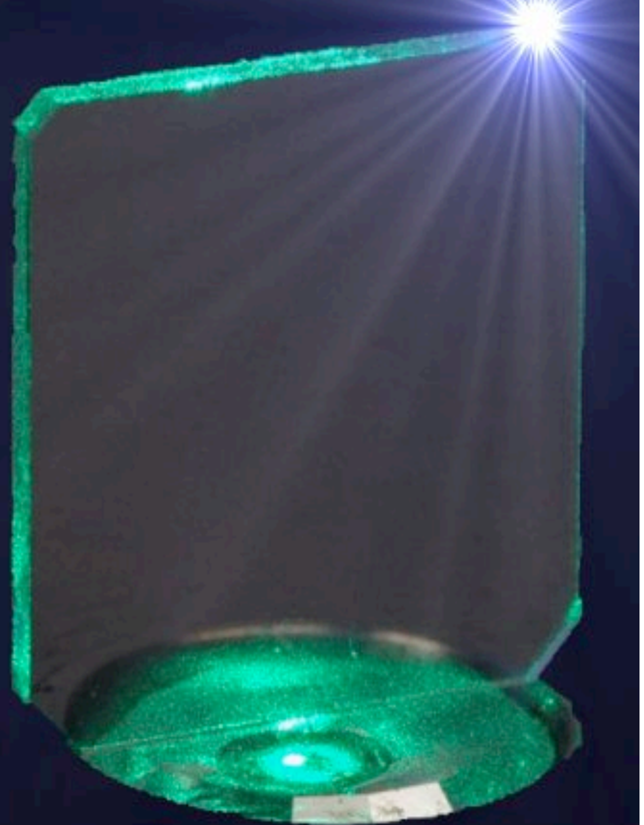
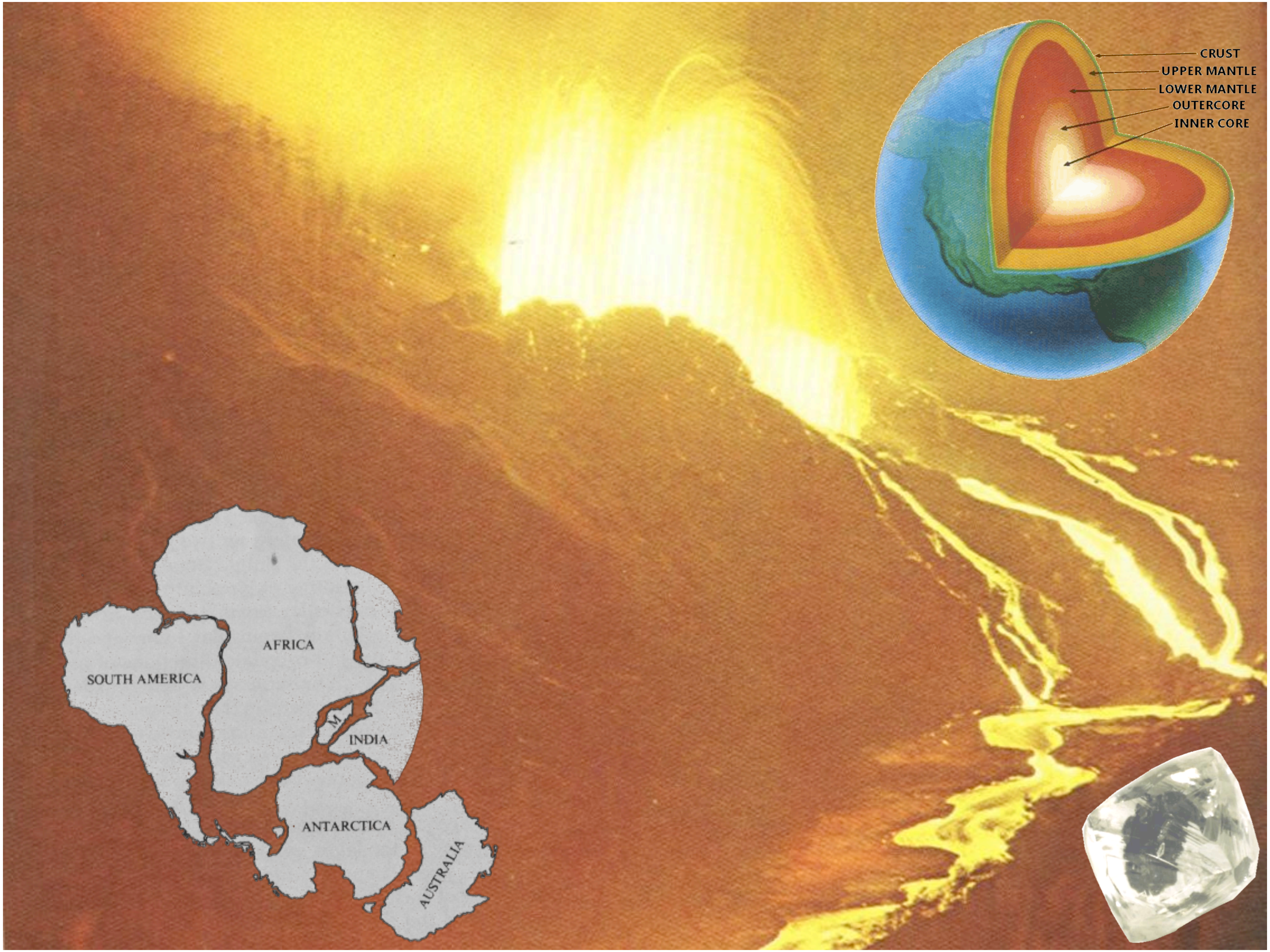
Channeling 2008 : Physics of Diamond

Prepared by SH Connell
University of Johannesburg
October 2008

1. Synthesis
2. Properties
3. Applications



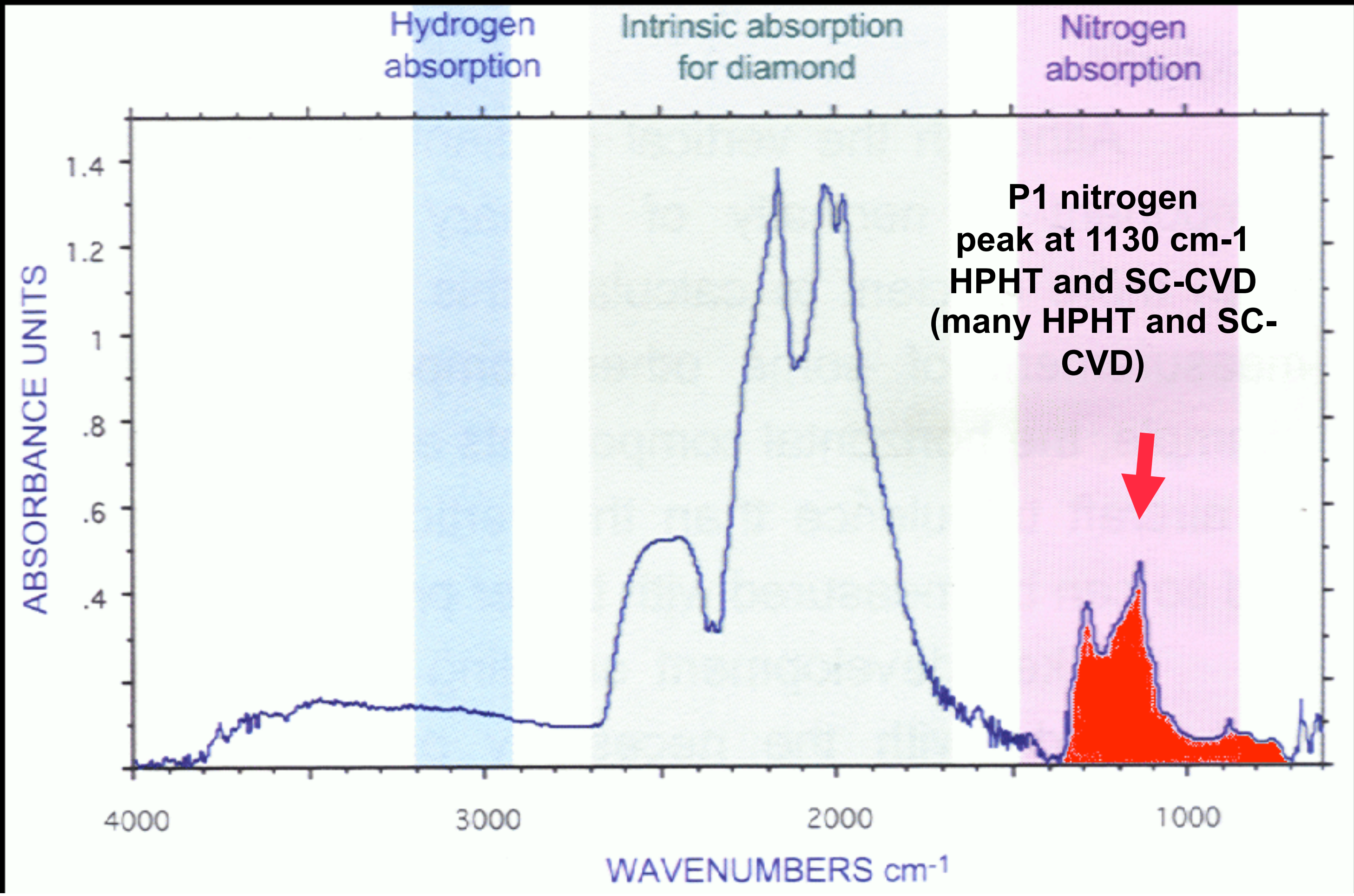

CRUST
UPPER MANTLE
LOWER MANTLE
OUTERCORE
INNER CORE
AFRICA
SOUTH AMERICA
M
INDIA
ANTARCTICA
AUSTRALIA

"…. It seems, indeed, to be a general truth, that there are comparatively few diamonds without cavities and flaws and that this mineral is a fouler stone than any other used in jewelry …."
Sir David Brewster
1862

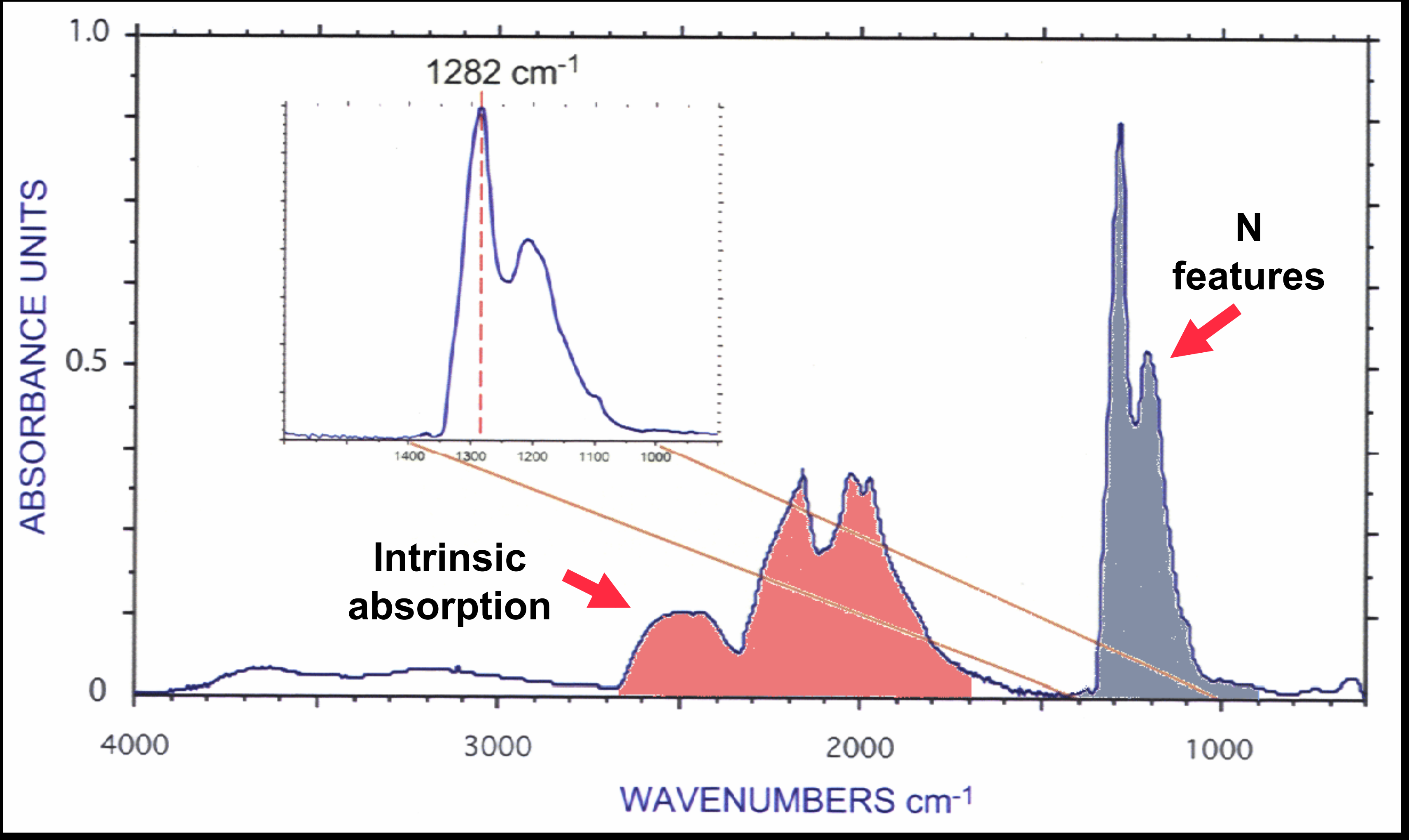
Courtesy J Hansen - Hansen Future Materials

Diamond

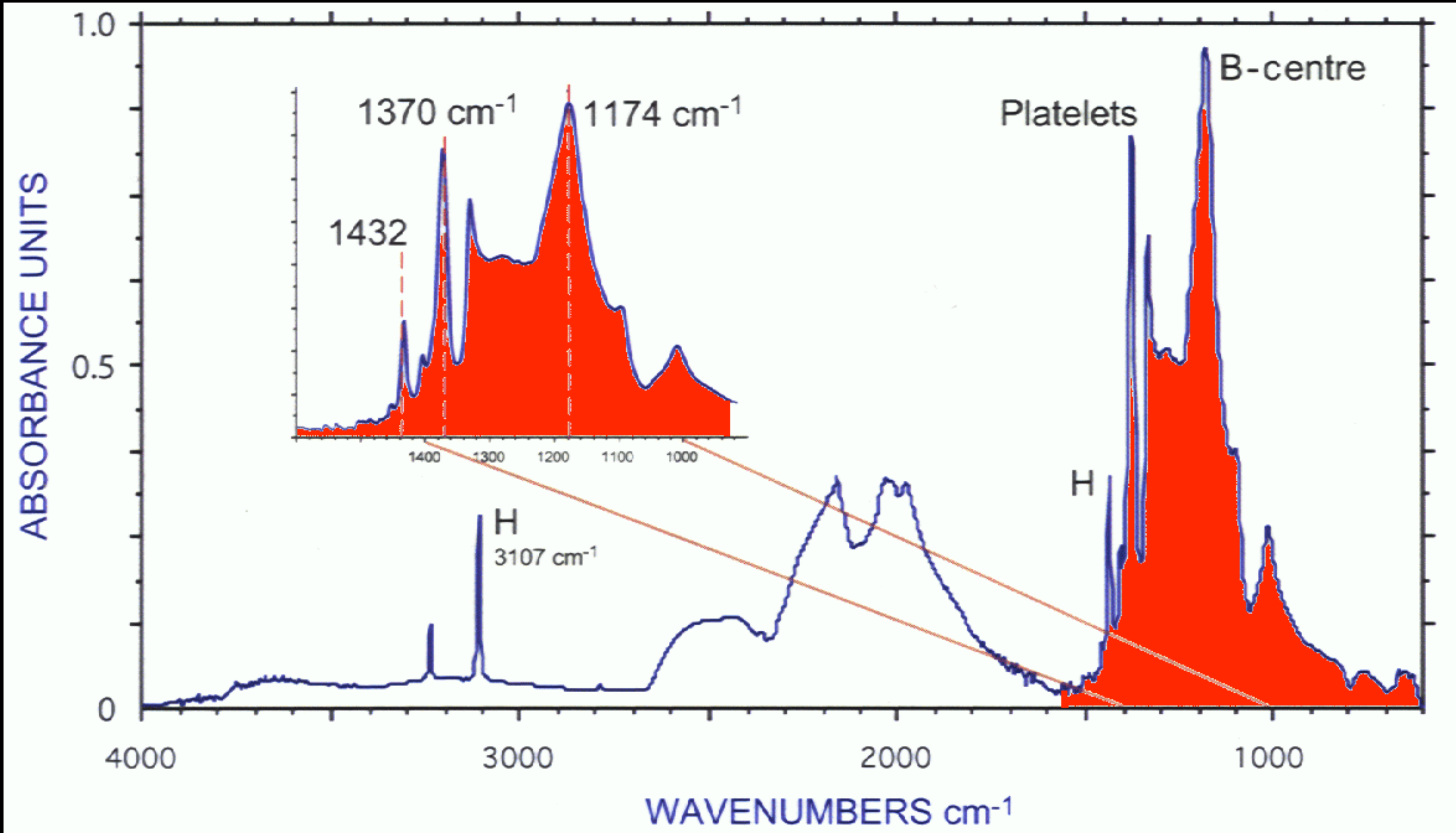
IR Spectra



In nature : nitrogen aggregates
The A-centre
(two neighbouring substitutional N atoms)



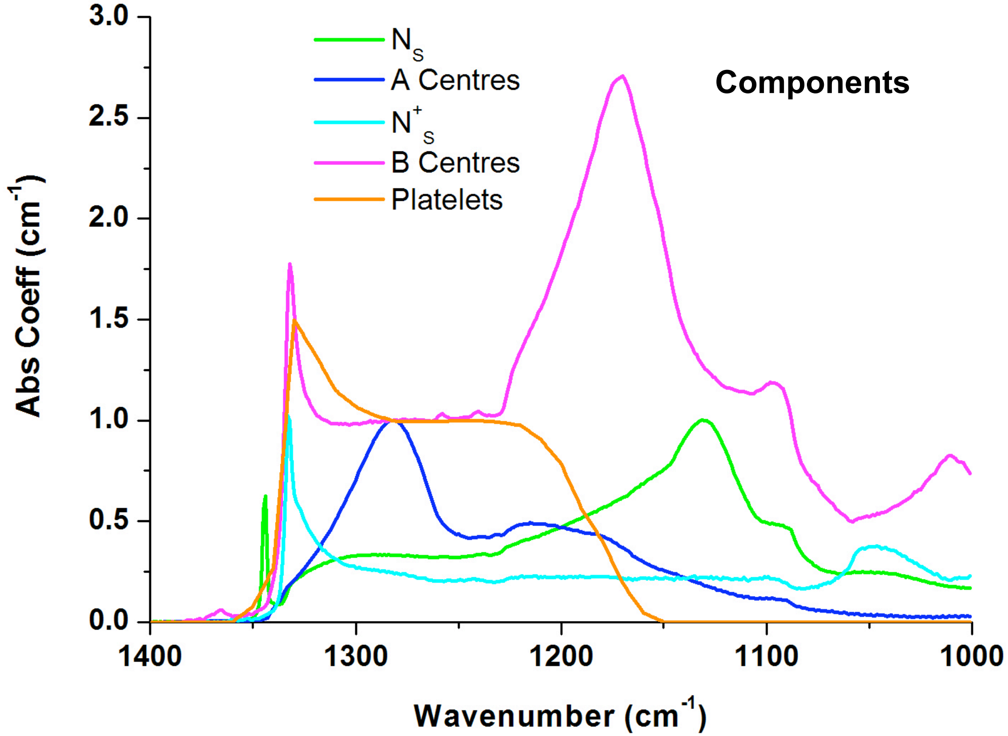
In nature : nitrogen aggregates
The B-centre : four N_S near a V

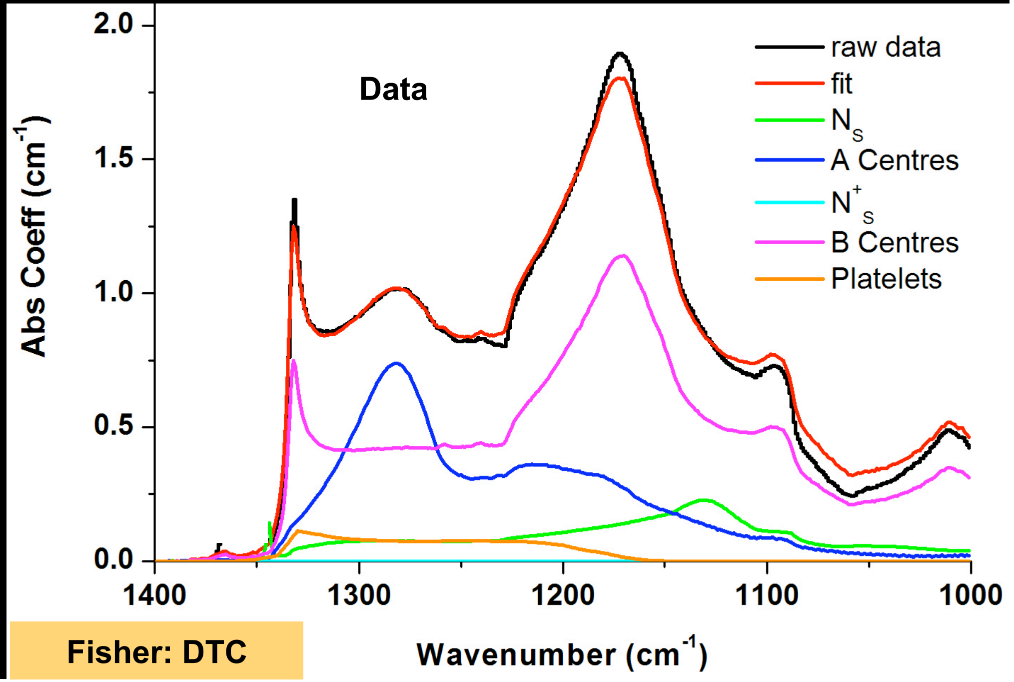


Decomposition of the IR Spectrum

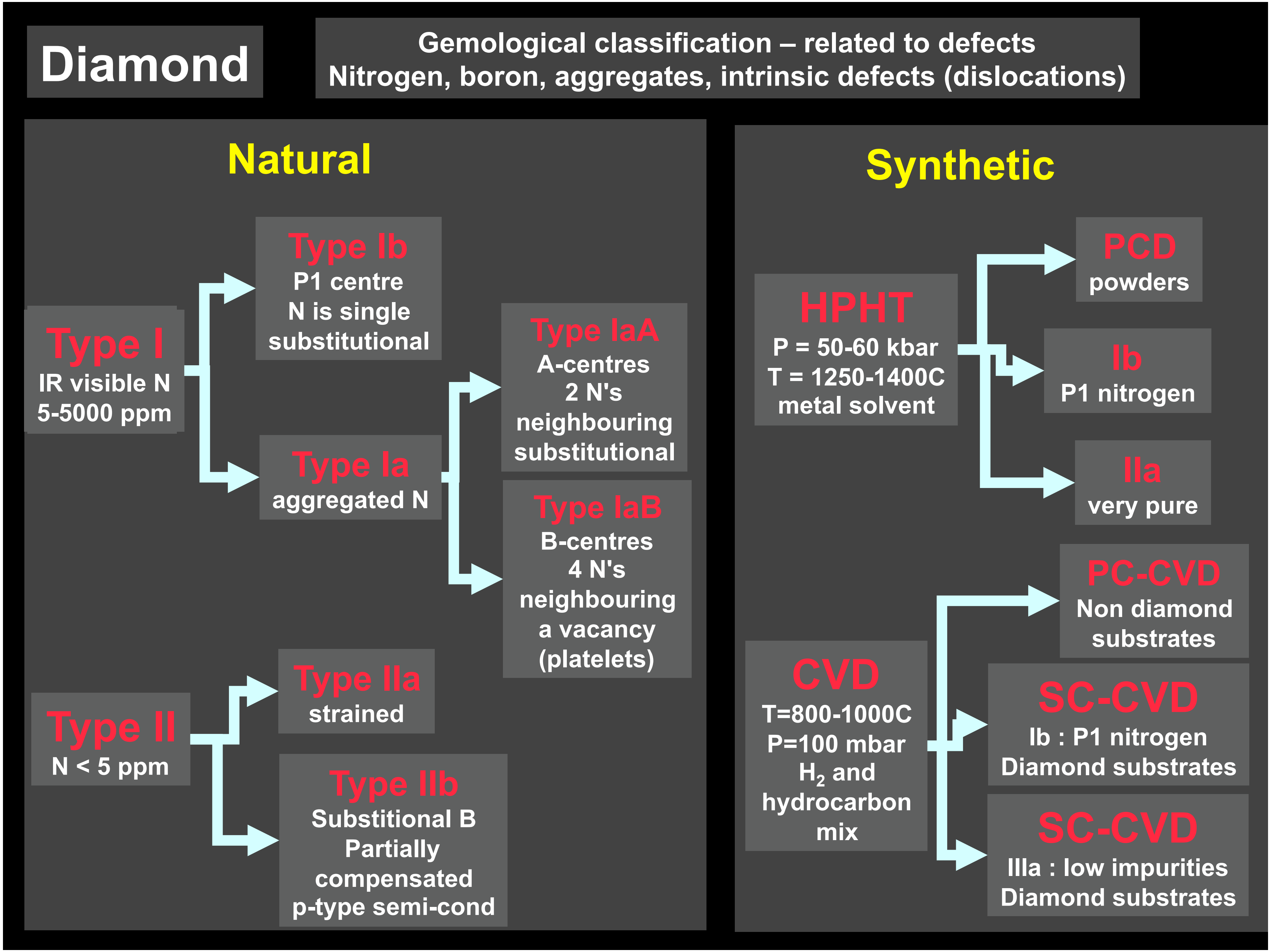
The functional forms of the absorption for
N_S – single substitutional N
A centers - pair of adjacent N_S
N_S+ - positively charged N_S
B centers – four N_S at a V
platelets
Are regarded as completely spanning the space of the nitrogen region absorption curve

Very rare to find even a small region within a very good natural diamond which approaches the quality (low impurities, low strain) of a very good modern synthetic diamond
…. see eg … papers by A Lang …..

