

# Welcome to CHE 384T: Computational Methods in Materials Science

## A Brief Introduction to Crystallography

LeSar App. B1-B5

Kittel      Intro to  
Solid-State

# Lecture Outline

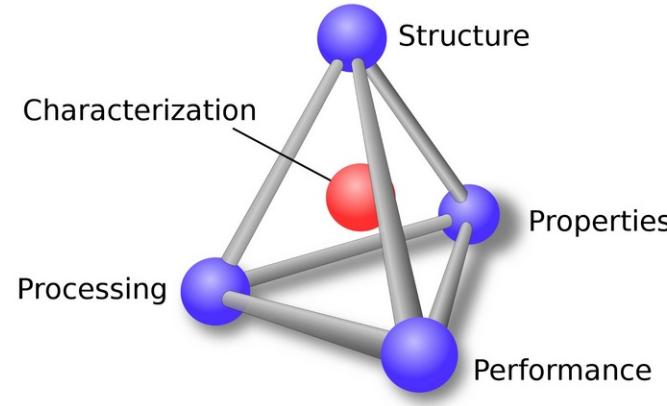
Crystal structure

Unit cell

Bravais Lattices

Example Crystal structures from the cubic space group

Brief on Crystallographic notation



# There are a lot of crystal structures out there

**› 210,000 crystal structures**

**› 165,000**  
experimental  
structures

**› 5,000**  
metal-organic  
structures

**› 13,000**  
theoretical  
structures

**~ 26,000**  
derived  
structures

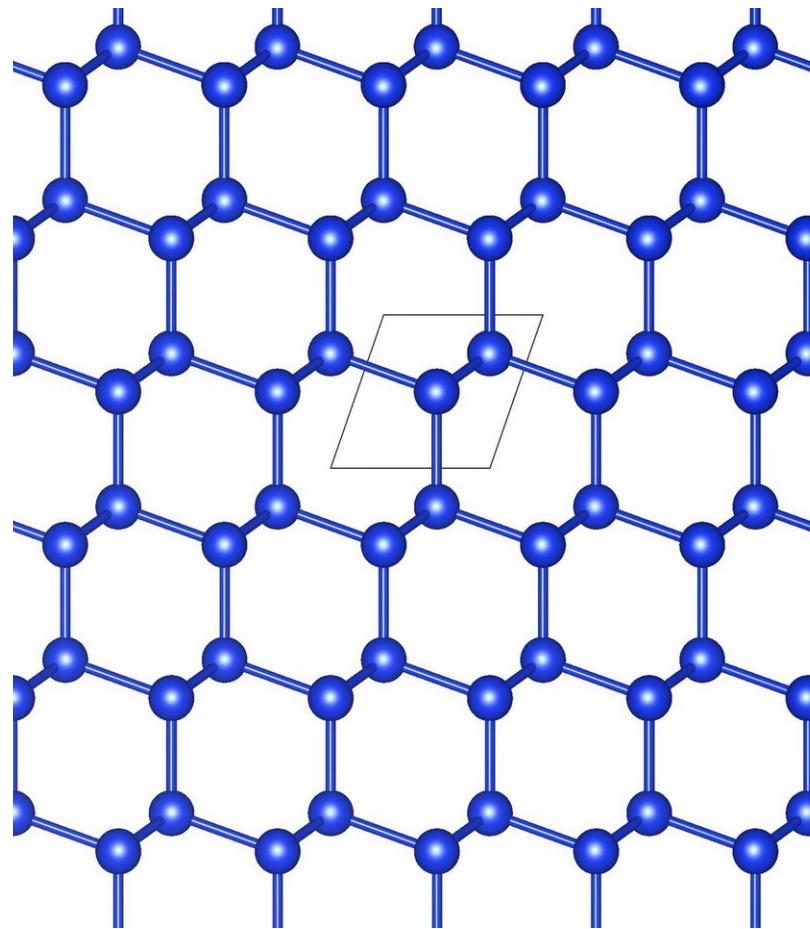
**› 9,000**  
structure  
types

**› 90,000**  
authors

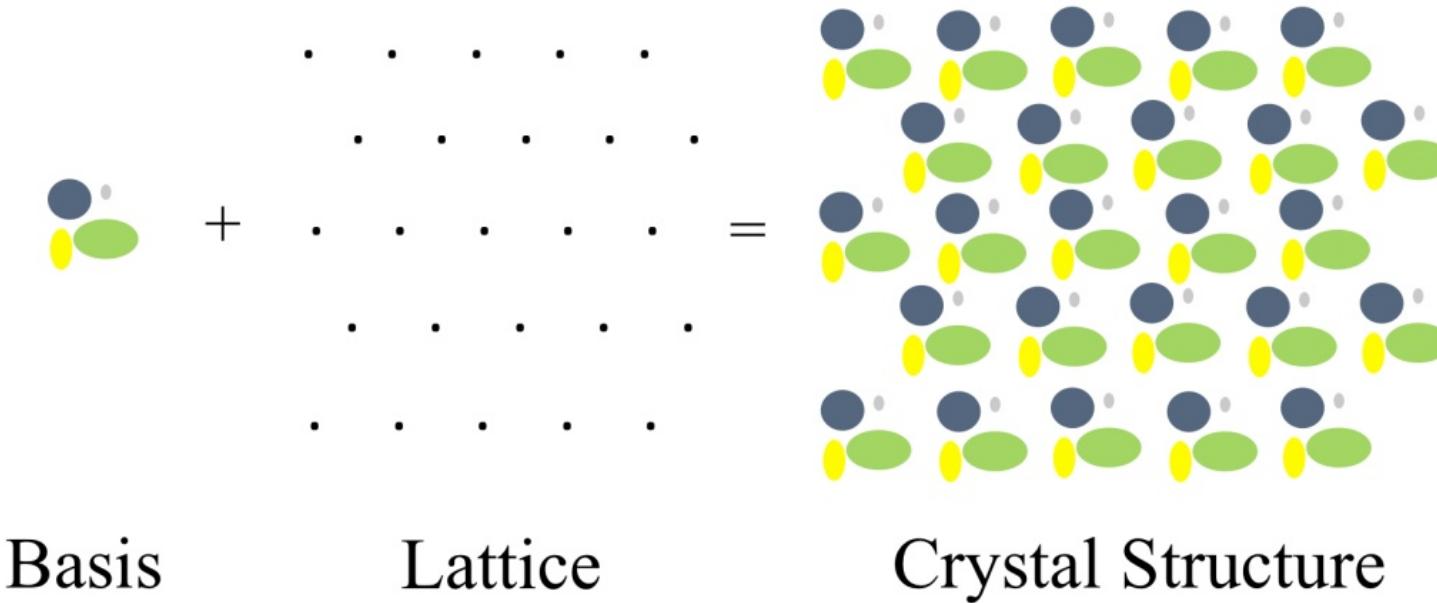
**› 80,000**  
articles

**› 1,600**  
journals

Crystals are described by periodicity of the unit cell

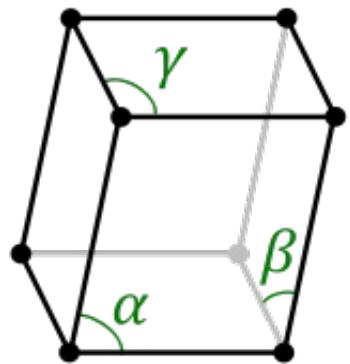


# Crystal Structure = Basis + Lattice

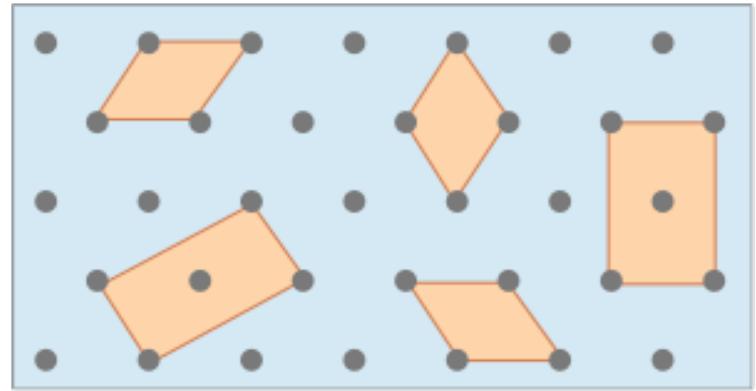
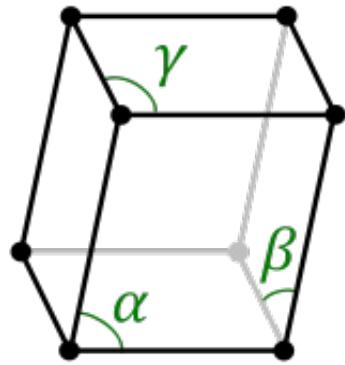


# The Unit Cell

$\alpha, \beta, \gamma \neq 90^\circ$



# The Unit Cell

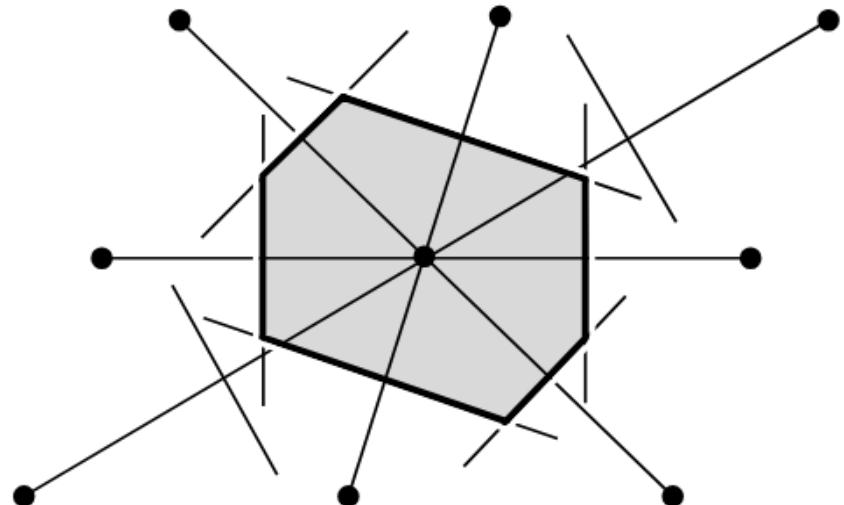


**Primitive Unit Cell**

**Conventional Unit Cell**

# The Unit Cell

**Figure 4** A primitive cell may also be chosen following this procedure: (1) draw lines to connect a given lattice point to all nearby lattice points; (2) at the midpoint and normal to these lines, draw new lines or planes. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All space may be filled by these cells, just as by the cells of Fig. 3.

