Preparing a magCIF file of a magnetic Structure for MAGNDATA. Example 2: Na2CuSO4Cl2

Reference:

Fujihala et al., Phys. Rev. B **105**, 144410 (2022), DOI: 10.1103/PhysRevB.105.144410

Parent structure at 303K in file: Parent_Na2CuSO4Cl2_303K.cif

The paper reporting the magnetic arrangement does not include information about the positions of the non-magnetic atoms. But the full positional structure at 303K was determined by the same group in a previous paper: Fujihala et al., Phys. Rev. B **101**, 024410 (2020), DOI: 10.1103/PhysRevB.101.024410

We will then use this 303K structure as parent structure with all atoms included. However, the cell parameters and Cu positions are however reported in the 2022 paper at 0.3K, the temperature at which the spin arrangement is determined.

The magnetic structure at 0.3K as reported in the reference (T_N=0.54K):

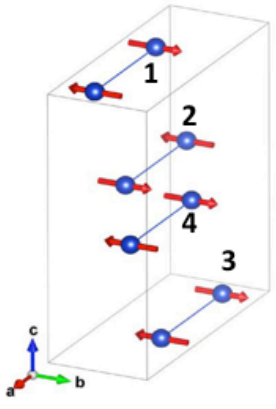
Cell parameters at 0.3K for the atomic positions (so-called nuclear structure under parent space group Pnma):

a = 6.9875(2) Å, b = 5.5657(2) Å, c = 15.9716(5) Å

Positions of the Cu atoms in this unit cell at 0.3K:

$\mathbf{r}_1$ = (0.636, 0.25, 0.966), $\mathbf{r}_2$ = (0.136, 0.25, 0.534)
$\mathbf{r}_3$ =(0.364, 0.75, 0.034), and $\mathbf{r}_4$ = (0.864, 0.75, 0.466)

Only collinear models along the main crystallographic axes were tested. The unit cell in the Figure is that of the magnetic structure: (2a,b,c), with respect to the unit cell indicated above.



k=(1/2,0,0)

Models (along a, b or c) tested in the refinement:

r_1	r_2	r_3	r_4
+	+	+	+
-	+	+	+
+	-	+	+
-	-	+	+

Best fit (along b)

The models tested are termed in the reference as: the "only four irreducible arrangements"

Moment value: 1 μB (apparently not refined). ***Note that the sequence in space along z of the atoms does not correspond to the sequence of numerical labels that the***

paper uses, the labels 3 and 4 being interchanged. This is important to take into account when describing the models in the form of the Table above, where the atoms are ordered according to their numerical labels.

We have above and in the provided CIF file all the necessary information 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 (a zip file with the pdf file: "instructions_to_prepare_mcif_file_v6.5.pdf"). According to these instructions, our situation is "Case 3", as we do not have yet any magCIF file. For the simple magnetic structure of this example the most rapid approach is to follow the 1st Procedure for "Case 3", which is recommended in the instructions, and use the program MAXMAGN. 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) As the paper reports the cell parameters and the atomic position of the Cu atom at 0.3K, which is the temperature of the measurement of the spin arrangement, introduce these values by hand in the provided CIF file of the structure at 303K, so that in the modified CIF file, to be used in the next step, only the non-magnetic atoms have approximate values corresponding to the measurement at 303K.

2) Use MAXMAGN: Introduce the k-vector and tick the option that "Structure data of the paramagnetic phase will be included". In the next step, upload the modified cif file produced in the previous step. The program will show that four maximal symmetries are compatible with the observed propagation vector, being described by four different magnetic space groups (MSGs). By clicking on the last column "Magnetic Structure" identify the only two MSGs, which allow a spin arrangement along b.

3) For the first MSG in the list compatible with moments along b, put values to the allowed moments and produce the corresponding mcif files. Use then the visualization tool of the program to identify that the two spin arrangements allowed by this MSG, if the arrangements are further restricted to have equal moment modulus, are:
+ - + + and + + - + (if atoms are ordered in the sequence 1,2,3,4 of the figure above). The first of these two possible arrangements corresponds to the one reported in the reference as the one that best fits the data. So we have already identified the MSG of the reported structure. Save therefore the corresponding mcif file, for further processing later. Save also the mcif file corresponding to the alternative (physically different!) possible arrangement + + - + under the same MSG.

4) The second arrangement obtained in the previous step + + - + does not appear among the four considered for refinement in the paper. If the paper is correct this must be due to the fact that this arrangement is fully equivalent to one of the four that were considered, being a domain related arrangement, i.e. related by some of the symmetry operations lost with respect to the symmetry of the parent paramagnetic structure. We can check this: upload the mcif file of the structure corresponding to the + + - + arrangement, saved in the previous step, in the program MVISUALIZE and using the

button "Domain related equivalent descriptions" and choosing the second possible equivalent (but different!) MSG that the program gives, produce the mcif file of corresponding equivalent description. Using the visualization tool that the program has, check that this equivalent structure has the arrangement + - - -, and therefore also equivalent to - + + +, which is indeed the one listed and tested in the paper. *This example shows that one should be very careful when trying to derive from the relative signs of the moments a specific local FM or AFM coupling. As shown here, this relative sign in many cases can vary depending on the way the structure is described.*

5) You have saved in step 3 a magCIF file of the model corresponding to the magnetic structure reported in the paper. You have therefore the necessary file to go now to the process explained as "Case 1" in the instructions mentioned above. Notice that the MSG of the structure is polar, with a breaking of the inversion symmetry of the parent paramagnetic phase. Therefore, if the compound is an insulator, it can have some spontaneous electric polarization induced by the magnetic ordering (multiferroic of type II). This can be included in the comments of the magCIF file being prepared.

6) The magCIF to be introduced in MAGNDATA has a small section about information on the irreps that are active. It is can be left untouched. But this information can easily be obtained using Get_mirreps. You will obtain there that only one 2-dim irrep is compatible with the magnetic arrangement of the structure, but restricted along a special direction. Therefore the two magnetic degrees of freedom present in the structure (the Cu site splits into two sites) correspond to this single irrep. Thus the assumption of equal moduli of the moments of all the Cu atoms is not forced by the restriction to a single irrep. It is an additional restriction. In fact, as you can check using the programs Basirreps or Sarah, the number of possible basis functions for the active irrep is four, and therefore assuming this irrep as active would imply four parameters to refine,. It is the constraint to the MSG (implying specific combinations of these four basis functions) that reduces the number of free parameters to two. The additional assumption of equal moduli then reduces the number of parameters to one.