The Abdus Salam
International Centre
for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

2359-27

Joint ICTP-IAEA Workshop on Physics of Radiation Effect and its Simulation for Non-Metallic Condensed Matter

13 - 24 August 2012

Some unexpected X-ray interactions with matter

Wim Bras

ESRF, Grenoble
France

Strada Costiera, 11 - 34151 - Trieste - Italy • Tel. +39 0402240111 • Fax. +39 040224163 • sci_info@ictp.it • www.ictp.it
ICTP is governed by UNESCO, IAEA, and Italy, and it is a UNESCO Category 1 Institute

Some unexpected X-ray interactions with matter

Wim Bras
DUBBLE @ ESRF
Netherlands Organization for Scientific Research (NWO)

Outline

- Glass ceramics
- Polymers
- Protein solutions

7.3.3 ALS
BM26A ESRF

Energy range

- Most SR experiments used for structure determination $2 < E < 30$ keV photons
- Electronic structure studies $E < 2$ keV

- I will be dealing with structure determination, i.e. photons around 20 keV

X-ray beam

- At modern sources size 20 – 500 micron
- On special microfocus lines < 2 micron
- Number of photons in beam 10^{10} – 10^{14}/sec
- absorption in sample most times ≈ 60%

- This means hardly any heating due to beam (10^{-4} K/sec)
  - This is only relevant at cryogenic temperatures

Radiation interaction

- Elastic/ inelastic scattering
  - All/most photon energy ‘leaves’ the sample
- Absorption
  - Mostly converted to photo electrons
  - Maximum electron energy is photon energy minus ionisation energy (i.e. E – tiny bit)
  - 30 keV photo electrons do not have sufficient energy to displace atoms in amorphous/crystalline state
  - In liquids/polymers free radicals can be created

Kinetic energy not enough for direct structural change

10 keV electron at most

Confession time!

I know hardly anything about radiation damage

Why talk here then?

Well, there is this guy Andre….

You mean THE Andre???….Say no more…..!!!

I'll stick to phenemological descriptions ….

Sensible!
I think this Andre guy owes you a pint….

Do we really deposit energy in samples?

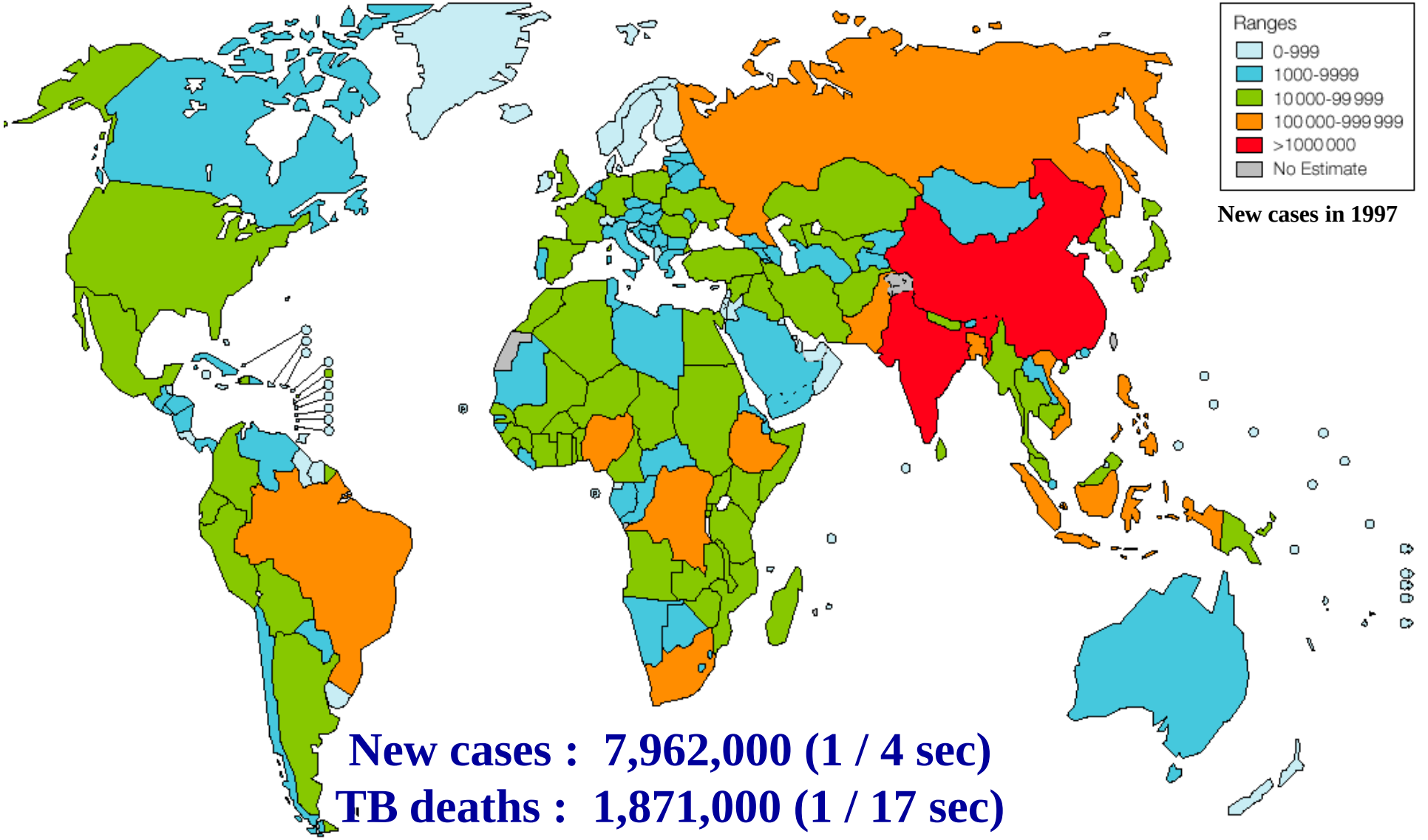
- The beams are intense but not extreme
- The photon energies are not enormous
- They have much less energy than compared with electron microscopy or ion bombardments

- So what is the big deal?

Protein crystallography

- Very popular at the moment
- In principle simple experiment
- Radiation damage issues widely studied
- Can be well controlled when sample are cryo-cooled (≈ 80 Kelvin)
- This freezes the free radicals
- This avoids major structural damage

Estimates of TB burden



New cases in 1997

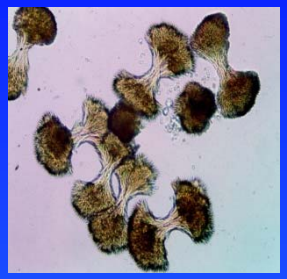
New cases : 7,962,000 (1 / 4 sec)

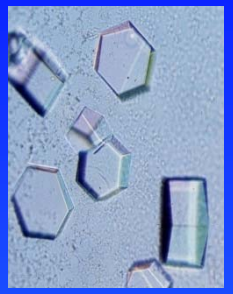
TB deaths : 1,871,000 (1 / 17 sec)

TB Crystals


Rv2610


Rv3628


Rv1908c


Rv2428

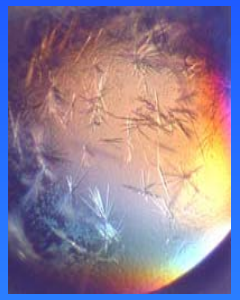

Rv2991


Rv2438c


$Rv0014c_{331}$

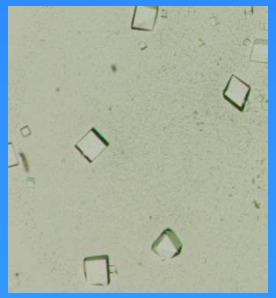

$Rv0014c_{279}$


Rv0813c


Rv0018c


Rv1846c


Rv0877


Rv2461c


Rv2276


Rv2883c


ML2640

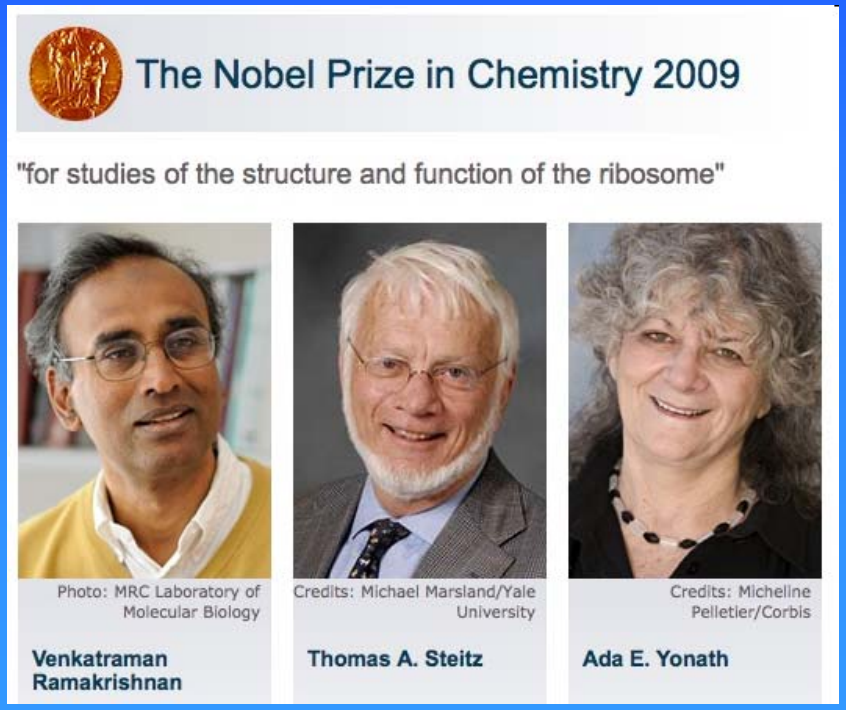

Rv2667


Rv0733

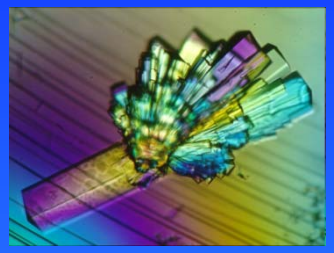

Rv2238

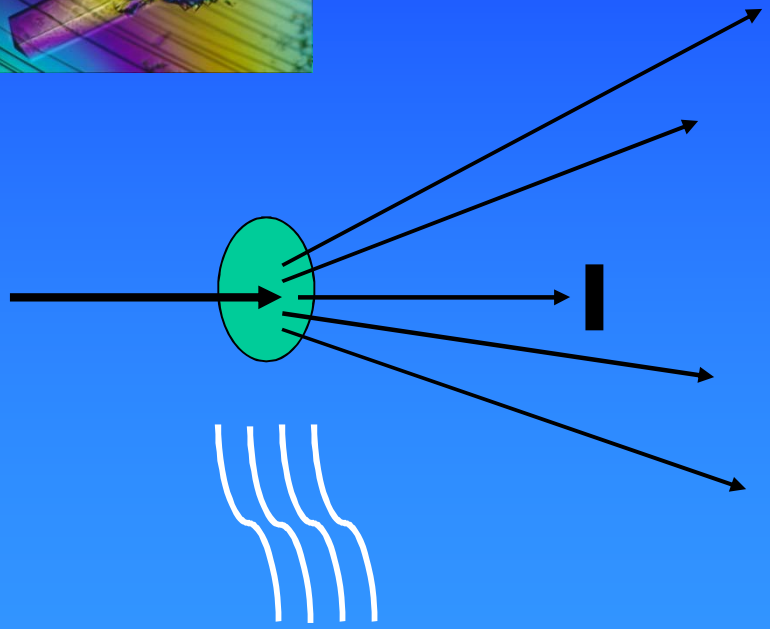
Protein crystallography

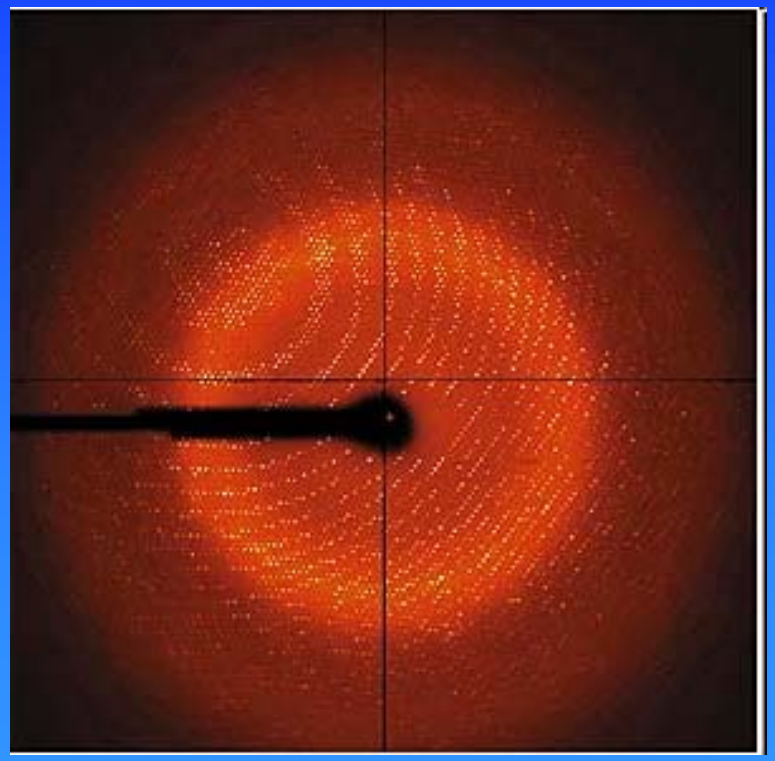
- One of the main applications of SR
- 25% of beam lines at the ESRF are dedicated to it



