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MS-72(6) (11:45-12:15)

# Particle Statistics in Powder Diffraction Method

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# Contents

## Motivation

Errors in Optimized Parameters (Lattice Const., Atomic Positions, etc) ?

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Too Small Errors in Optimized Parameters in the Output of Rietveld Analysis, particularly in the cases :

- Strong X-ray Source (Rotating Anode, Synchrotron)
- Long Measurement Time
- High-Resolution Optics (Crystal Analyzer or Monochromator)
- High-Sensitivity Detectors (1-D, 2-D)
- Samples with Good Crystallinity and/or Heavy Elements

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Experimental Errors are Under-Estimated !

→ Use Appropriate Values for Experimental Errors !

# Background/Theory (1/2)

"Sample powder should be very finely ground to obtain reproducible powder diffraction data"

Particle size for reproducible powder diffraction measurement

[Alexander *et al.*, *J. Appl. Phys.*, **19**, 742 (1948)]

| Reproducibility | organic compounds | siliceous minerals | PbO |
|---|---|---|---|
| ±1% | < 10 μm | < 5 μm | < 2 μm |
| ±2% | < 20 μm | < 8 μm | < 3 μm |

Typical particle size of powdered food

| wheat flour | potato starch | corn starch |
|---|---|---|
| 10 - 100 μm | 2 - 80 μm | 2 - 30 μm |

# Background/Theory (2/2)

## History of Particle statistics in Powder Diffraction Method (1)

Theory for a stationary specimen, integrated intensity (Alexander *et al.* 1948)

- statistical variance $\sigma_P^2 \propto \frac{\langle I \rangle^2 \sin\theta}{m}$
- four series of 10 refilled powder specimens, quartz 101/011-reflection

TABLE I. Intensity measurements on fractions of <325-mesh quartz powder. Tabulated values are areas in arbitrary units of the 3.33A maximum as counted with the Geiger-counter x-ray spectrometer using CuK$\alpha$ radiation.

| Specimen No. | 15–50-micron fraction | 5–50-micron fraction | 5–15-micron fraction | <5-micron fraction |
|---|---|---|---|---|
| 1 | 7,612 | 8,688 | 10,841 | 11,055 |
| 2 | 8,373 | 9,040 | 11,336 | 11,040 |
| 3 | 8,255 | 10,232 | 11,046 | 11 |
| 4 | 9,333 | 9,533 | 11,597 | 11 |
| 5 | 4,823 | 8,530 | 11,541 | 11 |
| 6 | 11,123 | 8,617 | 11,336 | 11,260 |
| 7 | 11,051 | 11,598 | 11,686 | 11,241 |
| 8 | 5,773 | 7,818 | 11,288 | 11,428 |
| 9 | 8,527 | 8,021 | 11,126 | 11,406 |
| 10 | 10,255 | 10,190 | 10,878 | 11,444 |
| Mean area: | 8,513 | 9,227 | 11,268 | 11,293 |
| Mean deviation: | 1,545 | 929 | 236 | 132 |
| Mean % deviation: | 18.2 | 10.1 | 2.1 | 1.2 |

TABLE II. Comparison of observed mean intensity deviations with theoretical values.
$p = 0.00386(0.031 + 13\Delta\theta_{\frac{1}{2}})$.
% $U_m = 1614(v_e/p)^{\frac{1}{3}}$.

| Size range (microns) | Effective particle volume, $v_e$ ($cm^3 \times 10^{10}$) | Calculated % $U_m$ for various values of $\Delta\theta_{\frac{1}{2}}$ 5′ | 10′ | 20′ | 30′ | Observed value of % $U_m$ |
|---|---|---|---|---|---|---|
| 15–50 | 394 | 23.1 | 19.6 | 15.8 | 13.3 | 18.2 |
| 5–50 | 329 | 21.1 | 18.0 | 14.4 | 12.2 | 10.1 |
| 5–15 | 32.1 | 6.6 | 5.6 | 4.5 | 3.8 | 2.1 |
| <5 | 0.40 | 0.7 | 0.6 | 0.5 | 0.4 | 1.2 |

Theoretically allowed values

Observed values

# Background/Theory (3/2)

## History of Particle statistics in Powder Diffraction Method (2)

Theory for a rotating specimen,
integrated & peak intensities
(de Wolff *et al.*, 1958, 1959)

Stationary : $\sigma_P^2 \propto \dfrac{\langle I \rangle^2 \sin\theta}{m}$

Rotating : $\sigma_P^2 \propto \dfrac{\langle I \rangle^2 \sin^2\theta}{m}$

- 10 refilled Si powder specimens
- in-plane rotation / scanning
- for peak / integrated intensities

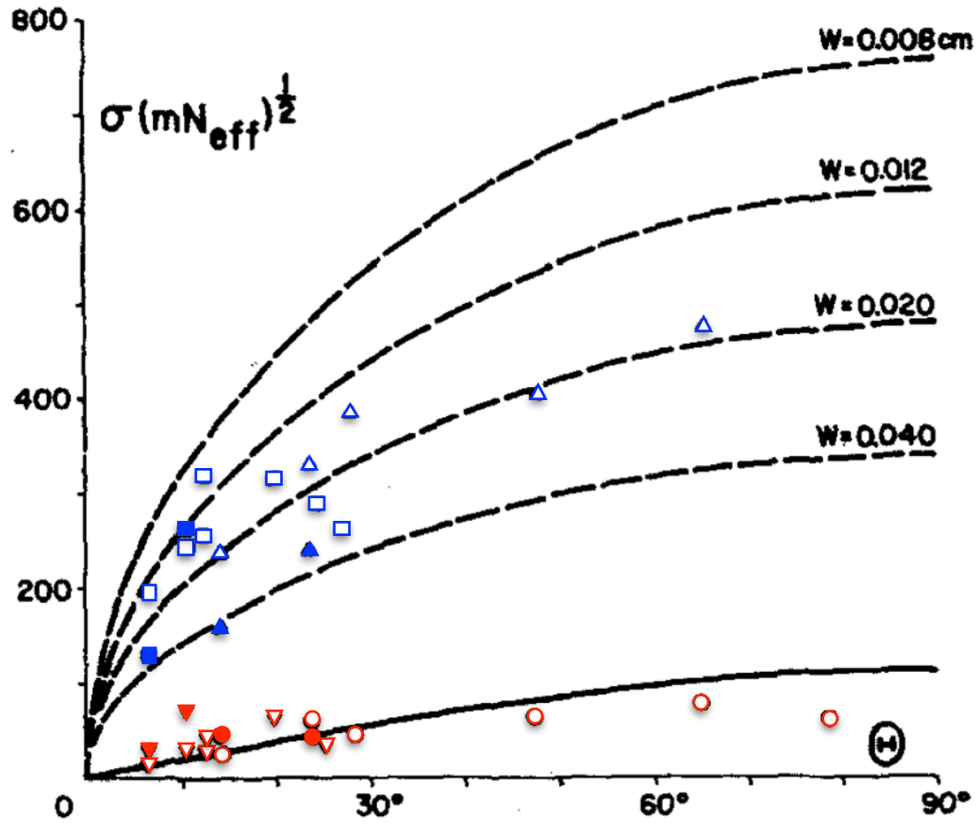


FIG. 8. Plot of $\sigma(mN_{\text{eff}})^{\frac{1}{2}}$ against $\theta$ with $N_{\text{eff}}=12.9\times10^4$ for CuK$\alpha$ and $125\times10^4$ for MoK$\alpha$ per degree of aperture. The dashed lines represent Eq. (1) for stationary specimens and the solid line Eq. (2) for rotating specimens. The points refer to the following experiments:

| | SP 1 | SI 10 | RP 1 | RI 10 |
|---|---|---|---|---|
| CuK$\alpha$ | △ | ▲ | ○ | ● |
| MoK$\alpha$ | □ | ■ | ▽ | ▼ |

stationary rotating

peak integ. peak integ.

(scan) (refill) (scan) (refill)

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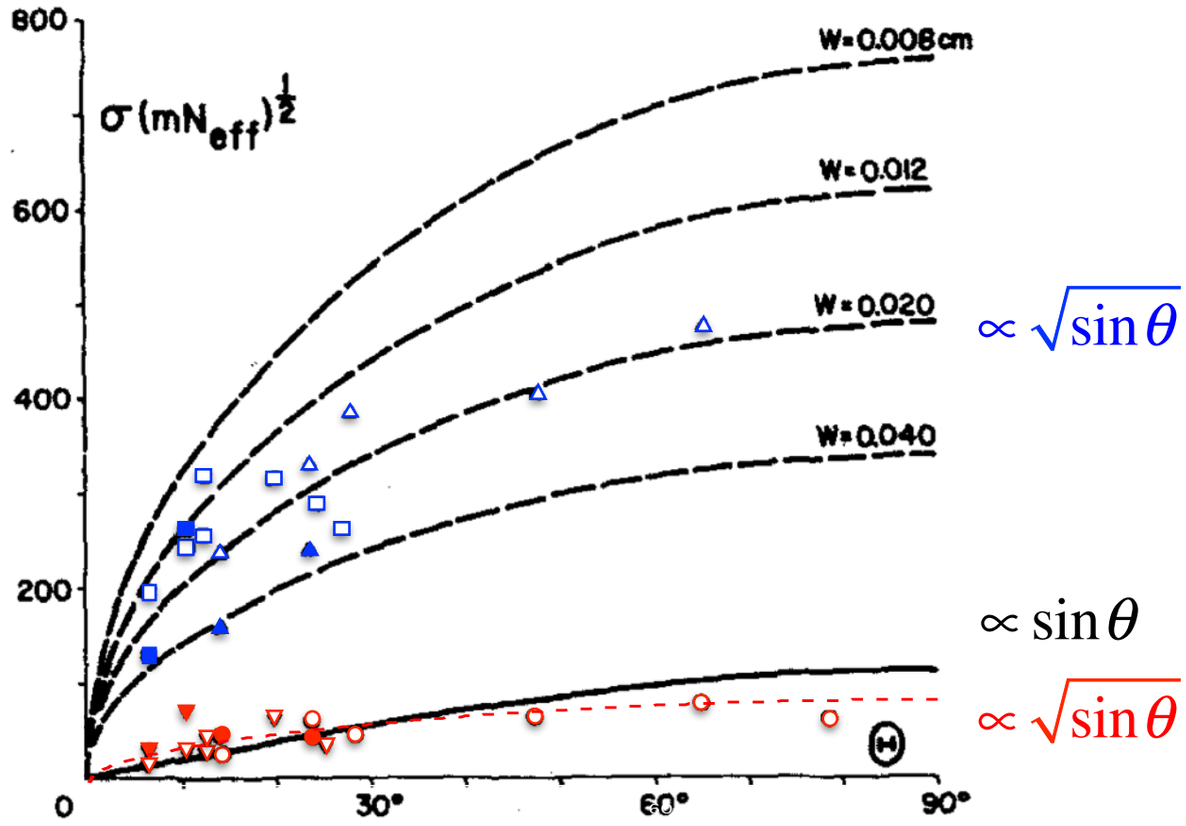


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# Background/Theory (4/3)

## Theory of Particle statistics in Powder Diffraction Method

Observed powder diffraction intensity is the sum of the diffraction intensity from each crystallite

$$I_{total} = I_1 + I_2 + \cdots + I_N \qquad N \approx 10^7$$

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Observed powder diffraction intensity is the **sum** of the diffraction intensity from each crystallite

$$I_{total} = I_1 + I_2 + \cdots + I_N \qquad N \approx 10^7$$

Probability density function of the observed intensity is the **convolution** of probability density functions of  intensity from each crystallite

$$P\left(I_{total}\right) = \int_0^\infty \cdots \int_0^\infty \delta\left(I - \sum_{j=1}^{N} I_j\right) p_1\left(I_1\right) \cdots p_N\left(I_N\right) \mathrm{d}I_1 \cdots \mathrm{d}I_N$$

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The cumulant of the convolution is the sum of the cumulants of the component functions

Cumulant

$$\kappa_\nu \equiv \lim_{\theta \to 0} \frac{\partial^\nu}{\partial \theta^\nu} \ln \int_{-\infty}^{\infty} \mathrm{e}^{\theta x} p(x) \mathrm{d}\, x$$

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$$\kappa_\nu \equiv \lim_{\theta \to 0} \frac{\partial^\nu}{\partial \theta^\nu} \ln \int_{-\infty}^{\infty} \mathrm{e}^{\theta x} p(x) \mathrm{d}x$$

$$\kappa_1 = \langle x \rangle \equiv \int_{-\infty}^{\infty} x p(x) \mathrm{d}x$$

$$\kappa_2 = \left\langle \left(x - \langle x \rangle\right)^2 \right\rangle = \int_{-\infty}^{\infty} \left(x - \langle x \rangle\right)^2 p(x) \mathrm{d}x$$

$$\kappa_3 = \left\langle \left(x - \langle x \rangle\right)^3 \right\rangle = \int_{-\infty}^{\infty} \left(x - \langle x \rangle\right)^3 p(x) \mathrm{d}x$$

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Observed powder diffraction intensity is the **sum** of the diffraction intensity from each crystallite

$$I_{total} = I_1 + I_2 + \cdots + I_N \qquad N \approx 10^7$$

Average observed intensity

$$\langle I_{total} \rangle = \langle I_1 \rangle + \cdots + \langle I_N \rangle = N \langle I_j \rangle$$

Variance of observed intensity

$$\left\langle \left( I_{total} - \langle I_{total} \rangle \right)^2 \right\rangle = N \left\langle \left( I_j - \langle I_j \rangle \right)^2 \right\rangle$$

Third central moment of observed intensity distribution

$$\left\langle \left( I_{total} - \langle I_{total} \rangle \right)^3 \right\rangle = N \left\langle \left( I_j - \langle I_j \rangle \right)^3 \right\rangle$$

