

RMCPow PRACTICAL

Modelling the magnetic structure of Ba_2FeWO_6

Files needed are found in the same zip file as this instruction. Copy or extract the files into a suitable directory and follow the instructions below. The different programs used can be accessed with the shell program called **WinNFLP**, available at ftp://ftp.studsvik.uu.se/Pub/WinNFLP/Win_NT/. To run, click on the WinNFLP icon, a browser window will then appear. Select your working directory by clicking on a file in that directory (any will do). Now you can access the programs you want to run from the menus **Useful** or **RMC**. If you do not have the WinNFLP program it is still possible to run the RMCPow simulations since all necessary input files are provided here.

The general approach of the practical is as follows:

- The average magnetic structure of Ba_2FeWO_6 in the long-range ordered antiferromagnetic phase at 15 K will be determined starting from a random configuration.

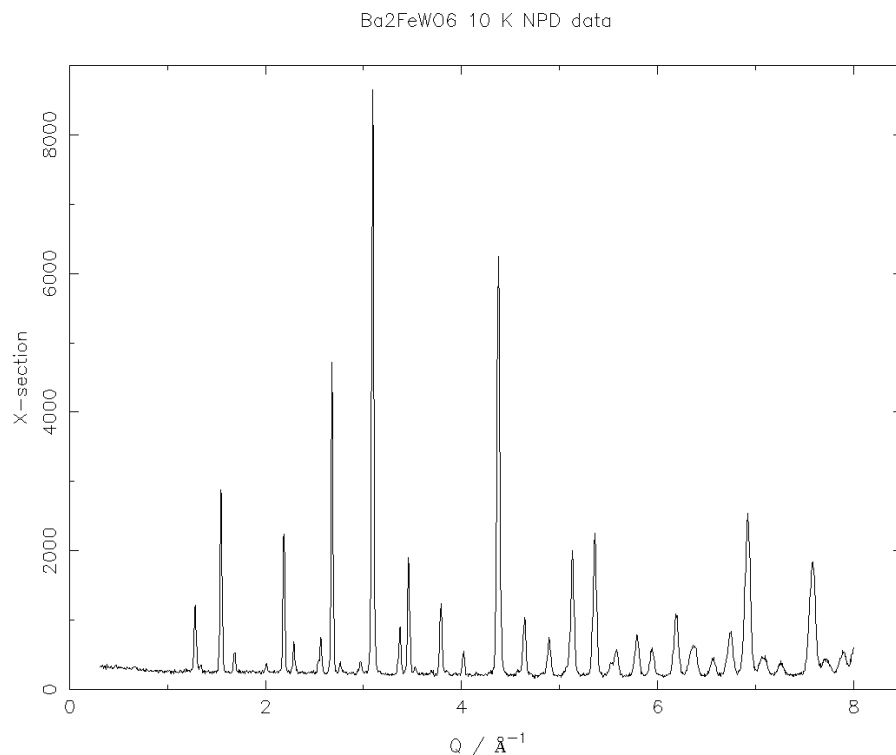
The times given in this practical, for running RMCPow is real time and NOT CPU time. The times may have to be increased on a slow computer. The output you get, will probably not be identical to the output in this example. The plotting and programs used in this practical can also be done with in principle any standard plotting program, such as Origin or SigmaPlot, since most data is easily imported as ASCII files.

1. Ba_2FeWO_6 is a double perovskite system with an ordered arrangement of Fe and W atoms. The structure is derived from the simple perovskite ABO_3 order with Ba occupying the A sites and Fe and W alternating along the (simple perovskite) cube edges on the B sites. At ambient temperature there is no long-range magnetic structure and the positions can be refined with the $I4/m$ space group. Below $T_N = 20$ K the atomic structure is still $I4/m$ but new Bragg peaks appear in the neutron diffractogram signalling onset of some antiferromagnetic ordering. From the location of the new peaks it is clear that the magnetic unit cell is doubled along one or more of the nuclear unit cell edges. In this practical we will use RMCPOW to find the size of the magnetic unit cell and the arrangement of spins. The model will be based on the neutron scattering data obtained at 10 K on the Neutron Powder Diffractometer NPD in Studsvik. The data is in the file `bafewo.fq`. Plot it with the program FqPlot. Useful \rightarrow User programs \rightarrow FqPlot.exe and type:

```
Filename [.fq] > bafewo.fq
bafewo.fq
Format? G(ENIE)/T(EXT)/D(ATA) > d
Graphics device/type (? to see list, default/W9):<RETURN>
```

