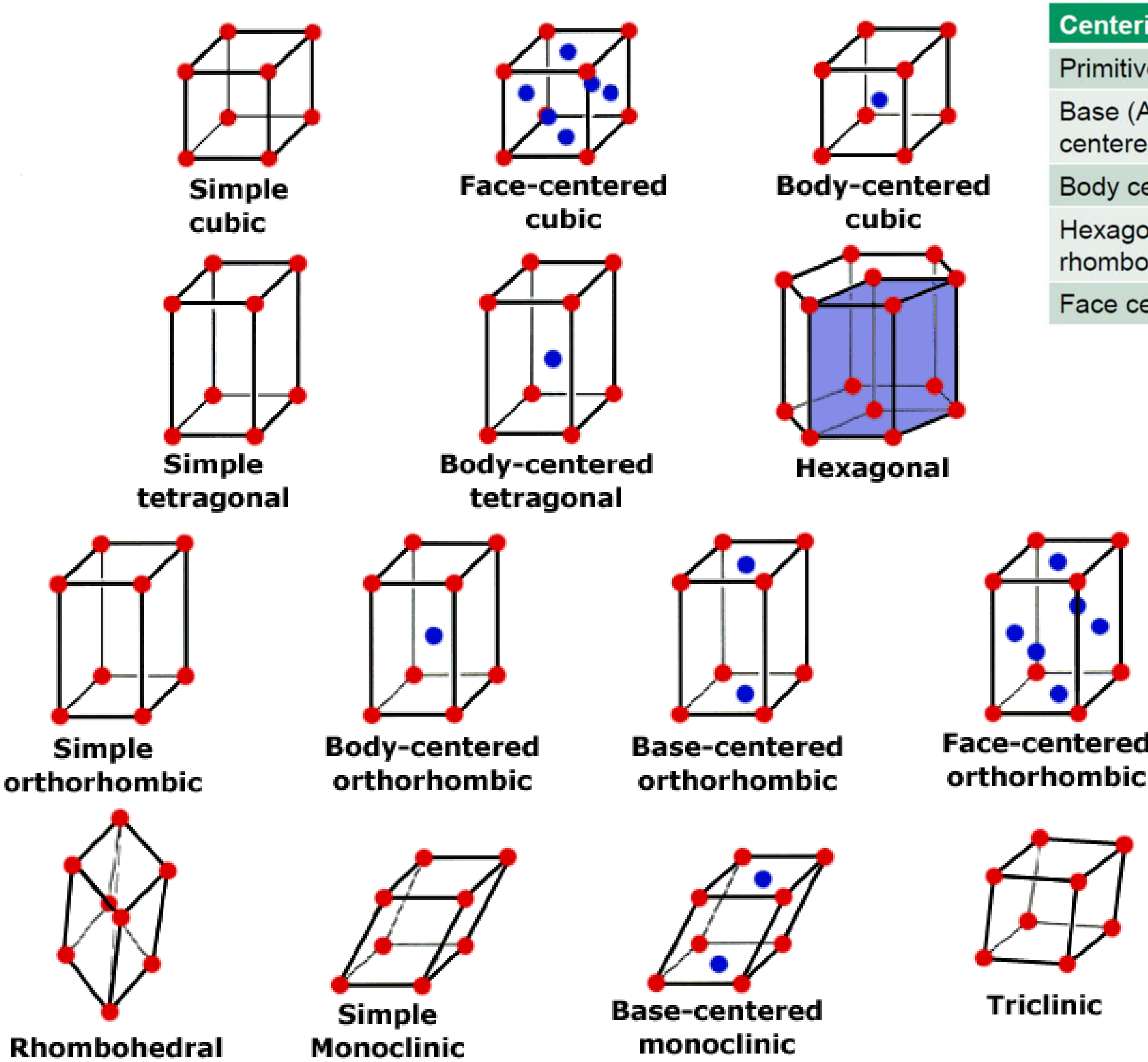
Triclinic
a # b # c
α # β # γ # 90^{o}

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

BRAVAIS LATTICES (14)

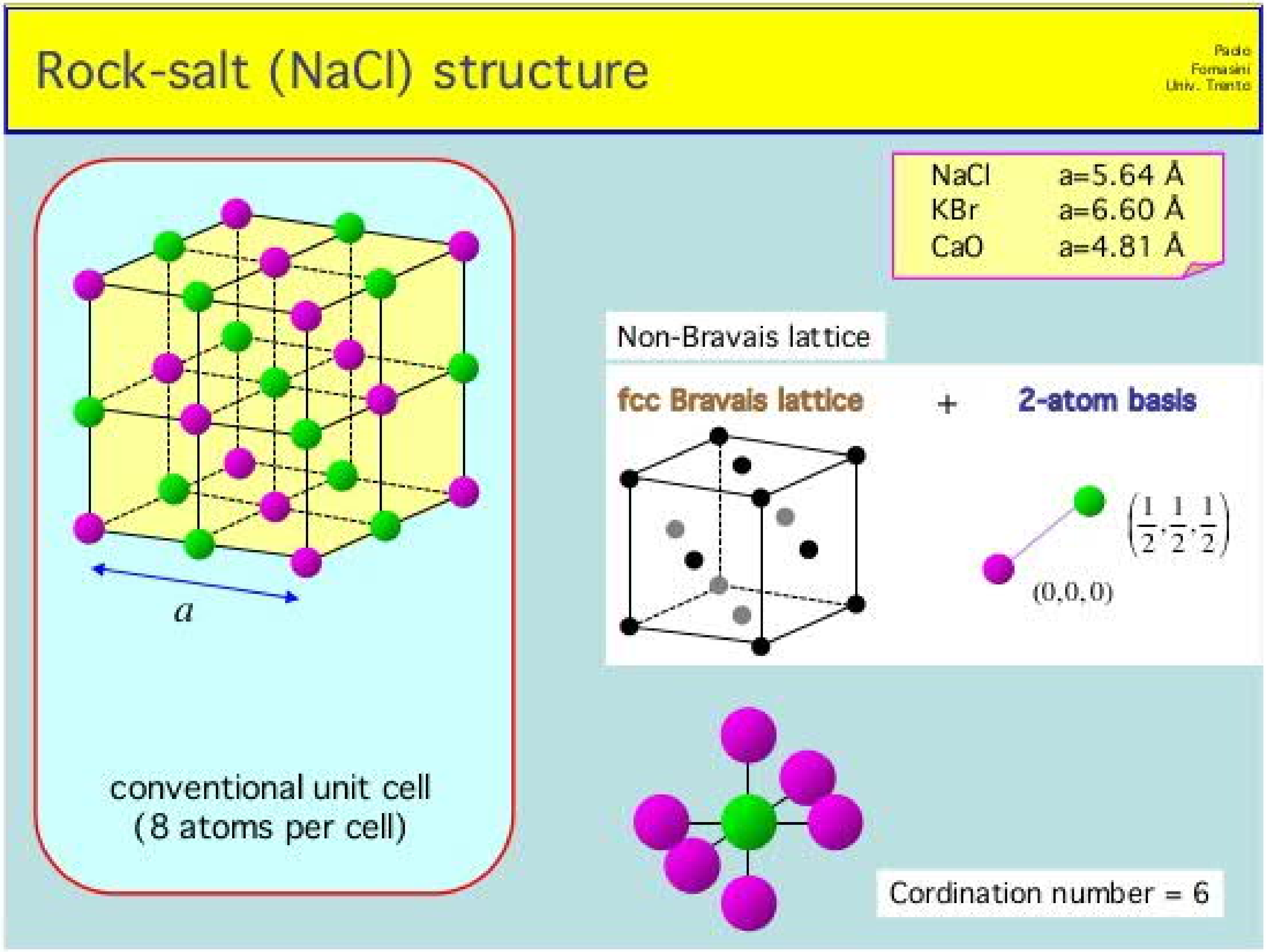
Positions of lattice sites (not atoms) included

