

# Welcome to Chem 263

## Materials Chemistry

<http://chem.ps.uci.edu/~lawm/chem263.html>

An introductory graduate level course in materials chemistry for students interested in the structure, preparation, characterization, and properties of crystalline inorganic solids in bulk, thin film, and nanoscale form. Emphasis is on a chemistry approach to periodic solids, beginning with a survey of descriptive crystal chemistry, bonding, and structure-property relationships. Students will learn common preparation methods, the characterization of solids by diffraction, and classical and quantum models of electronic structure, with a particular focus on the properties and applications of semiconductors.

# Chemistry 263

## Materials Chemistry

**Lecture:** MWF 11-11:50 am @ PSCB 240

**Instructor:** Professor Matt Law, 2127 NS II, lawm@uci.edu  
**Office Hour:** Tu 1:30-2:30 pm, and by appointment

**TA:** Nick Drago, 2138 NS II, dragon@uci.edu  
**Discussion Section:** Th 12:30-1:20 pm @ PSCB 240  
**Office Hour:** M 3-4 pm, and by appointment

**Text:** West: Solid State Chemistry and its Apps, 2<sup>nd</sup> Edition  
(purchase from UCI bookstore or online)

lecture slides and other readings available on website:  
<http://chem.ps.uci.edu/~lawm/chem263.html>

## **Main Texts**

West: Solid State Chemistry & Its Applications, 2nd. Ed. (Wiley 2014)\*

Ashcroft and Mermin: Solid State Physics (Cengage 2016)\*

Gersten/Smith: The Physics and Chemistry of Materials (Wiley 2001)\*

Hoffmann: Solids and Surfaces (VCH 1989)

Sze: Physics of Semiconductor Devices, 3<sup>rd</sup> Ed. (Wiley 2007)\*

Kittel: Introduction to Solid State Physics (Wiley 2004)

Burdett: Chemical Bonding in Solids (Oxford 1995)

Fahlman: Materials Chemistry (Springer 2011)

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 2012)

Wold and Dwight: Solid State Chemistry (Chapman Hall 1993)

\* = recommended for purchase through your favorite bookshop

## **Grading:**

<b>Problem Sets (4)</b>	<b>50%</b>
<b>Midterm Exam</b>	<b>25%</b>
<b>Term Paper</b>	<b>25%</b>

## **General Areas Covered:**

Structure and structural determination of crystalline solids

Chemical bonding in solids

Structure-property relationships

X-ray and electron diffraction

Synthesis methods

Phase equilibria

Electronic band structure

Semiconductors

Nanomaterials

# SYLLABUS

Week	Topic(s)	Assignment
1	real space lattices & crystals	
2	descriptive crystal chemistry	
3	descriptive crystal chemistry	
4	diffraction and the reciprocal lattice	problem set 1 (Jan 27)
5	diffraction and the reciprocal lattice	
6	synthesis	problem set 2 (Feb 12)
7	phase diagrams	midterm exam (Feb 19)
8	phase diagrams/free electron model	
9	band theory	problem set 3 (Mar 2)
10	band theory/semiconductors	
11	<i>finals week</i>	problem set 4 (Mar 16) term paper and presentations (Fri, Mar 20)

campus holidays (no class): Mon, Jan 20 (MLK Day)

Mon, Feb 17 (Presidents' Day)

# Term Paper

Choose a contemporary materials topic that interests you. For example:

- Hybrid Perovskites
- Metamaterials
- Multiferroics
- Graphene / 2D Materials
- Photonic Crystals
- Amorphous Metals
- Colossal Magnetoresistance
- Synthetic Biomaterials
- Infrared Photodetectors
- Conducting Polymers
- Inorganic Solar Cells
- Plasmonics
- High  $\kappa$  Dielectrics
- Quantum Dots

In  $\geq 10$  pages of double-spaced text (+ figures and references):

- 1) Quantitatively explain the basic principles/background
- 2) Summarize the state-of-the-art in synthesis, properties, and apps
- 3) Identify a key challenge facing the field and propose an original solution to this challenge

# CrystalMaker Software

Important visualization/measurement tool for crystals/molecules

The screenshot displays the CrystalMaker software interface. The main window shows a 3D model of a silicon crystal structure with green spheres representing atoms. A distance measurement of 95.750 Å is shown between two atoms labeled T1 and T2. The interface includes a menu bar (File, Edit, View, Model, Transform, Calculate, Window, Help), a toolbar with various tools (Axes, Cell, Scale, Centre, Range, Cluster, Tidy, Orient, Rotate, Spin, Annotate, Add H, Relax, Vibrate, Play), and a status bar. A sidebar on the left shows a thumbnail of the structure and the name 'Rm3\_1\_fromGISAXS'. A sidebar on the right displays crystallographic data:

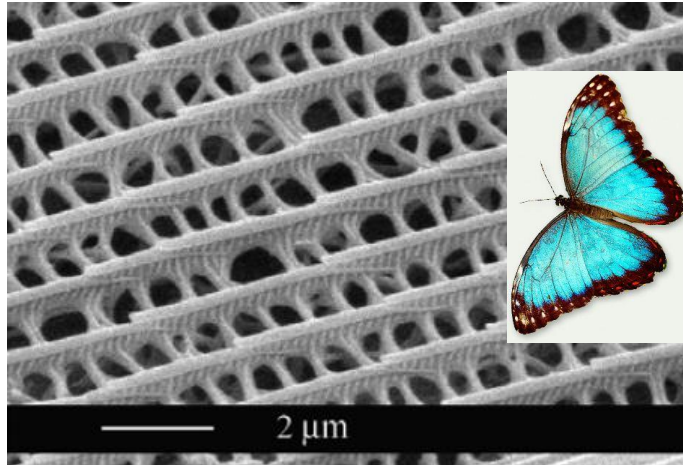
**Structure Type:** Crystal  
**Chemical Formula:** Si  
**Spacegroup:** P1  
(Allows Chirality: Polar)  
**Crystal System:** Triclinic  
**a = b = c:** 95.7500 Å  
 **$\alpha = \beta = \gamma:$**  81.000°  
**Asymmetric Unit:** 2 sites  
**Unit Cell:** 2 sites per unit cell  
**Site Density:** 0.0000 sites/Å<sup>3</sup>  
**Visible Atoms:** 9  
**Cell Volume:** 848488.306 Å<sup>3</sup>  
**Density:** 0.0001 g/cm<sup>3</sup>

# CLASSIFICATIONS OF SOLID MATERIALS

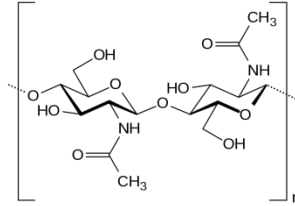
## Natural vs. artificial

Natural:

Wood  
Ivory  
Bone  
Fiber, Silk  
Rubber  
Minerals  
Ceramics  
Metals



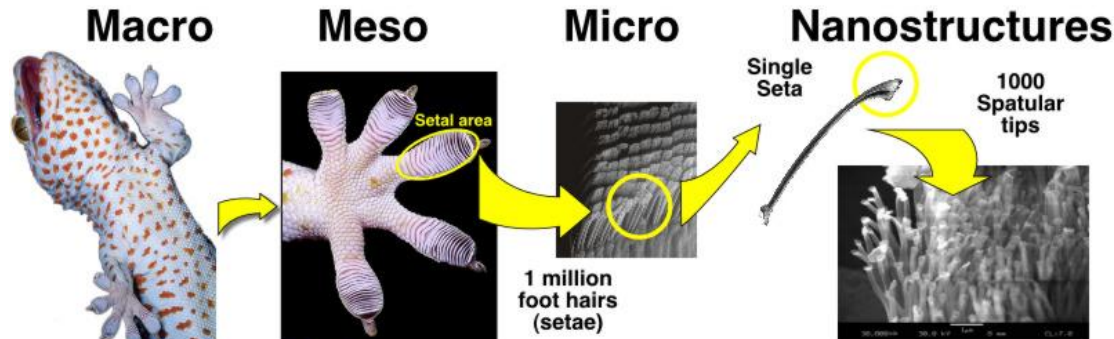
butterfly wing (chitin) Zs. Bálint



## By property

Semiconductors  
Metals and alloys  
Ceramics  
Polymers  
Dielectrics and ferroelectrics  
Superconductors  
Magnetic materials  
Optical materials

## Gecko adhesive system



## By application

High  $T_C$  superconductors  
Solar cells  
Microelectronics  
Surface engineering (Teflon)  
Photonic computing  
Magnetic disk materials  
Superalloys  
Structural composites



# QUEST FOR THE IDEAL MATERIAL

**Synthesis** → **composition + structure** → **properties**  
→ **applications of solid materials**

*Inorganic, organic, biological*

- ❖ **Experimentalist: Make/characterize/measure/remake**
- ❖ **Theoretician: predict structure/composition with particular properties (goal is “materials by design”)**

## **Characterization Techniques:**

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

**Solid state:** A to Z: X-ray/electron scattering, microscopy, spectroscopy, scanning probes, physical property characterization, optical/electrical/magnetic properties, others

# MATERIALS GENOME INITIATIVE (MGI)

government initiative to discover and commercialize new materials at least twice as fast as done today, at a fraction of the cost.

- massive computing power for materials modeling
- advanced, rapid experimental characterization tools
- big data

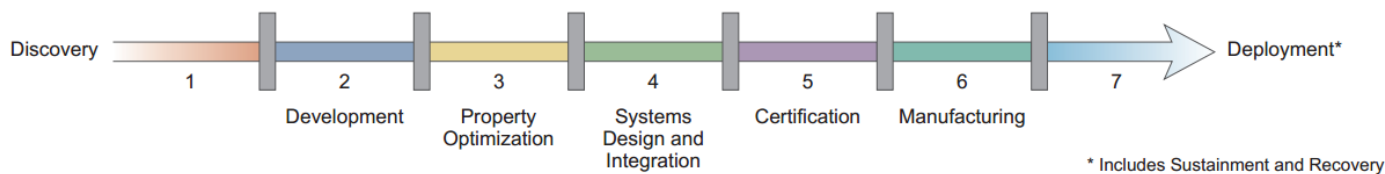


Figure 1: Materials development continuum

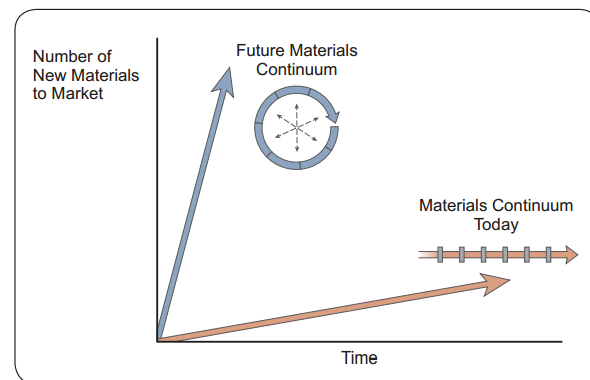


Figure 2: Initiative acceleration of the materials continuum

# Superconductors

1911, Kamerlingh-Onnes experiments on liquid He (a few ml)

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

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

La-Ba-Cu-O

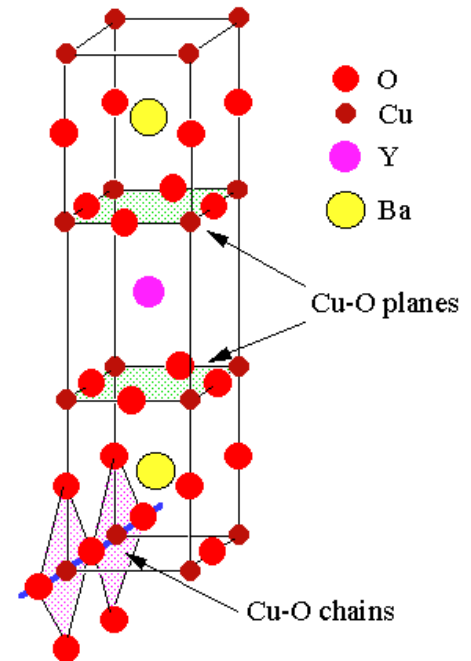
Oxide:  $T_c = 35$  K

1987 Nobel prize in Physics

Y-Ba-Cu-O (YBCO):  $T_c = 92$  K

best-to-date:  $T_c = 138$  K

2008:  $\text{La}_{1-y}\text{Sm}_y\text{O}_{1-x}\text{F}_x\text{FeAs}$   $T_c = 55\text{K}$



*Metals*, edited by D. H. Douglass (Plenum, New York and London, 1976), and by C. M. Varma and R. C. Dynes, *ibid.*

<sup>2</sup>We have chosen 0.5 eV somewhat arbitrarily to de-

fine  $D_2^6$ . It is the energy near the F.S., scattering within which leads to over 90% of most of the anomalies. <sup>10</sup>W. Kohn, *Phys. Rev. Lett.* **2**, 393 (1959); A. W. Overhauser, *Phys. Rev. Lett.* **4**, 415 (1960).

# Conducting Polymers

2000 Alan Heeger,  
Alan G. MacDiarmid,  
Hideki Shirakawa

Nobel Prize in Chemistry

- organic light-emitting diodes (OLED)
- organic field-effect transistors (OFET)
- organic photovoltaics (OPV)



## 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,<sup>(a)</sup> 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, bromine, or iodine, and with arsenic pentafluoride ( $\text{AsF}_5$ ). 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  $\sigma$  bonded to one hydrogen and two neighboring carbon atoms consistent with  $sp^2$  hybridization. The  $\pi$  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.<sup>1</sup> Bond alternation is present in the polymer and would be expected to lead to semiconducting behavior. However, Ovchinnikov<sup>1</sup> 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-workers<sup>2-6</sup> succeeded in synthesizing high-quality

polycrystalline films of  $(\text{CH})_x$ , and developed techniques for controlling the *cis/trans* content.<sup>4,5</sup> These materials are semiconductors<sup>6</sup>; the *trans* isomer is the thermodynamically stable form at room temperature.

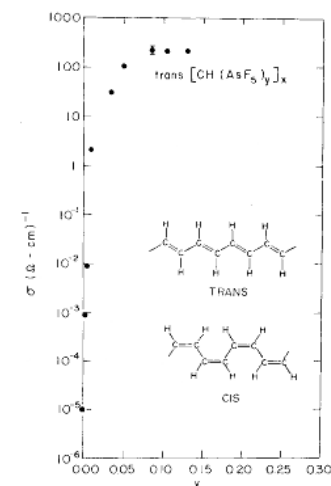
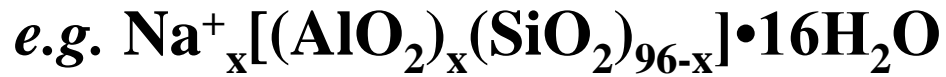


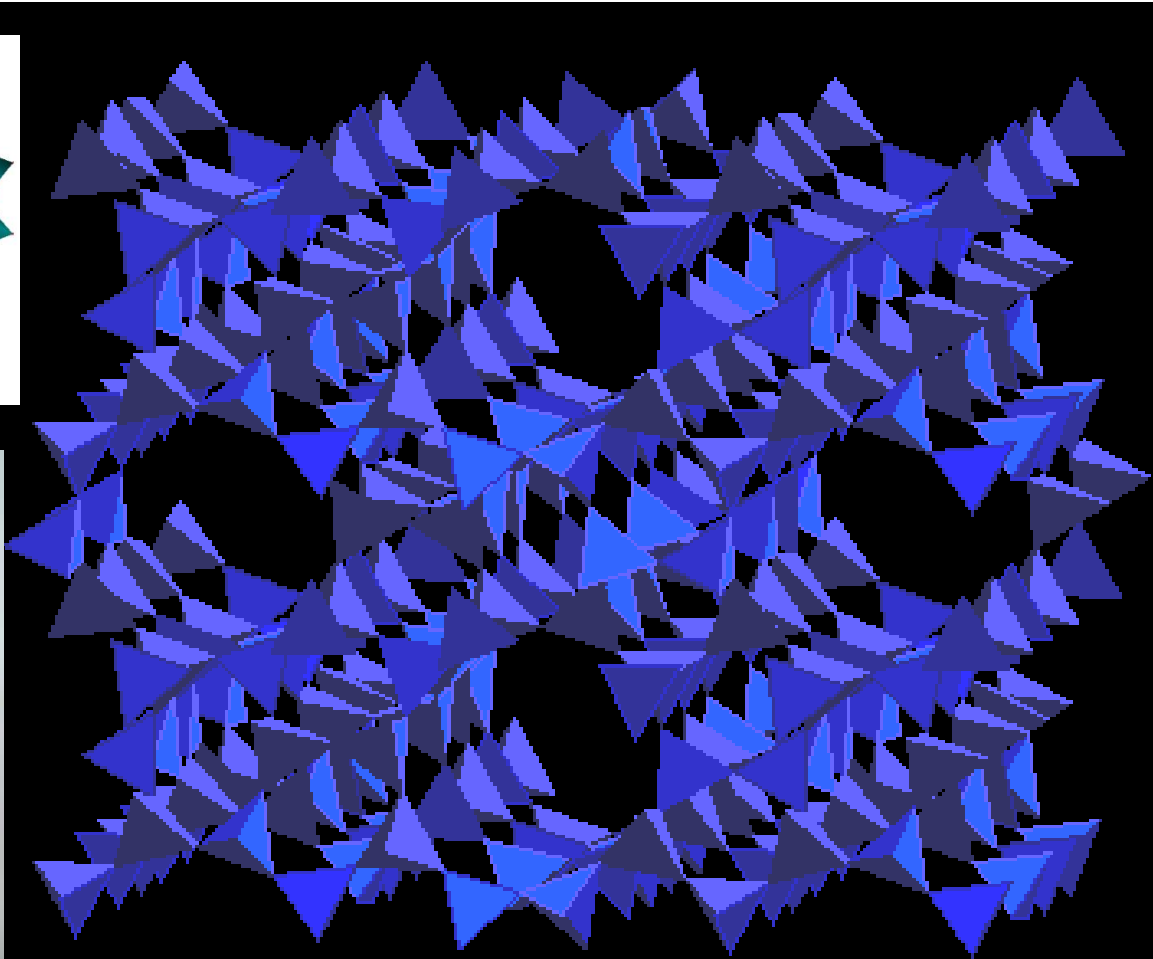
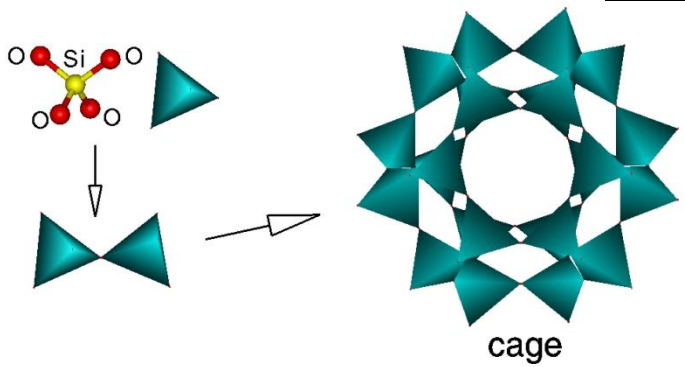
FIG. 1. Electrical conductivity of *trans*-( $\text{CH}$ )<sub>x</sub> as a function of ( $\text{AsF}_5$ ) dopant concentration. The *trans* and *cis* polymer structures are shown in the inset.

