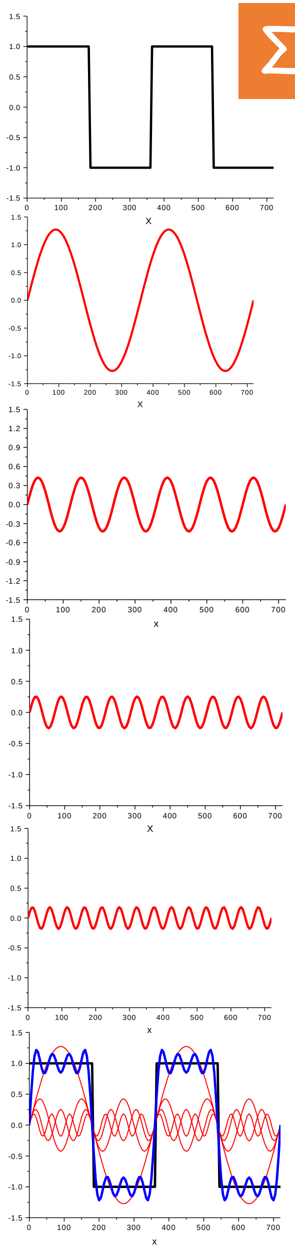
Σύνθεση Fourier

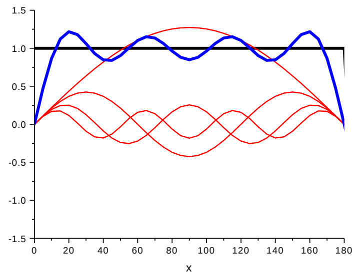


$4/\pi \quad \sin\omega_o\chi$

$4/3\pi \quad \sin 3\omega_o\chi$

$4/5\pi \quad \sin 5\omega_o\chi$

$4/7\pi \quad \sin 7\omega_o\chi$

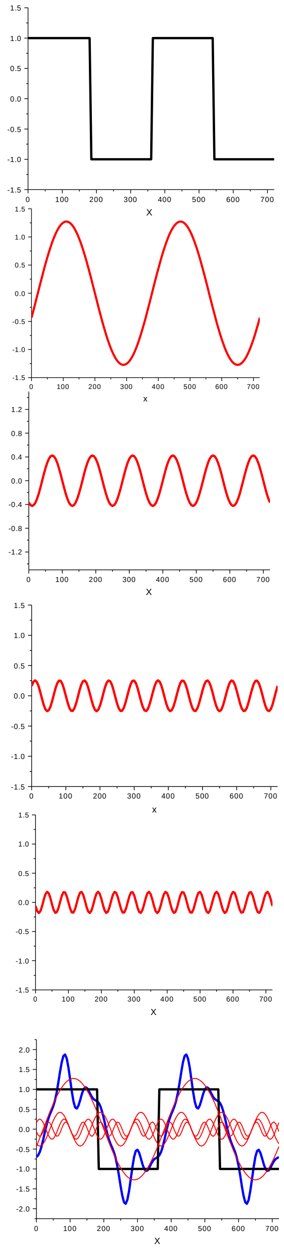


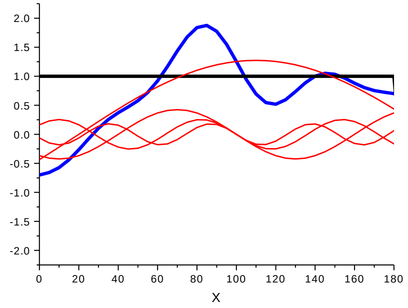
$4/\pi \quad \sin\omega_o\chi$

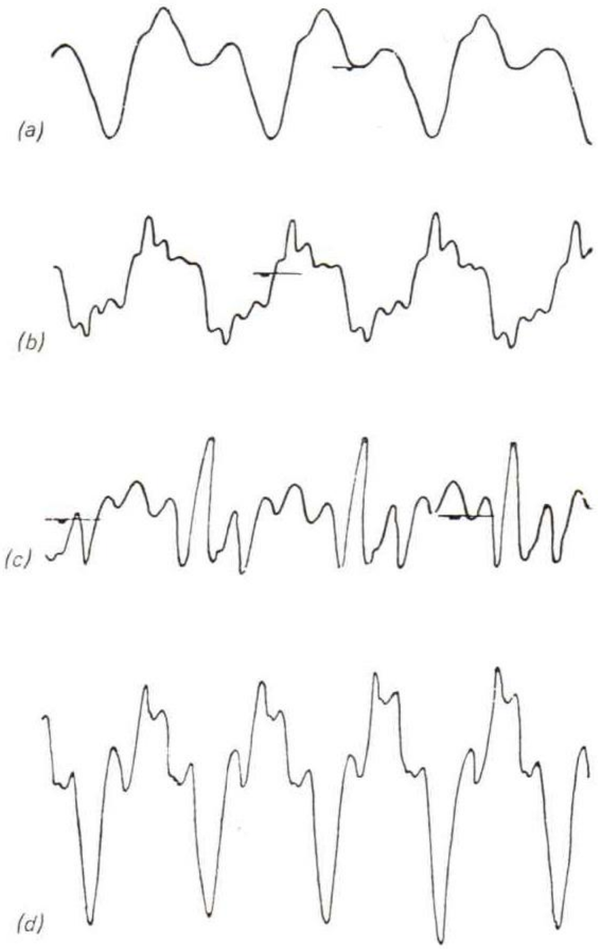
$4/3\pi \quad \sin 3\omega_o\chi$

$4/5\pi \quad \sin 5\omega_o\chi$

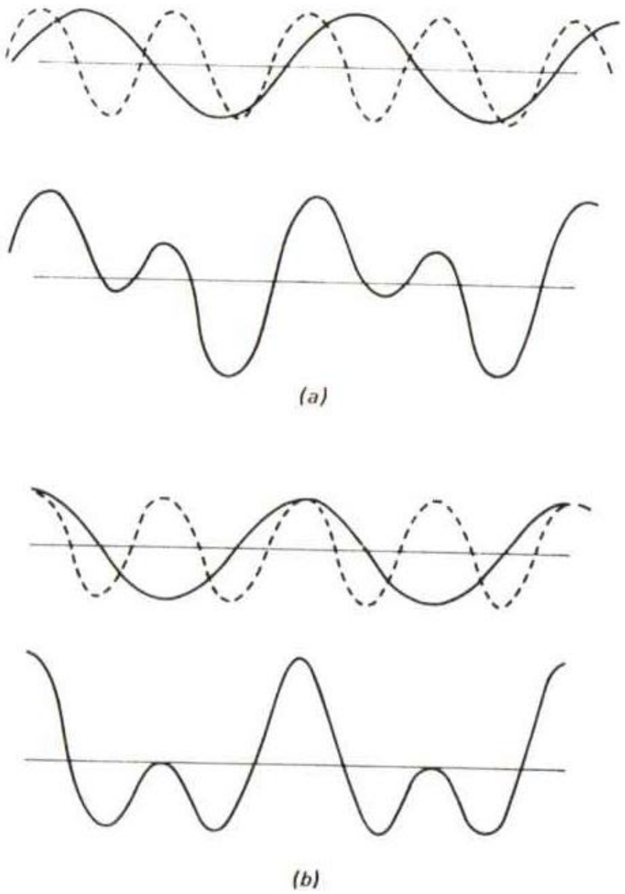
$4/7\pi \quad \sin 7\omega_o\chi$







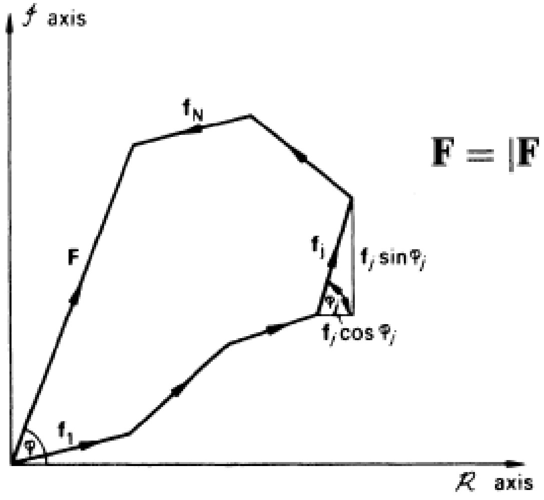
. 1. The variation in the pressure of the air for a note from (a) flute (b) clarinet, (c) oboe, (d) saxophone.