Centering	Lattice points/cell	Abbreviation
Primitive	1	P
Base (A,B, or C) centered	2	A,B or C
Body centered	2	I
Hexagonal rhombohedral	3	hR
Face centered	4	F



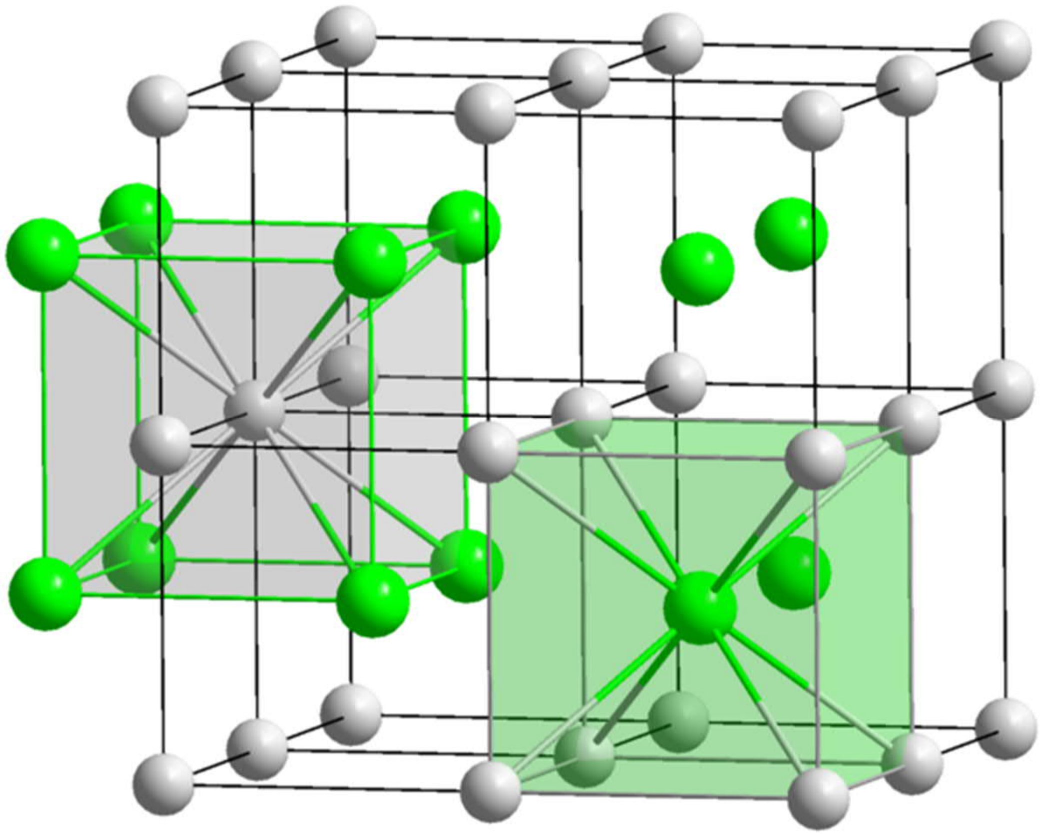
EXAMPLE

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



EXAMPLE

- **What is the Bravais lattice type of CsCl: Cubic P (basis: Cs-Cl)**



CRYSTAL CLASSES (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)

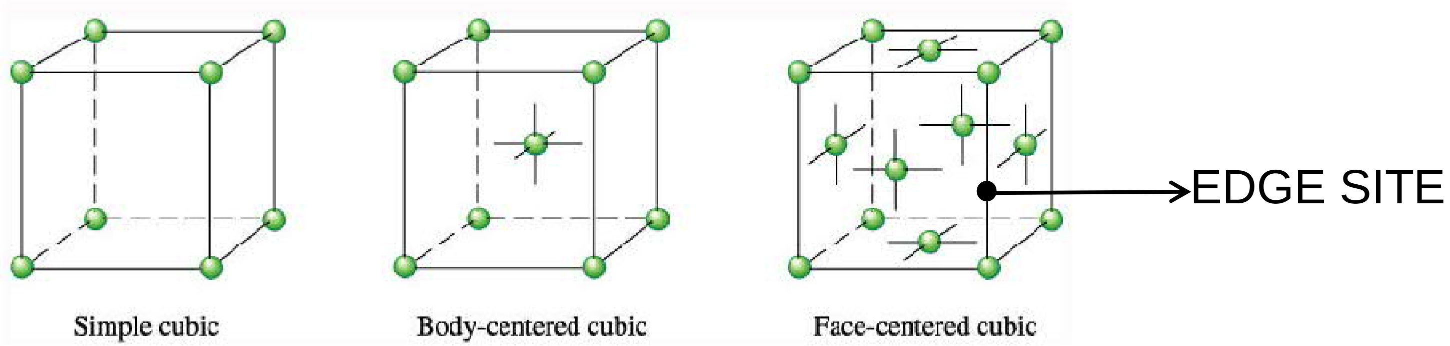
Crystal System	# of Point Groups	# of Crystal Lattices
Cubic	5	3
Tetragonal	7	2
Orthorhombic	3	4
Monoclinic	3	2
Triclinic	2	1
Hexagonal	7	1
Trigonal	5	1
Totals	32	14

