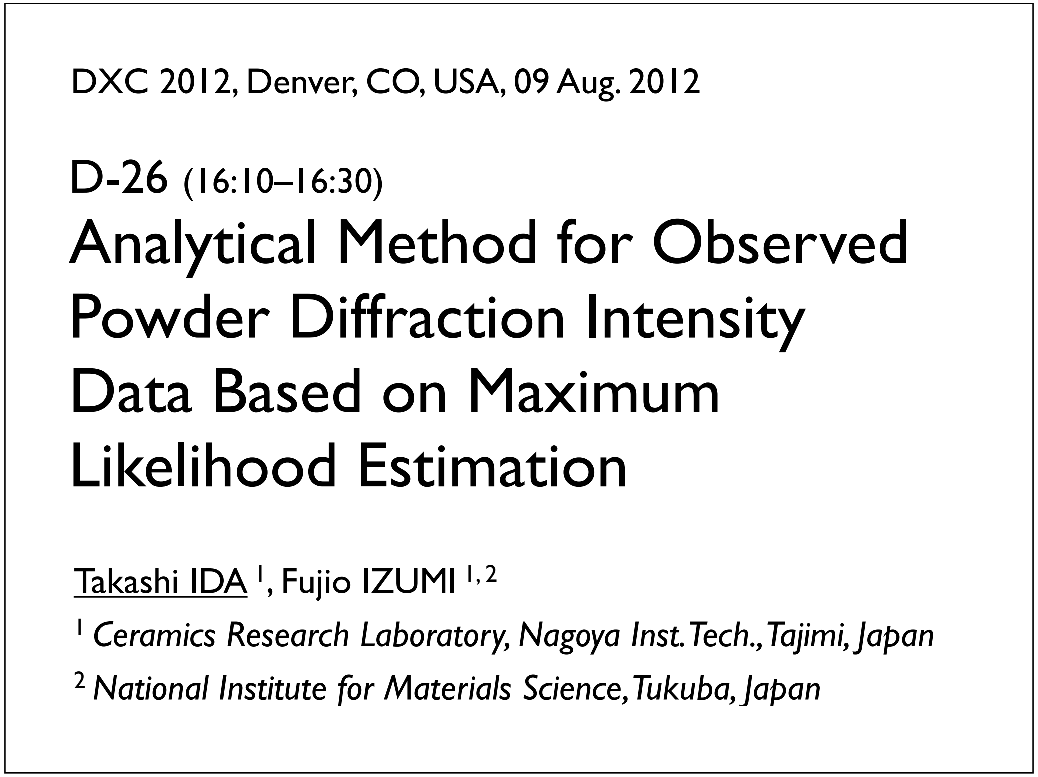


DXC 2012, Denver, CO, USA, 09 Aug. 2012

D-26 (16:10–16:30)

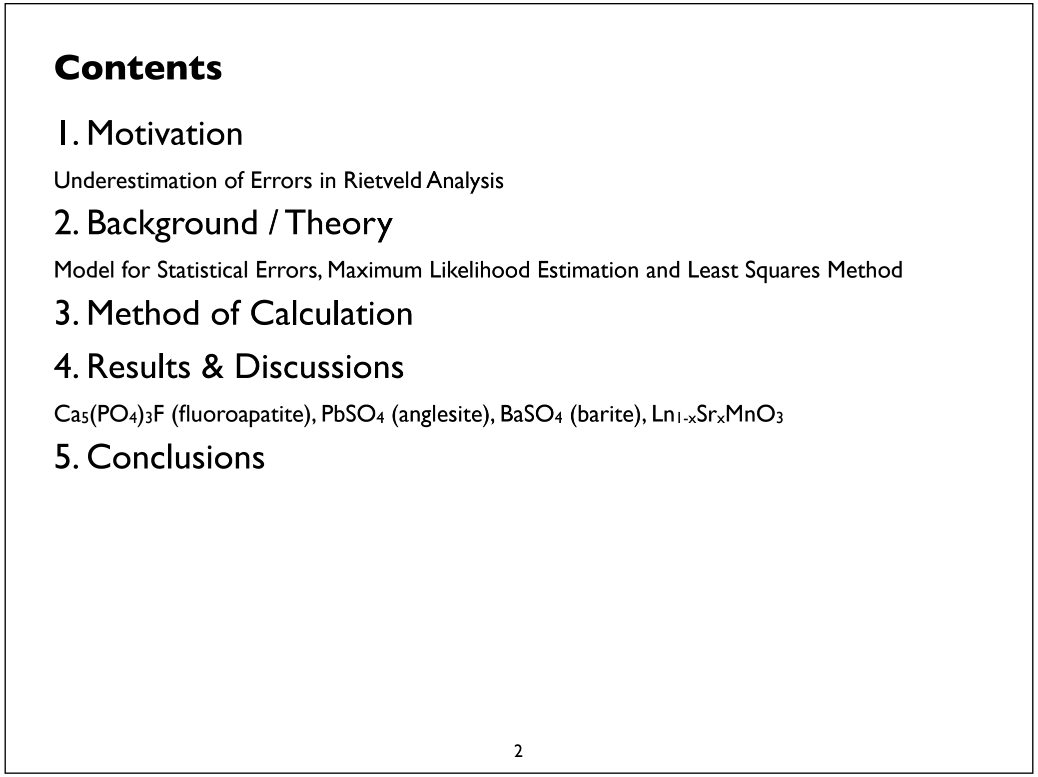
Analytical Method for Observed Powder Diffraction Intensity Data Based on Maximum Likelihood Estimation

Takashi IDA [1], Fujio IZUMI [1, 2]

[1] *Ceramics Research Laboratory, Nagoya Inst. Tech., Tajimi, Japan*

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

It is the first time I attend the Denver conference, I am really enjoying this meeting, and I am happy to make a talk here.
Thanks to the organizers and all the staffs on this meeting.
Now, I will be talking about a new method for analysis of observed powder diffraction data based on maximum likelihood estimation.



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Underestimation of Errors in Rietveld Analysis

2. Background / Theory

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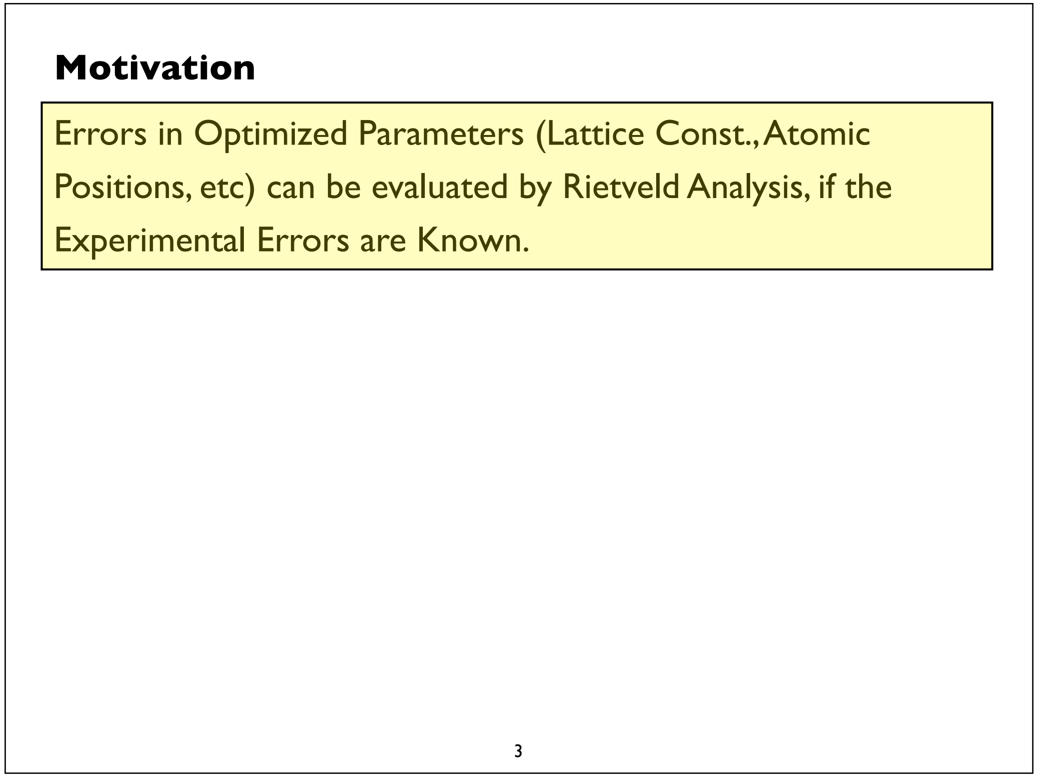
3. Method of Calculation

4. Results & Discussions

$Ca_5(PO_4)_3F$ (fluoroapatite), $PbSO_4$ (anglesite), $BaSO_4$ (barite), $Ln_{1-x}Sr_xMnO_3$

5. Conclusions

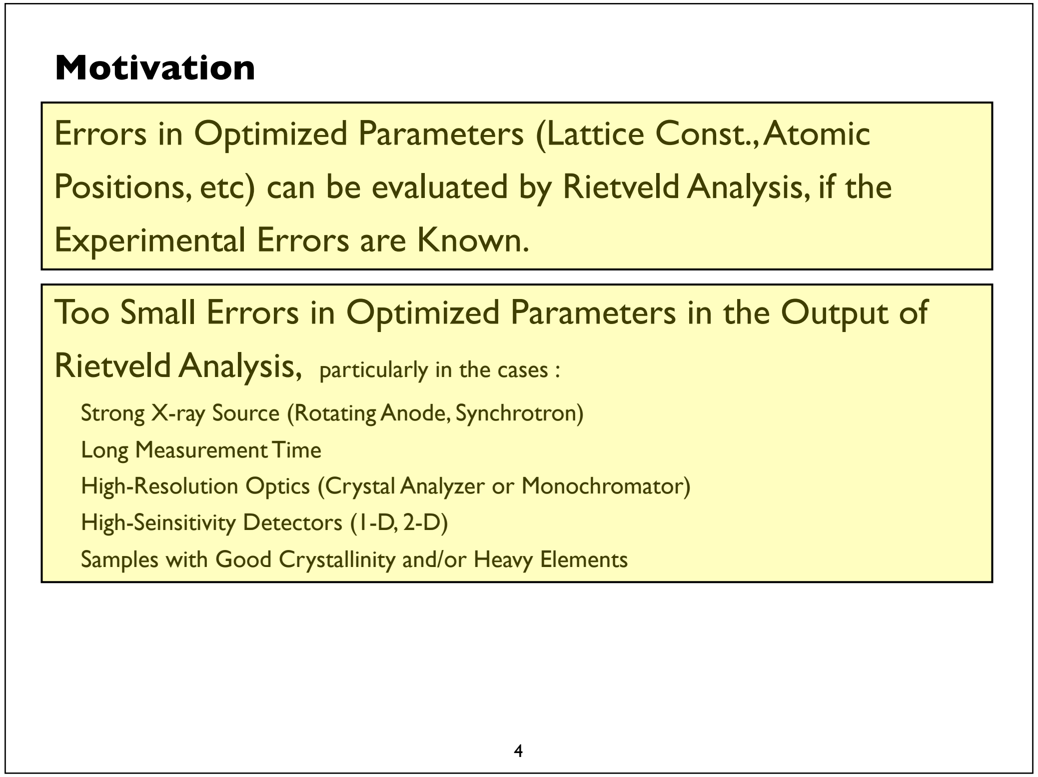
In this presentation, I will talk about the motivation of this study, theoretical aspects, method of calculation, and the results of structure refinement about 4 examples, and like to show the conclusions of the study.



Motivation

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

First, let me mention, why I started this study, because the conclusions, I will show you later, may appear somehow TRICKY to some Rietveld users, but the motivation of this study seems to be commonly acceptable !
In principle, errors in crystallographic parameters, such as lattice constants, atomic positions, and so on, can be evaluated by the Rietveld analysis, if the experimental errors are known quantities.



