Welcome to Chem 253

http://www.cchem.berkeley.edu/pdygrp/chem253.html

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Chemistry 253 A & B
Materials & Solid State Chemistry

Lecture: Tu. Thurs. 12:30-2:00 pm @ 425 Latimer

Instructor:
Professor Peidong Yang, B68 Hild.,
Office Hours:Friday 10:00-12:00pm or by appointment
p_yang@berkeley.edu

TA:
Michael Moore
michael.moore@berkeley.edu

Chong Liu
chongliu@berkeley.edu

Grading:

Problem sets (2)	**40%**
Final	**60%**

Description:

Structure and structure determination of crystalline solids;
Solid State Synthesis
Solid State Characterization
Electronic band structure;
Chemical bonding in solids;
Structure-property relationships.

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Main Reference Books

West: Basic solid state chemistry (Wiley, 1999).
West: Solid State Chemistry and its Applications (Wiley, 1988)
Gersten and Smith: The Physics and Chemistry of Materials (Wiley, 2001)
Hoffmann: Solids and Surfaces (VCH, 1988)
Burdett: Chemical Bonding in Solids (Oxford 1995)
Kittel: Introduction to solid State Physics (Wiley, 1996)
Ashcroft and Mermin: Solid State Physics (Saunders College, latest edition)
Cheetham and Day: Solid State Chemistry: Techniques (Oxford, 1987)
Cheetham and Day: Solid State Chemistry: Compounds (Oxford, 1992)
Cox: The Electronic Structure and Chemistry of Solids (Oxford, 1987)
Wells: Structural Inorganic Chemistry (Clarendon Press, 1984)
Wold and Dwight: Solid State Chemistry (Chapman Hall, 1993)

Materials Chemistry I

1).	No Lecture	
2).	Bravais Lattice, Reciprocal Lattice	Ashcroft: 4-7
3).	XRD, Structural Factor	Ashcroft: 4-7
4).	Diffraction	West: 5
5).	Descriptive crystal chemistry	West: 7,8
6).	Descriptive crystal chemistry	
7).	Crystal Chemistry, Phase diagrams	West: 11, 12
8).	Phase Diagram	Callister 9
9).	Phase Diagram	
10).	Final	

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Materials Chemistry II

11).	Free Electron Model	Ashcroft/Mermin: 1-3, 8-10, Kittel: 6-9
12).	Nearly free electron model, Fermi surface, Effective Mass, Exciton.	
13).	Fermi's Golden Rule, Optical Transition	
14).	Quantum well/wire/dot	Gersten, 7,11
15).	Tight Binding Model MO Theory	Hoffmann,Burdett 1-3
16).	Tight Binding Model	
17).	Tight Binding Model	
18).	Final	

Solid State and Materials Chemistry

Synthesis, structure,
properties, applications of solid materials

Inorganic, organic, biological

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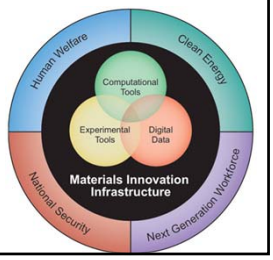
Materials by Design

Theoretician: predict structure/composition with particular properties

Chemist/Physicist: Make/measure/characterize

Materials Genome Initiative

http://www.whitehouse.gov/mgi



Characterization Techniques:

Organic/Organometallic: **NMR, IR, crystallography**

Solid state: **X-ray powder diffraction,**
Electron microscopy
Physical property characterization

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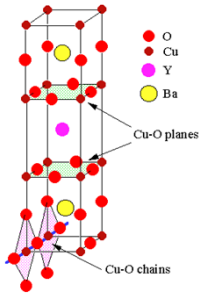
Superconductivity

1908, Kammerlingh-Onnes experiments on liquid He (a few ml)

Hg resistance: 0.08 ohm @ 5K to 0.000003 ohm @ 4.2 K

1986, J. G. Bednorz, K. H. Muller (IBM)
La-Ba-Cu-O
Oxide: Tc = 35 K
1997 Nobel prize in Physics

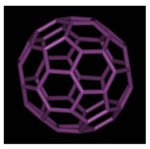
French Group (B. Raveau)

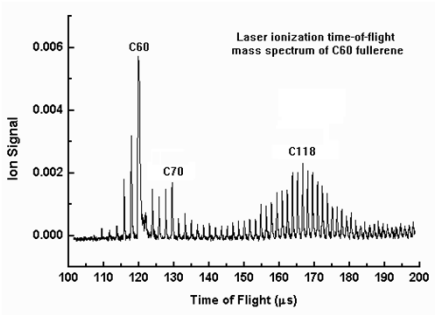


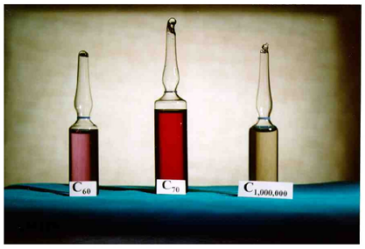
Bucky Ball; fullerene
1996 Nobel prize in chemistry

C_{60}

*J.R. Heath, S.C. O'Brien, H.W. Kroto, R.F. Curl, R.E. Smalley, Nature **318** , 162, (1985)*



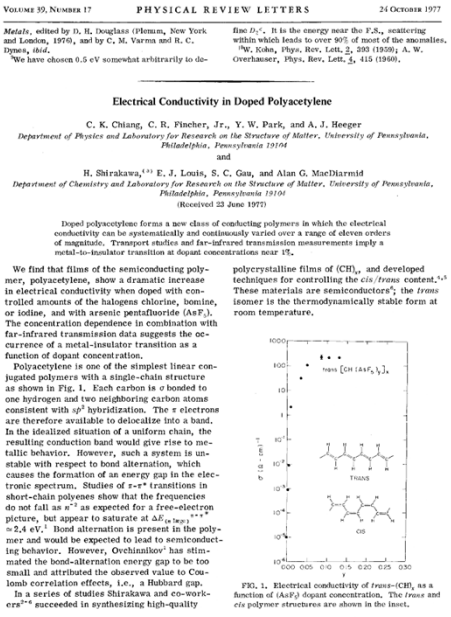




Conducting Polymer

2000 Alan Heeger,
Alan G. MacDiarmid,
Hideki Shirakawa

Nobel Prize in Chemistry



VOLUME 39, NUMBER 17 PHYSICAL REVIEW LETTERS 24 OCTOBER 1977

Metals, edited by D. H. Douglass (Plenum, New York and London, 1970), and by C. M. Varma and R. C. Dynes, *ibid.*

[9]We have chosen 0.5 eV somewhat arbitrarily to define D_1^c. It is the energy near the F.S., scattering within which leads to over 90% of most of the anomalies.

[10]W. Kohn, Phys. Rev. Lett. 2, 393 (1959); A. W. Overhauser, Phys. Rev. Lett. 4, 415 (1960).

Electrical Conductivity in Doped Polyacetylene

C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, and A. J. Heeger
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104
and
H. Shirakawa,[(a)] E. J. Louis, S. C. Gau, and Alan G. MacDiarmid
Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104
(Received 23 June 1977)

Doped polyacetylene forms a new class of conducting polymers in which the electrical conductivity can be systematically and continuously varied over a range of eleven orders of magnitude. Transport studies and far-infrared transmission measurements imply a metal-to-insulator transition at dopant concentrations near 1%.

We find that films of the semiconducting polymer, polyacetylene, show a dramatic increase in electrical conductivity when doped with controlled amounts of the halogens chlorine, bomine, or iodine, and with arsenic pentafluoride (AsF_5). The concentration dependence in combination with far-infrared transmission data suggests the occurrence of a metal-insulator transition as a function of dopant concentration.

