X-ray beam induced phase transitions at DUBBLE

observations at a bending magnet beamline

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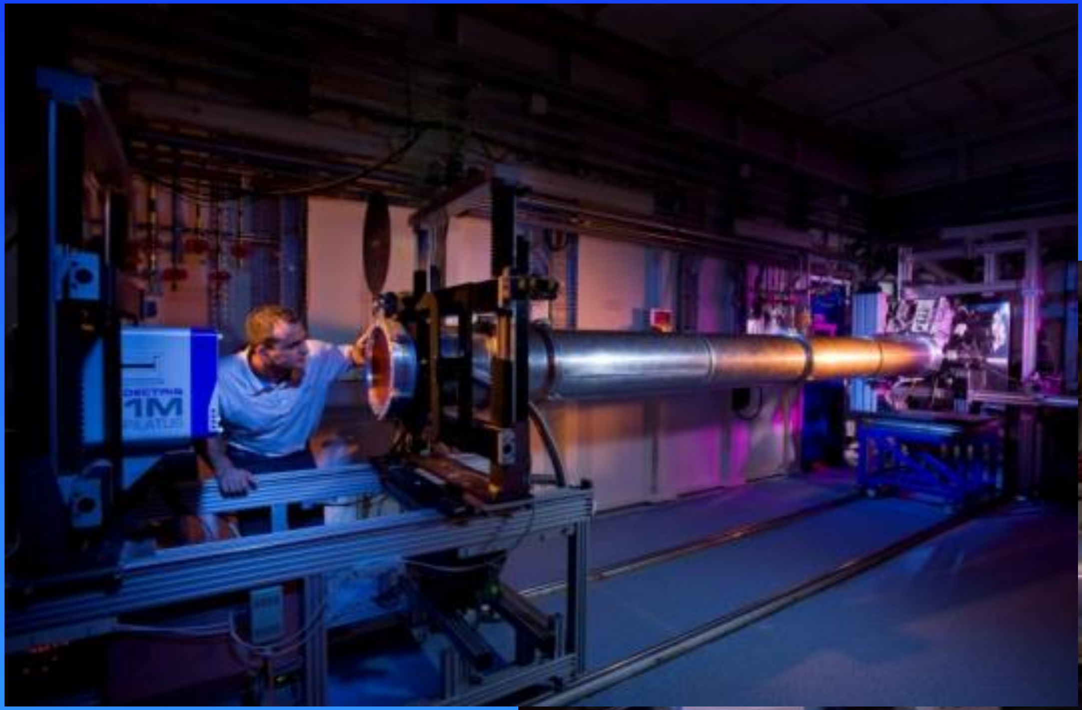
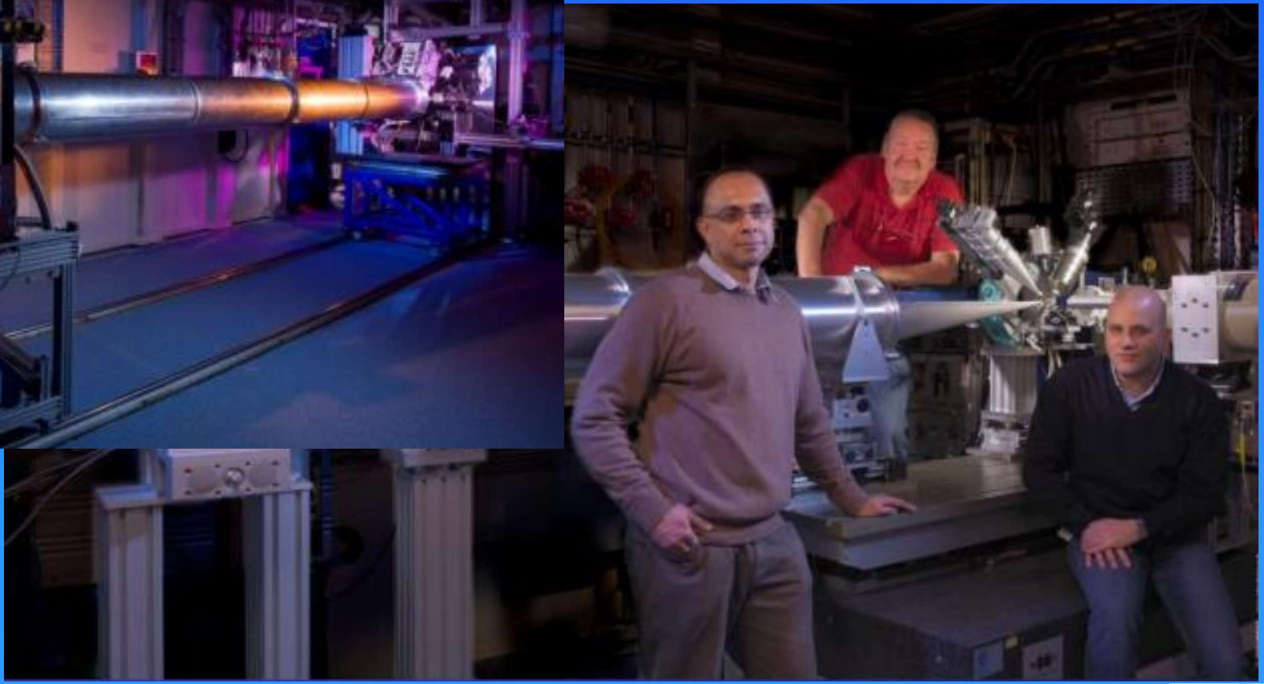
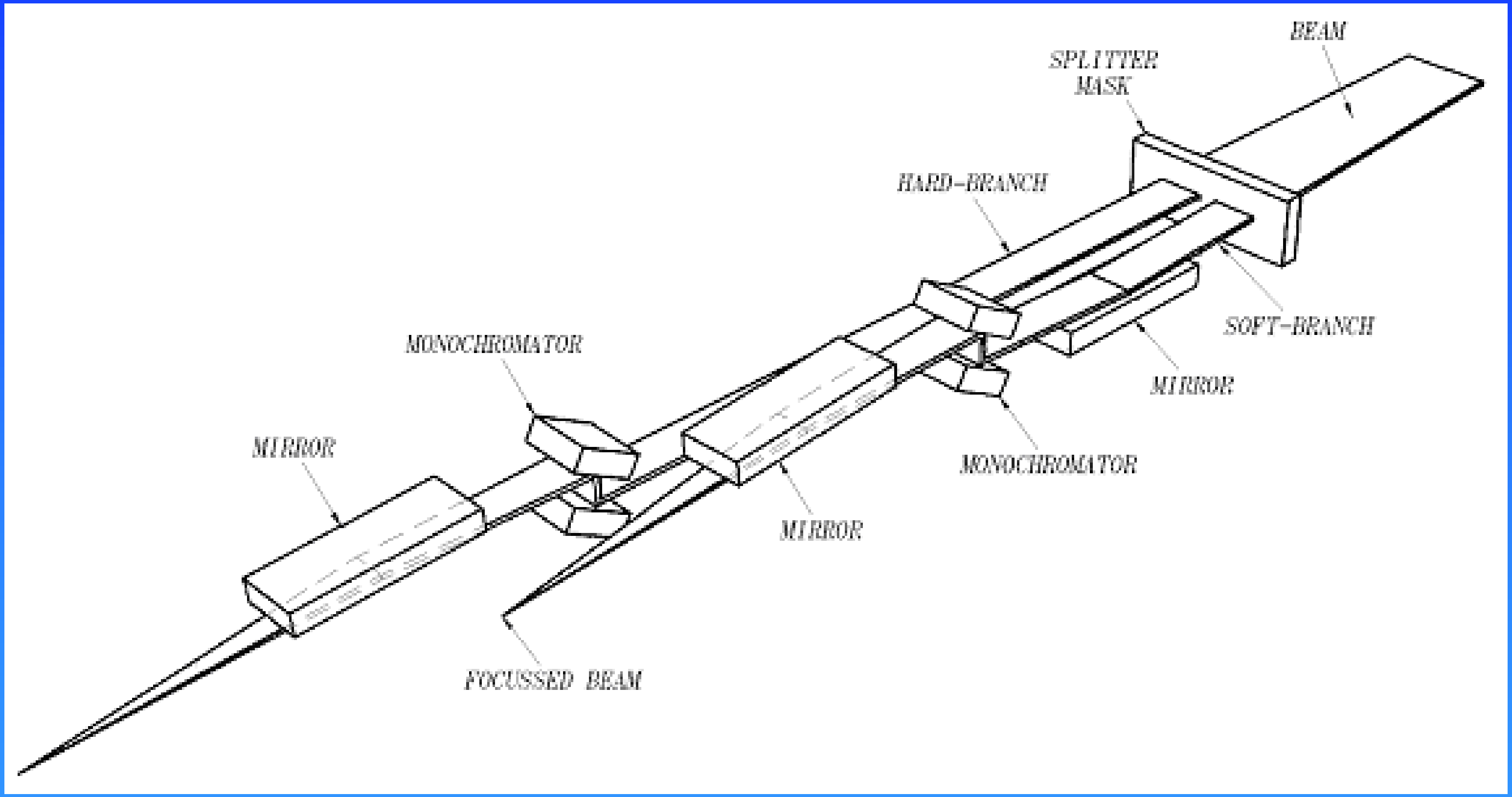
DUBBLE:

