Electron Diffraction

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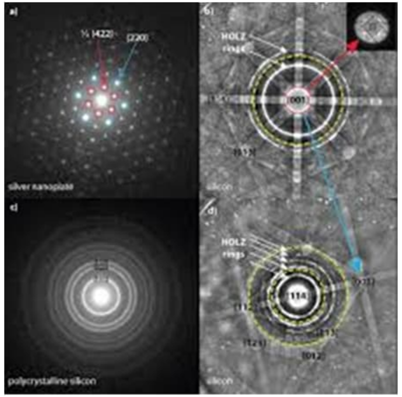
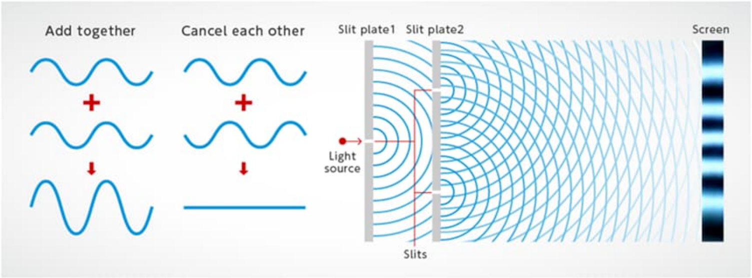


- History, principle of the technique
- Process explained, type of information gained
- More detail on certain steps
    - Explaining the rings/stars seen in the diffraction pictures
    - Reciprocal space
- Influential improvements (similar to aberration correction in TEM)
- Pros & cons

The Historical Evolution of Electron Diffraction

Discovery of Electrons (1897): J.J. Thomson's groundbreaking experiment led to the discovery of electrons, setting the stage for the development of electron diffraction [1].

Wave-Particle Duality (1924): Louis de Broglie proposed the theory of wave-particle duality, postulating that electrons can exhibit both particle-like and wave-like properties, a fundamental concept for electron diffraction



Source:https://photonterrace.net/en/photon/duality/

The Historical Evolution of Electron Diffraction

First Electron Diffraction Experiment (1927): Clinton Davisson and Lester Germer performed the first successful electron diffraction experiment, confirming de Broglie's hypothesis and paving the way for future developments

Development of Electron Microscopy (1930s): Ernst Ruska and Max Knoll developed the first electron microscope, which utilized the principles of electron diffraction to provide highly magnified images of specimens

https://en.wikipedia.org/wiki/Lester_Germer#/media/File:Davisson_and_Germer.jpg

The Historical Evolution of Electron Diffraction

Advancement of Electron Diffraction Techniques (1940s-1980s): Various techniques like selected area electron diffraction (SAED), convergent beam electron diffraction (CBED), and high-resolution electron microscopy (HRTEM) were developed during this period, broadening the applications of electron diffraction

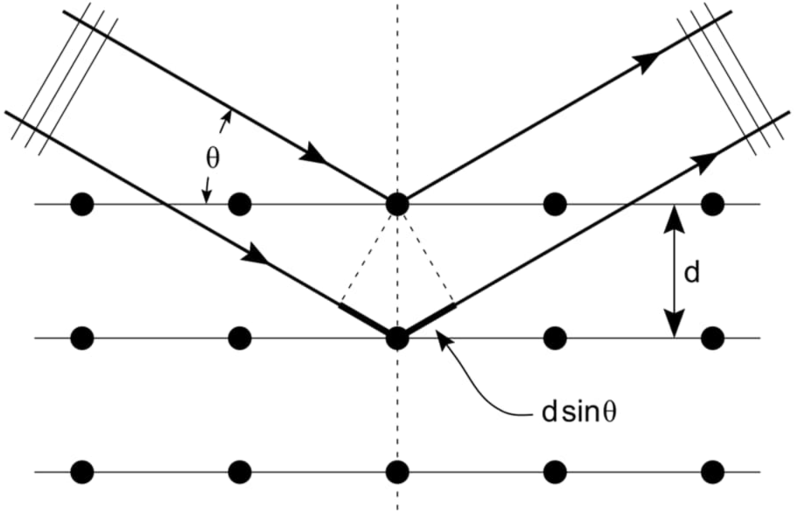
Electron Crystallography (1990s-Present): This method has gained prominence in recent years for its ability to determine the atomic structure of materials, especially those that are challenging to crystallize for X-ray crystallography [2].

https://en.wikipedia.org/wiki/Electron_diffraction#/media/File:Ernst_Ruska_Electron_Microscope_-_Deutsches_Museum_-_Munich-edit.jpg

Basic Principle of Electron Diffraction

Wave-Particle Duality: As per Louis de Broglie's hypothesis, electrons behave as both particles and waves. This wave-like behavior allows for their diffraction when passed through a crystal lattice

Bragg's Law: This fundamental law describes the angles for coherent and incoherent scattering from a crystal lattice. When incoming electron waves interact with the crystal lattice, they get diffracted, forming a pattern that can be analyzed [3].

