Modern Crystallography

Topics:

20.11. **Crystalline state**
definition, interaction types in crystalline materials
lattice types, symmetry operations, reciprocal lattice

27.11. **X-ray diffraction (kinematic theory)**
Bragg equation, Laue equations, Ewald sphere, atomic form factor, structure factor, absorption

4.12 **experimental X-ray structure determination**
experimental methods, phase problem, phase retrieval methods, structure refinement

11.12 **modern applications of crystallography**
protein crystallography, powder diffraction,
time-resolved crystallography (pump and probe)

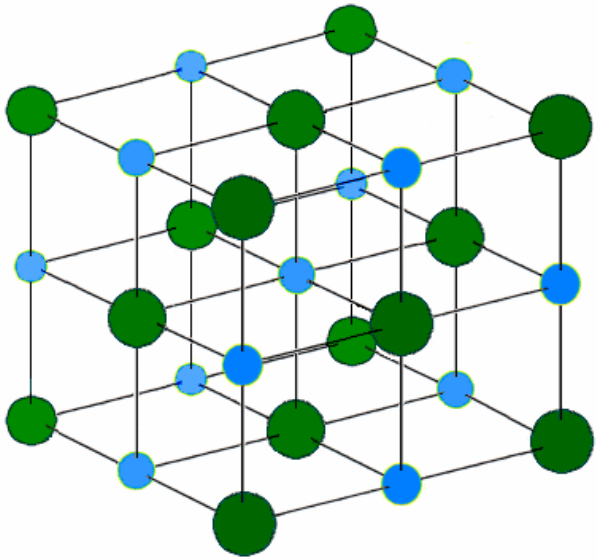
Recommended literature

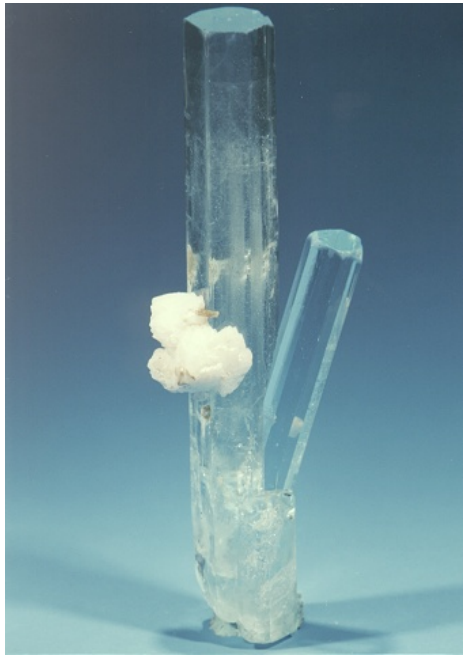
Michael M. Woolfson: An introduction to X-ray crystallography
(Cambridge University Press)

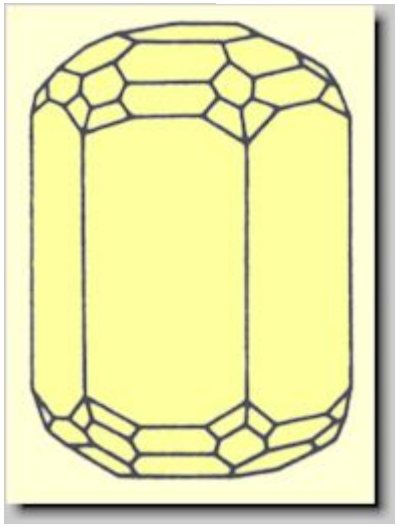
C. Ciaccovazzo: Fundamentals of Crystallography
(International Union of Crystallography)

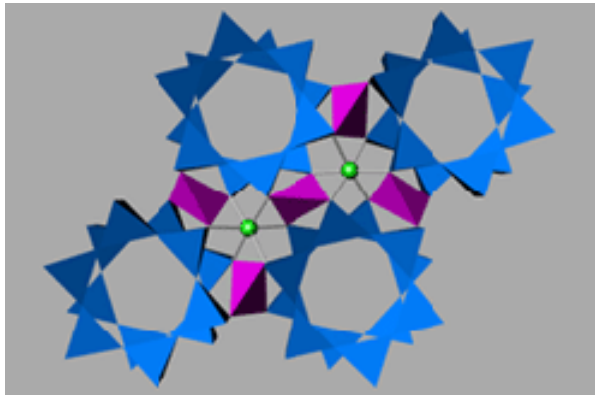
International Tables of Crystallography, Vol I
(International Union of Crystallography)

