

Review

Drude model – (free electron approximation) + (independent electron approximation) + (Maxwell Boltzmann statistics)

Sommerfeld model – (free electron approximation) + (independent electron approximation) + (Fermi Dirac statistics)

Next:

Band structure – (crystal potential) + (independent electron approximation) + (Fermi Dirac statistics)

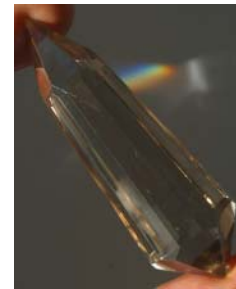
Crystal potential arises from the crystal structure made of atoms -- important for understanding the differences among metals, semiconductors, and insulators.

Crystal Structure

Crystal structure is evident from naturally formed facets of many mineral samples.

Based on x-ray diffraction:

Crystal structure = periodic,^(b) infinite^(a) repetition of structural units^(c)



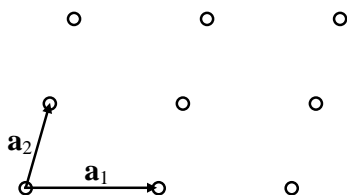
(a) Infinite: $N \sim 10^{23} \sim \infty$, bulk properties are independent of surfaces.

(b) Periodic: translational symmetry

Define **Bravais lattice** with **lattice vector** $\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$; $n_{1,2,3} = \text{integers}$

$\mathbf{a}_{1,2,3} \equiv$ **primitive lattice vectors** (noncoplanar); they generate the lattice.

2d example:



(c) Structural unit: **basis** = a set of atoms associated with each lattice point

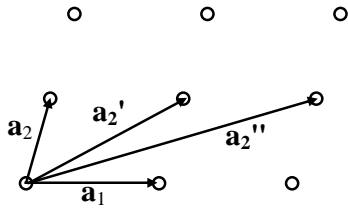
Summarize : crystal structure = Bravais lattice + basis

Theorem: A crystal looks the same from every Bravais lattice point.

$$TH T^{-1} = H \text{ (system is invariant under translation)}$$

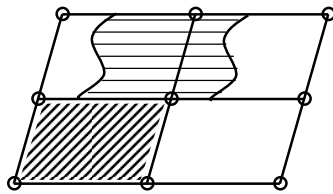
Theorem: Primitive vectors are not unique; there are ∞ ways of choosing them.

2d example:

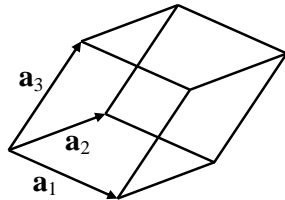


Definition: primitive unit cell = a region in space, when translated using all lattice vectors \mathbf{R} , fills neatly the whole space (w/o overlapping regions or voids)

2d examples: 2 possible choices out of ∞



3d example: (obvious choice)



Theorem: volume of primitive cell $v_c = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \frac{V}{N}$; V = volume of crystal, N = # of lattice points

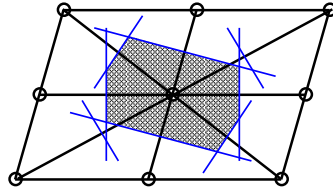
One unit cell contains one lattice point (on average).

Definition: Wigner-Seitz unit cell = the region of space that is closer to a selected lattice point (origin O) than to any other lattice points; it is a primitive unit cell.

Method of construction:

1. Draw lines from O to all nearby lattice points.
2. Draw \perp bisectors (planes in 3-d).
3. Find the smallest volume enclosed.

2d example:



Proof: Every point in space can be uniquely assigned to a W-S cell associated with a lattice point (except for those on the boundaries, but those have zero volume).
 Translational symmetry \rightarrow all W-S cells are the same.
 Since each point in space (other than those on boundaries) is accounted for once and only once, we have no overlapping regions or voids.

- W-S cell is a primitive cell.
- It does not depend on the choice of $\mathbf{a}_{1,2,3}$.
- As symmetric as the original lattice (e.g., 3-fold, 4-fold, mirror planes, ...).

