NanED Workshop II – Imperfect crystals, complementarity with XRPD,
Intellectual properties and patent in Science
Mainz, December 6.-8, 2022

XRPD structure solution and refinement strategies

R. E. Dinnebier

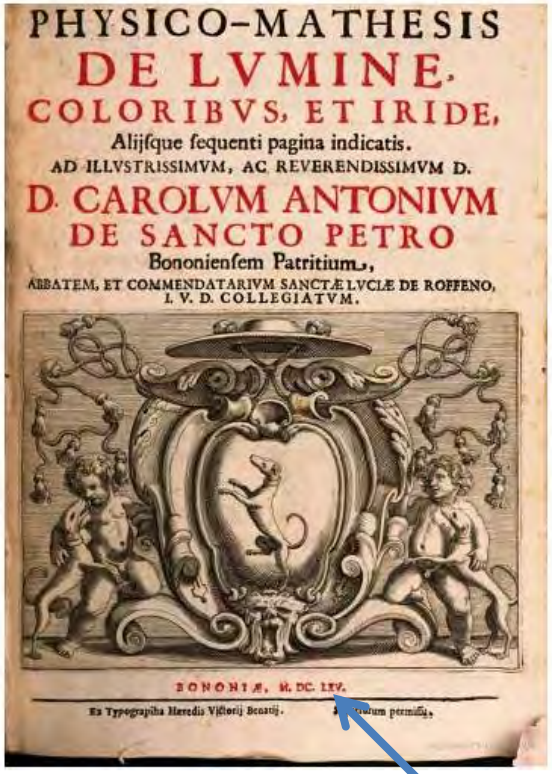
Max-Planck Institute for Solid State Research, Stuttgart, Germany

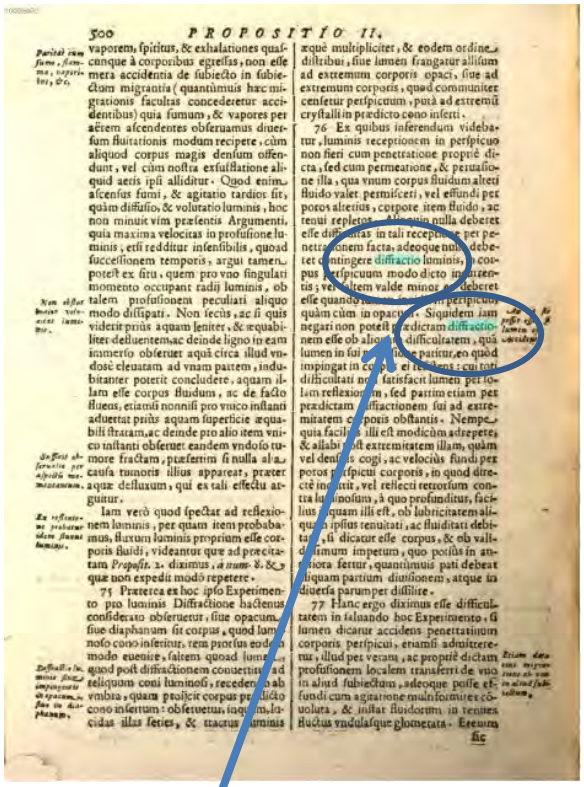


Slides of Wikipedia and other web sources are used in this lecture

Basics of diffractio(n)




PHYSICO-MATHESIS
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COLORIBVS, ET IRIDE,
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D. CAROLVM ANTONIVM
DE SANCTO PETRO
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I. V. D. COLLEGIATVM.
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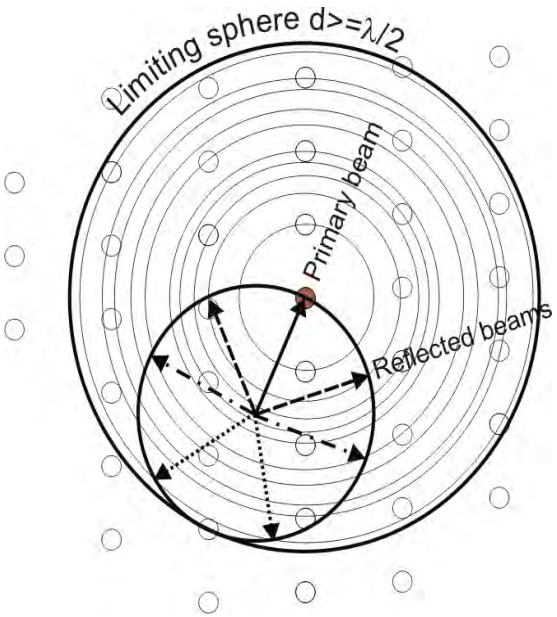

500 PROPOSITIO II.
diffractio

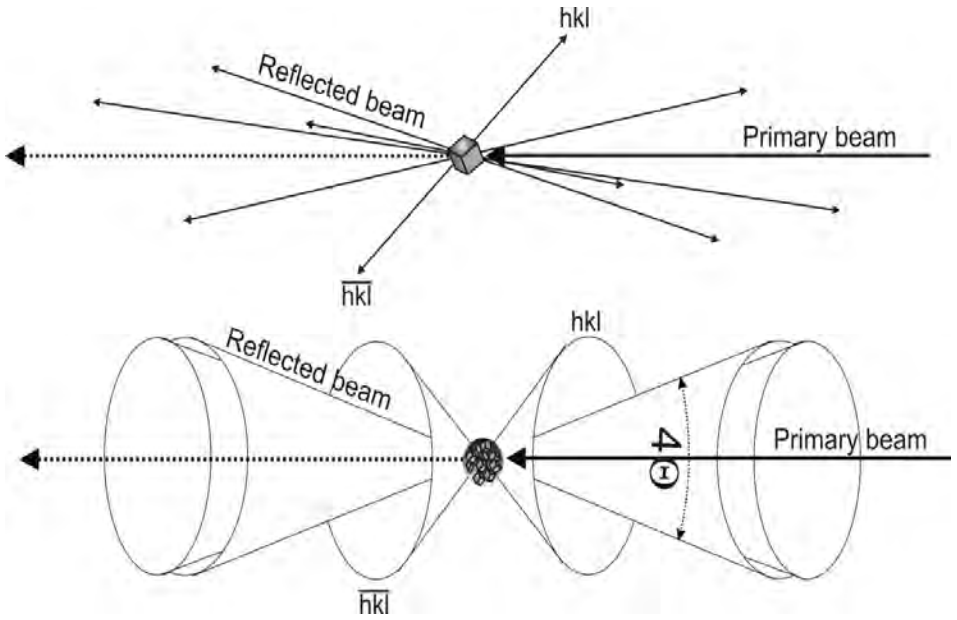
1665

diffractio

Francesco Maria Grimaldi (1618- 1663).
Italian jesuit, physisist, mathematician, and astronomer from Bologna.

Powder diffraction in reciprocal & real space



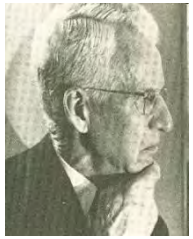




Peter J.W. Debye



Paul Scherrer



Albert W. Hull

About 4.8 million grains of 5 µm diameter in 1 mm^3 powder (assuming a packing density of 60%)

Debye, P.;Scherrer, P. (1916), Interferenzen an regellos orientierten Teilchen im Roentgenlicht, Physikalische Zeitschrift 17, 277-283
Hull, A. W. (1917), A New Method of X-Ray Crystal Analysis, Phys. Rev. 10, 661 - 696

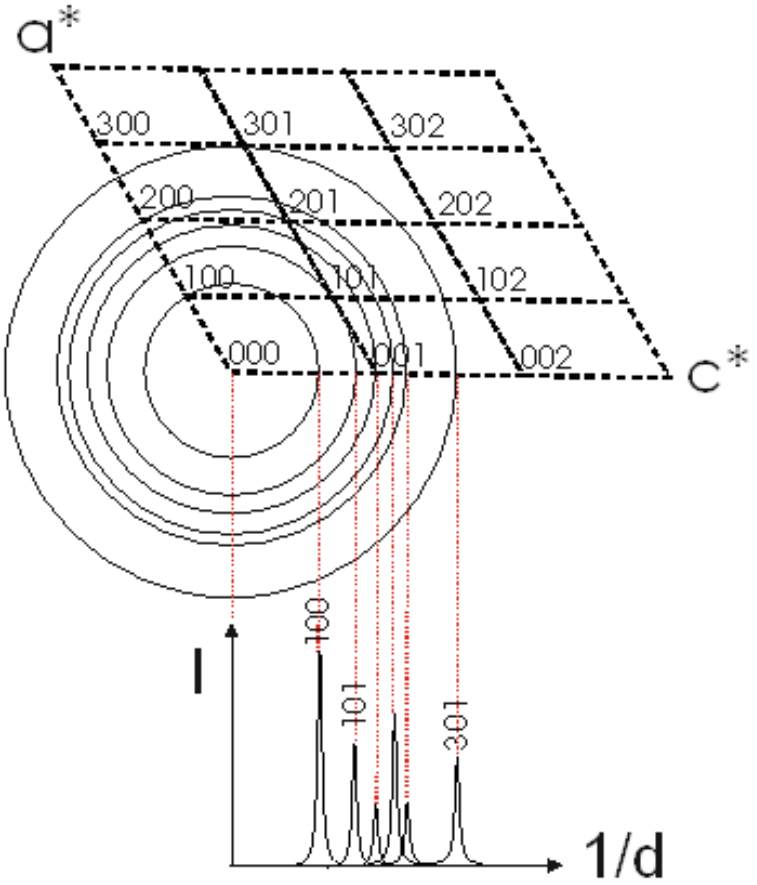
The problem of powder diffraction Summary

Powder: Single crystal reciprocal lattice is smeared into spherical shells

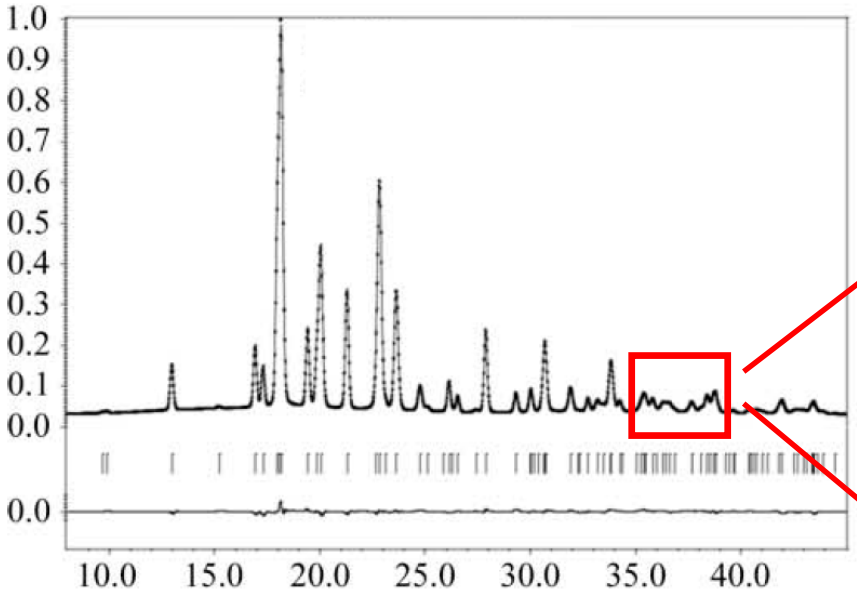
$$\mathbf{d} \Rightarrow |\mathbf{d}| = d \approx \sin\theta^{-1}$$

→Different degrees of overlap:
- systematic (e.g. 511, 333 in the cubic case and multiplicity)
- accidental (depending on lattice parameters and scattering angle)

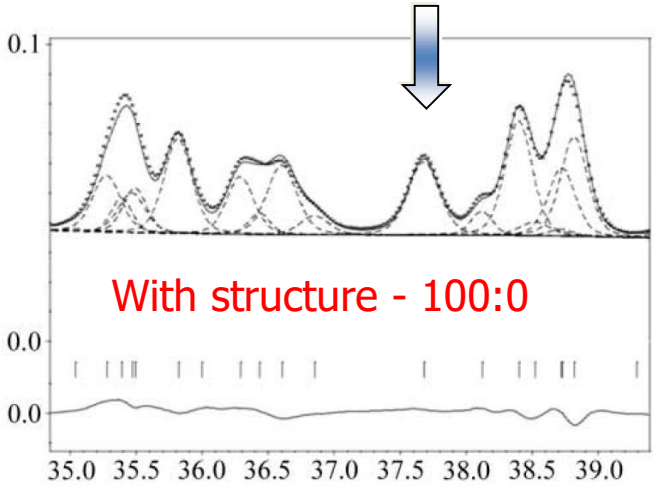
→Not only the phases of the structure factors are unknown, but also many amplitudes

