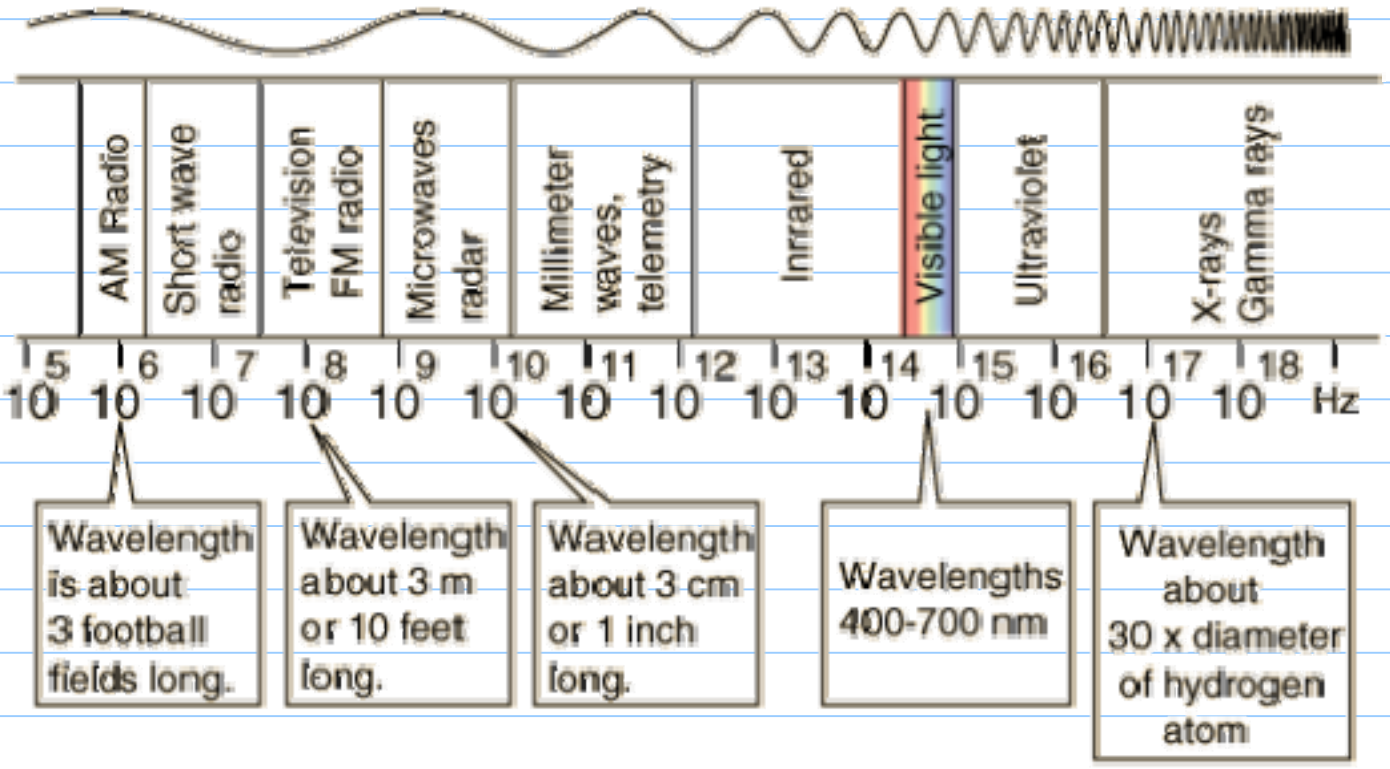
X – Rays

Note Title 4/10/2007

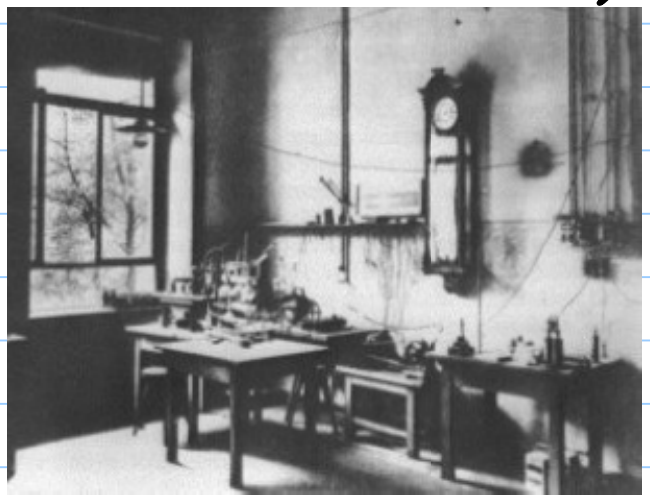


Wilhelm Conrad Röntgen

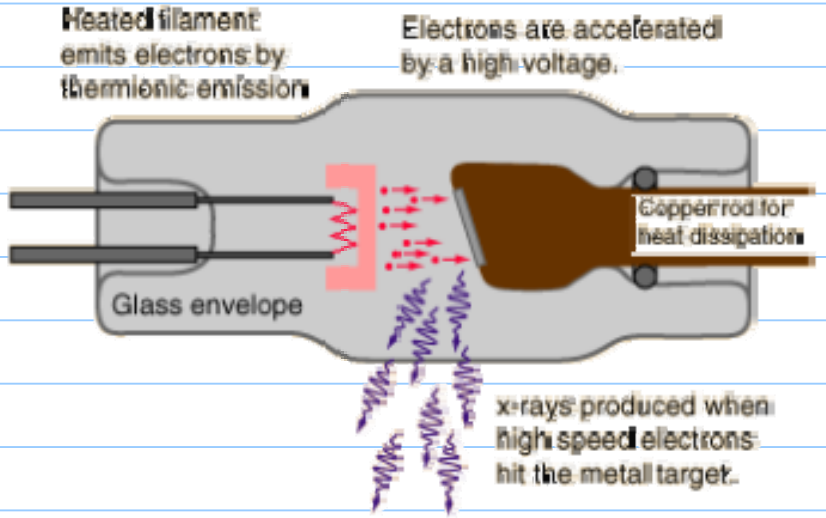
- discoverer of X-rays

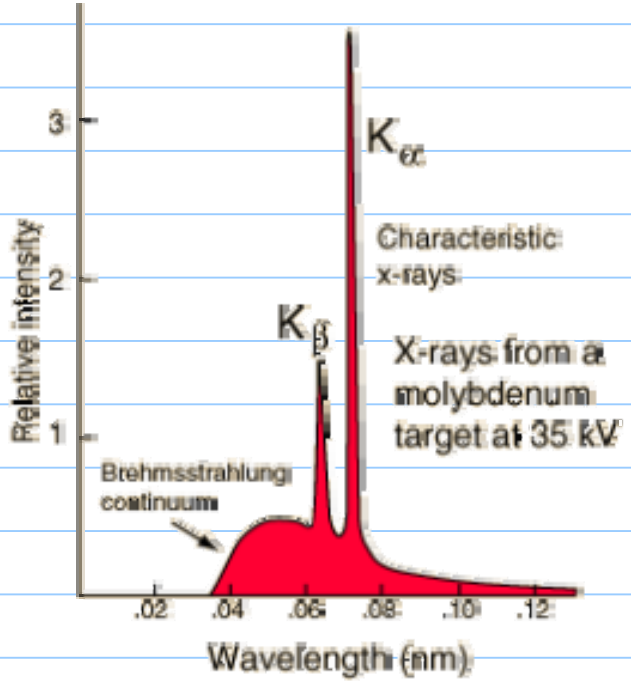
  Nov. 8, 1895

- called "Rontgen Rays"