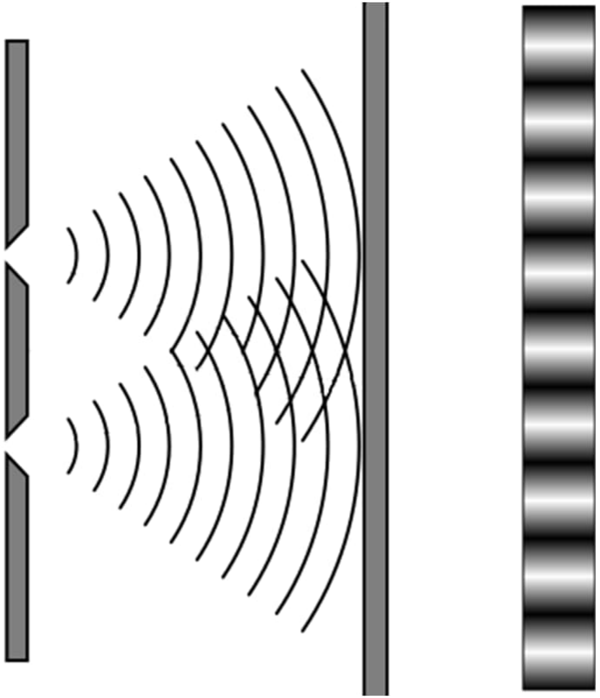


https://en.wikipedia.org/wiki/Bragg%27s_law#/media/File:Bragg_diffraction_2.svg

Principle - Interaction with the Sample

Electron-Atom Interactions: When a beam of electrons strikes a sample, various interactions can occur, including elastic and inelastic scattering. In the case of elastic scattering, the electrons retain their energy but change direction, contributing to the diffraction pattern

Diffraction Pattern: The resultant diffraction pattern is a consequence of the interference of diffracted electron waves. This pattern is unique to the atomic arrangement of the material under investigation, allowing for its structural analysis [4].

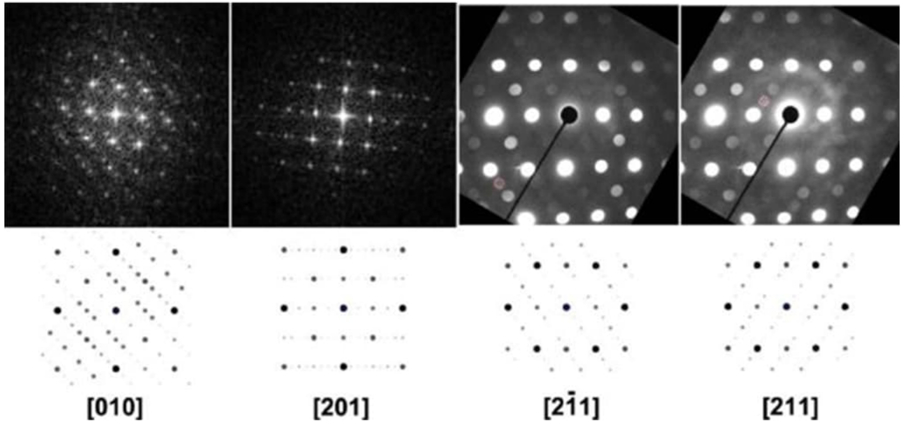


https://waves.neocities.org/diffractionpatterns

Principle - Interpretation of Diffraction Patterns

Fourier Transform: The diffraction pattern can be considered as the Fourier transform of the object's electron density. Thus, by interpreting the diffraction pattern, one can deduce the structural information about the sample [5].

Phase Problem: Determining the phases of the diffracted waves is a fundamental challenge in electron diffraction.



https://www.researchgate.net/profile/Judith-Macmanus-Driscoll

Information from Electron Diffraction

Defect Analysis: Electron diffraction can also help identify structural defects in a material. Dislocations, stacking faults, or twins can be identified through analysis of diffraction patterns [6].

Phase Identification: Electron diffraction is essential in phase identification, which determines the various crystalline phases present within a multi-phase material

Atomic Arrangement: Electron diffraction is a powerful tool for understanding the atomic arrangement within a material. The diffraction patterns can provide information about atomic spacing, crystal symmetry, and crystal orientation

Information from Electron Diffraction

Molecular Structure: Electron diffraction can be used to determine the structure of individual molecules. This includes bond lengths, bond angles, and the overall shape of the molecule

Dynamics and Vibrations: Electron diffraction can be used to study molecular dynamics and vibrations, particularly using time-resolved electron diffraction methods

Key Formulas in Electron Diffraction

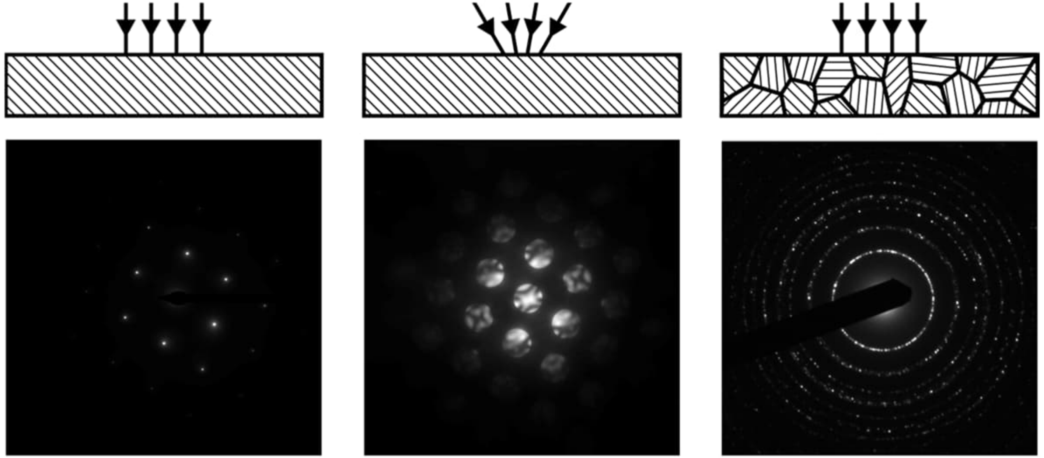
de Broglie Wavelength: The wavelength of electrons (λ) is given by de Broglie's equation: $\lambda = h / (p)$

