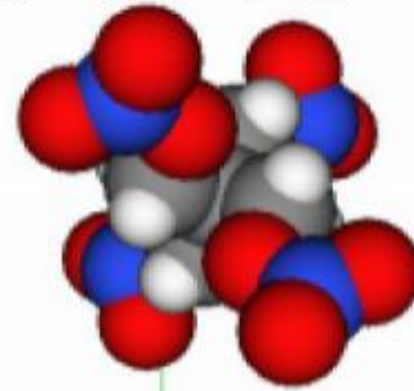


SYSTEMATIC DETERMINATION OF MAGNETIC STRUCTURES DRIVEN BY SPACE GROUPS IN GSAS-II

GSAS-2

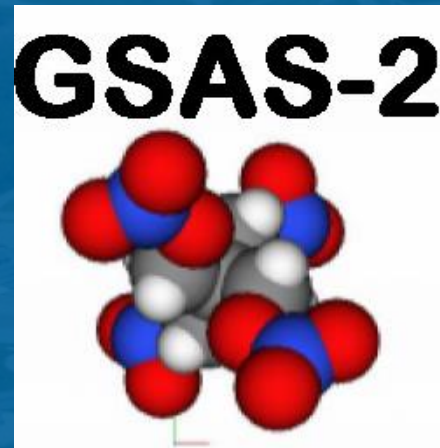


ROBERT VON DREELE
APS/ANL – retired!
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THANKS TO: BRIAN TOBY, J.M. PEREZ-MATO & COWORKERS

Oak Ridge, June 5, 2023

GSAS-II



GSAS-II: A MODERN ANALYSIS PACKAGE FOR ALL ASPECTS OF CRYSTALLOGRAPHY



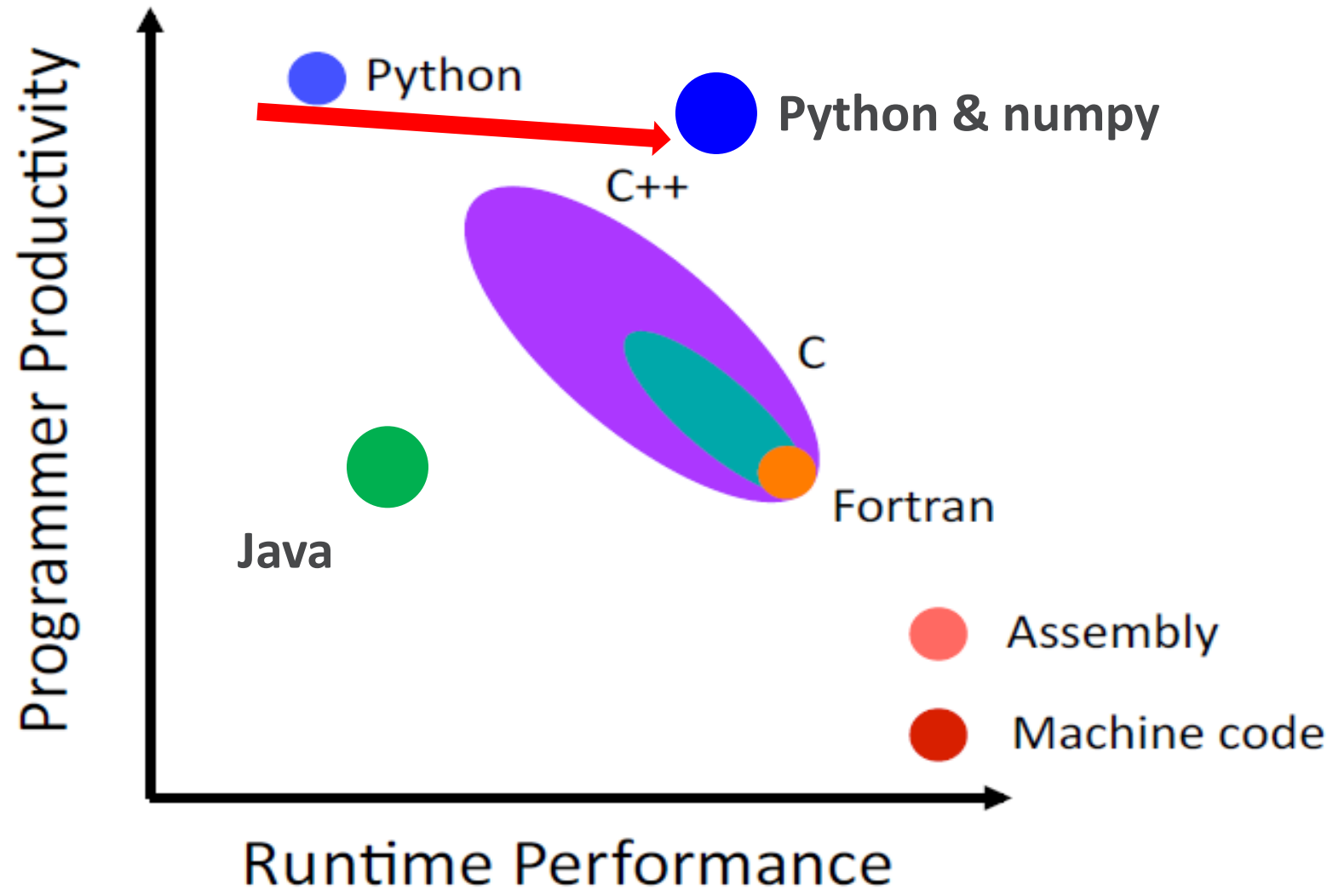
GSAS-II is intended to more than replace GSAS & EXPGUI with a new, modern, extensible, and open-source crystallographic analysis code

