

Exercises on Ho₂BaCuO₅

Nuclear and Magnetic Structures refinement using symmetry modes and sequential refinements. Use of TOF data with symmetry modes.

Summary of the provided data and known information

1. Powder data collected at ILL on low-resolution diffractometer D1B with $\lambda = 2.524 \text{ \AA}$, between 2K and 32K. The U, V and W parameters are: 1.689, -1.091 and 0.344 approximately.
2. The space group of Ho₂BaCuO₅ is *Pnma*, the cell parameters are $a \approx 12.176 \text{ \AA}$, $b \approx 5.659 \text{ \AA}$ and $c \approx 7.101 \text{ \AA}$ at RT.
3. Two magnetic phase transitions take place: from paramagnetic to ordered state at 17.5K and independent ordering of the Ho³⁺ ions at 8K.
4. Powder data collected at ISIS on WISH at 1.5K as an example of TOF data treatment in a different sample of that collected in D1B.

The initial structural parameters can be obtained from the input CIF file, **Ho2BaCuO5.cif**, located in the tutorial directory. This compound contains three magnetic sites: two Ho³⁺ and one Cu²⁺. Both types of ions are situated at the 4c Wyckoff positions of *Pnma* space group.

In this tutorial, there is a main directory named **Ho2BaCuO5**, which contains there subdirectories: **DyHo_PRB_2021**, **CW** and **TOF**. Additionally, a CIF file is included. This file provides the room-temperature crystal structure of Ho₂BaCuO₅ that can be used as starting point for structural analysis. The **Ho2BaCuO5** directory also contains this document.

For a comprehensive explanation of the symmetry and magnetic structures relevant to this example, refer to Physical Review **B 104**, 144401 (2021). The article and its supplemental material are available in the **DyHo_PRB_2021** subdirectory of this tutorial.

Input files:

The **CW** subdirectory includes data collected at D1B between 2K and 32K, which are stored in the **Data-D1B** subdirectory. The data files in **Data-D1B** are named **hog_nn.dat** (where **nn**=02, 03 ... 62) and follow the format corresponding to the variable **Ins = 3** in the PCR file of FULLPROF. Within the **Sequential-Modes** subdirectory, you will find PCR files designed to initiate the sequential refinements. Additionally, there is a file named **hk12.hkl**, which contains the peaks of the aluminium screens from the cryostat observed in the diffraction patterns. This file must be included as a spurious phase with **Jbt=3** and **Inf=2**. The phase is treated using the space group *Pmmm* and fake cell parameters: $a = 2.126 \text{ \AA}$, $b = 2.150 \text{ \AA}$, $c = 1.000 \text{ \AA}$, and is considered as a background component. An example of TOF refinement using four detector banks of WISH is provided in the **TOF** subdirectory. Here you will also find a complete PCR file ready for execution.

Exercises

In this document, the user is not provided with a systematic step-by-step-guide for completing the tasks. The approach to working through the material is similar to that of other tutorials, so the methods and actions required are familiar to the user. Within the provided directories and subdirectories, the user will find the solutions for the refinements. If the user prefers to start with an already prepared PCR file, it is recommended to make a copy of it first.

To successfully complete these exercises, it is important to read the PRB article and its supplemental information to become familiar with the problem at hand. This tutorial is designed as an extended exercise that can be revisited progressively as the user gains more knowledge and experience.

Begin the exercises by creating a **Testing** subdirectory within the root of the tutorial directory. Copy inside the CIF file containing the structure of $\text{Ho}_2\text{BaCuO}_5$ into this subdirectory. Additionally, copy one of the files from the **Data-D1B** subdirectory that corresponds to a pattern in the paramagnetic state. For example the file **hog_33.dat** corresponds to the temperature $T \approx 19\text{K}$, just above the first ordered state. Copy also the file **hkl2.hkl**, which represents a spurious phase with the characteristics described earlier. The purpose of the **Testing** subdirectory is to determine the propagation vectors of the two magnetic phases.

1: Using the information provided, construct a PCR file from the CIF file. To do this, use EDPCR and modify the created PCR file to include the correct values for the wavelength and profile parameters. Add a second phase using **Jbt=3** and **Irf=2**, and complete it with the values specified earlier. Open the file **hog_33.dat** using WINPLOTR-2006, select points to create a background file, and import this background into the PCR file using EDPCR. Run FULLPROF, varying the scale factor of the two phases (keeping the *c* parameter of the second phase fixed at 1.0) and the zero-shift, for 10 cycles. Run FULLPROF again to refine the cell parameters. Further improve the refinement as needed.

2: Copy the file **hog_18.dat** to the **Testing** directory and save the previous PCR file under a new name (e.g. **hog_18.pcr**). Run FULLPROF with this new PCR file using the data file **hog_18.dat**, fixing structural and background parameters. Re-select background points from the plot of the PRF with WINPLOTR-2006, import the new background, and refine the cell parameters. Identify the prominent magnetic reflections from the new plot and save them for running K-SEARCH.

