Single Crystal Diffraction

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National School on Neutron and X-Ray Scattering

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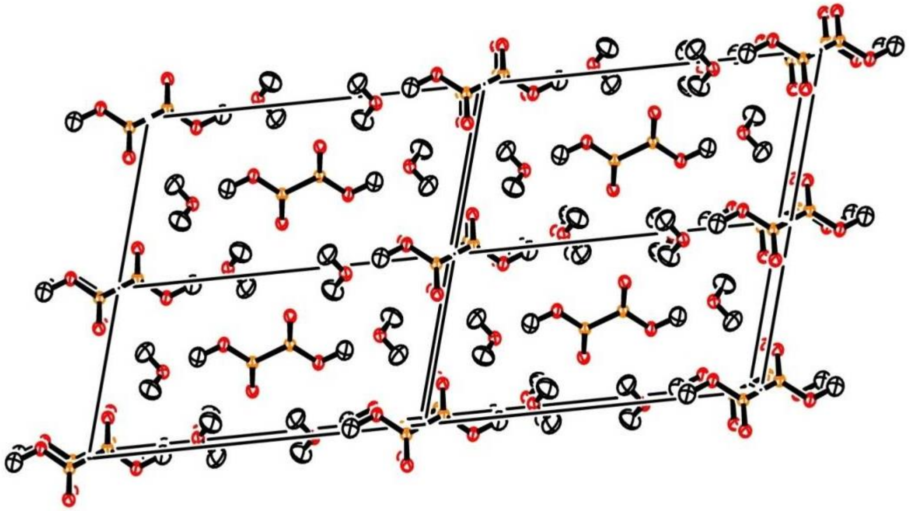
What is a crystal?

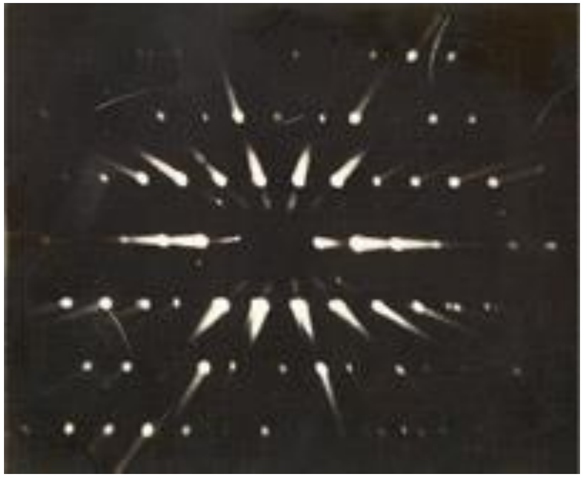


Unit cells of oxalic acid dihydrate

- Atoms (molecules) pack together in a regular pattern to form a crystal.
- Periodicity: we superimpose (mentally) on the crystal structure a repeating lattice or unit cell.
- A lattice is a regular array of geometrical points each of which has the same environment.

Quartz crystals

Why don’t the X-rays scatter in all directions?

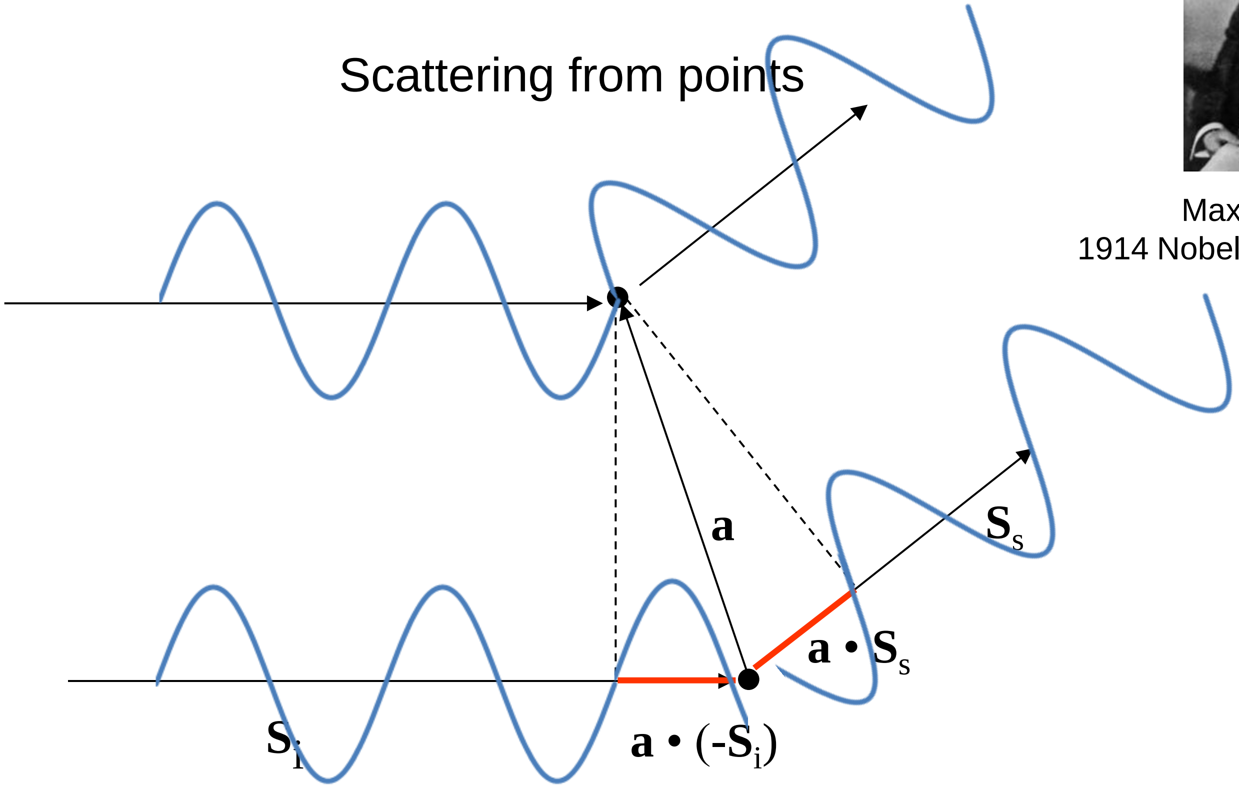


X-ray precession photograph
(Georgia Tech, 1978).

- X-rays (and neutrons) have wave properties.
- A crystal acts as a diffraction grating producing constructive and destructive interference.

Laue Equations

Max von Laue
1914 Nobel Prize for Physics



$$\mathbf{a} \cdot \mathbf{S}_s + \mathbf{a} \cdot (-\mathbf{S}_i) = \mathbf{a} \cdot (\mathbf{S}_s - \mathbf{S}_i) = h\lambda$$

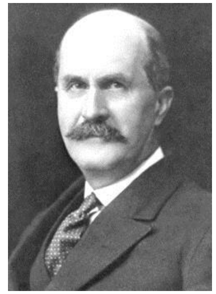
In three dimensions →

$$\mathbf{a} \cdot (\mathbf{S}_s - \mathbf{S}_i) = h\lambda$$

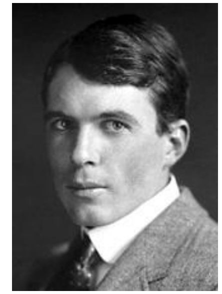
$$\mathbf{b} \cdot (\mathbf{S}_s - \mathbf{S}_i) = k\lambda$$

$$\mathbf{c} \cdot (\mathbf{S}_s - \mathbf{S}_i) = l\lambda$$

Bragg’s Law

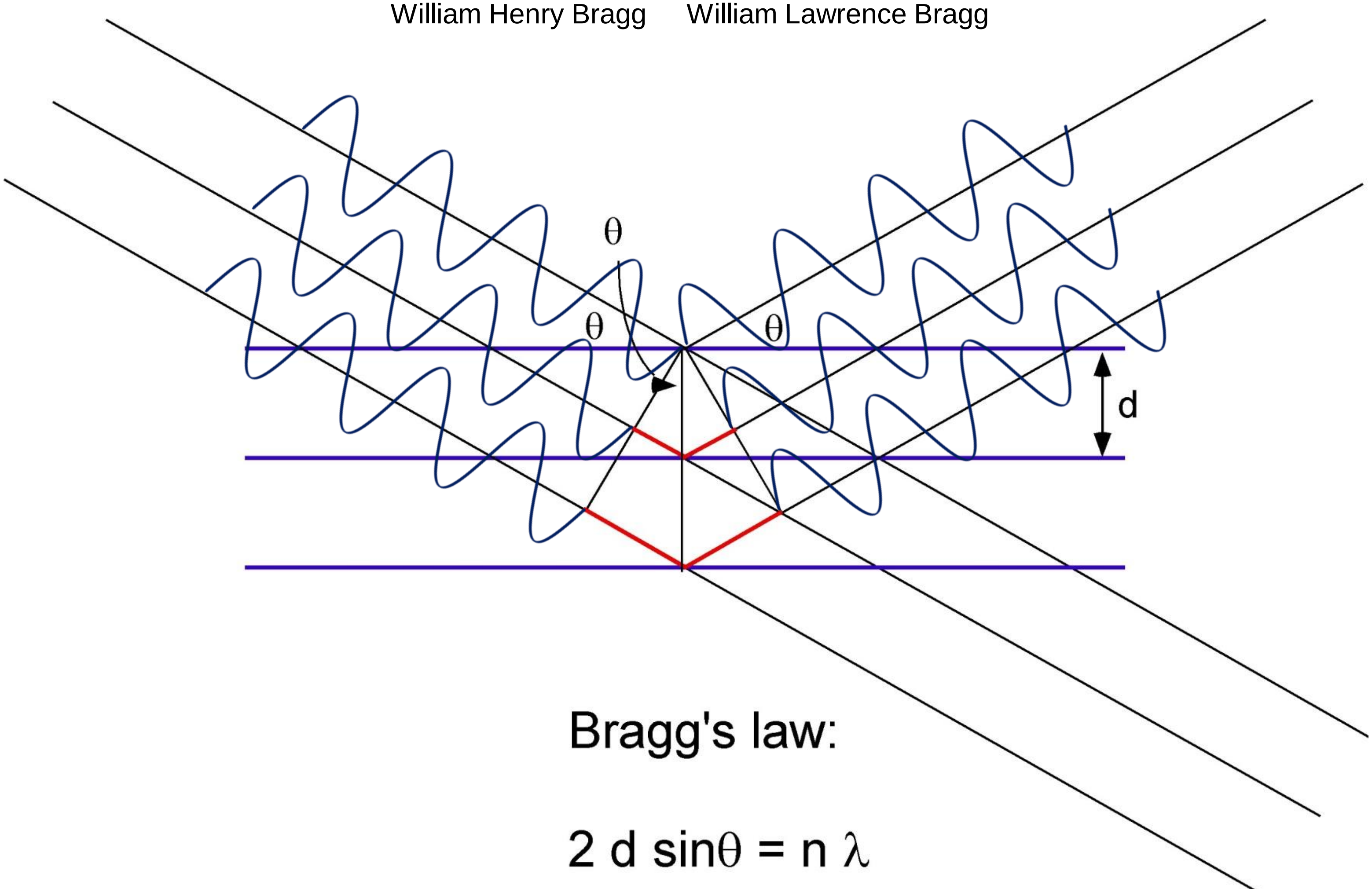


William Henry Bragg



William Lawrence Bragg

Jointly awarded the 1915 Nobel Prize in Physics

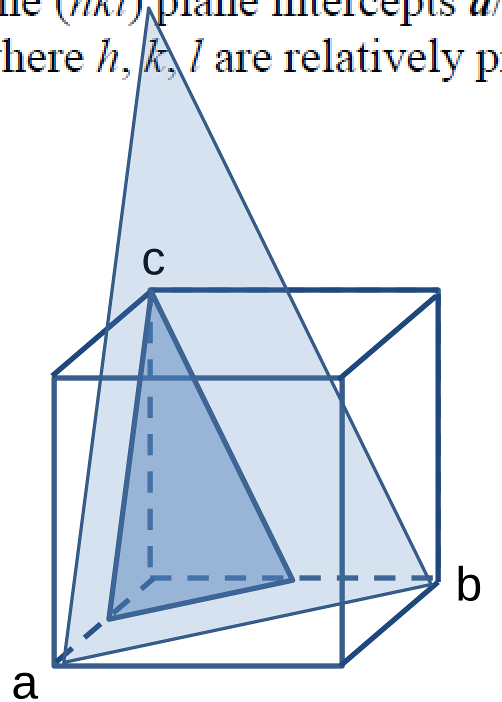


Bragg's law:

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

Crystallographic Planes and Miller Indices

The (hkl) plane intercepts $\boldsymbol{a}/h$, $\boldsymbol{b}/k$, $\mathbf{c}/l$ on crystallographic axes X, Y, Z, where h, k, l are relatively prime integers.