Definition: **conventional unit cells** (non-primitive cells): volume = $n \times$ volume of primitive cell; filling the whole space when translated using a subset of \mathbf{R} ; containing n lattice points per cell; often chosen for convenience.

Examples of Bravais lattices:

1. Simple cubic (sc)

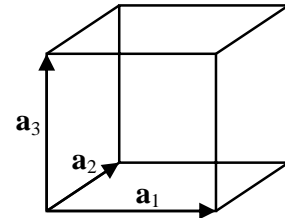
$\mathbf{a}_{1,2,3}$ mutually perpendicular; $a_1 = a_2 = a_3 = a$

a = lattice constant or lattice parameter

Primitive cell = cube = conventional cell

W-S cell is also cubic.

Po, the only one in the periodic table (under typical conditions)



2. Body centered cubic (bcc)

Conventional cell = sc + another atom at center of cube body

Primitive lattice vectors (symmetric form):

$$\mathbf{a}_1 = \frac{a}{2}(-\hat{x} + \hat{y} + \hat{z}) = \frac{a}{2}(-1, 1, 1)$$

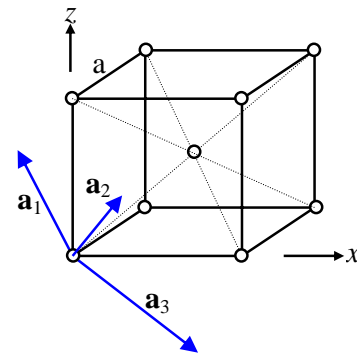
$$\mathbf{a}_2 = \frac{a}{2}(\hat{x} - \hat{y} + \hat{z}) = \frac{a}{2}(1, -1, 1)$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z}) = \frac{a}{2}(1, 1, -1)$$

a = lattice constant

Make sure all points are generated:

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 = \frac{a}{2}(n_2 + n_3 - n_1, n_3 + n_1 - n_2, n_1 + n_2 - n_3) = \frac{a}{2}(l_1, l_2, l_3)$$



$\ell_{1,2,3}$ = integers but not arbitrary; $n_{1,2,3}$ arbitrary.

$\ell_1 + \ell_2 = 2n_3 = \text{even}$, etc. So, $\ell_{1,2,3}$ either all even or all odd.

$\mathbf{R} = \frac{a}{2}(0,0,0)$ corner; $(2,0,0)$ corner; $(0,2,0)$ corner; ... $(1,1,1)$ body-center; ...

Wigner-Seitz cell: "truncated octahedron" (see textbook)

Conventional cell: $v = a^3$

Primitive cell: $v = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 = \frac{a^3}{8} \begin{vmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{vmatrix} = \frac{a^3}{2}$

Conventional cell = 2 x primitive cell

bcc = sc + a two-atom basis (useful for X-ray diffraction).

$\mathbf{a}_1 = a(1,0,0)$, $\mathbf{a}_2 = a(0,1,0)$, $\mathbf{a}_3 = a(0,0,1)$ Basis: $\mathbf{d}_0 = a(0,0,0)$ and $\mathbf{d}_1 = \frac{a}{2}(1,1,1)$

Examples: Ba, Cr, Li, etc.

3. Face centered cubic (fcc)

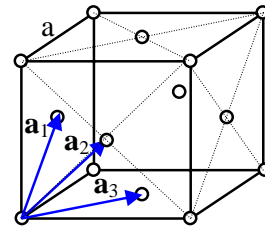
Conventional cell = sc + 6 atoms at faces centers

Bravais lattice

$$\mathbf{a}_1 = \frac{a}{2}(0,1,1)$$

$$\mathbf{a}_2 = \frac{a}{2}(1,0,1)$$

$$\mathbf{a}_3 = \frac{a}{2}(1,1,0)$$



$\mathbf{R} = \sum n_i \mathbf{a}_i \rightarrow$ generates the lattice (verify yourself).

Conventional cell: $v = a^3$ Primitive cell: $v = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 = a^3/4$

There are 4 lattice points per conventional cell

Counting	Lattice points	Weight	Total
	8 corner atoms	1/8	1
	6 face atoms	1/2	3
			4

Or, one could offset the cube slightly to avoid shared points.