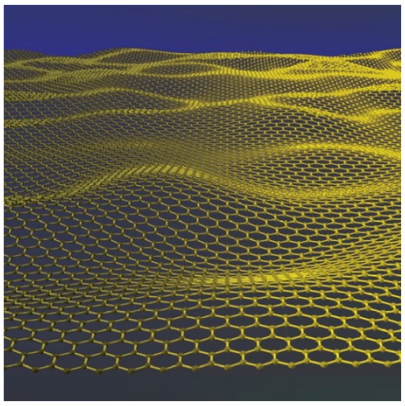
Polyacetylene is one of the simplest linear conjugated polymers with a single-chain structure as shown in Fig. 1. Each carbon is σ bonded to one hydrogen and two neighboring carbon atoms consistent with sp^2 hybridization. The π electrons are therefore available to delocalize into a band. In the idealized situation of a uniform chain, the resulting conduction band would give rise to metallic behavior. However, such a system is unstable with respect to bond alternation, which causes the formation of an energy gap in the electronic spectrum. Studies of π-π^* transitions in short-chain polyenes show that the frequencies do not fall as n^{-2} as expected for a free-electron picture, but appear to saturate at $\Delta E_{(n=\infty)}^{\pi-\pi^*} \approx 2.4$ eV.[1] Bond alternation is present in the polymer and would be expected to lead to semiconducting behavior. However, Ovchinnikov[7] has stimmated the bond-alternation energy gap to be too small and attributed the observed value to Coulomb correlation effects, i.e., a Hubbard gap.

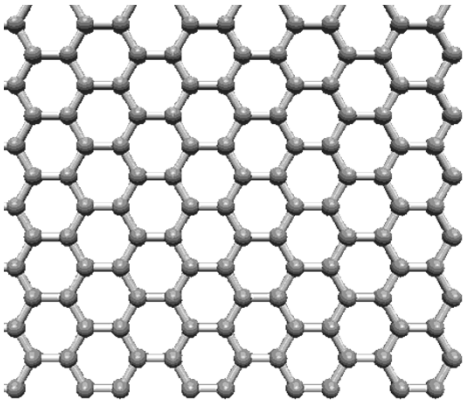
In a series of studies Shirakawa and co-workers[2-4] succeeded in synthesizing high-quality polycrystalline films of $(CH)_x$ and developed techniques for controlling the *cis*/*trans* content.[4,5] These materials are semiconductors[6]; the *trans* isomer is the thermodynamically stable form at room temperature.

FIG. 1. Electrical conductivity of *trans*-$(CH)_x$ as a function of (AsF_5) dopant concentration. The *trans* and *cis* polymer structures are shown in the inset.

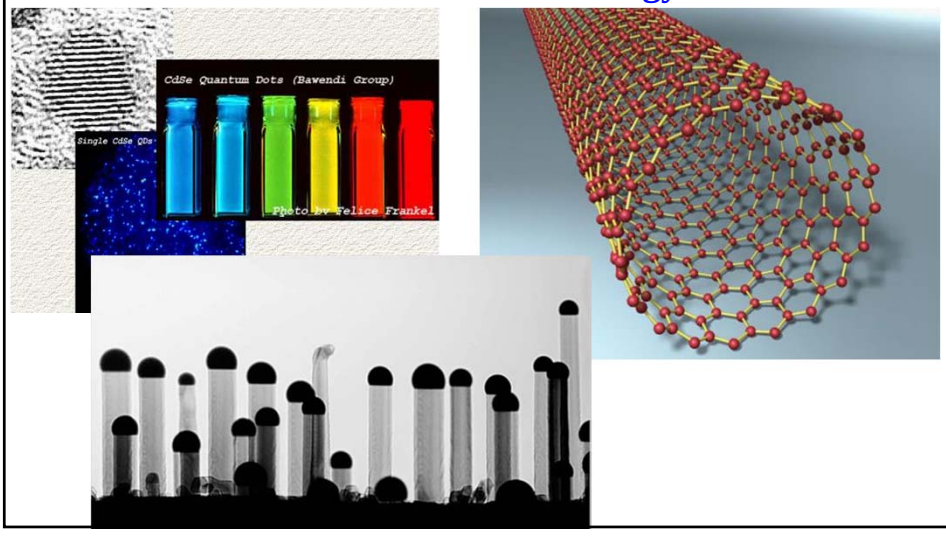
Graphene

The Nobel Prize in Physics 2010
Andre Geim, Konstantin Novoselov

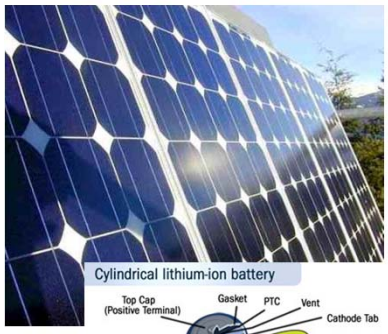


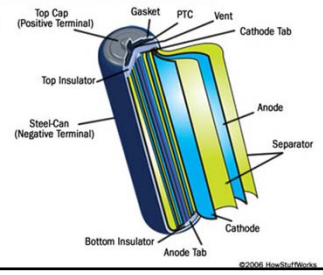


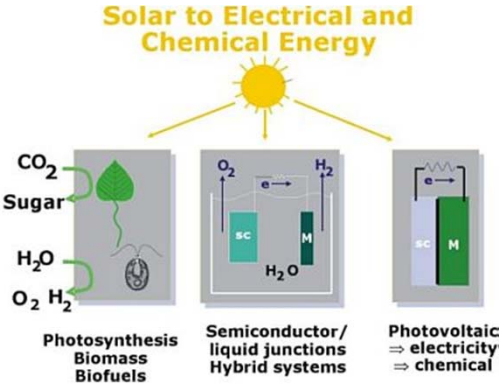
Materials Chemistry is the foundation for the field of Nanoscience and technology.



