

Welcome to Chem 253
Materials & Solid State Chemistry

<http://nanowires.berkeley.edu/teaching/chem253.html>

Chemistry 253 A & B & C
Materials & Solid State Chemistry

Lecture: Tu. Thurs. 2:00-3:30 pm @ 433 Latimer

Instructor:

Professor Peidong Yang, 239 Hild.,
Office Hours: Friday 10:00-12:00pm or by appointment
p_yang@berkeley.edu

TA:

Nick Kornienko
nick.kornienko.berkeley@gmail.com
Office Hours: TBA

Grading:

Problem sets (2) 40%

Final 60%

Course Description:

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

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). | Introduction | |
| 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 | |

March 2016

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
		1	2	3	4	5
6	7	8	9	10	11	12
13	14	15	16	17	18	19
20	21	22	23	24	25	26
	Spring Break					
27	28	29	30	31		
		Exam				

Materials Chemistry II

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

<p>Gersten, 7,11
Hoffmann,Burdett 1-3</p> |
|---|---|

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
April 2016					1	2
3	4	5	6	7	8	9
10	11	12	13	14	15	16
17	18	19	20	21	22	23
24	25	26	27	28 Exam	29	30
Notes:						

Solid State and Materials Chemistry

**Synthesis, structure,
Properties, applications of solid materials**

Inorganic, organic, biological

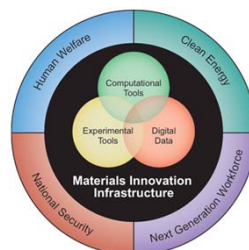
Materials by Design

**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

Superconductivity

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

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

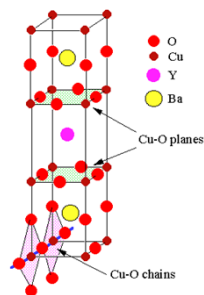
1986, J. G. Bednorz, K. H. Muller (IBM)

La-Ba-Cu-O

Oxide: $T_c = 35$ K

1997 Nobel prize in Physics

French Group (B. Raveau)

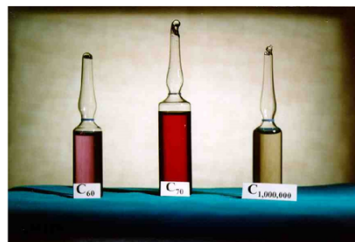
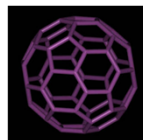
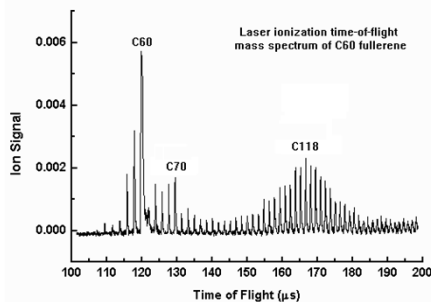


Bucky Ball; fullerene

1996 Nobel prize in chemistry



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



Models, edited by R. H. Douglas (Plenum, New York and London, 1976), and by C. M. Varma and R. C. Dymos, *ibid.*
We have chosen 0.5 eV somewhat arbitrarily to do-

first π^* . It is the energy near the F_{2g}^+ scattering within which leads to over 90% of most of the anomalies.
*W. Kohn, *Phys. Rev. Lett.* **2**, 293 (1959); A. W. Overhauser, *Phys. Rev. Lett.* **2**, 415 (1959).

Electrical Conductivity in Doped Polyacetylene

C. K. Chiang, C. R. Fischer, 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,^{1,2} 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 22 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 5%.

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, bromine, or iodine, and with arsenic pentafluoride (AsF₅). 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 $\pi-\pi^*$ 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 $\Delta E_{\pi-\pi^*} \approx 2.4$ eV.³ Bond alternation is present in the polymer and would be expected to lead to semiconducting behavior. However, Ovchinnikov⁴ has stimulated 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-workers⁵⁻⁷ succeeded in synthesizing high-quality

polycrystalline films of (CH)_x and developed techniques for controlling the *cis/trans* content.^{1,4} These materials are semiconductors⁸; the *trans* isomer is the thermodynamically stable form at room temperature.

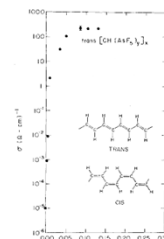


FIG. 1. Electrical conductivity of *trans*-(CH)_x as a function of (AsF₅) dopant concentration. The *trans* and *cis* polymer structures are shown in the inset.