# Background/Theory (4/3)

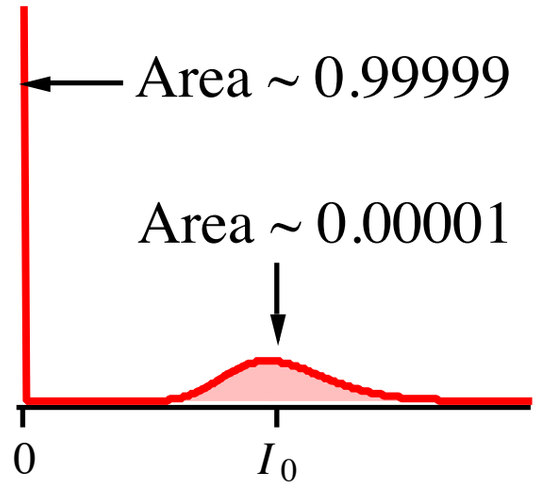
## Theory of Particle statistics in Powder Diffraction Method

Probability Density Function of the Diffraction Intensity from a Crystallite :

$$f_j\left(I_j\right) \approx (1-\rho)\delta\left(I_j\right) + \rho f_0\left(I_j\right)$$

Dirac's Delta Function

Probability Density Function for a Crystallite, Provided Diffraction Condition is Satisfied (Affected by Crystallite Size, Absorption, …)




Typical Value of Probability that a Crystallite Satisfies the Diffraction Condition

$$\rho = \frac{m \times \left(0.1^\circ \times \frac{\pi}{180^\circ}\right) \times \left(5^\circ \times \frac{\pi}{180^\circ} \times \frac{1}{2\sin\theta}\right)}{4\pi} = 10^{-6} \sim 10^{-5}$$

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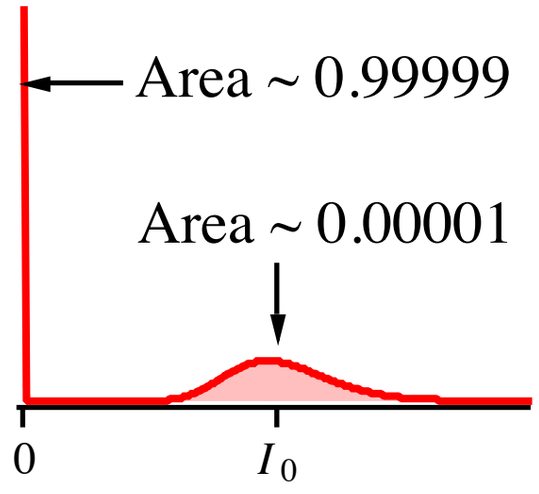


Average Total Intensity :

$$\left\langle I_j \right\rangle \approx N\rho I_0 \qquad I_0 \equiv \int_0^\infty I_j f_0\left(I_j\right) \mathrm{d}\, I_j$$

Variance of Total Intensity :

$$\left\langle \left( I_j - \left\langle I_j \right\rangle \right)^2 \right\rangle \approx N\rho I_0^2$$

Third-order Cumulant of Total Intensity :

$$\left\langle \left( I_j - \left\langle I_j \right\rangle \right)^3 \right\rangle \approx N\rho I_0^3$$

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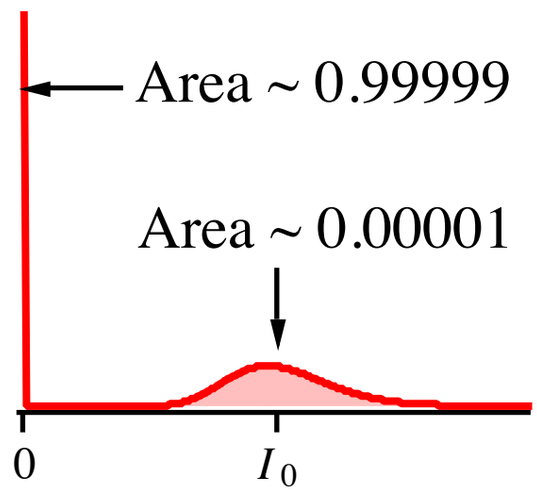


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Third-order Cumulant of Total Intensity :

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Effective Number of Diffracting Crystallites :

$$\frac{\left\langle I_{total} \right\rangle^2}{\left\langle \left( I_{total} - \left\langle I_{total} \right\rangle \right)^2 \right\rangle} = N\rho$$

$$\equiv n_{\text{eff}}$$

# Background/Theory (4/2)

## Statistical uncertainty of experimentally evaluated cumulants

Estimation of average : $$m = \frac{1}{n}\sum_{i=1}^{n}\left(I_{\mathrm{obs}}\right)_i$$

Variance of estimated average : $$\left\langle \left(m - \langle m \rangle\right)^2 \right\rangle \approx \frac{\sigma^2}{n}$$

Relative errors < 5% needs > 400 counts, (20 samples)

Estimation of variance : $$\sigma^2 = \frac{1}{n-1}\sum_{i=1}^{n}\left[\left(I_{\mathrm{obs}}\right)_i - m\right]^2$$

Variance of estimated variance : $$\left\langle \left(\sigma^2 - \langle \sigma^2 \rangle\right)^2 \right\rangle \approx \frac{1}{n}\sum_{i=1}^{n}\left[\left(I_{\mathrm{obs}}\right)_i - m\right]^4 - \frac{\sigma^2}{n}$$

Relative errors about variance < 5% on 400 counts needs n > 400 (400 samples)

# Background/Theory (1/2)

## Assumption about statistical errors on Rietveld analysis

$$\sigma_j^2 = (\sigma_c)_j^2$$

(1) $\sigma_c$ : Error caused by counting (Poisson) statistics for count-loss negligible case

= square root of count $\sigma_c = \sqrt{y_{calc}}$

# Background/Theory (1/2)

## A theoretical model for statistical errors

$$\sigma_j^2 \approx (\sigma_c)_j^2 + (\sigma_p)_j^2$$

(1) $\sigma_c$ : Error caused by counting (Poisson) statistics for count-loss negligible case

= square root of count $\sigma_c = \sqrt{y_{calc}}$

(2) $\sigma_p$ : Error caused by particle (sampling) statistics (Alexander *et al.* 1948)

$$\sigma_p^2 \approx C_p (y_{calc} - b)^2 \sin\theta / m_{eff}$$

$(y_{calc} - b)$ : peak intensity, $m_{eff}$ : effective multiplicity

Dependence on ($y_{calc}$ - $b$), 2θ and $m_{eff}$ (for symmetric reflection, stationary specimen) is acceptable.

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Proportionality factor $C_p$ , determined by crystallite size, absorption factors of the sample and geometry of the diffractometer,

can experimentally be evaluated for stationary specimens,

in symmetric-reflection mode, if a standard powder and a sample-spinning attachment are used (Ida *et al.*, 2009).

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## A theoretical model for statistical errors

$$\sigma_j^2 = (\sigma_c)_j^2 + (\sigma_p)_j^2 + (\sigma_r)_j^2$$

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Proportionality factor $C_p$ is unknown

(3) $\sigma_r$ : Error proportional to intensity (Toraya 1998, 2000)

Incompleteness of count-loss correction (?) and/or peak profile model (?)

$$\sigma_r^2 = C_r y_{calc}^2$$

Proportionality factor $C_r$ is unknown

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## A theoretical model for statistical errors

$$\sigma_j^2 = (\sigma_c)_j^2 + (\sigma_p)_j^2 + (\sigma_r)_j^2$$

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Incompleteness of count-loss correction (?) and/or peak profile model (?)

$$\sigma_r^2 = C_r y_{calc}^2$$

Proportionality factor $C_r$ is unknown

How can we optimize the statistical model including two unknowns $C_p$ & $C_r$ in variance to fit experimental data ?

# Background/Theory (2/2)

## Maximum likelihood estimation (MLE)

Maximization of the probability that the observed data should appear

Maximization of $$\prod_{j=1}^{N} \frac{1}{\sqrt{2\pi}\sigma_j} \exp\left(-\frac{\Delta_j^2}{2\sigma_j^2}\right)$$

Deviation of the observed value from calculated value : $\Delta_j = \left(Y_{\text{obs}}\right)_j - \left(y_{\text{calc}}\right)_j$

MLE can optimize not only $\left(y_{\text{calc}}\right)_j$ , but also the error $\sigma_j$

# Background/Theory (2/2)

## Maximum likelihood estimation (MLE)

Maximization of the probability that the observed data should appear

= Minimization of $\sum_{j=1}^{N}\left(\frac{\Delta_j^2}{\sigma_j^2}+\ln\sigma_j^2\right)$ $\Leftrightarrow$ Maximization of $\prod_{j=1}^{N}\frac{1}{\sqrt{2\pi}\sigma_j}\exp\left(-\frac{\Delta_j^2}{2\sigma_j^2}\right)$

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Unlikelihood

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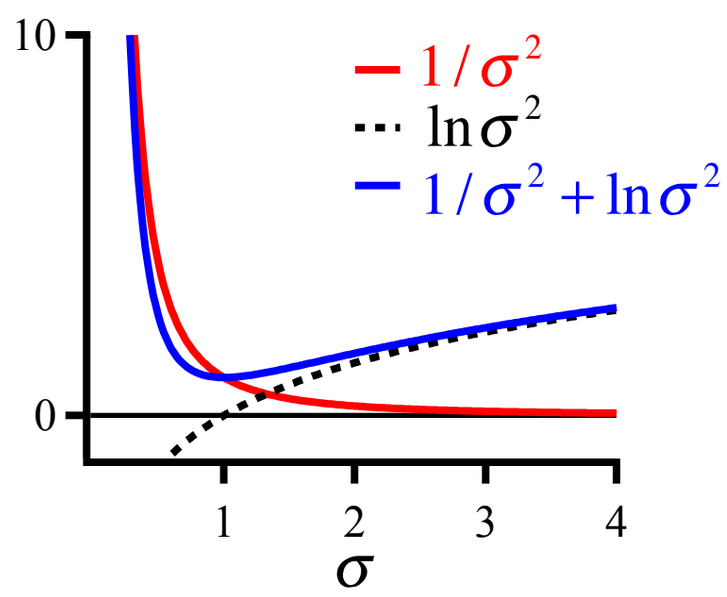
## Least-squares method (LSQ)

= Minimization of $\sum_{j=1}^{N}\frac{\Delta_j^2}{\sigma_j^2}$ ($\sigma_j$ : known error )

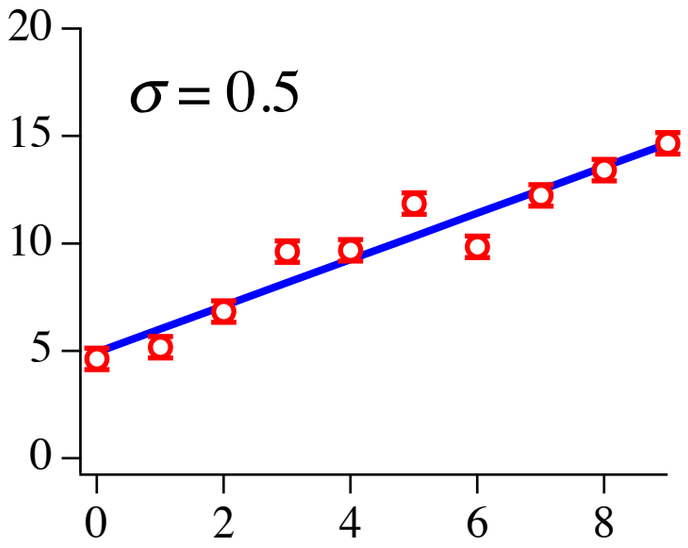
Weighted Sum of Squared Deviations

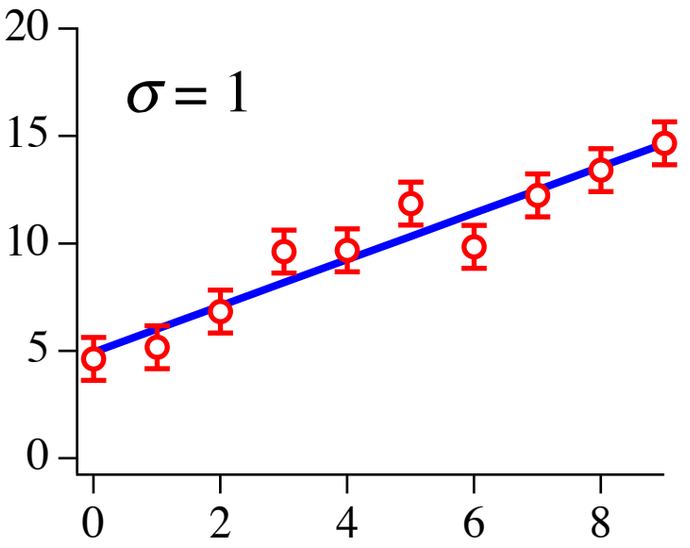


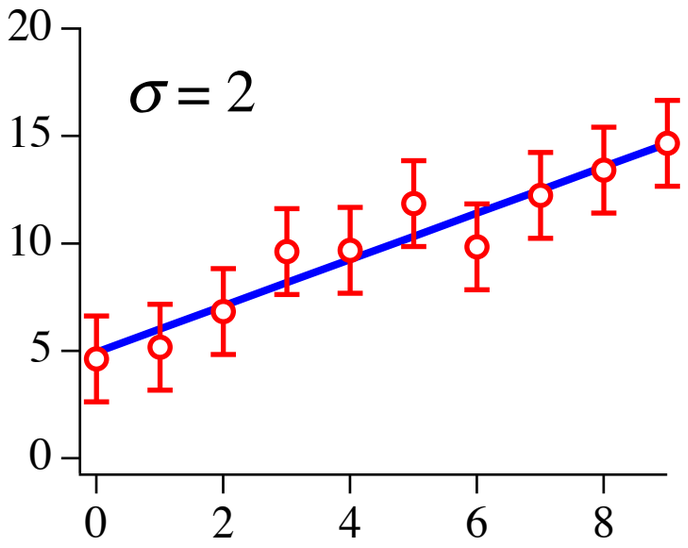
# Background/Theory (2/2)