Now you should have a plot on the screen. To plot with other limits select the FqPlot text input window and type

```
Change limits? [T/F] > t
Data limits are           : .020 10.300   .000 10.558
Current plotting limits are : .000 12.000  -.528 11.086
New limits > 0 10 0 11
```



To exit type

```
Change limits? [T/F] > f
Hardcopy output? [T/F] > f
Type <RETURN> to close graphics window # 1 <RETURN>
```

or if you first want a hardcopy output (e.g. a GIF file) type

```
Hardcopy output? [T/F] > t
Graphics device/type (? to see list, default/W9):name/gif
Output to name
```

where name will be the GIF filename.

2. We are now going to make a first attempt to determine the long-range magnetic order. We need to set up a configuration of atomic positions and another configuration with spin unit vectors. The atomic configuration will be made using the input file **bafewo.atom**:

```
.false.                ! apply to existing configuration?
87 1                   ! I4/m ispg,isetting
5.74528 5.74528 8.10935 90. 90. ! a1,a2,a3,g1,g2,g3
 1 2 2 2              ! isym,n1,n2,n3
n                      ! no displacements
4                      ! No. of atom types
 1                    ! No. of Fe Wyckoff sites
2b 0.0      0.0      0.5 ! Wyckoff site,x,y,z
 1                    ! No. of Ba Wyckoff sites
4d 0.0      0.5      0.25 ! Wyckoff site,x,y,z
 1                    ! No. of W Wyckoff sites
2a 0.0      0.0      0.0 ! Wyckoff site,x,y,z
 2                    ! No. of O Wyckoff sites
4e 0.0      0.0      0.24067 ! Wyckoff site,x,y,z
8h 0.23561 0.23634 0.0 ! Wyckoff site,x,y,z
.true.                ! Output in RMC coordinates
```

The lattice parameters (a1-a3,g1-g3) and atom positions have been obtained by a Rietveld refinement to the same data using only the high Q part (with negligible magnetic contribution). Create the configuration by running **Useful → CFG programs → Crystal.exe** with **bafewo.atom** as input and **bafewo.cfg** as output. This will set up a model consisting of 2×2×2 I4/m unit cells. Next we make a random spin configuration with **Useful → CFG programs → RandomSpins.exe**. There is only one type of magnetic atoms (Fe) and there should be 16 of them in the configuration. Give **bafewo.scfg** as output.

3. For running the RMCPOW simulation we also need the control file **bafewo.dat**:

```
Ba2FeWO6 I4/m
0 0                   ! ncoll,ncycles
100 0 5 5            ! iprint,iplot,timelim,timesav
5.74528 5.74528 8.10935 90. 90. 90. ! a1,a2,a3,g1,g2,g3
0 0 0 0 0 0          ! lattice parameters flags
1 2 2 2              ! isym,n1,n2,n3
```

