MGSTR 2022
Magnetic Structure Determination from Neutron Diffraction Data, ORNL

The following document is laid out in 2 sections. The first goes through the Windows version of SARAh and SARAh Refine. These are legacy codes and are no longer being developed. They can still prove useful, however, such as when searching for a k-vector or when using GSAS and Topas. SARAh-Refine with GSAS-1 is still a very effective way of analysing commensurate systems.

The second section introduces some aspects of SARAh-webRefine for FullProf. Do try the examples from Section 1 using the web interface!
-ASW 2022

1. SARAh and FullProf:

Technicalities:

- I am assuming that you are using the Windows version of SARAh and Sarah Refine that is available at: `http://fermat.chem.ucl.ac.uk/spaces/willsgroup/software/`
    - SARAh is installed in the default location of `C:\Program Files (x86)`
    - FullProf is installed at the default location of `C:\FullProf_Suite`
- Make shortcuts to SARAh-Rep Analysis and SARAh-Refine on the desktop.
- Make a shortcut to Notepad (or your favourite text editor) on the desktop.
- To run SARAh-Rep Analysis – Right click on the icon and select "Run as administrator", then 'Yes". (This is needed so that SARAh is allowed to write files to your hard drive. If no files are created, try this.)
- If SARAh doesn't run, try Right clicking and selecting "Troubleshoot compatibility". Windows 10 will run "Detecting issues". When this is finished click <Try recommended settings>, <Test program> (this opens up an instance of SARAh-Rep Analysis), close this instance, and click <Next> to continue in the CompatibilityTroubleshooter. Then click <Yes> to use the default settings, and <Close>
- It is helpful for you to associate files with the extension .fst with FullProf Studio (FPStudio). To do this, right click on the fst file, select "Open with…", the blue "More apps🡻", go to the bottom of the list and click "Look for another app on this PC", select to "`C:\FullProf_Suite\fp_studio2k.exe`" and click Open.
- Make a shortcut to `Notepad` (or your preferred editor for text files) on your desktop. We are going to do all of our text editing manually rather than use EdPcr within FullProf.
- Copy over the tutorial folder `2020MagStr` to `C:\`
- For these exercises the files are in `C:\2020MagStr\FullProf`
- The website for webSARAh is in the menu `Web Software` of http://fermat.chem.ucl.ac.uk/spaces/willsgroup/
- The walk through for Bertaut's method is at the bottom of the menu `Documents/Papers` of http://fermat.chem.ucl.ac.uk/spaces/willsgroup/

- (Funding for software development is not easy to get in the UK. The website runs on my desktop computer rather than a fast server, please be patient :-)

Let's start with some example calculations using representation theory

1. $LaMnO_3$: Space group : #62, Pnma : k = 0 0 0 : Mn @ 0 0 0.5
2. $Er_2Ti_2O_7$: Space group #227 Fd-3m : k = 0 0 0 : Er @ 0 0 0
3. $Gd_2Ti_2O_7$: Space group #227 Fd-3m : k = 0.5 0.5 0.5 : Gd @ 0 0 0

Use the web version of SARAh to perform the symmetry calculations.

Find the

- Different propagation vectors in the 1st Brillouin zone
- The match between the propagation vector and the description within the Brillouin zone that was used by Kovalev
- The star of the propagation vector – these are the k vectors that are related to that of your input by the symmetry operations of the space group.
    - These make a particular type of multi-k structures, that based on (symmetry) related or 'conjugate' k-vectors
- The positions related by the rotational/translational operations of your space group (the equivalent positions of the Wyckoff site).
    - Are all these positions generated by the operations of Gk? If not SARAh will add new ones for you automatically. If *n* is the number of the equivalent positions, 3*n* will be the number of basis vectors
- The IRs themselves.
    - Note the number, the dimension of the matrices, whether the numbers are real/imaginary/complex
- The epikernels (isotropy subgroups) for IRs with dimension >1, their stationary vector (we are not using Landau yet, so it is not an order parameter), their magnetic point group (made from normal and primed operations).
    - Look for symmetries common to different IRs.
- The decomposition of the magnetic representation.
    - The number in front of the Gamma is the number of times the IR repetition is repeated.
    - The number of basis vectors for an IR will be the repetition times by the order of the IR
    - Do the different input atoms share IRs?
        - If yes, they may order at the same transition
        - If no, they may[1] order at different transitions
- The basis vectors — as projected and combined into epikernel groups
    - Look at how the structures in different IRs are orthogonal (IRs are orthogonal symmetries) and how all the possibilities are separated and distributed across the IRs.
    - Are the components on different atom of the same magnitude?