Energy Research

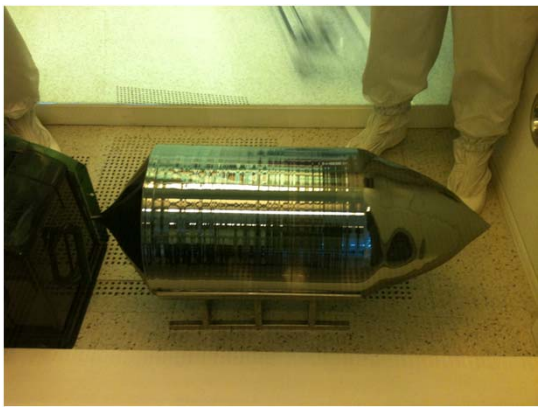


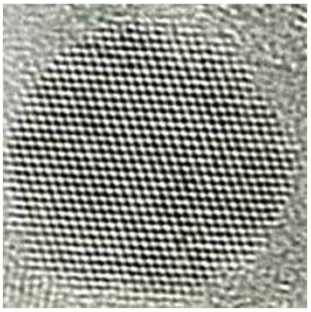




Crystal Structure

Reading: Ashcroft 4-7





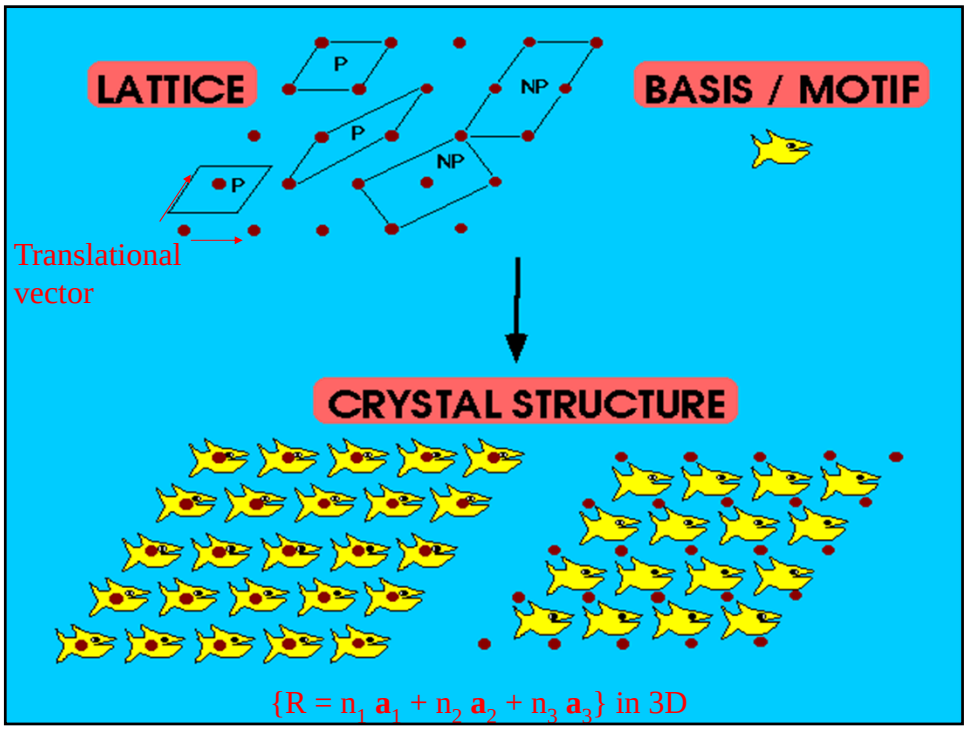
Crystal Structure

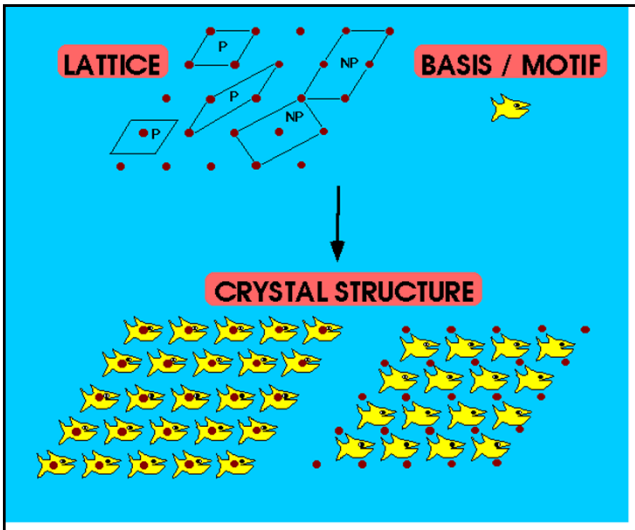
Reading: Ashcroft 4-7

Ideal Crystal: Contain periodical array of atoms/ions
Represented by a simple lattice of points
A group of atoms attached to each lattice points

Basis

LATTICE = *An infinite array of points in space, in which each point has identical surroundings to all others.*
CRYSTAL STRUCTURE = *The periodic arrangement of atoms in the crystal.*
It can be described by associating with each lattice point a group of atoms called the **MOTIF** (**BASIS**)



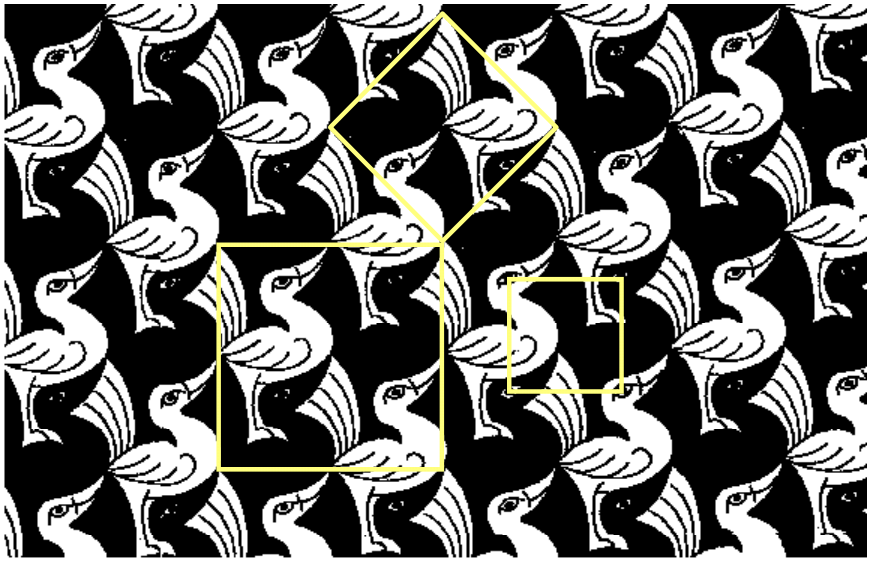


UNIT CELL = *The smallest component of the crystal, which when stacked together with pure translational repetition reproduces the whole crystal*

Primitive Cell: *simplest cell, contain one lattice point*
Not necessary have the crystal symmetry

White and black birds
by the artist, M. C. Escher

Unit Cells?



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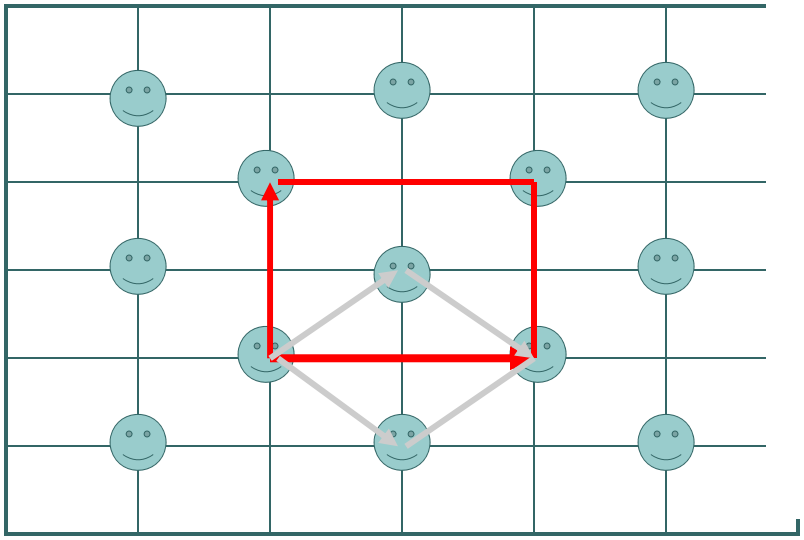

Conventional cell vs. Primitive Cell

Reflecting the symmetry

Different Basis

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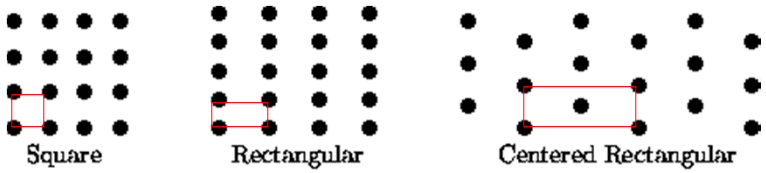
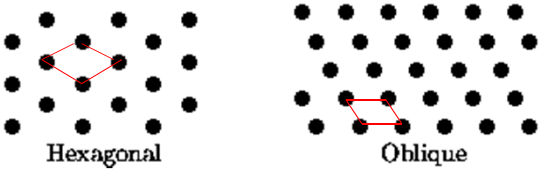
***Bravais Lattice*: an infinite array of discrete points with an arrangement and orientation that appears exactly the same from whichever of the points the array is viewed.**