Bragg's Law: This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing: $n\lambda = 2d \sin \theta$

Scherrer Equation: This equation is used to determine crystallite size (D) from the broadening of diffraction peaks: $D = K\lambda / (\beta \cos \theta)$, where K is a dimensionless shape factor, β is the full-width at half-maximum (FWHM) of the peak, and θ is the Bragg angle

Representation of Electron Diffraction Data

Diffraction Pattern: The most direct graphical representation of electron diffraction data is the diffraction pattern itself, which can be a series of spots, rings, or a combination of both, depending on the sample's crystallinity and orientation [7].

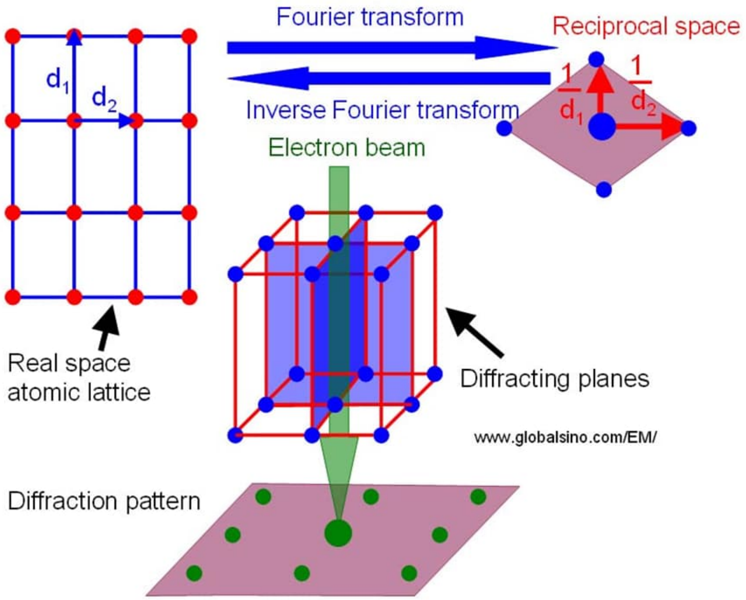


https://en.wikipedia.org/wiki/Electron_diffraction#/media/File:Difrakce.png

Interpreting Electron Diffraction Patterns

Spot Patterns: The positions of the spots in the diffraction pattern correspond to the reciprocal lattice of the sample. The angles and distances between spots can be used to determine the size and shape of the unit cell

Reciprocal Space: The patterns seen in electron diffraction represent the Fourier transform of the real-space structure and are displayed in what we call reciprocal space. Each point in reciprocal space corresponds to a plane in real space, with the point's distance from the origin inversely proportional to the plane's interatomic spacing [8].



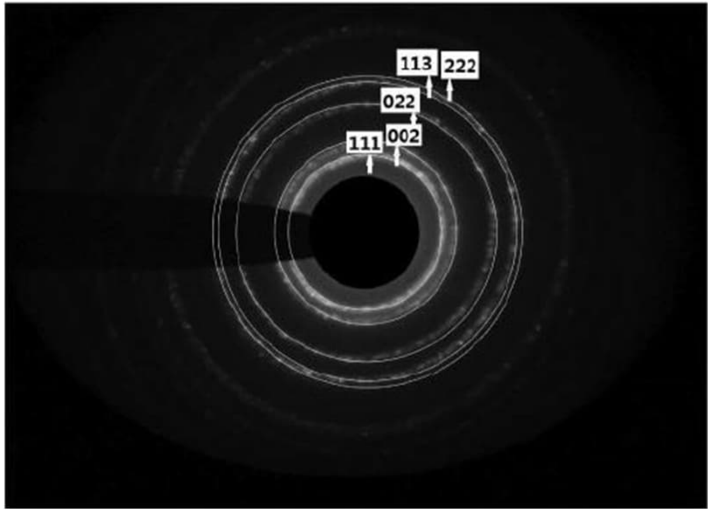
https://www.globalsino.com/EM/page2718.html

Interpreting Electron Diffraction Patterns

Ring Patterns: These patterns typically indicate the presence of an amorphous or polycrystalline material. The radii of the rings correspond to the interplanar spacing of the material's structure

Rings in Electron Diffraction: The presence of rings in an electron diffraction pattern is indicative of a polycrystalline or amorphous material. Each ring corresponds to a set of planes with a specific interatomic distance (d-spacing), with the center of the diffraction pattern corresponding to the direct beam (unscattered beam). [9].

