Diffraction Methods

- Diffraction methods are the most important approach to the analysis of crystalline solids
  - both phase and structural information
- Continuous solids usually can not be purified
  - elemental analysis not much use on its own
- Solid state NMR is a powerful technique
  - but does not provide a detailed picture

Types of diffraction experiment

- X-ray
  - Routinely used to provide structural information on compounds and to identify samples
  - Used with both powder and single crystal samples
  - X-rays produced in the home lab or using synchrotrons
    - Can also be used to examine liquids and glasses
- Electron diffraction
  - primarily used for phase identification, and unit cell determination on small crystallites in the electron microscope
  - also used for gas phase samples
- Neutrons
  - useful source of structural information on crystalline materials, but expensive
  - Also useful for spectroscopy and structure of liquids/glasses
Production of x-rays

- X-rays are produced in the laboratory by bombarding a metal target with high energy electrons.
- The high energy electrons knock electrons out of the core orbitals in target metal.
- These empty core orbitals are refilled by atomic transitions that lie in the x-ray region.

**Fig. 3.1** (a) Generation of Cu \(K_\alpha\) X-rays. A 1s electron is ionized; a 2p electron falls into the empty 1s level (□) and the excess energy is released as X-rays. (b) X-ray emission spectrum of Cu.
X-ray tube

Production of X-rays 3

- The wavelength of x-rays produced depends on the element the target is made from

<table>
<thead>
<tr>
<th>Target</th>
<th>kα₁</th>
<th>kα₂</th>
<th>kα</th>
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<tr>
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<td>2.2935</td>
<td>2.2909</td>
<td>V</td>
</tr>
<tr>
<td>Fe</td>
<td>1.936</td>
<td>1.9399</td>
<td>1.9373</td>
<td>Mn</td>
</tr>
<tr>
<td>Cu</td>
<td>1.5405</td>
<td>1.5443</td>
<td>1.5418</td>
<td>Ni</td>
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<td>0.7093</td>
<td>0.7135</td>
<td>0.7107</td>
<td>Nb</td>
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<td>Ag</td>
<td>0.5594</td>
<td>0.5638</td>
<td>0.5608</td>
<td>Pd</td>
</tr>
</tbody>
</table>
Producing Synchrotron Radiation

- High intensity
- Plane polarized
- Intrinsically collimated
- Wide energy range
- Has well defined time structure
The Advanced Photon Source

Inside the APS
Producing neutrons

- Produced using a nuclear reactor or a spallation source
- Spallation neutrons are produced by bombarding a metal target with pulses of protons
  - Gives different wavelength distribution to reactor
- Peak flux from pulsed source is high but time average flux is not so good
  - Need to use time structure of source to make up for this

A comparison of X-rays and neutrons

<table>
<thead>
<tr>
<th>X-rays</th>
<th>Neutrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic scattering power varies smoothly with atomic number</td>
<td>Atomic scattering power varies erratically with atomic number</td>
</tr>
<tr>
<td>Atomic scattering power decreases as the scattering angle increases</td>
<td>Atomic scattering power is constant as the scattering angle changes</td>
</tr>
<tr>
<td>Insensitive to magnetic moments</td>
<td>Scattered by magnetic moments</td>
</tr>
<tr>
<td>Readily available as intense beams</td>
<td>Low intensity beams</td>
</tr>
<tr>
<td>Typically, strongly absorbed by all but low Z elements</td>
<td>Weakly absorbed by most materials</td>
</tr>
</tbody>
</table>
The scattering of X-rays by electrons

- The charge on an electron interacts with electromagnetic radiation and can give rise to elastic scattering
- If the source, electron and detector lie in a plane perpendicular to the X-rays electric vector the scattering probability is isotropic
- If the electric vector lies in the plane the scattering is not isotropic

The scattering of unpolarized X-rays

- For an unpolarized beam of X-rays being scattered by an electron

\[ I \propto 0.5 \times (1 + \cos^2\theta) \]

- This is the physical origin of the polarization correction used in crystallography
Scattering of X-rays and neutrons by atoms

- X-rays are scattered electrons in atoms
  - the electron cloud is about the same size as the wavelength of the X-rays
- Neutrons are scattered by nuclei
  - nuclei are much smaller than the neutron wavelength
  - for magnetic materials electron spin interacts with neutron spin and gives scattering

X-ray scattering by atoms
X-ray and neutron form factor

- The form factor is related to the envelope function for an atom

![Diagram](image1.png)

