Solid State Physics (I)

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Yia-Chung CHANG
and
Chao-Cheng KAUN
(in the order of lectures)

Textbooks

- Main text: *Fundamentals of Solid State Physics* by J. Richard Christman (John Wiley & Sons, NY, 1988).

- Main reference: *Introduction to Solid State Physics 8th ed.* by Charles Kittel (Wiley, NY, 2004)

Grading

- Presence: 10%
- Homework: 30%
- Three exams: 20% each
  - The range of the three exams will not overlap

Part 1 (Lectures by K.K.Liang)

- Introduction
- Crystal lattices
- Crystal structures and reciprocal lattices
- X ray diffraction
- Crystal binding
- Elastic properties

Solid State Physics

- Understanding the **properties** of solid materials in terms of their constituent particles: **electrons** and **nuclei**
- Developing tailored-made materials and devices for particular applications

Solid State Theory

- Atoms   molecules   solids
  - Maxwell's equation for EM fields
  - Schrödinger equation for particles
- Schrödinger equation $\Rightarrow$ particle wavefunctions (eigenvector) + other dynamical quantities (such as energy, the eigenvalue) $\Rightarrow$ various material properties
- External forces (perturbations) may be added into the SE to study the responses

Solid State Theory Takes Care of:

- The structure of solids
  - Atomic equilibrium positions $\Rightarrow$ fixed structure of a solid
  - Distinction from liquids and gases
  - Classes of solids:
    - Crystalline
    - Amorphous
    - Polycrystalline
  - High symmetry makes crystals simpler to handle theoretically, as the SE need be solved only for points **within a single pattern** rather than throughout the crystal.

Solid State Theory Takes Care of:

- Electrons
  - The electrons are usually separated into core electrons and outer electrons
  - Outer electrons contribute the most to material properties:
    - Produce forces of attractions that hold atoms of the solid together
    - In conjunction with ion cores, they produce restoring forces that are responsible for the vibratory motion of the atoms
  - Core electrons are responsible for short-range forces of repulsion between atoms and so prevent the collapse of solids.
  - Transition elements with *d* and *f* subshells partially filled have to be considered on a case-by-case basis.

Solid State Theory Takes Care of:

- Atomic vibrations
  - Collective oscillations $\Rightarrow$ normal modes
  - Fixed allowed frequencies, determined by the equilibrium structure and strength of interactions between atoms (thus differ from solid to solid)
  - Quantized normal mode energies $\Rightarrow$ phonons
  - Number of phonons does not conserve
- Defects — anomalies in the atomic structure
  - Any deviations from regularity in pattern of atomic positions, or impurity, in a crystal
  - Impurity in amorphous materials
  - Defects influence nearly all properties of materials

Properties of Solids

- Mechanical
  - Mass density
  - Cohesive energy
  - Elastic properties (bulk modulus)
- Thermal
  - Heat capacity (C_v, C_p)
  - Thermal conductivity
  - Contributions from phonons and electrons
- Electrical
  - (electrical) conductivity
  - Dielectric constant

Properties of Solids

- Magnetic
  - Magnetic susceptibility (para, dia, ferro)
- Optical
  - Reflectance
 - Index of refraction
  - absorption

Solid State Experiments

- Scattering
  - X ray
  - Electrons
  - Neutrons
- Hall effect
- Optical
  - Absorption
  - Reflection
- Magnetic resonance
- De Haas – van Alphen effect

Crystal Lattice

- Idealized description of the geometry of crystals
- Mathematical techniques for precise definition of the meaning of crystalline periodicity
- The description and use of crystalline symmetry
- Notation for specifying directions and planes in crystals

Crystalline Periodicity

- In a crystalline material, the equilibrium positions of all the atoms form crystal

- Crystal = lattice + basis

- Lattice = 3D periodic array of points, unbounded in all directions
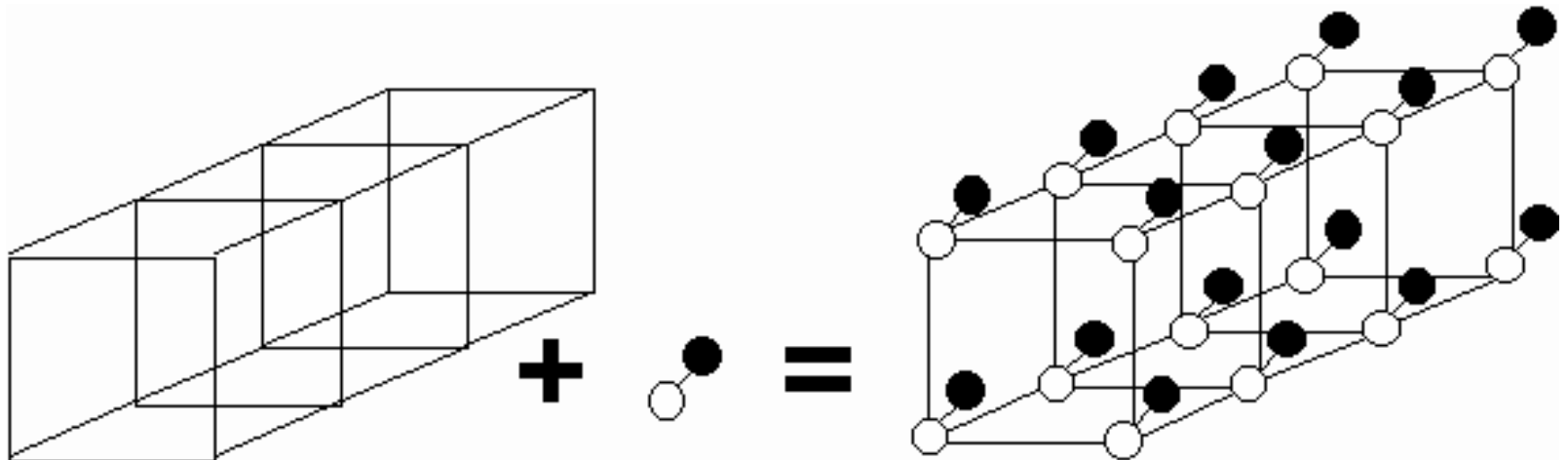
Bravais Lattice

- Definition 1: Periodic structure form by infinite number of points in the space. The distribution of other points in space, observed from any of the points, is exactly the same.