Relation between crystal habit, symmetry and structure



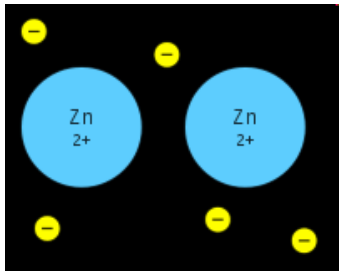




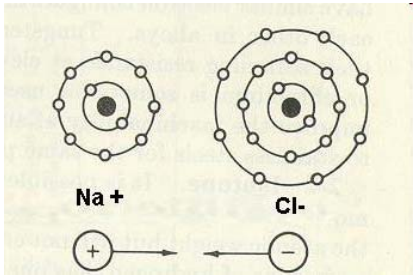


Chemical interaction forces in crystals

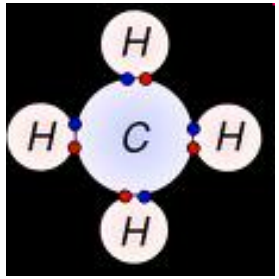
Metallic bond



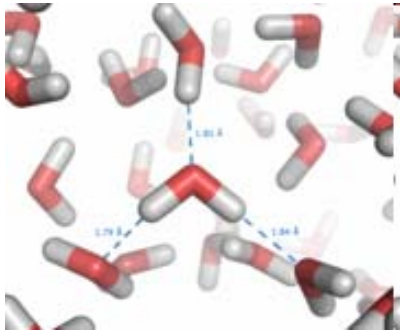
Ionic bond



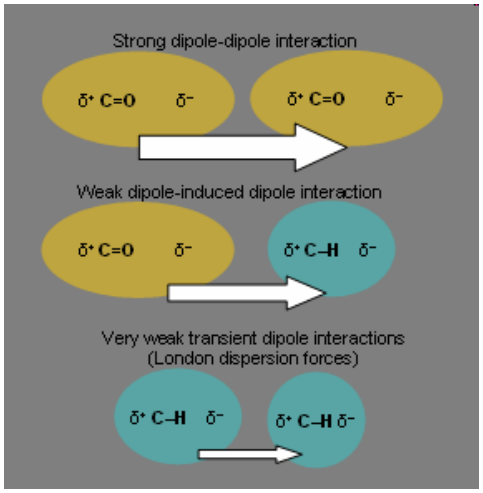
Covalent bond



Hydrogen bond

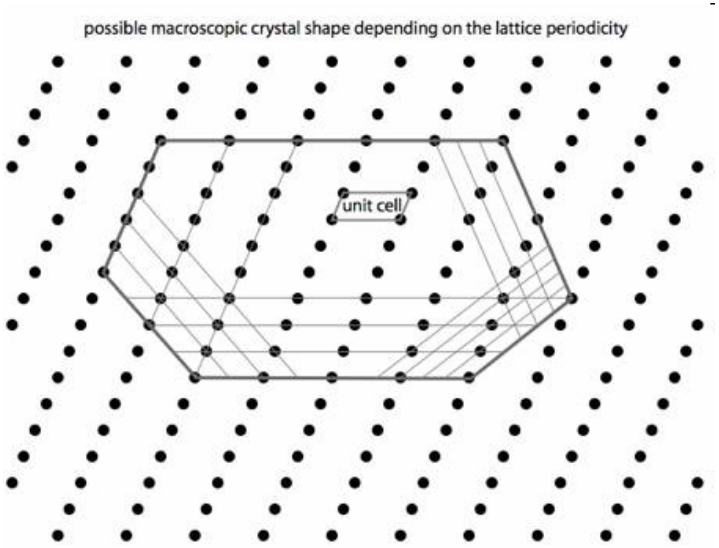


Van der Waals bond

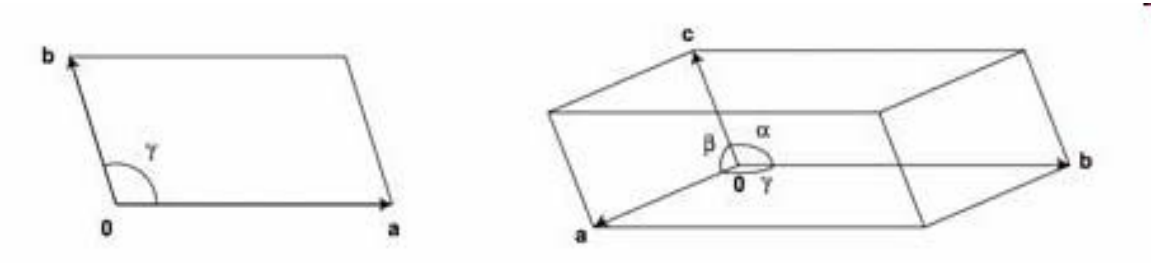


Definition of a crystal

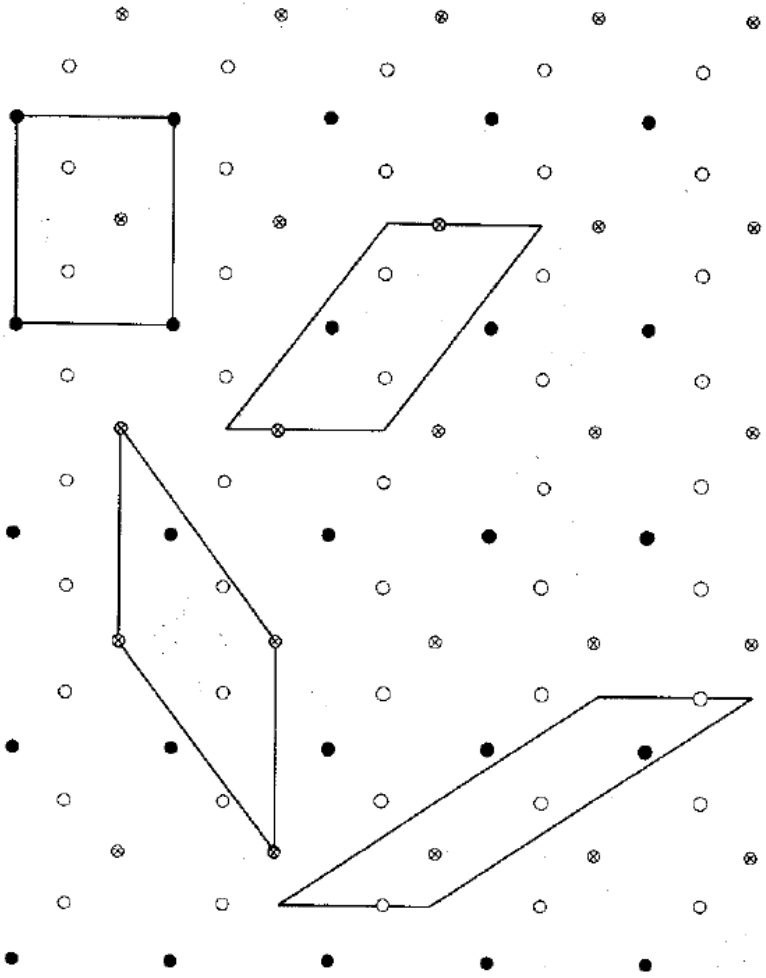
A crystal is made up of atoms, ions or molecules arranged in a regular and periodic fashion. The regular repetition in space is usually called a **periodic translation** and we shall specify the three independent directions of space by the translation vectors **a**, **b** and **c.**



The repeating unit in this three-dimensional structure is called "unit cell“, defined by the vectors **a**, **b**, and **c** and the angels **α**, **β**, and **γ.**

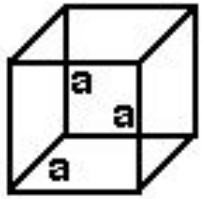


‘right’ unit cell choice

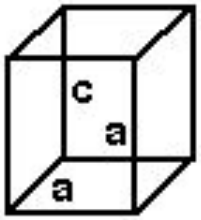


7 primitive crystal lattices

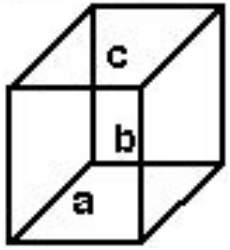
Cubic $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$



