Single Crystal Diffraction

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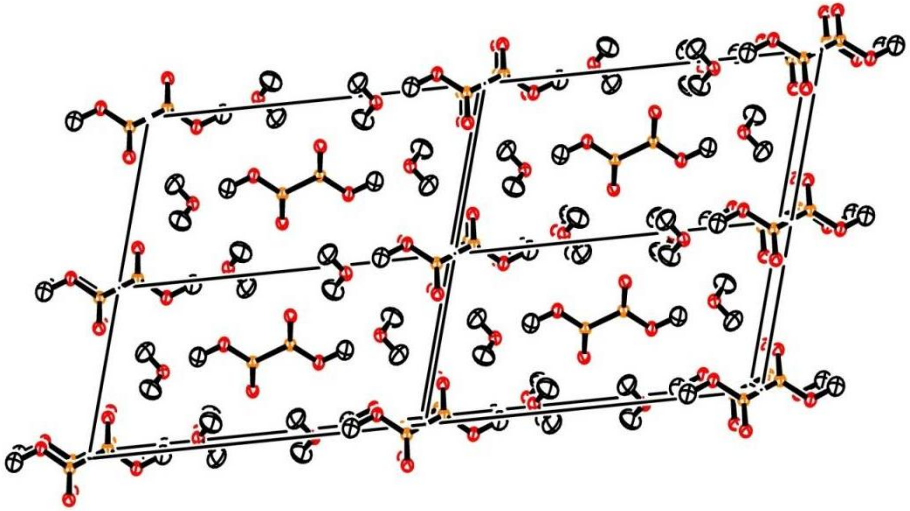
Argonne National Laboratory

National School on Neutron and X-Ray Scattering

June 24, 2010

What is a crystal?

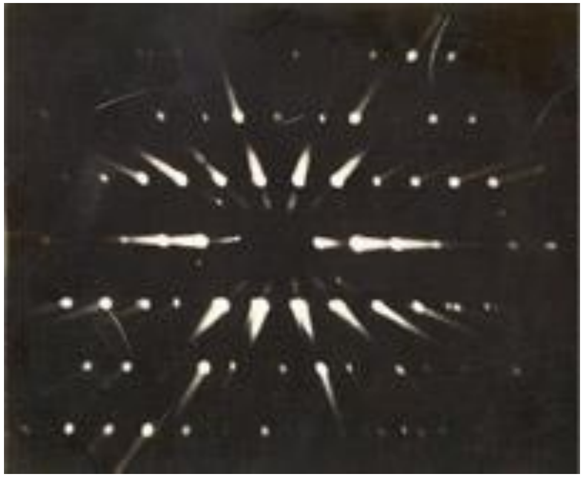


Unit cells of oxalic acid dihydrate

- 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

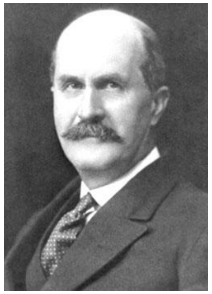
Why don’t the X-rays scatter in all directions?

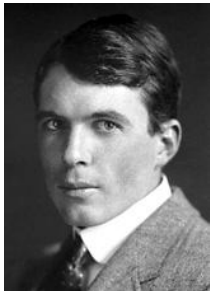


X-ray precession photograph
(Georgia Tech, 1978).

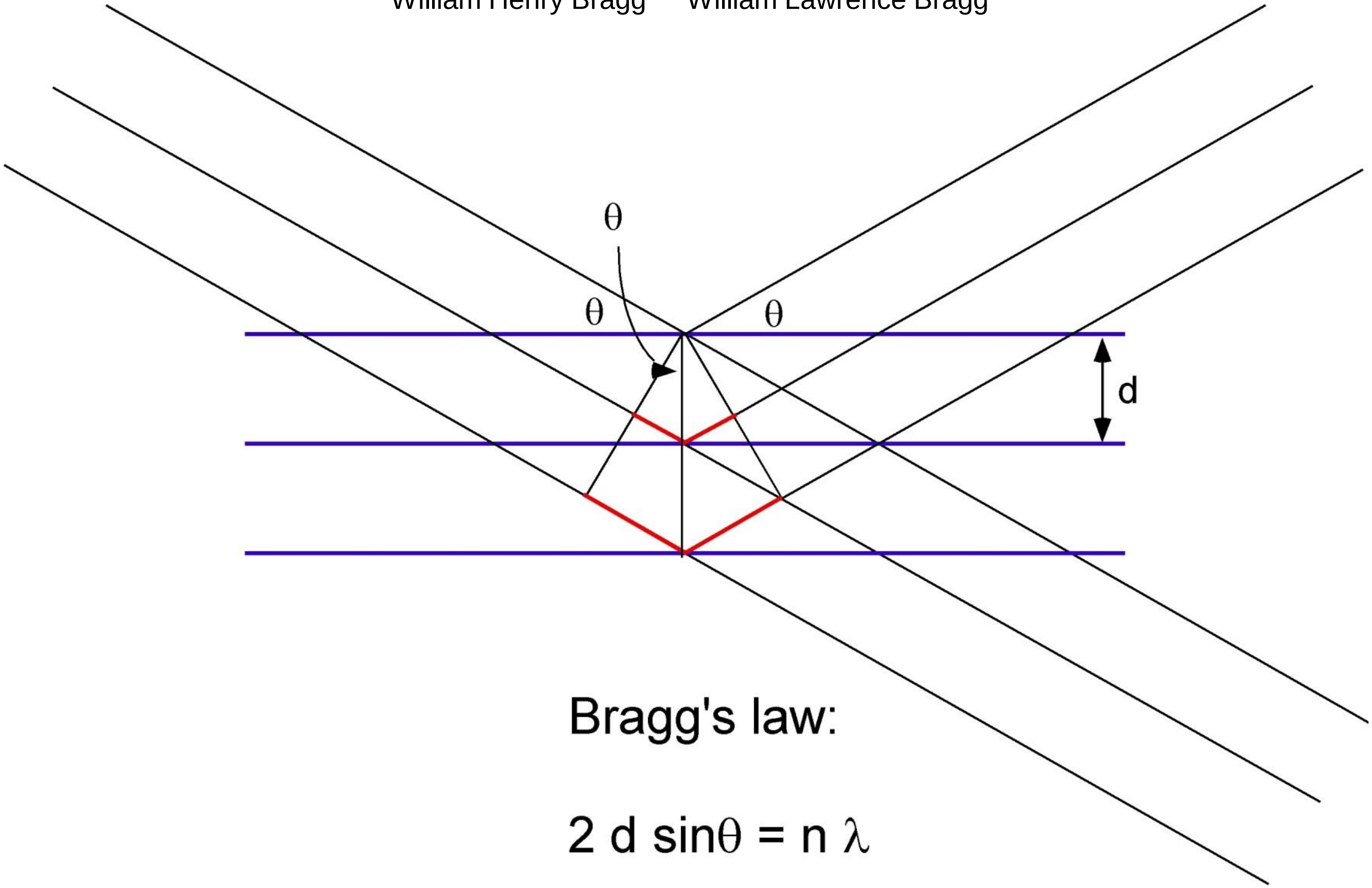
- X-rays and neutrons have wave properties.
- A crystal acts as a diffraction grating producing constructive and destructive interference.

Bragg’s Law


William Henry Bragg


William Lawrence Bragg

Jointly awarded the 1915 Nobel Prize in Physics

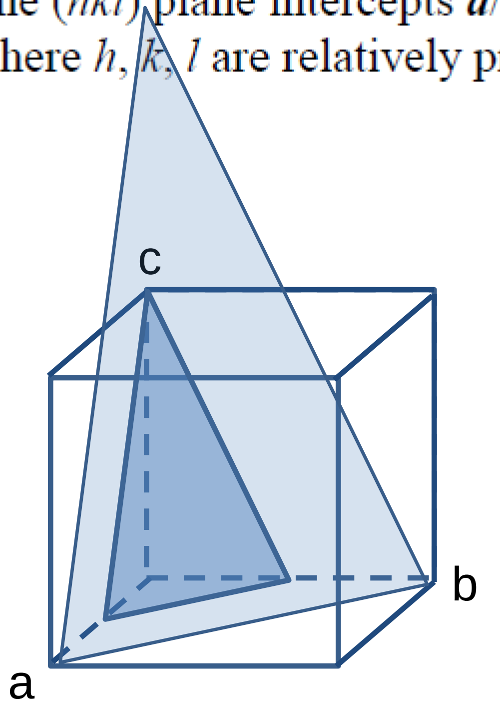


Bragg's law:

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

Crystallographic Planes and Miller Indices

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



(221)

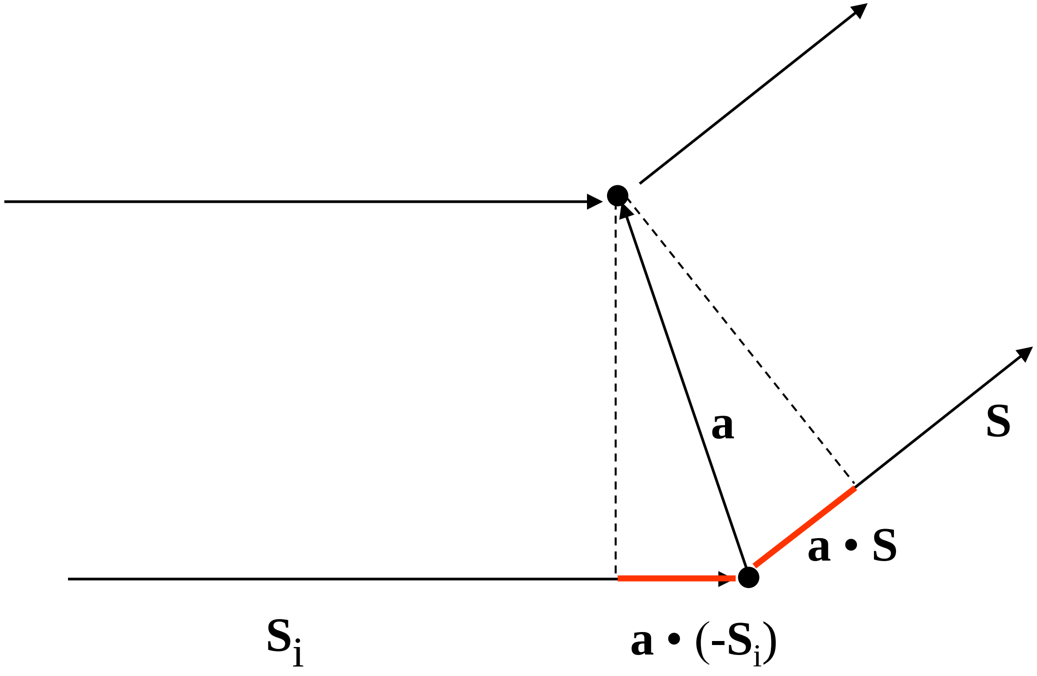
Intercepts	$\frac{a}{h}, \frac{b}{k}, \frac{c}{l}$
Fractional intercepts	$\frac{1}{h}, \frac{1}{k}, \frac{1}{l}$
Reciprocals of the fractional intercepts	h, k, l
Miller Indices *(prime integers)*	h, k, l

