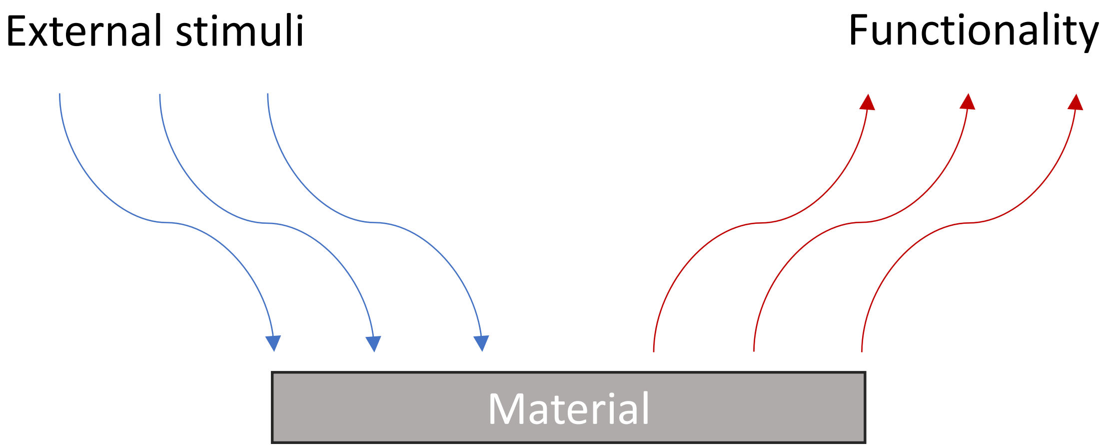
Responsive Functional Materials

Ass.-Prof. Dr. Heidi A. Schwartz

Photoactive Hybrid Materials

Universität Innsbruck

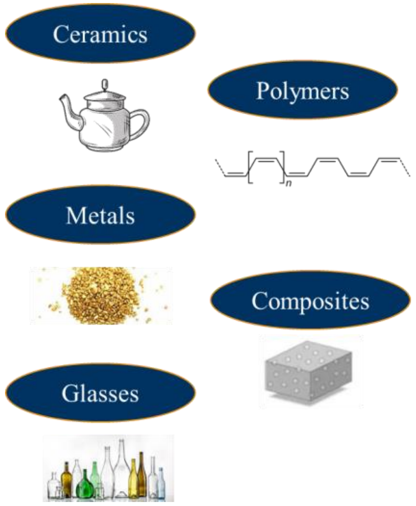


https://www.uibk.ac.at/en/aatc/ag-schwartz/

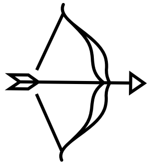
heidi.schwartz@uibk.ac.at

L01.063

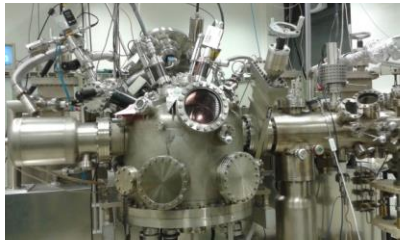
Outline for today´s lecture



1. Short conclusion of last lecture

2. Learning objectives 

- Analyzation tools and characterization methods I

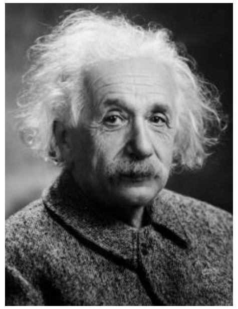


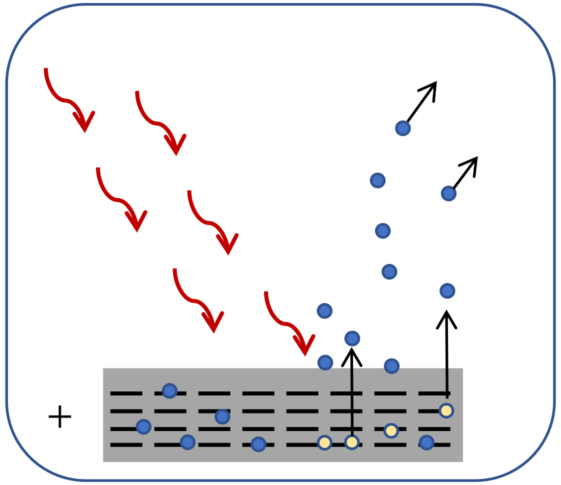
- Next time: Analyzation tools and characterization methods II

Photoelectric & photovoltaic effect

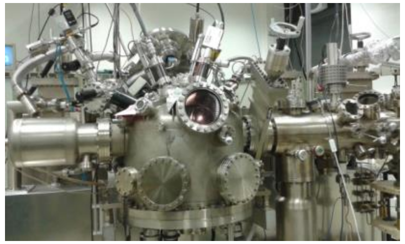
“excitation of electrons to a higher-energy state, when a material is exposed to electromagnetic radiation”

Note: An external stimulus is changing the material and therewith its properties!

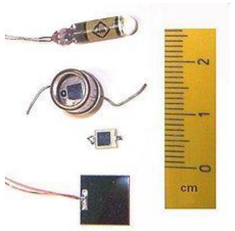

A. Einstein

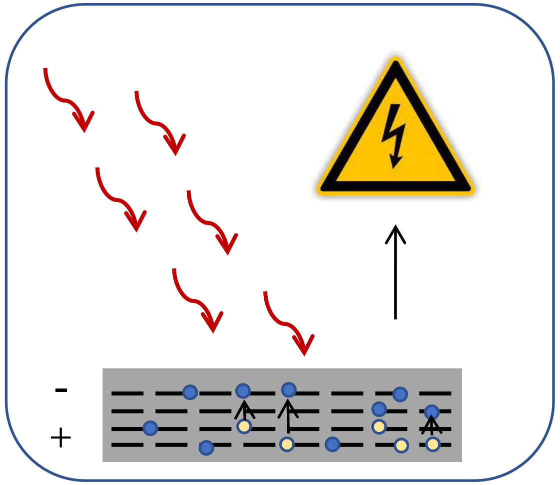


Electrons leave the material.


XPS.


Solar cell.


Photodiode.



Electrons stay within the material.


E. Becquerel

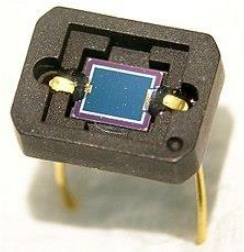
Photovoltaic effect is also called the inner photoelectric effect.

[Happy birthday Edmond Becquerel | IEC]() (4th March, 2023)

White Board

Photodiodes – what we need for detection or TV

Photodiodes are typically built up from Si, Ge.

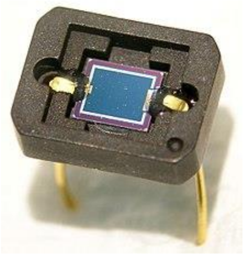


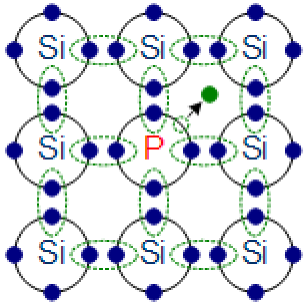
Photodiode – Wikipedia (5th March, 2023)
Dotieren: n- und p-Halbleiter - Grundlagen - Halbleitertechnologie von A bis Z - Halbleiter.org (5th March, 2023)

White Board

Photodiodes – what we need for detection or TV

Photodiodes are typically built up from Si, Ge.





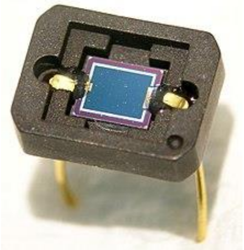
Doped semiconductors, whose conductivity originates from free **n**egative electrons.

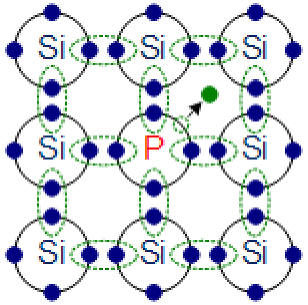
***n*-doping**

[Photodiode – Wikipedia](#) (5th March, 2023)
[Dotieren: n- und p-Halbleiter - Grundlagen - Halbleitertechnologie von A bis Z - Halbleiter.org](#) (5th March, 2023)

Photodiodes – what we need for detection or TV

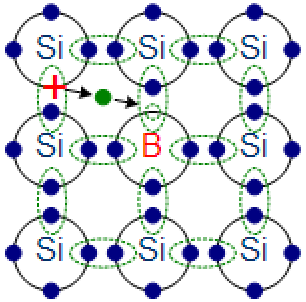
Photodiodes are typically built up from Si, Ge.





Doped semiconductors, whose conductivity originates from free **n**egative electrons.

***n*-doping**



Doped semiconductors, whose conductivity originates from the presence of **p**ositive holes.

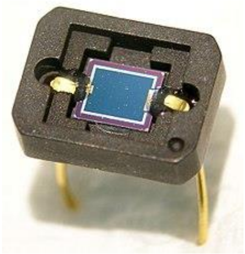
***p*-doping**

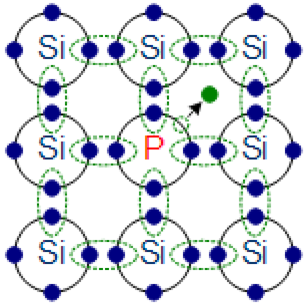
Photodiode – Wikipedia (5th March, 2023)

Dotieren: n- und p-Halbleiter - Grundlagen - Halbleitertechnologie von A bis Z - Halbleiter.org (5th March, 2023)

Photodiodes – what we need for detection or TV

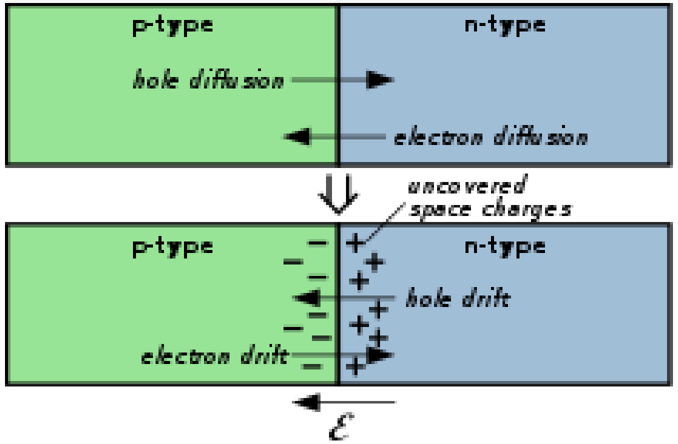
Photodiodes are typically built up from Si, Ge.



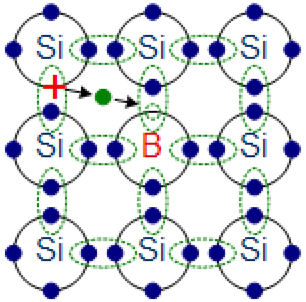


Doped semiconductors, whose conductivity originates from free **n**egative electrons.