- Support all aspects of diffraction data analysis (from raw data to publication), including capabilities not in GSAS/EXPGUI
- Facile processing of large numbers of similar datasets
- Written with modern code (Python)
- Incorporates extensive visualization
- Use parameters that “make sense”
- Designed around GUI
- Design goal: Novice friendly, but expert efficient

GSAS-II reads powder diffraction images from all appropriate synchrotron & neutron beamlines, as well as the Curiosity Rover on Mars!

B.H. Toby and R.B. Von Dreele, "GSAS-II: The Genesis of a Modern Open-Source All-Purpose Crystallography Software Package". *Journal of Applied Crystallography*. **46**: p. 544-9 (2013).

WHY PYTHON? – CHOICE OF LANGUAGES (~LOG SCALES!)



WHY PYTHON?

Code snippet – charge flipping all inside a “while” loop

NB: CEhkl is F_{hkl} expanded over full sphere & zero filled out to 1/resolution limit as an array
Start with random phases for CEhkl

```

CErho = np.real(fft.fftn(fft.fftshift(CEhkl)))*(1.+0j)           #fft Fhkl → ρ(xyz)
CEsig = np.std(CErho)                                           #get σ(ρ)
CFrho = np.where(np.real(CErho) >= flipData['k-factor']*CEsig,CErho,-CErho) #CF ρ → ρ'
CFrho = np.where(np.real(CErho) <= flipData['k-Max']*CEsig,CFrho,-CFrho)   #U atom CF!
CFhkl = fft.ifftshift(fft.ifftn(CFrho))                         #fft ρ(xyz) → F'(hkl)
CFhkl = np.where(CFhkl,CFhkl,1.0)                               #avoid divide by zero
phase = CFhkl/np.absolute(CFhkl)                               # get φ(hkl) from F'
CEhkl = np.absolute(CEhkl)*phase                               #apply φ to F
Ncyc += 1                                                       #count tries
sumCF = np.sum(ma.array(np.absolute(CFhkl),mask=Emask))         #Σ F
DEhkl = np.absolute(np.absolute(Ehkl)/sumE-np.absolute(CFhkl)/sumCF) #ΣDF
Rcf = min(100.,np.sum(ma.array(DEhkl,mask=Emask)*100.))        #R-value for CF

```

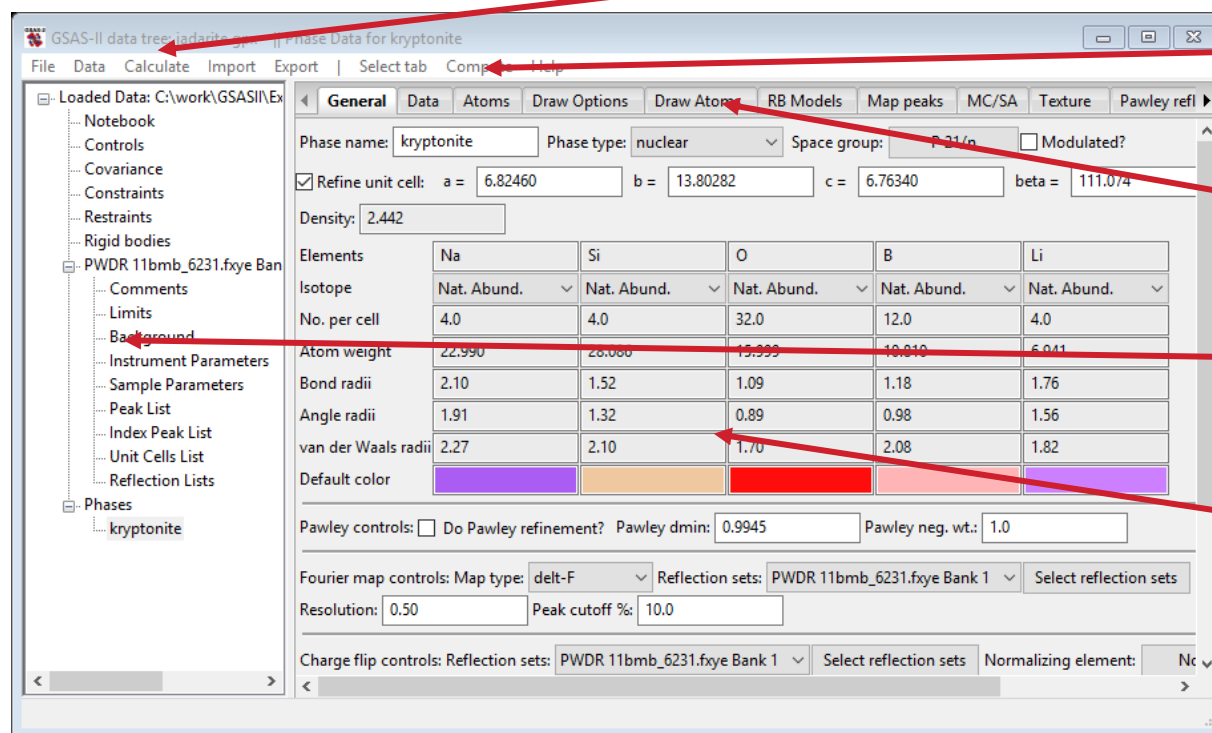
NB: the 4D version is almost identical except that $F_{hk\ell m}$ is used

