In-situ Quick-EXAFS

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XAFS theory: http://xafs.org/Tutorials?action=AttachFile&do=view&target=Newville_xas_fundamentals.pdf

Nano-particle example: JOURNAL OF PHYSICAL CHEMISTRY C,**114,** 9207-9215, 2010.

Fe on GaAs example: PHYSICAL REVIEW B **74,** 165405, 2006.

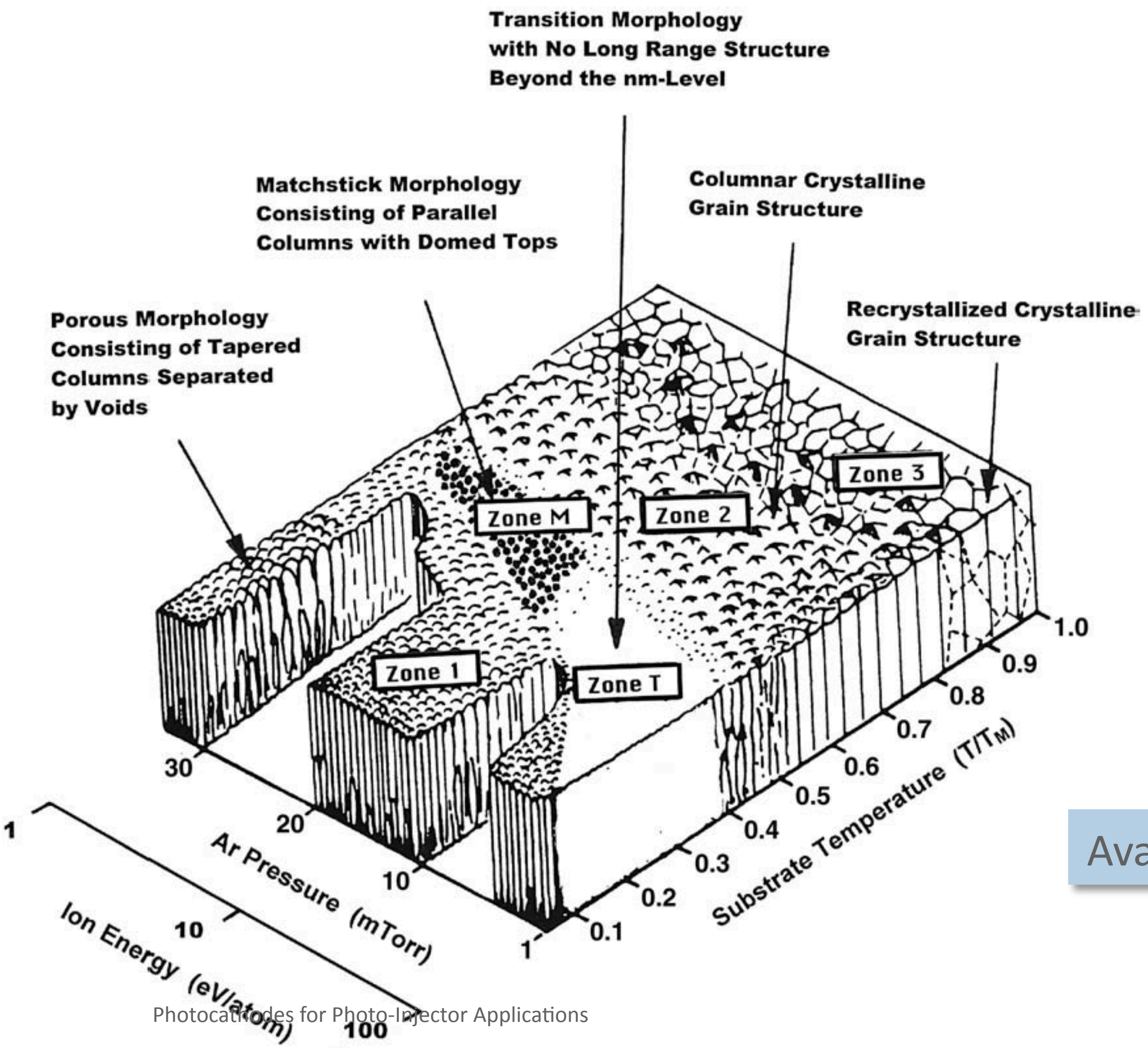
Overview

- Introduction: What we want to know?
  - The photocathode: a complex heterogeneous sample system.
  - Structure and chemical composition during growth.
  - The surface composition and its chemistry.
  - Changes during operation.
- XAFS
  - What is NEXAFS & EXAFS?
  - How does the experiment look like?
  - Examples:
    - doping of nano-particles
    - Characterization of spintronics interfaces (GaAs-Fe interface)
- Time resolved Experiments
  - QEXAFS & "ultrafast"
  - The proposed system at the APS
- Conclusion

Introduction: What we want to know?

Changes during operation.

J.H.E. Cartwright et al. / Thin Solid Films 518 (2010) 3422–3427



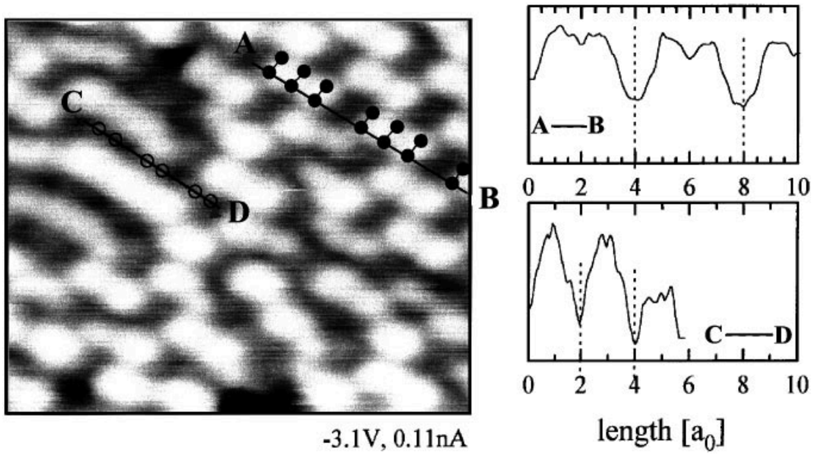
- What time scales are involved?
- How is the energy introduced: thermal/ non-thermal processes (melting)
- Which processes are reversible and which are irreversible
- Correlations between structure and functionality?

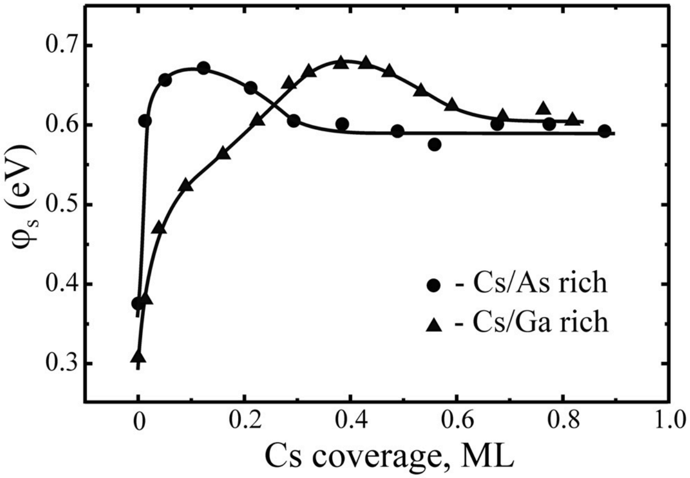
Available time resolution: 100ps-days

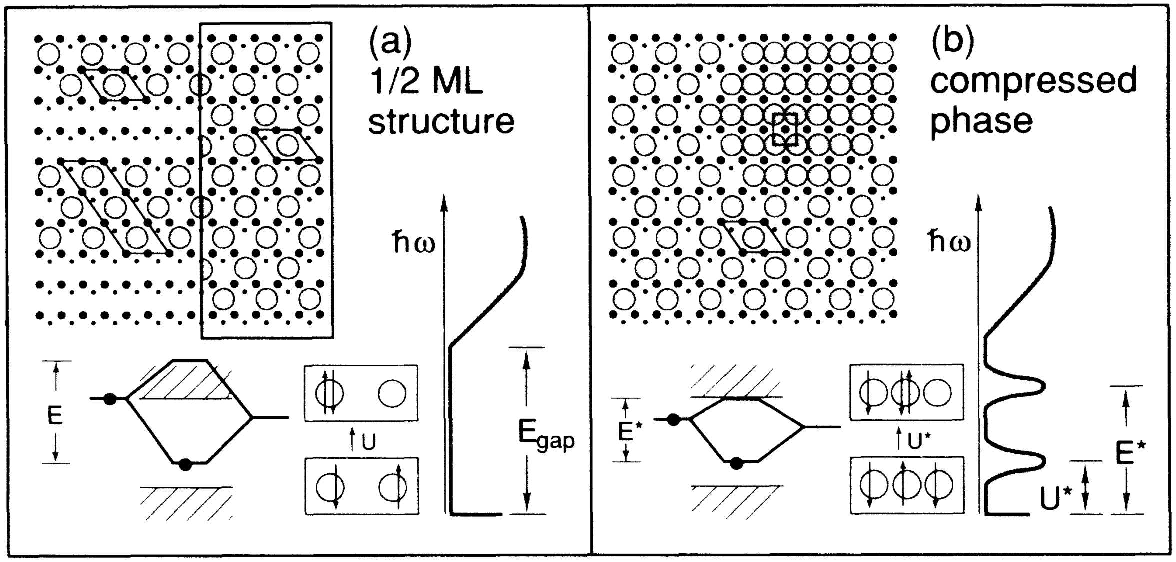
Introduction: What we want to know?

