# SCHEDULE

| | Date | | Topic |
|---|---|---|---|
| 1. | Tue | 14.09. | Lec-1: Introduction |
| 2. | Fri | 17.09. | Lec-2: Crystal Chemistry & Tolerance parameter |
| 3. | Fri | 17.09. | EXERCISE 1 |
| 4. | Tue | 21.09. | Lec-3: Crystal chemistry & BVS |
| 5. | Fri | 24.09. | Lec-4: Symmetry & Point Groups |
| 6. | Fri | 24.09. | EXERCISE 2 |
| 7. | Tue | 28.10. | Lec-5: Crystallography & Space Groups |
| 8. | Fri | 01.10. | Lec-6: XRD & Reciprocal lattice |
| 9. | Fri | 01.10. | EXERCISE 3 |
| 10. | Tue | 05.10. | Lec-7: ND & GI-XRD |
| 11. | Fri | 08.10. | Lec-8: Rietveld |
| 12. | Fri | 08.10 | EXERCISE 4: Rietveld |
| 13. | Tue | 12.10. | Lec-9: Synchrotron rad. & XAS & RIXS |
| 14. | Fri | 15.10. | Lec-10: EXAFS & Mössbauer |
| 15. | Fri | 15.10. | EXERCISE 5 |
| 16. | Tue | 19.10. | Seminars: XPS, FTIR, Raman, ED, HRTEM, SEM, AFM |
| 17. | Fri | 22.10. | Lec-11: XRR |
| 18. | Fri | 22.10. | EXERCISE 6: XRR |

**EXAM: Friday, Oct. 29th, 2021**

# 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** $\sigma$ **/** ***m***

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

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

# FROM MOLECULES TO CRYSTALS

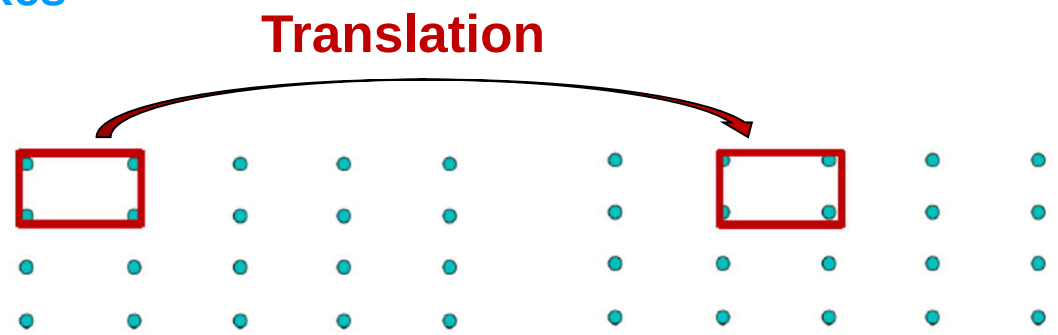
**There are two things which make macroscopic (infinite) crystals different from discrete molecules in terms of symmetry: Space-filling & Translation**

## Space-filling

- **Macroscopic crystals need to continuosly fill the space**
- **For molecules 5-fold rotation is possible, but not for crystals (except in quasicrystals)**

## 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**



## Additional translation symmetry elements in INFINITE LATTICES

### Translation

- Movement from one point to another point

### Screw axis

- Rotation plus translation

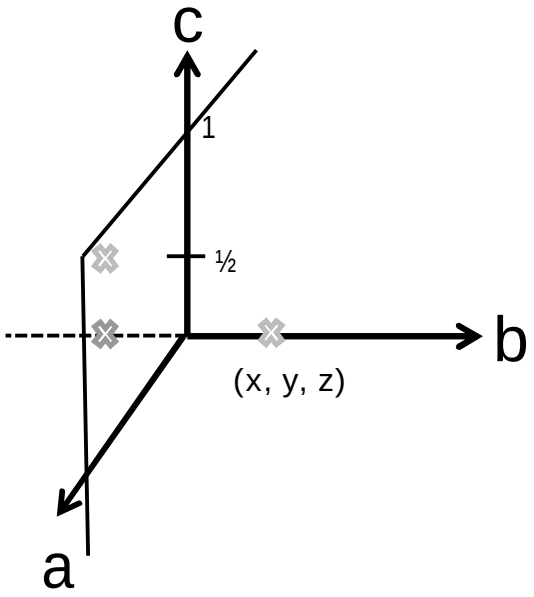
$n_m$ ($2_1$, $3_1$, $3_2$, $4_1$, $4_2$, $4_3$, $6_1$, $6_2$, $6_3$, $6_4$, $6_5$)
For example: $2_1$: rotation 180$^o$ and translation ½(*m*/*n*)

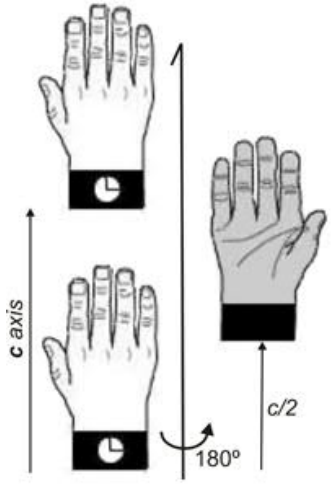
### Glide plane

- 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)

