Single Crystal Diffraction

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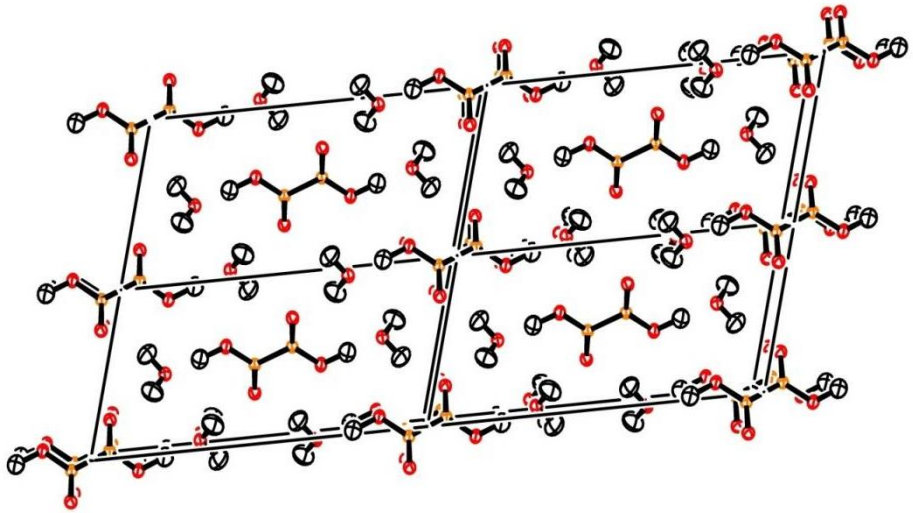
Argonne National Laboratory

National School on Neutron and X-Ray Scattering

June 4, 2009

What is a crystal?

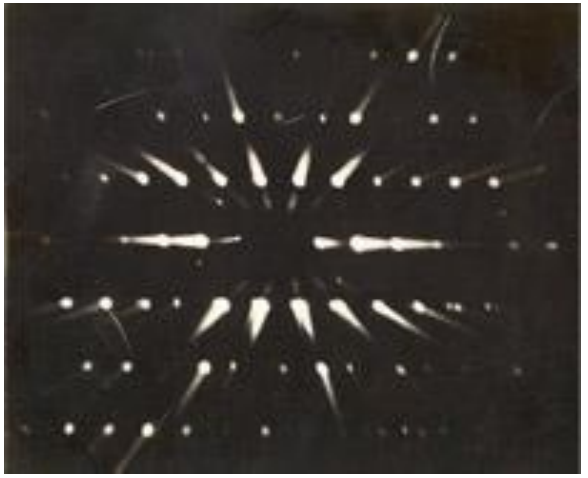


Unit cells of oxalic acid dihydrate

- 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?



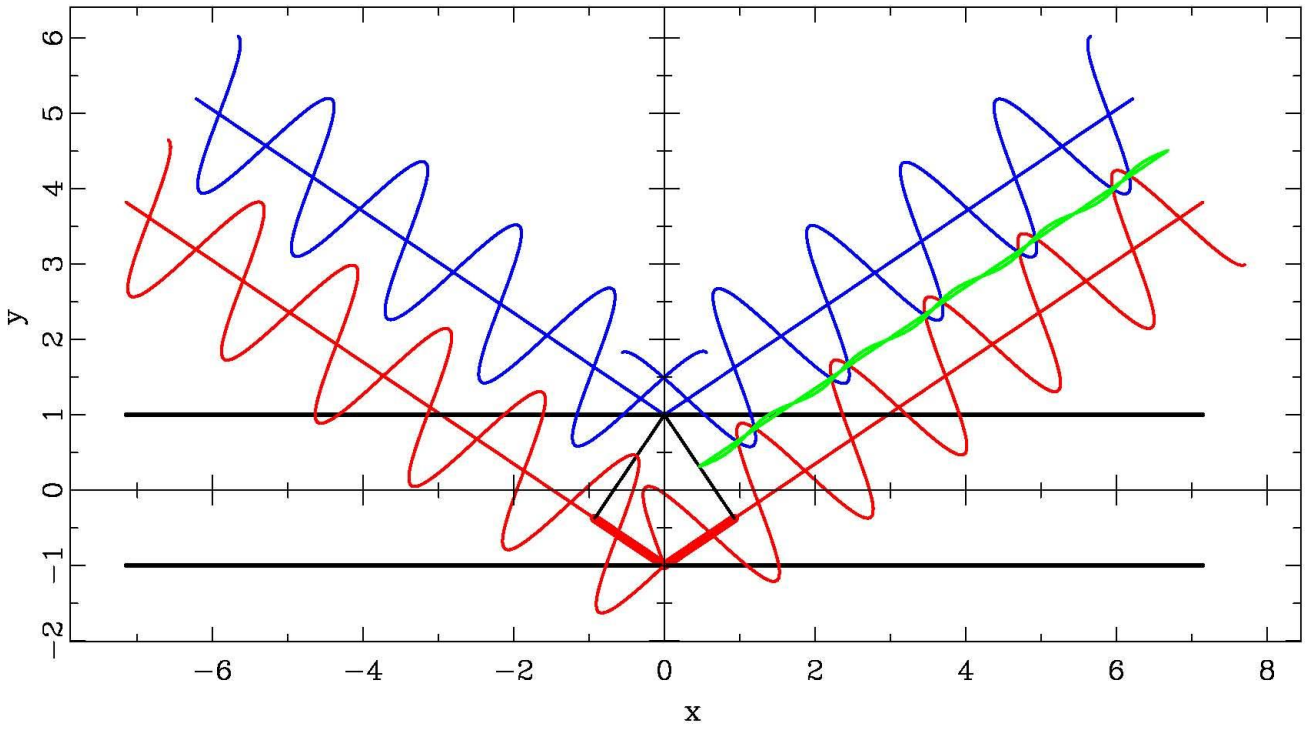
X-ray precession photograph
(Georgia Tech, 1978).

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

The Bragg Equation

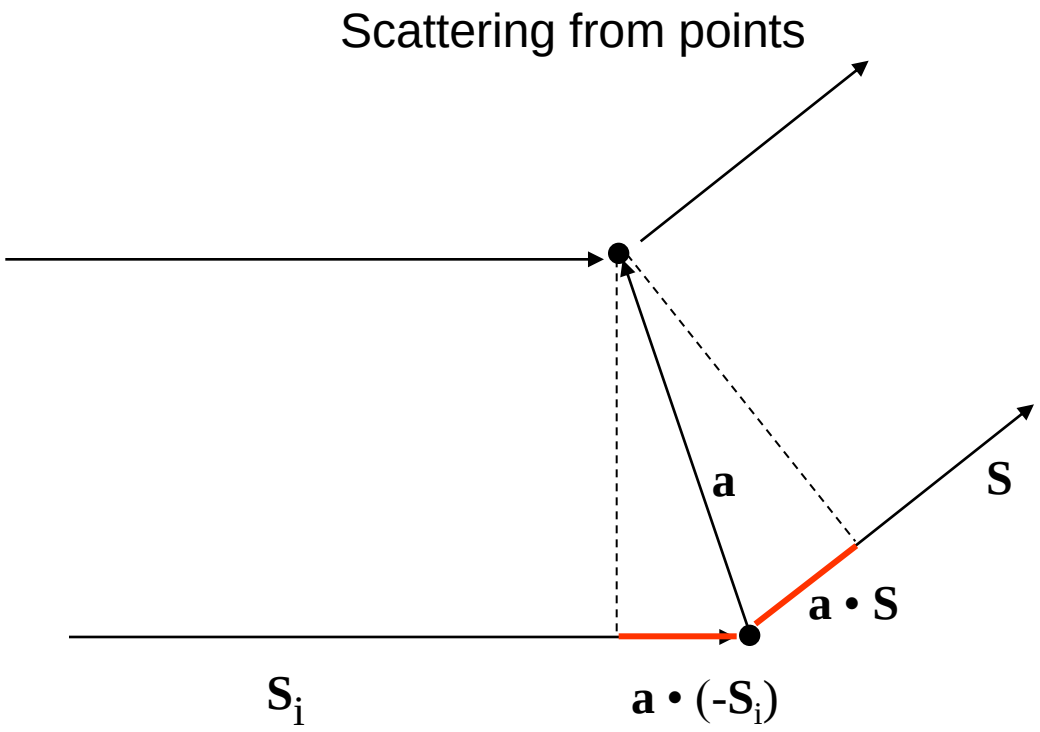
Reflection from a series of equally spaced planes:

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



wave length	1.500 A
vertical distance	2.000 A
horizontal position	0.000 A
theta	34.000 degrees
Phase difference	1.491 * wavelength
Amplitude	0.111

Laue Equations



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

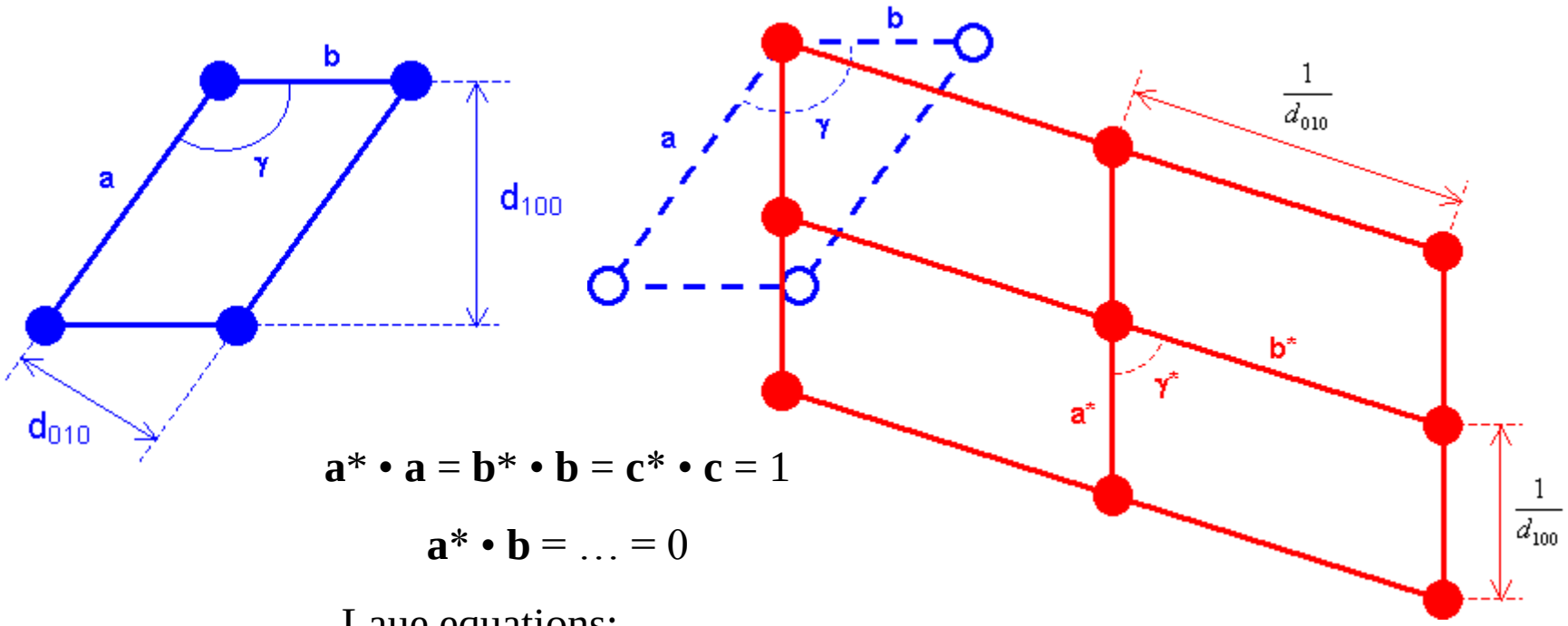
In three dimensions →

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

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

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

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:

