X-ray CoreLab Facilities at HZB

HyPerCell/HySPRINT Workshop, 12. 10. 2017

X-Ray CoreLab at HZB

- Methods and instruments
- Registration and booking

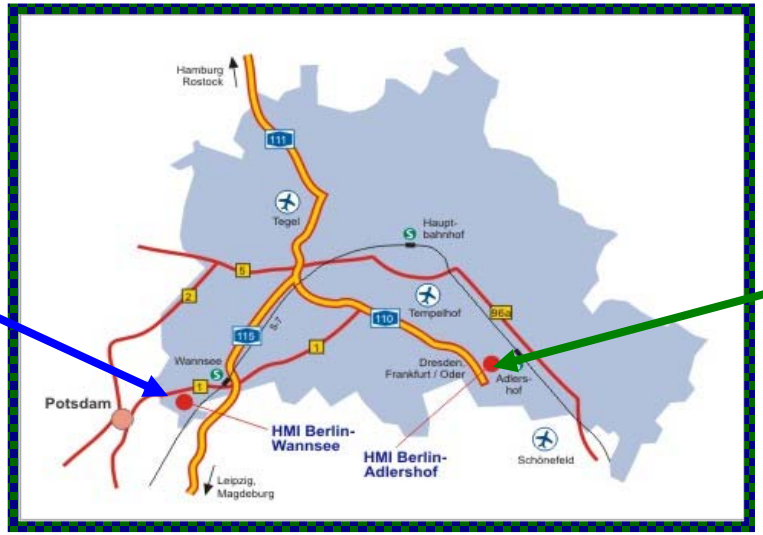
Susan Schorr
Chair of the X-Ray CoreLab Steering Committee

Mission statement

The **mission** of the X-Ray CoreLab is
to use and to anchor the methods of lab-scale X-ray diffraction
on an institutional and cross-cutting level in the HZB's strategy.

The X-ray CoreLab is supervised by a **Steering Committee**
Susan Schorr, chair (EM-ASD)
Christoph Genzel (EM-AME)
Roel van de Krol (EE-IF)
Bella Lake (EM-AQM)

LMC
Michael Tovar
(9 instruments)



WCRC
Christoph Genzel
(3 instruments)

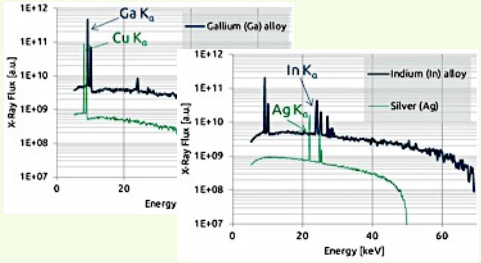
The fundamental pillars of the X-ray corelab

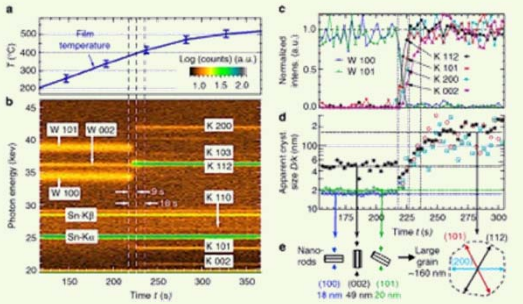
Cutting edge research

MetalJet X-ray tube

bichrome beam

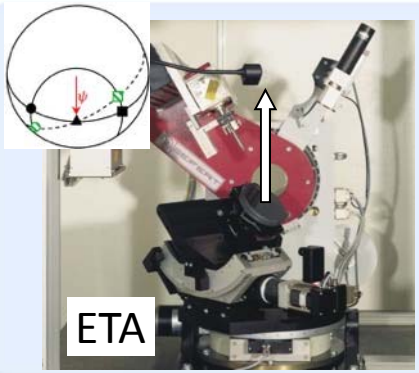
white beam

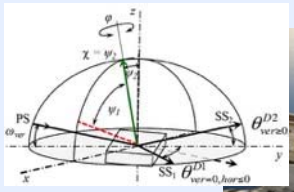


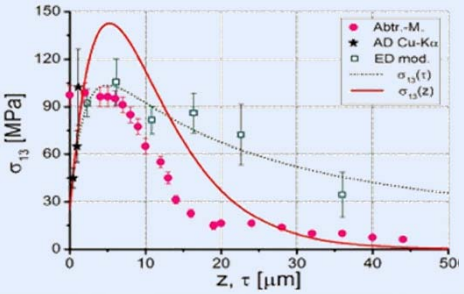


Mainz et al., Nature Comm. 4133 (2014)

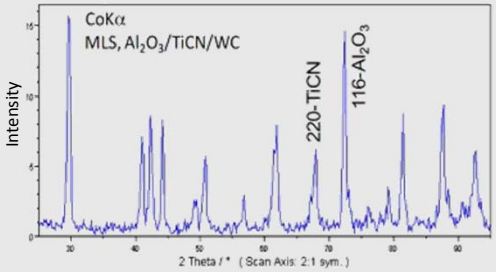
Prototyping & method development

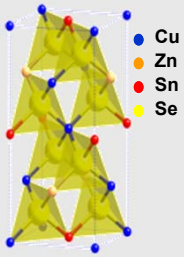


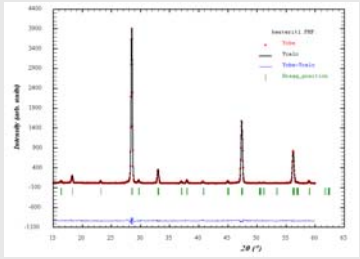


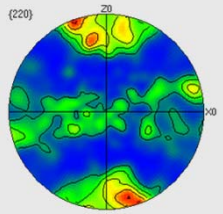


‚Bred & butter business'

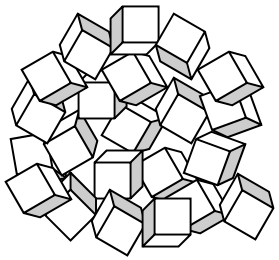






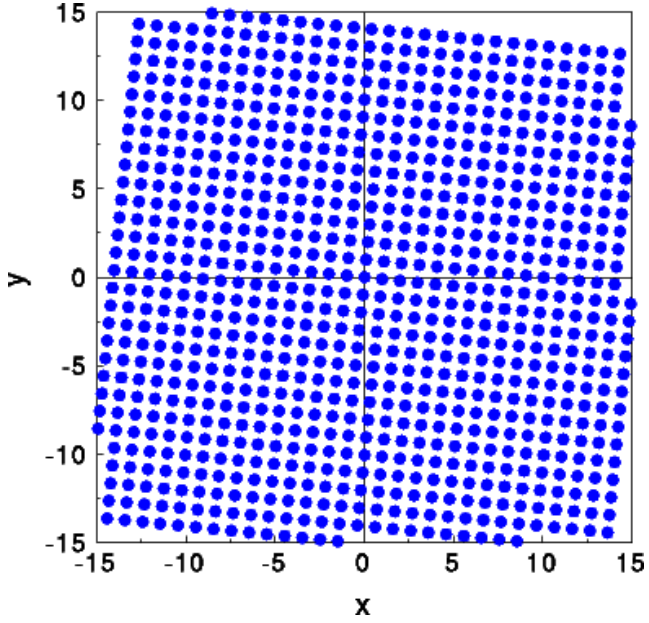


Investigation of polycrystalline samples

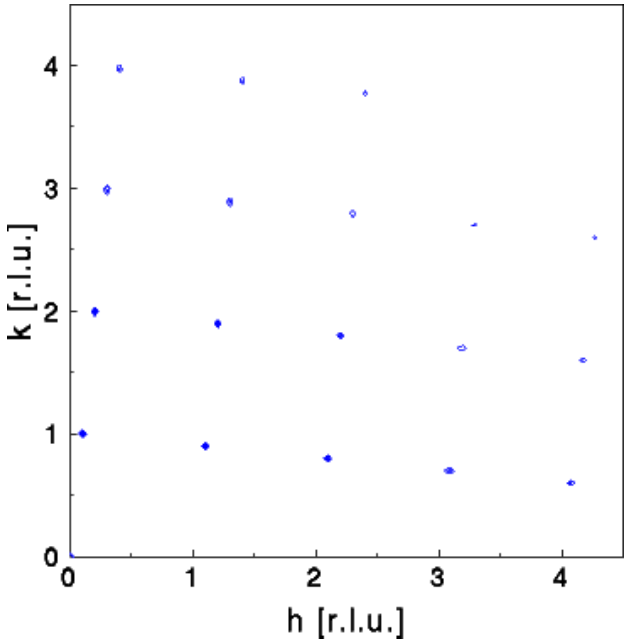


What is a polycrystalline material?

real space



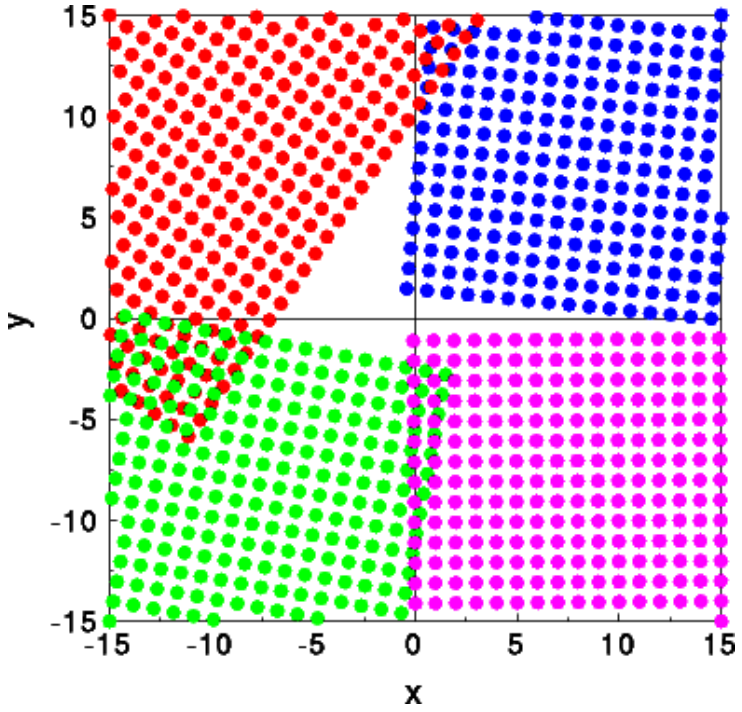
reciprocal space



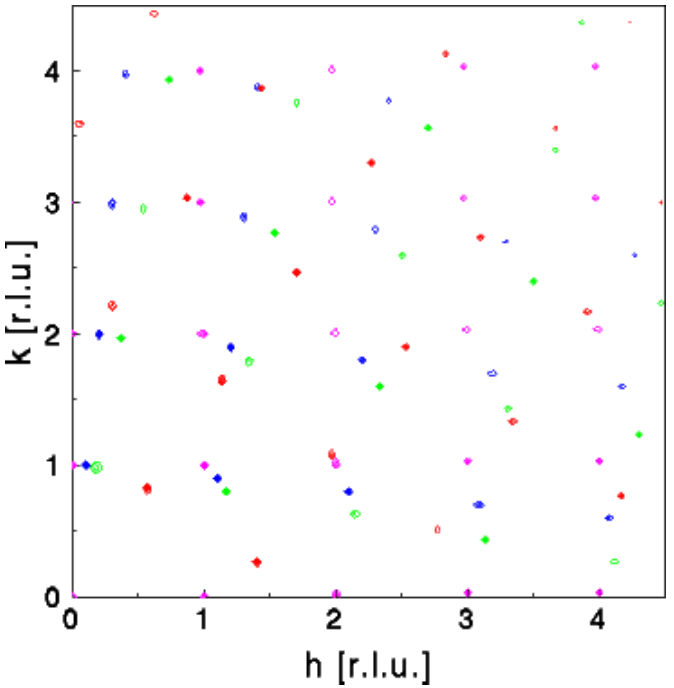
3D periodic arrangement
of atoms/ions/molecules