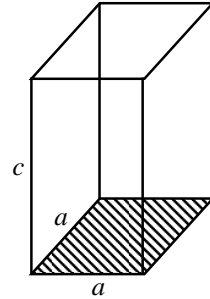
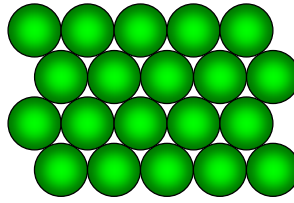
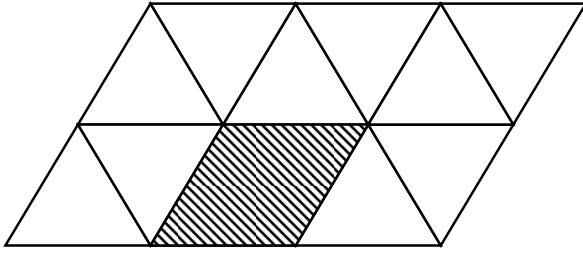
Examples: Ni, Cu, Ag, Au, Al, Pt, ...

4. Simple hexagonal (sh)

60° triangular net in 2d, stacked vertically directly atop $a_1 = a_2 = a$ $a_3 = c$

$$\mathbf{a}_1 = a \hat{x} \quad , \quad \mathbf{a}_2 = \frac{a}{2} \hat{x} + \frac{\sqrt{3}}{2} a \hat{y} \quad , \quad \mathbf{a}_3 = c \hat{z}$$

a, c : lattice constants; z-axis = c-axis



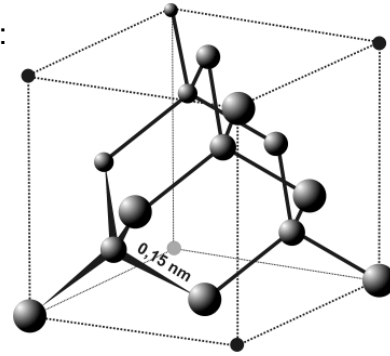
Examples of **lattice + nontrivial basis**, one kind of atom:

1. Diamond structure

fcc lattice (lattice constant a)

+ 2-atom basis at $(0,0,0)$ and $\frac{a}{4}(1,1,1)$

Coordination number = 4; tetrahedral bonding
Examples: diamond, Si, Ge, grey-Sn



2. Hexagonal close packed (hcp)

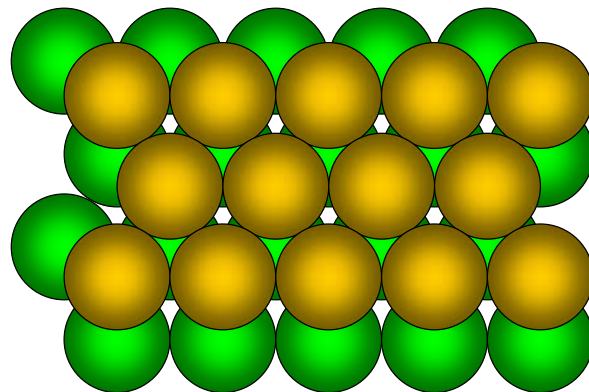
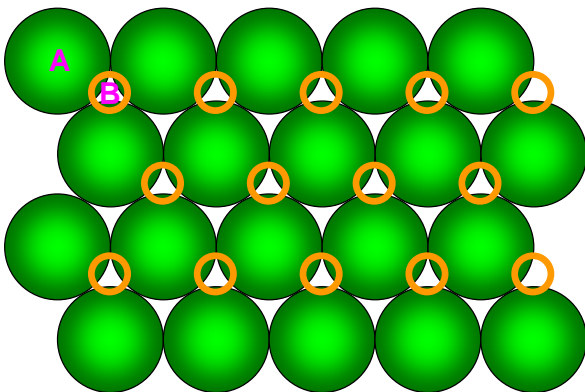
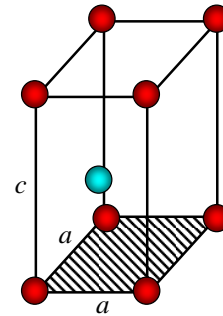
hcp = (simple hexagonal lattice)

+ 2-atom basis at $(0,0,0)$ and $\frac{1}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{a}_3$

For close packed hard spheres,

$$c/a = \sqrt{\frac{8}{3}} \quad (\text{ideal structure});$$

but most are not ideal.

