Lecture 2

X-ray Crystallography and Crystal Bonding

"X-ray" here is to be taken as any of

X-ray (~ 10 keV: "hard" X-ray)

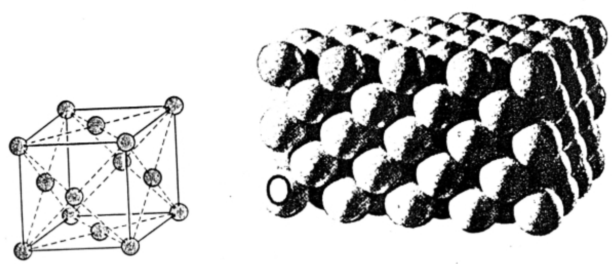
Electron (~ 100 eV: "low energy" electron)

Neutron (~ 10-100 meV: "cold" or thermal neutron)

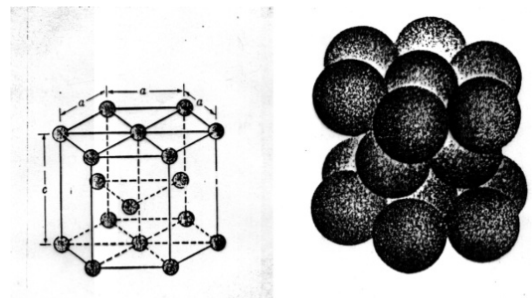
Learning question 1

Pages 11,14 of H&H

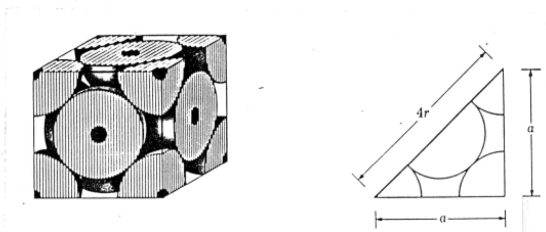
- Explain what are **fcc** (ccp) and **hcp** structures, and why they are called “close-packing” structures. (section 1.3.1)