Motivation

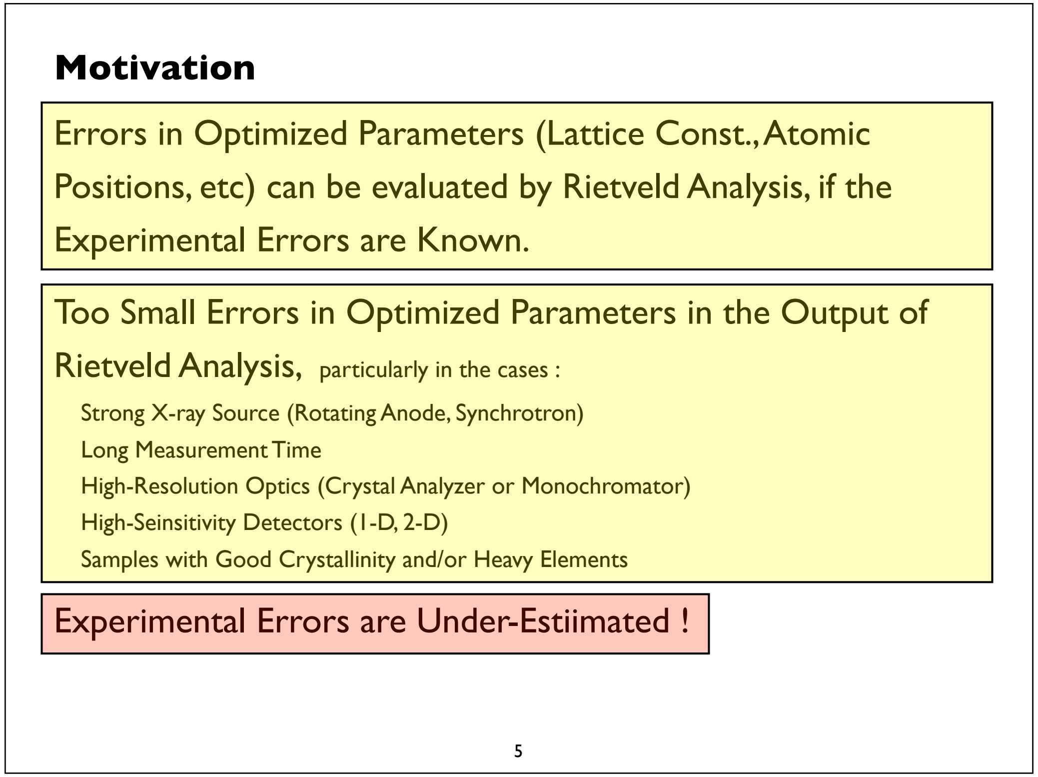
Errors in Optimized Parameters (Lattice Const., Atomic Positions, etc) can be evaluated by Rietveld Analysis, if the Experimental Errors are Known.

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

But we often get TOO small errors in the output of Rietveld analysis, particularly in the cases: Strong x-ray source, Long-Time Measurement, High-Resolution Optics, High-Sensitivity Detectors, and well-crystallized samples, or samples including heavy elements.

Most of them sound NICE, but we should be careful in those cases.



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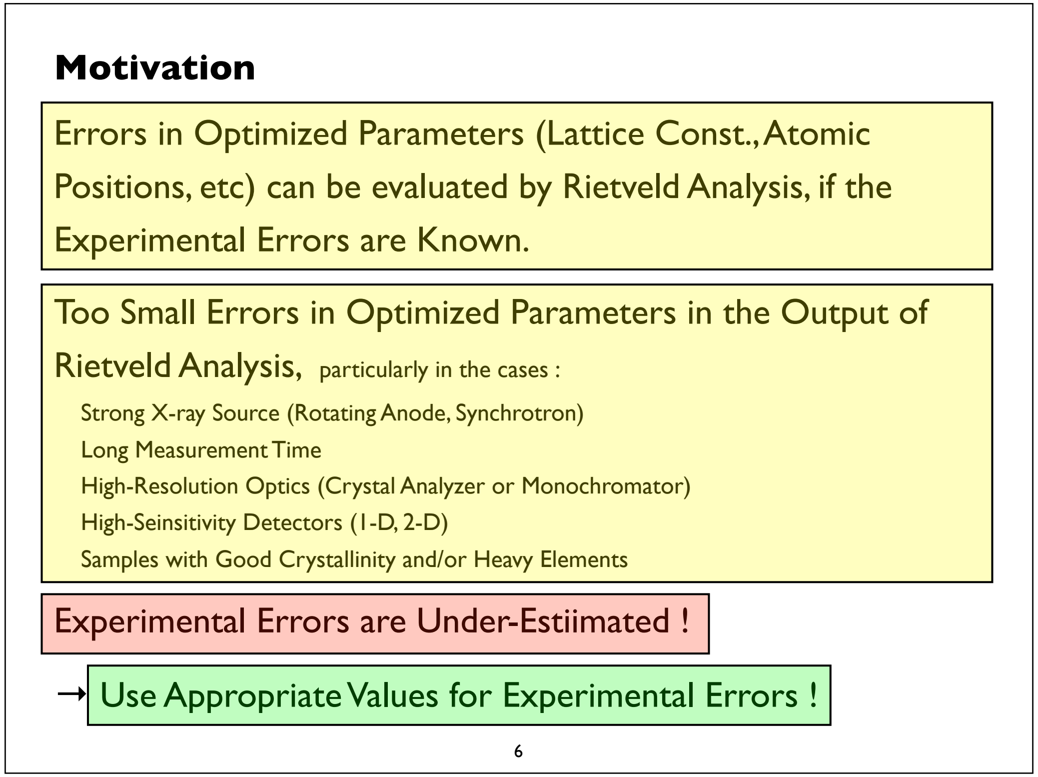
- High-Seinsitivity Detectors (1-D, 2-D)
- Samples with Good Crystallinity and/or Heavy Elements

Experimental Errors are Under-Estiimated !

The discrepancy is simply ascribed to the Under-Estimation of the Experimental Errors in those cases.



Motivation

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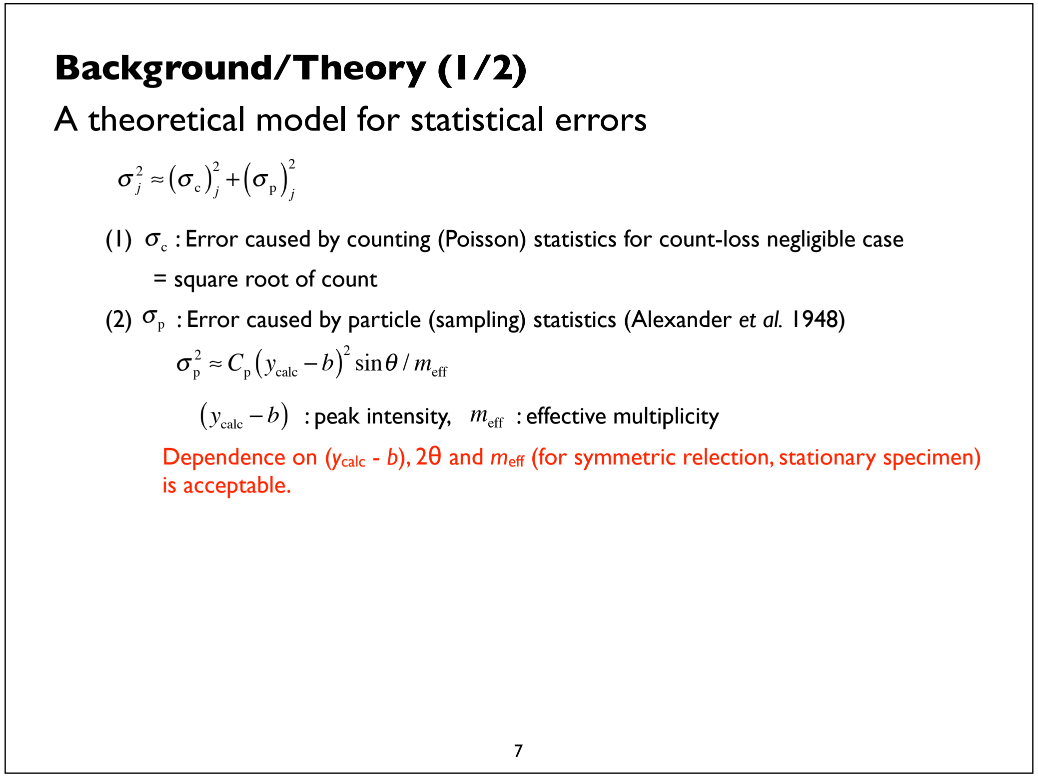
Samples with Good Crystallinity and/or Heavy Elements

Experimental Errors are Under-Estiimated !

→ Use Appropriate Values for Experimental Errors !

And the Solution should also be Simple: Just Use Appropriate Values for the Assumptions of 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

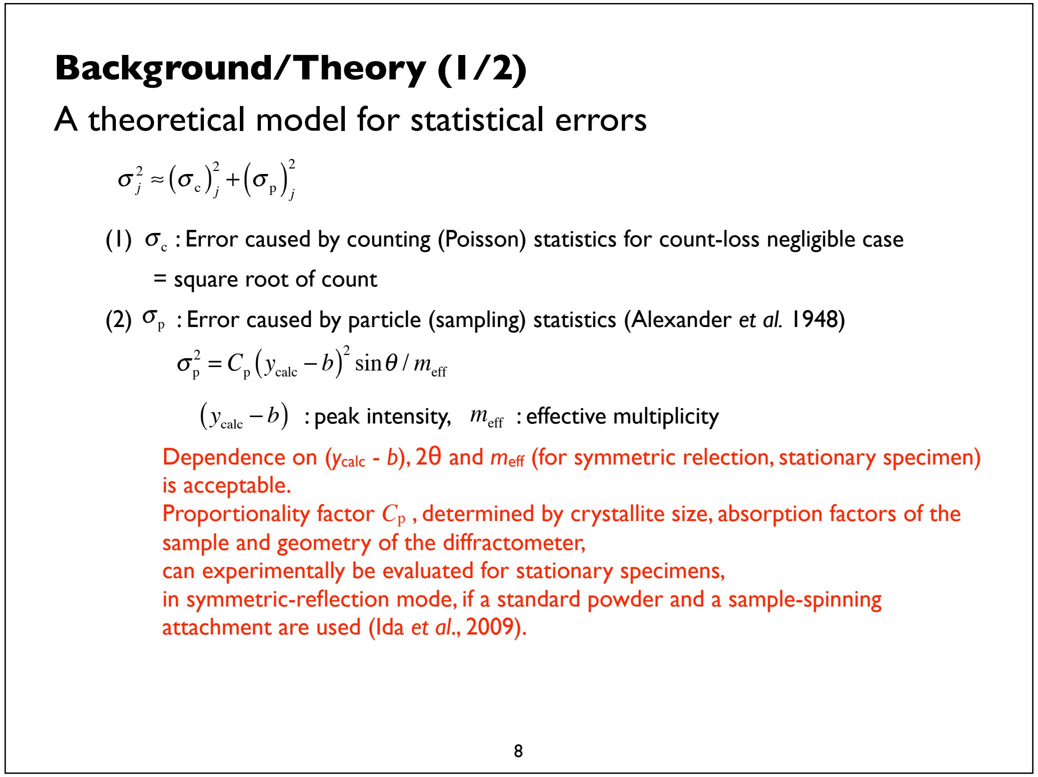
(2) σ_p : Error caused by particle (sampling) statistics (Alexander *et al.* 1948)

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

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

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

And it is already known, since more than FIFTY years ago, that the experimental errors in powder x-ray diffraction data are partly caused by counting statistics, but sometimes more dominantly affected by particle statistics. And I have experimentally confirmed that we can certainly apply the proposed dependence of the pariticle statistics, shown HERE, on the peak intensity, diffraction angle and the multiplicity of reflection.