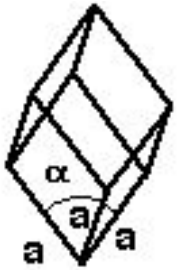
Tetragonal $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$



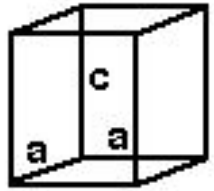
Orthorhombic $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$



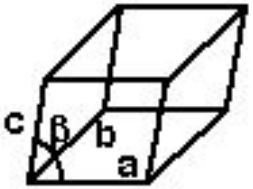
Rhombohedral $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$



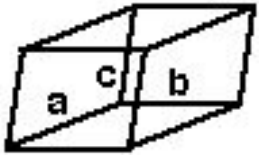
Hexagonal $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$



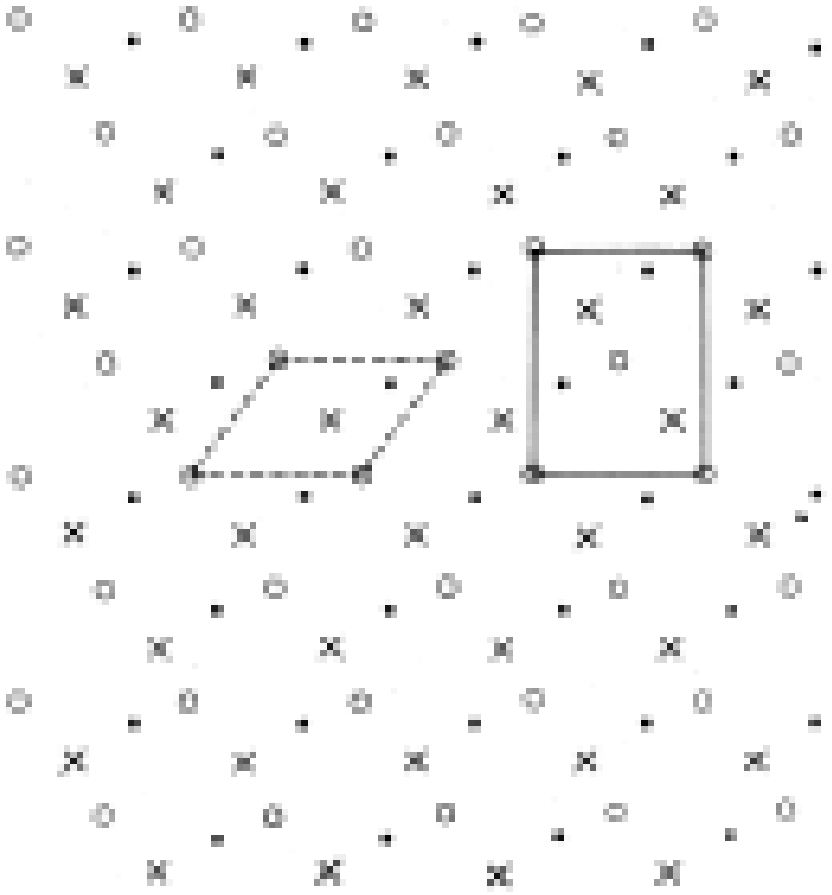
Monoclinic $a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$

