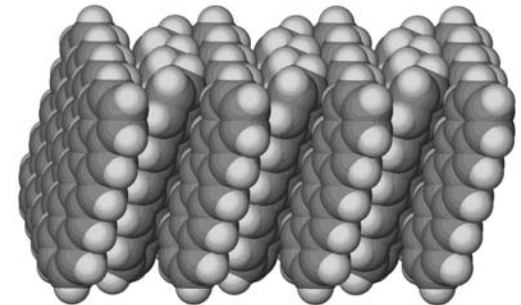
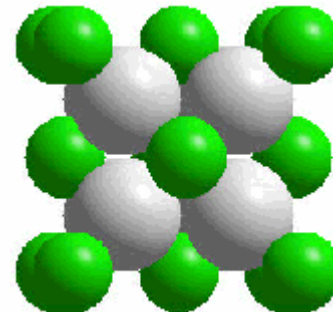
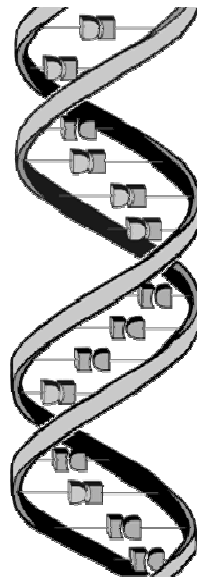
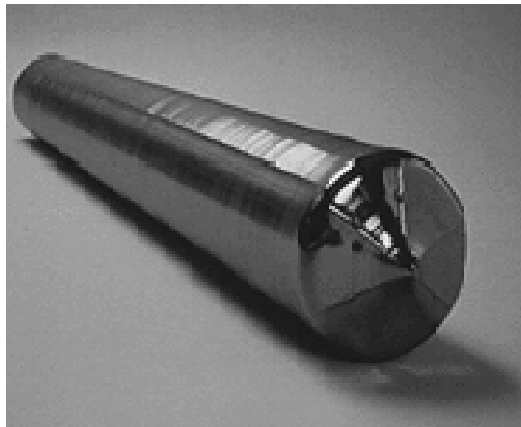


X-ray Diffraction

Mike Toney

Stanford Synchrotron Radiation Laboratory



Outline



1. Crystals and crystal geometry (planes)
2. Bragg's law
3. Reciprocal lattice & reciprocal space
 - definition and examples
 - relation to diffraction
4. Diffraction intensities and crystallography
5. Some examples from current research
 - Macromolecular Crystallography
 - Powder Diffraction – Zeolites
 - Strain: Eu films
 - Pentacene films

Bibliography

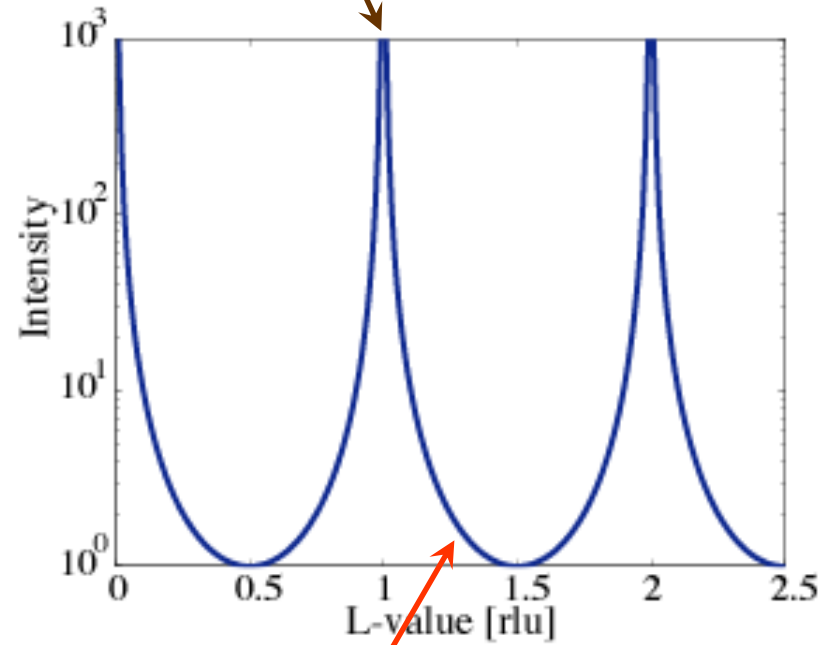
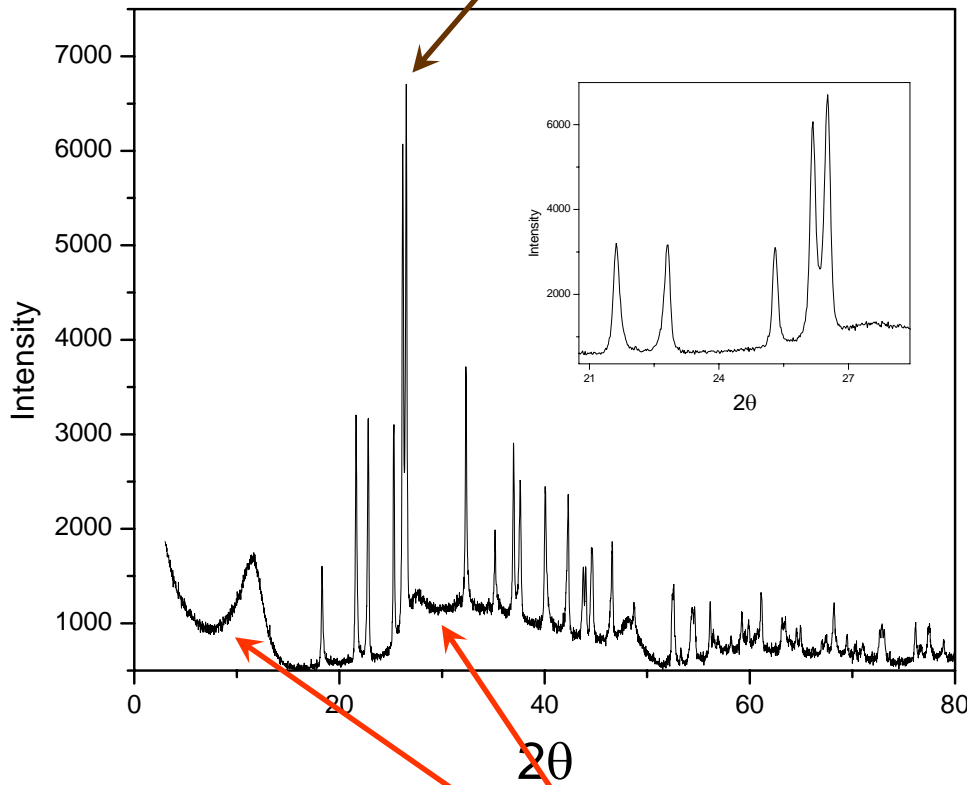


- B Warren, “X-ray Diffraction”, Dover (1990): \$11.87 & Eligible for FREE Super Saver Shipping on amazon.com.
- BD Cullity & SR Stock, “X-ray Diffraction”, Prentice Hall (2001).
- J Als-Nielsen & D McMorrow, “Elements of Modern X-ray Physics”, Wiley (2001).

Diffraction vs Scattering

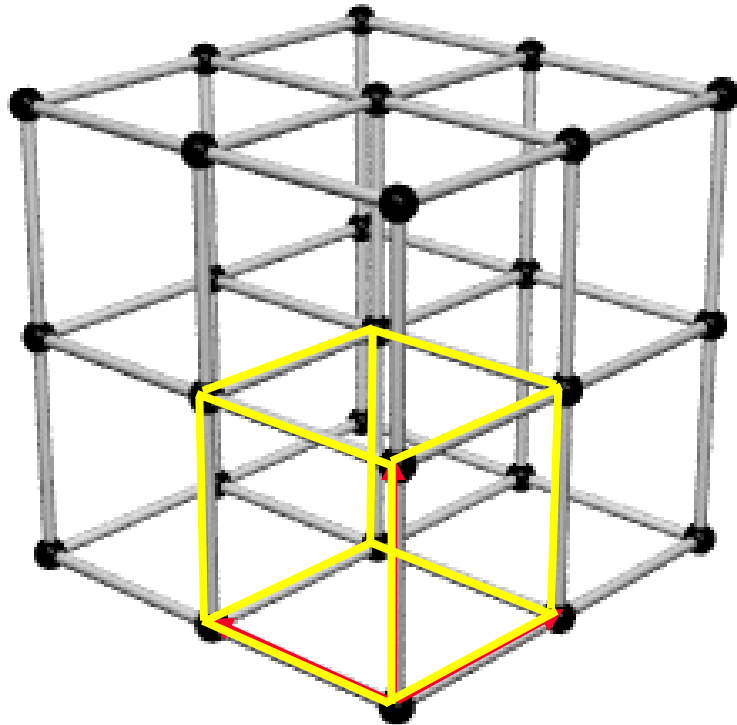


diffraction: Bragg peaks



scattering: the rest

Crystal Lattice



Crystal lattice: periodic,
repeating array

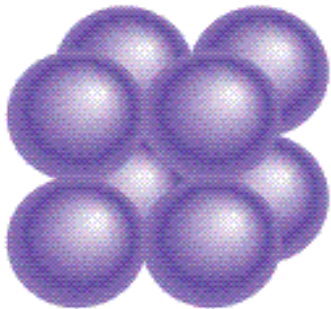
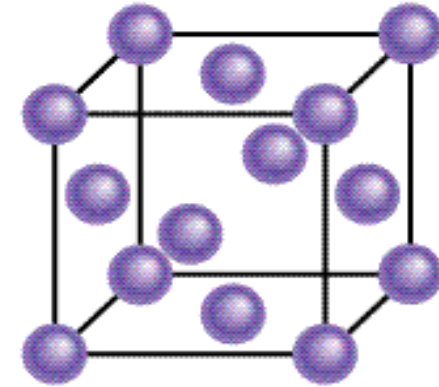
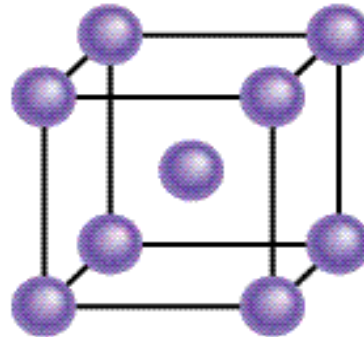
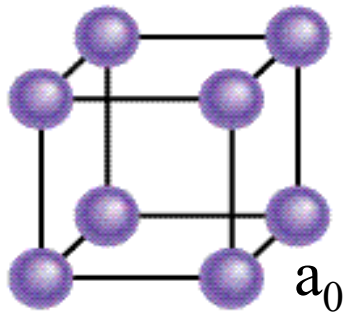
Lattice point – atom,
molecule, or fixed
arrangement of atoms,
or protein, fullerene, ...

Lattice Vectors span the
unit cell

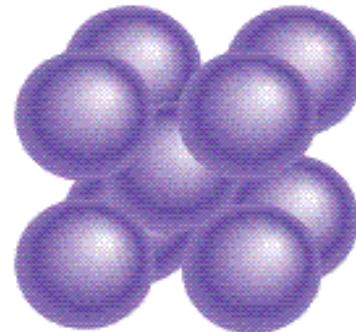
Crystal Lattice



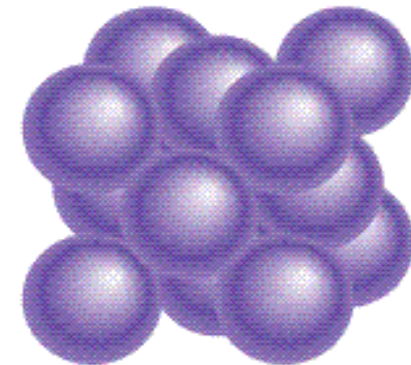
Three Types of Cubic Cells



Simple cubic

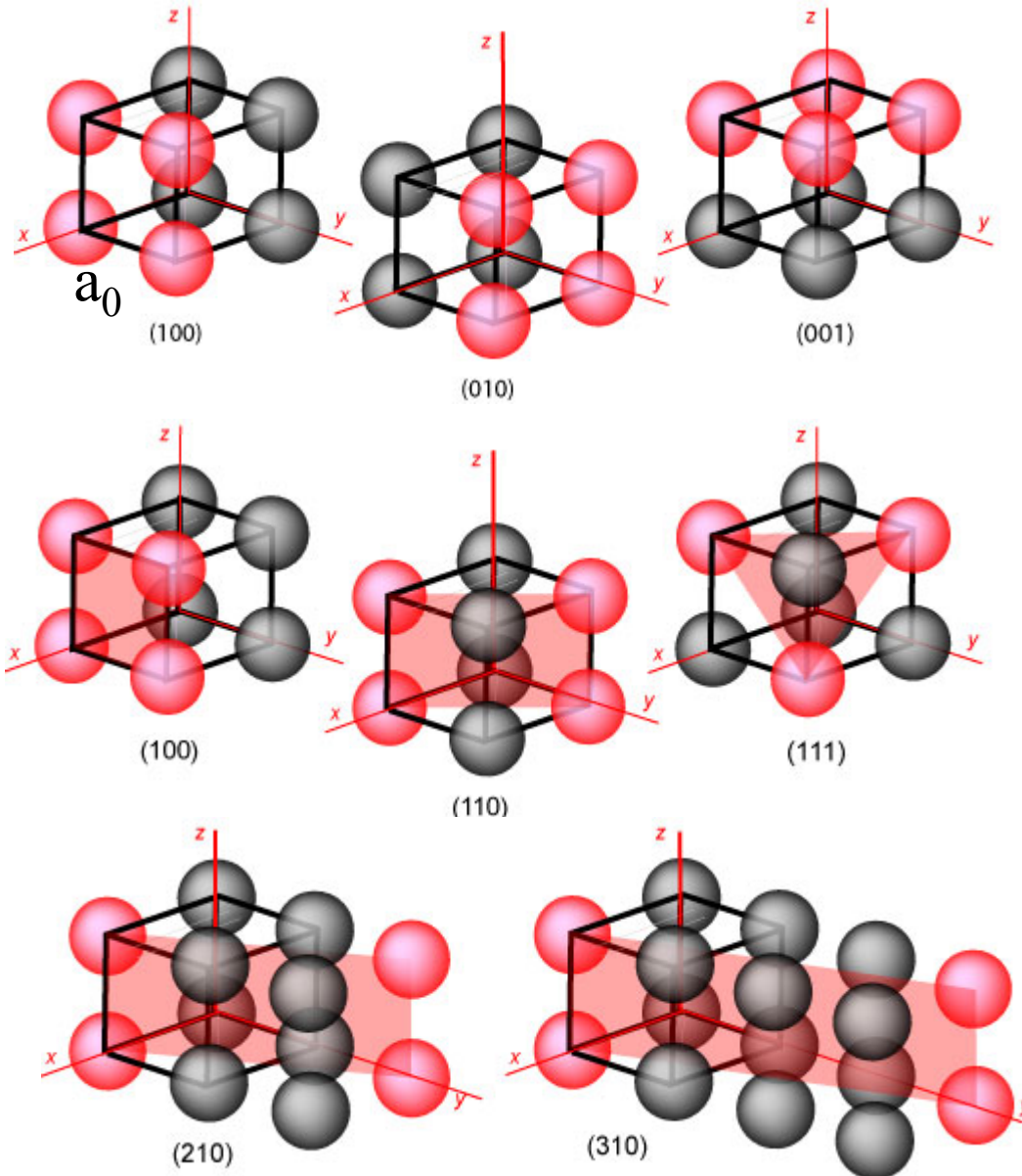


Body-centered cubic



Face-centered cubic

Crystal Planes



plane spacings (d):