single crystal

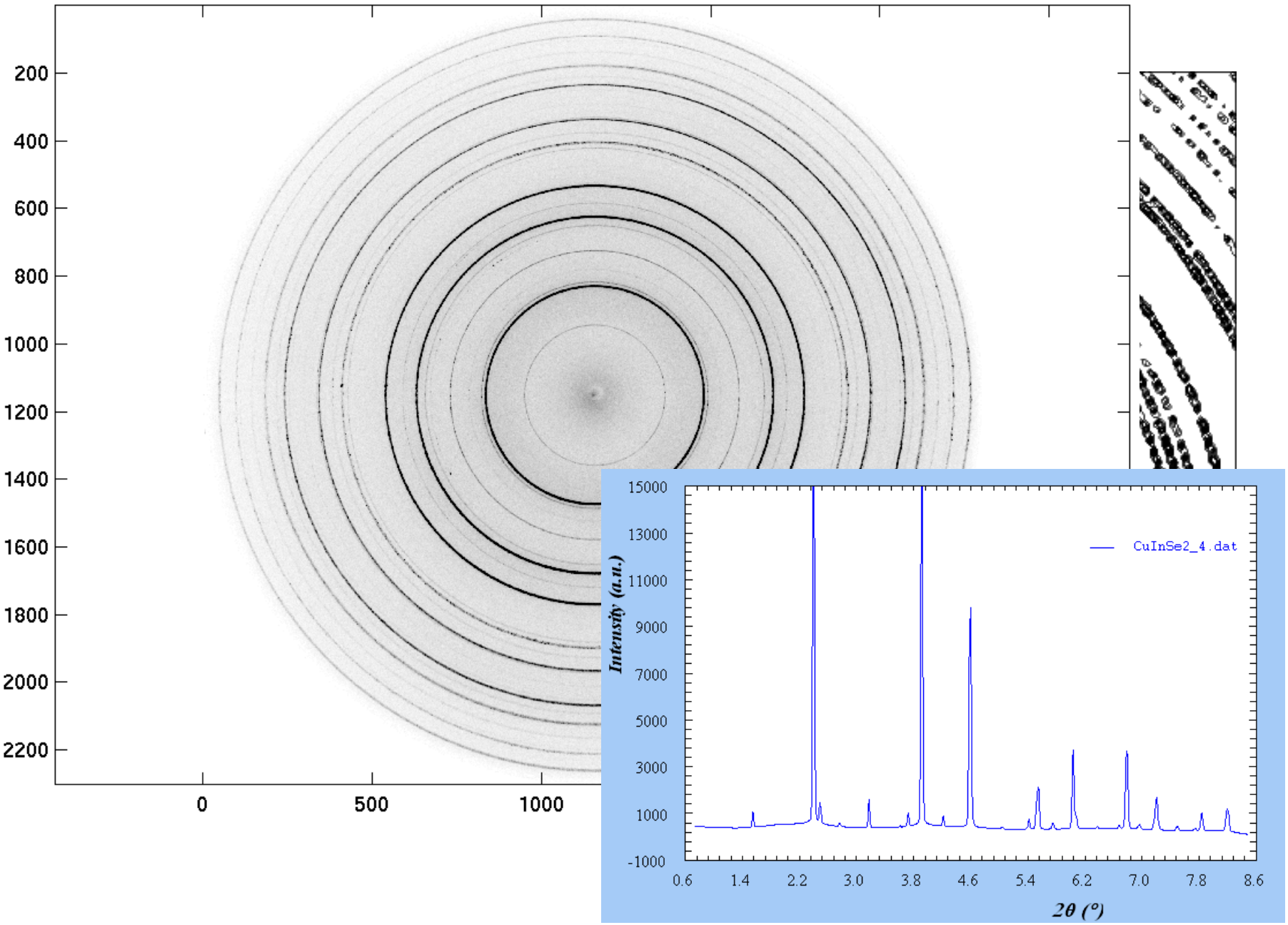
real space



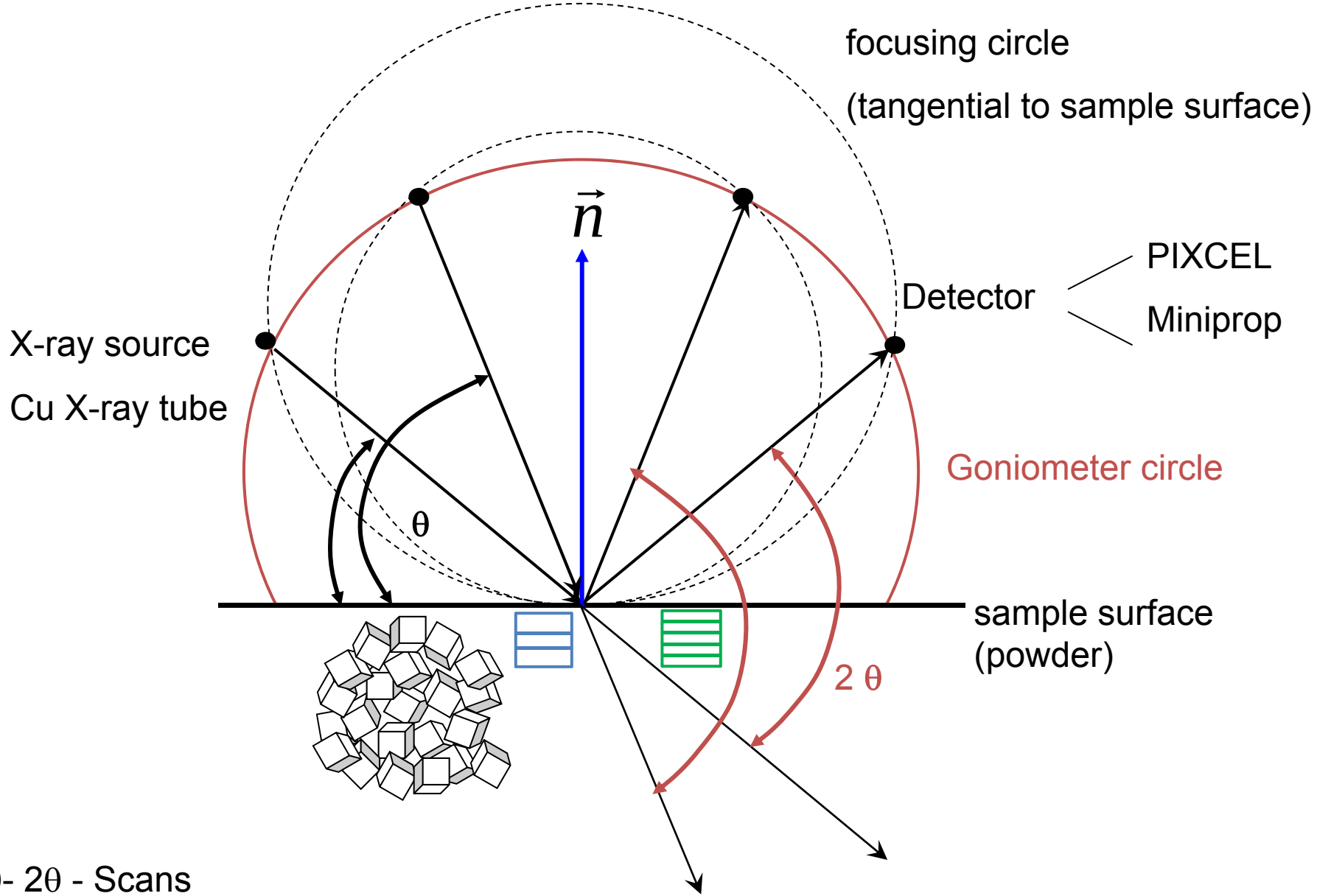
reciprocal space



four single crystals

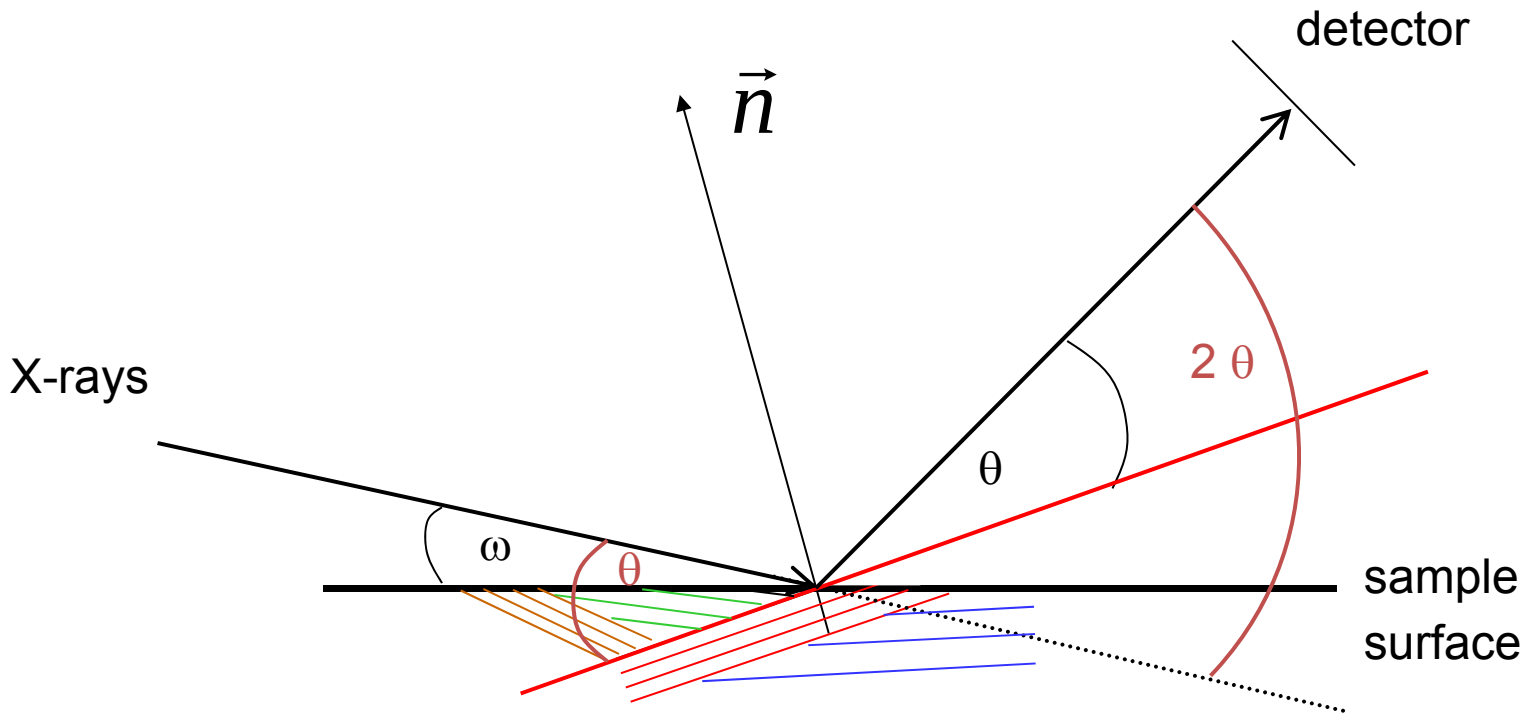

200
400
600
800
1000
1200
1400
1600
1800
2000
2200
0
500
1000
15000
13000
11000
9000
7000
5000
3000
1000
-1000
Intensity (a.u.)
CuInSe2_4.dat
0.6
1.4
2.2
3.0
3.8
4.6
5.4
6.2
7.0
7.8
8.6
2θ (°)

Powder Diffraction (Bragg – Brentano – Geometry)



θ- 2θ - Scans

grazing incidence X-ray diffraction - GIXRD



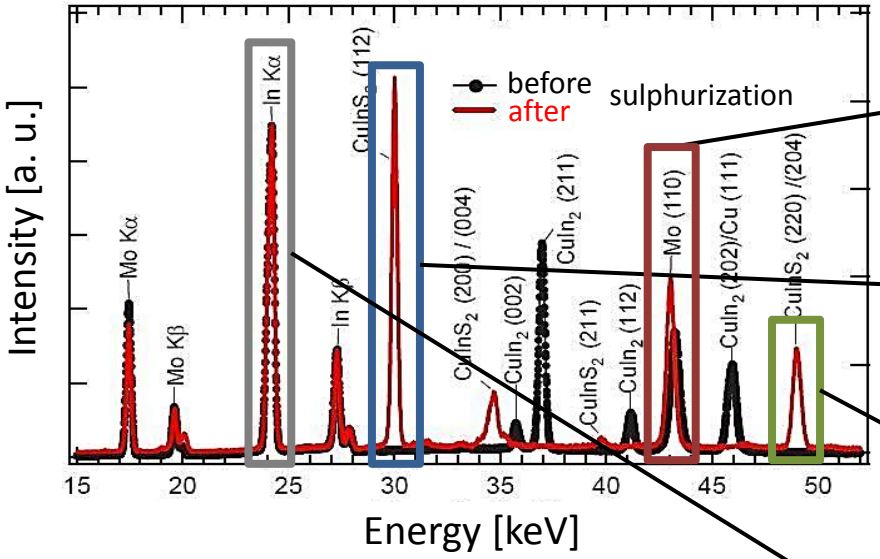
sample: polycrystalline thin film

- parallel beam
- fixed incidence angle ω
- detector - scan

Information content of X-ray diffractograms

Features of diffraction methods:

- ❑ non-destructive
- ❑ phase selective
- ❑ information depth nm ... cm



Line position and line shift:
- ❑ crystal structure
- ❑ residual stress

Line width and line shape
- ❑ micro strain, defects

Line intensity:
- ❑ crystallographic texture
- ❑ reaction kinetics

Fluorescence lines:
- ❑ element distribution

High energies >20 keV for:

- ❑ ... High information depth
- ❑ ... XRF close to K-edges of many elements

Instrumentation @ LMC

Bruker D8 Advance for analysis of thin films (l.) and powders (r.)

Instrumentation @ LMC

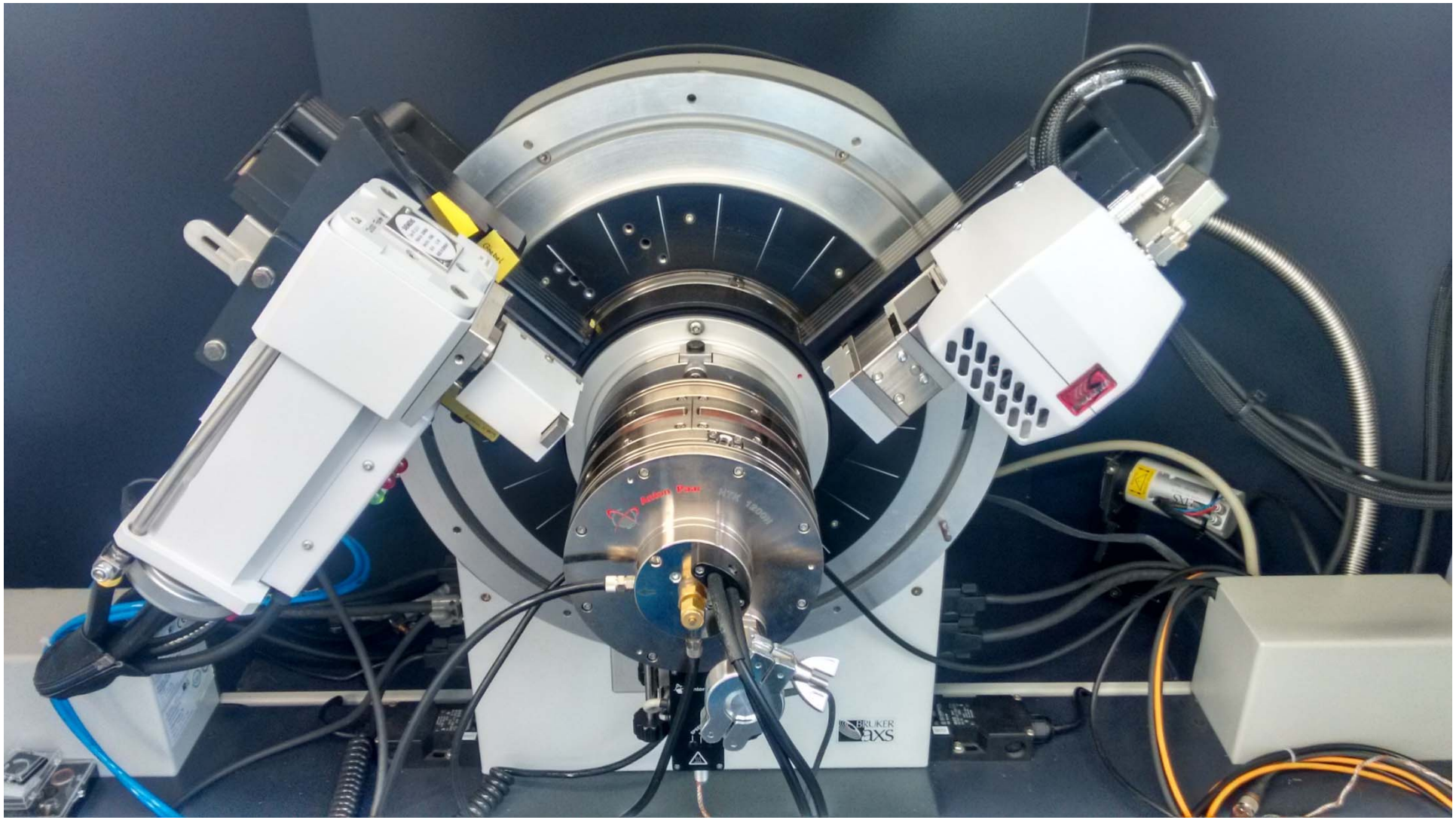
powder diffraction

- fast scans with LYNX Eye 1D detctor (~5-10 min)
- sample changer for high throughput
- *in situ* high temperature sample environment
- *Bruker EVA* and *TOPAS* for phase analysis
- ICDD-PDF-2 for phase analysis,
  upgrade to PDF-4 in progress
- web access to FIZ-ICSD

What can be done?

- qualitative phase analysis (search/match with database)
- quantitative phase analysis (Rietveld refinement with e. g. TOPAS)
- single peak fits: lattice parameter (rectangular crystal system)
  peak witdh (FWHM)
- structure refinement
  LeBail refinement (lattice parameter)
  Rietveld refinement (all structural parameters)

Anton Paar HTK 1200N High-Temperature Furnace-Chamber



Anton Paar HTK 1200N High-Temperature Furnace-Chamber

Specifications:

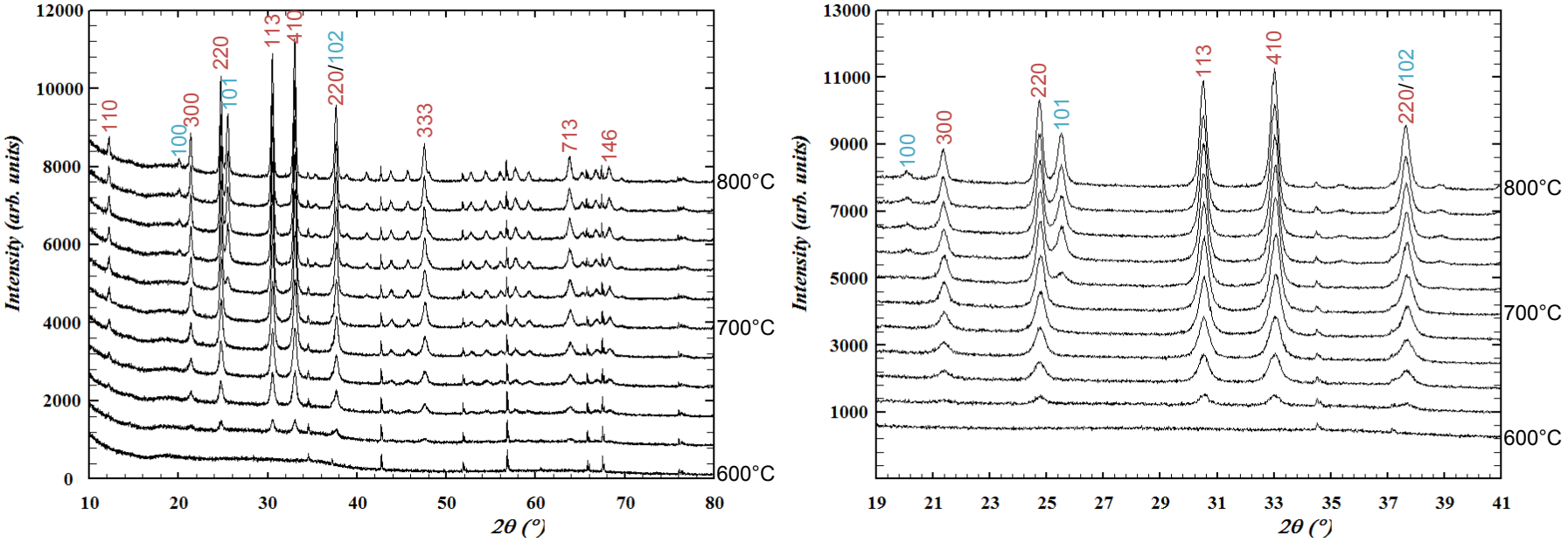
- RT ≤ T ≤ 1200°C, dT/dt ≈ 1K s^{-1}
- oscillating sample holder for enhanced grain statistics
- motorized z-alignment stage to compensate for sample thicknesses and thermal expansion
- p_{min} = 10^{-4} mbar, air and inert gas atmosphere*
- sample carriers for powders and thin films ($Ø_{max}$ = 20 mm)
- X-ray window: graphite/Kapton (10 mm width)