# Zeolites

catalysis, separation, purification, templating



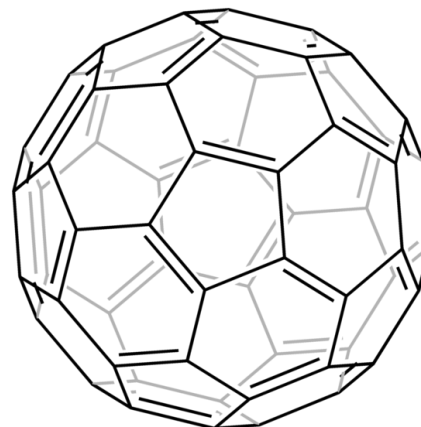
*Zeolite ZSM-5*



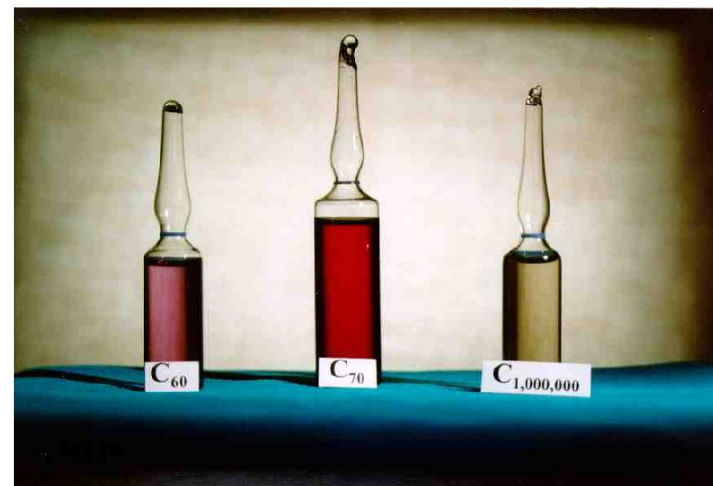
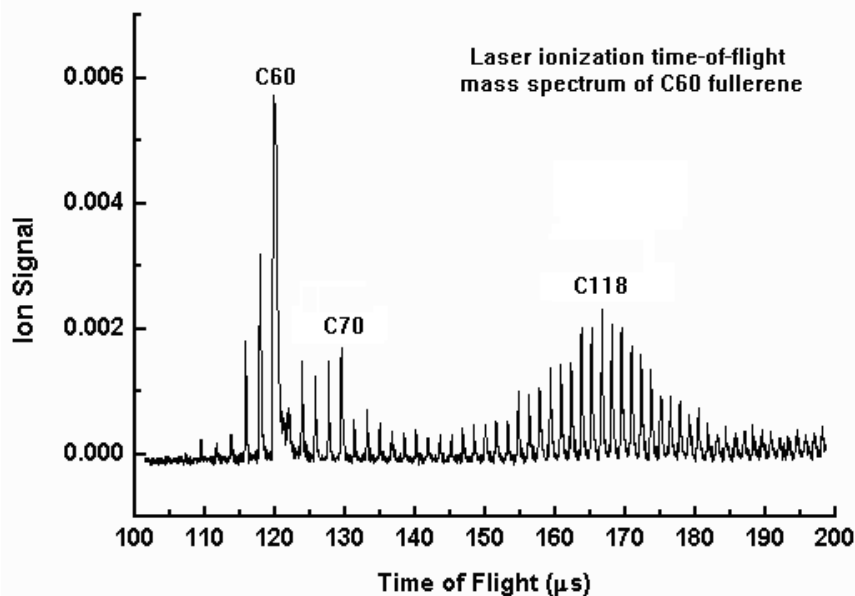
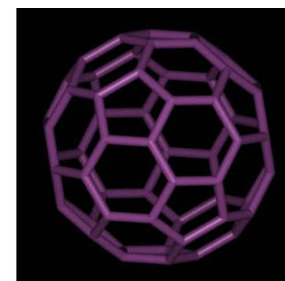


buckyball; spherical fullerene  
allotrope of carbon  
1996 Nobel prize in chemistry

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



20 hexagons  
12 pentagons



# Graphene

## The rise of graphene

A. K. GEIM AND K. S. NOVOSELOV  
 Manchester Centre for Mesoscience and Nanotechnology, University of  
 Manchester, Oxford Road, Manchester M13 9PL, UK  
 \*e-mail: geim@man.ac.uk; kostya@graphene.org

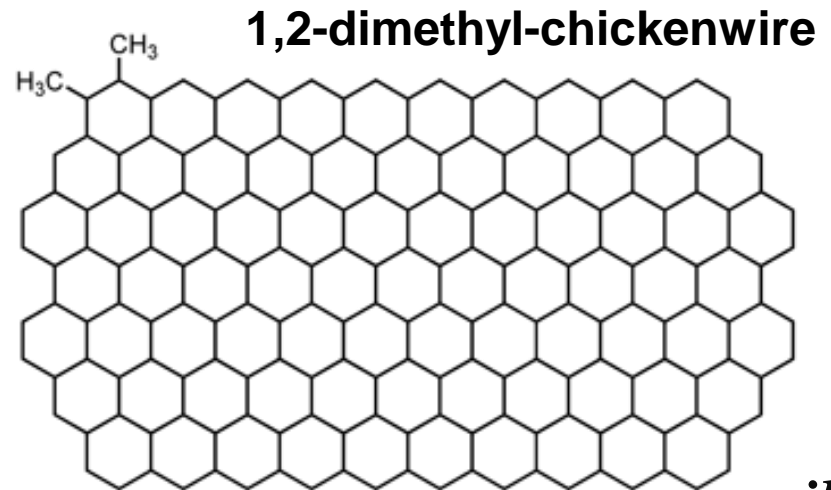
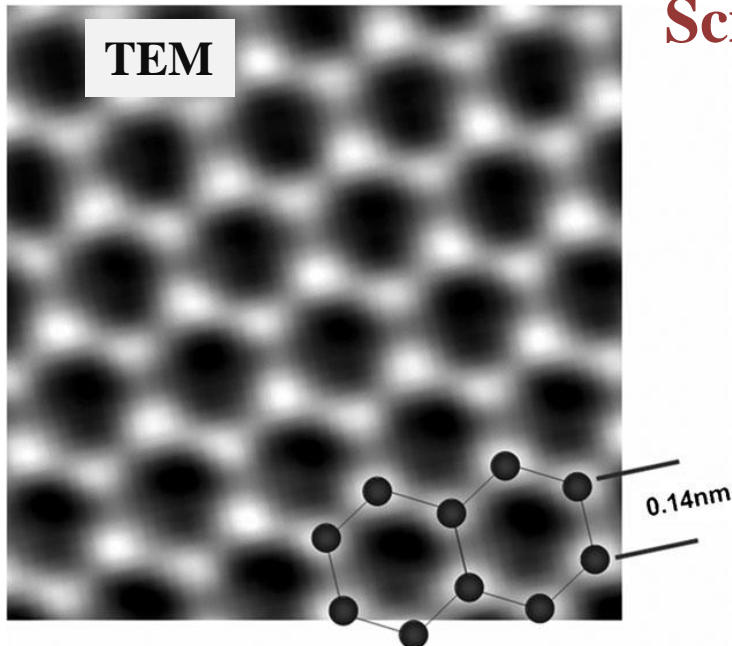
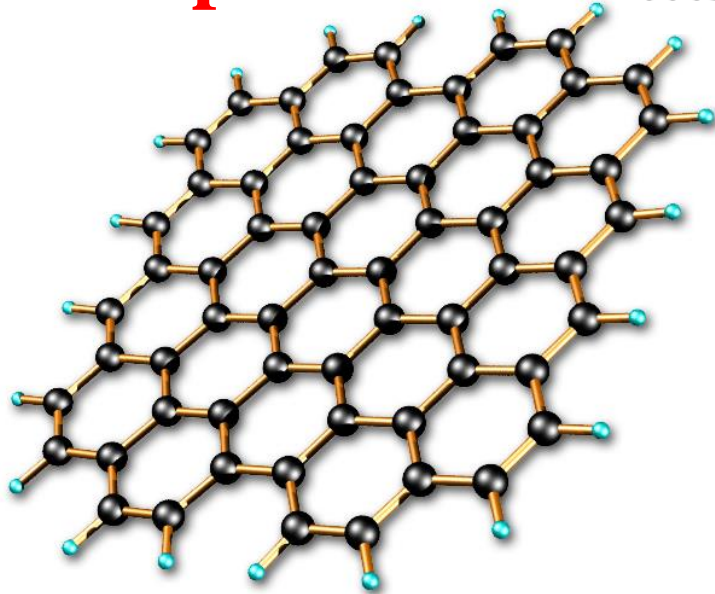
**Single atom thick sheet of  $sp^2$  C**  
**- all the rage since 2004**

2010 Nobel Prize in Physics awarded  
 A. Geim, K. Novoselov

RT mobilities  $>15,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

- **Extremely high freq. transistors**
- **spintronics**

**Science made possible by Scotch<sup>®</sup> tape**



wiki

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

## Semiconductor Quantum Dots

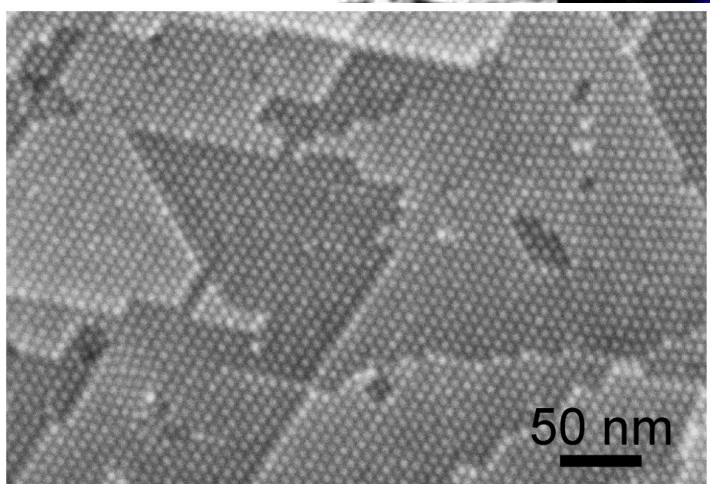


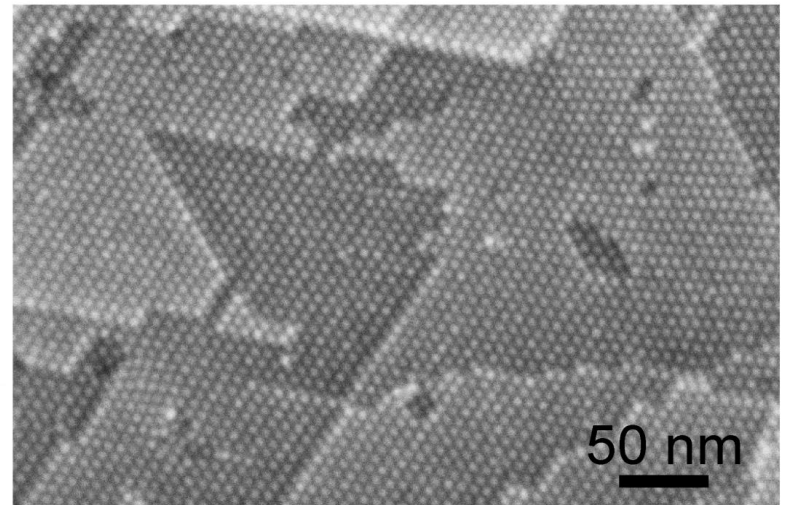
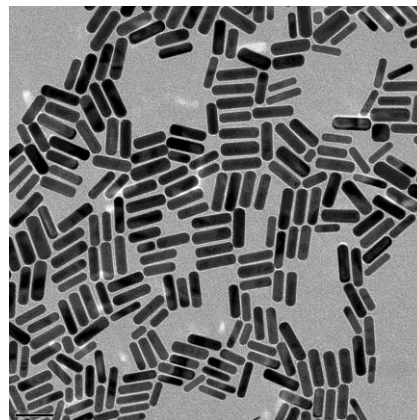
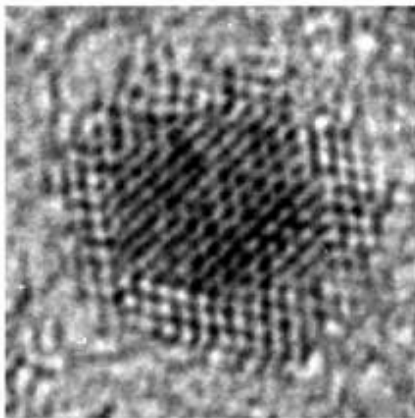
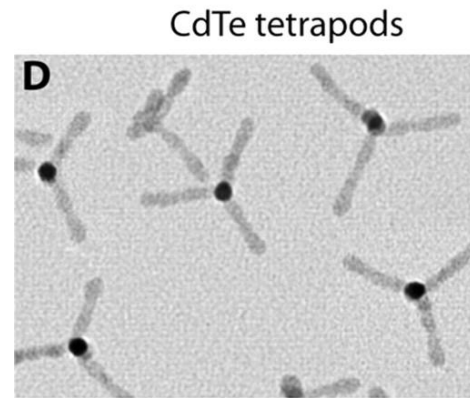
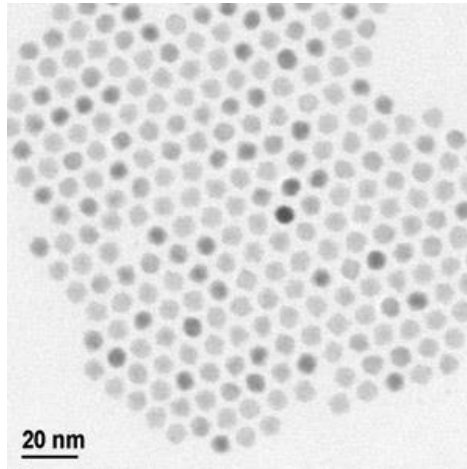
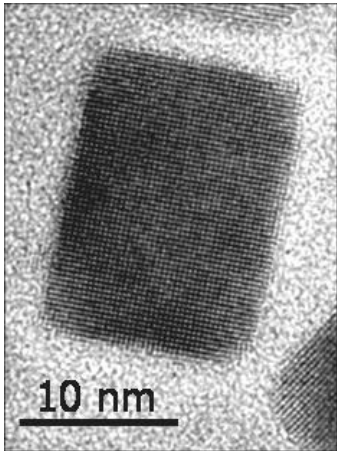
Photo Taken By R. Neuhauser

**Brus**  
**Bawendi**  
**Alivisatos**



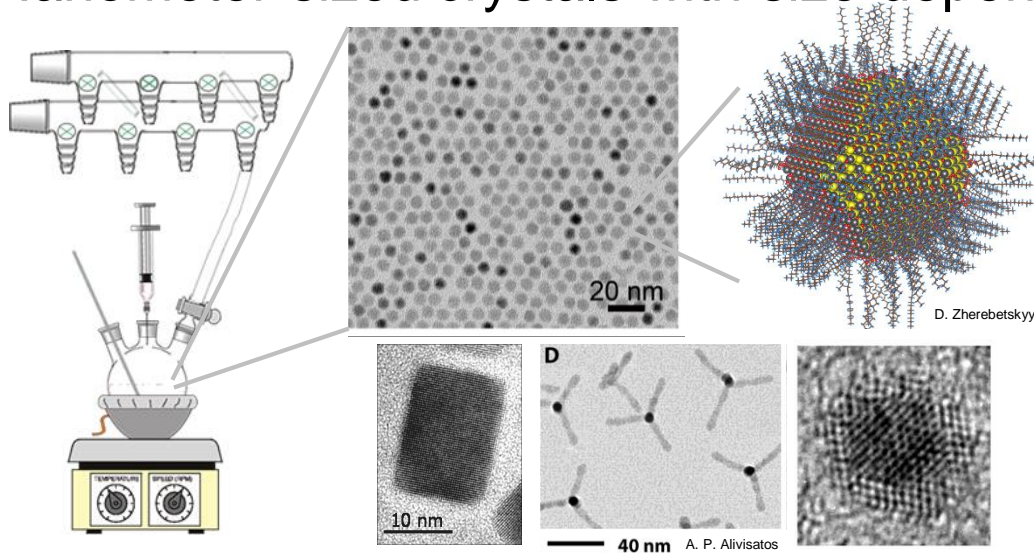
# Semiconductor quantum dots

Nanometer-sized crystals with size-dependent properties

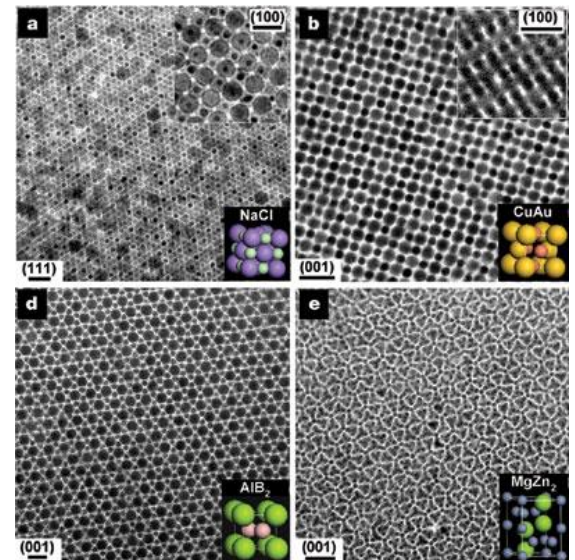
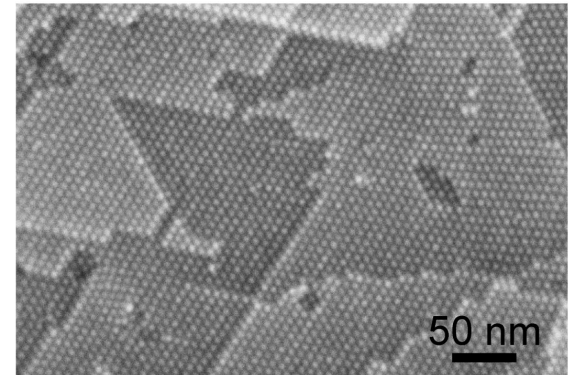


# Quantum Dot Basics

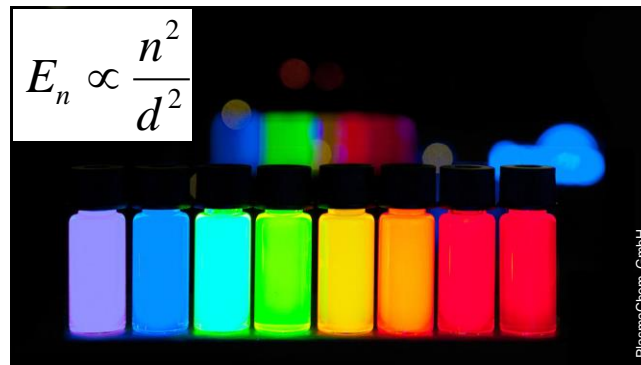
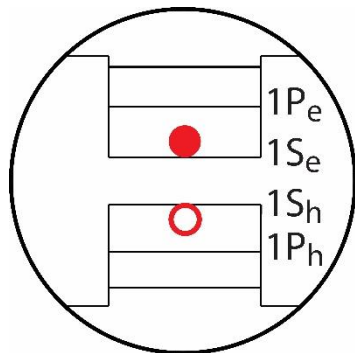
Nanometer-sized crystals with size-dependent properties



self-assembly from solution



quantum confinement - *particle in a box*



← smaller diameter

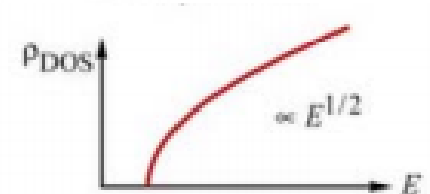
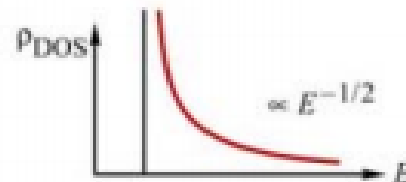
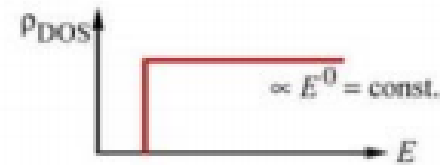
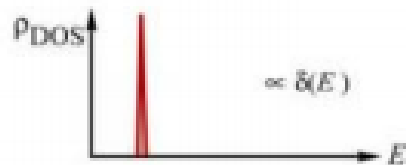
C. Murray, C. Kagan

# Electrons in solids of reduced dimensionality



TABLE 11.5 Properties of Electrons in Solids of Reduced Dimensionality

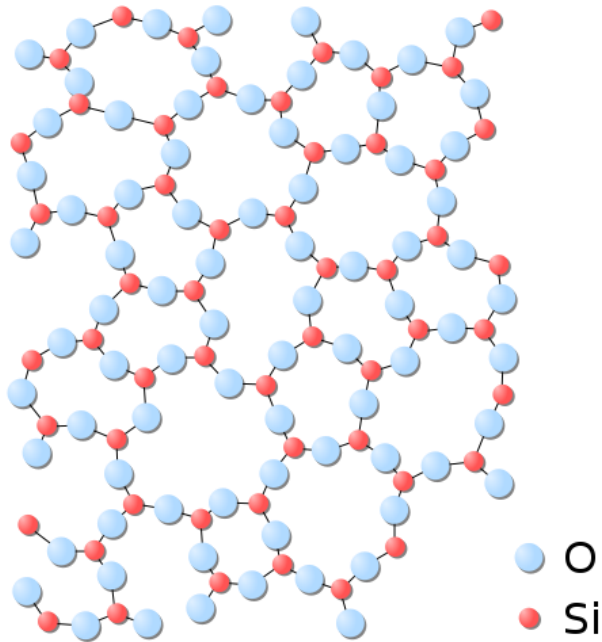
	Dimensionality			
	$d = 0$ (Quantum Dot)	$d = 1$ (Quantum Wire)	$d = 2$ (Quantum Well)	$d = 3$ (Bulk)
$\psi_{\mathbf{k}}(\mathbf{r})^a$	$A \sin k_x x (\sin k_y y) (\sin k_z z)$	$A \sin k_x x (\sin k_y y) e^{ik_z z}$	$A (\sin k_x x) e^{i(k_y y + k_z z)}$	$A e^{i(k_x x + k_y y + k_z z)}$
$E(\mathbf{k})^b = E(k_x) + E(k_y) + E(k_z); n_x, n_y, n_z = 1, 2, 3, \dots$	$\frac{\hbar^2}{8m_e^*} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$	$\frac{\hbar^2}{8m_e^*} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) + \frac{\hbar^2 k_z^2}{2m_e^*}$	$\frac{\hbar^2 n_x^2}{8m_e^* L_x^2} + \frac{\hbar^2 (k_y^2 + k_z^2)}{2m_e^*}$	$\frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m_e^*}$
$\rho_e(E)^{b,c}$	Discrete states	$\frac{\sqrt{2m_e^*}}{\pi \hbar L_x L_y} E^{-1/2}$	$\frac{m_e^*}{\pi \hbar^2 L_x}$	$\frac{1}{2\pi^2} \left( \frac{2m_e^*}{\hbar^2} \right)^{3/2} E^{1/2}$
$k_F^d$	—	$\frac{\pi n L_x L_y}{2}$	$\sqrt{2\pi n L_x}$	$(3\pi^2 n)^{1/3}$



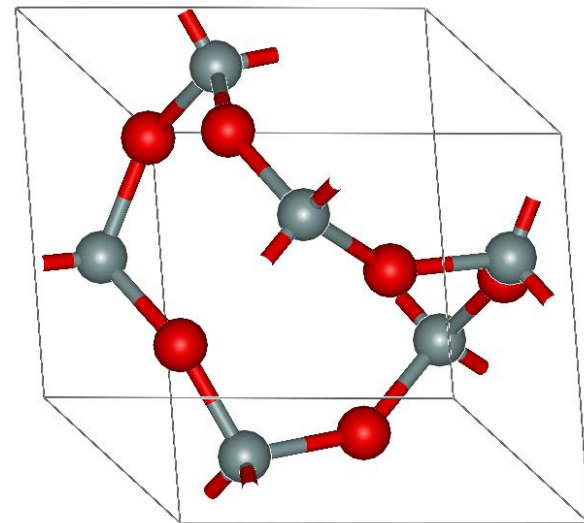
# AMORPHOUS VS. CRYSTALLINE SOLIDS

**Amorphous materials:** No long-range structural order

**Crystalline materials:** Possess long-range periodicity



**SiO<sub>2</sub> glass**



**SiO<sub>2</sub> crystal (α-quartz)**

trigonal crystal, space group  $P3_121$  or  $P3_221$

selective formation requires favourable kinetics

# STRUCTURE OF CRYSTALS

*Reading: New West Ch. 1  
AM Ch. 4, 7  
Old West Ch. 6  
GS Ch. 1*

**Ideal Crystal:** A perfect periodic array of atoms/ions/molecules.

- Represented by an infinite array of points (***the lattice***) with one or more atoms attached to each lattice point (***the basis***).

