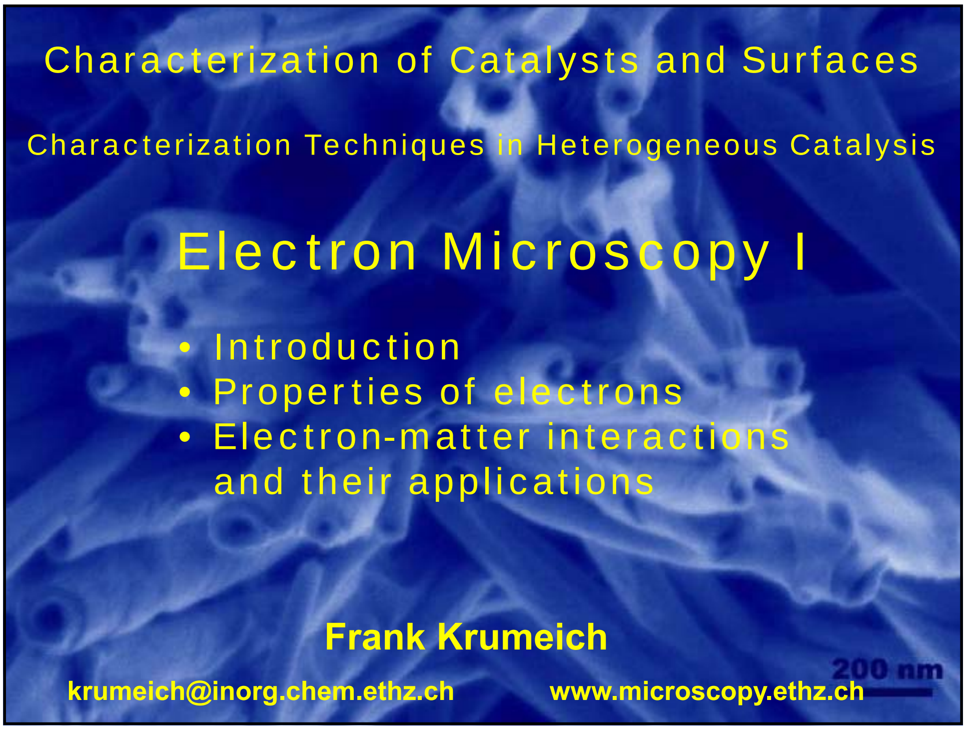


Characterization of Catalysts and Surfaces

Characterization Techniques in Heterogeneous Catalysis

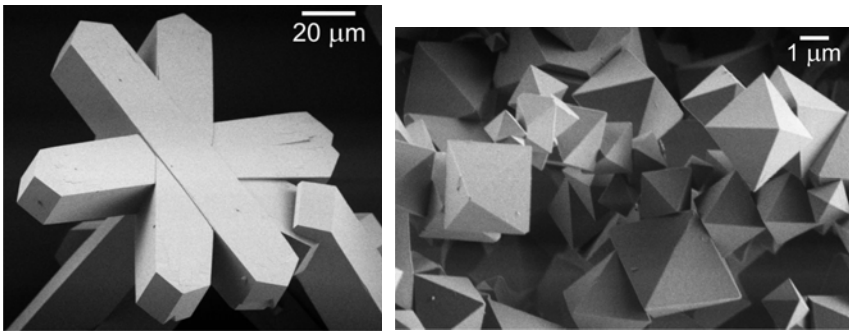
Electron Microscopy I

- Introduction
- Properties of electrons
- Electron-matter interactions and their applications

Frank Krumeich

krumeich@inorg.chem.ethz.ch www.microscopy.ethz.ch

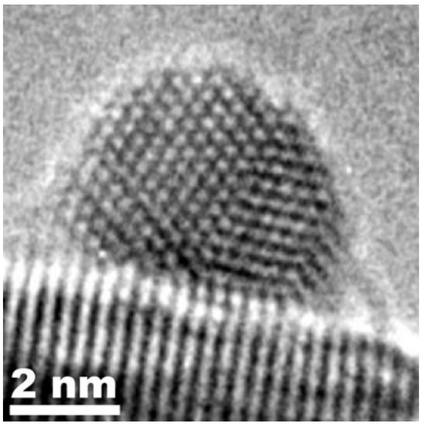
How do crystals look like? Shape?



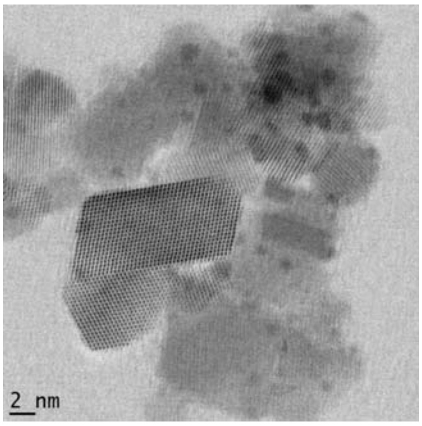
SEM images of zeolithes (left) and metal organic frameworks (MOF, right)

Examples: electron microscopy for catalyst characterization

How does the Structure of catalysts look like? Size of the particles?



HRTEM image of an Ag particle on ZnO

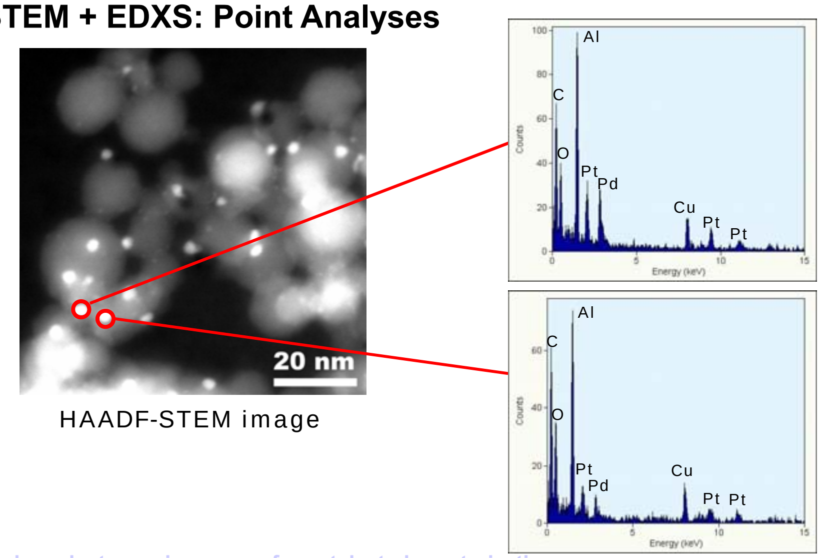


BF-STEM image of Pt particles on CeO_2

Examples: electron microscopy for catalyst characterization

Pd and Pt supported on alumina: Size of the particles? Alloy or separated?

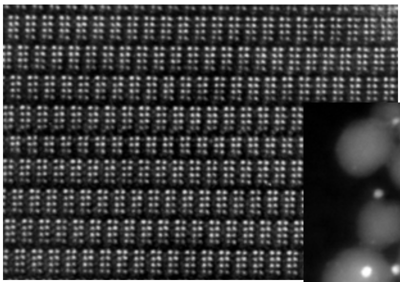
STEM + EDXS: Point Analyses



HAADF-STEM image

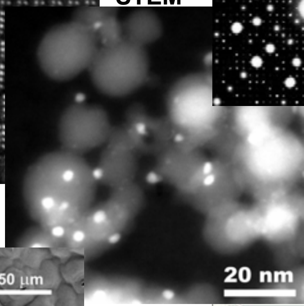
Examples: electron microscopy for catalyst characterization

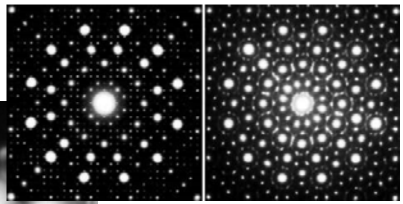
Electron Microscopy Methods (Selection)



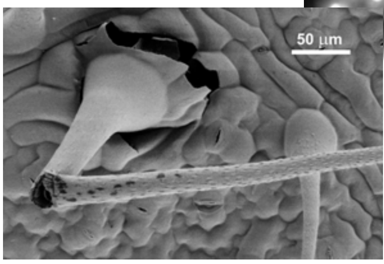
HRTEM

STEM



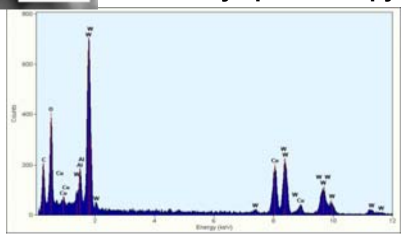


Electron diffraction

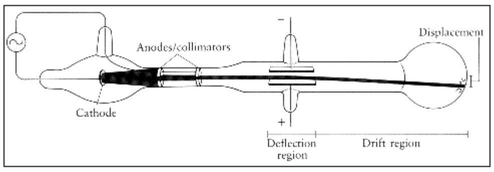


SEM

X-ray spectroscopy



Discovery of the Electron



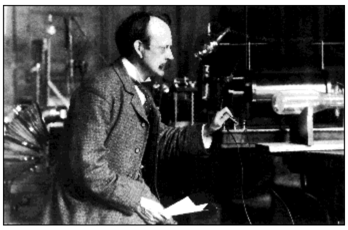
1897 J. J. Thomson:

Experiments with cathode rays

⇒ hypotheses:

(i) Cathode rays are charged particles ("corpuscles").