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

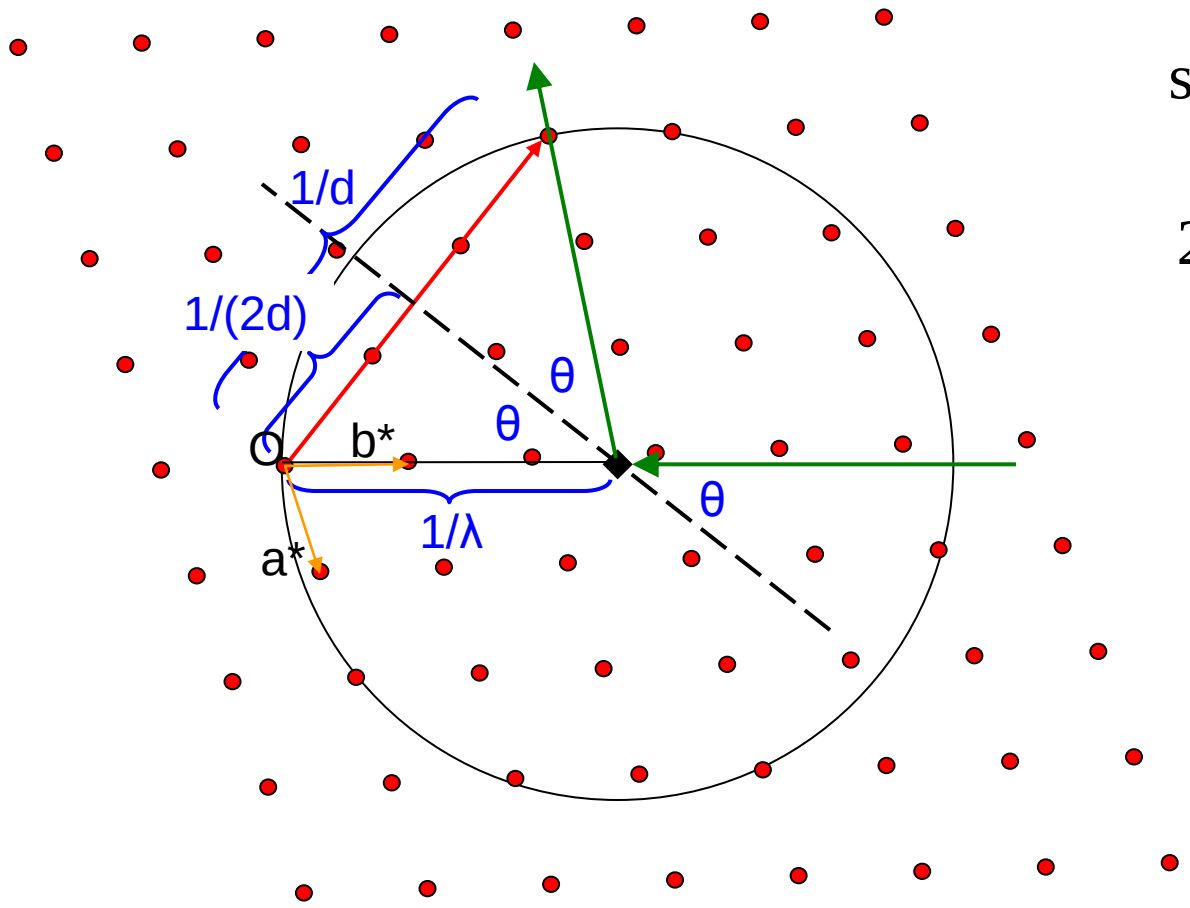
$\mathbf{b} \bullet (\mathbf{S}_o - \mathbf{S}_i) = k\lambda$, or $\mathbf{b} \bullet \mathbf{s} = k$

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

where

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

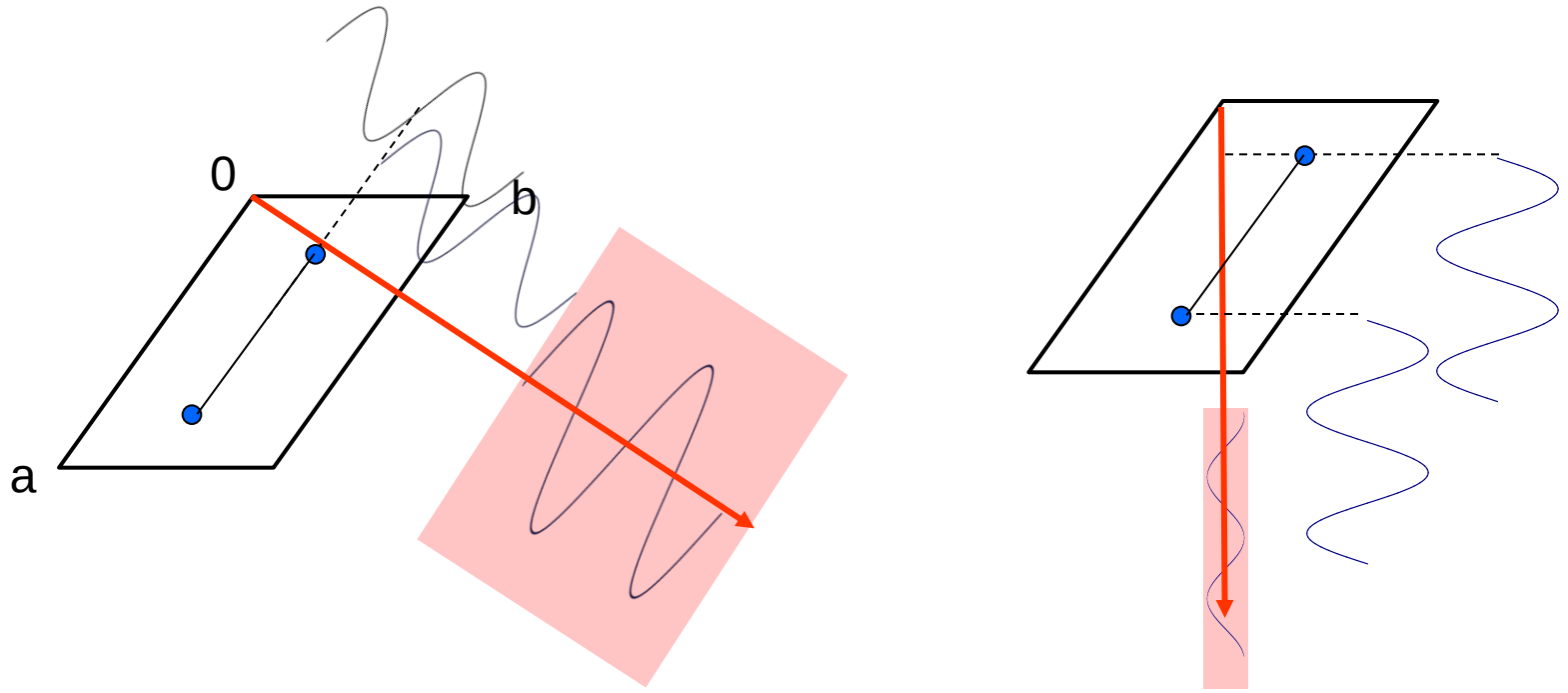
The Ewald Sphere



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

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

Bragg Peak Intensity



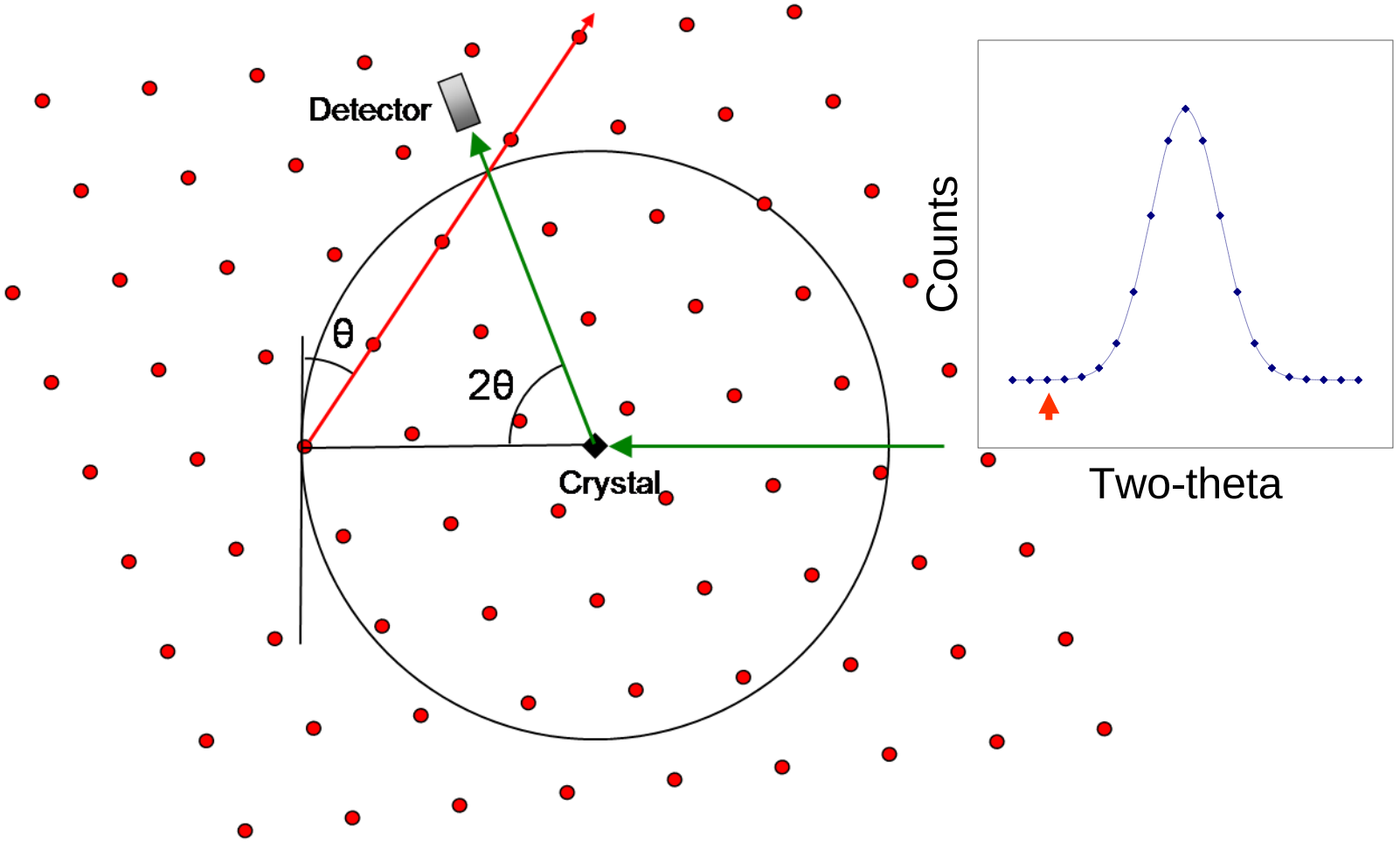
Relative phase shifts related to molecular structure.