Protein crystallography

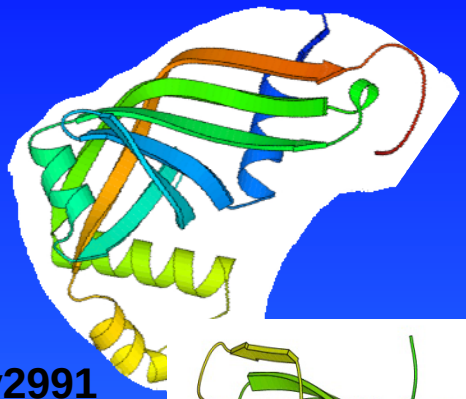




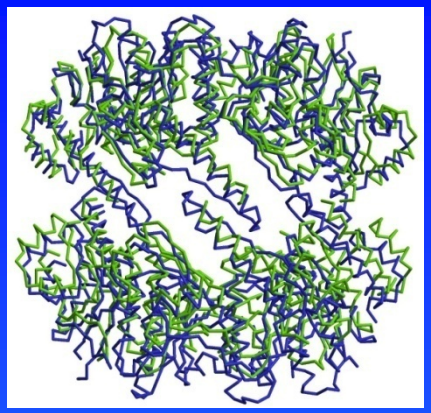


3D Structures

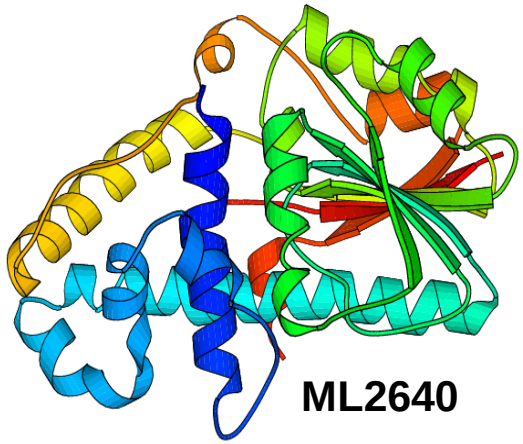
Rv3247c
tmK



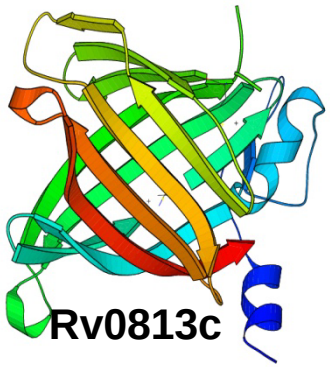
Rv2991



Rv2461c
clpP

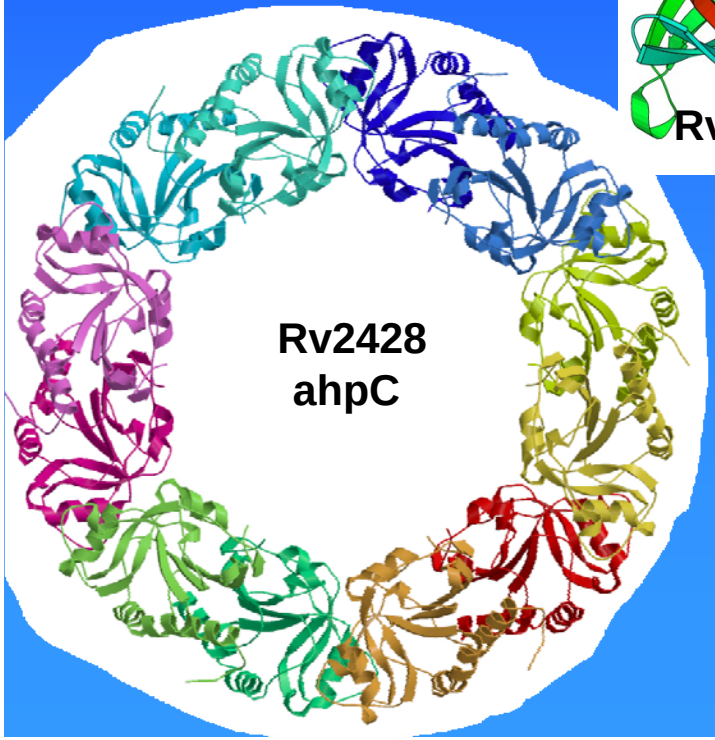


ML2640



Rv0813c

Rv0733
adK

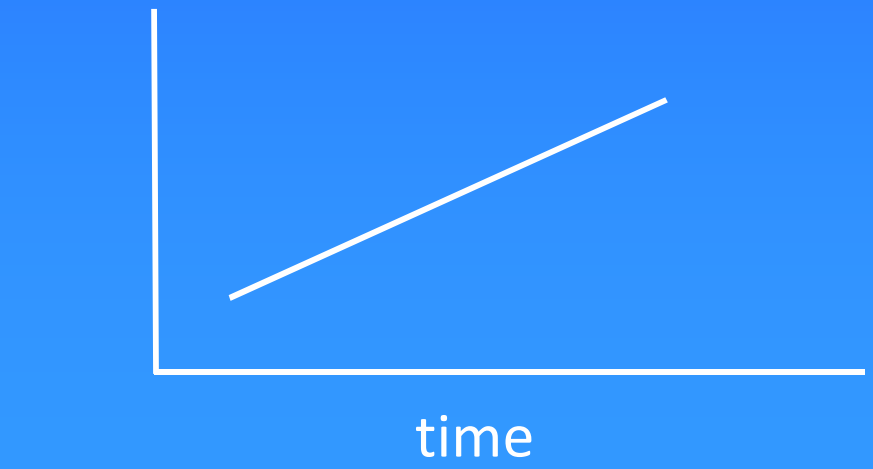


Rv2428
ahpC

Rv0014c
pknB

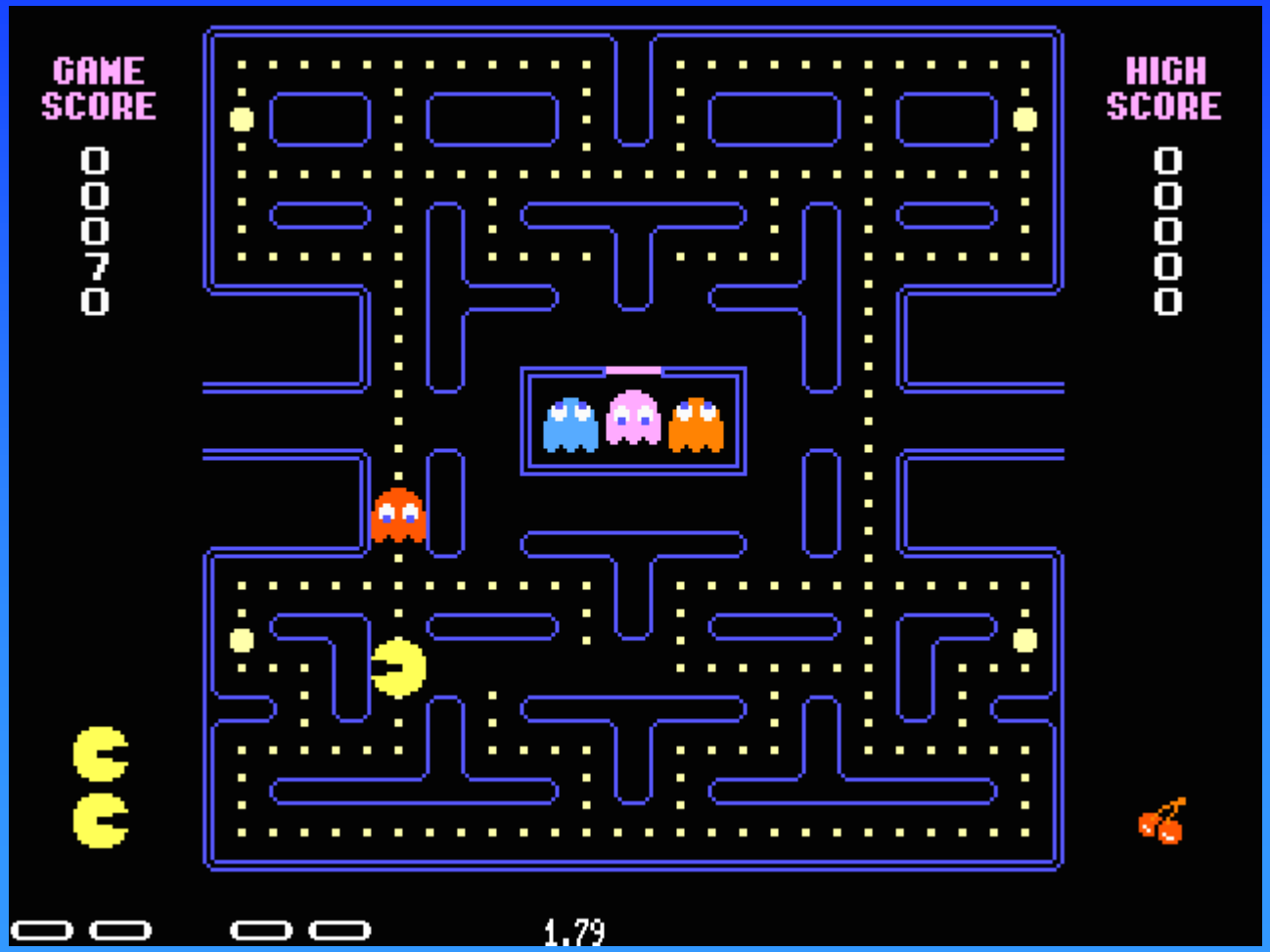
Protein crystal warmed up after experiment

Ed Mitchel/Sean McSweeney

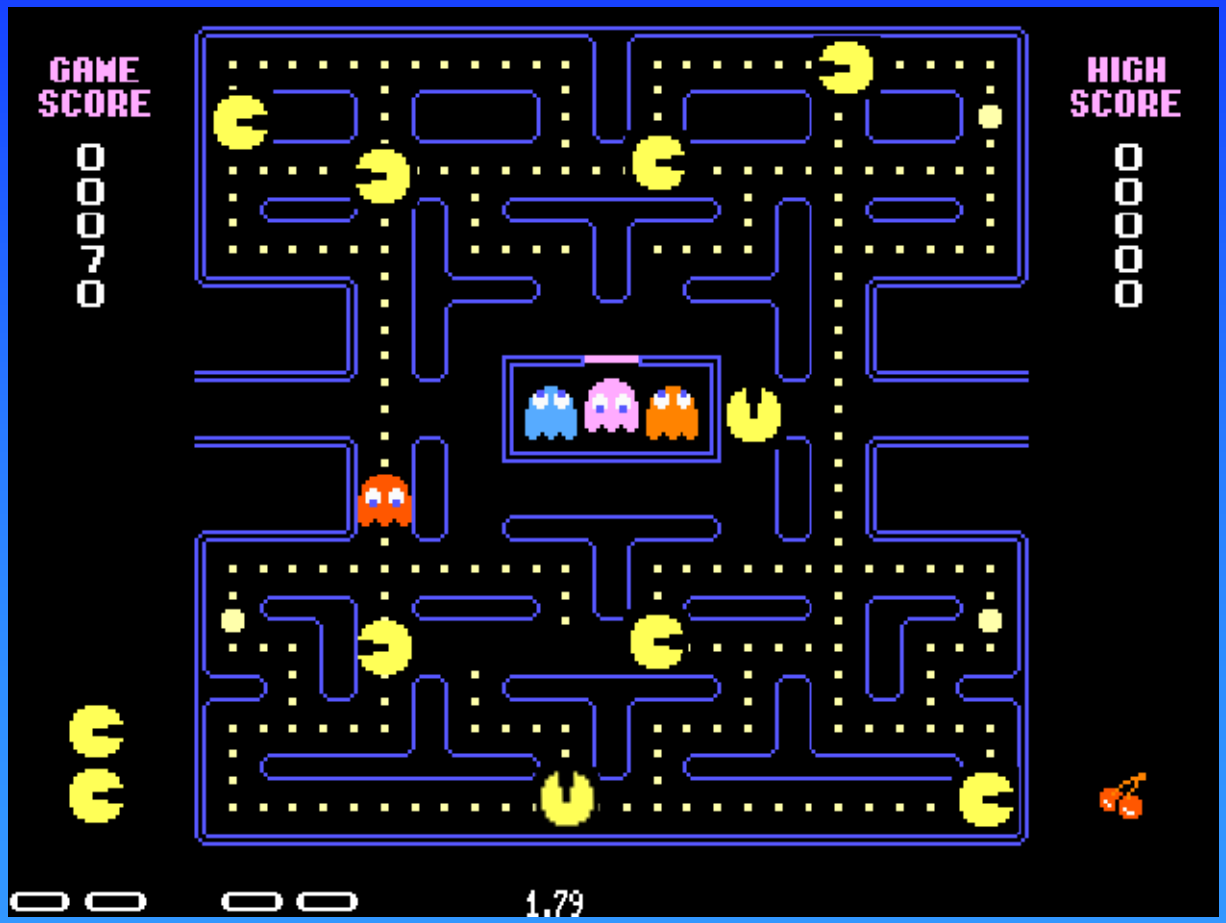


What happened?

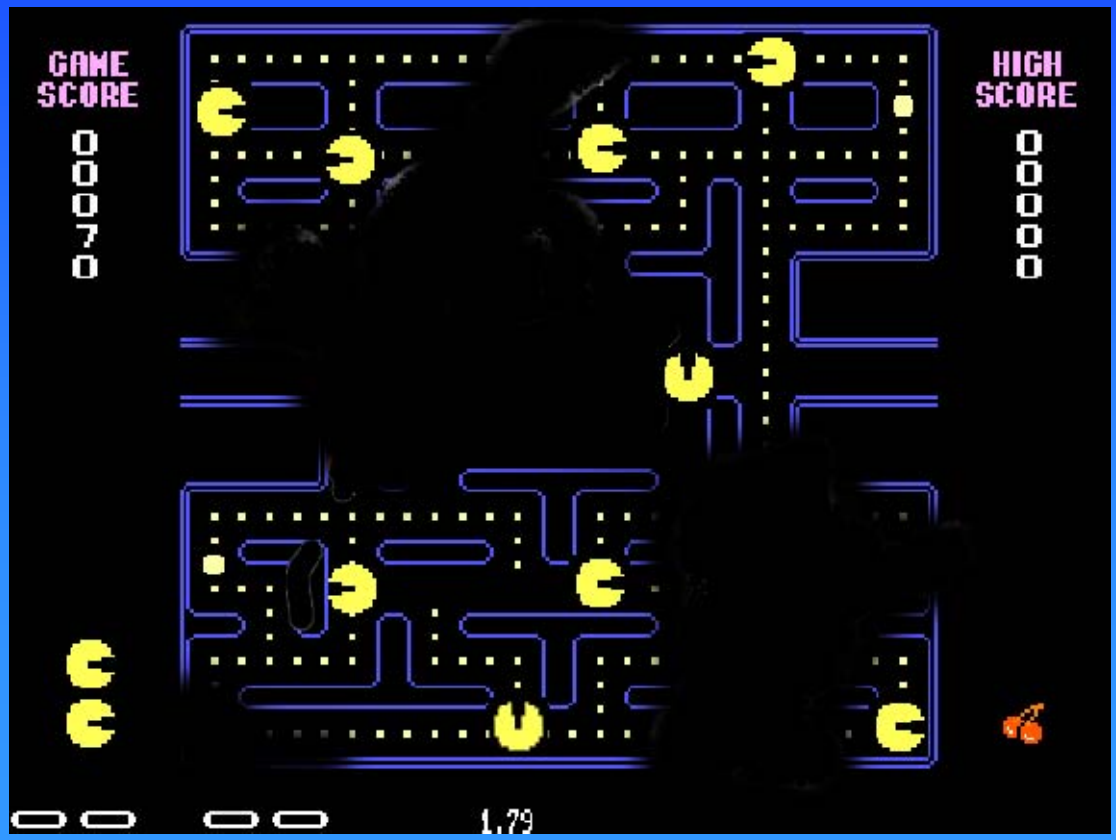
Free radicals become mobile



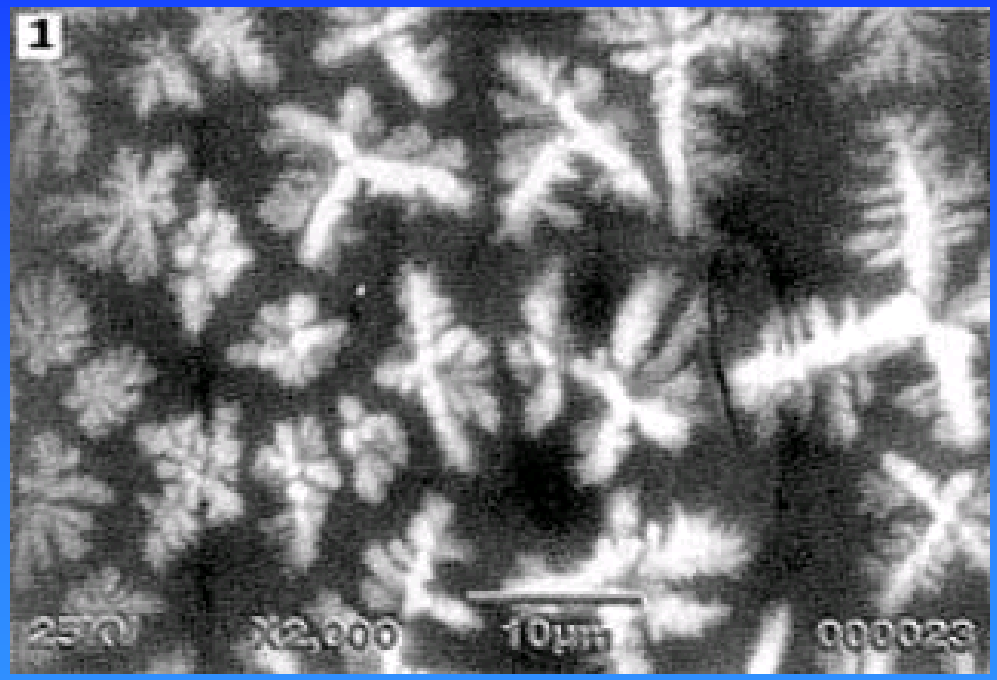
Not a single pac man but many



Pacman(s) didn’t only eat Blinky, Pinky, Inky and Clyde but they eat parts of the maze as well

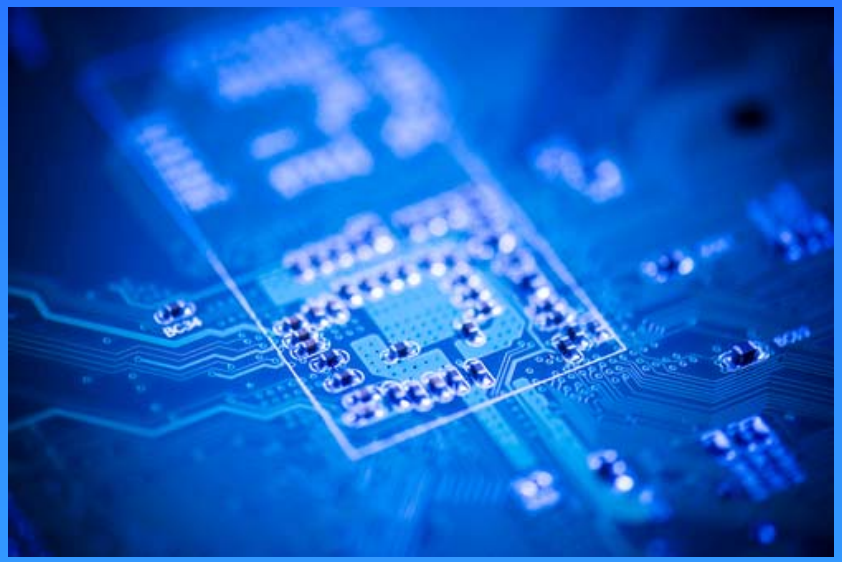


Glass ceramics

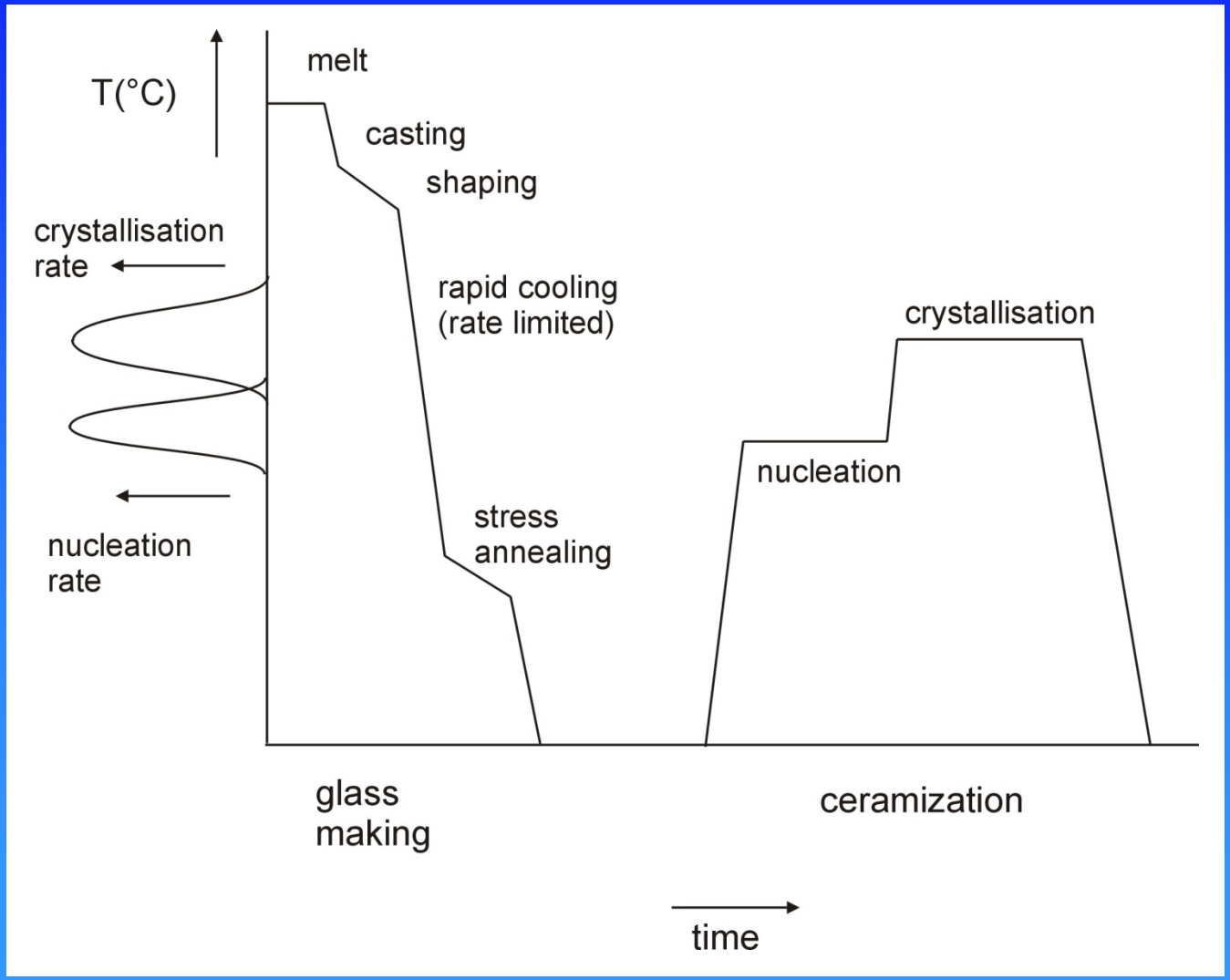


Composite material

$Li_2O \times Al_2O_3 \times nSiO_2$
$MgO \times Al_2O_3 \times nSiO_2$
$ZnO \times Al_2O_3 \times nSiO$



How to make them?



Lithium disilicate

$LiSi_2O_5$

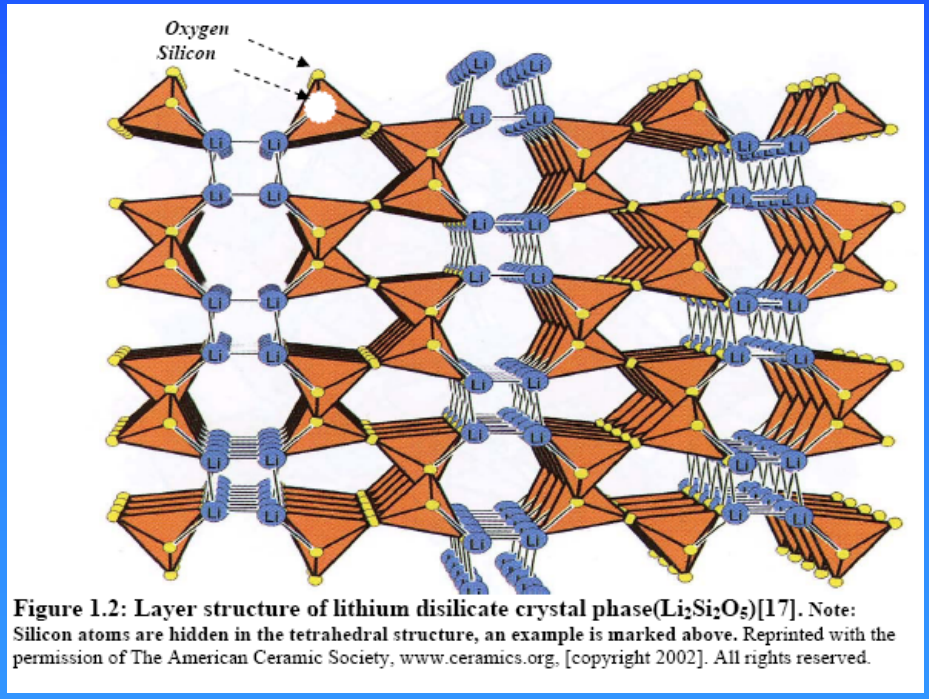


Figure 1.2: Layer structure of lithium disilicate crystal phase($Li_2Si_2O_5$)[17]. Note: Silicon atoms are hidden in the tetrahedral structure, an example is marked above. Reprinted with the permission of The American Ceramic Society, www.ceramics.org, [copyright 2002]. All rights reserved.