The surface composition and its chemistry.

e-J. Surf. Sci. Nanotech. Vol. 5 (2007) 80-88







Phys. Rev. Lett. 81, 721–724 (1998)

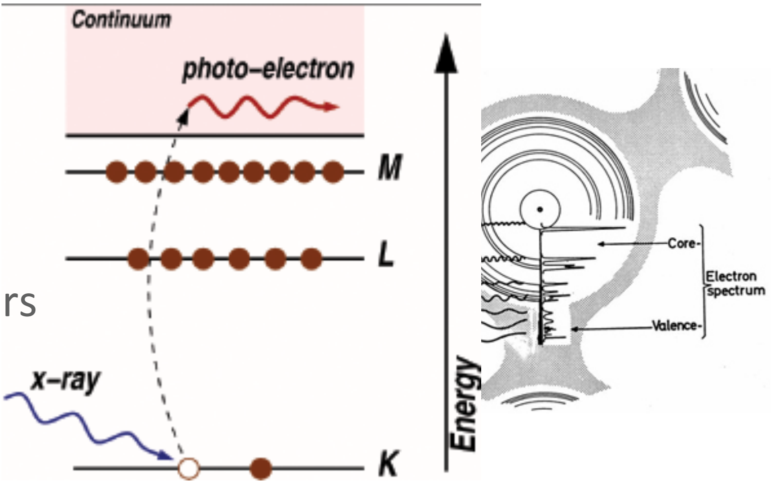
- Exact details of surface and Cs contribution determines electronic states of activation layer
- Dark counts are highly effected by these details
- Effects of morphology unknown
- Long term stability depends on exact composition

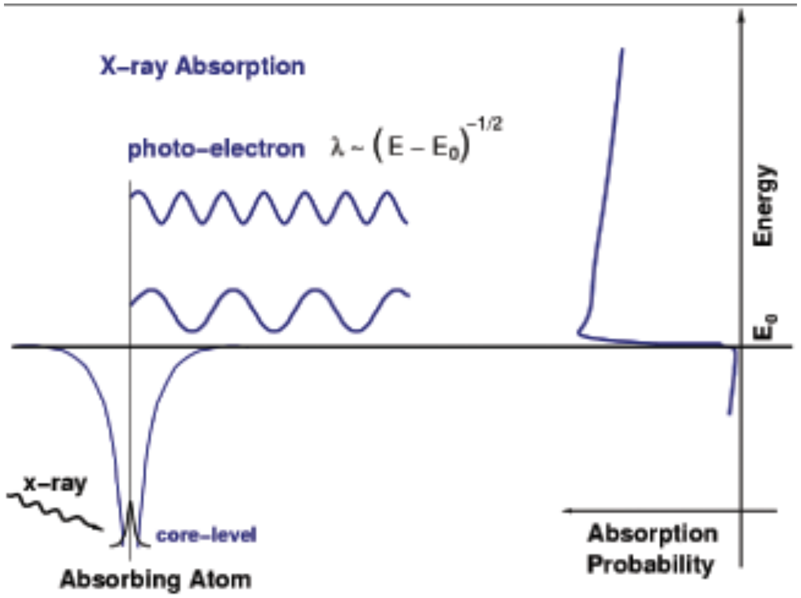
XAFS

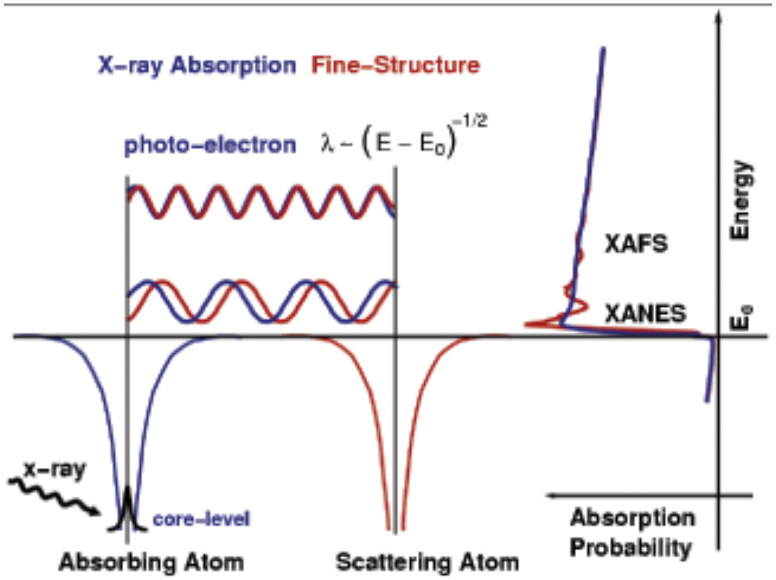
What is X-ray Absorption?

- Absorption is mostly treated in Two-Step-Model (absorption/relaxation)
- "Principle" difference: photo-electron in bonded (NEXAFS) are non-bonded (EXAFS) state
- NEXAFS probes electronic states – EXAFS next neighbors
- Good description can be found: http://xafs.org/Tutorials?action=AttachFile&do=view&target=Newville_xas_fundamentals.pdf

Initial absorption process



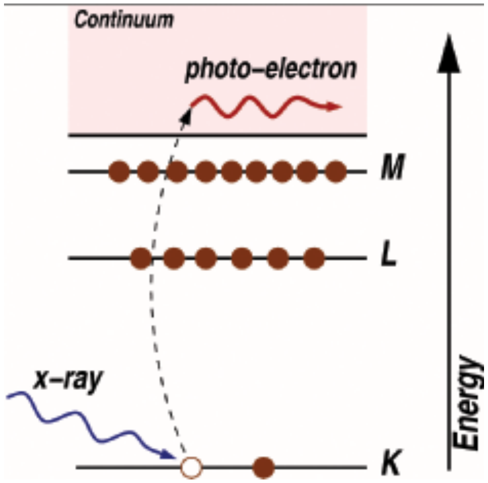




XAFS
How to Measure XAFS?

Transmission Experiment:

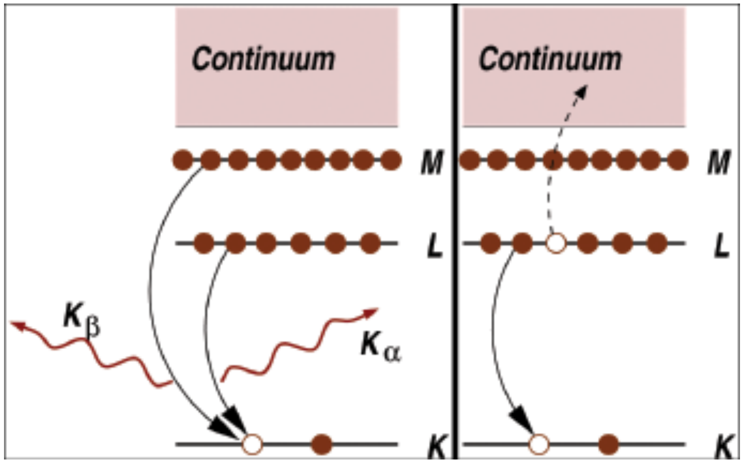
The missing photon! $I_T = I_0 \bullet e^{-\mu(E_{X-ray})d}$



$$\mu(E_{X-ray})d = \ln\left(\frac{I_0}{I_T}\right)$$

Relaxation process:

Secondary photon or electron



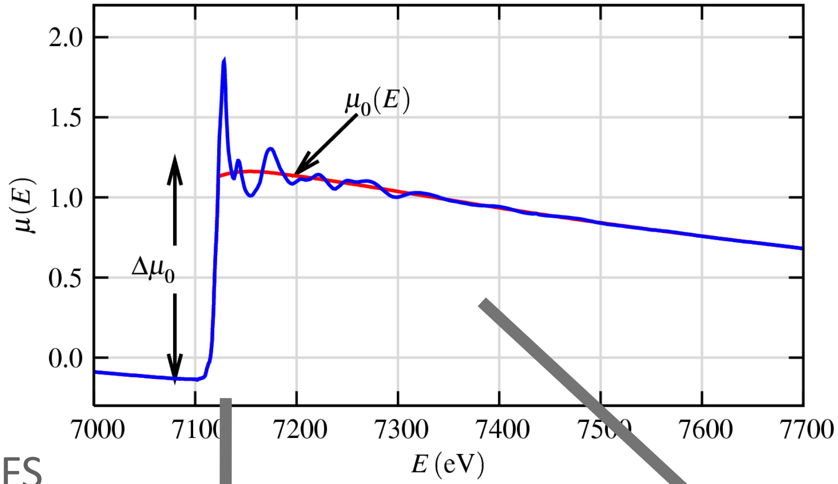
$$\mu(E_{X-ray})d = a \bullet \frac{I_{F/E}}{I_0}$$

- Detection method: Transmission (reflection), fluorescence (high yield for energies > 4KeV), electron yield/Auger (high yield for energies < 2KeV)
- Scanning of incidence energy
- Emitted photon/electron has constant energy and is typical for atomic species (in non resonant case)

