

# Characterization of Catalysts and Surfaces

Characterization Techniques in Heterogeneous Catalysis

## Electron Microscopy I

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

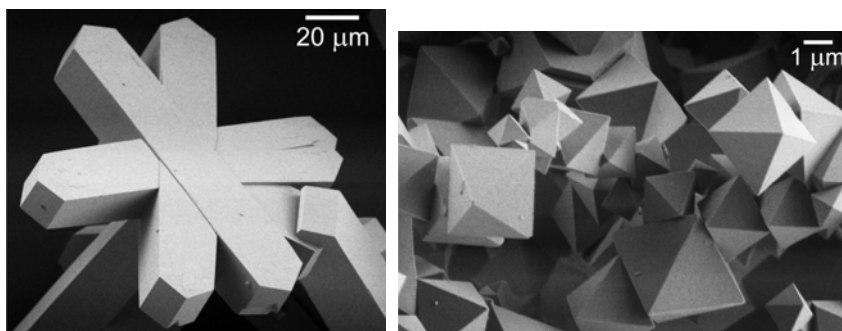
**Frank Krumeich**

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[www.microscopy.ethz.ch](http://www.microscopy.ethz.ch)

200 nm

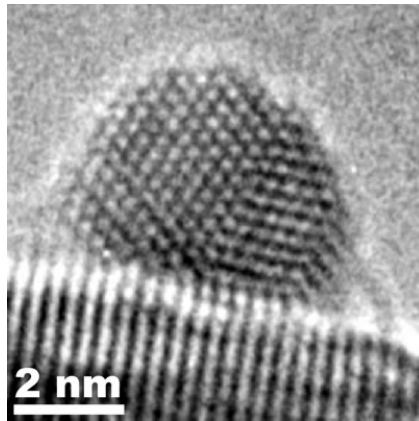
How do crystals look like? Shape?



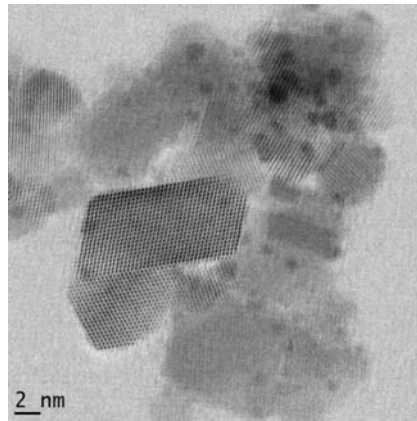
SEM images of zeolithes (left) and metal organic frameworks (MOF, right)

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

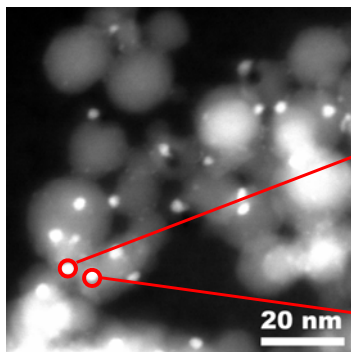


BF-STEM image of Pt particles on CeO<sub>2</sub>

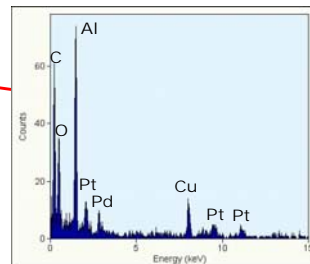
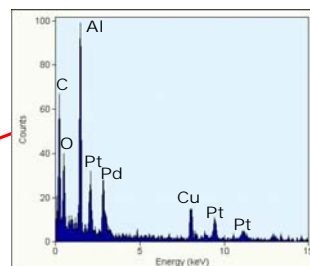
Examples: electron microscopy for catalyst characterization