For a polycrystalline sample, the rings result from the random orientation of many tiny crystallites. Each ring represents one specific family of lattice planes

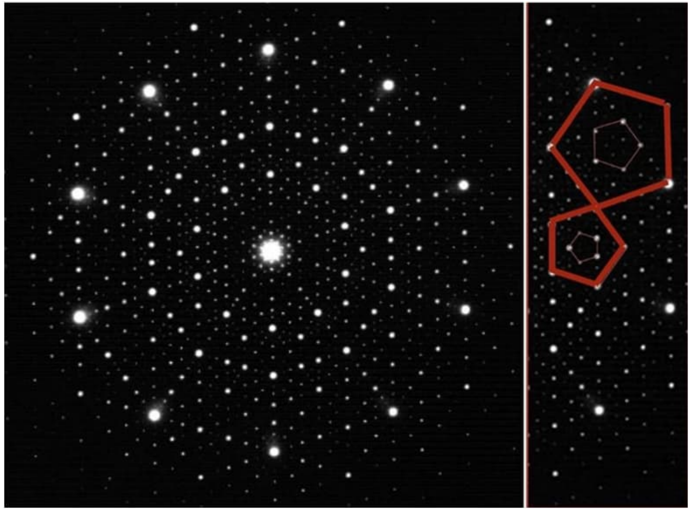


https://www.researchgate.net/profile/Mohammad-Eskandari-3

Interpreting Electron Diffraction Patterns

D-spacing Calculation: The distance between planes of atoms (d-spacing) can be calculated from the diffraction pattern using Bragg's law. This provides valuable insights into the crystal structure [4].

Stars in Electron Diffraction: The star-shaped patterns usually appear in selected area electron diffraction (SAED) of single crystals. This pattern results from the rotation of the crystal around an axis perpendicular to the electron beam. The diffraction spots form a series of arcs due to the continuous rotation of the crystal. Each point on these arcs corresponds to a specific crystal plane [3].

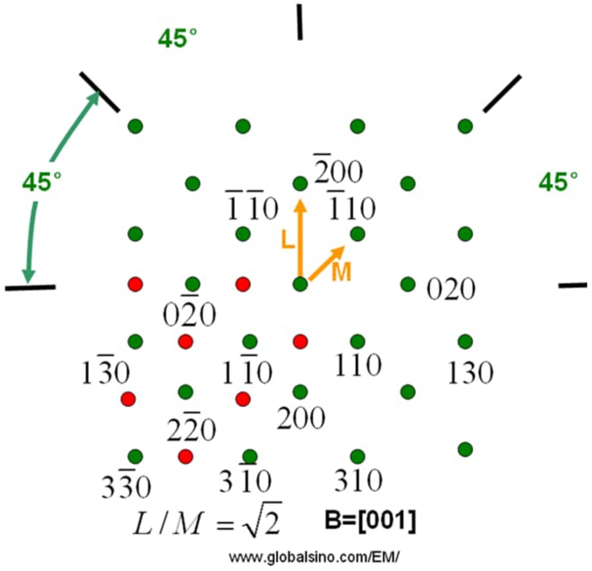


https://www.nist.gov/image/quasicrystals-kuojpg

Interpreting Electron Diffraction Patterns

Indexing: This involves assigning Miller indices (hkl) to the observed spots or rings in the diffraction pattern, which represent specific crystal planes. Indexing helps in identifying crystal symmetry and phases

Quantitative Phase Analysis: The intensities of the diffraction spots or rings can be used to determine the relative amounts of different phases in a multiphase material



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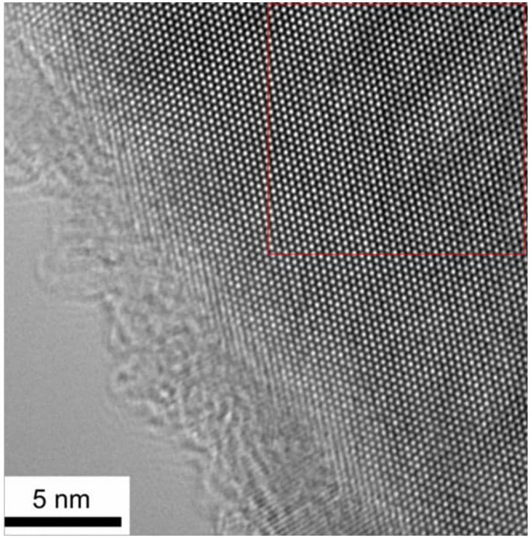
In Practice