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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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It can experimentally be evaluated for stationary specimens in symmetric-reflection mode measurements,
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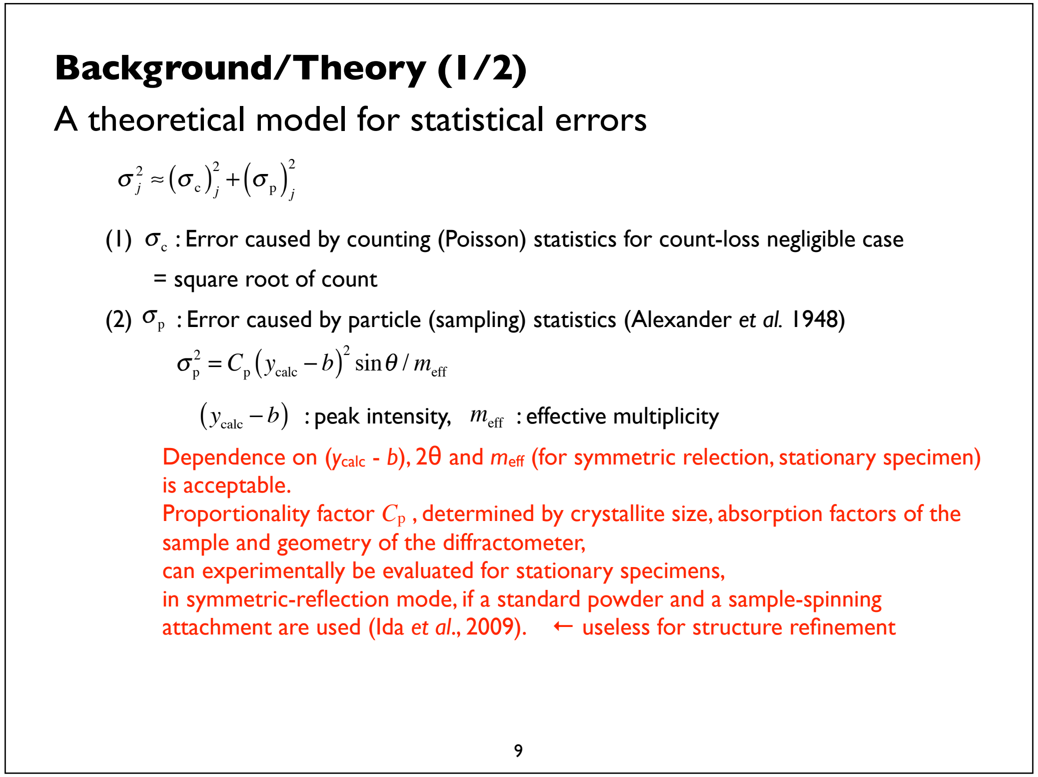

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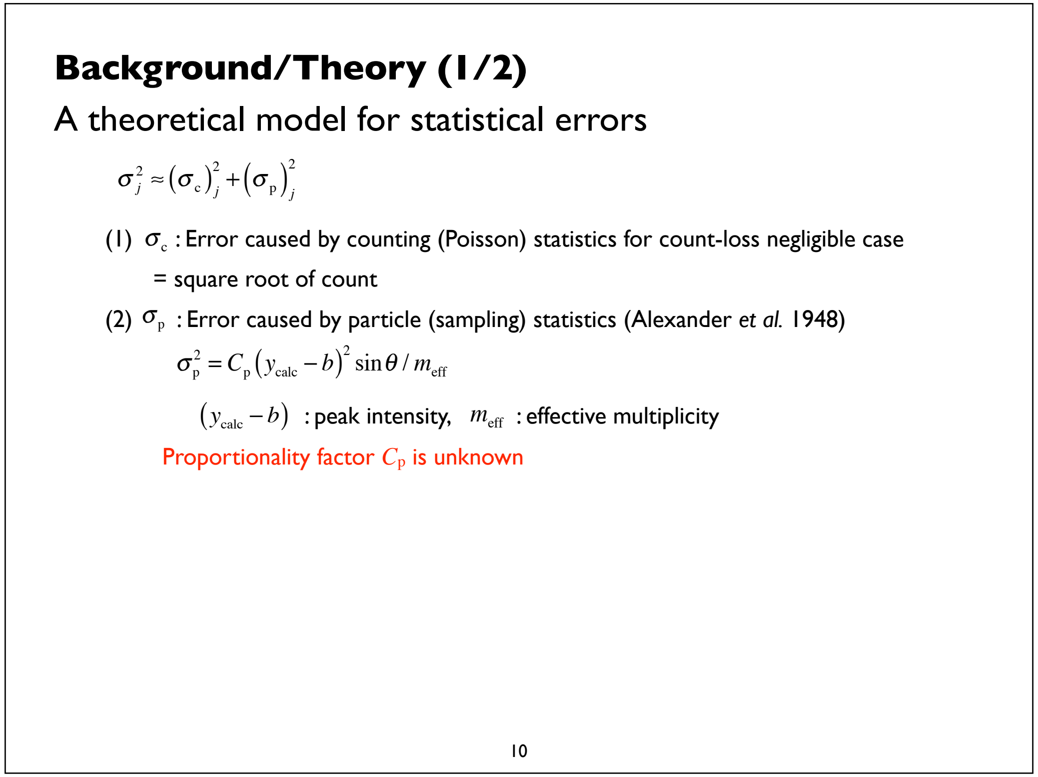
can experimentally be evaluated for stationary specimens,
in symmetric-reflection mode, if a standard powder and a sample-spinning attachment are used (Ida *et al.*, 2009). ← useless for structure refinement

But, it is useless for the purpose of structure refinement.
Because continuous rotation of the sample always improves the powder diffraction data for structure refinement.
I mean that there is no reason to keep the sample stationary, if we can spin the sample. AND, unfortunately, we have no reliable model for particle statistics about rotating samples at this moment.



Background/Theory (1/2)

A theoretical model for statistical errors

$$\sigma_j^2 \approx (\sigma_\mathrm{c})_j^2 + (\sigma_\mathrm{p})_j^2$$

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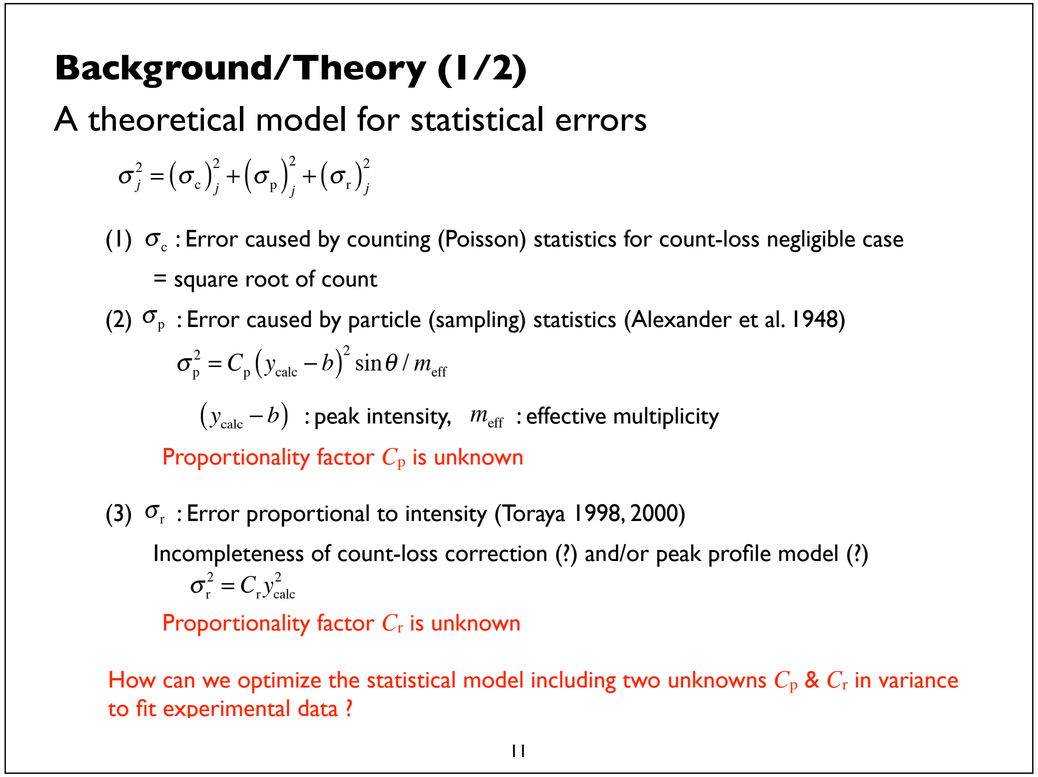
$\left(y_\mathrm{calc} - b\right)$: peak intensity, m_eff : effective multiplicity

Proportionality factor C_p is unknown

So we should think that the proportionality factor in the model of particle statistics is still 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

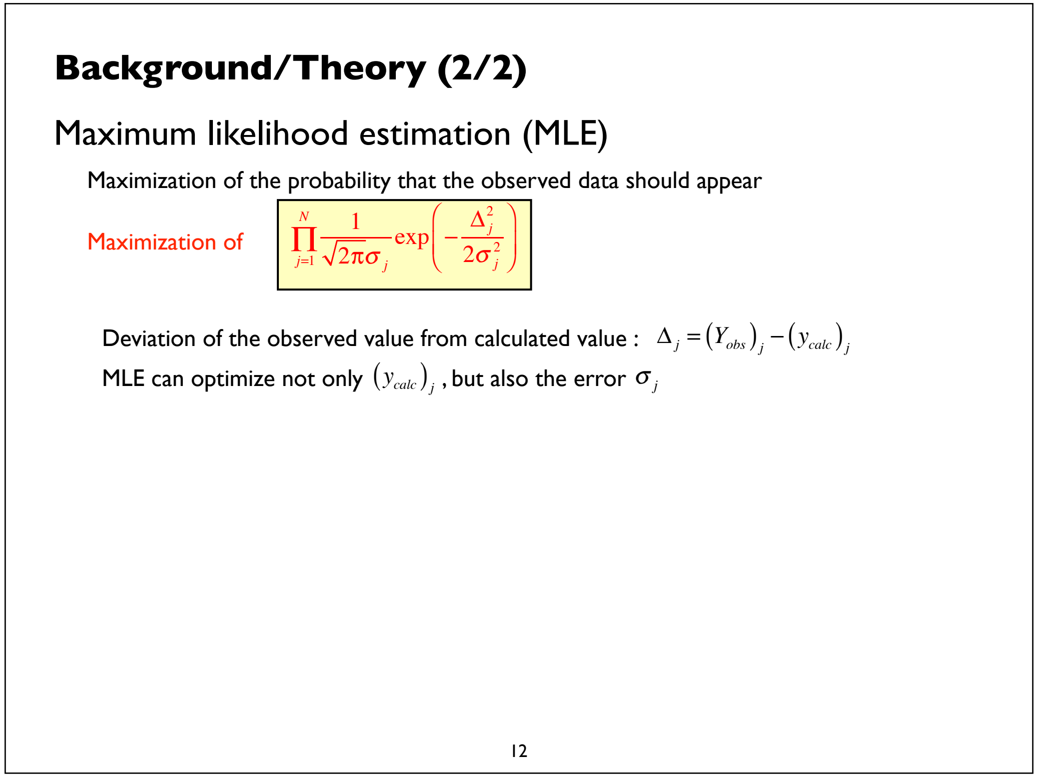
How can we optimize the statistical model including two unknowns C_p & C_r in variance to fit experimental data ?

And it is quite likely that the statistical errors include another term proportional to the intensity, NOT the square root of the intensity.

So I have assumed a three-term model including two unknown parameters, for statistical errors.

Now, the question is, how can we optimize the statistical model including two unknown parameters in variance from experimental data.

AND I have got an idea, Last Year, to Use Maximum Likelihood Estimation Instead of Least Squares Method.



Background/Theory (2/2)

Maximum likelihood estimation (MLE)

Maximization of the probability that the observed data should appear

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

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

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

Maximum likelihood estimation means that maximization of the probability that the observed experimental data should appear.

Background/Theory (2/2)

Maximum likelihood estimation (MLE)

Maximization of the probability that the observed data should appear

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

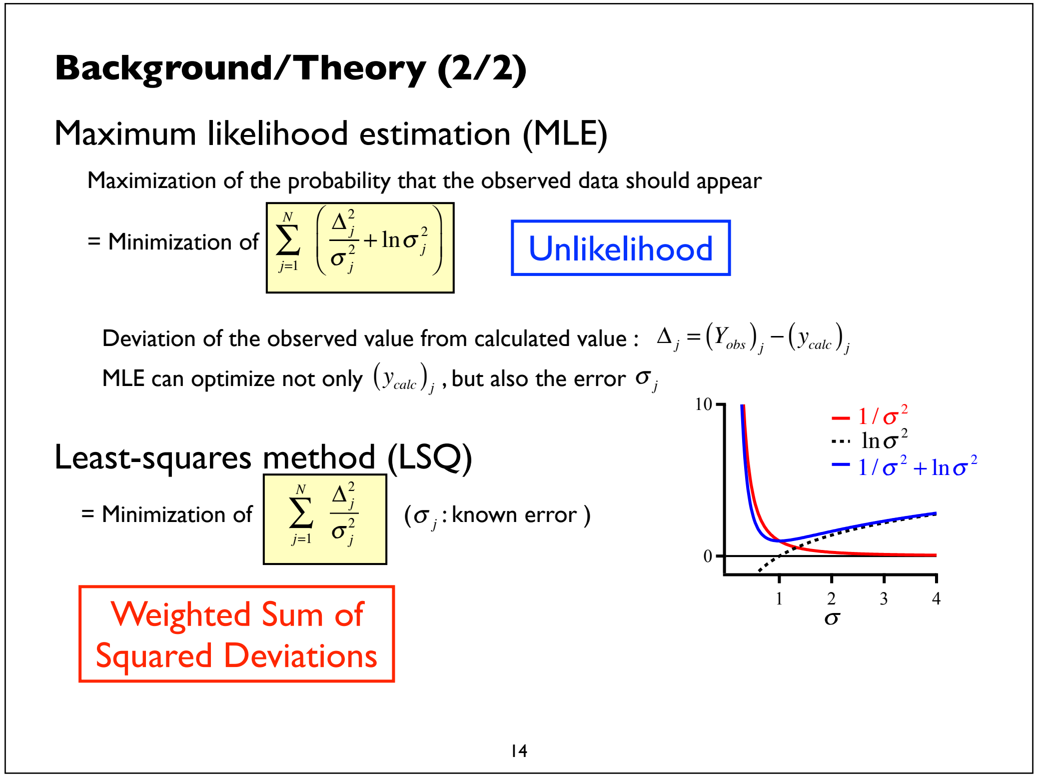
Deviation of the observed value from calculated value : $\Delta_j=\left(Y_{obs}\right)_j-\left(y_{calc}\right)_j$

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

Least-squares method (LSQ)

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

It is exactly equivalent to minimization of the sum of weighted squared deviations and logarithm of variance, if the normal distribution is assumed.