***n*-doping**



p-*n* junction
Formation of depletion zone



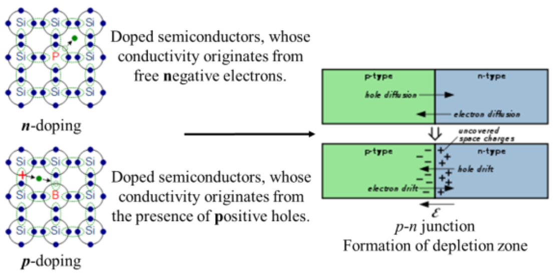
Doped semiconductors, whose conductivity originates from the presence of **p**ositive holes.

***p*-doping**

Photodiode – Wikipedia (5th March, 2023)
Dotieren: n- und p-Halbleiter - Grundlagen - Halbleitertechnologie von A bis Z - Halbleiter.org (5th March, 2023)

White Board

Photodiodes – what we need for detection or TV

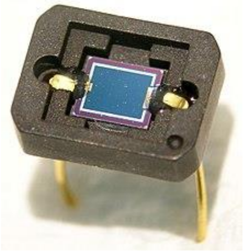


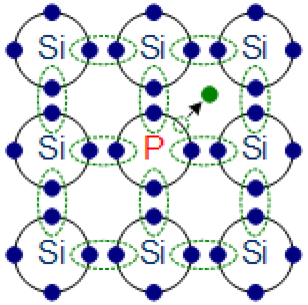
[p-n-Übergang - Halbleiterdiode | LEIFIphysik]

Photodiode – Wikipedia (5th March, 2023)
Dotieren: n- und p-Halbleiter - Grundlagen - Halbleitertechnologie von A bis Z - Halbleiter.org (5th March, 2023)

Photodiodes – what we need for detection or TV

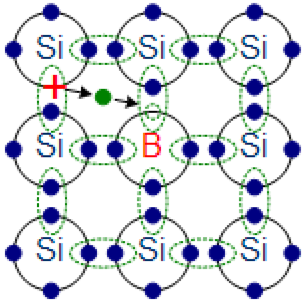
Photodiodes are typically built up from Si, Ge.





***n*-doping**

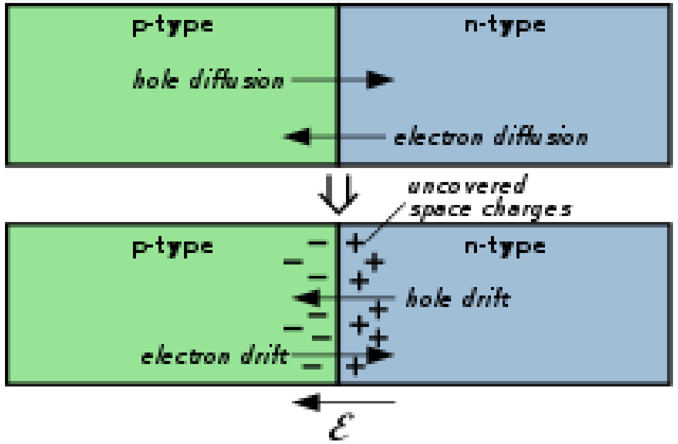
Doped semiconductors, whose conductivity originates from free **n**egative electrons.



***p*-doping**

Doped semiconductors, whose conductivity originates from the presence of **p**ositive holes.

Formation of local charges in *n*- and *p*-doped areas, which is called built-in voltage.
Diodes: Applying a voltage **in** forward direction creates an electric field: electric current!



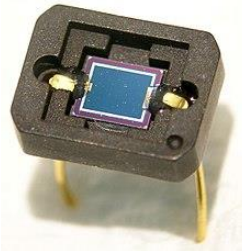
p-*n* junction
Formation of depletion zone

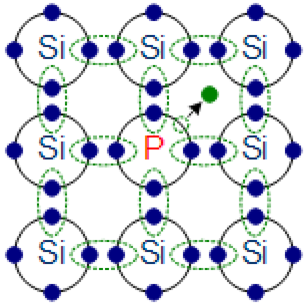
Photodiode – Wikipedia (5th March, 2023)
Dotieren: n- und p-Halbleiter - Grundlagen - Halbleitertechnologie von A bis Z - Halbleiter.org (5th March, 2023)

White Board

Photodiodes – what we need for detection or TV

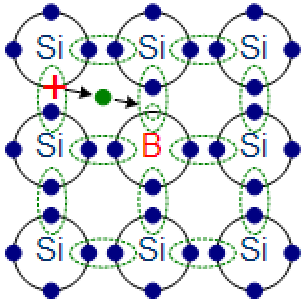
Photodiodes are typically built up from Si, Ge.





n-doping

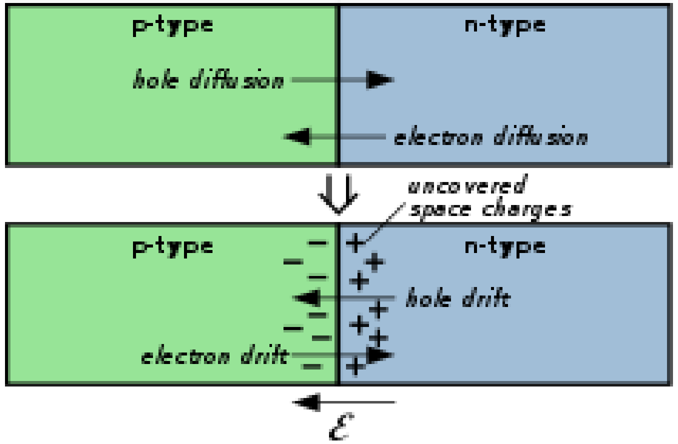
Doped semiconductors, whose conductivity originates from free **n**egative electrons.



p-doping

Doped semiconductors, whose conductivity originates from the presence of **p**ositive holes.

Formation of local charges in *n*- and *p*-doped areas, which is called built-in voltage.
Diodes: Applying a voltage **in** forward direction creates an electric field: electric current!



p-*n* junction
Formation of depletion zone

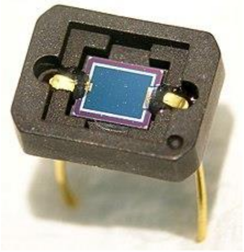
Photodiodes:
Voltage applied **against** forward direction!
Photons create electron-hole pairs, which are separated and measured as photo-current!

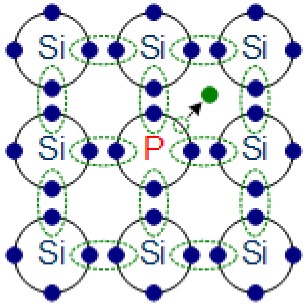
[Photodiode – Wikipedia](#) (5th March, 2023)
[Dotieren: n- und p-Halbleiter - Grundlagen - Halbleitertechnologie von A bis Z - Halbleiter.org](#) (5th March, 2023)

White Board

Photodiodes – what we need for detection or TV

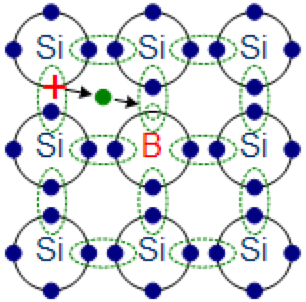
Photodiodes are typically built up from Si, Ge.





n-doping

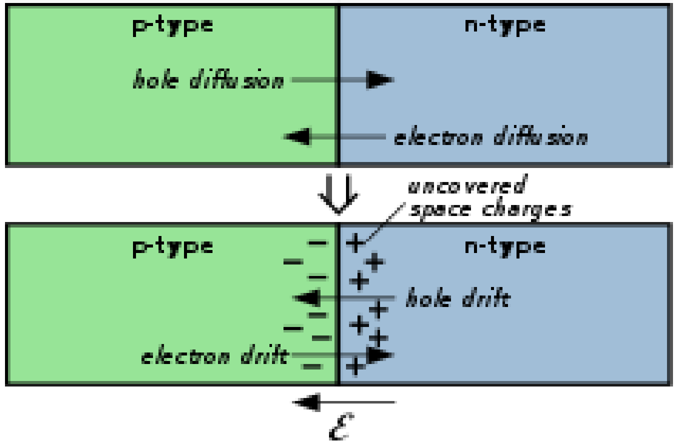
Doped semiconductors, whose conductivity originates from free **n**egative electrons.



p-doping

Doped semiconductors, whose conductivity originates from the presence of **p**ositive holes.

Formation of local charges in *n*- and *p*-doped areas, which is called built-in voltage.
Diodes: Applying a voltage **in** forward direction creates an electric field: electric current!



p-*n* junction
Formation of depletion zone

Photodiodes:
Voltage applied **against** forward direction!
Photons create electron-hole pairs, which are separated and measured as photo-current!

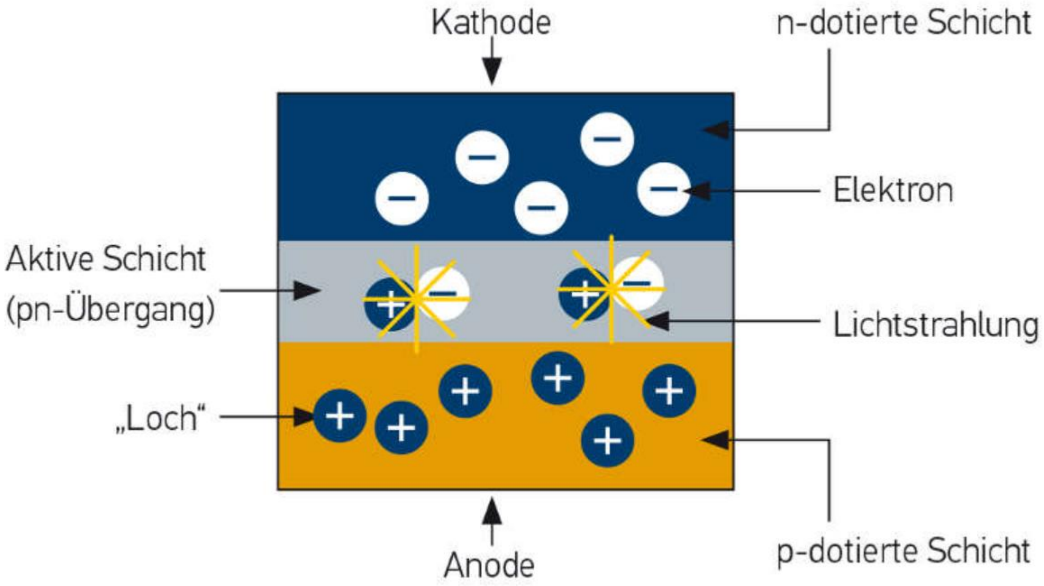
Photodiode – Wikipedia (5th March, 2023)
Dotieren: n- und p-Halbleiter - Grundlagen - Halbleitertechnologie von A bis Z - Halbleiter.org (5th March, 2023)

Working principle of a LED

Difference to “normal” non-emitting diode:

- built up from direct semi-conductor
- Recombination in diode occurs radiation-less

Indium and gallium.