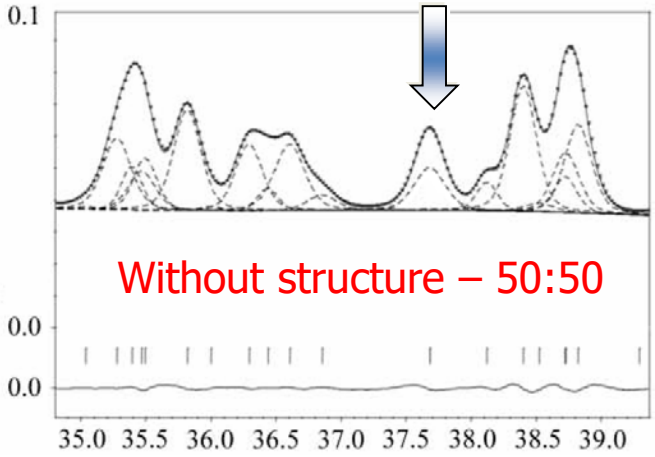


Powder diffraction: overlapping reflections

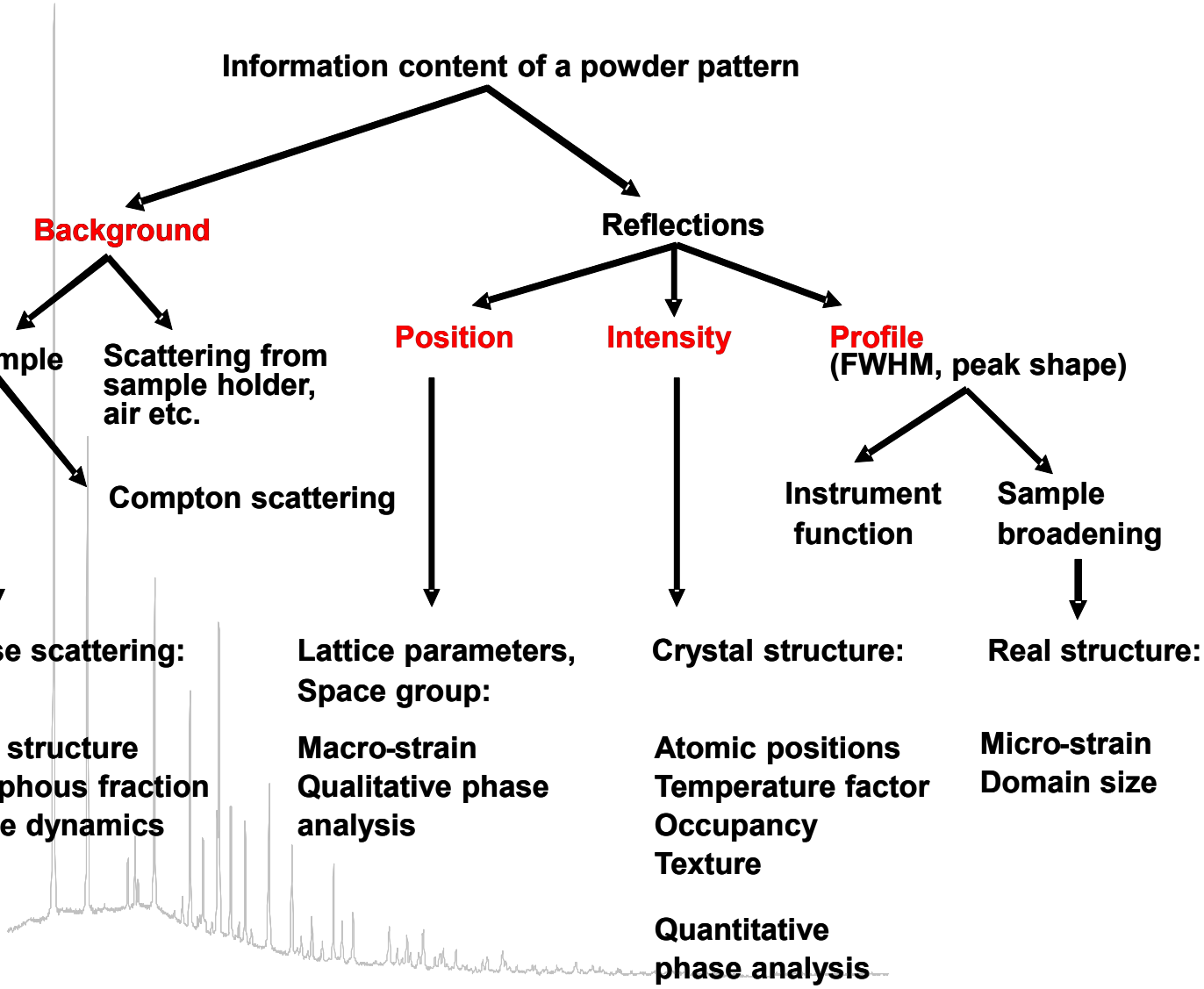


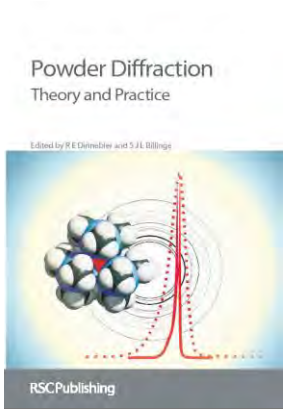
$K_2C_2O_4$





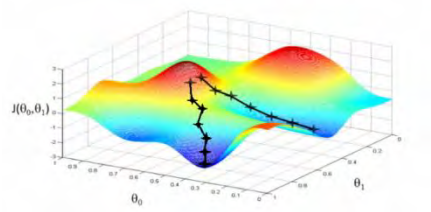
Information in a powder pattern

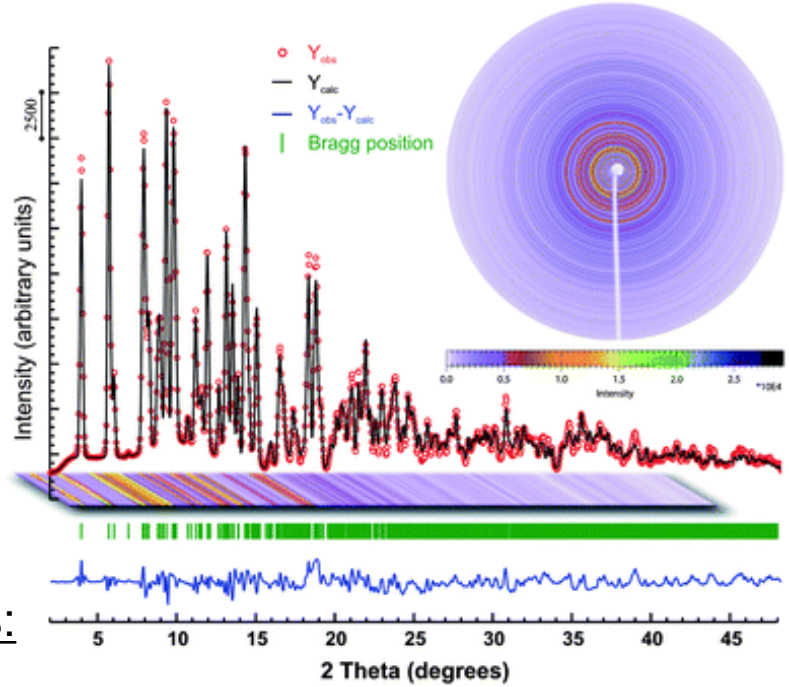


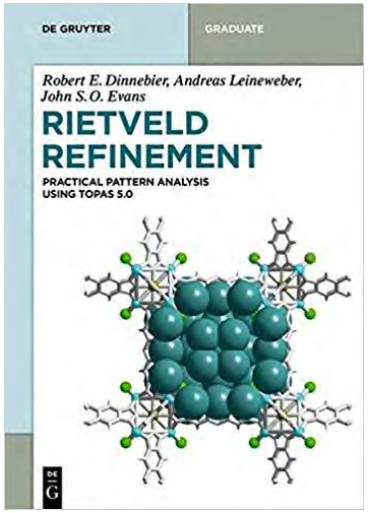


from:
Powder Diffraction, Theory & Practice, Dinnebier & Billinge, eds.,RSC, 2008

The Rietveld method, a local optimization method







<u>The famous two papers:</u>

H. M. Rietveld

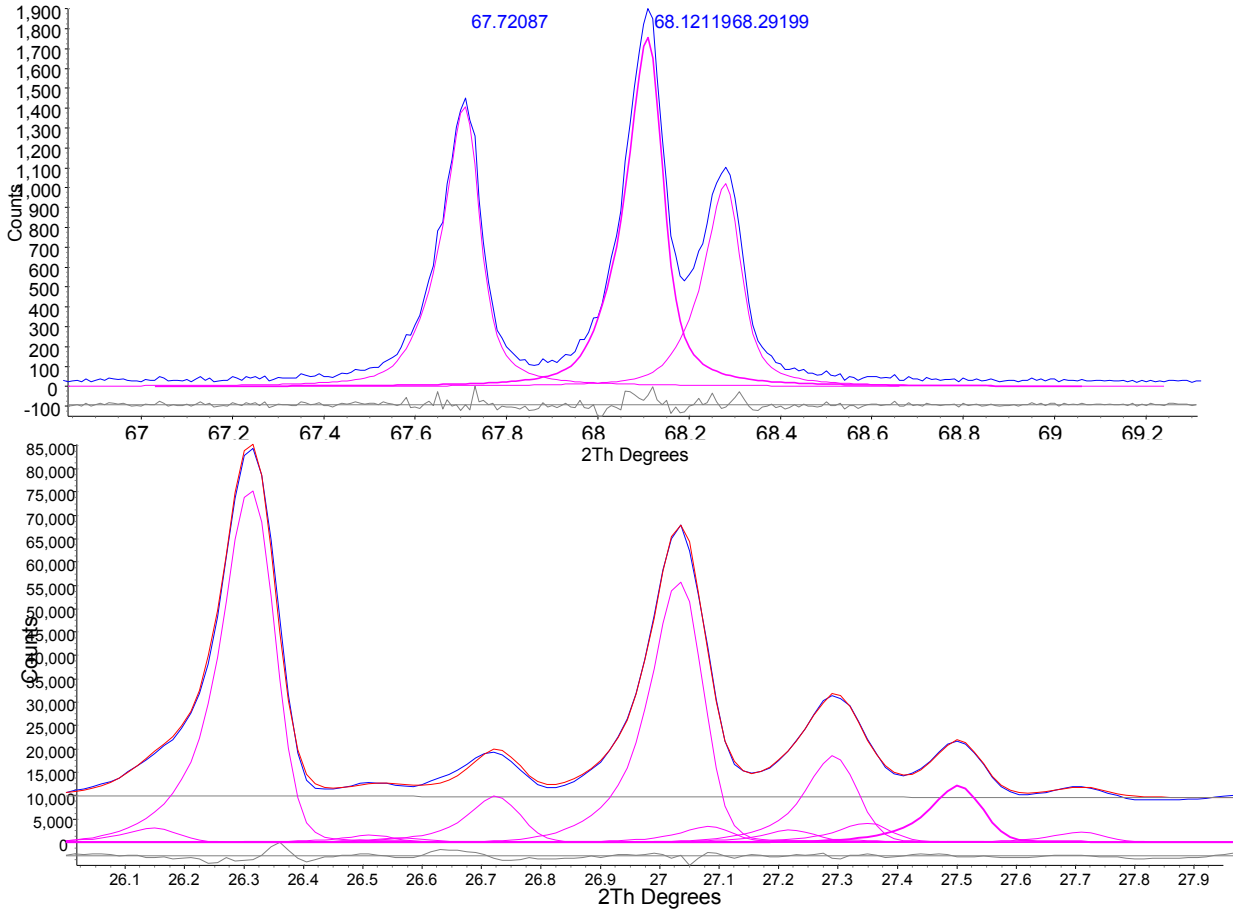
Acta Cryst. (1967). 22, 151-152, Line profiles of neutron powder-diffraction peaks for structure refinement

Appl. Cryst. (1969). 2, 65-71, A profile refinement method for nuclear and magnetic structures



First application on X-ray data: J. Appl. Cryst. (1977). 10, 7-11 Least-squares structure refinement based on profile analysis of powder film intensity data measured on an automatic microdensitometer, G. Malmros and J. O. Thomas

The overlap problem



The degree of overlap of individual reflection correlates with the uncertainty of their integrated intensities.

Rietveld‘s idea:
Modelling of the entire powder pattern while minimizing the difference to the measured powder pattern by LSQ‘s techniques takes the peak overlap intrinsically into account.

