Lecture 1

1.1 Crystal Lattices
1.2 The Reciprocal Lattice
1.3 Experimental Determination of Crystal Structure

Crystal:
a solid composed of atoms, ions, or molecules arranged in a pattern that is repeated in three dimensions.
A material in which atoms are situated in a repeating or periodic array over large atomic distances.

References:
1. Marder, Chapters 1-3
2. Kittel, Chapter 1 and 2
3. Ashcroft and Mermin, Chapter 4-6
4. Burns, Chapters 1-2
5. Ziman, Chapter 1

- Crystalline materials
  - atoms (ions or molecules) in repeating 3D pattern (a lattice)
  - long-range order; ex.: NaCl,

- Amorphous (noncrystalline) materials
  - Short range order, not periodic; ex.: liquid water, glass

- Fractals
  - long-range order, symmetry, but not repeating

- Liquid crystals
  - long range order of one type; disorder of another
  - nematic and smectic

Fractals

Liquid crystals
1.1 Crystal Lattices

Atomic Structure Questions:
• What is the basic structure of matter?
• How do atoms spontaneously organize?

Basic Answers:
• Scaling theory relates atom-scale units to macroscopic solids
• Atoms form crystalline arrays
• Idea comes from special class of solids: minerals

See vast numbers of minerals at http://webmineral.com/

1.1.1 Two-Dimensional Lattices

Definitions:
• Bravais lattice
• Primitive vector
• Basis vector
• Unit cell (primitive or not)
• Wigner-Seitz cell (Voronoi polyhedron)
• Translation, space and point groups

Bravais Lattices
Bravais Lattices

Questions

Are primitive vectors unique?

No

For hexagonal lattice

\[ \mathbf{a}_1 = a (1, 0) \]

\[ \mathbf{a}_2 = a \left( \frac{\sqrt{3}}{2}, \frac{1}{2} \right) \]

We can also choose

\[ \mathbf{a}_{1,alt} = a \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right) \]

\[ \mathbf{a}_{2,alt} = a \left( \frac{1}{2}, -\frac{\sqrt{3}}{2} \right) \]

Lattice with Basis

Note presence of glide plane, showing that space group is not the same as the product of translation and point group

Some, but not all symmetries of triangular lattice destroyed
Symmetries and The Space Group

The complete set of rigid body motions that takes a crystal into itself is called the space group:

\[ G = \alpha + R(\hat{\alpha}, \hat{\beta}) \]

Two subgroups: translation and point groups.

Translation: translation through all lattice vectors defined by \( n_1 \hat{\alpha}_1 + n_2 \hat{\alpha}_2 + \ldots \)

and it leaves the crystal unchanged (invariant).

Point group consists of rotations that leave the crystal invariant

... plus screw axis and glide planes.

Summary: Classification of 2D periodic Structures

Unit cell: a convenient repeating unit of a crystal lattice; the axial lengths and axial angles are the lattice constants of the unit cell.

Wigner – Seitz cell: place the symmetry centre in the centre of the cell; draw the perpendicular bisector planes of the translation vectors from the chosen centre to the nearest equivalent lattice site.

Unit cell is not unique!

Questions

How many distinct Bravais lattices are there?
Five

How many distinct two-dimensional lattices are there?
17

http://www2.spsu.edu/math/tile/symm/ident17.htm
1.1.2 Three–Dimensional Crystals

- Distribution of structures among elements
- A small number of popular crystal structures
- Crystal symmetries:
  - 7 crystal systems
  - 14 Bravais lattices
  - 32 point groups
  - 230 space groups

Crystallization of Pure Elements

From Marder:

Web of Elements:
http://www.webelements.com/crystal_structure.html

Allotropy

Allotropy – the ability of an element to exist in two or more crystalline structures

In case of compound it is called polymorphism

Carbon allotropes: ?

- diamond
- graphite
- fullerene or buckyballs
- nanotubes or buckysheets
Allotropy

Many elements adopt multiple crystal structures between 0 K and their melting temperatures. Plutonium has a rich phase diagram.