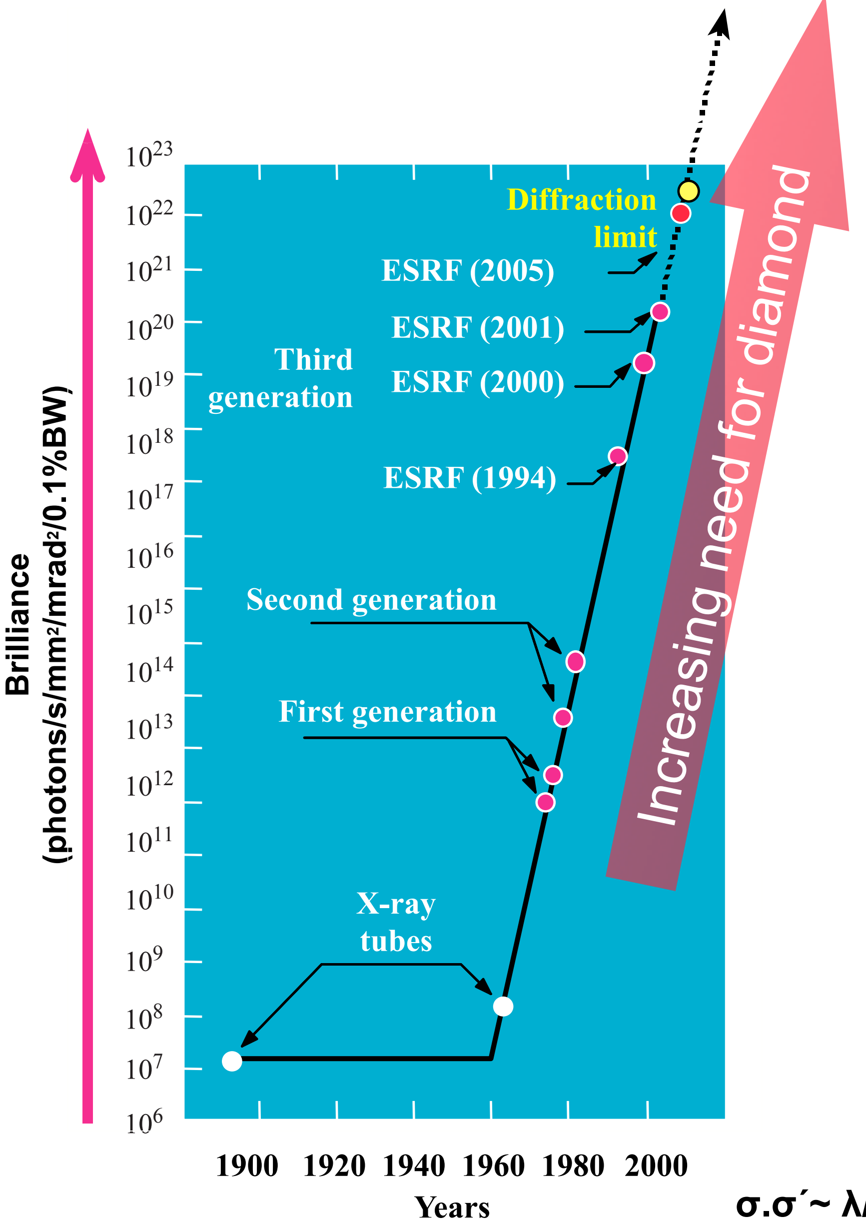


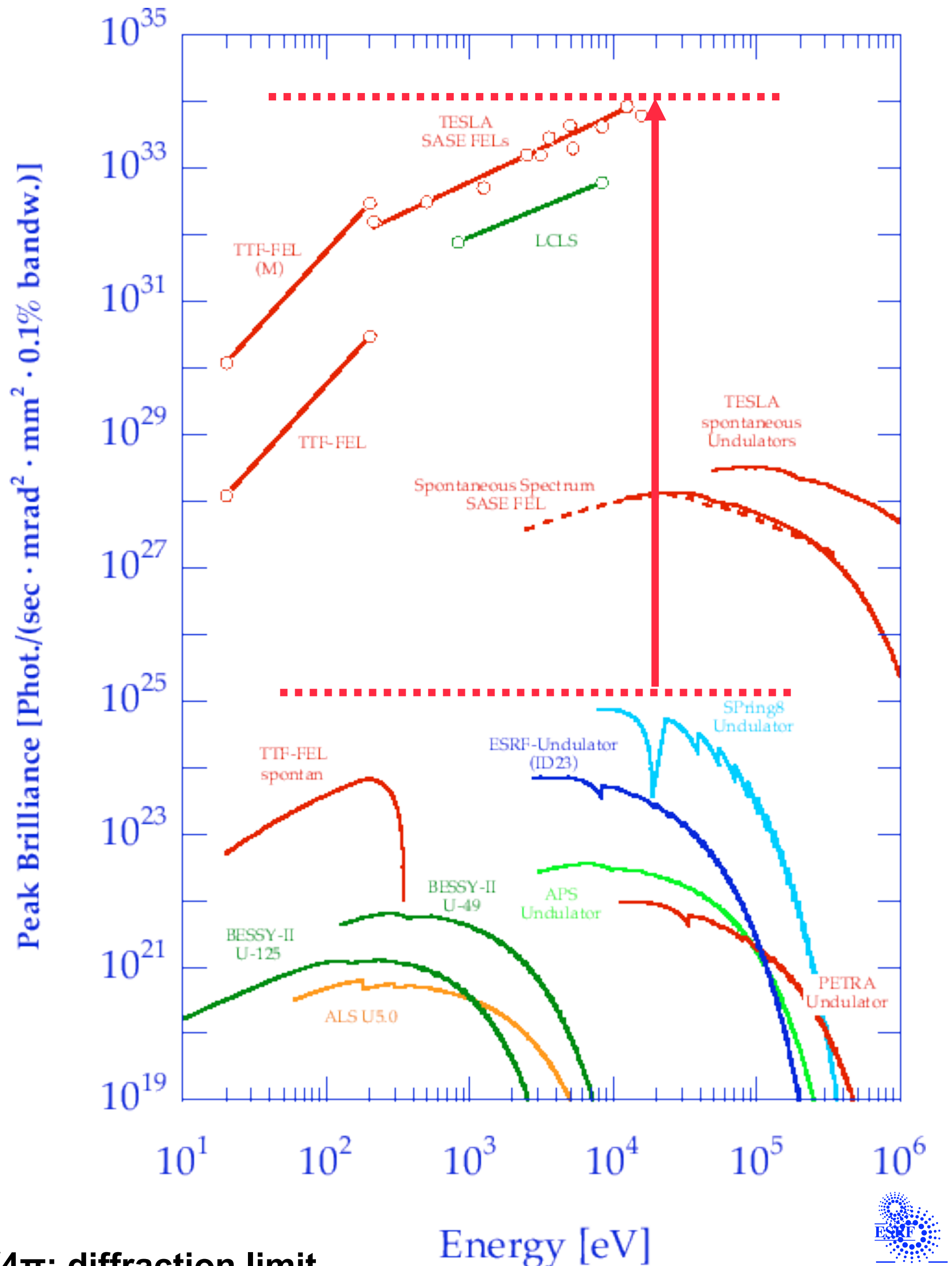


Fisher: DTC


Diamond
Gemological classification – related to defects
Nitrogen, boron, aggregates, intrinsic defects (dislocations)
Natural
Type I
IR visible N
5-5000 ppm
Type Ib
P1 centre
N is single
substitutional
Type Ia
aggregated N
Type IaA
A-centres
2 N's
neighbouring
substitutional
Type IaB
B-centres
4 N's
neighbouring
a vacancy
(platelets)
Type II
N < 5 ppm
Type IIa
strained
Type IIb
Substitional B
Partially
compensated
p-type semi-cond
Synthetic
HPHT
P = 50-60 kbar
T = 1250-1400C
metal solvent
PCD
powders
Ib
P1 nitrogen
IIa
very pure
CVD
T=800-1000C
P=100 mbar
H_2 and
hydrocarbon
mix
PC-CVD
Non diamond
substrates
SC-CVD
Ib : P1 nitrogen
Diamond substrates
SC-CVD
IIIa : low impurities
Diamond substrates

"Moore's Law" for the brilliance of Synchrotron X-Ray beams



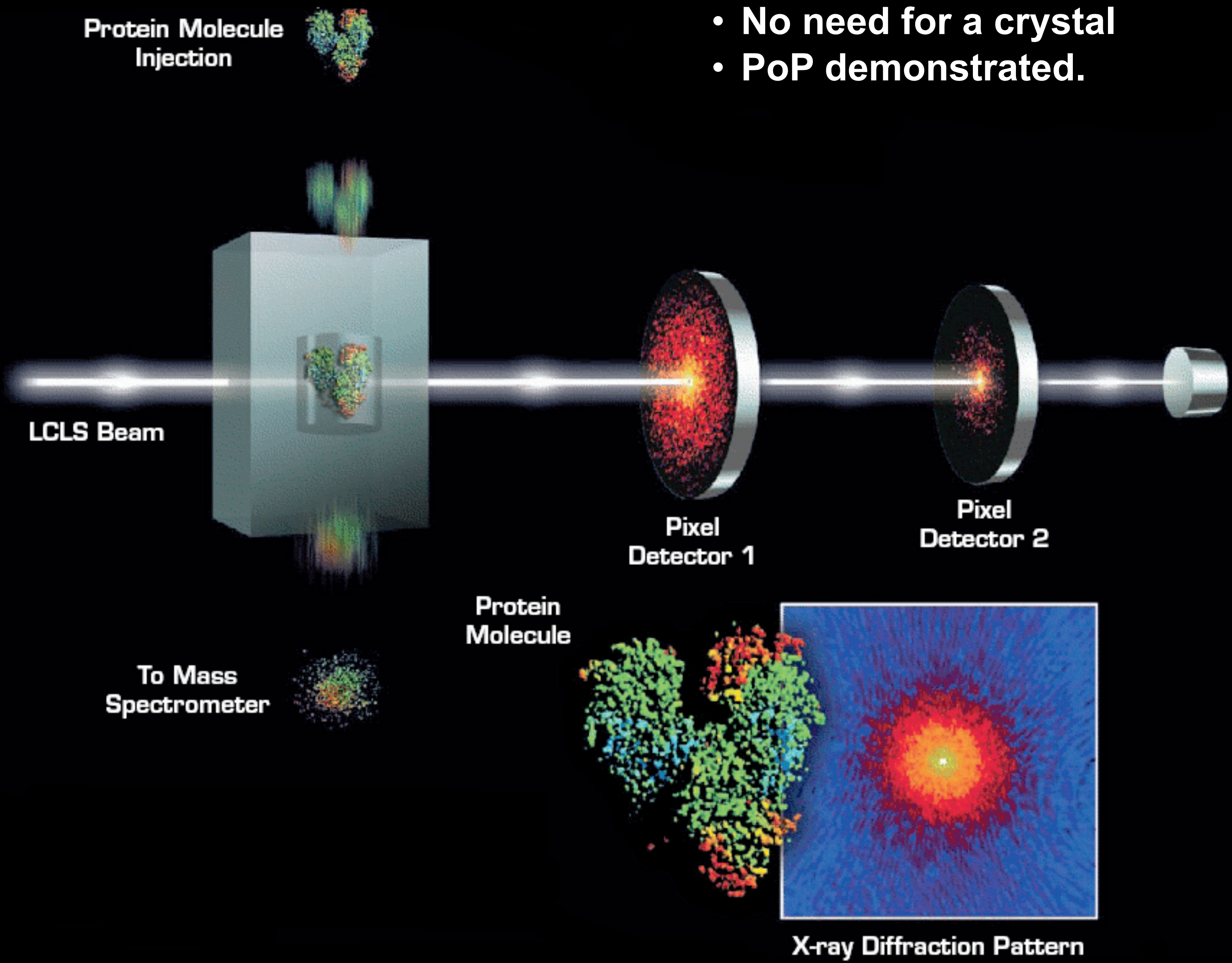


σ.σ´~ λ/4π: diffraction limit

ESRF

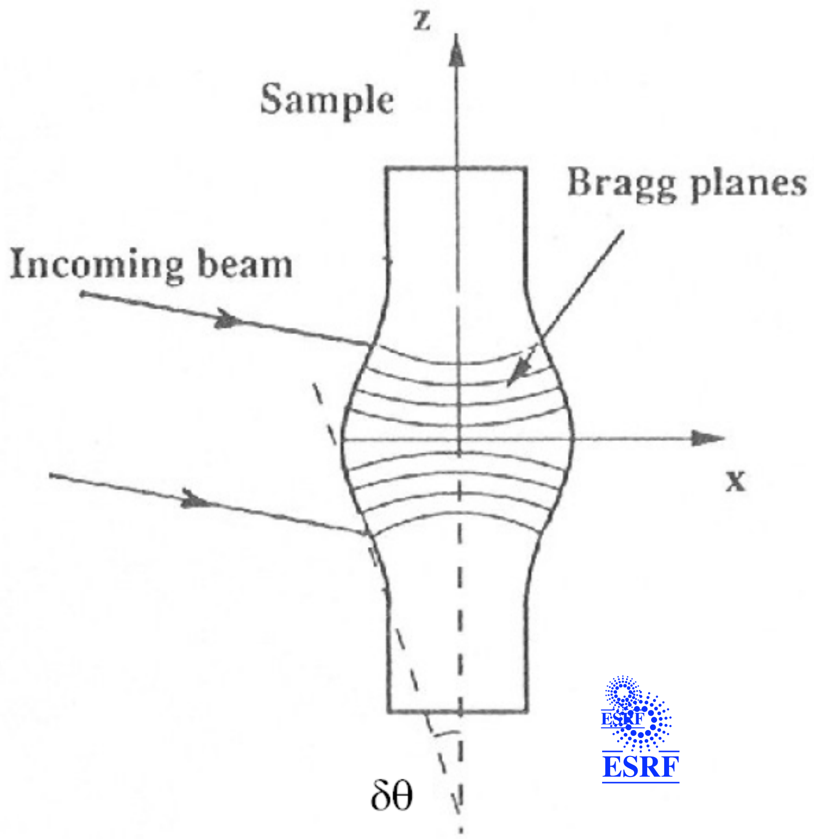
• Example of FEL Science

• Analyse a single bio-molecule with “one shot” per projection.
• No need for a crystal
• PoP demonstrated.



From LCLS brochure

Why diamond Beam Optical Elements



σ high thermal conductivity,
μ low linear X-ray absorption,
α low thermal expansion

$$\delta\theta \propto \left(\frac{\sigma}{\mu\alpha}\right)^{-1}$$

Diamond >> Silicon

500 x

For Silicon :
liquid N_2 cooling works up to 400 W/mm^2

For FEL :
Response to transients important

Properties of importance for X-ray applications

Material	Beryllium	Diamond	Silicon	Germanium
Atomic number Z	4	6	14	32
Debye Temp T_d, K	1188	1860	532	293
Absorption coefficient, μ at 8 keV (cm^{-1})	1.7	14	143	350
Thermal conductivity, κ, at 297K ($Wcm^{-1}K^{-1}$)	2.0	Type I: 5-18 Type IIa: 20-25 Iso-pure:35 PC:4-20	1.5	0.64
Thermal conductivity, κ, at 80K ($Wcm^{-1}K^{-1}$)		Ia: 20-40 IIa: 150 Iso-pure:2000	Nat 15 Iso-pure: 20	
Thermal exp coef, α at 297K ($10^{-6}K^{-1}$)	11	1	2.4	5.6
Figure of merit, 100·μκ/α at 297K (MW)	**11**	**36-180**	**0.44**	**0.03**

Additional properties for applications at FEL's

1. Requires thin crystals (time response) → framed plates
2. Time structure of beam –
   a. Time average heat load OK,
   b. Must dissipate high peak power on
      - 100 fs time scale (pulse)
      - 1ms time scale (bunch train)
3. Fast thermalisation time, damage resistant
4. Large head spreader, (isotopically enriched diamond)

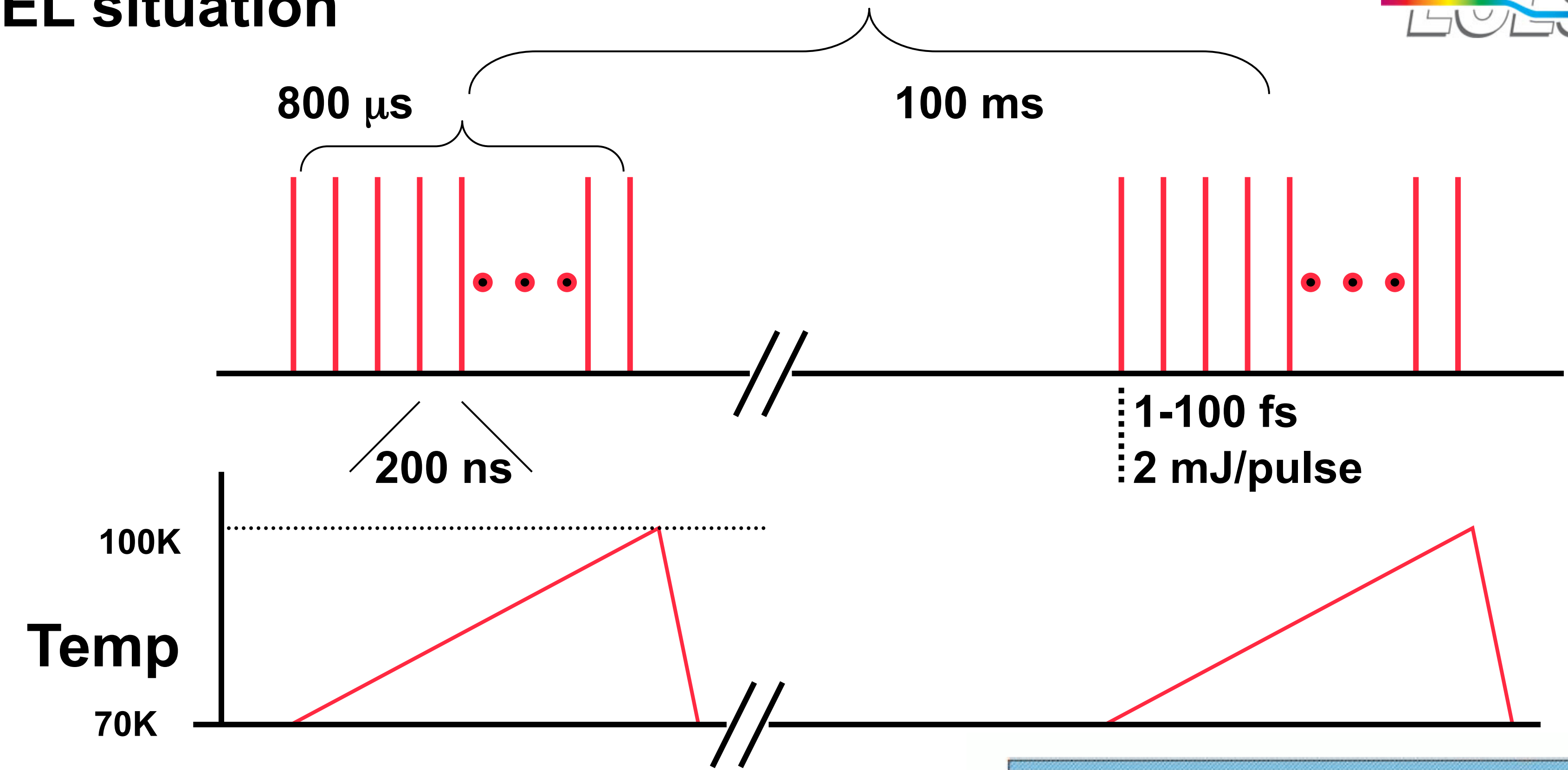
	Diamond (nat)	Diamond (0.07% ^{13}C)	Silicon	Copper
Diffusivity (cm^2/s)	12.4	18.5	0.86	1.25

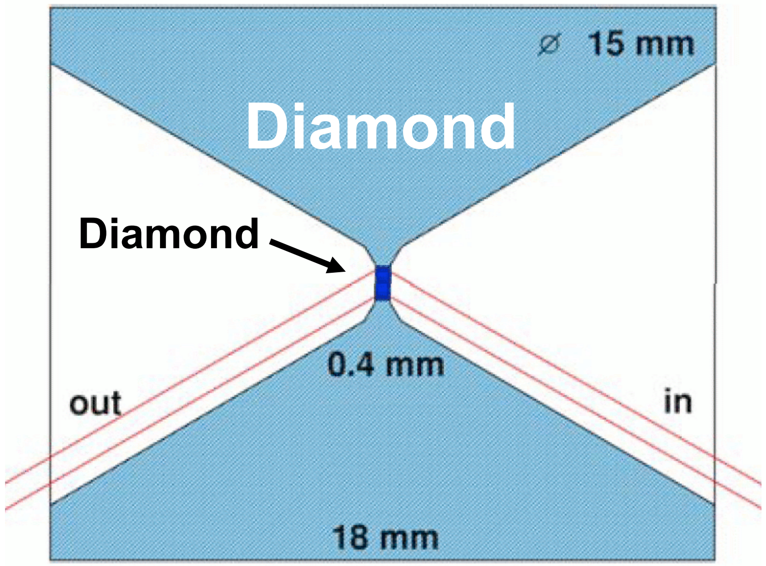
PRB42(1990)1104 – T Anthony et al

Laser ablation damage threshold for isotopically enriched diamond (0.1% ^{13}C) 10 x higher than for natural diamond.