3: Run K-SEARCH, which will determine that the propagation vector. The result is $\mathbf{k}=(0,1/2,0)$. To verify this, add a new third phase to the PCR file in Le Bail Fit (LBF) mode. This new phase should have the same cell parameters as phase 1, with the space group symbol set to *Pmmm* for generating all reflections. Set **Nat=0**, **Jbt=2**, **Irf=-1** and **Nvk=1**, and include the propagation vector. This can be done using EDPCR or by manually editing the PCR file.

4: Copy the file **hog_02.dat** to the **Testing** directory and save the previous PCR file under a new name (e.g. **hog_02.pcr**). Use WINPLOTR-2006 to select a new background using the data file **hog_02.dat**, and import it into the new PCR file. Fix all structural and background parameters, and refine the cell parameters. Observe that many prominent magnetic reflections overlap with nuclear reflection, while others correspond to the previous propagation vector $\mathbf{k}=(0,1/2,0)$. This indicates the presence of the additional propagation vector $\mathbf{k}=(0,0,0)$. Run the modified PCR file by setting **Irf=0**, so the LBF phase generates both satellites reflections and reflections corresponding to $\mathbf{k}=(0,0,0)$. Run the modified PCR file to confirm everything is correct.

5: It has been verified that between 8K and 18K, there is a magnetic phase with $\mathbf{k}=(0,1/2,0)$, and below 8K, a new magnetic phase contains two propagation vectors: (0,0,0) and (0,1/2,0). Next, prepare PCR files with different models for the magnetic structures using all possibilities provided by ISODISTORT. Use the data files **hog_18.dat** and **hog_02.dat** test these models. Load the CIF file **Ho2BaCuO5.cif** into ISODISTORT, remove the strain modes, and select Ho and Cu as magnetic atoms while keeping all the displacive modes.

6: Begin by searching for the possible MSG for the point Y (0,1/2,0) in the Brillouin Zone. Two 2D representations mY1 and mY2 are obtained. For each representation, three MSGs are possible: one orthorhombic and two monoclinic. Save a FULLPROF PCR file for each case (automatically named **fullprof.pcr** by ISODISTORT), using the parent-related setting with origin fixed at (0,0,0). Name the file informatively, for example **mY1-P3(a,a)14.80_P2_1_over_c.1'_a[P2_1c].pcr** (the name is extracted from the ISODISTORT page for saving the PCR file), removing unnecessary details such as the space group number and the UNI symbol extension (enclosed in square brackets). Store these files in a separate directory (e.g. **ISO_pcrs**). Let us refer to one of these PCR files as **ISOname.pcr** (where **name** varies for each model).

For each PCR file in **ISO_pcrs**, save a copy of the PCR used for testing the propagation vector (e.g. **hog_02.pcr**) with a corresponding name, such as **hog_02_ISOname.pcr**. Remove the third phase used for testing the propagation vector in LBF mode. To obtain the magnetic mode amplitudes in Bohr magnetons units, insert the following lines just below the name of the first phase:

```
COMMANDS
reference_cell    12.1667    11.3106    7.1135    90.0    90.0    90.0
END_COMMANDS
```

The reference cell is that of the subgroup used in generating the **ISOname.pcr** files. Copy the text from **ISOname.pcr**, starting with the phase name and ending at the beginning of the profile parameters, and paste it into the **hog_02_ISOname.pcr**, replacing the first phase. Test the different files against the experimental data (file **hog_02.dat**) by trial-and-error, starting with arbitrary values for the mode amplitudes.

7: Next, search for the possible MSGs for the coexistence of points GM(0,0,0) and Y (0,1/2,0) in the Brillouin Zone. Combine the *irreps* of the two 2D representations mY1 and mY2 with the eight *irreps* for GM(0,0,0): GM1+, GM2+, ...GM1-, ...GM4-. This results in 16 possible combinations, each with three MSGs. Download the PCR file for all cases, initially discarding the lowest symmetries. If hints from the previous phase analysis are available, select only symmetries that can be subgroups. Perform the same operations as in the previous case and determine the best solution by trial and error.

8: Compare the solutions found with the PCR files in the subdirectory **Sequential-Modes**. Run the scripts in this subdirectory to perform a sequential refinement. After running the scripts, files with the **.seq** extension will contain all refined parameters. Use WINPLOTR or WINPLOTR -2006 to visualise the evolution of the different mode amplitudes.

9: Verify that the above information aligns with the content of the PCR files prepared for TOF data. Perform a refinement of the full crystal and magnetic structure using the WISH data at 1.5K. Note that the provided PCR file treats some reflections as special because the complex function for positions and shape parameters may not fit all reflections well across large ranges of d-spacings.