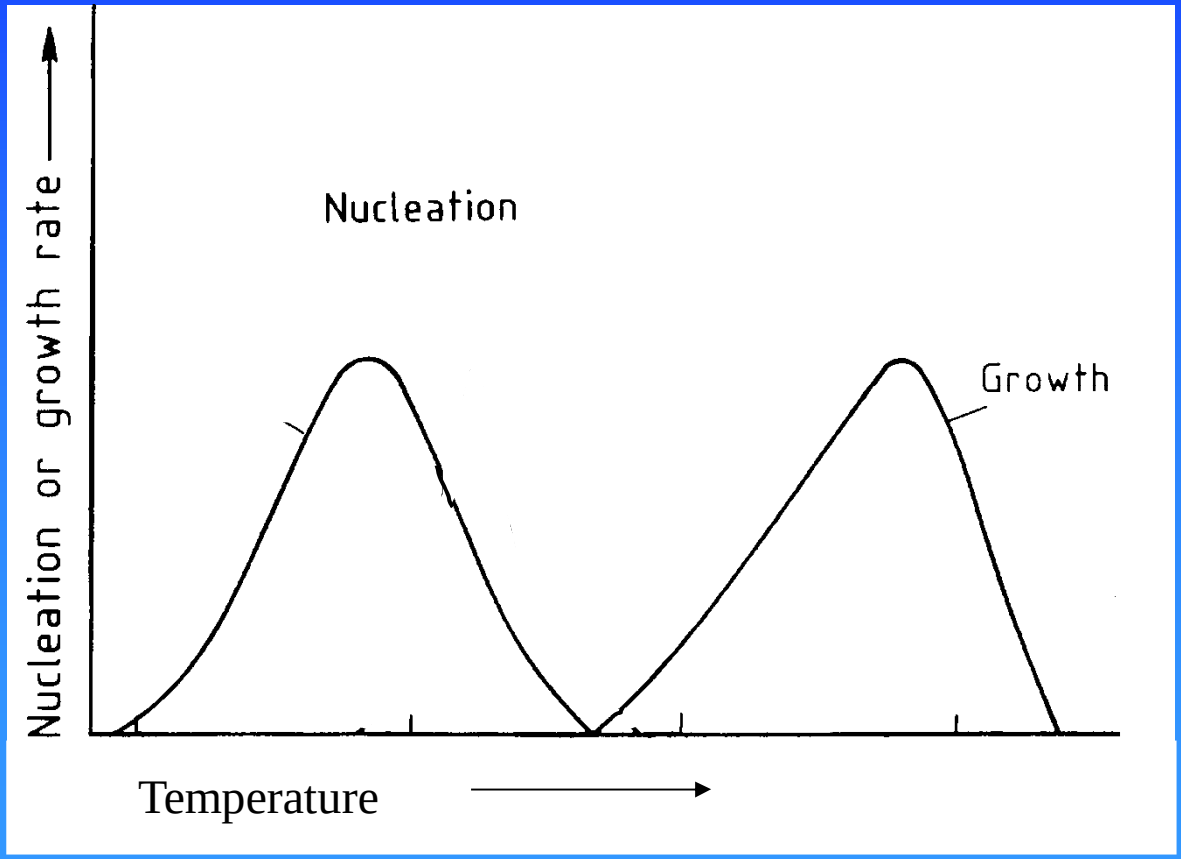
Accidentally developed when looking for materials for missile nose cones

More benign use

S. Donald Stookey
1953

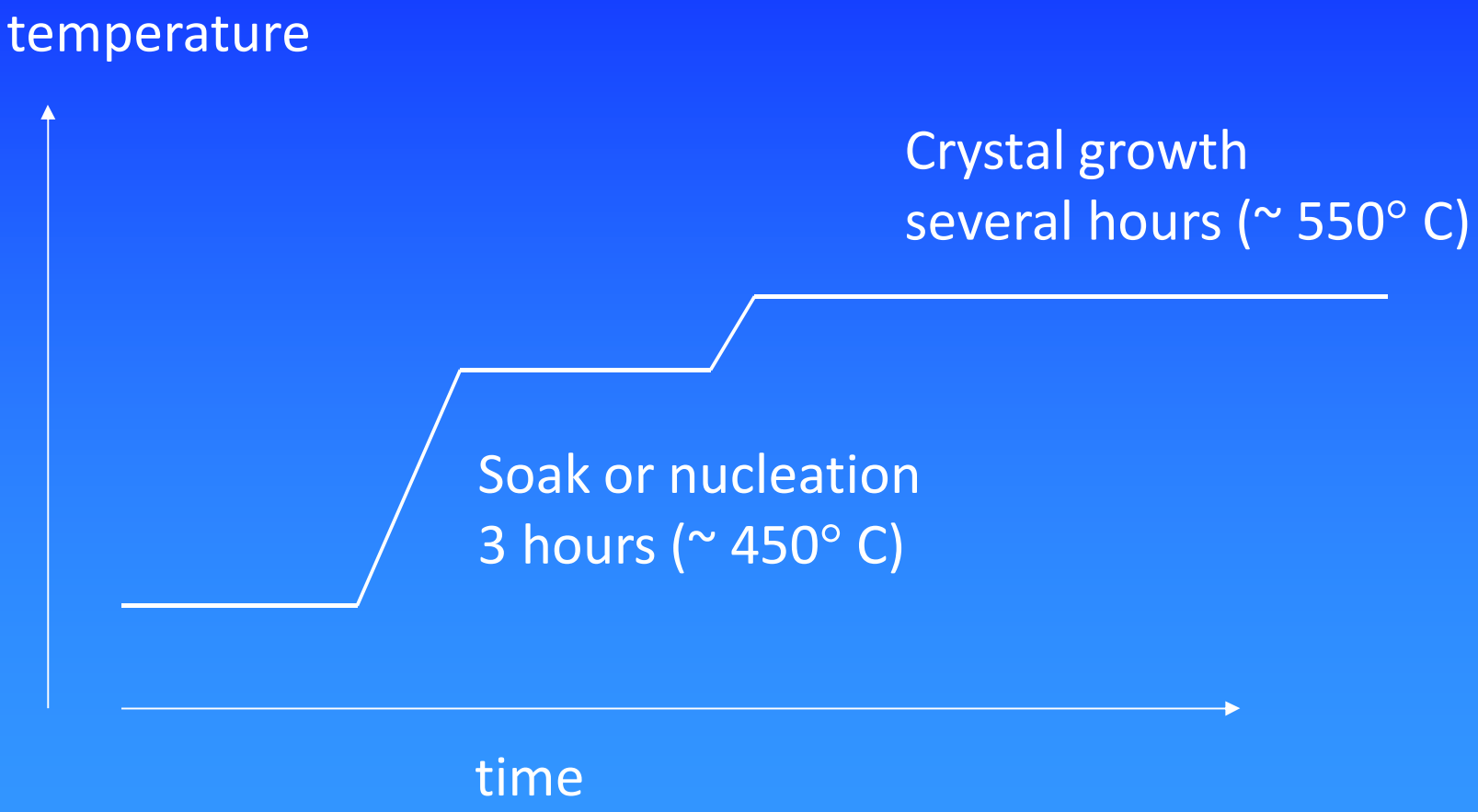
Early version of Corningware

Glass devitrification experiments



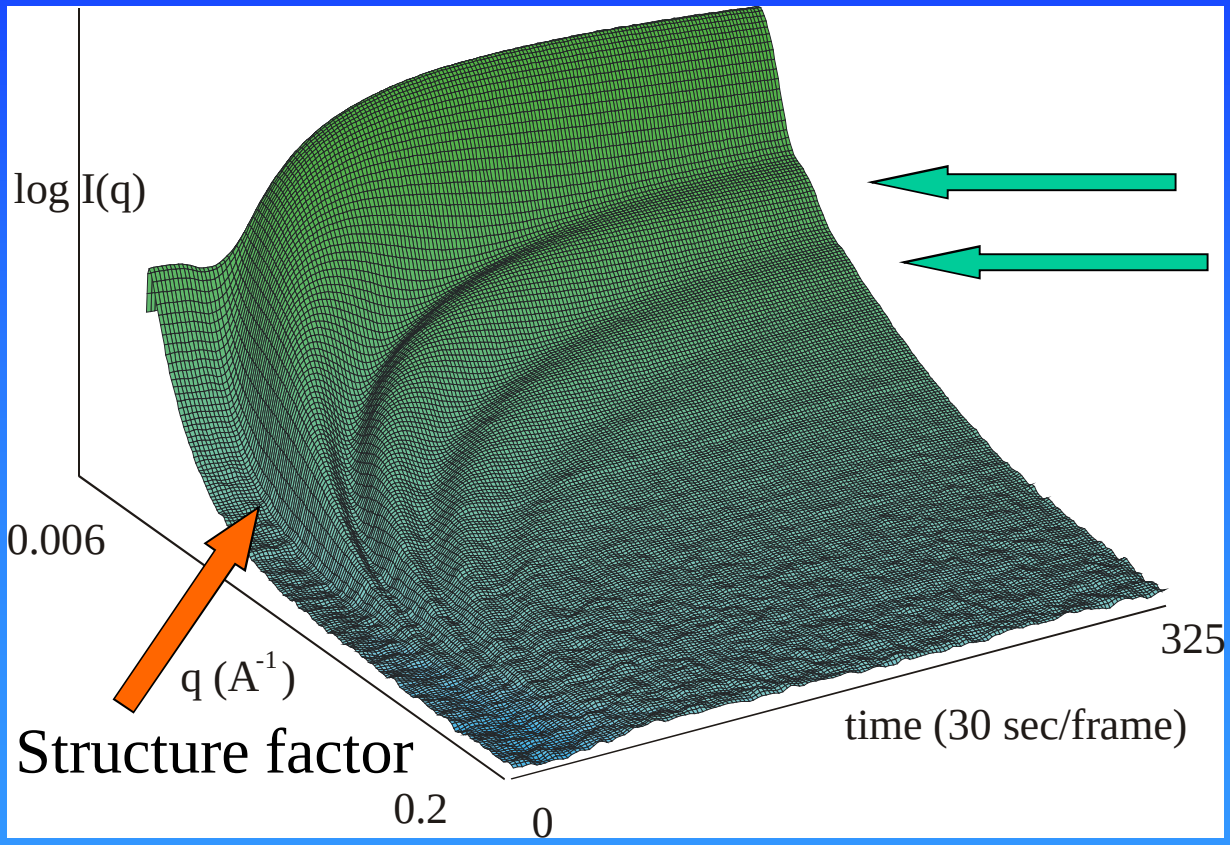
$LiSi_2O_5$

Experiment on 200 micron thick platelet



SAXS

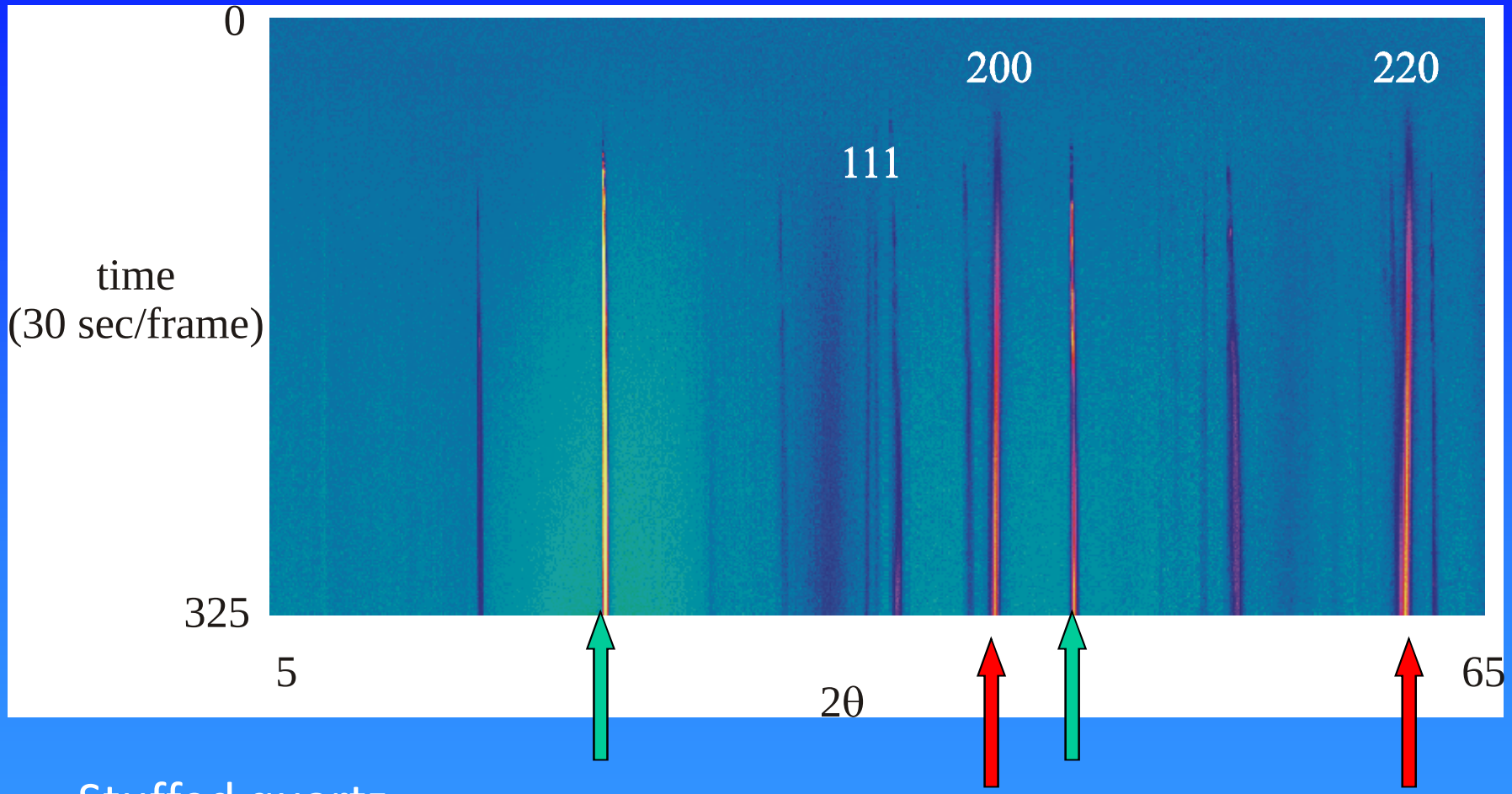
$$I(q) = S(q) * |F(q)|^2$$



Form factor peaks (up to 5th order)

$\Delta R/R \sim 0.04$

WAXS data



Stuffed quartz

Spinel unit cell increases in time

$MgOAl_2O_3$ FCC a = b = c = 8.06 Å

Spinel

Stuffed quartz unit cell decreases in time

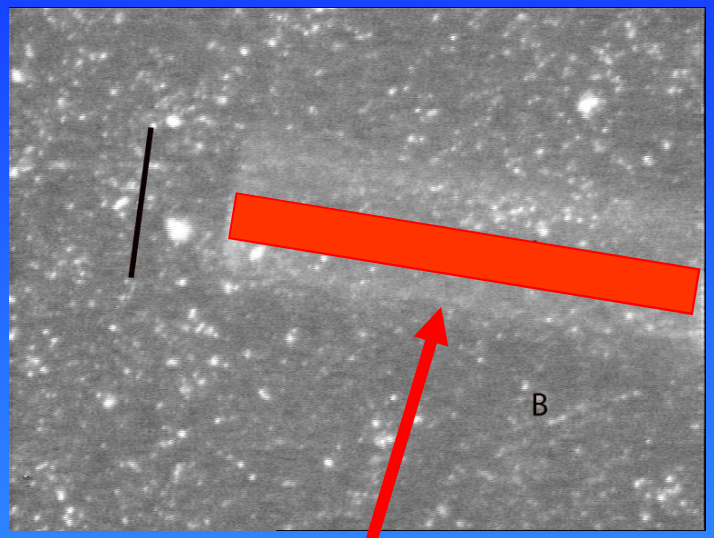
trigonal a = b = 5.13 Å c = 5.37 Å

Time-resolved SAXS and WAXS

- SAXS
  - Size of particles
  - Crystalline volume fraction
  - Diffusion or reaction limited process
- WAXS
  - Which phases
  - Crystallisation kinetics
  - Etc. etc. etc.