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

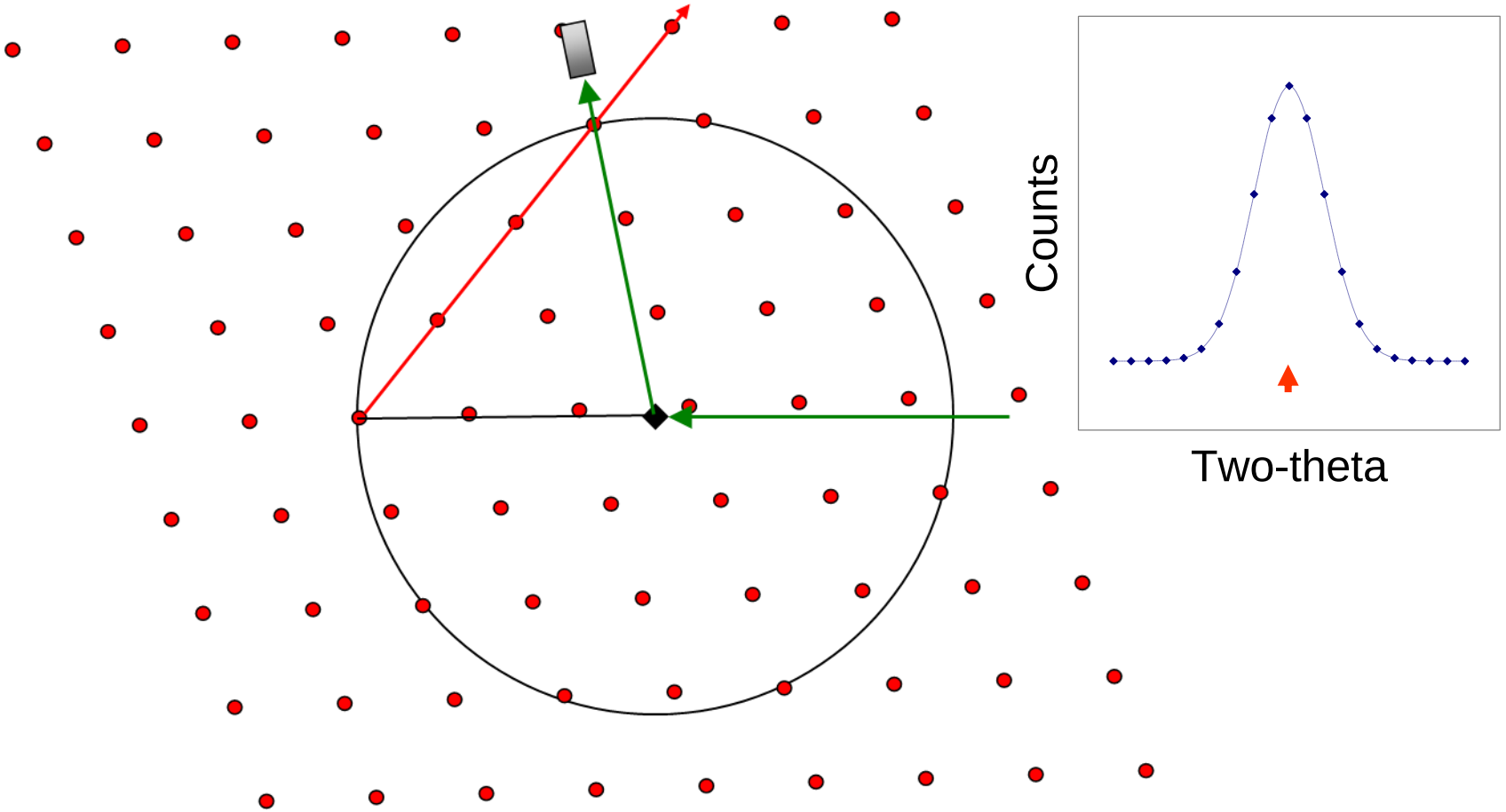
$$F_{hkl} = \sum_i b_i \exp[2\pi i(hx_i + ky_i + lz_i)]$$

$$F_{hkl}^2 \approx I_{hkl}$$

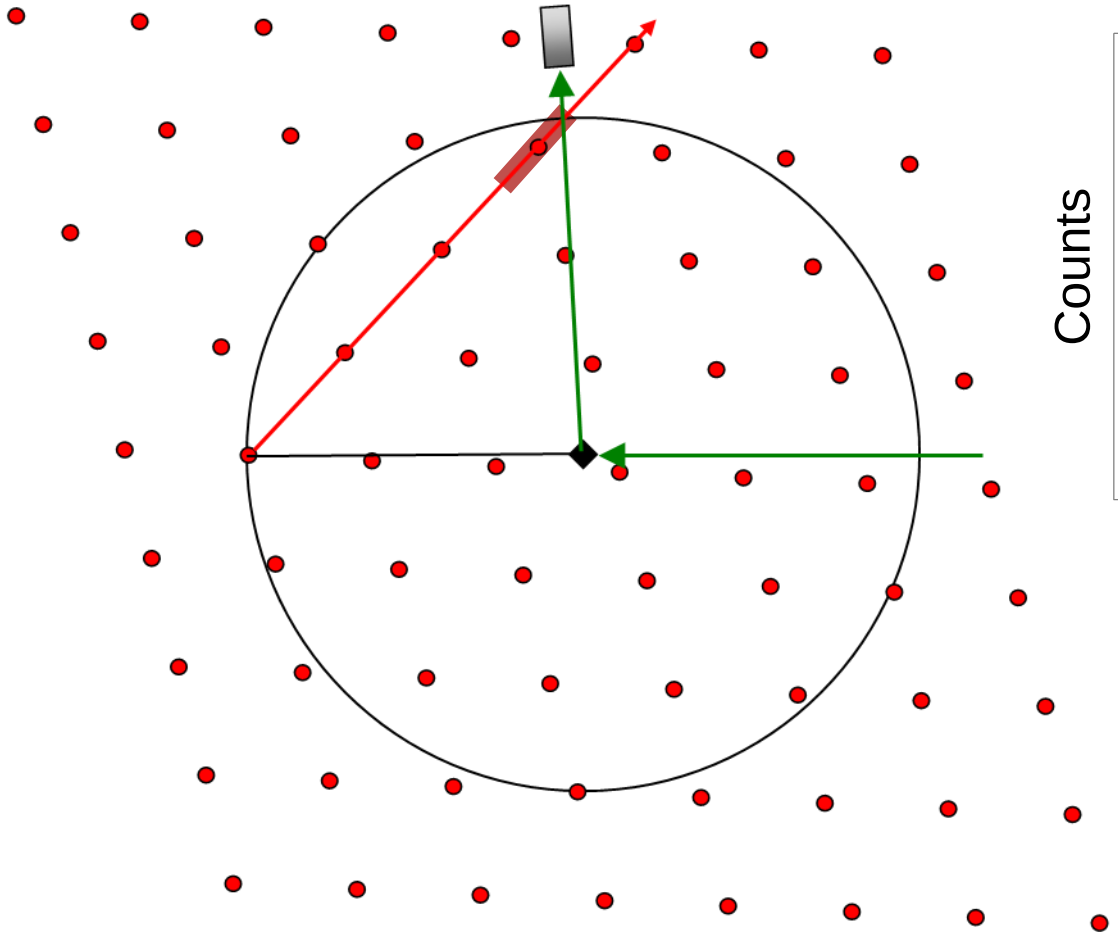
θ-2θ Step Scan (1)

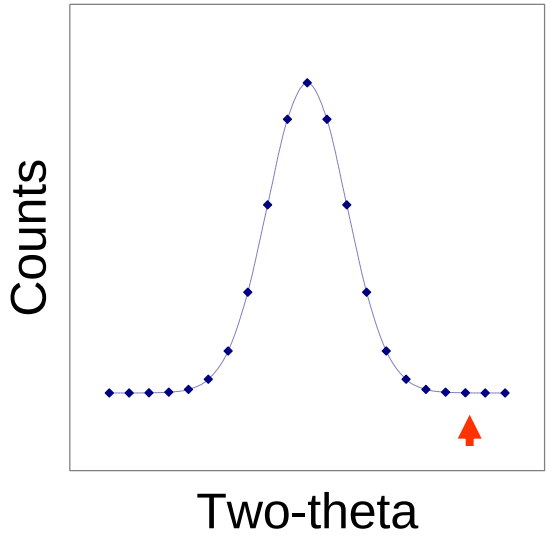


θ-2θ Step Scan (2)

