Neutron Structure Refinement – A Tutorial Using SHELX for Neutrons

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Outline

• Neutron single crystal diffraction
  Neutron Sources: Monochromatic vs. Time-of-flight Laue

• SHELX Instructions for refinement against neutron data

• Data format for neutron time-of-flight Laue

• Treatment of hydrogen atoms

• A short tutorial
  Import starting structure model
  Locate H atoms from difference Fourier map
  Refine hydrogen atom positions and ADPs
  Prepare cif for publication
Neutron single crystal diffraction

- **Neutron diffraction** *Weak* neutron ~ nuclear interaction $E = 81.8$ meV at $1.0$ Å
  - *Scattering length* $b$:
    - Fourier transform of the nuclear density of an atom
  - $b$ is isotope specific
    - H: -3.74 fm, D: 6.67 fm
    - A number that is independent of scattering angle and wavelengths
  - \[ Q = \frac{4\pi \sin \theta}{\lambda} \]

  **Magnetic scattering**
  
  Neutron *(spin $\pm$)* ~ (out-shell) electron interaction, strong Q dependence

- **X-ray diffraction** Photon ~ electron interaction, $E_{Mo \ K\alpha} = 17.5$ keV, $\lambda = 0.71$ Å
  - *Form factor* $f$:
    - Fourier transform of the atomic electron density of an atom
  - $f \propto$ Atomic Z
    - Decay as Q increases
Neutron scattering lengths

- SHELX Instructions

**NEUT**

```
! Placed before the first SFAC instruction with element names
```

**SFAC**

```
C H N O F P Fe
```

![Graph showing neutron scattering lengths](www.ncnr.nist.gov/resources/n-lengths/)
SFAC for element of individual isotopes

Create an isotope specific SFAC instruction form

**Example** $^{7}\text{Li}$ in enriched $^{7}\text{LiMnPO}_4$

https://www.ncnr.nist.gov/resources/n-lengths/

<table>
<thead>
<tr>
<th>Isotope</th>
<th>conc</th>
<th>Coh b</th>
<th>Inc b</th>
<th>Coh xs</th>
<th>Inc xs</th>
<th>Scatt xs</th>
<th>Abs xs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>---</td>
<td>-1.90</td>
<td>---</td>
<td>0.454</td>
<td>0.92</td>
<td>1.37</td>
<td>70.5</td>
</tr>
<tr>
<td>6Li</td>
<td>7.5</td>
<td>2.00-0.261i</td>
<td>-1.89+0.26i</td>
<td>0.51</td>
<td>0.46</td>
<td>0.97</td>
<td>940.4</td>
</tr>
<tr>
<td>7Li</td>
<td>92.5</td>
<td>-2.22</td>
<td>-2.49</td>
<td>0.619</td>
<td>0.78</td>
<td>1.4</td>
<td>0.0454</td>
</tr>
</tbody>
</table>

$\sigma = \sigma_s + \frac{\sigma_a}{1.798} \times \lambda$

- $\sigma$ is wavelength dependent
- $\sigma_s$ total bound scattering cross section
- $\sigma_a$ absorption cross section for 1.798 Å neutrons
- NEUT
- SFAC Li 0 0 0 0 0 0 0 0 -2.22 0 0 1.42 1.28 7.016
- SFAC Mn P O

The absorption cross section for H needs to be calculated differently with an empirical formula

SHELXL instructions for neutron data

name.ins

CELL 1.003 6.5120 18.9545 9.7582 90.0 108.921 90.0
ZERR 4 0.0001 0.0004 0.002 0.0 0.001 0.00

... NEUT ! Placed before the first SFAC instruction with element names
SFAC Ca Si Al O H
ACTA

... EXTI
FVAR

... HKLF 4 data from monochromatic source
Neutron time-of-flight Laue

- Combine de Broglie’s equation with Bragg’s law

\[ \lambda = \frac{h}{mv} = \frac{ht}{m(L_1 + l_2)} = 2d \sin \theta \]

\[ t = \frac{m}{h}(L_1 + l_2) \times 2d \sin \theta \]

Neutron Time-of-flight Laue
(Wavelength-resolved Laue)
3-D Reciprocal Space Mapping
HKLF 2 Instruction for Laue data

- **HKLF 2** ! + batch number (BN) and wavelength $\lambda$ for individual reflections
- **Data Format** 3I4, 2F8.2,I4,F8.4
- 1234123412341234567812345678123412345678
- $h \quad k \quad l \quad F_0^2 \quad \sigma(F_0^2) \quad BN \quad \lambda$

**Neutron Time of Flight Laue**
- Reflections are measure on a stationary single crystal sample.
- Integrated intensities are corrected for intensity distributions by neutron wavelengths, Lorentz and sample absorption.