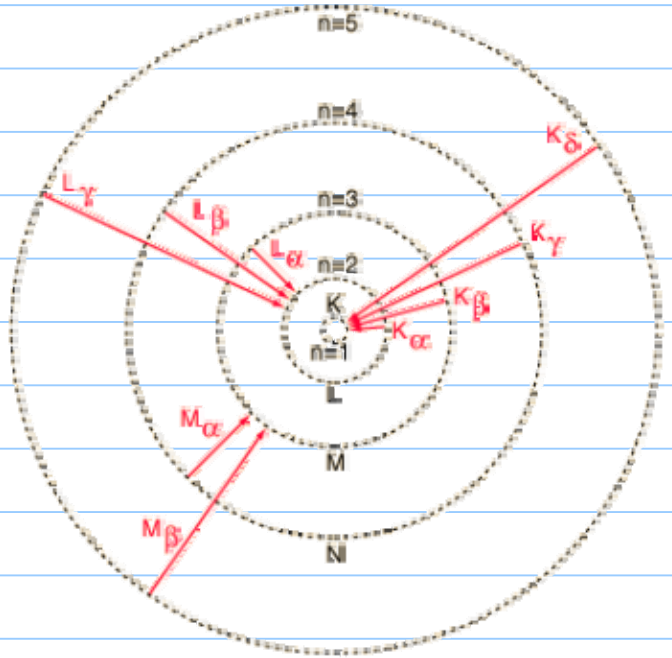


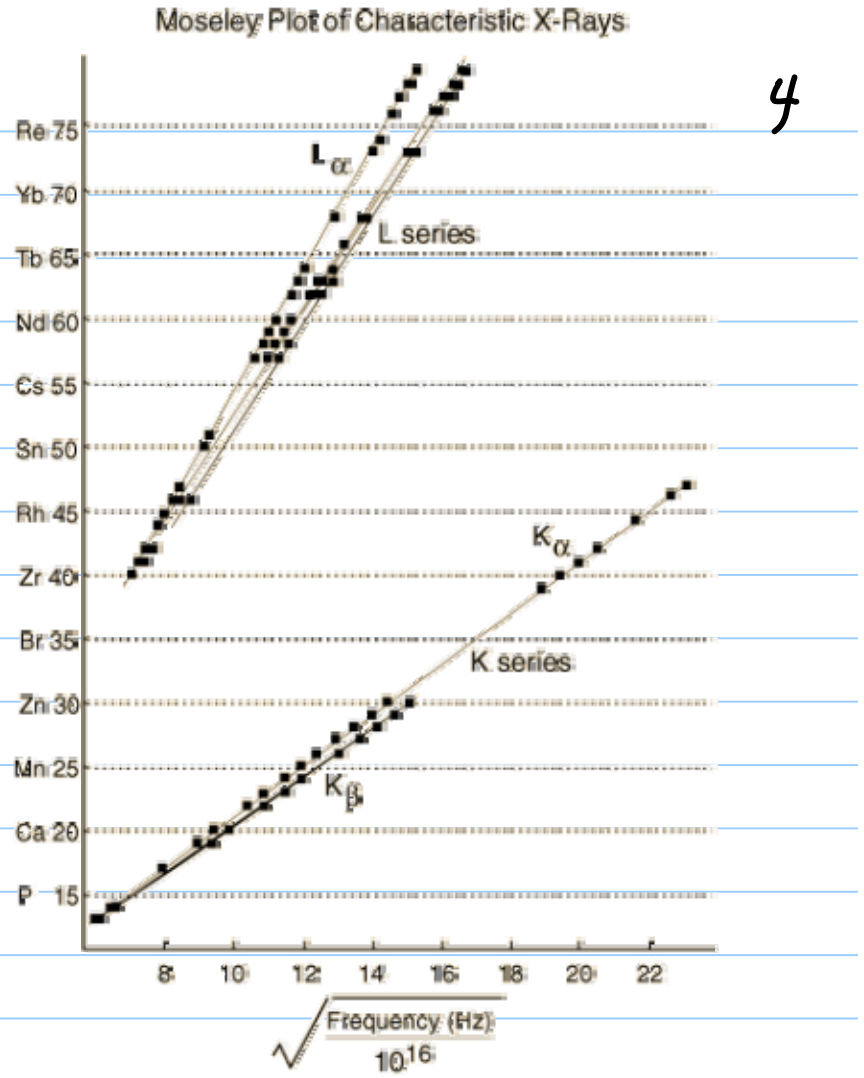
X-ray generation





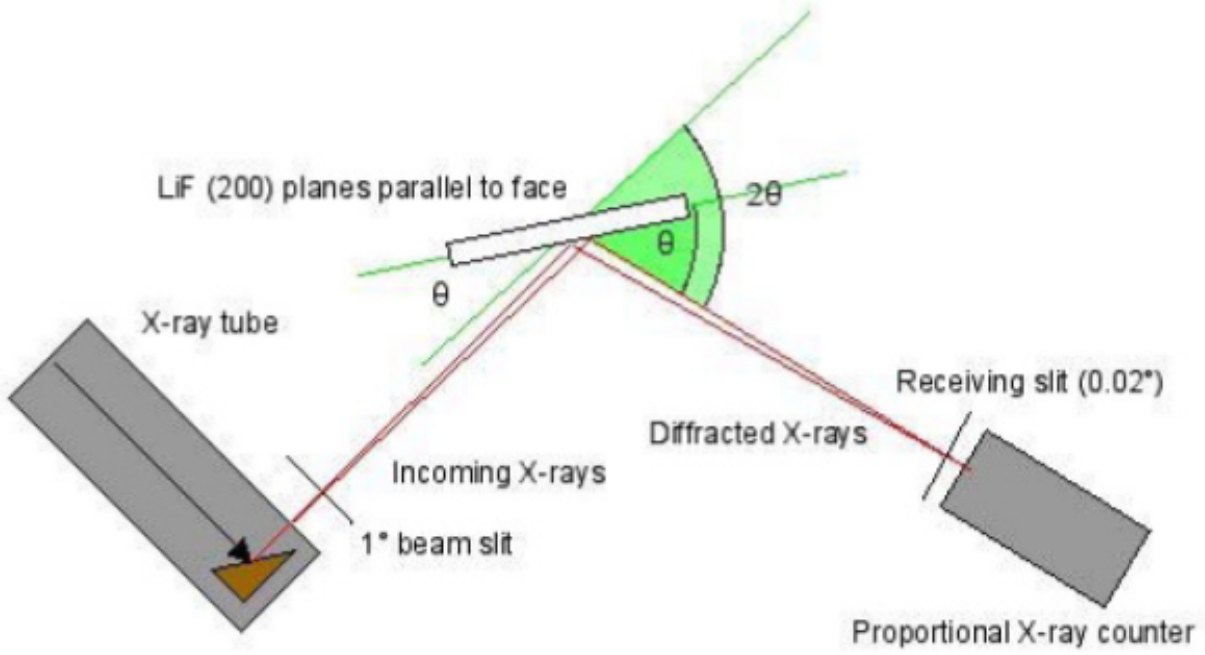
X-ray Terminology





Adapted from Moseley's original data (H. G. J. Moseley, Philos. Mag. (6) 27:703, 1914)

X-ray Diffraction with a Tube

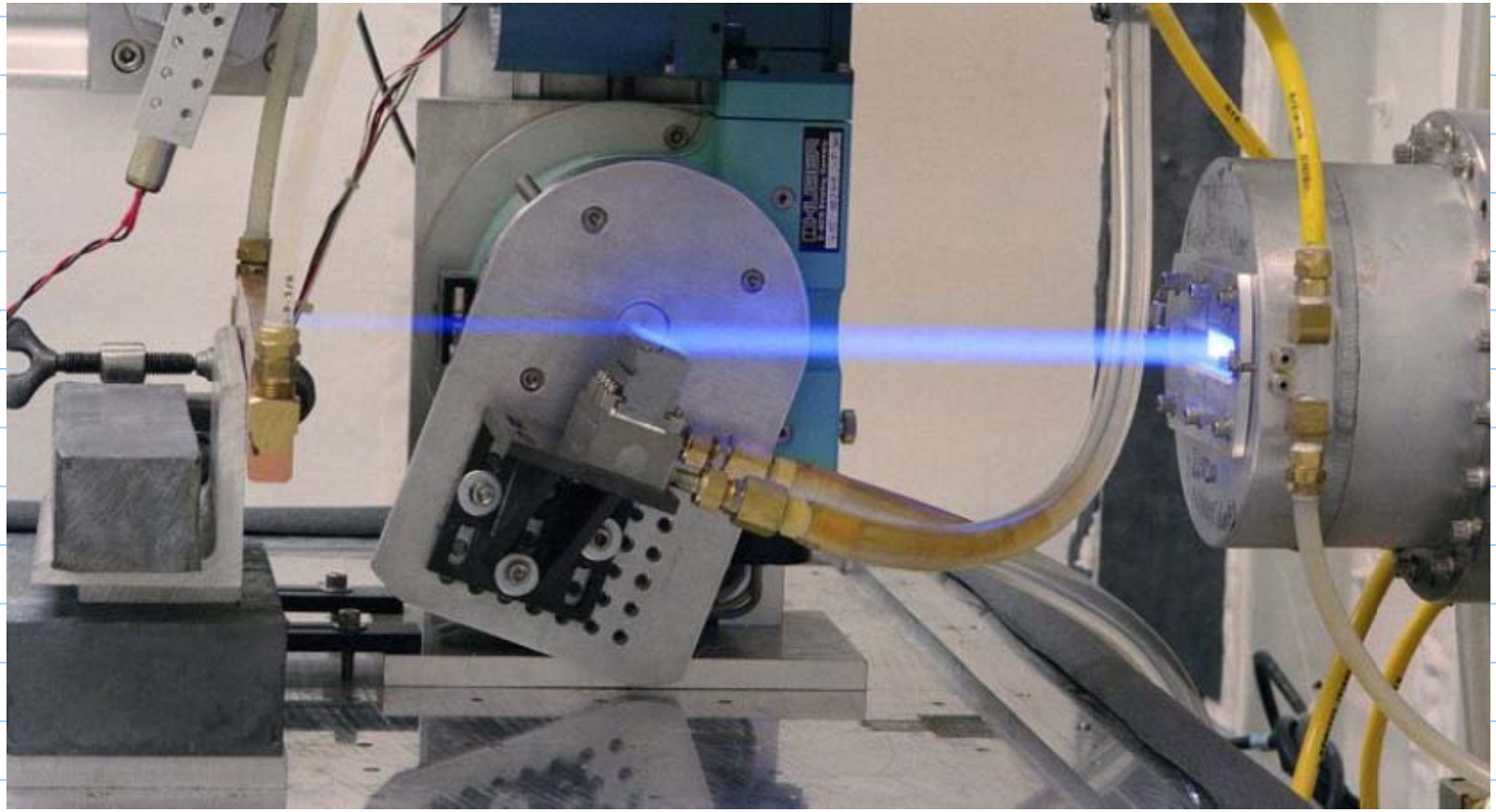


At this point, Bragg's law of diffraction will apply:

$$\lambda = 2d\sin\theta$$

Synchrotron Light Source

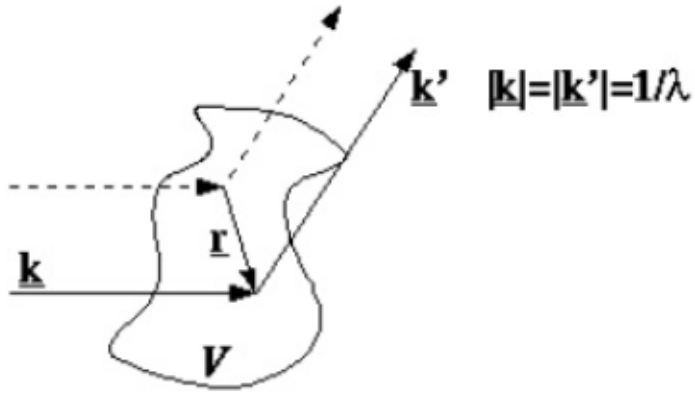
X-rays from a synchrotron light source 7



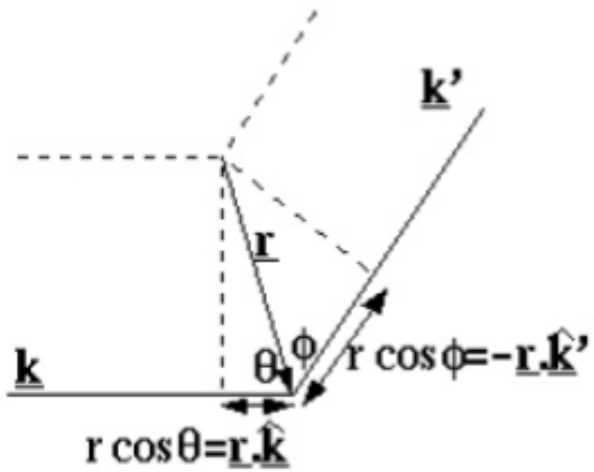
Scattering Theory

What is the relationship between X-ray diffraction and Fourier transforms?