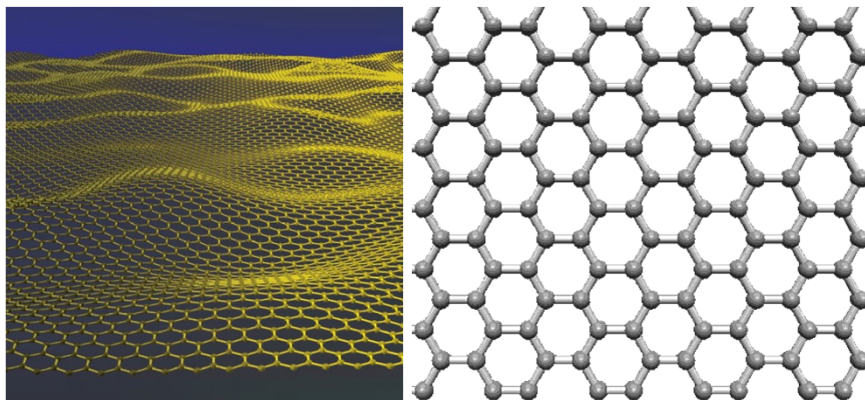
Conducting Polymer

[2000 Alan Heeger.](#)
[Alan G. MacDiarmid.](#)
[Hideki Shirakawa](#)

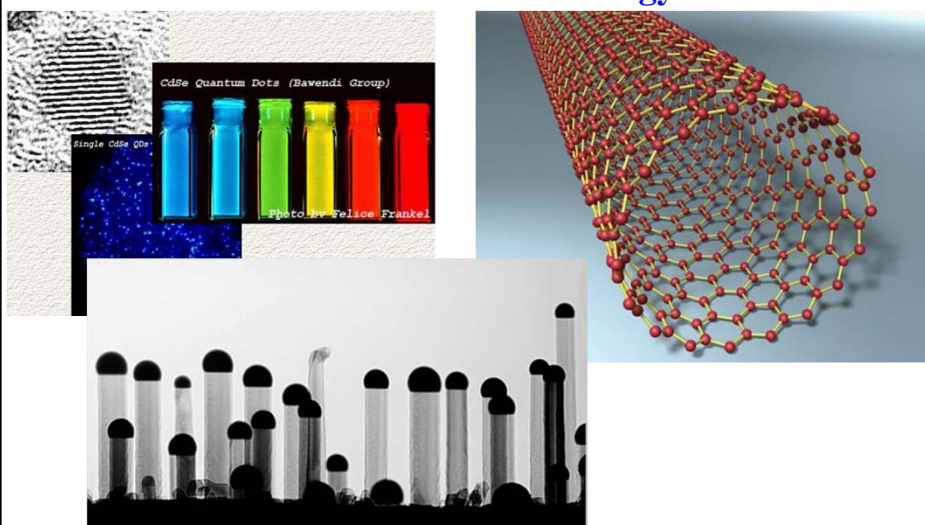
Nobel Prize in Chemistry

Graphene

The Nobel Prize in Physics 2010
Andre Geim, Konstantin Novoselov



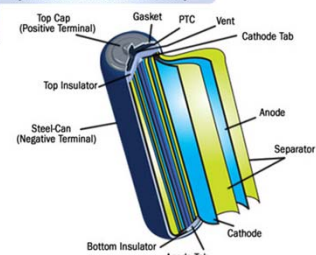
**Materials Chemistry is the foundation for the
field of
Nanoscience and technology.**



