Basic concepts of X-ray scattering and prospects

XTOP 2024 - High Resolution X-ray Diffraction and Imaging, Carry-le-Rouet, France, 18 March 2024

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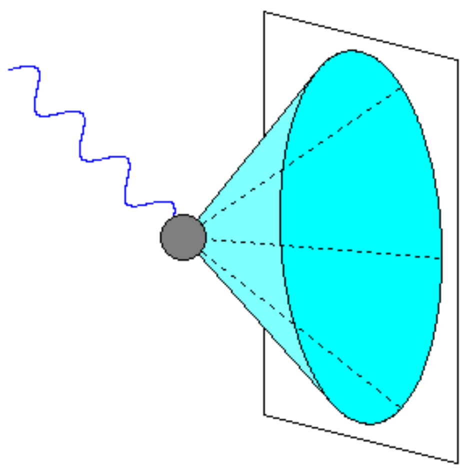
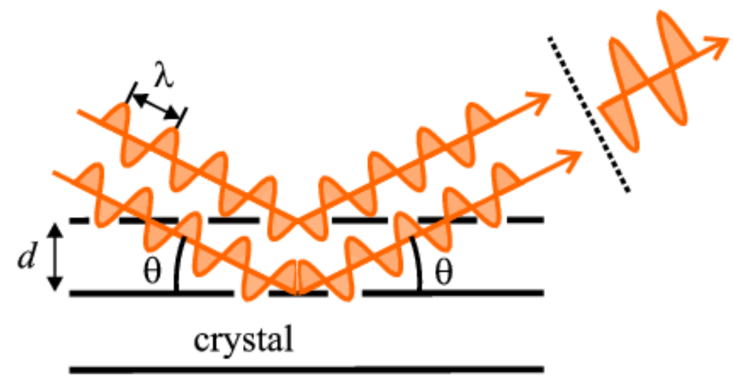
Tutorial Outline

- Powder diffraction methods “XRD”
- Williamson-Hall analysis of size and strain
- Surface diffraction and surface structure
- Extension to Coherent X-ray Diffraction
- XFEL study of thin film melting

X-ray Scattering vs Diffraction

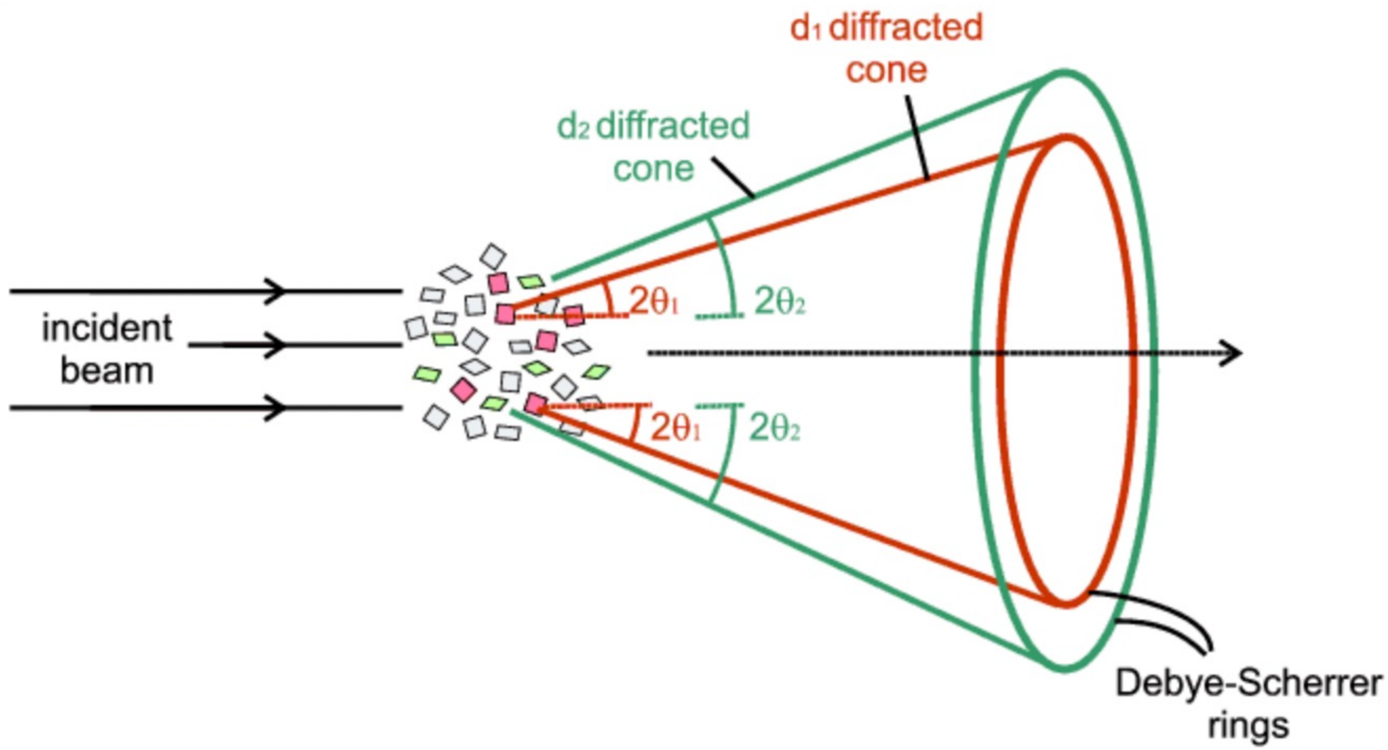




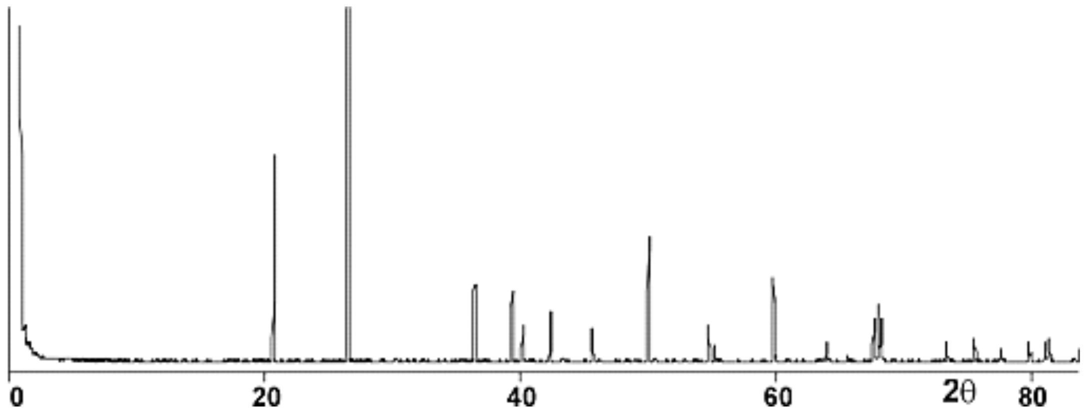
$2d \sin \theta = \lambda$

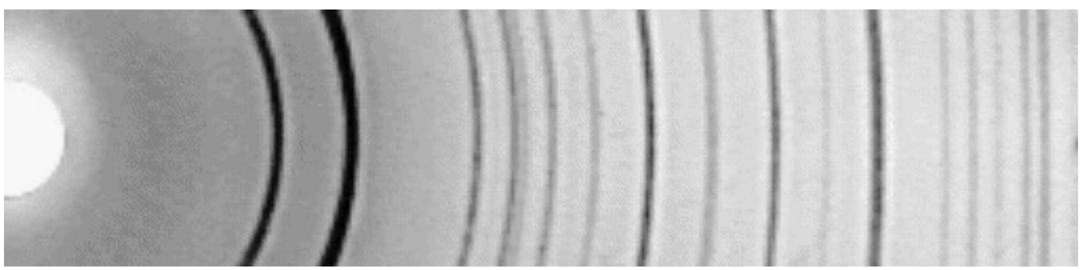
Bragg law

Powder diffraction

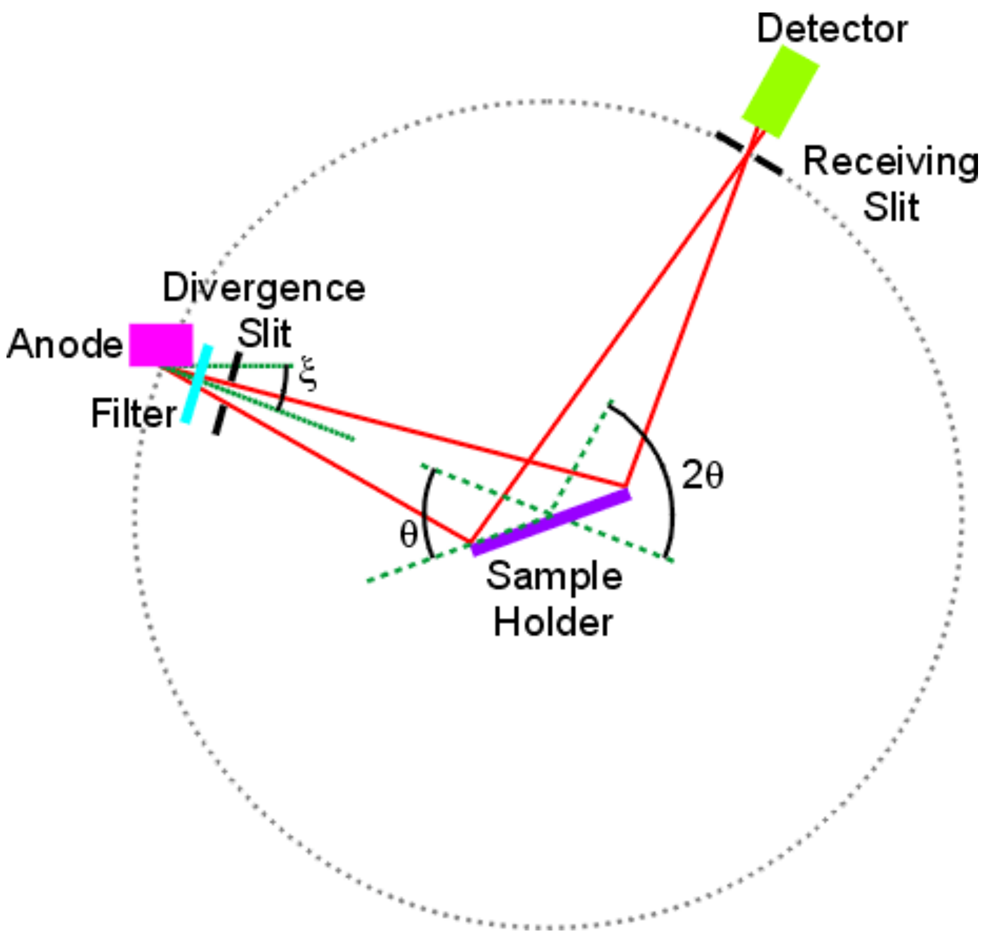


Quartz powder pattern

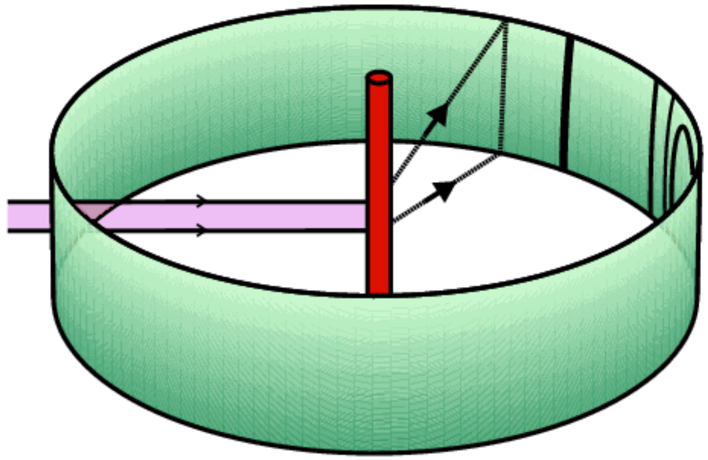


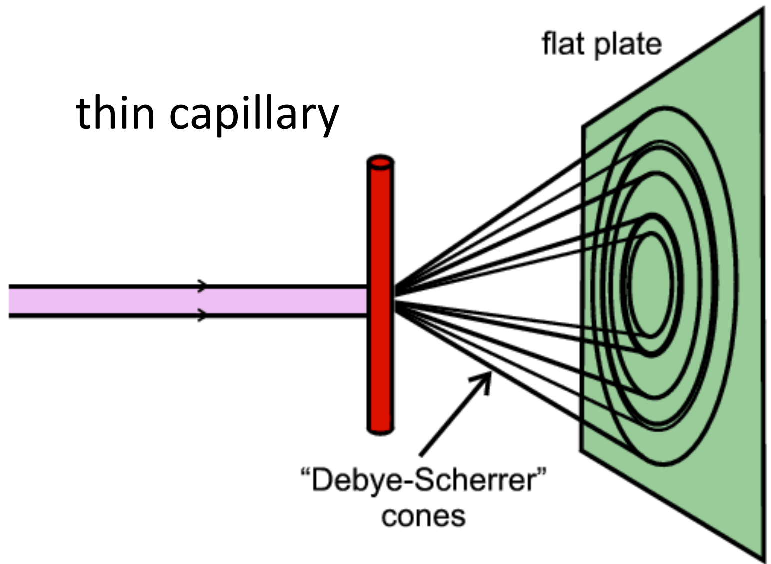


Bragg-Brentano geometry

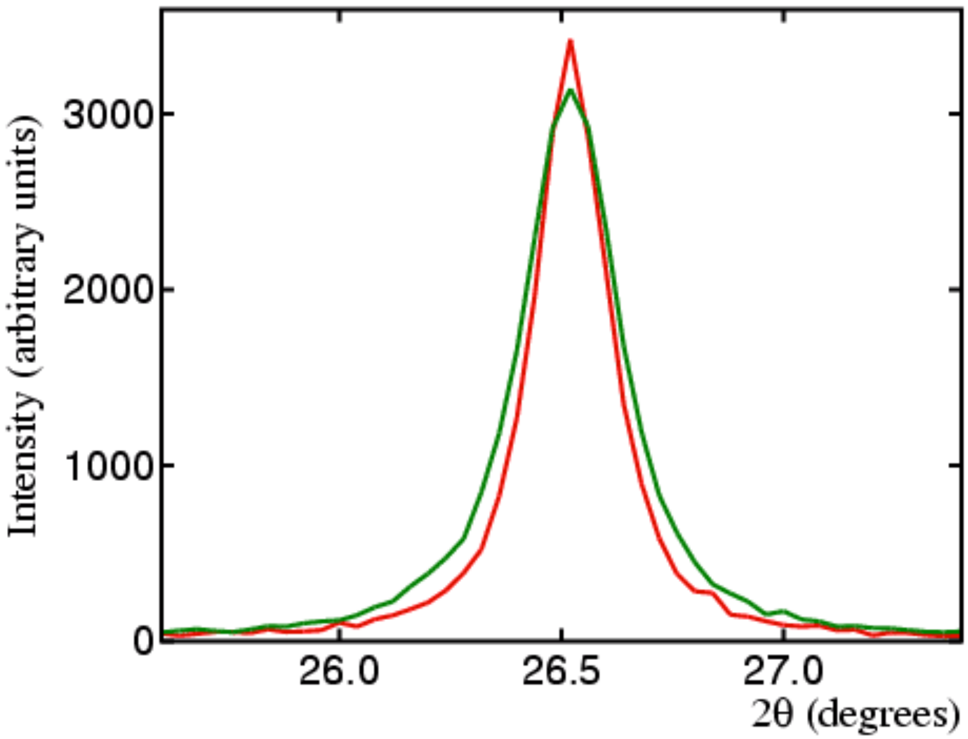


Debye Scherrer method





Size effect on lineshape

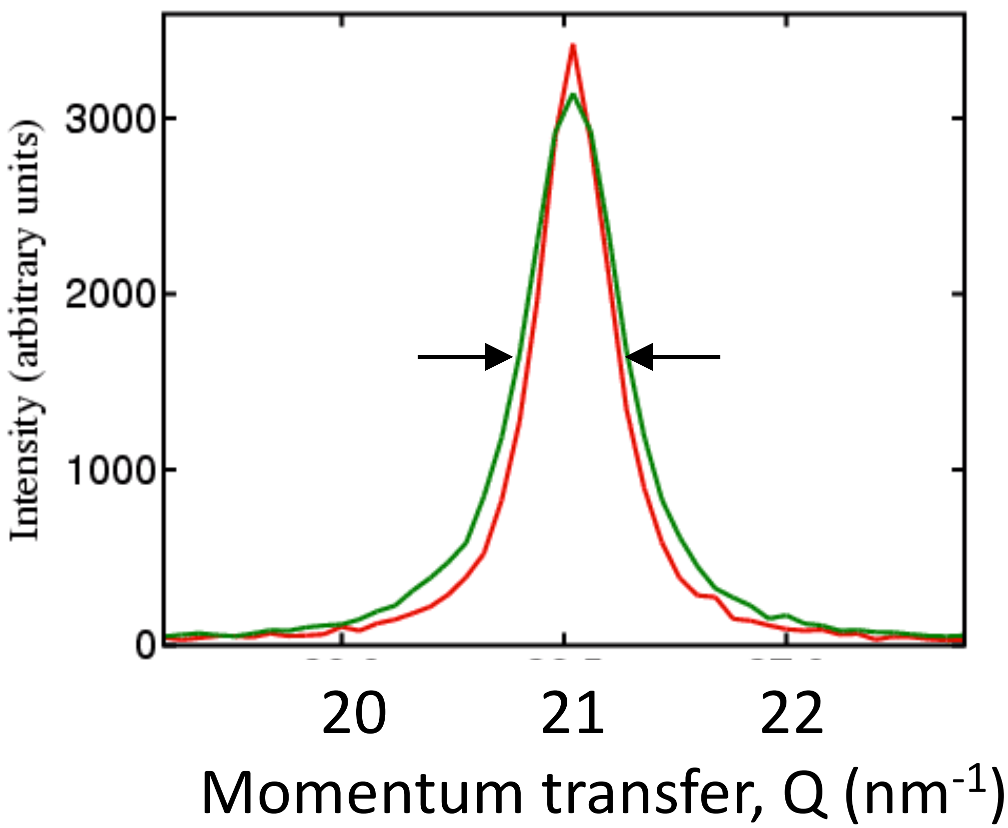


The Scherrer equation

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

τ = crystal size (nm)
λ = wavelength (nm)
β = full width half max (rad)
θ = Bragg angle
K = Scherrer shape factor
= 0.94 for spheres

“Physics” Notation may be Simpler



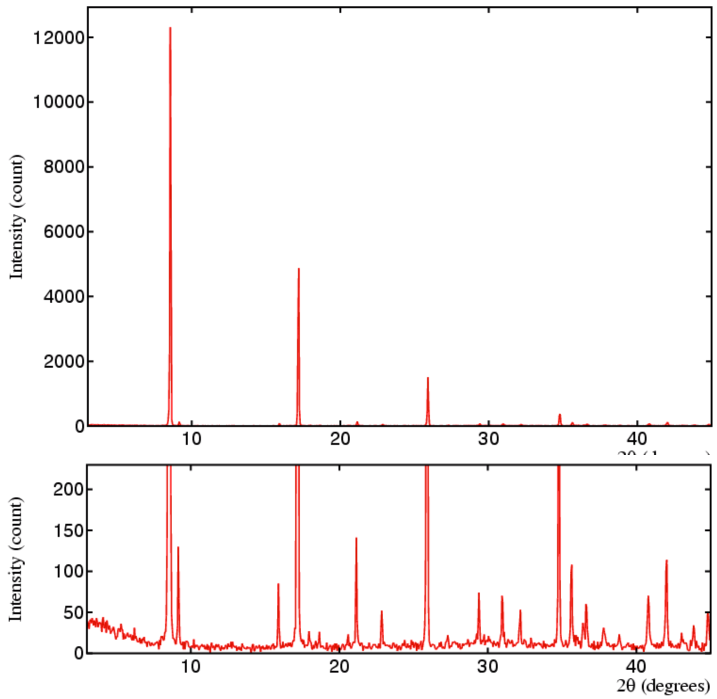
$Q = k_f - k_i$
$= 4\pi/\lambda \sin\theta$