(ii) Corpuscles are constituents of the atom.



Joseph John Thomson (1856-1940)
Nobel prize 1906

Properties of Electrons

Dualism wave-particle

De Broglie (1924): $\lambda = h/p = h/mv$

λ : wavelength; h: Planck constant; p: momentum

Accelerated electrons: $E = eV = m_0v^2/2$

V: acceleration voltage
e / m_0 / v: charge / rest mass / velocity of the electron

$$p = m_0v = (2m_0eV)^{1/2}$$

$$\lambda = h / (2m_0eV)^{1/2} \ (\approx 1.22 / V^{1/2} \text{ nm})$$

Relativistic effects:

$$\lambda = h / [2m_0eV (1 + eV/2m_0c^2)]^{1/2}$$

Electron

Properties of Electrons

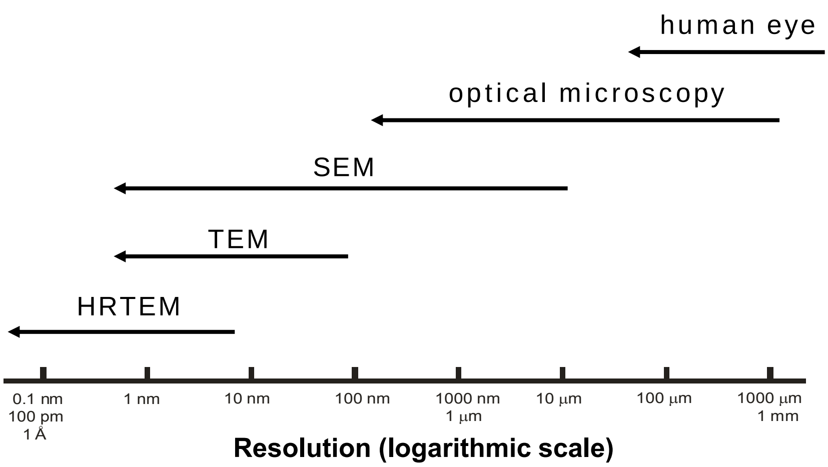
V_{acc} kV	Nonrel. λ pm	Rel. λ pm	Mass x m_0	V_{nonrel} x 10^8 m/s	v_{rel} x 10^8 m/s
100	3.86	3.70	1.20	1.88	1.64
200	2.73	2.51	1.39	2.65	2.09
300	2.23	1.97	1.59	3.25	2.33
400	1.93	1.64	1.78	3.75	2.48
1000	1.22	0.87	2.96	5.93	2.82

Rest mass of an electron: $m_0 = 9.109 \times 10^{-31}$ kg

Speed of light in vaccuum: $c = 2.998 \times 10^8$ m/s

Electron

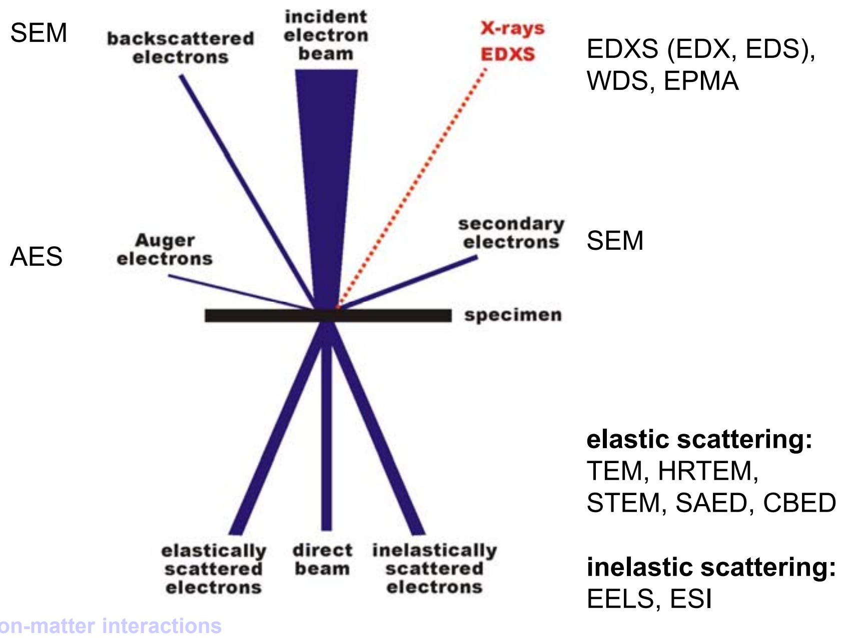
Working ranges of various types of microscopes



SEM: scanning electron microscopy

(HR)TEM: (high-resolution) transmission electron microscopy

Interactions of Electrons with Matter



Interactions of Electrons with Matter

- Elastic interactions

Incident electrons with energy E_0 pass through a sample or are scattered without energy transfer.

$$E_{el} = E_0$$

- Inelastic interaction

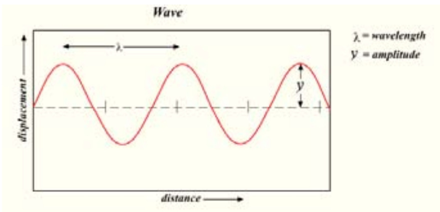
Transfer of energy from the electron to the matter, causing various effects, e.g., ionization.

$$E_{el} < E_0$$

Elastic Electrons-Matter Interactions

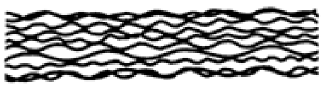
Elastic scattering of a incoming coherent electron wave:

- **Scattering of electrons by individual atoms**
  - ➢ **scattered waves are incoherent**
- **Scattering of electrons by a collective of atoms (crystal)**
  - ➢ **scattered waves are coherent**



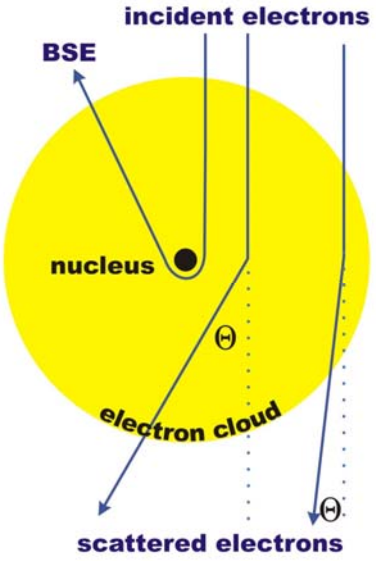
period: time for one complete cycle for an oscillation
frequency: periods per unit time (measured in Hertz)

Coherent waves have the same wave-length and are in phase with each other



Incoherent waves

Scattering of Electrons at an Atom



$F = Q_1Q_2 / 4\pi\varepsilon_0 r^2$

ε_0: dielectric constant

Weak Coulomb interaction within the electron cloud

⇒ low-angle scattering

Strong Coulomb interaction with the nucleus

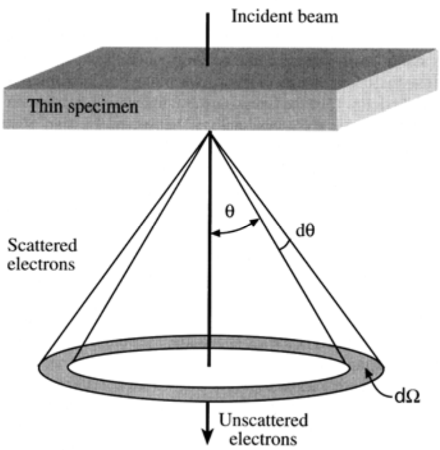
⇒ scattering into high angles or even backwards (Rutherford scattering)