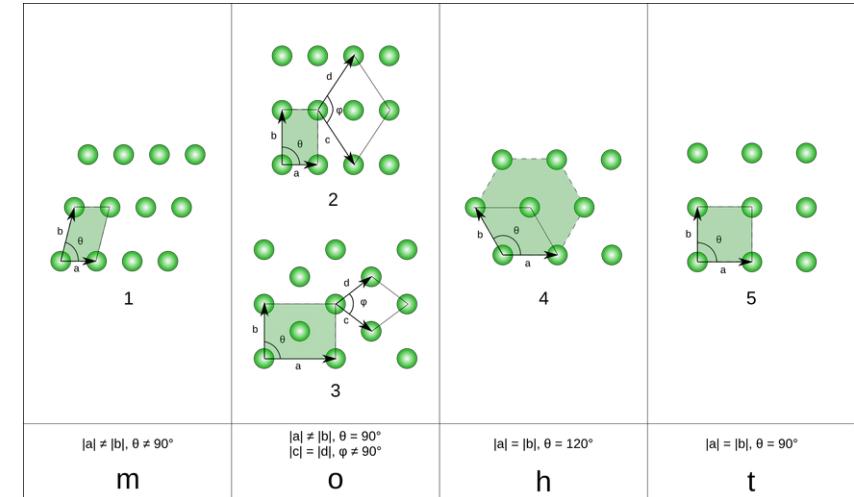


Physics: “Wigner-Seitz cell”

# Bravais Lattice (in 3D)

Bravais lattice cells	Axes and interaxial angles	Examples
Cubic P    Cubic I    Cubic F	Three axes at right angles; all equal: $a = b = c; \alpha = \beta = \gamma = 90^\circ$	Copper (Cu), silver (Ag), sodium chloride (NaCl)
Tetragonal P    Tetragonal I	Three axes at right angles; two equal: $a = b \neq c; \alpha = \beta = \gamma = 90^\circ$	White tin (Sn), rutile ( $\text{TiO}_2$ ), $\beta$ -spodumene ( $\text{LiAlSi}_2\text{O}_6$ )
P    C    I    F Orthorhombic	Three axes at right angles; all unequal: $a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$	Gallium (Ga), perovskite ( $\text{CaTiO}_3$ )
Monoclinic P    Monoclinic C	Three axes, one pair not at right angles, of any lengths: $a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta$	Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )
Triclinic P	Three axes not at right angles, of any lengths: $a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90^\circ$	Potassium chromate ( $\text{K}_2\text{CrO}_7$ )
Trigonal R (rhombohedral)	Rhombohedral: three axes equally inclined, not at right angles; all equal: $a = b = c; \alpha = \beta = \gamma \neq 90^\circ$	Calcite ( $\text{CaCO}_3$ ), arsenic (As), bismuth (Bi)
Trigonal and hexagonal C (or P)	Hexagonal: three equal axes coplanar at $120^\circ$ , fourth axis at right angles to these: $a_1 = a_2 = a_3 \neq c; \alpha = \beta = 90^\circ, \gamma = 120^\circ$	Zinc (Zn), cadmium (Cd), quartz ( $\text{SiO}_2$ ) [P]

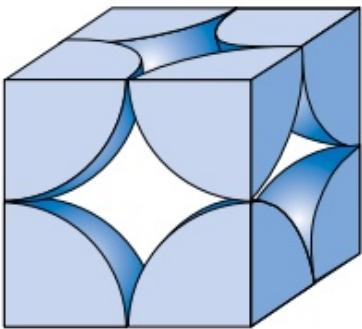
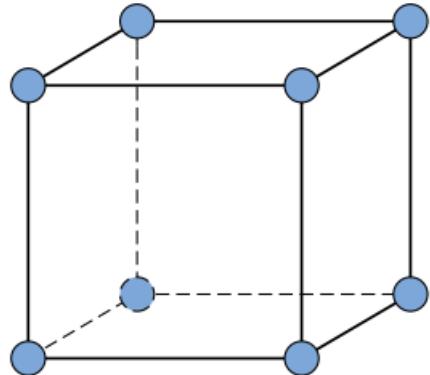
# Bravais Lattice (in 2D)



These assume single-atom basis

# Cubic crystal structures (monoatomic)

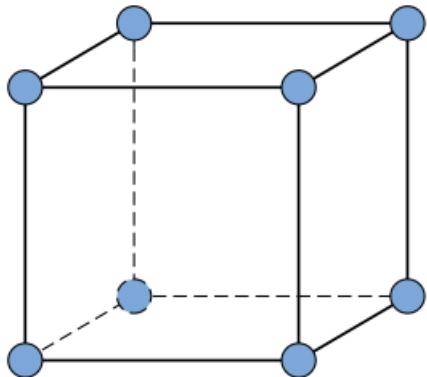
Simple Cubic



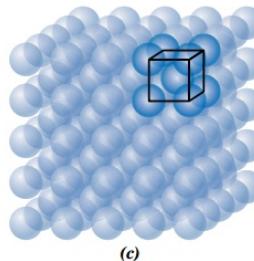
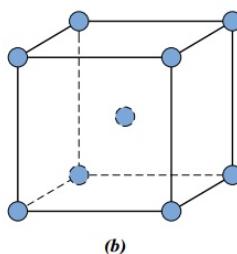
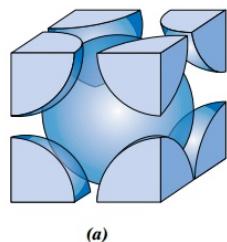
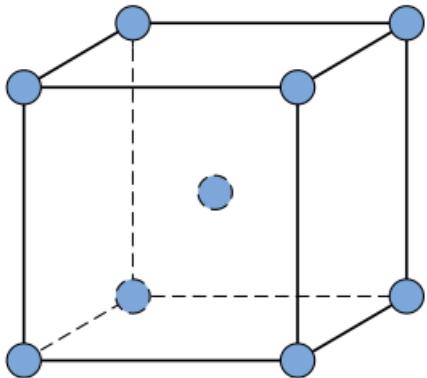
Fractional coordinates

# Cubic crystal structures (monoatomic)

Simple Cubic

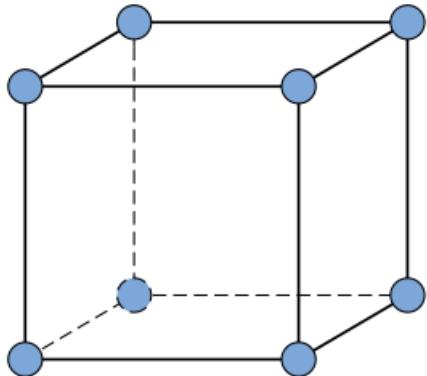


Body-Centered Cubic

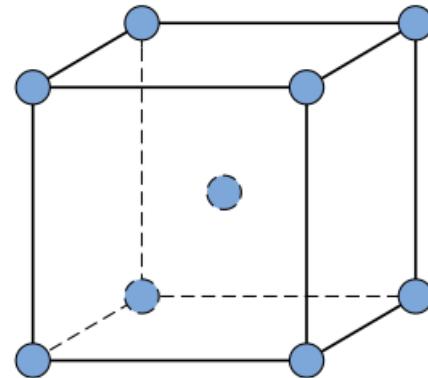


# Cubic crystal structures (monoatomic)

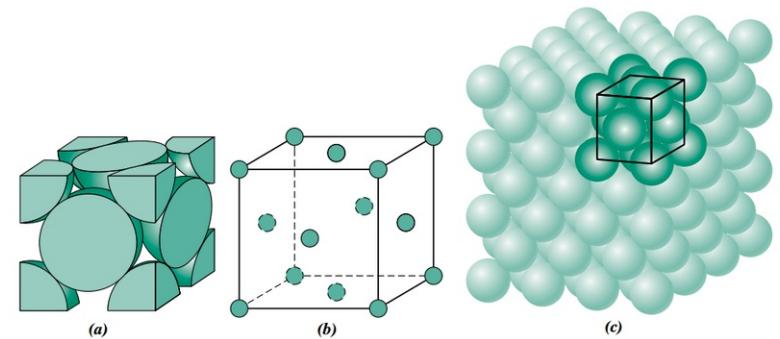
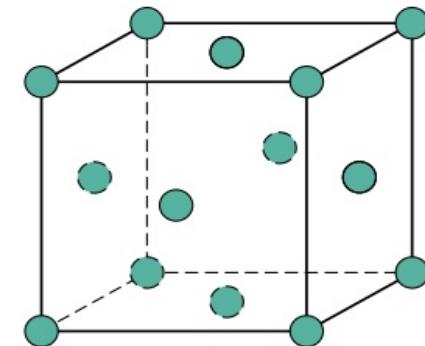
Simple Cubic



