Crystal Structures

{ Kittel Chpt 1
  Ashcroft + Mermin Chpt 4

In most solids, the ions sit at the sites of a well defined periodic lattice of points. We now seek to describe ~~the lattice of ions~~ the geometric structure of the lattice of ions.

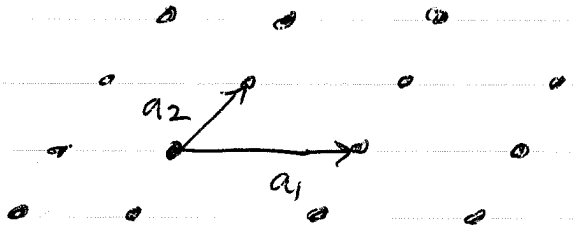
Bravais Lattice - specifies the periodic ~~of~~ array in which the ~~units~~ units of the crystal are organized. Two equivalent definitions of the Bravais lattice are:

a) An infinite array of discrete points where the arrangement and orientation appears exactly the same from whichever point the array is ~~set~~ viewed -

b) A 3-dimensional Bravais lattice consists of all points $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ where $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are not all in the same plane, and n_1, n_2, n_3 are any integers.

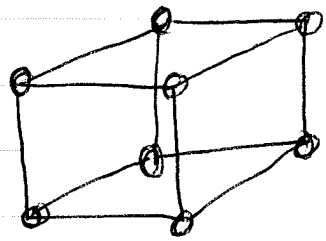
$\vec{a}_1, \vec{a}_2, \vec{a}_3$ are called the primitive vectors of the Bravais lattice - they are not unique. (primitive vectors sometimes called the basis vectors)

An example of a 2-d Bravais lattice with no special symmetry is given by $\vec{a}_1$, $\vec{a}_2$ of different length, with a angle $\alpha \neq \frac{2\pi}{\text{integer}}$ between them



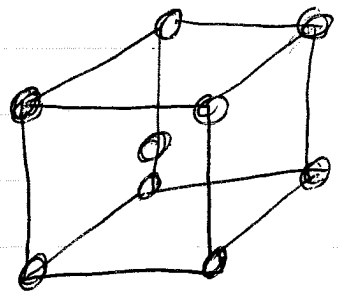
Examples of Bravais Lattices

3D simple cubic lattice $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = a\hat{y}$, $a_3 = a\hat{z}$



3D Body centered cubic (bcc)

take simple cubic and put an extra atom in the center of each cubic cell



looks like two interpenetrating simple cubic lattices

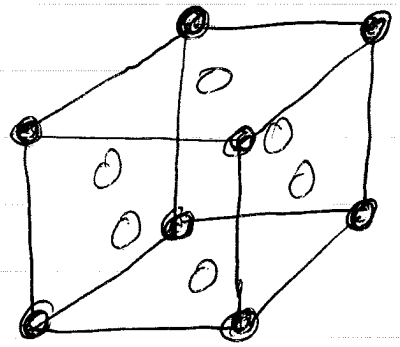
primitive vectors:

$$\vec{a}_1 = a\hat{x}\,,\ \vec{a}_2 = a\hat{y}\,,\ \vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$$

or a more symmetric choice:

$$\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z}-\hat{x})\,,\ \vec{a}_2 = \frac{a}{2}(\hat{z}+\hat{x}-\hat{y})\,,\ \vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}-\hat{z})$$

3D face centered cubic (fcc)



take a single cubic lattice and add an atom to the center of every face of each cubic cell

primitive vectors

$$\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z})$$
$$\vec{a}_2 = \frac{a}{2}(\hat{z}+\hat{x})$$
$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y})$$

bcc and fcc are very common lattice structures. Single cubic is very rare (only α-phase of polonium under normal conditions)

fcc: Ar, Ag, Al, Au, Ca, Ce, β-Co, Cu, Ir, Kr, La, Ne, Ni, Pb, Pd, Pr, Pt, δ-Pu, Rh, Sc, Sr, Th, Xe, Yb

lattice constant $a \sim 3-6$ Å

bcc: Ba, Cr, Cs, Fe, K, Li, Mo, Na, Nb, Rb, Ta, Tl, V, W

$a \sim 3-6$ Å

Bravais Lattice - this term can refer to either the set of points, or the set of vectors $\vec{R} = \sum_i n_i \vec{a}_i$.