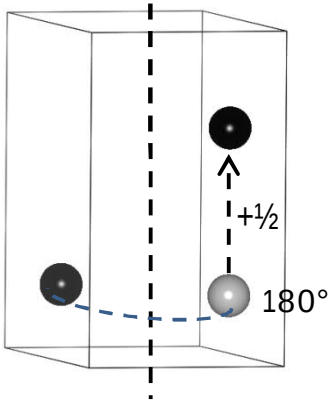


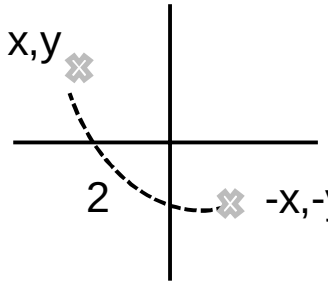

**Rotation (c) followed by translation (t)**

## SCREW AXIS

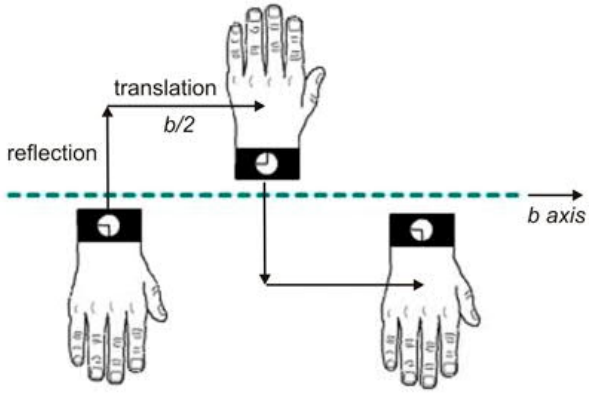
$2_1 \parallel c$

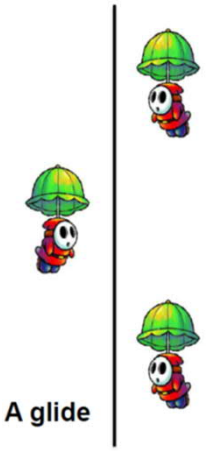



x,y,z -> -x, -y, z+½




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



(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**

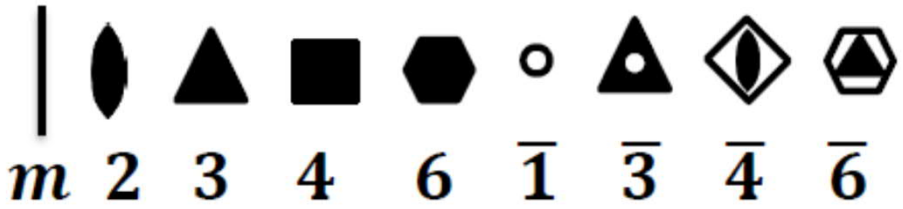



**Table 1.1** Symmetry elements of crystal point groups.

| 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 |
| | $C_S = C_{1h} = C_{1v}$ | $m$ | $I, \sigma$ | 2 |
| | $C_{2h}$ | $2/m$ | $I, C_2, \sigma_h, i$ | 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 |