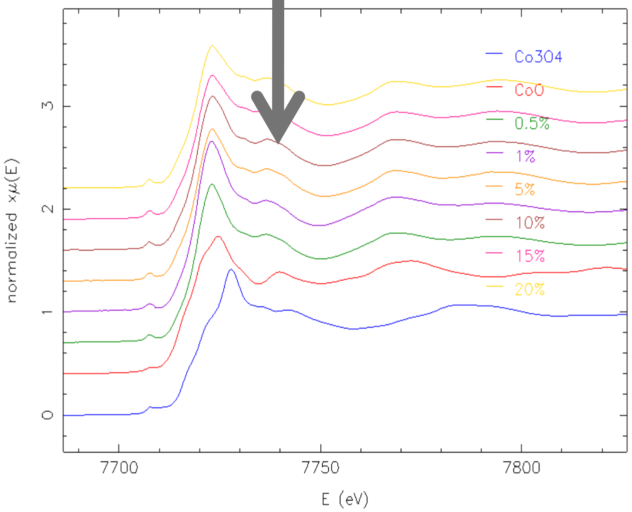
XAFS

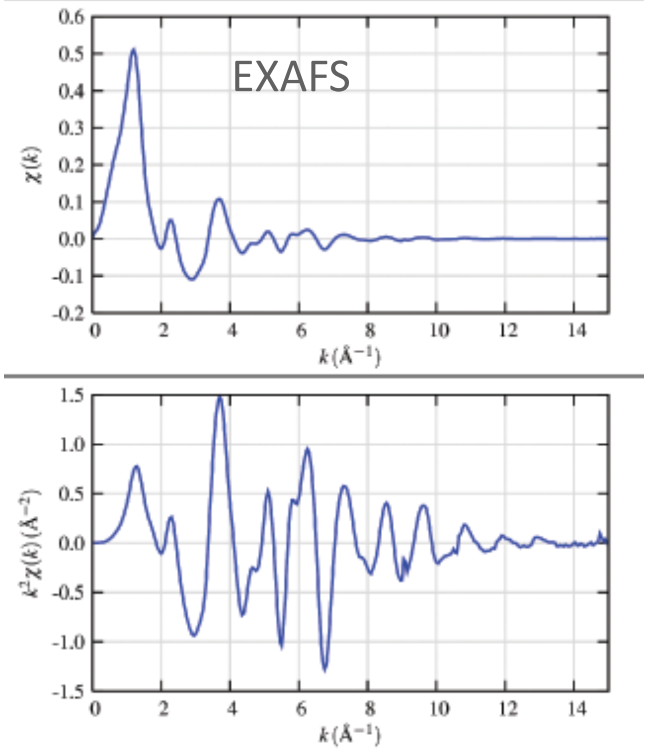
The signal: NEXAFS & EXAFS

- NEXAFS:
  - Finger print method using reference samples (local probe)
  - Comparison with theoretical calculation of spectrum (fit of model-reverse Monte Carlo)



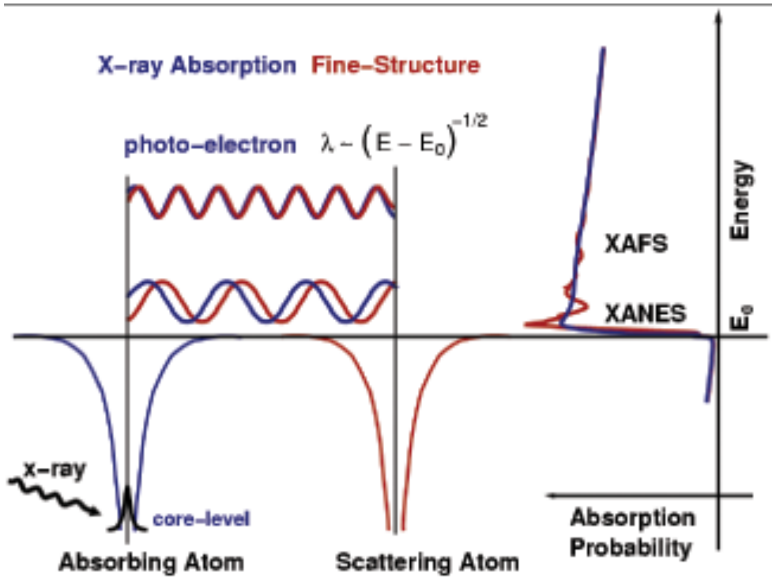
NEXAFS





XAFS

A closer look to the EXAFS range



- χ(k) depends:
  - Scatting strength of neighbor
  - Phase-shift during “reflection”
  - Is strongly reduced for “large R”
- Exafs is a local probe
- Fourier Transformation of χ(k) provides pair-distribution function (δ(k) is required.

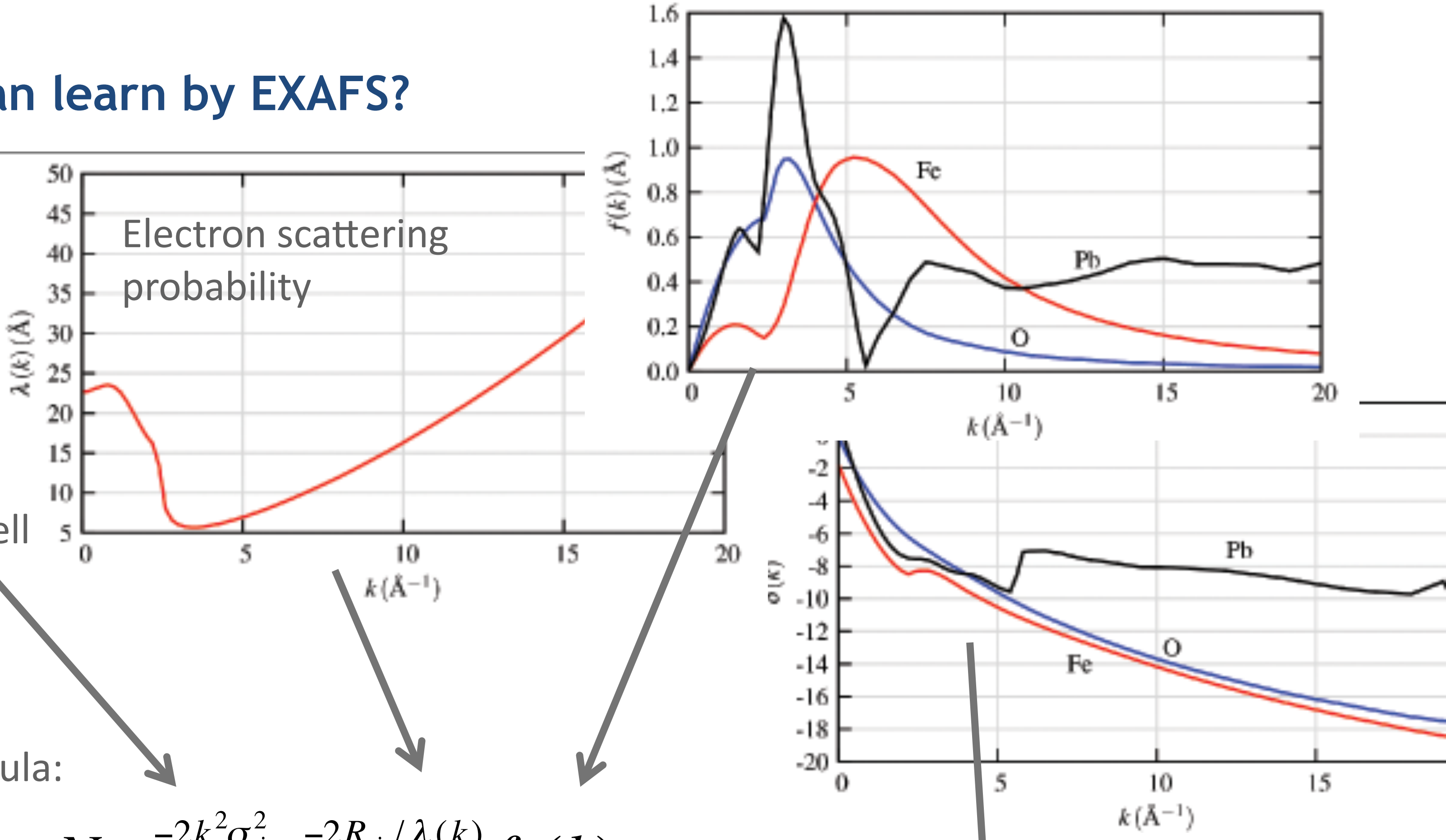
Out-going wave: $\varphi(k,r) = \dfrac{e^{ikr}}{kr}$

$$\chi(k) \propto \varphi_{(out\_going*reflected)}(k, r = 0)$$

$$\chi(k) \propto \frac{e^{ikR}}{kR} * \left[2kf(k)e^{i\delta(k)}\right] * \frac{e^{ikR}}{kR} + C.C. \longrightarrow \boxed{\chi(k) = \frac{f(k)}{kR^2}\sin(2kR + \delta(k))}$$

XAFS

What you can learn by EXAFS?