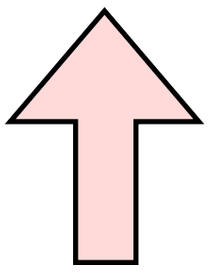
## Ability of Maximum Likelihood Method

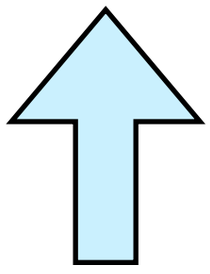
( = Minimum Unlikelihood Optimization )

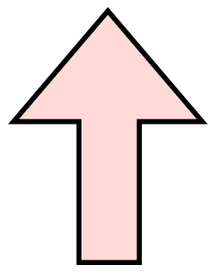






Unlikely

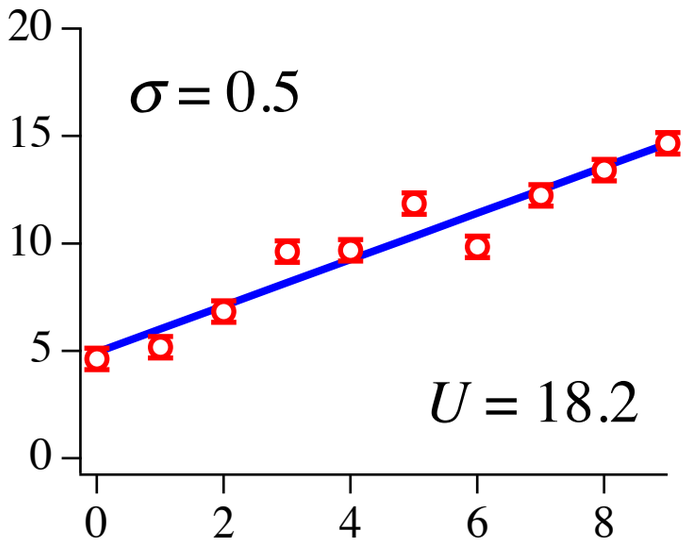
Likely

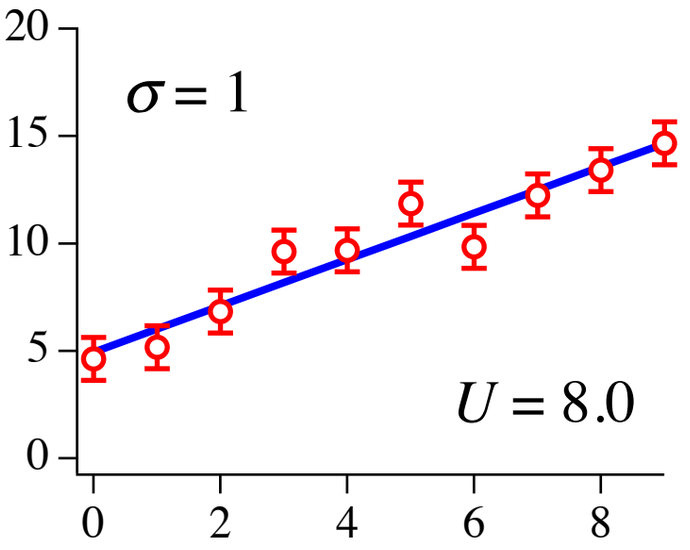
Unlikely

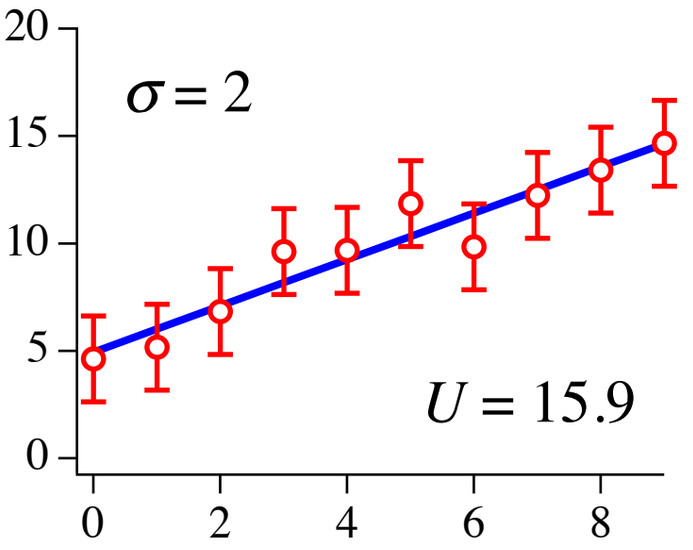
# Background/Theory (2/2)

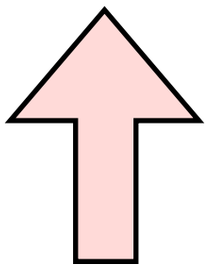
## Ability of Maximum Likelihood Method

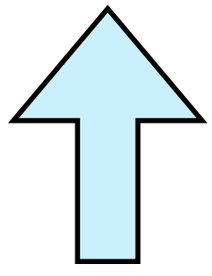
( = Minimum Unlikelihood Optimization )

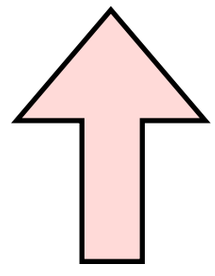






*U* = 18.2

*U* = 8.0

*U* = 15.9

# Background/Theory (2/2)

## Maximum likelihood estimation (MLE)

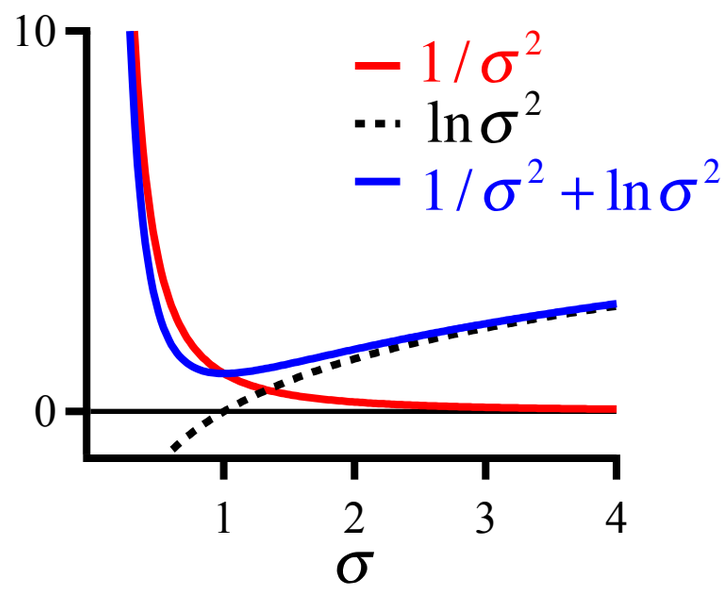
Maximization of the probability that the observed data should appear

= Minimization of $\sum_{j=1}^{N}\left(\frac{\Delta_j^2}{\sigma_j^2}+\ln\sigma_j^2\right)$

Unlikelihood

Deviation of the observed value from calculated value : $\Delta_j=\left(Y_{\mathrm{obs}}\right)_j-\left(y_{\mathrm{calc}}\right)_j$

MLE can optimize not only $\left(y_{\mathrm{calc}}\right)_j$, but also the error $\sigma_j$




## Least-squares method (LSQ)

= Minimization of $\sum_{j=1}^{N}\frac{\Delta_j^2}{\sigma_j^2}$ ($\sigma_j$ : known error )

Weighted Sum of Squared Deviations

# Method of MLE Calculation

## Step (1) : Structure refinement by the Rietveld method

Optimization of structure and profile models

(with *RIETAN-FP ver. 2.x*)

$\Delta, \{y_1, ..., y_M\}$

$\sigma$

## Step (2) : Error estimation by MLE method

Evaluation of effective multiplicity at each data point

Optimization of error model by downhill simplex method

Calculation of statistical errors

(coded with a graphing software *Igor Pro ver. 6.2* macro language)

## Iterations of steps (1) & (2)

Maximum-likelihood solution of structure, profile and error models will be obtained, when no change is observed on further iteration (typically 2~3 iterations are needed).

# Method of MLE Calculation

Step (1) : Structure refinement by the Rietveld method

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$\sigma$

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(with *RIETAN-FP ver. 2.x*)

$\Delta, \{y_1, ..., y_M\}$

$\sigma$

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Calculation of statistical errors

(coded with a graphing software *Igor Pro ver. 6.2* macro language)

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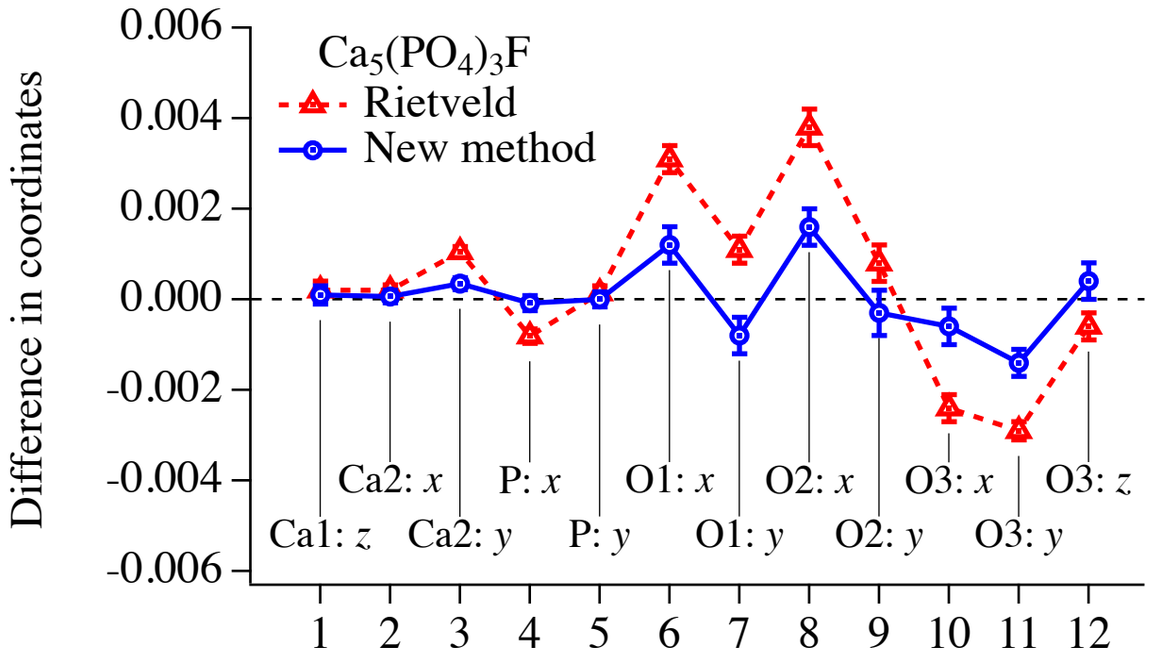
Maximum-likelihood solution of structure, profile and error models will be obtained, when no change is observed on further iteration (typically 2~3 iterations are needed).

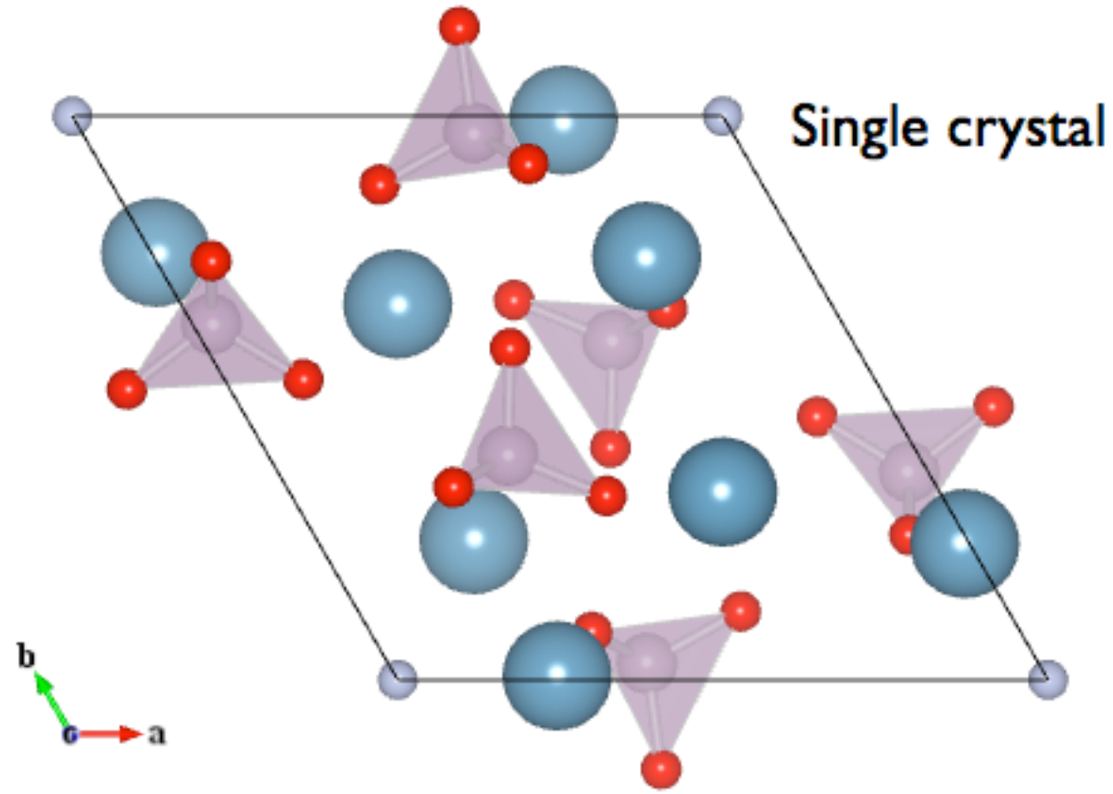
# Results (1/4) $Ca_5(PO_4)_3F$ (open powder data attached to *RIETAN-FP*)

