DXC 2012, Denver, CO, USA, 09 Aug. 2012

D-26 (16:10–16:30)

Analytical Method for Observed Powder Diffraction Intensity Data Based on Maximum Likelihood Estimation

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[2] *National Institute for Materials Science, Tukuba, Japan*

Contents

Motivation

Errors in Optimized Parameters (Lattice Const., Atomic Positions, etc) can be evaluated by Rietveld Analysis, if the Experimental Errors are Known.

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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-Seinsitivity Detectors (1-D, 2-D)
- Samples with Good Crystallinity and/or Heavy Elements

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Experimental Errors are Under-Estiimated !

→ Use Appropriate Values for Experimental Errors !

Background/Theory (1/2)

A theoretical model for statistical errors

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

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

= square root of count

(2) σ_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 relection, 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,

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Proportionality factor C_p is unknown

Background/Theory (1/2)

A theoretical model for statistical errors

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

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

= square root of count

(2) σ_p : Error caused by particle (sampling) statistics (Alexander et al. 1948)

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

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

Proportionality factor C_p is unknown

(3) σ_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

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 : $\Delta_j = \left(Y_{obs}\right)_j - \left(y_{calc}\right)_j$

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

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= 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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Least-squares method (LSQ)

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

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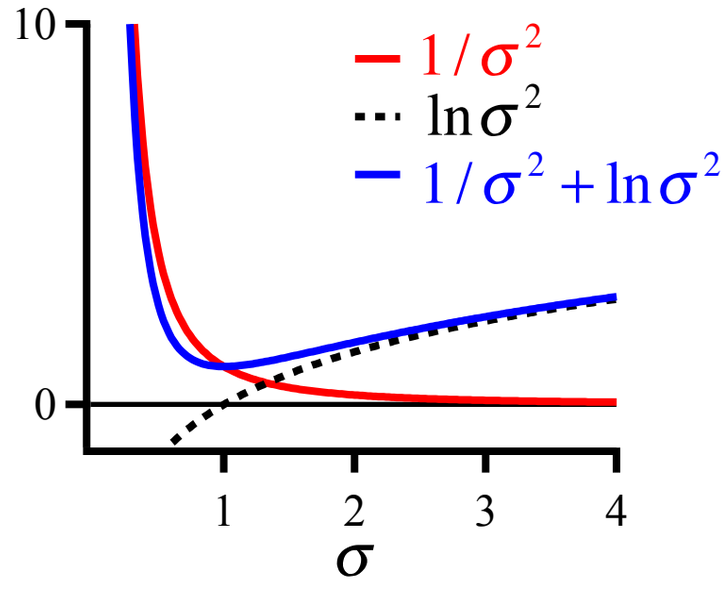
Weighted Sum of Squared Deviations



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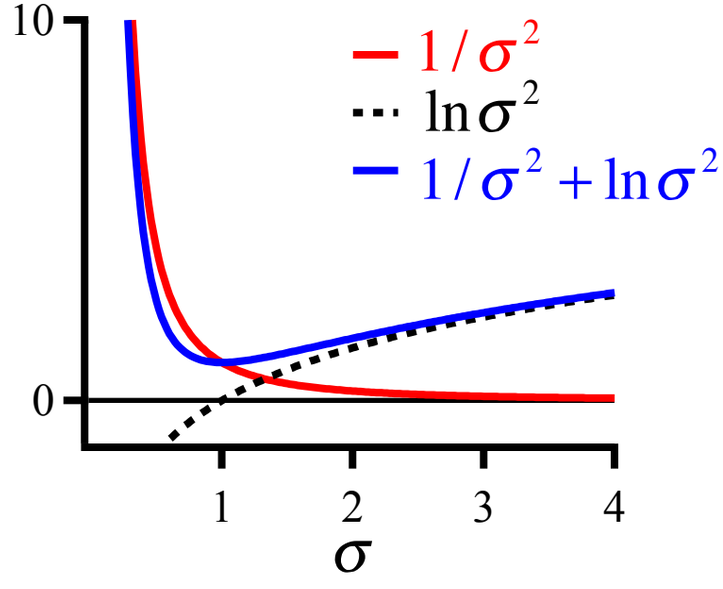

Just Minimize Unlikelihood !

Method of Calculation

Step (1) : Structure refinement by the Rietveld method

Optimization of structure and profile models

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

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

σ

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 Calculation

Step (1) … Rietveld method

Optimiza…

(wit…

Give me Δ & {y_1, …, y_M}, as OUTPUT, and Allow σ as INPUT

Δ, {y_1, …, y_M}

σ

Step (2) : Error estimation by M…

OK !

Evaluation of effective multiplicity at each da…

Optimization of error model by downhill simplex…

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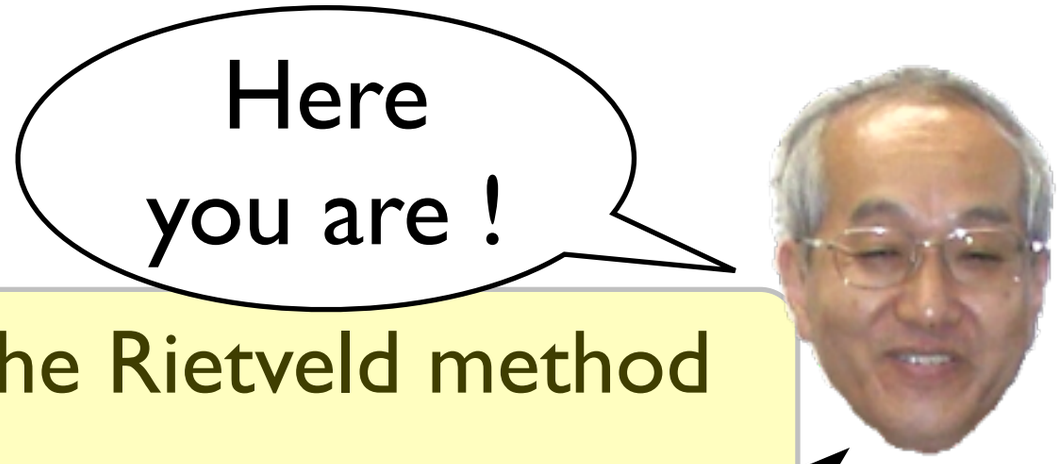

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F. Izumi

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T. Ida

Iterations of steps (1) & (2)