This stuff is fast! ~1s/cycle for 500K reflections/map points

GSAS-II DEVELOPMENT - PYTHON

Started Nov. 2008 – 1st usable version late 2011- early 2012

GSAS-II: modern GUI – 2 frames + console



Main menu

Submenu

Data tabs

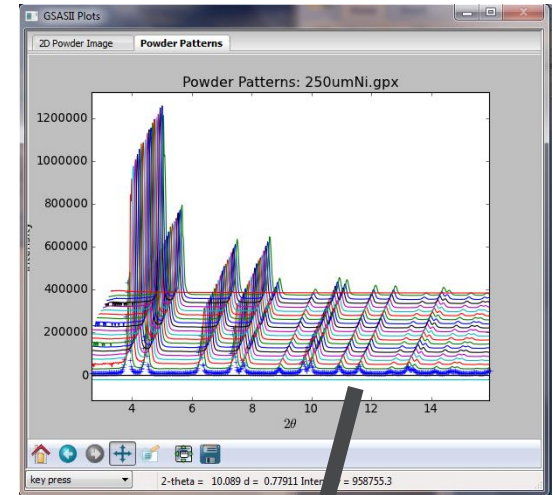
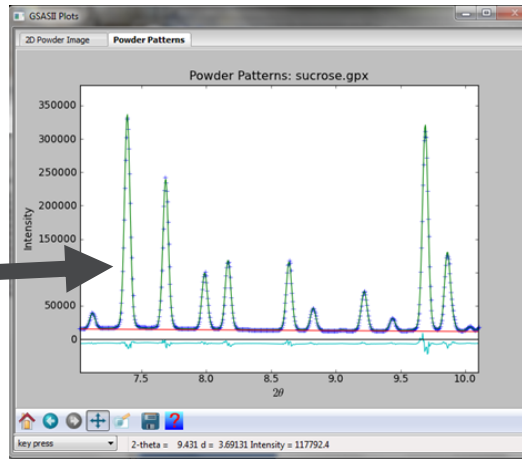
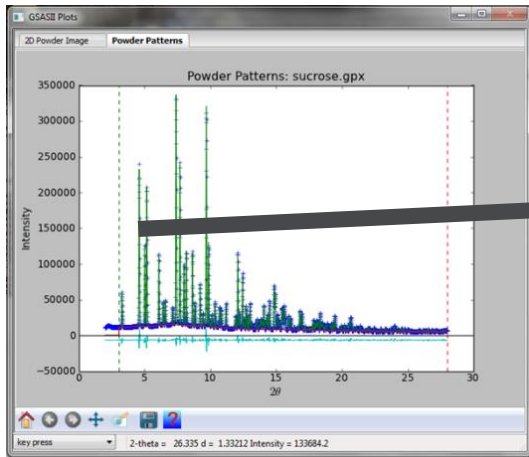
Data tree