x-ray scattering and spectroscopy





DUBBLE:
x-ray scattering and spectroscopy



BM26B:
SAXS/WAXS

BM26A:
EXAFS/XANES

“beamline energetics”

- typ. photon energy range 5 – 30 keV
- typ. flux: $10^{10} – 10^{11}$ s^{-1} (bending magnet)
- Beam spot size approx. 0.5 x 1 mm^2

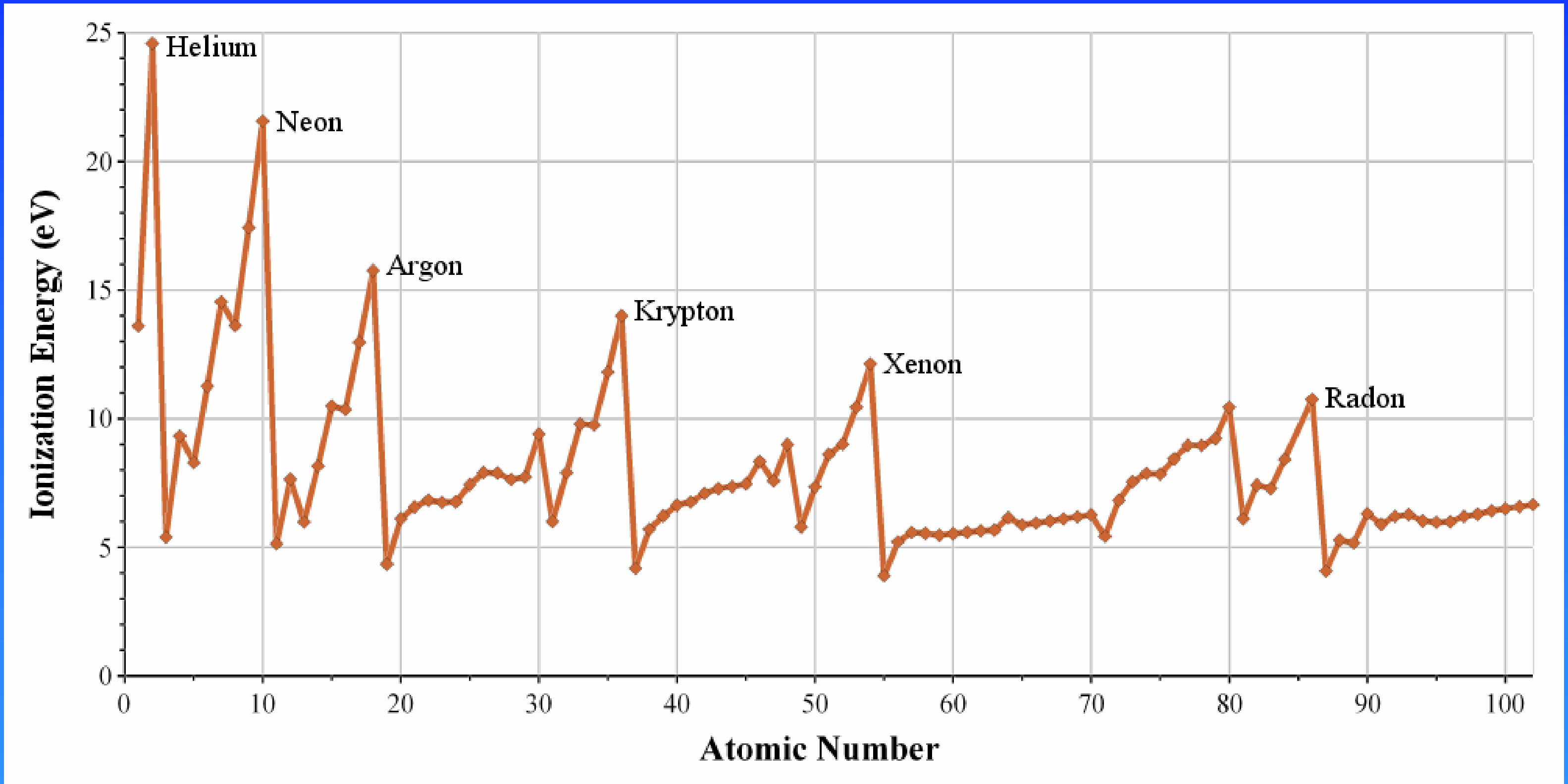
or 8 – 480 µW !