## Comparison with single-crystal data

Synthetic (Sudarsanan *et al.* 1972)




Difference in atomic coordinates
(from synthetic single crystal)




$P6_3/m$

# Results (1/4) $Ca_5(PO_4)_3F$ (open powder data attached to *RIETAN-FP*)

## Comparison with single-crystal data

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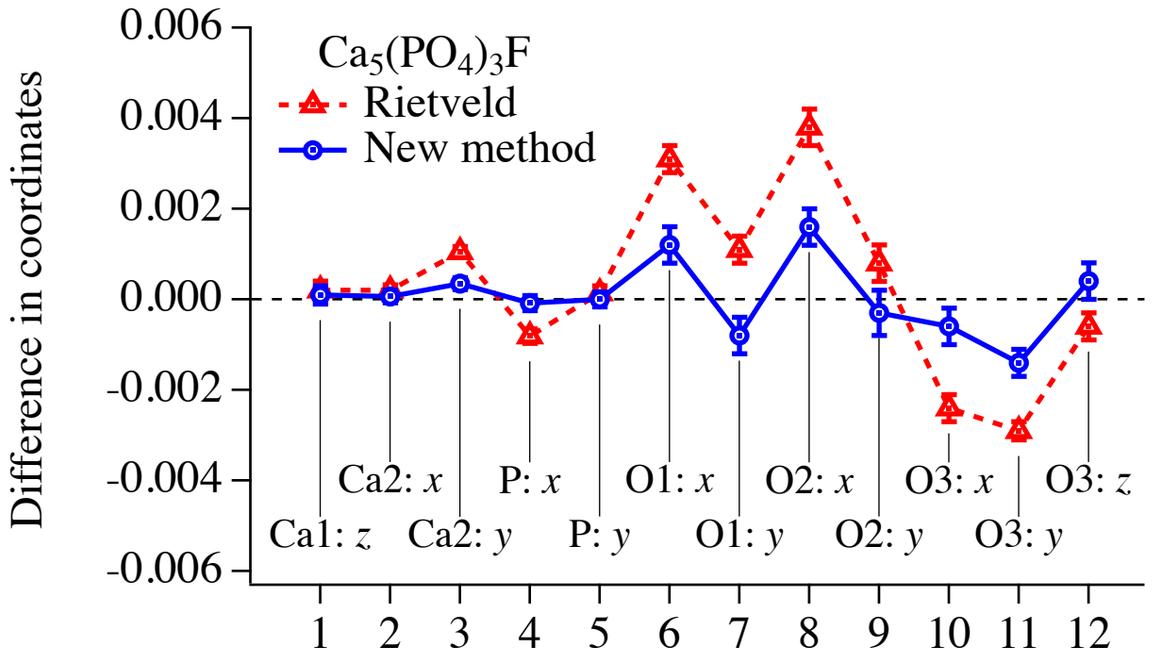
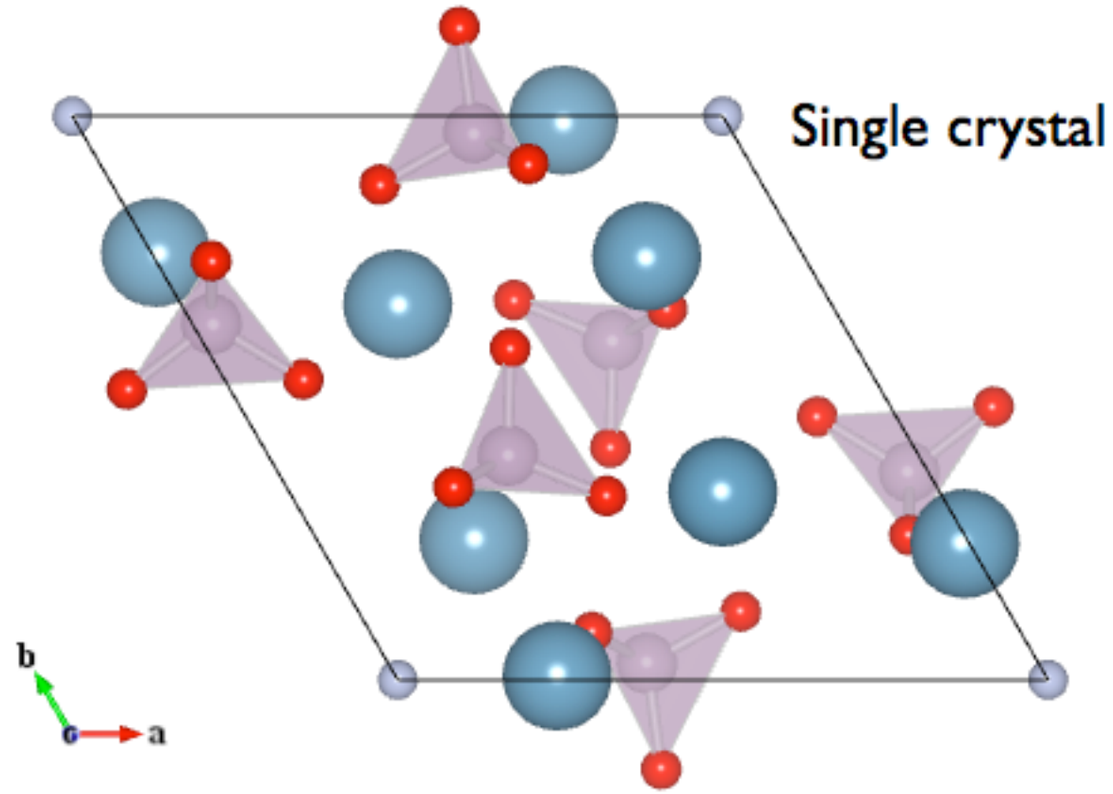



Difference in atomic coordinates
(from synthetic single crystal)



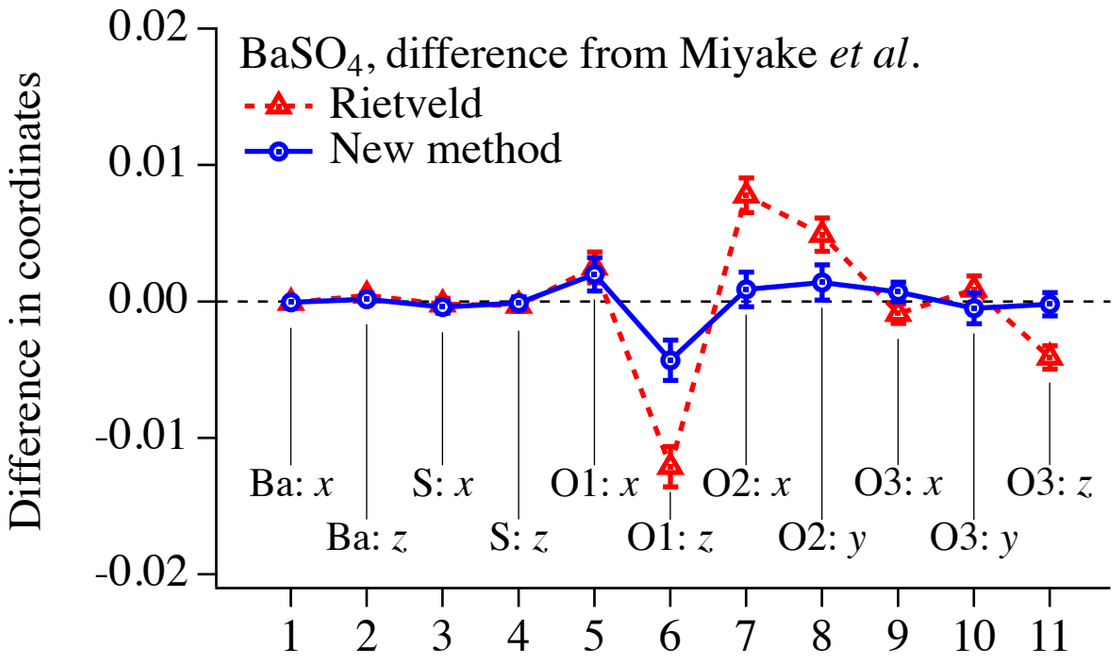

$P6_3/m$

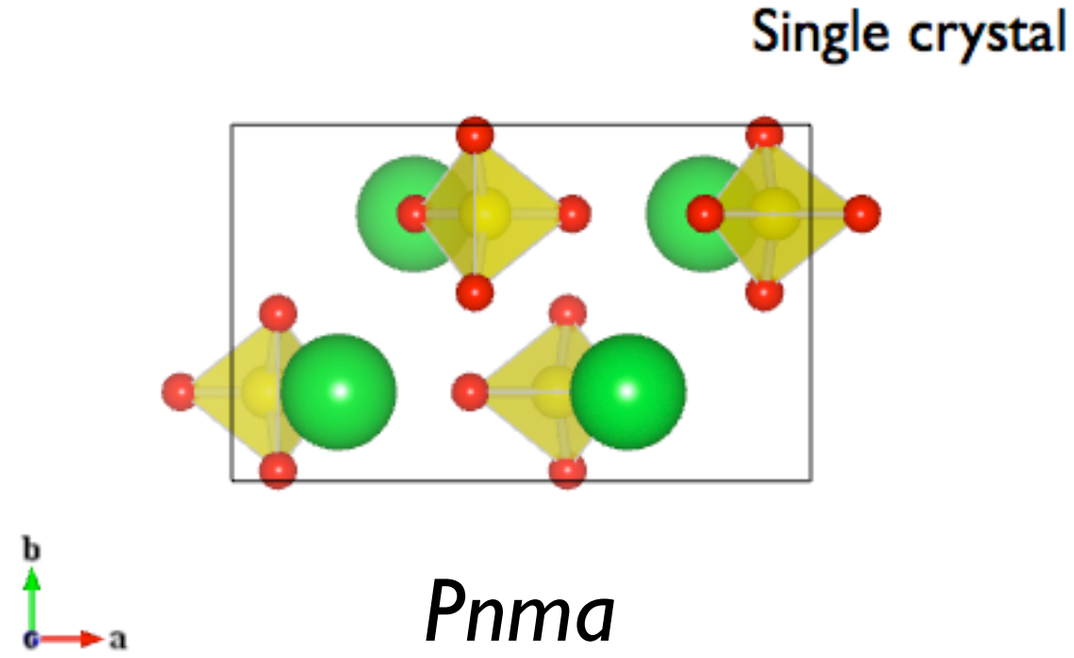
**The results of the new (MLE) method** are closer to **single-crystal data** rather than **the results of the Rietveld method** from the same data set !

# Results (2/4)　$BaSO_4$　(open powder data attached to *RIETAN-FP*)

## Comparison with single-crystal data

Spherical 0.15 mmΦ (Miyake *et al.* 1978),



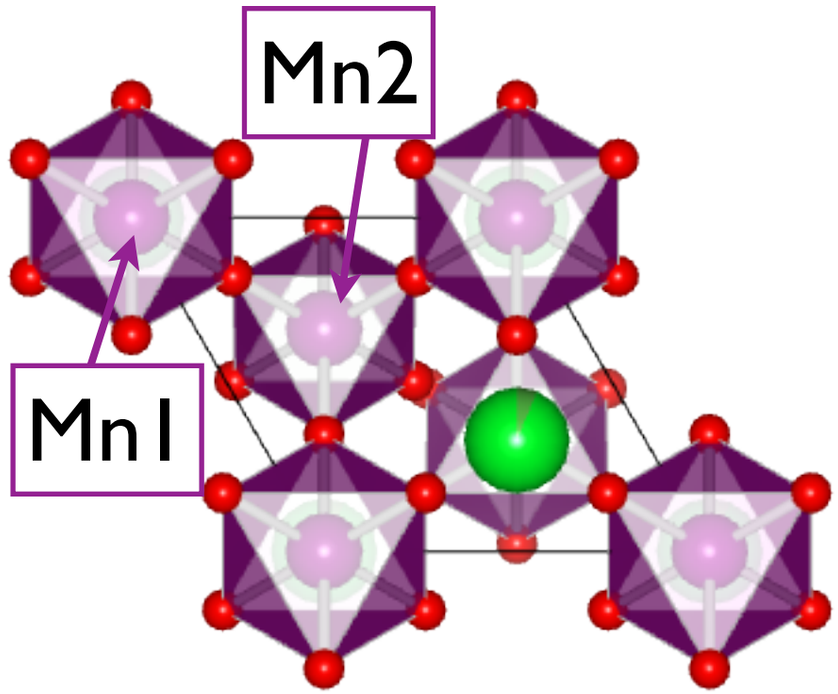




Difference in atomic coordinates
(from results by Miyake *et al.*)

**The results of the new (MLE) method** coincide with the **single-crystal data** except one structure parameter (O1: z), while the deviations in **the results of the Rietveld method** exceed the error range.