* vacuum (scroll pump, ≈10^{-4} bar) and Inert gas atmosphere (e.g. N_2 or user supplied gas mixtures) available

in situ temperature-dependent diffraction

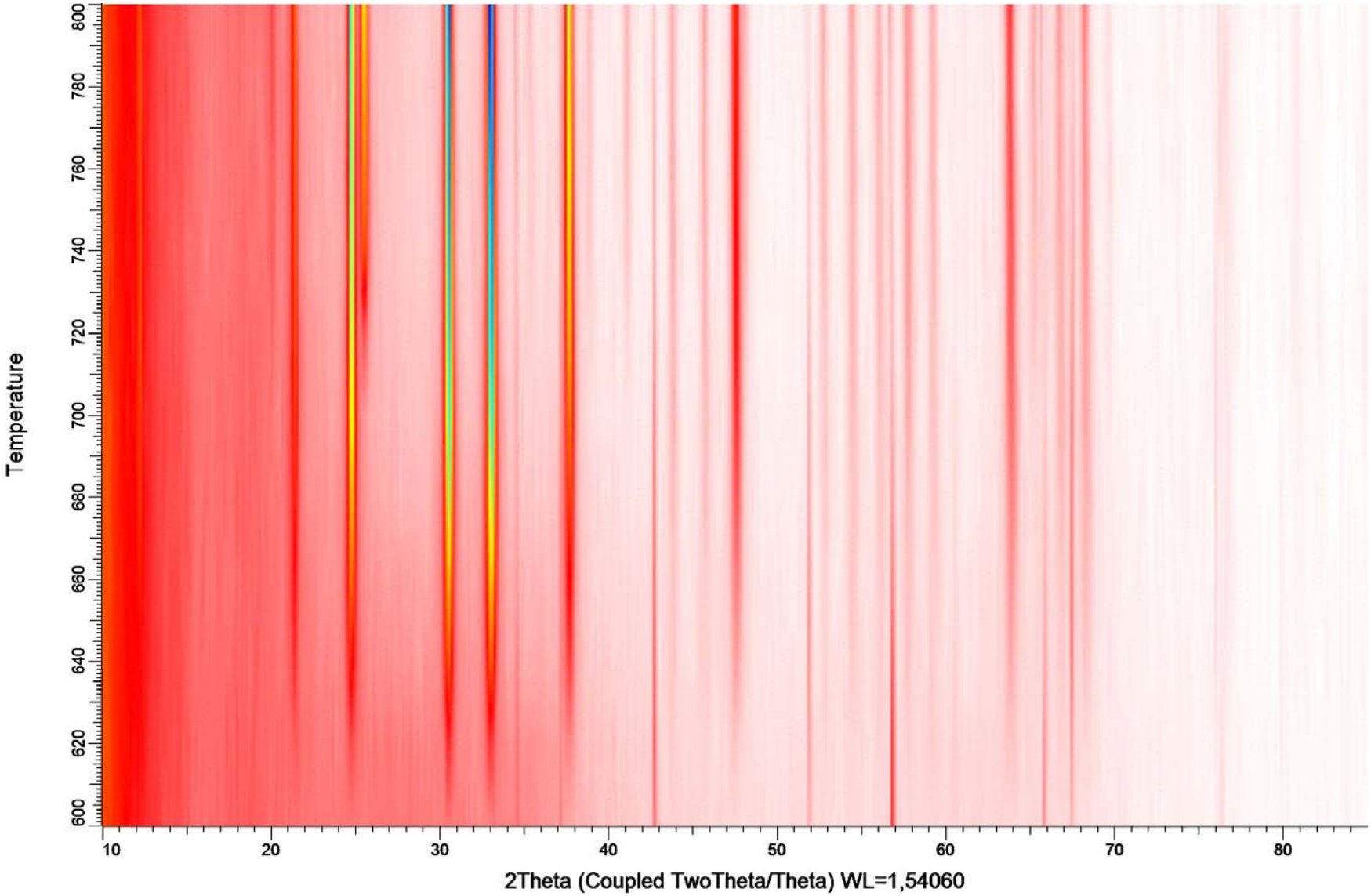
monitoring of crystallization of $ZnGe_2O_4$

- *in situ* XRD measurements performed on Bruker D8 epuipped with Anton Paar HTK1200N
- 2θ range = 10° – 80°
- temperature range = 600 – 800°C; 20 K steps; dT/dt ≈ 1 K s^{-1}; 20 min delay before measurements
- air atmosphere
- phases: $ZnGe_2O_4$, GeO_2 (α-quartz-type)



in situ temperature-dependent diffraction

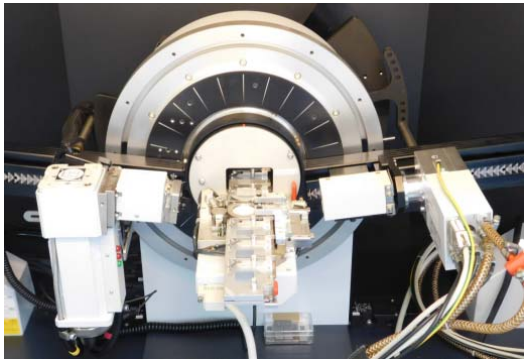
monitoring of crystallization of $ZnGe_2O_4$



Instrumentation @ LMC

grazing incidence diffraction (GIXRD)

- low background energy dispersive SOL-X detector
- sample changer for high throughput
- *Bruker EVA* for phase analysis
- sample hight cannot be adjusted (necessary for pattern refinement)



What can be done?

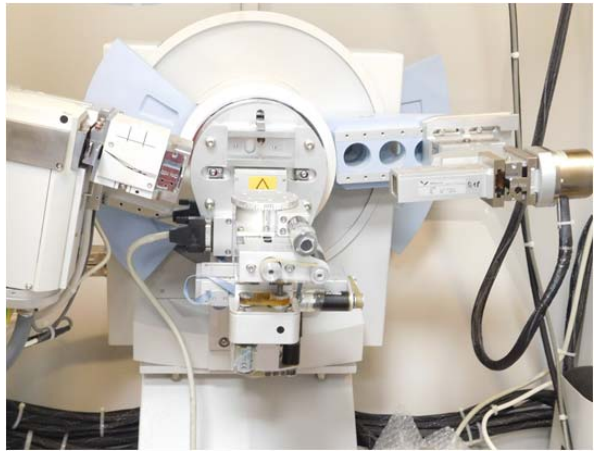
- qualitative phase analysis (search/match with database)
- single peak fits: lattice parameter (rectangular crystal system)
  peak witdh (FWHM)

Instrumentation @ LMC

PANalytical MRD (l.) and MPD (r.) for analysis of thin film and powders, for texture and epitaxy analysis and micro-diffraction

Instrumentation @ LMC

PANalytical MPD (multi purpose diffractometer)



- precise **GIXRD** measurements of thin films: parallel X-ray beam (X-ray mirror and Xe single counter), sample hight can be adjusted (z-scan)
- sample table for x-y scans allows scanning
- **reflectivity** option for film thickness and roughness
- fast **powder diffraction** with 1-D PIXcel detector

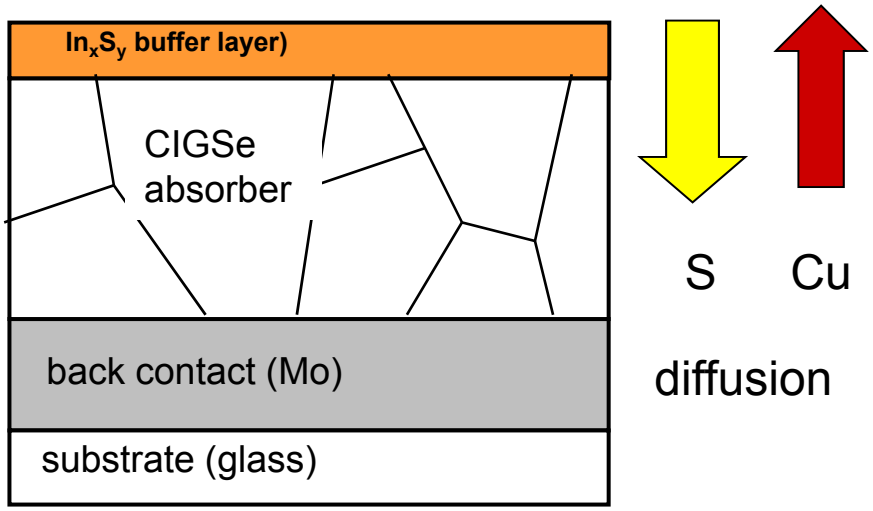
What can be done?

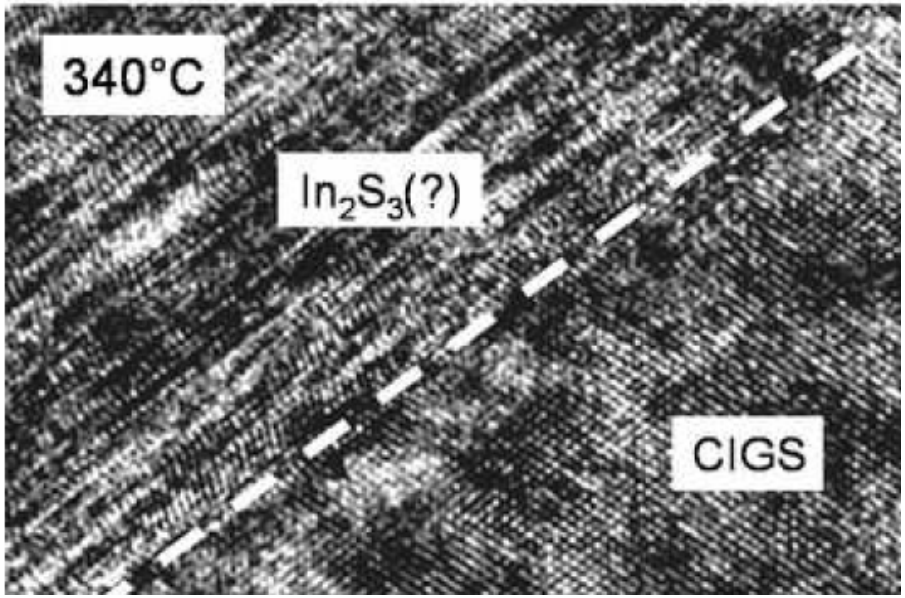
- qualitative phase analysis (search/match with database)
- quantitative phase analysis (Rietveld refinement with e. g. HIGHSCORE)
- single peak fits: lattice parameter (rectangular crystal system)
  peak witdh (FWHM)
- structure refinement
  LeBail refinement (lattice parameter)
  Rietveld refinement (all structural parameters)

With both XRD and GIXRD measurements!

Example: Depth-resolved phase analysis (qualitative)

sputtered In_xS_y layer
T_{sub}= 230°C, 340°C, no heating



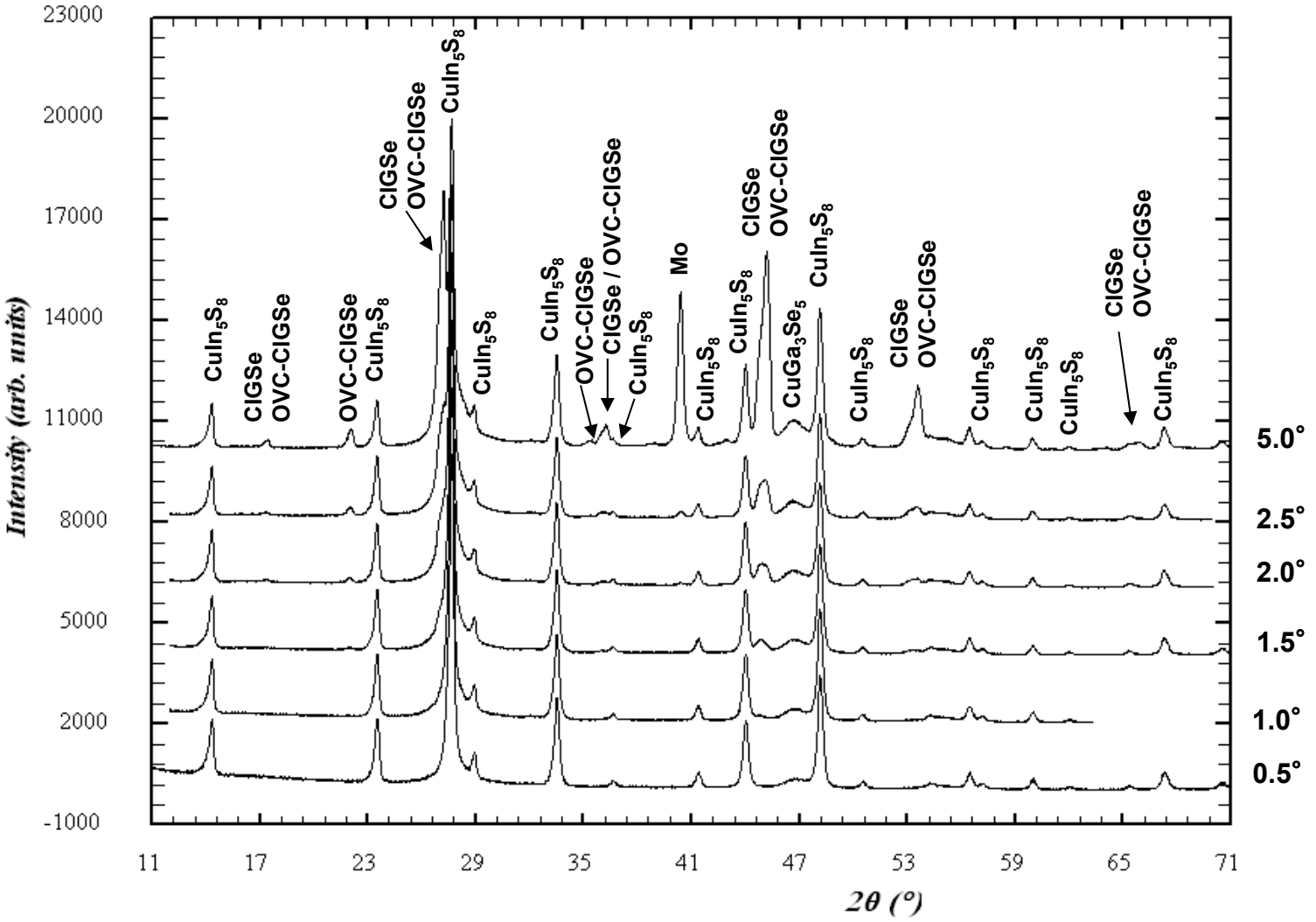


What happened with the sputtered In_xS_y layer?

D. Abou-Ras, G. Kostorz, D. Hariskos, R. Menner, M. Powalla, S. Schorr, A.N. Tiwari, Thin Solid Films 517 (2009) 2792.

In_xS_y / CIGSe (T_{sub} = 340° C)

diffusion of Cu and Ga from CIGSe into the buffer (In_xS_y) → formation of vacancy compounds



In_xS_y / CIGSe (T_{sub} = 340° C)

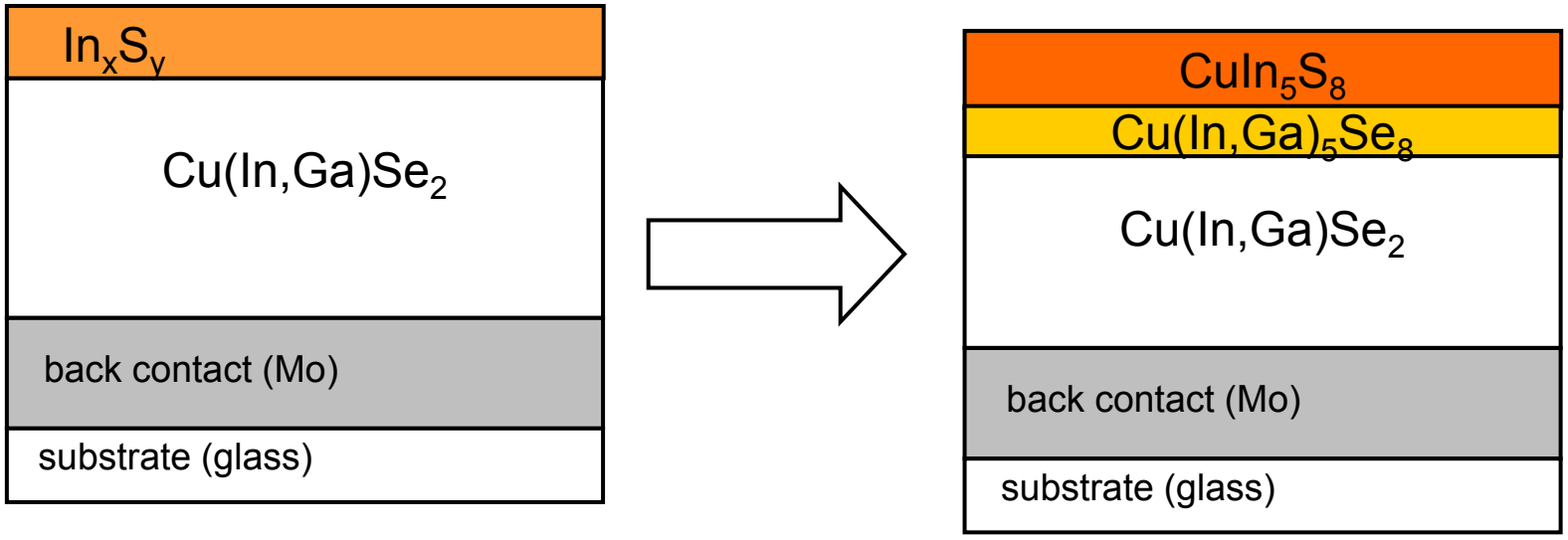
→ layer stacking:

$CuIn_5S_8$

$Cu(In,Ga)_5Se_8$

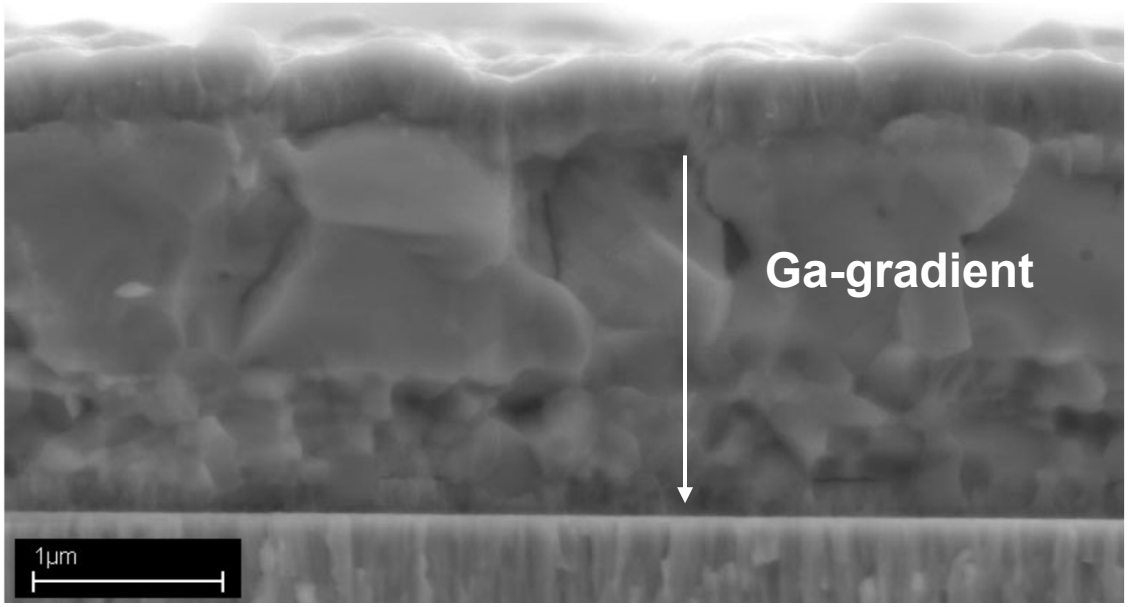
$Cu(In,Ga)Se_2$

additional:
$CuGa_3Se_5$
thin layer
or
small crystallites



Example: depth-resolved phase analysis (semi-quantitative)

Ga-gradient in $Cu(In,Ga)Se_2$ absorber layers



cross-sectional SEM image

ZnO window layer

CdS

CIGSe absorber

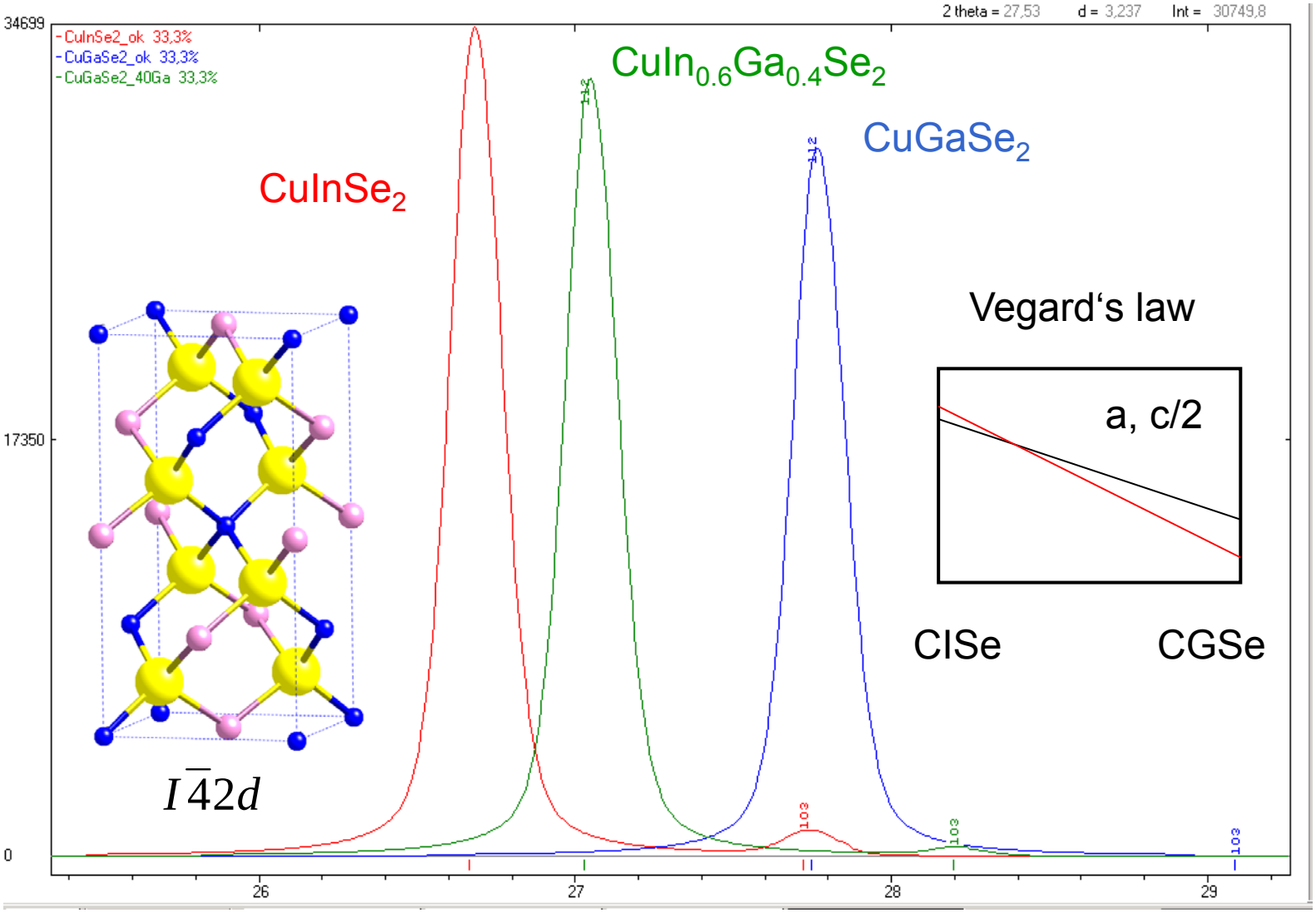
Mo back contact

glass substrate

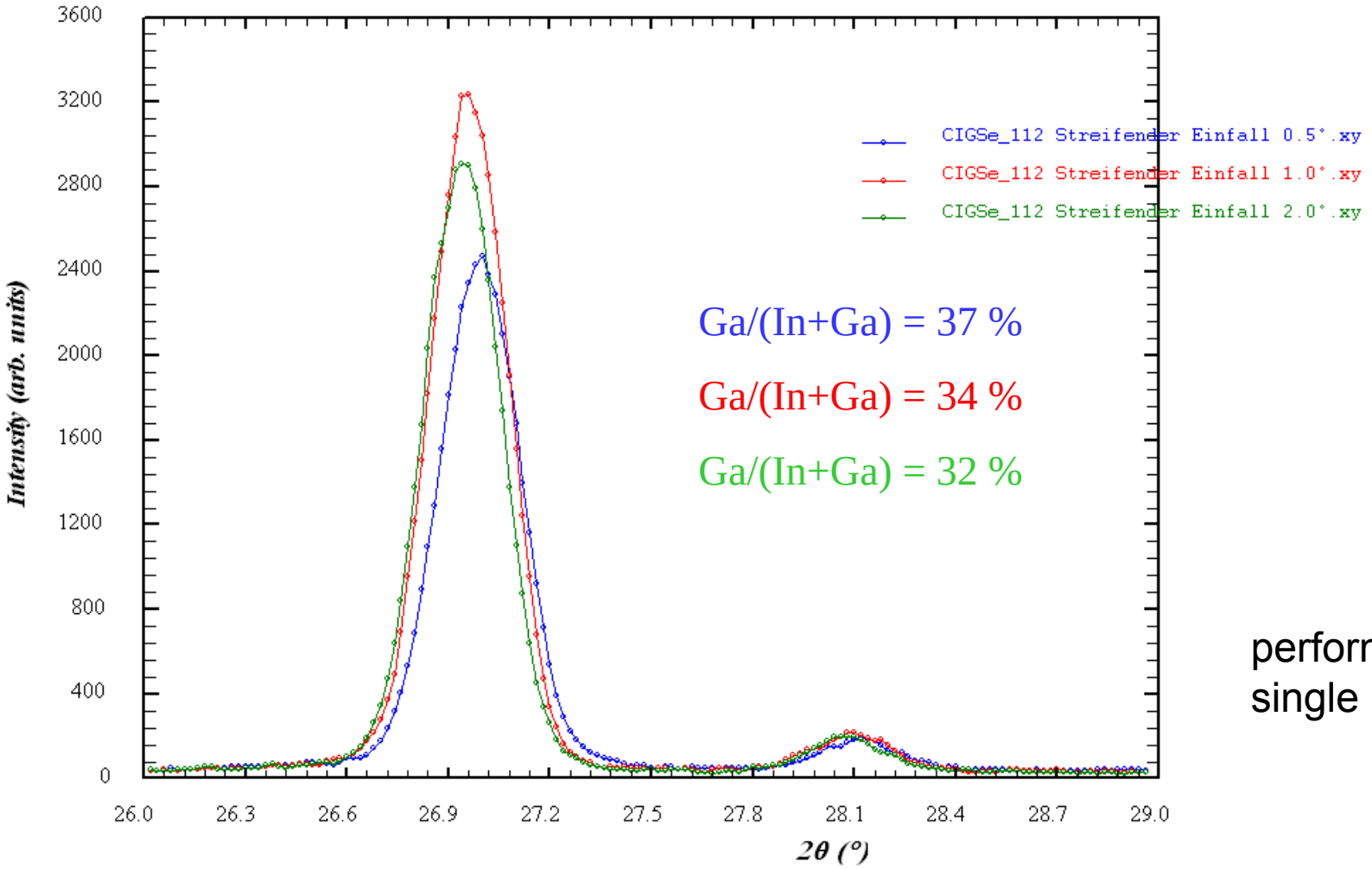
Ch. A. Kaufmann, R. Caballero, T. Unold, R. Hesse S. Schorr, M. Nichterwitz, H.-W. Schock, Sol. Energy Mat. & Sol. Cells (2008)

Simulated powder pattern: $Cu(In,Ga)Se_2$

112 Bragg peak

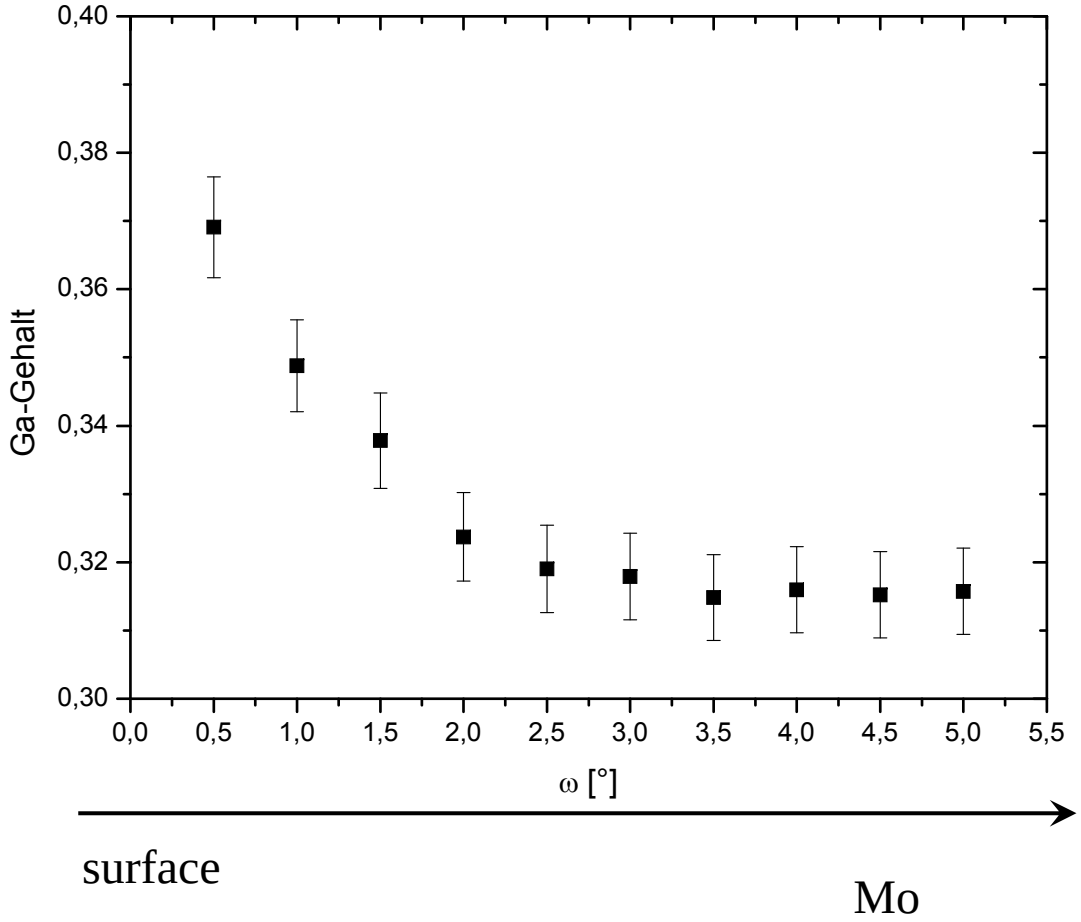


depth profiles of CIGSe thin films



perform
single peak fits

depth profiles of CIGSe thin films



Bragg equation:

$$\lambda = 2d_{hkl}\sin\theta$$

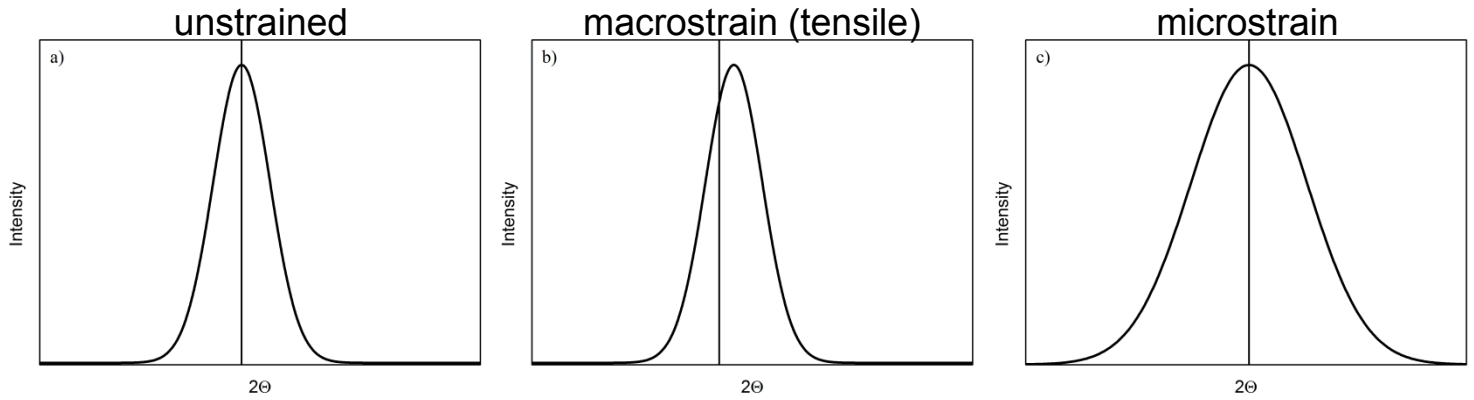
tetragonal crystal system:

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

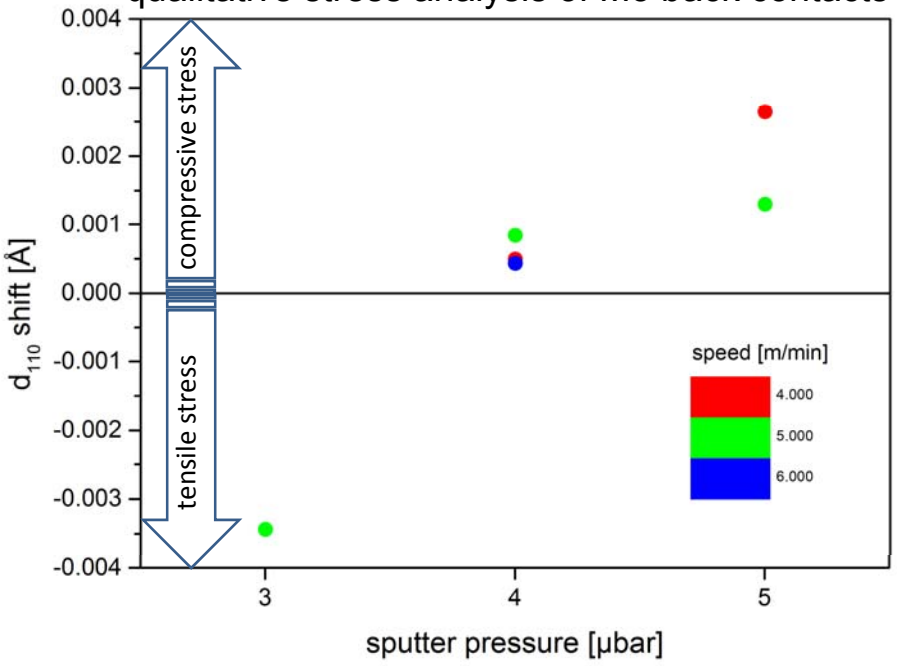
Vegard‘s law:

$$a_{AB} = a_A(1 - x_B) + a_B x_B$$

macrostrain and microstrain in thin films

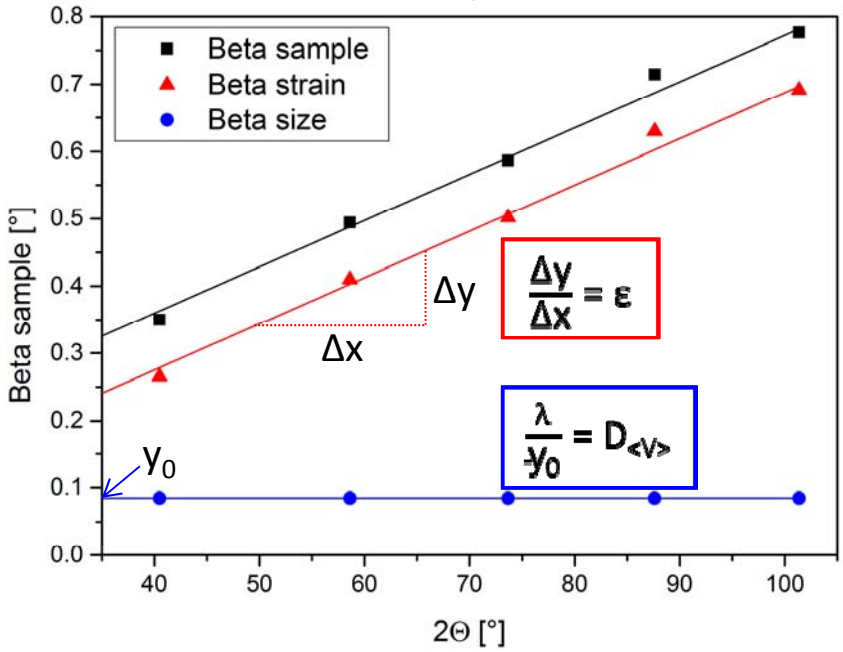


qualitative stress analysis of Mo back contacts



→ shift in peak position reveals stress regime

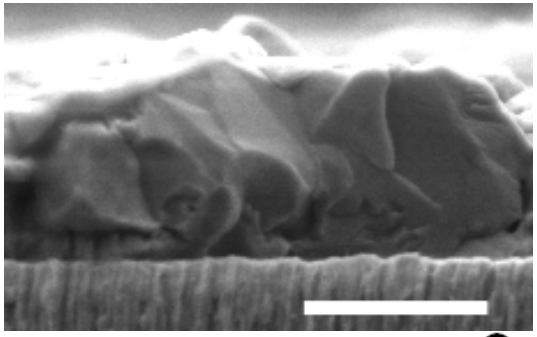
microstructure (WH) analysis of Mo back contacts



→ based on individual peak profile parameters
→ separation of size and strain broadening

Rietveld refinement of GIXRD data

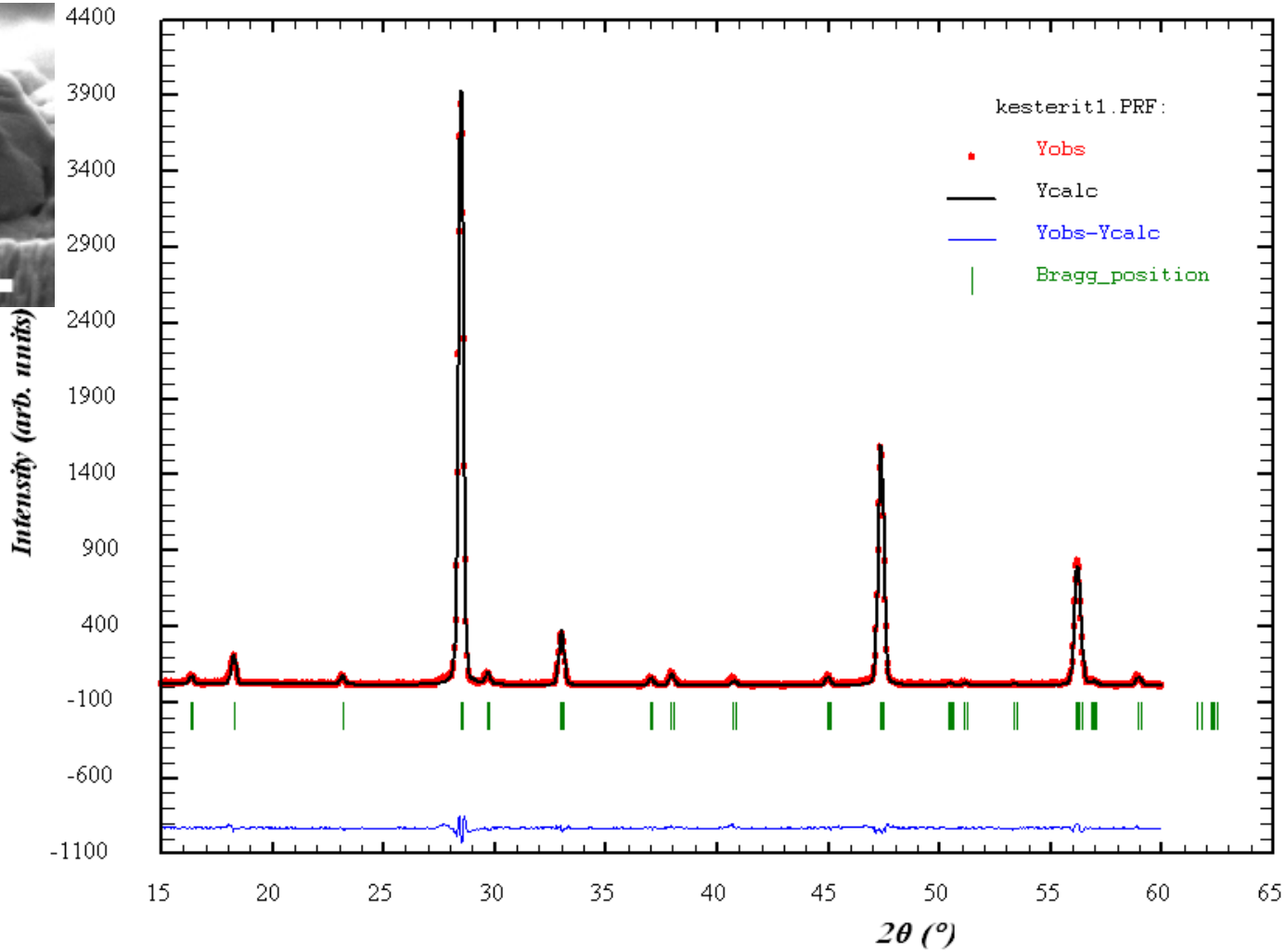
Cu_2ZnSnS_4 thin film grown by co-evaporation



single phase

no texture

determination of structural parameters

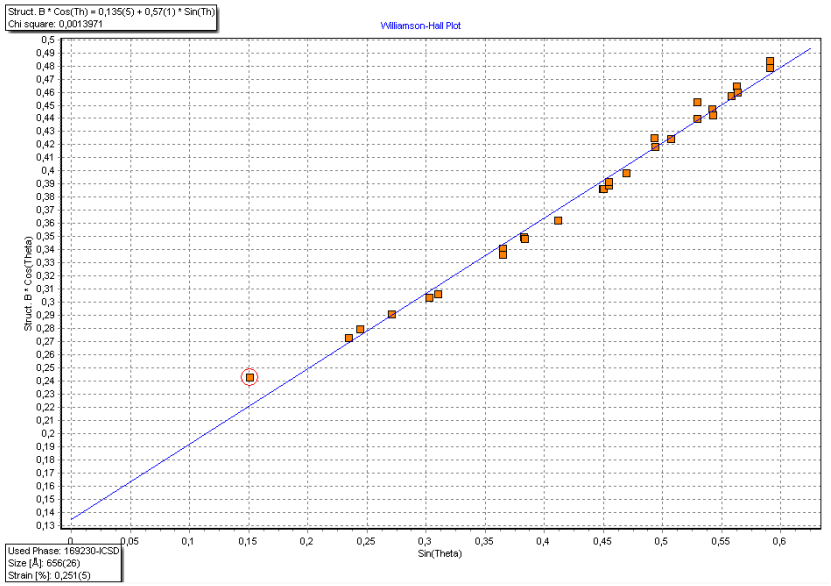


B. A. Schubert, B. Marsen, S. Cinque, T. Unold, R. Klenk, S. Schorr, H.-W. Schock, Progress in Photovolatics: Research and Application (2010)

microstructure analysis of thin films

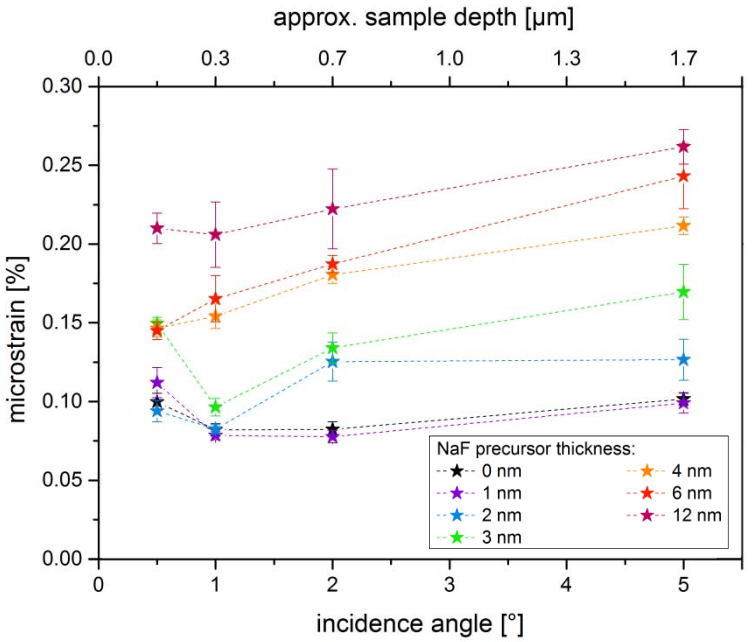
- microstructure analysis of CISe thin film absorber layers
- broadening of integral peak breadths β used to deduce microstrain and domain size
- depth-resolved characterization possible by varying incidence angles

Williamson-Hall analysis of CISe using pseudo-Voigt profile function to obtain β
(done with Highscore Plus, PANalytical)



→ linear equation used to obtain size and strain

microstructure analysis of CISe using Thompson-Cox-Hastings pseudo-Voigt profile function to obtain β
(done with Fullprof Suite software package)



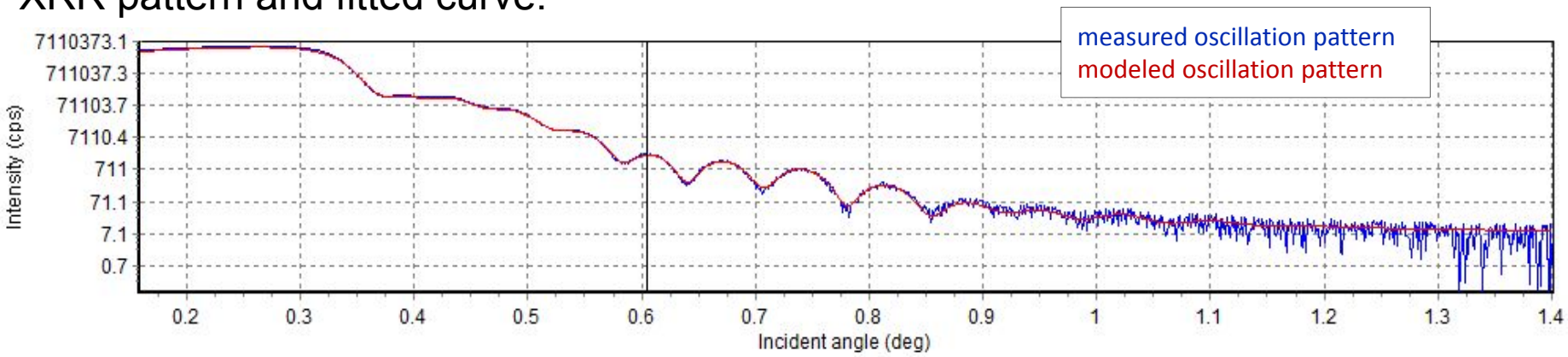
→ size and strain directly calculated from corresponding profile parameters

X-ray reflectivity (XRR)

estimation of thickness, density and roughness of thin films

- X-ray reflectometry is based on varying reflectivities of X-rays when traversing interfaces between dissimilar media (differing optical constants)
- resulting interference fringes allow modeling of thickness, density and roughness of thin layers
- higher contrasts in optical constants (for multi-layer systems) cause stronger oscillations
- layer thickness is inferred by the period of the oscillations

XRR pattern and fitted curve:



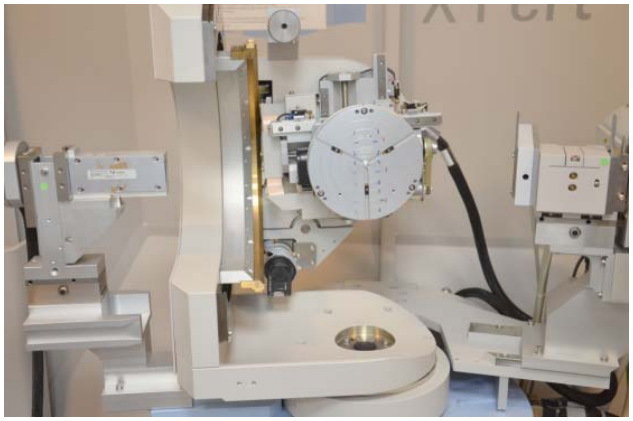
Results from modeling:

Layer	Layer Description	Density (g/cm3)	Thickness (nm)	Roughness (nm)
2, 0	DensityOnly, Fe3O4	5.18	12.845	2.173
1, 0	DensityOnly, CoO	6.45	44.143	1.862
Substrate	DensityOnly, SrTiO3	5.1	600000	0.993

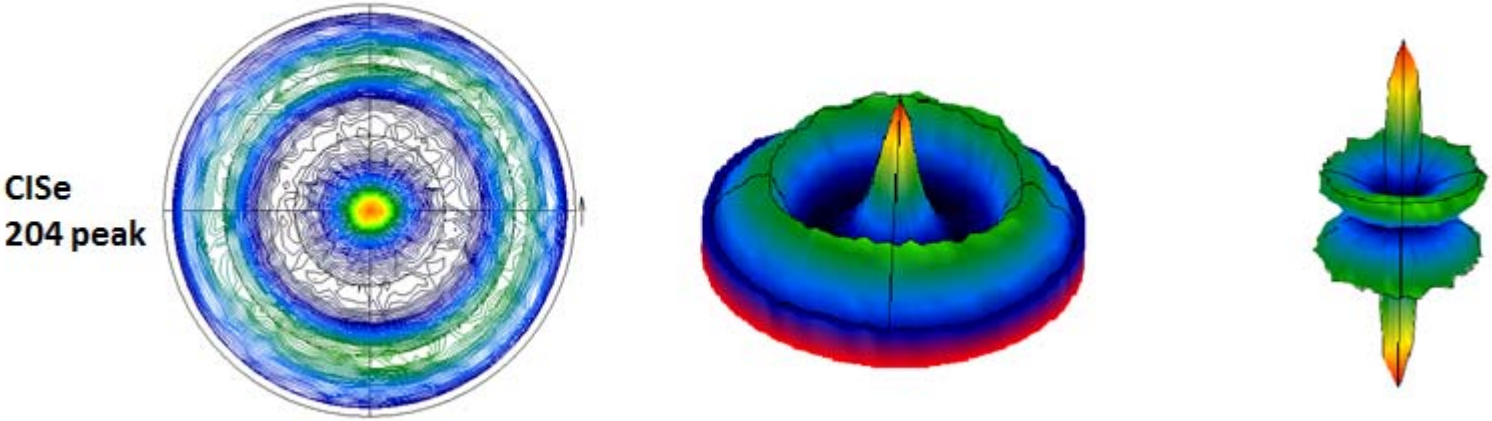
Instrumentation @ LMC

PANalytical MRD for texture analysis:

- X-ray lens for high intensive parallel beam
- Eulerian cradle for 3D sample orientation
- Xe single counter
- *X'Pert Texture* to create pole figures and orientation distribution functions (ODF)



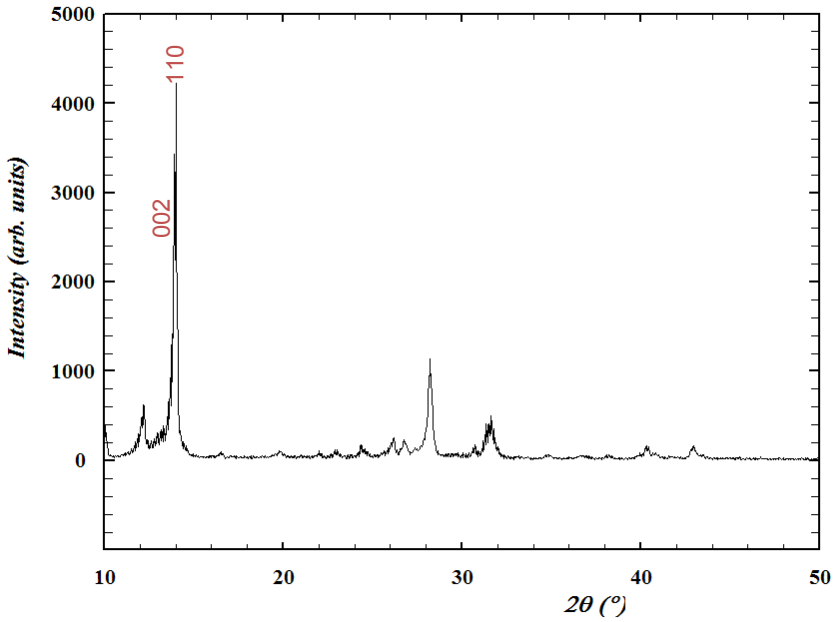
Pole figures recorded on $CuInSe_2$ (CISe) chalcopyrite-type thin film absorber layer

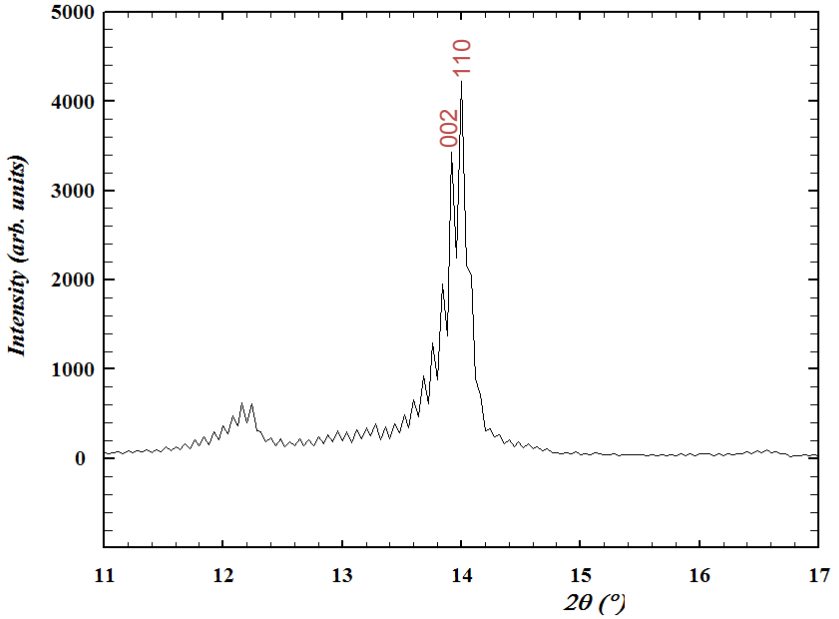


Orientation distribution functions (ODF) shown as contour plot and 3D plot for CISe Bragg peaks 112 and 204

texture of thin films

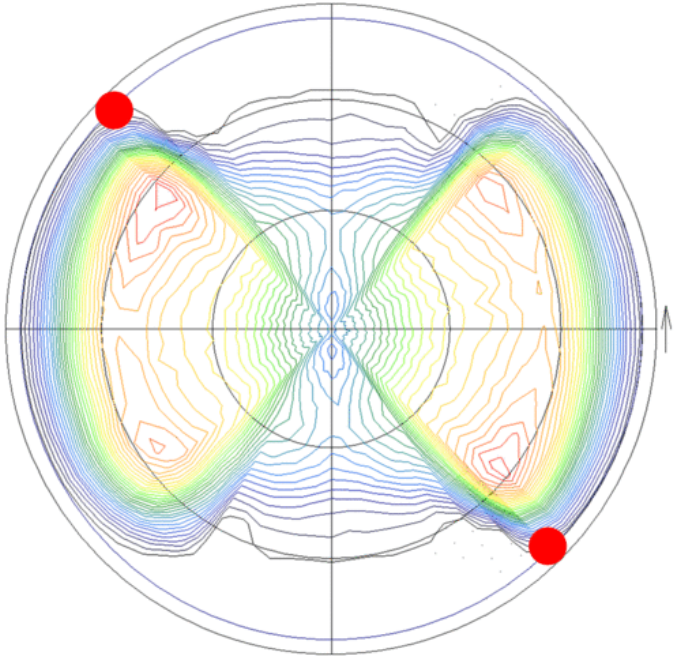
hybrid perovskite MAFACsPb(I_xBr_{1-x})$_3$ on glass substrate (C. Rehermann)





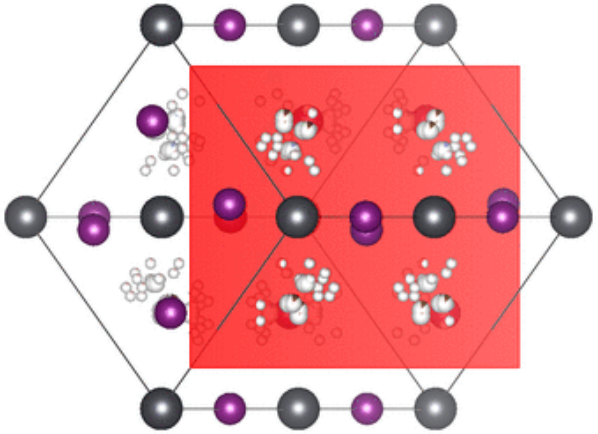
- accidental sample rotation during GIXRD measurement
- „sawtooth“ pattern due to highly textured thin film

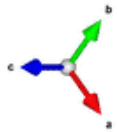
texture of thin films



110 pole figure @ 2Θ = 14.0756°

→ nearly epitaxial thin film





Instrumentation @ LMC

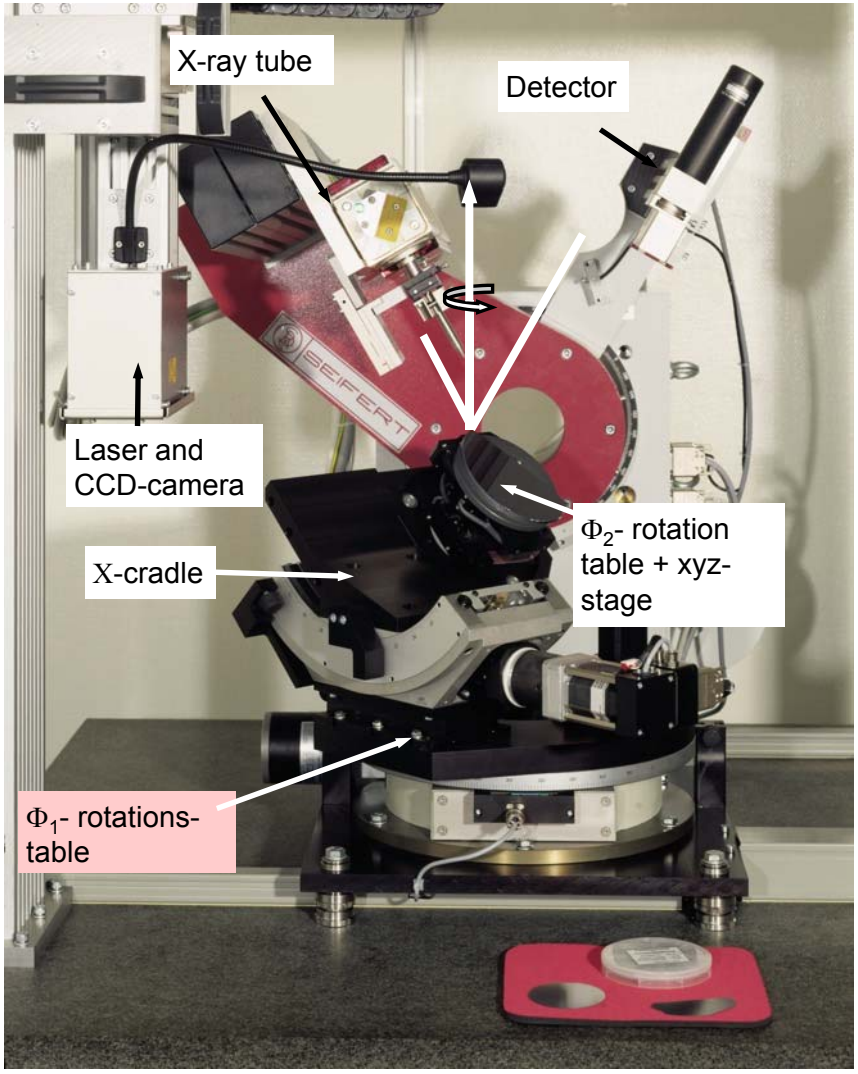
Panalytical MRD for epitaxy analysis and micro-diffraction

Monocapillary 230 x 0,1

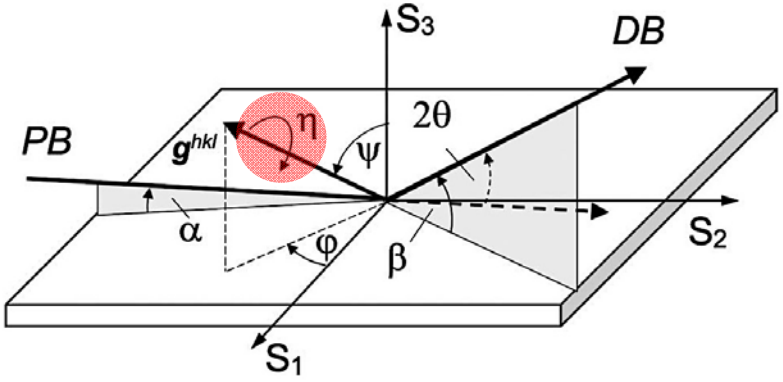
- length 230 mm
- thickness 0,1 mm
- divergence 0,3°

Instrumentation @ WCRC

The 5-axes diffractometer ETA for surface gradient analysis



- direct sample rotation around the scattering vector
- polycapillary optics and soller + secondary mononchromator for thin film analysis



Principle of residual stress analysis by diffraction methods

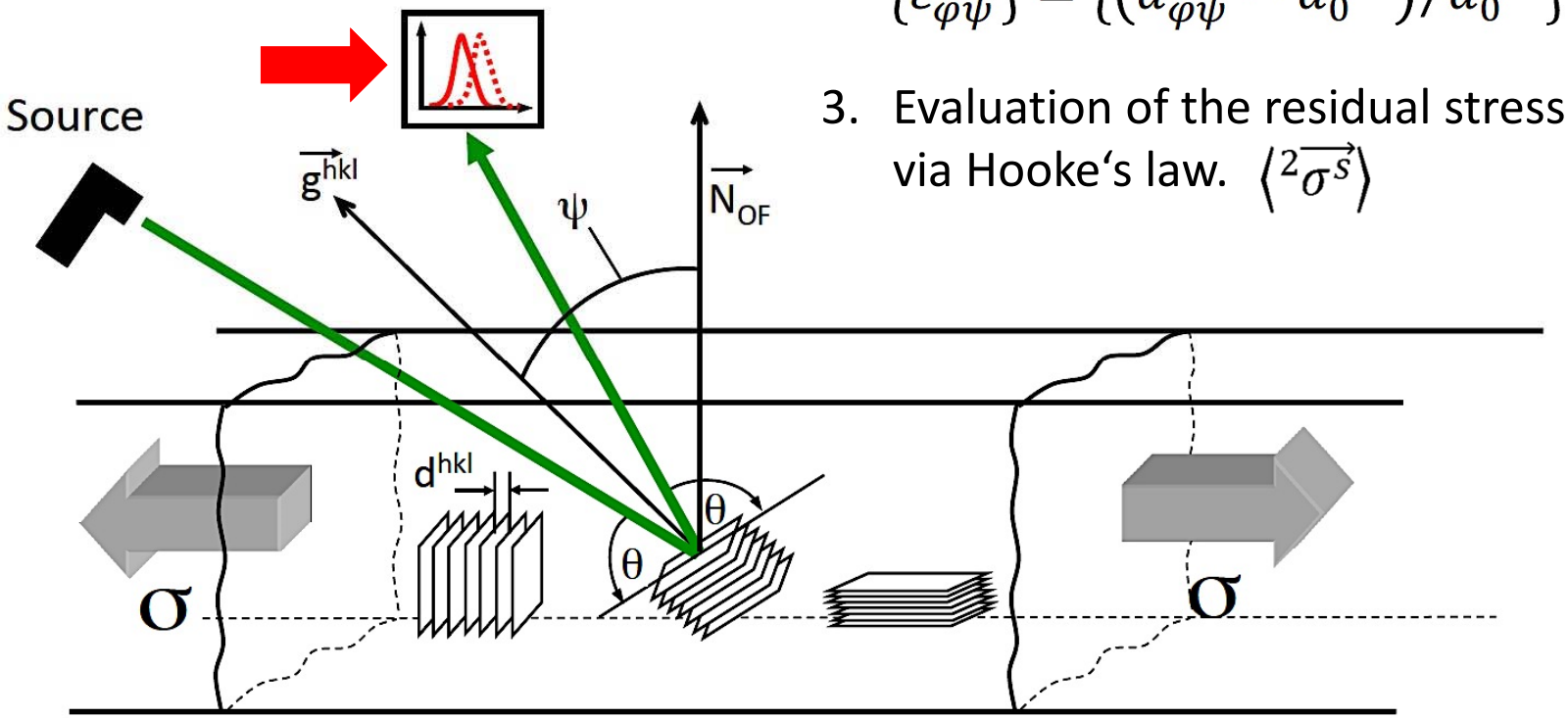
$$\{\varepsilon_{\varphi\psi}^{hkl}\} = \begin{Bmatrix} -\cot\theta^{hkl}\Delta\theta^{hkl} \\ -\Delta E^{hkl}/E^{hkl} \end{Bmatrix} \rightarrow \langle {}^2\overrightarrow{\sigma^s} \rangle$$

angle-/energy-dispersive

1. Measurement of the diffraction line shift for various orientations (φ, ψ)
2. Evaluation of the lattice strain

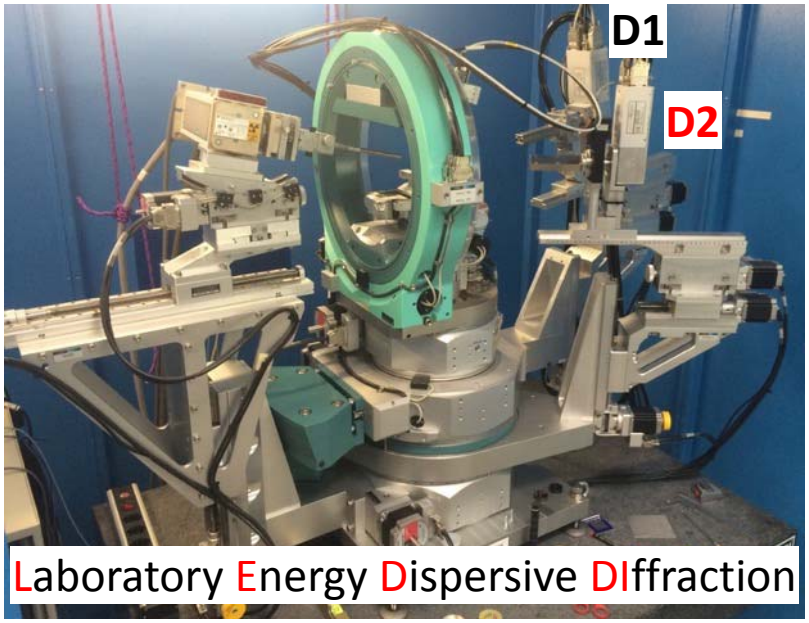
$$\{\varepsilon_{\varphi\psi}^{hkl}\} = \{(d_{\varphi\psi}^{hkl} - d_0^{hkl})/d_0^{hkl}\}$$

