X-ray characterisation of diamonds at the ESRF

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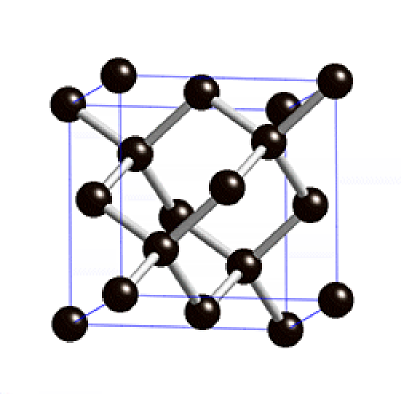
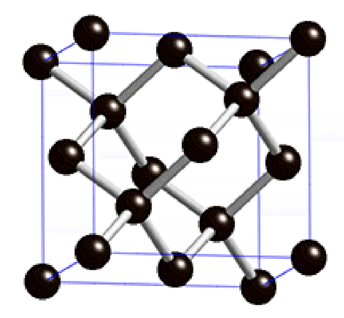
Co-workers



R. Burns, J.O. Hansen
Element Six Technologies (Johannesburg) – South Africa

S.H. Connell, M. Rebak, D. Dube, R. Setshedi, L. Mkhonza
University of the Witwatersrand – South Africa

P. Van Vaerenbergh, I. Gierz, F. Masiello, J. Hoszowska, A. Rommeveaux, A. Chumakov, G. Carbone, J. Morse
European Synchrotron Radiation Facility, Grenoble - France



Outline

1. Introduction
2. Looking more at the "bulk"
   - Bragg diffraction imaging ("X-ray topography")
   - High-resolution diffractometry
3. Looking closer to the "surface"
   - Reflectometry
   - Grazing incidence diffraction

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Diamonds at modern X-ray sources

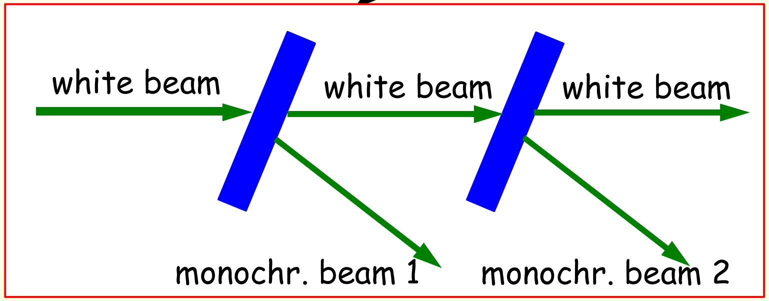
- Diamond anvils for high pressure generation
- Detectors, beam position monitors (John Morse)
- **X-ray optical elements**

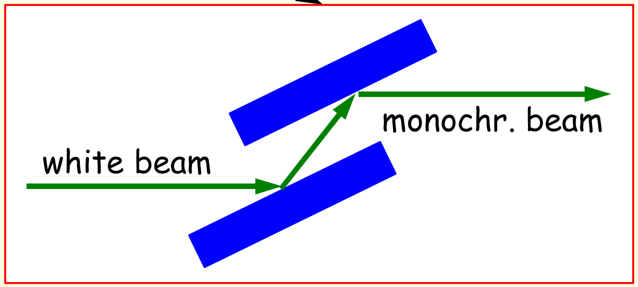
Optical elements at beamlines

- apertures, slits, pinholes
- filters, windows (amorphous, poly-crystals, crystals)
- monochromators (crystals, multi-layers)
- beam splitters (crystals), (are special monochromators)
- phase plates (crystals)
- mirrors
- lenses, zone plates (poly-crystals, crystals, ML)
- combined elements (ML gratings, Bragg-Fresnel-lenses)

Crystal based X-ray optical elements

- filters, windows
- phase plates
- beam splitters
- monochromators
- etc.



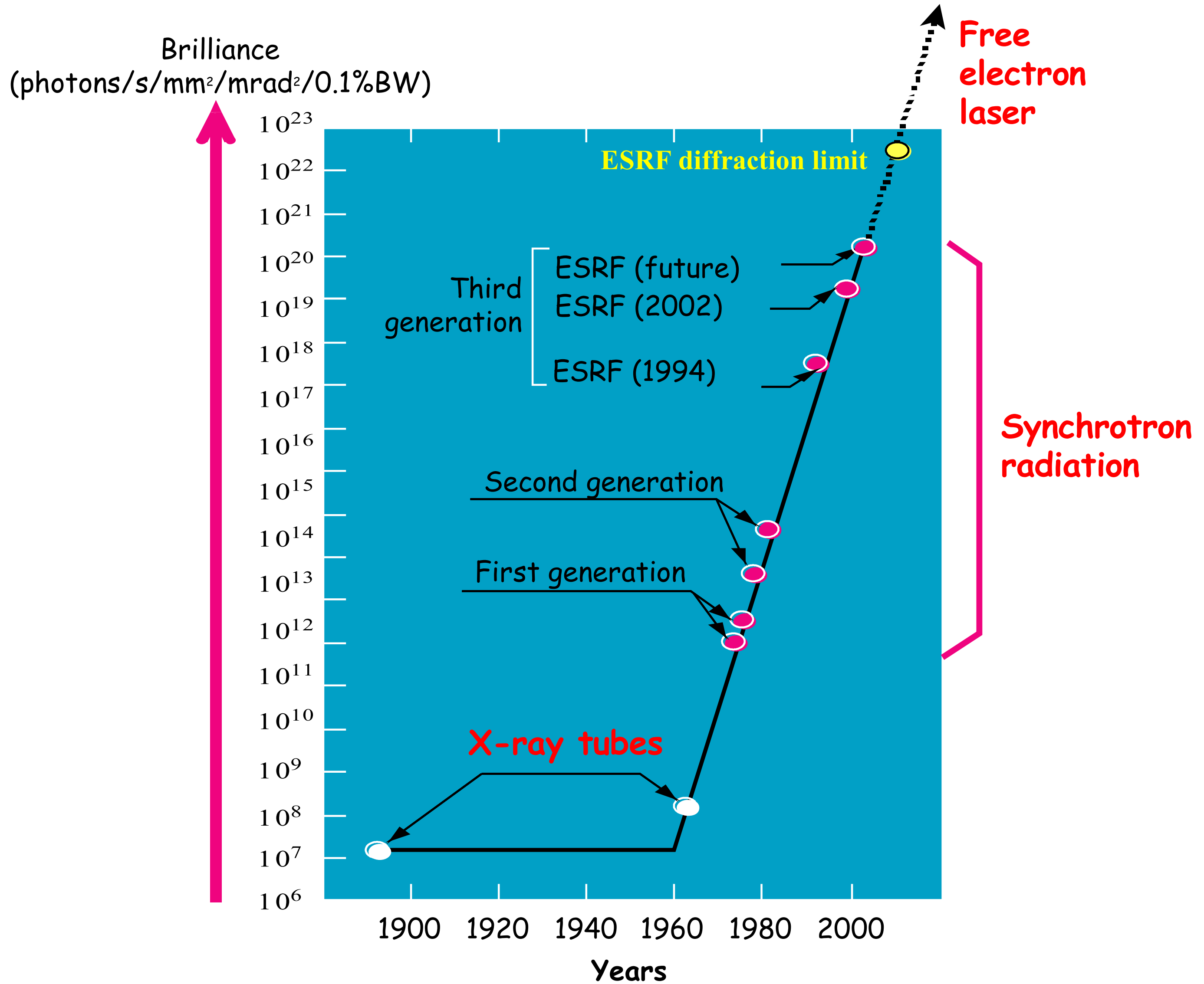


Why diamond?

Very interesting material properties

Mechanical, electronical, optical, thermal properties

History of Brilliance



With the modern sources:

Specific problems

heat load

coherence preservation

Consequences for used materials

for Bragg reflecting elements like monochromators

mainly silicon

diamond would be fine

(in few cases already used)

Limiting factors:

quality (bulk and surface)
dimension

The "perfection" of diamond

Firstly – nothing is perfect in nature!!!

Secondly – which are the defects we are sensitive to???

Surely not isolated defects on the atomic scale!

However, on them (and their resulting spectroscopic properties) the traditional classification is based (type Ia, Ib, IIa, IIB, III)

Classification and perfection of diamond

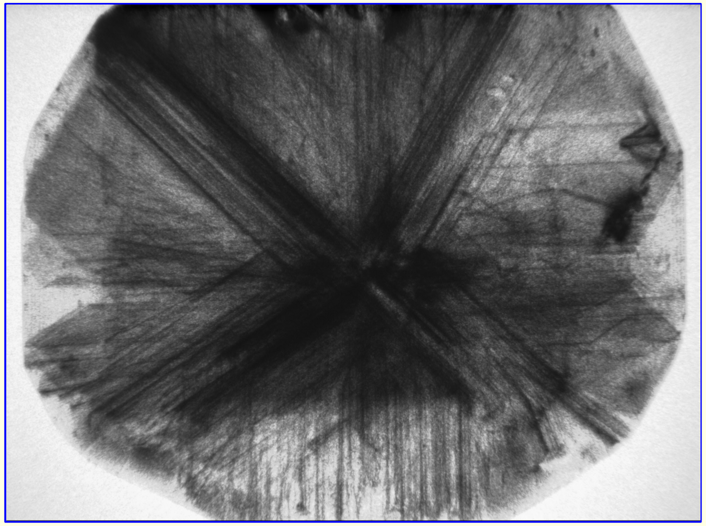
Traditional classification of diamond – spectroscopic properties

Based on defect structure, but on nanometric or atomic level

but

X-ray optics – defect structure up to a microscopic to millimetric level

No direct relation between both classifications!



0.5 mm

Gem quality IIa synthetic diamond

We need:

High bulk and surface quality!

Study of the defect structure of crystals

Why?

Interrelation between:

its origin ⟷ defect structure ⟷ its results

growth process,
growth conditions,
crystal processing, ...

Influence on physical properties

Techniques we used at ESRF

X-ray diffraction imaging (X-ray topography)

From white beam topography to monochtomatic-plane-wave topography; preferred techniques

Diffractometry and rocking curve widths

For comparison (and because people like it),
but integrating method (even if spatially resolved),
low single defect sensitivity

Surface sensitive techniques

Coherence measurements (Talbot effect)

ESRF

"Macroscopic" defects in diamond which we do **not** like:

Inclusions

Dislocation

Stacking faults

Impurities, but in the form of:

- concentration differences between sectors -

growth sector boundaries

- concentration changes within a sector -

growth striations

Best candidate for material with high perfection for X-ray optics applications

Highly pure type IIa HPHT material
(very low nitrogen content)

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ESRF

What is X-ray Bragg diffraction imaging?

X-ray Bragg diffraction imaging
historically called **X-ray topography**
is an imaging technique

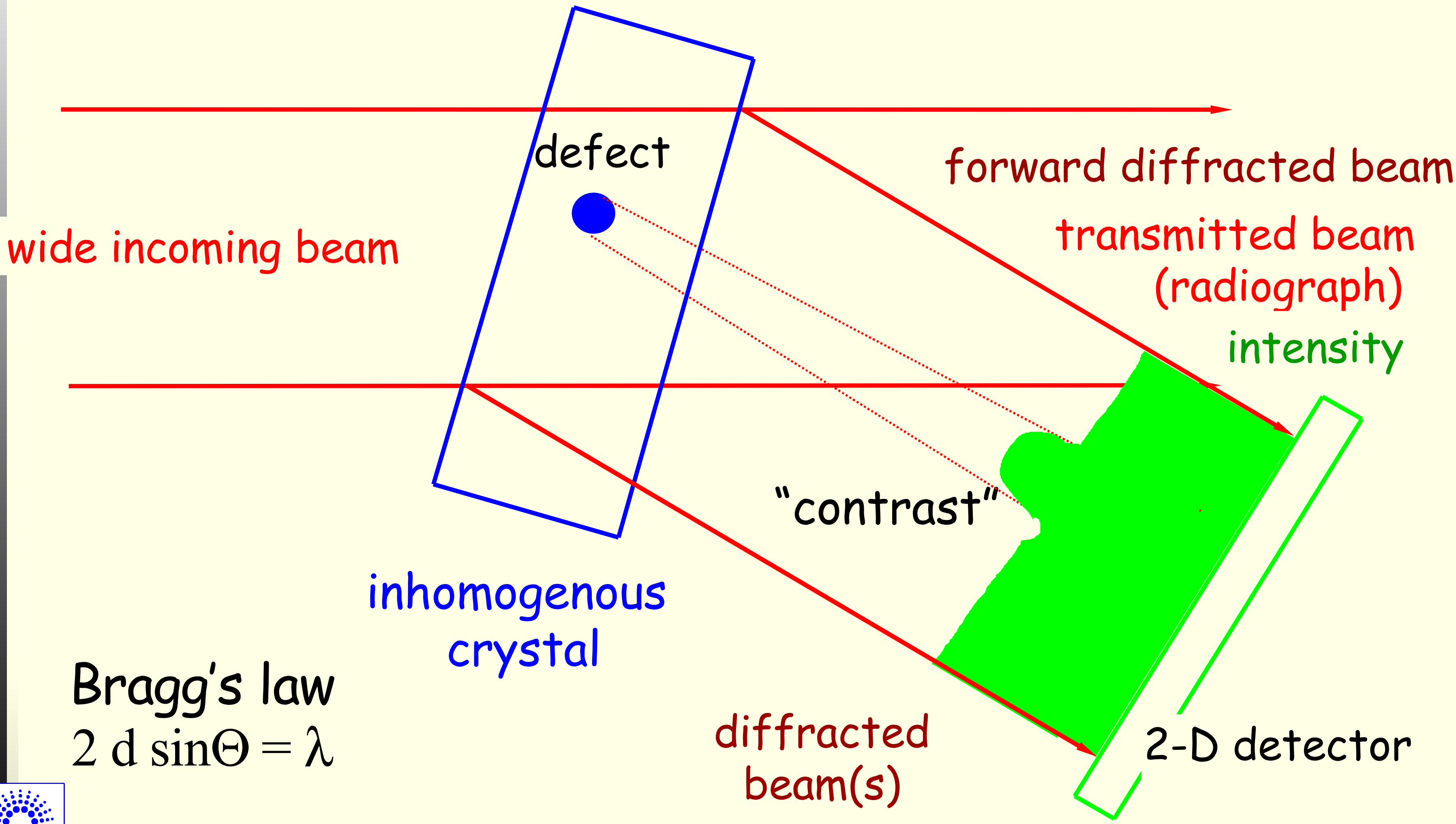
- based on Bragg diffraction
- which applies to single crystal samples
- which shows the *inhomogeneities in the crystal* (on a micrometric scale)

Which inhomogeneities can be observed, visualized?