But that is not today's story

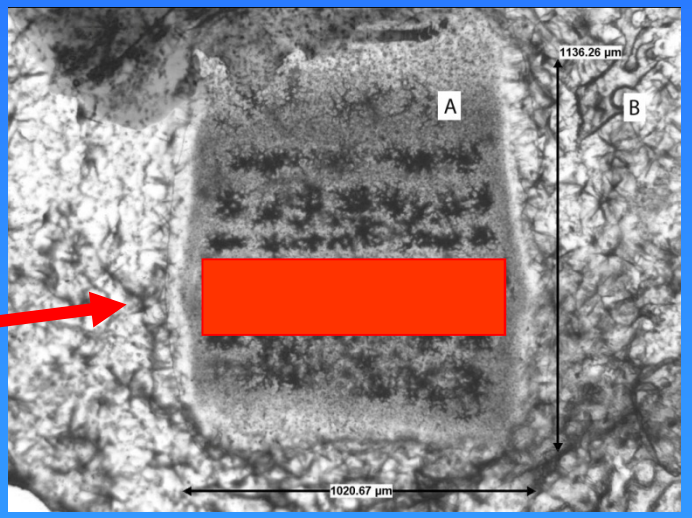
Post mortem optical microscopy

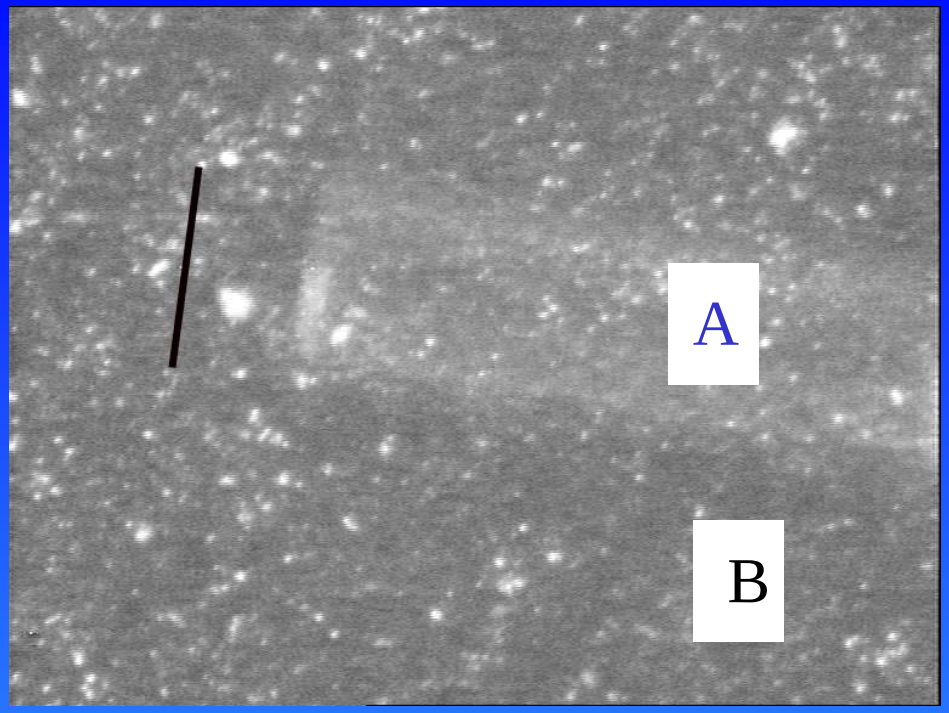


Partially crystallised

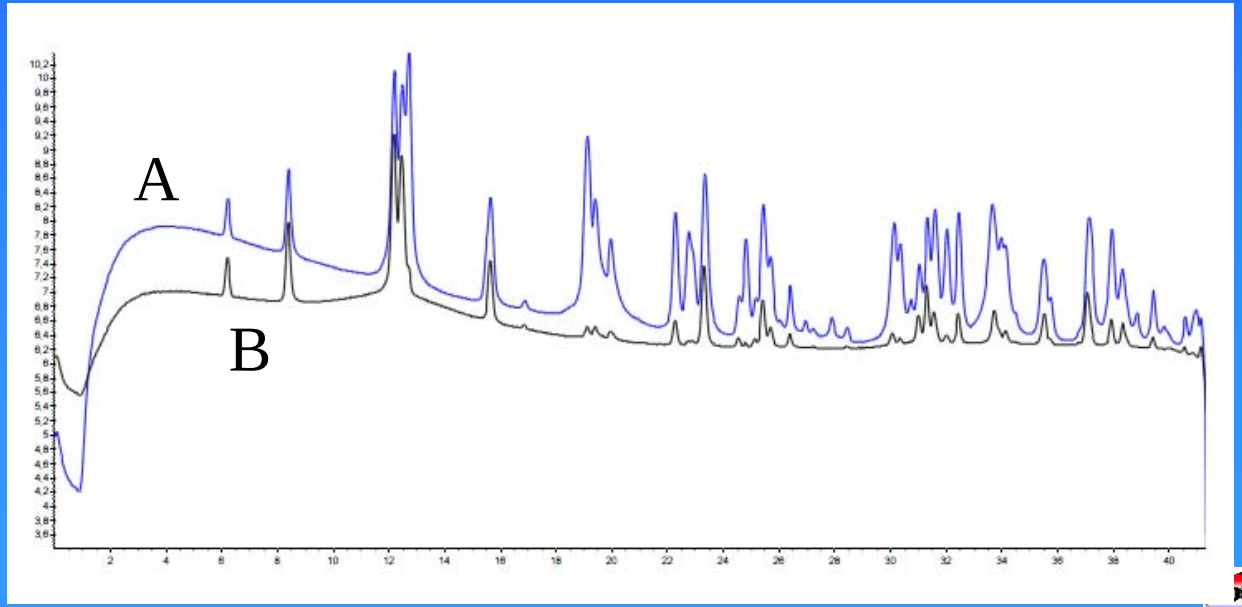
Real beam size

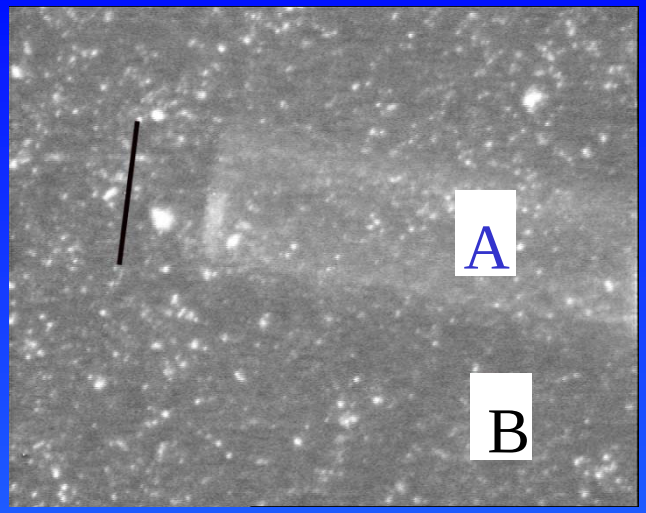
Fully crystallised





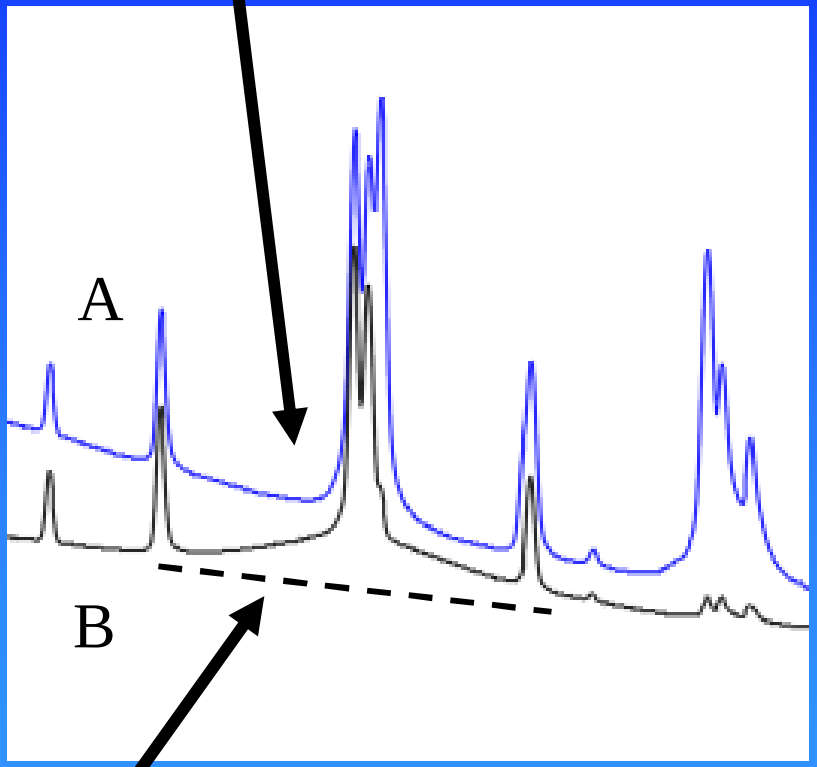
Post mortem powder diffraction





Sample should only be partially crystallised according to recipe

Amorphous halo absent

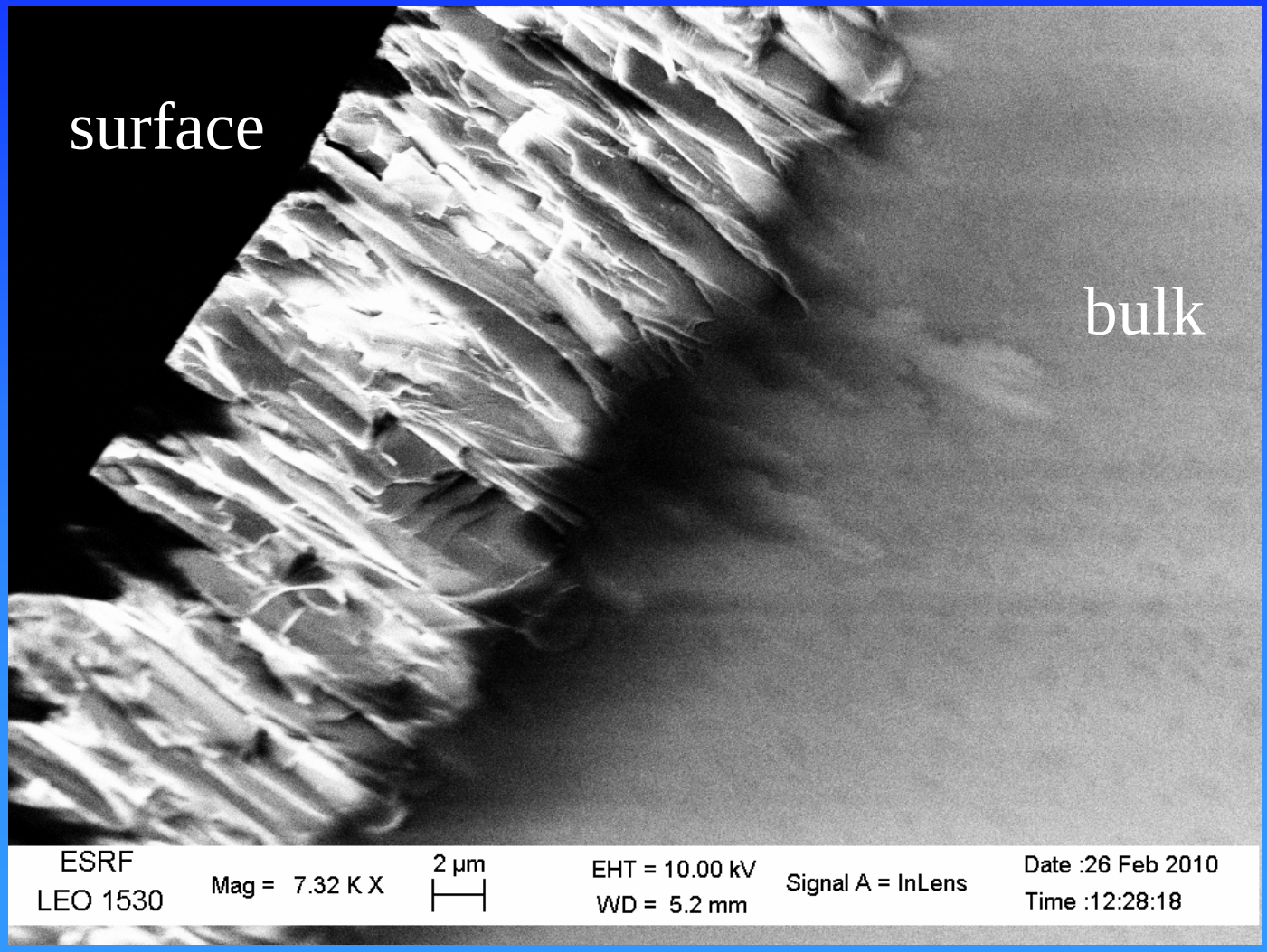


Amorphous halo still present

In irradiated region the sample has crystallised faster then in the non-irradiated region

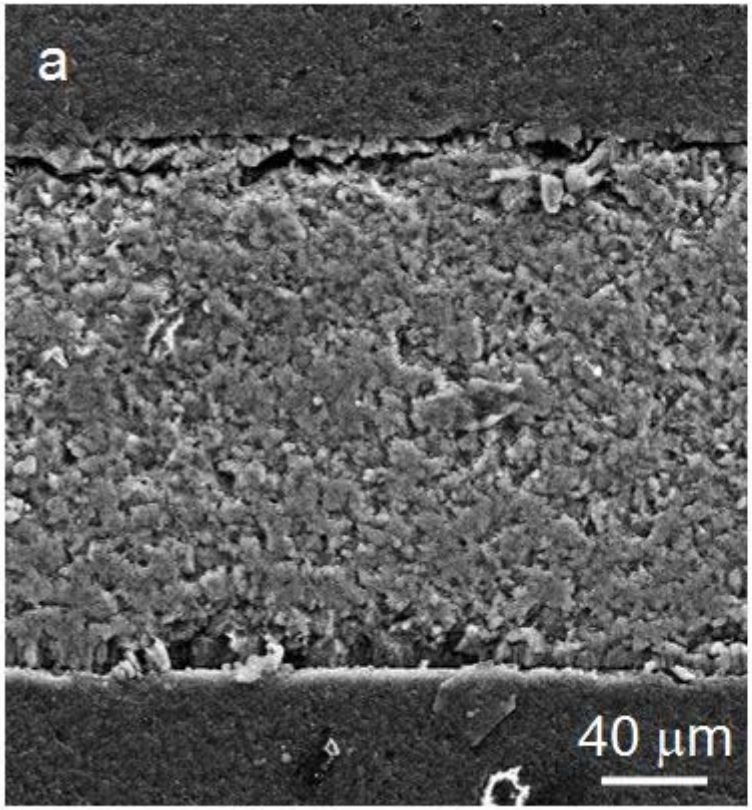
SEM partially crystallised

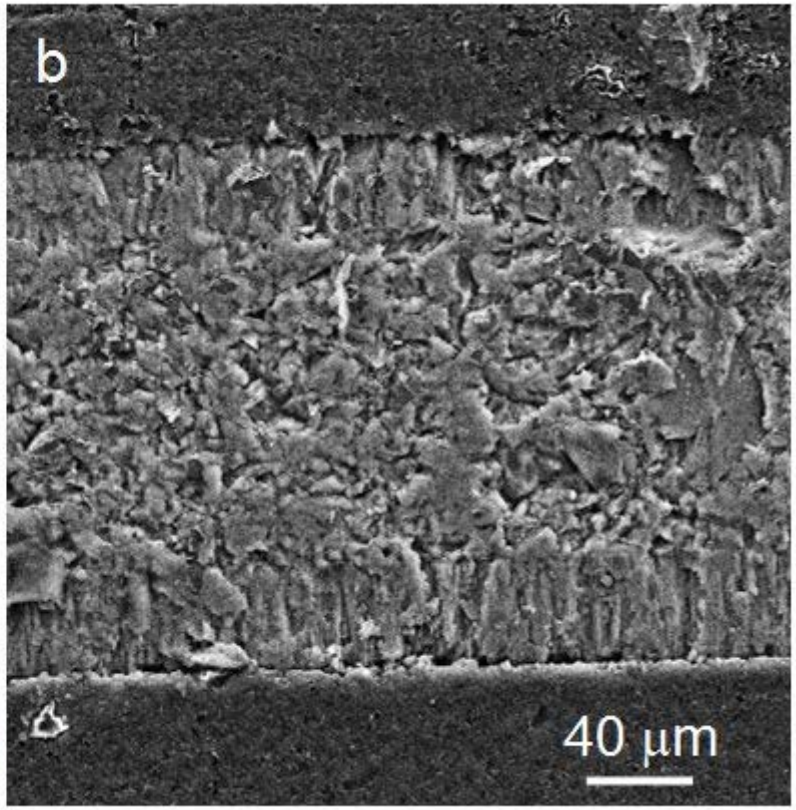
(not irradiated)



- Sample is in principle bulk crystallising
- There clearly is a textured crystalline layer on the surface
  - Not really all that uncommon
- The degree of crystallinity in surface layers is higher than in the bulk

SEM fully crystallised sample





Irradiated by X-rays

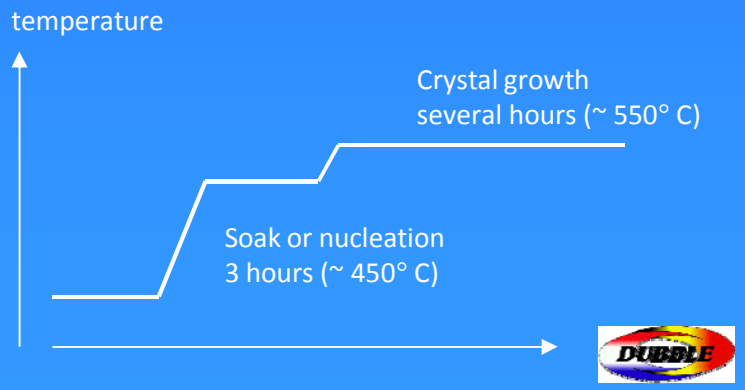
Not irradiated by X-rays

Powder diffraction

Irradiated

Not irradiated

- X-rays on during whole process
  - Fine morphology
  - No surface layer
  - Faster crystallisation
- X-rays on only during crystallisation
  - Texture increased
  - Surface layer less prominent
- X-rays off
  - Coarse morphology
  - (Textured) surface layer
  - Slower crystallisation



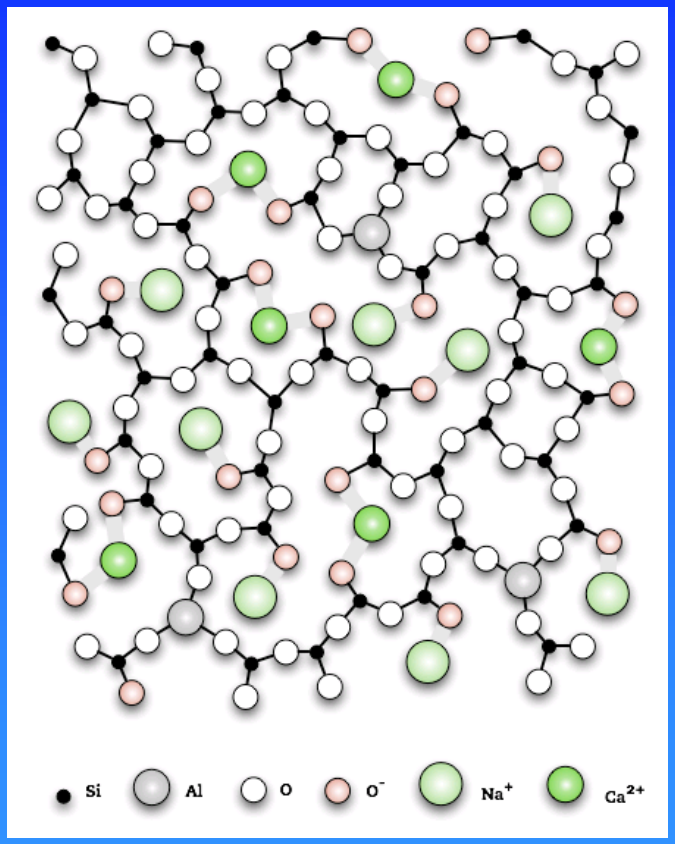
- The X-rays influence the crystallisation process
- The X-rays induce crystallisation
- Strongest effect during the thermal nucleation treatment
- Flux 10^{11} photons/sec in 0.3 x 2 mm^2

But:

- The X-rays influence the crystallisation in a larger area than the direct beam
- This only occurs in the vertical direction

What is happening?

- Local heating? Not sufficient energy deposited to influence kT dependent processes ($\uparrow 10^{-4}$ K/s)
- Most likely due to electrons liberated in sample (photo electric effect)
- One way or another these electrons help to create nucleation sites

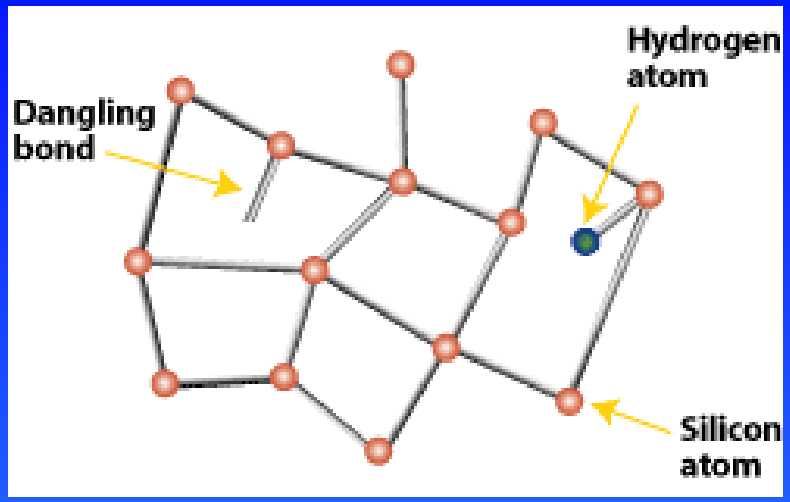


Mechanism of electron-irradiation-induced recrystallization in Si

Frantz, J. Tarus, K. Nordlund, and J. Keinonen
PHYSICAL REVIEW B, VOLUME 64, 125313

For electron irradiation, it has been recently shown that even quite low energy (25 keV) electron bombardment can produce recrystallization of amorphous pockets in silicon, germanium, and gallium arsenide.