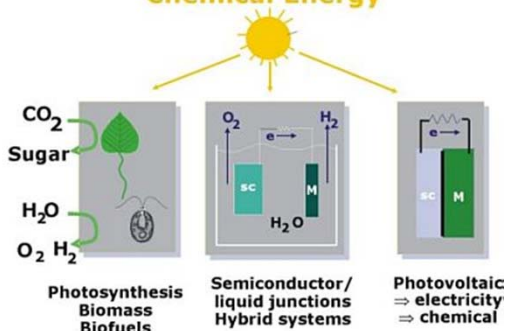
Energy Research



Cylindrical lithium-ion battery

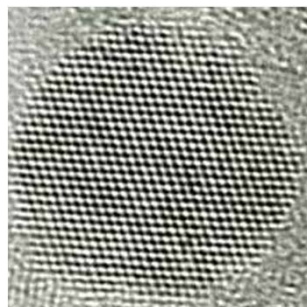


Solar to Electrical and Chemical Energy



Crystal Structure

Reading: Ashcroft 4-7



Crystal Structure

Reading: Ashcroft 4-7

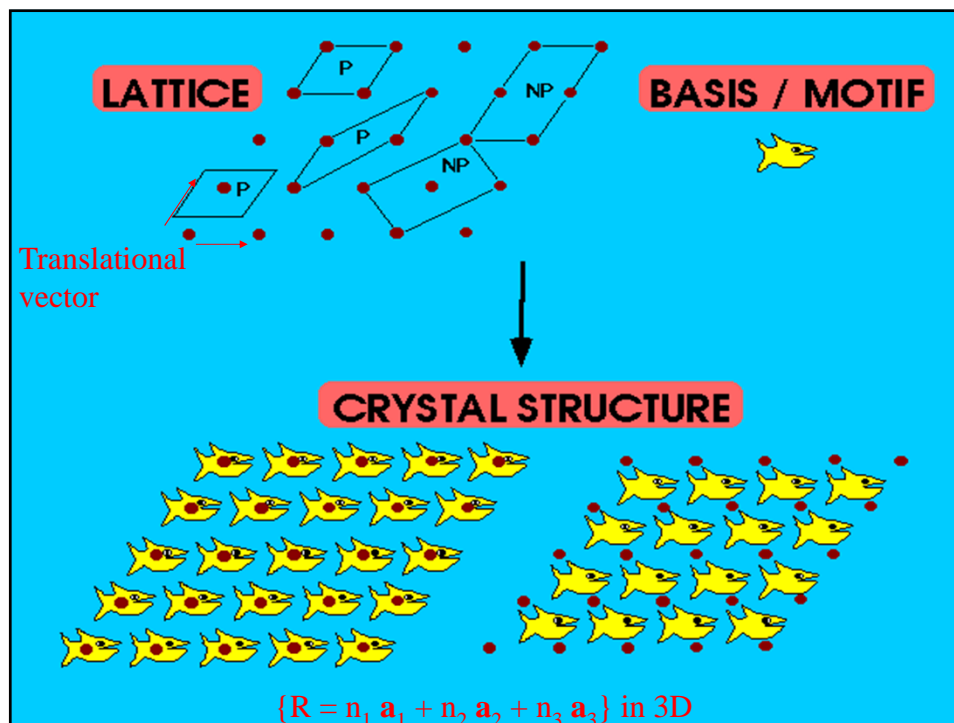
Ideal Crystal: Contain periodical array of atoms/ions
Represented by a simple lattice of points
A group of atoms attached to each lattice points