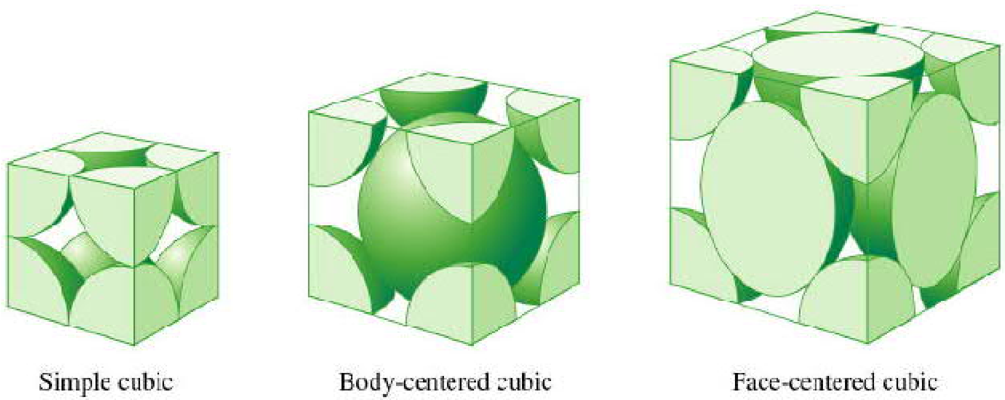
System	Minimum Requirements
Cubic	Four 3-fold rotation axis
Tetragonal	One 4-fold rotation (or RI) axis
Orthorhombic	Three perpendicular 2-fold axis
Rhombohedral	One 3-fold rotation (or RI) axis
Hexagonal	One 6 fold rotation (or RI) axis
Monoclinic	One 2 fold rotation axis or mirror plane
Triclinic	none

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, $\bar{1}$

NUMBER of FORMULA UNITS in UNIT CELL (Z)

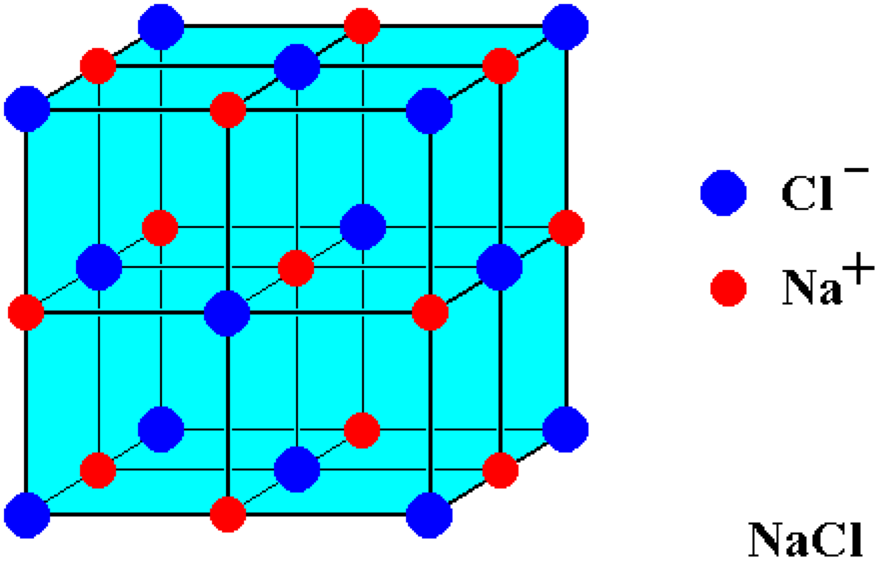
- **typically 1 – 6, but can be tens or even hundreds**
- **atom inside unit cell: belongs only to one unit cell**
- **atom on unit cell face: belongs to two unit cells**
- **atom on unit cell edge: belongs to four unit cells**
- **atom on unit cell corner: belongs to eight unit cells**





EXAMPLE

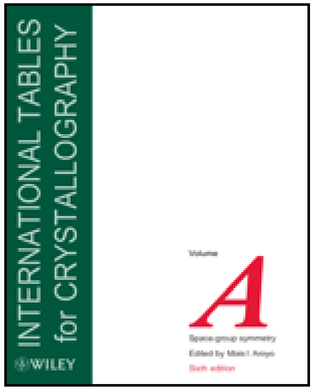
- **How many NaCl formula units in unit cell?**
- **Answer: 4**



SPACE GROUPS

- **From finite molecule (or macroscopic crystal) to infinite lattice → translation symmetry must be included**
- **Possible combinations of symmetry elements (including the translation symmetry elements): 230**
  → 230 space groups
- **Space groups (and the characteristic information in 2 pages) are listed in International Tables for Crystallography**
  → BIBLE of CRYSTALLOGRAPHY
- **Next-next slide: Space Group P4/mmm as an example**

https://it.iucr.org/



Triclinic

(For the enlarged unit cells, click here)

1. $P1$	2. $P\text{-}1$

Monoclinic

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

3. $P121$	4. $P12_11$	5. $C121$	6. $P1m1$	7. $P1c1$
8. $C1m1$	9. $C1c1$	10. $P12/m1$	11. $P12_1/m1$	12. $C12/m1$
13. $P12/c1$	14. $P12_1/c1$	15. $C12/c1$		

Orthorhombic

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

16. $P222$	17. $P222_1$	18. $P2_12_12$	19. $P2_12_12_1$	20. $C222_1$
21. $C222$	22. $F222$	23. $I222$	24. $I2_12_12_1$	25. $Pmm2$
26. $Pmc2_1$	27. $Pcc2$	28. $Pma2$	29. $Pca2_1$	30. $Pnc2$
31. $Pmn2_1$	32. $Pba2$	33. $Pna2_1$	34. $Pnn2$	35. $Cmm2$
36. $Cmc2_1$	37. $Ccc2$	38. $Amm2$	39. $Abm2$	40. $Ama2$
41. $Aba2$	42. $Fmm2$	43. $Fdd2$	44. $Imm2$	45. $Iba2$
46. $Ima2$	47. $Pmmm$	48. $Pnnn$	49. $Pccm$	50. $Pban$
51. $Pmma$	52. $Pnna$	53. $Pmna$	54. $Pcca$	55. $Pbam$
56. $Pccn$	57. $Pbcm$	58. $Pnnm$	59. $Pmmn$	60. $Pbcn$
61. $Pbca$	62. $Pnma$	63. $Cmcm$	64. $Cmca$	65. $Cmmm$
66. $Cccm$	67. $Cmma$	68. $Ccca$	69. $Fmmm$	70. $Fddd$
71. $Immm$	72. $Ibam$	73. $Ibca$	74. $Imma$	