<table>
<thead>
<tr>
<th>Transformation Temp, °C</th>
<th>Phase Structure (atoms per unit cell)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>112</td>
<td>α monoclinic (16)</td>
<td>19.8</td>
</tr>
<tr>
<td>185</td>
<td>β fcc monoclinic (34)</td>
<td>17.8</td>
</tr>
<tr>
<td>510</td>
<td>γ fcc orthorhombic (8)</td>
<td>17.1</td>
</tr>
<tr>
<td>450</td>
<td>δ fcc (4)</td>
<td>15.9</td>
</tr>
<tr>
<td>875</td>
<td>δ' fcc tetragonal (2)</td>
<td>16.0</td>
</tr>
<tr>
<td>640</td>
<td>ε bcc (2)</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table 1: Source: Atomic Weapons Establishment, Discovery Articles

Popular Lattices

>90% of elemental metals crystallize upon solidification into 3 densely packed crystal structures:

- **Body-centered cubic (bcc)**: ex.: Fe, W, Cr
- **Face-centered cubic (fcc)**: ex.: Cu, Ag, Au
- **Hexagonal close-packed (hcp)**: ex.: Zr, Ti, Zn

Important to know:

- **Distance between atoms (d)**
  - in terms of $a$
- **Number of atoms in the unit cell**
  - each corner atom shared by 8 cells: 1/8
  - each face atom shared by 2 cells: 1/4
  - each edge atom shared by 4 cells: 1/4
- **Coordination number**
  - Number of nearest neighbours (n.n.); for metals all equivalent
- **Atomic Packing Factor (APF)**
  \[ APF = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell (}a^3)} \]
Diamond and Silicon dioxide

C (diamond)
Si, Ge

Cristobalite (SiO$_2$)
Si C.N. = 4  SiO$_4^4$
O C.N. = 2

Sodium Chloride – NaCl (Rocksalt)

Layer 1
Layer 2
Layer 3 \(=\) Layer 1

Cesium Chloride - CsCl

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

Layer 1
Layer 2
Layer 3 \(=\) Layer 1
Interstitial Sites in fcc Crystal Lattice

Zinc Blend (ZnS) crystal structure

Calcium Fluoride – CaF₂
CaF$_2$ - coordination

Perovskite – CaTiO$_3$

14 Bravais Lattices and 7 Crystal Systems
Symmetry Elements

Symmetry of Lattices

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Number</th>
<th>Principal Axes</th>
<th>Operations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>43m</td>
<td>4</td>
<td>3 4 6</td>
</tr>
<tr>
<td>Tetrakaidekaedra</td>
<td>13m</td>
<td>13</td>
<td>3 4 6</td>
</tr>
<tr>
<td>Triclinic</td>
<td>T</td>
<td>4</td>
<td>3 4 6</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>O</td>
<td>4</td>
<td>3 4 6</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>M</td>
<td>2</td>
<td>3 4 6</td>
</tr>
<tr>
<td>Trigonal</td>
<td>3</td>
<td>3</td>
<td>3 4 6</td>
</tr>
<tr>
<td>Cubic</td>
<td>432</td>
<td>4</td>
<td>3 4 6</td>
</tr>
</tbody>
</table>

Schönflies and International Notations

Schönflies
- C = Cyclic; allows successive rotation about main axis.
- D = Dihedral; contains two-fold axes perpendicular to main axis.
- S = Spiegel; unchanged after combination of reflection and rotation.
- T = Tetragonal.
- O = Octahedral.

A subscript $n=1 \ldots 6$ denotes the order of a rotational axis, and subscripts denote the three types of mirror plane on previous slide.

International
- Associates each group with a list of its symmetry axes.
- Notation such as 6m refers to a mirror plane containing a six-fold axis, while 6/m refers to a mirror plane perpendicular to the six-fold axis.

32 Crystallographic Point Groups

Learn more here:
- http://www.uwgb.edu/dutchs/SYMMETRY/3DSPACE/3DSPGRP.HTM
Symmetry Operations

- **Symmetry operation** for a molecule or crystal is an operation that interchanges the positions of the various atoms in such a way that the molecule or crystal appear exactly as before the operation.

Find of the symmetry operations:

- 3 rotations around P-F axis
- 3 mirror planes Cl, P and different F atoms
- 1 mirror plane with P and F atoms
- Rotation by 120° and 240° around c-axis
- Identity operation

Note: the axis of highest symmetry of a molecule or crystal is called the principle axis or c-axis or z-axis.

HW task #1: draw a stereogram for PF3Cl2

Ideal flat surface: truncating the bulk structure of a perfect crystal

Miller indices, revisited

- For plane with intersections at \( b_x, b_y, b_z \)
- Write reciprocals: \( \left[ \frac{1}{a}, \frac{1}{b}, \frac{1}{c} \right] \)
- If all quotients are rational integers or 0, this is Miller index

- E.g.: \( b_x, b_y, b_z = 1, 1, 0.5 \) \( \Rightarrow (112) \)
- In general

  Miller index \( \langle i, j, k \rangle \) \( \frac{1}{\text{cd}} \) where cd = common divisor of \( b_x, b_y, b_z \)

