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Perspectives - Summer School 2014

Materials Science

Crystal and Atomic Arrangements

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OUMC
Summer Class

Materials Science
Crystal and Atomic Arrangements

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University of Cambridge

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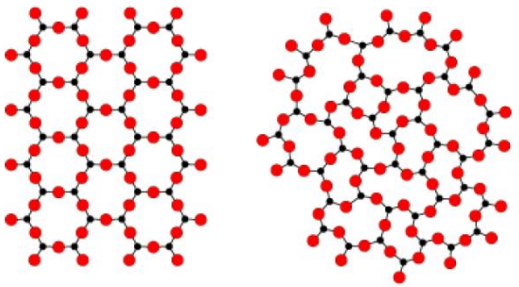
Useful Websites: www.doitpoms.ac.uk & http://www.crystalmaker.com/

Most if not all of these course materials are extracted and transcribed from the University of Cambridge's department notes: http://www.msm.cam.ac.uk/teaching/partIA/courseA/AH.pdf. Any questions can be directed to* ***Celine Wan* *at saw83@cam.ac.uk*

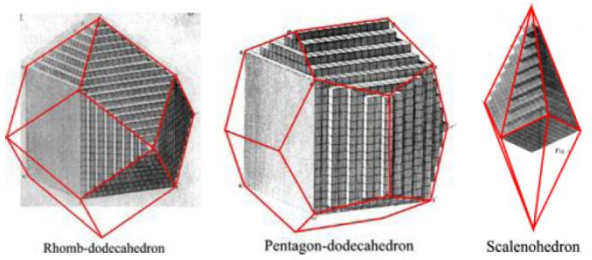
Introduction

- In this course we will concentrate solely on solids and in particular **crystalline solids**
- Solid materials can be classified into many different types and in many different ways depending on whether you want to stress, for example, their **structure** or their **mechanical** or **electrical** properties
- Traditionally we might talk about: **metals, ceramics, and polymers**, which again are very broad descriptions and with lots of overlap. For example many ceramics are good conductors and thus in some sense could be called ‘metallic’
- We could also talk about groups of materials stressing for example their **electrical and magnetic properties,** so we talk about: semiconductors, superconductors, hard and soft magnetic materials, ferroelectric materials and so on
- In addition we study solids that are **crystalline** (that have a crystal structure) and **non-crystalline.**
- A crystalline solid is one in which the atoms are arranged in a periodic fashion – we talk about ‘long-range order’.
- A non-crystalline material is non-periodic it does not have long-range order but can have ‘short range order’ where the local arrangement of atoms (and the local bonding) is approximately the same as in a crystal.



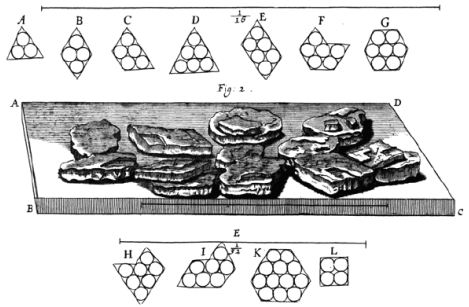
crystalline

non-crystalline



← Unit cells

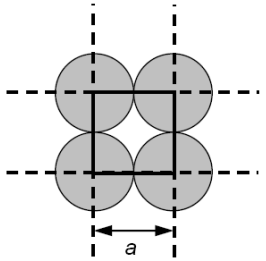
Packing of atoms to form crystals →



Packing of Atoms in 2D

- The efficiency of this 2D packing is easily calculated by considering the filling of the 2D plane with circles:

Square Packing



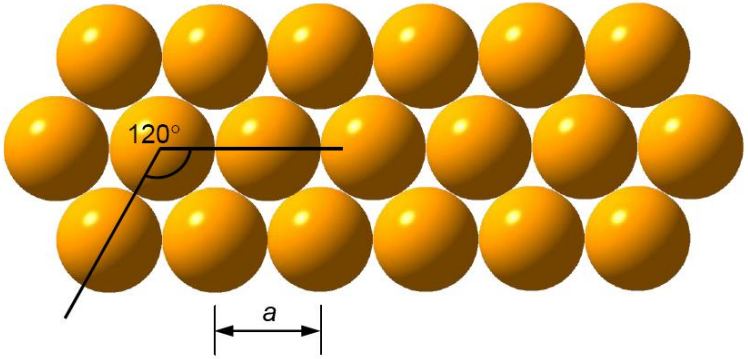
square of side *a*

circle diameter *a*

Packing of Atoms in 3D

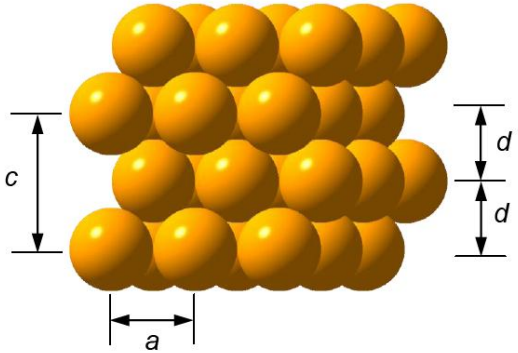
Let's extend this picture to 3D and consider the packing of spheres (to represent atoms).

