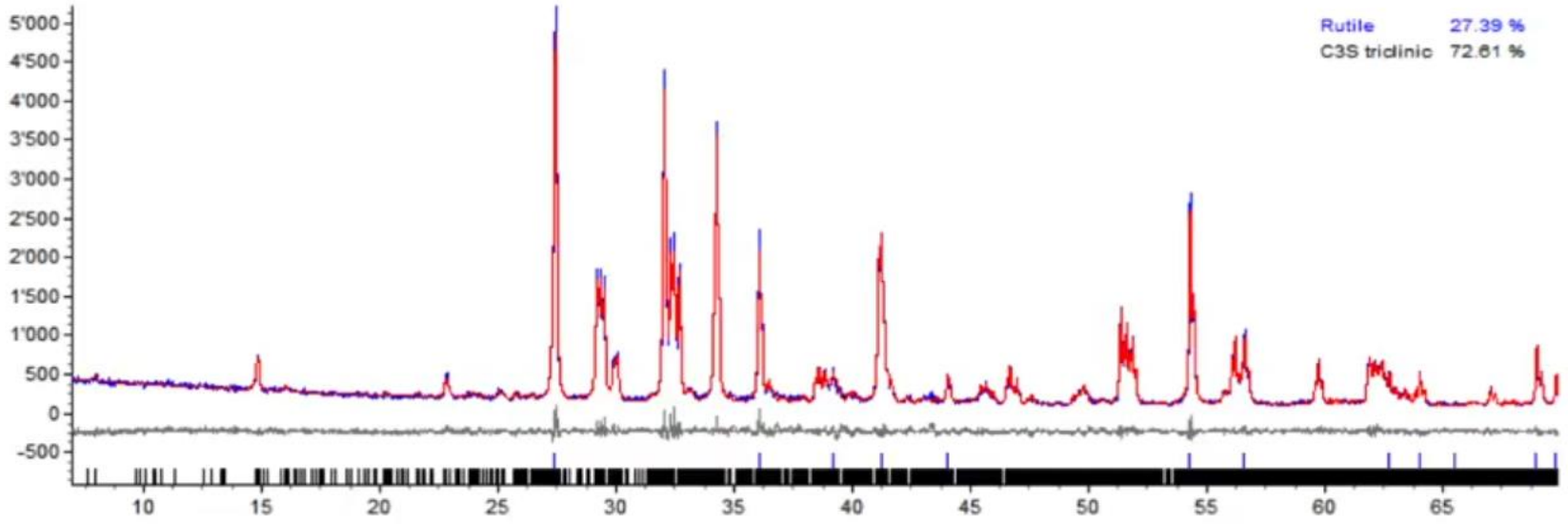
Rietveld refinement - method and parametrisation

