Diffraction microscopy - from millimeter to nanometer

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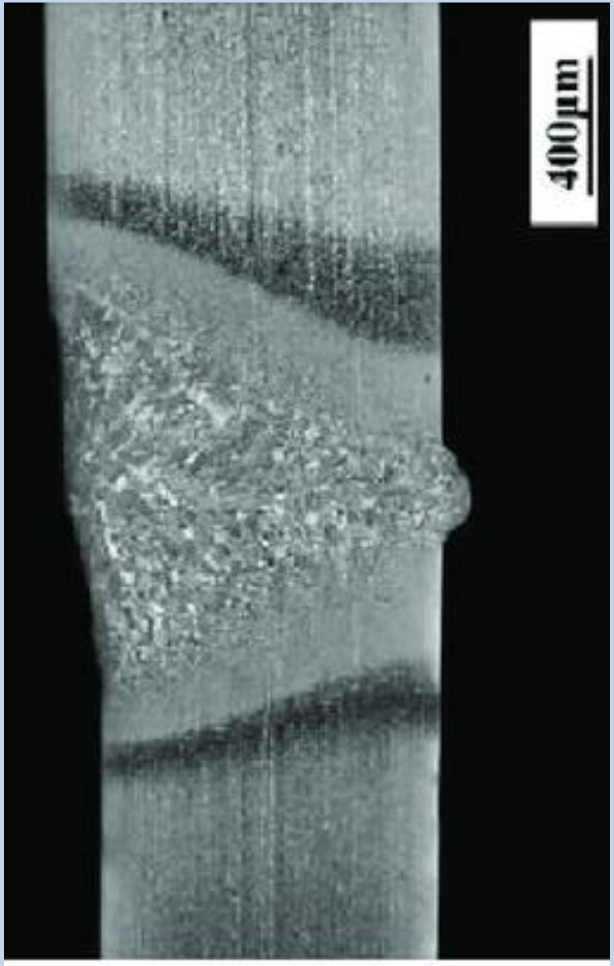
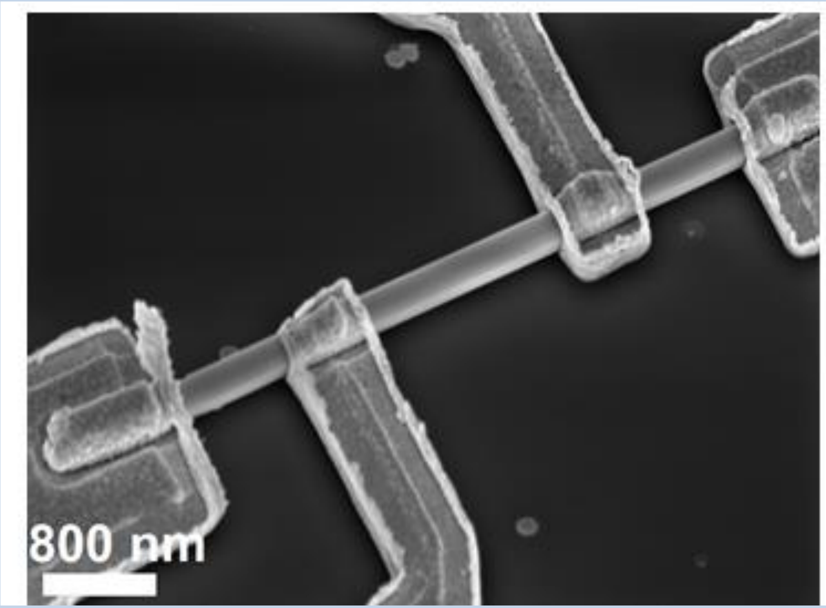
The need for spatial resolution

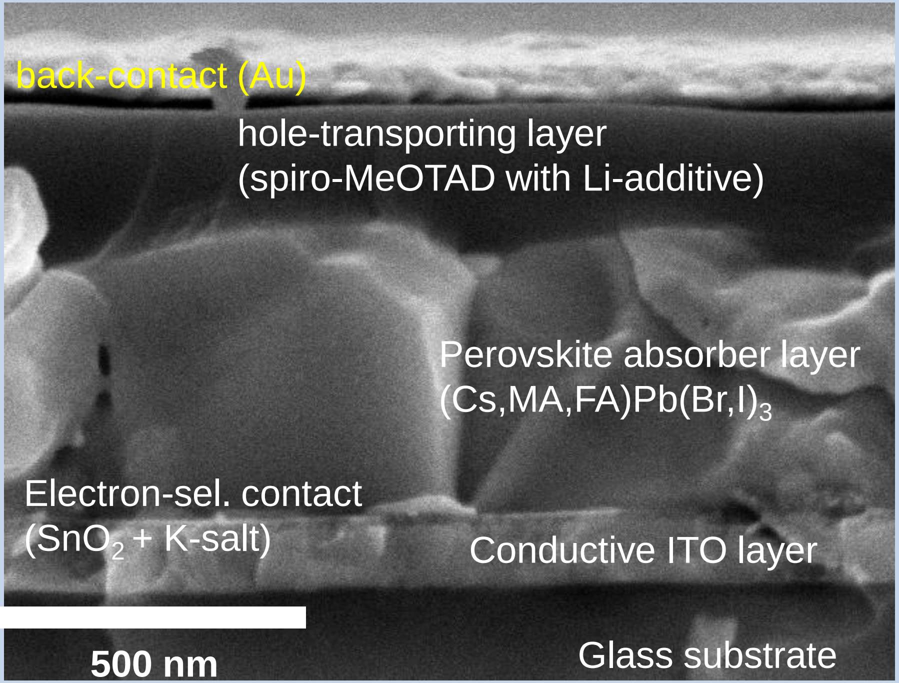
- Most samples show internal variation:
  - Composition
  - Crystal structure
  - Strain
  - ….
- X-ray methods have traditionally had poor real space resolution
- New synchrotrons and new X-ray optics allow focusing below 100 nanometer



The need for *nanoscale* resolution

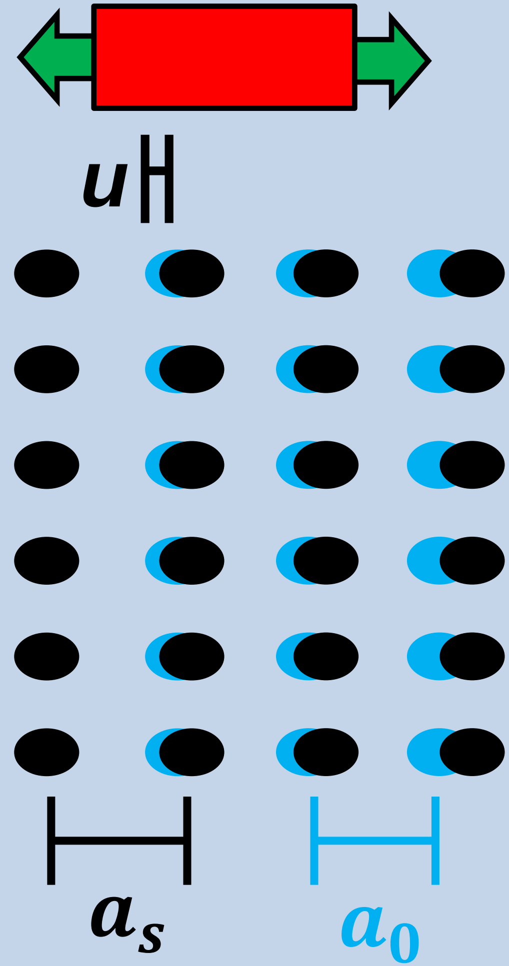
- Nanostructured materials have unique properties.
- Polycrystalline materials such as metals are nanostructured, with grain sizes from 10 nm to 10 µm
- Measuring *individual nanostructures* or *individual grains* gives a different insight compared with low-resolution, averaging methods

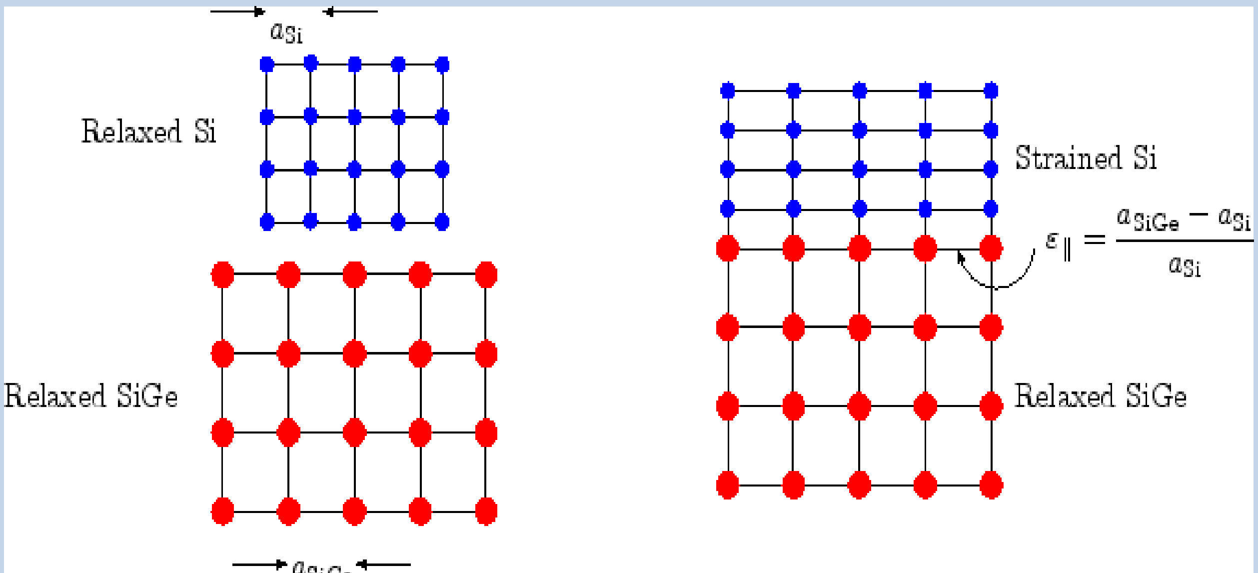




Strain in a crystal from stress or lattice mismatch

- A crystal under stress will be strained
- On an atomic level, this will change the atomic distances
- Strain can also come from lattice mismatch in a heterostructure