Tetragonal

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

75. $P4$	76. $P4_1$	77. $P4_2$	78. $P4_3$	79. $I4$
80. $I4_1$	81. $P\text{-}4$	82. $I\text{-}4$	83. $P4/m$	84. $P4_2/m$
85. $P4/n$	86. $P4_2/n$	87. $I4/m$	88. $I4_1/a$	89. $P422$
90. $P42_12$	91. $P4_122$	92. $P4_12_12$	93. $P4_222$	94. $P4_22_12$
95. $P4_322$	96. $P4_32_12$	97. $I422$	98. $I4_122$	99. $P4mm$
100. $P4bm$	101. $P4_2cm$	102. $P4_2nm$	103. $P4cc$	104. $P4nc$
105. $P4_2mc$	106. $P4_2bc$	107. $I4mm$	108. $I4cm$	109. $I4_1md$
110. $I4_1cd$	111. $P\text{-}42m$	112. $P\text{-}42c$	113. $P\text{-}42_1m$	114. $P\text{-}42_1c$
115. $P\text{-}4m2$	116. $P\text{-}4c2$	117. $P\text{-}4b2$	118. $P\text{-}4n2$	119. $I\text{-}4m2$
120. $I\text{-}4c2$	121. $I\text{-}42m$	122. $I\text{-}42d$	123. $P4/mmm$	124. $P4/mcc$
125. $P4/nbm$	126. $P4/nnc$	127. $P4/mbm$	128. $P4/mnc$	129. $P4/nmm$
130. $P4/ncc$	131. $P4_2/mmc$	132. $P4_2/mcm$	133. $P4_2/nbc$	134. $P4_2/nnm$
135. $P4_2/mbc$	136. $P4_2/mnm$	137. $P4_2/nmc$	138. $P4_2/ncm$	139. $I4/mmm$
140. $I4/mcm$	141. $I4_1/amd$	142. $I4_1/acd$		

Trigonal

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

143. $P3$	144. $P3_1$	145. $P3_2$	146. $R3$	147. $P\text{-}3$
148. $R\text{-}3$	149. $P312$	150. $P321$	151. $P3_112$	152. $P3_121$
153. $P3_212$	154. $P3_221$	155. $R32$	156. $P3m1$	157. $P31m$
158. $P3c1$	159. $P31c$	160. $R3m$	161. $R3c$	162. $P\text{-}31m$
163. $P\text{-}31c$	164. $P\text{-}3m1$	165. $P\text{-}3c1$	166. $R\text{-}3m$	167. $R\text{-}3c$

Hexagonal

168. $P6$	169. $P6_1$	170. $P6_5$	171. $P6_2$	172. $P6_4$
173. $P6_3$	174. $P\text{-}6$	175. $P6/m$	176. $P6_3/m$	177. $P622$
178. $P6_122$	179. $P6_522$	180. $P6_222$	181. $P6_422$	182. $P6_322$
183. $P6mm$	184. $P6cc$	185. $P6_3cm$	186. $P6_3mc$	187. $P\text{-}6m2$
188. $P\text{-}6c2$	189. $P\text{-}62m$	190. $P\text{-}62c$	191. $P6/mmm$	192. $P6/mcc$
193. $P6_3/mcm$	194. $P6_3/mmc$			

Cubic

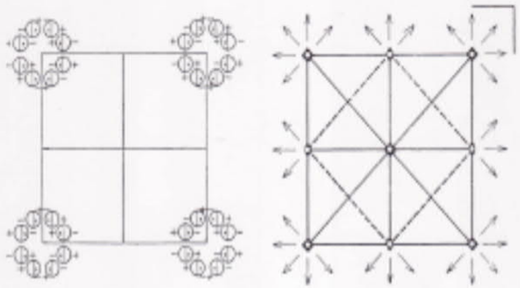
195. $P23$	196. $F23$	197. $I23$	198. $P2_13$	199. $I2_13$
200. $Pm\text{-}3$	201. $Pn\text{-}3$	202. $Fm\text{-}3$	203. $Fd\text{-}3$	204. $Im\text{-}3$
205. $Pa\text{-}3$	206. $Ia\text{-}3$	207. $P432$	208. $P4_232$	209. $F432$
210. $F4_132$	211. $I432$	212. $P4_332$	213. $P4_132$	214. $I4_132$
215. $P\text{-}43m$	216. $F\text{-}43m$	217. $I\text{-}43m$	218. $P\text{-}43n$	219. $F\text{-}43c$
220. $I\text{-}43d$	221. $Pm\text{-}3m$	222. $Pn\text{-}3n$	223. $Pm\text{-}3n$	224. $Pn\text{-}3m$
225. $Fm\text{-}3m$	226. $Fm\text{-}3c$	227. $Fd\text{-}3m$	228. $Fd\text{-}3c$	229. $Im\text{-}3m$
230. $Ia\text{-}3d$				

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

$P\,4/m\,m\,m$ D^1_{4h} $4/m\,m\,m$ 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 $0\le x\le \frac{1}{2}$; $0\le y\le \frac{1}{2}$; $0\le z\le \frac{1}{2}$; $x\le y$

Symmetry operations

(1) 1	(2) 2 0,0,z	(3) 4^+ 0,0,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]$P\,4/m\,c\,c$ ($\mathbf{c}'=2\mathbf{c}$); [2]$P\,4_2/m\,m\,c$ ($\mathbf{c}'=2\mathbf{c}$); [2]$P\,4_2/m\,c\,m$ ($\mathbf{c}'=2\mathbf{c}$); [2]$C\,4/a\,m\,d$ ($\mathbf{a}'=2\mathbf{a},\mathbf{b}'=2\mathbf{b}$)($P\,4/n\,b\,m$); [2]$C\,4/m\,m\,d$ ($\mathbf{a}'=2\mathbf{a},\mathbf{b}'=2\mathbf{b}$)($P\,4/m\,b\,m$); [2]$C\,4/a\,m\,m$ ($\mathbf{a}'=2\mathbf{a},\mathbf{b}'=2\mathbf{b}$)($P\,4/n\,m\,m$); [2]$F\,4/m\,m\,m$ ($\mathbf{a}'=2\mathbf{a},\mathbf{b}'=2\mathbf{b},\mathbf{c}'=2\mathbf{c}$)($I\,4/m\,m\,m$); [2]$F\,4/m\,m\,c$ ($\mathbf{a}'=2\mathbf{a},\mathbf{b}'=2\mathbf{b},\mathbf{c}'=2\mathbf{c}$)($I\,4/m\,c\,m$)