→ *not high power*
(or high power density) !

Dissociation?

Bond	Bond	Bond-dissociation energy at 298 K			Comment
		(kcal/mol)	(kJ/mol)	(eV/Bond)	
C–C	Carbon	83–85	347–356	3.60–3.69	Strong, but weaker than C–H bonds
Cl–Cl	Chlorine	58	242	2.51	Indicated by the yellowish colour of this gas
Br–Br	Bromine	46	192	1.99	Indicated by the brownish colour of Br_2 Source of the $Br^{\bullet}$ radical
I–I	Iodine	36	151	1.57	Indicated by the purplish colour of I_2 Source of the $I^{\bullet}$ radical
H–H	Hydrogen	104	436	4.52	Strong, nonpolarizable bond Cleaved only by metals and by strong oxidants
O–H	Hydroxide	110	460	4.77	Slightly stronger than C–H bonds
OH–H	Hydroxide-Hydron	64	268	2.78	Far weaker than C–H bonds
C–O	Monoxide	257	1077	11.16	Far stronger than C–H bonds
O–CO	Dioxide	127	532	5.51	Slightly stronger than C–H bonds
O=O	Oxygen	119	498	5.15	Stronger than single bonds Weaker than many other double bonds
N≡N	Nitrogen	226	945	9.79	One of the strongest bonds Large activation energy in production of ammonia

Ionisation Energy



Hydrogen radicals?

Courtesy: Ed Mitchell, ESRF

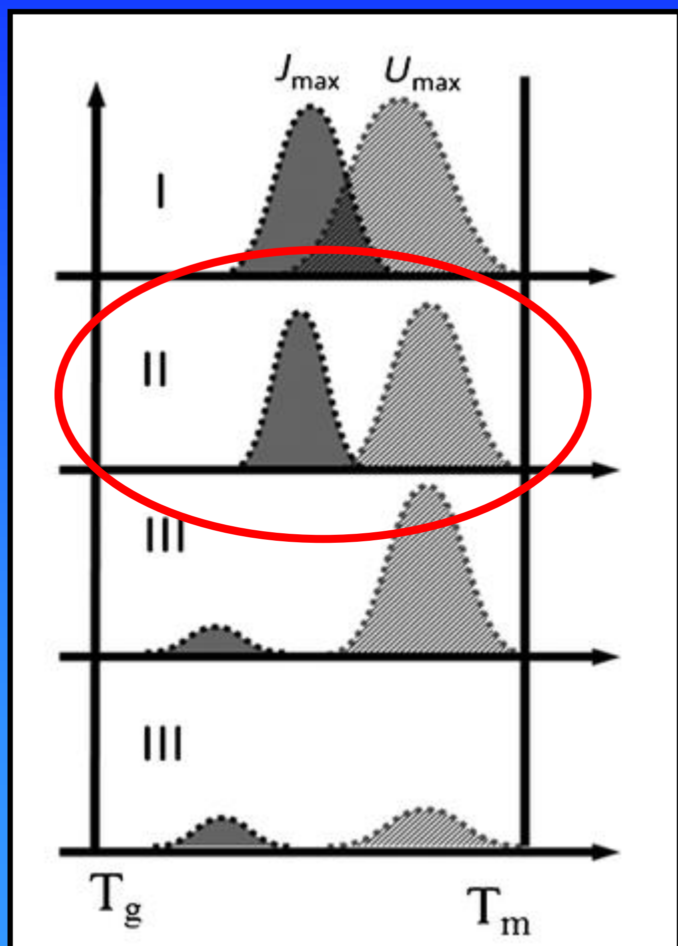
Protein diffraction:

Crystals cooled during experiment

Switch of cryo-stream

Crystal warms and what happens?

