Pushing the limits of Modern Powder Diffraction

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1 As a reminder: „Yesterday today was tomorrow, but tomorrow today will be yesterday“
Content

- Instrumentation 1917
- Instrumentation 2011
- Exploring 2D powder patterns
- Parametric Rietveld refinement
- MEM + CF
The pioneers of powder diffraction 1916/1917

Debye, P.; Scherrer, P. (1916), Interferenzen an regellos orientierten Teilchen im Roentgenlicht, Physikalische Zeitschrift 17, 277-283
Hull, A. W. (1917), A New Method of X-Ray Crystal Analysis, Phys. Rev. 10, 661 - 696

Outline of Method.

The method consists in sending a narrow beam of monochromatic X-rays (Fig. 2) through a disordered mass of small crystals of the substance to be investigated, and photographing the diffraction pattern produced. Disorder, as regards orientation of the small crystals, is essential. It is at-
Crystal structure from ‘in situ’ powder diffraction: The beginning...

An early 'in-situ' powder xray diffraction experiment on the structure of $\alpha$-N$_2$

Debye-Scherrer film of $\alpha$-N$_2$ at 34K

Exposure time: 18h

Schematic drawing of the used cryo-camera

$\alpha$-N$_2$ Pa-3

The next big step: towards higher resolution

The first “modern” powder diffractometer

Norelco powder, X-ray goniometers. First installed in 1949 at the Geophysical Laboratory (Design patented by William Parrish in 1947)

Standard Bragg-Brentano geometry
Modern laboratory powder diffractometers

- Bruker D8-Advance, Våntag PSD
- Stoe-Stadi-P with 140° IP-PSD
- PANalytical, X'pert PRO with Accelerator
- Stoe-Stadi-P, 6° PSD's and Mythen
- Inel CPS120 with 120° PSD

High speed, high resolution PSD's in Debye-Scherrer geometry
Modern powder diffractometers at synchrotron beamlines

- ID31, ESRF
- ID9, ESRF
- MF-Beamline, Anka
- SLS X04SA
- X7B, NSLS

Multi-analyzer crystals or 2D detectors in Debye-Scherrer geometry
Advantages of the Debye-Scherrer method

• Less grain size effects
• Little preferred orientation
• Small amounts of material
• Handling of extremely sensitive samples
• Simple correction functions
• No overspill effect
• Simple line profile (→ fundamental parameters)
• Easy adaptation of reaction cells for non-ambient conditions, gas flow etc.
• Perfect for structure determination

Disadvantages of the Debye-Scherrer method

• Absorption (for Z > 20)
• High background
• Peak to background ratio

Solution → Using a high resolution Mo diffractometer with Ge(220) primary beam monochromator and a high efficiency detector
LaB$_6$ reference pattern of the Mo-K$_{\alpha 1}$ radiation high resolution Debye-Scherrer diffractometer

LaB$_6$ line profile standard measured with Mo-Ka1 radiation (Bruker D8 Advance with Ge(220) primary beam monochromator and Lynx-Eye detector with 0.5 mm thick silicon stripes, 17 h counting time)

- Wavelengths distribution (Lorentzian)
- Receiving slit width (Hat)
- Source, sample, slit lengths (exp.)
- Gaussian strain

Resolution in 2$\theta$ < 0.04° 2$\theta$
Minimum d-spacing < 0.4 Å

4 refined parameters only
Starting from an unknown chemical composition: a new nitridoosmate from lab data (Stoe-Stadi-P, Mo-Kα₁)

Known composition before simulated annealing: Ba/Os = 3:1 plus several nitrogen atoms

“Ba₃OsN₃”
R-wp 6.690  R-Bragg 1.95

(Ba₆O)(OsN₃)₂
R-wp 6.486  R-Bragg 1.67

Alternatively: \((\text{Ba}_6\text{O})(\text{OsN}_3)_2\)

“\(\text{Ba}_3\text{OsN}_3\)”

\((\text{Ba}_6\text{O})(\text{OsN}_3)_2\)

\(\text{Ba}_3\text{FeN}_3\) exists!
### CRYSTAL06 (DFT)-Calculations – Hybrid-Funktional B3PW

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<th>exp.</th>
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<td>((\text{Ba}_6\text{O})(\text{OsN}_3)_2)</td>
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<td><strong>Position</strong></td>
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<tr>
<td>3b</td>
<td>O</td>
<td>-</td>
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<tr>
<td>3a</td>
<td>-</td>
<td>-</td>
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<td><strong>Distance / Å</strong></td>
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<tr>
<td>Ba – 3a</td>
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<td><strong>Binding energy / (kJ / mole)</strong></td>
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<td>578</td>
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<td><strong>Partial charges/ Spin charges</strong></td>
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<td></td>
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<tr>
<td>OsN(_3)^-</td>
<td>-2.8 / +1.9</td>
<td>-2.6 / +1.6</td>
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<tr>
<td>Ba</td>
<td>+1.2 / -0.1</td>
<td>+1.3 / +0.1</td>
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<tr>
<td>Pos. 3b</td>
<td>-0.7 / -0.6</td>
<td>-1.9 / 0</td>
</tr>
<tr>
<td>Pos. 3a</td>
<td>-0.7 / -0.6</td>
<td>-0.5 / +0.5</td>
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Calculations by Ulrich Wedig, MPI-FKF, Stuttgart
Data reduction & filtering:
A high pressure phase of the NLO – compound BiB$_3$O$_6$ (BiBO)