The Rietveld method: How to

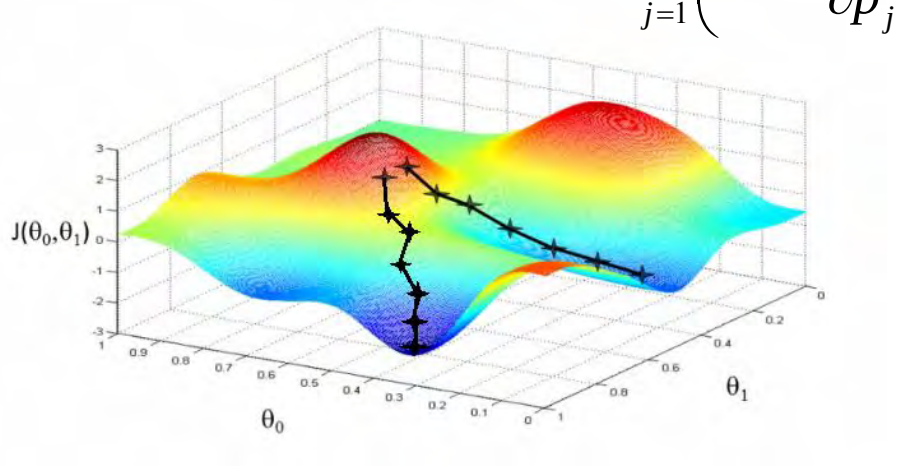
The idea of least squares

$$Min = \sum_i \left(w_i \left(y_{calc}(2\theta_i) - y_{obs}(2\theta_i) \right)^2 \right)$$

$$\sum_{i=0}^{n-1} \left(w_i \left(Yobs_i - Ycalc_i(p_1..p_m) \right) \frac{\partial Ycalc_i}{\partial p_j} \right) = 0$$

using Taylor series expansion

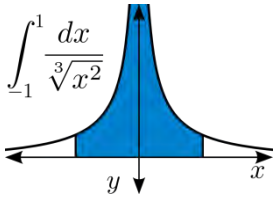
$$Ycalc_i(p_{1..m}) = Ycalc_i(p_{10..m0}) + \sum_{j=1}^{m} \left(\frac{\partial Ycalc_i(p_{1..m})}{\partial p_j} \left(p_{j0} - p_j \right) \right)$$



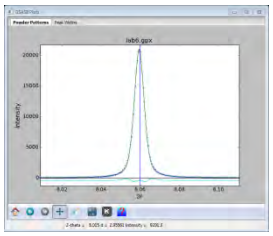
>> 100 Degrees of freedom possible (proteins !)

The Rietveld formula: 5 main contributions

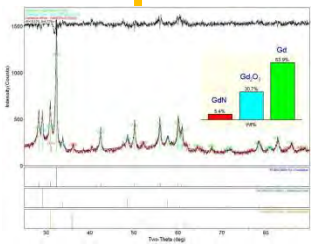
Peak intensity



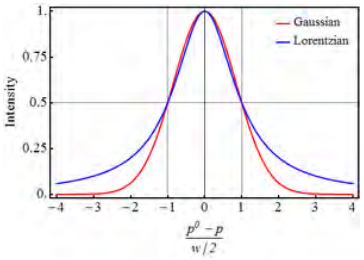
Peak position



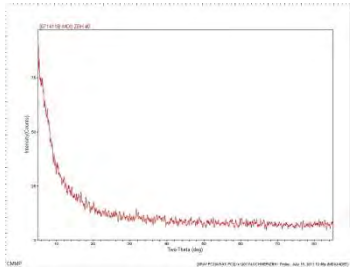
$$y_{calc}(2\theta_i) = \sum_p \left(S_p \sum_{(hkl)p} \left(\left|F_{calc}((hkl)p)\right|^2 \cdot \Phi_{(hkl)p}\left(2\theta_i - 2\theta_{(hkl)p}\right) \cdot Corr_{(hkl)p}(2\theta_i) \right) \right) + \mathrm{Bkg}(2\theta_i)$$



Scale factors



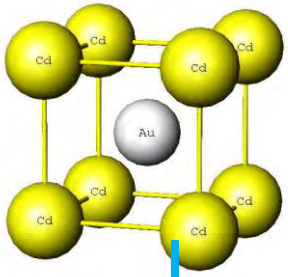
Peak profile



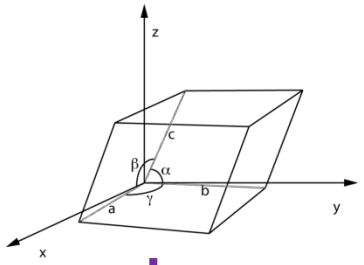
Background

The Rietveld formula: 5 models

Crystal structure



Unit cell & space group



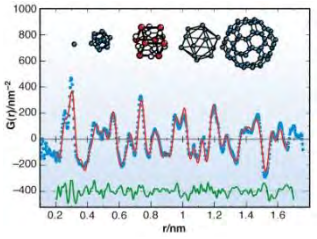
$$y_{calc}(2\theta_i) = \sum_p \left(S_p \sum_{(hkl)p} \left(|F_{calc}((hkl)p)|^2 \cdot \Phi_{(hkl)p}(2\theta_i - 2\theta_{(hkl)p}) \cdot Corr_{(hkl)p}(2\theta_i) \right) \right) + \mathrm{Bkg}(2\theta_i)$$



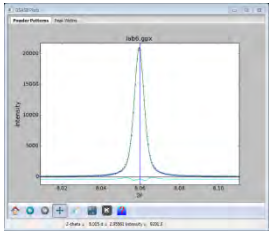
QPA



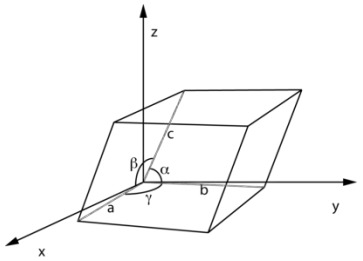
IRF & microstructure



PDF & instrument

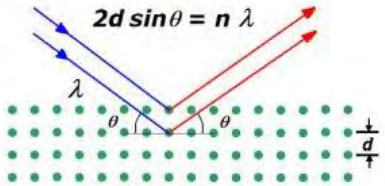


Peak position



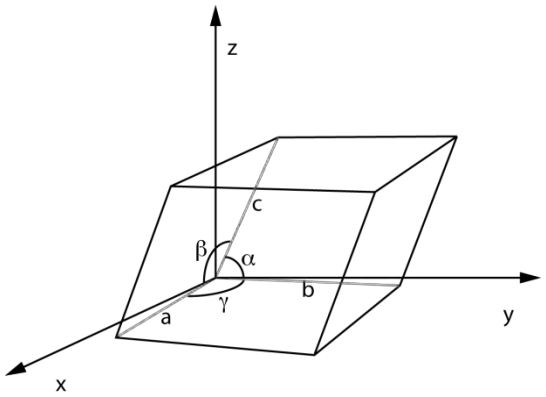
The Rietveld formula: peak position

The position of a Bragg reflection can be calculated from Bragg's equation:



$$2\theta_{hkl} = 2\arcsin\left(\frac{\lambda}{2}\frac{1}{d_{hkl}}\right) + 2\theta_{Corr}$$

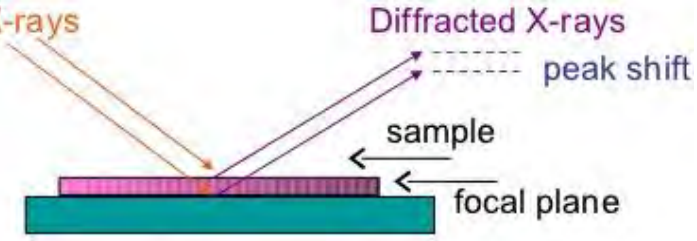
using the lattice parameters a, b, c, α, β, and γ

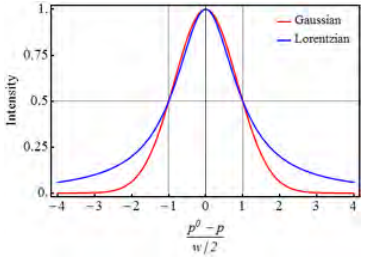


$$\frac{1}{d_{hkl}} = \frac{1}{V}\sqrt{\left[\begin{array}{c} a^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin^2\gamma + 2hkabc^2\left(\cos\alpha\cos\beta - \cos\gamma\right) \\ + 2kla^2bc\left(\cos\beta\cos\gamma - \cos\alpha\right) + 2hlab^2c\left(\cos\alpha\cos\gamma - \cos\beta\right) \end{array}\right]}$$

corrected zero shift and sample displacement:

$$2\theta_{Corr} = 2\theta_0 - 2\left(\frac{\pi}{180}\right)c\frac{\cos(\theta)}{Rs}$$



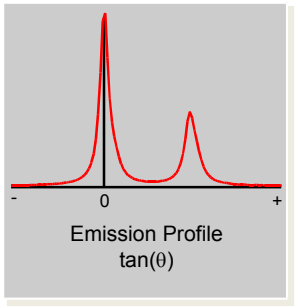


Peak profile

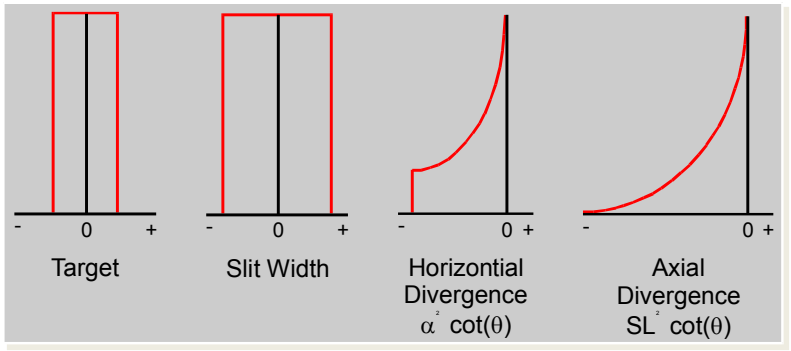


The Rietveld formula: peak profile

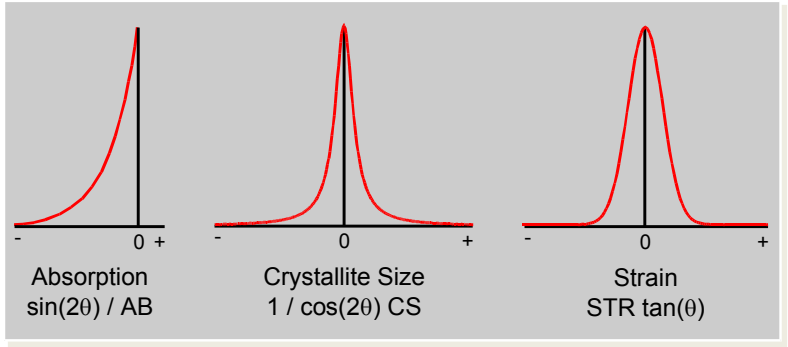
W

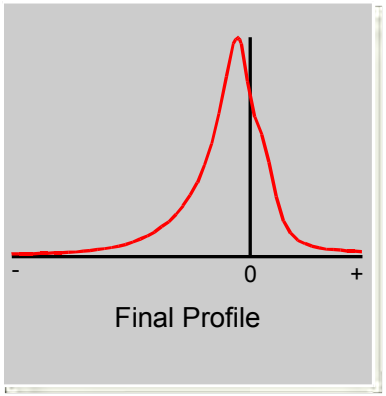


G



S





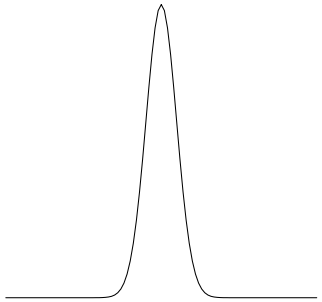
$$\mathbf{Y(2\theta) = (W \otimes G) \otimes S}$$

H. P. Klug, L. E. Alexander (1974), „X-ray diffraction procedures for polycrystalline and amorphous materials". John Wiley and Sons, New York.

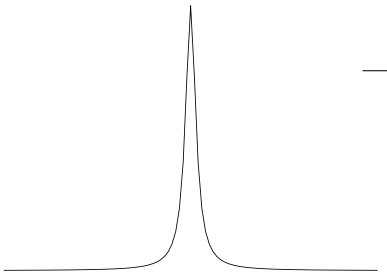
Cheary, R. W., Cline, J. P., Coelho, A. A. (2004) Fundamental Parameters Line Profile Fitting in Laboratory Diffractometers. 109(1).

