Crystal Structure

- Recall the Hamiltonian describing a system of ions, etc, that form a crystal. It has the full symmetry of 3D space (rigid motions: rotations, reflections, translations)

- Translation is particularly crucial: $\vec{r} \to \vec{r} + \vec{a}$ is a symmetry for all vectors $\vec{a}$.

- A crystal is invariant only under discrete subset of translations: $\{T_{\vec{R}}\}$, where $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$.

- Example of spontaneous symmetry breaking: physical system has less symmetry than the Hamiltonian that describes it.

  - Happens for crystalline solids, but not for liquids & gases, which are homogeneous & isotropic.

Mathematical Group Theory — Language of Symmetry

- Physicist's definition: A group is a set of symmetry operations, that is closed under composition of operations in the set.

- Precise definition:

A group is a set of elements $\{g_i\}$, and a rule for multiplying two g_i's, with the following properties:

(1) $g_i g_j = g_k$; g_k is also a group element (closure)

(2) There is a special element e satisfying
$e g_i = g_i e = g_i$. (Identity transformation)

(3) For every g_i, there is a unique g_i^{-1} satisfying
$g_i^{-1} g_i = g_i g_i^{-1} = e$. (Inverse transformations.)

(4) $(g_i g_j) g_k = g_i (g_j g_k)$. (Associativity)

NB: In general, $g_i g_j \neq g_j g_i$ (Not commutative.)

Examples of groups: Rigid motions of space, continuous translations, discrete translations, rotations, ...

- Subgroup: A subgroup is a subset of some group, which is itself also a group. (In particular, it is closed under multiplication.)

Example: Discrete translations $\{T_{\vec{R}}\}$ ($\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$) is a subgroup of the group of all translations.

- Spontaneous symmetry breaking: A larger symmetry group (e.g. continuous translations)

- Precise statement of spontaneous symmetry breaking:
  - Hamiltonian has a symmetry described by some group G.
  - The system itself has a lower symmetry described by a group H, where H is a subgroup of G.

Description of Crystal Structure

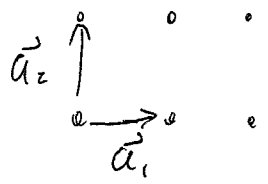
- Bravais lattice:
  - Set of points $\{\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3\}$
    - n_i integers
    - $\vec{a}_i$ must be linearly independent
    - $d=1$: $\{\vec{R} = n_1\vec{a}_1\}$
    - $d=2$: $\{\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2\}$
- Useful when $\{\vec{R}\}$ are precisely the translation vectors that are crystal symmetries.

- Simplest monatomic crystals: $\{\vec{R}\}$ give the atomic positions.

Example Bravais Lattices:

- Start with $d = 2$ (for ease of drawing)

(a) Square lattice

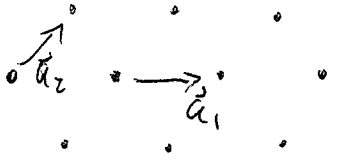


"lattice constant"

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

$$\vec{a}_2 = a\hat{y}$$

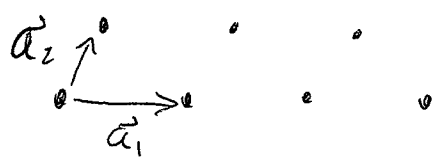
(b) Hexagonal lattice (a.k.a. triangular lattice)



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

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

(c) Oblique lattice (no special symmetries — generic choice of $\vec{a}_1 \& \vec{a}_2$)

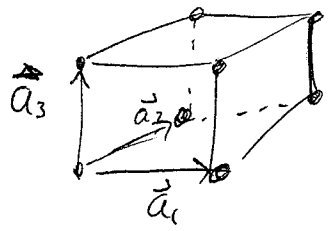


- $\vec{a}_1, \vec{a}_2 \rightarrow$ "primitive vectors"
- Choice of primitive vectors is not unique for a given lattice.

