1. Crystal Structures

Idealized abstraction. We've assumed that the atoms are at fixed points in space – so we are ignoring zero-point effects and thermal effects.

1.1 Translational Symmetry & Bravais Lattices

This is at the heart of solid state (crystal) physics – assumption of translational symmetry. Take an infinite structure in 3D, or pattern in 2D. Make some non-trivial translation, and you should end up with the same thing.

We choose a and b as non-colinear relations which map the pattern onto itself. From this, we can say that $\underline{R} = n_1\underline{a} + n_2\underline{b}$ will also map the pattern onto itself.

Equivalent Points

Look at a honeycomb pattern. All of the points in this pattern are the same, but for some of them (50%) the environment is in a different orientation (rotated through 180 degrees).

Equivalent points have the same environment in the same orientation.

If we choose one of these points as a lattice point, only the other equivalent points are lattice points. Translation between equivalent points is not a symmetric translation of that pattern.

The set of lattice vectors $\{\underline{R}\}$ is the set of position vectors of equivalent points.

If we separate out the equivalent points from the honeycomb, then we get a special type of lattice. The angle between a and b ($|a| = |b|$) (i.e. distances to other points nearby) is $\gamma = 120°$. Recall that $\underline{R} = n_1\underline{a} + n_2\underline{b}$.

Translational symmetry in 2D can be characterized by a 2D lattice, or net. In 3D, it can be characterized by a Bravais lattice.

There are two equivalent interpretations of a Bravais lattice;

1. It is an infinite array of points, which appears exactly the same (in the same orientation) when viewed from any one of the points.
2. It consists of all points with position vectors $\underline{R}$ of the form $\underline{R} = n_1\underline{a} + n_2\underline{b} + n_3\underline{c}$, where $\underline{a}$, $\underline{b}$ and $\underline{c}$ are any three non-coplanar vectors and the n's range through all positive or negative integer values.

1.2 Basis and Unit Cell

Back to the honeycomb lattice. What is it that repeats itself with the translational symmetry to give you the whole pattern? Take a rhombus (a parallelogram with equal sides). If you take what is in this shape, and repeat it at each position defined by the lattice, then you will get the whole pattern. In this case, the two blobs in each rhombus are what we need to generate the whole pattern. Notice that the corners of these parallelograms form a lattice themselves; they are equivalent points, all at the centre of the hexagon of the honeycomb lattice.

Lattice + Basis = Structure

In 3D, use the 3D version of a parallelogram, a parallelepiped (or another tessellating shape).

Start with a parallelogram whose edges are the lattice vectors. Associate the contents, the basis, with all lattice points.

Note that the choice is not unique, just like the choice of lattice vectors. Sometimes, the basis is defined within a shape other than a parallelogram (parallelepiped) provided that it tessellates the plane, or the equivalent in 3D – i.e. it fills all of space without overlapping of leaving gaps.

A *crystal structure* consists of identical copies of the *basis* located at all points of a Bravais lattice.

A *primitive unit cell* is the box that contains the basis.

A unit cell may be chosen to contain more than one copy of the basis. In this case, we would describe it as a *non-primitive unit cell*. This is often done to preserve orthogonality, or to reflect some symmetry that is there in the structure but which may not be apparent in the primitive unit cell.

The choice of unit cell and the lattice vectors are inseparable.

A *unit cell* is a region that fills all of space without either overlapping or leaving voids, when translated through some subset of the vectors of a Bravais lattice. The unit cell is *primitive* if the same is true for all of the vectors of a Bravais lattice.

A *conventional unit cell* may be chosen which is non-primitive, usually to preserve the orthogonality of the lattice vectors.

1.3 Classifying Lattices: Symmetry (1) 2D

If we take any lattice, we can look to see what symmetry it has. Lattices may be classified by the symmetries that they possess.

The *square lattice* has $|\underline{a}| = |\underline{b}|$, and $\gamma = 90°$. It also has a four-fold rotational symmetry. There are also various mirror planes.

Symmetry operations are operations that map the pattern (structure in 3D) into itself. These can be rotation, reflection, translation and inversion $(\underline{r} \to -\underline{r})$.

A $\frac{2\pi}{n}$ rotation is called an n-fold rotation. A square lattice has a 4-fold axis. $n = 2, 3, 4, 6$ for nets and Bravais lattices.

The square lattice also has 4 generic mirror planes – x, y, and two diagonal ones.