- Better conversion efficiency than BBO ($\beta$-BaB$_2$O$_4$) or LBO (LiB$_3$O$_5$)
- Better resistance to laser damage than KTP
- Tunable laser 240nm – 1000nm

R. E. Dinnebier, B. Hinrichsen, A. Lennie, and M. Jansen, The high pressure crystal structure of the NLO compound BiB$_3$O$_6$ from 2D powder diffraction data. (2009), Acta Cryst. B65, 1-10 (see also IUCr newsletter June 2009)

Known phases of BiBO

α (C2)

NLO

β (P2₁/n)

γ (P2₁/n)

δ (Pca2₁)
Raw data at high pressure...

2D image plate powder diffraction data set of BiB$_3$O$_6$ at high pressure
How about counting statistics with 2D XRPD data?

A very large number of equally sized and randomly oriented crystallites to the diffraction pattern would lead to an ideal binomial intensity distribution over the entire Bragg cone.

Probability \( P_B \) of exactly \( n \) successes out \( N \) trials where each trial has the probability of success \( p \) and probability of failure \( q=1-p \)

\[
P_B(n | N) = \begin{pmatrix} N \end{pmatrix} p^n q^{N-n} = \frac{N!}{n!(N-n)!} p^n (1 - p)^{N-n}
\]

- \( n \to \infty; \ p = \text{const} \)
- \( n \to \infty; \ p = 0; \ Np = \nu > 0 \)

Image plate

Continuous Gaussian distribution

Counter

Discrete Poisson distribution
Intensity distribution in a bin

histogram of the intensities contributing to one bin* of air scattering intensity

The distribution of the air scattering intensity as a function of the azimuth

* A bin is a container into which pixels are grouped. It spans a 2D region of $2\theta$ which is identical to the $2\theta$ step width of the integrated pattern. The intensities of the pixels within a bin determine the corresponding intensity of a step in the integrated pattern.
The simpler the better ... Fractile filtering

We propose a robust type of band pass filter based on fractile statistics. A fraction $x$ of the low intensity data and a fraction $y$ of the high intensity data are removed:

$$I_{\text{min}} + x(I_{\text{max}} - I_{\text{min}}) \geq I_{\text{filtered}} \geq I_{\text{min}} + (1-y)(I_{\text{max}} - I_{\text{min}})$$
Effect of fractile filtering on the intensities of an almost ideal Bragg reflection as it would contribute to a two-theta bin.
The effect of filtering on high pressure XRPD data

The intensity is shown as a function of the azimuth for a high pressure powder diffraction data set. (+) highest data fraction removed by the filter. (•) lowest data fraction removed by the filter.
The azimuthal intensity distribution of a Bragg peak

Most promising description of the intensity distribution is the Pareto distribution (80/20 rule) convoluted with the normal distribution.

(At values of $a > 20$, the Pareto distribution tends toward a Dirac delta function, thereby reducing a convoluted normal-Pareto (NP) function to the normal distribution of perfectly monodisperse grains.)
Estimating the high intensity fraction to be filtered

For high values of parameter \( a \) the normal fraction approaches 1 asymptotically.

For a filter setting which would reduce the Pareto distribution to a roughly normal distribution \( (1\text{-normal fraction}) \) of the highest intensities should be removed.
Finally, the filtered data...

The effect of filtering on the diffraction image is shown in this figure. Intensities per integration bin:
- Green mask \rightarrow top 48%
- Blue mask \rightarrow bottom 2%
- Yellow mask \rightarrow beam stop

Screenshot of Powder3D-IP
http://www.fkf.mpg.de/xray/
The effect of filtering

Red: integrated pattern (left) and standard deviation (right) of the unfiltered image
Blue: 48% of the highest intensities and 2% of the lowest intensities removed
Filtered diffraction patterns of BiBO at high pressure

Simulated Guinier-plot of BiB$_3$O$_6$ in the pressure range from 0 to 12 GPa (using Powder3D).
Structure determination of $\varepsilon$-BiBO (TOPAS)

The toolbox:
1. Global optimization (Simulated annealing)
2. Optimized cost function
3. Modified weighting scheme
4. Anti-bumping penalties
5. Distance restraints
6. Occupancy merging

$\chi^2 = \sum \sum (I_h - c|F_h|^2)(V^{-1})_{hk}(I_k - c|F_k|^2)$


How do the lone pairs react on pressure...