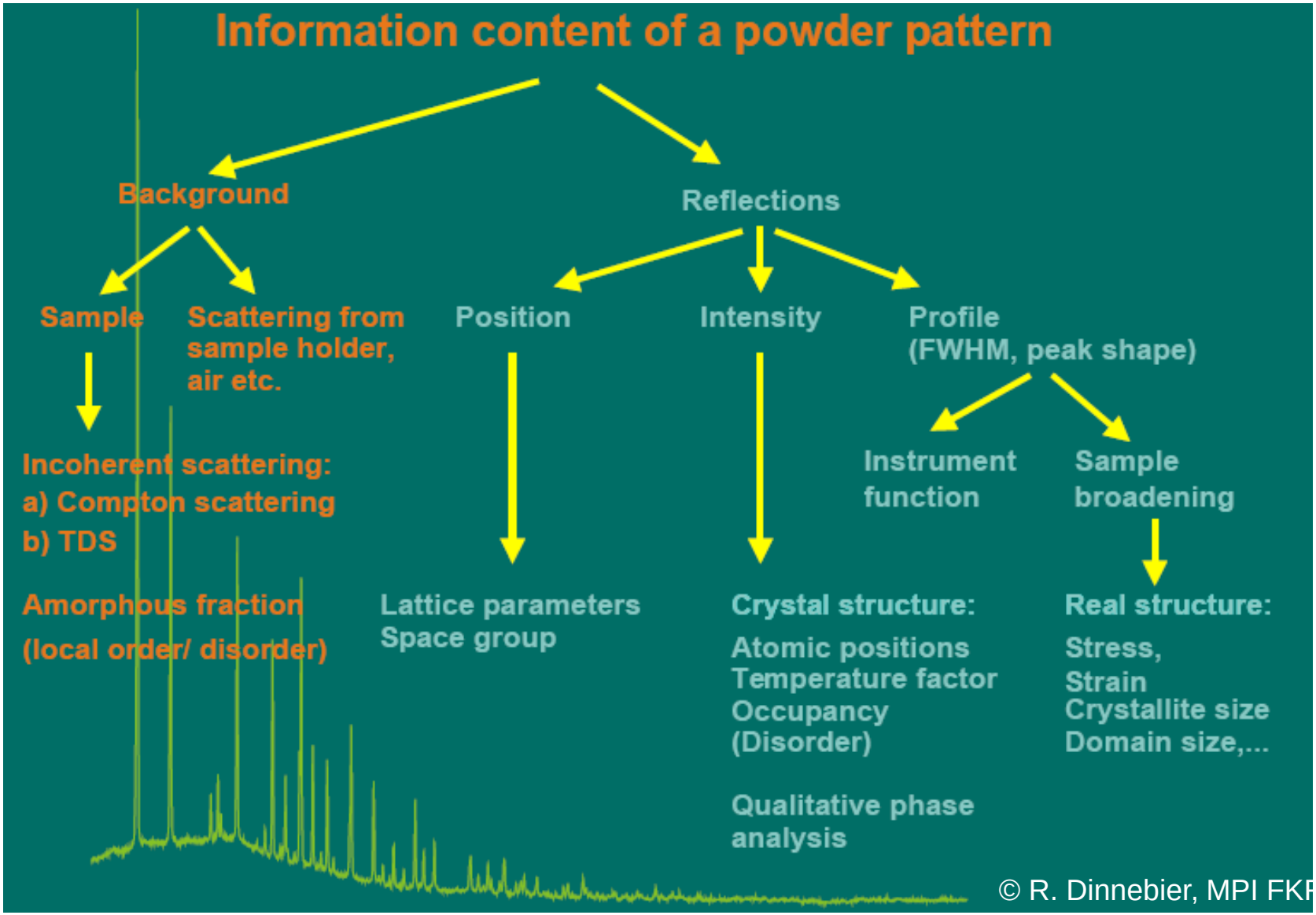
Anatoliy Senyshyn

The Rietveld method

- Rietveld (1969): diffraction pattern analysis by a curve fitting procedure
- First proposed for neutron diffraction
- Least-squares minimization between observed and calculated profiles
- Extended to XRD profiles in the 1970's

Hugo Rietveld (1932-2016)




Information content of a powder pattern
Background
Reflections
Sample
Scattering from sample holder, air etc.
Position
Intensity
Profile (FWHM, peak shape)
Incoherent scattering:
a) Compton scattering
b) TDS
Amorphous fraction
(local order/ disorder)
Instrument function
Sample broadening
Lattice parameters
Space group
Crystal structure:
Atomic positions
Temperature factor
Occupancy
(Disorder)
Qualitative phase analysis
Real structure:
Stress,
Strain
Crystallite size
Domain size,...
© R. Dinnebier, MPI FKF

Calculated profile of powder diffraction data

Single phase, single pattern case
i – angle, **h** - reflection

$$y_{ci} = \sum_{\{\mathbf{h}\}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

$$I_{\mathbf{h}} = I_{\mathbf{h}}(\boldsymbol{\beta}_{\mathbf{I}})$$

Contains structural information: atom positions, magnetic moments, etc

$$\Omega = \Omega(x_{\mathbf{h}i}, \boldsymbol{\beta}_{\mathbf{P}})$$

Contains micro-structural information: instr. resolution, defects, crystallite size…

$$b_i = b_i(\boldsymbol{\beta}_{\mathbf{B}})$$

Background: noise, incoherent scattering diffuse scattering, ...