Hexagonal Lattice, $|\underline{a}| = |\underline{b}|$, $\gamma = 120°$

Rectangular Lattice, $|\underline{a}| \neq |\underline{b}|$, $\gamma = 90°$

Centered Rectangular Lattice, $|\underline{a}| \neq |\underline{b}|$, $\gamma = 90°$

Oblique Lattice, None of the above.

1.4 Classifying Lattices: Symmetry (2) in 3D

There are 14 Bravais lattices. See e.g. the 8th edition of Kittel, p9.

The convention is that, if you have 3 non-coplanar vectors, $\underline{a}$, $\underline{b}$ and $\underline{c}$, the angles between them are known as α (between b and c) β (between a and c) and γ (between a and b)

Four special cases:

$|\underline{a}| = |\underline{b}| = |\underline{c}|$; $\alpha = \beta = \gamma = 90°$:

Simple cubic
Body-centered cubic
Face-centered cubic

$|\underline{a}| = |\underline{b}| \neq |\underline{c}|$; $\alpha = \beta = 90°$, $\gamma = 120°$.

Hexagonal lattice

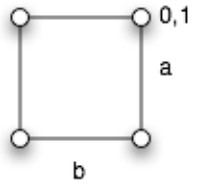
Projected Crystal Structures

The method for representing 3D unit cells is to project down the c-axis. Label with fractional c-coordinates.

$\underline{r} = x\underline{a} + y\underline{b} + z\underline{c}$

Polonium

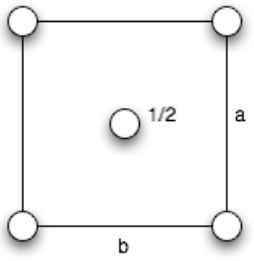
(each dot is a Po atom)



What is the Lattice? Simple cubic.

What is the basis? One Po atom $(x, y, z) = (0,0,0)$

Chronium



$a = b$

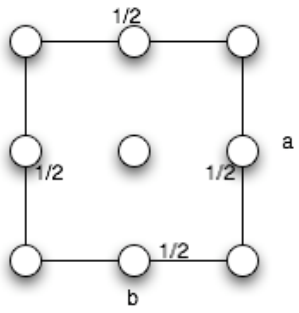
This denotes a cube with at atom at each corner, plus one in the center… (I think)

What is the Lattice? Body-centered cubic

What is the basis? One Ch atom at $(0,0,0)$. The one in the centre is generated by the symmetry of the lattice.

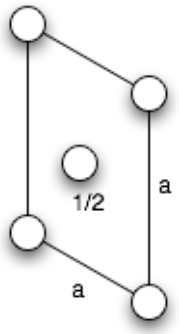
Also adopted by αFe (one of the two types of iron), Na, W (Tungsten), etc.

Nickel



$a = b$
This represents a cube with atoms at corners, the middle of each face (the one in the centre is the one that is in the middle of the face facing us; the others (denoted by 0.5) are in the other faces…) (I think)
Lattice: face-centered cubic
Basis: one nickel atom at $(0,0,0)$. Total number of atoms in the unit cell: 4.
Also adopted by Au, Pt, γFe, Pb, Le.

Cobalt



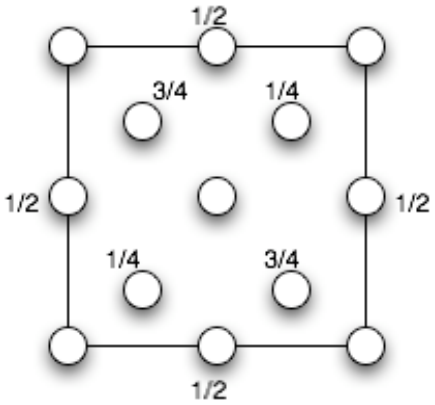
Angle is $120°$.
Lattice: hexagonal
Basis: two Co atoms, one at $(0,0,0)$ other at $\left(\frac{2}{3},\frac{1}{3},\frac{1}{2}\right)$
The structure is called Hexagonal close-packed.
Also adopted by Be, Zn, Cd.

Note on "close-packing":
Hexagonal close packed (hcp) and monatomic fcc pack hard spheres at high density.
For fcc, $|\underline{a}| = |\underline{b}| = |\underline{c}|$.
For hcp, $|\underline{a}| = |\underline{b}|$. No symmetry requirement for c unless you stack spheres, where is it $|\underline{c}| = \sqrt{\frac{8}{3}}|\underline{a}| \sim 1.63|\underline{a}|$.