Glass devitrification experiments

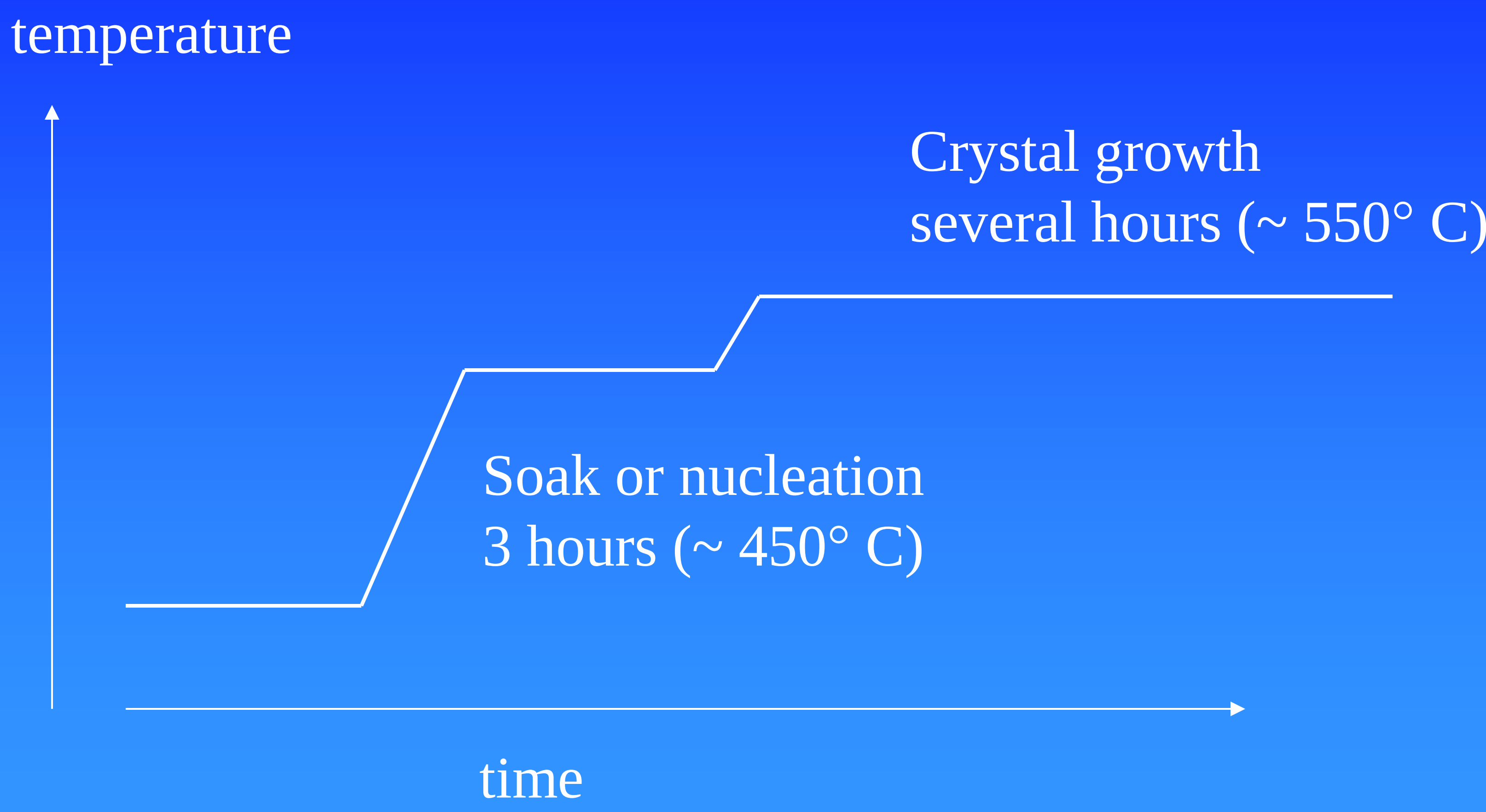


$LiSi_2O_5$

Bulk nucleating material:

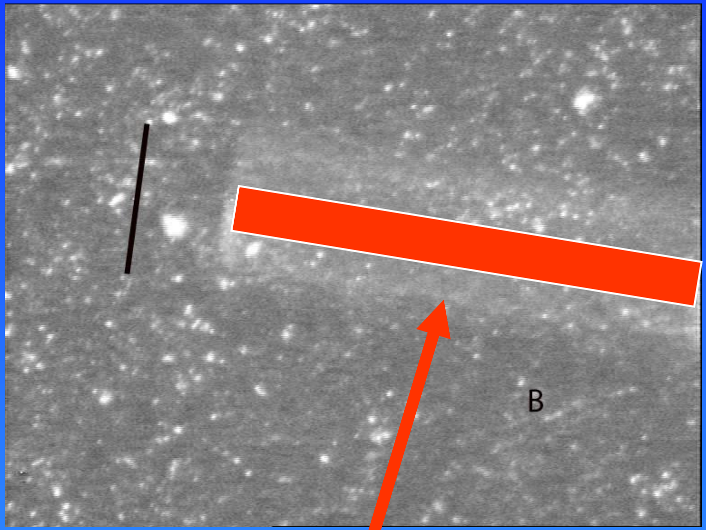
J - nucleation rate
U - growth rate

Experiment on 200 micron thick platelet

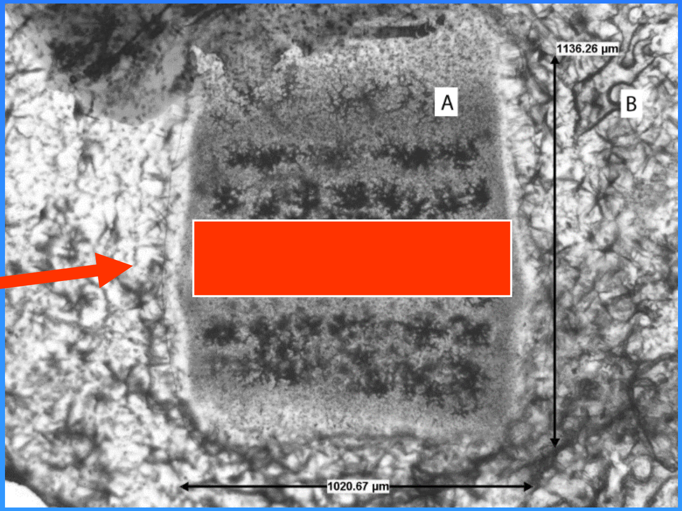


Post mortem optical microscopy

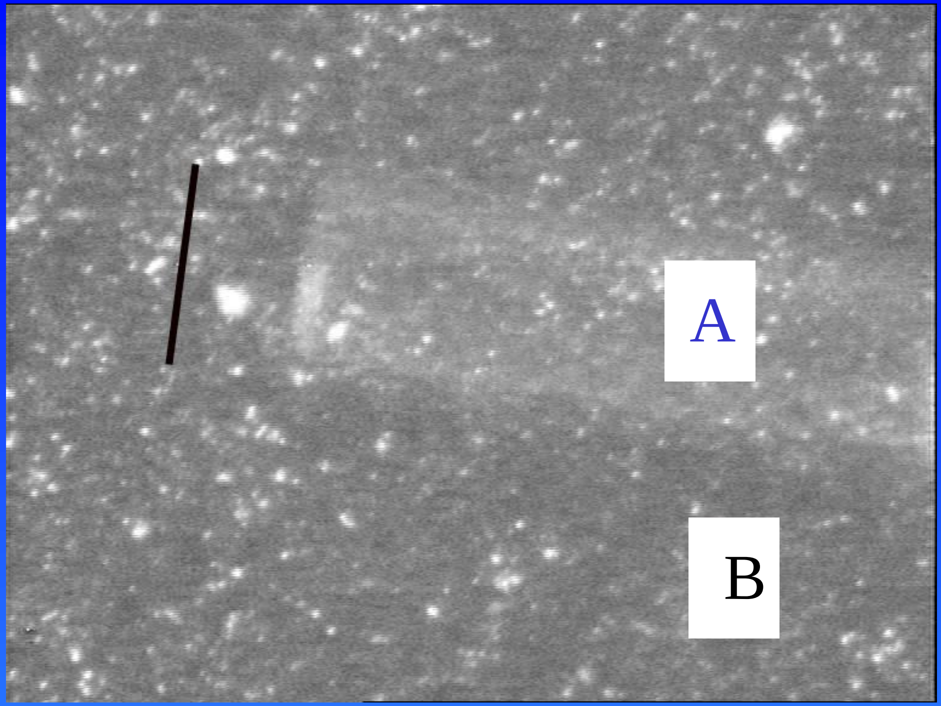
Partially crystallised



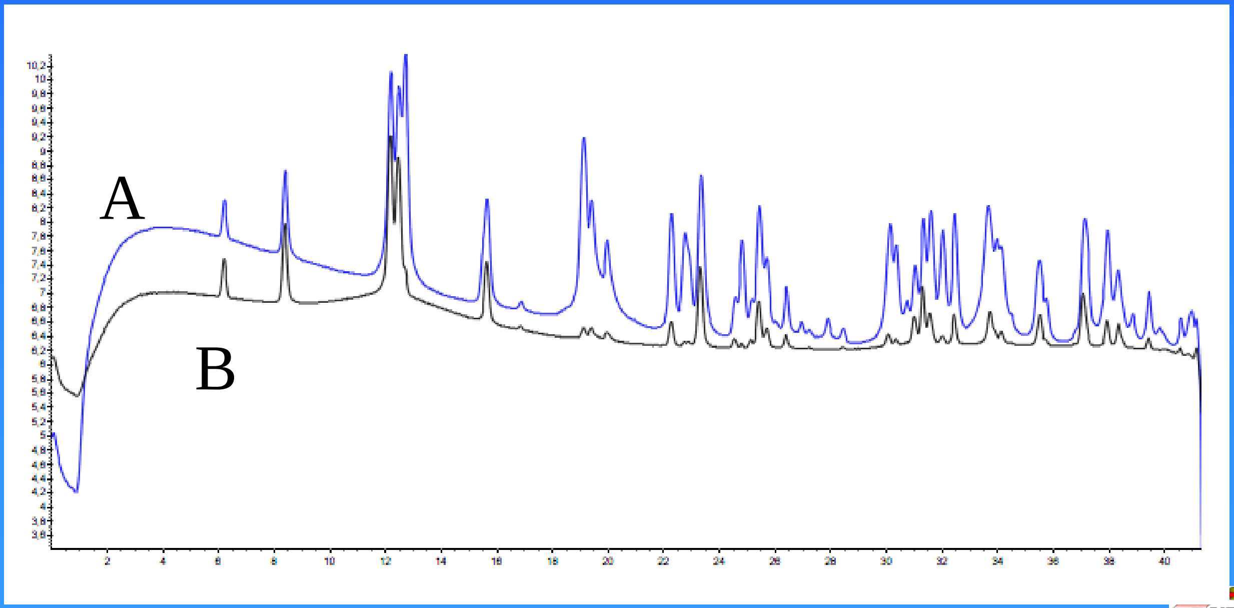
Fully crystallised

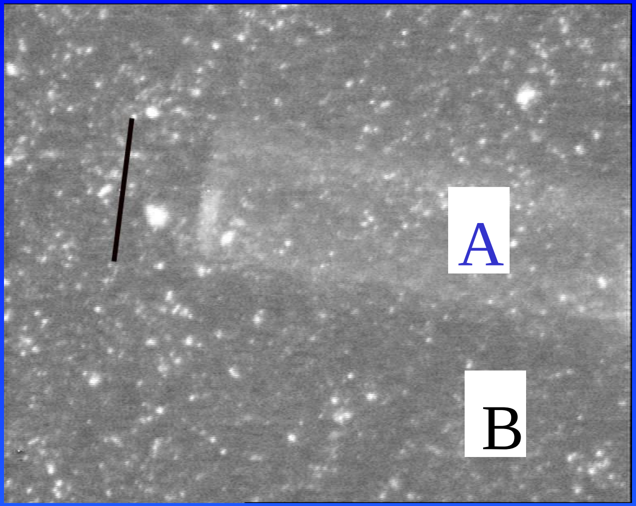


