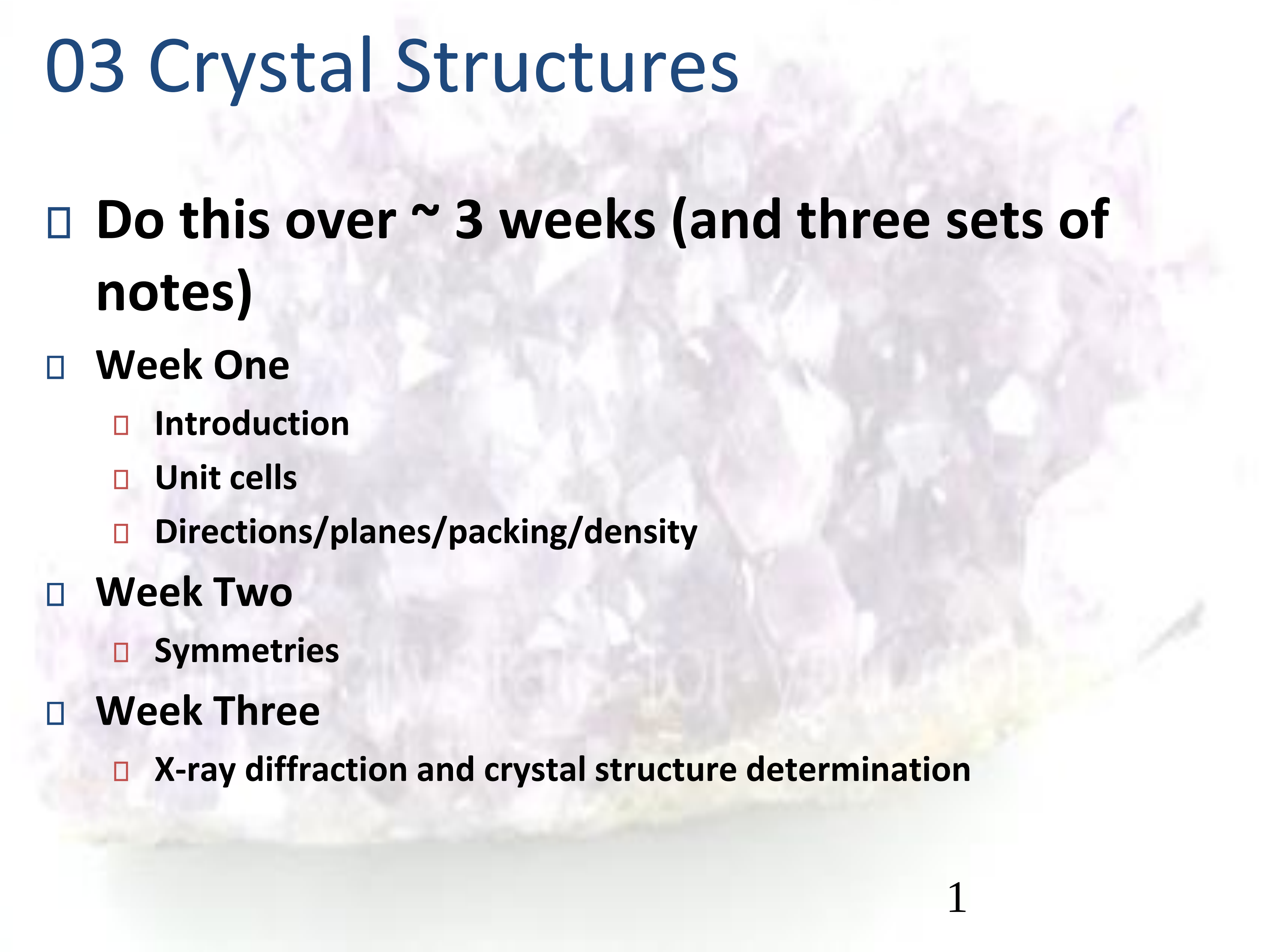
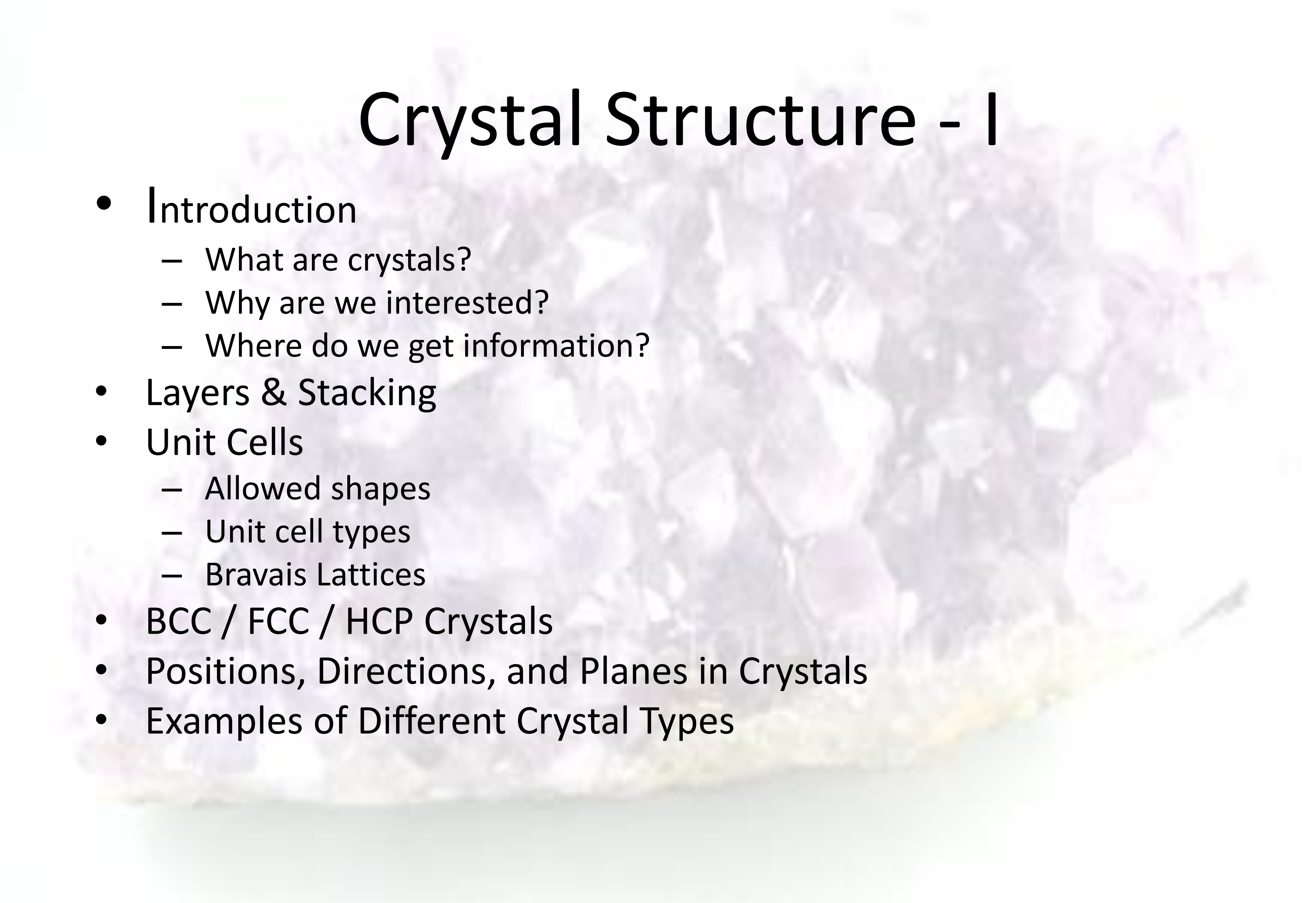
03 Crystal Structures



