Argonne NATIONAL LABORATORY

... for a brighter future

U.S. Department of Energy

THE UNIVERSITY OF CHICAGO

Office of Science U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory managed by The University of Chicago

Combined Rietveld Refinements: Where 1+1 can be > 2

Brian H. Toby
Robert B. Von Dreele

Outline

- Motivation to use more than a single measurement
  - Anomalous dispersion (resonant scattering)
  - X-rays + neutrons
  - Hard & soft constraints
- Combined refinement case studies
- What can go wrong with combined refinements

What are "combined" refinements?

- Traditional "single-crystal" paradigm:
  - collect a set of data ==> determine a structure

Complex problems may require more information than can be obtained from a single set of diffraction measurements

  - ***Particularly true for powder diffraction.***

- **Options:**
  - give up
  - use multiple sets of measurements: more observations
  - build external "knowledge" or assumptions into model
    - •disadvantage: loss of "independence from bias" associated with crystallography

Why? -- Limitations of a single diffraction measurement

All a single x-ray diffraction measurement can tell you is how many electrons are present at an atomic site.

Example: find amounts of Fe & Ti sharing a site in a perovskite

$f_{site} = n_{Fe} f_{Fe}(Q) + n_{Ti} f_{Ti}(Q)$ where $f_{Fe}(Q)/26 \cong f_{Ti}(Q)/22$

one observable: f_{site} but two unknowns: n_{Fe} and n_{Ti}

One approach to solving this: assumptions

Assume no vacancies: $n_{Fe} = 1 - n_{Ti}$

Assume total composition is known: works if only one Fe/Ti site

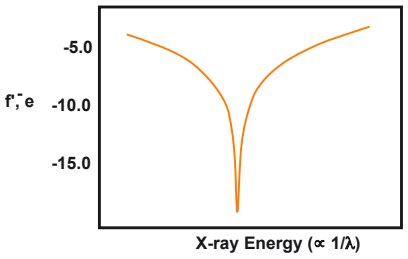
Why do Multiple X-ray Measurements?

Anomalous Dispersion (better name Resonant Scattering):

Changing the x-ray λ can allow us to "tweak" $f_{Fe}(Q)$ and/or $f_{Ti}(Q)$ near the appropriate absorption edge

$f_{total} = f(Q) + f' + if''$

(sometimes written as $\Delta f'$ and $\Delta f''$)

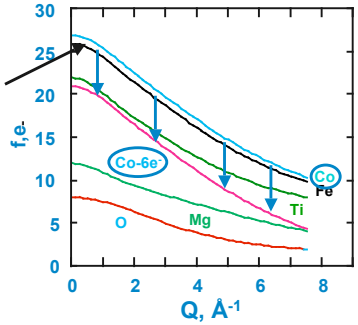


The effect of using a wavelength near an absorption edge

Curves show "form factor" (scattering length) for a few types of atoms

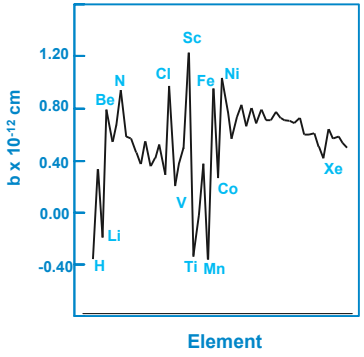
Note: Co and Fe differ by 1 electron

Choosing a wavelength just below the Co absorption edge effectively creates a 6 electron difference in Co x-ray scattering

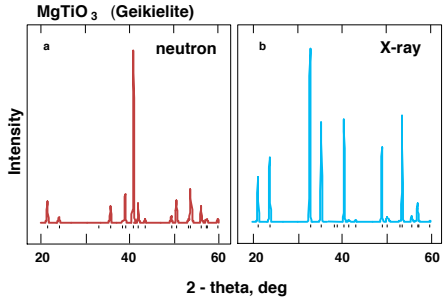


Neutron diffraction has different atomic scattering lengths than x-rays

- Neutron scattering lengths (b) vary erratically across Periodic Table
- Most "light" elements scatter well
- some atoms have "Negative" (phase inverted) b values
- b usually varies by isotope
  - H (-0.37) vs. D (0.67)
- b does not vary with Q: more intense "high angle" scattering
  - more accurate models
  - better discrimination of occupancies



