Chapter 4

X-Ray and EUV Methods



X-Ray and EUV Methods

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4.1 X-Rays and Extreme UV Photons

X-rays and EUV photons have a much higher energy hv > 20 eV and much shorter wavelengths than visible or infrared photons.



As a result:

- 1. <u>Phase differences</u> between the x-rays lead scattered by the atoms lead to a *diffraction pattern* that yields precise information on the arrangement of the atoms with sub 0.01Å resolution
- Higher energy electronic transitions involving tightly bound core electrons come into reach. These depend only weakly on the chemical bonding and atom environment and are therefore <u>element specific</u>.
 <u>non-destructive chemical analysis</u> by <u>x-ray absorption</u> or <u>x-ray fluorescence</u> spectroscopy.
- <u>hv is larger than the binding energies of electrons</u> in solids (work functions of ~few eV). Thus, bound electrons can be photo-excited into continuum states and emitted from the solid = <u>photo emission</u> <u>spectroscopy</u>. These electrons can be analyzed for (i) chemical analysis (XPS, ESCA) as well as (ii) mapping of the energy-momentum dispersion E(k) of the electronic band structure.



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G. Springholz - Nanocharacterization I

Example: X-Ray Diffraction

For x-ray photons the wavelength $\lambda \sim A$ is of the order of the interatomic distances in solids.

As a result, **strong interference** between x-ray waves scattered from the individual atoms occurs, which depends on the direction of the incident and scattered x-rays.

This gives rise to a <u>diffraction pattern $I(\omega, \theta)$ </u> that is measured by <u>X-ray diffraction</u>.

Critical wavelength needed: Bragg's law $n\lambda = 2 d \sin \theta \gg \lambda < 2d$ since $\sin \theta$ always < 1



⇒ The diffraction pattern strongly depends on the arrangement of the atoms and their interatomic distances in the crystal lattice.

Thus, diffraction yields precise information on the atomic structure of materials with *picometer resolution,* from which the kind of materials as well as their structural properties can be identified.

X-ray diffraction set-up

Diffraction spectrum = angular intensity distribution

Photons with hv >> several eV can <u>knock-out</u> bound valence electrons with typical binding energies of 5 – 20 eV from the sample as well as core electrons with binding energies > 100eV

This leads to generation of secondary electrons that can be emitted from the sample.



- ⇒ The photoemission spectrum yields information on the binding energies of the electrons
- ⇒ Ionization is the main reason for the harmful nature of EUV and X-ray radiation !

Example: X-Ray Fluorescence

Knock-out of strongly bonded *inner core shell electrons* by x-ray absorption leads to a core shell vacancy that is subsequently filled by recombination of an electron from an outer shell.



The fluorescence spectrum thus features sharp lines at element specific positions. Measuring the positions yields information on which elements are contained in the sample and from the intensity rations the chemical composition can be obtained.

Probe - in	Interaction	Probe - out	➡ Measurement Method
X-rays	elastic	x-rays	Angular distribution = x-ray diffraction & scattering (XRD),
~ keV	inelastic excitation	x-rays electrons	Energy spectrum = x-ray fluorescence (XRF) Energy Spectrum = x-ray photoelectron spectroscopy (XPS)

Limitation of XR and EUV Methods

An important limitation is the *lack of effective optical elements* for focusing, shaping and manipulation of x-ray beams because for all materials, at short wavelengths the **refractive index** approaches $n \sim 1$ and the reflectivity is close to zero, i.e., R < 0.1 %!



In addition:

 All materials show some kind of absorption for EUV and X-ray radiation.

X-rays = ionizing radiation » radiation damage =

- harmful nature XRs
- » safety measures required (radiation protection)

Further limitation: Limited availibility of high intensity and tunable light sources » synchrotrons.

4.2 X-Ray Absorption

Absorption of high energy photons has similar properties as for visible photons.

XRD: $E_{XR} \sim 0.5 - 50 \text{keV}$, $\lambda \sim 3 - 0.03 \text{ nm}$; **UV:** $E_{UV} \sim 5 - 200 \text{ eV}$, $\lambda \sim 200 - 5 \text{ nm}$ Due to the higher energy, however, also *high-energy excitations* come into reach.

