EEE 6212
Semiconductor Materials

Lecture 2: crystal structures

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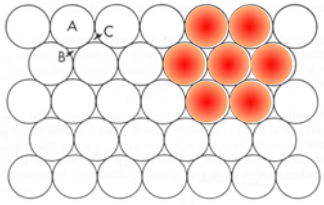
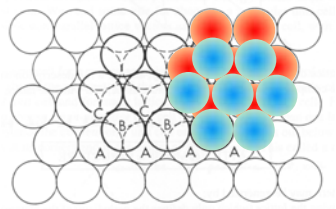
- close packing of spheres in 3D – cubic vs. hexagonal stacking
- concept of lattice, unit cell and Miller indices
- lattice planes, Weiss zone law and calculation of angles
- symmetry operations
- definition of a crystal as lattice ⊗ motif
- the 14 Bravais lattices
- semiconductor crystals

Cubic vs. hexagonal stacking sequences



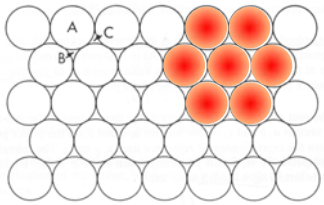
most efficient way to stack equally sized spheres in 2D: each touches
6 neighbouring spheres, forming layer A

2 types of hollows are formed: B & C



in 3D, the 2nd layer can be stacked on top of either B sites (shown) or C sites

Cubic vs. hexagonal stacking sequences



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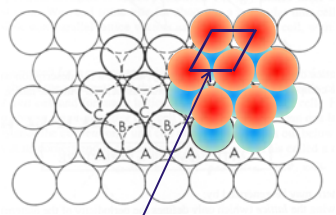


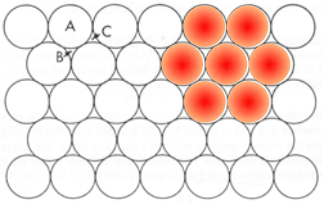
in 3D, the 2nd layer can be stacked on top of either B sites (shown) or C sites

the 3rd layer can be stacked upon B using again either A sites

-> AB(ABAB): **hexagonal**

rhombus in top view

Cubic vs. hexagonal stacking sequences



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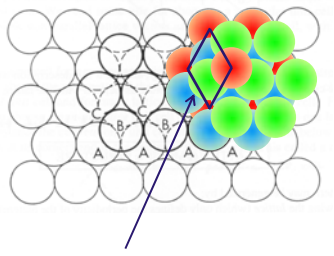


square in oblique side view

in 3D, the 2nd layer can be stacked on top of either B sites (shown) or C sites

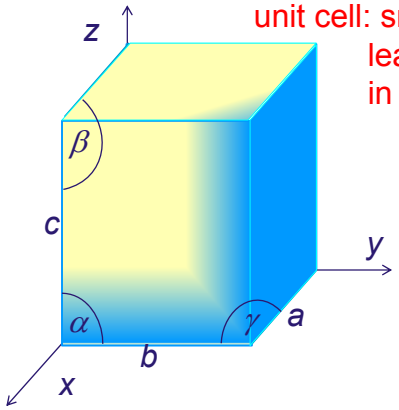
the 3rd layer can be stacked upon B using again either A sites or C sites

-> ABC(ABC): **cubic**

Concept of lattice and unit cell

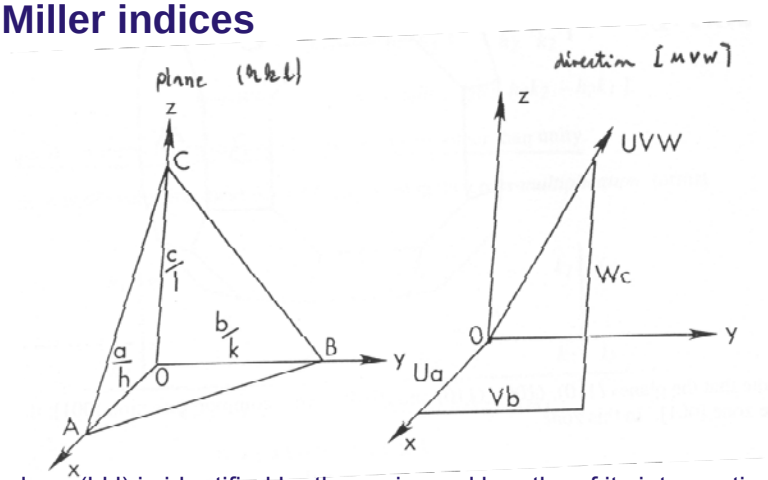
lattice: periodic array of points that completely fills 3D space

unit cell: smallest box that contains at least one atom and is repeated in this lattice, e.g. as shown