Doses low enough to avoid sample heating due to electron beam



By geometric rearrangement we mean that after a bond between atoms *i* and *j* breaks, the atom *i* can reform the bond with some other atom *k* in the local neighbourhood and similarly with *j* and some other atom *l).* Although this is quite unlikely to occur in the crystalline state, in an amorphous state produced by irradiation there are weak bonds which are relatively easy to break.

Frantz, J. Tarus, K. Nordlund, and J. Keinonen
PHYSICAL REVIEW B, VOLUME 64, 125313

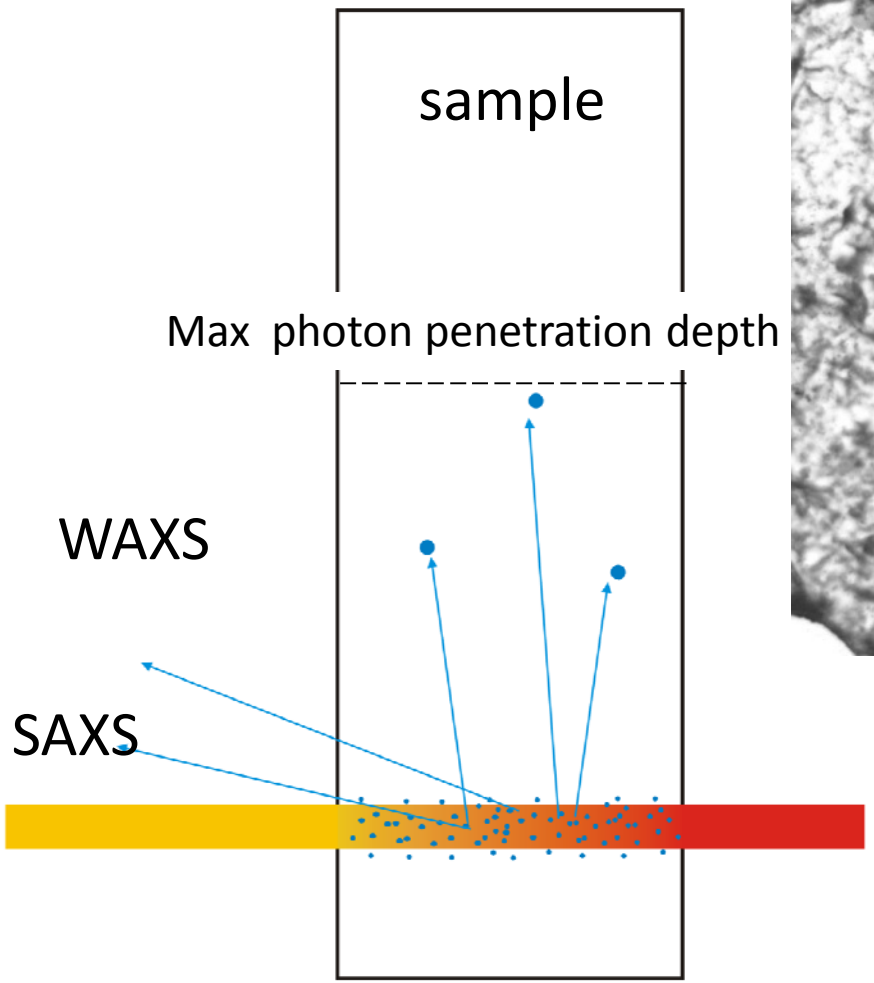
But…

- This would not explain the vertical extension of the affected region
- This is around 200 micron (either vertical side of beam)
- The path length of scattered electrons is at most microns

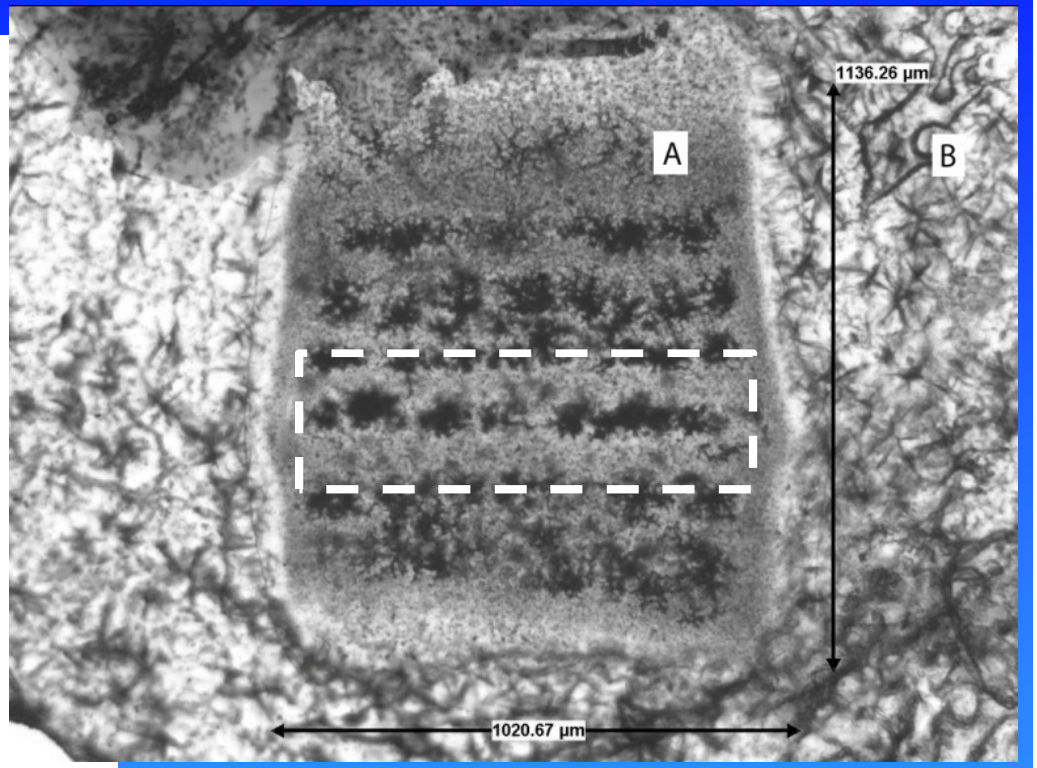
But…

- 10 keV photons can travel around 200 micron in this sample
- The synchrotron photons are polarized
- They will be scattered in the vertical direction (both elastic as well as inelastic)

Side view

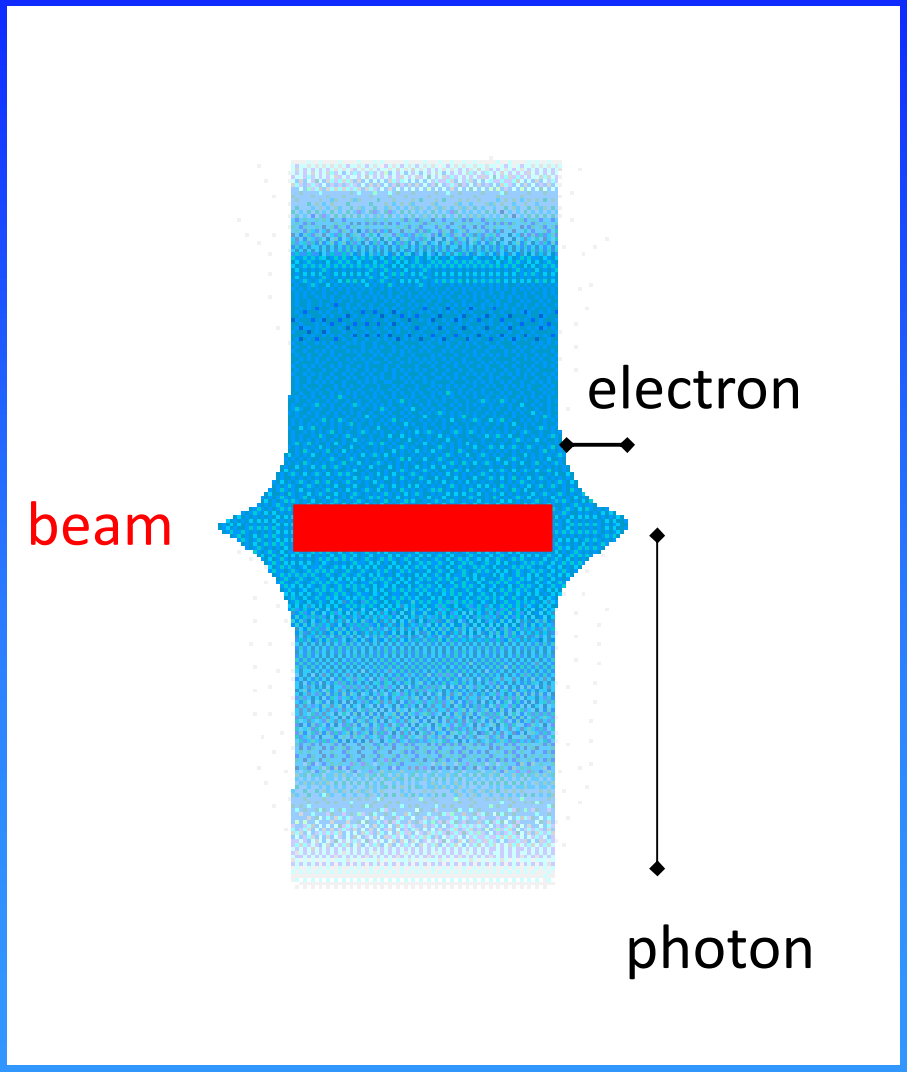


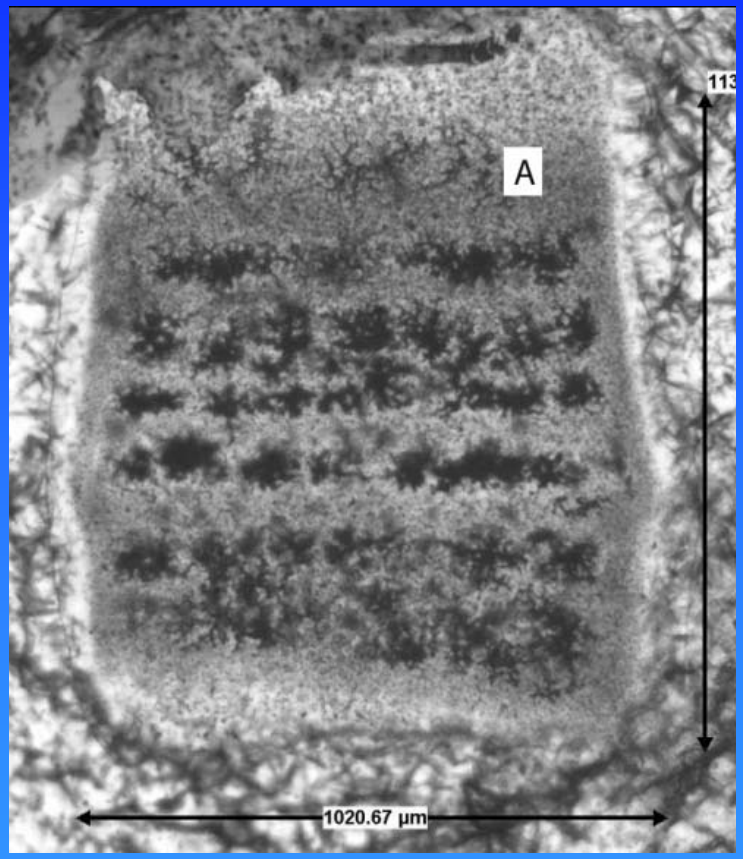
Beam direction view



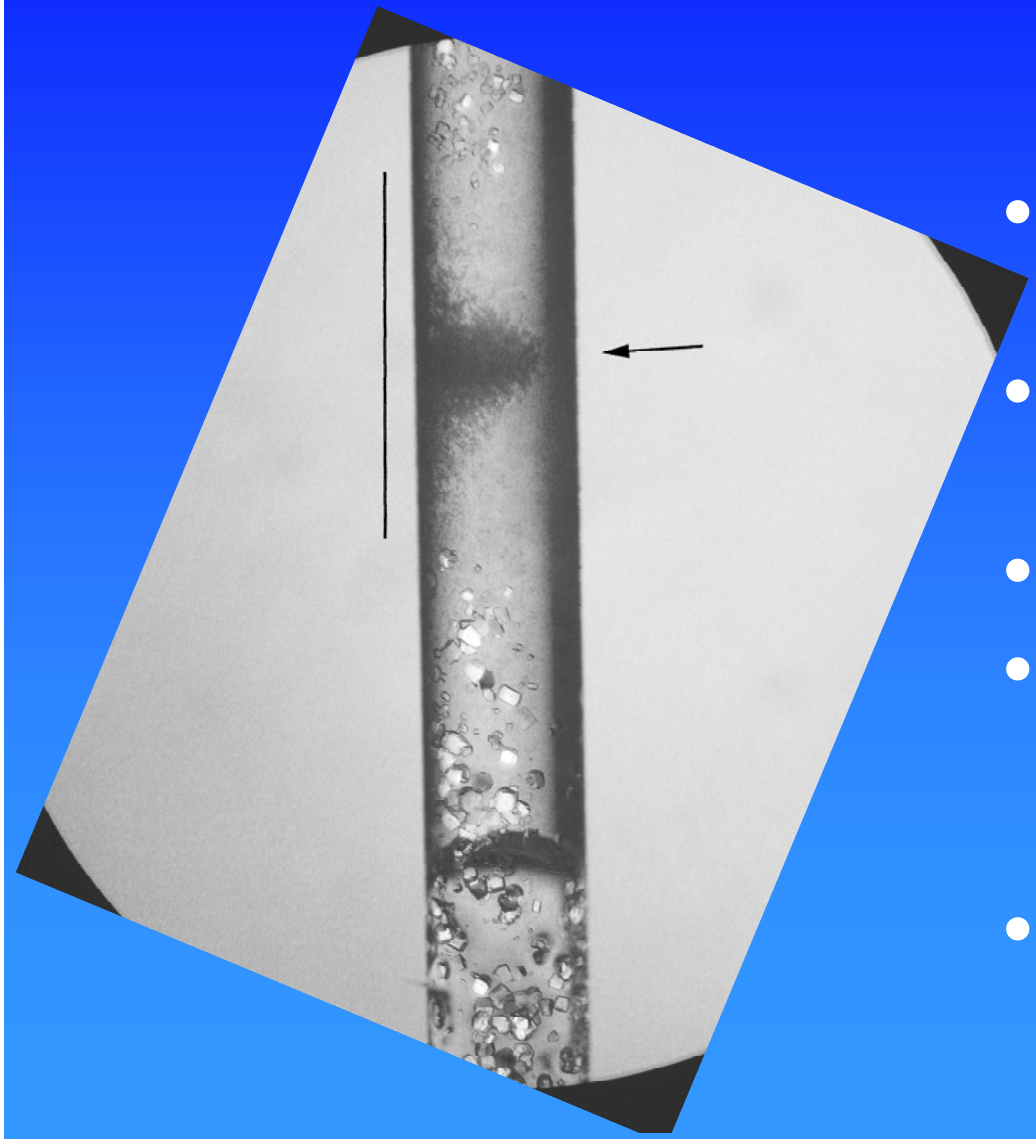
What is most likely:

- Part of photons in direct beam get absorbed and release electrons
- Part of photons scatter inside sample
- These ultimately get absorbed and release electrons


beam
electron
photon


A
1020.67 µm

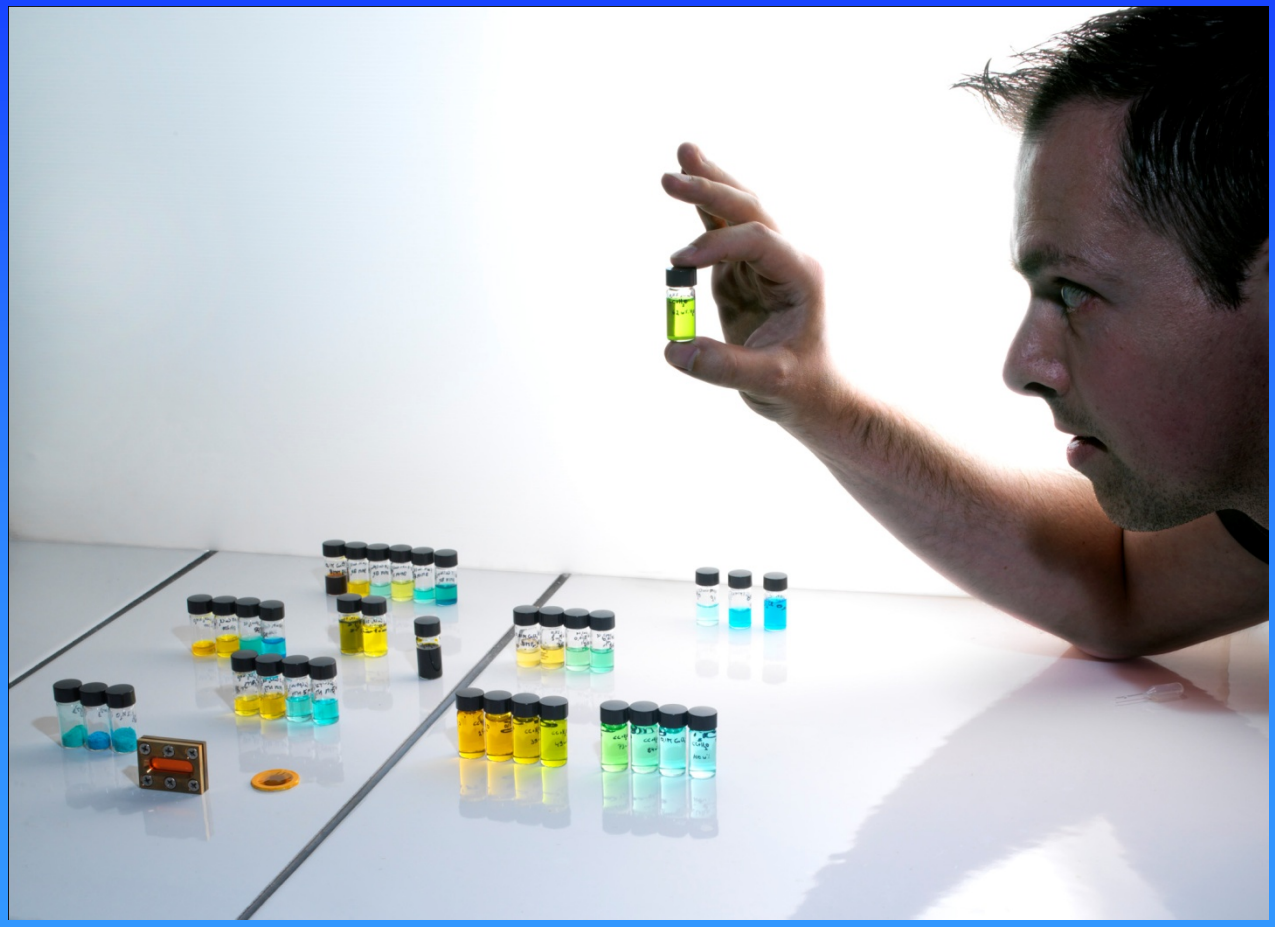
Earlier work



- On-line lysozome crystallisation
- Radiation damage in beam spot
- 8 keV photons
- No crystallisation in region of 500 mm above/below beam
- Hydrolysis products don’t ‘travel’ that far (2 micron)