[1] *'may' depends on the details of the Landau free energy expansion, such as how high the powers of the order parameter goes.*

  - Convince yourself that all the basis vectors add together to describe all possible structures
- Finally, look in the tables below for more useful information.

Now we will move to a simple refinement using SARAh with FullProf

The problem is in the directory `AgFe`
We are going to use a working directory for refinements to keep our files tidy.

- Copy the files from `C:\2020MagStr\FullProf\AgFe` to `2020MagStr\working`
- Set `2020MagStr\working` as your working directory
- In the `working` directory open `46048a.pcr` with Notepad
- We will use FullProf simply, with WinPLOTR and the buttons <Pcr> and <FP>

You will find a simple refinement of a nuclear phase, with no magnetism and no refined parameters turned on. Run FP and look at the refinement graph to see the missing intensity for the magnetic phase. Look at the pcr file, to see the atoms in the nuclear structure.

There is one magnetic atom :

```
Fe1  FE      0.50000  0.50000 0.50000  0.46104   0.42753   0   0   0    0
```

This is an Fe3+ at 0.5 0.5 0.5. The space group is 166, R-3m in the hexagonal setting, and the k vector is (0 0 1.5). *(Does this k vector component sound odd to you?)*

We need to put this information into SARAh Representational Analysis.

- Put this information into SARAh (opening it as Administrator), and Run. Reading any pop-ups and pressing <OK> as the default.
- The last step, "Identify Shubnikov space groups" is very slow (and targeted for removal :-). Please be patient.
- The files will be made in the SARAh install directory and have the name format sarah***.list1, where *** is the number of the space group in the International Tables
- The following files are made
  - lst1 – gives the details of the calculations of the IRs using Kovalev's tables and Karep. This also shows the different k-vectors in the Brillouin zone and the star of the propagation vector. All k vectors are turned into the setting of the crystal structure that the user selected.
  - list2 – takes the selected IRs (irreducible representations) and projects the basis vectors. You will see the permutation tables, axial vector representation, etc
  - mat – the file for SARAh Refine
  - tex – a useful summary file with formatted tables in LaTeX

- _summary.txt – the information that my group felt was the most important

Look through the lst1 file to see how information is pulled together to get the IRs

Copy the files that SARAh made from `C:\Program Files (x86)\SARAh\`
- to `2020MagStr\working`
- Open in notepad `46048a.pcr`

Launch SARAh-Refine (as admininstrator)
- Click <FullProf Controls>
- Select the file that you copied `2020MagStr\working\sarah166.mat`
- Select **one** basis vector on the left, and on the right click '1) Generate model PCR phase', with 'powder' selected.

In the working directory you will have made `sarah166.pcr`. Open it in Notepad. You will find a template for a basic magnetic phase – remembering that SARAh doesn't know anything about lattice parameters, profile, scale, etc.

Now edit the refinement pcr to introduce the magnetic phase:
- Make a copy of `46048a.pcr` as a backup in case something goes wrong
- Open `46048a.pcr` in Notepad as well.

- Above:

```
!   2Th1/TOF1     2Th2/TOF2   Pattern # 1
        9.030       88.830        1
```

- Press <Return> to make some empty lines:

```
!-------> Profile Parameters for Pattern #  1
!  Scale         Shape1       Bov       Str1       Str2       Str3    Strain-Model
  4.5661        0.24180    1.03890    0.00000    0.00000    0.00000        0
     0.00000      0.000      0.000      0.000      0.000      0.000
!       U          V           W           X           Y         GauSiz    LorSiz Size-
Model
   1.419960  -0.715270   0.229350  -0.003480   0.000000   0.000000   0.000000     0
      0.000      0.000      0.000      0.000      0.000      0.000      0.000
!     a           b           c         alpha       beta       gamma       #Cell Info
   7.350883   7.350883  16.509501  90.000000  90.000000 120.000000
    0.00000    0.00000    0.00000    0.00000    0.00000    0.00000
!  Pref1     Pref2       Asy1      Asy2      Asy3      Asy4
  0.00000   0.00000   0.00000   0.00000   0.00000   0.00000
     0.00      0.00      0.00      0.00      0.00      0.00


!  2Th1/TOF1     2Th2/TOF2   Pattern # 1
       9.030       88.830        1
```

- Into this space paste the entire text from `sarah166.pcr`

- In the nuclear phase, copy everything from:

```
!  Scale         Shape1       Bov       Str1       Str2       Str3    Strain-Model
```

up to the line before the first:

```
!-----------------------------------------------------------------------
```

and replace the corresponding text in phase 2.