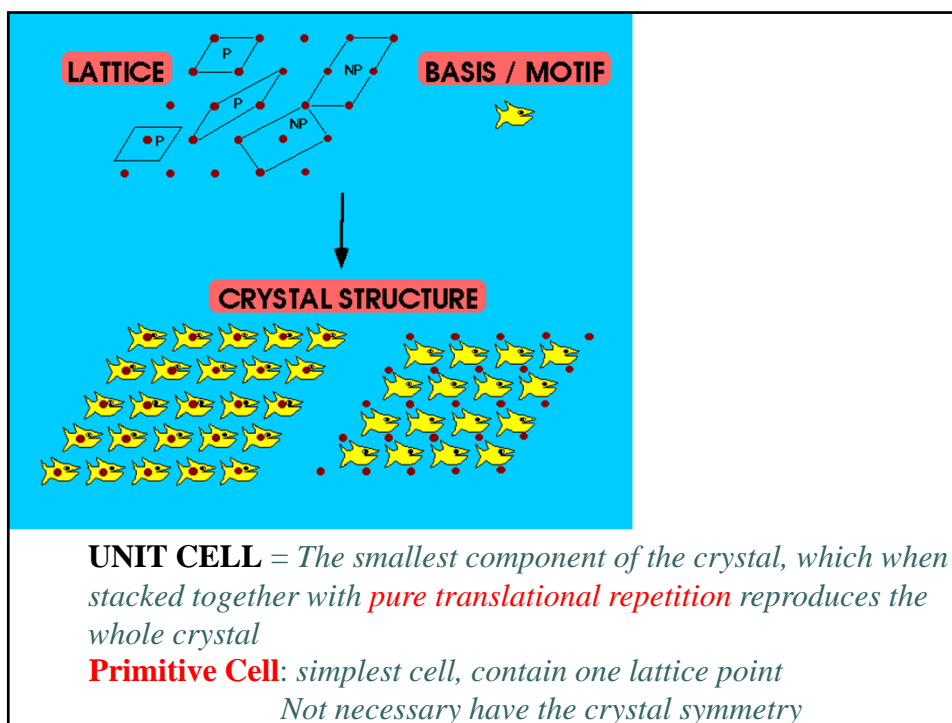
Basis

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)**

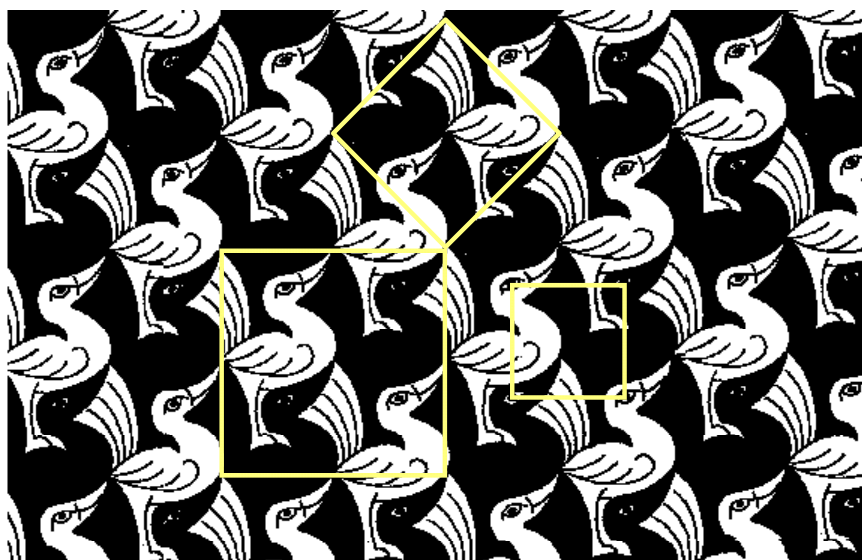


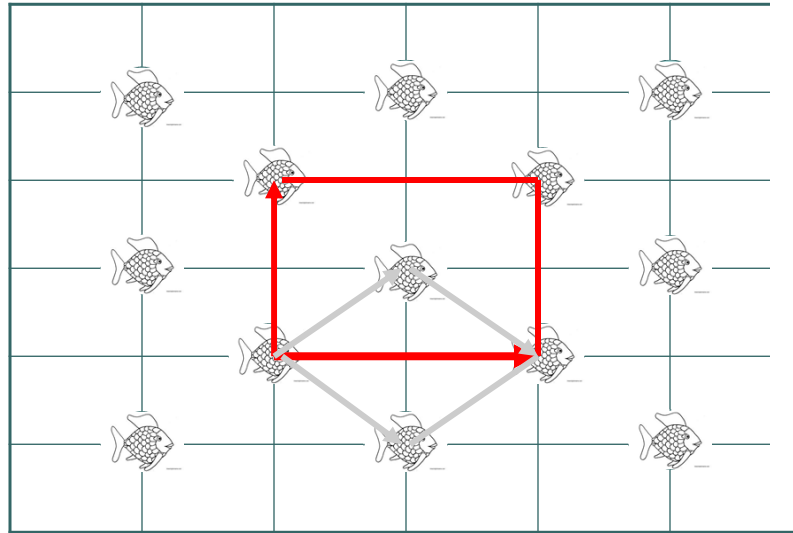


Chem 253, UC, Berkeley ● ● ●

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

Unit Cells?



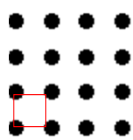


Conventional cell vs. Primitive Cell

Reflecting the symmetry

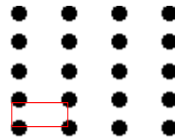
Different Basis

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.



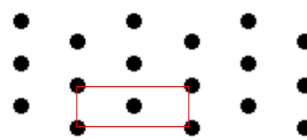
Square

P



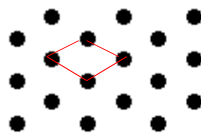
Rectangular

P

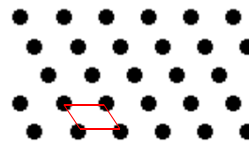


Centered Rectangular

NP



Hexagonal



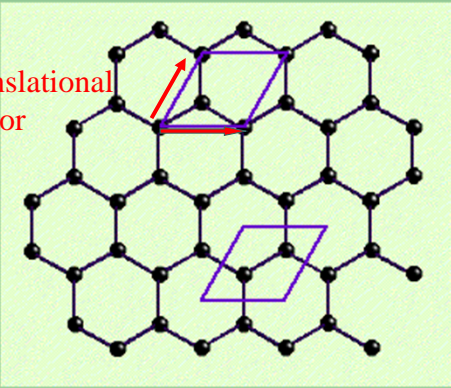
Oblique

5 Bravais Lattice in 2D

Square	$a=b$	$\gamma=90$
Rectangular	$a \neq b$	$\gamma=90$
Centered Rectangular	$a \neq b$	$\gamma=90$
Hexagonal	$a=b$	$\gamma=120$
Oblique	$a \neq b$	$\gamma \neq 90$

5 Bravais Lattice in 2D

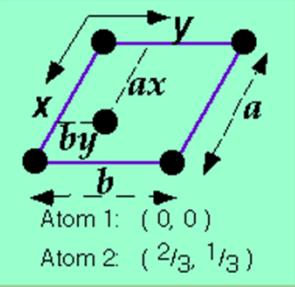
2D LATTICE



Translational vector

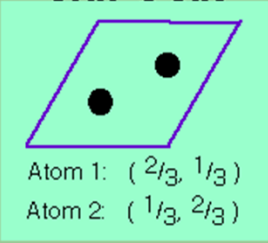
Lattice + Basis

Graphene



Atom 1: $(0, 0)$
Atom 2: $(\frac{2}{3}, \frac{1}{3})$

Unit Cells



Atom 1: $(\frac{2}{3}, \frac{1}{3})$
Atom 2: $(\frac{1}{3}, \frac{2}{3})$

FRACTIONAL Atomic (x,y) coordinates
(As a fraction of unit cell dimension)
i.e. true dimensions are ax and by

3D: 14 Bravais Lattice, 7 Crystal System

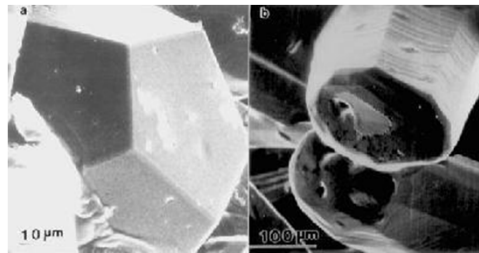
Name	Number of Bravais lattices	Conditions
Triclinic	1 (P)	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2 (P, C)	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = 90^\circ \neq \gamma$
Orthorhombic	4 (P, F, I, A)	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2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