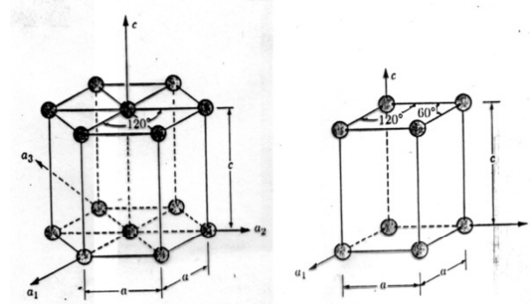


Face Centered Cubic Lattice



Hexagonal Lattices



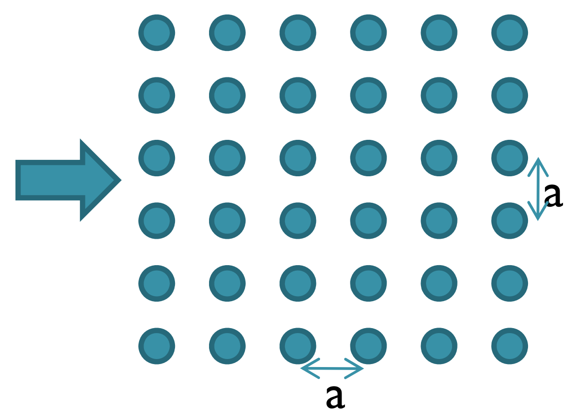


http://www.ae.iitm.ac.in/~sriram/as401/materials

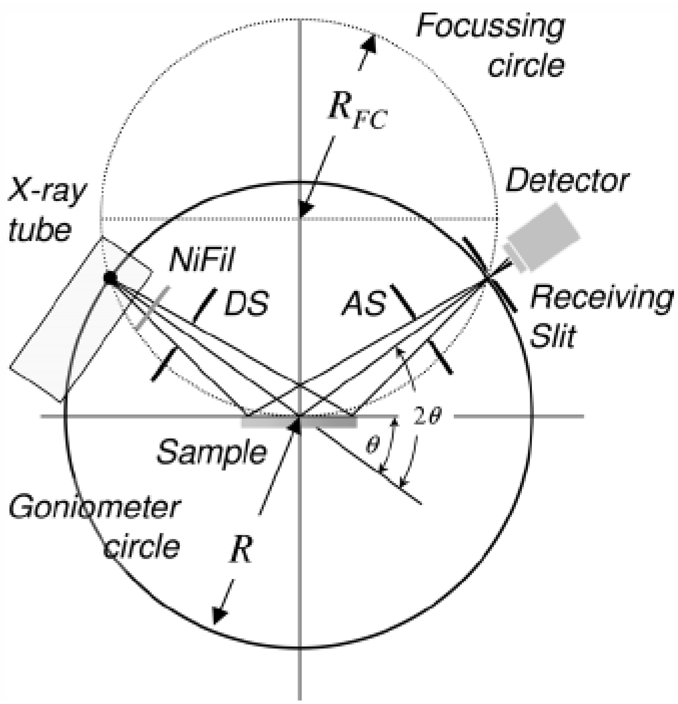
Learning question 2

Sections 1.4.1,2, of H&H

- Derive **Bragg's law**, $2d \sin \theta = n \lambda$, by considering a stack of planes, as in Figure 1.16 b.
- Consider a simple cubic lattice with light impinging on the crystal like this. Identify 2 different stacks of non-vertical lattice planes, and show outgoing light arrows for each case. Give Miller indices of your lattice planes. Determine values of d.
- Write down Bragg's law for n=1 for each of the two different kinds of lattice planes identified. Explain what may actually occur
  (1) for a single value of λ
  (monochromatic light)
  (2) for all λ values available in the beam
  (**Laue method**)
  (3) for all θ values available at the same time
  (imagine a collection of crystallites with different orientation)
  with but for monochromatic light
  (**powder method**)