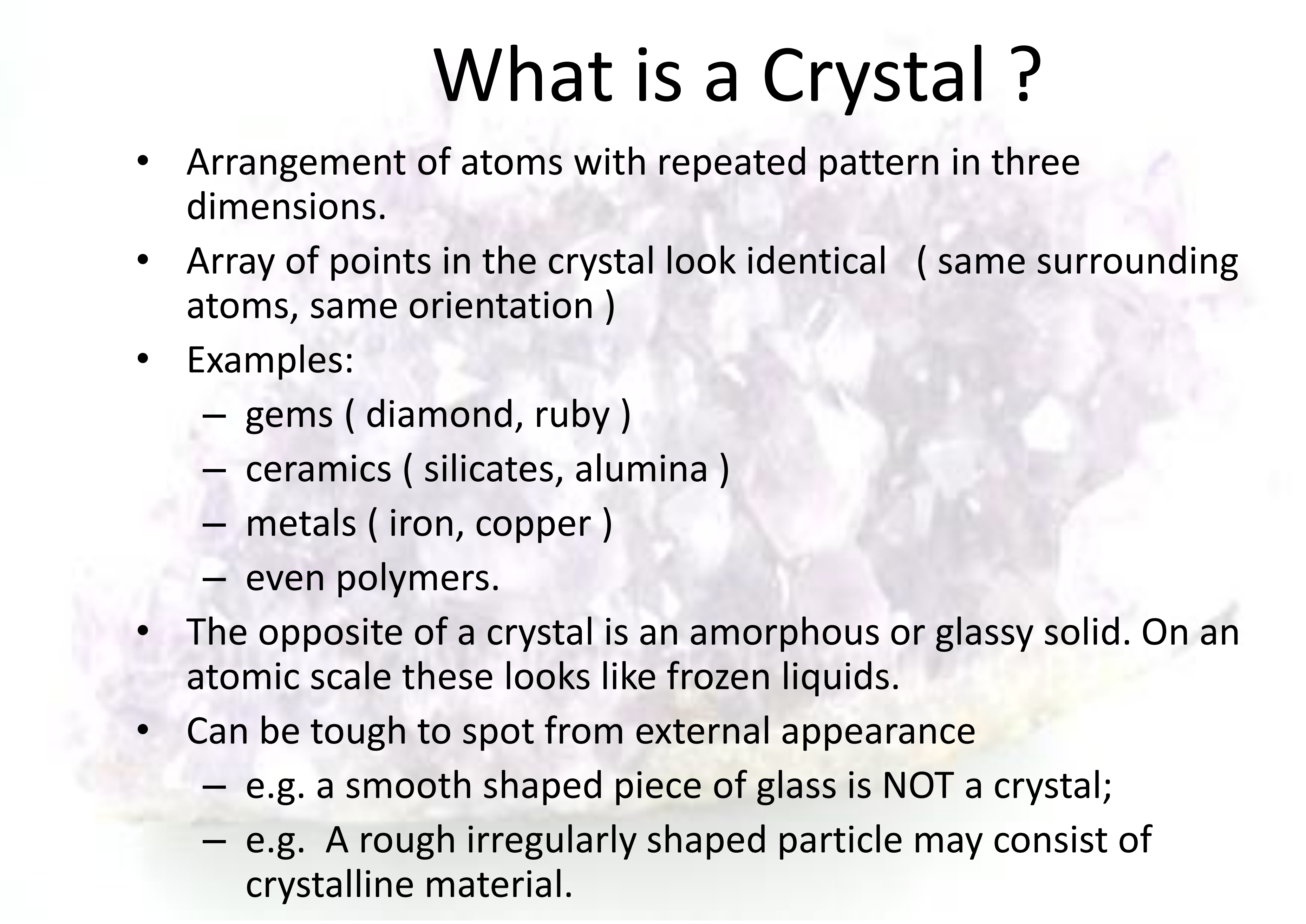
- **Do this over ~ 3 weeks (and three sets of notes)**
- **Week One**
  - **Introduction**
  - **Unit cells**
  - **Directions/planes/packing/density**
- **Week Two**
  - **Symmetries**
- **Week Three**
  - **X-ray diffraction and crystal structure determination**

Crystal Structure - I



- Introduction
  - What are crystals?
  - Why are we interested?
  - Where do we get information?
- Layers & Stacking
- Unit Cells
  - Allowed shapes
  - Unit cell types
  - Bravais Lattices
- BCC / FCC / HCP Crystals
- Positions, Directions, and Planes in Crystals
- Examples of Different Crystal Types

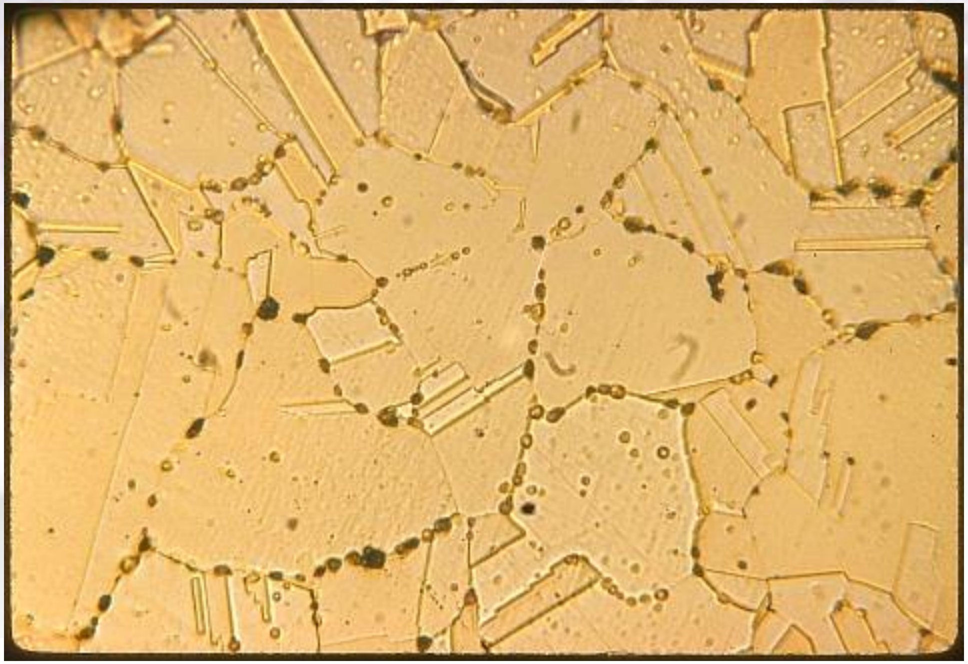
What is a Crystal ?



- Arrangement of atoms with repeated pattern in three dimensions.
- Array of points in the crystal look identical (same surrounding atoms, same orientation)
- Examples:
  - gems (diamond, ruby)
  - ceramics (silicates, alumina)
  - metals (iron, copper)
  - even polymers.
- The opposite of a crystal is an amorphous or glassy solid. On an atomic scale these looks like frozen liquids.
- Can be tough to spot from external appearance
  - e.g. a smooth shaped piece of glass is NOT a crystal;
  - e.g. A rough irregularly shaped particle may consist of crystalline material.

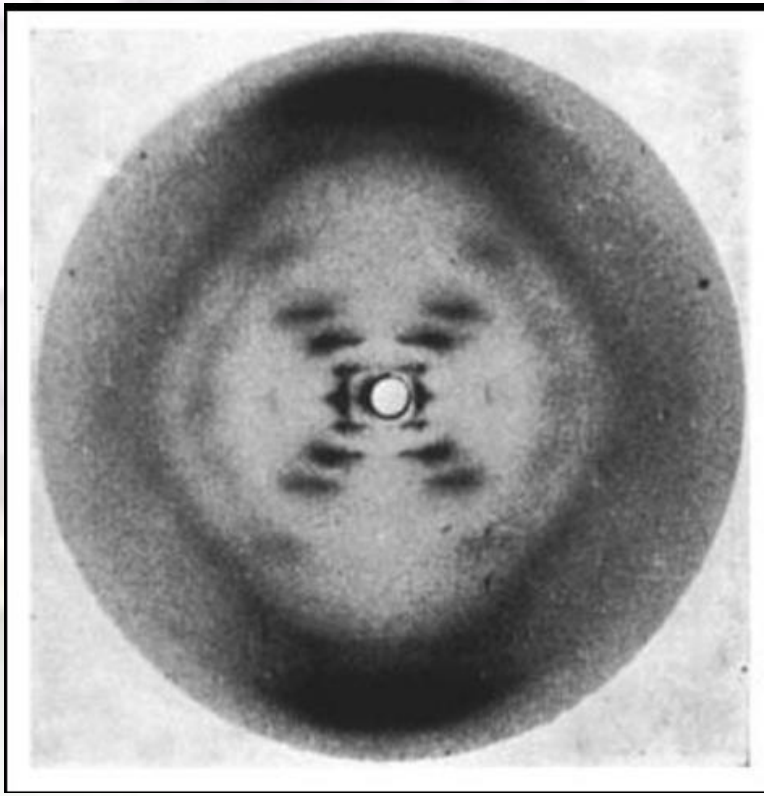
Metals have Crystals

- Image below shows crystal grains in copper
- Polish and etch to reveal grain boundaries