$$\rho(\mathbf{x}) = \frac{1}{V}\sum_{\mathbf{h}} \mathbf{F}(\mathbf{h})\exp(-2\pi i\mathbf{h}\cdot\mathbf{x})$$

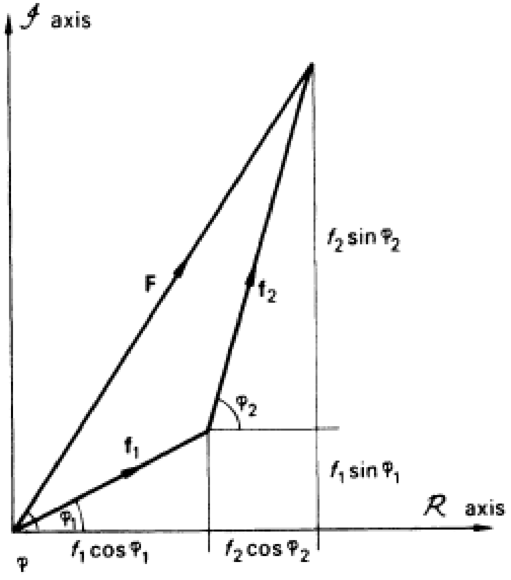
$$\rho(XYZ) = \frac{1}{V_c} \sum\sum\sum_{\text{all } h,k,l} |F| \cos\left[2\pi(hX + kY + lZ) - \alpha\right].$$

$$F\left(\vec{\mathbf{H}}\right) = F_{(h,k,l)} = \sum_{j=1}^{N} f_j \cdot e^{2\pi i \vec{\mathbf{H}}\cdot\vec{r}_j} \; :$$

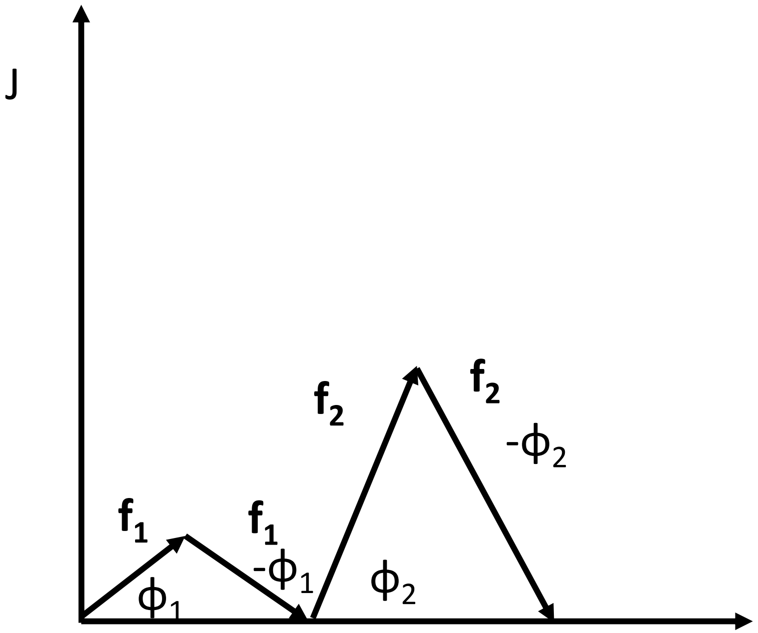


$$\mathbf{F} = |\mathbf{F}| \exp(i\phi)$$

$$\mathbf{F} = f_1 \exp(i\phi_1) + f_2 \exp(i\phi_2) + \cdots + f_j \exp(i\phi_j) + \cdots = \sum_{j=1}^{n} f_j \exp(i\phi_j)$$