Disorder Term of shell (thermal or static)

General EXAFS-formula:

$$\chi(k) = \sum_j \frac{N_j e^{-2k^2\sigma_j^2} e^{-2R_j/\lambda(k)} f_j(k)}{kR_j^2} * \sin\left[2kR_j + \delta_j(k)\right]$$

j: Shell-index

R: Distance

XAFS
What you can learn from XAFS:

- NEXAFS (element selective):
  - Speciation
  - Empty Density of States (DOS)
  - Local symmetry of absorber atom
- EXAFS (element selective):
  - Pair-distribution function of next neighbors (~3Å-5Å)
  - Thermal & static disorder of neighbors
  - Interstitial or substitutions for dopents
  - Differentiation between light and heavy neighbors (amplitude)
- Both techniques are powerful if :
  - System has a high degree of disorder
  - The grain size is below ~10nm
  - Theory is available to create model structures
- Is typically combined with:
  - PDF (x-ray scattering of high energetic photons) similar to powder diffraction
  - XRD (X-ray diffraction)
  - Electron diffraction & microscopy (TEM/AFM/STM)

Examples:

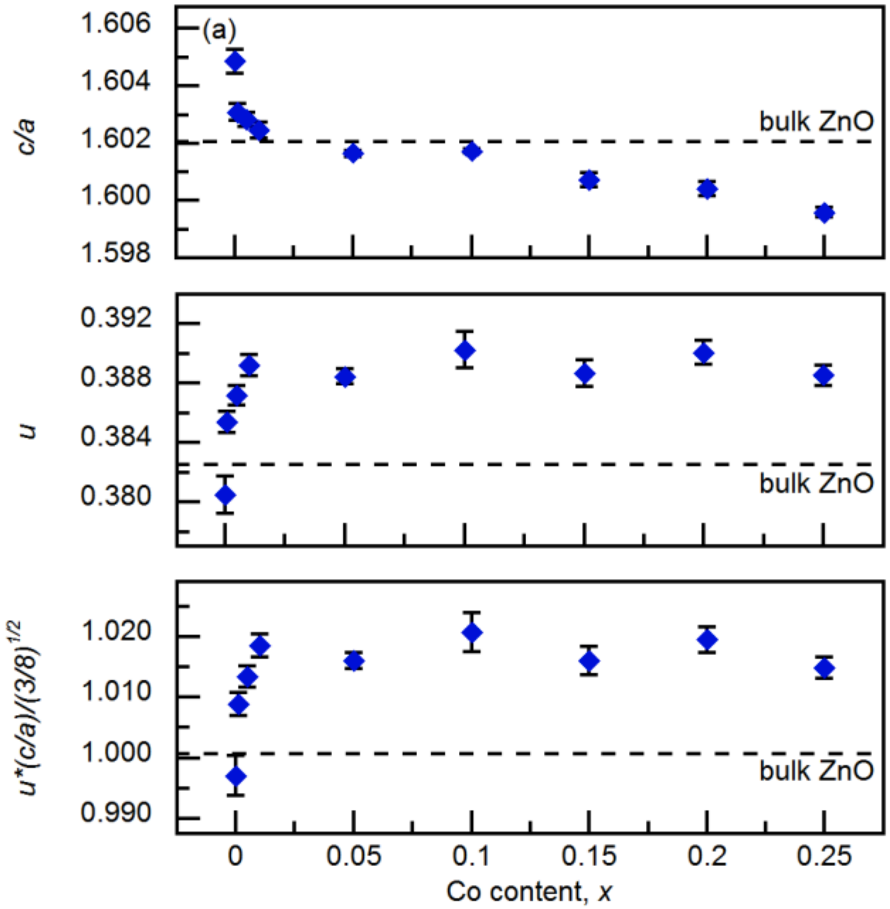
Doping of nano particles: $Zn_{1-x}Co_xO$

- Particle size about 2nm
- Problem:
  - Is Co substituting Zn?
  - Is there a concentration when Co phase-segregates?
  - Is surface composition identical to “bulk”?
  - Is Co substitution creating a lattice relaxation?
- To solve the problem:
  - XAFS measurement taken at:
    - Co K-edge
    - Zn K-edge
  - XRD
  - Analysis with
    - Conventional Fourier-analysis
    - Reverse Monte Carlo
- Publication: JOURNAL OF PHYSICAL CHEMISTRY C,**114,** 9207-9215, 2010.

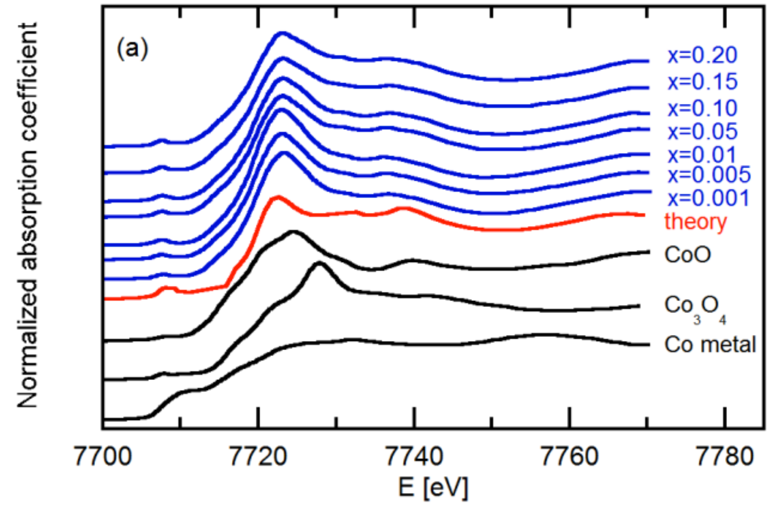
Examples:

Doping of nano particles: $Zn_{1-x}Co_xO$

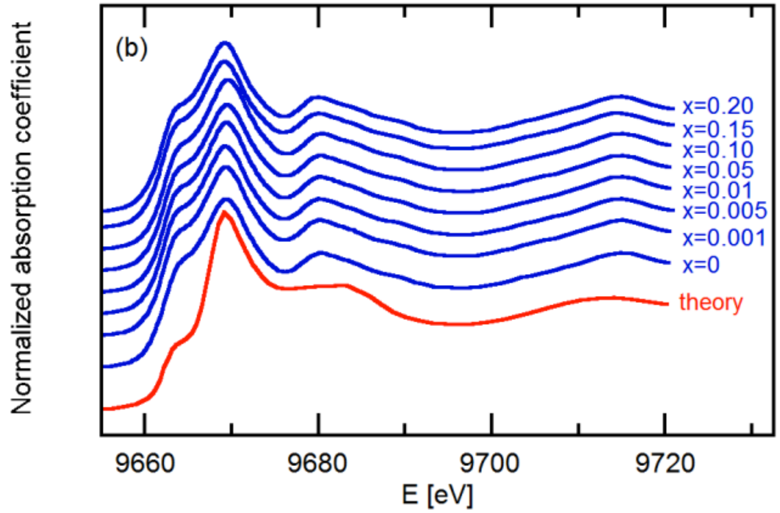
XRD



Co K-edge



Zn K-edge



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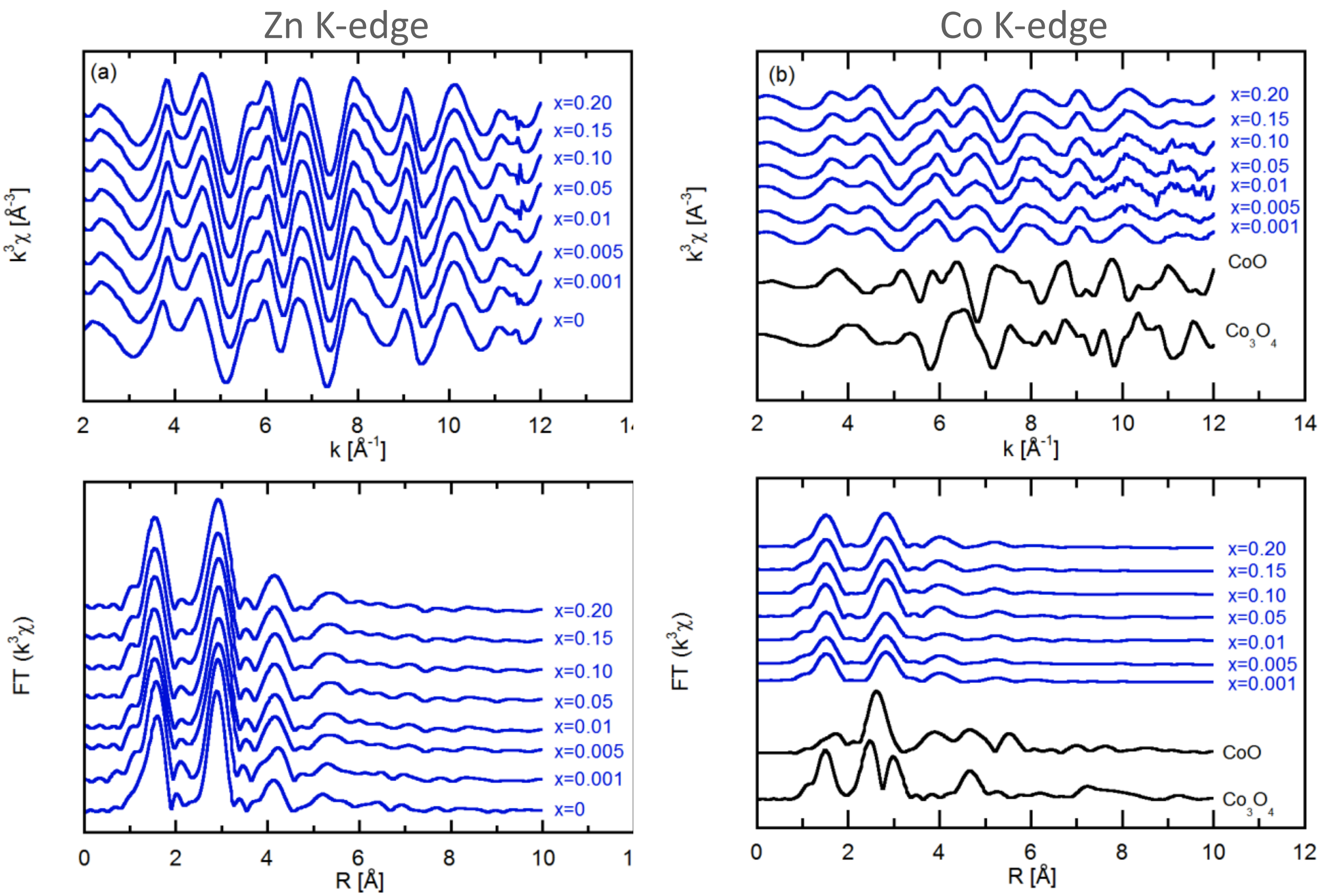