**Lattice:** An infinite array of points in space

**Crystal structure:** The periodic arrangement of atoms/ions/molecules in a crystal.

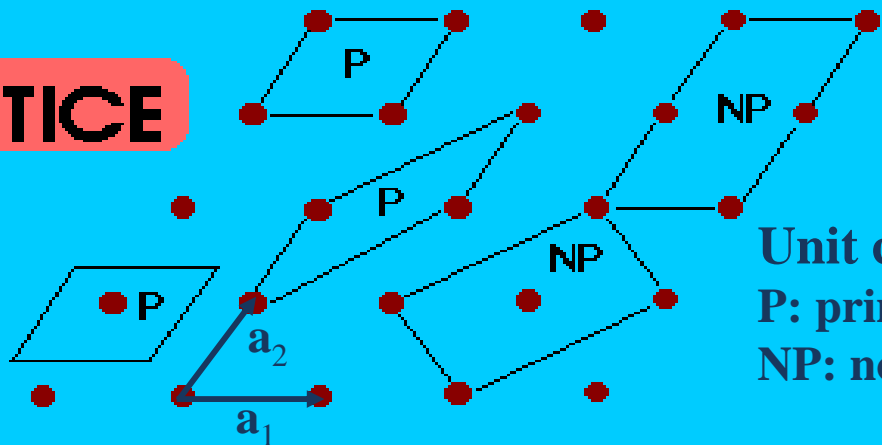
It can be described by associating with each lattice point a group of atoms called the **basis** (or **motif**)

**Unit Cell:** A volume of the crystal that, via pure translational repetition, generates the entire crystal without overlaps or voids.

**Primitive Cell:** *smallest cell, contains one lattice point, needn't reflect full symmetry*

**Conventional Cell:** *nonprimitive, bigger unit cell that reflects full crystal symmetry*

# LATTICE



# BASIS / MOTIF

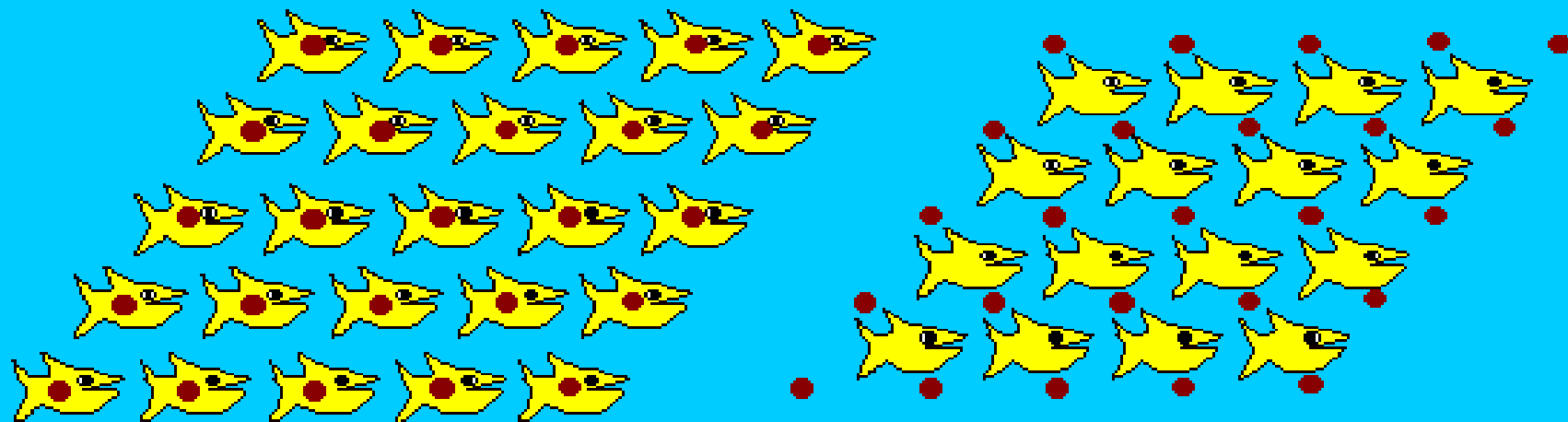
Unit cells  
P: primitive  
NP: not primitive



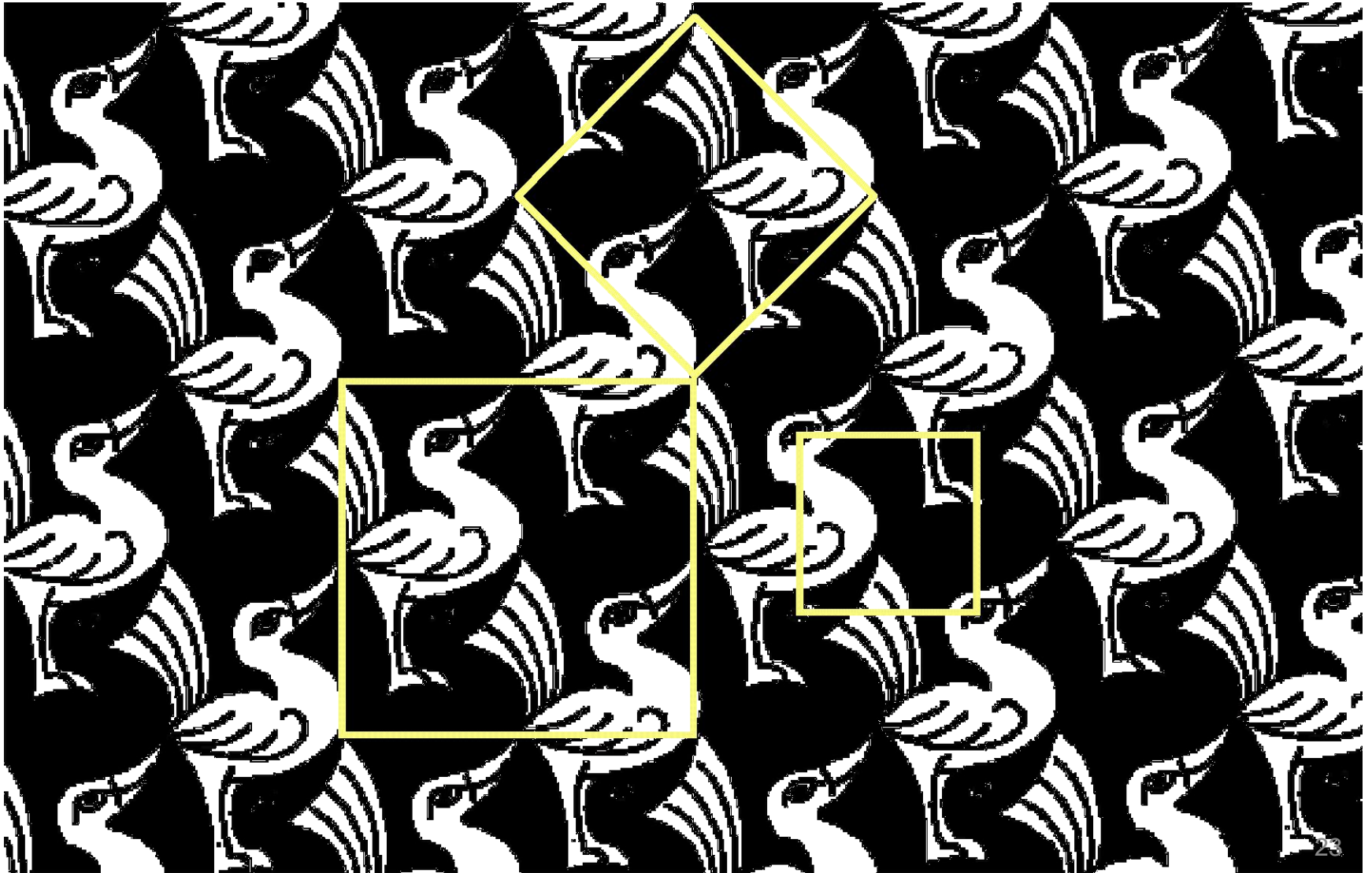
Translation vectors  
 $\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2$

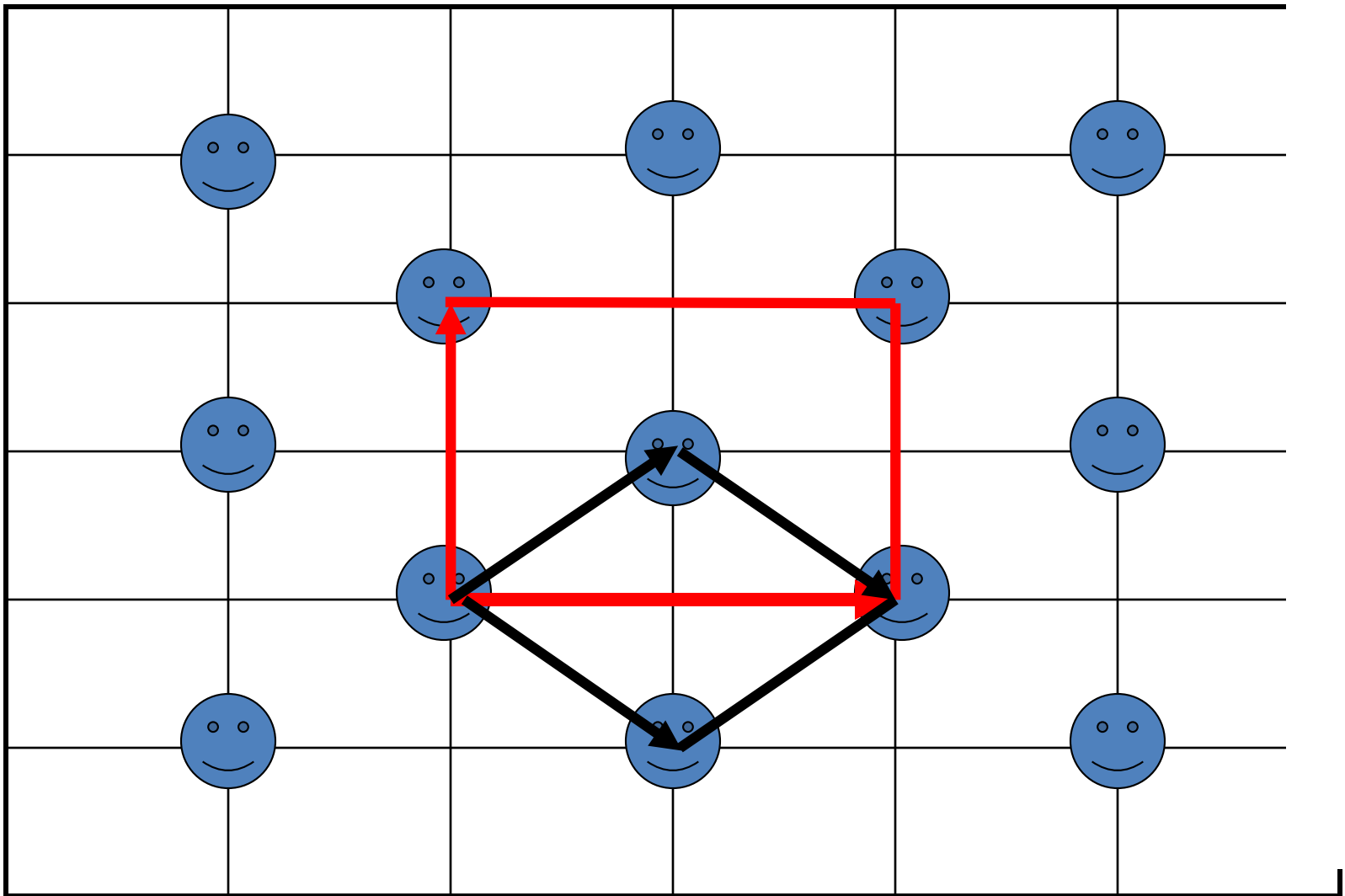


# CRYSTAL STRUCTURE



# Unit Cells?





**Conventional cell** vs. **Primitive Cell**

*Reflecting the symmetry*

*Different Basis*



# 2D BRAVAIS LATTICES

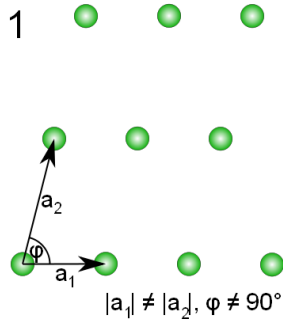
Bravais Lattice: An infinite array of points with an arrangement and orientation that looks exactly the same from any lattice point

5 possibilities in 2D space

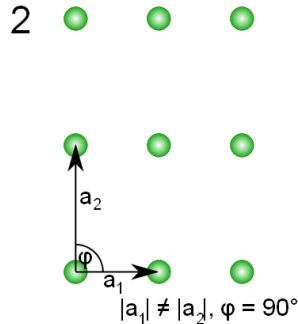


**Bravais**  
(~1850)

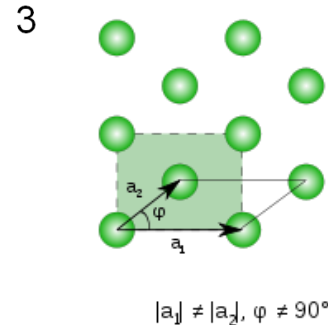
**Oblique**



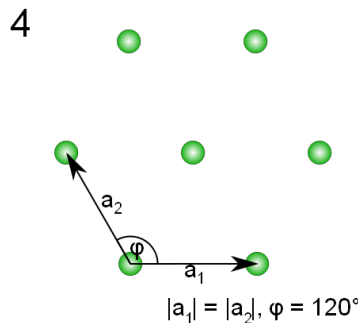
**Rectangular**



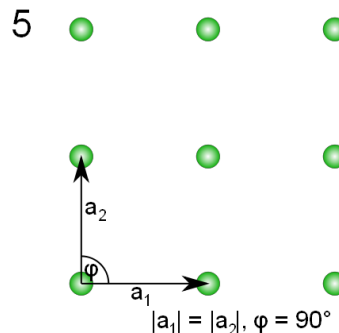
**Centered Rectangular**



**Hexagonal**



**Square**



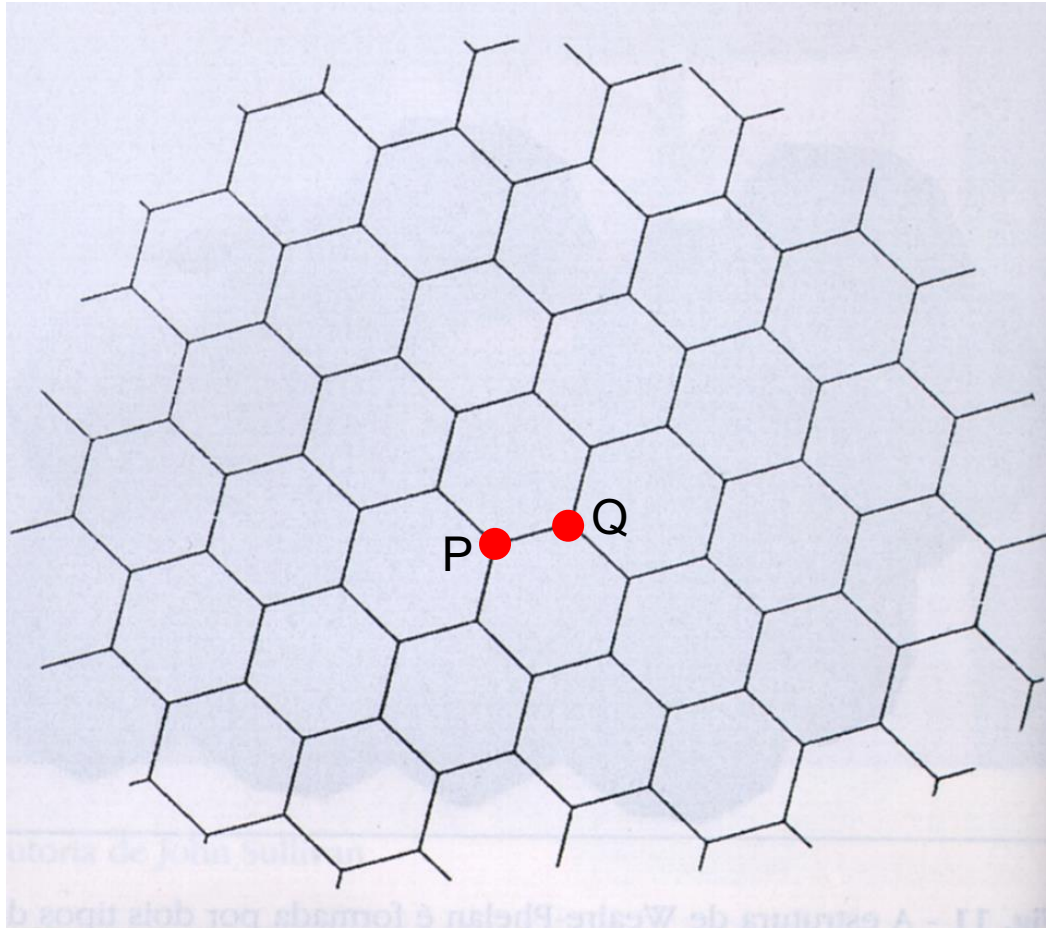
Points are generated by  
*translation operations*

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2$$

- $\mathbf{a}_i$  are primitive vectors
- $n_1, n_2$  are integers

# EXAMPLE OF A NON-BRAVAIS LATTICE

## The 2D honeycomb

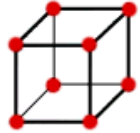


*different orientations at points P and Q  $\rightarrow$  not a Bravais lattice  
(it's a hexagonal lattice with a 2-point basis)*

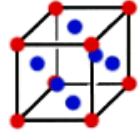
# 3D BRAVAIS LATTICES

The symmetry-unique lattices that fill space without gaps or overlaps between cells.