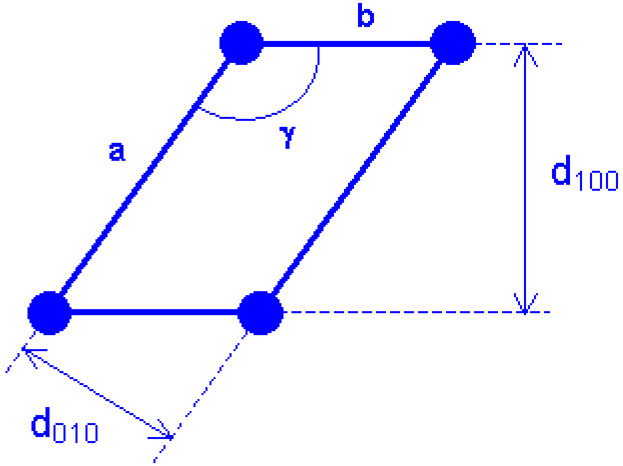


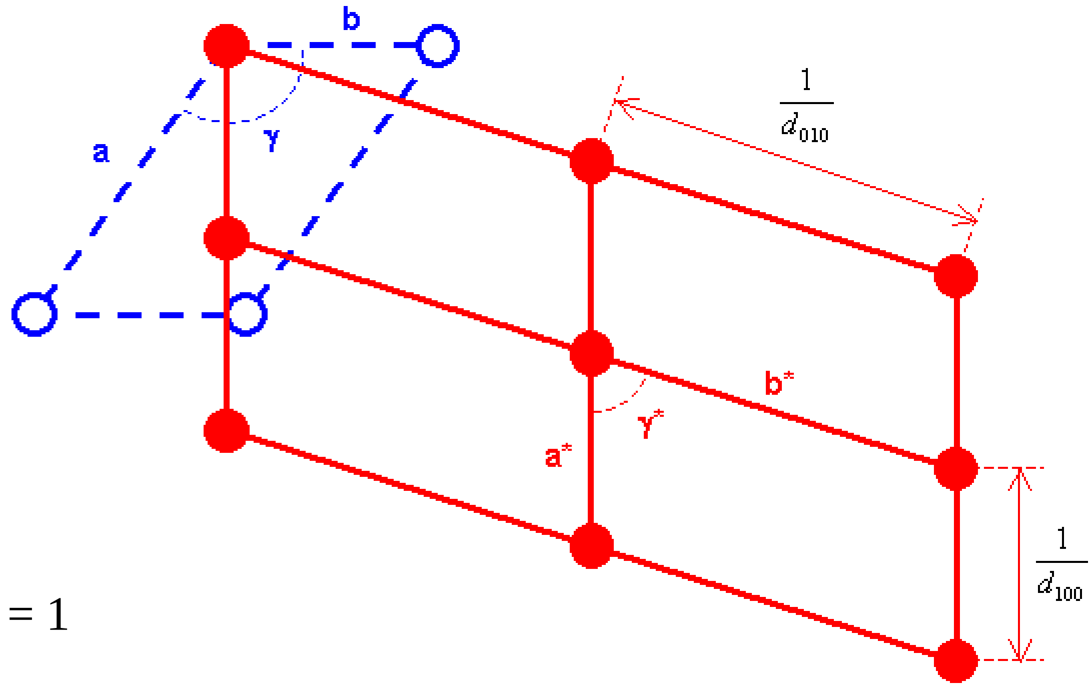
(221)

Intercepts	$\frac{a}{h}, \frac{b}{k}, \frac{c}{l}$
Fractional intercepts	$\frac{1}{h}, \frac{1}{k}, \frac{1}{l}$
Reciprocals of the fractional intercepts	h, k, l
Miller Indices (*prime integers*)	h, k, l

d-spacing = spacing between origin and first plane or between neighboring planes in the family of planes.

Real and reciprocal Space





$$\mathbf{a}^* \bullet \mathbf{a} = \mathbf{b}^* \bullet \mathbf{b} = \mathbf{c}^* \bullet \mathbf{c} = 1$$

$$\mathbf{a}^* \bullet \mathbf{b} = \ldots = 0$$

Laue equations:

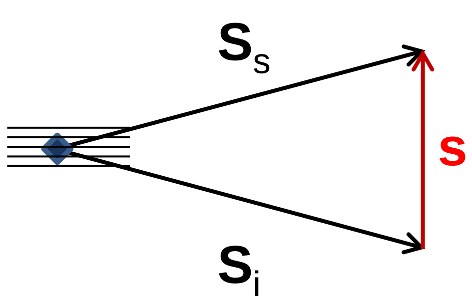
$\mathbf{a} \bullet (\mathbf{S}_s - \mathbf{S}_i) = h\lambda$, or $\mathbf{a} \bullet \mathbf{s} = h$

$\mathbf{b} \bullet (\mathbf{S}_s - \mathbf{S}_i) = k\lambda$, or $\mathbf{b} \bullet \mathbf{s} = k$

$\mathbf{c} \bullet (\mathbf{S}_s - \mathbf{S}_i) = l\lambda$, or $\mathbf{c} \bullet \mathbf{s} = l$

where

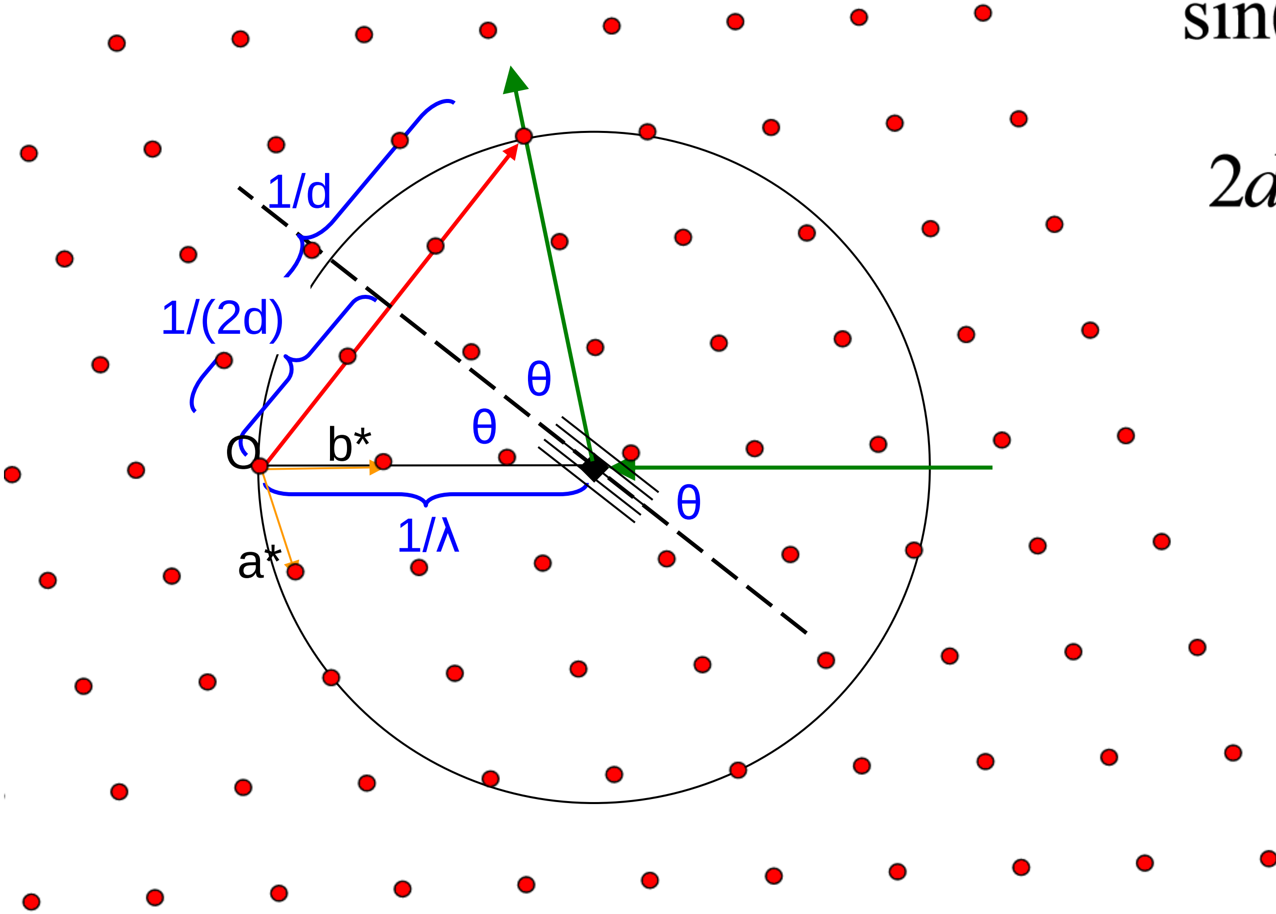
$\mathbf{s} = (\mathbf{S}_s - \mathbf{S}_i)/\lambda = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$



$|\mathbf{S}| = 1/\lambda$

$|\mathbf{s}| = 1/d$

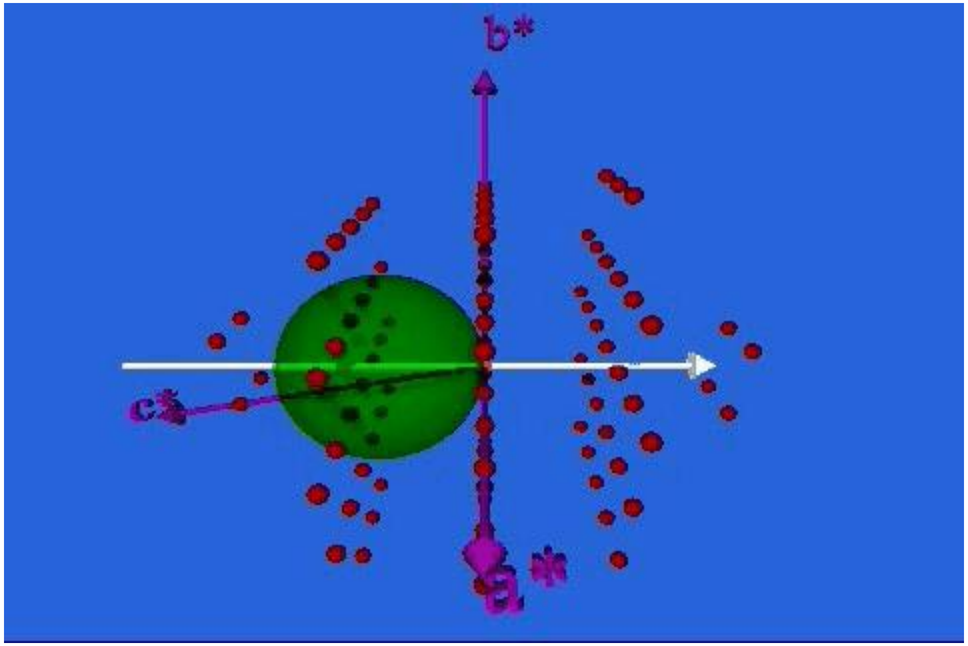
The Ewald Sphere



$$\sin(\theta) = \frac{1/(2d)}{1/\lambda}$$

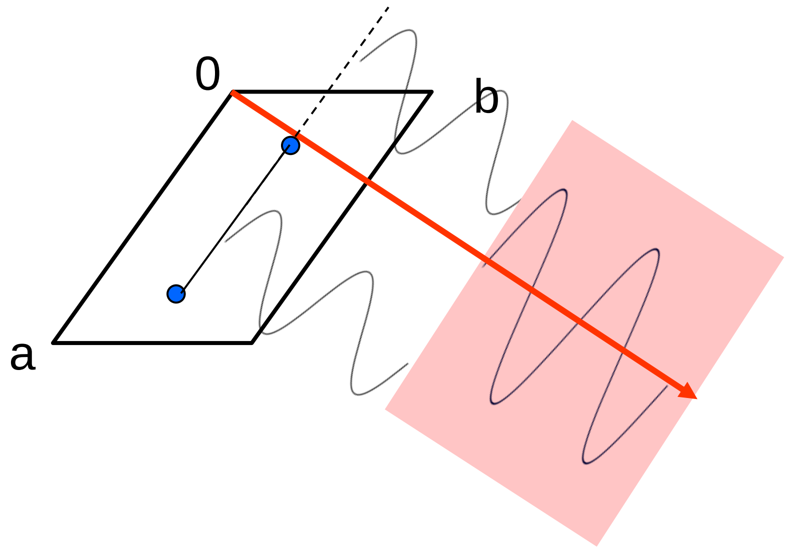
$$2d\sin(\theta) = \lambda$$

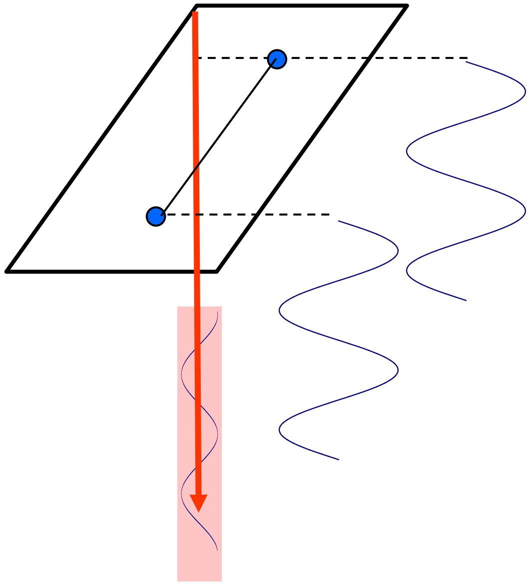
The Ewald sphere: the movie



Courtesy of the CSIC (Spanish National Research Council).
http://www.xtal.iqfr.csic.es/Cristalografia/index-en.html

Bragg Peak Intensity





Relative phase shifts related to molecular structure.

$$F_{hkl} = \sum_i b_i \exp(2\pi i \mathbf{s} \bullet \mathbf{r})$$

$$F_{hkl} = \sum_i b_i \exp[2\pi i(hx + ky + lz)]$$

$$\rho(xyz) = \frac{1}{V} \sum_{hkl} F_{hkl}\, e^{-2\pi i(hx+ky+lz)}$$

b_i is the neutron scattering length.
It is replaced by f_i, the x-ray form factor.

