Diffraction based techniques
-
X-ray, neutron, and electron based methods
Topics

• The basic idea
• Sources
• X-ray diffraction
  – Phase analysis
  – Texture and stress measurements
• Electron diffraction
  – General remarks
  – Electron backscatter diffraction (EBSD)
  – Selected area diffraction (SAD)
• Neutron diffraction
  – General remarks
Basic definition of diffraction

• **Diffraction** is the bending, spreading and interference of waves when they pass by an obstruction or through a gap. It occurs with any type of wave, including sound waves, water waves, electromagnetic waves such as light and radio waves, and matter displaying wave-like properties according to the wave–particle duality.
Brief historic overview

- Diffraction effects were first carefully observed and characterized in 1665 by Francesco Maria Grimaldi, who also coined the term *diffraction*.

- **Isaac Newton** studied these effects and attributed them to *inflexion* of light rays.

- **James Gregory** (1638–1675) observed the diffraction patterns caused by a bird feather, effectively the first diffraction grating.

- **Thomas Young** observed two-slit diffraction in 1803 and deduced that light must propagate as waves.

- **Augustin Jean Fresnel** did more definitive studies and calculations of diffraction, published in 1815 and 1818, and thereby gave great support to the wave theory of light that had been advanced by Christian Huygens and reinvigorated by Thomas Young, against Newton's theories.
Brief historic overview

• **X-rays**
  Wilhelm Conrad Röntgen (1845-1923)
  first Nobel laureate 1901.

• **Von Laue formulation of X-ray diffraction**
  Max von Laue (1879-1960)
  Nobel laureate 1914

• **Bragg diffraction**
  Sir William Henry Bragg (1862-1942) and Sir William Lawrence Bragg (1890-1971)
  Nobel laureate 1915
# Nobel laureates (based on Röntgen’s work)

<table>
<thead>
<tr>
<th>Year</th>
<th>Field</th>
<th>Laureate(s)</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1901</td>
<td>Physik</td>
<td>W.C. Röntgen</td>
<td>Entdeckung der Röntgenstrahlen</td>
</tr>
<tr>
<td>1914</td>
<td>Physik</td>
<td>Max von Laue</td>
<td>Beugung von Röntgenstrahlen an Kristallen</td>
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<tr>
<td>1915</td>
<td>Physik</td>
<td>W.H. Bragg W.L. Bragg</td>
<td>Analyse von Kristallstrukturen mit Hilfe von Röntgenstrahlen</td>
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<tr>
<td>1917</td>
<td>Physik</td>
<td>Charles G. Barkla</td>
<td>Entdeckung der charakteristischen Röntgenstrahlen der Elemente</td>
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<tr>
<td>1924</td>
<td>Physik</td>
<td>Manne Siegbahn</td>
<td>Entwicklung der hochauflösenden Elektronenspektroskopie</td>
</tr>
<tr>
<td>1927</td>
<td>Physik</td>
<td>Arthur H. Compton</td>
<td>Entdeckung des Comptoneffektes</td>
</tr>
<tr>
<td>1936</td>
<td>Chemie</td>
<td>Peter J.W. Debye</td>
<td>Untersuchungen zu Dipolmomenten und zur Beugung von Röntgenstrahlung</td>
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<tr>
<td>1956</td>
<td>Physiologie/Medizin</td>
<td>André Frédéric Cournand, Werner Forssmann, Dickinson W. Richards</td>
<td>Entdeckung der Katheterisierung des Herzens und den pathologischen Veränderungen im zirkularen System</td>
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<tr>
<td>1962</td>
<td>Chemie</td>
<td>Max F. Perutz, John C. Kendrew</td>
<td>Strukturanalyse von globularen Proteinen (Hämoglobin).</td>
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<tr>
<td>1962</td>
<td>Physiologie/Medizin</td>
<td>James D. Watson, Francis H. C. Crick, Maurice H.F. Wilkins</td>
<td>Entdeckung der molekularen Struktur der DNS in Form einer Doppelhelixstruktur und ihre Bedeutung für den genetischen Informationsaustausch in lebendem Gewebe</td>
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<tr>
<td>1964</td>
<td>Chemie</td>
<td>Dorothy C. Hodgkin</td>
<td>Bestimmung der biochemischen Struktur des Vitamin B12 mit Hilfe der Röntgen-Kristallographie</td>
</tr>
<tr>
<td>1979</td>
<td>Physiologie/Medizin</td>
<td>Allan M. Cormack, Godfrey N. Hounsfield</td>
<td>Entwicklung der Computertomographie</td>
</tr>
<tr>
<td>1985</td>
<td>Chemie</td>
<td>Herbert A. Hauptman, Jerome Karle</td>
<td>Entwicklung von direkten Methoden der Röntgen-Kristallographie zur Analyse chemischer Reaktionen</td>
</tr>
<tr>
<td>1988</td>
<td>Chemie</td>
<td>Johann Deisenhofer, Robert Huber, Martmut Michel</td>
<td>Bestimmung der dreidimensionalen Strukturen des photosynthetischen Reaktionszentrums</td>
</tr>
</tbody>
</table>
Particle wavelengths (reminder)
X-ray sources

