Materials

A. Atomic structure of materials

- Crystalline solids are periodic (ie long range order). In contrast, non-crystalline materials may only have short-range order
  ↳ typically non-crystalline are weaker because stress can concentrate on irregularities.
- Atom-atom interactions ~~can~~ determine material properties. sp^3 hybridized carbon forms strong bonds with low packing density.
- Packing efficiency can be calculated by considering the smallest repeating unit

large holes are called interstices
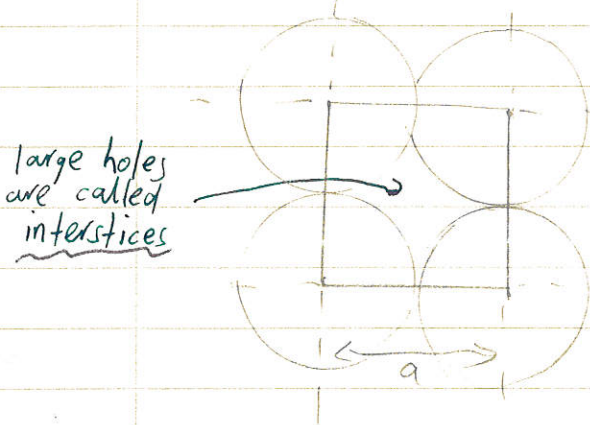
2D square packing:

$$\text{packing efficiency} = \frac{\pi a^2/4}{a^2} = \frac{\pi}{4} \approx 78.5\%$$

- For the close-packed hexagonal arrangement, the rhombus is the best repeating unit
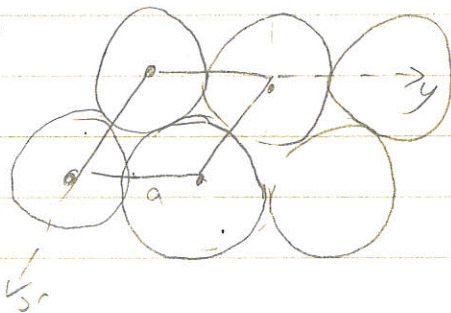
*triangle doesn't tesselate.

- In 3D, stacking these hex layers directly gives a simple hexagonal structure. But it is energetically more favourable to shear the top layer into the interstices
- However, after the 2nd layer is added, there are 2 holes that the new layer can fit into:
  - ABAB gives rise to hexagonal close packing (hcp)
  - ABC gives cubic close packing (ccp)

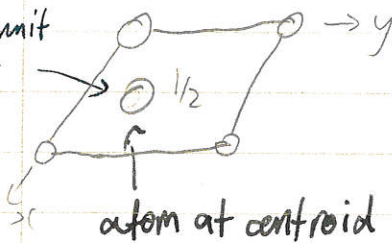· Crystal structures can be represented with plan views,
i.e z projections.

simple
hex
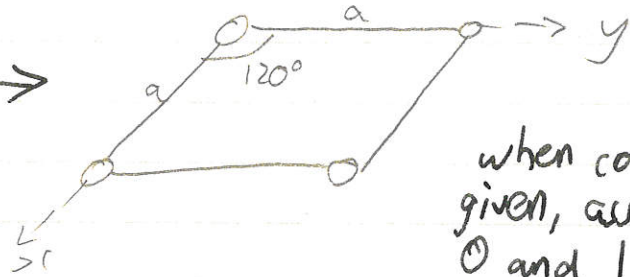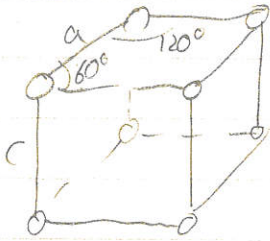
when coords not
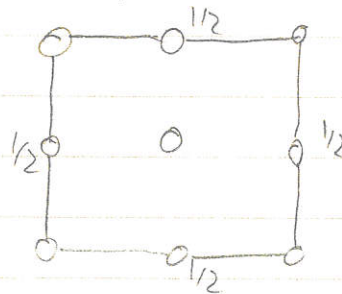given, assume at
0 and 1 (z).

hcp

ccp

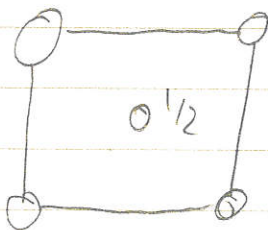height in unit
cell coords

atom at centroid

· The packing eff. of 3D structures can be calculated by
counting the number of full atoms in a unit cell and finding
their radius in terms of a. Then Vol_{atoms}/Vol_{cell}

· The body-centred cubic (bcc) structure is formed from
square layers.

atoms are ~~most~~ touching along
the body diagonal: this fact is
used to calculate packing
eff.