- Crystal defects (their diffraction images!):
  dislocations, twins, stacking faults,
  growth sector boundaries, growth striations,
  inclusions, precipitates, …
- and macroscopic deformations:
  bending, acoustic waves, heat bump, …

Basic principle of X-ray diffraction topography

for an extended, homogeneous, white or monochromatic beam



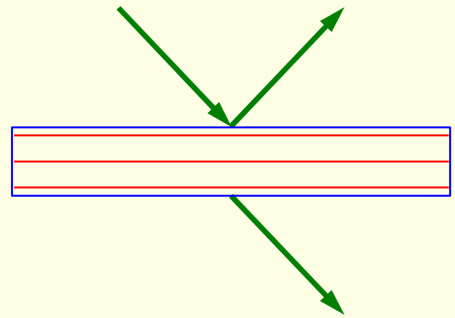
Bragg's law

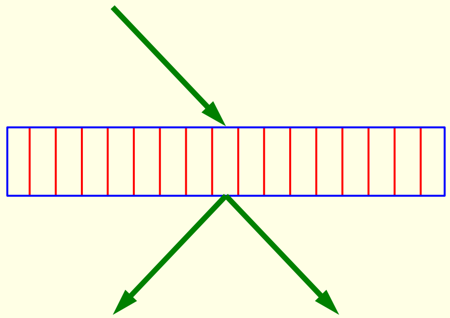
$2\, d \sin\Theta = \lambda$

Various techniques and variants exist

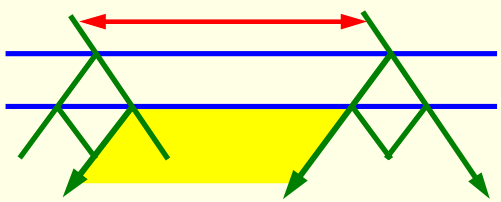
Most basic "classification"

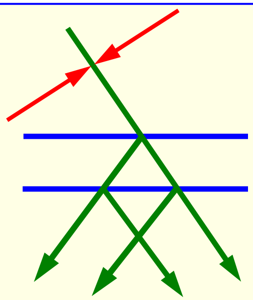
Reflection (Bragg) geometry - transmission (Laue) geometry





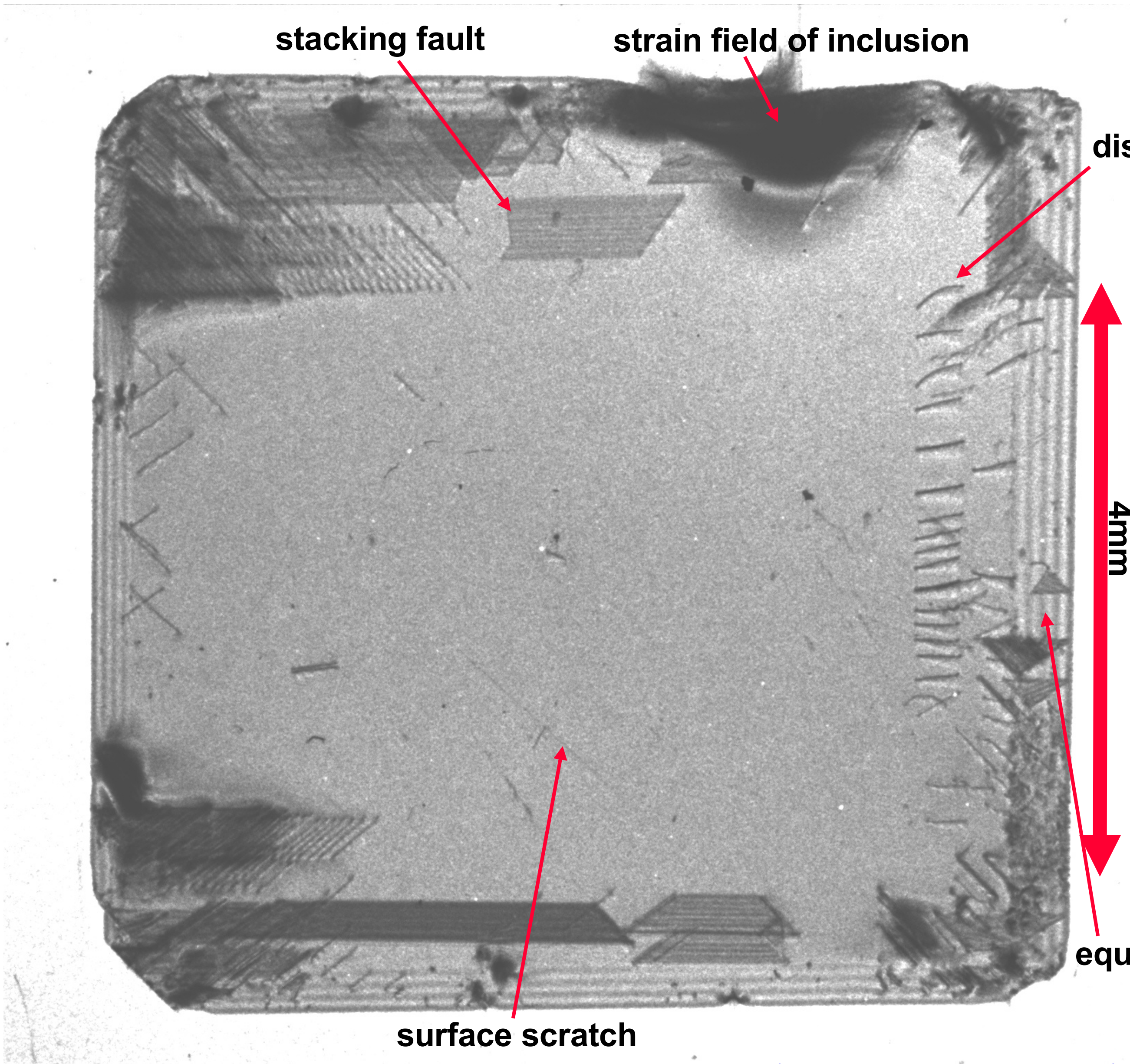
extended beam - limited beam





integrated wave topography (e.g. white beam topography) - plane monochromatic wave topography

How a X-ray topograph may look like (1):

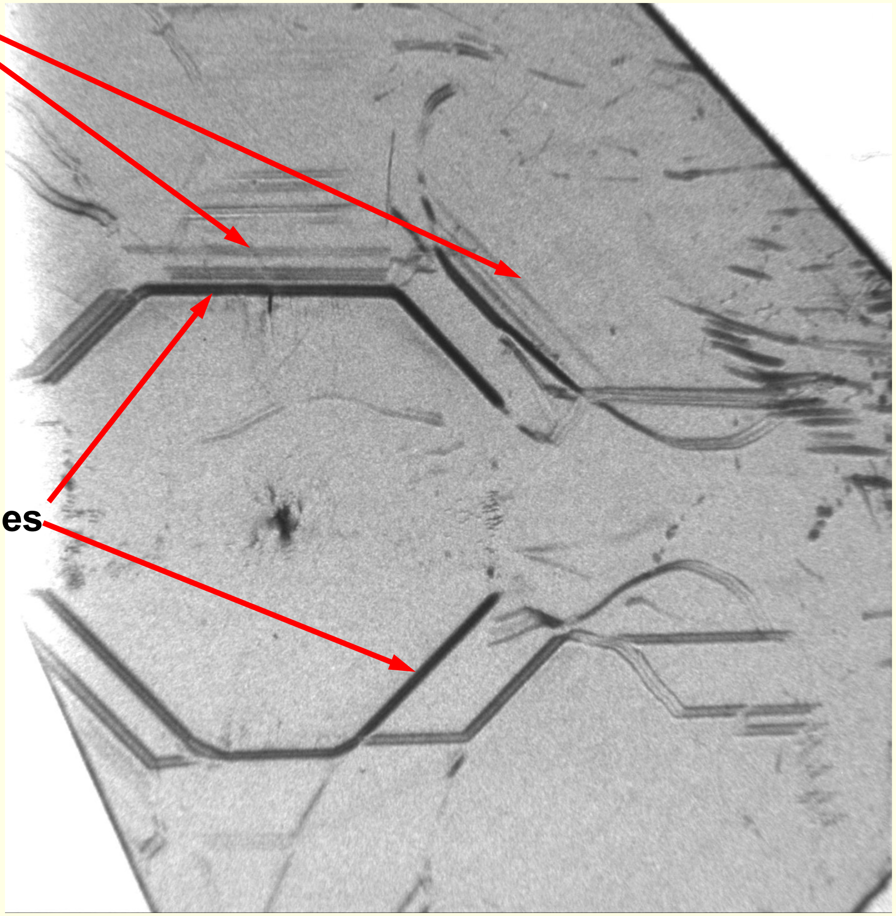


Highly pure HPHT type IIa 100-oriented diamond

(first new series)

White beam topography (transmission geometry)

How defects may look like in a X-ray topograph (2):



growth striations

growth sector boundaries

$[2\bar{2}0]$

2 mm

Nitrogen rich
HPHT type Ib
100-oriented
diamond

White beam topography (transmission geometry)

X-ray topography versus TEM

Complementary methods

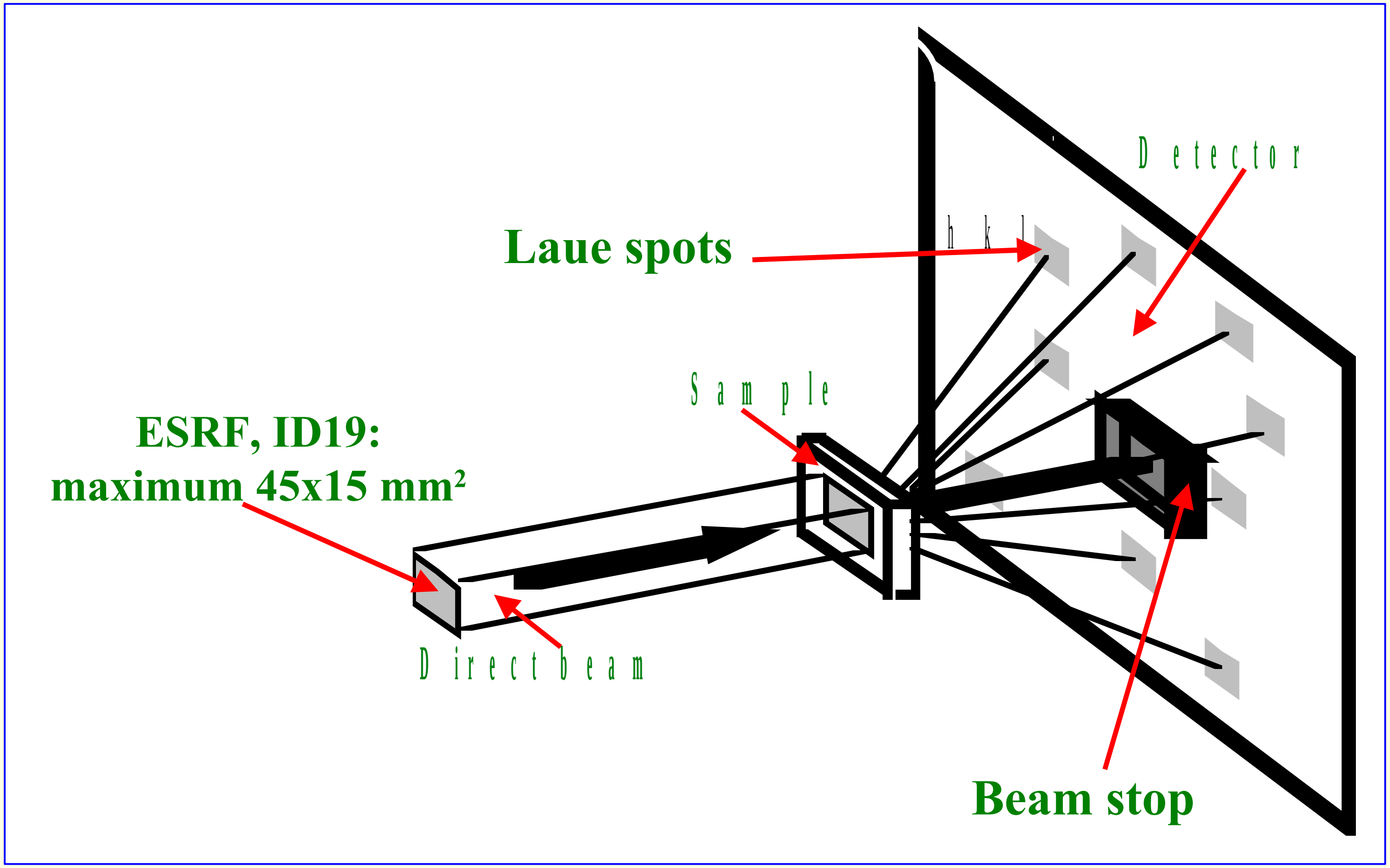
	X-ray topography	TEM
Spatial resolution:	µm	nm
Field of view:	mm … dm	µm
Strain sensitivity:	(10^{-3}) 10^{-4} … 10^{-7} (10^{-9})	10^{-2} … 10^{-3}
Defect densities: (dislocations)	0 … 10^{-5} cm/cm³	10^{-4} … 10^{-10} cm/cm³
	large samples possible	small samples
	non-destructive	destructive

White beam topography

White Beam Topography

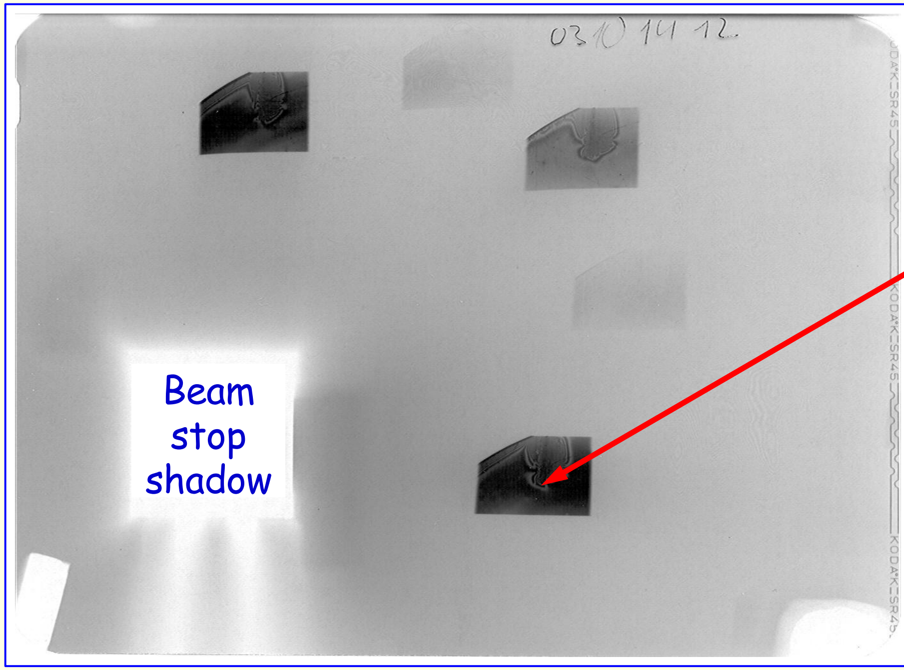
Most popular integrated wave technique at synchrotrons:

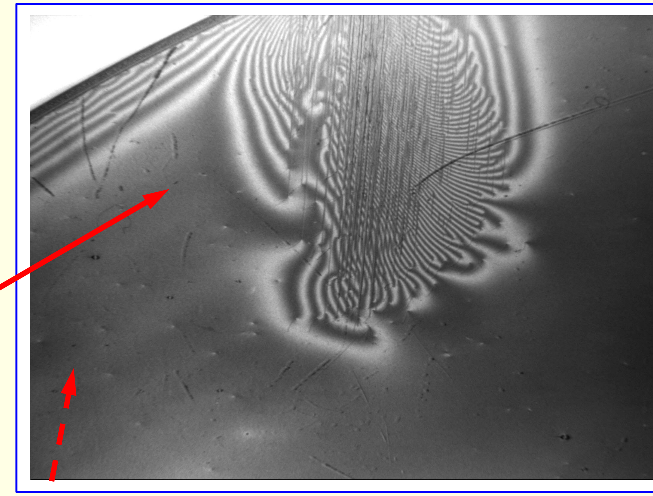
- principle (for transmission geometry) -



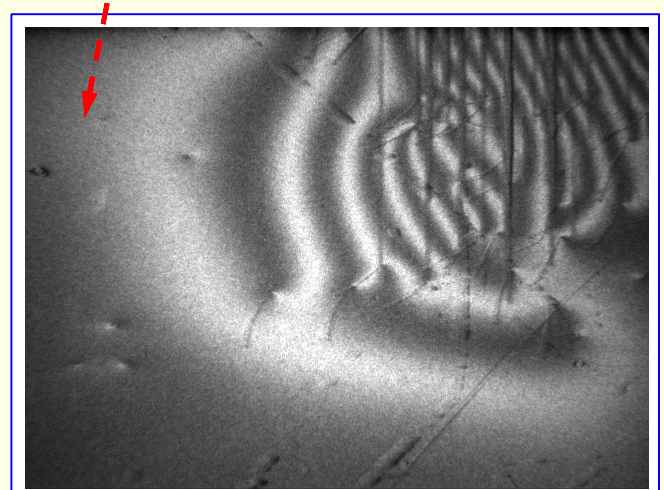
How it works - example

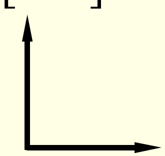
18 cm





One individual "spot"
- a topograph





Film with Laue spots

part of a low dose SIMOX* wafer

*Separation by IMplantation of OXygen

Action of lattice distortion on diffraction

Defect – long-range **strain field**

⬇

Departure of the local Bragg angle $\Theta(\mathbf{r})$
from that for a perfect reference crystal region Θ_B

Effective misorientation:

$$\delta\theta(\mathbf{r}) = \Theta(\mathbf{r}) - \Theta_B = -(\lambda/\sin 2\theta_B)\cdot\partial(h\cdot u(\mathbf{r}))/\partial s_h$$

h : undistorted reciprocal lattice vector

$u(\mathbf{r})$: displacement vector

$\partial/\partial s_h$: differentiation along reflected beam direction

Remember: $\delta\theta(\mathbf{r}) = f(h \cdot u(\mathbf{r}))$

With the local dilatations and rotations

More descriptive form:

$$\delta\theta(\vec{r}) = -\tan\Theta_B \frac{\delta d}{d}(\vec{r}) \pm \delta\varphi(\vec{r})$$

$\delta d(\mathbf{r})/d$ – local relative change of the lattice parameter

$\delta\varphi(\mathbf{r})$ - local inclination angle of the reflecting lattice planes with respect to the perfect lattice

(these are strain tensor components)

U. Bonse, Z. Phys. 153,278 (1958)

("combined local strain" = -δθ, the now accepted term "effective missorientation" after A. Authier 1967)

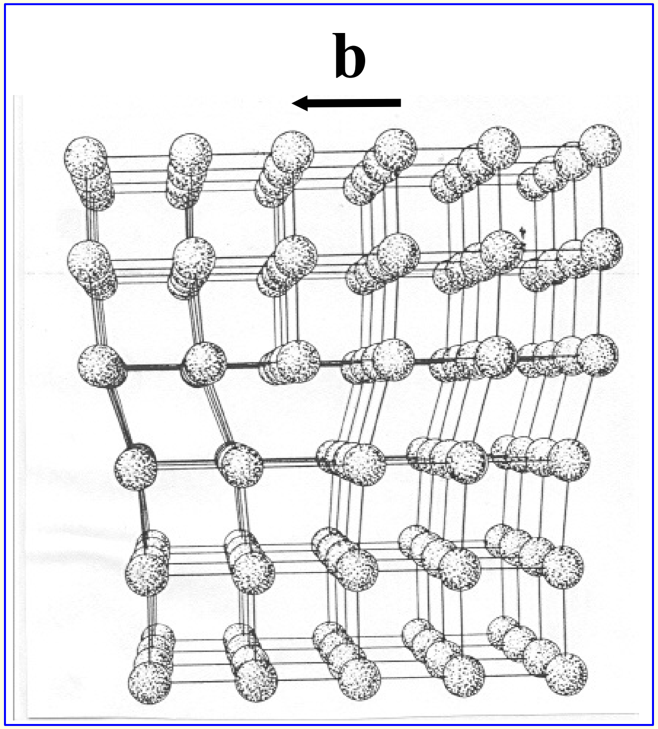
The double sign has to be chosen taking into account if the Bragg angle is locally increased or decreased by the deformation.

Consequence:

$\delta\theta = 0$ if $\mathbf{u}$ perpendicular to $\mathbf{h}$:

defect not visible on the topograph

(diffracting lattice planes are NOT deformed!)



Example: dislocation not visible

when $\mathbf{h}\cdot\mathbf{b} = 0$

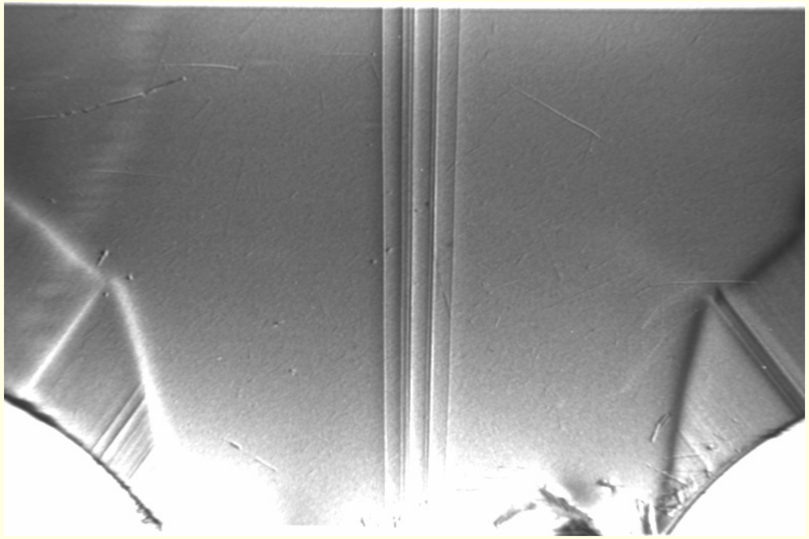
b - Burgers vector

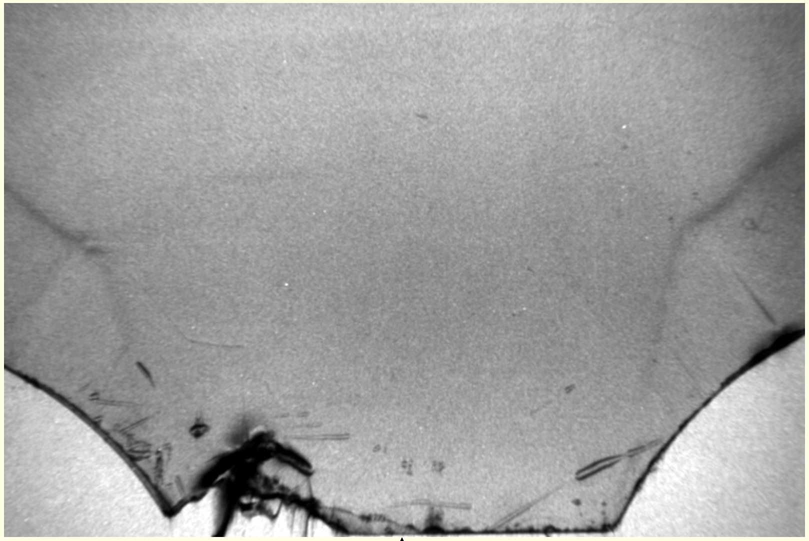
(strong contrast extinction for $h \perp$ image plane)

Example: white beam topography of GaAs

Dislocations in high quality GaAs

(grown by the Vertical Gradient Freeze technique
by B. Birkmann & G. Müller, University of Erlangen)





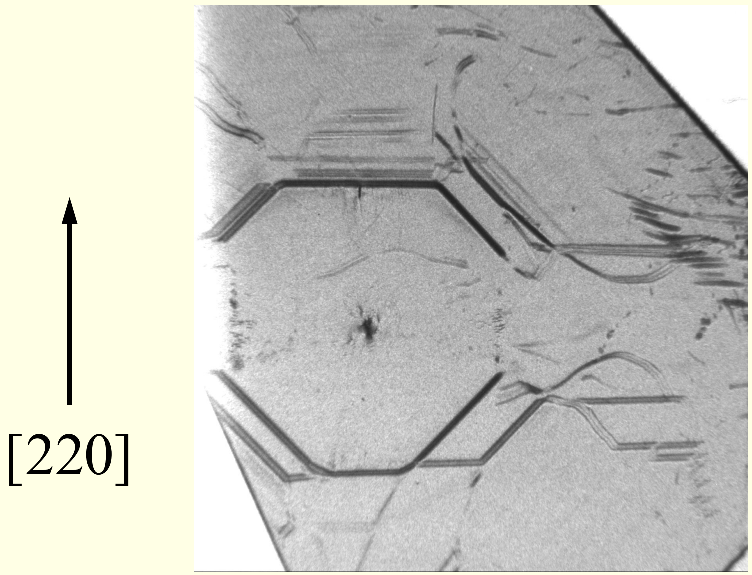
[2-20]

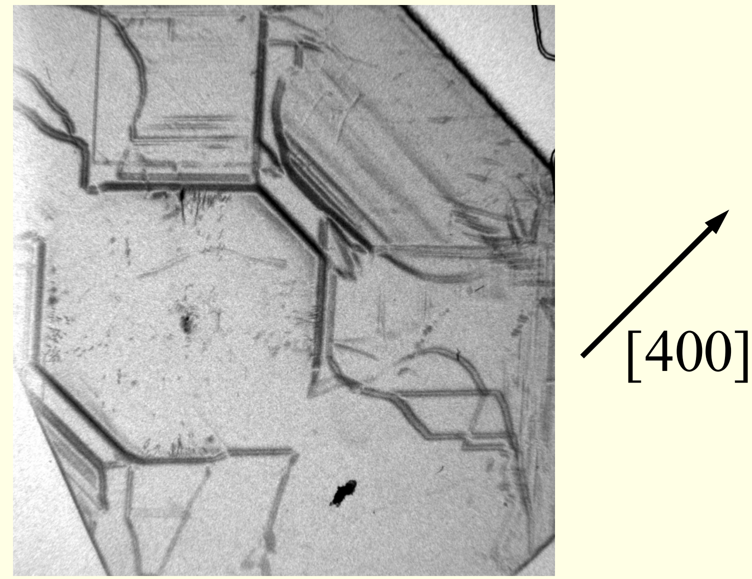
5 mm

[004]