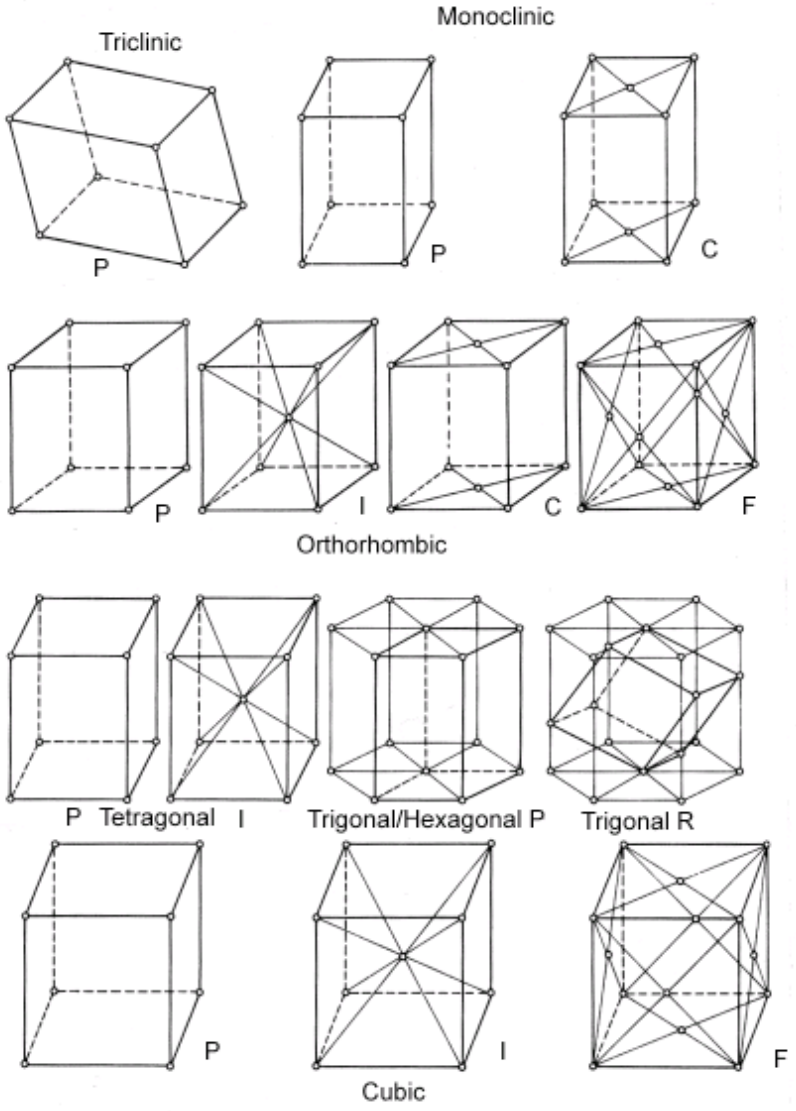


Triclinic $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$

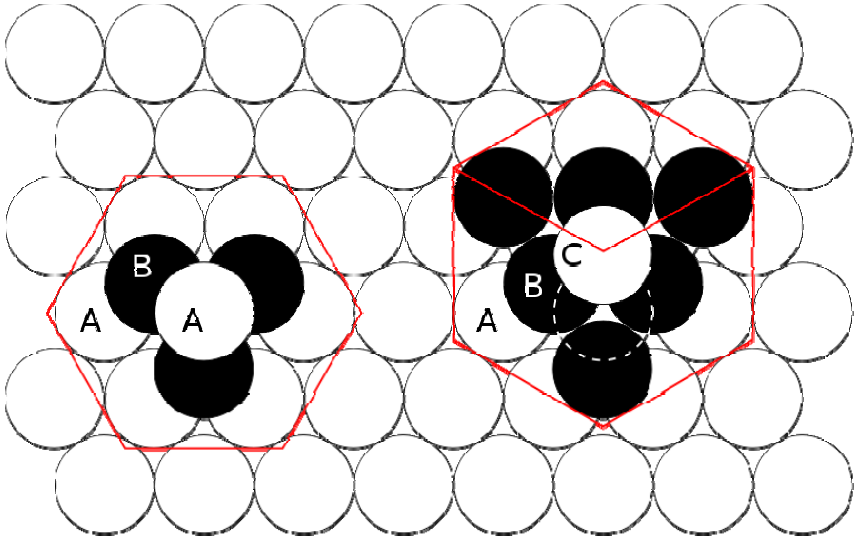


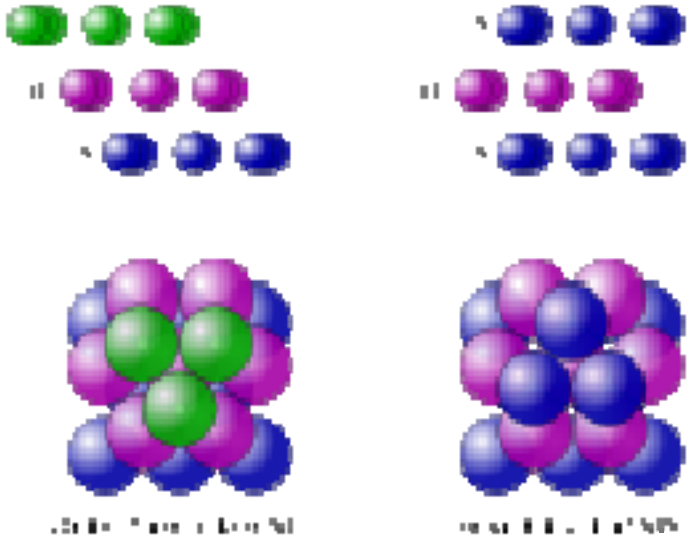
Centered unit cells -> 14 Bravais lattices





Close packing of spheres (metals)



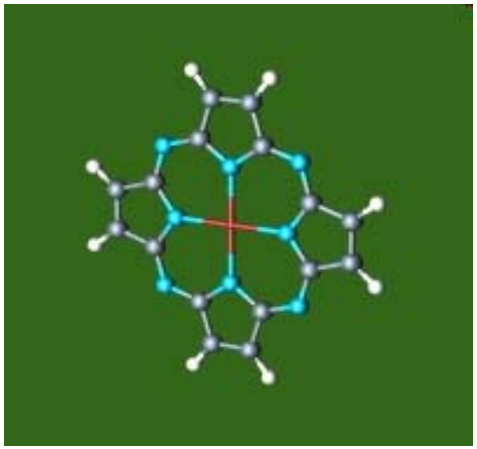


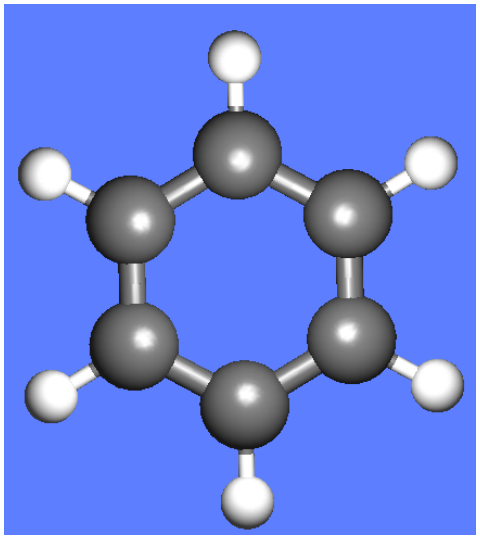
parameter	fcc	Bcc
Symmetry	Cubic	Hexagonal
Coordination number	12	12
Packing density	0.7405	0.7405

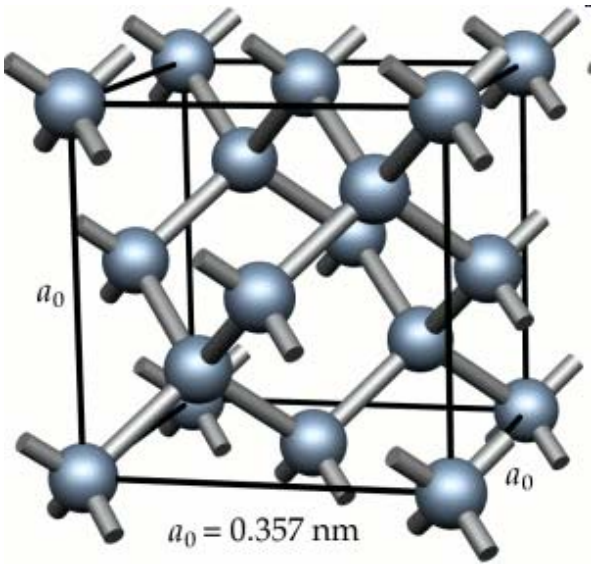
packing density:

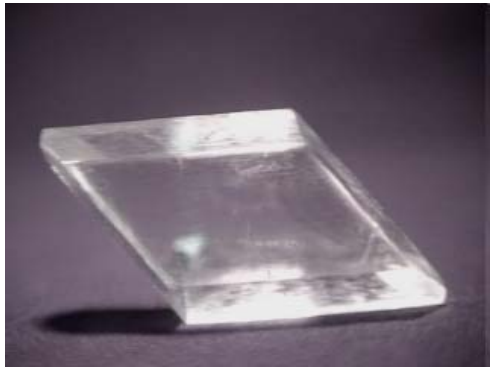
$$\frac{\pi}{3\sqrt{2}} \simeq 0.74048.$$

Symmetries in molecules and crystals









Symmetry elements in crystallography

Definition

A **symmetry operation** on an object is a displacement, which maps the object onto itself such that the mapped object cannot be distinguished from the object in the original state.