Examples:

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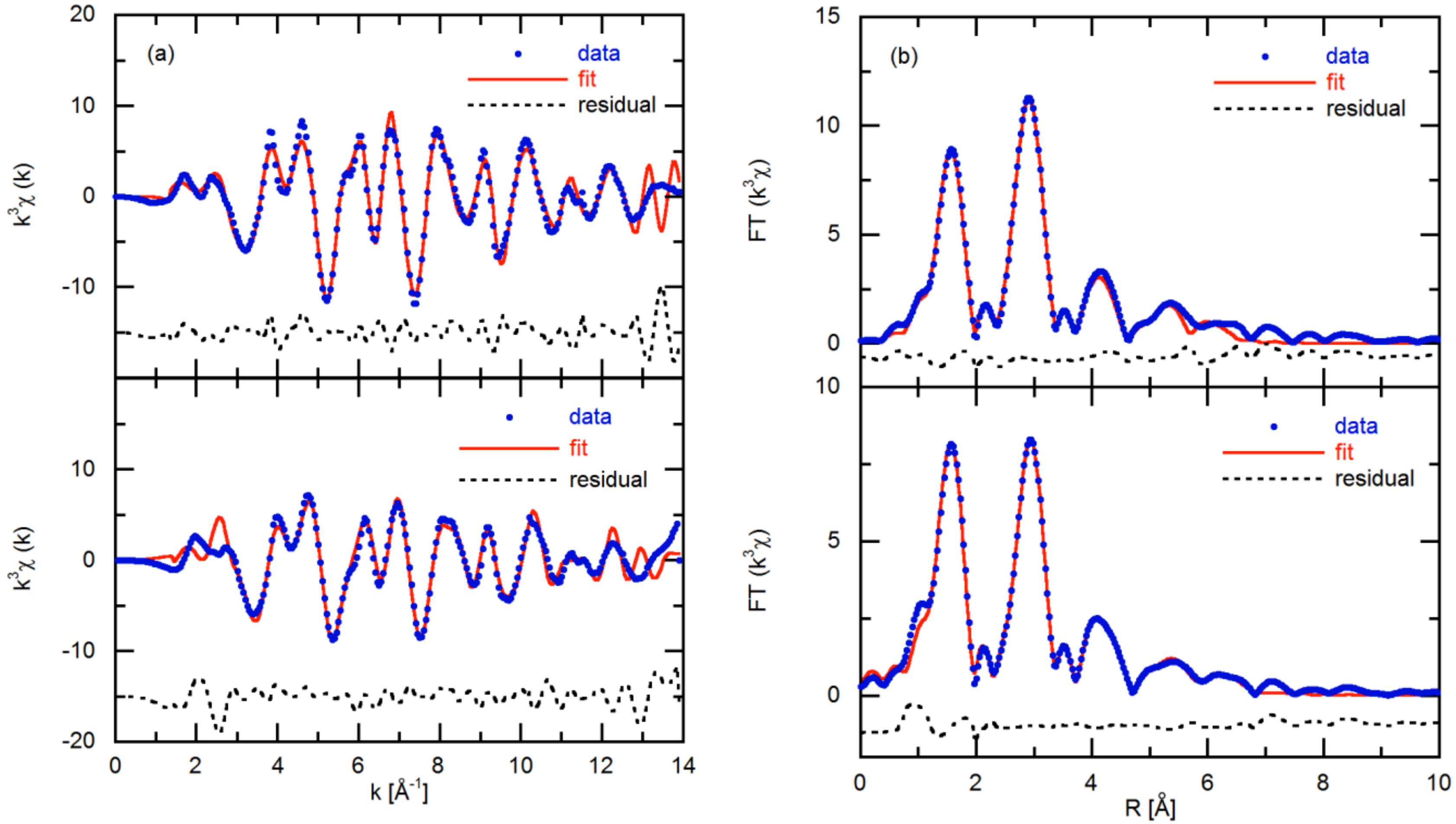

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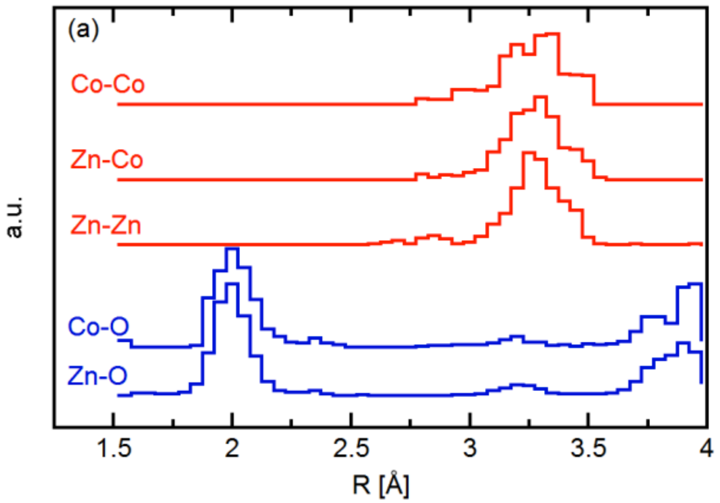
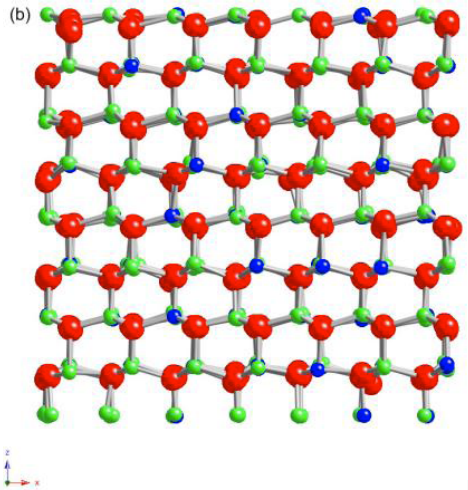
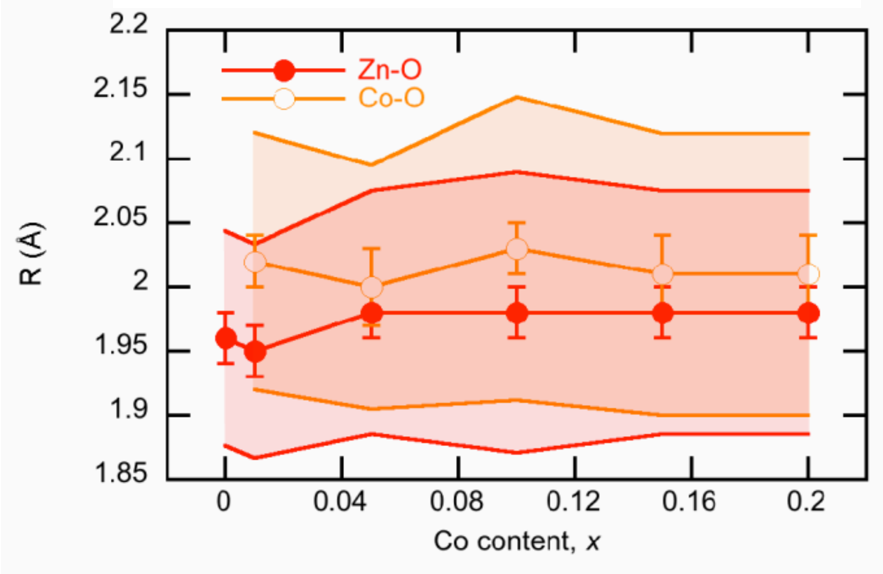
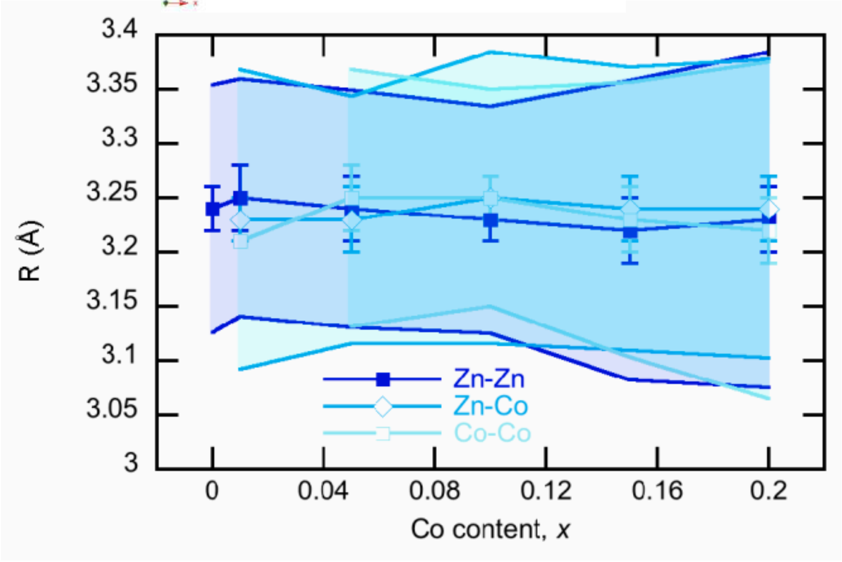