Energy regime of Gamma- und X-ray radiation overlap – naming criteria is the heritage: X-ray is created by electron processes whereas Gamma radiation is a nuclear reaction product.

Typically X-ray radiation is generated by deceleration of electrons.
**X-ray sources (Synchrotron)**

Synchrotron radiation is emitted by charged relativistic particles deflected by a magnetic field tangentially to their path of motion.

In order to generate synchrotron radiation so called storage rings are used that keep the kinetic energy of the charged particles constant in order to conserve a constant energy spectrum of the radiation.

Worldwide, about 30 laboratories are able to generate synchrotron radiation. In Germany there are, among others, BESSY in Berlin, HASYLAB in Hamburg, DELTA at Universität Dortmund and ANKA in Karlsruhe.

A known natural source of synchrotron radiation is for example Jupiter which bombards its moons with synchrotron radiation.
Electron sources (reminder)

Electron guns:

- Various examples of gun design
  - Thermionic
  - Schottky
  - Field emission
- Cathode material
  - Tungsten
  - Lanthanum hexaboride (LaB$_6$)
  - Others...
- Cathode material determines emission current density

Energy scheme of various gun types
Neutron sources

Nuclear reactor
• Usually fission reactors are used to generate kinetic neutrons to serve in diffraction experiments

Spallation source
• Nuclear spallation is one of the processes by which a particle accelerator may be used to produce a beam of neutrons. A mercury, tantalum or other heavy metal target is used, and 20 to 30 neutrons are expelled after each impact of a high energy proton. Although this is a far more expensive way of producing neutron beams than by a chain reaction of nuclear fission in a nuclear reactor, it has the advantage that the beam can be pulsed with relative ease.
Bragg relation

• The diffraction equation postulated by Bragg and his son in 1914 (Nobel laureate in 1915)

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

Waves that satisfy this condition interfere constructively and result in a reflected wave of significant intensity.
The phenomenon of crystal diffraction can also be formulated in other equivalent ways. One such example is the von Laue formulation of X-ray diffraction. In this model, the crystal is instead seen as a set of identical ions resting at the sites defined by the Bravais lattice, each of which reradiate incident radiation isotropically. The condition for constructive interference in this formulation is given by:

$$\vec{R} \cdot (\vec{k} - \vec{k}') = 2\pi n,$$

where $n$ is again an integer, $k$ is the wave vector describing the incoming wave, $k'$ is the wave vector describing the outgoing wave, and $R$ is any Bravais lattice vector. This can be equivalently stated as

$$\vec{k} \cdot \vec{G} = \frac{1}{2} G^2$$

by defining $G$ to be a reciprocal lattice vector, and assuming that $|k| = |k'|$
Peak intensity depends on

\[ I = S \cdot (L \cdot P \cdot G) \cdot (A \cdot E) \cdot [H \cdot T^2 \cdot f_{hkl}^2 \cdot G_{hkl}^2] \]

- **S**: Scaling factor, depends on primary intensity, wavelength used, and scattering process involved
- **A**: Absorption
- **E**: Extinction
- **L** and **G**: Lorentz and geometry factor, reflect the fact that the incoming X-rays are non-monochromatic and not each atom is at its ideal theoretical position in space
- **P**: Polarization factor, radiation characteristics of the atomistic dipoles in the lattice
- **H**: Factor depending on the number of identical crystallographic planes
- **T**: Temperature or Debye-Waller-factor
Peak intensity depends on

\[ I = S \cdot (L \cdot P \cdot G) \cdot (A \cdot E) \cdot \left[ H \cdot T^2 \cdot f_{hkl}^2 \cdot G_{hkl}^2 \right] \]

- \( f_{hkl} \): Atomic form factor, depending on the charge density distribution of involved shell electrons
- \( G_{hkl} \): Phase factor, based on the positions of atoms in the unit cell
- \( F_{hkl} = f_{hkl} \ G_{hkl} \): Structure factor

... in this context, please remember existing extinction rules
Where to use which technique?

