

# Second FullProf School 2023: Diffraction data analysis of energy materials



## Microstructural effects in diffraction patterns

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# Outline



1. Diffraction patterns of real crystals. Intrinsic general shape of Bragg peaks
2. Simplified methods for studying the microstructure of materials: size and strain using the double-Voigt approximation
3. How to create an IRF for the study of microstructure
4. Examples in literature

**Live presentation:** Complete creation of an IRF file using the case of spinel  $\text{MgAl}_2\text{O}_4$

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# Microstructure: defects in crystals

- Instrumental broadening

- Finite crystallite size

$FWHM \propto \cos^{-1}(\theta)$   
size < 1  $\mu\text{m}$

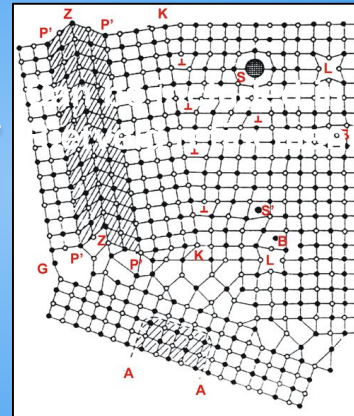
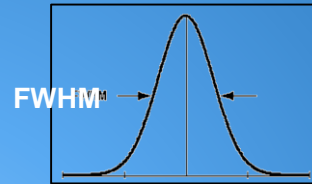
- Lattice microstrains

$FWHM \propto \tan(\theta)$   
fluctuations in cell parameters

- Extended defects / Disorder

- Antiphase boundaries
- Vacancies / Atomic disorder

- Stacking Faults
- Turbostraticity
- Interstratification



2 $\theta$  ( $^\circ$ )

- A antiphase domain
- B interstitial atom
- G, K grain boundary
- L vacancy
- S substitutional impurity
- S' interstitial impurity
- P, Z stacking faults
- $\perp$  dislocations

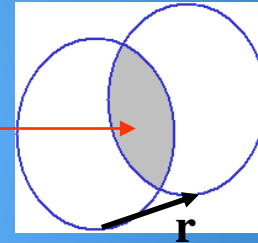


# Scattered Intensity of a Finite Crystal

Shape function:  $g(\mathbf{r})$  is defined as  $g(\mathbf{r})=1$  for  $\mathbf{r}$  inside the crystal, and  $g(\mathbf{r})=0$  for  $\mathbf{r}$  outside  $\Rightarrow G(\mathbf{s})=FT\{g(\mathbf{r})\}$ .

$G^2(\mathbf{s})=FT\{g(\mathbf{r})\otimes g(-\mathbf{r})\}$  is Fourier transform of the auto-correlation function:

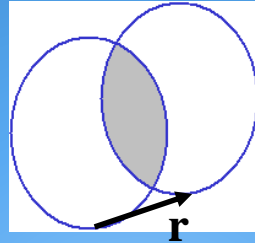
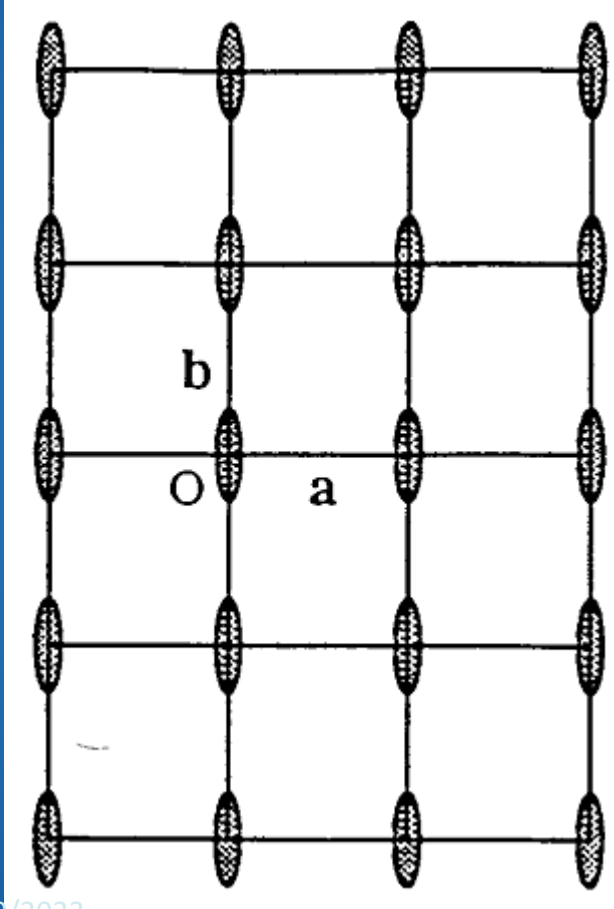
$$V \cdot A_S(\mathbf{r}) = \int g(\mathbf{u})g(\mathbf{r} + \mathbf{u})d^3\mathbf{u}$$



$A_S(\mathbf{r})$  is the fraction of the total volume shared in common between the object and its "ghost" displaced by the vector  $\mathbf{r}$ .  $A_S(0)=1$  and decreases as  $\mathbf{r}$  increases.  $G^2(\mathbf{s})=V FT\{A_S(\mathbf{r})\}$

$$I(\mathbf{s}) \propto \frac{N}{VV_c} F(\mathbf{s})F^*(\mathbf{s}) \sum_{\mathbf{H}} G^2(\mathbf{s} - \mathbf{H})$$

# Size effects in reciprocal space



$$VA_S(\mathbf{r}) = \int g(\mathbf{u})g(\mathbf{r}+\mathbf{u})d^3\mathbf{u}$$

$$A_S(\mathbf{r}) = \frac{1}{V} FT^{-1}\{G^2(\mathbf{s})\}$$

$$G^2(\mathbf{s}) = FT\{g(\mathbf{r}) \otimes g(-\mathbf{r})\} = V FT\{A_S(\mathbf{r})\}$$

$$\sum_{\mathbf{H}} G^2(\mathbf{s} - \mathbf{H}) \rightarrow G_{\mathbf{H}}^2(\Delta\mathbf{s}) = G^2(\Delta\mathbf{s})$$

**$G$  determines the shape of the peak profile and it is the same for all reciprocal nodes**

**Width of peak increases in  $2\theta$  space as  $(\cos\theta)^{-1}$ .**  
Except for spheres, the width depends on the direction in reciprocal space

# Size effects in reciprocal space

$$G^2(\mathbf{s}) = FT\{g(\mathbf{r}) \otimes g(-\mathbf{r})\} = V FT\{A_S(\mathbf{r})\}$$

$$I(\mathbf{s}) \propto \frac{N}{VV_c} F(\mathbf{s})F^*(\mathbf{s}) \sum_{\mathbf{H}} G^2(\mathbf{s} - \mathbf{H}) \Rightarrow I(\mathbf{s}_H) \propto \frac{N}{V_c} F(\mathbf{H})F^*(\mathbf{H}) \frac{G^2(\mathbf{s}_H)}{V}$$

$$I(\mathbf{s}_H) \propto \frac{N}{V_c} F(\mathbf{H})F^*(\mathbf{H}) \int A_S(\mathbf{r}) \exp\{2\pi i \mathbf{s}_H \mathbf{r}\} d^3\mathbf{r}$$

Normalised profile of a single crystal spot in reciprocal space: Fourier transform of the size function  $A_S(\mathbf{r})$

$$i(\mathbf{s}_H) = \int A_S(\mathbf{r}) \exp\{2\pi i \mathbf{s}_H \mathbf{r}\} d^3\mathbf{r}$$

In powder diffraction we obtain a similar equation restricted to columns perpendicular to diffracting planes



# Real Crystals: diffuse scattering

Average structure factor:  $F = \langle F \rangle = 1/N \sum_m F_m$

local fluctuation of the structure factor:  $\phi_n = F - F_n$

$$p_n = F^2 + \langle \phi_m \phi_{m+n}^* \rangle = F^2 + \Phi_n,$$

The intensity formula can be transformed to:

$$I(\mathbf{s}) = I_{\text{Bragg}} + I_{\text{Diffuse}} =$$

$$N F^2 \sum_n A_S(\mathbf{R}_n) \exp\{2\pi i \mathbf{s} \cdot \mathbf{R}_n\} + N \sum_n A_S(\mathbf{R}_n) \Phi_n \exp\{2\pi i \mathbf{s} \cdot \mathbf{R}_n\} =$$

$$N F^2 / (V V_c) \sum_{\mathbf{H}} G^2(\mathbf{s} - \mathbf{H}) + N \sum_n \Phi_n \exp\{2\pi i \mathbf{s} \cdot \mathbf{R}_n\}$$

In the last expression, we have made the approximation  $A_S(\mathbf{R}_n) = 1$  because  $\Phi_n$  decreases with  $n$  much faster than  $A_S(\mathbf{R}_n)$ .



# Strained Crystals

A crystal is said to be “strained” if the structure factor of the cell  $m$  can be written in the form:

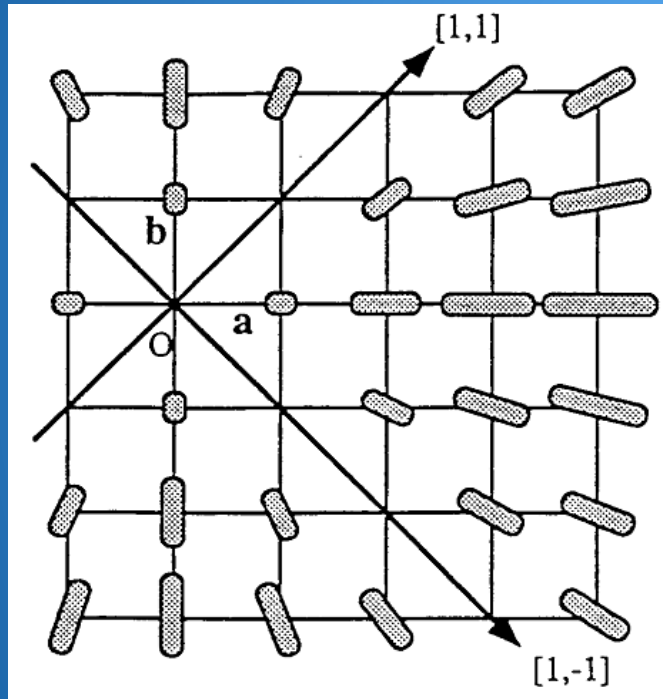
$$F_m = F \exp\{2\pi i \mathbf{s} \mathbf{u}_m\}, \quad \left( \text{with } F = \frac{1}{N} \sum_n F_n \right)$$

Defining the quantity:  $A_D(\mathbf{R}_n, \mathbf{s}) = \langle \exp\{2\pi i \mathbf{s} (\mathbf{u}_m - \mathbf{u}_{m+n})\} \rangle$

$$I(\mathbf{s}) = NF^2 \sum_n A_S(\mathbf{R}_n) A_D(\mathbf{R}_n, \mathbf{s}) \exp\{2\pi i \mathbf{s} \mathbf{R}_n\}$$

$$I_H(\Delta\mathbf{s}) = NF_H^2 \sum_n A_S(\mathbf{R}_n) A_{DH}(\mathbf{R}_n) \exp\{2\pi i \Delta\mathbf{s} \mathbf{R}_n\} \approx F_H^2 f_H(\Delta\mathbf{s})$$

# Strain effects in reciprocal space



The interpretation of the peak shape in the case of strains is not so straightforward as that of size because there are many possible physical origins for strain broadening: dislocations, interstitials, vacancies, compositional fluctuations, etc.

The important point is that the peak shape and width depend on both the particular reflection and the direction in reciprocal space.