- It is possible to refine the scale factors BN for different sets of reflections measured at different sample orientations / or on different detectors

**TWIN** instruction cannot be used for refinement against data in **HKLF 2** format
- ** ILLEGAL TWIN/HKLF COMBINATION **
Example

- Scolecite
  - ORNL SNS TOPAZ Time of Flight Laue data
  - SHELX HKLF 2 Format [First 7 columns]

A data set were measured using 39 sample orientations to achieve > 98% completeness
SHELXL instructions for TOF neutron data

name.ins

CELL 0.600 6.5125 18.9371 9.7575 90.0 108.953 90.0

ZERR 4 0.0001 0.0002 0.0001 0.0 0.001 0.00

...

NEUT ! Needs to be placed before the first SFAC instruction

SFAC Ca Si Al O H

MERG 0

SUMP 6 0.0001 2 1 3 1 4 1 6 1 ! Constrain the sum of batch factors 6.

BASF 1.0 1.0 1.0 1.0 1.0 ! Refine 5 scale factors out of 6 in HKLF 2 data set.

EXTI

FVAR 0.666 ! Overall scale factor.

....

HKLF 2 ! Laue data
SHELXL instructions for nuclear density

**name.ins**

**FMAP** -2  \( ! \) Include negative difference nuclear density

**PLAN** 10  \( ! \) Generate 10 negative and positive Q peaks

**LIST** 4  \( ! \) \( F_o^2 \) scaled to \( F_c^2 \), extinction correction included

**ACTA**

✓ **LIST** 4

output *name.fcf* ; required by the IUCr, optional for CCDC and ICSD

✓ **LIST** 3

For viewing density map in WinGX

✓ **LIST** 6

For viewing density map in Olex2, Shelxle, Coot…

Unit of neutron scattering density: \( \text{fm} \ \text{Å}^{-3} \)
Extinction correction

- **EXTI** $x$
  - Extinction is wavelength dependent

\[ k \left[ 1 + \frac{0.001 F_c^2 \lambda^3 x}{\sin(2\theta)} \right]^{\frac{1}{4}} \]

When $x$ approaches 0 (no extinction correction applied):
Negligible difference in refinements against TOF Laue data in either HKLF 2 or 4 format.
Locate and refine hydrogen atom positions

- Difference map
  - **FMAP** -2 ! List positive and negative peaks, unit for neutron data: fm Å⁻³
  - **PLAN** 10 ! Copy largest 10 peaks by the absolute value of peak heights to .res

**HFIX mn or AFIX mn**

Apply geometry constraints to reduce refined parameters
- m for geometry constraints calculated before the refinement cycle
- n = 3 no refinement of coordinates ➔ Riding model; no extra parameters
- n = 4 X-H distance is free to refine
Comments on sample absorption correction

- The neutron attenuation coefficient consists of two parts
  - Total scattering and True absorption

\[ \mu = \left[ \mu_s + \frac{\mu_a}{1.798} \times \lambda \right] \text{ cm}^{-1} \]

TOPAZ Scolecite data

_exptl_absorpt_special_details

;  
Neutron linear absorption coefficient is wavelength dependent.  
For each peak, the absorption coefficient \( \mu \) is calculated as:  

\[ \mu = 0.6710 + 0.7340/1.8 \times \text{wavelength} \ [\text{cm}^{-1}] \]

where  
0.6710 cm\(^{-1}\) is the absorption coefficient for total scattering;  
0.7340 cm\(^{-1}\) is the absorption coefficient for true absorption at 1.8 A.

The value of 0.1079 (mm\(^{-1}\)) shown in _exptl_absorpt_coefficient_mu  
is the sample absorption coefficient for neutron wavelength at 1.0 \%A.