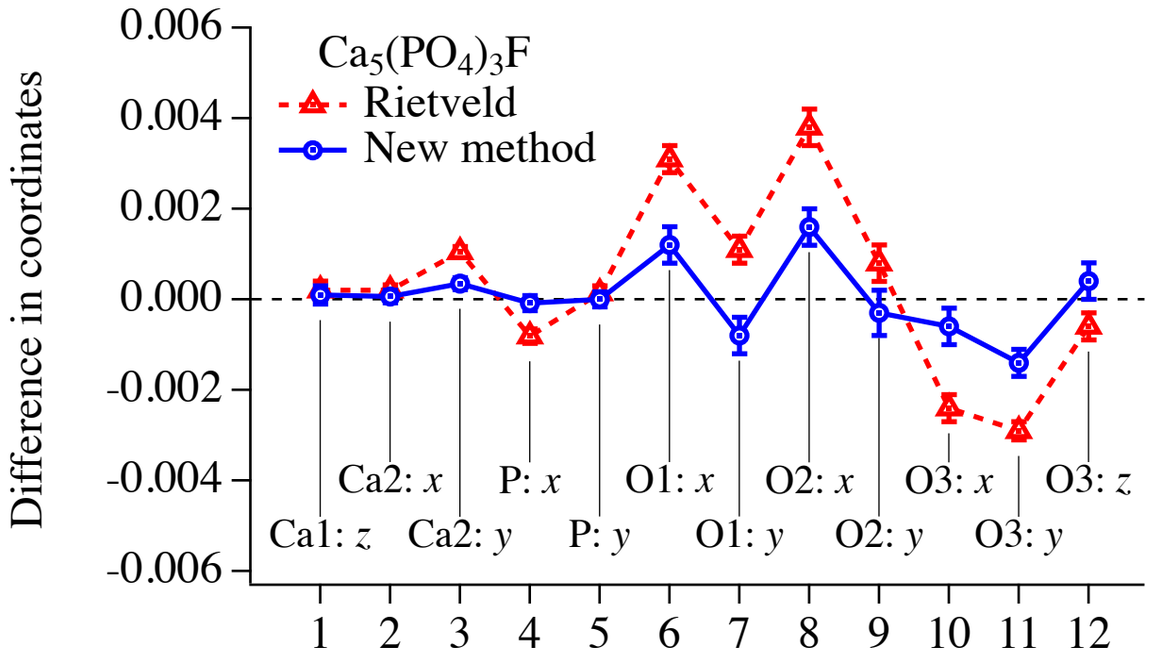
Maximum-likelihood solution of structure, profile and error models will be obtained, when no change is observed on further iteration (typically 2~3 iterations are needed).

Ida-Izumi cycle (!)

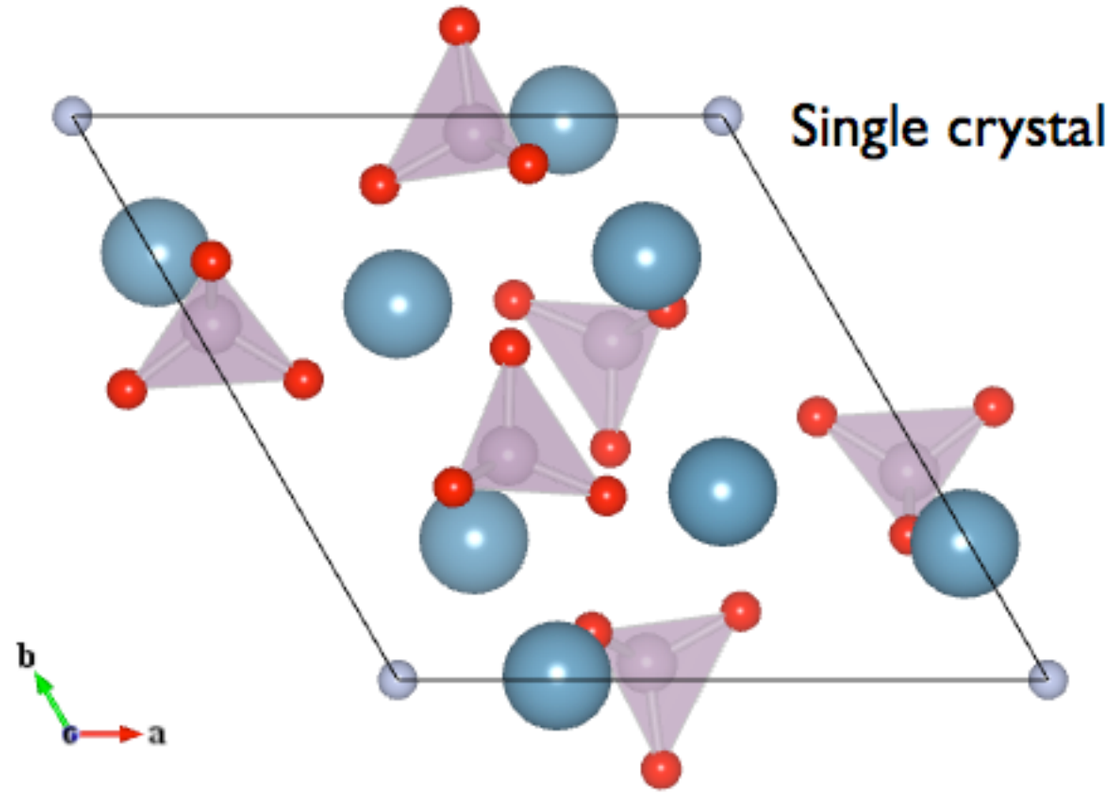
Results (1/4) $Ca_5(PO_4)_3F$ (powder data attached to *RIETAN-FP*)

Comparison with single-crystal data

Mineral & synthetic (Sudarsanan *et al.* 1972)



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 !

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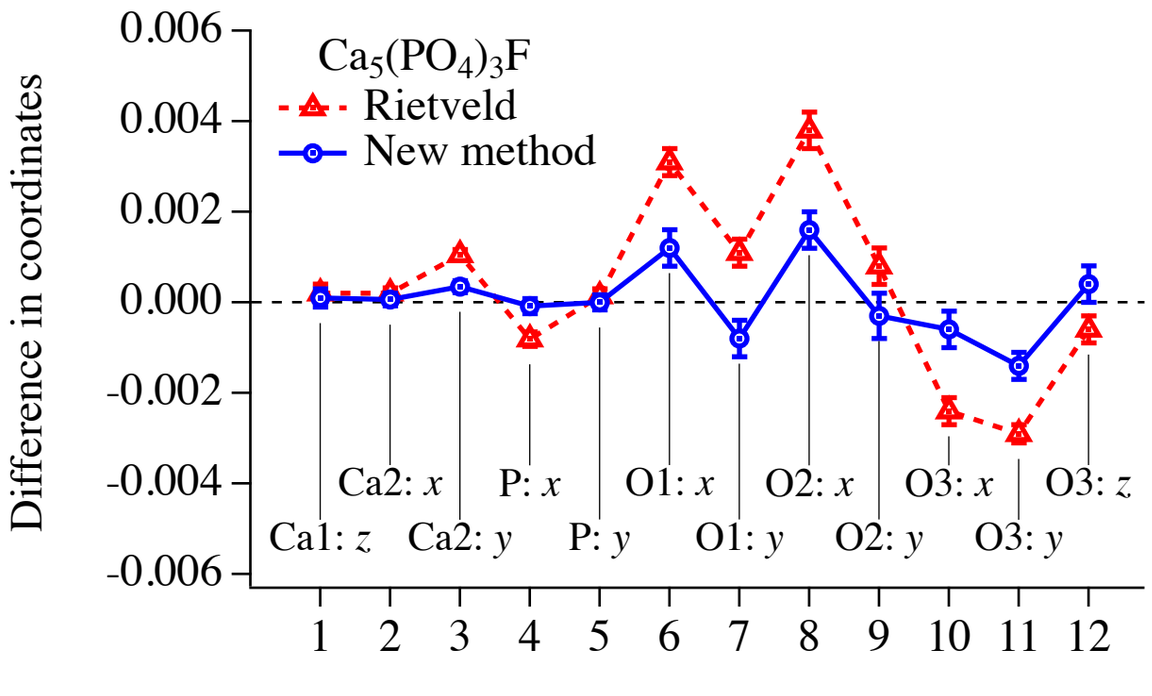