3. Evaluation of the residual stress tensor via Hooke's law. $\langle {}^2\overrightarrow{\sigma^s} \rangle$

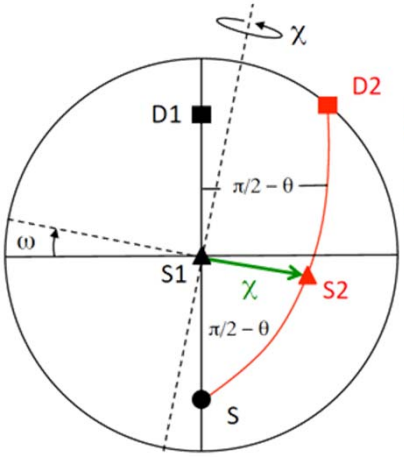


Instrumentation @ WCRC

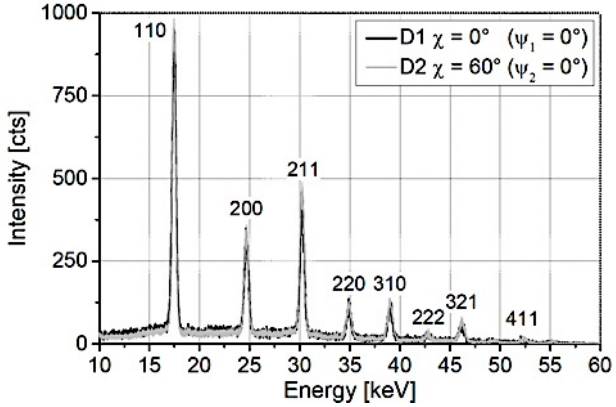
The energy-dispersive 8-circle diffractometer LEDDI



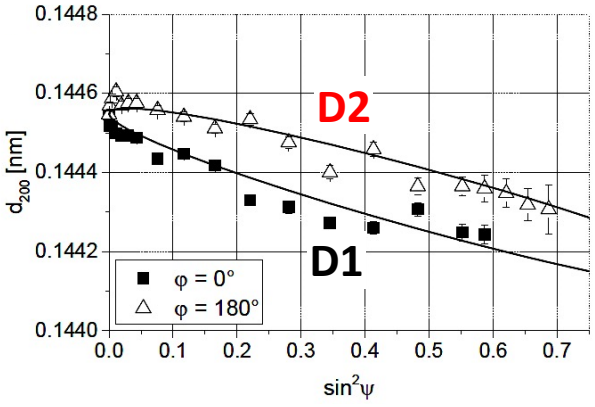
Mode 2

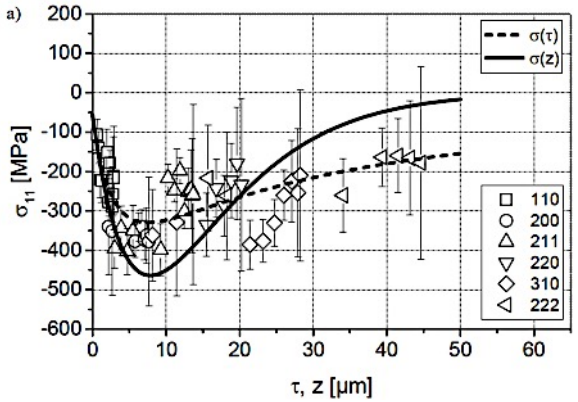


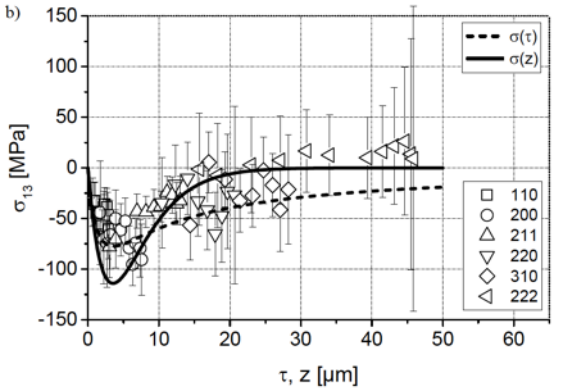
$\theta_1 = \theta_2$; $\chi = 60°$



simultaneous data acquisition with two detectors







in- and out-of-plane residual stress depth profiles from a single χ-scan

Full support : Planning and conducting experiments & data evaluation

EDDI-LEDDI

Ein MATHEMATICA®-Progammsystem zur energiedispersiven Eigenspannungsanalyse

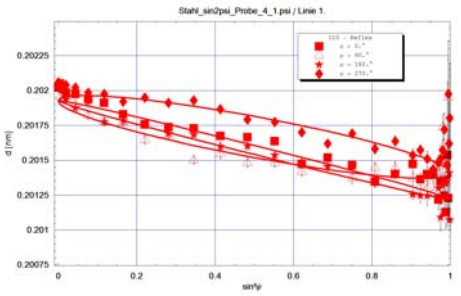
Notebookdatei: EDDI-LEDDI.nb
Packagedatei: EDDIbasicLEDDI.m
Letzte Änderung: 24. August 2016

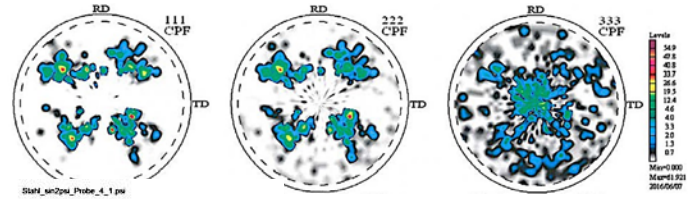
Listen mit diffraktionselastischen Konstanten (DEK)

EDDI

- Radioaktives Präparat
- Detektor im Labor
- Nützliche Tools ...
- Vorbereitung von ED-Messungen an EDDI
- Auswertung von ED-Beugungsspektren
- Linienlagenkorrekturen
- Darstellung von Ergebnissen
- Quantitative Phasenanalyse zweiphasiger Gefüge
- Texturmessungen
- Ermittlung von Eigenspannungen und Eigenspannunstiefenverteilungen

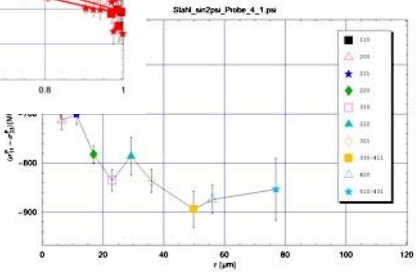
Mathematica

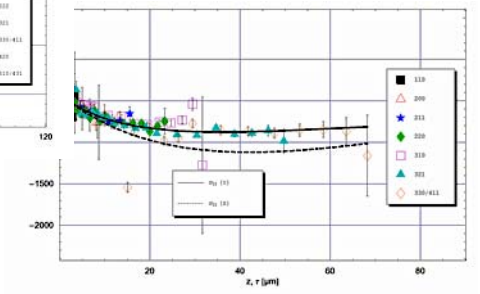


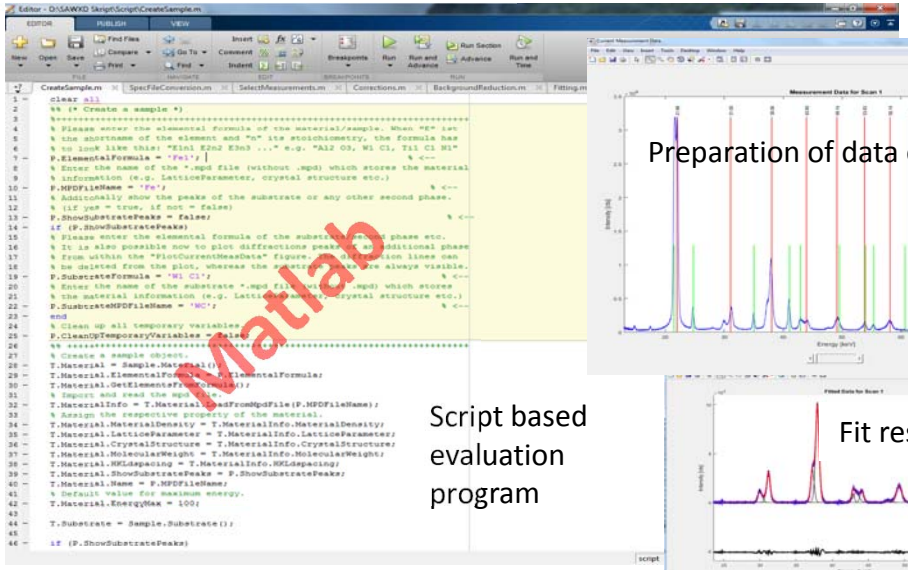


Texture analysis

Residual stress analysis





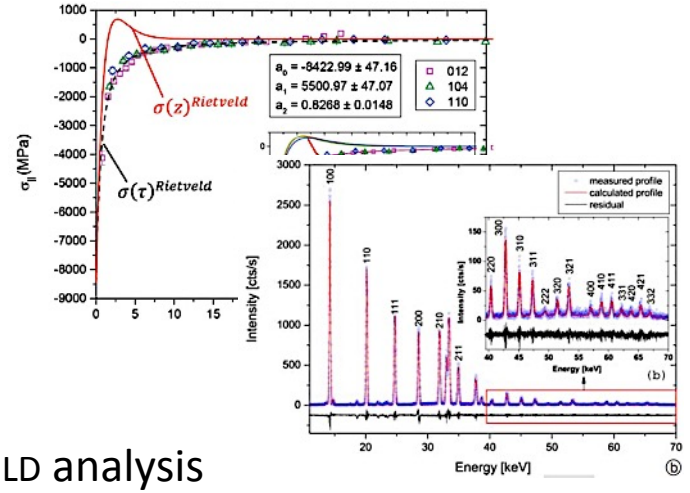


Matlab

Script based evaluation program

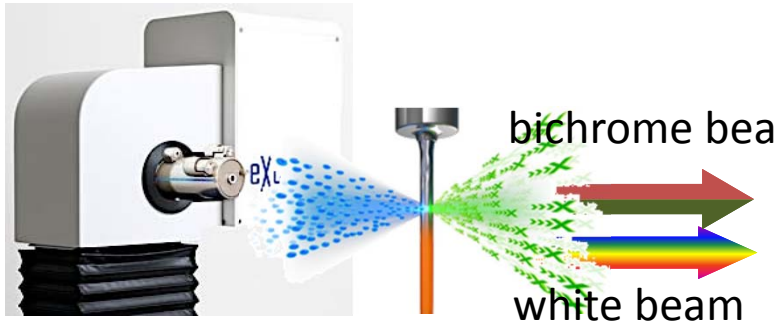
Preparation of data evaluation

Fit results

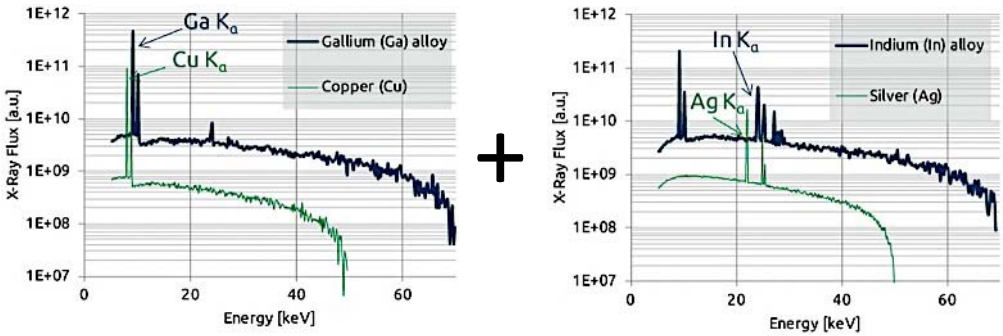


RIETVELD analysis (stress, microstructure)

Synchrotron-like conditions in the lab?



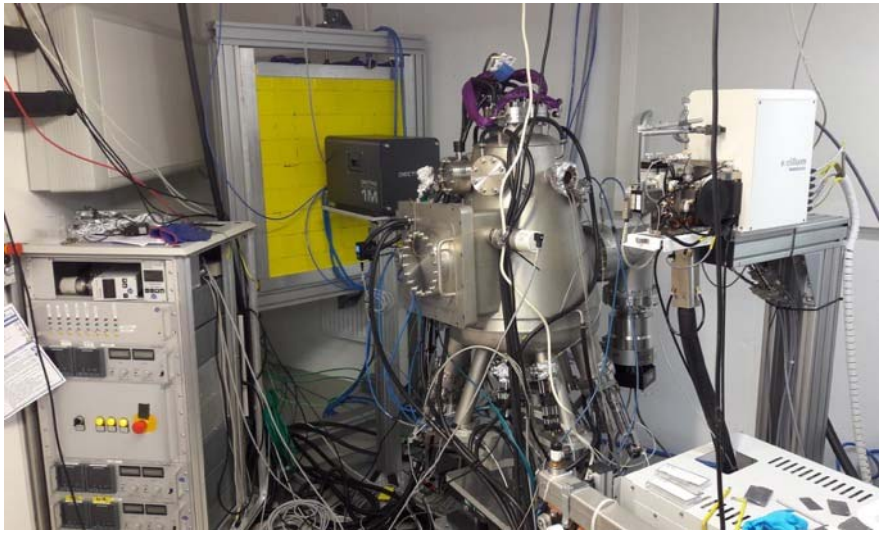
MetalJet X-ray tube



Ga-Kα: 9.2 keV

In-Kα: 24.2 keV

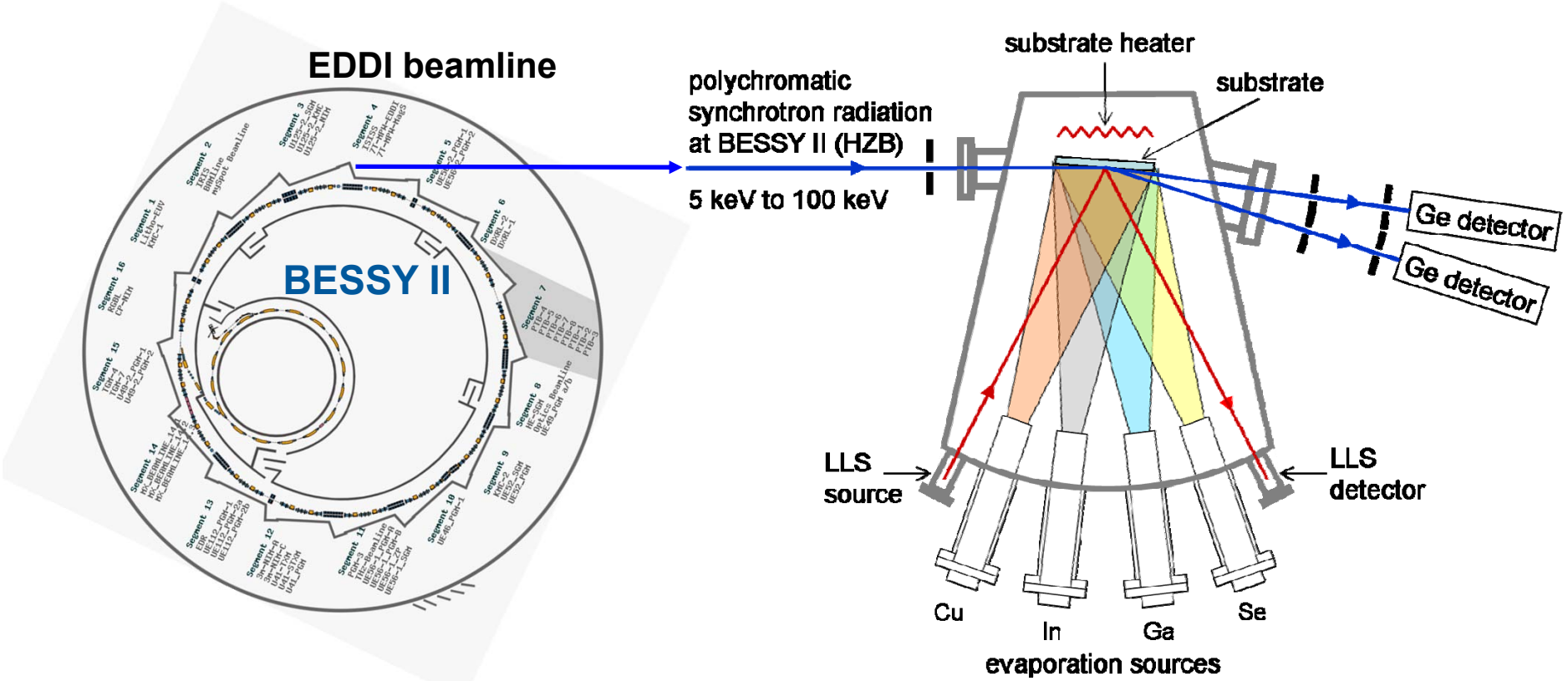
WCRC/EMIL: 160 kV source



LMC: 70 kV source

in situ EDXRD/XRF during thin film growth

Energy-dispersive X-ray diffraction and fluorescence (EDXRD/XRF)