α-BiBO

e-BiBO
Direct access to the order parameter

Parametric Rietveld refinement using spontaneous strain, symmetry modes and polyhedral tilting as a function of external variables
Sequential ↔ parametric Rietveld refinement

**Sequential Rietveld refinement:**
Each parameter in each pattern is refined individually

\[
y_{\text{calc}}(2\theta_{\text{pattern}(1)}) = \text{function}(p_{(1),1}, p_{(1),2}, \ldots, p_{(1),m})
\]

\[
y_{\text{calc}}(2\theta_{\text{pattern}(n)}) = \text{function}(p_{(n),1}, p_{(n),1}, \ldots, p_{(n),1})
\]

Minimization for each powder pattern independently

\[
\text{Min} = \sum_{i} \left( w_i \left( y_{\text{calc}}(2\theta_i) - y_{\text{obs}}(2\theta_i) \right)^2 \right)
\]

**Parametric Rietveld refinement:**
Some parameters in each pattern are functions of external variable(s)

\[
y_{\text{calc}}(2\theta_{\text{pattern}(1)}) = \text{function}(p_{(1),1}, p_2 = f(T_1, T_2, \ldots, T_i), \ldots, p_{(1),m})
\]

\[
y_{\text{calc}}(2\theta_{\text{pattern}(n)}) = \text{function}(p_{(n),1}, p_{(n),2} = f(T_1, T_2, \ldots, T_i), \ldots, p_{(n),1})
\]

Minimization over all powder patterns simultaneously

\[
\text{Min} = \sum_{\text{pattern}=1}^{n} \left( \sum_{i} \left( w_i \left( y_{\text{calc}}(2\theta_{\text{pattern}i}) - y_{\text{obs}}(2\theta_{\text{pattern}i}) \right)^2 \right) \right)
\]

Single refinement

Multiple refinement
Advantages of "parametric Rietveld refinement"

The idea:
The evolution of parameters in Rietveld refinement is described by functions in dependence on external variables (temperature, time, pressure, ...). The parameters of these functions are treated as global parameters and are subjected to "surface" Rietveld refinement (all powder patterns are refined simultaneously).

Advantages:

- the correlation between parameters and the final standard uncertainty can be reduced
- physically meaningful constraints and restraints can be introduced easily
- non-crystallographic parameters can be refined (e.g. rate constants, temperatures, ...)

The order parameter

Many crystalline solids can be considered as distorted versions of a higher symmetry parent structure. This parent structure can either be virtual or real. A group-subgroup relation must exist between the structures. All symmetry elements of the low-symmetry phase are already present in the high symmetry phase.

A new thermodynamic variable is necessary to specify the thermodynamic state of the low symmetry phase: order parameter $\eta$.

E.g. spontaneous strain, critical stress, birefringence, …

Landau theory is believed to describe the main physical features of ferroelastic and co-elastic phase transitions.

Excess Gibbs (free) energy is the difference in Gibbs energy between both phases, stabilizing the low symmetry phase: \( G_e = G_e(T, P, N, \eta) \)

Equilibrium condition: \( \frac{\partial G}{\partial \eta} = 0 \rightarrow G = G(T, P, N) \)

Trivial solution \( G(T) = 0 \) (for high temperature phase)

All quantities are measured with respect to the high temperature phase as excess quantities.

Landau assumed that the excess free energy (Landau potential) can be described in a Taylor series for small values of \( \eta \). Assumption: polynomial form of \( G \) is a good approximation over an extended temperature interval and for large values of \( \eta \).

\[ G = G_0 + \alpha \eta + A\eta^2 + C\eta^3 + B\eta^4 + ... \quad G_0, \alpha, A, B, C = f(P, T) \quad G_0 \neq f(\eta) \]
Power law behavior of the order parameter

\[ \eta = \text{constant \ (} T_c - T)^{\beta} \]

\[ \beta = \frac{1}{2} \ \text{(2}\text{nd order}) \]

\[ \beta = \frac{1}{4} \ \text{(tricritical)} \]

Temperature evaluation of structural order parameters \( \eta \) for several 2\text{nd} order and tricritical phase transitions (from Salje, 1993)
Access to the order parameter via spontaneous strain

Fig. 8. Spontaneous-strain data for the tetragonal = orthorhombic transition in As$_2$O$_3$ (data from Redfern & Salje, 1988; Redfern, 1988). (a) Lattice-parameter variation with temperature. (b) Variation of unit-cell volume with temperature, showing a small volume change due to the transition. The straight lines drawn in would imply $V \propto T$. (c) The square of the symmetry-adapted form of the symmetry-breaking strain is linear with $T$, implying $Q^2 \propto T$ and, hence, second-order behaviour.