Real beam size

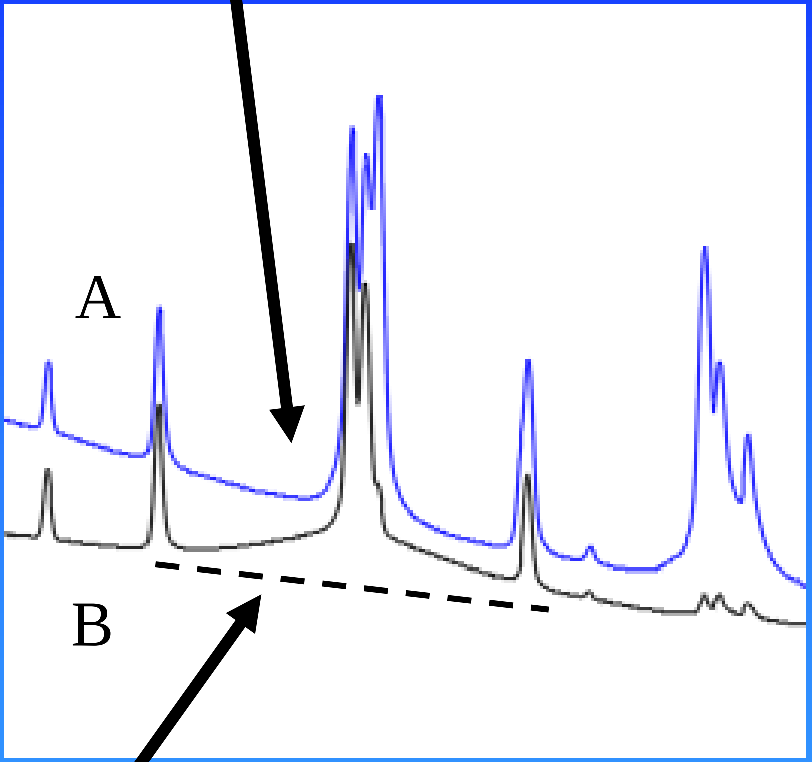


Post mortem
powder diffraction





Amorphous halo absent



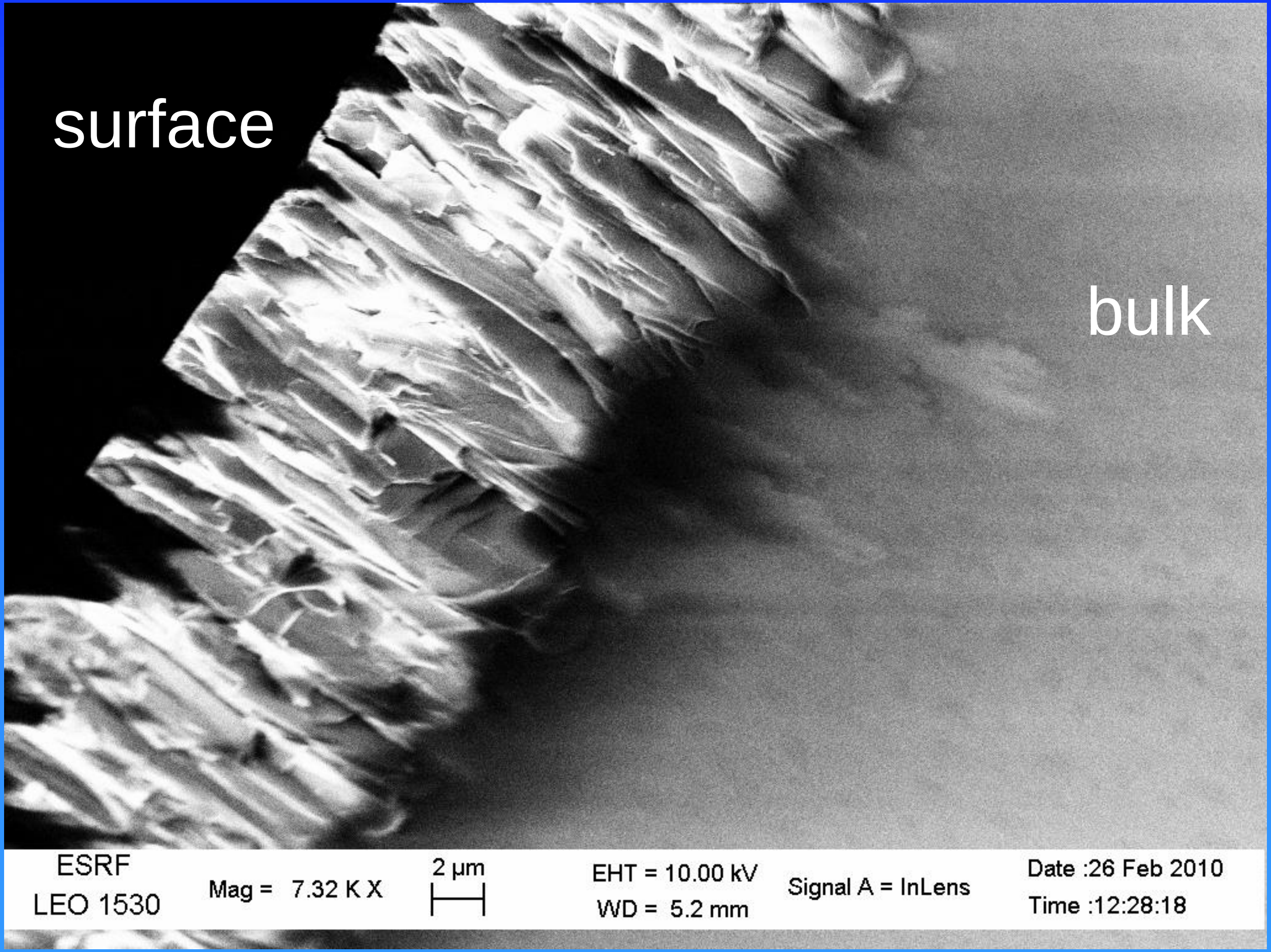
Sample should only be partially crystallised according to recipe

Amorphous halo still present

- in irradiated region the sample has crystallised faster than in the non-irradiated region!