The phase problem

$$I_{hkl} = F_{hkl}\overline{F_{hkl}} = |F_{hkl}|e^{i\phi}|F_{hkl}|e^{-i\phi} = |F_{hkl}|^2$$

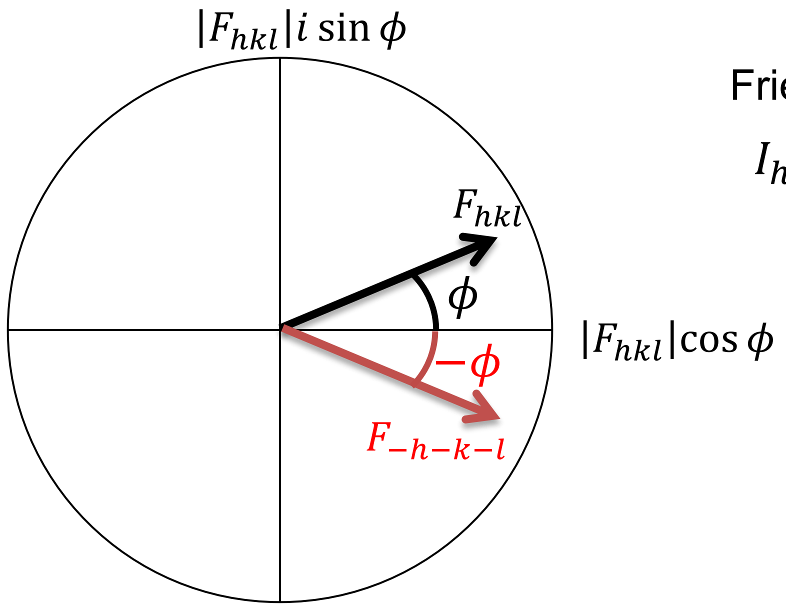
Euler's formula:

$$F_{hkl} = |F_{hkl}|e^{i\phi} = |F_{hkl}|(\cos\phi + i\sin\phi) = A + iB$$

$$F_{hkl} = |F_{hkl}|e^{-i\phi} = |F_{hkl}|(\cos\phi - i\sin\phi) = A - iB$$

$$\tan\phi = B/A$$

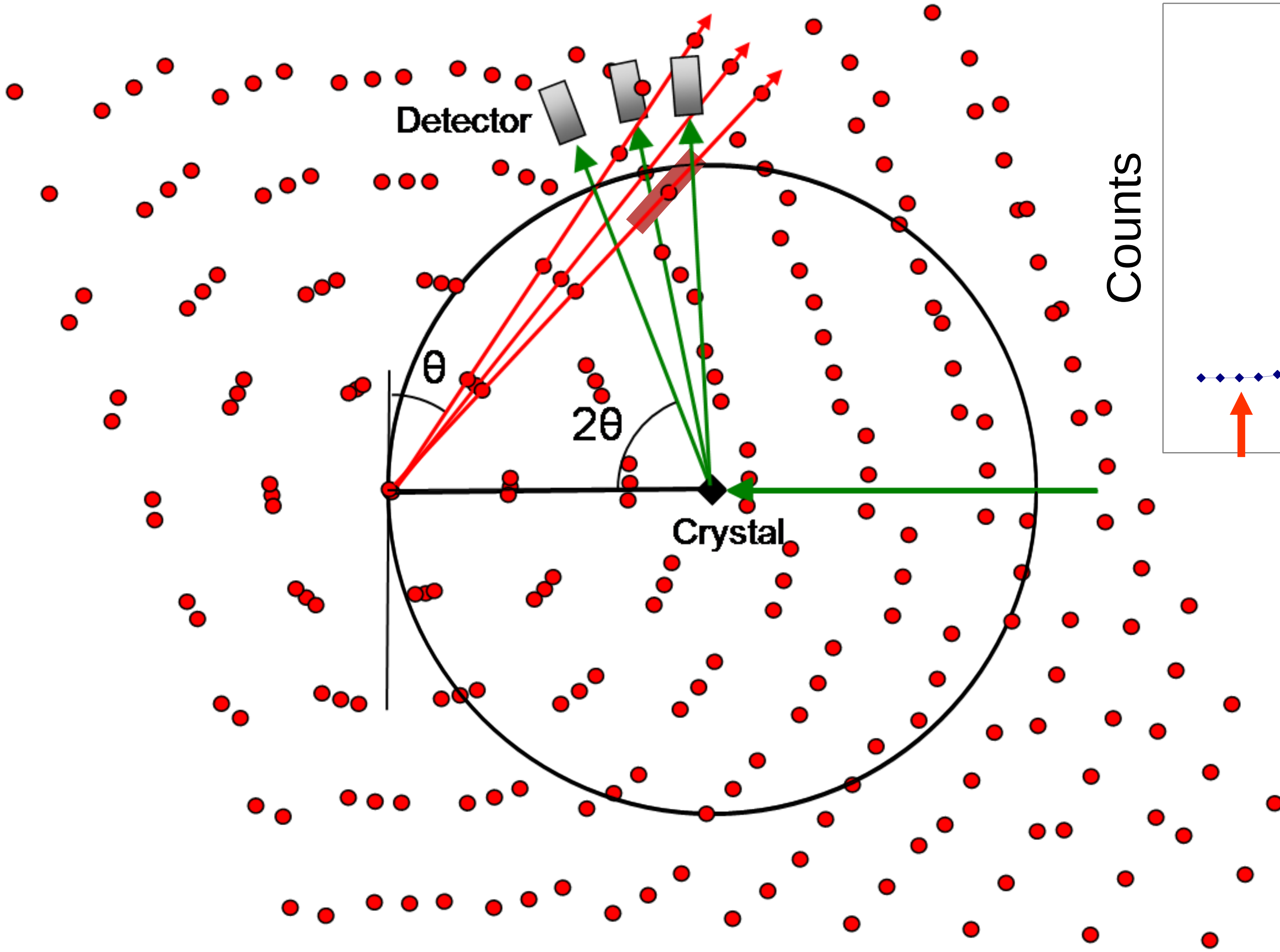
$$I_{hkl} = (A + iB)(A - iB) = A^2 + B^2$$

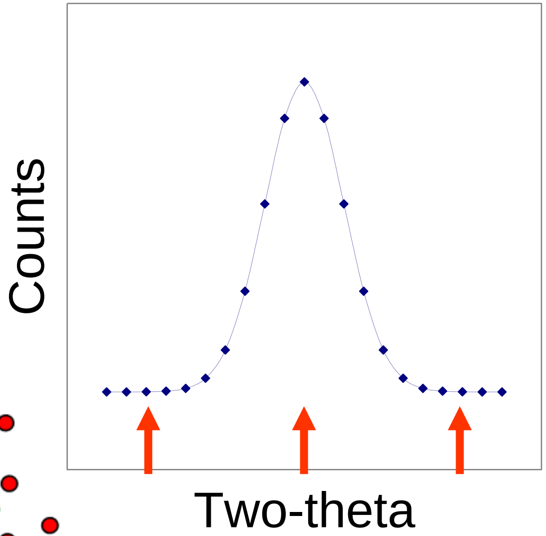


Friedel's law:

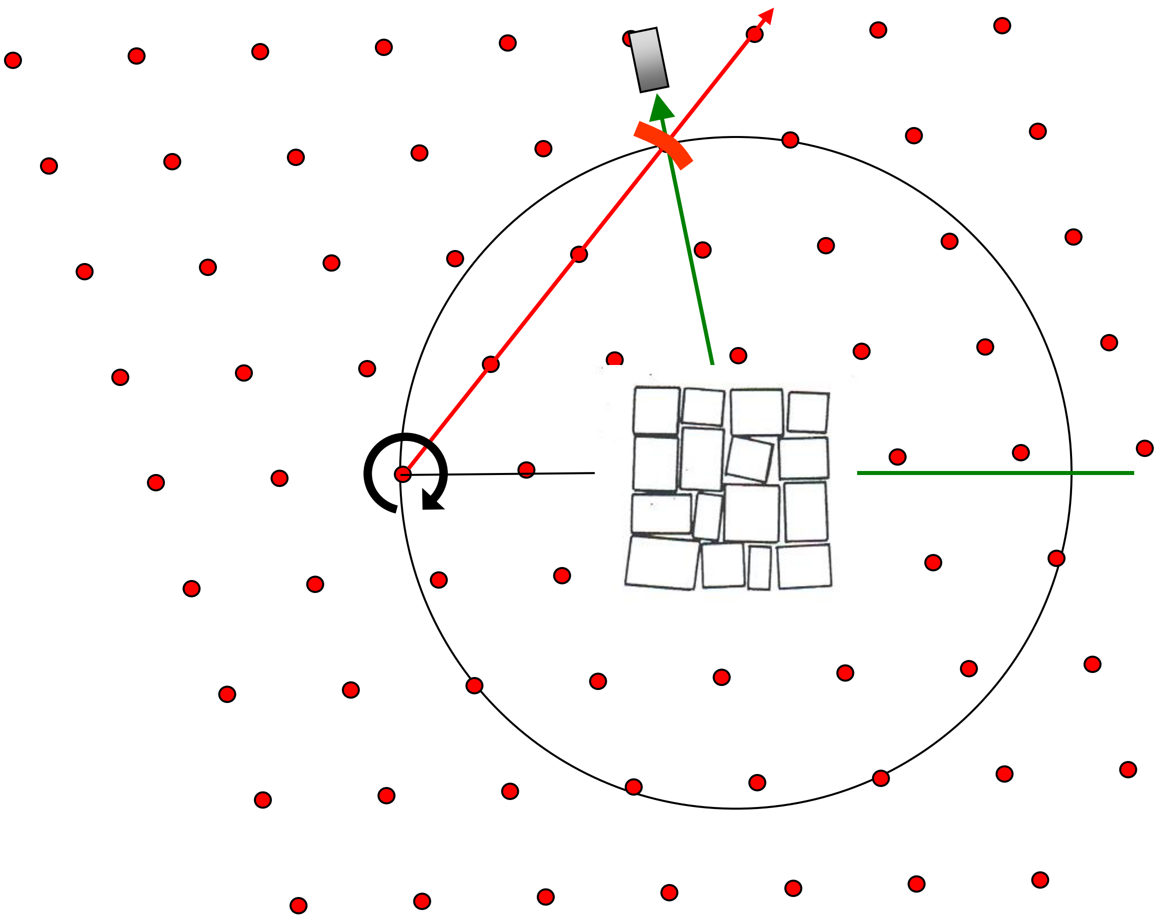
$$I_{hkl} = F_{hkl}\overline{F_{hkl}} = F_{hkl}F_{-(hkl)} = I_{-(hkl)}$$

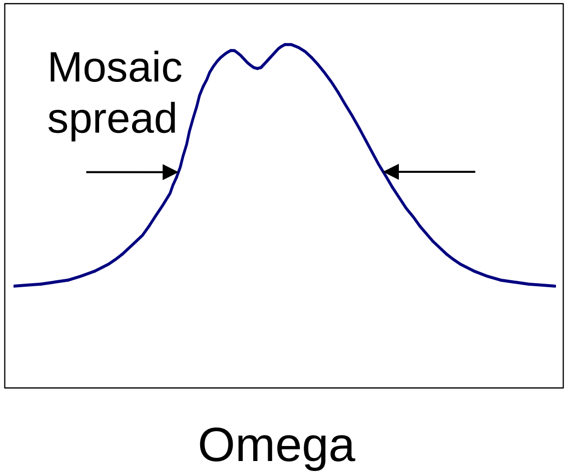
θ-2θ Step Scan





Omega Step Scan

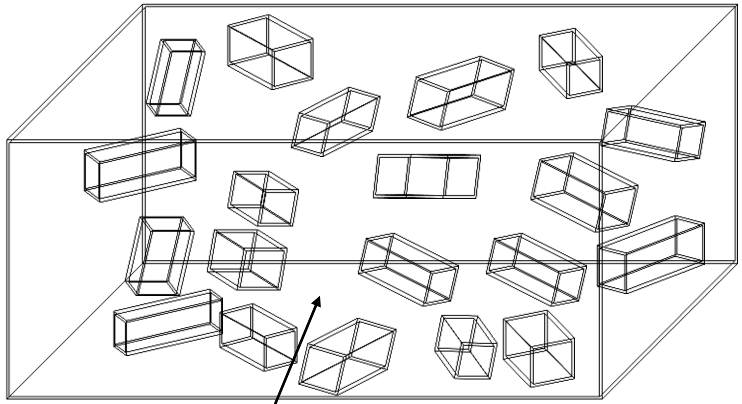




1. Detector stationary at 2θ angle.
2. Crystal is rotated about θ by +/- ω.
3. FWHM is the mosaic spread.

Something completely different - polycrystallography

What is a powder? - polycrystalline mass



All orientations of crystallites possible

Sample: 1μl powder of 1μm crystallites - ~10^9 particles

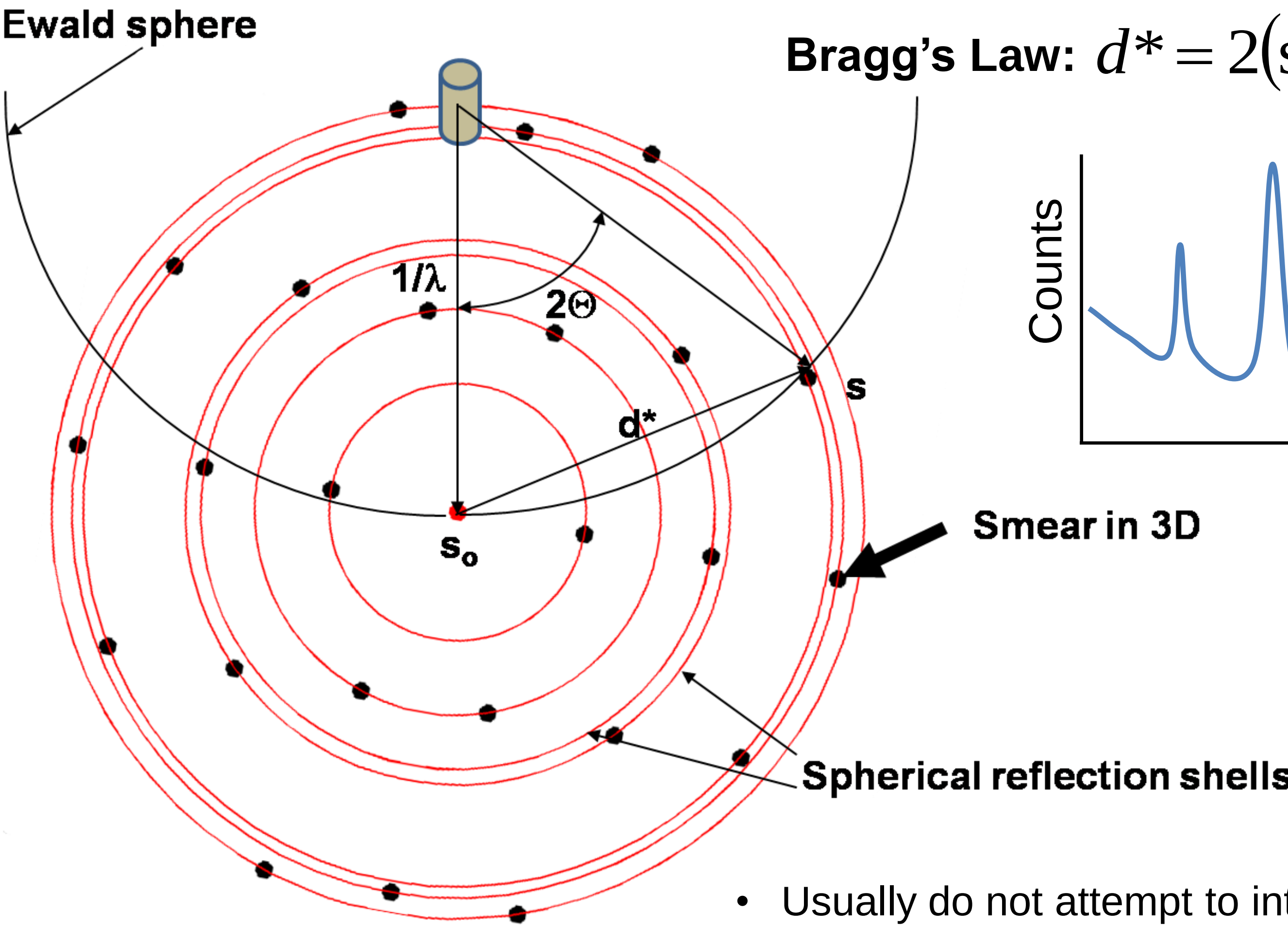
Packing efficiency – typically 50%
Spaces – air, solvent, etc.