Access to the order parameter via symmetry/distortion modes

Distorted Structure = High-symmetry Struct + “frozen” modes

distortion mode = Amplitude x polarization vector

Description of a “mode”:

\[ u(\text{atoms}) = Q \varepsilon \]

amplitude polarization vector

\[ e = (e_1, e_2, e_3, e_4) \]

normalization: \[ |e_1|^2 + |e_2|^2 + |e_3|^2 + 2 |e_4|^2 = 1 \]

\[ r_j^{LS} = r_j^{HS} + \sum_m c_m Q_m e(j|m) \]

The concept of polyhedral tilting, as an alternative way of describing distortions

Double-tetrahedra-group with 3 internal deg. of freedom as main structural building unit:
- average Fe-O bond length
- tilt1 torsion angle between the tetrahedra
- tilt2 rotation angle of one tetrahedron with respect to the other

Example I: CsFeO$_2$ (HT)


In-situ XRPD data of CsFeO$_2$, recorded at SLS with the 1D-Mythen-detector (4*10 seconds for each scan)
Aristotype: filled $\beta$-cristobalite structure

$\text{CsFeO}_2$ (HT)  $\beta$-Cristobalite
Phase transformation of CsFeO$_2$

HT-phase $Fd-3m$

LT-phase $Pbca$

Structural distortion mainly driven by rotation of the Fe$_2$O$_7$ double tetrahedra & translation of Cs atoms
Distortion modes amplitudes of CsFeO$_2$

(Main) distortion mode amplitudes of CsFeO$_2$

**ISODISPLACE: view distortion**

Graphical rendering of selected crystal [help]

Difficulty: some modes are coupled!
Distortion modes & amplitudes for CsFeO$_2$

1. Fd-3m[0,0,0]GM5+(a,0,0)[cs:b]T2(a) -0.0113(3)
2. Fd-3m[0,3/2,0]DT5(0,0,0,0,0,0,0,a,-0.414a,0.414a,a)[cs:b]T2_1(a) -0.0506(3)
3. Fd-3m[0,3/2,0]DT5(0,0,0,0,0,0,0,a,-0.414a,0.414a,a)[cs:b]T2_2(a) 0.1358(4)
4. Fd-3m[1/2,1/2,0]SM2(0,a,0,0,0,0,0,0,0,0)[cs:b]T2(a) -0.2839(4)
5. Fd-3m[1/2,1/2,1/2]L3+(0,0,0,a,-a,-a,a)[cs:b]T2(a) 0.0132(4)
6. Fd-3m[0,1,0]X1(0,a,0,0,0,0)[cs:b]T2(a) 0.0138(3)
7. Fd-3m[0,0,0]GM5+(a,0,0)[Fe:a]T2(a) -0.0020(5)
8. Fd-3m[0,3/2,0]DT5(0,0,0,0,0,0,0,0,a,-0.414a,0.414a,a)[Fe:a]T2_1(a) -0.1180(4)
9. Fd-3m[0,3/2,0]DT5(0,0,0,0,0,0,0,0,a,-0.414a,0.414a,a)[Fe:a]T2_2(a) 0.0168(4)
10. Fd-3m[1/2,1/2,0]SM2(0,a,0,0,0,0,0,0,0,0,0,0)[Fe:a]T2(a) -0.1948(5)
11. Fd-3m[1/2,1/2,1/2]L3+(0,0,0,a,-a,-a,a)[Fe:a]T2(a) 0.0132(4)
12. Fd-3m[0,1,0]X1(0,a,0,0,0,0)[Fe:a]T2(a) 0.0138(3)
13. Fd-3m[0,3/2,0]DT5(0,0,0,0,0,0,0,0,a,-0.414a,0.414a,a)[O:c]A2u(a) 0.057(2)
14. Fd-3m[0,3/2,0]DT5(0,0,0,0,0,0,0,0,a,-0.414a,0.414a,a)[O:c]Eu_1(a) -0.432(3)
15. Fd-3m[0,3/2,0]DT5(0,0,0,0,0,0,0,0,a,-0.414a,0.414a,a)[O:c]Eu_2(a) 0.052(4)
16. Fd-3m[1/2,1/2,0]SM2(0,a,0,0,0,0,0,0,0,0,0,0)[O:c]A2u(a) 0.188(3)
17. Fd-3m[1/2,1/2,0]SM2(0,a,0,0,0,0,0,0,0,0,0,0)[O:c]Eu_1(a) 0.059(2)
18. Fd-3m[1/2,1/2,0]SM2(0,a,0,0,0,0,0,0,0,0,0,0)[O:c]Eu_2(a) 0.503(3)
19. Fd-3m[1/2,1/2,1/2]L2+(0,0,a,-a)[O:c]Eu(a) 0.611(2)
20. Fd-3m[1/2,1/2,1/2]L3+(0,0,0,0,a,-a,-a,a)[O:c]A2u(a) -0.611(2)
21. Fd-3m[1/2,1/2,1/2]L3+(0,0,0,0,a,-a,-a,a)[O:c]Eu_1(a) -0.611(2)
22. Fd-3m[1/2,1/2,1/2]L3+(0,0,0,0,a,-a,-a,a)[O:c]Eu_2(a) -0.611(2)
23. Fd-3m[0,1,0]X1(0,a,0,0,0,0)[O:c]A2u(a) 0.001(2)
24. Fd-3m[0,1,0]X1(0,a,0,0,0,0)[O:c]Eu(a) 0.046(2)
Parameterization of lattice strains, distortion modes and polyhedral tilting in dependence on temperature by multiple simultaneous Rietveld refinement
Parameterised strain modes in dependence on temperature