;
Tutorial: Neutron structure refinement using Shelx

• SHELX-2013
  http://shelx.uni-ac.gwdg.de/SHELX/download.php

• Graphic User Interfaces
  ► ShelXle
    https://www.shelxle.org/shelx/eingabe.php
  – WinGX Program System
    http://www.chem.gla.ac.uk/~louis/software/
  – Olex² Crystallography Software
    http://www.olexsys.org/Software

• Workshop Talks

• George Sheldrick: SHELXL for neutrons (TOPAZ Oak Ridge 2015)
  http://shelx.uni-ac.gwdg.de/SHELX/shelxl_for_neutrons.pdf

• Xiaoping Wang: Refinement of small molecules against neutron data (ACA, 2016)
  http://shelx.uni-ac.gwdg.de/SHELX/neutrons_SM_ACA2016.pdf
Tutorial Sample No. 1

• Scolecite

• Aims of the neutron experiment: Use neutron single crystal diffraction to locate missing water (H$_2$O) (pink, red) molecules in the large channels of the aluminosilicate framework.

View of the structure of scolecite in the $bc$ plane. Ca (yellow); Si (blue) and Al (cyan) atoms form interconnected tetrahedral with corner sharing O(red) atoms.
Neutron data for scolecite

- Copy TOPAZ neutron TOF Laue single crystal diffraction dataset in shared subfolder to your work directory

- \Tutorial\scolecite\exercise
  - `scolecite.hkl` TOPAZ neutron data set saved in HKLF 2 format
  - `topaz_anvred3.cif` TOPAZ Instrument cif
  - `latcon.out` Lattice parameter from neutron experiment

- X-ray CIF from ICSD
  - `ICSD_95391.cif` Shelxl ins file
  - `ICSD_95391_std.ins` Starting model to be used for neutron refinement
Need a starting model for neutron refinement

- Import from X-ray structures
  - Use X-ray .res from shelx
  - Convert .cif to .res
    - **Platon, Mercury, Olex2, Vesta, WinGX**
    - **Example** Create a res file using Vesta

- Solve a unknown structure
  - Not necessary in most cases since the basic structure model is usually known from X-ray diffraction.
  - If needed, neutron structure can be solved using charge and band flipping method *Acta Cryst. (2007). A63, 156-163*
  - SHELXT uses X-ray form factors only for structure solution
Structure refinement in ShelXle

- Launch **ShelXle**
- Open ICSD_95391_std.ins  ! H atoms are missing for the atom list
- Update the lattice parameter from TOPAZ neutron experiment *latcon.out*
- Add NEUT before SFAC
- Place HKLF 2 before END of ins file

TITL Scolecite from Neutron TOF Laue
REM  Space group Cc
CELL  0.50000  6.5125  18.9371  9.7575  90.0 108.953  90.0
ZERR  4  0.0001  0.0002  0.0001  0.0  0.001  0.0
LATT  -7
SYMM  +X,-Y,1/2+Z
NEUT
SFAC Ca Si Al O H
UNIT 4 12 8 52 24
TEMP  -173
ACTA
MERG 0
SIZE  1.63 1.19 0.62
Locate H atoms from difference Fourier

- Setup for difference Fourier synthesis

  L.S. 5
  FMAP -2
  PLAN 10
  BOND $H
  CONF
  LIST 6
  ACTA
  HTAB

  WGHT 0.1
  FVAR 0.5

- Save input instruction file as scolecite.ins

- Click XL Refine in ShelXle
Locate H atoms from difference Fourier map

- The first 6 Q peaks with the most negative peak heights are the H atoms for the 3 water molecules in the crystal structure

REM Scolecite from Neutron TOF Laue
REM R1 = 0.1446 for 21745 Fo > 4sig(Fo) and 0.1543 for all 23654 data
REM 77 parameters refined using 2 restraints
END

WGHT 0.1707 239.1128

REM No hydrogen bonds found for HTAB generation
REM Highest difference peak 9.030, deepest hole-22.594, 1-sigma level 1.017
Q1 1 0.4010 0.2553 0.0862 11.00000 0.05 -22.59
Q2 1 0.0359 0.4686 0.1321 11.00000 0.05 -22.34
Q3 1 0.4185 0.1585 0.8687 11.00000 0.05 -21.48
Q4 1 0.2968 0.3112 -0.0431 11.00000 0.05 -19.53
Q5 1 0.3322 0.1998 0.7263 11.00000 0.05 -19.04
Q6 1 -0.0119 0.3949 0.0600 11.00000 0.05 -18.38
Q7 1 0.0555 0.4335 0.1138 11.00000 0.05 -5.34
Q8 1 0.1414 0.4101 0.1280 11.00000 0.05 -5.26
Q9 1 0.3364 0.1783 0.8003 11.00000 0.05 -4.57
Q10 1 0.4245 0.2057 0.2104 11.00000 0.05 -4.36
Refine H positions