Applying a voltage **in** forward direction:

- Charge carriers move towards each other; e^- from *n* to *p-n* junction
- Recombination in depletion zone under light emission

LED-Scheinwerfer - Funktionweise & Einstellen | HELLA (8th March, 2024) p–n junction – Wikipedia (8th March, 2024)
Licht ins Dunkel bringen | Make Magazin | heise magazine (8th March, 2024)

Solar cells – special photodiodes

Solar panels of the ISS.

Solar cells are built up like photodiodes, except that they are not operated as a radiation detector, but as power source.

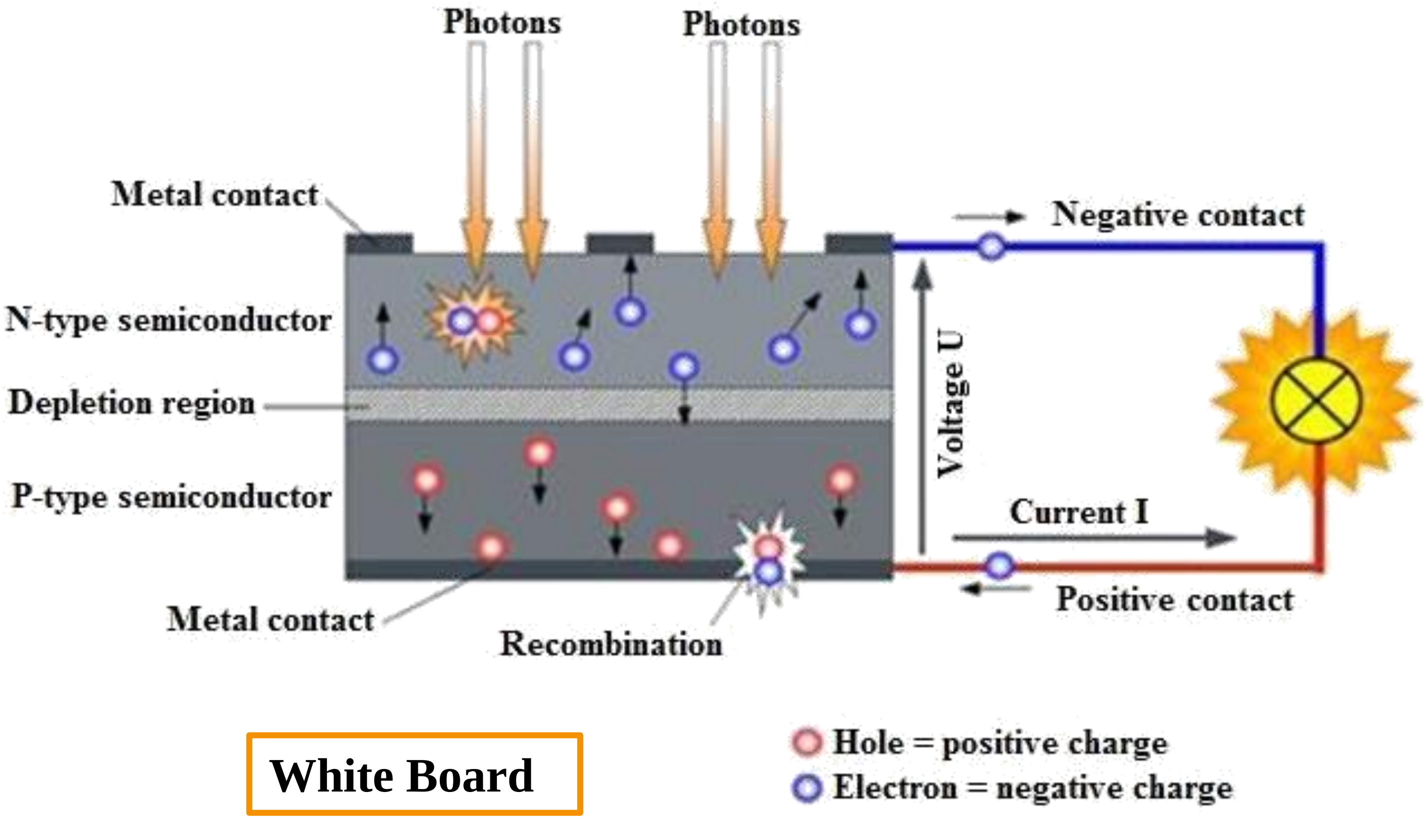
White Board

Kavaz, A & Hodžić, S & Hubana, Tarik & Curevac, Semra & Đozić, N & Merzic, Hamza & Tanković, H & Dervišević, K & Alihodžić, E & Sikira, E & Rahić, D & Kavazovic, Nihad & Tanković, Faris & Šestan, B. (2014). Solar Tree Project.

Solar cells – special photodiodes

Solar panels of the ISS.

Solar cells are built up like photodiodes, except that they are not operated as a radiation detector, but as power source.



White Board

Kavaz, A & Hodžić, S & Hubana, Tarik & Curevac, Semra & Đozić, N & Merzic, Hamza & Tanković, H & Dervišević, K & Alihodžić, E & Sikira, E & Rahić, D & Kavazovic, Nihad & Tanković, Faris & Šestan, B. (2014). Solar Tree Project.

Solar cells – special photodiodes

universität innsbruck

Solar panels of the ISS.

Solar cells are built up like photodiodes, except that they are not operated as a radiation detector, but as power source.

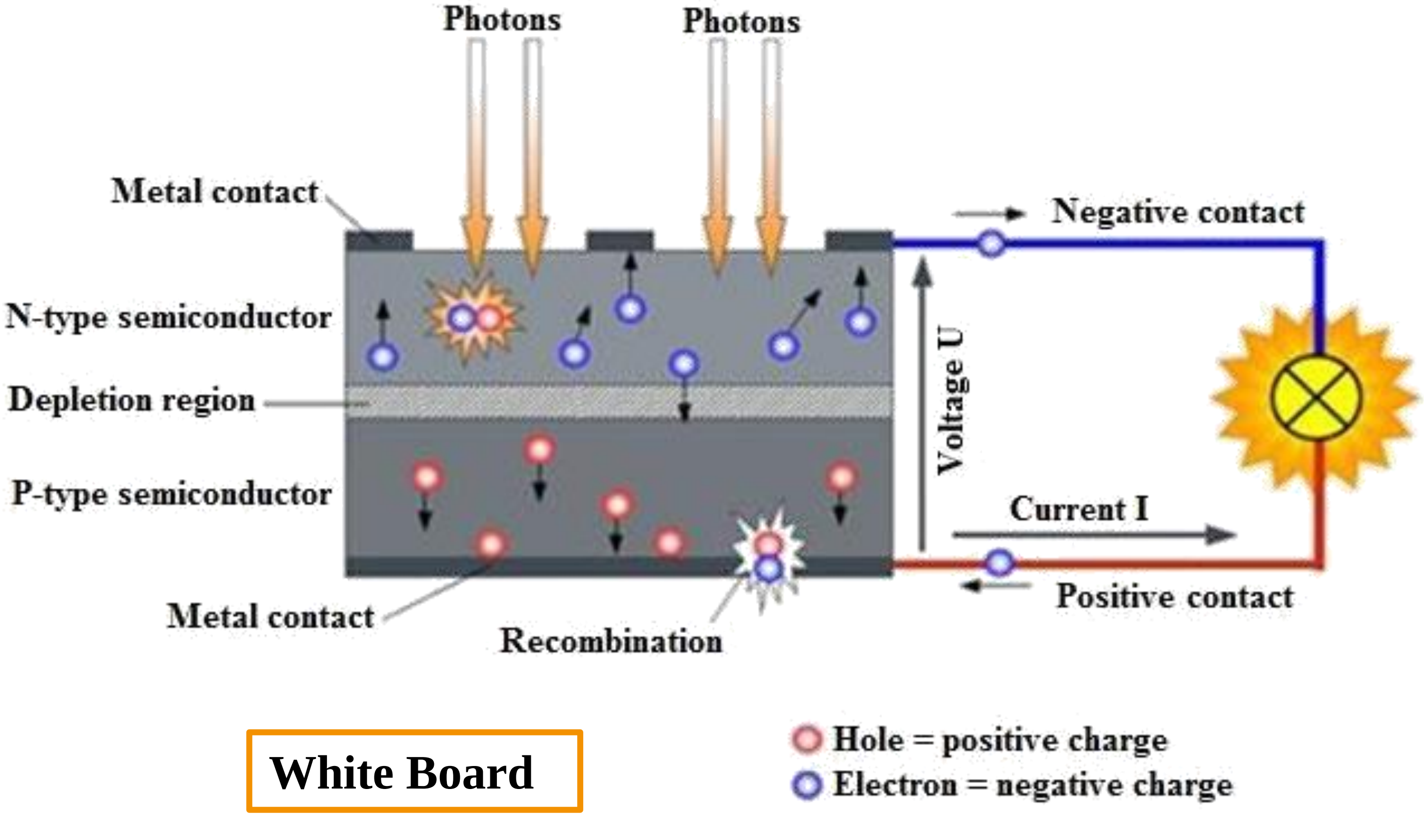
Photons separate electron-hole pairs in the depth of the depletion zone

↓

e^- travel to ***n***-layer, holes to ***p***-layer

↓ Travelling electrons

Recombination in depletion zone



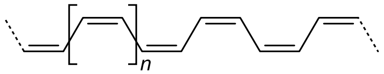
White Board

Kavaz, A & Hodžić, S & Hubana, Tarik & Curevac, Semra & Đozić, N & Merzic, Hamza & Tanković, H & Dervišević, K & Alihodžić, E & Sikira, E & Rahić, D & Kavazovic, Nihad & Tanković, Faris & Šestan, B. (2014). Solar Tree Project.