Other sources of shift in lattice distance

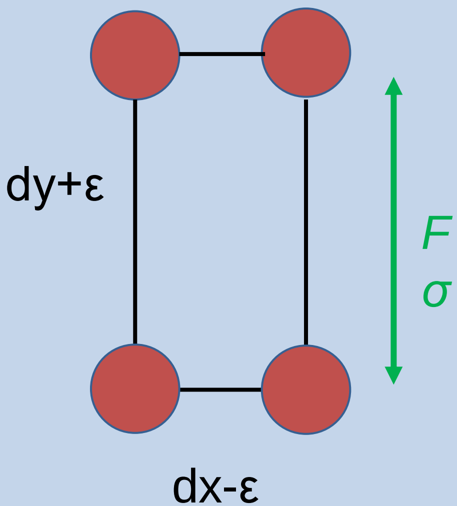
- Compound composition, e.g. in Si_xGe_{1-x}
- Piezoelectric fields
- Heating / cooling (thermal expansion)
- Manufacturing damage, e.g. from cutting
- Surface stress

All of these change the lattice, which can be measured by XRD

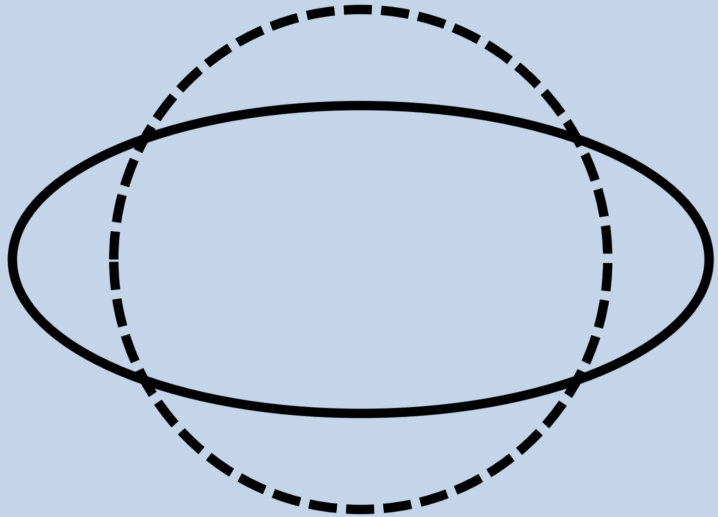
=> We can use XRD as a gauge of other processes

- These effects generally vary in space.
  How can we characterize this?

Effect of strain on powder XRD / WAXS

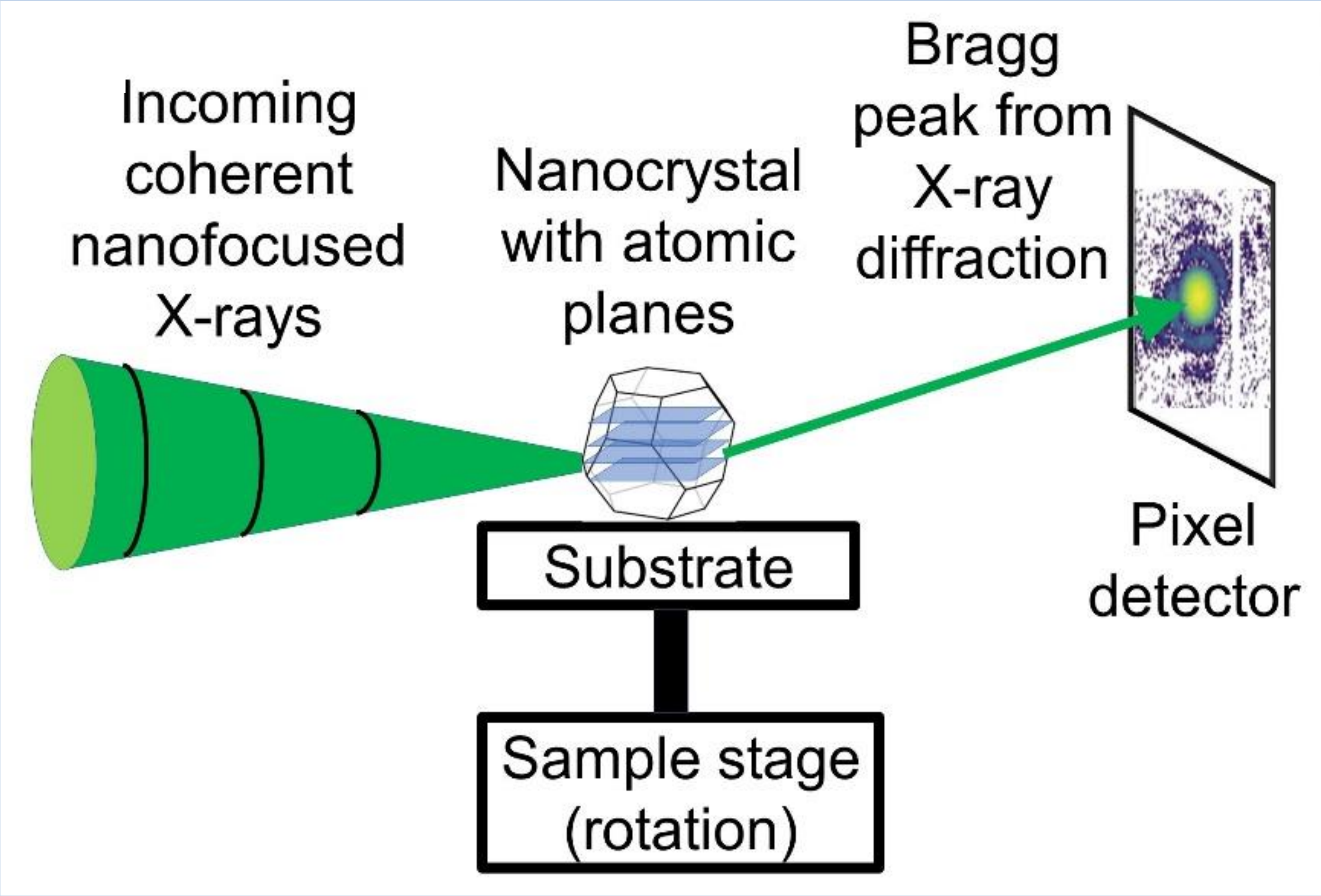


Change in powder ring

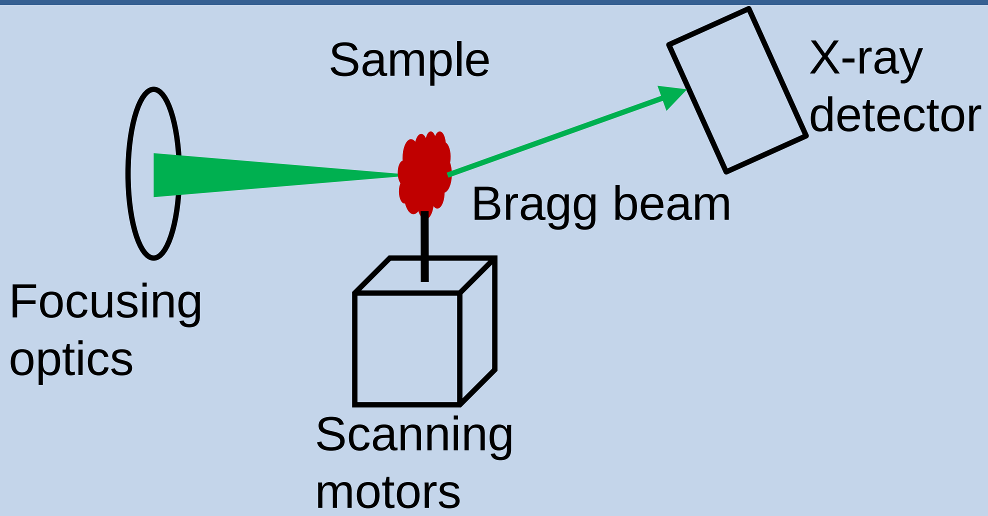


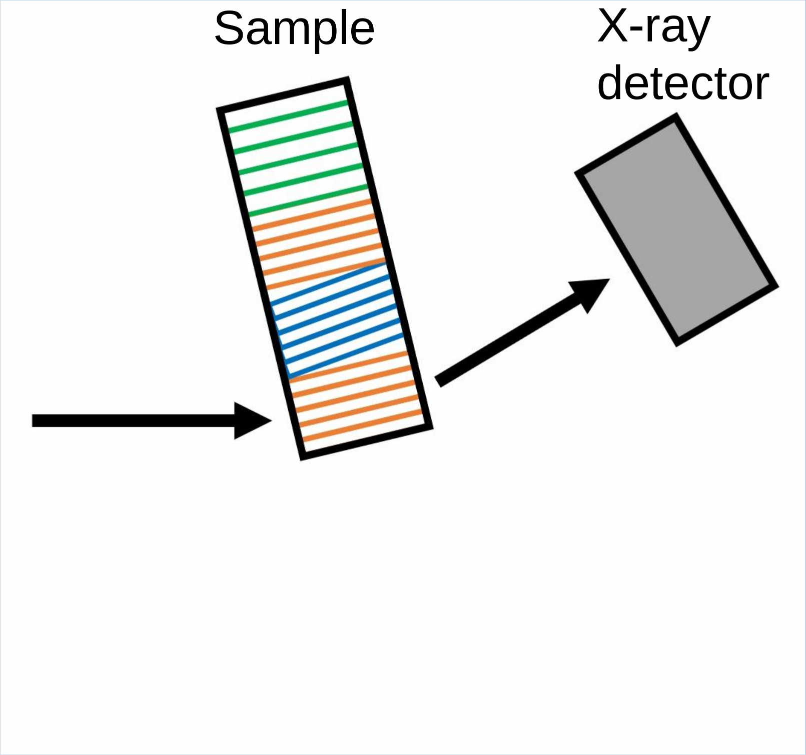
- Change can be quantified and converted to strain

Focused X-rays



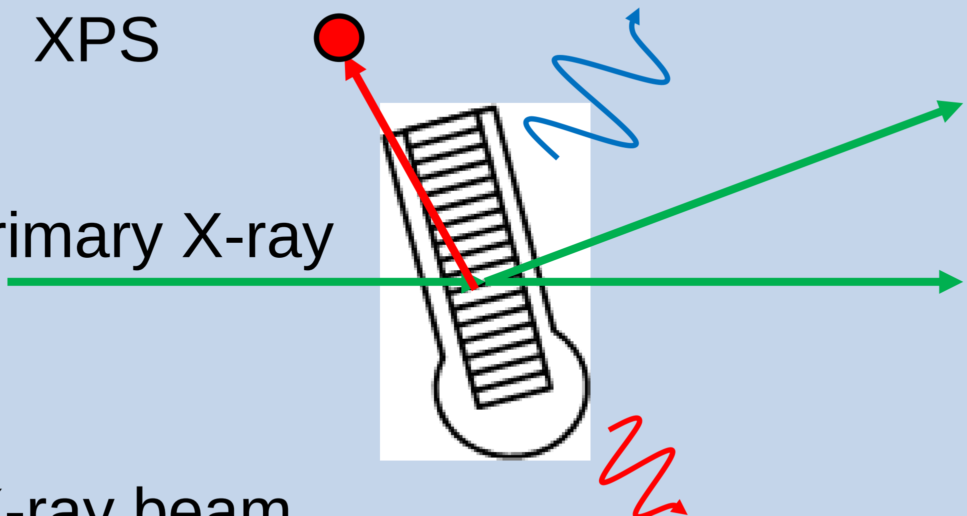
Scanning X-ray diffraction (XRD)