Incident beam with a vector $\vec{k}$ and and diffracted beam $\vec{k}'$



Sum scattering from entire solid



- difference in path length is phase difference between the two waves

– substitute new vector $\vec{s}$ for the difference between $\vec{k}$ and $\vec{k'}$
– each point $p(r)$

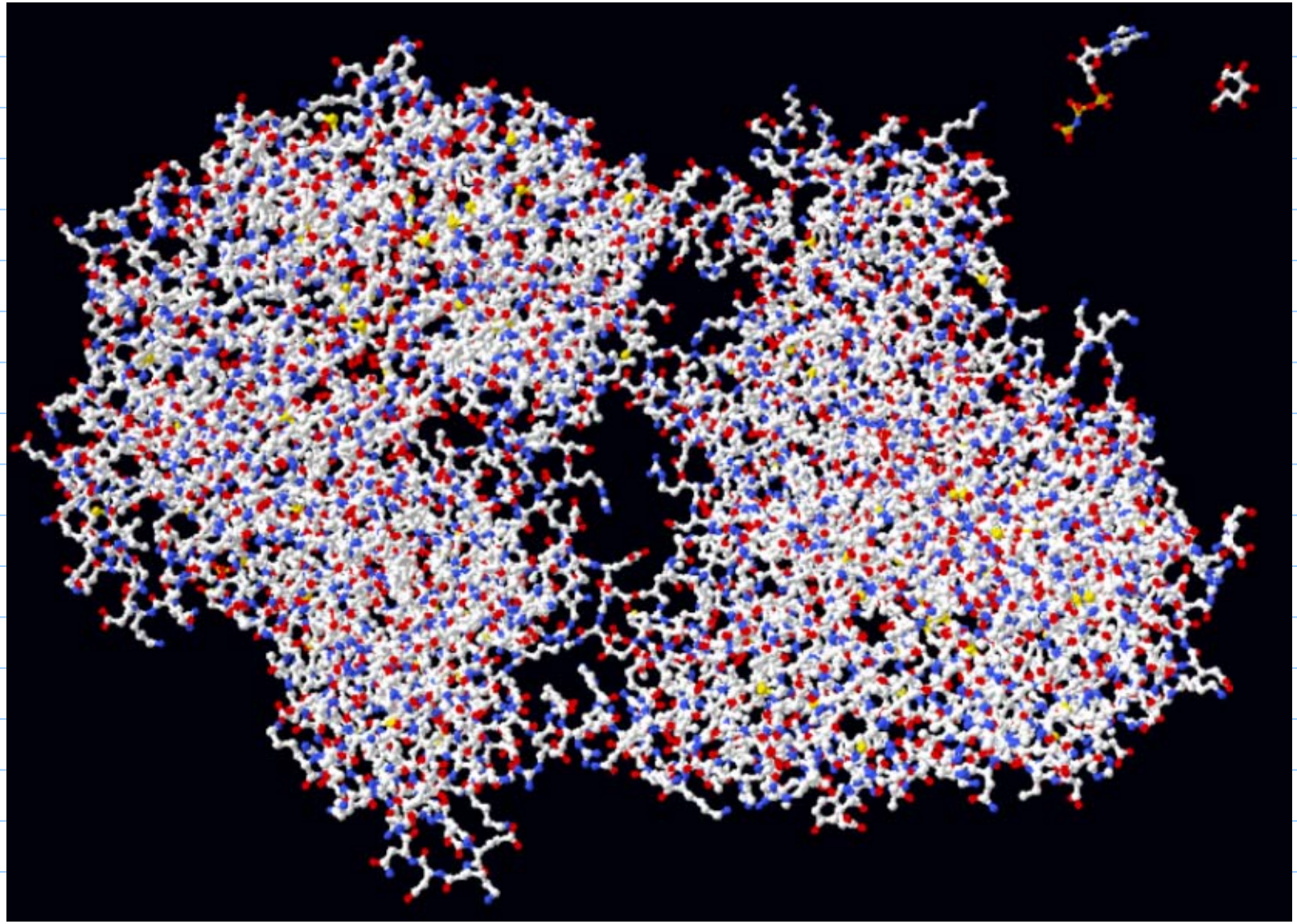
path difference = $\underline{r}.\hat{\underline{k}} - \underline{r}.\hat{\underline{k}}' = \underline{r}.(\hat{\underline{k}} - \hat{\underline{k}}')$

phase difference = $2\pi/\lambda$ x path difference
$= 2\pi/\lambda\ \underline{r}.(\hat{\underline{k}} - \hat{\underline{k}}') = 2\pi \underline{r}.(\underline{k} - \underline{k}')$

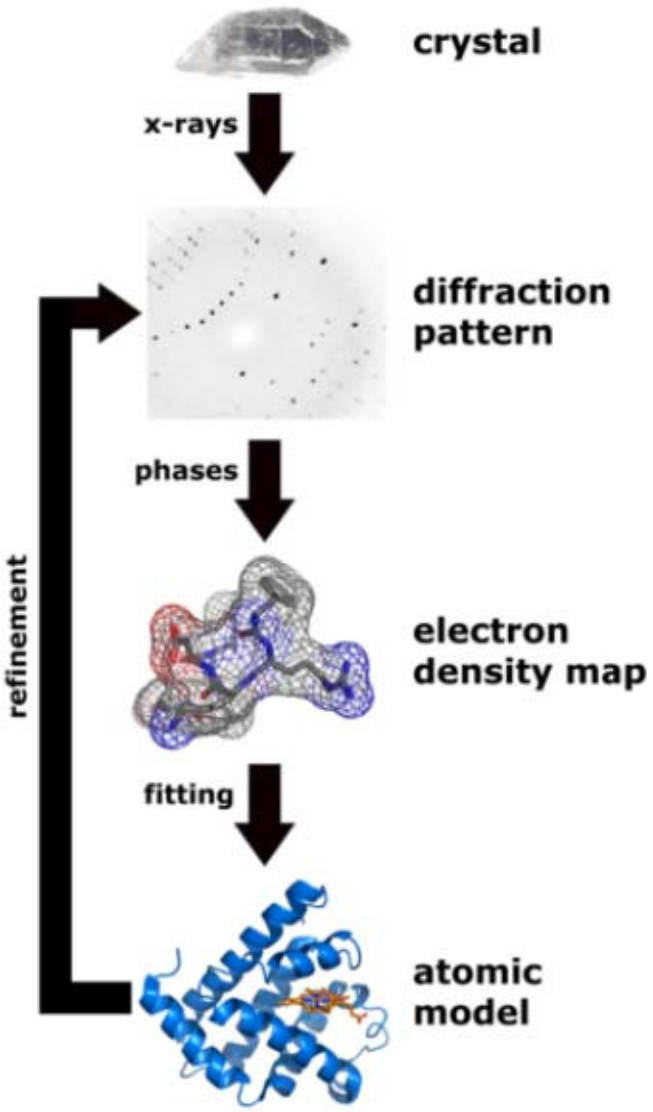
Define $\underline{s} = \underline{k} - \underline{k}'$, sum over all $\underline{r}$

$$F(\underline{s}) = \int_V p(\underline{r})\ \exp(2\pi i\, \underline{r}.\underline{s})\ d\underline{r}$$

Hexokinase Structure

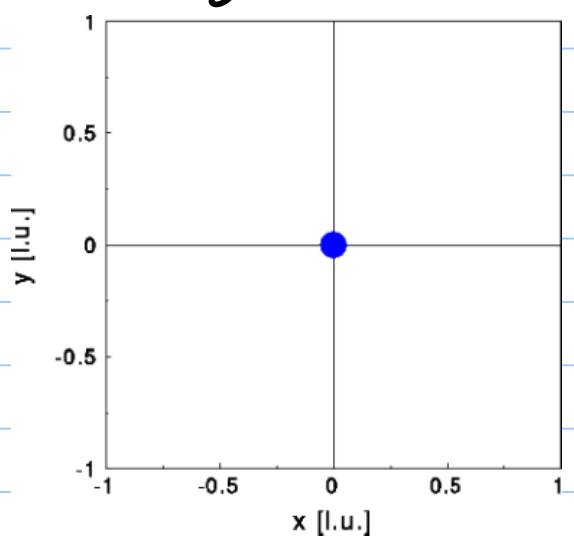


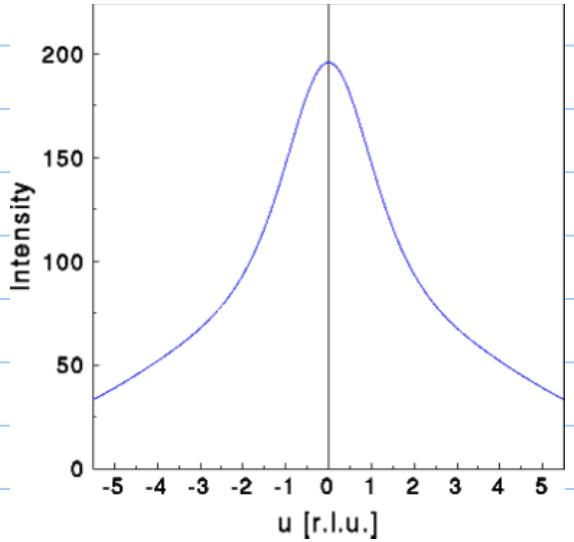
Process of determining complex crystal structures