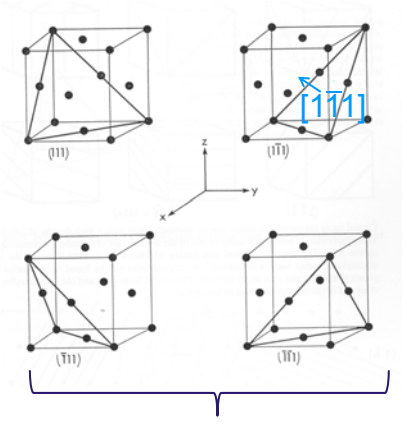
The unit cells is character-ised by its lengths of *a*,*b*,*c* along the *x*,*y*,*z* axes and the angles α,β,γ between the axes (here: all 90°). ***a*,*b*,*c*** are called base vectors.

Miller indices

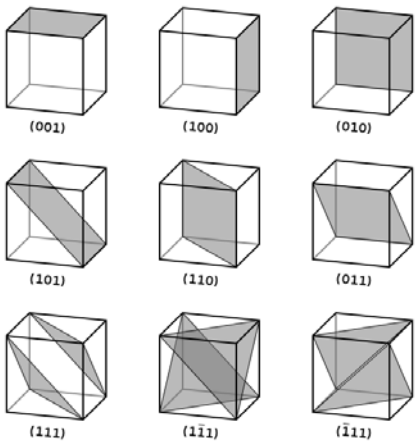


Each plane (hkl) is identified by the reciprocal lengths of its intersections with the three axes. Each direction [uvw] is identified by the multiples of its extensions along the three axes. For cubic systems [hkl] is the normal to (hkl).

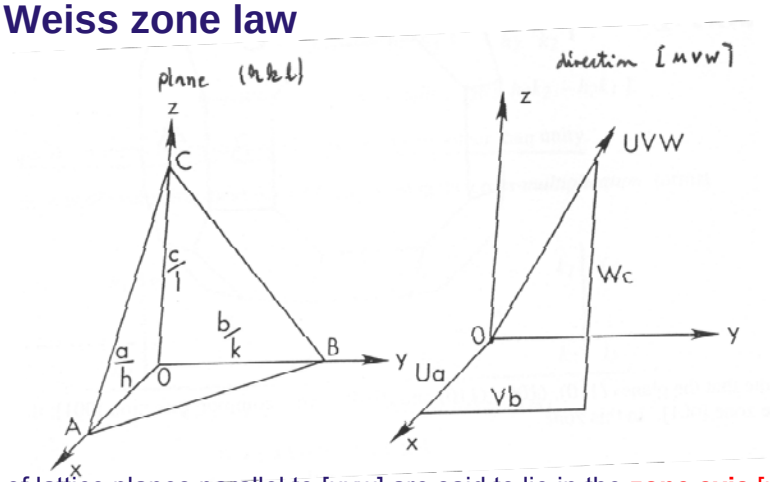
Miller indices in the cubic system



crystallographically equivalent: {111}

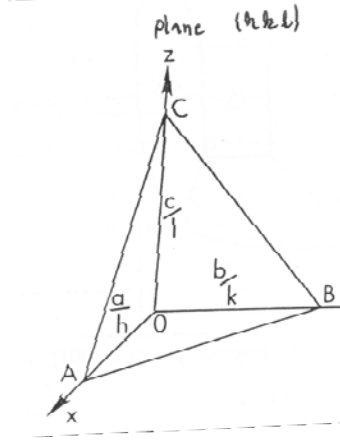


Weiss zone law



A set of lattice planes parallel to [uvw] are said to lie in the **zone axis** [uvw]. The condition for a direction ***d***=[uvw] to be parallel to a lattice plane ***p***=(hkl) is called the Weiss zone law or **zone equation**: ***d***·***p***=hu+kv+lw=0