Selected components of a peak function

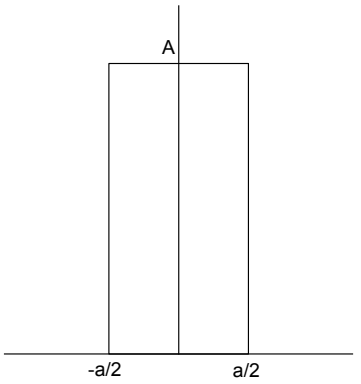
$$G(2\theta - 2\theta_{hkl}) = \left(\frac{2\sqrt{\ln(2)/\pi}}{fwhm}\right)\exp\left(\frac{-3\ln(2)(2\theta - 2\theta_{hkl})^2}{fwhm^2}\right)$$



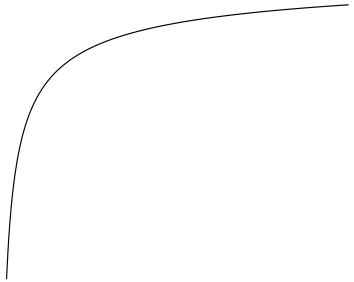
$$L(2\theta - 2\theta_{hkl}) = \left(\frac{2/\pi}{fwhm}\right)/\left(\frac{1+4(2\theta - 2\theta_{hkl})^2}{fwhm^2}\right)$$



$$H(2\theta - 2\theta_{hkl}) = \begin{cases} A \text{ for } -\frac{a}{2} < (2\theta - 2\theta_{hkl}) < \frac{a}{2} \\ 0 \text{ for } (2\theta - 2\theta_{hkl}) \le -\frac{a}{2} \text{ and } (2\theta - 2\theta_{hkl}) \ge -\frac{a}{2} \end{cases}$$

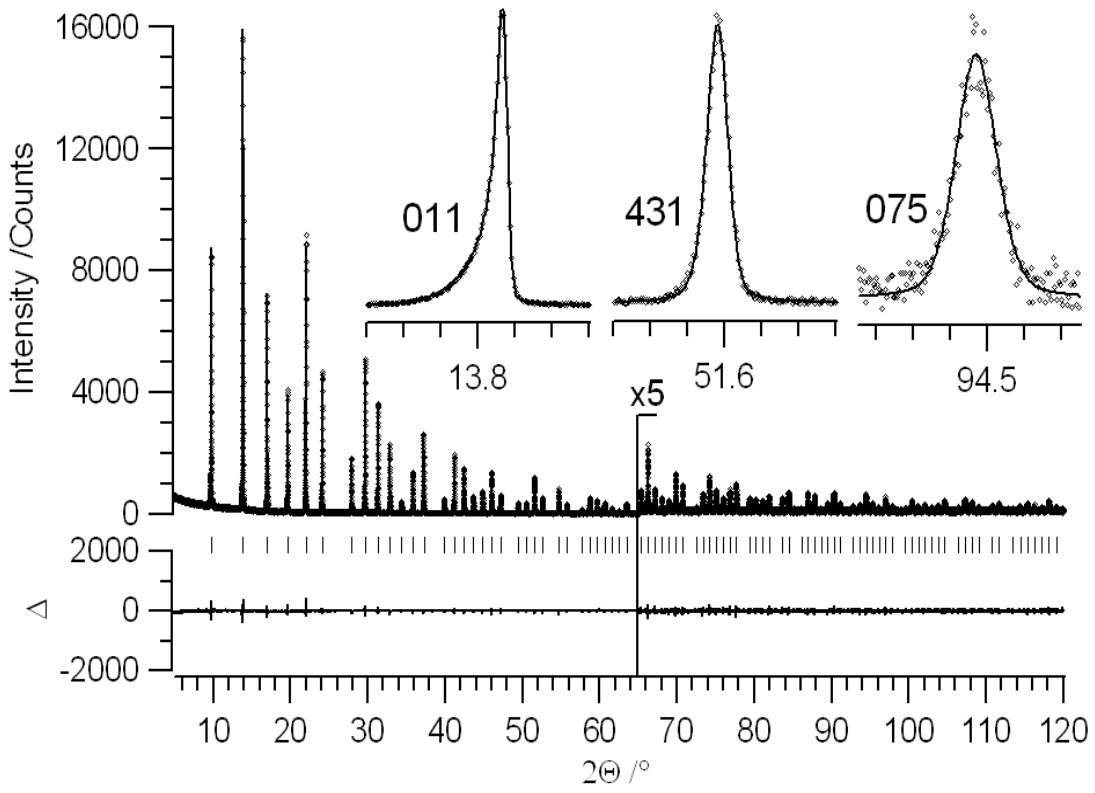


$$C(2\theta - 2\theta_{hkl}) = \left(1 - \sqrt{\left|\frac{\varepsilon_m}{(2\theta - 2\theta_{hkl})}\right|}\right) \text{ for } (2\theta - 2\theta_{hkl}) = 0..\varepsilon_m$$

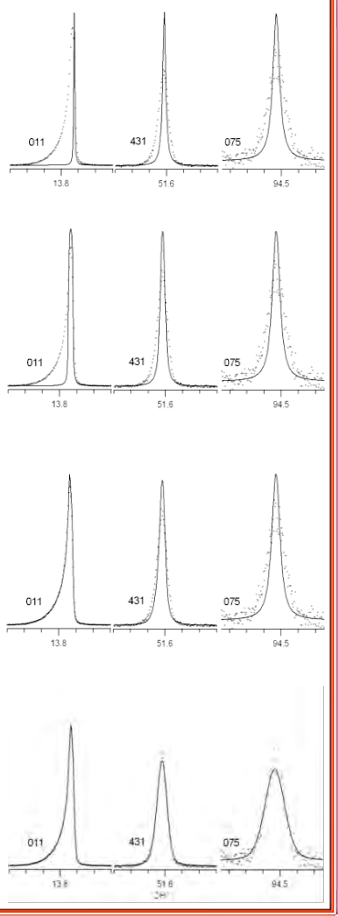


The Rietveld formula: peak profile

LaB_6 line profile standard (Mo-$K_{\alpha 1}$, Ge(220), Lynx-Eye)

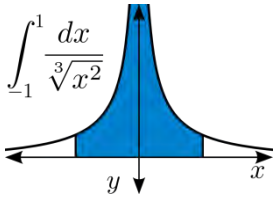


- wavelengths distribution (Lorentzian)
- Receiving slit width (Hat)
- Source, sample, slit lengths (exp.)
- Gaussian strain

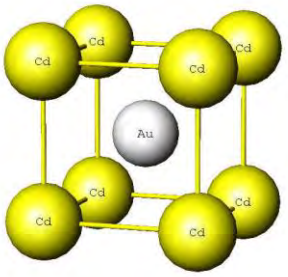


Resolution in 2 θ < 0.04° 2 θ
Minimum d-spacing < 0.4 Å

Only 4 fundamental parameters

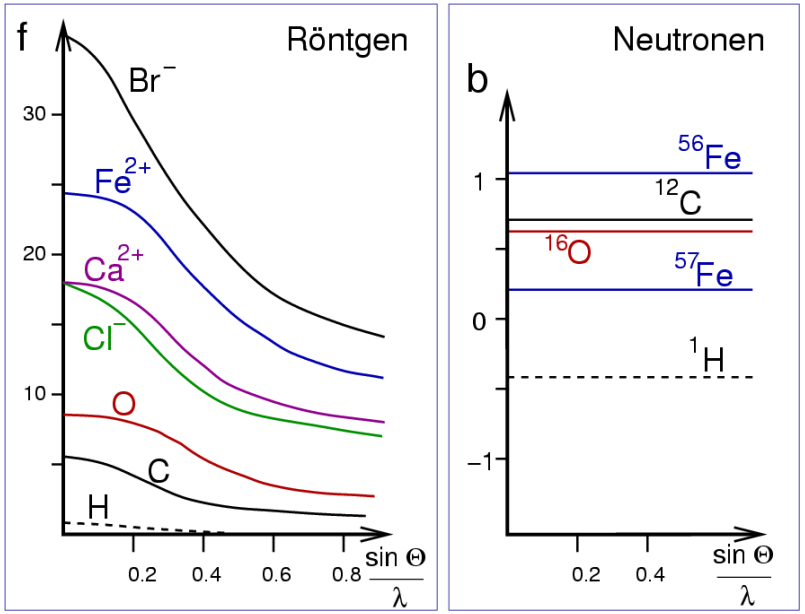


Peak intensity

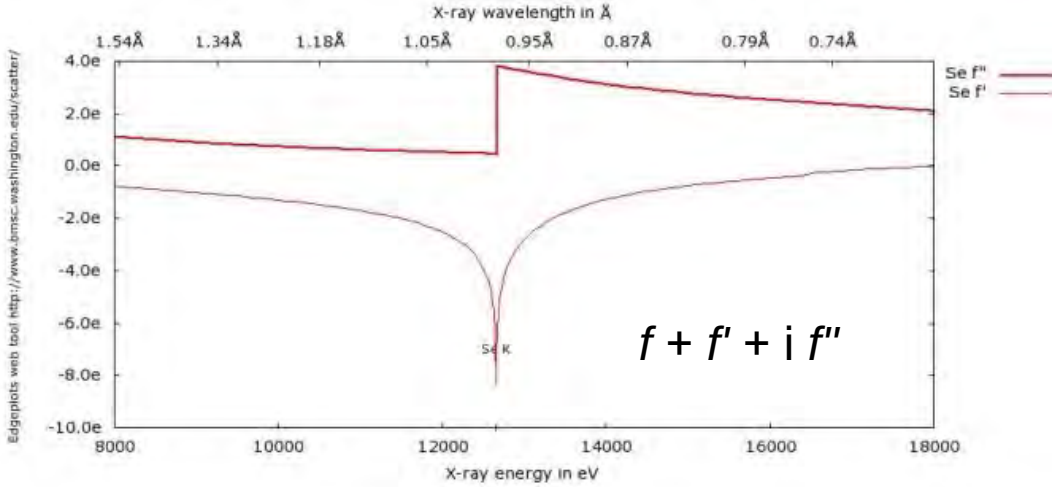


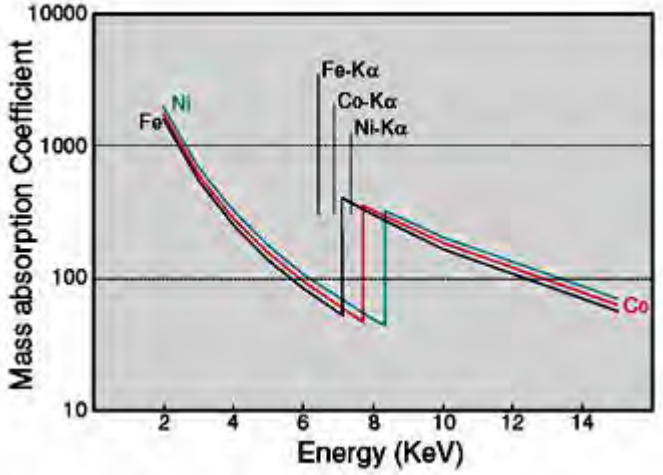
The Rietveld formula: intensity

Atomic form factor



Anomalous dispersion



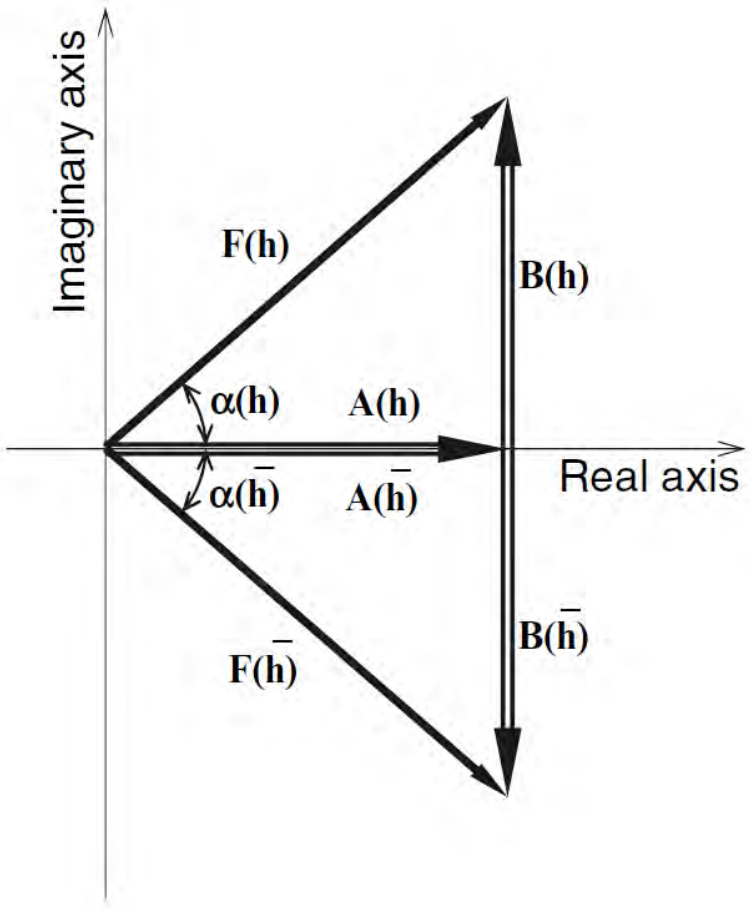


The structure factor

$$\left|F_{calc}(hkl)\right|^2 = \left|A(hkl)\right|^2 + \left|B(hkl)\right|^2 = \left[\left|A(hkl)\right| + i\left|B(hkl)\right|\right]\left[\left|A(hkl)\right| - i\left|B(hkl)\right|\right]$$

$$A(hkl) = \sum_j \left(f_j(2\theta_{hkl}) \cos\left[2\pi\left(hx_j + ky_j + lz_j\right)\right]\right)$$

$$B(hkl) = \sum_j \left(f_j(2\theta_{hkl}) \sin\left[2\pi\left(hx_j + ky_j + lz_j\right)\right]\right)$$