- Delete any empty lines that you have before:

```
!  2Th1/TOF1    2Th2/TOF2  Pattern # 1
       9.030      88.830       1
```

We need to give the refinement some intensity to try

- Remember that you have only 1 basis vector
- So set the value of C1 to 1.00 and the refinement parameter to 11.00

```
!Atom   Typ  Mag Vek    X       Y       Z       Biso    Occ      C1      C2      C3
!     C4     C5     C6      C7      C8      C9      MagPh
FE1    MFE3  1  0  0.50000 0.50000 0.50000 0.30000  1.00000    1.0    0.000   0.000
                      0.00    0.00    0.00    0.00     0.00   11.00    0.00    0.00
```

- At the top of the pcr file, tell FullProf that you have 2 phases. In the line:

```
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   5   1   0   1   0   0   1   0   0   1   0   0   0   0   0   0   0   1
```

- Change the phase NPh from 1 to 2.

- Save and close the pcr file.

As there is only 1 refined parameter, the refinement should converge. Let's check that everything works before looking at the details of the format for the magnetic structure

- Launch FP
- Click Pcr to edit the pcr. Look at the basis vectors

```
! Real(0)-Imaginary(1) indicator for Ci
  0  0
!
SYMM X, Y, Z
BASR        2       -2        0
BASI        0        0        0
SYMM -Y+1, X-Y, Z
BASR        2        4        0
BASI        0        0        0
SYMM -X+Y, -X+1, Z
BASR       -4       -2        0
BASI        0        0        0
```

The number 0 below '`! Real`' means that the coefficients are real numbers.

The lines `BASR` and `BASI` are the moment components along the a,b,c directions. `SYMM` is the symmetry operator that is applied to the position of the moment-bearing ion to generate the symmetry related position. For example `SYMM X, Y, Z` is the identity operation and generates the position given in the main part of the phase 2. The `BASR` and `BASI` are the components of the basis vector for that position.

- The components for all the atoms generated by the symmetry operations define the complete basis vector.

For the position generated by the symmetry operator above.

- Further below, as the pcr is updated during the refinement, the refined value of the mixing coefficient can be found

We have one BV selected. Let's try changing it:

- In SARAh-Refine uncheck the selected BV, and check the second BV
- Now in the box labelled "2)" click <Select PCR> and select `46084a.pcr`
- Click <Edit File> and select the magnetic phase. <OK>

- Reopen the pcr file with the Pcr button of WinPLOTR
- You will see the BV has changed and the structure is one with the moments along the c-axis

Only the BV relevant lines were changed. So, the atom and the settings for the mixing coefficients are unchanged. In this way, you have complete control of all of the other parameters and possibilities within FullProf.

We can rerun FP and see that the single BV2 cannot fit the data.

In a similar way we can insert different BVs for an IR.

- Whichever basis vectors you select will be inserted into `46084a.pcr` . You are NOT limited to those of a single IR of Gk. The choice is yours and for your refinement strategy, such as how far you push the order of the order parameter within Landau theory.
- *If you change the number of BVs in the pcr, ensure that you to change the number of refined mixing coefficients and set to zero any coefficient parameters that you have turned off.*

FAQ. What do I do if I don't know the wave vector? Where do I start?

A. You can start by using k-search in FP to help you find it. For more challenging cases (weak data, few peaks, etc) I use <k-Vector Search> in the SARAh-Refine FullProf menu.

It runs using reverse Monte Carlo refinements of model that uses no symmetry except that of the k vector that is being tested. For each k-vector the moments (using polar notation) are freely refined, and so it tests thoroughly whether that k vector is able to fit model the data. SARAh_Refine knows the Brillouin zone and can move through the points, lines and planes of symmetry as you need.

Refinements can be run automatically in batches so I suggest that you go for a coffee/lunch and come back. As it uses the full profile it is slow, but you have full control over FullProf parameters and you are able to extract the maximum information from the data.

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2. SARAh-webRefine for FullProf:

This section provides a quick overview of the technical side of SARAh-webRefine. You are encouraged to use it with the example information above.

Technicalities:

Your bowser needs to be set up to allow you to chose a location to save the generated file and to allow a pcr file to be overwritten (edited). Below is some information from the SARAh-webRefine.