**WHAT WE LIKE TO KNOW ABOUT THE CRYSTAL STRUCTURE**

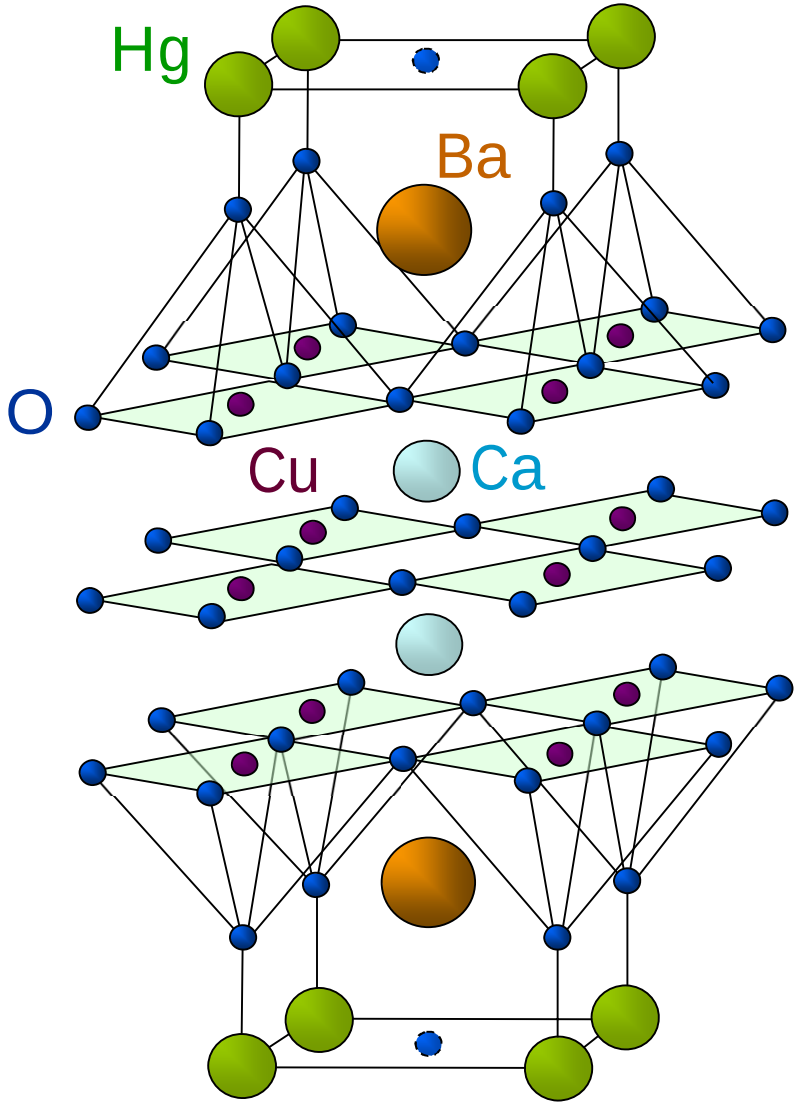
**CRYSTALLOGRAPHY**

- **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.**

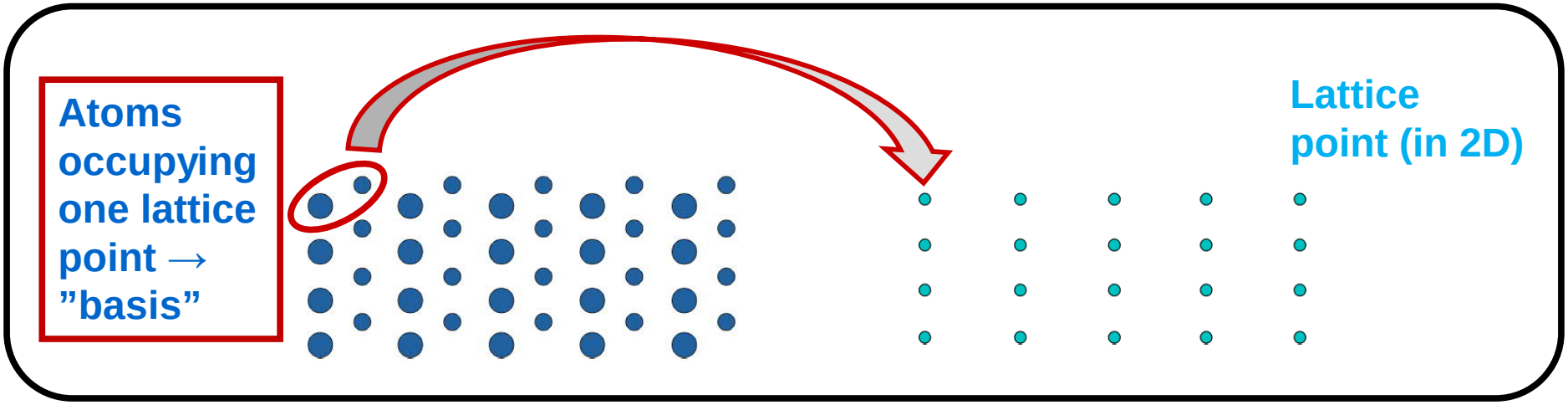
**Discussed in Lecture 2!**




$HgBa_2Ca_2Cu_3O_{9-\delta}$

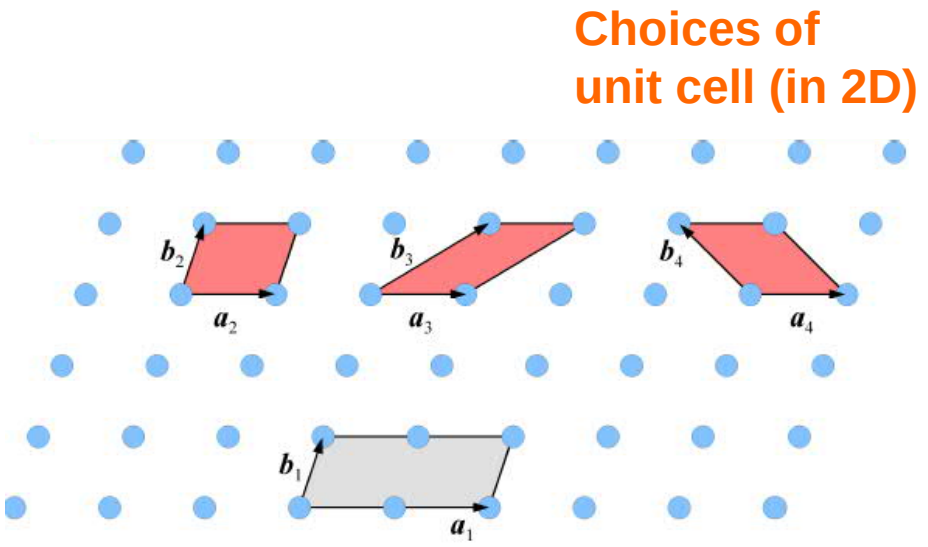
# CRYSTAL LATTICE

- **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)**

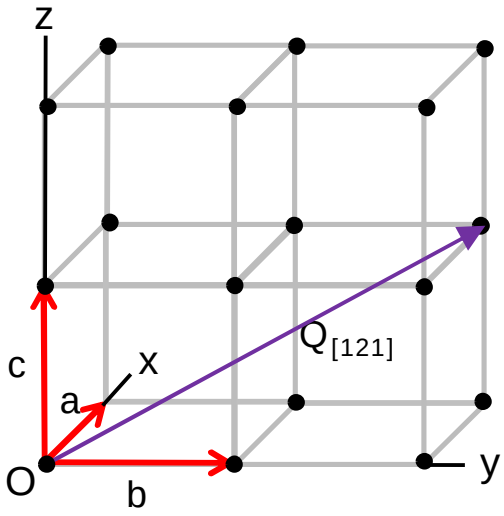



# UNIT CELL

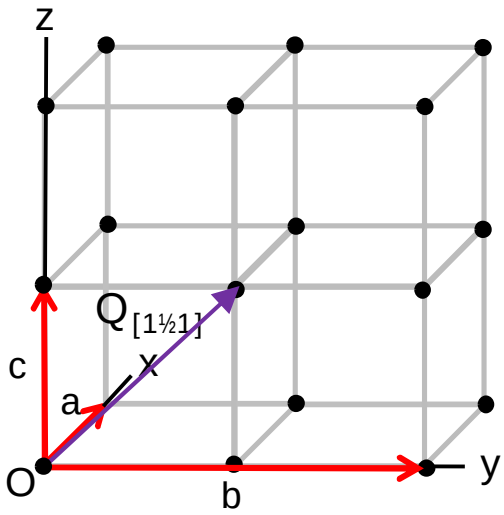
- Smallest possible microscopic 3D part of the crystal lattice that repeats itself periodically and completely fills the lattice volume, and is enough to describe the lattice perfectly
- Choice of the unit cell not always unambicious: several possible choices



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



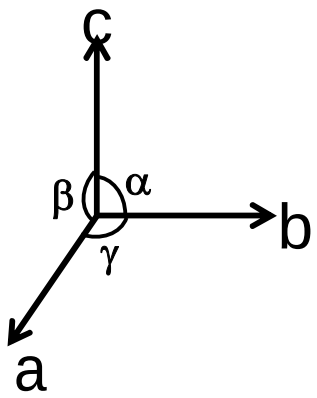

Unit cell: YES




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)

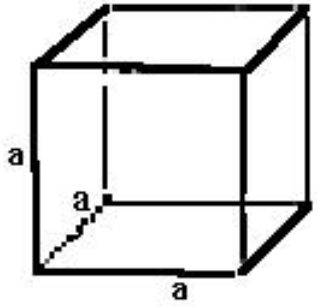
**CRYSTAL SYSTEM & SYMMETRY (most important in crystallography)**

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

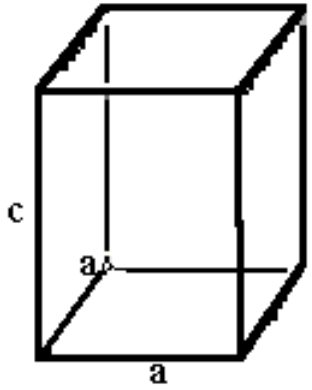
  There are an infinite number of **three-dimensional point groups**, but the crystallographic restriction results in there being only 32 crystallographic point groups.
- Considering also the translational symmetry operations in 3D
  → **230 space groups**

# CRYSTAL SYSTEMS (7)

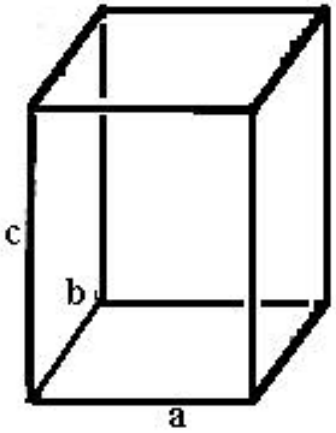
**No information of the positions of atoms**



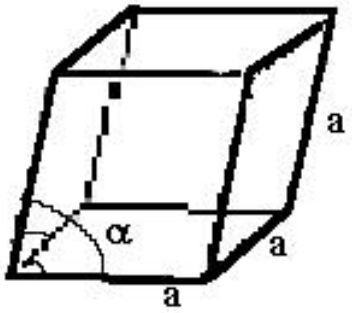

Cubic
a = b = c
α = β = γ = 90 °
NaCl, $MgAl_2O_4$



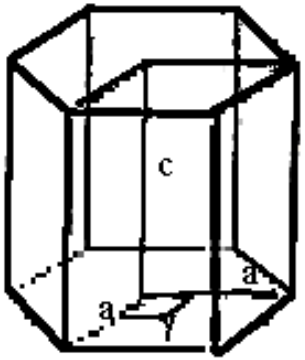

Tetragonal
a = b # c
α = β = γ = 90 °
$TiO_2$, $K_2NiF_4$



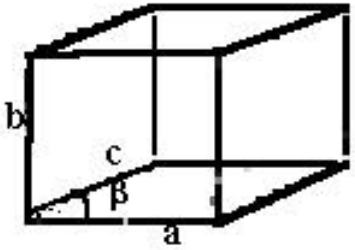

Orthorhombic
a # b # c
α = β = γ = 90 °
$YBa_2Cu_3O_7$



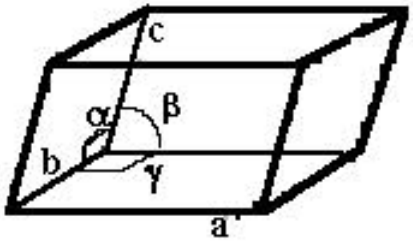

Rhombohedral
a = b = c
α = β = γ # 90 °
$BaTiO_3$ (low-T)