**Width of peaks increases in  $2\theta$  space as  $\tan\theta$  in most of the cases.**

# Powder peak profiles

For a powder (after spherical averaging), the total profile is a superposition of the profiles of the set of equivalent nodes and the distribution function for size and strain effects:

$$I_{\{\mathbf{H}\}}(\Delta s) \approx \sum_{\{\mathbf{H}\}} F_{\mathbf{H}}^2 f_{\mathbf{H}}(\Delta s)$$

Usual notation in literature:

$$f_{hkl}(\Delta s) \approx \sum_n \left\{ A_n^S A_n^D \exp(2\pi i \Delta s n d_{hkl}) \right\}$$

$$f_{hkl}(s) \approx \int_{L=0}^{L=\infty} A_S(L) A_D(L, s) \exp\{2\pi i sL\} dL$$

*Microstructure Analysis from Diffraction*

Edited by R. L. Snyder, H. J. Bunge, and J. Fiala, International Union of Crystallography, 1999

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# Calculation of the full profile of a powder diffraction pattern

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

$$I_{\mathbf{h}} = \left\{ L p O A C F^2 \right\}_{\mathbf{h}}$$

Structural information: atomic positions, magnetic moments, etc

$$\Omega = \Omega(x_{hi}, \beta_P)$$

Contains micro-structural information: size, ...  
instr. resolution.  $\int_{-\infty}^{+\infty} \Omega(x) dx = 1$

$$\Omega(x) = g(x) \otimes f(x) = \text{instrumental} \otimes \text{intrinsic profile}$$

$$b_i = b_i(\beta_B)$$

Background: noise, diffuse scattering, ...

## Simplified methods for treating the intrinsic profile as implemented in FullProf

The method of Warren-Averbach, based in the Fourier series representing the intrinsic profile of a powder diffraction peak, has drawbacks when overlap is strong. Moreover, not enough statistics make the de-convolution method extremely unstable

$$\beta(\text{size}) = \frac{\lambda}{D \cos \theta}$$
$$\beta(\text{strain}) = 4e \tan \theta$$

**Integral breadth methods, combined with an analytical approximation for  $f$ ,  $g$  and  $\Omega$ , are, by far, much more simple and robust: strain and size parameters are volume averaged quantities**

# Broadening due to size effects

The intrinsic profile of a particular reflection due to size effect has an integral breadth  $\beta_S$ , the Scherrer formula:

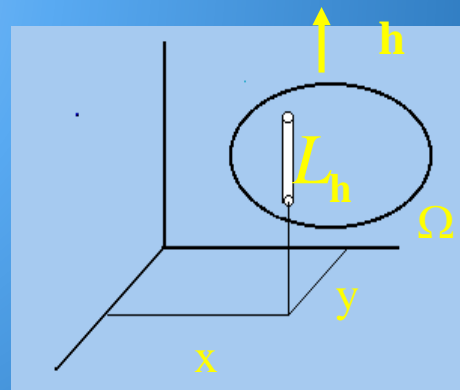
$$\langle D \rangle_V = \frac{\lambda}{\beta_S \cos \theta} = \frac{1}{\beta_S^*}$$

gives the volume-averaged apparent size of the crystallites in the direction normal to the scattering planes. This apparent size has a perfectly defined physical interpretation:

$$\langle D \rangle_V = \frac{1}{N} \sum_{i=1, \dots, N} \frac{1}{V_i} \iiint_{C_i} L_{\mathbf{h}}(x, y) d^3 \mathbf{r}$$

in terms of the normalized column-length distribution  $p_V(L)$ :

$$\langle D \rangle_V = \int_0^{\infty} L p_V(L) dL$$





# Size effects in reciprocal space: powder case

$$A_S(0) = 1 = \int_0^\infty p_V(L) dL$$

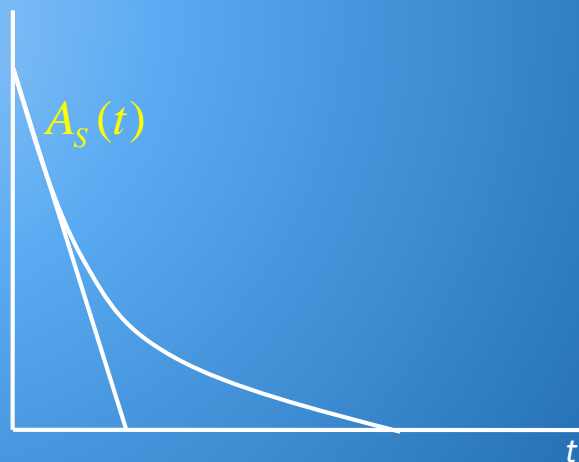
$$A_S(t) = \int_0^\infty \left(1 - \frac{|t|}{L}\right) p_V(L) dL$$

$$\left. \frac{dA_S(t)}{dt} \right|_{t=0} = -\frac{1}{V} \int d\sigma = -\frac{1}{\bar{D}_S}$$

*Surface Averaged column length*  $\bar{D}_S$ : height of a cylinder of section equal to the projection of the grain perpendicular to planes  $(hkl)$  having the same volume as the grain

Normalised column-length distribution

$$p_V(L) = L \left( \frac{d^2 A_S(t)}{dt^2} \right)_{t=L}$$



# The Voigt Function

$$V(x) = V_1(x) \otimes V_2(x)$$

The Voigt function has proven to be a very good experimental approximation in many cases (I. Langford)

$$\beta_L = \beta_{1L} + \beta_{2L}$$

Lorentzian breadths simply have to be summed

$$\beta_G^2 = \beta_{1G}^2 + \beta_{2G}^2$$

Gaussian breadths have to be summed quadratically

$$\beta_{fL} = \beta_{hL} - \beta_{gL}$$

$$\beta_{fG}^2 = \beta_{hG}^2 - \beta_{gG}^2$$

Correction for instrumental broadening  
(‘Double Voigt’, D. Balzar)

# Column lengths distributions when using Voigt functions for approximating the line profile

$$p_V(L) = L \left( \frac{d^2 A_S(t)}{dt^2} \right)_{t=L}$$

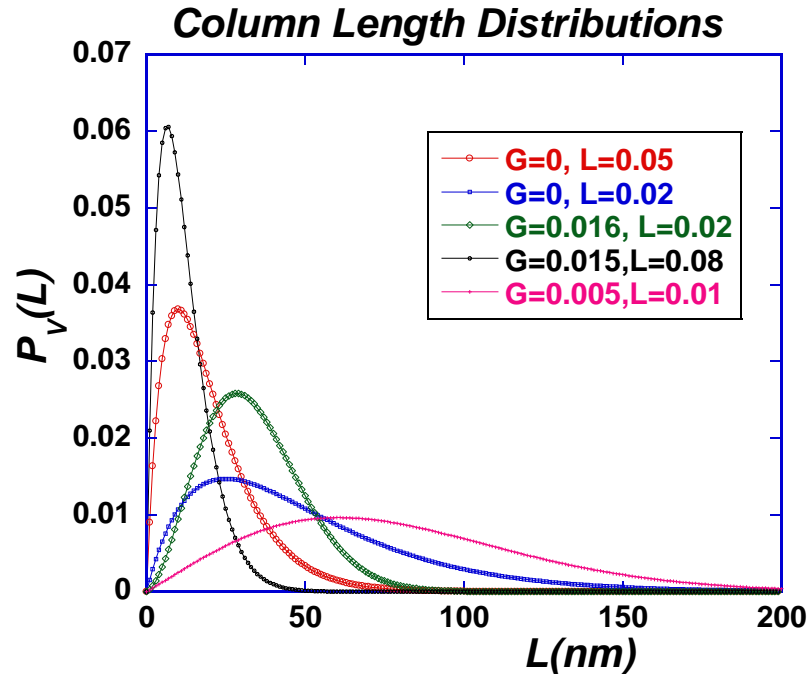
Fourier size coefficients corresponding to the Voigt function

$$A_S(t) = \int i(s_0) e^{-2\pi i s_0 t} ds_0 = FT^{-1}\{V(s_0)\} = \exp\{-2t\beta_L - \pi\beta_G^2 t^2\}$$

Normalised distribution of column lengths

$$p_V(L) = 2L[2\beta_L^2 - \pi\beta_G^2 + 4\pi\beta_L\beta_G^2 L + 2\pi^2\beta_G^4 L^2] \exp\{-2L\beta_L - \pi\beta_G^2 L^2\}$$

# Column lengths distributions when using Voigt functions for approximating the line profile



Size distributions corresponding to Voigt profiles are quite flexible and are positive for all lengths provided that:

$$\beta_L > \sqrt{\frac{\pi}{2}} \beta_G \approx 1.25332 \beta_G$$

# Definitions of strain in microstructural analysis

⇒ The apparent strain was defined by Wilson as the quantity:

$$\eta_{\beta} = \beta_D \cot \theta$$

⇒ The so-called maximum strain is related to the apparent strain by the relation:

$$e = \frac{\Delta d}{d} = \frac{\eta}{4} = \frac{1}{2} \beta_D d = \frac{\beta_D}{2s}$$

⇒ Local average strain:  $\varepsilon(L) = \Delta L / L$  between two cells separated a distance  $L$  along a column perpendicular to  $(hkl)$  planes

⇒ Root mean square strain:

$$e_{rms} = \langle \varepsilon^2(L) \rangle^{1/2}$$

For a Gaussian distribution  $e \approx 5/4 e_{rms}$

See chapter 7 of ***Microstructure Analysis from Diffraction*** by Davos Balzar

# Definitions of strain in microstructural analysis

$$A_D(\mathbf{R}_n, \mathbf{s}) = \langle \exp\{2\pi i \mathbf{s} (\mathbf{u}_m - \mathbf{u}_{m+n})\} \rangle$$

Local average strain:  $\varepsilon(L) = \Delta L / L$  between two cells separated a distance  $L$  along a column perpendicular to  $(hkl)$  planes

$$A_D(L, s) = \langle \exp\{2\pi i s \Delta L\} \rangle = \langle \exp\{2\pi i s L \varepsilon(L)\} \rangle$$

$$A_D(L, s) = \langle \exp\{2\pi i s L \varepsilon(L)\} \rangle \approx \exp\{-2\pi^2 s^2 L^2 \langle \varepsilon^2(L) \rangle\}$$

$$f_{hkl}(s) \approx \int_{L=0}^{L=\infty} A_D(L, s_{hkl}) \exp\{2\pi i s L\} dL$$

## Definitions of strain in microstructural analysis

Local average strain:  $\varepsilon(L) = \Delta L / L$  between two cells separated a distance  $L$  along a column perpendicular to  $(hkl)$  planes

$$A_D(L, s) = \langle \exp\{2\pi i sL \varepsilon(L)\} \rangle \approx \exp\{-2\pi^2 s^2 L^2 \langle \varepsilon^2(L) \rangle\}$$

$$A_D(L, s) = FT^{-1}\{f_{hkl}(s)\} = FT^{-1}\{V(s)\} = FT^{-1}\{L(s) \otimes G(s)\}$$

$$A_D(L, s) = FT^{-1}\{L(s)\}FT^{-1}\{G(s)\} = \exp\{-2L\beta_{LD}\} \exp\{-\pi L^2 \beta_{GD}^2\}$$

$$2\pi^2 s^2 L^2 \langle \varepsilon^2(L) \rangle = 2L\beta_{LD} + \pi L^2 \beta_{GD}^2$$

$$\langle \varepsilon^2(L) \rangle = \frac{1}{s^2} \left( \frac{\beta_{LD}}{\pi^2 L} + \frac{\beta_{GD}^2}{2\pi} \right)$$



# Simplified methods for treating the intrinsic profile as implemented in FullProf

Parameters controlling the Full-Width at half maximum (isotropic case)

$U, V, W, I_G, X, Y$

$$h(x) = g(x) \otimes f(x)$$

$$H_{hG}^2 = (U_g + U_f) \tan^2 \theta + V_g \tan \theta + W_g + \frac{I_{fG}}{\cos^2 \theta}$$

$$H_{hL} = (X_g + X_f) \tan \theta + \frac{Y_g + Y_f}{\cos \theta}$$

# Simplified methods for treating the intrinsic profile as implemented in FullProf

General  $2\theta$  dependence of the instrumental broadening (determined by a standard sample)

$$H_{hG}^2 = (U_f + (1 - \xi_f)^2 D_{fST}^2(\alpha_D)) \tan^2 \theta + \frac{I_{fG}}{\cos^2 \theta} + H_{gG}^2$$
$$H_{hL} = (X_f + \xi_f D_{fST}(\alpha_D)) \tan \theta + \frac{[Y_f + F_f(\alpha_S)]}{\cos \theta} + H_{gL}$$

The Gaussian and Lorentzian components of the instrumental Voigt function are interpolated between empirically determined values.