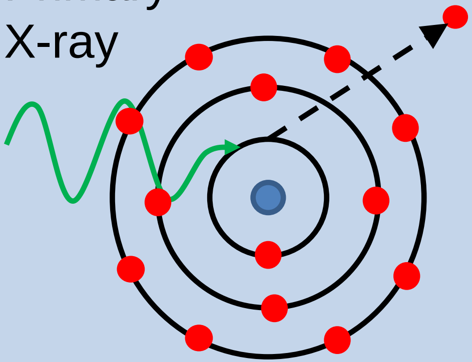


- Focused X-ray beam => local XRD
- Investigate the local crystal structure
- Create maps of local lattice plane distance and direction
- Spatial resolution limited by focus size

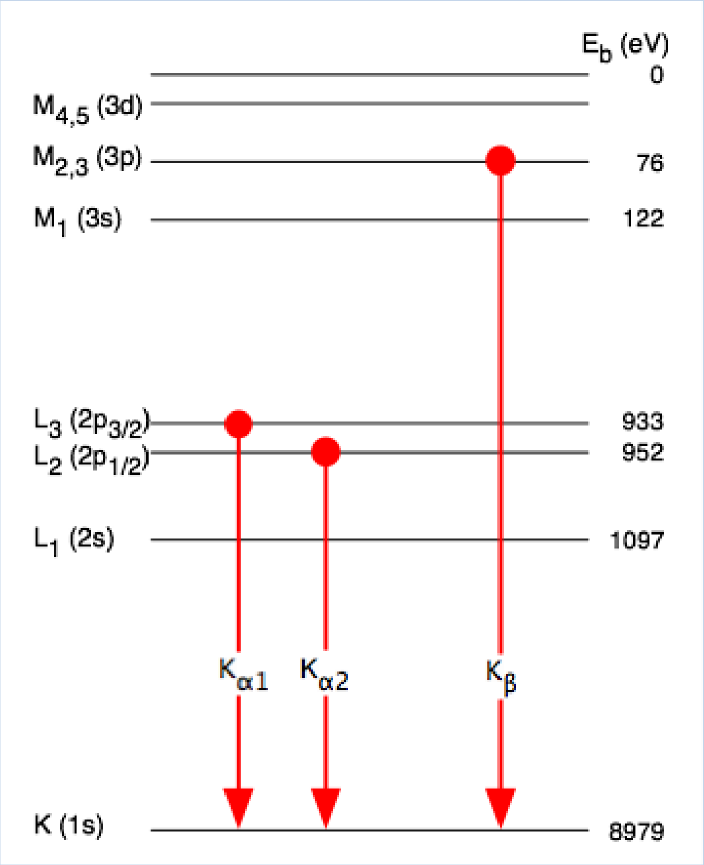
X-ray contrast mechanisms

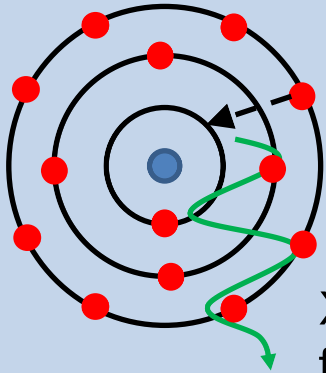


X-ray fluorescence



XRF energy: Elemental fingerprint





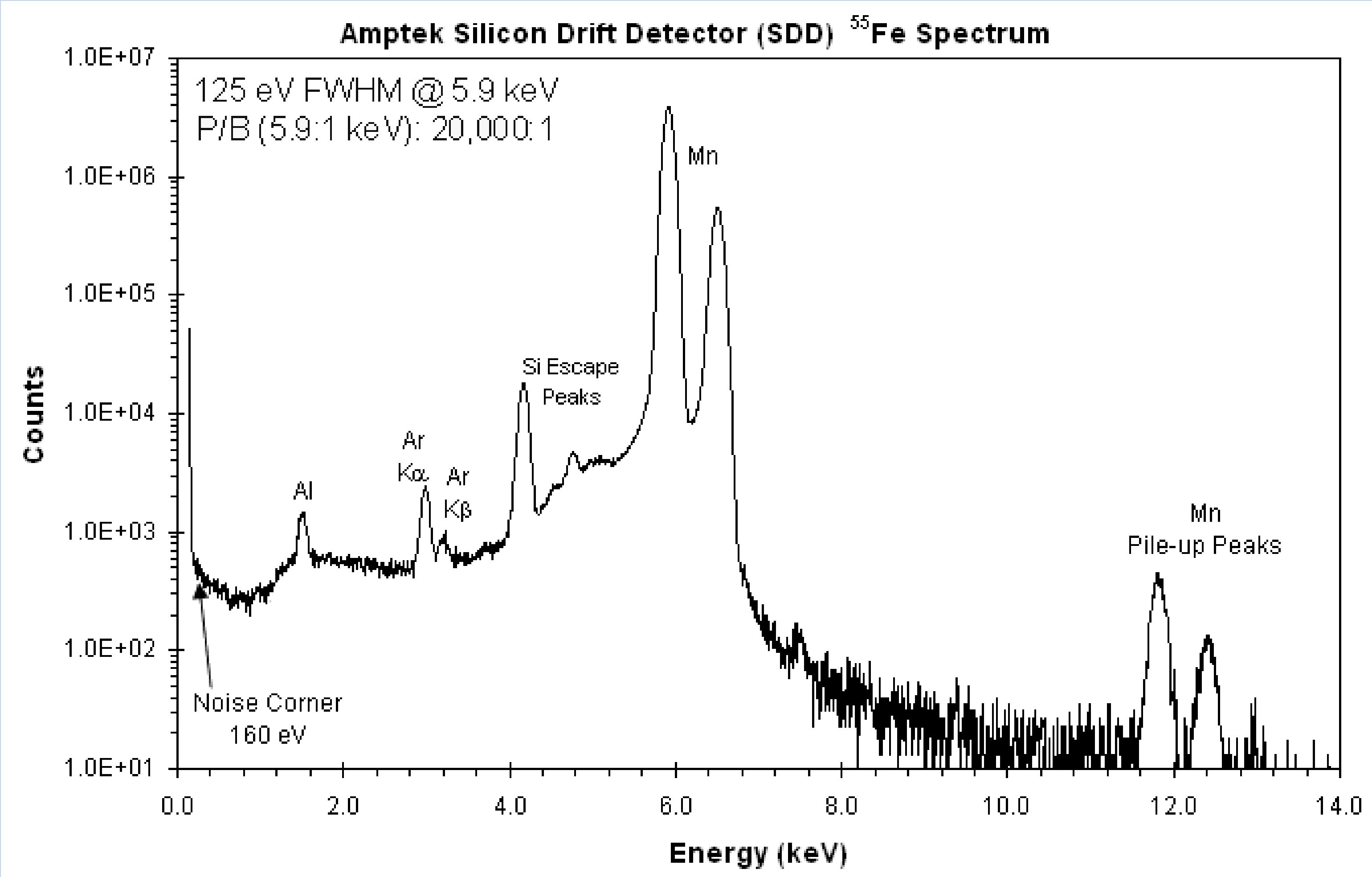
X-ray fluorescence (XRF)

- The emitted XRF photons have energies which are characteristic for the element
- List sorted by element here http://www.med.harvard.edu/jpnm/physics/refs/xrayemis.html
- Tables can be found for instance in the *X-ray data booklet*, which can also be found on http://xdb.lbl.gov/

Table 1-2. *Energies of x-ray emission lines (continued).*

Element	$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$L\alpha_1$	$L\alpha_2$	$L\beta_1$	$L\beta_2$	$L\gamma_1$	$M\alpha_1$
63 Eu	41,542.2	40,901.9	47,037.9	5,845.7	5,816.6	6,456.4	6,843.2	7,480.3	1,131
64 Gd	42,996.2	42,308.9	48,697	6,057.2	6,025.0	6,713.2	7,102.8	7,785.8	1,185
65 Tb	44,481.6	43,744.1	50,382	6,272.8	6,238.0	6,978	7,366.7	8,102	1,240
66 Dy	45,998.4	45,207.8	52,119	6,495.2	6,457.7	7,247.7	7,635.7	8,418.8	1,293
67 Ho	47,546.7	46,699.7	53,877	6,719.8	6,679.5	7,525.3	7,911	8,747	1,348
68 Er	49,127.7	48,221.1	55,681	6,948.7	6,905.0	7,810.9	8,189.0	9,089	1,406
69 Tm	50,741.6	49,772.6	57,517	7,179.9	7,133.1	8,101	8,468	9,426	1,462
70 Yb	52,388.9	51,354.0	59,370	7,415.6	7,367.3	8,401.8	8,758.8	9,780.1	1,521.4
71 Lu	54,069.8	52,965.0	61,283	7,655.5	7,604.9	8,709.0	9,048.9	10,143.4	1,581.3

Example spectrum from Silicon drift detector



XRF detection limit

- The lowest detectable concentration is called the detection limit
- Depends on:
  - Element (high *Z* better)
  - Detector
  - Primary X-ray flux & energy
  - Overlapping XRF lines from other elements.
    => Sample-dependent
- Often in the parts per million (ppm) range – usually much better than EDS (~%)

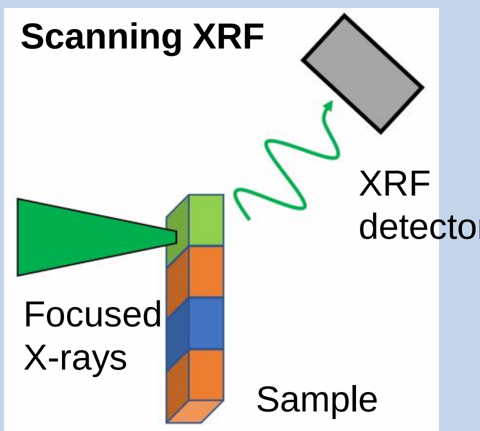
Material	Elements	LOD（PPM）
Take example of SO2 for Mineral and rear earth elements）	Mg	8976
	Al	309
	Si	864
	P	212
	S	170
	Cl	126
	K	84
	Ca	45
	Ti	88
	V	10
	Cr	15
	Mn	10
	Fe	7
	Co	7
	Ni	5
	Cu	4
	Zn	5
	As	1.5
	Pb	3.5
	Br	2
	Rb	1.5
	Sr	2.3
	Zr	1.2
	Nb	1.1
	Mo	15
	Ag	10
	Cd	20
	Sn	25