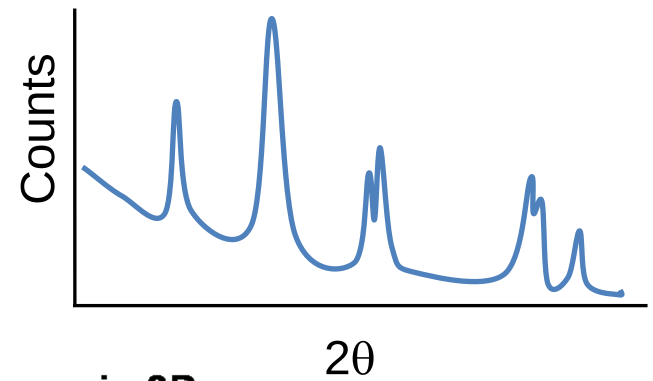
Single crystal reciprocal lattice
- smeared into spherical shells

Courtesy of R. Von Dreele

Powder Diffraction

Bragg's Law: $d^* = 2(\sin\theta)/\lambda$





- Usually do not attempt to integrate individual peaks.
- Instead, fit the spectrum using Rietveld profile analysis. Requires functions that describe the peak shape and background.

Why do single crystal diffraction (vs. powder diffraction)?

- Smaller samples
  - neutrons: 1-10 mg vs 500-5000 mg
  - x-rays: µg vs mg
- Larger molecules and unit cells
- Neutrons: hydrogen is ok for single crystals, powders generally need to be deuterated
- Less absorption
- Fourier coefficients are more accurate – based on integrating well-resolved peaks
- Uniquely characterize non-standard scattering – superlattice and satellite peaks (commensurate and incommensurate), diffuse scattering (rods, planes, etc.)

But:

- Need to grow a single crystal
- Data collection can be more time consuming

Some history of single crystal neutron diffraction

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 19, NUMBER 11 NOVEMBER, 1951

The Use of Single-Crystal Neutron Diffraction Data for Crystal Structure Determination*

S. W. PETERSON AND HENRI A. LEVY
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received August 30, 1951)

Intensities of neutron reflections from single crystal specimens of several substances have yielded structure factors in close agreement with calculation and with those measured by the usual powder method. Specimens whose dimensions were in the millimeter range were used. Three materials yielded low results, probably because of extinction in the single crystal specimens. The use of single crystal neutron reflections for crystal structure determination appears practical in many cases.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 20, NUMBER 4 APRIL, 1952

A Single Crystal Neutron Diffraction Determination of the Hydrogen Position in Potassium Bifluoride*

S. W. PETERSON AND HENRI A. LEVY
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received December 10, 1951)

Neutron diffraction measurements on KHF_2 single crystals show that the hydrogen atom occupies the central position, within 0.1A, in the linear F—H—F ion. The data also indicate asymmetry in thermal motion, which suggests that the bifluoride ion undergoes rotatory oscillation with appreciable amplitude. The study demonstrates the usefulness of single crystal neutron diffraction data for crystal structure determination.

- 1951 – Peterson and Levy demonstrate the feasibility of single crystal neutron diffraction using the Graphite Reactor at ORNL.
- 1950s and 1960s – Bill Busing, Henri Levy, Carroll Johnson and others wrote a suite of programs for singe crystal diffraction including ORFLS and ORTEP.
- 1979 – Peterson and coworkers demonstrate the single crystal neutron time-of-flight Laue technique at Argonne’s ZING-P’ spallation neutron source.

The Orientation Matrix

Acta Cryst. (1967). **22**, 457

Angle Calculations for 3- and 4- Circle X-ray and Neutron Diffractometers*

BY WILLIAM R. BUSING AND HENRI A. LEVY

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, *U.S.A.*

(*Received* 13 *June* 1966)

Methods are derived for calculations useful in the operation of 3- and 4-circle X-ray or neutron single-crystal diffractometers. These include: (1) establishing the sample orientation from the cell parameters and the observed angles for two reflections, or from the observed angles for three reflections only, (2) calculating the angles for observing a given reflection either in a special setting or at a specified azimuthal angle, (3) obtaining the vectors needed for calculating absorption corrections, and (4) using observations of several reflections to refine cell and orientation parameters by the method of least squares.

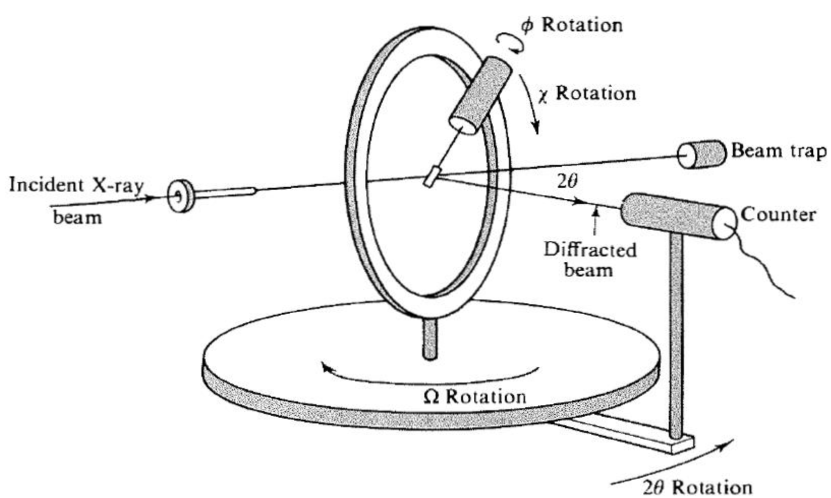


Fig. 5.29. A typical four-circle diffractometer. The counter rotates about the 2θ axis in one plane and the crystal may be orientated in any way by the three axes of rotation ϕ, χ and Ω.

$$\mathbf{B} = \begin{pmatrix} b_1 & b_2 \cos\beta_3 & b_3 \cos\beta_2 \\ 0 & b_2 \sin\beta_3 & -b_3 \sin\beta_2 \cos\alpha_1 \\ 0 & 0 & 1/a_3 \end{pmatrix}$$

U is a rotation matrix relating the unit cell to the instrument coordinate system.

The matrix product **UB** is called the *orientation matrix*.

Picker 4-Circle Diffractometer

Kappa Diffractometer

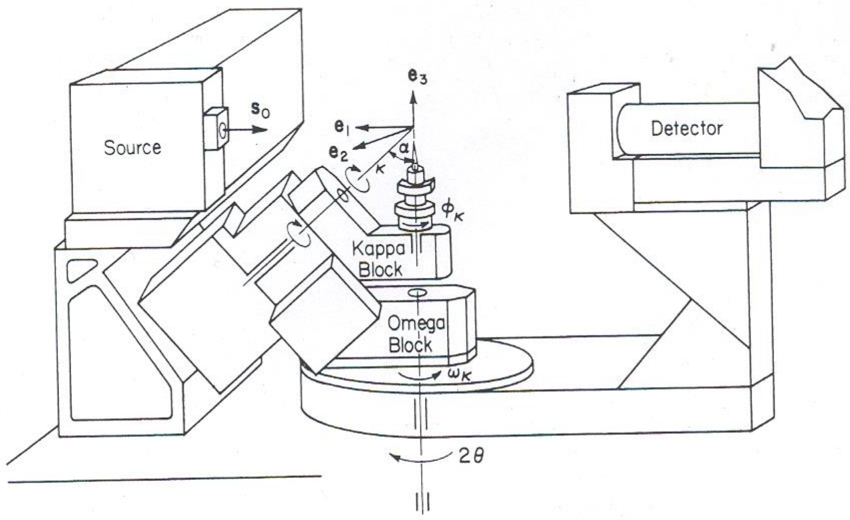
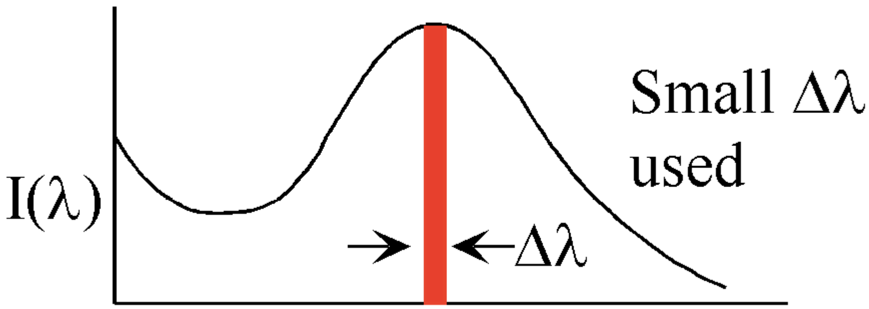


FIGURE 6–13. Kappa geometry. Adapted from operating manual for ENRAF–NONIUS CAD 4 diffractometer (angles ω, ϕ, and $\varkappa$ are opposite in sign to those of Enraf–Nonius). (By permission of ENRAF-NONIUS Service Corp., Bohemia, New York.)

Brucker AXS: KAPPA APEX II

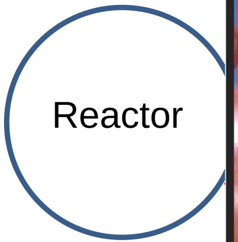
- Full 360° rotations about ω and φ axes.
- Rotation about κ axis reproduces quarter circle about χ axis.

Monochromatic diffractometer

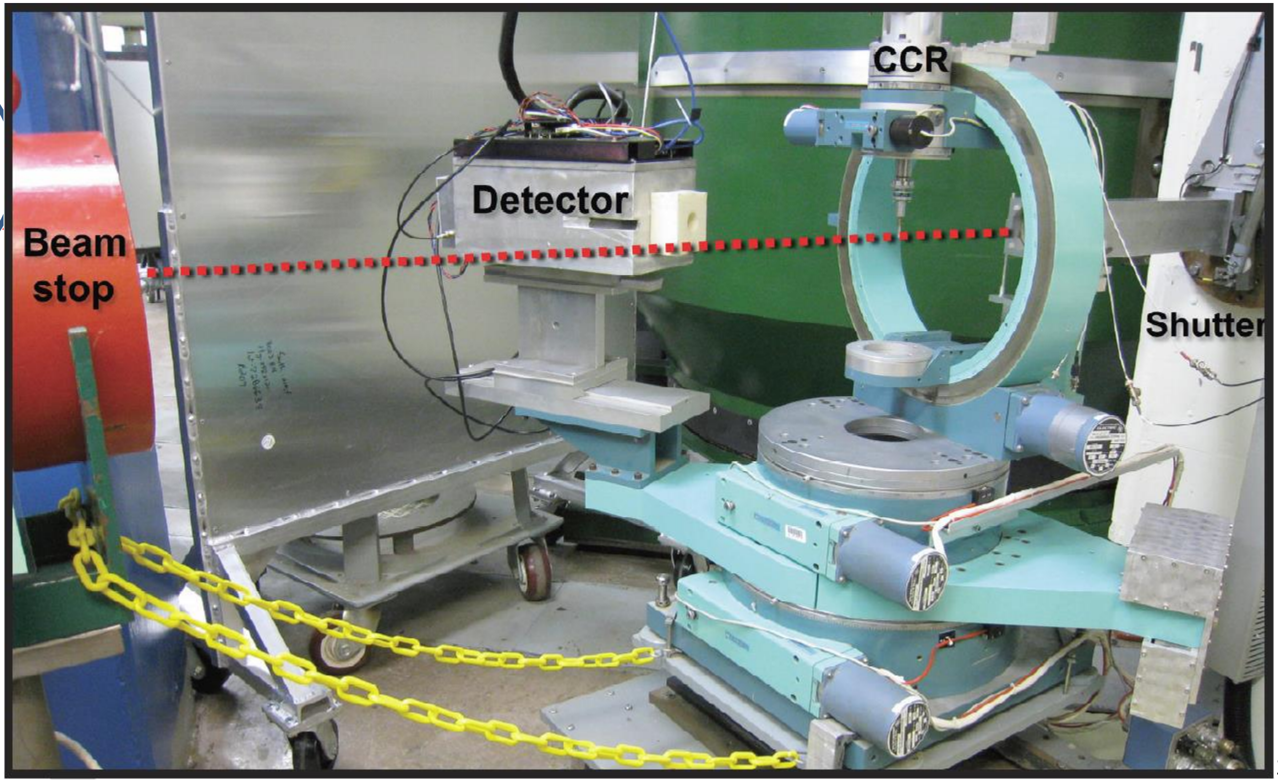


- Rotating crystal
- Vary $\sin\theta$ in the Bragg equation:

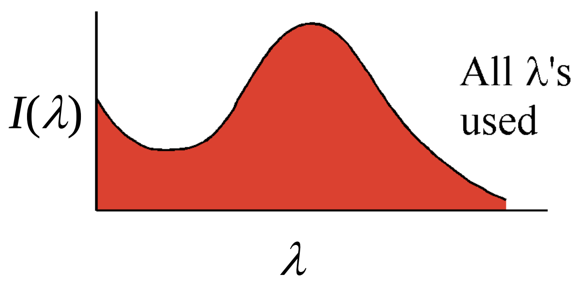
$$2d\sin\theta = n\lambda$$



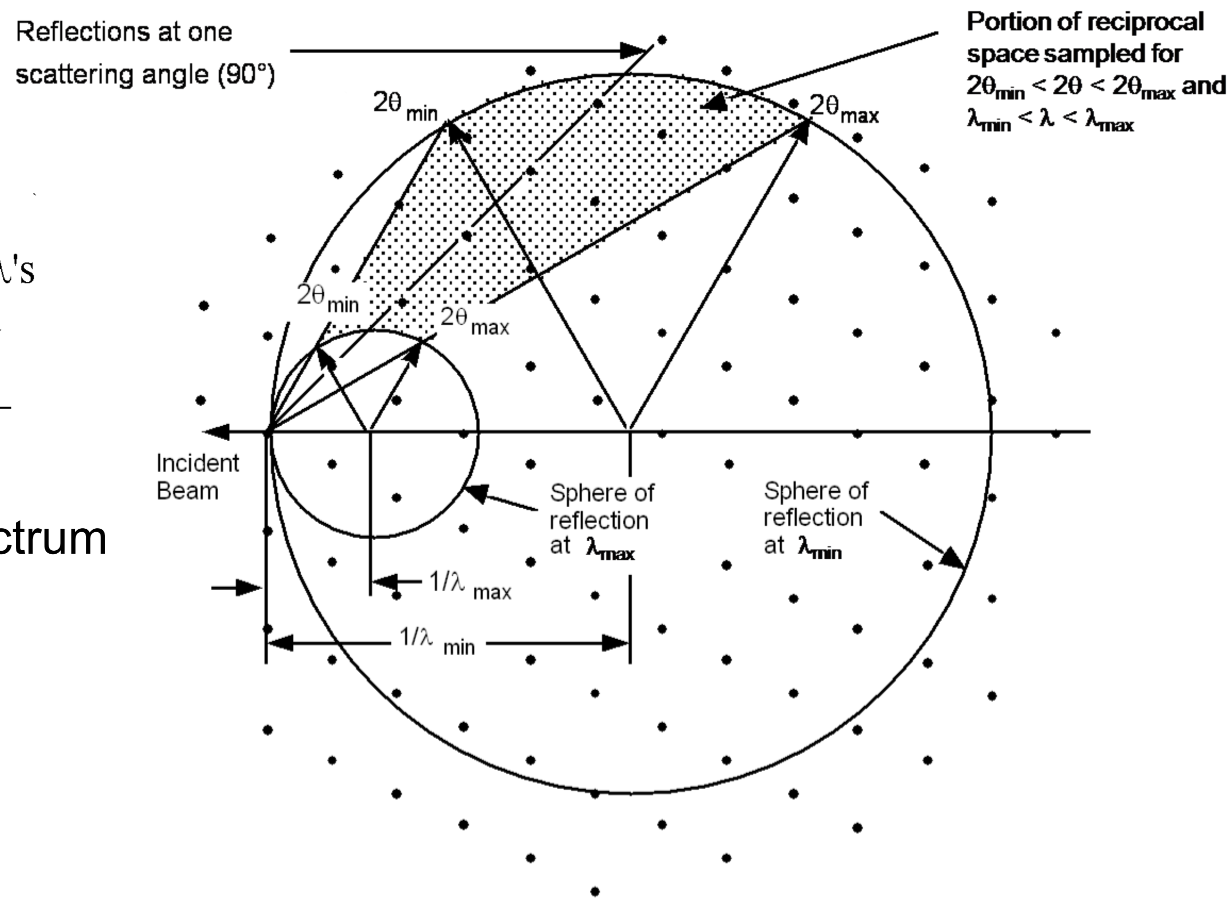
HFIR 4-Circle Diffractometer



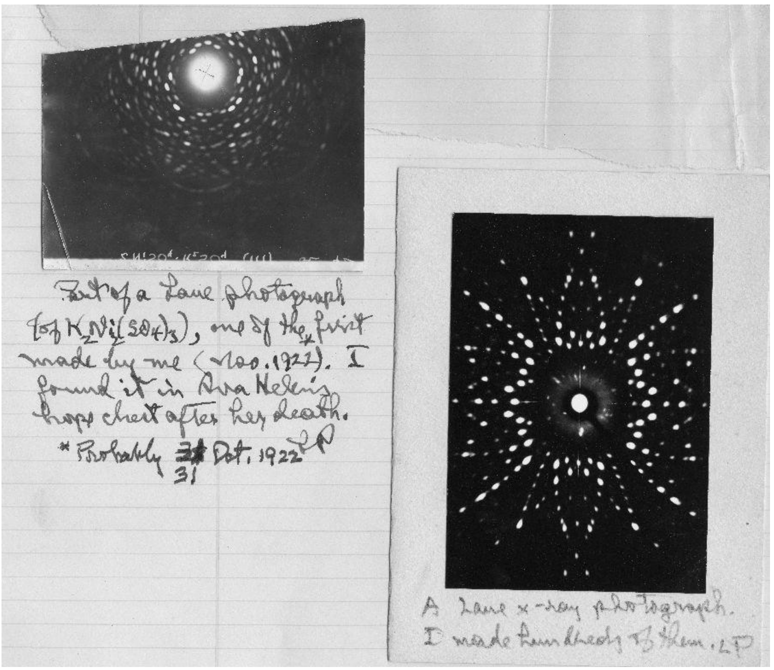
Laue diffraction



Polychromatic "white" spectrum

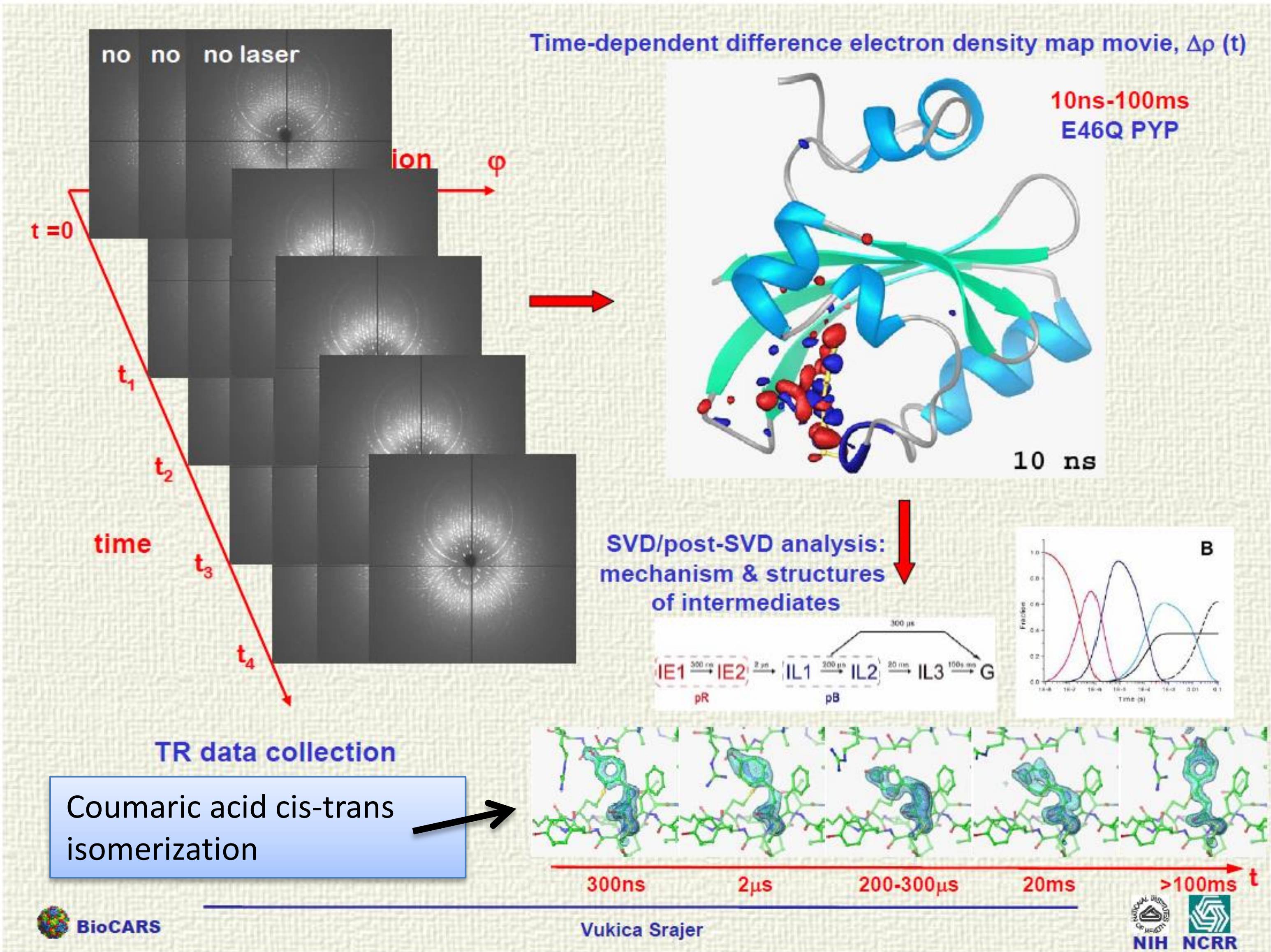


Laue photo from white radiation

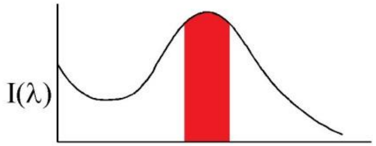


X-ray Laue photos taken
by Linus Pauling

Time-resolved X-ray Laue diffraction of photoactive yellow protein at BioCARS using pink radiation



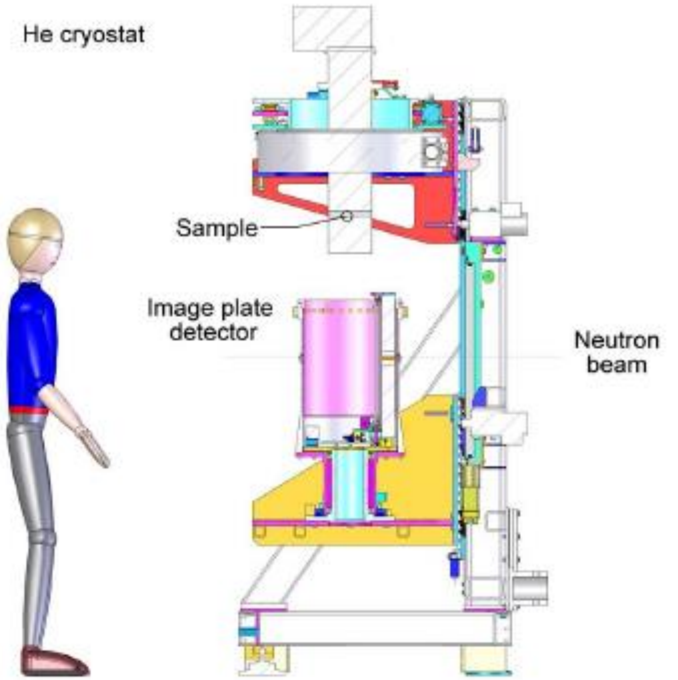
Quasi-Laue Neutron Image Plate Diffractometer



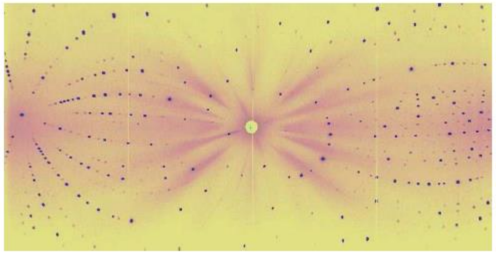
Select $\Delta\lambda/\lambda$ of 10-20%

IMAGINE @ HFIR, ORNL

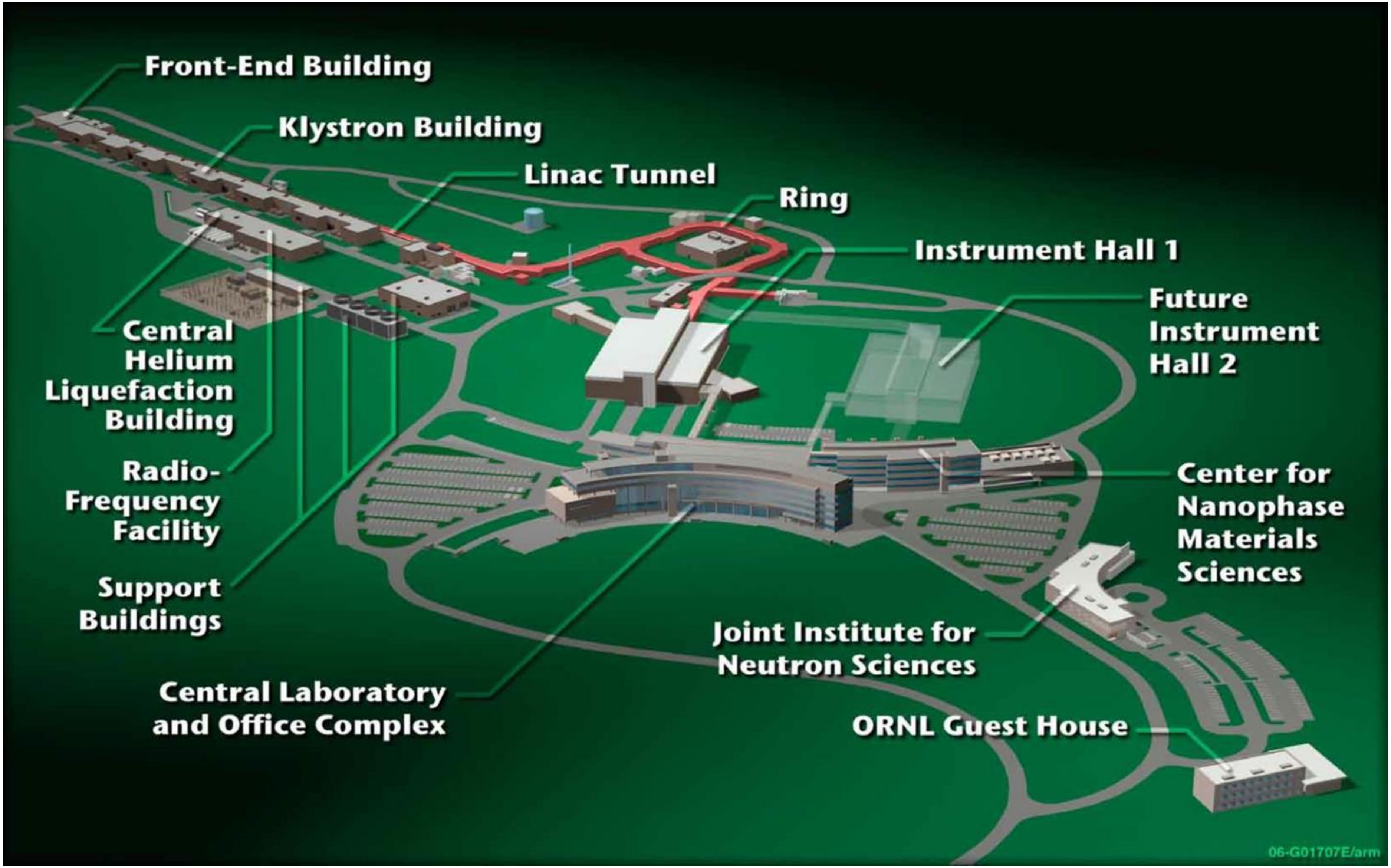
General view of the QLD



QLD schematic (open position)