If needed, axial divergence is convoluted numerically with the resulting profile.

# Anisotropic strains

Phenomenological model: strains considered as fluctuations and correlation between metric parameters

J. Rodríguez-Carvajal, M.T. Fernández-Díaz and J.L. Martínez  
J. Phys. Cond. Matt. **3**, 3215 (1991)

$$M_{hkl} = \frac{1}{d_{hkl}^2} = M(\alpha_i; hkl)$$

The metric parameters  $\alpha_i$  (direct, reciprocal or any combination) are considered as stochastic variables with a Gaussian distribution characterized by:

- the mean  $\langle \alpha_i \rangle$  and
- the variance-covariance matrix  $C_{ij}$

# The mean and the variance of the function

$M_{hkl}$  are given by :

$$\langle M_{hkl} \rangle = M(\langle \alpha_i \rangle; hkl)$$

$$\sigma^2(M_{hkl}) = \sum_{i,j} C_{ij} \frac{\partial M}{\partial \alpha_i} \frac{\partial M}{\partial \alpha_j}$$

$C_{ij}$  contains 21 parameters,  
15 independent

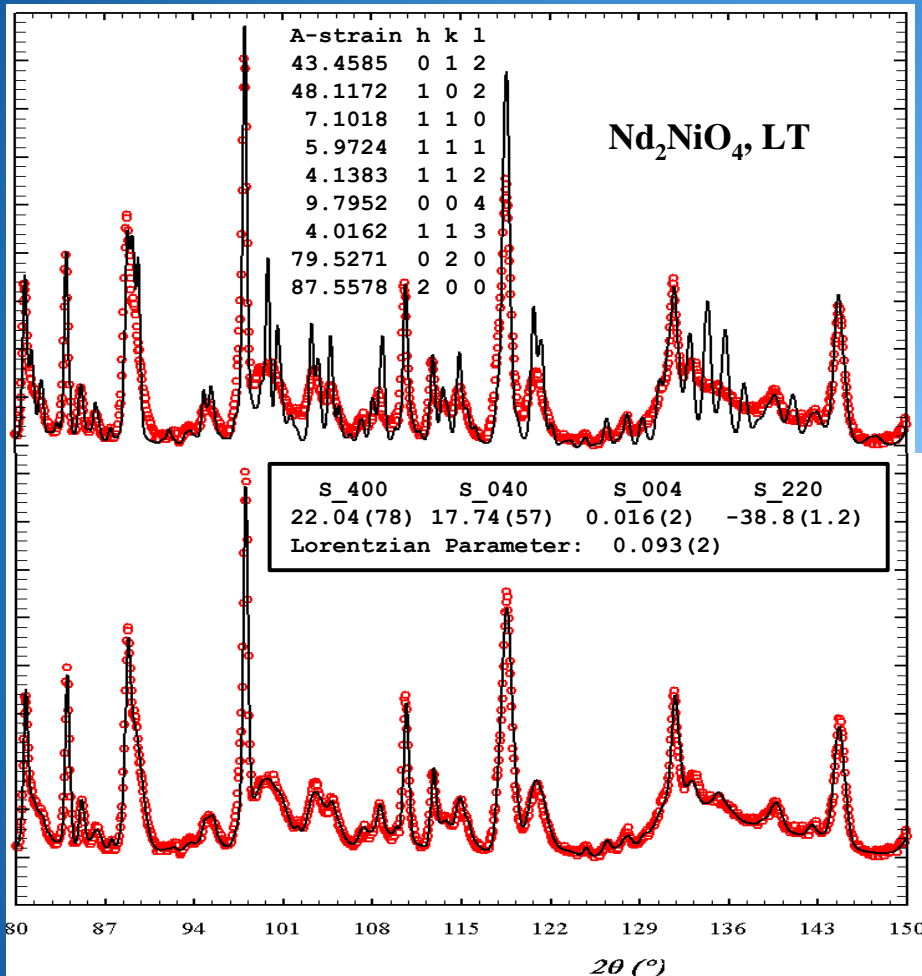
If the metric parameters are taken as the coefficients of the quadratic form:

$$\frac{1}{d_{hkl}^2} = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk$$

$$\sigma^2(M_{hkl}) = \sum_{\substack{HKL \\ \{H+K+L=4\}}} S_{HKL} h^H k^K l^L$$

$$\{\alpha_i\} = \{A, B, C, D, E, F\}$$

P. W. Stephens,  
J. Appl. Cryst. 32, 281 (1999)



Example of microstrain generated after a series of phase transitions

# Different models to simulate the average shape of crystallites

Ellipsoidal shapes of crystallites .

$$\frac{1}{D_h} = k_s d_h^2 (\alpha_1 h^2 + \alpha_2 k^2 + \alpha_3 l^2 + 2\alpha_4 hk + 2\alpha_5 hl + 2\alpha_6 kl)$$

Arbitrary shapes of crystallites can be simulated using spherical harmonics.

$$\frac{1}{D_h} = \sum_{lmp} a_{lmp} P_{lm} (\cos \Theta_h) \begin{cases} \cos m\Phi_h \\ \sin m\Phi_h \end{cases}; \quad p = + / -$$

$$\beta_s = \frac{\lambda}{\cos \theta} \sum_{lmp} a_{lmp} P_{lm} (\cos \Theta_h) \begin{cases} \cos m\Phi_h \\ \sin m\Phi_h \end{cases}$$

Volume averaged shape of crystallites is obtained from the refined parameters

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# The knowledge of your diffractometer is crucial for the success of Rietveld refinement

If you have a Bragg-Brentano diffractometer take the diffraction pattern of a standard sample not having size or strain broadening (e.g.  $\text{LaB}_6$  from NIST). The diffraction pattern should be taken in exactly the same conditions as your problem sample.

You can prepare your own standard if you are able to prepare a sample with similar absorption coefficient as your problem sample and very good crystallinity.

For capillary samples  $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$  (NAC or Nacalf, from Le Mans, France) is appropriate.

# How to create IRF files

Collect a powder diffraction pattern of the standard sample: for different conditions of the diffractometer (combination of slits) a new diffraction pattern is needed

Analyze the diffraction pattern determining the peak shape parameters that have to be stored in the IRF file:

1: Individual peak refinements (List of  $H_G$  and  $H_L$  for each peak Res=4, 8)

2: Le Bail fits

$(U_{ins}, V_{ins}, W_{ins}, X_{ins}, Y_{ins})$  Res=1

3: Rietveld refinement

# The format of the file containing the Instrumental Resolution Function

The instrumental resolution function file may contain keywords that change some variables in the input PCR file if they are used. Now it is possible to read an IRF file for other profiles than NPROF=7.

The most simple format for the case RES  $\neq$  4,8 is the following:

**Line 1:** General title

**Next lines** containing ! are comments

**Lines containing one of the keywords:**

**JOBT, WAVE, PROF, ASYM** (order does not matter)

**One or two lines** containing the variables (see manual):  $U_{ins}$ ,  $V_{ins}$ ,  $W_{ins}$ ,  $X_{ins}$ ,  $Y_{ins}$

In case of two lines the second corresponds to instrumental parameters for the second wavelength.

# The format of the file containing the Instrumental Resolution Function

The keywords in the IRF are accompanied by values as follows:

1: **JOBT** **job** (character variable)

with **job** = 'neuc' or 'NEUC' for **jobtyp** = 3

**job** = 'neut' or 'NEUT' for **jobtyp** = 1

**job** = 'tof' or 'TOF' for **jobtyp** = -1

**job** = 'tofc' or 'TOFC' for **jobtyp** = -3

**job** = 'xr' or 'XR' for **jobtyp** = 0

**job** = 'xrc' or 'XRC' for **jobtyp** = 2

2: **WAVE** **lambda1, lambda2, ratio** (three real values)

3: **PROF** **nprofile, shape1, shape2, shape3** (1 integer and 3 real numbers)

4: **ASYM** **S\_L, S\_D** (two real numbers)

# How to work with FullProf when microstructural effects are important

- Select profile function: `NPROF=7`, TCH pVoigt function convoluted with axial divergence
- Reference sample data analysis → Instrumental Resolution Function (create an IRF file)
- Broad pattern analysis: IRF is fixed through `RES` parameter and read in the `FILERES` file
- Use FullProf with IRF (`RES/=0`), putting to zero all profile parameters
- Select a model for microstructure and refine only the profile parameters related to the sample
- The program generates micro-structural files with all the relevant information concerning size and strain parameters

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# Battery materials: Ni-hydroxides



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)



Journal of Power Sources 174 (2007) 414–420

JOURNAL OF  
**POWER  
SOURCES**

[www.elsevier.com/locate/jpowsour](http://www.elsevier.com/locate/jpowsour)

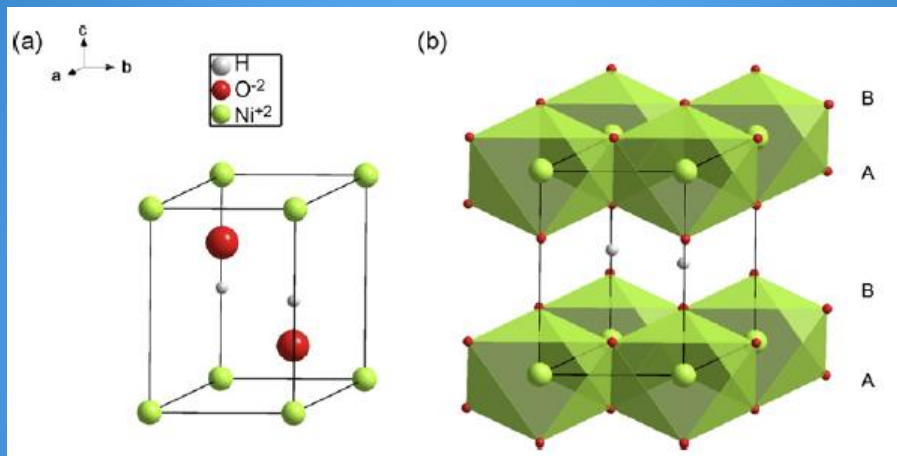
Microstructural characterisation of battery materials using powder diffraction data: DIFFaX, FAULTS and SH-FullProf approaches

M. Casas-Cabanas<sup>a</sup>, J. Rodríguez-Carvajal<sup>b</sup>, J. Canales-Vázquez<sup>a</sup>,  
Y. Laligant<sup>c</sup>, P. Lacorre<sup>c</sup>, M.R. Palacín<sup>a,\*</sup>

**A comparison of conventional Rietveld refinement completed with microstructural analysis and the more sophisticated method implemented in DIFFaX and FAULTS**