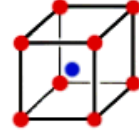
14 possibilities in 3D space



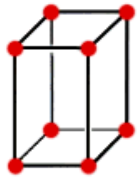
Simple cubic



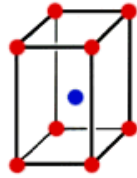
Face-centered cubic



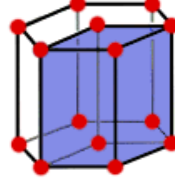
Body-centered cubic



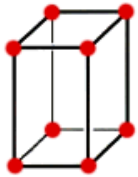
Simple tetragonal



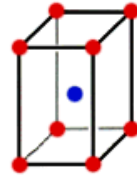
Body-centered tetragonal



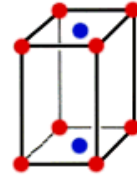
Hexagonal



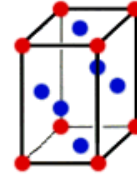
Simple orthorhombic



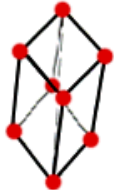
Body-centered orthorhombic



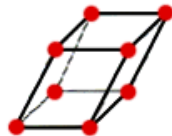
Base-centered orthorhombic



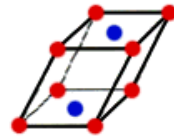
Face-centered orthorhombic



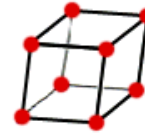
Rhombohedral  
(aka trigonal)



Simple Monoclinic



Base-centered monoclinic

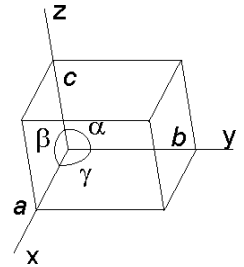


Triclinic

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

$$\mathbf{R} = n_1 a \hat{\mathbf{a}}_1 + n_2 b \hat{\mathbf{a}}_2 + n_3 c \hat{\mathbf{a}}_3$$

- $a, b, c$  are *lattice constants*
- $\mathbf{a}_i$  are primitive vectors
- $\hat{\mathbf{a}}_i$  are unit vectors

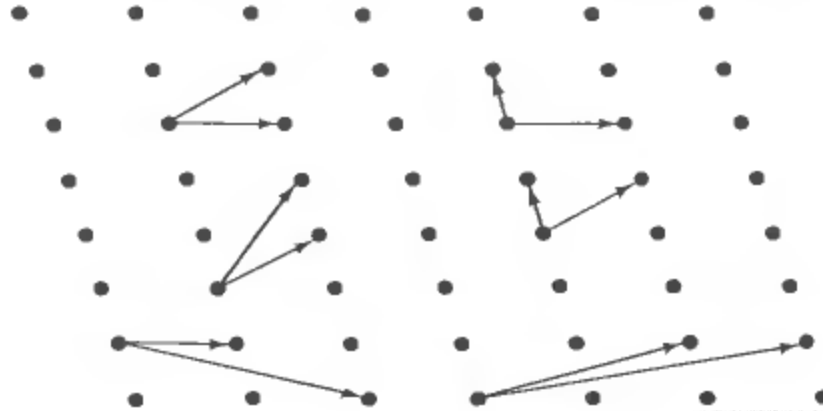


System	Number of Lattices	Lattice Symbols	Restrictions on Conventional Cell Axes and Angles
Triclinic	1	$P$	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$P, C$	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	4	$P, C, I, F$	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	$P, I$	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Cubic	3	$P$ or $sc$ $I$ or $bcc$ $F$ or $fcc$	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal	1	$R$	$a = b = c$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	1	$P$	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$

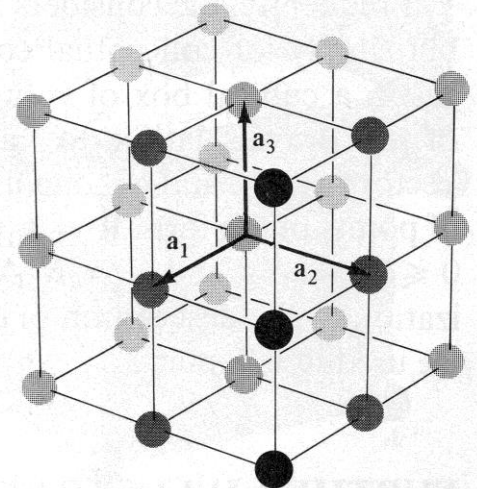
# PRIMITIVE VECTORS

*The choice of primitive vectors is not unique*

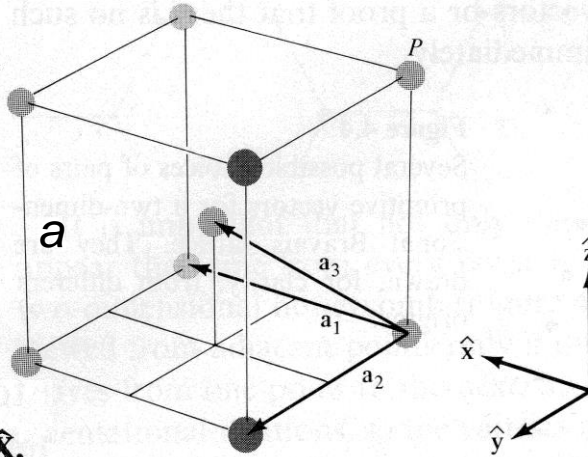
*The oblique net:*



*Simple cubic*



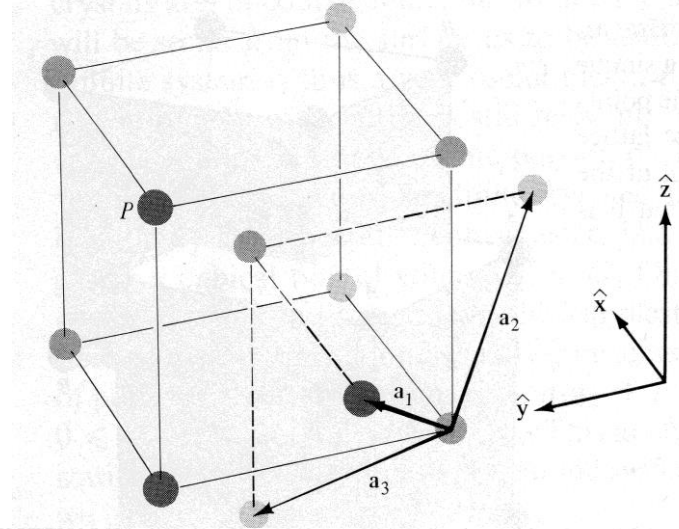
*Body-centered cubic (BCC) lattice:*



$$\mathbf{a}_1 = a\hat{\mathbf{x}},$$

$$\mathbf{a}_2 = a\hat{\mathbf{y}}, \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}).$$

*or*

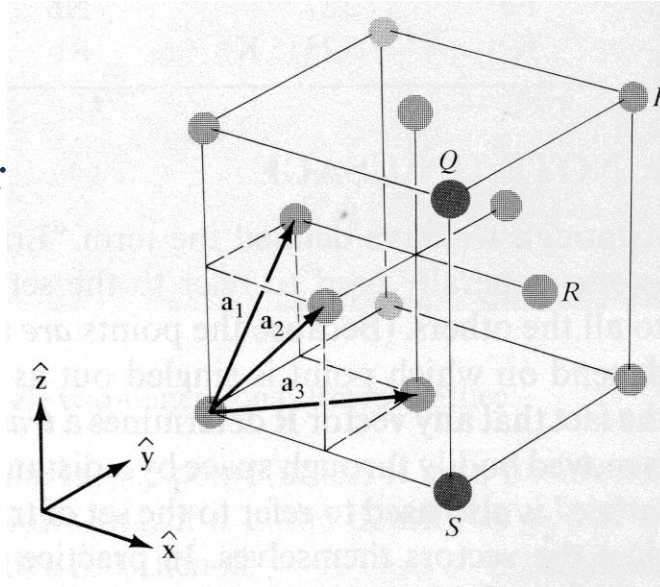


$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}),$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}).$$

# PRIMITIVE VECTORS CONT.

*Face-centered cubic (FCC) lattice:*



Primitive vectors:

$$\mathbf{a}_1 = \frac{a}{2}(\hat{y} + \hat{z}),$$

$$\mathbf{a}_2 = \frac{a}{2}(\hat{z} + \hat{x}),$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y}).$$

*Monatomic BCC and FCC lattices are very common*

Table 4.2  
ELEMENTS WITH THE MONATOMIC BODY-CENTERED  
CUBIC CRYSTAL STRUCTURE

ELEMENT	$a$ (Å)	ELEMENT	$a$ (Å)	ELEMENT	$a$ (Å)
Ba	5.02	Li	3.49 (78 K)	Ta	3.31
Cr	2.88	Mo	3.15	Tl	3.88
Cs	6.05 (78 K)	Na	4.23 (5 K)	V	3.02
Fe	2.87	Nb	3.30	W	3.16
K	5.23 (5 K)	Rb	5.59 (5 K)		

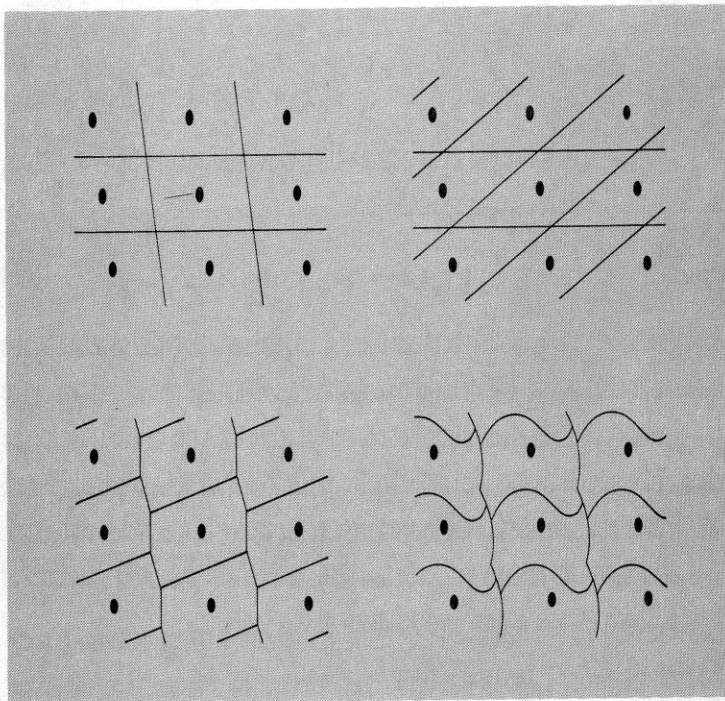
Table 4.1  
ELEMENTS WITH THE MONATOMIC FACE-CENTERED  
CUBIC CRYSTAL STRUCTURE

ELEMENT	$a$ (Å)	ELEMENT	$a$ (Å)	ELEMENT	$a$ (Å)
Ar	5.26 (4.2 K)	Ir	3.84	Pt	3.92
Ag	4.09	Kr	5.72 (58 K)	$\delta$ -Pu	4.64
Al	4.05	La	5.30	Rh	3.80
Au	4.08	Ne	4.43 (4.2 K)	Sc	4.54
Ca	5.58	Ni	3.52	Sr	6.08
Ce	5.16	Pb	4.95	Th	5.08
$\beta$ -Co	3.55	Pd	3.89	Xe (58 K)	6.20
Cu	3.61	Pr	5.16	Yb	5.49

# PRIMITIVE UNIT CELLS

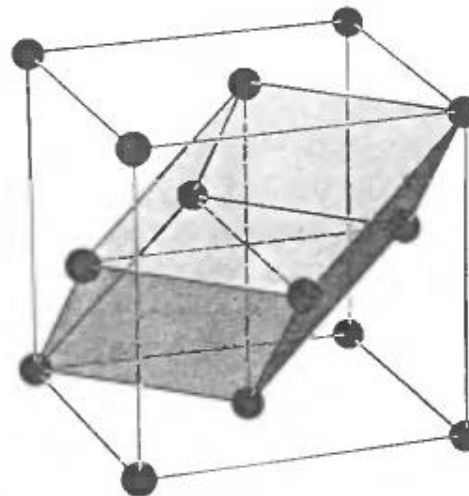
The smallest volume of space that can generate the entire crystal when translated through all primitive translation vectors of the Bravais lattice

- *contains only one lattice point*
- *not unique*
- *any two primitive cells of a given lattice have equal areas/volumes*



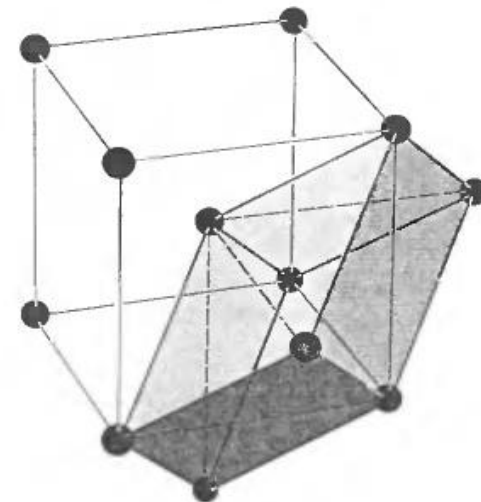
area or volume =  $1/n$   
 $n$  = lattice point density

**primitive\* and conventional  
cells for FCC**



**P.C. is  $1/4$  the volume**

**and for BCC**

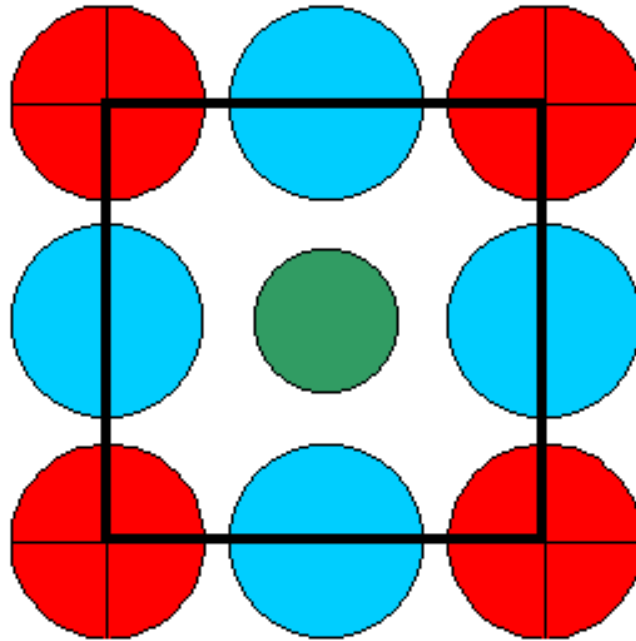


**P.C. is  $1/2$  the volume**

**\*8 lattice points shared by 8 cells = 1 point per cell**

# Unit cell contents

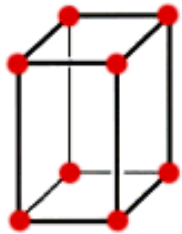
Counting the number of atoms belonging to the unit cell



Many atoms are shared between unit cells

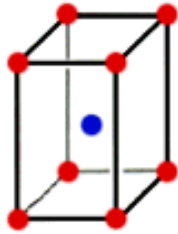
# UNIT CELL ATOM ACCOUNTING

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



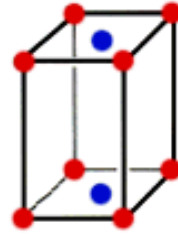
**Simple  
orthorhombic**

$$8 \times 1/8 = 1$$



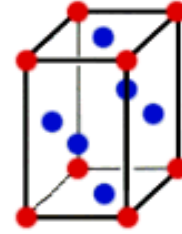
**Body-centered  
orthorhombic**

$$8 \times 1/8 + 1 \times 1 = 2$$



**Base-centered  
orthorhombic**

$$8 \times 1/8 + 2 \times 1/2 = 2$$

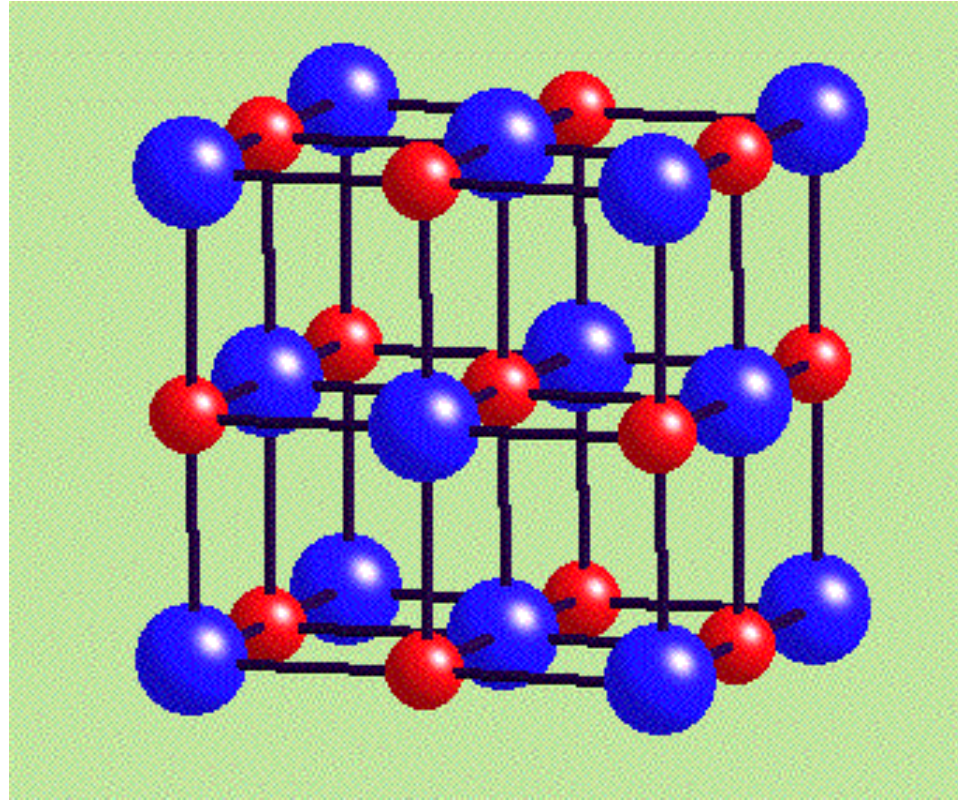


**Face-centered  
orthorhombic**

$$8 \times 1/8 + 4 \times 1/2 = 4$$



Consider  
sodium chloride:  
*rock salt*  
(not Bravais)



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

Na at edge centers  $(12 \times 1/4) = 3$

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

Na at body centre = 1

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

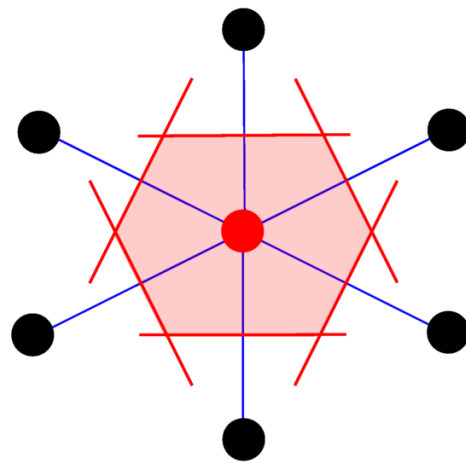
# WIGNER-SEITZ PRIMITIVE CELL

Primitive cell with the full symmetry of the Bravais lattice

- *contains one lattice point at its center + full symmetry*

To construct:

- 1) pick a lattice point
- 2) draw lines to all neighboring lattice points
- 3) draw perpendicularly bisecting planes



*enclosed region is W-S cell  
for 2D hexagonal lattice*



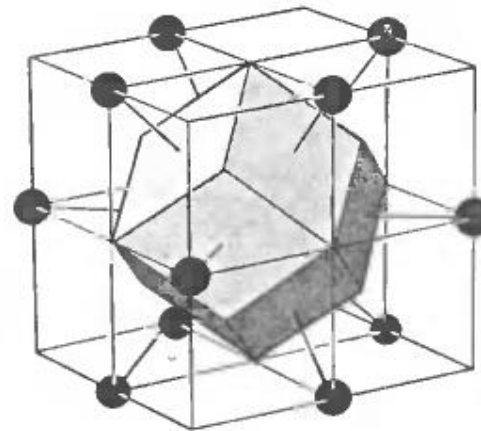
**Wigner**  
(laureate)



**Seitz**

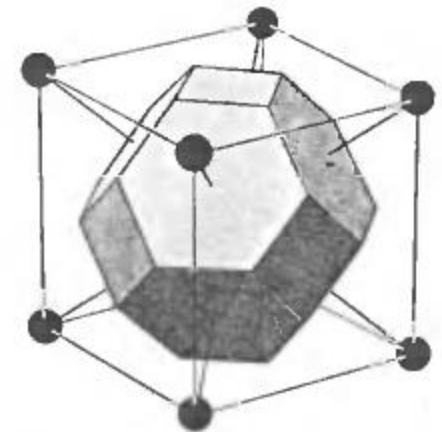
**FCC:**

a rhombic dodecahedron



**BCC:**

a truncated octahedron

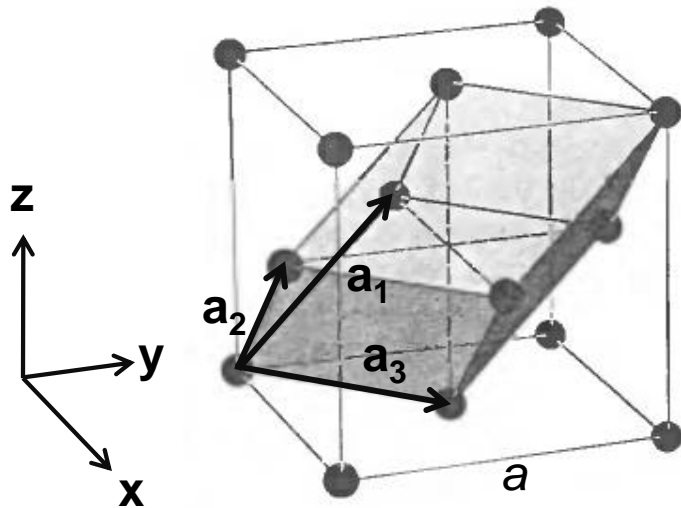


# CONVENTIONAL UNIT CELLS

A larger volume of space that possesses the full crystal symmetry and generates the entire crystal when translated through some subset of the primitive lattice vectors