Multiphase single pattern case:
$\phi = 1, \ldots n_\phi$

$$y_{ci} = \sum_{\phi} s_\phi \sum_{\{\phi\mathbf{h}\}} I_{\phi,\mathbf{h}} \, \Omega(T_i - T_{\phi,\mathbf{h}}) + b_i$$

Multiphase and multipattern case
$\phi = 1, \ldots n_\phi$,
$p = 1, \ldots n_p$

$$y_{ci}^{p} = \sum_{\phi} s_\phi^{p} \sum_{\{\phi\mathbf{h}\}} I_{\phi,\mathbf{h}}^{p} \, \Omega^{p}(T_i - T_{\phi,\mathbf{h}}) + b_i^{p}$$

Calculated profile of powder diffraction data

Single phase, single pattern case
i – angle, **h** - reflection

$$y_{ci} = \sum_{\{\mathbf{h}\}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

$$I_{\mathbf{h}} = S\{LpOACF^2\}_{\mathbf{h}}$$

Scale Factor

Lorentz polarization

preferred orientation

absorption

other "corrections"

Definition of structure factor F(h)

$$F(\mathbf{h}) = \sum_{j=1}^{n} O_j f_j(h) T_j \sum_s exp\left\{2\pi i\left[\mathbf{h}\{S|\mathbf{t}\}_s \mathbf{r}_j\right]\right\}$$

Structure factor (isotropic case)

Number of atoms

$$F(\mathbf{h}) = \sum_{j=1}^{n} O_j f_j(h) T_j \sum_s exp\left\{2\pi i\left[\mathbf{h}\left\{S|\mathbf{t}\right\}_s \mathbf{r}_j\right]\right\}$$

Occupation factor

Form factor

Debye-Waller factor

$$\mathbf{r}_j = (x_j, y_j, z_j)$$

Anisotropic crystal approximation

As in the simplest case plus additional (or alternative) parameters:

- Anisotropic temperature (displacement) factors
- Anharmonic temperature factors
- Special form-factors (Symmetry adapted spherical harmonics), TLS for rigid molecules, etc.
- Magnetic moments, coefficients of Fourier components of magnetic moments , basis functions, etc.

Calculated profile of powder diffraction data

Single phase, single pattern case
i – angle, **h** - reflection

$$y_{ci} = \sum_{\{\mathbf{h}\}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

$$\Omega(x_{\mathbf{h}i}, \beta_{\mathbf{P}}) = \Omega(T_i - T_{\mathbf{h}}, \beta_{\mathbf{P}}) \qquad \int_{-\infty}^{+\infty} \Omega(x)dx = 1$$

Gaussian function

$$G(x) = a_G \exp(-b_G x^2)$$

$$a_G = \frac{2}{H}\sqrt{\frac{\ln 2}{\pi}} \qquad b_G = \frac{4\ln 2}{H^2}$$

Integral breadth: $\beta_G = \frac{1}{a_G} = \frac{H}{2}\sqrt{\frac{\pi}{\ln 2}}$

Lorentzian function

$$L(x) = \frac{a_L}{1 + b_L x^2}$$

$$a_L = \frac{2}{\pi H} \qquad b_L = \frac{4}{H^2}$$

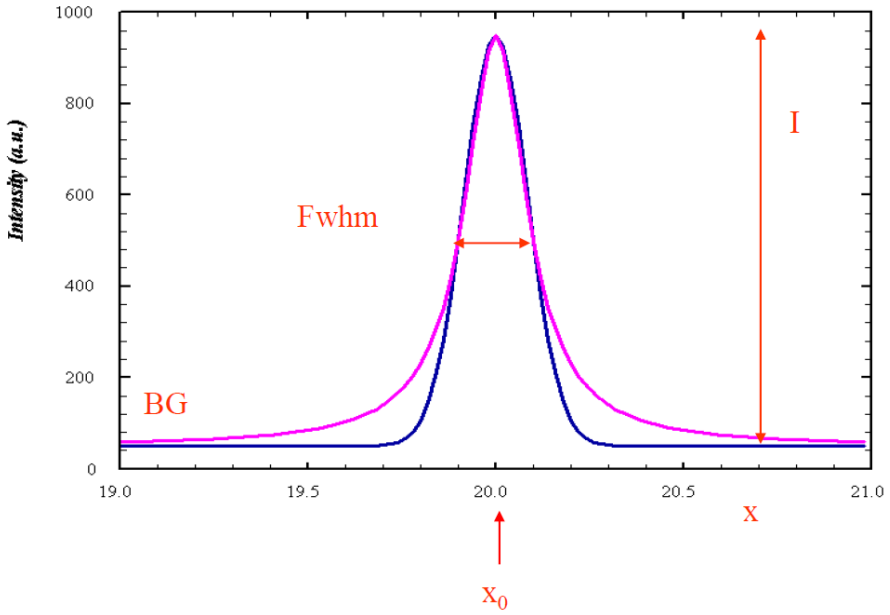
Integral breadth: $\beta_L = \frac{1}{a_L} = \frac{\pi H}{2}$