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

### STEM + EDXS: Point Analyses

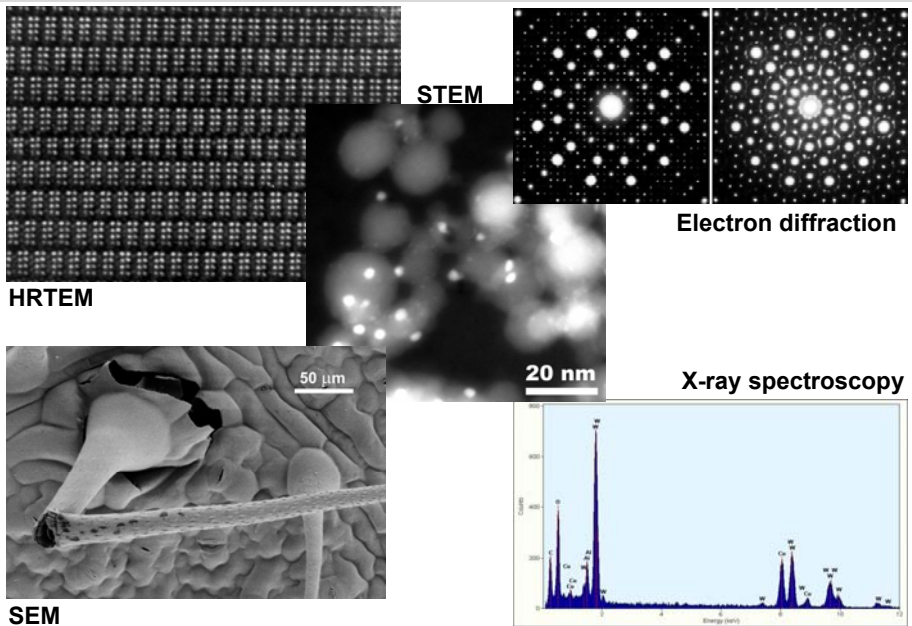


HAADF-STEM image

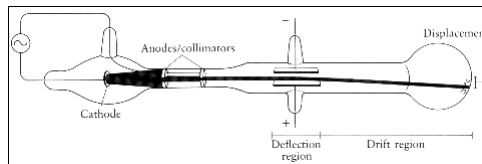


Examples: electron microscopy for catalyst characterization

## Electron Microscopy Methods (Selection)



## Discovery of the Electron



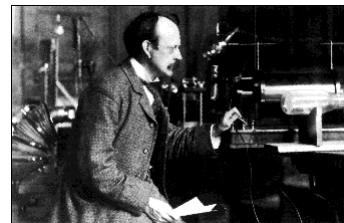
**1897 J. J. Thomson:**

**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**

Electron

## Properties of Electrons

### Dualism wave-particle

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

$\lambda$  : 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

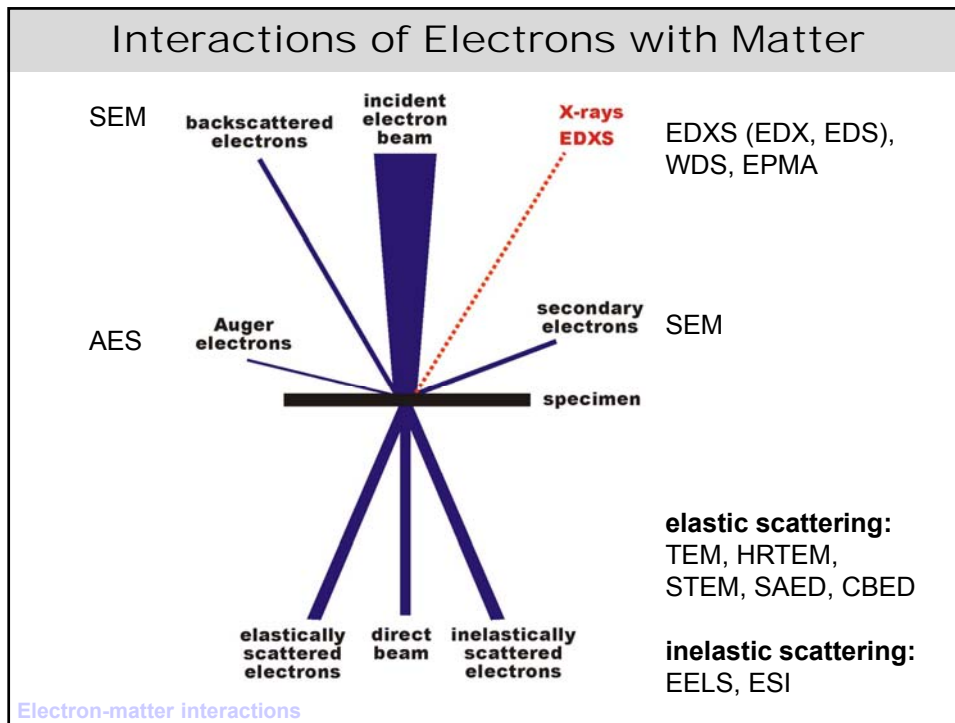
## Properties of Electrons

| $V_{acc}$<br>kV | Nonrel. $\lambda$<br>pm | Rel. $\lambda$<br>pm | Mass x $m_0$ | $V_{nonrel} \times$<br>$10^8 \text{ m/s}$ | $V_{rel} \times$<br>$10^8 \text{ m/s}$ |
|-----------------|-------------------------|----------------------|--------------|---|--|
| 100             | 3.85                    | 3.70                 | 1.20         | 1.85                                      | 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:  $m_0 = 9.109 \times 10^{-31} \text{ kg}$

Speed of light in vacuum:  $c = 2.998 \times 10^8 \text{ m/s}$

Electron



### 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.**

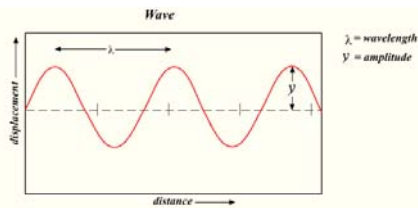
$$E_{el} < E_0$$

*Electron-matter interactions*

## 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)



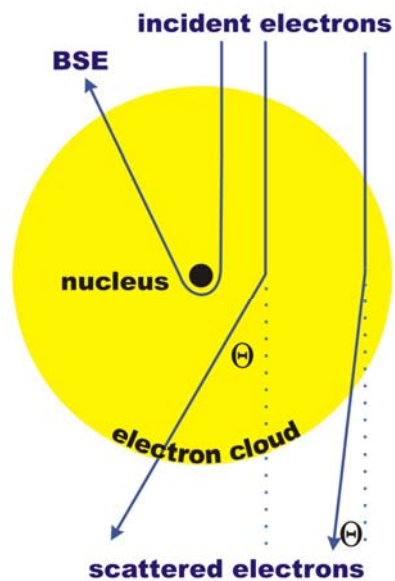
Coherent waves have the same wave-length and are in phase with each other



Incoherent waves

Elastic interactions

## Elastic Scattering of Electrons by an Atom



$$F = Q_1 Q_2 / 4\pi\epsilon_0 r^2$$

$\epsilon_0$ : dielectric constant

Weak Coulomb interaction within the electron cloud

⇒ low-angle scattering

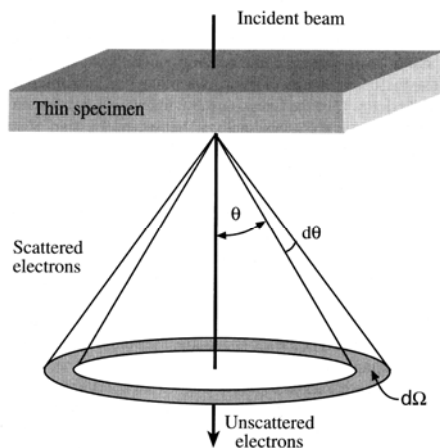
Strong Coulomb interaction close to the nucleus

The interaction of electrons with matter is strong! Much stronger than that of X-rays

$$\frac{d\sigma_e}{d\Omega} \propto Z^2$$

Elastic interactions

## Electron Scattering



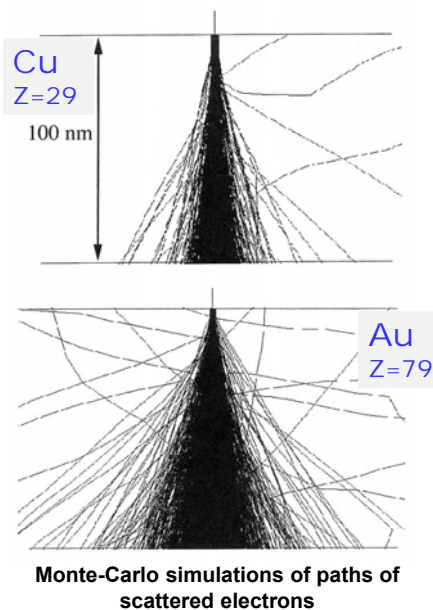
Interaction cross section  $\sigma$  = probability that a scattering event will occur

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

Differential cross section  $d\sigma/d\Omega$  = angular distribution of scattering  
often: measured quantity

Elastic interactions

## Elastic Scattering of Electrons



Monte-Carlo simulations of paths of scattered electrons

Elastic interactions

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

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

⇒ decreases with increasing electron energy

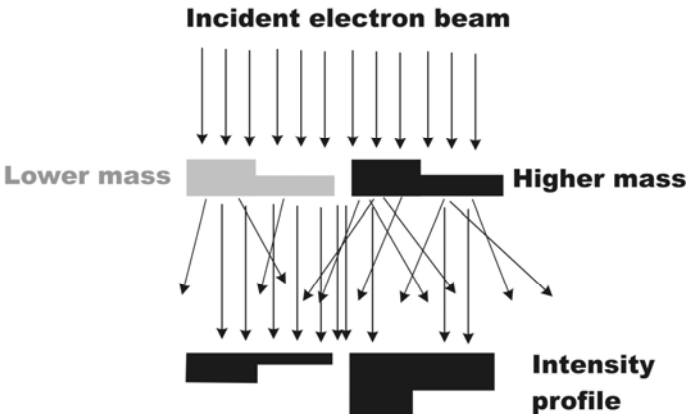
As a general effect of scattering events, the incoming electron beam is weakened and broadened