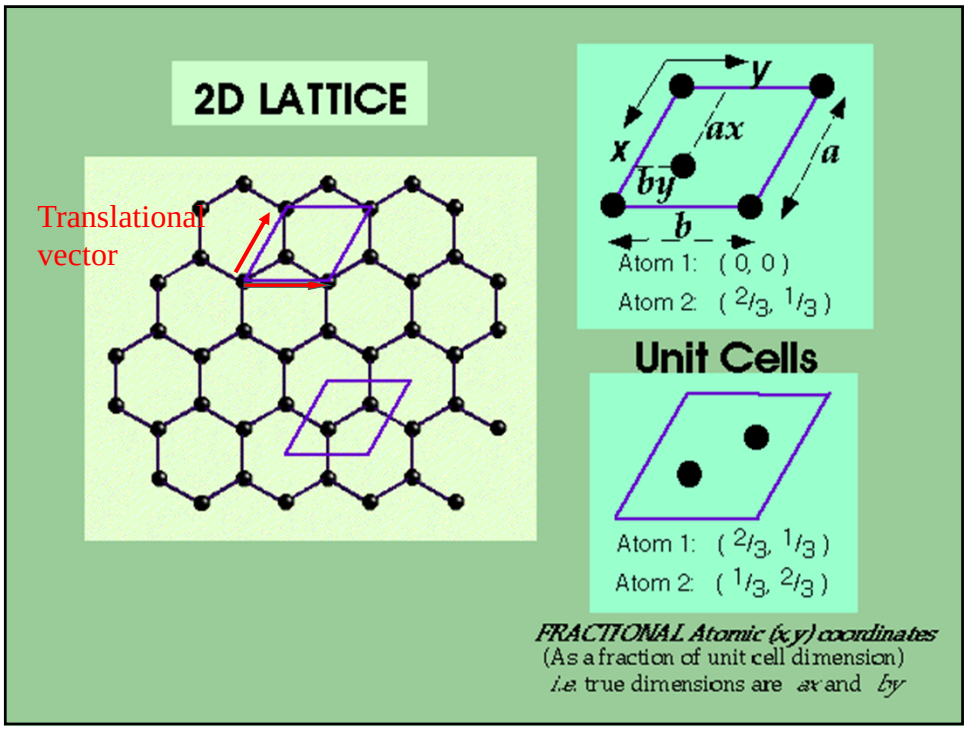
P **P** **NP**



5 Bravais Lattice in 2D

Square	a=b	γ =90
Rectangular	a≠ b	γ=90
Centered Rectangular	a ≠b	γ=90
Hexagonal	a=b	γ =120
Oblique	a ≠b	γ ≠90

5 Bravais Lattice in 2D



3D: 14 Bravais Lattice, 7 Crystal System

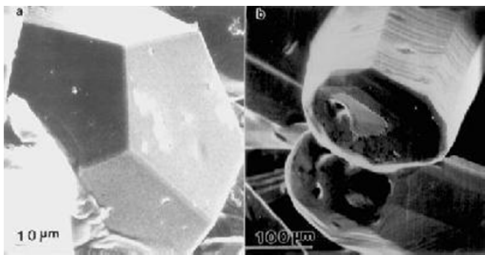
Name	Number of Bravais lattices	Conditions
Triclinic	1 (P)	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2 (P, C)	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = 90° \neq \gamma$
Orthorhombic	4 (P, F, I, A)	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Tetragonal	2 (P, I)	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Cubic	3 (P, F, I)	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90°$
Trigonal	1 (P)	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120° \neq 90°$
Hexagonal	1 (P)	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90°$ $\gamma = 120°$

Allowed rotation axis:

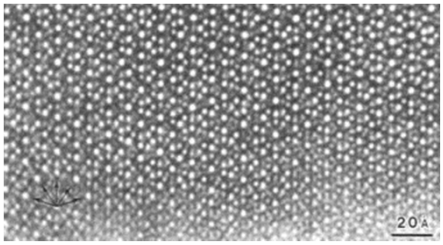
1, 2, 3, 4, 6

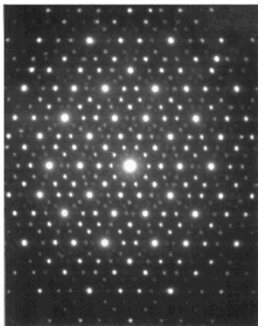
NOT 5, > 6

Quasicrystal: *AlFeCu*



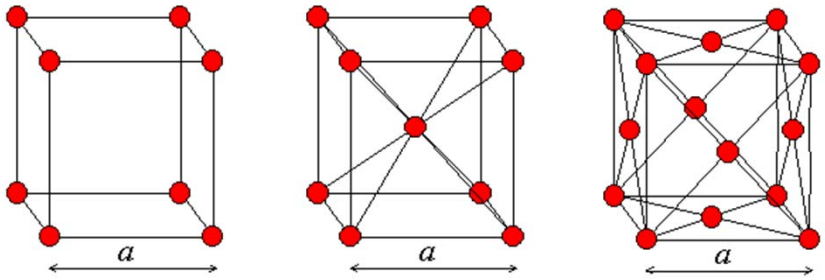
Shechtman, D., Blech, I., Gratias, D. & Cahn, J. W. *Phys. Rev. Lett.* **53**, 1951-1953 (1984).





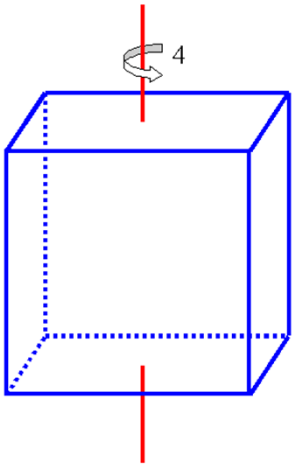
The Nobel Prize in Chemistry 2011
Dan Shechtman

Cubic: four 3-fold + three 4-fold



(a) (b) (c)

Unit cell symmetries - cubic

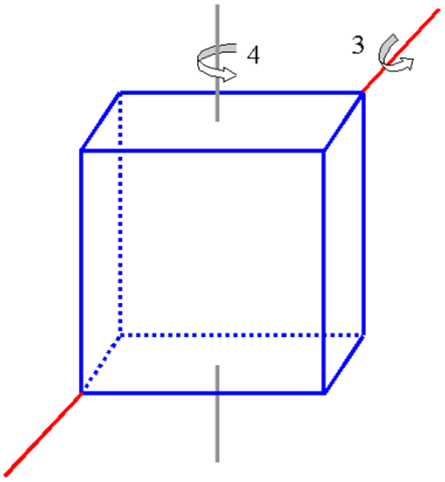


- **4 fold rotation axes**

(passing through pairs of opposite face centers, parallel to cell axes)

TOTAL = 3

Unit cell symmetries - cubic



- 4 fold rotation axes
  TOTAL = 3

- **3-fold rotation axes**
  (passing through cube body diagonals)
  TOTAL = 4

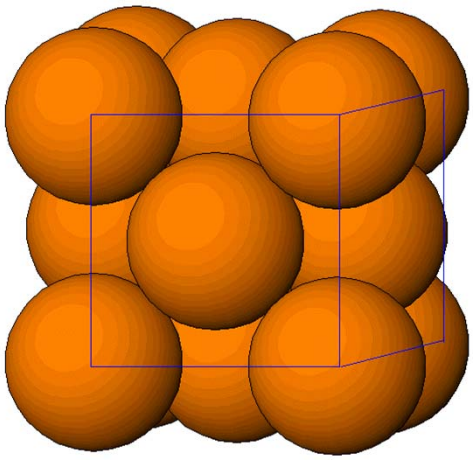
FCC Lattice

Copper metal is **face-centered cubic**

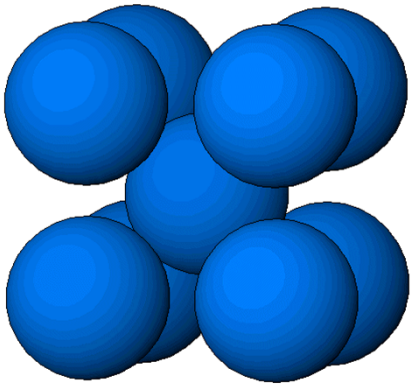
Identical atoms at corners and at face centers

Lattice type F

also Ag, Au, Al, Ni...



BCC Lattice



α-Iron is **body-centered cubic**

Identical atoms at corners and body center (nothing at face centers)

Lattice type I

Also Nb, Ta, Ba, Mo...