Low symmetry orthorhombic phase (supercell)

\[
e_{11s} = \frac{a_s}{a_{s0}} - 1 = \frac{a_s}{a_{p0} / \sqrt{2}} - 1
\]
\[
e_{22s} = \frac{b_s}{b_{s0}} - 1 = \frac{b_s}{\sqrt{2}a_{p0}} - 1
\]
\[
e_{33s} = \frac{c_s}{c_{s0}} = \frac{c_s}{2a_{p0}} - 1
\]

High symmetry cubic phase

\[
e_{11p} = e_{22p} = e_{33p} \quad \text{and} \quad e_{12p} = e_{23p} = e_{13p} = 0
\]
\[
e_{11p} = e_{22p} = \varepsilon_\Gamma^+ - \frac{1}{2} \varepsilon_\Gamma^+ = \frac{a_p}{a_{p0}} - 1 = \frac{b_p}{a_{p0}} - 1
\]
\[
e_{33p} = \varepsilon_\Gamma^+ + \varepsilon_\Gamma^+ = \frac{c_p}{a_{p0}} - 1
\]
\[
e_{12p} = e_{21p} = \frac{1}{2} \varepsilon_\Gamma^+ = \frac{\pi}{2} - \gamma_p
\]

relationship between the strain of the supercell and the cubic strain

If \((T < T_{\text{crit}})\) then \(\varepsilon_\Gamma (T) = f_\Gamma (T_{\text{crit}} - T)^{\beta_\Gamma}\), else \(\varepsilon_\Gamma = 0\)
Parameterised strain modes in dependence on temperature

Temperature-dependent supercell parameters for CsFeO$_2$ as calculated from parametrically-refined power-law models of the strain parameters.

Temperature-dependent supercell strains for CsFeO$_2$ as calculated from their parametrically-refined power-law models.
Order parameter $\eta$ derived from parametric Rietveld refinement

$$\eta = A(T_c - T)^\beta$$

$\beta = [0.07..0.125]$
Order parameter $\eta$ derived from parametric Rietveld refinement

$$\eta = A (T_c - T)^\beta$$
$$\beta = [0.07..0.125]$$

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<td>a3</td>
<td>0.27 (1)</td>
<td>Cs 1 y</td>
<td>0.21(1)</td>
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<td>a4</td>
<td>0.08(1)</td>
<td>Cs 2 x</td>
<td>0.08(1)</td>
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<td>a10</td>
<td>0.11 (1)</td>
<td>tilt-1</td>
<td>0.125(2)</td>
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<tr>
<td>a15 / a19</td>
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<td>tilt-2</td>
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<td>$\varepsilon_1$</td>
<td>0.125(6)</td>
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<td>$\varepsilon_3$</td>
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<td>0.15(1)</td>
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<td>$\varepsilon_S$</td>
<td>0.23(1)</td>
<td>$\varepsilon_S$</td>
<td>0.23(1)</td>
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</table>

Some results:
- order parameters derived from polyhedral tilting and distortion modes are equivalent.
- The spontaneous strain $\varepsilon_S$ is coupled linear-quadratic with the $a10$ distortion mode and the angle $\text{tilt-1}: \varepsilon_S \sim \eta^2$
- The spontaneous strain $\varepsilon_S$ is coupled linear-cubic for $a4$ and Cs2x: $\varepsilon_S \sim \eta^3$
- The phase transition is clearly of first order.
Example II: \( \text{As}_2\text{O}_5 \) (HP)

\[
a = \sqrt[3]{V(P)} = V_{0a} \left(1 + \frac{K'_a P}{K_{0a}} \right)^{-\frac{1}{3K'_a}}
\]

“Linear” Murnaghan parameterisation of lattice parameters in dependence on high pressure.

Comparison of relative unit cell parameters in dependence on pressure obtained by independent refinement (red) and by Murnaghan parameterisation (black).