⇒ brightness of the direct beam depends on the material

⇒ contrast between different materials



# Contrast Formation

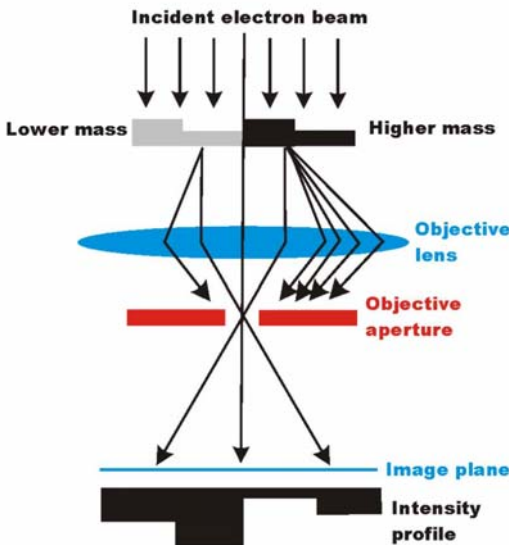


A strong decrease of incoming electron beam intensity occurs

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

Elastic interactions

# Mass-Thickness Contrast



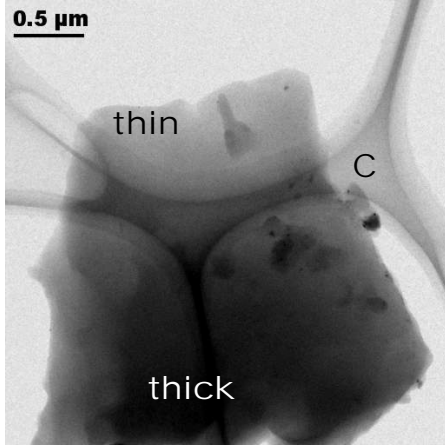
Dark contrast in BF-TEM images appears

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

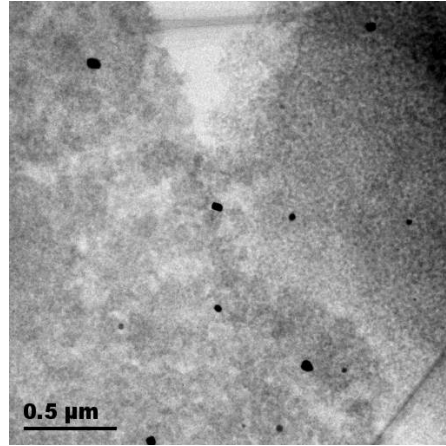
Elastic interactions



## Bright Field TEM Images



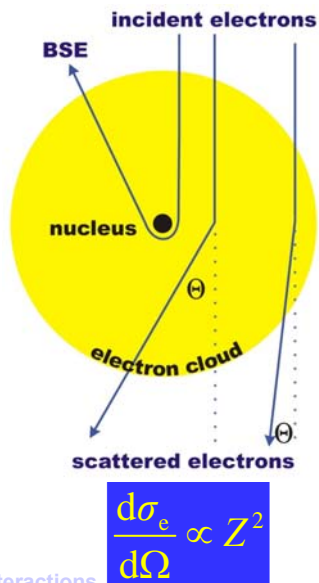
Amorphous SiO<sub>2</sub> on C foil  
Mainly thickness contrast



Au particles on TiO<sub>2</sub>  
Mainly mass contrast

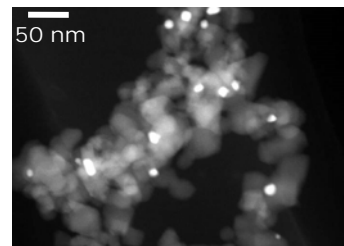
Elastic interactions

## Elastic Scattering of Electrons by an Atom

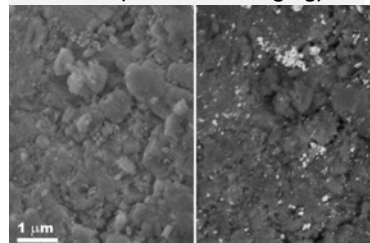


Elastic interactions

## Applications



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

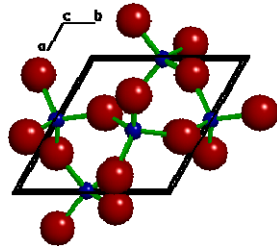


SEM of Pt particles on alumina: imaging with secondary electrons (left) and back-scattered electron (right)

## Crystals



Image of quartz crystals



Crystal structure of quartz  $\text{SiO}_2$   
Unit cell outlined; Si blue; O red

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.

Crystallographic data of quartz

symmetry: trigonal; space group:  $P3_221$

lattice parameters:

$$a = b = 4.892, c = 5.388 \text{ \AA}$$

$$\alpha = \beta = 90^\circ, \gamma = 120^\circ$$

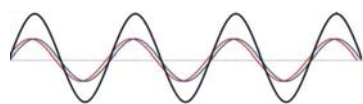
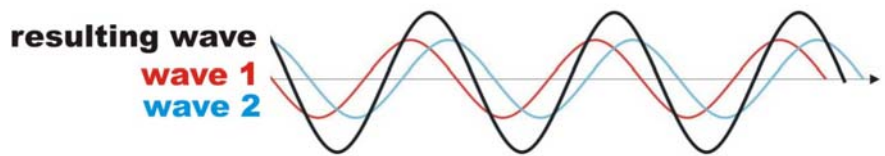
atomic positions:

$$\text{Si } 0.468; 0.0; 0.667$$

$$\text{O } 0.413; 0.271; 0.784$$

## Interference of Waves

linear superposition



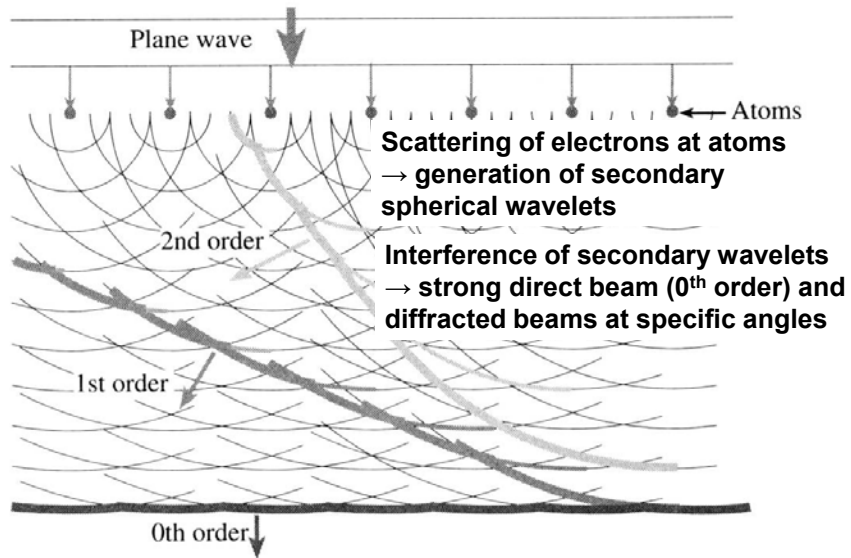
waves in phase  
 $\Rightarrow$  constructive interference



waves not in phase  
 $\Rightarrow$  destructive interference

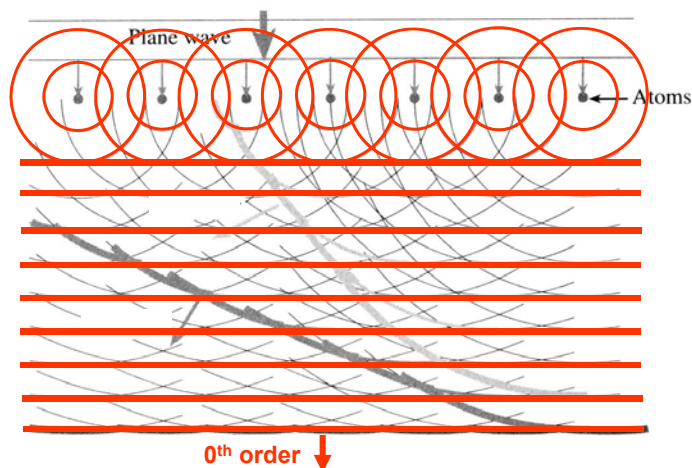
Elastic interactions

## Coherent Scattering



Elastic interactions

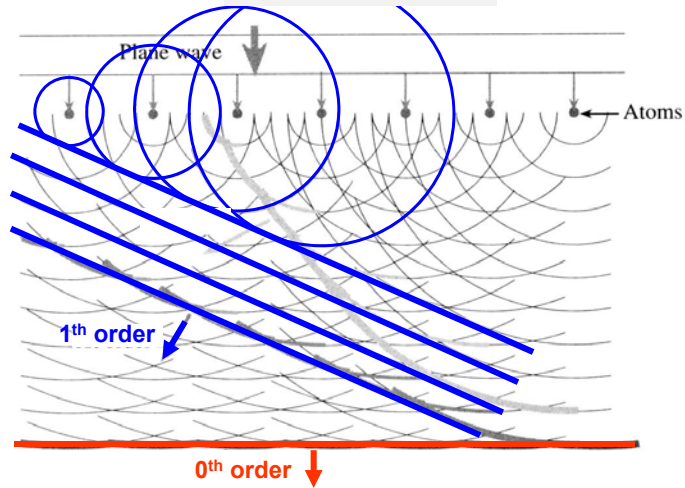
## Coherent Scattering



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.