- Definition 2: In a 3-D lattice, the position vector of one of the points can be written as the linear combination of three fundamental vectors with integral coefficients.

Lattice and Fundamental Vectors

- The fundamental vectors are chosen non-uniquely to describe the lattice
- The fundamental vectors form the *unit cell* (*)
- If both the volume of the unit cell and the basis are chosen to be the smallest, they are *primitive*
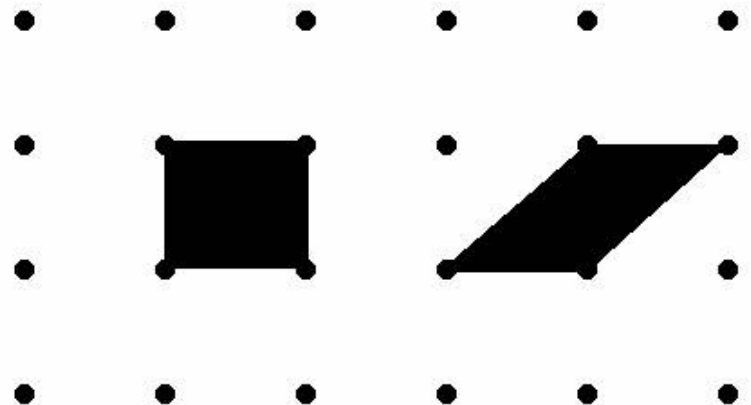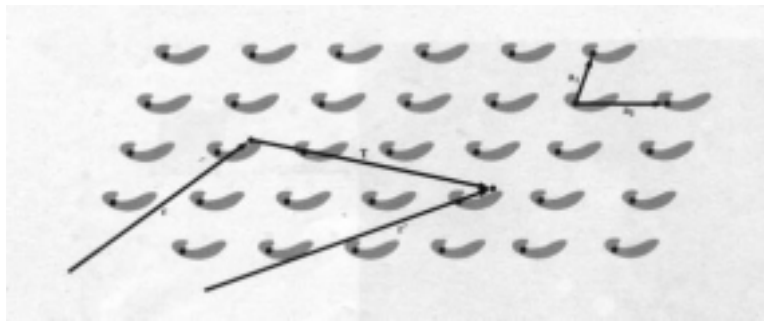
Unit Cells

- Unit cell: A volume which, through translation by all of the lattice vectors, can fill the space without overlapping between the replica.

- Primitive unit cell: unit cell with the smallest volume

- Unit cell can form from fundamental vectors, but it can also be constructed by other methods (*e. g.* Wigner-Seitz primitive cell).

- As long as the fundamental vectors are fixed, all the unit cells have the same volume (why?)

Crystal Symmetry Operations

- Symmetry operations: Operations under which there is no change in the spatial distances and angles, and there is no distortion, compression or extension, and yet after application of the operation, there is still a lattice point where there were a lattice point and there is not a lattice point where there were no lattice point.
  - Translation
  - Rotation
  - Reflection
  - Inversion

Crystal Symmetry

- Any symmetry operation of a Bravais lattice = a translation + point group operators

- A collection of these operations forms a symmetry group of the Bravais lattice.

Frequently used symmetry op notations (Schönflies notations)

- E : Identity
- i : Inversion
- C_n : n-fold axis (rotation over 2π / n)
- σ (σ_h and σ_v): reflection (horizontal or vertical w.r.t. C_n axis)
- D_n, D_{nh}, D_{nd} : $C_n \times C_2'$, $C_{nh} \times C_2'$, $S_n \times C_2'$ (C_2' axis is perpendicular to the C_n axis)
- $S_n = \sigma_h C_n$

Rotation axes

$C_2(2)$

Inversion through a center

$i(\bar{1})$

$C_3(3)$

Rotatory inversion axes

$i(\bar{1})$ = inversion
$\sigma(\bar{2})$ = mirror plane
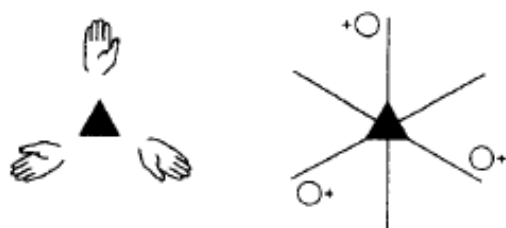
$C_4(4)$ $C_6(6)$
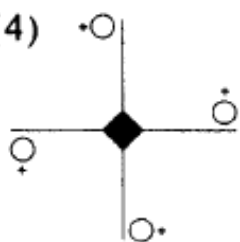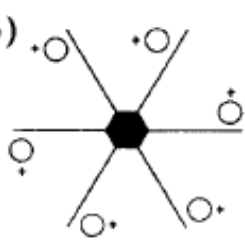
$S_4{}^3(\bar{4})$