Need also data for the melt limit and photo-ionisation cross section

X-FEL situation





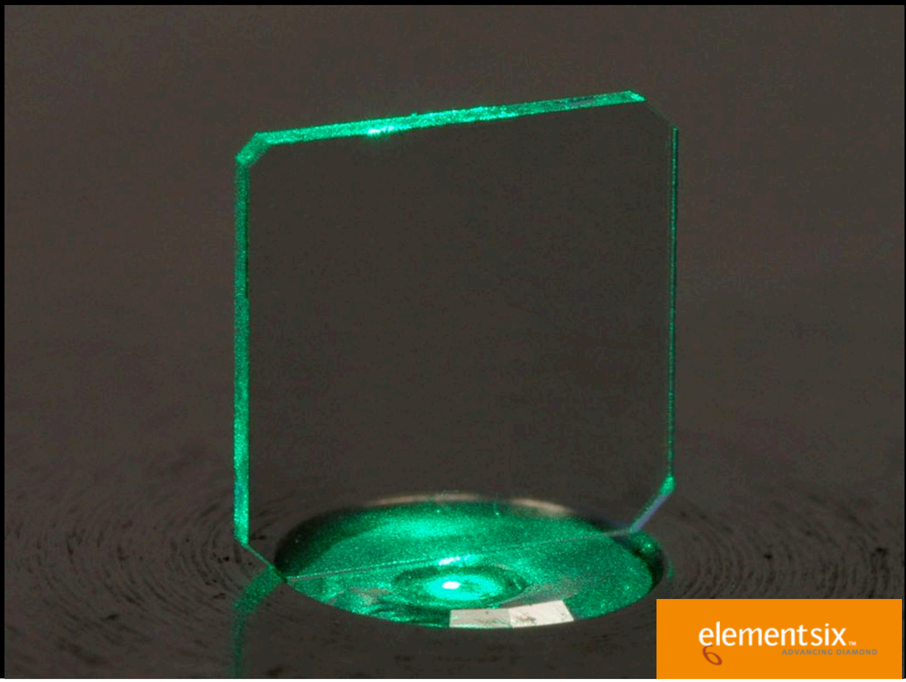
10-100 GW/pulse
75 W/mm^2 continuous (500m from undulator)

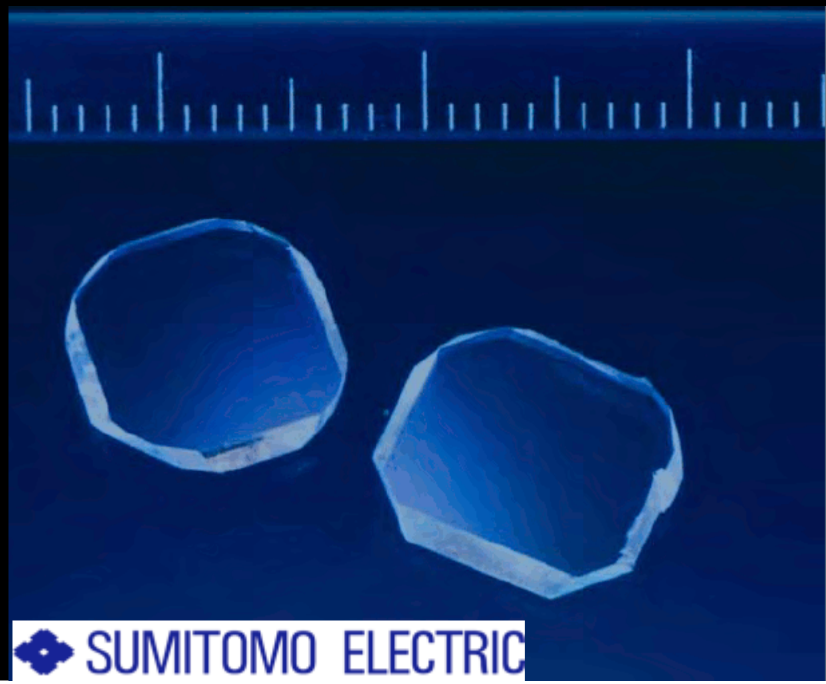
Assume
1. Scaling from experiments with λ=100nm
2. Inst ablation threshold ~ 0.01 eV/atom
3. Need to be ~ 1000m from undulator
4. Diamond > 10 x better than Si
5. Situation still marginal

Low strain diamond

Conclusions : "Diamond in Modern Light Sources 1 & 2"

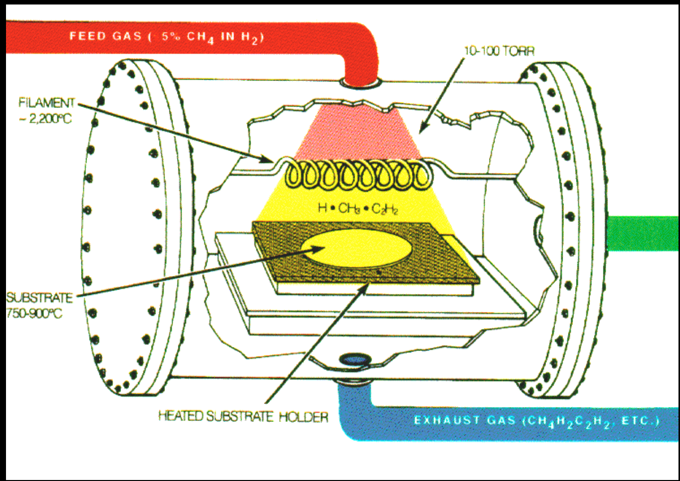
1. Diamond is a very attractive material for Synchrotron applications
2. Symbiosis : optical and electronic (and many others)
3. Synthesis quality improving
4. Type IIa for more demanding applications
5. Require larger plate area and variety of orientations (100), (110), (111)
6. Require lower strain (low + homogenous impurities, no dislocations etc)
7. Coherence preservation not yet established
8. Surface quality must be improved !
9. Diamond mounting technologies

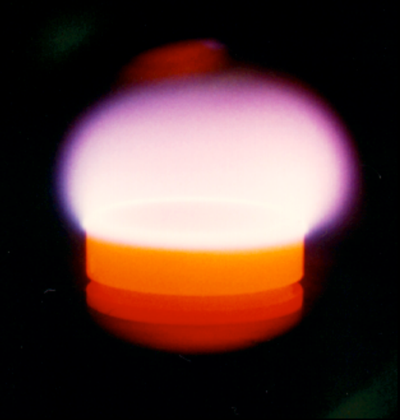




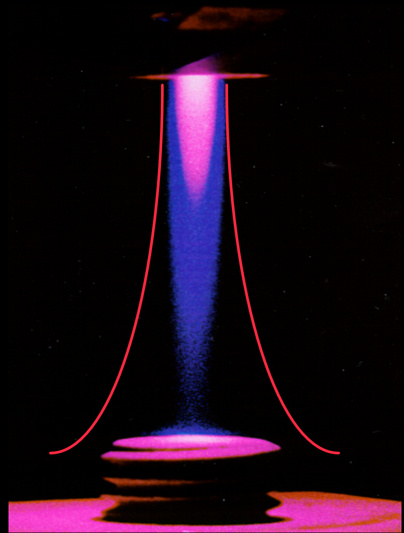
CVD Deposition Methods

Hot Filament



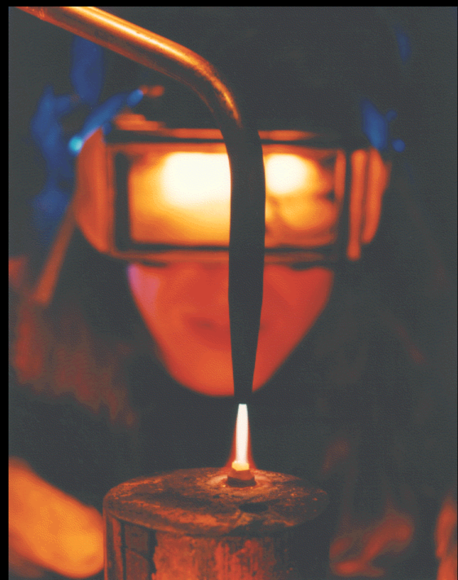


Microwave Plasma



dc arcjet

Combustion Torch



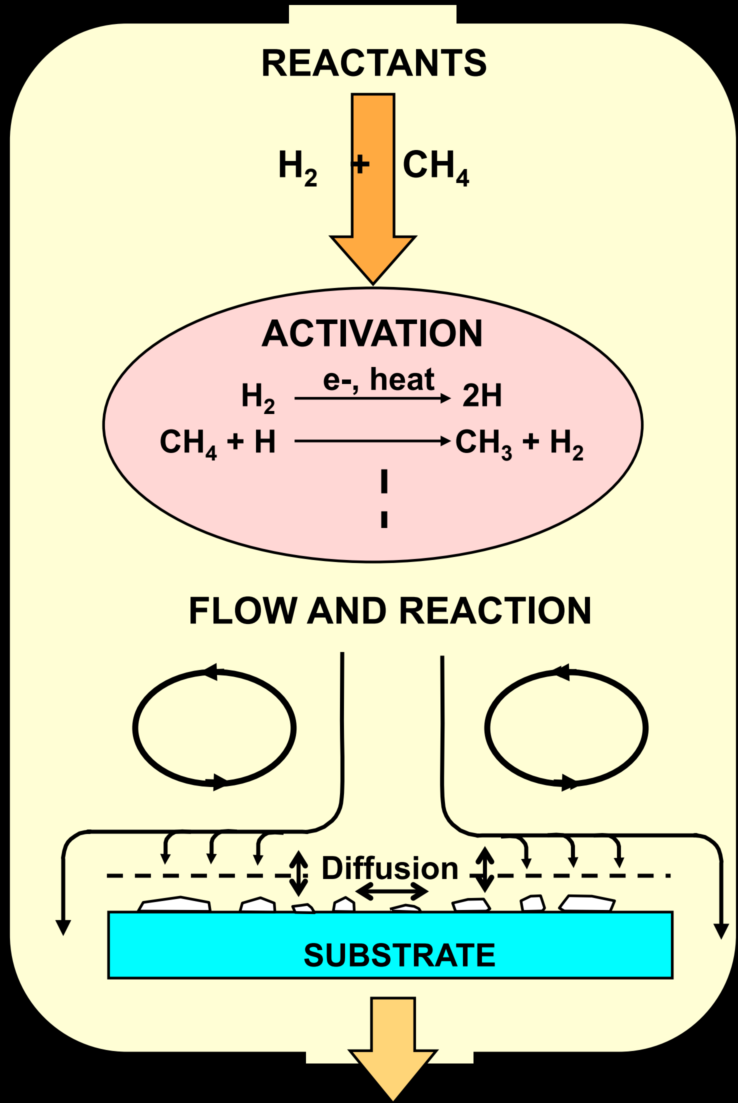
Diamond
Chemical Vapor Deposition

Gaseous Reagents

Gaseous Processes

Surface Processes

Bulk Processes and Properties



Electronic grade SC-CVD

(100 – 200 $ /mm^3)

Optical grade PC-CVD

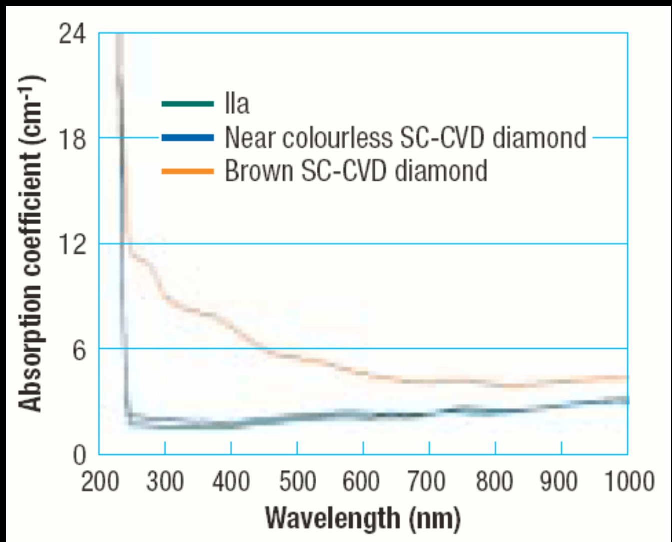
(10 – 20 $ /mm^3)

Nano diamond

elementsix

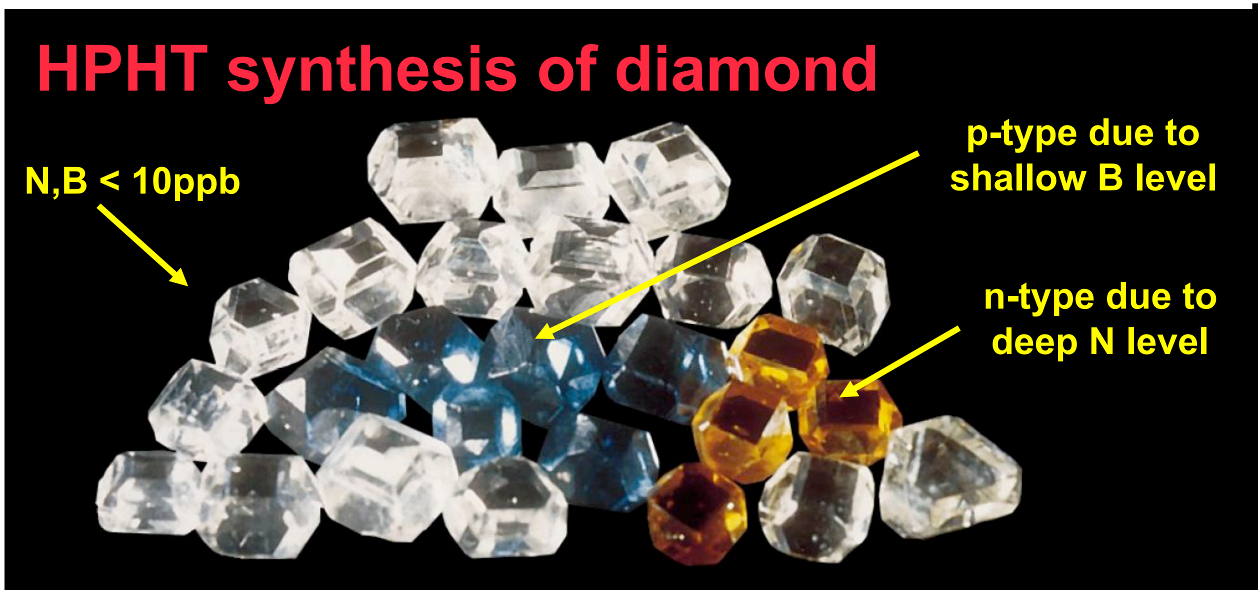
How good can CVD get ?

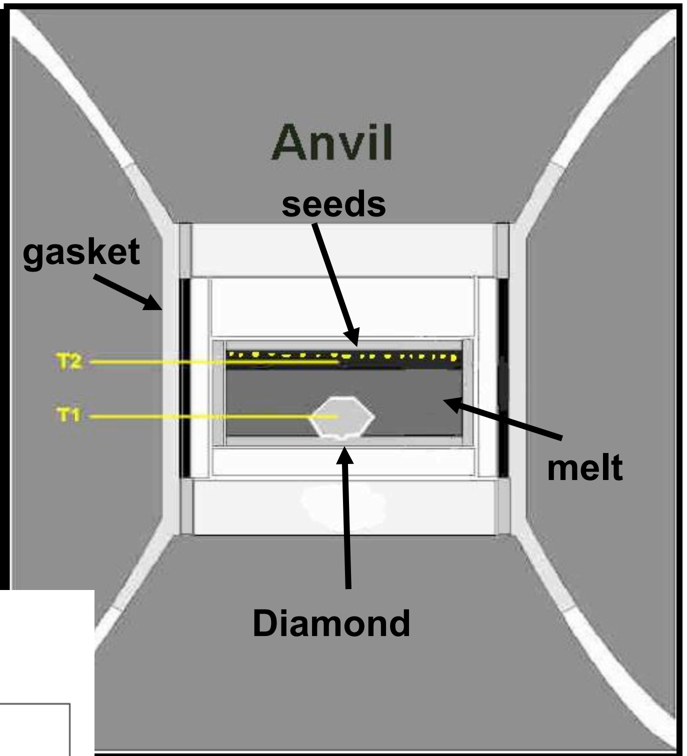
1. **Size** ☺
2. **Purity** ☺
3. **Strain** (not as good as HPHT yet)

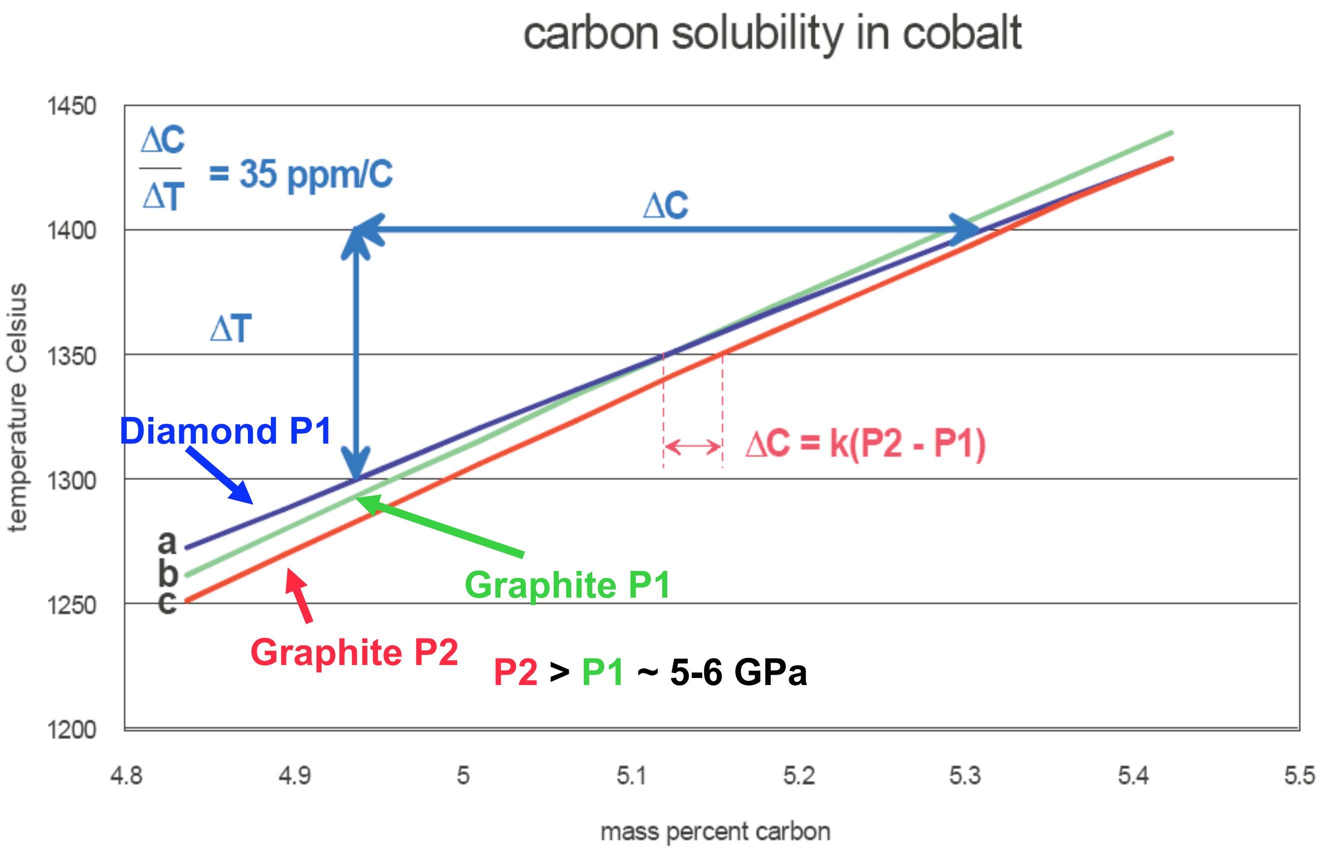


Ind Diam Rev 1(2006)28 Carniegie Inst

HPHT synthesis of diamond





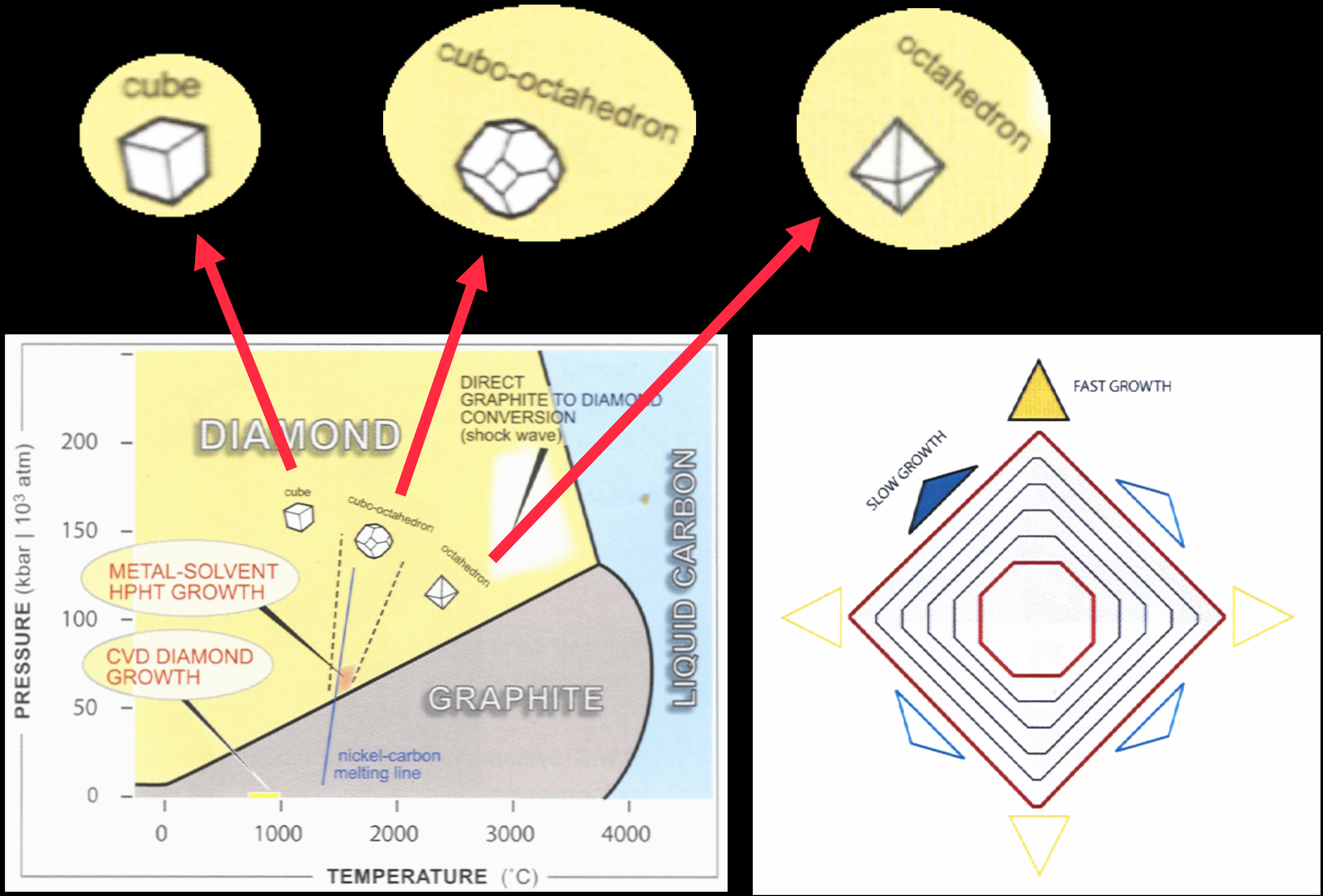


Reconstitution method

- Temperature driven
- Dissolution from diamond seeds
- Temperature gradient $T_2 > T_1$
- Type IIa ~ 300 hours

elementsix ADVANCING DIAMOND

Sectoral variation and striata - (HPHT)



HPHT Diamond

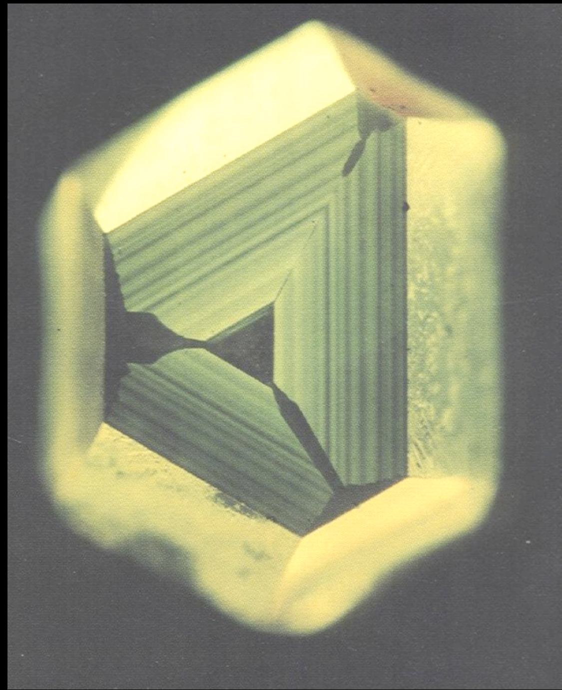
Growth rate related to surface density of atoms

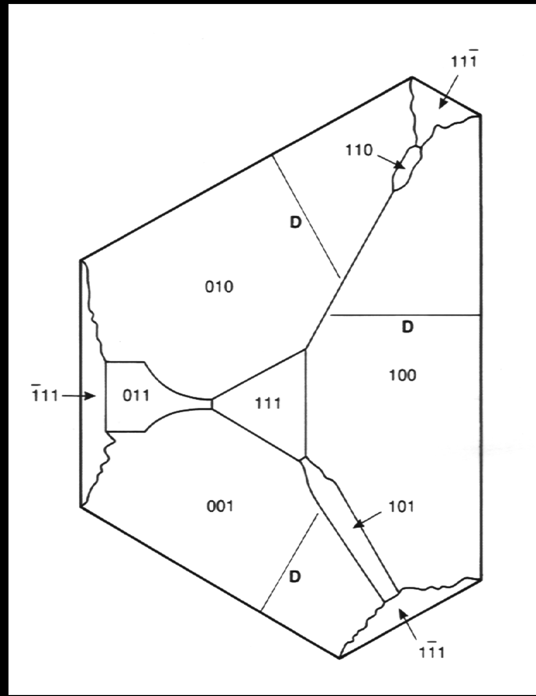
Growth sector dependence of N concentration, [111]>[100]>[113]>[110]