Quantum dots

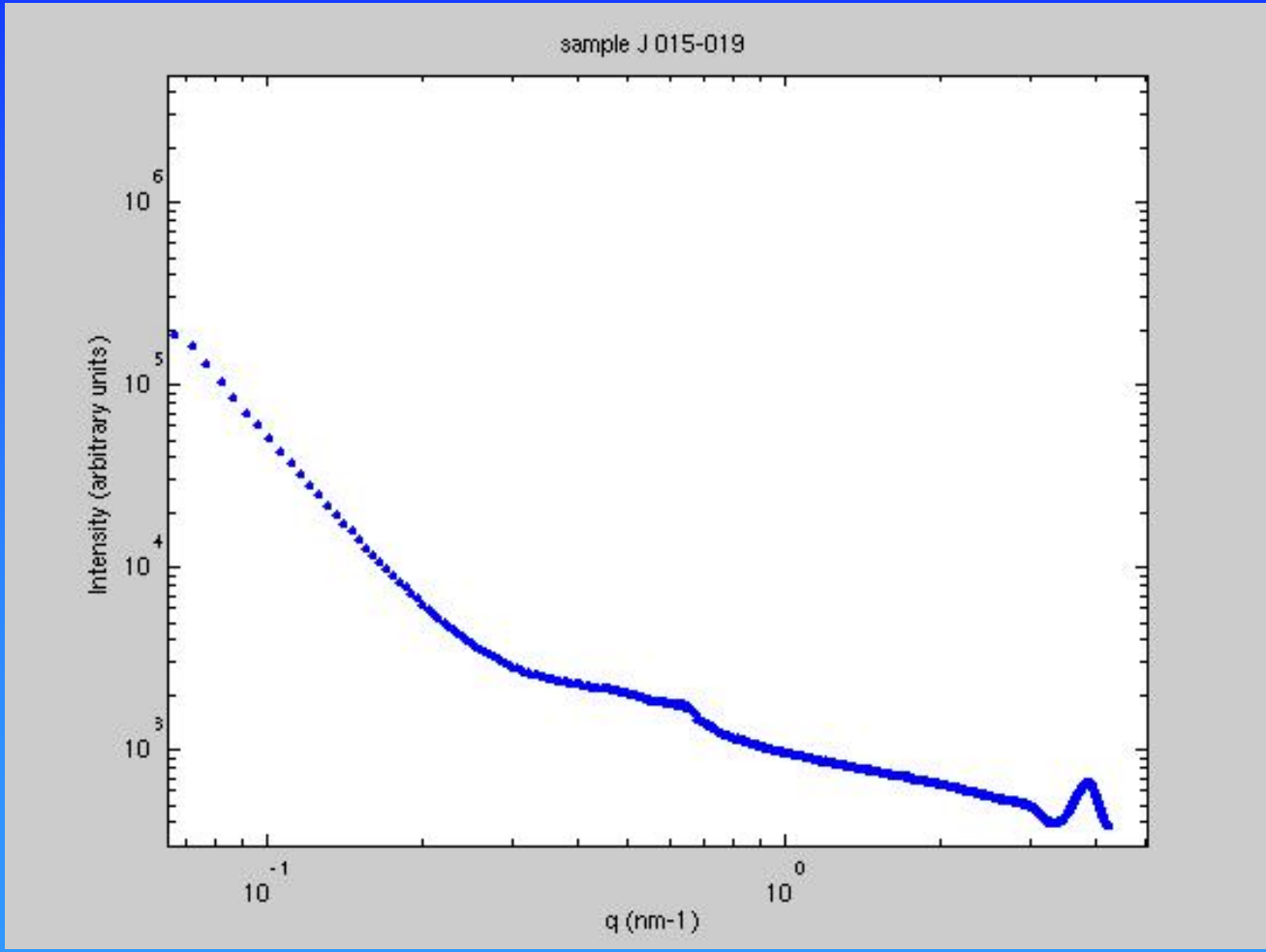
Just for aesthetics a second picture



Quantum dots

- Interesting for their optical properties
- Small size (≈ 1 nm)
- Preferably monodisperse, i.e. all the same size
- Can be made with thermal treatments of glass
- PbS in silica glass matrix is well studied system

Real time SAXS

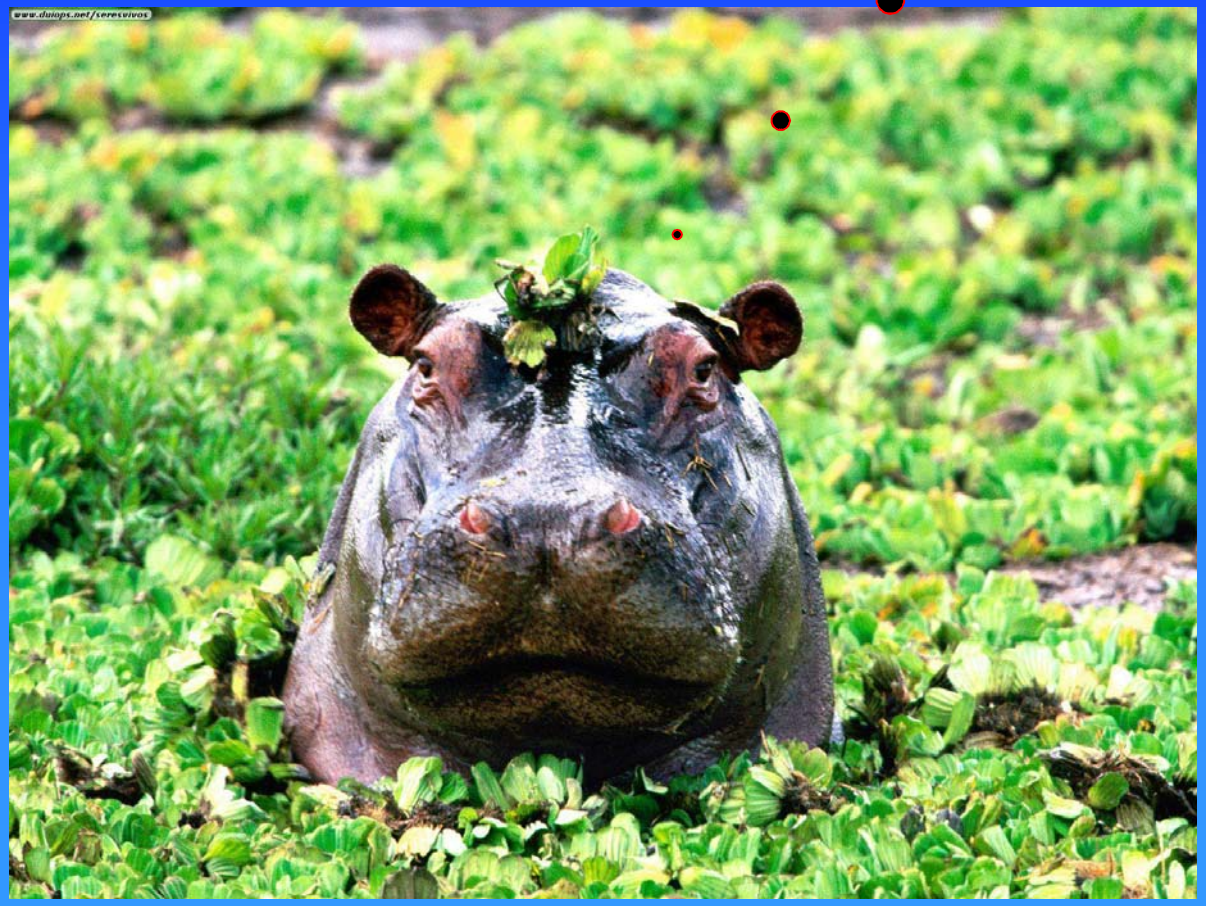


That looks ok!

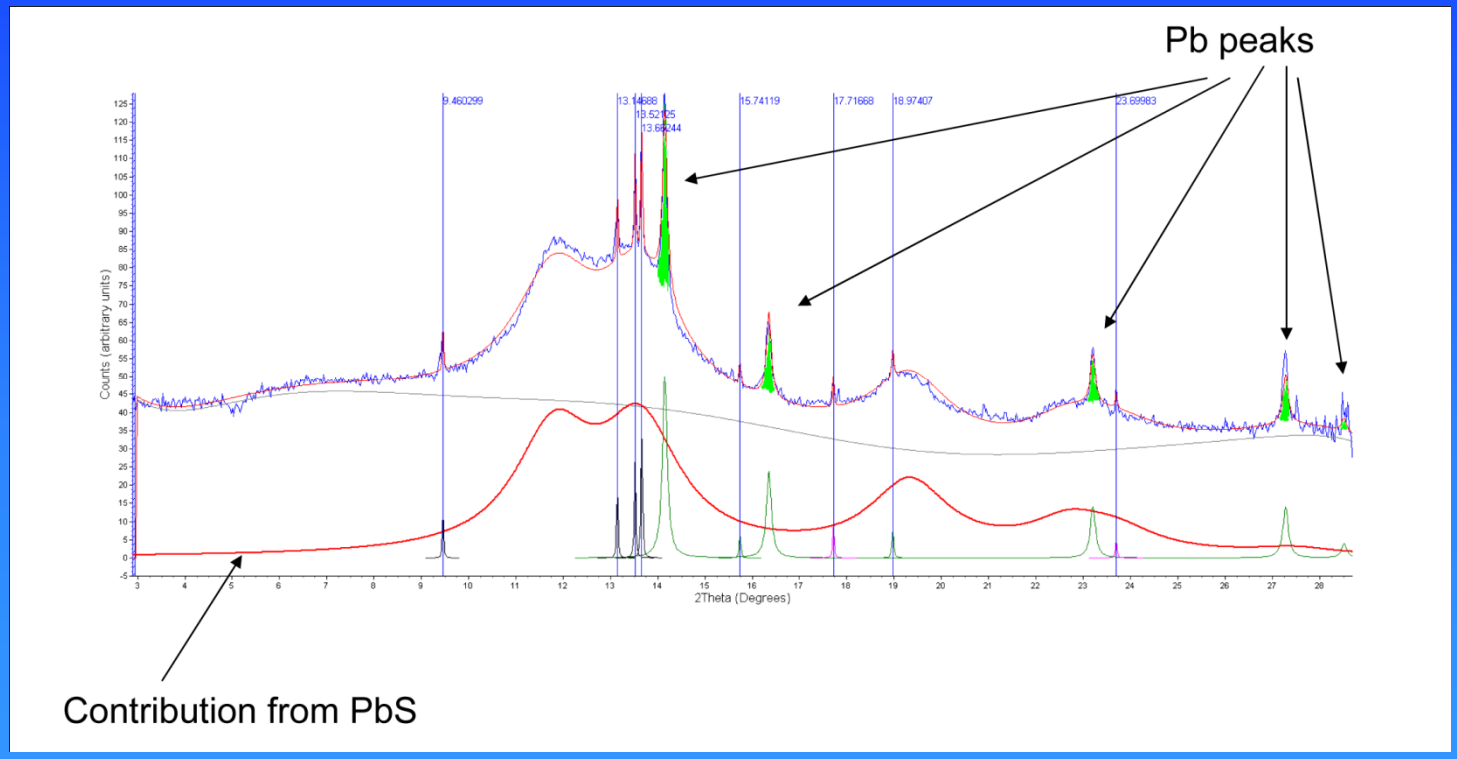
- Particles grow
- Finite size
- Very monodisperse

- Everything is ok, isn't it?

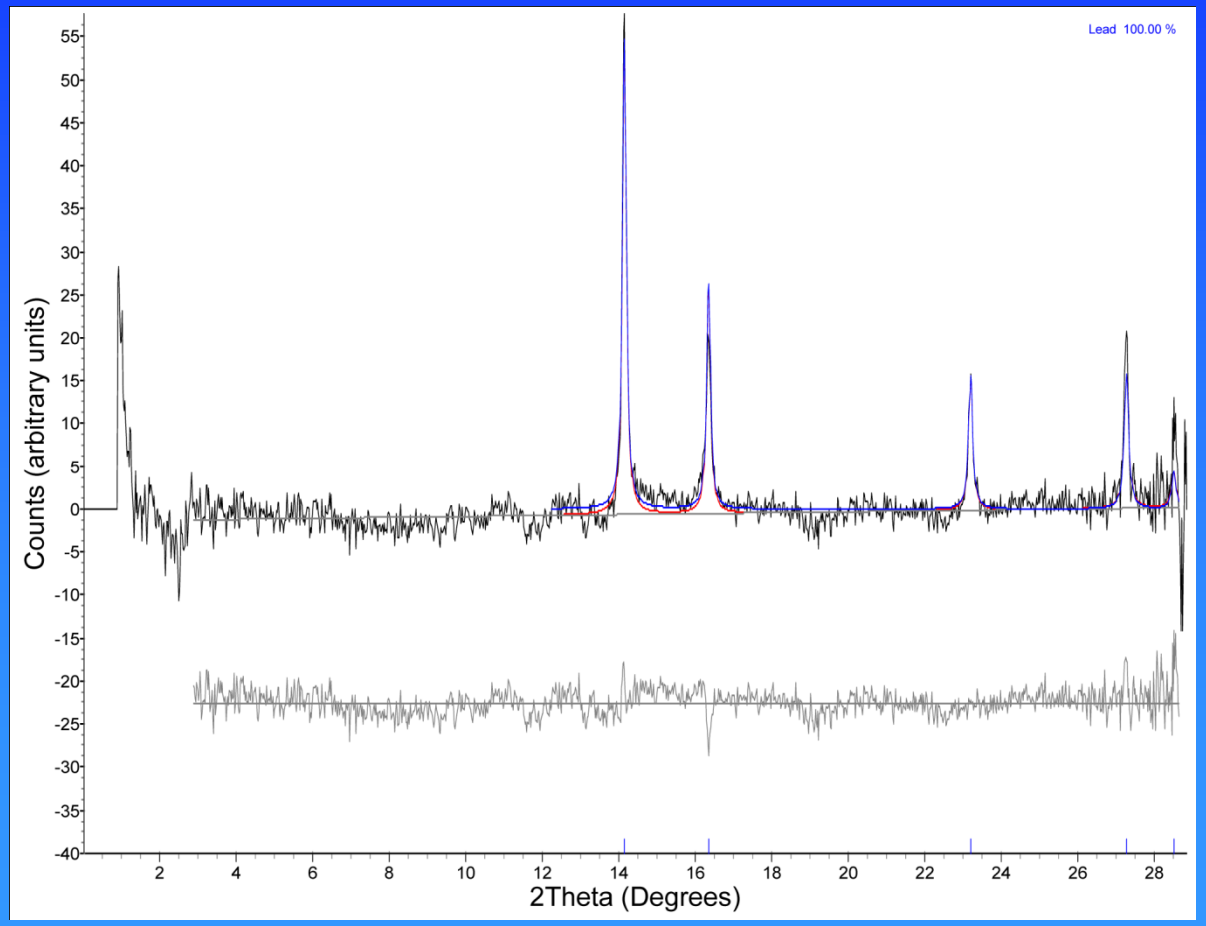
No it is not ok



WAXS/powder diffraction



The difference between exposed- not exposed

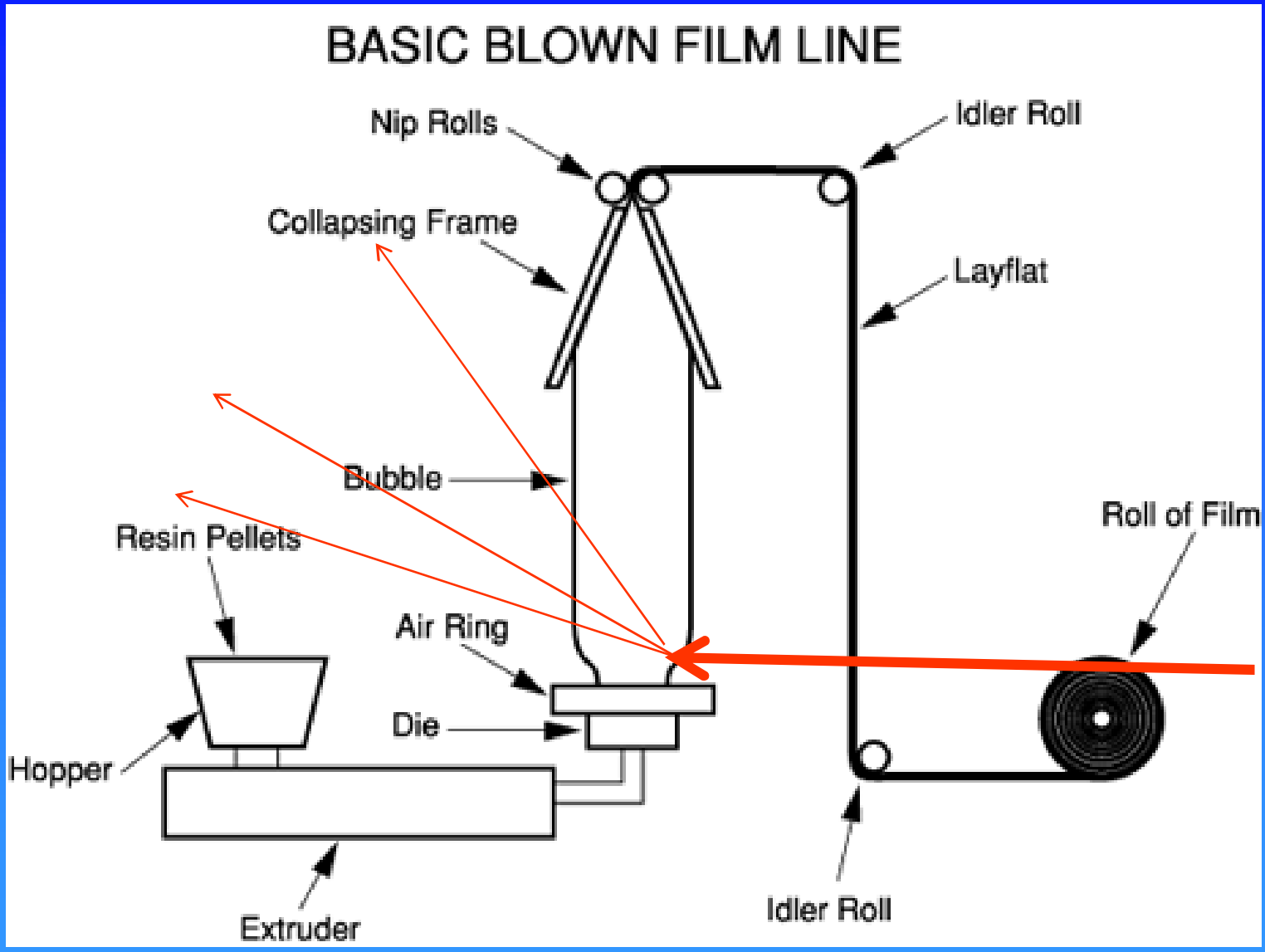


The conclusion:

- PbS quantum dots grow
- Scattering pattern dominated by metallic lead particles!!
- Only small volume fraction but large contrast
- Metallic Pb is not found outside of the irradiated spot.
- Metallic Pb R = 40 nm, PbS R = 2 nm