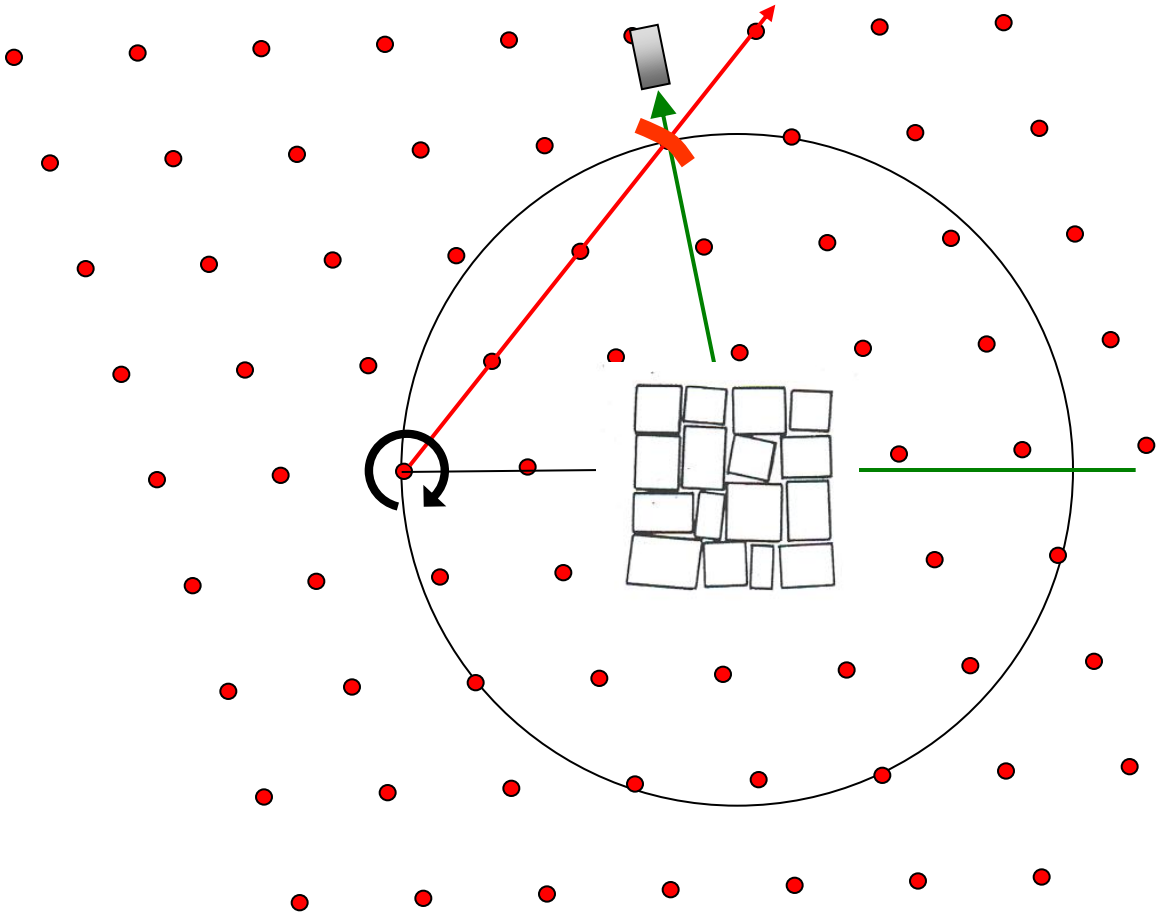


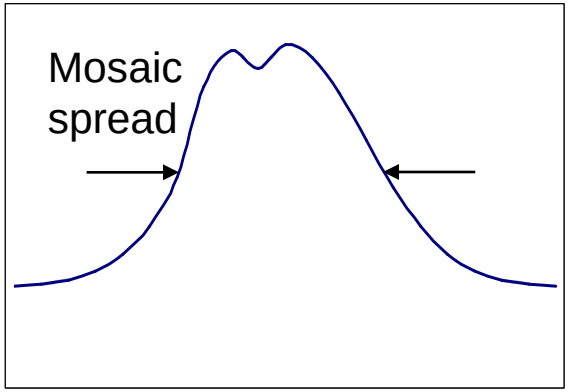
θ-2θ Step Scan (3)





Omega Step Scan





Omega

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

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.

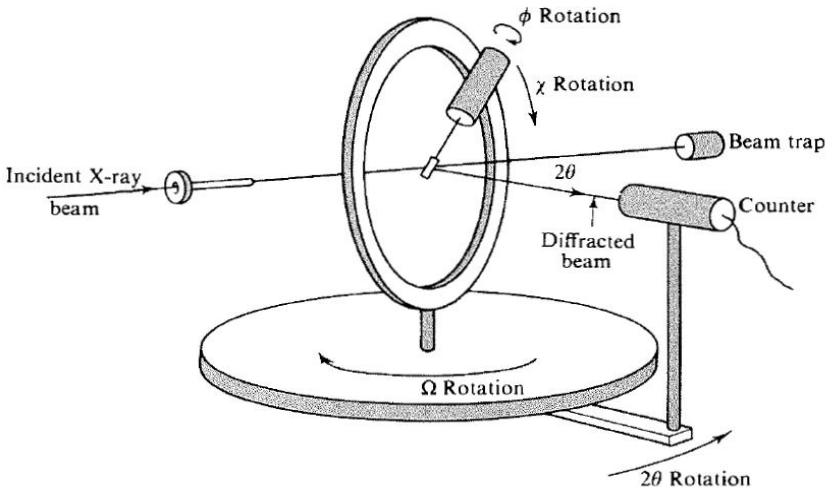


Fig. 5.29. A typical four-circle diffractometer. The counter rotates about the 2θ axis in one plane and the crystal may be orientated in any way by the three axes of rotation ϕ, χ and Ω.

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

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

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

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)

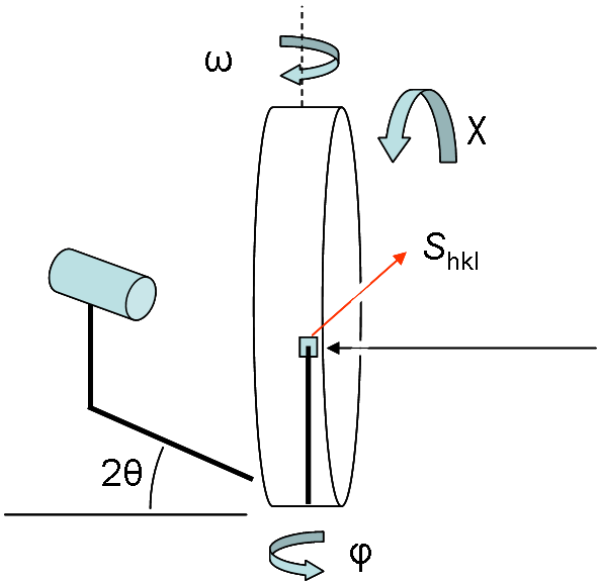
Neutron diffraction measurements on KHF_2 single crystals show that the hydrogen atom occupies the central position, within 0.1A, in the linear F—H—F ion. The data also indicate asymmetry in thermal motion, which suggests that the bifluoride ion undergoes rotatory oscillation with appreciable amplitude. 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 – Busing, 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.

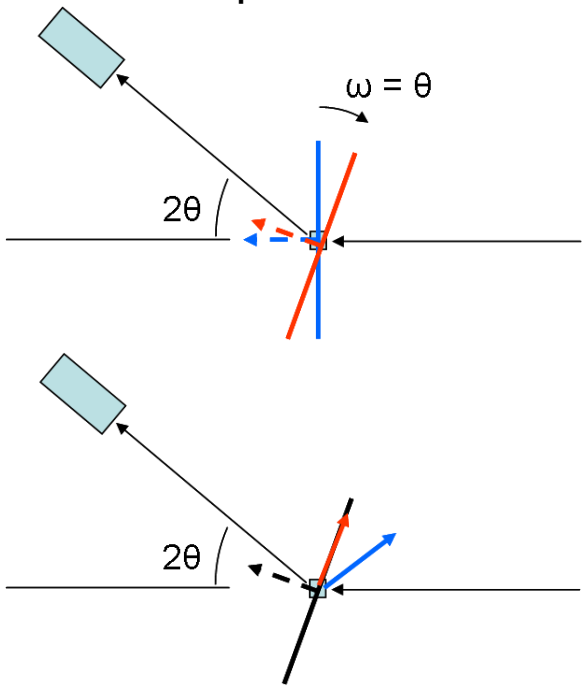
Picker 4-Circle Diffractometer

4-Circle Diffractometer: Euler Angle Rotations

Perspective view
in horizontal plane



Tops views

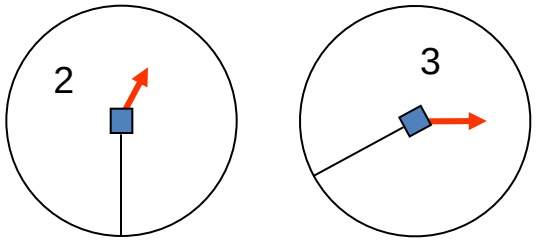


1. Rotate ω by θ so that the normal to the χ plane bisects 2θ.

2. Rotate φ so that the diffraction vector S_{hkl} is in the plane of the χ circle.

3. Rotate χ so that S_{hkl} is in the horizontal plane of the incident and diffracted beam.

View normal to χ circle from source for steps 2 and 3.



Kappa Diffractometer

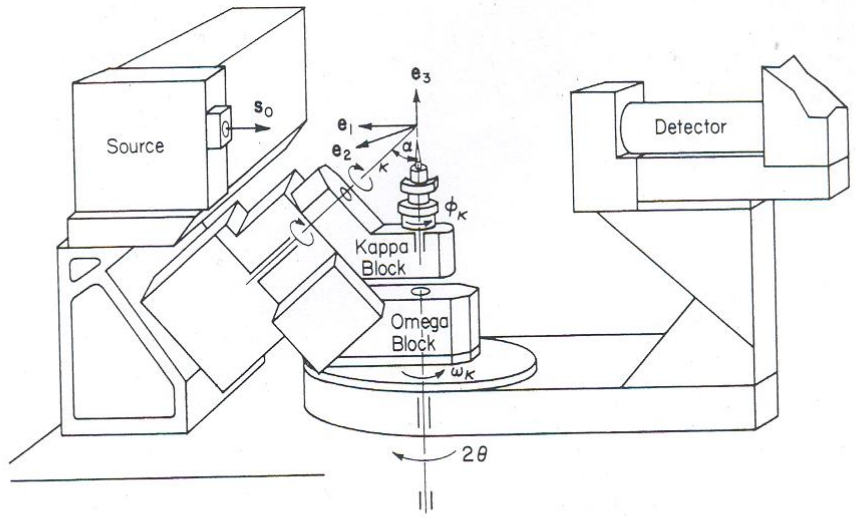
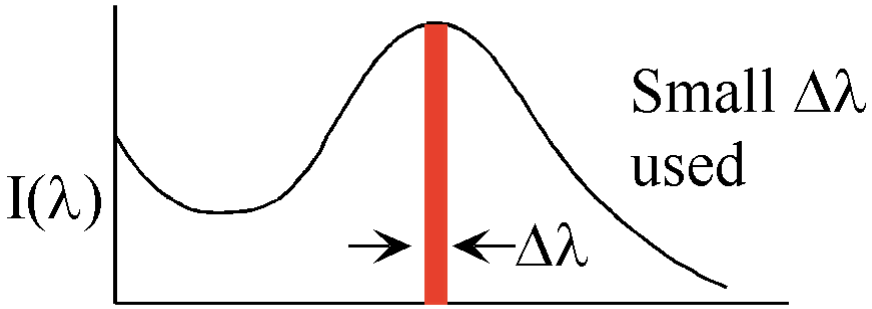


FIGURE 6–13. Kappa geometry. Adapted from operating manual for ENRAF–NONIUS CAD 4 diffractometer (angles ω, ϕ, and κ are opposite in sign to those of Enraf–Nonius). (By permission of ENRAF-NONIUS Service Corp., Bohemia, New York.)