Data window

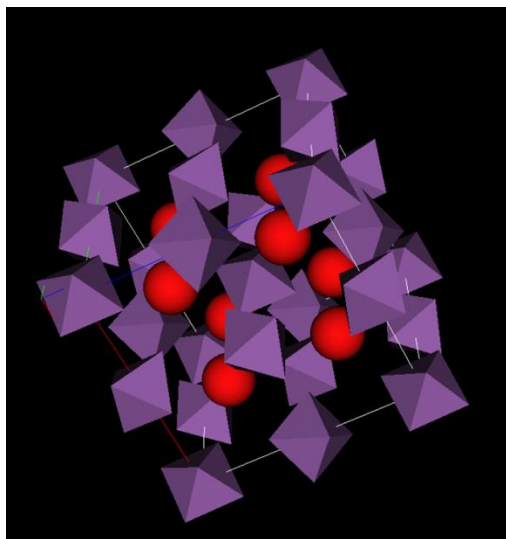
Plot & console in separate frames

THE PLOTS - ADVANCED VISUALIZATION

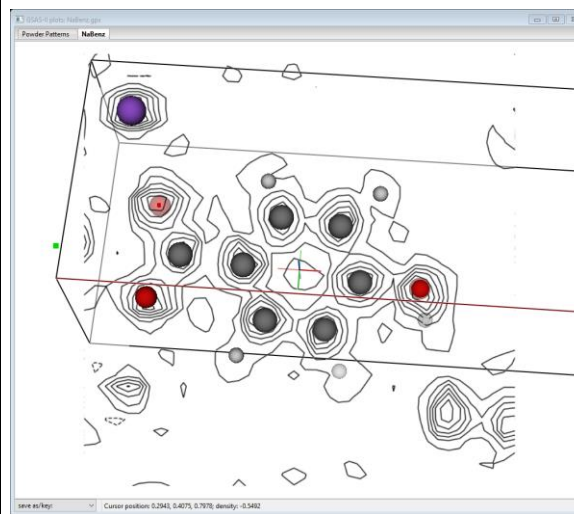
Powder profile – easy zoom



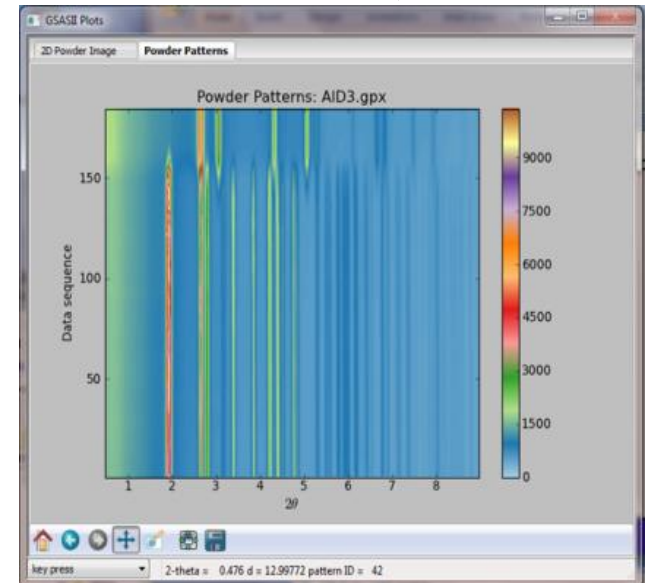
Waterfall plot



Structure drawing



contoured density thru any plane



Contour plot

INTRODUCTION TO MAGNETISM IN GSAS-II

MAGNETISM – SOME BASICS

Assumptions: powder sample, unpolarized neutrons, elastic scattering – no cross term; sum intensities

Nuclear structure factor

Magnetic structure factor

$$|F_{\mathbf{h}}|^2 = \left| \sum_n b_n \exp\{2\pi i(\mathbf{h} \cdot \mathbf{r})\} \right|^2 + \left| \sum_m \mathbf{q}_m p_m \exp\{2\pi i(\mathbf{h} \cdot \mathbf{r})\} \right|^2$$

All atoms

Magnetic ions only

GSAS-II: 2 phases

- 1) “chemical” nuclear – all atoms
- 2) only magnetic ions

Need not be same lattice/space group, but describe same atomic arrangement for magnetic ions.

STRUCTURE FACTOR – POWDERS & NO POLARIZATION

The p's & q's? (after Bacon, 1975)

$$\mathbf{q}_m = \boldsymbol{\varepsilon}_h (\boldsymbol{\varepsilon}_h \cdot \mathbf{K}_m) - \mathbf{K}_m$$

$$p_m = \left(\frac{e^2 \gamma}{m_N c^2} \right) S_m f_m$$

$\boldsymbol{\varepsilon}_h$ – unit vector $\parallel \mathbf{h}$ – diffraction vector

\mathbf{K}_m – unit vector \parallel magnetic moment on atom m

$\therefore \mathbf{q}$ small for $\mathbf{h} \parallel \mathbf{K}$ & large for $\mathbf{h} \perp \mathbf{K}$

$0.539 \times 10^{-12} \text{cm}$ – similar to b_n

e – electron charge

γ – neutron magnetic moment

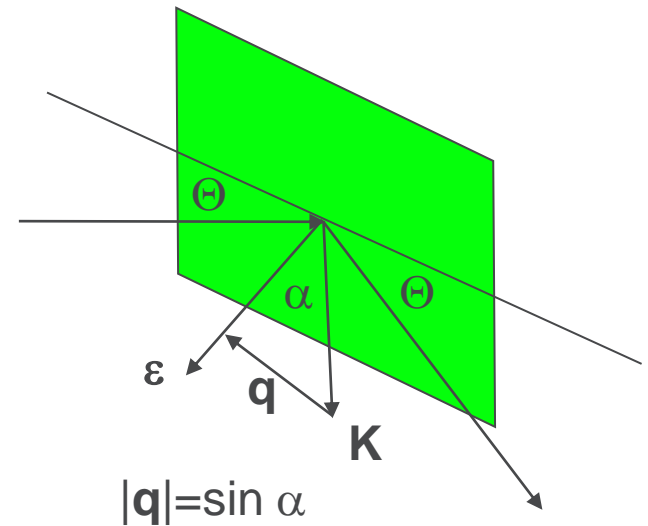
m_N – neutron mass

c – speed of light

S – magnetic moment (Bohr magnetons)

f – 1-electron magnetic form factor

Important point: Magnetic $|F|$ proportional to $|q|$




MAGNETIC FORM FACTOR - f_m

Fourier transform of unpaired e^- density:
valence e^- ; outer shell
Sharp fall off with Q (small d, etc.)