X-Ray vs. Neutron Diffraction



X-ray & neutron data - very different pattern of intensities
Combination - stronger restriction on structure model

Fe & Ti site-sharing example revisited

With x-ray and neutron information combined:

$f_{site} = n_{Fe} f_{Fe}(Q) + n_{Ti} f_{Ti}(Q)$ (x-rays)

$\mathbf{b}_{site} = n_{Fe} \mathbf{b}_{Fe} + n_{Ti} \mathbf{b}_{Ti}$ (neutrons)

two observables: f_{site} and $\mathbf{b}_{site}$ and two unknowns: n_{Fe} and n_{Ti}

- Note: $\mathbf{b}_{Fe} = 0.94$ and $\mathbf{b}_{Ti} = -0.34$ so Fe/Ti contrast is excellent

Constraints: Use of a priori *knowledge*

- Rigid bodies: assumption that the relative atom positions for a molecule or molecular fragment (e.g. phenyl ring) is known
  - define the group (in cartesian coordinates) and define location & orientation (refinable); possible to refine some scaling terms
- Group parameters: assume that all O atoms have same U_{iso}
- "Soft Constraints" (Restraints): fit is degraded if restraint is not met
  - interatomic distances
  - bond angles
  - composition

Minimization function (for protein refinement)

$$M = \sum w_i (I_{oi} - I_{ci})^2$$ **Powder profile (Rietveld)**

$$+ f \sum w_i (a_{oi} - a_{ci})^2$$ **Bond angles**

$$+ f \sum w_i (d_{oi} - d_{ci})^2$$ **Bond distances**

$$+ f \sum w_i (t_{oi} - t_{ci})^2$$ **Torsion angles**

$$+ f \sum w_i (- p_{ci})^2$$ **Plane RMS displacements**

$$+ f \sum w_i (v_{oi} - v_{ci})^2$$ **van der Waals distances**

$$+ f \sum w_i (h_{oi} - h_{ci})^2$$ **Hydrogen bonds**

$$+ f \sum w_i (x_{oi} - x_{ci})^2$$ **Chiral volumes**

$$+ f \sum w_i (-R_{ci})^2$$ **"ϕ/ψ" pseudopotential**

$w_i = 1/\sigma^2$ weighting factor, f - weight (typically 0.1-3)

Combined Experiments: case studies

1. Multiple λ x-ray
2. Synchrotron/Neutron
3. X-ray single crystal/Neutron
4. Synchrotron/Neutron with isotope labeling & rigid bodies
5. Texture via multiple "views" of sample

Example 1: resonant x-ray diffraction, $La_{0.9}Gd_{0.9}Sr_{0.2}CuO_4$

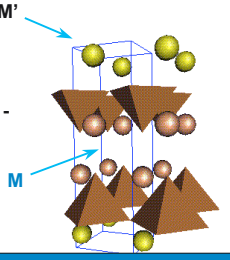
T* - phase - "middle" of La(Sr)CuO_4; "top" of Nd(Ce)CuO_4
Issue - M site preferences for Sr, La & Gd (strong neutron absorber)

Data collection - all x-ray

Sr K	0.767956(9)	f'(Sr) = -5.60
La L	1.98944(11)	f'(La) = -8.45
Gd L	1.71688(4)	f'(Gd) = -15.53
Cu Ka	1.540598	

Site occupancy results - 2 sites/3 atoms - constrain by chemistry

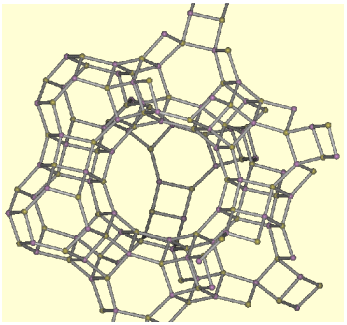
	M	M'	Σ – const
Sr	0.24(7)	-0.04(7)	0.20
La	0.80(9)	0.10(9)	0.90
Gd	-0.01(5)	0.91(5)	0.90
Σ	1.03	0.97	



Uncertainties on combinations of parameters (such as these compositions) can be computed in program GEOMETRY

Example 2: CaLSX ($Ca_{0.5}AlSiO_4$)