Allowed rotation axis:

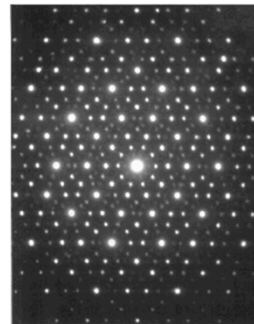
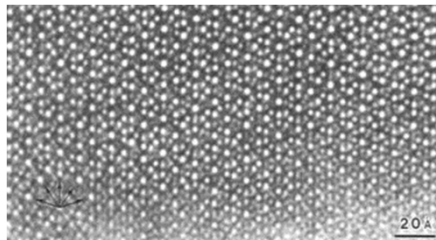
1, 2, 3, 4, 6

NOT allowed: 5, > 6

Quasicrystal: AlFeCu

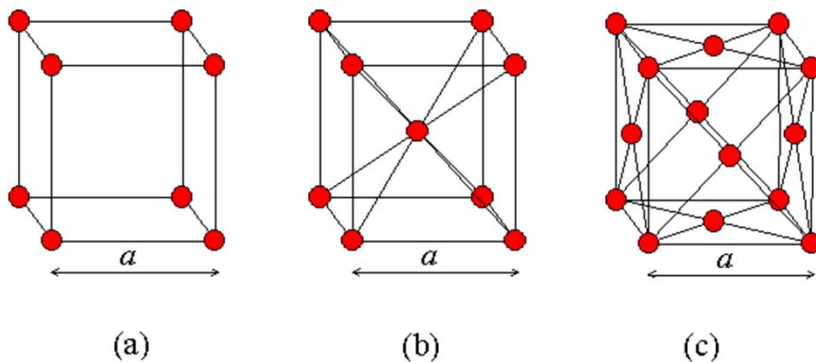


Shechtman, D., Blech, I., Gratias, D. & Cahn, J. W.
Phys. Rev. Lett. **53**, 1951-1953 (1984).

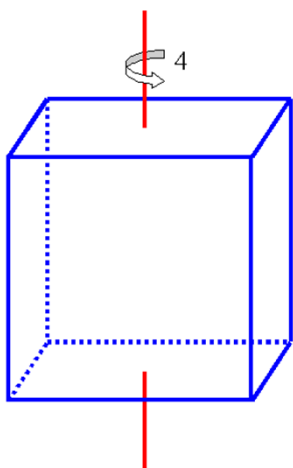


The Nobel Prize in Chemistry 2011
Dan Shechtman

Cubic: four 3-fold + three 4-fold

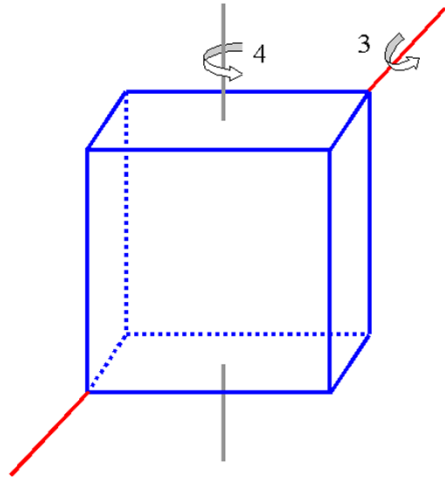


Unit cell symmetries - cubic



● **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

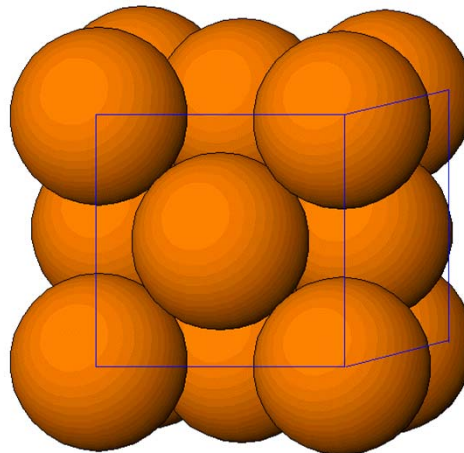
FCC Lattice

Copper metal is
**face-centered
cubic**

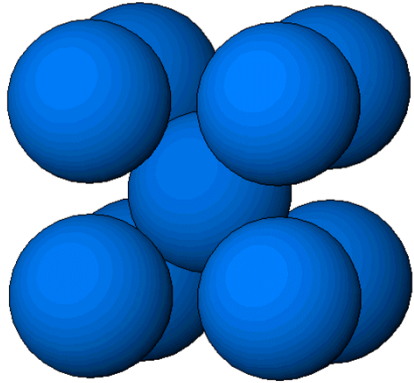
Identical atoms at
corners and at face
centers

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...