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




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

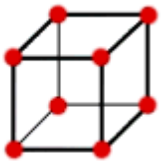



Triclinic
a # b # c
α # β # γ # 90 °

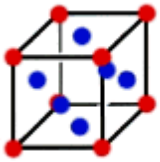
| Element | What it does | Possible in crystal system |
|---|---|---|
| Identity (1) | - | All |
| Inversion ($\bar{1}$) | Inversion | All |
| Mirror plane (m) | Mirror | All but triclinic |
| 2- fold rotation (2) | Rotate 180° | All but triclinic |
| 3-fold rotation (3) | Rotate 120° | Trigonal, Hexagonal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

# BRAVAIS LATTICES (14)

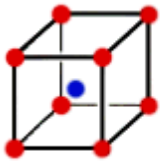
**Positions of lattice sites (not atoms) included**



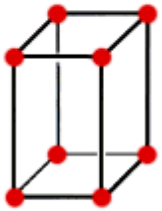
Simple cubic



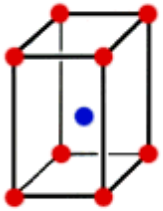
Face-centered cubic



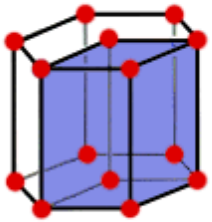
Body-centered cubic



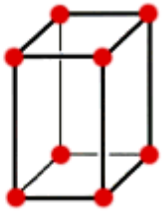
Simple tetragonal



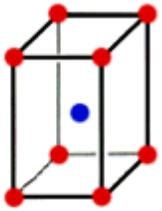
Body-centered tetragonal



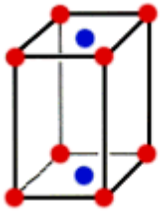
Hexagonal



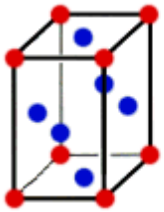
Simple orthorhombic



Body-centered orthorhombic

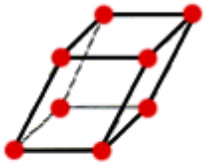


Base-centered orthorhombic

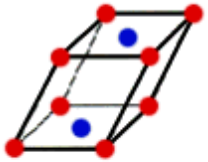


Face-centered orthorhombic

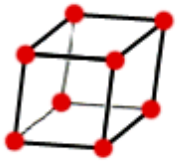
Rhombohedral



Simple Monoclinic



Base-centered monoclinic

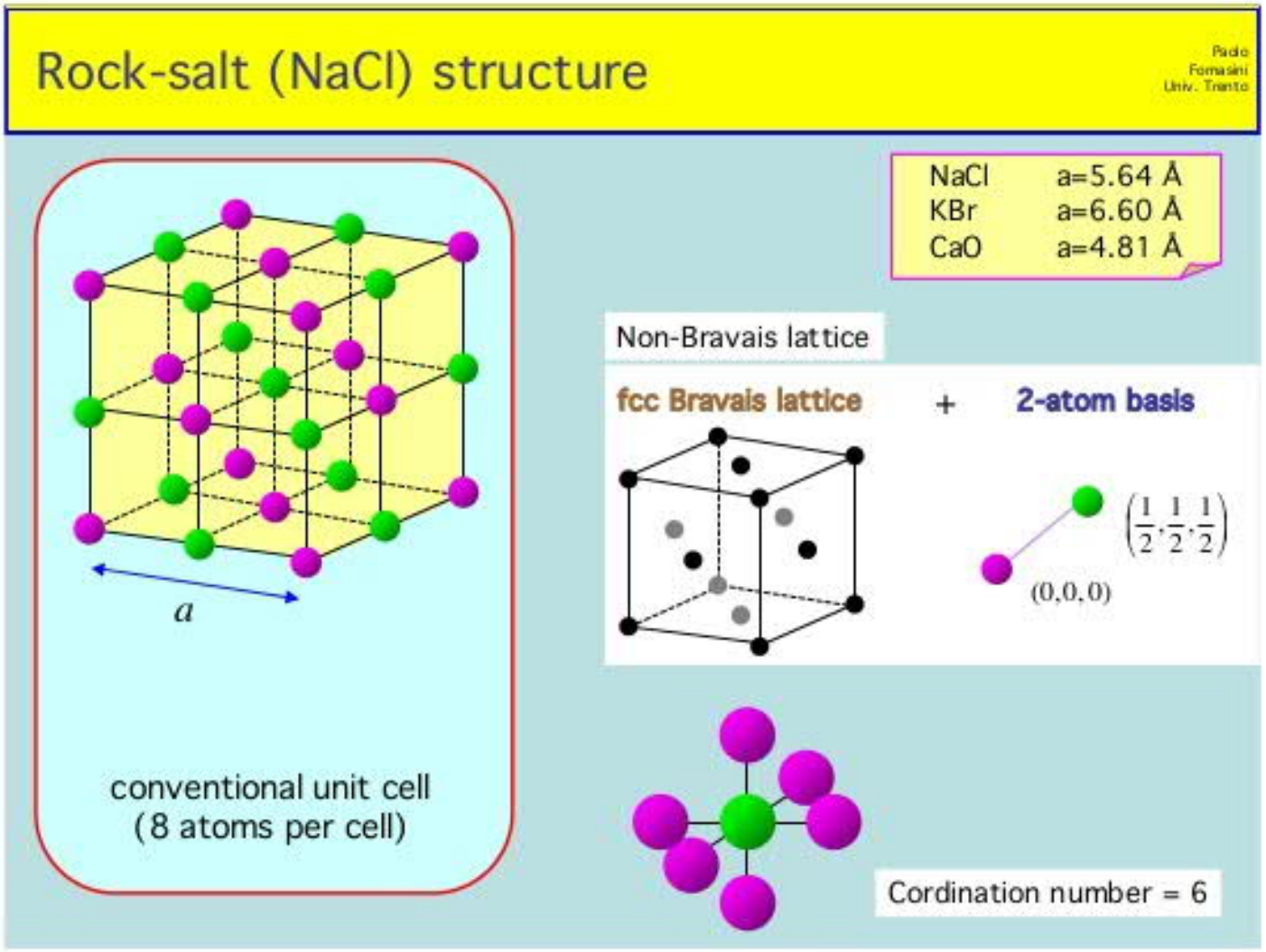


Triclinic