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

Laue Equations

Max von Laue
1914 Noble Prize for Physics

Scattering from points



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

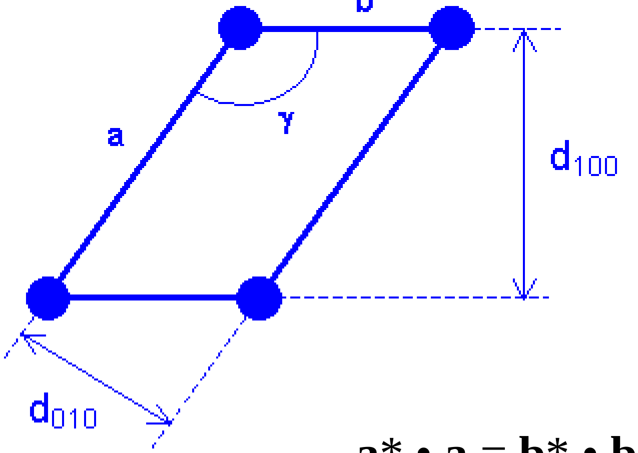
In three dimensions →

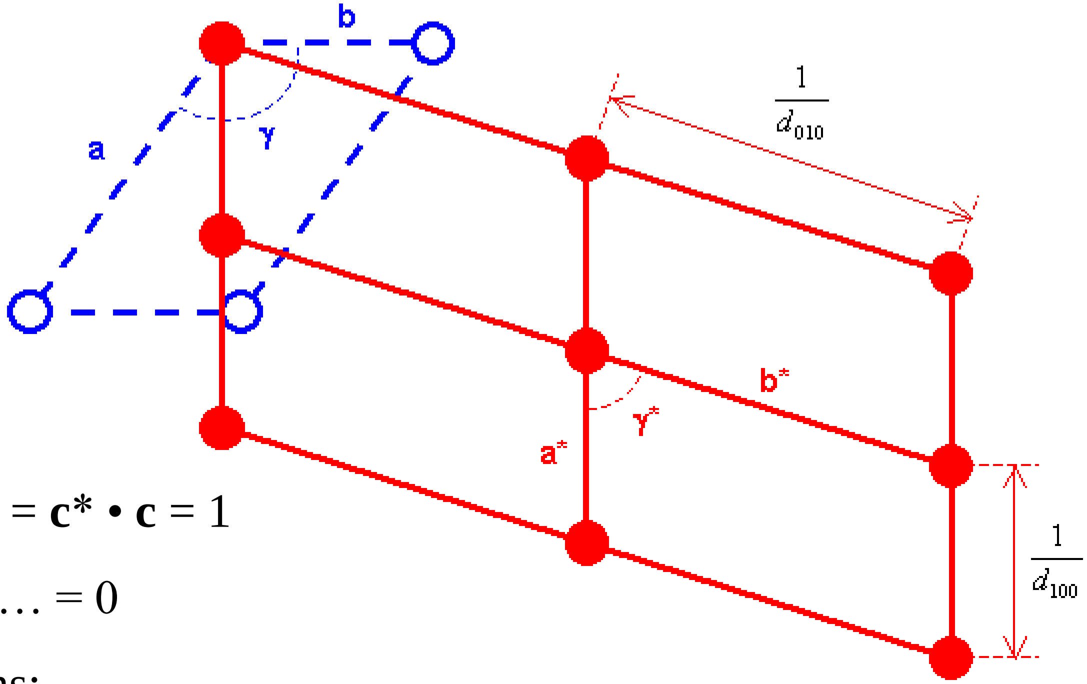
$$\mathbf{a} \cdot (\mathbf{S} - \mathbf{S}_i) = h\lambda$$

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

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

Real and Reciprocal Space





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

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

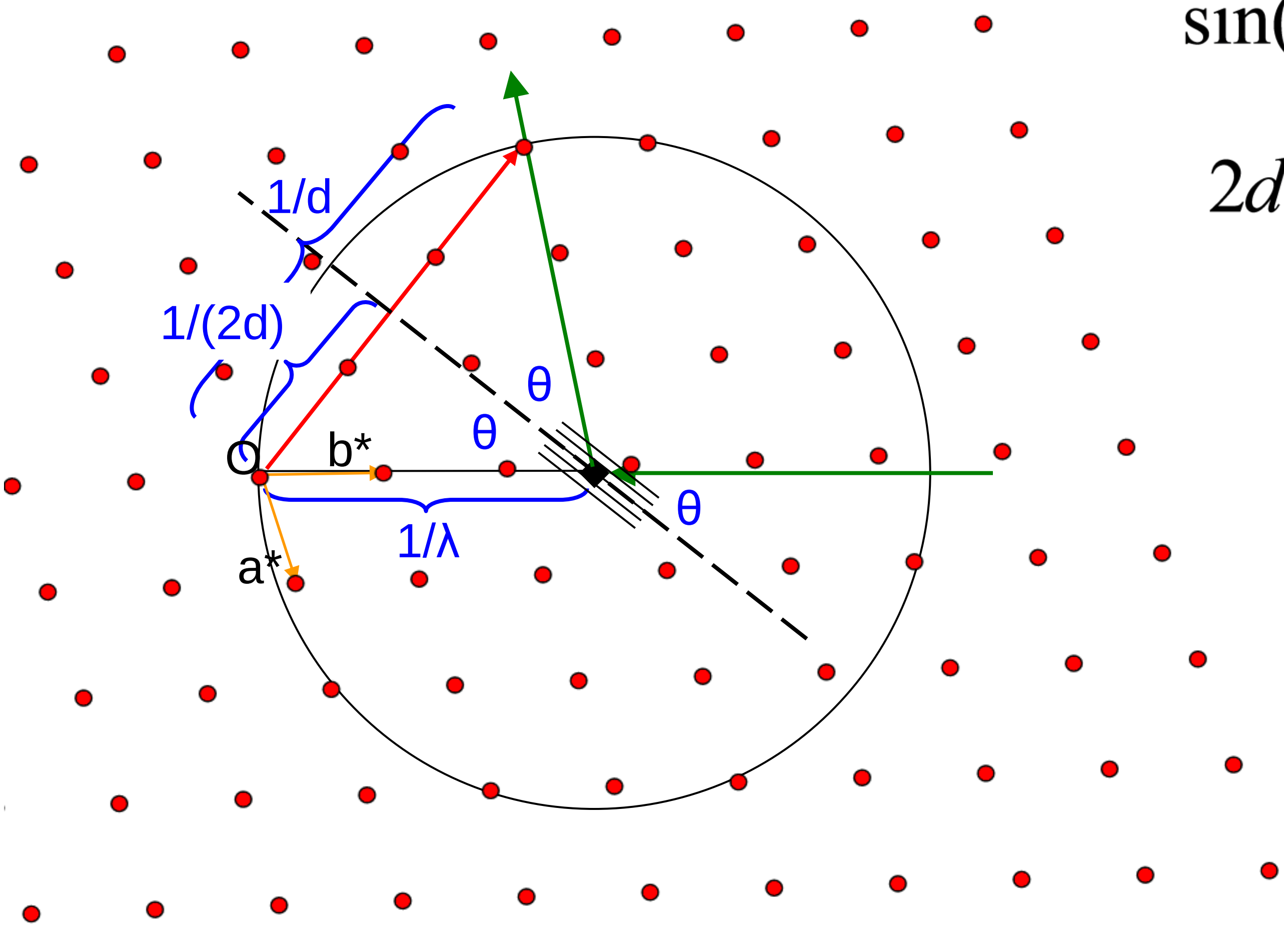
Laue equations:

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

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

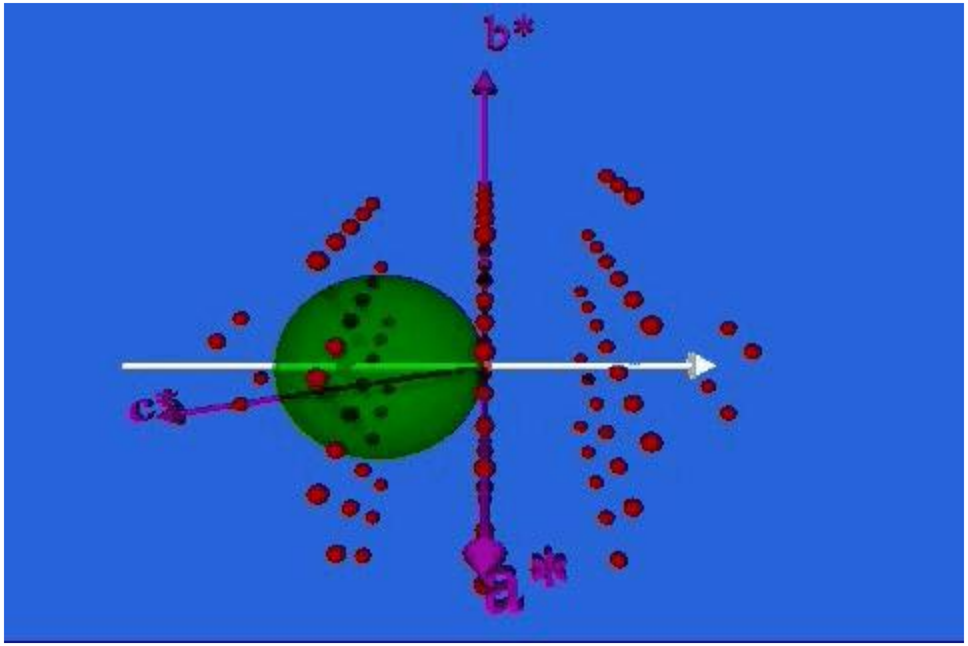
The Ewald Sphere



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

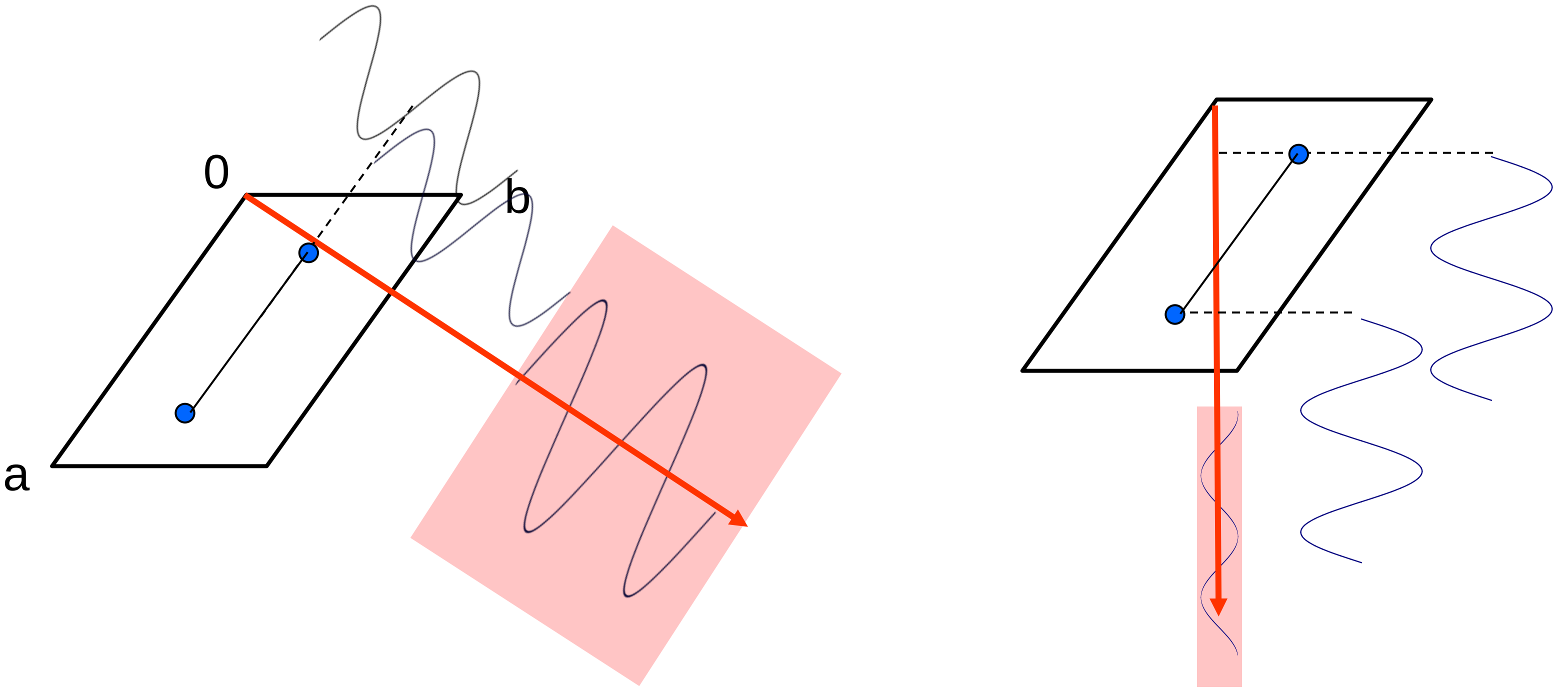
$$2d\sin(\theta)=\lambda$$

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



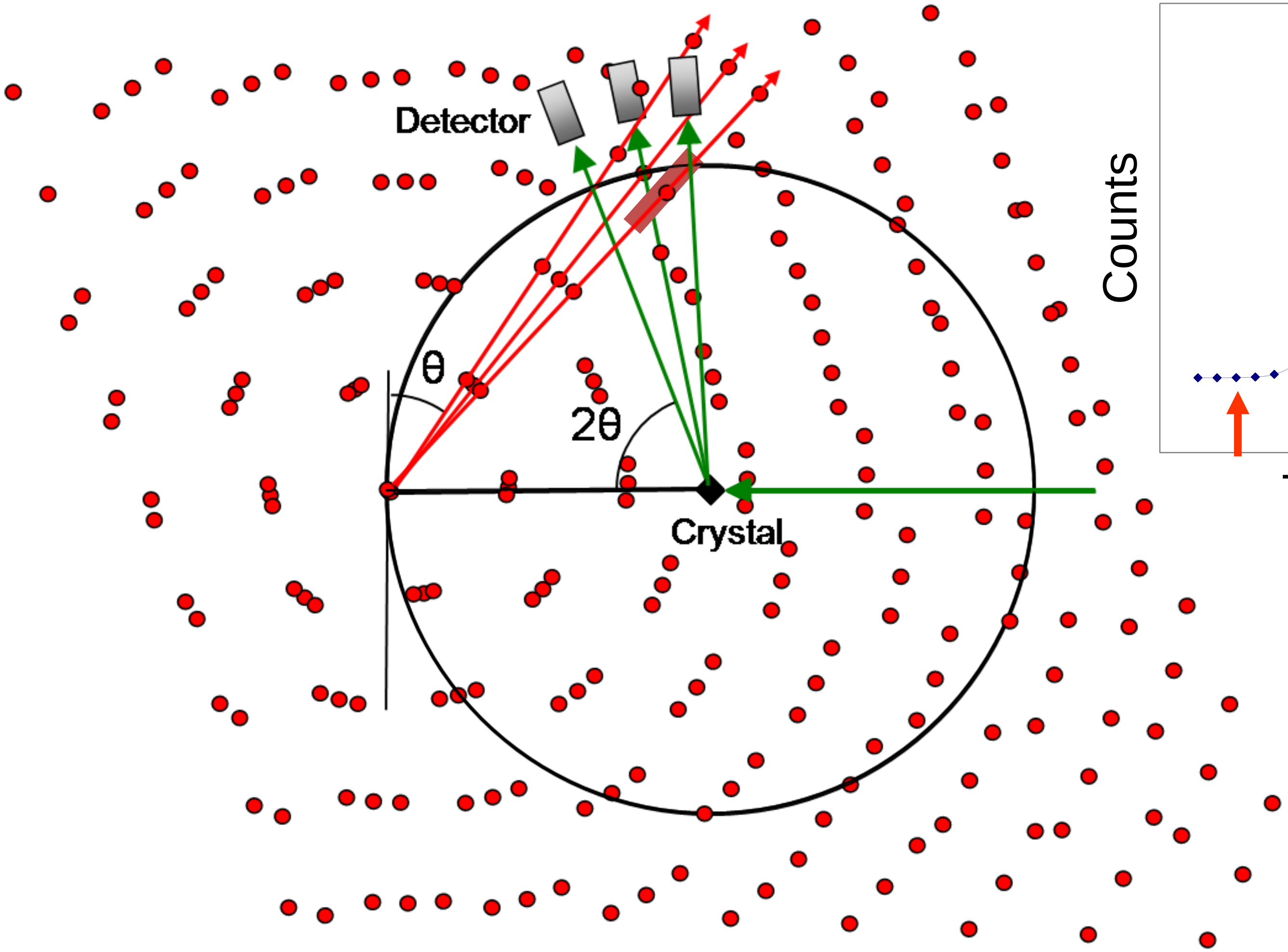
Relative phase shifts related to molecular structure.

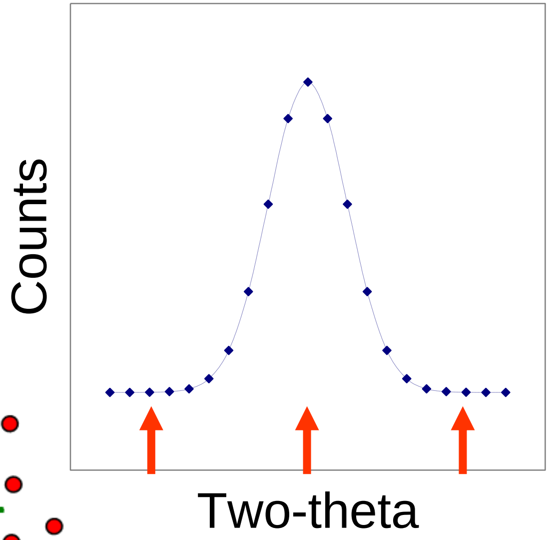
$$F_{hkl} = \sum_i b_i \exp(2\pi i \mathbf{s} \bullet \mathbf{r})$$