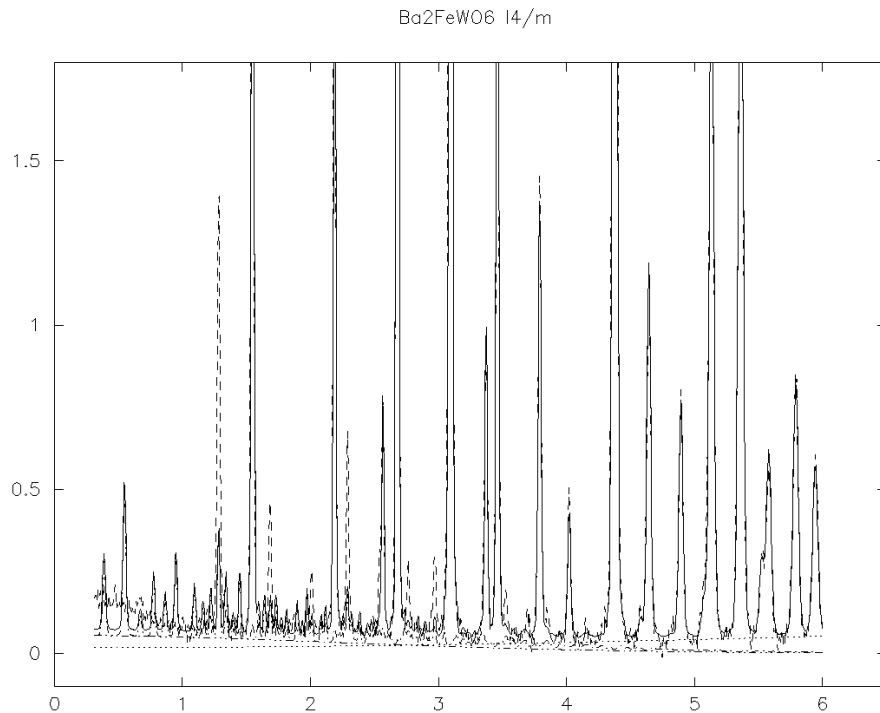
```

4 1          ! ntypes, ntypesm
1           ! attypes
0. 0. 0. 0. ! delta
40.0        ! deltam
0 0.0       ! nswap, swapfrac
0 0.0       ! nref, reffrac
1.0 1.0 1.0 1.0
      1.0 1.0 1.0
            1.0 1.0
                  1.0      ! rcut
0           ! ncoord
0           ! navc
0           ! nval
0           ! naval
0           ! navm
0           ! nsc
0           ! nasc
0           ! nmpot
1 0 0       ! nexpn, nexpx, nsx
5.0 0.2     ! rwdt, swdt
2 0         ! ijob, iexist
0.0015 0.0015 0.0015 0.004      ! msd's
      0      0      0      0      ! msd flags
3.5         ! muz
0           ! flag
bafewo.fq
1.0 6.0     ! Qmin, qmax
0           ! nexcl  2.62 2.72 3.03 3.20
2 0.5       ! isign, sigman
2 0         ! nbpol, nbfix
200. 0.0 1 1 ! alpha0, flag
600. 1      ! beta, flag
1.47 1.0    ! wave, qwmax
1.43278 -0.73675 0.17372 0.0 0.15 ! U,V,W,IG,eta
      0      0      0      0      ! resolution flags
0           ! wextn
1           ! Fe noccn
Fe 1.0      ! coccn, bcoh, siginc
1           ! Ba noccn
Ba 1.0      ! coccn, bcoh, siginc
1           ! W noccn
W 1.0       ! coccn, bcoh, siginc
1           ! O1/O2 noccn
O 1.0       ! coccn, bcoh, siginc
6.0         ! Q2m
1           ! noccn
1.0 4.9     ! magsym, coccn, mueff
0.3972 13.2442 0.6295 4.9034 -0.0314 0.3496 0.0 0.0
0.0044      ! form factor parameters

```

Note that atomic positions are kept fixed, parameters delta are 0, whereas spins can maximally be moved 40° , parameter `deltam`. The simulation is run with the `ijob=2` option. This means that we will add diffuse scattering based on analytic approximations, see the RMCPOW manual, using the mean square displacements, parameters `msd` [\AA^2], and the ordered spin component, parameter `muz` [μ_B]. The NPD data used here is not really suitable for fitting also the diffuse scattering because no background subtraction or multiple scattering corrections etc. have been performed. Since we are going to model the long-range order only, and there doesn't appear to be any major features in the diffuse scattering it is not crucial in this case (though it can be for other data). Parameters `msd`, `mueff` and `muz` needs some further explanation. The `msd` parameters are chosen according to the Rietveld results for the high Q data. Since Fe is presumed to be divalent in this case (Ba is 2+ and W is 4+) it is in a $3d^4$ state. The spin only total magnetic moment is then $g\sqrt{S(S+1)} = 4.9$ with $S = 4/2$ and we use this value for `mueff`. The maximum ordered component is $gS = 4$ which is what we expect for fully ordered spins at $T = 0$ K. Here we are almost halfway to the critical temperature so we use a somewhat reduced value, 3.5.