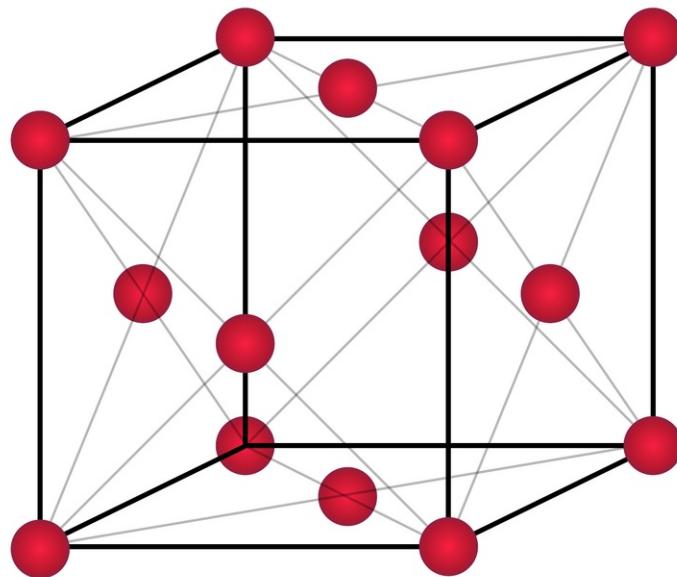
Body-Centered Cubic



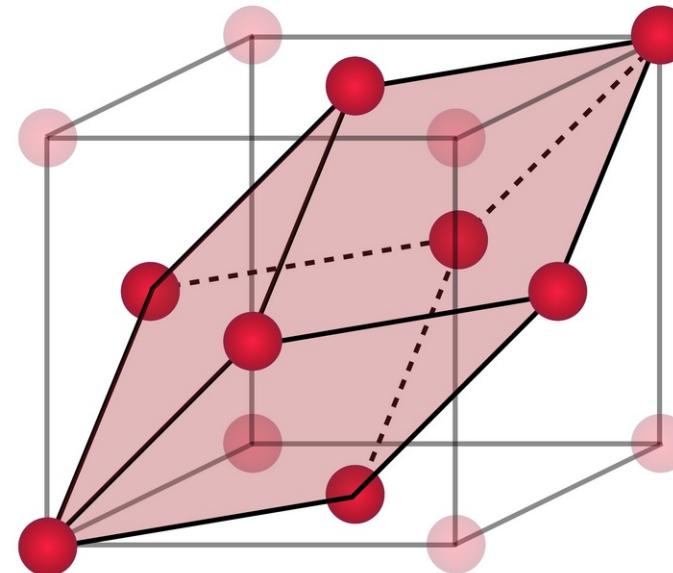
Face-Centered Cubic



# Cubic crystal structures (monoatomic)



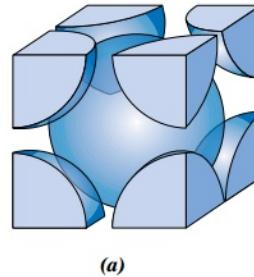
(a) conventional unit cell



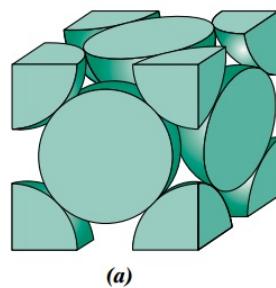
(b) primitive unit cell

# How many (whole) atoms per unit cell?

Body-Centered Cubic

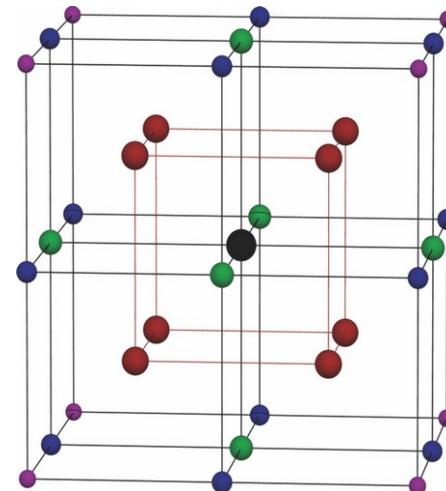


Face-Centered Cubic

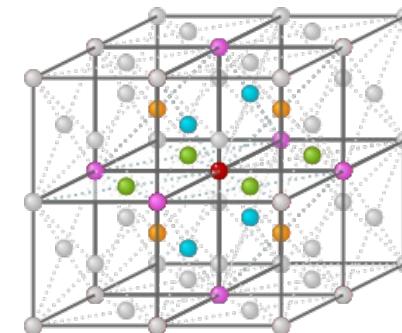


# How many nearest neighbors?

Body-Centered Cubic



Face-Centered Cubic



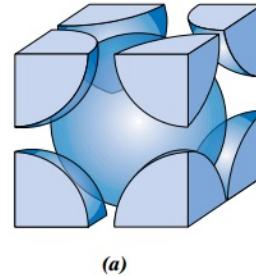
# How many nearest neighbors?

**Table 2 Characteristics of cubic lattices<sup>a</sup>**

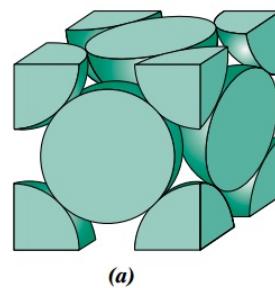
	Simple	Body-centered	Face-centered
Volume, conventional cell	$a^3$	$a^3$	$a^3$
Lattice points per cell	1	2	4
Volume, primitive cell	$a^3$	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	$a$	$3^{1/2} a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	$a$	$a$
Packing fraction <sup>a</sup>	$\frac{1}{6}\pi$ $=0.524$	$\frac{1}{8}\pi\sqrt{3}$ $=0.680$	$\frac{1}{6}\pi\sqrt{2}$ $=0.740$

# Fractional v cartesian coordinates

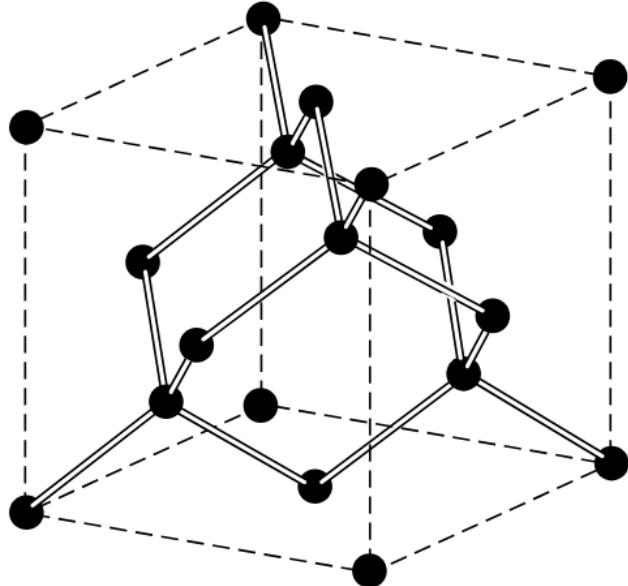
Body-Centered Cubic



Face-Centered Cubic

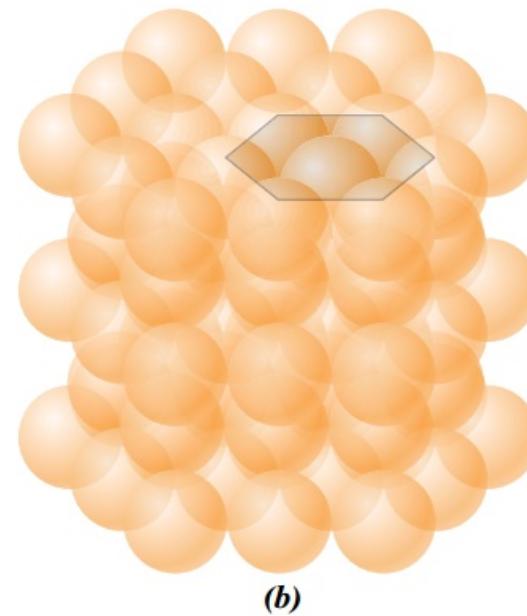
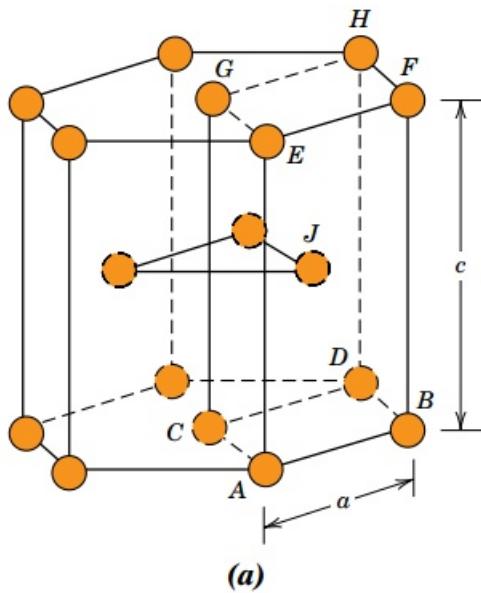


# What are the fractional coordinates of the basis set atoms of diamond?

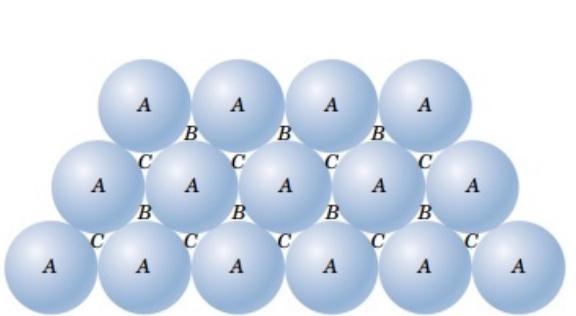


**Figure 23** Crystal structure of diamond, showing the tetrahedral bond arrangement.

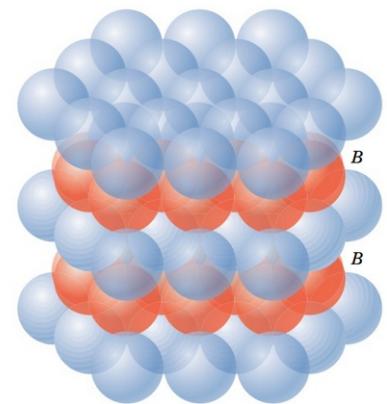
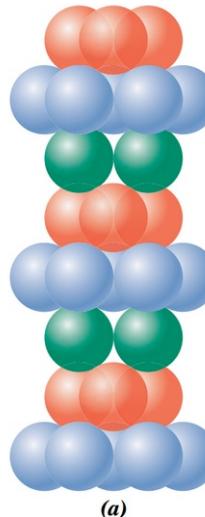
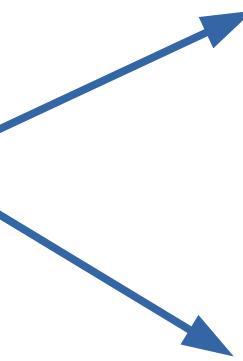
# Hexagonal closed-packed (HCP)