Consider again the close-packed hexagonal arrangement in one layer:



If the 3rd layer atoms 'slip' into the interstices of the 2nd layer then they may end up directly above the atoms of the 1st layer.

The stacking sequence is then ABAB and this is called the **hexagonal close-packed** (hcp) structure. Seen from the side:



In the ideal hcp structure, as shown, then $d = \sqrt{\frac{2}{3}}a$ (see question sheet!)

Let's define d as the spacing between the layers (or '**planes**') of atoms, then

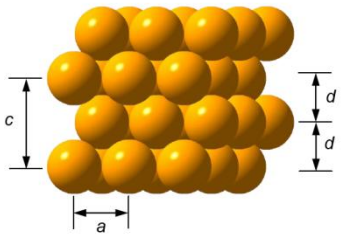
$$c = 2d = 2\sqrt{\frac{2}{3}}a = 1.633a$$

Interatomic forces in real crystals cause deviations from the ideal c/a ratio but metals such as Be, Mg and Co have hcp structures with c/a ratio close to the ideal.

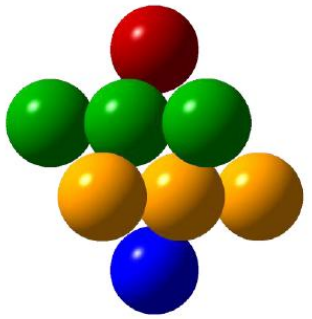
Metal	c/a ratio
Mg	1.623
Co	1.622
Be	1.567

But there is an alternative interstice in the 1st layer – let's label it as C. Atoms in the 3rd layer could be placed above C and not A.

Then the sequence would be ABCABC and the resultant structure is called the cubic close-packed (ccp) structure.



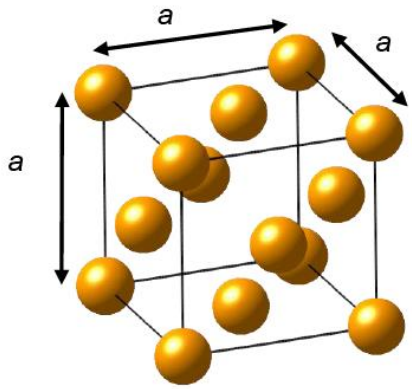
Hexagonal closed packed

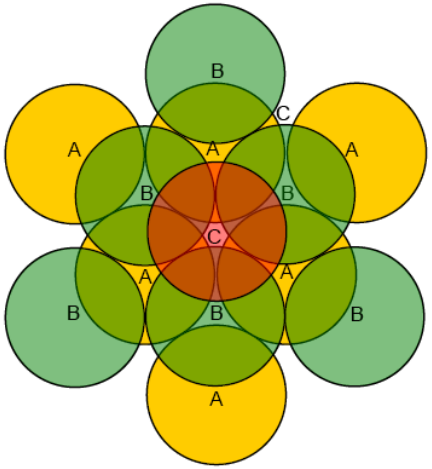


Cubic closed packed

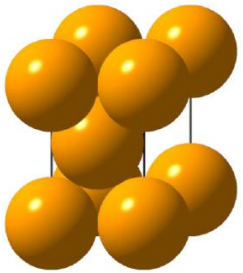
Unit Cells of the HCP and CCP Structures

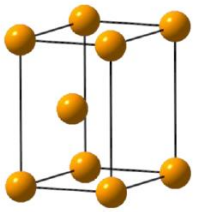
Cubic Close-Packed (ccp)