Mirror plane

$\sigma(m)$

Looking
parallel   perpendicular
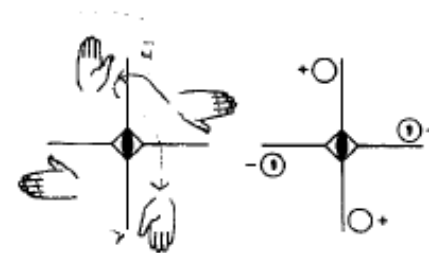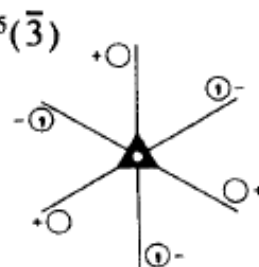
$S_6{}^5(\bar{3})$ $S_3{}^5(\bar{6})$
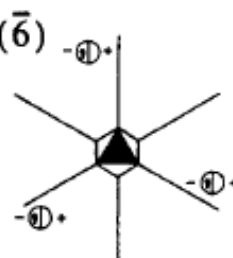
Classification of the Crystal Systems
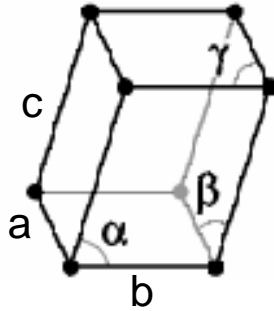
- Point group (only rotation or reflection) $\Rightarrow$ 7 crystal systems
  - Cubic (a = b = c, $\alpha = \beta = \gamma = 90°$)
  - Tetragonal (a = b $\neq$ c, $\alpha = \beta = \gamma = 90°$)
  - Orthorhombic (a $\neq$ b $\neq$ c, $\alpha = \beta = \gamma = 90°$)
  - Monoclinic (a $\neq$ b $\neq$ c, $\alpha = \beta = 90° \neq \gamma$)
  - Triclinic (a $\neq$ b $\neq$ c, $\alpha \neq \beta \neq \gamma = 90°$)
  - Trigonal (a = b = c, $\alpha = \beta = \gamma < 120° \neq 90°$)
  - Hexagonal (a = b $\neq$ c, $\alpha = \beta = 90°$, $\gamma = 120°$)

Bravais Lattices

- Space group (point group + translation)
  - Considering the addition of lattice points by certain centering conditions
  - Check if it is still a lattice
  - Check if it is a new lattice

- 14 Bravais lattices:
  - P (primitive) (6) : 7 lattice systems, but primitive trigonal = primitive hexagonal
  - I (3) : Body-centered, cubic, tetragonal, orthorhombic
  - F (2) : Face-centered, cubic, orthorhombic
  - A, B, or C (2) : One-side-centered, monoclinic-B, orthorhombic-C
  - R (1) : Special-centering, trigonal-R

Alternative grouping

- Cubic (3) : simple cubic, body-centered cubic, face-centered cubic
- Tetragonal (2) : simple, body-centered
- Orthorhombic (4) : simple, base-centered, face-centered, body-centered
- Monoclinic (2) : simple, base-centered
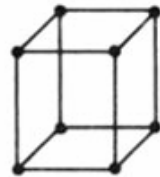- One for triclinic, trigonal and hexagonal each. (simple)
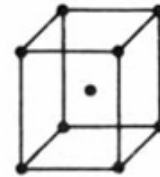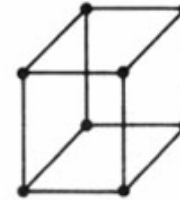
14 Bravais Cells
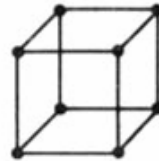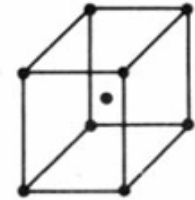

Simple cubic
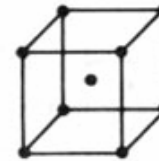
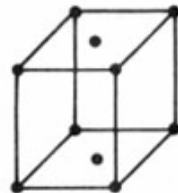Body-centered cubic
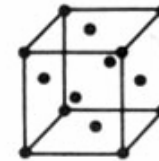
Face-centered cubic
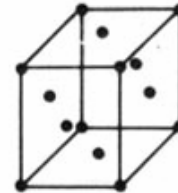
Simple tetragonal

Body-centered tetragonal

Simple orthorhombic

Body-centered orthorhombic
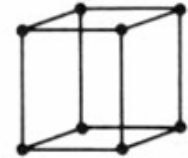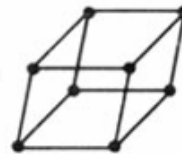
Base-centered orthorhombic

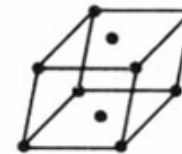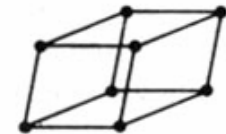Face-centered orthorhombic

Rhombohedral

Hexagonal

Simple monoclinic

Base-centered monoclinic

Triclinic

Crystal

- Lattice + Basis $\Rightarrow$
  - 32 point groups
  - 230 space groups

Lattice Planes

- Lattice plane: a plane passing three non-co-linear points

- Description of lattice plane
  - Choose the lattice origin (not on the plane considered) and lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ (primitive if possible, otherwise conventional)
  - The plane intersects the crystal axes at 3 points: $x_1\mathbf{a}_1$, $x_2\mathbf{a}_2$, $x_3\mathbf{a}_3$. x_1, x_2, and x_3 are integers if the lattice vectors are primitive.
  - Take the inverse of x_1, x_2 and x_3 ($H=1/x_1$, $K=1/x_2$, $L=1/x_3$) and multiply by the LCM of x_1, x_2 and x_3 $\Rightarrow$ (h, k, l)
  - (h, k, l) = Miller indices of the plane

Properties of Miller Indices

- (h, k, l) may denote not only one but a set of parallel planes
- { h, k, l } = the set of planes equivalent to (h, k, l). For example, { 1 0 0 } in cubic system = (1 0 0) + (0 1 0) + (0 0 1) + (-1 0 0) + (0 -1 0) + (0 0 -1)
- (2 0 0) = (1 0 0) ?
- [h k l] denotes a direction ($h\mathbf{a}_1 + k\mathbf{a}_2 + l\mathbf{a}_3$). In cubic system [h k l] $\perp$ (h k l)

Inter-Planar Distance

- The distance *d* between adjacent planes with the same Miller indices (h k l) is given by

$$d = \frac{\tau}{|\mathbf{g}|}$$

where t is the volume of the primitive unit cell and

$$\mathbf{g} = h\mathbf{b} \times \mathbf{c} + k\mathbf{c} \times \mathbf{a} + l\mathbf{a} \times \mathbf{b}$$

Some more terms

- Coordination number: number of nearest neighboring lattice points
  - sc : 6
  - bcc : 8
  - fcc : 12
- Conventional unit cell
  - Cubic systems : sc, bcc, fcc
  - The length of the sides of the underlying sc is chosen as the *lattice constant.*
  - The fundamental vectors of the underlying sc are chosen as the fundamental vectors