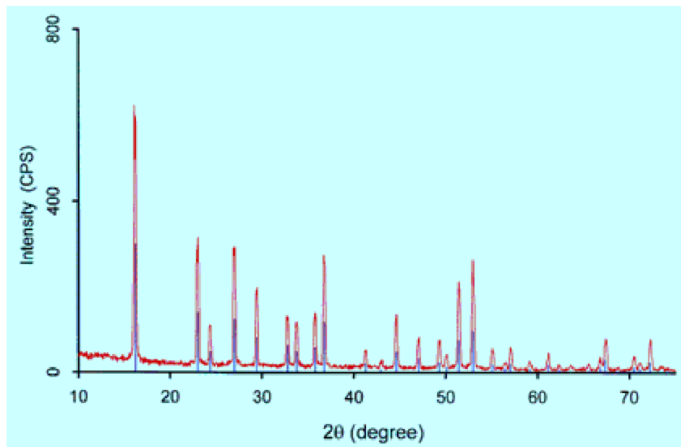
X-Ray Diffraction in Practice



www.wiley-vch.de/templates/pdf/3527310525_c01.pdf

"θ-2θ" Scan

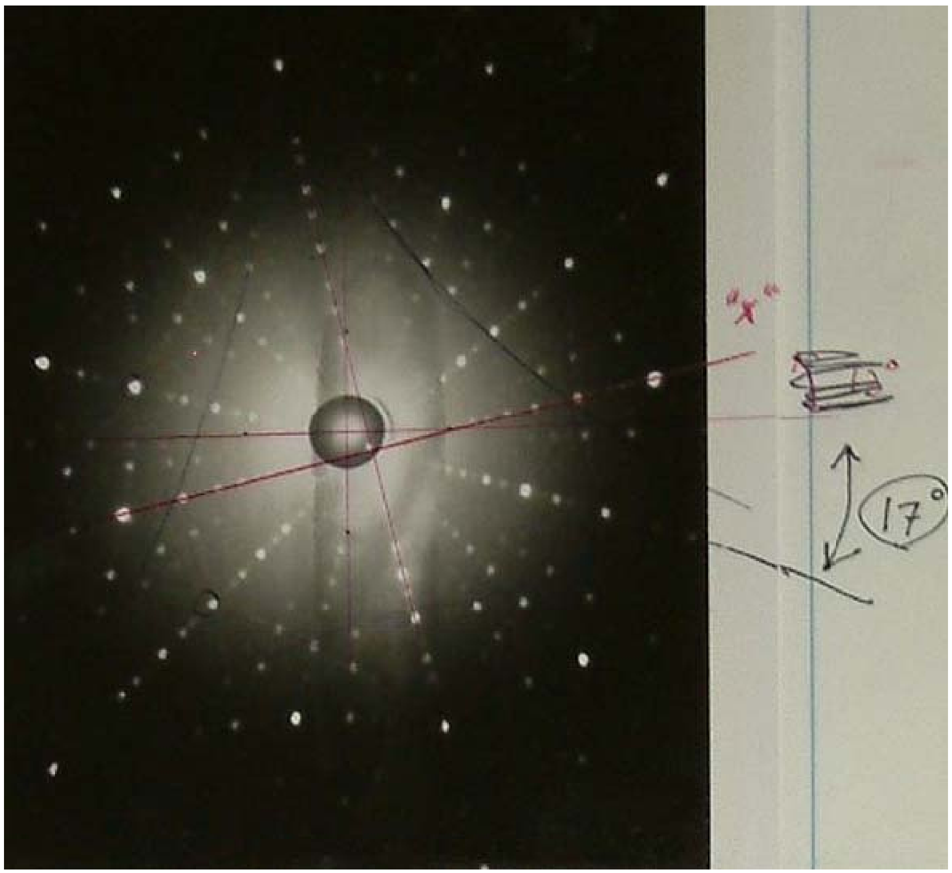
- Monochromatized or filtered light
- For detailed structure solving
- Can use powder sample



XRD Caption 1: Powder X-ray Diffraction of $AlF_3 \cdot 3H_2O$ mineral.
The vertical lines indicate the positions and peak intensities of the powder diffraction standard from JCPDS database.

http://www.mastest.com/xrdxrr.htm

X-Ray Diffraction in Practice



Laue method

- Cheap and easy
- Unfiltered white light
- Polaroid film
- Used for single crystal orientation, or check on the single crystallinity

Crystal Bonding

- Measurement of bonding strength
  - *Cohesive energy*

    Energy to separate crystal into neutral free atoms.
  - *Lattice energy* (ionic crystal)

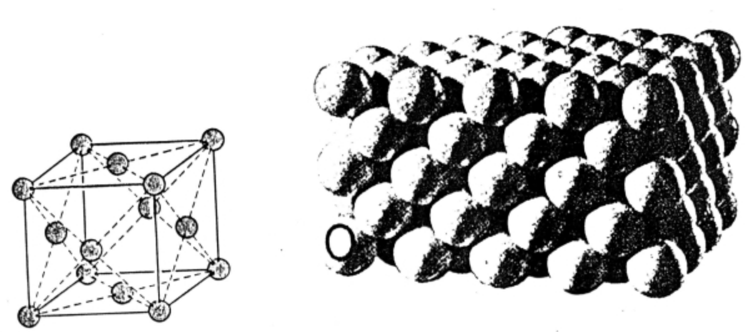
    Energy to separate crystal into infinitely separated ions (related to "*Madelung potential, energy, constant*")
- All due to electrons and protons and statistics

  (Many-body electrostatics problem)

Crystal Bonding – van der Waals

Inert Gas Elements
He, Ne, Ar, Kr, Xe

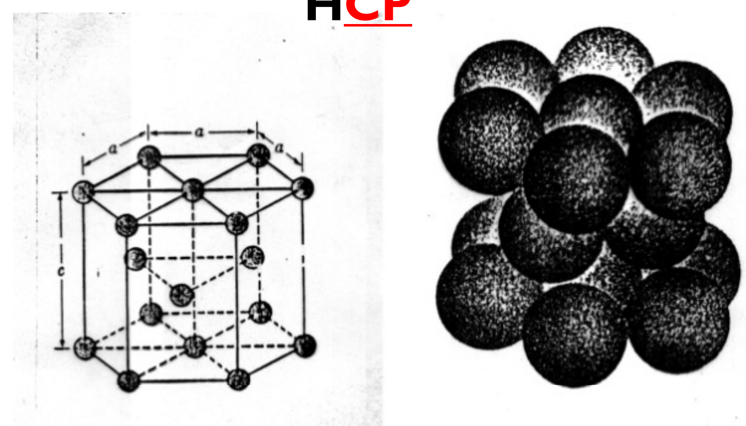
FCC (C<u>CP</u>)