- Change Q 1 to 6 to hydrogen atoms
- Use Unique in Shelxle to bring the water molecules near Ca

H5  5  -0.103388  0.755400  0.085831  11.00000  0.02144
H3  5   0.034655  0.468647  0.131058  11.00000  0.02190
H1  5  -0.083772  0.658561  -0.130082  11.00000  0.02226
H6  5  -0.207767  0.809191  -0.043109  11.00000  0.02787
H2  5  -0.172161  0.700047  -0.273411  11.00000  0.02721
H4  5  -0.012793  0.394421   0.060589  11.00000  0.02690
HKLF 2

REM  Scolecite from Neutron TOF Laue
REM  R1 = 0.0876 for 21745 Fo > 4sig(Fo) and 0.0960 for all 23654 data
REM  101 parameters refined using 2 restraints
Refine scale factors for TOF Laue data

• Apply SUMP and BASF in refinement

SUMP 38.0 0.001 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 =
1 16 1 17 1 18 1 19 1 20 1 21 1 22 1 23 1 24 1 25 1 26 1 27 1 28 1 29 =
1 30 1 32 1 33 1 34 1 35 1 36 1 37 1 38 1 39

BASF 1 1 1 1 1 1 1 1 1 1
BASF 1 1 1 1 1 1 1 1 1 1
BASF 1 1 1 1 1 1 1 1 1 1
BASF 1 1 1 1 1 1 1 1 1 1
Refine extinction coefficient

- Apply EXTI

SUMP 38.0 0.001 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 =
1 16 1 17 1 18 1 19 1 20 1 21 1 22 1 23 1 24 1 25 1 26 1 27 1 28 1 29 =
1 30 1 32 1 33 1 34 1 35 1 36 1 37 1 38 1 39

WGHT 0.100000
BASF 0.99143 1.15869 1.10400 0.93727 1.10778 0.92781 0.95867
BASF 1.07476 1.13240 1.14795 1.12599 0.85335 1.16327 0.96090
BASF 0.88745 0.82943 0.86730 1.10580 0.85269 1.08825 0.99675
BASF 0.82155 1.22637 1.24223 0.92484 1.07557 1.11123 1.00243
BASF 1.16305 1.05114 0.92820 1.18664 0.88681 1.13989 1.16102
BASF 0.85764 0.97949 1.01975
EXTI 0.1
FVAR 0.17405

REM Scolecite from Neutron TOF Laue
REM R1 = 0.0706 for 21745 Fo > 4sig(Fo) and 0.0793 for all 23654 data
REM 139 parameters refined using 3 restraints

END
WGHT 0.0803 28.0119
Refine all parameters

• Apply ANIS to all atoms, including H atoms

WGHT     0.0241   38.0936
EXTI     0.006207

ANIS

REM Scolecite from Neutron TOF Laue
REM R1 = 0.0405 for 21745 Fo > 4sig(Fo) and 0.0481 for all 23654 data
REM 265 parameters refined using 3 restraints

• Update WGHT

END

• Update HTAB

WGHT     0.0049   0.0000

REM Instructions for potential hydrogen bonds
EQIV $1 x+1/2, -y+1/2, z+1/2
HTAB O13 O10_$1
EQIV $2 x, -y+1, z+1/2
HTAB O12 O4_$2
HTAB O12 O7
EQIV $3 x-1, y, z
HTAB O12 O8_$3
Refine until WGHT converges

R1 = 0.0404 for 21745 Fo > 4sig(Fo) and 0.0481 for all 23654 data
wR2 = 0.0849, GooF = S = 1.011, Restrained GooF = 1.011 for all data
0 atoms may be split and 0 atoms NPD
R1 = 0.0251 for 4751 unique reflections after merging for Fourier
Highest peak 0.72 at 0.4676 0.7588 0.0843 [0.96 A from O1]
Deepest hole -0.89 at 0.4856 0.3772 0.4700 [0.54 A from O3]

+ scolecite finished at 12:07:54 Total elapsed time: 3.62 secs +

Converged: Yes after 4 runs.

