Lecture 4

Waves in Crystal – continued

Crystal Bonding

Phonons – Soft and Hard

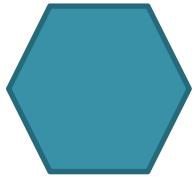
Crystal is nature's diffraction grating

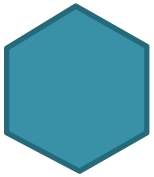
for any wave, i.e. for any particle!

Quiz

- Which is most likely the reciprocal unit cell of the unit cell  ?

A.  B.  C. 

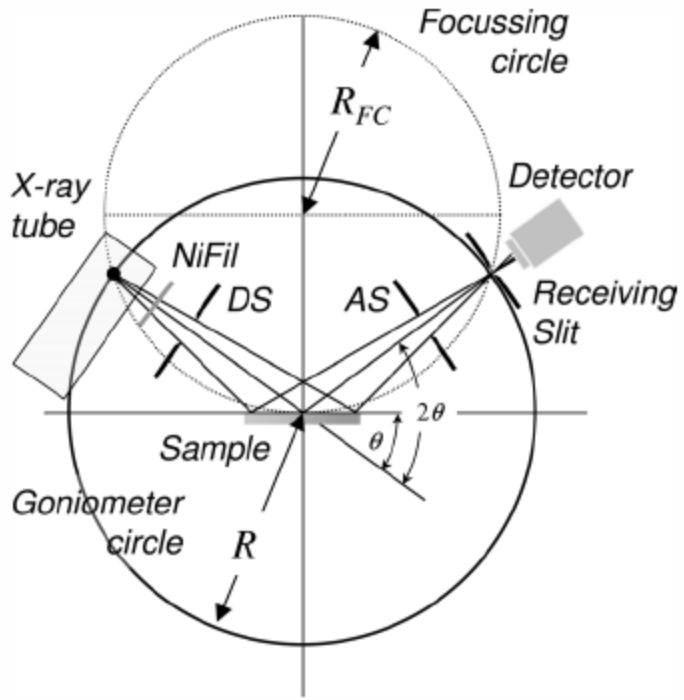
- Which is most likely the the reciprocal WS cell of the WS unit cell  ?

A.  B.  C. 

Quasi-Crystal

- Crystals give Bragg diffraction spots
- But not all materials giving Bragg diffraction spots are crystals
- People suggest that "Quasi-Crystals" can be defined as those non-crystals giving Bragg diffraction spots
- In the language used so far, QC has no Bravais lattice and an infinite size unit cell!
- Nature and human make QCs (penrose tiles, photonic QC)