A functional material could be defined as being prepared from a "target-motivated" approach

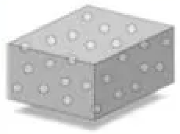
Ceramics

Polymers

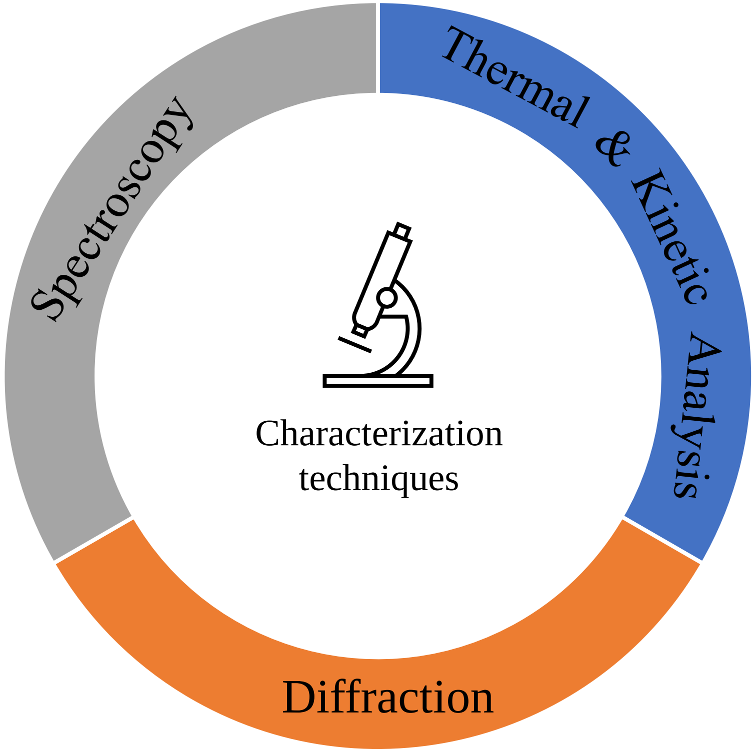


Metals

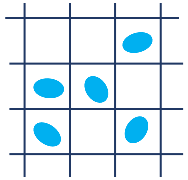
Composites



Glasses



Innovative Materials



Biomaterials

Nanomaterials

Semiconductors

…

Porous materials

Functional Material - an overview | ScienceDirect Topics (3rd March, 2023)

Group-/Tandem-Work

What can we learn from different analyzation techniques?

Shortly sum up, which methods you know and what kind of information you can extract!

10 min

Characterization methods – there are so many…

There are various methods to determine the average and the local structure: diffraction and spectroscopic methods.

Diffraction / no change in electronic structure

- X-ray diffraction
- Neutron diffraction
- Pair Distribution Function (PDF)

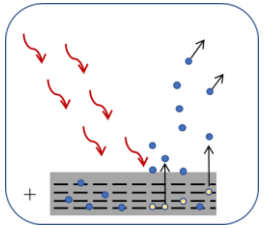
Characterization methods – there are so many…

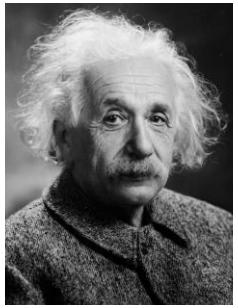
There are various methods to determine the average and the local structure: diffraction and spectroscopic methods.

Diffraction / no change in electronic structure

- X-ray diffraction
- Neutron diffraction
- Pair Distribution Function (PDF)

Photoelectric effect





- XAS, XPS (AES) & UPS

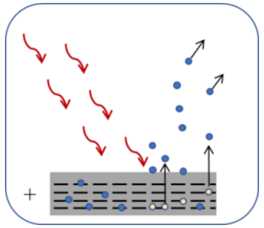
Characterization methods – there are so many…

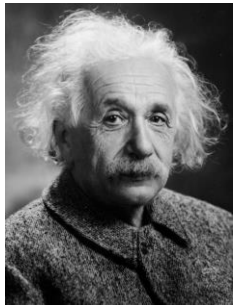
There are various methods to determine the average and the local structure: diffraction and spectroscopic methods.

Diffraction / no change in electronic structure

- X-ray diffraction
- Neutron diffraction
- Pair Distribution Function (PDF)

Photoelectric effect





- XAS, XPS (AES) & UPS

Vibrations and Rotations

- IR and Raman

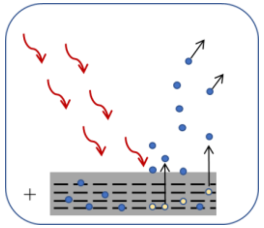
Characterization methods – there are so many…

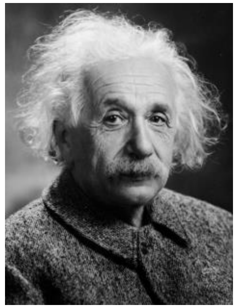
There are various methods to determine the average and the local structure: diffraction and spectroscopic methods.

Diffraction / no change in electronic structure

- X-ray diffraction
- Neutron diffraction
- Pair Distribution Function (PDF)

Photoelectric effect



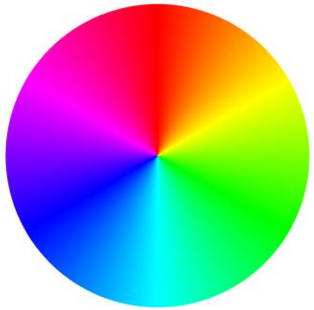


- XAS, XPS (AES) & UPS

Vibrations and Rotations

- IR and Raman

Electronic, nuclear transitions



- UV/Vis spectroscopy
- NMR spectroscopy

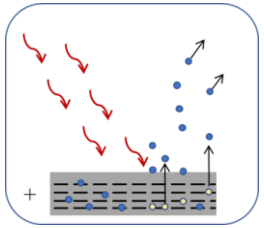
Characterization methods – there are so many…

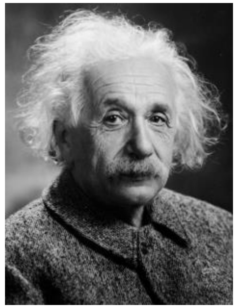
There are various methods to determine the average and the local structure: diffraction and spectroscopic methods.

Diffraction / no change in electronic structure

- X-ray diffraction
- Neutron diffraction
- Pair Distribution Function (PDF)

Photoelectric effect



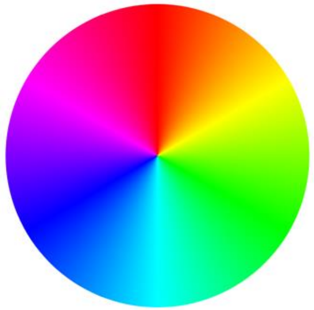


- XAS, XPS (AES) & UPS

Vibrations and Rotations

- IR and Raman

Electronic, nuclear transitions



- UV/Vis spectroscopy
- NMR spectroscopy

Further methods: EDX, mass spectrometry, DSC-TGA, BET.

universität innsbruck

Group-/Tandem-Work

For this week, set up a table with method, sample requirement, information gained and limitations.

5 min

Fundamentals of diffractional methods

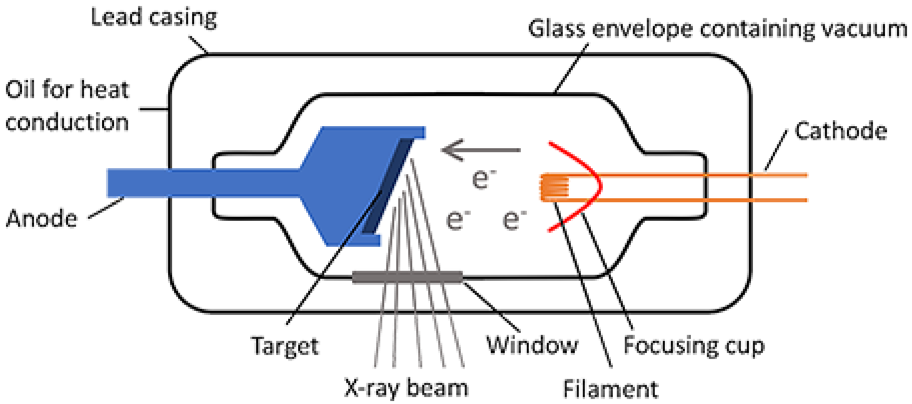
X-ray diffraction – scattering at the electrons

X-rays were discovered by Wilhelm Conrad Röntgen in 1895, for which he was awarded with the Nobel Prize in Physics in 1901.

http://ruby.chemie.uni-freiburg.de/Vorlesung/methoden_II_3.xhtml (11th June 2018)
W. Massa, Kristallstrukturbestimmung, *Teubner GmbH*, **2002**.

X-ray diffraction – scattering at the electrons

X-rays were discovered by Wilhelm Conrad Röntgen in 1895, for which he was awarded with the Nobel Prize in Physics in 1901.



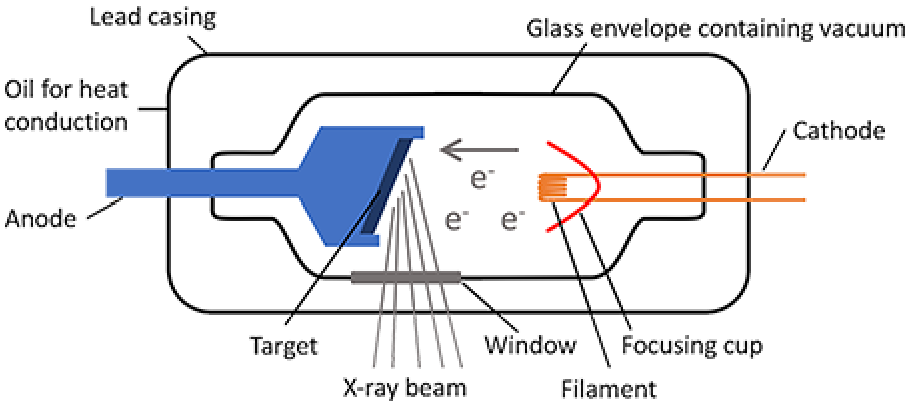
http://ruby.chemie.uni-freiburg.de/Vorlesung/methoden_II_3.xhtml (11th June 2018)

W. Massa, Kristallstrukturbestimmung, *Teubner GmbH*, **2002**.

Production of X-rays - Radiology Café (27th March 2023)

X-ray diffraction – scattering at the electrons

X-rays were discovered by Wilhelm Conrad Röntgen in 1895, for which he was awarded with the Nobel Prize in Physics in 1901.



Electrons are accelerated onto anode material in a high vacuum

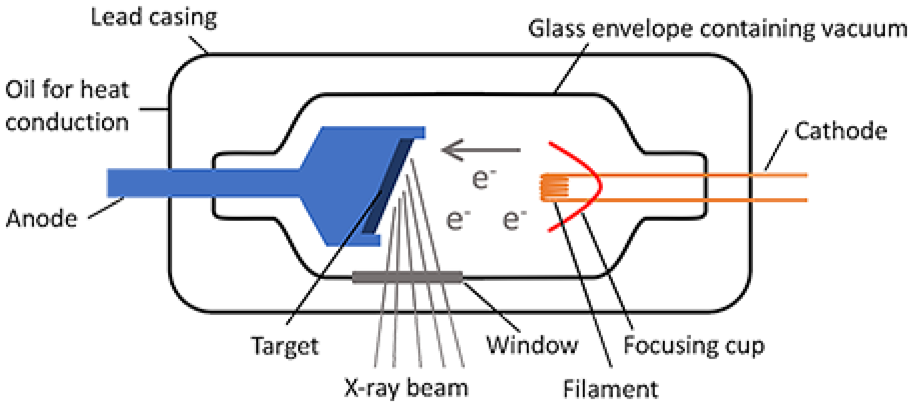
Cu $K_{\alpha 1}$: 1.54 Å

Mo $K_{\alpha 1}$: 0.70 Å

http://ruby.chemie.uni-freiburg.de/Vorlesung/methoden_II_3.xhtml (11th June 2018)
W. Massa, Kristallstrukturbestimmung, *Teubner GmbH*, **2002**.
Production of X-rays - Radiology Café (27th March 2023)

X-ray diffraction – scattering at the electrons

X-rays were discovered by Wilhelm Conrad Röntgen in 1895, for which he was awarded with the Nobel Prize in Physics in 1901.