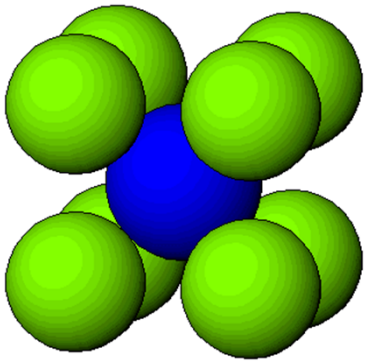
Simple Cubic Lattice

Caesium Chloride (CsCl) is **primitive cubic**

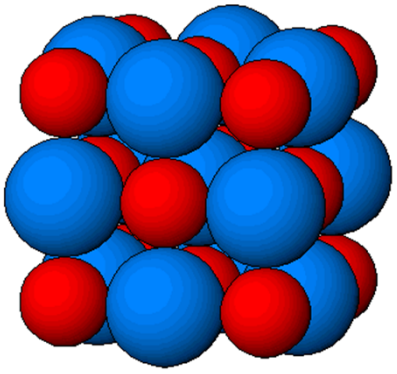
Different atoms at corners and body center. NOT body centered, therefore.

Lattice type P

Also CuZn, CsBr, LiAg



FCC Lattices



Sodium Chloride (NaCl) - Na is much smaller than Cs

Face Centered Cubic

Rocksalt structure

Lattice type F

Also NaF, KBr, MgO….

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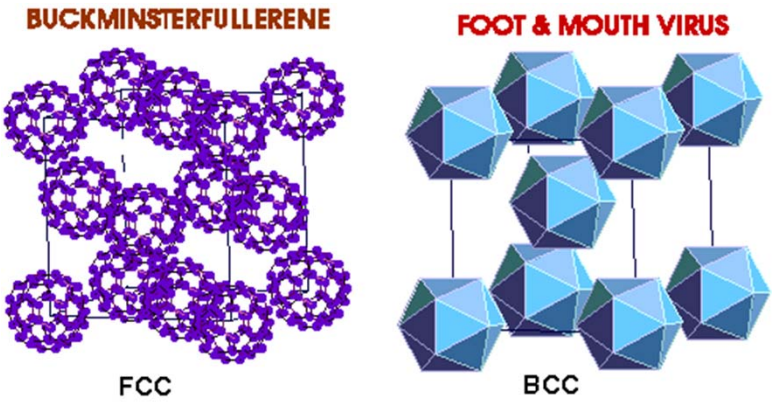
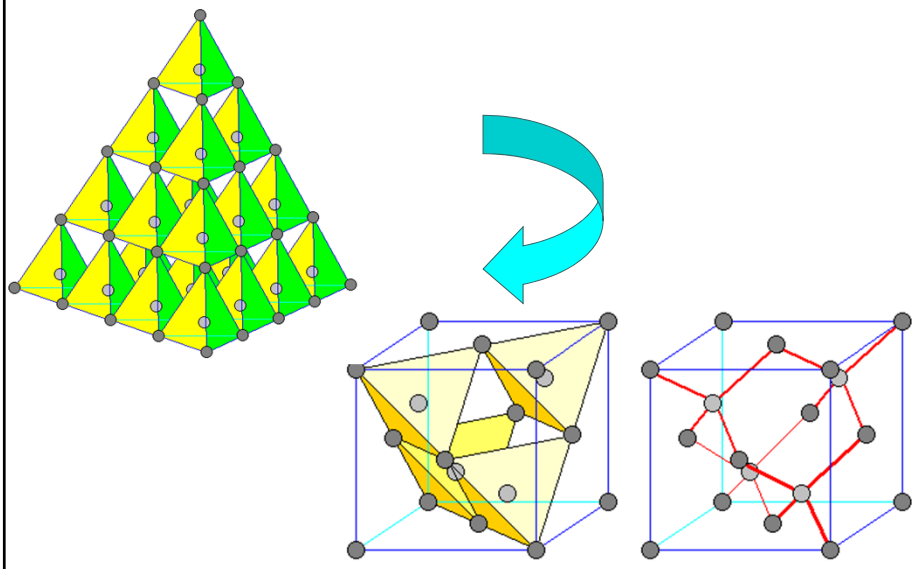
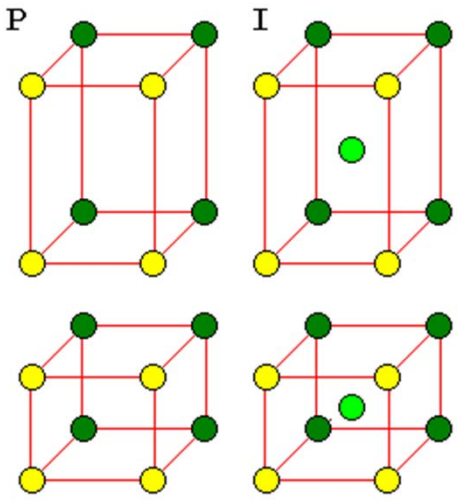


Nature **353**, 147 - 149 (12 Sep 1991)

Diamond Structure: two sets of FCC Lattices



Tetragonal: P, I

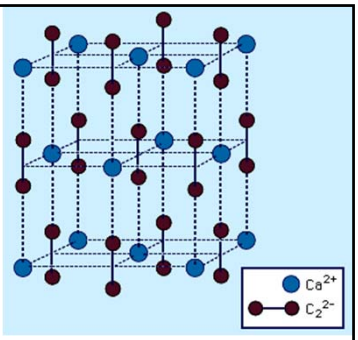


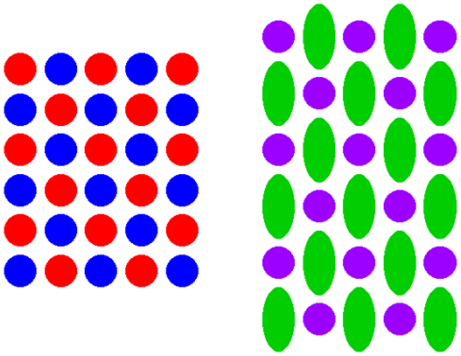
One 4-fold axes

Why not F tetragonal?

Example

CaC_2 - has a rocksalt-like structure but with non-spherical carbides

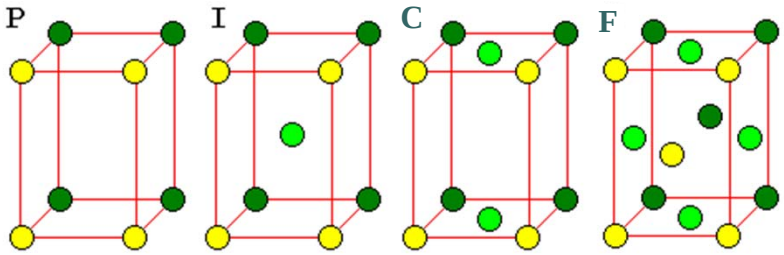




Carbide ions are aligned parallel to **c**

$\therefore$ **c** > **a,b** $\rightarrow$ tetragonal symmetry

Orthorhombic: P, I, F, C



Another type of centering

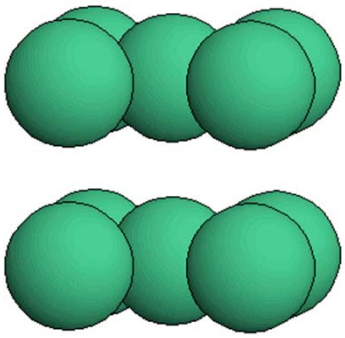
Side centered unit cell

Notation:

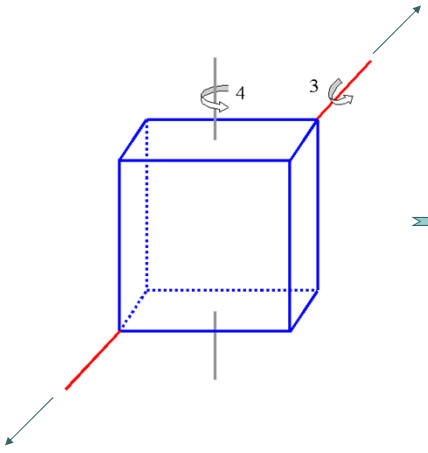
A-centered if atom in bc plane

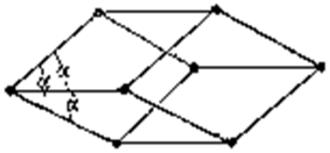
B-centered if atom in ac plane

C-centered if atom in ab plane



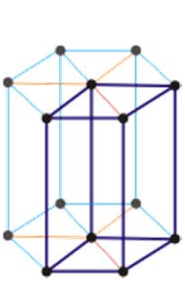
Trigonal: P : 3-fold rotation

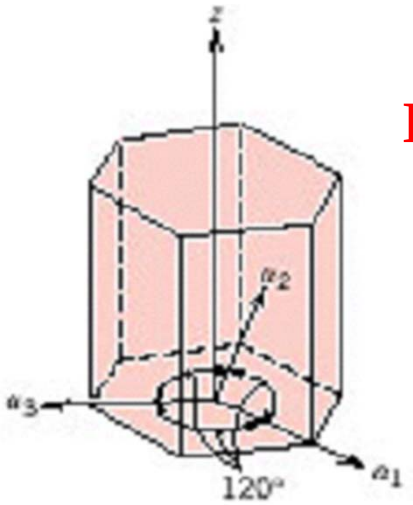




Rhombohedral
R

a1 = a2 = a3
α = β = γ < 120° ≠ 90°

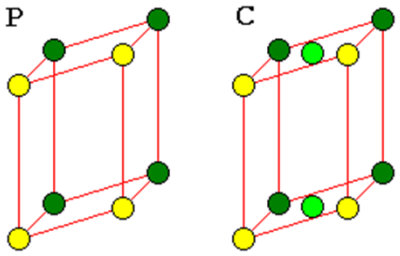




Hexagonal

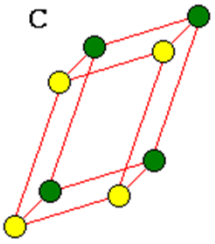
$a_1 = a_2 \neq a_3$
$\alpha = \beta = 90°$
$\gamma = 120°$

Monoclinic

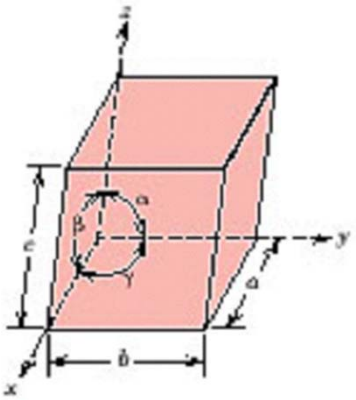


a1 ≠ a2 ≠ a3
α = β = 90° ≠ γ

Triclinic



a1 ≠a2≠ a3
α ≠β≠ γ

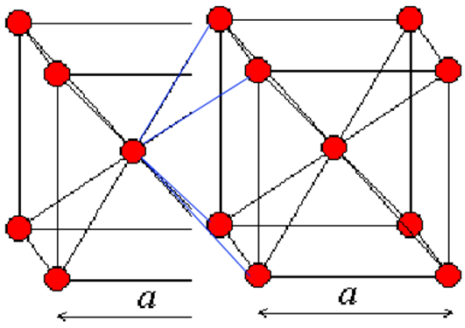


Lattice parameters:
a, b, c; α, β, γ

7 Crystal Systems

Table 3.2 Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems

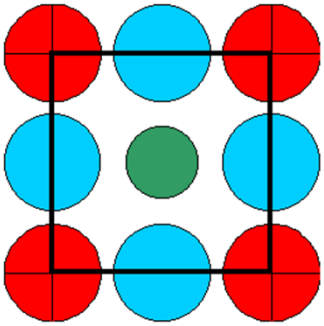
Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	



The choice of unit cell: reflect the crystal symmetry

Unit cell contents

Counting the number of atoms within the unit cell



Many atoms are shared between unit cells

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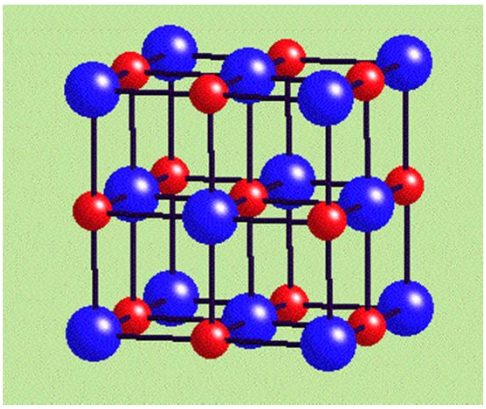
Atoms	Shared Between:	Each atom counts:
corner	8 cells	1/8
face center	2 cells	1/2
body center	1 cell	1
edge center	4 cells	1/4

lattice type	cell contents	
P	1	[=8 x 1/8]
I	2	[=(8 x 1/8) + (1 x 1)]
F	4	[=(8 x 1/8) + (6 x 1/2)]
C	2	[=(8 x 1/8) + (2 x 1/2)]



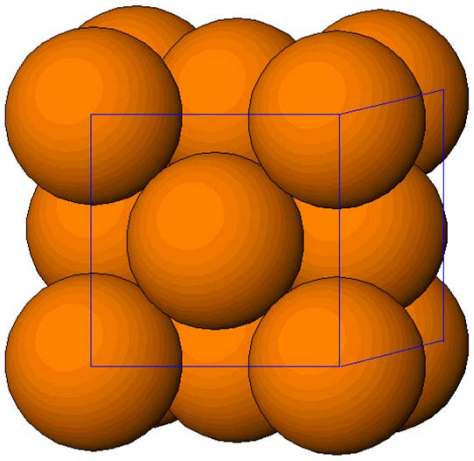
e.g. NaCl

Na at corners: (8 × 1/8) = 1 Na at face centres (6 × 1/2) = 3

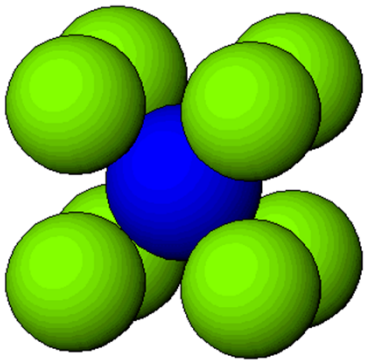
Cl at edge centres (12 × 1/4) = 3 Cl at body centre = 1

Unit cell contents are $4(Na^+Cl^-)$

Fractional Coordinates



(0,0,0)
(0, ½, ½)
(½, ½, 0)
(½, 0, ½)



Cs (0,0,0)
Cl (½, ½, ½)

Density Calculation

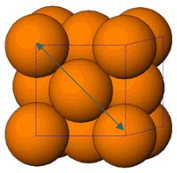
$$\rho = \frac{nA}{V_C N_A}$$

n: number of atoms/unit cell

A: atomic mass

V_C: volume of the unit cell

N_A: Avogadro's number (6.023×10^{23} atoms/mole)



Calculate the density of copper.