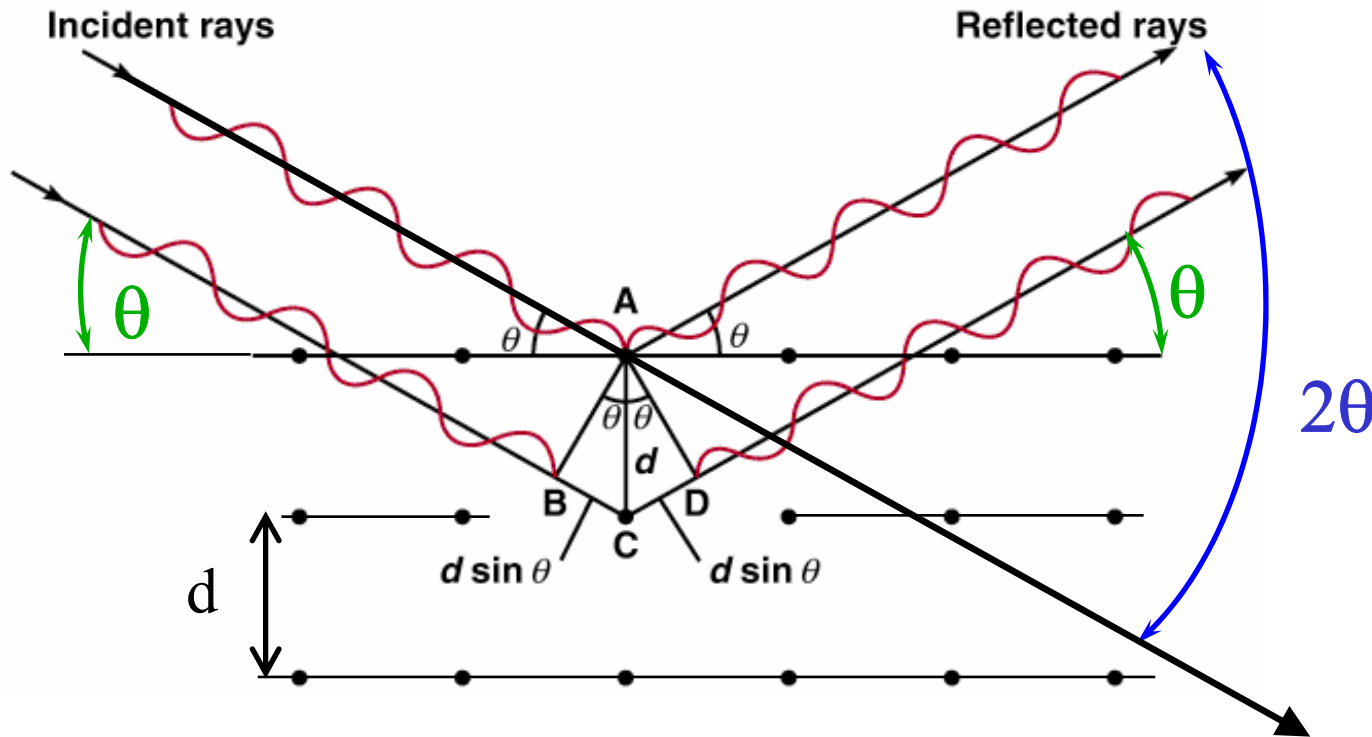
$$(100): d = a_0$$

$$(110): d = a_0/\sqrt{2}$$

$$(111): d = a_0/\sqrt{3}$$

$$(hkl): d = a_0/\sqrt{h^2 + k^2 + l^2}$$

Bragg's Law



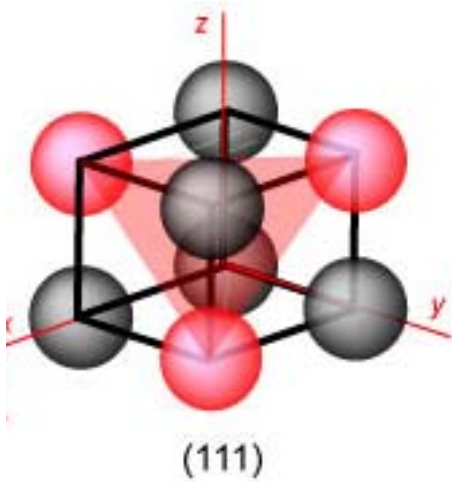
$2\theta =$
scattering angle

$\lambda =$ incident wavelength ($=hc/E$)

$$n \lambda = 2d \sin (\theta)$$

Bragg's Law:
constructive interference
of reflected X-rays

Bragg's Law

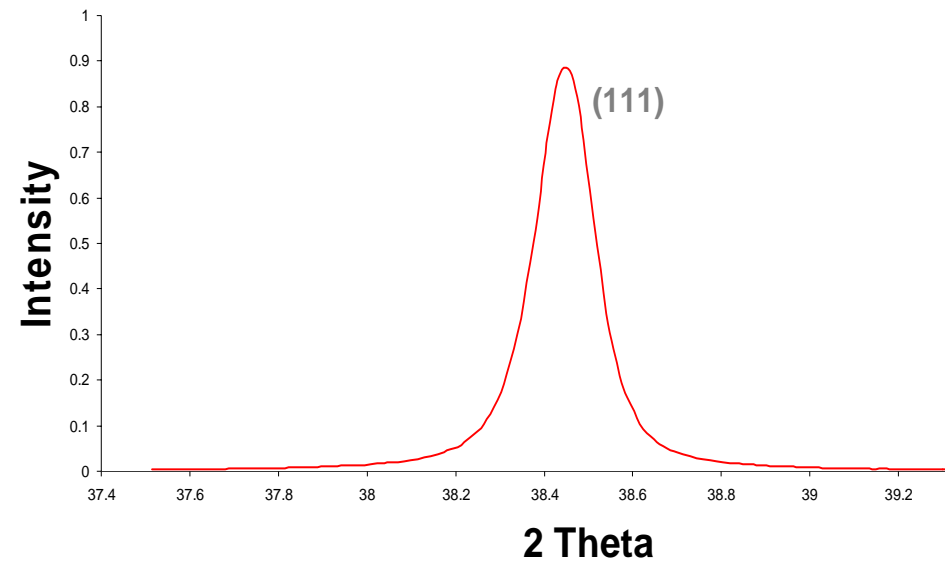
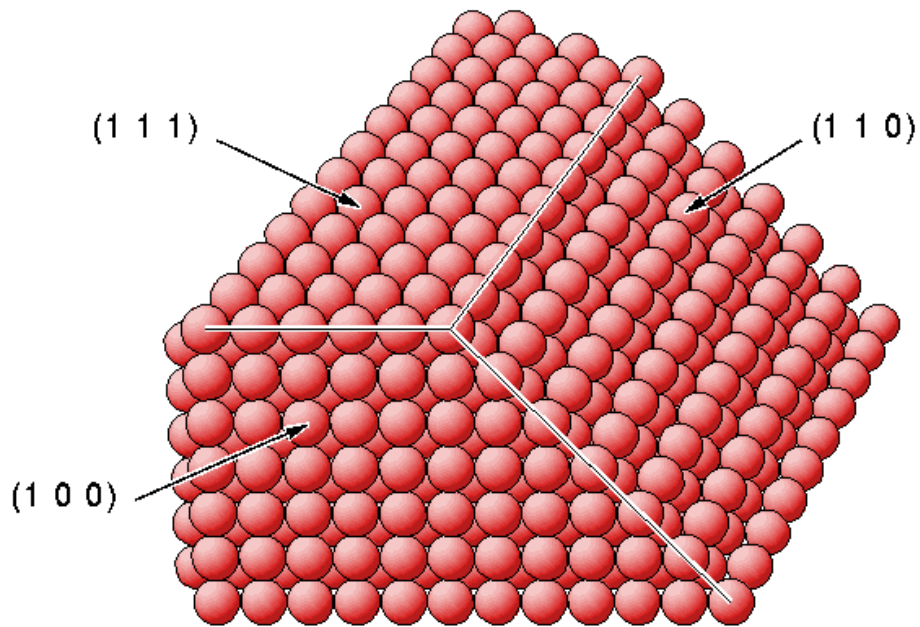


Au: $a_0 = 4.0786 \text{ \AA}$

$d(111) = 2.3548 \text{ \AA}$

for $\lambda = 1.5498 \text{ \AA}$,

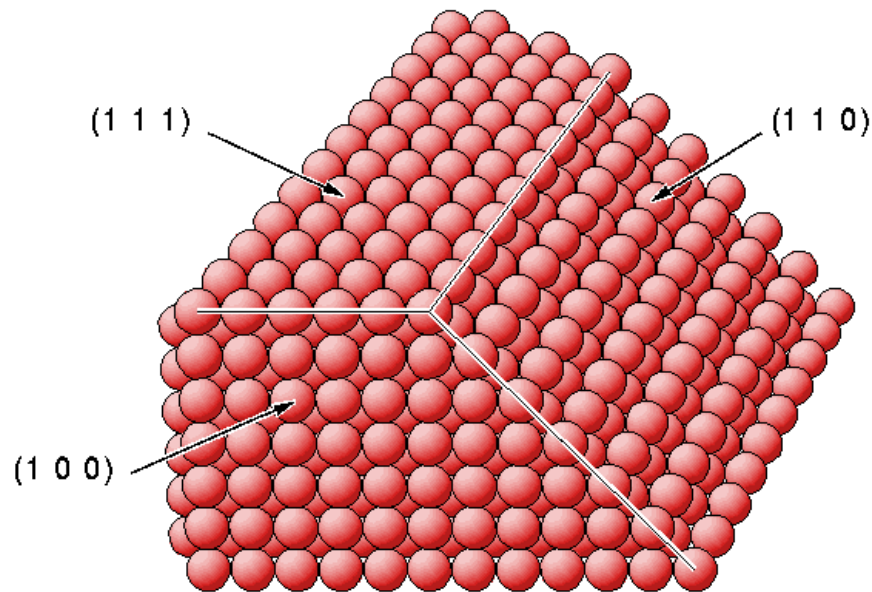
$2\theta = 38.425 \text{ deg.}$



Bragg's Law



$$n \lambda = 2d \sin(\theta)$$



need:

- crystal oriented to give diffracting planes perpendicular to incoming & diffracted X-rays
- incoming X-rays at θ
- diffracted X-rays at θ
- AND $n \lambda = 2d \sin \theta$

Reciprocal Lattice



Reciprocal: “complementary”

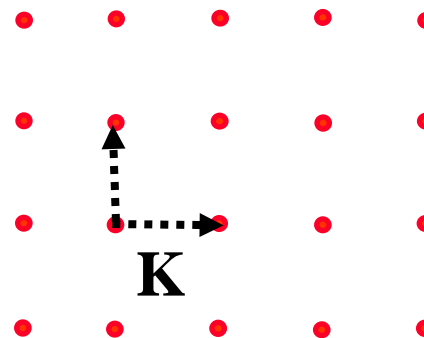
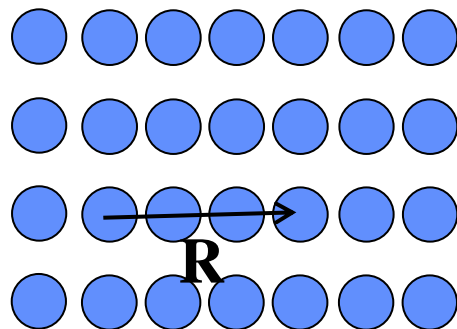
Webster’s Dictionary

The reciprocal lattice is set
of vectors \mathbf{K} so that:

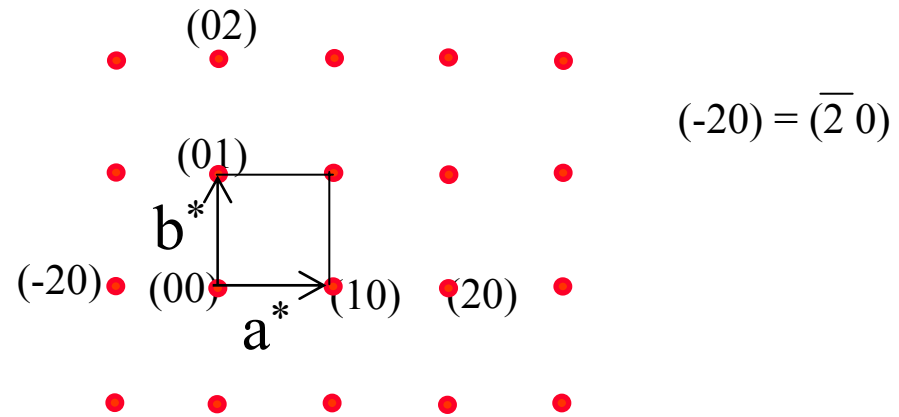
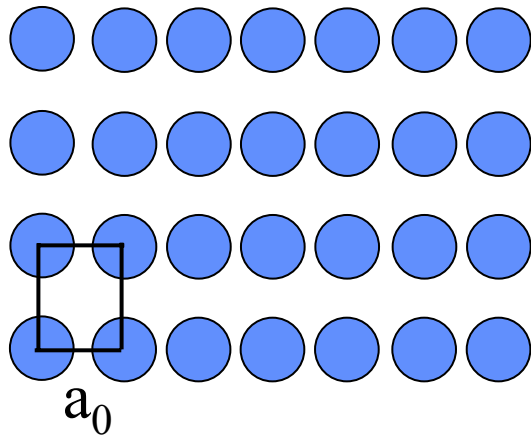
$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1,$$

where \mathbf{R} is any lattice vector

Reciprocal lattice (space):
language to describe
diffraction and scattering



Reciprocal Lattice



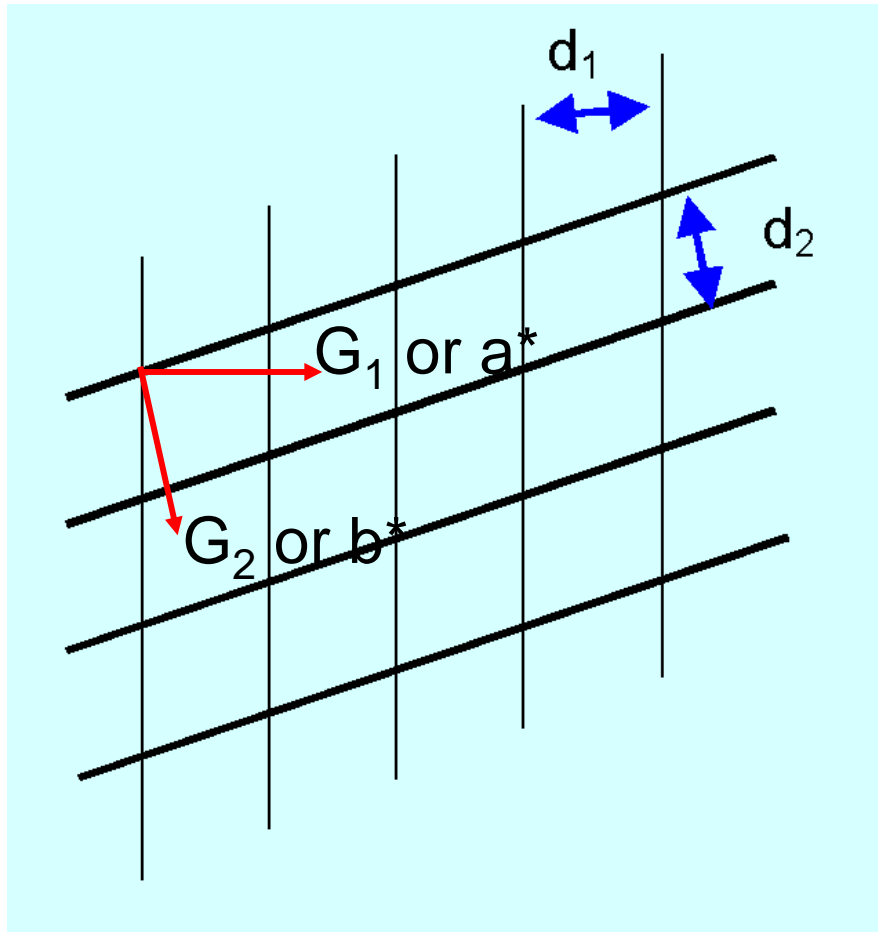
$$e^{i \mathbf{K} \cdot \mathbf{R}} = 1,$$