Electron Diffraction

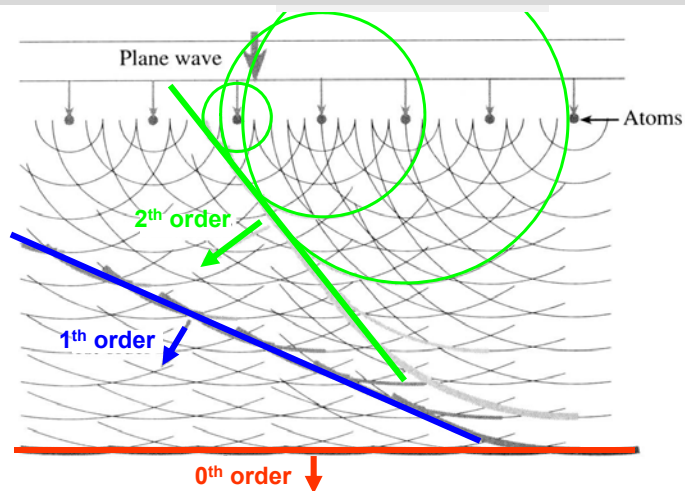
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Electron Diffraction

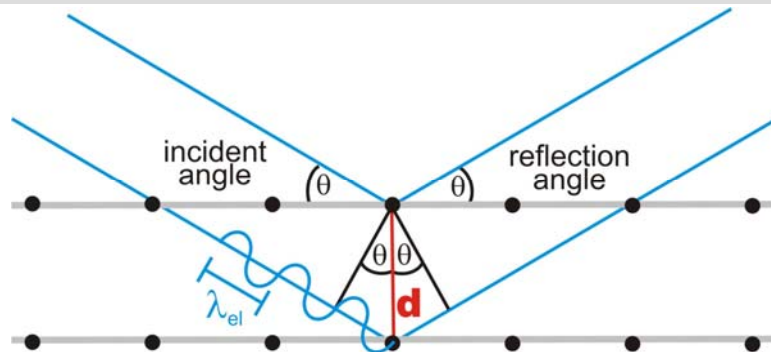
## Coherent Scattering



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.

Electron Diffraction

## Bragg Description of Diffraction

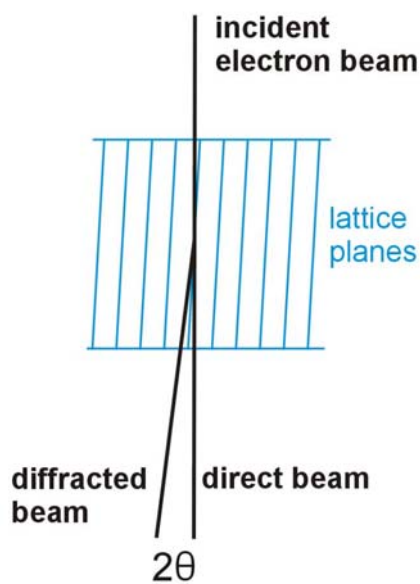


Constructive interference between the waves reflected with an angle  $\theta$  at atom planes of spacing  $d$  occurs if the path difference between the two waves is  $2d \sin\theta$ .

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

Electron Diffraction

## Electron Diffraction



**Bragg law:**

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

$$\lambda_{el} = 0.00197 \text{ nm (1.97 pm)}$$

for 300 kV

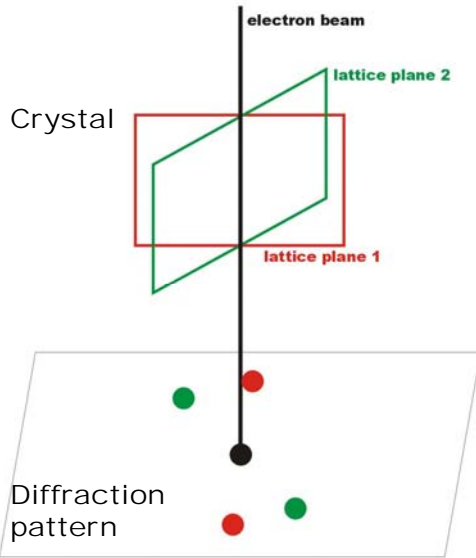
$$\text{If } d = 0.2 \text{ nm} \Rightarrow \Theta = 0.28^\circ$$

$$\Rightarrow 0 > \Theta > 1$$

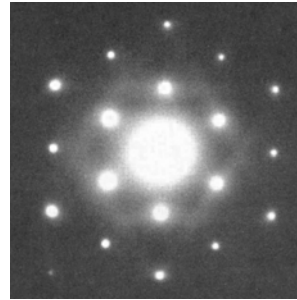
$\Rightarrow$  Reflecting lattice planes are almost parallel to the direct beam

Electron Diffraction

## Electron Diffraction on a Lattice



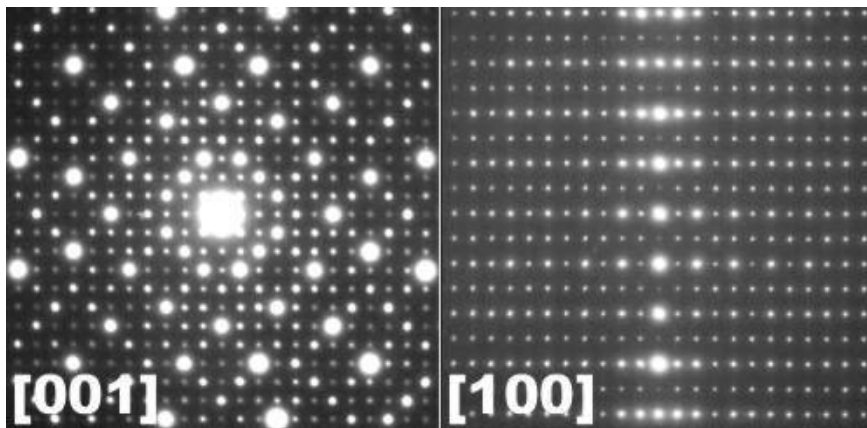
Because of small diffraction angles, the electron beam is parallel to the zone axis of the diffracting lattice planes



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

Elastic interactions

## Electron Diffraction: Examples



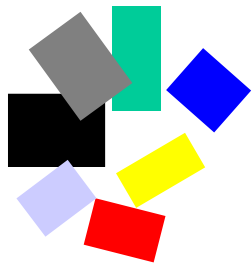
SAED patterns of single micro-crystals of  $\text{Ta}_{97}\text{Te}_{60}$  (tetragonal;  $a = 2.76 \text{ nm}$ ,  $c = 2.06 \text{ nm}$ )

[http://www.microscopy.ethz.ch/TEM\\_ED\\_examples.htm](http://www.microscopy.ethz.ch/TEM_ED_examples.htm)

