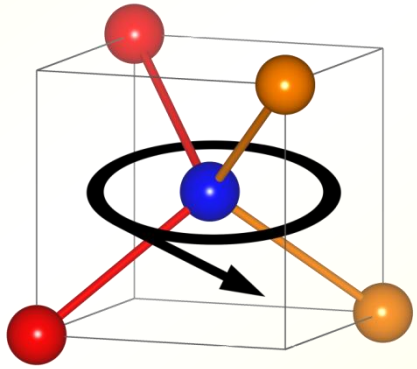
X-ray absorption spectroscopy and its application to chalcopyrite and kesterite materials



Claudia S. Schnohr

Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Germany

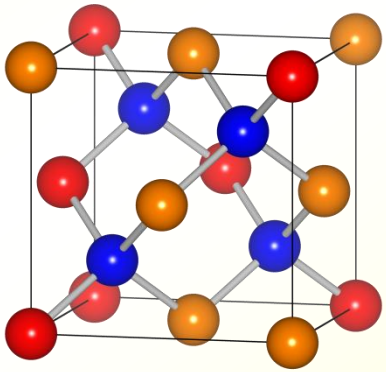
Part I **Basics of XAS**

Part II **Experimental aspects of XAS**

Part III **Applications of XAS to chalcopyrite and kesterite materials**

X-ray absorption spectroscopy (XAS)

powerful technique for structural analysis



complementary to other techniques
such as diffraction or electron microscopy

applicable to crystalline and disordered materials,
liquids and even gases

physics, chemistry, material science, geology,
biology, environmental science, ...

Literature

Books

S. Calvin, *XAFS for Everyone*, CRC Press, 2013

G. Bunker, *Introduction to XAFS*, Cambridge University Press, 2010

S. D. Kelly et al., *Analysis of Soils and Minerals Using X-ray Absorption Spectroscopy*, Book Chapter, Soil Science Society of America Book Series No. 5, 2008

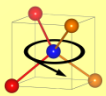
C.S. Schnohr, M.C. Ridgway, *X-ray Absorption Spectroscopy of Semiconductors*, Springer, 2015

Internet

http://www.ixasportal.net/ixas/

→ http://www.ixasportal.net/wiki/doku.php

http://xafs.org/



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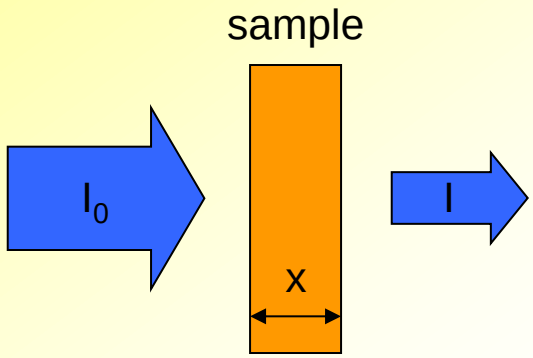
EXAFS

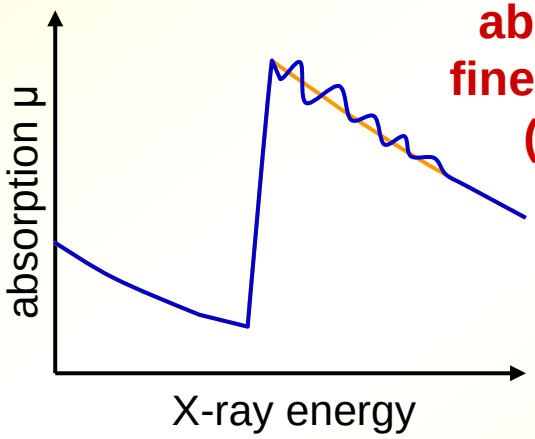
Summary

Basic principle

X-ray absorption



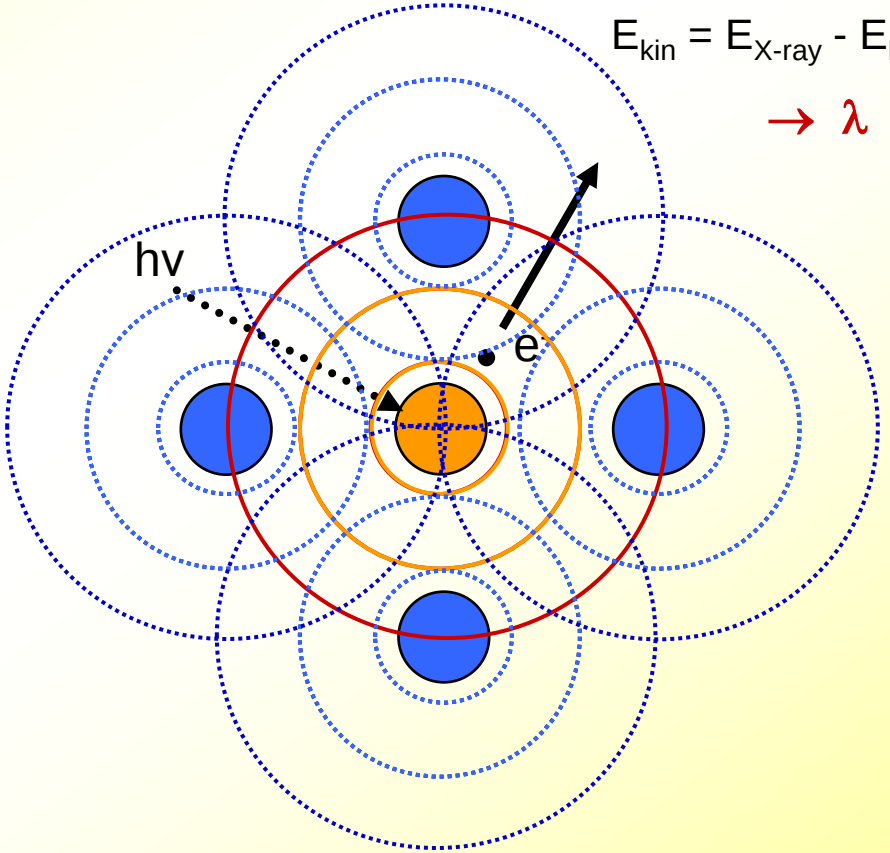
$$I = I_0 e^{-\mu x}$$



X-ray absorption fine structure (XAFS)

$E_{kin} = E_{X\text{-}ray} - E_B$

$\rightarrow \lambda$

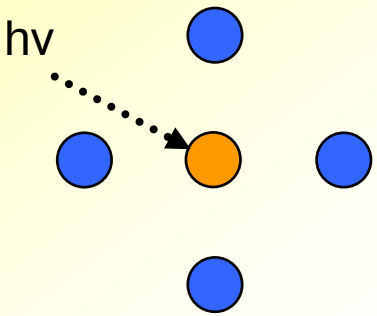


final state $\rightarrow$ superposition of outgoing and scattered waves

Basic principle

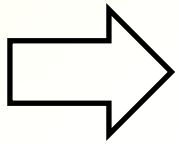
Fermi‘s Golden Rule

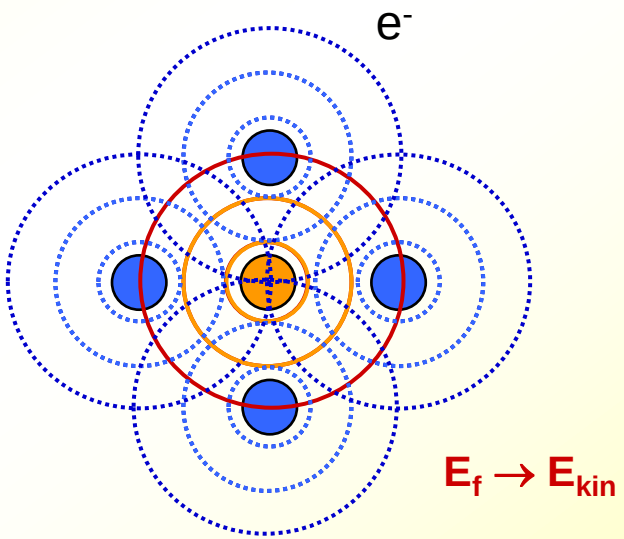
quantum mechanics



initial state $\boldsymbol{i}$

transition





final state $\boldsymbol{f}$

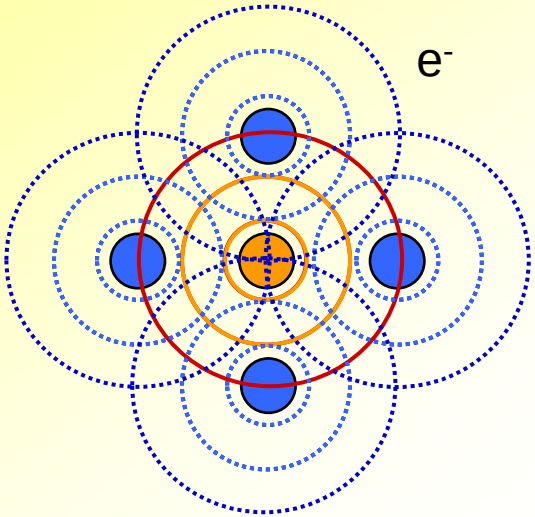
transition probability:

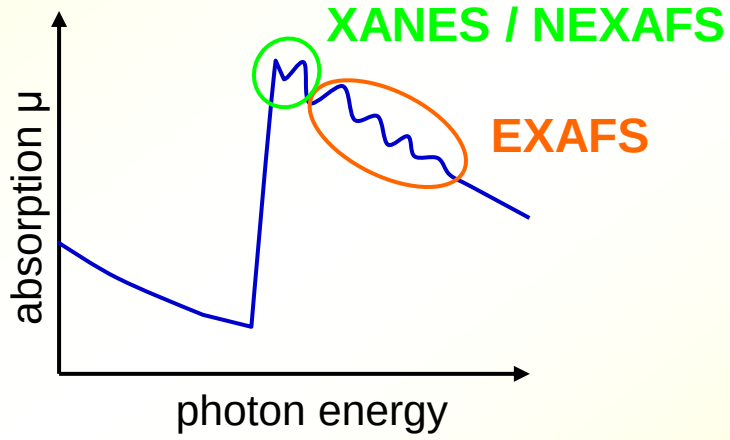
$$\mu \propto \left|\langle f|H_{X-ray}|i\rangle\right|^2 \rho(E_f)$$

matrix element M_{if} density of states

Basic principle

Characteristics of XAS





fine structure of a particular absorption edge

→ **element-specific**

short range probe (~ 10 Å)

→ **no long-range order needed**

instantaneous configuration around the absorber

→ **correlated motion**

Contents – Part I

Basic principle ✓

XANES

EXAFS

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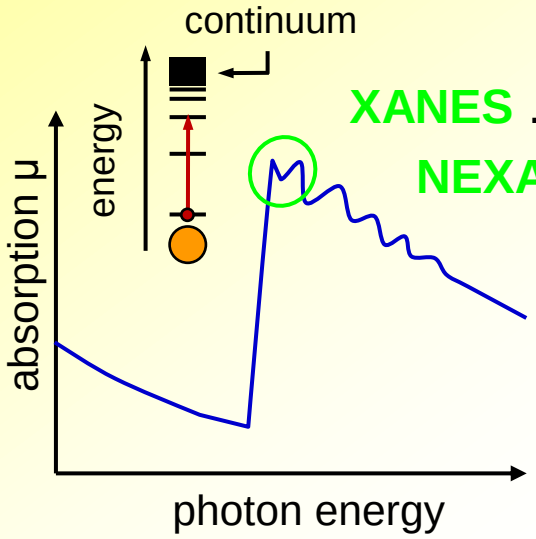
XANES

Characteristics



XANES ... X-ray Absorption Near Edge Structure

NEXAFS ... Near Edge X-ray Absorption Fine Structure

$$\mu \propto \underbrace{\left|\langle f|H_{X-ray}|i\rangle\right|^2}_{\text{matrix element } M_{if}} \underbrace{\rho(E_f)}_{\text{density of states}}$$

$\rho(E_f)$ ⇨ excitation to unoccupied bound states

→ **density of states, chemical bonding**

dipole transition → selection rules

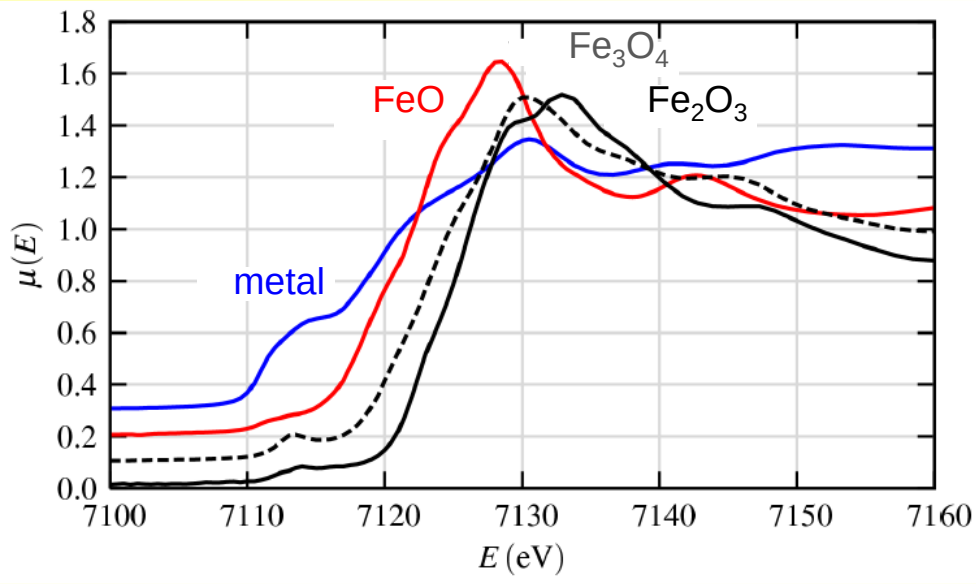
M_{if} ⇨ multiple scattering effects

→ **crystal or cluster symmetry**

XANES

Chemical bonding

Fe K-edge of Fe oxides and Fe metal



Newville, Fundamentals of XAFS
www.xafs.org/Tutorials

valence state of the absorber

&

number and kind of nearest neighbours

⇩

position and shape of edge region

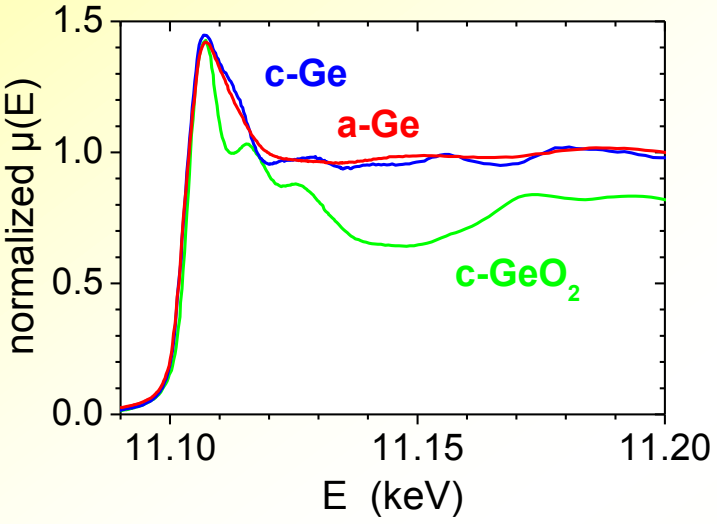
XANES → density of states, chemical bonding, valence state