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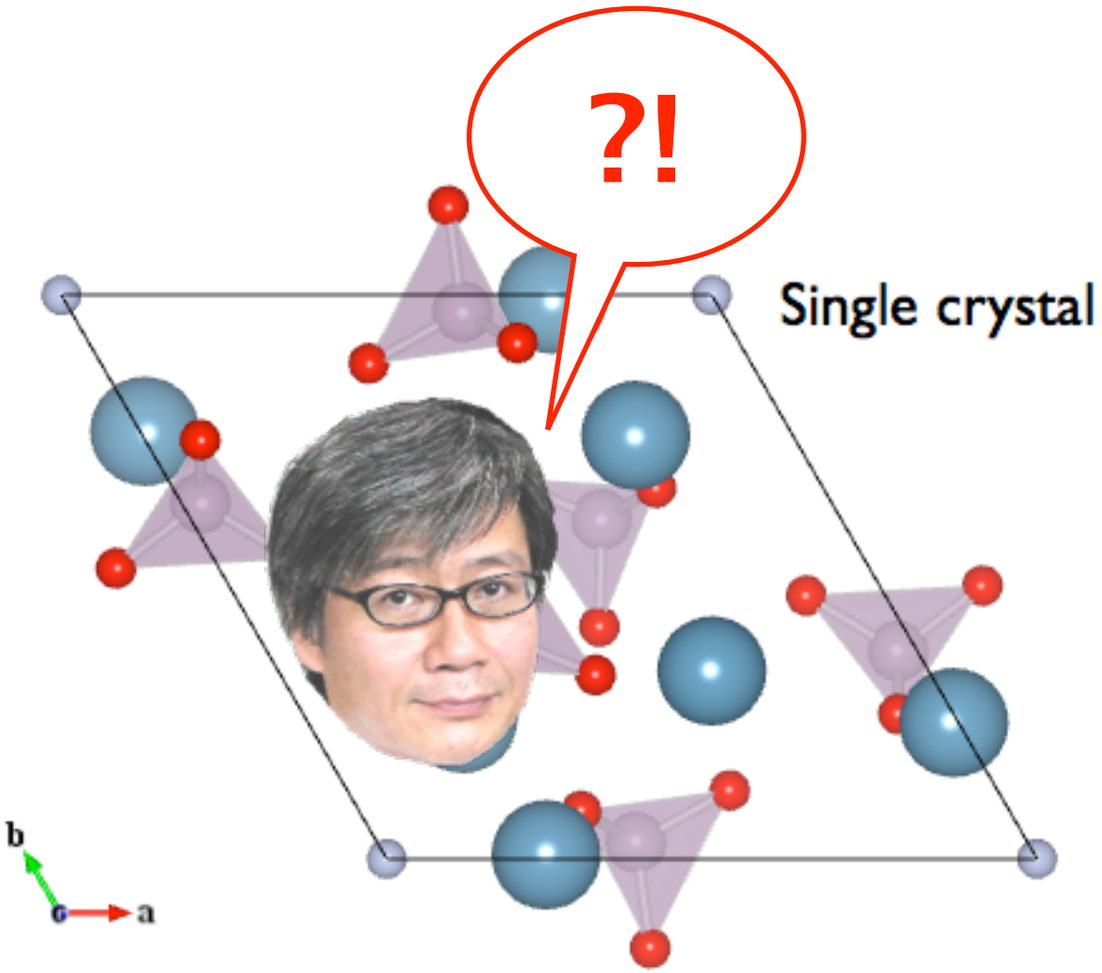


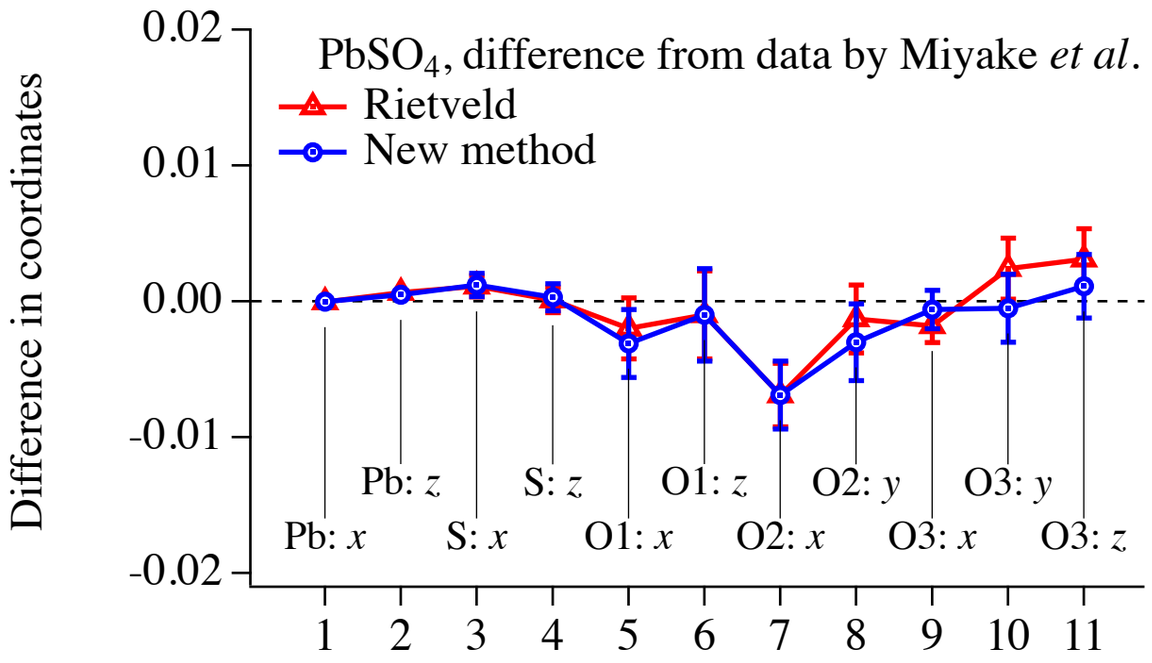
*P*6$_3$/*m*

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 !