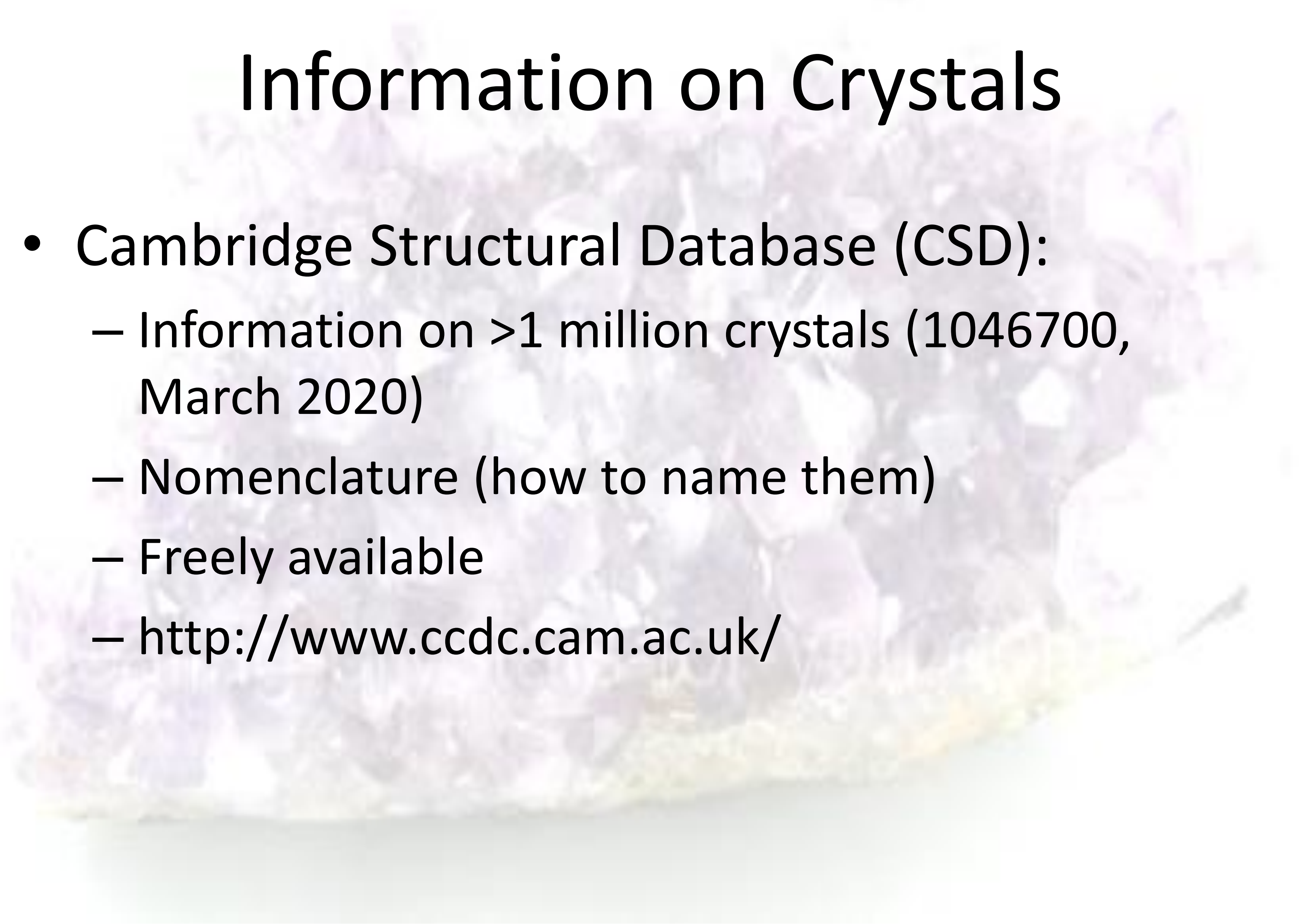


Why do we care

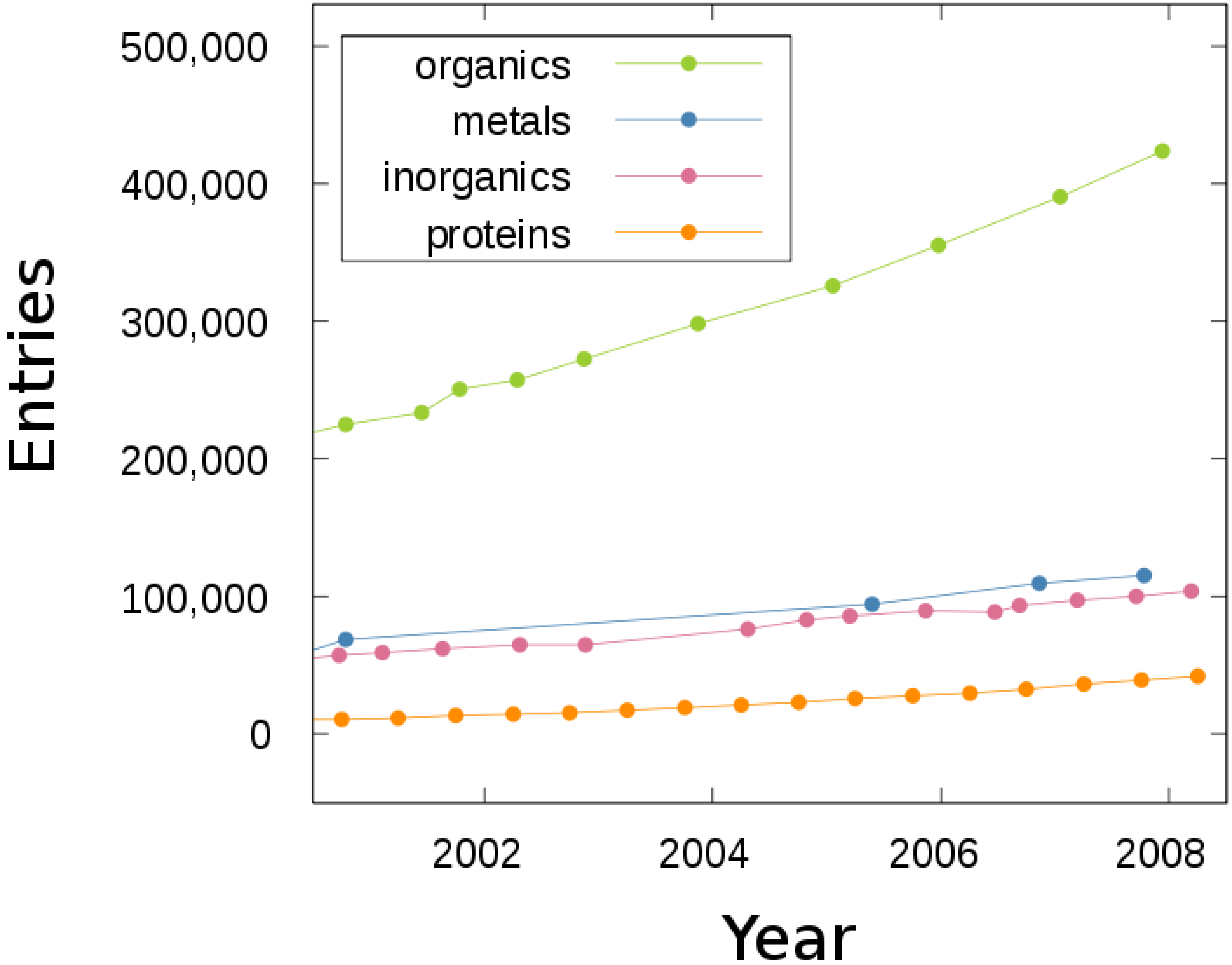
- The anisotropy of crystals has many important applications in Pharma industry:
  - The actual crystal structure of an API is critical (a particular polymorph only can be patented)
  - The appearance of an unknown crystal form may make the drug unmarketable