XANES

Structure

Ge K-edge of Ge

crystalline vs. amorphous



Araujo et al., PRB 78, 2008

structure

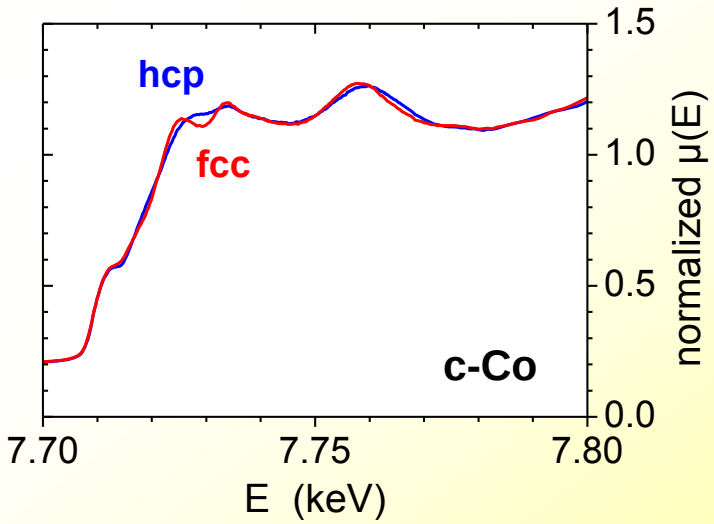
&

symmetry

shape of edge region

Co K-edge of Co

hcp vs. fcc



Sprouster et al., PRB 80, 2009

XANES → crystal or cluster symmetry

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EXAFS

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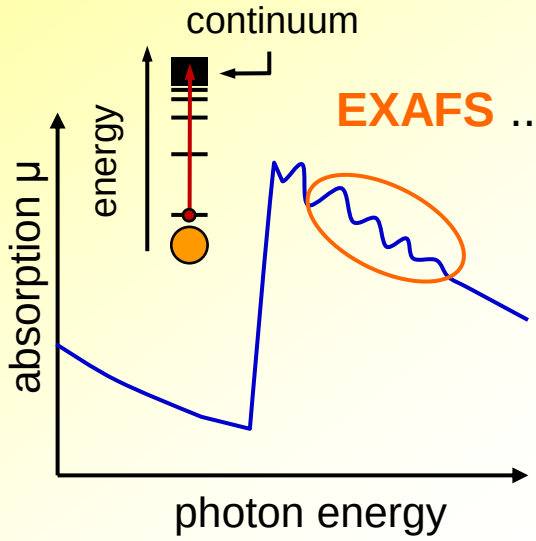


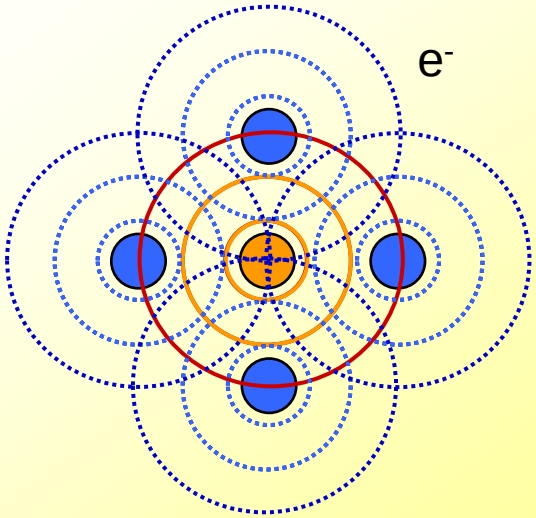
EXAFS ... Extended X-ray Absorption Fine Structure

~ 30 ... 1000 eV above the edge

$$\mu \propto \underbrace{\left|\langle f|H_{X-ray}|i\rangle\right|^2}_{\text{matrix element } M_{if}} \underbrace{\rho(E_f)}_{\text{density of states}}$$

M_{if} ⇨ structural environment of absorber

→ **coordination number,**
bond lengths,
disorder,
...



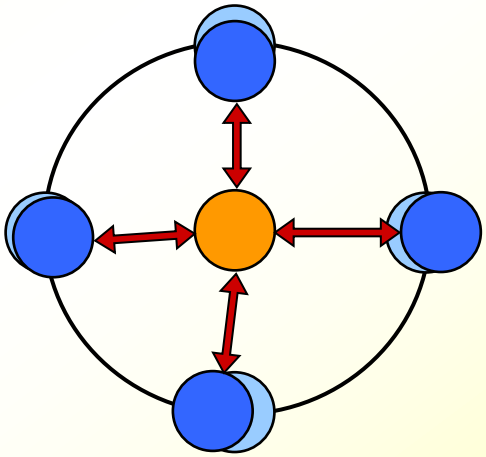
EXAFS

Structural parameters

EXAFS measures instantaneous configuration

thermal vibrations & static disorder

→ **distance distribution**



parameters

mean value (d)

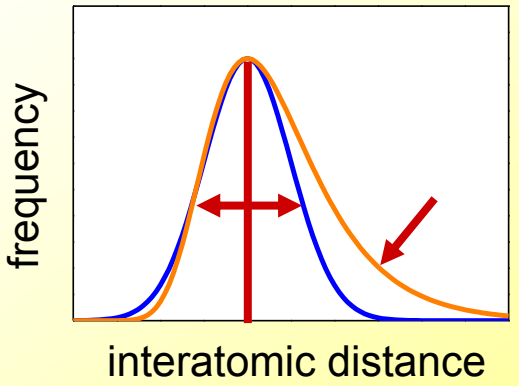
→ **average distance, i.e. bond length**

standard deviation (σ)

→ **variation of distances**

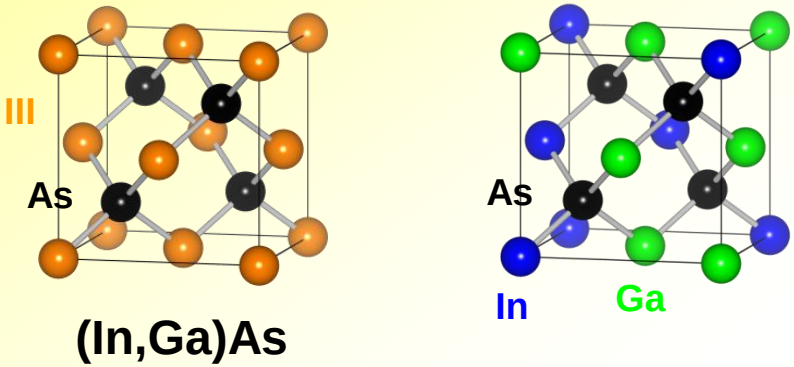
asymmetry (C3)

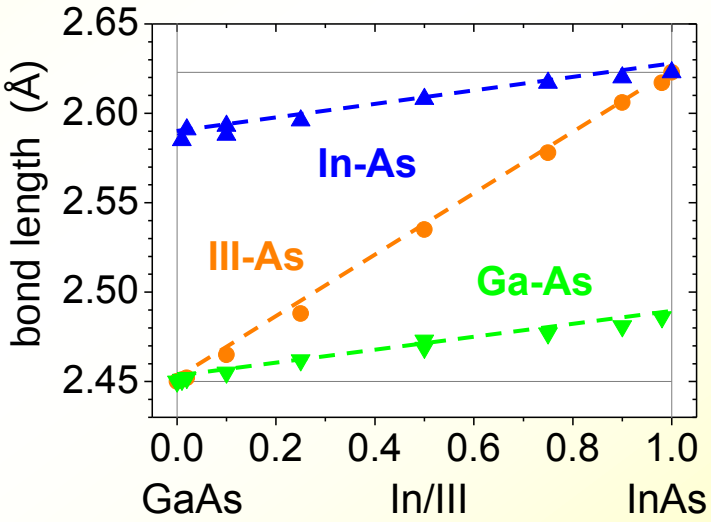
→ **excess of shorter or longer distances**



EXAFS

Bond lengths





Mikkelsen & Boyce, PRL 49, 1982

→ In-As and Ga-As bond lengths are very different from average III-As distance

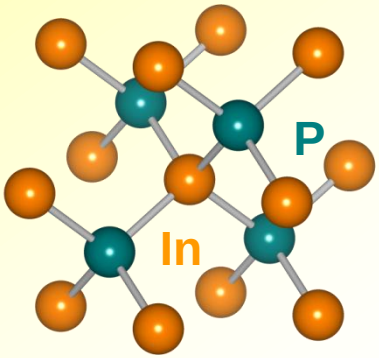
→ local atomic arrangements deviate from crystallographic structure

EXAFS → element-specific bond lengths

EXAFS

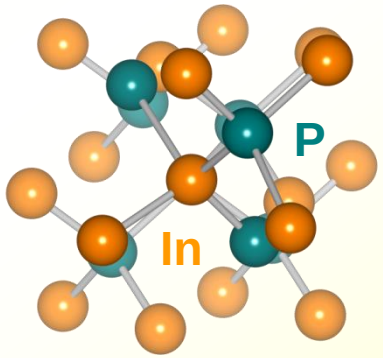
Coordination number and disorder

crystalline InP



Schnohr et al.,
PRB 77, 2008
PRB 79, 2009

amorphous InP

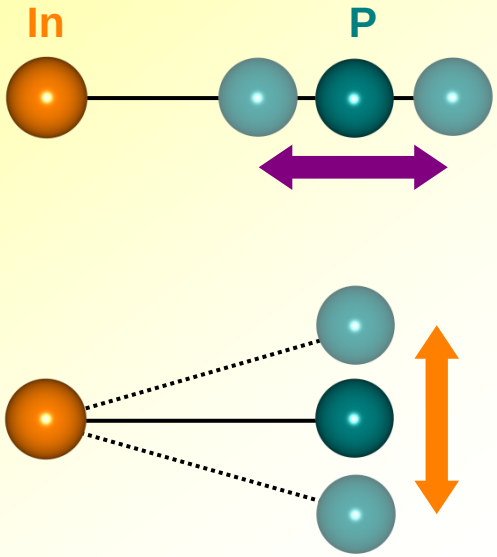


	structural parameters	
4	N	3.4 (3) 0.7 (3)
2.541 (5)	d (Å)	2.584 (3) 2.799 (6)
2.5 (2)	σ^2 (10^{-3} Å^2)	5.6 (2) 5.8 (2)
0	C3 (10^{-5} Å^3)	22 (7) 10 (20)

EXAFS → structural parameters of crystalline and disordered materials

EXAFS

Atomic vibrations

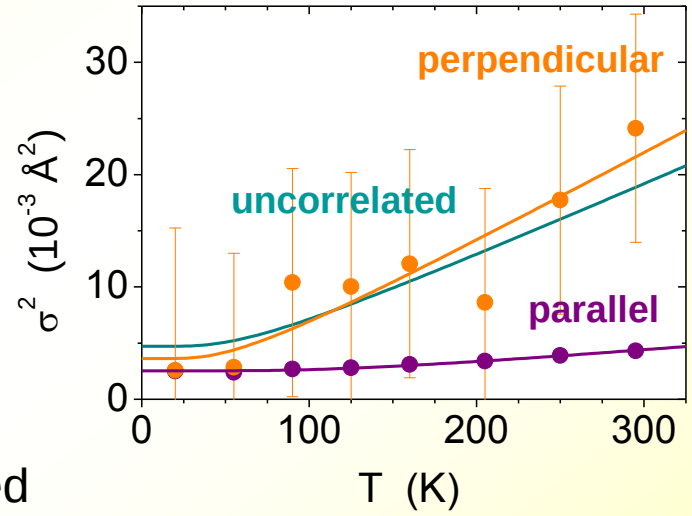


parallel

→ mostly in phase

perpendicular

→ mostly uncorrelated



Schnohr et al., PRB 79, 2009

→ bond stretching requires more energy than bond bending

→ force constants for correlated motion

EXAFS → relative vibrations of neighbouring atoms

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EXAFS ✓

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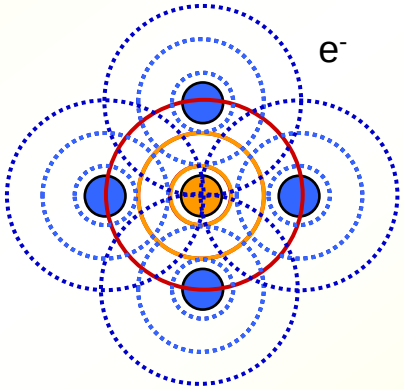
Summary

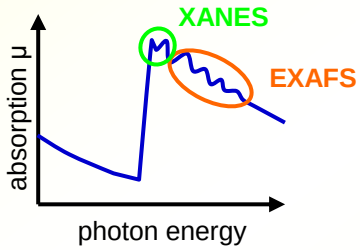


X-ray absorption spectroscopy (XAS)

→ structural analysis on sub-nm scale

→ crystalline and disordered solids, liquids, ...