## FCC lattice

- *trigonal primitive cell*
- *4-fold larger cubic conventional cell*



Primitive vectors:

$$\mathbf{a}_1 = \frac{a}{2}(\hat{y} + \hat{z}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{z} + \hat{x}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y}).$$

## Two ways to fill space

translate primitive cell:

$$\mathbf{R}_{\text{prim}} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

translate conventional cell:

$$\mathbf{R}_{\text{conv}} = n_1 a \hat{\mathbf{x}} + n_2 a \hat{\mathbf{y}} + n_3 a \hat{\mathbf{z}}$$

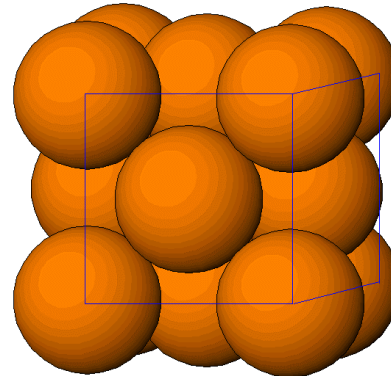
# CONVENTIONAL UNIT CELLS

A Bravais lattice can be described as a lattice with a basis by choosing a conventional unit cell

## FCC lattice

simple cubic lattice spanned by  $a\hat{x}$ ,  $a\hat{y}$ , and  $a\hat{z}$  with a 4-point basis

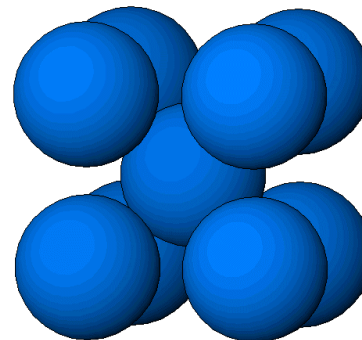
$$\mathbf{0}, \quad \frac{a}{2}(\hat{x} + \hat{y}), \quad \frac{a}{2}(\hat{y} + \hat{z}), \quad \frac{a}{2}(\hat{z} + \hat{x})$$



## BCC lattice

simple cubic lattice spanned by  $a\hat{x}$ ,  $a\hat{y}$ , and  $a\hat{z}$  with a 2-point basis

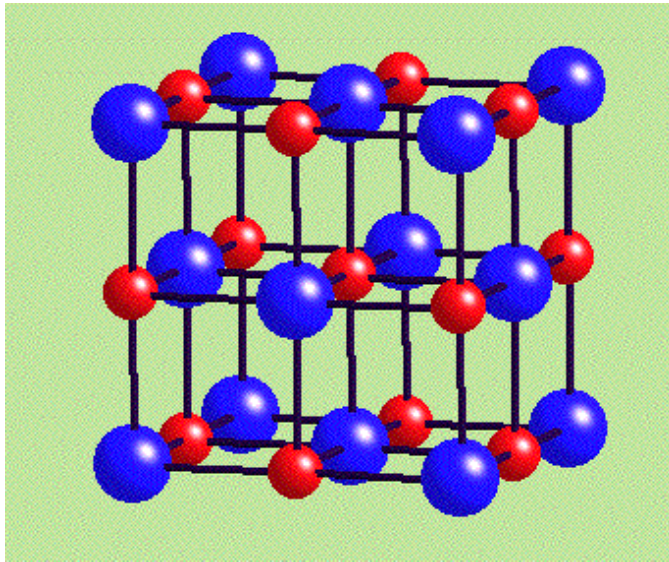
$$\mathbf{0}, \quad \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})$$



# IMPORTANT NON-BRAVAIS LATTICES

A non-Bravais crystal structure can be described as a Bravais lattice with a basis

## NaCl structure

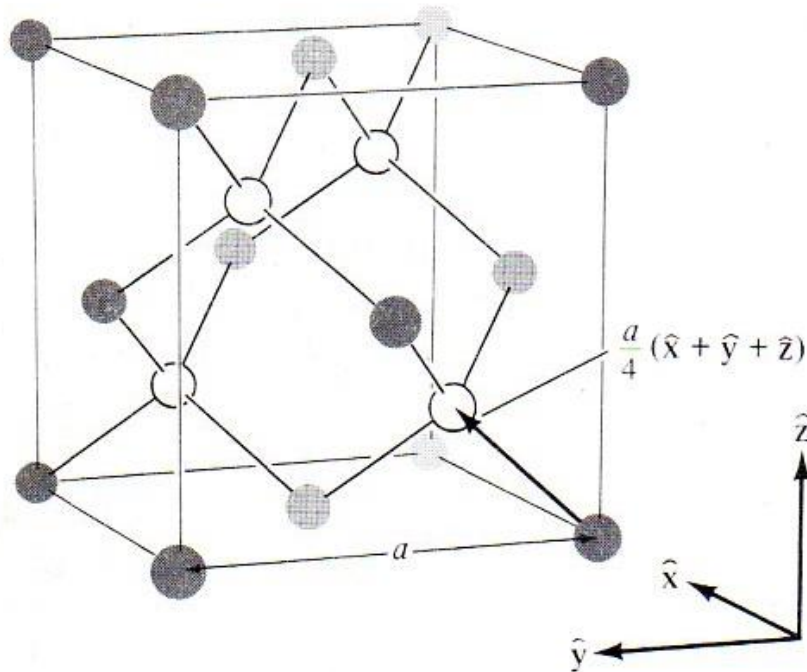


## alternative descriptions

- FCC lattice with a two-point basis  $\mathbf{0}$  (Cl) and  $(a/2)(\hat{x} + \hat{y} + \hat{z})$  (Na)
- two interpenetrating FCC lattices offset by  $\frac{1}{2}$  of a body diagonal

# IMPORTANT NON-BRAVAIS LATTICES

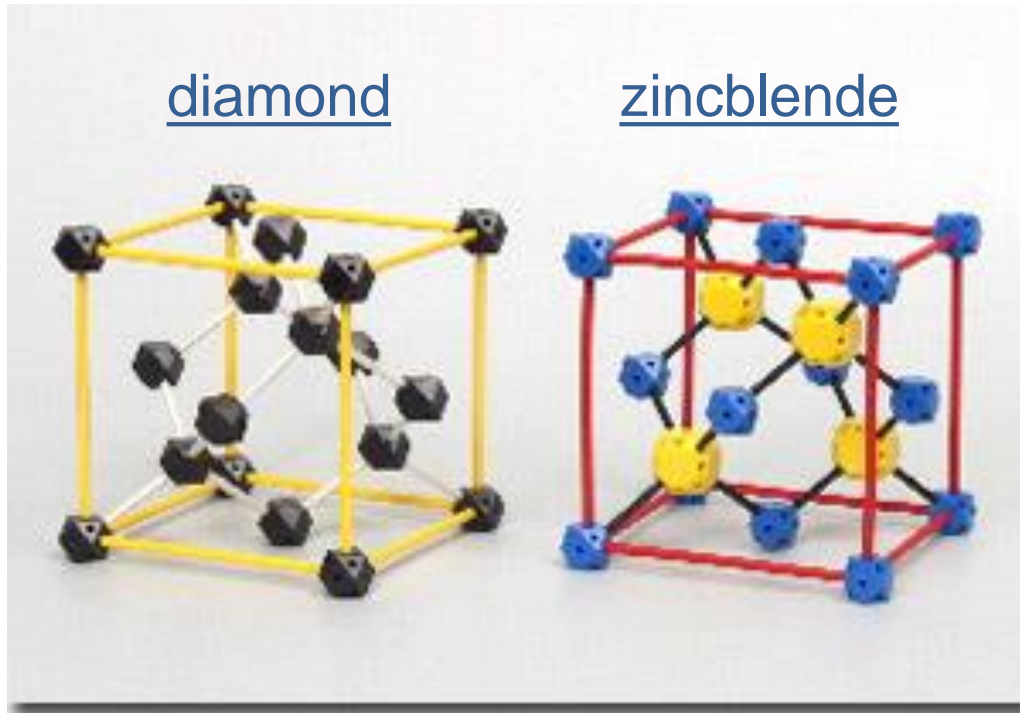
## diamond structure



- FCC lattice with a two-point basis  $\mathbf{0}$  and  $(a/4)(\hat{x} + \hat{y} + \hat{z})$
- two interpenetrating FCC lattices offset by  $1/4$  of a body diagonal

# IMPORTANT NON-BRAVAIS LATTICES

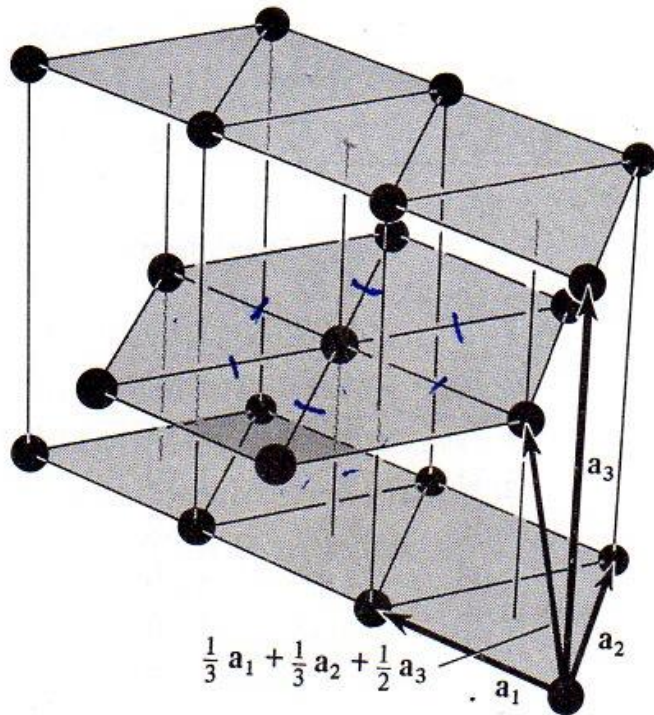
## zincblende (ZnS) structure



- FCC lattice with a two-point basis  $\mathbf{0}$  (Zn) and  $(a/4)(\hat{x} + \hat{y} + \hat{z})$  (S)
- two interpenetrating FCC lattices with different atoms, offset by  $1/4$  of a body diagonal

# IMPORTANT NON-BRAVAIS LATTICES

## hexagonal close packed (hcp) structure



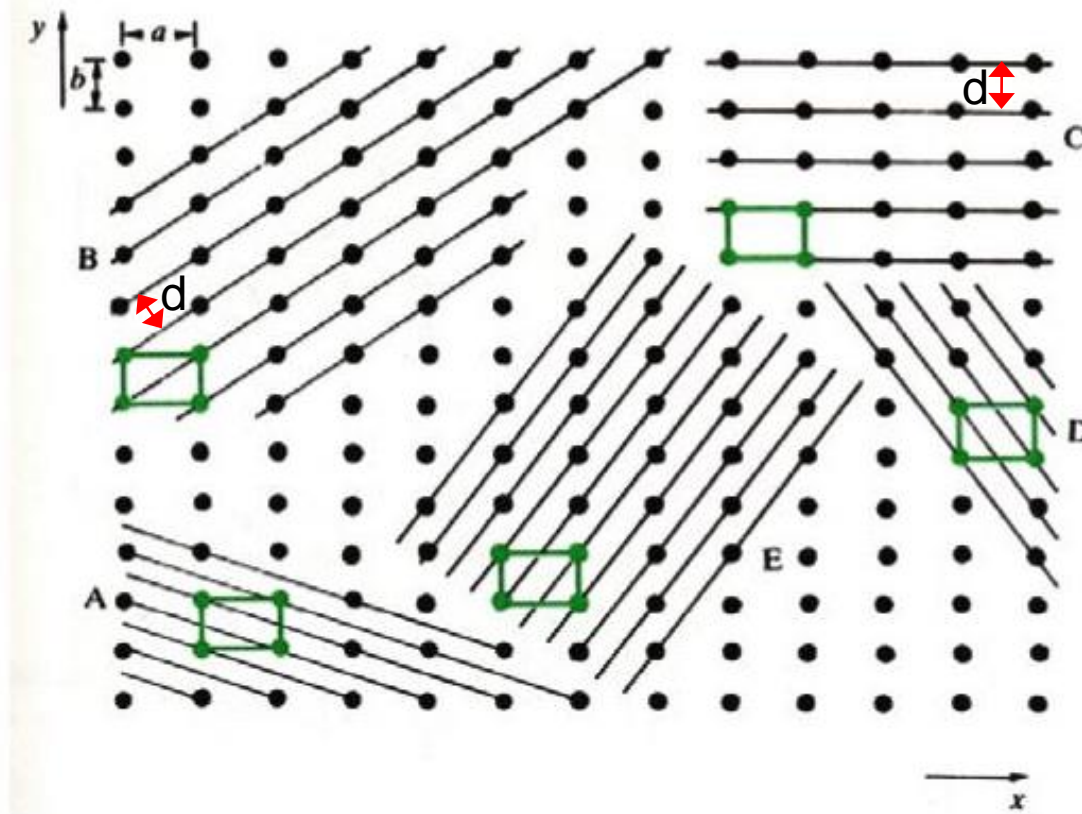
- A simple hexagonal lattice with a two-point basis,  $\mathbf{0}$  and  $\mathbf{a}_1/3 + \mathbf{a}_2/3 + \mathbf{a}_3/2$
- two interpenetrating simple hexagonal lattices offset by  $\mathbf{a}_1/3 + \mathbf{a}_2/3 + \mathbf{a}_3/2$



# MILLER INDICES

In crystallography, it is convenient to describe planes and directions with respect to the crystal lattice using a set of three integers ( $hkl$ ) called *Miller indices (1839)*

*This lattice is divided into many different sets of rows, each with a different  $d$ -spacing*

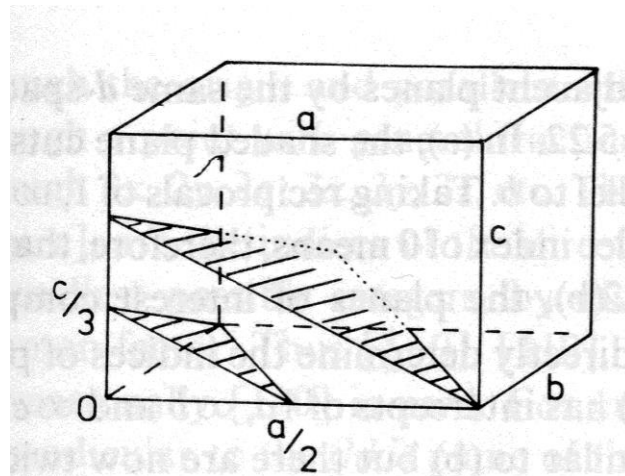


*In 3D, these rows become sets of planes*

# MILLER INDICES FOR PLANES

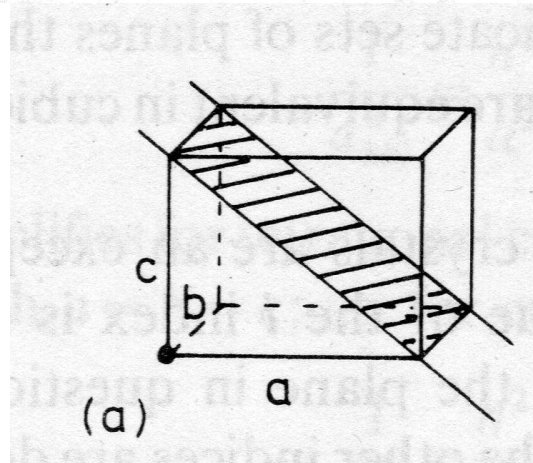
Definition #1: inverse intercepts in the real lattice

- 1) Find the intercepts with the cell axes as fractions of the lattice constants  $a$ ,  $b$ ,  $c$
- 2) Take the reciprocals of these numbers to give three integers, denote them  $(hkl)$



Intercepts:  $1/2, 1, 1/3$   
Reciprocals:  $2, 1, 3$

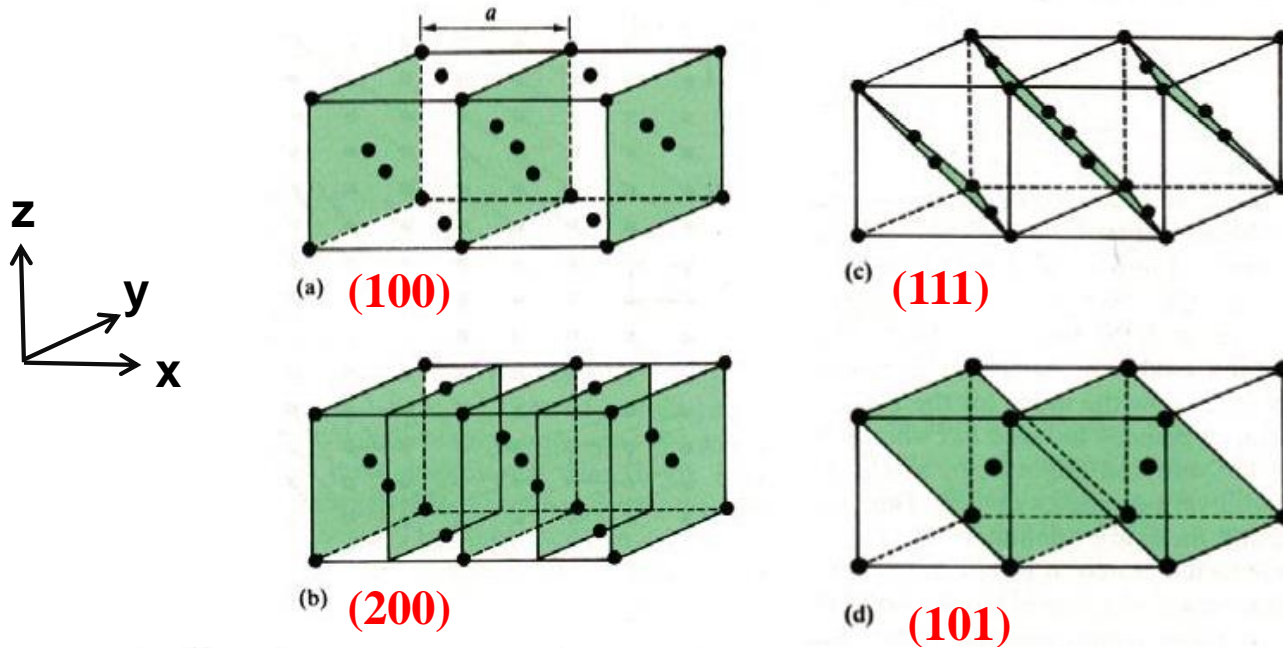
**Miller index: (213)**



Intercepts:  $1, \infty, 1$   
Reciprocals:  $1, 0, 1$

**Miller index: (101)**

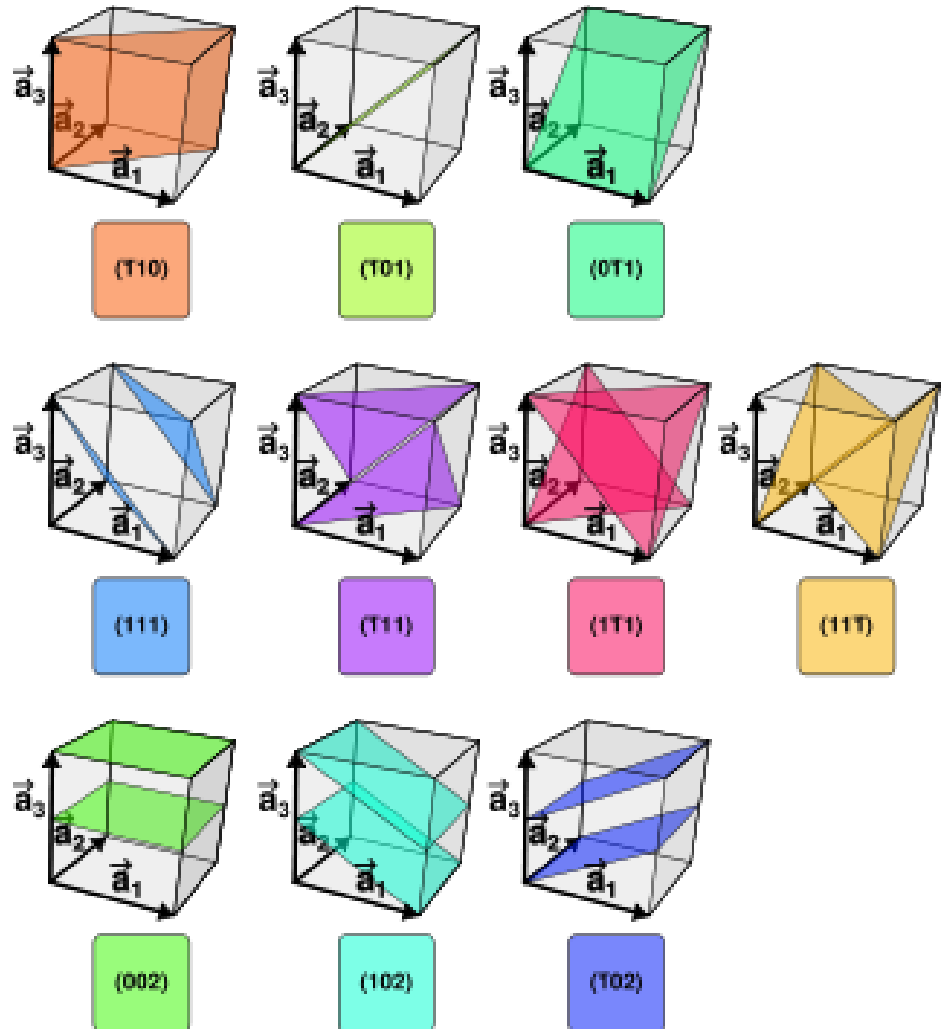
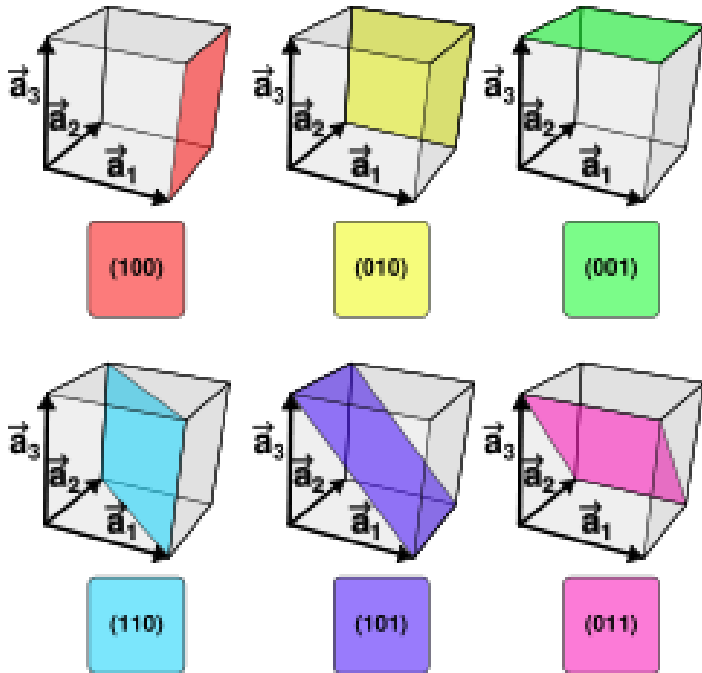
# MILLER INDICES