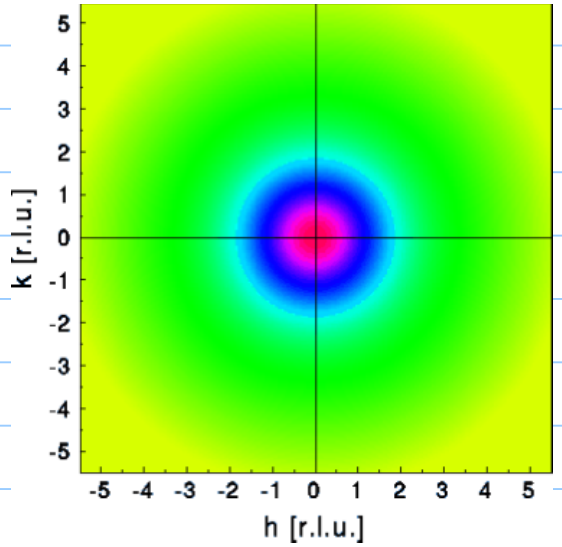


Start simple

Single Atom

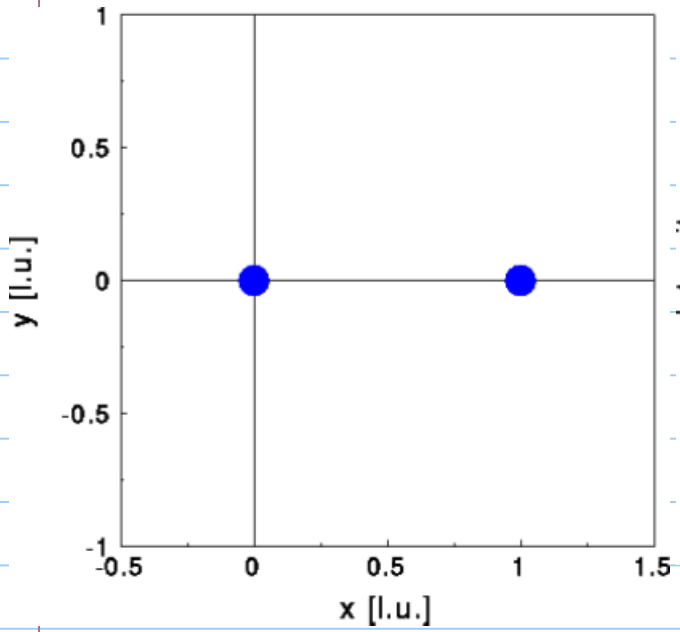




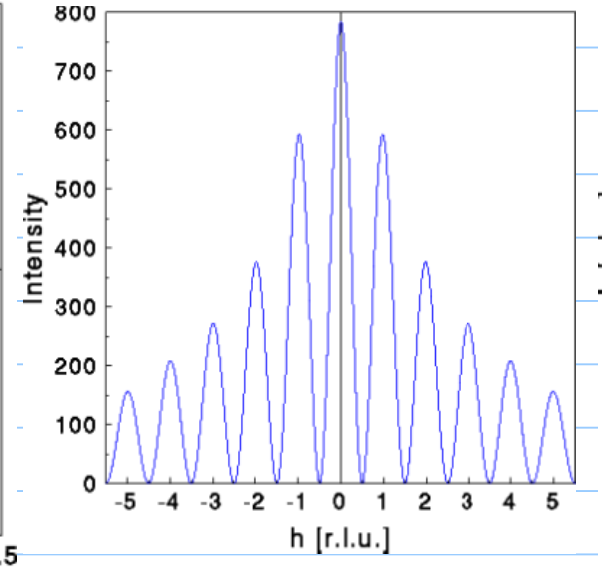


Pair of Atoms

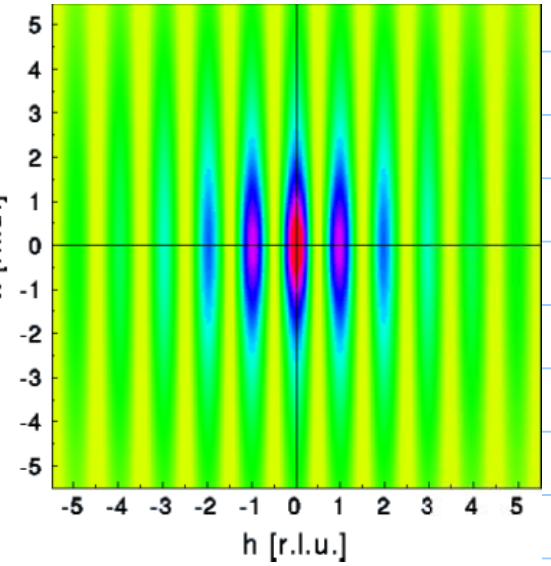
2 atoms



1D FT

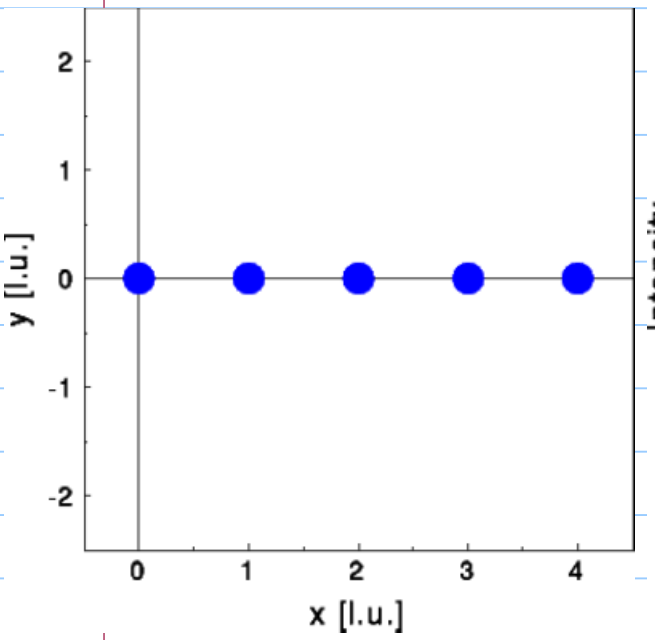


2D FT

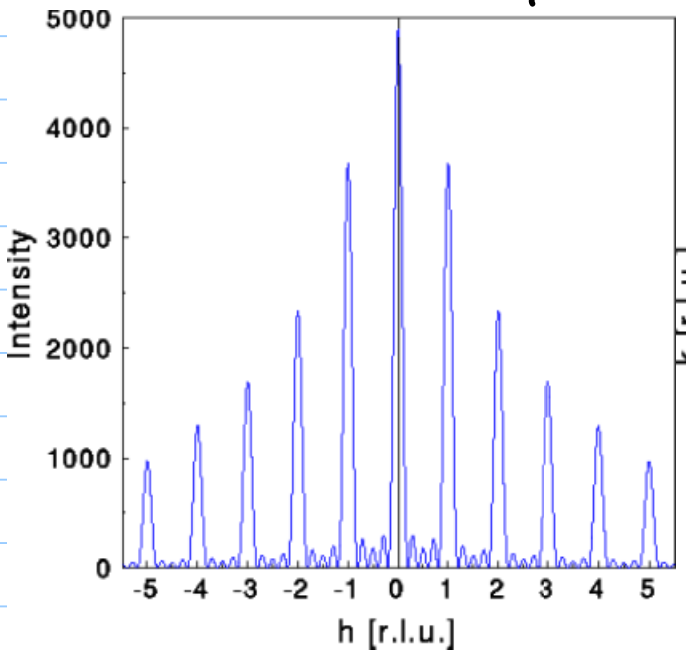


Row of Atoms

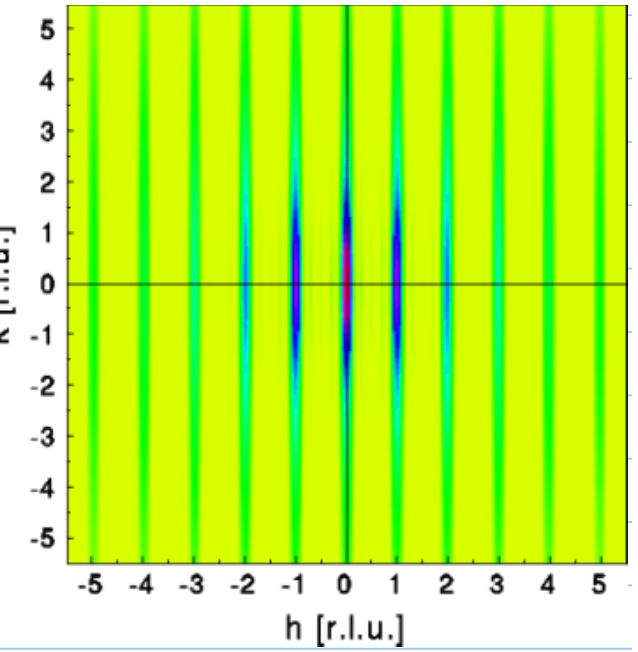
Row of Atoms



1D FT

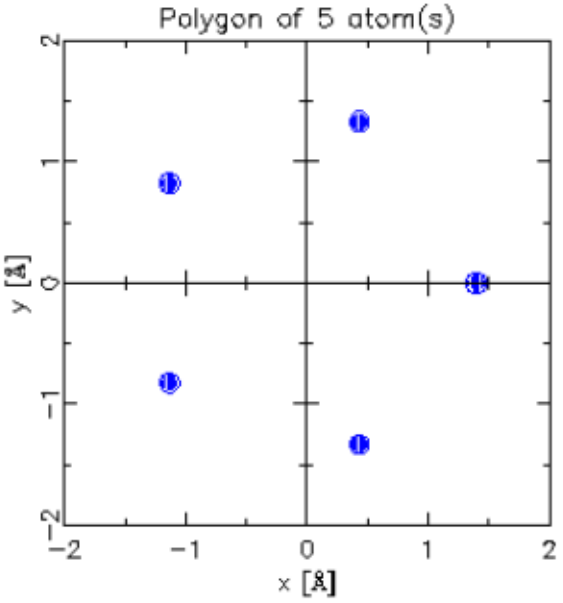


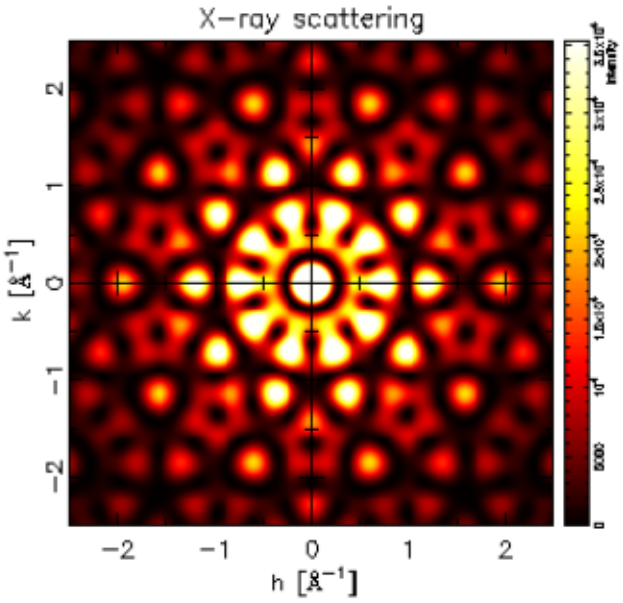
2D FT



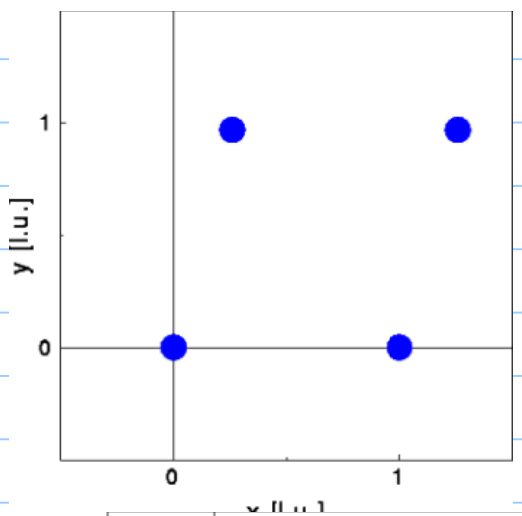
Polygon of Atoms