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

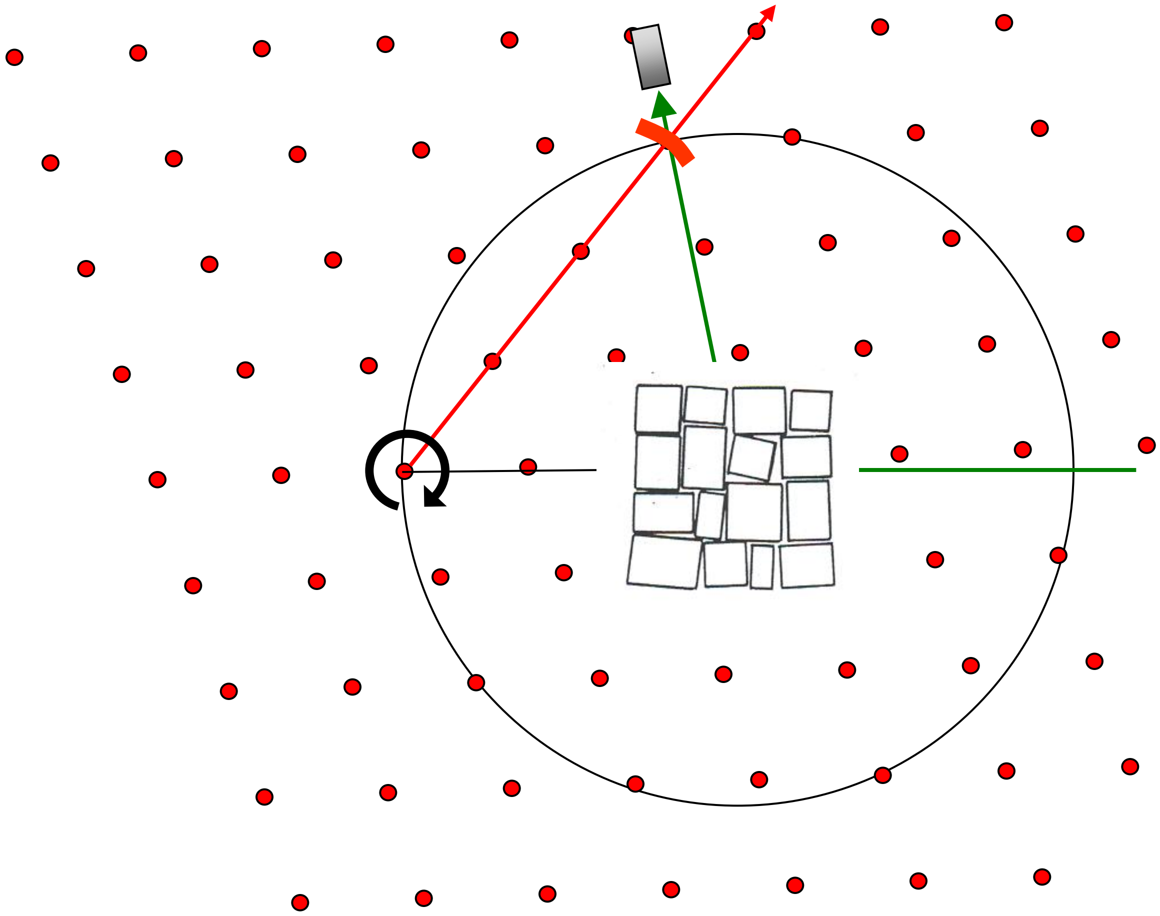
$$F_{hkl}^2 \approx I_{hkl}$$

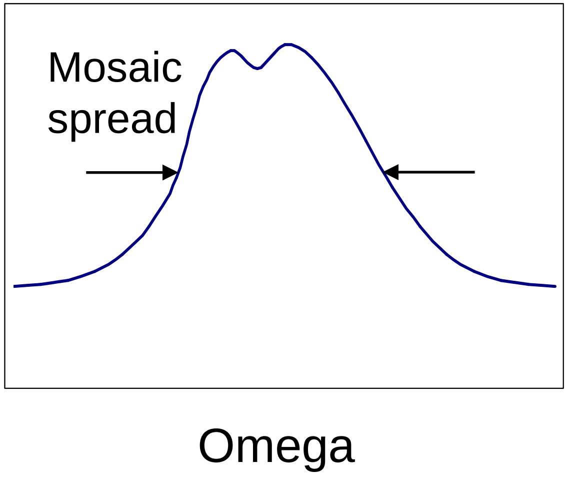
θ-2*θ* Step Scan





Omega Step Scan

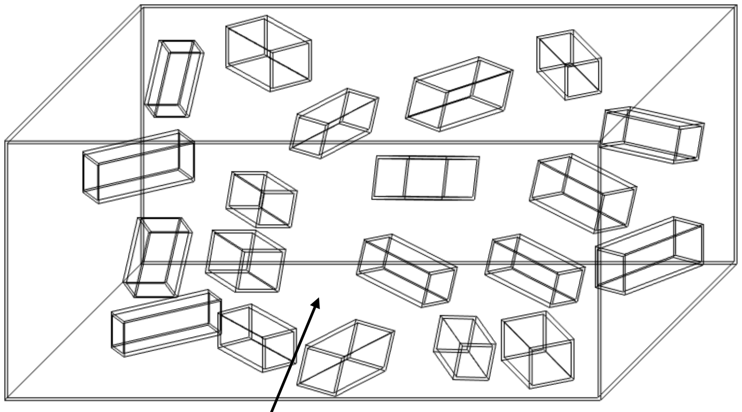




1. Detector stationary at 2θ angle.
2. Crystal is rotated about θ by +/- ω.
3. FWHM is the mosaic spread.

Something completely different - polycrystallography

What is a powder? - polycrystalline mass



All orientations of crystallites possible

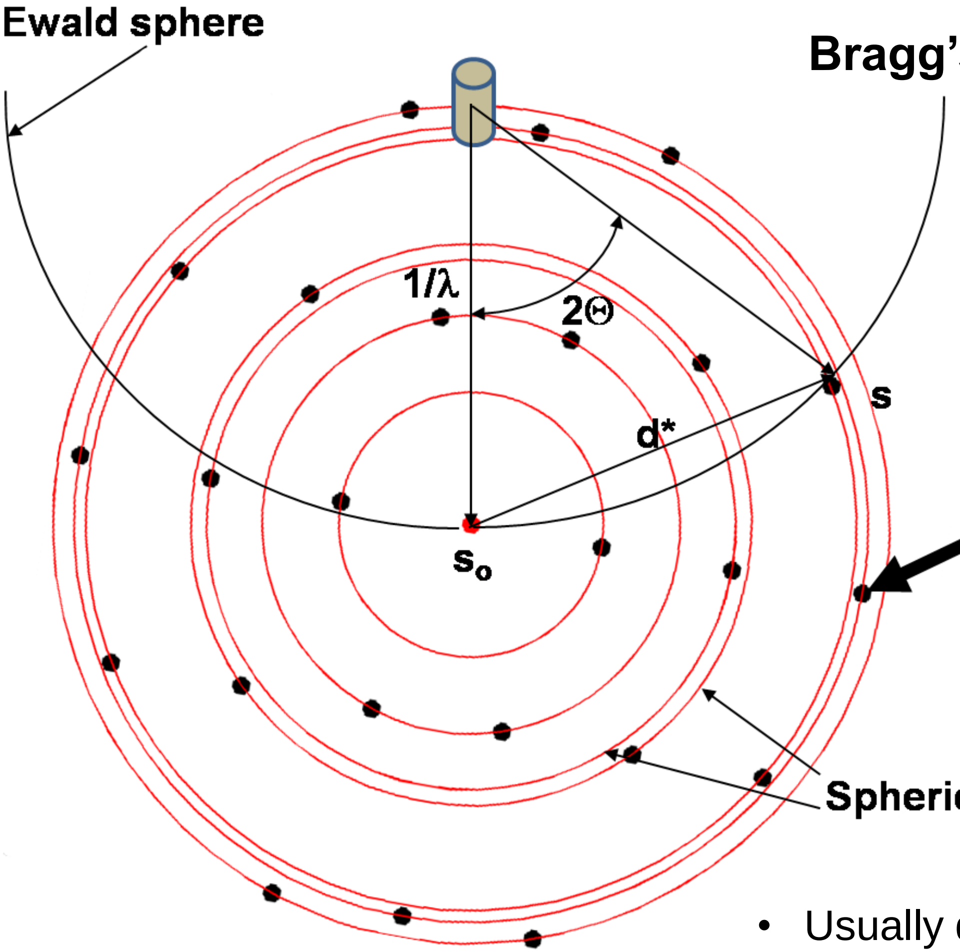
Sample: 1μl powder of 1μm crystallites - $\sim 10^9$ particles

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

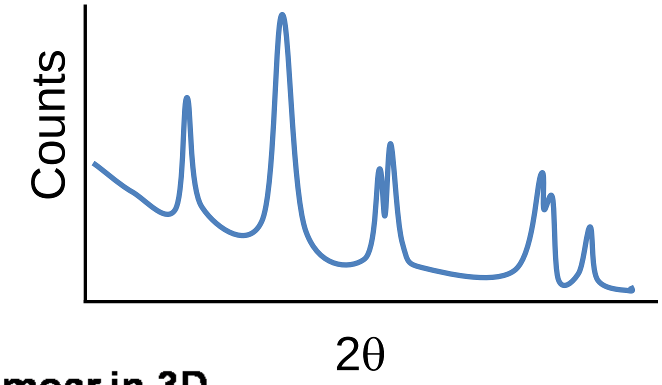
Single crystal reciprocal lattice
- smeared into spherical shells

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.

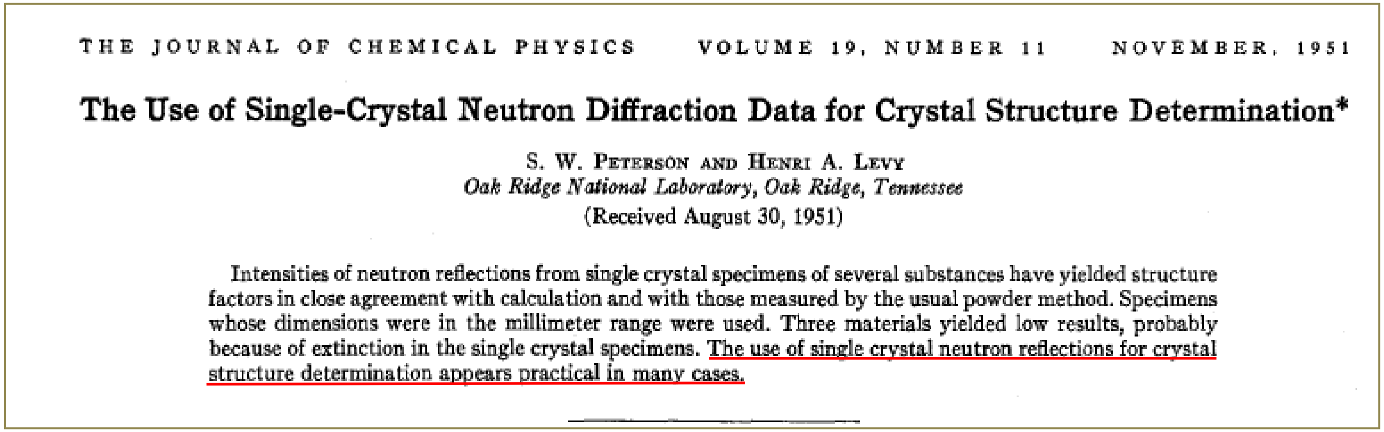
Why do single crystal diffraction (vs. powder diffraction)?

- Smaller samples – 1-10 mg vs 500-5000 mg
- Larger molecules and unit cells
- Hydrogen is ok – generally does not 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

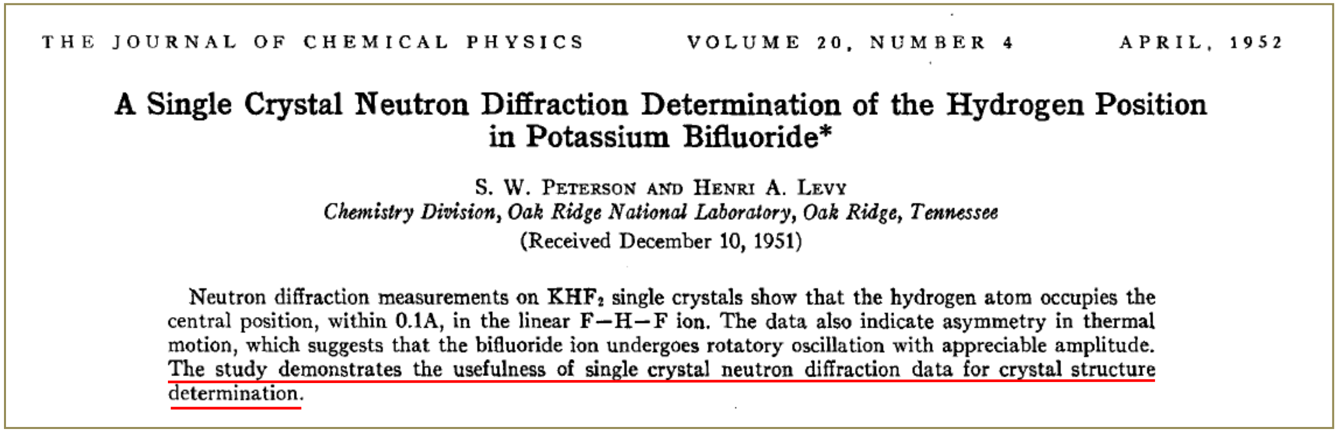


THE JOURNAL OF CHEMICAL PHYSICS VOLUME 19, NUMBER 11 NOVEMBER, 1951

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

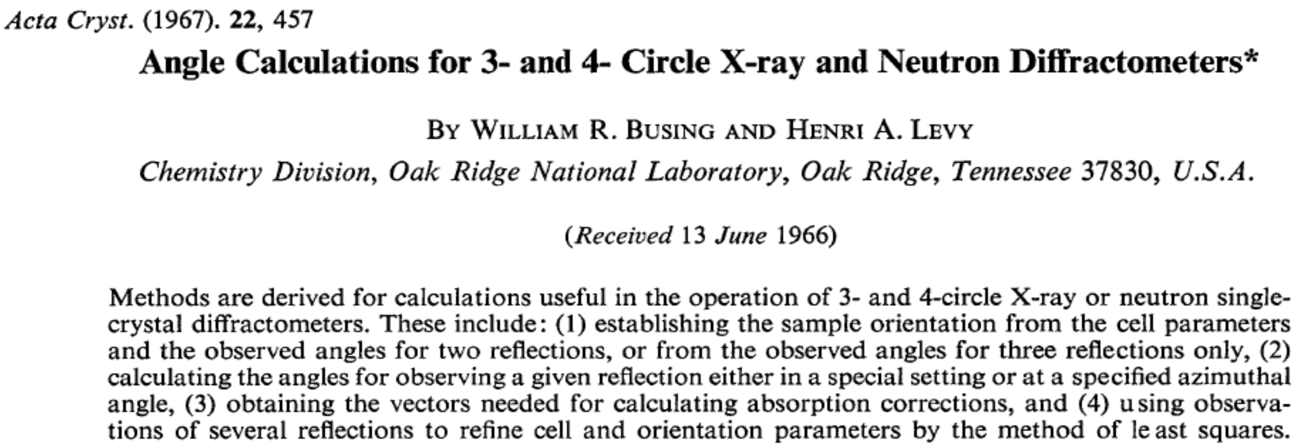
A Single Crystal Neutron Diffraction Determination of the Hydrogen Position in Potassium Bifluoride*

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.

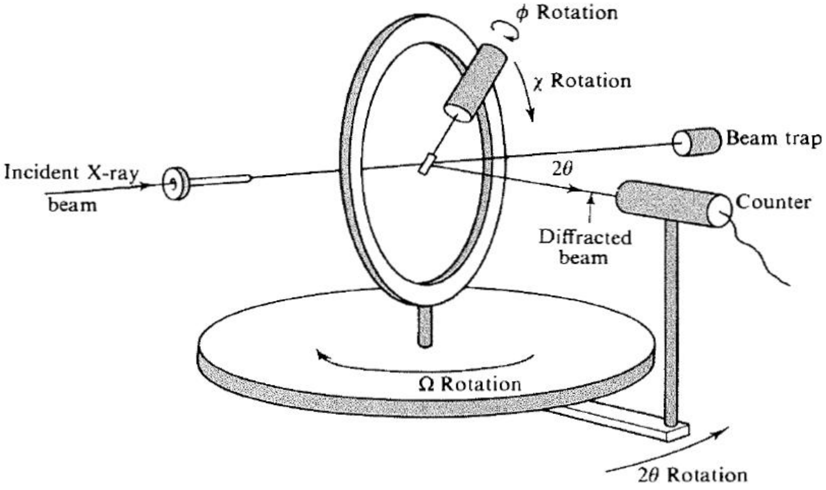


Fig. 5.29. A typical four-circle diffractometer. The counter rotates about the 2θ axis in one plane and the crystal may be orientated in any way by the three axes of rotation ϕ, χ and Ω.