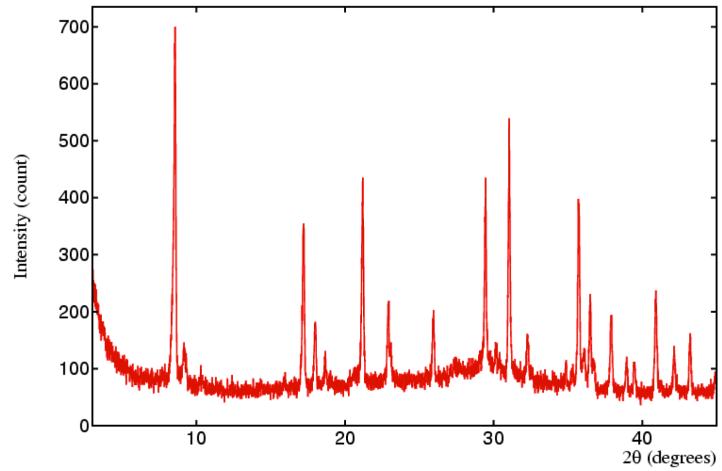
$\tau = 2\pi / \Delta Q$

τ = crystal size (nm)
λ = wavelength (nm)
θ = Bragg angle
ΔQ = full width half max

Preferred orientation = texture

hydrated cement phase $Ca_4Al_2(SO_4)O_6.16H_2O$





left: flat plate holder
right: capillary holder

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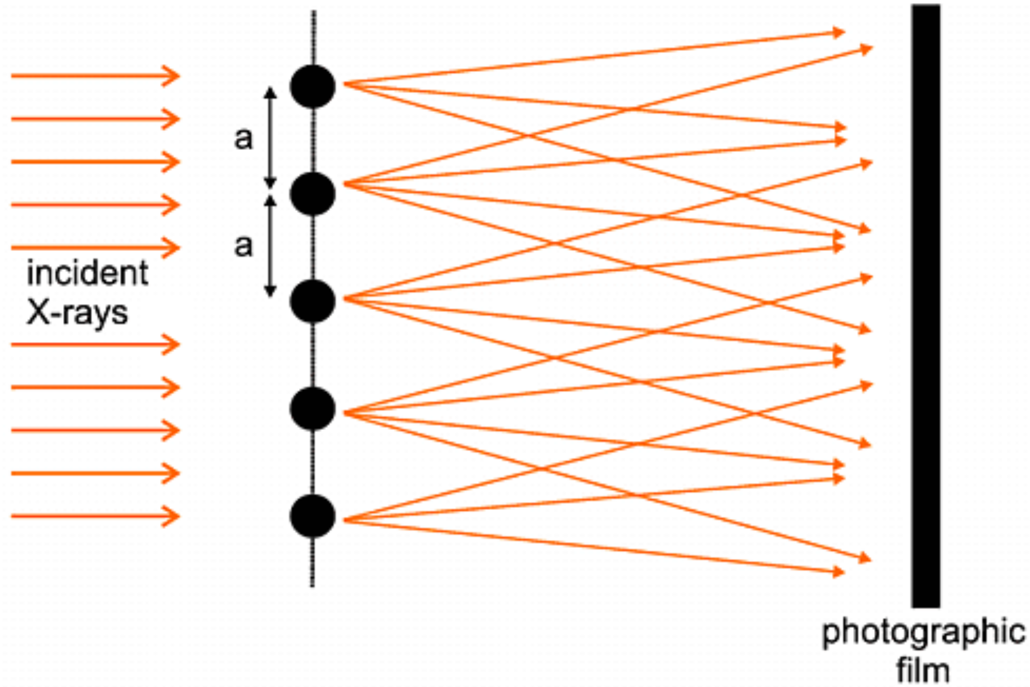
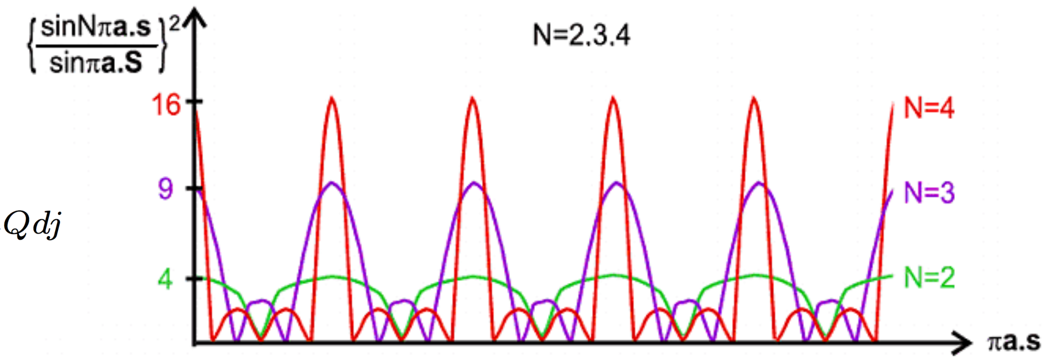
Scattering from array of unit cells

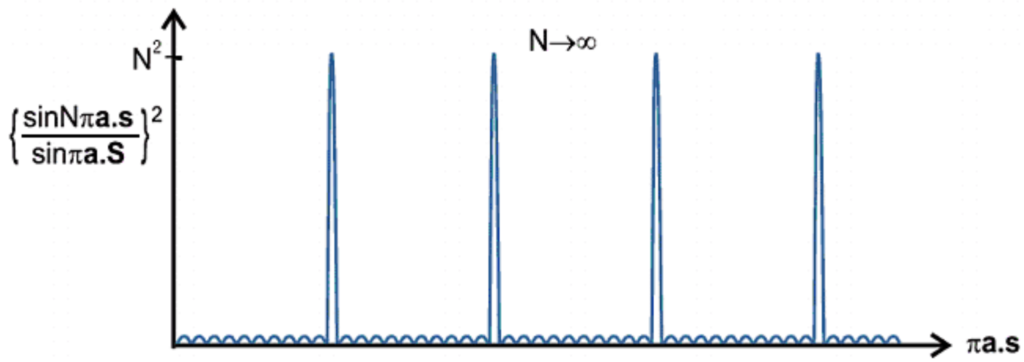


Interference sum over unit cells

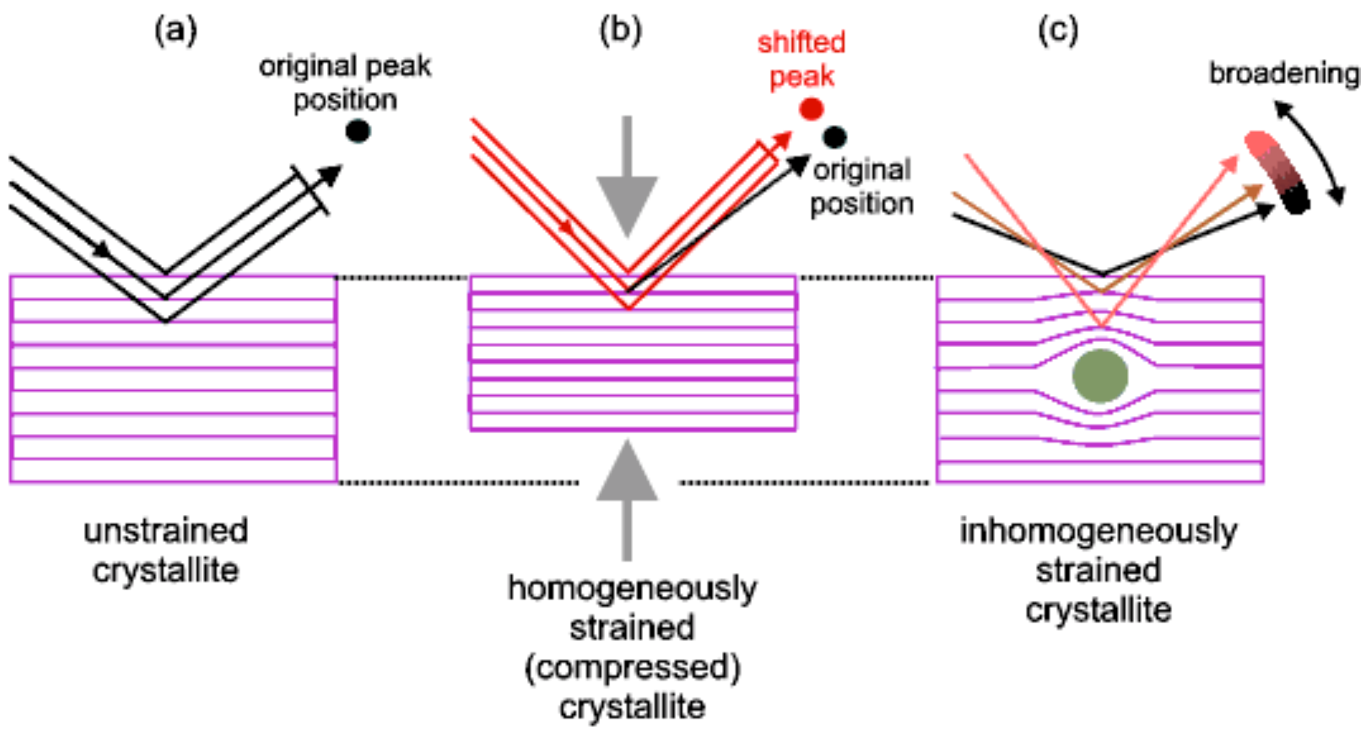
$$R_N(Q) = A \sum_{j=0}^{N-1} e^{iQdj}$$

$$= A \frac{1 - e^{iQdN}}{1 - e^{iQd}}$$





Effect of Strain on Diffraction



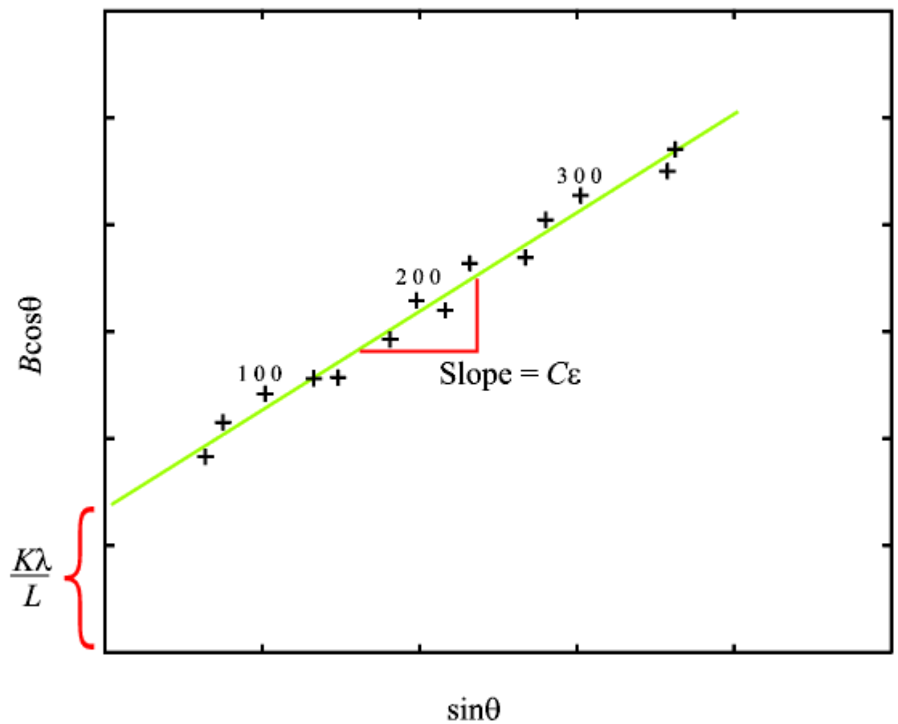
G.K.Williamson and W.H.Hall
Acta Metall. 1, 22-31 (1953)

Scherrer equation

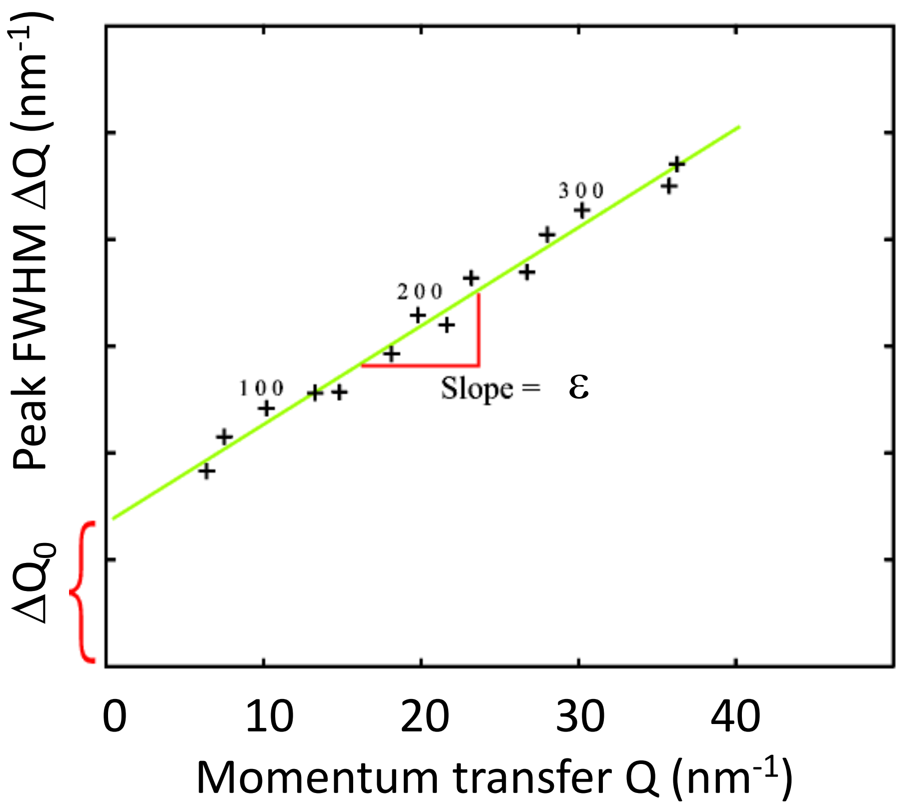
$$\beta_L = \frac{\mathbf{K}\lambda}{L\cos\theta}$$

$$\beta_e = \mathbf{C}\varepsilon \tan\theta$$

$$\beta_{tot} = \beta_e + \beta_L = \mathbf{C}\varepsilon \tan\theta + \frac{\mathbf{K}\lambda}{L\cos\theta}$$



W-H Size-Strain in "Physics" Notation



4

$Q = k_f - k_i$
$= 4\pi/\lambda \sin\theta$

$\tau = 2\pi / \Delta Q_0$ = size

τ = crystal size (nm)
λ = wavelength (nm)
θ = Bragg angle
ΔQ = full width half max

$\varepsilon = \delta d/d$ = "microstrain"
= range of local strains

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First UHV Experiments (1981)

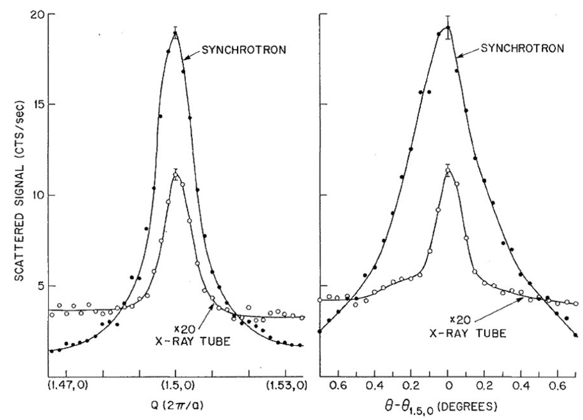
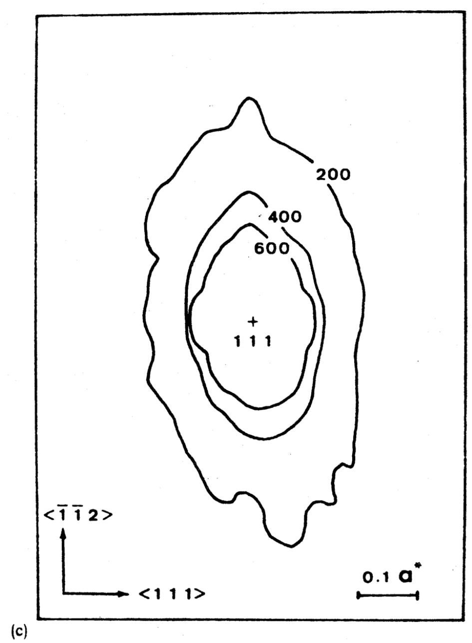


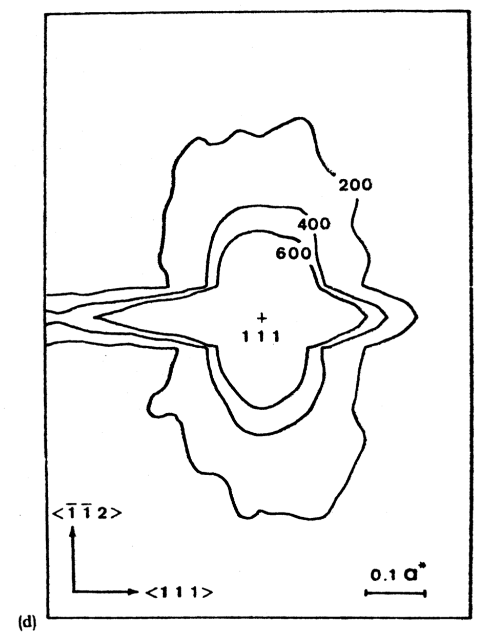
FIG. 1. A plot of the $(\frac{3}{2}, 0)$ Bragg reflection as a function of the momentum transfer $Q(2\pi/a)$ and the crystal's mosaic spread (deg).

P. Eisenberger and W. C. Marra,
PRL **46** 1081 (1981)
experiments done at SSRL

Diffuse Scattering from Si Wafer



Unpolished wafer



40 microns removed

N. Kashiwagara, J. Harada and M. Ogino, J. Appl. Phys 54 2706 (1983)

Scattering of X-rays From Crystal Surfaces

S. R. Andrews and R. A. Cowley JPCM **18** 6427 (1985)

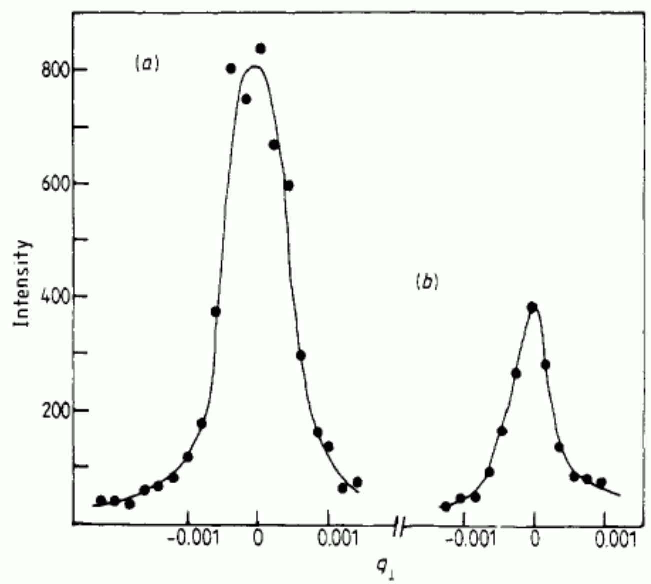


Figure 1. The intensity of scattering, as a function of q, (*a*) for $\boldsymbol{Q} = (0, 0, 4.005)$ (vertical scale in counts per 2 s) and (*b*) $\boldsymbol{Q} = (0, 0, 4.025)$ (vertical scale in counts per 300 s) in the GaAs sample with an (001) surface corresponding to figure 2, curve B.