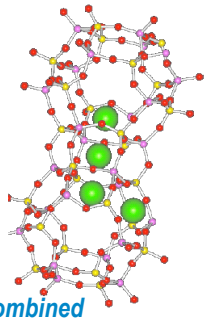
- LSX ==> low silica X
  - e.g. Al:Si = 1:1
- X ==> Faujasite
- "simple" structure
  - cubic, F d -3
  - 9 atoms/asym. Unit
- Diffracts beautifully
  - (for a zeolite)



Vitale, G., Bull, L. M., Morris, R. E., Cheetham, A. K., Toby, B. H., Coe, C. G., and MacDougall, J. E., "Combined Neutron and X-Ray-Powder Diffraction Study of Zeolite Ca LSX and A ^{2}H NMR Study of Its Complex with Benzene", *Journal of Physical Chemistry* **99**, 16087 (1995).

CaLSX: Why Combined?

- Neutrons alone:
  - detailed & precise framework geometry
  - inaccurate Ca positions
  - wrong Ca occupancies!
- Synchrotron X-ray data alone:
  - insensitive to framework atoms



Excellent fit with Neutrons & X-rays combined

Example 3: $KFe_3(D_2VO_2)_3(SO_4)_2$ (Jarosite structure)

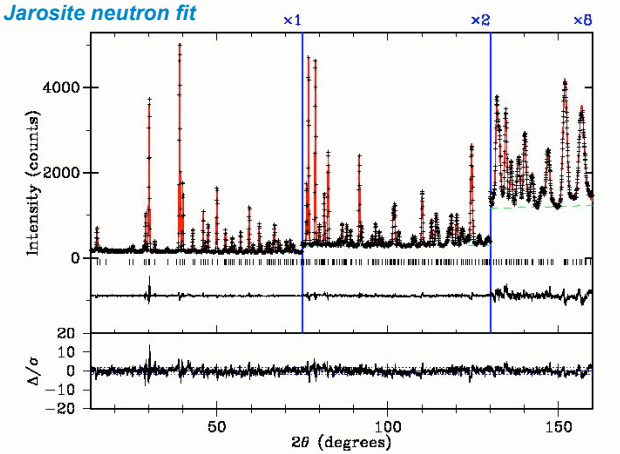
- Nice single crystal structure – but no hydrogen site information
- Good powder neutron data, but for vanadium, b ≅ 0

Combined refinement was simple. Removal of each set of data gave virtually no improvement in R-factor for remaining set.

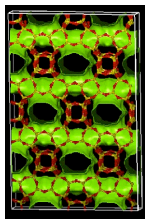
  - Combined refinement improved crummy x-ray anisotropic U_{ij}'s

D. Grohol, Q.Z. Huang, B.H. Toby, J.W. Lynn, Y.S. Lee, and D.G. Nocera, "Powder Neutron Diffraction Analysis and Magnetic Structure of Kagome-type Vanadium Jarosite $NaV_3(OD)_6(SO_4)_2$". *Physical Review B.* **68**(9): p. 094404 **(2003)**.

Jarosite neutron fit



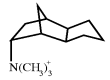
Example 4: Combining a priori knowledge with diffraction data



CIT-1 is a molecular sieve that illustrates interesting zeolite-SDA (template) interactions

◂ 1 Makes CIT-1 (~1% stacking faults)

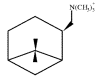
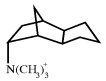
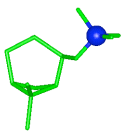
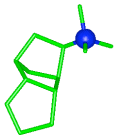
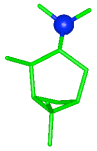
2 Makes SSZ-33 (similar to CIT-1, but with >30% stacking faults) ▸



◂ 3 Cannot be used to make either CIT-1 or SSZ-33

Why?