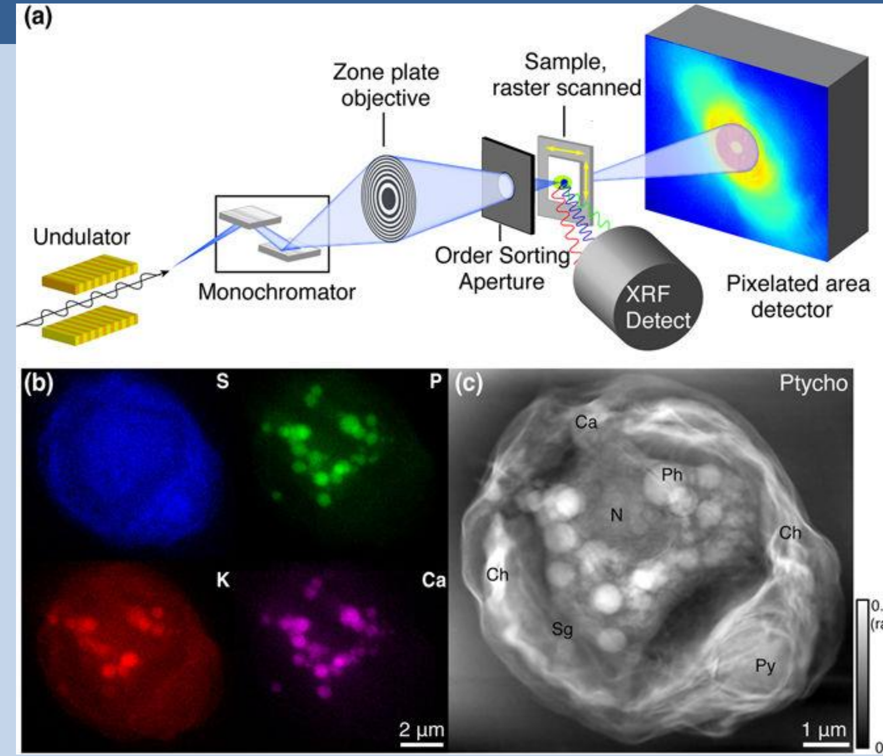
Element	LOD（PPM）
Sn	25.3
Sb	22.3
Th	5
Nb	3.7
Ba	17
Ba	12
W	15
Au	20
Pt	15
Rh	15
Hg	5
Sc	35
Y	4.5
La	35.7
Ce	26.4
Pr	36
Nd	35.7
Pm	35
Sm	34.5
Eu	34.7
Gd	34
Tb	33.2
Dy	32.5
Ho	32
Er	31.3
Tm	30
Yb	28.5
Lu	27

Example: Handheld XRF device, soil

Scanning XRF

- Sample scanned in focused beam
- XRF spectrum measured at each point
- Composition evaluated, creating a 2D map
- Resolution limited by focus





J. Deng, D. J. Vine, S. Chen, Q. Jin, Y. S. G. Nashed, T. Peterka, S. Vogt, and C. Jacobsen, *"X-ray ptychographic and fluorescence microscopy of frozen-hydrated cells using continuous scanning"* **Scientific Reports** 7 (1), 445 (2017) 10.1038/s41598-017-00569-y

Nano-XRF of ore from Liikavaara Östra Cu-(W-Au) deposit

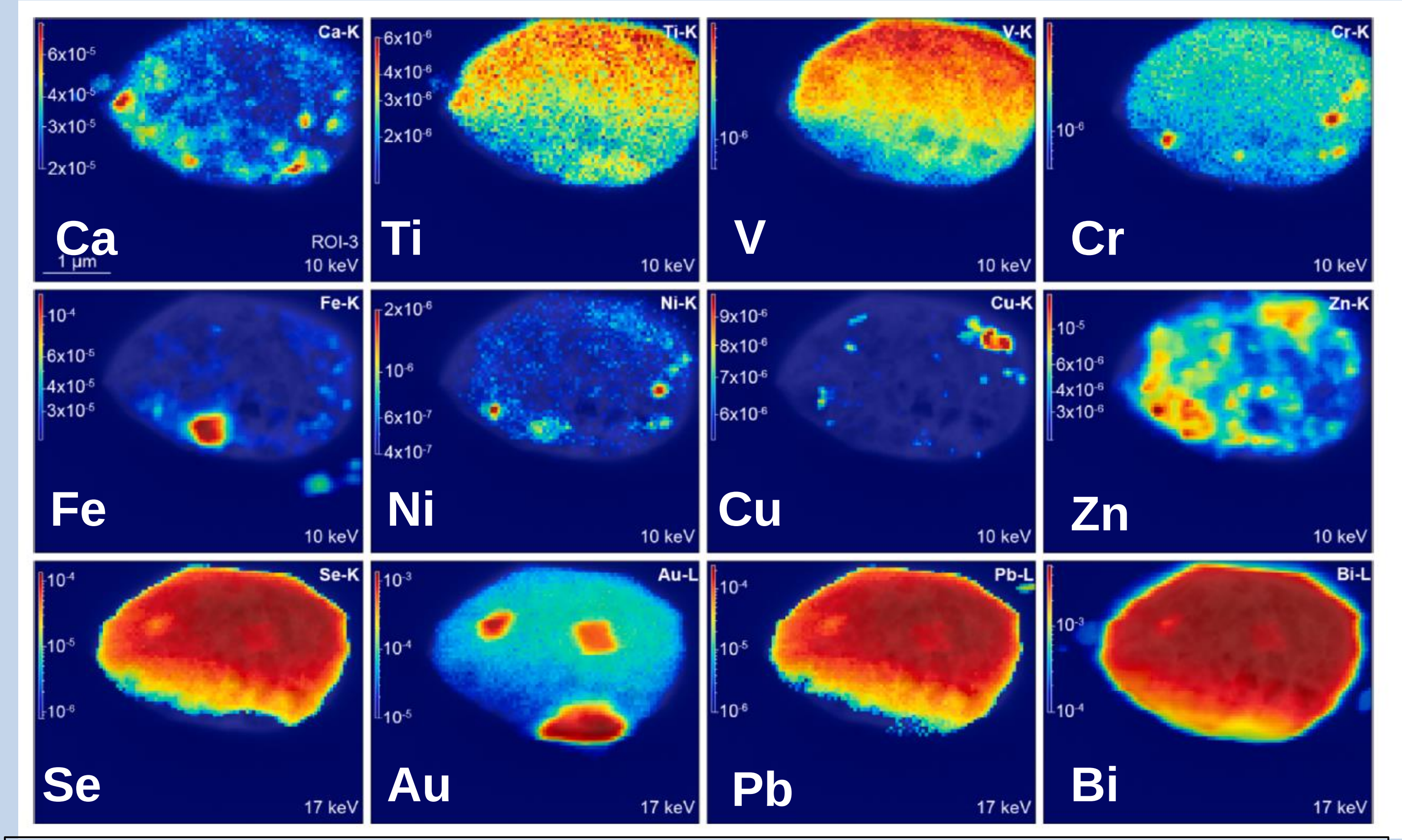
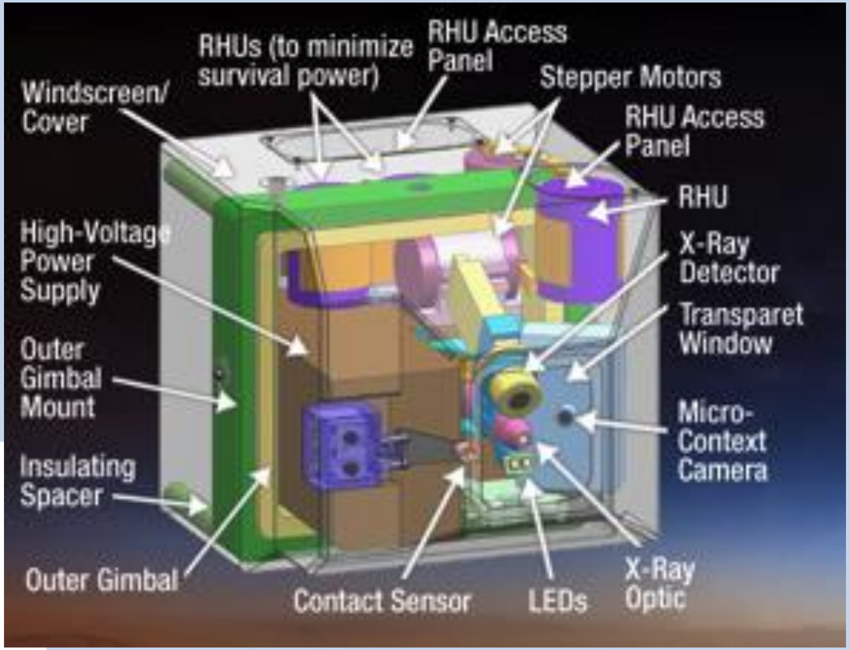


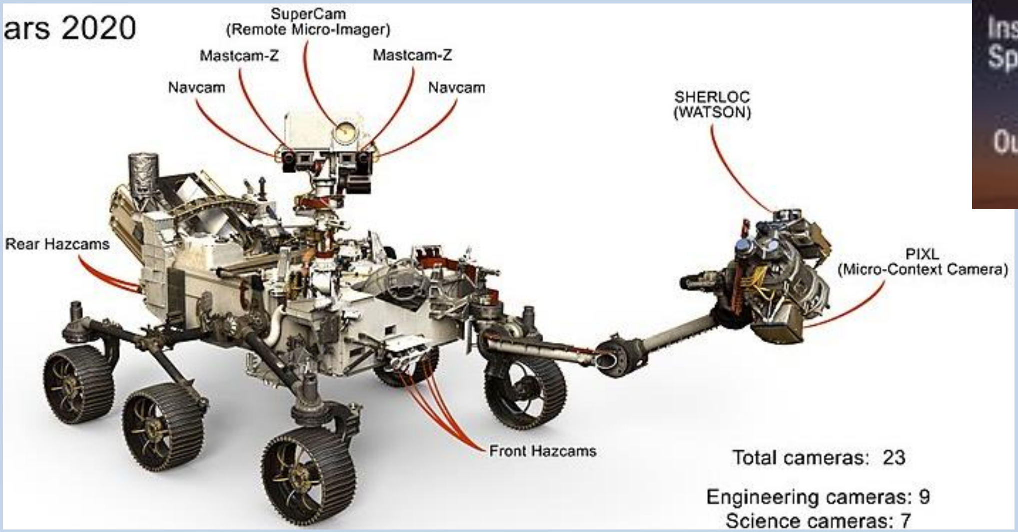
Image size 4x5 µm

M. Warlo, G. Bark, C. Wanhainen, I. McElroy, A. Björling, and U. Johansson, *"Extreme-resolution synchrotron X-Ray fluorescence mapping of ore samples"* **Ore Geology Reviews** 140, 104620 (2022) https://doi.org/10.1016/j.oregeorev.2021.104620