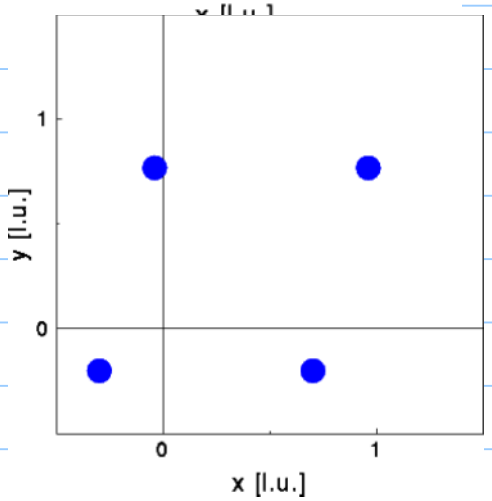
2D FT

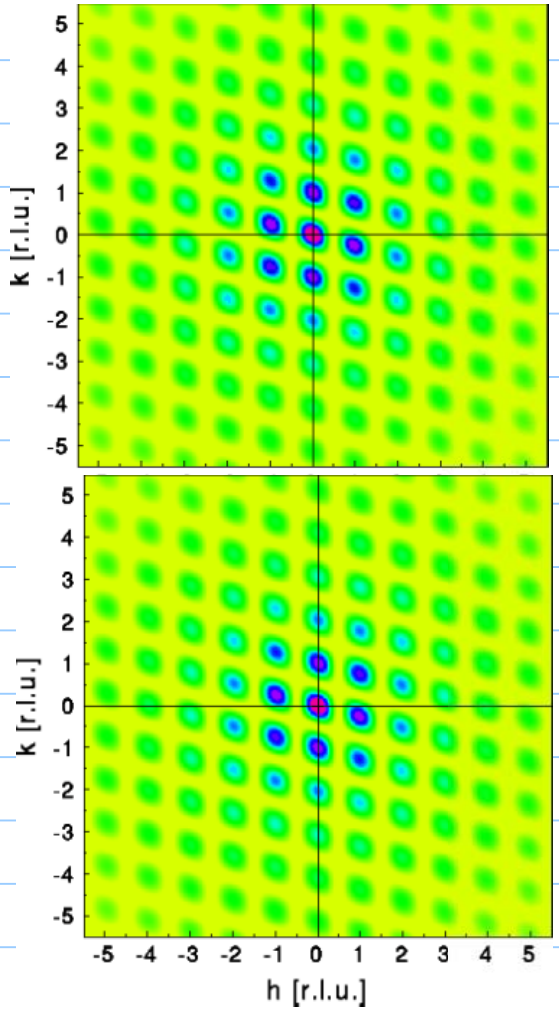




Translation

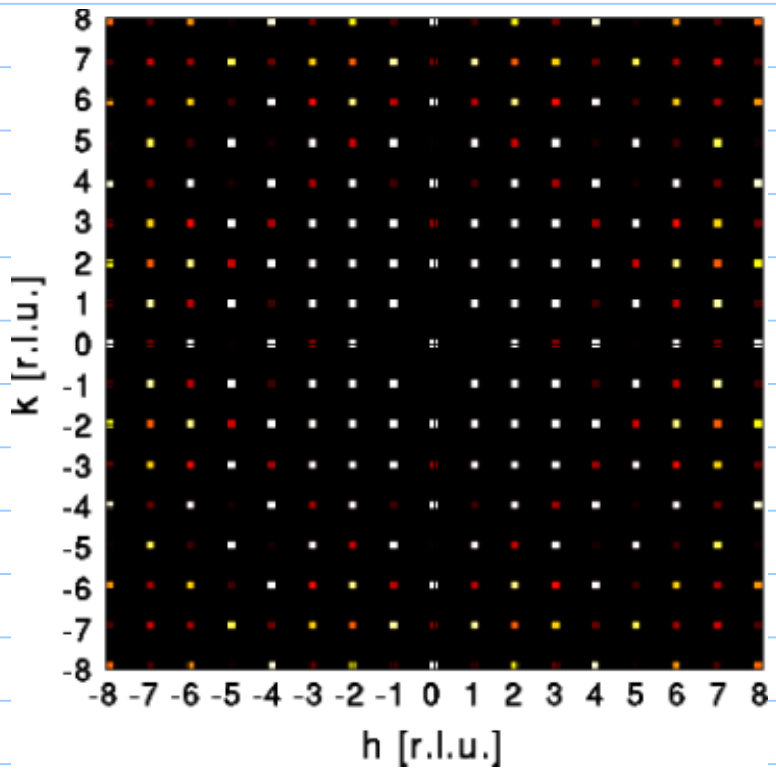






Diffraction Pattern Unchanged

Solve a Crystal Structure



What information can we extract from the diffraction pattern

Bragg Condition

$$\lambda = 2d\sin\theta$$

determines spacing

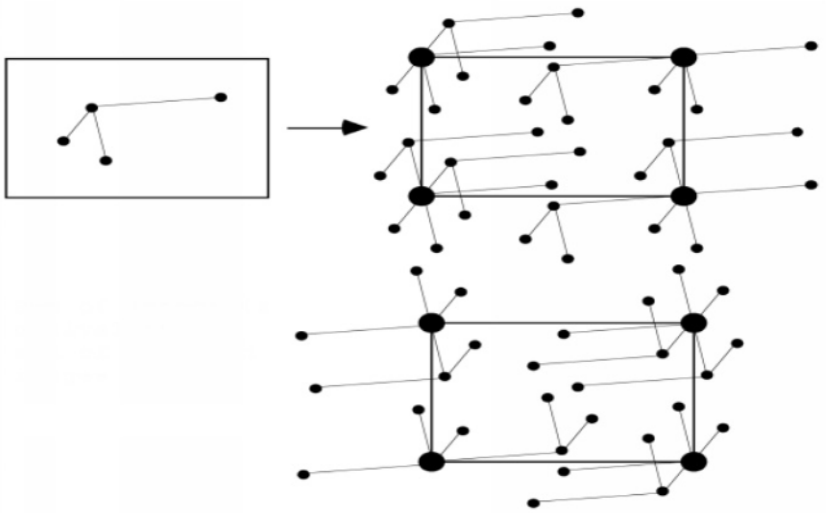
Symmetry Pmm4

Add. from/ Information Needed

- Need Chemistry $Zr Ti O_4$
- Should know density

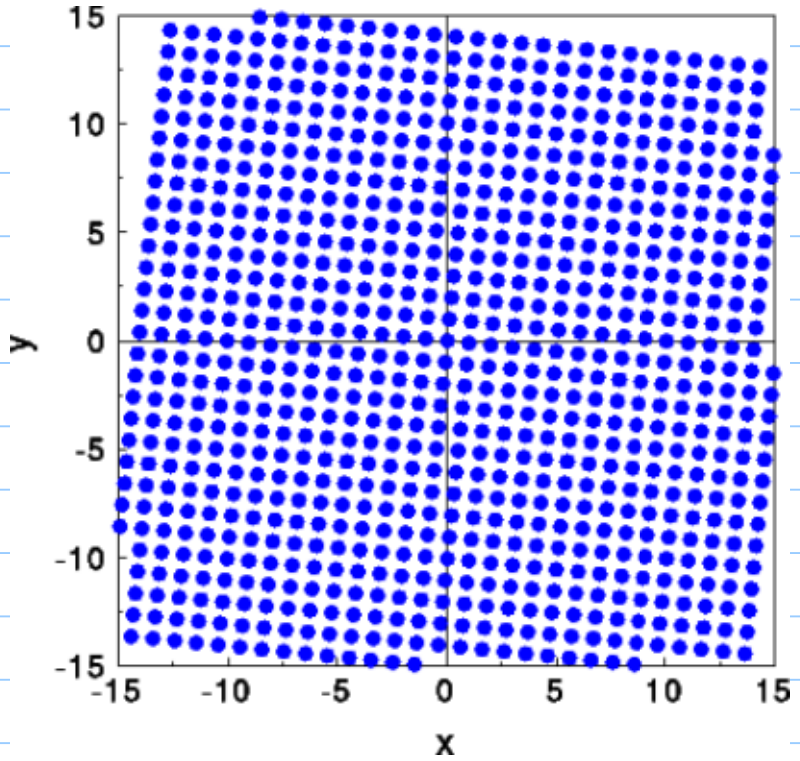
Patterson synthesis