Background/Theory (2/2)

Maximum likelihood estimation (MLE)

Maximization of the probability that the observed data should appear

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

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

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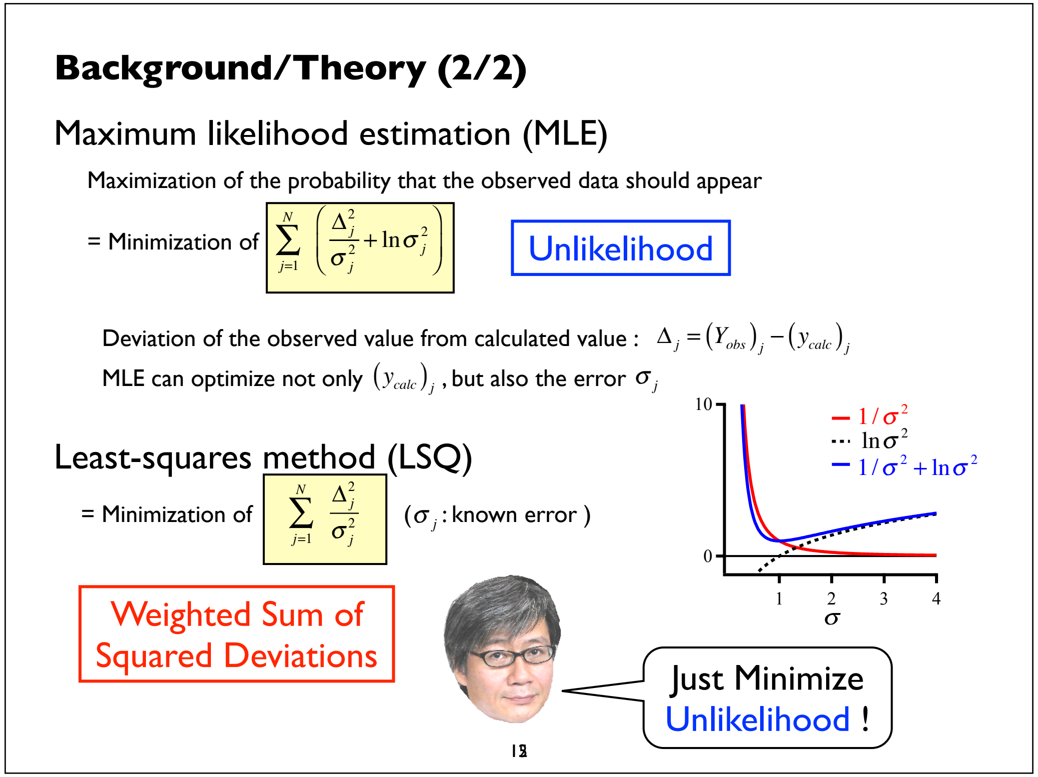
Least-squares method (LSQ)

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

Weighted Sum of Squared Deviations

We can call it “Unlikelihood estimator” or “Unlikelihood function”. You can see that it looks very similar to the least-squares method, but it is definitely different from the least-squares method, because the maximum likelihood method can optimize the model for the errors, “SIGMA”.

The plot shown HERE, demonstrates this TRICK. Unlikelihood function always has minimum at a finite value of sigma, by adding the logarithm of variance to the weighted squared deviation.



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Maximization of the probability that the observed data should appear

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

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

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

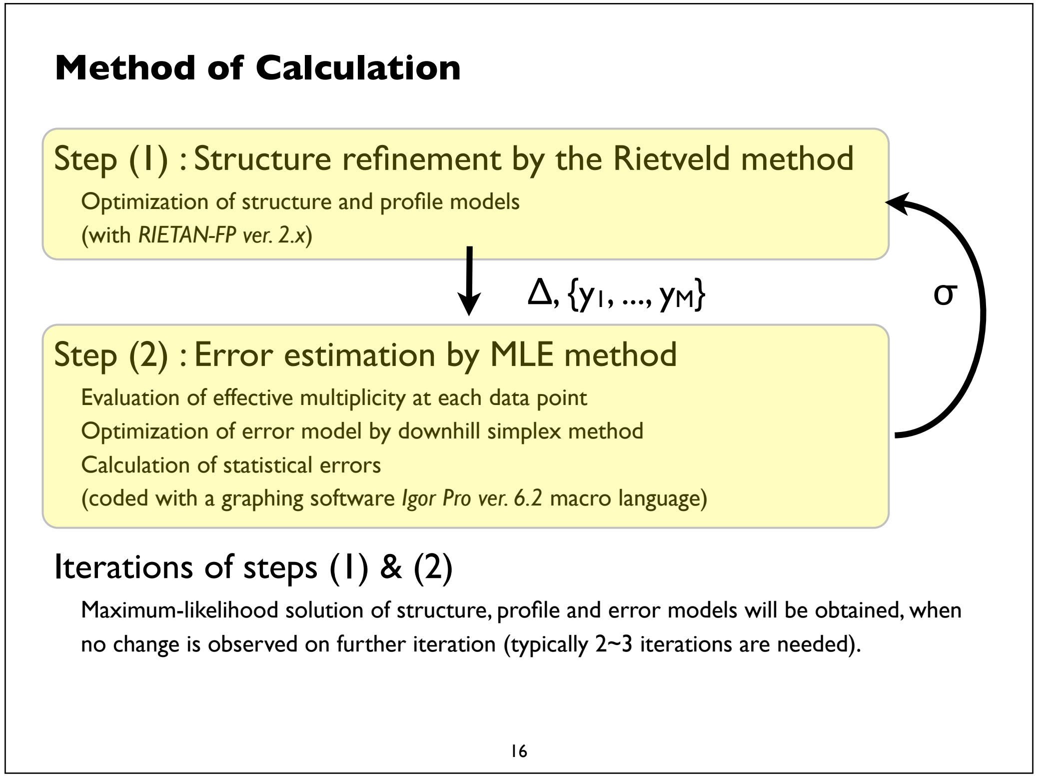
Least-squares method (LSQ)

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

Weighted Sum of Squared Deviations

Just Minimize **Unlikelihood** !

So I have decided to Throw Away the Concept: “Minimize the Weighted Sum of Squares Deviations”, but Apply a New Simple Concept: “Just Minimize the Unlikelihood” !



Method of Calculation

Step (1) : Structure refinement by the Rietveld method

Optimization of structure and profile models
(with *RIETAN-FP ver. 2.x*)

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

σ

Step (2) : Error estimation by MLE method

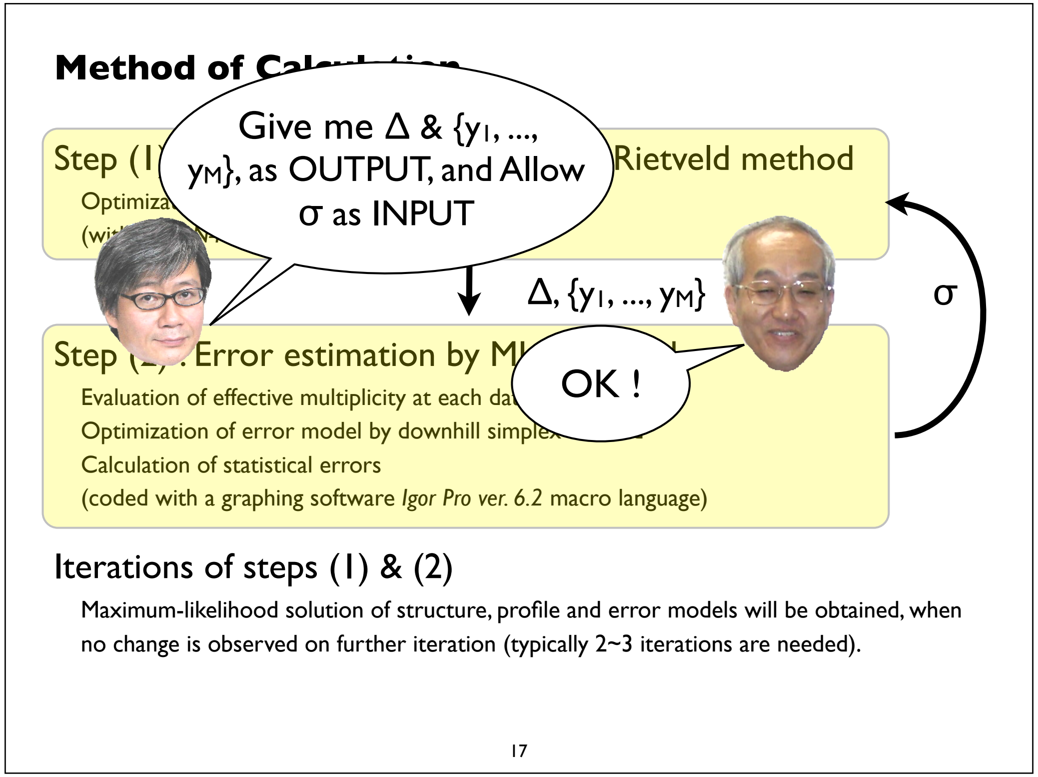
Evaluation of effective multiplicity at each data point
Optimization of error model by downhill simplex method
Calculation of statistical errors
(coded with a graphing software *Igor Pro ver. 6.2* macro language)

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).

Of course, the Rietveld codes are still useful. We can divide the maximum likelihood procedure into two steps.

First, apply the Rietveld refinement, Next, estimate errors by the MLE from the results of the Rietveld refinement, and use the optimized errors in the next Rietveld step, and so on.



Method of Ca

Step (1 … Rietveld method

Optimiza

(wit

Give me Δ & $\{y_1, ..., y_M\}$, as OUTPUT, and Allow σ as INPUT

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

σ

Step (2 … Error estimation by ML

OK !

Evaluation of effective multiplicity at each da

Optimization of error model by downhill simplex

Calculation of statistical errors

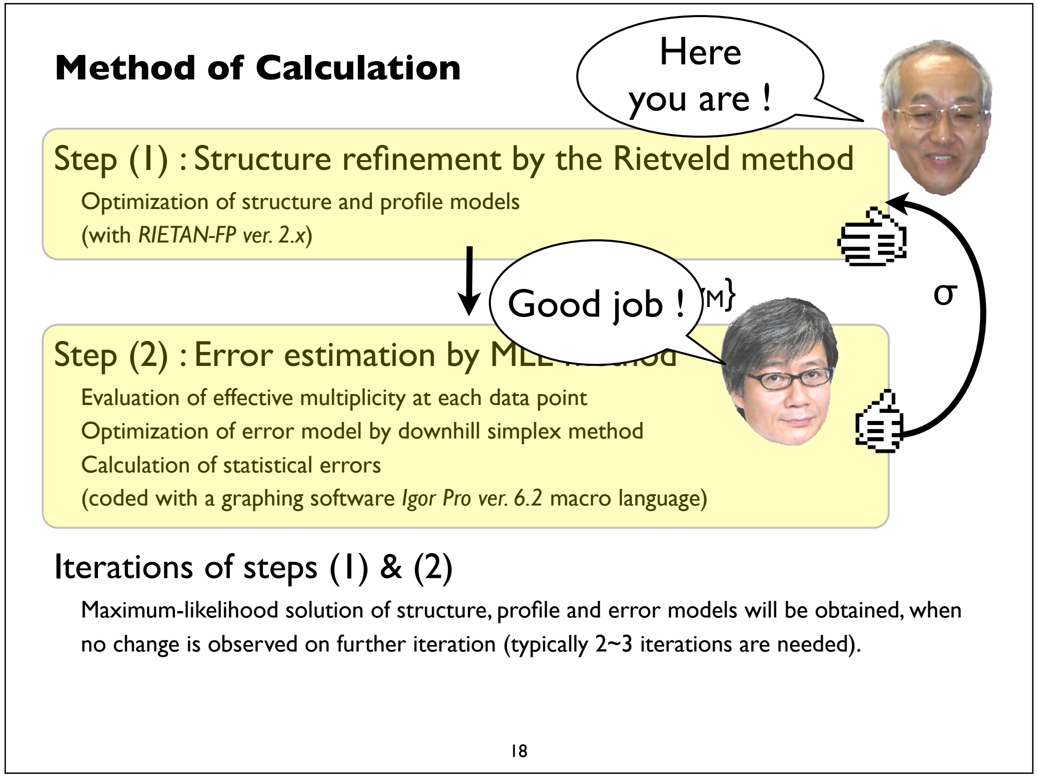
(coded with a graphing software *Igor Pro ver. 6.2* macro language)

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).