Face Centered Cubic Lattice

Inert Gas Elements
He

H<u>CP</u>

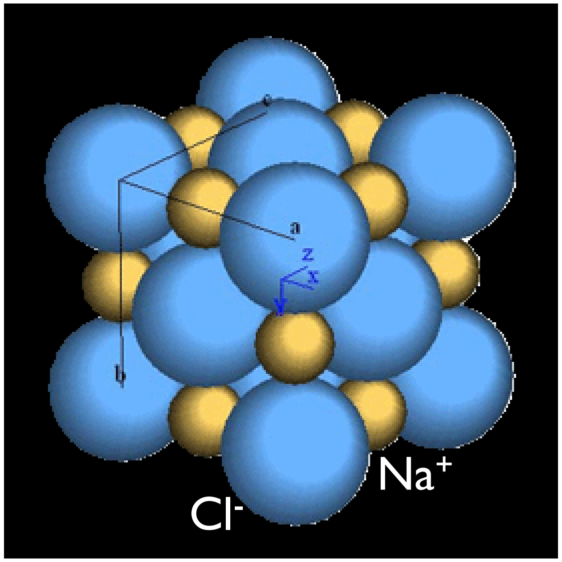


Hexagonal Lattices

http://www.ae.iitm.ac.in/~sriram/as401/materials

Crystal Bonding – Ionic Bonding

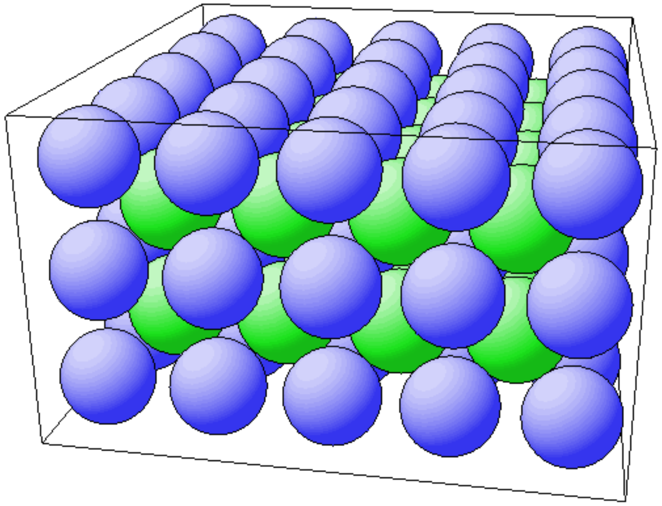
- NaCl



http://www.matsci.ucdavis.edu/MatSciLT/ENG-45L/images/CaRIne.gif

Cl⁻ bigger than Na⁺, by a factor of 2
Looks like close packing of bigger ions
fcc with two atom basis