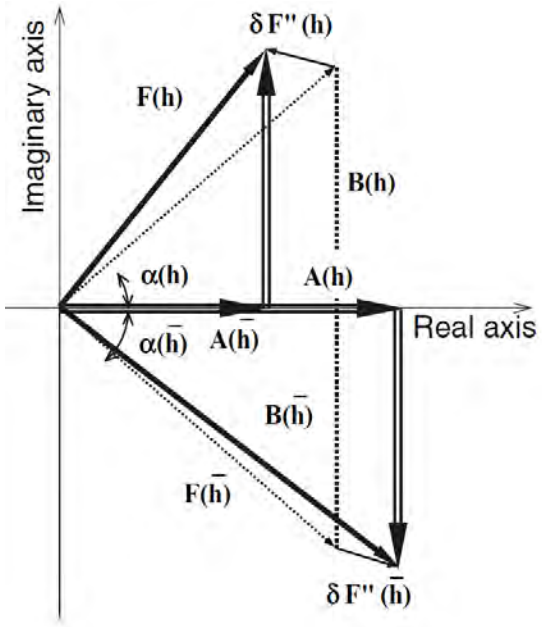


Anomalous dispersion

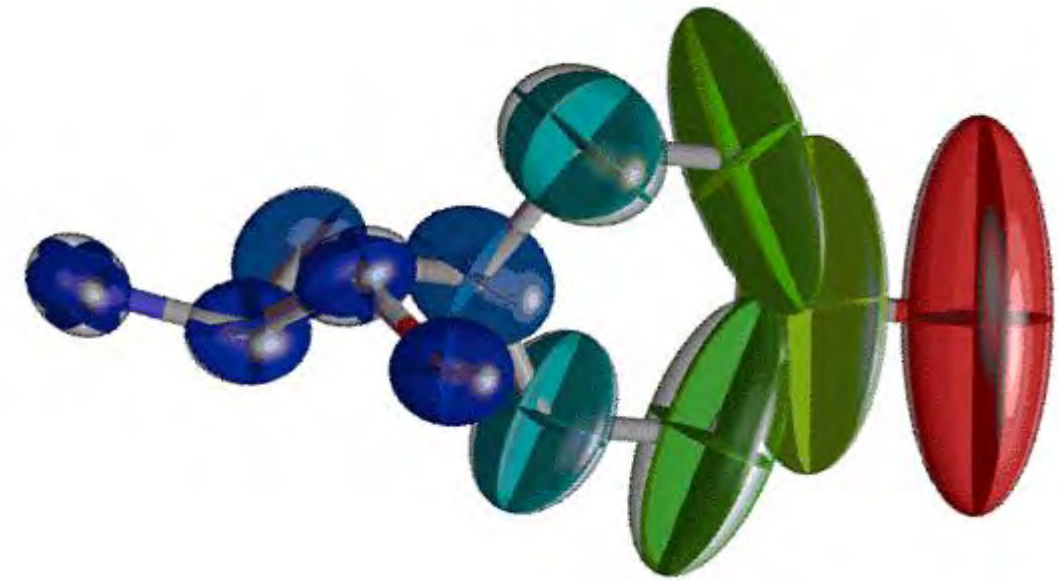
$$f_j(2\theta_{hkl}) = f_j^0(2\theta_{hkl}) + \Delta f_j' + i\Delta f_j''$$

$$A(hkl) = \sum_j \left(\left(f_j(2\theta_{hkl}) + \Delta f_j' \right) \cos\left[2\pi \left(hx_j + ky_j + lz_j \right) \right] \right) - \sum_j \left(\Delta f_j'' \sin\left[2\pi \left(hx_j + ky_j + lz_j \right) \right] \right)$$

$$B(hkl) = \sum_j \left(\left(f_j(2\theta_{hkl}) + \Delta f_j' \right) \sin\left[2\pi \left(hx_j + ky_j + lz_j \right) \right] \right) + \sum_j \left(\Delta f_j'' \cos\left[2\pi \left(hx_j + ky_j + lz_j \right) \right] \right)$$



Displacement parameter



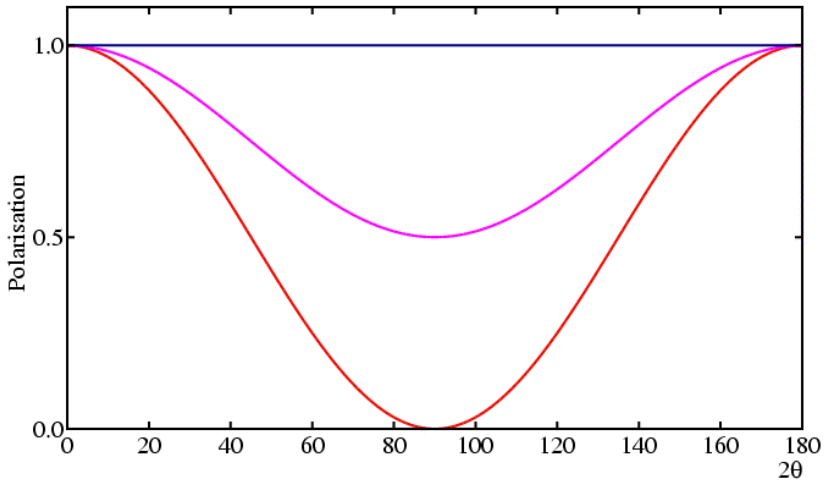
$$t_j(2\theta_{hkl}) = \exp\left(-B_j \frac{\sin^2\theta_{hkl}}{\lambda}\right)$$

$$B_j = 8\pi^2\left(u^2\right)_j$$ in [Å^2]

$$B_{ij} = \begin{pmatrix} B_{11} & B_{12} & B_{13} \\ B_{21} & B_{22} & B_{23} \\ B_{31} & B_{32} & B_{33} \end{pmatrix}$$

Selected correction functions in powder diffraction

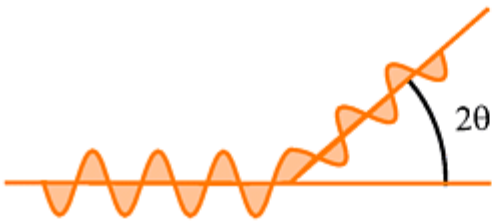
Polarization factor

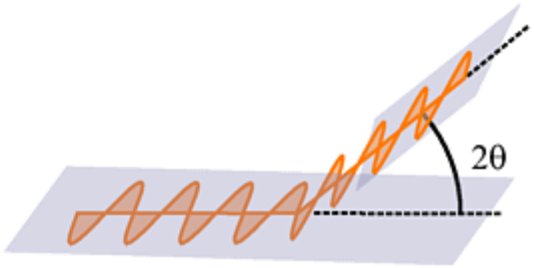


Case (1): Polarisation in plane of scattering, $P = \cos^2 2\theta$

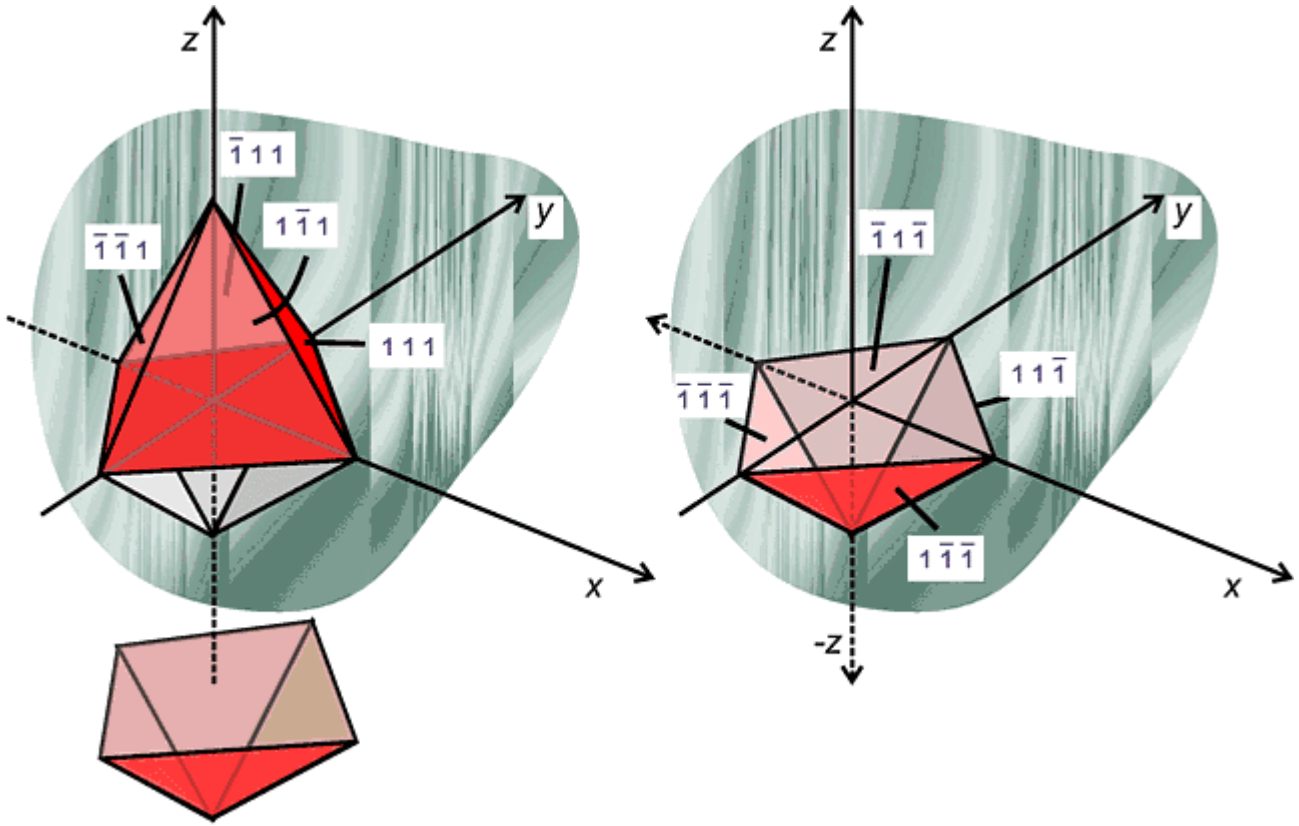
Case (2): Polarisation perpendicular to plane of scattering, $P = 1$

Case (3): Unpolarised X-rays, $P = (1 + \cos^2 2\theta)/2$



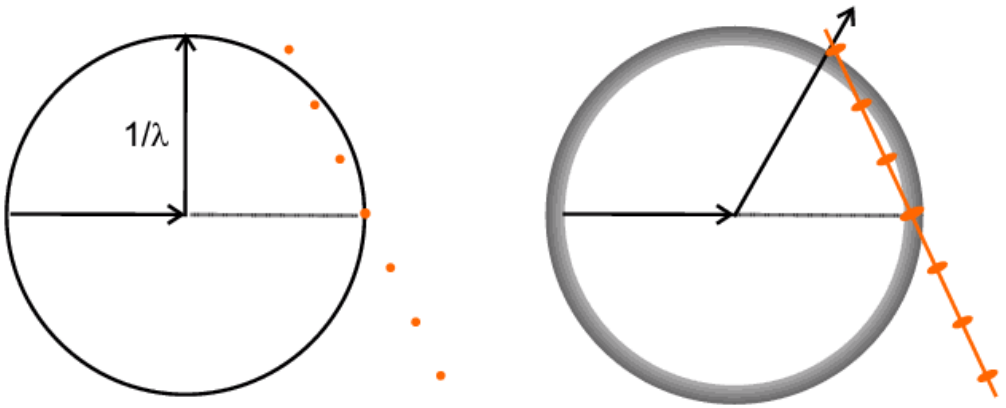


Multiplicity

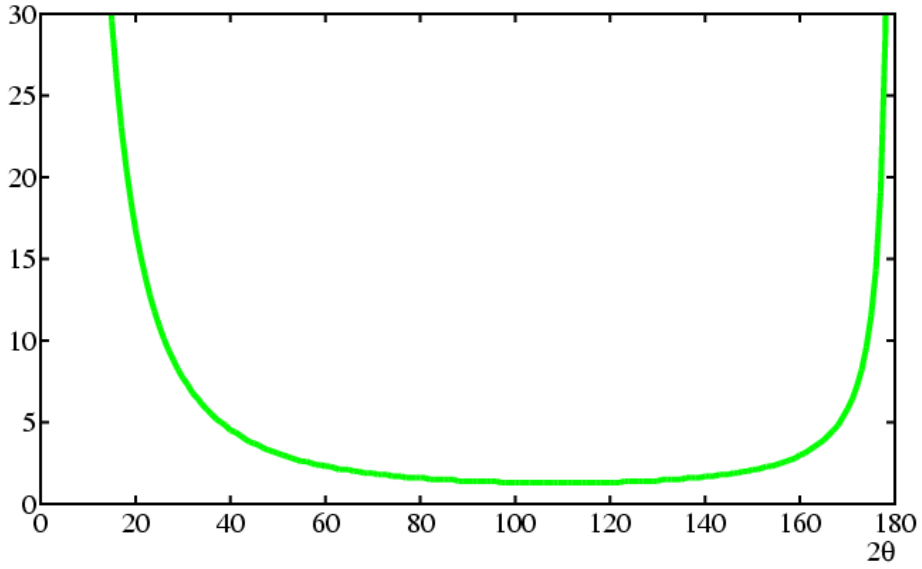


$$\mathbf{d} \Rightarrow |\mathbf{d}| \quad \mathrm{M} = 8\,(\text{faces of an octahedron})$$