Examples of Crystal Structures

- Body-centered cubic (bcc)
  - Conventional lattice fundamental vectors:

    a_1 = a (1, 0, 0); a_2 = a (0, 1, 0); a_3 = a (0, 0, 1)

    2 atoms per unit cell (bases at (0, 0, 0) and a (1, 1, 1) / 2)
  - Bravais lattice vectors (primitive, coord# = 8):

    a_1 = a (-1, 1, 0) / 2; a_2 = a (1, -1, 1) / 2; a_3 = a (1, 1, -1) / 2
  - The usually seen bcc crystals are all metals:
   - Ba, Cr, Cs, Fe, K, Li, Mo, …

Examples of Crystal Structures

- Face-centered cubic (fcc)
  - Conventional lattice fundamental vectors:

    4 atoms per unit cell (bases at (0, 0, 0), a (0, 1, 1) / 2, a (1, 0, 1) / 2 and a (1, 1, 0) / 2)
  - Bravais lattice vectors (primitive, coord# = 12):

    a_1 = a (0, 1, 1) / 2; a_2 = a (1, 0, 1) / 2; a_3 = a (1, 1, 0) / 2
  - All kinds of materials including noble gases may form fcc crystal because the larger the coord# the more stable the structure:
   - Ca, Ce, Ag, Al, Au, Cu, Ni, Pb, Pt, and Ar, Ne, Xe, Kr at low temperature, …

Examples of Crystal Structures

- Diamond structure (not a Barvais lattice)
  - fcc lattice with a 2-point basis at (0, 0, 0) and a (1, 1, 1) / 4
  - Primitive: 2 atoms / unit cell
  - Conventional: 8 atoms / unit cell
  - Coordination # = 4
  - Next-nearest neighbors (nnn) = 12
  - Few neighbors, but since it is suitable for covalent bonding, it is stiff. Usually semiconductors (valence 4 materials):
    - C (diamond), Si, Ge, α-Sn, …

Diamond structure
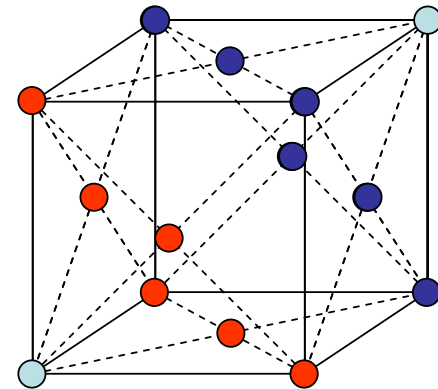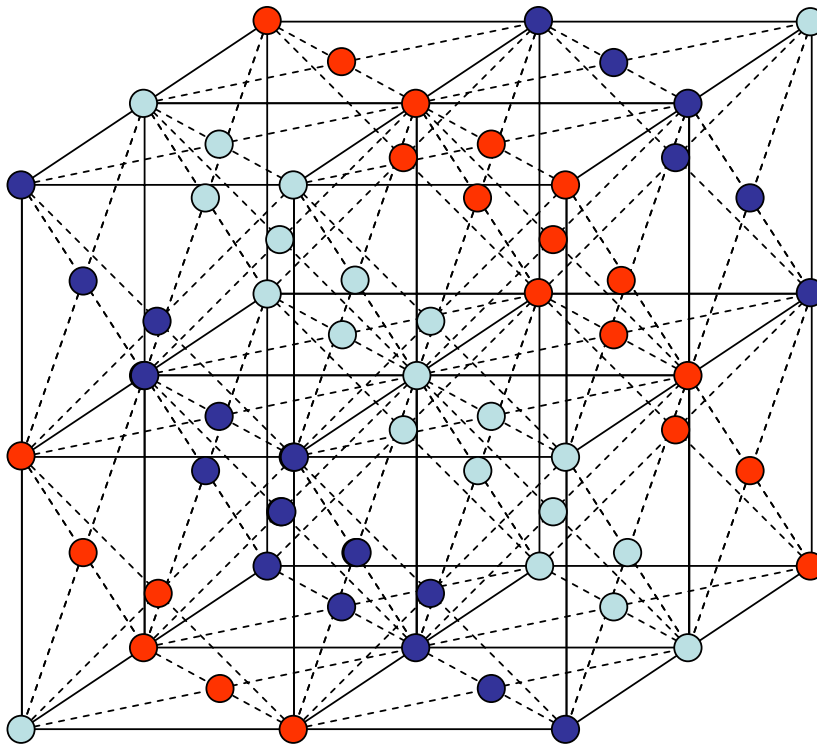