  - E.g., cd = 12; \( \langle 12 12 12 \rangle \) \( \Rightarrow (643) \) plane 1

Angles between the planes

- \( [ijk] = [lmn] \times [opq] \)
- Cross products of two vectors in a plane defines direction perpendicular to plane

- \( [lmn] \) and \( [opq] \) are both vectors in plane \( [ijk] \)

Angle between two planes (directions) \( \cos \Theta = \frac{[ijk] \cdot [lmn]}{\sqrt{l^2 + m^2 + n^2} \cdot \sqrt{o^2 + p^2 + q^2}} \)

- E.g., for [111], [211]:

  \( \cos \Theta = \frac{2 + 1 + 1}{\sqrt{4} \cdot \sqrt{4}} \Rightarrow \Theta = 19.47° \)
Planes in hexagonal crystals

4 coordinate axes ($a_1$, $a_2$, $a_3$, and $c$) of the HCP structure (instead of 3)

Miller-Bravais indices - ($h$, $k$, $l$) - based on 4 axes coordinate system

$a_1$, $a_2$, and $a_3$ are 120° apart: $h$, $k$, $l$
$c$ axis is 90°: $i$

3 indices (rarely used):
$h + k = - l$
$(h$, $k$, $l) \Rightarrow (h$, $k$, $l)$

Note: in hcp, (001) ≠ (100)

Basal and Prizm Planes

Basal planes:
$a_1 = \infty$; $a_2 = \infty$; $a_3 = \infty$; $c = 1$
$\Rightarrow (0$, $0$, $01)$

Prizm planes: ABCD
$a_1 = +1$; $a_2 = \infty$; $a_3 = -1$; $c = \infty$
$\Rightarrow (1$, $0$, $-10)$

Comparison of crystal structures

FCC and HCP metal crystal structures

• (111) planes of fcc have the same arrangement as (001) plane of hcp crystal
• 3D structures are not identical; stacking has to be considered
FCC and HCP crystal structures

B plane placed in a void of plane A
Next plane placed in a void of plane B, making a new C plane
Stacking: ABCABC…

B plane placed in a void of plane A
Next plane placed in a void of plane B, making a new A plane
Stacking: ABAB…

Stereographic Projections

Project normals onto planar surface

Stereogram for PF₃Cl₂

C₉, C₃, S₂, S₃, S₅, S₆, S₇, S₈
1.2 Reciprocal Space

Reciprocal space is also called Fourier space, $k$-space, or momentum space in contrast to real space or direct space.

The reciprocal space lattice is a set of imaginary points constructed in such a way that the direction of a vector from one point to another coincides with the direction of a normal to the real space planes and the separation of those points (absolute value of the vector) is equal to the reciprocal of the real interplanar distance.

⇒ The things which are larger in real space are smaller in reciprocal space by definition.

1.2 Reciprocal Space Lattices

- Given a unit cell with basis vectors $(\vec{a}_1, \vec{a}_2)$
- There is a complementary reciprocal lattice $(\vec{a}_1^*, \vec{a}_2^*)$

\[ \vec{a}_i \cdot \vec{a}_j^* = \delta_{ij}, \quad (i,j=1,2) \Rightarrow \vec{a}_i^* \perp \vec{a}_i \quad \text{and} \quad \vec{a}_i^* \perp \vec{a}_j \]

\[ A = |\vec{a}_1 \cdot \vec{a}_2^*| = |\vec{a}_2 \cdot \vec{a}_1^*| = \frac{|\vec{a}_1 \cdot \vec{a}_2|}{\sin \theta} \]

Area of unit cell $A$

\[ A^* = \frac{1}{A} \]

Rectangular Lattice

Non-rectangular lattice

1.3 Experimental Determination of Crystal Structures
History

Experiments and theory in 1912 finally revealed locations of atoms in crystalline solids.

Essential ingredients:
- Theory of diffraction grating
- Skiing, and physics table at Café Lutz
- X-ray tubes, photographic plates, and first experiments with their use
- Persistence
- Coherent experiments with incoherent theory along behind

Incident particles to consider:

<table>
<thead>
<tr>
<th>Incident Particle</th>
<th>X-rays</th>
<th>Neutrons</th>
<th>Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (g)</td>
<td>0</td>
<td>0</td>
<td>0.910938</td>
</tr>
<tr>
<td>Charge</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>Typical energy (eV)</td>
<td>12,400</td>
<td>0.025 eV</td>
<td>100 eV</td>
</tr>
<tr>
<td>Typical wavelength (Å)</td>
<td>1 Å</td>
<td>1 Å</td>
<td>0.1 Å</td>
</tr>
<tr>
<td>Typical momentum (Å)</td>
<td>1 Å</td>
<td>1 Å</td>
<td>0.1 Å</td>
</tr>
</tbody>
</table>