$$P(\vec{u}) = \frac{1}{V} \sum_{i=1}^{N} I(h) \, e^{-2\pi i h \vec{u}}$$

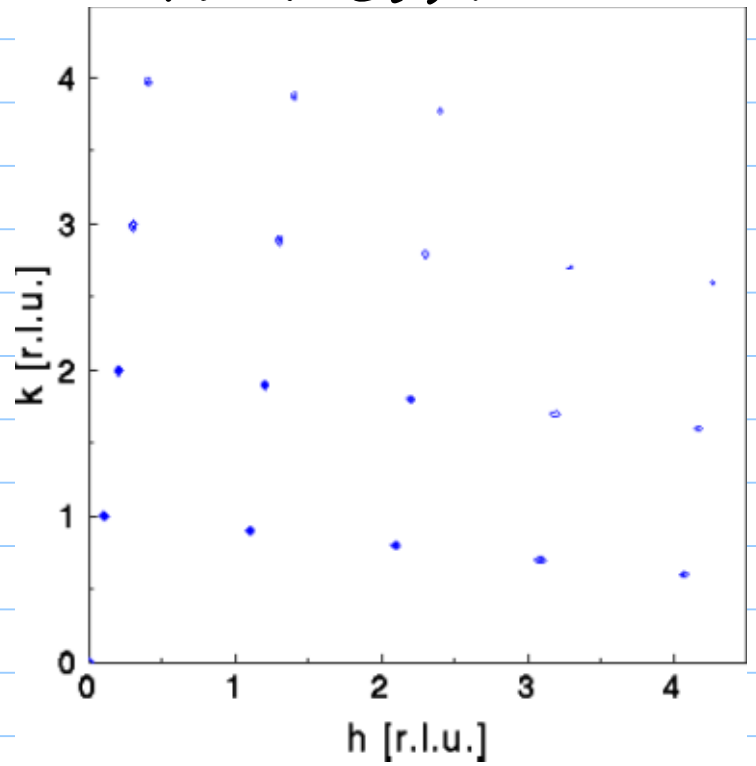


Powder Diffraction

Rotated Crystal

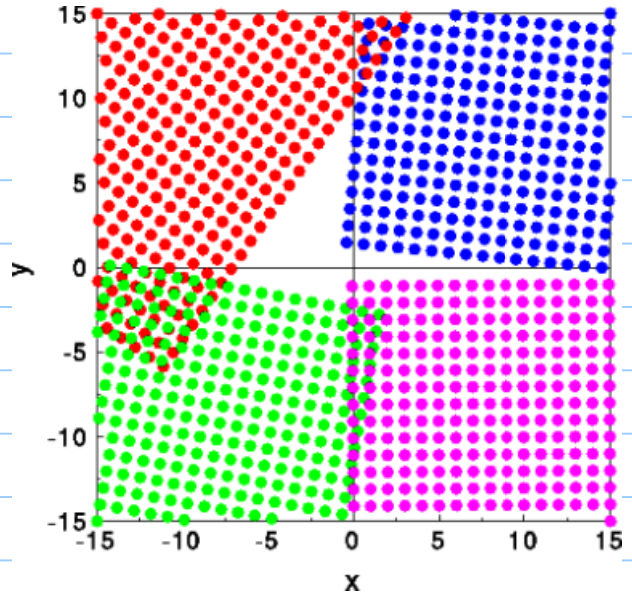


Rotated Diffraction Pattern

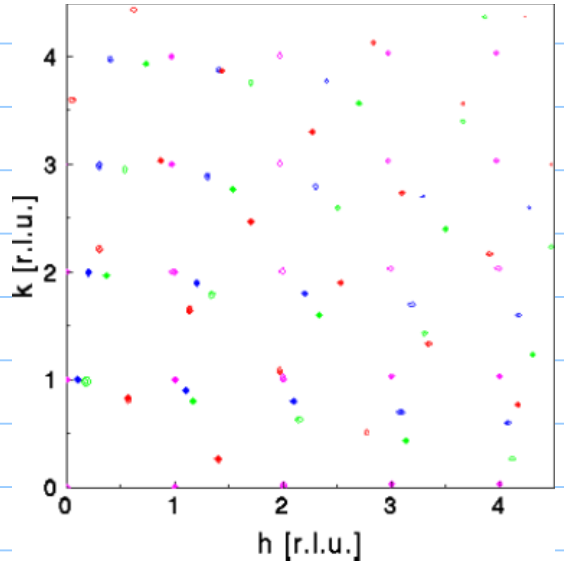


Powder Diffraction

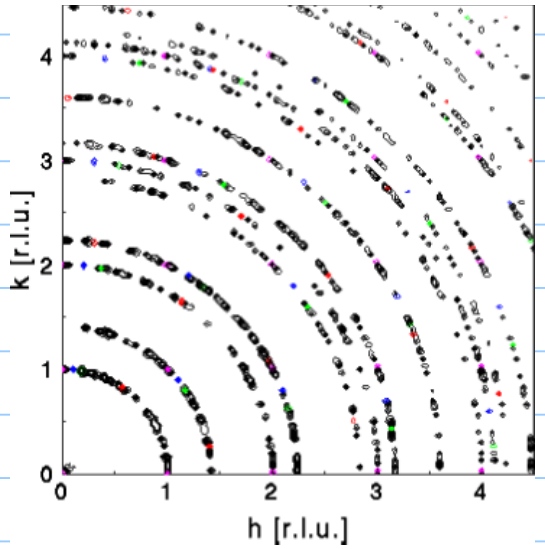
4 crystals



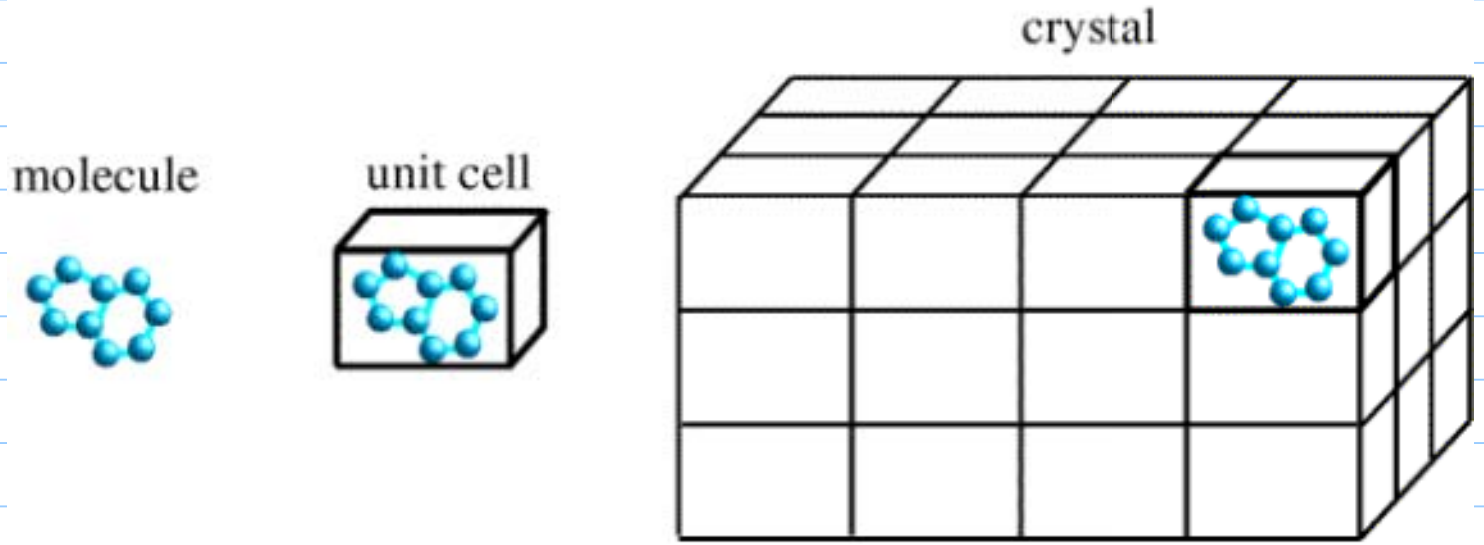
4 crystal Diffraction Pattern



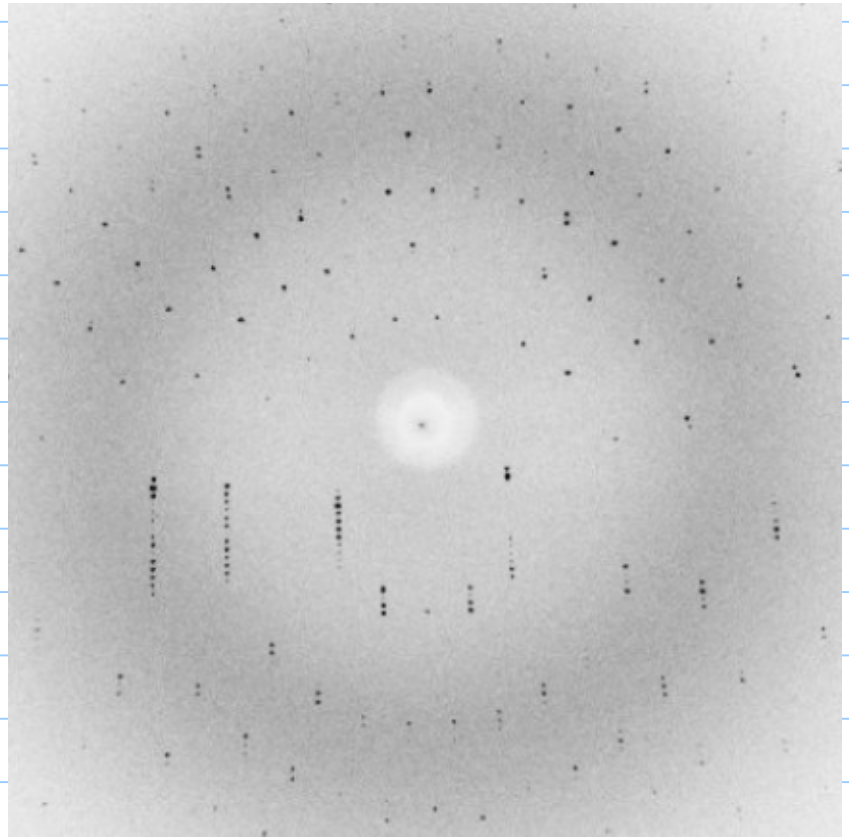
40 crystal Diff Pattern



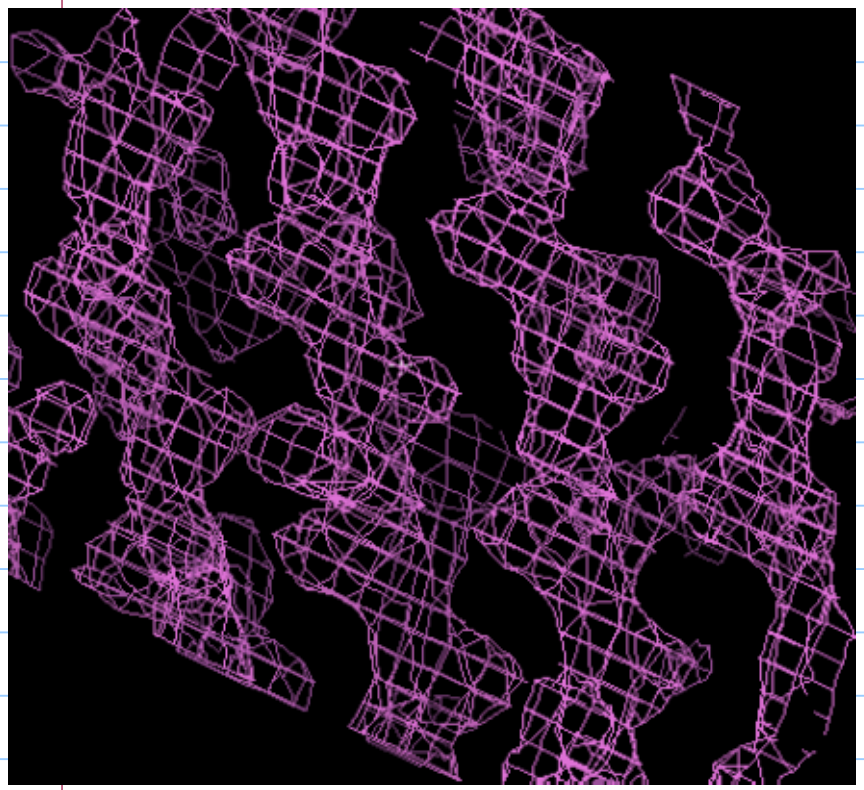
Why crystals?