These are ionization (creation of unbound photoelectrons) and core shell excitations.



For both cases, initially *bound electrons* are excited into *unbound continuum states* with arbitrary final energy. Therefore, the absorption spectrum at high photon energies consists of a <u>broad continuum</u> with a superimposed fine structure (<u>absorption edges</u>) at which the photon energy reaches the binding energy of certain strongly bound core shell electrons.

Note: Because the refractive index *n* of all materials is $n \sim 1$ for high energy photons, the reflectivity is very small and can be practically neglected (except for diffraction experiments).

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4.2.1 Absorption Edges due to Core-Shell Excitations

Photons with **energy > 100 eV** are able to *knock-out* also strongly bonded *inner core shell electrons* in the sample.

The <u>critical ionization energy</u> E_{crit} is the minimal energy required to remove an inner electron with quantum number *n* bound to the nucleus.

This energy is more or less the binding energy of the core electron E_{core} with primary quantum number *n* is given by:

 $E_{\text{crit}}(n) = E_{\text{Fermi}} - E_{\text{core}} \approx - E_{\text{core}}(n) \quad \text{because the}$

Fermi energy is usually small compared to E_{core} .



For an *atom with just one electron*, the **binding energy** of an electron with principle quantum number *n* simply corresponds to the corresponding electron energy in the hydrogen atom, *corrected* by the given nucleus charge *Z* of the atom that is the order number of the atom, i.e.,

$$E_n(Z) = \frac{m_e}{8c\varepsilon_0 h^3} \frac{(Ze)^2 e^2}{n^2} = R_H \frac{Z^2}{n^2}$$
 where $R_H = 13.6 \text{eV}$ (=Rydberg constant)

For a neutral atom, the number of bound electrons is equal to the nucleus charge Z.

For the outer electrons, the nucleus charge Z is therefore partially screened, so that the electrons in an outer shell see only an *effective nucleus charge* $(Z - \sigma_n)$ where σ_n is the screening factor that is more or less equal to the number of electrons in the more inner shells.

4.2.2 Critical ionization energies of atoms as a function of Z number

Taking into account the partial screening of the nucleus charge Z, the electron binding energies and thus the critical ionization energies can be approximated by:

 $E_{crit}(Z,n) = -R_H (Z - \sigma_n)^2 / n^2$ $R_H = 13.6 \text{ eV} = Rhydberg constant.$

 \Rightarrow **n** = 1, 2, 3, ... = principle quantum number *n* of the removed electron for K, L, M, N, O shells

- \Rightarrow (Z σ_n) = effective nucleus charge seen by the core electron,
 - = nucleus charge Z minus the charge σ_n that is screened by the electrons of the more inner shells.



When $E_{probe} > E_{crit}$ exceeds the critical ionization energy, the absorption coefficient abruptly ⇔ increases compared to $E_{probe} < E_{crit}$, forming <u>absorption edges</u> in the spectra.

⇒ Core level transitions are element specific and thus, well suited for *chemical* analysis !

Ionization Energy of

2500

e٧

Absorption edges: Core-level absorption sets in at photon or particle energies $E > E_{crit}(n)$. This gives rise to discrete steps in the absorption spectra, named *absorption edges*.



⇒ Position of core level edges are element specific and thus, allow identification of chemical elements !

4.2.3 Fine Structure of the Absorption edges (EXAFS, NEXAFS)

There exist also a *fine structure* of the *absorption edges* because at $E \sim E_{crit}$ the core electrons are excited into unoccupied bound or antibonding states, which are influenced by the chemical environment of the atoms.

⇒ This can be employed to derive not only the chemical composition, but also information on the local **bond configuration of the atoms** in the samples.

XANES = X-Ray <u>Absorption Near Edge Structure</u>, also known as near edge X-ray absorption fine structure (NEXAFS) caused by interference effects with surrounding atoms. Information on local atomic coordination and chemical / oxidation state.

EXAFS: Interference between incoming and outgoing wave. Yields information on bond lengths and nearest neighbor coordination.