Contrast extinction for **b** ⊥ **h** ➡ Edge dislocation with **b || [2-20]**

White beam topography - use of contrast extinction



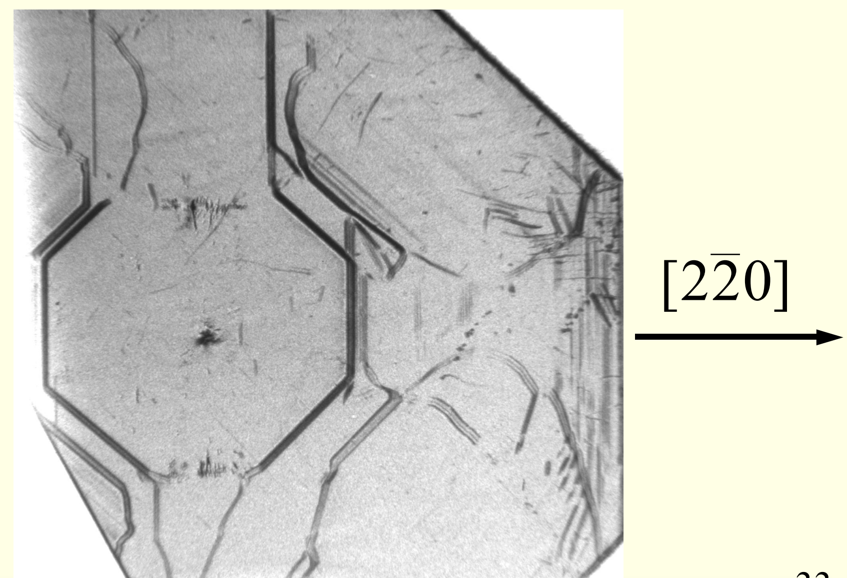


2 mm

Nitrogen rich HPHT type Ib

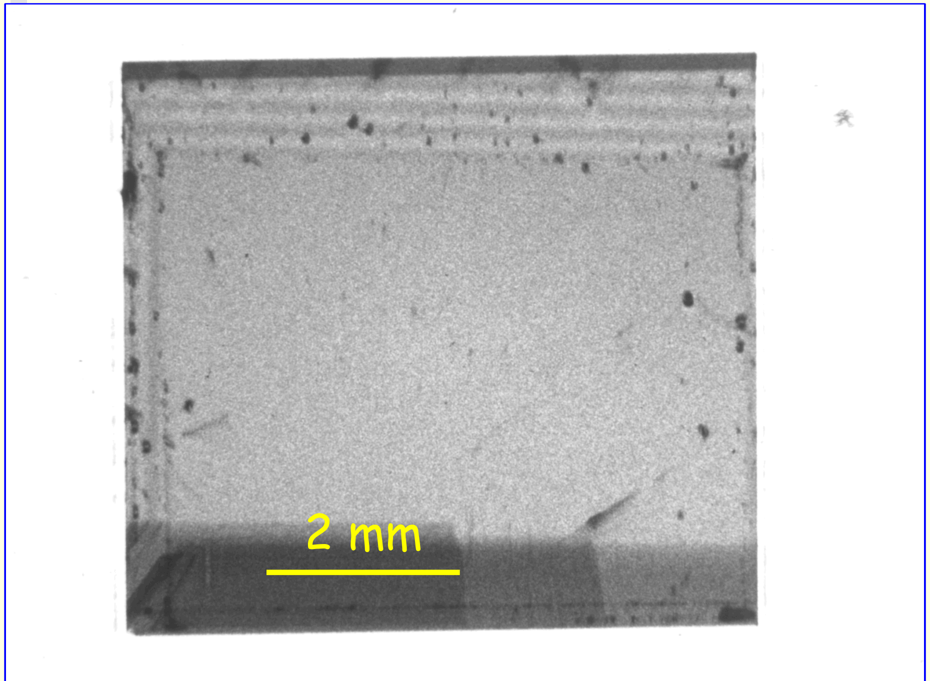
100-oriented

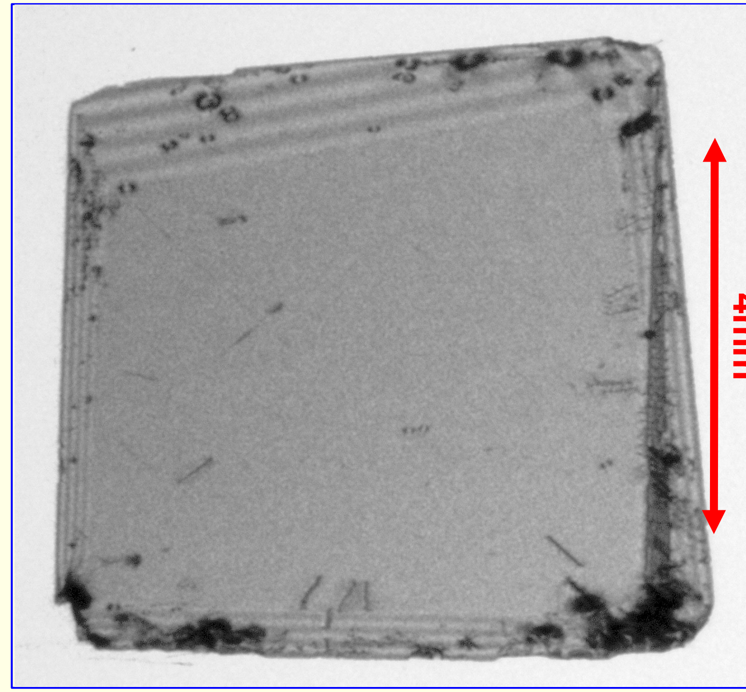
transmission (Laue) geometry



New type IIa HPHT material

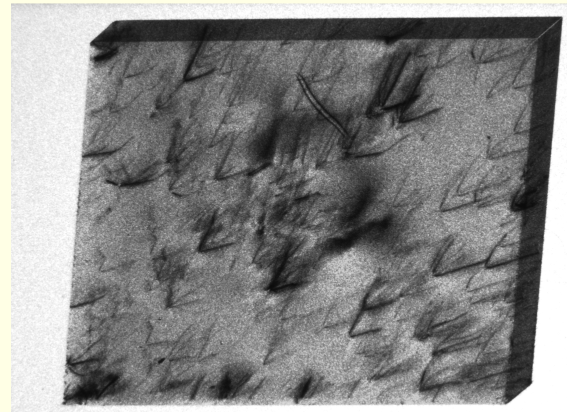
The best we could do up to now – X-ray topography





Central regions of high bulk quality
Confirmed by monochromatic beam (double crystal) topography
$\Delta d/d \leq 10^{-7}$
Promising for synchrotron X-ray optical applications
But dimension, coherence preservation?

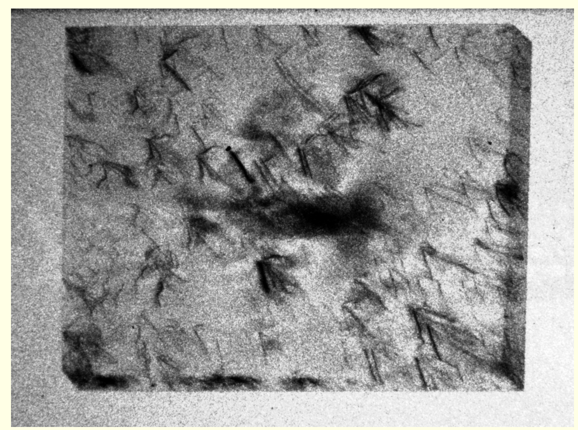
CVD material for detector applications



1mm

001-oriented plates

"top view"



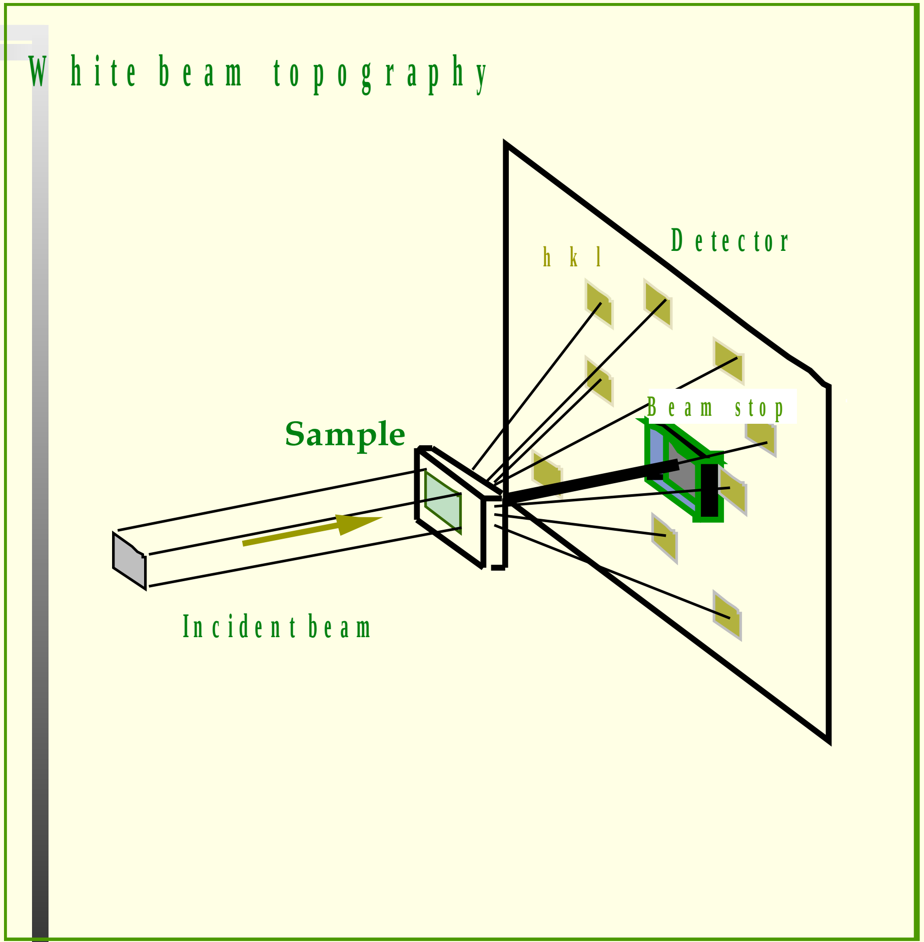
Local RC broadening – 0.9" … 2.4"
(ideal width 1" (FWHM))

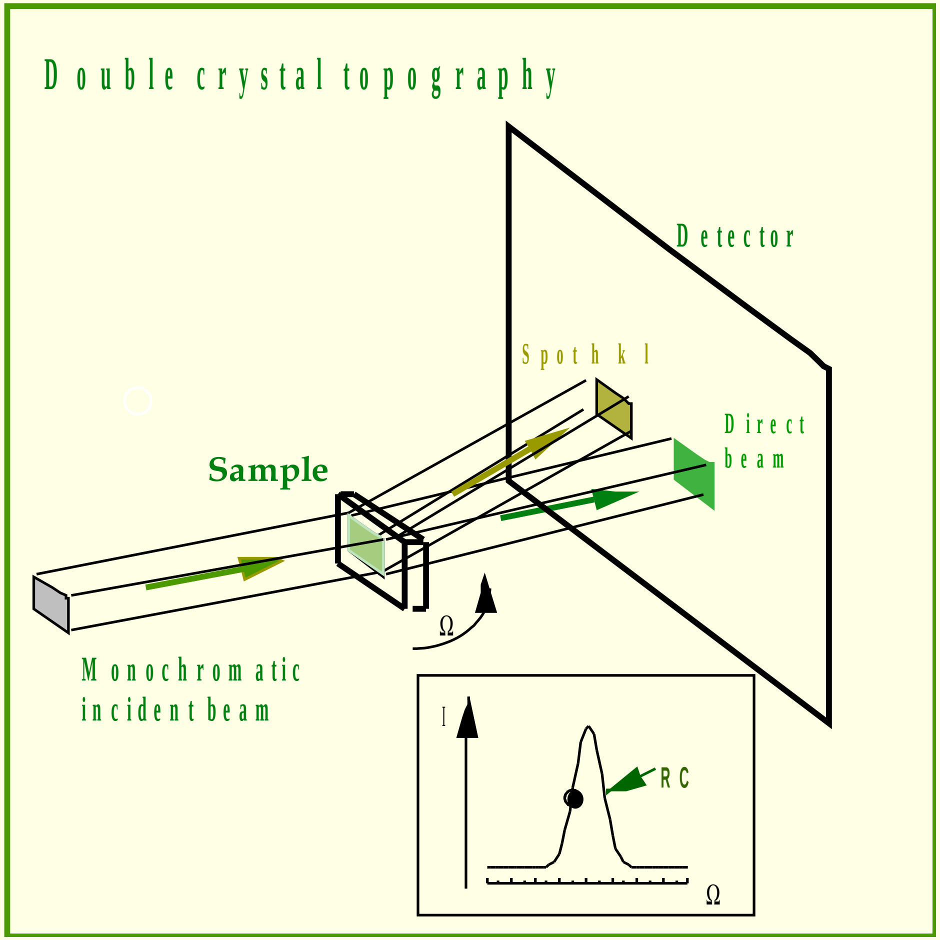
"Monochromatic" beam topography

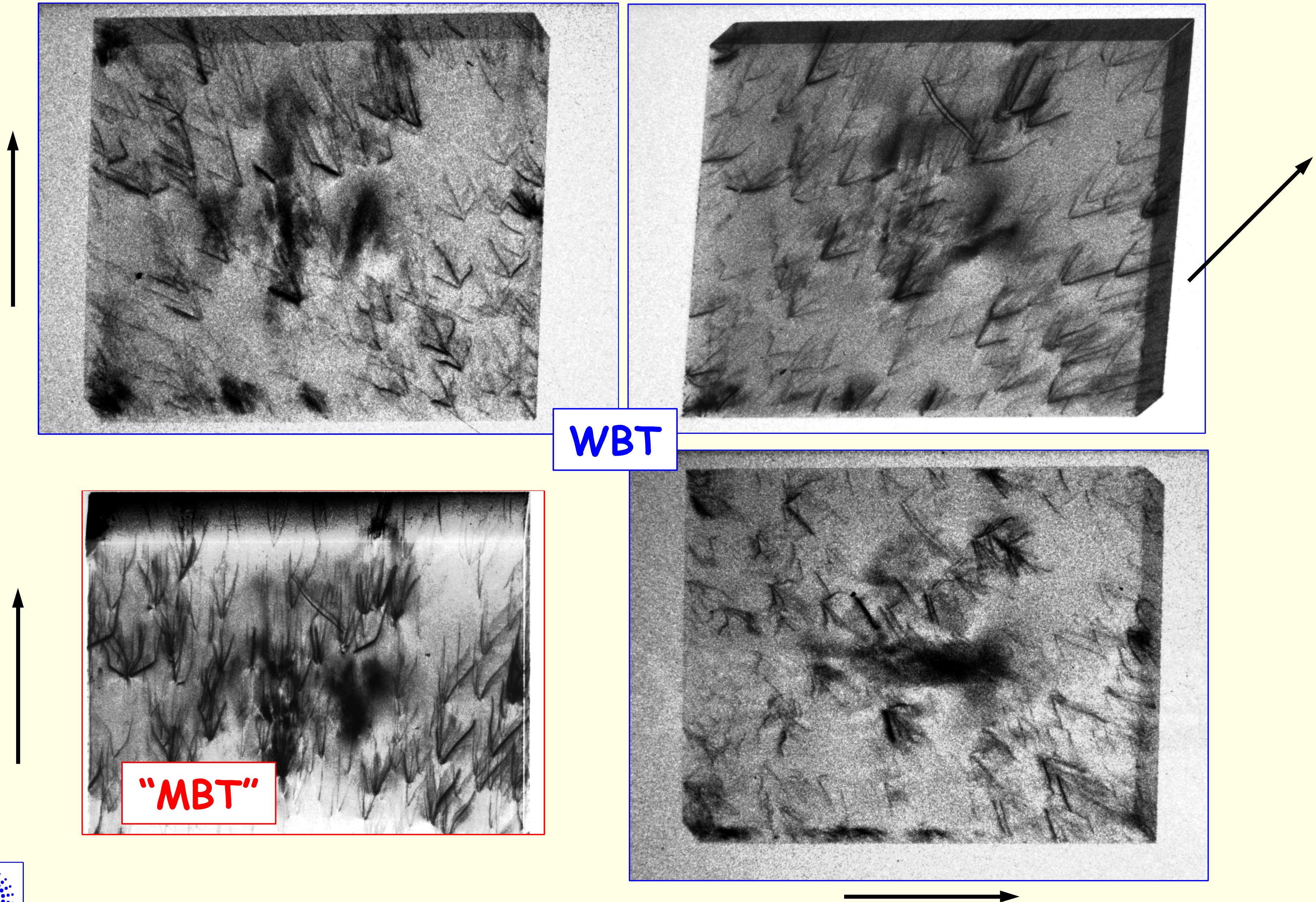
Laboratory – spectral lines ($K_{\alpha 1}$-lines)

Synchrotron – silicon 111 double monochromator

But still integrate wave methods!!!