WGHT
WGHT
Converged: Yes
after 4 runs.

WGHT
Converged: Yes
after 4 runs.
Data CIF

Neutron Time-of-Laue example

TOPAZ data

Measured in neutron time-of-flight Laue that uses a band width chopper to select a range of neutrons for data collection.

Scattered neutrons from single crystal sample are detected in event mode using an $^6$Li-glass neutron detector with fast readout time (<1 μSecond).


Prepare CIF for publication

• Change LIST from 6 to 4 to write fcf IUCr check cif
• Refine the following instructions included
  ACTA
  LIST 4
• Merge data cif with cif from SHELXL refinement
Tutorial Sample No. 2

- Structure of hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$
  - Heavy elements with very high X-ray absorption $\mu = 526.82 \text{ cm}^{-1}$
  - Transparent to neutrons $\mu = 0.654 + 0.508\lambda \text{ cm}^{-1}$
- Tetragonal phase at 295 K
- Space group $I4/mcm$
- Twinned due to tetragonal distortion
- Disordered $\text{CH}_3\text{NH}_3^+$
- Apply enhanced rigid bond restraints
  **RIGU**
- Combine with riding model for H
  **AFIX** 137
  Improve the model without adding additional parameters

Tutorial Sample No. 2

- **CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} (MAPbI\textsubscript{3})**

- **Aims of the neutron experiment**: Solve and refine the position of CH\textsubscript{3}NH\textsubscript{3} cation in MAPbI\textsubscript{3}.

- Copy the neutron dataset in shared subfolder to your work directory
  
  `\Tutorial\MAPbI3\exercise`
  
  - **i4mcm.hkl** TOPAZ neutron data set saved in HKLF 2 format

- **X-ray CIF from ICSD**
  
  - **CSD_MAPBTI05.cif**
  
  - Convert the X-ray .cif to SHELXL .ins
    
    Update the lattice parameter for the neutron experiment
    
    ```
    CELL 0.6000 8.8796 8.8796 12.6266 90.0 90.0 90.0
    ZERR 4 0.0006 0.0006 0.0018 0.0 0.0 0.0
    ```

- Proceed following the steps for the refinement of scolecite structure
Modeling of disordered neutron structures

Disordered model for CH$_3$NH$_3^+$ in MAPbI$_3$

REM N atom in MA at Wyckoff site 16 I

SUMP 0.5 0.0001 1 2 1 3
REM rigid bond restraints on MA

RIGU N1 > H2C


FVAR 0.42848 0.06819 0.43180
N1 3 21.000000 31.000000 0.285842 10.12500 0.07436 0.08261 =
 0.09761 -0.00316 0.00406 0.00627

AFIX 137
H1A 2 0.172347 0.467410 0.311569 10.12500 0.08308 0.10802 =
 0.12138 -0.00718 -0.00252 0.06619
H1B 2 0.080849 0.338705 0.238002 10.12500 0.08766 0.09184 =
 0.10971 -0.00971 0.00605 0.01300
H1C 2 0.002437 0.404188 0.350178 10.12500 0.09789 0.10033 =
 0.10382 -0.00405 0.01065 -0.00158

AFIX 0
C2 1 -0.004495 0.552932 0.225745 10.12500 0.06675 0.08960 =
 0.09151 -0.00431 0.00867 0.00880

AFIX 137
H2A 2 -0.026886 0.644979 0.276828 10.12500 0.09120 0.09524 =
 0.08942 -0.00511 -0.00343 0.02156
H2B 2 -0.106990 0.512969 0.193152 10.12500 0.06822 0.12527 =
 0.08125 -0.01130 0.01633 0.00454
H2C 2 0.067838 0.588431 0.163803 10.12500 0.08004 0.09576 =
 0.10115 0.00293 0.01835 0.01506

AFIX 0

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SHELX

The SHELX homepage http://shelx.uni-ac.gwdg.de/SHELX


Neutron time-of-flight laue single crystal diffraction

TOPAZ Single-Crystal Diffractometer at ORNL https://neutrons.ornl.gov/topaz

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The ORNL Spallation Neutron Source