⇒ XAFS: Single Scattering, NEXAFS: Multiple Scattering



Fine structure measurements is a fingerprint of the local environment but requires tuneable x-ray sources available only by synchrotrons



4.2.4 Instrumentation for X-Ray Spectroscopy

Laboratory x-ray sources: X-ray tubes – only discreet emission lines, limited intensity, divergent beams



Detectors: Gas discharge detectors, scintillators, photomultiplier and semiconductor detectors. **Optics**: No refractive optics, only weak diffractive or reflective focusing elements. **Spectrometers**: Diffraction of single crystals, energy dispersive detectors with S ~ hv.

4.3 X-ray Fluorescence: Characteristic X-Ray Emission

Knock-out of strongly bonded *inner core shell electrons* by x-ray absorption leads to a core shell vacancy that is subsequently filled by recombination of an electron from an outer shell.

The energy difference between initial and final state is emitted as *characteristic x-ray* photon.

This fluorescence photon energy is given by:

Nomenclature for characteristic X-rays:

- Capital letter indicates shell of vacancy: K, L, M shells, corresponds to n = 1,2,3 ...
- **\diamond** Greek letter indicates difference Δn of principle quantum number between the involved shell transitions $\alpha = \Delta n = 1; \beta = \Delta n = 2; \gamma = \Delta n = 3; \dots$
- Subscript number: Related to energy levels within each shell due to orbital (I) and spin (s,j) quantization with the possible transitions between sublevels following from the selection rules: $\Delta I = +-1$, $\Delta j = 0, +-1$,



 $E_{photon} = E_{2,o} - E_{1,i}$

 $K\alpha_1$, $K\alpha_2$, $K\beta_1$, $L\alpha_1$, $L\beta_1$, $M\alpha_1$,

Neglecting the sub-shell structure, in a first approximation the x-ray energies for a n₁ - n₂ transition

is given by:

 $E_{x-ray}(n_1 - n_2) = R_H (Z - \sigma_{n2})^2 / n_2^2 - R_H (Z - \sigma_{n1})^2 / n_1^2)$ Moseley's law

with $R_{\rm H} = 13.6 \text{ eV} = \text{Rhydberg constant and}$ (*Z* - $\sigma_{\rm n}$) = effective nucleus charge = (*Z* number - shell screening $\sigma_{\rm n}$) K-radiation: $\sigma_{\rm n} = 1$ and $n_1 = 1$, L-radiation: $\sigma_{\rm n} = 7.4$ and $n_2 = 2$



Because inner shell transitions are not much influenced by the chemical bonding, the characteristic x-ray energies do not depend much on the environment of the atoms !

Note: Chemical effects, however, are observable in the fine structure (~eV) of electronic transitions involving outer electrons.

Fluorescence intensity: (1) Increases with K, L, M number due to higher ionization crosssection (higher number of shell electrons) although transition probability decreases (2) *decreases* within a shell with increasing α, β, γ and subscript index, i.e., $I_{\alpha} > I_{\beta} > I_{\gamma}$...

Advantage of XRF versus XR absorption spectroscopy: No no tunable x-ray source is required.

Examples for Characteristic X-Ray Emission Spectra:



Figure on the right: X-ray fluorescence yield ω as a function of Z and of K, L, M shell number.

Ζ

4.4 Photo-Electron Emission (XPS, UPS)

Photoelectrons emitted as a result of x-ray or EUV absorption carry valuable information on the <u>electronic properties</u> as well as <u>chemical composition</u> of the sample.

This is because when monochromatic photons with well defined energy are used for excitation and the electrons are emitted without further scattering, the **photoelectron energy spectrum** represents a direct *replication* of the *electronic density of states* in the sample. Typically

Photon energies of hv = 10 to 100 eV (=UPS) or 100 eV – 10 keV (=XPS) are used.

Due to **energy conservation**, the kinetic energy of the emitted photoelectrons is given by:

 $E_{kin} = hv - E_{el, binding} - \phi_{Det}$ (*hv* = photon energy,

 $\phi_{\text{Det}} \sim 3\text{eV} = \text{work function of electron detector}$

This applies as long as the electrons do not loose the energy transferred from the photons on their way to the sample surface where they are emitted.