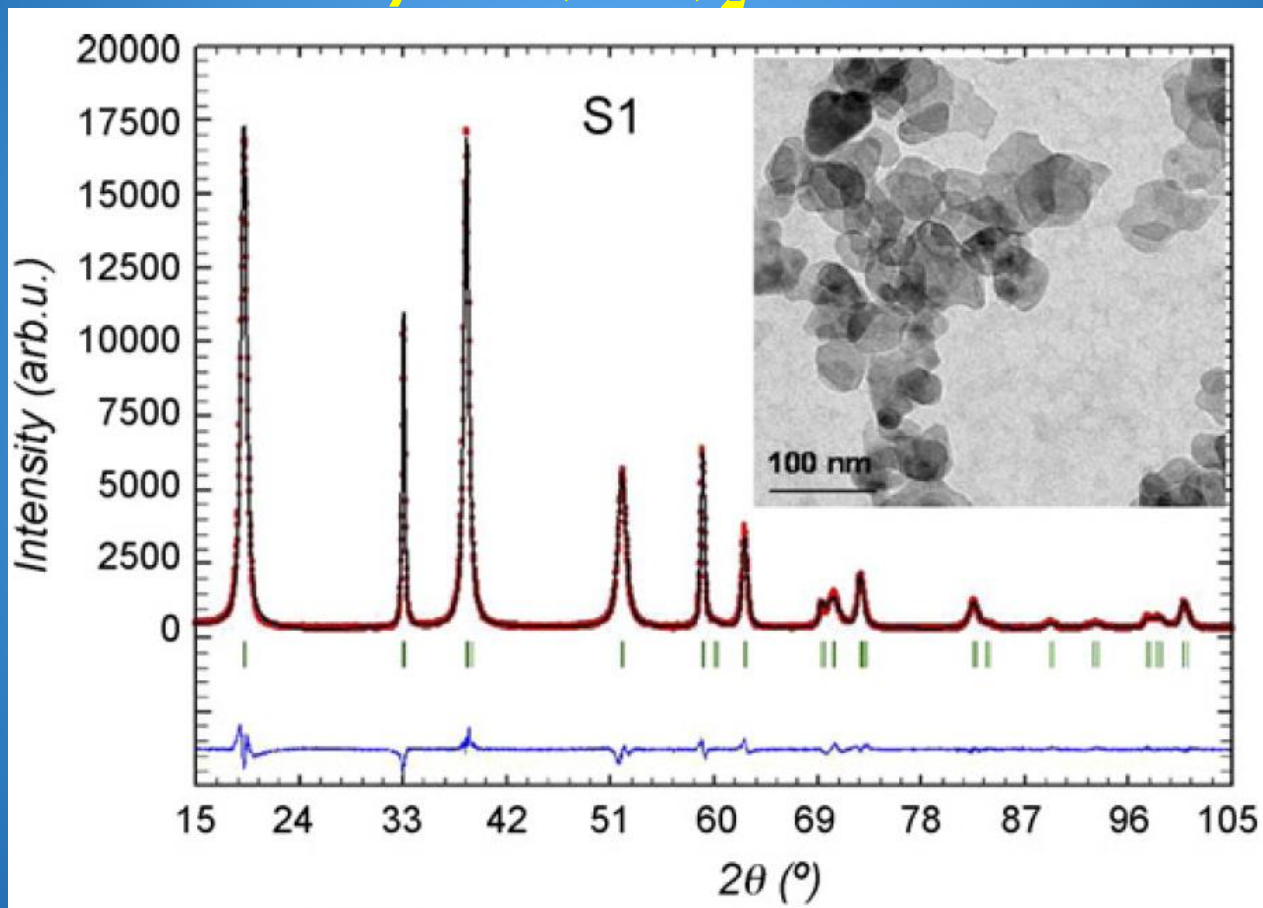


# Structure of $\beta$ -Ni(OH)<sub>2</sub>

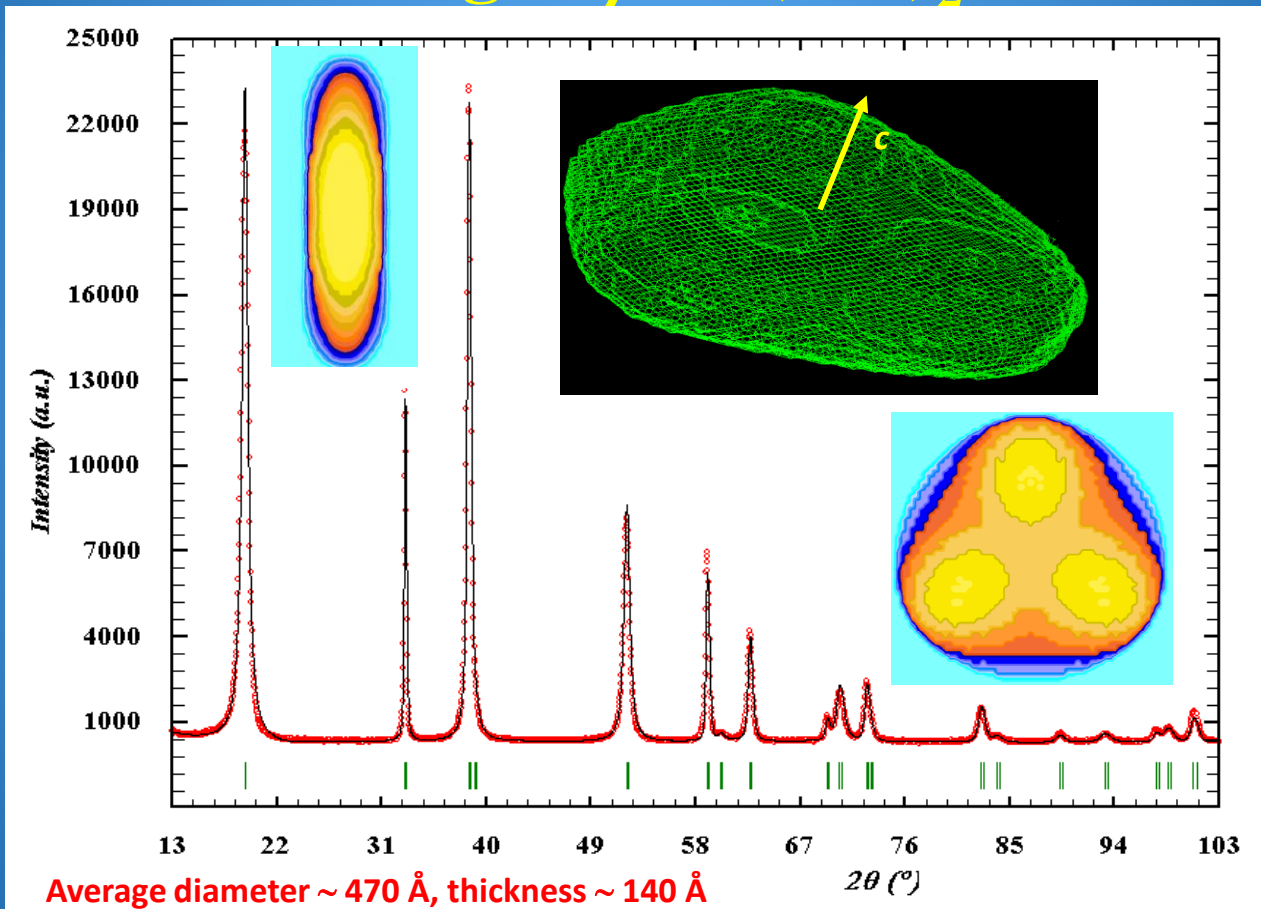


$\beta$ -Ni(OH)<sub>2</sub>:  $a=3.13\text{\AA}$ ,  $c=4.61\text{\AA}$ , SPG:  $P\bar{3}m1$

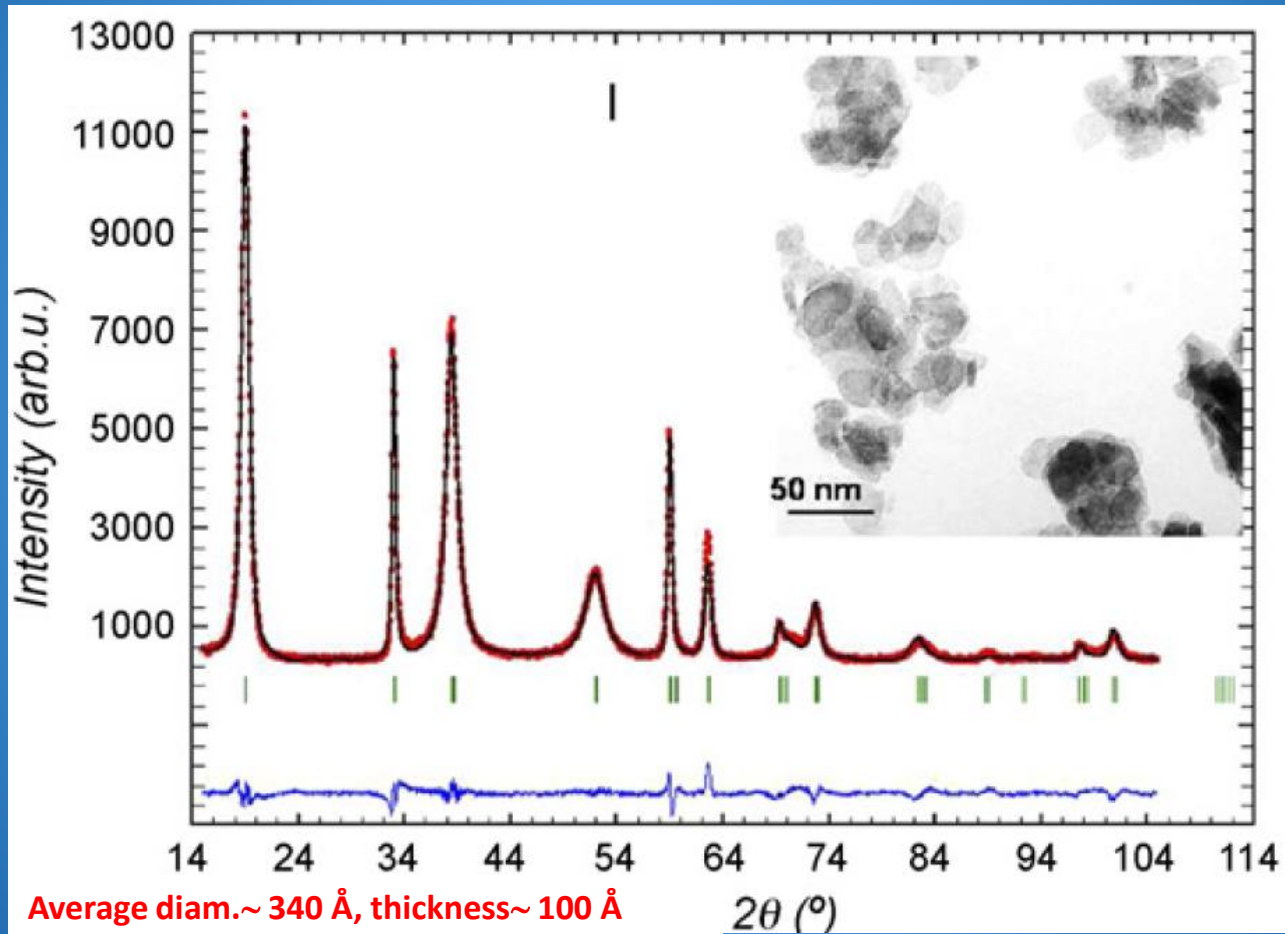
# Structure of $\beta$ -Ni(OH)<sub>2</sub>