Polymer processing

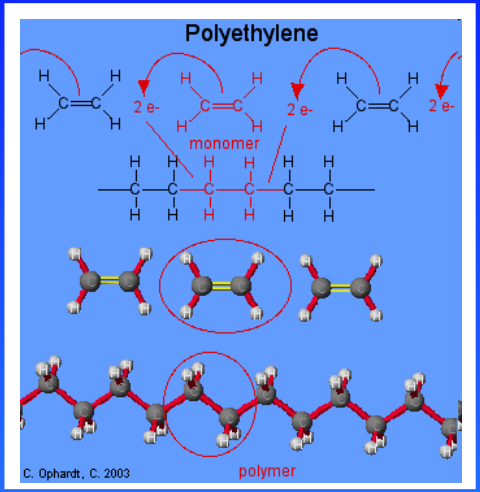
BASIC BLOWN FILM LINE



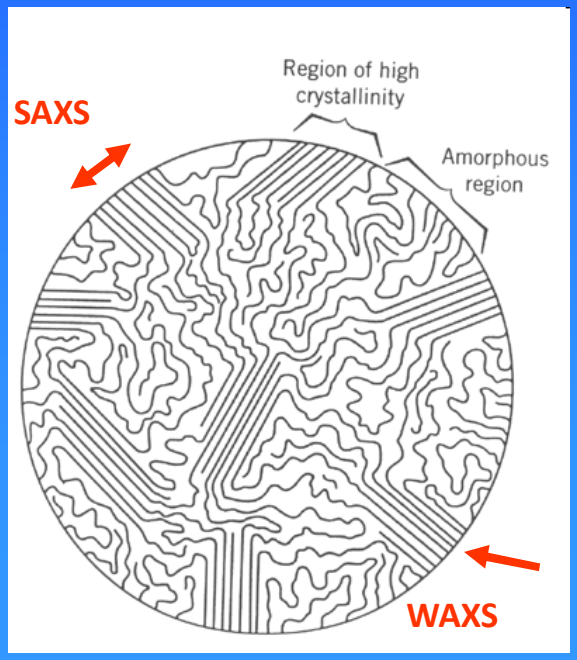
Semi crystalline polymers

- Polyethylene, polypropylene, nylon, PVC, i.e. 95% of the world polymer consumption

polyethylene



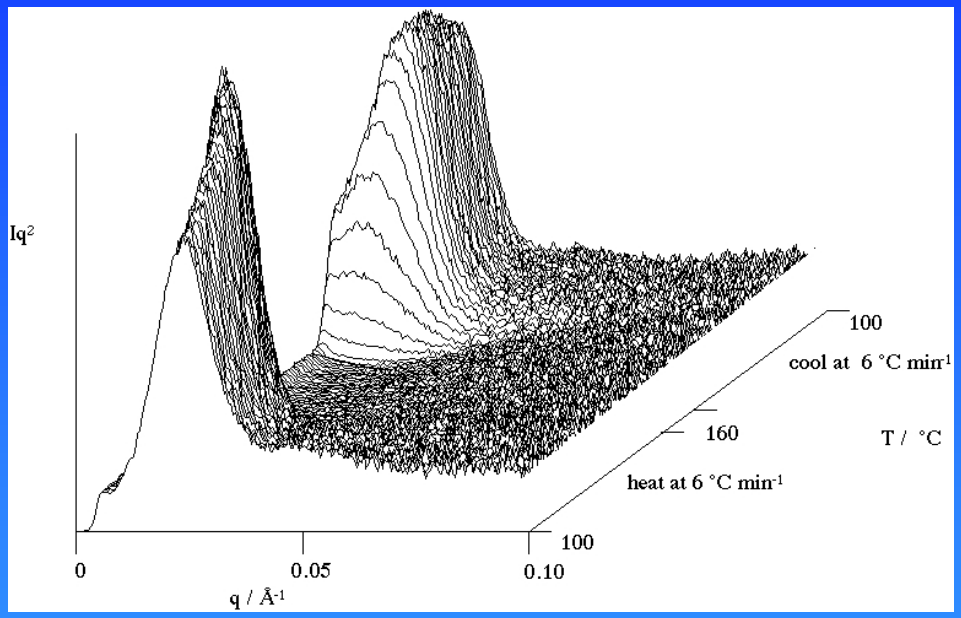
Molten it looks like spaghetti

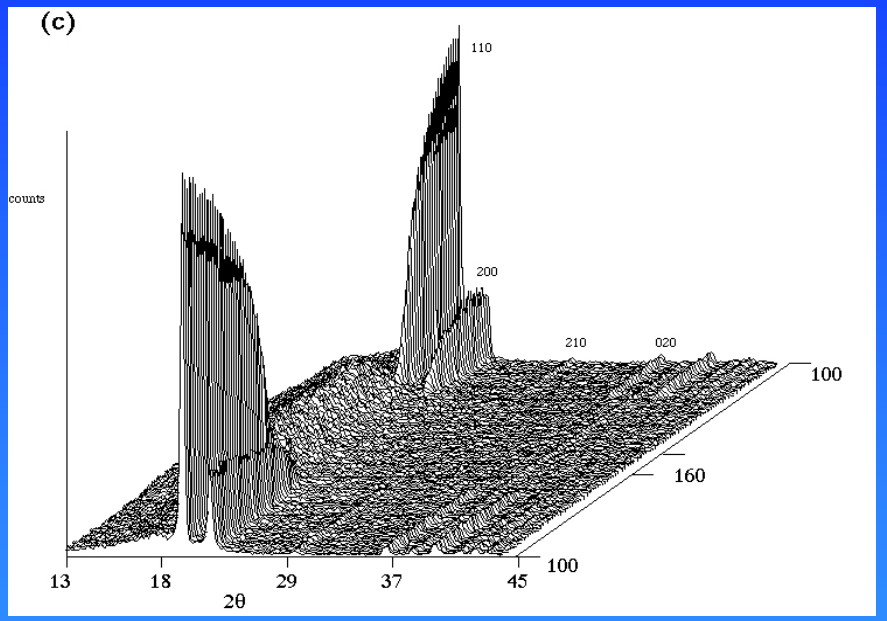


In solid state semi-crystalline
- amorphous parts
- crystalline parts

The ratio amorphous/crystalline and the spatial orientation determine the macroscopic properties

Heating/cooling cycle on HDPE





SAXS
(lamellar spacing)

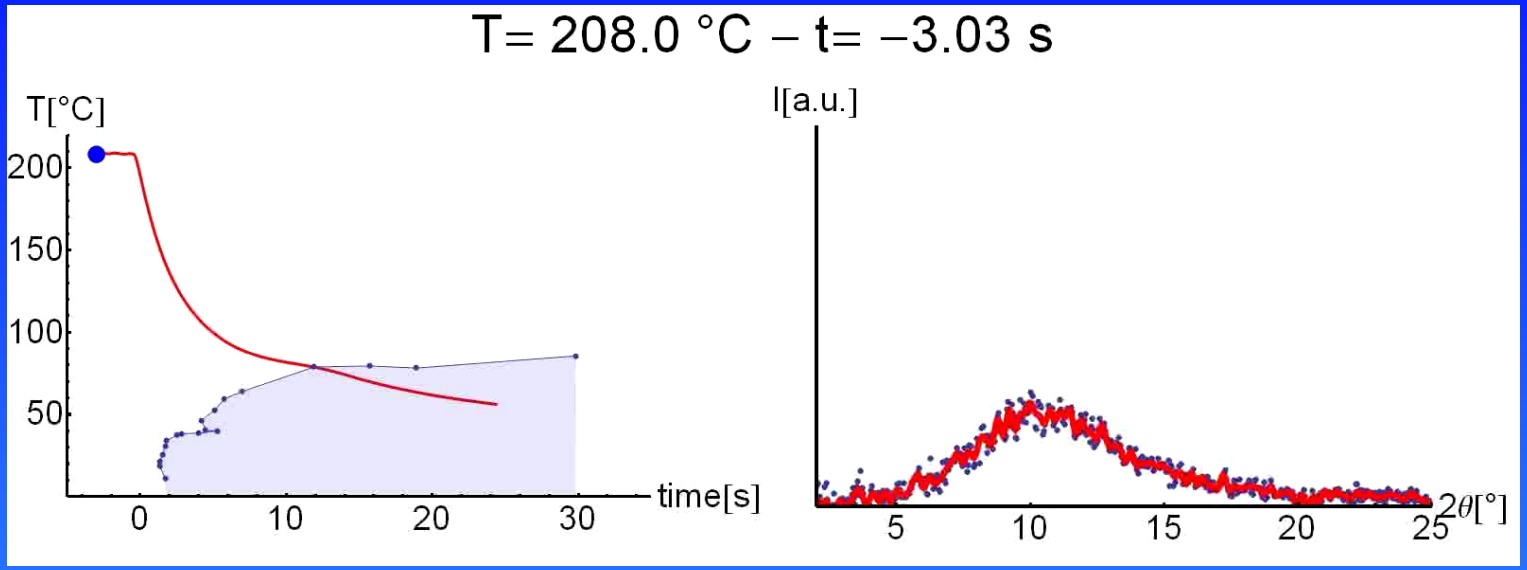
WAXS
(crystalline order)

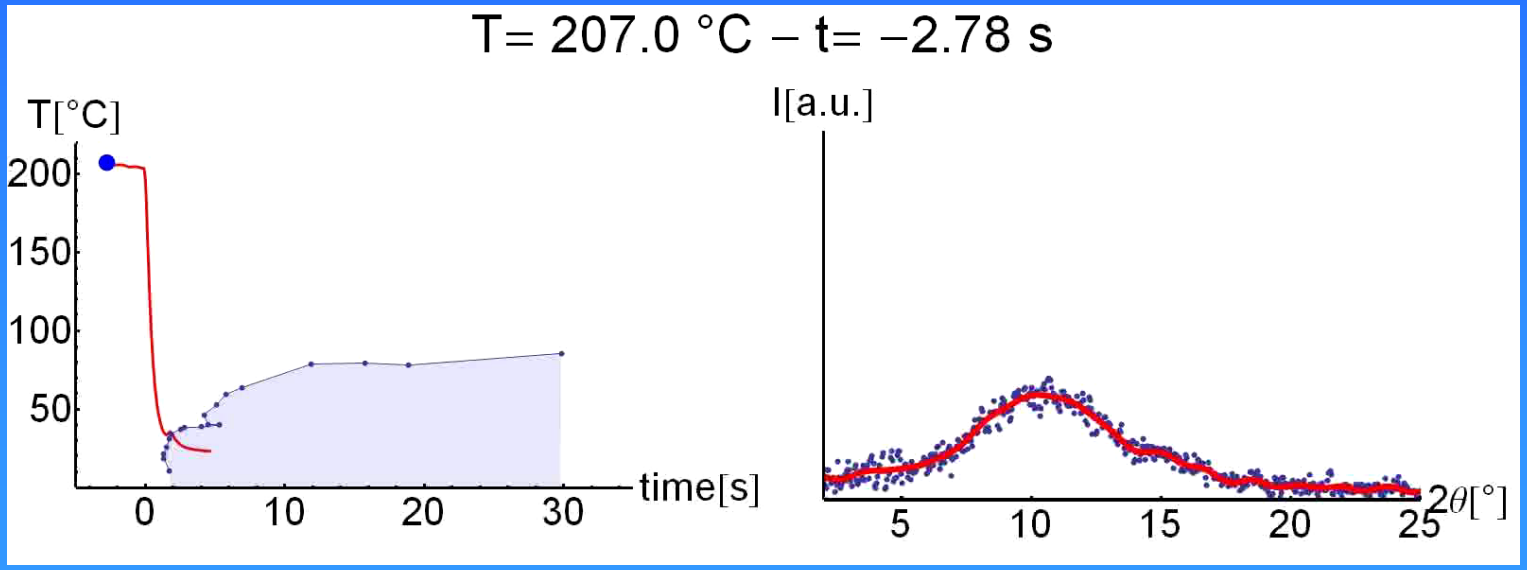
Fundamental question

- What is the crystallisation process?
  - Nucleation and growth
  - Spinodal decomposition like

- Nucleation and growth
  - Lamellae and crystallinity develop at same time
  - SAXS and WAXS signals increase simultaneous
- ‘Spinodal’
  - Long range density fluctuations first
  - SAXS signal increases before WAXS

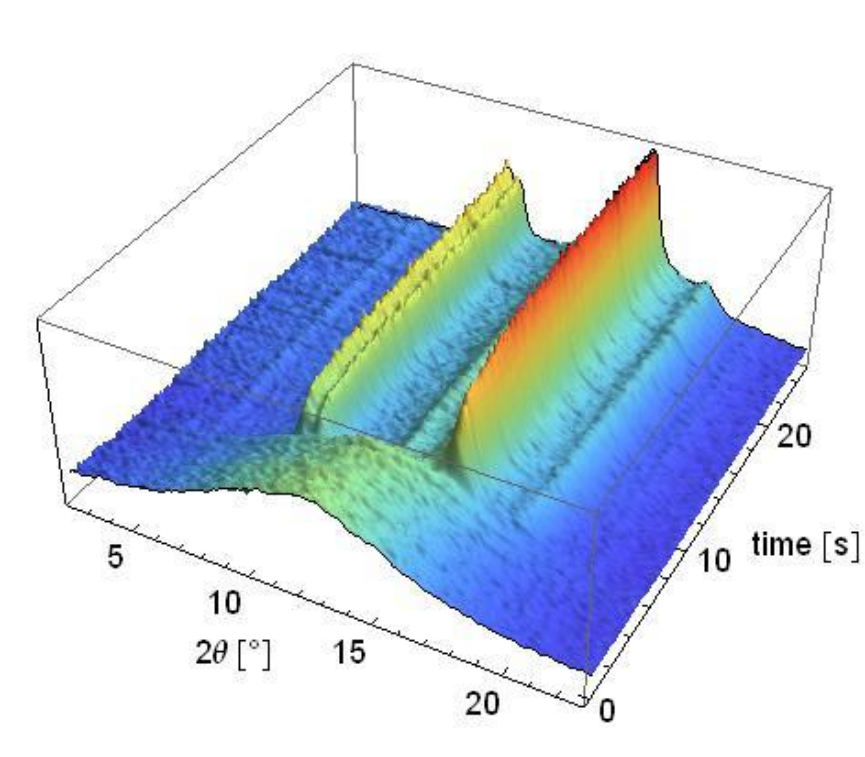
On-line WAXD during quenching



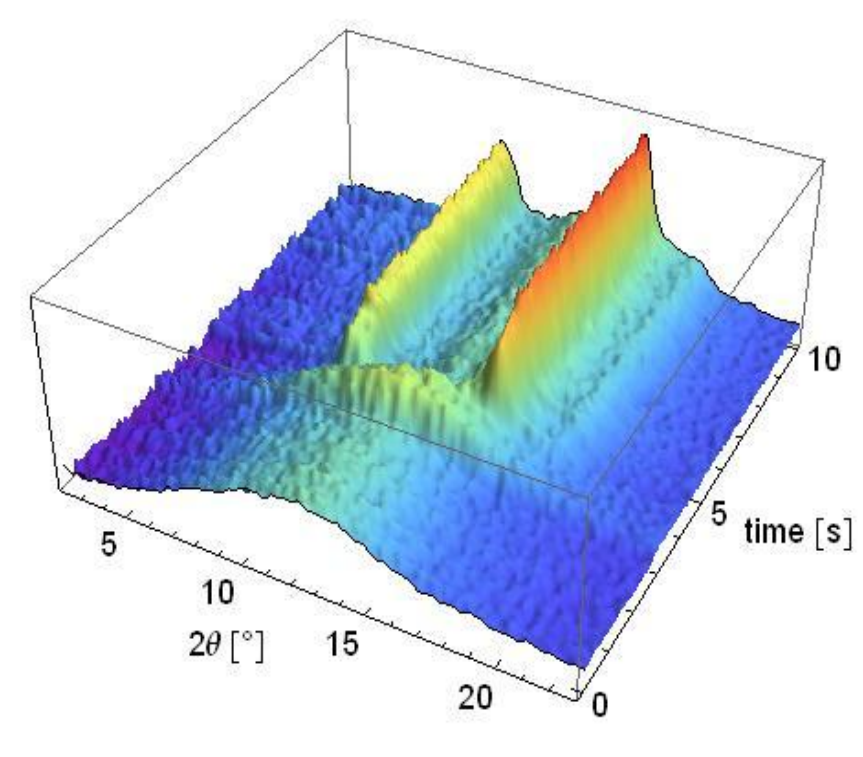


The hidden mesophases

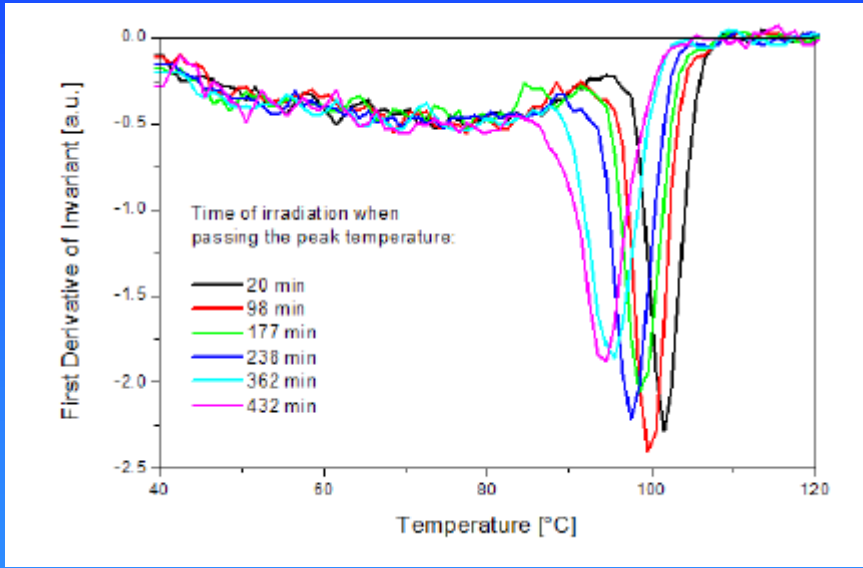
30 °C/s

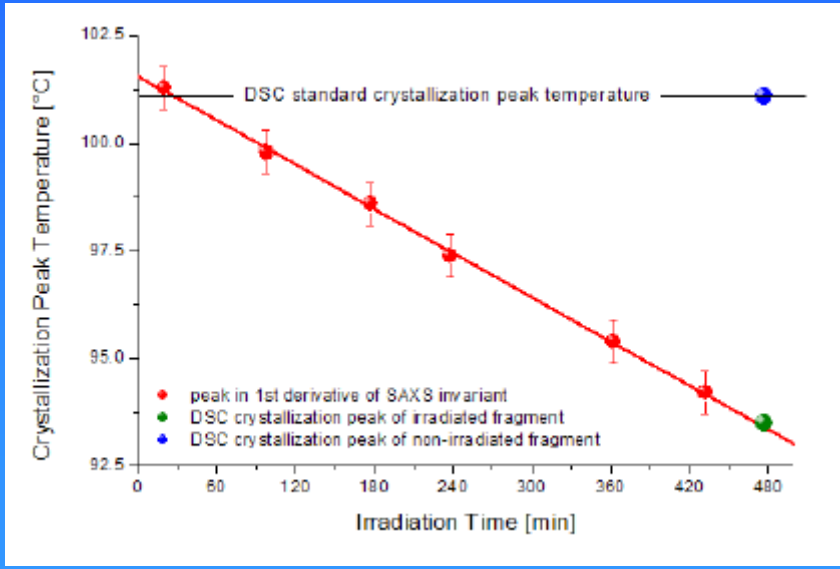


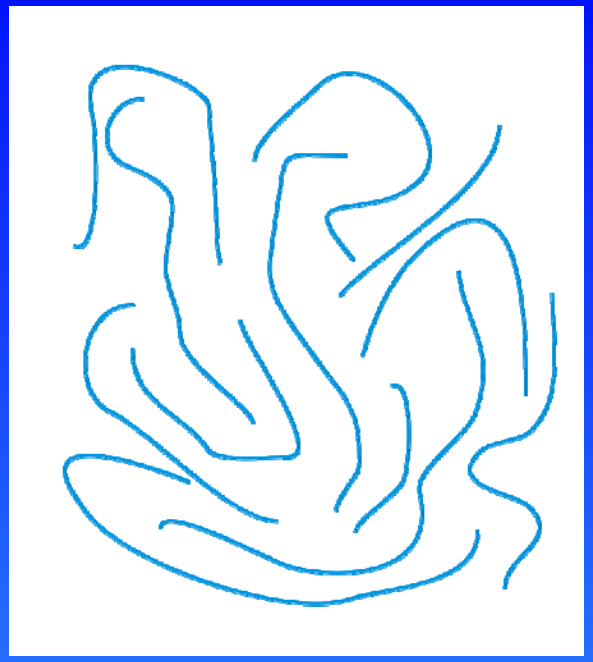
100 °C/s



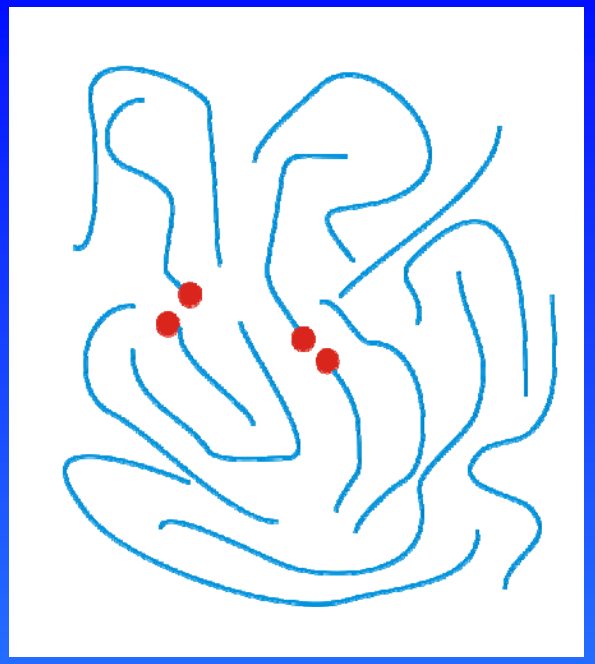
But what happens when one is not careful……