Electron Diffraction

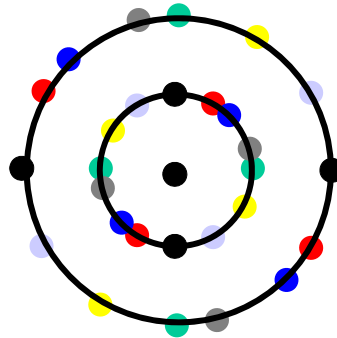
## Diffraction of Polycrystalline Samples

Crystals



FT →

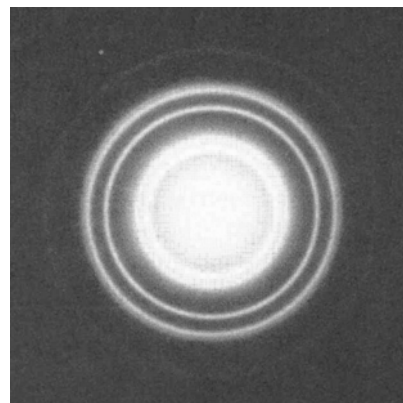
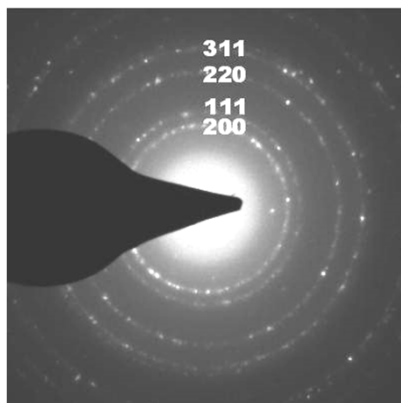
Reciprocal lattice



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

Electron Diffraction

## Electron Diffraction: Examples



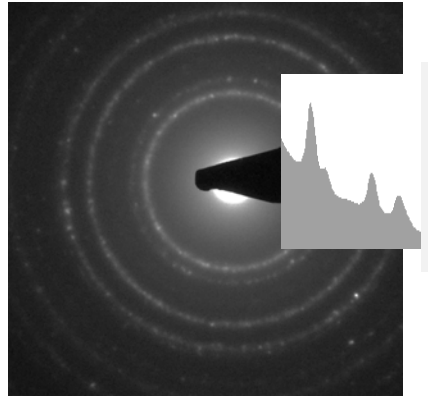
SAED patterns of polycrystalline platinum (left) and gold (right).

[http://www.microscopy.ethz.ch/TEM\\_ED\\_examples.htm](http://www.microscopy.ethz.ch/TEM_ED_examples.htm)

Electron Diffraction



## Diffraction of Polycrystalline Samples



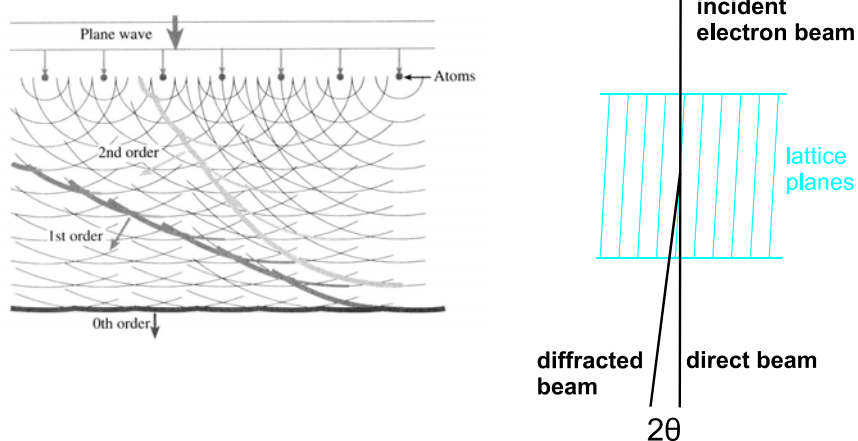
Rotational averaging of intensity → scattering angle vs. intensity (cf. XRD)

Applications of  
electron diffraction

- **determination of Phases**
- **sample crystallinity**
- **lattice parameters**
- **crystal symmetry**

## Bragg or Diffraction Contrast

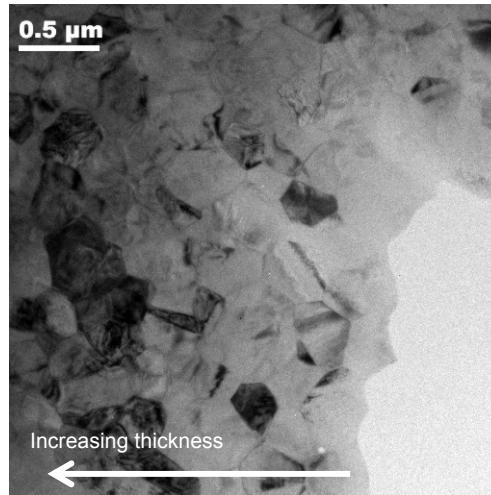
### Coherent scattering



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

Elastic interactions

## BF-TEM Image

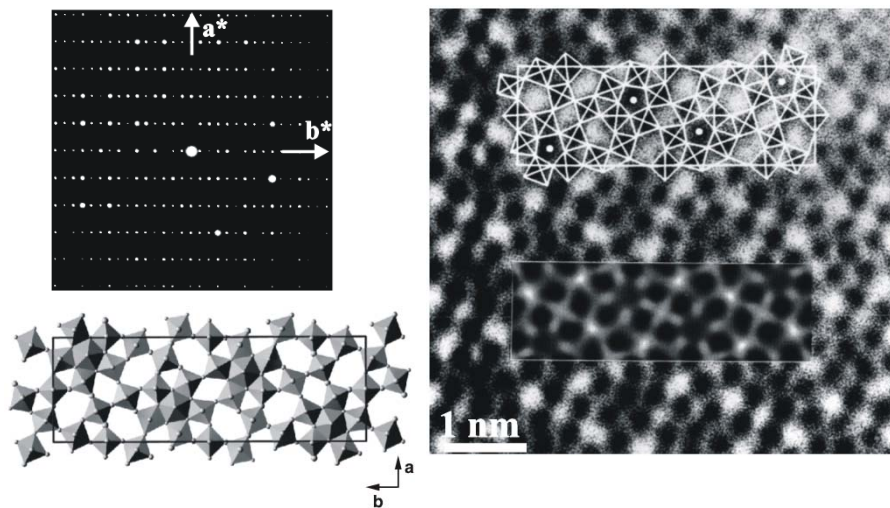


ZrO<sub>2</sub> micro crystals; crystals orientated close to zone axis appear dark

Mainly Bragg contrast

Elastic interactions

## Electron Diffraction + High Resolution Transmission Electron Microscopy



Nb<sub>7</sub>W<sub>10</sub>O<sub>47</sub> – threefold superstructure of the tetragonal tungsten bronze type

Elastic interactions

## Inelastic Electron-Matter Interactions

Energy is transferred from the electron to the specimen causing:

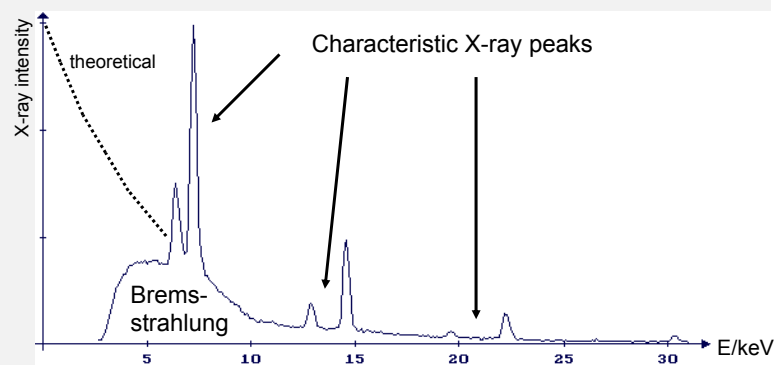
- 1. Bremsstrahlung**  
uncharacteristic X-rays
- 2. Inner-shell ionisation**  
generation of characteristic X-rays and Auger Electrons
- 3. Secondary electrons**  
low energy ( $< 50$  eV)  
loosely bound electrons (e.g., in the conduction band)  
can easily be ejected (application: SEM)
- 4. Phonons**  
lattice vibrations (heat) ( $\Rightarrow$  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**

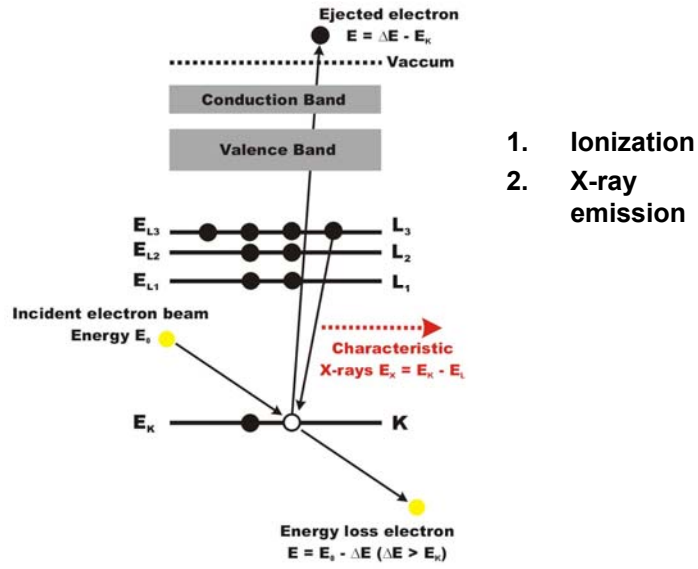
$\Rightarrow$  **Emission of X-ray carrying the surplus energy  $\Delta E$  (Bremsstrahlung, continuum X-rays)**