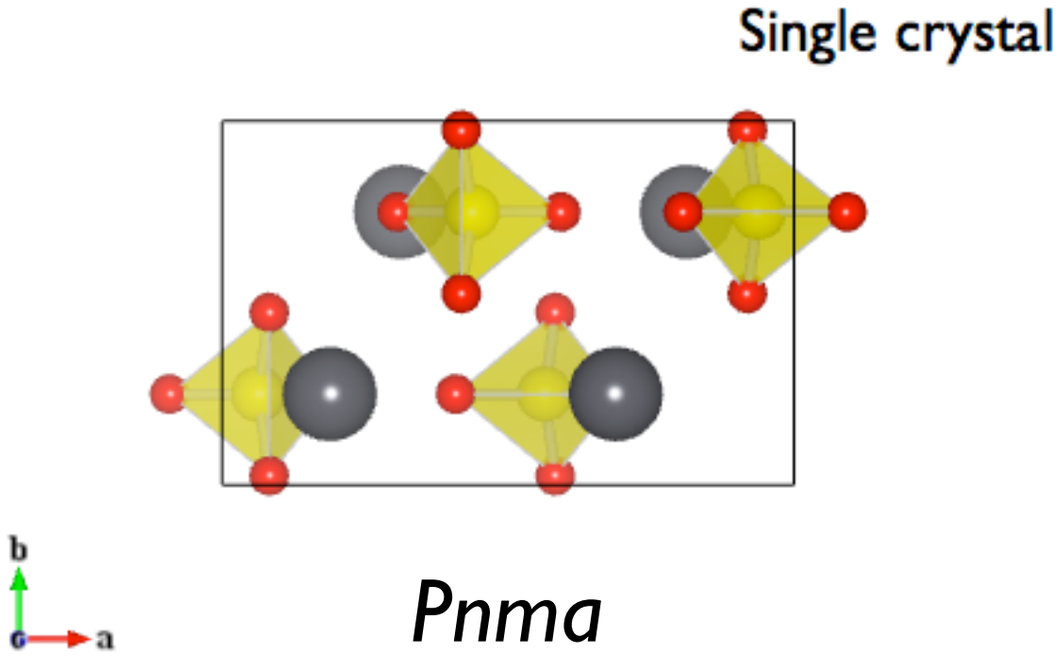
Results (2/4) $PbSO_4$ (powder data attached to *FULLPROF*, used for RRRR)

Comparison with single-crystal data

Lamellar 0.17×0.17×0.03 mm^3 (Miyake *et al.* 1978), 0.1×0.08×0.06 mm^3 (Lee *et al.* 2005)



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



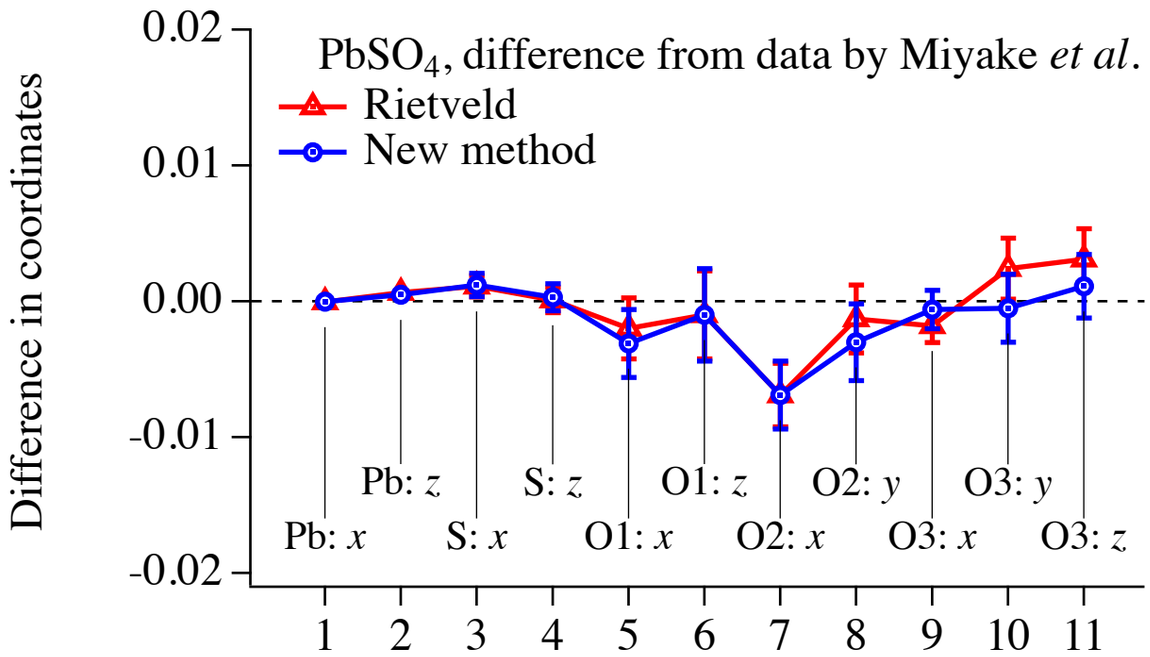
The difference between **the results of the Rietveld method** and **the results of the new (MLE) method** is not significant, in this case.

Results (2/4) $PbSO_4$ (powder data attached to *FULLPROF*, used for RRRR)

Comparison with single-crystal data

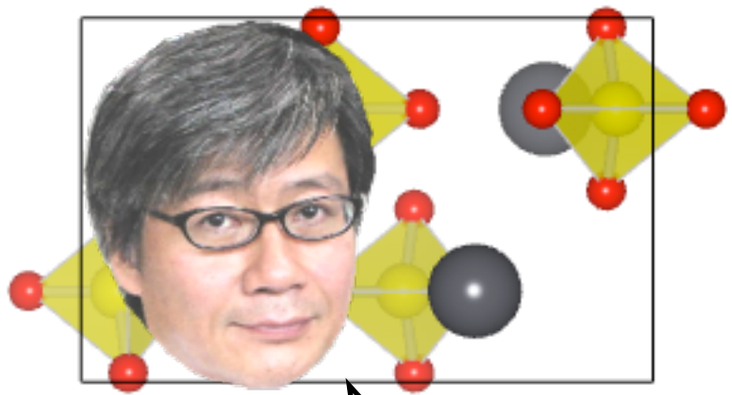
Lamellar 0.17×0.17×0.03 mm^3 (Miyake *et al.* 1978), 0.1×0.0[illegible]2005)

Disappointed ?