Maximal isomorphic subgroups of lowest index

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

Minimal non-isomorphic supergroups

I [3]$P\,m\,\bar{3}\,m$

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 (5) $\bar{x},y,\bar{z}$ (9) $\bar{x},\bar{y},\bar{z}$ (13) $x,\bar{y},z$	(2) $\bar{x},\bar{y},z$ (6) $x,\bar{y},\bar{z}$ (10) $x,y,\bar{z}$ (14) $\bar{x},y,z$	(3) $\bar{y},x,z$ (7) $y,x,\bar{z}$ (11) $y,\bar{x},\bar{z}$ (15) $\bar{y},\bar{x},z$	(4) $y,\bar{x},z$ (8) $\bar{y},\bar{x},\bar{z}$ (12) $\bar{y},x,\bar{z}$ (16) y,x,z	no conditions
							Special:
8	t	$.m.$	$x,\frac{1}{2},z$ $\bar{x},\frac{1}{2},\bar{z}$	$\bar{x},\frac{1}{2},z$ $x,\frac{1}{2},\bar{z}$	$\frac{1}{2},x,z$ $\frac{1}{2},x,\bar{z}$	$\frac{1}{2},\bar{x},z$ $\frac{1}{2},\bar{x},\bar{z}$	no extra conditions
8	s	$.m.$	$x,0,z$ $\bar{x},0,\bar{z}$	$\bar{x},0,z$ $x,0,\bar{z}$	$0,x,z$ $0,x,\bar{z}$	$0,\bar{x},z$ $0,\bar{x},\bar{z}$	no extra conditions
8	r	$..m$	x,x,z $\bar{x},x,\bar{z}$	$\bar{x},\bar{x},z$ $x,\bar{x},\bar{z}$	$\bar{x},x,z$ $x,x,\bar{z}$	$x,\bar{x},z$ $\bar{x},\bar{x},\bar{z}$	no extra conditions
8	q	$m..$	$x,y,\frac{1}{2}$ $\bar{x},y,\frac{1}{2}$	$\bar{x},\bar{y},\frac{1}{2}$ $x,\bar{y},\frac{1}{2}$	$\bar{y},x,\frac{1}{2}$ $y,x,\frac{1}{2}$	$y,\bar{x},\frac{1}{2}$ $\bar{y},\bar{x},\frac{1}{2}$	no extra conditions
8	p	$m..$	$x,y,0$ $\bar{x},y,0$	$\bar{x},\bar{y},0$ $x,\bar{y},0$	$\bar{y},x,0$ $y,x,0$	$y,\bar{x},0$ $\bar{y},\bar{x},0$	no extra conditions
4	o	$m2m.$	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	no extra conditions
4	n	$m2m.$	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	no extra conditions
4	m	$m2m.$	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	no extra conditions
4	l	$m2m.$	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	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] $p\,4\,m\,m$
$\mathbf{a}'=\mathbf{a}$ $\mathbf{b}'=\mathbf{b}$
Origin at 0,0,z

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

Along [110] $p\,2\,m\,m$
$\mathbf{a}'=\frac{1}{2}(-\mathbf{a}+\mathbf{b})$ $\mathbf{b}'=\mathbf{c}$
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* ; *s*howing the symmetry elements (4-fold rotation axis, mirror planes)**
- **Crystal family: tetragonal**
- **Lattice type: P (primitive)**
- **Site symmetry of the highest-symmetry site: D_{4h}**
- **Asymmetric unit: 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

CONTINUED No. 123 $P4/mmm$

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 (5) $\bar{x},y,\bar{z}$ (9) $\bar{x},\bar{y},\bar{z}$ (13) $x,\bar{y},z$	(2) $\bar{x},\bar{y},z$ (6) $x,\bar{y},\bar{z}$ (10) $x,y,\bar{z}$ (14) $\bar{x},y,z$	(3) $\bar{y},x,z$ (7) $y,x,\bar{z}$ (11) $y,\bar{x},\bar{z}$ (15) $\bar{y},\bar{x},z$	(4) $y,\bar{x},z$ (8) $\bar{y},\bar{x},\bar{z}$ (12) $\bar{y},x,\bar{z}$ (16) y,x,z	no conditions
							Special:
8	*t*	$.m.$	$x,\frac{1}{2},z$ $\bar{x},\frac{1}{2},\bar{z}$	$\bar{x},\frac{1}{2},z$ $x,\frac{1}{2},\bar{z}$	$\frac{1}{2},x,z$ $\frac{1}{2},x,\bar{z}$	$\frac{1}{2},\bar{x},z$ $\frac{1}{2},\bar{x},\bar{z}$	no extra conditions
8	*s*	$.m.$	$x,0,z$ $\bar{x},0,\bar{z}$	$\bar{x},0,z$ $x,0,\bar{z}$	$0,x,z$ $0,x,\bar{z}$	$0,\bar{x},z$ $0,\bar{x},\bar{z}$	no extra conditions
8	*r*	$..m$	x,x,z $\bar{x},x,\bar{z}$	$\bar{x},\bar{x},z$ $x,\bar{x},\bar{z}$	$\bar{x},x,z$ $x,x,\bar{z}$	$x,\bar{x},z$ $\bar{x},\bar{x},\bar{z}$	no extra conditions
8	*q*	$m..$	$x,y,\frac{1}{2}$ $\bar{x},y,\frac{1}{2}$	$\bar{x},\bar{y},\frac{1}{2}$ $x,\bar{y},\frac{1}{2}$	$\bar{y},x,\frac{1}{2}$ $y,x,\frac{1}{2}$	$y,\bar{x},\frac{1}{2}$ $\bar{y},\bar{x},\frac{1}{2}$	no extra conditions
8	*p*	$m..$	$x,y,0$ $\bar{x},y,0$	$\bar{x},\bar{y},0$ $x,\bar{y},0$	$\bar{y},x,0$ $y,x,0$	$y,\bar{x},0$ $\bar{y},\bar{x},0$	no extra conditions
4	*o*	$m2m.$	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	no extra conditions
4	*n*	$m2m.$	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	no extra conditions
4	*m*	$m2m.$	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	no extra conditions
4	*l*	$m2m.$	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	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] $p4mm$
$\mathbf{a}'=\mathbf{a}$ $\mathbf{b}'=\mathbf{b}$
Origin at $0,0,z$

Along [100] $p2mm$
$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}$
Origin at $x,0,0$

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

(*Continued on preceding page*)

EXAMPLE: Potassium tetrachloroplatinate(II): K_2PtCl_4

Space group: *P4/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)

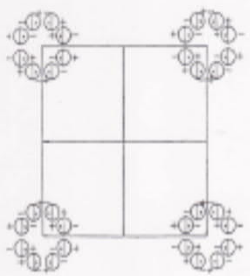
(d) Calculate the distances: Pt-Pt, Pt-K, Pt-Cl.