Weiss zone law



derivation:

Any lattice vector [uvw] in the plane **ABC** can be written as linear combination of two vectors ***AB*** and ***AC***:

u***a***+v***b***+w***c*** = x ***AB*** +y ***AC***

where

AB = 1/k ***b*** –1/h ***a***

AC = 1/ℓ ***c*** –1/h ***a***

Inserting into above yields:

u***a***+v***b***+w***c*** = x(1/k ***b*** –1/h ***a***)+ y(1/ℓ ***c*** –1/h ***a***)

= (-x/h-y/h)***a*** + x/k ***b*** + y/ℓ ***c***

Comparing coefficients:

u=-(x+y)/h, v=x/k, w=y/ℓ

Hence,

hu+kv+ℓw = -(x+y)+x+y = 0 q.e.d.

note: derivation does **not** require orthogonal axes!

Weiss zone law

applications:

1. Find direction [uvw] common to two planes $(h_1k_1\ell_1)$ and $(h_2k_2\ell_2)$ using the cross-product (in any crystal):
   $h_1u+k_1v+\ell_1w=0$
   and
   $h_2u+k_2v+\ell_2w=0$
   yields:
   $[uvw]=[k_1\ell_2-k_2\ell_1,\ \ell_1h_2-\ell_2h_1,\ h_1k_2-h_2k_1]=(h_1k_1\ell_1)\ \mathbf{x}\ (h_2k_2\ell_2)$

2. Find angles between lattice directions (vectors) $\underline{\boldsymbol{p}}=[u_1v_2w_1]$ & $\underline{\boldsymbol{q}}=[u_2v_2w_2]$ **for orthogonal axes** using the dot product:

$$\cos\theta = [u_1u_2a^2+ v_1v_2b^2+w_1w_2c^2]/[(u_1^2a^2+v_1^2b^2+w_1^2c^2)(u_2^2a^2+v_2^2b^2+w_2^2c^2)]^{1/2}$$
$$= \underline{\boldsymbol{p}}\cdot\underline{\boldsymbol{q}}/(pq)$$

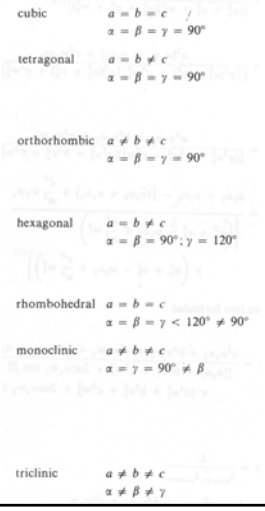
(& angles between planes are the angles between their normals!)

Shape of the unit cell defines 7 lattice systems

The lattice systems are distinguished according to the form of their unit cells. We have the following 7 lattice systems:

1. cubic
2. tetragonal
3. orthorhombic
4. hexagonal
5. rhombohedral
6. monoclinic
7. triclinic

where the symmetry decreases from top to bottom.



The 4 most important lattice systems

Crystal system		Interplanar spacing of the (hkl) plane
cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	$\frac{1}{d^2} = \frac{1}{a^2}(h^2 + k^2 + l^2)$
tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	$\frac{1}{d^2} = \frac{1}{a^2}(h^2 + k^2) + \frac{1}{c^2}l^2$
orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	$\frac{1}{d^2} = \frac{1}{a^2}h^2 + \frac{1}{b^2}k^2 + \frac{1}{c^2}l^2$
hexagonal	$a = b \neq c$ $\alpha = \beta = 90°; \gamma = 120°$	$\frac{1}{d^2} = \frac{4}{3a^2}(h^2 + hk + k^2) + \frac{1}{c^2}l^2$