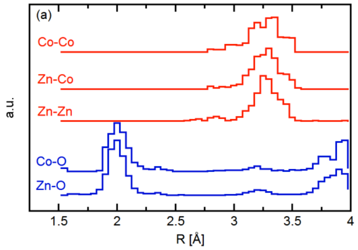




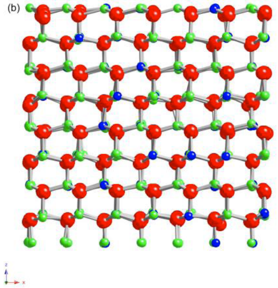
Results:

- What was necessary:
  - Measuring of multiple edges
  - Measuring under multiple conditions (concentration)
  - Analysis with conventional XAFS analysis and RMC analysis

- Results:
  - Quantitative description of pair-distribution function



  - Detailed model how the Co is distributed in the particles (dependent on concentration)

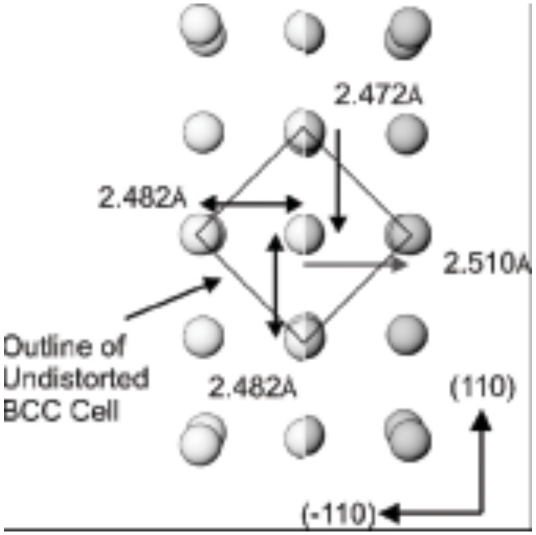


  - No segregation (bulk or surface) was detected (NEXAFS & EXAFS)
  - Zn and Co have same valence state

Examples:

Effects of 5 mono layers of Fe on GaAs (Spintronics example)

- Single crystal, UHV in-situ experiment; single crystal GaAs and MBE growth of Fe
  - (001) substrate orientation
  - Ga-rich surface
  - 4x6 surface reconstruction
- Problem:
  - How is the surface reconstruction influenced?
  - *Is there an anisotropic in-plane strain?*
  - Island growth or layer growth?
- To solve the problem:
  - XAFS at the Fe-Kedge
  - measurement taken at 2 different polarizations
- Publication: PHYSICAL REVIEW B **74,** 165405, 2006.



Examples:

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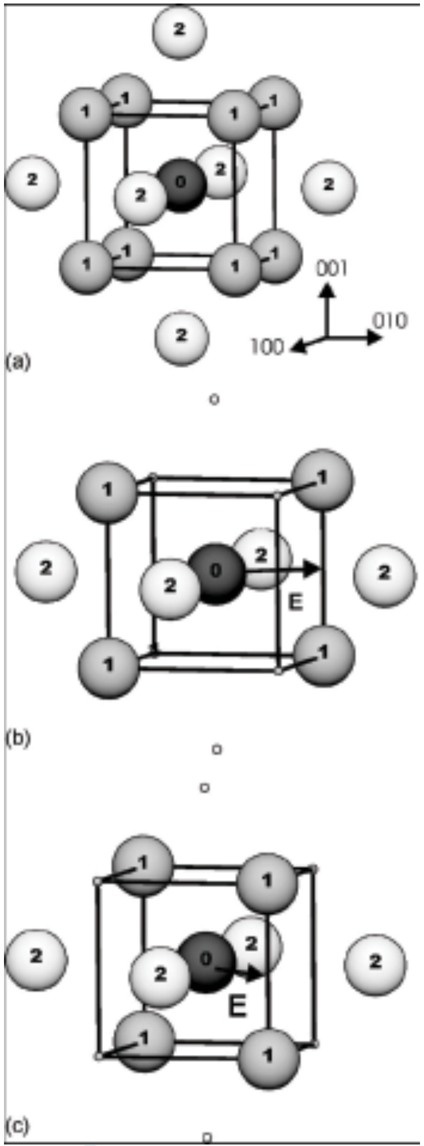

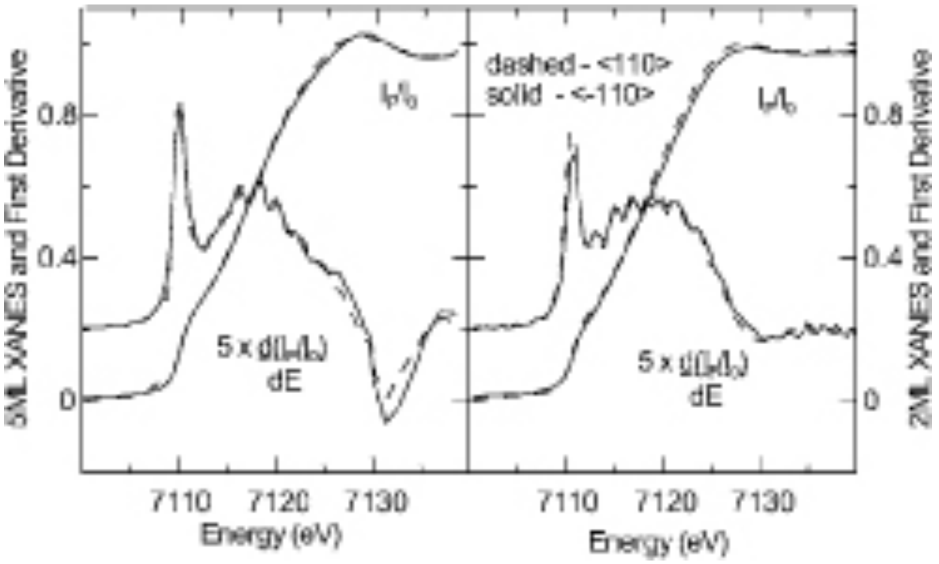

Examples:

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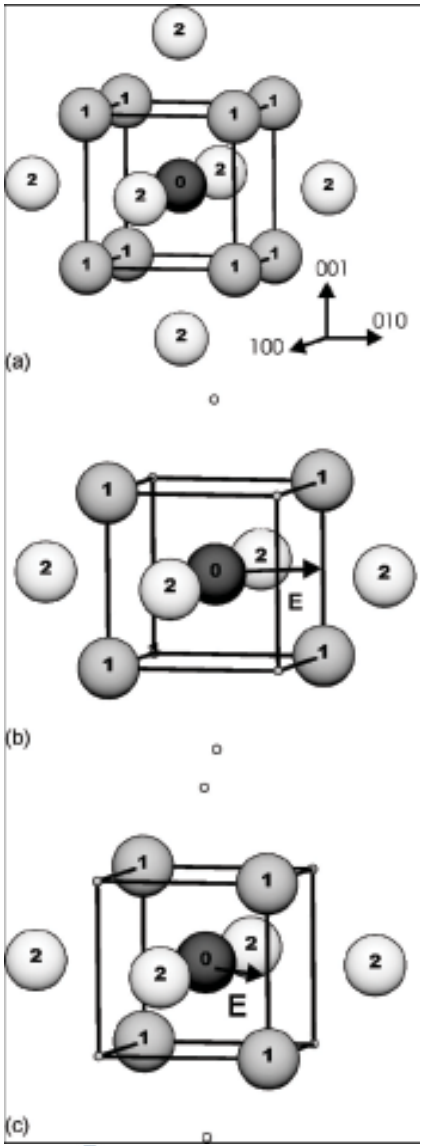
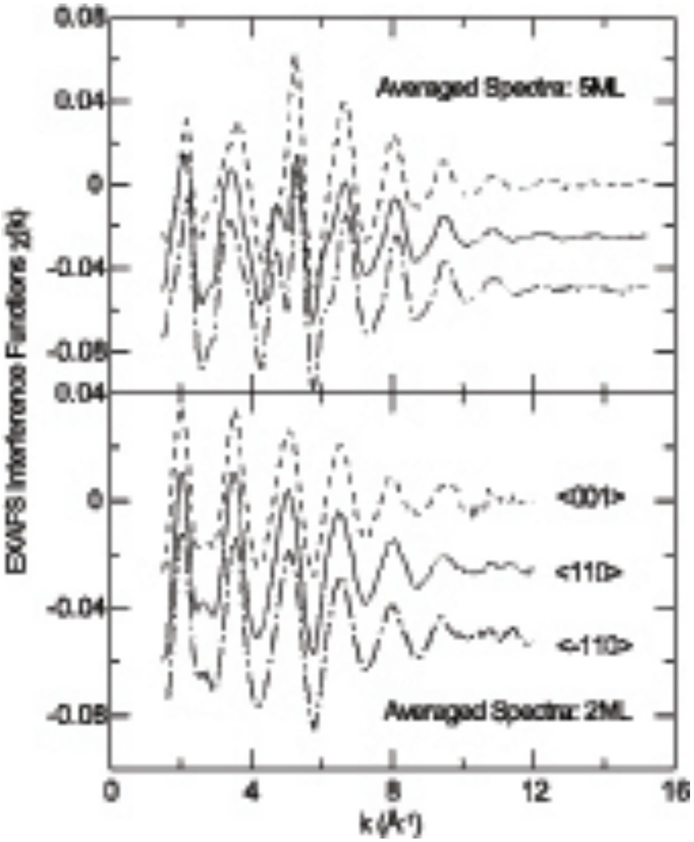
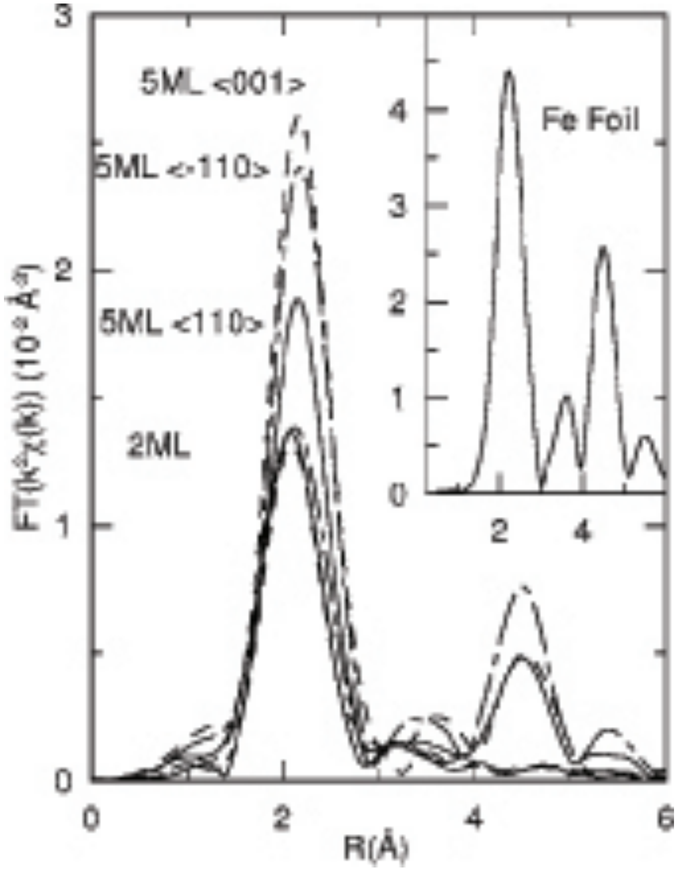