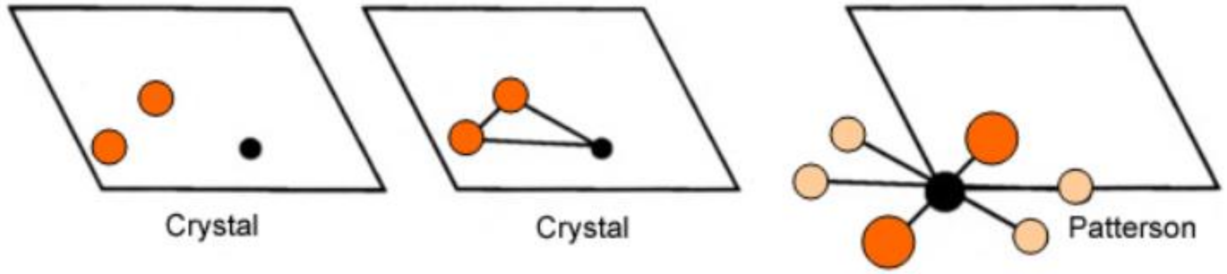
$\bar{r}_j \qquad -\bar{r}_j$



$$F(\bar{H}) = \sum_{j=1}^{N/2}\left(f_j\, e^{2\pi i \bar{H}\cdot\bar{r}_j} + f_j e^{-2\pi i \bar{H}\cdot\bar{r}_j}\right) = \pm\left|F(\bar{H})\right|$$

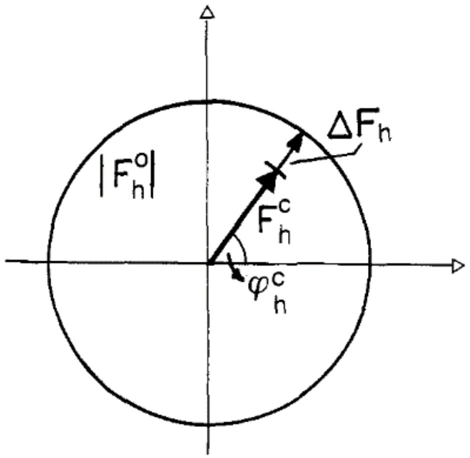
Συνάρτηση Patterson

$$P(u) = \int \rho(x) . \rho(x+u) du = \frac{1}{V} \sum_h |F_{obs}(h)|^2 . e^{-2\pi i h.u}$$



Συνθεση Fourier διαφορών

$$\Delta\rho(x,y,z) = \frac{2}{V_c} \sum_h \sum_k \sum_l (|F_o| - |F_c|) \cos[2\pi(hx + ky + lz) - \phi_c]$$



Άμεσες μέθοδοι

Κανονικοποιημένοι παράγοντες δομής

$$\left|E(\vec{h})\right|^2 = \frac{\left|F_{rel}(\vec{h})\right|^2 K(S)}{\varepsilon \sum_{j=1}^{N} f_j^2}$$

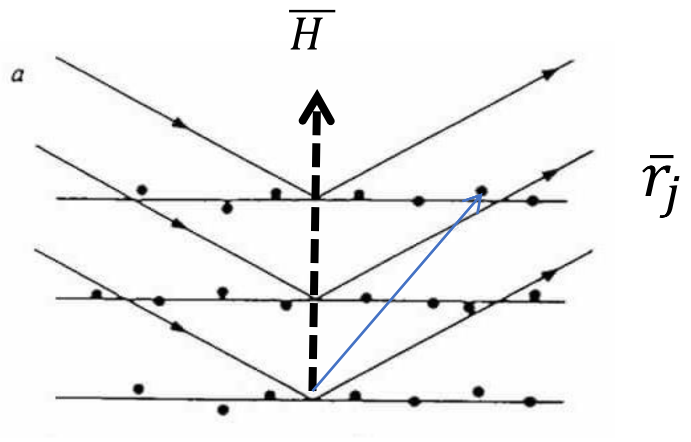
$$S\left[E\left(\vec{h}_1\right)\right] S\left[E\left(\vec{h}_2\right)\right] S\left[E\left(\vec{h}_3\right)\right] \cong +1$$

Κεντροσυμμετρικές δομές

$$\varphi\left(\vec{h}_1\right)+\varphi\left(\vec{h}_2\right)+\varphi\left(\vec{h}_3\right) \cong 0$$