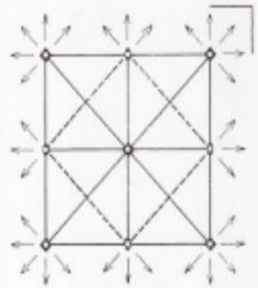
(e) What is the coordination number of platinum ?

(f) What is the site symmetry of platinum ?

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

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





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

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

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

Maximal isomorphic subgroups of lowest index

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

Minimal non-isomorphic supergroups

I $[3]P\,m\,\bar{3}\,m$

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

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

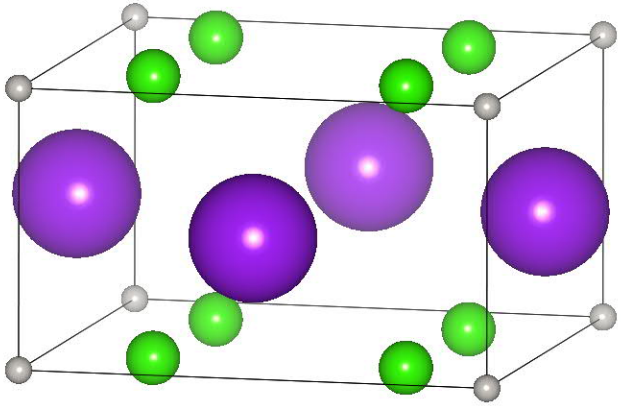
Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
16	u	1	(1) x,y,z (5) $\bar{x},y,\bar{z}$ (9) $\bar{x},\bar{y},\bar{z}$ (13) $x,\bar{y},z$	(2) $\bar{x},\bar{y},z$ (6) $x,\bar{y},\bar{z}$ (10) $x,y,\bar{z}$ (14) $\bar{x},y,z$	(3) $\bar{y},x,z$ (7) $y,x,\bar{z}$ (11) $y,\bar{x},\bar{z}$ (15) $\bar{y},\bar{x},z$	(4) $y,\bar{x},z$ (8) $\bar{y},\bar{x},\bar{z}$ (12) $\bar{y},x,\bar{z}$ (16) y,x,z	no conditions
							Special:
8	t	$.\,m\,.$	$x,\tfrac12,z$ $\bar{x},\tfrac12,\bar{z}$	$\bar{x},\tfrac12,z$ $x,\tfrac12,\bar{z}$	$\tfrac12,x,z$ $\tfrac12,x,\bar{z}$	$\tfrac12,\bar{x},z$ $\tfrac12,\bar{x},\bar{z}$	no extra conditions
8	s	$.\,m\,.$	$x,0,z$ $\bar{x},0,\bar{z}$	$\bar{x},0,z$ $x,0,\bar{z}$	$0,x,z$ $0,x,\bar{z}$	$0,\bar{x},z$ $0,\bar{x},\bar{z}$	no extra conditions
8	r	$.\,.\,m$	x,x,z $\bar{x},x,\bar{z}$	$\bar{x},\bar{x},z$ $x,\bar{x},\bar{z}$	$\bar{x},x,z$ $x,x,\bar{z}$	$x,\bar{x},z$ $\bar{x},\bar{x},\bar{z}$	no extra conditions
8	q	$m\,.\,.$	$x,y,\tfrac12$ $\bar{x},y,\tfrac12$	$\bar{x},\bar{y},\tfrac12$ $x,\bar{y},\tfrac12$	$\bar{y},x,\tfrac12$ $y,x,\tfrac12$	$y,\bar{x},\tfrac12$ $\bar{y},\bar{x},\tfrac12$	no extra conditions
8	p	$m\,.\,.$	$x,y,0$ $\bar{x},y,0$	$\bar{x},\bar{y},0$ $x,\bar{y},0$	$\bar{y},x,0$ $y,x,0$	$y,\bar{x},0$ $\bar{y},\bar{x},0$	no extra conditions
4	o	$m\,2\,m\,.$	$x,\tfrac12,\tfrac12$	$\bar{x},\tfrac12,\tfrac12$	$\tfrac12,x,\tfrac12$	$\tfrac12,\bar{x},\tfrac12$	no extra conditions
4	n	$m\,2\,m\,.$	$x,\tfrac12,0$	$\bar{x},\tfrac12,0$	$\tfrac12,x,0$	$\tfrac12,\bar{x},0$	no extra conditions
4	m	$m\,2\,m\,.$	$x,0,\tfrac12$	$\bar{x},0,\tfrac12$	$0,x,\tfrac12$	$0,\bar{x},\tfrac12$	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	$m\,.\,2\,m$	$x,x,\tfrac12$	$\bar{x},\bar{x},\tfrac12$	$\bar{x},x,\tfrac12$	$x,\bar{x},\tfrac12$	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	$2\,m\,m\,.$	$0,\tfrac12,z$	$\tfrac12,0,z$	$0,\tfrac12,\bar{z}$	$\tfrac12,0,\bar{z}$	$hkl: h+k=2n$
2	h	$4\,m\,m$	$\tfrac12,\tfrac12,z$	$\tfrac12,\tfrac12,\bar{z}$			no extra conditions
2	g	$4\,m\,m$	$0,0,z$	$0,0,\bar{z}$			no extra conditions
2	f	$m\,m\,m\,.$	$0,\tfrac12,0$	$\tfrac12,0,0$			$hkl: h+k=2n$
2	e	$m\,m\,m\,.$	$0,\tfrac12,\tfrac12$	$\tfrac12,0,\tfrac12$			$hkl: h+k=2n$
1	d	$4/m\,m\,m$	$\tfrac12,\tfrac12,\tfrac12$				no extra conditions
1	c	$4/m\,m\,m$	$\tfrac12,\tfrac12,0$				no extra conditions
1	b	$4/m\,m\,m$	$0,0,\tfrac12$				no extra conditions
1	a	$4/m\,m\,m$	$0,0,0$				no extra conditions