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

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

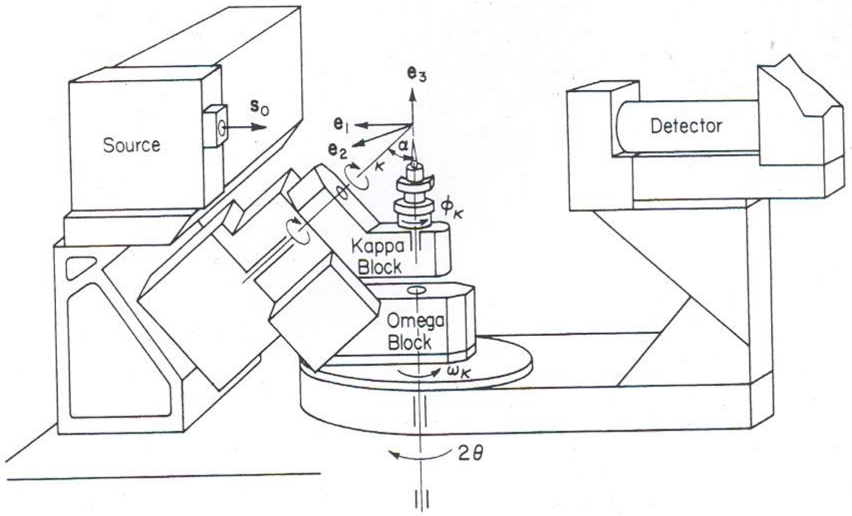
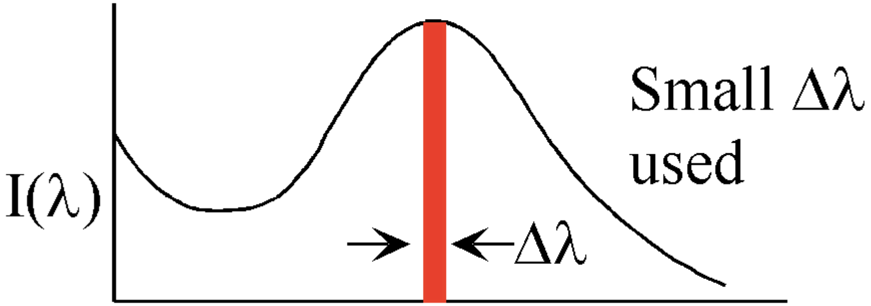


FIGURE 6-13. Kappa geometry. Adapted from operating manual for ENRAF-NONIUS CAD 4 diffractometer (angles ω, ϕ, and κ are opposite in sign to those of Enraf-Nonius). (By permission of ENRAF-NONIUS Service Corp., Bohemia, New York.)

Brucker AXS: KAPPA APEX II

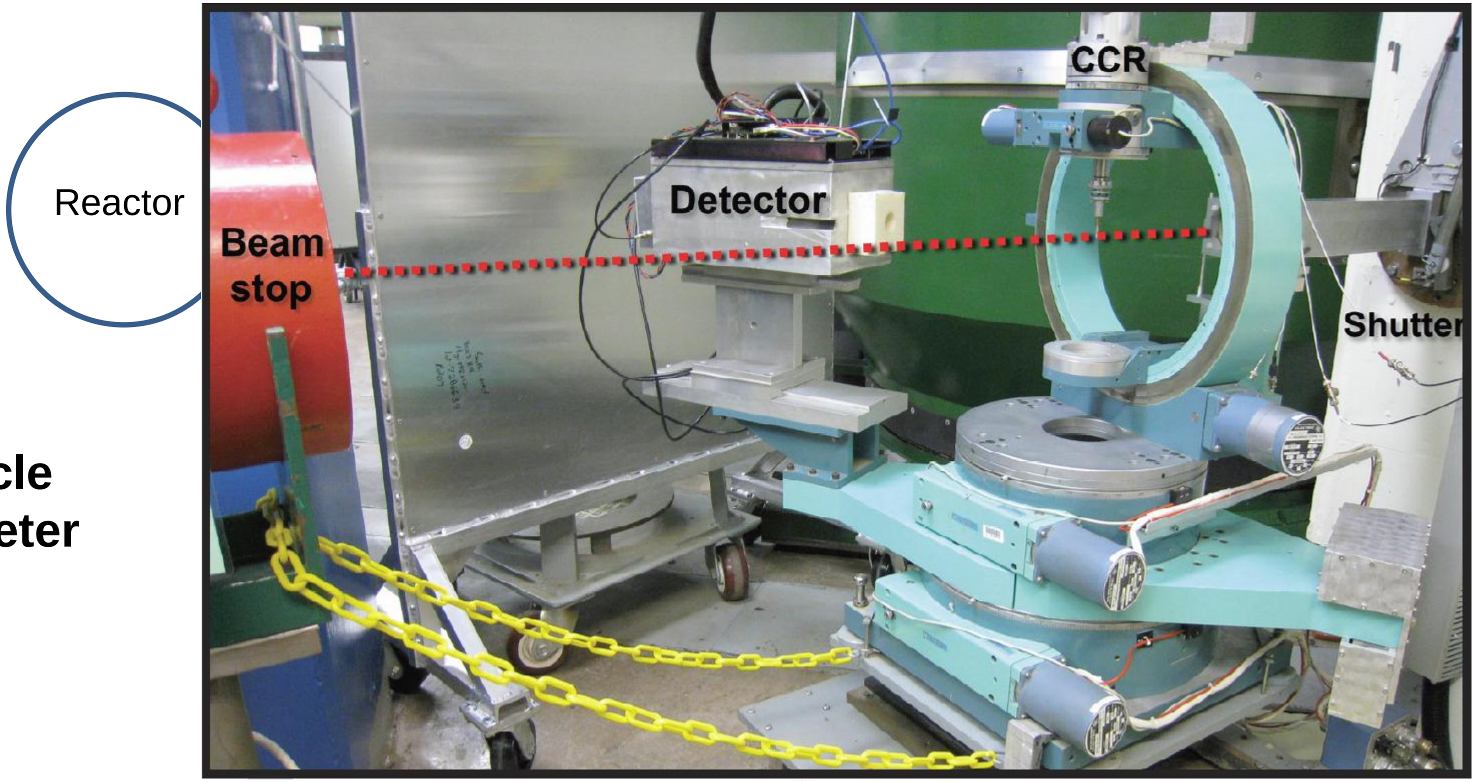
- Full 360° rotations about ω and φ axes.
- Rotation about κ axis reproduces quarter circle about χ axis.

Monochromatic diffractometer



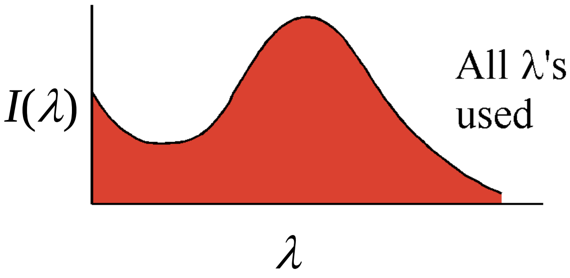
- Rotating crystal
- Vary $\sin\theta$ in the Bragg equation:

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

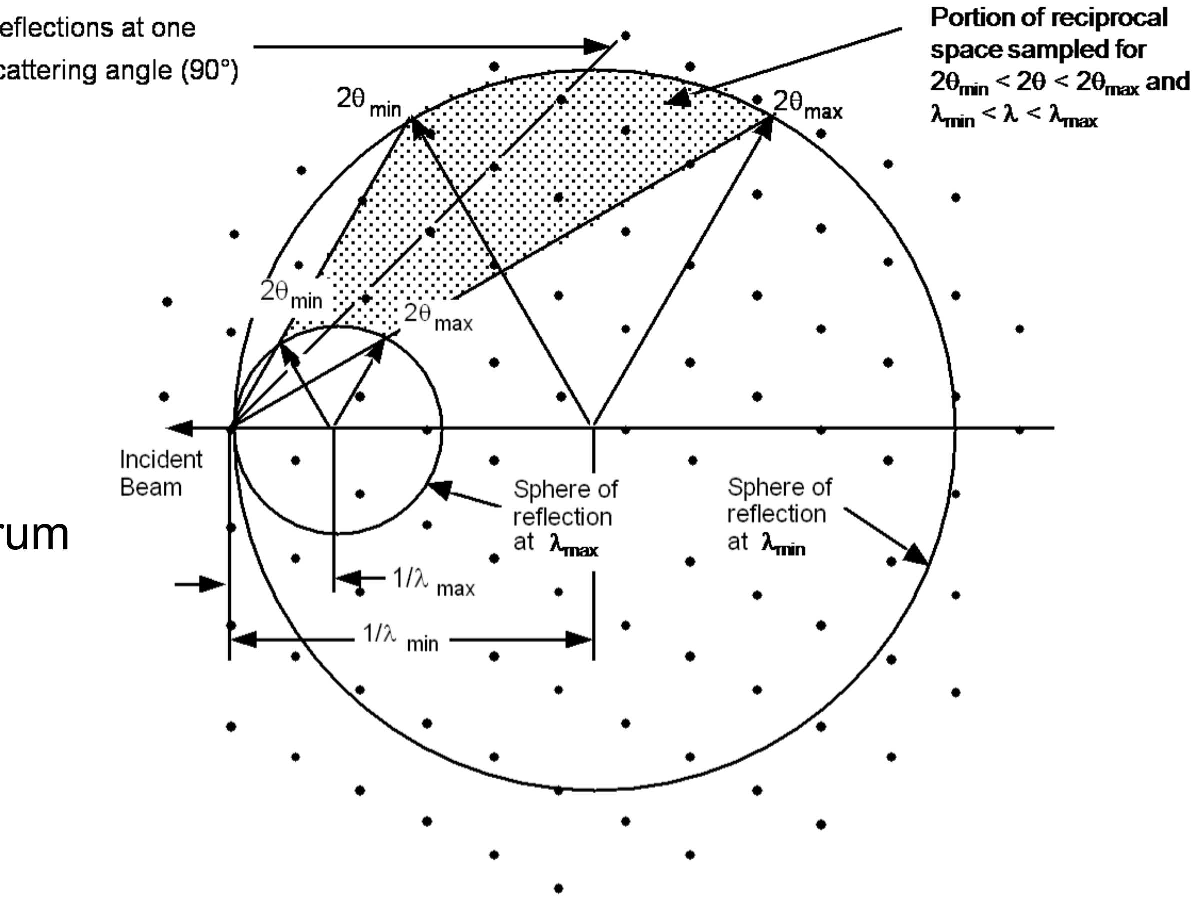


HFIR 4-Circle Diffractometer

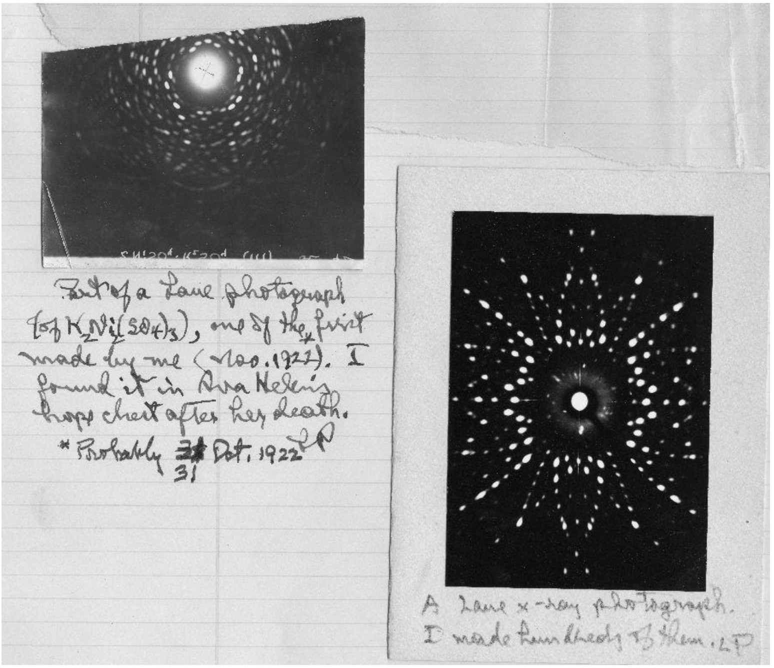
Laue diffraction



Polychromatic “white” spectrum



Laue photo from white radiation



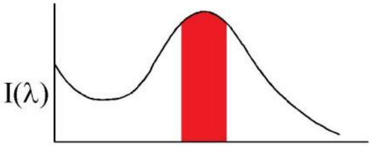
Part of a Laue photograph [of $K_2Ni_2(SO_4)_3$), one of the first* made by me (Nov. 1922). I found it in Ava Helen's hope chest after her death.