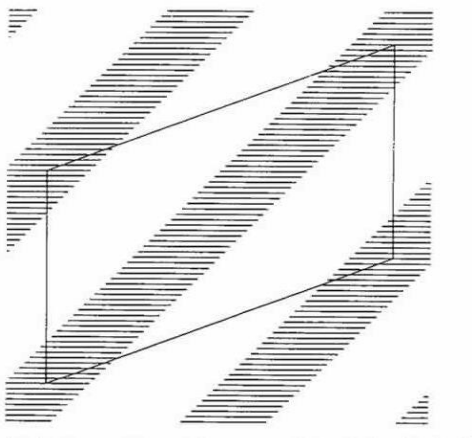
μη Κεντροσυμμετρικές δομές

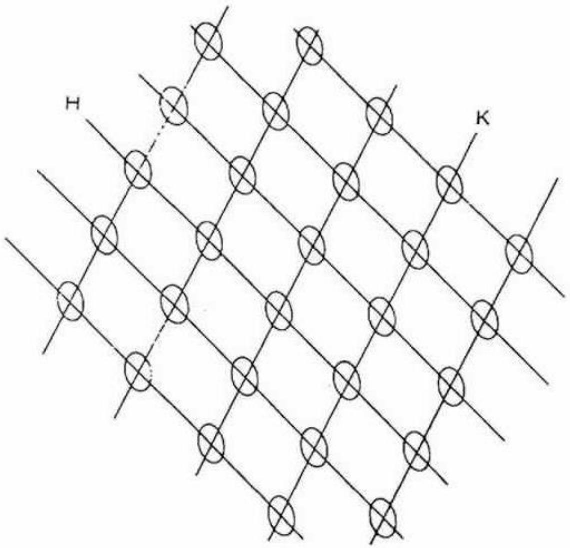
$$\vec{h}_1+\vec{h}_2+\vec{h}_3 = 0$$

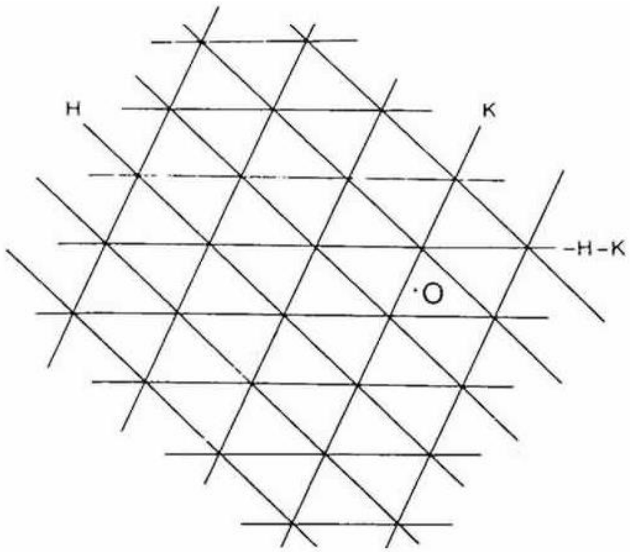


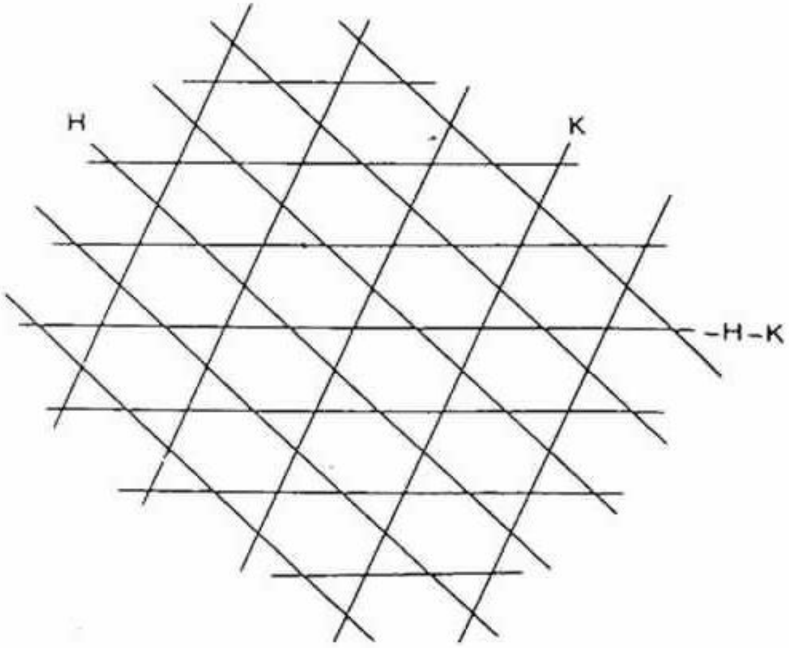
$$F\left(\vec{\mathbf{H}}\right) = F_{(h,k,l)} = \sum_{j=1}^{N} f_j \cdot e^{2\pi i \vec{\mathbf{H}} \cdot \vec{\mathbf{r}}_j} \; ;$$

$$F(\overline{H}) = \sum_{j=1}^{N} f_j \, e^{2\pi i \left(\frac{1}{d}\cdot\right)(nd)} \approx \sum_{j=1}^{N} f_j$$









$$\vec{h}_1 + \vec{h}_2 + \vec{h}_3 = 0$$

$\varphi_{\bar{\mathrm{H}}1}$ $\varphi_{\bar{\mathrm{H}}2}$ $\varphi_{\bar{\mathrm{H}}3}$ $\bar{H}1 + \overline{H}\,2 + \overline{H}\,3 = 0$

$\varphi_{\bar{\mathrm{H}}4}$ $\varphi_{\bar{\mathrm{H}}5}$ $\bar{H}1 + \overline{H}\,4 + \overline{H}\,5 = 0$

. . .

. . .

. . .