Diffraction as a Surface Integral

Die äußere Form der Kristalle in ihrem Einfluß auf die Interferenzerscheinungen an Raumgittern

Von M. v. Laue

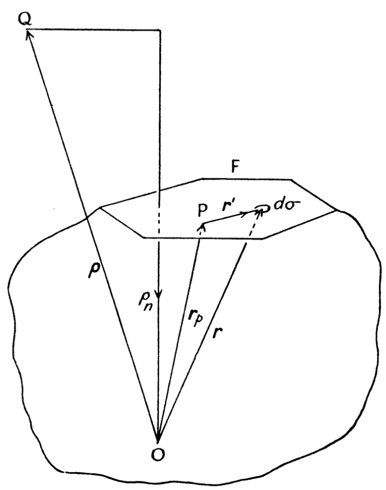
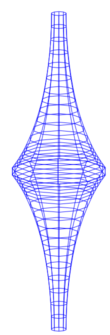


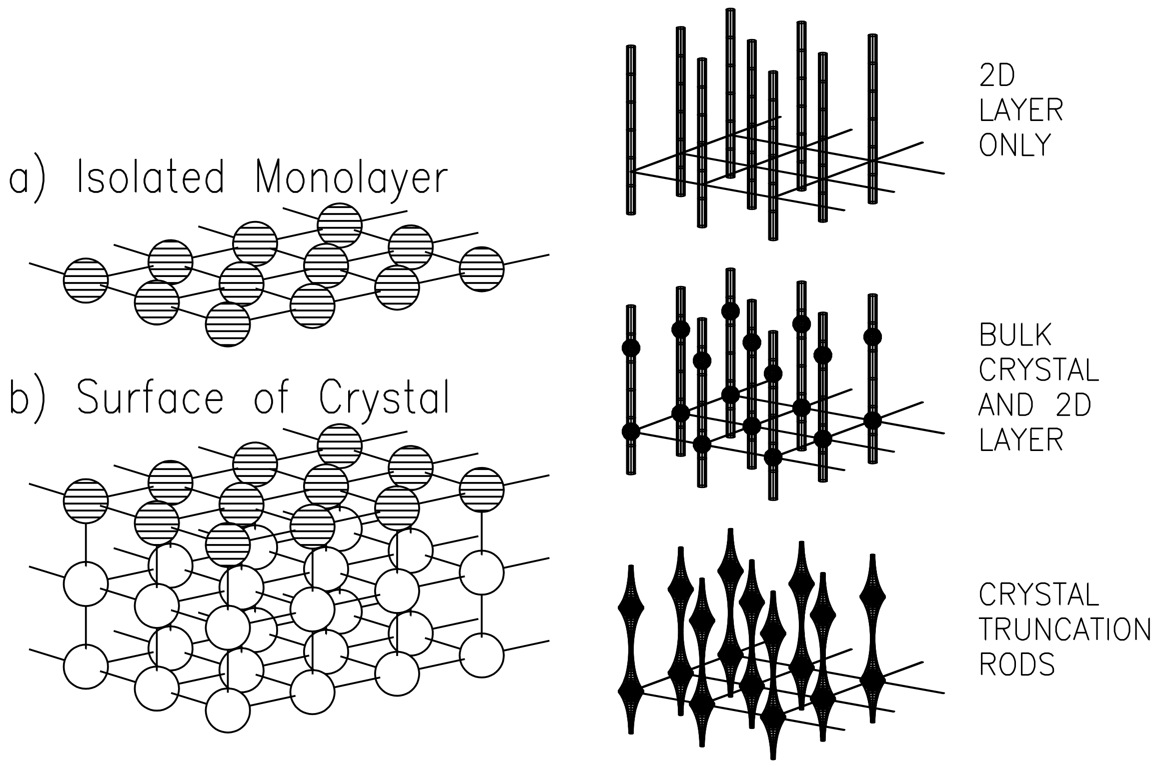
FIG. 200

Annalen der Physik [5] 26 55 (1936)

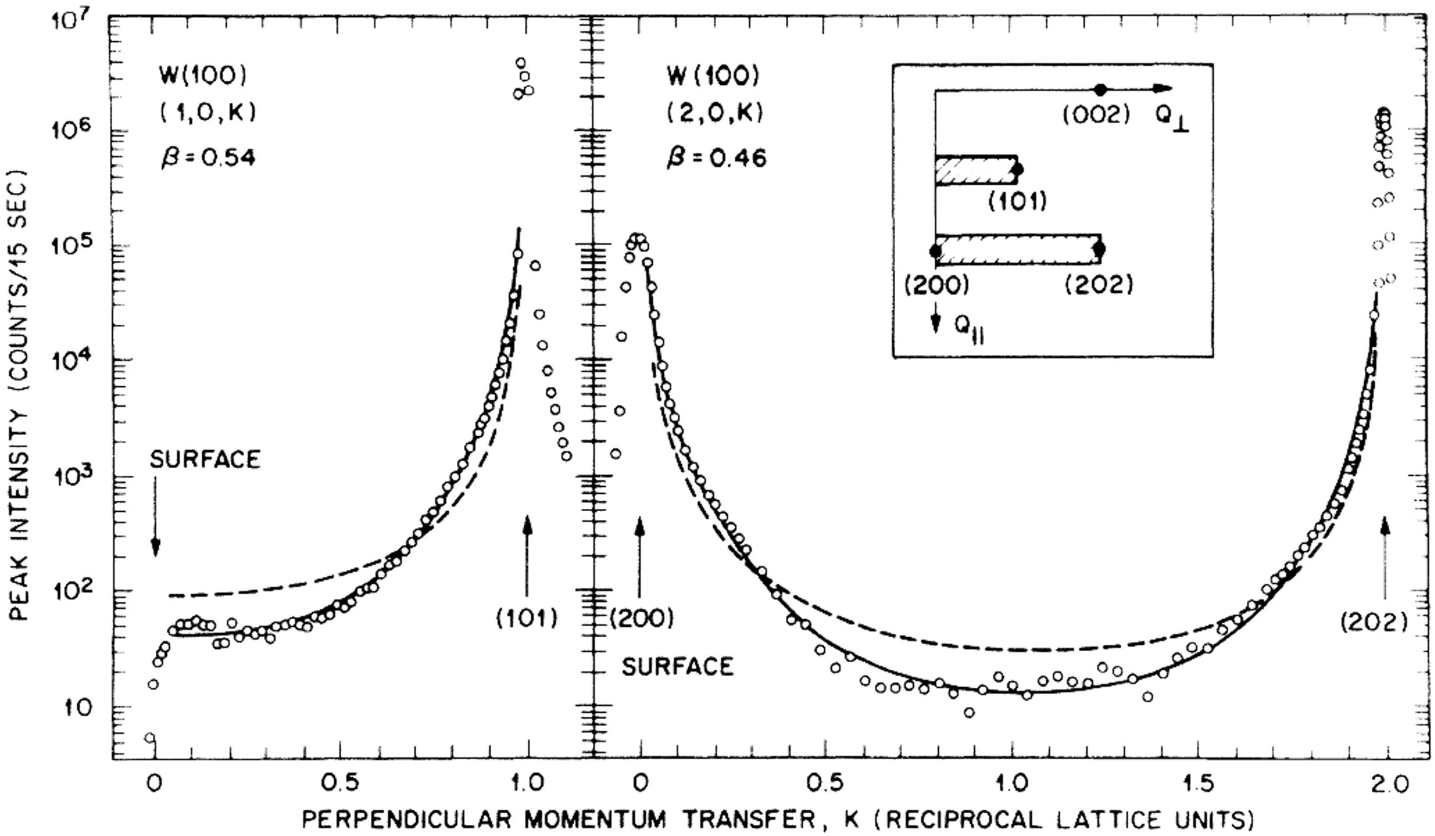


"Stacheln"

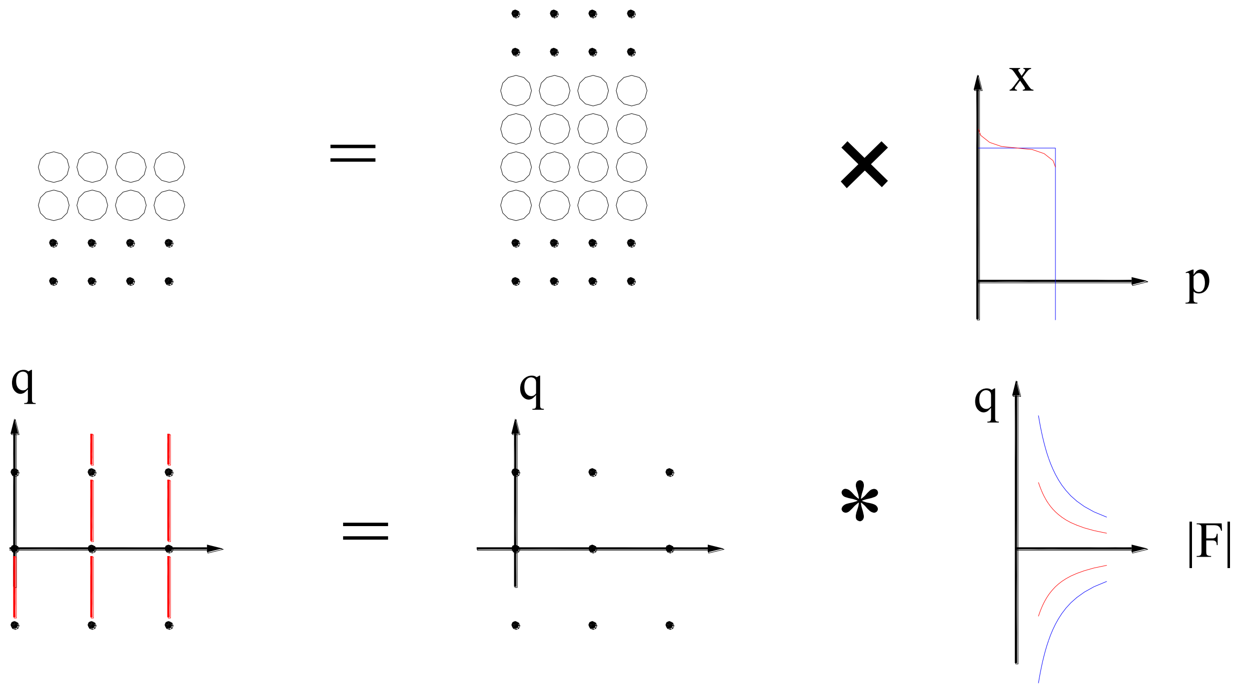
Crystal Truncation Rods (1986)



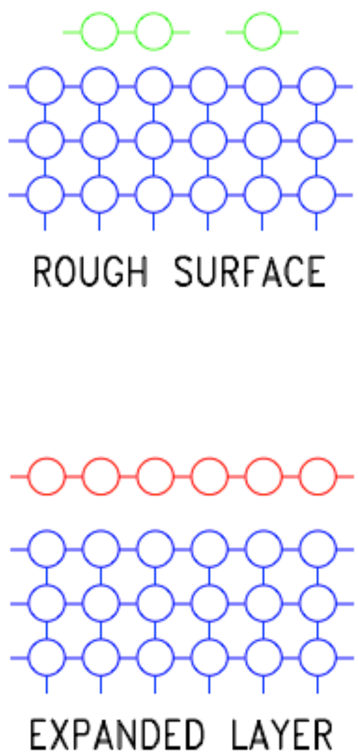
CRYSTAL TRUNCATION RODS AND SURFACE ROUGHNESS

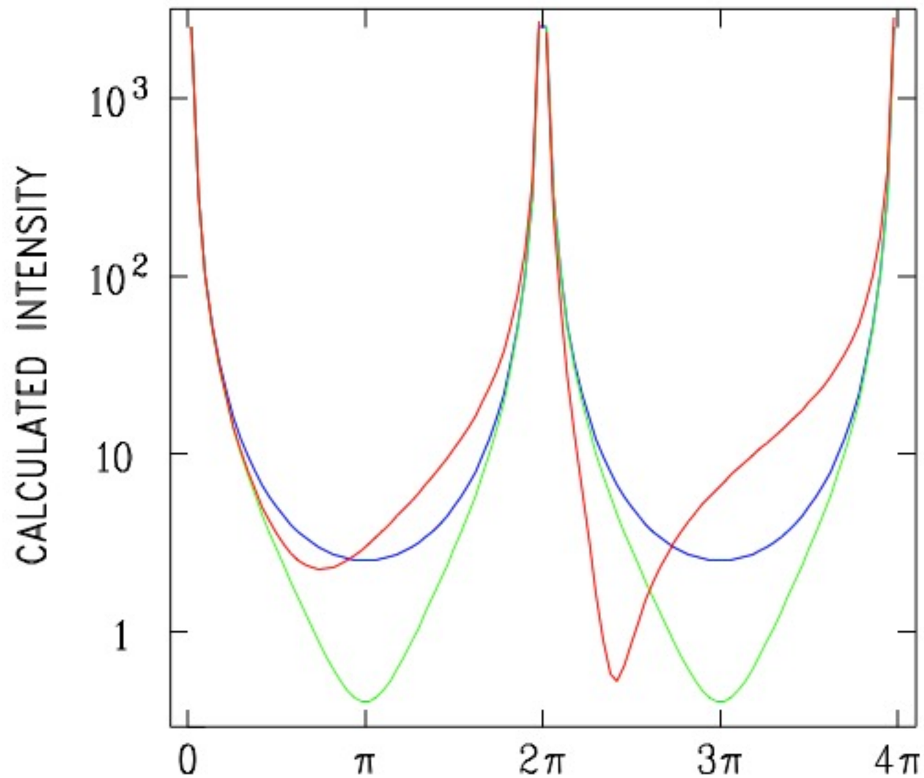


CTR as Convolution

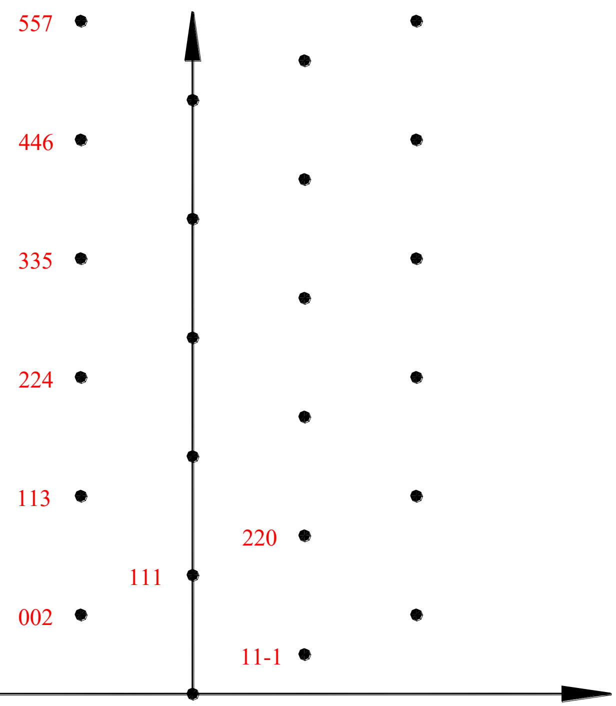


CTR is Sensitive to Surface Structure

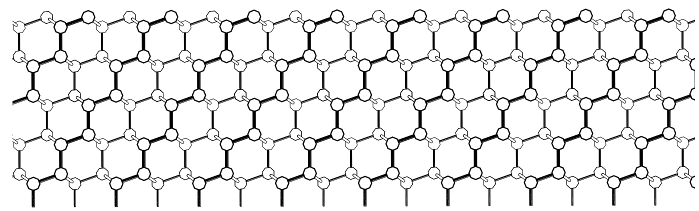


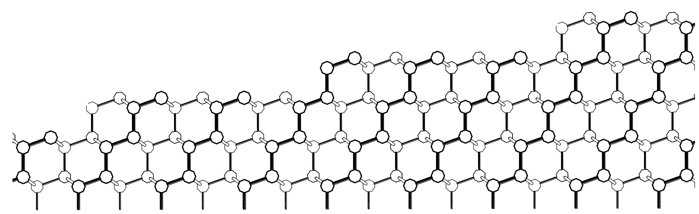


Crystallography of Stepped Surfaces



Silicon (111)