where \mathbf{R} is any lattice vector

$$a^* = 2\pi/a_0$$

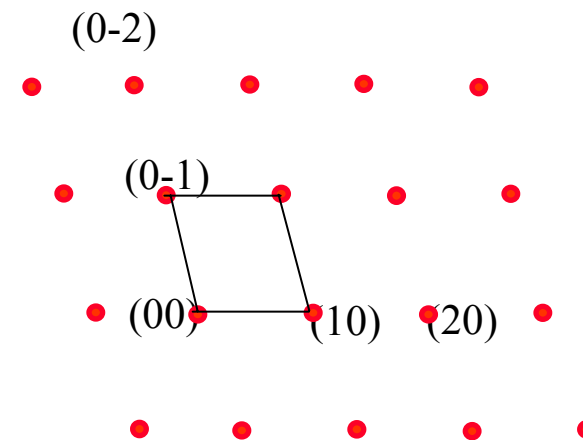
$$b^* = 2\pi/a_0$$

Reciprocal Lattice



$$G_1 \cdot d_1 = 2\pi$$

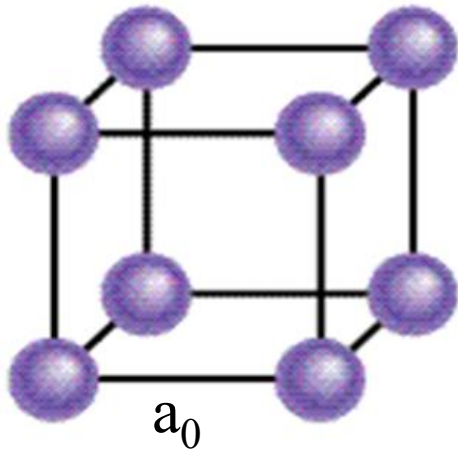
$$G_2 \cdot d_2 = 2\pi$$



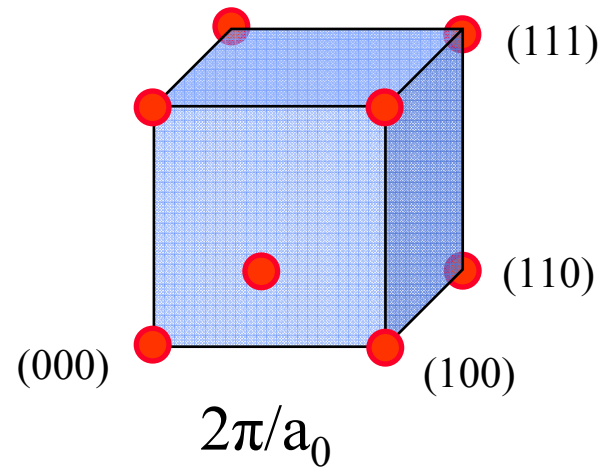
Reciprocal Lattice



real space:
simple cubic



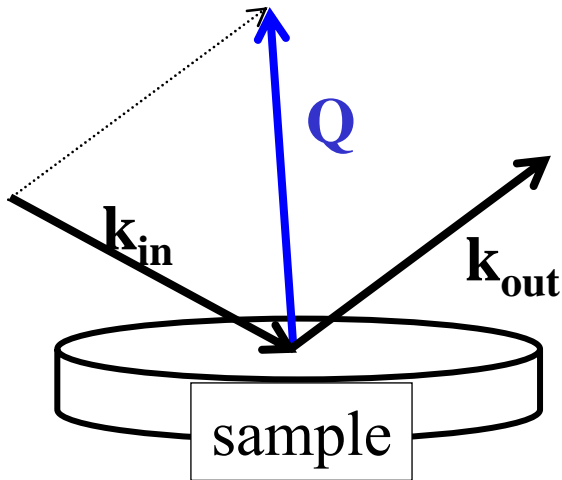
reciprocal space:
simple cubic



$$e^{i \mathbf{K} \cdot \mathbf{R}} = 1,$$

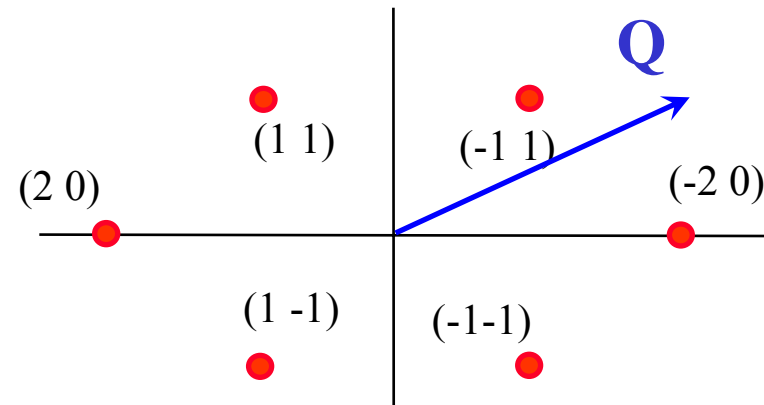
where \mathbf{R} is any lattice vector

Reciprocal Lattice & Diffraction



- Constructive interference of X-rays (diffraction peaks) requires that $e^{i\mathbf{Q}\cdot\mathbf{R}} = 1$.
- So $\mathbf{Q} = \mathbf{K}$, where \mathbf{K} is a reciprocal lattice vector

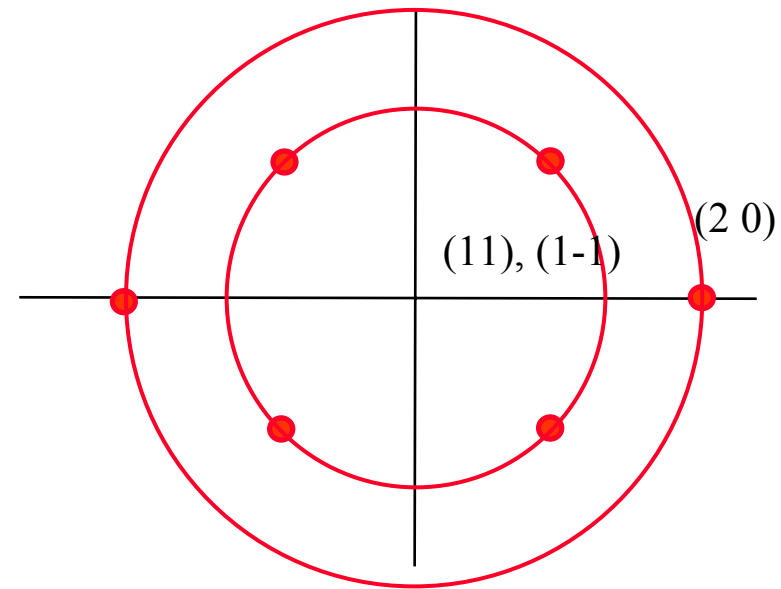
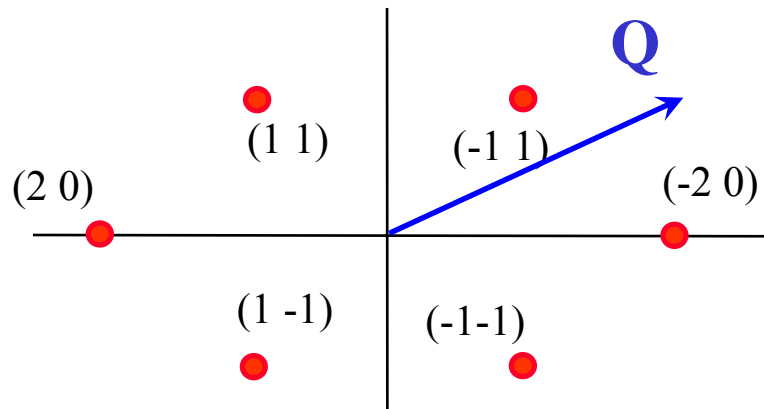
\mathbf{Q} = scattering vector
 $= \mathbf{k}_{in} - \mathbf{k}_{out}$



Reciprocal Lattice



Diffraction: $\mathbf{Q} = \mathbf{K}$



Stringent condition!

- Rotating crystal (macromolecular crystallography)
- Powder diffraction
- Live with it (single crystal)

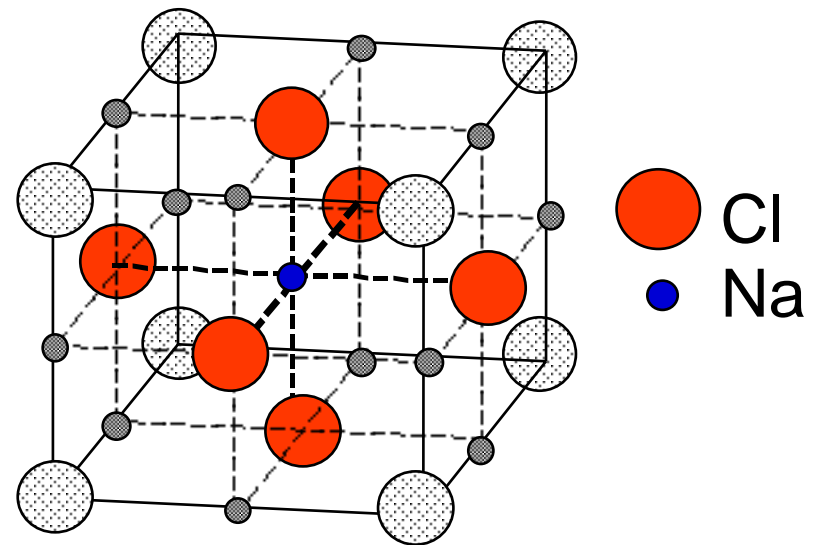
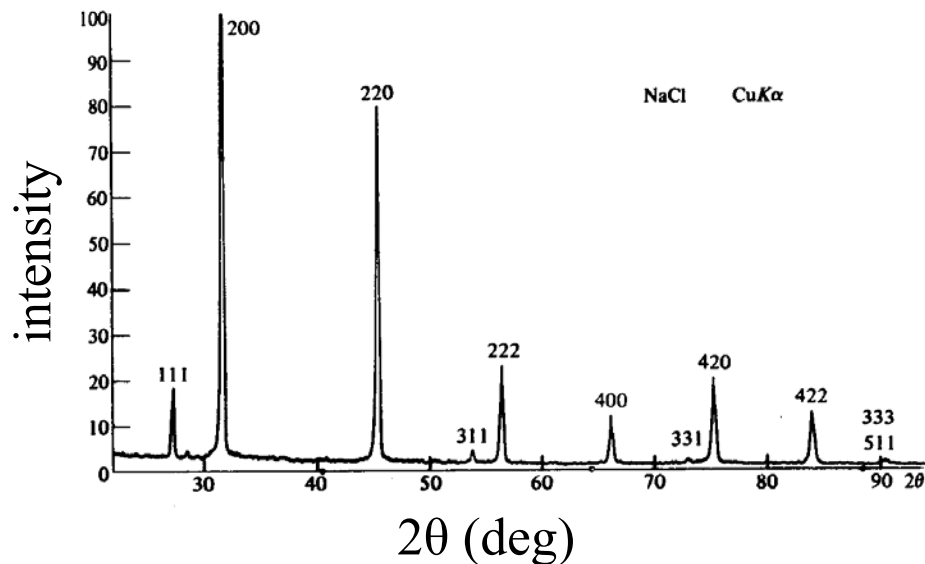
Diffraction Intensities



I have neglected something important.

What have I missed?

Diffraction intensities: These depend on atomic positions within the unit cell. => Crystallography



Diffraction Intensities



The structure factor, F , is defined as:

$$F = \sum_n f_n e^{i\vec{Q}\cdot\vec{r}_n}$$

$$\text{Intensity} = |F|^2$$

where f_n is the atomic scattering factor;

Phase problem

\vec{r}_n is the position of the n^{th} atom in the unit cell.

Explain better & show x , y , z and h k l

This can be reduced to:

$$F = \sum_n f_n e^{(2\pi i)(hx_n + ky_n + lz_n)}$$

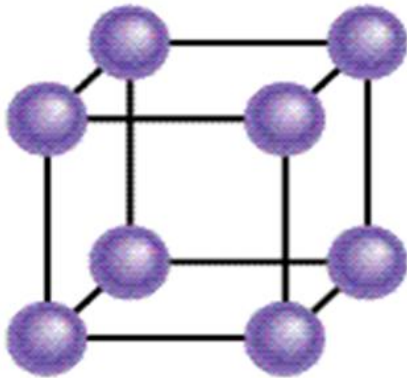
where $\vec{r}_n = (x_n + y_n + z_n)$

and h, k, l are peak indices.

Diffraction Intensities



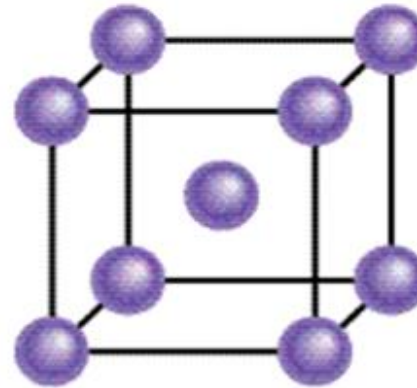
$$F = \sum_n f_n e^{(2\pi i)(hx_n + ky_n + lz_n)}$$



Simple cubic lattice:

$$(x, y, z) = (0, 0, 0)$$

$$\Rightarrow F = f_n$$



bcc lattice:

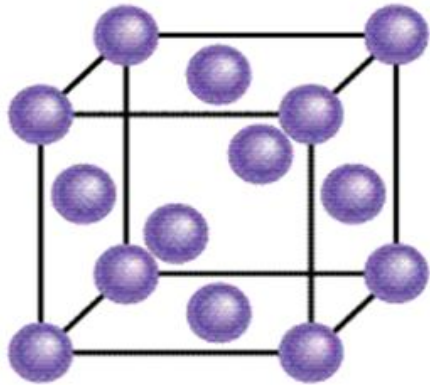
$$(x, y, z) = (0, 0, 0) \text{ \& } (1/2, 1/2, 1/2)$$

$$\Rightarrow F = f_n \{1 + e^{i\pi(h+k+l)}\}$$

$$\Rightarrow F = 2 f_n \text{ for } h+k+l = \text{even}$$

$$= 0 \text{ otherwise}$$

Diffraction Intensities



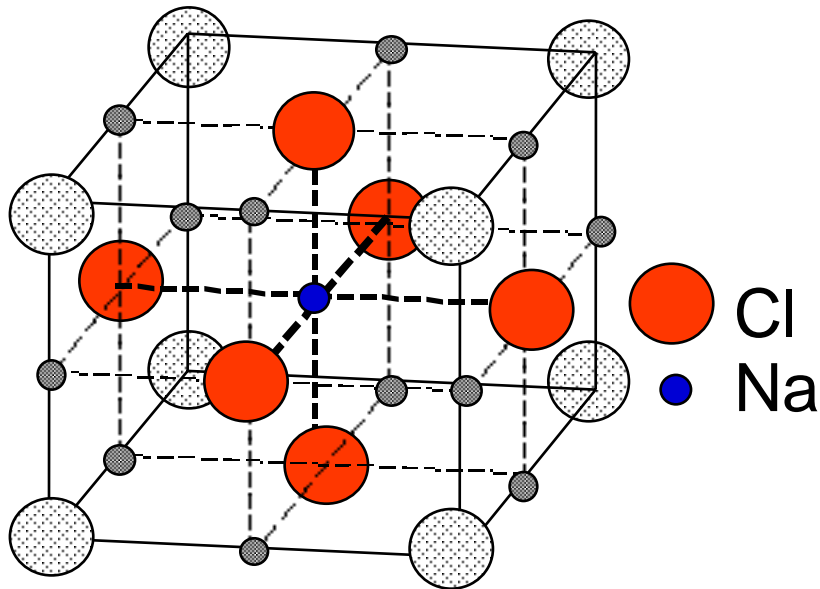
fcc lattice:

$$(x, y, z) = (0, 0, 0), \left(\frac{1}{2}, \frac{1}{2}, 0\right), \\ \left(\frac{1}{2}, 0, \frac{1}{2}\right) \text{ \& } \left(0, \frac{1}{2}, \frac{1}{2}\right)$$

$$\Rightarrow F = f_n \{1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + \\ e^{i\pi(k+l)}\}$$

$$\Rightarrow F = 4f_n: h,k,l \text{ all even or odd} \\ = 0, \text{ otherwise}$$