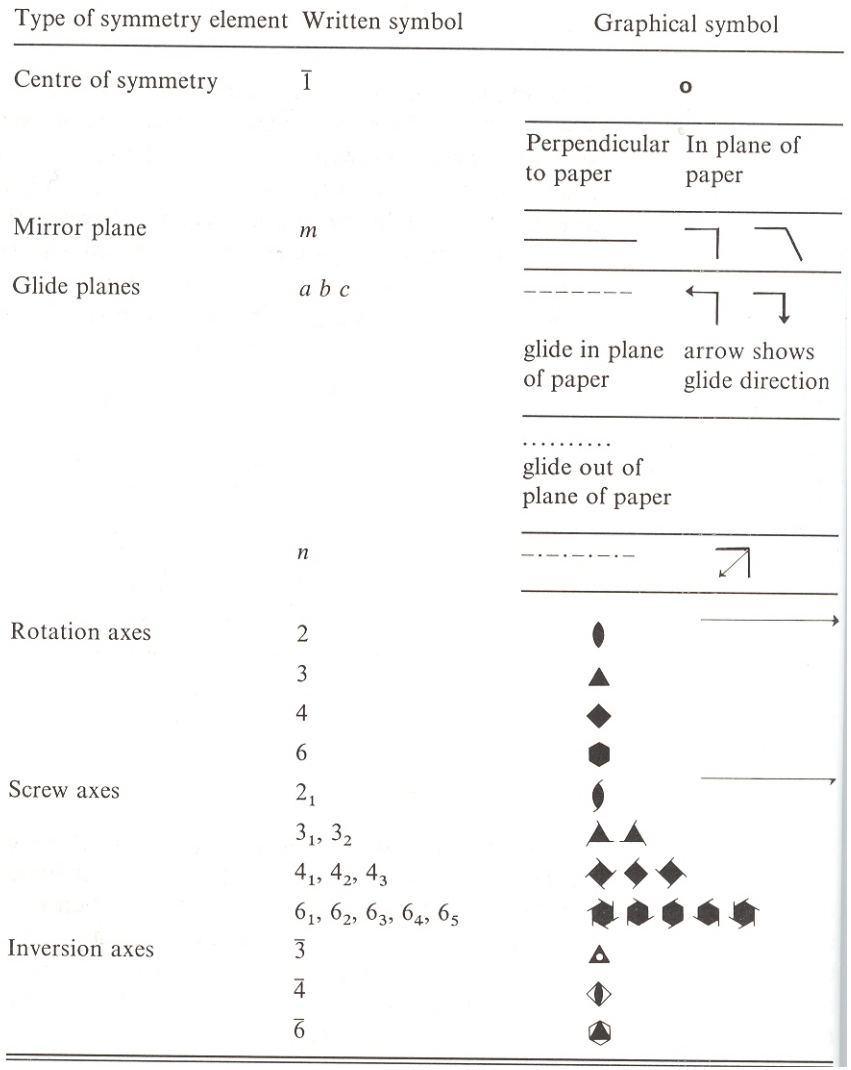
2 different types:

without translation

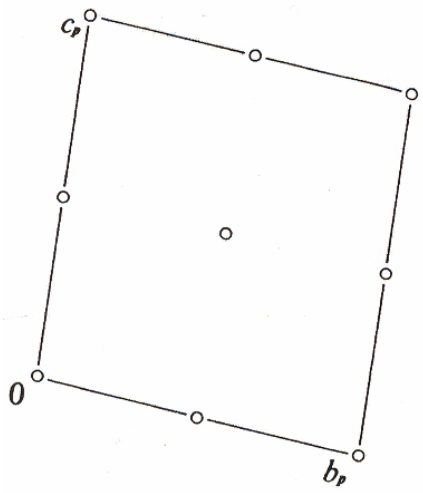
- rotation axes
- mirror planes

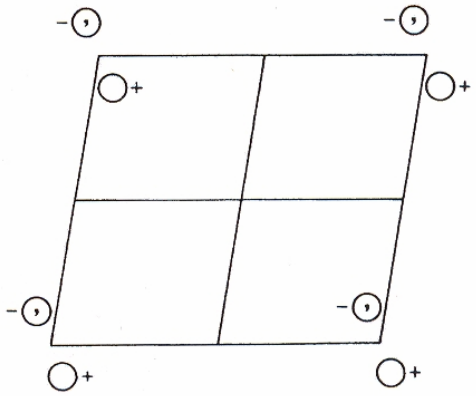
with translational component:

- screw axes
- mirror glide planes



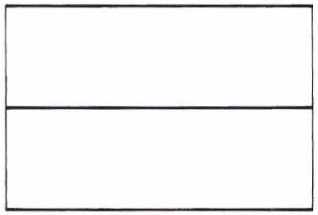
center of inversion and mirror planes

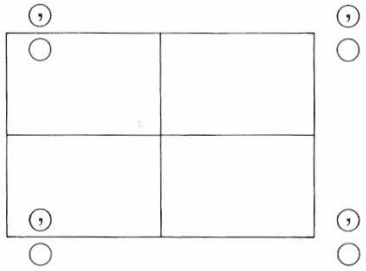




pm *m* Rectangular

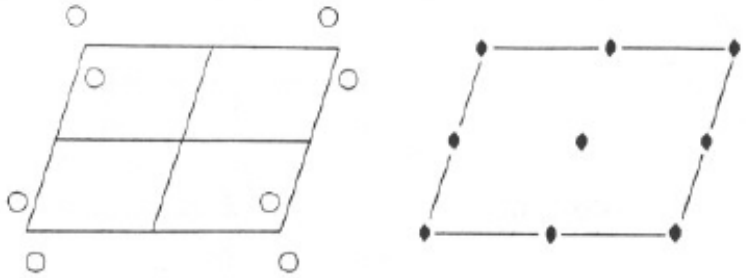
No. 3 *p*1*m*1 Patterson symmetry *p*2*mm*