So I asked a Rietveld programmer, Dr. Izumi, to Modify His Program to give me the delta (deviation) & individual peak profile as OUTPUT, and to allow user-defined errors as INPUT.

and he said “O.K., it’s easy !”



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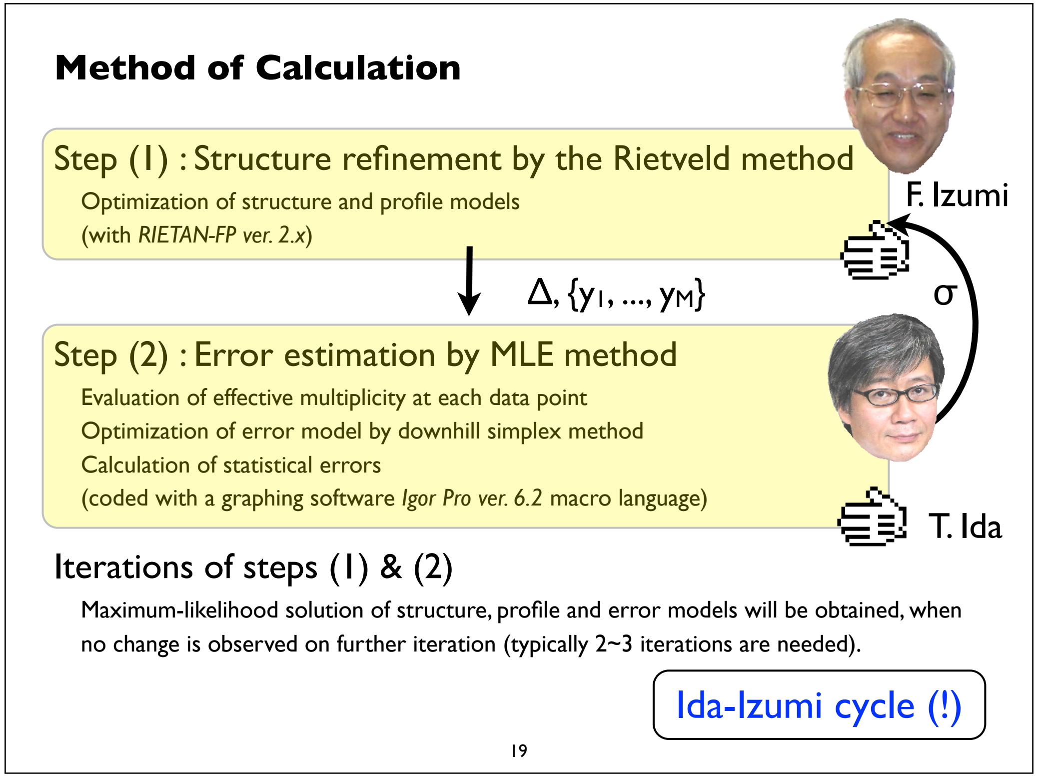
Iterations of steps (1) & (2)

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).

A few days later he gave me a modified version of his Rietveld program.
Then, All I should do was minimization of the Unlikelihood function in Two dimension.
It was not difficult for me, and I have also finished the coding in a few days.



Method of Calculation

Step (1) : Structure refinement by the Rietveld method

Optimization of structure and profile models

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

F. Izumi

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

σ

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Calculation of statistical errors

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

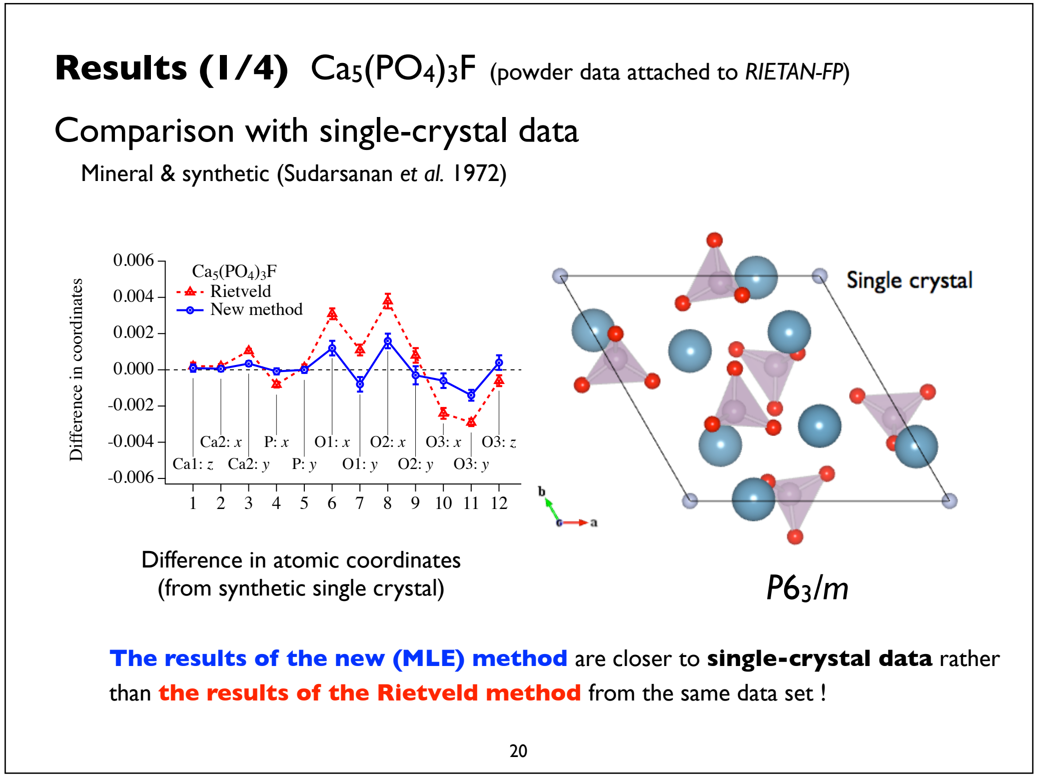
T. Ida

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 (!)

You can call it as IdaIzu-mi cycle, if you like.



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)

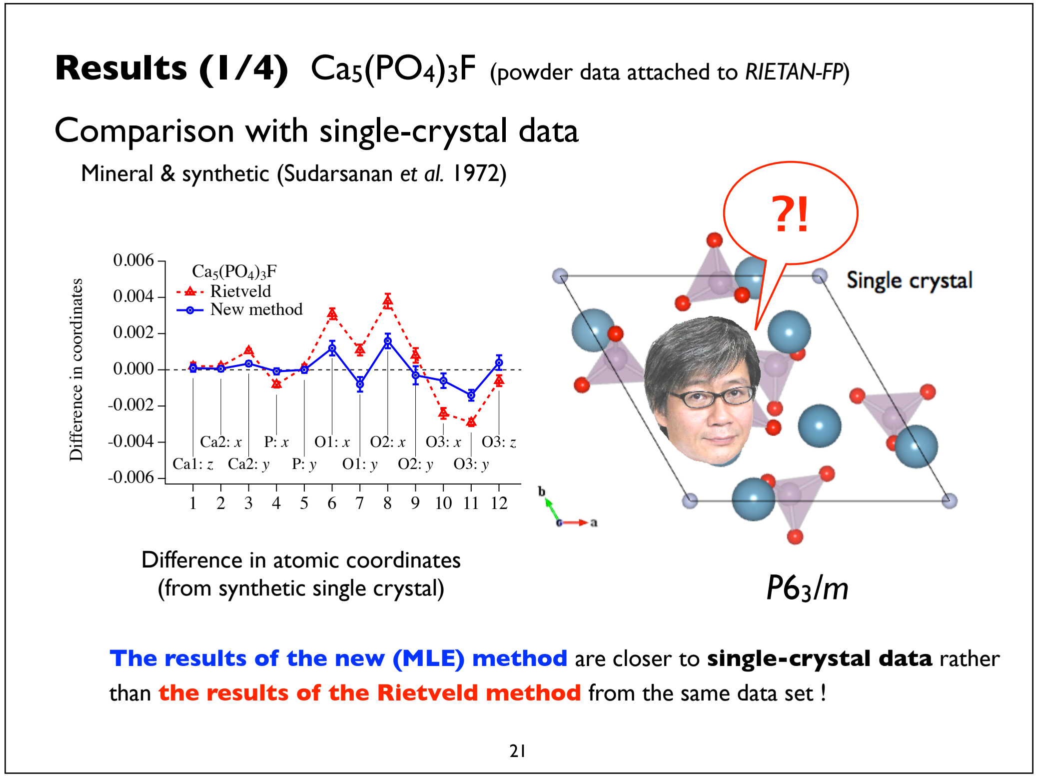
Difference in atomic coordinates
(from synthetic single crystal)

*P*6₃/*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 !

On this slide, I am showing the comparison about the atomic coordinates in the results of the Rietveld as red, maximum likelihood method as blue, it means differences in atomic coordinates from single crystal data about fluoro-apatite.

You can see that the atomic coordinates optimized by the new method are closer to single-crystal data rather than the results of the Rietveld method.



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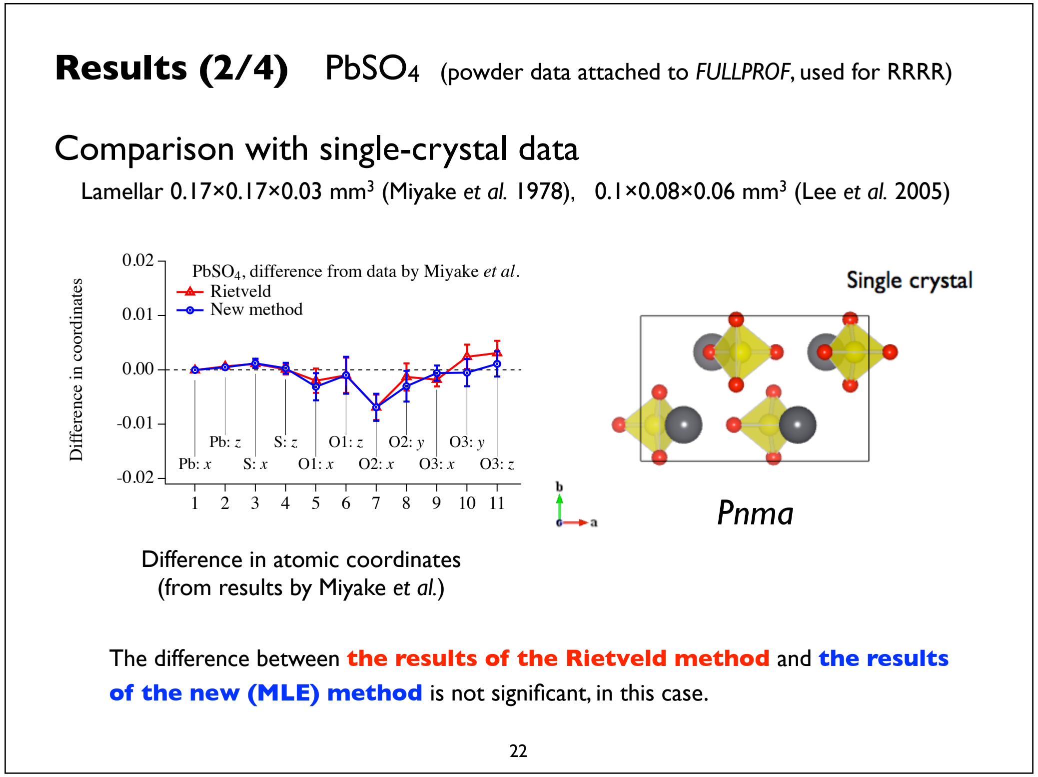
The result was quite different from what I expected.
What I expected was the length of the error-bars should become longer by increasing the statistical errors, and I did NOT really expect the improvement of the accuracy.