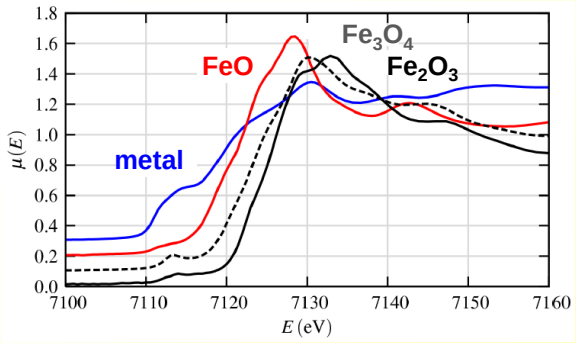
→ element-specific



XANES

→ density of states, chemical bonding

→ crystal or cluster symmetry



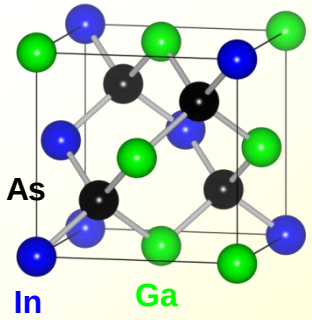
EXAFS

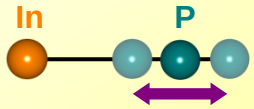
→ coordination number

→ bond lengths

→ static disorder

→ atomic vibrations





Part I **Basics of XAS**

Part II **Experimental aspects of XAS**

Part III **Applications of XAS to chalcopyrite and kesterite materials**

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Experimental techniques

Sample preparation

Data analysis

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- EXAFS

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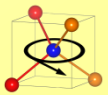


X-ray sources

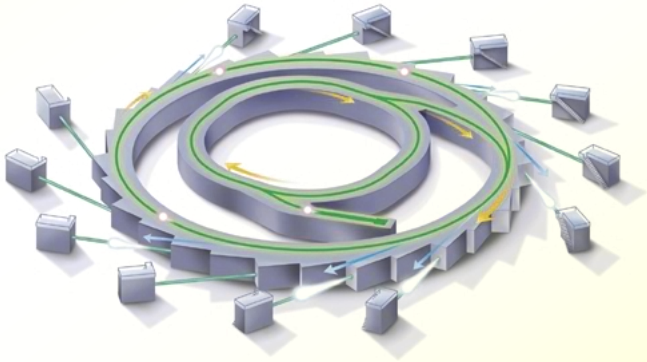
Synchrotron radiation

continuous energy spectrum and high X-ray flux

→ **synchrotron radiation**

DESY, BESSY, ESRF, SLS, …

but: application process
limited number of samples
long time scale



http://www.sync.monash.edu.au

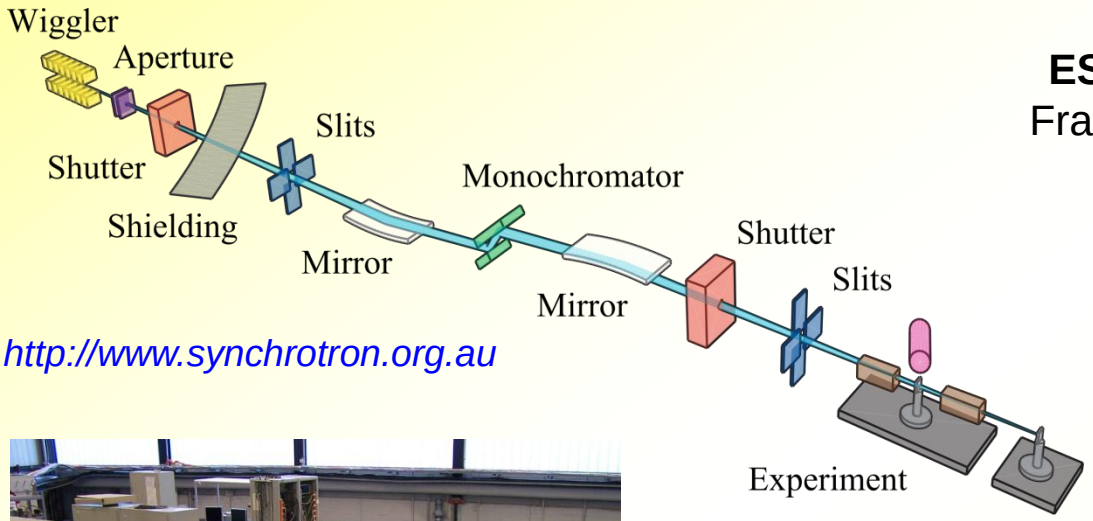
<u>elements</u> Ti (Z=22) … Ag (Z=47) … Xe (Z=54) → K-edges
Cs (Z=55) … U (Z=92) → L-edges
Sc (Z=21) and below → K-edges, but **difficult**

<u>absorption length</u>

$Cu(In,Ga)Se_2$	Cu K-edge	8.979 keV	~ 15 µm	} →	**bulk technique**
	In K-edge	27.940 keV	~ 80 µm		

X-ray sources

XAS beamlines



http://www.synchrotron.org.au

ESRF
France

DESY
Hamburg

SLS
Switzerland

Contents – Part II

X-ray sources ✓

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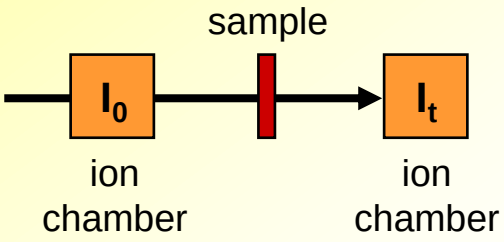
Detection modes

Transmission

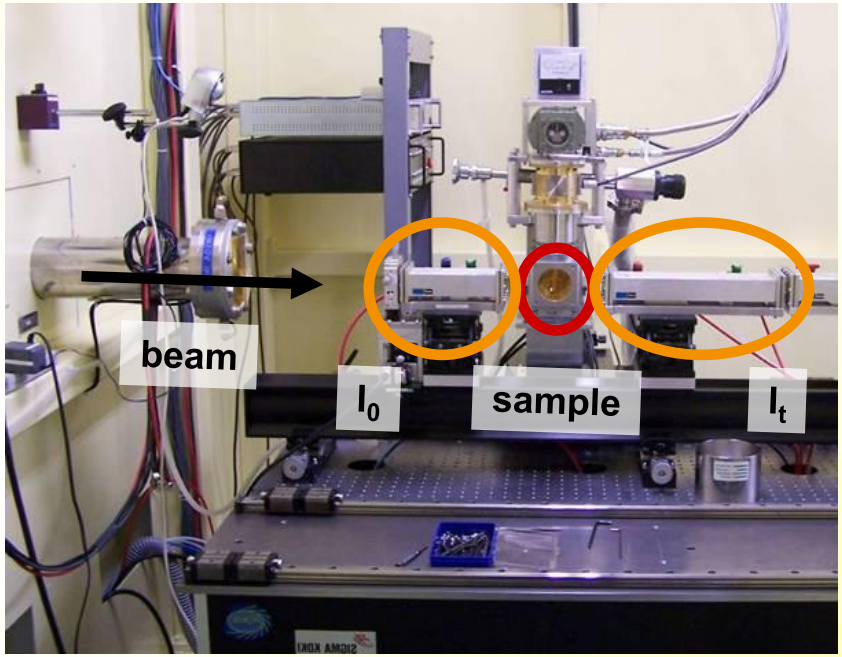


→ bulk sensitive

→ simple setup
high quality data

→ but samples must be:
concentrated
thick (10...50 µm)
uniform

→ **typically powder samples**

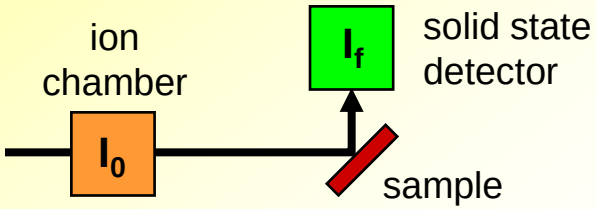


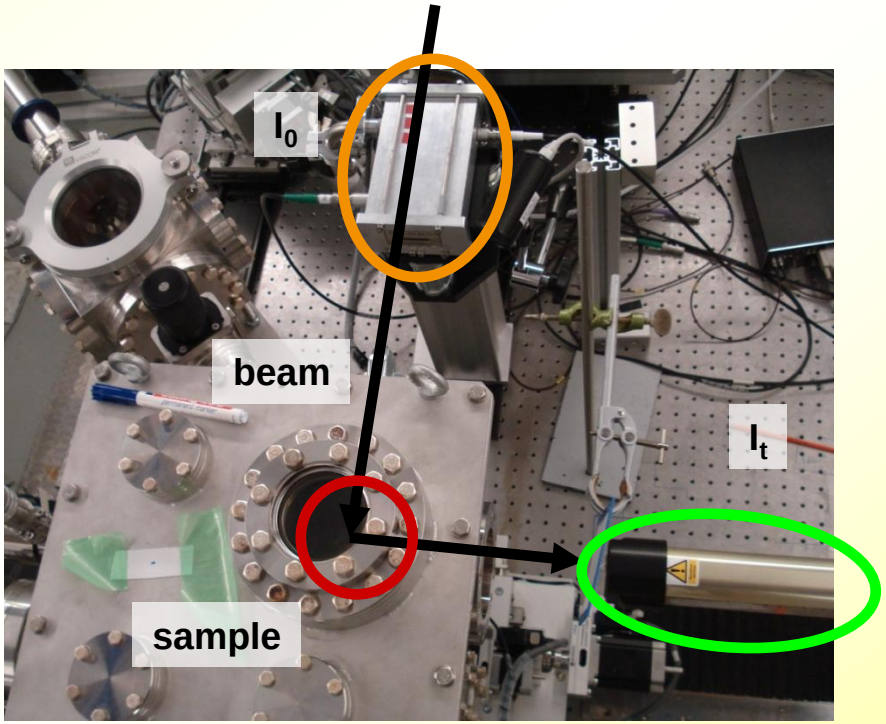
NW10-A, **Photon Factory**, Japan

Experimental techniques

Detection modes

Fluorescence





SuperXAS, **SLS**, Switzerland

→ bulk sensitive

→ sophisticated detector
limited count rate

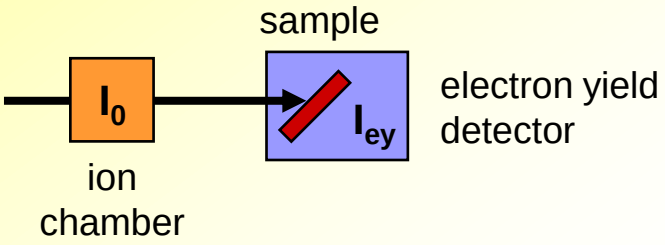
→ but samples can be:
diluted
thin (≤ 2 µm)
nonuniform

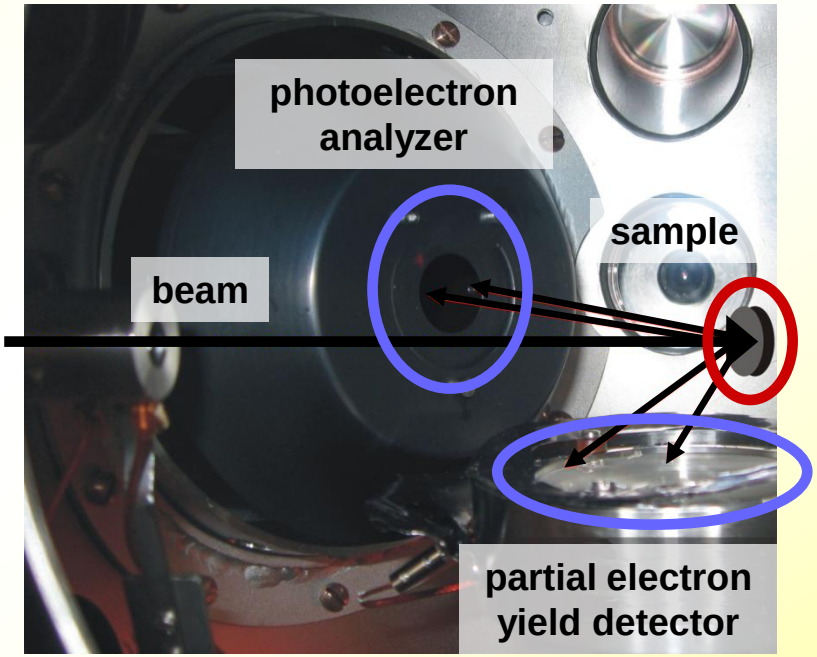
→ **thin films, nanoparticles, ...**

Experimental techniques

Detection modes

Electron yield





D1011, **MAX II**, Sweden

www.maxlab.lu.se/node/458

→ surface sensitive (~ 100 nm)

→ sophisticated detector

ultra high vacuum

→ **suitable for light elements (soft X-ray regime)**

but surface treatment of sample may be necessary

Experimental techniques

Specialized techniques - I

Grazing incidence XAS

reduced penetration depth

→ highly surface sensitive (tens of nm)

Total external reflection XAS

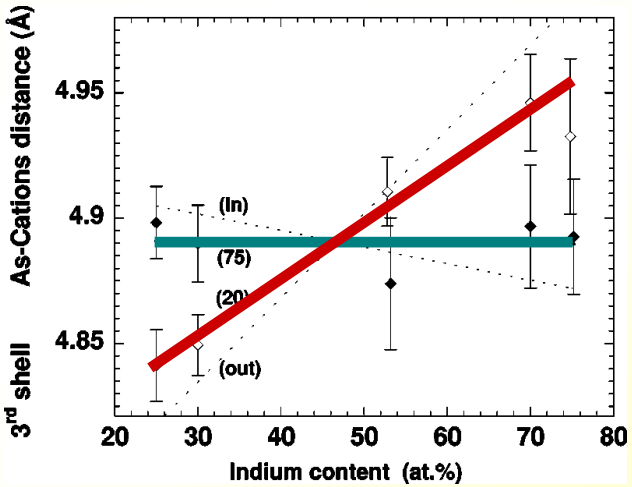
penetration depth further reduced

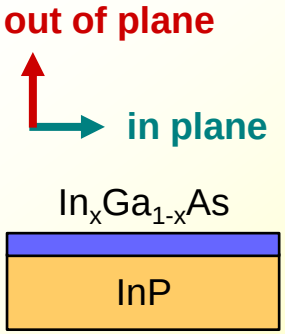
→ extremely surface sensitive (some nm)

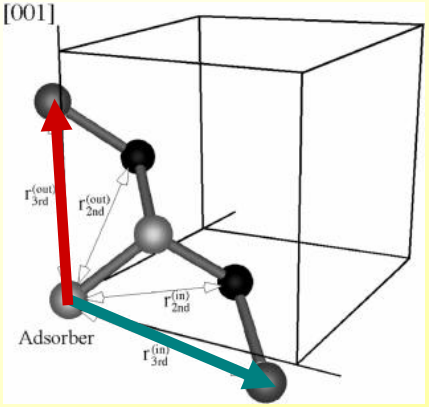
Polarization-dependent XAS

absorption coefficient depends on X-ray polarization

→ structural parameters parallel and perpendicular to sample normal







Tormen et al., PRB 63, 2001

Experimental techniques

Specialized techniques - II

Diffraction anomalous fine structure (DAFS)

measures intensity of a particular Bragg reflection as function of the X-ray energy

→ same structural information as XAS

→ can provide site or spatial selectivity

e.g. $In_xGa_{1-x}As$ layer on GaAs substrate

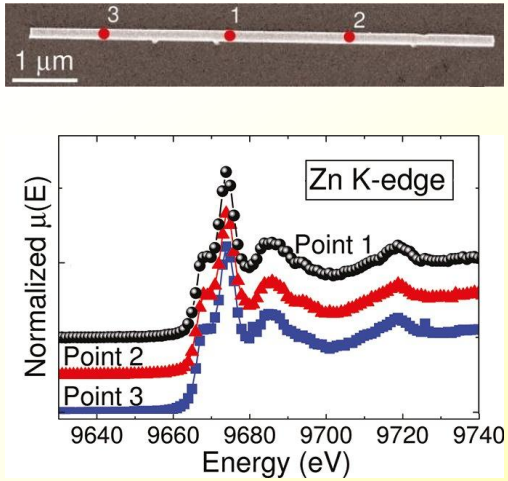
QuickXAS and energy-dispersive XAS

→ time-resolved studies (s ... min)

MicroXAS

→ spatially resolved studies (tens of nm ... µm)

Co-doped ZnO nanowire



Segura-Ruiz et al., Nano Lett. 11, 2011

but: all techniques require specialized setup and much experience

Contents – Part II

X-ray sources ✓

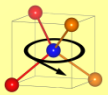
Experimental techniques ✓

Sample preparation

Data analysis

- XANES
- EXAFS

Summary

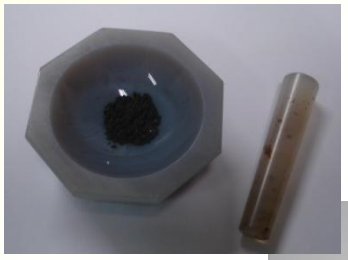


Sample preparation

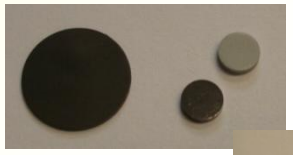
<u>powders</u>

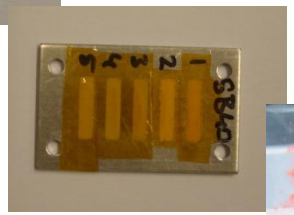
grinding and dilution with binder,
e.g. BN, graphite or cellulose

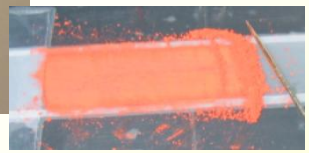
→ ball mill or mortar



pressing into pellets
or sample holder
or dispersion on tape





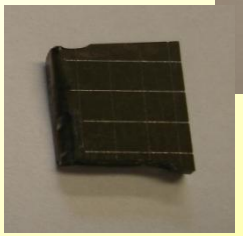


Matt Newville

<u>thin films</u>

measure as-grown on substrate
or lifted off on tape

alternatively: scrape off and process
as powder sample



many more options for other types of samples ...