Polyatomic Crystal: Rock Salt



like fcc lattice:

Na at $(0, 0, 0)$

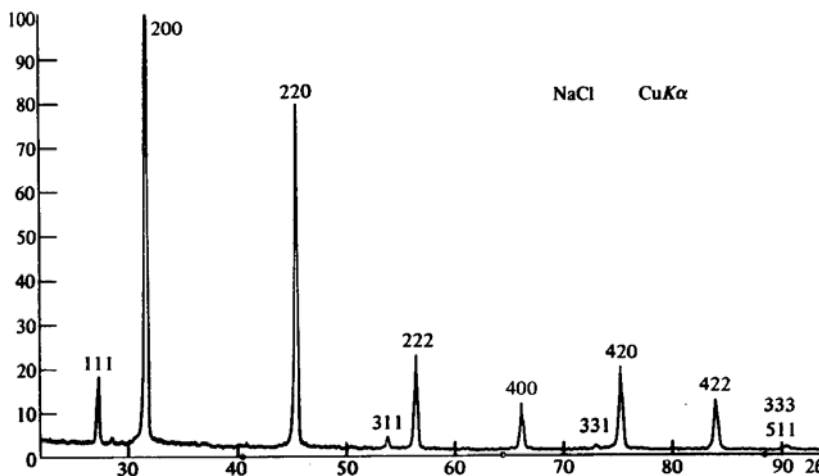
Cl at $(\frac{1}{2}, 0, 0)$

$$\Rightarrow F = \{f_{\text{Na}} + e^{i\pi h} f_{\text{Cl}}\} F_{\text{fcc}}$$

$$\Rightarrow F = 4 \{f_{\text{Na}} + f_{\text{Cl}}\} F_{\text{fcc}} : h, k, l \text{ even}$$

$$= 4 \{f_{\text{Na}} - f_{\text{Cl}}\} F_{\text{fcc}} : h, k, l \text{ odd}$$

$$= 0, \text{ otherwise}$$

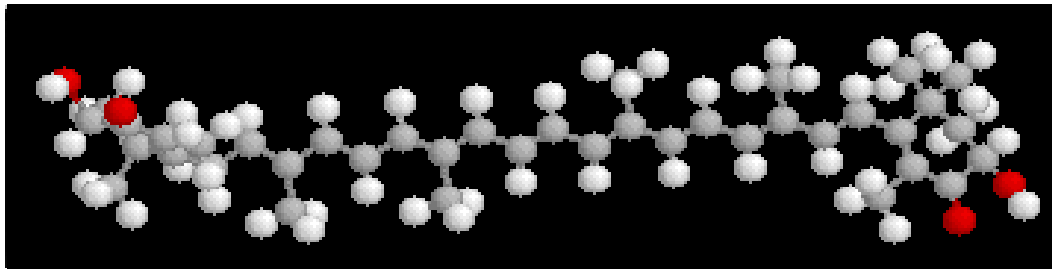


Macromolecular Crystallography



Macromolecule = big molecule,
mostly biological.

Protein, virus, vitamins, ...

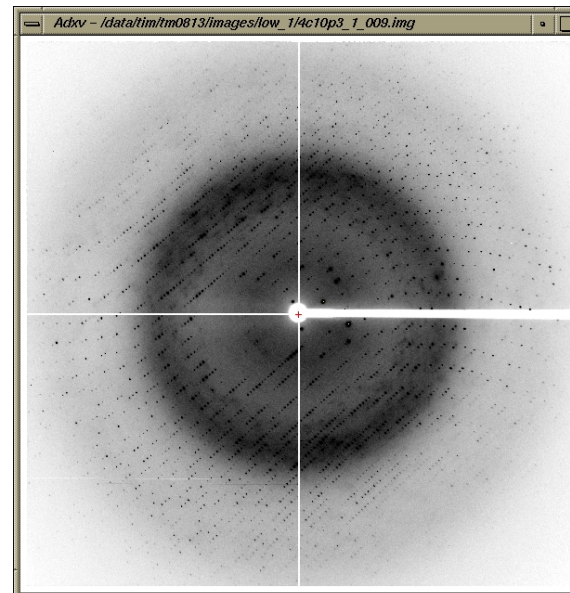
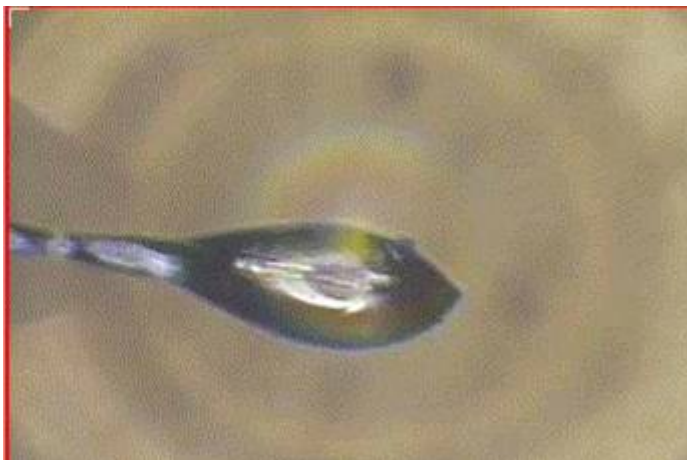
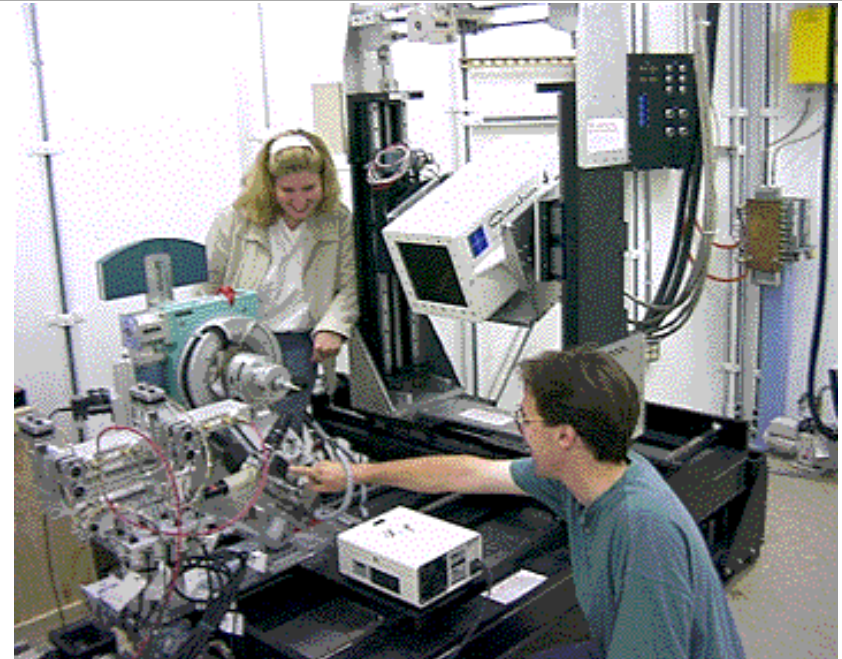
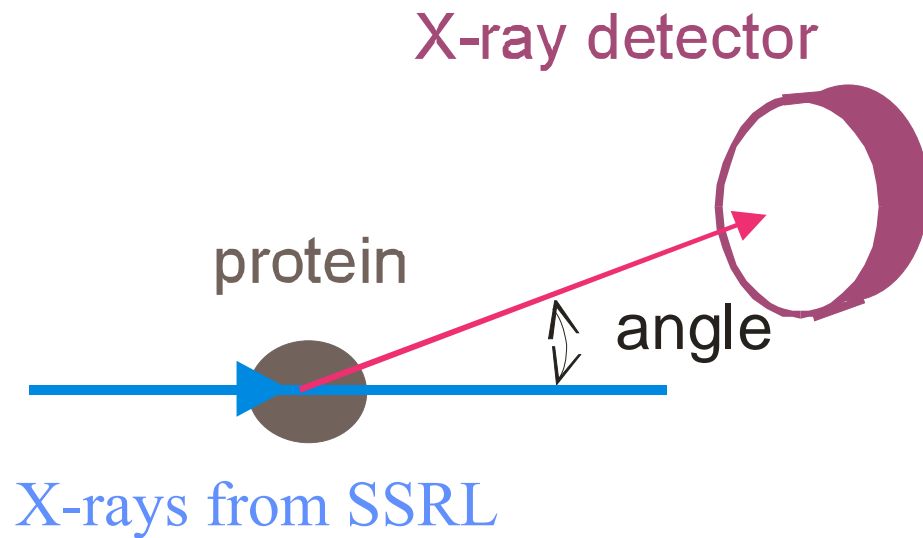


astaxanthin
pigment

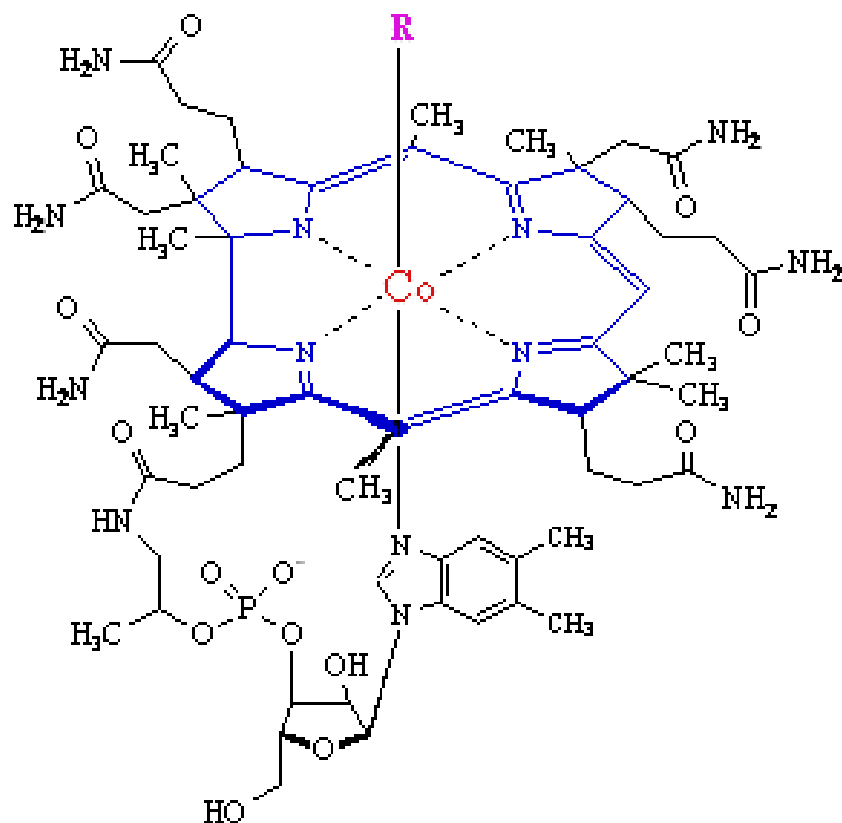
- = oxygen
- = carbon
- = hydrogen

Molecular structure
determines function,
how it works

Macromolecular Crystallography



Vitamin B12



Vitamin B12
Solved in 1956

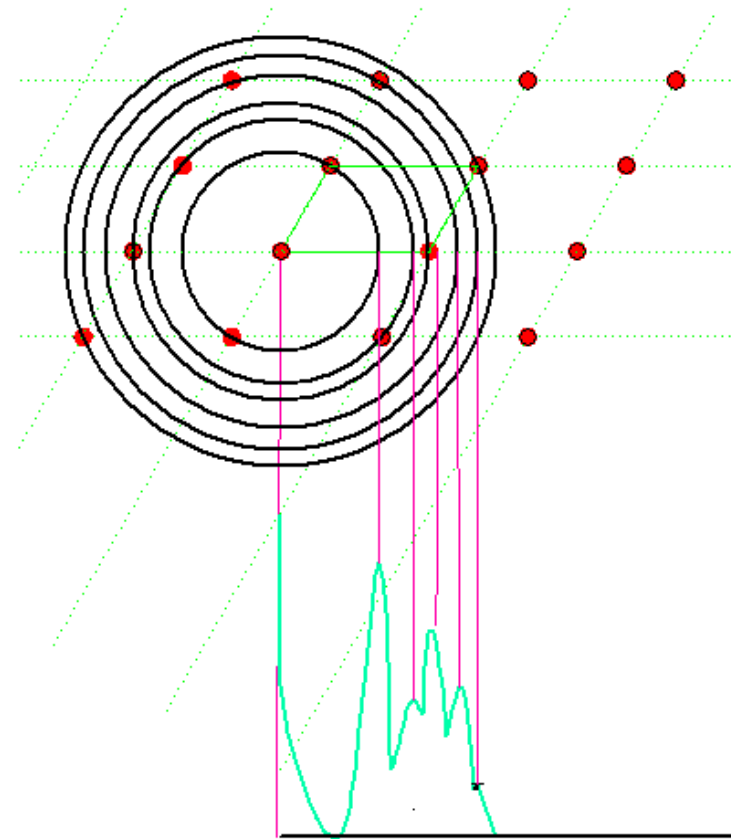
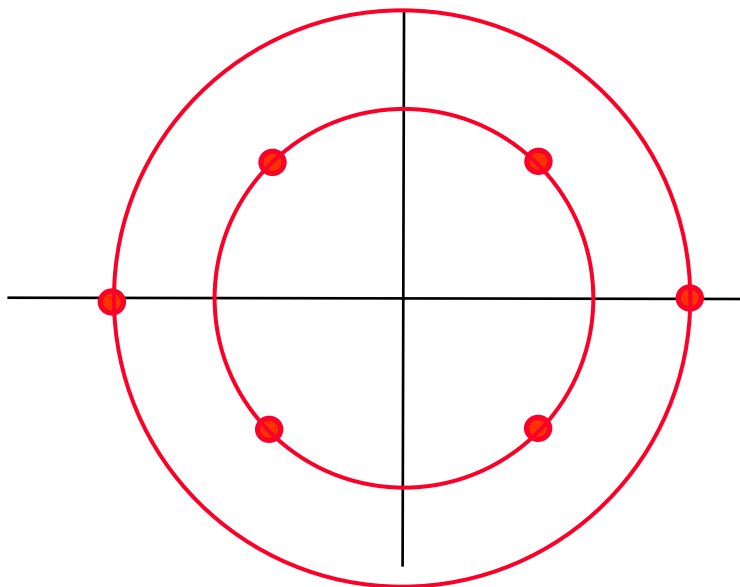
Dorothy Hodgkin (1910-1994)
Nobel Prize, 1964