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

Comparison with single-crystal data

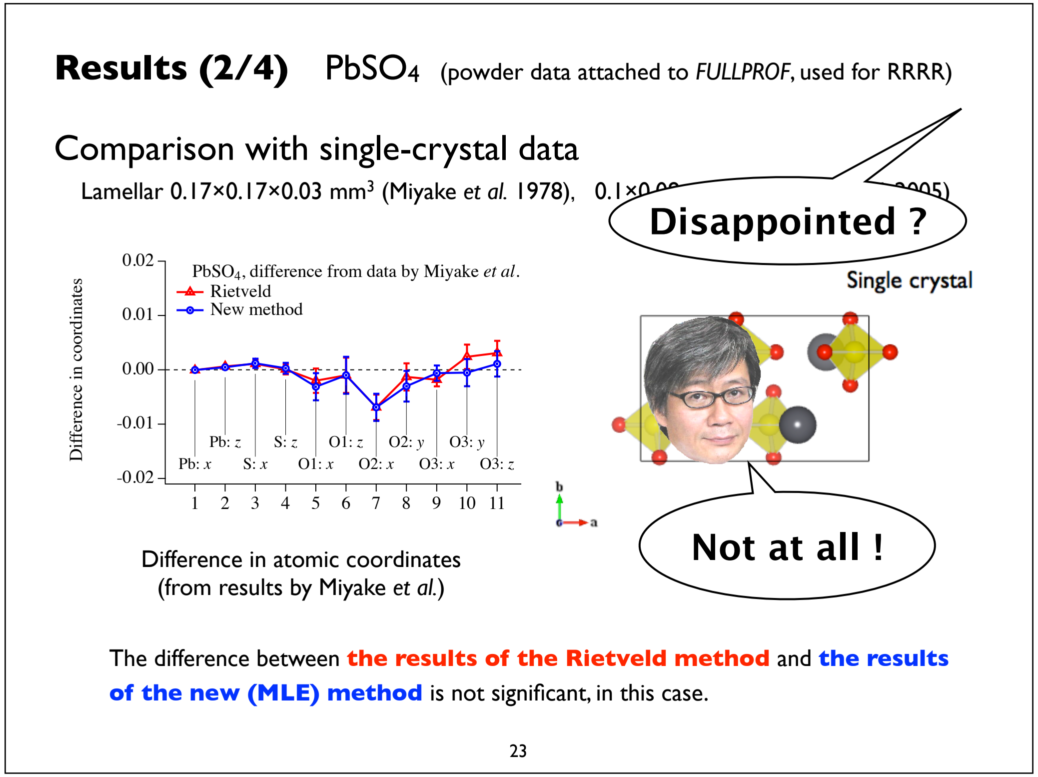
Lamellar 0.17×0.17×0.03 mm^3 (Miyake *et al.* 1978), 0.1×0.08×0.06 mm^3 (Lee *et al.* 2005)

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

Pnma

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

The second example is lead sulfate (anglesite), and it shows no significant difference between Rietveld and new methods, and it suggests that the data are collected almost in idealistic condition for Rietveld analysis.
Actually this powder diffraction data set is from Rietveld Refinement Round Robin.



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

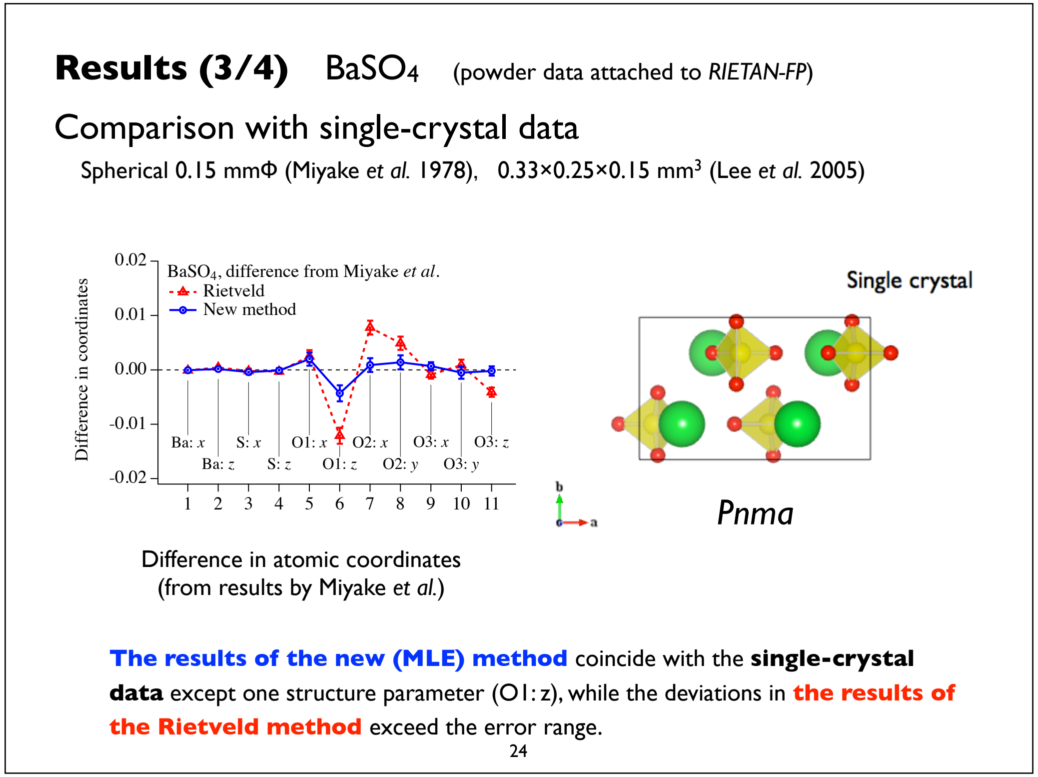
Comparison with single-crystal data

Lamellar 0.17×0.17×0.03 mm^3 (Miyake *et al.* 1978), 0.1×0.0 005)

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.

One may think that I was disappointed by this result, but absolutely NO, because we do not want the results of the Rietveld refinement to be changed, when we have already got good results by the Rietveld method.
So it suggests another FAVORABLE behavior of this new method,
that is, You can sometimes confirm the reliability of the Rietveld results, by applying the maximum likelihood estimation.



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

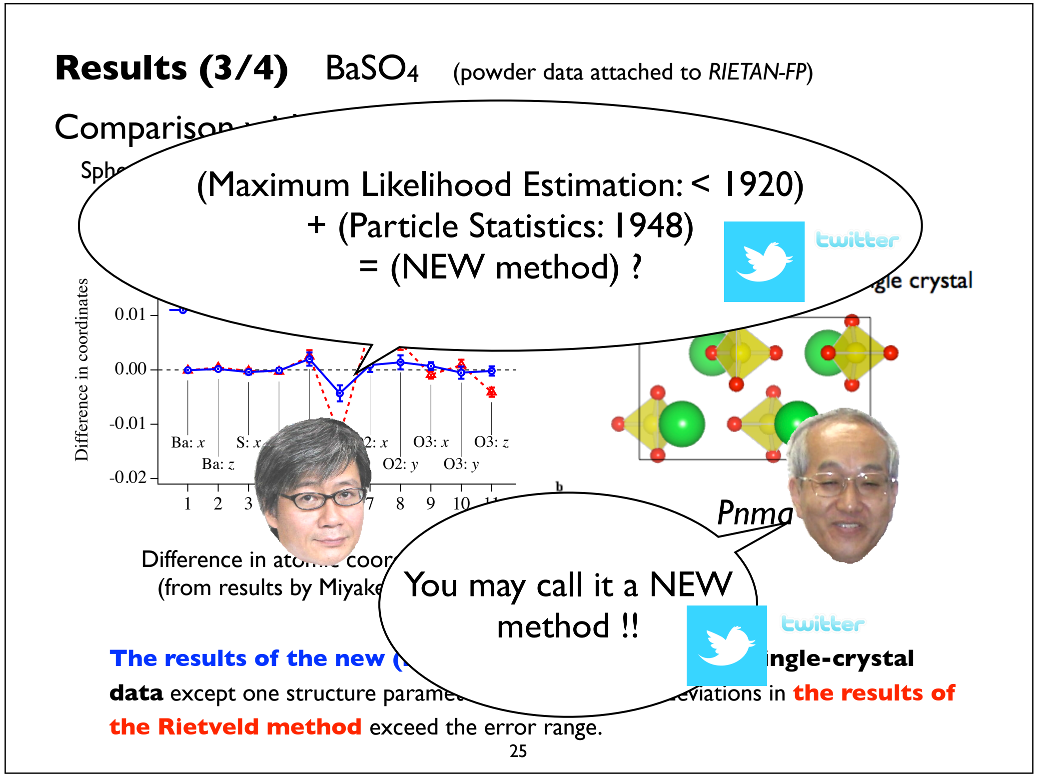
Comparison with single-crystal data

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

Difference in atomic coordinates
(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.

The third example is barium sulfate (barite), it is isostructural to lead sulfate (anglesite).
This result shows MOST SIGNIFICANT improvement obtained by the maximum likelihood estimation.
You can see that the differences from single crystal data has become almost ZERO, when we apply the MLE.



Results (3/4) BaSO4 (powder data attached to *RIETAN-FP*)

Comparison

Sph

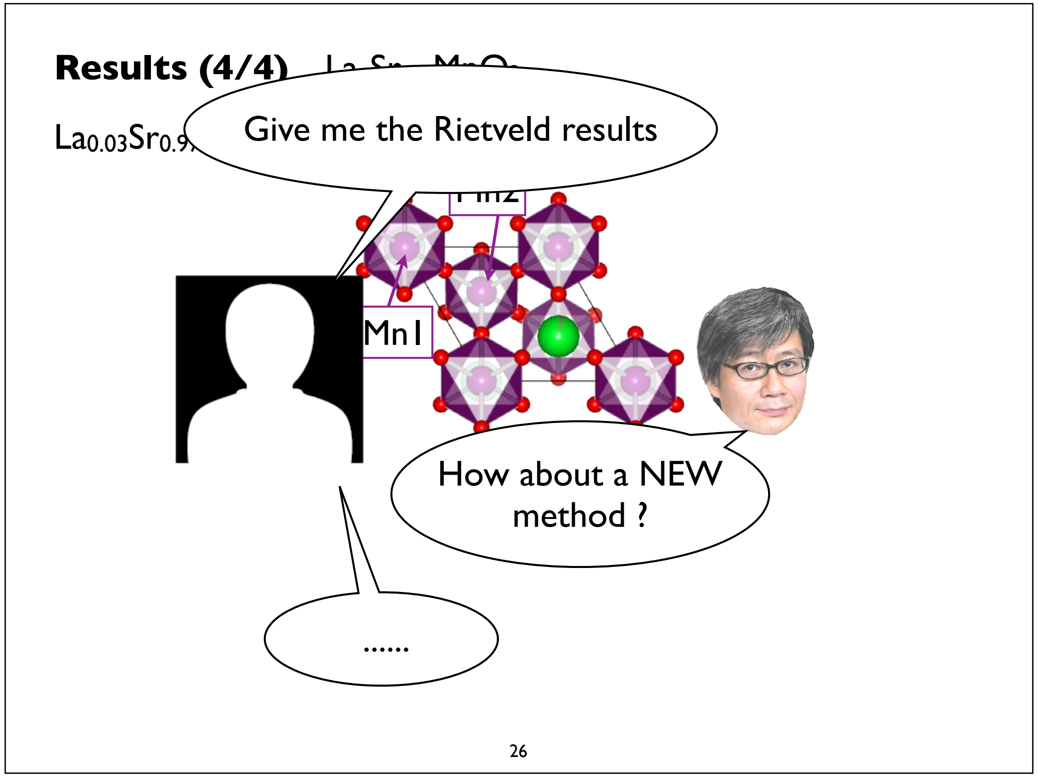
(Maximum Likelihood Estimation: < 1920)
+ (Particle Statistics: 1948)
= (NEW method) ?

Difference in ato coor
(from results by Miyake

You may call it a NEW
method !!

The results of the new (**ingle-crystal data** except one structure parame eviations in **the results of the Rietveld method** exceed the error range.

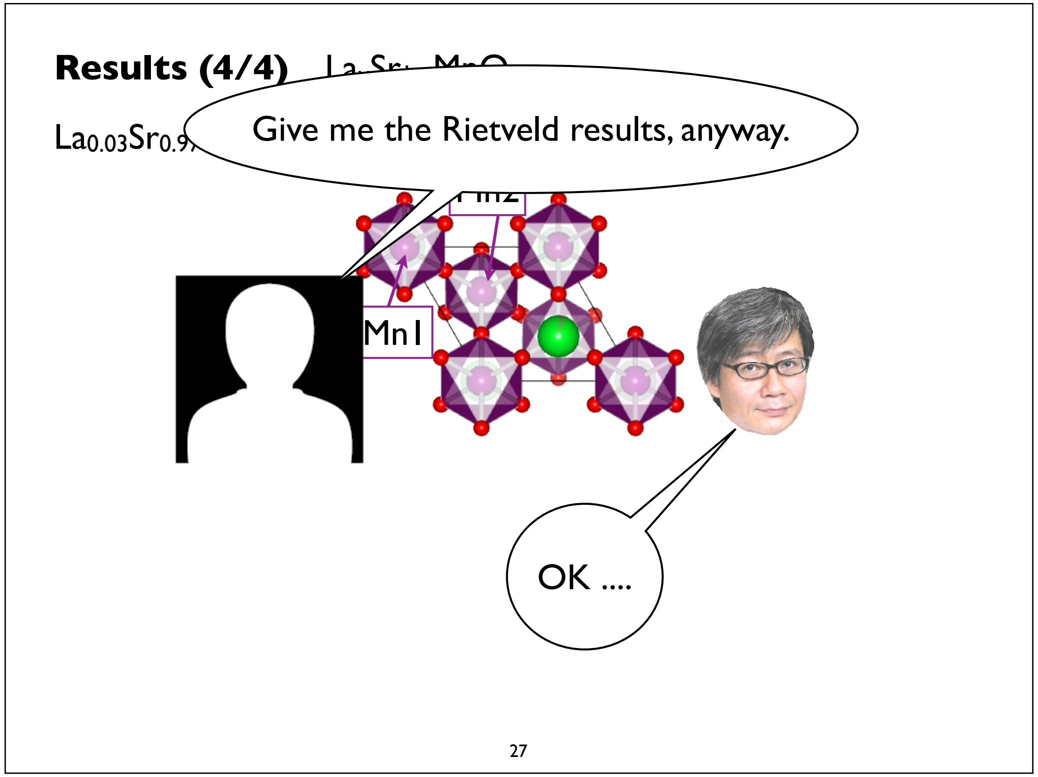
But this method is JUST a combination of classical methods.
Maximum likelihood estimation was proposed almost a hundred years ago, and the Theory about Particle Statistics was proposed more than FIFTY years ago.
Can I call it a NEW method ? - I Tweeted,
And Dr. Izumi Tweeted, You May Call it a new method, in reply.