The measured energy spectrum of photo-electrons can be converted into the **spectrum of the electronic states**

within the solid using:

 $E_{el,binding} = hv - E_{kin,meas} - \phi_{Det}$



⇒ If a monochromatic x-ray or UV photon beam is used for excitation, the energy spectrum of the photo-electrons directly corresponds to the energy distribution of the bound electronic states within the material, shifted upward by the used photon energy as shown in the figure above.

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X-Ray versus UV-induced Photoelectrons

The accessible electronic states are limited by the photon energy.

Thus, for XPS (E_{ph} >1keV) core level peaks appear in the electron spectrum, whereas for UPS ($E_{ph} \sim 10 - 100 \text{ eV}$) mainly the valence band structure appears.

 \Rightarrow Thus, XPS is mainly used for chemical analysis, whereas UPS mainly for determination of the electronic band structure (valence & conduction band).



Instrumentation:

The energy spectrum of the photoelectrons



4.5 Chemical Analysis by X-Ray Photoelectron Spectroscopy

The photoelectrons excited from core levels have specific energy kinetic energies from which the electron binding energies (BE) can be calculated using: $E_{el,binding} = hv - E_{kin,meas}$



⇒ Exact values of binding energies are tabulated in XPS and AES data bases

Example: XPS spectrum from Ni-Cu alloy



	Binding Energy (eV)			
Element	2p _{3/2}	3р	Δ	
Fe	707	53	654	
Со	778	60	718	
Ni	853	67	786	
Cu	933	75	858	
Zn	1022	89	933	

Surface sensitivity:

Due to the short mean free path of electrons resulting in a small escape depth, XPS and UPS are very surface sensitive, contrary to EDX where characteristic photons come from the large excitation volume. Thus, for XPS, UPS, AES the information comes from only a few nm thick layer of the sample surface, i.e., no bulk information is obtained.



Note that in the photo-electron spectra, also the peaks due to Auger electron emission appear.

Sensitivity

Detection limit (minimal concentrations) for elemental analysis



Peak fine structure: Chemical effects

Like for the x-ray or electron absorption edges, the XPS peak positions and structure also slightly depends on the binding environment of the different atoms within the sample (= *ESCA* analysis).



4.6 Mapping of the Electronic Band Structure by ARPES

In **ARPES** (= Angle Resolved Photo-Electron Spectroscopy), not only the **emission energy** but also the **emission angle** of the photoelectrons is measured.

This yields both the binding energy as well as the k vector of the electrons within the electronic bands of the material, i.e., the **E(k) dispersion** of the bands.

Measurement geometry and angle to k-vector conversion:



⇒ This allows to record complete **2D or 3D maps of the electronic band structure** of materials.



Practical Implementation of ARPES



owerrur reatures. High resolution and last data acquisition using 2D detecto

- full 3D map of band structure by variation of tilt & azimuth directions
- ◆ **<u>Resolution</u>**: $\Delta E < 1 \text{ meV}$, 1 300K, $\Delta k < 0.005 \text{ Å} < 10^{-2}$ of BZ

1. Energy Spread of Photons $\Delta E = (\Delta \lambda / \lambda) \cdot E_0$: which we have a solution of the sources needed



3. Thermal broadening:

» low temperatures (small k_BT) required

Example: Band structure of topological insulator



Example: ARPES of topological insulator BiTISSe as a function of composition



Spin-Resolved ARPES



Quantum Confined States in PbSnSe QWs measured by ARPES



Battery operated UHV vacuum suitcase for sample transportation



In situ cleavage or growth/regrowth at the synchrotron

- ⇒ Portable effusion cell (quadruple source)
- ⇒ PbSe, PbTe, PbSnSe, Te, Sn, Bi,
- ⇒ Substrates with pregrown buffer layers
- \Rightarrow Allows to control the surface termination





In situ cleavage or exfoilation of 2D materials

4.7 X-Ray Diffraction

Diffraction arises from the wave nature of the probe beam and is caused by the interference of the excited secondary spherical waves in the sample.

This leads to a preferred scattering (i.e. constructive interference only in certain discreet angular directions = "diffraction pattern" of intensity maxima.