*Probably ~~3~~ 31 Oct. 1922 LP

A Laue x-ray photograph. I made hundreds of them. LP

X-ray Laue photos taken
by Linus Pauling

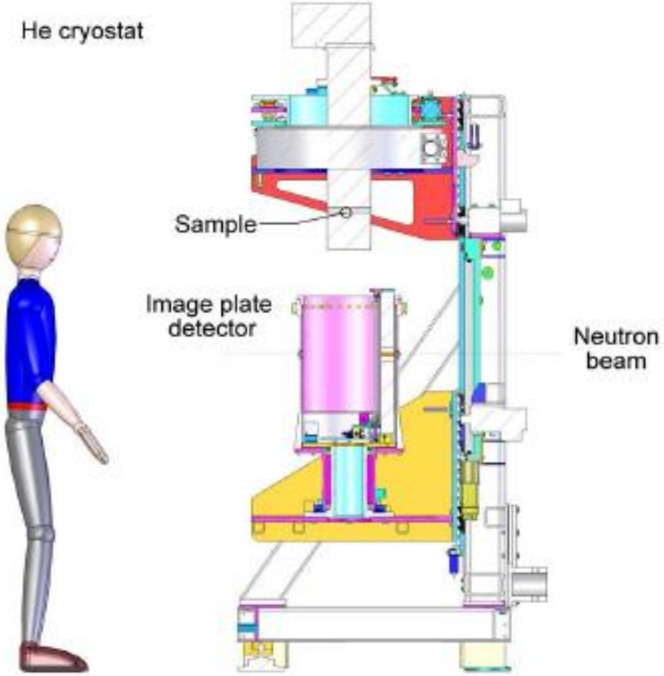
Quasi-Laue Neutron Image Plate Diffractometer



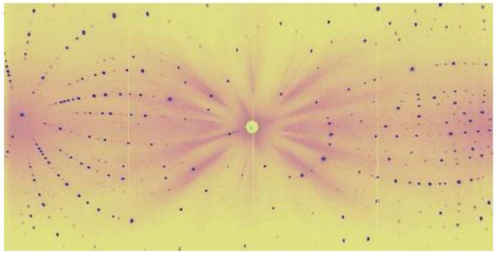
Select Δλ/λ of 10-20%

2011 at HFIR: IMAGINE

General view of the QLD

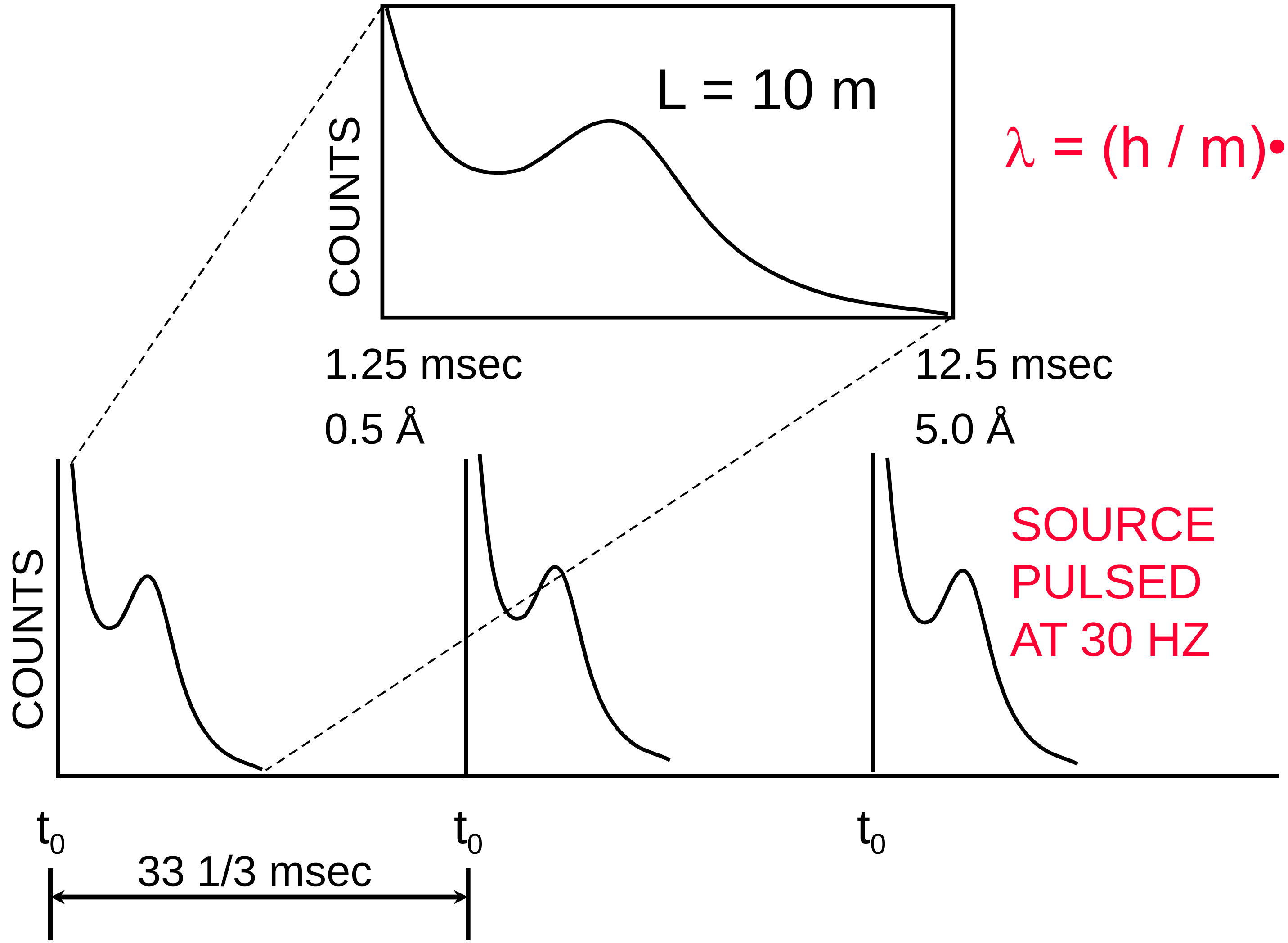


QLD schematic (open position)



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

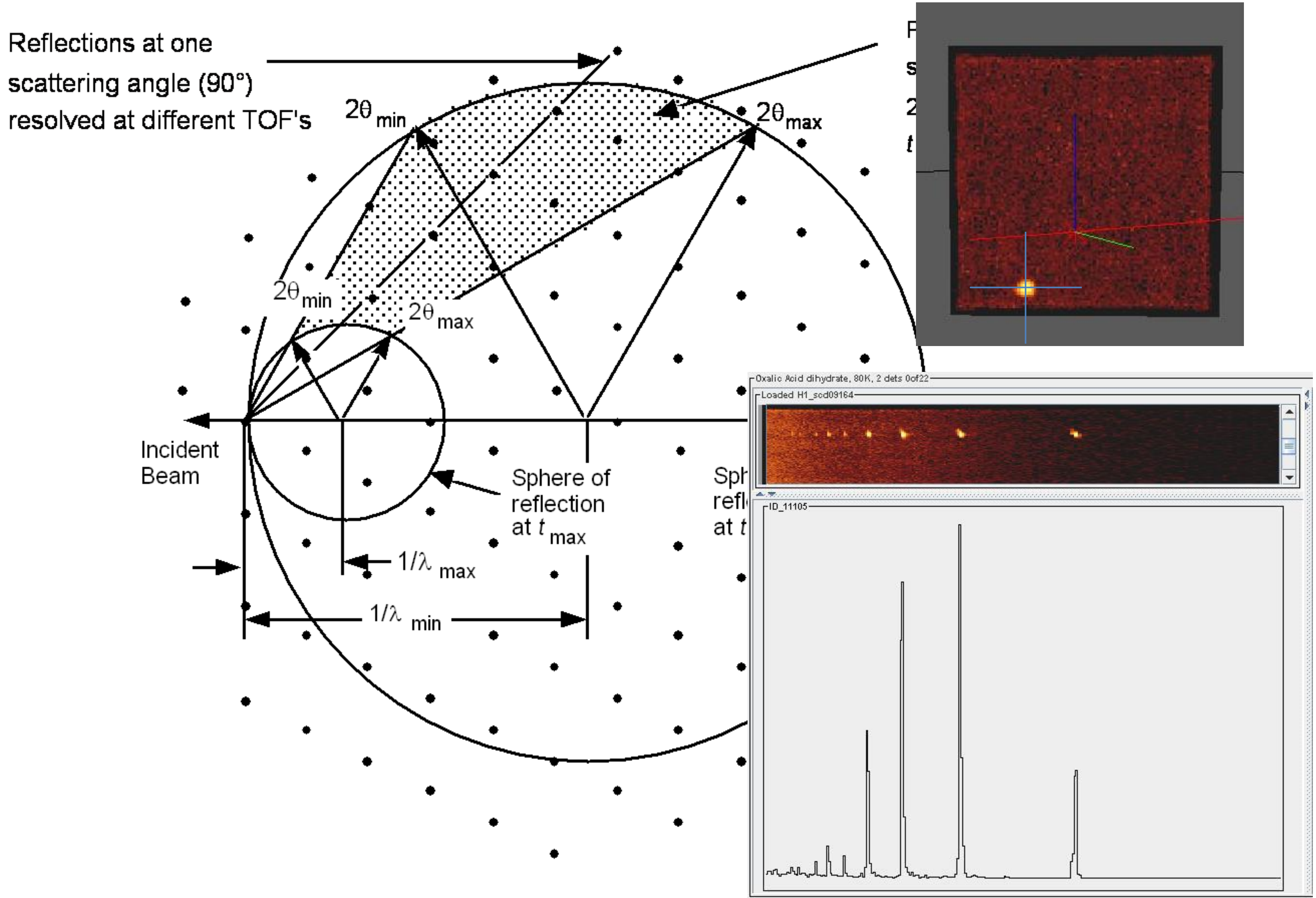
Pulsed Neutron Incident Spectrum



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

SOURCE
PULSED
AT 30 HZ

Time-of-Flight Laue Technique



Reflections at one scattering angle (90°) resolved at different TOF's

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

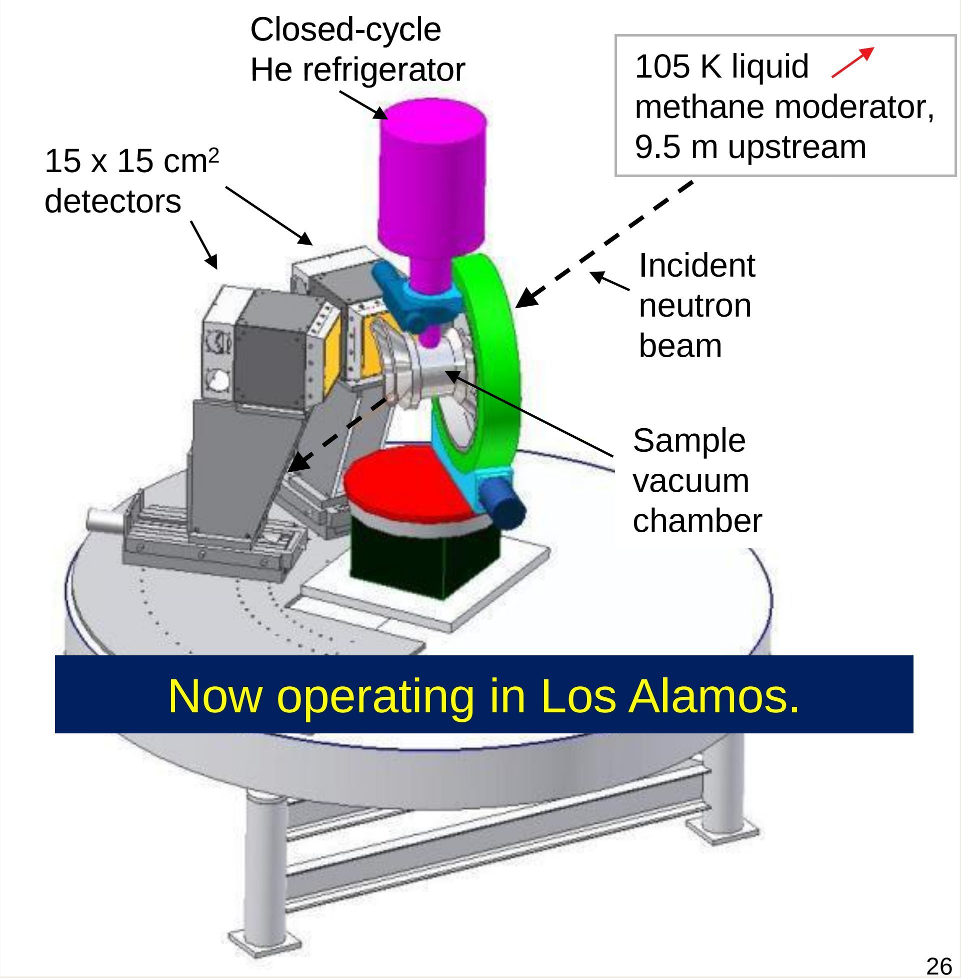
Hot-Stage Displex: 4-900 K

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.