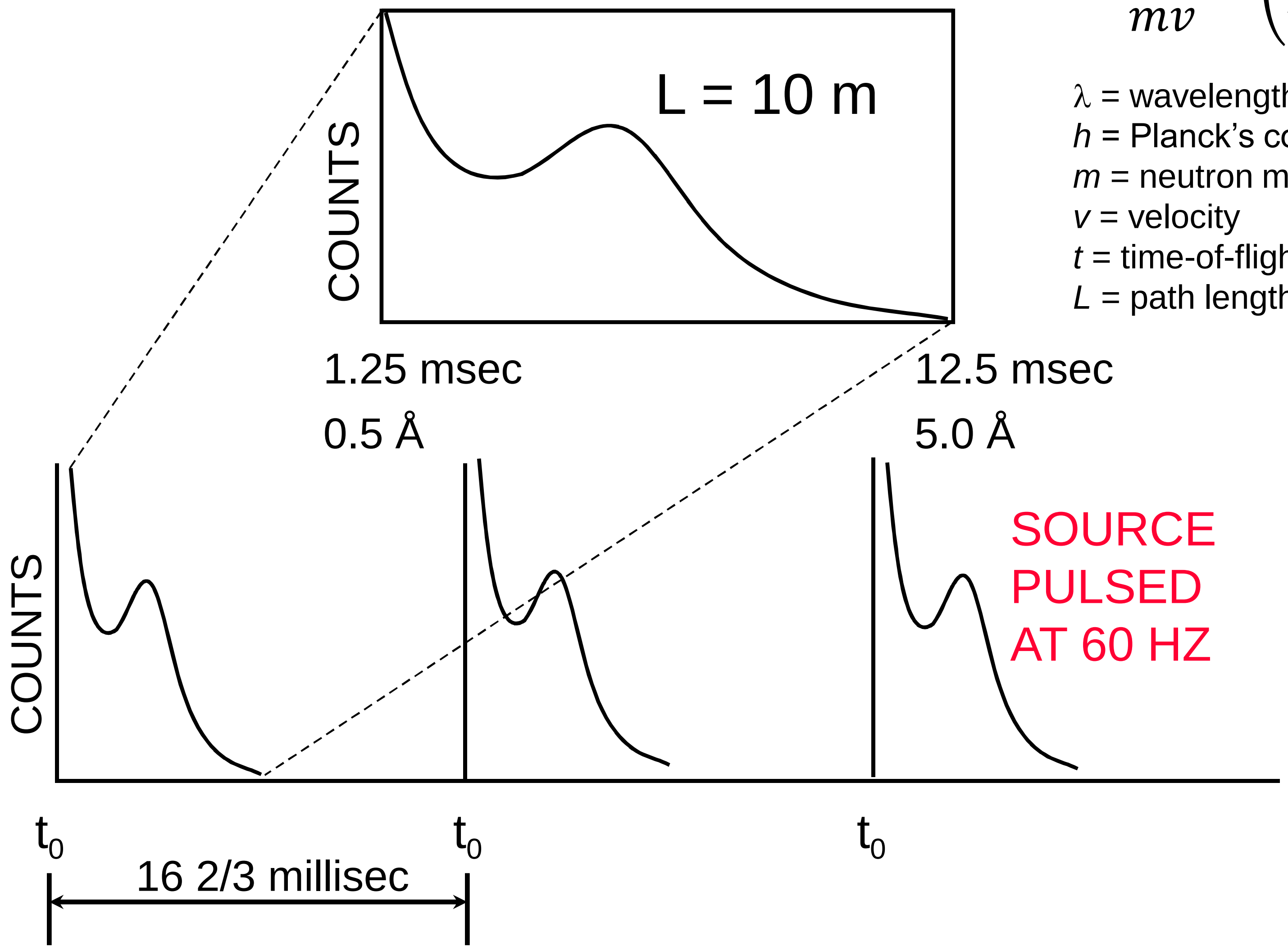
A typical Laue diffraction pattern from $FeTa_2O_6$ just above the 3-D ferroelectric ordering temperature (Chung et al. J. Phys.: Condens. Matter, 16 (2004) 1-17). The faint cross of radial streaks about the central hole, which allows passage of the transmitted neutron beam, arises from 2-D magnetic ordering. Results from the Laue diffractometer VIVALDI at the ILL


Front-End Building
Klystron Building
Linac Tunnel
Ring
Instrument Hall 1
Future Instrument Hall 2
Central Helium Liquefaction Building
Radio-Frequency Facility
Support Buildings
Center for Nanophase Materials Sciences
Joint Institute for Neutron Sciences
Central Laboratory and Office Complex
ORNL Guest House
06-G01707E/arm

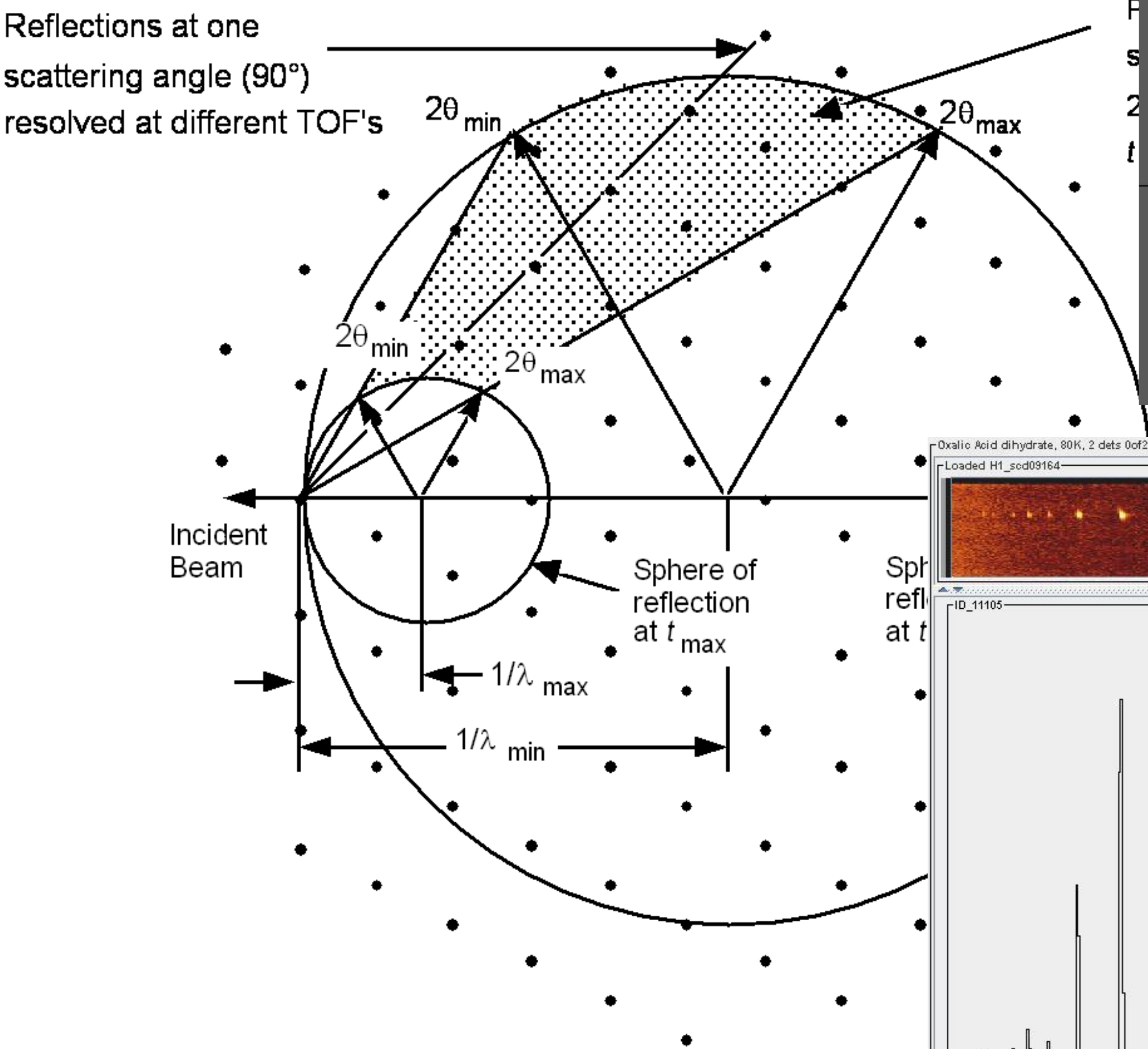
Pulsed Neutron Incident Spectrum

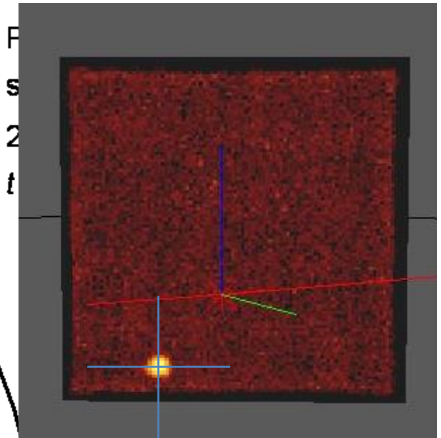
$$\lambda = \frac{h}{mv} = \left(\frac{h}{m}\right)\left(\frac{t}{L}\right)$$

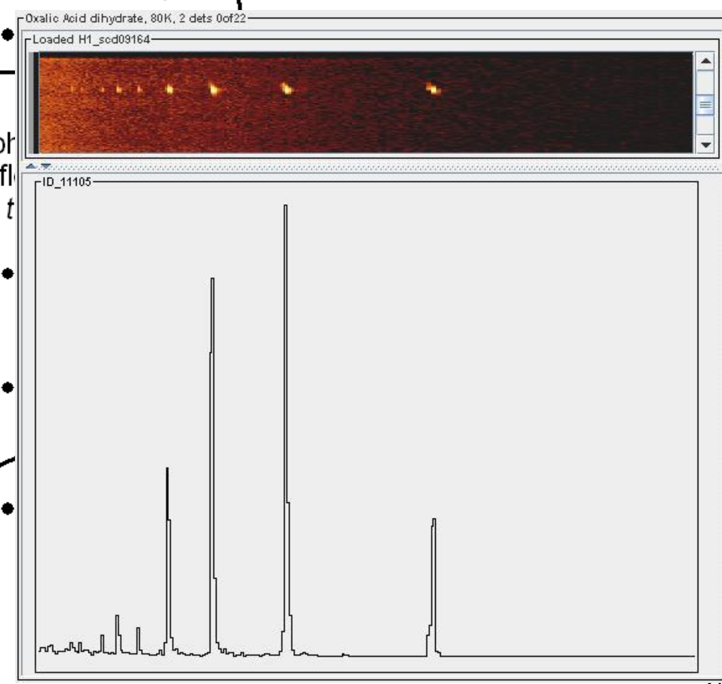
λ = wavelength
h = Planck's constant
m = neutron mass
v = velocity
t = time-of-flight
L = path length