Information on Crystals

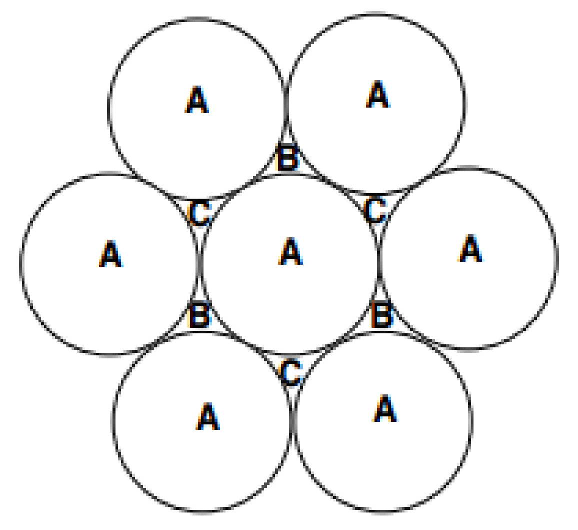


- Cambridge Structural Database (CSD):
  - Information on >1 million crystals (1046700, March 2020)
  - Nomenclature (how to name them)
  - Freely available
  - http://www.ccdc.cam.ac.uk/


organics
metals
inorganics
proteins
Entries
500,000
400,000
300,000
200,000
100,000
0
2002
2004
2006
2008
Year

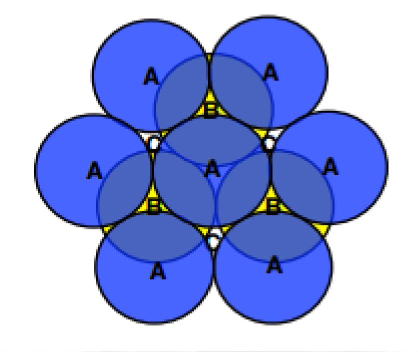
Layers and Stacking

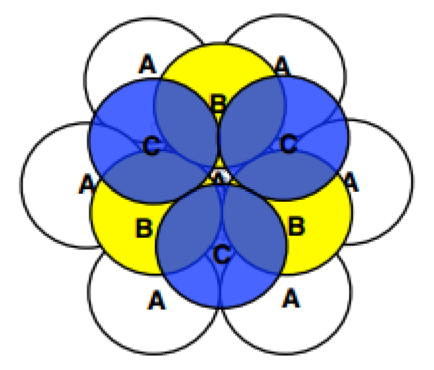
- We’ll talk about metals here
  - Not so fussy about direction of bonds
  - Behave like hard spheres
- Lay spheres out on a table so they are packed as close as possible in one layer
  - Two possibilities for next layer



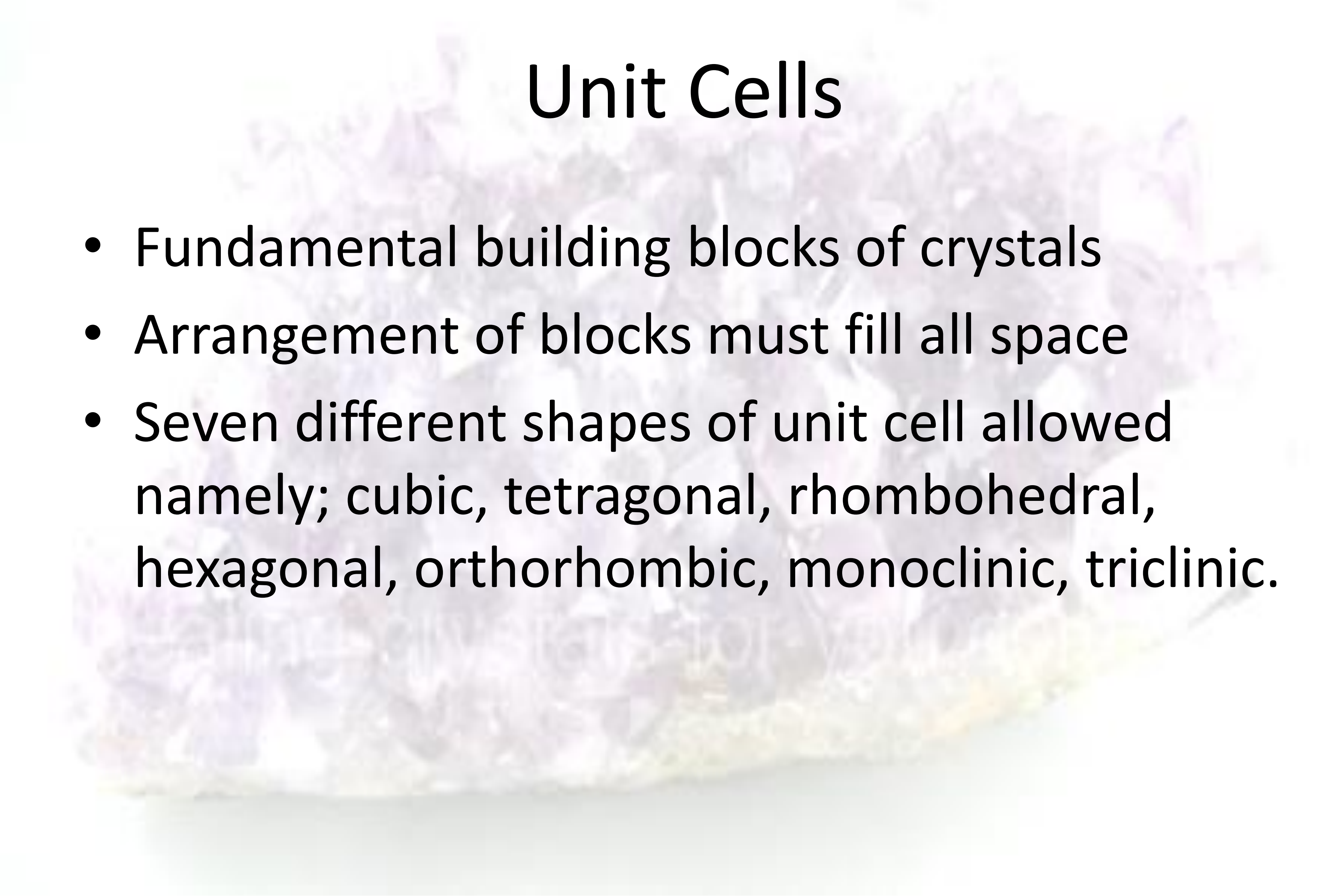
Layers and Stacking

- There are two ways to stack layers
  - ABABABABA
    - Creates form called Hexagonal Close Packed (HCP)
  - ABCABCABC
    - Creates form called Face Centred Cubic(FCC)





- Any other stacking is less compact



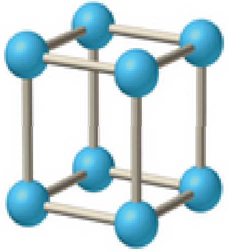
Unit Cells

- Fundamental building blocks of crystals
- Arrangement of blocks must fill all space
- Seven different shapes of unit cell allowed namely; cubic, tetragonal, rhombohedral, hexagonal, orthorhombic, monoclinic, triclinic.