$$\frac{a}{4}\left(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}\right)$$
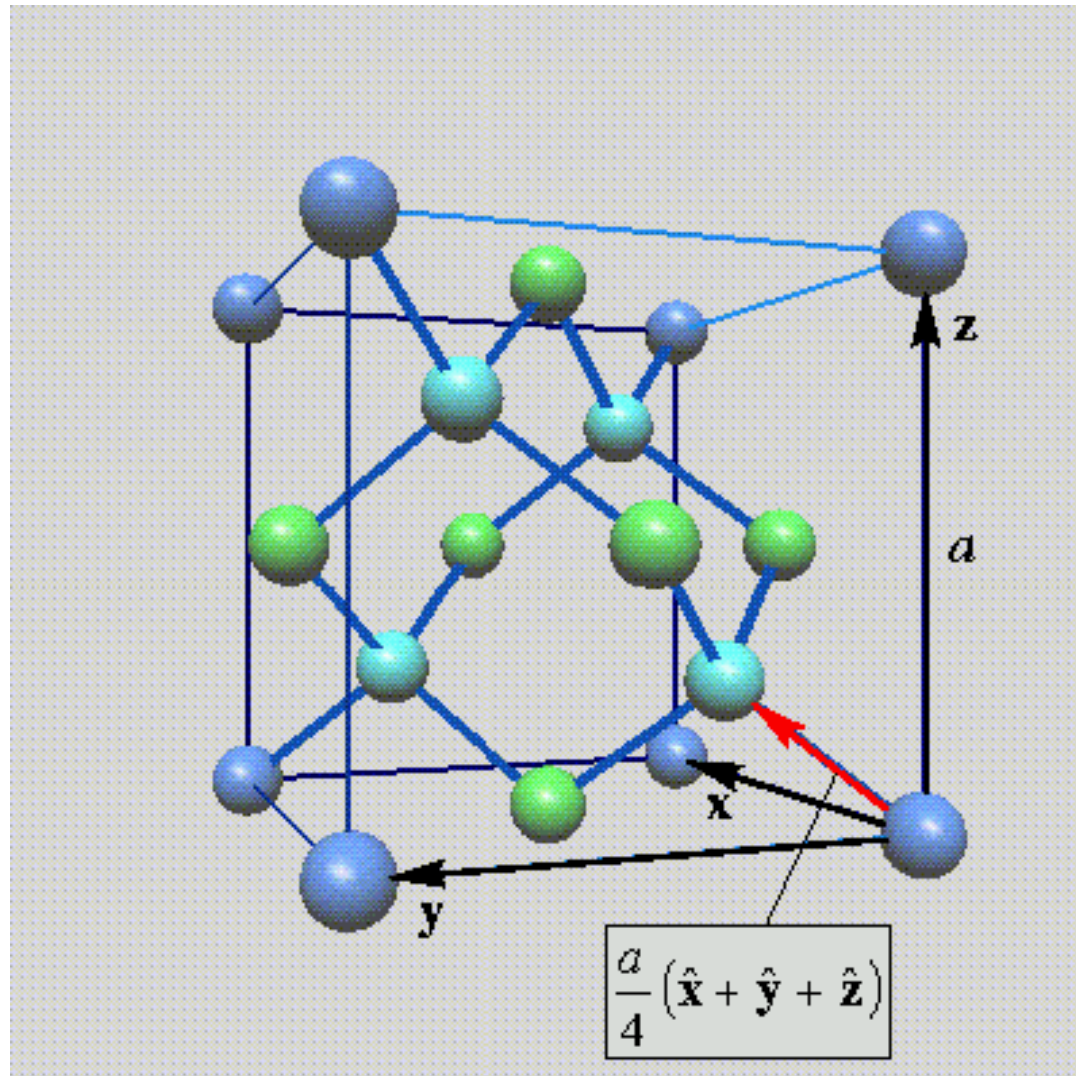
2-D Closest-Packed Structures
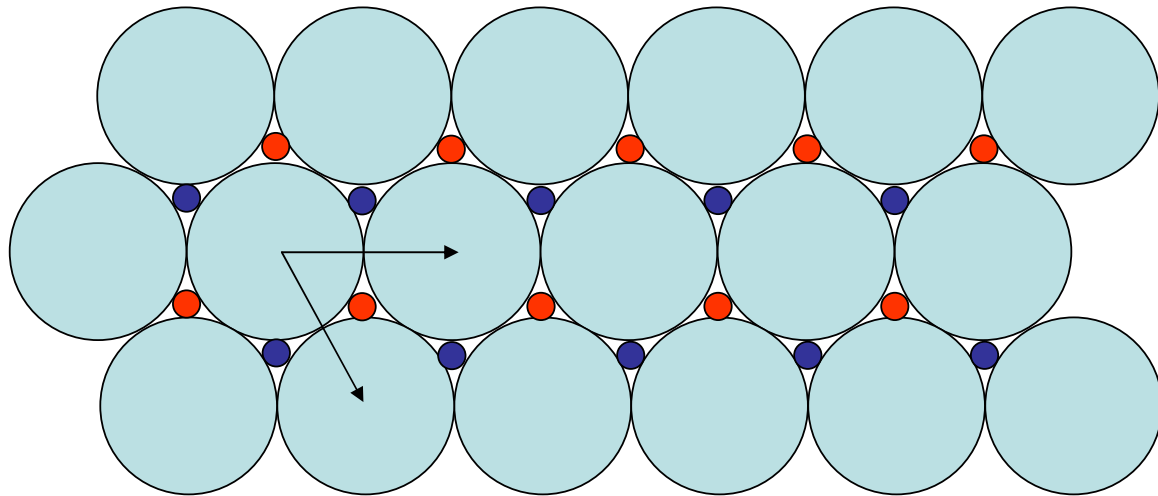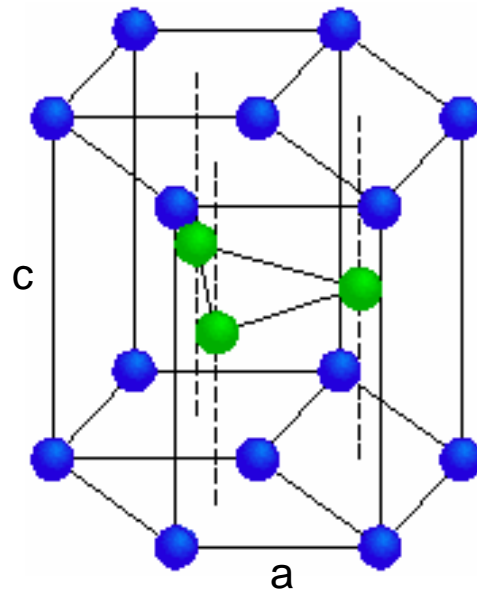
FCC Closest-Packed Structure
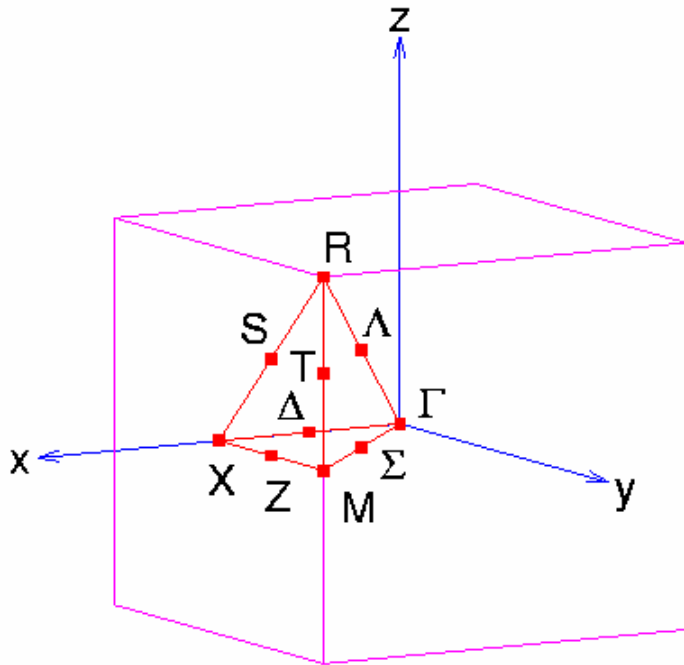
- Plane stacking order: ABCABC stacking