Closed-cycle He refrigerator

105 K liquid methane moderator, 9.5 m upstream

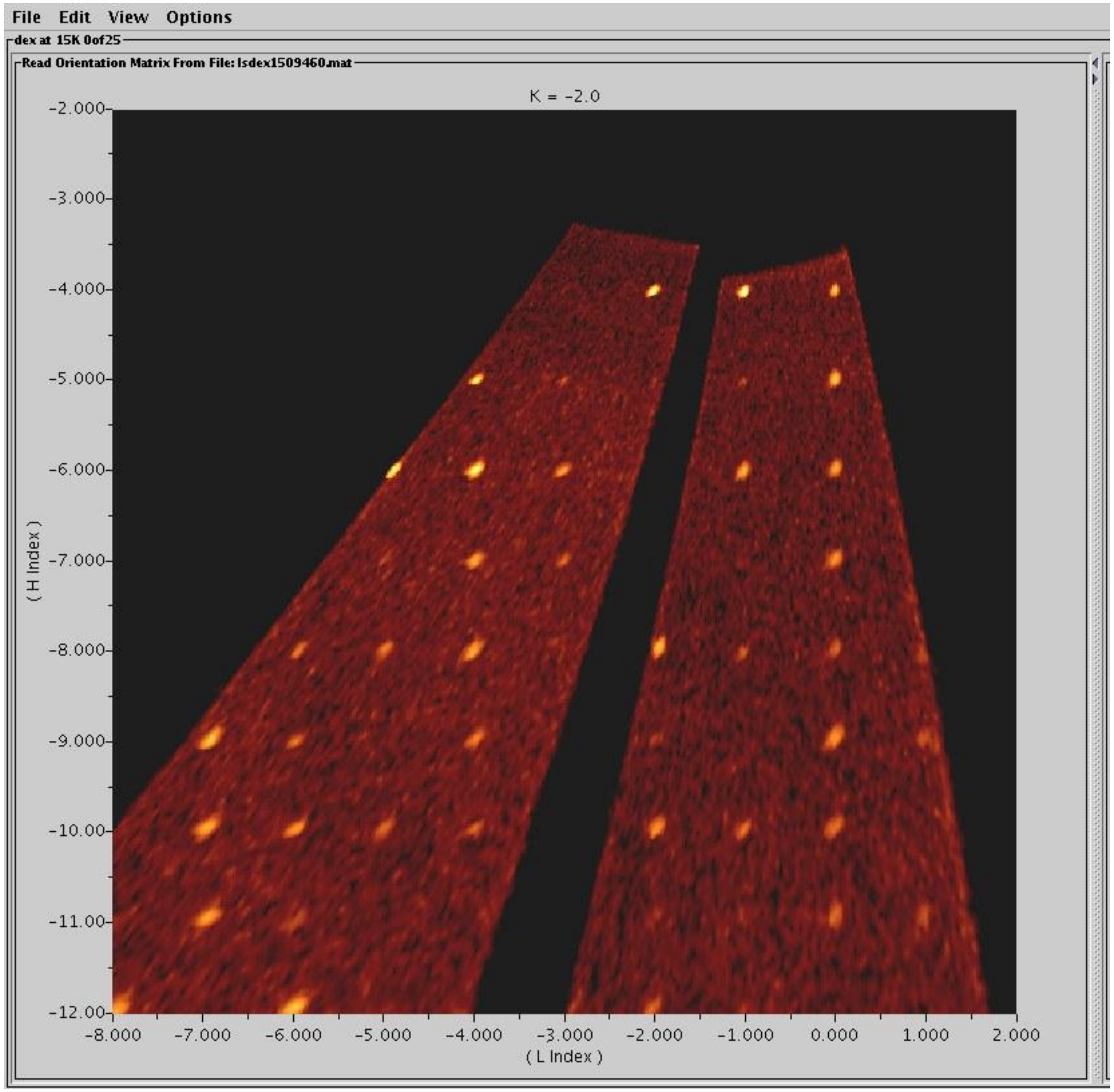
15 x 15 cm^2 detectors

Incident neutron beam

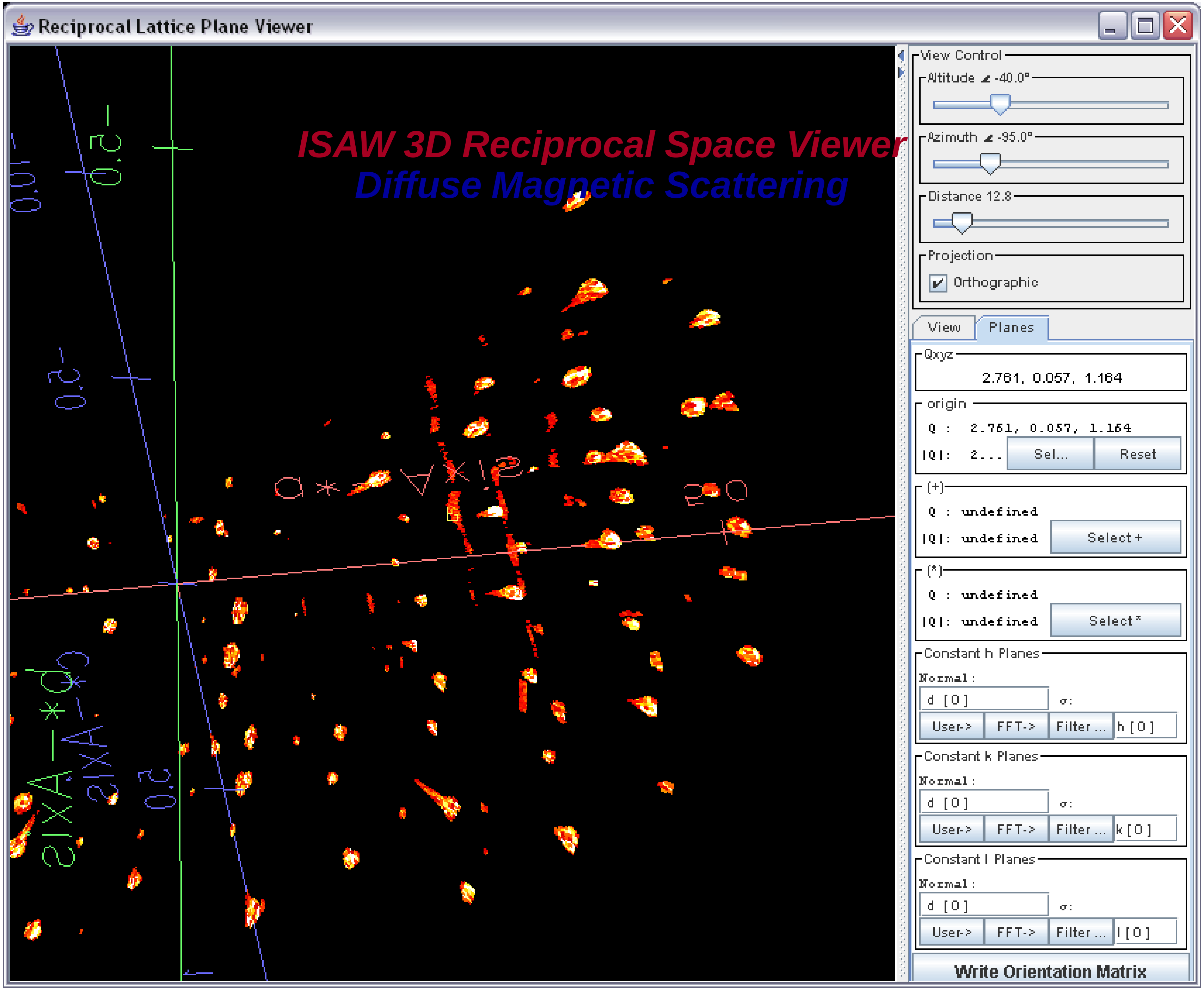
Sample vacuum chamber

Now operating in Los Alamos.

ISAW hkl plot



ISAW 3D Reciprocal Space Viewer
Diffuse Magnetic Scattering



Altitude -40.0°

Azimuth -95.0°

Distance 12.8

Projection: ☑ Orthographic

Qxyz: 2.761, 0.057, 1.164

origin
Q : 2.761, 0.057, 1.164
|Q|: 2...

(+)
Q : undefined
|Q|: undefined

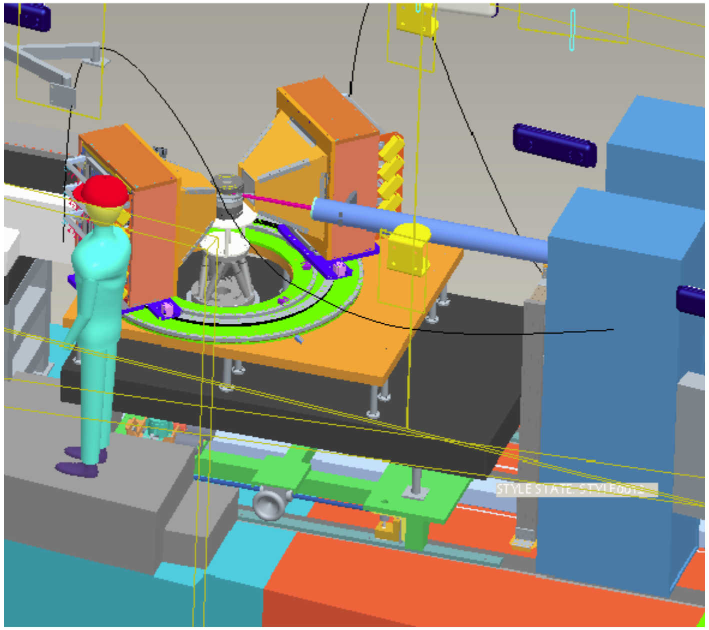
(*)
Q : undefined
|Q|: undefined

Constant h Planes
Normal: d [0] σ: h [0]

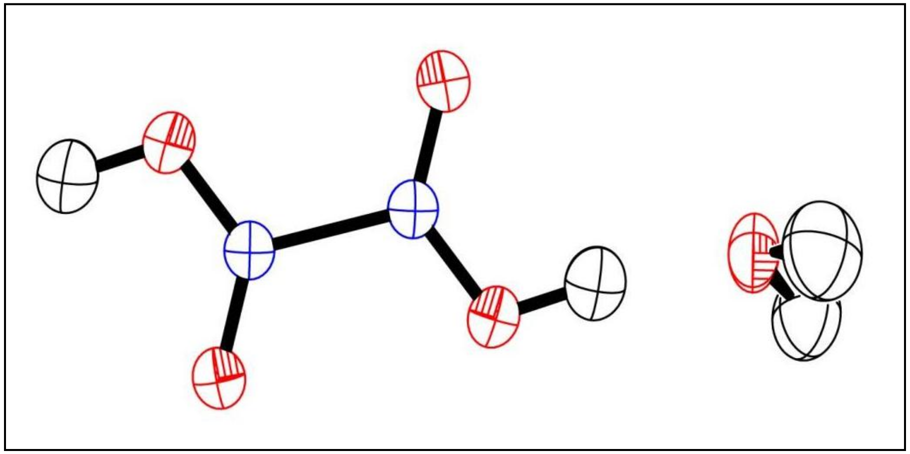
Constant k Planes
Normal: d [0] σ: k [0]