(e.g. $\vec{a}_1 = a\hat{x}$; $\vec{a}_2 = a(\hat{x}+\hat{y})$ also works for square lattice)

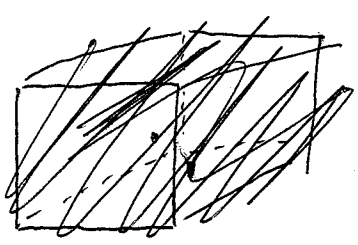
d = 3 Lattices

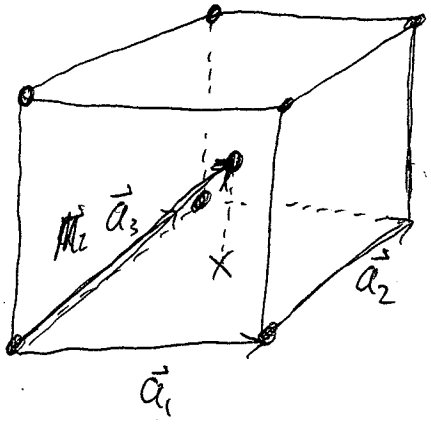
(a) Simple cubic (example material: Po)



$$\vec{a}_1 = a\hat{x}$$
$$\vec{a}_2 = a\hat{y}$$
$$\vec{a}_3 = a\hat{z}$$

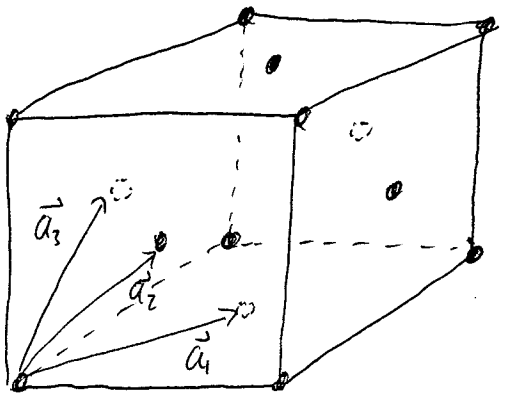
(b) BCC (ex: alkali metals Li, Na, K, ... ; Fe)





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

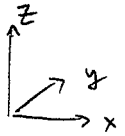
(c) FCC (ex: Cu, Ag, Au ; noble gases Ne, Ar, Kr, ...)



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

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

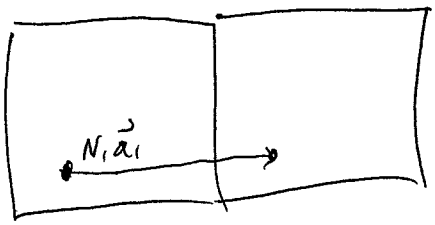
$$\vec{a}_3 = \frac{a}{2}(\hat{y}+\hat{z})$$



- Non-infinite crystals: convenient to consider putting the crystal in a periodic box ("periodic boundary conditions"):
  - $\{\vec{R}\}$; $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

    $0 \le n_1 \le N_1 - 1$
    $0 \le n_2 \le N_2 - 1$
    $0 \le n_3 \le N_3 - 1$

    } $N = N_1 N_2 N_3$ total lattice sites
  - Translation by $N_1\vec{a}_1$, $N_2\vec{a}_2$ or $N_3\vec{a}_3$ returns to same point.

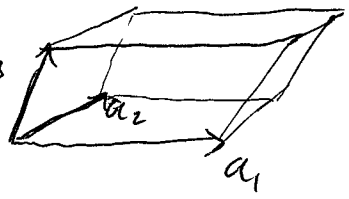


Unit Cells

- Primitive unit cell: Volume that fills space (with no overlaps) when translated by Bravais lattice vectors $\{\vec{R}\}$.

  - example: $\{x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3 \mid 0 \le x_i \le 1\}$

    parallelepiped



    cell volume $= |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$

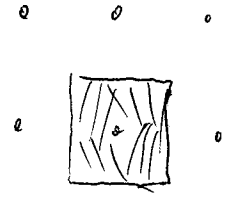
  - Infinite number of different possible primitive cells.
    (examples)
  - All primitive unit cells have same volume.
    (since each contains exactly 1 lattice point.)

- Non-Primitive Unit Cell: Volume that fills space (no overlaps) when translated by some subset of $\{\vec{R}\}$.