Brucker AXS: KAPPA APEX II

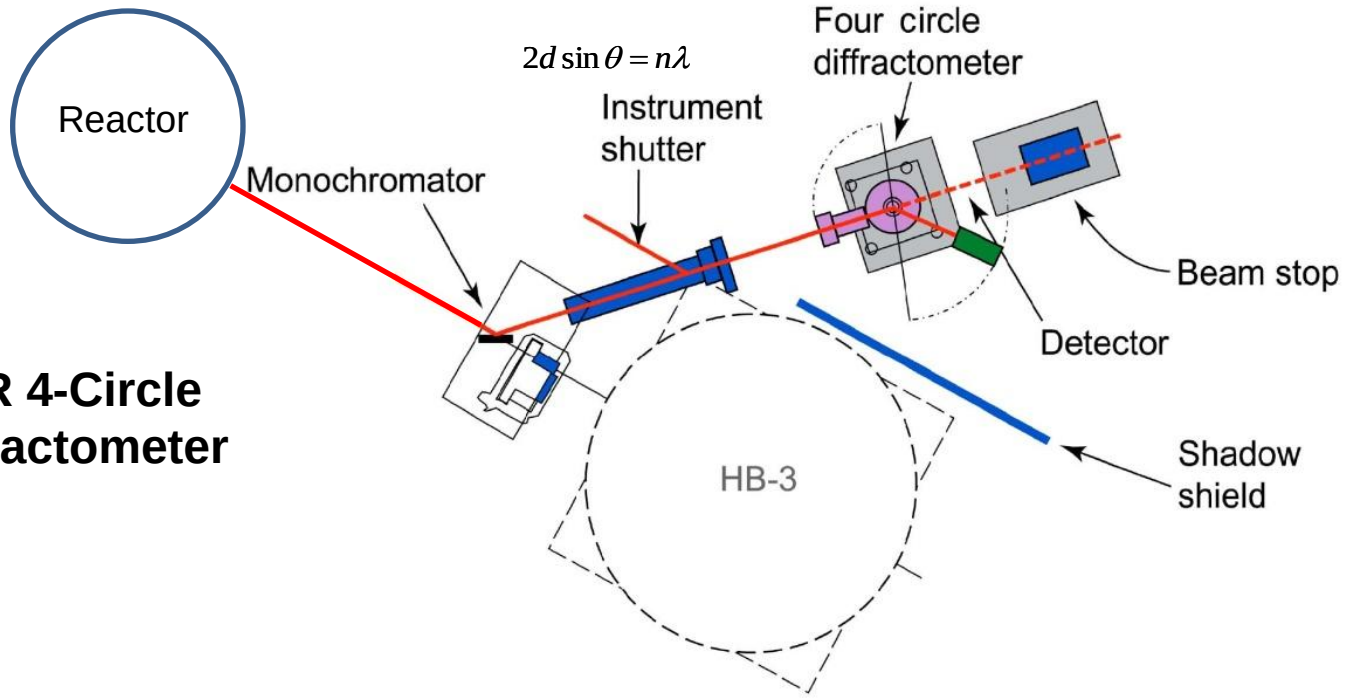
- Full 360° rotations about ω and φ axes.
- Rotation about κ axis reproduces quarter circle about χ axis.

Monochromatic diffractometer



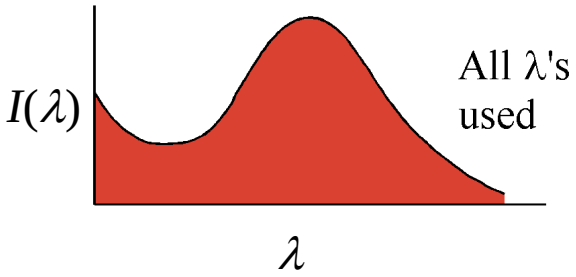
- Rotating crystal
- Vary $\sin\theta$ in the Bragg equation:

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

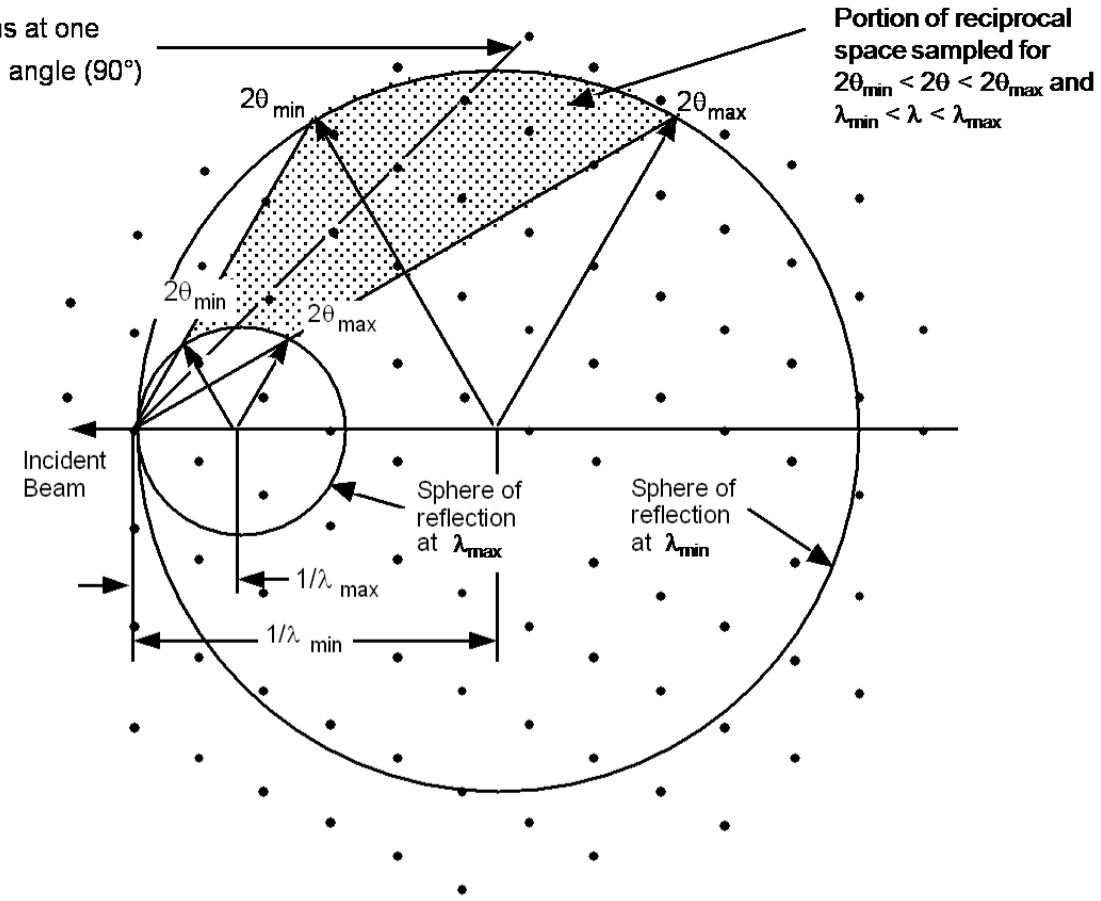


HFIR 4-Circle Diffractometer

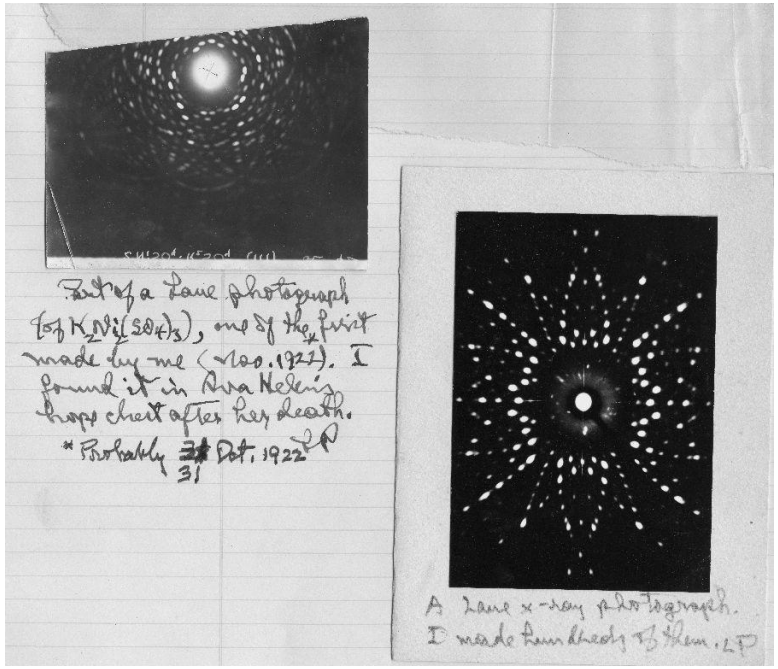
Laue diffraction



Polychromatic “white” spectrum

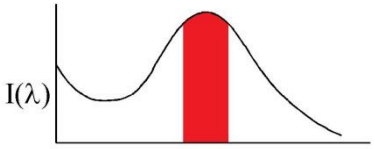


Laue photo from white radiation



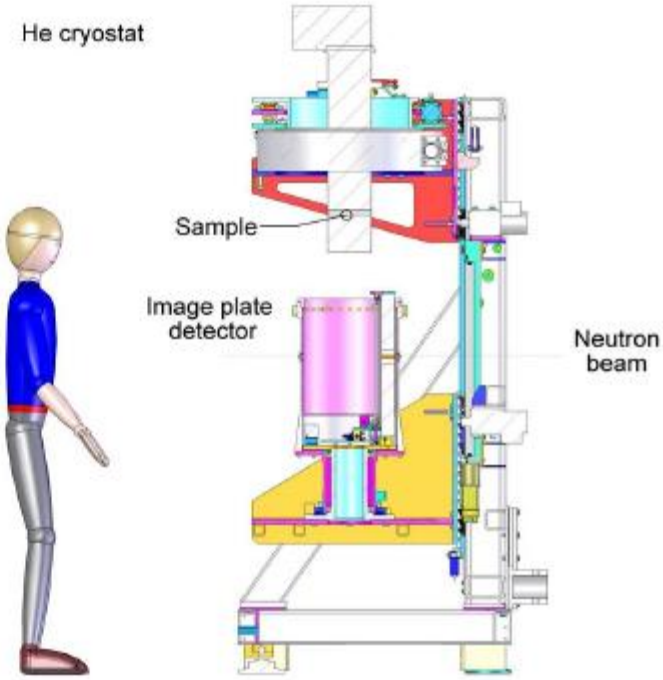
X-ray Laue photos taken
by Linus Pauling