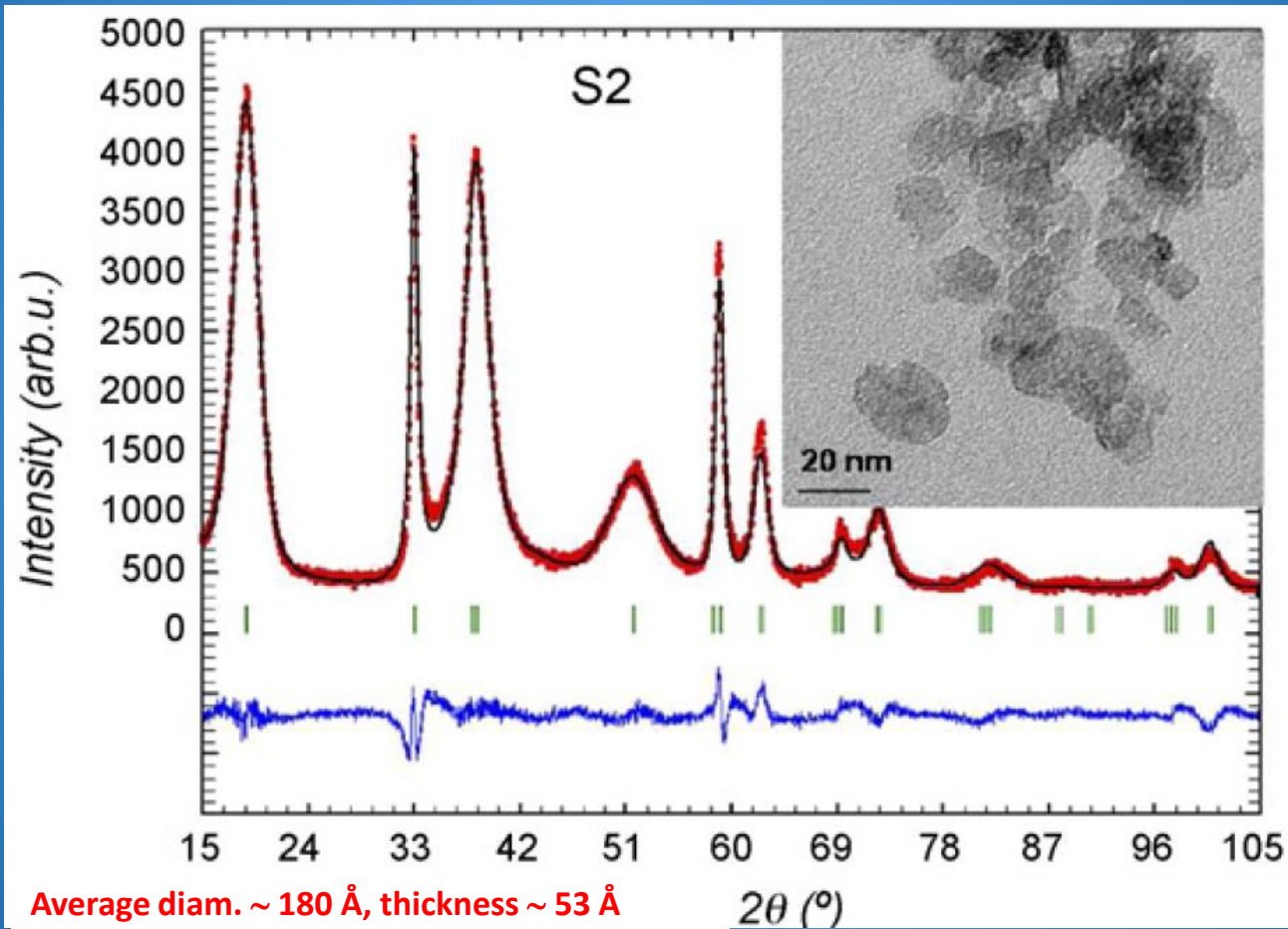
# Size broadening in $\beta$ -Ni(OH)<sub>2</sub>



## Size broadening in $\beta$ -Ni(OH)<sub>2</sub>



## Size broadening in $\beta$ -Ni(OH)<sub>2</sub>



# $\beta$ -NiOOH in batteries: nanopowders

J|A|C|S  
COMMUNICATIONS

Published on Web 04/14/2007

## Deciphering the Structural Transformations during Nickel Oxyhydroxide Electrode Operation

Montse Casas-Cabanas,<sup>†</sup> Jesús Canales-Vázquez,<sup>†</sup> Juan Rodríguez-Carvajal,<sup>‡</sup> and M. Rosa Palacín<sup>\*†</sup>

*Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB E-08193 Bellaterra, Catalonia, Spain, and Institut Max Von Laue-Paul Langevin, BP 156 Grenoble Cedex 9, F-38042 France*

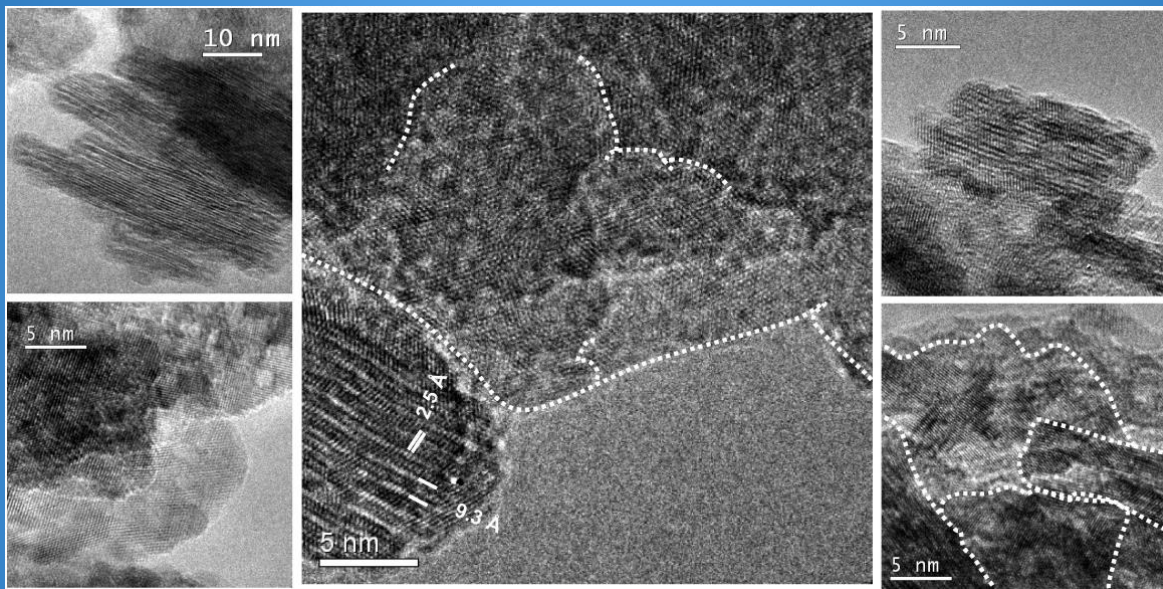
**An example of structure determination applying approximate conventional methods:**

$\beta$ -Ni(OH)<sub>2</sub>:  $a=3.13\text{\AA}$ ,  $c=4.61\text{\AA}$ , SPG:  $P\bar{3}m1$

**After oxidation of  $\beta$ -Ni(OH)<sub>2</sub> to  $\beta$ -NiOOH, the original crystallites break into nano-domains**

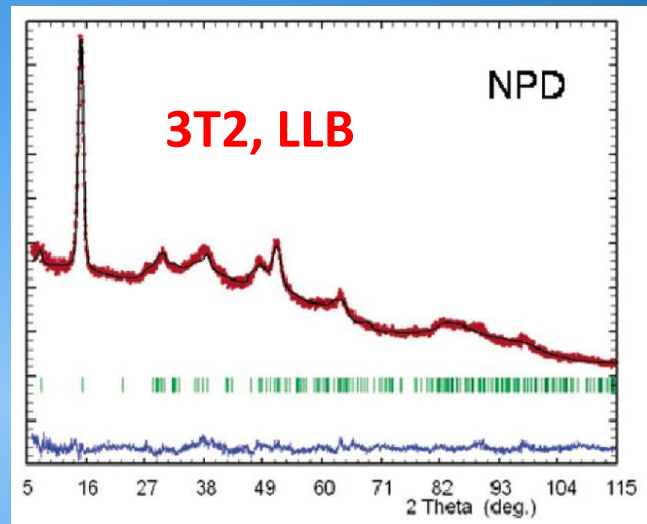
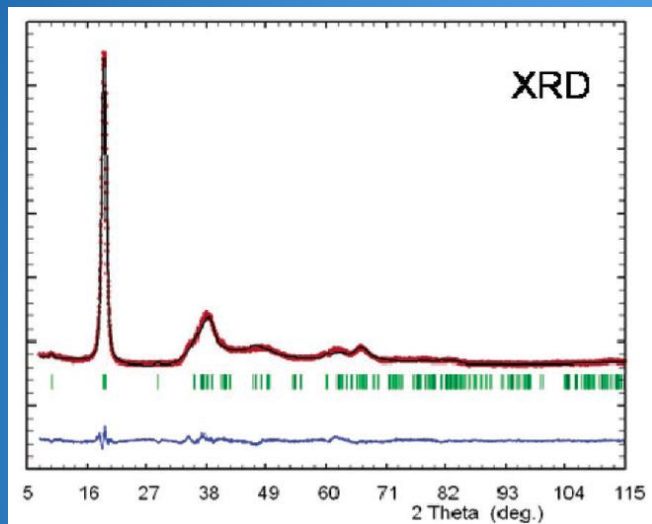


# $\beta$ -NiOOH in batteries: nanopowders



The nano-domain structure of particles, as well as micro-strains and the doubling of periodicity along the stacking direction is seen clearly in the central image

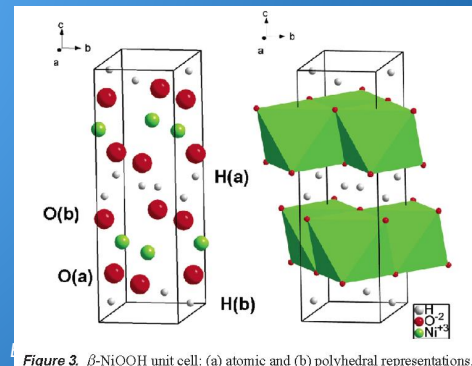
# $\beta$ -NiOOH in batteries: nanopowders



Joint refinements considering ABCA stacking models and common micro-structural parameters: ellipsoidal average crystallites + anisotropic strains (spherical harmonics)

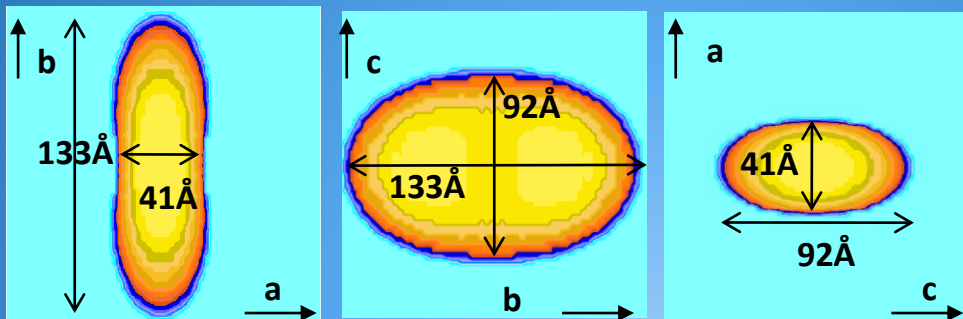
$a=4.883(5)\text{\AA}$ ,  $b=2.920(8)\text{\AA}$ ,  $c=9.24(1)\text{\AA}$ ,  $\beta=88.8(1)^\circ$ ,