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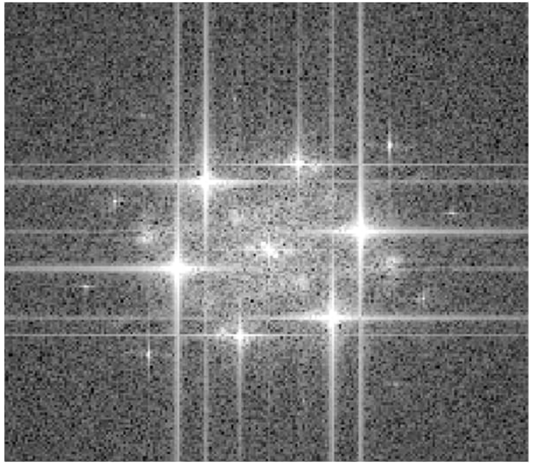
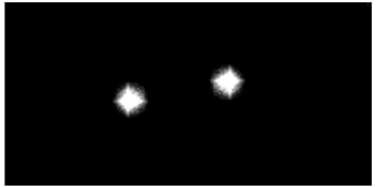
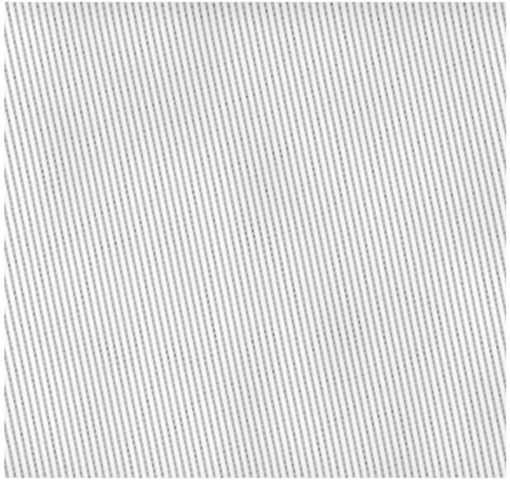
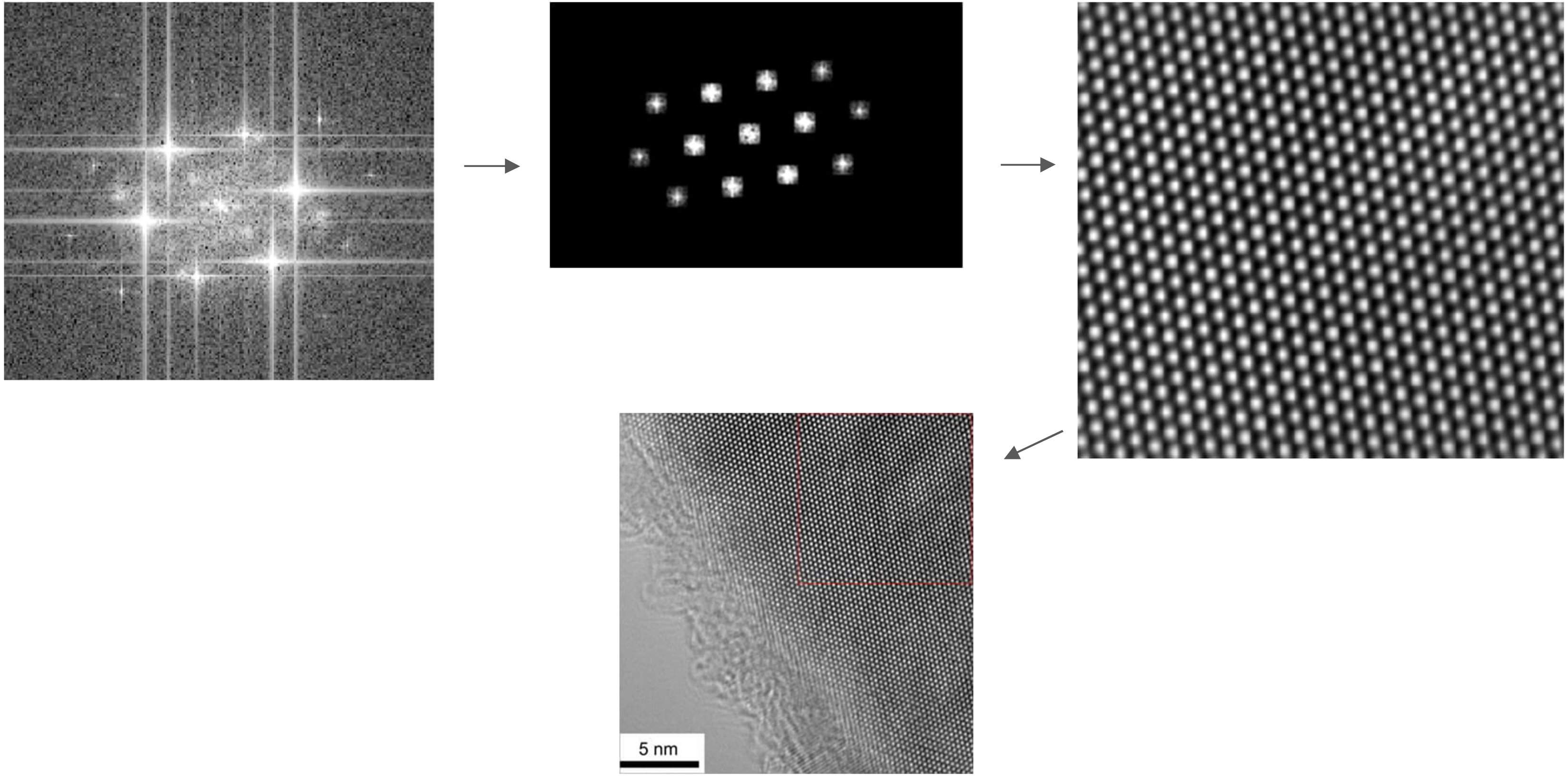