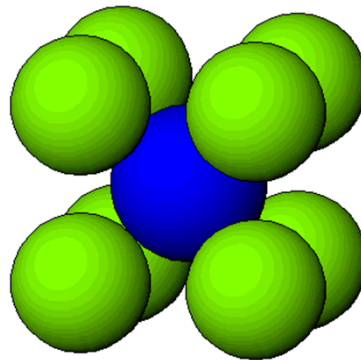
Simple Cubic Lattice

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

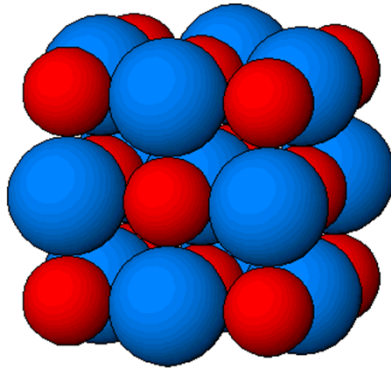
Different atoms at corners and body center. **NOT** body centered, therefore.

Lattice type P

Also CuZn, CsBr, LiAg



FCC Lattices



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

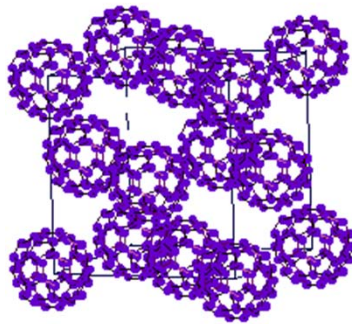
Face Centered Cubic

Rocksalt structure

Lattice type F

Also NaF, KBr, MgO....

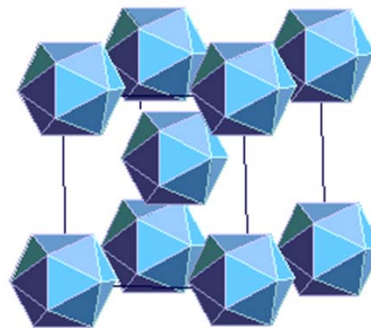
BUCKMINSTERFULLERENE



FCC

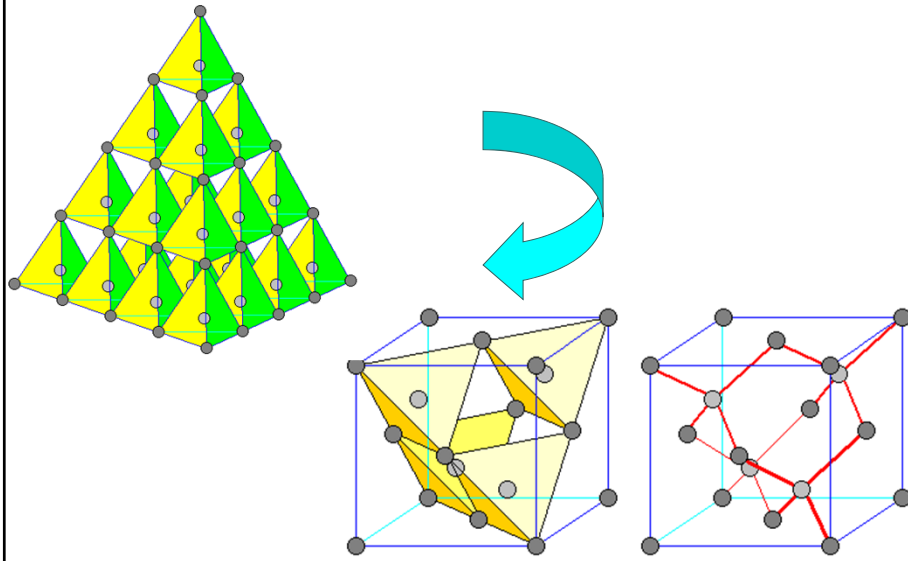
Nature **353**, 147 - 149 (12 Sep 1991)

FOOT & MOUTH VIRUS

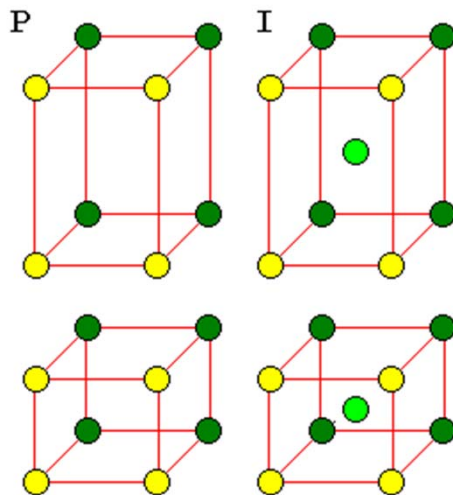


BCC

Diamond Structure: two sets of FCC Lattices



Tetragonal: P, I



One 4-fold axes

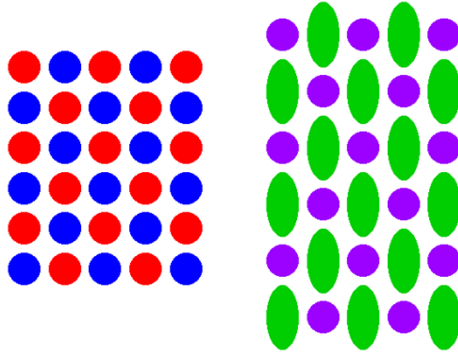
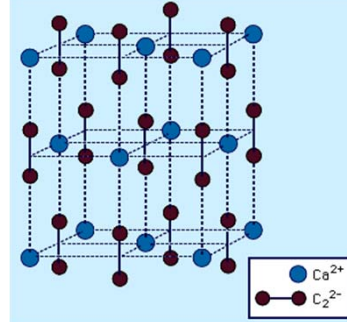
$$a_1 = a_2 \neq a_3$$

$$\alpha = \beta = \gamma = 90^\circ$$

Why not F tetragonal?