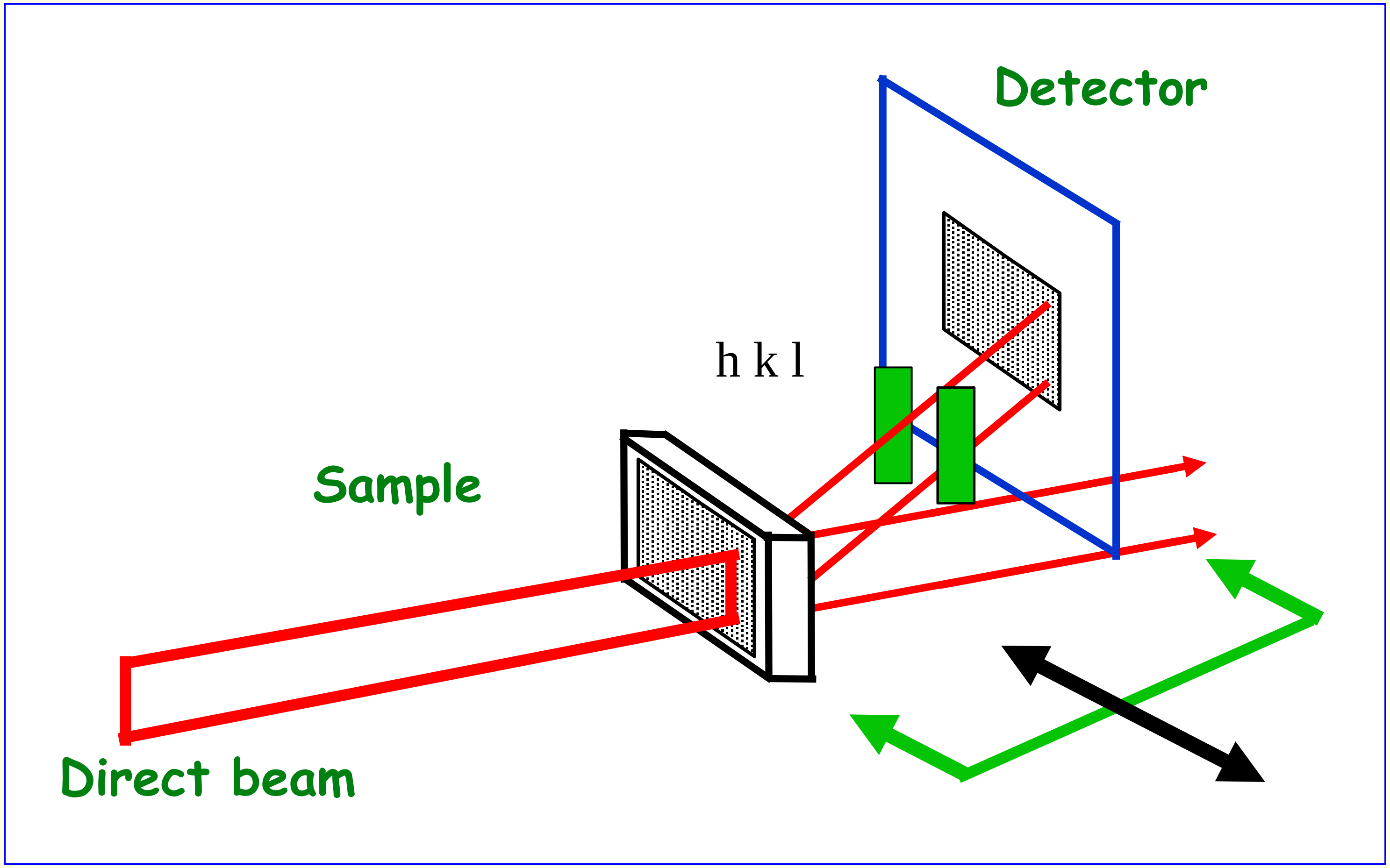

White beam topography
h k l
Detector
Beam stop
Sample
Incident beam

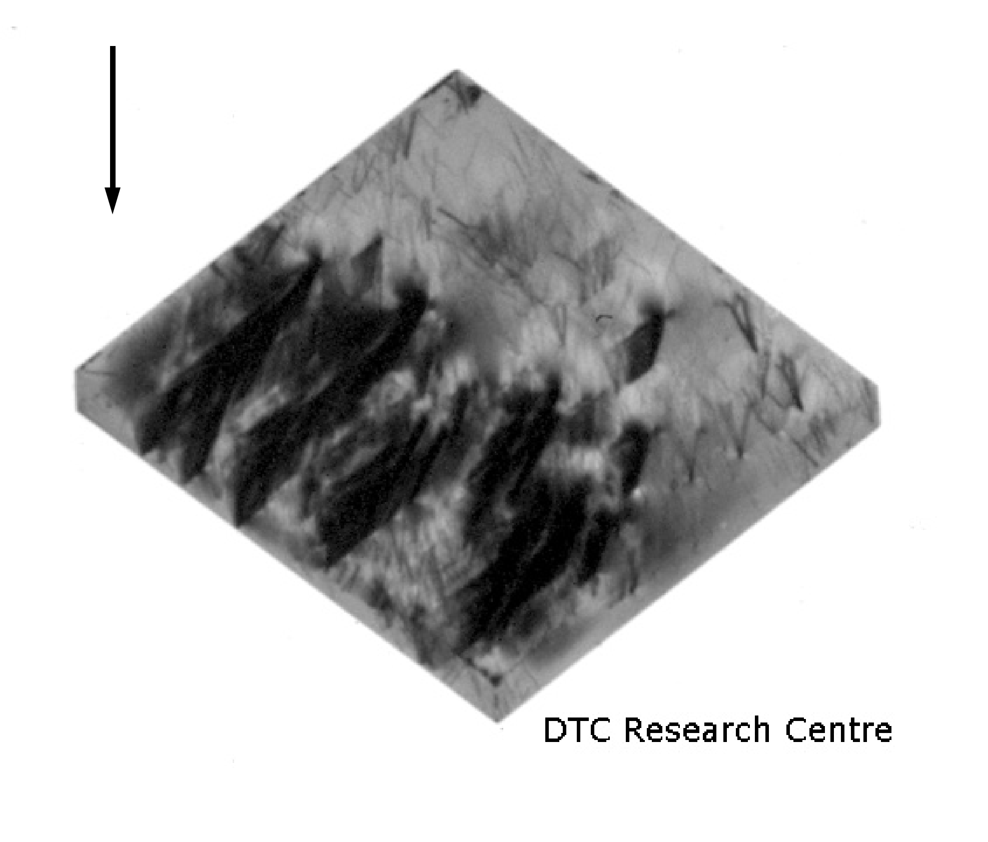

Double crystal topography
Detector
Spot h k l
Direct beam
Sample
Ω
Monochromatic incident beam
I
RC
Ω


WBT
"MBT"

Laboratory technique

Lang's technique – principle (transmission geometry)



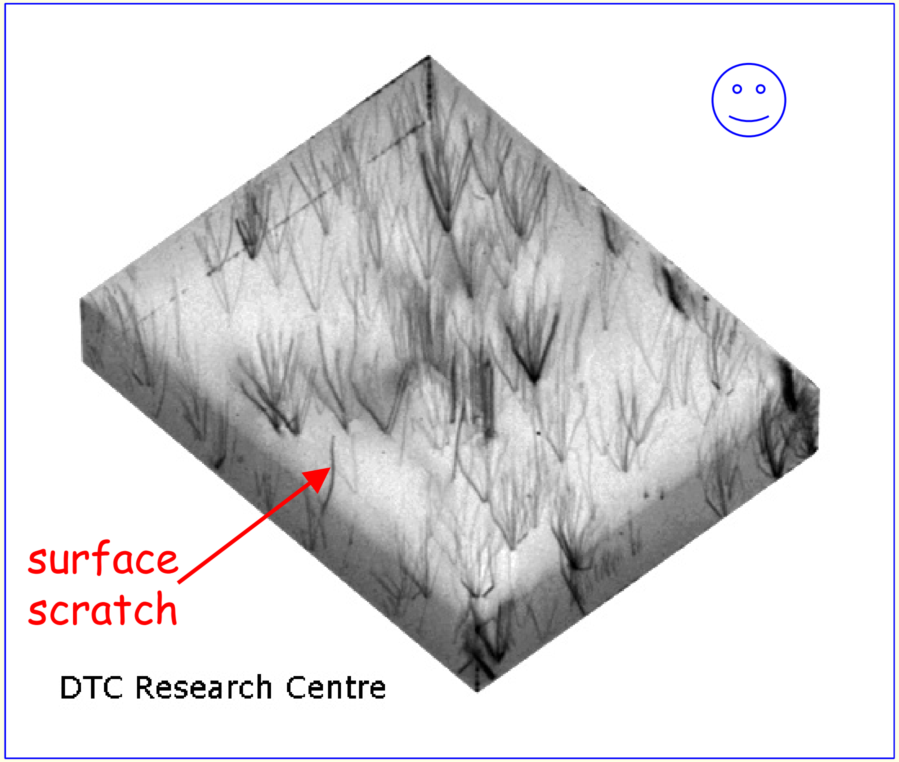


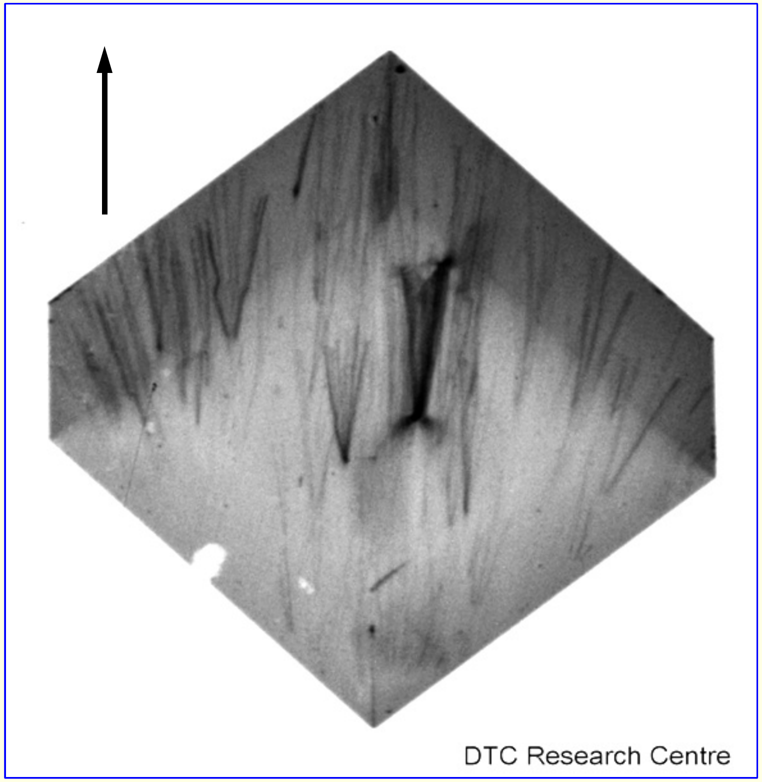
{111} Lang topograph

001-oriented CVD layer (with substrates removed).

CVD layer grown on a poorly processed substrate

Mike Gaukroger and Philip Martineau (DTC Research Centre, Maidenhead, UK)





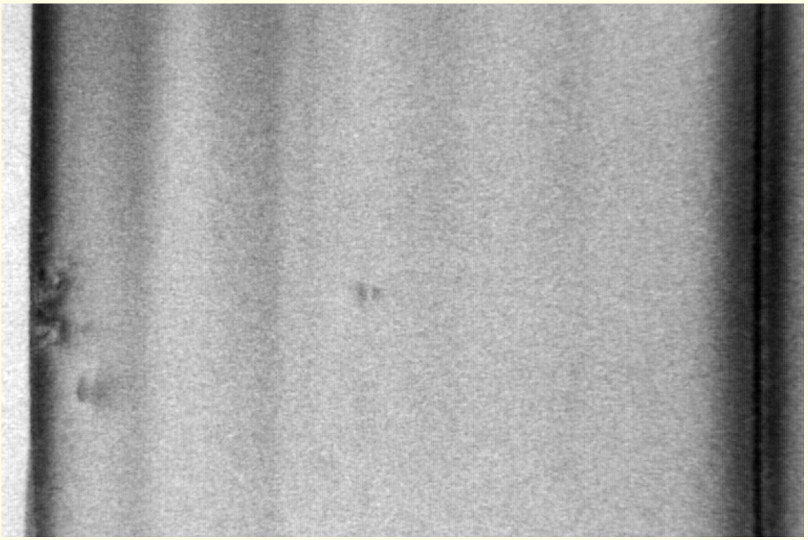
{111} Lang topographs
(1-11- or -111-reflection)
001-oriented CVD layers (with substrates removed)
CVD layers grown on carefully processed substrates

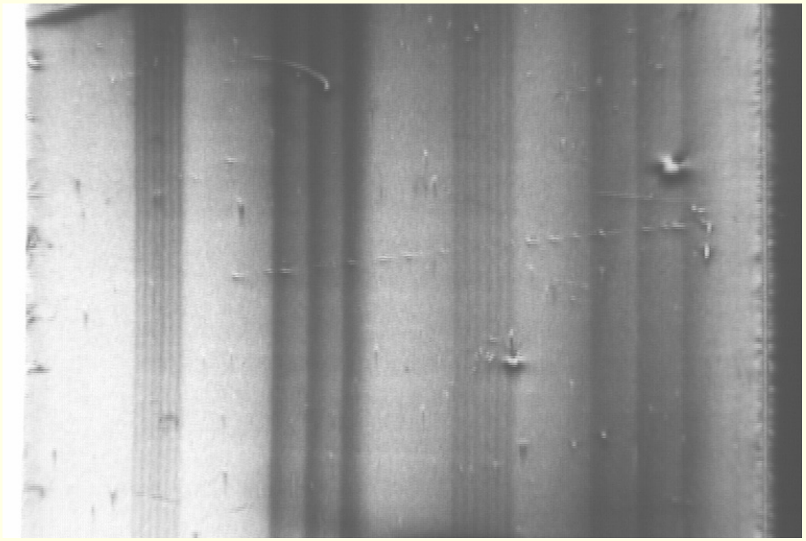
Mike Gaukroger and Philip Martineau (DTC Research Centre, Maidenhead, UK)