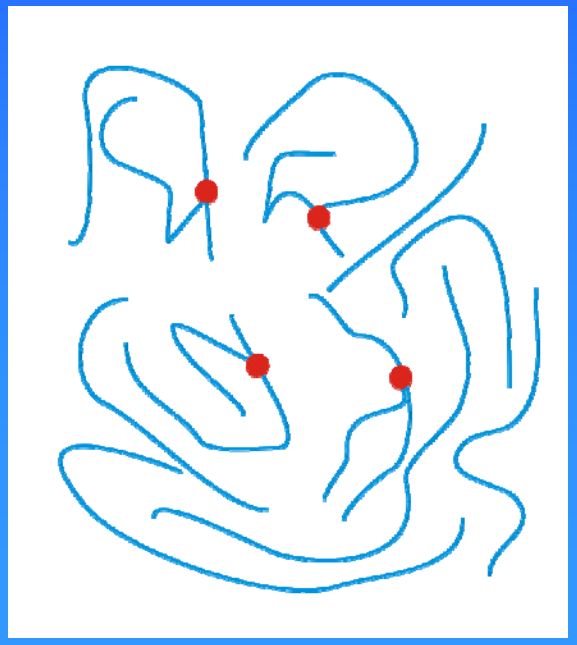






$\bar{M}_w = x$

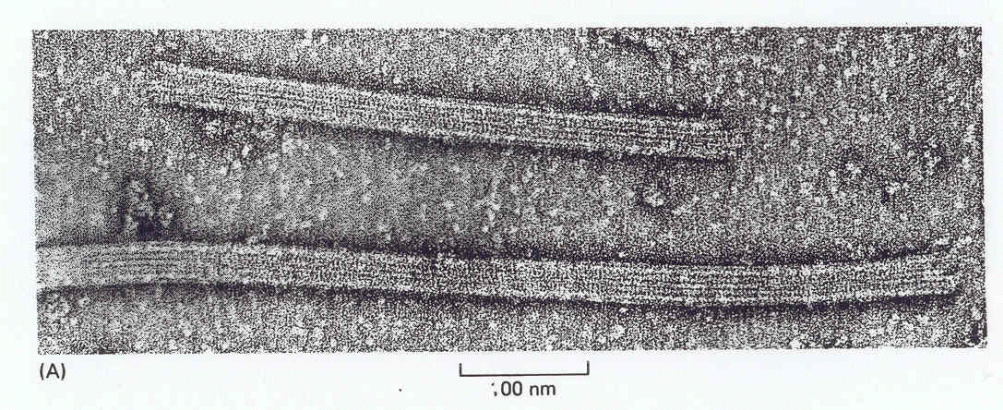


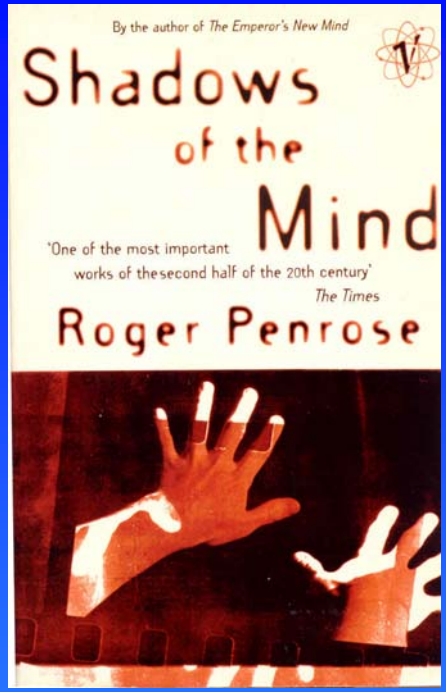


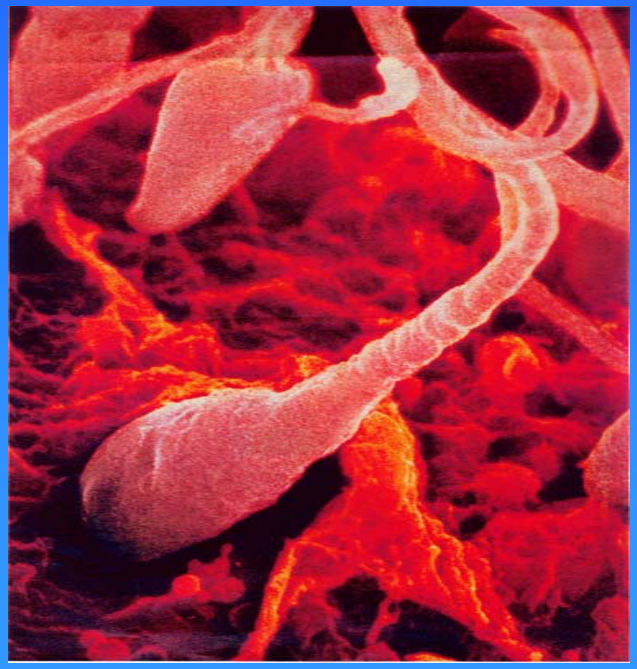
$\bar{M}_w > x$

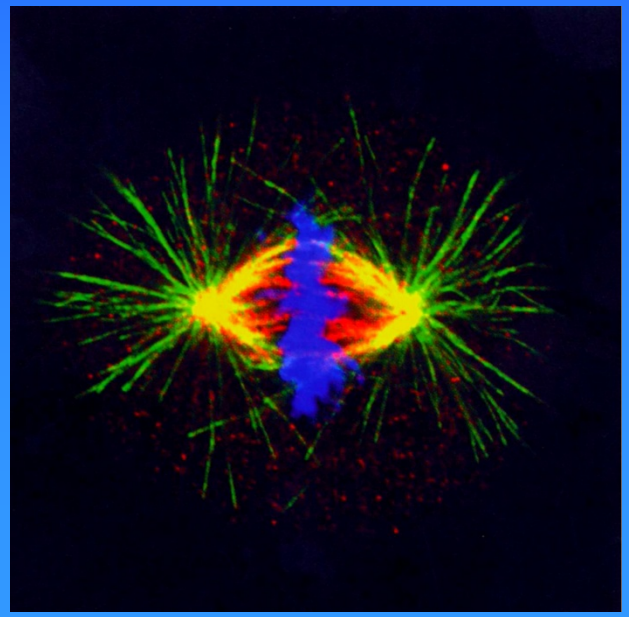
Problem:

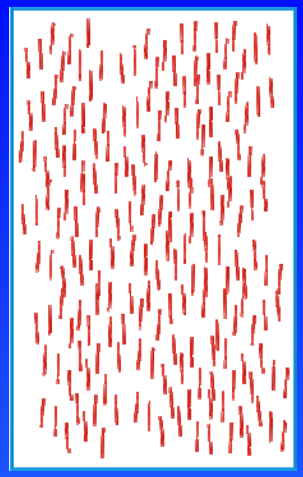
- One finds this back in the DSC data
- This means that instead of being a local ‘problem’ the total affected volume is much larger then the irradiated area

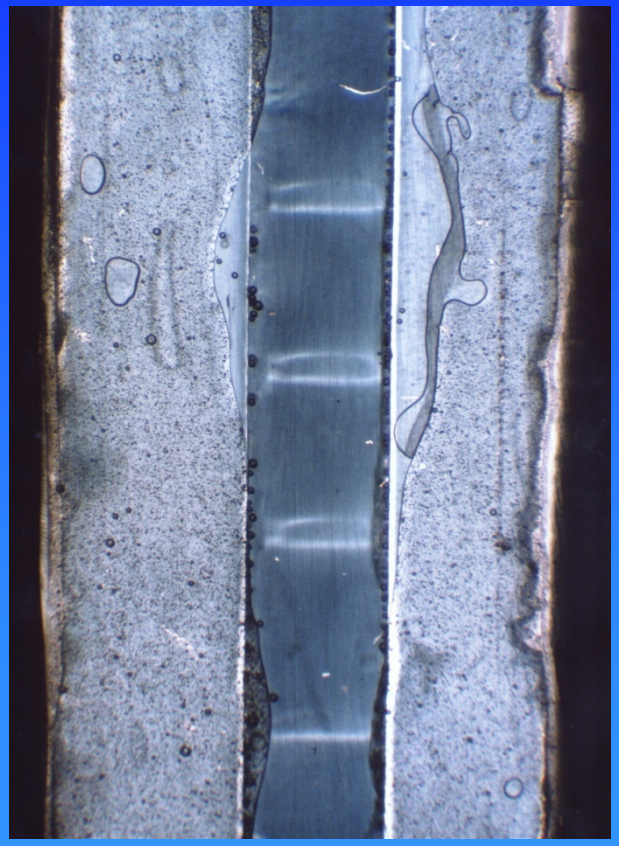

(A)
;00 nm


By the author of The Emperor's New Mind
Shadows
of the
Mind
'One of the most important
works of the second half of the 20th century'
The Times
Roger Penrose





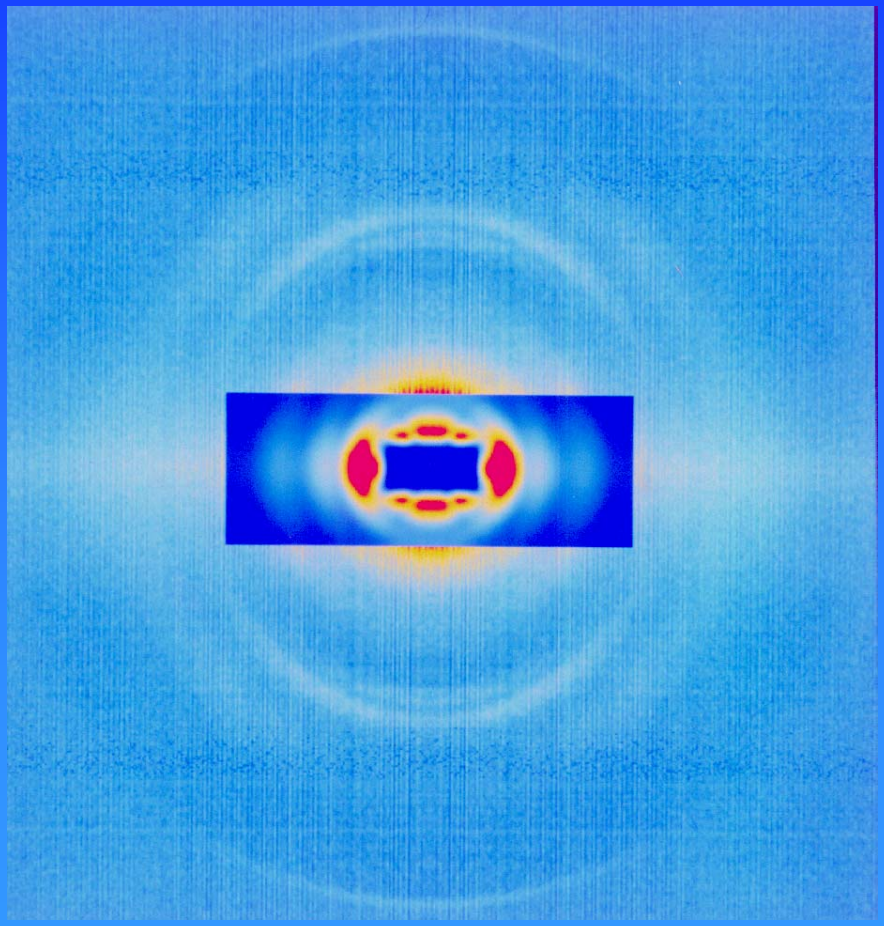


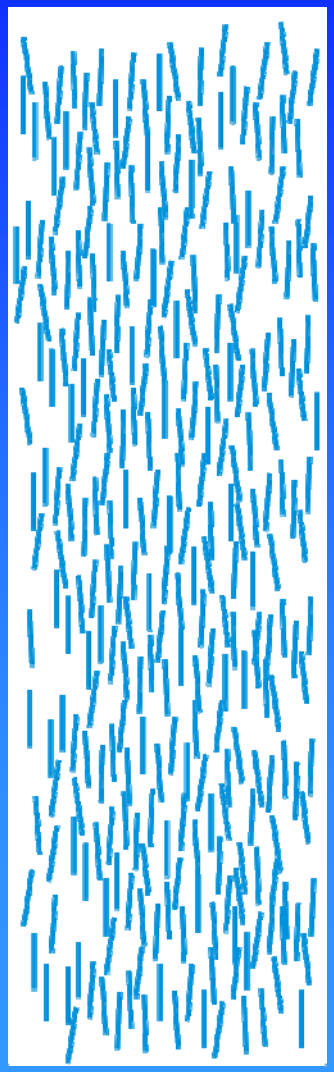


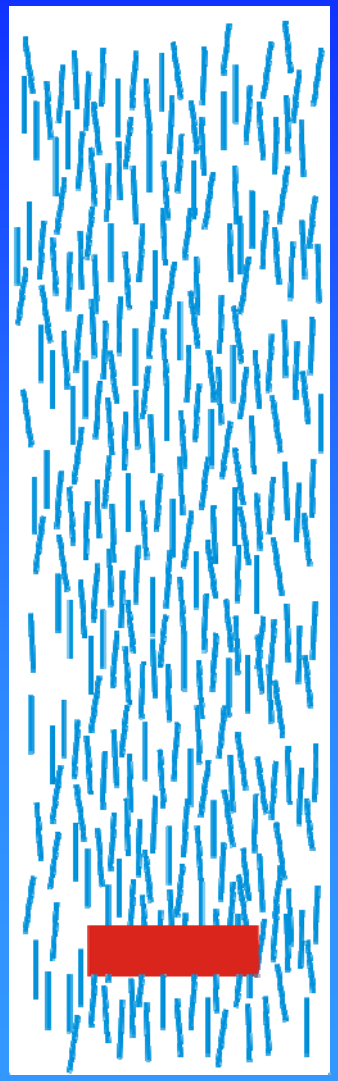
5 mm

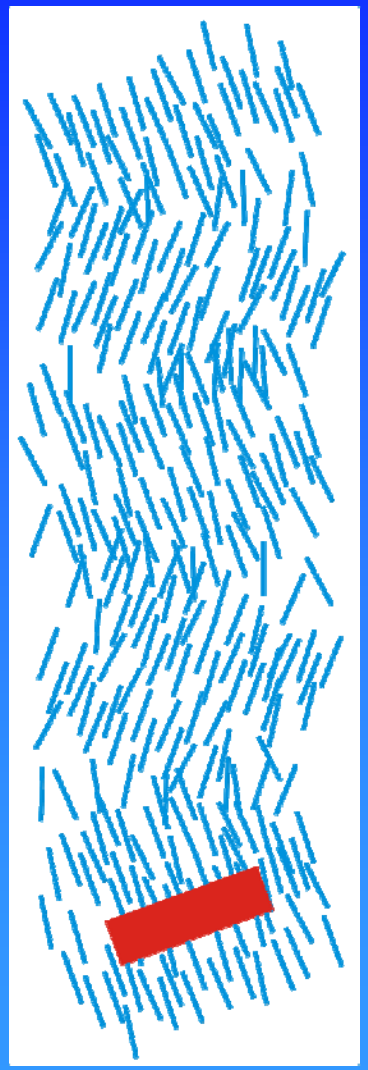
- Microtubule (rigid rod) polymer solutions
- Beam spot 300 micron vertical
- Radiation damage around 1 mm vertical direction

Fibre diffraction pattern









Worrying detail

- Calculations show only 0.1 weight% of material is damaged
- In most cases this would not change macroscopic morphology of sample
- Here it definitely does

Further results in the literature

- Au particles formation and Ostwald ripening
- Surface crystallisation at cryogenic temperatures
- Water evaporation due to lowered surface tension
- And probably more that I'm not aware of…

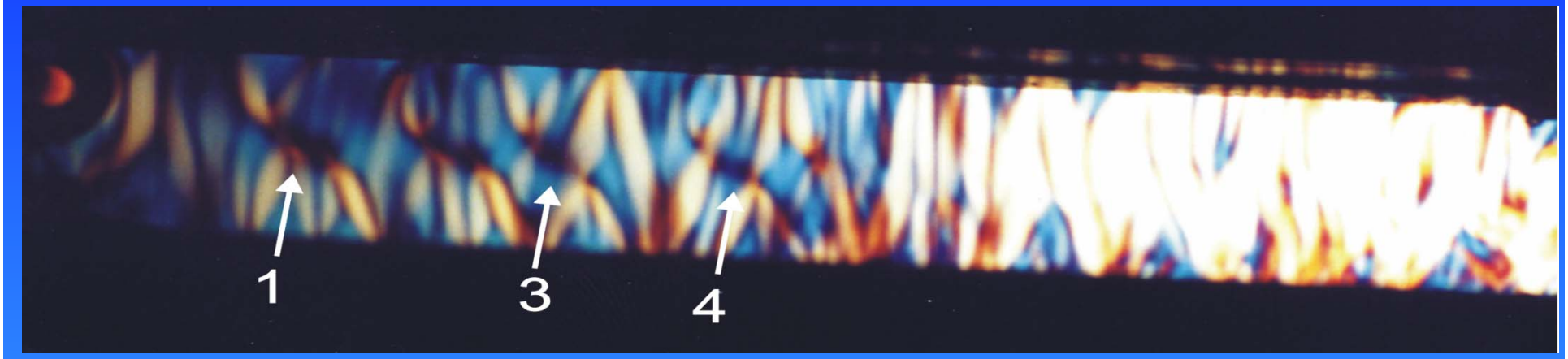
Prof. Rontgen says:

Don’t underestimate the power of my rays!

Thanks for your attention

So:

- Even in hard condensed matter samples 10 keV photons can screw up a time-resolved experiment
- Not only direct footprint area of beam affected but area perpendicular in photon polarization direction as well


1
3
4