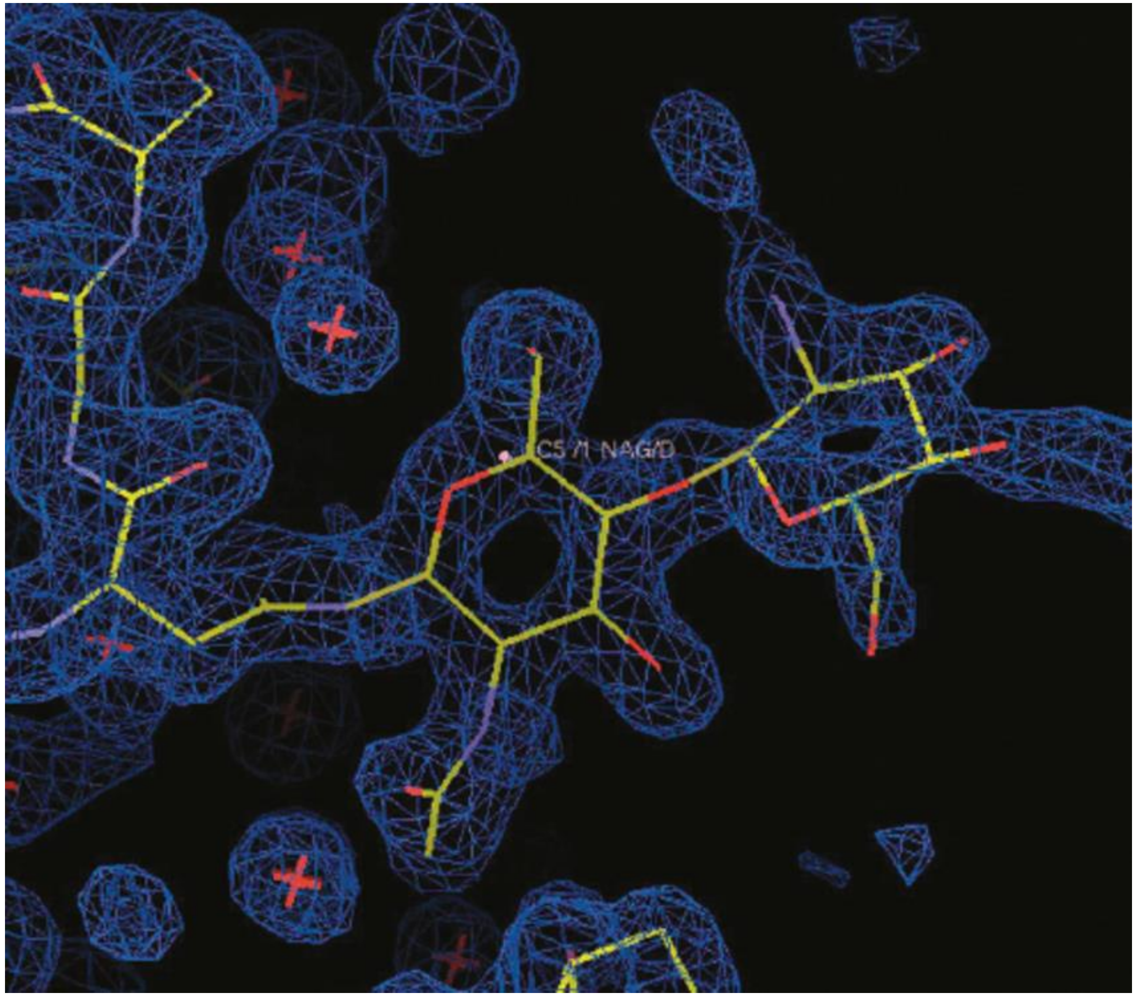
$\varphi_{\bar{\mathrm{H}}n1}$ $\varphi_{\bar{\mathrm{H}}n2}$ $\bar{H}1 + \overline{H}\,4 + \overline{H}\,5 = 0$

https://www-structmed.cimr.cam.ac.uk/Course/Fourier/Fourier.html

Jerome Karle

Herbert A. Hauptman

Nobel price in Chemistry
1985



$$\rho(XYZ) = \frac{1}{V_c} \sum_{\text{all } h,k,l}\sum\sum |F| \cos\left[2\pi(hX + kY + lZ) - \alpha\right].$$

….Linear fit

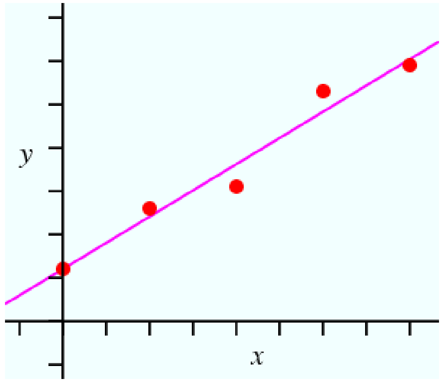


Figure B

$$y = m\,x + c$$

….non Linear fit

$$M = \sum w(|F_o| - |F_c|)^2$$

$$f(x + \Delta x) = f(x) + \Delta x \frac{\mathrm{d}f(x)}{\mathrm{d}x} + \frac{(\Delta x)^2}{2!}\frac{\mathrm{d}^2 f(x)}{\mathrm{d}x^2} + \frac{(\Delta x)^3}{3!}\frac{\mathrm{d}^3 f(x)}{\mathrm{d}x^3} + \ldots$$

Birkbeck College, University of London.

During the integration of the reflections (peaks), the intensities are determined by $\mathbf{I} = \mathbf{I}_{\mathbf{reflection}} - \mathbf{I}_{\mathbf{background}}$

For weak reflections the result can be negative.

Reflections with $0 > I > -3\sigma(I)$ contain useful information. ($I = 0$ is in the margin of errors for these reflections.)

Merging of Reflections – R(int)

R(int): Merging error (measure of the precision/reproducibility)

$$R_{\text{int}} = \frac{\sum \left| F_o^2 - F_o^2(mean) \right|}{\sum F_o^2}$$

Possible error sources (high R(int) value):

- Incorrect Laue group
- Bad or missing absorption correction
- Crystal decomposition
- Twinning
- Goniometer problems (covered reflections, misalignment)

Merging of Reflections – R(sigma)

R(sigma) - Measure of the signal-to-noise ratio

$$R_{sigma} = \frac{\sum \sigma(F_o^2)}{\sum F_o^2}$$

$$M = \sum w(|F_o| - |F_c|)^2$$

(The lower M, the better is the agreement of our model with the experimental data.)

$$w_{hkl} = 1/[\sigma^2(F_{o,hkl}^2) + (a\ P)^2 + b\ P\ ]$$

The values for a and b are chosen to give an even distribution of the variances across all groups of data based on the relative intensities

But: M increases with the number of reflections and with their intensity. It is thus structure dependent, with well diffracting structures with high redundancy giving the highest M values. We thus need a structure independent value.

$$M' = \sum w(|F_o|^2 - |F_c|^2)^2$$

R2 →

Confidence factor, Residual, R-factor:

$$wR_2 = R_w(F^2) = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$$

For statistical reasons, refinement against F^2 gives R-factors approximately twice as high than those for refinement against F. To facilitate comparison (and to increase acceptance of the new method) SHELXTL calculates also the R-factor based on F.

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

← **R1**

SHELXL calculates 4 confidence values:

- **wR2 (all data)**
- **wR2 (observed data, I>2σ(I))**
- **R1 (all data)**
- **R1 (observed data, I>2σ(I))**

Refinement against F^2 requires a correct weighing scheme

The weighing schemes optimised for refinement against F^2 cannot be used for the calculation of R1.

The important values are **wR2 (all data)** (since we do the refinement with all data) and **R1 (observed data)**, for comparison with the old method.