“Monochromatic plane” wave topography

“double ” crystal topography

quartz sample with induced growth striations (strain 2.5 … 4 10^{-7})
(Y-cut plate, ≈ 1 mm thick)





h = [0003] ←

1 mm

$\mathbf{k}_{||}$ ↑

$\mathbf{R_I = 2400m}$

White beam topograph

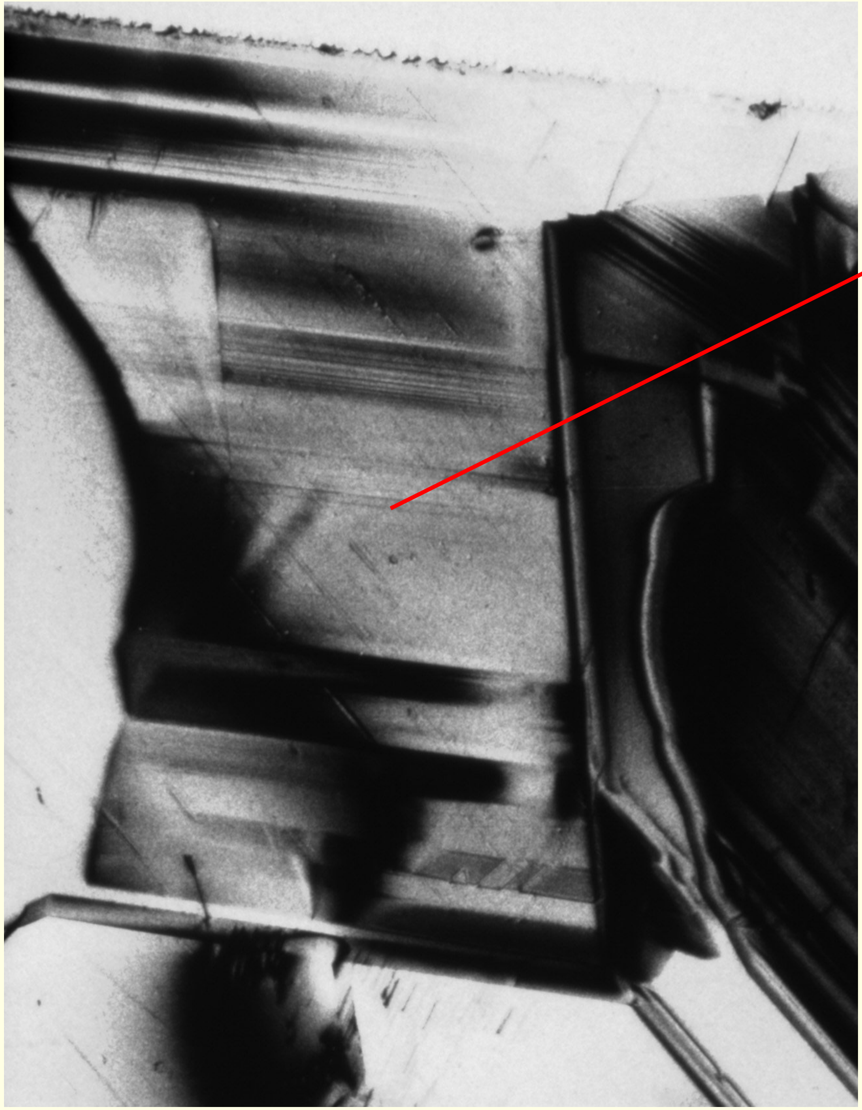
Double crystal topograph

sample 80·0 reflection (Bragg case), FWHM = 0.07″
bent Si monochromator, 448 reflection (Bragg case), FWHM = 0.31″, asymmetry angle α = -17.6°, high angle flank of rocking curve, E = 17.7 keV

HPHT Ib

High in Nitrogen

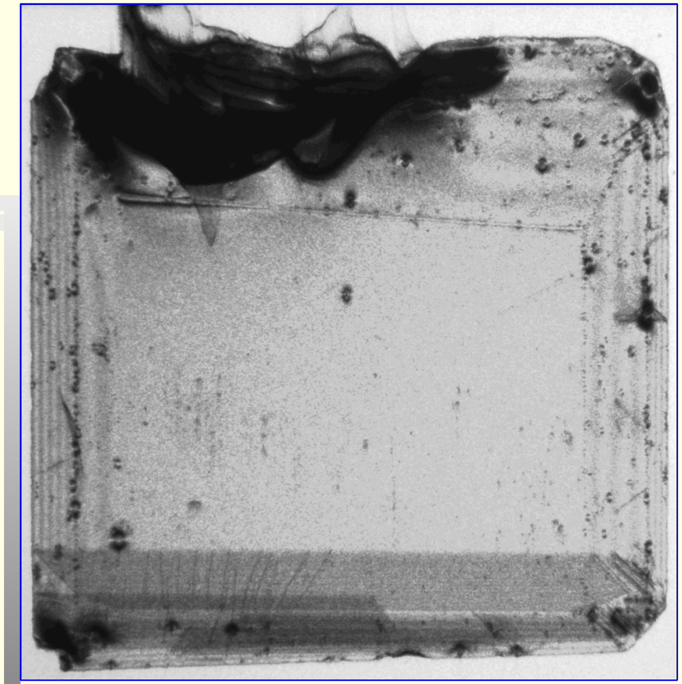
"better" Ib sample (100-oriented)



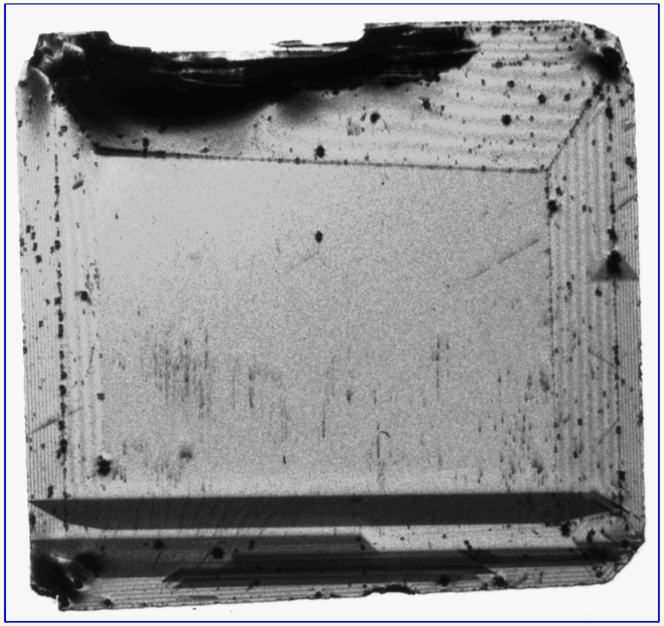
Double crystal topography
(reflection geometry)

Now many inhomogeneities within "homogeneous" parts visible

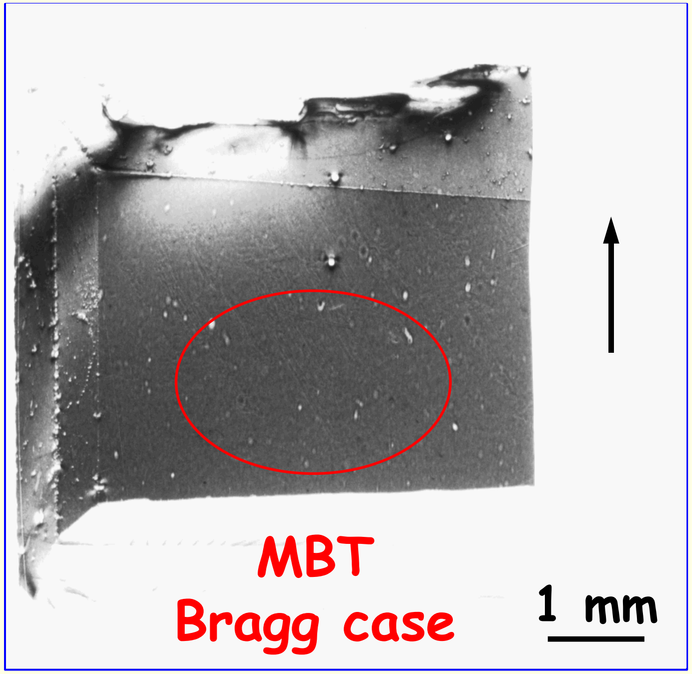
High bulk quality
$\Delta d/d < 10^{-7}$



WBT
Laue case



MBT
Laue case



X-ray characterisation of diamonds

1. Introduction

2. Looking more at the "bulk"

   Bragg diffraction imaging ("X-ray topography")

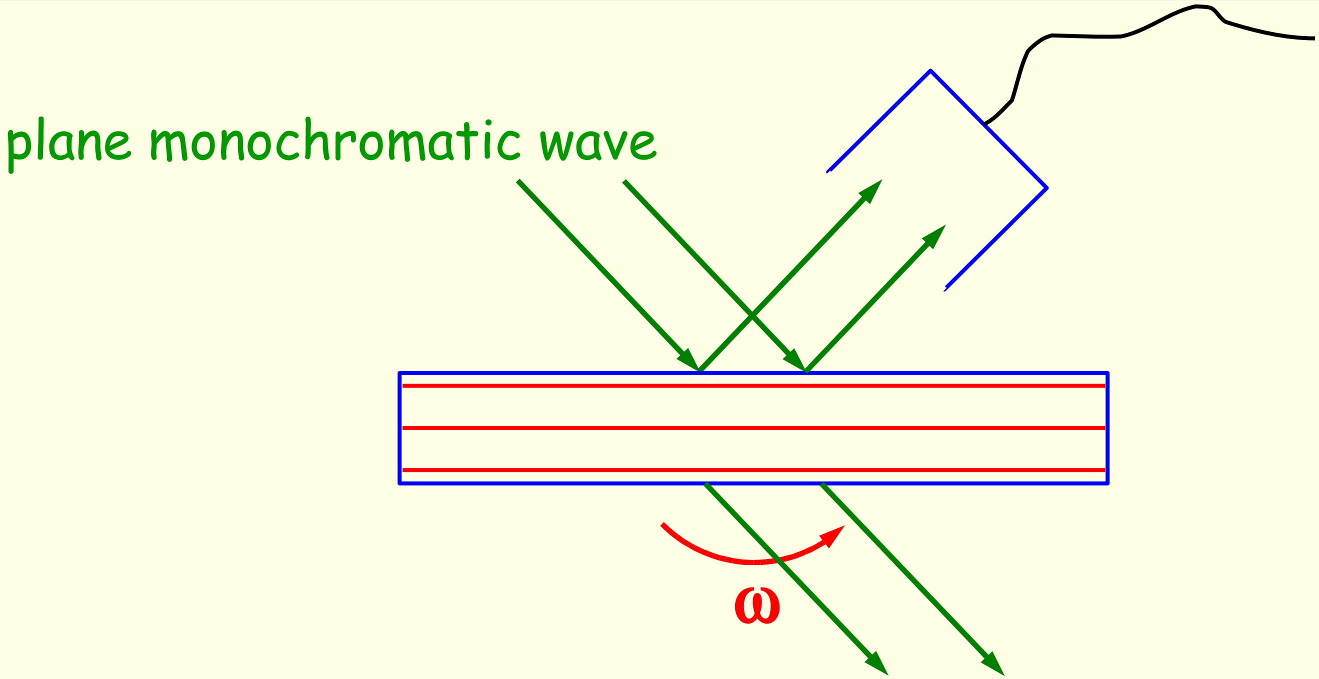
   High-resolution diffractometry

3. Looking closer to the "surface"

   Reflectometry

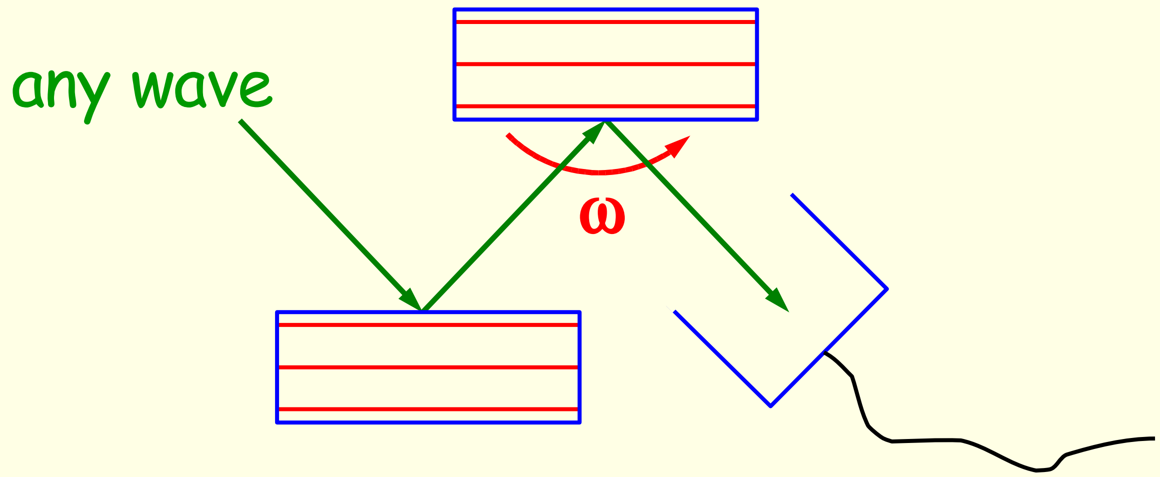
   Grazing incidence diffraction

Reflectivity (and transmissivity) curve
How to measure it?