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

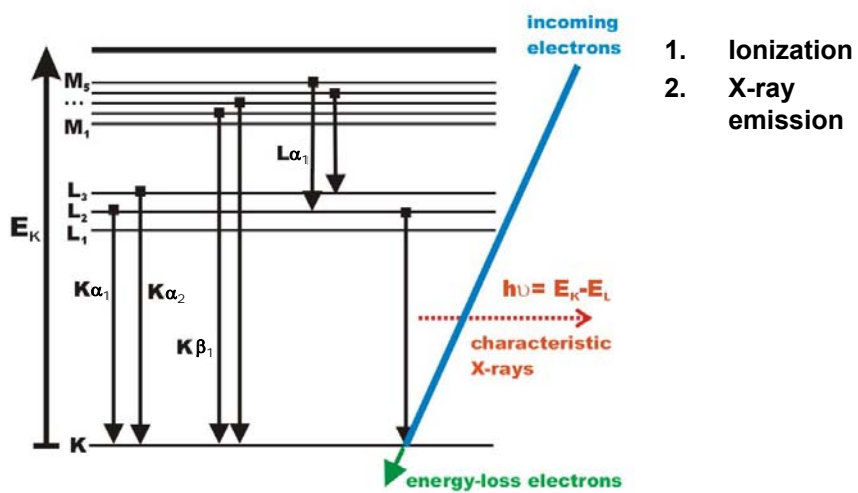
Inelastic interactions

## Generation of Characteristic X-rays



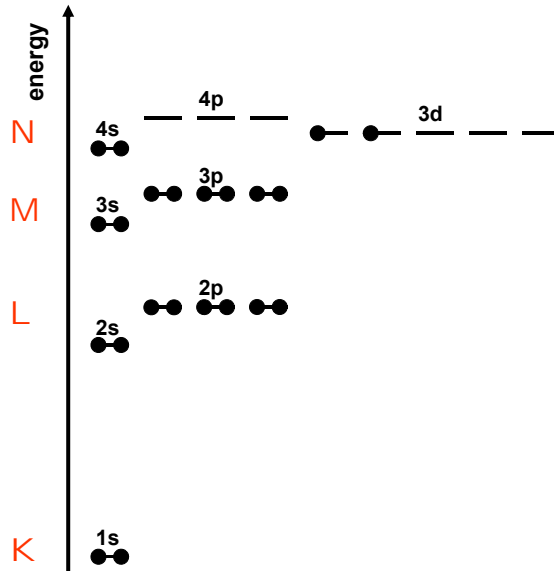
Inelastic interactions

## Generation of Characteristic X-rays



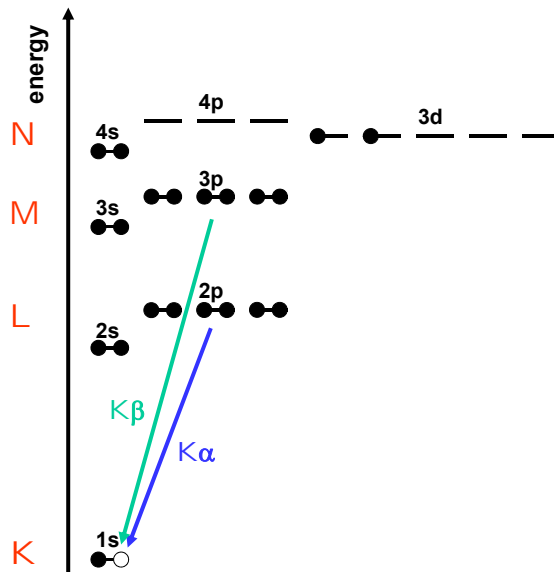
Inelastic interactions

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



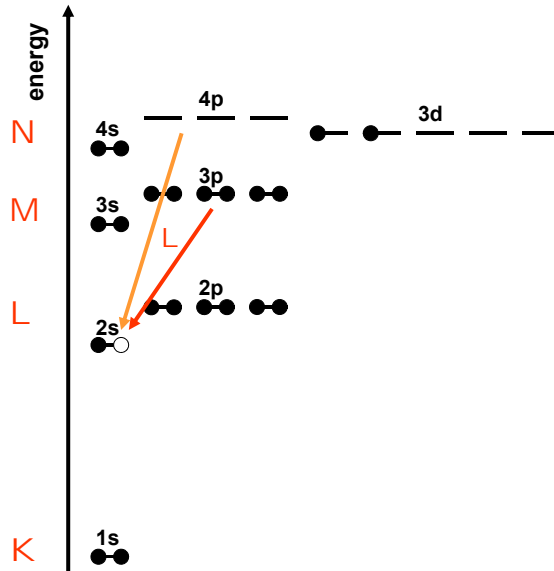
Inelastic interactions

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



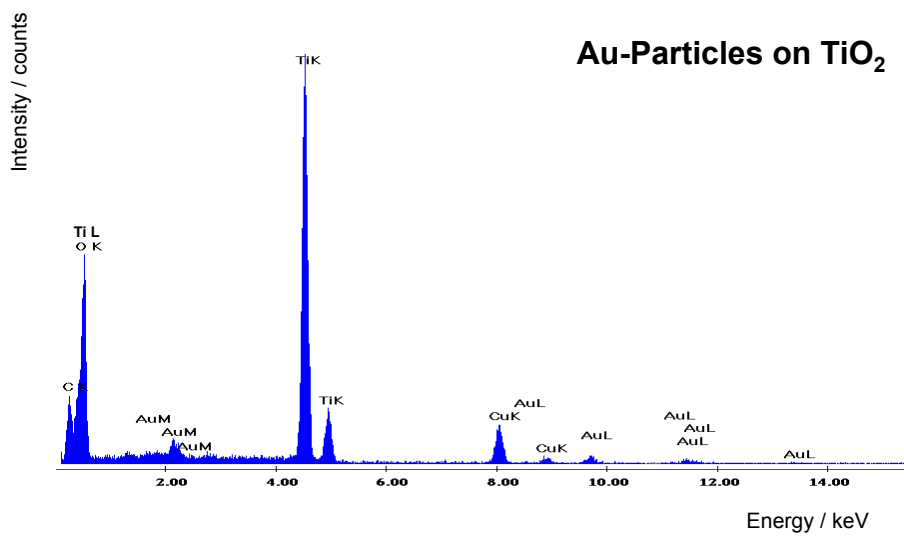
Inelastic interactions

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



Inelastic interactions

### Energy-Dispersive X-ray Spectroscopy (EDXS)



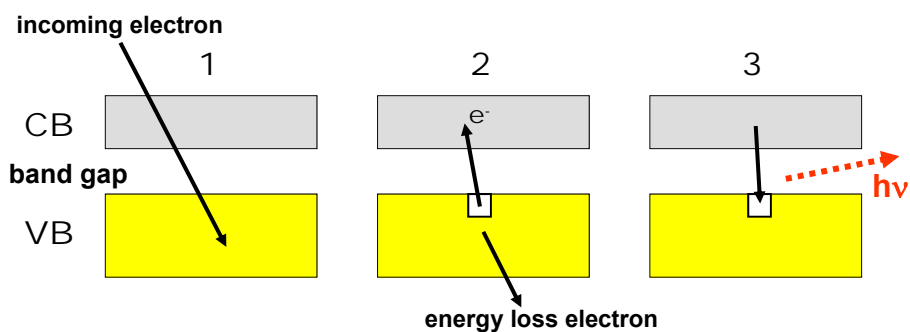
Inelastic interactions





## 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

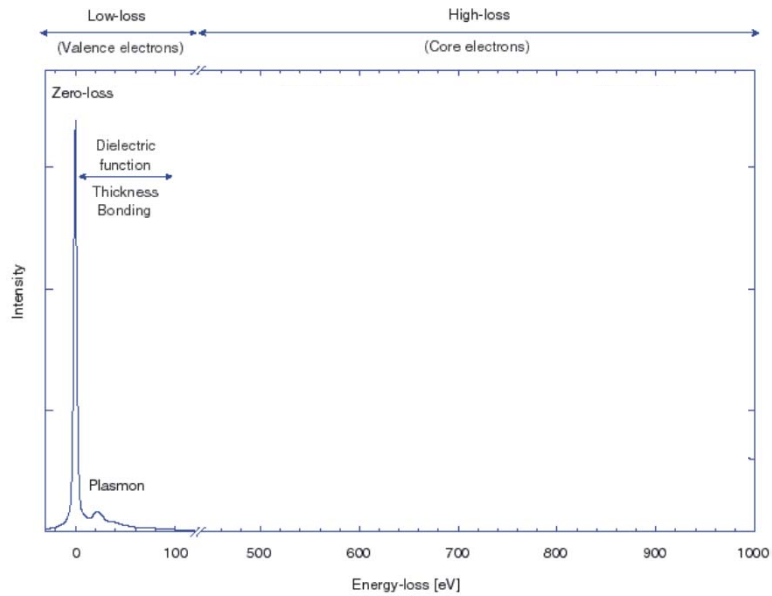
Energy is transferred from the electron to the specimen causing:

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.

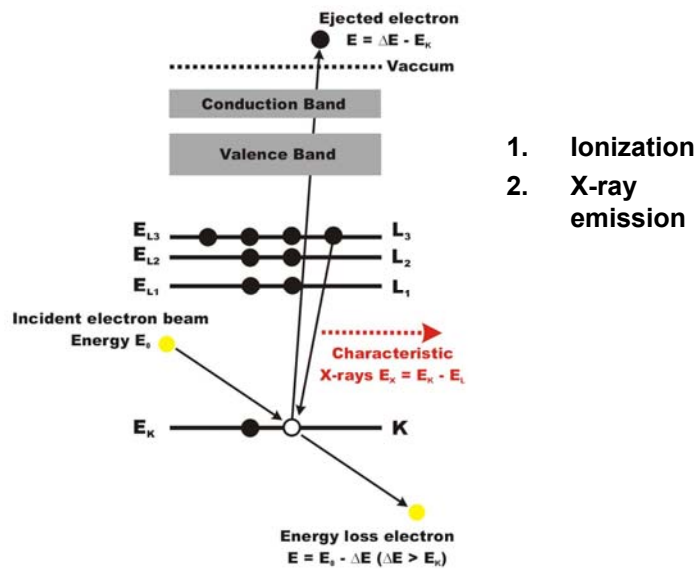
Inelastic interactions

## Electron Energy Loss Spectroscopy



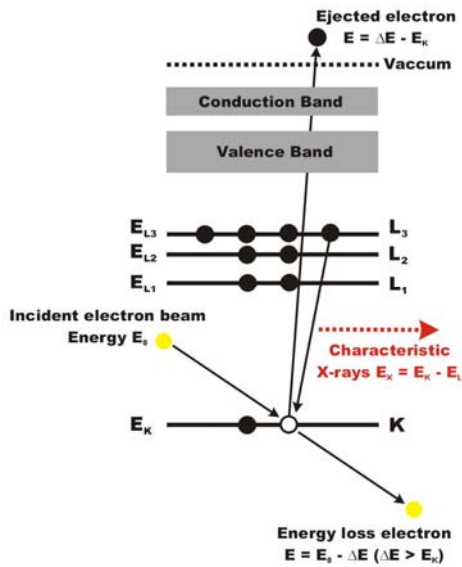
Inelastic interactions

## Generation of Characteristic X-rays



Inelastic interactions

## Threshold Energy in EELS

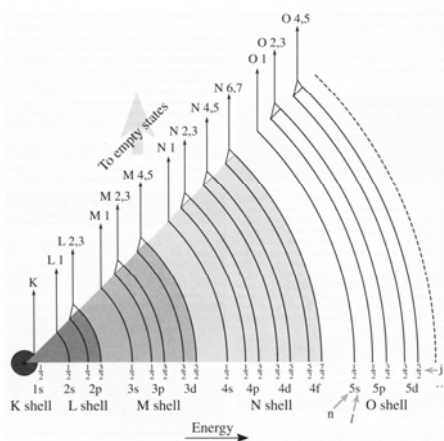


**Threshold (or binding) energy:**  
Minimum energy necessary to transfer an electron from its initial to the lowest unoccupied state