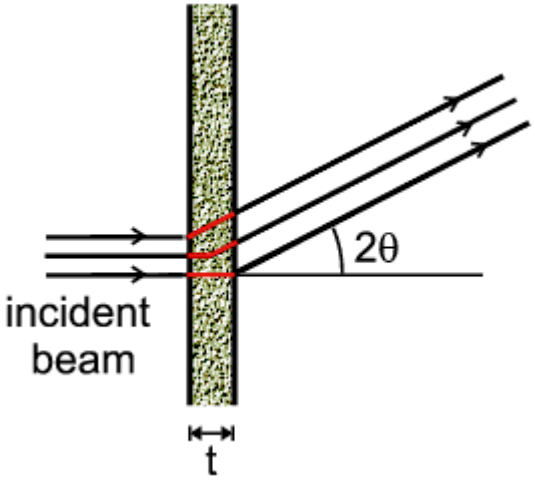
Lorentz factor

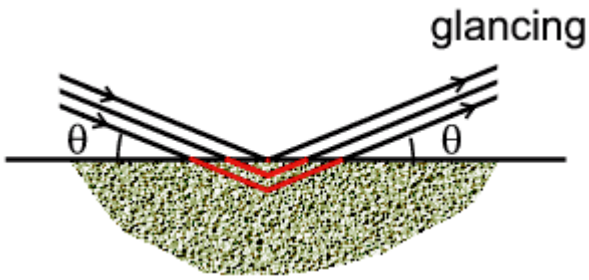


$L = c / (\sin\theta \sin 2\theta)$

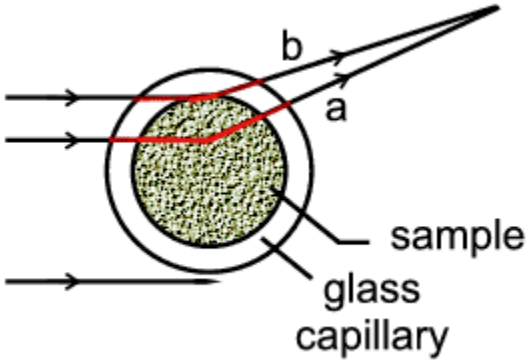


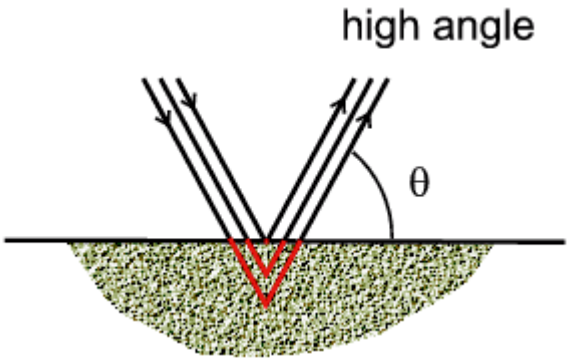
Absorption correction



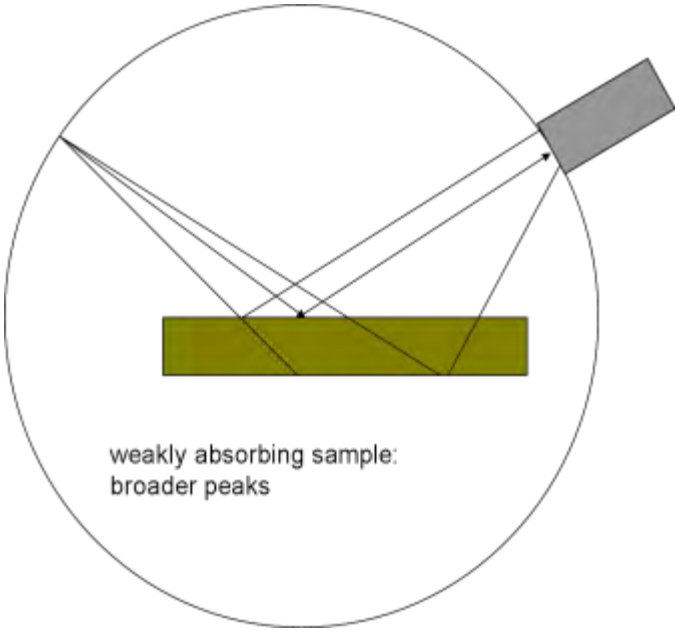


$$I = I_0 e^{-\mu\rho t}$$





Transparancy effect



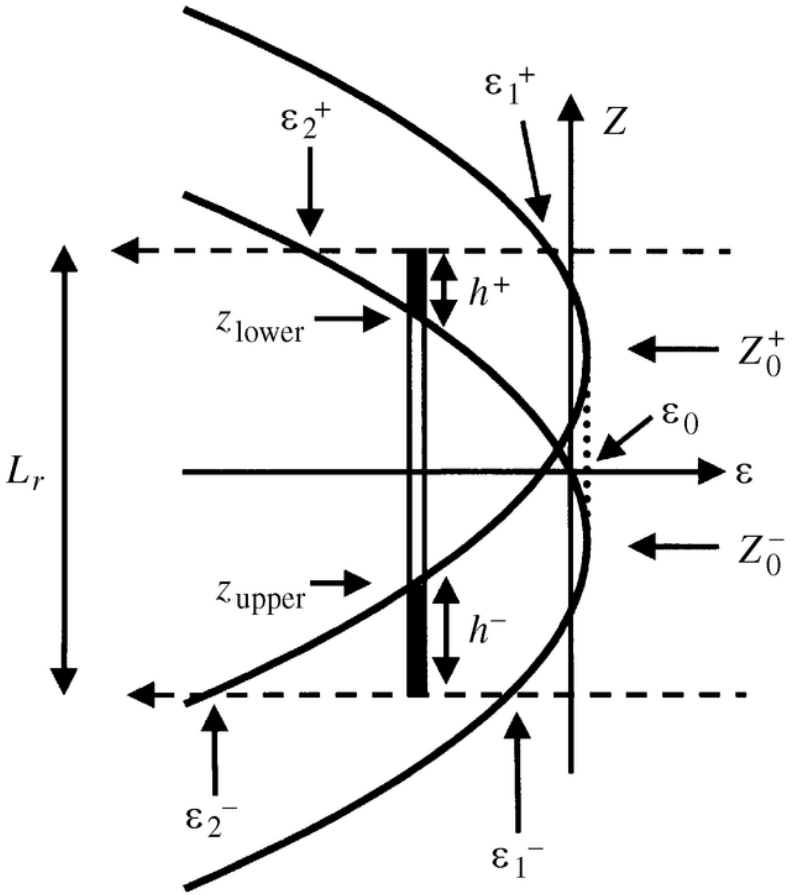
$$w_{\mathrm{T}}(x;\mu,T,R,2\theta) = \begin{cases} \dfrac{1}{\gamma_{\mathrm{T}}}\exp\left(\dfrac{x}{\gamma_{\mathrm{T}}}\right) & \text{for } -x_{\mathrm{T}} < x < 0, \\ 0 & \text{elsewhere} \end{cases}$$

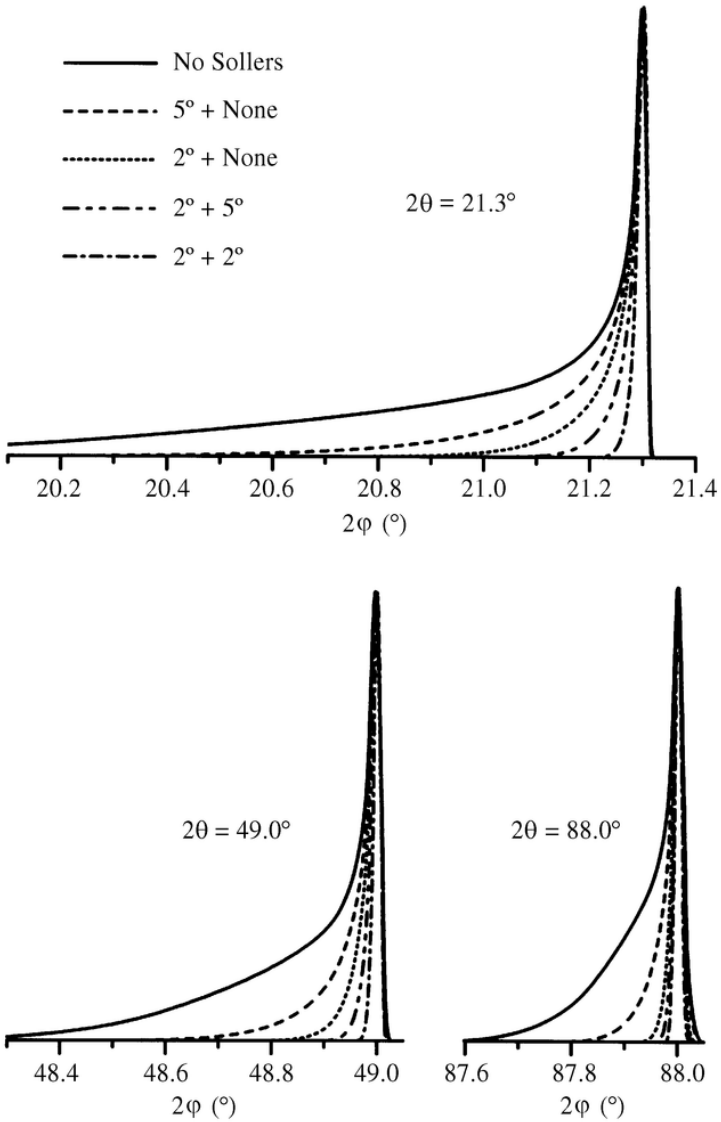
where x is the deviation from the peak position,
μ is the linear absorption coefficient of the specimen,
T is the thickness of the specimen,
R is the goinometer radius,
2θ is the diffraction angle,

$$\gamma_{\mathrm{T}} \equiv \frac{\sin 2\theta}{2\mu R}, \quad x_{\mathrm{T}} \equiv \frac{2T\cos\theta}{R}.$$

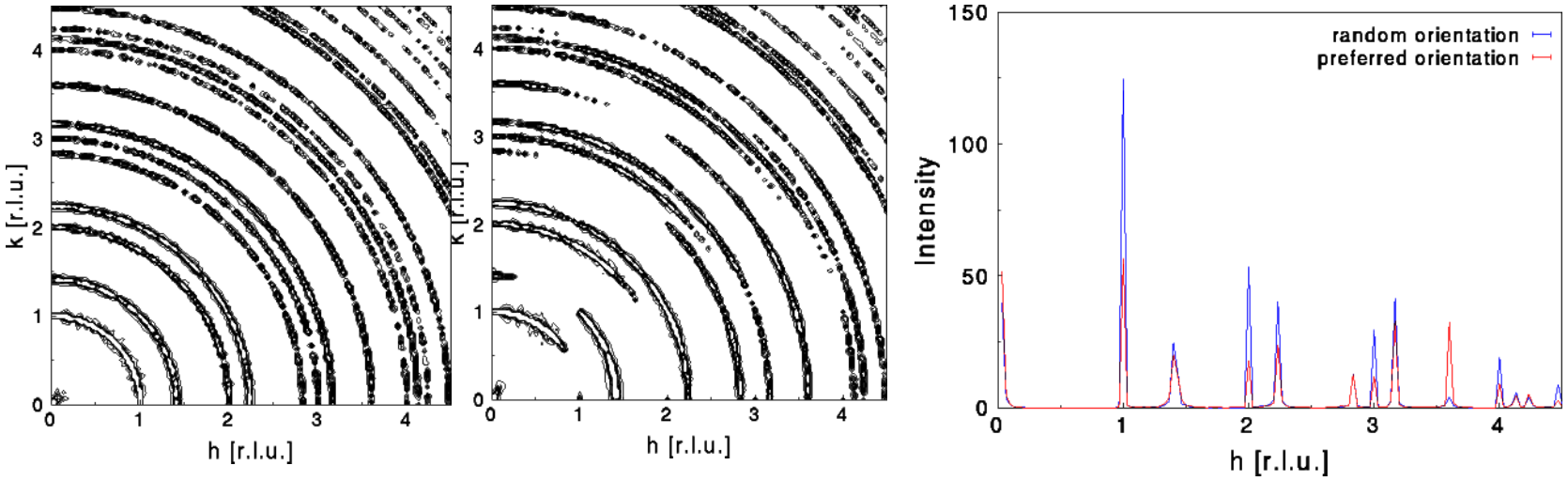
T. Ida and K. Kimura, *J. Appl. Cryst.*, **32**, 982-991 (1999)

Axial divergence





Preferred orientation



$$P_h = G_2 + (1 - G_2)\left[(G_1 \cos\alpha)^2 + \frac{\sin\alpha_h}{G_1}\right]^{-3/2}$$

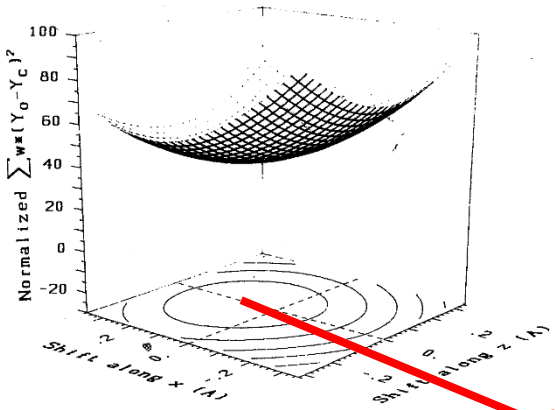
W. A. Dollase, J. Appl. Cryst. (1986). 19, 267-272. *Correction of intensities for preferred orientation in powder diffractometry: application of the March model.*