SPG:  $C2/m$

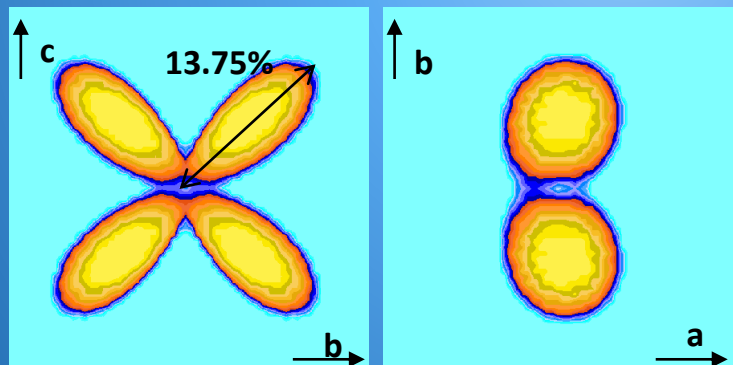




# $\beta$ -NiOOH in batteries: nanopowders

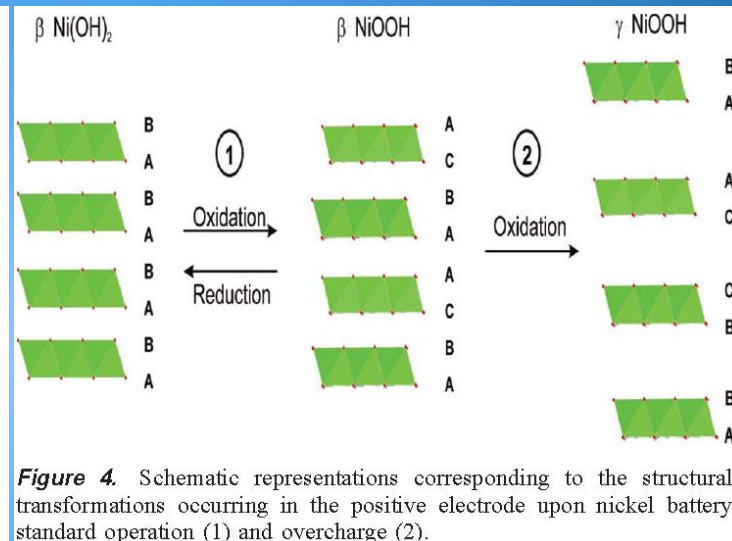
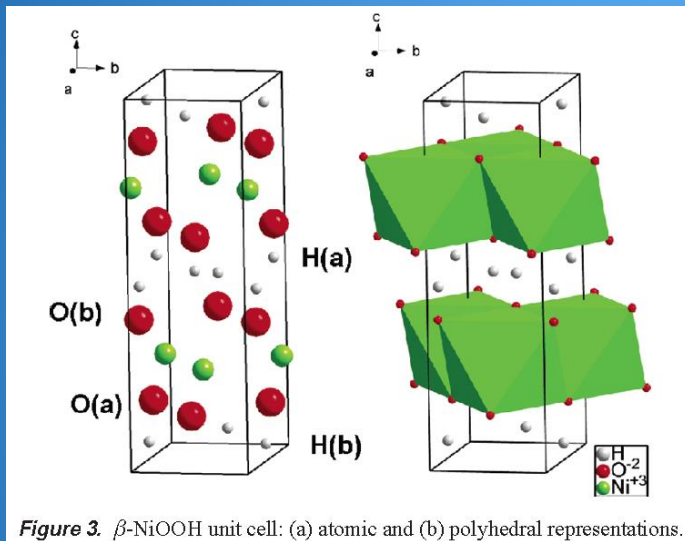


Apparent average shape



Anisotropic strain

# $\beta$ -NiOOH in batteries: nanopowders



Details of the oxidation-reduction process between  $\beta$ -Ni(OH)<sub>2</sub> and  $\beta$ -NiOOH and the over-oxidation giving rise to irreversible formation of  $\gamma$ -NiOOH

## Example of size effects characterised using FullProf

DOI: 10.1021/cg901441p

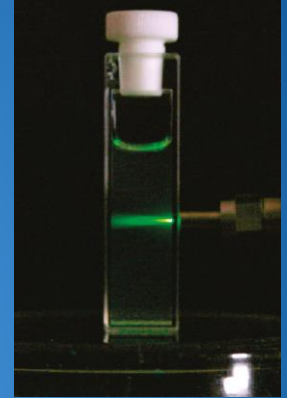
### Synthesis and Characterization of Upconversion Fluorescent Yb<sup>3+</sup>, Er<sup>3+</sup> Doped RbY<sub>2</sub>F<sub>7</sub> Nano- and Microcrystals

Helmut Schäfer,\* Pavel Ptacek, Benjamin Voss, Henning Eickmeier, Jörg Nordmann, and Markus Haase

*University of Osnabrück, Institute of Chemistry, Barbarastrasse 7, D-49069 Osnabrück, Germany*

CRYSTAL  
GROWTH  
& DESIGN  
Article

2010, Vol. 10  
2202-2208



Lanthanide-doped RbY<sub>2</sub>F<sub>7</sub> nanocrystals synthesized at 185° C in the high boiling organic solvent N-(2-hydroxyethyl)-ethylenediamine (HEEDA) using ammonium fluoride, rare earth chlorides, and a solution of rubidium alkoxide of N-(2-hydroxyethyl) ethylenediamine in HEEDA as precursors.

Microwave synthesis gives larger crystallites.

Heat-treatment of these nano-crystals (600° C for 45 min) led to bulk material which shows highly efficient light emission upon continuous wave (CW) excitation at 978 nm.

# RbY<sub>2</sub>F<sub>7</sub>: synthesis from nanocrystals

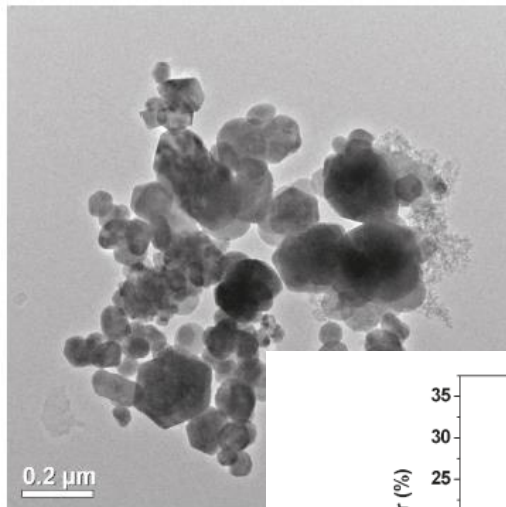
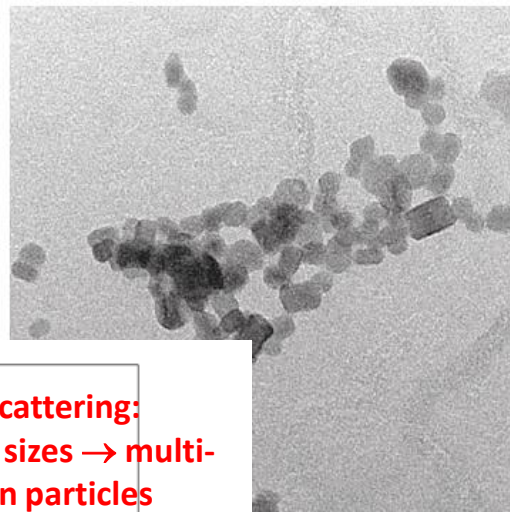


Figure 3. TEM image of RbY<sub>2</sub>F<sub>7</sub> nanocrystals generated in the micelle.



RbY<sub>2</sub>F<sub>7</sub>:78% Y, 20% Yb, 2.0% Er  
A.

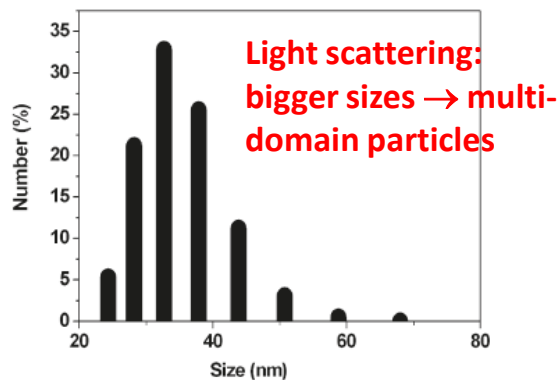
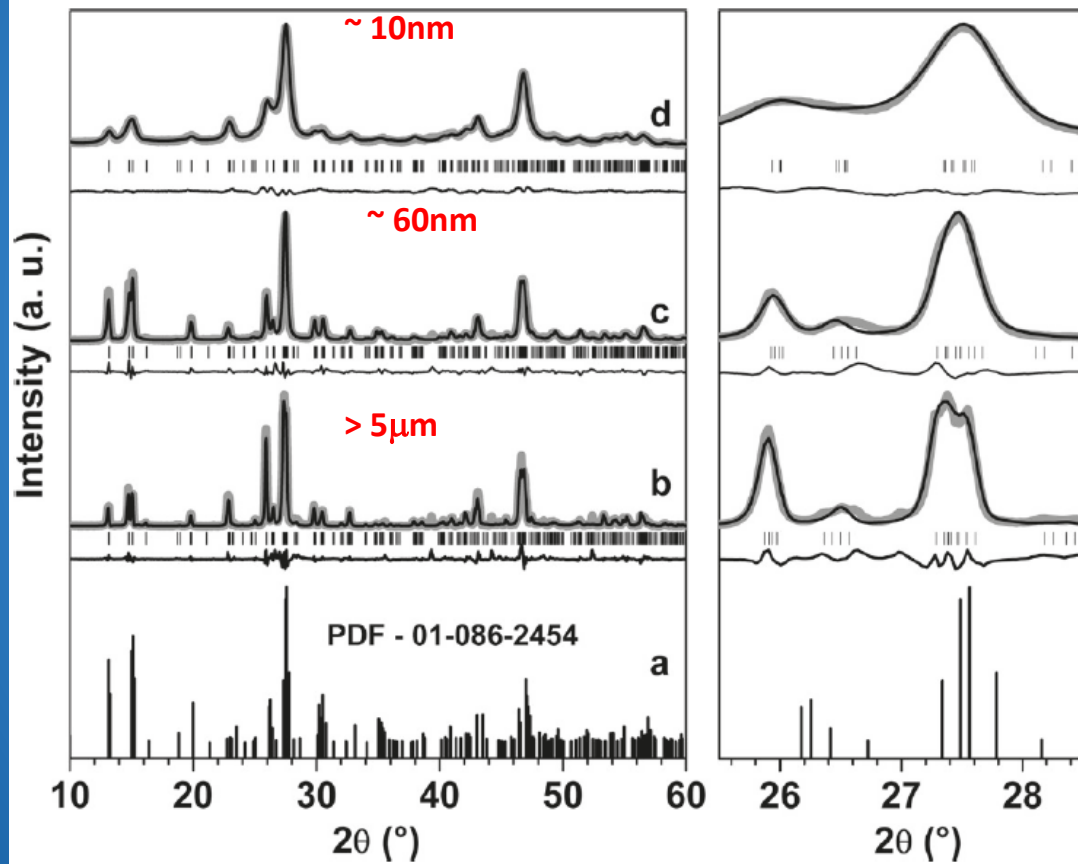


Figure 5. Characterization by dynamic light scattering: particle size and size distribution of RbY<sub>2</sub>F<sub>7</sub>:78% Y, 20% Yb, 2.0% Er nanocrystals (HEEDA synthesis) in 2-propanol.