- **X-ray**: generic, surface sensitive, phase, texture and stress analysis
- **Electrons**: Surface sensitive, local texture and stress measurement
- **Neutrons**: global texture and stress measurement, larger volumes
X-ray diffraction

Four circle goniometer

- At the LOT a XRD 3000 PTS, provided by Seifert is used.

- Anodes used are Cr- and Cu-tubes with either fine point or line focus.

- Possible coupled or independent axes movements ($2\theta$, $\omega$ (omega), $\chi$ (Chi) and $\phi$ (Phi)) are: $2\theta$: -3 to 164°, $\omega$: -4 to 180°, $\chi$: -90 to 90° and $\phi$ with unlimited rotation and adjustable rotation speeds.

- A flat graphite monochromator, variable slits and soller systems are available to improve the quality of patterns measured. The NaI(Tl) scintillation detector is piloted by the 2 theta–arm.
X-ray diffraction

What kind of information is accessible via a diffractogramm?

- Diffractogramm → Phase analysis
- Peak intensities → Texture
- Detailed peak positions → Macro strain
- FWHM → Grain size
- Peak profile → Micro strain
**Rietveld method** (Hugo Rietveld (1932-)) allows a quantitative phase analysis in the context of X-ray and neutron diffractogramms

- Analysis of the whole diffractogramm
- Refinement of structure- as well as real-structure-parameters
  - Quantitative phase analysis
  - Lattice parameters and temperature effects
  - Grain size and micro strain
- Its not a structure analysis!
  - Basic lattice parameters,
  - phase composition, and
  - Space group needs to be known
• Motivation: In today's materials design highly textured materials are desired in order to achieve optimal performance with respect to certain applications.

• Knowledge about orientation statistics is important in the context of mechanical, electrical, magnetic, optical, and piezo-electric devices.
X-ray diffraction - texture

Heteroepitactical diamond film


{111} X-ray-Pole figure
Electron diffraction SEM/TEM

Benefits

• The wavelength of electron accelerated in a SEM/TEM is much smaller than that of the radiation usually used for X-ray diffraction experiments. A consequence of this is that the radius of the Ewald sphere is much larger in electron diffraction experiments than in X-ray diffraction. This allows the diffraction experiment to reveal more of the two dimensional distribution of reciprocal lattice points.

• Furthermore, the electron lenses allows the geometry of the diffraction experiment to be varied. The conceptually simplest geometry is that of a parallel beam of electrons incident on the specimen. However, by converging the electrons in a cone onto the specimen, one can in effect perform a diffraction experiment over several incident angles simultaneously. This technique is called Convergent Beam Electron Diffraction (CBED) and can reveal the full three dimensional symmetry of the crystal.

• In a TEM, a single crystal grain or particle may be selected for the diffraction experiments. This means that the diffraction experiments can be performed on single crystals of nanometer size, whereas other diffraction techniques would be limited to studying the diffraction from a multicrystalline or powder sample. Furthermore, electron diffraction in TEM can be combined with direct imaging of the sample, including high resolution imaging of the crystal lattice, and a range of other techniques. These include chemical analysis of the sample composition through energy-dispersive X-ray spectroscopy and investigations of electronic structure and bonding through electron energy loss spectroscopy.
Limitations

- Electron diffraction in TEM is subject to several important limitations. First, the sample to be studied must be electron transparent, meaning the sample thickness must be of the order of 100 nm or less. Careful and time consuming sample preparation may therefore be needed. Furthermore, many samples are vulnerable to radiation damage caused by the incident electrons.

- The study of magnetic materials is complicated by the fact that electrons are deflected in magnetic fields by the Lorentz force. This may sometimes make crystal structure determination virtually impossible.

- Furthermore, electron diffraction is often regarded as a qualitative technique suitable for symmetry determination, but too inaccurate for determination of lattice parameters and atomic positions. In principle, this is not quite the case: lattice parameters of high accuracy can in fact be obtained from electron diffraction, relative errors less than $10^{-3}$ have been demonstrated. However, the right experimental conditions may be difficult to obtain, and these procedures are often viewed as too time consuming and the data too difficult to interpret. X-ray or neutron diffraction are therefore often the preferred methods for determining lattice parameters and atomic positions.