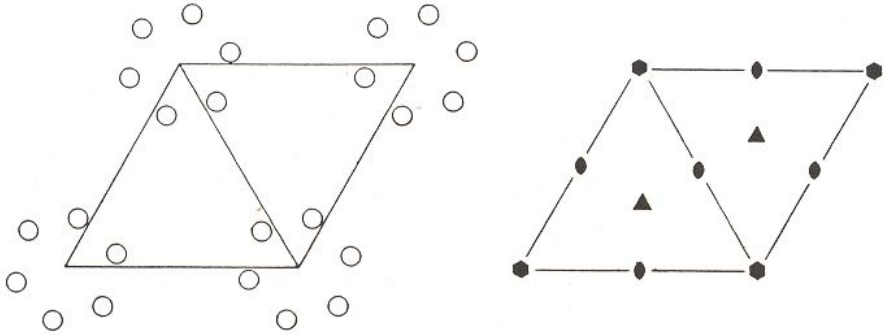
Rotation axes

p 2 No. 2 *p* 2 1 1 2 Oblique



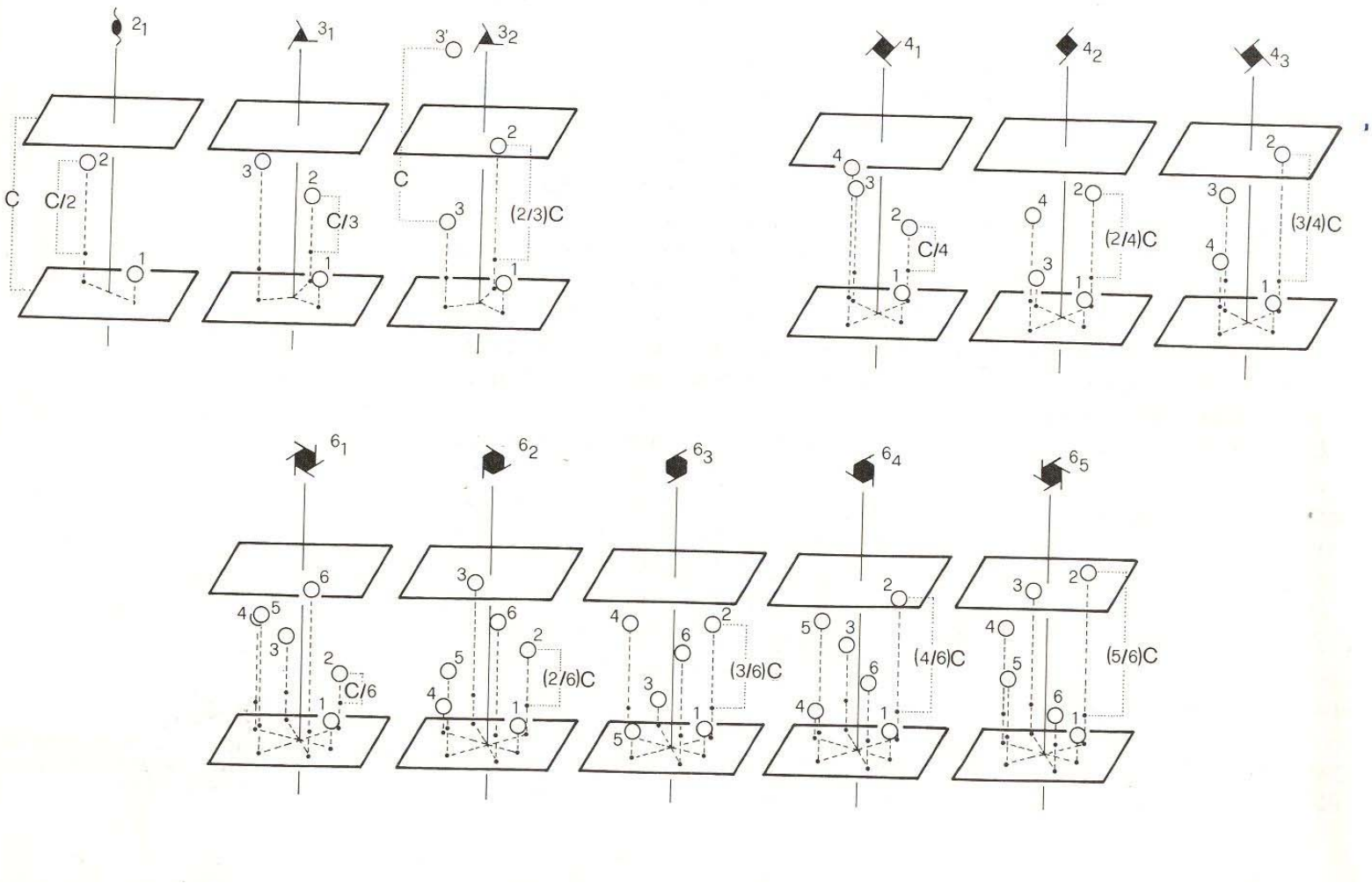
Origin at 2

Hexagonal 6 *p* 6 No. 16 *p* 6



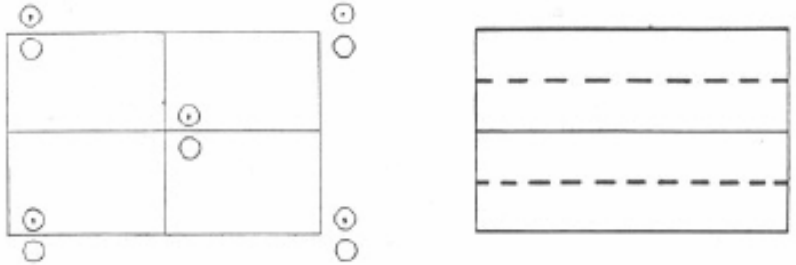
Origin at 6

Screw axes


2₁
3₁
3₂
C
C/2
C/3
(2/3)C
4₁
4₂
4₃
C/4
(2/4)C
(3/4)C
6₁
6₂
6₃
6₄
6₅
C/6
(2/6)C
(3/6)C
(4/6)C
(5/6)C

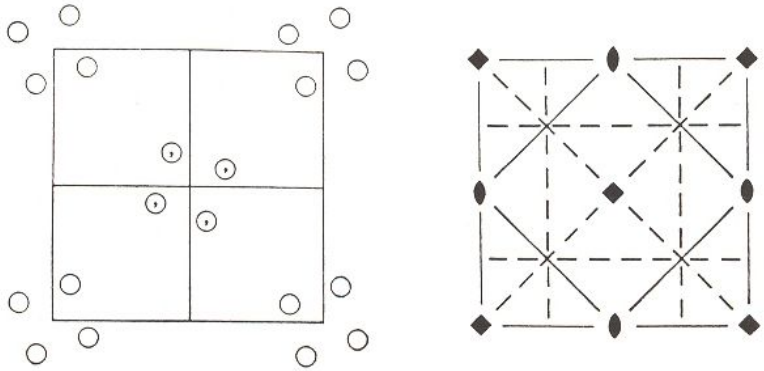
mirror glide planes

c m No. 5 *c* 1 *m* 1 *m* Rectangular



Origin on *m*

Square 4 *m m* *p* 4 *g m* No. 12 *p* 4 *g*



Origin at 4

Lattice symmetry directions directions

popular symmetry directions
in real space:

[1 0 0] along a-axis
[0 1 0] along b-axis
[0 0 1] along c-axis
[1 1 1] along body diagonal
[1 1 0] along face diagonal

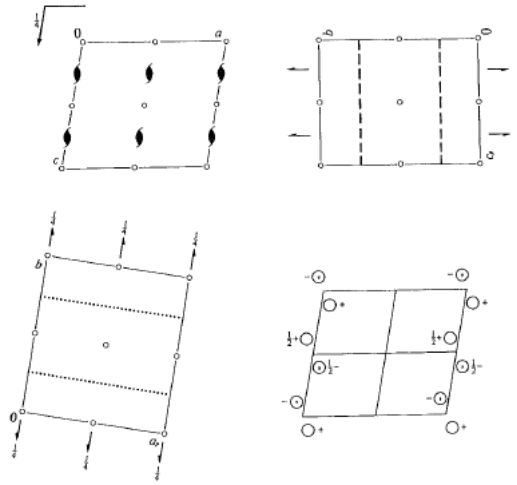
Three dimensions			
Triclinic	None		
Monoclinic*	[010] ('unique axis *b*') [001] ('unique axis *c*')		
Orthorhombic	[100]	[010]	[001]
Tetragonal	[001]	{[100], [010]}	{[1$\bar{1}$0], [110]}
Hexagonal	[001]	{[100], [010], [1$\bar{1}$0]}	{[1$\bar{1}$0], [120], [2$\bar{1}$0]}
Rhombohedral (hexagonal axes)	[001]	{[100], [010], [1$\bar{1}$0]}	
Rhombohedral (rhombohedral axes)	[111]	{[1$\bar{1}$0], [01$\bar{1}$], [$\bar{1}$01]}	
Cubic	{[100], [010], [001]}	{[111], [1$\bar{1}\bar{1}$], [$\bar{1}$1$\bar{1}$], [$\bar{1}\bar{1}$1]}	{[1$\bar{1}$0] [110], [01$\bar{1}$] [011], [$\bar{1}$01] [101]}

space group symbols

$P2_1/c$ C_{2h}^5 $2/m$ Monoclinic

No. 14 $P12_1/c1$ Patterson symmetry $P12/m1$

UNIQUE AXIS b, CELL CHOICE 1



Origin at $\bar{1}$

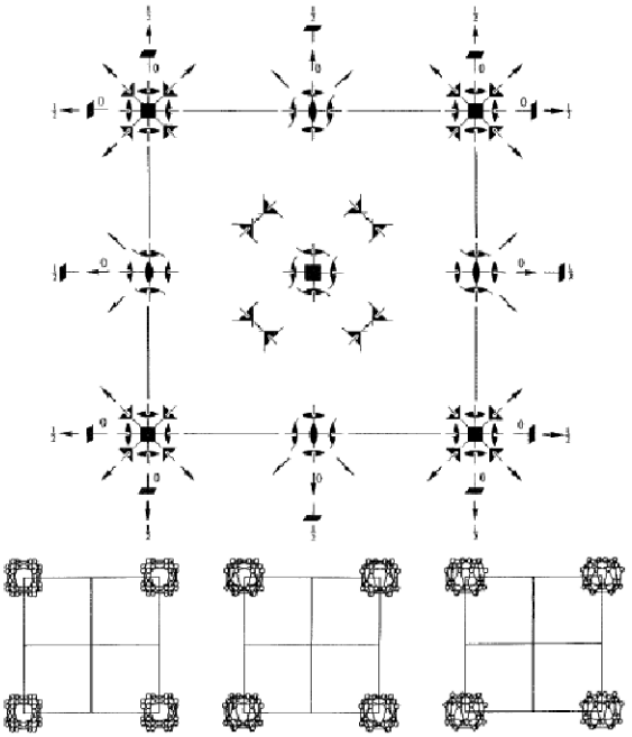
Asymmetric unit $0 \le x \le 1;\quad 0 \le y \le \frac{1}{4};\quad 0 \le z \le 1$

Symmetry operations

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

$P432$ O^1 432 Cubic

No. 207 $P432$ Patterson symmetry $Pm\bar{3}m$



Origin at 432

Asymmetric unit $0 \le x \le 1;\quad 0 \le y \le \frac{1}{2};\quad 0 \le z \le \frac{1}{2};\quad y \le \min(x, 1-x);\quad z \le y$

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

Symmetry operations

(1) 1	(2) 2 0,0,z	(3) 2 0,y,0	(4) 2 x,0,0
(5) 3^+ x,x,x	(6) 3^+ $\bar{x},x,\bar{x}$	(7) 3^+ $x,\bar{x},\bar{x}$	(8) 3^+ $\bar{x},\bar{x},x$
(9) 3^- x,x,x	(10) 3^- $x,\bar{x},\bar{x}$	(11) 3^- $\bar{x},\bar{x},x$	(12) 3^- $\bar{x},x,\bar{x}$
(13) 2 x,x,0	(14) 2 $x,\bar{x}$,0	(15) 4^- 0,0,z	(16) 4^+ 0,0,z
(17) 4^- x,0,0	(18) 2 0,y,y	(19) 2 0,$y,\bar{y}$	(20) 4^+ x,0,0
(21) 4^+ 0,y,0	(22) 2 x,0,x	(23) 4^- 0,y,0	(24) 2 $\bar{x}$,0,x