In GSAS-II:

Form factor coefficients $\langle j_0 \rangle$ and $\langle j_2 \rangle$ (higher terms ignored)

$$f_m = C + \sum_{i=1}^4 A_i \exp\left(-B_i \sin^2 \Theta / \lambda^2\right) + \left(\frac{2}{g} - 1\right) \left[C' + \sum_{i=1}^4 A'_i \exp\left(-B'_i \sin^2 \Theta / \lambda^2\right) \right] \sin^2 \Theta / \lambda^2$$


*Landé g factor = 2 for 1st row transition elements:
quenched orbital contribution*

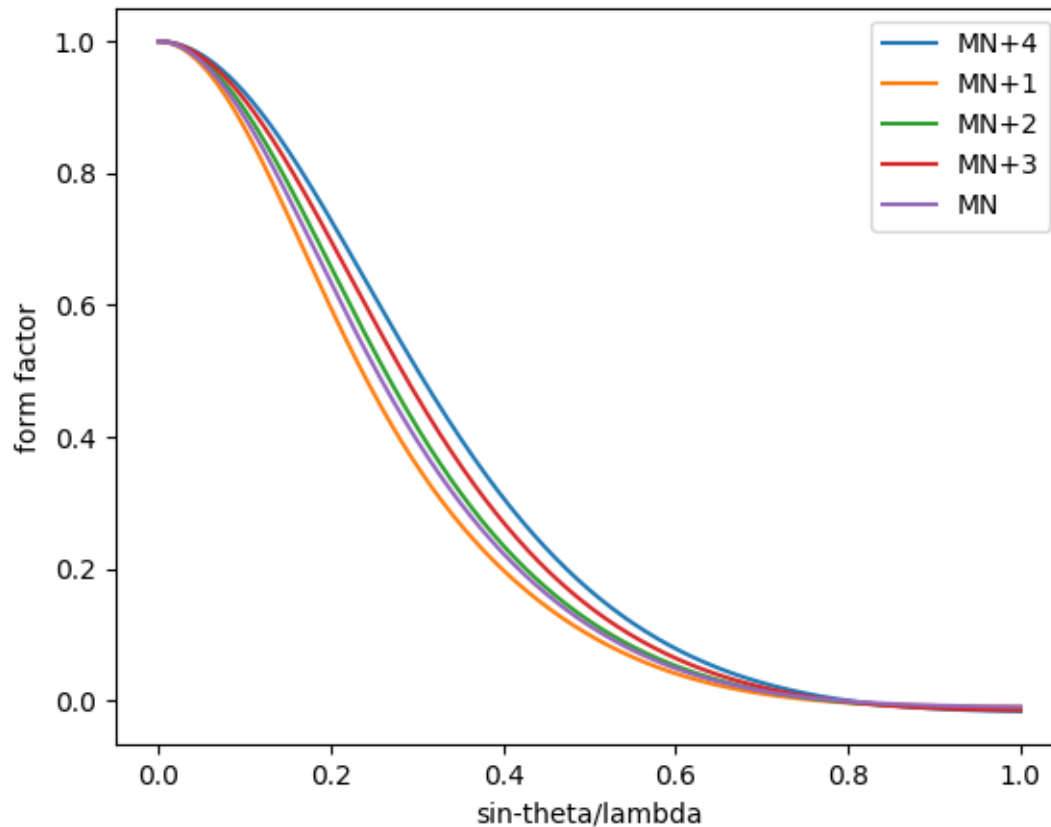
In general $f_m \rightarrow 0$ for $\sin \Theta / \lambda > 0.5$; $d < 1.0$

Tables from J. Brown (ITC-C) & Kobayashi K, Nagao T, Ito M. (Acta A67, 473-480, 2011)

(No input for user tables; might allow additions/substitutions in coeff. tables if there is interest)

MAGNETIC FORM FACTORS

E. g. for Mn & ions – some valence sensitivity



GSAS-II uses the high spin versions where there is a choice – 3rd row transition elements (W-Ir) given by Kobayashi, et al.

MAGNETIC SYMMETRY IN GSAS-II

Symbol driven; 2nd setting (if appropriate); BNS settings (not OG)