Term

- Miller indices
- Reciprocal lattice

Structure Determination
- Bragg scattering, elastic and inelastic
- Bragg angle, Bragg peak and crystal planes
- Atomic form factor
- Structure factor
- Extinctions

Experimental Methods:
- Ewald construction
- Laue method
- Debye-Scherrer method, powder diffraction

Theory of Scattering from Crystals

**Geometry of scattering experiment**

Elastic scattering: frequency of outgoing radiation is the same as that of incoming radiation of wave vector $\mathbf{k}$, arrives at a sample, introducing a circular ring of radiation from each atom.

If $\mathbf{K}$ is chosen just right, the scattering radiation from the atoms adds constructively in certain directions.

- X-ray = EM
- $\nu$, $e$ - CM
Scattering from a particle

At the origin
Schiff, page 115 or Jackson Eq. 9.8
\[ \psi = Ae^{-i\omega t}e^{i\mathbf{r}\cdot\mathbf{\tau}} \]
\[ f(r) \] is atomic form factor
Contains details of interactions between the scattering potential and the scattered wave
Let’s assume we know \( f(r) \)
At \( \mathbf{R} \)
\[ \psi = Ae^{-i\omega t}e^{i\mathbf{r}\cdot\mathbf{\tau}} + f(r) \frac{e^{i\mathbf{R}\cdot\mathbf{\tau}}}{\mathbf{R}} \]
For sufficiently large \( r \),
\[ k_x \mathbf{R} + \mathbf{k}_x - \mathbf{k}_x \frac{e^{i\mathbf{R}\cdot\mathbf{\tau}}}{\mathbf{R}} \]
Using Eq. above and defining
\[ k = \frac{q}{\tau} \]
and \[ q = \frac{2 \pi}{\tau} \sin \theta \]
\[ \mathbf{q} \] - momentum transfer between incoming and outgoing waves
\[ \theta \] - Bragg angle

Let’s assume we know \( f(r) \)

Many scattering particles

Assuming multiple scattering and inelastic scattering can be ignored
\[ \psi = Ae^{-i\omega t}e^{i\mathbf{r}\cdot\mathbf{\tau}} + \sum f(r) \frac{e^{i\mathbf{R}\cdot\mathbf{\tau}}}{\mathbf{R}} \]
In direction away from incident beam
\[ \psi = Ae^{-i\omega t} \sum f(r) \frac{e^{i\mathbf{R}\cdot\mathbf{\tau}}}{\mathbf{R}} \]
Intensity per unit solid angle
\[ I = \sum f(r)^2 e^{2i\mathbf{R}\cdot\mathbf{\tau}} \]
Equation above is true no matter how atoms are arranged!
Scattering from crystal

If all of the scatters are identical and arranged in a Bravais lattice:

\[ I = I_0 \sum e^{i\mathbf{q}\cdot\mathbf{R}} \]

Laue condition: find \( \mathbf{q} \) so that for all atom locations \( \mathbf{R}_i \)

\[ e^{i\mathbf{q}\cdot\mathbf{R}_i} = 1 \]

One-Dimensional Sum: lattice points must be of the form \( la \)

\[ \sum_{l=0}^{\infty} e^{i\mathbf{q}\cdot(la)} = \frac{\sin \left( \frac{2\pi l a \mathbf{q}}{a} \right)}{l \sin \frac{\pi \mathbf{q}}{a}} \]

(follow Marder, p. 48)

Scattering for one-dimension

Peak when \( \frac{\pi}{2} l \pi \Rightarrow q = \frac{2\pi}{a} \)

Assuming delta functions:

\[ \sum_{l=0}^{\infty} e^{i\mathbf{q}\cdot(la)} = 2 \pi \delta(q - \frac{2\pi}{a}) \]

Scattering in three dimensions

Main result: when \( \mathbf{q} = \mathbf{K} - \mathbf{K} = \tilde{\mathbf{K}} \) satisfies

\[ e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \] or \( \mathbf{K} \cdot \tilde{\mathbf{K}} = 2\pi \theta \)

there is a strong peak

The scattering sum can be written

\[ \sum_{l} e^{i\mathbf{q}\cdot\mathbf{R}_l} = \sum_{\mathbf{K}} N \left( \frac{2\pi}{a} \right)^2 \delta(q - \mathbf{K}) \]

When the vectors \( \mathbf{R} \) lie in a Bravais lattice, then vectors \( \mathbf{K} \) satisfying equation above also lie in a lattice – the reciprocal lattice
Lattice with a Basis

\[ \mathbf{g} = \mathbf{b}_1 + \mathbf{b}_2 \]