XRF on new Mars 2020 rover

- Focused X-ray source (25 kV)
- Scanning micro-XRF
- Spatial resolution 300 µm

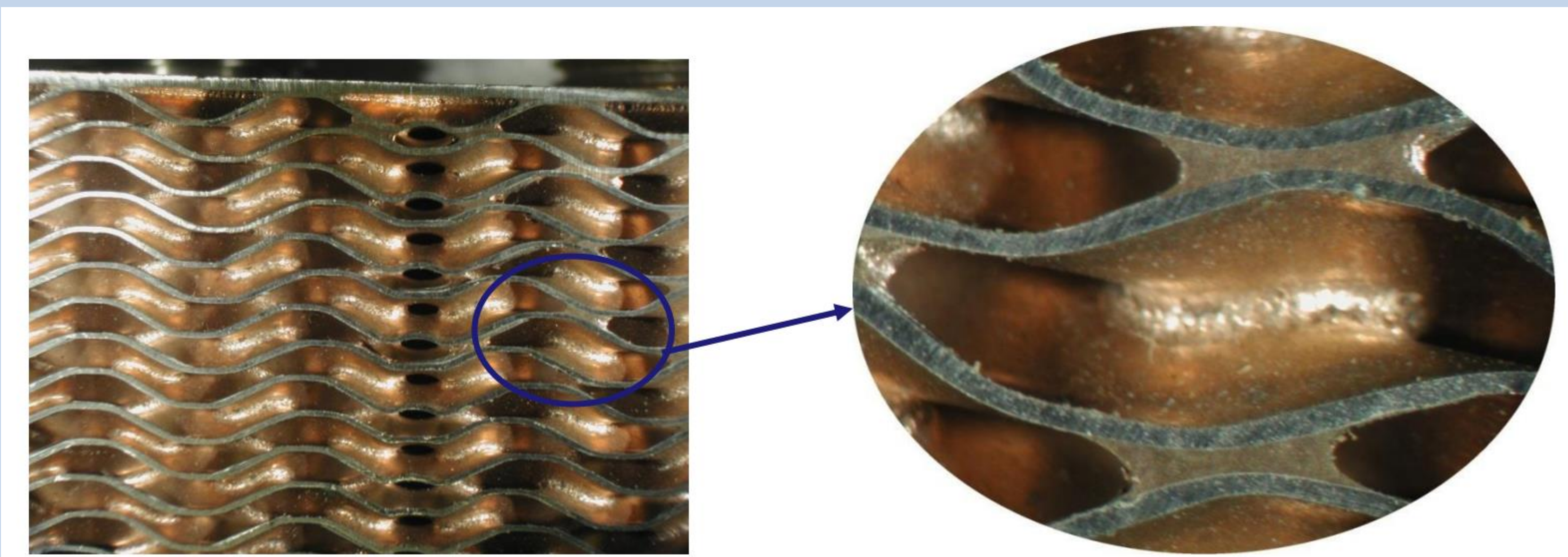




https://astrobiology.nasa.gov/news/pixl-a-new-nasa-instrument-for-ferreting-out-clues-of-ancient-life-on-mars/

Example with micrometer resolution: Brazed joint

- Collaboration between Filip Lenrick, LTH, and AlfaLaval.
- Two metals joined by brazing, to create heat exchangers
- Cross-sectional foil
- Applied stress until failure
- Data analysis in the summer by students. Still work in progress!

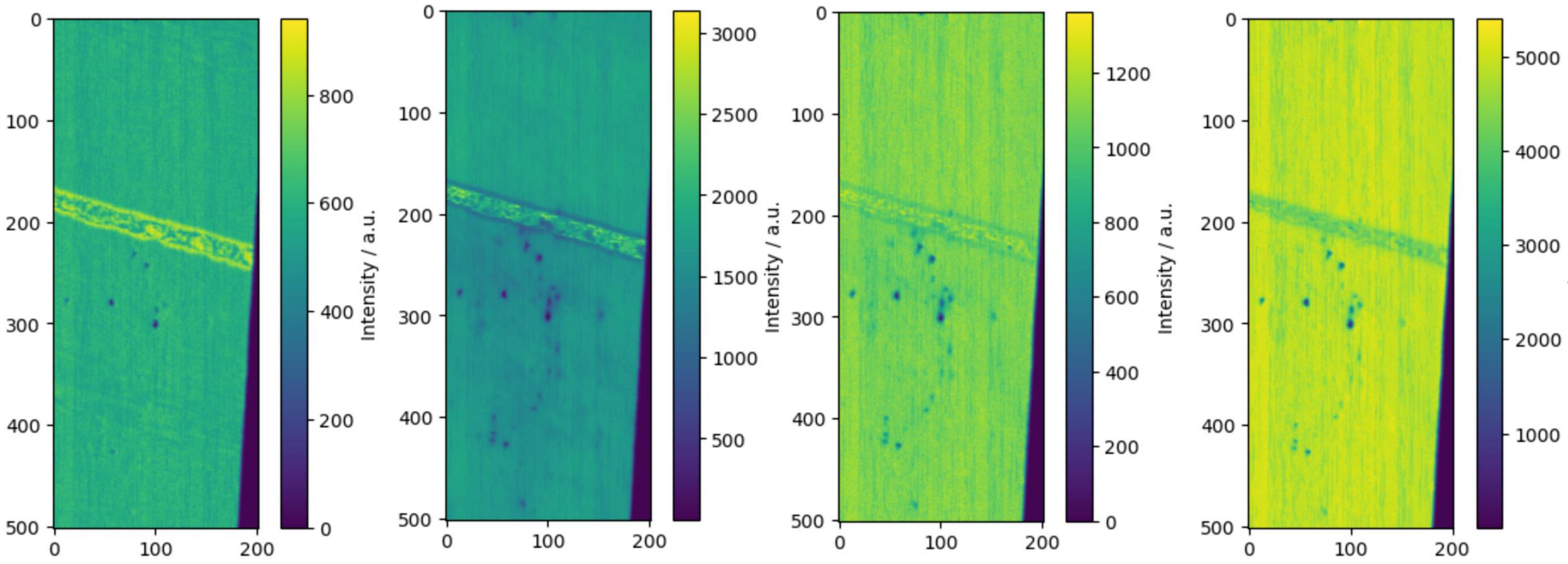


Experimental setup at DanMax

- Vertical stress
- Measure in transmission
- Scanning X-ray diffraction / WAXS + XRF