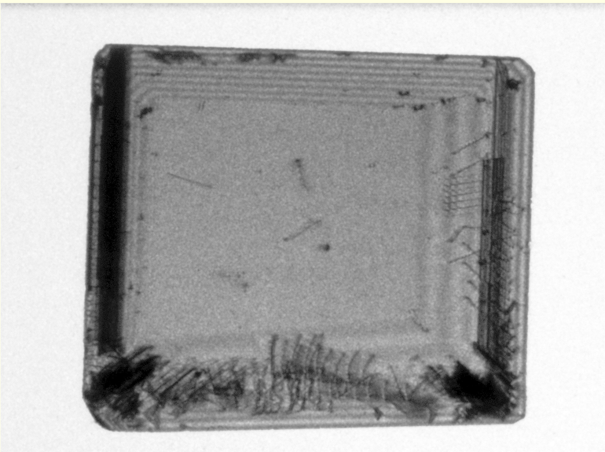
Plane & monochromatic incoming wave
changing its angle of incidence
counting all photons

Rocking curve



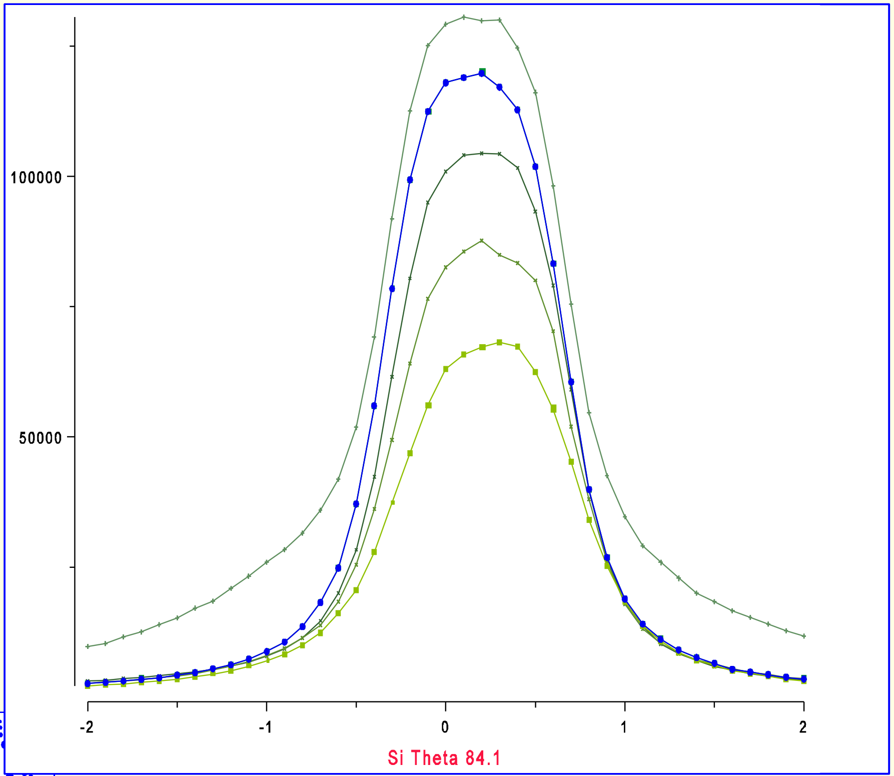
Real situation

Convolution (autocorrelation) of reflectivity curve with instruments/apparatus function (other reflectivity curves, and wavelength (energy) distribution, and divergence distribution)



Some results

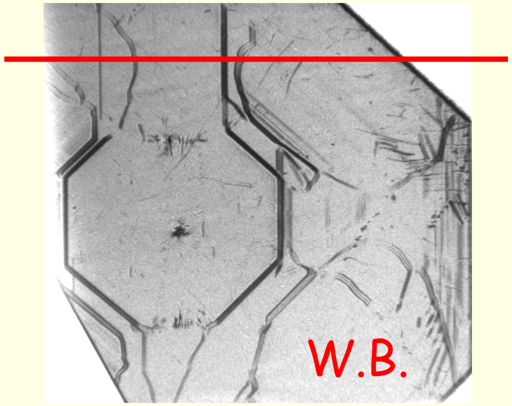
N° 1: 100 IIa

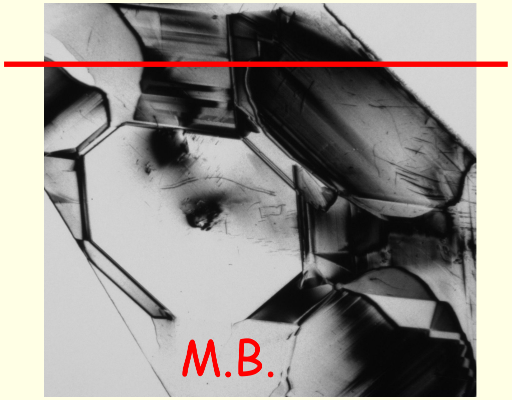


FWHM of the "defects broadening":

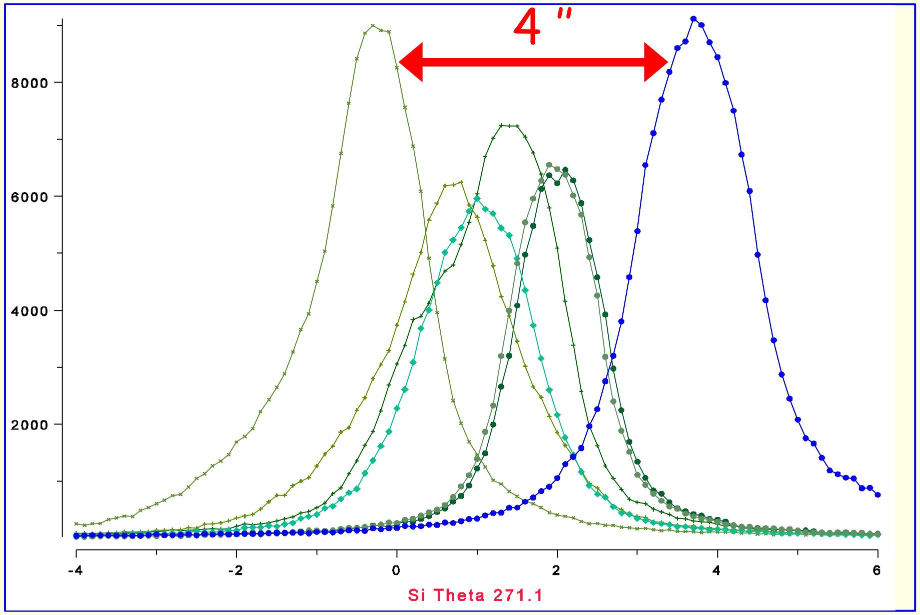
0.10 " - 0.39 "

Less broadened one:
FWHM: 0.10 "
FW20%M: 0.32 "
FW2%M: 0.61 "





N° 2: 100 Ib

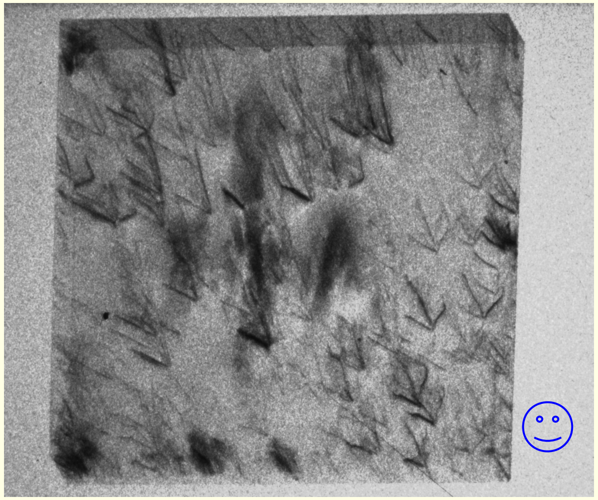


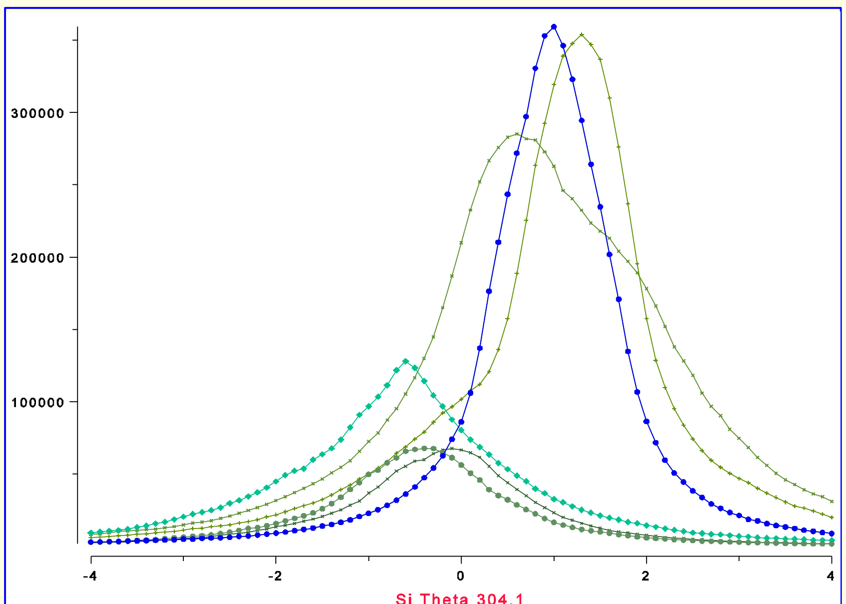
FWHM of the "defects broadening":

1.09 "

FWHM: 1.09 "
FW20%M: 1.79 "
FW2%M: 3.09 "

$\Delta d/d = 1.2\ 10^{-5}$



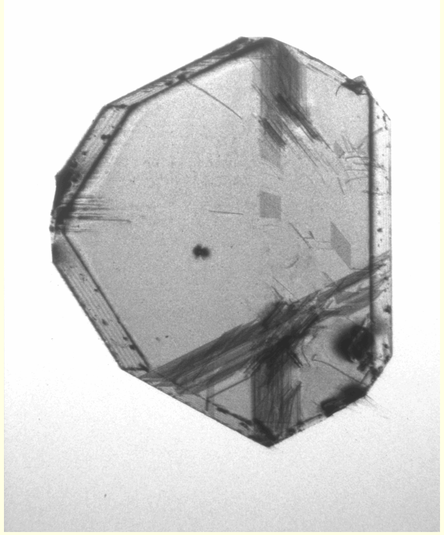


N° 3: 100 CVD

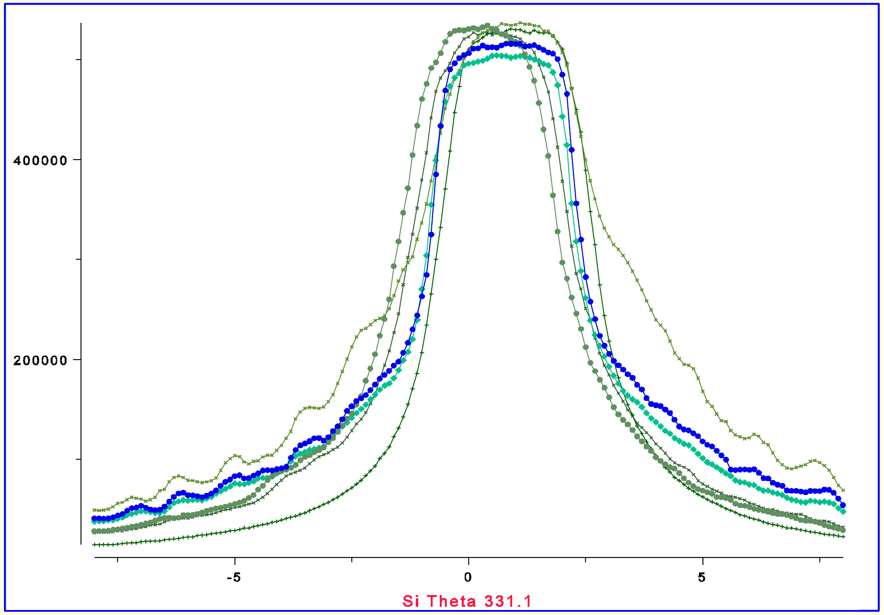
FWHM of the "defects broadening":

0.83 "

FWHM: 0.83 "
FW20%M: 1.32 "
FW2%M: 2.47 "



N° 4: 111 IIa



FWHM of the "defects broadening":

0.44 "

FWHM: 0.44 "
FW20%M: 0.71 "
FW2%M: 6.83 "

Summary of some results

	N° 1 100 IIa	N° 2 100 Ib	N° 3 100 CVD	N° 4 111 IIa
FWHM	0.10"	1.09"	0.83"	0.44"
FW20%M	0.32"	1.79"	1.32"	0.71"
FW2%M	0.61"	3.09"	2.47"	6.83"

Information about surface quality in the tails of the rocking curves

ESRF

X-ray characterisation of diamonds

1. Introduction

2. Looking more at the "bulk"

 Bragg diffraction imaging ("X-ray topography")

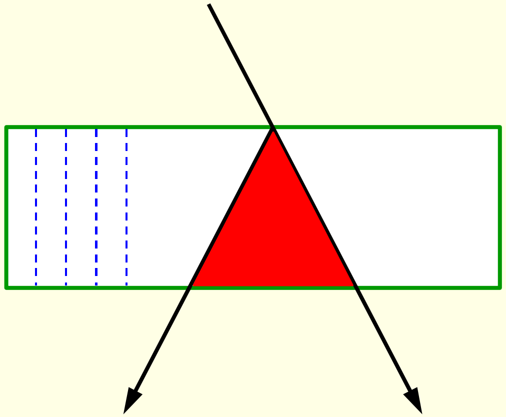
 High-resolution diffractometry

3. Looking closer to the "surface"

 Reflectometry

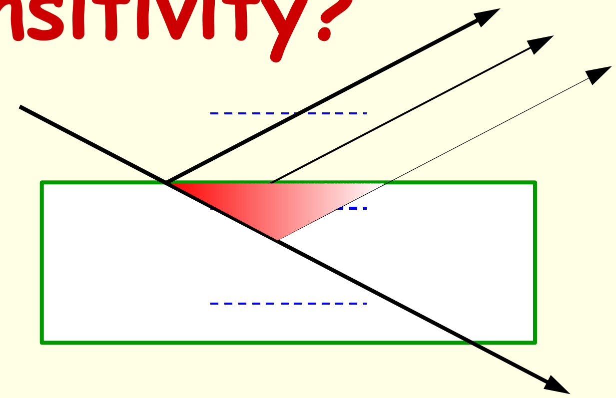
 Grazing incidence diffraction

"Surface" sensitivity?



Laue case/transmission geometry

We "see" mainly the bulk



Bragg case/reflection geometry

We "see" bulk and "surface

Bragg case, diamond 400-reflection, E = 14.413keV:

t_{ext} = 4µm, t_{abs} = 1140µm !!!