⇒ atomic-number (*Z*) contrast

$$d\sigma/d\Omega \sim Z^2$$

Elastic interactions

Electron Scattering



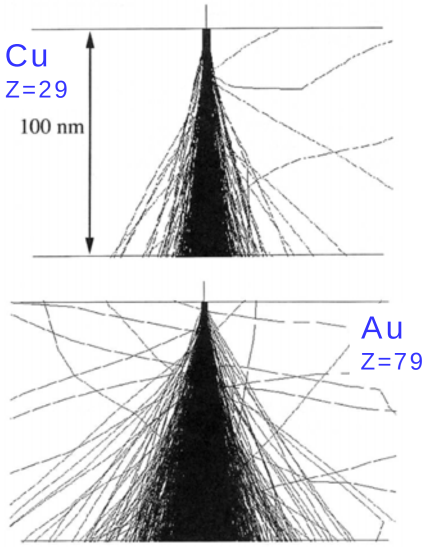
Interaction cross section σ = probability that a scattering event will occur

$$\sigma_{total} = \sigma_{elastic} + \sigma_{inelastic}$$

Differential cross section
dσ/dΩ = angular distribution of scattering
often: measured quantity

Elastic interactions

Elastic Scattering of Electrons



Monte-Carlo simulations of paths of scattered electrons

Amount of high-angle scattering or even backscattering of incident electrons

⇒ increases with increasing atomic number (e. g., scattering cross section $\sigma_{Au} >> \sigma_{Cu}$)

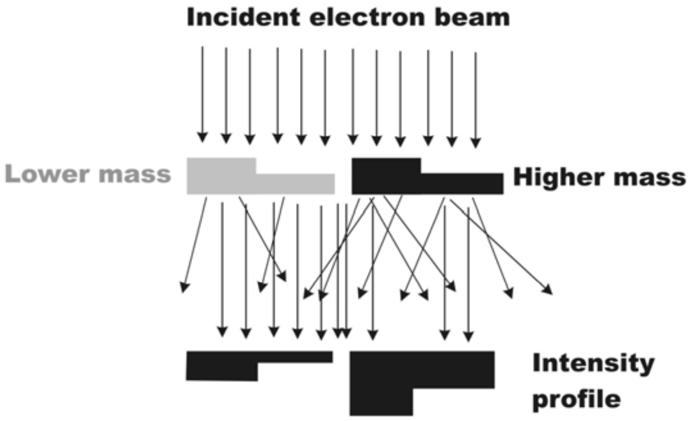
⇒ decreases with increasing electron energy

As a general effect of scattering events, the incoming electron beam is weakened and broadened

⇒ brightness of the direct beam depends on the material

⇒ contrast between different materials

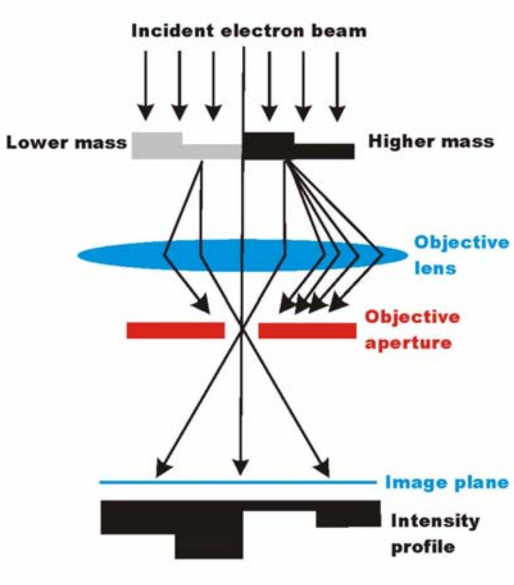
Contrast Formation



A strong decrease of incoming electron beam intensity occurs

- if many atoms scatter, i.e. in thick areas
- if heavy atoms scatter

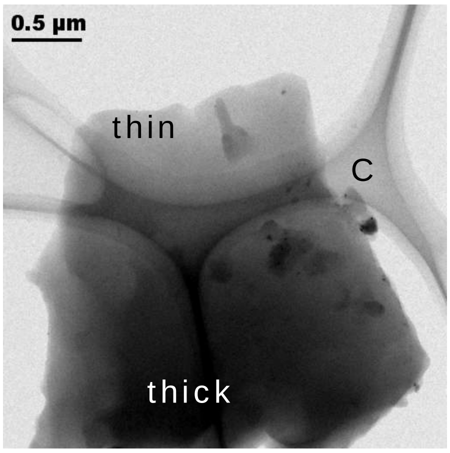
Mass-Thickness Contrast



Dark contrast in BF-TEM images appears

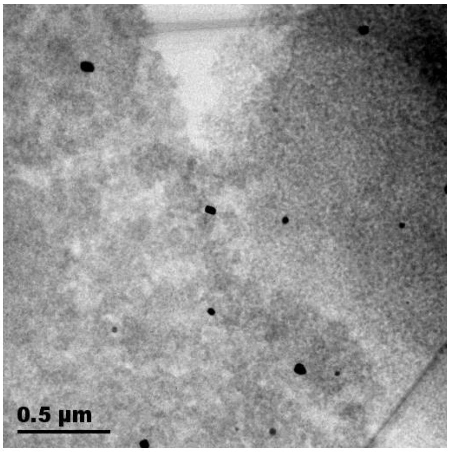
- **if many atoms scatter (thick areas darker than thin areas)**
- **if heavy atoms scatter (areas with heavy atoms darker than such with light atoms)**

Bright Field TEM Images



Amorphous SiO_2 on C foil

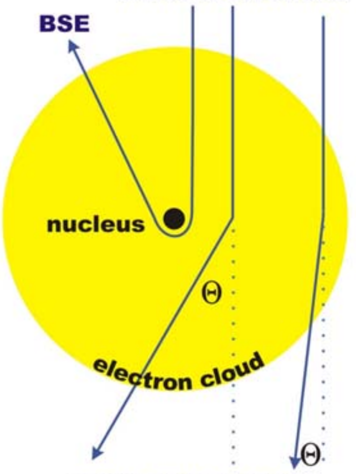
Mainly thickness contrast



Au particles on TiO_2

Mainly mass contrast

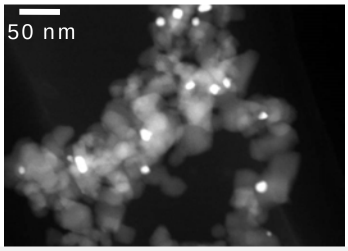
Elastic Scattering of Electrons by an Atom



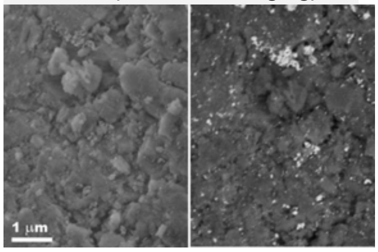
$d\sigma/d\Omega \sim Z^2$

Elastic interactions

Applications



HAADF-STEM of Au particles on titania (Z contrast imaging)

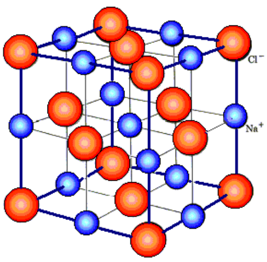


SEM of Pt particles on alumina: imaging with secondary electrons (left) and back-scattered electron (right)

Crystals

Image of rocksalt crystals

A crystal is characterized by an array of atoms that is periodic in three dimensions. Its smallest repeat unit is the unit cell with specific lattice parameters, atomic positions and symmetry.



Crystal structure of NaCl

Na blue; Cl red

Crystallographic data of NaCl

symmetry: cubic; space group: $Fm\bar{3}m$

lattice parameters:

$a = b = c = 5.639$ Å

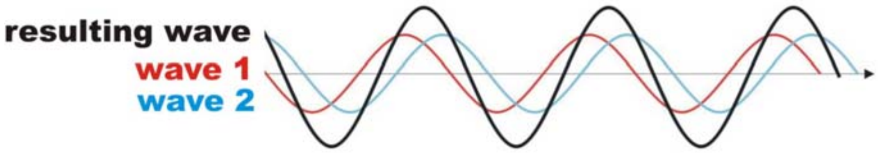
$\alpha = \beta = \gamma = 90°$

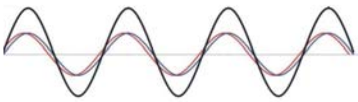
atom positions:

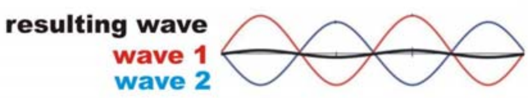
Na	½, ½, ½
Cl	0, 0, 0

Interference of Waves

linear superposition







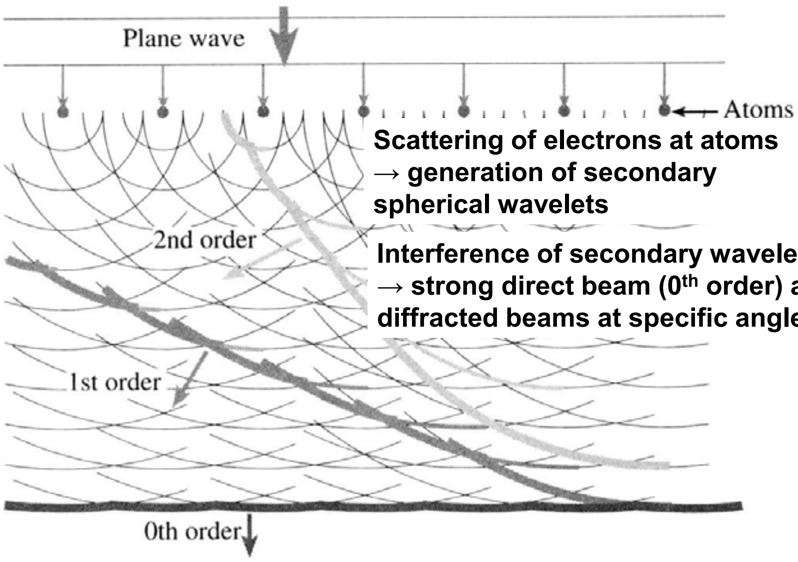
waves in phase

⇒ constructive interference

waves not in phase

⇒ destructive interference

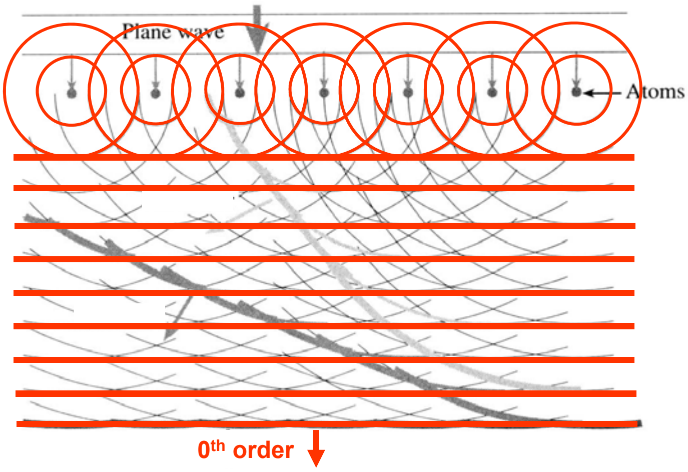
Coherent Scattering



Scattering of electrons at atoms → generation of secondary spherical wavelets

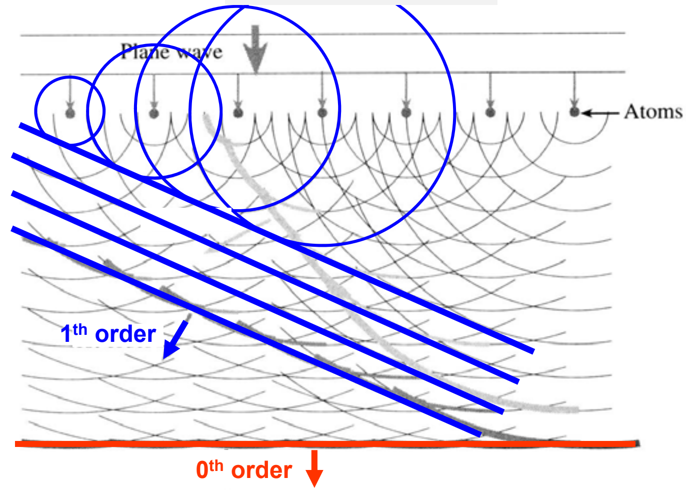
Interference of secondary wavelets → strong direct beam (0th order) and diffracted beams at specific angles

Coherent Scattering



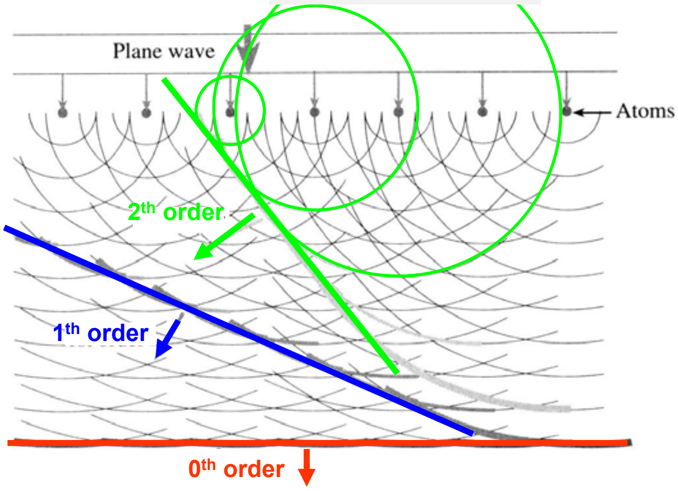
Plane electron wave generates secondary wavelets from periodically ordered scattering centers (atoms in a crystal lattice). Constructive interference of these wavelets leads to scattered beams.

Coherent Scattering



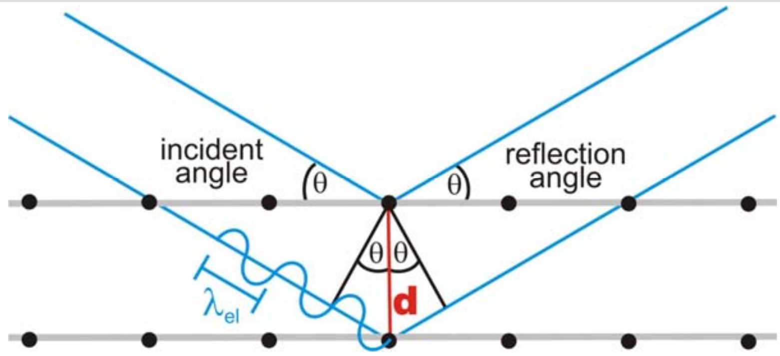
Plane electron wave generates secondary wavelets from periodically ordered scattering centers (atoms in a crystal lattice). Constructive interference of these wavelets leads to scattered beams.

Coherent Scattering



Plane electron wave generates secondary wavelets from periodically ordered scattering centers (atoms in a crystal lattice). Constructive interference of these wavelets leads to scattered beams.

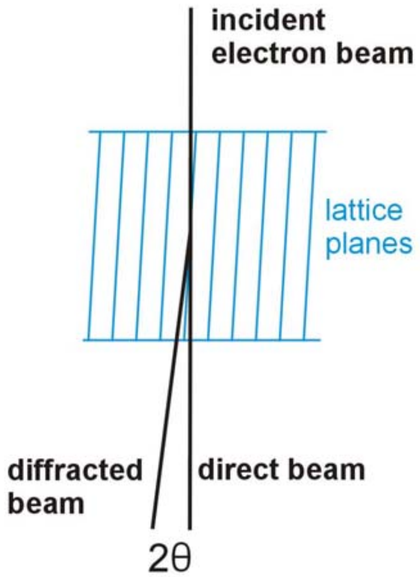
Bragg Description of Diffraction



Constructive interference between the waves reflected with an angle θ at atom planes of spacing d occurs if the path difference between the two waves is 2d sinθ.

Bragg law: $2d\sin\theta = n\lambda$

Electron Diffraction



Bragg law:

$$2d\sin\Theta = n\lambda$$

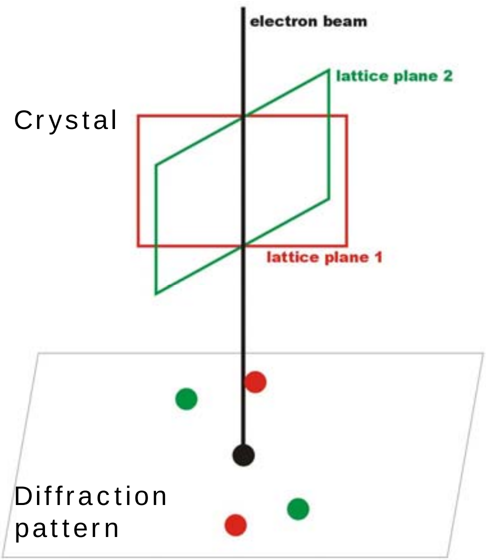
λ_{el} = 0.00197 nm (1.97 pm) for 300 kV