Electrons are accelerated onto anode material in a high vacuum

Cu $K_{\alpha 1}$: 1.54 Å

Mo $K_{\alpha 1}$: 0.70 Å

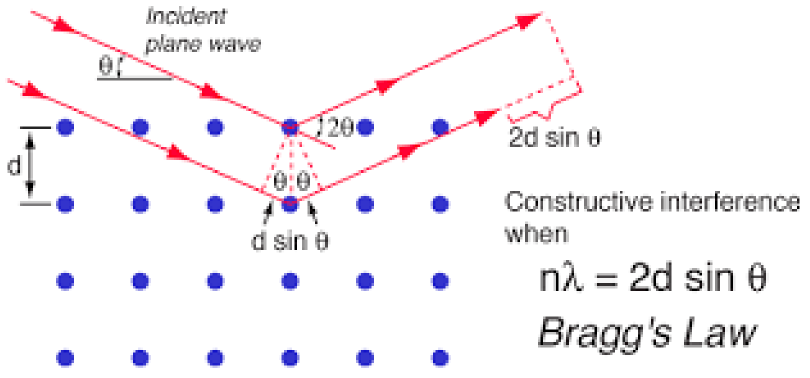
X-ray diffraction provides **electron density maps**

http://ruby.chemie.uni-freiburg.de/Vorlesung/methoden_II_3.xhtml (11th June 2018)
W. Massa, Kristallstrukturbestimmung, *Teubner GmbH*, **2002**.
Production of X-rays - Radiology Café (27th March 2023)

X-ray diffraction – scattering at the electrons

X-rays were discovered by Wilhelm Conrad Röntgen in 1895, for which he was awarded with the Nobel Prize in Physics in 1901.

Sample requirement: long-range order.



Scattering at net planes – **electron shell**

X-ray diffraction provides **electron density maps**

http://ruby.chemie.uni-freiburg.de/Vorlesung/methoden_II_3.xhtml (11th June 2018)
W. Massa, Kristallstrukturbestimmung, *Teubner GmbH*, **2002**.

X-ray diffraction – scattering at the electrons

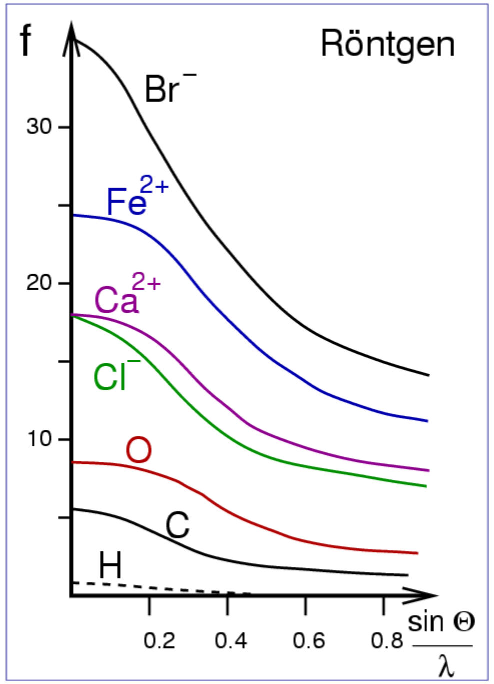
X-rays were discovered by Wilhelm Conrad Röntgen in 1895, for which he was awarded with the Nobel Prize in Physics in 1901.

Sample requirement: long-range order.

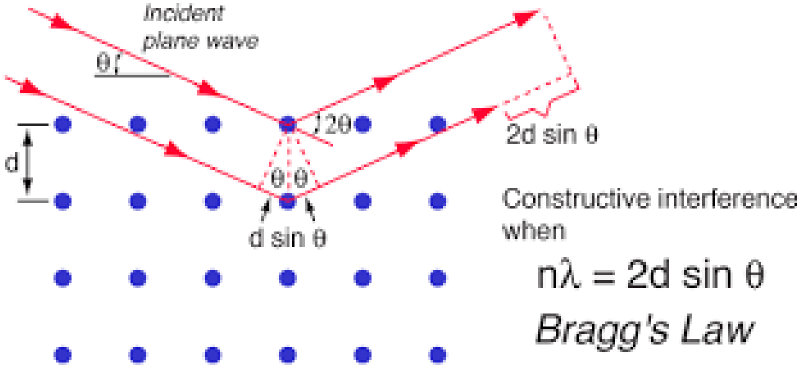
Challenges in X-ray diffraction

- Determination of proton positions difficult
- Differentiation of atoms with the same or similar number of electrons hardly possible

X-ray diffraction provides **electron density maps**



Intensity is dependent of atomic form factor



Scattering at net planes – **electron shell**

http://ruby.chemie.uni-freiburg.de/Vorlesung/methoden_II_3.xhtml (11th June 2018)
W. Massa, Kristallstrukturbestimmung, *Teubner GmbH*, **2002**.

Neutron diffraction – scattering at the nucleus

Neutron radiation is generated in two ways: Either a nuclear reaction (^{235}U) or spallation sources are used.

Sample requirement: long-range order.

ILL Grenoble

- Scattering of neutrons by the point-like nucleus
- Absorber: Cadmium, Boron, Hafnium, Europium

ORNL Oak Ridge

Neutron diffraction – scattering at the nucleus

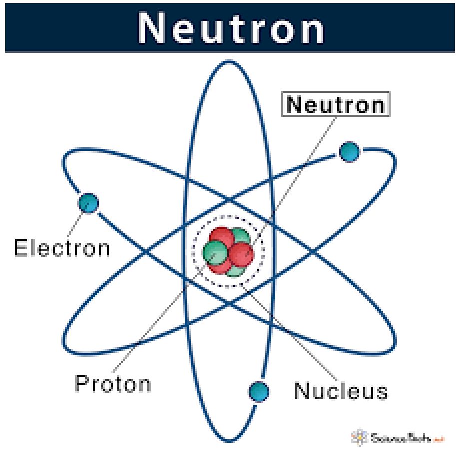
Core reactions

- Neutrons are continuously produced from the fission of uranium: very fast (high-energy) neutrons

- Can be adjusted by moderators:

I. thermic neutrons, 1.5 Å, heavy water
II. hot neutrons:, 0.5 Å, graphite at 2500 °C
III. cold neutrons, 5 Å, liquid H_2

Neutrons are guided through waveguides (Ni mirrored glass tubes) / monochromators also applied



Welt der Physik: Mit Neutronen zu neuen Materialien (28th March 2023)
Kernreaktor – Wikipedia (28th March 2028)

Neutron diffraction – scattering at the nucleus

universität innsbruck

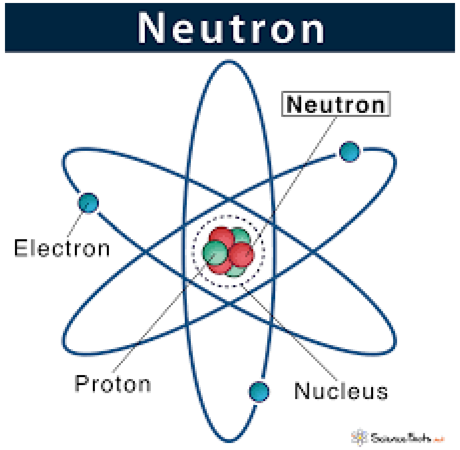
Core reactions

- Neutrons are continuously produced from the fission of uranium: very fast (high-energy) neutrons

- Can be adjusted by moderators:

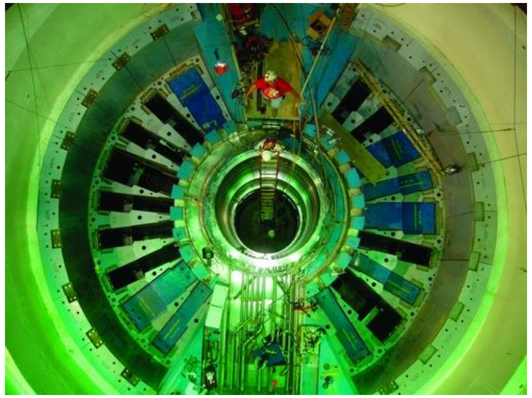
I. thermic neutrons, 1.5 Å, heavy water
II. hot neutrons:, 0.5 Å, graphite at 2500 °C
III. cold neutrons, 5 Å, liquid H_2

Neutrons are guided through waveguides (Ni mirrored glass tubes) / monochromators also applied



Spallation sources

I. Pulsed proton beam (50 Hz) from synchrotron hits heavy metal target (U, Pb, Hg, Ta) and ejects around 50 neutrons per proton
II. Velocity is known and related to E and λ: no monochromator required!



Welt der Physik: Mit Neutronen zu neuen Materialien (28th March 2023)
Kernreaktor – Wikipedia (28th March 2028)

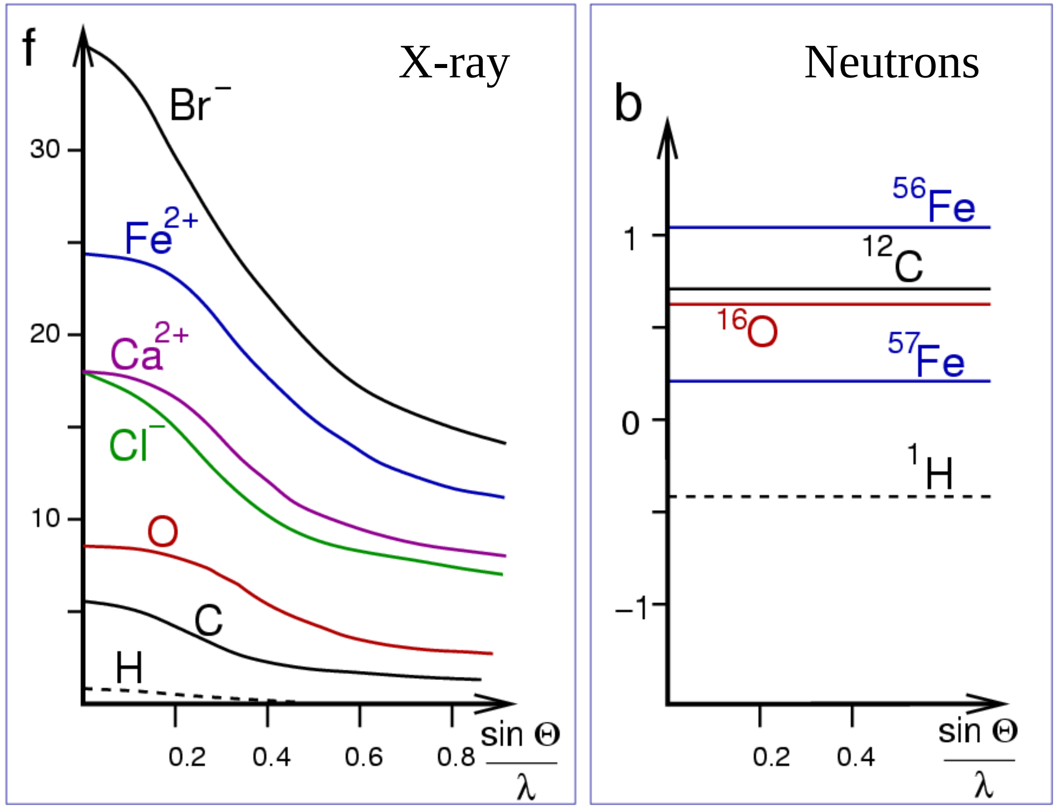
Neutron diffraction – scattering at the nucleus

Neutron scattering lengths hardly decrease with increasing diffraction angle.