Maxima positions are described by the **Bragg condition**:



Lattice plane spacing (cubic):

The resulting angular intensity distribution contains precise information on the interatomic distances on the 0.002 Å scale ! (XRD)

 $\frac{1}{d_{(h,k,l)}^{2}} = \frac{h^{2}}{a^{2}} + \frac{k^{2}}{b^{2}} + \frac{l^{2}}{c^{2}}$

<u>Note</u>: Because for constructive interference the phase differences $s \sim 2d$ from neighboring atoms must be equal to the wavelength λ . Thus, λ must be comparable or smaller than the atomic distances (~1 Å) in the sampe, i.e. $\lambda < 2d_{hkl} \gg \lambda < 10$ Å

This is fulfilled for **photons** with $h_V > 1$ keV and **particles** with $E_{kin} > 1$ eV.

4.7.1 Diffraction in the Kinematic Fraunhofer Far-Field Approximation

When the detector is sufficiently far away from the sample (= Fraunhofer diffraction) and multiple scattering in the sample is neglected (Born approximation), constructive interference of the excited secondary waves and thus, maximum diffraction intensity occurs at scattering angles given by the

Braggs law: $2d_{hkl} \sin \theta = \lambda$ where d_{hkl} is the lattice plane spacing of the (*hkl*) lattice planes.

Alternatively, constructive interference can be also represented by the

Laue condition: $\Delta \vec{k} = \vec{k_i} - \vec{k_0} = \vec{G}_{hkl}$ where $|\vec{k_0}| = 2\pi/\lambda$ and \vec{G}_{hkl} is a reciprocal lattice vector, meaning that the scattering vector Δk must be equal to a reciprocal lattice vector

The diffraction process can be represented and visualized by the *Ewald construction*.



4.7.2 Scattering Units

(1) Scattering by Electrons

The elementary scattering unit for x-rays is an electron.

Classical scattering by a single free electron (Hertz dipole) is decribed by the Thomson scatterin model:

$$E_{rad}(R) = -$$

Intensity:

$$\frac{e^{2}}{2}}{e^{2}}E_{in}\frac{e^{ikR}}{R}\sin\Psi}{=I_{0}\frac{e^{4}}{m^{2}c^{4}R^{2}}\left(\frac{1+\cos^{2}2\theta}{2}\right)} \text{ If } R = \text{few cm:} \quad \frac{I}{I_{0}}\approx10^{-26}$$





Scattering by Atoms – Atomic Form Factor

Electrons are distributed around the nucleus in an electron cloud with electron density p.

From each point, the x-rays are scattered with an amplitude proportional to the local electron density.

Defining the atomic form factor as:

 $f = \frac{\text{amplitude of the wave scattered by an atom}}{\text{amplitude of the wave scattered by one electron}}$

Assuming a spherically symmetry electron density in an atom with a number n = Z electrons,

the scatting amplitude, i.e. atomic form factor is given by the intergration of scattering over the cloud:

$$f = \sum_{n} f_{en} = \sum_{n} \int_{0}^{\infty} 4\pi r^{2} \rho_{n}(r) \frac{\sin kr}{kr} dr$$

Scattering by Atoms ...

 $f = \sum_{n} f_{en} = \sum_{n} \int_{0}^{\infty} 4\pi r^{2} \rho_{n}(r) \frac{\sin kr}{kr} dr$

Due to the finite extent of the electron cloud, there is a phase difference between the x-rays scattered at different positions within the cloud. This reduces the scattering amplitude at higher angles. For a sherical electron distribution:



- ⇒ The atomic scattering factor is f = Z in the forward direction (2 θ = 0): I(2 θ =0) =Z₂
- \Rightarrow As θ increases *f* decreases



- → functional dependence of the decrease depends on the details of the distribution of electrons around an atom (sometimes called the form factor)
- ⇒ Thus, *f* must be calculated using quantum mechanics

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(3) Scattering by a Crystallographic Unit Cell – Structure Factor

A crystal unit cell typcially consists of several atoms located at different positions within a unit cell.

The structure factor, i.e., scattering amplitude of the unit cells is accordingly defined as:



The phase difference, i.e., interference between the waves scattered from the individual atoms causes an additional modulation of the total scattered intensity.