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

Single crystal



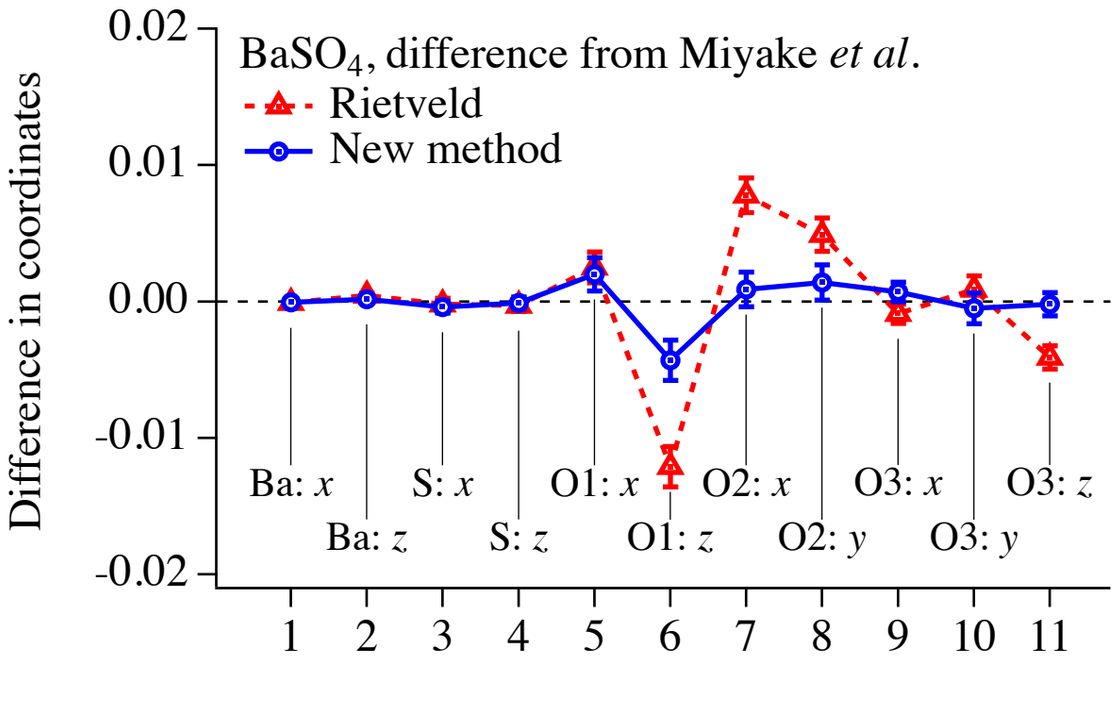
Not at all !

The difference between **the results of the Rietveld method** and **the results of the new (MLE) method** is not significant, in this case.

Results (3/4) $BaSO_4$ (powder data attached to *RIETAN-FP*)

Comparison with single-crystal data

Spherical 0.15 mmΦ (Miyake *et al.* 1978), 0.33×0.25×0.15 mm^3 (Lee *et al.* 2005)



Difference in atomic coordinates
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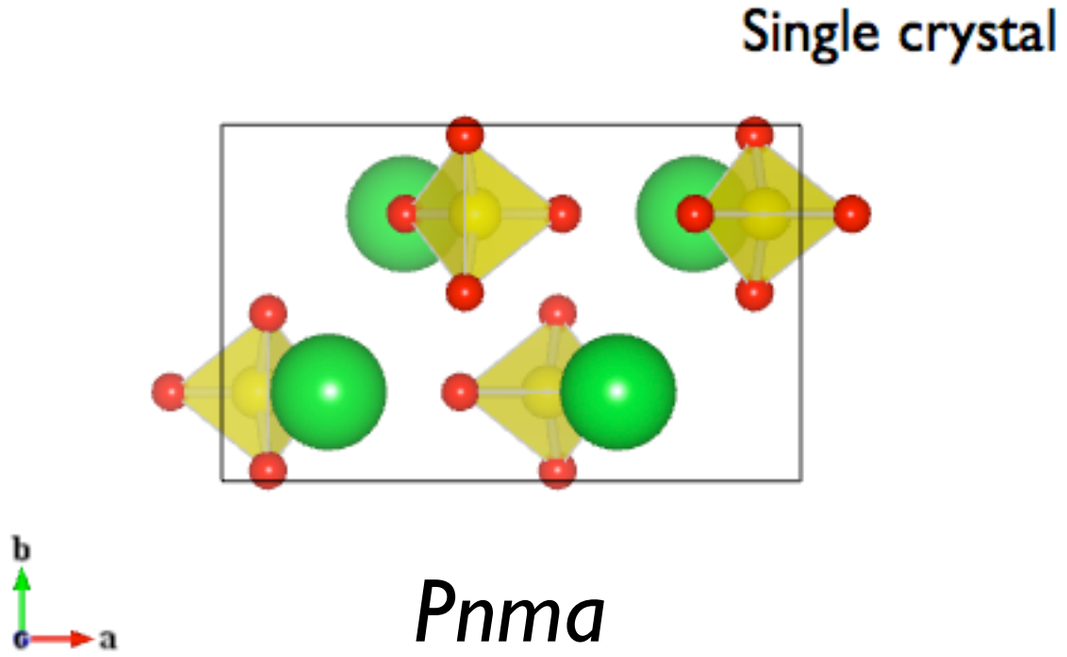


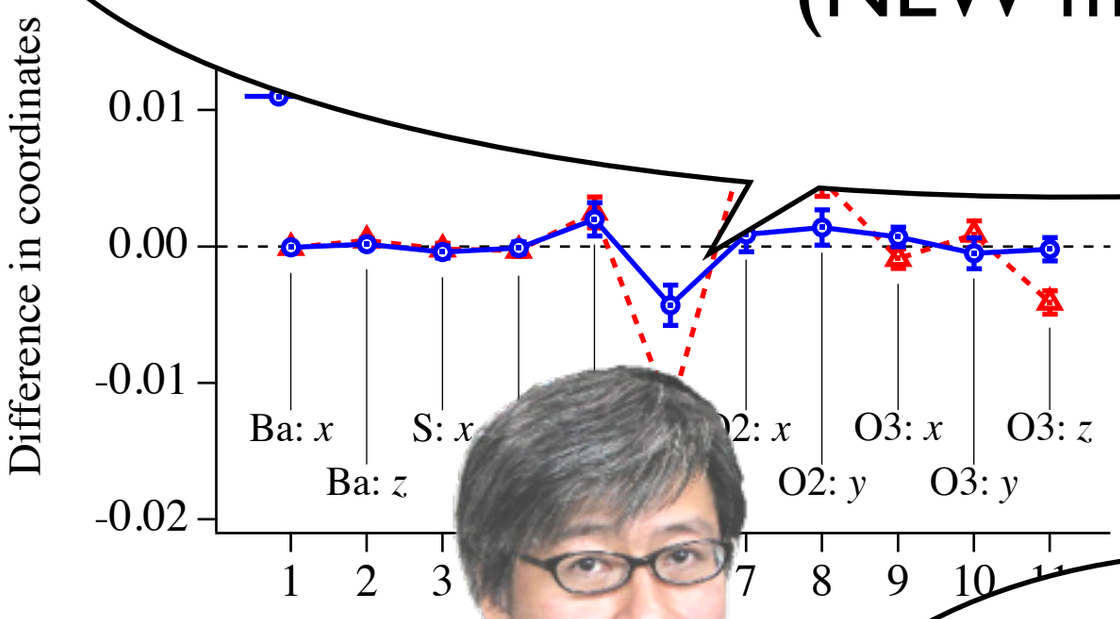
The results of the new (MLE) method coincide with the **single-crystal data** except one structure parameter (O1: z), while the deviations in **the results of the Rietveld method** exceed the error range.

Results (3/4) $BaSO_4$ (powder data attached to *RIETAN-FP*)

Comparison

Sph

(Maximum Likelihood Estimation: < 1920)
+ (Particle Statistics: 1948)
= (NEW method) ?