	Good	Acceptable	Problematic	Really problematic
R1	< 5%	< 7%	>10%	>15%
wR2	< 12%	< 20%	>25% (ou > 2*R1)	>35%
S	0.9-1.2	0.8-1.5	<0.8 ou >2	<0.6 ou >4

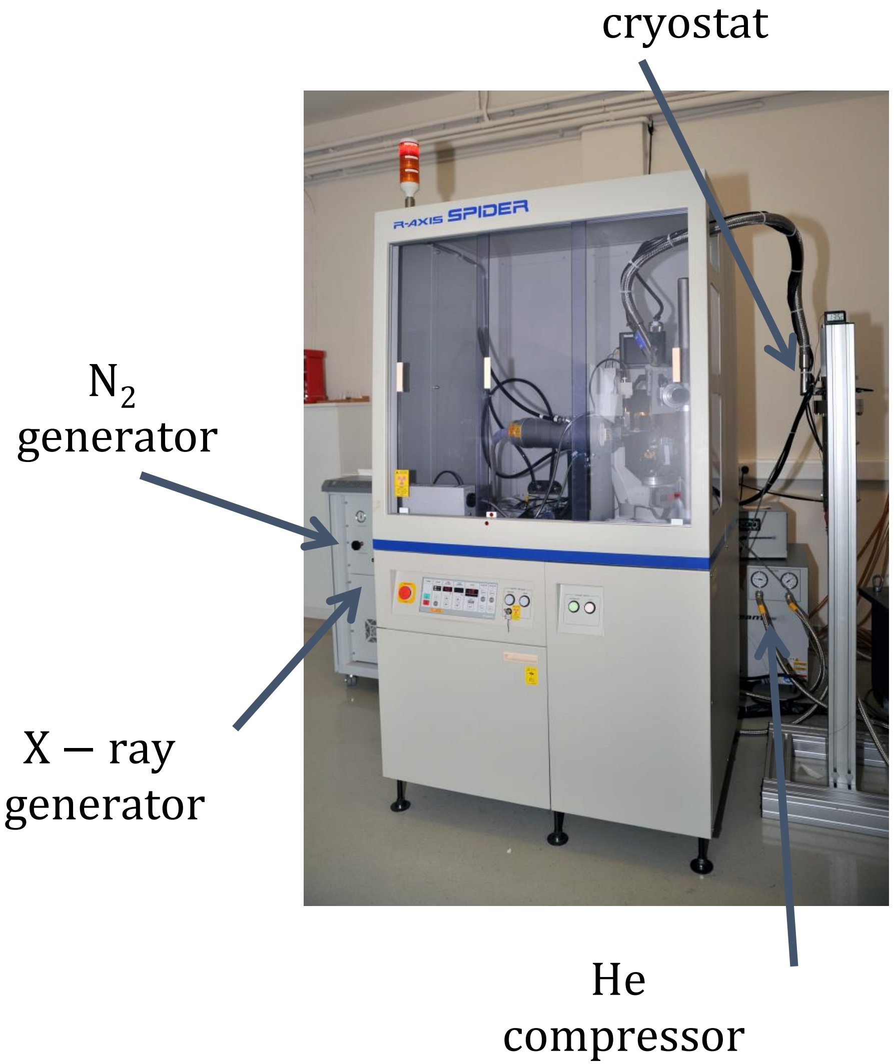
Goodness-of-Fit - S

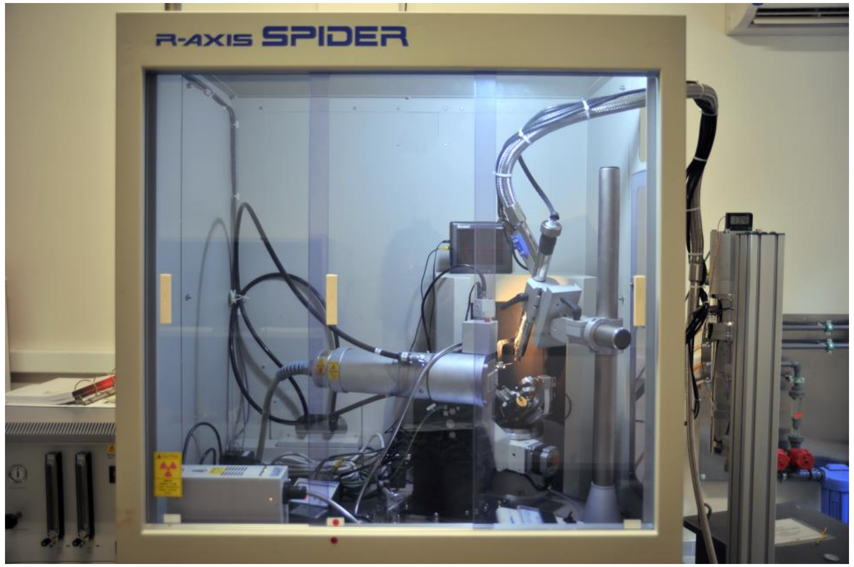
The GoF or GooF is another value which describes the quality of our model:

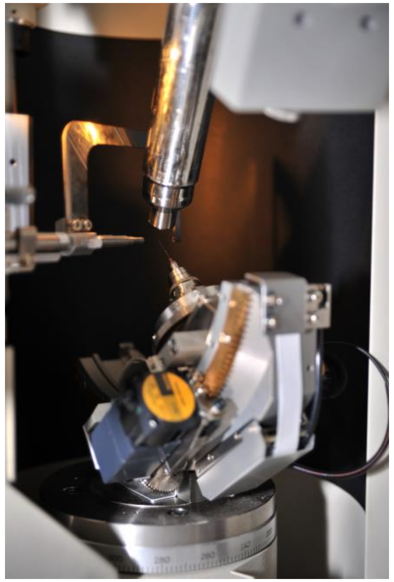
$$GooF = S = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{N_{Ref.} - N_{Par.}}}$$