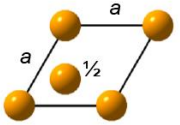


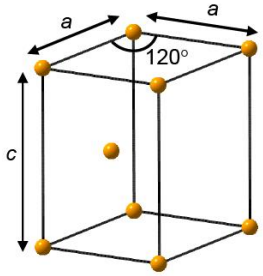
Hexagonal Close-Packed (hcp)





plan view





Unit Cell Angles = 90°, 120°

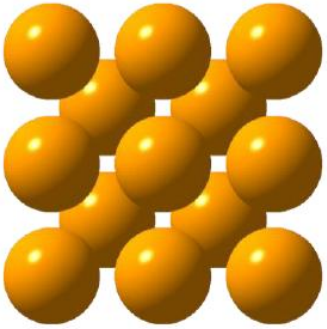
*Plan View Tips

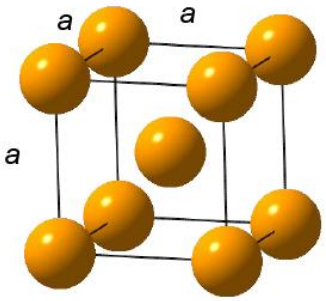
- Big, clear diagrams! Use ruler for right scale! (square etc)
- Label the atoms
- Label the axis
- BE NEAT
- Usually 4 unit cells, examples below (see data book):

Packing Efficiency of HCP

Packing Efficiency of CCP

Square Layers of Atoms





Unit Cell Angles = 90°

Here if we consider the unit cell as shown then the atoms of the 2nd layer are in the centre of the cube – we call this structure body-centred cubic (bcc).
Many metals take this structure, e.g. Cr, Mo, Ti (high temperature form), Fe (low temperature form).
In the bcc structure the atoms are most closely packed in the diagonal plane with atoms touching only along the body diagonal.

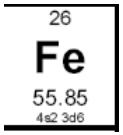
Plan View of BCC:

Question Sheet

1. Determine the packing efficiency of a 2D hexagonal array of solid circles (0.907)
2. Determine the packing efficiency of a b.c.c. structure (68%)
3. For the ideal h.c.p. structure, show that the layer spacing, d, as defined in lectures, is equal to 2/3a
4. Iron is known to be able to crystallise with three different structures: α-Fe is body centred cubic, γ-Fe is cubic close-packed and ε-Fe is hexagonal close-packed. Lattice parameters quoted in the scientific literature for these three polymorphs of Fe are a = 2.87 Å (bcc), a = 3.67 Å (ccp) and a = 2.50 Å, c = 4.02 Å (hcp).
   a) Sketch a plan view of one unit cell of each structure, as viewed down the crystallographic z-axis.
   b) Calculate the number of Fe atoms in each unit cell and the volume of each unit cell. Hence calculate the density of each polymorph of iron. (7.86Mgm-3,7.51Mgm-3, 8.52Mgm-3)

Data Book Extract

N_A Avogadro's number (mol^{-1}) **(= 6.023×10^{23})**



Structure Types

Name	Formula	System	Lattice	Motif
hcp	-	hexagonal	P	0,0,0; $^{2}/_{3},^{1}/_{3},^{1}/_{2}$
bcc	-	cubic	I	0,0,0
ccp	-	cubic	F	0,0,0
diamond	C	cubic	F	C: 0,0,0; $^{1}/_{4},^{1}/_{4},^{1}/_{4}$
caesium chloride	CsCl	cubic	P	Cl: 0,0,0; Cs: $^{1}/_{2},^{1}/_{2},^{1}/_{2}$
sodium chloride	NaCl	cubic	F	Cl: 0,0,0; Na: 0,0,$^{1}/_{2}$
zinc blende	ZnS	cubic	F	S: 0,0,0; Zn: $^{1}/_{4},^{1}/_{4},^{1}/_{4}$
wurtzite	ZnS	hexagonal	P	S: 0,0,0; $^{2}/_{3},^{1}/_{3},^{1}/_{2}$ Zn: 0,0,$^{1}/_{2}+u$; $^{2}/_{3},^{1}/_{3},u$ $(u \approx {}^{1}/_{8})$
nickel arsenide	NiAs	hexagonal	P	As: 0,0,0; $^{2}/_{3},^{1}/_{3},^{1}/_{2}$ Ni: $^{1}/_{3},^{2}/_{3},^{1}/_{4}$; $^{1}/_{3},^{2}/_{3},^{3}/_{4}$
fluorite	CaF_2	cubic	F	Ca: 0,0,0; F: $\pm(^{1}/_{4},^{1}/_{4},^{1}/_{4})$
rutile	TiO_2	tetragonal	P	Ti: 0,0,0; $^{1}/_{2},^{1}/_{2},^{1}/_{2}$ O: $\pm(u,u,0)$; $\pm(^{1}/_{2}+u,^{1}/_{2}-u,^{1}/_{2})$ $(u \approx 0.30)$
perovskite	$CaTiO_3$	cubic	P	Ti: 0,0,0; Ca: $^{1}/_{2},^{1}/_{2},^{1}/_{2}$ O: $^{1}/_{2}$,0,0; 0,$^{1}/_{2}$,0; 0,0,$^{1}/_{2}$