Sample requirement: long-range order.

- light and heavy elements have comparable scattering force
- different b-lengths of elements with similar atomic number
- Slow decrease of b → measurements at high resolution

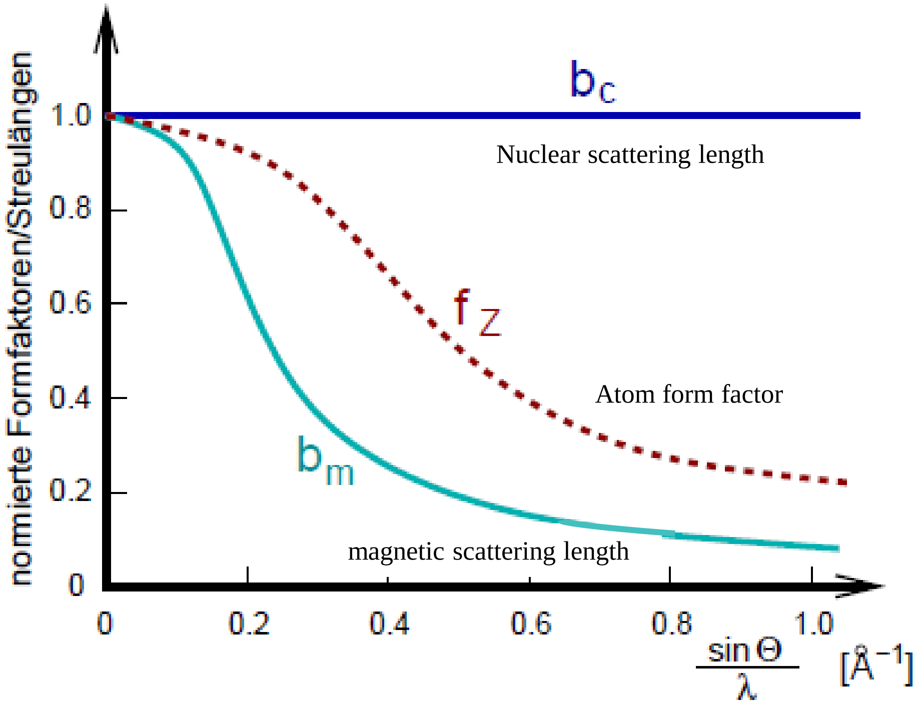
Neutron diffraction provides **core density maps**



http://ruby.chemie.uni-freiburg.de/Vorlesung/methoden_II_3.xhtml (11th June 2018)
Vorlesung Methoden der Festkörperchemie: „Neutronenbeugung“, WS 16/17, Röhr

Neutron diffraction – it´s much more!

Not only core density maps are yielded, but also information about the magnetic structure is obtained.



- Interaction with magnetic field (spin and orbital moments of electrons of the atomic shell)
- Electron shell is not point like: Θ dependence as known from X-ray diffraction

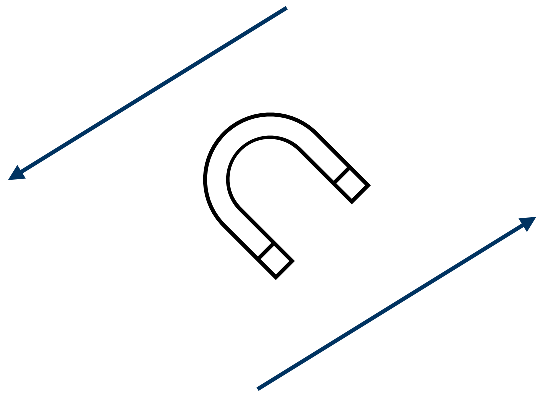
Magnetic scattering: Neutron has magnetic moment of μ = ½

http://ruby.chemie.uni-freiburg.de/Vorlesung/methoden_II_3.xhtml (11th June 2018)
Vorlesung Methoden der Festkörperchemie: „Neutronenbeugung“, WS 16/17, Röhr

Neutron diffraction – it´s much more!

Differentiation between ferro- and antiferromagnetism due to additional peaks!

Ferromagnetic material

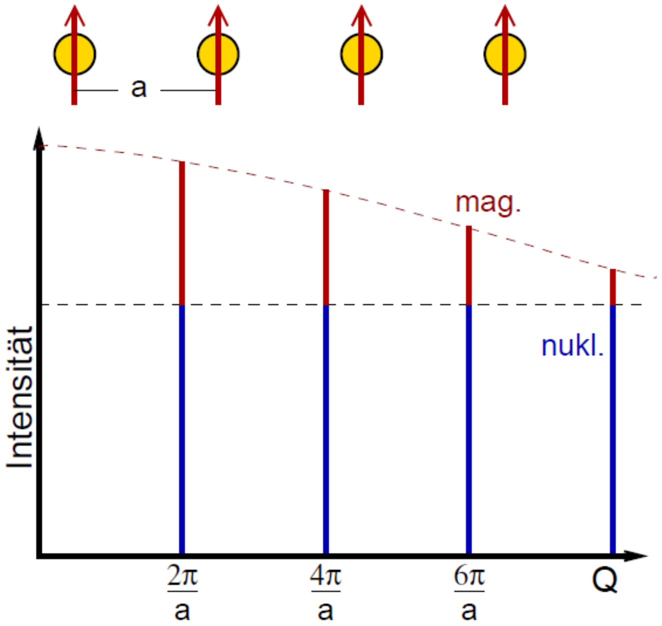


Antiferromagnetic material

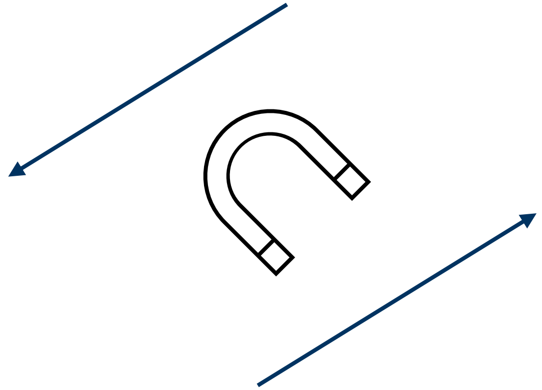
Magnetic scattering: Neutron has magnetic moment of $\mu = ½$

Neutron diffraction – it´s much more!

Differentiation between ferro- and antiferromagnetism due to additional peaks!



Ferromagnetic material



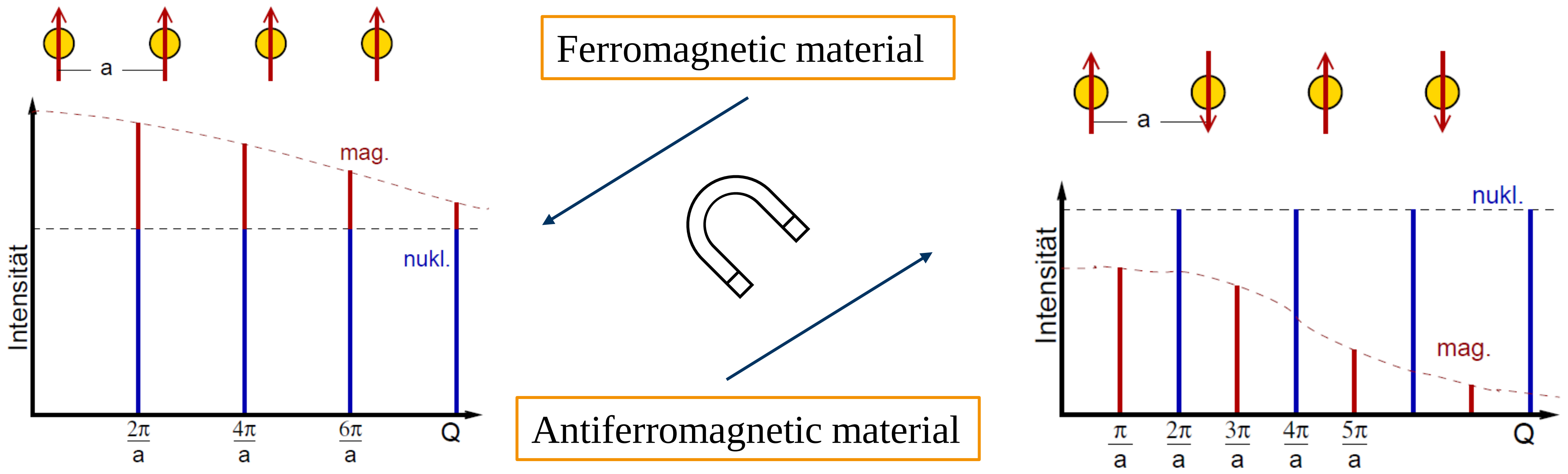
Antiferromagnetic material

- magnetic Bragg peaks at the same positions as nuclear peaks
- Θ dependence of magnetic structure

Magnetic scattering: Neutron has magnetic moment of $\mu = ½$

Neutron diffraction – it´s much more!

Differentiation between ferro- and antiferromagnetism due to additional peaks!



- magnetic Bragg peaks at the same positions as nuclear peaks
- Θ dependence of magnetic structure

- magnetic Bragg peaks between nuclear peaks
- formation of magnetic superstructure

Magnetic scattering: Neutron has magnetic moment of $\mu = ½$

Neutron diffraction vs. X-ray diffraction

Highly penetrating due to 0 charge.
Probing internal structure of sample.

X-rays are carrying no charge, provide data on the surface structure mainly.

Neutron diffraction

X-ray diffraction

Neutron diffraction vs. X-ray diffraction

Highly penetrating due to 0 charge.
Probing internal structure of sample.

Interacts with nuclei: scatters strongly from both light and heavy atoms and can differentiate between isotops.