Example

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



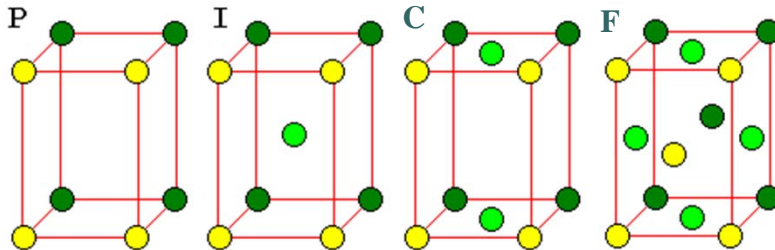
Carbide ions are aligned parallel to **c**

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

Orthorhombic: P, I, F, C

$$a_1 \neq a_2 \neq a_3$$

$$\alpha = \beta = \gamma = 90^\circ$$



Another type of centering

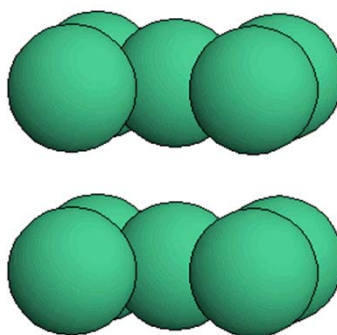
Side centered unit cell

Notation:

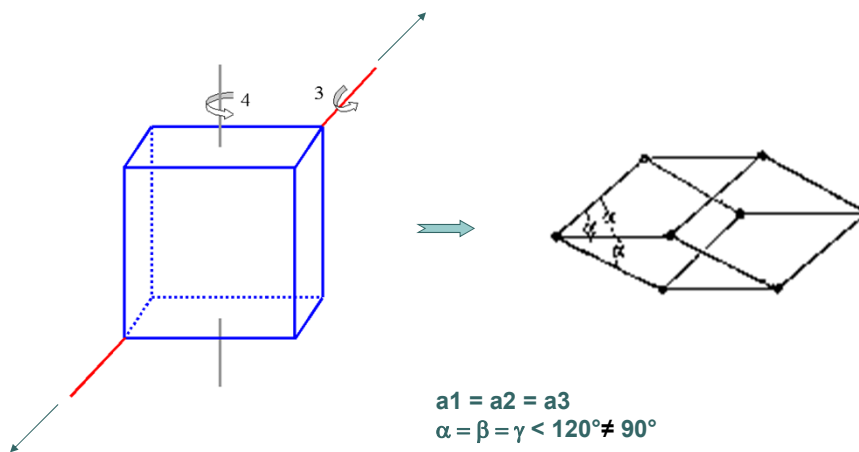
A-centered if atom in bc plane

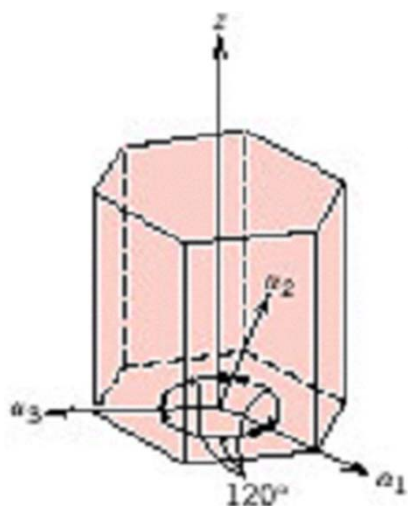
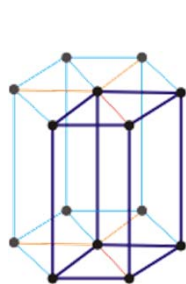
B-centered if atom in ac plane

C-centered if atom in ab plane



Trigonal: P : 3-fold rotation

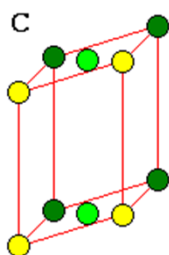
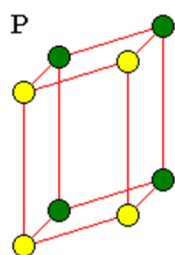




Hexagonal

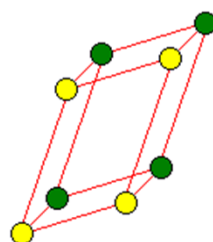
$$\begin{aligned} a_1 &= a_2 \neq a_3 \\ \alpha &= \beta = 90^\circ \\ \gamma &= 120^\circ \end{aligned}$$