coordination number - the number of points in a Bravais lattice that are closest to a given point is the coordination number z. These closest points are the "nearest neighbors" of the given point. Each point has the same coordination number

s.c. $z = 6$

b.c.c $z = 8$

fcc $z = 12$

primitive cell - a volume of space, that when translated by all vectors $\vec{R}$ in the Bravais lattice, will fill all of space without any overlaps or voids.

the primitive cell is not unique just as the choice of primitive vectors $\vec{a}_i$ ~~are not~~ is not unique.

For a given set of primitive vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ then the volume swept out by the set of points

$$\vec{r} = x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3$$

with $0 \le x_i \le 1$, is an example of a primitive cell.

Since the primitive cell must contain only one Bravais lattice point, the volume

v of a primitive cell must be such that

$V = Nv$ $\quad N$ = total number of lattice points

V = total volume

$\Rightarrow v = \frac{V}{N} = \frac{1}{n}$ $\quad n$ = density of BL points.

↖ v is independent of choice of the primitive cell

The primitive cell need not have the full symmetry of the crystal

unit cell or conventional cell – a volume that fills up all space without overlaps or voids when translated by some particular subset of vectors of the Bravais lattice. The unit cell is bigger than the primitive cell, and usually chosen for convenience with the symmetry of the lattice.

For example, for bcc or fcc one can take as the unit cell the single cubic cell which is decorated to form the bcc or fcc structure. The parameters that specify the size of the unit cell are called the lattice constants

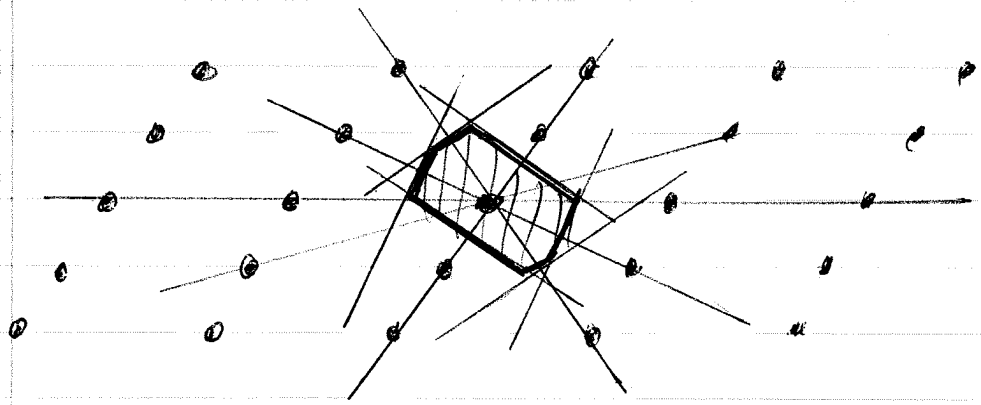
Wigner Seitz cell

This is a uniquely defined choice for a primitive cell that has the full symmetry of the Bravais lattice. We define it as follows:

Choose a point $\vec{P}$ in the Bravais lattice. The region of space closer to $\vec{P}$ than to any other point $\vec{P}'$ in the Bravais lattice is the Wigner Seitz cell.

Since above definition makes no reference to any particular set of primitive vectors, the W-S cell has all the same symmetries of the Bravais lattice.