Time-of-Flight Laue Technique

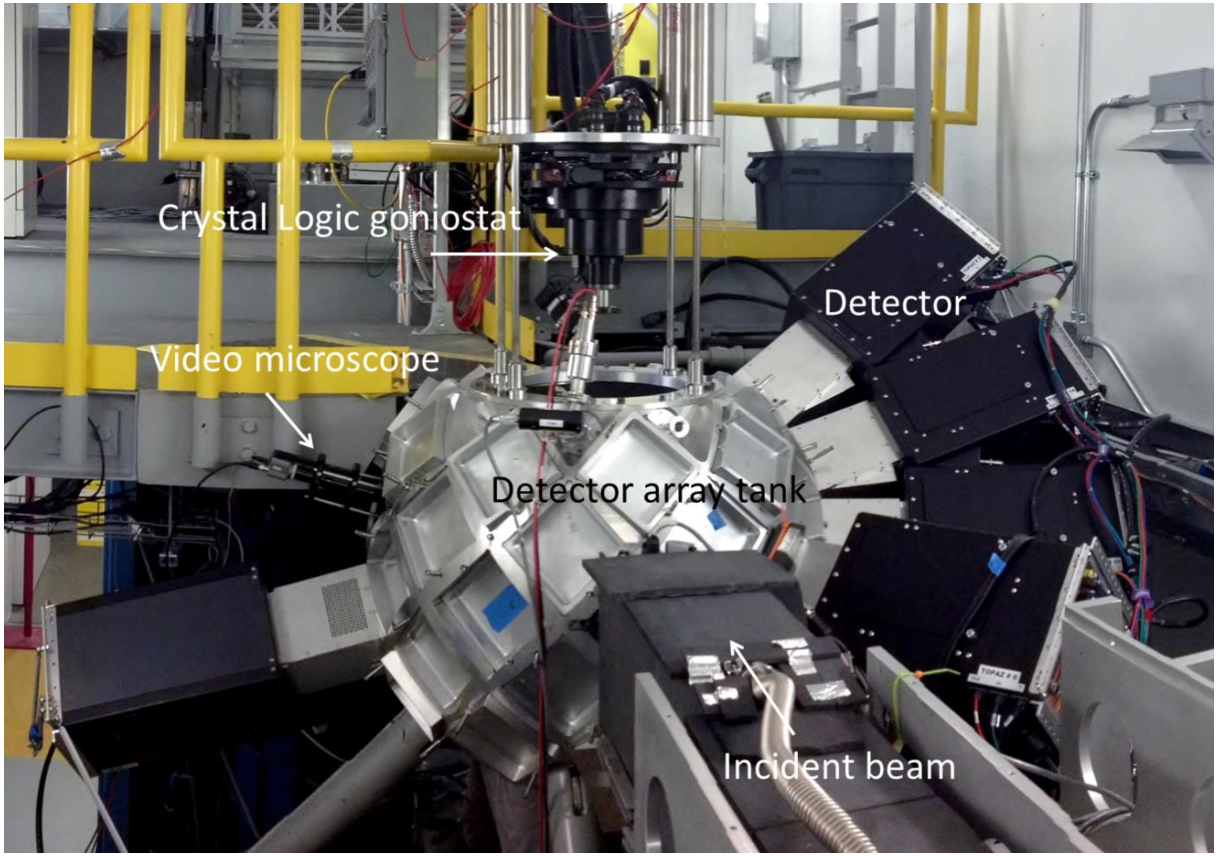




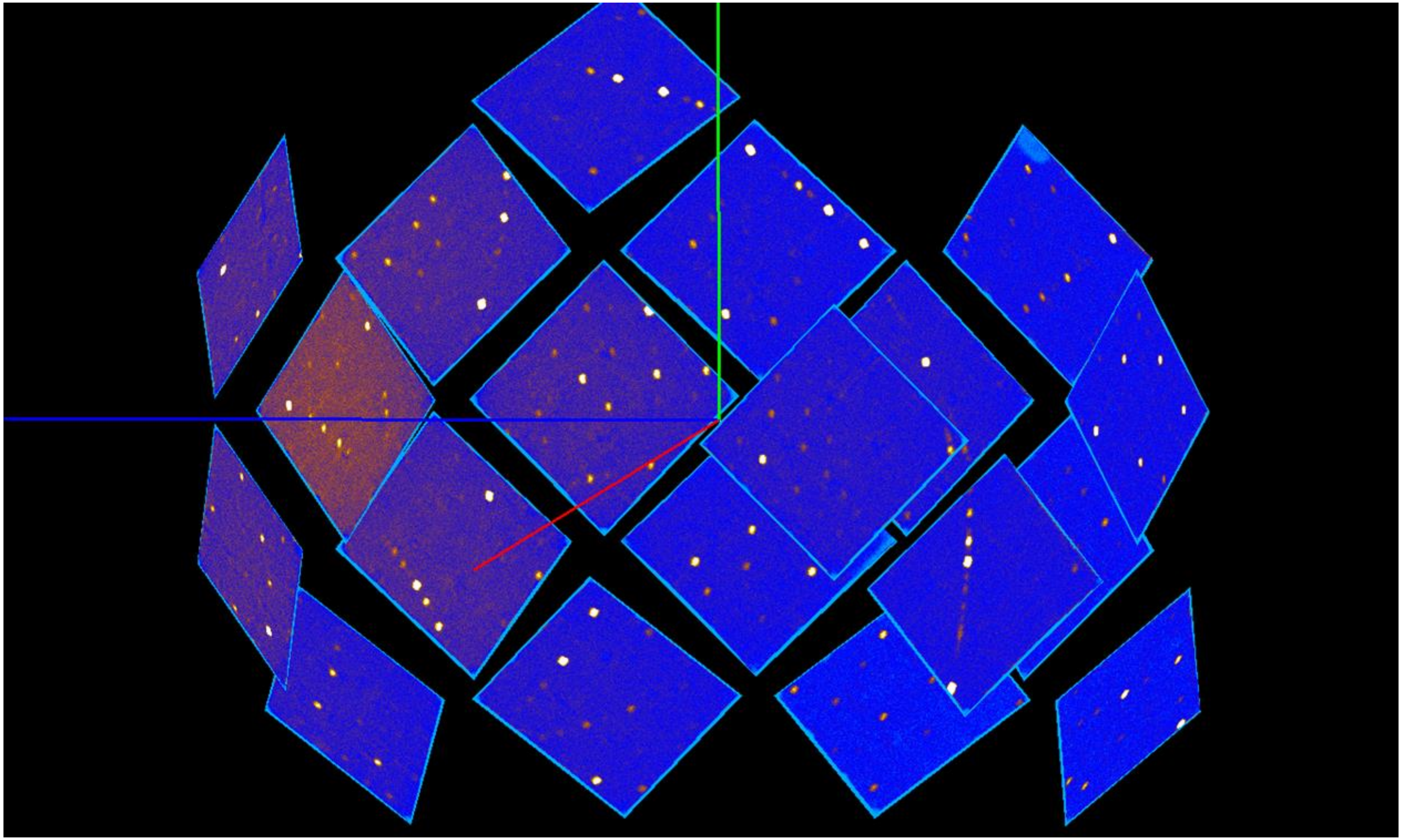


Topaz at the SNS

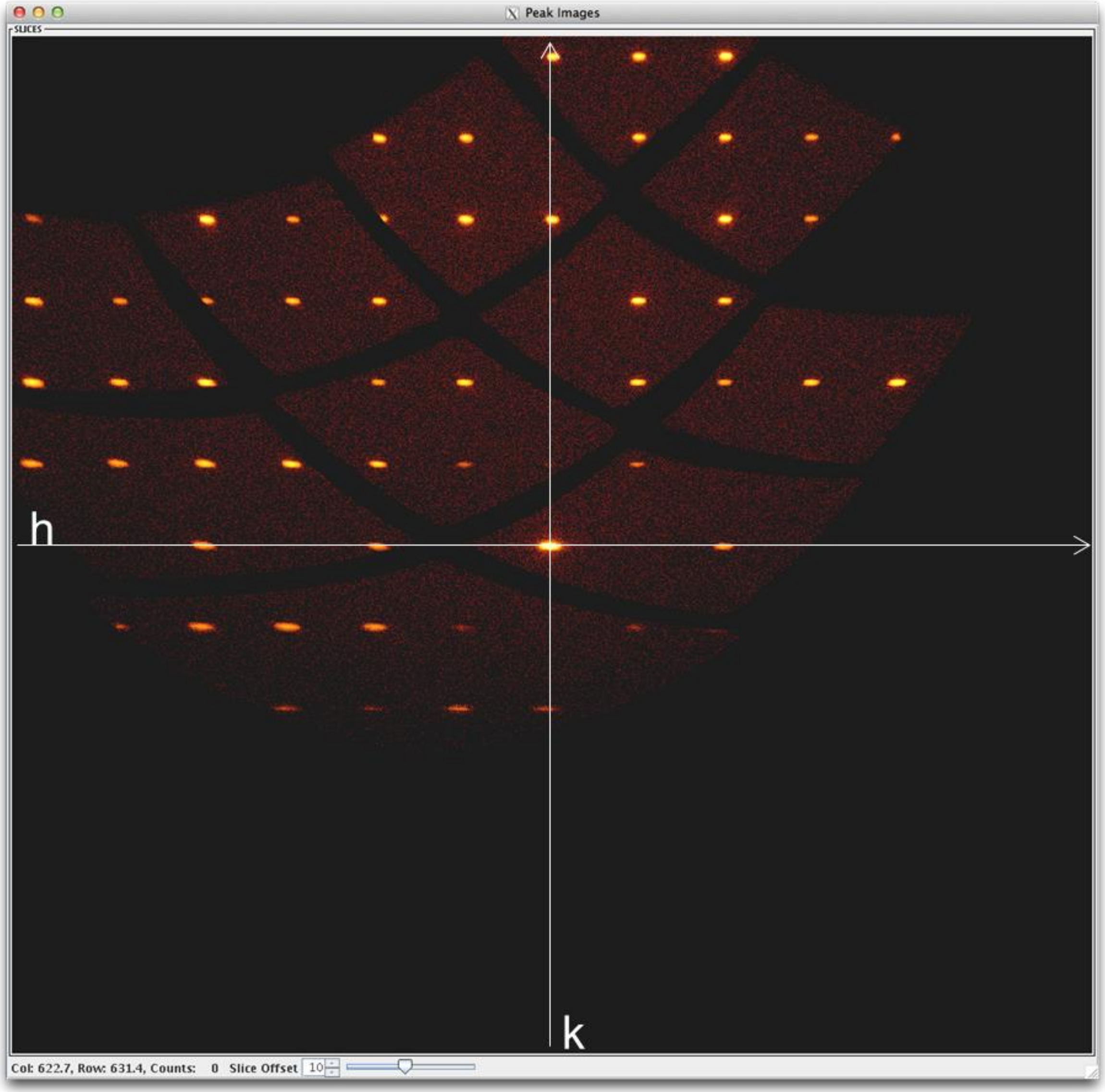
- The TOPAZ detector array tank with 13 detectors
- Each detector active area is 15 x 15 cm^2.
- Crystal to detector distance varies from 40 to 450 cm.
- Moderator to crystal distance is 18 m.
- The Crystal Logic goniostat is raised from the tank to mount crystals and lowered into the tank for data collection

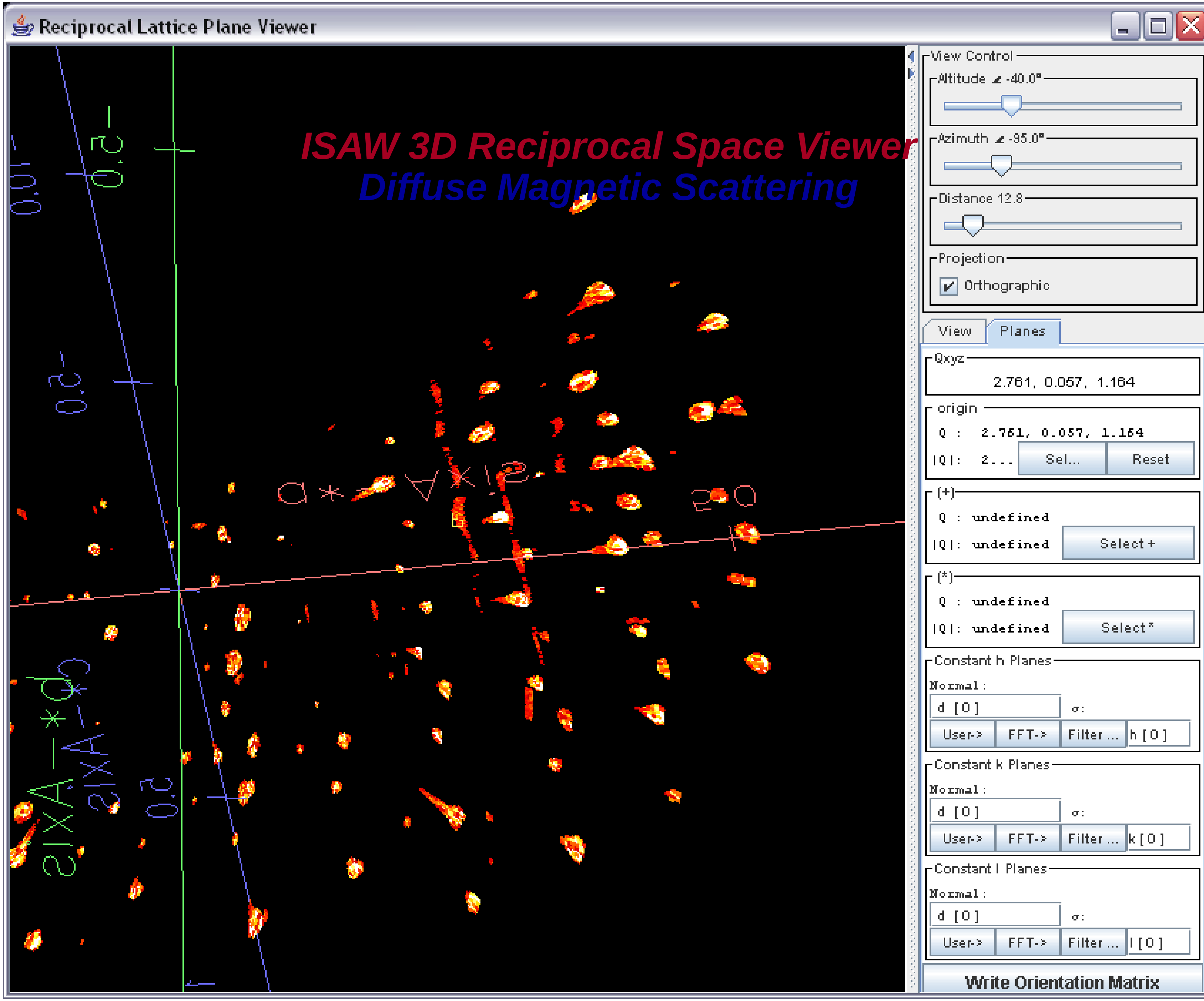


TOPAZ Instrument View with Mantid



Slice View: *l* = 5 reciprocal lattice plane





Reciprocal Lattice Plane Viewer
ISAW 3D Reciprocal Space Viewer
Diffuse Magnetic Scattering
View Control
Altitude -40.0°
Azimuth -95.0°
Distance 12.8
Projection
Orthographic
View
Planes
Qxyz
2.761, 0.057, 1.164
origin
Q : 2.761, 0.057, 1.164
|Q| : 2...
Sel...
Reset
(+)
Q : undefined
|Q| : undefined
Select +
(*)
Q : undefined
|Q| : undefined
Select *
Constant h Planes
Normal :
d [0]
σ:
User->
FFT->
Filter ...
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Constant k Planes
Normal :
d [0]
σ:
User->
FFT->
Filter ...
k [0]
Constant l Planes
Normal :
d [0]
σ:
User->
FFT->
Filter ...
l [0]
Write Orientation Matrix

Outline of single crystal structure analysis

- Collect some initial data to determine the unit cell and the space group.
  - Auto-index peaks to determine unit cell and orientation
  - Examine symmetry of intensities and systematic absences
- Measure a full data set of observed intensities.
- Reduce the raw integrated intensities, I_{hkl}, to structure factor amplitudes, $|F_{\mathrm{obs}}|^2$.
- Solve the structure.
- Refine the structure.