| 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 |

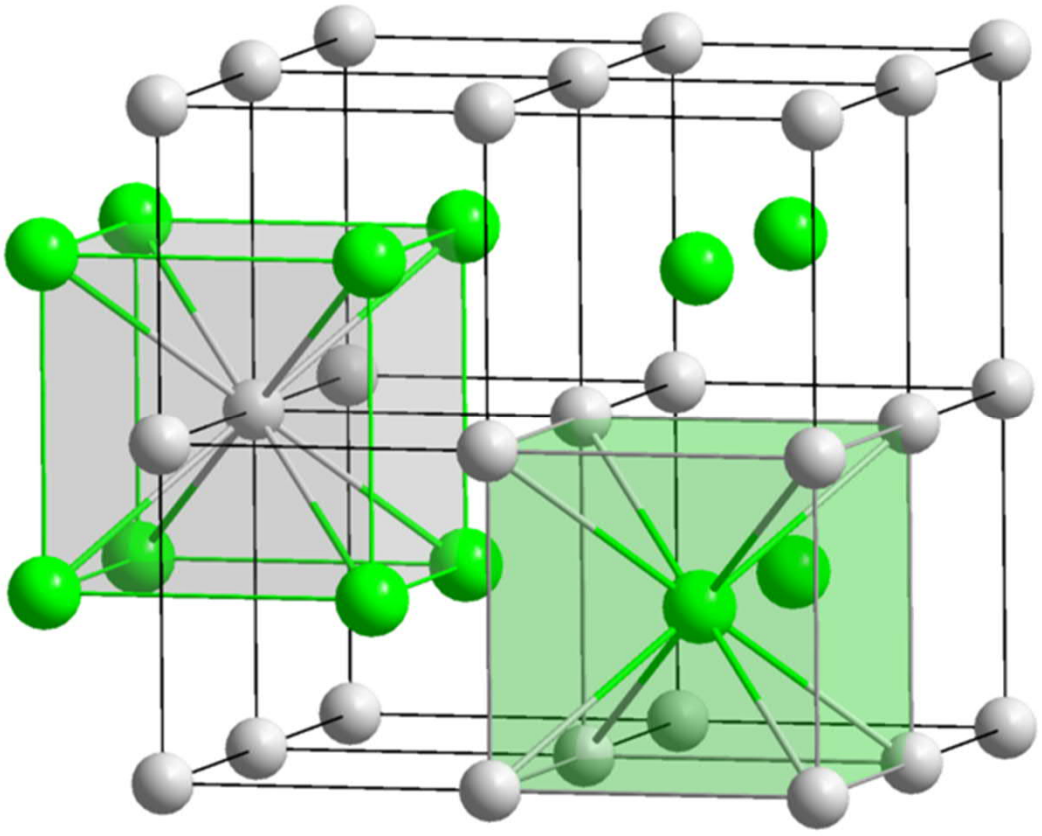
# EXAMPLE

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



# Your EXERCISE question

- **What is the Bravais lattice type of CsCl**



# 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 ($C_\sigma$) | 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 ($D_6$) | $m\bar{3}m$ ($O_h$) |

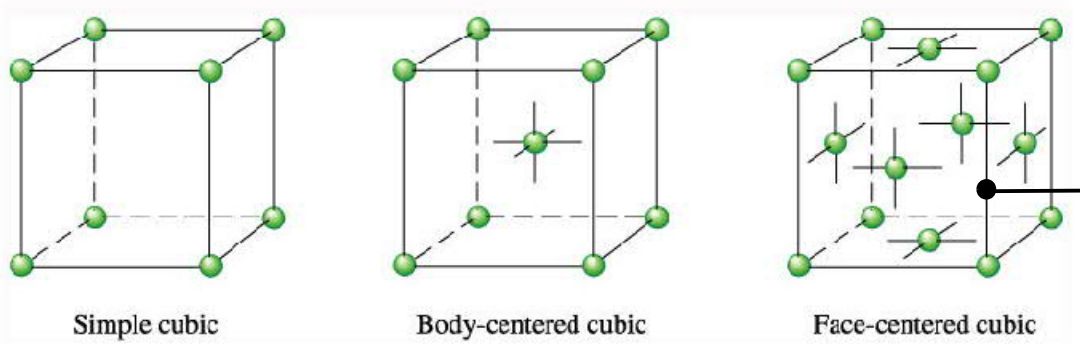
| Crystal System | # of Point Groups | # of Crystal Lattices |
|---|---|---|
| **Cubic** | **5** | **3** |
| **Tetragonal** | **7** | **2** |
| **Orthorhombic** | **3** | **4** |
| **Monoclinic** | **3** | **2** |
| **Triclinic** | **2** | **1** |
| **Hexagonal** | **7** | **1** |
| **Trigonal** | **5**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

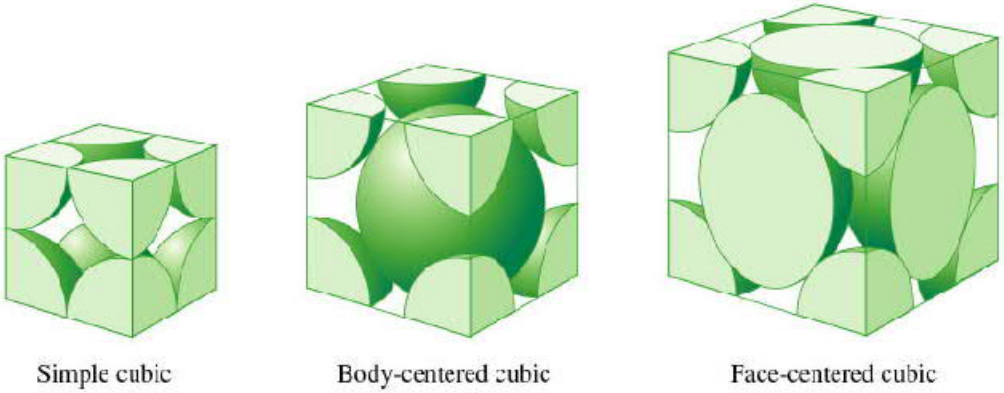
| System | Minimum Requirements |
|---|---|
| Cubic | Four 3-fold rotation axis |
| Tetragonal | One 4-fold rotation (or RI) axis |
| Orthorhombic | Three perpendicular 2-fold axis |
| Rhombohedral | One 3-fold rotation (or RI) axis |
| Hexagonal | One 6 fold rotation (or RI) axis |
| Monoclinic | One 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)

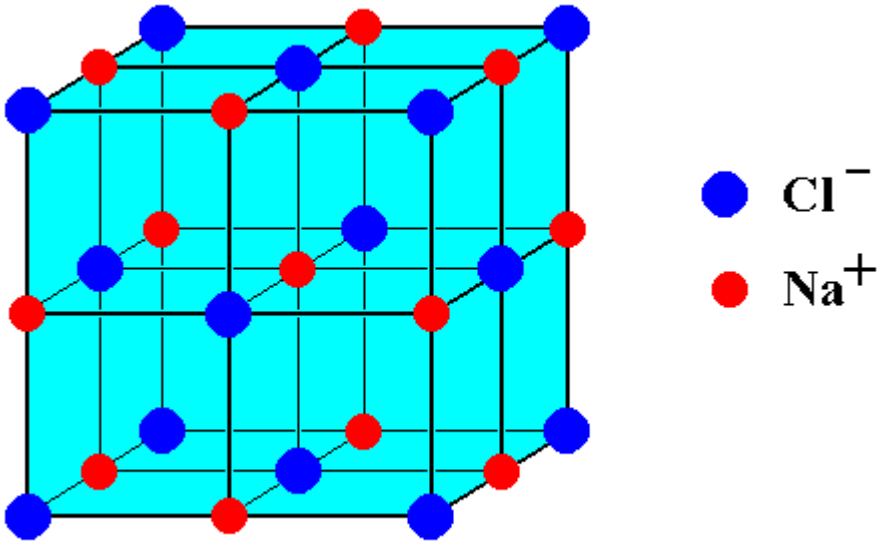
- typically 1 – 6, but can be tens or even hundreds
- atom inside unit cell: belongs only to one unit cell
- atom  on unit cell face: belongs to two unit cells
- atom on unit cell edge: belongs to four unit cells
- atom on unit cell corner: belongs to eight unit cells