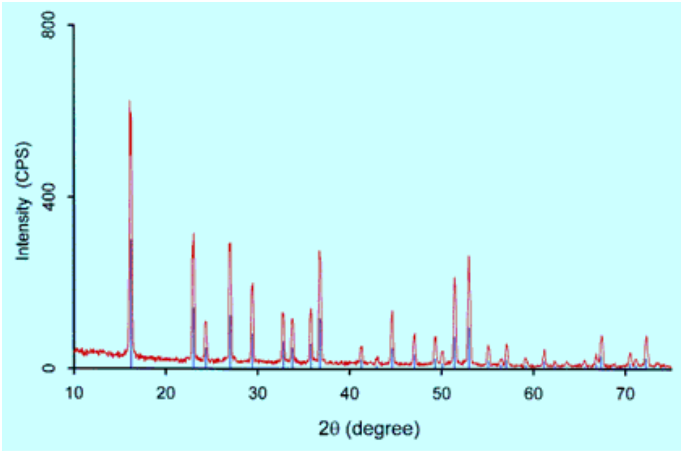
X-Ray Diffraction in Practice



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

"θ-2θ" Scan

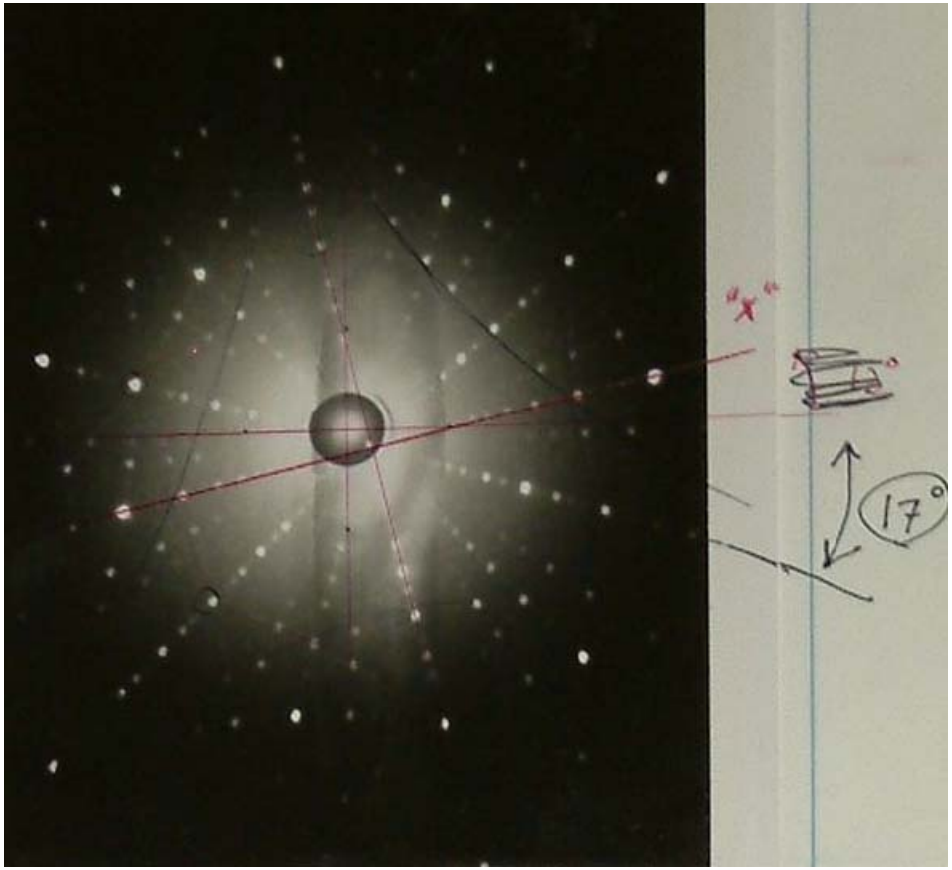
- Monochromatized or filtered light
- For detailed structure solving
- Can use powder sample



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

Structural Factor

- Scattering amplitude (for one atom basis)

  $= \sum_{\mathbf{R}} \exp(i\,\mathbf{k_f}\cdot(\mathbf{r}-\mathbf{R}))\exp(i\,\mathbf{k_i}\cdot\mathbf{R})\,f(\mathbf{q})$

  $\propto f(\mathbf{q}) \sum_{\mathbf{R}} \exp(-i\,\mathbf{q}\cdot\mathbf{R})$

- For general case (multiple atom basis)

  Scattering amplitude

  $\propto \sum_{\mathbf{R}} \exp(-i\,\mathbf{q}\cdot\mathbf{R}) \times \sum_m f_m(\mathbf{q})\exp(-i\,\mathbf{q}\cdot\mathbf{r}_m)$

  S(q)

  $\mathbf{r}_m$: position of basis atoms relative to $\mathbf{R}$

  f_m : atomic scattering factor

Crystal Bonding

- Measurement of bonding strength
  - *Cohesive energy*

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

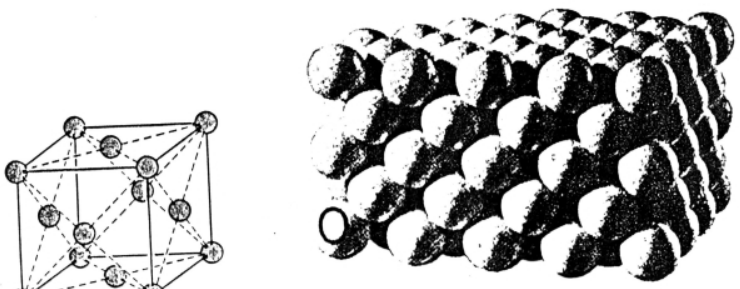
    Energy to separate crystal into infinitely separated ions (related to "*Madelung potential, energy, constant*")
- All due to electrons and protons and statistics

  (Many-body electrostatics problem)

Crystal Bonding – van der Waals

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

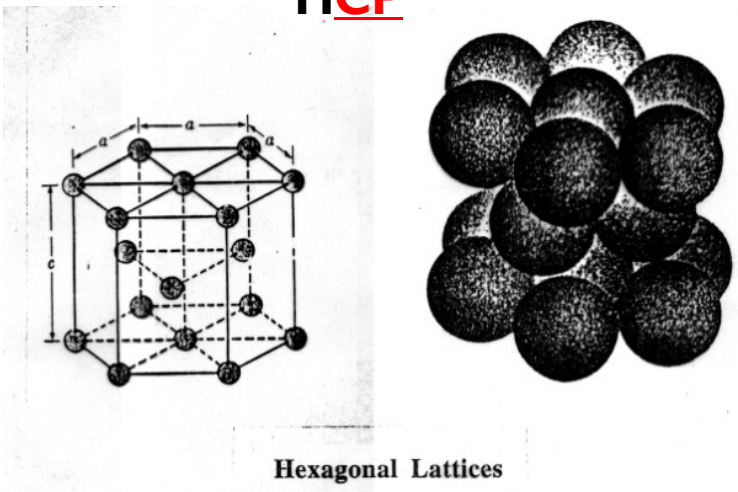
FCC (CCP)