There is no obvious difference between the SDA cations

no faults	*faults*	*neither*
		
		
1	2	3

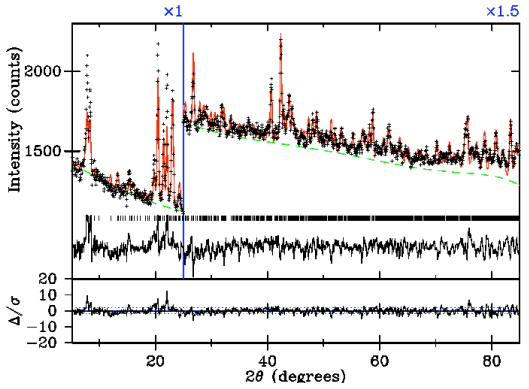
CIT-1: Questions

- Synchrotron x-ray and neutron powder data
  - CIT-1 with SDA **1** -- "as synthesized"
  - SDA deuterated on the $N(CD_3)_3$ end
- Even so, insufficient data to model the framework positions
  - Use soft-constraints of 1.64±0.02 Å on Si-O bonds
- Goal: learn siting of SDA cations:
  - Disorder problem: symmetry is much lower than host
  - Use rigid body model for SDA cation (from molecular modeling)
    - *can fit 13 non-H atom SDA with only 7 parameters (3 position, 3 angles, U_{iso})*

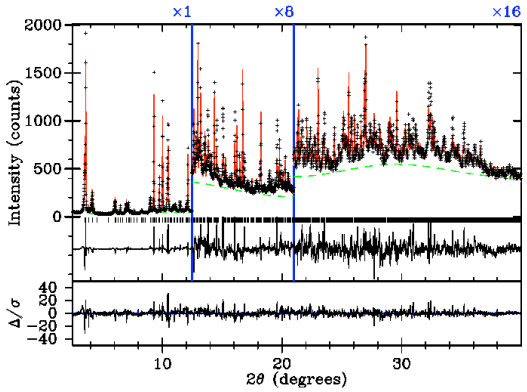
CIT-1: Results

- First attempt: ("Old-fashioned" approach), view difference Fourier map in 3-D and look for how SDA cation might fit.
  - Result with single SDA site poor, added a 2nd SDA site
  - Gave reasonable fit to x-ray & neutron data (not great)
  - ~4 template molecules/unit cell (3 in literature)
- Are there other solutions with reasonable or even better agreement to the data?

Final Neutron Fit



Final X-ray Fit



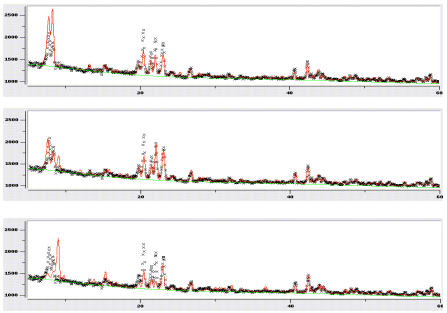
CIT-1: Model Template Packing

Perform an exhaustive search for possible SDA sites in CIT-1

- Generate models with MSI Solids Docking (Monte-Carlo MM)
  - Obtained no reasonable models with 4 templates per cell
  - Numerous models with 3 molecules per cell
- Analysis of MM models with reasonable "energy":
  - SDA sites in only 3 orientations (labeled as A, B & C)

How do these models fit the data?

Which of the three fits the data?



A

B

C

None of the above!

3A+1B works!

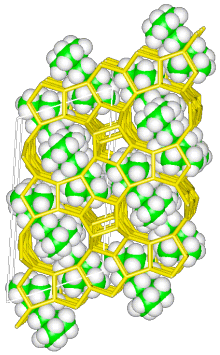
- Using all three orientations and refining occupancies yields a good (not great) fit:
  - ~ 3 molecules/cell in orientation A
  - ~ 1 molecule/cell in orientation B
  - ~ 0 molecules/cell in orientation C
- A & B are equivalent except for orientation of $N(CD_3)_3$ group
  - A & B could not be distinguished by x-rays, only neutrons
- Refined positions ~same as "difference Fourier" results

But, can four molecules really fit?

Use MM to optimize packing of 4 SDA **1** cations/cell
- compact structure
- No "bumps" (overlapping atoms)
- ~ same result as crystallographic model

Answer: Yes!

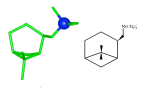
- prompt-γ: 4 SDA/Cell
- repeat TGA: 3.4 SDA/Cell



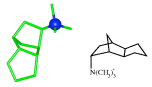
How do SDA 1, 2 & 3 Compare?