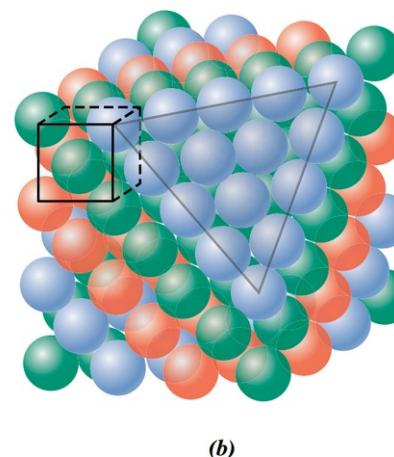
# Relation between HCP & FCC



3D animation #1  
3D animation #2

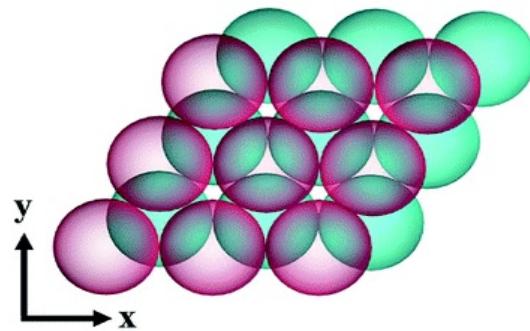


B  
A  
C  
B  
A  
C  
B  
A

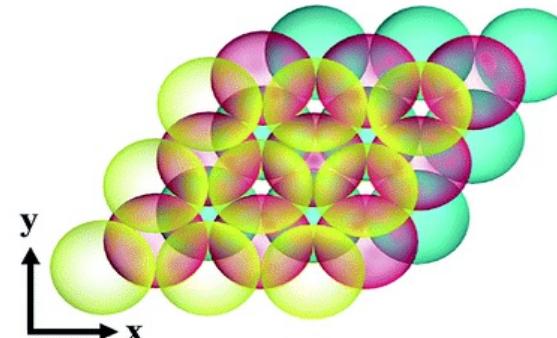


# Relation between HCP & FCC

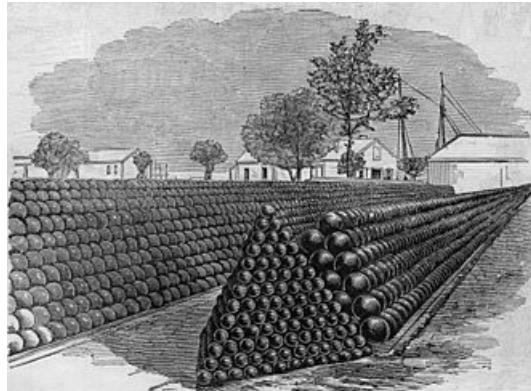
HCP



FCC



N.A. Mahynski et al. Soft Matter, 2015, 11, 280-289 10.1039/C4SM02191F



The Cannonball problem

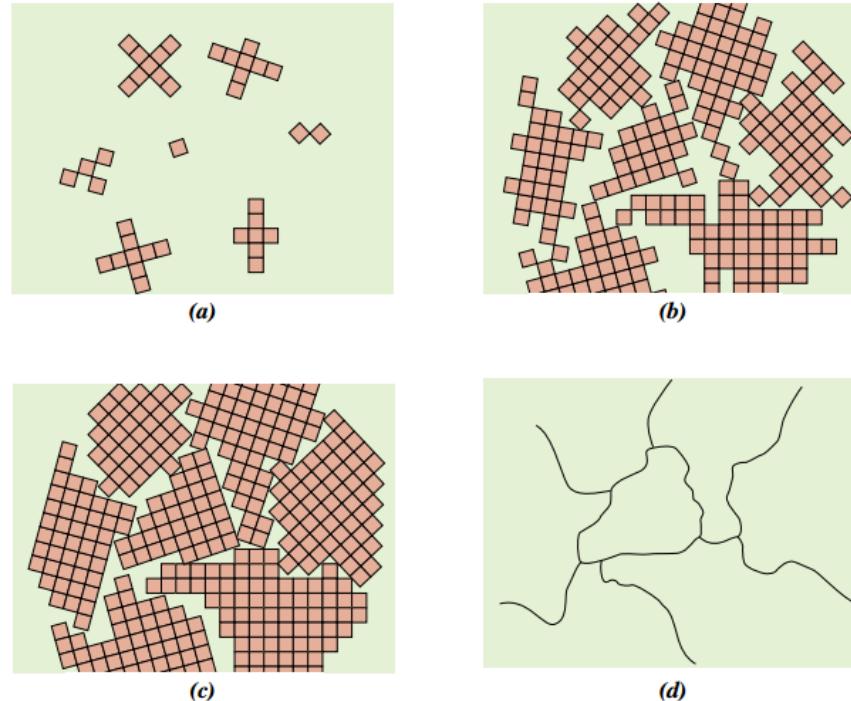
Youtube video: Hard sphere packing problem



Front HCP, Rear FCC  
(Image from Yvette Cendes, CC0)

# Non-crystalline systems

## Polycrystalline materials

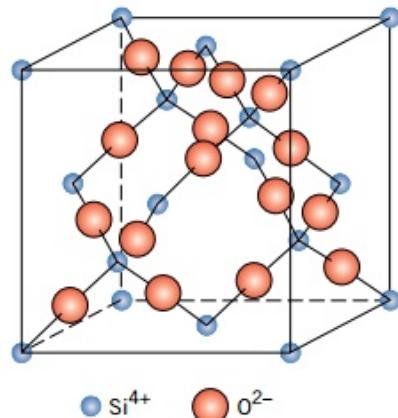


**Figure 3.20** Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (a) Small crystallite nuclei. (b) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (c) Upon completion of solidification, grains having irregular shapes have formed. (d) The grain structure as it would appear under the microscope; dark lines are the grain boundaries.

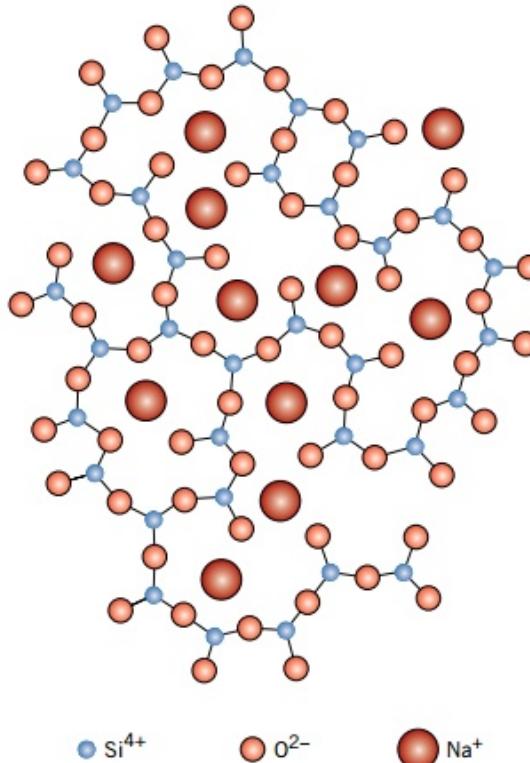
(Adapted from W. Rosenhain, *An Introduction to the Study of Physical Metallurgy*, 2nd edition, Constable & Company Ltd., London, 1915.)

# Non-crystalline systems

## Amorphous materials



**Figure 12.10** The arrangement of silicon and oxygen atoms in a unit cell of cristobalite, a polymorph of SiO<sub>2</sub>.



**Figure 12.11** Schematic representation of ion positions in a sodium-silicate glass.

# A side note on Reciprocal Space:

The electron density is a periodic function of the lattice

$$n(\bar{r} + \bar{T}) = n(\bar{r})$$

"  
 $\bar{R}$

$$\text{1D: } n(x) = n_0 + \sum_{p>0} \left[ c_p \cos\left(\frac{2\pi}{a} px\right) + s_p \sin\left(\frac{2\pi}{a} px\right) \right], \quad p \in \mathbb{Z}^+$$