⇒ The structure factor contains the information regarding the types (f) and locations (u, v, w) of atoms within a unit cell. These can be obtained by comparision of measured and calculated (hkl) peak intensities, which however must be corrected for experimental and geometric effects

The scattered amplitude is obtained by integrating the scattering amplitude E over the whole crystal

volume V

$$E_{out} \propto \frac{E'_0}{R'} \int\limits_V n(\mathbf{r}) e^{i(\mathbf{k_{in}} - \mathbf{k_{out}}) \cdot \mathbf{r}} dV = \frac{E'_0}{R'} \int\limits_V n(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} dV$$

where the scattering vector q is defined as: $q = k_{out} - k_{in}$

The amplitude of the scattered wave is therefore proportional to the Fourier transformation of the electron density.

The phase problem of diffraction:

In diffraction experiments one can not detect the amplitude but only the intensity of the scattered wave, thus loosing the phase information.

$$I \propto \frac{|E_0|^2}{R'^2} \left| \int_V n(\mathbf{r}) \,\mathrm{e}^{-i\mathbf{q}\cdot\mathbf{r}} \,\mathrm{d}V \right|^2$$

- ⇒ Therefore the electron density distribution (real space structure) can not be simply obtained by an inverse Fourier transformation of the obtained diffraction pattern.
- ⇒ For this reason an inductive approach is used, where model structures are assumed from which the expected diffraction is calculated, which is then compared with the experimental spectra. The model parameters are then varied in order to find the best fit to the experiments.

$$\frac{Periodic Crystals:}{I \propto \frac{|E_0|^2}{R'^2}} \left| \sum_{\mathbf{G}} n_{\mathbf{G}} \int_{V} e^{i(\mathbf{G}-\mathbf{q})\cdot\mathbf{r}} dV \right|^2 = \begin{cases} l_x l_y l_z = V & \text{for } \mathbf{q} = \mathbf{G} \\ \approx 0 & \text{otherwise} \end{cases} \quad \text{for } l_x, l_y, l_z \text{ large}$$

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Definition of reciprocal lattice vectors:

 a^* , b^* , c^* = basic vectors in reciprocal space; a, b, c = basic vectors in real space, *h*, *k*, *I* are integer numbers of the Miller indices

<u>Cubic lattices</u>: $d_{hkl}^{cubic} = a_0 / \sqrt{h^2}$

$$l_{hkl}^{cubic} = a_0 / \sqrt{h^2 + k^2 + l^2}$$

$$\left| \Delta \vec{k} \right| = 2 \left| \vec{k}_0 \right| \sin \theta = \frac{4\pi}{\lambda} \sin \theta$$

$$\vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

$$\vec{a}^* = \frac{\vec{b} \times \vec{c}}{\vec{a} \times \vec{b} \cdot \vec{c}} \qquad \vec{b}^* = \frac{\vec{c} \times \vec{a}}{\vec{a} \times \vec{b} \cdot \vec{c}} \qquad \vec{c}^* = \frac{\vec{a} \times \vec{b}}{\vec{a} \times \vec{b} \cdot \vec{c}}$$

$$\left| \Delta \vec{k} \right| = \frac{4\pi}{\lambda} \sin \theta = \left| G_{hkl} \right| = \frac{2\pi}{a} \sqrt{h^2 + k^2 + l^2}$$

Summary:

Information obtained from positions and intensity of diffraction maxima:

- ⇒ Lattice structure (type) and symmetries, lattice constants, sample orientation,
- ⇒ strains and lattice distortions (=changes in lattice plane distances and lattice parameters),
- ⇒ structural phases (=material identification), etc. ..

Intensities for different (hkl) Bragg peaks:

Determined by structure factor of unit cell (= internal structure of the unit cell) and atomic form factor.

<u>Multiple scattering</u> becomes only important for very perfect single crystals where the probability that an electron is scattered several times before leaving the sample is large. In this case, dynamical scattering theory must be applied for description of the intensity distribution. This applies also for *electron diffraction* where the scattering is much stronger than for x-rays.

Additional information is encoded in

the *shape* of the diffraction maxima, i.e., intensity distribution around reciprocal lattice points.