Regrouping of basic sums first carried out by Lune:

\[
\sum_{\mathbf{g}} e^{i \mathbf{g} \cdot \mathbf{r}} = \sum_{\mathbf{G}} e^{i \mathbf{G} \cdot (\mathbf{r} + \mathbf{r}_0)} \\
= \left( \sum_{\mathbf{G}} e^{i \mathbf{G} \cdot \mathbf{r}_0} \right) \left( \sum_{\mathbf{G}} e^{i \mathbf{G} \cdot \mathbf{r}} \right) \\
= I \propto \left( \sum_{\mathbf{G}} e^{-i \mathbf{G} \cdot (\mathbf{r} - \mathbf{r}_0)} \right) \left( \sum_{\mathbf{G}} e^{i \mathbf{G} \cdot \mathbf{r}_0} \right).
\]

Structure factor for the unit cell is

\[ F_0 = \left| \sum_{\mathbf{G}} e^{i \mathbf{G} \cdot \mathbf{r}_0} \right|^2. \]

When \( F_0 \) vanishes, have an extinction. Lune overlooked this possibility, leading to years of confusion in interpreting patterns.

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Experimental Methods

Ewald construction

Shining generic monochromatic X-ray upon crystal gives no scattering peaks.

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Laue Method

Intensity vs. Wavelength

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Rotating Crystal Method

Powder Diffraction

And the radius $r$ on film of the scattering ring due to the reciprocal lattice vector $K$ is

$$r = D \tan(2\theta)$$

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Powder diffraction

Main method for determining crystal structure

Consider an X-ray of wavelength $\lambda$ hits a set of planes separated by $d$ under an angle $\Theta$

- some of the X-rays go straight through
- some are reflected (scattered), but only if specific conditions met

Consider a material to be a stack of planes at a constant separation - $d$

$$2d \sin \Theta$$

Out of phase

In phase

whole number

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Bragg’s law

The diffraction (the coherent elastic scattering of waves by the crystal lattice) condition

\[ n \lambda = 2d \sin \Theta \]

\textbf{Bragg’s law (X-rays, neutrons, electrons)}

where \( \lambda \) – wavelength of X-ray beam, \( d \) – spacing of reflecting planes, \( \Theta \) – angle of incidence and reflection, \( n \) – order of diffraction (for most of the cases we discuss \( n=1 \))

The lattice plane spacing \( d \) depends on the crystal structure and indices \( \{hkl\} \) of the planes.

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

\( d \) – set by the crystal
\( \lambda \) – set by apparatus (constant for a given setup)
can change \( \Theta \) (theta) or often \( 2\Theta \)

Kittel, pp.29 - 30

Constructive and destructive interference

X-ray waves scatter in phase (constructive interference): \( \lambda, 2\lambda, 3\lambda, \ldots, n\lambda \) (n – whole number)

Out of phase (destructive interference): \( 1/2\lambda, 3/2\lambda, 5/2\lambda, \ldots \)

What about the other planes?
- If in phase condition holds for plane 1 and 2, it also holds for the plane 3, 4, etc.
- If plane 1 and 2 are out of phase, the 3rd will be in phase with the 1st, … but the 4th will cancel it out

Other planes are also important:

1. \( \lambda/2 \)
2. \( \lambda/4 \)
3. \( \lambda/4 \)
4. \( \lambda/2 \)

Unless constructive interference condition met \( n \) (n – whole number), there is very little intensity at a given angle.

Additional rules

- Consider diffraction from the (100) face of the fcc crystal

\[ 2d \sin \Theta = \lambda \] (i.e., \( n=1 \))

but there is always another plane at \( (n=1/2) \)

\( \Rightarrow \) no intensity...

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Possible peaks for cubic structures

\[ d_{\text{hkl}} = \frac{\alpha}{\sqrt{h^2 + k^2 + l^2}} \]

<table>
<thead>
<tr>
<th>Family of planes</th>
<th>ac</th>
<th>fcc</th>
<th>bcc</th>
</tr>
</thead>
<tbody>
<tr>
<td>({100})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Powder diffraction

- Use polycrystalline sample
  - All possible planes are at angle \(\Theta\) to beam
  - Only ones satisfying Bragg's condition provide diffraction
  - Need to change angle \(\Theta\) to detect all "Bragg peaks"

Experimental details (powder diffraction)

- Source
- Collimator (slits)
- Sample holder (need rotation)
- Detector (moves in arc around sample; intensity vs \(2\Theta\) is recorded)