Now start the RMCPOW program: **RMC → RMC programs → RMCPOW.exe** and give **bafewo.dat** as input file. The simulation should converge within the 5 minutes specified in the control file. You should obtain a $\chi^2 \sim 8.6$. If necessary continue the simulation by simply restarting RMCPOW. Look at the fit with the RMCPlot program: **Useful → Plot programs → RMCPlot.exe** and give **bafewo.out** as the file to plot. In the plot you will find the experimental and RMCPOW fit curves as well as various contributions to the RMCPOW fit. The fit should be quite good. Compare this to a plot of the RMCPOW output for a random spin configuration, change `timelim` to 0 to just save the initial configuration. An example for a random spin configuration is shown below.



4. We will now use ConfPlot to visualize the magnetic order: **Useful → Plot programs → ConfPlot.exe** and at the ConfPlot prompt type

```
> open bafewo.cfg
Reading file: bafewo.cfg
Configuration contains 160 atoms of 5 types.
> spin bafewo.scfg
Reading file: bafewo.scfg
Configuration contains 16 spins of 1 types.
> spl
Warning: Atom type 2 contains different number of atoms
and spins
Warning: Atom type 3 contains different number of atoms
and spins
Warning: Atom type 4 contains different number of atoms
and spins
Warning: Atom type 5 contains different number of atoms
and spins
Configuration: bafewo.cfg
Spin config. : bafewo.scfg
PLEASE WAIT...
Type: 1
```

The warning messages are just because atom types 2-5 are not magnetic. This first plot will be along the c (001) direction. Use the **dir** command to plot the configuration along a and b also to determine if the magnetic cell is doubled along all edges. We can also use the dot command to tell ConfPlot to colour code the spins from red to blue depending on their projection on the chosen direction. Use this to try to find out if there is some unique axis along which spins are ordered

5. At this stage you have probably obtained an ordered but non-colinear model. If the simulation is repeated, starting from a new random spin configuration, we will probably get a similar result but with pairs of spins in other directions. Obviously the quality of the data is not good enough to permit distinction between various non-colinear solutions. We will now see if we can narrow down the possible solutions by restricting spins to be co-linear. To facilitate this we use, in addition to fit the data, a series of constraints to exclude the possibility of spin pairs with non-colinear arrangement. We turn this on by setting the number of spin co-ordination constraints, parameter `nsc` in the control file, to 3. Directly after the `nsc` line we introduce new lines:

```
1 1 0.0 7.0 1 18 -.5 .5 0.0 0.0001
1 1 0.0 7.0 1 18 -.7 .7 0.0 0.001
1 1 0.0 7.0 1 18 -.9 .9 0.0 0.01
```

```
! Parameters are:
! sctypes, sctypen, rsc, scno, cthsc, scfrac, sigmasc
```

The first line will put a penalty on having `scno` = 1 to 18 spin neighbours of `sctypen` = 1 (i.e. Fe), with a spin-spin cosine `cthsc` = -0.5 to 0.5, within `rsc` = 0 to 7 Å separation from spins of `sctypes` = 1. `scfrac` = 0.0 is then the desired fraction of spins with such neighbours. `sigmasc` = 0.0001 is a weighting factor for this constraint and should be of this size in order for the constraint to be effective. The 2nd and 3rd lines are then used to create a gradient towards even more co-linearity. Note that these constraints are weaker than the first. Restart the simulation and run until all three constraints are fulfilled. The current fractions of each constraint can be monitored during the simulation as they are written to new lines in the summary on the screen and in the log file.

The spin configuration should now have all spin almost parallel or anti-parallel. We could go on sharpening the constraint even further but the fraction of accepted moves will then gradually decrease so that simulation takes longer time. At this stage it is probably better to use the information we have obtained as input to a Rietveld refinement. The important thing is that we now have a constrained, co-linear model with about the same agreement with experimental as had the previous, unconstrained, model. In fact there should now be a very well-defined propagation vector and also direction of moments, which are they?

Since these simulations are very fast to converge it is strongly recommended to repeat the runs, and experiment with other conditions. Change for example `deltam` to a small or large angle or play around with the co-linearity constraints!