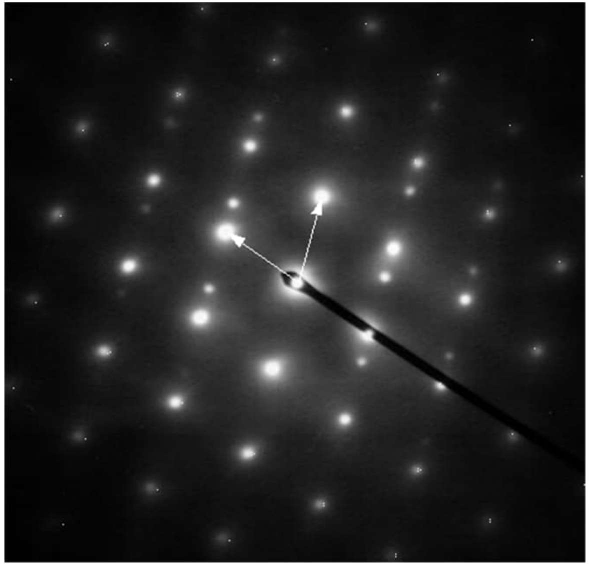


Pictures made using DigitalMicrograph from Gatan

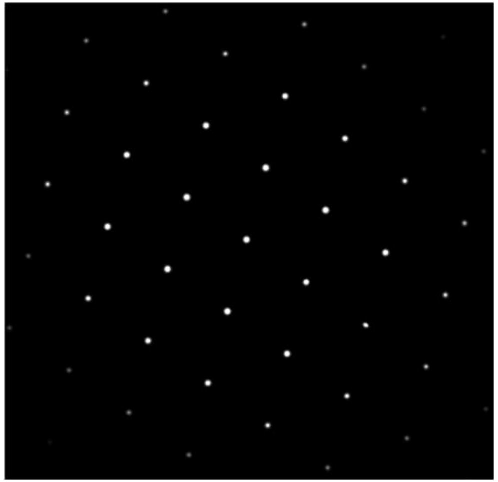
Diffraction pattern = Image

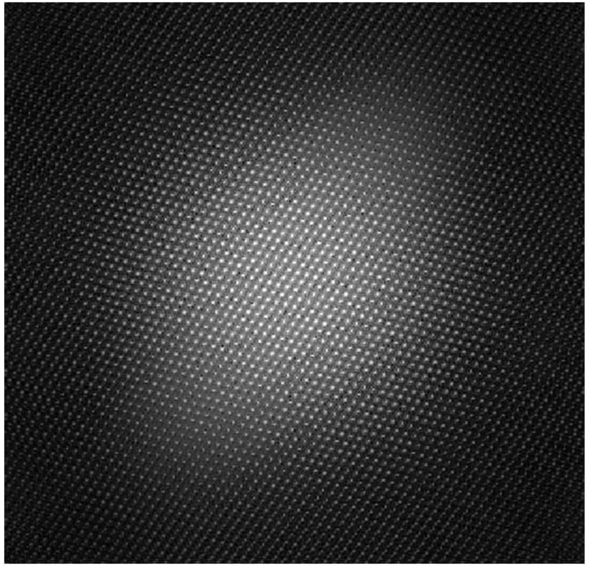


Another Example



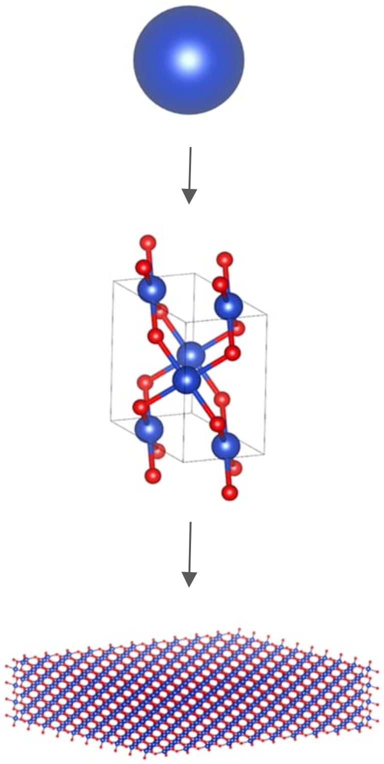
https://en.wikipedia.org/wiki/Electron_diffraction#/media/File:Austenite_ZADP.jpg





Diffraction Intensity and Geometry analysis

Intensity: The intensity of a diffraction spot can be understood by three different concepts, atomic scattering factor, structure factor, and crystal shape factor. The atomic scattering factor describes the effects of a single atom. The Structure factor describes the effects of a unit cell. The crystal shape factor describes the effects of the real crystal.



Atomic scattering factor

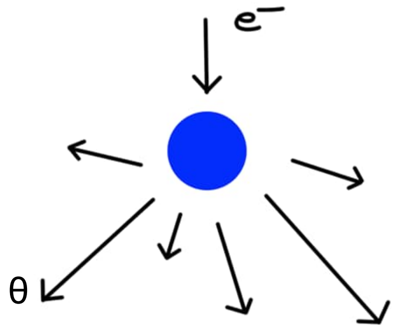
The atomic scattering factor measures the scattering of an electron wave by a single atom. It is defined by the following equation:

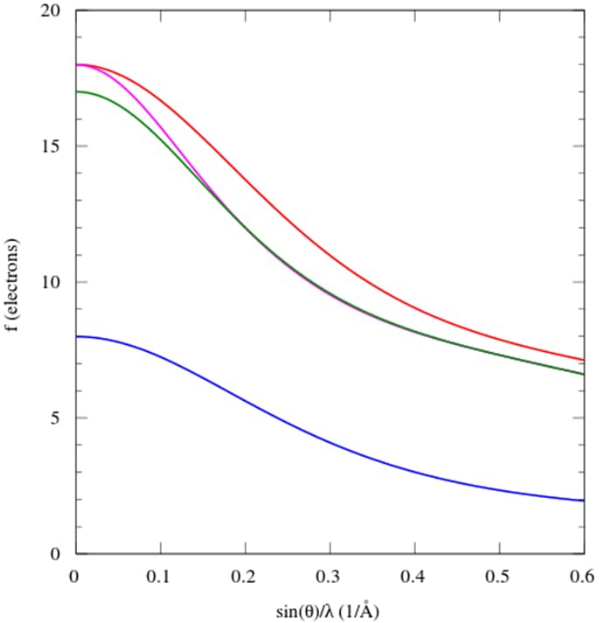
$f(\mathbf{Q}) = \int \rho(\mathbf{r})\, e^{i\mathbf{Q}\cdot\mathbf{r}}\, d^3\mathbf{r}.$

Momentum transfer: $\mathbf{Q} = 4\pi \sin(\theta)/\lambda$

Spatial density: $\rho(\mathbf{r}) \propto Z$

$f(\mathbf{Q})$ decreases when θ increases, Z is low, and λ decreases (high-voltage)





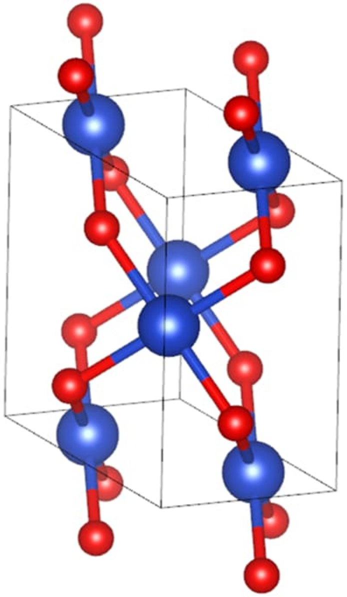
Structure Factor

The structure factor describes contributions from all the atoms in a unit cell. These include atom locations, types, and amounts.

$F(hkl) = \sum f_j^e \exp[2\pi i(hx_j + ky_j + lz_j)]$

Each atom has an atomic scattering factor, f_j^e, and a location, (x_j, y_j, z_j).

The structure factor relates to the amplitude of electrons diffracted from some (*hkl*) lattice plane.



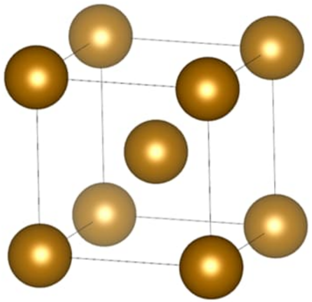
Example: b.c.c Iron

$F(hkl) = \sum f_{Fe}^{e} \exp[2\pi i(hx_j + ky_j + lz_j)]$

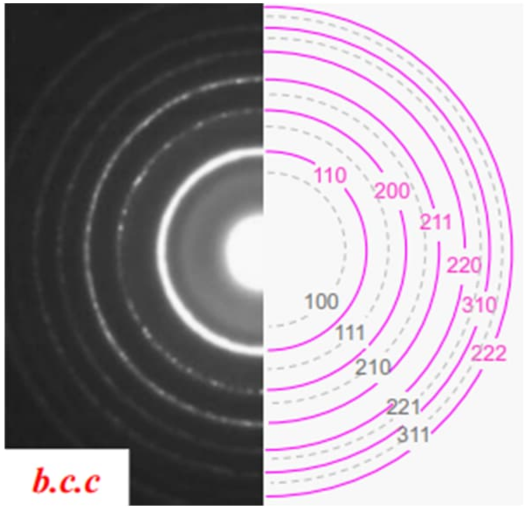
$= f_{Fe}^{e} \exp[2\pi i(0+0+0)] +$
$f_{Fe}^{e} \exp[2\pi i(0.5h+0.5k+0.5l)]$

$= f_{Fe}^{e} + f_{Fe}^{e} \exp[\pi i(h+k+l)] = f_{Fe}^{e} + f_{Fe}^{e} (-1)^{(h+k+l)}$

Contains atoms at
0,0,0, and 0.5, 0.5, 0.5



⇒ if h+k+l is uneven, structure factor is zero

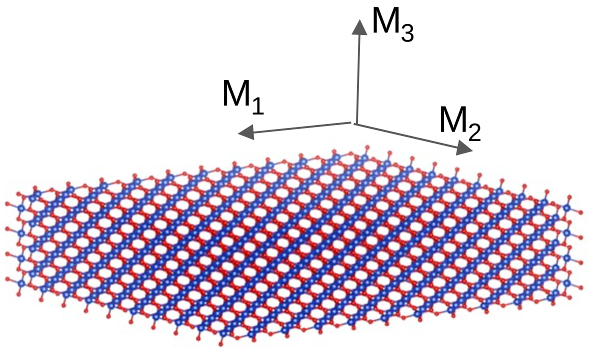


Diffraction rules

The structure factor can be used to calculate the electron diffraction rules:

Simple Cubic	All h, k, l
Body-centered Cubic	$h + k + l = 2n$
Face-centered Cubic	h, k, l all odd, or all even
Hexagonal Close-packed	$h + 2k \neq 3n$, or $h + 2k = 3n$ and l is even

Crystal shape factor



All the individual unit cells contribute towards the amplitude of a diffracted beam.