230 space groups

among them:

non-centro-symmetric space groups

no inversion center, no mirror planes

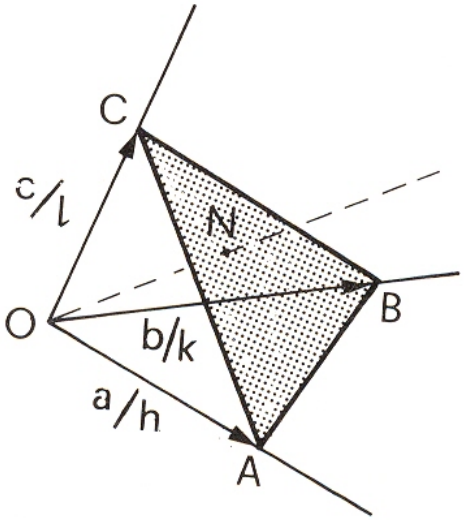
- molecules of biological relevance, e.g. amino acids, proteins
- optical activity

22 (21) polar space groups

only polar axes, no inversion center

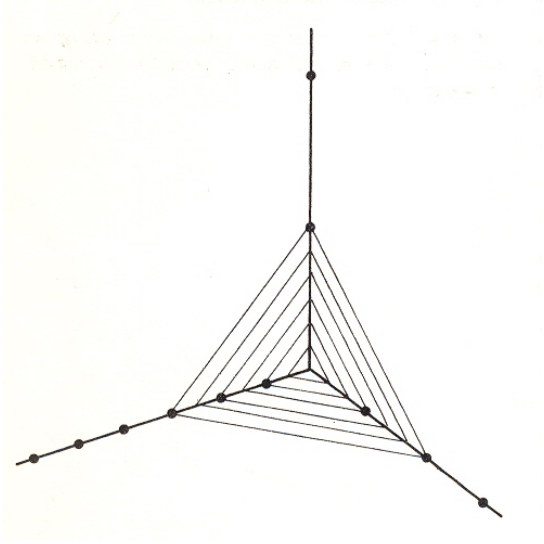
- piezo electric effect
- second harmonic generation

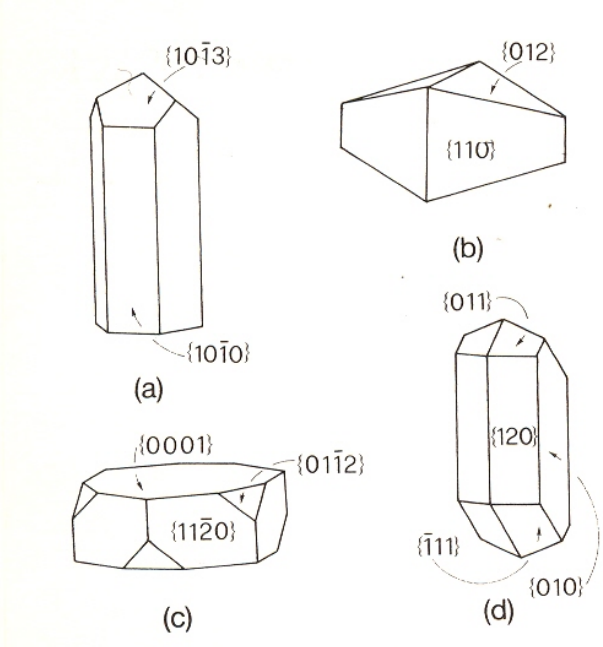
Crystallographic planes – Miller indices



Three lattice points define a crystallographic plane. Intersection with the three crystallographic axes at points
A= c / l, B = b / k, and C = c / l

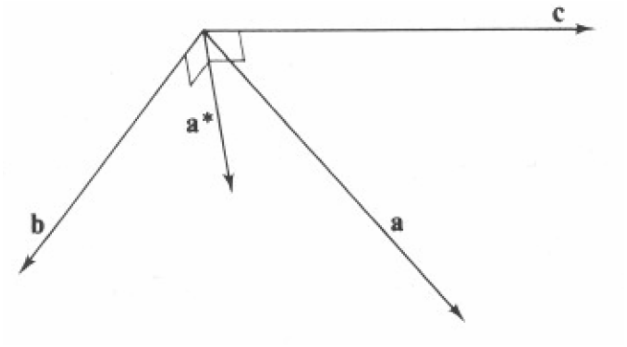
(h k l) => Miller Indices, h,k,l integers, no common divider.





Concept of the reciprocal lattice

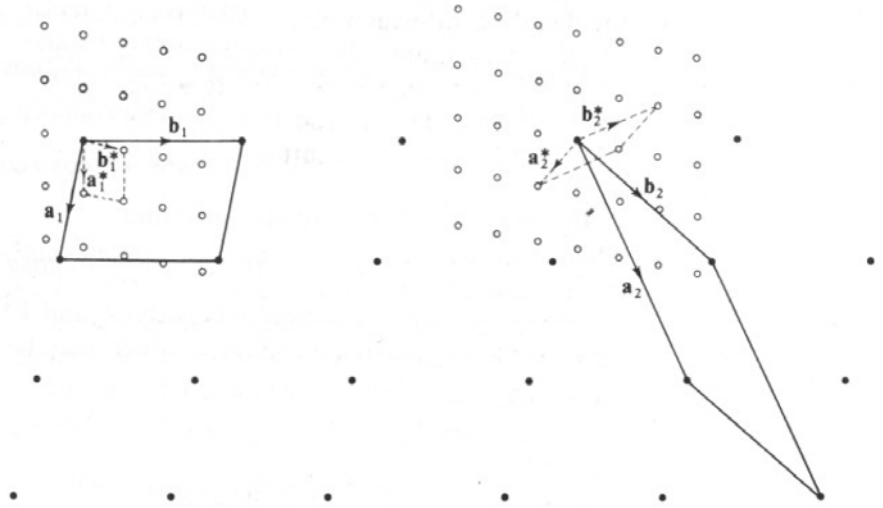
reciprocal lattice defined by the three lattice vectors: a*, b*, c*



$$a \cdot a^* = 1 \quad b \cdot a^* = 0 \quad c \cdot a^* = 0$$
$$b \cdot a^* = 0 \quad b \cdot b^* = 1 \quad c \cdot b^* = 0$$
$$c \cdot a^* = 0 \quad c \cdot b^* = 0 \quad c \cdot c^* = 1$$

reciprocal lattice vector:

$$\vec{s} = h \cdot \vec{a}^* + k \cdot \vec{b}^* + l \cdot \vec{c}^*$$



attention:

$$\vec{Q} = \frac{2\pi}{\lambda}\vec{s}$$