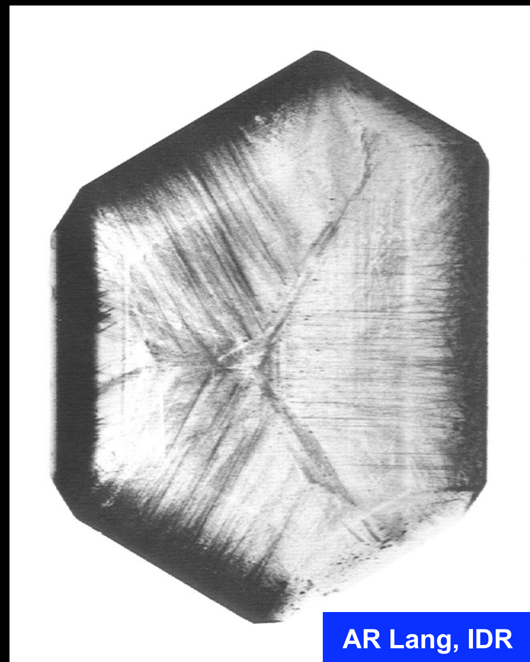
B concentration, [111]>[110]>[100]=[113]>[115]

Ni concentration, [111]

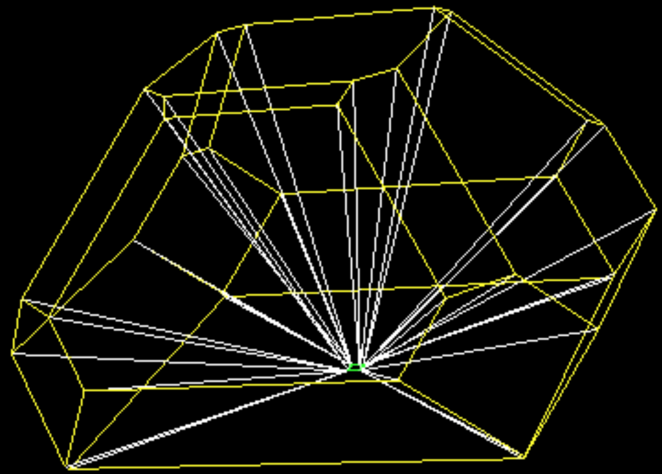
Cube growth sectors have A high denisty of perp. dislocations

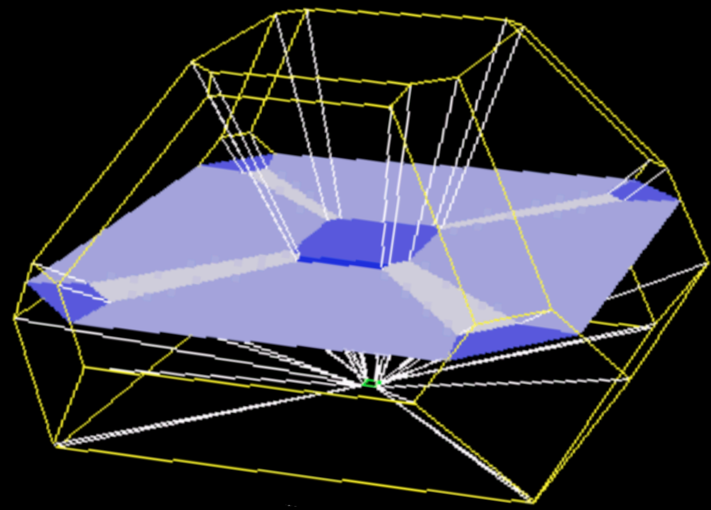




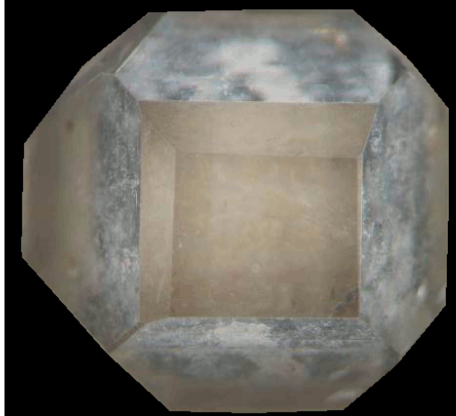


AR Lang, IDR

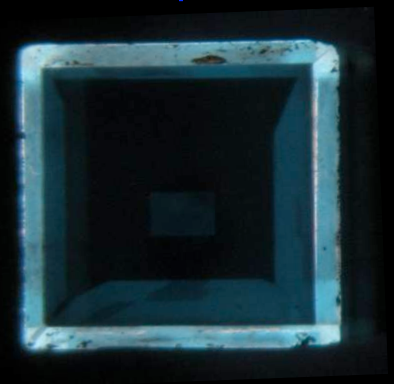




Images from Growth program of the DTC

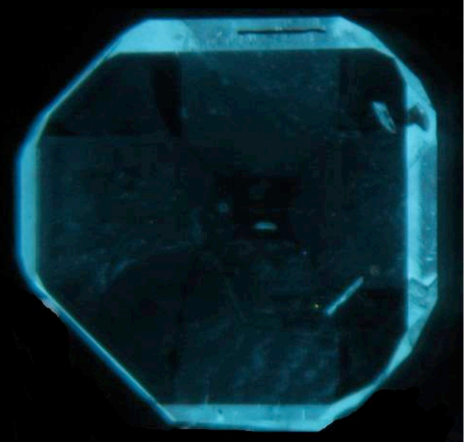


top

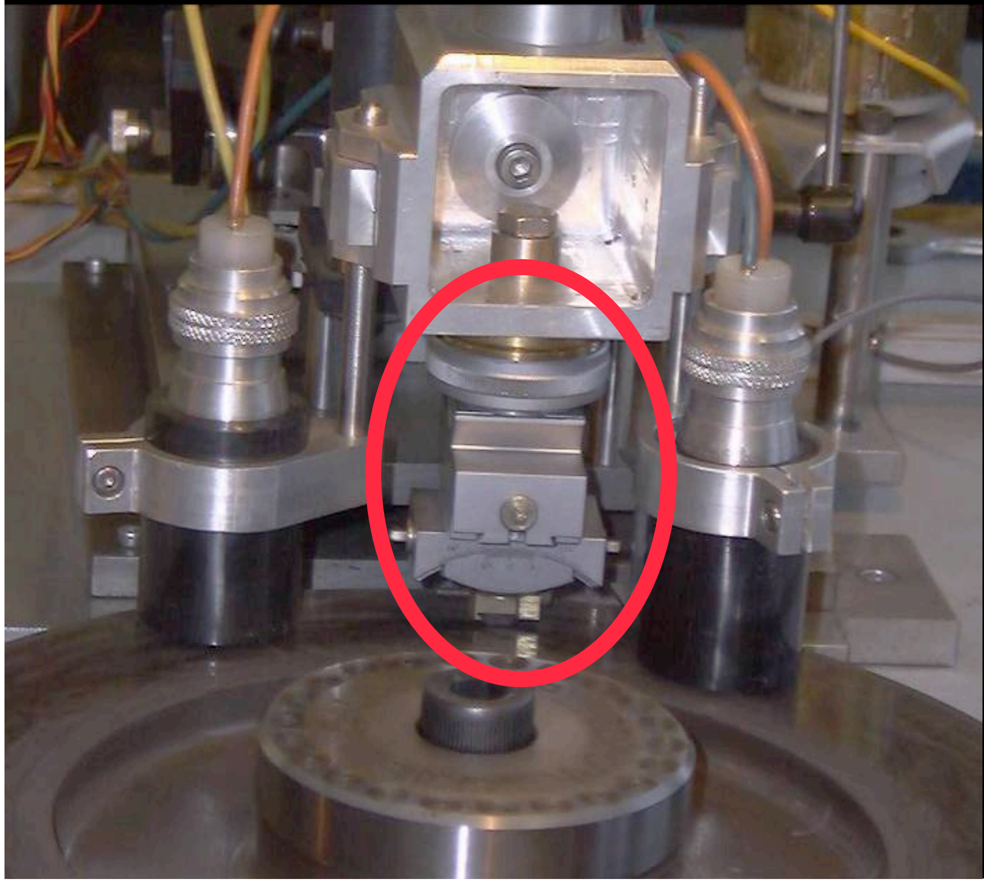


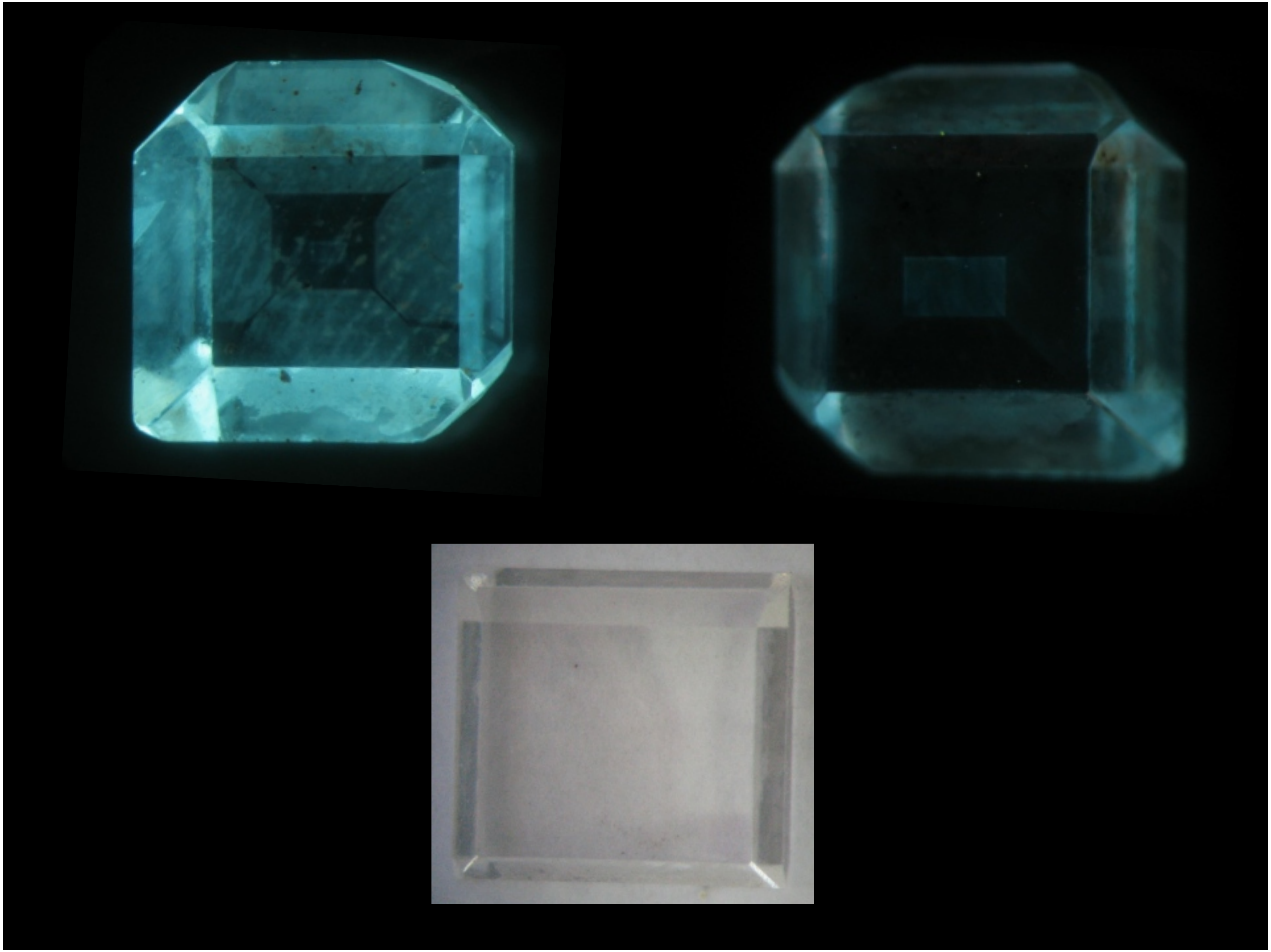
middle

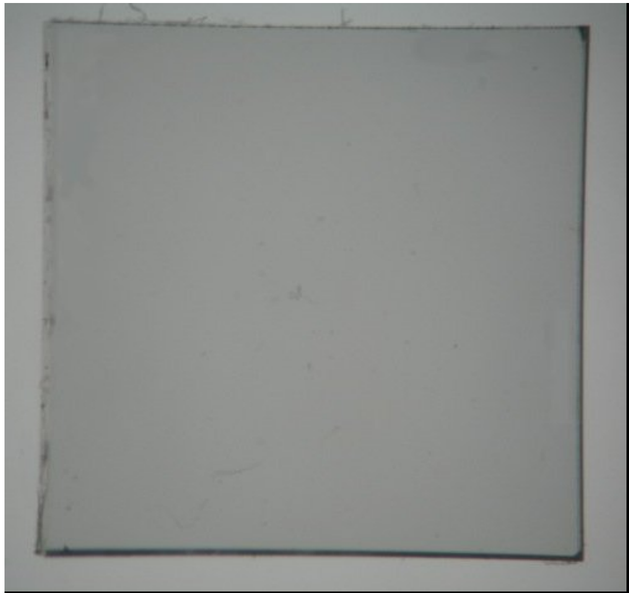
bottom



Courtesy J Hansen -
Hansen Future Materials



Clockwise

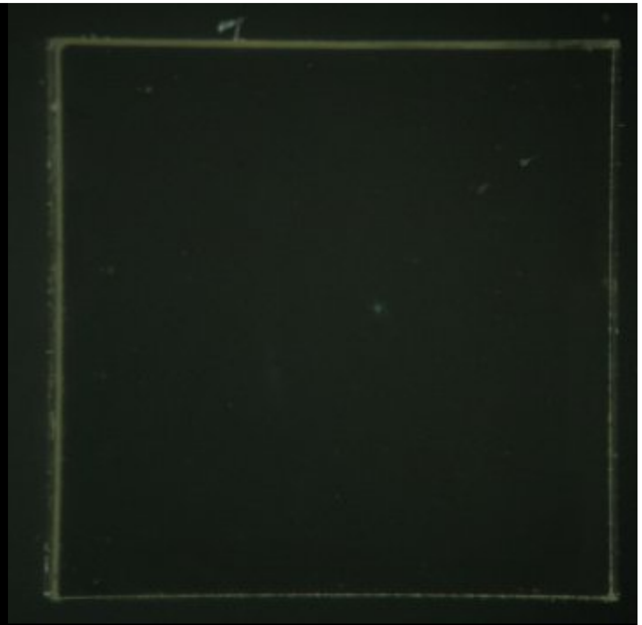
Visible

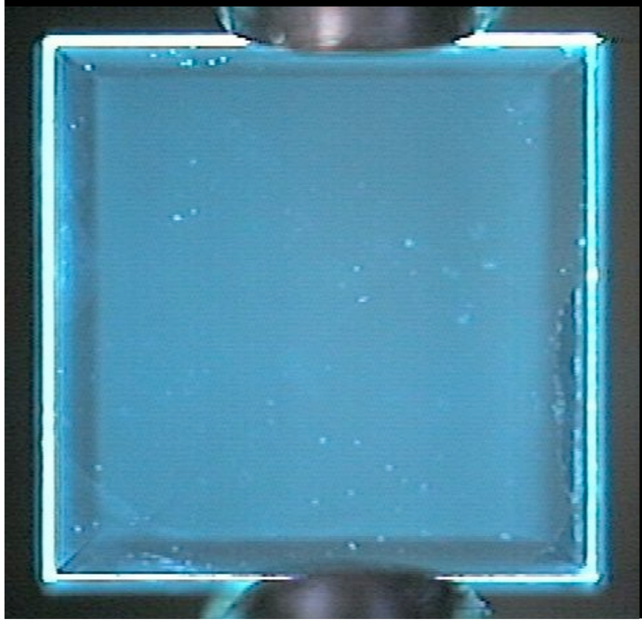
Birefringence

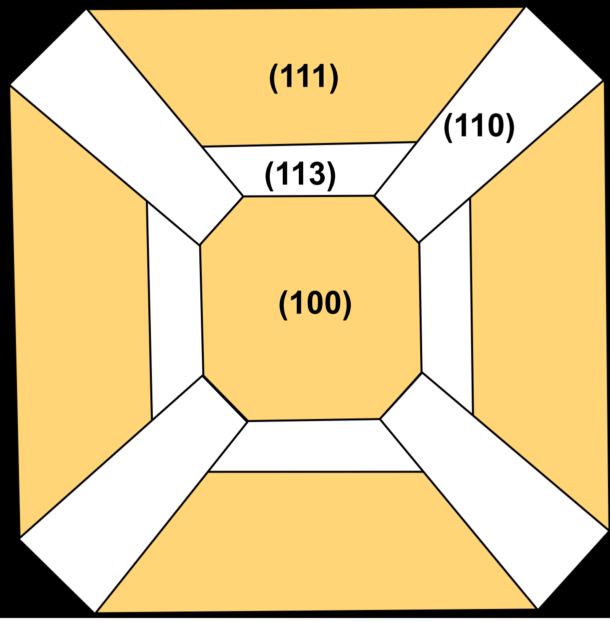
Top-face UV

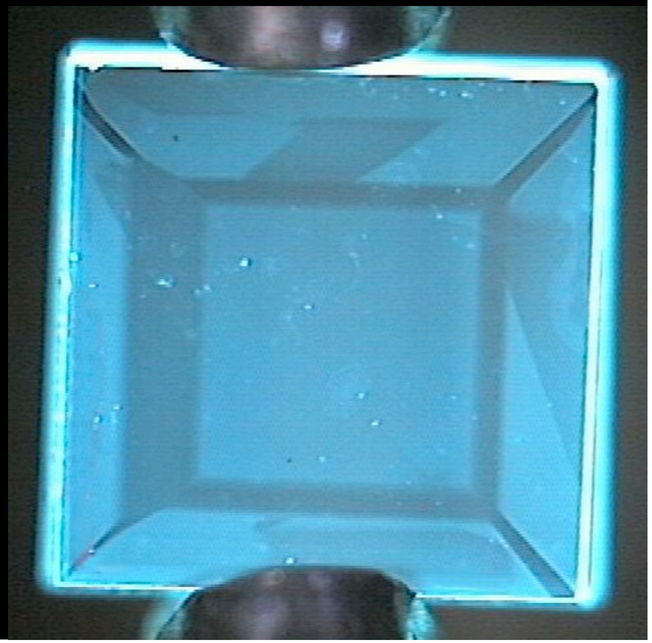
Schematic

Bot-face UV





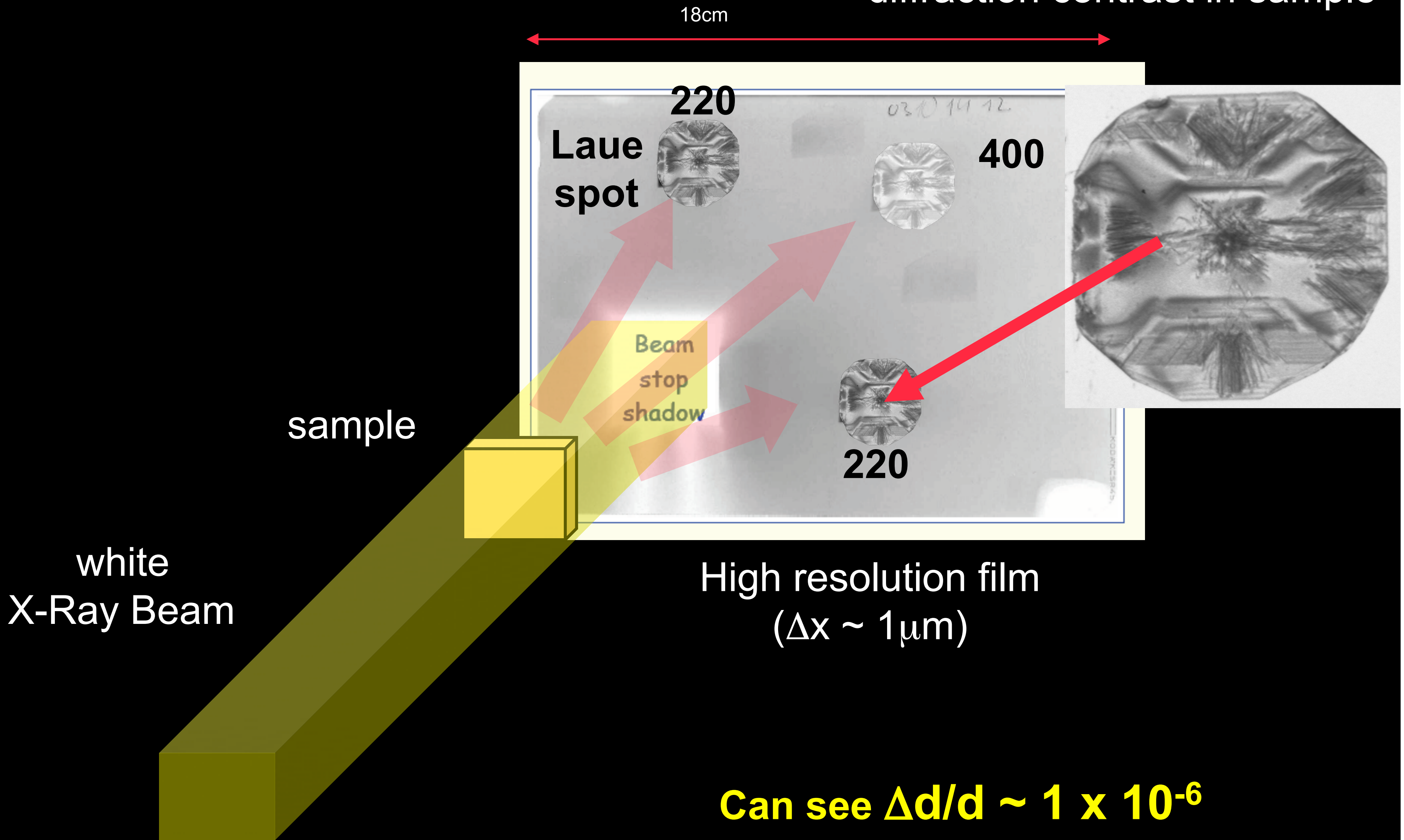




White Beam X-ray Topography

Transmission (Laue) geometry

Each Laue spot is a topographic image of diffraction contrast in sample



High resolution film ($\Delta x \sim 1\mu m$)

Can see $\Delta d/d \sim 1 \times 10^{-6}$

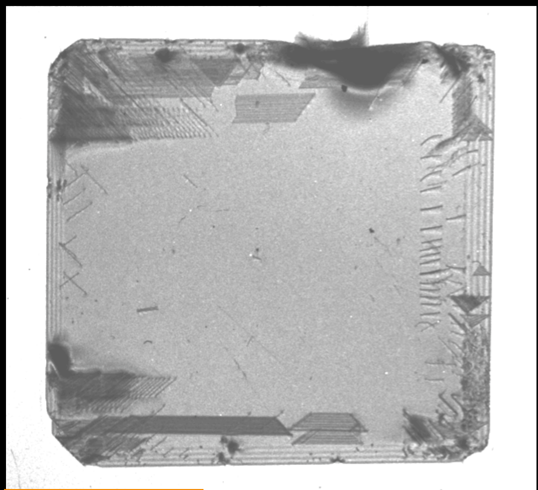
HPHT vs CVD

Techniques are complimentary – both are necessary

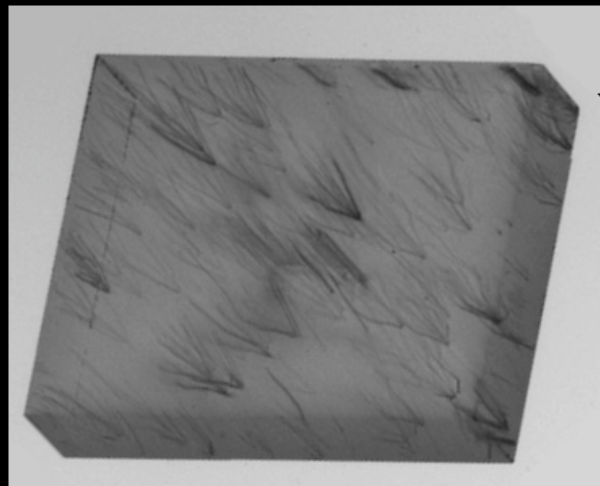
1. CVD growth conditions cold for diamond – allow better control of impurities however, defects can freeze in.
   Leads to purer diamond (c<1ppb), but residual strain is compromised (bundles of dislocations emanating from defects in substrate, maybe more still $\Delta\theta > 10^{-6}$).
   Niche is Electronic Applications

2. HPHT growth conditions hotter, and in the pressure capsule its more difficult to control impurities, growth is in “annealing” conditions.
   Leads to low strain diamond $\Delta\theta \sim 10^{-8}$, but more impurities, c<10ppb.
   Niche is Optical Applications