- CsCl

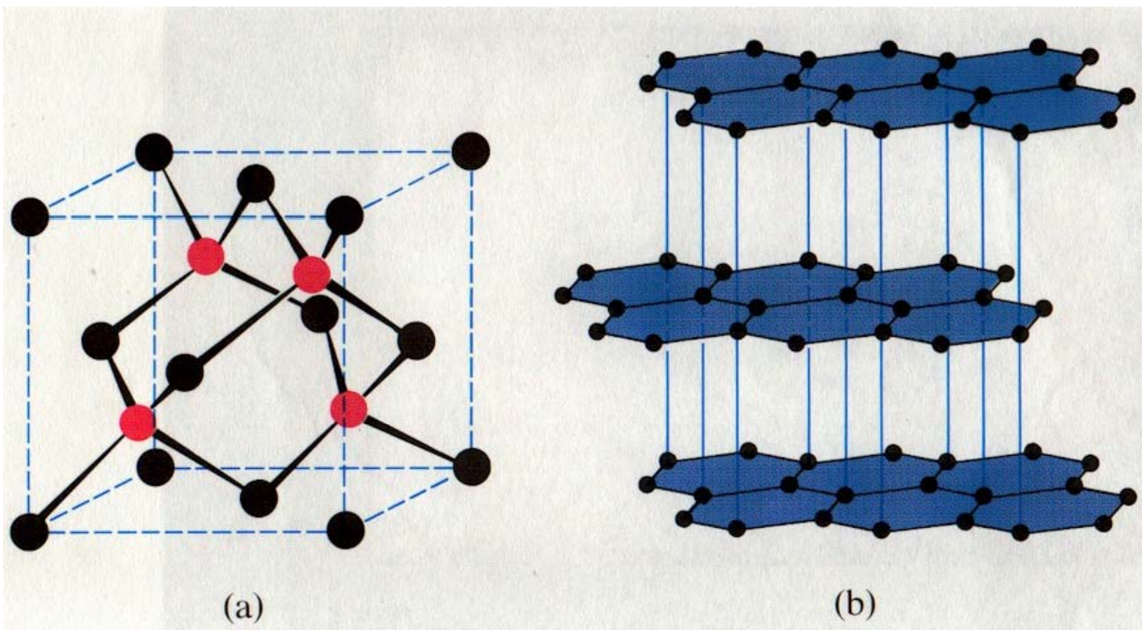


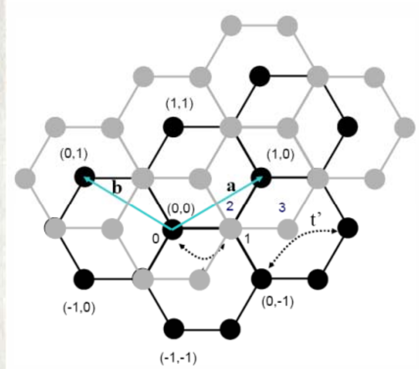
http://www.cmmp.ucl.ac.uk/~ijf/3c25/CsCl.gif

sc (simple cubic) with two atom basis

Crystal Bonding – Covalent Bonding

- Diamond
- Graphite





Top view
Gray=top
Black=next layer

http://library.tedankara.k12.tr/chemistry/vol2/allotropy/h76.jpg

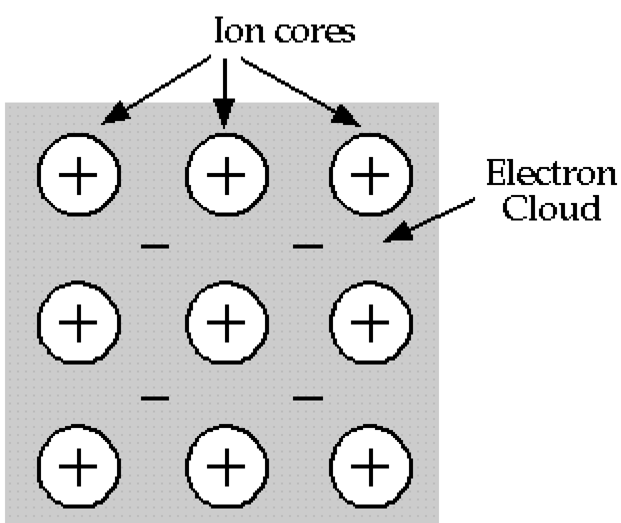
fcc with two atom basis
000 and ¼, ¼, ¼
ZnS, Si, Ge, GaAs
sp3 covalent bonding

Hexagonal with four atom basis
sp2 bonding
Weak inter-plane bonding ("Van der Waals")
More stable than diamond!

Crystal Bonding – Metallic Bonding and Hydrogen Bonding

- Metallic Bonding: Electrons are released freely from atom and spend most of their time freely. Energy lowering can be viewed as "kinetic energy lowering."

  Na, Cu, Al, …



- Hydrogen Bonding: DNA, Water (Ice)!