Parameters for Unit Cells

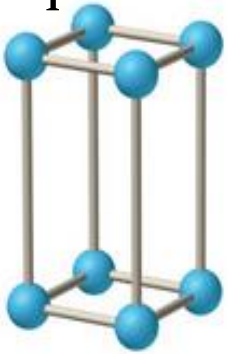
- cubic; $a=b=c$, $\alpha= \beta= \gamma=90^0$
- tetragonal; $a=b\neq c$, $\alpha= \beta= \gamma=90^0$
- orthorhombic; $a\neq b\neq c$, $\alpha= \beta= \gamma=90^0$
- rhombohedral; $a=b=c$, $\alpha= \beta= \gamma\neq 90^0$
- hexagonal; $a=b\neq c$, $\alpha= \beta= 90^0$ $\gamma=120^0$
- monoclinic; $a\neq b\neq c$, $\alpha= \gamma= 90^0 \neq\beta$
- triclinic;$a\neq b\neq c$, $\alpha\neq \beta\neq \gamma\neq 90^0$

cube



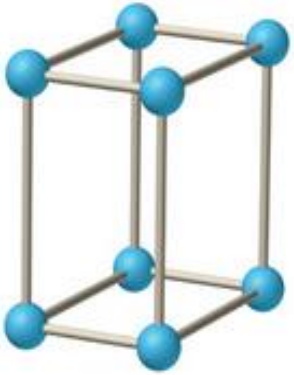
Cubic

square top



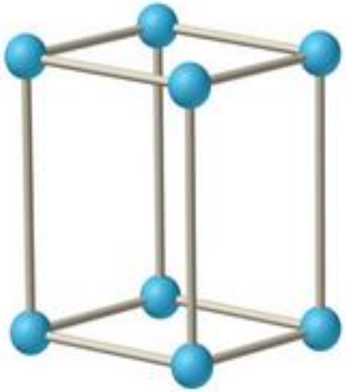
Tetragonal

shoe box

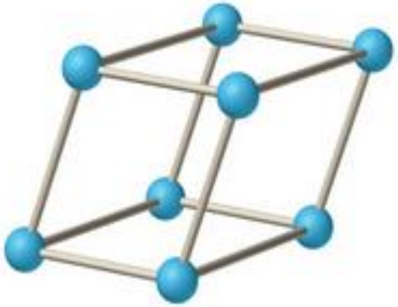


Orthorhombic

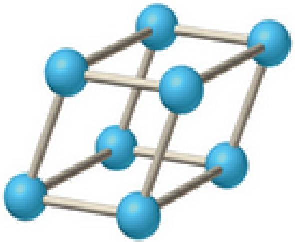
slanted shoe box



Monoclinic

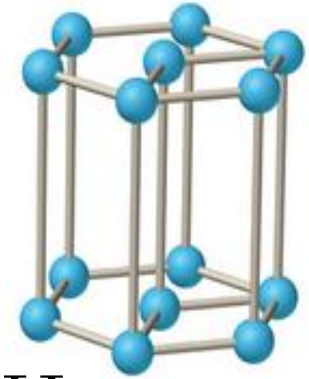


Rhombohedral



Triclinic

honeycomb

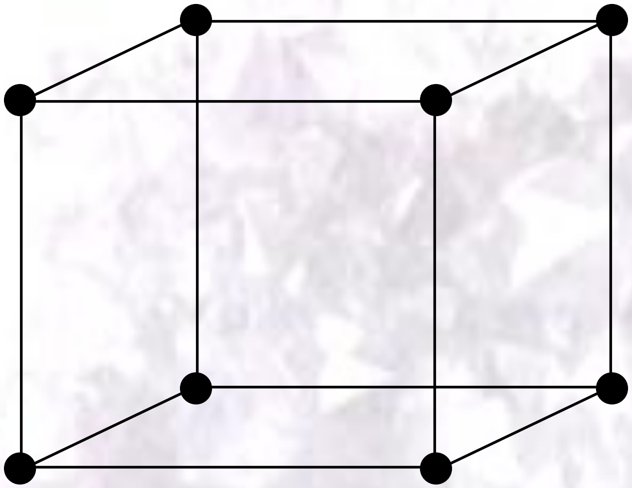


Hexagonal

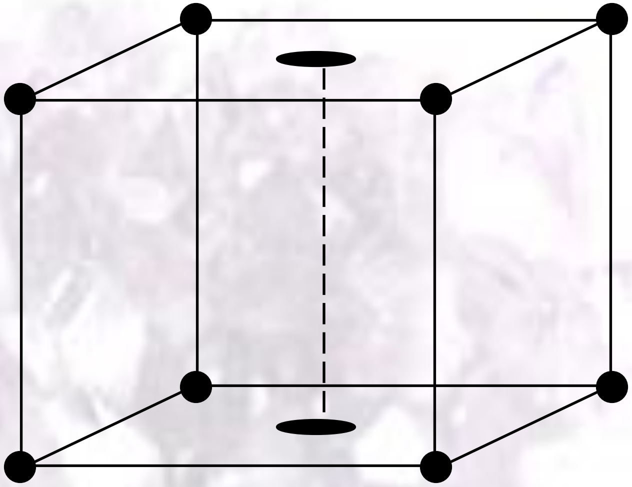
Symmetries within Unit Cells

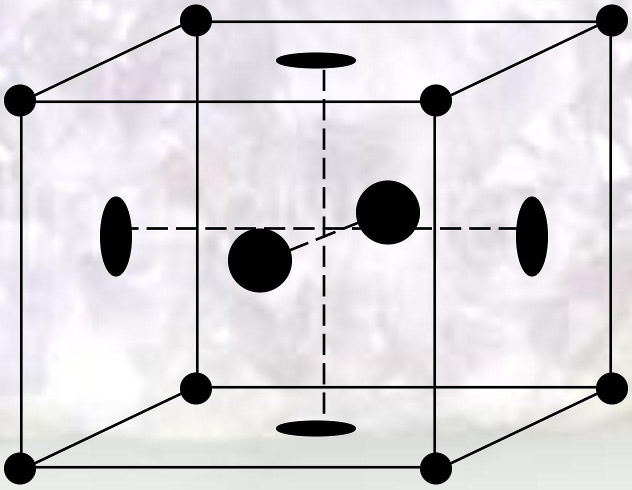
- As well as the symetries of their shapes, unit cells can have symmetries due to their internal structures
- Gives four types of unit cell: simple (P), face centered (F), body centered (I), and base centered (C)

Simple (P)

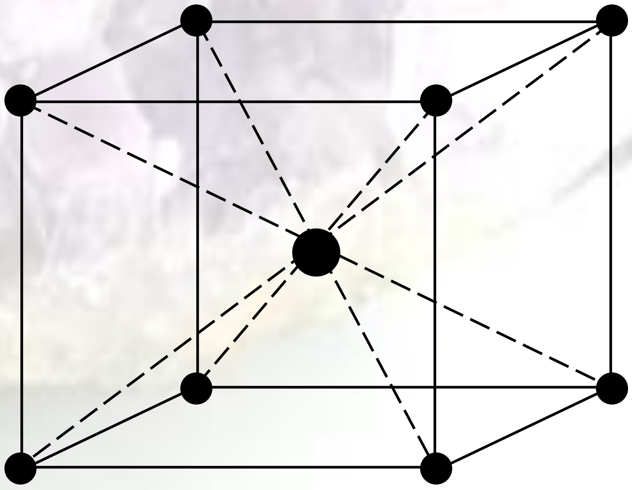


Base Centered (C)





Face Centered (F)



Body Centered (I)

Bravais Lattices

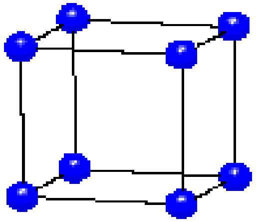
- Not all of the seven cell shapes can have all four types of internal symmetry
- For instance, the face centered tetragonal structure can be reduced to the body centered tetragonal structure
- There are fourteen distinct possibilities called the *Fourteen Bravais lattices*
- The fourteen lattices contain all the necessary *translational* symmetries to describe every possible crystal structure in nature

CUBIC

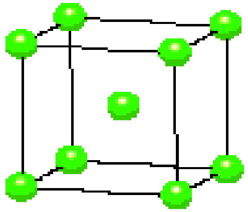
$a = b = c$

$\alpha = \beta = \gamma = 90°$

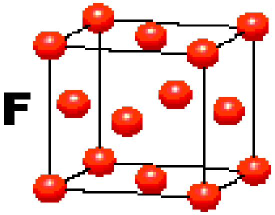
P



I



F

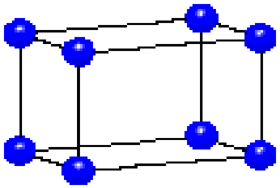


TETRAGONAL

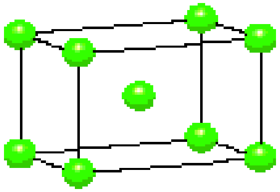
$a = b \neq c$

$\alpha = \beta = \gamma = 90°$

P



I

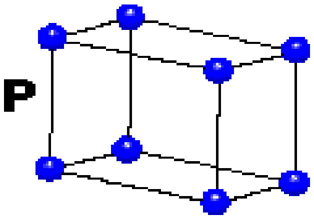


ORTHORHOMBIC

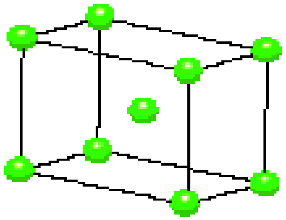
$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