Examples:

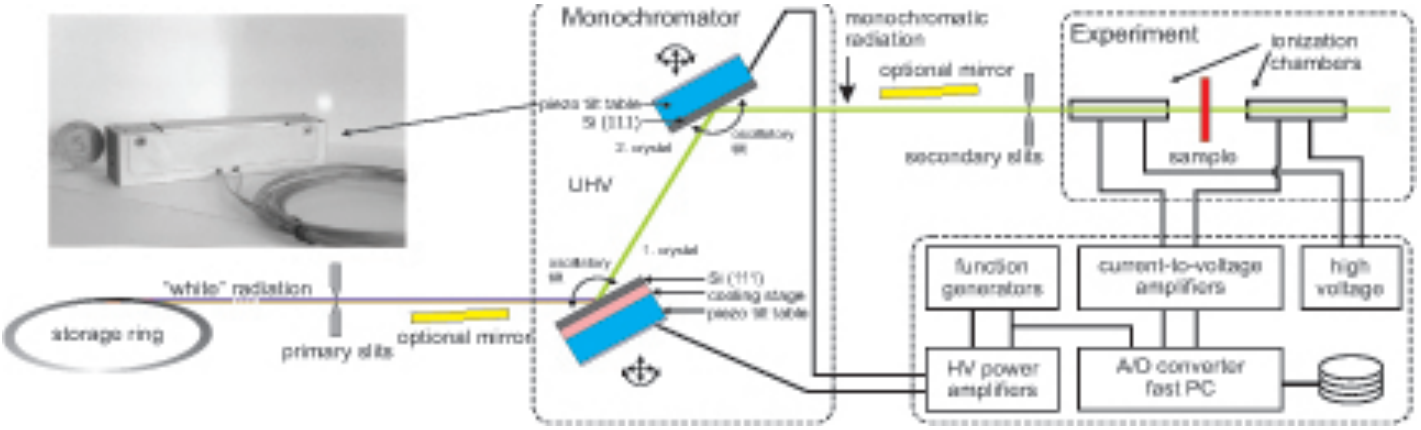
Effects of 5 mono layers of Fe on GaAs (Spintronics example)

- What was necessary:
  - Measuring of multiple polarizations and orientations
  - Gracing incidence measurement
  - Theory with predictions
- Results:
  - Transition from island growth to film growth
  - Epitaxial growth
  - Measured distortion is smaller than predicted (if existing)
  - Zn and Co have same valence state

Time resolved Experiments

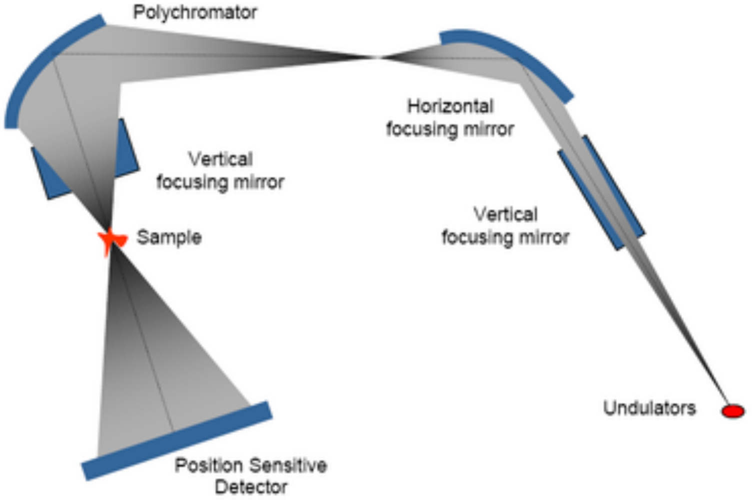
QEXAFS & “ultrafast”

- QEXAFS: Quick EXAFS
  - Time resolution: 100ms-s



J. Synchrotron Rad. (2001). **8, 354–356**

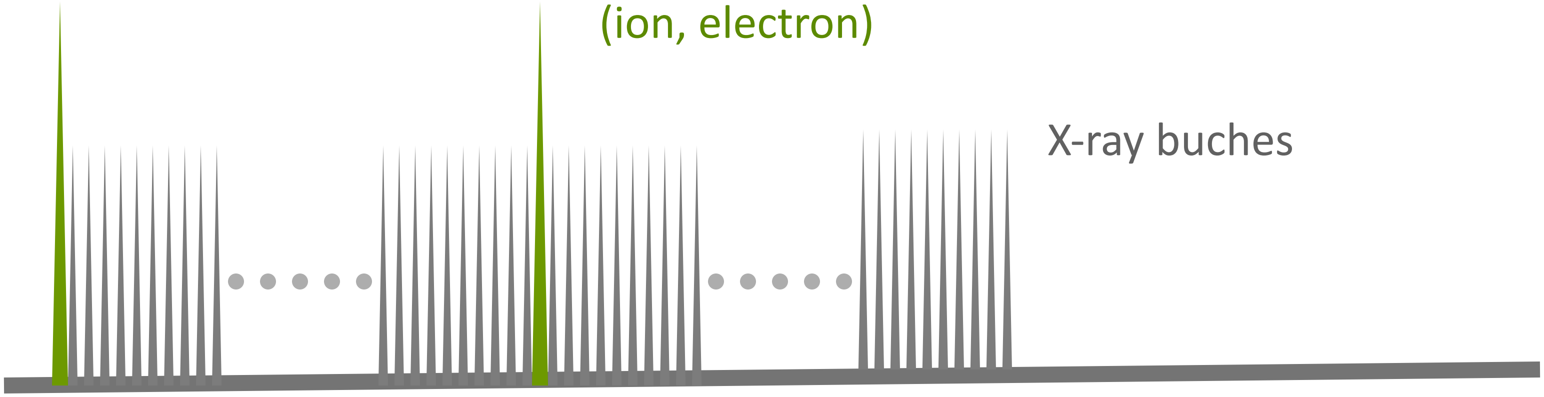
- DEXAFS: Dispersive EXAFS
  - Time resolution: 1μs-s



Time resolved Experiments

QEXAFS & “ultrafast”

- “ultrafast approach” or how to make a movie:
  - – Time resolution: 100ps-s



Laser pulse
(ion, electron)