Powder Diffraction



“Powder” average by
random orientation of
crystals



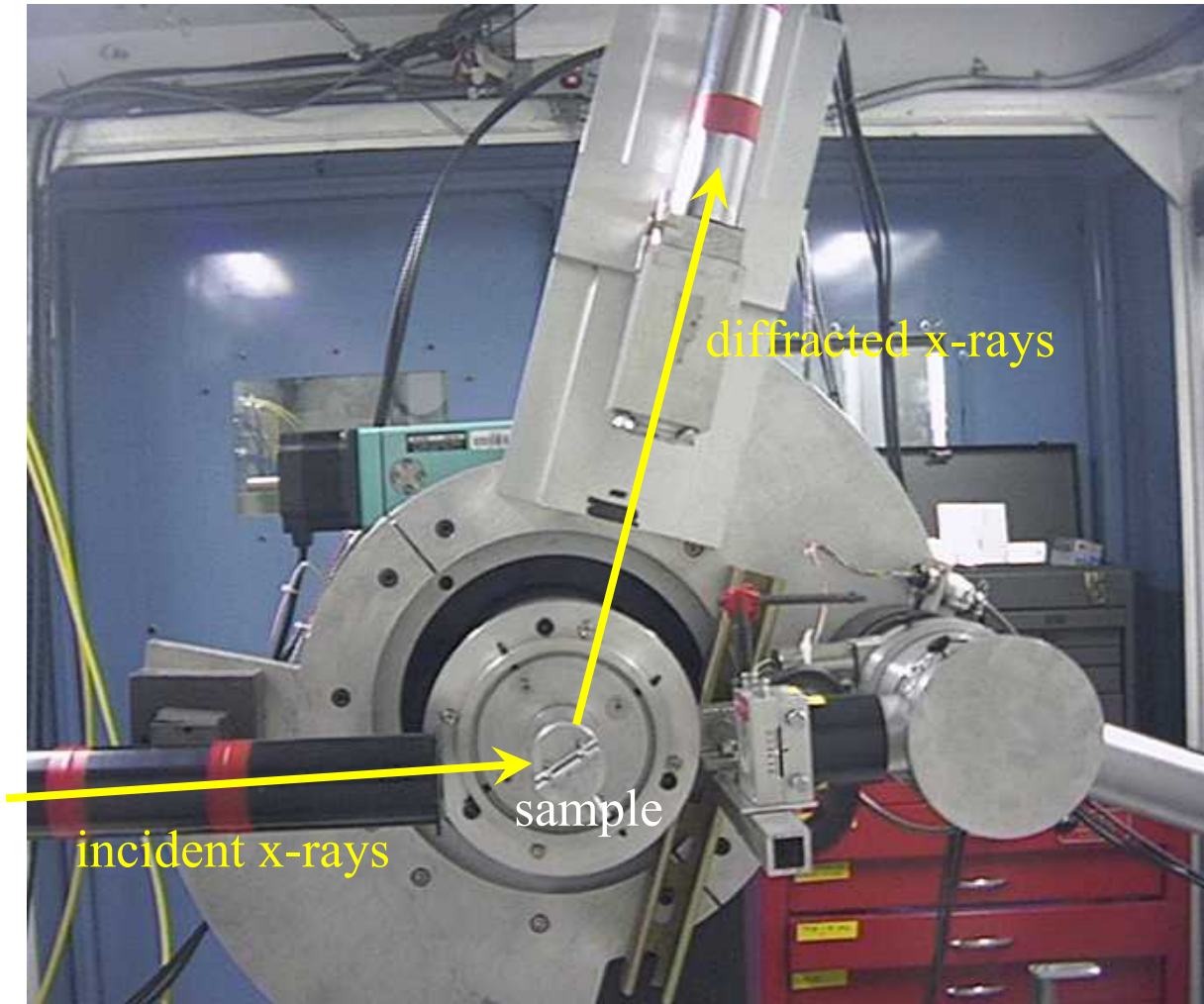
Problems due to
peak overlap

Powder Diffraction



SSRL 2-1:

Dedicated for
powder diffraction



Powder Diffraction: Zeolites



Zeolites: microporous aluminosilicates used as catalysis, adsorbents,

Rare single crystals

SSZ-58: novel zeolite developed by Chevron-Texaco Research

SSZ-58 structure 'solved' with advanced *ab initio* methods

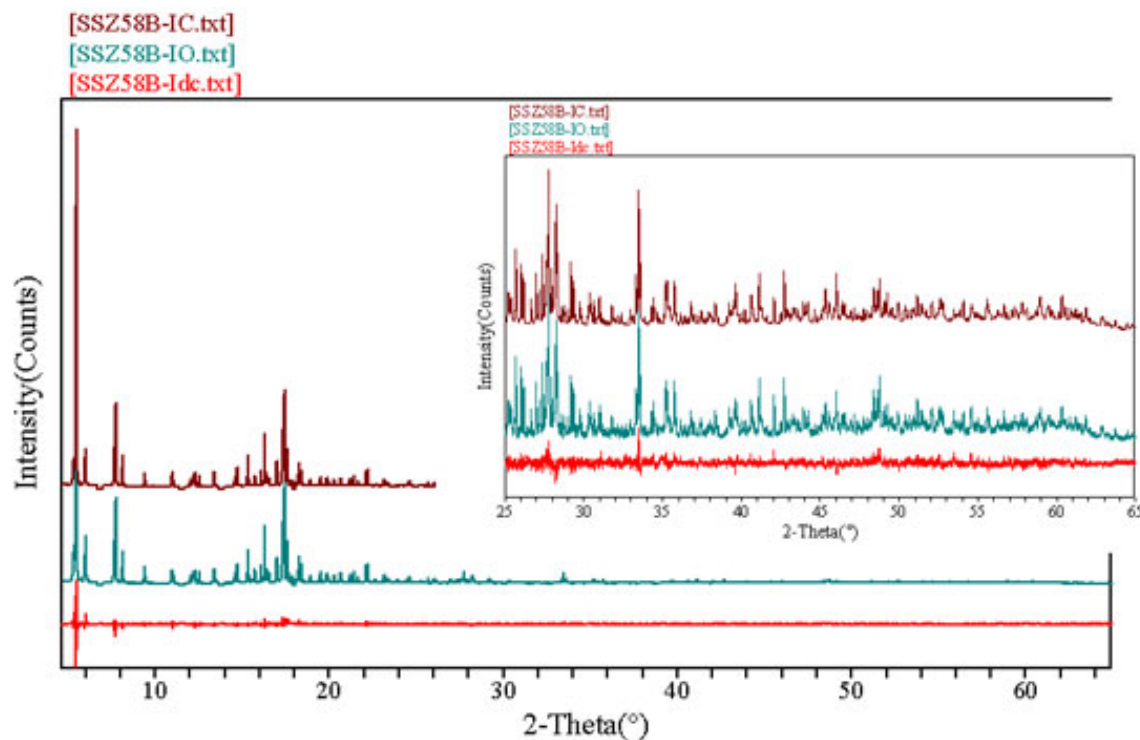


Figure 1. The simulated, experimental, and difference profiles of the synchrotron powder x-ray diffraction pattern ($\lambda = 1.1996$ Angstrom) of SSZ-58.

A Burton et al., JACS 125, 1633 (2003)

Powder Diffraction

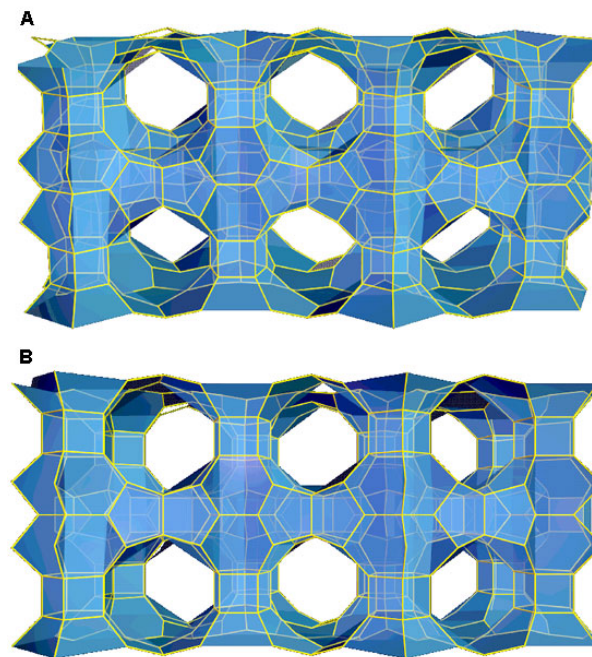
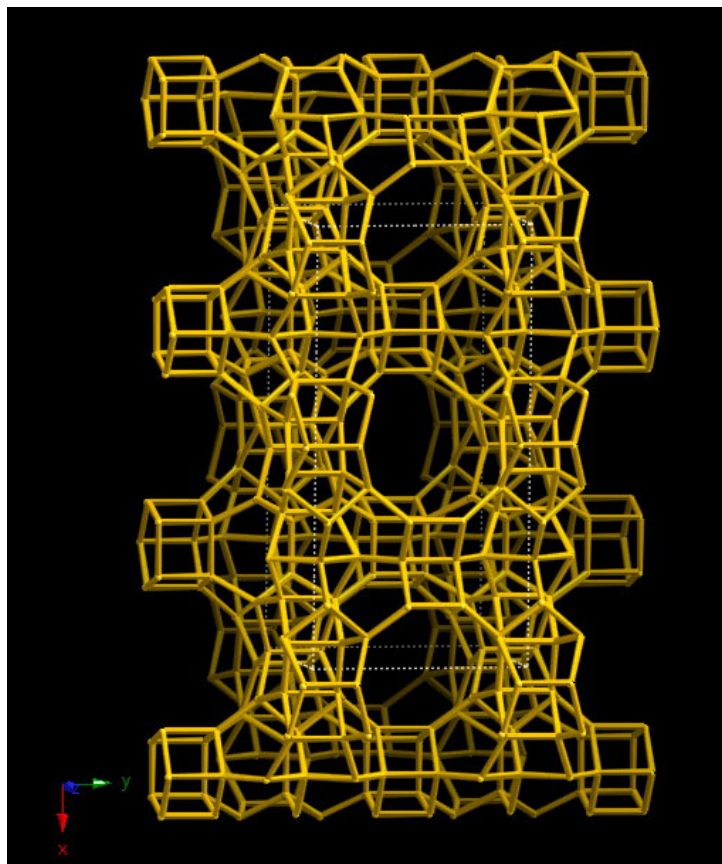


Figure 2. Models showing the two-dimensional pore system in SSZ-58 (a) along the c-axis and (b) along the a-axis. Tetrahedral atoms are represented by intersections of line segments. Oxygen atoms have been removed for visual clarity.

10-membered ring pores
huge surface area

A Burton et al., JACS 125, 1633 (2003)

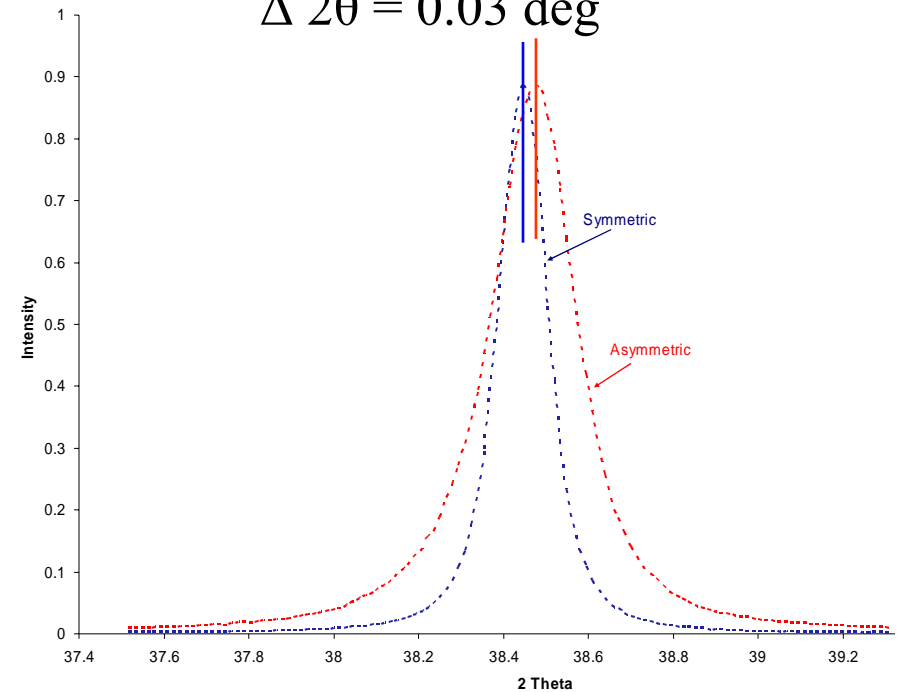
Diffraction Measurements of Strain



Many materials properties depend on strain: magnetostriction, mobility, pizeoelectricity

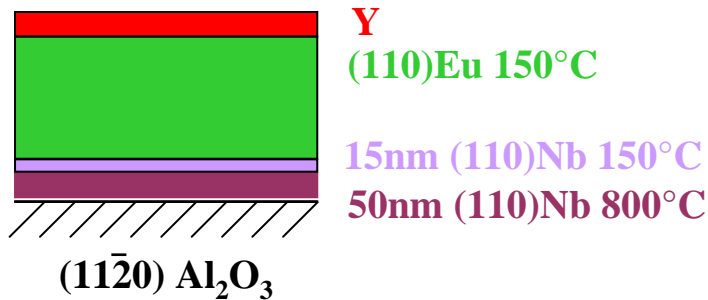
X-ray diffraction provides a very accurate & precise method of strain measurement

$\Delta 2\theta = 0.03$ deg

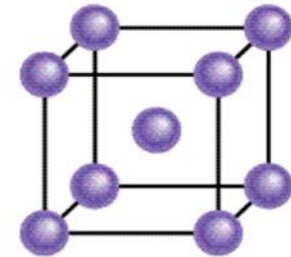


- $Q = (4\pi/\lambda) \sin \theta$
- typical 2θ resolution is 0.001-0.1 deg
- gives Q resolution of 0.0001-0.01 \AA^{-1}
- translates to d resolution of 0.005-0.00005 \AA (0.5-0.005 pm)

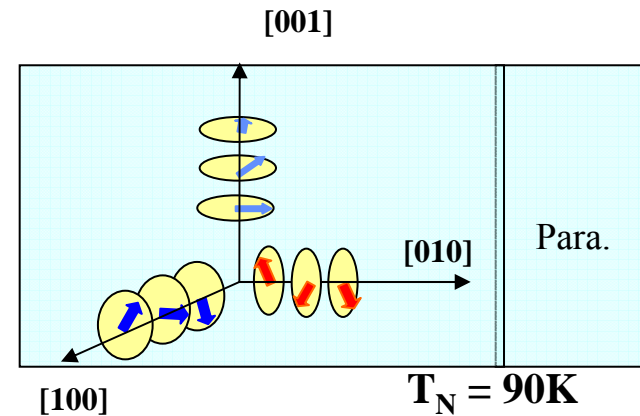
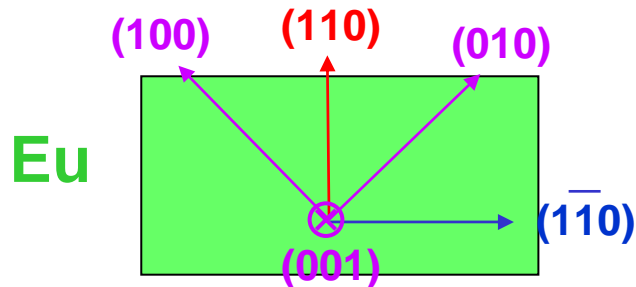
Eu Thin Films: Strain



Bulk Eu: bcc



Molecular beam epitaxy ($4 \cdot 10^{-11}$ Torr)