Quasi-Laue Neutron Image Plate Diffractometer

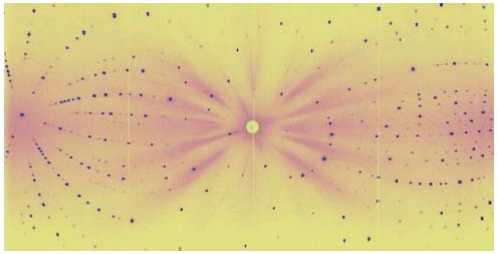


Select $\Delta\lambda/\lambda$ of 10-20%

General view of the QLD

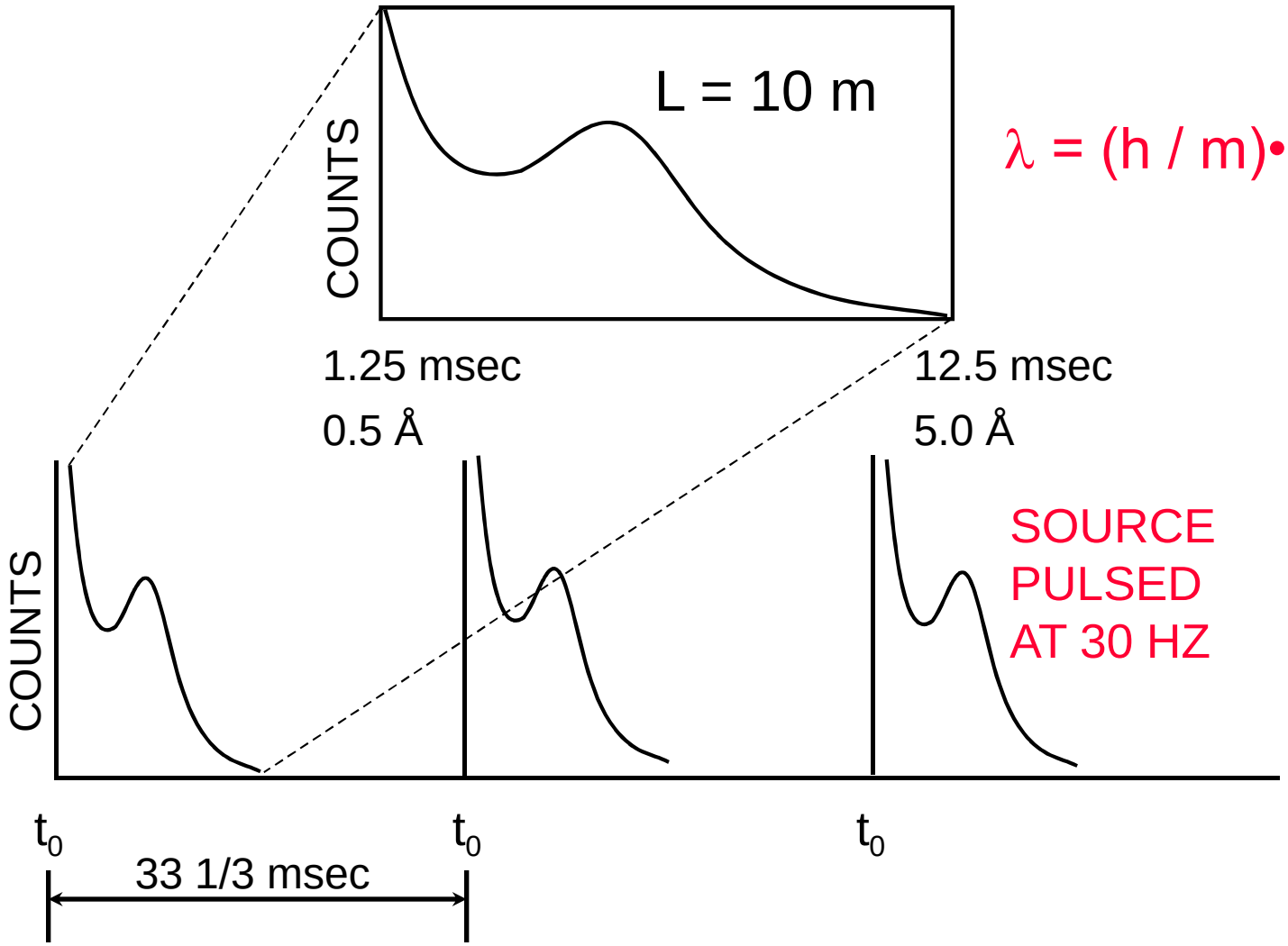


QLD schematic (open position)



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

Pulsed Neutron Incident Spectrum



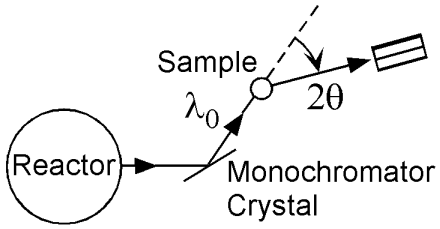
$\lambda = (h / m) \bullet (t / L)$

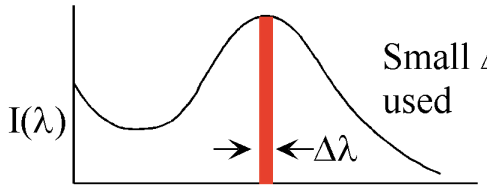
NEUTRON DIFFRACTION

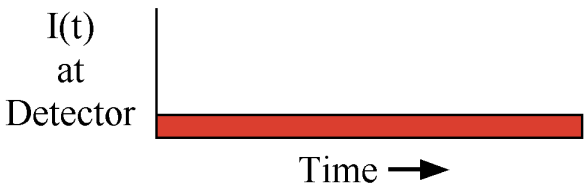
MEASURE F(d)

$$d = \frac{\lambda}{2\sin\theta}$$

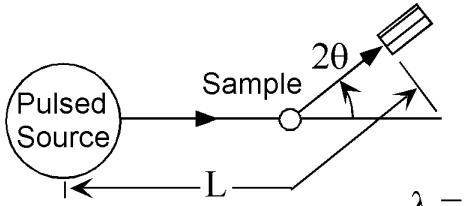
STEADY STATE TECHNIQUE



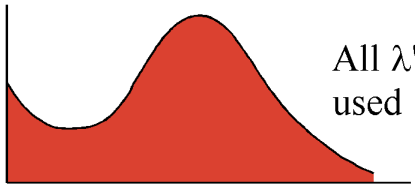


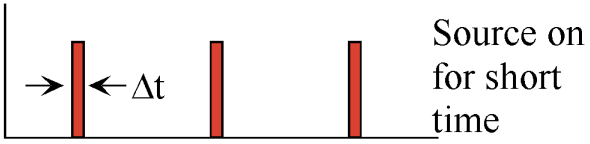


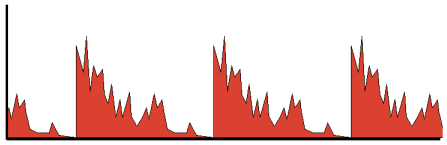
TIME OF FLIGHT TECHNIQUE



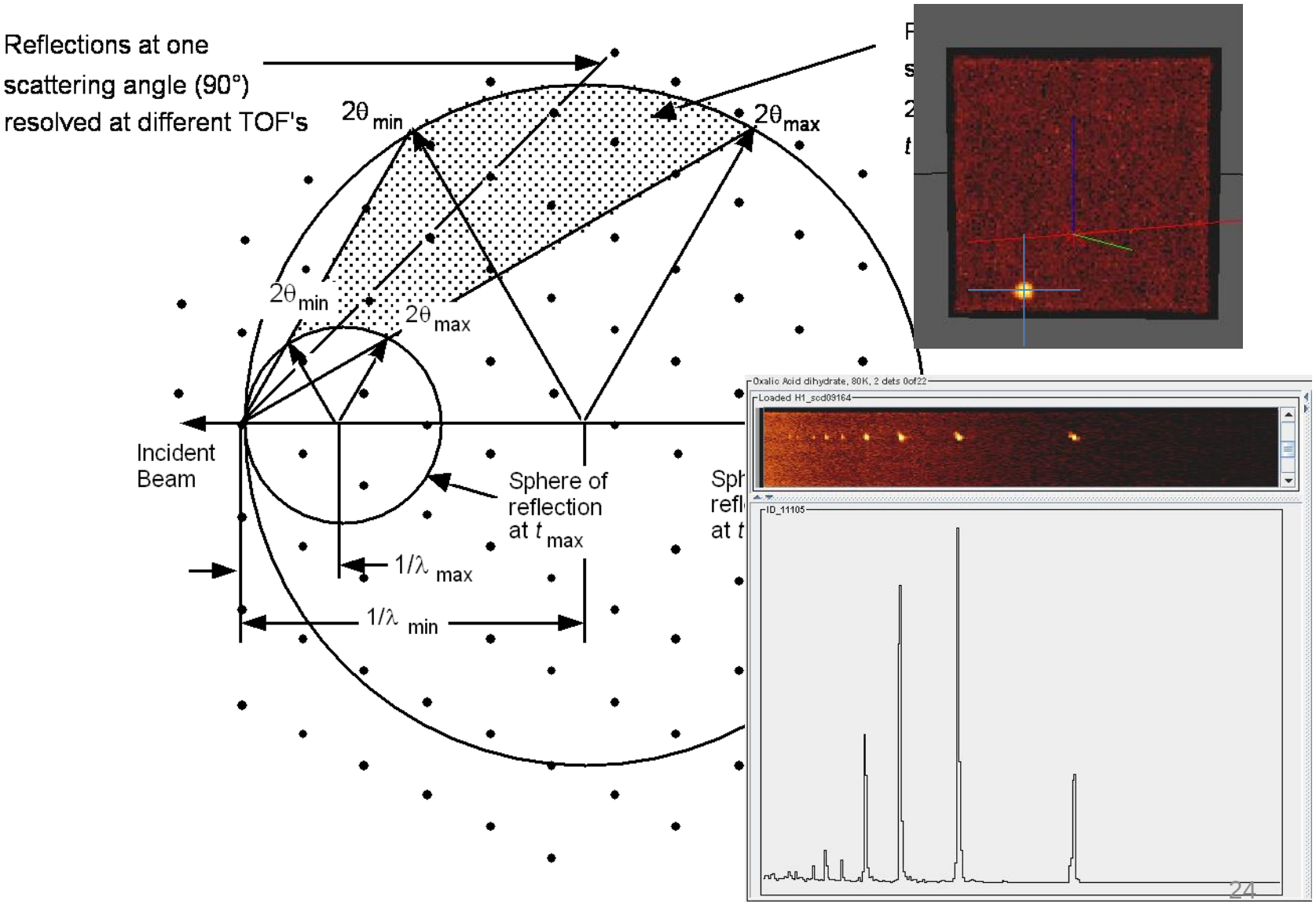
$\lambda = (h/m)\cdot(t/L)$







Time-of-Flight Laue Technique



SCD Instrument Parameters

Moderator	liq. methane at 105
Source frequency	30 Hz
Sample-to-moderator dist.	940 cm
Number of detectors	2
Detector active area	155 x 155 mm^2
Scintillator	GS20 ^{6}Li glass
Scintillator thickness	2 mm
Efficiency @ 1 Å	0.86
Typical detector channels	100 x 100
Resolution	1.75 mm
Detector 1:	
angle	75˚
sample-to-detector dist.	23 cm
Detector 2:	
angle	120˚
sample-to-detector dist.	18 cm
Typical TOF range	1–25 ms
wavelength range	0.4–10 Å
d-spacing range	~0.3–8 Å
TOF resolution, Δ*t*/*t*	0.01