Resulting EoS from parameterised lattice parameters

As$_2$O$_5$ (HP)
polynomial parameterization of coordinates

$$a = A_0 + A_1 P + A_2 P^2 + A_3 \sqrt{P}$$

Joint plot of all the powder patterns of As$_2$O$_5$ in dependence on pressure refined with polynomial parameterisation of coordinates

Overlapped projections of the crystal structures of As$_2$O$_5$ obtained by (red) independent refinement and (blue) refinement using polynomial parameterisation of coordinates at the pressure of 20 GPa.
Example III: CuInSe$_2$

phase transition is driven by:

1) **anti site ordering** of copper and indium atoms
2) translation of selenium atoms

The modes

three different types of modes: strain, displacive, occupancy

Parameterization of strain, displacive, and occupancy modes
Some results of parametric refinement

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<th>critical exponent</th>
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<td>$a_1$</td>
<td>0.24(1)</td>
<td>tricritical displacive phase transition</td>
</tr>
<tr>
<td>$s_1$</td>
<td>0.49(2)</td>
<td>linear quadratic coupling</td>
</tr>
<tr>
<td>$s_2$</td>
<td>0.16(5)</td>
<td>maybe order-disorder transitions?</td>
</tr>
<tr>
<td>occupancy</td>
<td>0.28(1)</td>
<td>3D ordering phenomenon (Ising model)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>temperature factor</th>
<th>critical exponent</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>cations</td>
<td>0.24(1)</td>
<td>same as $a_1$</td>
</tr>
<tr>
<td>anion</td>
<td>0.49(2)</td>
<td>same as $s_1$</td>
</tr>
</tbody>
</table>

Phase transition combines an order-disorder (cation lattice) and a displacive (anion lattice) transition.
Towards automation:
Powder 3D\(^1\) - Parametric


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Handling TOPAS input files with Powder3D-Parametric
Sequential refinements with 
Powder3D-Parametric

Applications:
- Reaction kinetics
- Lattice parameters
- Distortion

Models:
- Linear, quadratic, cubic, Avrami, etc.

Sequentially refined parameters
Graphics

Sequential refinements with Powder3D-Parametric

Models: Linear, quadratic, cubic, Avrami, etc.
Parametric refinements of CuPc (isothermal) with Powder3D-Parametric

90% alpha and 10% beta CuPc at 250°C

Weight fraction Vs Time at 250°C

Avrami parameters for parametric refinements:

\[ n = 0.82163 \quad (1-130) \]
\[ k = 0.00227 \]

Sequential refinements for comparison:

\[ n = 0.97 \]
\[ k = 0.00178 \]
“True” disorder from XRPD by MEM and charge flipping

The method of MEM

\[
S = -\sum_{j=1}^{N} \rho_j \log \left( \frac{\rho_j}{\omega_j} \right)
\]

- \( N \) number of pixels in the unit cell;
- \( \rho_j \) electron density in pixel \( j \);
- \( \omega_j \) initial value of the electron density or prior

Collins (1982)
The method of charge flipping with histogram matching

\[
\rho(xyz) = \frac{1}{V} \sum_{hkl} |F_{hkl}| \cos(2\pi(hx + ky + lz) - \phi_{hkl})
\]

The high temperature phases of rubidium oxalate by \textit{in situ} powder diffraction

T: 25°-450°-25°

200 scans in 3½ hrs

R. E. Dinnebier, S. Vensky, M. Jansen, and J. Hanson, Crystal Structures of and Topological Aspects on the High Temperature Phases and the Decomposition Products of the Alkali Oxalates \(M_2\text{[C}_2\text{O}_4\text{]}\), \(M=\text{(K, Rb,Cs)}\), \textit{2005, Chemistry, a European Journal, 11, 1119 – 1129.}

A. Samy, R. E. Dinnebier, S. van Smaalen, and M. Jansen, The Maximum Entropy Method and Charge Flipping, a powerful combination to visualize the true nature of structural disorder from \textit{in situ} X-ray powder diffraction data. \textit{(2010) Acta Cryt. B.}
Crystal structures of the different phases of Rb$_2$C$_2$O$_4$ and Rb$_2$CO$_3$
Example: Rietveld plot of $\alpha$-$\text{Rb}_2\text{C}_2\text{O}_4$

Rietveld refinement: $\text{GOF}=1.57$, $R_p=1.70$, $R_{wp}=2.77$
Example: LeBail plot of $\alpha$-Rb$_2$C$_2$O$_4$

LeBail: GOF= 0.59, $R_p$=0.74, $R_{wp}$=1.03
Observed structure factors & model-biased effects

Rietveld refinement $\rightarrow F_{\text{obs}}$ - model-bias

$$A(\text{obs})_1 = \sum_{i=1}^{n} \frac{A(\text{calc})_1 \times q_1(i)}{A(\text{calc})_1 \times q_1(i) + A(\text{calc})_2 \times q_2(i)} (\text{obs}(i) - \text{back}(i))$$

$$A(\text{obs})_2 = \sum_{i=1}^{n} \frac{A(\text{calc})_2 \times q_2(i)}{A(\text{calc})_1 \times q_1(i) + A(\text{calc})_2 \times q_2(i)} (\text{obs}(i) - \text{back}(i))$$

LeBail algorithm

$$A_{m}^{r+1}(\text{obs}) = \sum_{i=1}^{N} \frac{A'_m(\text{obs}) \times q_m(i)}{\sum_{m=1}^{N} A'_m(\text{obs}) \times q_m(i)} (\text{obs}(i) - \text{back}(i)),$$

where, $A_{m}^{r+1}=1$, $n=1,...,N$
Ways of reconstructing the different types of electron density maps.