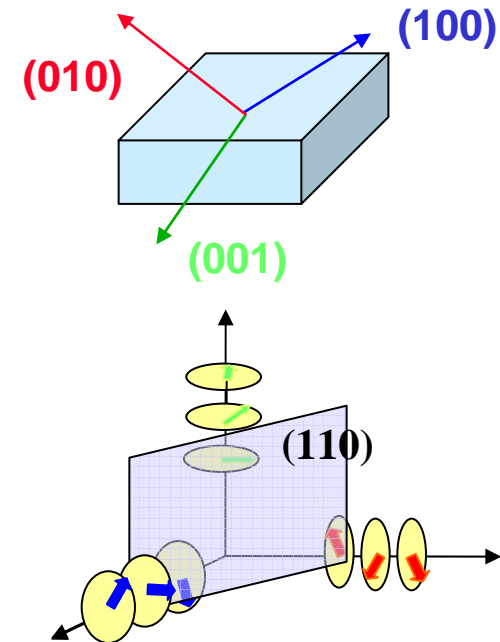
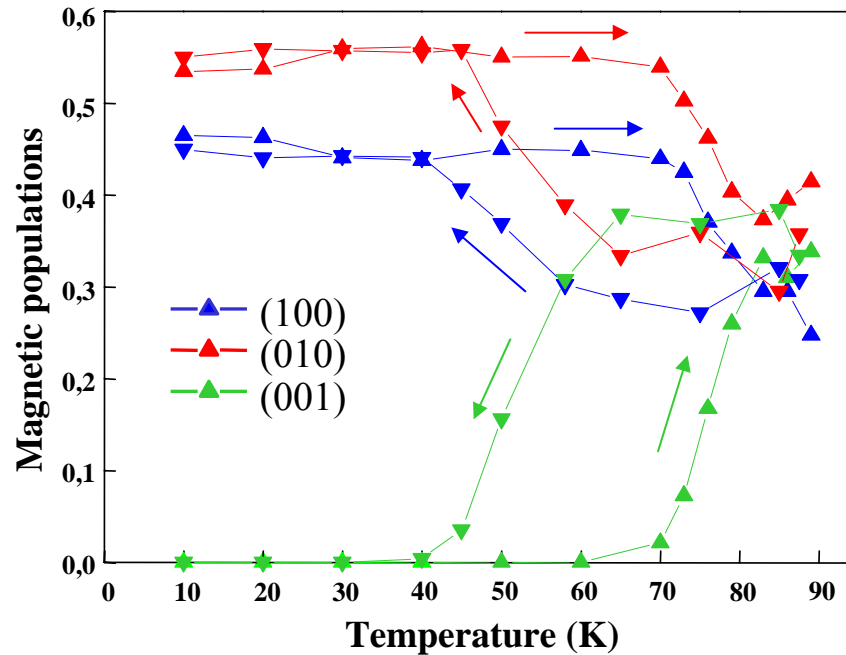


S. Soriano, K. Dumesnil, C. Dufour, T. Gourieux, A. Stunault, M. Hennion, J.A. Borchers, Ph. Mangin, Laboratoire de Physique des Matériaux (LPM) – Nancy, Institut Laue Langevin (ILL) – ESRF - Grenoble, Laboratoire Leon Brillouin (LLB) (Saclay), NIST Center for Neutron Research (NCNR)

Magnetic State of Eu Thin Films



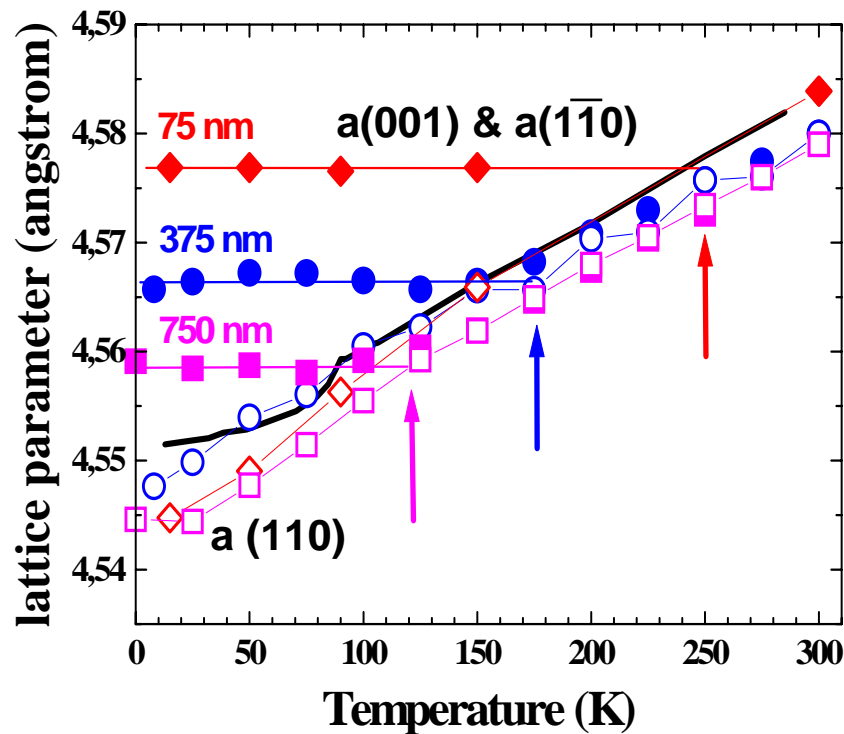
375 nm thick films



- Disappearance of one of the magnetic helices ($\tau//[001]$) in favor of the two others: $\tau//[100]$ and $\tau//[010]$
- Thermal hysteresis

RXMS
ESRF - BM28
Eu L₂ edge

Eu Thin Films: Lattice Clamping



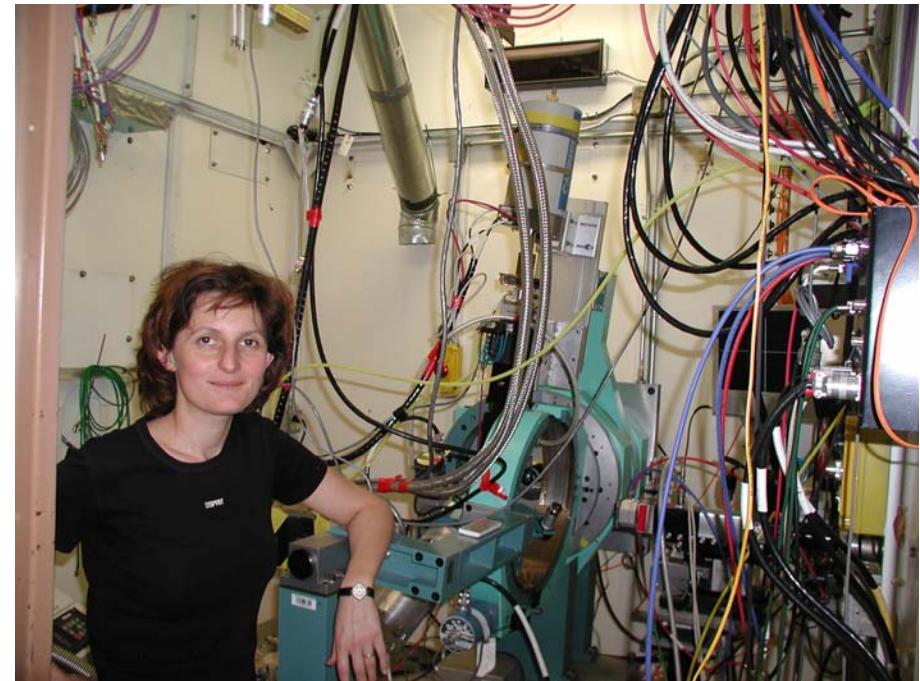
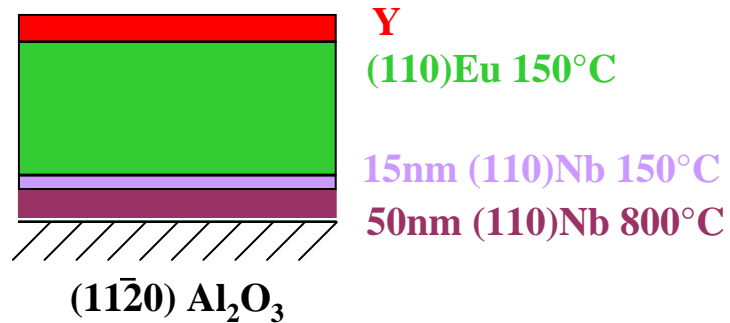
neutron diffraction data

- $a_{\perp} = a_{(110)}$: match bulk 300K-10K
- $a_{//} = a_{(002)} = a_{(110)}$:
 - match bulk $T > T_{cl}$
 - for $T < T_{cl}$ constant to 10 K
- T_{cl} depends on the film thickness
- The amplitude of the strains increase with decreasing temperature and reduced film thickness.

Eu Thin Films: Strain



- Use diffraction to accurately assess strain state
- Depth dependent strain

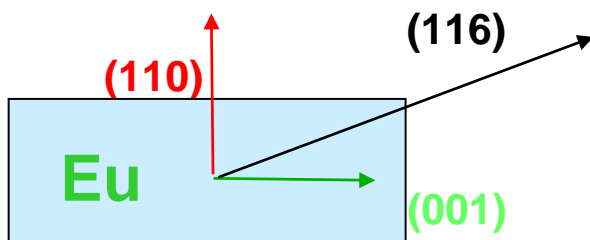
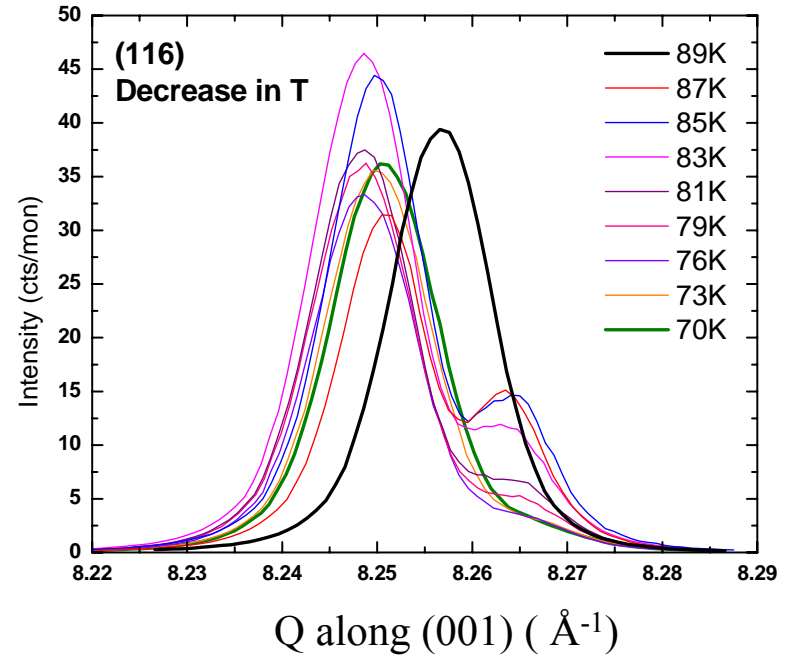
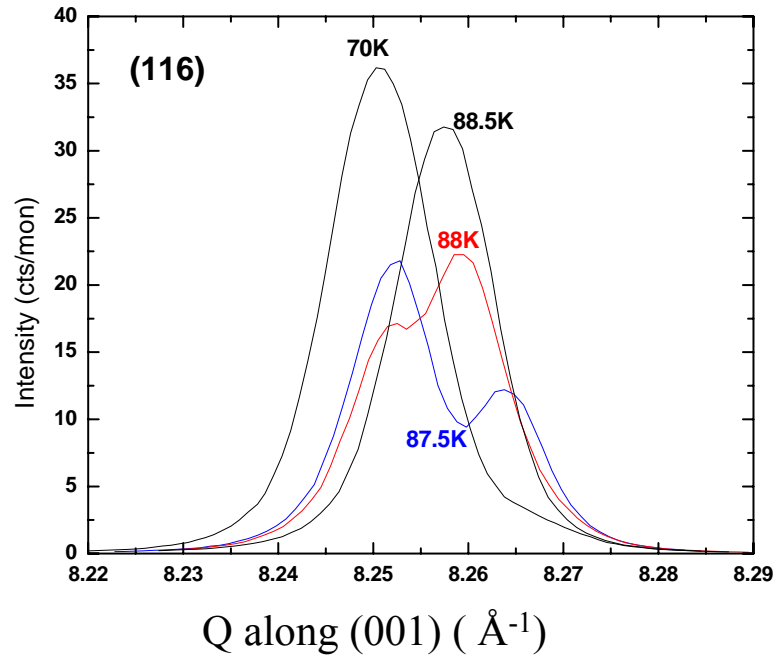


Karine Dumesnil, Université H. Poincaré - Nancy, France on SSRL beam line 7-2

Eu Thin Films: Strain

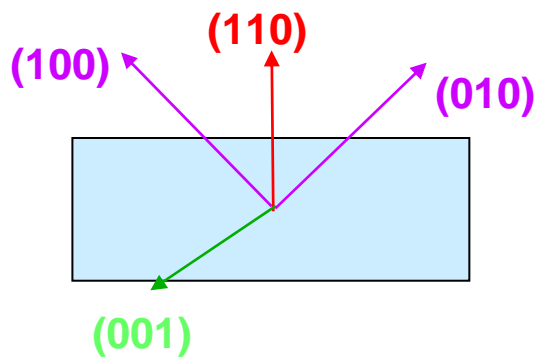


decreasing temperature



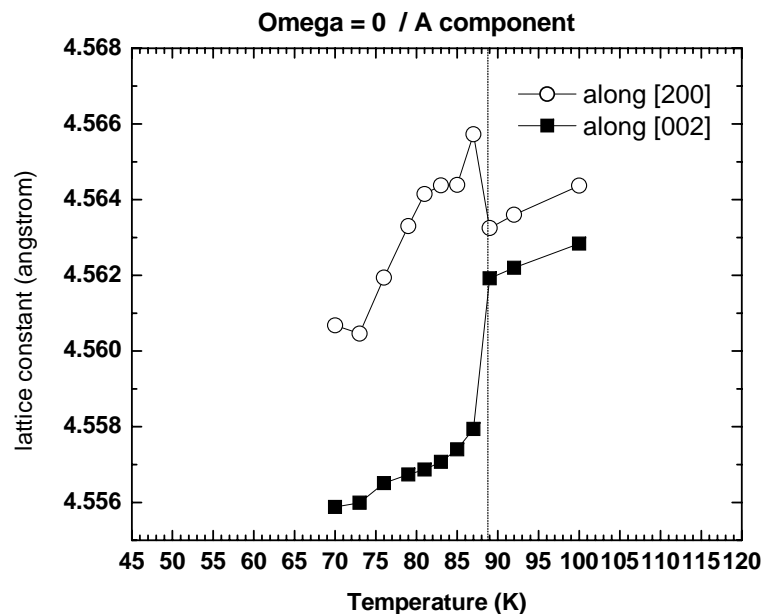
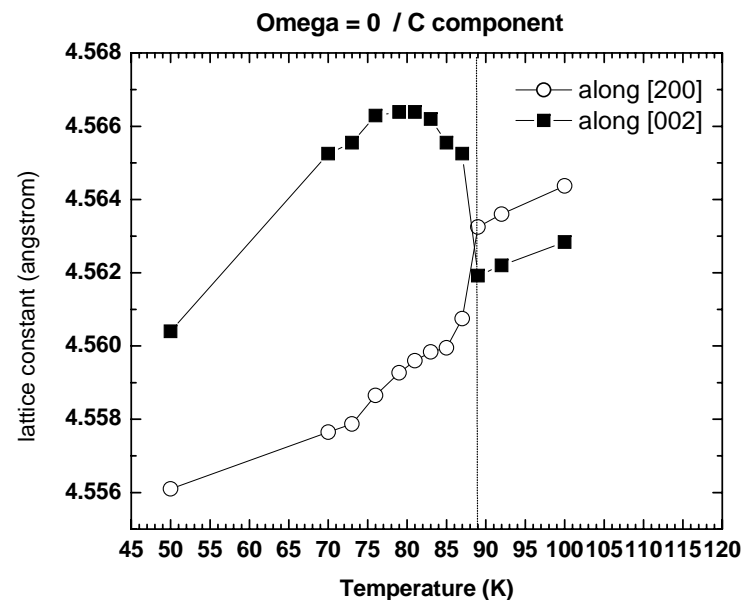
=> two domains with different strain states