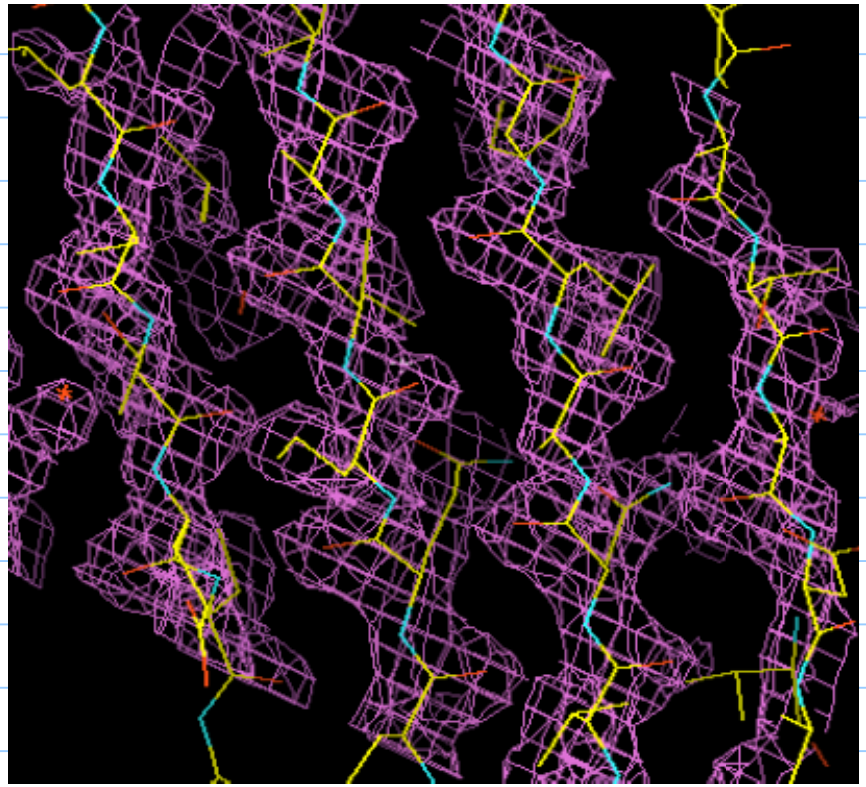
Diffraction Pattern



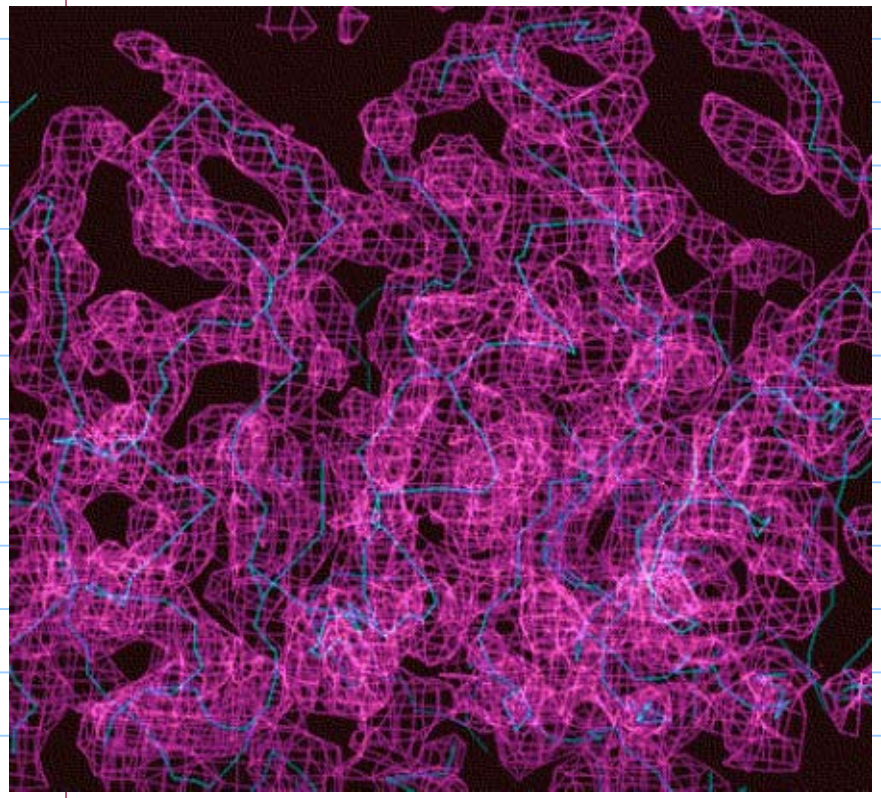
Electron Density Map



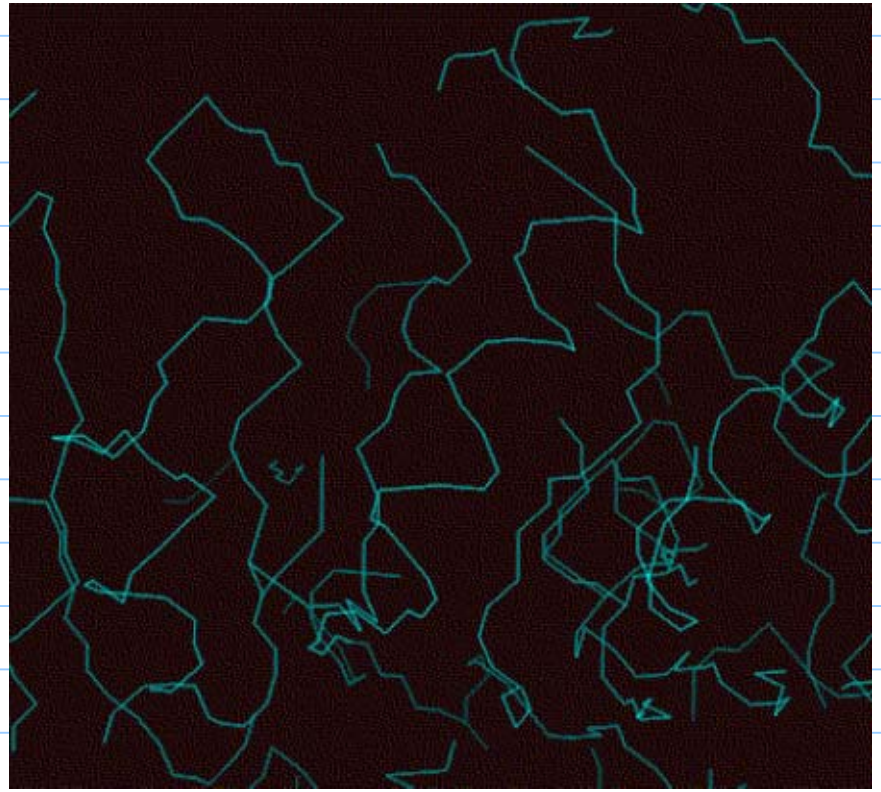
Add atoms



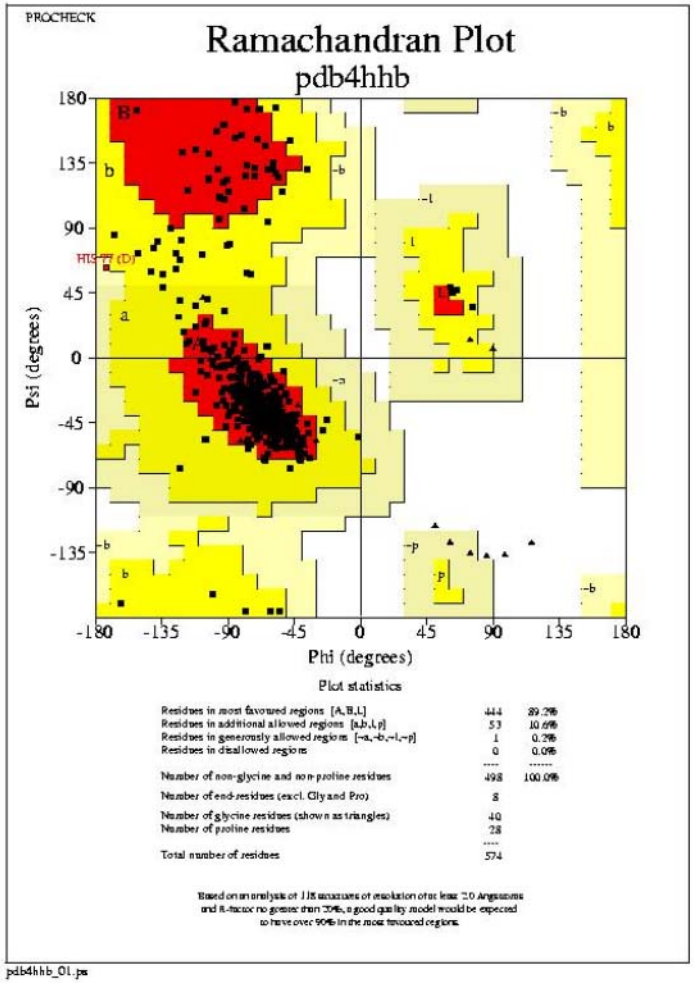
Complex Map



"Bones"



Validation

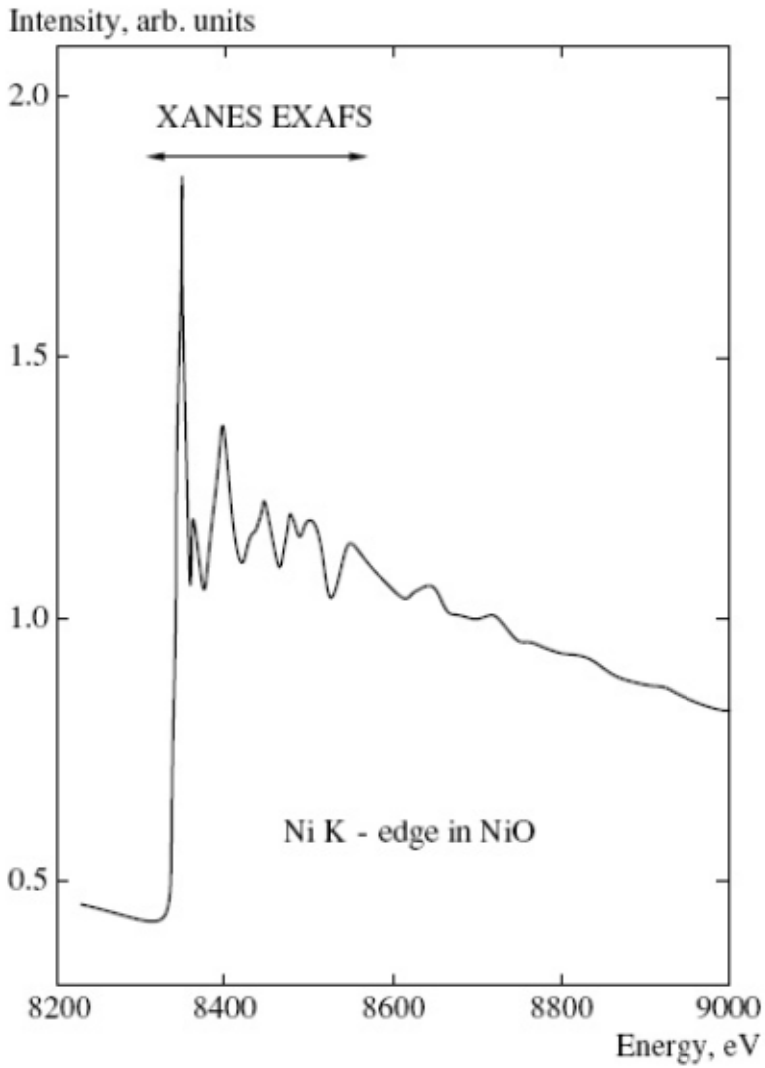

PROCHECK
Ramachandran Plot
pdb4hhb
Psi (degrees)
Phi (degrees)
180
135
90
45
0
-45
-90
-135
-180
HIS-77 (D)
Plot statistics
Residues in most favoured regions [A,B,L] 444 89.2%
Residues in additional allowed regions [a,b,l,p] 53 10.6%
Residues in generously allowed regions [~a,~b,~l,~p] 1 0.2%
Residues in disallowed regions 0 0.0%
Number of non-glycine and non-proline residues 498 100.0%
Number of end-residues (excl. Gly and Pro) 8
Number of glycine residues (shown as triangles) 40