Contents – Part II

X-ray sources ✓

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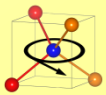
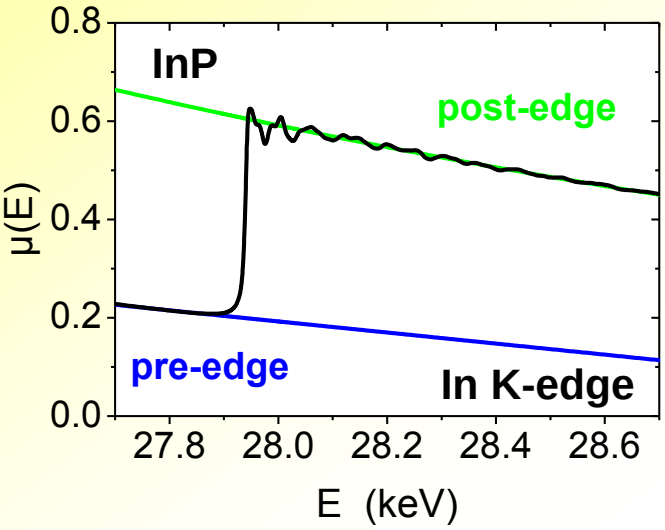


XANES analysis

Normalization



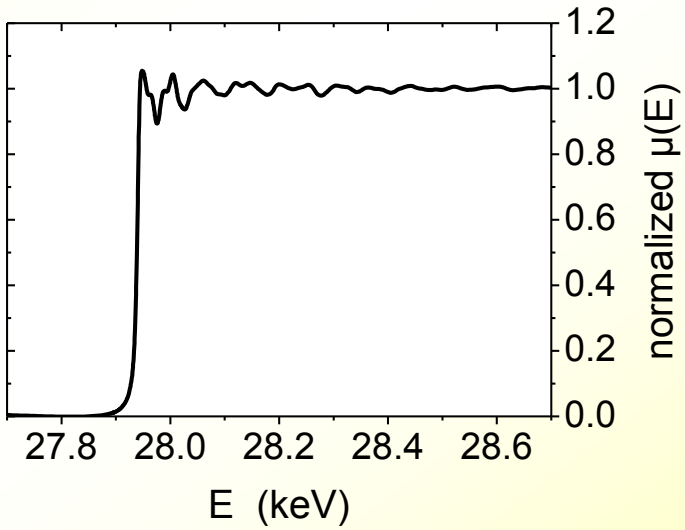
Schnohr et al., PRB 79, 2009

IFEFFIT software package:

ATHENA

Newville & Ravel

http://cars9.uchicago.edu/ifeffit



energy calibration

alignment of spectra

→ reference samples

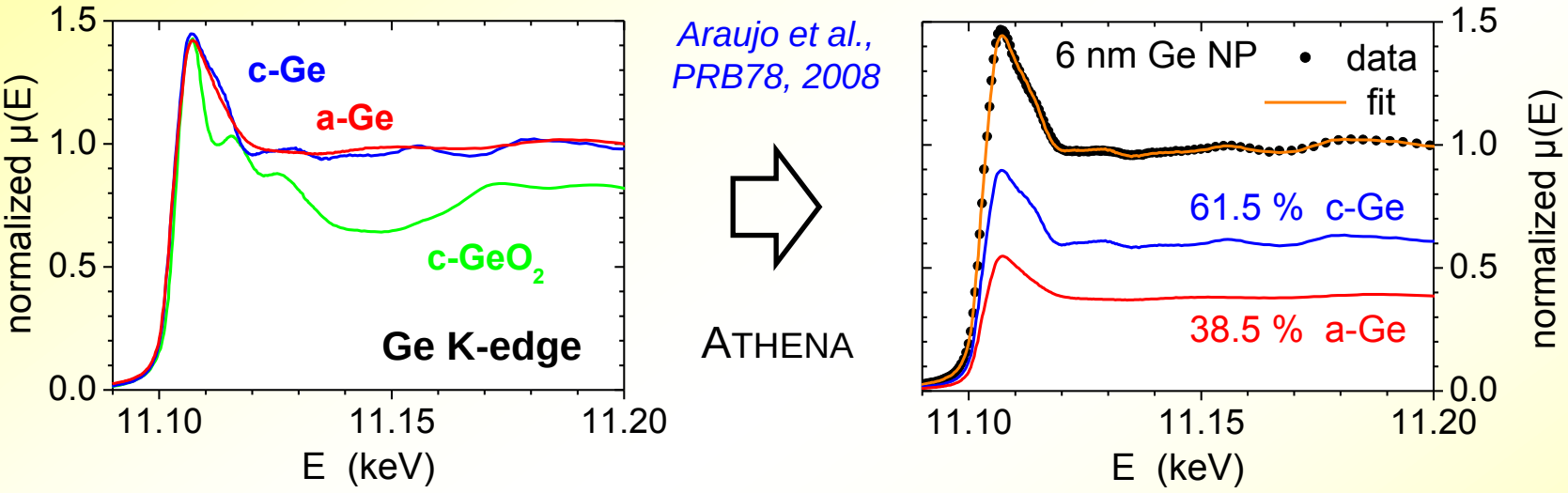
normalization of spectra

→ uses pre-edge and post-edge lines

→ **possible to compare spectra of different samples**

XANES analysis

Linear combination fitting



comparison of measured spectra to those of known standards

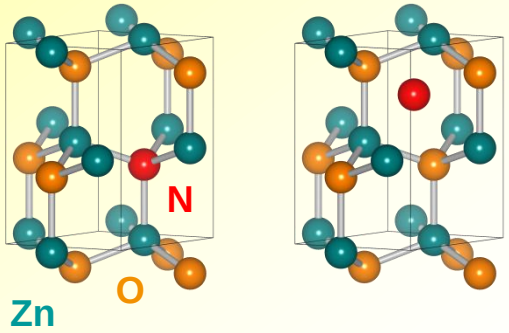
→ **linear combination fitting**

but: existence and measurement of suitable standards is crucial

XANES analysis

Theoretical calculations

different structural models



N in ZnO

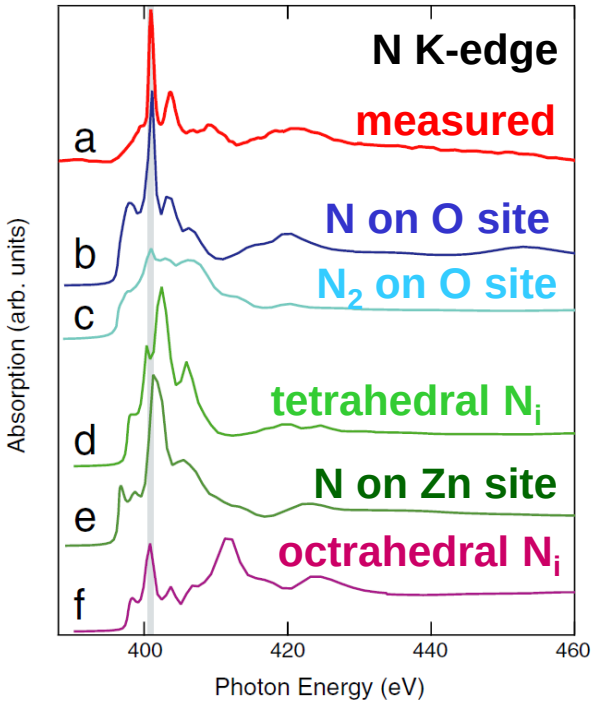
e.g. from density functional theory (DFT)

calculation of theoretical spectra

computer code FEFF

Rehr et al.

http://www.feffproject.org/



Fons et al., PRL 96, 2006

comparison of calculated with measured spectra

→ acceptance or rejection of structural models

but: complicated and accuracy is sometimes limited

Contents – Part II

X-ray sources ✓

Experimental techniques ✓

Sample preparation ✓

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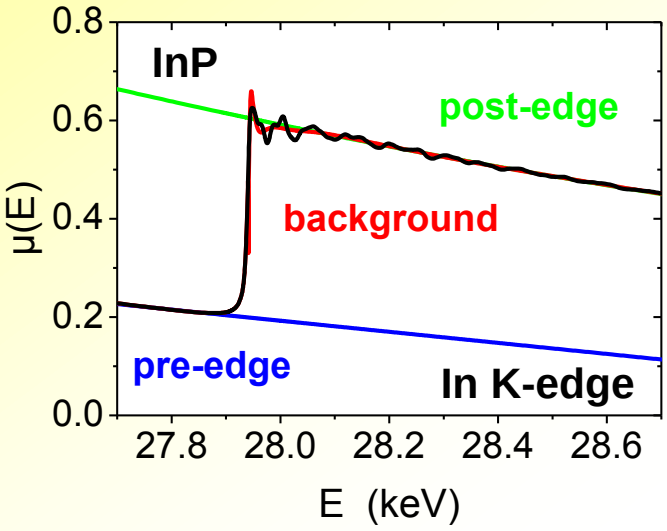
XANES

EXAFS

Summary

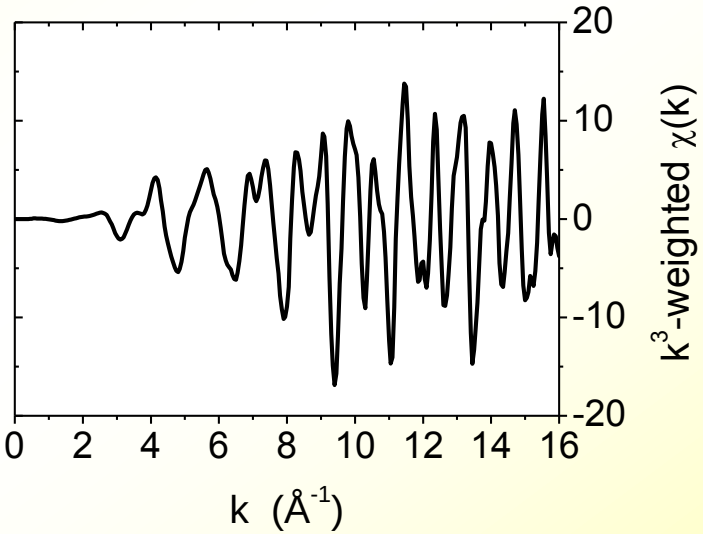
EXAFS analysis

Data processing



Schnohr et al., PRB 79, 2009

ATHENA



background subtraction

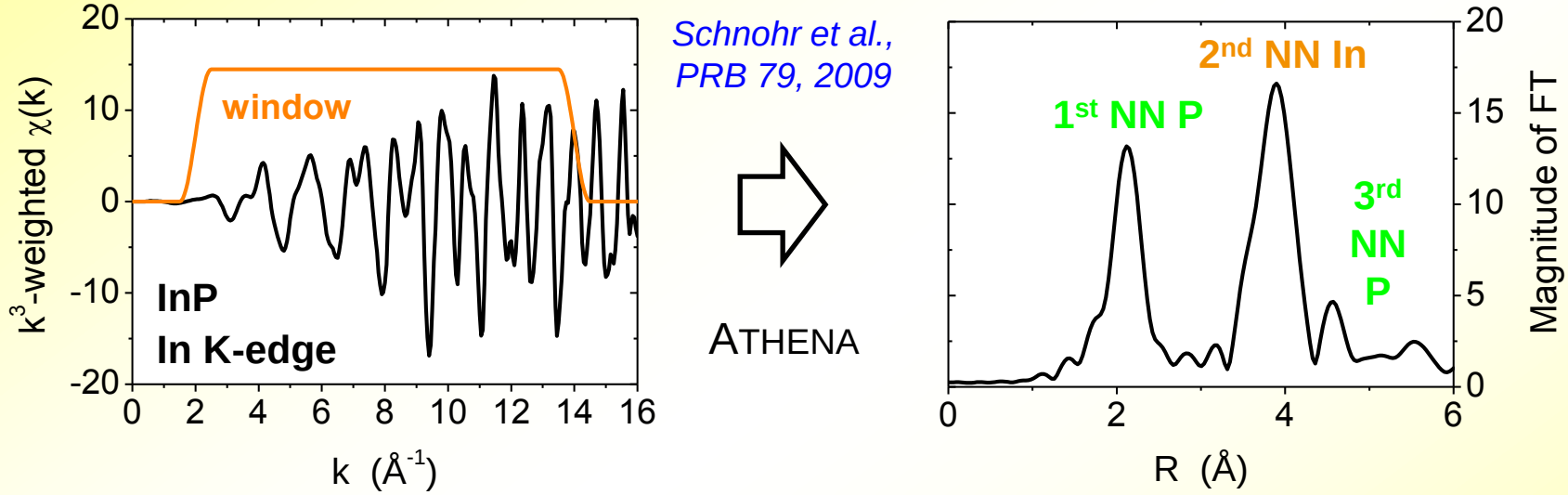
→ isolated fine structure

energy scale is converted to photoelectron wave number

$k = \sqrt{2m_e(E - E_B)}/\hbar$

EXAFS analysis

Data processing



background subtraction

→ isolated fine structure

Fourier transformation (FT)

→ visualization of different scattering contributions

→ **analysis of different scattering contributions**

EXAFS analysis

Ratio Method

analysis of difference between
unknown sample and known reference

amplitude:

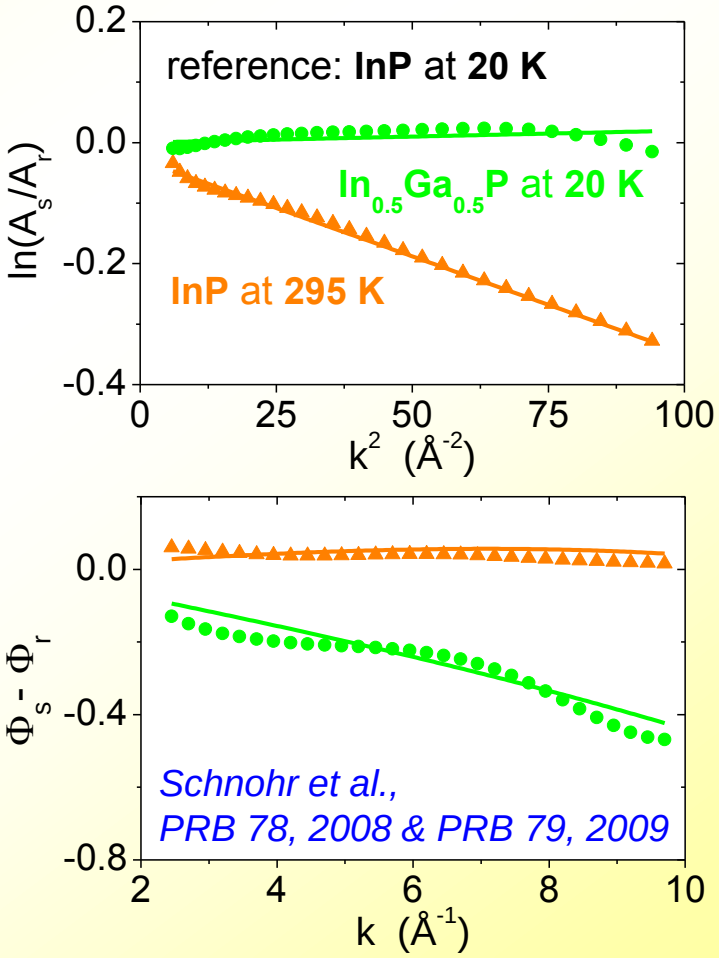
$$ln\left|\frac{A_s(k)}{A_r(k)}\right| = C - 2k^2(\sigma_s^2 - \sigma_r^2) + \ldots$$

phase:

$$\Phi_s(k) - \Phi_r(k) = 2k(R_s' - R_r') - \ldots$$

→ **no structural model needed**

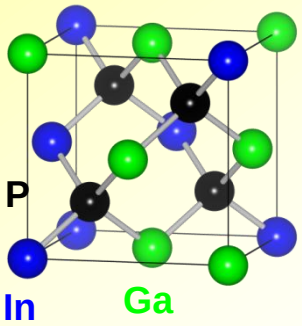
but: limited to first shell
requires suitable reference



EXAFS analysis

Path fitting

structural model



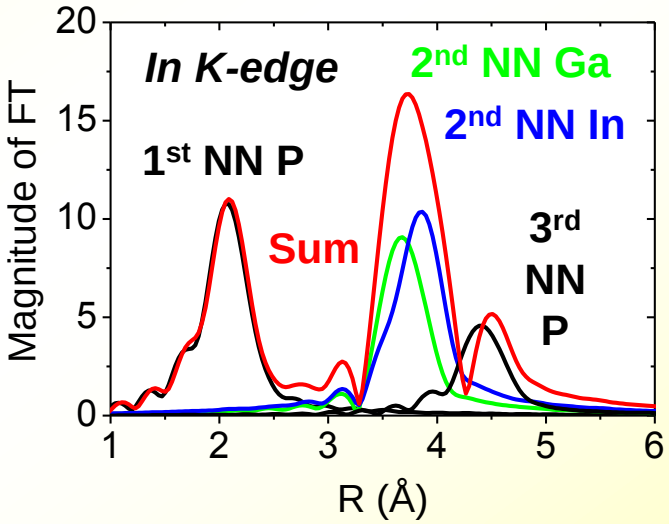
$In_{0.5}Ga_{0.5}P$

calculation of theoretical spectrum

computer code FEFF

Rehr et al.

http://www.feffproject.org/



refinement of structural parameters by fitting calculated to measured spectra

→ **analysis of mixed and higher shells**
no reference material needed

but: requires structural model

IFEFFIT software package: ARTEMIS

Newville & Ravel

http://cars9.uchicago.edu/ifeffit

Contents – Part II

X-ray sources ✓

Experimental techniques ✓

Sample preparation ✓

Data analysis ✓

- XANES
- EXAFS

Summary

Summary

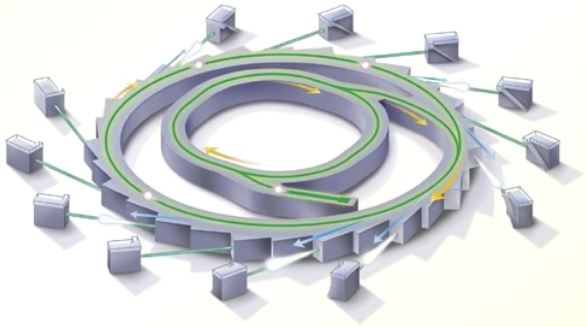
XAS measurements

→ synchrotron radiation

→ transmission, fluorescence or electron yield mode

→ specialized techniques

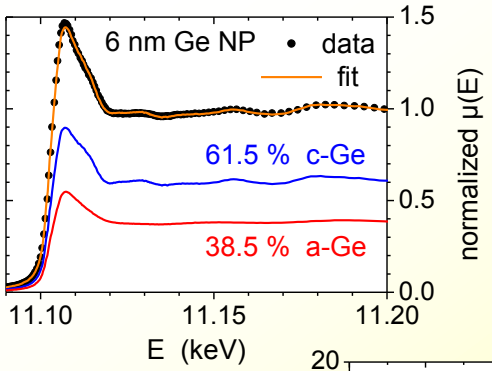
→ powders, thin films, ...

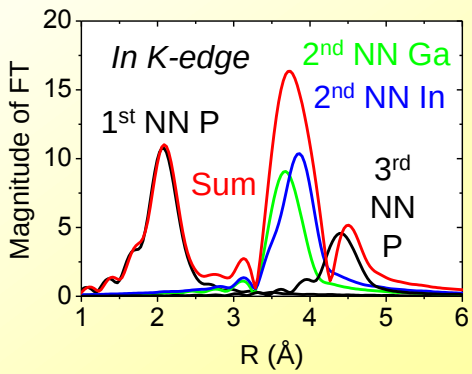


analysis

XANES → data normalization
→ linear combination fitting
→ theoretical calculations

EXAFS → data processing
→ Ratio Method
→ path fitting





Part I **Basics of XAS**

Part II **Experimental aspects of XAS**

Part III **Applications of XAS to chalcopyrite and kesterite materials**

Contents – Part III

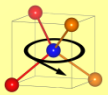
Chalcopyrites

- Atomic-scale structure and band gap bowing
- Local versus global electronic properties
- Cu content and Cu-poor phases

Kesterites

- Secondary phases
- Cation disorder
- Atomic-scale structure

Conclusions

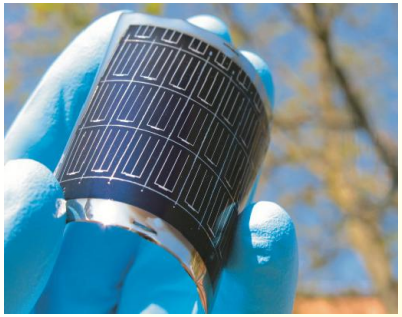


$Cu(In,Ga)Se_2$

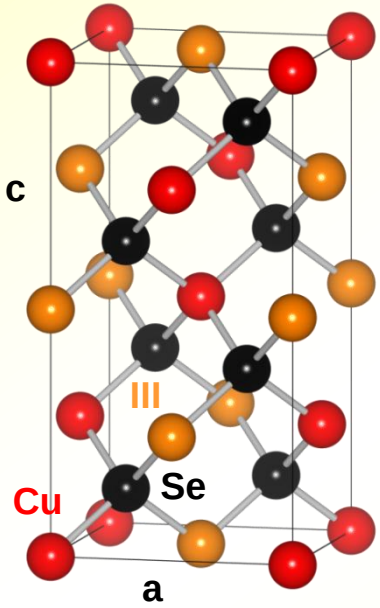
Crystal structure

thin film solar cells with record efficiencies above 20 %
on glass and polymer foils

Jackson et al., PPRA 19, 2011
Chirila et al., Nature Mat. 12, 2013



Chalcopyrite structure



space group $I\bar{4}2d$

a and c change linearly with In/III (Vegard's Law)

anion (Se) displacement

$CuGaSe_2$ $d_{Cu\text{-}Se} \sim d_{Ga\text{-}Se}$ → Se not displaced

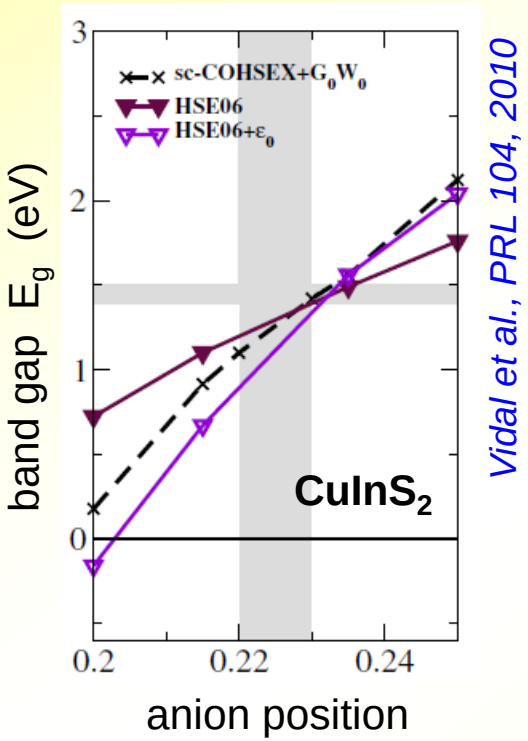
$CuInSe_2$ $d_{Cu\text{-}Se} < d_{In\text{-}Se}$ → Se displaced

$Cu(In,Ga)Se_2$ → Se position ?

$Cu(In,Ga)Se_2$

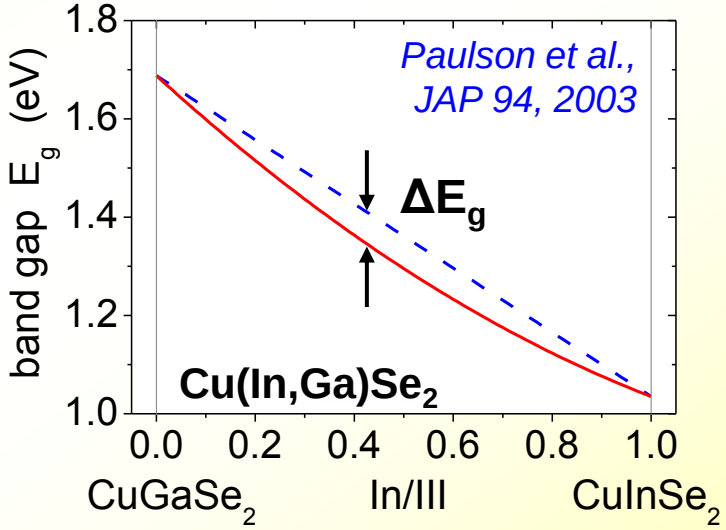
Anion displacement and band gap

anion position strongly influences band gap



Vidal et al., PRL 104, 2010

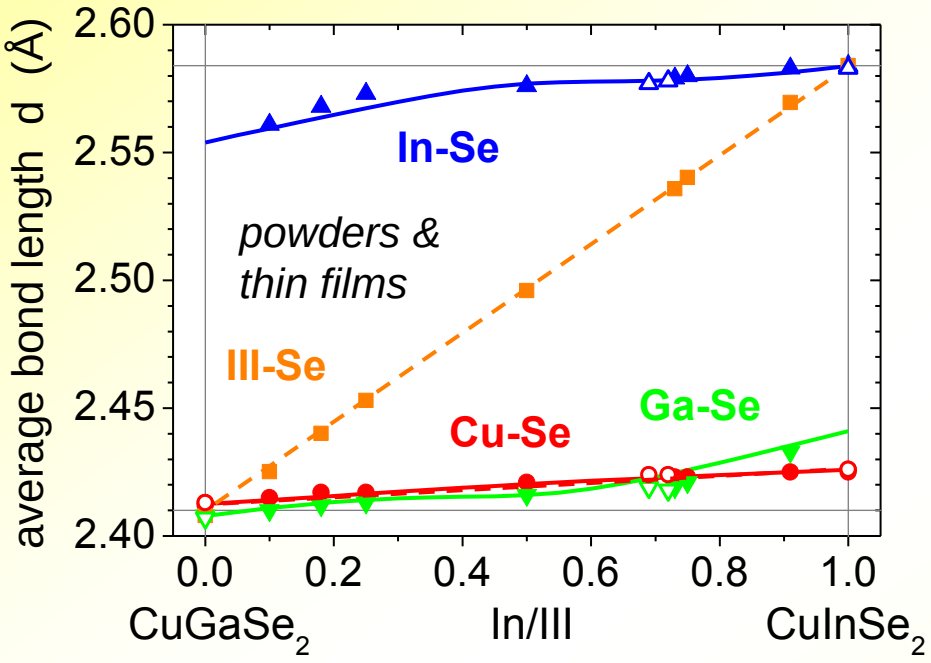
band gap changes nonlinearly with In/III
→ band gap bowing ΔE_g