XRF maps

Step size 10 micrometer



Nickel: 7.45 keV peak

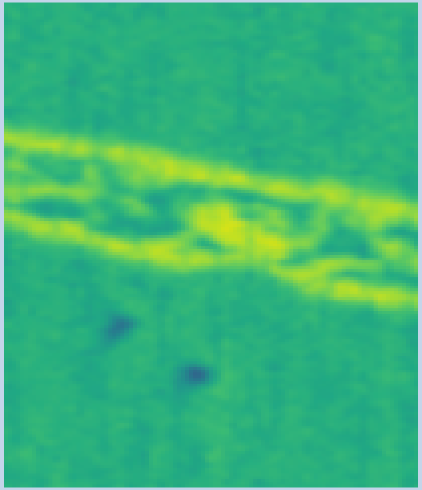
Molybdenum: 17.45 keV peak

Chromium: 5.39 keV peak

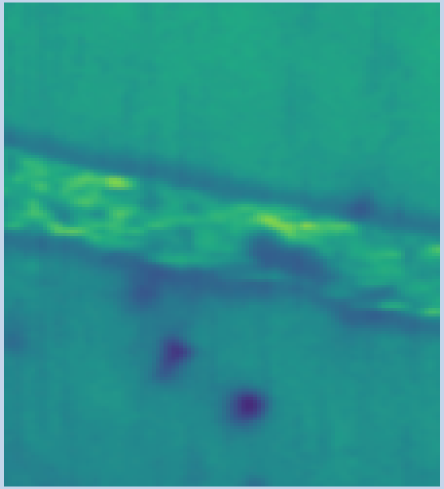
Iron: 6.38 keV peak

XRF maps, details

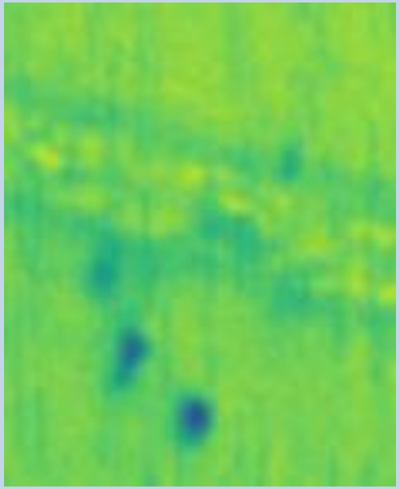
Step size 10 micrometer



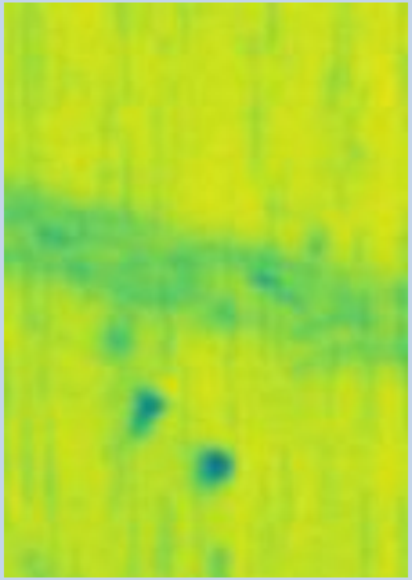
Nickel: 7.45 keV peak



Molybdenum: 17.45 keV peak

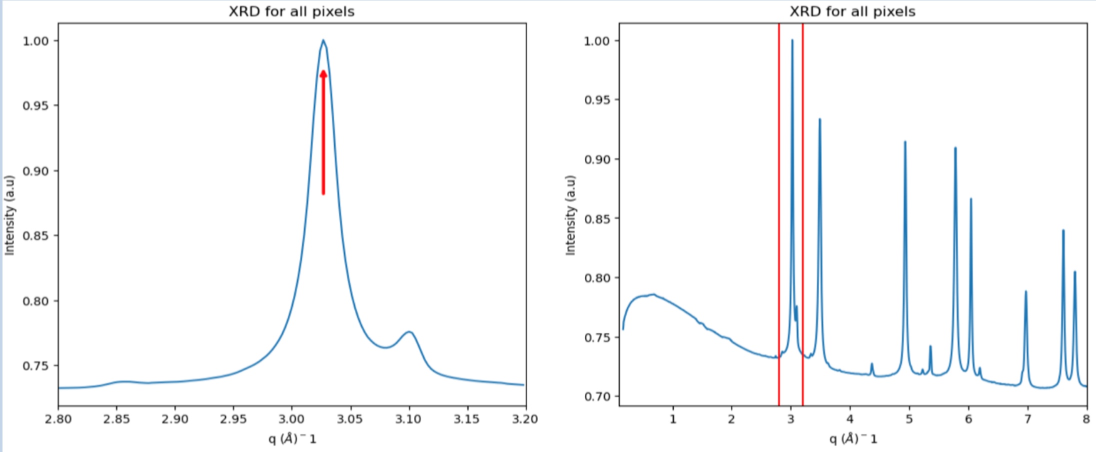


Chromium: 5.39 keV peak

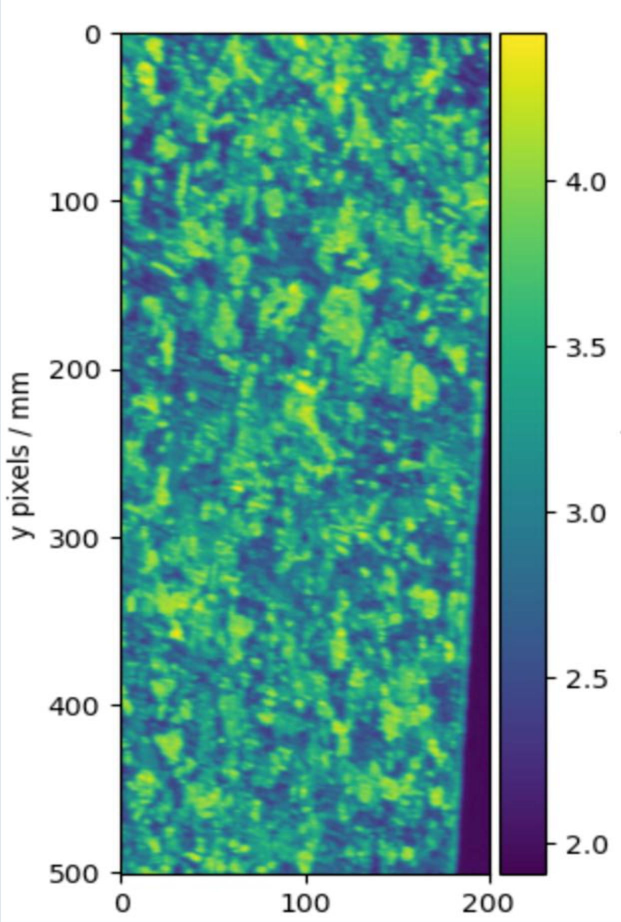


Iron: 6.38 keV peak

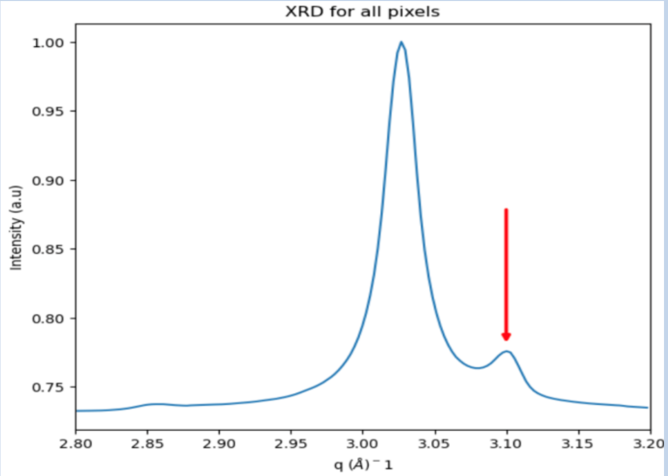
X-ray diffraction (XRD): Fe (111)

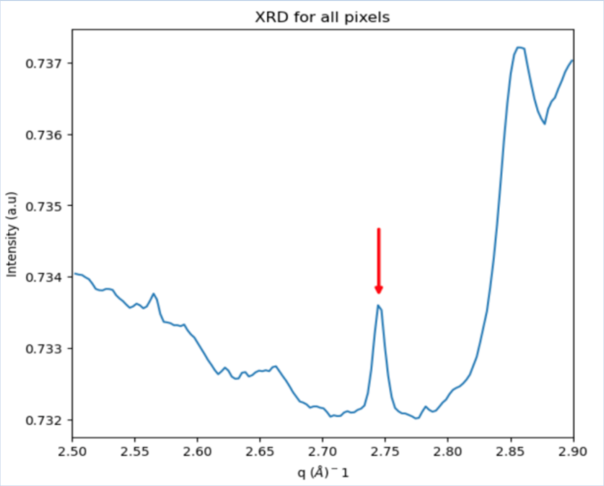


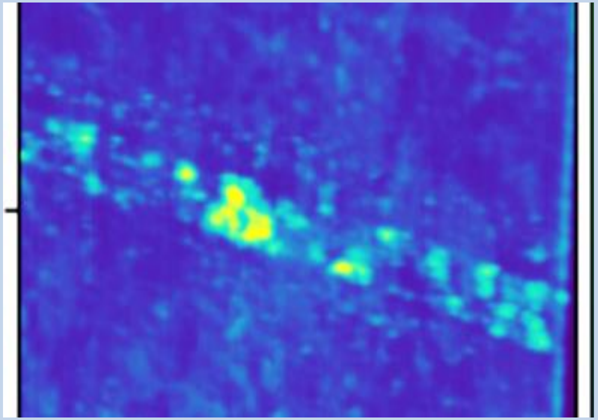
Map of intensity for each position

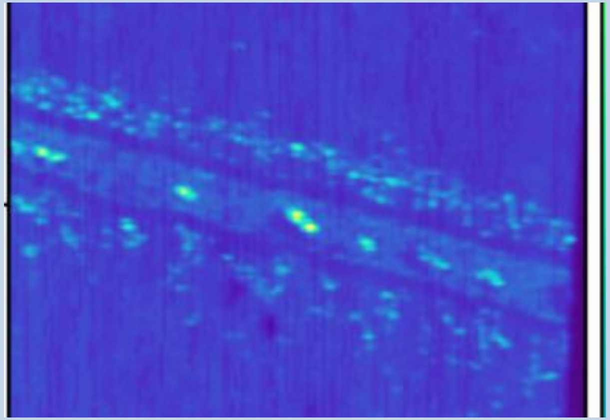


Other peaks in XRD





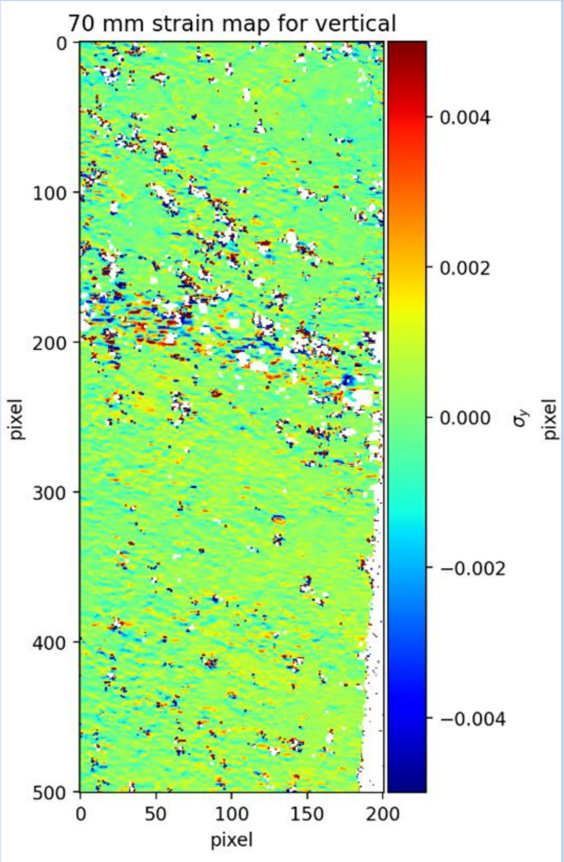




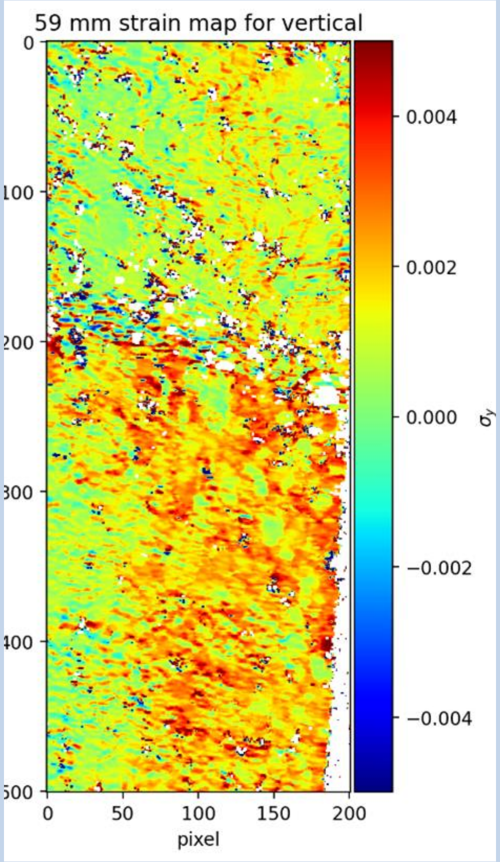
- These peaks could disappear in a low-resolution averaging method
- Spatial distribution crucial to understand the material!