Difference in atomic coor
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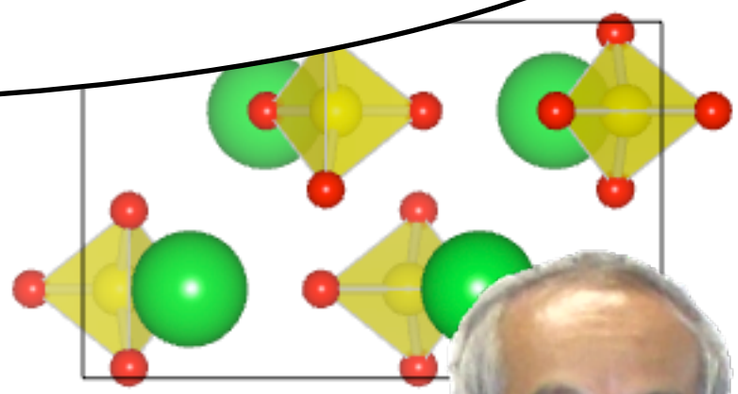
gle crystal



Pnma

You may call it a NEW method !!

The results of the new (

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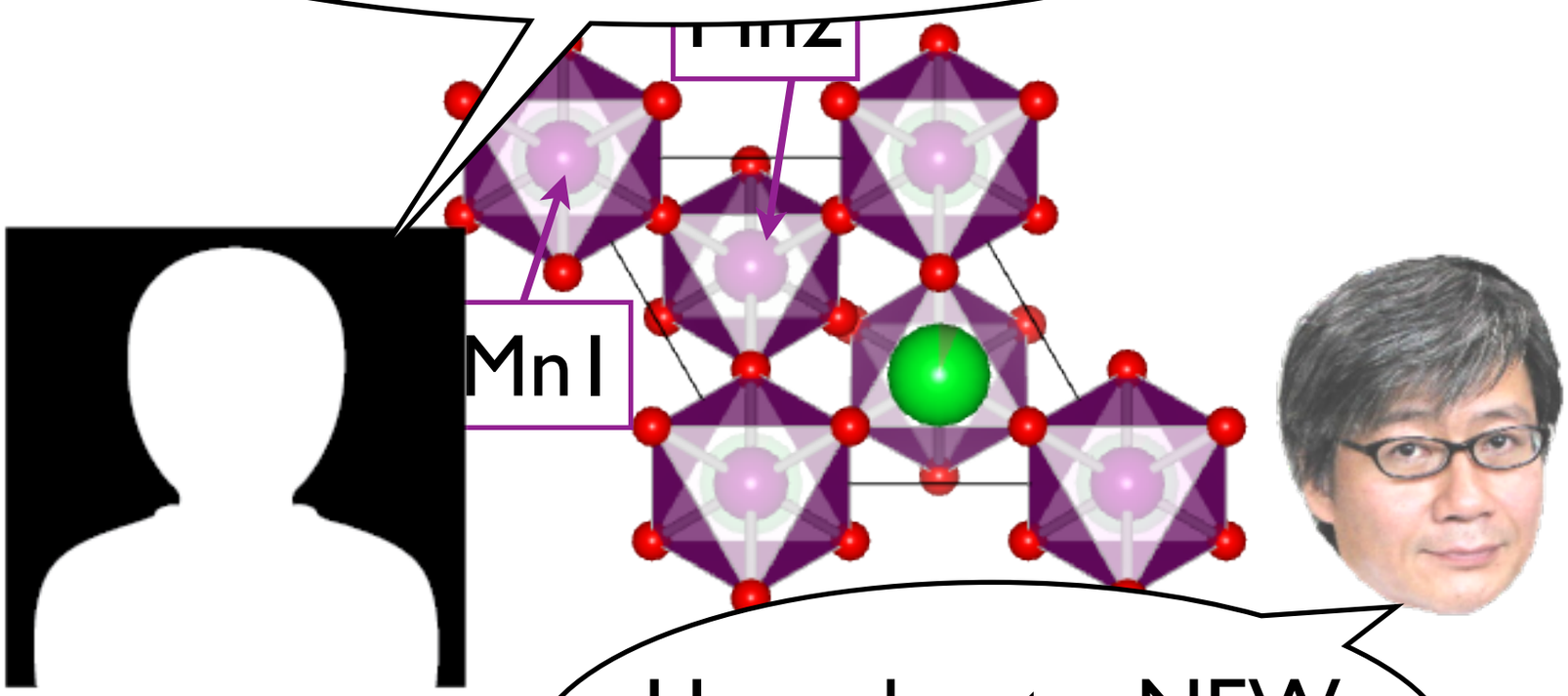
eviations in **the results of the Rietveld method** exceed the error range.

Results (4/4)

$La_{0.03}Sr_{0.9}$

Give me the Rietveld results



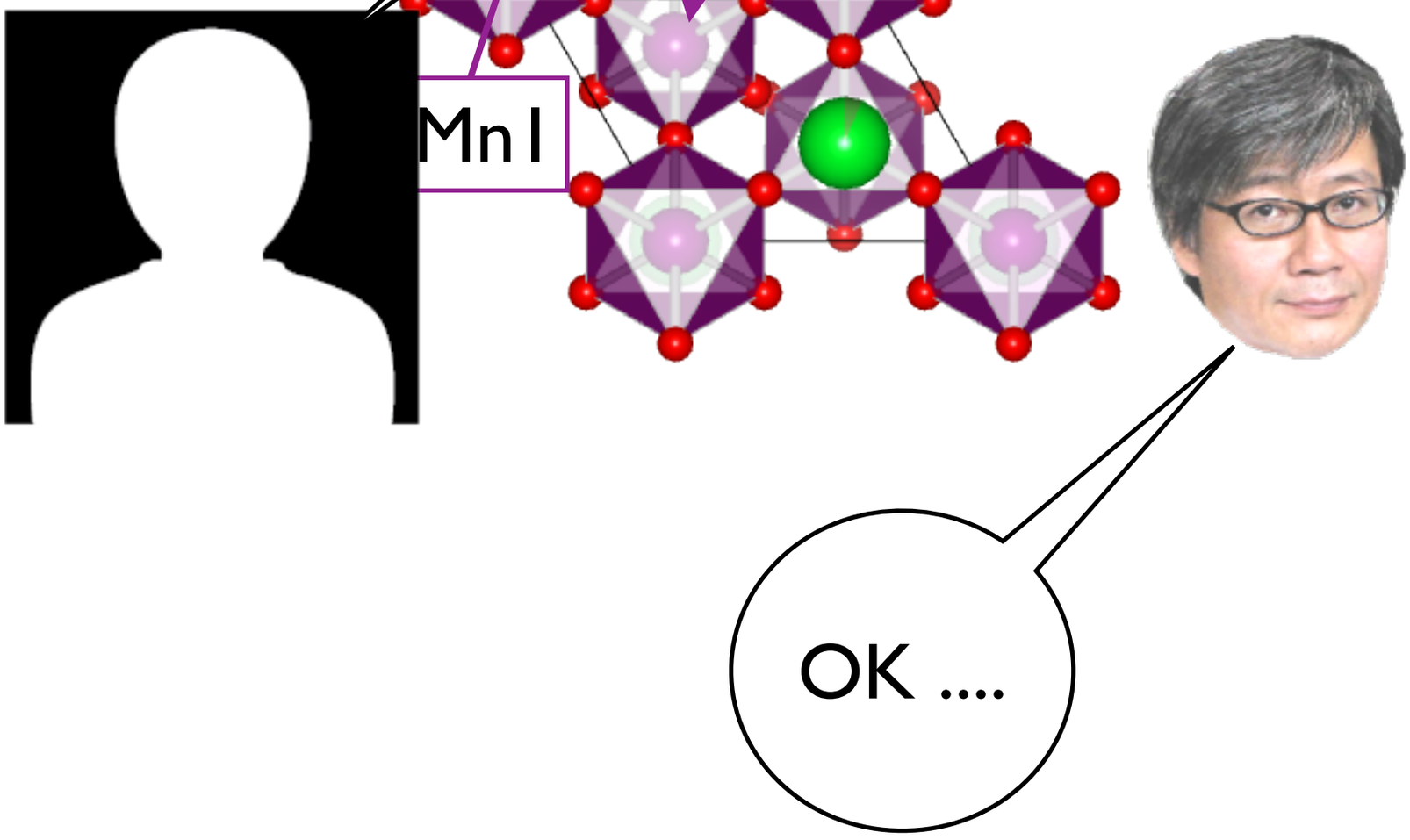
How about a NEW method ?