- Use MM to optimize packing of each SDA with 4 molecules/cell
  - SDA **1** & **2** agree within 4.5 kcal
  - SDA **3** is 55 kcal less stable

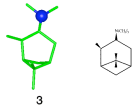
*Explains why SDA **3** does not make CIT-1*



1



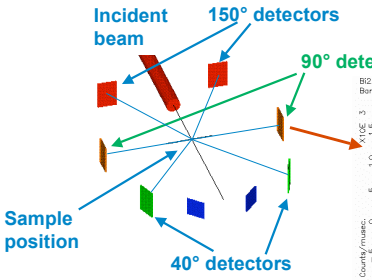
2



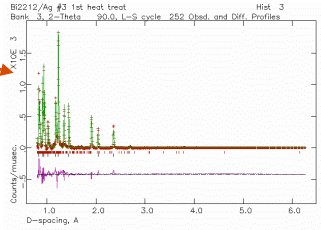
3

Toby, Khosrovani, Dartt, Davis and Parise, "Structure-directing Agents and Stacking Faults in the CON System: A Combined Crystallographic and Computer Simulation Study.", *Microporous and Mesoporous Materials* **39**, 77 (2000).

Measurement of Texture using HIPD (or HIPPO) at LANSCE



Fixed 2Θ, TOF ∝ λ ∝ d



- 10-20 sample orientations
- 4 (or 6) different "looks"at the texture
- 50-90 "powder" patterns
- full patterns - many reflections
- fit by Rietveld refinement

LANSCE
Los Alamos Neutron Science Center

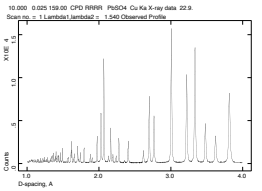
What can go wrong with combined refinements?

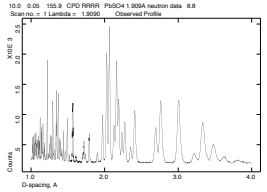
Combined refinements pitfalls

- Are the samples the same?
  - Beware of single crystals for variable composition phases: specimen may not be representative of bulk material
  - Surface vs. bulk differences: neutrons sample the entire bulk, while for high-μ materials, x-rays sample the surface
- Incompatible wavelength calibration
  - vary λ (DIFA & DIF`C) for all but one histogram type
- Are the measurement temperatures the same?
  - Differential thermal expansion for non-cubic materials may result in irreconcilable differences in peak positions

Incompatible data -- example $PbSO_4$

X-ray Diffraction - CuKα
Phillips PW1710
- **Higher resolution**
- **Intensity falloff at small d spacings**
- **Better at resolving small lattice distortions**





Neutron Diffraction - D1a, ILL
λ=1.909 Å
- **Lower resolution**
- **Much higher intensity at small d-spacings**
- **Better atomic positions/thermal parameters**

Incompatible data -- example $PbSO_4$

Classic failure - $PbSO_4$ Rietveld Round Robin
2 data sets - CuKα x-ray and CW neutron
both excellent but at different temperatures
(x-ray at 298K, neutron at 295K?)
Important experimental controls not followed-
Same temperature
Same sample
Combined Rietveld Refinement not the best -
Thermal expansion - orthorhombic
Changed atom positions
Changed thermal motion
• Poorer fit than individual refinements -
R_{wp} ca 2% high for X-ray data
• Inconsistent results - e.g. neutron λ = 1.9105Å

Quality assurance

Testing Constraints

- If using 2+ data sets: are they consistent with each other?
  - Try removing individual data sets from the refinement (may need to lock some parameters)
    - *Parameter values will change but changes to R_{wp} should be fairly small*
- Soft constraints: are the assumptions valid?
  - Reduce the weights (or increase uncertainties)
    - *Parameter values will change but changes to R_{wp} should be fairly small*
    - *What % of total χ^2 comes from constraints? Should be <10-20%*
- Hard constraints: can be hard to test
  - Try removing them – do the results suggest any conclusions?

Be sure to document Hard & Soft Constraints in publications

Conclusions

- A single powder diffraction measurement may not provide enough information to fully determine a structure
- Use of additional observations may allow for more to be learned
- Be careful that your derived result is not a direct outcome from your assumptions
- When using multiple measurements, make sure the observations are consistent