- However, the main limitation of electron diffraction in TEM remains the comparatively high level of user interaction needed. Whereas both the execution of powder X-ray (and neutron) diffraction experiments and the data analysis are highly automated and routinely performed, electron diffraction requires a much higher level of user input.
Electron backscatter diffraction (EBSD)

• Its possible to fully automate this technique (including indexing)
• Measurement time on the order of hours
• Achievable lateral resolution on the order of 30 nm
Kikuchi lines (first reported in 1928)

- Electrons which have been inelastically scattered can subsequently be diffracted.
- Two sets of electrons will be able to do this - those at $+\theta_B$ and those at $-\theta_B$.
- This diffraction results in intensity changes in the background. Because there are more electrons at A than B (since electrons passing through A are closer to the incident direction than those through B) one bright line is developed (the excess line) together with one dark line (the deficit line).
- Because the electrons are inelastically scattered in all directions, the diffracted electrons will form a cone, not a beam.
Electron backscatter diffraction (EBSD)

- Possible to fully automate this technique (including indexing)
- Measurement time on the order of hours
- Achievable lateral resolution on the order of 30 nm
3D Electron backscatter diffraction (3D-EBSD)

- State of the art in orientation microscopy
<table>
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<tr>
<th></th>
<th>FEG-SEM / EBSD</th>
<th>Analytical TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spatial resolution</strong></td>
<td>2 nm</td>
<td>0.5 nm</td>
</tr>
<tr>
<td>Image</td>
<td>30 nm (Fe)</td>
<td>0.5...0.01°</td>
</tr>
<tr>
<td>Diffraction</td>
<td>60 nm (Al)</td>
<td></td>
</tr>
<tr>
<td><strong>Angular resolution</strong></td>
<td>0.5...0.1°</td>
<td>0.5...0.01°</td>
</tr>
<tr>
<td><strong>Visibility of lattice defects</strong></td>
<td>for $\Delta g &gt; 0.1^\circ$</td>
<td>all</td>
</tr>
<tr>
<td>Grain boundaries</td>
<td>rarely or indirectly</td>
<td>direct observation</td>
</tr>
<tr>
<td>Line defects</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample preparation</td>
<td>easy</td>
<td>complicated</td>
</tr>
<tr>
<td>Observable areas</td>
<td>large (up to cm$^2$)</td>
<td>small (&lt; 50 x 50 μm$^2$)</td>
</tr>
<tr>
<td>Automation</td>
<td>high</td>
<td>medium</td>
</tr>
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</table>
Selected area diffraction (SAD)

- Selected area diffraction, abbreviated as SAD, is a crystallographic experimental technique that can be performed inside a transmission electron microscope (TEM).
- As a diffraction technique, SAD can be used to identify crystal structures and examine crystal defects. It is similar to x-ray diffraction, but unique in that areas as small as several hundred nanometres in size can be examined, whereas x-ray diffraction typically samples areas several centimetres in size.
- SAD is used primarily in material science and solid state physics, and is one of the most commonly used experimental techniques in those fields.
Selected area diffraction (SAD)

Copper-filled multi-walled carbon nanotube. The growth direction of the Cu-nanowire is $<111>$. 
Neutron diffraction

General

• Neutrons as quantum particles can exhibit wave phenomena we typically associate with light or sound. Diffraction is one of these phenomena; it occurs when waves encounter obstacles whose size is comparable with the wavelength.

Benefits of neutron diffraction

• The scattering cross section of a neutron depends on the individual properties of the nucleus it is scattered at. Therefore it may vary for each nucleus as well as different isotopes
• In contrast to this X-rays are scattered mainly at the electron cloud and have, therefore, an increasing interaction cross-section with increasing atomic number. Hydrogen is nearly invisible for X-rays
• In many biological sample X-ray diffraction analysis is complemented by neutron scattering in order to determine the position of Hydrogen within the structures
• Neutrons have a magnetic moment and scatter at magnetic grids. Because of that, neutron diffraction is an invaluable tool to characterize magnetic structures
• Slow neutrons feature energies of only a few meV. Their energy is on the same order as that of phonons and magnons. Inelastic neutron diffraction is thus a standard tool in characterizing phonon and magnon dispersion
Final remarks

• Diffraction techniques, based on instrumentation development, are still invaluable tools in determining materials structure
• Based on SAD in a TEM it's possible to determine the crystallographic orientation of nanostructures such as metal nanowires and others
• X-ray diffraction is still the standard tool to access structure and phase compositions of crystalline materials (electron and neutron diffraction are in general reserved for specific applications)

• No results have been shown in the context of amorphous materials
• Radiation damage has been ignored