.....

Results (4/4)

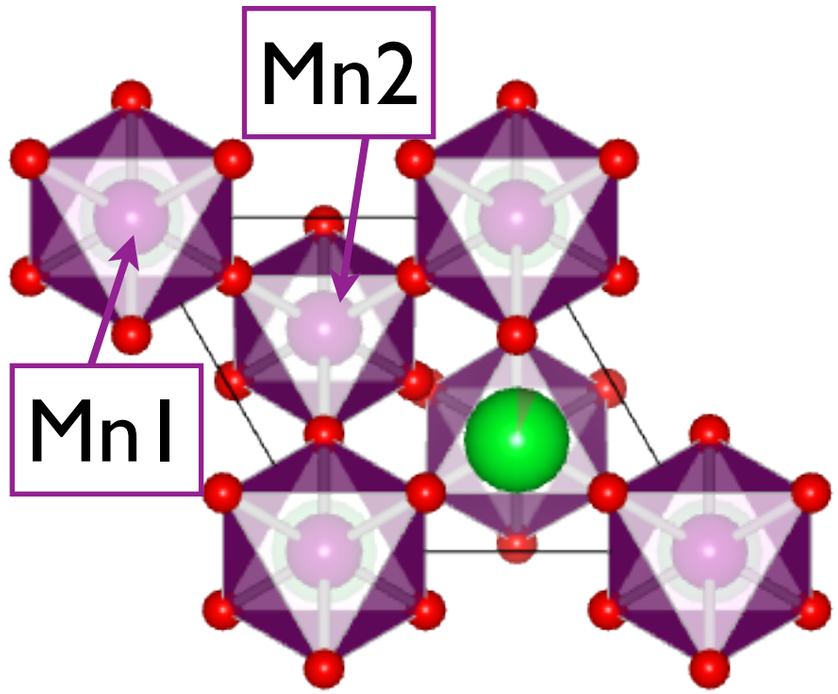
$La_{0.03}Sr_{0.9}$

Give me the Rietveld results, anyway.



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

$La_{0.03}Sr_{0.97}MnO_3$, *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 (4/4) $La_xSr_{1-x}MnO_3$

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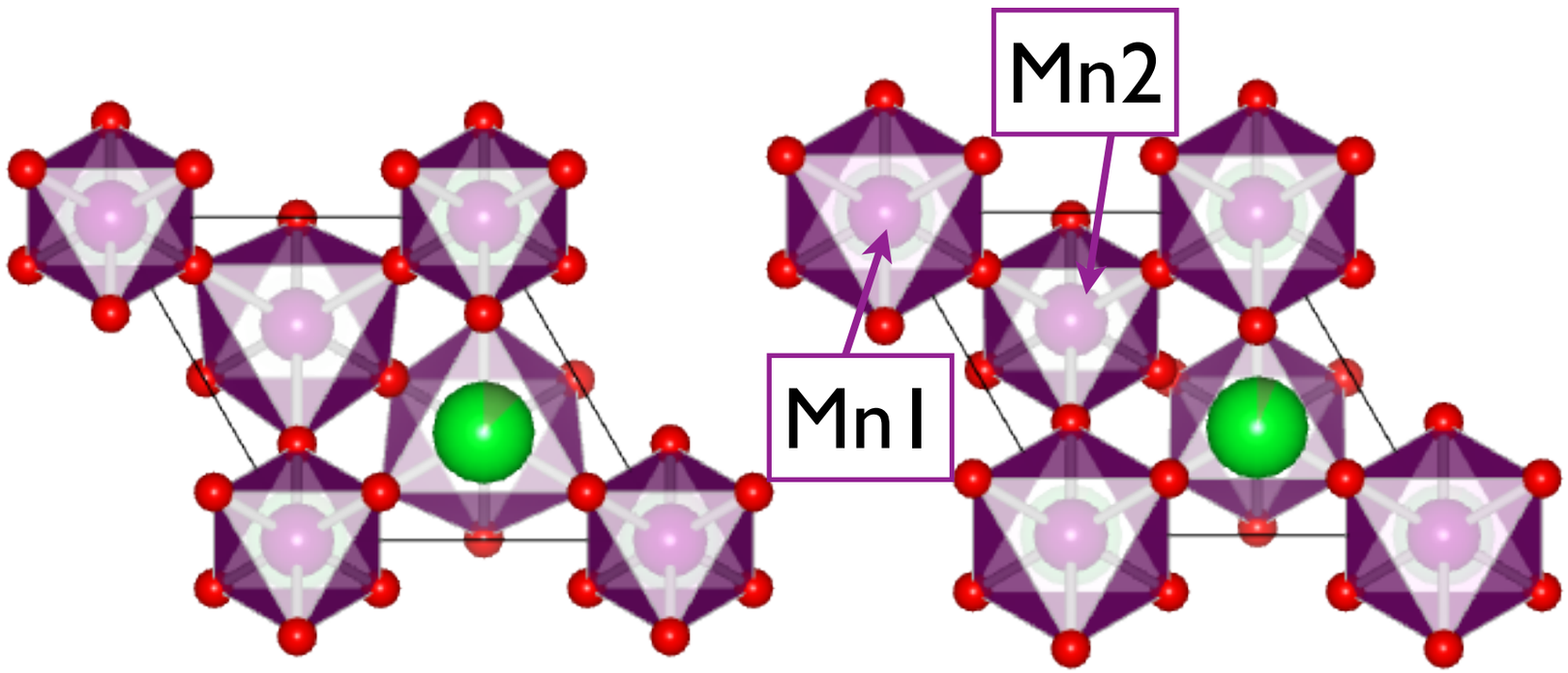

PDF#04-010-5038
(Star Quality)
$La_{0.1}Sr_{0.9}MnO_3$
Rietveld
BVS(Mn1) = +4.65
BVS(Mn2) = +3.04