Neutron diffraction

X-ray diffraction

X-rays are carrying no charge, provide data on the surface structure mainly.

Interacts with electron clouds: scatters strongly from heavier elements with bigger electron clouds.

Neutron diffraction vs. X-ray diffraction

universität innsbruck

Highly penetrating due to 0 charge. Probing internal structure of sample.

Interacts with nuclei: scatters strongly from both light and heavy atoms and can differentiate between isotops.

Neutrons are spin ½ and carry magnetic moment: study of magnetism over short ranges.

Neutron diffraction

X-ray diffraction

X-rays are carrying no charge, provide data on the surface structure mainly.

Interacts with electron clouds: scatters strongly from heavier elements with bigger electron clouds.

X-rays can be utilized to investigate magnetism but are less accurate.

Neutron diffraction vs. X-ray diffraction

Neutron diffraction	X-ray diffraction
Highly penetrating due to 0 charge. Probing internal structure of sample.	X-rays are carrying no charge, provide data on the surface structure mainly.
Interacts with nuclei: scatters strongly from both light and heavy atoms and can differentiate between isotops.	Interacts with electron clouds: scatters strongly from heavier elements with bigger electron clouds.
Neutrons are spin ½ and carry magnetic moment: study of magnetism over short ranges.	X-rays can be utilized to investigate magnetism but are less accurate.
Expensive and lot of sample amount is needed.	Less expensive and small sample amounts are possible.

Neutron diffraction vs. X-ray diffraction

Neutron diffraction	X-ray diffraction
Highly penetrating due to 0 charge. Probing internal structure of sample.	X-rays are carrying no charge, provide data on the surface structure mainly.
Interacts with nuclei: scatters strongly from both light and heavy atoms and can differentiate between isotops.	Interacts with electron clouds: scatters strongly from heavier elements with bigger electron clouds.
Neutrons are spin ½ and carry magnetic moment: study of magnetism over short ranges.	X-rays can be utilized to investigate magnetism but are less accurate.
Expensive and lot of sample amount is needed.	Less expensive and small sample amounts are possible.
Requires the use of high energy synchrotrons.	Can also be performed in house – no need for synchrotrons.

What diffraction methods cannot serve for…

- Average crystal structure is obtained – no statements on the local structure
- No structural solution of non-crystalline materials
- No structure solution of disordered materials
- Limited structure solution of nano-crystalline substances (poorly defined Bragg peaks)

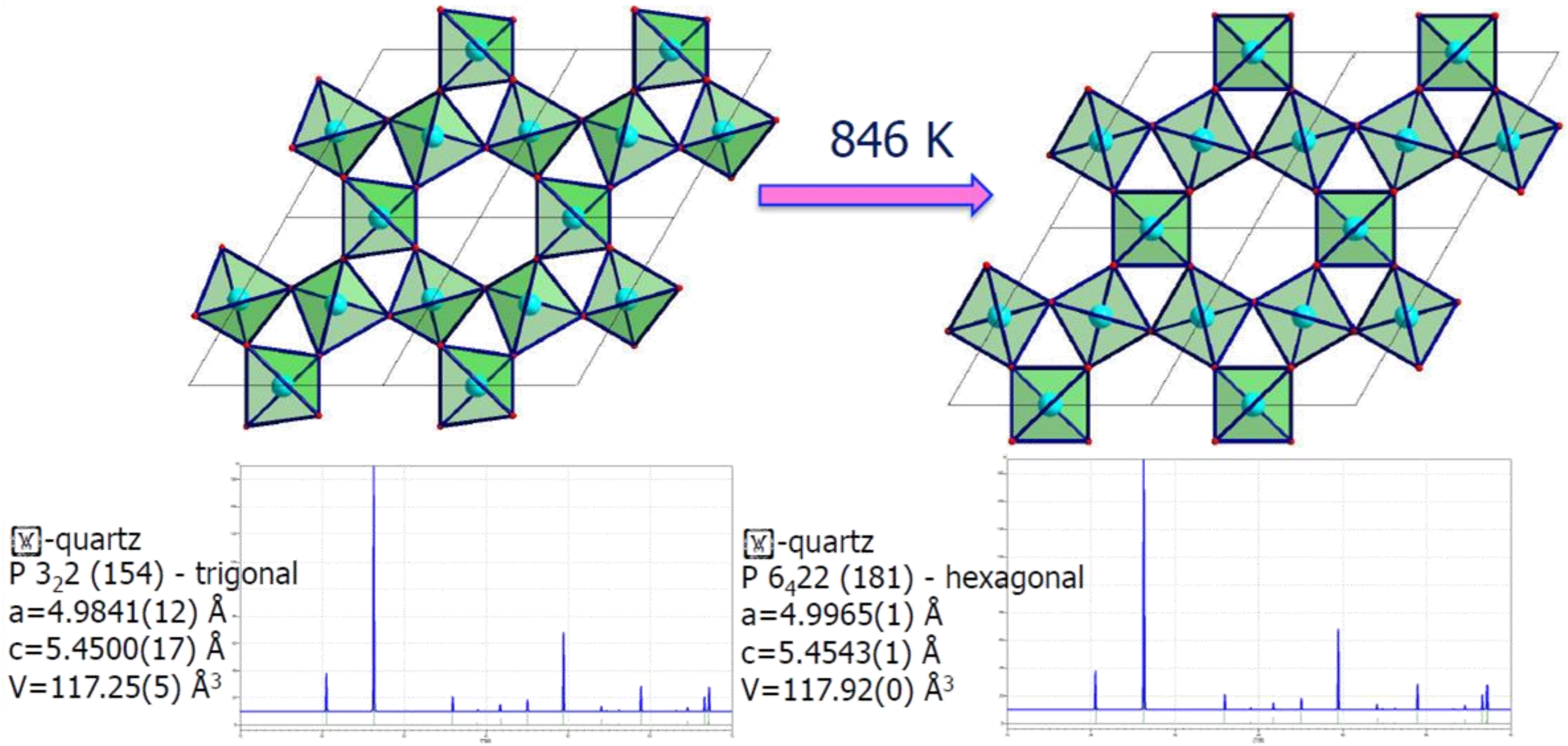
↓

Methods for exact determination of the local structure – short range order.

universität innsbruck

The problem with the local structure….

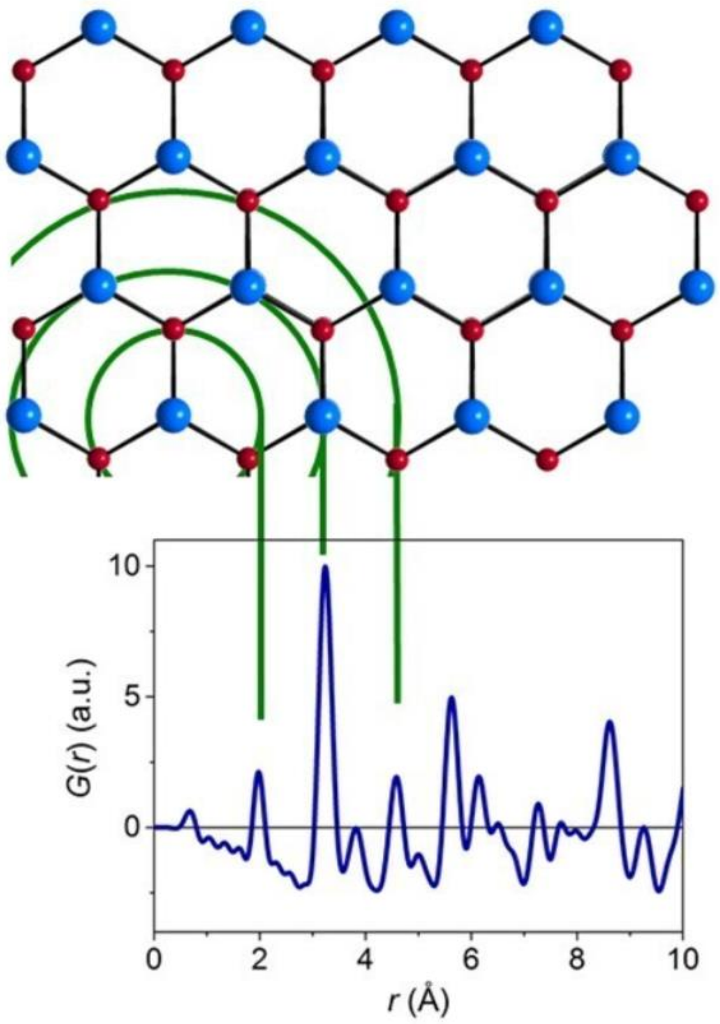
Average crystallographic structure is obtained *via* X-ray or neutron scattering – no statements on the local structure can be made.



When we want to look closer - PDF

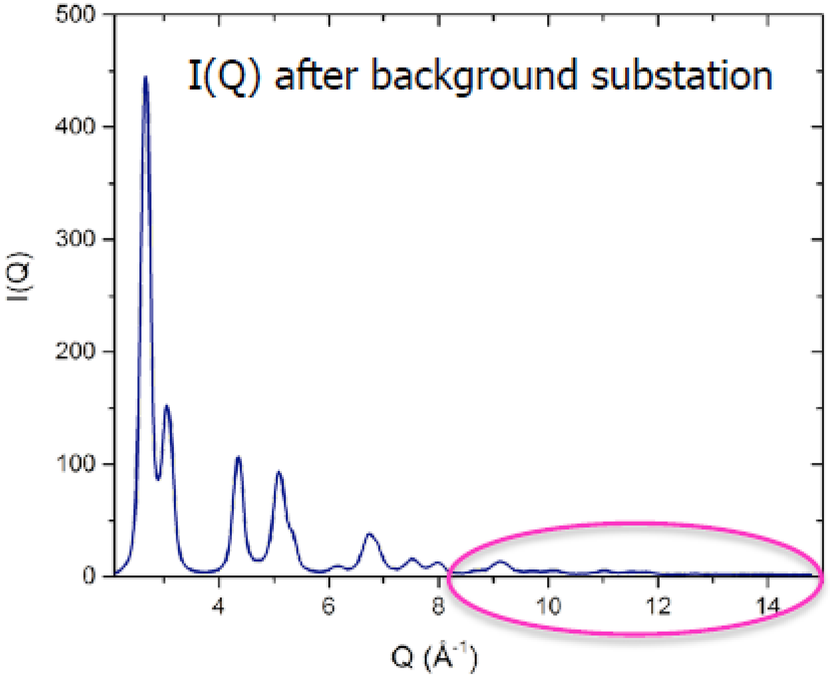
Both Bragg scattering and the underlying diffuse scattering are determined. The arrangement of atoms in the long range can be inferred from the Bragg peaks in an X-ray diffraction pattern. The short-range arrangement, i.e., the local atomic structure, is visible in the broad, less well-defined features of the diffraction pattern. This local structure is quantitatively described by the atomic pair distribution function.