Interstitial structures

· Often, smaller atoms/ions (normally cations) will fit in the interstices between larger atoms.
· Goldschmidt's packing principle states that the no. of anions surrounding a cation tends to be as large as possible (but they should touch the cation).

e.g ccp

— octahedral interstice (6-fold coordination).

— tetrahedral interstice (4-fold coordination)
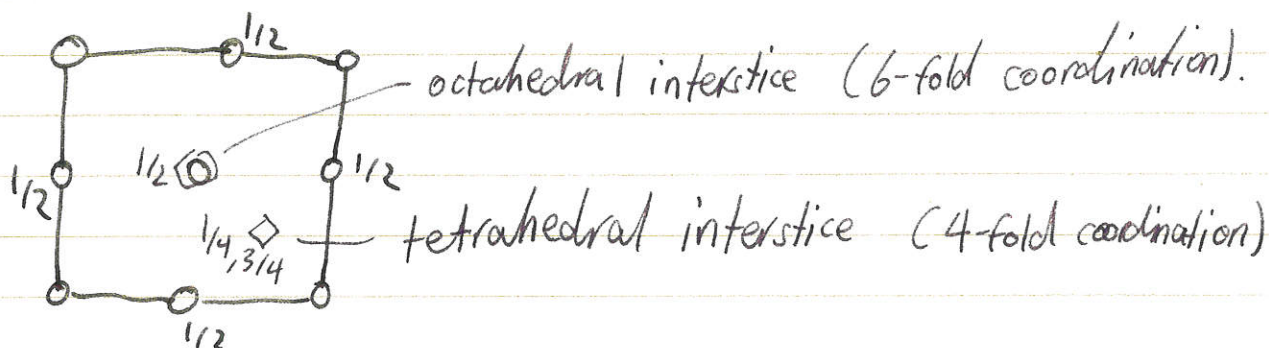
· The ideal size ratio can be calculated by looking at where the different ions touch.

A2. Patterns, lattices and symmetry

A lattice is an infinite array of points repeated periodically throughout space. The view from each lattice point is the same.

At each lattice point we can place a motif, i.e a repeating unit of pattern.
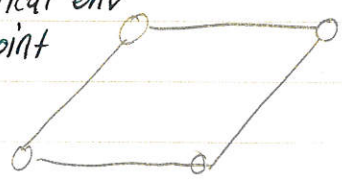
i.e structure = lattice + motif.

In this scheme, a unit cell is a parallelepiped with vertices on lattice points.

- There are only a small number of possible lattices.
- A lattice is primitive if we only have one lattice point per unit cell
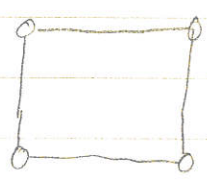
* each point in identical env
* only one lattice point per cell.

simple cubic (P)   simple hexagonal (P)

- Both face-centred cubic and bcc are lattices, but they are non-primitive.
  ↳ face-centred : F lattice
  ↳ body-centred : I lattice ← "in the middle".

- HCP is not a lattice.   hcp = hex P lattice + motif

- The Bravais Lattices are the 14 ant possible 3D lattices, often separated into 7 crystal systems depending on their rotational symmetry.
- Cubic is the most symmetric, with P, I, F lattices.

Rotational symmetry

2-fold : diad

3-fold : triad

4-fold : tetrad

6-fold : hexad

The crystallographic restriction theorem shows that there are no other ~~sy~~ rotational symmetries that form periodic structures.

mirror symmetry   Я | R
                      m

Glide lines and screw axes

· A glide line combines translation and mirror symmetry.
· In 3D, this becomes a glide plane

· A screw axis combines rotation and translation,
  i·e a generalised version of rotation.
· Represented by R_n, where R is the order of
  rotation and n is the number of translations for
  one complete turn of the helix.

e·g O $^{1/2}$ — notation: diad + tails.