Number of proline residues 28
Total number of residues 574
Based on an analysis of 118 structures of resolution of at least 2.0 Angstroms and R-factor no greater than 20%, a good quality model would be expected to have over 90% in the most favoured regions.
pdb4hhb_01.ps

EXAFS Extended X-Ray Absorption Fine Structure

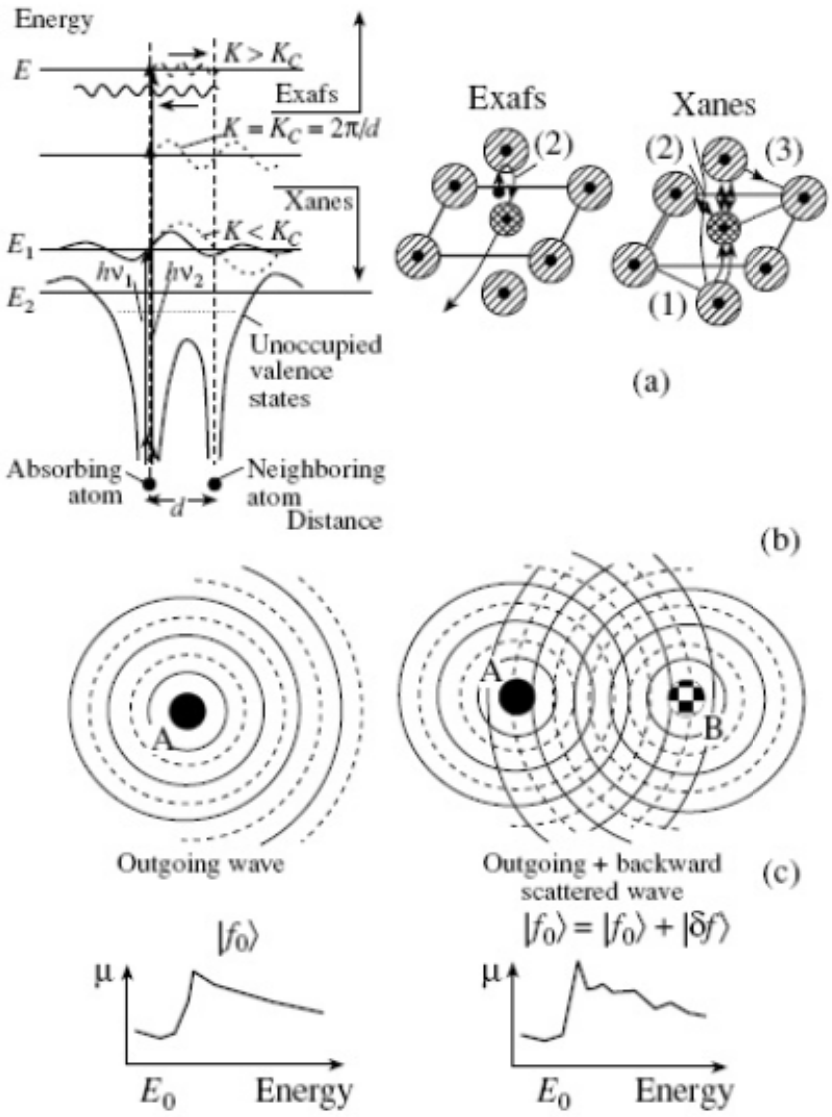
XANES X-Ray Near Edge Structure

XANES ~ 50 – 100 eV beyond an absorption edge

EXFAS ~ 400 ~ 2000 eV beyond the edge



Nickel K Edge Absorption Spectrum


Energy
E
K > K_C
Exafs
K = K_C = 2π/d
Xanes
E_1
K < K_C
hν_1
hν_2
E_2
Unoccupied valence states
Absorbing atom
Neighboring atom
d
Distance
Exafs
Xanes
(2)
(2)
(3)
(1)
(a)
(b)
A
A
B
Outgoing wave
Outgoing + backward scattered wave
(c)
|f_0⟩
|f_0⟩ = |f_0⟩ + |δf⟩
μ
μ
E_0
Energy
E_0
Energy