Calculated profile of powder diffraction data

Single phase, single pattern case
i – angle, **h** - reflection

$$y_{ci} = \sum_{\{\mathbf{h}\}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

Comparison of **Gaussian** and **Lorentzian** peak shapes of the same peak height "I" and same width "Fwhm"



Convolution properties of profile functions

$$L(x,H_1)\otimes L(x,H_2)=L(x,H_1+H_2)$$

$$G(x,H_1)\otimes G(x,H_2)=G(x,\sqrt{H_1^2+H_2^2})$$

$$L(x,H_L)\otimes G(x,H_G)=V(x,H_L,H_G)$$

Voigt function

$$V(x)=L(x)\otimes G(x)=\int_{-\infty}^{+\infty}L(x-u)G(u)du$$

$$V(x)=V(x,H_L,H_G)=V(x,\beta_L,\beta_G)$$

Pseudo-Voigt function (Npr=5)

$$pV(x)=\eta L'(x)+(1-\eta)G'(x)$$

$$pV(x)=pV(x,\eta,H)$$

Pseudo-Voigt - Voigt Thomson-Cox-Hasting formulation

$$(H,\eta) = F(H_G, H_L) \quad \Leftrightarrow \quad (H_G, H_L) = F^{-1}(H,\eta)$$

$$H = (H_G^5 + 2.69269 H_G^4 H_L + 2.42843 H_G^3 H_L^2 + 4.47163 H_G^2 H_L^3 + 0.07842 H_G H_L^4 + H_L^5)$$

$$\eta = 1.36603 \frac{H_L}{H} - 0.47719 \left(\frac{H_L}{H}\right)^2 + 0.11116 \left(\frac{H_L}{H}\right)^3$$

$$\frac{H_L}{H} = 0.72928\eta + 0.19289\eta^2 + 0.07783\eta^3$$

$$\frac{H_G}{H} = (1 - 0.74417\eta - 0.24781\eta^2 - 0.00810\eta^3)^{1/2}$$

Parameters controlling the Full-Width at half maximum

U, V, W, I_G, X, Y

$$H_G^2 = U \tan^2\theta + V \tan\theta + W + \frac{I_G}{\cos^2\theta}$$

$$H_L = X \tan\theta + \frac{Y}{\cos\theta}$$

The Rietveld method

Rietveld Method: refinement of crystal (and/or magnetic) structure by minimising the weighted squared difference between the observed and the calculated pattern against the parameter vector: β

$$\chi^2 = \sum_{i=1}^{n} w_i \left\{ y_i - y_{ci}(\beta) \right\}^2 \qquad w_i = \frac{1}{\sigma_i^2}$$

σ_i^2: **is the variance of the "observation"** y_i ⇒ In Poisson's statistics, $\sigma \approx \sqrt{y_i}$

Minimisation of the relationship $\frac{\partial \chi^2}{\partial \beta} = 0$

- The least squares procedure provides (when it converges) the value of the parameters constituting the local minimum closest to the starting point
- A set of good starting values for all parameters is needed
- If the initial model is bad for some reasons the LSQ procedure will not converge, it may diverge