**Table 1** Miller Indices and Their Represented Plane or Direction of a Crystal Surface

Miller Indices	Description of plane or direction
$(hkl)$	For a plane that intercepts $1/h$ , $1/k$ , $1/l$ on the $x$ -, $y$ -, and $z$ -axis, respectively.
$(\bar{h}kl)$	For a plane that intercepts the negative $x$ -axis.
$\{hkl\}$	For a full set of planes of equivalent symmetry, such as $\{100\}$ for $(100)$ , $(010)$ , $(001)$ , $(\bar{1}00)$ , $(0\bar{1}0)$ , and $(00\bar{1})$ in cubic symmetry.
$[hkl]$	For a direction of a crystal such as $[100]$ for the $x$ -axis.
$\langle hkl \rangle$	For a full set of equivalent directions.
$(hki)$	For a plane in a hexagonal lattice (such as wurtzite) that intercepts $1/h$ , $1/k$ , $1/i$ , $1/l$ on the $a_1$ -, $a_2$ -, $a_3$ -, and $z$ -axis, respectively (Fig. 1g).

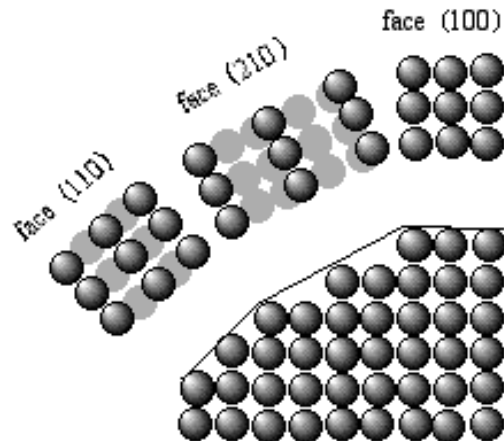
# MILLER INDICES FOR PLANES



# MILLER INDICES FOR PLANES

## Important points:

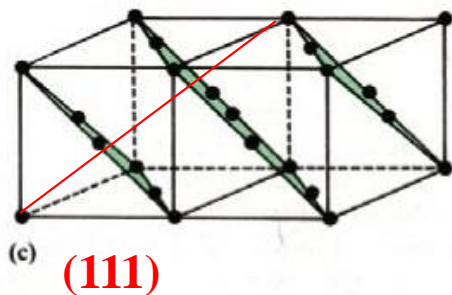
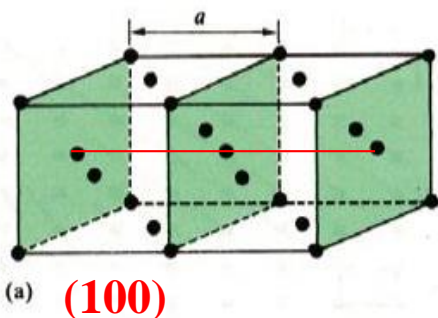
- Lattice planes need not coincide with a layer of atoms
- $(hkl)$  refers to the *entire set* of parallel planes with the same  $d$ -spacing
- If a Miller index is zero, the plane is parallel to that axis
- Multiplying or dividing  $(hkl)$  by a constant has no effect on the orientation of the plane, but it does change the  $d$ -spacing
- Miller indices with four integers  $(hkil)$  are often used for hexagonal lattices
- The most common surfaces are those with low Miller indices, since such planes have the highest concentrations of atoms (lowest energy)



# D-SPACINGS: Cubic Example

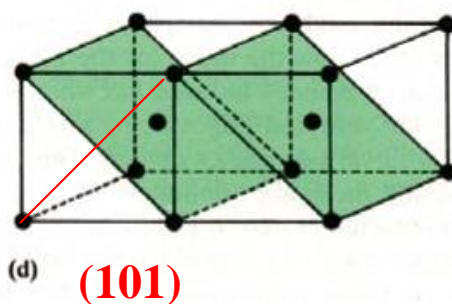
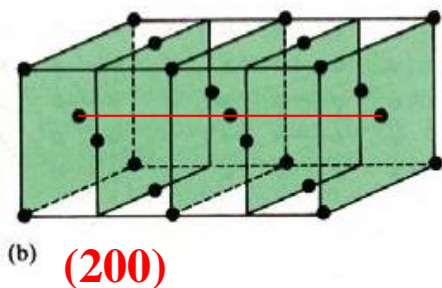
for Silicon (cubic with  $a = 5.43 \text{ \AA}$ ):

(100)	$d_{100} = 5.43 \text{ \AA}$
(200)	$d_{200} = a/2 = 2.72 \text{ \AA}$
(111)	$d_{111} = a/\sqrt{3} = 3.14 \text{ \AA}$
(101)	$d_{101} = a/\sqrt{2} = 3.84 \text{ \AA}$



Length of body diagonal:  $a\sqrt{3}$

{111} d-spacing:  $\frac{a\sqrt{3}}{3}$



Length of face diagonal:  $a\sqrt{2}$

{101} d-spacing:  $\frac{a\sqrt{2}}{2}$

# D-SPACINGS

*d-spacing formulae for any lattice symmetry:*

Cubic 
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal 
$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Orthorhombic 
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Hexagonal 
$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

Monoclinic 
$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$

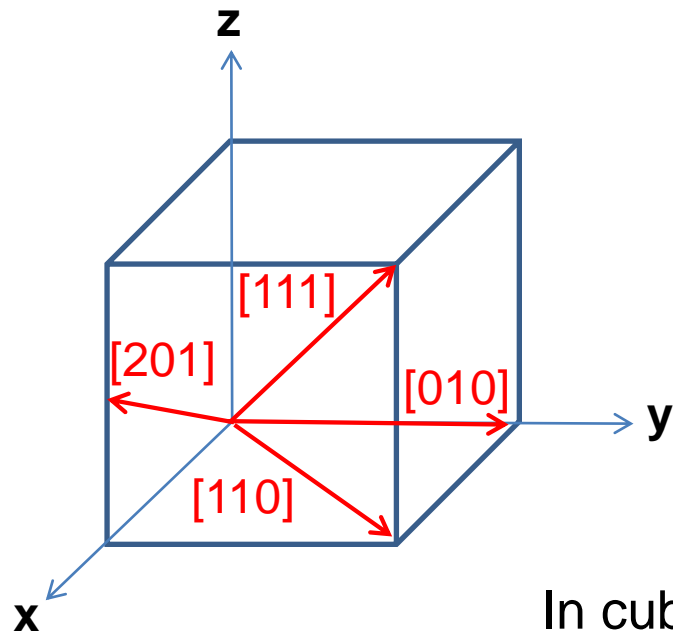
Triclinic 
$$\frac{1}{d^2} = \frac{1}{V^2} [h^2 b^2 c^2 \sin^2 \alpha + k^2 a^2 c^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma + 2hkabc^2 (\cos \alpha \cos \beta - \cos \gamma) + 2kla^2 bc (\cos \beta \cos \gamma - \cos \alpha) + 2hlab^2 c (\cos \alpha \cos \gamma - \cos \beta)]$$

Table 5.4 Calculated *d*-spacings for an orthorhombic cell, for  $a = 3.0$ ,  $b = 4.0$ ,  $c = 5.0 \text{ \AA}$

<i>hkl</i>	<i>d</i> ( $\text{\AA}$ )
001	5.00
010	4.00
011	3.12
100	3.00
101	2.57
110	2.40
111	2.16

# CRYSTALLOGRAPHIC DIRECTIONS

$[hkl]$  indicates a direction in a crystal, defined in the normal way from the origin

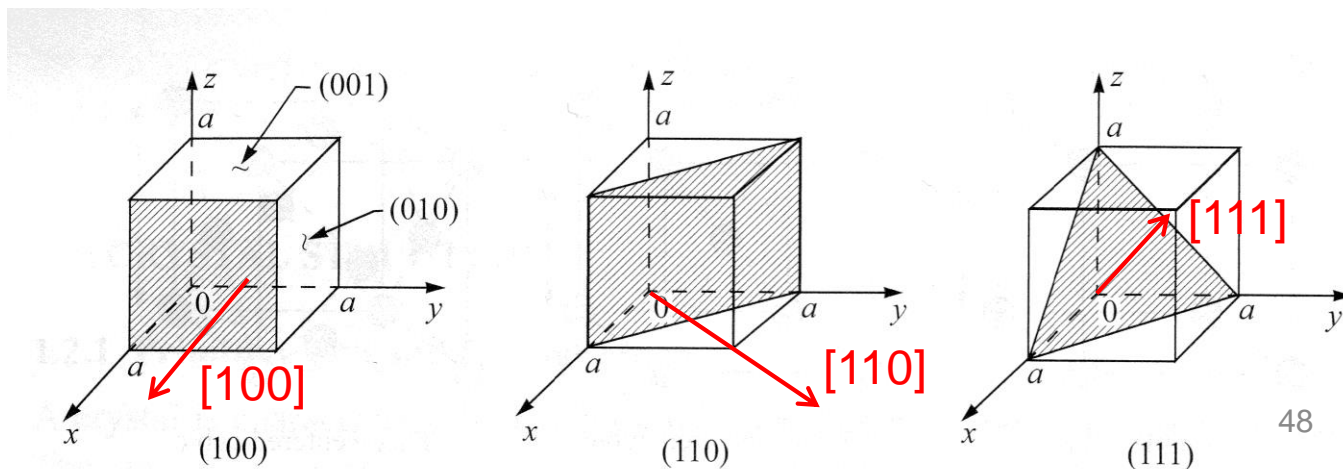


## Lattice Directions

*Individual directions:*  $[hkl]$

*Set of equivalent directions:*  $\langle hkl \rangle$

In cubic crystals,  $[hkl]$  is perpendicular to  $(hkl)$ .



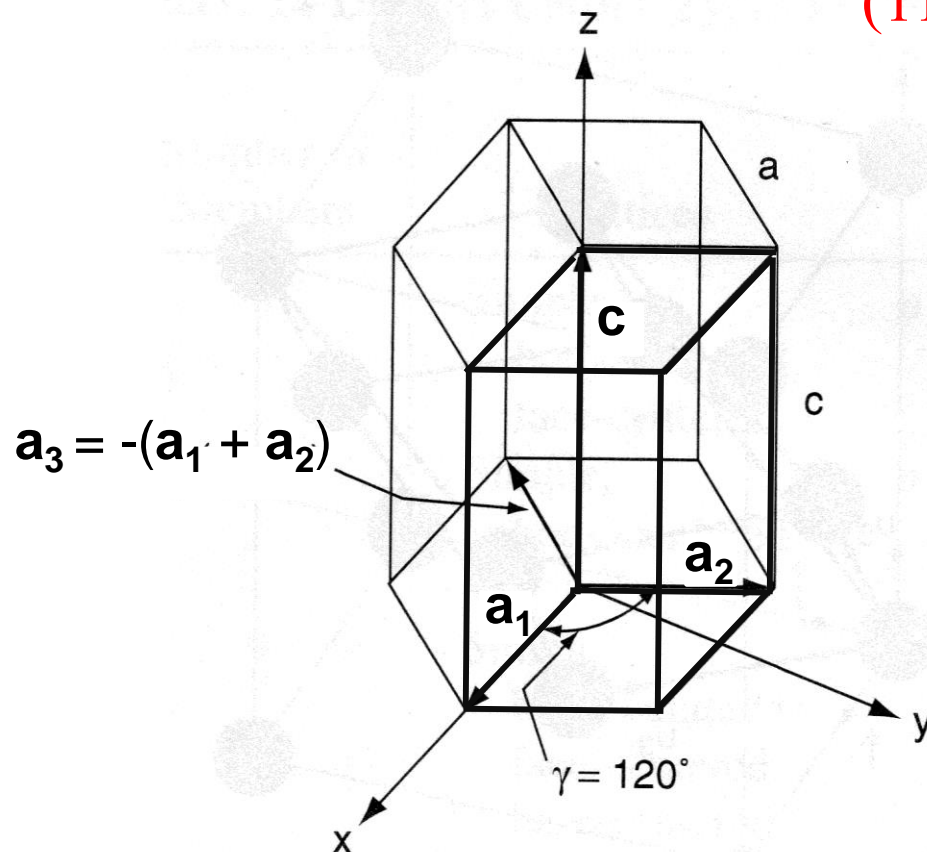


# INDICES for HEXAGONAL LATTICES

It is best to use four indices ( $hkil$ ) to describe hexagonal lattices since the non-orthogonal equatorial axes make ( $hkl$ ) notation ambiguous

For example,  $(110)$  and  $(\bar{1}20)$  are equivalent planes in hex. systems, but this is not obvious unless the four-index notation is used.

$$(110) \equiv (11\bar{2}0) \quad (\bar{1}20) \equiv (\bar{1}2\bar{1}0)$$



- Primitive cell in bold
- Conventional cell also shown
- Lattice constants:  $a$ ,  $c$
- 4 vectors:  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$  and  $\mathbf{c}$

## Primitive vector transformations

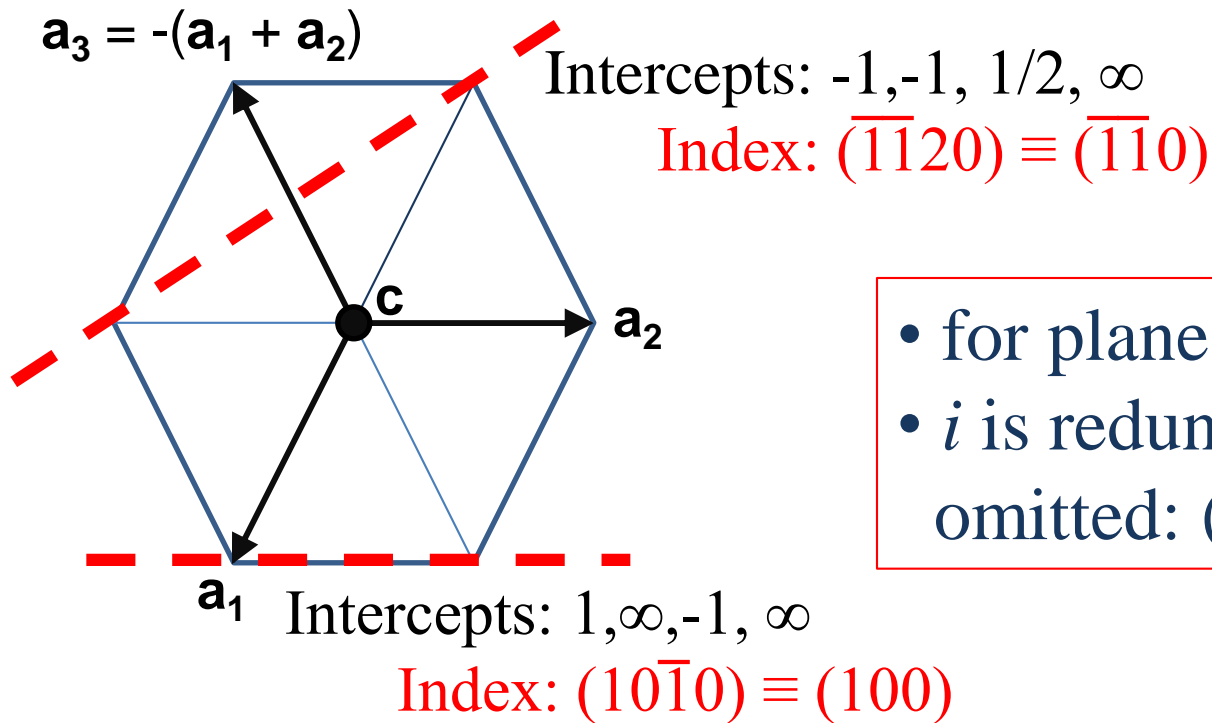
$$\mathbf{a}_1 = a\hat{\mathbf{x}}$$

$$\mathbf{a}_2 = a[-\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}]/2$$

$$\mathbf{c} = c\hat{\mathbf{z}}$$

# HEXAGONAL LATTICE PLANES

## plan view of 4-axis basis



- for planes,  $h + k + i = 0$
- $i$  is redundant and can be omitted:  $(hkil) \rightarrow (hkl)$

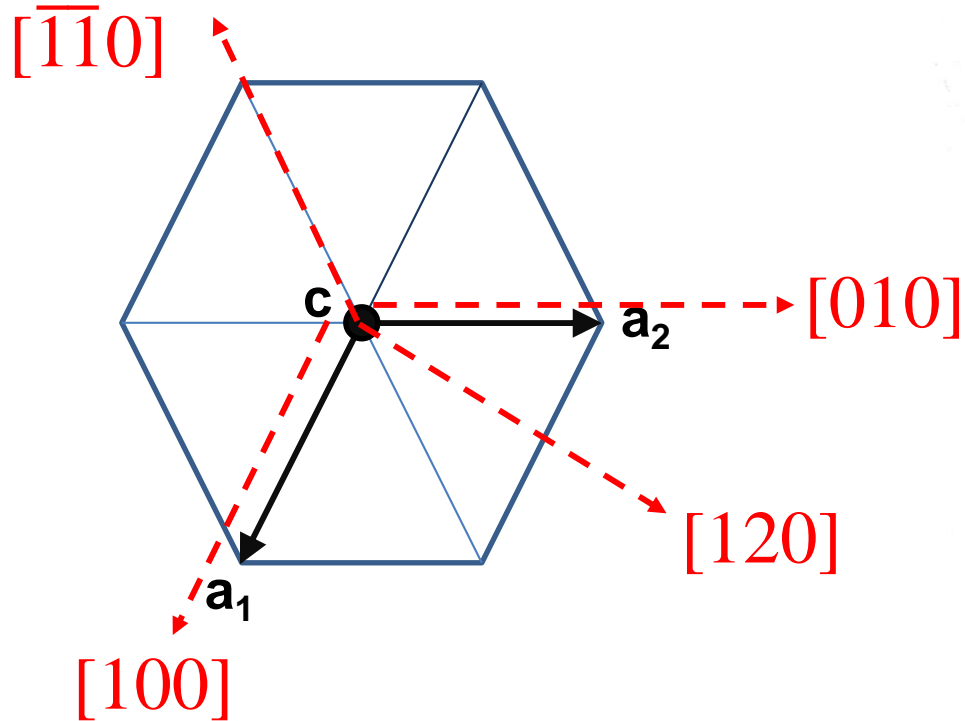
there are six  $\{100\}$ , six  $\{110\}$  planes,  
 and two basal planes,  $\{0001\}$

$$\begin{aligned} \{100\} = & (10\bar{1}0), \\ & (\bar{1}010), (1\bar{1}00), \\ & (\bar{1}100), (01\bar{1}0), \\ & (0\bar{1}10) \end{aligned}$$