4.7.3 Shape of Diffraction Spots: Influence of Size and Geometry

For an infinitely large, defect-free single crystal, the reciprocal lattice points (RELP) and diffraction maxima $I(\theta)$ would be infinitesimal sharp delta functions. However, due to structural imperfections as well as finite size, the reciprocal lattice points are broadened and have a certain extension.



4.7.4 Intensity around Bragg Points: Reciprocal Space Mapping

The shape of the reciprocal lattice points can be determined by high-resolution <u>reciprocal space</u> <u>mapping</u>, by which the 3D intensity distribution around individual Bragg points is measured. This allows to determine the geometrical shape and morphology of nanostructures.

Reciprocal space mapping = intensity distribution measured in small steps around Bragg reflections



High resolution requires:

- Highly monochromatic x-ray beam: Channel cut Barthels monochromator
- Very small beam divergence (parallel beam)
- Very high angular resolution of detector
- High precise goniometer



Example #1: X-Ray diffraction from 1D Nanowires revealing the NWR shape function



Example #12: Diffraction from Low Dimensional 2D Layers $d_{film} = \lambda / 2\Delta\omega\cos\theta$



Example #3: XR Scattering from Graded layers and superlattices



Example 3: Ensemble diffraction of colloidal nanocrystals by X-ray diffraction

X-ray are difficult to focus and the scattering is weak. Therefore, usually only ensemble measurement are possible. However, the width of the diffraction peaks still allows to determine the average size of nanostructure ensembles using the Scherrer formula that describes the broadening of the diffraction peaks due to the crystal size.

Example for colloidal PbTe nanocrystals with sizes ranging from 5 to 32 nm





Figure 3. (a)–(f) XRD patterns obtained from powders composed of PbTe nanocrystals of different sizes. The sizes indicated in (a)–(f) are calculated values from the Scherrer equation based on analysis of the width of the [100] peak.

The average crystal size can be determined from the *width of the Bragg peaks* using the <u>Scherrer formula</u> that relates the FWHM β of the x-ray peaks to the crystallite size *D* with θ = diffraction angle.

$$D_p = \frac{0.94\lambda}{\beta_{\frac{1}{2}}\cos\theta}$$

4.8 Summary

 x-rays give access to higher energy excitations compared to photons including core level excitations.

These can be probed by x-ray absorption spectroscopy (XAS) at synchrotrons as well as by photoelectron spectroscopy (XPS).

Recombination of electrons into the excited core levels gives rise to characteristic x-ray fluorescence.

Since the electronic transitions involving core electrons are element specific all three methods can be used for non-destructive <u>chemical analysis</u>. In addition, the fine structure shifts and splitting also yield information on the local bonding configuration (ESCA, EXAFS, NEXAFS).

- EUV excited angle resolved photoelectron spectroscopy allows direct imaging and analysis of the electronic band structure of the valence band.
- Elastic scattering of x-rays with wavelength comparable to the lattice spacing gives rise to an <u>x-ray diffraction pattern</u> consisting of diffraction maxima observed at different incidence and exit angles.

The position and intensity of the diffraction maxima give very precise information on the crystal lattice parameters and structure with picometer resolution.

The intensity distribution around the diffraction peaks, i.e., the shape of the reciprocal lattice point yields information on the size and shape of nanometer sized structures.

Limitations: Due to the lack of efficient optical elements due to absorption and negligible reflection, focusing of x-rays is difficult and thus, nanometer spatial resolution difficult to achieve.

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X-ray methods provide valuable information on:

- + very highly precision for lattice parameters & layer thicknesses,
- + core level excitations for chemical analysis (XRD, XPS)
- + fine structure of absorption edges (XAFS, XANES)
- + band structure mapping photoelectron spectrosc.
- + non-destructive and high penetration depth,

Disadvantages:

- Wavelength tunable and high power x-ray sources for spectroscopy available only at synchrotrons.
- No efficient focusing elements available, thus, only **limited spatial resolution**.

Spatial imaging only achieved using special focusing optics such as Fresnel zone plates, microfocusing refractive optics, curved multilayer mirrors, but these are only weak focusing elements. Currently achievable smallest probe size ~50nm.

- Diffraction measurements yield no *direct* real space information, requires extensive simulations.