Metal	c/a
Co	1.62
Be	1.56
Zn	1.86
Gal	1.59

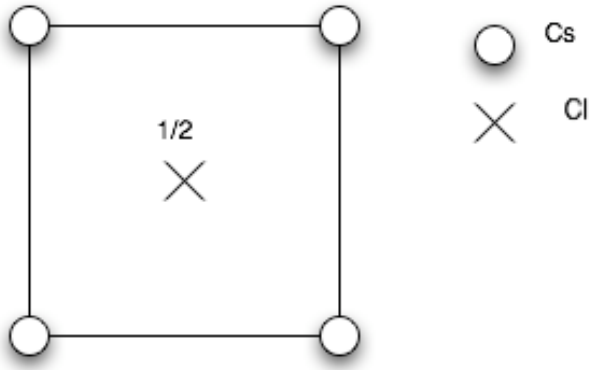
If we take hexagonal rafts of hard spheres, and start with layer A. The next layer nestles as layer B. The third layer can either go over the layer A, or be in a new position C.
hcp: ABABAB… $[AB]_n$
fcp: ABCABC… $[ABC]_n$

1.5 More Crystal Structures
Silicon



Lattice: fcc
Basis: Two Si atoms at $(0,0,0)$ and $\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$.
$\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$ is not a lattice point if $(0,0,0)$ is, as there is no centre atom.
Structure is the diamond structure – also C (diamond), Ge.

CsCl

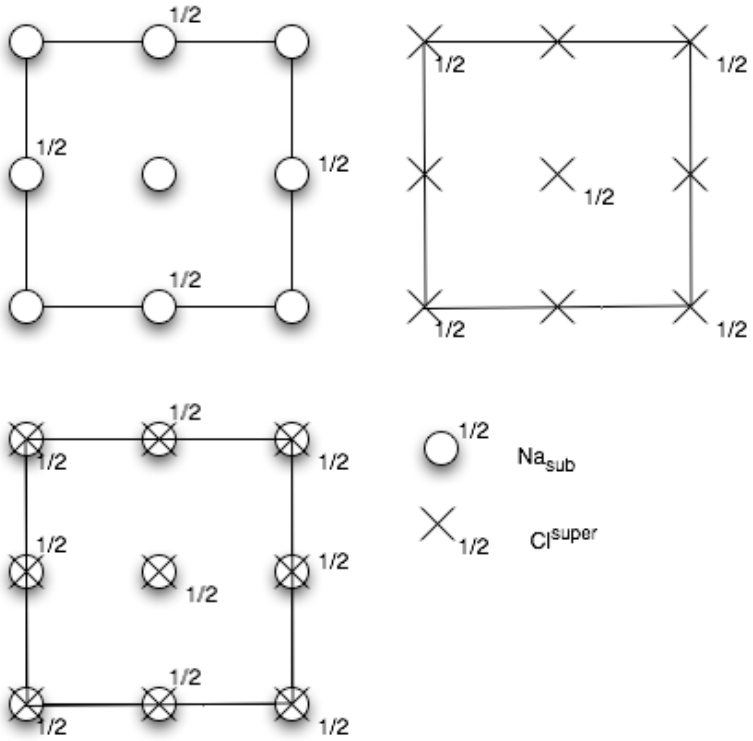


Lattice: simple cubic

Basis: one Cs atom at $(0,0,0)$, one Cl at $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$.

Coordination # is the number of nearest neighbours of the opposite sort. Here, it is 8.

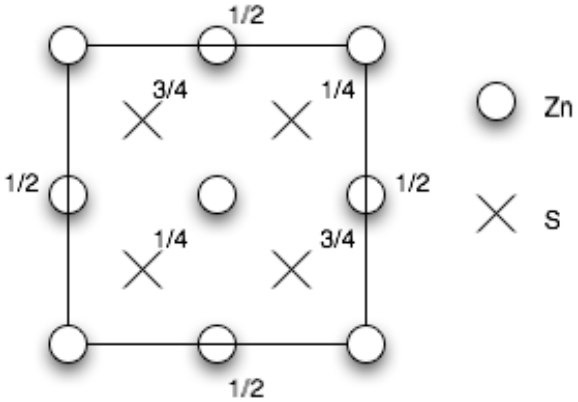
NaCl



Lattice: fcc. Basis: one Na at $(0,0,0)$, one Cl at $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$

Rocksalt structure – coordinate number 6.

ZnS, Zincblende



Lattice fcc. Basis: one Zn at $(0,0,0)$. One S at $\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$.

Coordinate number = 4.

For more info, Wychoff, "Crystal Structures", 4th edition, 1974. ("stamp collecting").