Situation evolves



HPHT

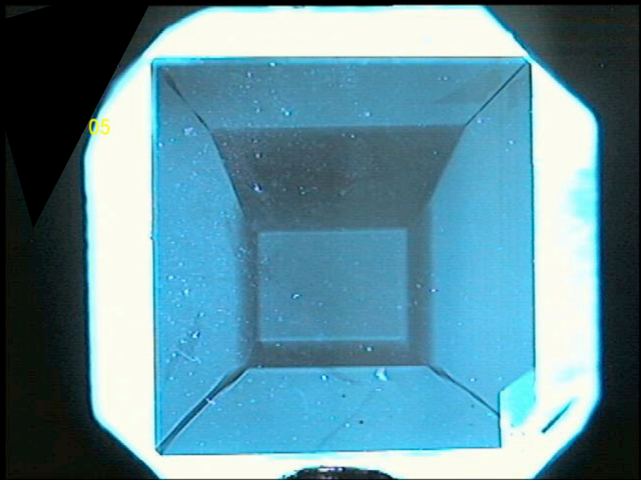


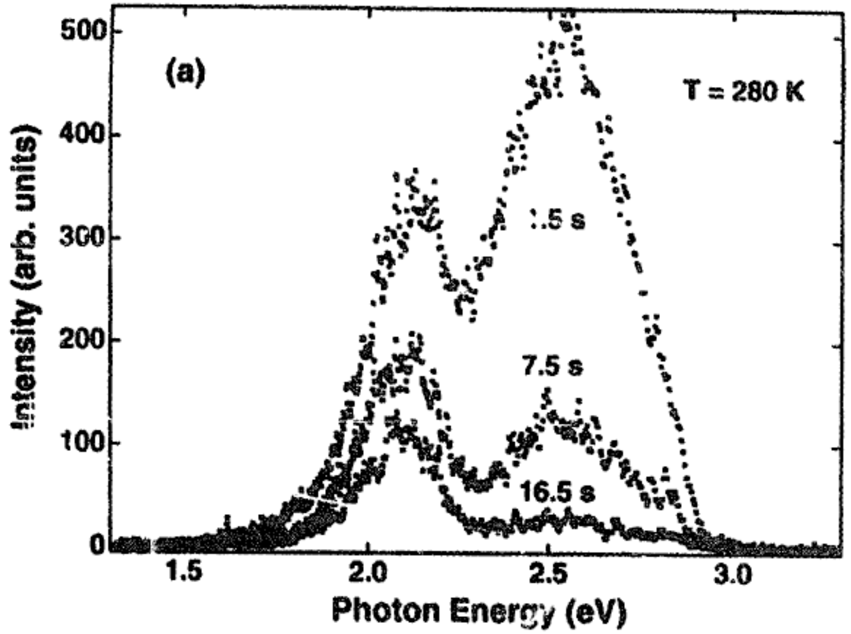
CVD

DRM17(2008)262

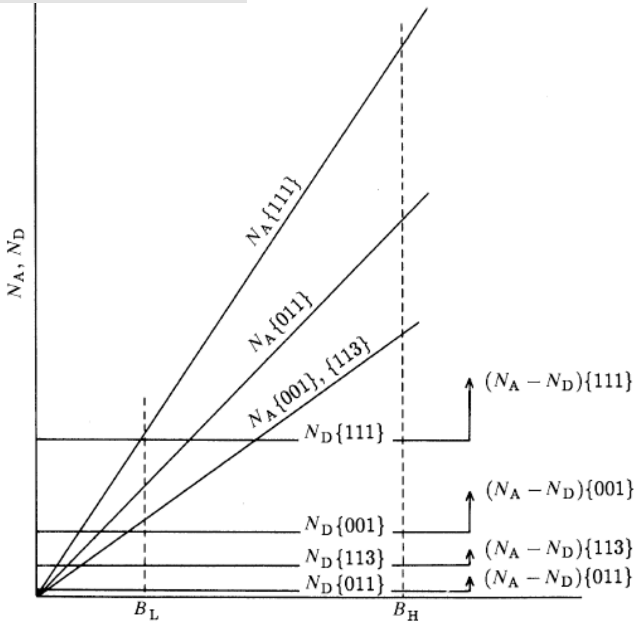
White Beam Topographs - In each case illustrative samples (not the best available)

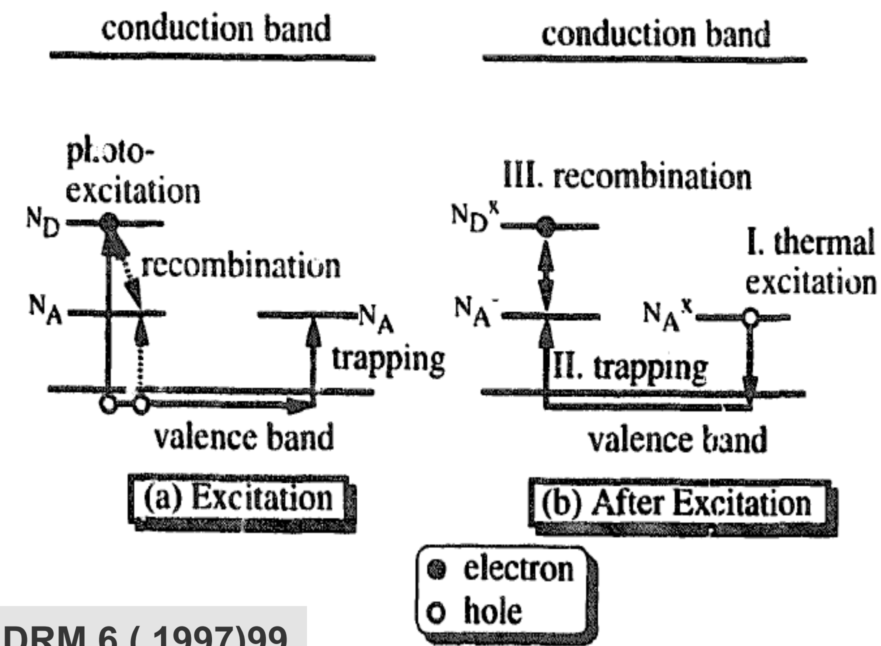
Very strong PL features





Burns (1990)





DRM 6 (1997)99

For very pure diamond

Point defects

1. Boron (acceptor, $E_A = 0.37eV$)
2. Nitrogen (deep donor, $E_D = 1.7$ eV)
3. Hydrogen
4. Vacancy
   a. GR1 (neutral for Type IIa)
   b. ND1 (negative for Type Ib)
5. NV (in CVD)
6. Ni and Co (in HPHT)

Annealing leads to aggregation

B, N are soluble (size)

Defect Characterisation

….. low strain diamond …. considering central cubic region of top plate

Classical Techniques

1. EPR (defect concentration in ppb region)
2. IR-Vis-UV Abs Spectroscopy (defect concentration in ppm region)
3. Photo / Cathodo - Luminescence / Phosphorescence (defect concentration in ppb region)
4. Birefringence – for strain sensitivity … down to ppm
5. Raman Spectroscopy – for strain sensitivity … down to ppm
6. SIMS (some defects down to ppb region)

Difficulty

- Beyond MDL of many techniques
- No single technique can quantify all impurities, or all molecular forms or even charge states of the same impurity …..

Birefringence

Contrast

Phase difference

$$\delta = \frac{2\pi}{\lambda} Cd \cdot \Delta S$$

stress-Optic coefficient

differential strain

$$C = 3.24 \times 10^{-12} \text{ Pa}^{-1}$$

$$\delta = \frac{2\pi d \Delta n}{\lambda}$$

$$S \approx Y \frac{\Delta d}{d}$$

$$Y = 10.54 \times 10^{11} \text{ Pa}$$

$$\Delta n \approx 3 \frac{\Delta d}{d}$$

Metripol : MDL , $\Delta n \sim 10^{-6}$

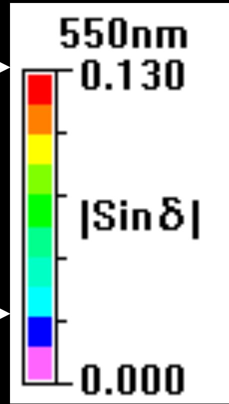
Can't characterise low strain diamond

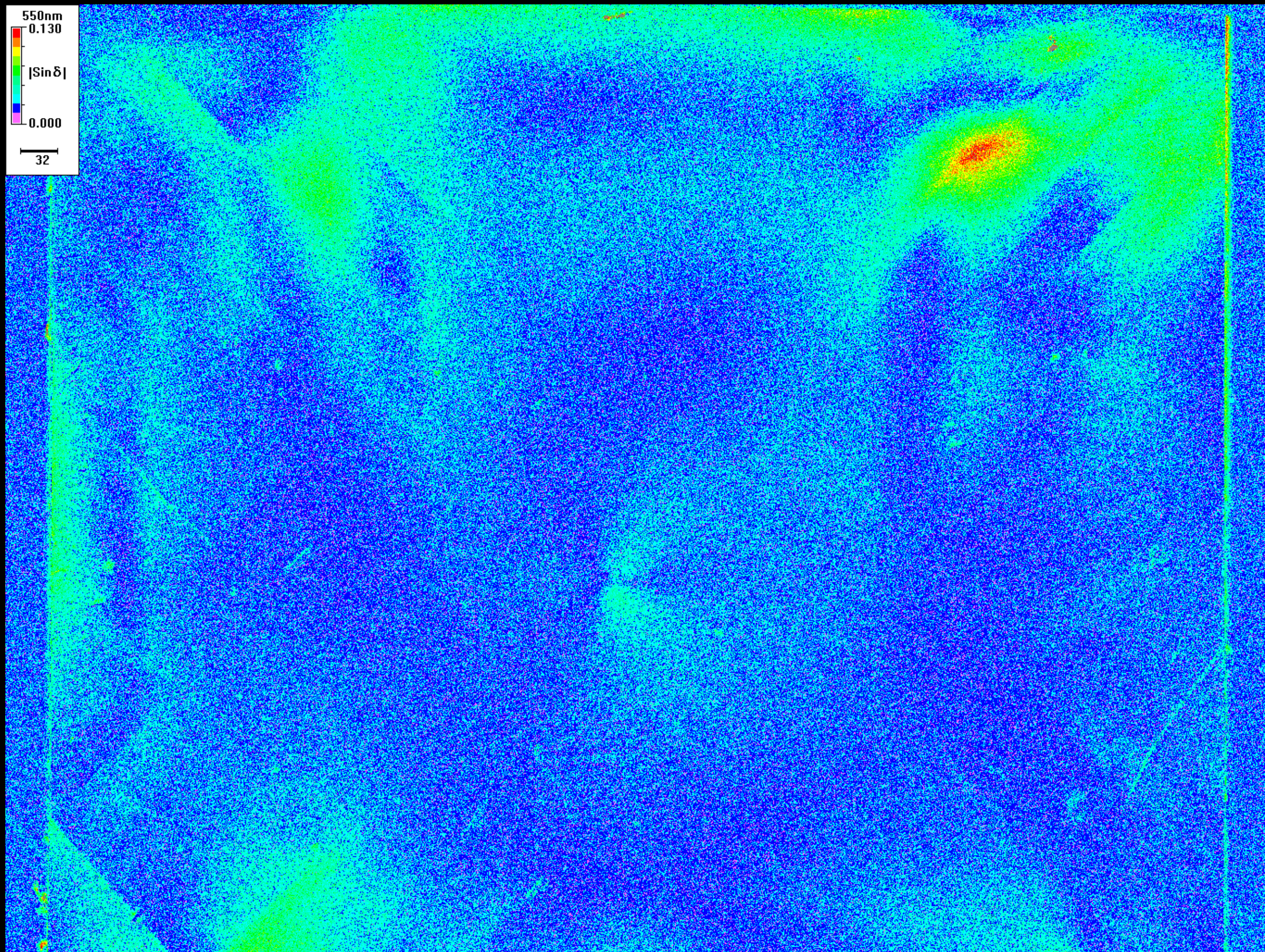
s357-01a

Metripol image – strain induced birefringence

Δn = 1.8×10^{-5}

Δn = 3.7×10^{-6}

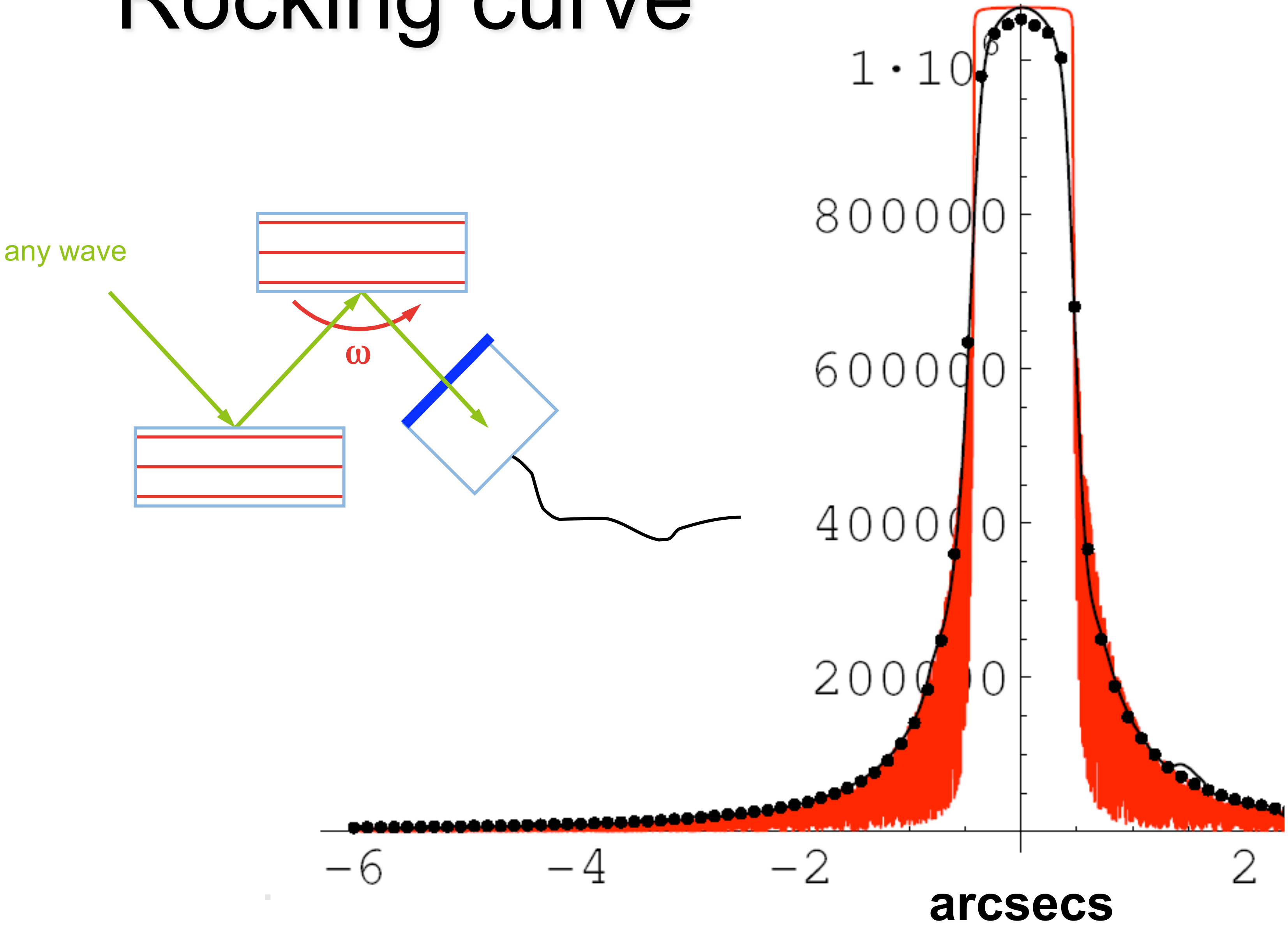




Thickness = 0.619 mm

Ian Friel, Element Six

Rocking curve

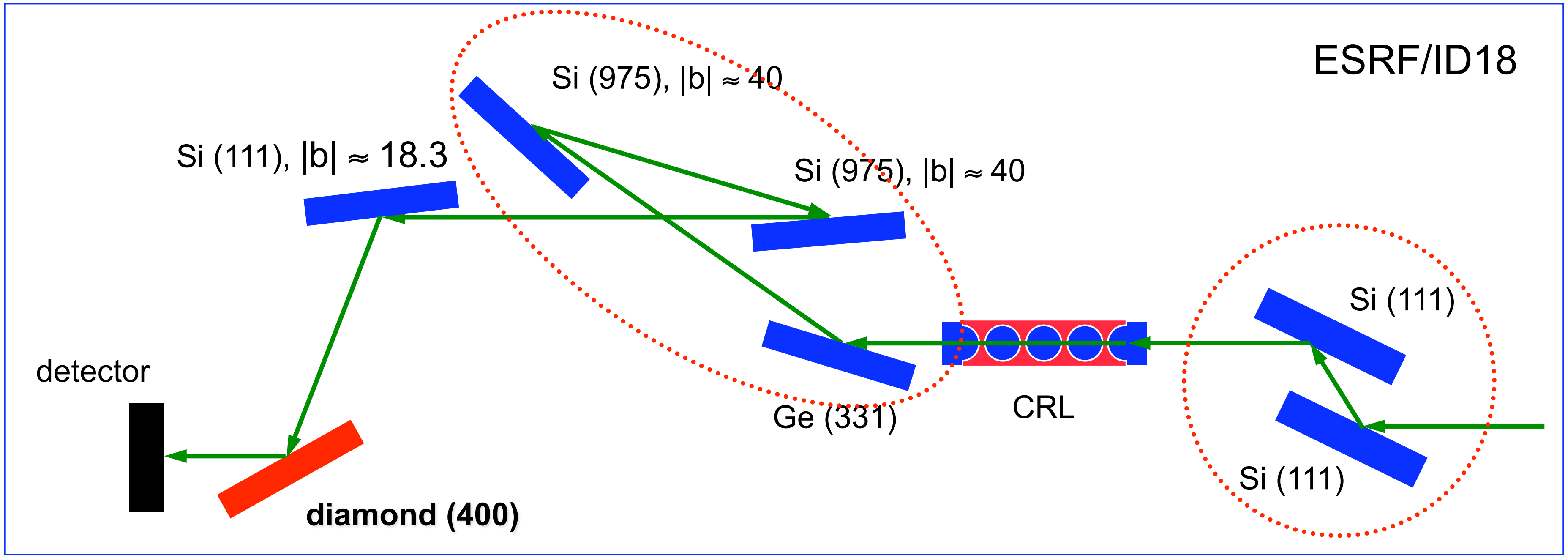


Rocking Curves

- Beam divergence – $\Delta\theta \sim 0.2''$
- Beam energy resolution $\Delta\lambda/\lambda \sim 10^{-8} \rightarrow \Delta\theta' \sim 0.0023''$

sample	theoretical width	exp. width full beam	broadening full beam	exp. width 100 µm center	broadening center
1173 – 001a	1.045”	1.15”	0.48”	1.10”	**0.20”**
1173 – 001b	0.986”	1.39”	0.98”	1.03”	**0.30”**
1173 – 001d	1.056”	1.30”	0.76”	0.97”	**0.0”**
1173 – 001e	1.018”	2.36”	2.13”	1.03”	**0.30”**
1186 – 001a	1.021”	1.09”	0.38”	1.04”	**0.20”**
1186 – 001c	1.021”	1.14”	0.52”	1.09”	**0.38”**
1186 – 001d	1.012”	2.47”	2.25”	1.73”	**1.40”**
1149/13R	1.059”	1.33”	0.80”	1.13”	**0.39”**

High-resolution diffractometry set-up



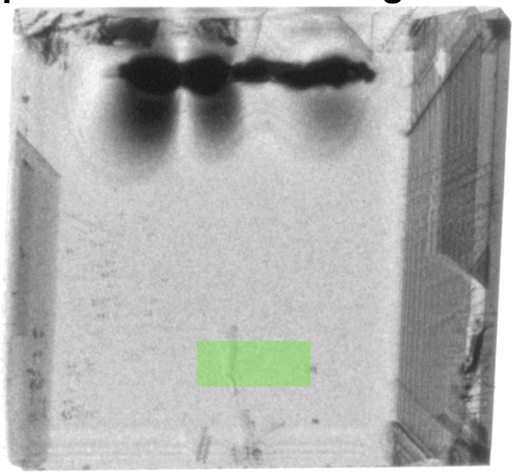
E = 14.413 keV

Δλ/λ ≈ 10^{-8} (≅ 0.0023”)

δθ ≈ 0.18”

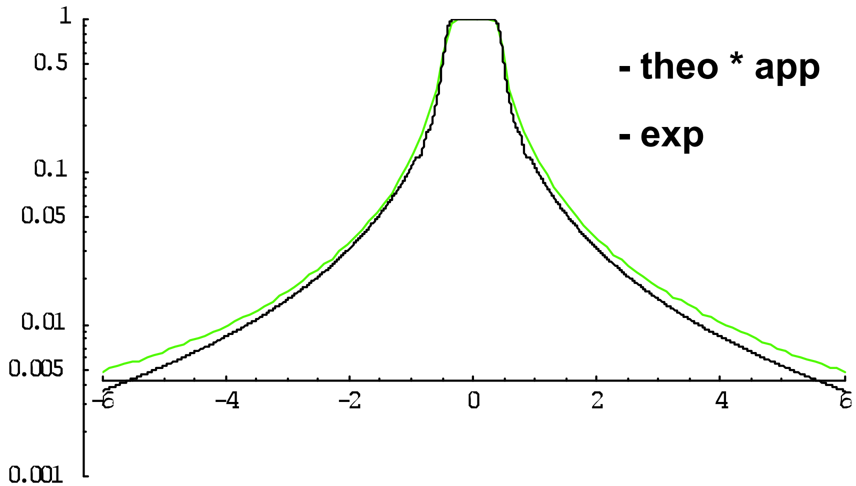
WHITE BEAM TOPOGRAPHY

type IIa HPHT with a large inclusion

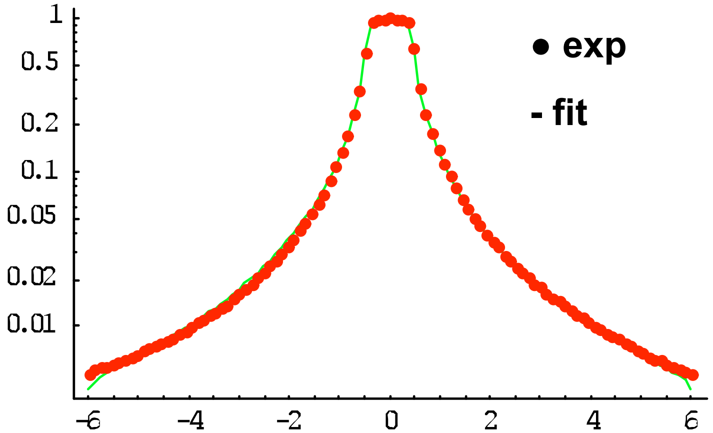


h **1 mm**

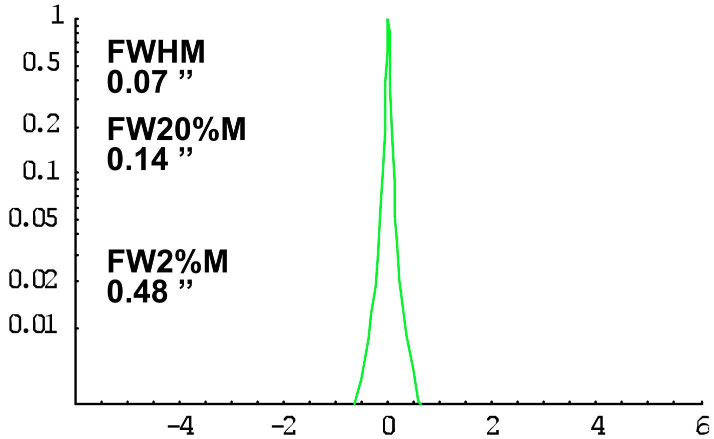
footprint = 1 x 0.4 mm



fit after convolution “defects broadening”



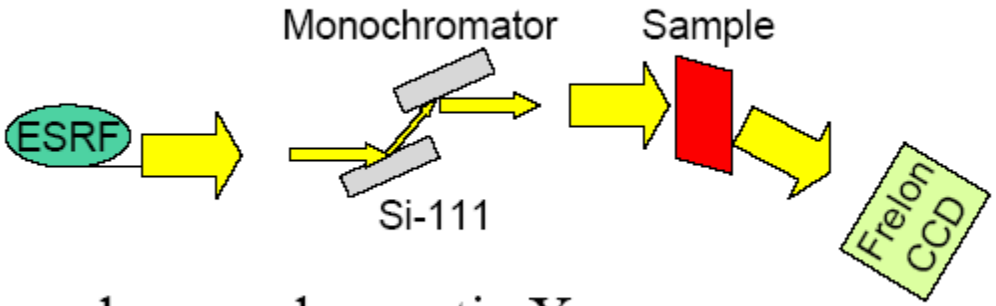
“defects broadening” function



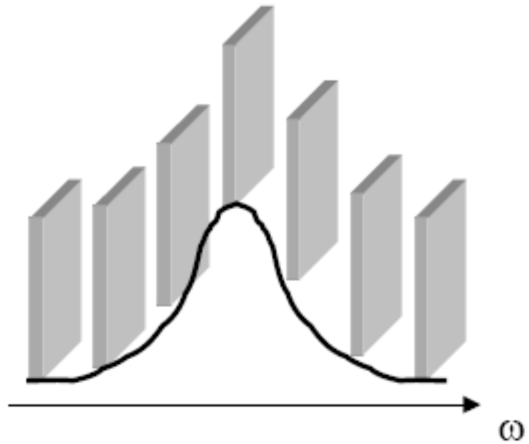
ESRF

Rocking Curve Imaging: Principle

- Wide, parallel X-ray beam
  ID19 @ ESRF: 15 x 40 mm



- Record monochromatic X-ray topographs digitally
- „Rock“ sample; take one exposure per angular position



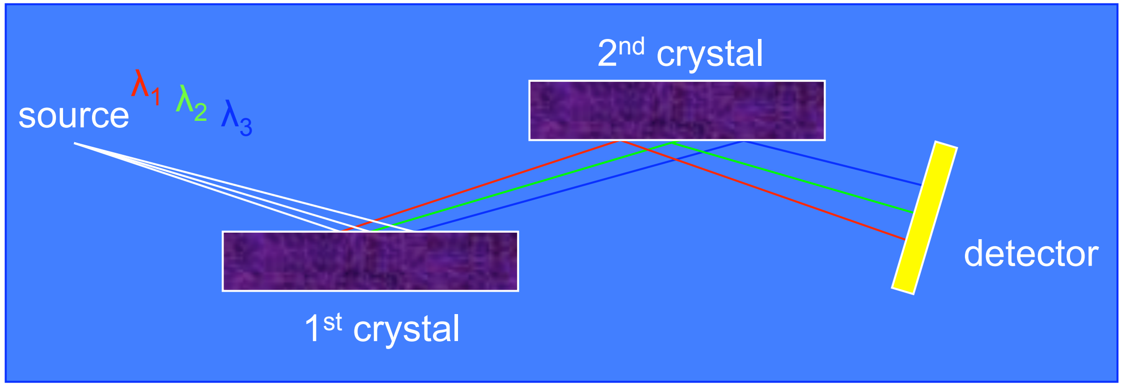
- $(\Delta\omega)^2_{obs} = (\Delta\omega)^2_{def} + (\Delta\omega)^2_{Darwin} + (\Delta\omega)^2_{source}$

vert. gradient const.