Sample Environments

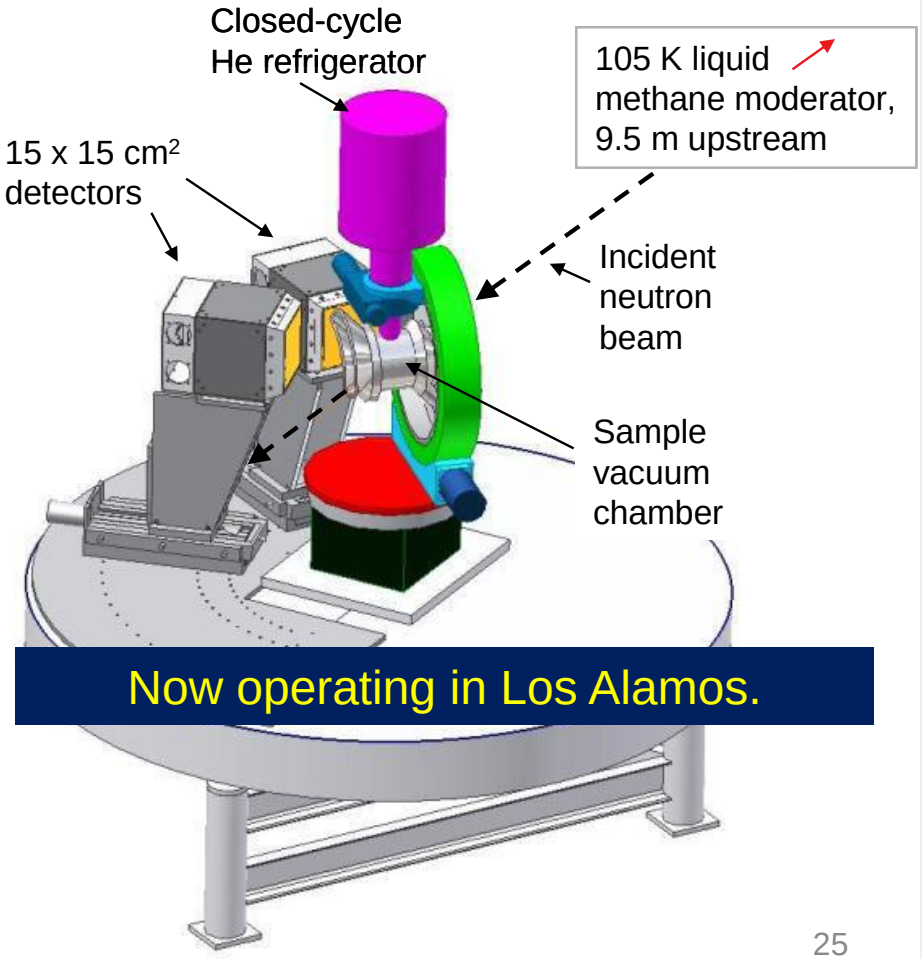
Hot-Stage Displex: 4-900 K

Displex Closed Cycle Helium Refrigerator: 12–473 K

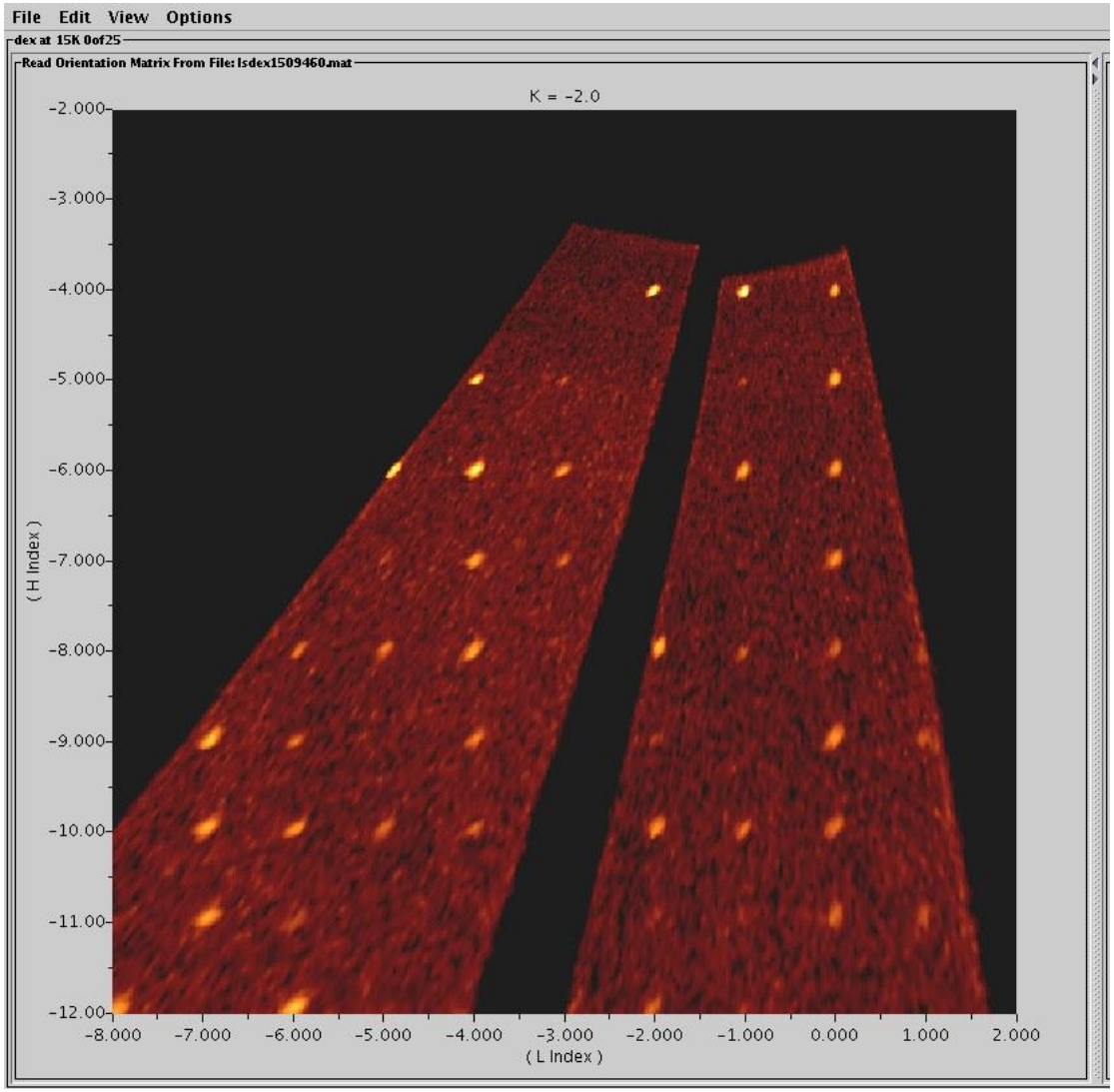
Furnaces: 300–1000 K

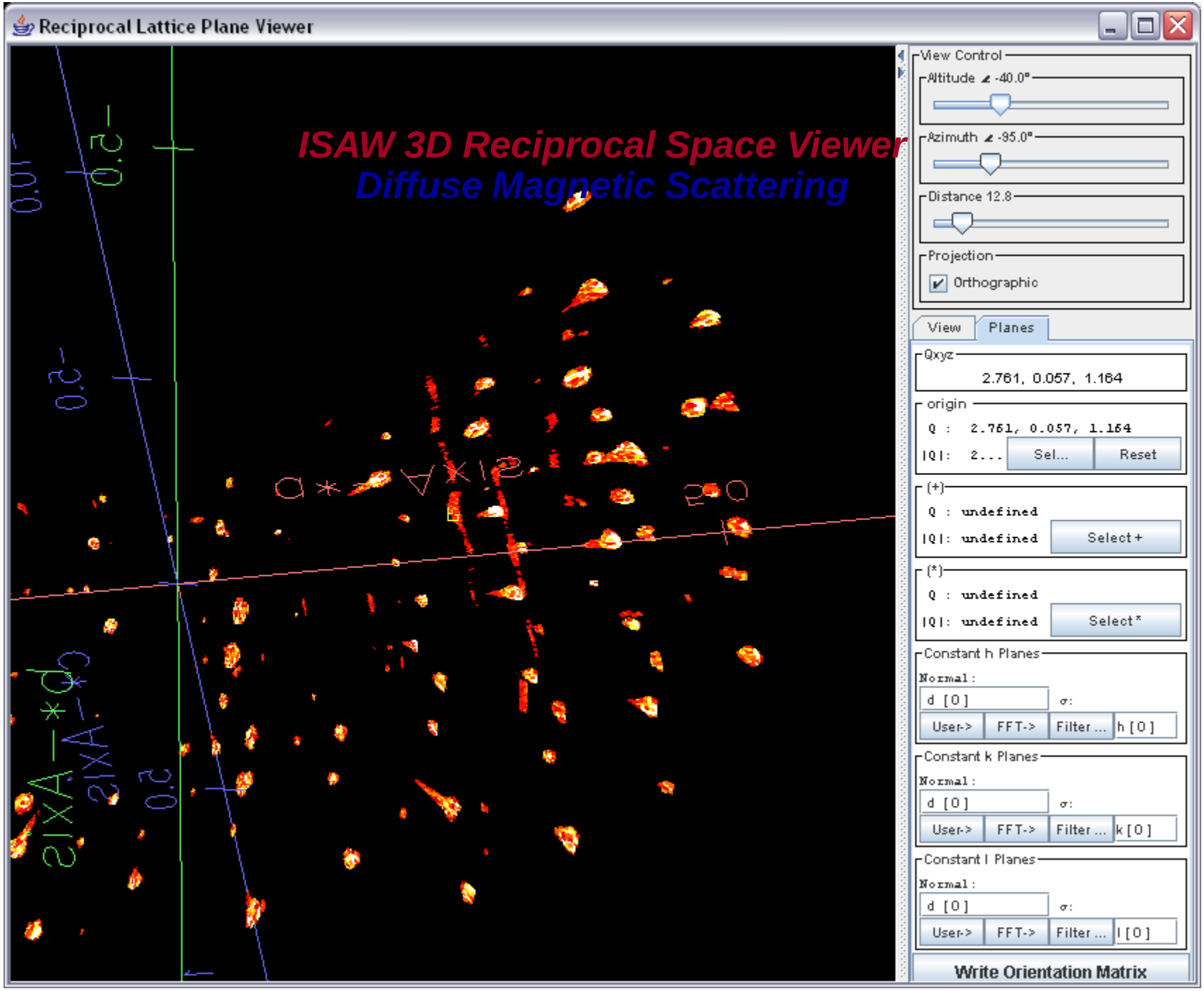
Helium Pressure Cell Mounted on Displex: 0–5 kbar @ 4–300 K

Detector distances on locus of constant solid angle in reciprocal space.