If d = 0.2 nm ⇒ Θ = 0.28°

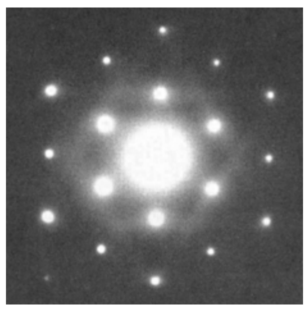
⇒ 0 > Θ > 1

⇒ Reflecting lattice planes are almost parallel to the direct beam

Electron Diffraction on a Lattice

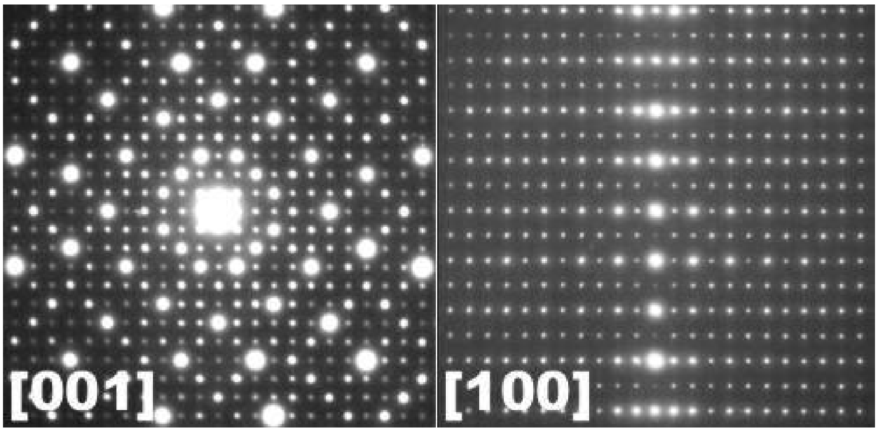


Because of small diffraction angles, the electron beam is parallel to the zone axis of the diffracting lattice planes



Electron diffraction pattern of a single crystal of Al along [111]

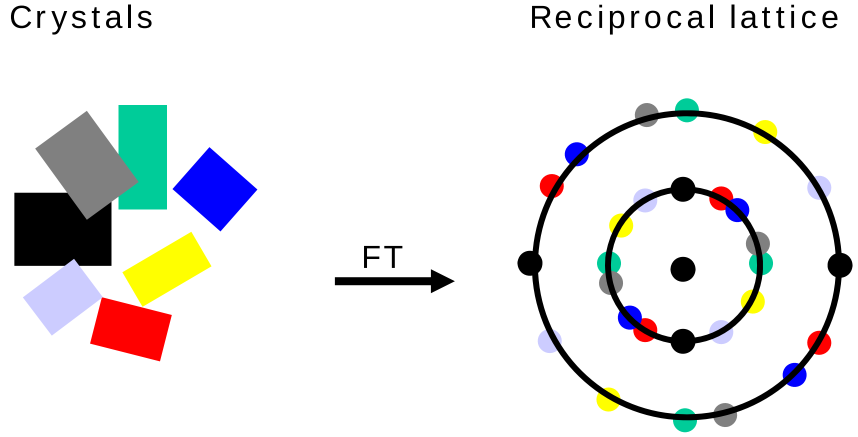
Electron Diffraction: Examples



SAED patterns of single micro-crystals of $Ta_{97}Te_{60}$ (tetragonal; a = 2.76 nm, c = 2.06 nm)

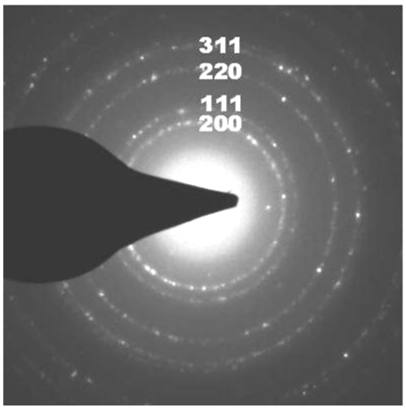
http://www.microscopy.ethz.ch/TEM_ED_examples.htm

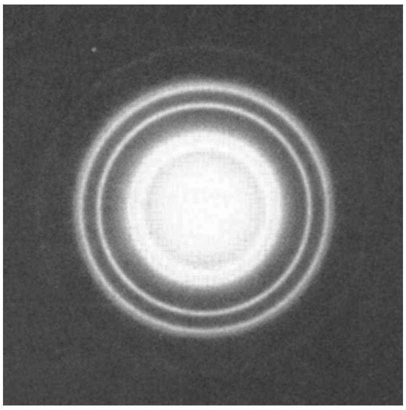
Diffraction of Polycrystalline Samples



Superposition of the diffractograms of many small crystals gives rise to a ring pattern (powder diffractogram).

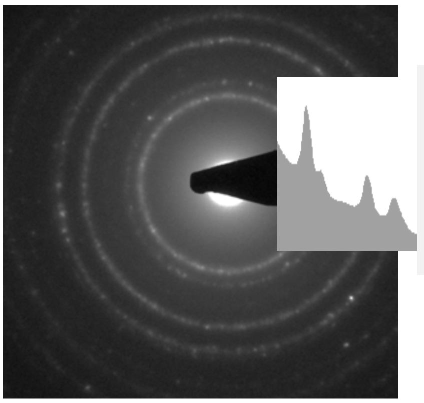
Electron Diffraction: Examples





SAED patterns of polycrystalline platinum (left) and gold (right).

Diffraction of Polycrystalline Samples

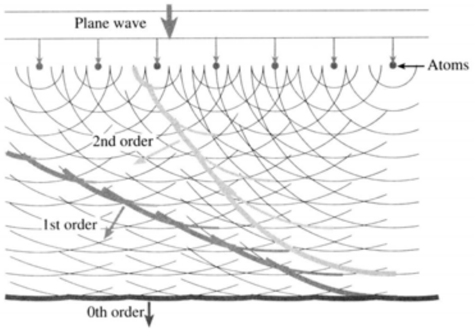


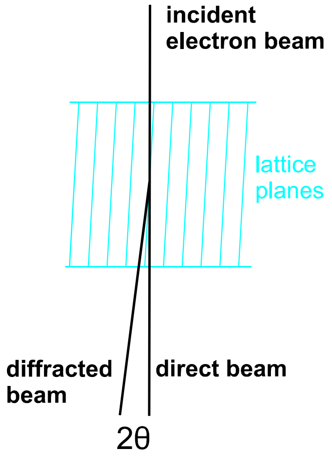
Rotational averaging of intensity → scattering angle vs. intensity (cf. XRD)

Applications of electron diffraction
- **determination of Phases**
- **sample crystallinity**
- **lattice parameters**
- **crystal symmetry**

Bragg or Diffraction Contrast

Coherent scattering

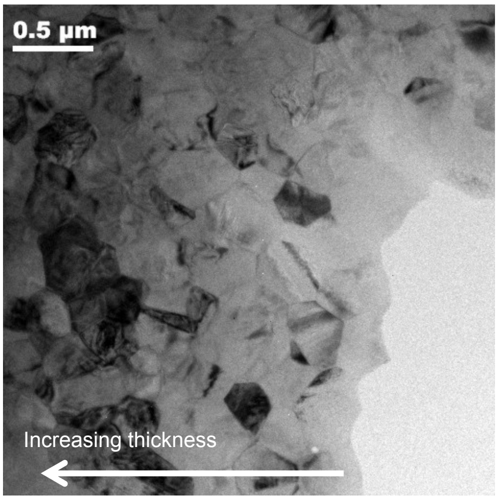




Diffracted beams lead to a decreased intensity of crystalline areas (crystalline areas appear darker than amorphous areas)

Elastic interactions

BF-TEM Image

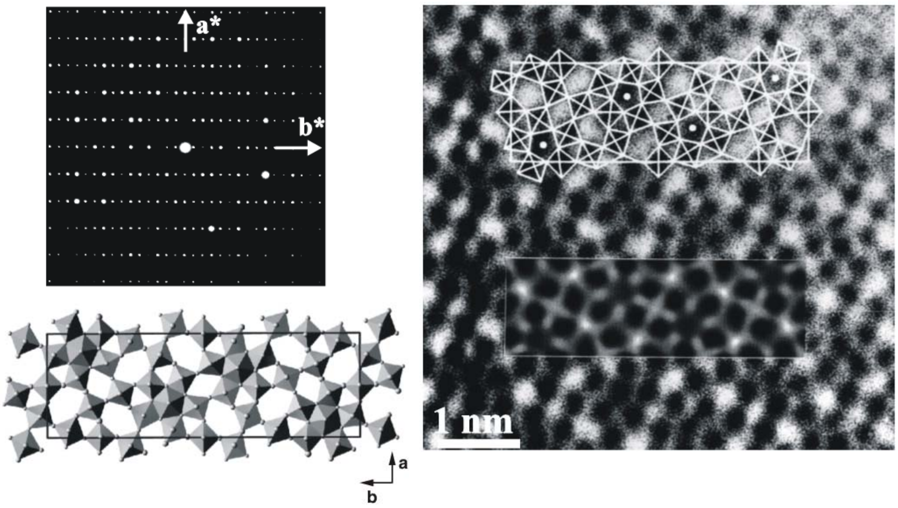


ZrO_2 micro crystals; crystals orientated close to zone axis appear dark

Mainly Bragg contrast

Elastic interactions

Electron Diffraction + High Resolution Transmission Electron Microscopy



$Nb_7W_{10}O_{47}$ – threefold superstructure of the tetragonal tungsten bronze type