$d_{hkl} = a/\sqrt{h^2+k^2+\ell^2}$

The 4 most important lattice systems

Crystal system		Angle ϕ between $(h_1k_1l_1)$ and $(h_2k_2l_2)$
cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	$\cos\phi = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)\}^{1/2}} = \frac{\underline{d}_{h_1k_1\ell_1} \cdot \underline{d}_{h_2k_2\ell_2}}{\lvert d_{h_1k_1\ell_1} \rvert \, \lvert d_{h_2k_2\ell_2} \rvert}$
tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	$\cos\phi = \frac{\frac{1}{a^2}(h_1h_2 + k_1k_2) + \frac{1}{c^2}l_1l_2}{\left[\left\{\frac{1}{a^2}(h_1^2 + k_1^2) + \frac{1}{c^2}l_1^2\right\}\left\{\frac{1}{a^2}(h_2^2 + k_2^2) + \frac{1}{c^2}l_2^2\right\}\right]^{1/2}}$
orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	$\cos\phi = \frac{\frac{1}{a^2}h_1h_2 + \frac{1}{b^2}k_1k_2 + \frac{1}{c^2}l_1l_2}{\left\{\left(\frac{1}{a^2}h_1^2 + \frac{1}{b^2}k_1^2 + \frac{1}{c^2}l_1^2\right)\left(\frac{1}{a^2}h_2^2 + \frac{1}{b^2}k_2^2 + \frac{1}{c^2}l_2^2\right)\right\}^{1/2}}$
hexagonal	$a = b \neq c$ $\alpha = \beta = 90°; \gamma = 120°$	$\cos\phi = \frac{h_1h_2 + k_1k_2 + \frac{1}{2}(h_1k_2 + k_1h_2) + \frac{3}{4}\frac{a^2}{c^2}l_1l_2}{\left\{\left(h_1^2 + k_1^2 + h_1k_1 + \frac{3}{4}\frac{a^2}{c^2}l_1^2\right)\left(h_2^2 + k_2^2 + h_2k_2 + \frac{3}{4}\frac{a^2}{c^2}l_2^2\right)\right\}^{1/2}}$

The 4 most important lattice systems

Crystal system		Angle ρ between directions $[u_1v_1w_1]$ and $[u_2v_2w_2]$
cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	$\cos\rho = \dfrac{u_1u_2 + v_1v_2 + w_1w_2}{\{(u_1^2 + v_1^2 + w_1^2)(u_2^2 + v_2^2 + w_2^2)\}^{1/2}}$
tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	$\cos\rho = \dfrac{a^2(u_1u_2 + v_1v_2) + c^2w_1w_2}{[\{a^2(u_1^2 + v_1^2) + c^2w_1^2\}\{a^2(u_2^2 + v_2^2) + c^2w_2^2\}]^{1/2}}$
orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	$\cos\rho = \dfrac{a^2u_1u_2 + b^2v_1v_2 + c^2w_1w_2}{\{(a^2u_1^2 + b^2v_1^2 + c^2w_1^2)(a^2u_2^2 + b^2v_2^2 + c^2w_2^2)\}^{1/2}}$
hexagonal	$a = b \neq c$ $\alpha = \beta = 90°; \gamma = 120°$	$\cos\rho = \dfrac{u_1u_2 + v_1v_2 - \frac{1}{2}(u_1v_2 + v_1u_2) + \frac{c^2}{a^2}w_1w_2}{\left\{\left(u_1^2 + v_1^2 - u_1v_1 + \frac{c^2}{a^2}w_1^2\right) \times \left(u_2^2 + v_2^2 - u_2v_2 + \frac{c^2}{a^2}w_2^2\right)\right\}^{1/2}}$

Symmetry operations in a crystal

The symmetry operations of a crystal lattice are:

1. translation (per definition of periodicity)

2. rotational symmetry around an n-fold axis
   - a) n=2: diads  or C_2
   - b) n=3: triads  or C_3
   - c) n=4: tetrads  or C_4
   - d) n=6: hexads  or C_6

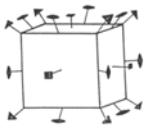
3. inversion symmetry around a point = point symmetry (sign: $\bar{1}$)

4. roto-inversion symmetry = 2.& 3. combined
   (signs: $\bar{2}$= plane with mirror symmetry (m); $\bar{3}$, $\bar{4}$ or $\bar{6}$)

Symmetry operations in a cubic crystal

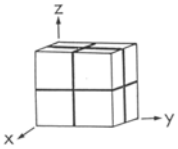
Rotation axes of symmetry

Three tetrads normal to the cube faces. $3 \times C_4$
Four triads along the body diagonals. $4 \times C_3$
Six diads through the mid points of opposite edges. $6 \times C_2$



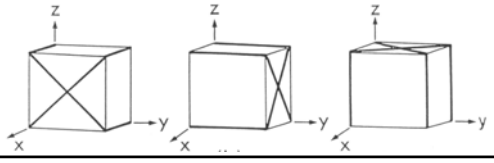
Planes of symmetry parallel to:

(100), (010) and (001).



and

(011) and (011) (101) and (101) (110) and (110).