$$= \sum_p n_p \exp\left(i \frac{2\pi}{a} px\right)$$

a+ib

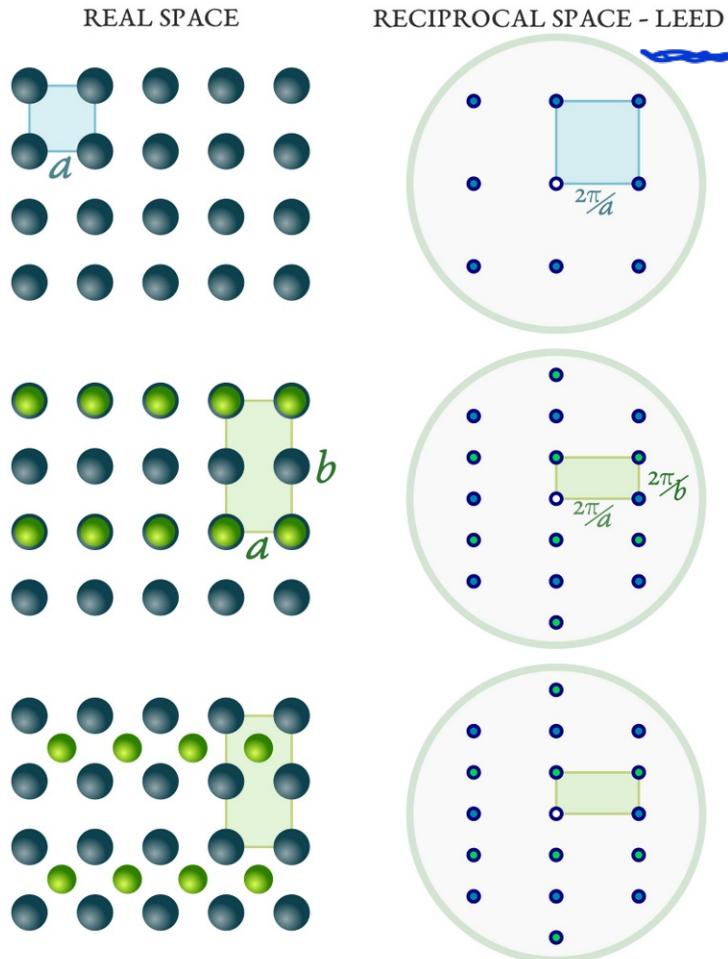
$$n_p = n_{-p}^*$$

$$n_p \rightarrow a+ib$$

$$n_p^* \rightarrow a-ib$$

$$\text{3D: } n(\bar{r}) = \sum g_i \exp(-i \bar{G}_i \cdot \bar{r})$$

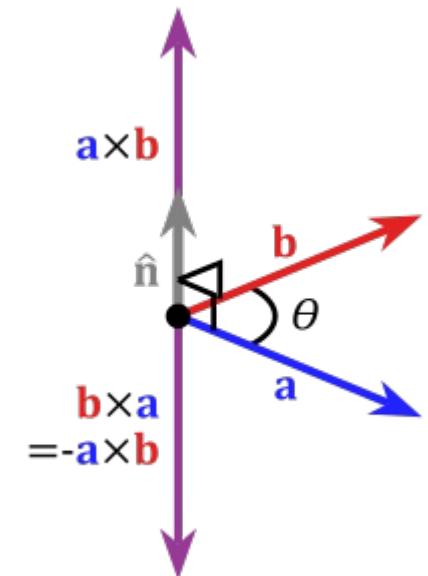
# A side note on Reciprocal Space:



$$\mathbf{b}_1 = \frac{2\pi}{V} \mathbf{a}_2 \times \mathbf{a}_3$$

$$\mathbf{b}_2 = \frac{2\pi}{V} \mathbf{a}_3 \times \mathbf{a}_1$$

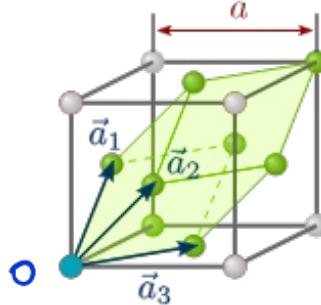
$$\mathbf{b}_3 = \frac{2\pi}{V} \mathbf{a}_1 \times \mathbf{a}_2$$



$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$$

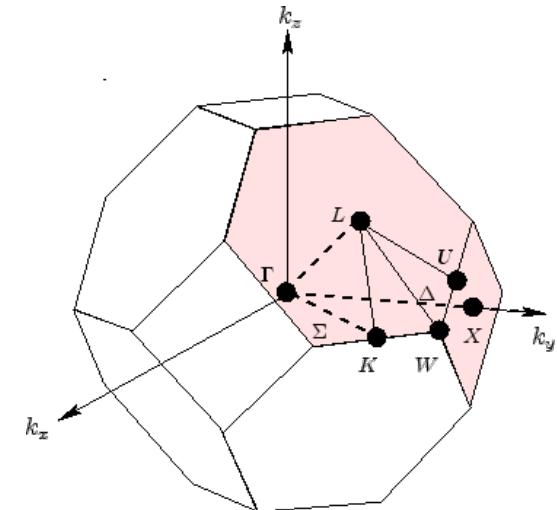
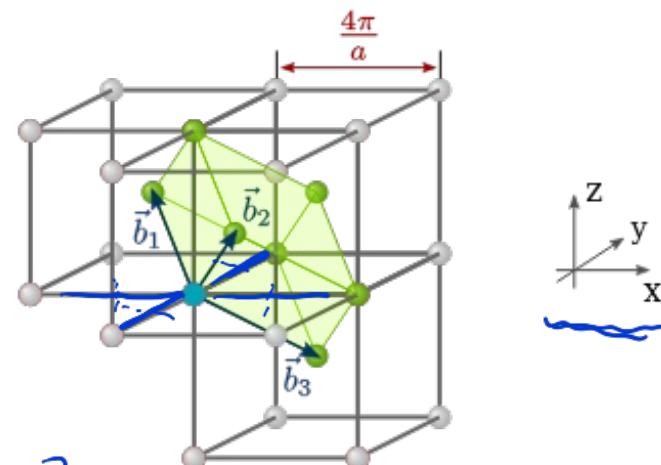
# A side note on Reciprocal Space:

**direct lattice:**  
fcc with edge length  $a$



$$\vec{a}_1 = \frac{1}{2} [0 \ 1 \ 1]$$

**reciprocal lattice:**  
bcc with edge length  $4\pi/a$



Reciprocal cell of FCC lattice,  
aka first Brillouin Zone

$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$$

# A side note on Reciprocal Space:

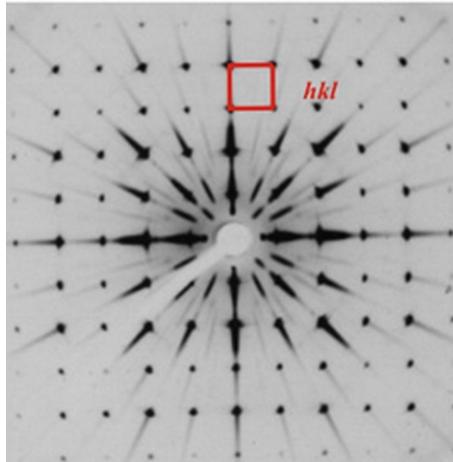
Why bother with reciprocal space?

Falls out naturally in the math (complex exponentials)

Corresponds to experimental measurements  
(where you probe the sample with light or beam source)

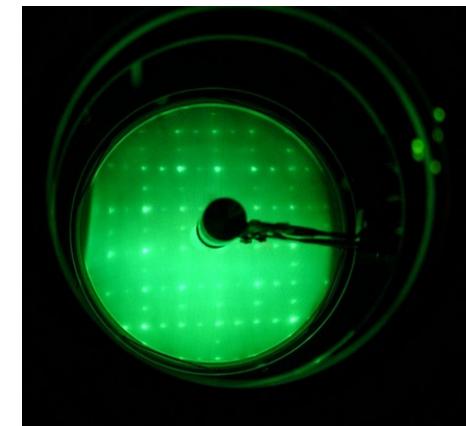
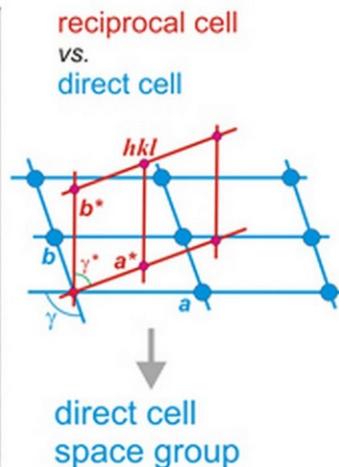
X-ray diffraction → Bulk crystal structure

Reciprocal space



Low-energy electron diffraction (LEED)

→ Surface crystal structure



# Discovery of the X-ray



Wilhelm Conrad Röntgen

Awarded the inaugural Nobel Prize  
"in recognition of the extraordinary  
services he has rendered by the  
discovery of the remarkable rays  
subsequently named after him"

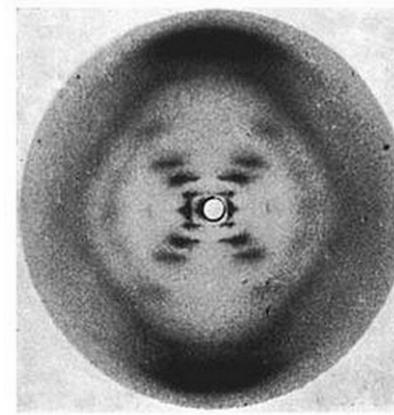


Image from K. Kelly, American Comes Alive!

# XRD in the history of science

Table 1. Nonexhaustive List of the Nobel Prizes Involving X-ray Crystallography

Discipline, Year of Prize	Winners	Motivation Cited by the Nobel Prize Committee
Physics, 1901	W.C. Röntgen	Discovery of X-rays
Physics, 1914	M. von Laue	Discovery of X-ray diffraction by crystals
Physics, 1915	W.H. and W.L. Bragg	Use of X-rays to determine crystal structures
Chemistry, 1962	J.C. Kendrew, M. Perutz	Studies of the structures of globular proteins
Medicine or Physiology, 1962	F. Crick, J. Watson, M. Wilkins	Helical structure of DNA
Chemistry, 1964	D. Crowfoot Hodgkin	Structure of many biochemical substances, including vitamin B <sub>12</sub>
Chemistry, 1976	W.N. Lipscomb	Structure of boranes
Chemistry, 1985	H. Hauptman, J. Karle	Development of direct methods for solving crystal structures
Chemistry, 1988	J. Deisenhofer, R. Huber, H. Michel	Determination of the 3D structure of a photosynthetic reaction center
Physics, 1992	G. Charpak	Discovery of the multiwire proportional chamber
Chemistry, 1996	R. Curl, H. Kroto, and R. Smalley	Discovery of the fullerene form of carbon
Chemistry, 2009	V. Ramakrishnan, T.A. Steitz, A.E. Yonath	Studies of the structure and function of the ribosome
Physics, 2010	A. Geim, K. Novoselov	Experiments regarding the 2D material graphene
Chemistry, 2011	D. Shechtman	Discovery of quasicrystals
Chemistry, 2012	R.J. Lefkowitz, B.K. Kobilka	Studies of G-protein-coupled receptors