Constant l Planes
Normal: d [0] σ: l [0]

SNAP



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



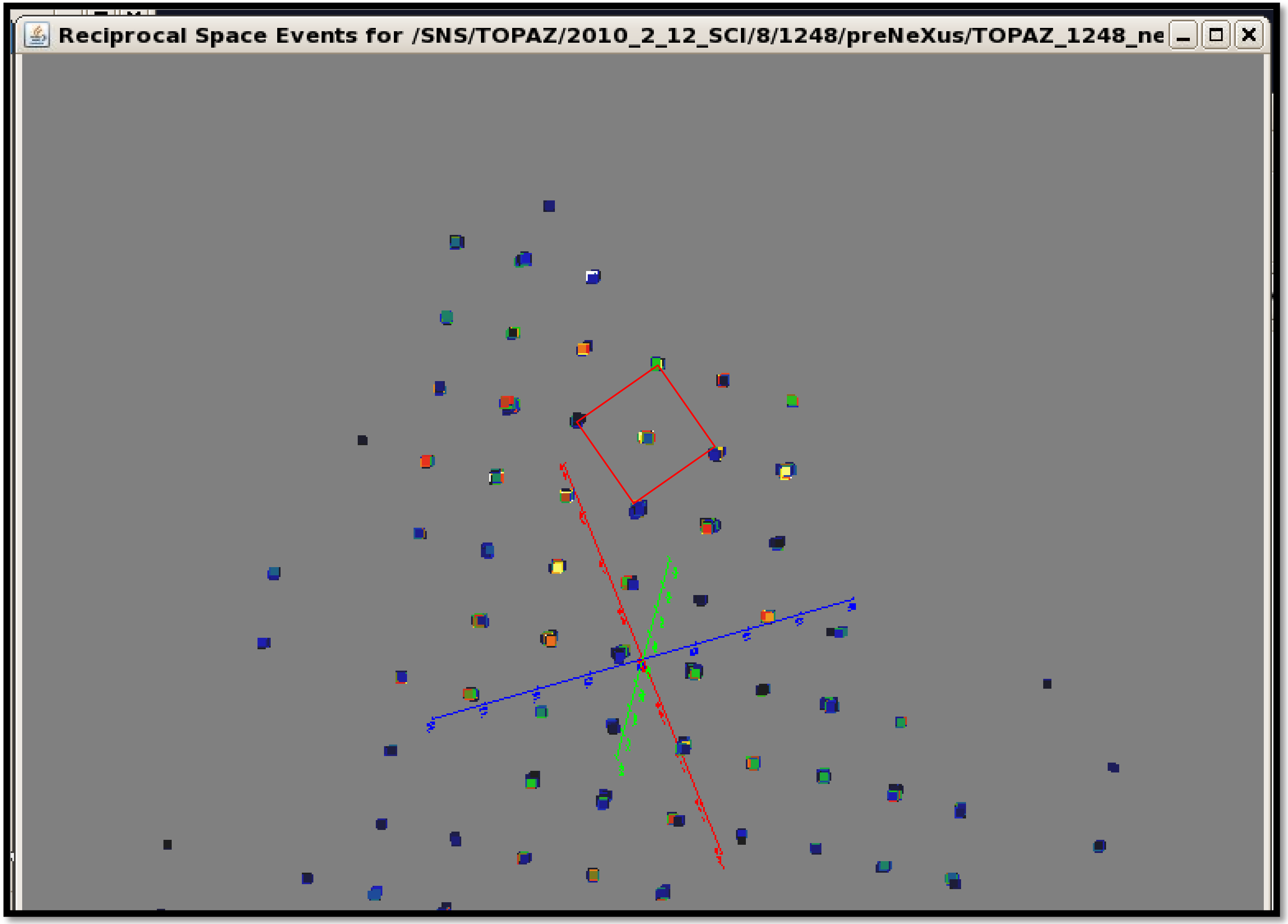
Topaz

- 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.

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.

Unit cell and space group



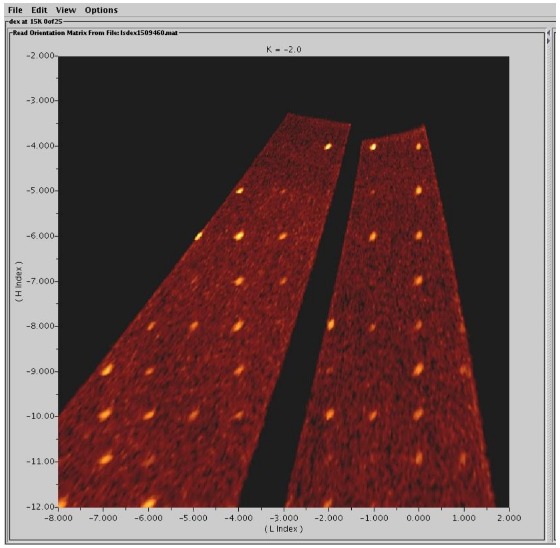
Data Reduction

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

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

k = scale factor
$\tau(\lambda)$ = deadtime loss
$\phi(\lambda)$ = incident flux spectrum, obtained by measuring the incoherent scattering from a vanadium sample
$\varepsilon(\lambda,\boldsymbol{r})$ = detector efficiency calculated as a function of wavelength λ and position $\boldsymbol{r}$ on the detector for each Bragg peak since the slant path through the flat ^{6}Li glass varies with $\boldsymbol{r}$
$A(\lambda)$ = 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

Fourier transforms



dex at 15K 0of25

Read Orientation Matrix From File: lsdex1509460.mat

K = -2.0

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

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

$(COOD)_2 \cdot 2D_2O$ *

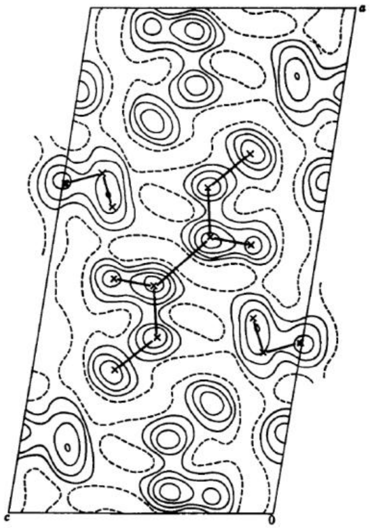


Fig. 3. Neutron scattering density projection along the *b* axis. The contours are at intervals of 4×10^{-13} cm.Å^{-2}, and broken lines are zero contours.

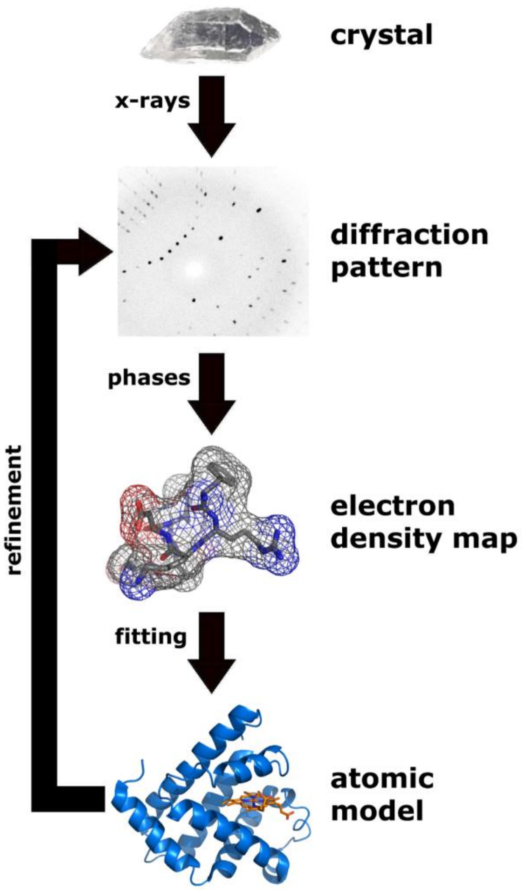
$$F_{hkl} = \int_{cell} \rho_{xyz}\, e^{2\pi i(\boldsymbol{s}\cdot\boldsymbol{r})} d\boldsymbol{v} = \sum_j b_j\, e^{2\pi i(hx_j+ky_j+lz_j)}$$

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.

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

Friedel's law

$$F_{\mathrm{hkl}} = F^*_{-(\mathrm{hkl})}$$
$$I_{\mathrm{hkl}} = I_{-(\mathrm{hkl})}$$

F(hkl) is equal to the complex conjugate of F(-h-k-l).

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

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

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

The structure factor of hkl and –(hkl) are complex conjugates.

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

$$\rho(xyz) = \frac{2}{V}\sum_{hemi} |F_{hkl}|\cos\bigl(\phi - 2\pi(hx + ky + lz)\bigr)$$

Centrosymmetric crystals

$$F_{hkl} = \sum_j b_j \, e^{2\pi i (hx_j + ky_j + lz_j)}$$

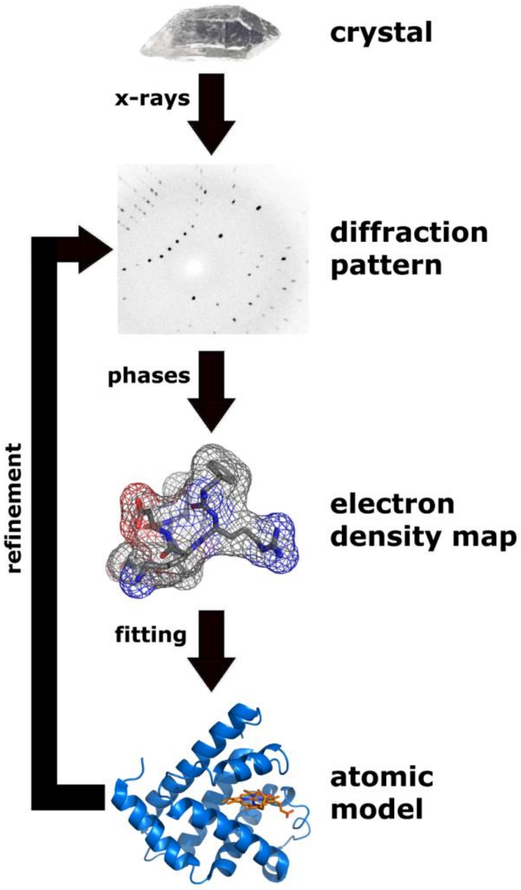
$$= \sum_j b_j \left(\cos 2\pi(hx + ky + lz) + i \xcancel{\sin 2\pi(hx + ky + lz)}\right)$$

- In a centrosymmetric crystal, for any atom at x,y,z, there is an equivalent atom at -x,-y,-z.
- Since sin(A) = -sin(-A), the sine term cancels.
- Phase angles are either 0 or π.

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



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

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

GSAS, SHELX, CRYSTALS…
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.

Books and on-line tutorials

- George E. Bacon, *Neutron Diffraction*, 3rd ed., Clarendon Press, 1975.
- Colin G. Windsor, *Pulsed Neutron Scattering*, Taylor & Francis, 1981.
- Chick C. Wilson, *Single Crystal Neutron Diffraction From Molecular Crystals*, World Scientific, 2000.

- 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.

- Interactive Tutorial about Diffraction: www.totalscattering.org/teaching/
- IPNS SCD tutorial by Paula Piccoli: www.pns.anl.gov/instruments/scd/subscd/scd.shtml