Results (4/4)

$La_{0.03}Sr_{0.9}$

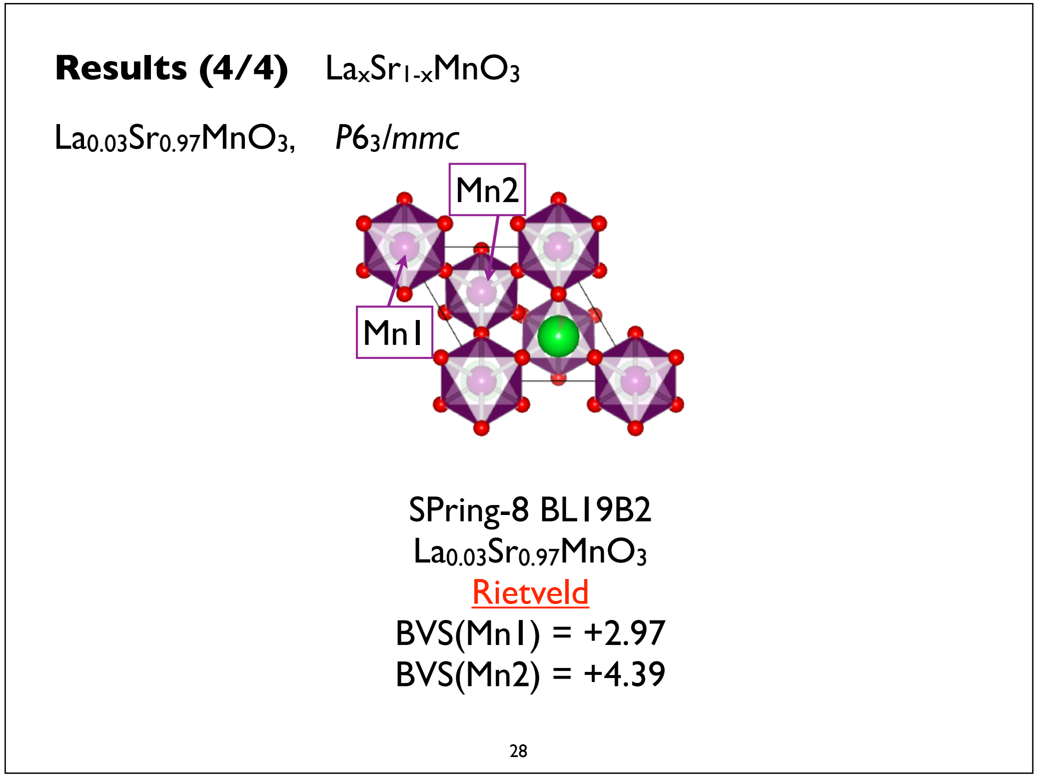
After that, a person working in an industrial company, asked me to analyze his data by the Rietveld method. And I told him, “I think I have found an alternative method...” ,



Results (4/4) $La Sr MnO$

$La_{0.03}Sr_{0.9}$

and he said “I do not understand your new method, anyway we like to have the Rietveld results”.

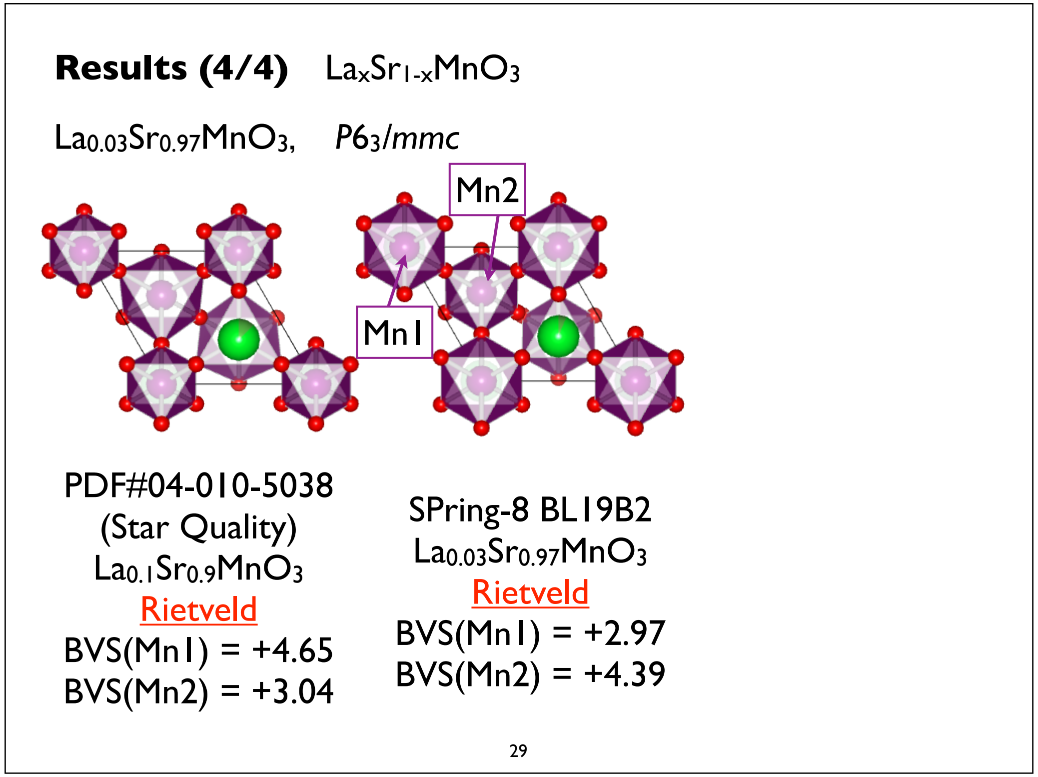


Results (4/4) $La_xSr_{1-x}MnO_3$

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

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

So I have analyzed his data of Lanthanum Strontium Manganite by the Rietveld method, and calculated the bond valence sums of two different sites of Manganese.
The valence of Mn1-site was about THREE, and the valence of Mn2-site was about 4.5 ... It may be possible, because the two sites are not equivalent.



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

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

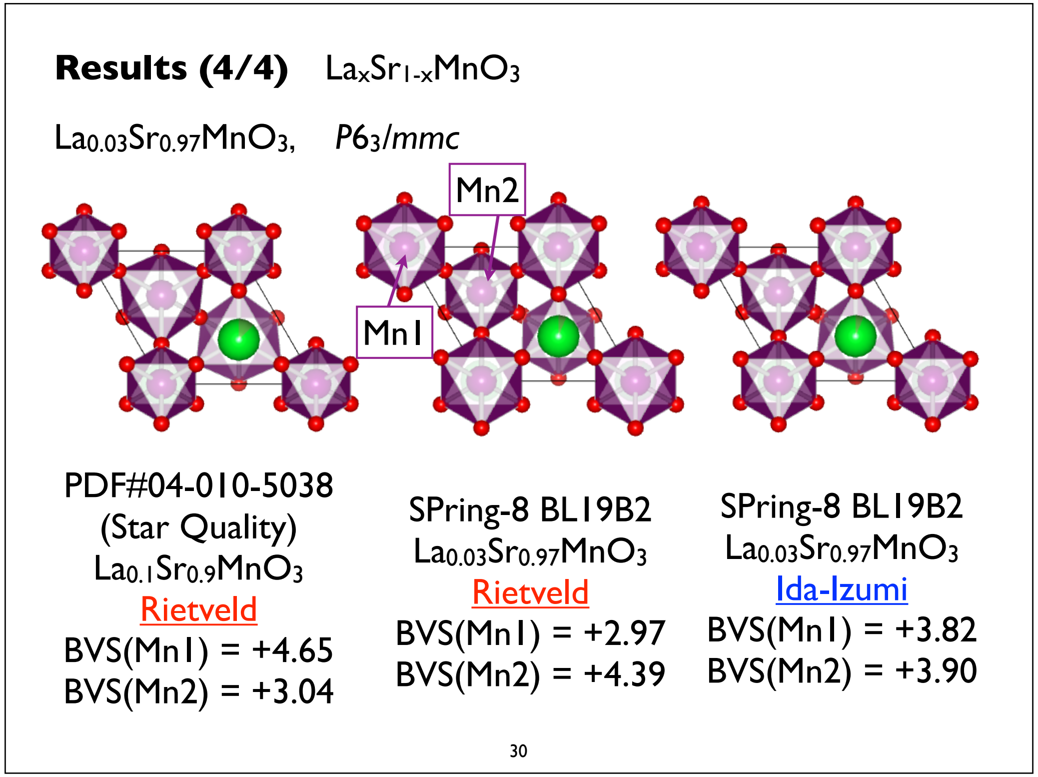
PDF#04-010-5038
(Star Quality)
$La_{0.1}Sr_{0.9}MnO_3$
Rietveld
BVS(Mn1) = +4.65
BVS(Mn2) = +3.04

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

Then I have searched the ICDD-PDF4+ database, and found STAR Quality Data from neutron diffraction, and calculated bond valence sums from the atomic coordinates.

In this case, Mn1-site has the valence about 4.5 and Mn2-site has the valence about THREE.

OK, It may also be possible, because the samples are different.



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

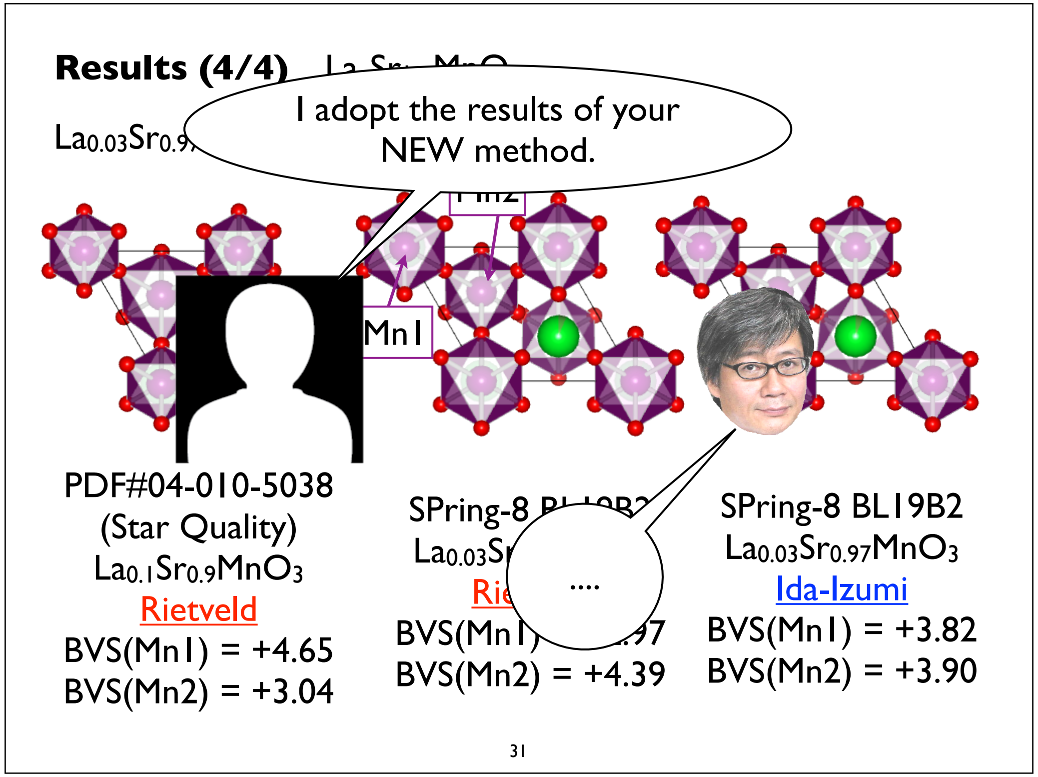
$La_{0.03}Sr_{0.97}MnO_3$, $P6_3/mmc$

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

Finally, I have tried to apply the new method.
Then, the valence of Mn1-site was estimated at about 4,
and the valence of Mn2-site was also estimated about 4.