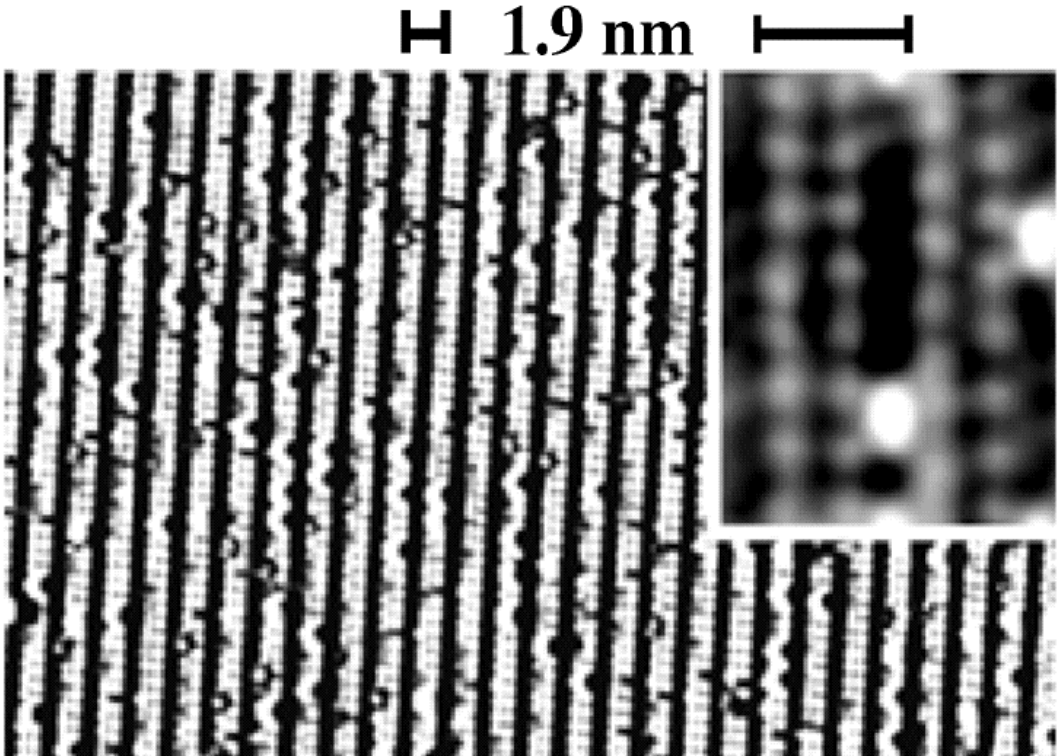


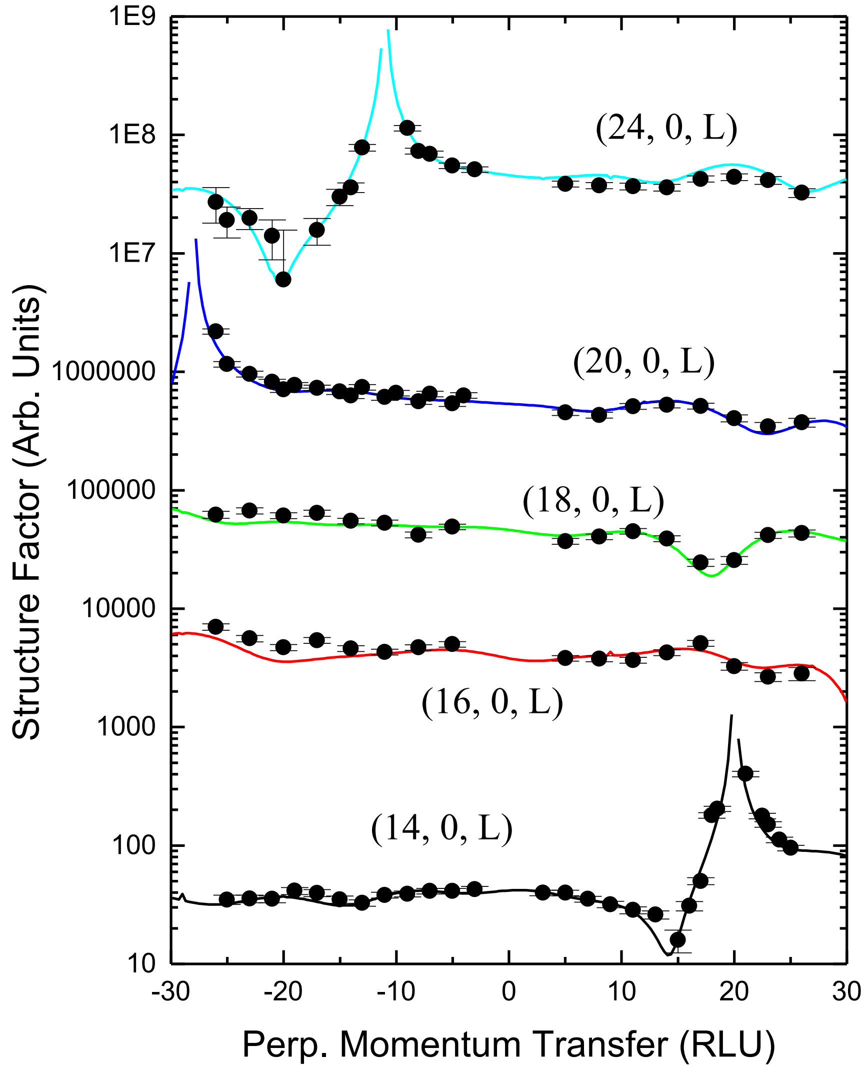


Si(557) surface

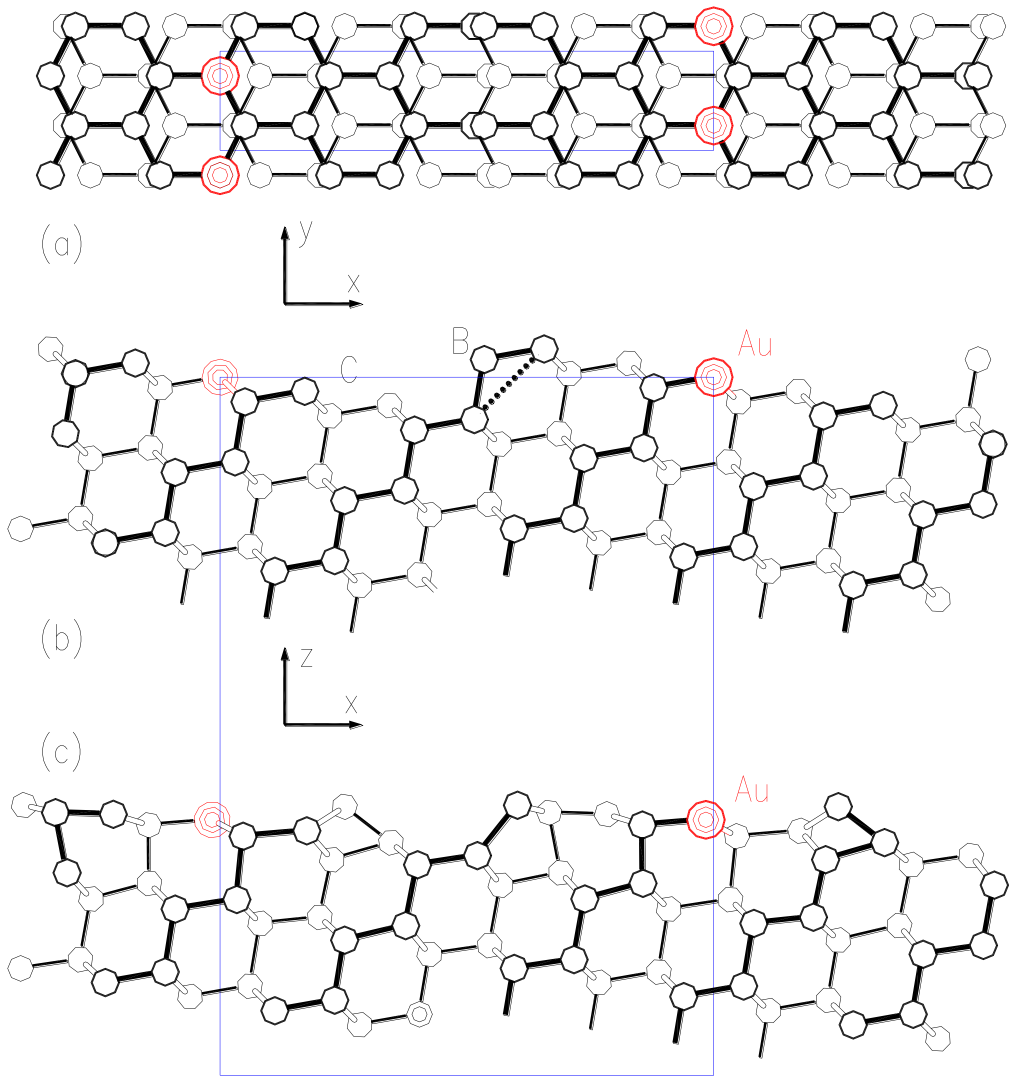
Si(557) coated with Au

R. Losio, et. al., Phys. Rev. Lett. 86 4632 (2001)

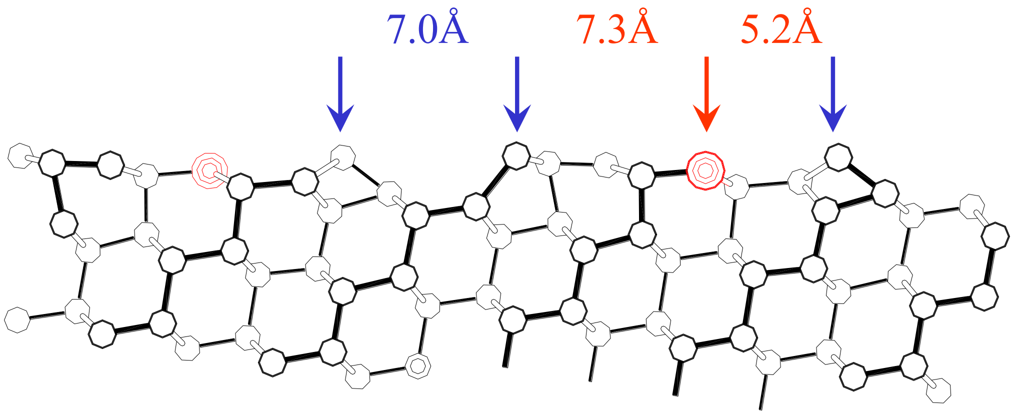


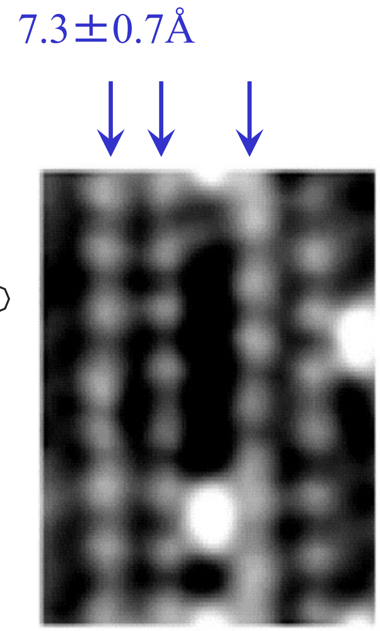


1E9
1E8
1E7
1000000
100000
10000
1000
100
10
Structure Factor (Arb. Units)
(24, 0, L)
(20, 0, L)
(18, 0, L)
(16, 0, L)
(14, 0, L)
-30
-20
-10
0
10
20
30
Perp. Momentum Transfer (RLU)

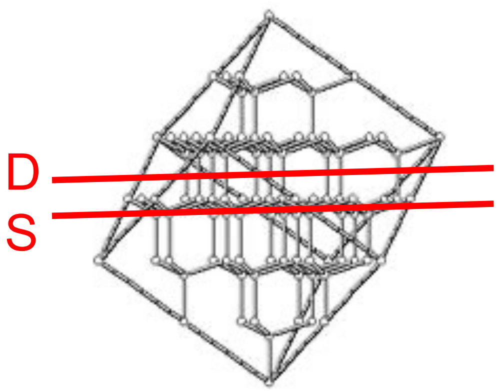

(a)
y
x
B
C
Au
(b)
z
x
(c)
Au

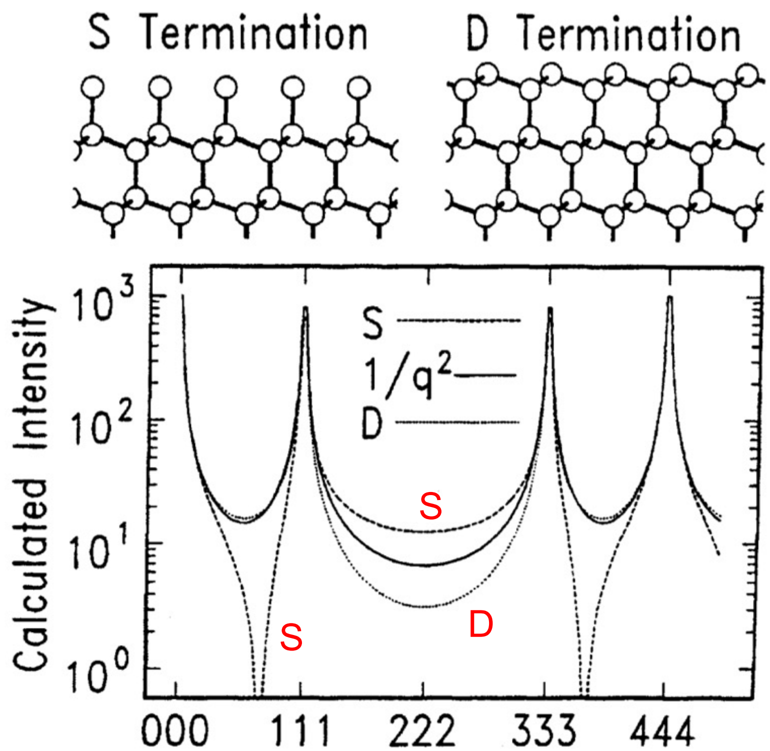
Comparison with STM





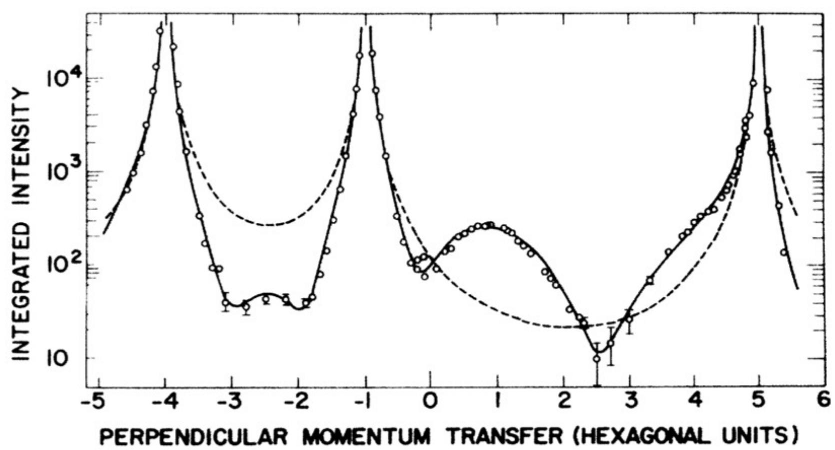
(111) Surface of Diamond Lattice

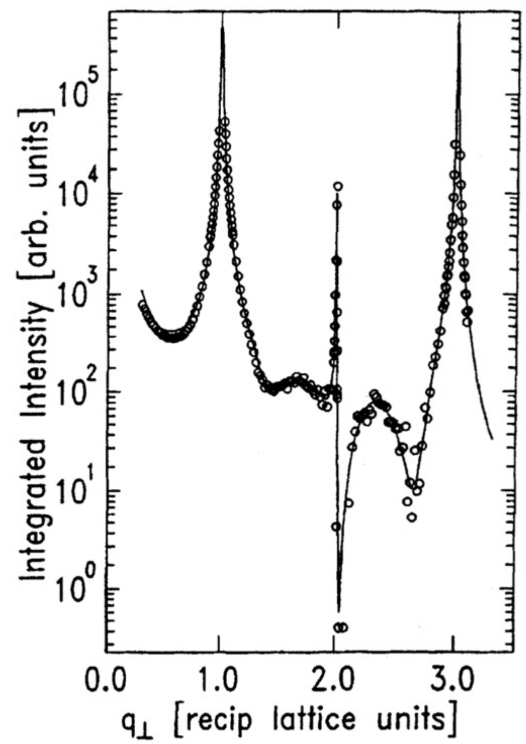




(111) Surface of Diamond Lattice

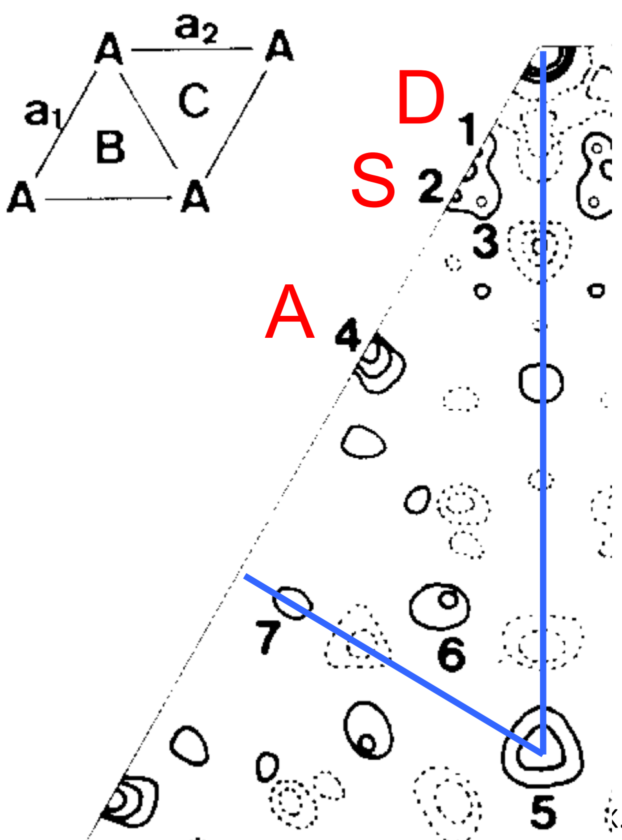
Si(111) 7x7 buried under a-Si
PRL 57 2714 (1986)

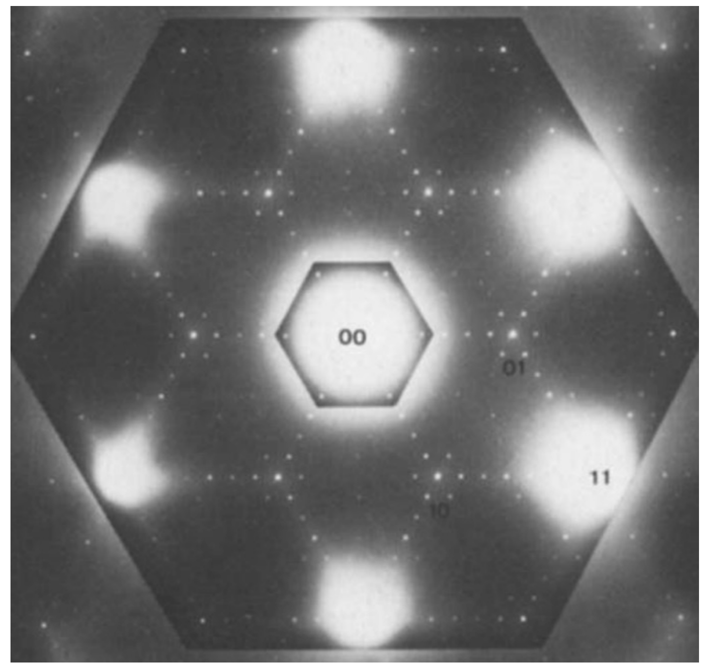




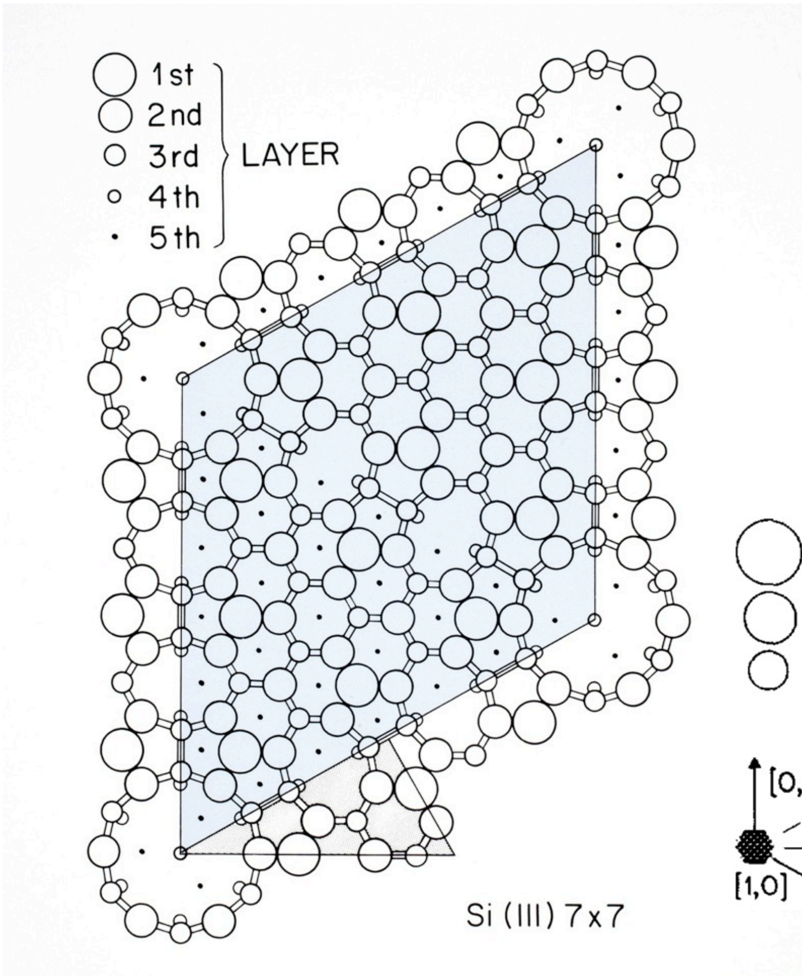
Patterson: Dimer-Adatom-Stacking-Fault

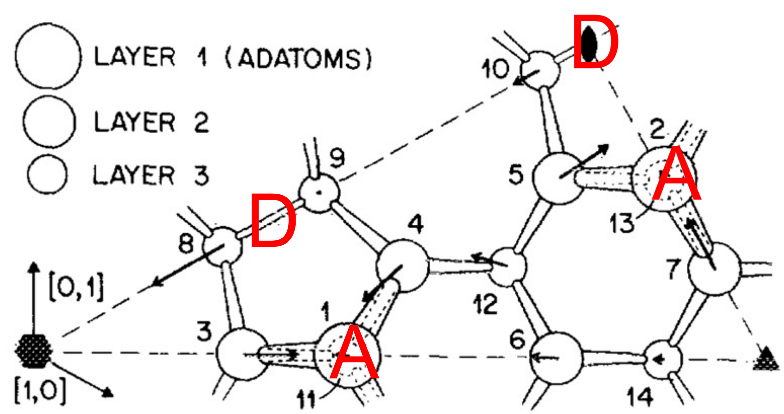
K. Takayanagi et al, Surf. Sci. 164 367 (1985)





DAS Model
Si(111) 7x7





Surface X-ray Diffraction Collaborators

Peter Eisenberger	Bell Labs
Paul Fuoss	Stanford
Peter Bennett	Arizona
Doon Gibbs	Brookhaven
Ben Ocko	Brookhaven
Peter Eng	Chicago
Robert Feidenhans'l	Copenhagen
Jens Als-Nielsen	Copenhagen
Jakob Bohr	Copenhagen
Mike Altman	HKUST
Elias Vlieg	Nijmegen
Sunil Sinha	San Diego
Don Walko	Urbana
Franz Himpsel	Wisconsin