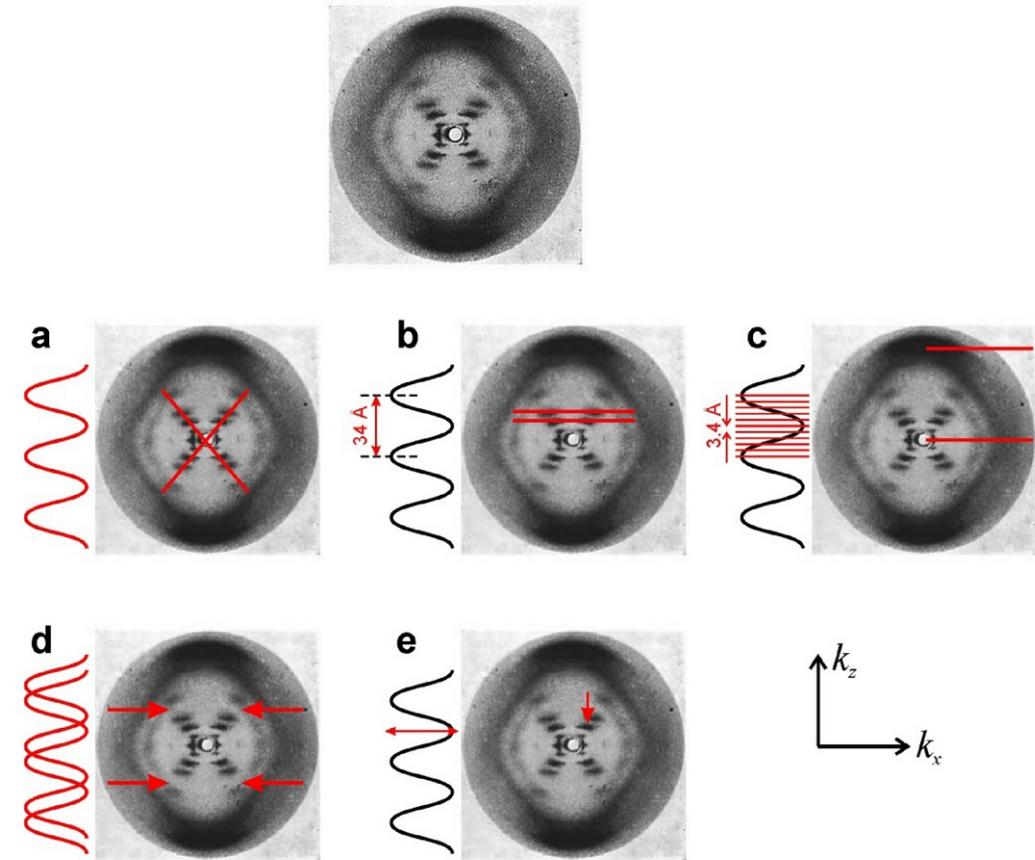
Rosalind Franklin   Francis Crick   James Watson   Maurice Wilkins

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10.1021/ed500343x

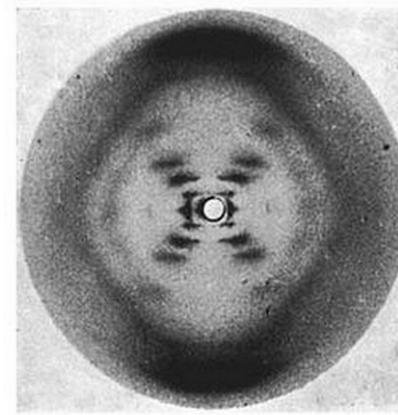


Evidence of (a) helical structure, (b) period of helical turns, (c) small periodic features (base pairs), (d) double helix from missing diffraction spots, (e) radius of helix  
T. Latychevskaia and H-W Fink, Opt. Express 26, 30991-31017 (2018)

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Medicine or Physiology, 1962	F. Crick, J. Watson, M. Wilkins	Helical structure of DNA
Chemistry, 1964	D. Crowfoot Hodgkin	Structure of many biochemical substances, including vitamin B <sub>12</sub>
Chemistry, 1976	W.N. Lipscomb	Structure of boranes
Chemistry, 1985	H. Hauptman, J. Karle	Development of direct methods for solving crystal structures
Chemistry, 1988	J. Deisenhofer, R. Huber, H. Michel	Determination of the 3D structure of a photosynthetic reaction center
Physics, 1992	G. Charpak	Discovery of the multiwire proportional chamber
Chemistry, 1996	R. Curl, H. Kroto, and R. Smalley	Discovery of the fullerene form of carbon
Chemistry, 2009	V. Ramakrishnan, T.A. Steitz, A.E. Yonath	Studies of the structure and function of the ribosome
Physics, 2010	A. Geim, K. Novoselov	Experiments regarding the 2D material graphene
Chemistry, 2011	D. Shechtman	Discovery of quasicrystals
Chemistry, 2012	R.J. Lefkowitz, B.K. Kobilka	Studies of G-protein-coupled receptors



**Crick, Watson, and Wilkins were awarded the Nobel Prize for Franklin's work.**



"As Watson was to write candidly, 'Rosy, of course, did not directly give us her data. For that matter, no one at King's realized they were in our hands.' When this admission appeared in Watson's best-selling, much-acclaimed book of the discovery, *The Double Helix*, published in 1968 (ref. 1), he was a Harvard professor and Nobel laureate (he had shared the prize for medicine and physiology in 1962, with Crick and Maurice Wilkins of King's College.) By then Franklin had died — in 1958, at the age of 37, from ovarian cancer."

— Maddox, B. *Nature* 421, 407–408 (2003).

# XRD in the history of science

Table 1. Nonexhaustive List of the Nobel Prizes Involving X-ray Crystallography

Discipline, Year of Prize	Winners	Motivation Cited by the Nobel Prize Committee
Physics, 1901	W.C. Röntgen	Discovery of X-rays
Physics, 1914	M. von Laue	Discovery of X-ray diffraction by crystals
Physics, 1915	W.H. and W.L. Bragg	Use of X-rays to determine crystal structures
Chemistry, 1962	J.C. Kendrew, M. Perutz	Studies of the structures of globular proteins
Medicine or Physiology, 1962	F. Crick, J. Watson, M. Wilkins	Helical structure of DNA
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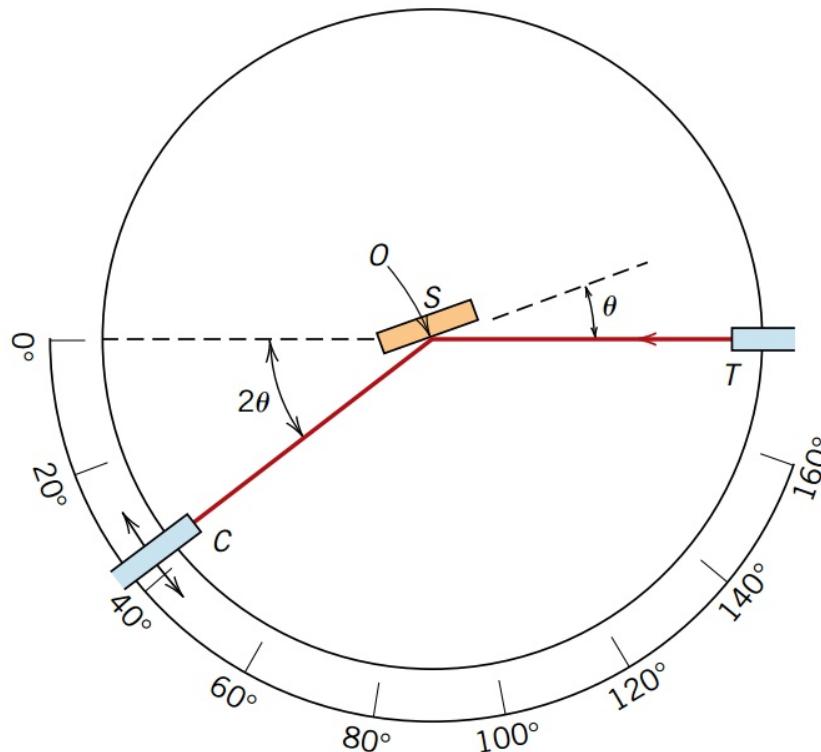
Exfoliation of graphene



Andre Geim and Konstantin Novoselov

# How XRD works

**Figure 3.23** Schematic diagram of an x-ray diffractometer;  $T$  = x-ray source,  $S$  = specimen,  $C$  = detector, and  $O$  = the axis around which the specimen and detector rotate.