Symmetry operations define 7 crystal systems

Each crystal system possesses one or more symmetry elements that impose a given shape of unit cell onto the lattice:

1. cubic	four triads parallel {111}
2. tetragonal	one tetrad along [001]
3. orthorhombic	three mutually perpendicular diads
4. hexagonal	one hexad along [001]
5. *trigonal**	one triad along [001]
6. monoclinic	one diad along [010]
7. triclinic	none

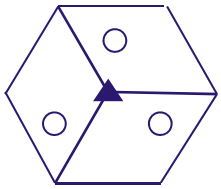
where again the symmetry decreases from top to bottom.
**Note the trigonal crystal system ($a=b\neq c$, $\alpha=\beta=90°$, $\gamma=120°$) here replaces the rhombohedral lattice system ($a=b=c$, $\alpha=\beta=\gamma\neq 90°$), which itself is a sub-set of the trigonal system. Quartz is trigonal but not rhombohedral!*

Definition of crystal

A crystal consists of a lattice on which a motif of a certain symmetry is repeated periodically, i.e.

$$\text{crystal} = \text{lattice} \otimes \text{motif}$$

example in 2D: hexagon with triade

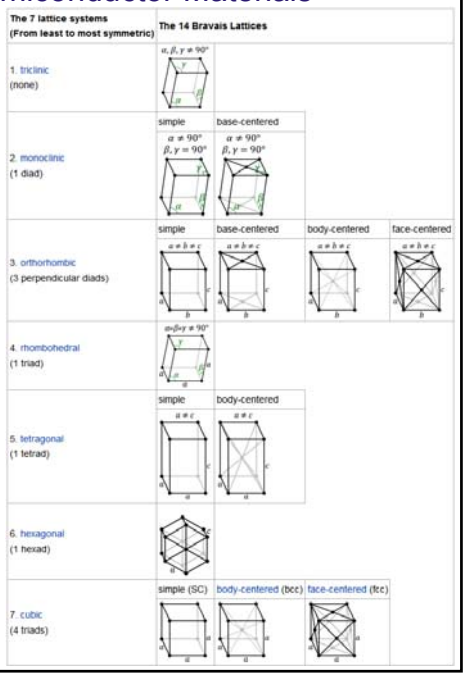


The 14 Bravais Lattices

The 14 Bravais lattices come about due to combinations of point symmetry (7 lattice systems) with 4 space centerings:

notation:	lattice points at 0,0,0 and
P: primitive	-
C: base centred	½, ½,0
I: body centred	½, ½, ½
F: face centred	½,½,0; ½,0,½; 0,½,½
R:	$^2/_3,^1/_3,^1/_3$; $^1/_3,^2/_3,^2/_3$

Note: trigonal R can be hexagonal P or rhombohedral.



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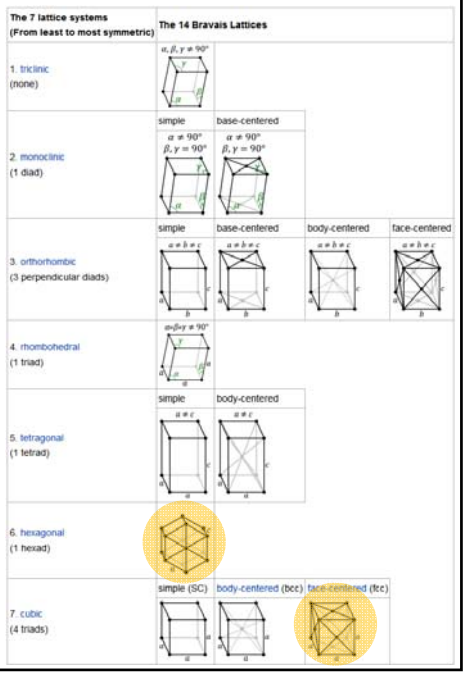
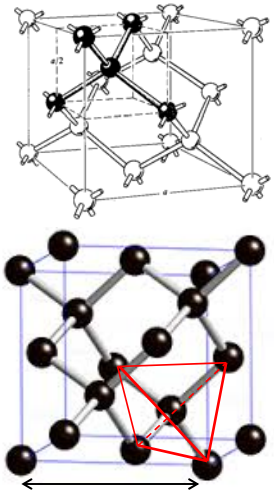