Elastic interactions

Inelastic Electron-Matter Interactions

Energy is transferred from the electron to the specimen causing:

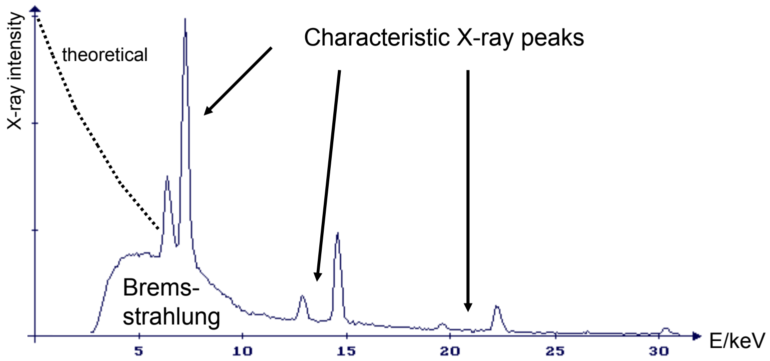
1. **Bremsstrahlung**
   uncharacteristic X-rays
2. **Inner-shell ionisation**
   generation of characteristic X-rays and Auger Electrons
3. **Secondary electrons**
   low energy (< 50 eV)
   loosely bound electrons (e.g., in the conduction band)
   can easily be ejected (application: SEM)
4. **Phonons**
   lattice vibrations (heat) (⇒ beam damage)
5. **Plasmons**
   oscillations of loosely bound electrons in metals
6. **Cathodoluminescence**
   photon generated by recombination of electron-hole
   pairs in semiconductors

Inelastic interactions

Bremsstrahlung (Braking Radiation)

Deceleration of electrons in the Coulomb field of the nucleus

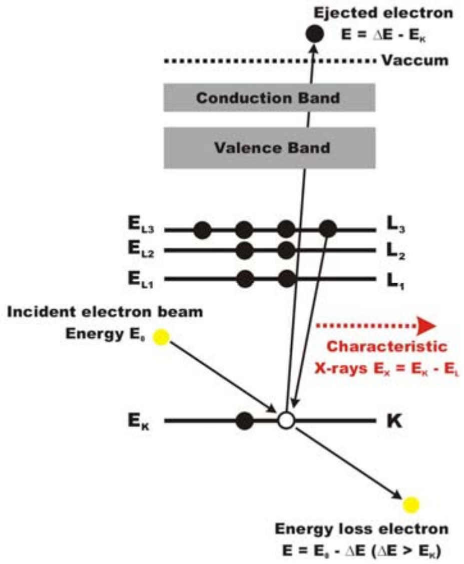
⇒ Emission of X-ray carrying the surplus energy ΔE (Bremsstrahlung, continuum X-rays)



X rays of low energy are completely absorbed in the sample and the detector

Inelastic interactions

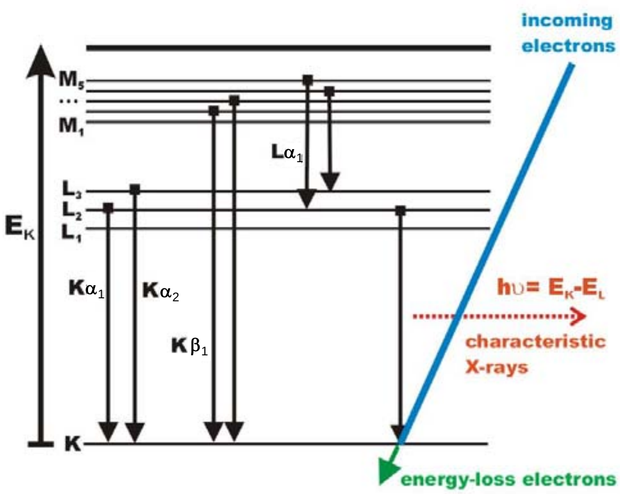
Generation of Characteristic X-rays



1. **Ionization**
2. **X-ray emission**

Inelastic interactions

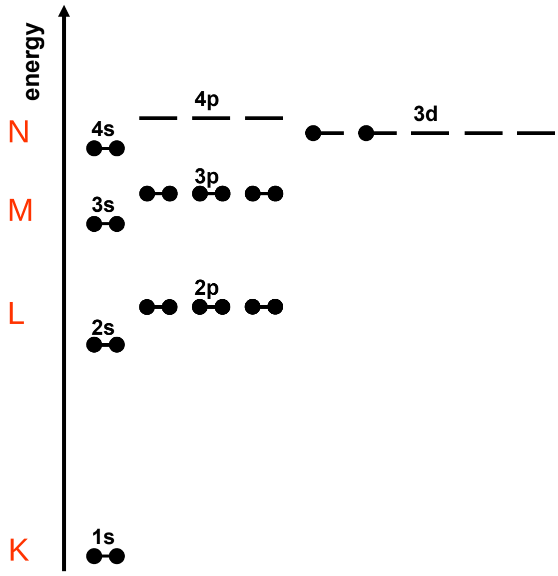
Generation of Characteristic X-rays



1. Ionization
2. X-ray emission

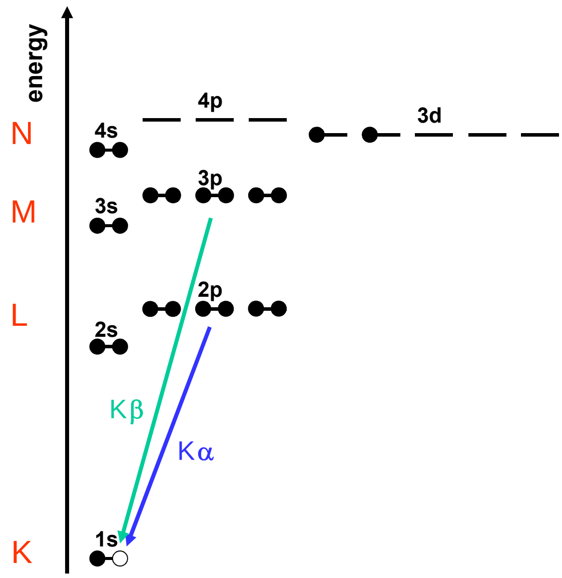
Inelastic interactions

Electron Configuration of Ti: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$



Inelastic interactions

Electron Configuration of Ti: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$



Inelastic interactions

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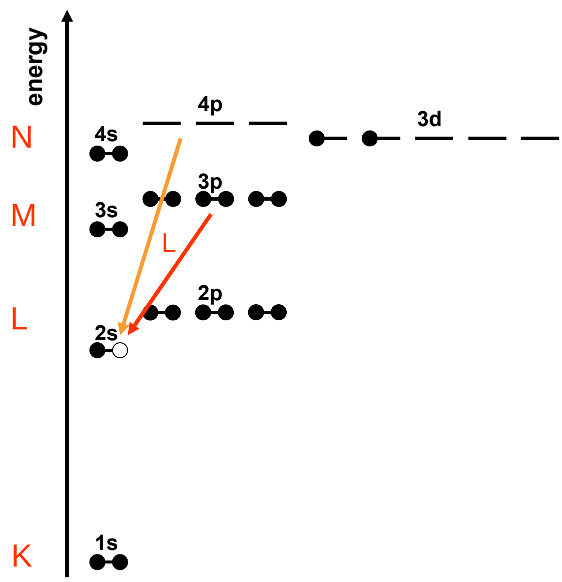
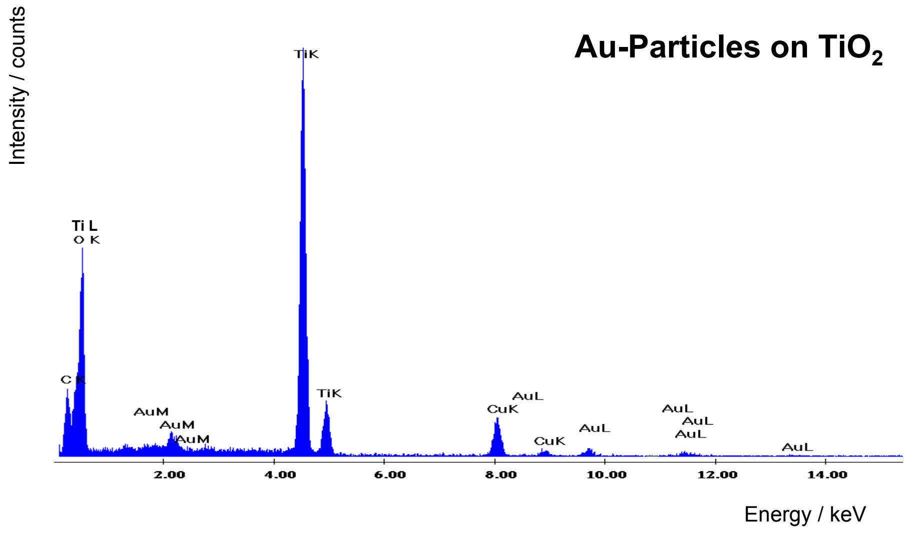