To construct the W-S cell, draw lines from $\vec{P}$ to all other points $\vec{P}'$ in the Bravais lattice. Bisect each such line with a plane. The inner envelope of these planes is the surface of the W-S cell.



example in 2D
shaded region is W-S cell

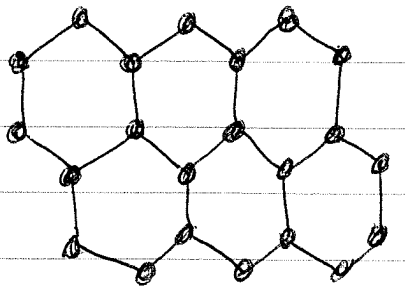
see Kittel or AM for W-S cells of 3D BL

Crystal Structure – Bravais Lattice with a basis

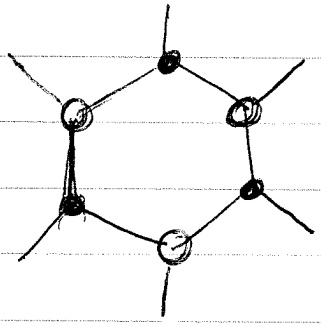
Crystals can form periodic structures which are NOT Bravais lattices – all points are not equivalent, ~~exactly~~ either due to positioning of atoms or because different atoms occupy different sites

Such structures are called a lattice with a basis and are described by an underlying B-L plus a set of basis vectors that give the positions of the atoms with respect to each B-L site $\vec{R}$

example: honeycomb lattice in 2D



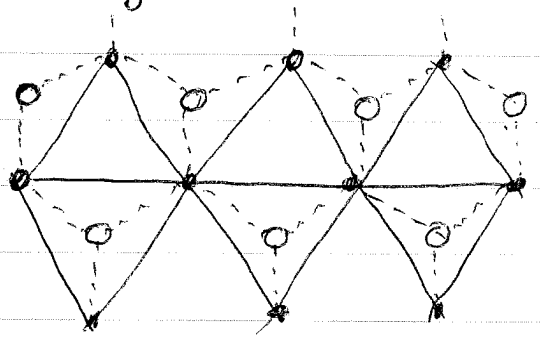
← this is not a Bravais-lattice!



the ● sites are all equivalent and the ○ ~~sites~~ sites are all equivalent, but the ● sites are NOT equivalent to the ○ sites!

Note: ○ ~~atoms~~ sites all have a ● neighbor to the upper right  whereas ● sites do not – they have a neighbor to the lower left  . Hence the orientational environment of ● sites is different from that of ○ sites

But we can describe the honeycomb lattice as a 2D triangular lattice with a two point basis. Let the • sites describe the sites $\vec{R}$ of a triangular B-L.



dashed lines show the honeycomb structure. solid lines show the underlying triangular BL

primitive vectors $\begin{cases} \vec{a}_1 = a\hat{x} \\ \vec{a}_2 = a\left(\frac{\hat{x}}{2} + \frac{\sqrt{3}}{2}\hat{y}\right) \end{cases}$

basis vectors $\begin{cases} \vec{d}_1 = 0 & \text{gives • sites} \\ \vec{d}_2 = \frac{a}{\sqrt{3}}\hat{y} & \text{gives o sites} \end{cases}$

sites of honeycomb lattice given by

$\{\vec{R} + \vec{d}_1,\ \vec{R} + \vec{d}_2\}$ with $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2$,

n_1, n_2 integers

We could describe the fcc and bcc Bravais lattices as a single cubic lattice with a basis

$\Rightarrow$ primitive vectors $\begin{cases} \vec{a}_1 = a\hat{x} \\ \vec{a}_2 = a\hat{y} \\ \vec{a}_3 = a\hat{z} \end{cases}$

basis vectors bcc: 2 point basis $\begin{cases} \vec{d}_1 = 0 \\ \vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z}) \end{cases}$

basis vectors fcc: 4 point basis $\begin{cases} \vec{d}_1 = 0 \\ \vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}) \\ \vec{d}_3 = \frac{a}{2}(\hat{y}+\hat{z}) \\ \vec{d}_4 = \frac{a}{2}(\hat{z}+\hat{x}) \end{cases}$

Diamond structure

Two interpenetrating fcc lattices displaced along the body diagonal of the cubic unit cell by 1/4 the length of the diagonal
(See Ashcroft + Mermin Fig 4.18

fcc Bravais lattice with two point basis

$$\vec{d}_1 = 0$$
$$\vec{d}_2 = \frac{a}{4}(\hat{x}+\hat{y}+\hat{z})$$

coordination number $z = 4$ - tetrahedral bonds
examples: C, Si, Ge, α-Sn

Bonde lengths from aton at $\vec{d}_1 = \frac{a}{4}(\hat{x}+\hat{y}+\hat{z})$ to origin and faces are the same.