## Results (3/4) $La_xSr_{1-x}MnO_3$

$La_{0.03}Sr_{0.97}MnO_3$, *P*6$_3$/*mmc*




SPring-8 BL19B2

$La_{0.03}Sr_{0.97}MnO_3$

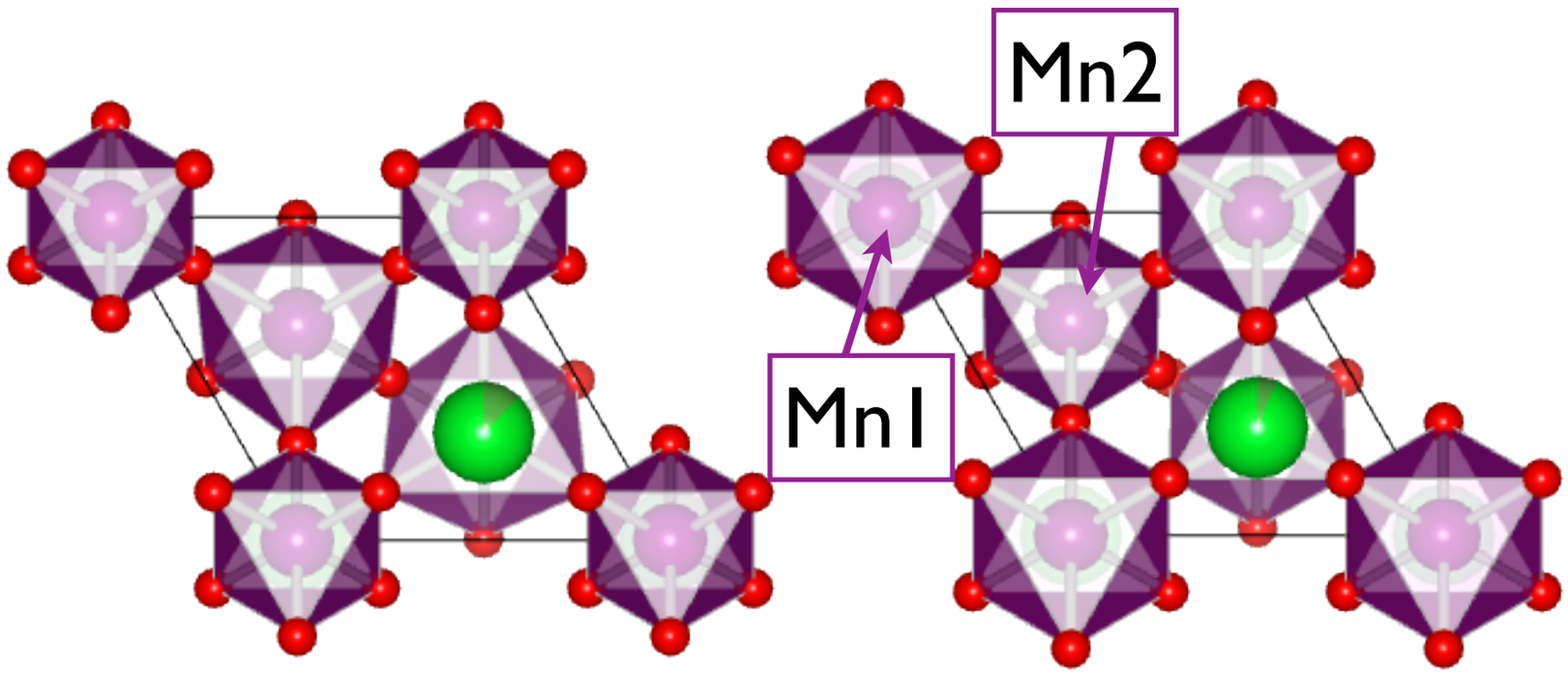
Rietveld

BVS(Mn1) = +2.97

BVS(Mn2) = +4.39

## Results (3/4) $La_xSr_{1-x}MnO_3$

$La_{0.03}Sr_{0.97}MnO_3$, *P*6$_3$/*mmc*

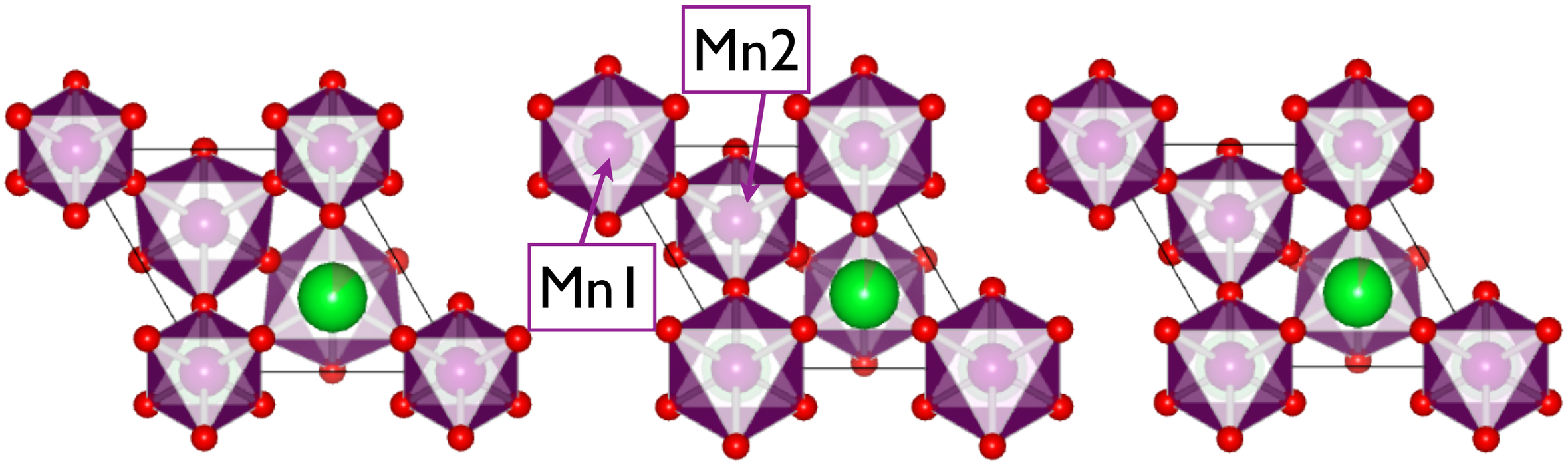



PDF#04-010-5038
(Star Quality / ND)
$La_{0.1}Sr_{0.9}MnO_3$
Rietveld
BVS(Mn1) = +4.65
BVS(Mn2) = +3.04

SPring-8 BL19B2
$La_{0.03}Sr_{0.97}MnO_3$
Rietveld
BVS(Mn1) = +2.97
BVS(Mn2) = +4.39

## Results (3/4) $La_xSr_{1-x}MnO_3$

$La_{0.03}Sr_{0.97}MnO_3$, *P*6$_3$/*mmc*

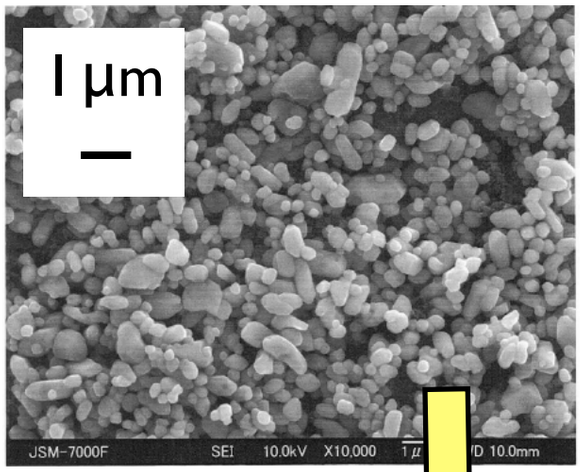



PDF#04-010-5038
(Star Quality)
$La_{0.1}Sr_{0.9}MnO_3$
Rietveld
BVS(Mn1) = +4.65
BVS(Mn2) = +3.04

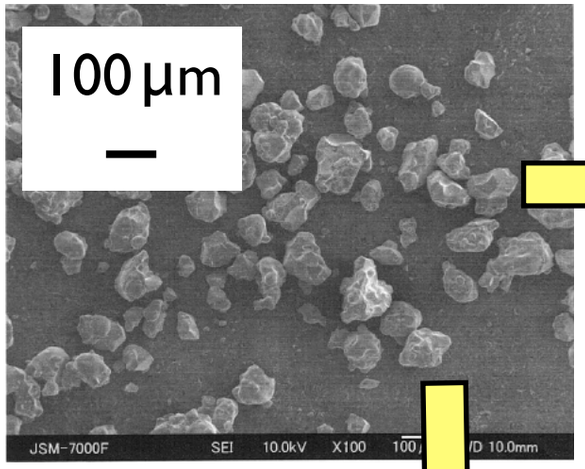
SPring-8 BL19B2
$La_{0.03}Sr_{0.97}MnO_3$
Rietveld
BVS(Mn1) = +2.97
BVS(Mn2) = +4.39

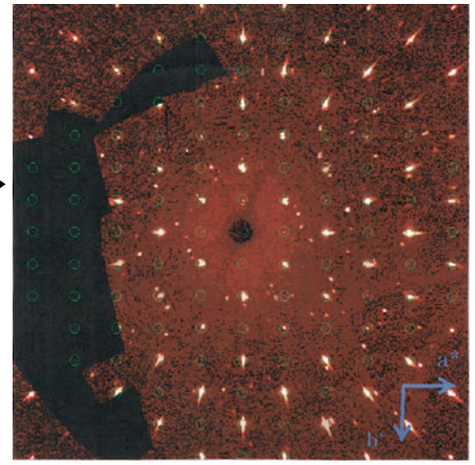
SPring-8 BL19B2
$La_{0.03}Sr_{0.97}MnO_3$
MLE
BVS(Mn1) = +3.82
BVS(Mn2) = +3.90