→ **study atomic-scale structure and influence on band gap in $Cu(In,Ga)Se_2$**

$Cu(In,Ga)Se_2$

Element-specific bond lengths



→ distinctly different and nearly constant

→ average III-Se distance matches diffraction results

Schnohr et al., PRB 85, 2012

→ same bond lengths for powders and thin films

Schnohr et al., TSF, 2014

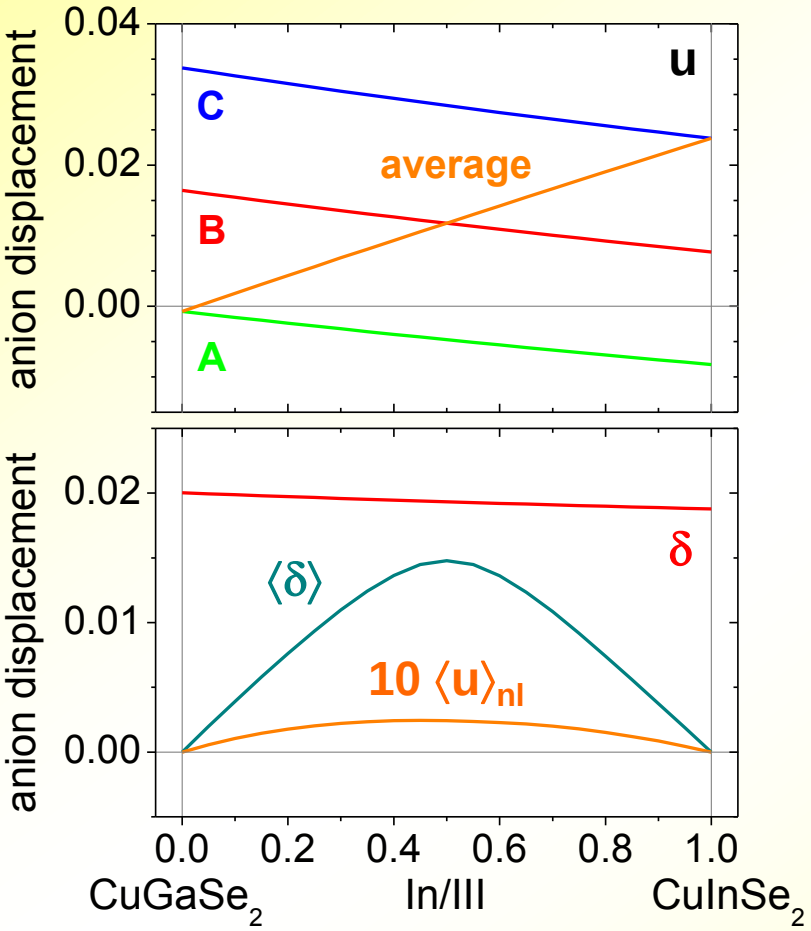
→ **short-range atomic arrangements deviate significantly from long-range crystallographic structure**

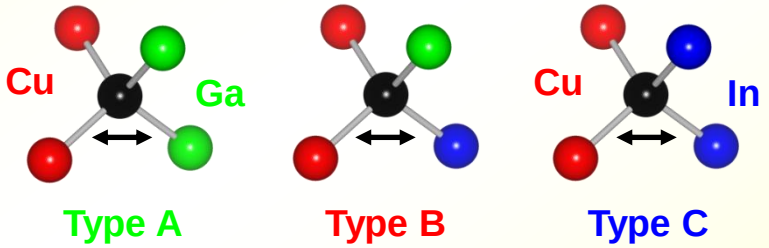
typical for tetrahedrally coordinated semiconductors

Schnohr et al., PRB 78, 2008

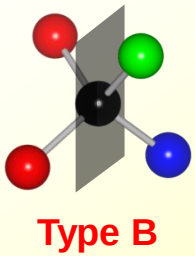
$Cu(In,Ga)Se_2$

Anion displacement





displacement **u** between Cu and III



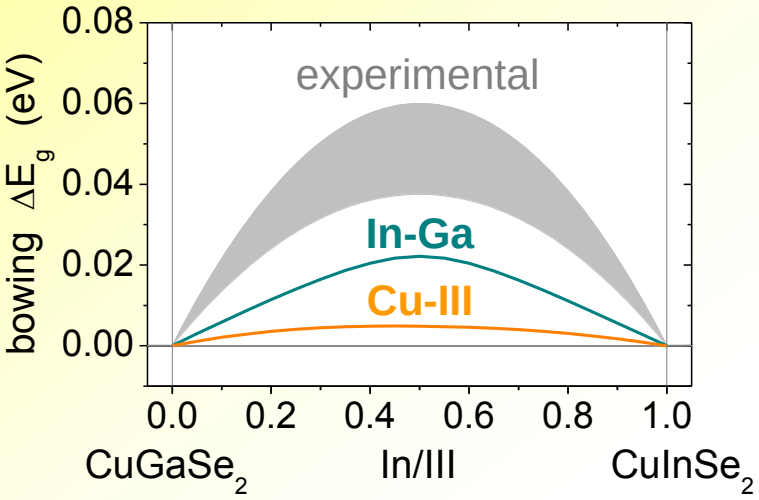
displacement δ between In and Ga

→ **two different relaxation effects both are nonlinear with In/III**

$Cu(In,Ga)Se_2$

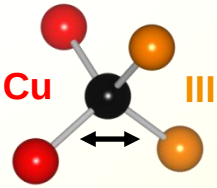
Band gap bowing

Wei & Zunger, JAP 78, 1995



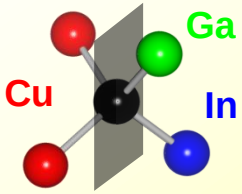
$$\Delta E_g^{Cu-III} = 20eV \cdot \langle u \rangle_{nl}$$

Vidal et al., PRL 104, 2010



$$\Delta E_g^{In-Ga} = 1.5eV \cdot \langle \delta \rangle$$

Schnohr, JPCM 24, 2012



Schnohr et al., PRB 85, 2012

atomic-scale structure strongly influences material properties

three sources

→ volume deformation

→ charge redistribution

→ **anion relaxation**

Bernard & Zunger., PRB 36, 1987

→ **similar results for $Cu(In,Ga)S_2$**

Eckner et al., APL 103, 2013

Contents – Part III

Chalcopyrites

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Kesterites

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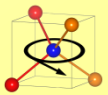
- Cation disorder
- Atomic-scale structure

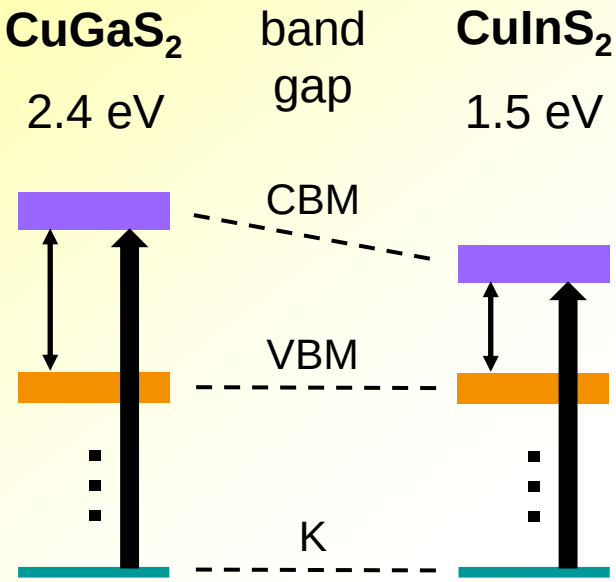
Conclusions



$Cu(In,Ga)S_2$

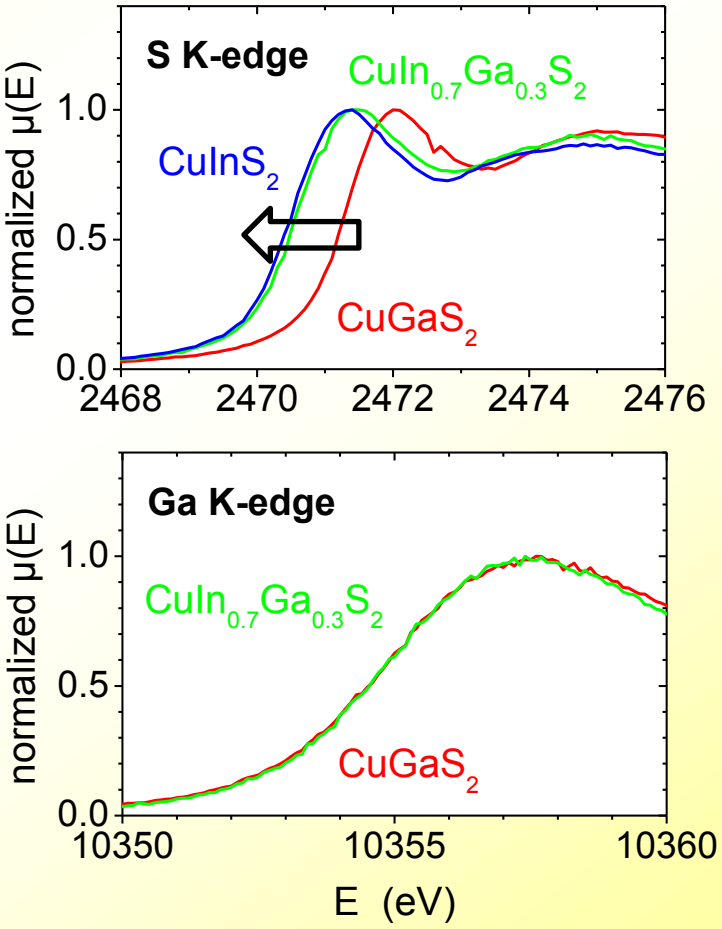
XANES

Johnson et al.
JES 190, 2013



→ absorption edge should shift with changing In/III

⇨ **S → edge shifts**
Ga, In, Cu → no shift



$Cu(In,Ga)S_2$

Density of states

ab initio DFT-based calculations

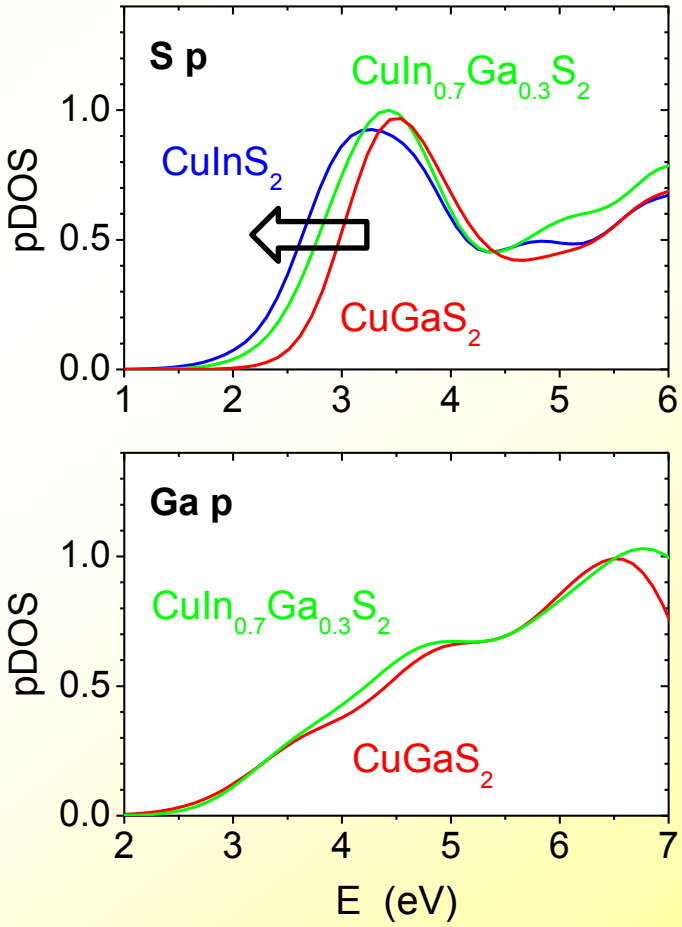
using hybrid functionals and
special quasi-random structures

Sarmiento-Pérez et al., JAP 116, 2014

→ projected partial density of states (pDOS)
corresponding to unoccupied states probed by XANES

⇨ **S → edge shifts**
Ga, In, Cu → no shift

despite change in band gap
cation edges don‘t shift → Why ?

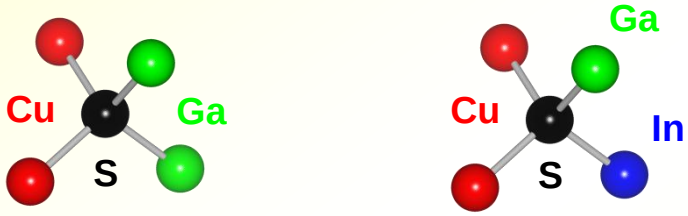


$Cu(In,Ga)S_2$

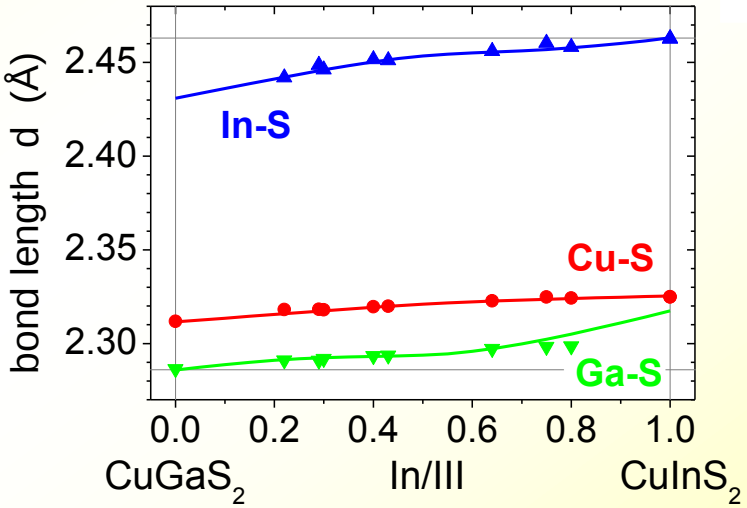
Local atomic environment

$CuGaS_2$ $Cu(Ga,In)S_2$

→ no change for Ga, In and Cu



→ local environment around S changes



Eckner et al., APL 103, 2013

Sarmiento-Pérez et al., JAP 116, 2014

→ **local environment determines local electronic states**
change in band gap due to changing spatial average

Contents – Part III

Chalcopyrites

- Atomic-scale structure and band gap bowing ✓
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Kesterites

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- Cation disorder
- Atomic-scale structure

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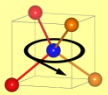
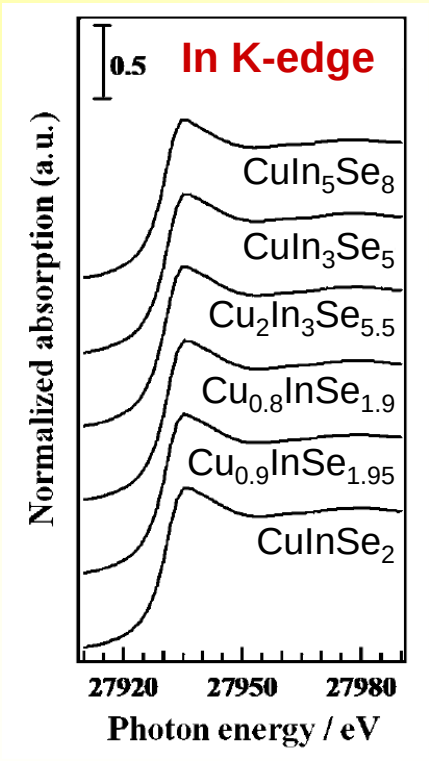