The Rietveld method

The shifts of the parameters obtained by solving the normal equations are added to the starting parameters giving rise to a new set

$$\boldsymbol{\beta}_1 = \boldsymbol{\beta}_0 + \boldsymbol{\delta}_{\beta_0}$$

A Taylor expansion of $y_{ic}(\boldsymbol{\beta})$ around $\boldsymbol{\beta}_0$ allows the application of an iterative process. The shifts to be applied to the parameters at each cycle for improving χ^2 are obtained by solving a linear system of equations (normal equations)

$$\mathbf{A}\boldsymbol{\delta}_{\beta_0} = \mathbf{b}$$

$$A_{kl} = \sum_i w_i \frac{\partial y_{ic}(\boldsymbol{\beta}_0)}{\partial \beta_k} \frac{\partial y_{ic}(\boldsymbol{\beta}_0)}{\partial \beta_l}$$

$$b_k = \sum_i w_i (y_i - y_{ic}) \frac{\partial y_{ic}(\boldsymbol{\beta}_0)}{\partial \beta_k}$$

The variances of the adjusted parameters are calculated by the expression

$$\sigma^2(\beta_k) = (\mathbf{A}^{-1})_{kk} \chi_\nu^2$$

$$\chi_\nu^2 = \frac{\chi^2}{N - P + C}$$

Goodness of fit parameters

$$R_{Bragg} = \frac{\sum |I_{hkl}(obs) - I_{hkl}(calc)|}{\sum I_{hkl}(obs)}$$

I_{hkl} is the intensity of each reflection

$$R_p = \frac{\sum |y_i(obs) - y_i(calc)|}{\sum y_i(obs)}$$

y is the intensity of each data point

$$R_{wp} = \left\{ \frac{\sum w_i \left(y_i(obs) - y_i(calc)\right)^2}{\sum w_i \left(y_i(obs)\right)^2} \right\}^{1/2}$$

$w_i = 1/\sigma_i(y_i)$ is the weighting of each data point (and σ_i is roughly proportional to $\sqrt{y_i}$

$$R_{exp} = \left(\frac{M - N}{\sum w_i \left(y_i(obs)\right)^2} \right)^{1/2}$$

M is the number of data points
N is the number of parameters

$$Goodness\ of\ fit = \chi = \frac{R_{wp}}{R_{exp}}$$

Ideally $\chi = 1$ for a perfect fit

Goodness of fit parameters

$$R_B = 100 \frac{\sum_k \left| {}'I_{obs,k}{}' - I_{calc,k} \right|}{\sum_k \left| {}'I_{obs,k}{}' \right|}$$

Bragg R-factor

$$R_F = 100 \frac{\sum_k \left| {}'F_{obs,k}{}' - F_{calc,k} \right|}{\sum_k \left| {}'F_{obs,k}{}' \right|}$$

Crystallographic R_F-factor.

- The sums over “i” may be extended only to the regions where Bragg reflections contribute
- The denominators in R_P and R_{WP} may or not contain the background contribution

Usage of Rietveld method

- **Phase identification** (crystalline and amorphous)
- Crystal structure refinement
- Crystal structure determination (not trivial)
- **Quantitative phase analysis**
- Microstructural analyses (crystallite size – microstrain)

Kinetic studies

Thermal expansion

Polymorphism

In-situ chemistry

Phase transitions

FullProf Suite

Crystallographic tools for Rietveld, profile matching & integrated intensity refinements of X-Ray and/or neutron data

- 02.05-03.05.2023 (09:00-17:00) GATE Garching

(advanced) – microstructure, magnetic structures, single crystals JRC + OF

https://indico.frm2.tum.de/event/414/

FullProf Workshop

(Gate Garching, Lichtenbergstrasse 8, D-85748 Garching b. München)

Tuesday, May, 02, 2023

09:00 Welcome and organisational details

09:05 Lecture 1: Brief introduction to the FullProf suite. Overview of new features and capabilities.

10:00 Lecture 2: Magnetic structures. Description of magnetic structures using the formalism of propagation vectors. Symmetry analysis: Magnetic Space Groups and Representation theory.

10:30 Coffee break

10:50 (cont.) Lecture 2: Magnetic structures. Description of magnetic structures using the formalism of propagation vectors. Symmetry analysis: Magnetic Space Groups and Representation theory.

12:30 Lunch break (lunch at Gate)

14:00 Lecture 3: Options for analyzing magnetic structures in FullProf. Utilities for magnetic space groups. Super space group formalism (nuclear and magnetic)

15:30 Coffee break

15:50 **Tutorial:** *Introduction to Magnetic Structure determination (number 10)*

Tutorial: *Different examples of Magnetic Structures (number 12)*

17:30 Day 1: closing remarks

19:00 Joint dinner at Garchinger Augustiner (Freisinger Landstraße 4, 85748 Garching bei München)

Wednesday, May, 03, 2023

09:00 Lecture 4: Microstructural studies, from mathematical foundations to real examples.