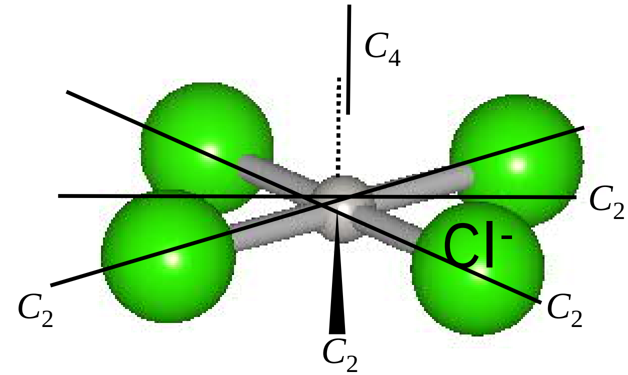
Symmetry of special projections

Along [001] $\ p\,4\,m\,m$	Along [100] $\ p\,2\,m\,m$	Along [110] $\ p\,2\,m\,m$
$\mathbf{a}'=\mathbf{a}\quad \mathbf{b}'=\mathbf{b}$	$\mathbf{a}'=\mathbf{b}\quad \mathbf{b}'=\mathbf{c}$	$\mathbf{a}'=\tfrac12(-\mathbf{a}+\mathbf{b})\quad \mathbf{b}'=\mathbf{c}$
Origin at $0,0,z$	Origin at $x,0,0$	Origin at $x,x,0$

(*Continued on preceding page*)

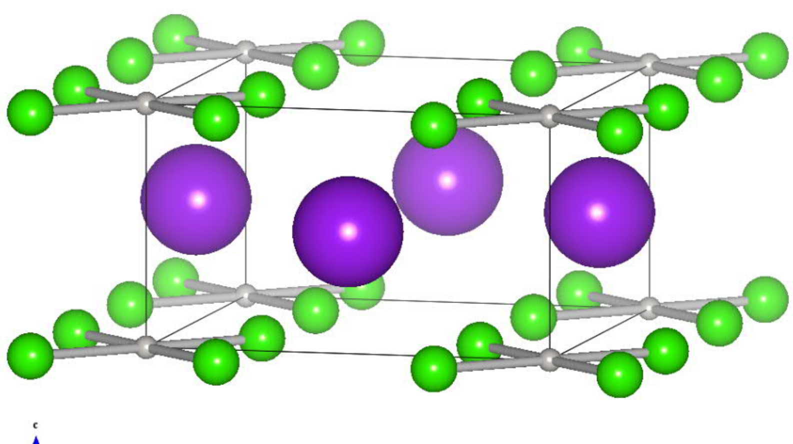


Pt: 1 atom in unit cell
K: 2 atoms in unit cell
Cl: 4 atoms in unit cell

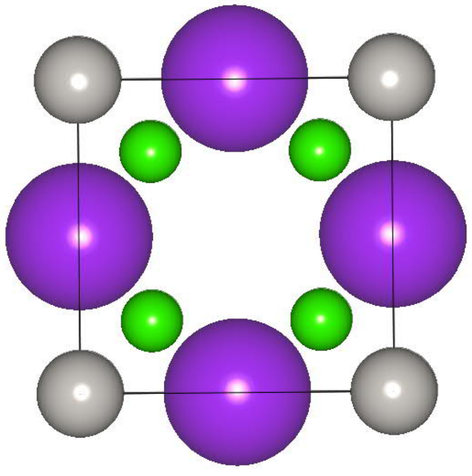


Site symmetry of Pt: D_{4h}

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



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



K_2PtCl_4

- ρ = 3.37 x 10^6 g/m^3
- V = 7.023 Å x 7.023 Å x 4.1486 Å = 204.62 x 10^{-30} m^3
- M = (2 x 39.098 + 195.22 + 4 x 35.453) g/mol = 415.228 g/mol
- Z = (V x ρ x 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
- PI site symmetry: D_{4h}

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**

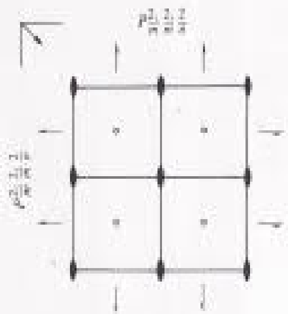
(c) Calculate BVS for chromium.

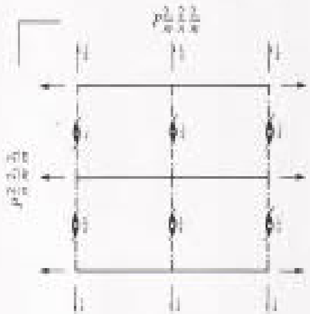
[R^0 values: Cr^{III}-O^{-II}: 1.724, Cr^{III}-Cl^{-I}: 2.08]

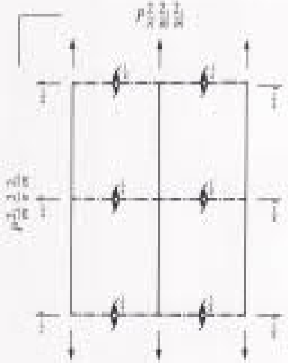
$Pmmn$ D_{2h}^{13} mmm Orthorhombic

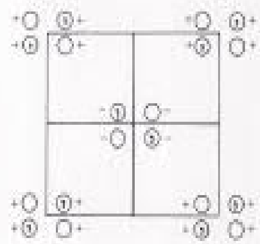
No. 59 $P\,2_1/m\,2_1/m\,2/n$ Patterson symmetry $Pmmm$