# How XRD works

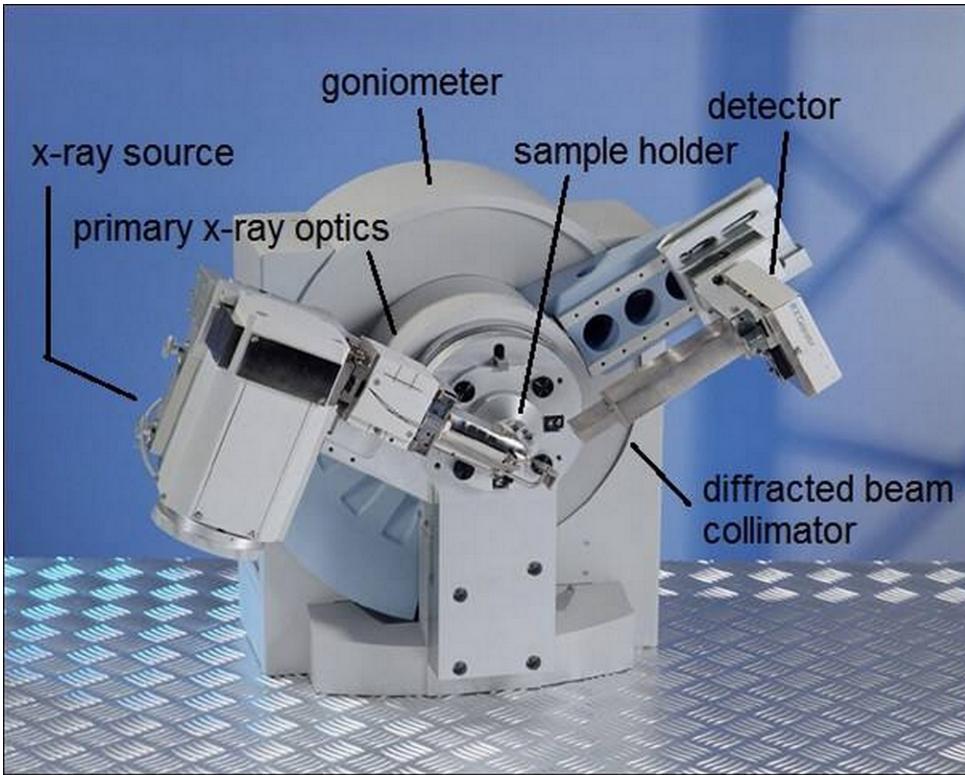


Image from [link](#)

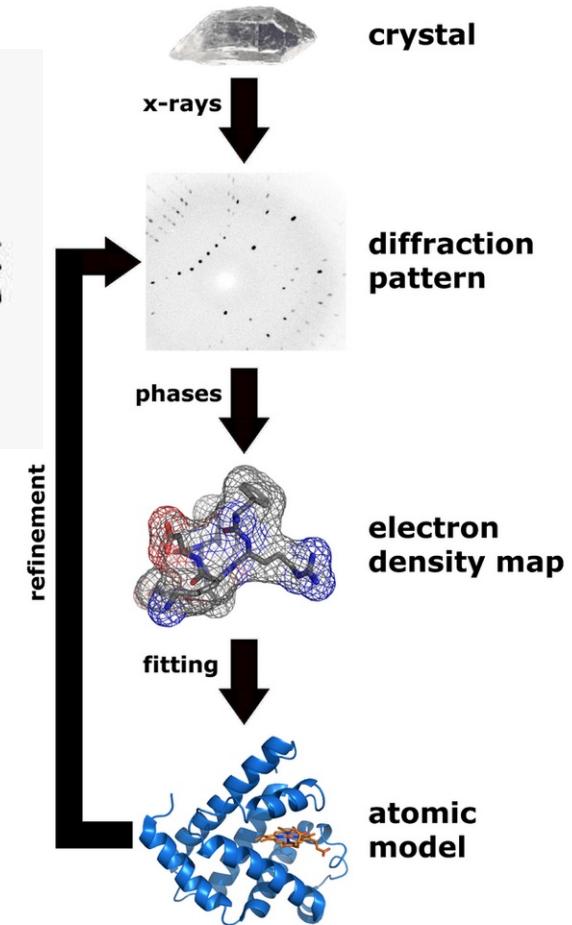
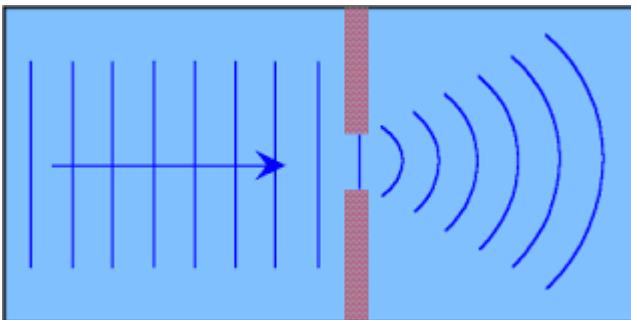
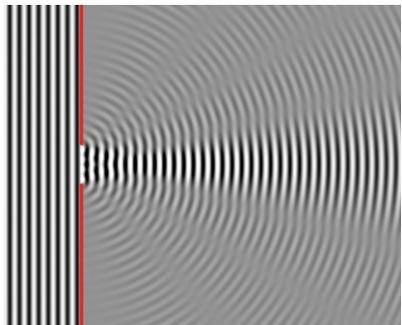
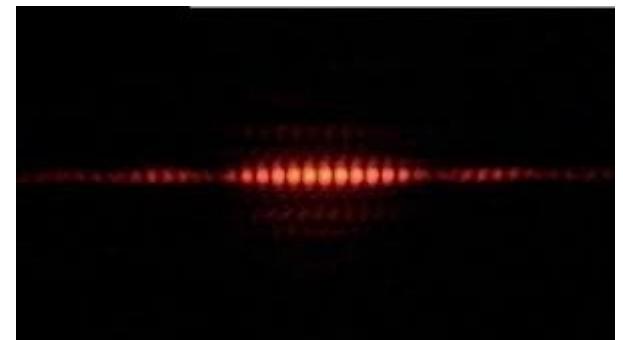
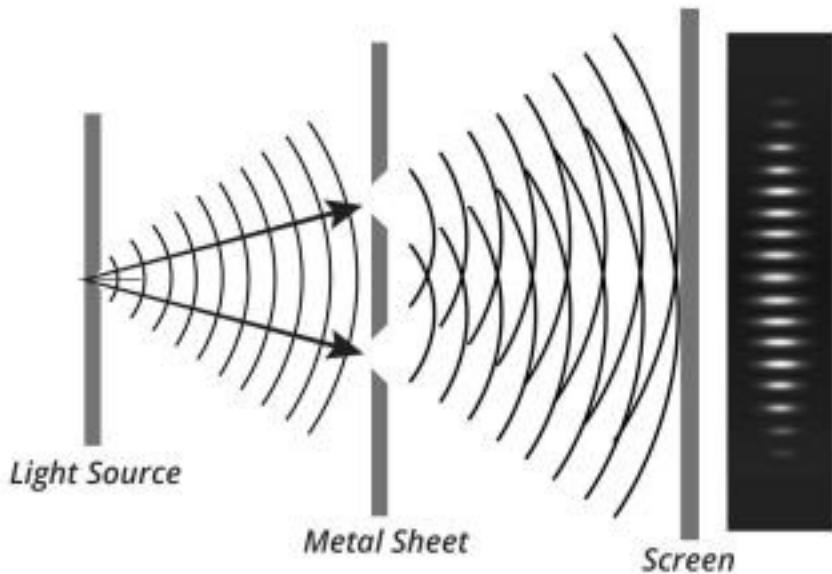


Image from [Bio Libretext, CC BY-NC-SA 3.0](#)

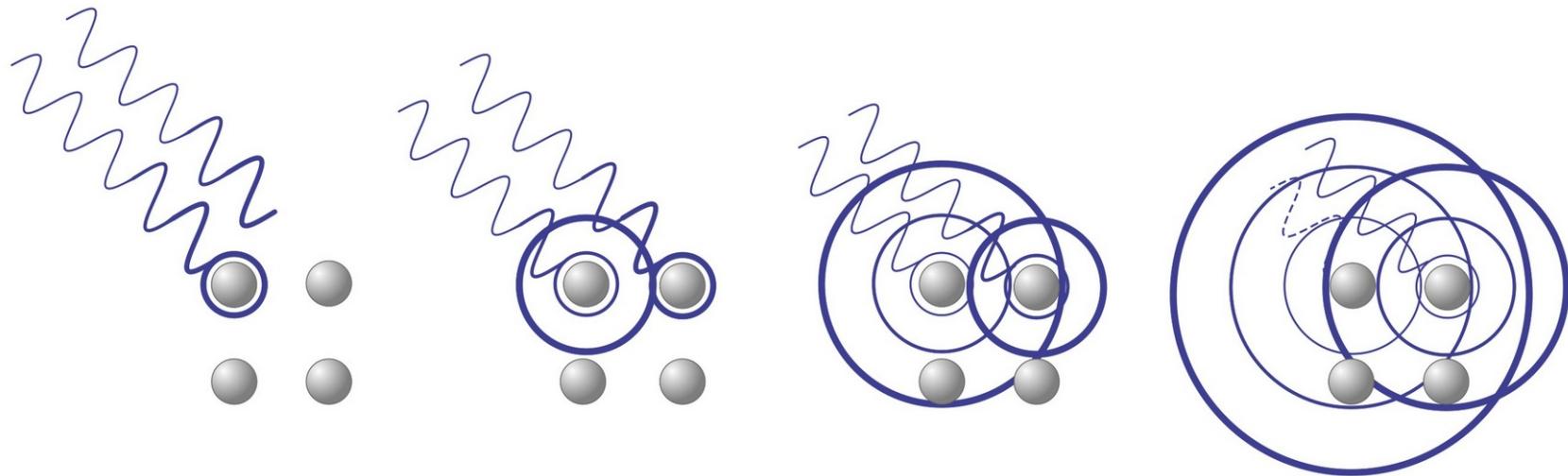
# Light-Matter Interactions: Diffraction



# Light-Matter Interactions: Diffraction



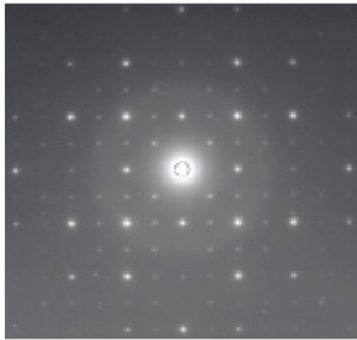
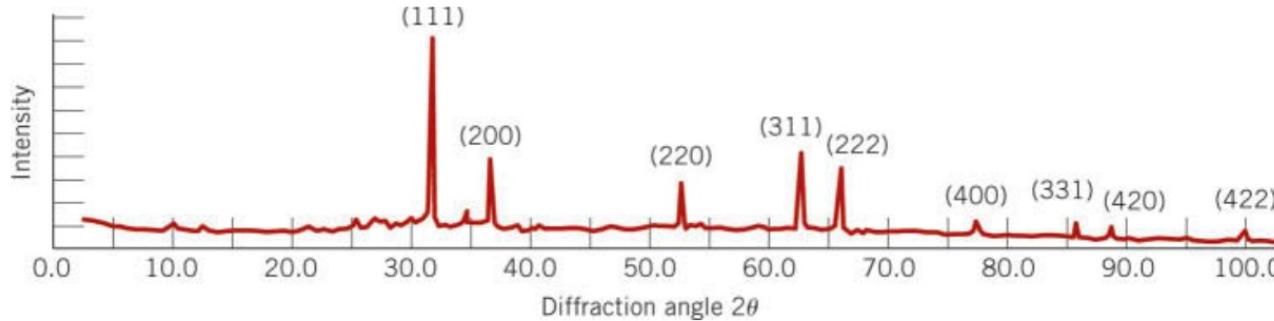
# Diffraction by a grating of atoms