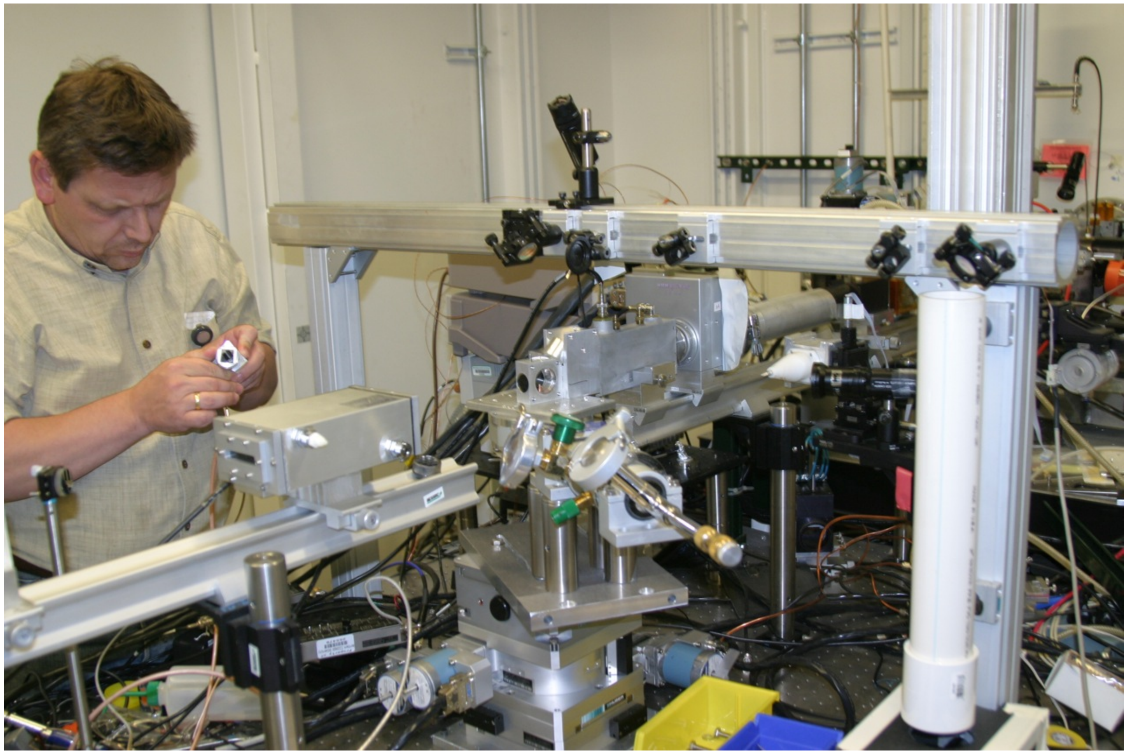
X-ray buches

Time

- Using natural bunching of ring:
  - Signal of every bunch will be stored independently (currently 6500 bunches over 1ms)
  - Final signal will be averaged over multiple excitation pulses
  - Maximum time-resolution depends on ring structure
  - Maximum record length depends on trigger-rep-rate and available electronics
  - Time-slices can be binned to result better statistics

Time resolved Experiments

The proposed system at the APS



- Combined SAXS/WAXS/XAFS approach
- In-situ growth chamber is in preparation
- Scattering detection is done with PILATUS 2M (30Hz readout)
- Spectroscopy detection system integrated with “ultrafast aproach”
- Gracing incidence technique

Conclusion

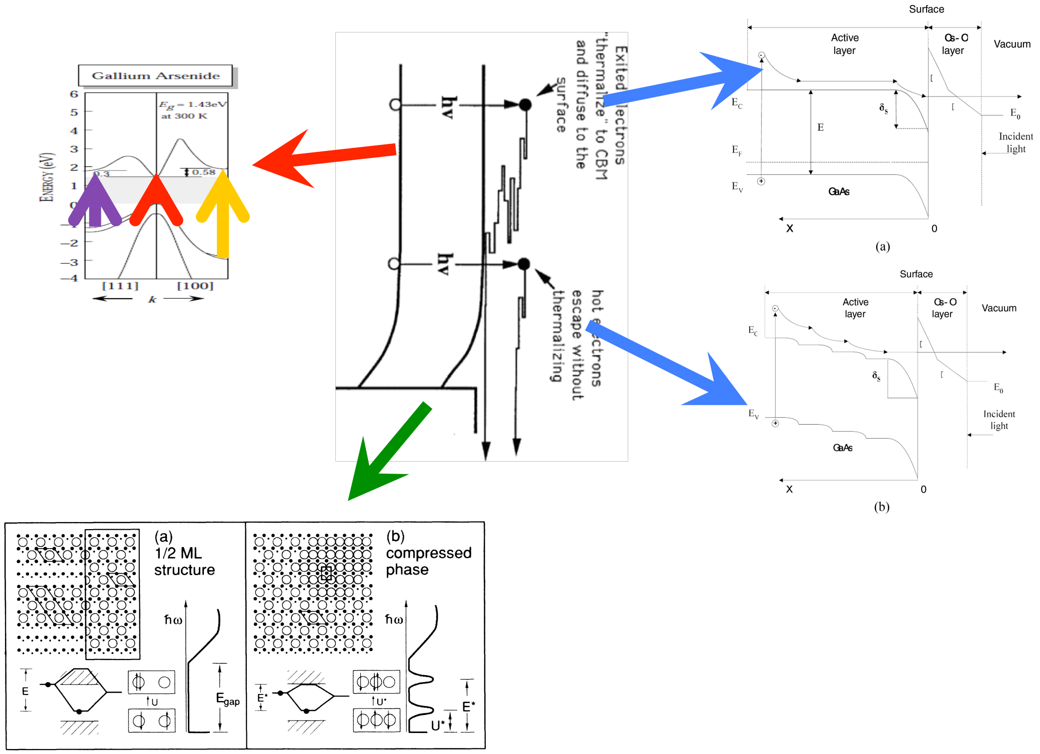
- X-ray techniques can help to characterize:
  - complex phase segregations during growth and use of PC's
  - And develop an atomistic model of the cathode-vacuum interface

- Combined X-ray techniques provide:
  - Elemental, chemical, structural information on crystalline, poly-crystalline and nano-materials.
  - Questions of interface sciences can be addressed.
  - Combination with theory provides powerful method to derive microscopic models of complex heterogeneous systems

- Experimental facilities are under construction
  - Combined studies will be possible at BNL and ANL
  - Time resolution from 100ps to s possible
  - This is a starting point, more efforts are essential

Introduction: What we want to know?

The photocathode: a complex heterogeneous sample system.

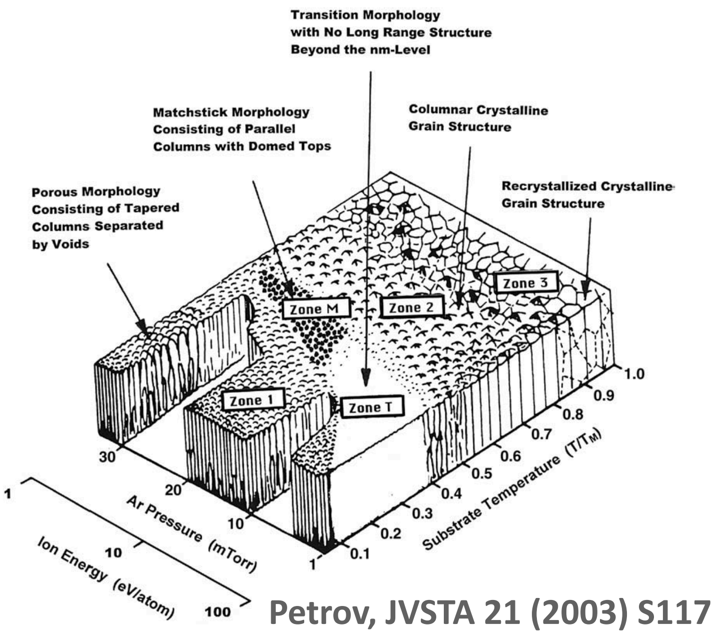


- Typical "thickness" of active area (fast cathodes): 10nm-100nm
- Most "high efficiency" cathodes are semiconductor cathodes (III-V, or bi- and multi-alkali)
- Functionality of semiconductor cathodes depends on band-structure of substrate, doping profile, segregation effects, and surface composition

Introduction: What we want to know?

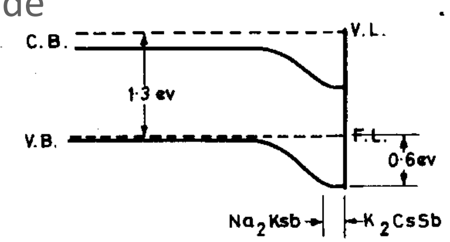
Structure and chemical composition during growth.

J.H.E. Cartwright et al. / Thin Solid Films 518 (2010) 3422–3427



Petrov, JVSTA 21 (2003) S117

K-Na-Cs/Sb: segregation effects yields to electric field inside the cathode



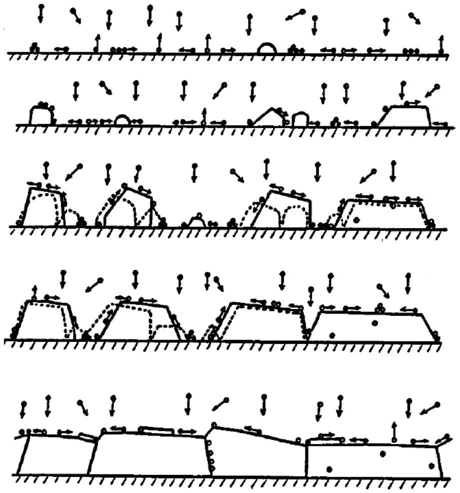
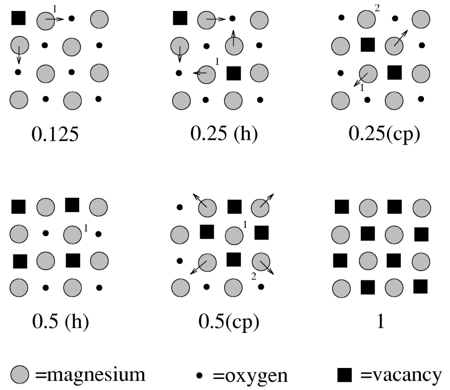


FIG. 1. Schematic diagram illustrating fundamental growth processes controlling microstructural evolution: nucleation, island growth, impingement and coalescence of islands, grain coarsening, formation of polycrystalline islands and channels, development of a continuous structure, and film growth (see Ref. 9).



Phys. Rev. B 59, 5178–5188 (1999)

- Amorphous versus poly- and crystalline growth
- Growth characteristic depends:
  - Thickness of layer
  - Rest-gas composition
  - Morphology and chemistry of substrate
- Amorphous may be good (?):
  - High mobility of ions
  - Chemical potential determines composition
  - Should work for strong covalent states