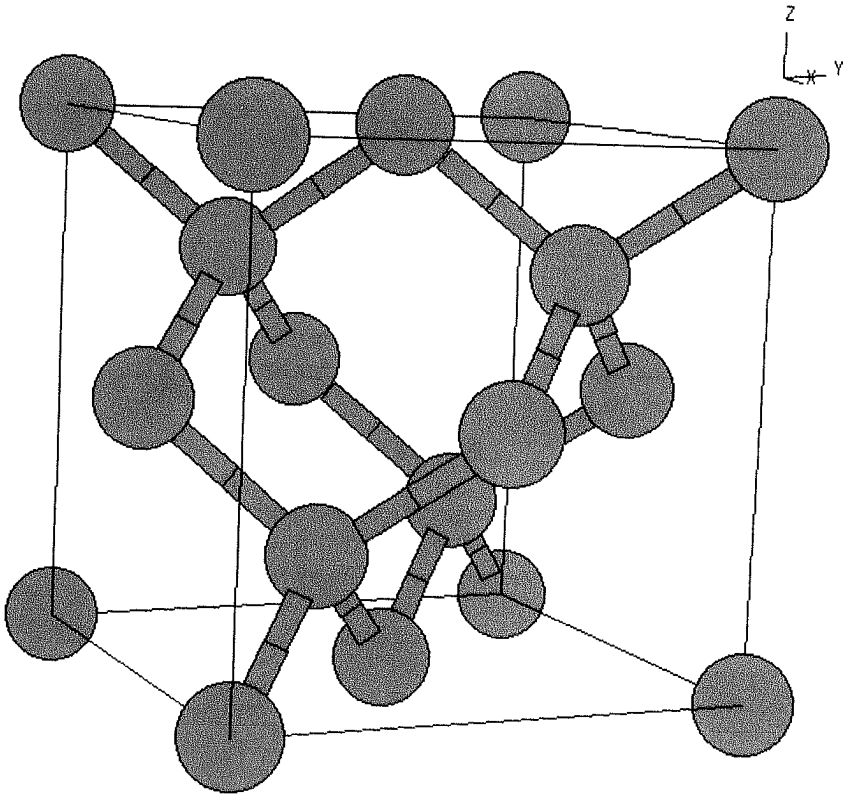
$$|\vec{d}_1| = \frac{\sqrt{3}}{4}a$$

$$\left|\vec{d}_1 - \frac{a}{2}(\hat{x}+\hat{y})\right| = \left|-\frac{a}{4}\hat{x} - \frac{a}{4}\hat{y} + \frac{a}{4}\hat{z}\right| = \frac{\sqrt{3}}{4}a$$

$$\left|\vec{d}_1 - \frac{a}{2}(\hat{x}+\hat{z})\right| = \left|-\frac{a}{4}\hat{x} + \frac{a}{4}\hat{y} - \frac{a}{4}\hat{z}\right| = \frac{\sqrt{3}}{4}a$$

$$\left|\vec{d}_1 - \frac{a}{2}(\hat{y}+\hat{z})\right| = \left|\frac{a}{2}\hat{x} - \frac{a}{2}\hat{y} - \frac{a}{2}\hat{z}\right| = \frac{\sqrt{3}}{4}a$$

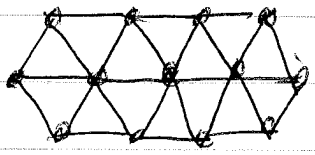
each atom of diamond structure has 4 equal length bonds to 4 nearest neighbors ~~These bonds form the edges of a tetrahedron~~

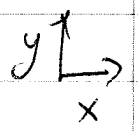


Hexagonal close packed

simple hexagonal B-lattice - obtained by stacking 2D triangular lattices directly above each other.