Semiconductor crystals



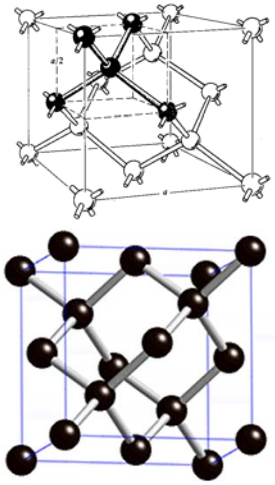
1. diamond (C, Si, Ge, α-Sn)

consists of two face-centred cubic crystals shifted by ¼ of the body diagonal; all 8 atoms are identical and connected via 4 neighbours via bonds forming tetrahedra.

space group 227: $Fd\bar{3}m$
1 atom at corners: 8 x $^1/_8$
3 atoms at centre of faces: 6 x ½
4 atoms at tetrahedral sites: 4 x 1

a=0.381nm (C), 0.543nm (Si), 0.566nm (Ge)

Semiconductor crystals



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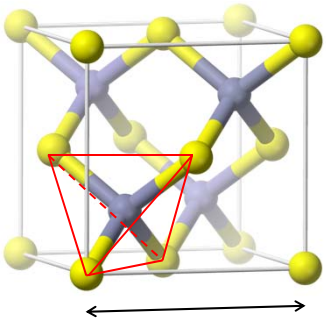
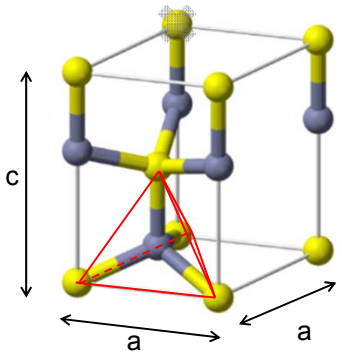


a=0.542nm (c-ZnS)
0.565nm (GaAs),
0.587nm (InP),
0.648nm (InSb),
0.450nm (c-GaN),

2. sphalerite or zinc blende (ZnS, GaP, InP, GaAs, AlAs, InAs, GaSb, InSb, ZnSe, HgTe,…)
consists of two face-centred cubic crystals shifted by ¼ of the body diagonal; both sub-lattices are occupied by different atoms which again are tetrahedrally connected to their 4 neighbours.

space group 216: $F\bar{4}3m$
1 atom at corners: 8 x $^1/_8$
3 atoms at centre of faces: 6 x ½
4 atoms at tetrahedral sites: 4 x 1

Semiconductor crystals



a=0.381nm, c=0.623nm (h-ZnS),
a=0.319nm, c=0.519nm (h-GaN),

3. wurtzite (ZnS, GaN, ZnO, BeO,…) consists of two hexagonal crystals (dihexagonal pyramidal) shifted by $^3/_8$ *c* (+δ) along ***c***-axis;
both sub-lattices are occupied by different atoms which again are tetrahedrally connected to their 4 neighbours.

space group 186: $P6_3mc$
1 atom at corners (0, 0,0)
1 atom at position ($^1/_3$,$^2/_3$,$^1/_2$)
1 atom at position (0,0,$^3/_8$)
1 atom at position ($^1/_3$,$^2/_3$,$^7/_8$)

Summary

- hexagonal and cubic structures only differ in their stacking sequence
- unit cell is the smallest box periodically repeated in a crystal lattice
- Miller indices describe planes (hkl) and directions [uvw] in a lattice
- Weiss zone equation states which planes lie in a zone axis, i.e. are perpendicular to a certain direction
- common direction for two planes can be calculated by cross-product
- shape of the unit cell defines 7 lattice systems
- symmetry operations defines 7 crystal systems (similar to above), of which the one with the highest symmetry is the cubic system
- a crystal is given by a motif repeated on a lattice
- there are 14 Bravais lattices defined by symmetry and centerings
- semiconductors crystallise in diamond, sphalerite or wurtzite structure