FCC Closest-Packed Structure

- Plane stacking order: ABAB stacking

$$\text{Ideally } \frac{c}{a} = \sqrt{\frac{8}{3}}$$
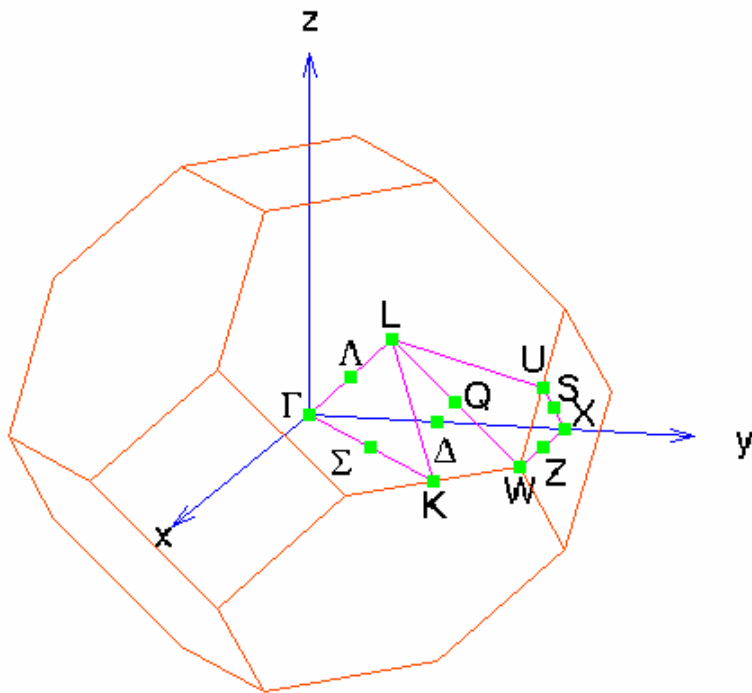
Points of Symmetry in BZ (SC)

SC

Most commonly used:

- M: center of an edge
- R: corner point
- X: center of a face
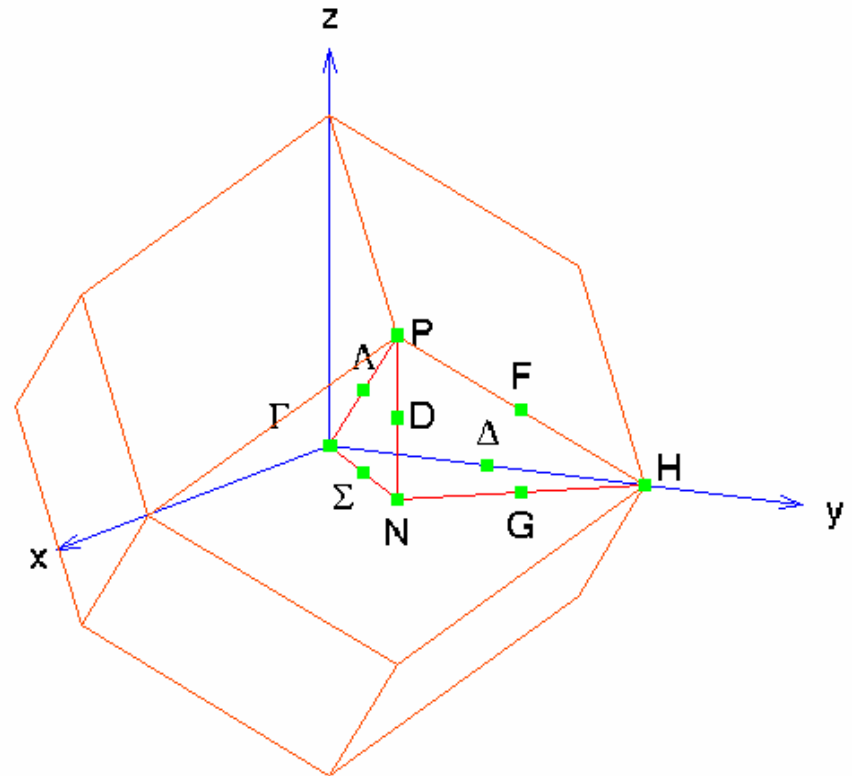
Points of Symmetry in BZ (FCC)

FCC

Most commonly used:

- K: middle of an edge joining two hexagonal faces
- L: center of a hexagonal face
- U: middle of an edge joining a hexagonal and a square face
- W: corner point
- X: center of a square face

Points of Symmetry in BZ (BCC)

Most commonly used:

- H: corner point joining four edges
- N: center of a face
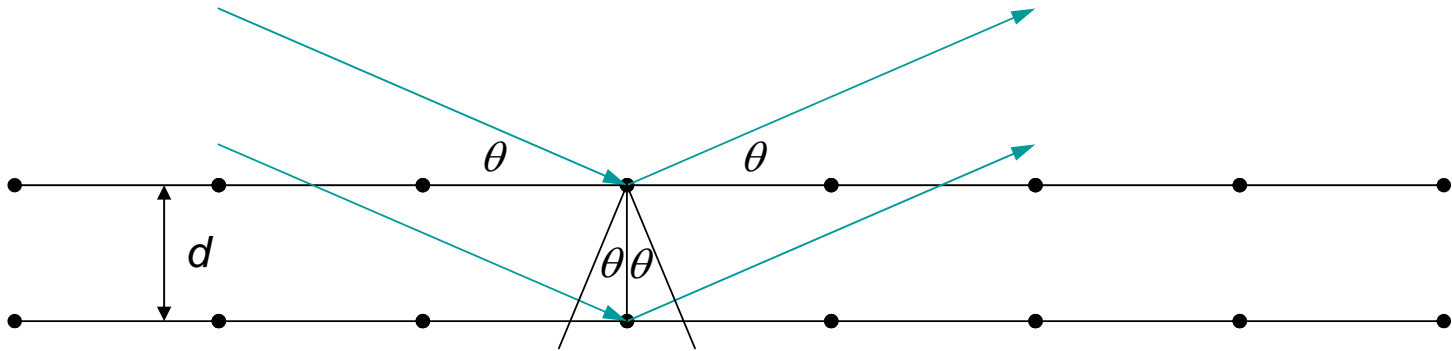- P: corner point joining three edges

BCC

Points of Symmetry in BZ (HCP)

- Most commonly used:
- A: center of a hexagonal face
- H: corner point
- K: middle of an edge joining two rectangular faces
- L: middle of an edge joining a hexagonal and a rectangular face
- M: center of a rectangular face

HEX

Bragg's formulation

Assumptions:
- Static ions (atoms)
- Elastic scattering ($\lambda = \lambda$')
- Specular reflection from a crystal plane ($\theta = \theta$')

Laue's formulation
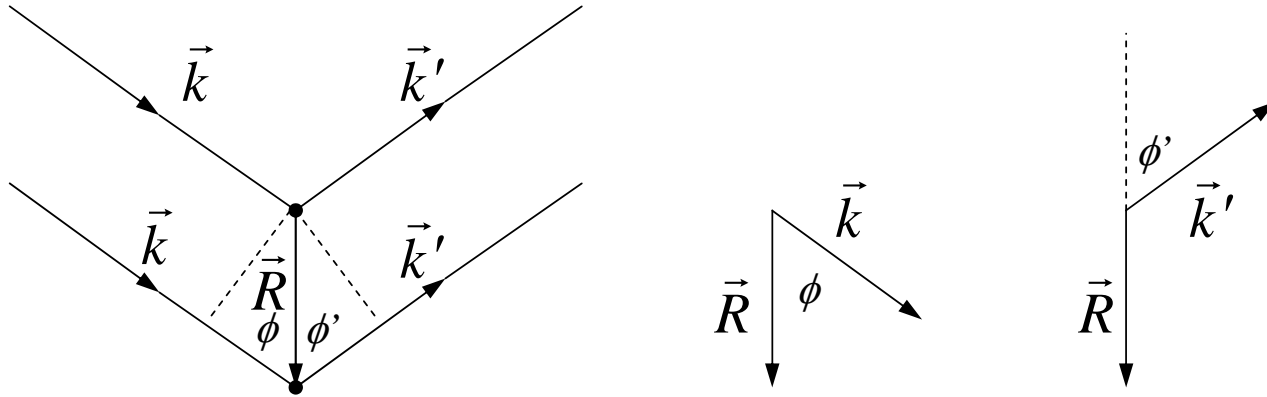
Assumptions:
- Static ions (atoms)
- Elastic scattering
- Each ion reflects the incident wave into all directions

Ewald Construction

- Draw the incident wave vector $\vec{k}$, it starts from a reciprocal lattice point O.

- Draw a sphere with radius $\left|\vec{k}\right|$ and centered at the other end of $\vec{k}$.

- If there is a reciprocal lattice point on the sphere, then the vector connecting this point to the center of the sphere is the allowed diffraction wave vector $\vec{k}'$.

Ewald Construction (Fig.)
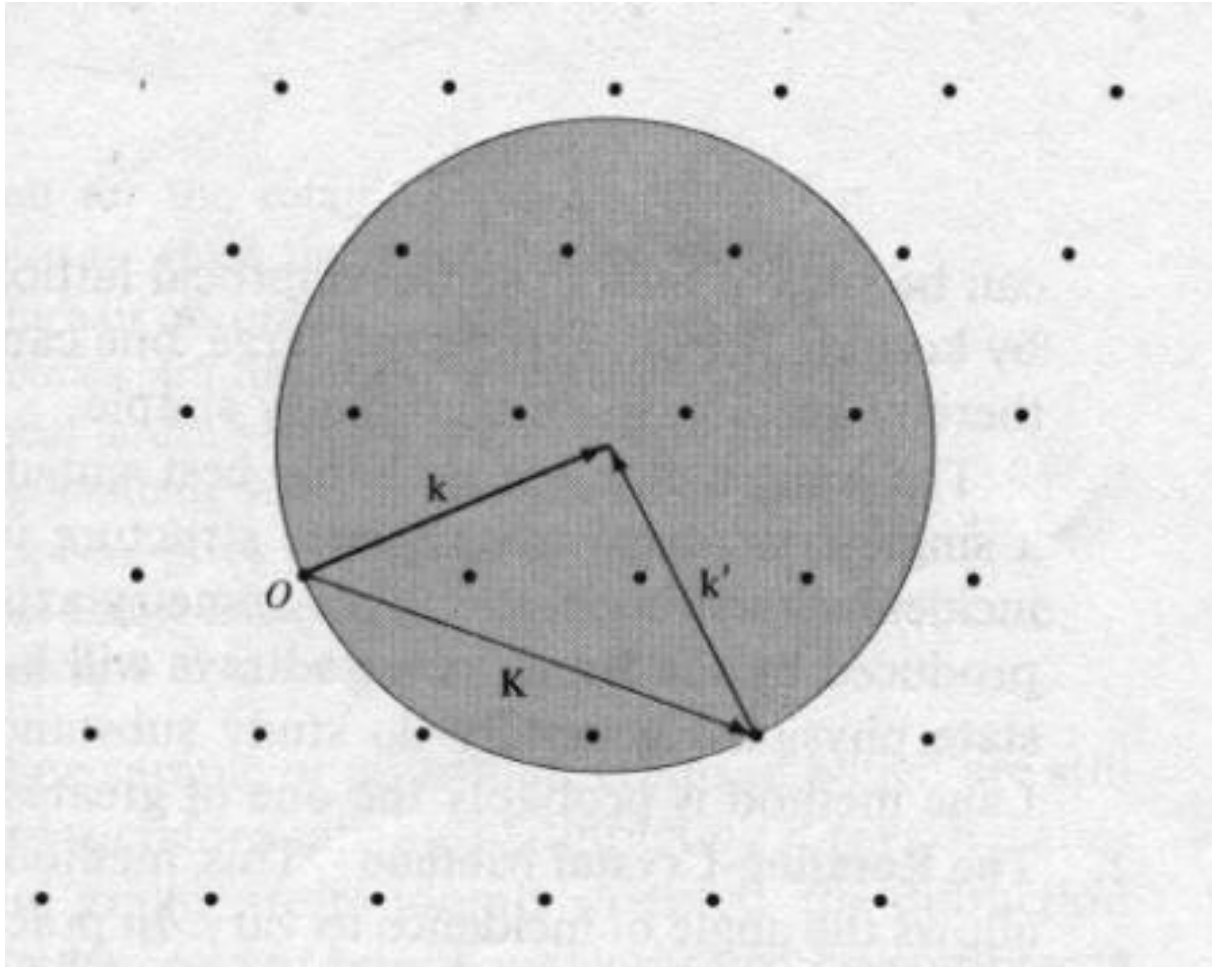
Experiment: Laue Method