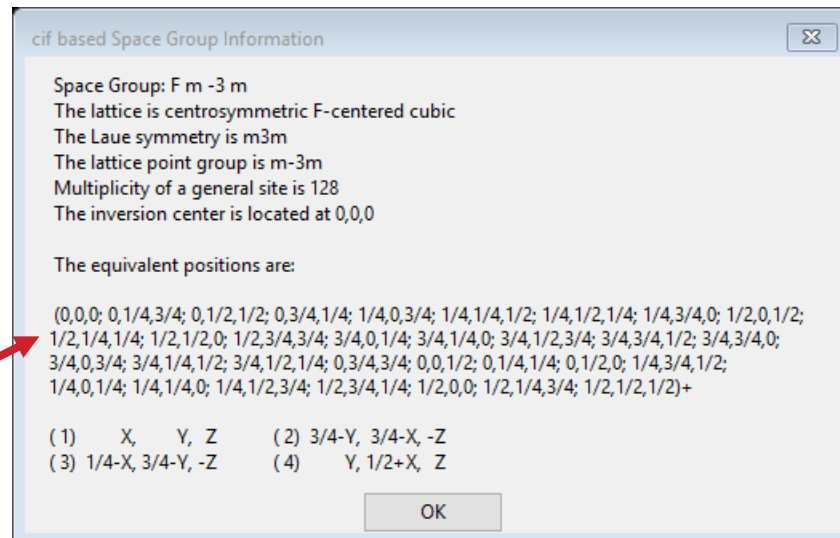
- Symbol based: allows nonstandard space groups – symbol interpretation yields operators (ITXC Vol I version! Thx to A. C. Larson's code)
- NB: does know that e.g. “F m -3 m” is really Fm3m & “C m c e” is really Cmca
- Spin flip designation on generators (e.g. symbol components)
- Magnetic type IV – by transformation from chemical cell (with constraints) & selection of magnetic centering type
- Grey groups by adding 1' to symbol (incommensurate only)
- → all std & nonstd BNS designations are reachable in GSAS-II
- Can be changed after input
- On the other hand:

Import Bilbao magnetic cif files:
operators from mcif file

(fixed – can't change 'em)

Occasionally peculiar:

NiO mcif has 32 centering ops!



BNS vs OG

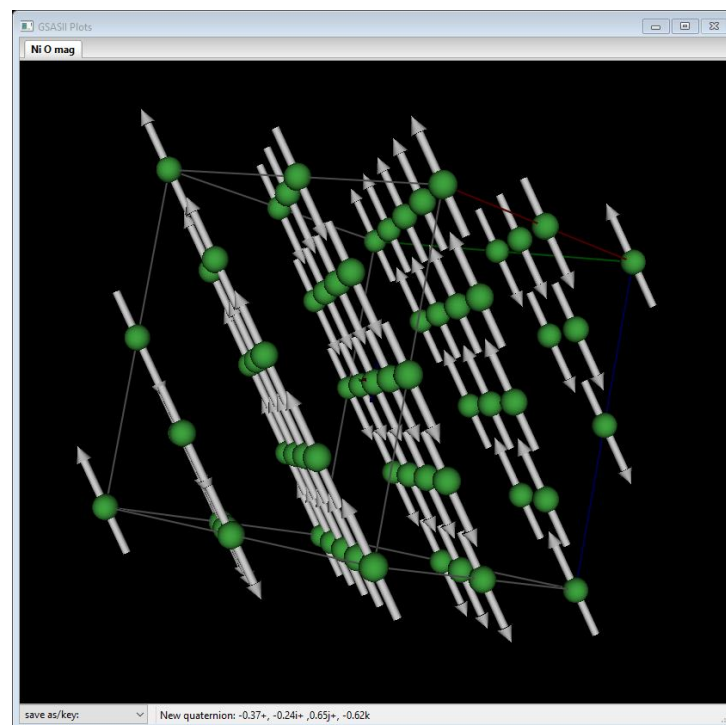
GSAS-II choice: BNS

- OG – Opechowski-Guccione(1965): 1651 unique magnetic space groups in book (Litvin, 2013 available on line from IUCr; NB: >11,000 pages!). 1651 = 1191magnetic+230 gray+230 nonmagnetic groups. For type IV magnetic structures the unit cell does not generate the lattice of magnetic moments & requires fractional hkl for reciprocal lattice.
- BNS – Belov-Neronova-Smirnova(1957): unit cell does generate complete magnetic lattice (e.g. type IV cell doubling with added lattice centering operations); hkl always integers. BNS set in Shubnikov, Belov, et al. book *Colored Symmetry* (1964).
- Stokes & Campbell compiled BNS/OG mag space group data – computer readable (but only std versions & 1st setting).
- GSAS-II allows non-std versions (that can be symbol interpreted, e.g. “F d” – a variant of Cc; something like “R 2/c” won’t work). NB: GSAS-II always uses 2nd setting (inversion @ origin).
- Spin flips → Pnma: Pn’m’a, Pnm’a’, etc. by choice; can be non-std
- Type IV – Transformation tool to new cell & add lattice centering; moves atoms
Pnma: P_anma, P_bnma, P_cnma, etc.

BILBAO MCIF FILES

~2000 structures (Gallego, et al. JAC 49, 1750-1776, 2016)

