

*This was supposed to be a brief note, but I got carried away...  
-ASW while on D2b, 7/2012.*

### **Introduction**

The k-vector search algorithm [AS Wills, Z. Kristallogr. Suppl., **30**, 39 (2009)] in *SARAh* is unique because it combines direct space, reciprocal space and global fitting algorithms. Why did I invent it?

### **Traditional techniques:**

The determination of a k vector is typically carried out in reciprocal space using only the lattice parameters and lattice type. The positions of a set of observed reflections matched against predictions based on simple nice fractional values (e.g.  $\frac{1}{2}$ ) and then a grid search is used if the fit was not good.

This technique is fast, but it is pretty wasteful in terms of information: 1) it fails to use the proper symmetry of the Brillouin zone and what it represents, 2) the projection of the magnetic powder diffraction spectrum to only a set of reflection positions throws away a lot of useful information.

### **How I do it in SARAh:**

*1) I perform a k-vector search based around the Brillouin zone information.*

Points, lines and planes should be explored in this order. k-vectors define the translational properties of a magnetic structure. The Brillouin zone defines the symmetry types of these k-vectors and in many cases the translational symmetry of the eigenfunction of the Hamiltonian that is the magnetic structure. The points of symmetry correspond to magnetic structures that propagate through the structure with a high-symmetry (by which I mean direction an repetition) periodicity. These are the simplest structures. Lines correspond to structures where competing energy scales in the magnetic Hamiltonian lead to more complex translational properties. Planes of symmetry, are yet more sophisticated.

Using the Brillouin zone will help you understand why a particular k-vector occurs and whether it is stable, e.g. to being incommensurate. *SARAh* uses the k-vector types and the Brillouin zone defined by Kovalev. The k vectors are then transformed to the user-chosen setting of the International Tables (IT). I recommend understanding a k vector in the primitive setting and then to work with it in the IT setting (this is why the primitive k vector is given in all of *SARAh*'s output). I have spent years pushing the importance of this. Why? Because the IT setting has nothing to do with physics; it is simply easier to think there. The physics follows the primitive setting. Working in the primitive setting makes things clear, e.g. it shows why  $k=(000)$  and  $k=(100)$  are not the same in an I-centred space group.

(Grid searches are used for lines and planes of symmetry)

*2) I use direct space information and a global optimisation algorithm*

In *SARAh*, the magnetic structure is defined by moments at the correct crystallographic positions of the nuclear unit cell. These moments are expressed using spherical coordinates where atoms of the same type have their moment magnitudes

set to be the same. (In FullProf I have made the refinement stable by constraining these moment types to be positive.) For a given k-vector (defined according to the explanation given above) the moment orientations are refined by a Monte Carlo algorithm based on the goodness-of-fit of the predicted and experimental powder diffraction patterns.

This means that for a given k-vector, the algorithm will try its best to fit the data. If it cannot, the k-vector is wrong, assuming, of course, that your profile function, etc, are appropriate. (After identifying a reasonable k-vector, you may need to refine the profile function or other parameters in the magnetic phase in order to get a good fit, as you would normally do in FullProf.)

### **Putting it all together**

I built the k-vector search algorithm in SARA*h* to be as close to the physics of the relevant processes as possible. This means that magnetic powder diffraction patterns that involve several k-vectors can be easily treated. As the contributions from the different k-vectors are independent, you will find that SARA*h* is able to fit some peaks well but not others. If this happens, don't worry. Accept the k-vector that SARA*h* used to fit some of your peaks, then add another magnetic phase (change the phase number on Tab 1) with another k vector, and continue. You will find that the next k-vector trials will fit some more peaks. Keep going until you have fitted all the peaks!

\*If this does not work, then one or more of your core assumptions is wrong. These are: 1) the space group, 2) the moment positions. My money would be on the space group being lower symmetry than you thought (*e.g.* it is primitive rather than centred) and the magnetism is revealing this to you more easily than the crystal structure data. I propose that you refine your nuclear structure in a lower symmetry space group and then start again.