Synchrotron X-ray Powder Diffraction data using image-plate detector

LeBail method (profile matching)

Crystal system information and space group

Charge Flipping (CF) and histogram matching (HM) using $F_{LeBail}$ with random phases $\phi$

Rigid Rietveld analysis

With reference model

$\rho_{Pro}$ (strong model-bias)

$\phi_{model}, F_{Calc}$, MEM Flat-prior

$\rho_{MEM}$ (Model-bias)

$F_{Calc}$

$\rho_{MEM}$ (Model-bias)

$F_{obs}$

$\rho_{MEM}$ (partially model-bias)

$F_{obs}$

$\phi_{CF}, F_{LeBail}$

$\phi_{CF}, F_{obs}$

$\phi_{CF}, F_{LeBail}$

MEM algorithm: Sakata&Sato (1990); Computer programs: BayMEM, Jana, Superflip
Results of MEM-calculations based on model-Rietveld-refinement

Prior: IAM
Strong-biased

MEM-Fcalc:
All F biased

MEM-Fobs:
$F_{\text{obs}}$ partially biased

MEM-Fobs-G-constr.
Less biased

$\delta$-K$_2$C$_2$O$_4$ ($Pbam$) ordered
$T = 295$ K

$\alpha$-Rb$_2$C$_2$O$_4$ ($P6_3/mmc$) disordered
$T = 683$ K

$\alpha$-Rb$_2$CO$_3$ ($P6_3/mmc$) disordered
$T = 860$ K
Results of the combination of MEM with phases of CF

Not perfect, but a powerful combination to solve disordered crystal structures from powder data directly...
Many experiments which were only be possible at the synchrotron can now be done in the laboratory (e.g. Mo K$_{\alpha 1}$ in Debye-Scherrer geometry).

Future Rietveld-programs: toolboxes, macros, self learning, user community.

Determination from powder data is becoming routine. (for small and medium sized structures).

Parametric Rietveld refinement opens a new world (determination of non-structural parameters, e.g. kinetics, order parameters).

Accurate electron density distributions using MEM method from XRPD.

Complex structure determination from powder data by the combination of CF and MEM.

High speed (<1 s) + high resolution is now available at the synchrotron (ESRF, SLS, Petra III, Diamond, etc.)

High pressure powder diffraction and PDF analysis in the laboratory....
Acknowledgement

To where the money came from

MPG, FCI, BMFT

To the facilities providing beamtime

NSLS, ANKA, ESRF, APS

To collaborators

Peter Stephens (SUNY at Stony Brook), John Hanson (NSLS), Sander van Smaalen (Bayreuth), Bernd Hasse (Incoatec), Ralph Weigel (ANKA), Andy Fitch (ESRF), Haozhe Liu (APS), Branton Campbell (BYU) …

To current and former group members
Constraints in MEM

1. Normalization of $\rho$ to the expected number of electrons per unit cell volume ($F_{000}$)

$$\int_V \rho dV - N_{el} = 0$$

2. $F$-constraints $C_F$ with central moment $m_n$. The resulting error distribution must be obeying the Gaussian distribution function

$$C_{F_n} = -1 + \frac{1}{m_n(\text{Gauss})} \frac{1}{N_F} \sum_{i=1}^{N_F} \left( \frac{F_{\text{obs}}(H_i) - F_{\text{MEM}}(H_i)}{\sigma(F_{\text{obs}}(H_i))} \right)^n$$

3. $G$-constraints, sometimes phases or even amplitudes of individual structure factors cannot be determined reliably. This is often the case for powder diffraction data, where systematic and/or accidental overlap of reflections is common.

$$G_G = -1 + \frac{1}{N_G} \sum_{i=1}^{N_G} \left( \frac{G_{\text{obs}}^i - G_{\text{MEM}}^i}{\sigma(G_{\text{obs}}^i)} \right)^2$$

$$G^i = \sqrt{\sum_{j=1}^{N_g} \frac{m_j}{\sum m_j} \left| F(H_j) \right|^2}$$

Sakata & Takata, 1996
Maximize:

\[ Q(\rho) = S(\rho) - \sum_{j=1}^{N_c} \lambda_j C_j(\rho), \quad \frac{\partial Q}{\partial \rho_i} = 0 \]

\[ \rho_i = \frac{N_{el}N_{pix}}{V} \tau_i \exp\left( -\lambda_F \frac{\partial C_F}{\partial \rho_i} \right) / \sum_{i=1}^{N_{pix}} \tau_i \exp\left( -\lambda_F \frac{\partial C_F}{\partial \rho_i} \right) \quad (3) \]