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

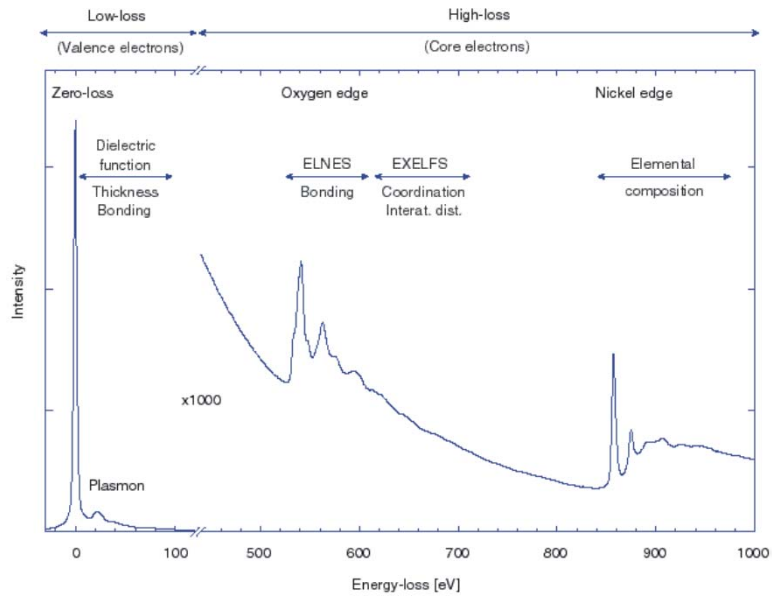
⇒ EELS is limited to the appr. energy range 50 - 2000 eV

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

Inelastic interactions

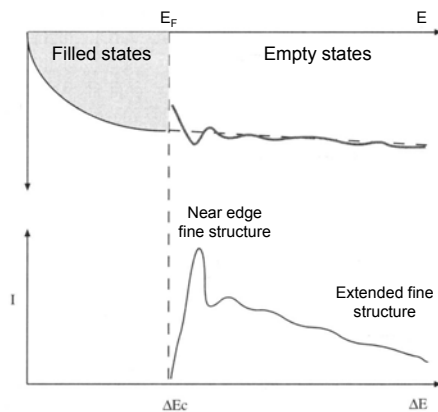
## Electron Energy Loss Spectroscopy



Inelastic interactions

## Electron Energy Loss Spectroscopy

Relationship between the EEL Spectrum and a Core-Loss Excitation 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

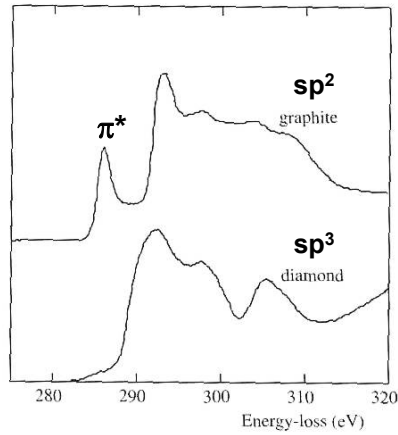
### EXELFS:

#### Extended Energy Loss Fine Structure

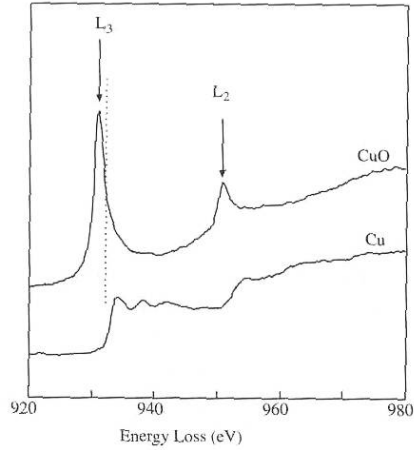
- information on local atomic arrangements
- corresponds to EXAFS in X-ray absorption spectroscopy

Inelastic interactions

## Observation of Fine Structures in EELS



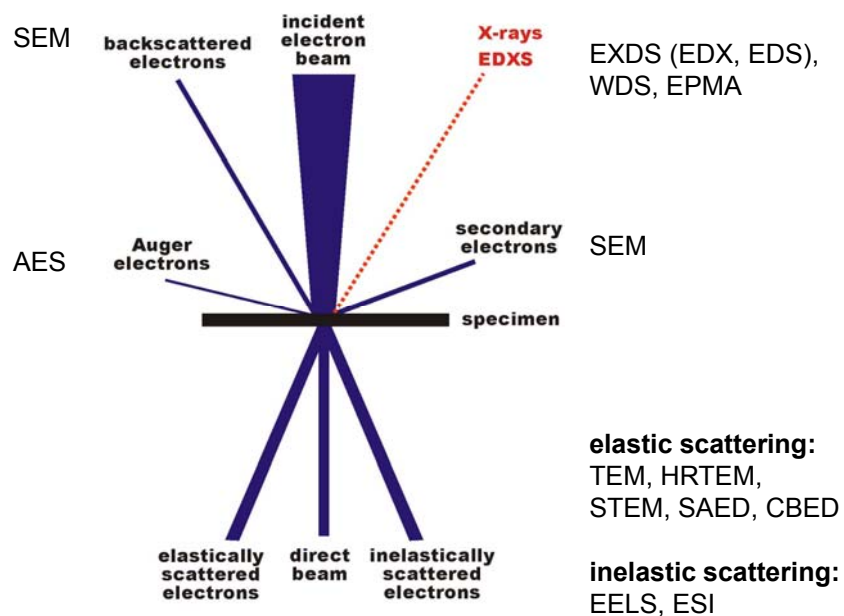
Characteristics of the C\_K edge depend on hybridization



Characteristics of the Cu\_L<sub>2,3</sub> edges depend on oxidation state of Cu

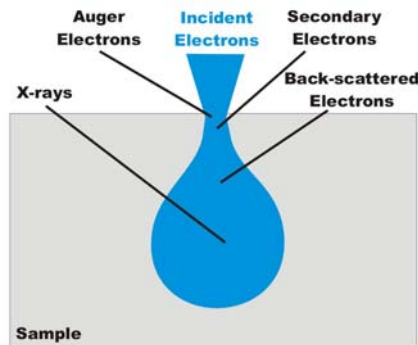
Inelastic interactions

## Interactions of Electrons with Matter



Electron-matter interactions

## Interaction Volume in Compact Samples



### Secondary electrons (SE)

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

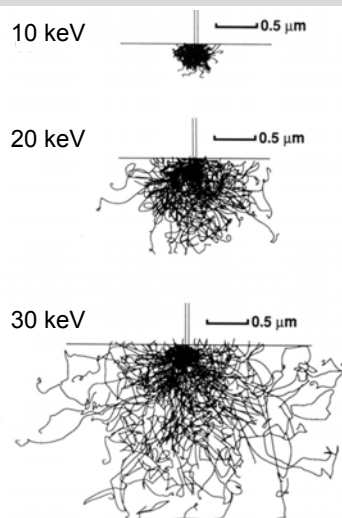
### Back-scattered electrons (BSE)

- High energy  $\cong E_0$  (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](http://www.matter.org.uk/tem/electron_scattering.htm)

Monte-Carlo simulations of electron trajectories in Fe

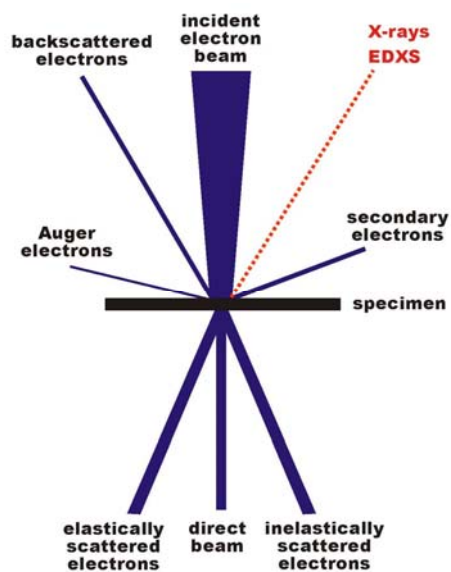
[Electron-matter interactions](#)

## 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

Electron-matter interactions

## Summary



Electron-matter interactions

- 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