- Single crystal
- Fixed direction of k but with continuous values of k (from k_0 to k_1)
- Used for determination of the orientation of a single crystal with known structure
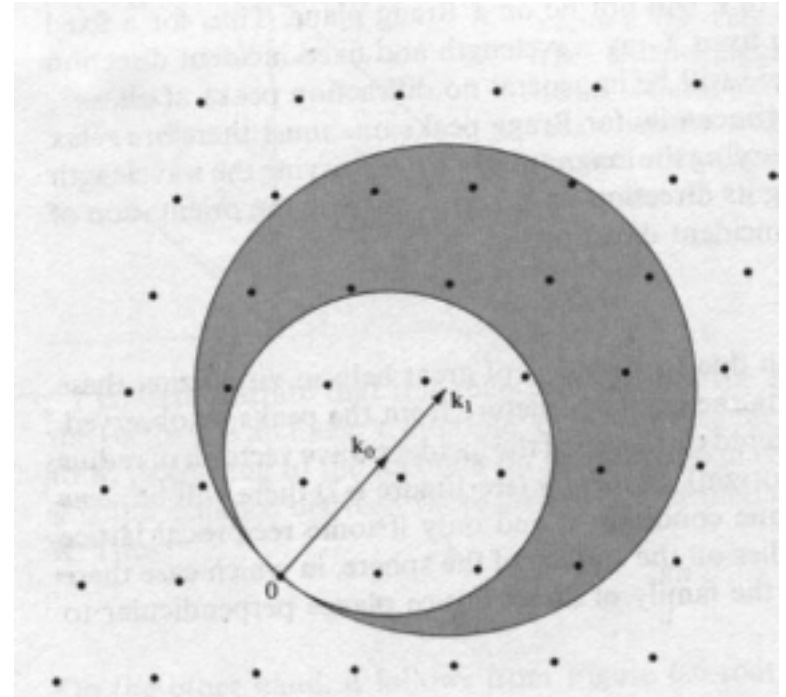
Experiment: Rotating-Crystal Method

- Monochromic wave (fixed magnitude of k)

- A single crystal rotating about a fixed axis

- Used for crystal structure determination
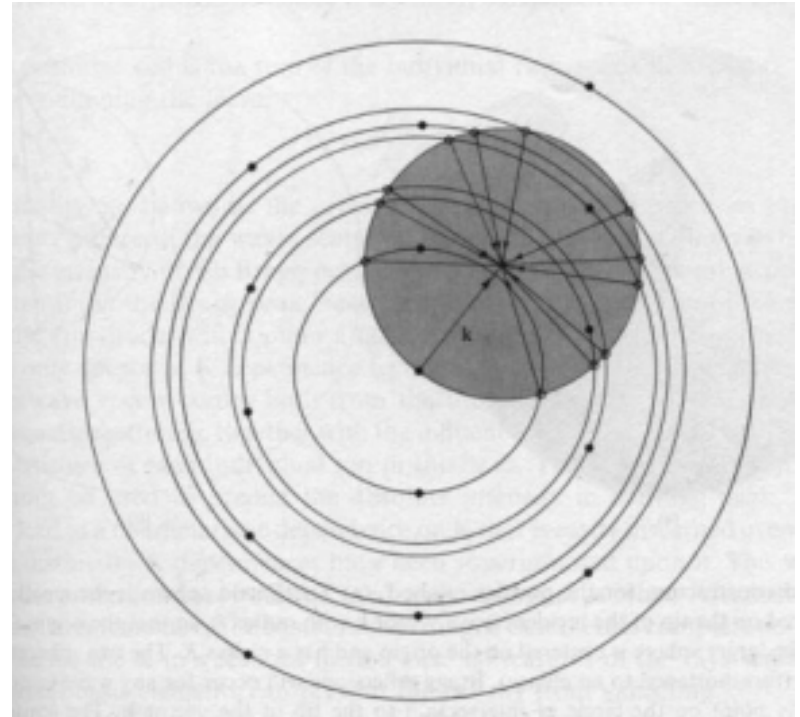
Experiment: Powder (Debye-Scherrer) Method

- Fixed magnitude of k

- Powdered sample (or a polycrystalline sample) $\Rightarrow$ continuous crystal orientation; otherwise the same as the rotating-crystal method

- With different diffraction rings, DSM measures all the size of K which are shorter than 2k