  - example: Conventional cubic unit cells for BCC & FCC lattices

- Wigner-Seitz Cell: Special primitive unit cell constructed by taking a given lattice point. The W-S cell is the volume enclosing that point where every point in the W-S cell is closer to the given lattice point than any other point.

ex: square:



hexagonal:

The W-S cell has the full symmetry of the lattice.

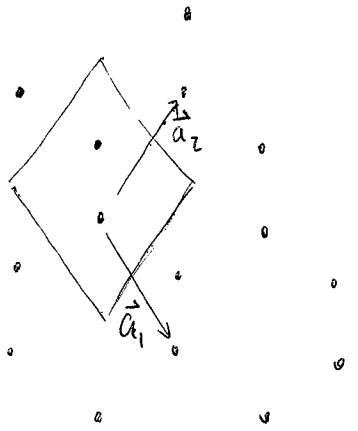
More General Crystal Structures:

- Given a Bravais lattice, can put anything in a primitive unit cell:

?	?	?
?	?	?

- Lattice with Basis
  - Basis $\begin{cases} = \text{whatever we put in unit cell} \\ = \text{some set of atoms.} \end{cases}$

Example: Honeycomb lattice (graphene)



~ $\vec{a}_1$ & $\vec{a}_2$ are primitive vectors for hexagonal Bravais lattice

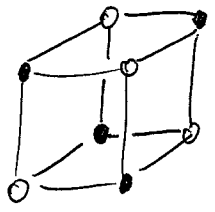
NB: All points of honeycomb lattice are equivalent by symmetry ... but not translation symmetry.

~~Specify~~

- To specify basis (of k atoms):
  - $\{\vec{c}_i\}$; $i = 1, \ldots, k$ give positions within unit cell
  - General atomic positions are $\{\vec{R} + \vec{c}_i\}$ ($\vec{R}$: Bravais lattice vectors)

- More examples (see crystal maker files online for images)

  - Diamond lattice (C (diamond), Si, Ge)
    - FCC with 2-site basis.
  - Zincblende structure (GaAs)
    - Like diamond, but 2 atoms in the basis are different.
  - Sodium Chloride structure



simple cubic, with 1/2 atoms of one type, 1/2 of other type

(Can view as FCC with 2-site basis.)

- Hexagonal Close Packed Lattice (HCP): (Mg, Ti, Zn, ...)

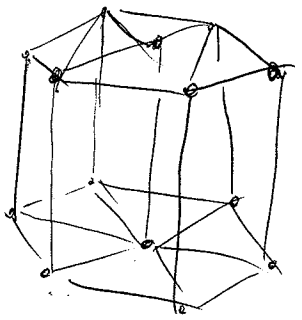
(3d)

- Based on hexagonal Bravais lattice, generated by:

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

$$\vec{a}_2 = a\left(\frac{1}{2}\hat{x} + \frac{\sqrt{3}}{2}\hat{y}\right)$$

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

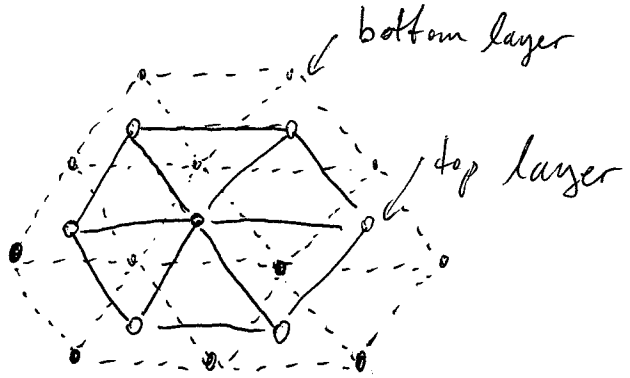


- Stacked triangular lattices.

- HCP is hexagonal Bravais lattice with basis

$$\vec{C}_1 = 0$$

$$\vec{C}_2 = \frac{\vec{a}_1}{3} + \frac{\vec{a}_2}{3} + \frac{\vec{a}_3}{2}$$



- Perovskite structure ($BaTiO_3$)
  - based on simple cubic Bravais lattice