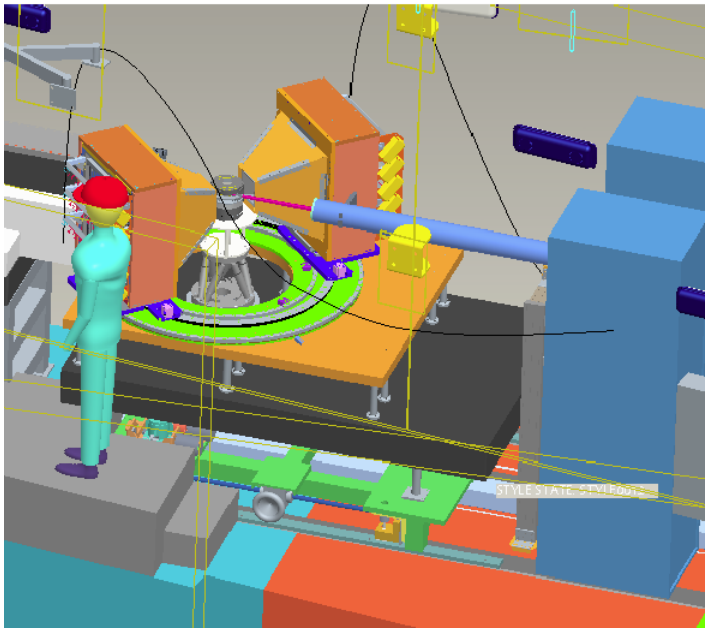


ISAW hkl plot

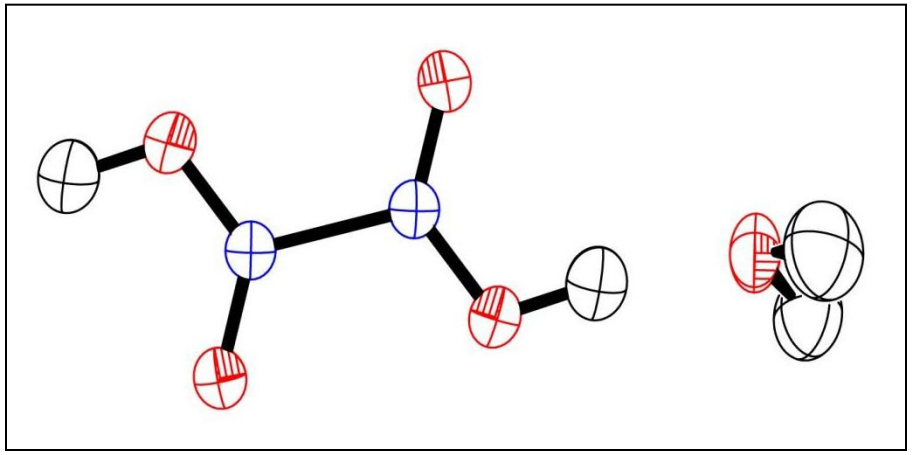



Reciprocal Lattice Plane Viewer
ISAW 3D Reciprocal Space Viewer
Diffuse Magnetic Scattering
View Control
Altitude -40.0°
Azimuth -95.0°
Distance 12.8
Projection
Orthographic
View
Planes
Qxyz
2.761, 0.057, 1.164
origin
Q : 2.761, 0.057, 1.164
|Q|: 2...
Sel...
Reset
(+)
Q : undefined
|Q|: undefined
Select+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

SNAP

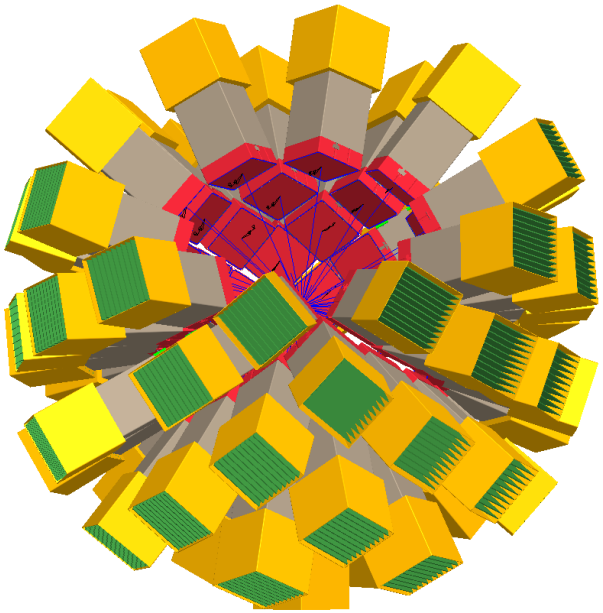


ORTEP of oxalic acid dihydrate from data measured on SNAP in December, 2008.



Topaz Detector Coverage

- Project Execution Plan requires a minimum of 2 steradian (approx. 23 detectors) coverage.
- Each detector active area is 150 mm x 150 mm.
- Secondary flight path varies from 400 mm to 450 mm radius and thus cover from 0.148 to 0.111 steradian each.



Data Reduction

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

$$I_{hkl} = k\ \tau(\lambda)\ \phi(\lambda)\ \varepsilon(\lambda,\mathbf{r})\ A(\lambda)\ y(\lambda)\ |F_{hkl}|^2\ \lambda^4 / \sin^2\Theta$$

k = scale factor

$\tau(\lambda)$ = deadtime loss

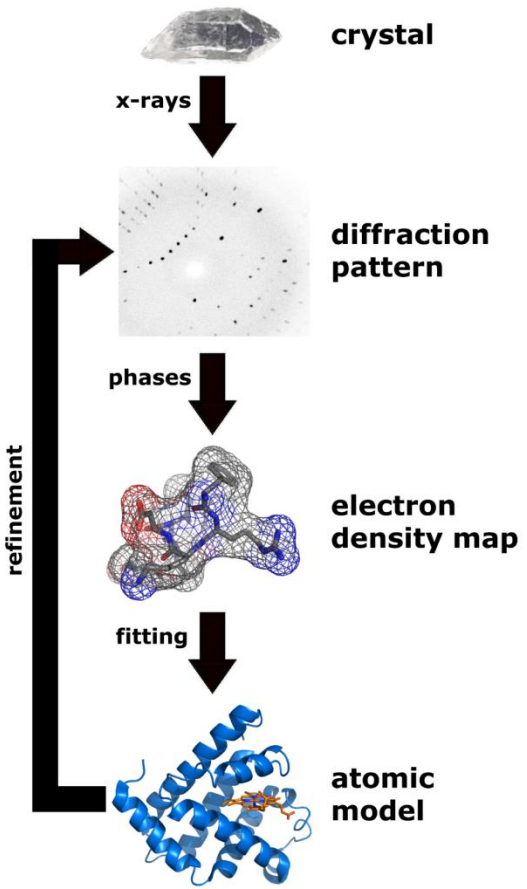
$\phi(\lambda)$ = incident flux spectrum, obtained by measuring the incoherent scattering from a vanadium sample

$\varepsilon(\lambda,\mathbf{r})$ = detector efficiency calculated as a function of wavelength λ and position $\mathbf{r}$ on the detector for each Bragg peak since the slant path through the flat ^{6}Li glass varies with $\mathbf{r}$

$A(\lambda)$ = sample absorption; includes the wavelength dependence of the linear absorption coefficients

$y(\lambda)$ = extinction correction is evaluated during the least-squares refinement of the structure

Structure solution and Fourier syntheses



Measured intensity

$$I_{hkl} \propto |F_{hkl}|^2$$

Electron (X-ray) or nuclear (neutron) density at point x,y,z in the unit cell

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

Phase angle

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

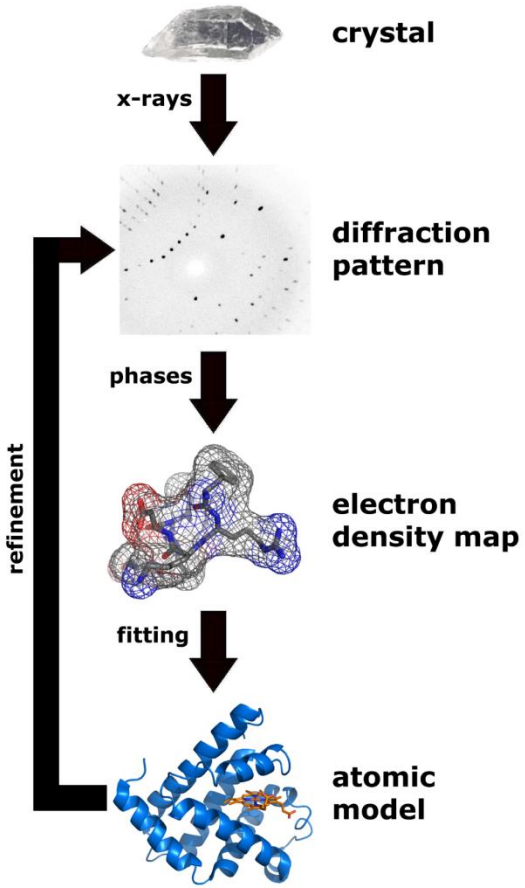
$$\phi = \tan^{-1}\frac{B}{A}$$

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

Sum over j atoms in the unit cell

Neutron scattering length or X-ray form factor for j^{th} atom

Structure Refinement



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

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

GSAS, SHELX, CRYSTALS…
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.

On-line Tutorials

- Th. Proffen, R. Neder, S. Billinge: http://www.totalscattering.org/teaching/
- Dissemination of IT for the Promotion of Materials Science (DoITPoMS): http://www.doitpoms.ac.uk/tlplib/xray-diffraction/index.php
- Bragg's Law (Stony Brook): http://www.eserc.stonybrook.edu/ProjectJava/Bragg/index.html
- X-ray 101 by Bernard Rupp: http://www.ruppweb.org/Xray/101index.html
- IPNS SCD tutorial by Paula Piccoli: http://www.pns.anl.gov/instruments/scd/subscd/scd.shtml