Non-dispersive and dispersive set-ups

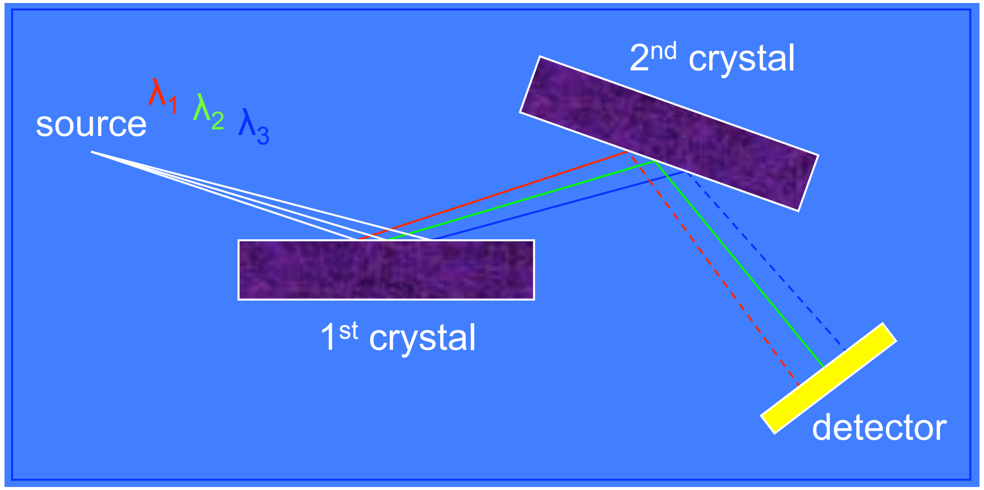
(n,-n) set-up

range of wavelengths on detector
what passed 1st crystal passes 2nd
full beamwidth reflected larger than source width



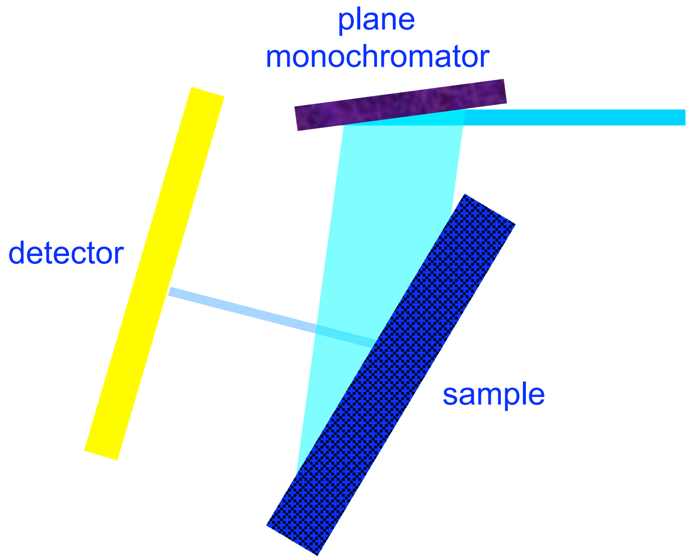
(n,-m) set-up

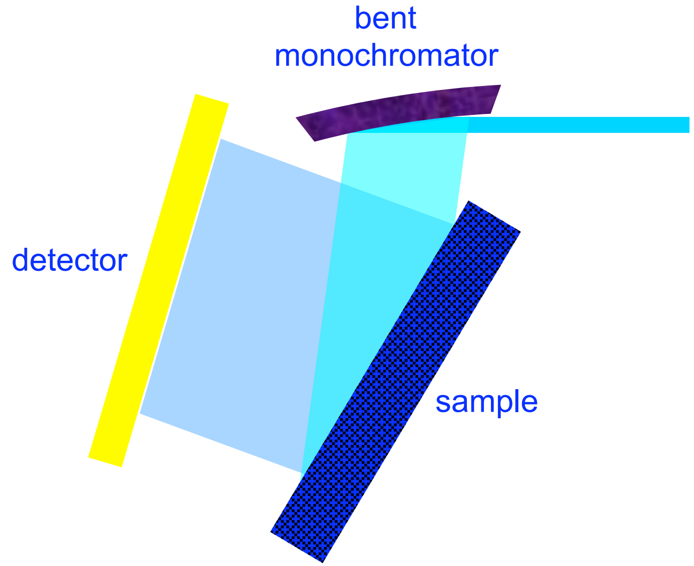
small range of wavelengths on detector
Only small band passes 2nd crystal
narrow beam reflected



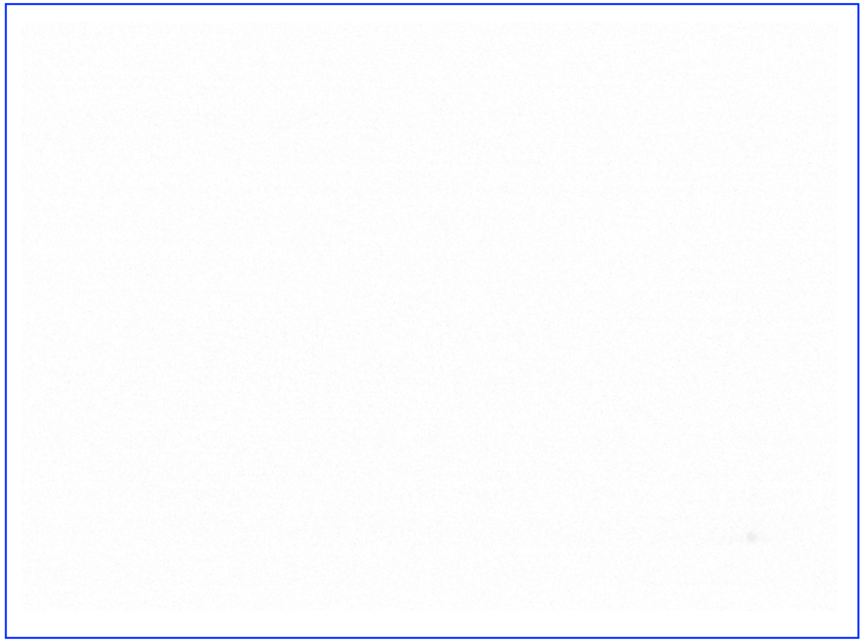
also (n,+n) and (n,+m) set-ups

Curved Crystal Topography (CCT)



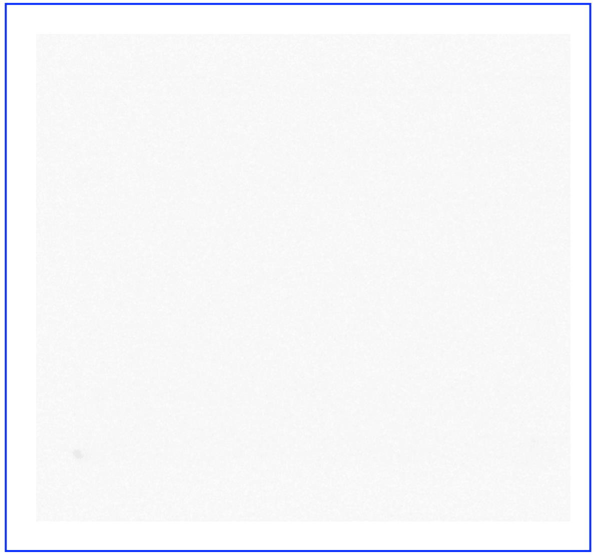


The consequence of dispersion



110-oriented plate

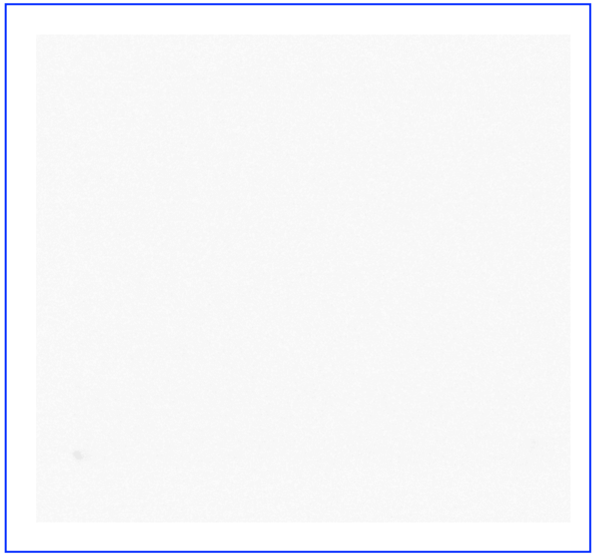
slightly distorted



100-oriented plate

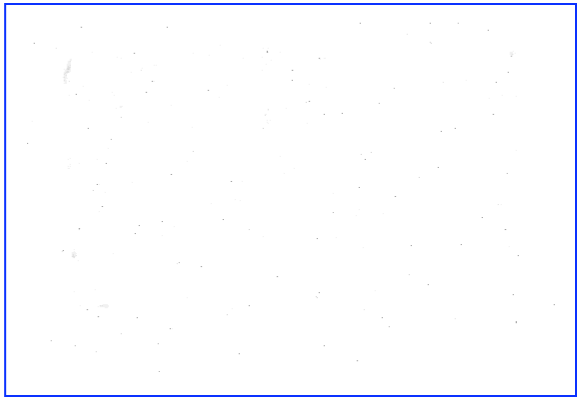
non-distorted

Dispersive – non-dispersive



100-oriented plate

dispersive set-up

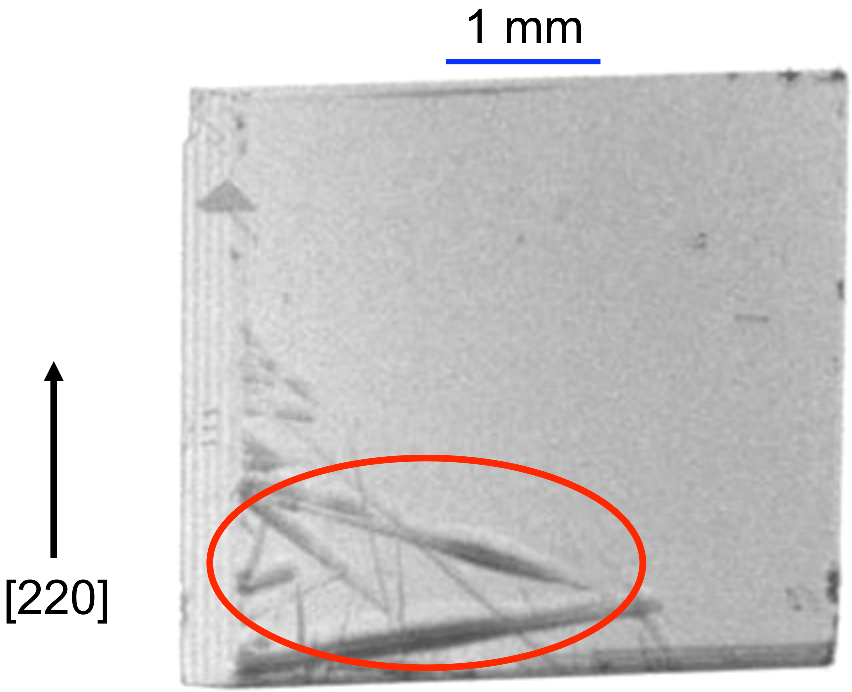


100-oriented plate

non-dispersive set-up

Non-dispersive set-up:

whole crystal illuminated for one angular position, higher strain sensitivity

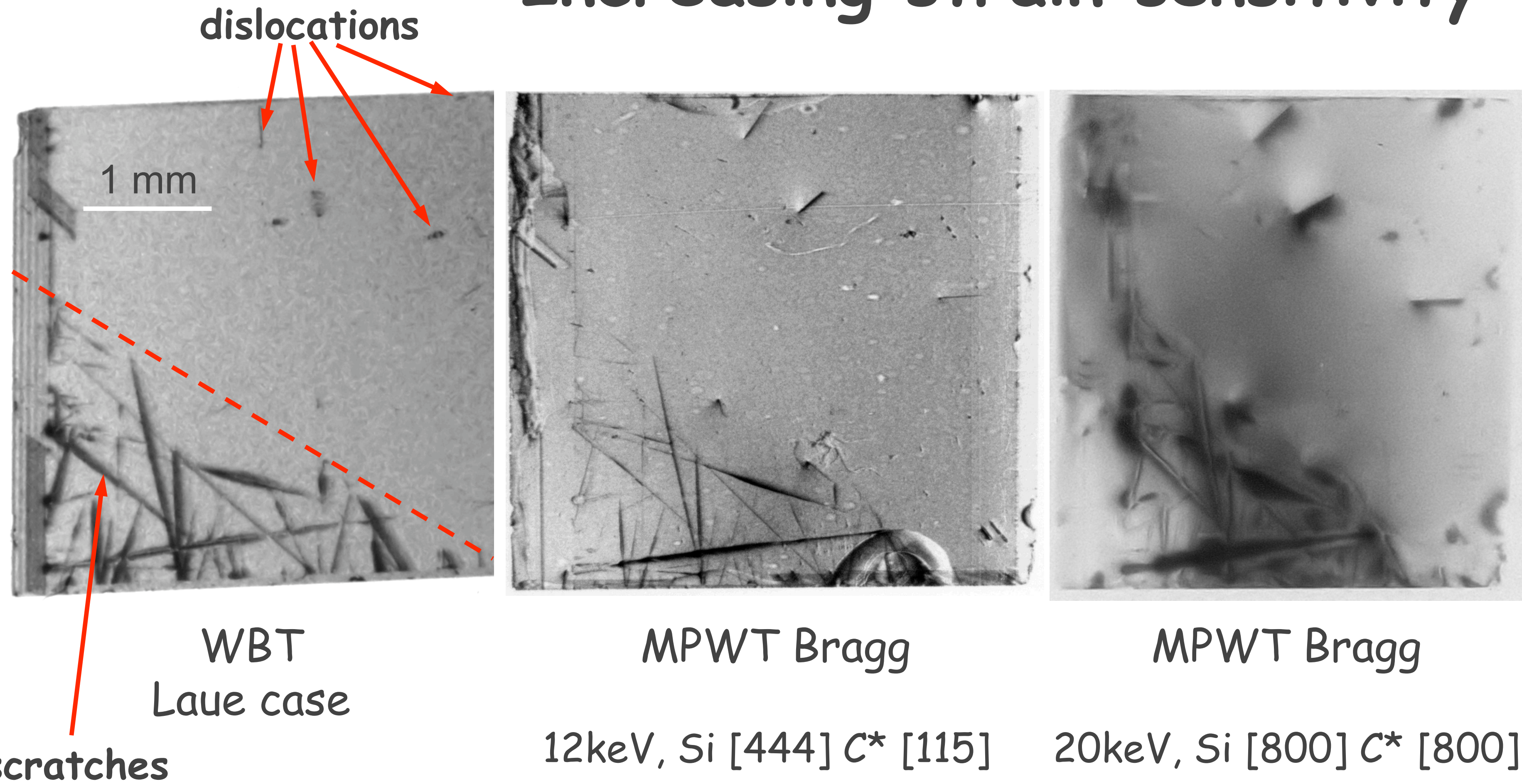


White beam topograph of a HPHT “last” diamond (Laue)

Rocking curve imaging with the **Curved Collimator** (Bragg)

E= 12keV
Si [444] - C* [-115]
$\Delta d/d >$ 3.7 10^{-8}
(detection limit)

Increasing strain sensitivity



WBT
Laue case

MPWT Bragg

12keV, Si [444] C* [115]
$\Delta d/d >$ 4 10^{-8}

MPWT Bragg

20keV, Si [800] C* [800]
$\Delta d/d >$ 1.2 10^{-8}

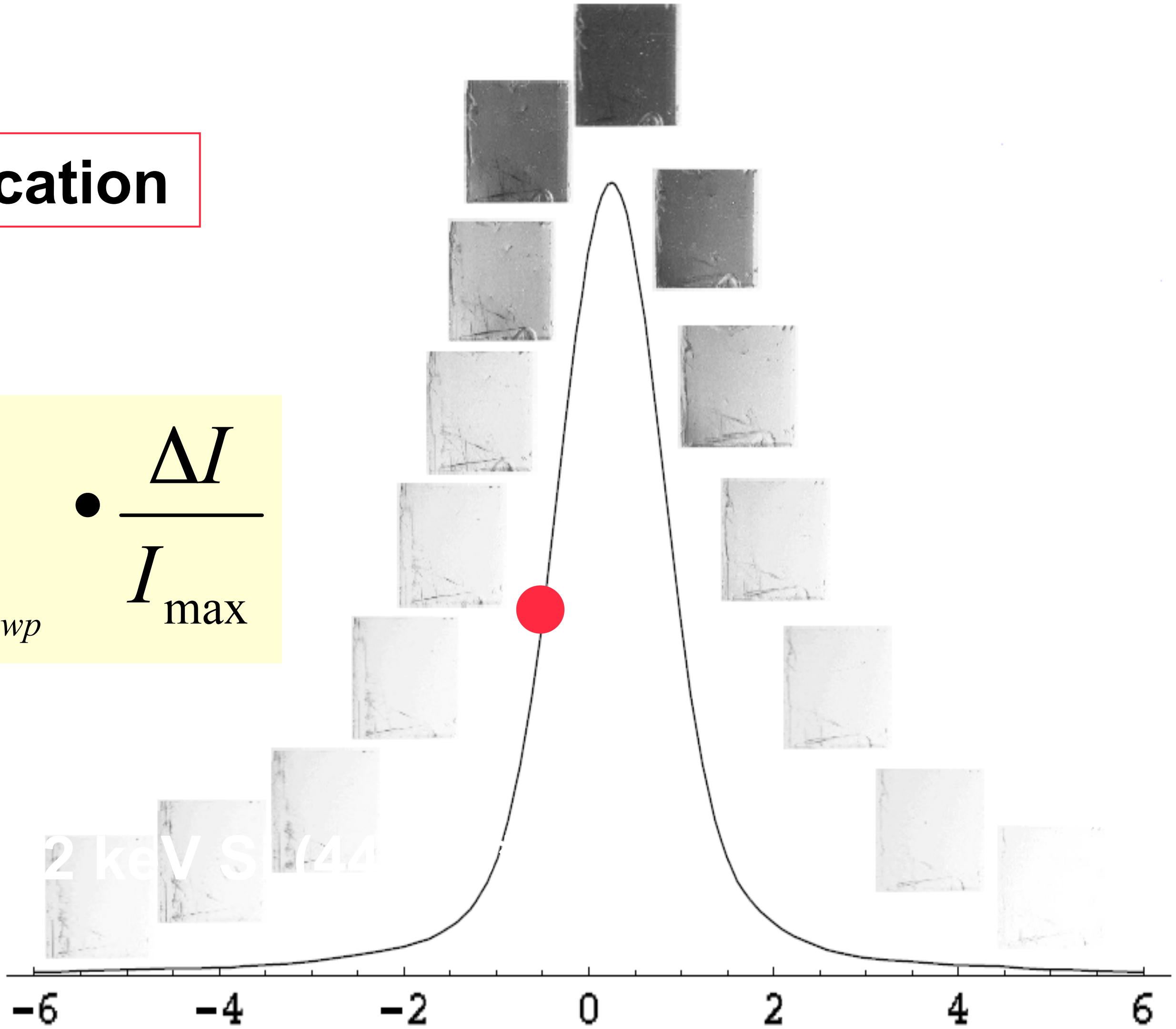
Also with this **very high strain sensitivity**
a **rather homogenous zone** is present,
there crystal quality **close to that of silicon**

ESRF
Newsletter
45(2007))27

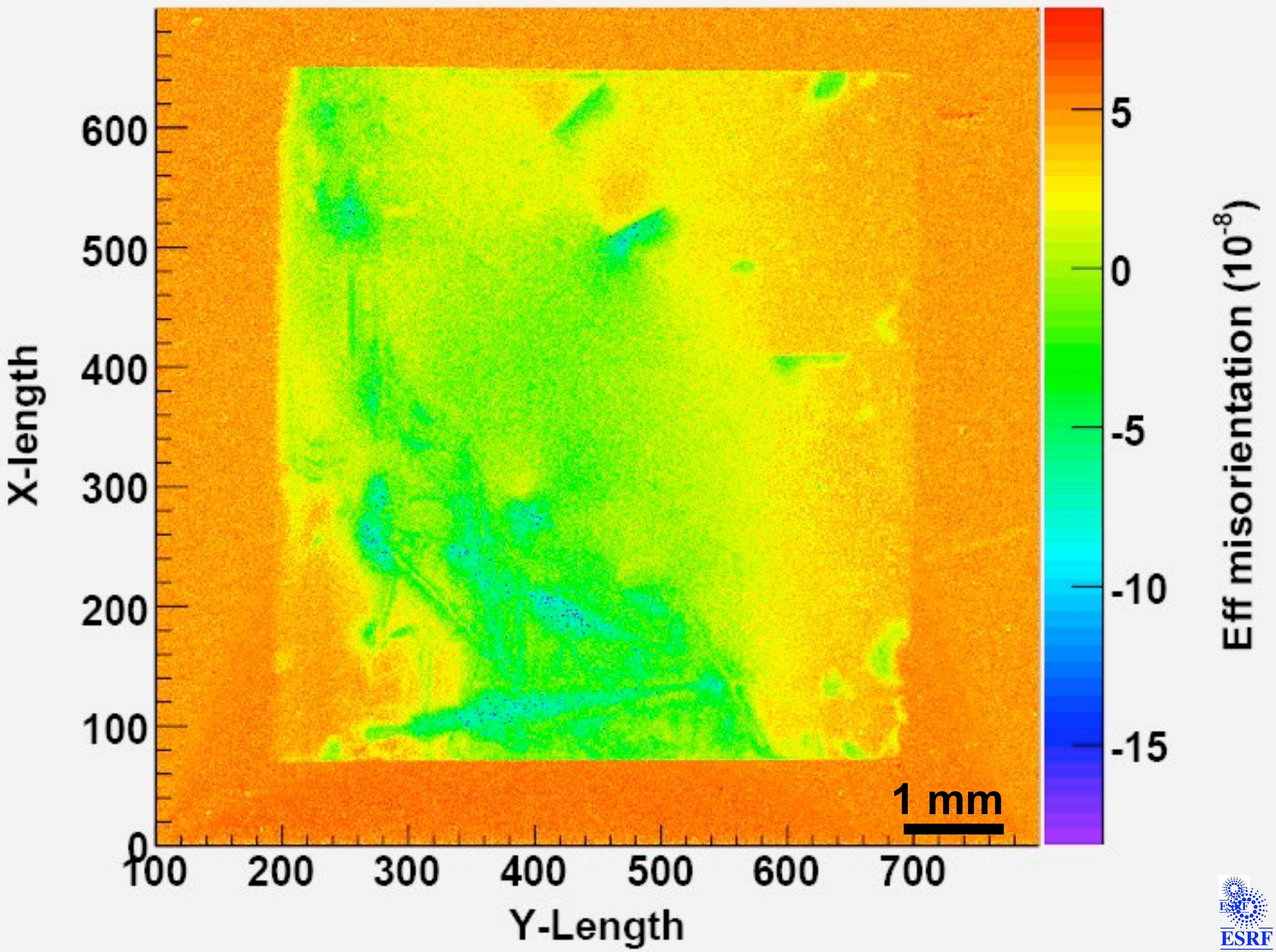
$$\delta\theta(\vec{r}) = \theta - \theta_B^{perf} - \tan\theta_B \frac{\Delta d}{d}(\vec{r}) \pm \Delta\varphi(\vec{r})$$