Results (4/4) La Sr MnO

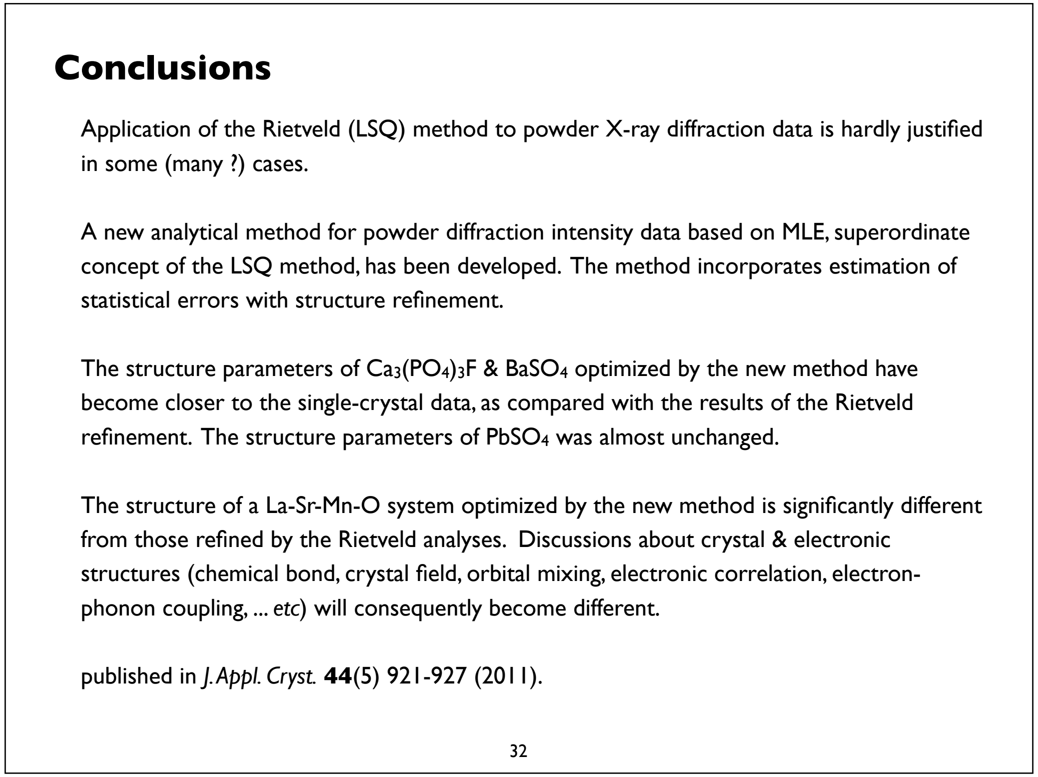
$La_{0.03}Sr_{0.9}$

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
$La_{0.03}S$
Rie
BVS(Mn1) .97
BVS(Mn2) = +4.39

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

I have shown all the results to the person who wanted me to give him the Rietveld results.
and he said, “I will adopt the results of your new method”.
I don’t know the exact reason...



Conclusions

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

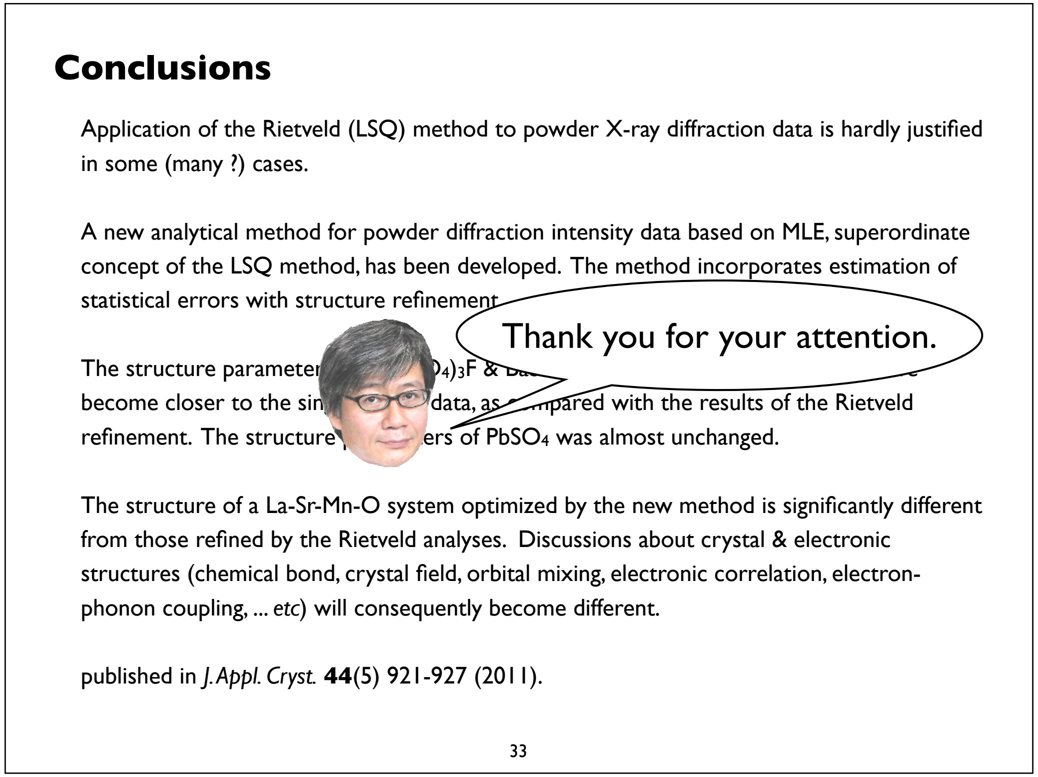
A new analytical method for powder diffraction intensity data based on MLE, superordinate concept of the LSQ method, has been developed. The method incorporates estimation of statistical errors with structure refinement.

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).

In conclusion, application of the Rietveld method is hardly justified in some cases.
A new analytical method based on maximum likelihood estimation has been developed.
The structures of FLUORO-APITITE and BARITE optimized by the new method have become closer to single-crystal data, while that of ANGLESITE was almost unchanged.
The structure of a La-Sr-Mn-O system optimized by the new method is significantly different from that optimized by the Rietveld method.
And the discussions about crystal & electronic structures, such as chemical bond, crystal field, orbital mixing, electronic correlation, electron-phon coupling et cetra should become different.
The framework of the new method has already been published in October last year.



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.

Thank you for your attention.

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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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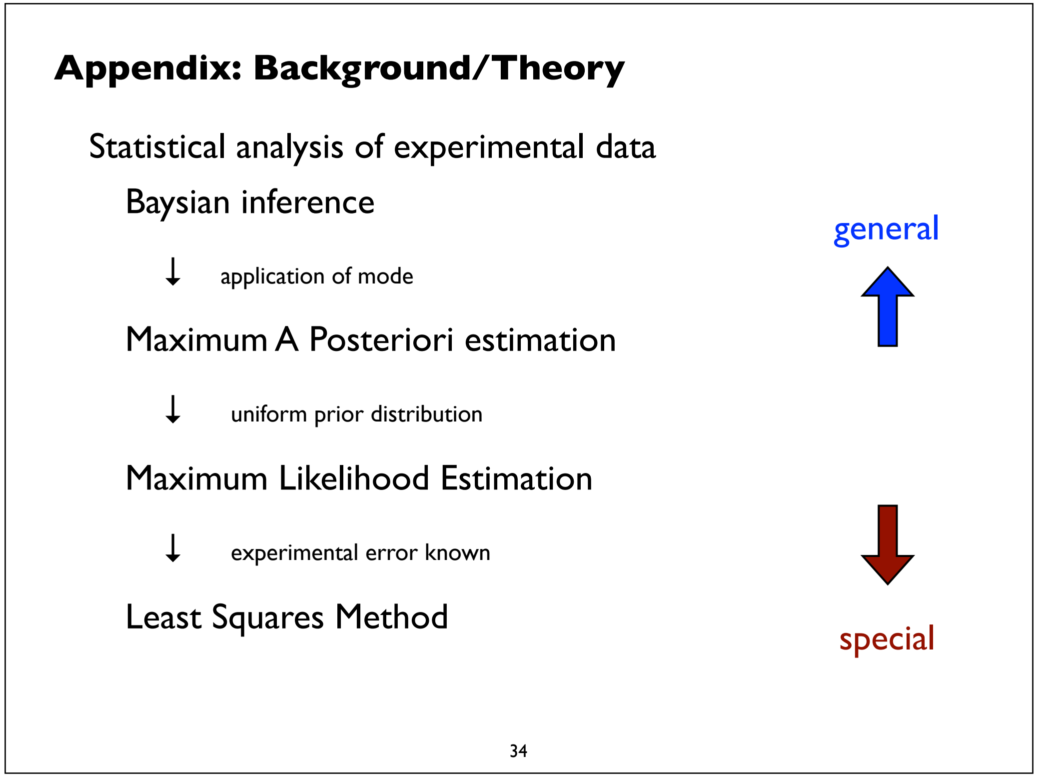
Thank you for your attention.



Appendix: Background/Theory

Statistical analysis of experimental data

Baysian inference

↓ application of mode

Maximum A Posteriori estimation

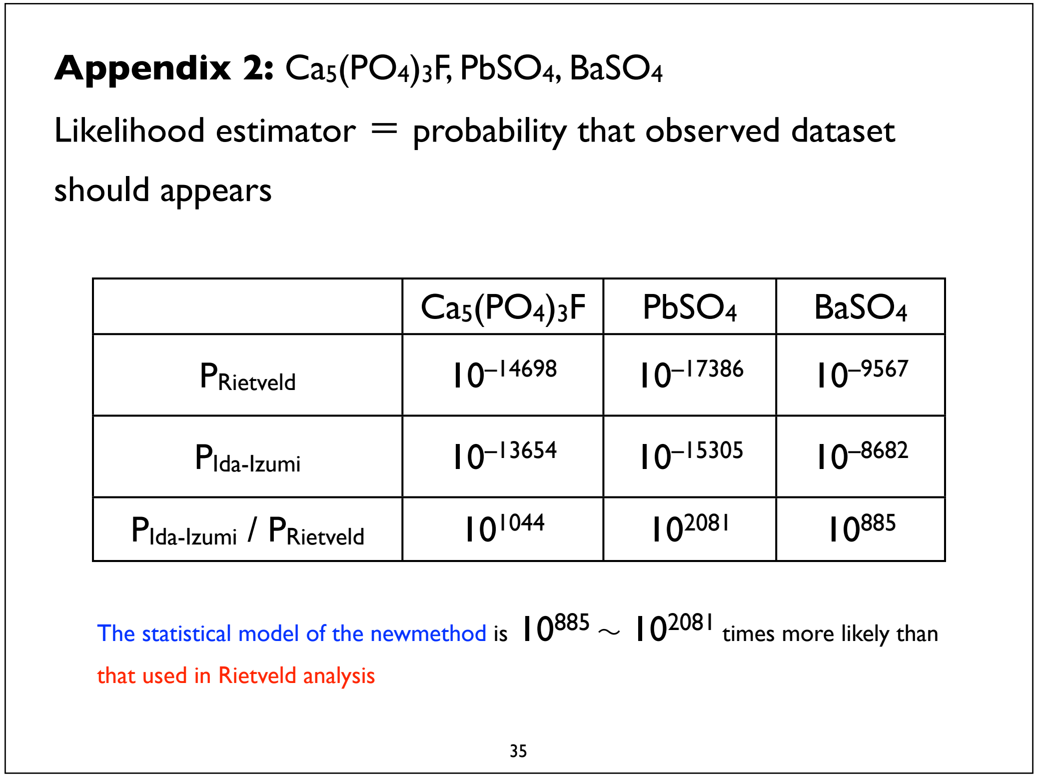
↓ uniform prior distribution

Maximum Likelihood Estimation

↓ experimental error known

Least Squares Method

(skipped)



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}
$P_{\text{Ida-Izumi}}$	10^{-13654}	10^{-15305}	10^{-8682}
$P_{\text{Ida-Izumi}} / P_{\text{Rietveld}}$	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

(skipped)

Discussions:

Q1 (Jim Kaduk, chairman): "Hmmm... Your talk makes us to think too 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 show HERE (slide 11), I have changed the treatment of the peak profile intensity, but NOT changed the treatment of the back ground 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."