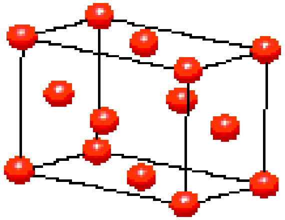
P



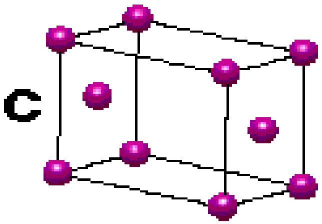
I



F



C



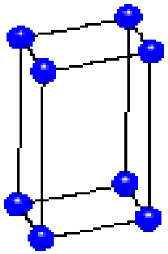
HEXAGONAL

$a = b \neq c$

$\alpha = \beta = 90°$

$\gamma = 120°$

P

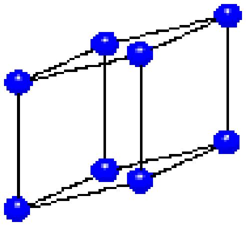


TRIGONAL

$a = b = c$

$\alpha = \beta = \gamma \neq 90°$

P



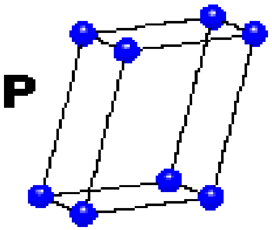
MONOCLINIC

$a \neq b \neq c$

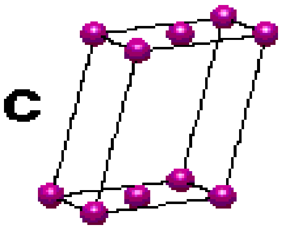
$\alpha = \gamma = 90°$

$\beta \neq 120°$

P



C

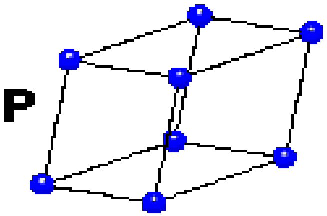


TRICLINIC

$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°$

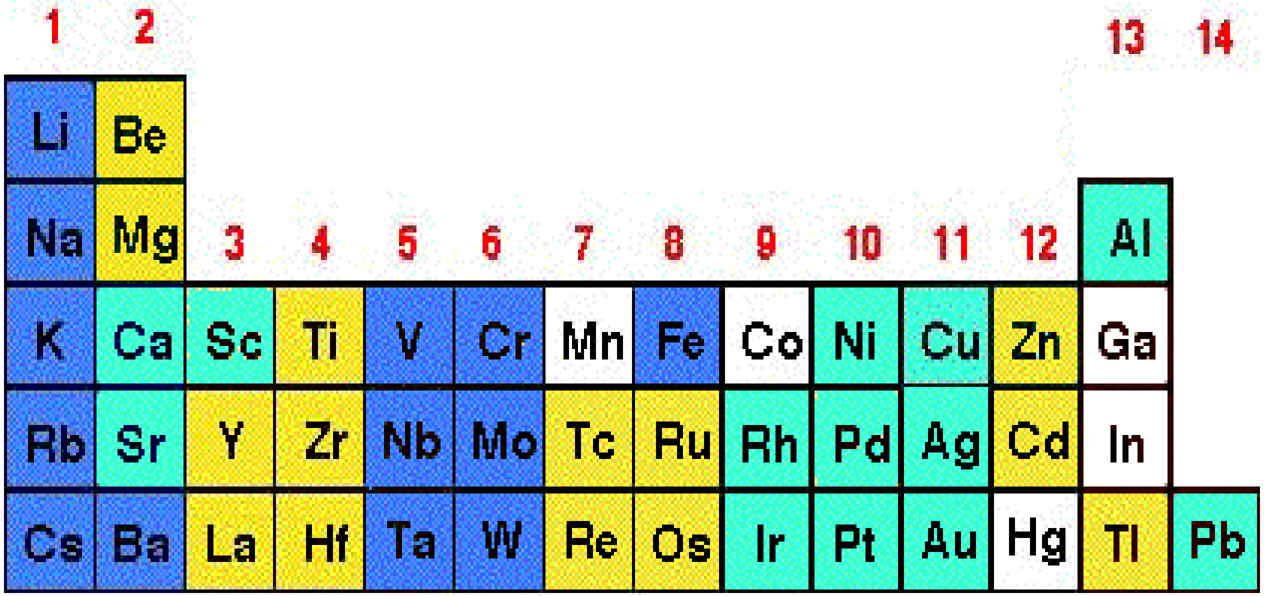
P



4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

Principle Metallic Crystal Structures

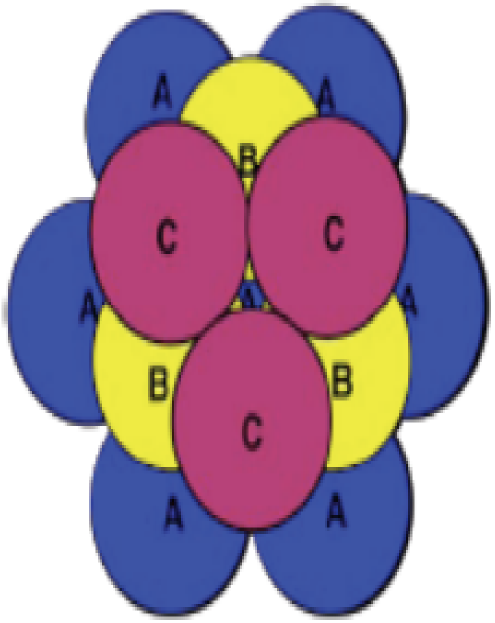
- Because of the nature of the metallic bond the principle requirement is for a high density
- Three arrangements satisfy this criterion: body centered cubic (**BCC**), face centered cubic (**FCC**), and hexagonal close packed (**HCP**).



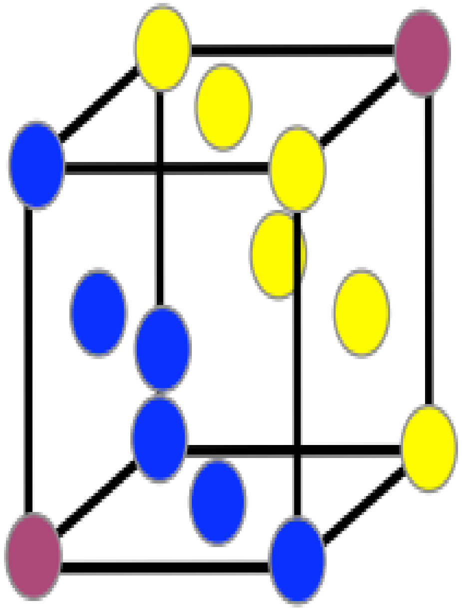
1	2	3	4	5	6	7	8	9	10	11	12	13	14
Li	Be												
Na	Mg											Al	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb

- Hexagonal Close Packed
- Body Centered Cubic
- Face Centered Cubic

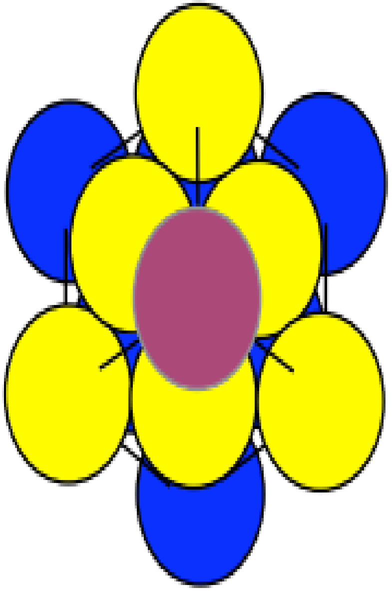
FCC Structure & Layer Stacking



ABC stacking



Fcc cell



View along diagonal (<111>)