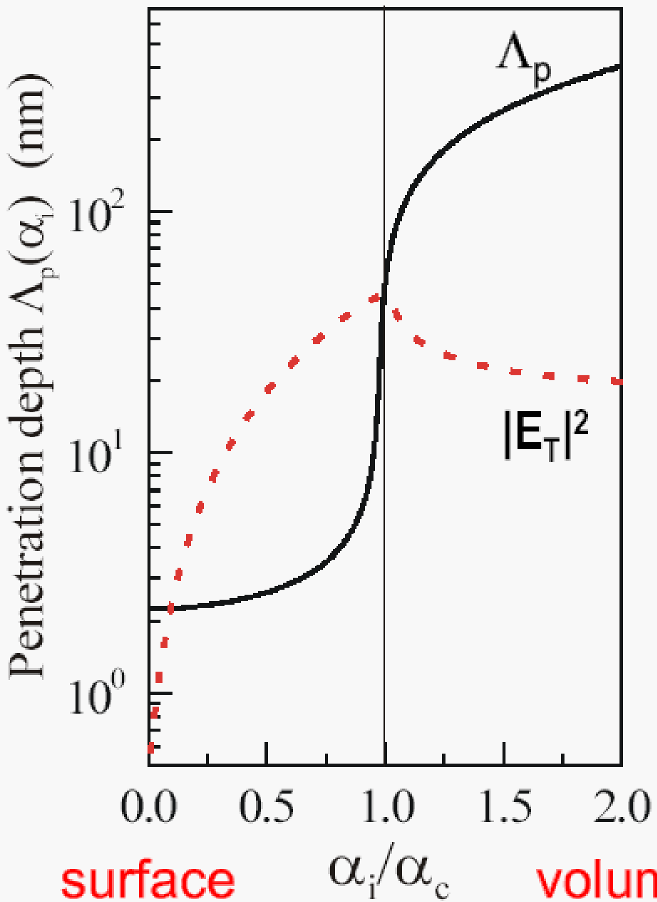
Can we diminish the penetration depth and control it?

Surface sensitivity of GI Methods

X-ray wavelength range

refraction index: $n = 1 - \delta + i\beta$

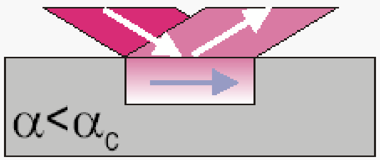
$n < 1$, and $\delta, \beta << 1$

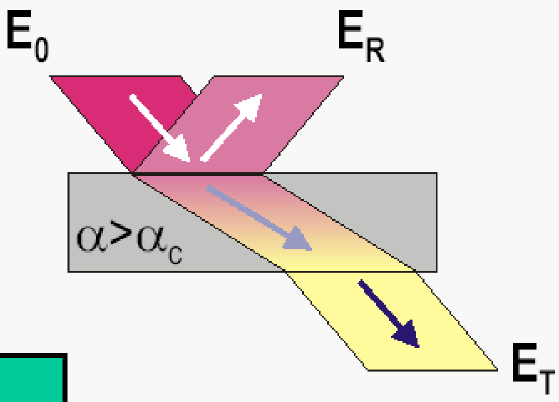


surface sensitive

volume

total external reflection





$$\frac{1}{e} = \left|\frac{E_T}{E_0}\right|^2 \approx e^{-2k\,\mathrm{Im}(\alpha')\Lambda_p}$$

$$\Lambda_p = 1 / 2k\,Im(\alpha_i)$$

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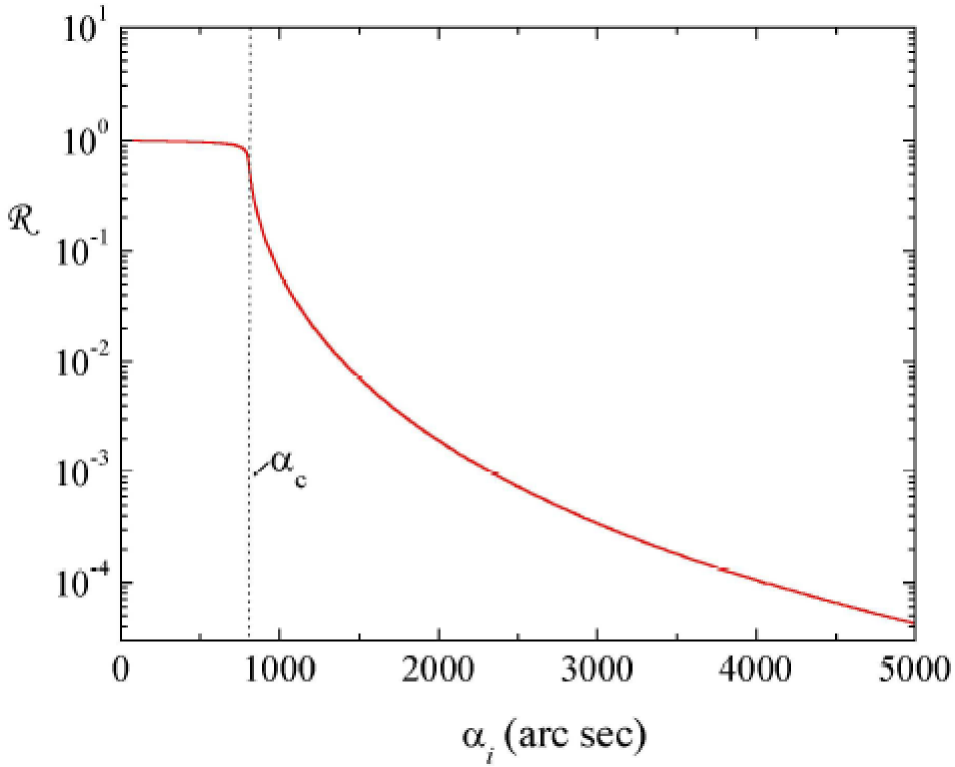
20th of September 2005

Reflection curve of a Si surface, CuKα1 radiation

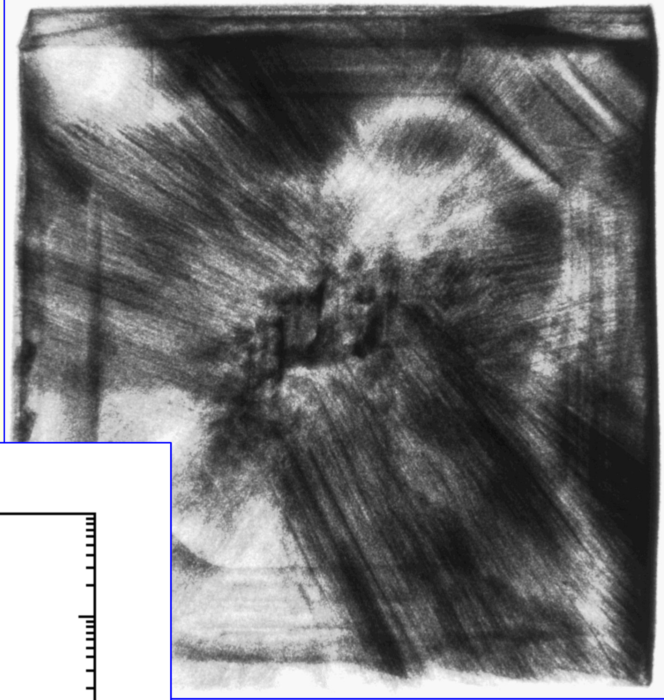


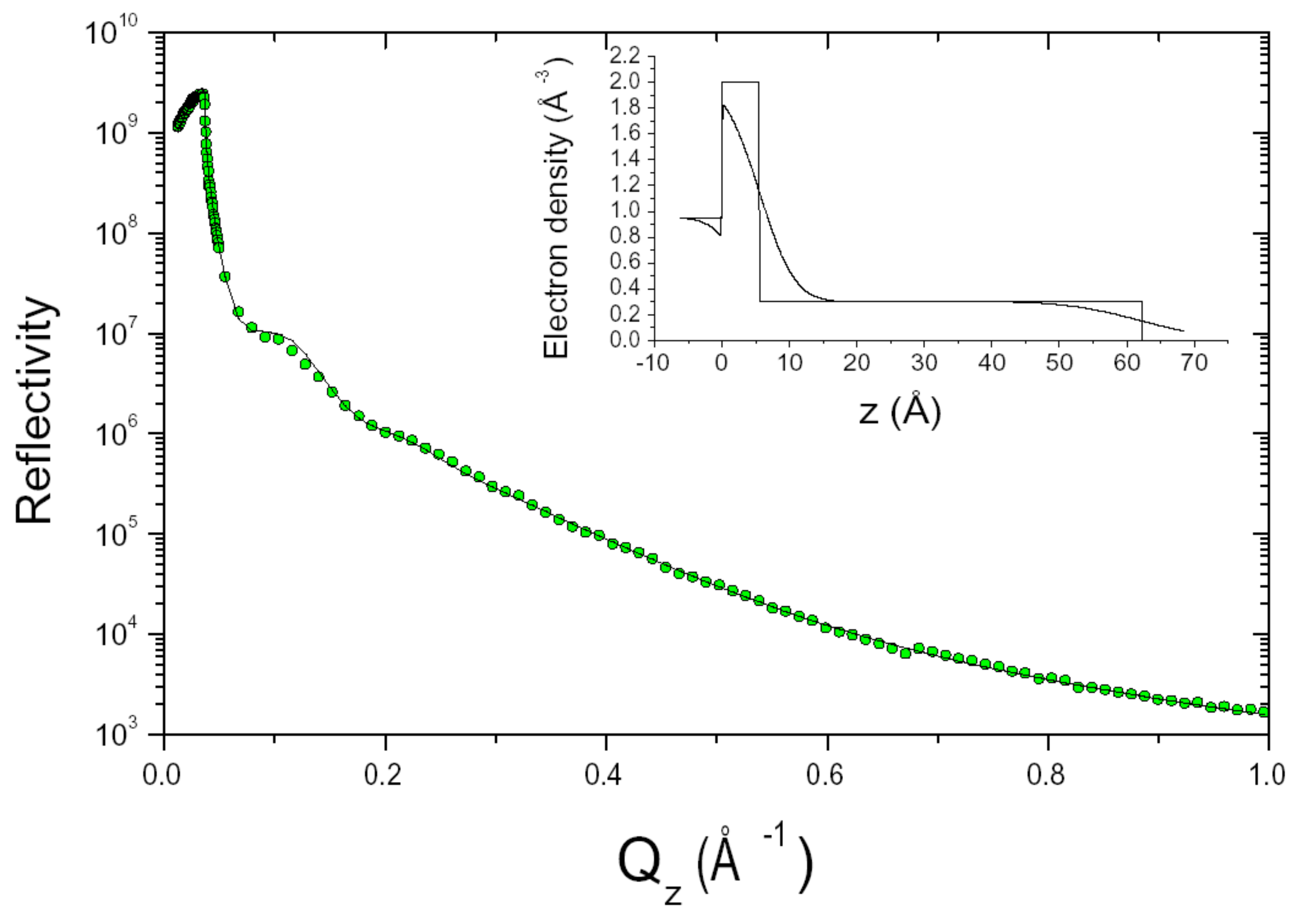
Critical angle of total external diffraction

$$\alpha_c \approx \sqrt{2\delta}, \quad \alpha_c \sim \lambda\sqrt{\langle\rho\rangle}$$

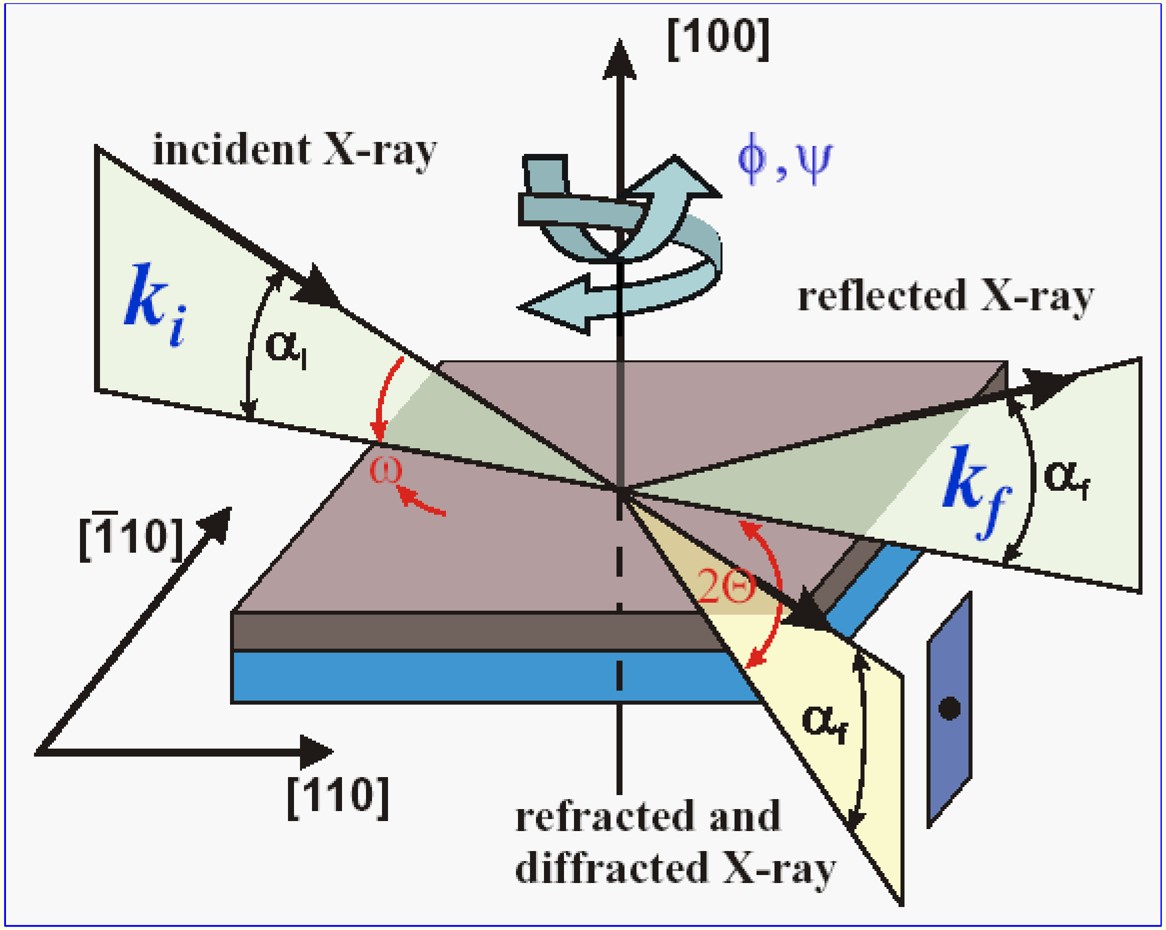
Ib diamond,

"bad" bulk, very well polished surface (3Å optical rms)





Grazing incidence diffraction



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20th of September 2005

Thank you for your attention!

fin

end

Ende