Neutron scattering lengths

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>$X$ rays $\sin \theta/\lambda = 0$</th>
<th>$X$ rays $\sin \theta/\lambda = 0.5/\AA$</th>
<th>Neutrons* $b (10^{-12}$ cm)</th>
<th>Neutrons** (normalized to -1.00 for $^1$H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>$^1$H</td>
<td>1.0</td>
<td>0.07</td>
<td>-0.38</td>
<td>-1.00</td>
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<tr>
<td></td>
<td>$^2$H (=D)</td>
<td>1.0</td>
<td>0.07</td>
<td>0.65</td>
<td>1.71</td>
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<tr>
<td>Li</td>
<td>$^6$Li</td>
<td>3.0</td>
<td>1.0</td>
<td>0.18 +0.025i</td>
<td>0.71 +0.066i</td>
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<tr>
<td></td>
<td>$^7$Li</td>
<td>3.0</td>
<td>1.0</td>
<td>-0.25</td>
<td>-0.66</td>
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<tr>
<td>C</td>
<td>$^{12}$C</td>
<td>6.0</td>
<td>1.7</td>
<td>0.66</td>
<td>1.74</td>
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<tr>
<td></td>
<td>$^{13}$C</td>
<td>6.0</td>
<td>1.7</td>
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<tr>
<td>O</td>
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<td>Fe</td>
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<td>11.5</td>
<td>0.42</td>
<td>1.11</td>
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<td></td>
<td>$^{56}$Fe</td>
<td>26.0</td>
<td>11.5</td>
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<tr>
<td></td>
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<tr>
<td>U</td>
<td>$^{238}$U</td>
<td>92.0</td>
<td>53.0</td>
<td>0.85</td>
<td>2.24</td>
</tr>
</tbody>
</table>
Neutron scattering lengths

Diffraction

- X-rays are scattered from the atoms in the sample. The x-rays scattered from the different atoms interfere with one another either constructively or destructively
- For crystalline solids this interference pattern has sharp well defined peaks
  - The positions of the peaks are determined by the lattice for crystalline solid
Scattering patterns for different substances

Interference between waves

(a)

(b)

(c)
in phase (constructive interference)

out of phase (destructive interference)

partially out of phase
Double slit experiment

Bragg’s law \(2d \sin \theta = \lambda\)

- Can consider crystal to contain repeating ‘reflecting’ planes (lattice planes)
- Interference between x-rays scattered from different planes leads to peaks in the diffraction pattern
d-spacing formulae

- For a unit cell with orthogonal axes
  \[ \frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \]

- Hexagonal unit cells
  \[ \frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + k^2 + hk}{a^2} \right) + \frac{l^2}{c^2} \]

Powder diffraction

\[ Q = \frac{4\pi \sin \theta}{\lambda} \]

\( Q \) is the Bragg angle

\( 2\theta \) is the Bragg angle

\( \lambda \) is the wavelength

\( Q \) is the scattering vector
Energy and angle dispersive diffraction

- An X-ray diffraction pattern is a measurement of X-ray intensity versus d-spacing
  - d-spacing, scattering angle and $\lambda$ are related by Bragg’s law
    - $2d \sin \theta = \lambda$

**Detector**

Incoming X-rays

2$\theta$

Energy dispersive diffraction
Fix $2\theta$ and vary $\lambda$
Quick experiment with fixed sampling volume, but low resolution

Angle dispersive diffraction
Fix $\lambda$ and vary $2\theta$
High resolution but slow and sampling volume varies

Instrument geometries

- There are several different ways of collecting powder diffraction patterns
  - Debye Scherrer
  - Bragg-Brentano (flat plate)
  - Guinier etc.

- The Bragg-Brentano geometry is the most commonly used
The Debye-Sherrer camera

Fig. 3-12 Debye-Scherrer powder method: (a) relation of film to specimen and incident beam; (b) appearance of film when laid out flat.

Bragg-Brentano diffractometer

Fig. 5-14. (b) Optical arrangement used in early x-ray diffractometer. (b) Present-day optical arrangement with a "line" x-ray source and Saalfeld slits to limit axial divergence.
Powder X-ray diffraction

- Powder XRD is used routinely to assess the purity and crystallinity of materials
- Each crystalline phase has a unique powder diffraction pattern
- Measured powder patterns can be compared to a database for identification

Powder patterns for different substances

- Can distinguish between the same compound with different structures and different compounds with the same structure

![Graphs of powder patterns for NaCl, KCl, Brookite TiO₂, Anatase TiO₂, and Rutile TiO₂]
Information from powder XRD

- Phase purity
  - both qualitative and quantitative
- Crystallinity
  - amorphous content, particle size and strain
- Unit cell size and shape
  - from peak positions
- Crystal structure in simple cases

Indexing a powder pattern

- The process of figuring out what Miller indices belong to each peak or “d-spacing” in a powder pattern is called indexing
- During the indexing process the unit cell constants are also determined
- Indexing can be done by hand or by computer
  - indexing by hand is only sensible for materials that are thought to have high symmetry
Indexing the powder pattern of NaBr