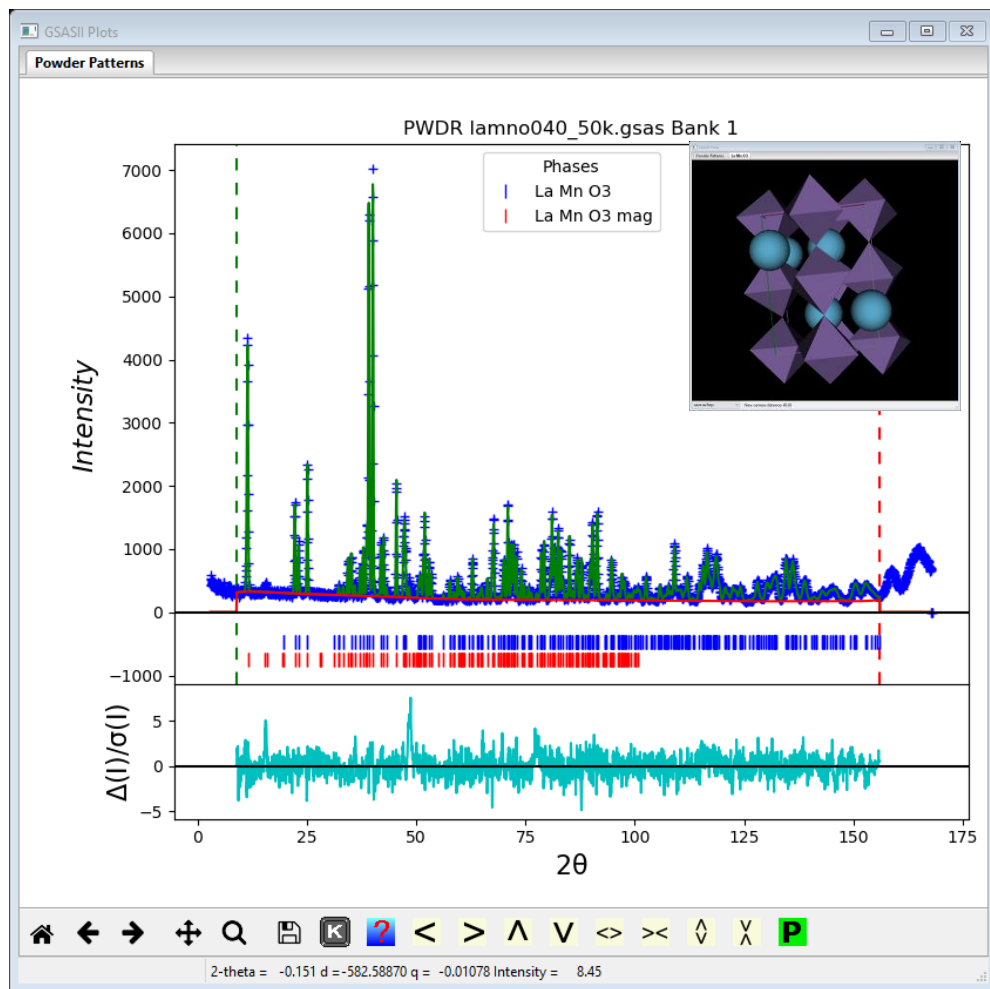
- Tables: zero propagation vector, Type III, Type IV, 2 & 3 propagation vectors, & incommensurate magnetic structures (more later)
- All single phase with Jmol viewer to visualize; full set sym. ops. & lattice centering ops all with “time reversal” (+/- 1) operator; uses BNS system
- Thus, chemical cell & magnetic cell coincident; nonstandard settings (occasionally quite odd, cf. NiO example)
- GSAS-II uses ops (overrides symbol Interpretation) → draw structures & compute powder patterns, etc.
- Magnetic moments – crystal axes components; Bohr magnetons. GSAS-II uses this convention.
NB: old GSAS used Cartesian magnetic moment components



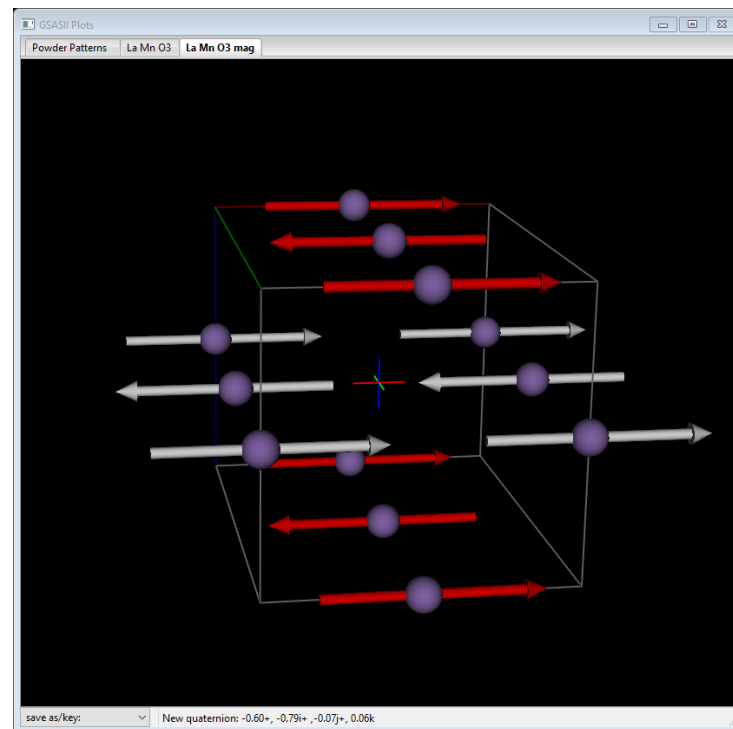
MAGNETIC STRUCTURE ANALYSIS IN GSAS-II

Magnetic Rietveld refinement – 2 phase

- Simple example – LaMnO_3 @50K (NIST- BT1)