$A(hkl) = F(hkl) \sum \sum \sum \exp[2\pi i(s_1 u+s_2 v+s_3 w)]$ ⇔ Sum of scattering by all unit cells

The intensity for hkl is equal to amplitude squared:

$I(hkl) = |A(hkl)|^2 =$

$|F(hkl)|^2 \times \sin^2(\pi M_1 s_1)/\sin^2(\pi s_1) \times \sin^2(\pi M_2 s_2)/\sin^2(\pi s_2) \times \sin^2(\pi M_3 s_3)/\sin^2(\pi s_3) =$
$= |F(hkl)|^2 \times |G(s_1,s_2,s_3)|^2$.

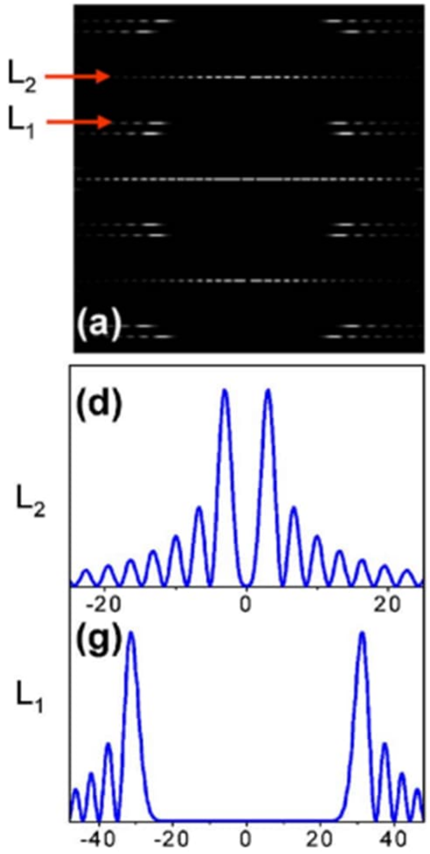
The crystal shape factor, $G(s_1,s_2,s_3)$, basically combines the structure factor of one unit cell with however many cells there are in the sample

Electron Diffraction in Research 1

Using electron diffraction to determine the (n,m) indices of single-walled carbon nanotubes [10].

A calibration-free method to find the (n,m) indices with high precision. Works well also for diffraction patterns of relatively low resolution.

They used the L1 and L2 functions to calculate some characteristic ratios whose values can be converted to the (n,m) indices using their table for Bessel factors.



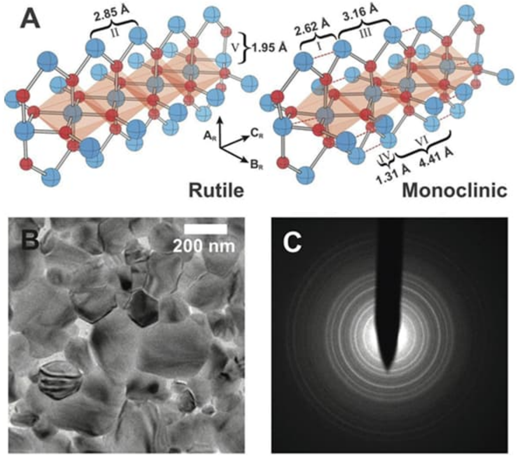
[10]

Electron Diffraction in Research 2

Using ultrafast electron diffraction to reveal the switch from semiconductor to metal for VO_2 [11].

A combination of ultrafast electron diffraction and infrared transmissivity experiments was able to show the lattice and charge density reorganizations from semiconductor to metal.

They were also able to make a metastable state with the lattice characteristics of the semiconductor and metal-like mid-infrared optical properties.



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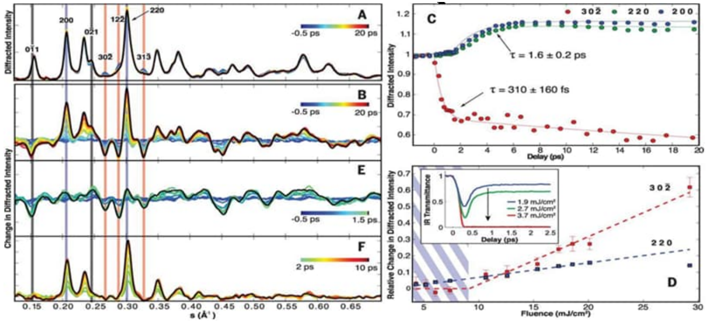

Pros & Cons

- \+ A diffraction pattern contains lots of information about the crystal structure of a material
- \+ The fourier transformation of a diffraction pattern is the image of the sample
- \+ Electrons have a shorter wavelength than x-rays, which leads to a higher resolution and smaller possible sample size

- \- Electron diffraction is often a part of TEM, which is expensive
- \- Only shows lattice planes visible from current crystal orientation. Needs multiple crystals or images to show all the lattice planes
- \- Requires an extremely thin sample so that electrons can pass through
- \- High vacuum is necessary to remove atoms surrounding the sample that might interfere with the scattering

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