# Results (4/4)　$BaSO_4$, heat-treated coarse-grain powder

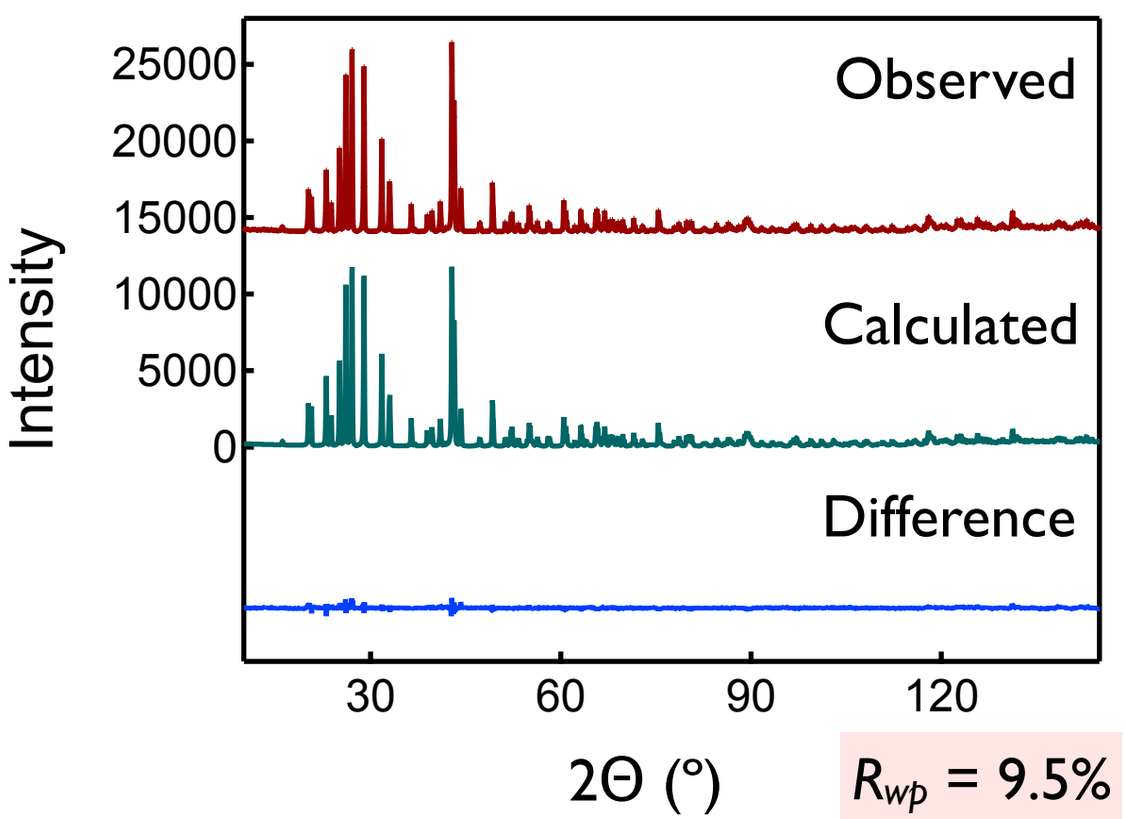



1000°C



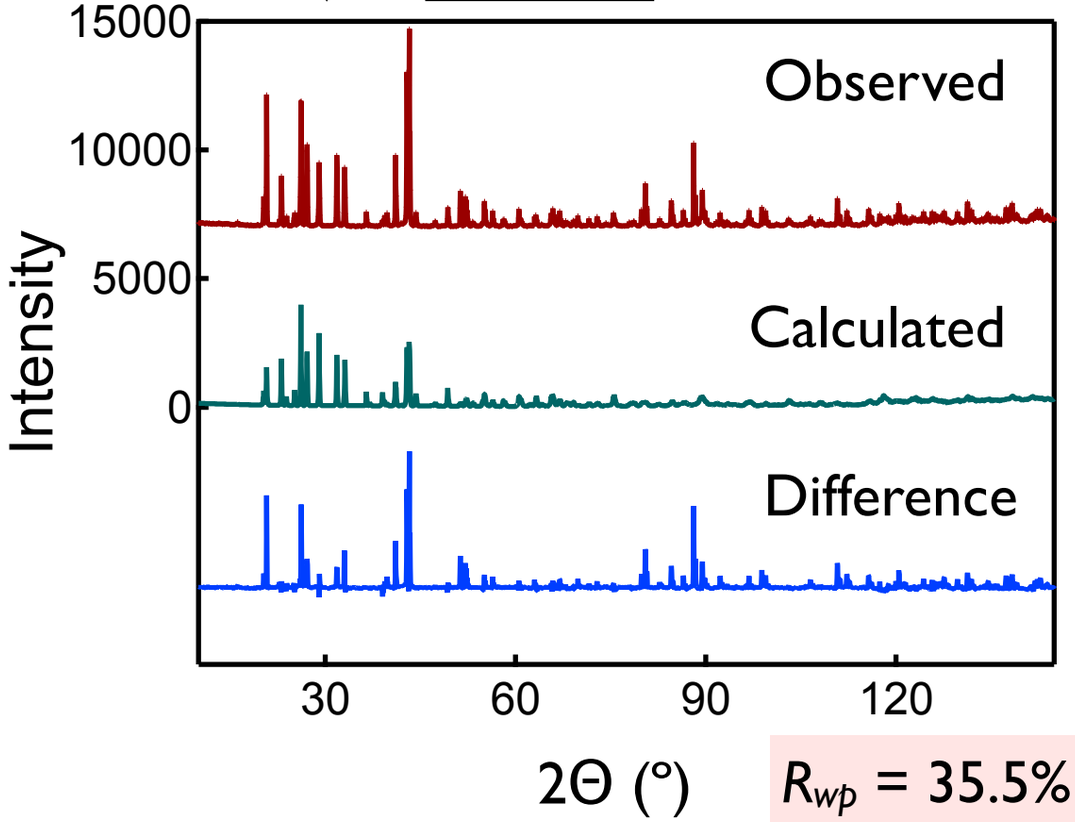



Rietveld



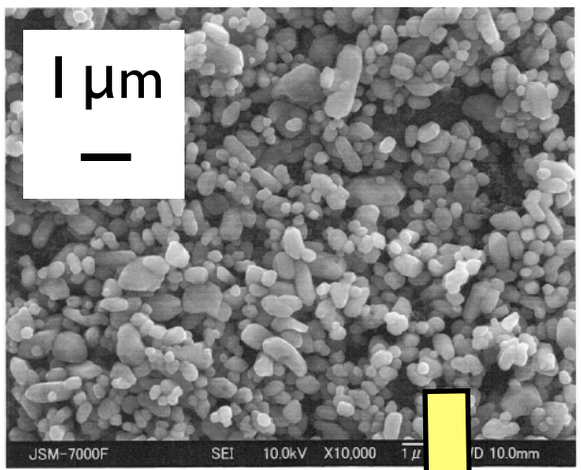

$R_{wp}$ = 9.5%

Rietveld

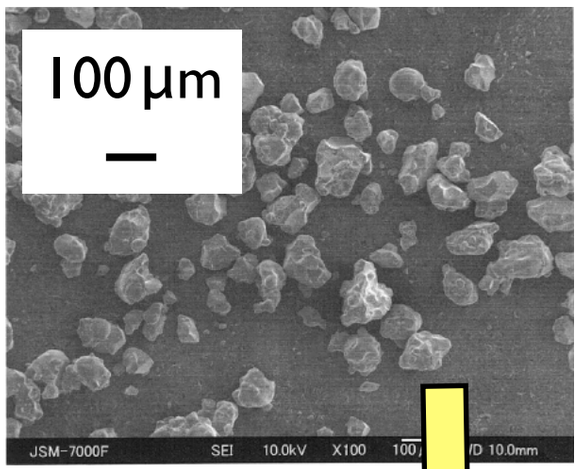



$R_{wp}$ = 35.5%

# Results (4/4)　$BaSO_4$, heat-treated coarse-grain powder

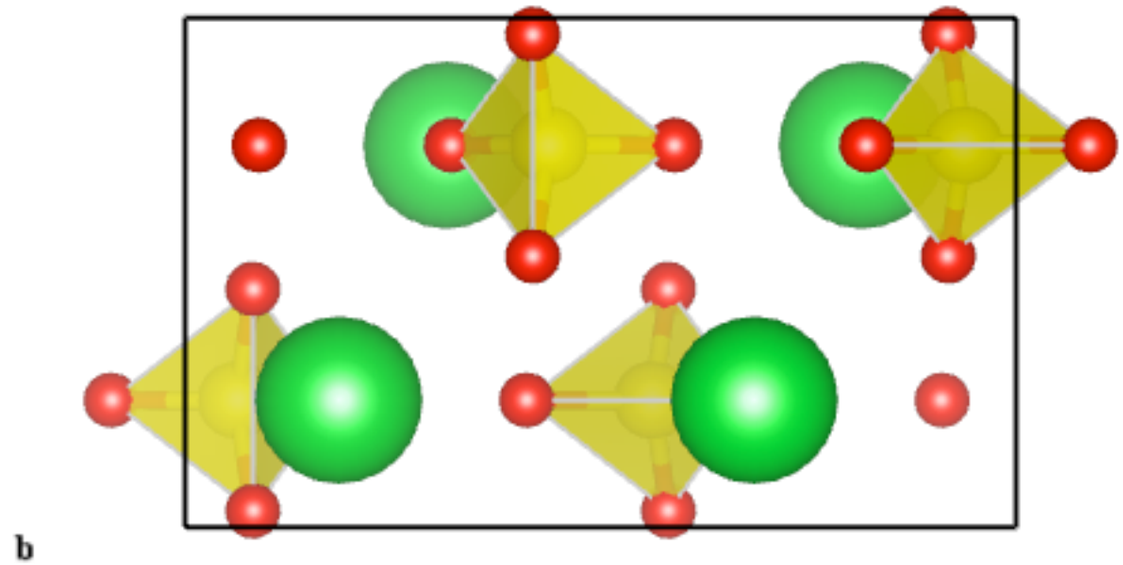


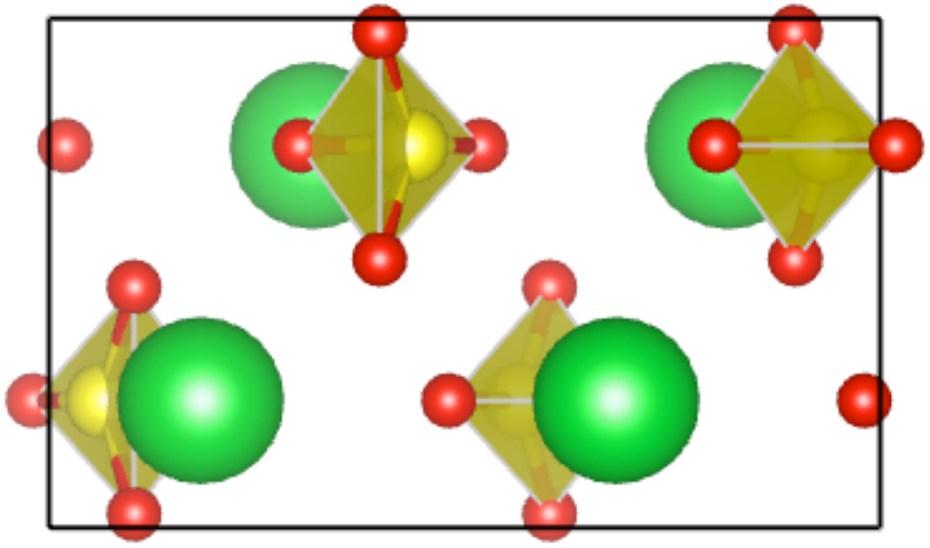

1000°C




Rietveld

Rietveld

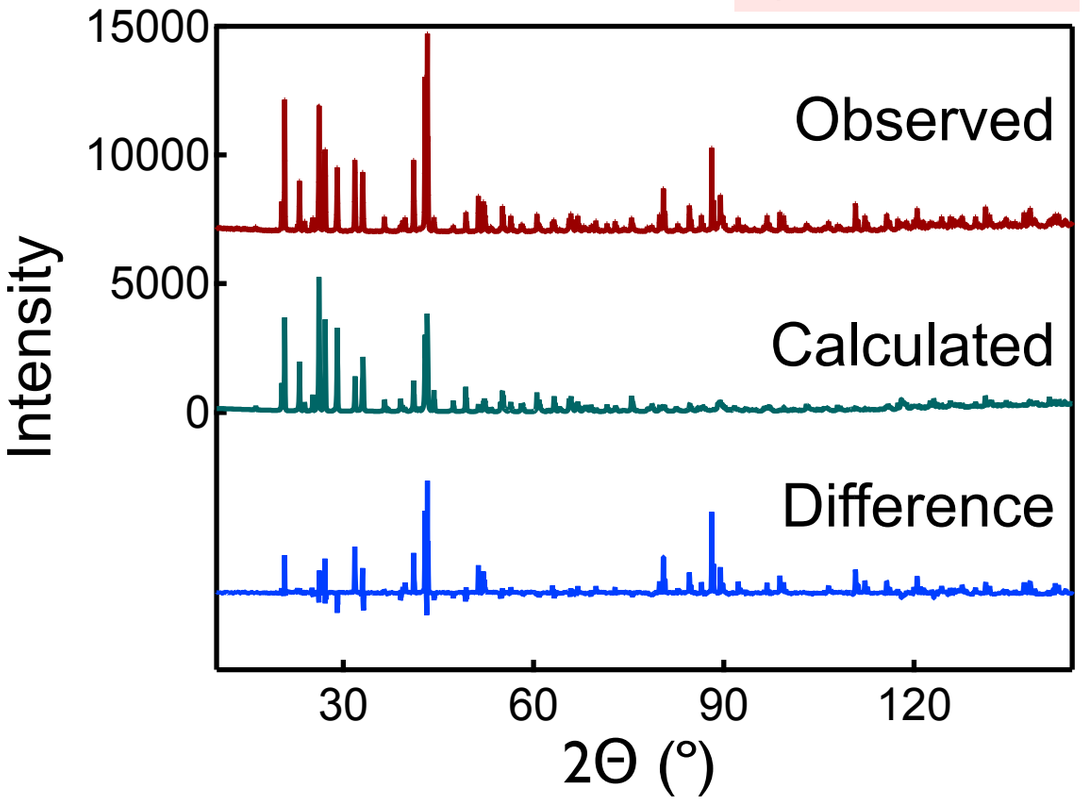


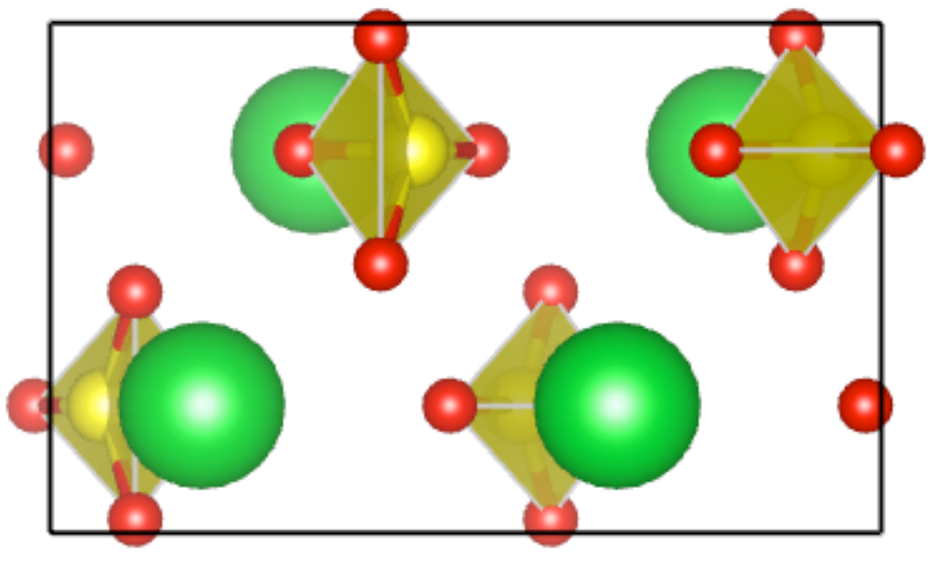



# Results (4/4)　$BaSO_4$, heat-treated coarse-grain powder

Rietveld

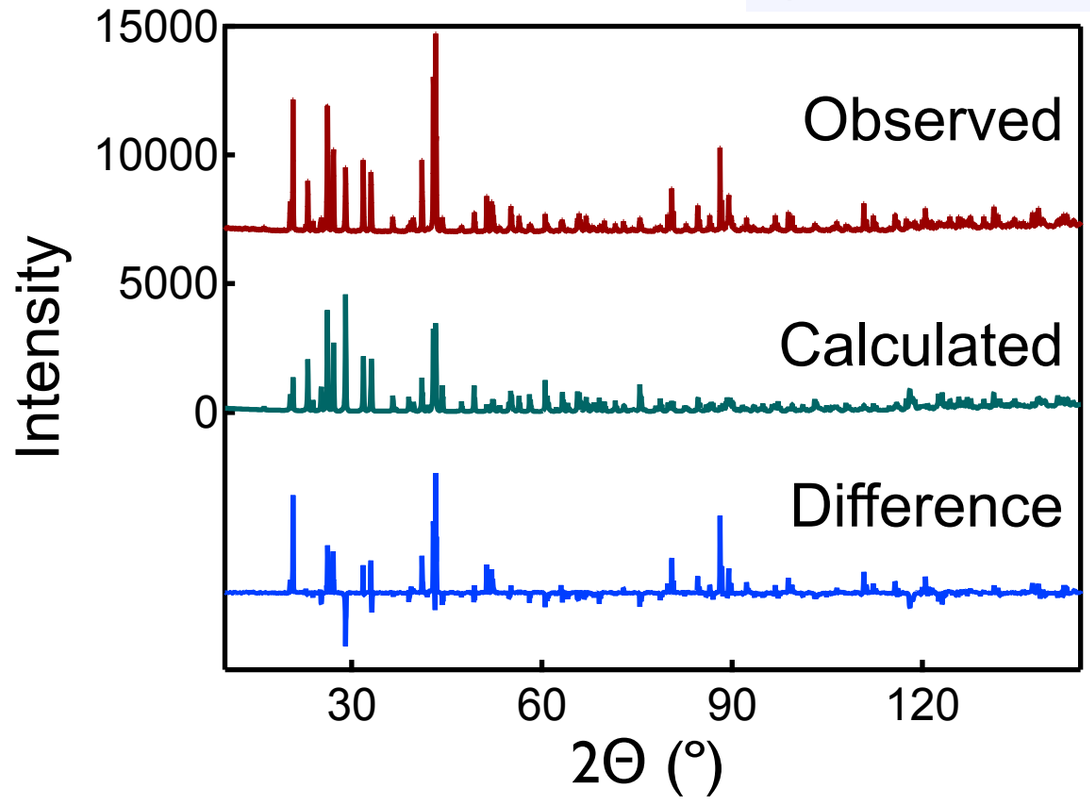
$R_{wp}$ = 35.5 %
$R_p$ = 27.5 %

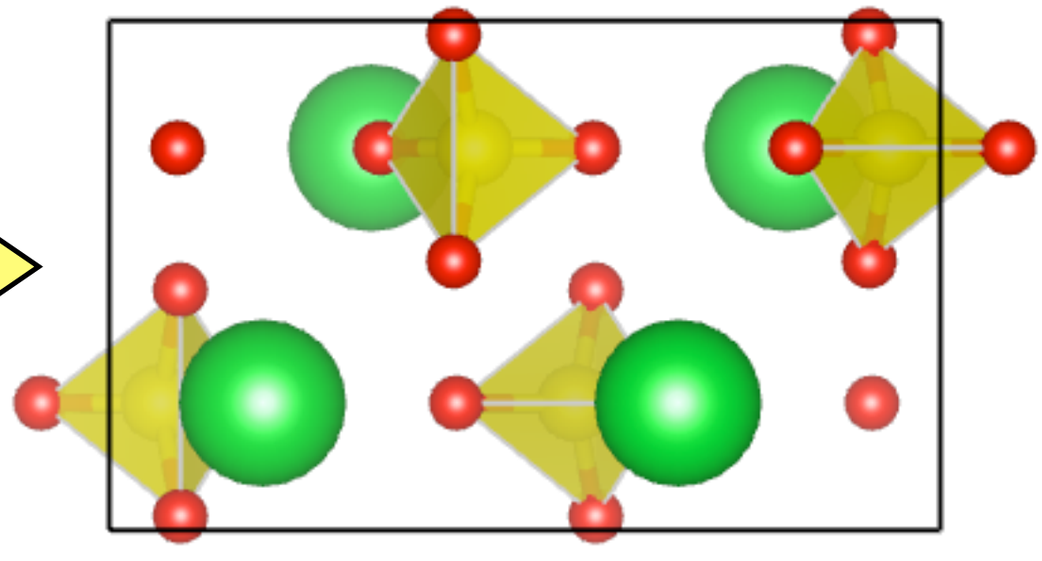


ML Optimization

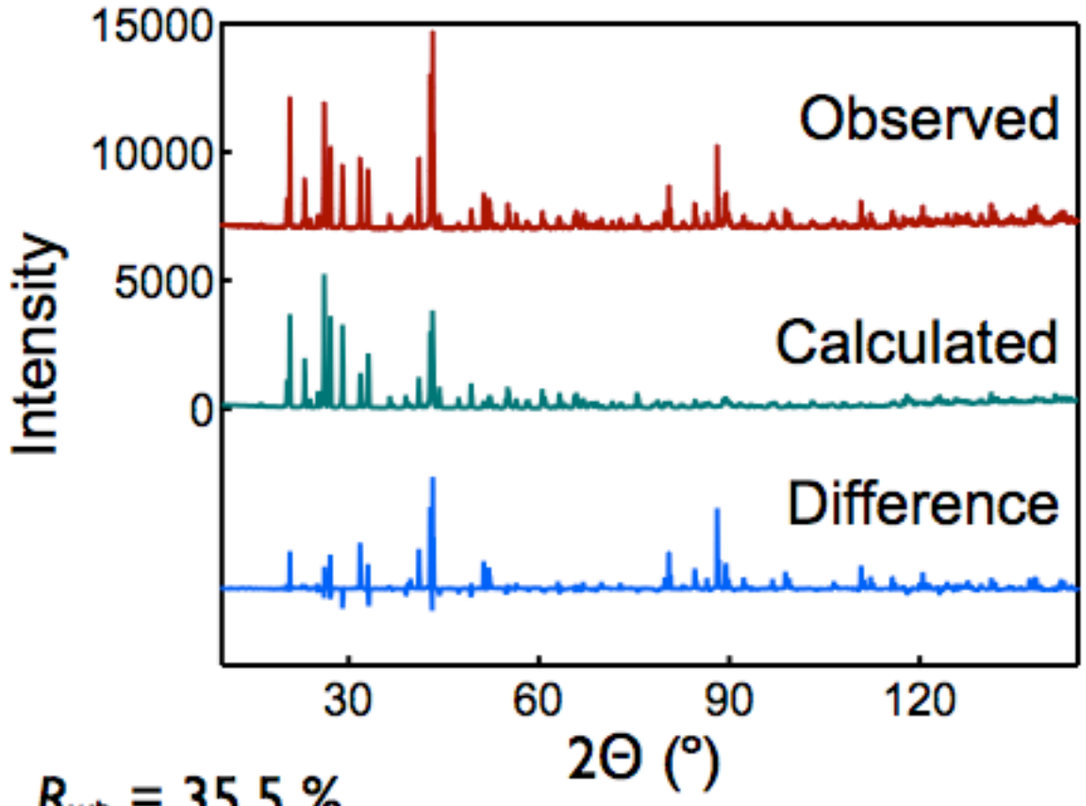
$R_{wp}$ = 21.5 %
$R_p$ = 30.6 %



# Results (4/4)  $BaSO_4$, heat-treated coarse-grain powder

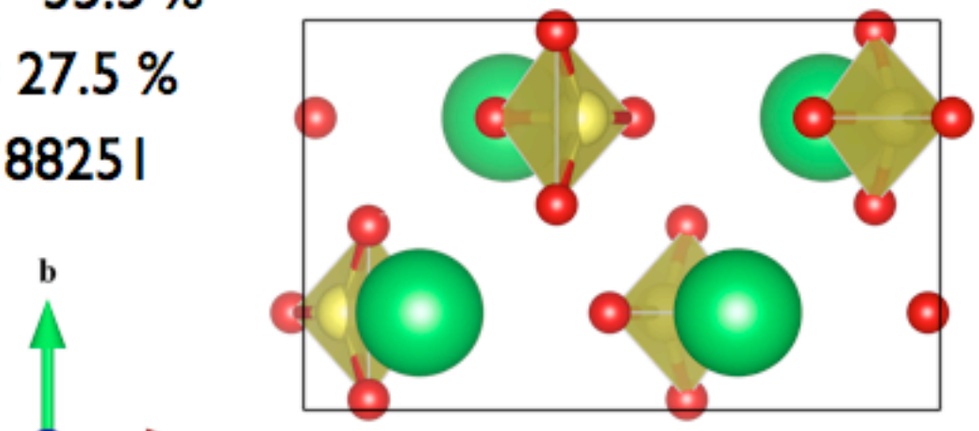
Rietveld




$R_{wp}$ = 35.5 %

$R_p$ = 27.5 %

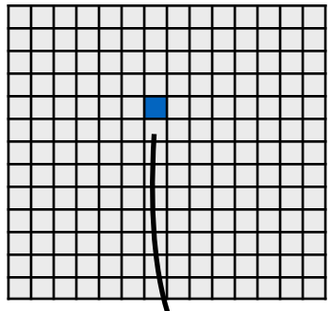
$U$ = 88251




| | Rietveld | MLE | single crystal |
|---|---|---|---|
| Bond length (Å) | | | |
| S–O1 | 2.04 | 1.39 | 1.47 |
| S–O2 | 1.47 | 1.41 | 1.47 |
| S–O3 | 1.84 | 1.6 | 1.49 |
| Bond angles (°) | | | |
| O1-S-O2 | 74.6 | 112.2 | 111.9 |
| O1-S-O3 | 137.8 | 114.2 | 109.6 |
| O2-S-O3 | 107.7 | 109.3 | 108.9 |
| O3-S-O3’ | 82.9 | 96.5 | 107.9 |

# Another Method for Structure Refinement

**Pixel-Mapping Method (Sulyanov 1994)**

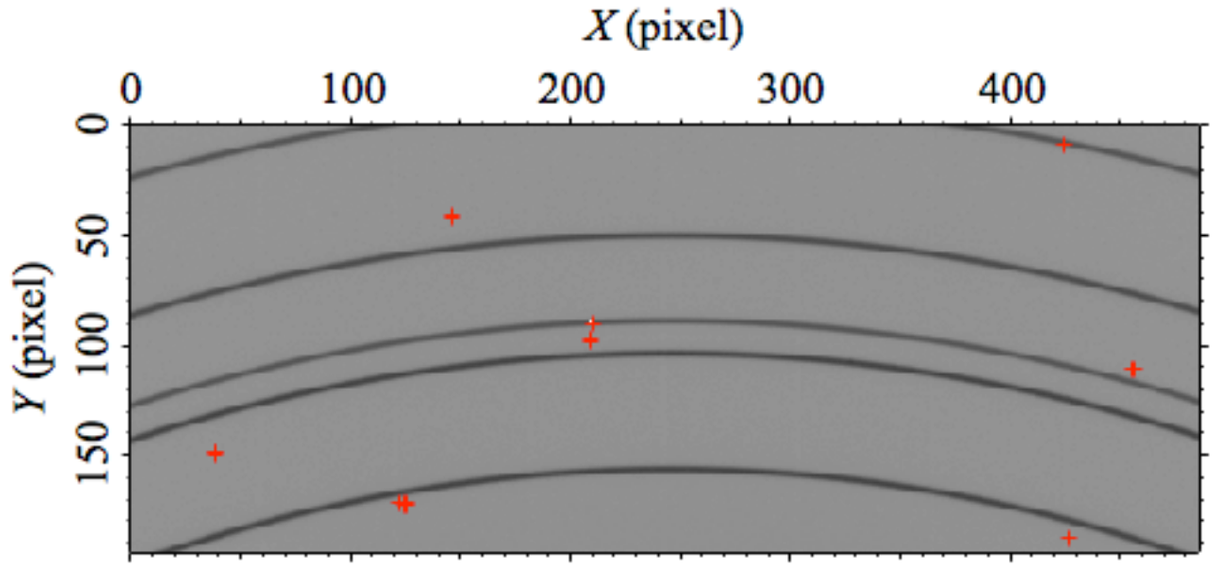


$$\left(X_j, Y_j\right) \rightarrow \left(2\theta_j, \varphi_j\right)$$