Monoclinic

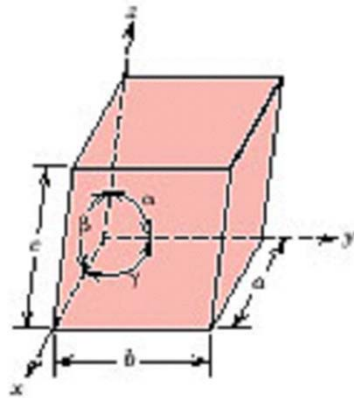


$$\begin{aligned} a_1 &\neq a_2 \neq a_3 \\ \alpha &= \beta = 90^\circ \neq \gamma \end{aligned}$$

Triclinic



$$\begin{aligned} a_1 &\neq a_2 \neq a_3 \\ \alpha &\neq \beta \neq \gamma \end{aligned}$$

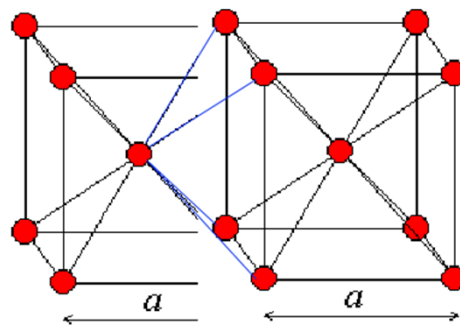


Lattice parameters:
 $a, b, c; \alpha, \beta, \gamma$

7 Crystal Systems

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

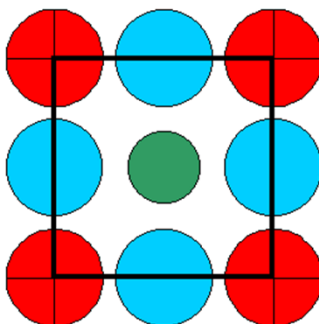
Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Rhombohedral	$a = b = c$	$\alpha =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



The choice of unit cell: reflect the crystal symmetry

Unit cell contents

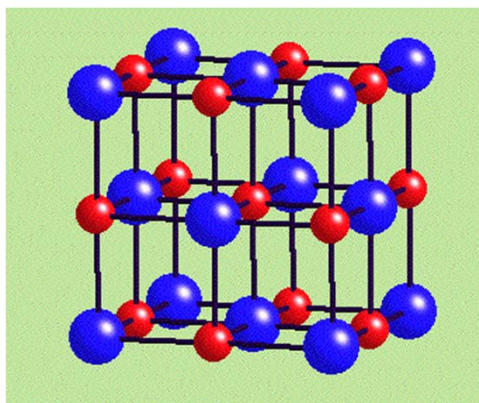
Counting the number of atoms within the unit cell



Many atoms are shared between unit cells

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 $[=8 \times 1/8]$
I	2 $[=(8 \times 1/8) + (1 \times 1)]$
F	4 $[=(8 \times 1/8) + (6 \times 1/2)]$
C	2 $[=(8 \times 1/8) + (2 \times 1/2)]$



e.g. NaCl

Na at corners: $(8 \times 1/8) = 1$

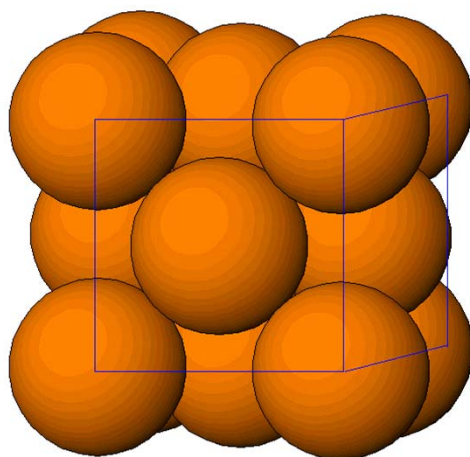
Na at face centres $(6 \times 1/2) = 3$

Cl at edge centres $(12 \times 1/4) = 3$

Cl at body centre = 1

Unit cell contents are $4(\text{Na}^+\text{Cl}^-)$

Fractional Coordinates

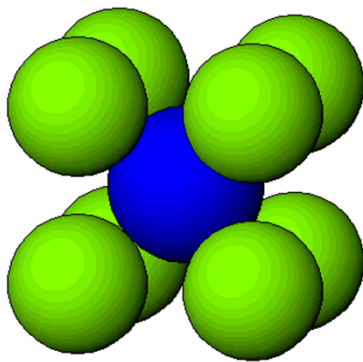


$(0,0,0)$

$(0, 1/2, 1/2)$

$(1/2, 1/2, 0)$

$(1/2, 0, 1/2)$



Cs (0,0,0)
Cl (1/2, 1/2, 1/2)

Density Calculation

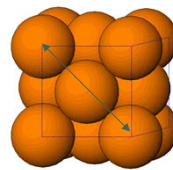
$$\rho = \frac{nA}{V_C N_A}$$

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.

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

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

$$\rho = \frac{(4)(63.5)}{[16\sqrt{2}(1.28 \times 10^{-8})^3 \times 6.023 \times 10^{23}]} = 8.89 \text{ g/cm}^3$$

8.94 g/cm³ in the literature