Eu Thin Films: Strain

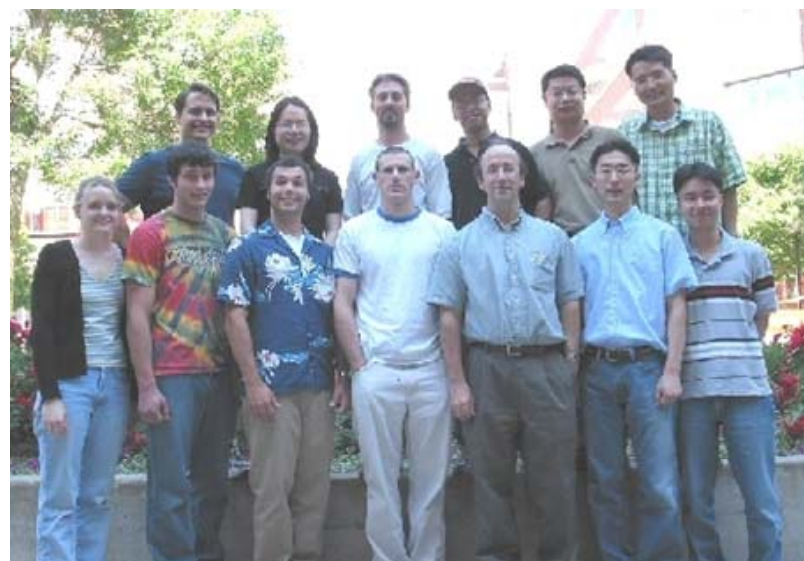


Domain C: (100) and (010)
compressed compared to (001)

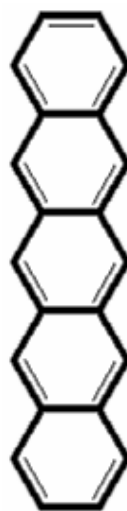
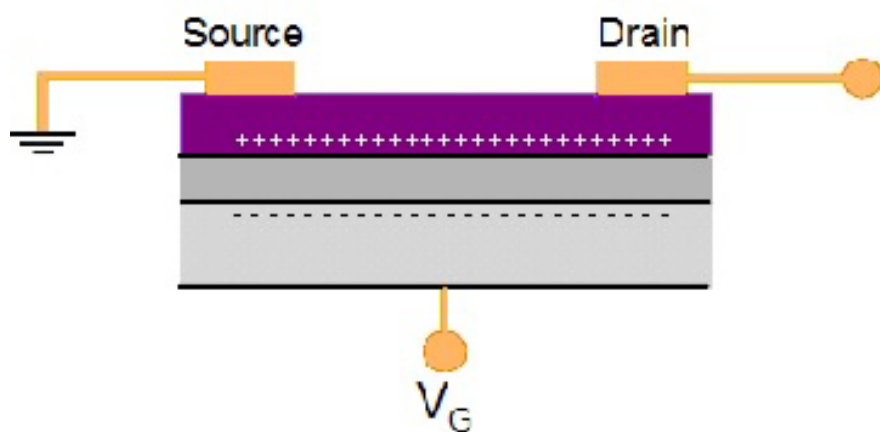
Domain A: (001) compressed
compared to (100) and (010)



Organic Thin Films



Organic FET

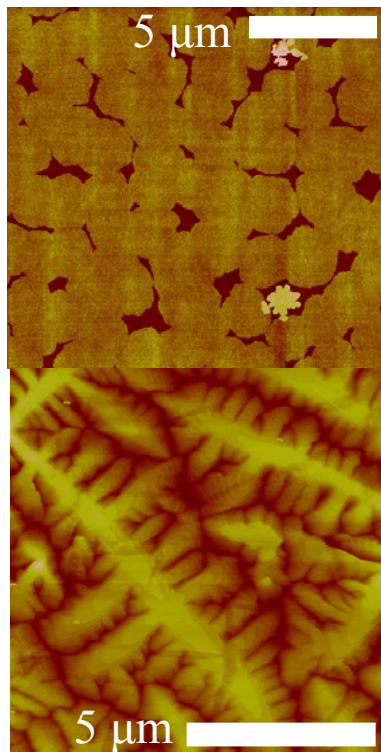


Sandra Fritz,
C. Daniel Frisbie,
Mike Ward,
Chemical Engineering
and Materials Science
University of Minnesota

Pentacene Thin Films



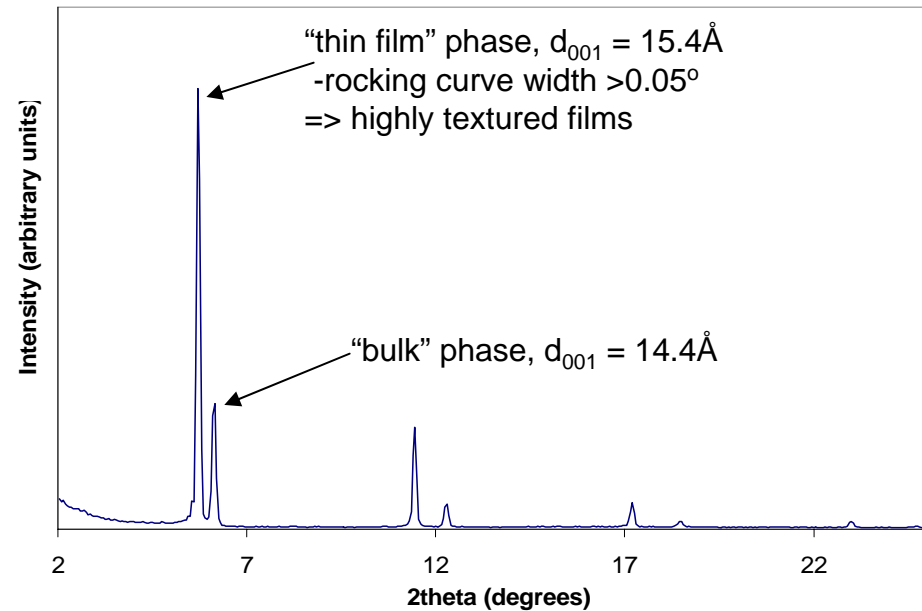
- Thermal evaporation of pentacene
- Film morphology and structure dependant on substrate temperature, deposition rate and film thickness



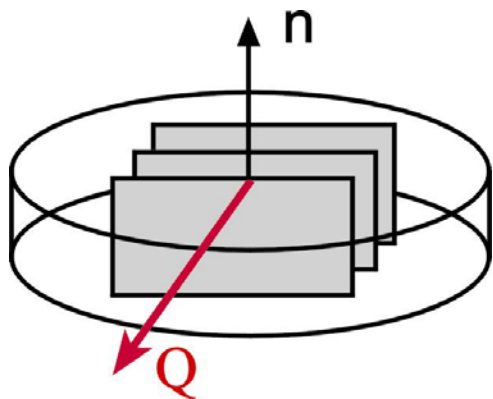
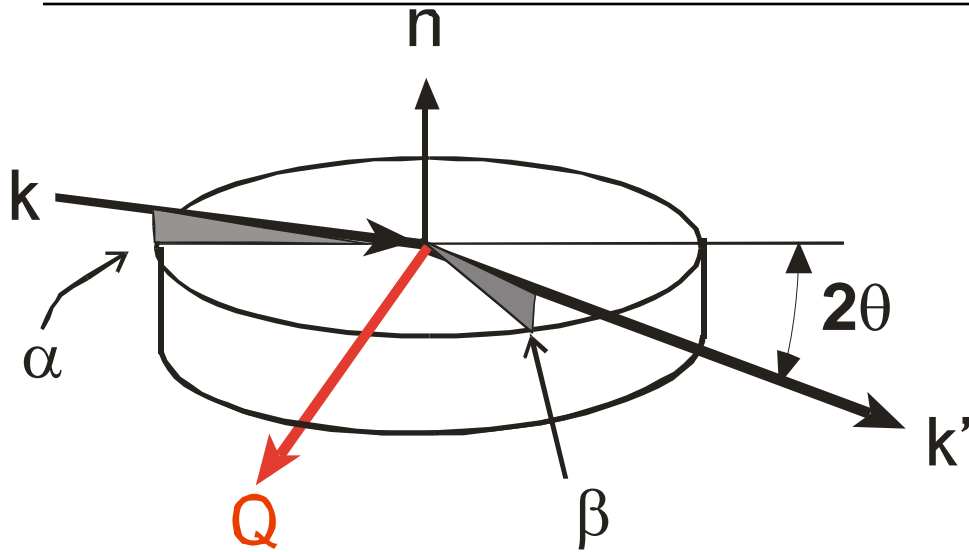
1.5 nm - one layer

30 nm – ca 15 layers

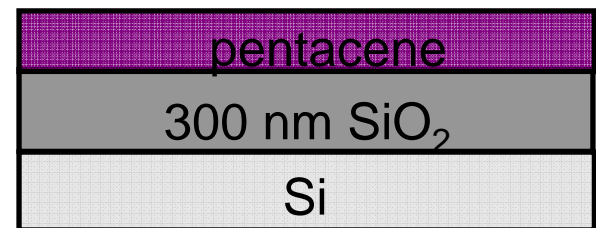
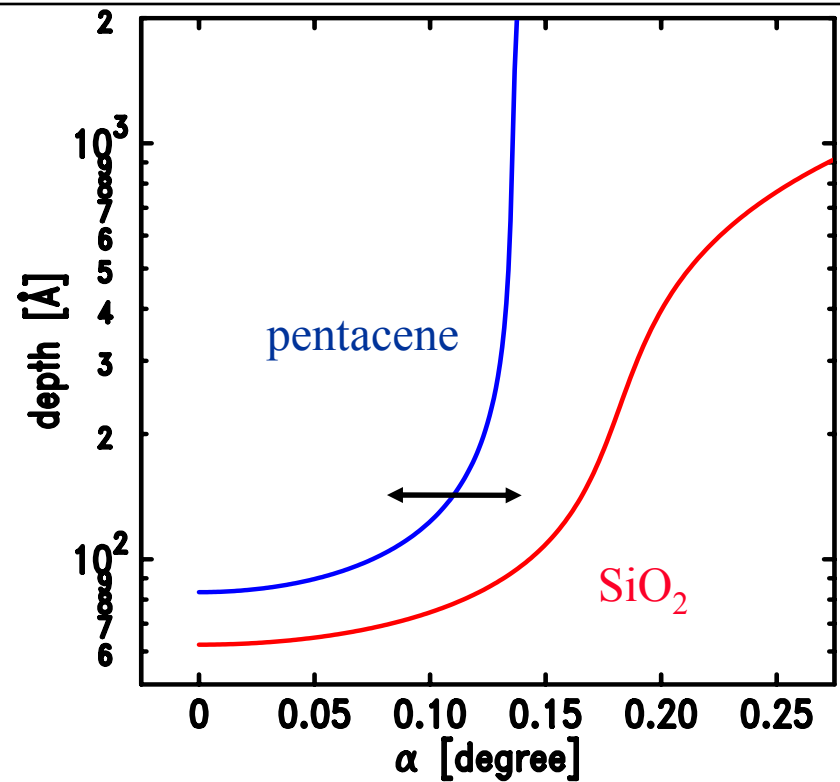
$\theta/2\theta$ XRD: ca 50 nm film



Grazing Incidence Diffraction

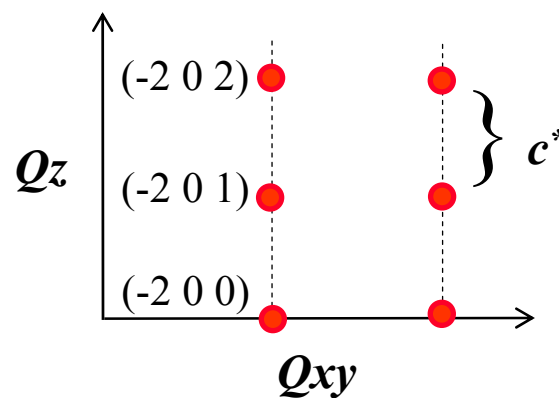
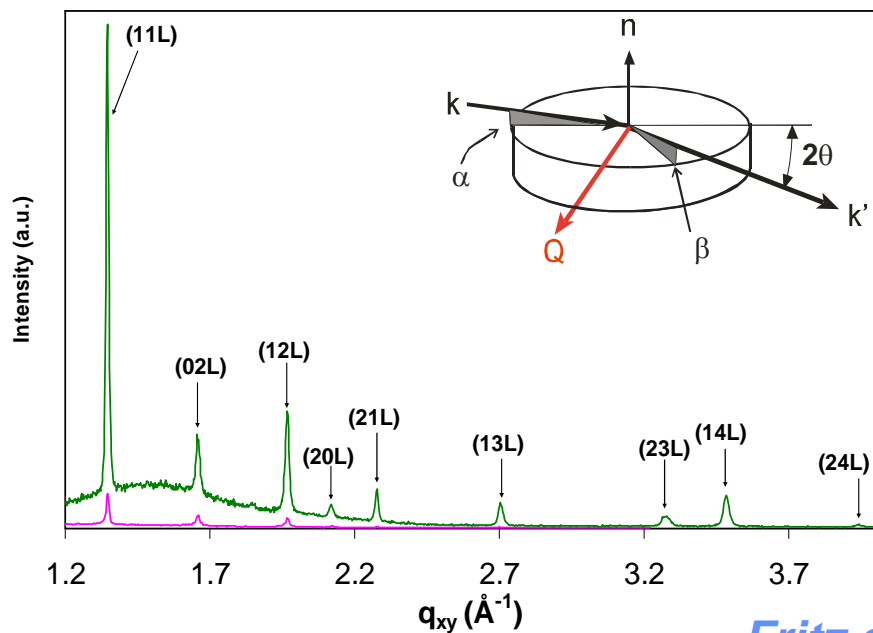
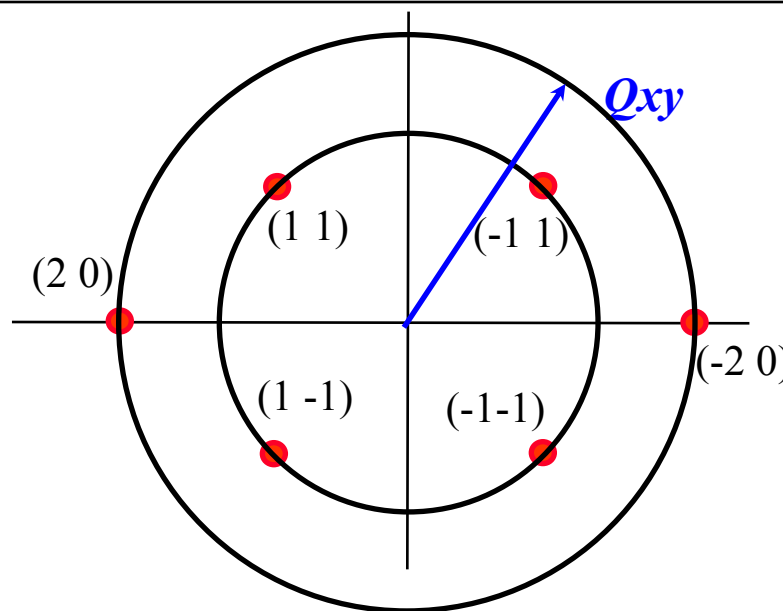
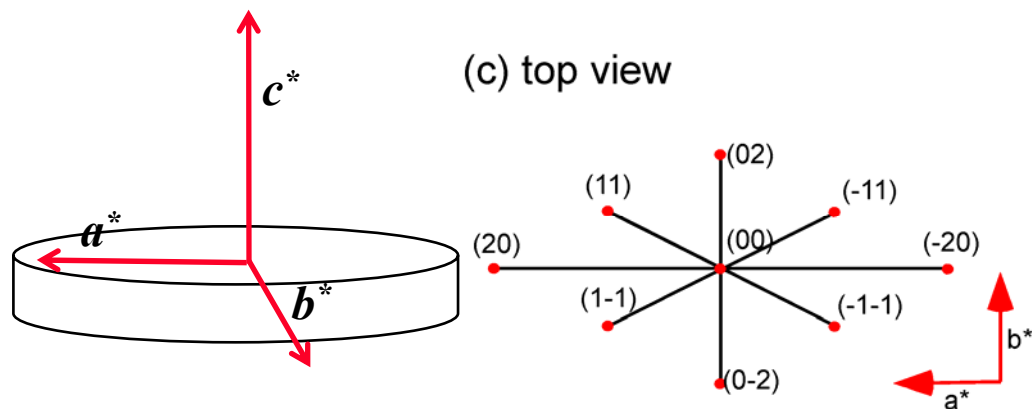