$CuInSe_2$ ... $CuIn_5Se_8$

XANES



→ **no change**

Cu poor phases

different crystal structures

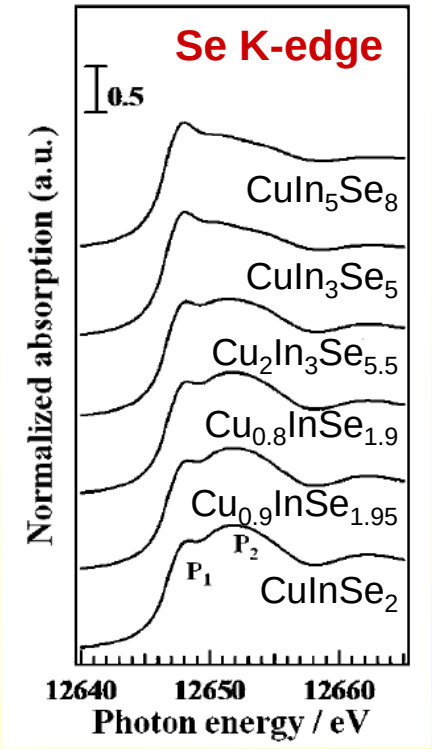
but still tetrahedral coordination

→ each In or Cu has four Se neighbours

bond lengths are similar for all compounds

→ each Se has Cu, In and vacancy neighbours

ratio strongly changes for different compounds

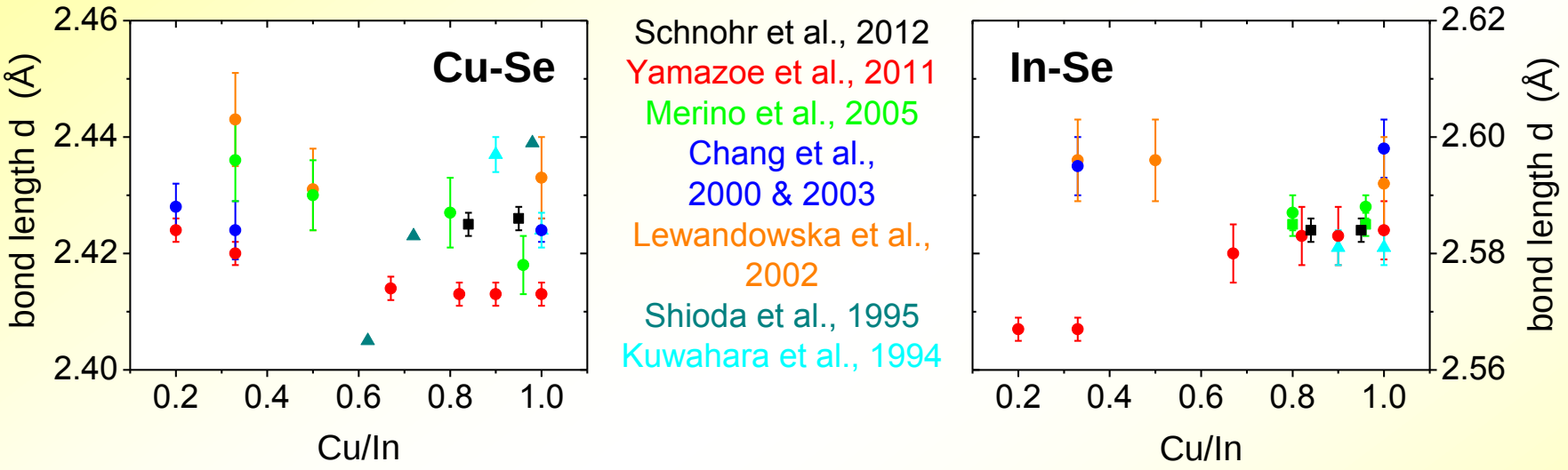


→ **strong change**

Yamazoe et al., JMR 26, 2011

$CuInSe_2$ ... $CuIn_5Se_8$

Element-specific bond lengths



→ mostly constant for $0.8 \leq Cu/In \leq 1.0$, i.e. chalcopyrite range

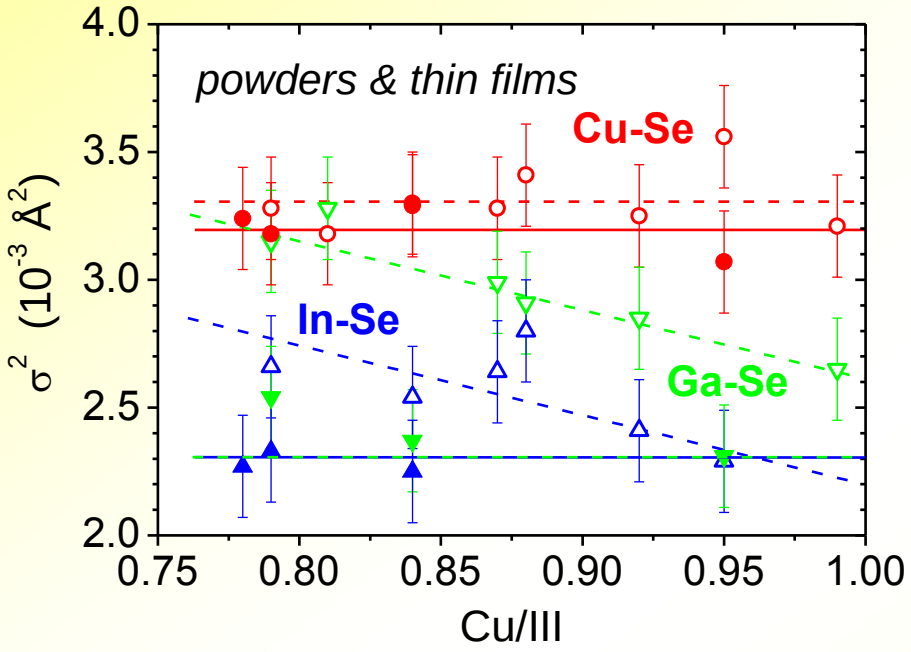
→ small increase or decrease for $Cu/In \leq 0.8$

but: partly contradicting results and only Cu-In-Se system

→ **detailed study of $Cu(In,Ga)_3Se_5$ and $Cu(In,Ga)_5Se_8$**

$Cu(In,Ga)Se_2$

Bond length variation



Schnohr et al., TSF, 2014

<u>powders</u>

→ Cu-Se ≥ Ga-Se ≥ In-Se
bond stretching force constants

→ increase with decreasing Cu/III
increasing amount of defects

<u>thin films</u>

→ Ga-Se and In-Se smaller than powders especially for low Cu/III
different Cu history, i.e. Cu-rich state during co-evaporation

→ **bond length variation depends on cation-anion pair and probably on Cu/III history during preparation**

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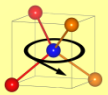


Cu_2ZnSnS_4

Crystal structure

thin film solar cells made of earth-abundant and non-toxic elements

record efficiency for $Cu_2ZnSn(S,Se)_4$ 12.6 %

Wang et al., AEM 4, 2014

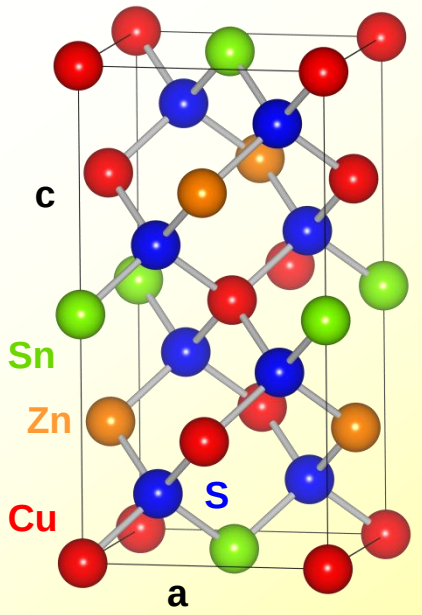
but: preparation often yields admixture of

(a) secondary phases with different composition
e.g. ZnS, CuS, SnS_2, ...

(b) secondary phases with different crystal structure that features different cation ordering
e.g. Stannite (space group $I\bar{4}2m$), ...

Kesterite structure

space group $I\bar{4}$



secondary phases affect electronic properties → have to be avoided

Cu_2ZnSnS_4

XANES

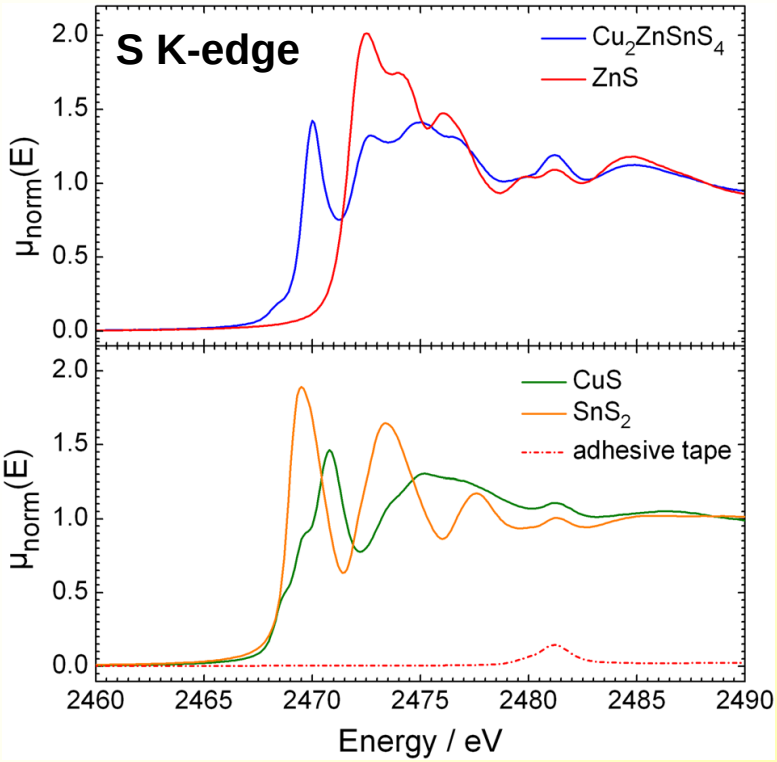
admixture of ZnS to Cu_2ZnSnS_4 very difficult to detect with diffraction

→ different method needed

S K-edge XANES spectra

→ distinctly different for Cu_2ZnSnS_4 and ZnS, CuS, SnS_2

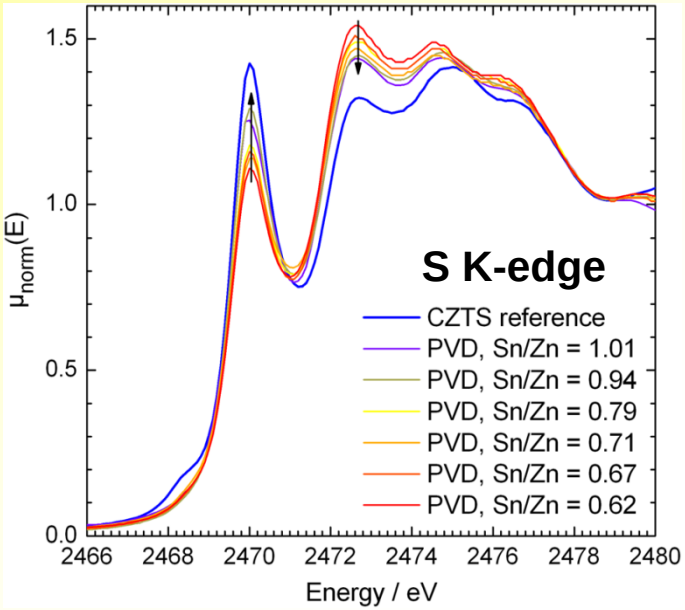
quantitative determination of secondary phases, e.g. ZnS, by linear combination fitting

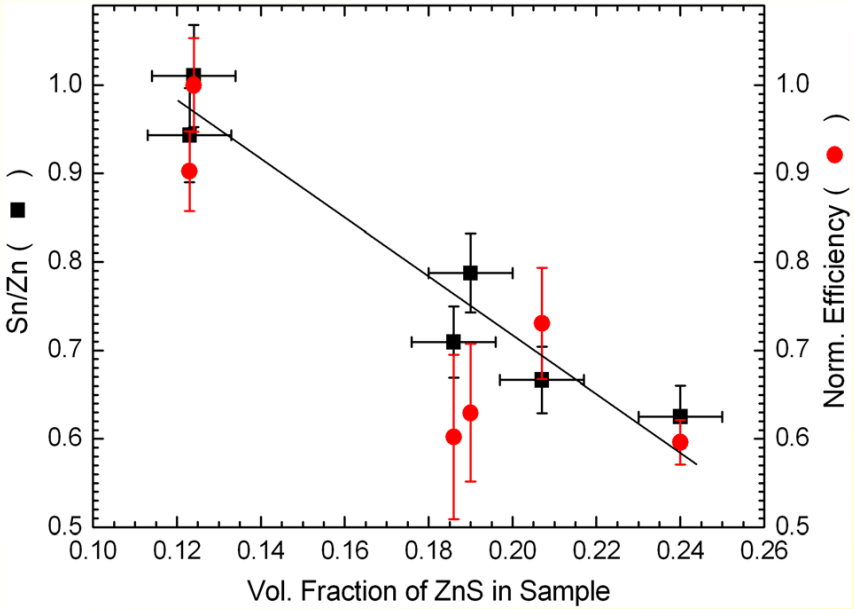


Just et al., APL 99, 2011

Cu_2ZnSnS_4

Amount of ZnS secondary phase





Just et al., APL 99, 2011

→ **amount of ZnS increases for decreasing Sn/Zn ratio**

→ **efficiency decreases for increasing amount of ZnS**

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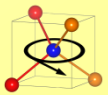


Cu_2ZnSnS_4

Cation disorder

nanoparticle synthesis *Zillner et al., APL 102, 2013*

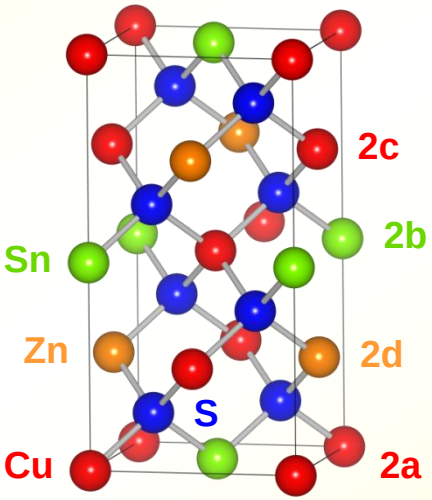
$Cu_2SnS_3 + ZnS \rightarrow Cu_2ZnSnS_4$

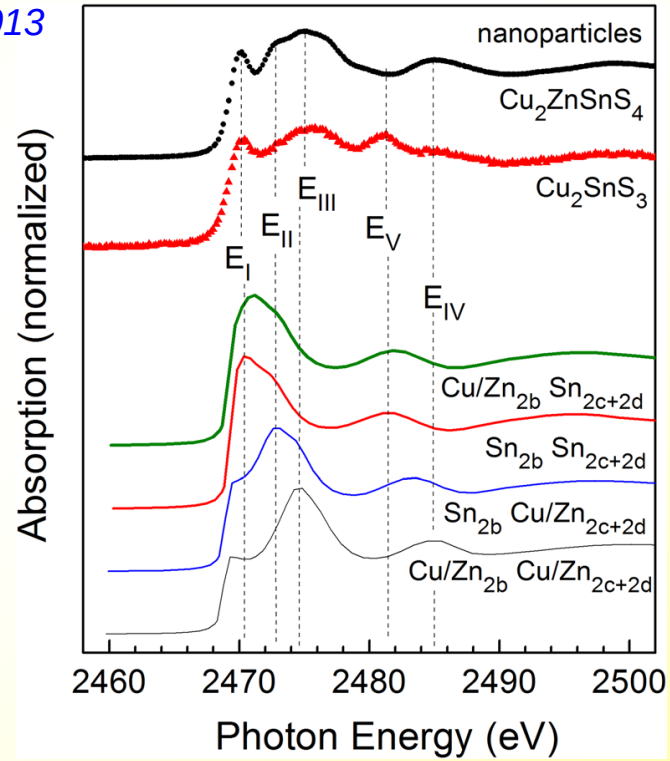
→ cation distribution ?