SPring-8 BL19B2
$La_{0.03}Sr_{0.97}MnO_3$
Rietveld
BVS(Mn1) = +2.97
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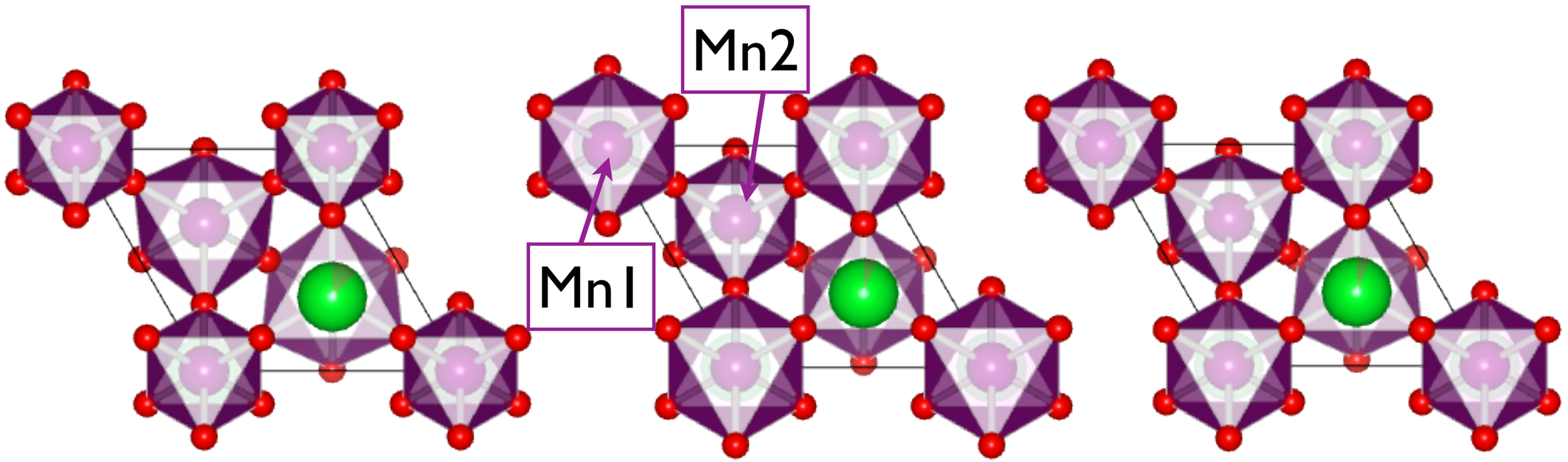
Results (4/4) $La_xSr_{1-x}MnO_3$

$La_{0.03}Sr_{0.97}MnO_3$, $P6_3/mmc$



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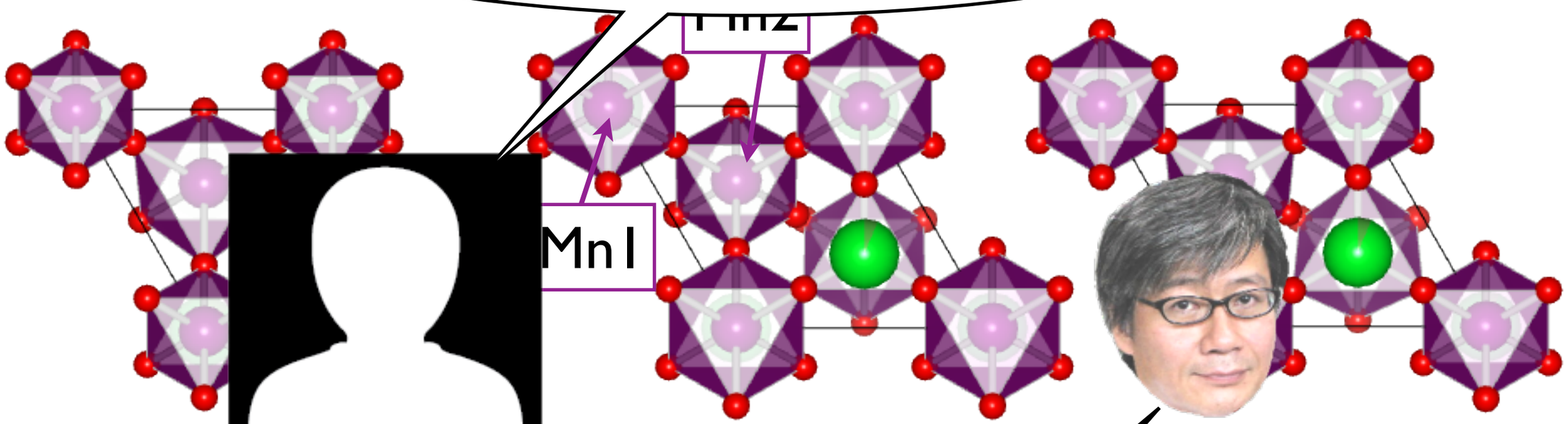
SPring-8 BL19B2
$La_{0.03}Sr_{0.97}MnO_3$
Ida-Izumi
BVS(Mn1) = +3.82
BVS(Mn2) = +3.90

Results (4/4)

$La_{0.03}Sr_{0.9}$

I adopt the results of your NEW method.



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SPring-8 BL19B2
$La_{0.03}Sr$
Rie
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....

SPring-8 BL19B2
$La_{0.03}Sr_{0.97}MnO_3$
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Conclusions

Application of the Rietveld (LSQ) method to powder X-ray diffraction data is hardly justified in some (many ?) cases.

A new analytical method for powder diffraction intensity data based on MLE, superordinate concept of the LSQ method, has been developed. The method incorporates estimation of statistical errors with 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 parameters of $PbSO_4$ was almost unchanged.

The structure of a La-Sr-Mn-O system optimized by the new method is significantly different from those refined by the Rietveld analyses. Discussions about crystal & electronic structures (chemical bond, crystal field, orbital mixing, electronic correlation, electron-phonon coupling, ... *etc*) will consequently become different.

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

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The structure parameter[illegible]$O_4)_3F$ & Ba[illegible] become closer to the sin[illegible] data, as compared with the results of the Rietveld refinement. The structure[illegible]ers of $PbSO_4$ was almost unchanged.

The structure of a La-Sr-Mn-O system optimized by the new method is significantly different from those refined by the Rietveld analyses. Discussions about crystal & electronic structures (chemical bond, crystal field, orbital mixing, electronic correlation, electron-phonon coupling, ... *etc*) will consequently become different.

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Appendix: Background/Theory

Statistical analysis of experimental data

Baysian inference

↓ application of mode

Maximum A Posteriori estimation

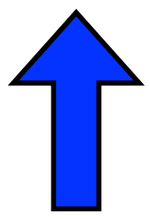
↓ uniform prior distribution

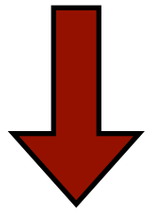
Maximum Likelihood Estimation

↓ 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

	$Ca_5(PO_4)_3F$	$PbSO_4$	$BaSO_4$
$P_{Rietveld}$	10^{-14698}	10^{-17386}	10^{-9567}
$P_{Ida\text{-}Izumi}$	10^{-13654}	10^{-15305}	10^{-8682}
$P_{Ida\text{-}Izumi}$ / $P_{Rietveld}$	10^{1044}	10^{2081}	10^{885}

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