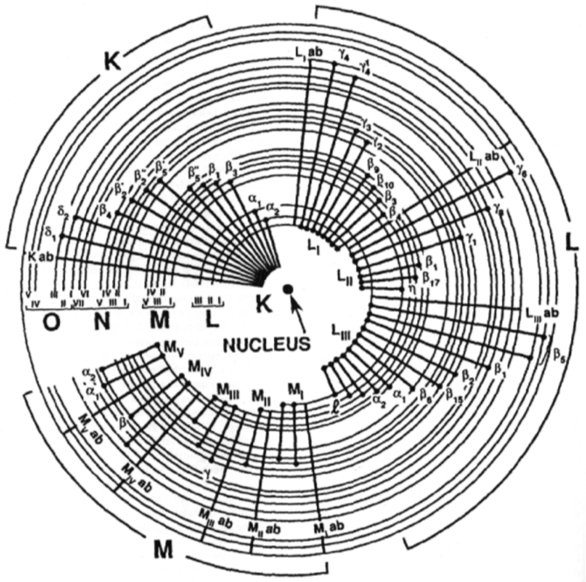
Inelastic interactions

Energy-Dispersive X-ray Spectroscopy (EDXS)



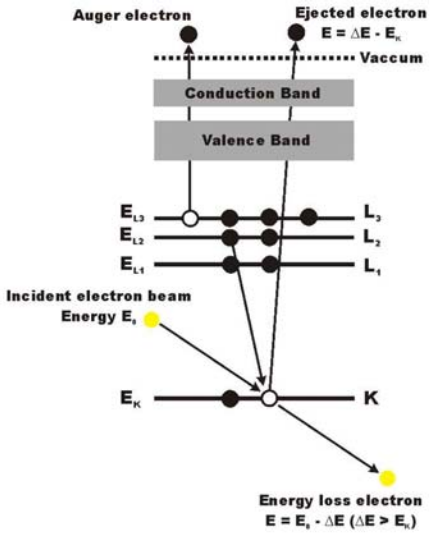
Inelastic interactions

Possible Transitions Between Electron Shells Causing Characteristic K, L, and M X-rays



Inelastic interactions

Generation of Auger Electrons



1. Ionization
2. Electron hole is filled by L_1 electron that transfers surplus energy to another electron (here: L_3)
3. Auger electron emission

Energy of Auger electron is low (ca. 100 to some 1000 eV).

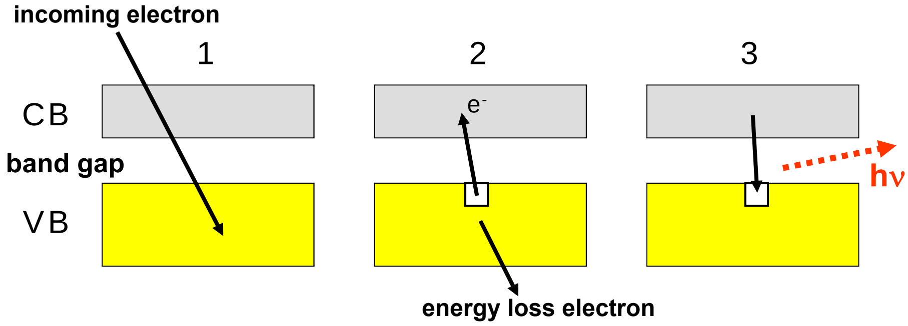
Strong absorption in sample

⇒ Surface technique

Inelastic interactions

Cathodoluminescence

1. Incoming electron interacts with electrons in the valence band (VB)
2. Electron is promoted from the VB to the conduction band (CB), generating electron-hole pairs
3. Recombination: hole in the VB is filled by an electron from the CB with emission of surplus energy as photon (CL)



Important in semiconductor research: determination of band gaps

Inelastic Scattering of Electrons

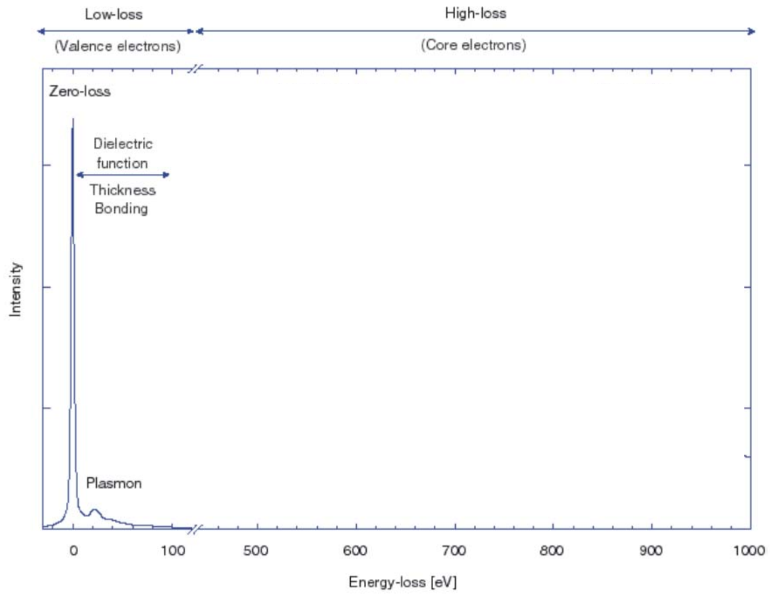
Energy is transferred from the electron to the specimen causing:

1. **Inner-shell ionization**
2. **Bremsstrahlung**
3. **Secondary electrons**
4. **Phonons**
5. **Plasmons**
6. **Cathodoluminescence**

Because of energy transfer to the specimen, the electron has a diminished kinetic energy $E < E_0$ after any inelastic scattering event.

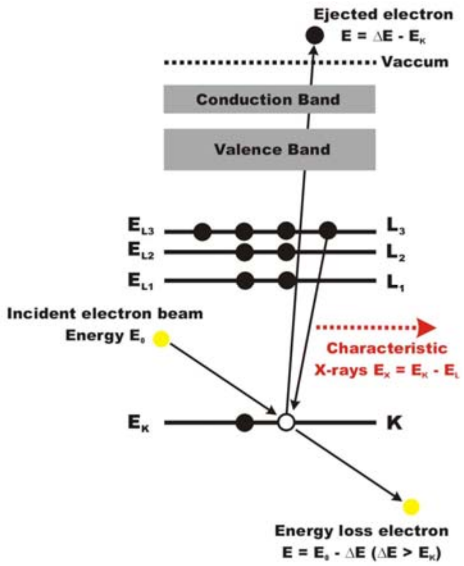
Inelastic interactions

Electron Energy Loss Spectroscopy



Inelastic interactions

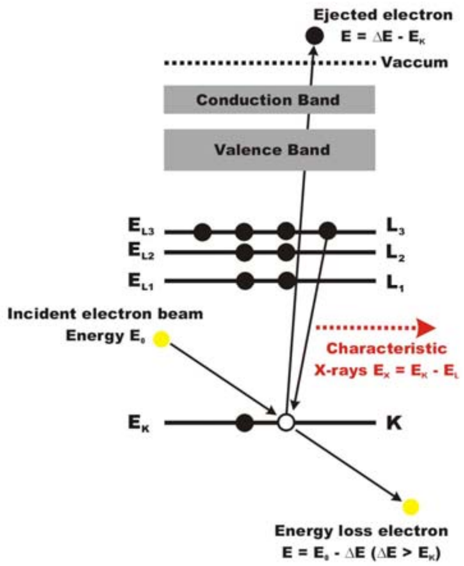
Generation of Characteristic X-rays



1. Ionization
2. X-ray emission

Inelastic interactions

Threshold Energy in EELS

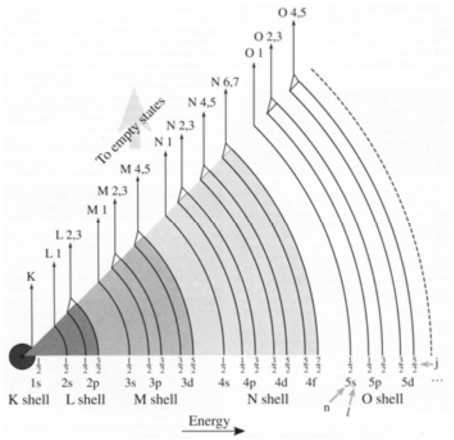


Threshold (or binding) energy: Minimum energy necessary to transfer an electron from its initial to the lowest unoccupied state

This excited electron can carry any amount of excess energy (kinetic energy of ejected electrons)
⇒ signal is extended above the threshold energy building up an edge