2θ is scattering angle
 Q = scattering vector
 $Q = k' - k$
 $Q = (4\pi/\lambda) \sin \theta$
 α = incidence angle
 β = exit angle



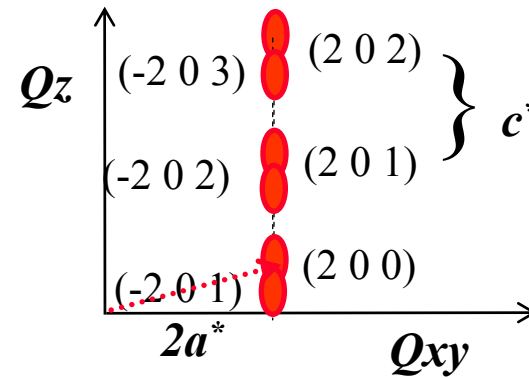
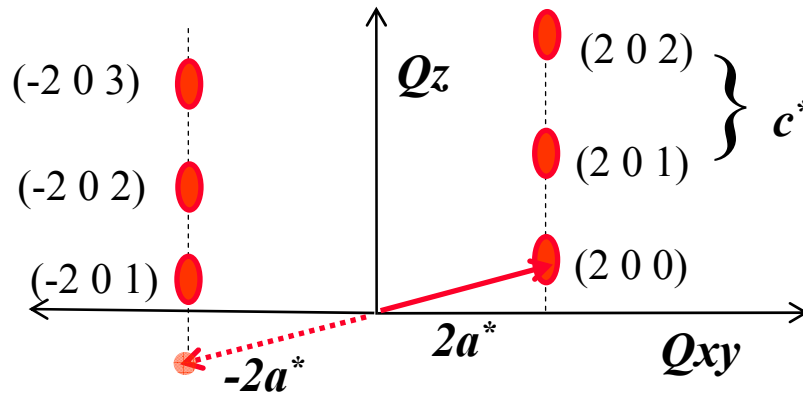
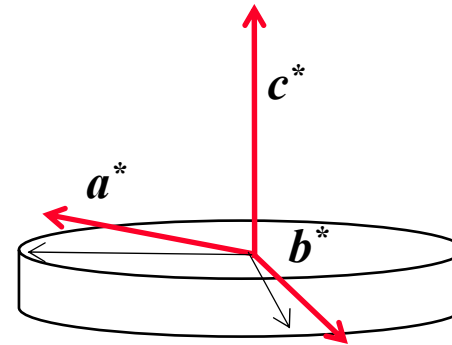
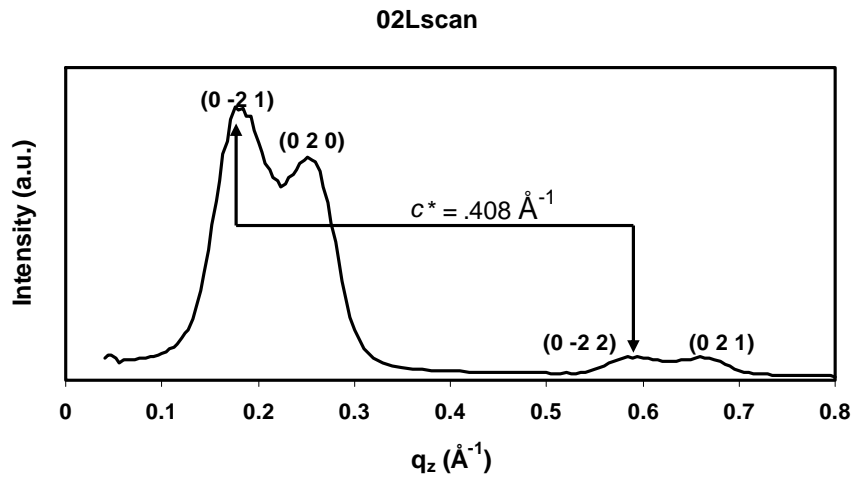
- Vary penetration depth by changing incidence angle α
- Needs good collimation

Pentacene Thin Films



Fritz et al., unpublished

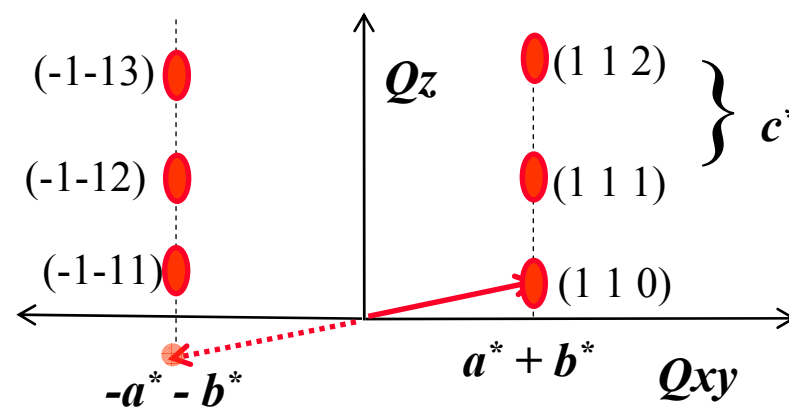
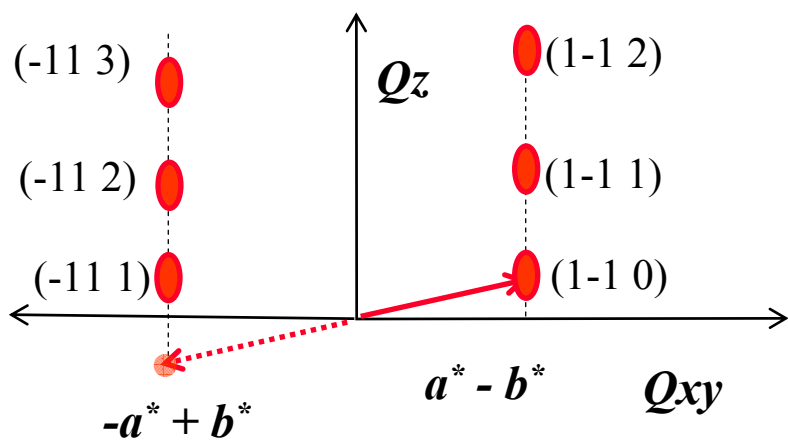
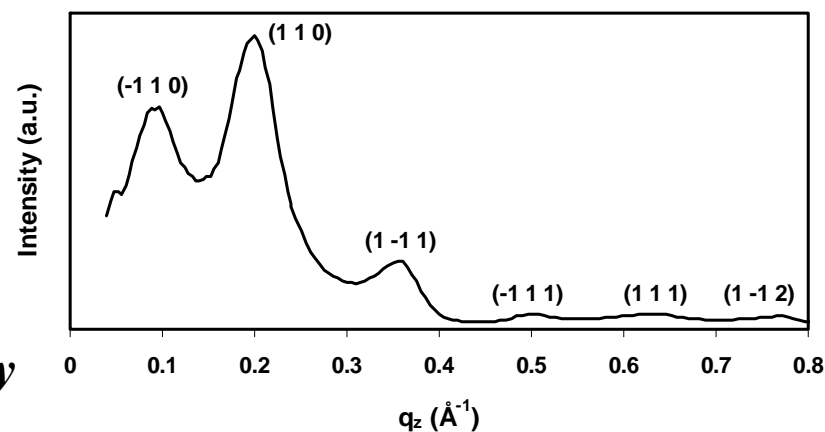
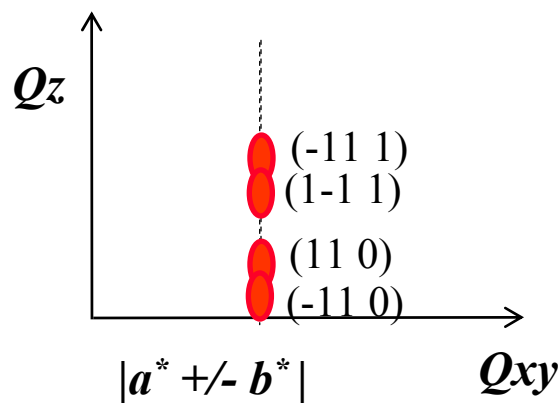
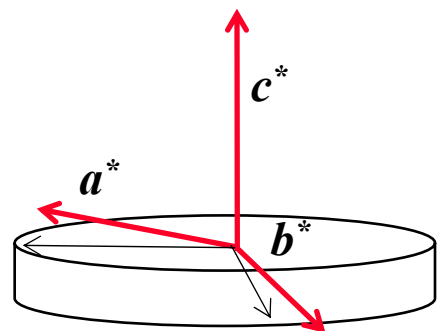
Pentacene Thin Films



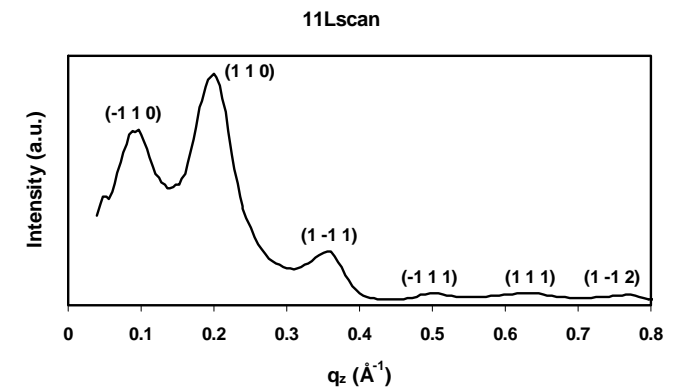
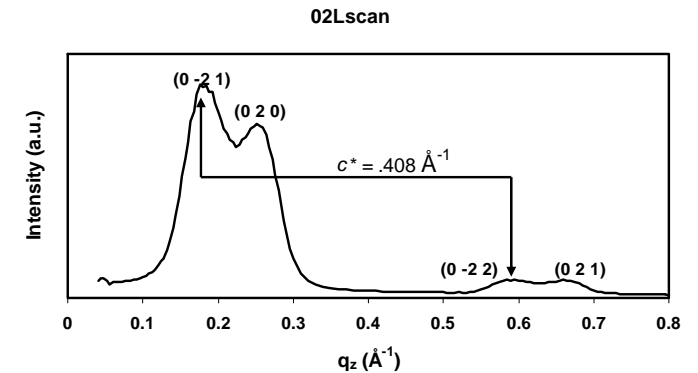
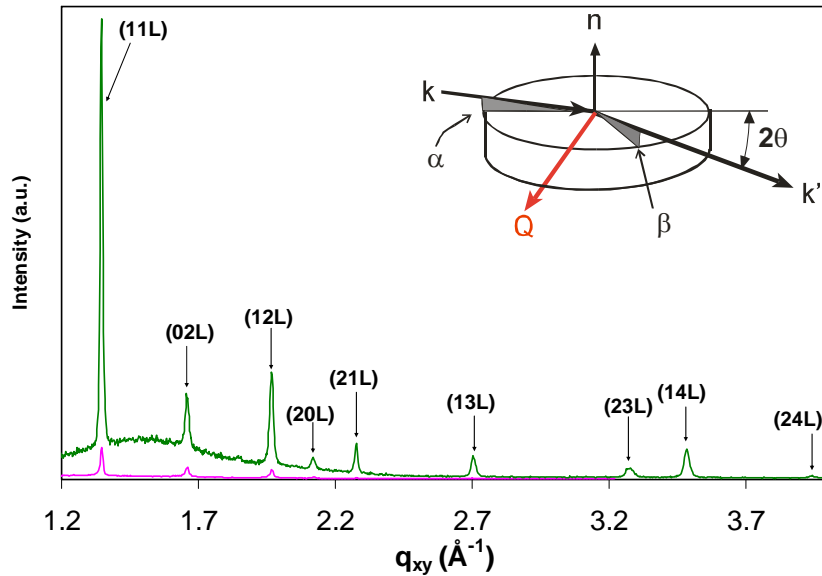
Pentacene Thin Films



11Lscan



Pentacene Thin Films



lattice parameters:

$$a = 5.933 (3) \text{ \AA}$$

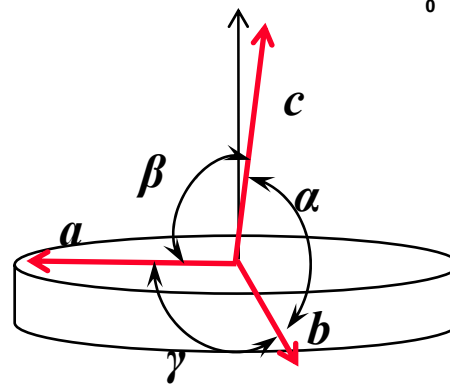
$$b = 7.540 (3) \text{ \AA}$$

$$c = 15.51 (1) \text{ \AA}$$

$$\alpha = 93.2 \text{ deg}$$

$$\beta = 95.9 \text{ deg}$$

$$\gamma = 90 \text{ deg}$$

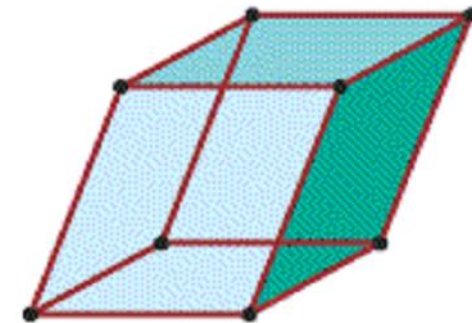


Fritz et al., unpublished

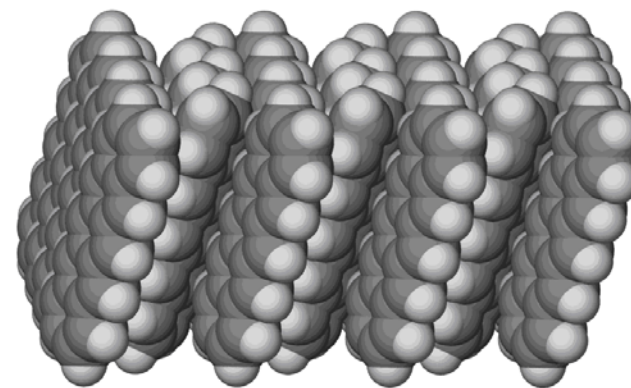
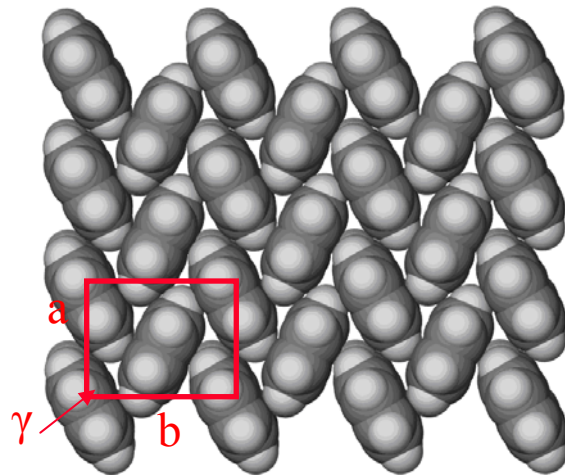
Pentacene Thin Films



- Pentacene thin films on SiO_2 are crystalline, but distinct from bulk
- Thin Film: herringbone motif with molecules tilted a few-ten degrees



Triclinic
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



Fritz et al., unpublished

Summary



- Crystals and geometry
- Bragg's law
- Reciprocal lattice & reciprocal space
 - definition and examples
 - relation to diffraction
- Diffraction intensities and crystallography
- Few Examples
 - Molecular & Crystal structure
 - Strain