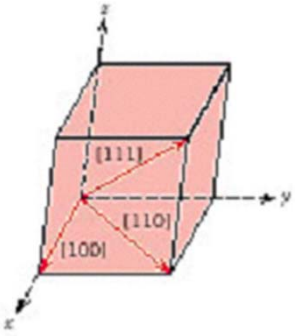
R_{Cu} =0.128nm, Crystal structure: FCC, A_{Cu}= 63.5 g/mole

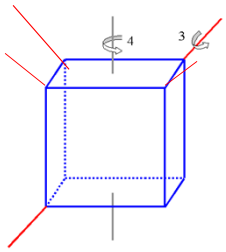
n = 4 atoms/cell, $V_C = a^3 = (2R\sqrt{2})^3 = 16\sqrt{2}R^3$

$$\rho = \frac{(4)(63.5)}{[16\sqrt{2}(1.28\times10^{-8})^3 \times 6.023\times10^{23}]} = 8.89 g/cm^3$$

8.94 g/cm^3 in the literature

Crystallographic Directions And Planes





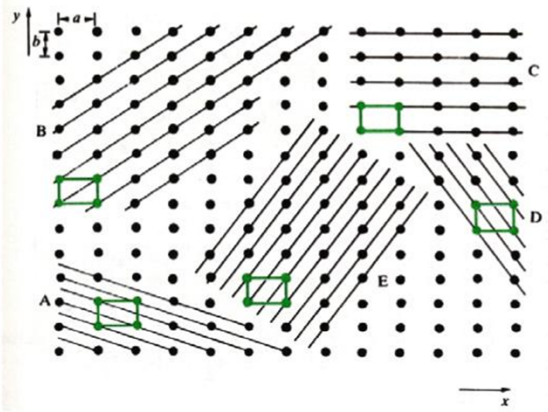
Lattice Directions

Individual directions: [uvw]

Symmetry-related directions: <uvw>

Lattice planes

- It is possible to describe certain directions and planes with respect to the crystal lattice using a set of three integers referred to as Miller Indices



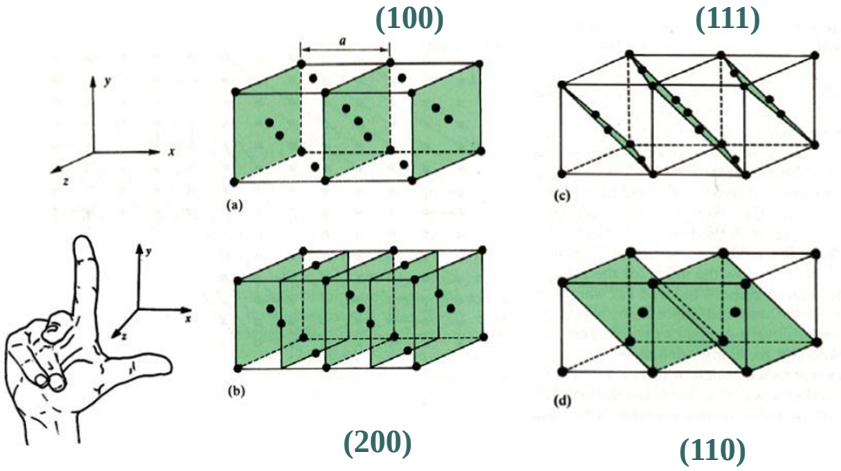
Crystallographic Directions And Planes

Miller Indices:

1. Find the intercepts on the axes in terms of the lattice constant a, b, c
2. Take the reciprocals of these numbers, reduce to the three integers having the same ratio
   (hkl)

Set of symmetry-related planes: {hkl}

Examples of Miller indices

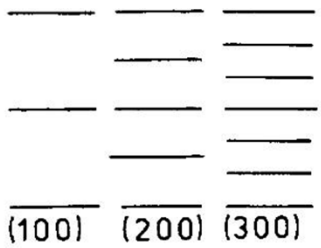


Families of planes

- Miller indices describe the orientation a spacing of a family of planes
  - The spacing between adjacent planes in a family is referred to as a "d-spacing"

Three different families of planes

d-spacing between (300) planes is one third of the (100) spacing



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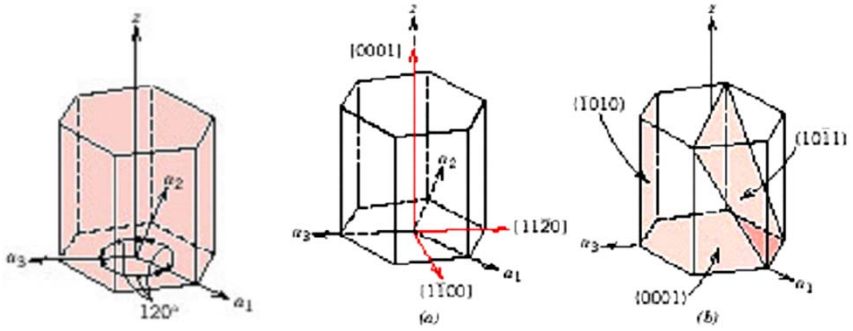
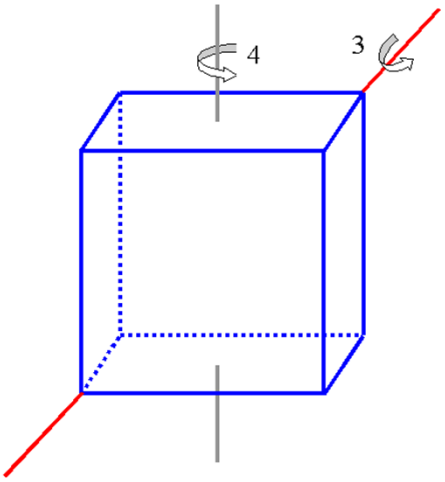
Crystallographic Directions And Planes



Miller-Bravais indices

[uvtw], (hkil)

t=-(u+v) *i=-(h+k)*



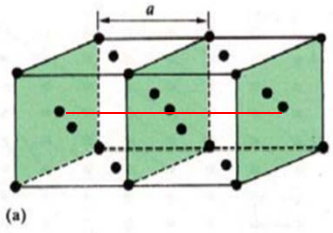
In cubic system,

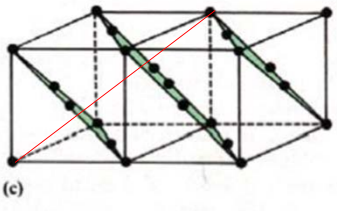
[hkl] direction perpendicular to (hkl) plane

Lattice spacing

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

For cubic system





d-spacing formulae

- For a unit cell with orthogonal axes
  - $(1 / d^2_{hkl}) = (h^2/a^2) + (k^2/b^2) + (l^2/c^2)$
- Hexagonal unit cells
  - $(1 / d^2_{hkl}) = (4/3)([h^2 + k^2 + hk]/ a^2) + (l^2/c^2)$

Crystal Structure Analysis

X-ray diffraction

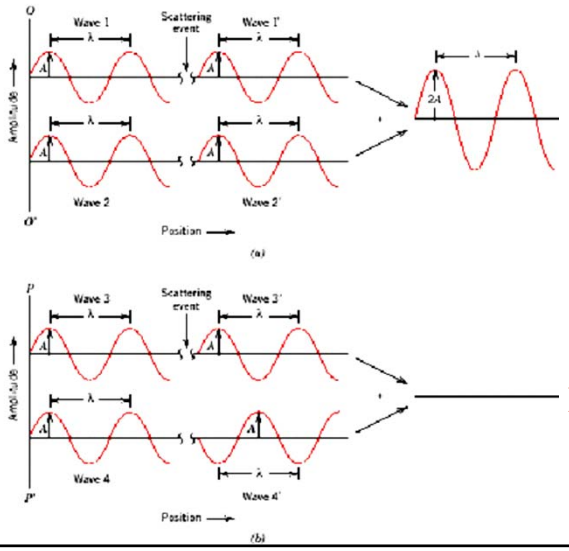
Electron Diffraction

Neutron Diffraction

Essence of diffraction: Bragg Diffraction

Light

Interference fringes

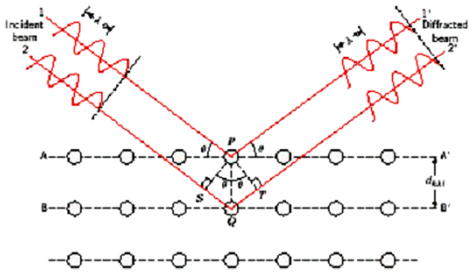


Constructive

Destructive

Bragg's Law

$$n\lambda = \overline{SQ} + \overline{QT}$$
$$= d_{hkl}\sin\theta + d_{hkl}\sin\theta$$
$$= 2d_{hkl}\sin\theta$$



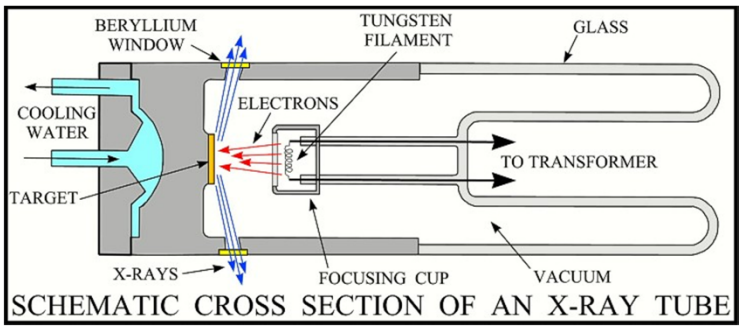
For cubic system:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

But not all planes have the diffraction !!!