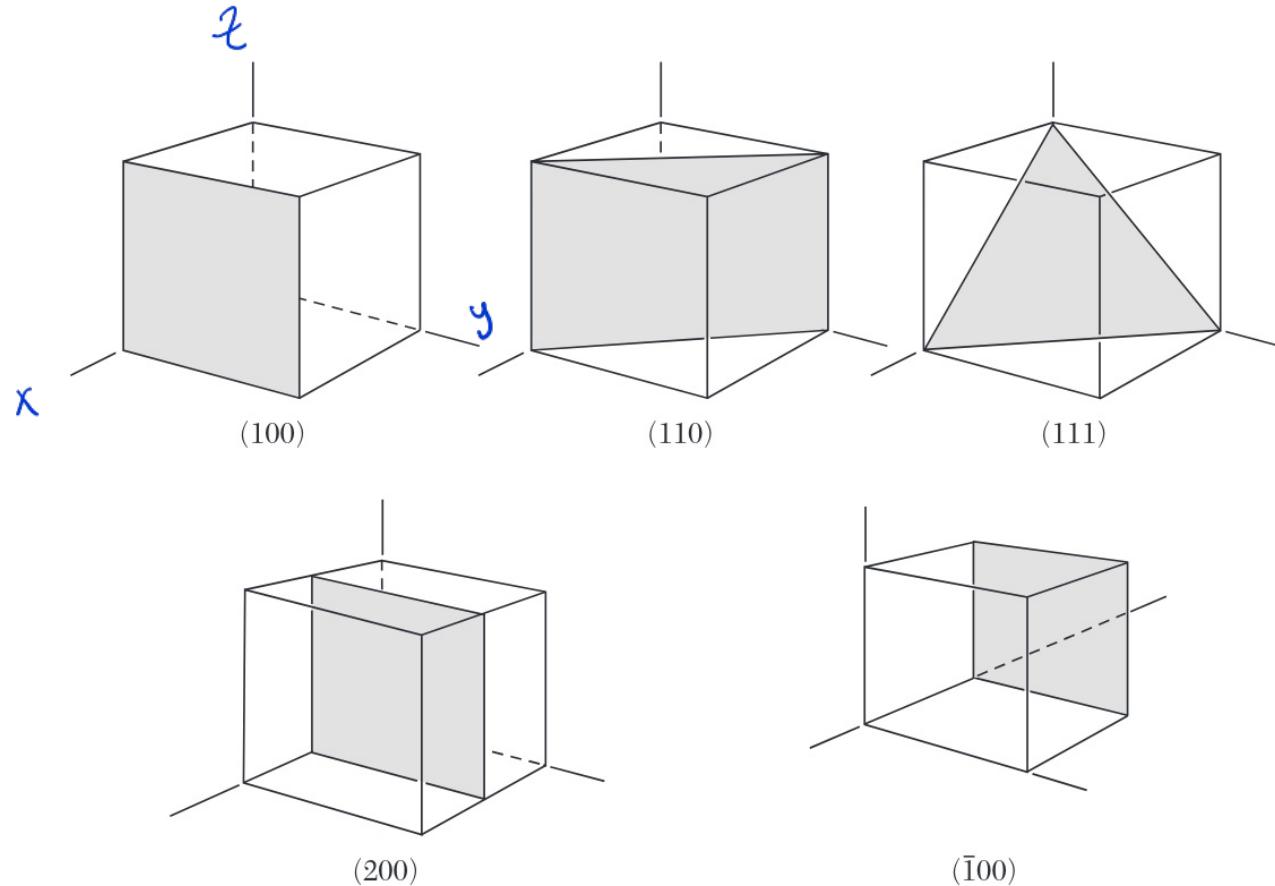
# Examples XRD data

**Figure 3.24**

Diffraction pattern  
for powdered lead.  
(Courtesy of Wesley  
L. Holman.)



**Figure 2** An X-ray  
diffraction pattern from  
the single crystal of  
sodium chloride.



**Figure 14** Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (001).

# How many nearest neighbors?

**Table 2 Characteristics of cubic lattices<sup>a</sup>**

	Simple	Body-centered	Face-centered
Volume, conventional cell	$a^3$	$a^3$	$a^3$
Lattice points per cell	1	2	4
Volume, primitive cell	$a^3$	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	$a$	$3^{1/2} a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	$a$	$a$
Packing fraction <sup>a</sup>	$\frac{1}{6}\pi$ $=0.524$	$\frac{1}{8}\pi\sqrt{3}$ $=0.680$	$\frac{1}{6}\pi\sqrt{2}$ $=0.740$

# A side note on space groups

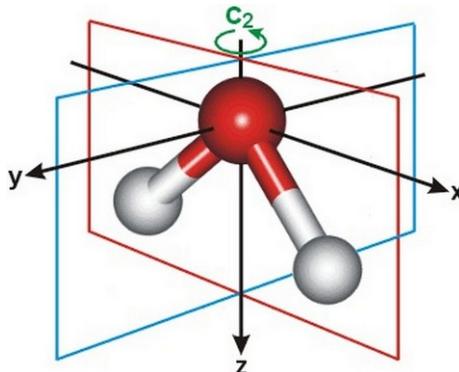
## Neumann's principle:

'the symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal'.

## Space group:

combination of crystallographic point groups + Bravais lattice  
(230 combinations in 3D, if count chiral structures distinct)

Example: crystallographic point group of water molecule



Common notation: Hermann-Mauguin or Schoeflies used

Looking up info on space space groups  
e.g., <http://img.chem.ucl.ac.uk/sgp/medium/sgp.htm>

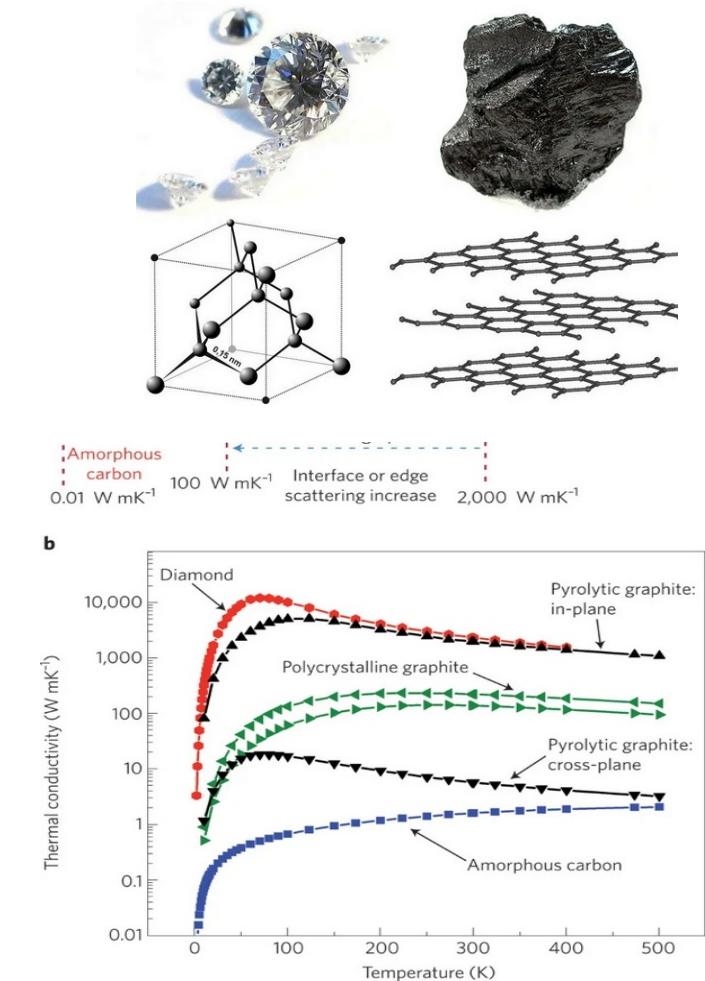
# Why is understanding crystallography important?

## Material anisotropy- material properties have directionality

**Table 3.4**  
**Modulus of Elasticity  
Values for Several  
Metals at Various  
Crystallographic  
Orientations**

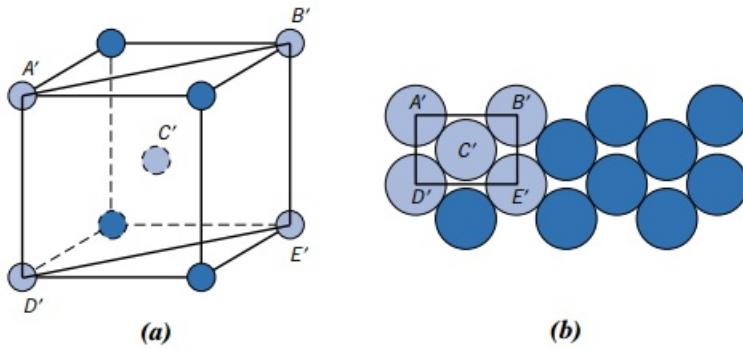
Metal	Modulus of Elasticity (GPa)		
	[100]	[110]	[111]
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

**Source:** R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition.  
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# Crystallographic planes and surface facets

(110) plane for BCC



(110) plane for FCC