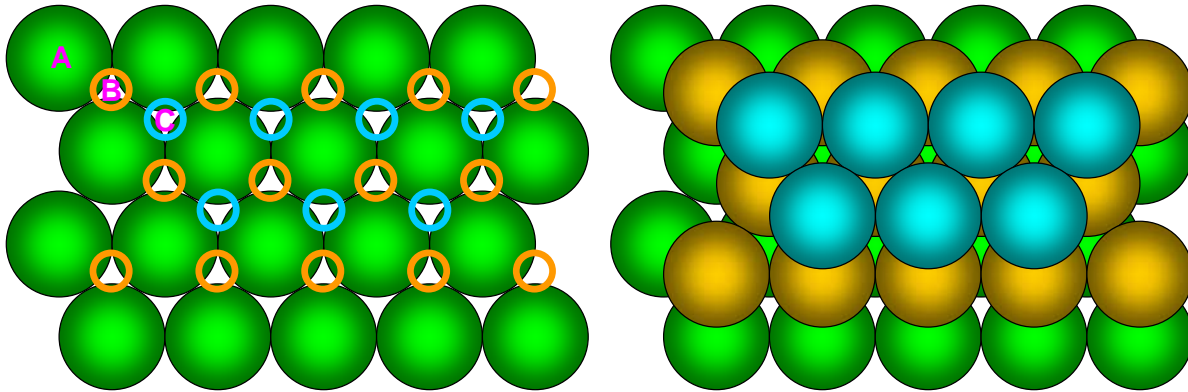


Green: first layer. Gold: second layer. The third layer repeats the first layer positions.

Stacking sequence: ABAB

Examples: Ru, Cd, Re, Y, Hf, Gd, etc.

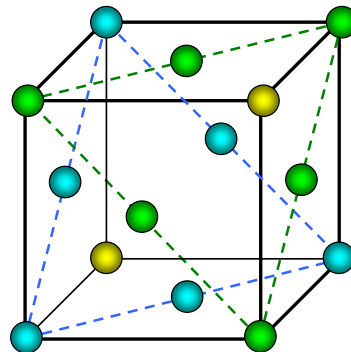
Changing the stacking sequence to ABCABC yields the fcc structure.



First layer at A sites; second layer at B sites, third layer at C sites; fourth layer at A sites; etc.

Looking along the body diagonal, the fcc structure can be viewed as a close stacking of atomic layers.

fcc and hcp have the same packing density (close packed).



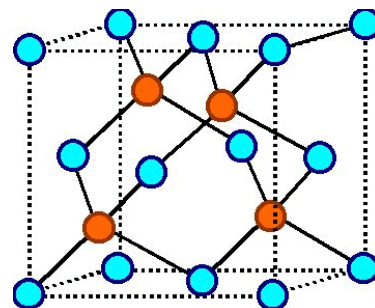
Examples of **lattice + nontrivial basis**, different kinds of atoms

1. Zinc blende (ZnS)

fcc lattice + 2-atom basis, Zn at $(0,0,0)$, S at $\frac{a}{4}(1,1,1)$

Replacing Zn and S by C \rightarrow diamond structure

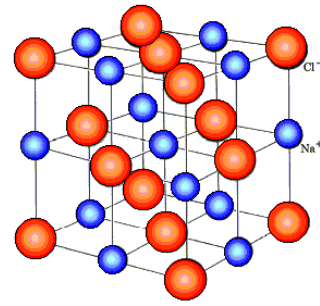
Coordination number = 4



2. NaCl structure

fcc lattice + 2-atom basis, Na at $(0,0,0)$, Cl at $\frac{a}{2}(1,1,1)$

Two interpenetrating fcc lattices.