Face Centered Cubic Lattice

Inert Gas Elements
He

HCP

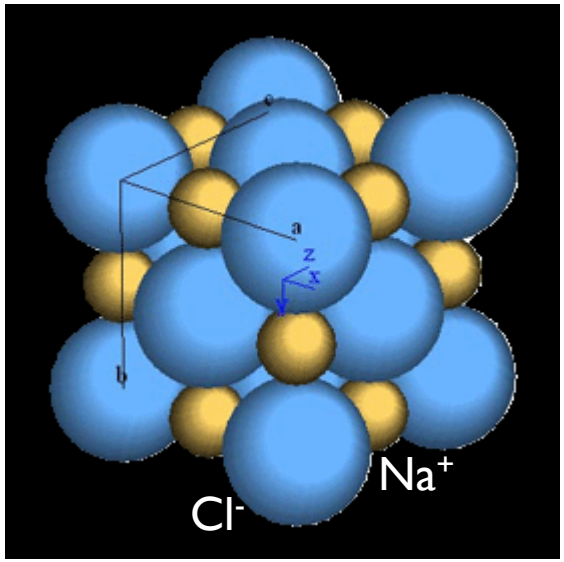


Hexagonal Lattices

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

Crystal Bonding – Ionic Bonding

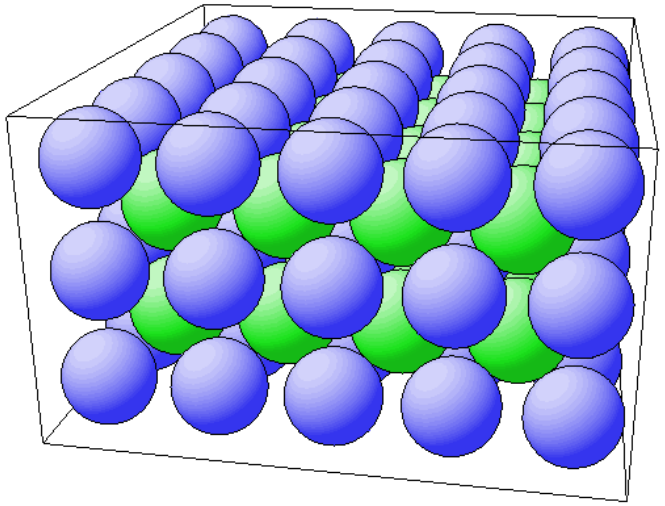
- NaCl



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

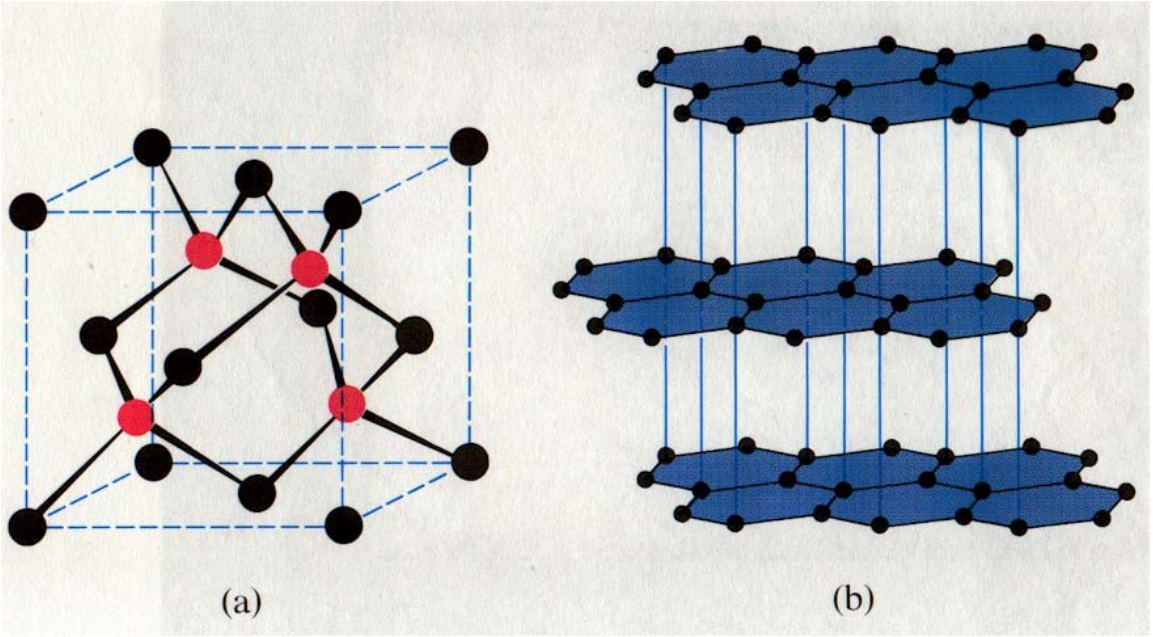


http://www.cmmp.ucl.ac.uk/~ijf/3c25/CsCl.gif

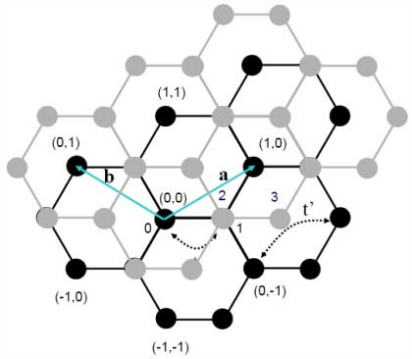
sc (simple cubic) with two atom basis

Crystal Bonding – Covalent Bonding

- Diamond
- Graphite



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



Top view
Gray=top
Black=next layer

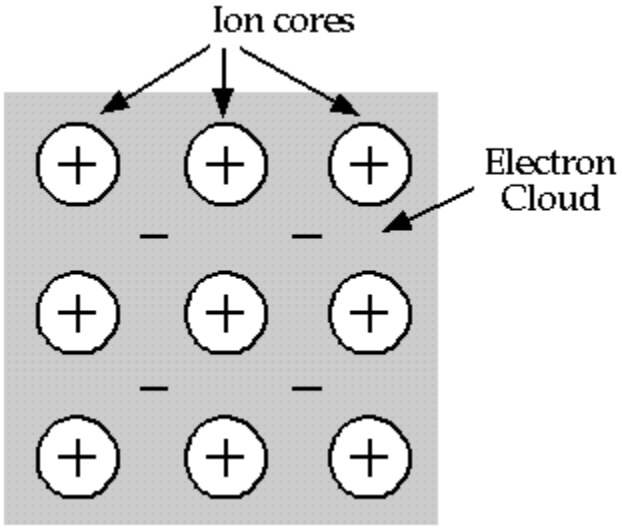
fcc with two atom basis
000 and ¼, ¼, ¼
ZnS, Si, Ge, GaAs
sp3 covalent bonding

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, …

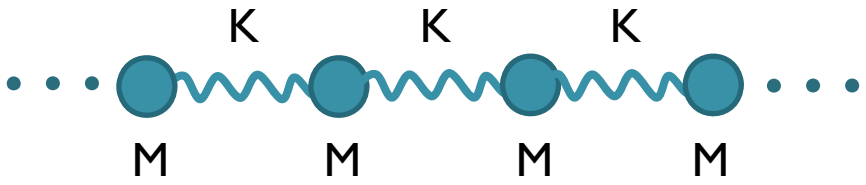


- Hydrogen Bonding: DNA, Water (Ice)!

Crystal Dynamics: Questions

(soft phonon and hard phonon; it is all classical mechanics for now!)

- Consider a monatomic crystal that can be modeled like this with total N (>> 1) atoms:



1. How many normal modes exist?
2. Consider a long wave length normal mode, in which locally the crystal simply undergoes a uniform translation. What is its frequency as wave length goes to infinity?
3. Consider a mode in which adjacent atoms move exactly in opposite ways. I.e. displacement of n-th atom is given by $(-1)^n u$. What is the frequency?

Born – Von Karman Boundary Condition

http://www.mcescher.com/

Born – Von Karman Boundary Condition

- Crystal is modeled as Circle (1D), Torus (2D), Hyper-Torus (3D), …
- Very useful for bulk properties of crystals
- Is not applicable to surface physics or nano-scale physics
- $\sum_{\mathbf{R}} \exp(-i\,\mathbf{q}\cdot\mathbf{R}) = N\,\delta_{\mathbf{q},\mathbf{G}}$ holds rigorously with this boundary condition