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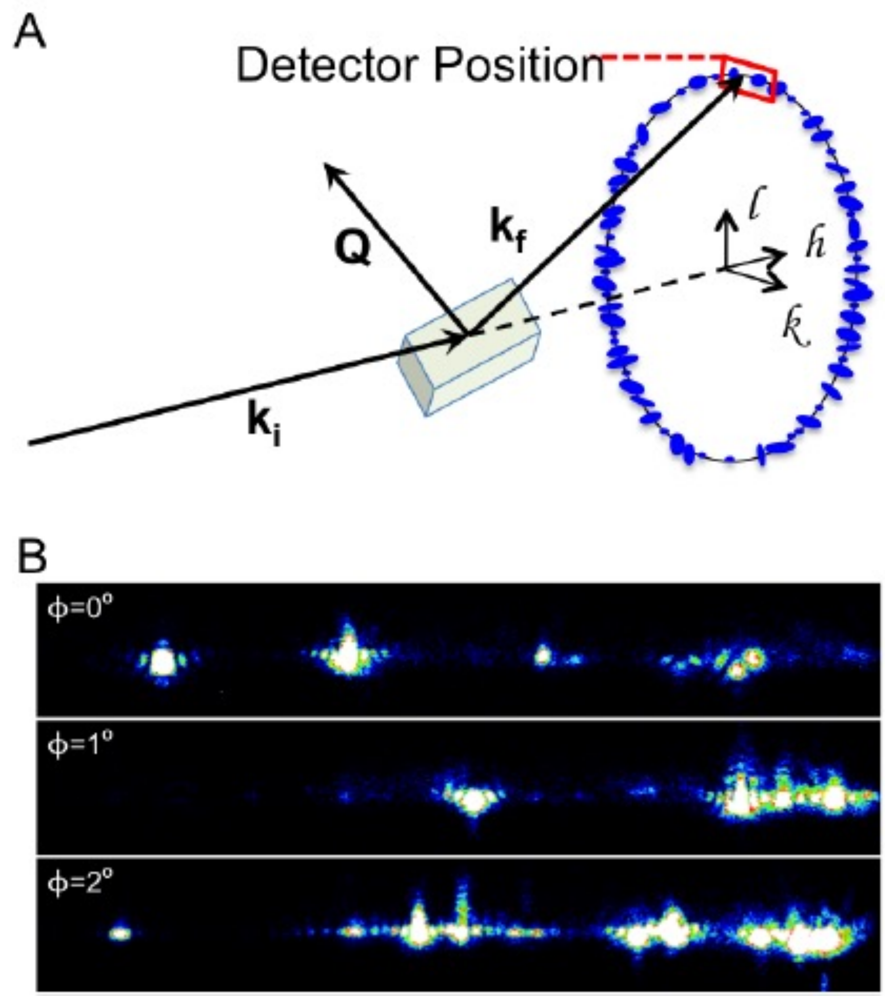
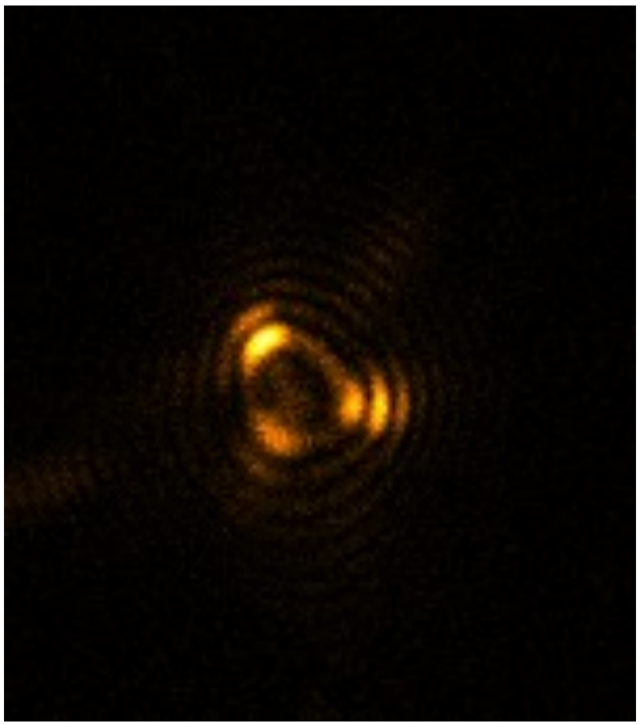
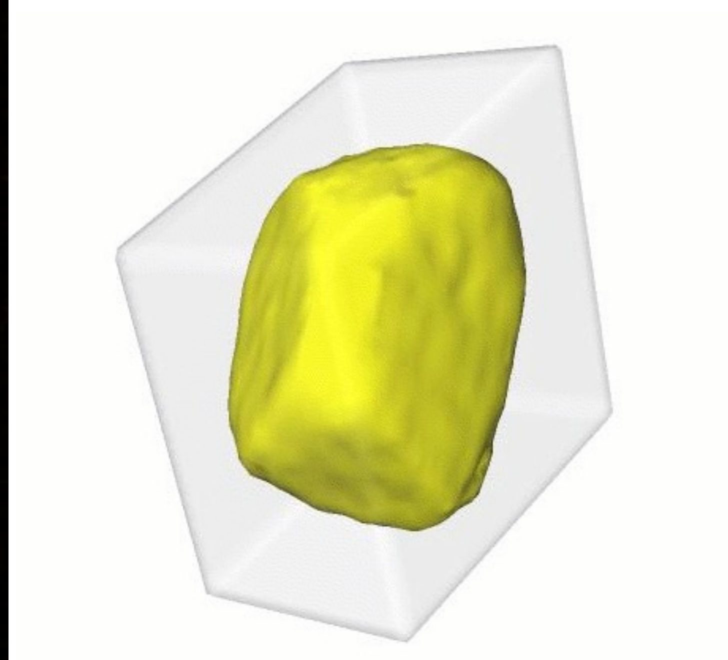

A
Detector Position
Q
k_f
k_i
l
h
k
B
ϕ=0°
ϕ=1°
ϕ=2°

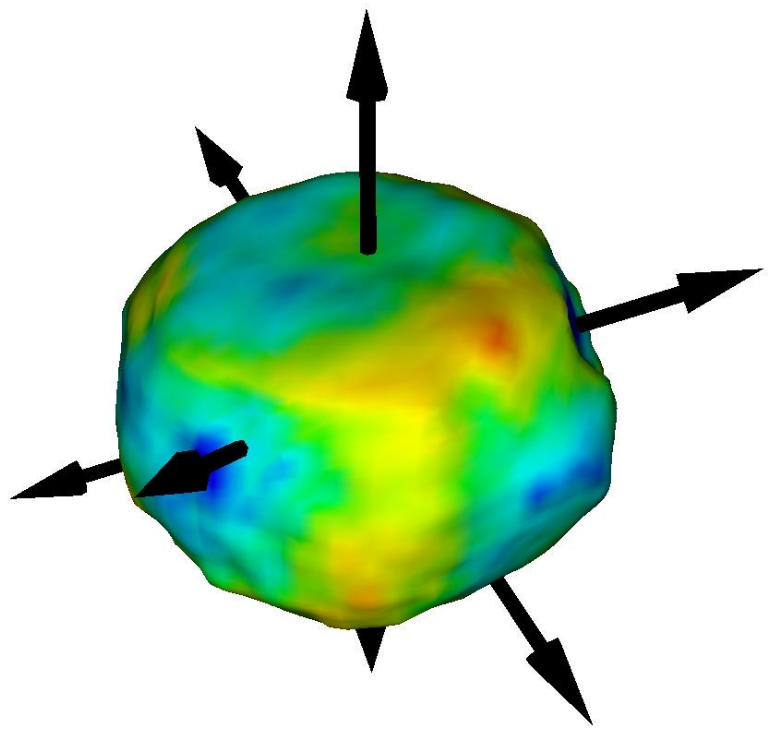
Gold nanocrystal reconstruction

showing support used for 20 HIO followed by 10 ER



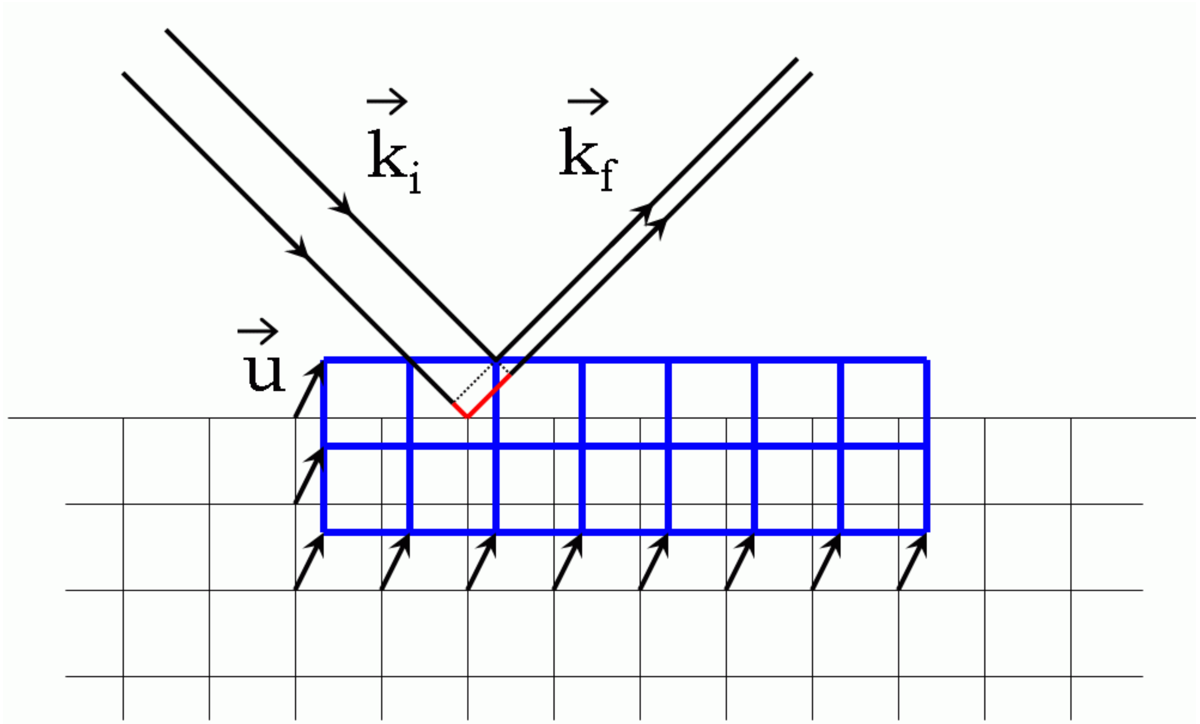


Phase isosurface of residual strain

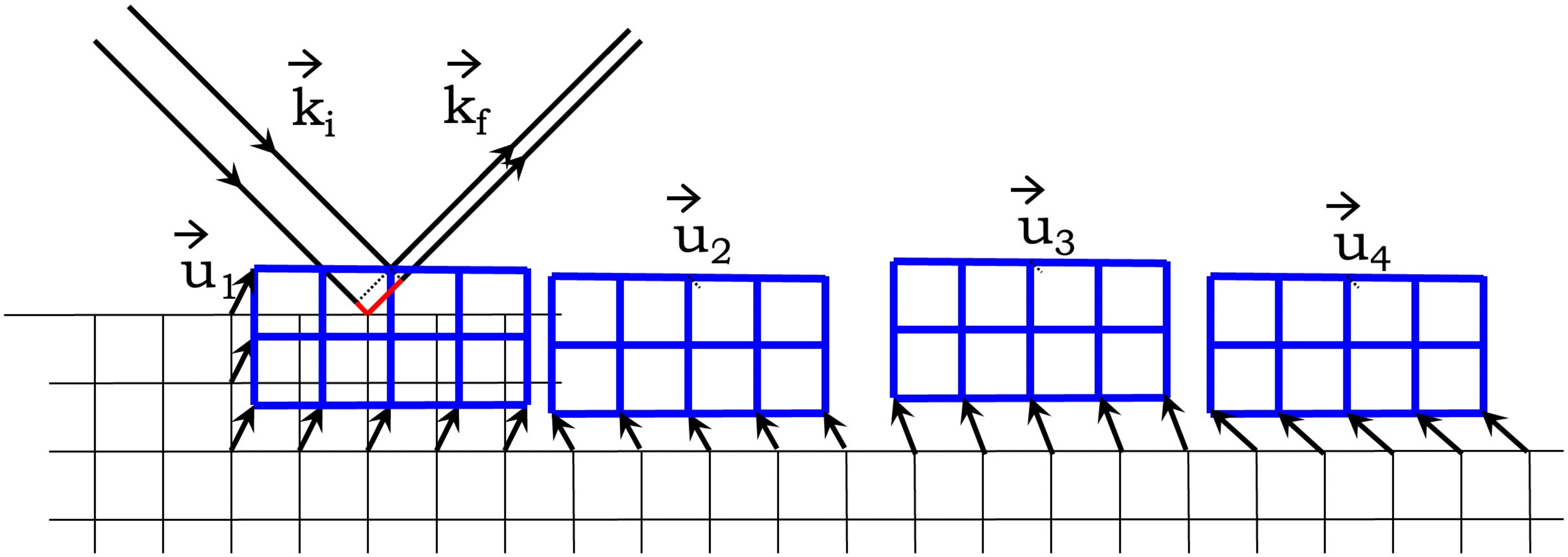


Sensitivity to strain

$\Delta\phi = \mathbf{k}_f \cdot \mathbf{u} - \mathbf{k}_i \cdot \mathbf{u} = \mathbf{Q} \cdot \mathbf{u}$



Generalization to Phase Domains



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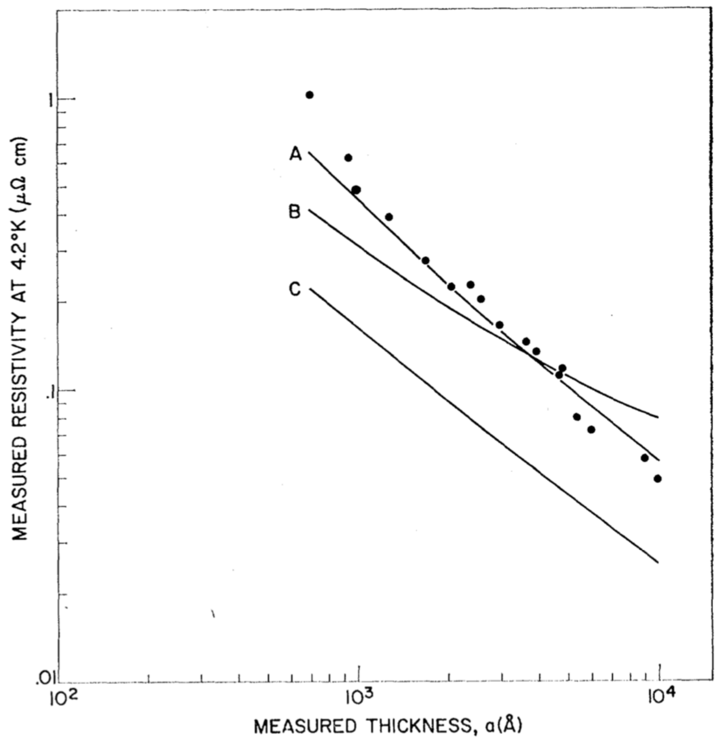
Resistivity of Al Thin Films

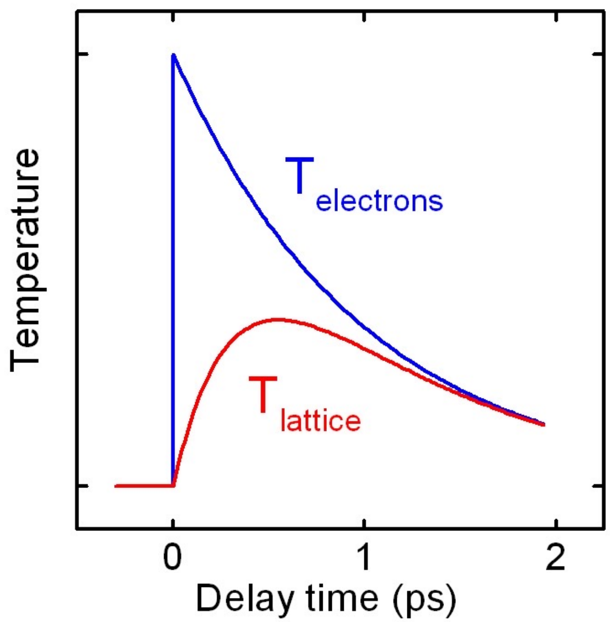
A. F. Mayadas and M. Shatzkes, PRB **1** 1382 (1970)



- "Universal curve" of MFP vs electron energy
- Thermal MFP removed at low temperature
- Grain size proportional to thickness (model)

"Two-temperature" model (2TM)

I. K. Robinson et al, Journal of Optics **18** 054007 (2016)
J. K. Chen et al, Int J. Heat Transfer **49** 307 (2006)



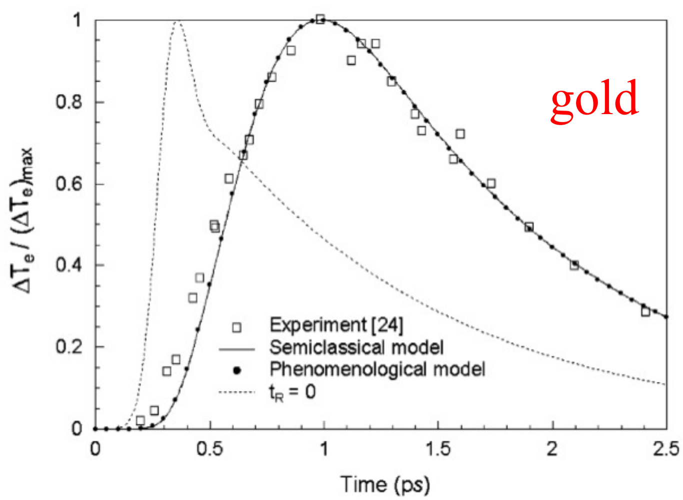


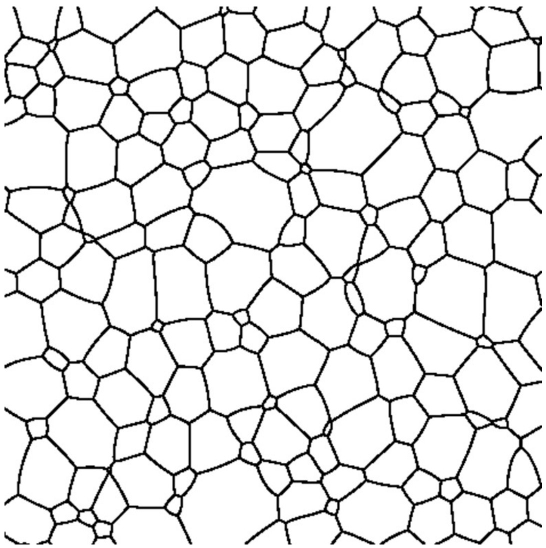
Fig. 2. Comparison of the change in electron temperature at the front surface of an 80-nm gold film irradiated by a 2.8 mJ/cm^2, 800 nm, 150-fs laser pulse.

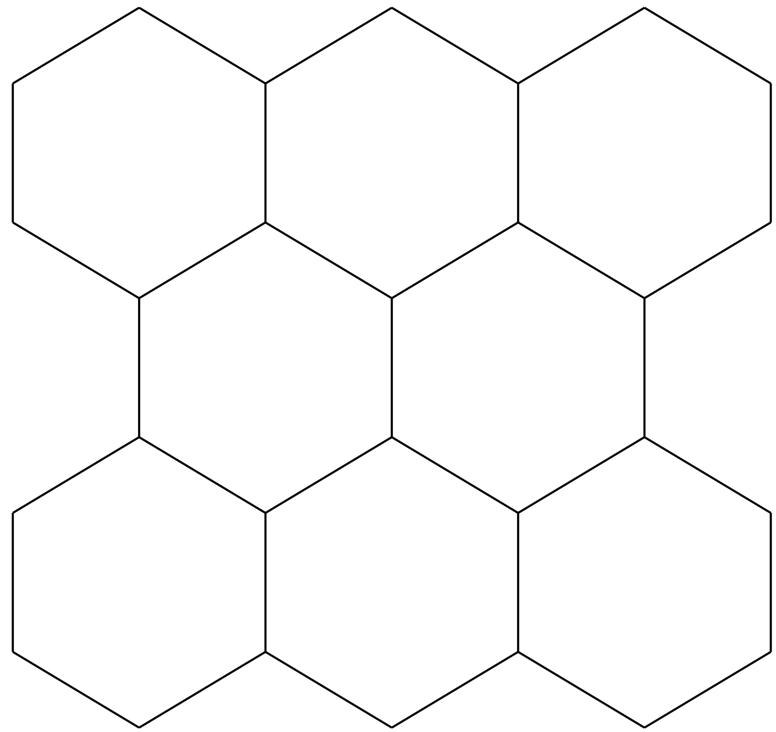
XFEL Questions about Melting

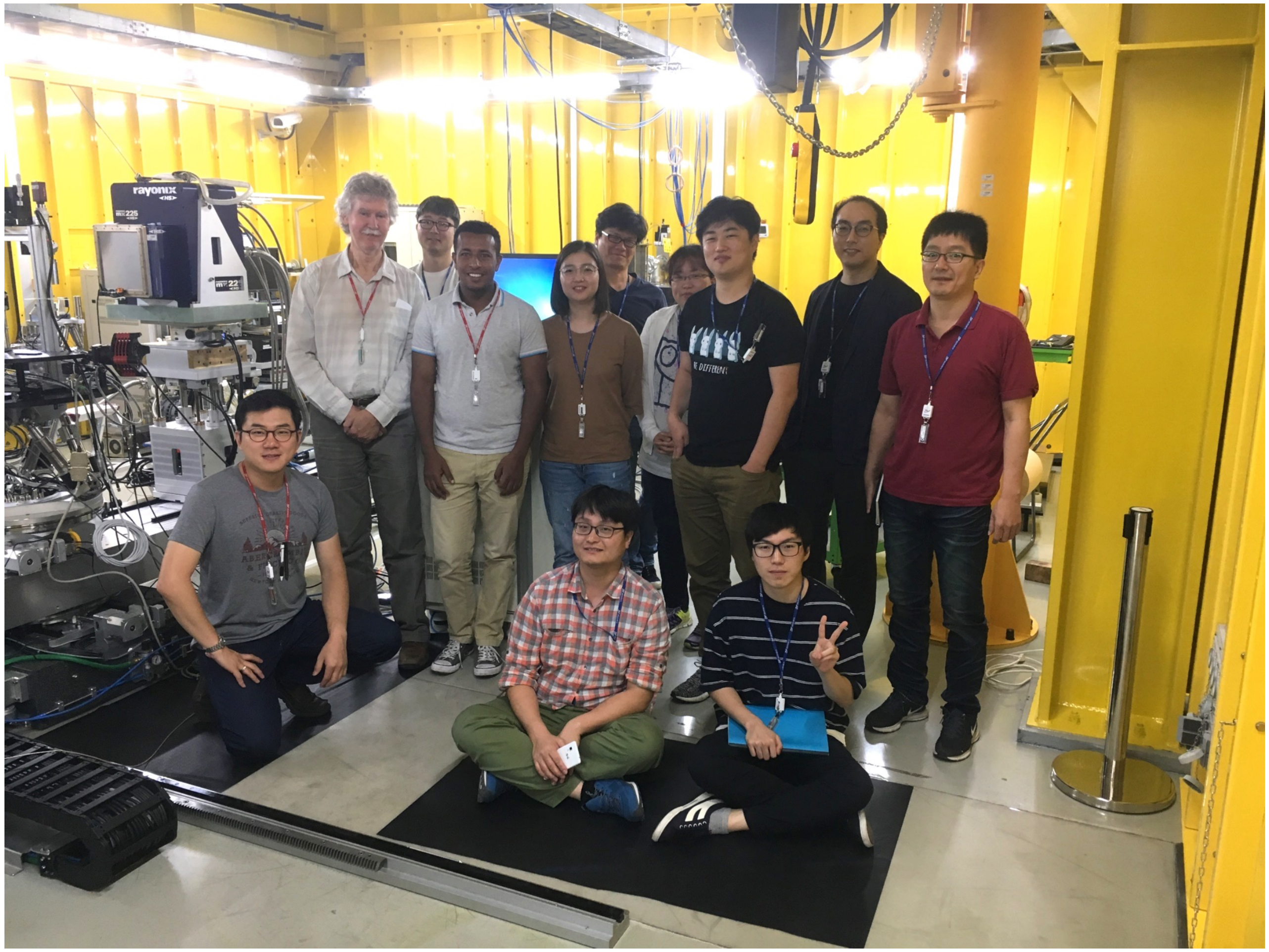
XFEL Questions about Melting

- Where does the melting start?
- How does the 2TM couple to the lattice?
- Role of sample geometry?
- Can we see the liquid phase?
- Are there transient liquid structures?
- How fast does melting take place?