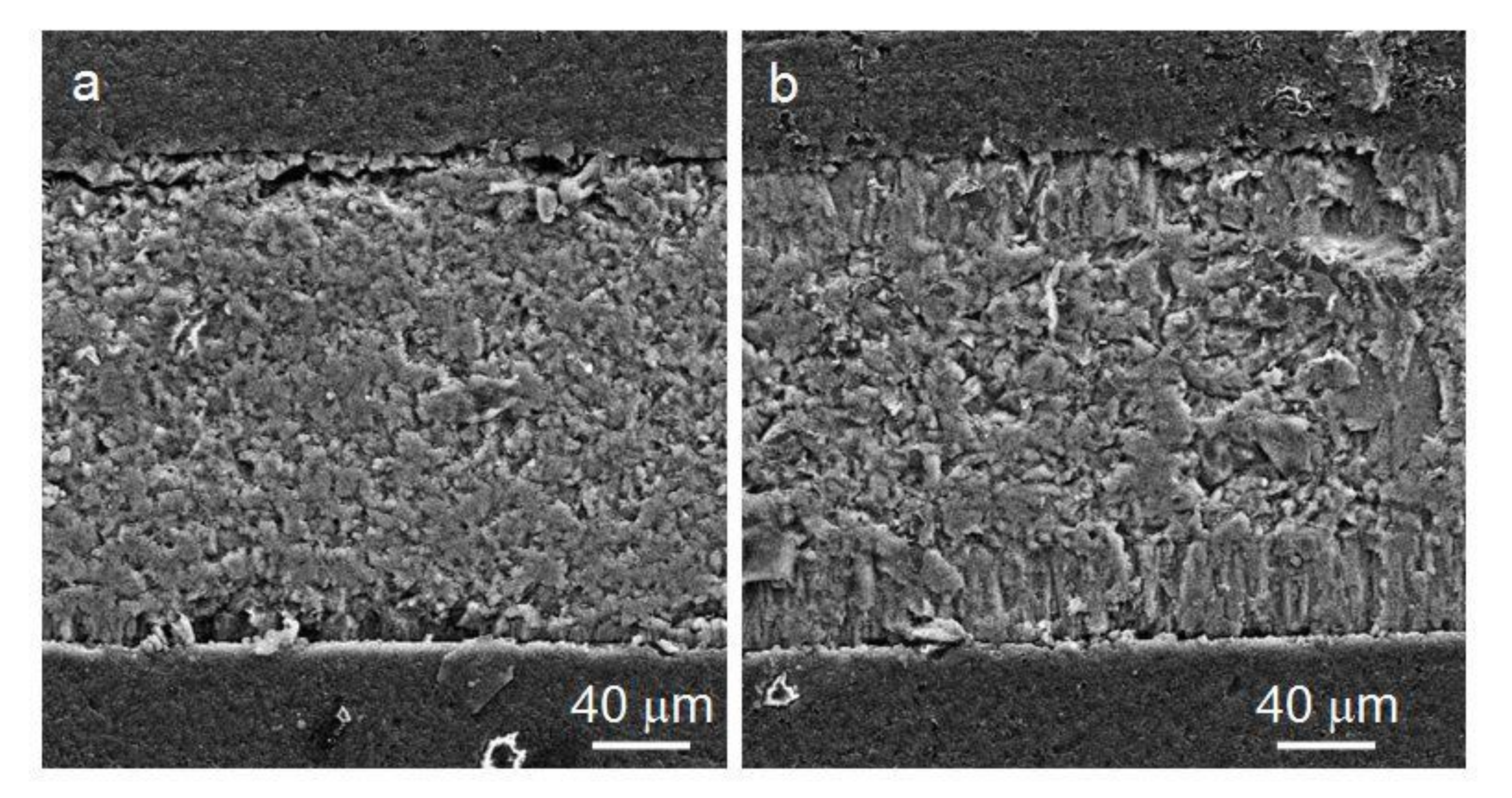
…. depth specific ???

SEM partially crystallised



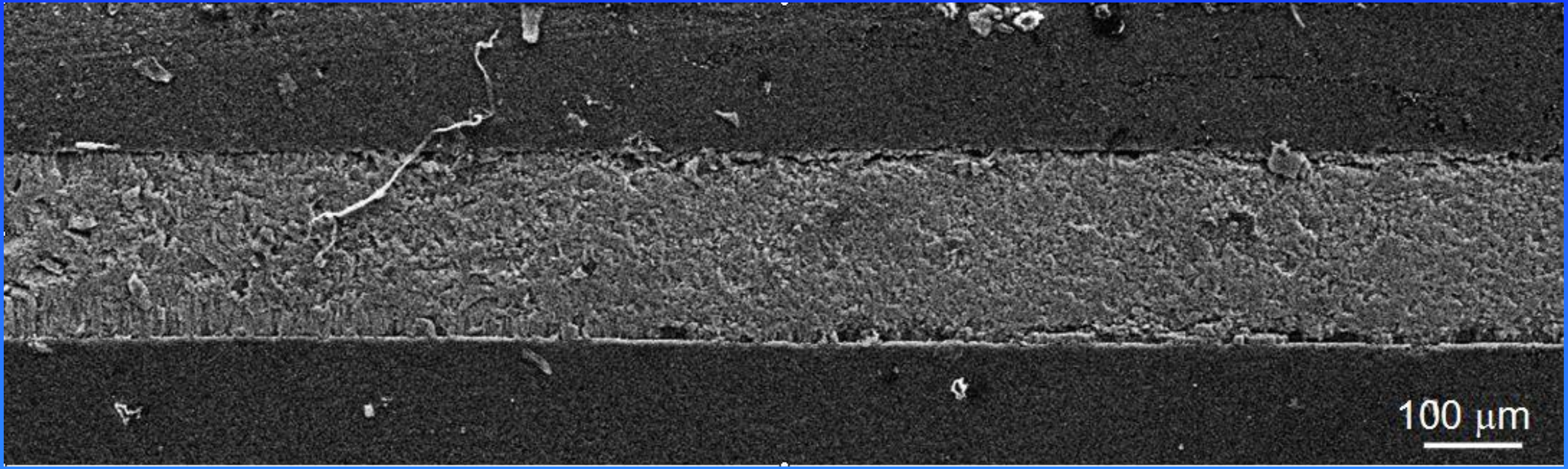
- Sample should bulk crystallise
- There clearly is a textured crystalline layer
- The degree of crystallinity is higher than in the bulk

SEM fully crystallised sample



Irradiated by X-rays

Not irradiated by X-rays



Not irradiated → Irradiated

Powder diffraction

Irradiated

Not irradiated

- X-rays on during whole process
  - Fine morphology
  - No surface layer
  - Faster crystallisation
  - No texture
- X-rays on only during crystallisation
  - Texture increased
  - Surface layer absent
- X-rays off
  - Coarse morphology
  - Surface layer
  - Slower crystallisation
  - texture

- It is clear that the X-rays influence the crystallisation process
- The X-rays induce crystallisation
- Strongest effect during the thermal nucleation treatment
- Flux 10^{11} photons/sec in 0.3 x 2 mm^2
- The X-rays influence the crystallisation in a larger area than the direct beam
- This only occurs in the vertical direction

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What is happening?