Con/restraints

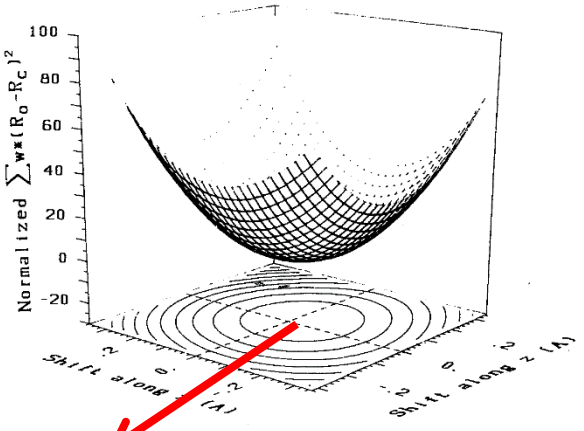
The Rietveld method: introducing chemical knowledge

$$M = \sum w_{Yi}\left(Y_{oi} - Y_{ci}\right)^2 + f_a \sum w_{ai}\left(a_{oi} - a_{ci}\right)^2 + f_d \sum w_{di}\left(d_{oi} - d_{ci}\right)^2 + f_p \sum w_{pi}\left(- p_{ci}\right)^2$$

Rietveld

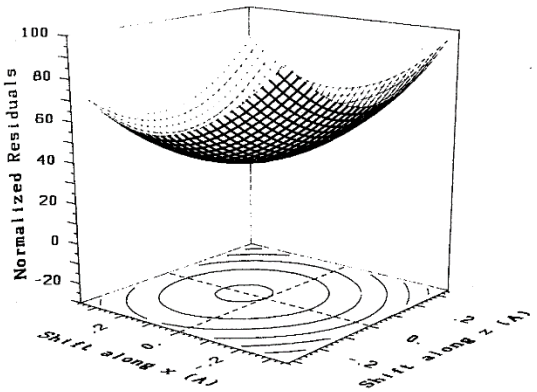


Restraints

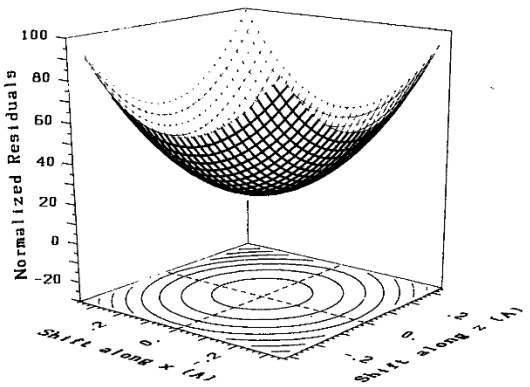


$$Min = \sum_i \left(w_i \left(y_{calc}(2\theta_i) - y_{obs}(2\theta_i) \right)^2 \right) + w_p \sum_p penalties$$

Rietveld and Restraints



Rietveld and Restraints



Agreement factors

The Rietveld method: Some agreement factors

$$R_p = \frac{\sum_{i=0}^{n-1} \left| Yobs_i - Ycalc_i \right|}{\sum_{i=0}^{n-1} Yobs_i}$$

$$w_i = \frac{1}{\sigma\left(Yobs_i\right)^2}$$

$$R'_p = \frac{\sum_{i=0}^{n-1} \left| Yobs_i - Ycalc_i \right|}{\sum_{i=0}^{n-1} \left| Yobs_i - b_i\left(obs\right) \right|}$$

$$R_{wp} = \sqrt{\frac{\sum_i w_i \left(Yobs_i - Ycalc_i\right)^2}{\sum_k w_i Yobs_i{}^2}}$$

$$R'_{wp} = \sqrt{\frac{\sum_i w_i \left(Yobs_i - Ycalc_i\right)^2}{\sum_k w_i \left(Yobs_i - b_i\left(obs\right)\right)^2}}$$

$$R_{\exp} = \sqrt{\frac{\sum_i M - P}{\sum_k w_i Yobs_i{}^2}}$$

$$R'_{\exp} = \sqrt{\frac{\sum_i M - P}{\sum_k w_i \left(Yobs_i - b_i\left(obs\right)\right)^2}}$$

$$\chi^2 = \frac{R_{wp}}{R_{\exp}} = \sqrt{\frac{\sum_i w_i \left(Yobs_i - Ycalc_i\right)^2}{M - P}}$$

$$R_{Bragg} = \frac{\sum_k \left| Iobs_k - Icalc_k \right|}{\sum_k Iobs_k}$$

QPA

The Rietveld formula: QPA

Integrated intensity I of a reflection *hkl* for phase *α* in a multi-phase mixture measured on a flat plate sample with „infinite thickness“:

$$I_{(hkl)\alpha} = \left[\frac{I_0 \lambda^3}{32\pi r}\frac{e^4}{m_e^2 c^4}\right] \cdot \left[\frac{M_{hkl}}{2V_\alpha^2}\left|F_{(hkl)\alpha}\right|^2 \left(\frac{1+cos^2 2\theta cos^2 2\theta_m}{sin^2\theta cos\theta}\right)\right] \cdot \left[\frac{W_\alpha}{\rho_\alpha \mu_m^*}\right]$$

Which can be simplified using a constant for reflection *hkl* in a particular experimental setup

$$I_{(hkl)\alpha} = C_{(hkl)\alpha} \cdot \frac{1}{V_\alpha^2} \cdot \left[\frac{W_\alpha}{\rho_\alpha \mu_m^*}\right]$$

In Rietveld analysis, all reflection intensities of a phase α are proportional to the corresponding scale factor:

$$I_{(hkl)\alpha} \propto S_\alpha$$

This leads to an with a scaling factof K which depends exclusively on the instrumental conditions and not on the sample/phases. :

$$S_\alpha = \mathrm{K} \cdot \frac{1}{V_\alpha^2} \cdot \left[\frac{W_\alpha}{\rho_\alpha \mu_\alpha^*}\right]$$

The Rietveld formula: QPA

Using the X-ray density

$$\rho_\alpha = 1.6604 \cdot \frac{ZM_\alpha}{V_\alpha}$$

the scale factor of phase α can be rewritten as:

$$S_\alpha = \mathrm{K} \cdot \frac{1}{V_\alpha^2} \cdot \left[\frac{W_\alpha V_\alpha}{1.6604 \cdot ZM_\alpha \mu_m^*} \right]$$

from which the weight fraction of phase α can be calculated

$$W_\alpha = \frac{S_\alpha (ZMV)_\alpha \mu_m^*}{K'}$$

assuming all phases to be crystalline, the following normalization relation can be used:

$$\sum_\alpha W_\alpha = 1$$

allowing to eliminate the instrument constant and the mass absorption coefficient of te sample:

$$W_\alpha = \frac{S_\alpha (ZMV)_\alpha}{\sum_{p=1}^{n} S_p (ZMV)_p}$$

The Rietveld formula: QPA

Amorphous/unknown content can be determined by adding an internal standard *s*:

$$W_{\alpha(meas)} = W_{s(meas)} \cdot \frac{S_{\alpha(meas)}\left(ZMV\right)_{\alpha(meas)}}{S_{s(meas)}\left(ZMV\right)_{s(meas)}}$$

The absolute weight fractions of the known materials can then be can calculated by:

$$W_{\alpha(abs)} = W_{\alpha(meas)} \times \frac{W_{std(known)}}{W_{std(meas)}}$$

The weight fraction of the unknown material (e.g. amorphous content) follows directly by:

$$W_{(unk)} = 1.0 - \sum_{k=1}^{n} W_{k(abs)}$$

The Rietveld formula: PONCKS partial or none crystalline standard

Determine a set of intensities (group of single peaks, Pawley or LeBail)
with an overall fixed scale factor (=1.0) and apply a Lorenz-Polarisation correction:

$$I'_{meas} = \frac{I_{meas}}{Lp}$$

With help of an internal standard s, an artificial ZM can be calculated:

$$(ZM)_\alpha = \frac{w_\alpha}{w_s} \cdot \frac{s_s}{s_\alpha} \cdot \frac{(ZMV)_s}{V_\alpha}$$

using $V_\alpha = 1$ for group of peaks

the „correct“ ZM value requires knowledge of the density of the unknown material

$$(ZM)_{\alpha(true)} = \frac{\rho_\alpha V_\alpha}{1.6604}$$

Peak intensities can then be scaled by:

$$\frac{(ZM)_{\alpha(true)}}{(ZM)_\alpha}$$

Parametric Rietveld refinement

Parametric Rietveld refinement

Sequential Rietveld refinement:
Each parameter in each pattern is refined individually

$$y_{calc}(2\theta_{pattern(1)}) = function(p_{(1),1}, p_{(1),2}, ..., p_{(1),m})$$
$$...$$
$$y_{calc}(2\theta_{pattern(n)}) = function(p_{(n),1}, p_{(n),1}, ..., p_{(n),1})$$

Parametric Rietveld refinement:
Some parameters in each pattern are functions of external variable(s)

$$y_{calc}(2\theta_{pattern(1)}) = function(p_{(1),1}, p_2 = f(T_1, T_2, ..T_t), ..., p_{(1),m})$$
$$...$$
$$y_{calc}(2\theta_{pattern(n)}) = function(p_{(n),1}, p_{(n),2} = f(T_1, T_2, ..T_t), ..., p_{(n),1})$$

Minimization for each powder pattern independently

$$Min = \sum_i \left(w_i \left(y_{calc}(2\theta_i) - y_{obs}(2\theta_i) \right)^2 \right)$$

Minimization over all powder patterns simultaneously

$$Min = \sum_{pattern=1}^{n} \left(\sum_i \left(w_i \left(y_{calc}(2\theta_{pattern,i}) - y_{obs}(2\theta_{pattern,i}) \right)^2 \right) \right)$$

Stinton G. W. & Evans J. S. O. (2007) J. Appl. Cryst. **40,** 87-95.

Reducing the number of degrees of freedom: rigid bodies (RB)

Number of refined parameters for a tetrahedron AX_4:

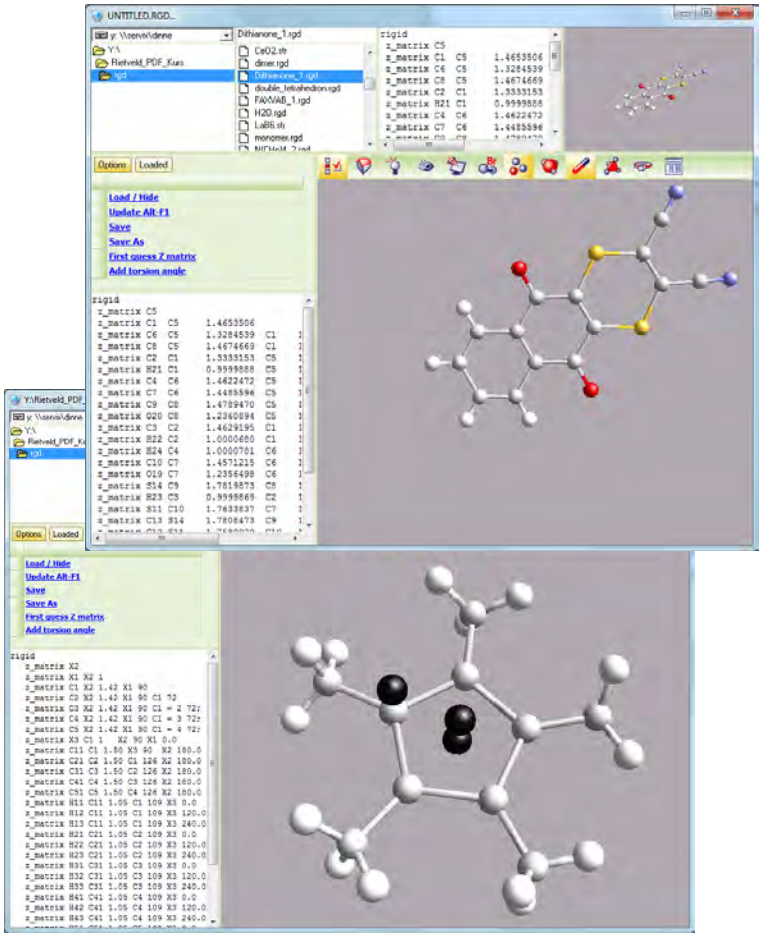
- ✓ free refinement (3*N) → 15
- ✓ 3 rotations + 3 translations → 6
- ✓ + AX average bond length → 7
- ✓ + Jahn-Teller distortion → 8
- ✓ + ...