Inelastic interactions

EELS: Observable Ionization Edges



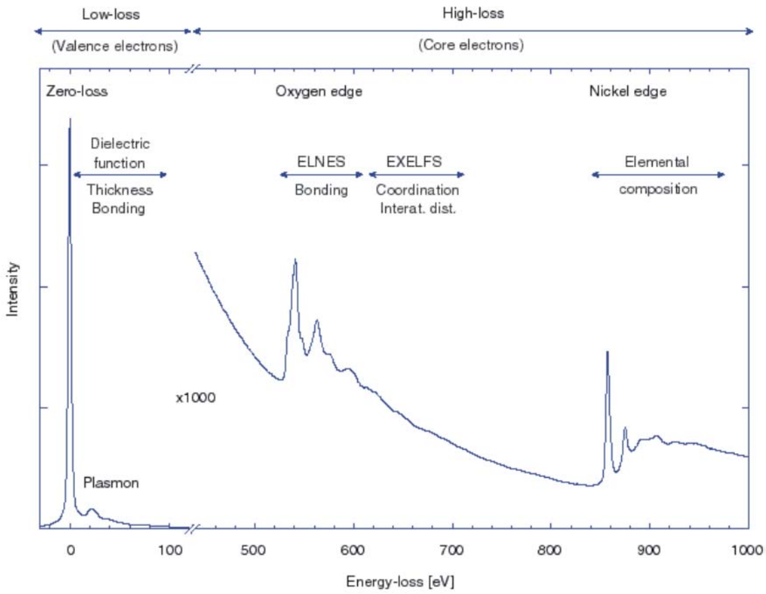
Edge intensity drops with increasing energy loss

⇒ EELS is limited to the appr. energy range 50 - 2000 eV

Almost all elements have observable edges in this energy range:

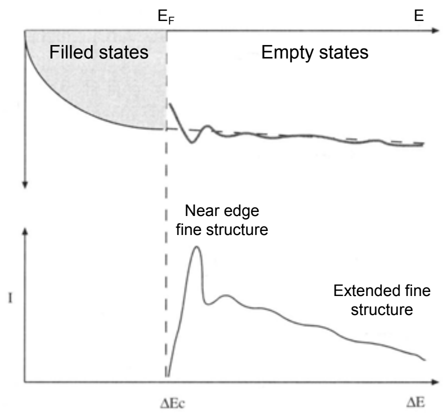
K edges: Li-Si
L edges: Mg-Sr
M edges: Se-Os
N edges: Os-U

Electron Energy Loss Spectroscopy



Electron Energy Loss Spectroscopy

Relationship between the EEL Spectrum and a Core-Loss Exication within the Band Structure



ELNES:

Electron Energy Loss Near Edge Structure

- reflects local density of unoccupied states (DOS)

- corresponds to XANES in X-ray absorption spectroscopy

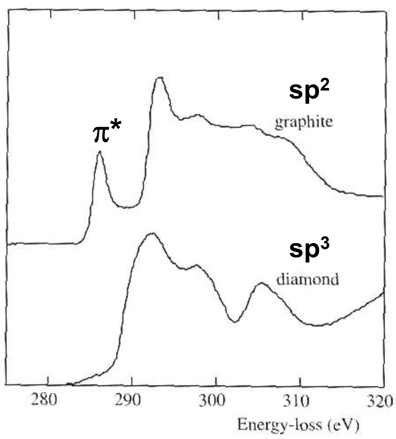
EXELFS:

Extended Energy Loss Fine Structure

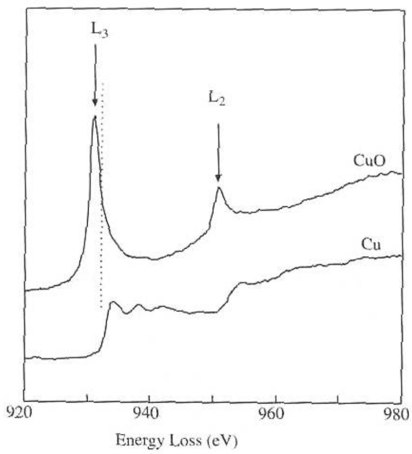
- information on local atomic arrangements

- corresponds to EXAFS in X-ray absorption spectroscopy

Observation of Fine Structures in EELS

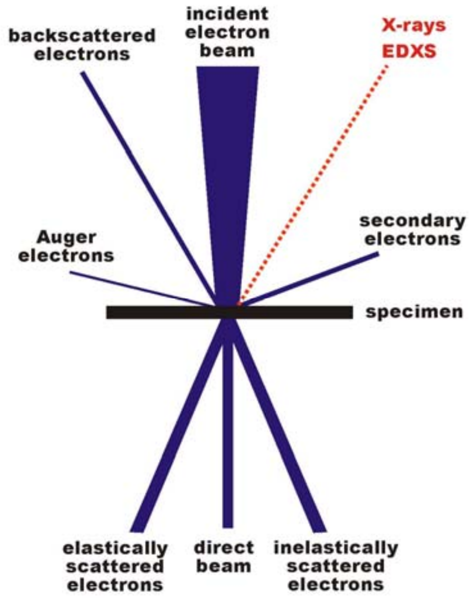


Characteristics of the C_K edge depend on hybridization



Characteristics of the $Cu\_L_{2,3}$ edges depend on oxidation state of Cu

Interactions of Electrons with Matter



SEM (backscattered electrons)

EXDS (EDX, EDS), WDS, EPMA (X-rays)

AES (Auger electrons)

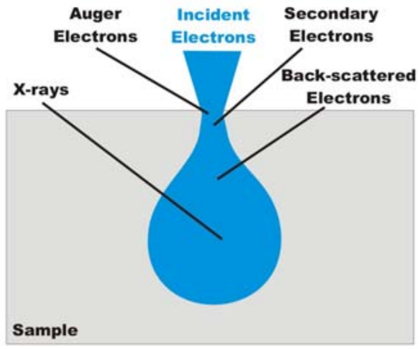
SEM (secondary electrons)

elastic scattering:
TEM, HRTEM, STEM, SAED, CBED

inelastic scattering:
EELS, ESI

Electron-matter interactions

Interaction Volume in Compact Samples



Secondary electrons (SE)

- Low energy < 50 eV (inelastic interactions)
- Information about topology and morphology

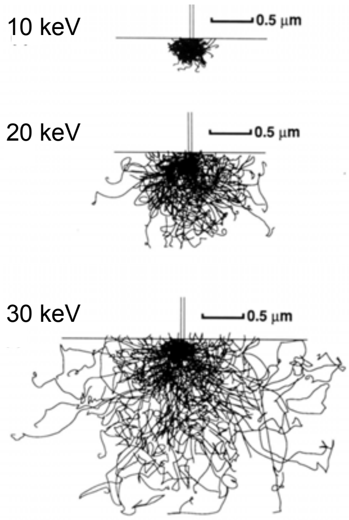
Back-scattered electrons (BSE)

- High energy ≅ E_0 (mostly elastic interactions)
- Morphology and chemical information

Electron-matter interactions

Dependence of Interaction Volume on Electron Energy

Penetration depth increases with increasing electron energy



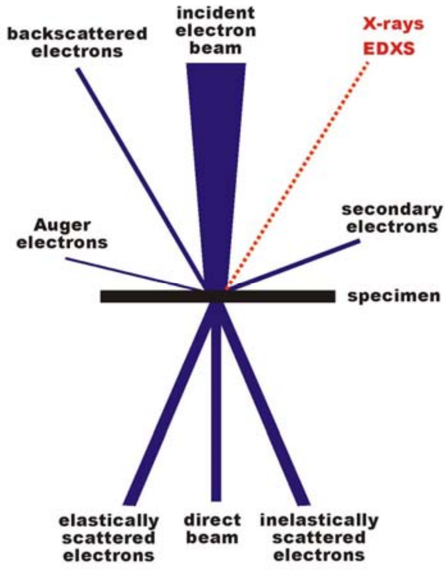
www.matter.org.uk/tem/electron_scattering.htm

Monte-Carlo simulations of electron trajectories in Fe

Beam Damage

- Radiolysis
  - **Ionization**
    ⇒ breaking of chemical bonds (e.g., in polymers)
- Knock-on damage
  - **Displacement of atoms in crystal lattice**
    ⇒ point defects (metals)
- Phonon generation
  - **Specimen heating**
    ⇒ sample drift, structure destruction, melting
- Charging

Summary



- Elastic interactions

  ⇒ ***no energy transfer***
  - **coherent scattering on crystals (diffraction)**
  - **incoherent scattering on atoms**

- Inelastic interactions

  ⇒ ***energy is transferred from the incident electron to the sample***
  - **X-rays**
  - **secondary electrons (low energy SE, Auger electrons)**
  - **phonons, plasmons, cathodoluminescence**