	APF	CN	atoms/cell
BCC	0.68	8	2
FCC	0.74	12	4
HCP	0.74^*	12	6

$$\textbf{APF = atomic packing fraction} = \frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}}$$

CN = coordination number

**** ideal, when c/a = 1.633***

Lattice Constants of Some BCC Metals

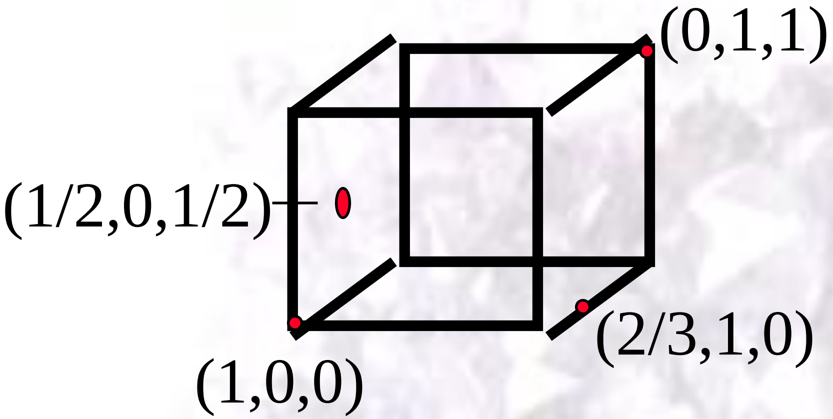
		Lattice Constant	Density
Metal	**atomic mass**	**a (nm)**	**(g cm^{-3})**
Chromium	52.00 amu	0.289	7.19
Iron	55.85 amu	0.287	7.86
Molybdenum	95.94 amu	0.315	10.2
Potassium	39.10 amu	0.533	0.86
Sodium	22.99 amu	0.429	0.97
Tantalum	180.95amu	0.330	16.6
Tungsten	183.85amu	0.316	19.3
Vanadium	50.94 amu	0.304	6.1

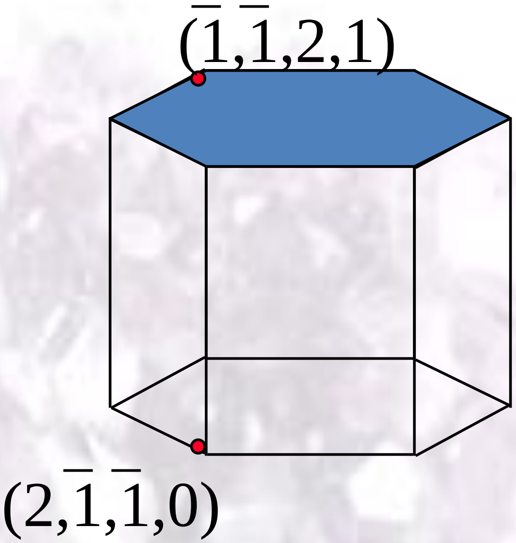
Lattice Constants of Some FCC Metals

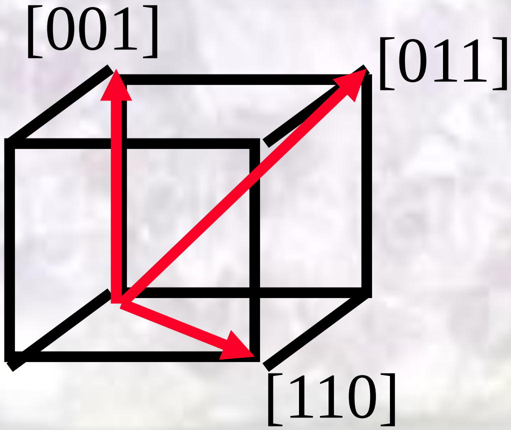
		Lattice Constant	Density
Metal	**atomic mass**	**a (nm)**	**(g cm^{-3})**
Aluminium	26.98amu	0.405	2.70
Copper	63.55 amu	0.3615	8.96
Gold	196.97amu	0.408	19.3
Lead	207.18amu	0.495	11.4
Nickel	58.71 amu	0.352	8.9
Platinium	195.09amu	0.393	21.4
Silver	107.87amu	0.409	10.5

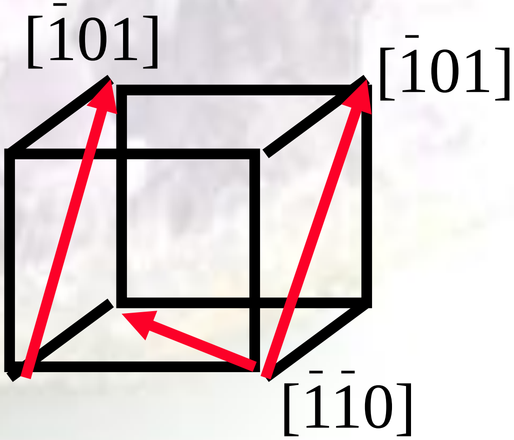
Positions, Directions, and Planes within Crystals

- **Position:** specifies a point within a unit cell. Expressed as fractions of lattice vectors. Notation is (1/4, 0, $-2^{1}/_{2}$)
- **Direction:** specifies the direction of a line. Expressed as a set of integers. Notation is [210] where 1 means -1.
- **Planes:** specifies surfaces within the crystal. Expressed as a set of integers known as the Miller indices. Notation is (210).


(0,1,1)
(1/2,0,1/2)
(2/3,1,0)
(1,0,0)

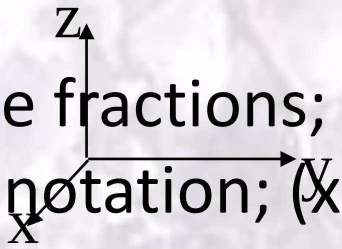

$(\bar{1},\bar{1},2,1)$
$(2,\bar{1},\bar{1},0)$


[001]
[011]
[110]