10:30 Coffee break

10:50 **Tutorial:** *Introduction to Magnetic Structure determination (number 10)*

Tutorial: *Different examples of Magnetic Structures (number 12)*

Tutorial: *Study of the micro-structural effects by powder diffraction (number 14)*

12:30 Lunch break (lunch at Gate)

14:00 Lecture 5: Single crystal diffraction using FullProf. Data reduction of single crystal data using DataRed and nDataRed.

15:30 Coffee break

15:50 **Tutorial: Tutorial:** *Introduction to Magnetic Structure determination (number 10)*

Tutorial: *Different examples of Magnetic Structures (number 12)*

Tutorial: *Study of the micro-structural effects by powder diffraction (number 14)*

Tutorial: *Use of FullProf for Single crystals: hybrid compounds*

17:30 Day 2: closing remarks and wrap up

Ende des Dokuments

bilbao crystallographic server

- 28-30.06.2023 (09:00-18:00) Glass Palace

Block I . 28 June 2023 afternoon (4 hours):

Crystallographic Symmetry - brief overview (MIA)

- Crystallographic point groups and their group-subgroup relations. Wyckoff positions of point groups. Supergroups and normalizers.
- Space groups and their descriptions in International Tables for Crystallography, Vol. A. Transformations of the coordinate systems: change of origin and orientation. Conventional and non-conventional descriptions of space groups; ITA-settings.

BCS: hands-on session on the computer databases and access tools to crystallographic symmetry data for space groups (GENPOS, WYCKPOS, IDENTIFY GROUP)

Block II. 29 June 2023 morning (4 hours)

Symmetry relations between space groups (MIA)

Group-subgroup relations between space groups: Subgroups of space groups; maximal subgroups and Hermann theorem.

Domain-structure analysis (initial steps)in structural phase transitions.

- Relations of Wyckoff positions for a group-subgroup pair.
- Supergroups of space groups. Normalizers.

BCS: Hands-on session with the computer databases and computer tools in the study of group-subgroup relations of space groups (SUBGROUPGRAPH, SUBGROUPS, HERMANN, WYCKSPLIT, MINSUP, SUPERGROUPS).

Block III 29 June afternoon (4 hours):

Computer structure tools of the Bilbao Crystallographic Server (GdF)

- Crystal-structure descriptions. Descriptions of crystal structures with respect to different ITA settings of the space groups (the program SETSTRU). Equivalent crystal structure descriptions (the program EQUIVSTRU). Crystal-structure descriptions compatible with symmetry reduction (the program TRANSTRU).
- Comparison btw different structure descriptions (the program (COMPSTRU).
- Crystal-structure relationships. Family trees (Baernighausen trees) of crystal structures: arystotype (basic) and hettotypes (derivative structures) (STRUCTURE RELATIONS).
- Possible symmetries of a distorted structure knowing only its non-distorted symmetry and the distorted lattice (SUBGROUPS)
- Structural pseudosymmetry. Pseudosymmetry search for new ferroics. Application structural phase transitions (PSEUDO). New developments of PSEUDO relacionados con el problema de twinning.

Block iV 30 June morning (2+2 hours)

Magnetic symmetry (MIA): 2 hours

- Magnetic point operations and magnetic point groups. Tensor properties of magnetic crystals
- Magnetic space groups. Types of magnetic space groups. BNS and OG settings in type IV magnetic space groups. Wyckoff positions of magnetic space groups
- BCS: Hands-on session with the basic computer tools on magnetic symmetry: MPOINT, MGENPOS, IDENTIFY MAGNETIC GROUP, BNS2OG, MWYCKPOS, MTENSOR

Magnetic Crystallography (GdF): 2 hours

- Possible maximal magnetic space groups for a given parent symmetry and a propagation vector and resulting magnetic structures (Tutorial on the use of MAXMAGN)
- Tutorial on the use of k-SUBGROUPSMAG plus MAGMODELIZE
- Database of magnetic structures on the Bilbao Crystallographic Server. (MAGNDATA)