Data reduction - single crystal TOF Laue

Data reduction: convert raw integrated intensities, I_{hkl}, into relative structure factor amplitudes, $|F_{hkl}|^2$.

$$I_{hkl} = k\,\phi(\lambda)\,\varepsilon(\lambda)\,A(\lambda)\,y(\lambda)\,(V_s/V_c^2)\,|F_{hkl}|^2\ \lambda^4/\sin^2\theta$$

k = scale factor

$\phi(\lambda)$ = incident flux spectrum

$\varepsilon(\lambda)$ = detector efficiency as a function of wavelength λ

$A(\lambda)$ = sample absorption

$y(\lambda)$ = secondary extinction correction

V_s = sample volume

V_c = unit cell volume

Intensity vs. sample volume and unit cell volume

$$I_{hkl} = k\ \phi(\lambda)\ \varepsilon(\lambda)\ A(\lambda)\ y(\lambda)\ (V_s/\boxed{V_c^2})\ |F_{hkl}|^2\ \ \lambda^4/\sin^2\theta$$

$$I_{hkl} = k\ \phi(\lambda)\ \varepsilon(\lambda)\ A(\lambda)\ y(\lambda)\ (V_s/\boxed{V_c})\ (|F_{hkl}|^2/\boxed{V_c})\ \ \lambda^4/\sin^2\theta$$

$$I_{hkl} = k\ \phi(\lambda)\ \varepsilon(\lambda)\ A(\lambda)\ y(\lambda)\ \boxed{N_s}\ (|F_{hkl}|^2/V_c)\ \ \lambda^4/\sin^2\theta$$

Number of unit cells in the sample

Scattering per unit volume approximately constant

Wilson plot

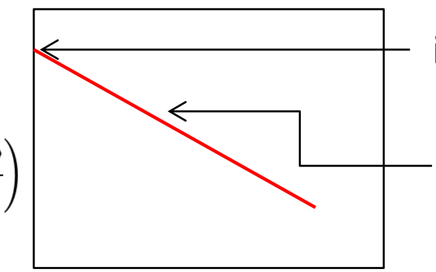
$$\langle |F_{hkl}|^2 \rangle = \sum_{j=1}^{n} b_j^2 = n\langle b_j^2 \rangle$$

n = number of atoms in the unit cell
b_j = neutron scattering length, or
f_j = x-ray form factor

$$\langle |F_{obs}|^2 \rangle = K \sum_{j=1}^{n} b_j^2 e^{-2B\,(\sin^2\theta)/\lambda^2}$$

K = scale factor
B = temperature or thermal parameter

$$\ln\left(\frac{\langle |F_{obs}|^2 \rangle}{\sum_{j=1}^{n} b_j^2}\right) = \ln K - 2B\,(\sin^2\theta)\,/\lambda^2$$



$$V_c = \sum_{j=1}^{n} v_j = n\langle v_j \rangle$$

V_c = unit cell volume
v_j = volume of atom j

$$\langle |F_{hkl}|^2 \rangle / V_c = \langle b_j^2 \rangle / \langle v_j \rangle$$

For crystals containing similar types of atoms in similar ratios, this is a constant.

A. J. C. Wilson, "Determination of absolute from relative x-ray intensity data," *Nature* **150** (1942) 152.

Lorentz factor

The Lorentz factor is geometric integration factor related to the time or angular range during which a peak is reflecting.

Laue integration:

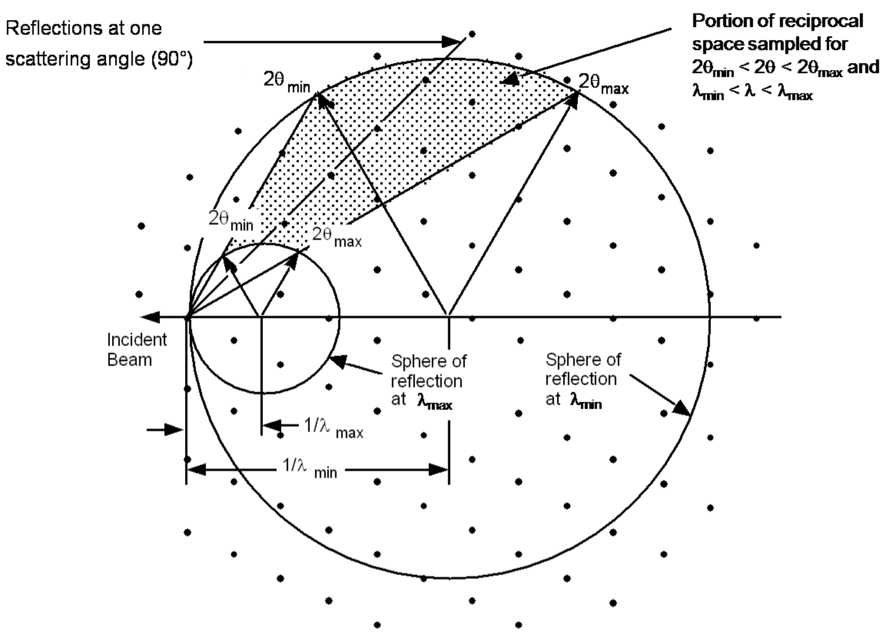
$$I_{hkl} = k\,\phi(\lambda)\,\varepsilon(\lambda)\,A(\lambda)\,y(\lambda)\,N_s\,(|F_{hkl}|^2/V_c)\,\boxed{\lambda^4/\sin^2\theta}$$

$$I_{hkl} = k\,\phi(\lambda)\,\varepsilon(\lambda)\,A(\lambda)\,y(\lambda)\,N_s\,(|F_{hkl}|^2/V_c)\lambda^2\,d^2/4$$

Constant wavelength integration:

$$I_{hkl} = k\,\phi(\lambda)\,\varepsilon(\lambda)\,A(\lambda)\,y(\lambda)\,N_s\,(|F_{hkl}|^2/V_c)\,\boxed{\lambda^3/\sin 2\theta}$$

$$I_{hkl} = k\,\phi(\lambda)\,\varepsilon(\lambda)\,A(\lambda)\,y(\lambda)\,N_s\,(|F_{hkl}|^2/V_c)\;\lambda^2 d/\cos\theta$$



Fourier transforms

$$\rho(xyz) = \frac{1}{V}\sum_{hkl} F_{hkl}\, e^{-2\pi i(hx+ky+lz)}$$

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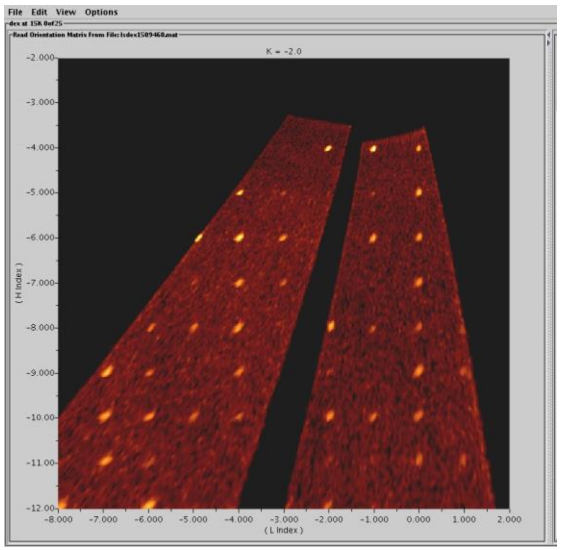


$I_{\mathrm{hkl}} \propto |F_{\mathrm{hkl}}|^2$
$F_{\mathrm{hkl}} = |F_{\mathrm{hkl}}|e^{i\varphi}$

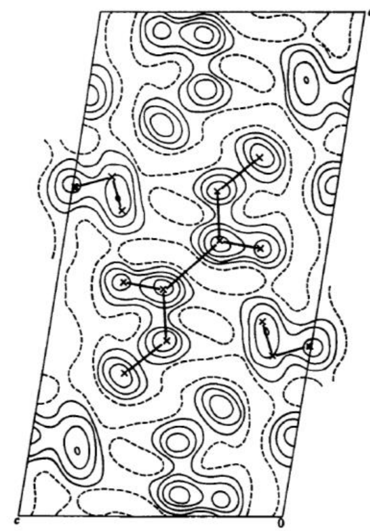


Fig. 3. Neutron scattering density projection along the b axis. The contours are at intervals of 4×10^{-13} cm.Å^{-2}, and broken lines are zero contours.

$$F_{hkl} = \int_{cell} \rho_{xyz}\, e^{2\pi i(\boldsymbol{s}\cdot\boldsymbol{r})}\, d\boldsymbol{v} = \sum_j b_j\, e^{2\pi i(hx_j+ky_j+lz_j)}$$

Sum over j atoms in the unit cell.

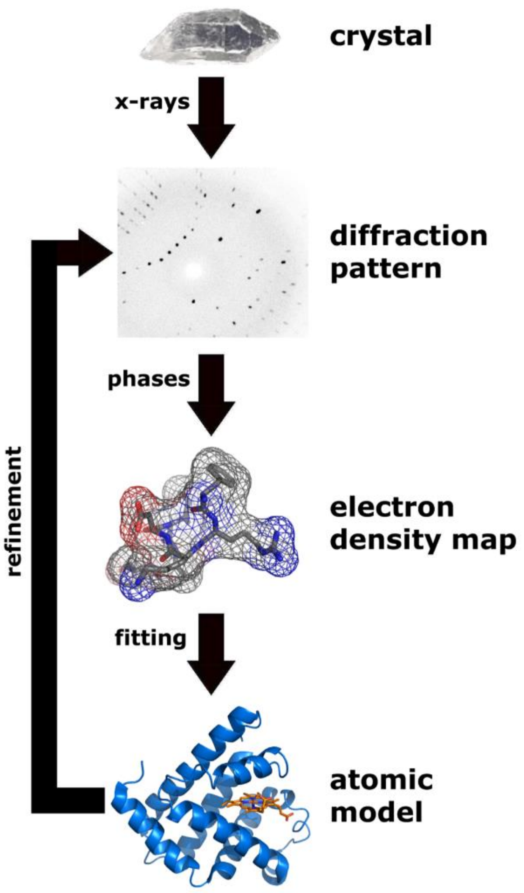
Neutron scattering length of the j^{th} atom,

* Iwasaki, Iwasaki and Saito, *Acta Cryst.* **23**, *1967*, 64.

Solutions to the phase problem

- Patterson synthesis using the $|F_{obs}|^2$ values as Fourier coefficients
  - Map of inter-atom vectors
  - Also called the heavy atom method
- Direct methods
  - Based on probability that the phase of a third peak is equal to the sum of the phases of two other related peaks.
  - J. Karle and H. Hauptman received the 1985 Nobel Prize in Chemistry
- Shake-and-bake
  - Alternate between modifying a starting model and phase refinement
- Charge flipping
  - Start out with random phases.
  - Peaks below a threshold in a Fourier map are flipped up.
  - Repeat until a solution is obtained
- MAD
  - Multiple-wavelength anomalous dispersion phasing
- Molecular replacement
  - Based on the existence of a previously solved structure with of a similar protein
  - Rotate the molecular to fit the two Patterson maps
  - Translate the molecule

Structure Refinement



Workflow for solving the structure of a molecule by X-ray crystallography (from http://en.wikipedia.org/wiki/X-ray_crystallography).

$$\chi^2 = \sum_{hkl} w\left(\left|F_0\right| - \left|F_c\right|\right)^2$$

$$F_{hkl} = \sum_i b_i \exp\left[2\pi i\left(hx_i + ky_i + lz_i\right)\right]\exp\left[-8\pi^2 U_i \sin^2\theta / \lambda^2\right]$$

GSAS, SHELX, CRYSTALS, OLEX2, WinGX… Nonlinear least squares programs. Vary atomic fractional coordinates x,y,z and temperature factors U (isotropic) or u_{ij} (anisotropic) to obtain best fit between observed and calculated structure factors.

Neutron single crystal instruments in the US

- **SNAP** @ SNS: high pressure sample environment (http://neutrons.ornl.gov/instruments/SNS/SNAP/)
- **TOPAZ** @ SNS: small molecule to small protein, magnetism, future polarized neutron capabilities (http://neutrons.ornl.gov/instruments/SNS/TOPAZ/)
- **Four-Circle Diffractometer (HB-3A)** @ HFIR: small molecule, high precision, magnetism (http://neutrons.ornl.gov/instruments/HFIR/HB3A/)
- **MaNDi** (Macromolecular Neutron Diffractometer) @ SNS: neutron protein crystallography, commissioning in 2012 (http://neutrons.ornl.gov/instruments/SNS/MaNDi/)
- **IMAGINE** (Image-Plate Single-Crystal Diffractometer) @ HFIR: small molecule to macromolecule crystallography , commissioning in 2012 (http://neutrons.ornl.gov/instruments/HFIR/imagine/)
- **SCD** @ Lujan Center, Los Alamos: general purpose instrument, currently not available due to budget constraints (http://lansce.lanl.gov/lujan/instruments/SCD/index.html)
- **PCS** (Protein Crystallography Station) @ Lujan Center, Los Alamos: neutron protein crystallography (http://lansce.lanl.gov/lujan/instruments/PCS/index.html)

Books and on-line tutorials

- M. F. C. Ladd and R. A. Palmer, *Structure Determination by X-ray Crystallography, Third Edition*, Plenum Press, 1994.
- J. P. Glusker and K. N. Trueblood, *Crystal Structure Analysis: A Primer*, 2nd ed., Oxford University Press, 1985.
- M. J. Buerger, *Crystal-structure analsysis*, Robert E. Krieger Publishing, 1980.

- George E. Bacon, *Neutron Diffraction*, 3rd ed., Clarendon Press, 1975.
- Chick C. Wilson, *Single Crystal Neutron Diffraction From Molecular Crystals*, World Scientific, 2000.

- Interactive Tutorial about Diffraction: www.totalscattering.org/teaching/
- An Introductory Course by Bernhard Rupp: http://www.ruppweb.org/Xray/101index.html