X-Ray Diffraction

$$E = h\nu = hc/\lambda$$



Mo: *35KeV ~ 0.1-1.4Å*

Cu K 1.54 A

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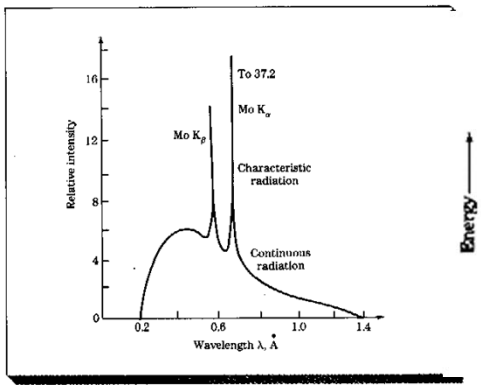
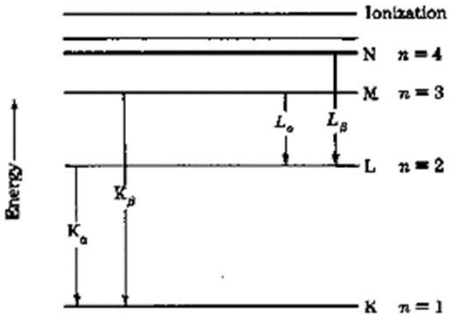
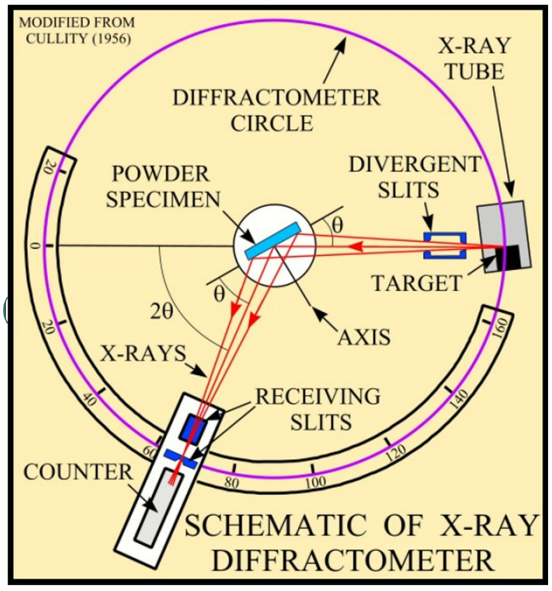
X-Ray Diffraction

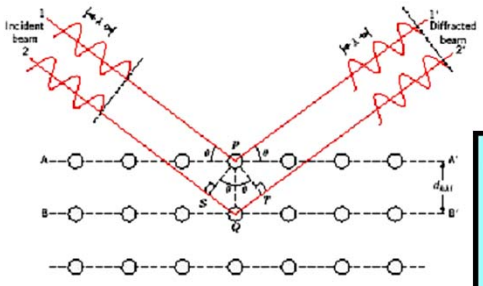




Powder diffraction



Powder diffraction



BRAGG LAW

$$2d(\sin\theta) = \lambda_o$$

where:

d = lattice interplanar spacing of the crystal

θ = x-ray incidence angle (Bragg angle)

λ = wavelength of the characteristic x-rays

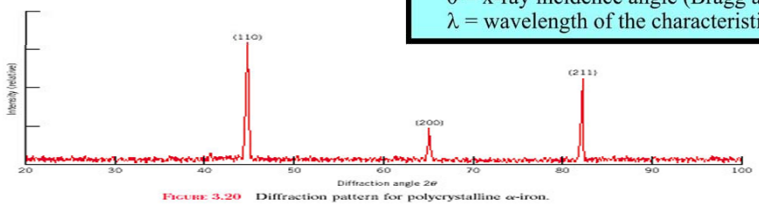
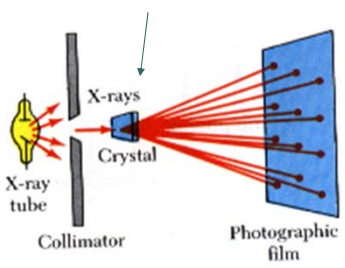
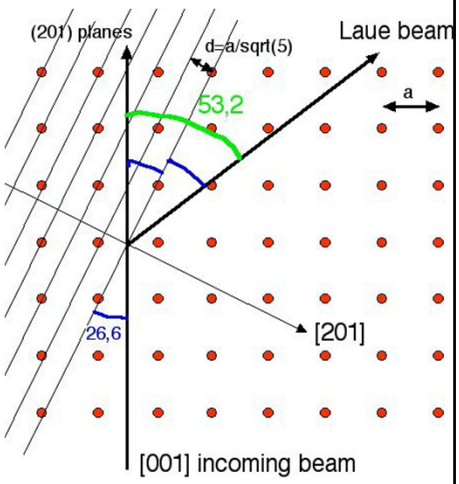


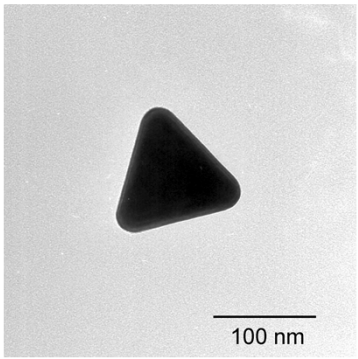
FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

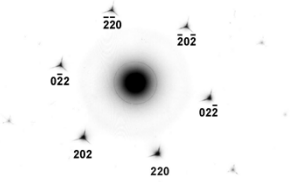
Laue Diffraction





Electron Diffraction



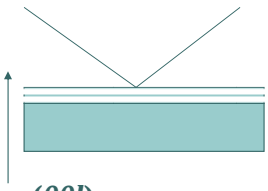


Layered Cuprates
Thin film, growth oriented along c axis

Example: La_2CuO_2

$$2d \sin\theta = n\lambda$$

2*theta	d	(hkl)
7.2	12.1	(001)
14.4	6.1	(002)
22	4.0	(003)



(00l)

c=12.2 A

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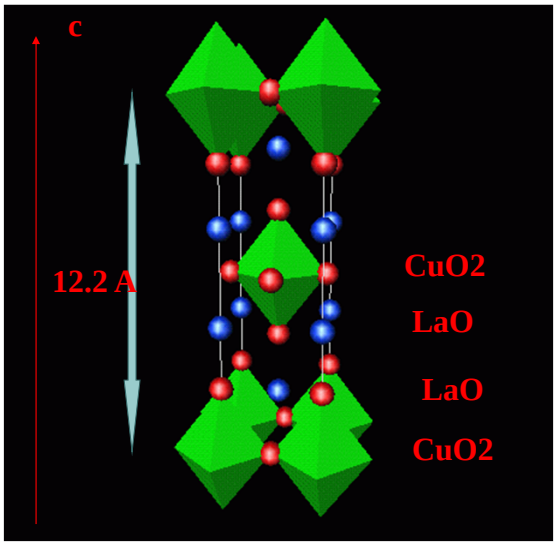
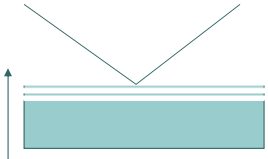


Example: $Ca_{0.5}Sr_{0.5}CuO_2$

Layered Cuprates
Thin film, growth oriented along c axis

$$2d \sin\theta = n\lambda$$

2*theta	d	(hkl)
12.7	6.96	(001)
26	3.42	(002)
42.2	2.15	(003)



(00l)

c=6.96 Å

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