Applied stress experiment

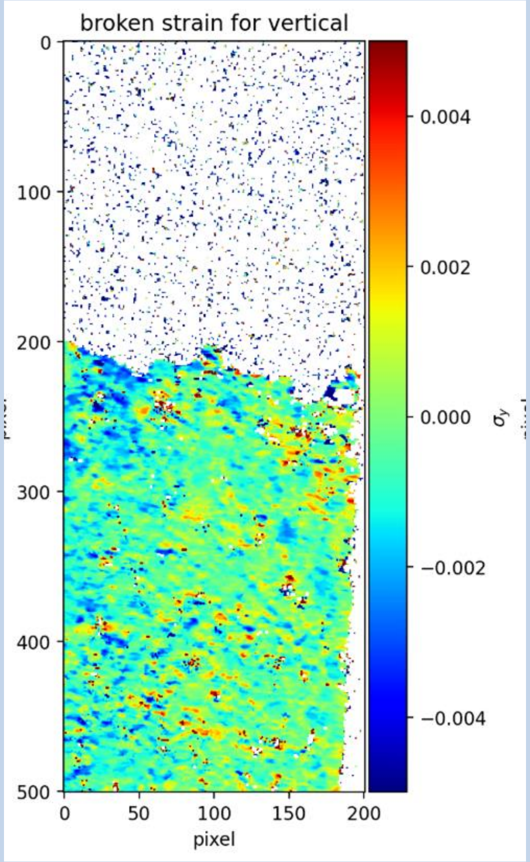
Small stress



High stress

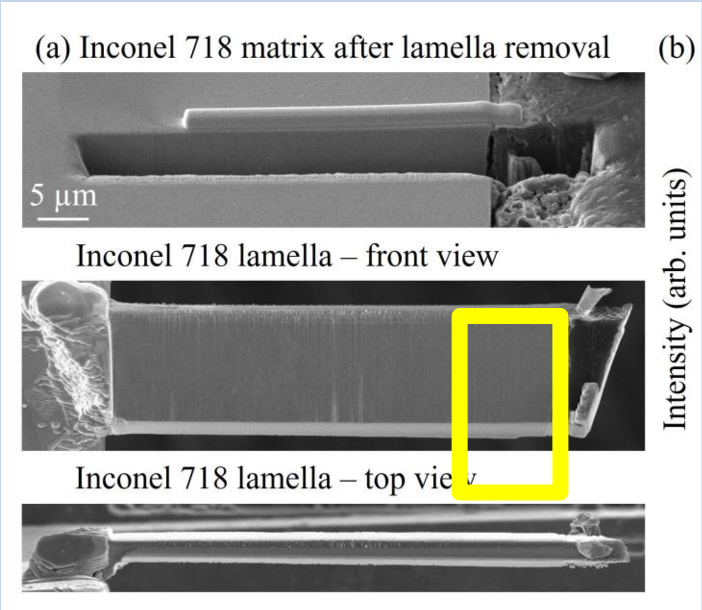


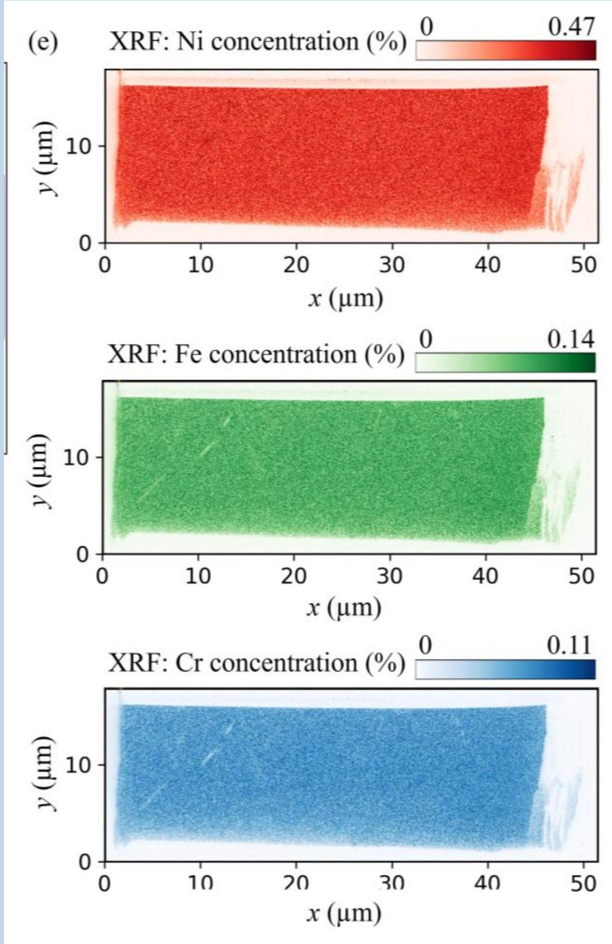
After failure

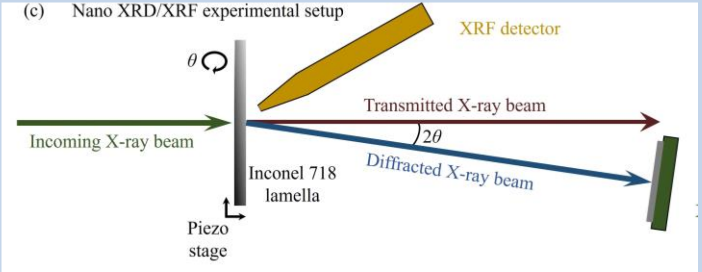


Nanobeam investigations: Inconel White layer

- White layer formed in Inconel 718 super alloy by machining
- Thin lamella extracted by focused ion beam (FIB)
- Investigated at NanoMax beamline, ~ 90 nm beam

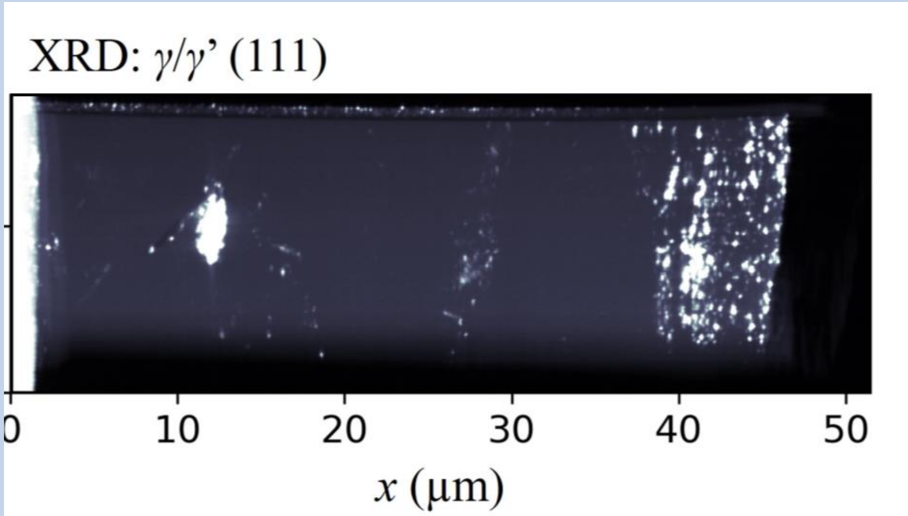


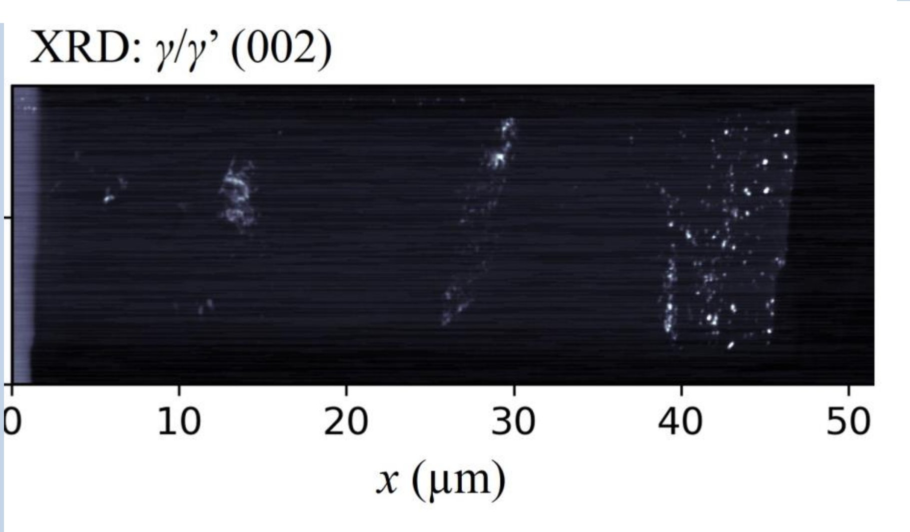


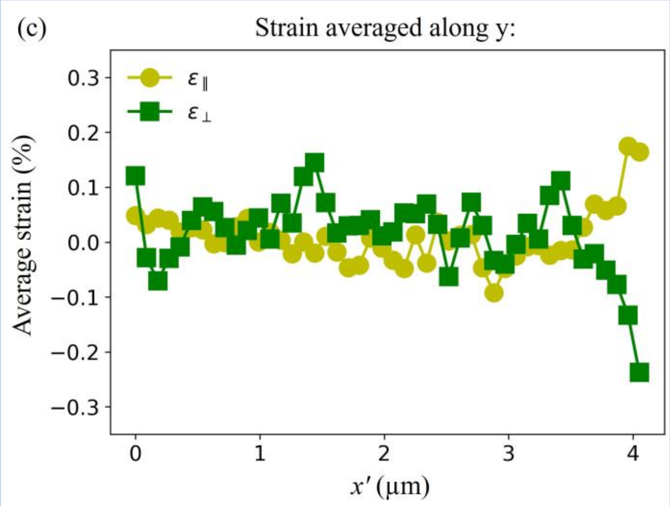


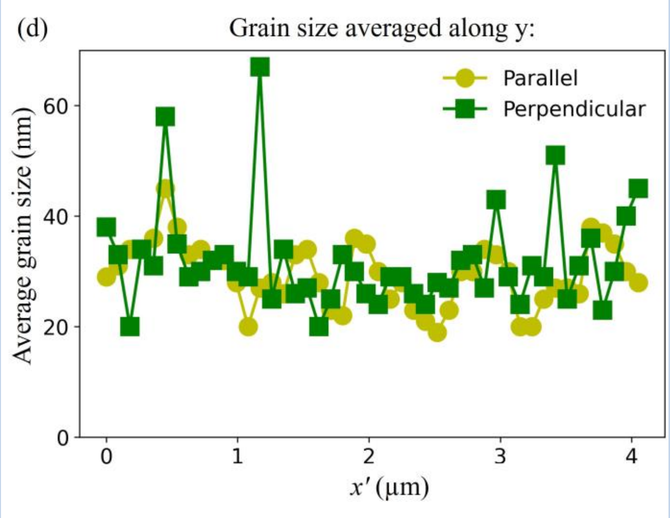
L. Marcal, et al., " **Materials & Design** 239, 112789 (2024)
https://doi.org/10.1016/j.matdes.2024.112789