Possible definition of a MX_4 tetrahedron



r = 2.17
a = 70.5288 (= arcsin(1/ √3)

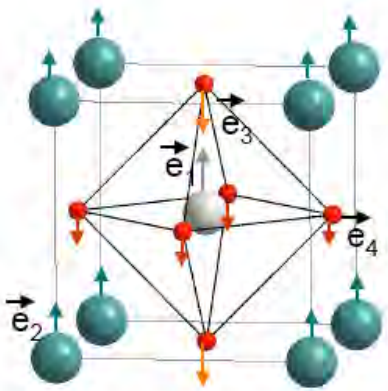
M
X1 z = r;
X2 x = sin(a) r; z = - cos(a) r;
X3 x = - sin(a)/2 r; y = √3 sin(a)/2 r; z = - cos(a) r;
X4 x = - sin(a)/2 r; y = - √3 sin(a)/2 r; z = - cos(a) r;



Reducing the number of degrees of freedom:
Symmetry (SM) modes

Distorted Structure = High-symmetry Struct + "frozen" modes

distortion mode = Amplitude x polarization vector



Description of a "mode": $\mathbf{r}_j^{LS} = \mathbf{r}_j^{HS} + \sum_m c_m Q_m \boldsymbol{\varepsilon}(j|m)$

$\vec{u}(\text{atoms}) = Q\,\vec{e}$

amplitude | polarization vector

$\mathbf{e} = (\vec{e}_1, \vec{e}_2, \vec{e}_3, \vec{e}_4)$

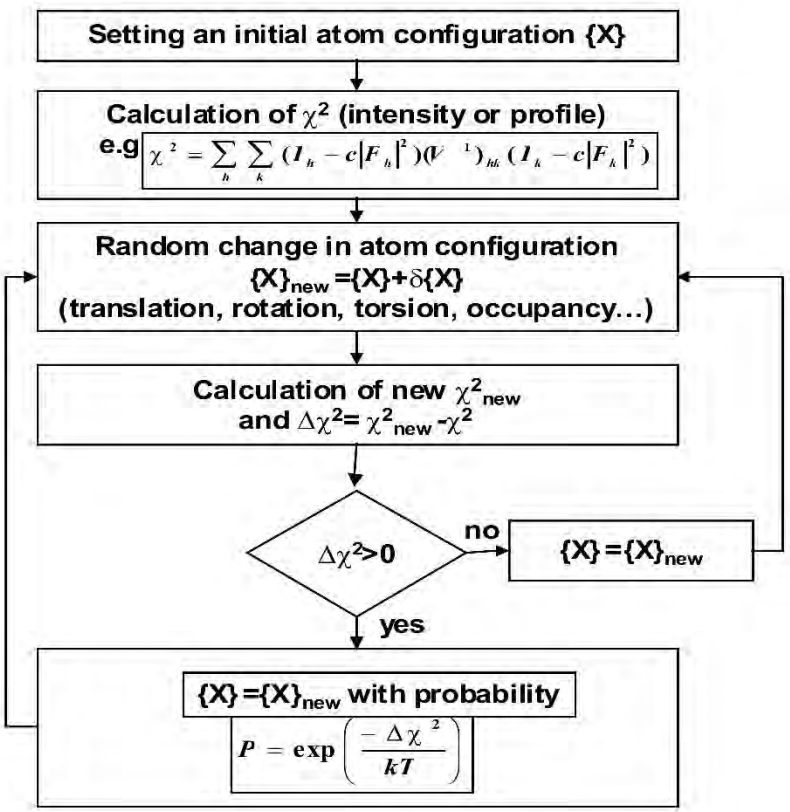
normalization: $|\vec{e}_1|^2 + |\vec{e}_2|^2 + |\vec{e}_3|^2 + 2\,|\vec{e}_4|^2 = 1$
(within a unit cell)

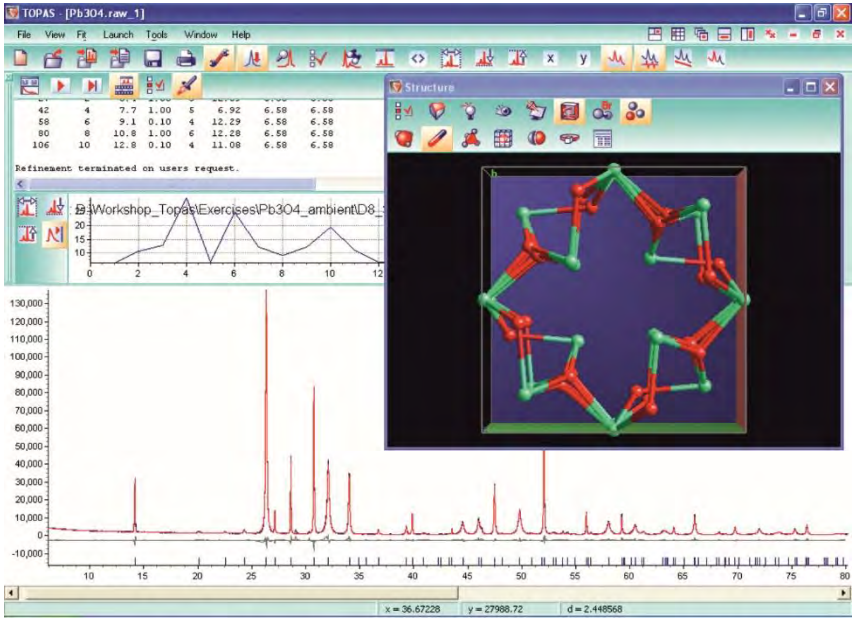
Modes with an amplitude close to zero can be neglected

Mois I. Aroyo, J. M. Perez-Mato and Danel Orobengoa, Universidad del Pais Vasco, Bilbao, Spain, THE BILBAO CRYSTALLOGRAPHIC SERVER: COMPUTER TOOLS FOR STRUCTURAL PHASE TRANSITIONS, lecture at "International School on the use and application of the Bilbao Crystallographic Server", 21-27 June 2009 Lekeitio (Spain)

Global optimization

Global optimization: Simulated annealing

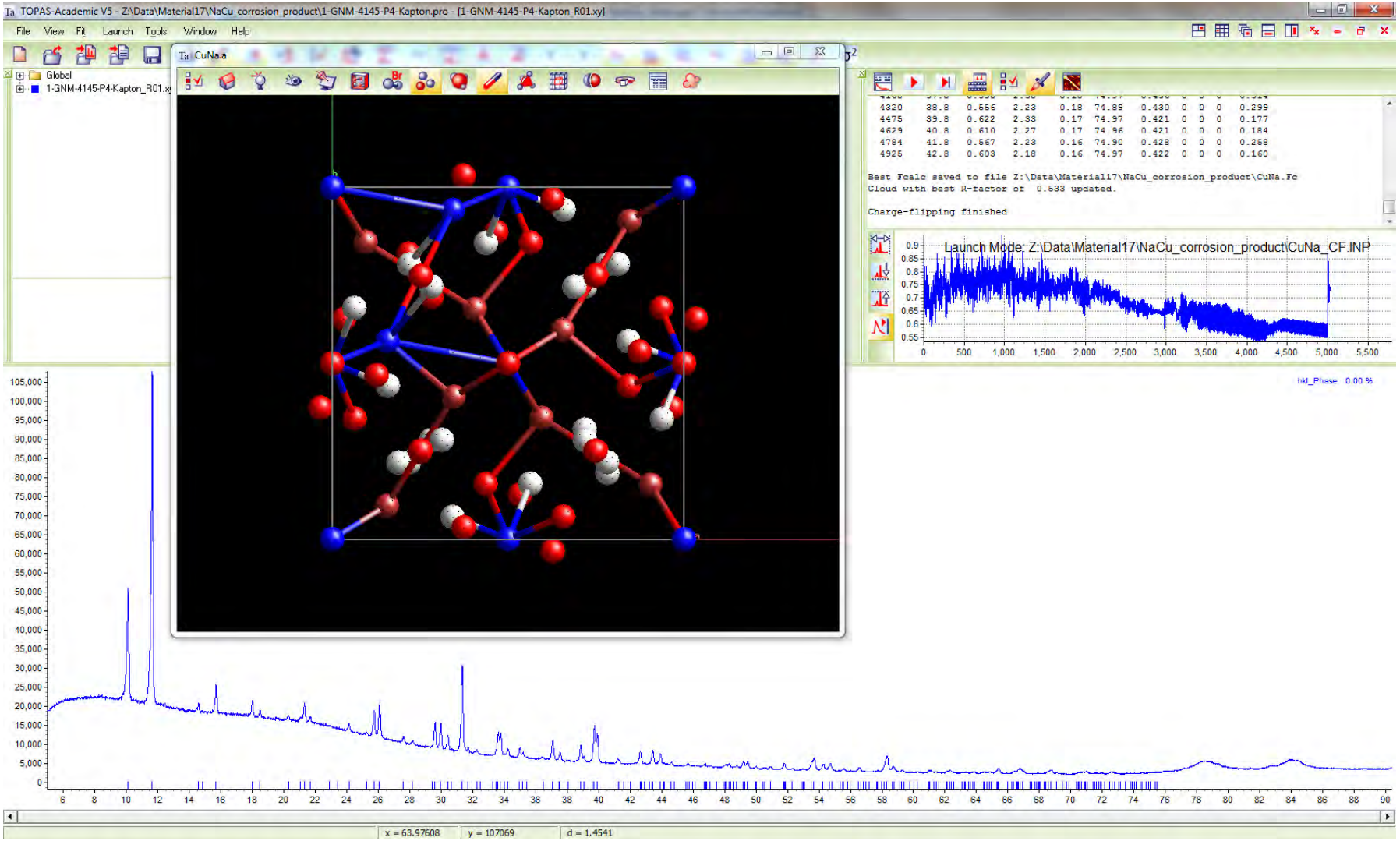




Easy update to global optimization using simulated annealing possible by Introduction of Metropolis algorithm using the Boltzmann criterion $\exp\left(-\frac{\Delta R}{kT}\right)$

N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller und E. Teller: Equation of State Calculations by Fast Computing Machines. In: Journal of Chemical Physics. 21, 1953, S. 1087-1092,.

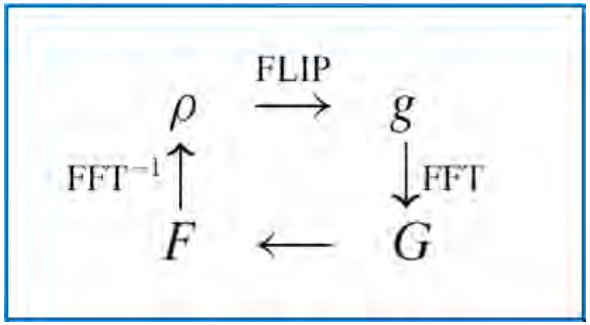
… a sodium copper hydroxy formate hydrate



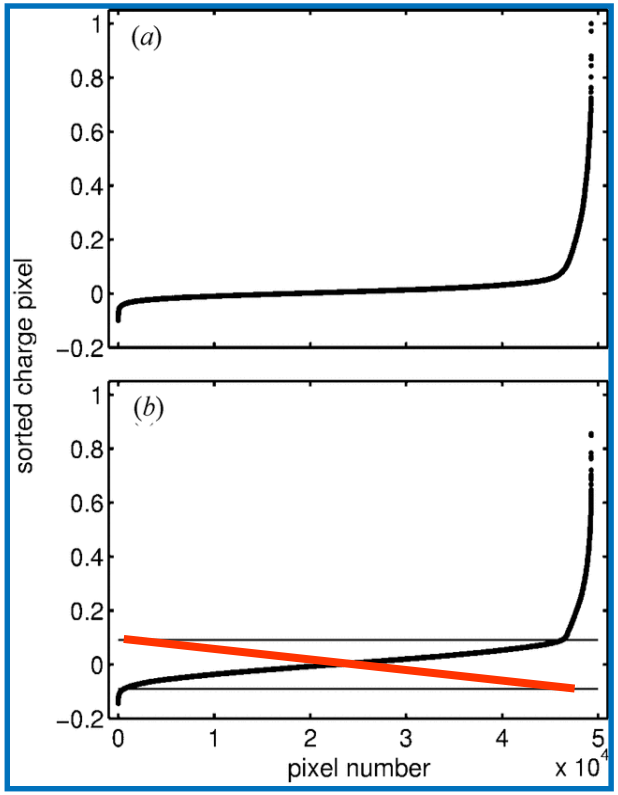
Solved by charge flipping, simulated annealing and difference Fourier analysis

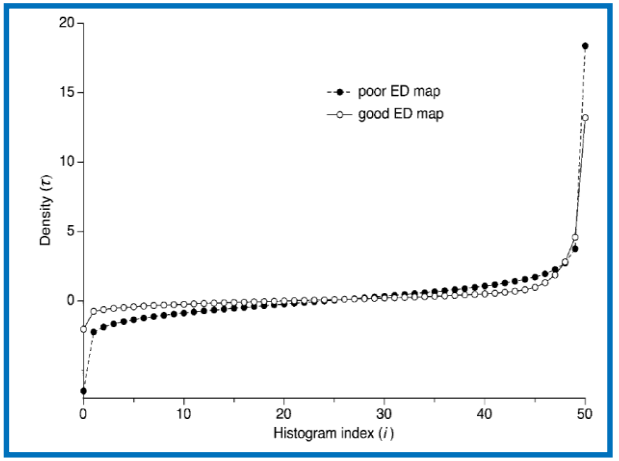
Charge flipping

The method of charge flipping with histogram matching



$$\rho(xyz) = \frac{1}{V}\sum_{hkl}|F_{hkl}|\cos(2\pi(hx+ky+lz)-\phi_{hkl})$$





Oszlányi and Sütő Acta Cryst. (2004). A60, 134-141

Baerlocher, McCusker and Palatinus *Z.Krist.* (2007). **222** 47-53