XFEL Grain Boundary Melting ?

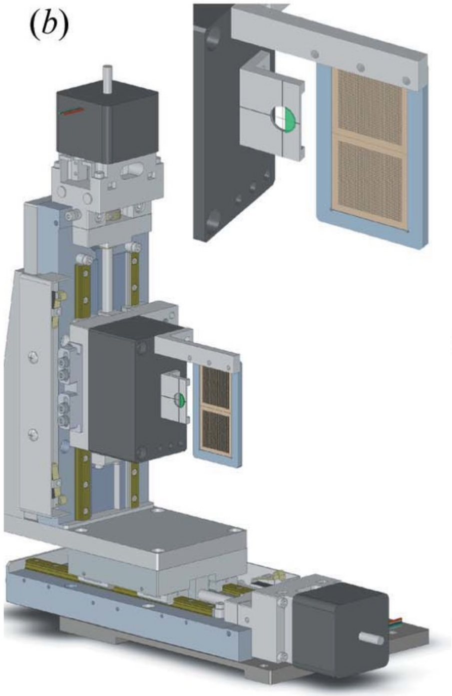


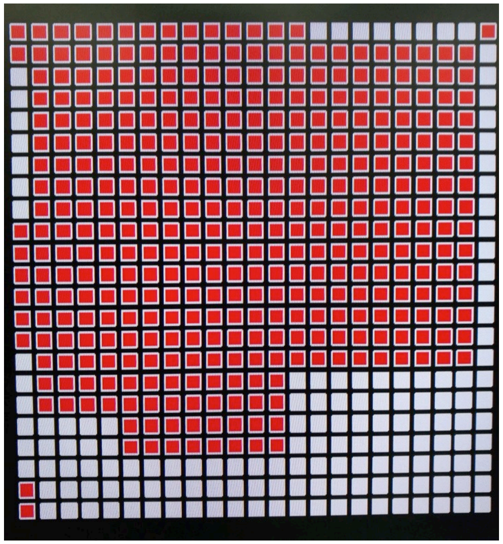



rayonix

Scan Stage for MAXIC chamber

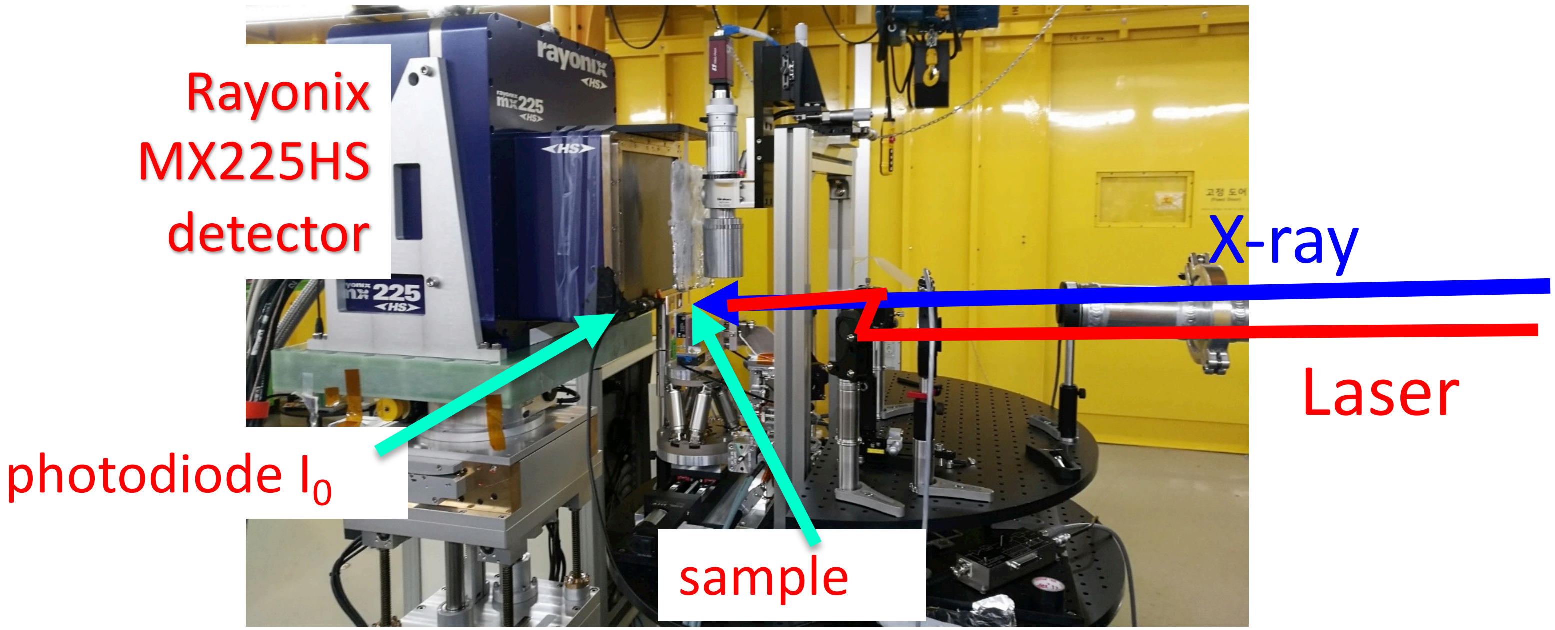
Changyong Song et al, J. Appl. Cryst. **47** 188 (2014)
Daewoong Nam, scanning software



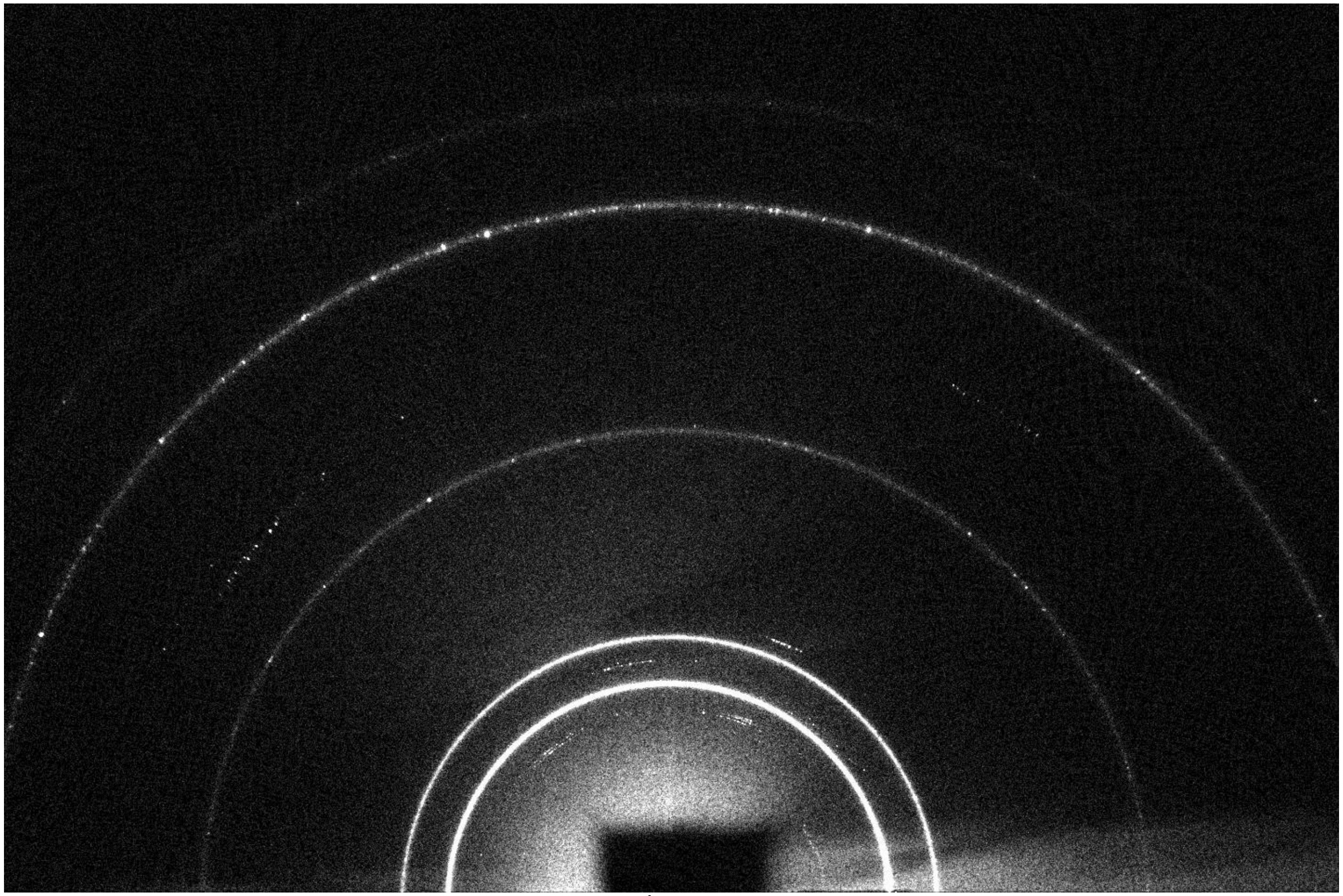


23x23 windows

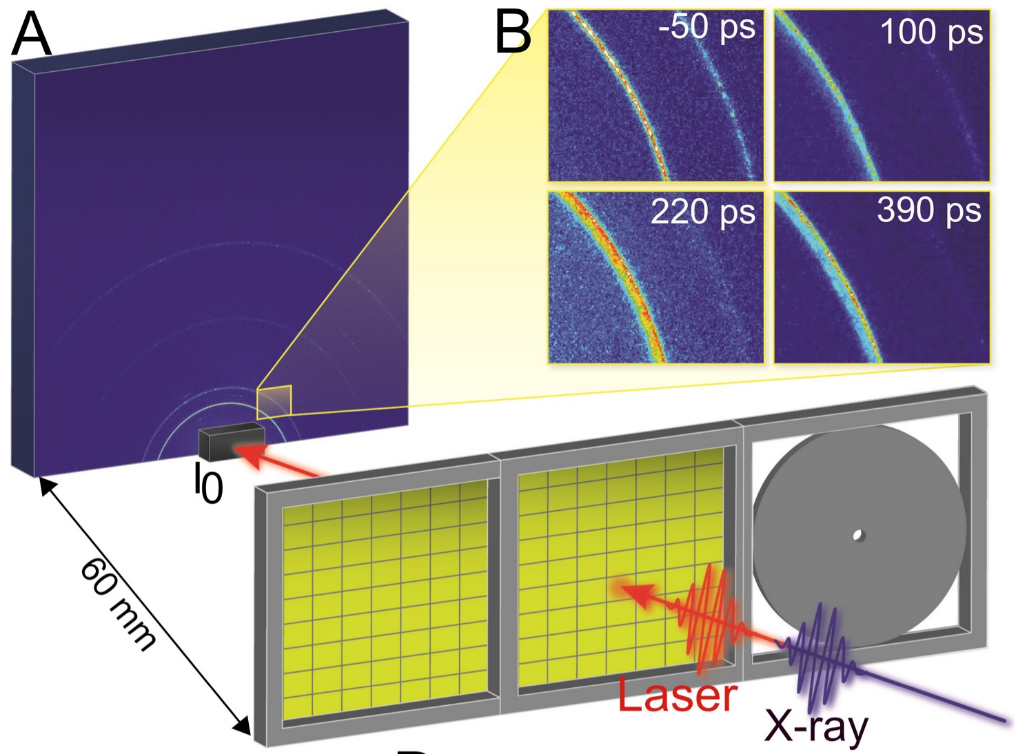
Experimental set-up at PAL-XFEL September 2017