$[\bar{1}01]$
$[\bar{1}01]$
$[\bar{1}\bar{1}0]$

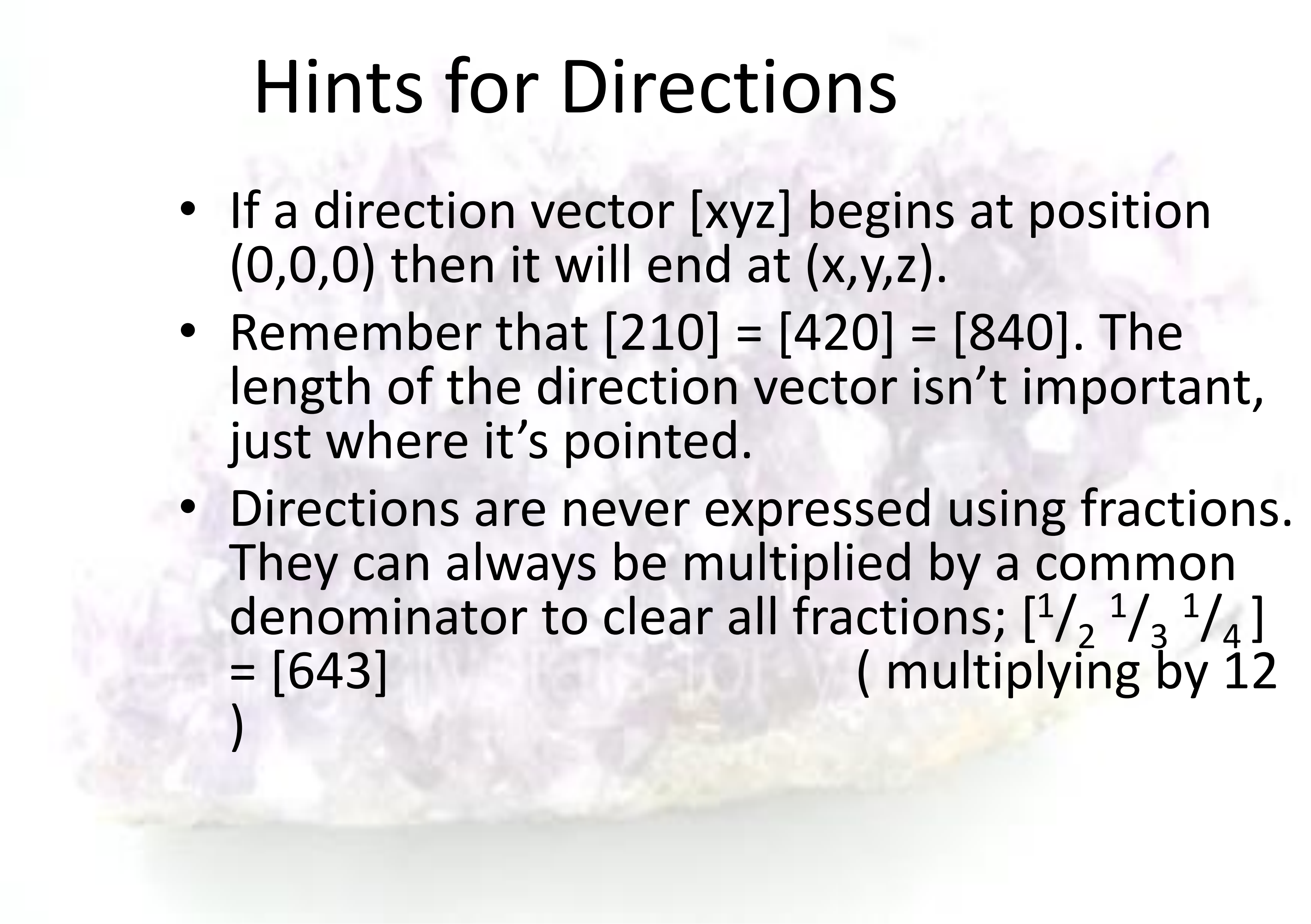
Hints for Positions

- by convention, take the position (0,0,0) to be in the bottom left hand corner at the back
- remember which axes point in which directions.



- positions can be fractions; $2^{1}/_{2}$, $-^{3}/_{4}$, $^{8}/_{3}$, etc
- remember the notation; (x,y,z)
- positions with negative indices or indices >1 will be outside the unit cell

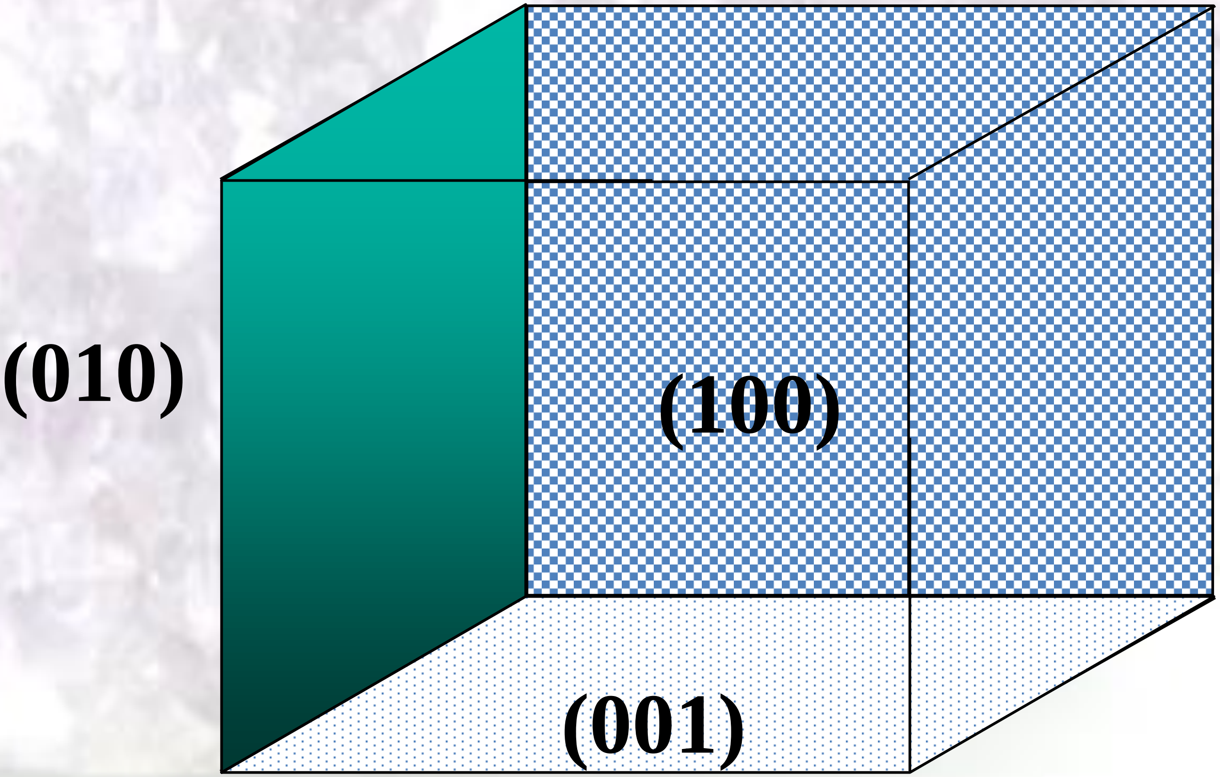
Hints for Directions

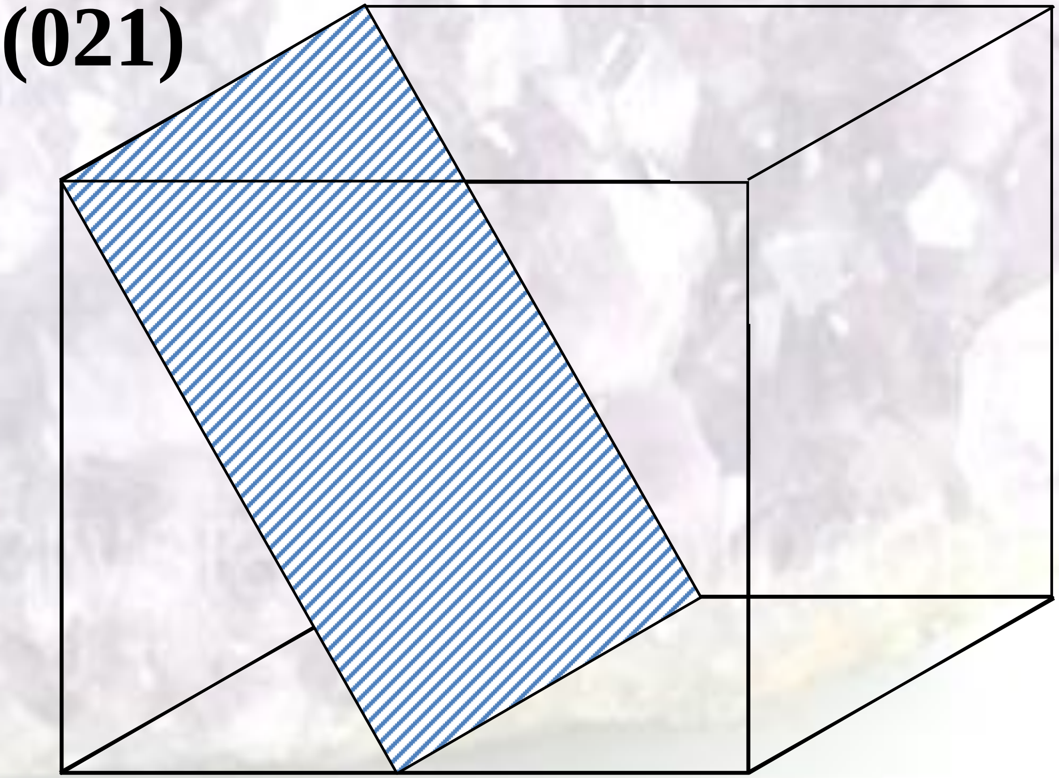


- If a direction vector [xyz] begins at position (0,0,0) then it will end at (x,y,z).
- Remember that [210] = [420] = [840]. The length of the direction vector isn’t important, just where it’s pointed.
- Directions are never expressed using fractions. They can always be multiplied by a common denominator to clear all fractions; [$^1/_2$ $^1/_3$ $^1/_4$] = [643] (multiplying by 12)

Hints for Planes

- sets of parallel planes all have the same Miller indices
- choose one of the planes that does not pass through the point (0,0,0)
- see where the plane cuts the x, y, and z axes (the intercepts, could be infinity)
- get the reciprocals of these intercepts
- clear fractions


(010)
(100)
(001)


(021)