- Local heating? Not sufficient energy deposited to influence kT dependent processes
- Most likely due to electrons liberated in sample (photo electric effect)
- One way or another these electrons help to create nucleation sites

But…

- This would not explain the vertical extension of the affected region
- This is around 100 micron (either side of beam)
- The path of scattered electrons is at most microns

But…

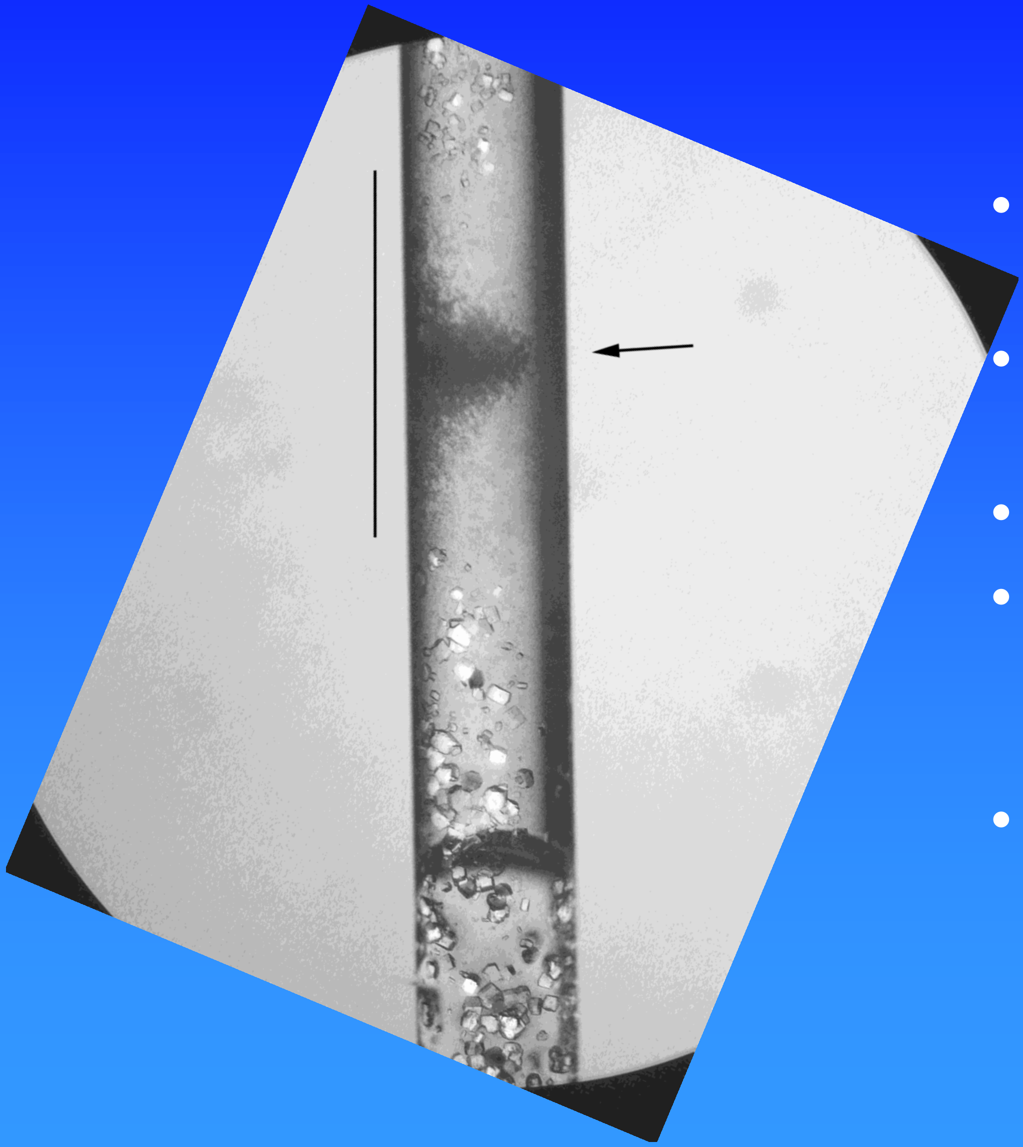
- 10 keV photons can travel around 100 micron in this sample

- The synchrotron photons are polarized
- They will be scattered in the vertical direction

What is most likely:

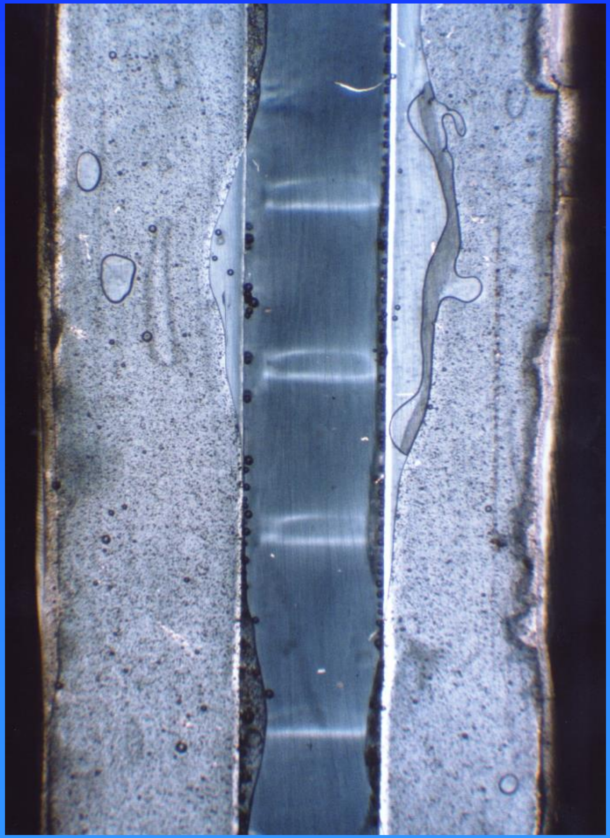
- Part of photons in direct beam get absorbed and release electrons
- Part of photons scatter but still have enough energy
- These get absorbed and release electrons
- How exactly the electrons create nucleation sites is <u>not well</u> understood

Earlier work



- On-line lysozyme crystallisation
- Radiation damage in beam spot
- 8 keV photons
- No crystallisation in region of 1 mm above/below beam
- Hydrolysis products don’t ‘travel’ that far

Earlier work



- Microtubule (rigid rod) solutions
- Beam spot 300 micron vertical
- Radiation damage around 1 mm vertical direction

Take home message:

- The effects of radiation in your sample can extend way beyond the size of the beam spot
- Exact nature of exchange of photon energy to sample is complex and depends on several parameters

Thank you for your attention!

- SR allows tuning of photon energy & spot size and intensity over a large range with full control !
- More than lithography ?