- The pair distribution function (PDF) corresponds to a histogram of interatomic distances
- Each atom in the sample serves as an arbitrary centre from which all interatomic distances to all other atoms are measured
- All interatomic distances are summed and projected over the radius r



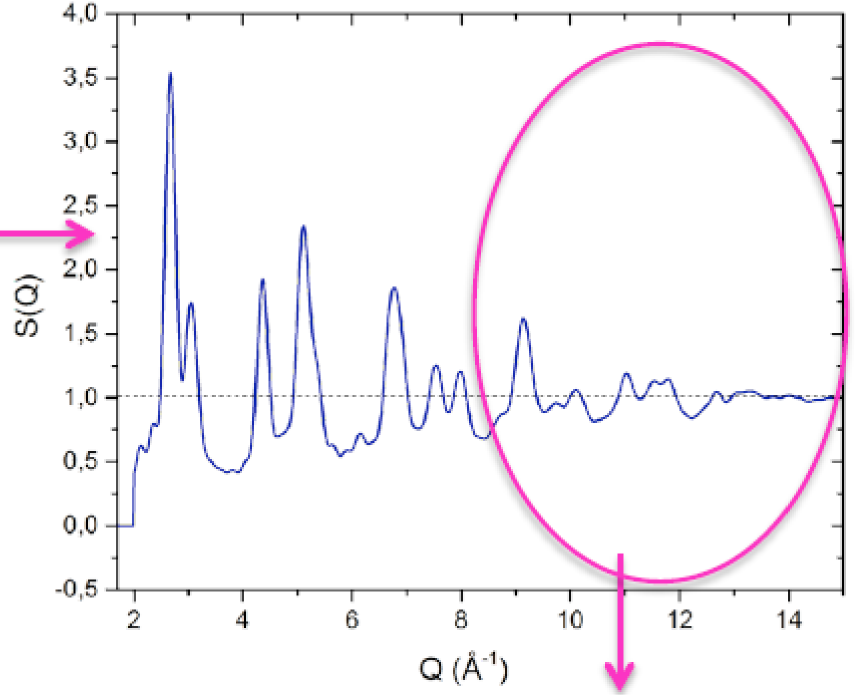
Paarverteilungsfunktion (PDF) - RWTH AACHEN UNIVERSITY Institut für Kristallographie – Deutsch (10th March, 2025)

PDF - Pair Distribution Function



Total scattering structure function

$$S(Q) = 1 + \frac{I(Q) - \langle f^2(Q) \rangle_{composition}}{\langle f(Q) \rangle^2_{composition}}$$

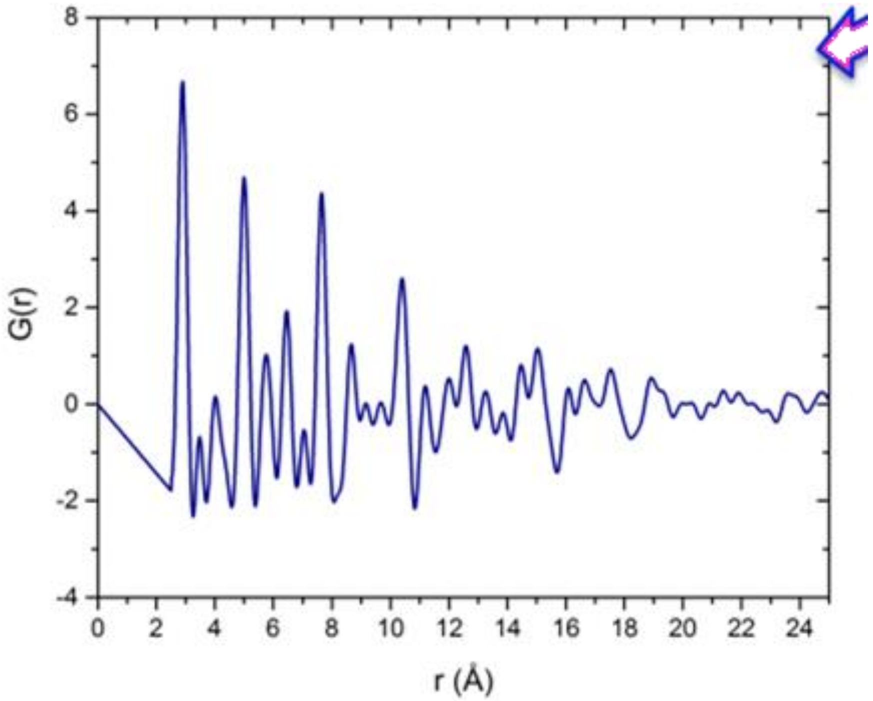


Reduced total scattering structure function

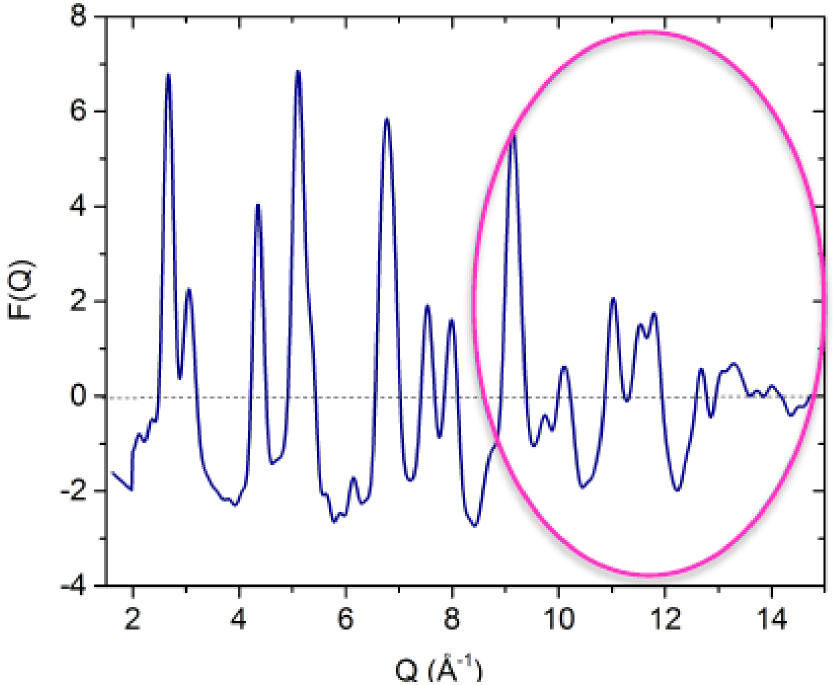
$$F(Q) = Q[S(Q) - 1]$$

Lecture series: Modern Methods in Heterogeneous Catalysis Research, Analysis of Local Structure by Atomic Pair Distribution Function, E. Willinger

PDF - Pair Distribution Function

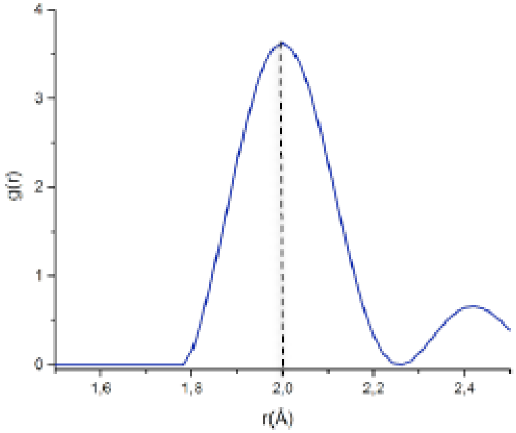


$$G(r) = \frac{2}{\pi}\int_0^\infty F(Q)\sin(Qr)\,dQ$$



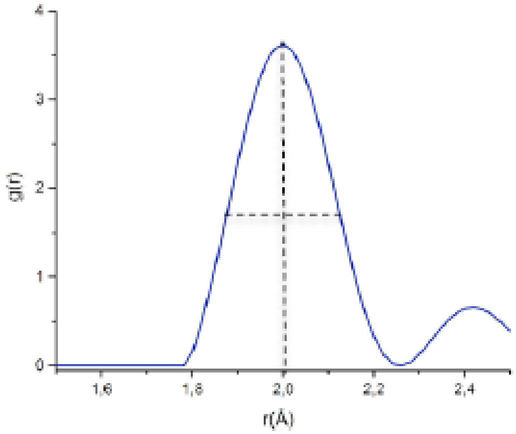
Fourier-Transformation

PDF - Pair Distribution Function



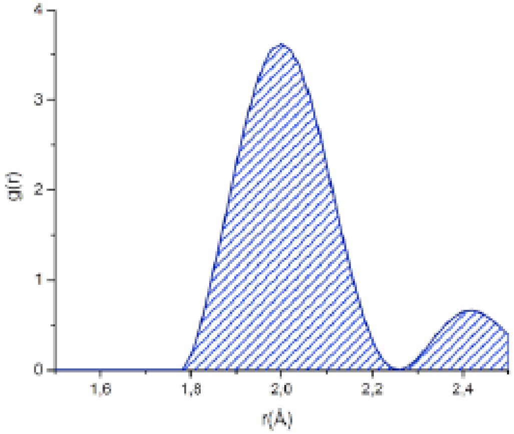
Peak positions

Average interatomic distances



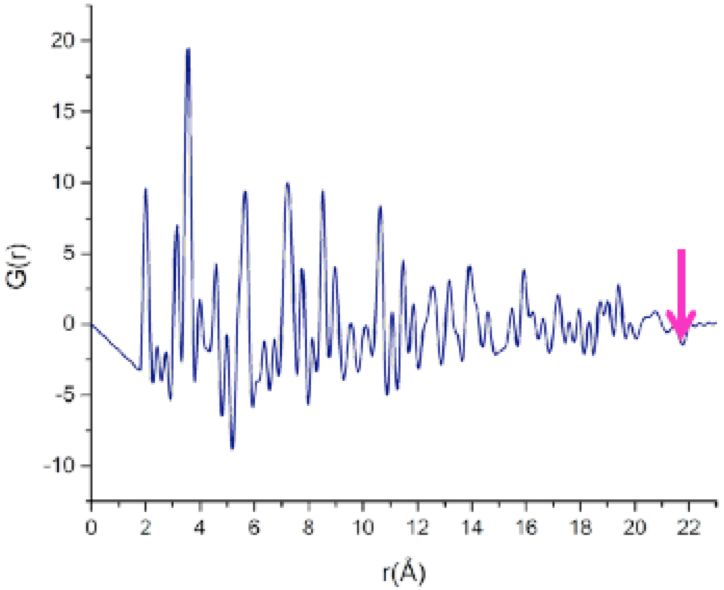
Peak Width

Structural disorders



Integrals

Average coordination properties



Cut-Off PDF

Particle size effect

Lecture series: Modern Methods in Heterogeneous Catalysis Research, Analysis of Local Structure by Atomic Pair Distribution Function, E. Willinger

Plenum

Methods-Table: Comparison results

10 min

Questions?