2-fold rotation — 2_1 O
                      ↳ A vertical translation
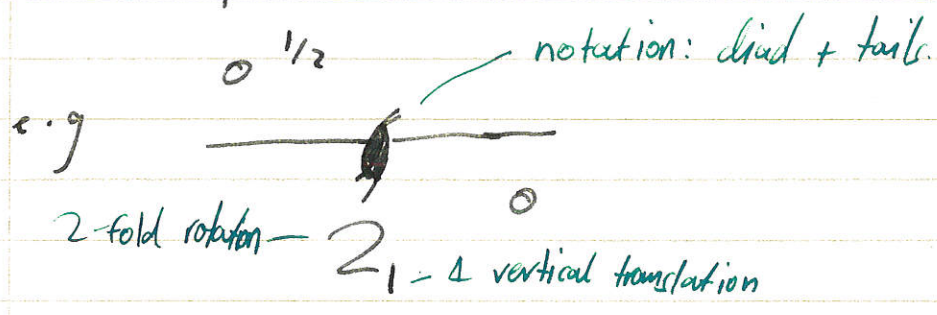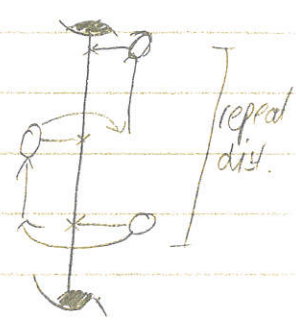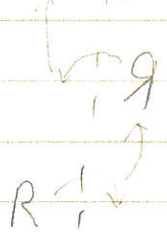
· If a crystal posseses a centre of symmetry, any line passing through
  this centre will connect equivalent faces or atoms.
· Centrosymmetric crystals are not polarised by deformation, so
  are not piezo electric.

A3. <u>Describing Crystals</u>

· A general unit cell has non-orthogonal basis vectors $\underline{a}, \underline{b}, \underline{c}$.
· Directions are expressed using integers in square brackets

e.g $[1 \ 0 \ 2] \equiv \underline{a} + 2\underline{c}$, $[1 \ \bar{2} \ 3] \equiv \underline{a} - 2\underline{b} + 3\underline{c}$

negative

· The interzonal angle is the angle between unit vectors.
   - difficult for non-orthogonal basis
   - if orthogonal : $[U \ V \ W] = U\underline{a} + V\underline{b} + W\underline{c}$
                       $= Ua\hat{\underline{i}} + Vb\hat{\underline{j}} + Wc\hat{\underline{k}}$

cubic, tetragonal, orthrhombic

   then the angle can be found with dot products.

· A <u>lattice plane</u> is a plane that passes through any three lattice points which are not in a straight line.
· A parallel set of lattice planes is referred to by Miller Indices (hkl).
· To find Miller Indices:
   1. Find intercepts on axis in terms of basis (this can be done for any origin as long as the directions are preserved)
   2. Take the reciprocals of each to give integers
   3. Put into round brackets to give $(h \ k \ l)$
· Thus a plane with index $(h \ k \ l)$ intercepts the axes at $a/h, \ b/k, \ c/l$.

· In a cubic crystal, the lattice directions are equivalent by symmetry, i.e $\pm \underline{a} = \pm \underline{b} = \pm \underline{c}$. Thus, these directions form a family, denoted by $\langle 1 \ 0 \ 0 \rangle$
· For a general $\langle U V W \rangle$, there are $3! \times 2^3 = 48$ variants.

· We can argue likewise for planes. The 6 plane faces of a cube are $(100), (\bar{1}00), (010), (0\bar{1}0), (001), (00\bar{1})$ and these are related by symmetry. This group is called a form, denoted by $\{100\}$. ← the number of variants is known as the multiplicity of the form, M_{hkl}

· It is not true in general that $[uvw] \perp (uvw)$ - only if the system is cubic.

· We can find the interplanar spacing d_{hkl} by considering the (hkl) plane closest to the origin and projecting the normal onto the axes.

direction cosines:

$x: \quad \cos\phi = \frac{h}{a} d_{hkl}$

$y: \quad \cos\theta = \frac{k}{b} d_{hkl}$

$z: \quad \cos\psi = \frac{l}{c} d_{hkl}$

If axes are orthogonal, $\cos^2\phi + \cos^2\theta + \cos^2\psi = 1$ (pythag).

$$\therefore \quad \boxed{\frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}$$

Weiss Zone Law

If $[UVW]$ is contained in a (hkl) plane, then
$$hU + kV + lW = 0. \qquad \begin{pmatrix} h \\ k \\ l \end{pmatrix} \cdot \begin{pmatrix} U \\ V \\ W \end{pmatrix} = 0$$

To find a direction common to multiple planes, solve:

$h_1 U + k_1 V + l_1 W = 0$

$h_2 U + k_2 V + l_2 W = 0$

$$[UVW] = \begin{pmatrix} h_1 \\ k_1 \\ l_1 \end{pmatrix} \times \begin{pmatrix} h_2 \\ k_2 \\ l_2 \end{pmatrix}$$