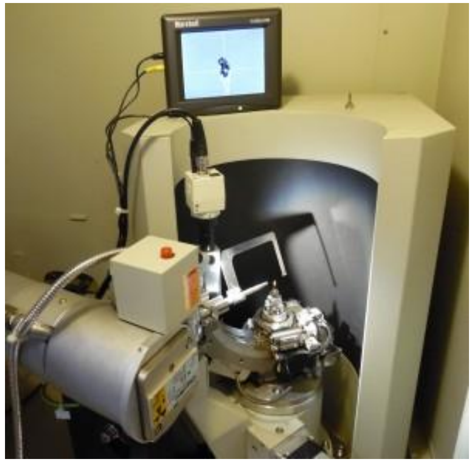
$N_{Ref.}$: number of independent reflections, $N_{Par.}$: number of parameters

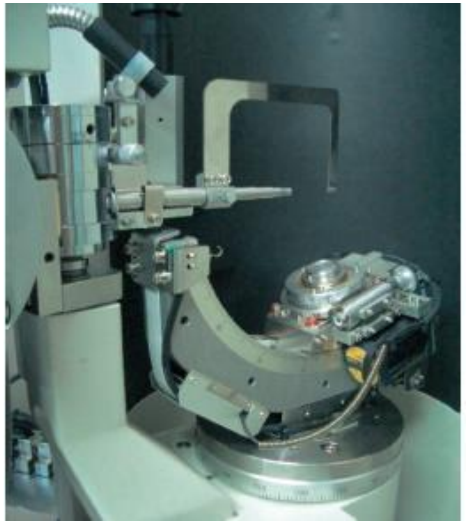
S should be around 1 for a good structure
- S > 1: bad model or bad data/parameter ratio
- S < 1: model is better than the data - problems with the absorption correction, outlier reflections at low resolution