Now that you have your k-vector, you can perform the symmetry calculations for possible structures using SARA*h*-Representational Analysis.

### **References:**

This indexing technique was developed out of need to analyse problem data that my friends and collaborators had. It was written up in: A.S. Wills, *Z. Kristallogr. Suppl.*, **30**, 39 (2009). Please reference this in your papers.

### **History:**

The journey began with

- J.R. Stewart, A.S. Wills, C.J. Leavey, B.D. Rainford and C. Ritter. *J. Phys.: Condens. Matter.* **19**, 145291 (2007).

Then further developments were made for:

- G. King, A. S. Wills, and P.M. Woodward, *Phys. Rev. B* **79**, 224428 (2009).

The following is a lovely examples of using the program for a pattern with 2 commensurate and 1 incommensurate magnetic phases:

- O.A. Petrenko, G. Balakrishnan, D.M. Paul, M. Yethiraj, G.J. McIntyre, A.S. Wills, *J. Phys.: Conf. Ser.* **145**, 012026 (2009).

The most recent examples include:

- H.J. Silverstein, K.Cruz-Kan, A.M. Hallas, H.D. Zhou, R.L. Donaberger, B.C. Hernden, M. Bieringer, E.S. Choi, J.M. Hwang, A.S. Wills, and C.R. Wiebe, *Chem. Mater.*, **24**, 664 (2012).

### **How do I use it:**

*The simplest way to start*

- 1) The assumed starting point is a nuclear refinement with NO magnetic phase. Get as far as you can. Turn off all variables (turn them on again when the magnetic refinement is fitting well)
- 2) In Tab 1, click <Select pcr>. The magnetic atoms are found automatically – delete any that you know have no moment by selecting them and clicking <Delete atom>.
- 3) Click <Make phase>. The magnetic phase will be set-up. Note that a constraint will have been added to force the moment sizes (Rm) to be positive. If you change the moment size variables, make sure you update the constraint or FullProf will not work.
- 4) Go to Tab 4
- 5) If you have WinPlotR open with the relevant refinement, minimise it. If it is left open WinPlotR will hold onto some files when processing them, which can cause a hand-shake error when SARAh tries to edit the pcr file.
- 6) In section1, click <RMC> and <Zero variables>, then click <Run>. Go and have a coffee.
- 7) When you return, the table will have the best  $\chi^2$  values for the different points of the Brillouin zone. Listed in the IT setting on the left and primitive under Info\_1.
- 8) Click on  $\chi^2$  in the table to order the list. (Note that low  $\chi^2$  values for  $k=0$  trials can occur because the magnetic refinement is improving problems with the nuclear structure.)
- 9) Select the k vector in the table that has the lowest  $\chi^2$  value.
- 10) In section 2, click <RMC> and click <Replace/ FP> to substitute this k-vector into the pcr and launch FP.
- 11) Look at the fit in WinPlotr. If the k-vector looks right, use FullProf as normal to improve the refinement.
- 12) If the fit is bad, look at the other k-vectors in the table. If non are good, try a in section 1, click on <One variable> to explore lines of symmetry. These can take hours – so go off and do something else
- 13) If required, try planes of symmetry.

*SARAh also allows you to look at the points, lines and planes manually. This is controlled in Tab 2.*

- 1) Select a point, line, plane (these are in Kovalev's primitive setting) in section 1, and click <Run>, also in section 1.
- 2) The results appear in section 2. Order the k-vectors by  $\chi^2$  and select that which you wish to trial. Click <Replace/FP> also in section 2.
- 3) You may also define a line or plane manually, e.g. 0.5, 0.5, u.

*Set-up of the RMC and Fullprof controls is done in Tab 3.*

- 1) Looping over different phases is useful when you have several k-vectors in your pcr. SARA $h$  will RMC refine the phases listed in sequence and will then loop back to the first as many times as defined.

*Returning to a refinement*

- 1) Load in the pcr file using Tab 1 and then move directly to Tabs 4 or 2.