# EXAMPLE

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



## Your EXERCISE question

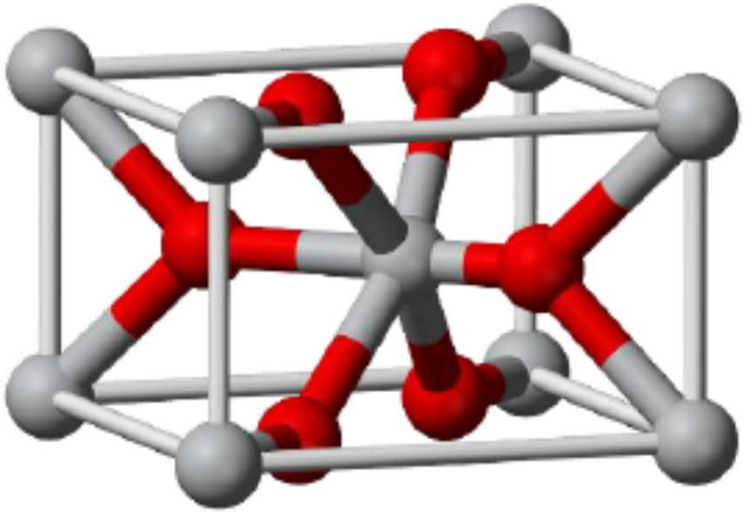
**White balls are Ti atoms, red balls are oxygen atoms.**

**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 ?**

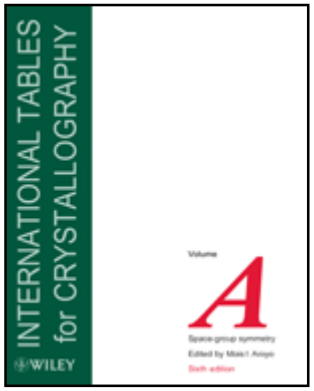
**(c) Please calculate the density.**



# 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. 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 $4_2$ / m 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 $6_1$ 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

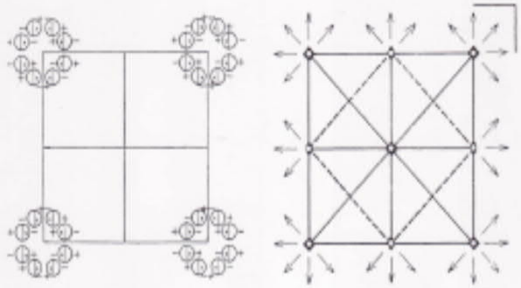
195. P 2 3 196. F 2 3 197. I 2 3 198. P $2_1$ 3 199. I $2_1$ 3
200. P m -3 201. P n -3 202. F m -3 203. F d -3 204. I m -3
205. P a -3 206. I a -3 207. P 4 3 2 208. P $4_2$ 3 2 209. F 4 3 2
210. F $4_1$ 3 2 211. I 4 3 2 212. P $4_3$ 3 2 213. P $4_1$ 3 2 214. I $4_1$ 3 2
215. P -4 3 m 216. F -4 3 m 217. 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

# $P\,4/m\,m\,m$ $D_{4h}^{1}$ $4/m\,m\,m$ 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 |
|---|---|---|---|---|---|
| 16 $u$ 1 | (1) $x,y,z$ | (2) $\bar{x},\bar{y},z$ | (3) $\bar{y},x,z$ | (4) $y,\bar{x},z$ | General: |
| | (5) $\bar{x},y,\bar{z}$ | (6) $x,\bar{y},\bar{z}$ | (7) $y,x,\bar{z}$ | (8) $\bar{y},\bar{x},\bar{z}$ | no conditions |
| | (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 |
| | $\bar{x},\frac{1}{2},\bar{z}$ | $x,\frac{1}{2},\bar{z}$ | $\frac{1}{2},\bar{x},\bar{z}$ | $\frac{1}{2},x,\bar{z}$ | |
| 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$m$$m$. | $0,\frac{1}{2},z$ | $\frac{1}{2},0,z$ | $0,\frac{1}{2},\bar{z}$ | $\frac{1}{2},0,\bar{z}$ | $hkl$ : $h+k=2n$ |
| 2 $h$ 4$m$$m$ | $\frac{1}{2},\frac{1}{2},z$ | $\frac{1}{2},\frac{1}{2},\bar{z}$ | | | no extra conditions |
| 2 $g$ 4$m$$m$ | $0,0,z$ | $0,0,\bar{z}$ | | | no extra conditions |
| 2 $f$ $m$$m$$m$. | $0,\frac{1}{2},0$ | $\frac{1}{2},0,0$ | | | $hkl$ : $h+k=2n$ |
| 2 $e$ $m$$m$$m$. | $0,\frac{1}{2},\frac{1}{2}$ | $\frac{1}{2},0,\frac{1}{2}$ | | | $hkl$ : $h+k=2n$ |
| 1 $d$ $4/m$$m$$m$ | $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ | | | | no extra conditions |
| 1 $c$ $4/m$$m$$m$ | $\frac{1}{2},\frac{1}{2},0$ | | | | no extra conditions |
| 1 $b$ $4/m$$m$$m$ | $0,0,\frac{1}{2}$ | | | | no extra conditions |
| 1 $a$ $4/m$$m$$m$ | $0,0,0$ | | | | 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: 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 |
|---|---|---|---|---|---|---|---|
| 16 | *u* | 1 | (1) $x,y,z$ | (2) $\bar{x},\bar{y},z$ | (3) $\bar{y},x,z$ | (4) $y,\bar{x},z$ | General: |
| | | | (5) $\bar{x},y,\bar{z}$ | (6) $x,\bar{y},\bar{z}$ | (7) $y,x,\bar{z}$ | (8) $\bar{y},\bar{x},\bar{z}$ | no conditions |
| | | | (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*m m*. | $0,\frac{1}{2},z$ | $\frac{1}{2},0,z$ | $0,\frac{1}{2},\bar{z}$ | $\frac{1}{2},0,\bar{z}$ | $hkl: h+k=2n$ |
| 2 | *h* | 4*m m* | $\frac{1}{2},\frac{1}{2},z$ | $\frac{1}{2},\frac{1}{2},\bar{z}$ | | | no extra conditions |
| 2 | *g* | 4*m m* | $0,0,z$ | $0,0,\bar{z}$ | | | no extra conditions |
| 2 | *f* | *m m m*. | $0,\frac{1}{2},0$ | $\frac{1}{2},0,0$ | | | $hkl: h+k=2n$ |
| 2 | *e* | *m m m*. | $0,\frac{1}{2},\frac{1}{2}$ | $\frac{1}{2},0,\frac{1}{2}$ | | | $hkl: h+k=2n$ |
| 1 | *d* | 4/*m m m* | $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ | | | | no extra conditions |
| 1 | *c* | 4/*m m m* | $\frac{1}{2},\frac{1}{2},0$ | | | | no extra conditions |
| 1 | *b* | 4/*m m m* | $0,0,\frac{1}{2}$ | | | | no extra conditions |
| 1 | *a* | 4/*m m m* | $0,0,0$ | | | | no extra conditions |

**Symmetry of special projections**

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

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

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

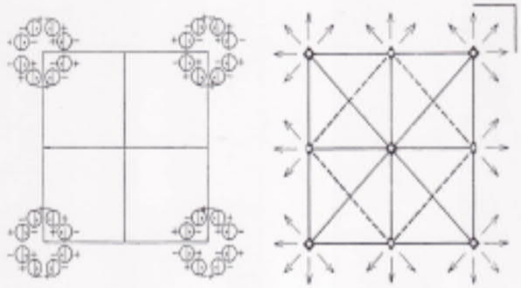
(d) Calculate the distances: Pt-Pt, Pt-K, Pt-Cl.