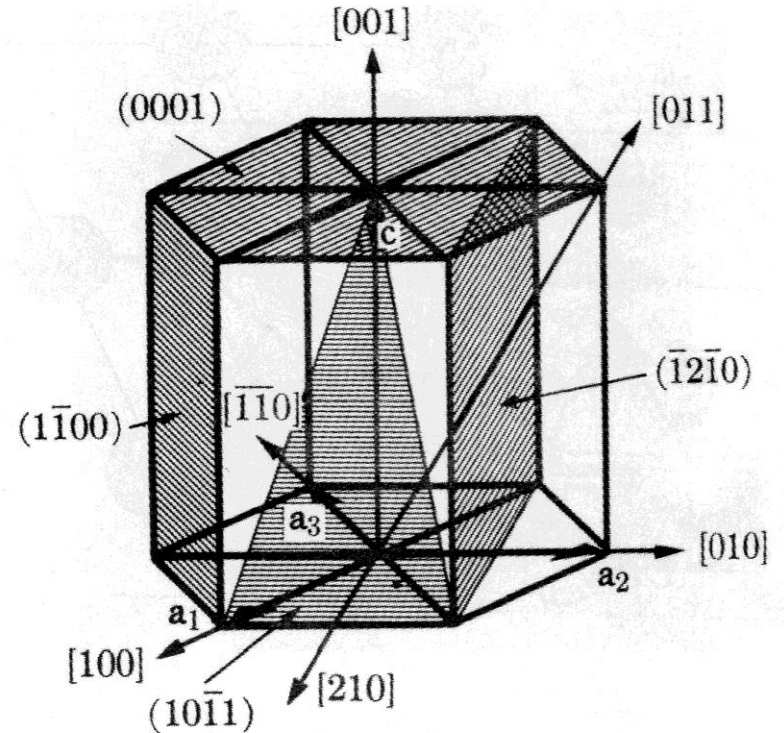
# HEXAGONAL LATTICE DIRECTIONS

We use  $[hk\bar{l}]$  rather than  $[hki\bar{l}]$  to specify lattice directions

plan view of 3-axis basis



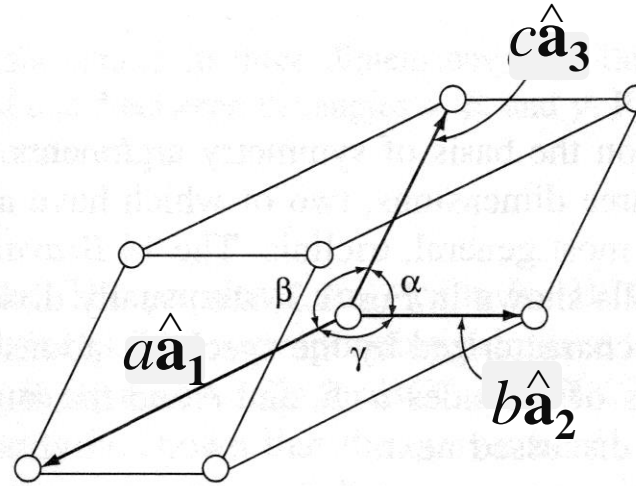
3D view



# UNIT CELL VOLUMES

*general formula  
(parallelepiped):*

$$V_{cell} = |a\hat{a}_1 \cdot (b\hat{a}_2 \times c\hat{a}_3)|$$



*lattice specific formulae:*

Cubic

$$V = a^3$$

Tetragonal

$$V = a^2c$$

Orthorhombic

$$V = abc$$

Hexagonal

$$V = (\sqrt{3}a^2c)/2 = 0.866a^2c$$

Monoclinic

$$V = abc \sin \beta$$

Triclinic

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2\cos \alpha \cos \beta \cos \gamma)^{1/2}$$

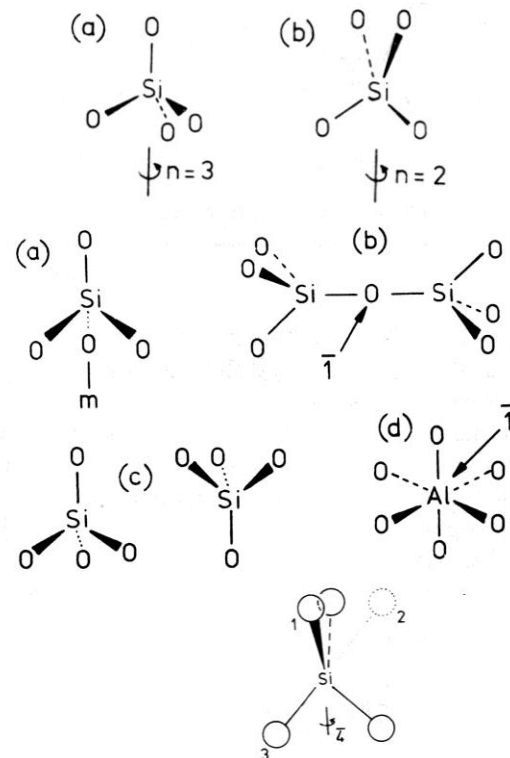
# SYMMETRY OF BRAVAIS LATTICES

By definition, all 14 Bravais lattices have *translational invariance*

Each Bravais lattice also has *point symmetry* (invariance under point operations)

Point symmetry refers to symmetry elements in which at least one point stays fixed during the symmetry operation

	Symmetry element	Notation	
		Hermann–Mauguin (crystallography)	Schönflies (spectroscopy)
Point symmetry	Mirror plane	$m$	$\sigma_v, \sigma_h$
	Rotation axis	$n$ ( $= 2, 3, 4, 6$ )	$C_n$ ( $C_2, C_3$ , etc.)
	Inversion axis	$\bar{n}$ ( $= \bar{1}, \bar{2}$ , etc.)	—
	Alternating axis (rotoreflection)	—	$S_n$ ( $S_1, S_2$ , etc.)
	Centre of symmetry	$\bar{1}$	$i$
Space symmetry	Glide plane	$n, d, a, b, c$	—
	Screw axis	$2_1, 3_1$ , etc.	—



All normal crystals belong to one of 32 possible *point groups* based on the combination of point symmetry elements they possess

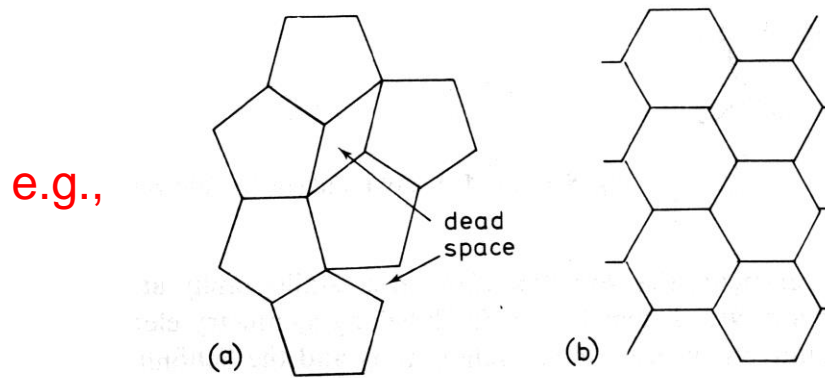
# POINT SYMMETRY

Table 5.2 *The seven crystal systems*

Crystal system	Unit cell shape <sup>†</sup>	Essential symmetry	Space lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Three twofold axes or mirror planes	P, F, I, A(B or C)
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	One threefold axis	P
(b)	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	One threefold axis	R
Monoclinic*	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	None	P

\* Two settings of the monoclinic cell are used in the literature. The one given here, which is most commonly used, and the other  $a \neq b \neq c, \alpha = \beta = 90^\circ, \gamma \neq 90^\circ$ .  
<sup>†</sup> The symbol  $\neq$  means not necessarily equal to. Sometimes, crystals possess *pseudo-symmetry* in which, say, the unit cell is geometrically cubic but does not possess the essential symmetry elements for cubic symmetry, and the symmetry is lower, perhaps tetragonal.

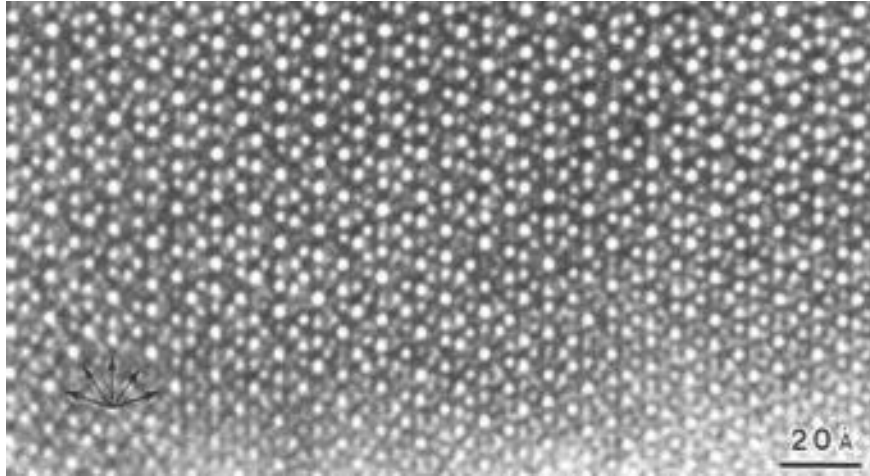
- Crystals may display rotational symmetries of 1, 2, 3, 4, or 6.  
 (other possibilities cannot fill space without voids)



**Fig. 5.11** (a) The impossibility of forming a close packed array of pentagons. (b) A close packed layer of hexagons.

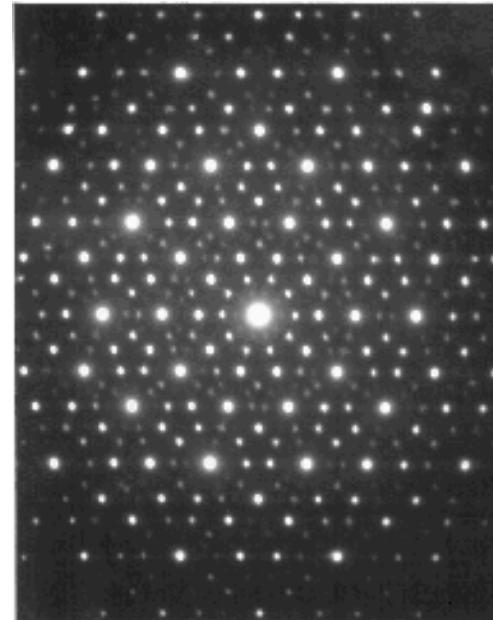
# QUASICRYSTALS

Ordered but aperiodic (“quasi-periodic”) crystals first discovered in 1982



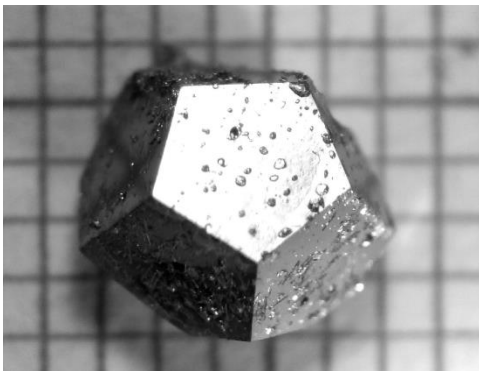
*Al<sub>0.86</sub>Mn<sub>0.14</sub> alloy*

Shechtman et al. *PRL* **53**, 1951 (1984).



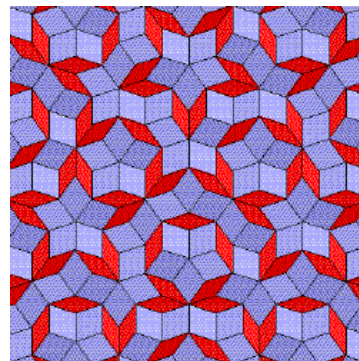
2011 Nobel Prize  
Chemistry  
D. Shechtman

10-fold  
symmetry!

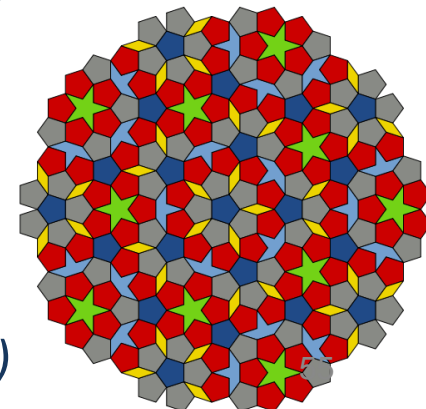


*YMgCd* Ian Fisher

Often binary or ternary intermetallic compounds  
- poor conductors, very hard



Quasicrystals  
are topologically  
similar to  
***Penrose tilings***  
(*aperiodic tilings*)



# POINT GROUPS

Point symmetry elements allowed in crystals:  $1, 2, 3, 4, 6, \bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{6}, m$

Table 2.4. The 32 Crystallographic Point Groups

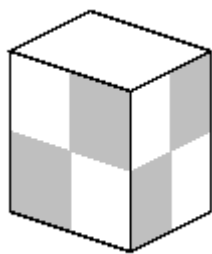
Crystal system (bravais lattices)	Crystallographic point groups <sup>a</sup> (molecular point groups <sup>b</sup> )
Cubic ( $P, I, F$ )	$23, m\bar{3}, 432, \bar{4}3m, m\bar{3}m$ ( $T, T_h, O, T_d, O_h$ )
Tetragonal ( $P, I$ )	$4, \bar{4}, 4/m, 422, 4mm, \bar{4}2m, 4/mmm$ ( $C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}, D_{4h}$ )
Orthorhombic ( $P, C, I, F$ )	$222, mm2, mmm$ ( $D_2, C_{2v}, D_{2h}$ )
Trigonal/Rhombohedral ( $P$ )	$3, \bar{3}, 32, 3m, \bar{3}m$ ( $C_3, C_{3i}, D_3, C_{3v}, D_{3d}$ )
Hexagonal ( $P$ )	$6, \bar{6}, 6/m, 622, 6mm, \bar{6}m2, 6/mmm$ ( $C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}, D_{6h}$ )
Monoclinic ( $P, C$ )	$2, m, 2/m$ ( $C_2, C_s, C_{2h}$ )
Triclinic ( $P$ )	$1, \bar{1}$ ( $C_1, C_i$ )

/ denotes a mirror plane perpendicular to the rotation axis

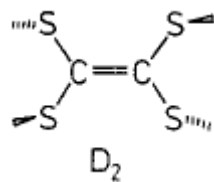
<sup>a</sup>The H-M symbolism derived from crystal symmetry operations. For image and movie representations of each point group, see the website: <http://neon.memscmu.edu/degraeef/pg/index.html>

<sup>b</sup>The analogous Schoenflies symbolism derived from molecular symmetry operations.

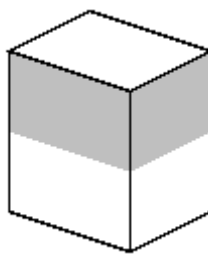
3D representations of the 3 orthorhombic point groups:



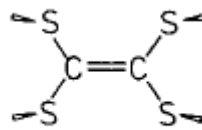
222  
 $D_2$



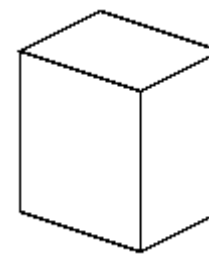
$D_2$



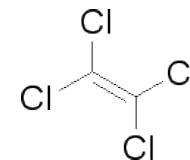
mm2  
 $C_{2v}$



$C_{2v}$



mmm  
 $D_{2h}$

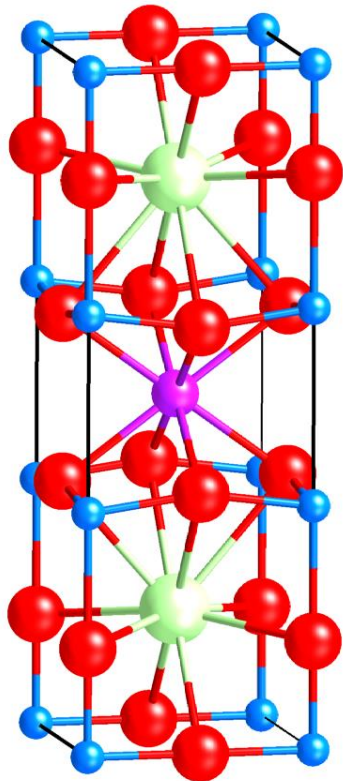


$D_{2h}$



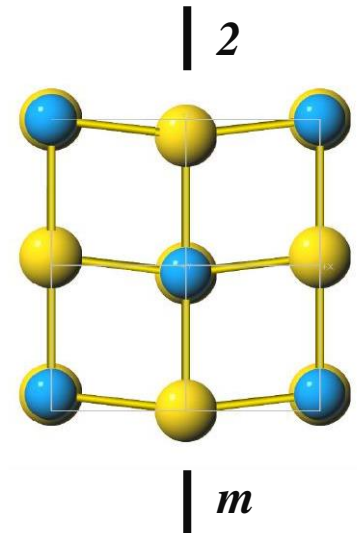
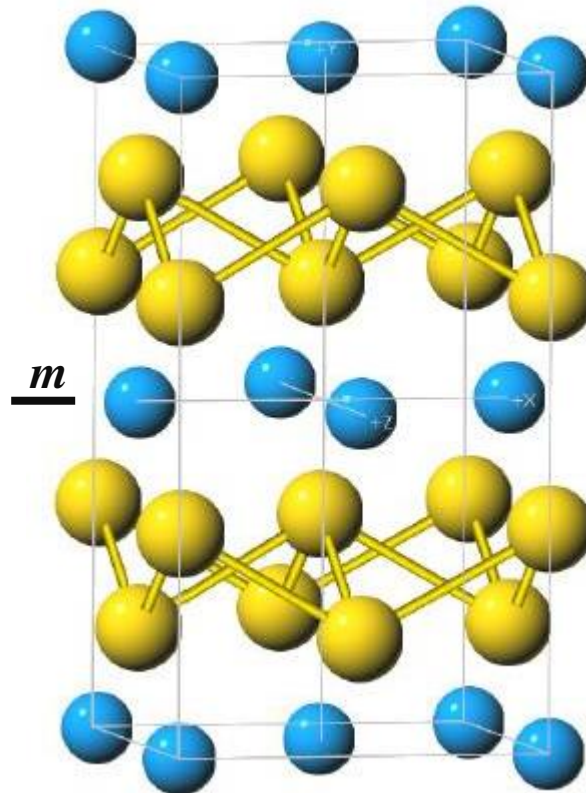
# EXAMPLES

mmm



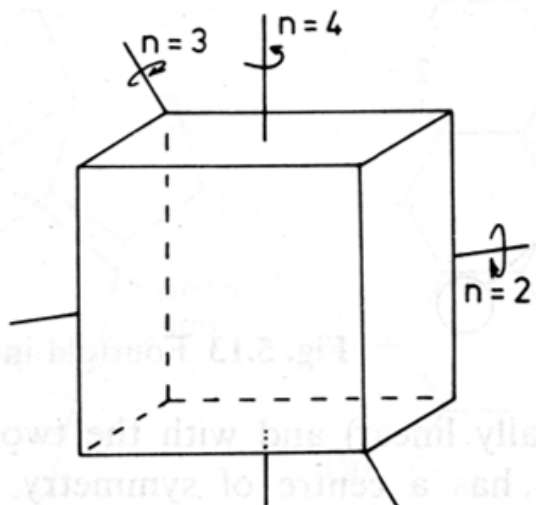
$$\begin{aligned} a &= 3.8240 \text{ \AA} \\ b &= 3.8879 \text{ \AA} \\ c &= 11.6901 \text{ \AA} \end{aligned}$$

mm2



• *slight buckle eliminates 3<sup>rd</sup> mirror plane*

# CUBIC POINT SYMMETRY

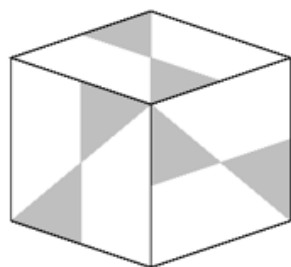


**Fig. 5.14** Two-, three- and four-fold axes of a cube

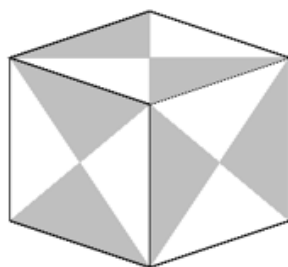
## Schönflies symbols

	Symbol	Meaning
Classification according to rotation axes and principal mirror planes	$T$	4 three- and 3 two-fold rotation axes as in a tetrahedron
	$O$	4 three- and 3 four-fold rotation axes as in an octahedron
Additional symbols for mirror planes	$h$	horizontal = perpendicular to the rotation axis
	$v$	vertical = parallel to the main rotation axis
	$d$	diagonal = parallel to the main rotation axis in the plane bisecting the 2-fold rotation axes

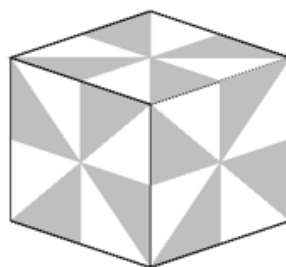
## The five cubic point groups in 3D:



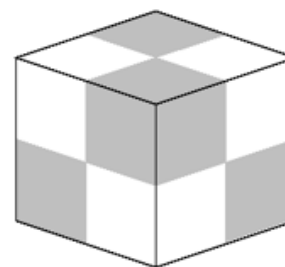
$23$   
 $T$



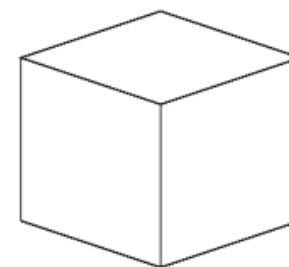
$m\bar{3}$   
 $T_h$



$432$   
 $O$

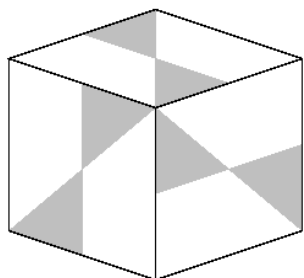


$\bar{4}3m$   
 $T_d$

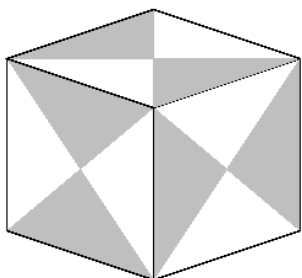


$m\bar{3}m$   
 $O_h$

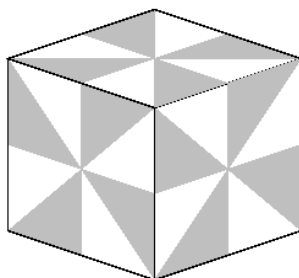
# The five cubic point groups in 3D:



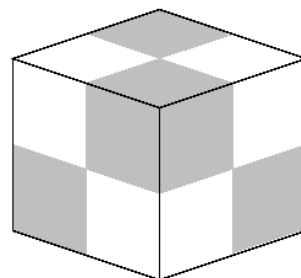
$23$   
T



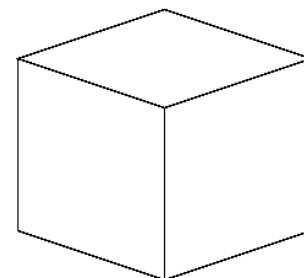
$m\bar{3}$   
Th



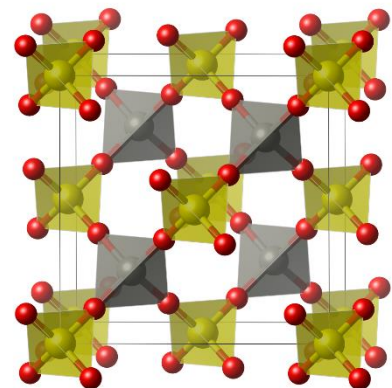
$432$   
O



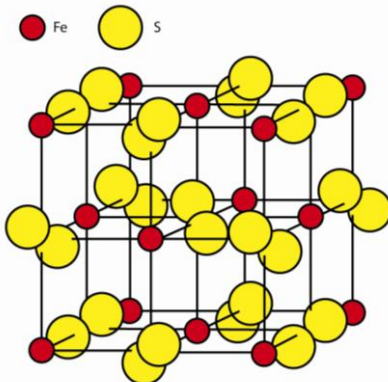
$\bar{4}3m$   
Td



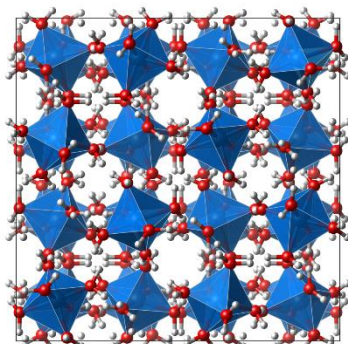
$m\bar{3}m$   
Oh



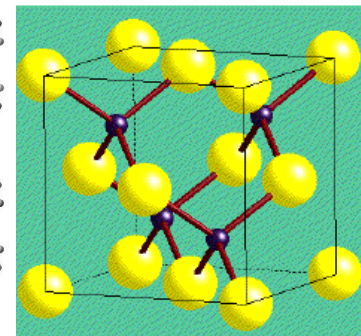
ZnSO<sub>4</sub>



pyrite (FeS<sub>2</sub>)

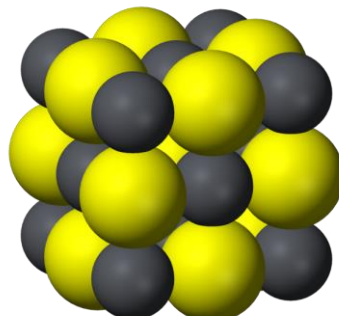


Te(OH)<sub>6</sub>



ZnS

diamond



galena (PbS)

fcc & bcc



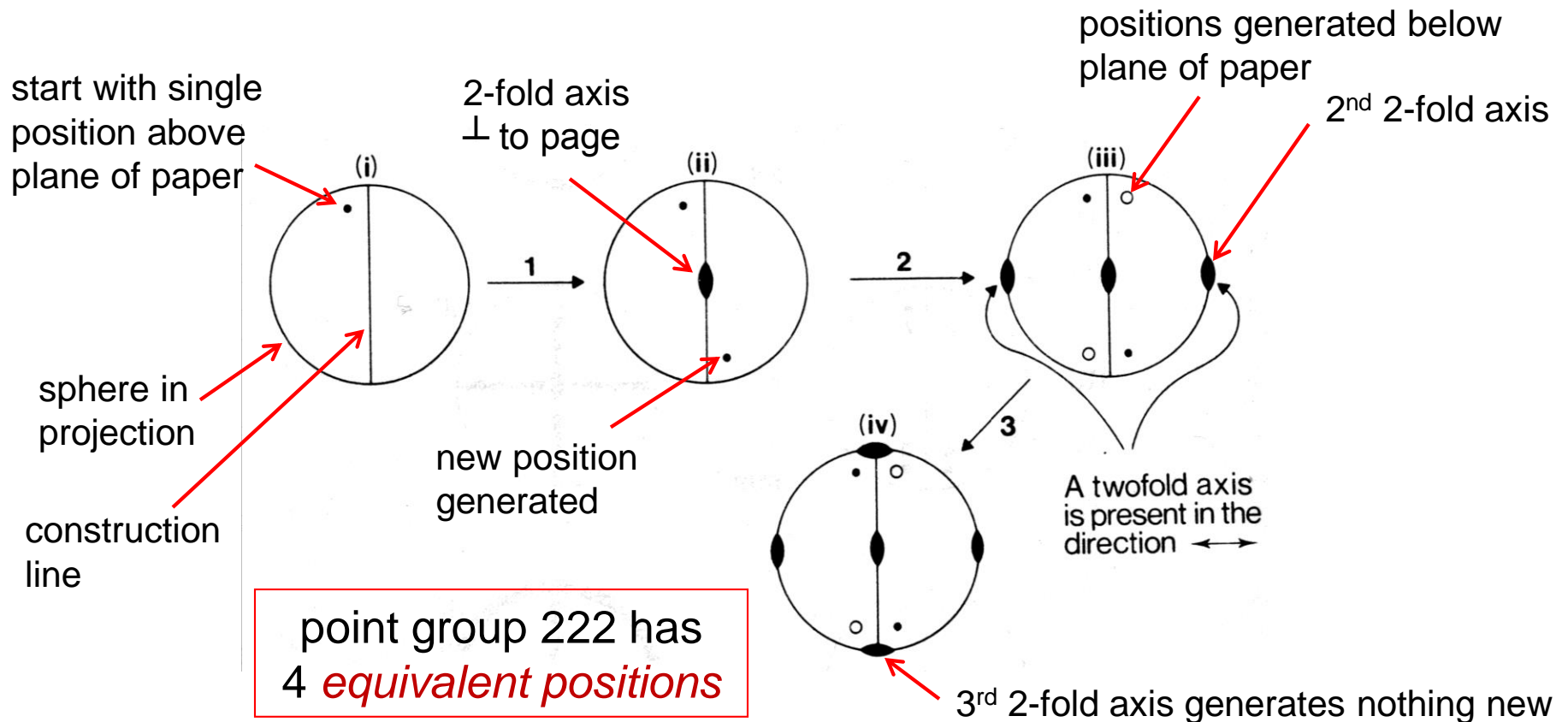
??



# STEREOGRAMS

Stereograms are semi-archaic representations of point groups, useful in crystallography and geology

Example: construct the stereogram for the 222 point group  
(3 mutually perpendicular 2-fold axes)



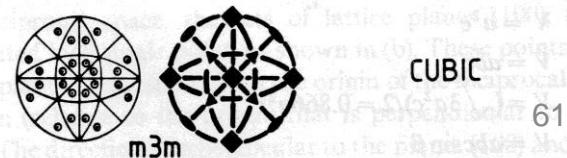
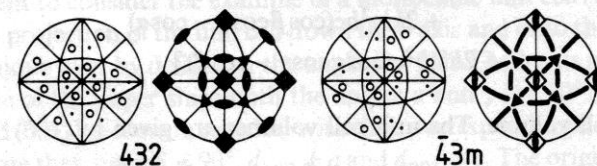
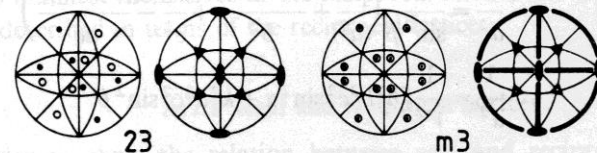
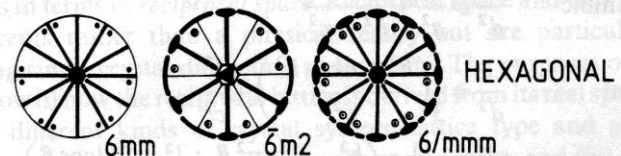
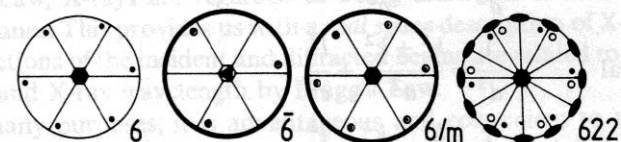
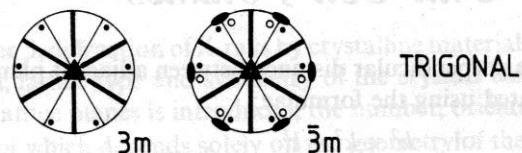
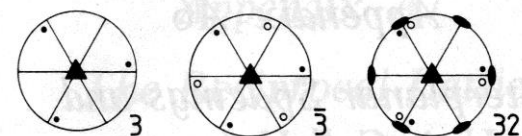
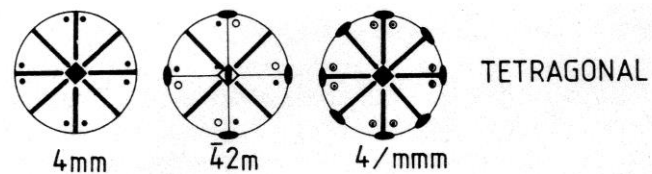
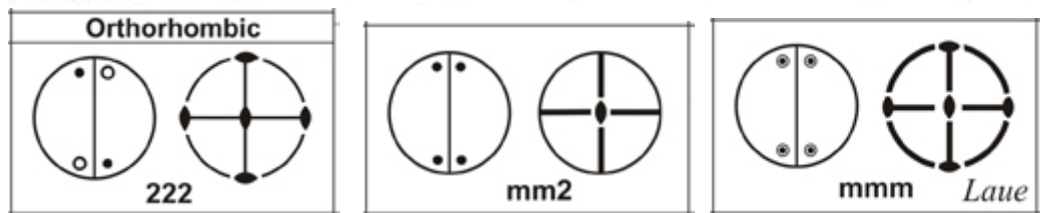
# STEREOGRAM NOTATION

Table 6.1 Point symmetry elements

Symmetry element	Written symbol	Graphical symbol
Rotation axes	1	None
	2	
	3	
	4	
	6	
Inversion axes	$\bar{1}$	None* — <sup>†</sup>
	$\bar{2} (\equiv m)$	
	$\bar{3} (\equiv 3 + \bar{1})$	
Mirror plane	4	
	$\bar{6} (= 3/m)$	
Mirror plane	$m$	—

\* The inversion axis,  $\bar{1}$ , equivalent to a centre of symmetry, is represented as  $\circ$  in space groups but does not have a formal graphical representation in point groups, even though it is present in many point groups.

† The inversion axis  $\bar{2}$  does not have a separate graphical symbol other than that of the mirror plane equivalent to it.



# TABLE OF POINT GROUPS

Correspondence between crystallographic and spectroscopic (“normal”) notation:

- *Hermann-Mauguin for crystallography*
- *Schönflies for spectroscopy*
- *21 out of the 32 have no center of symmetry (centrosym. groups in red)*

H-M	Schönflies	H-M	Schönflies	H-M	Schönflies
1	$C_1$	$m\bar{3}$	$T_h$	6mm	$C_{6v}$
2	$C_2$	$2/m$	$C_{2h}$	$m\bar{3}m$	$O_h$
222	$D_2$	$mmm$	$D_{2h}$	$\bar{4}2m$	$D_{2d}$
4	$C_4$	$4/m$	$C_{4h}$	$\bar{6}2m$	$D_{3h}$
3	$C_3$	32	$D_3$	$4/mmm$	$D_{4h}$
6	$C_6$	$6/m$	$C_{6h}$	$6/mmm$	$D_{6h}$
23	T	432	O		
$\bar{1}$	$C_i$	422	$D_4$		
m	$C_s$	3m	$C_{3v}$		
mm2	$C_{2v}$	622	$D_6$		
$\bar{4}$	$S_4$	$\bar{4}3m$	$T_d$		
$\bar{3}$	$S_6$	4mm	$C_{4v}$		
$\bar{6}$	$C_{3h}$	$\bar{3}m$	$D_{3d}$		

# SPACE SYMMETRY OPERATIONS

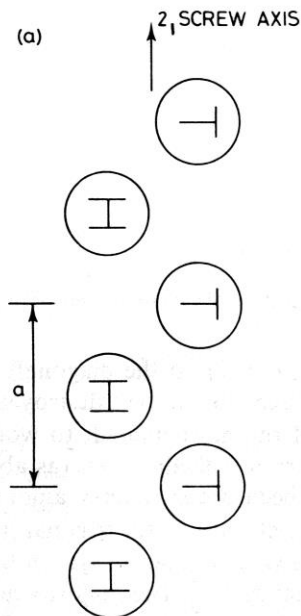
*finite molecules* have point symmetry only

*crystals* have point symmetry + extra operations that include translation

*point group* + *space symmetry elements* → *space group*

## Screw axis

- translation and rotation along the same axis



symbol



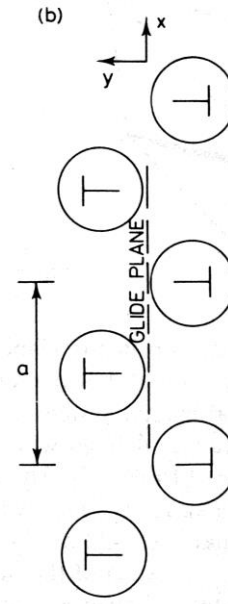
- translate by  $Y/X$  of unit cell edge
- rotate by  $360^\circ/X$

e.g.

$6_3 = \frac{1}{2}$  translation,  
60° rotation

## Glide plane

- translation and reflection in a parallel plane



types

*a, b & c glides*  
*n* (face dia.)  
*d* (body dia.)

an *a* glide plane with  
reflection  $\perp$  to *b* axis

# INTERNATIONAL SPACE GROUP SYMBOLS

All periodic crystals can be classified into one of 230 possible space groups, which summarize their crystal system, lattice, and point and space symmetries

*14 Bravais lattices + 32 crystall. point groups + space ops. → 230 space groups*

The first letter in the int'l symbol refers to Bravais lattice type:

P (primitive); F (face-centered); I (body centered); A, B, or C (base centered)

The remaining characters are the H-M symbols (with space symmetry added and ordered from most important axis to least important axes, or xyz)

**quartz:** P3<sub>1</sub>21 – primitive trigonal with 3<sub>1</sub> screw axis and 2-fold rotation axis

**diamond:** Fd $\bar{3}$ m – FCC with glide planes along the body diags. and 3-fold rotoinversion axes

**CaTiO<sub>3</sub> :** Pnma – primitive orthorhombic with an *n*-glide plane  $\perp$  to x-axis, a mirror plane  $\perp$  to y-axis, and an *a*-glide plane  $\perp$  to c axis



# CONCEPTUAL RELATIONSHIPS

## POINT AND SPACE GROUPS OF BRAVAIS LATTICES AND CRYSTAL STRUCTURES

	BRAVAIS LATTICE (BASIS OF SPHERICAL SYMMETRY)	CRYSTAL STRUCTURE (BASIS OF ARBITRARY SYMMETRY)
Number of point groups:	7 ("the 7 crystal systems")	32 ("the 32 crystallographic point groups")
Number of space groups:	14 ("the 14 Bravais lattices")	230 ("the 230 space groups")



groups possible when basis  
is of maximum symmetry  
(a sphere on each lattice point)



groups possible when basis  
can have arbitrary symmetry

# SELECT SPACE GROUPS

Cubic (36)	23	P23, F23, I23, P2 <sub>1</sub> 3, I2 <sub>1</sub> 3
	m $\bar{3}$	Pm $\bar{3}$ , Pn $\bar{3}$ , Fm $\bar{3}$ , Fd $\bar{3}$ , Im $\bar{3}$ , Pa $\bar{3}$ , Ia $\bar{3}$
	432	P432, P4 <sub>2</sub> 32, F432, F4 <sub>1</sub> 32, I432, P4 <sub>3</sub> 32, P4 <sub>1</sub> 32, I4 <sub>1</sub> 32
	$\bar{4}3m$	P $\bar{4}$ 3m, F $\bar{4}$ 3m, I $\bar{4}$ 3m, P $\bar{4}$ 3n, F $\bar{4}$ 3c, I $\bar{4}$ 3d
	m $\bar{3}m$	Pm $\bar{3}m$ , Pn $\bar{3}n$ , Pm $\bar{3}n$ , Pn $\bar{3}m$ , Fm $\bar{3}m$ , Fm $\bar{3}c$ , Fd $\bar{3}m$ , Fd $\bar{3}c$ , Im $\bar{3}m$ , Ia $\bar{3}d$
Hexagonal (27)	6	P6, P6 <sub>1</sub> , P6 <sub>5</sub> , P6 <sub>2</sub> , P6 <sub>4</sub> , P6 <sub>3</sub>
	$\bar{6}$	P $\bar{6}$
	6/m	P6/m, P6 <sub>3</sub> /m
	622	P622, P6 <sub>1</sub> 22, P6 <sub>5</sub> 22, P6 <sub>2</sub> 22, P6 <sub>4</sub> 22, P6 <sub>3</sub> 22
	6mm	P6mm, P6cc, P6 <sub>3</sub> cm, P6 <sub>3</sub> mc
	$\bar{6}m2$	P $\bar{6}m2$ , P $\bar{6}c2$ , P $\bar{6}2m$ , P $\bar{6}2c$
	6/mmm	P6/mmm, P6/mcc, P6 <sub>3</sub> /mcm, P6 <sub>3</sub> /mmc
Orthorhombic (59)	mm2	Pmm2, Pmc2 <sub>1</sub> , Pcc2, Pma2, Pca2 <sub>1</sub> , Pnc2, Pmn2 <sub>1</sub> , Pba2, Pna2 <sub>1</sub> , Pnn2, Cmm2, Cmc2 <sub>1</sub> , Ccc2, Amm2, Aem2, Ama2, Aea2, Fmm2, Fdd2, Imm2, Iba2, Ima2
	mmm	Pmmm, Pnnn, Pccm, Pban, Pmma, Pnna, Pmna, Pcca, Pbam, Pccn, Pbcm, Pnmm, Pmnm, Pbcn, Pbca, Pnma, Cmcm, Cmce, Cmmm, Cccm, Cmme, Ccce, Fmmm, Fddd, Immm, Ibam, Ibca, Imma

find the rest @ [http://en.wikipedia.org/wiki/Space\\_group](http://en.wikipedia.org/wiki/Space_group)

# CRYSTAL SYMMETRY SUMMARY

Crystal family	Crystal system	Required symmetries of point group	point groups	space groups	bravais lattices	Lattice system
Triclinic		None	2	2	1	Triclinic
Monoclinic		1 twofold axis of rotation or 1 mirror plane	3	13	2	Monoclinic
Orthorhombic		3 twofold axes of rotation or 1 twofold axis of rotation and two mirror planes.	3	59	4	Orthorhombic
Tetragonal		1 fourfold axis of rotation	7	68	2	Tetragonal
Hexagonal	Trigonal	1 threefold axis of rotation	5	7	1	Rhombohedral
	Hexagonal	1 sixfold axis of rotation		18		Hexagonal
Cubic		4 threefold axes of rotation	5	36	3	Cubic
<b>Total: 6</b>	<b>7</b>		<b>32</b>	<b>230</b>	<b>14</b>	<b>7</b>