Preparing a magCIF file of a magnetic Structure for MAGNDATA. Example 4: $CdCu_3(OH)_6(NO_3)_2 \cdot H_2O$

Reference:
Ihara et al., PHYSICAL REVIEW B **106**, 024401 (2022)
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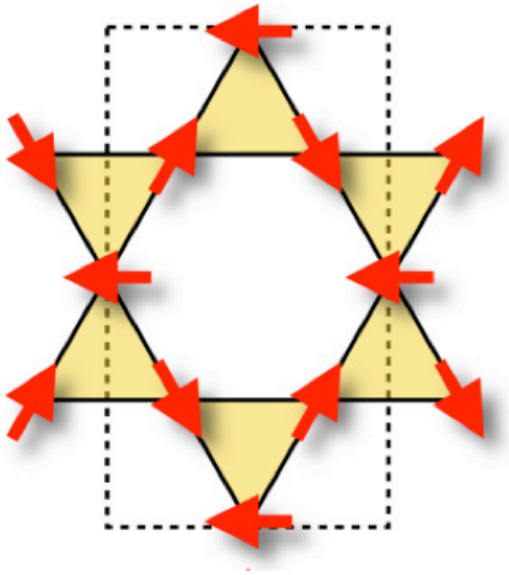
Parent P-3m1 structure at 10K in file: Parent_paper_P-3m1_10K.cif
The article reports the positional structure at 10K, in the paramagnetic phase. We will use this positional structure parent structure, and also as approximately valid for the magnetic arrangement measured at 1.6K.

The magnetic structures at 1.6K as reported in the reference (T_N=4K):
The propagation vector is identified as **k**=(0 0 0) and the MSG as C2/m, with unit cell (2a+b, b, c) with respect to the trigonal parent unit cell. The spin arrangement is only described by means of a graphical scheme in Figure 2:



where the centered orthorhombic unit cell is outlined.

Moment modulus: 0.21(1) μ_B at 1.6K and T_N= 4K

The information above, together with the provided CIF file is sufficient to produce a magCIF file that can be uploaded in MAGNDATA.

First of all, if you do not have them, download the instructions available in the webpage of MAGNDATA. There you will obtain a zip file that includes the pdf file: "instructions_to_prepare_mcif_file_v6.5.pdf". According to these instructions, our situation for this example is "Case 3", as we do not have yet any magCIF file. For the magnetic structure of this example the most rapid approach is to follow the 1st Procedure for "Case 3", which is recommended in the instructions. In the case of parent symmetries with 3-fold operations, the MSGs associated with single irreps with dim>1 can be non-maximal, and therefore the program MAXMAGN does not directly provide these MSGs, except if one uses the more complex option of lowering the symmetry. In

this example it is therefore more convenient to use the program k-SUBGROUPSMAG combined with MAGMODELIZE, which will provide all possible symmetries compatible with the propagation vector, not only the maximal ones. This will be sufficient to produce an initial magCIF file and then follow the steps explained in the instructions for "Case 1", i.e. when one has already a magCIF file consistent with the MSG of the structure.

1) Open k-SUBGROUPSMAG and introduce the number corresponding to the parent space group P-3m1 (164) and the k-vector (0 0 0). Then, click on "Wyckoff" to introduce the Wyckoff position of the magnetic atom. Then submit. The program will then list all possible non-equivalent MSGs that the structure may have. You can check that the list includes the four possible symmetries discussed in the paper.

2) Tick on the last column of the listing the case of C2/m to transport it to MAGMODELIZE, tick below in "Include structure of the parent phase" to indicate that a CIF file of the parent phase will be uploaded, and submit to MAGMODELIZE. Upload the parent CIF file in the following menu, and indicate that Cu is the magnetic atom in the next page. You will then obtain a page where some information about the chosen subgroup C2/m is given. By clicking in the last column, a magnetic structure under this MSG can be obtained.

3) Click on "Show" in the last column "Magnetic Structure" of the last page obtained in the previous step. You obtain then a listing of the atomic positions with a unit cell and the allowed magnetic moments under this MSG. You can see that the Cu site splits into two independent sites, with one having the moment restricted along b, but the other one fully free. In order to produce the model proposed in the paper one has to choose a very specific direction for this free moment. But the paper describes the structure using the standard orthorhombic unit cell of the MSG C2/m, while the program is still using by default a description under the parent trigonal unit cell. We can however go directly to the standard description by clicking on "Go to setting standard (2a+b,b,c;0,0,0)". We have now a new listing of the atomic positions and allowed moments under the C2/m standard setting. Under this unit cell, the free moment in the reported model for the particular independent site chosen by the program is along the direction (-sqrt(3),1,0) ≈ (-1.732,1,0). Fill in an arbitrary scale the moment values for the two independent Cu sites, so that they have same modulus, and using the visualization tool of the program, check that indeed this is the stucture proposed in the paper, except for the specific value of the moment modulus. Save the corresponding mcif file produced by the program.

4) You have saved in the previous step a magCIF file of the model corresponding to the magnetic structure that is proposed in the paper. You have therefore the necessary file to go now to the process that is explained as "Case 1" in the instructions, and obtain following these instructions the desired magCIF file ready for uploading in MAGNDATA.

5) The magCIF to be introduced in MAGNDATA has a small part about information on the irreps that are active. It is can be left untouched, without information, if wished. But in this particular case, it is important to fill it, in order to understand why the MSG allows a fully free moment in one of the two independent Cu sites, while in the reported model, this moment is fully correlated with the other one, according to a 120º arrangement on the xy plane. To get this information you can use ISODISTORT in its "Method 4", using as input the parent CIF file and the mCIF file that you have produced

in step 3. As this second file is in the standard setting of the MSG, it can be used directly in the program. Take care of un-ticking in the initial menu all structural distortions and strain, so that the output is simpler and only shows the amplitudes of magnetic irrep modes.
You will obtain that the proposed model corresponds to an arrangement according to the 2-dim irrep mGM3+, but restricted along a special direction. The mGM3+ arrangement restricted to the MSG C2/m has however two degrees of freedom on the plane xy. An additional FM mode along y for the same irrep is possible (see step below) and its presence would break the specific 120º orientation of the two independent moments and its equal modulus. These two features are therefore not forced by the restriction to a single irrep. Also the mGM3+ irrep allows a non zero mz component in one of the two sites. A secondary irrep mGM1+ mode, fully breaking the correlation between the moments of the two sites on the xy plane, is also symmetry allowed, and completes the number of degrees of freedom present in a fully general C2/m model.

6) For the possible comments in the final magCIF file one should take into account that the monoclinic axis is along b (or symmetry equivalent directions), and therefore a FM component is possible along this direction. This FM mode is in fact part of the set of degrees of freedom for the mGM3+ irrep. Hence, weak FM, which cannot be detected in the diffraction experiment, is to be expected, and it is mentioned in the paper as experimentally observed.