# RbY<sub>2</sub>F<sub>7</sub>: different stages in synthesis

*Crystal Growth & Design*, Vol. 10, No. 5, 2010 2203



Crystal structure solved by isomorphism with KEr<sub>2</sub>F<sub>7</sub>:

$a=11.97 \text{ \AA}$   
 $b=13.46 \text{ \AA}$   
 $c=7.7 \text{ \AA}$

SPG: *Pnam*



# LnPO<sub>4</sub> (Ln:La, Eu) nanoparticles

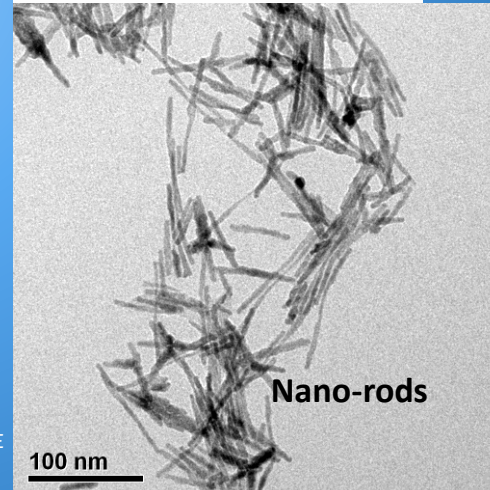
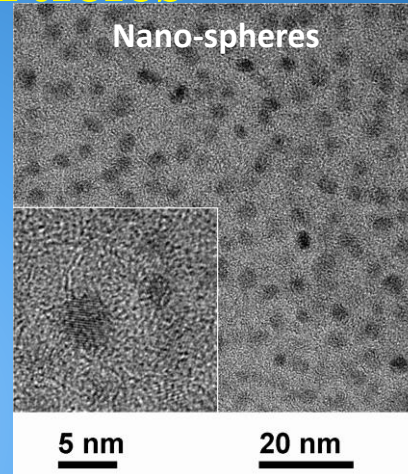
Helmut Schafer, et al. (2011)

Lanthanide phosphates are unique class of materials having versatile properties such as high temperature stability, chemically inertness, catalytic and photoluminescence. Bulk and nanosize lanthanide phosphates have been found to act as excellent host/matrices for lanthanides and the optical properties of these NPs can also be tuned by the lanthanide dopants.

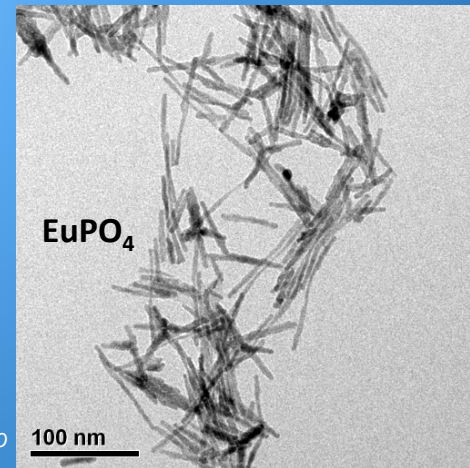
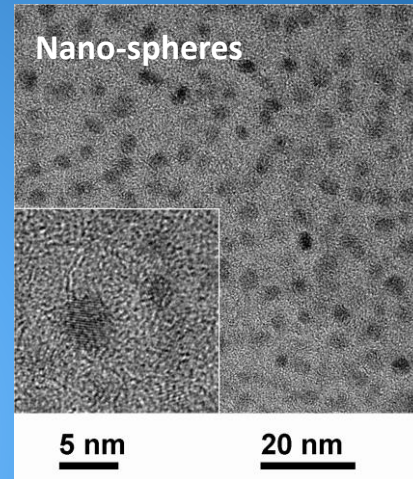
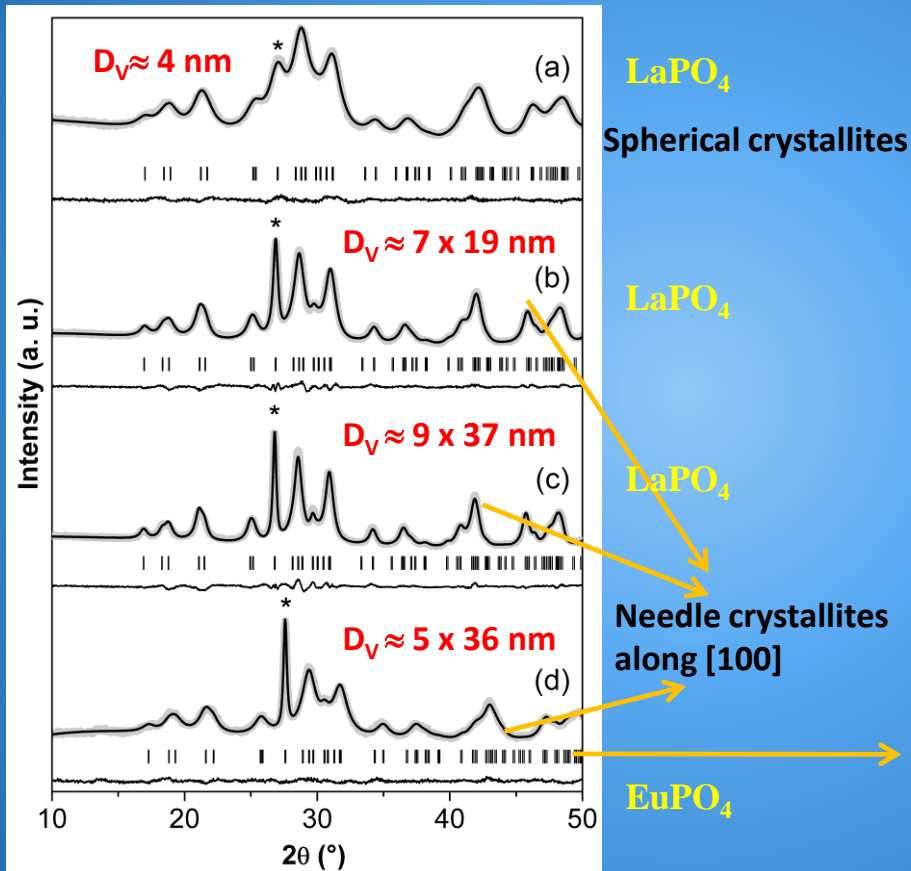
Notable examples of demonstrated applications include field-effect transistors (FETs), light-emitting diodes (LEDs), single-electron transistors, biological and chemical sensors, photo-detectors, electron emitters, and ultraviolet lasers