<table>
<thead>
<tr>
<th>2 Theta</th>
<th>d-spacing</th>
<th>1/d^2</th>
<th>diff</th>
<th>1/d^2 div 0.0280</th>
<th>h2 + k2 +l2</th>
<th>hkl</th>
<th>a</th>
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<td>35.08000416</td>
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<td>531</td>
<td>5.969325</td>
</tr>
</tbody>
</table>

Systematic absences and centering

- The presence of a centered lattice leads to the systematic absence of certain types of peak in the diffraction pattern
  - For I centered lattices: \( h + k + l = 2n \) for a line to be present
  - For an F centered lattice: \( h + k = 2n, k + l = 2n \) and \( h + l = 2n \)
- For a C centered lattice:
  - \( h + k = 2n \)
Phase identification

- Powder X-ray diffraction is often used for phase identification
  - this can be done by calculating the unit cell and then search the NIST crystal data database for known compounds with the same or similar unit cells
  - usually done by comparing the measured pattern against the ICDD/JCPDS powder diffraction file data base. This contains powder patterns for a very large number of compounds.

Processing powder data

- Phase identification is usually done using a list of peak positions and intensities rather than the raw data
- Peaks can be located automatically
- Always check that the list of peaks you are going to use is a reasonable match to the raw data!
Strategies for search match

- Identification using the PDF can be done manually using the Hanawalt method
  - based of three strongest lines
- Identification can be done by computer
  - should narrow search down to elements of interest
- Problems can arise from the presence of multiple phases in a sample
  - strongest peaks may not be from the same phase

Phase identification

- Illustrate approach using analysis of solid found at bottom of vessel while carrying out Na$_2$SO$_4$ corrosion experiments on type I Portland cement paste
Examine raw data

Perform background subtraction and peak search
Search PDF for likely match

What constitutes a match?

- For a PDF card to be considered a good match to your experimental data there should be no strong peaks on the PDF card that are missing from your data
- Extra peaks in the data may indicate the presence of additional phases
Carefully check possibilities against the data
Quantitative phase analysis

- The relative amount of the phases in a mixture can be determined by comparing the intensities of peaks in the sample with those from reference materials.

Particle size

- The width of the peaks in a powder pattern contain information about the crystallite size in the sample (and also the presence of microstrain).
- \( L = \left( K \frac{\lambda}{\beta \cos \theta} \right) \) : Scherrer equation
  - \( L \) - mean size of crystallites
  - \( K \) - constant roughly 1: depends on shape of crystallites
  - \( \beta \) - width of reflection in radians
Peak intensities

- Phase identification is done primarily by comparing peak positions
  - Although if a match between a database pattern and an experiment is to be considered good the relative intensities of the peaks should be similar
- Peak positions are determined by the lattice
- Peak intensities are determined by the positions of the atoms in the unit cell
  - Can use intensities to figure out where the atoms are

Diffracted intensity and the structure factor

- The intensity of a reflection is related to the structure factor for that reflection
  - $I(hkl) \propto F(hkl)^2$
  - $F(hkl) = |F(hkl)|\exp(i\alpha_{hkl}) = A(hkl) + iB(hkl)$
  - $A(hkl) = \Sigma f_j \cos 2\pi(hx_j + ky_j + lz_j)$
  - $B(hkl) = \Sigma f_j \sin 2\pi(hx_j + ky_j + lz_j)$
- Note the structure factor is a sum of terms
  - There is a term corresponding to the scattering from each of the atoms in the unit cell
Fourier synthesis and electron density

- The electron density in a crystal is related to the diffraction pattern of the crystal through a Fourier synthesis like procedure

\[ \rho(x, y, z) = \frac{1}{V} |F(hkl)| \cos [2\pi(hx + ky + lz) + \alpha_{\text{ext}}] \]

- or usually,

\[ \rho(x, y, z) = \frac{1}{V} |F(hkl)| \exp(i\alpha) \exp[-i2\pi(hx + ky + lz)] \]

Electron density synthesis for NaCl

![Electron density map for NaCl](image)
Microscopy and X-ray diffraction

The phase problem

- If we know the structure factors for a structure we can calculate an electron density and “see” where the atoms are
  - However, the x-ray data only give us structure factor magnitudes. We are missing the phases. The processes of solving a crystal structure from x-ray diffraction data boils down to figuring out what the missing phases are
Solving crystal structures

- Crystal structures can be solved in a variety of different ways
  - In many cases quite highly automated
- Typically, structures are solved from single crystal diffraction patterns not power diffraction patterns
  - More structure factors can be measured and you do not have to worry about the overlap of Bragg reflections that are not equivalent to one another