ORIGIN CHOICE 1









Origin at $mm2/n$, at $\frac{1}{4},\frac{1}{4},0$ from $\bar{1}$

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 $0,0,z$	(3) $2(0,\frac{1}{2},0)$ $\frac{1}{4},y,0$	(4) $2(\frac{1}{2},0,0)$ $x,\frac{1}{4},0$
(5) $\bar{1}$ $\frac{1}{4},\frac{1}{4},0$	(6) $n(\frac{1}{2},\frac{1}{2},0)$ $x,y,0$	(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
					General:
8 g 1	(1) x,y,z (5) $\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$	(2) $\bar{x},\bar{y},z$ (6) $x+\frac{1}{2},y+\frac{1}{2},\bar{z}$	(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) $\bar{x},y,z$	$hk0$: $h+k=2n$ $h00$: $h=2n$ $0k0$: $k=2n$
					Special: as above, plus
4 f $.m.$	$x,0,z$	$\bar{x},0,z$	$\bar{x}+\frac{1}{2},\frac{1}{2},\bar{z}$	$x+\frac{1}{2},\frac{1}{2},\bar{z}$	no extra conditions
4 e $m..$	$0,y,z$	$0,\bar{y},z$	$\frac{1}{2},y+\frac{1}{2},\bar{z}$	$\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$	no extra conditions
4 d $\bar{1}$	$\frac{1}{4},\frac{1}{4},\frac{1}{2}$	$\frac{3}{4},\frac{3}{4},\frac{1}{2}$	$\frac{3}{4},\frac{1}{4},\frac{1}{2}$	$\frac{1}{4},\frac{3}{4},\frac{1}{2}$	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 $mm2$	$0,\frac{1}{2},z$	$\frac{1}{2},0,\bar{z}$			no extra conditions
2 a $mm2$	$0,0,z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			no extra conditions

Symmetry of special projections

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

Along [100] $p2mg$
$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}$
Origin at $x,\frac{1}{4},0$

Along [010] $p2gm$
$\mathbf{a}'=\mathbf{c}$ $\mathbf{b}'=\mathbf{a}$
Origin at $\frac{1}{4},y,0$

Maximal non-isomorphic subgroups

I [2]$P2_12_12$ 1; 2; 3; 4
[2]$P112/n$ ($P2/c$) 1; 2; 5; 6
[2]$P12_1/m1$ ($P2_1/m$) 1; 3; 5; 7
[2]$P2_1/m11$ ($P2_1/m$) 1; 4; 5; 8
[2]$Pmm2$ 1; 2; 7; 8
[2]$Pm2_1n$ ($Pmn2_1$) 1; 3; 6; 8
[2]$P2_1mn$ ($Pmn2_1$) 1; 4; 6; 7

IIa none

IIb [2]$Pcmn$ ($\mathbf{c}'=2\mathbf{c}$)($Pnma$); [2]$Pmcn$ ($\mathbf{c}'=2\mathbf{c}$)($Pnma$); [2]$Pccn$ ($\mathbf{c}'=2\mathbf{c}$)

Maximal isomorphic subgroups of lowest index

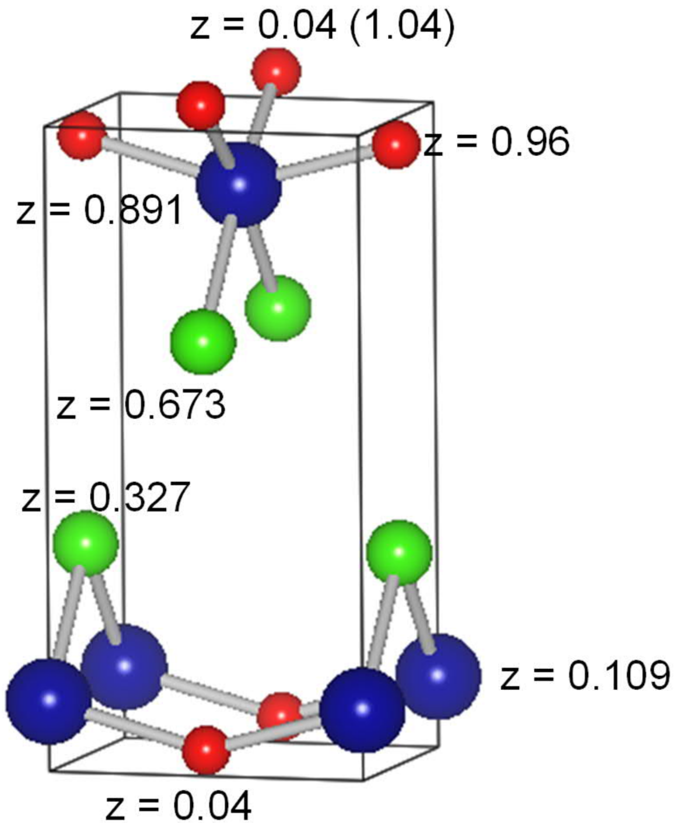
IIc [3]$Pmmn$ ($\mathbf{a}'=3\mathbf{a}$ or $\mathbf{b}'=3\mathbf{b}$); [2]$Pmmn$ ($\mathbf{c}'=2\mathbf{c}$)

Minimal non-isomorphic supergroups

I [2]$P4/nmm$; [2]$P4_2/nmc$

II [2]$Amma$ ($Cmcm$); [2]$Bmmb$ ($Cmcm$); [2]$Cmmm$; [2]$Immm$; [2]$Pmmb$ ($2\mathbf{a}'=\mathbf{a}$)($Pmma$); [2]$Pmma$ ($2\mathbf{b}'=\mathbf{b}$)

CrOCl



Chromium bonding

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

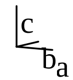
2 x Cr-O: $\sqrt{\{(0.960-0.891) \times 7.72\ \text{Å}\}^2 + \{0.5 \times 3.88\ \text{Å}\}^2} = 2.0118\ \text{Å}$

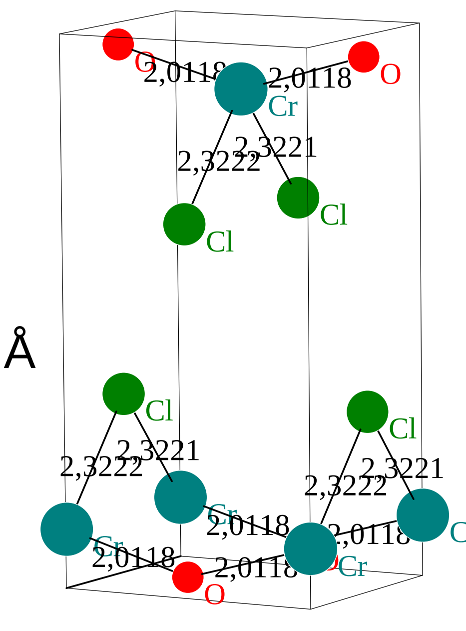
2 x Cr-O: $\sqrt{\{[(1-0.891)+0.04] \times 7.72\ \text{Å}\}^2 + \{0.5 \times 3.20\ \text{Å}\}^2} = 1.9706\ \text{Å}$

CN(Cr) = 6

Cr site symmetry: C_{2v}

BVS(Cr): +2.985





CrOCl: simulated XRD pattern based on the structure data