conformal mapping

$$I_j \rightarrow I'_j$$

solid-angle correction
(camera length + incident angle)
polarization correction




17 dead pixels in 487 x 195 pixels

equatorial pixel intensity

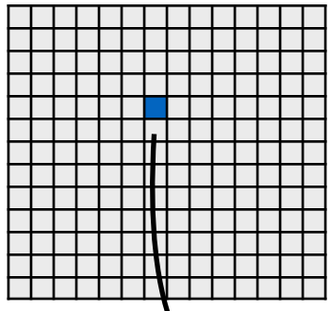
$$I_i = \frac{\sum_{2\Theta_i < 2\theta_j < 2\Theta_{i+1}} I'_j}{n_i} = \frac{\sum_{2\Theta_i < 2\theta_j < 2\Theta_{i+1}} I'_j}{\sum_{2\Theta_i < 2\theta_j < 2\Theta_{i+1}} 1}$$

statistical variance

$$\sigma_i^2 = \frac{1}{n_i - 1} \sum_{2\Theta_i < 2\theta_j < 2\Theta_{i+1}} \left(I'_j - I_i\right)^2$$

# Another Method for Structure Refinement

**Pixel-Mapping or Histogram Method**
**(Sulyanov *et al.* 1994)**



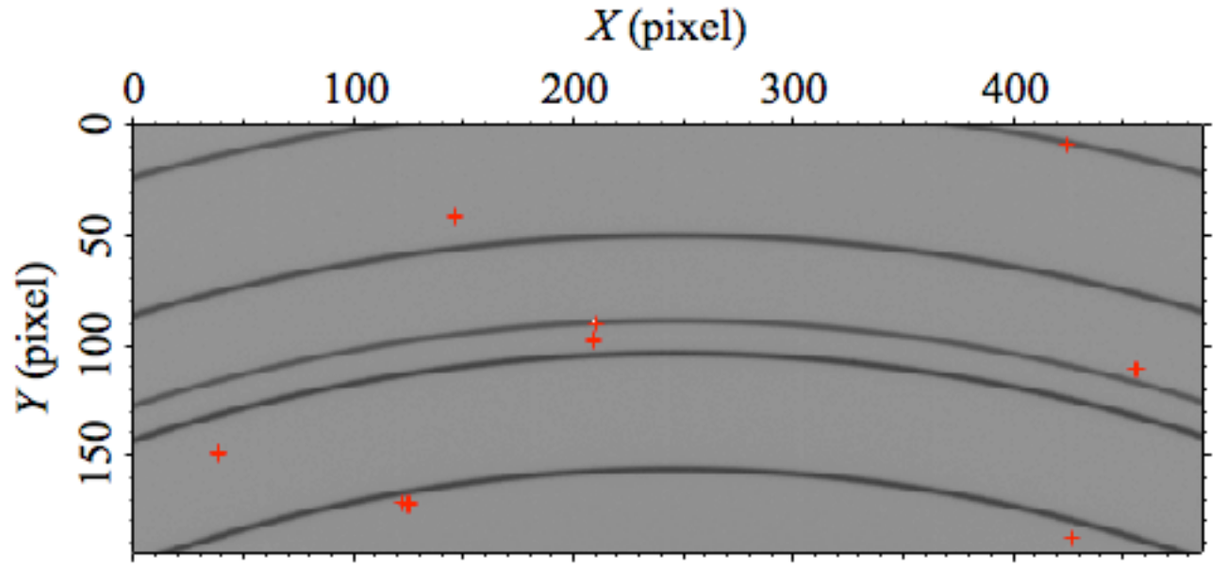
$$\left(X_j, Y_j\right) \rightarrow \left(2\theta_j, \varphi_j\right)$$

conformal mapping

$$I_j \rightarrow I'_j$$

solid-angle correction
(camera length + incident angle)
polarization correction

pretend to be located at
"equatorial position"




17 dead pixels in 487 x 195 pixels

"equatorial pixel average intensity"

$$I_i = \frac{\sum_{2\Theta_i < 2\theta_j < 2\Theta_{i+1}} I'_j}{n_i} = \frac{\sum_{2\Theta_i < 2\theta_j < 2\Theta_{i+1}} I'_j}{\sum_{2\Theta_i < 2\theta_j < 2\Theta_{i+1}} 1}$$

statistical variance

$$\sigma_i^2 = \frac{1}{n_i - 1} \sum_{2\Theta_i < 2\theta_j < 2\Theta_{i+1}} \left(I'_j - I_i\right)^2$$

# Conclusion

A new analytical method for powder diffraction intensity data based on MLE, superordinate concept of the LSQ method, has been developed. The method includes estimation of statistical errors on structure refinement.