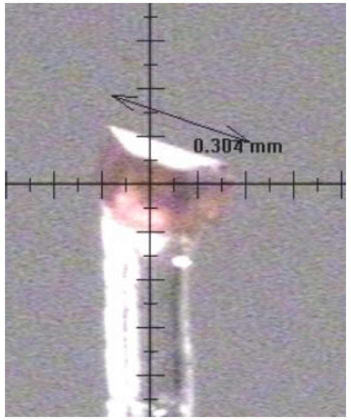

cryostat
N_2 generator
X – ray generator
He compressor
R-AXIS SPIDER

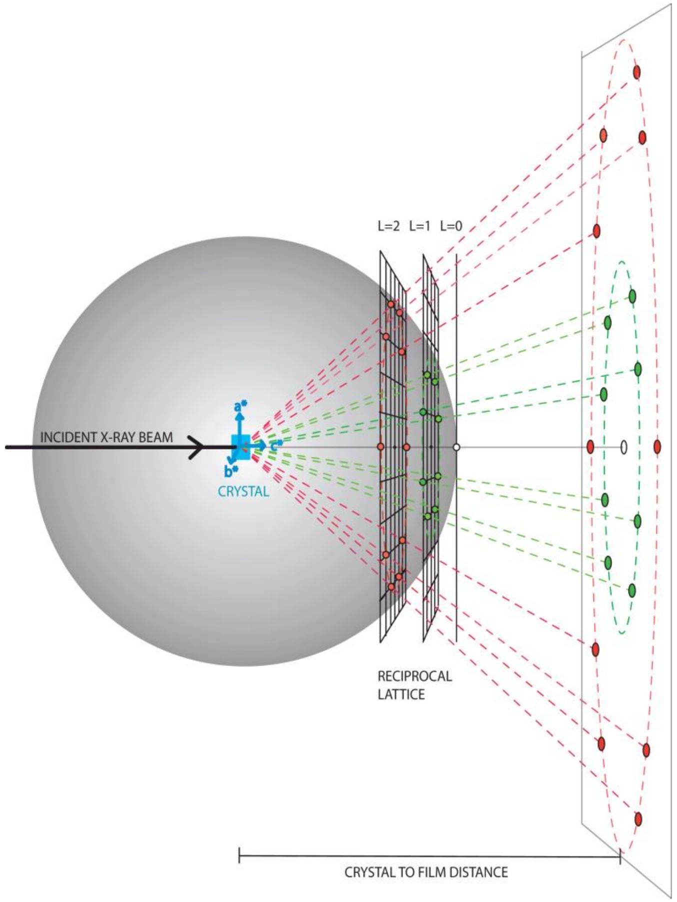

R-AXIS SPIDER



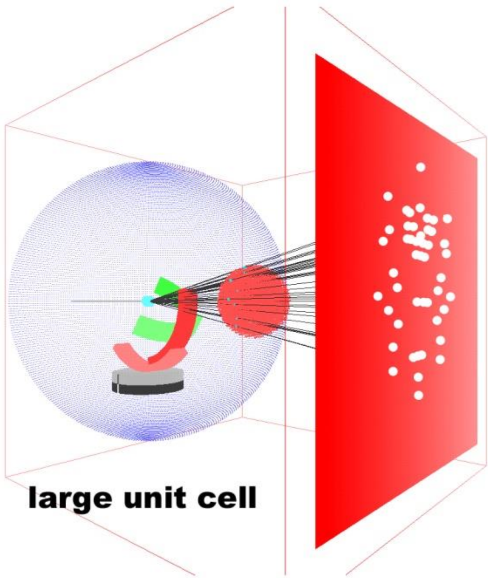


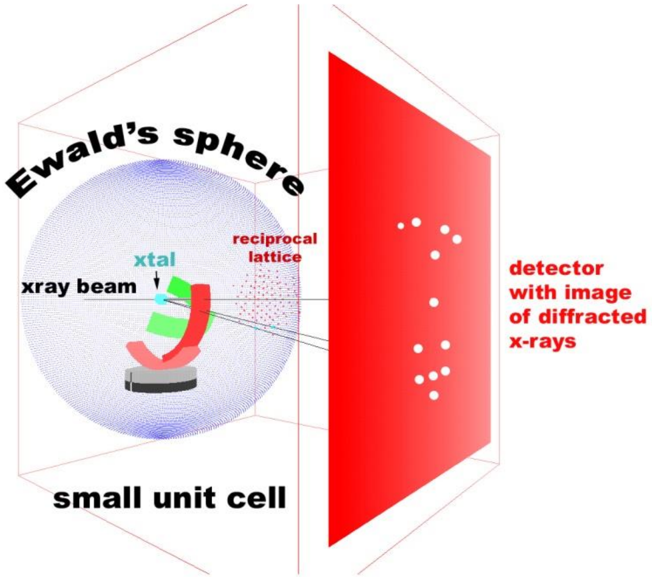



0.304 mm


INCIDENT X-RAY BEAM
CRYSTAL
L=2 L=1 L=0
RECIPROCAL LATTICE
CRYSTAL TO FILM DISTANCE
0

OSCILLATION ANGLE

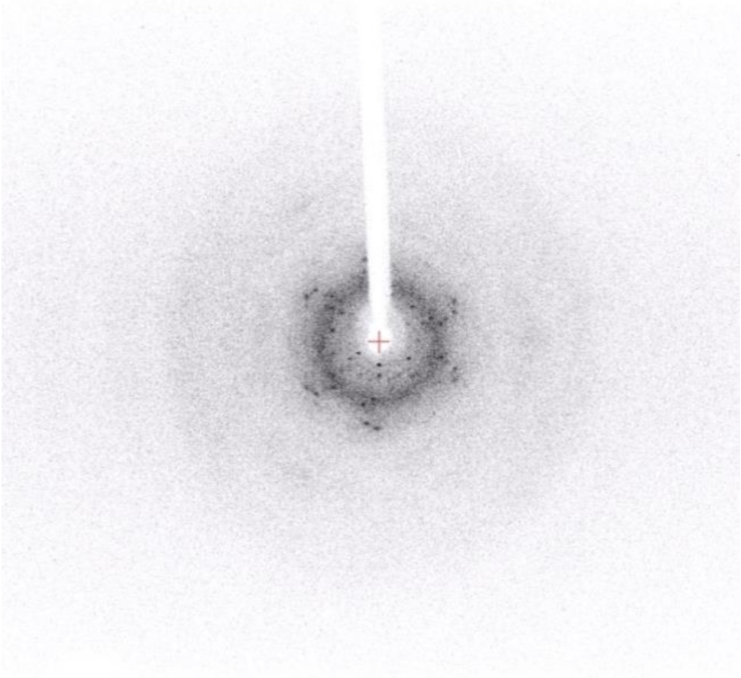


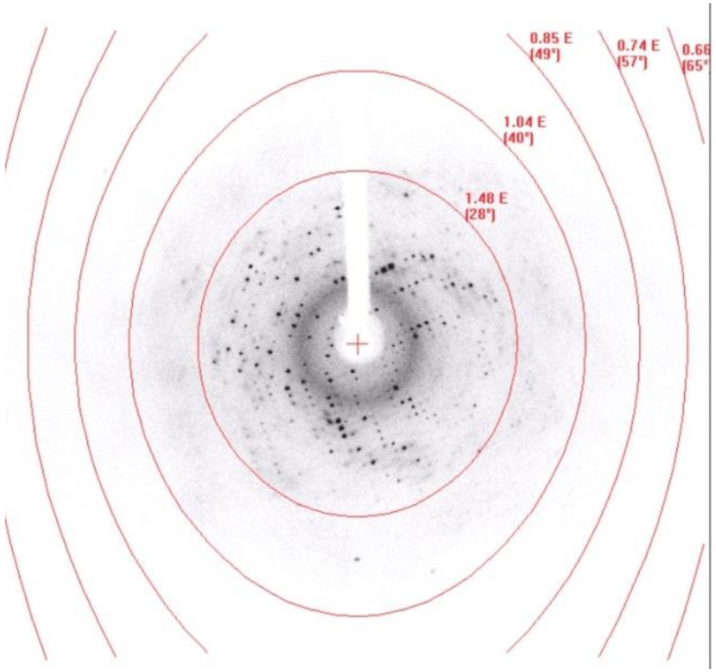


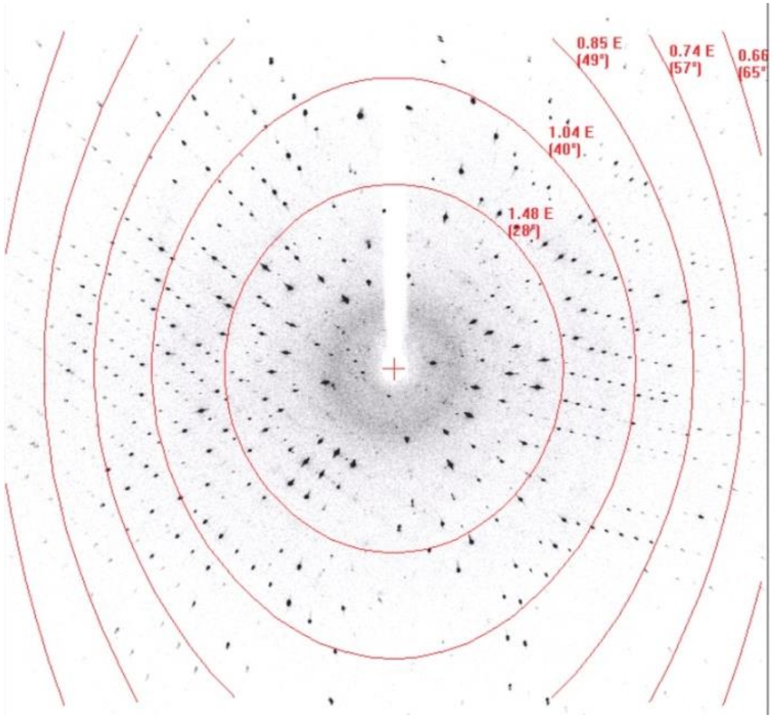
fewer degrees oscillation — **more degrees oscillation**

+ less risk of spot overlap
- requires more exposures, time consuming
+ more accurate intensity measurements

more risk of spot overlap -
requires fewer exposures, quicker collection +
less accurate measurements -




0.85 E
(49°)
0.74 E
(57°)
0.66
1.04 E
(40°)
1.48 E
(28°)


0.85 E
(49°)
0.74 E
(57°)
0.66
1.04 E
(40°)
1.48 E
(28°)