(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 |
|---|---|---|---|---|---|
| 16 $u$ 1 | (1) $x,y,z$ | (2) $\bar{x},\bar{y},z$ | (3) $\bar{y},x,z$ | (4) $y,\bar{x},z$ | General: |
| | (5) $\bar{x},y,\bar{z}$ | (6) $x,\bar{y},\bar{z}$ | (7) $y,x,\bar{z}$ | (8) $\bar{y},\bar{x},\bar{z}$ | no conditions |
| | (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 |
| | $\bar{x},\frac{1}{2},\bar{z}$ | $x,\frac{1}{2},\bar{z}$ | $\frac{1}{2},\bar{x},\bar{z}$ | $\frac{1}{2},x,\bar{z}$ | |
| 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$m$$m$. | $0,\frac{1}{2},z$ | $\frac{1}{2},0,z$ | $0,\frac{1}{2},\bar{z}$ | $\frac{1}{2},0,\bar{z}$ | $hkl$ : $h+k=2n$ |
| 2 $h$ 4$m$$m$ | $\frac{1}{2},\frac{1}{2},z$ | $\frac{1}{2},\frac{1}{2},\bar{z}$ | | | no extra conditions |
| 2 $g$ 4$m$$m$ | $0,0,z$ | $0,0,\bar{z}$ | | | no extra conditions |
| 2 $f$ $m$$m$$m$. | $0,\frac{1}{2},0$ | $\frac{1}{2},0,0$ | | | $hkl$ : $h+k=2n$ |
| 2 $e$ $m$$m$$m$. | $0,\frac{1}{2},\frac{1}{2}$ | $\frac{1}{2},0,\frac{1}{2}$ | | | $hkl$ : $h+k=2n$ |
| 1 $d$ $4/m$$m$$m$ | $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ | | | | no extra conditions |
| 1 $c$ $4/m$$m$$m$ | $\frac{1}{2},\frac{1}{2},0$ | | | | no extra conditions |
| 1 $b$ $4/m$$m$$m$ | $0,0,\frac{1}{2}$ | | | | no extra conditions |
| 1 $a$ $4/m$$m$$m$ | $0,0,0$ | | | | no extra conditions |

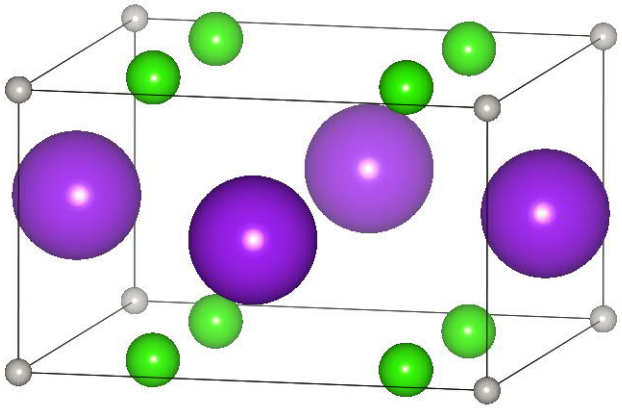
**Symmetry of special projections**

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

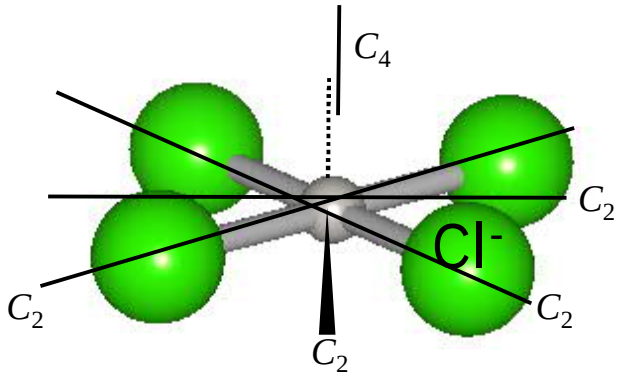
Along [100] $p\,2m\,m$
$a'=b$ $b'=c$
Origin at $x,0,0$

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

(*Continued on preceding page*)

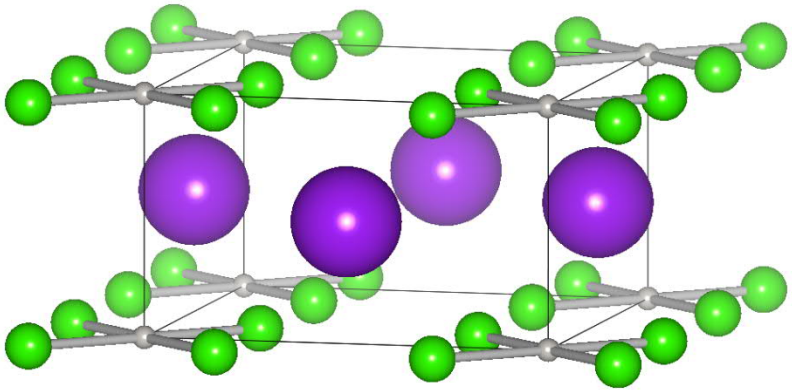


**Pt: 1 atom in unit cell**
**K: 2 atoms in unit cell**
**Cl: 4 atoms in unit cell**

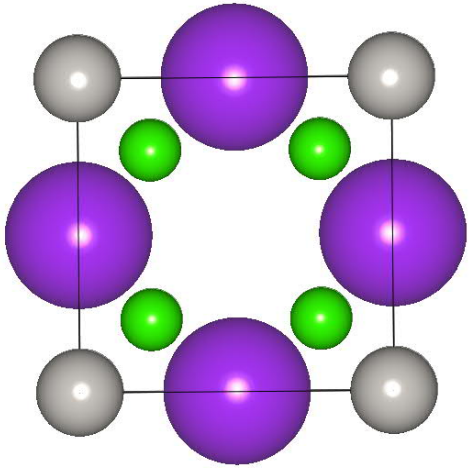



Site symmetry of Pt: $D_{4h}$

**Bond lengths:**
**Pt-Pt: $(1\text{-}0)^2 \cdot 4.15$Å**
**Pt-K: $\sqrt{[(0.5\text{-}0)^2 \cdot 7.023\text{Å} + (0.5\text{-}0)^2 \cdot 4.149\text{Å}]} = 4.08$Å**
**Pt-Cl: $\sqrt{[(0.232\text{-}0)^2 \cdot 7.023\text{Å} + (0.232\text{-}0)^2 \cdot 7.023\text{Å}]} = 2.30$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 = $204.62 \times 10^{-30}$ 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: $D_{4h}$