The structure parameters of $Ca_3(PO_4)_3F$ & $BaSO_4$ optimized by the new method have become closer to the single-crystal data, as compared with the results of the Rietveld refinement. The structure of a La-Sr-Mn-O system optimized by the new method is clearly different from those refined by the Rietveld analyses.

Reasonable structure parameters was obtained from powder diffraction data of coarse $BaSO_4$ powder by applying the ML optimization.

published in *J. Appl. Cryst.* 44(5) 921-927 (2011).

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# Appendix: Background/Theory

Statistical analysis of experimental data

Baysian inference

↓ application of mode

Maximum A Posteriori estimation

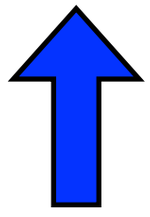
↓ uniform prior distribution

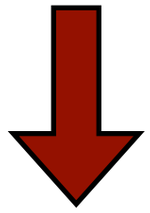
Maximum Likelihood Estimation

↓ experimental error known

Least Squares Method

general





special

**Appendix 2:** $Ca_5(PO_4)_3F$, $PbSO_4$, $BaSO_4$

Likelihood estimator = probability that observed dataset should appears

| | Ca | PbSO | BaSO |
|---|---|---|---|
| P | 10 | 10 | 10 |
| P | 10 | 10 | 10 |
| P | 10 | 10 | 10 |

The statistical model of the newmethod is $10^{885} \sim 10^{2081}$ times more likely than that used in Rietveld analysis

# Appendix: errors in the goniometer angles

## A theoretical model for statistical errors

$$\sigma_j^2 = (\sigma_c)_j^2 + (\sigma_p)_j^2 + (\sigma_r)_j^2 + (\sigma_{2\Theta})_j^2$$

(1) $\sigma_c$ : Error caused by counting (Poisson) statistics for count-loss negligible case
(2) $\sigma_p$ : Error caused by particle (sampling) statistics (Alexander et al. 1948)
(3) : Error proportional to intensity (Toraya 1998, 2000)
(4) $\sigma_r$ : Error caused by statistical error in goniometer angle

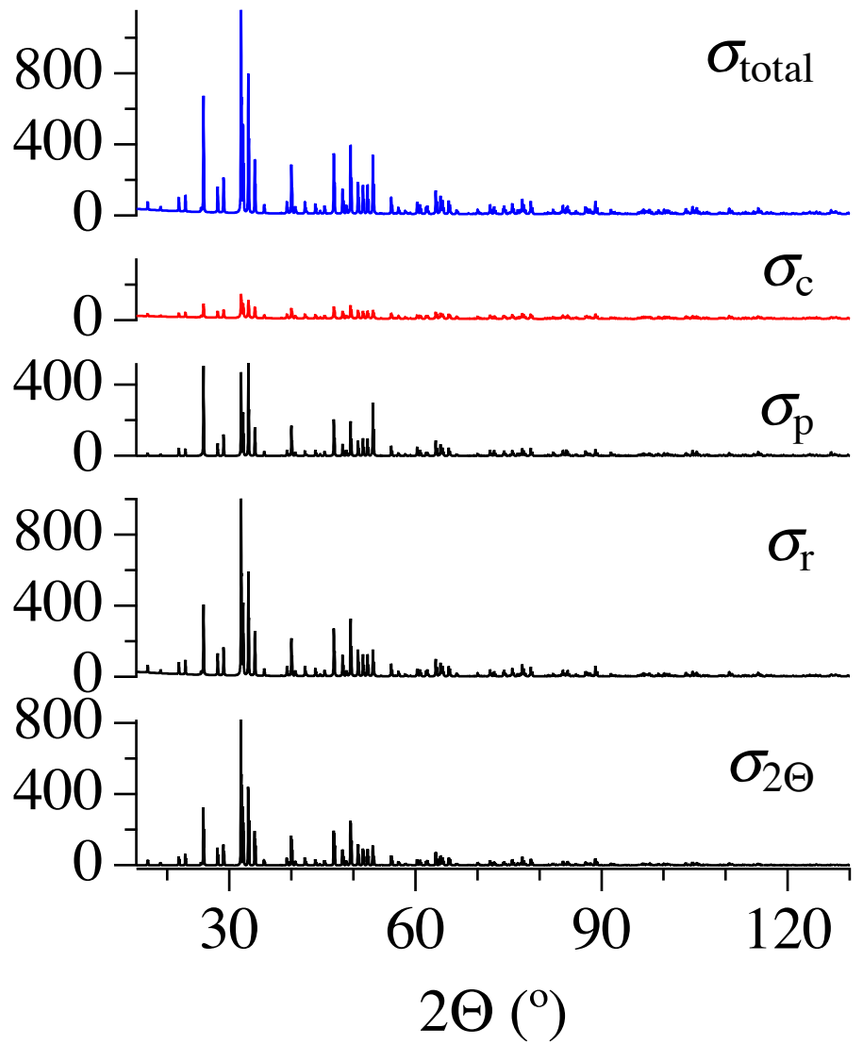
$\sigma_{2\Theta}$

$$\sigma_{2\Theta} = C_{2\Theta}(\Delta 2\Theta)$$

$$C_{2\Theta} = \left( \frac{\partial y_{\mathrm{calc}}}{\partial 2\Theta} \right)^{-1}$$

# Errors in 2Θ ? (1) $Ca_5(PO_4)_3F$ (open powder data)

## Optimized errors in 2Θ : Δ2Θ = 0.0030°




← Total errors evaluated by the maximum likelihood estimation

← Counting statistical errors

← Particle statistical errors

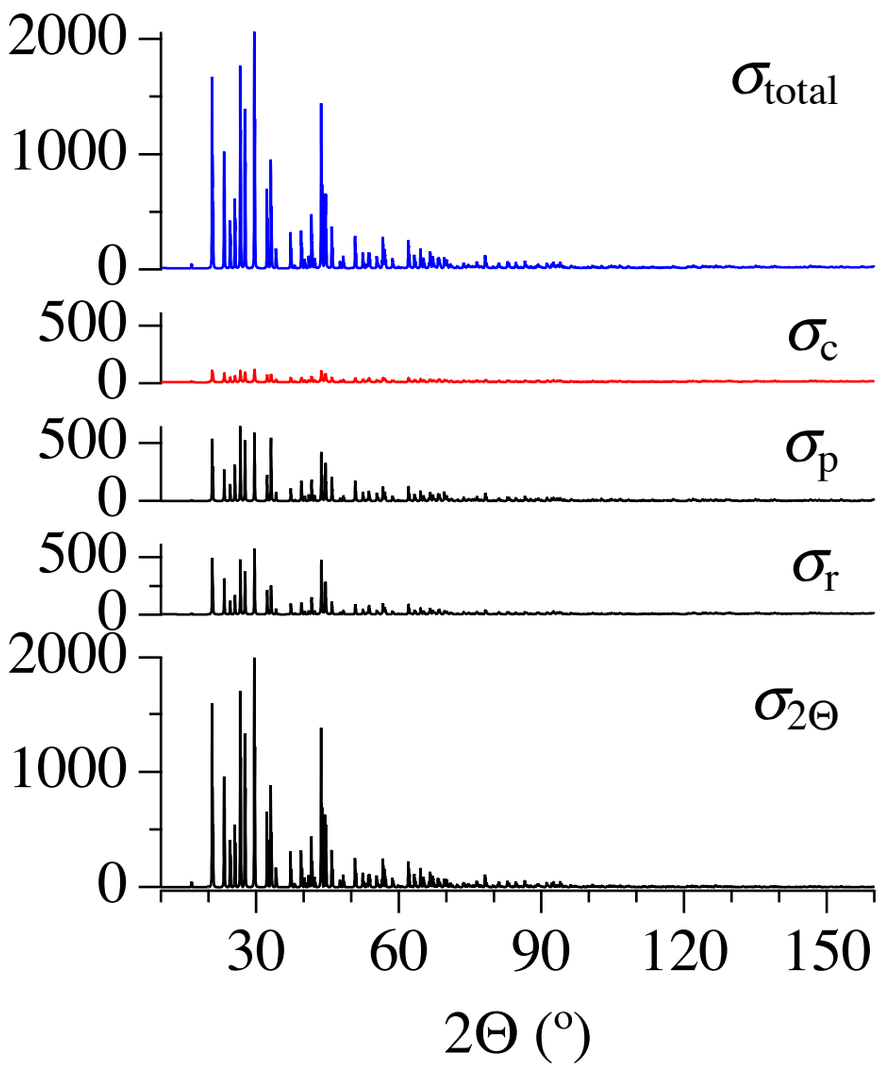
← Errors proportional to intensities

← Errors calculated with Δ2Θ = 0.003°

Total & component errors optimized by maximum likelihood estimation

# Errors in 2Θ ? (2) $PbSO_4$ (open powder data attached to *FULLPROF*)

## Optimized errors in 2Θ : Δ2Θ = 0.0099°




Total & component errors optimized by maximum likelihood estimation

← Total errors evaluated by the maximum likelihood estimation

← Counting statistical errors

← Particle statistical errors

← Errors proportional to intensities

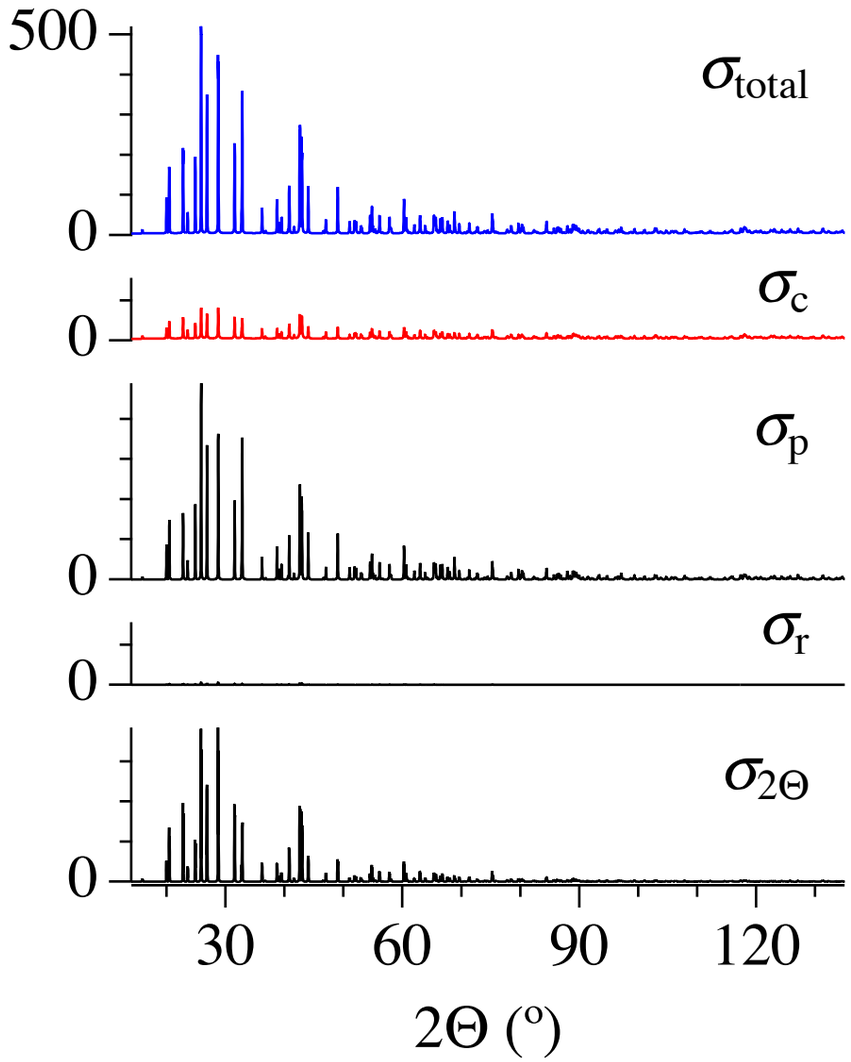
← Errors calculated with Δ2Θ = 0.0099°

*a* = 9.37102(10) Å
*c* = 6.88533(6) Å ⇐ MLE

*a* = 9.37124(10) Å
*c* = 6.88548(6) Å ⇐ Rietveld

# **Errors in 2Θ ? (3)** (open powder data attached to *RIETAN-FP*)

## Optimized errors in 2Θ : Δ2Θ = 0.0036°




Total & component errors optimized
by maximum likelihood estimation

← Total errors evaluated by the maximum likelihood estimation

← Counting statistical errors

← Particle statistical errors

← Errors proportional to intensities

← Errors calculated with Δ2Θ = 0.0036°

# Discussions on DXC 2012:

Q1 (Jim Kaduk, chairman): "Your talk makes us think many things before the excursion. There have been some suggestions to change how to weight the data in the Rietveld analysis, and do you think adjustment of weighting scheme can make similar results as your method ?"
A1: "Yes, I think it is possible, but I think the maximum likelihood method is easier."

Q2 (D. Balzar): "As you have mentioned, the errors in the optimized parameters were almost unchanged. Do you have any idea to explain that ?"
A2: "Good question... Actually, the results are different from what I expected, and I am not sure about the reason... But as I showed in equations, I have changed the treatment of the PEAK PROFILE intensity, but NOT changed the treatment of the BACKGROUND intensity in the statistical model. You know most of the powder diffraction intensity data are background intensity, so I think that can be a reason why the estimated errors are not significantly changed... but I am not sure about that now."