The iteration is started with \( \rho_i^{(1)} = \tau_i \) and the new density \( \rho_i^{(n+1)} \) is calculated from the prior density \( \rho_i^{(n)} \), the value of the constraint decreases each cycle until the condition of \( C_F \leq 1 \) is fulfilled.

\[ \tau_i^{n+1} \approx \rho_i^n \]

Set of \( N_{pix} \) nonlinear equations
The parameters of MEM-calculations

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>(-\text{K}_2\text{C}_2\text{O}_4)</th>
<th>(-\text{Rb}_2\text{C}_2\text{O}_4)</th>
<th>(-\text{Rb}_2\text{CO}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of voxels</td>
<td>108 64 36</td>
<td>96 96 108</td>
<td>54 54 72</td>
</tr>
<tr>
<td>Pixel size /Å</td>
<td>0.101 0.095 0.096</td>
<td>0.067 0.067</td>
<td>0.109 0.109 0.10</td>
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<tr>
<td></td>
<td></td>
<td>0.076</td>
<td>8</td>
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<tr>
<td>Electrons per unit cell</td>
<td>164</td>
<td>236</td>
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<td>Lagrange multiplier</td>
<td>0.05</td>
<td>0.05</td>
<td>automated</td>
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<td>Initial density</td>
<td>Flat-prior</td>
<td>Flat-prior</td>
<td>Flat-prior</td>
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<tr>
<td>F-constraints</td>
<td>86</td>
<td>46</td>
<td>42</td>
</tr>
<tr>
<td>G-constraints</td>
<td>9</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>

Initial density (flat-prior) = \(\frac{N_{el}}{N_{pix}}\)

Algorithm: Sakata&Sato (1990)

Computer program: BayMEM (van Smaalen, 2003)
Simulated annealing and disorder

CsCp*: perfect fit in \( \alpha_4 \alpha_\text{amd} \) (\( a = 7.54 \text{Å}, \text{and} \ c = 19.97 \text{Å} \)), but problems in solving the crystal structure (Cs at 0 0 0, Cp* (as pseudo atom) at 0 1/4 1/8 ???)

10 years after the measurement ....

Structure determination "by hand" in maximal translationengleiche subgroup $I2d \ (C2/c)$

Optimum results for bent Cp*-Cs-Cp* chains with two-fold rotational disorder of the Cp* rings
Why tetragonal?

Most likely stacking faults perpendicular to the ac-plane lead to pseudotetragonal appearance (supported by anisotropic microstrain broadening with the maximum “strain” occurring long the vector $a \pm c$ and shape of thermal ellipsoids).
Temperature dependence of the order parameter for 2\textsuperscript{nd} order phase transitions

\( T > T_c : \eta \to 0 \quad \Rightarrow \quad \text{Minimum of free energy at } \eta = 0 \Rightarrow \dot{\eta} = 0; A > 0 \)

\( T < T_c : \eta > 0 \quad \Rightarrow \quad \text{Minimum of free energy at } \eta \neq 0 \Rightarrow \dot{\eta} = 0; A < 0, B(P,T) > 0 \)

Simplest choice: \( A(P,T) = a(T_c-T) \)

Assumption: \( C = 0 \)

\( \Rightarrow \quad G = G_0 + a(T-T_c)\eta^2 + B\eta^4 \quad (2\text{-}4 \text{ potential}) \)

\( \Rightarrow \frac{\dot{G}}{\dot{\eta}} = 0 \Rightarrow 2a(T-T_c)\eta = -4B\eta^3 \Rightarrow \eta^2 = a/(2B)(T_c-T) \Rightarrow \eta = c(T_c-T)^{1/2} \quad (T < T_c) \)

\( \Rightarrow \eta = 0 \)
Assumption: $C = 0$  $\Rightarrow$ $G(P,T) = A(P,T)\eta^2 + B(P,T)\eta^4$

Assumption: $B(P,T_c) < 0$  $\Rightarrow$ higher order terms are necessary to allow for a minimum of the free energy at any finite value of $\eta$

Assumption: $B = 0$

$\Rightarrow$ $G = G_0 + a(T-T_c)\eta^2 + D\eta^6$ (2-6 potential)

$\Rightarrow \frac{\partial G}{\partial \eta} = 0 \Rightarrow 2a(T-T_c)\eta = -6D\eta^5$  $\Rightarrow \eta^4 = a/(3D)(T_c-T)$  $\Rightarrow \eta = c (T_c-T)^{1/4}$  $(T < T_c)$

$\Rightarrow \eta = 0$  $(T > T_c)$

At the point where $B(P,T)$ changes sign, a 2nd order phase transition goes over to a 1st order phase transition (tri-critical point)