Quantification

$$\delta\theta = \left.\frac{d\theta}{dR}\right|_{\theta_{wp}} \bullet \frac{\Delta I}{I_{\max}}$$



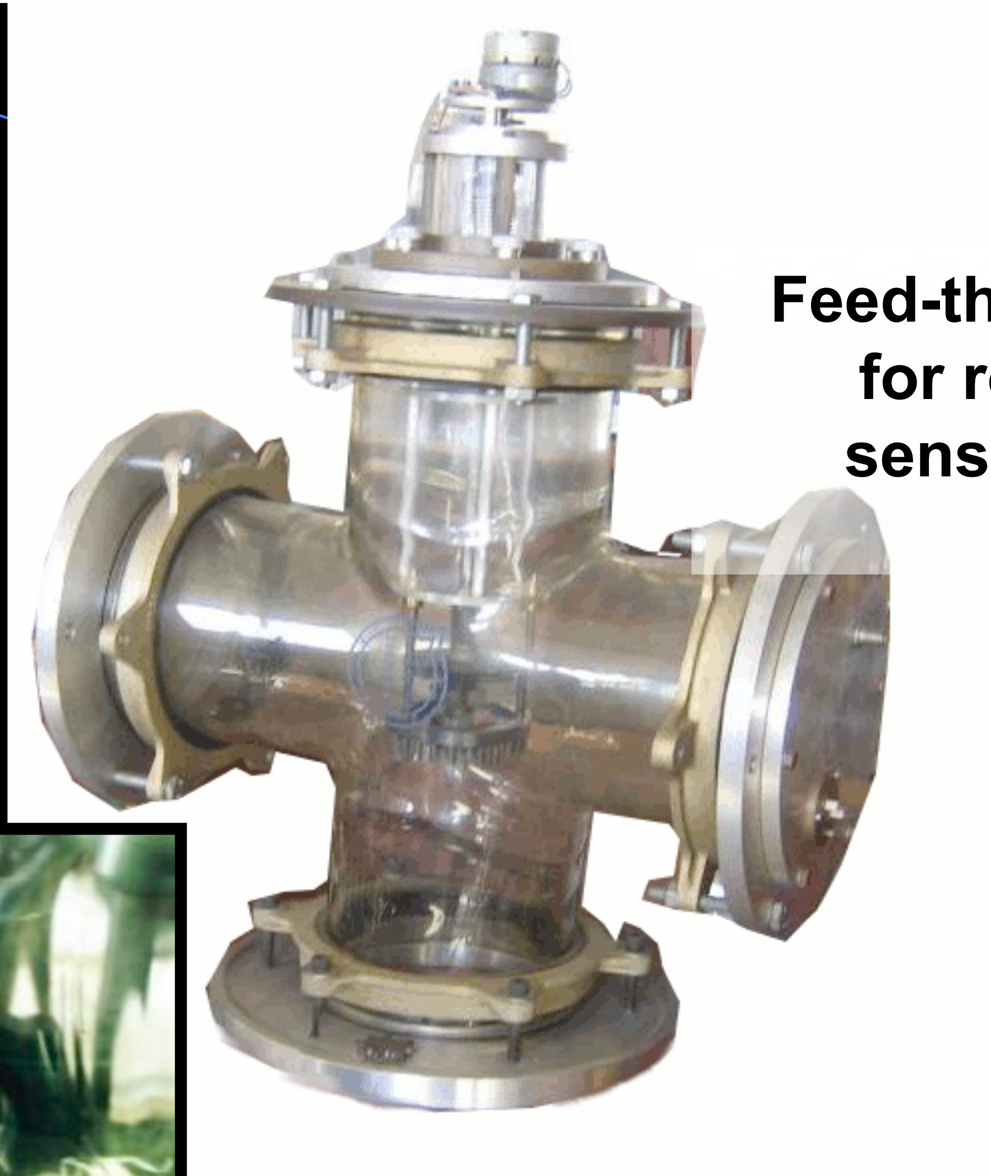
ESRF



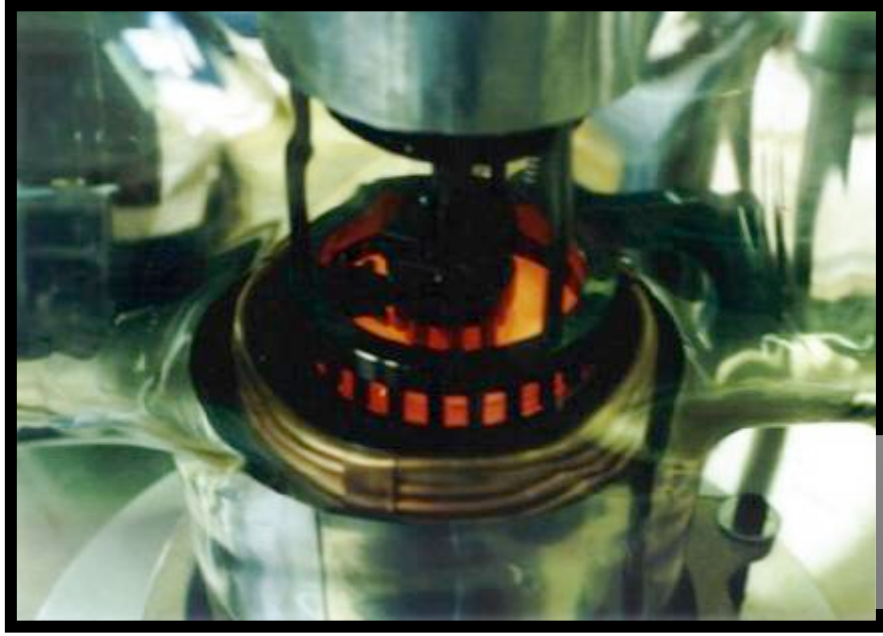
X-length
600
500
400
300
200
100
0
100
200
300
400
500
600
700
Y-Length
1 mm
5
0
-5
-10
-15
Eff misorientation (10^{-8})

ESRF

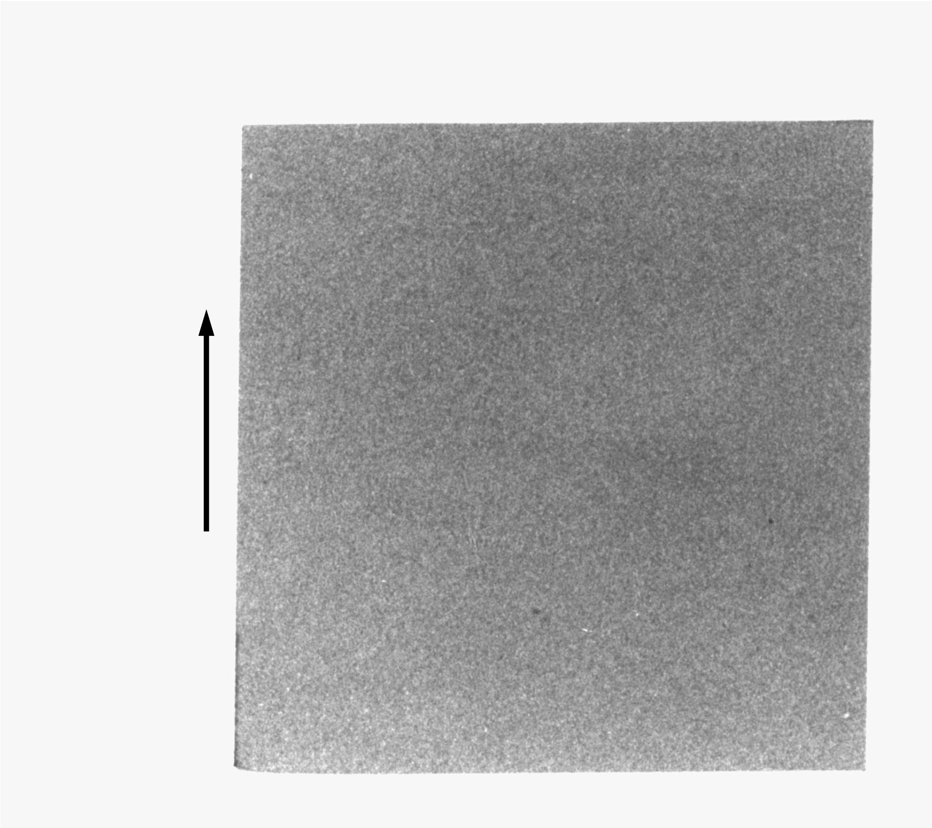
Thermo-chemical-mechanical Processing

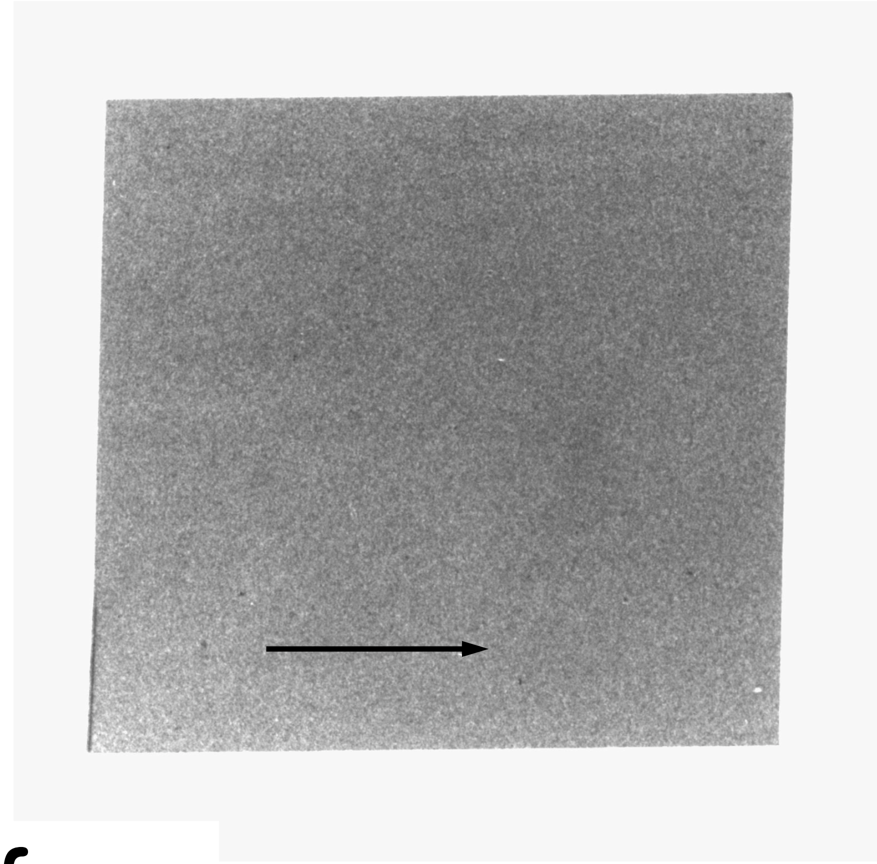


Feed-throughs for rotation, sensing and power



Insert shows hot metal polishing in operation





Dislocation free

-220 and 220-reflections

sample dimension 4x4 mm^2

The crystal quality seen with the strain sensitivity of white beam topography is very good! No macroscopic defects like dislocations are visible.

White beam topographs in transmission

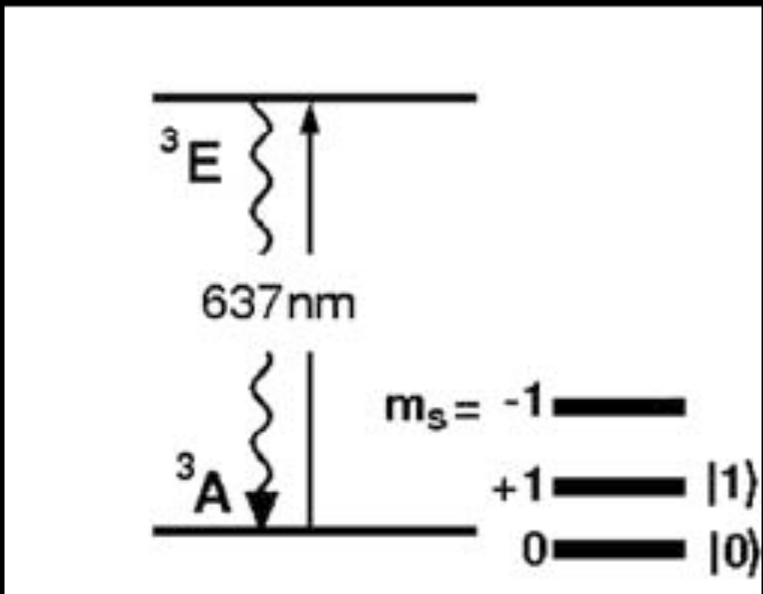
ESRF

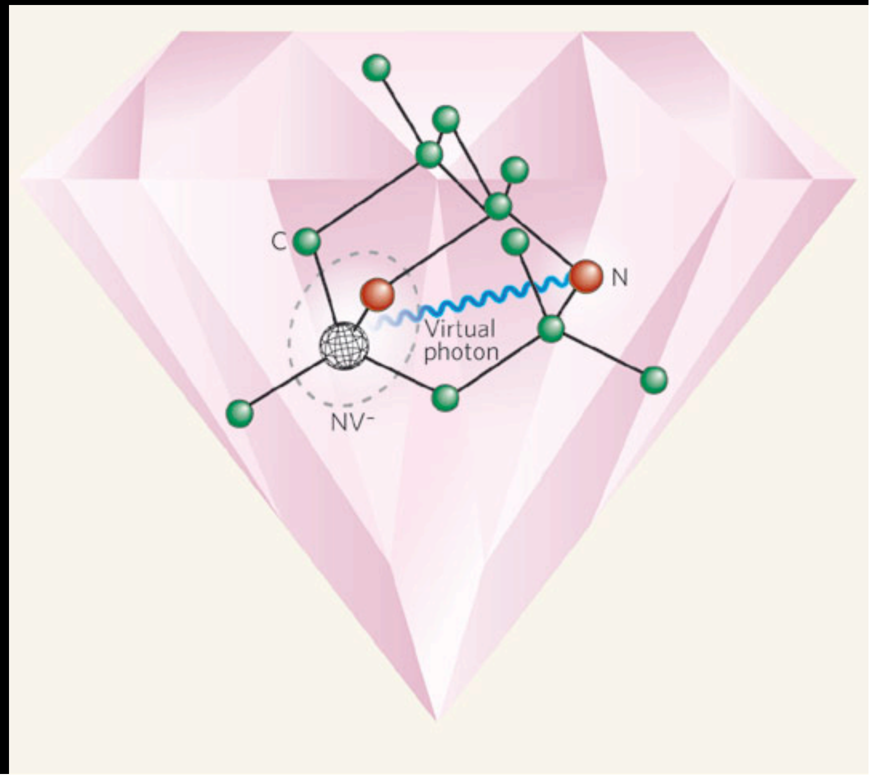
Quantum Communication

1. Photoluminescence
2. Polarised
3. Triggered
4. Photostable
5. Monochromatic (nm)
6. Short Lifetime (ns)

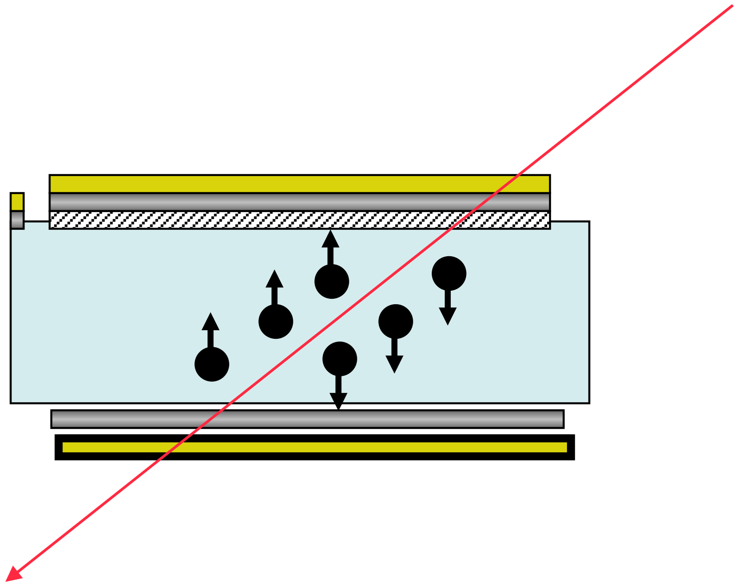
N-V

1. N-V, spin-encoded
2. $\tau \sim 58$ μs atomic → 20 hr nuclear
3. Single and two qubit gates
4. So far 5 states coupled

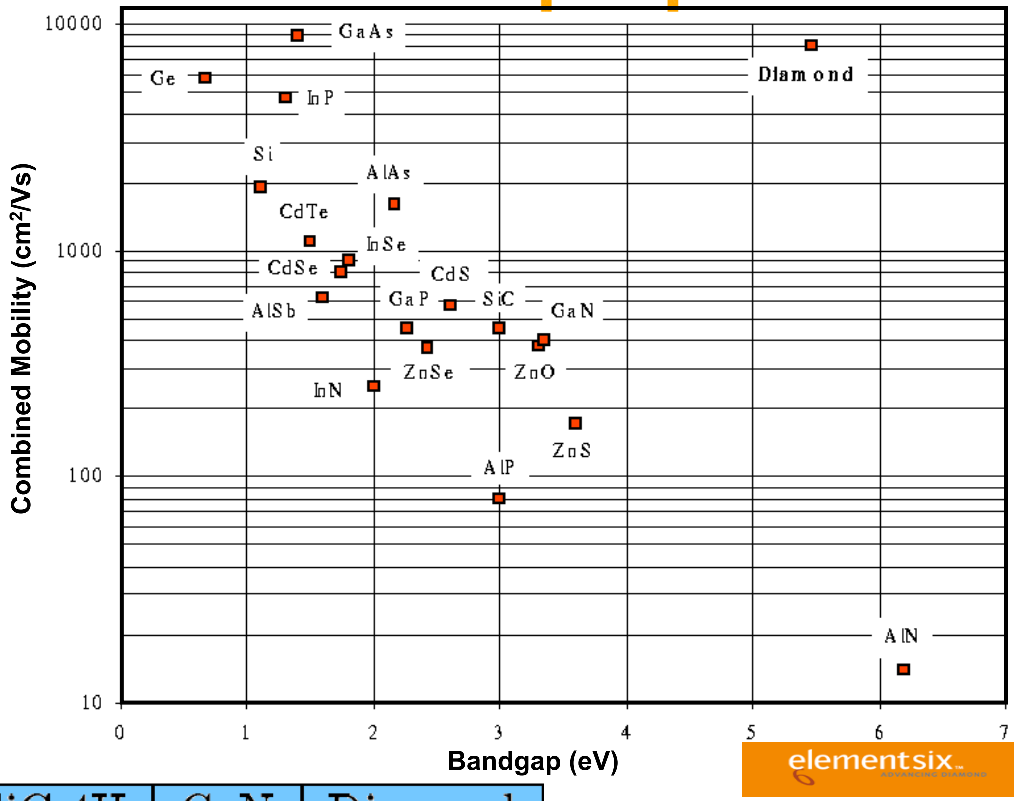




Diamond detectors



Diamond's unique position



Properties	Si	SiC-4H	GaN	Diamond
Band gap (eV)	1.1	3.2	3.44	5.5
Breakdown field (MV/cm)	0.3	3	5	10**
Electron mobility (cm^2/Vs)	1450	900	440	4500
Hole mobility (cm^2/Vs)	480	120	200	3800
Dielectric constant	11.7	9.7	8.9	5.68
Thermal conductivity (W/cmk)	1.5	5	1.3	24
Johnson's Figure of merit	1	410	280	8200
Keyes' Figure of merit	1	5.1	1.8	32
Baligas Figures of Merit	1	290	910	17200

Study

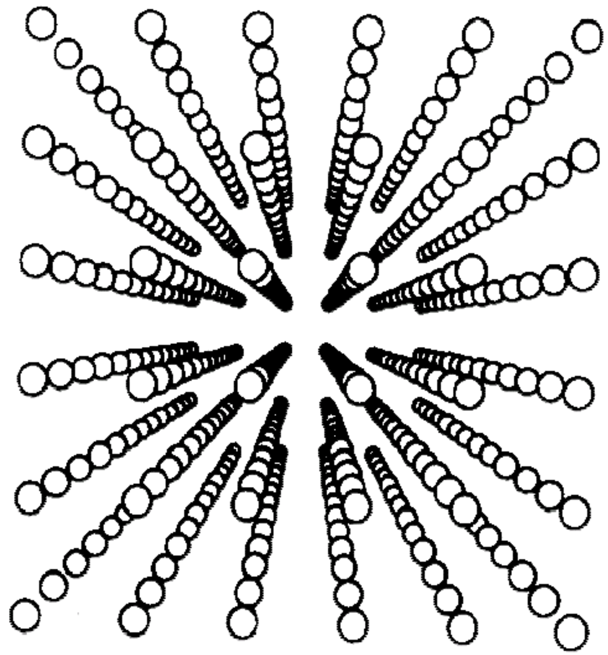
- Charge carrier dynamics
- Near surface defects
- Electrically active defects

High Energy Photon physics

Technology –

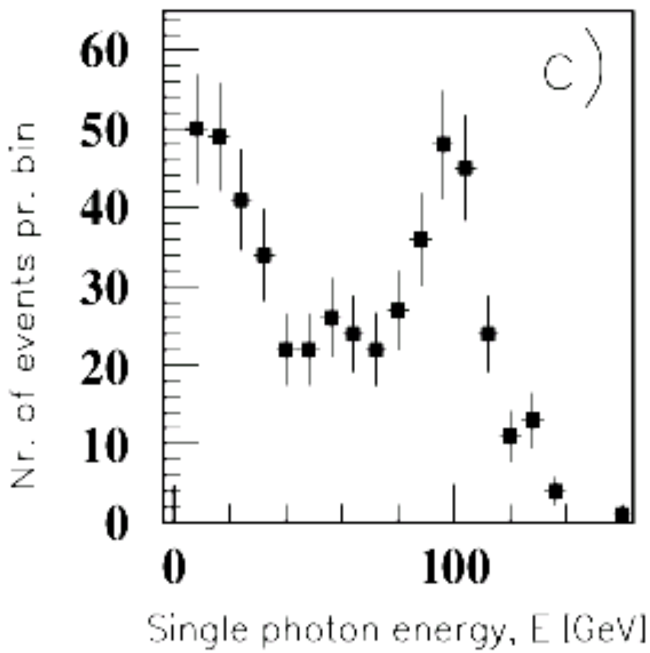
use aligned particle incidence on diamond to