Example: EuPO<sub>4</sub>

P 2<sub>1</sub>/n, a ≈ 6.66Å, b ≈ 6.89Å, c ≈ 6.37Å, β=104,05°



# LnPO<sub>4</sub> (Ln:La, Eu) nanoparticles



# Microstructure helps to solve the crystal structure ...

**Example: Refinement of a TaOF<sub>3</sub> sample  
(from MPI Stuttgart)**

**The data were collected in a powder  
diffractometer using Debye-Scherrer geometry**

with

**Neutrons:  $b(\text{O})=b(\text{F})$**

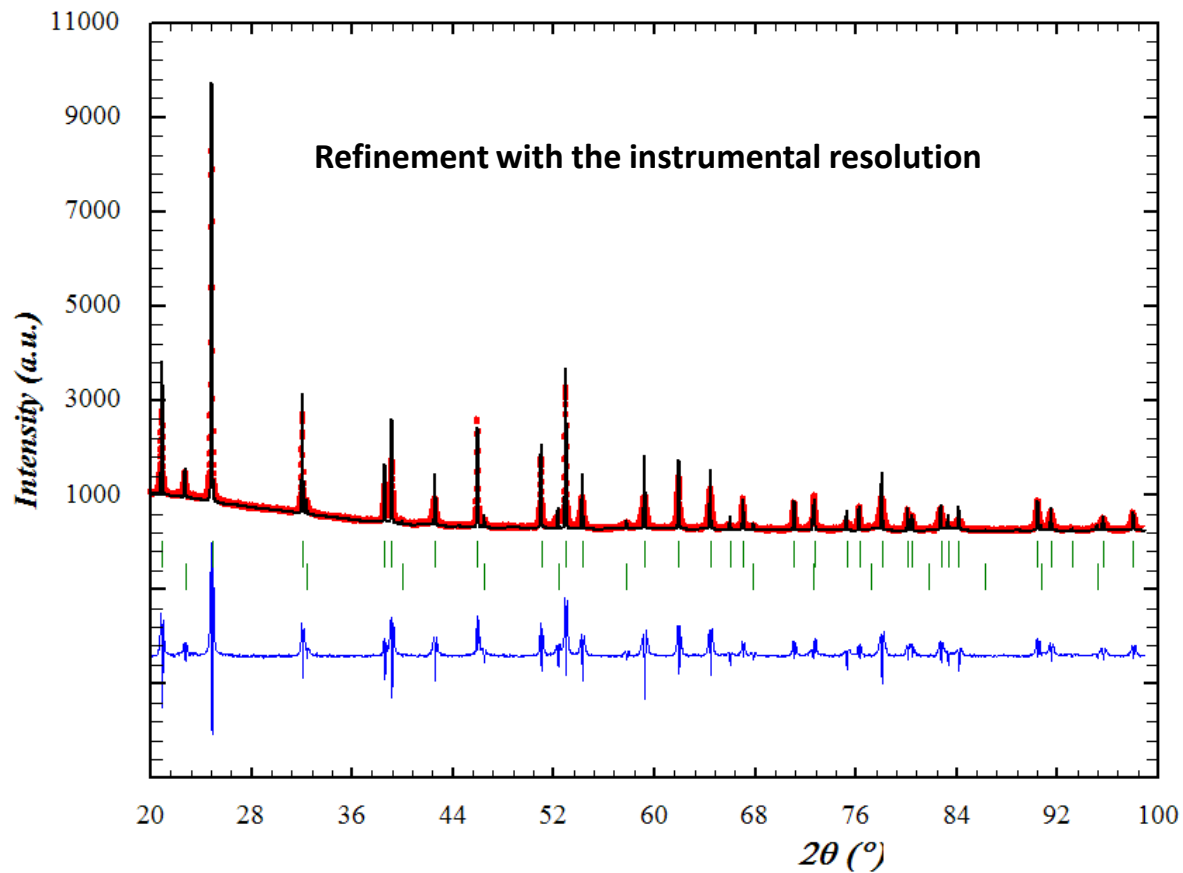
**$\text{K}_{\alpha 1}$**

**X-rays:  $f(\text{O})=f(\text{F})$**

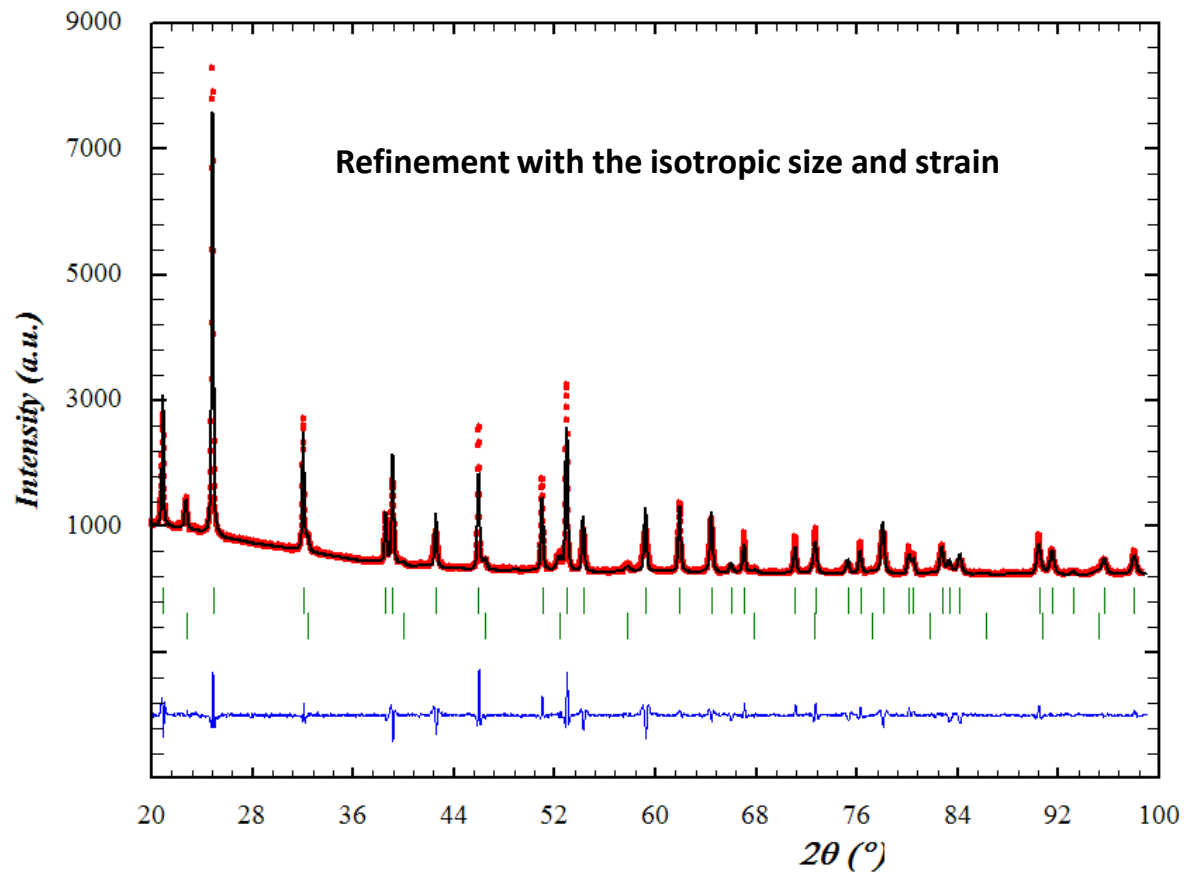
**Data reduction: the diffraction pattern has been  
presumably smoothed using a Fourier filtering)  
The sample presents anisotropic peak broadening**



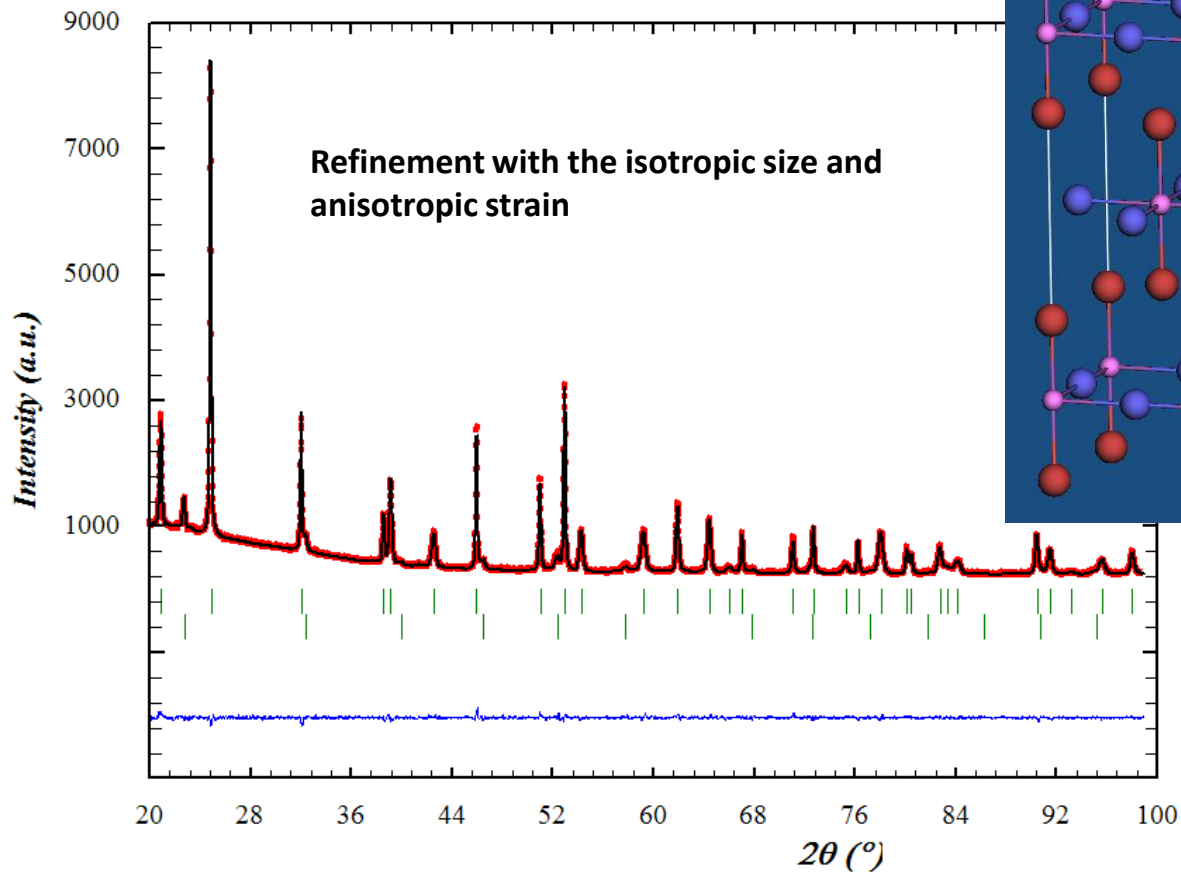
# TaOF<sub>3</sub> d=0.02 mm / Cu



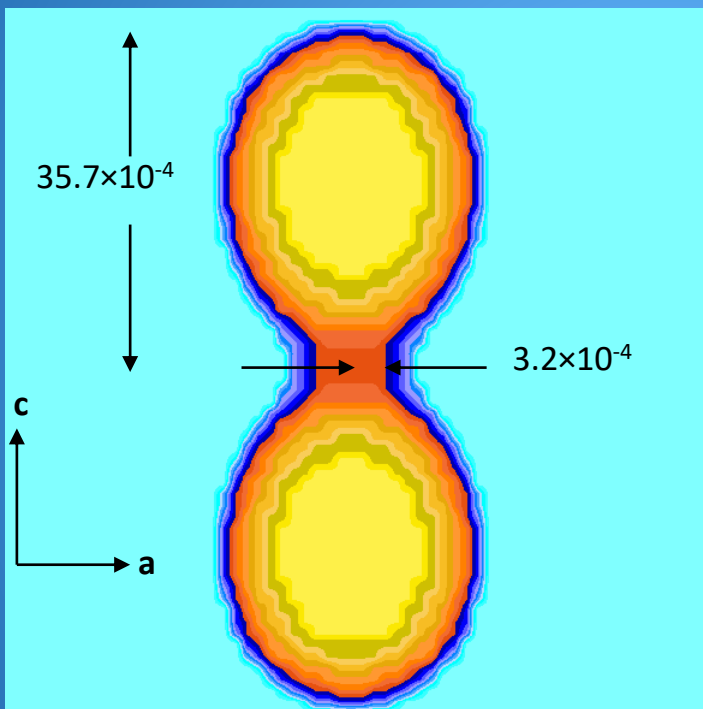
# TaOF<sub>3</sub> d=0.02 mm / Cu



TaOF3 d=0.02 mm / Cu



# Microstructure helps to solve the crystal structure ...

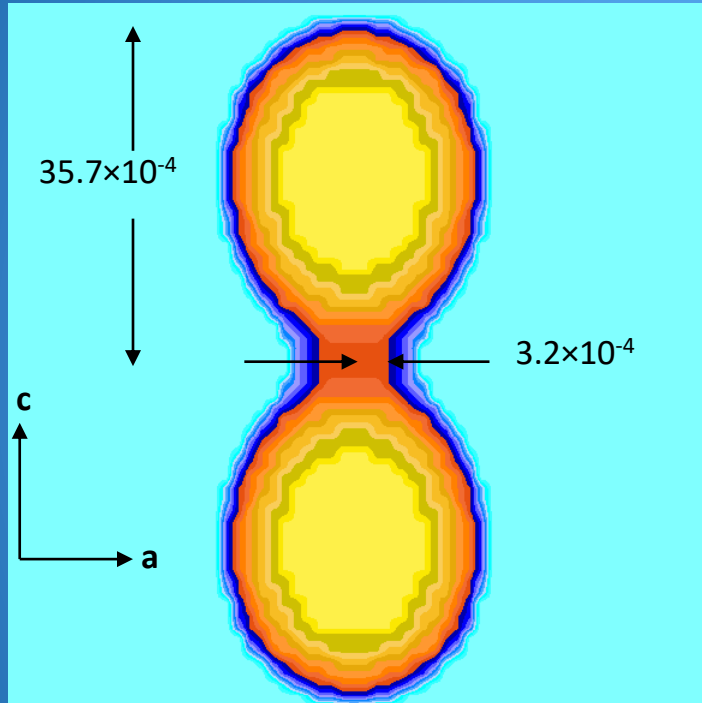


Apparent size: 848 Å  
(isotropic)

Average max. strain: 17.7×10<sup>-4</sup>  
Anisotropy : 10.5×10<sup>-4</sup>

TaOF<sub>3</sub>  
*I4/mmm*,  $a=3.945$  Å,  $c=8.486$  Å

# Microstructure helps to solve the crystal structure ...



TaOF<sub>3</sub>

$I4/mmm$ ,  $a=3.945 \text{ \AA}$ ,  $c=8.486 \text{ \AA}$

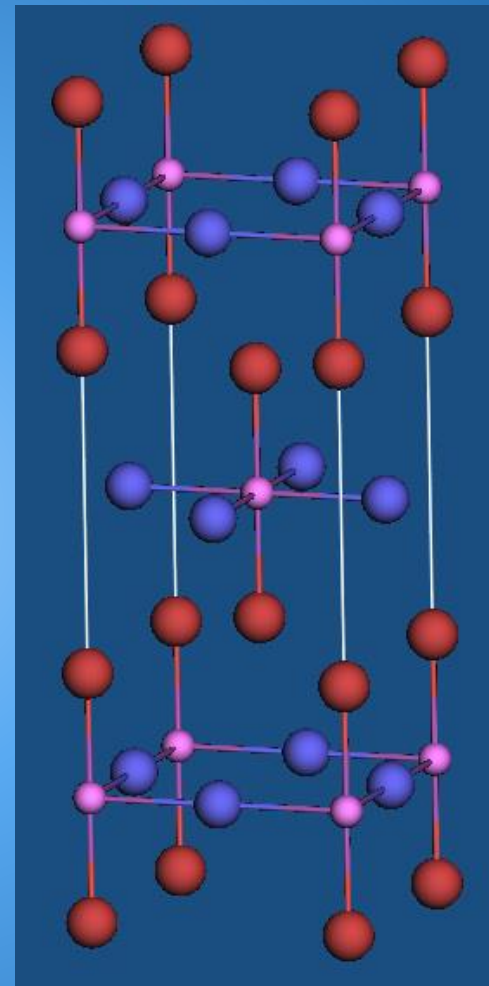
Ta, F

O, F

Ta, F

O, F

Ta, F



# Outline



1. Diffraction patterns of real crystals. Intrinsic general shape of Bragg peaks
2. Simplified methods for studying the microstructure of materials: size and strain using the double-Voigt approximation
3. How to create an IRF for the study of microstructure
4. Examples in literature

**Live presentation:** Complete creation of an IRF file using the case of spinel  $\text{MgAl}_2\text{O}_4$