2D triangular lattice

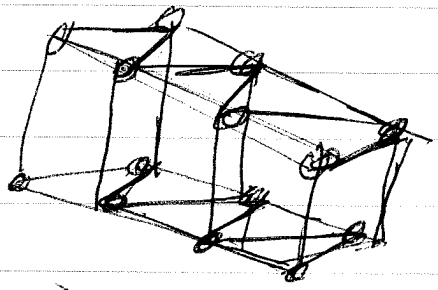




$\vec{a}_1 = a\hat{x}$

$\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$

all angles 60°



stacked triangular lattices

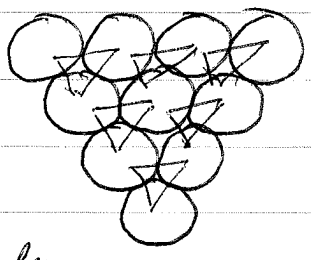
$\vec{a}_3 = c\hat{z}$

Hexagonal close packed -

two interpenetrating simple hexagonal Bravais lattices displaced by $\vec{d}_2 = \frac{\vec{a}_1}{3} + \frac{\vec{a}_2}{3} + \frac{\vec{a}_3}{2}$

with $c = \sqrt{\frac{8}{3}}\,a = 1.63299\,a$

obtained by close packing of hard spheres

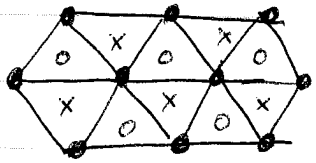


1st layer

put 2nd layer on top of "holes" in 1st layer - there are two choices how to do this - one choice is given by the triangles in picture on the left.

For the 3rd layer, put the sphere on the "holes" in the 2nd layer, so that they lie directly above the spheres in the 1st layer. This gives the hexagonal close-packed structure.

For each layer, there are always two choices



Let • be sites of 1st layer. Then can always put next layer down on top of the O's or the X's.

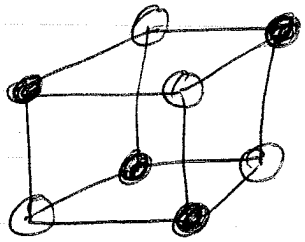
If put 2nd layer on the O's, then the 3rd layer can go on either the X's or the •'s. We can call these three sets of sites, A, B, C (for •, O, X).

Then the close packing corresponding to the stacking sequence ABABAB.... is the hexagonal closed packed. The stacking sequence ABCABCABC... turns out to give the fcc Bravais lattice!

Certain rare earth crystals have stacking ABACABAC...

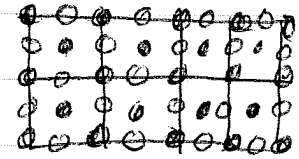
Could in principle ~~do~~ make the choice between the two possibilities at each layer randomly. This would give a random close packed structure.

NaCl structure



Space points where atoms sit is a single cubic Bravais lattice BUT sites are not equivalent since they are alternately occupied by different atoms (Na and Cl for salt)

Need to describe this as a fcc Bravais lattice with two point basis $\vec{d}_1 = 0$, $\vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$



- Na at sites of fcc
- Cl at center of cube

(See A+M Fig 4.24)

Cesium Chloride Structure

equal numbers of cesium and chlorine at points of a bcc lattice so that each has 8 neighbors of the other kind.

described by single cubic Bravais lattice of Cs with Cl at center of unit cube

$\vec{d}_1 = 0$ Cs

$\vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$ Cl

Zincblend Structure equal nubers of zinc and sulfur on a deamond lattice so that each has 4 nearest neighbors of the other type.