Other diffraction methods

- Single crystal X-ray diffraction
  - routinely used to get crystal structures
- Electron diffraction
  - useful for very small particles of material
  - can give you unit cell and space group
- Neutron diffraction
  - good for looking at light atoms
  - sensitive to magnetic moments
  - good when sample “environment” is used
A single crystal of about 0.1 mm in all dimensions is required

Several thousand “reflections” (intensities) are measured to solve an xtal structure

Uses the space group symmetry of the solid to aid the process
  – a crystal contains an enormous number of atoms
  – without using symmetry we would have an underdetermined problem

Experiment measures intensities for many reflections with different Miller indices

Unit cell is determined from measured reflection angles (or positions)

The space group is assigned from systematic absences and other information
  – tells you about both translational and point symmetry in the solid
Determining crystal structures

- Going from measured intensities to a final structure (set of atomic coordinates) is a two step process
- Solve the structure
  - get an initial estimate of where the atoms are
- Refine the structure
  - change the atom positions so that the calculated diffraction pattern matches what you measured as well as possible

R-factors

- We determine “how good a structure is” by comparing the measured structure factor magnitudes with those that we would calculate for our model structure. We try and improve the agreement as much as we can
- We judge how good the agreement is using “R-factors” such as

\[
R = \frac{\sum |F_{\text{obs}}| - |F_{\text{calc}}|}{\sum |F_{\text{obs}}|}
\]

Sum is over all measured reflections
Electron diffraction

- Very high energy electrons are employed to examine small crystals of materials
- Electrons interact strongly with matter
  - can only use thin samples to observe a diffraction pattern in transmission
- Not good for solving crystal structures due to multiple scattering

Neutron diffraction

- Neutrons are very expensive
  - from nuclear reactor or a “spallation” source
- They are uniquely suited to studying magnetic materials
- Very good for looking at weak X-ray scatterers like H, or O in the presence of heavy metals
- Good for crystal structure refinement from powder diffraction data
Magnetic structures

- Neutrons have a magnetic moment and they are scattered by unpaired electron spins
  - Normal neutron scattering is scattering off the nucleus
  - Neutrons scattering patterns are sensitive to the arrangement of unpaired electron spins in a material
    » If the unpaired spins on atoms and ions are ordered throughout the material scattering from these spins will contribute to the neutron diffraction pattern

The magnetic structure of MnO

- MnO, NiO and FeO order antiferromagnetically
- After taking into account the arrangement of unpaired spins the unit cell is twice as big as the atomic arrangement would suggest
  - So you get extra peaks in the neutron diffraction pattern
Powder neutron diffraction data for MnO

- Extra peaks are only present in the neutron diffraction pattern at temperatures where the unpaired spins are ordered (below Neel temperature).

Comparison of X-ray and neutron patterns

Lab X-ray data

Reactor neutron data
Time-of-flight diffraction

- Time from source to detector is determined by neutron wavelength
  \[ v = \frac{(L + L_1)}{t} \quad \text{and} \quad mv = \frac{h}{\lambda} \quad \text{so} \quad t = \frac{m(L + L_1)\lambda}{h} \]

- Can measure \( I(Q) \) without scanning detector
  \[ Q = \frac{4\pi m(L + L_1)\sin \theta}{ht} \]

- Use many separate detectors and sum the counts recorded in each to measure \( I(Q) \) with good counting statistics in less time

SEPD – Special Environment Powder Diffractometer

- Only small fraction of total solid angle covered

<table>
<thead>
<tr>
<th>2 theta</th>
<th>Solid angle (str)</th>
</tr>
</thead>
<tbody>
<tr>
<td>± 145°</td>
<td>0.086</td>
</tr>
<tr>
<td>± 90°</td>
<td>0.086</td>
</tr>
<tr>
<td>± 60°</td>
<td>0.052</td>
</tr>
<tr>
<td>± 30°</td>
<td>0.017</td>
</tr>
<tr>
<td>- 15°</td>
<td>0.017</td>
</tr>
</tbody>
</table>
TOF neutron data for cubic ZrMo$_2$O$_8$

The Rietveld method

- Powder diffraction patterns can be curve fit so as to obtain structural information
  - this process is called Rietveld refinement
  - it is not a method of solving structures. It is a method for refining structures
- Refine a model containing:
  - structural parameters
  - peak shape
  - unit cell size
Small angle scattering

- The arguments used in discussing the form factor for atoms can be applied to other systems
  - polymer particles, globular proteins, voids in samples
- The low angle scattering from a sample of something like a colloid tells you about the size and shape of the particles

Example small angle scattering curve