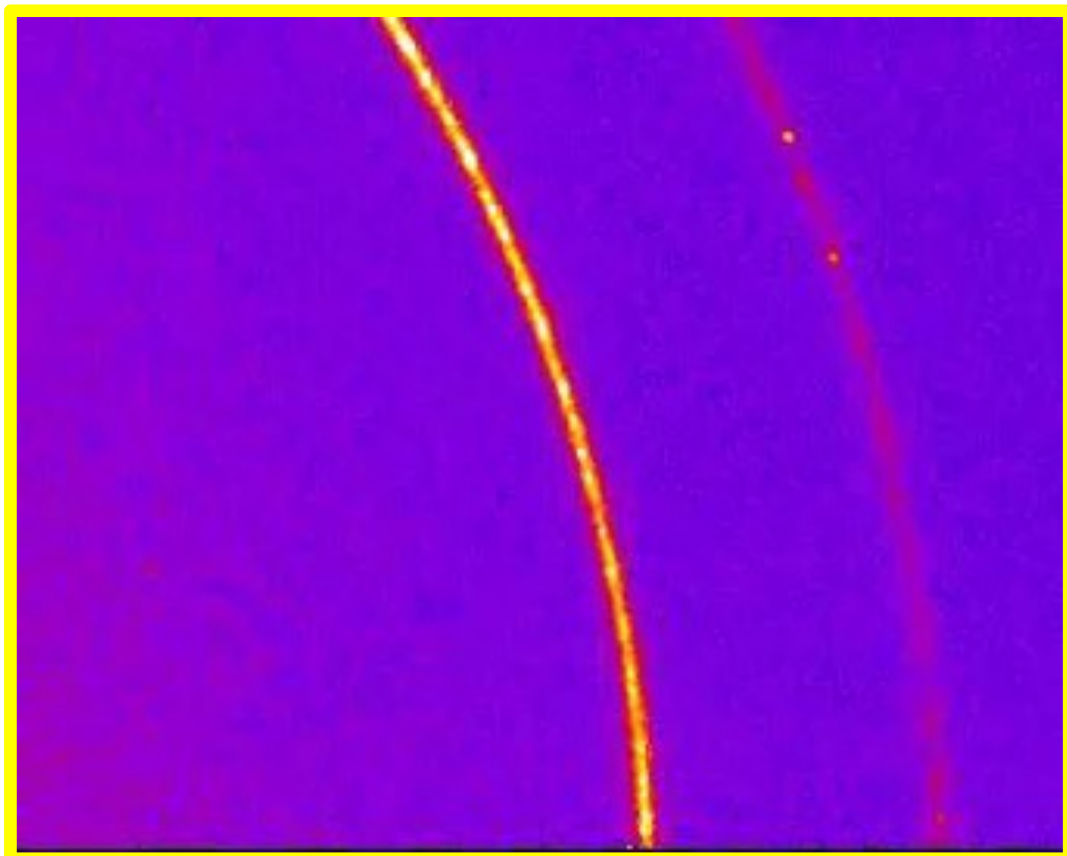
Raw data #397 300nm film



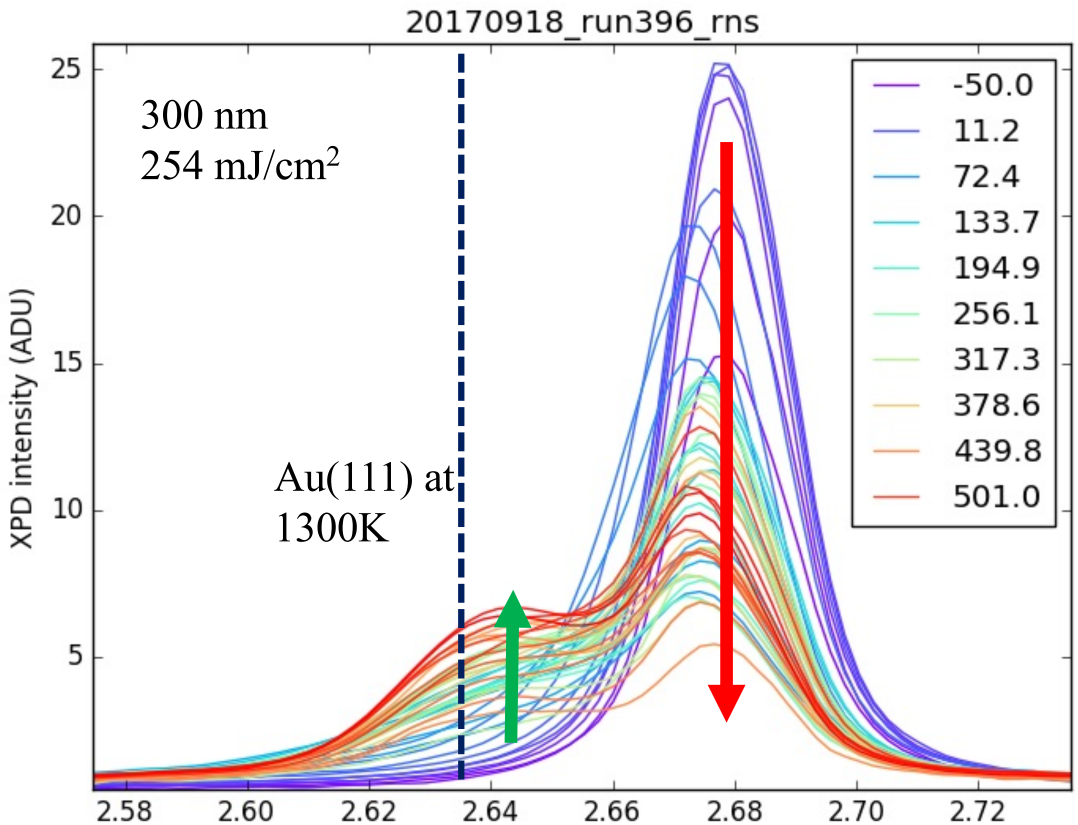
Powder Diffraction Geometry



Raw data #396 300nm film, 254 mJ/cm^2



PyFAI integration around ring



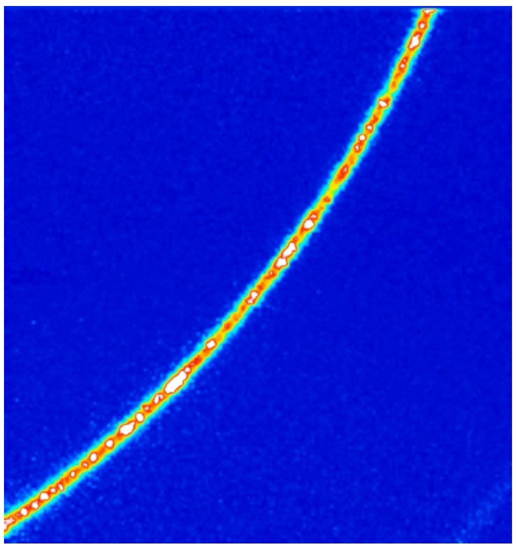
Average grain size ≥ 30nm

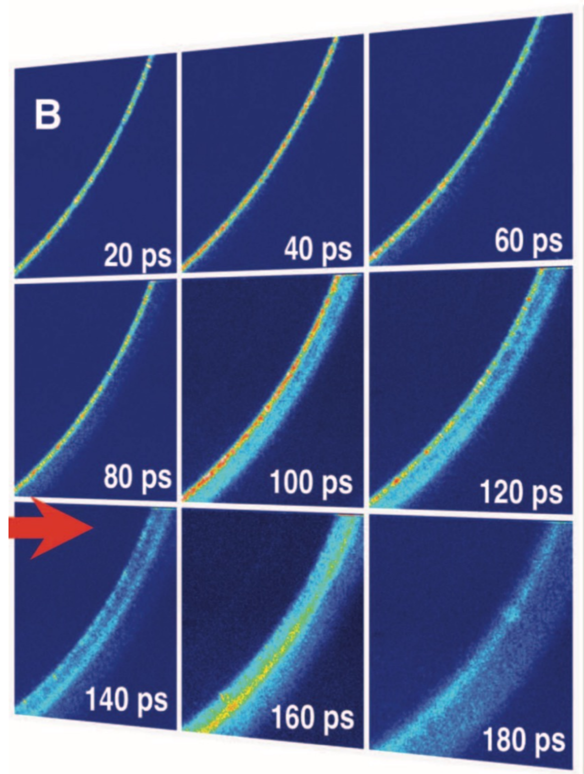
New peak ~3x broader

Thin Film of Cu at CXI, LCLS

D. Milathianaki et al, Science **342** 220 (2013)

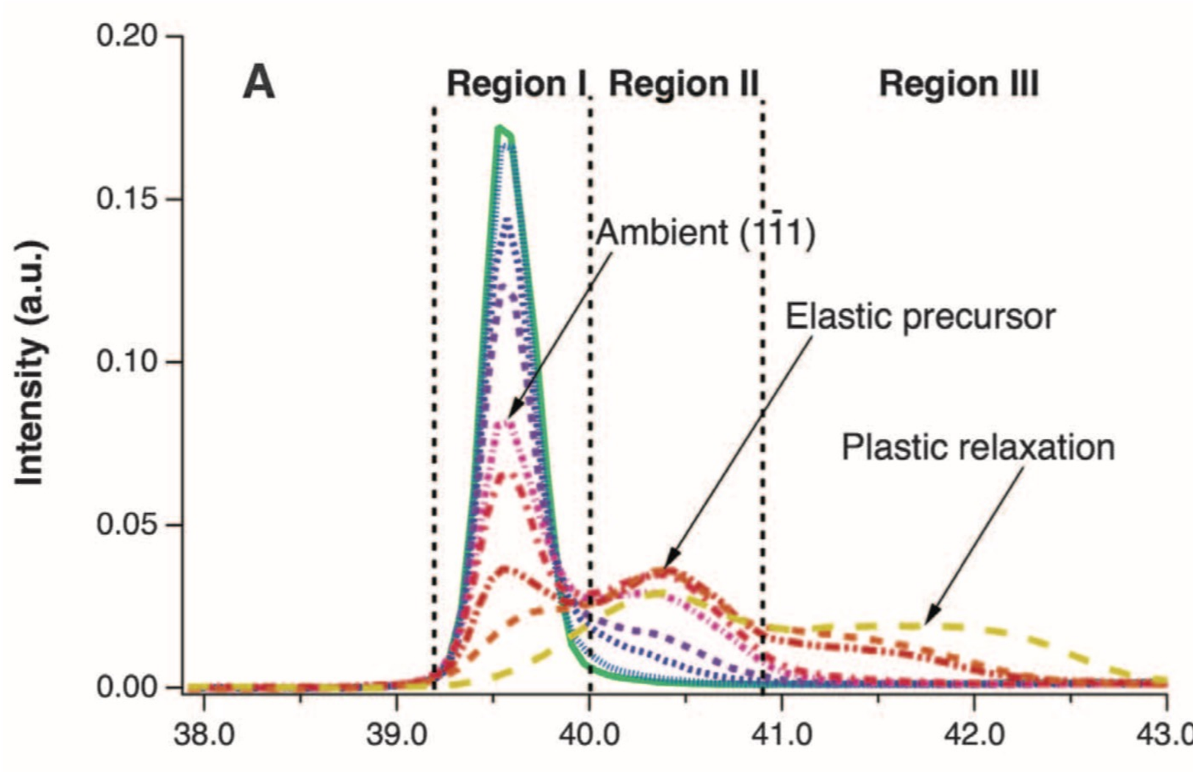
Laser
38 J/cm^2
170ps





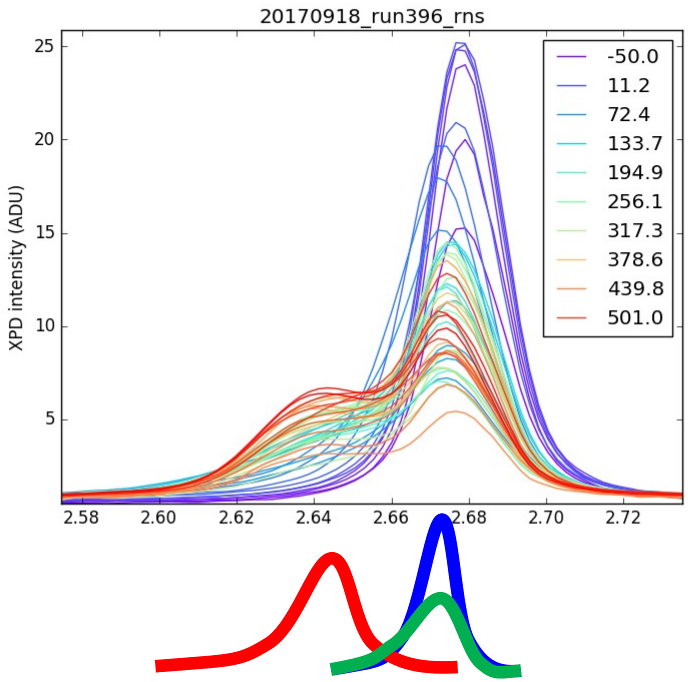
Thin Film of Cu at CXI, LCLS

D. Milathianaki et al, Science **342** 220 (2013)



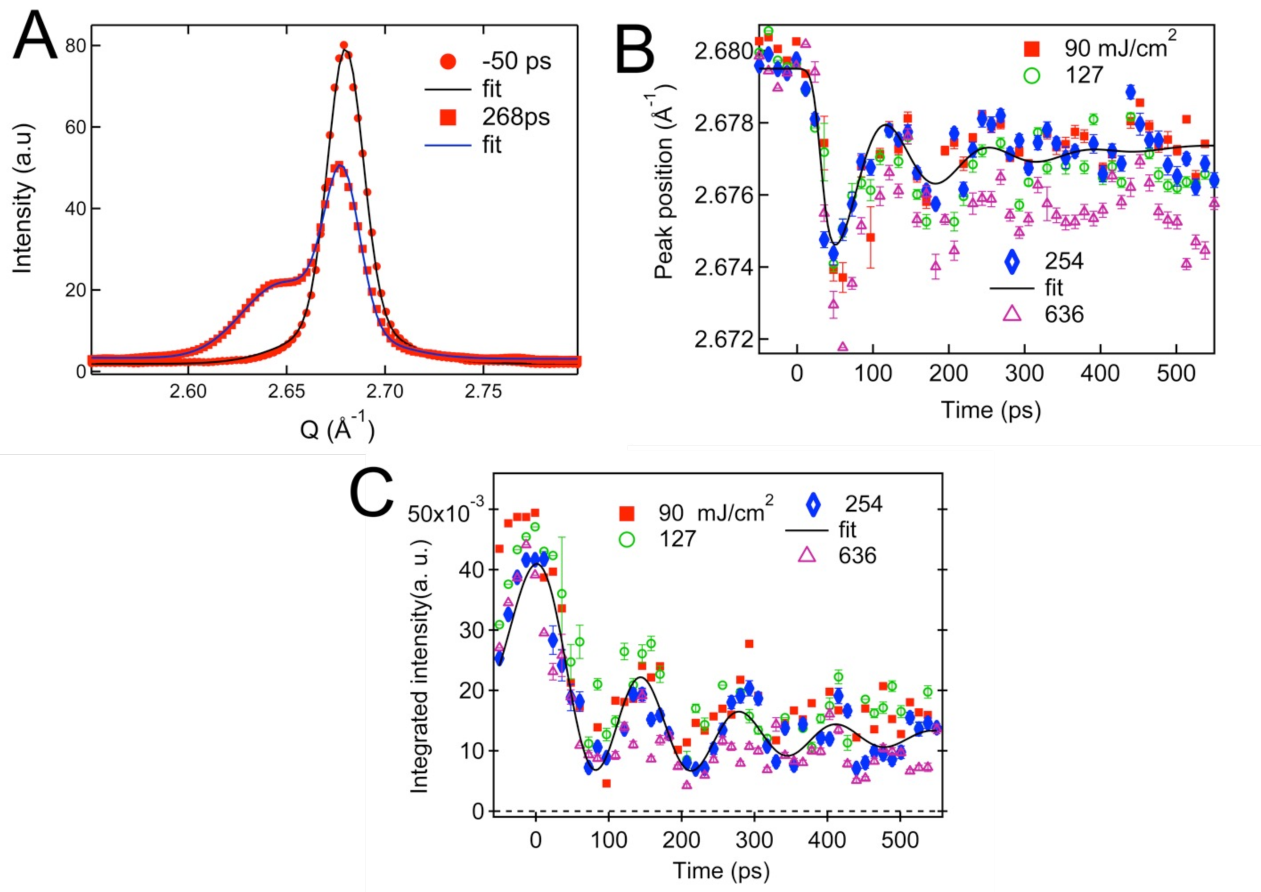
Laser
38 J/cm^2
170ps

Gaussian ftting procedure



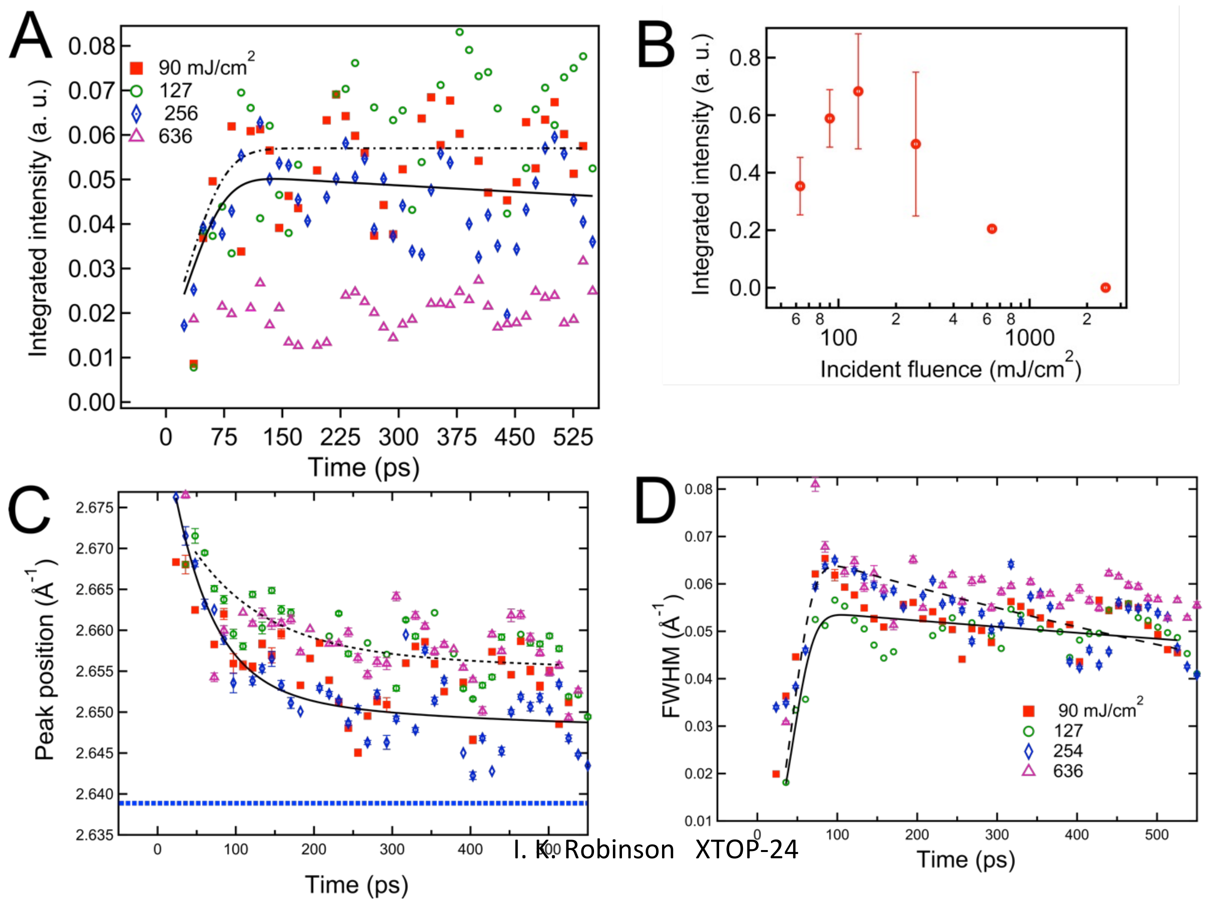
- Crystal Peaks (2x)
  - fixed widths
  - fixed height ratio
  - variable position
- "New" Peak
  - variable width
  - variable height
  - variable position

Response of the Crystal 111 peak



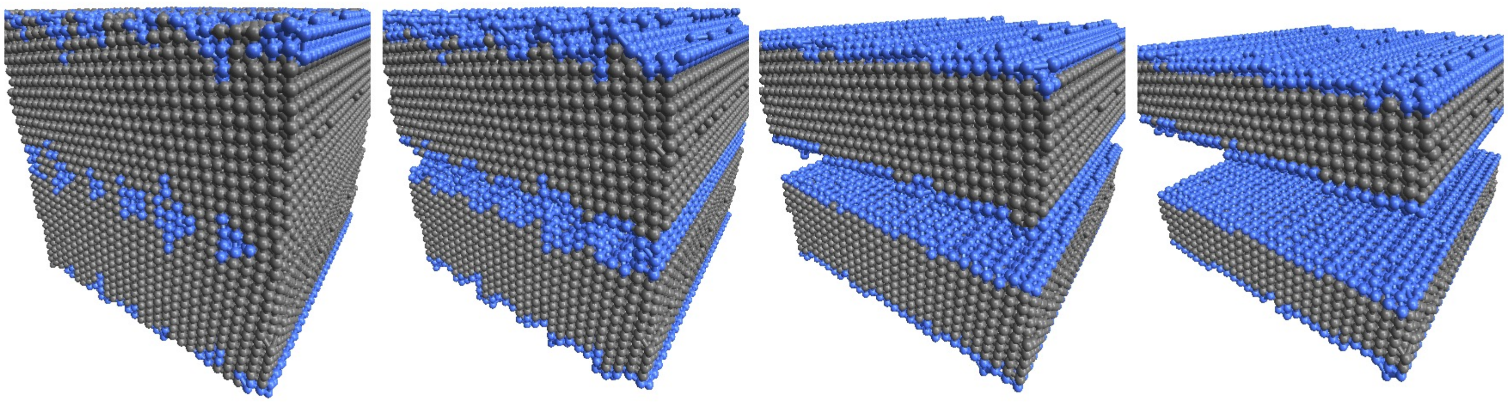
Response of New Melt-front Peak

Material trapped at the melting point



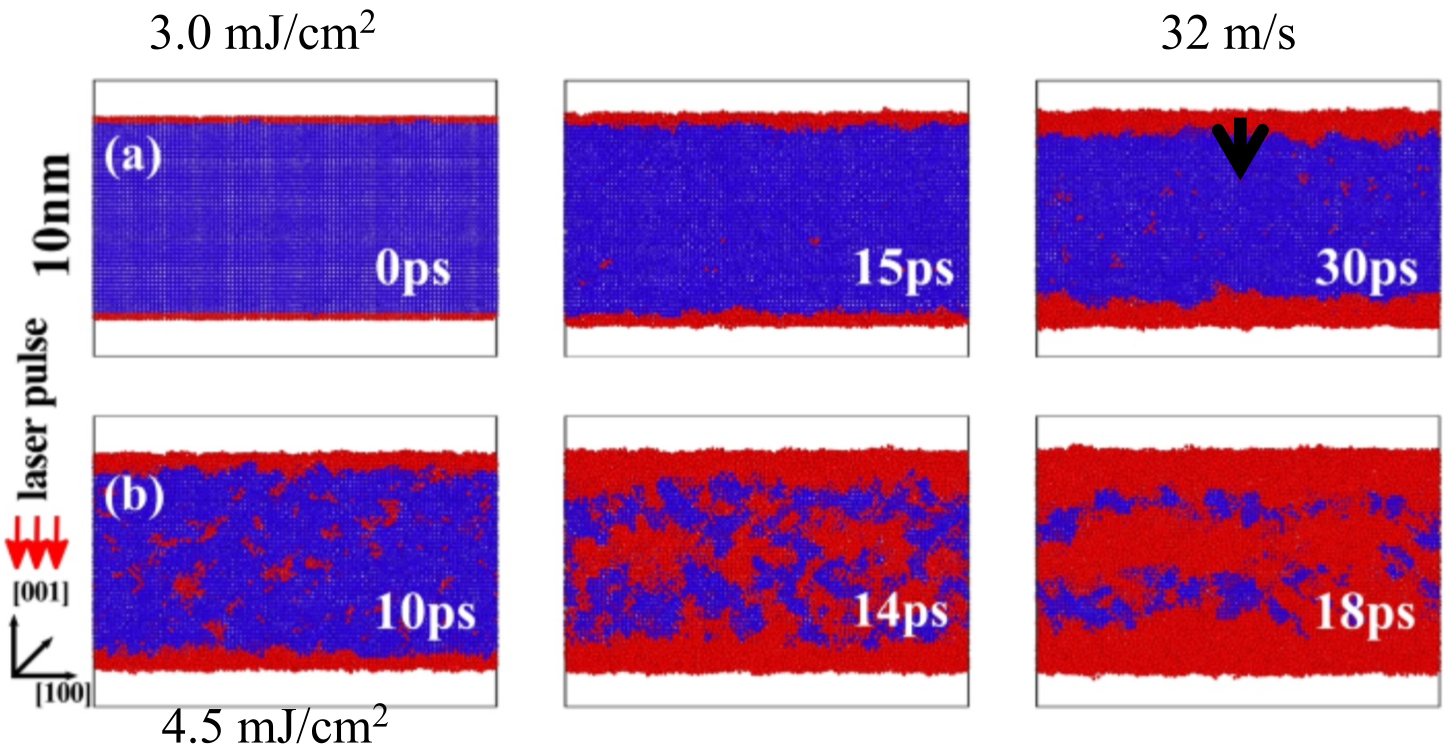
Force-Field Simulation of GB melting

J. Berry, K. Elder and M. Grant, PRB 77 224114 (2008)

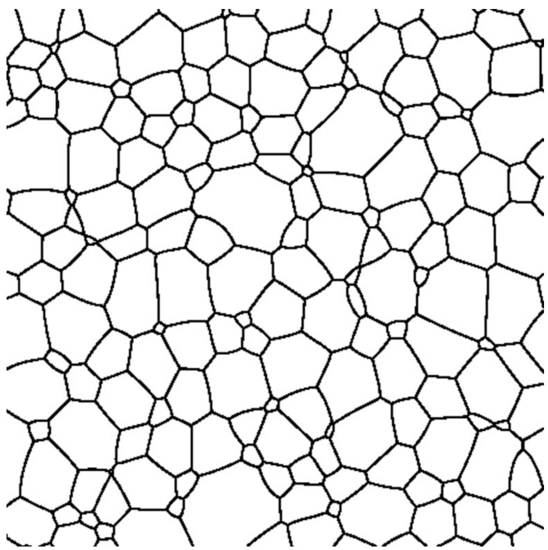


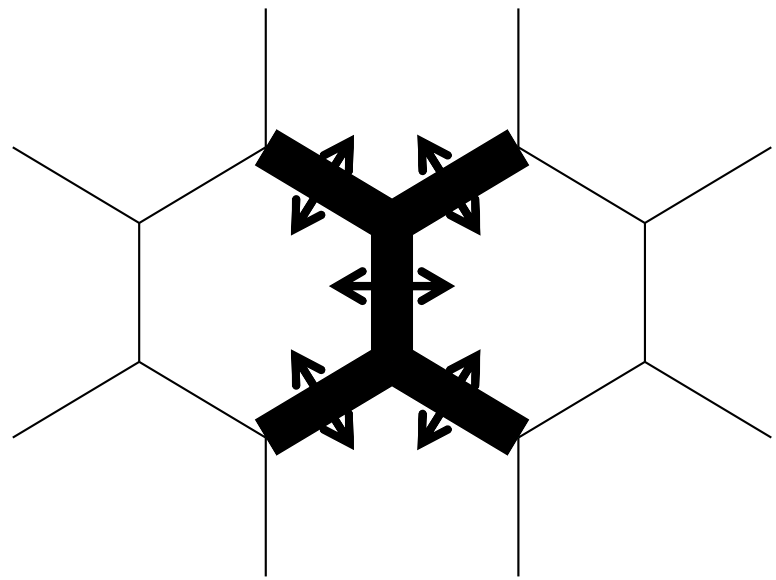
2TM-MD (EAM) simulation Au slab

Giret et al, APL **103** 253107 (2013)