# 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** | ***2a*** | ***z* = 0.109** |
| | **Cl** | ***2b*** | ***z* = 0.327** |
| | **O** | ***2b*** | ***z* = 0.960** |

**(a) Draw the unit cell.**

**(b) Give for chromium:**
- **bond lengths**
- **coordination numbers**
- **site symmetry**

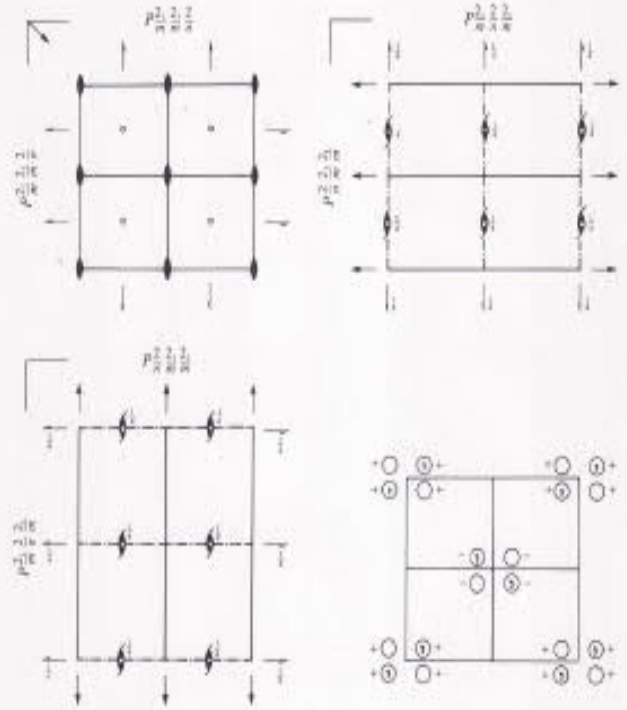
**(c) Calculate BVS for chromium.**

**[$R^0$ 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 $mm2/n$, at $\frac{1}{4},\frac{1}{4},0$ from $\bar{1}$

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

**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* | (2) $\bar{x},\bar{y},z$ | (3) $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$ | (4) $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z$ | General: |
| | (5) $\bar{x},\bar{y},\bar{z}$ | (6) $\frac{1}{2}+x,\frac{1}{2}+y,\bar{z}$ | (7) *x*,$\bar{y}$,*z* | (8) $\bar{x}$,*y*,$\bar{z}$ | *hk*0: $h+k=2n$<br>*h*00: $h=2n$<br>0*k*0: $k=2n$ |
| | | | | | Special: as above, plus |
| 4 *f* .*m*. | *x*,0,*z* | $\bar{x}$,0,*z* | $\frac{1}{2}+x,\frac{1}{2},\bar{z}$ | $\frac{1}{2}-x,\frac{1}{2},\bar{z}$ | no extra conditions |
| 4 *e* *m*.. | 0,*y*,*z* | 0,$\bar{y}$,*z* | $\frac{1}{2},\frac{1}{2}+y,\bar{z}$ | $\frac{1}{2},\frac{1}{2}-y,\bar{z}$ | 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,*z* | | | no extra conditions |
| 2 *a* *mm*2 | 0,0,*z* | $\frac{1}{2},\frac{1}{2},z$ | | | no extra conditions |

**Symmetry of special projections**

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

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

Along [010] *p* 2*g*m
$a'=c$ $b'=a$
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]$Pcmn$($c'=2c$)($Pnma$); [2]$Pmcn$($c'=2c$)($Pnma$); [2]$Pccn$($c'=2c$) | |

**Maximal isomorphic subgroups of lowest index**

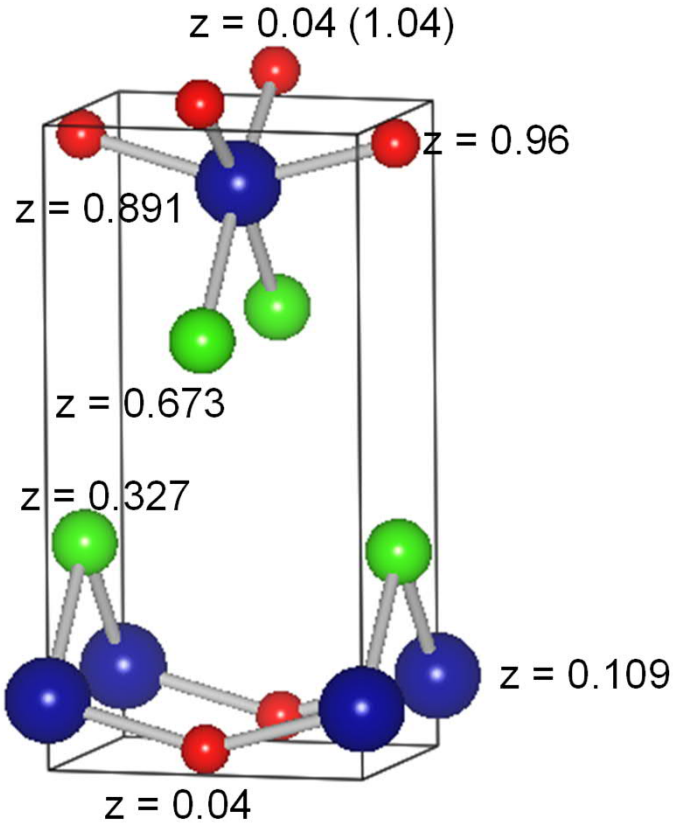
IIc [3]$Pmmn$($a'=3a$ or $b'=3b$); [2]$Pmmn$($c'=2c$)

**Minimal non-isomorphic supergroups**

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

II [2]$Ammm$($Cmcm$); [2]$Bmmb$($Cmcm$); [2]$Cmmm$; [2]$Immm$; [2]$Pmmb$($2a'=a$)($Pmma$); [2]$Pmma$($2b'=b$)

# CrOCl




## Chromium bonding

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

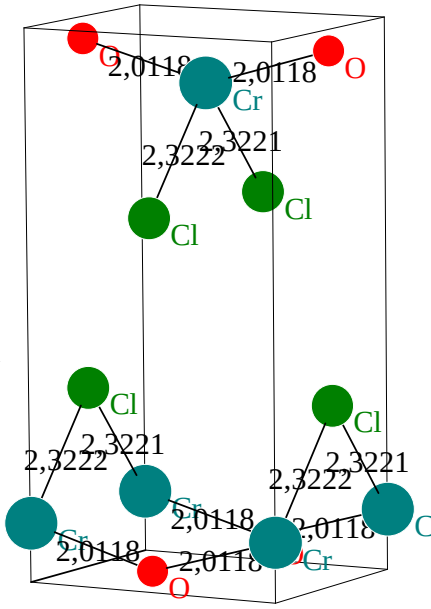
2 x Cr-O: $\sqrt{\{(0.960-0.891)\times 7.72\ \text{Å}\}^2 + \{0.5\times 3.88\ \text{Å}\}^2} = 2.0118\ \text{Å}$

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