Scanning X-ray diffraction

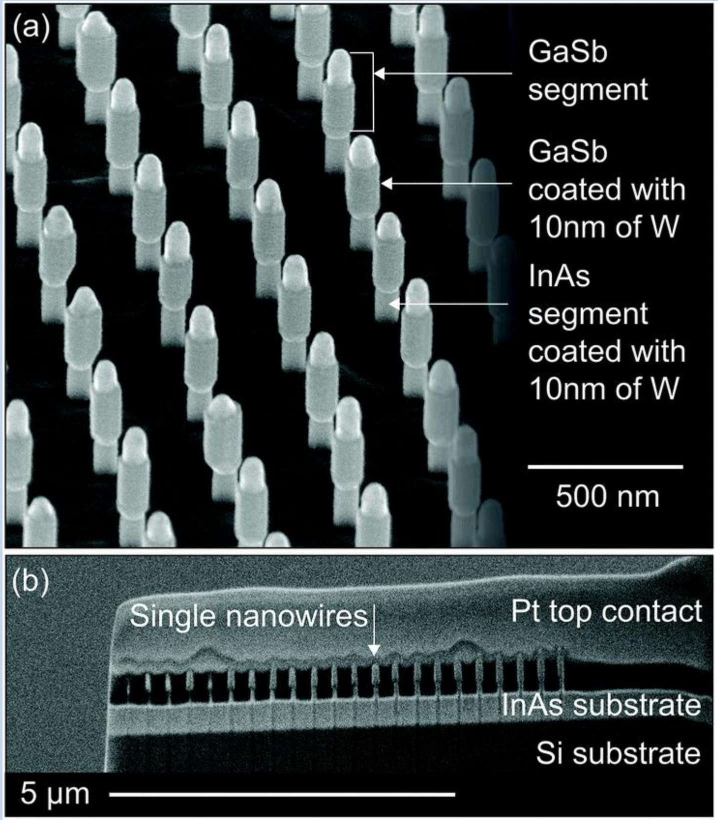


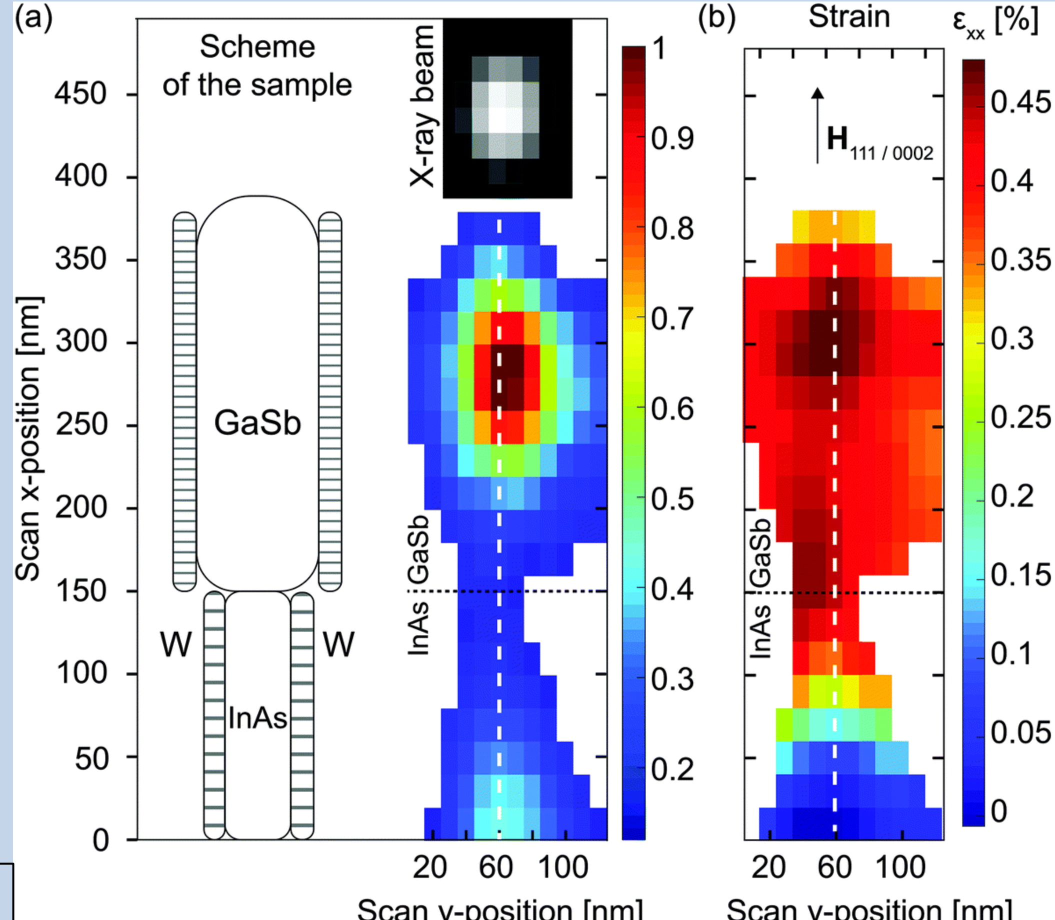






Nanobeam experiment at NanoMax: Strain within single crystal nanowire transistor

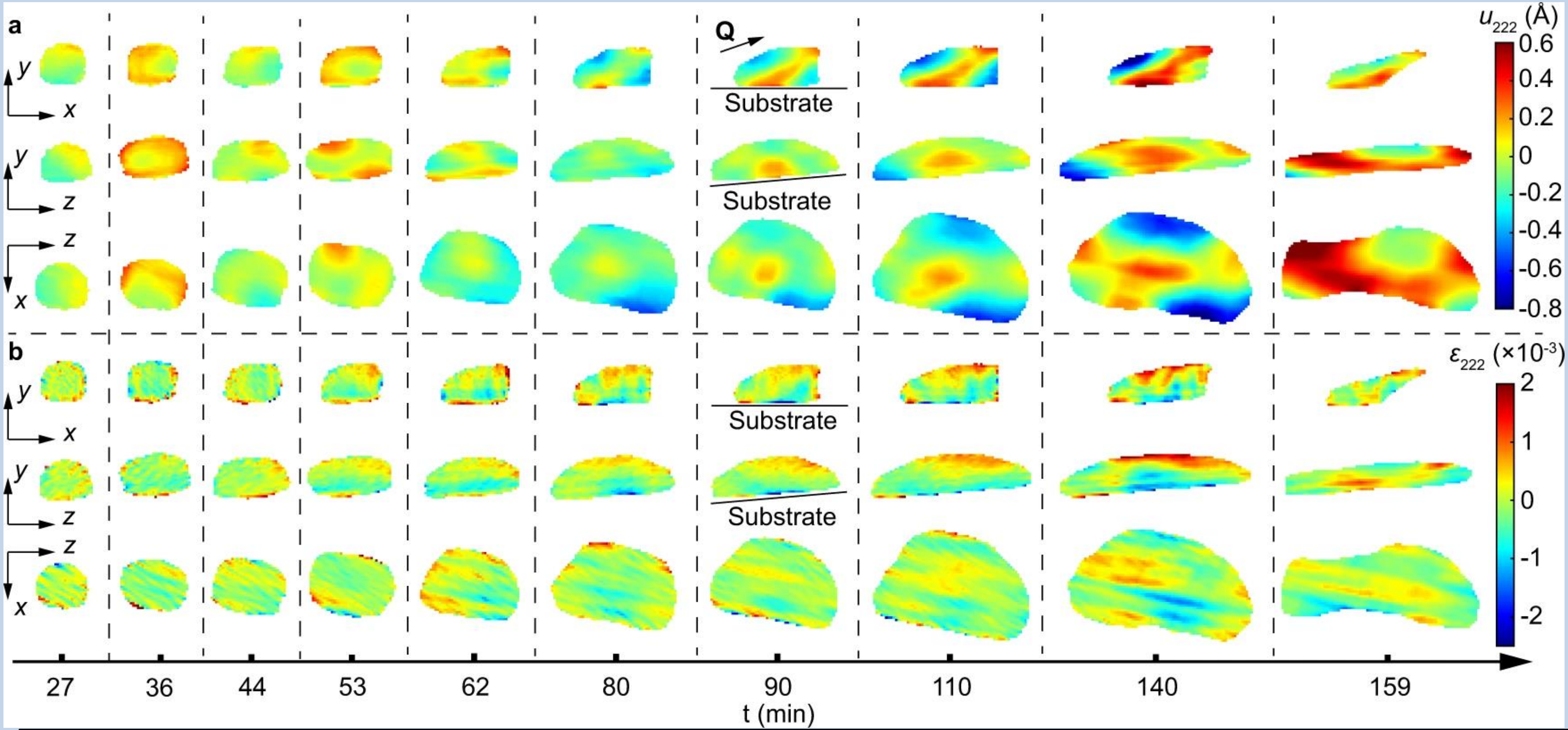




D. Dzhigaev, et al, **Nanoscale** 12 (27), 14487 (2020) http://doi.org/10.1039/D0NR02260H

In situ imaging of InO single grain growth

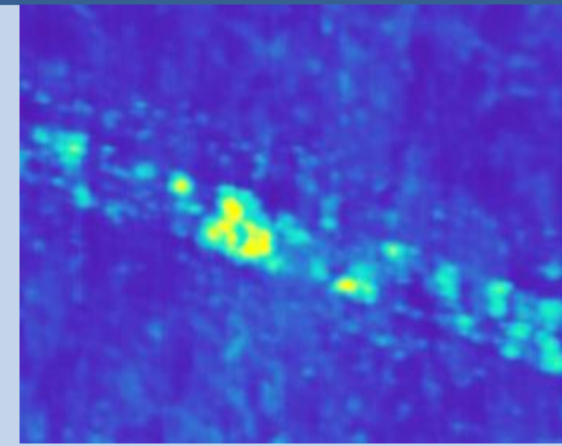
- 3D imaging single grain growth from ~100 nm to ~500 nm
- Shape and strain

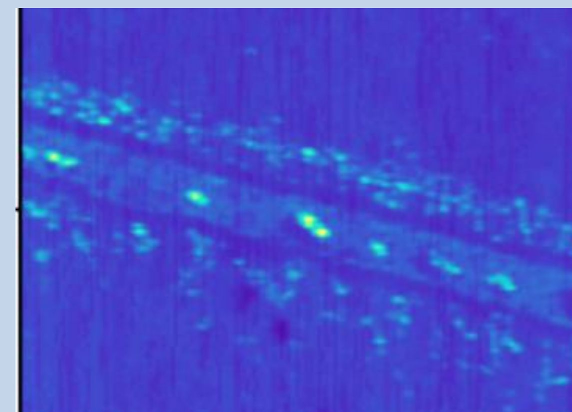


D. Dzhigaev, et al., *"Three-dimensional in situ imaging of single-grain growth in polycrystalline In2O3:Zr films"* **Communications Materials** 3 (1), 38 (2022) http://doi.org/10.1038/s43246-022-00260-4

Summary

- Synchrotrons can now give real-space resolution ranging from 10 micron down to <100 nm
- Spatial resolution can give new, often unexpected, insight into materials
- Local measurements can discover rare phases
- Measuring composition with XRF can be important to understand XRD results
- Can be combined with operando / in situ setups





Thank you for your attention

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- Lucas Marcal, now at the Brazilian Synchrotron
- Dmitry Dzhigaev, now at Bosch
- Aksel Mihailov and Ingrid Klint, summer students
- NanoMax & DanMax teams

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