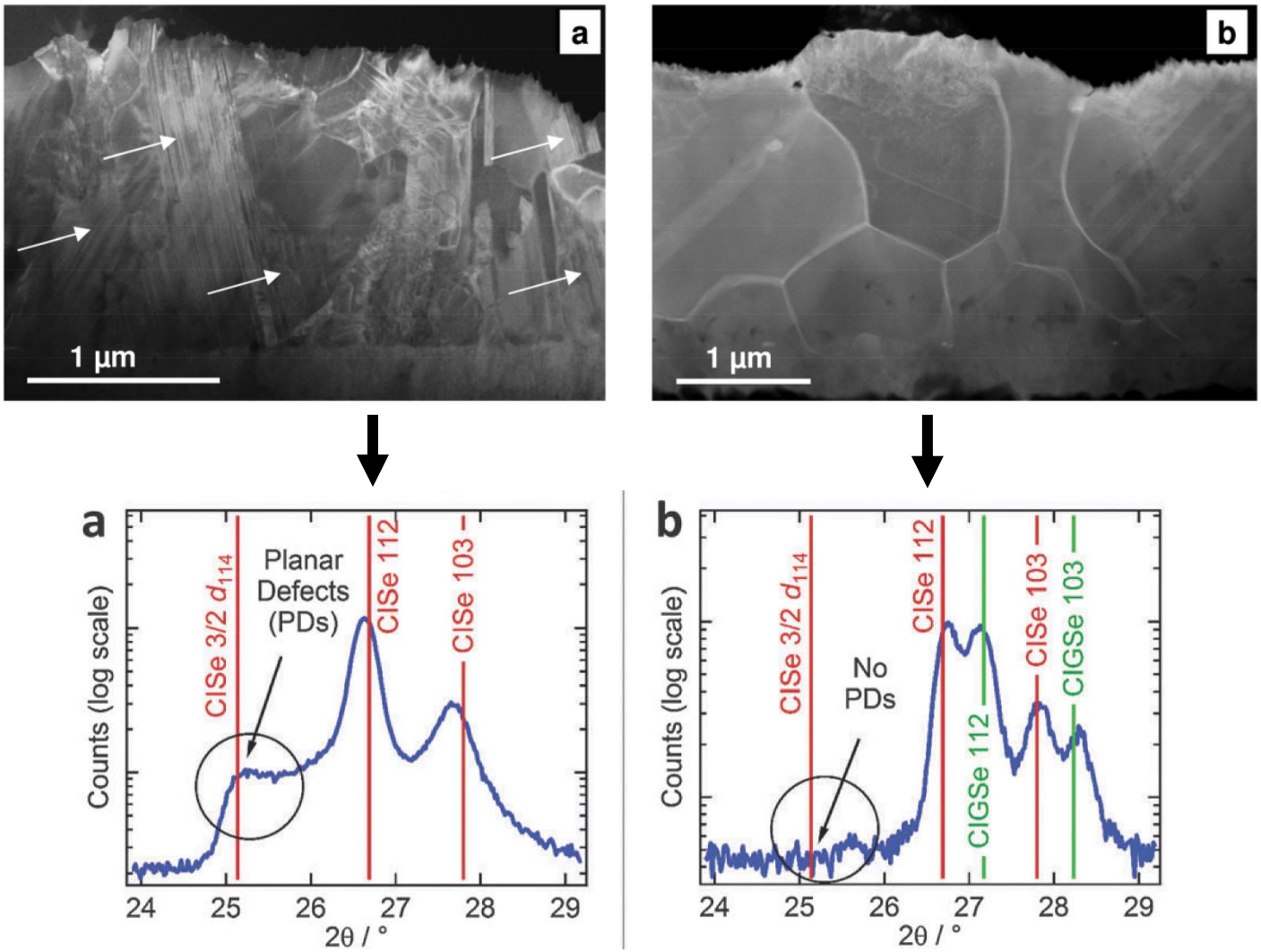
3-stage process for $Cu(In,Ga)Se_2$ thin film growth:

I) In-Ga-Se co-evaporation
II) Cu-Se co-evaporation (Cu-rich stage)
III) In-Ga-Se co-evaporation (Cu-poor stage)

H. Rodriguez-Alvarez, A. Weber, J. Lauche, C. A. Kaufmann, T. Rissom, D. Greiner, M. Klaus, T. Unold, C. Genzel, H.-W. Schock, R. Mainz. Advanced Energy Materials **3**, 1381-1387 (2013).

Planar defects in $Cu(In,Ga)Se_2$ create a diffraction signal

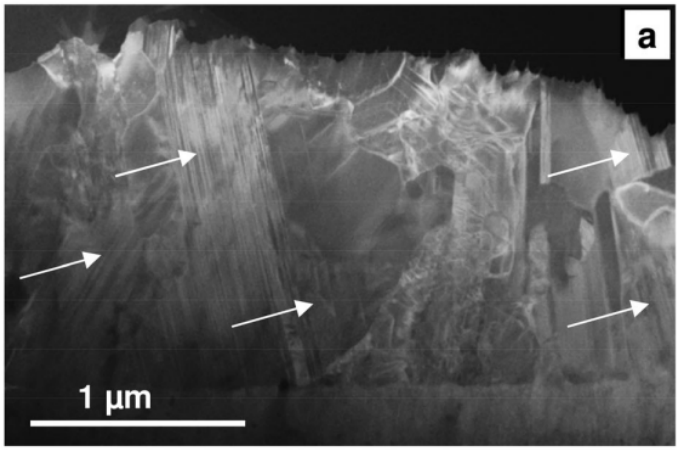
without Cu-rich stage | **with Cu-rich stage**



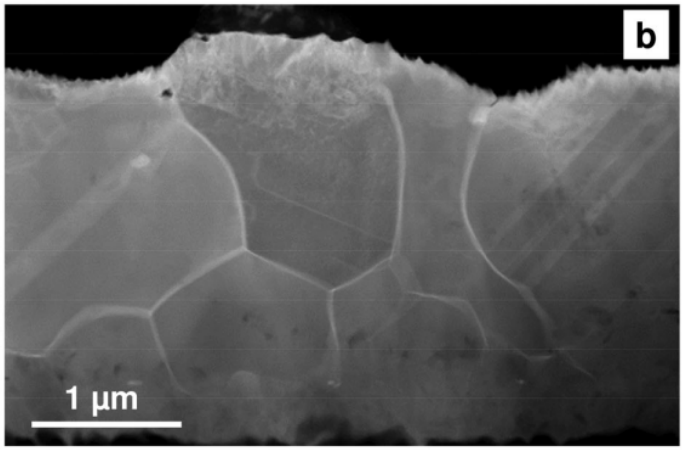
R. Mainz et al., *Energy Environ. Sci.* **9**, 1818 (2016)

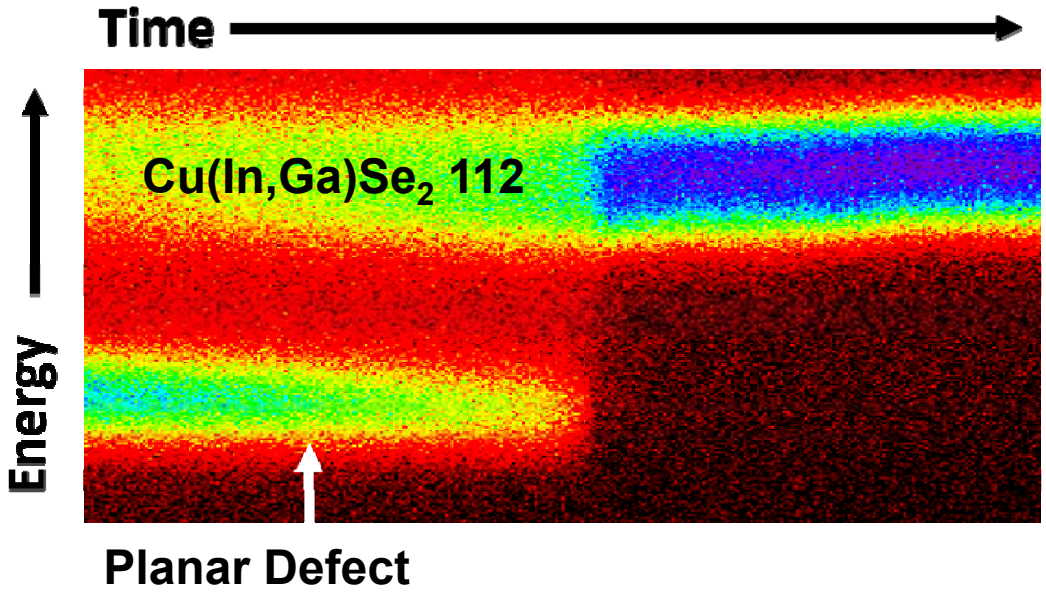
Monitoring PD annihilation by real-time XRD

without Cu-rich stage



with Cu-rich stage

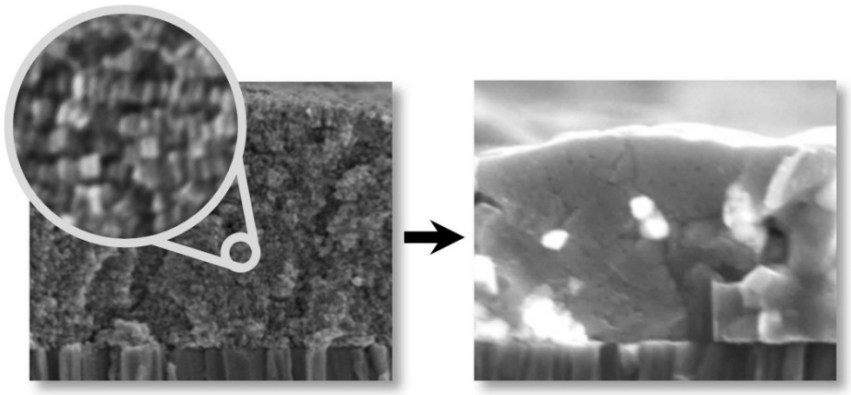




R. Mainz et al., *Energy Environ. Sci.* **9**, 1818 (2016)

Cu_2ZnSnS_4 film formation from wurtzite nanorods

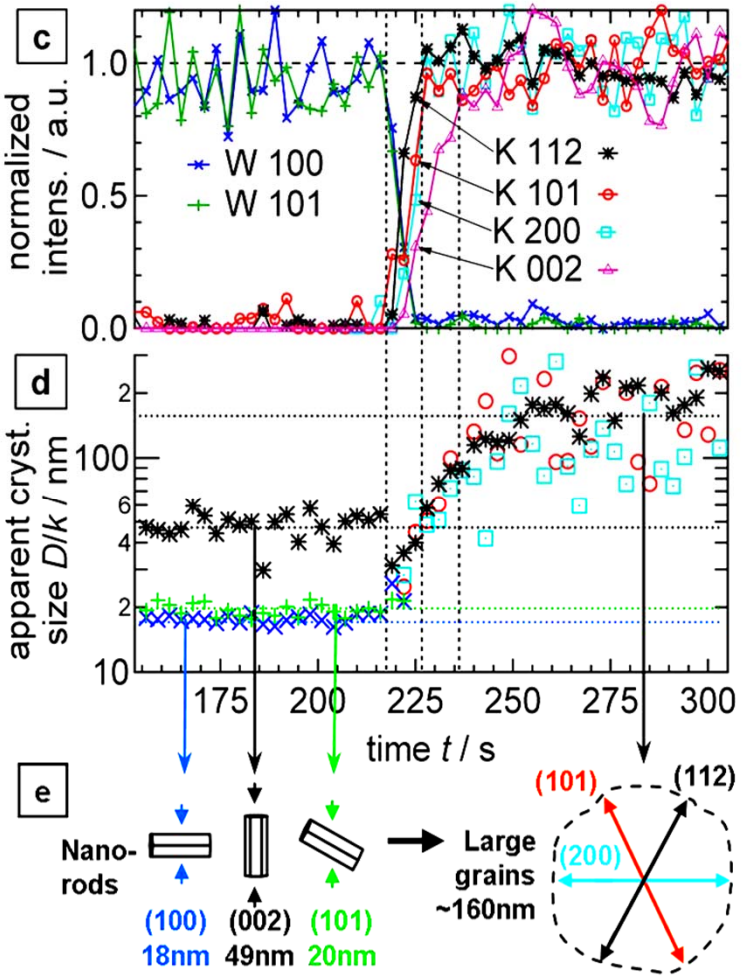
Wurtzite-type Cu_2ZnSnS_4 → **Kesterite-type Cu_2ZnSnS_4**



From nanorods to large grains within a few seconds!

→ correlation of phase formation and domain growth

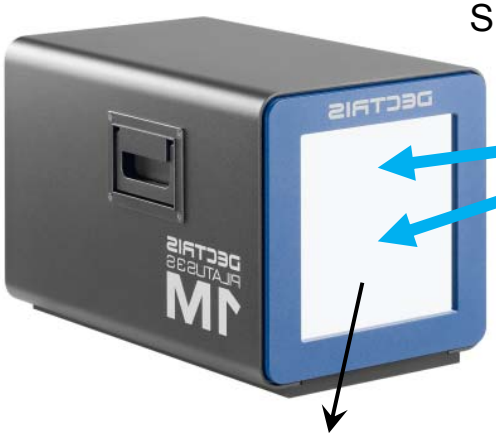
→ phase-transition-driven grain growth

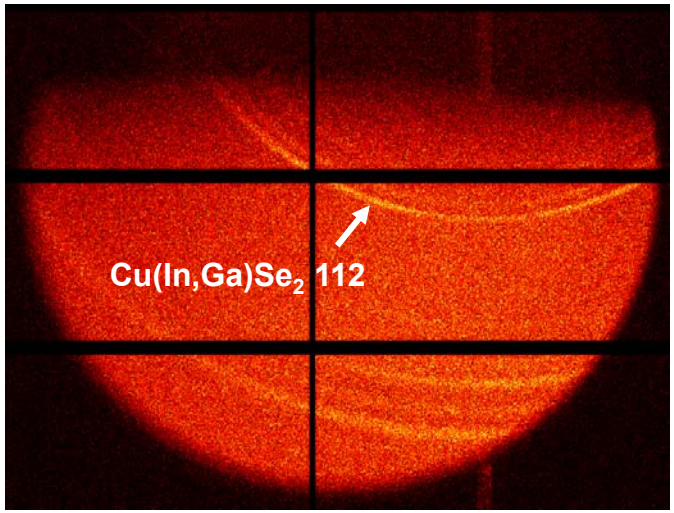


R. Mainz, A. Singh et al. Nature Commun. **5**, 3133 (2014)

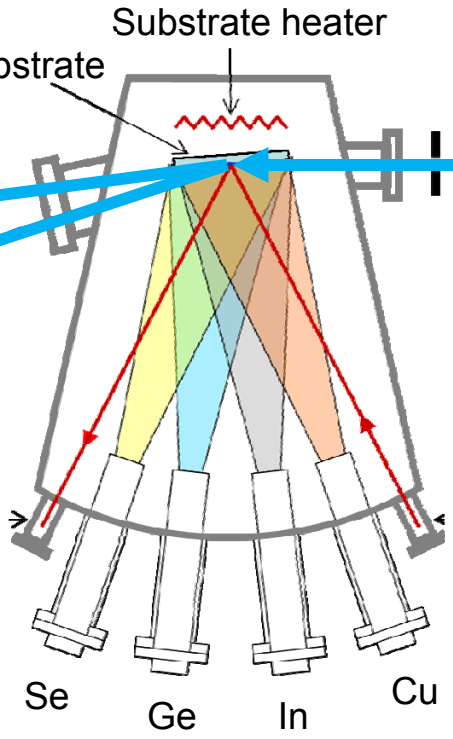
new *in situ* X-ray laboratory

2D photon detection





thin film growth



high-flux X-ray metal-jet source

first in-situ measurement during Cu(In,Ga)Se_2 film growth with metal-jet X-ray source

Latest news …

New X-ray diffractometer for powder diffraction and GIXRD was ordered for WCRC!

course on X-ray diffraction (for PhD students) will be organized next year (June 2018) @LMC

User access – fast and easy!

Scientists from all HZB divisions as well as external users have access to the X-Ray CoreLab.

1st step → each potential user has to register online
the user has to declare to follow the lab rules

2nd step → booking an instrument of the CoreLab via the online calendar system
user should give a short description of the planned experiment
and the samples he/she wants to study

3rd step → check by the scientific lab manager to make sure, that the user has chosen the suitable instrument for his/her problem

4th step → scientific lab manager confirms the booking and the user gets access to the X-Ray CoreLab

LMC → after introduction by the lab manager the user can do the experiments
WCRC → user experiments supported by instrument experts

Welcome to the X-Ray CoreLab!

Thank you for your attention!