calculation of S K-edge XANES for different cation distributions

→ cannot distinguish Cu and Zn

→ but is sensitive to Sn-Cu/Zn antisites and Sn vacancies





→ **cation distribution depending on synthesis and/or treatment**

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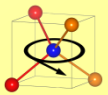
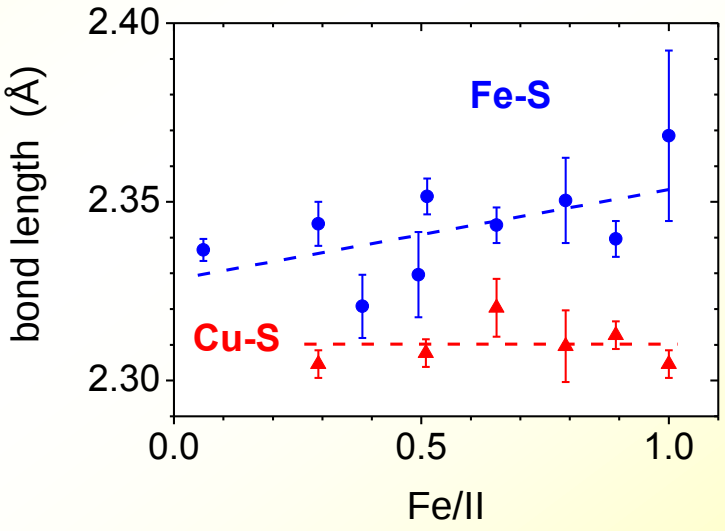


$Cu_2(Zn,Fe)SnS_4$

Element-specific bond length

kesterite	stannite
Cu_2ZnSnS_4	Cu_2FeSnS_4

$Cu_2(Zn,Fe)SnS_4$



Cu-S and Fe-S bond lengths

→ different from each other

→ different slope with Fe/II

→ **different behaviour than chalcopyrites** *Zalewski et al., JAC 492, 2010*

→ **detailed study of mixed kesterites**
influence of atomic-scale structure on band gap

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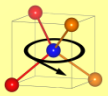
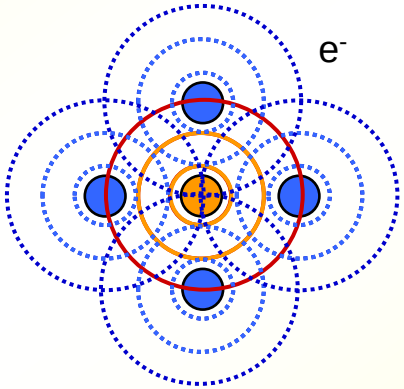


Conclusions

Basics of XAS

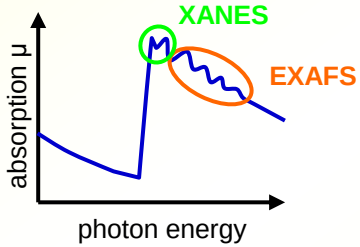


X-ray absorption spectroscopy (XAS)

→ structural analysis on sub-nm scale

→ crystalline and disordered solids, liquids, ...

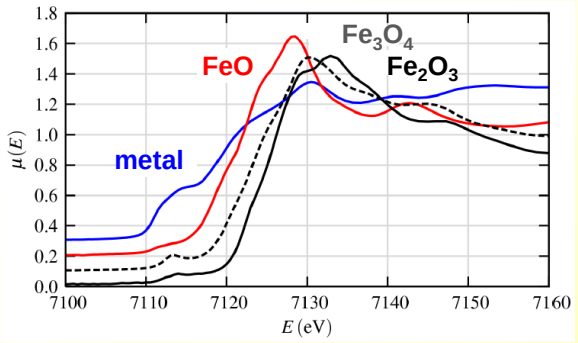
→ element-specific



XANES

→ density of states,
chemical bonding

→ crystal or cluster symmetry



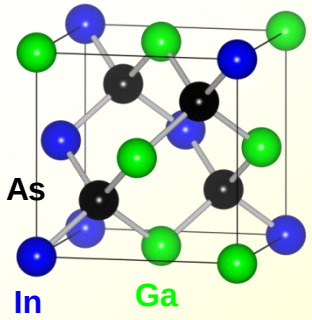
EXAFS

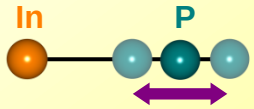
→ coordination number

→ bond lengths

→ static disorder

→ atomic vibrations





Experimental aspects

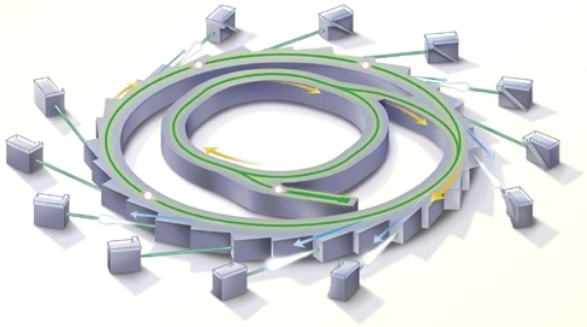
XAS measurements

→ synchrotron radiation

→ transmission, fluorescence or electron yield mode

→ specialized techniques

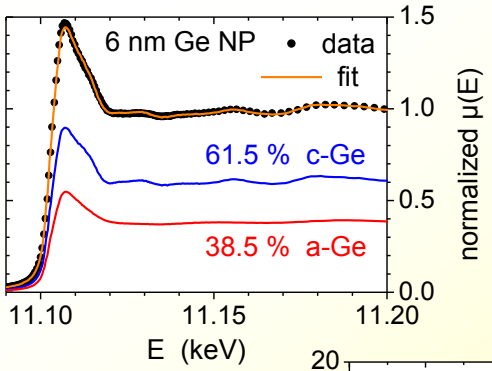
→ powders, thin films, ...

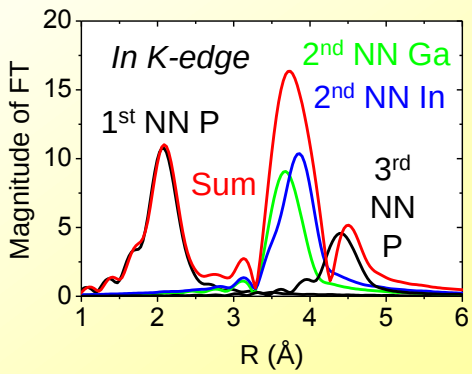


analysis

XANES → data normalization
→ linear combination fitting
→ theoretical calculations

EXAFS → data processing
→ Ratio Method
→ path fitting



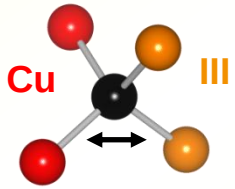


Chalcopyrites

element-specific bond lengths

→ very different and nearly constant

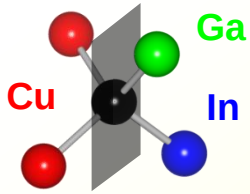
→ local arrangements deviate from crystallographic structure



anion displacement

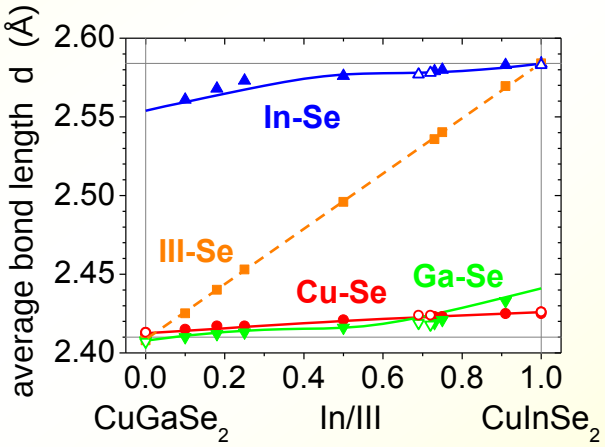
→ depends on cation configuration

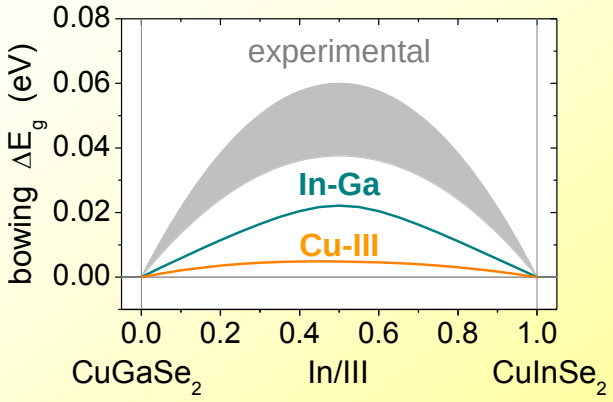
→ two different displacement mechanisms



band gap bowing

→ both displacement mechanisms contribute to band gap bowing but in different ways



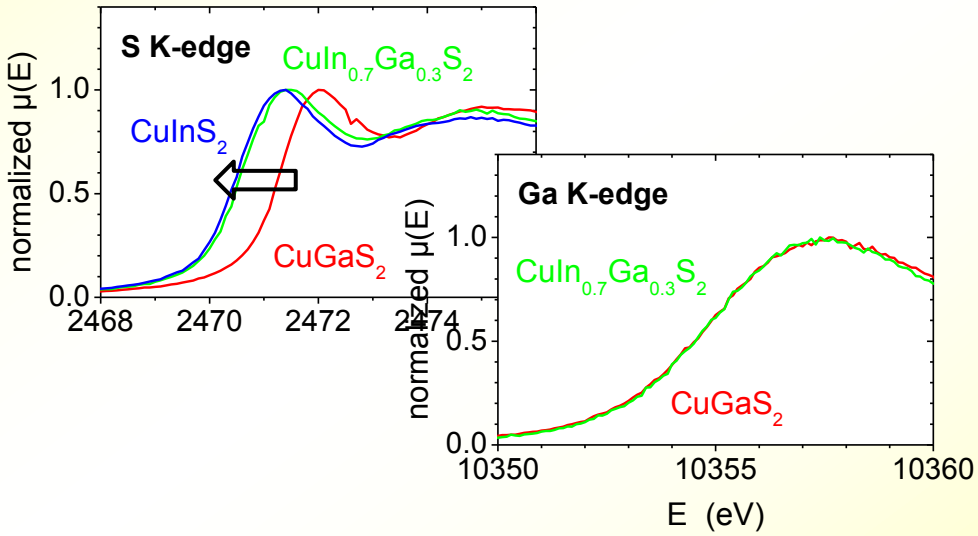


Chalcopyrites

electronic states

→ local states determined by local environment

→ global properties like band gap arise from spatial average

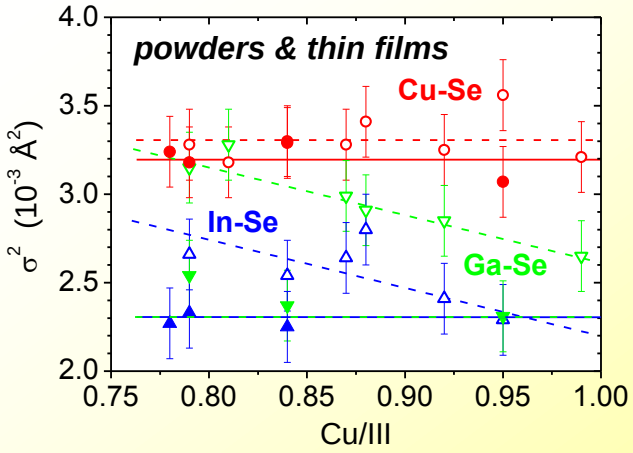


bond length variation

→ depends on cation-anion pair

→ different for powders and thin films

→ probably depends on Cu/III history during preparation

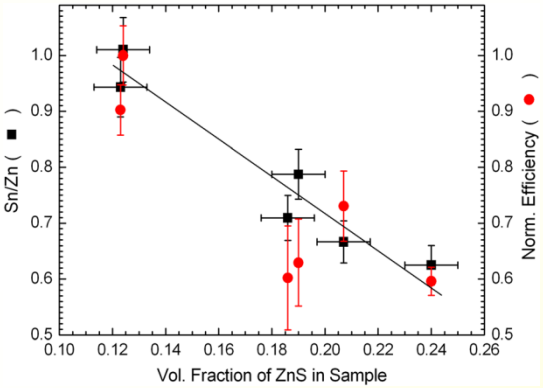


Kesterites

<u>secondary phases</u>

→ S K-edge XANES very different for Cu_2ZnSnS_4 and ZnS, CuS, SnS_2, ...

→ quantitative determination of secondary phase, e.g. ZnS

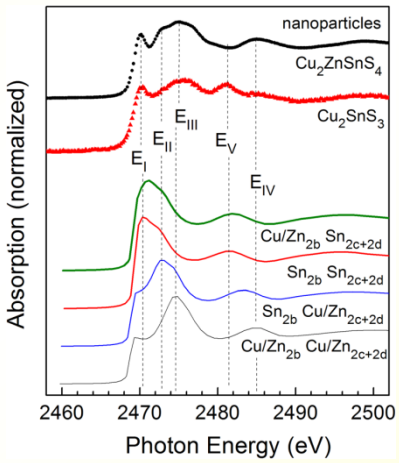


Just et al., APL 99, 2011

<u>cation disorder</u>

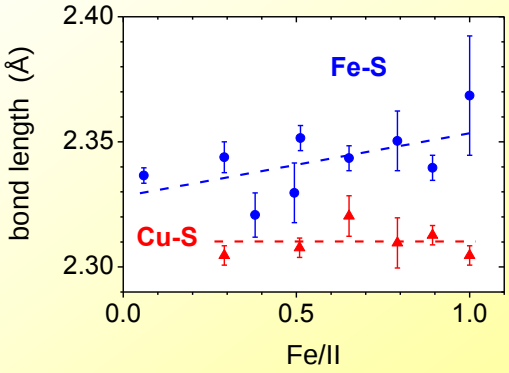
→ S K-edge XANES depends on cation distribution

→ Sn-Cu/Zn antisites and Sn vacancies



Zillner et al., APL 102, 2013

Zalewski et al., JAC 492, 2010



<u>element-specific bond lengths</u>

→ similarities but also differences to chalcopyrite materials for $Cu_2(Zn,Fe)SnS_4$

Thank you !