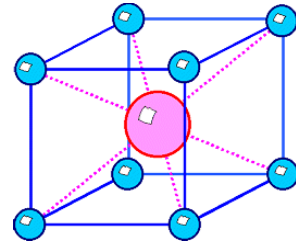


3. CsCl structure

sc lattice + 2-atom basis, Cs at $(0,0,0)$, Cl at $\frac{a}{2}(1,1,1)$

Replacing Cl by Cs \rightarrow bcc Cs

Coordination # = 8

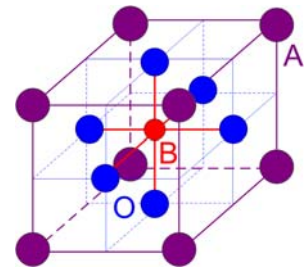


4. Perovskite structure (CaTiO₃, or ABO₃ generally)

sc lattice + 5-atom basis

Ca²⁺ at A site, Ti⁴⁺ at B site, and 3 O atoms

Key feature: oxygen cage. Many closely related variations.
Examples: complex oxides, high-temp superconductors,
colossal magnetoresistive materials, ferroelectrics,



Symmetry (Brief review in terms of group theory)

Space group: all symmetry operations $\{P|T\}$ that leave the crystal invariant, where P is a point operation (leaving one point fixed) including rotation, inversion, reflection, and combos, and T is a translation. T might be a translation by $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, but it could also involve a nontrivial fraction of \mathbf{R} in more complicated cases:

Glide planes – mirror reflection + translation by, for example, $\frac{1}{2}$ of a primitive lattice vector

Screw axes – rotation by π + translation by, for example, $\frac{1}{2}$ of a primitive lattice vector

Translation group: all translations by $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$; an invariant subgroup of the space group (*invariant* under all symmetry transformations). Note $\{I|T\}$ (I being the identity operator) is not necessarily the translation group, as there can be additional translations involving a nontrivial fraction of \mathbf{R} associated with glide planes and screw axes.

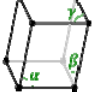



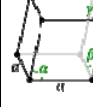
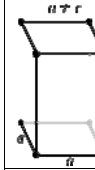




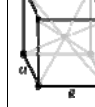



Point group: all operations $\{P|I\}$. Not necessarily a subgroup of the space group because of glide planes and screw axes. It leaves the point lattice & Wigner Seitz cell invariant.

Factor group: (Space group) \div (Translation group); isomorphic to the point group.

	Bravais lattice	Crystal structure
Point group	7 (crystal systems)	32
Space group	14 (lattice structures)	230

Listed in M.J. Berger, **Elementary Crystallography**, Wiley, NY, 1963.

See textbook or http://en.wikipedia.org/wiki/Crystal_structure

7 crystal systems	Triclinic	Monoclinic	Orthorhombic	Hexagonal	Rhombohedral (trigonal)	Tetragonal	Cubic
14 Bravais lattices	$\alpha, \beta, \gamma \neq 90^\circ$ 	Simple $\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$ 	Simple $a \neq b \neq c$ 	$a \neq c$ 	$\alpha, \beta, \gamma = 90^\circ$ 	Simple $a \neq b \neq c$ 	Simple 
		Base-centered $\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$ 	Base-centered $a \neq b \neq c$ 			Body-centered $a \neq b \neq c$ 	Body-centered 
			Body-centered $a \neq b \neq c$ 				Face-centered 
			Face-centered $a \neq b \neq c$ 				

Bravais lattices:

Consider the highest symmetry, the cubic point group O_h (full symmetry group of a cube); there are 3 Bravais lattices having this point group symmetry: sc, fcc, and bcc.

Distorting the system in various ways results in additional crystal systems and lattice structures that have lower symmetries (fewer symmetry operations).

The triclinic structure has the lowest symmetry.

For systems with one atom per unit cell, there are only 14 possible structures (Bravais lattices).

Crystal structures:

The number of possible structures explodes to 230 as you add a basis (which tends to reduce the number of symmetry operations).

For enumerating all possible structures, the exercise is to reduce the symmetry in a systematic manner. Make sure that all structures are distinct. It is an interesting but time-consuming exercise.