Most browsers have a default directory where they save files. SARAh-webRefine works best if you can select the location for each download. This will enable you to save the template magnetic phase .pcr file to your current refinement directory or to edit a file by replacing it. If you use more than one browser, perhaps for compatibility or as part of your internet security, it may be easiest to have one set to using a default folder and another that asks each time for the download location.

Below are some settings for common browsers that turn on 'Ask where to save each file before downloading':

Google Chrome : 1) Click the menu icon (aka 3 dots) in the upper right corner of the Chrome window. 2) Select 'Settings'. 3) Scroll down and click 'Show Advanced Settings'. 4) Scroll down to the 'Downloads' section and click 'Ask where to save each file before downloading'

Firefox - Mac: 1) Select 'Firefox' → 'Preferences' from the menu bar. 2) In the General panel scroll down to 'Files and Applications'. 3) In Downloads select 'Always ask where to save files'

Firefox - Windows 11: 1) Click the menu button (the 3 line burger button) and select 'Settings'. 2) In the General panel scroll down to 'Files and Applications'. 3) In Downloads select 'Always ask where to save files'

Safari - Mac: 1) Select 'Safari' → 'Preferences' from the menu bar. 2) In the General tab, click the dropdown menu next to 'File download location'. 3) Select 'Ask for Each Download'

Edge - Windows 11: 1) Go to 'Settings' → 'Downloads'. 2) Where it says 'Ask me what to do with each download', turn the slider to the ON position'

Automatically making and inserting a magnetic phase
SARAh-webRefine uses the last phase in the pcr file to provide templating information for lattice constants, profile etc. For ease, this should match the magnetic basis vector phase that is being inserted. Not everything is straight forward to set up because of the flexibilities within the pcr format. In particular, references to the propagation vector and the oxidation state of the magnetic ions (used to define the magnetic form factor) should be checked.

Editing a pcr file
SARAh-webRefine identifies the phase for editing from the propagation vector, the Jbt value and the atomic coordinates. To be recognised correctly, the magnetic phase should have the **same coordinates** as the SARAh calculations. For ease, you can copy the atom and coordinates directly from the .pcr file into SARAh-webRefine page that gives the input for the symmetry calculations.

Suggested refinement strategy (ASW version Feb 2022 :-)

- 1. Go through irreps in turn to see which put magnetic intensity at the experimentally observed positions. Irreps can have systematic absences
- 2. Within a chosen irrep, explore first the epikernels (and stationary vectors) that have the highest number of symmetry operations and the smallest number of BVs. This strategy comes from Asher [E Ascher and J Kobayashi 1977 J. Phys. C: Solid State Phys. 10 13], who postulated that an epikernel with the highest symmetry is more likely to result from a phase transition. This preference for the maximal group of the irreducible representation corresponds to the epikernel with the highest number of symmetry operations. More recently the Bilbao group have described maximal subgroups of the paramagnetic grey group for a single propagation vector as 'k-maximal' and these will have a mapping onto the highest symmetry epikernels of the irreps of G_k that are used here
- 3. Increase complexity as needed by then testing epikernels, and stationary vectors, that involve fewer symmetry operations and more basis vectors. Non-maximal groups do occur, but are markedly less common
- 4. Coupling irreps - part 1. For low-spin orbit coupling atoms, start with those within an exchange multiplet. Exchange multiplets were originally developed by Izyumov [Yu.A. Izyumov 1980 J. Magn. Magn. Mater. 15-18 497-498]
- 5. Coupling irreps - part 2. The same epikernels (defined here as black and white point groups) can occur in different irreps. These are expected to couple with one irrep (primary) driving the transition and others (secondary) induced by it to contribute. The latter may order more slowly with reducing temperature
- 6. Coupling irreps - part 3. Irreps related by antiunitary symmetry (e.g. complex conjugation or time-reversal) can join to make an irreducible corepresentation [E.P. Wigner 1959 'Group theory and its application to atomic spectra', Academic Press, New York and London]. This is the more complete symmetry description and can be expressed simply for single-k structures in terms of irreps of G_k
- 7. Coupling irreps - part 4. As well as the above, irreps of G_k can couple if there are suitable energy terms in the Landau energy expansion. This analysis requires working with the irreducible corepresentations of the space group G and exploring the energy polynomial to a given level of approximation. Within this framework the use of epikernels and kernel symmetries still applies. (If you end up here, I suggest that you consult an expert...)