1. Produce >100 GeV quasi-monochromatic photons
2. Manipulate polarisation
3. Measure polarisation



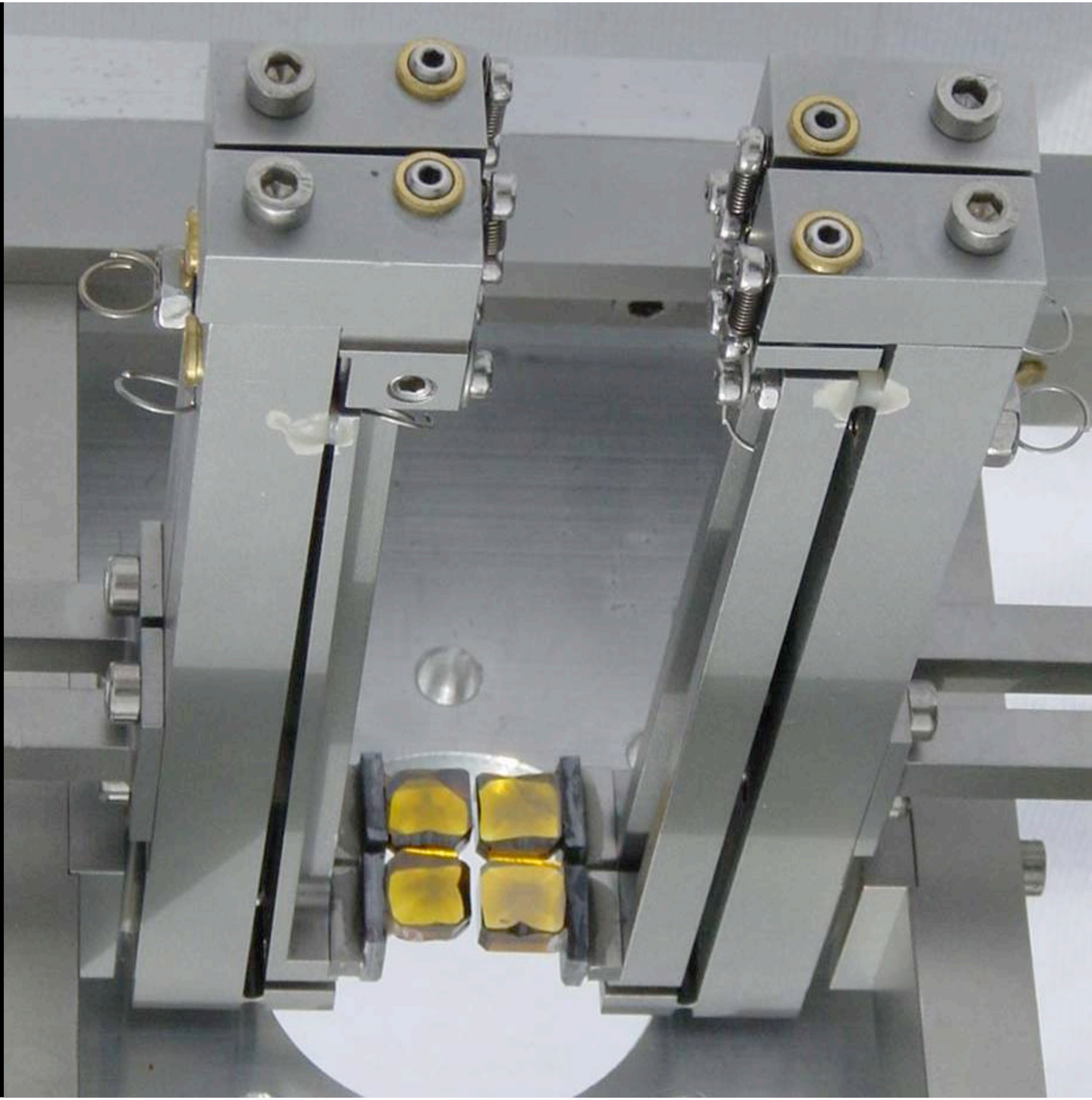
Physics (QED) -

1. Strong field effects (Lorentz boost)
2. Coherent enhancements



Polarised photons from Coherent Bremsstrahlung by 200 GeV electrons incident on aligned diamond → quasi monochromatic tagged photons

NA43
NA59
NA63



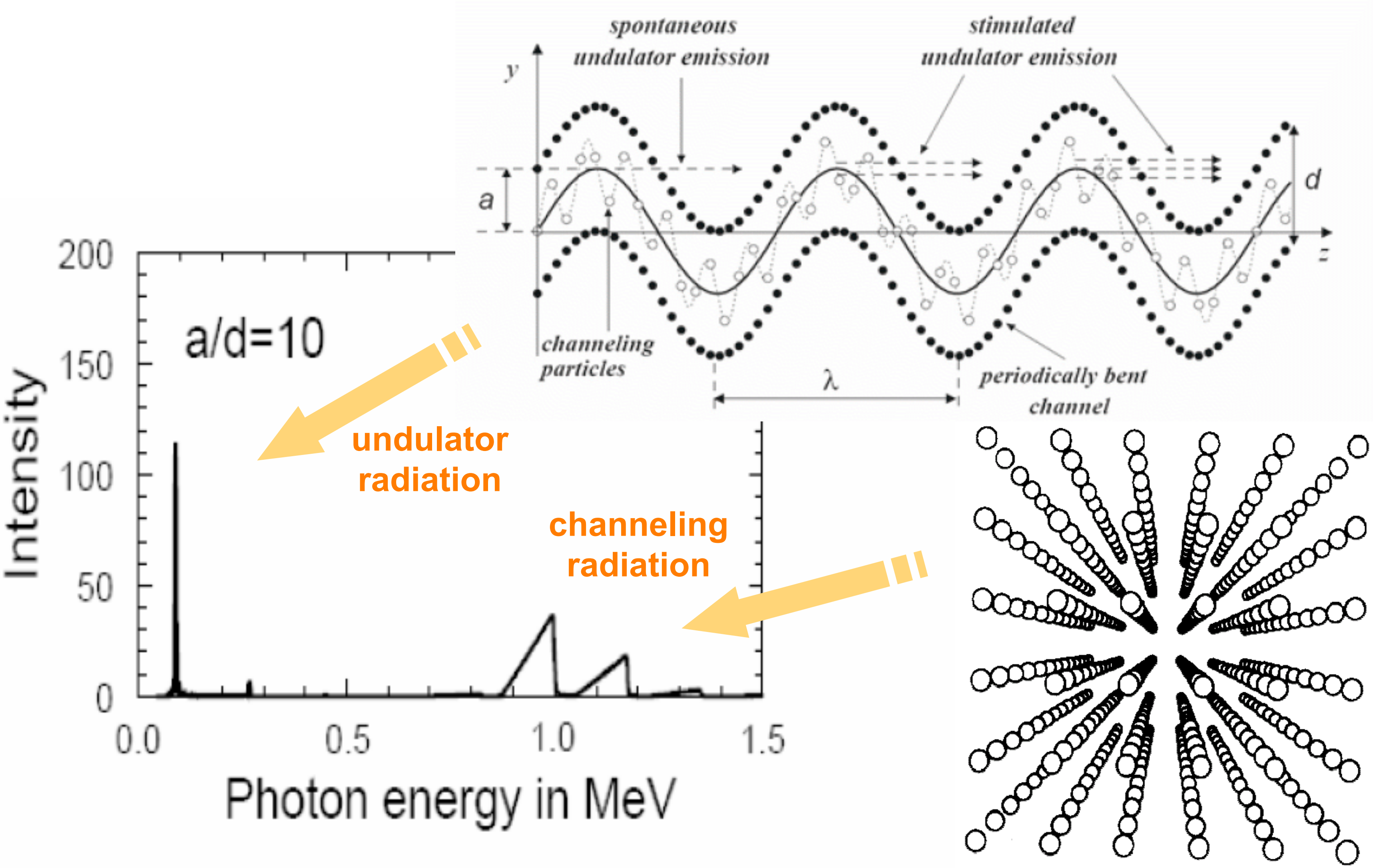
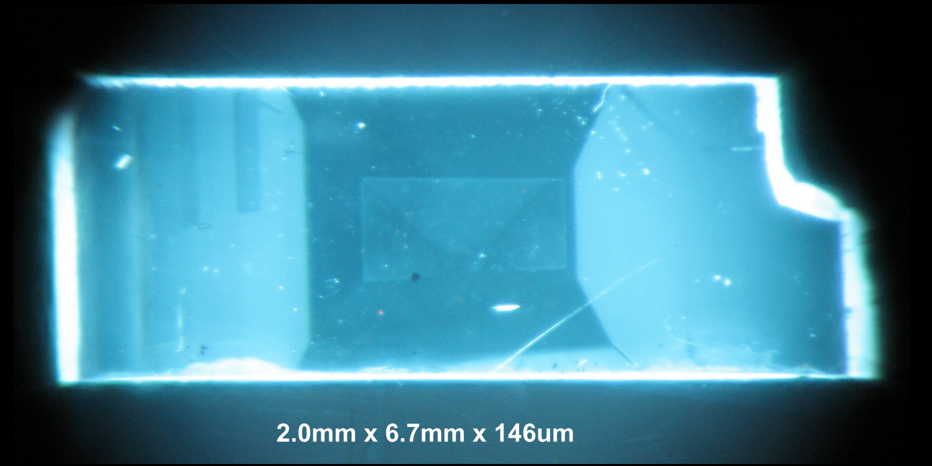


Fig. 2. Spectral distributions of the total radiation emitted in forward direction for $\varepsilon = 500$ MeV positrons channeling in Si along the (1 1 0) crystallographic planes for $a/d = 10$.

Krause et al. NIM A 482 (2002) 455-460

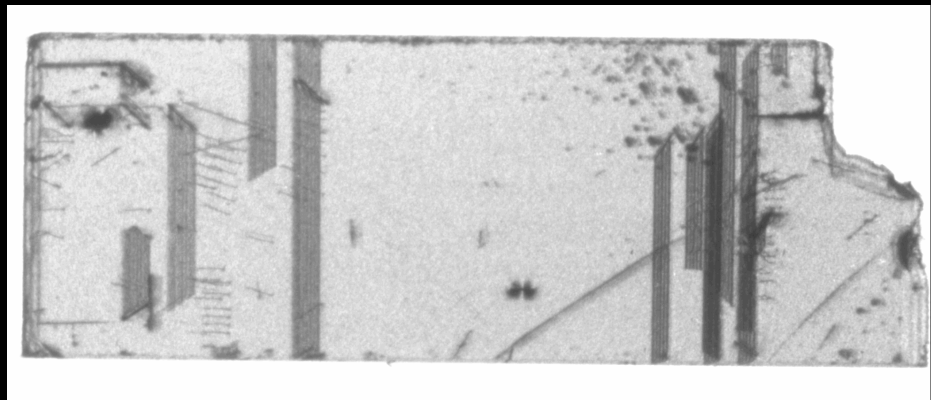


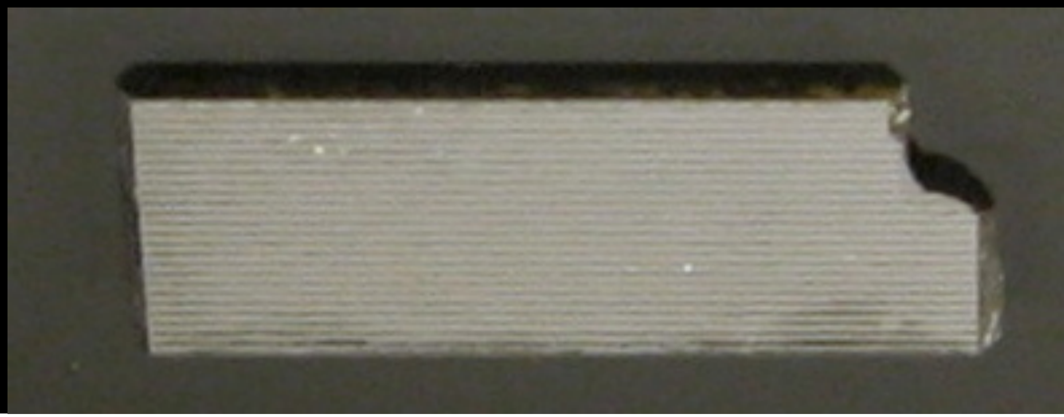
CL image

WB Topo

220 reflection

14 keV



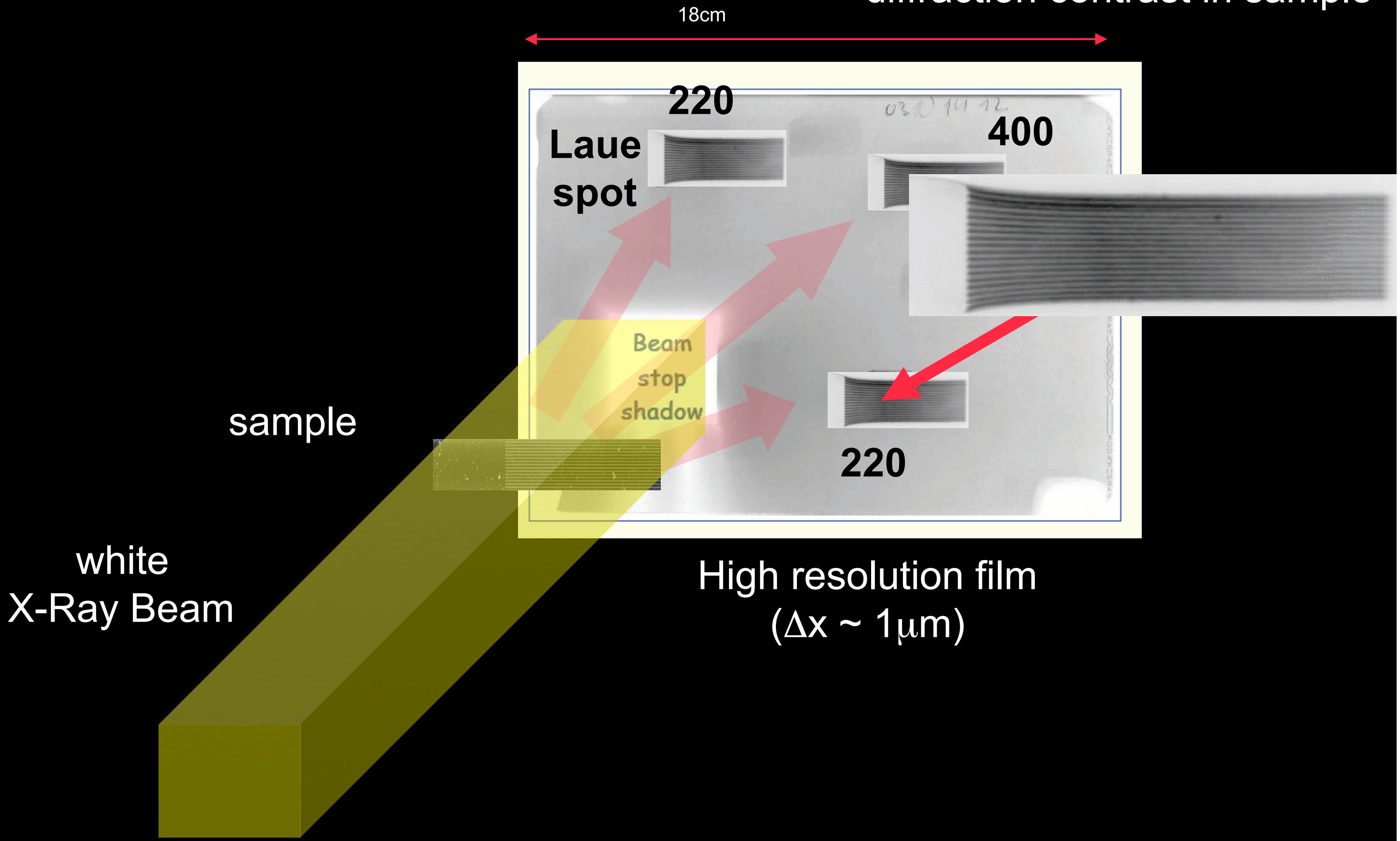


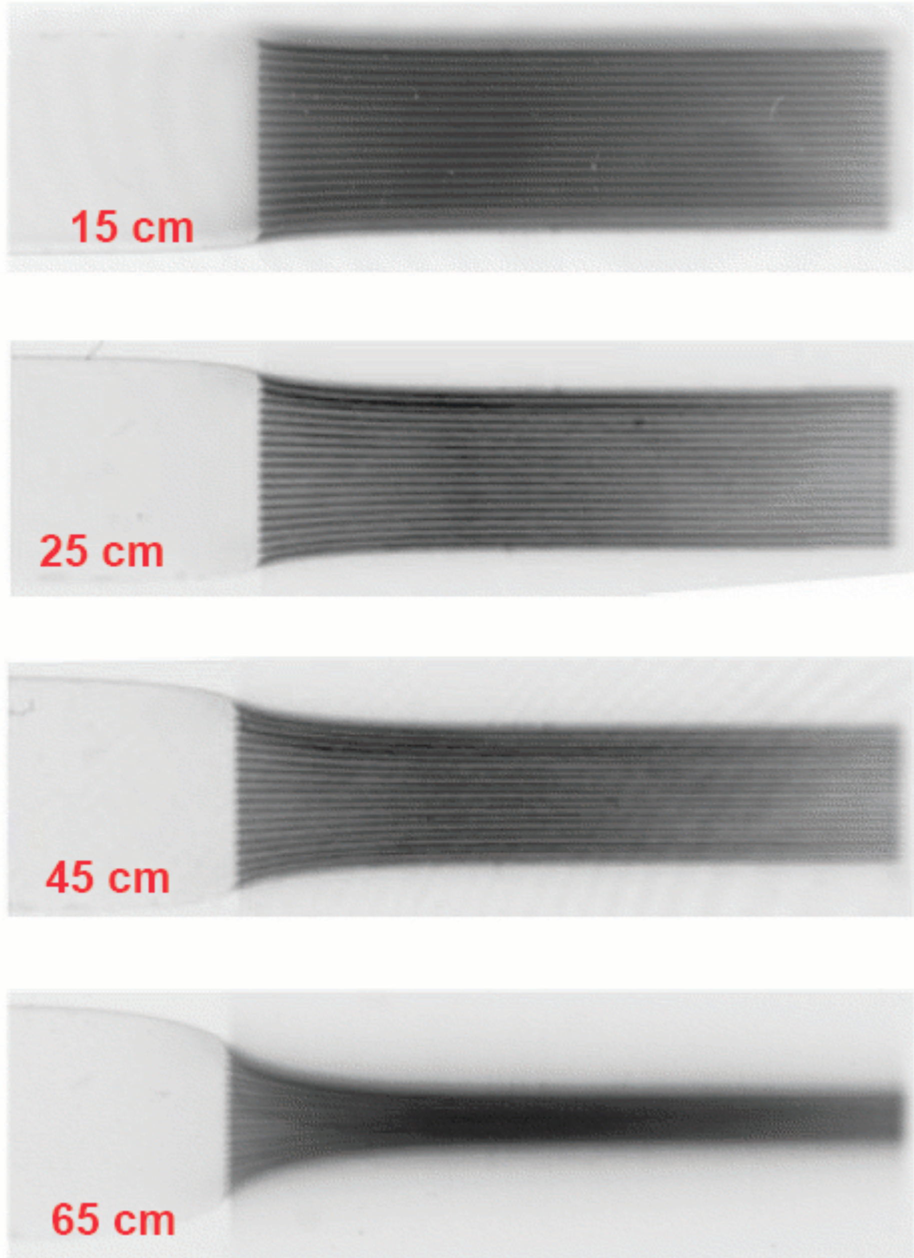
With laser trenches

White Beam Topography

Transmission (Laue) geometry

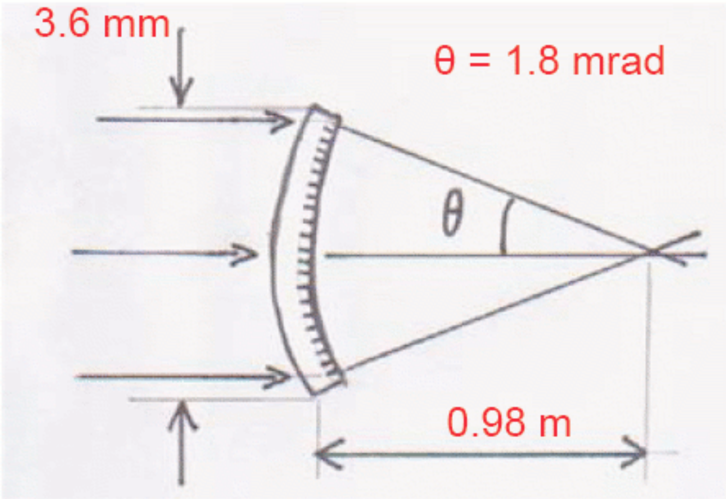
Each Laue spot is a topographic image of diffraction contrast in sample

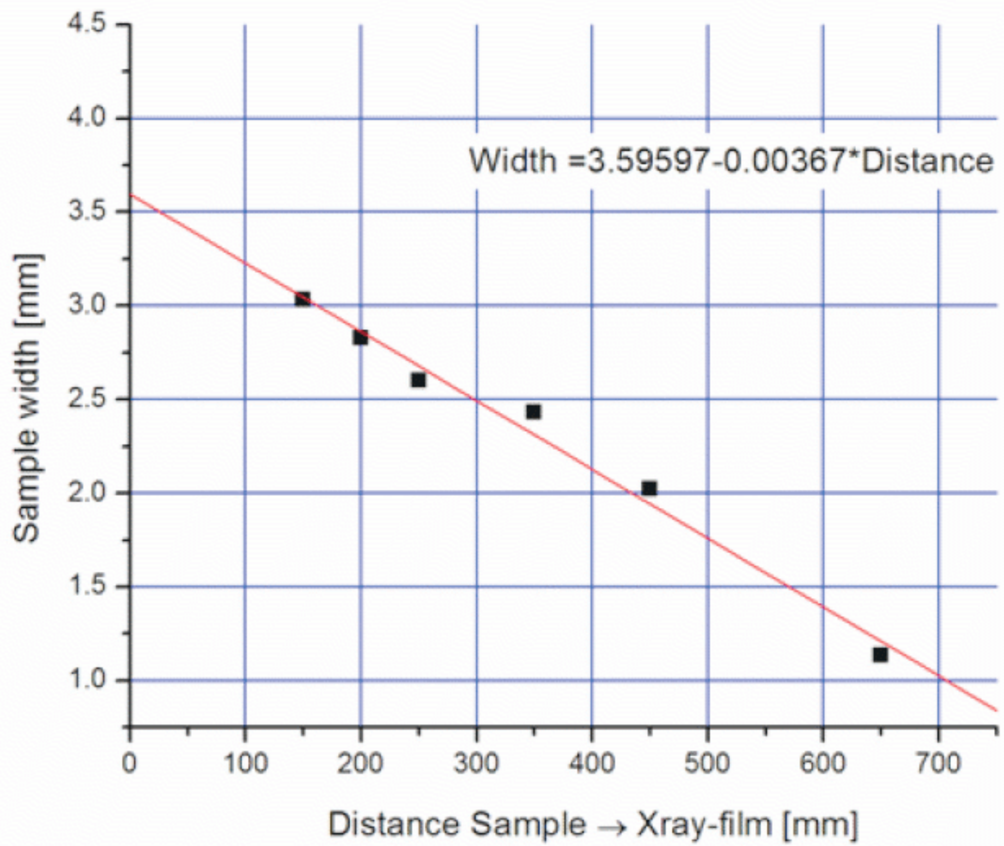



15 cm
25 cm
45 cm
65 cm

Focussing in vertical plane

Bending across crystal corresponds to:
1 mrad/mm crystal!





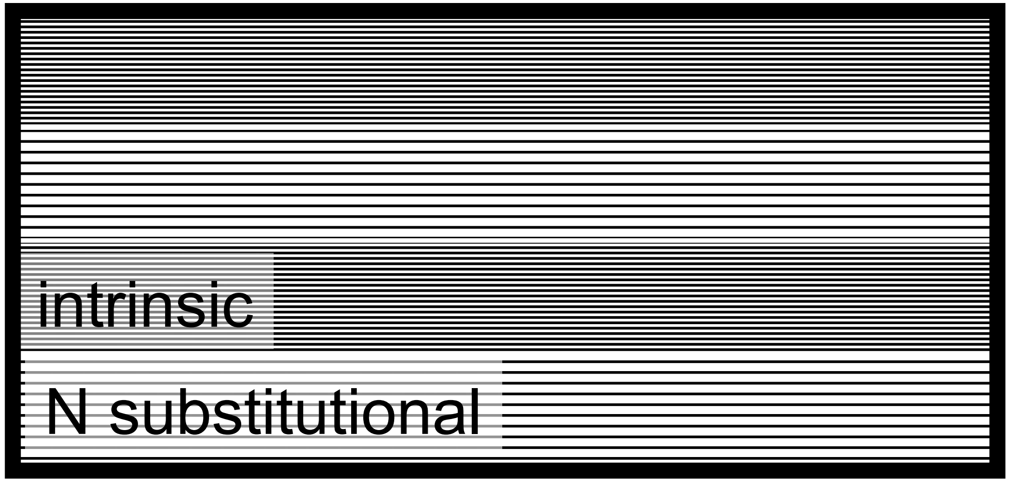
Diamond Superlattice

Lang Dilatation Formula

Doping with nitrogen → expands the lattice

$$\frac{\Delta a}{a_0} = 0.116 \pm 0.02 \times C_N$$

← C_N in ppm



KEY PHYSICAL PARAMETERS:
Undulator wavelength = λ_u (≈ 0.1 mm)
Undulator amplitude = a (≈ 50 Å)
Interplanar distance = d (≈ 1-2 Å)
Crystal thickness = t (≈ 1-4 mm)
Number of undulator oscillations = $N_u = t/\lambda_u$ (> 10)

Conclusions

Showed improvements in diamond targets to eff misorientation of few 10^{-8}

Acknowledgements

J Härtwig, P Van Vaerenbergh, F Masiello

U Uggerhøj (Århus) and the CRYSTAL collaboration

R Burns, JO Hansen
And Hansen Future Materials