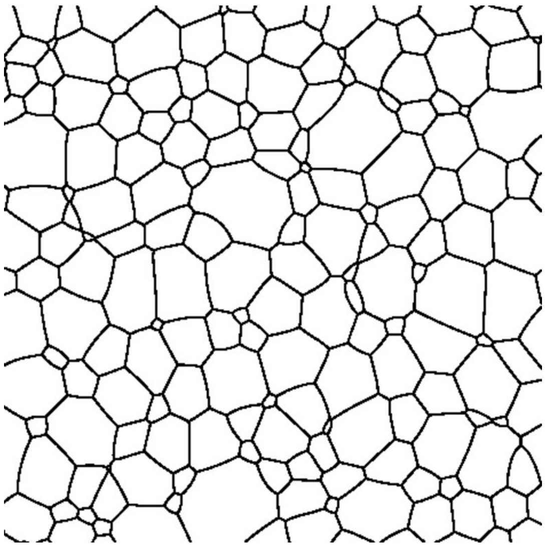


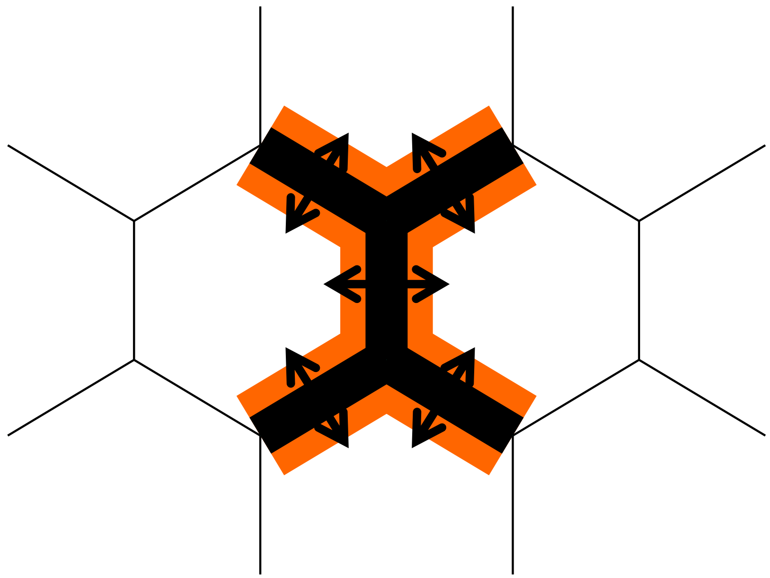
Grain Boundary Melting





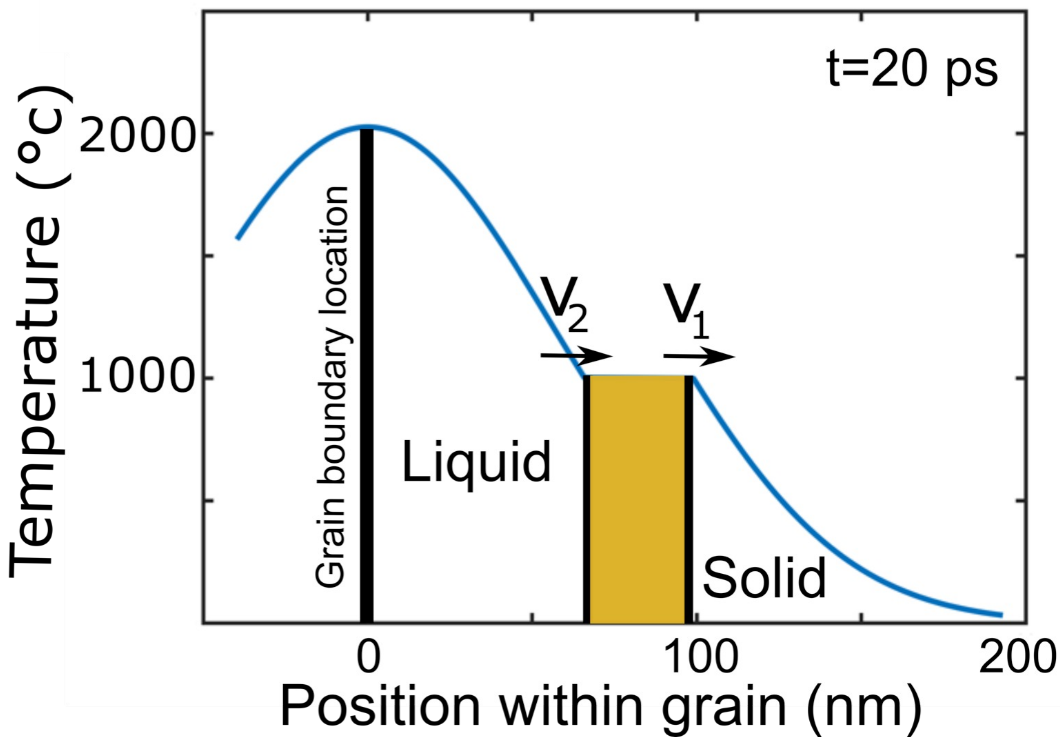
Grain Boundary Melting





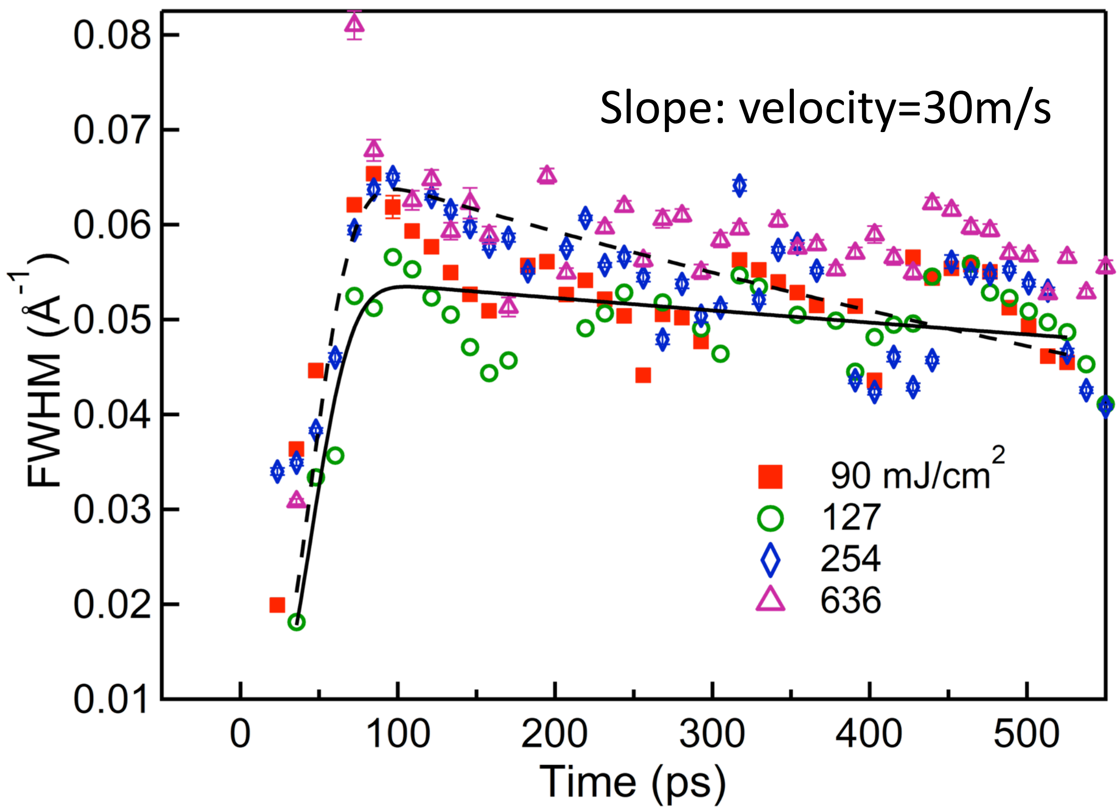
Grain Boundary Induced Melting

T. A. Assefa et al Science Advances 6 eaax2445 (2020)



Width of new "Melt-Front" Peak

T. A. Assefa et al Science Advances 6 eaax2445 (2020)

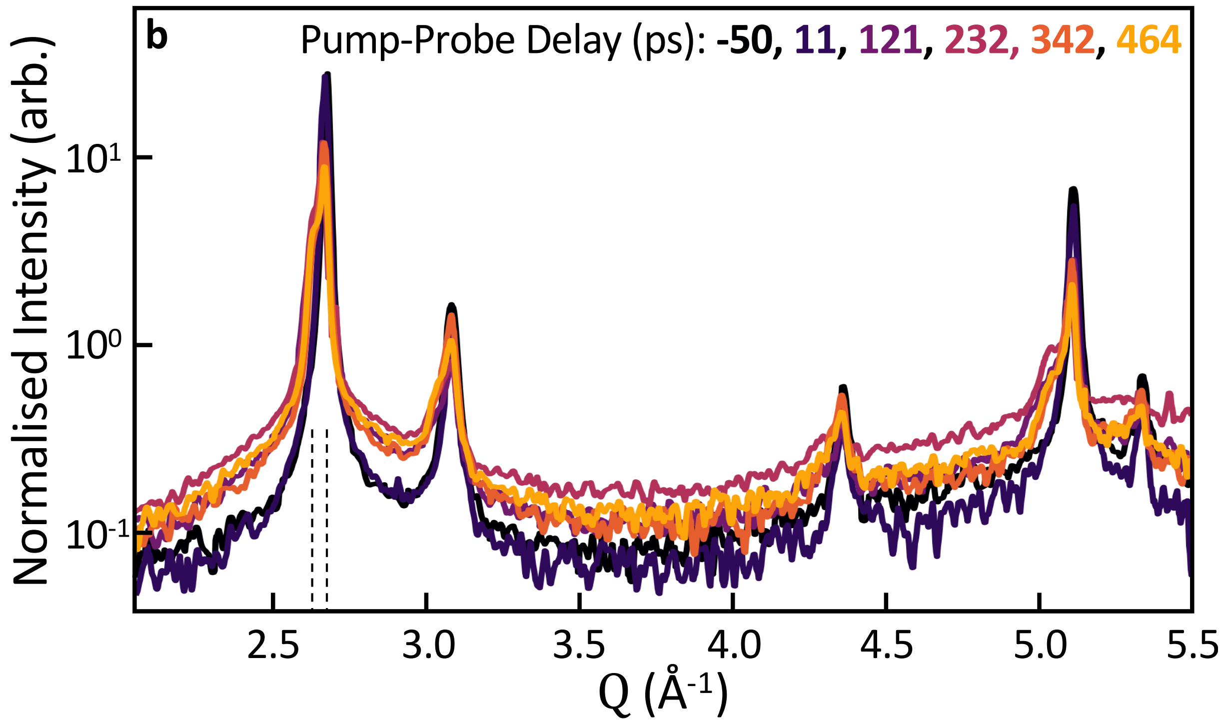


$\tau = 2\pi / \Delta Q$

= 12 nm

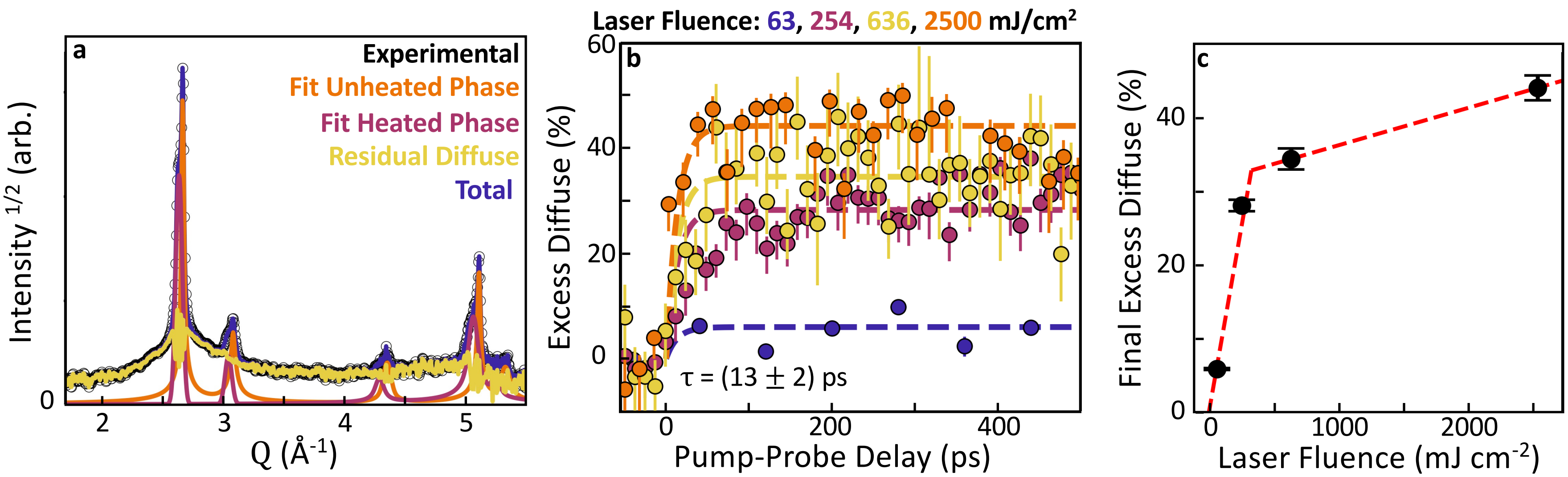
Liquid structure factor

I. K. Robinson, et al, IUCrJ 10 656–661 (2023)

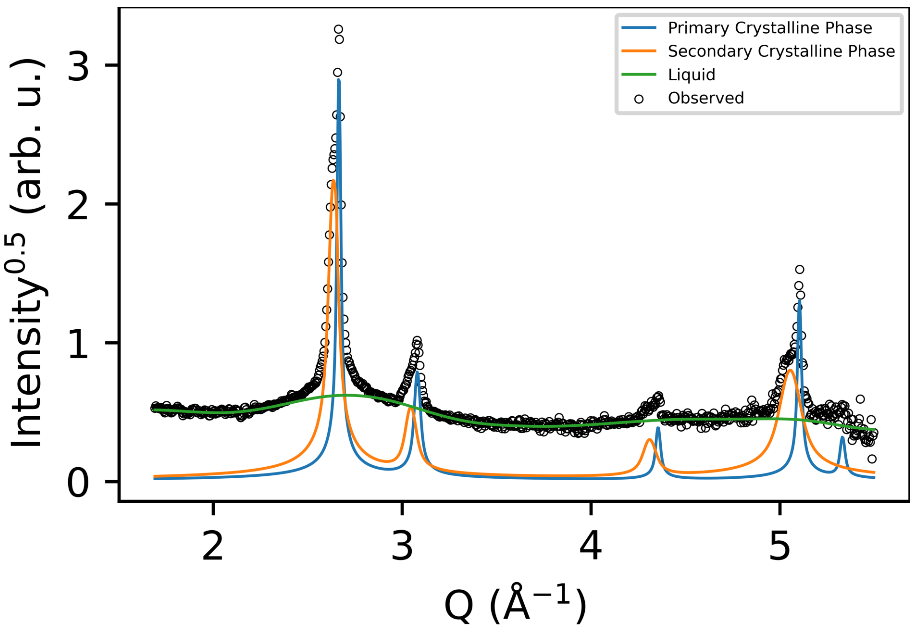


Extracting Liquid structure factor

I. K. Robinson, et al, IUCrJ 10 656–661 (2023)



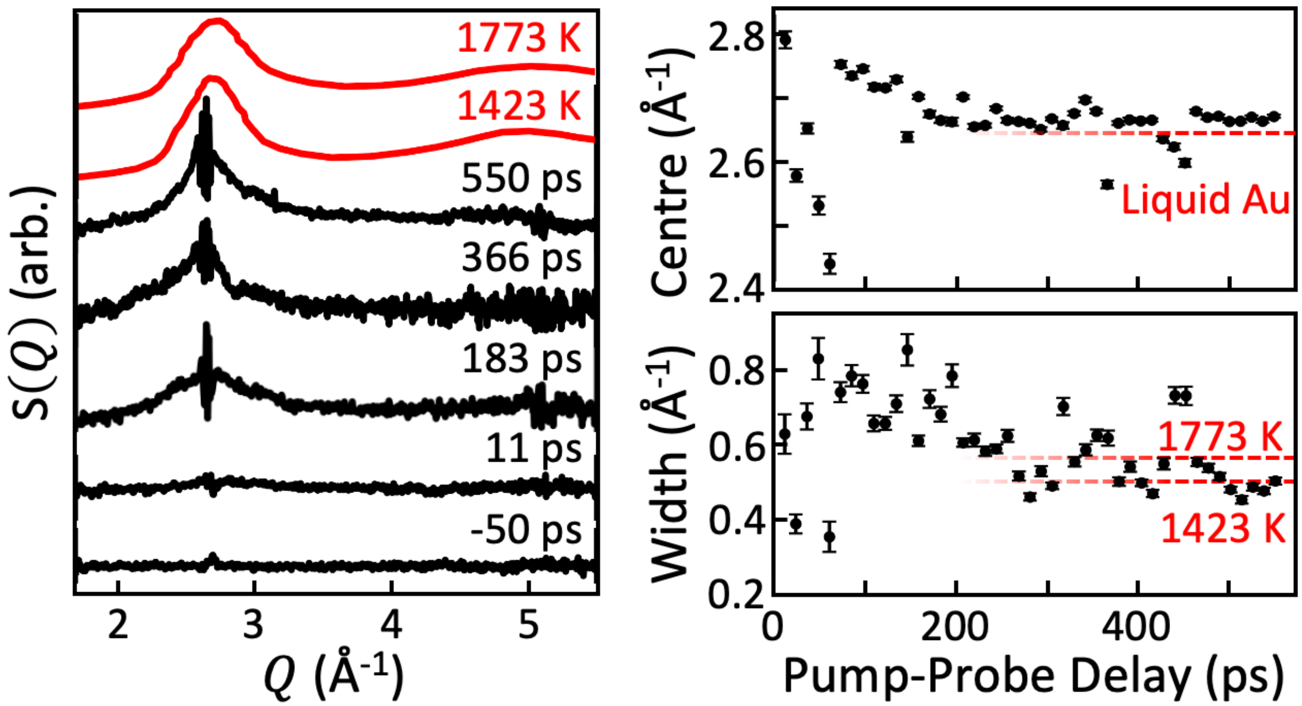
Extracting the diffuse signal



- Raw data plotted, 231 ps, square root intensity scale
- Unconstrained peak fitting approach
- Remove Bragg components

Liquid structure factor

I. K. Robinson, et al, IUCrJ 10 656–661 (2023)



Melt-front description of melting in polycrystalline materials

- Laser induced disorder
- Three phases: liquid, solid, melt
- 2-phase inhomogeneous melting
- Energy transfer at Grain Boundaries
- Interface melting like nanoparticles
- Measured structure of Melt Front

Thin-film melting collaborators

Tadesse Assefa
Jack Griffiths
Yue Cao
Emil Bozin
Rob Koch
Pavol Juhas
Simon Billinge

Dongjin Kim
Sungwon Kim
Hyunjung Kim
Changyong Song

Sunam Kim
Jae Hyuk Lee
Yongsam Kim
Jaeku Park
Sang-Youn Park
Intae Eom
Hyojung Hyun
Tae-Yeong Koo
Jaehun Park
Daewoong Nam
Sang Soo Kim

Summary

- Powder diffraction methods "XRD"
- Williamson-Hall analysis of size and strain
- Surface diffraction and surface structure
- Extension to Coherent X-ray Diffraction
- XFEL study of thin film melting