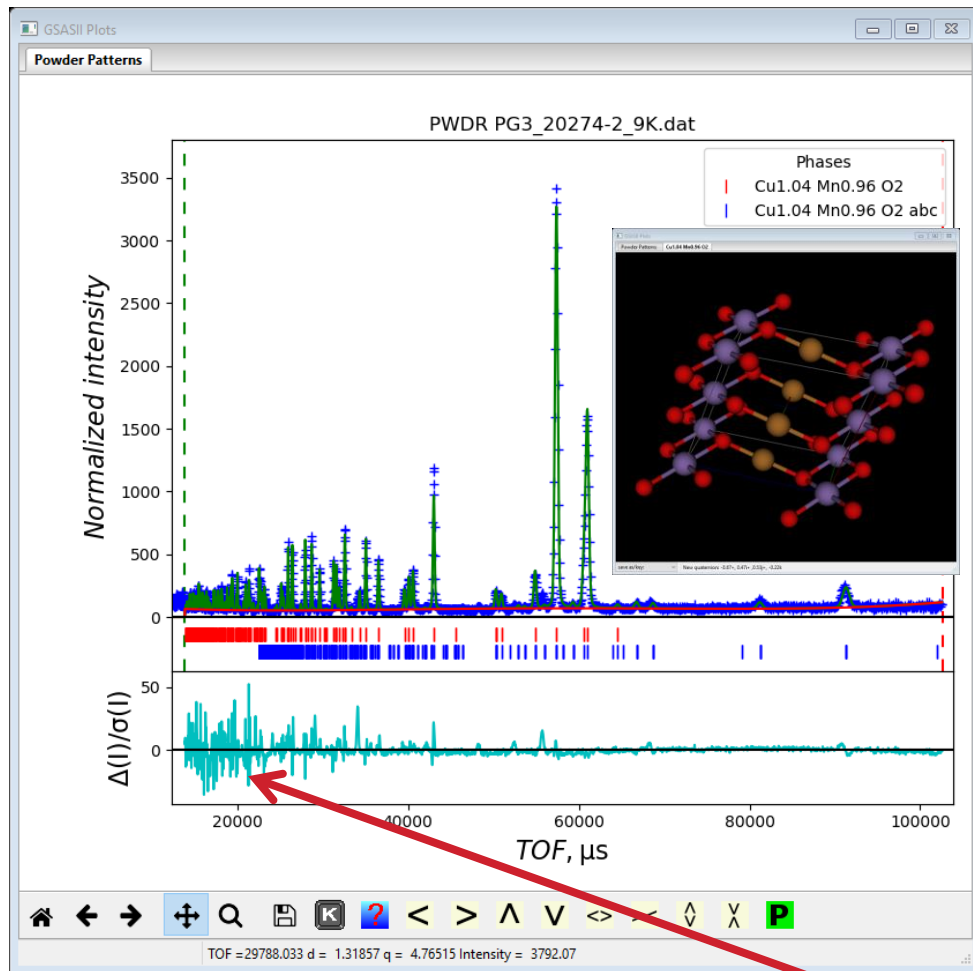


Antiferromagnet $Pn'ma'$
Fe @ 0,0,1/2 M_x, M_y, M_z
allowed but only $M_x > 0$
 $M_x = 3.678(19)\mu_B$



POWGEN DATA EXAMPLE

$\text{Cu}_{1.04}\text{Mn}_{0.96}\text{O}_2$ Type IV antiferromagnet (Bilbao 1.178 similar)

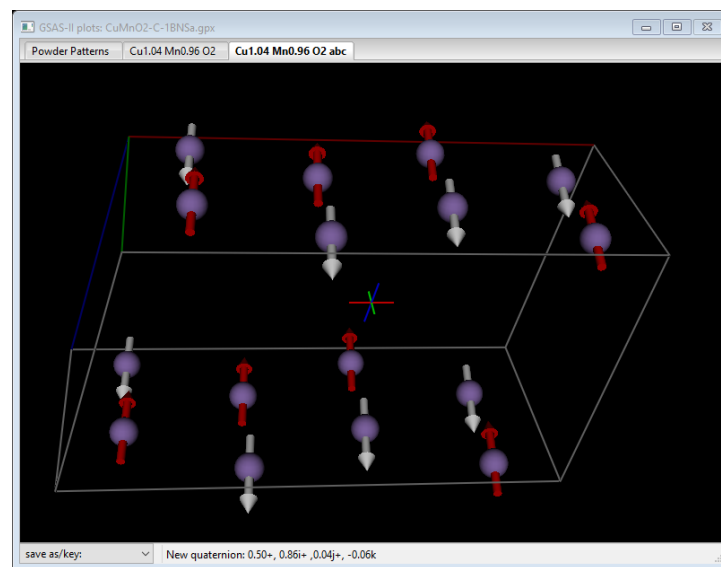


$C2/m$ (Mn @ 0,0,0)

5.554,2.885,5.902,104.354 \rightarrow

$C_a \bar{1}'$ (non-std! not grey!)

11.0866,5.7707,5.902, 90,104.354,90



Shifted Mn atom: @ 1/8,1/8,0:

$M_x, M_y, M_z = 0, 1.925, 0.53$

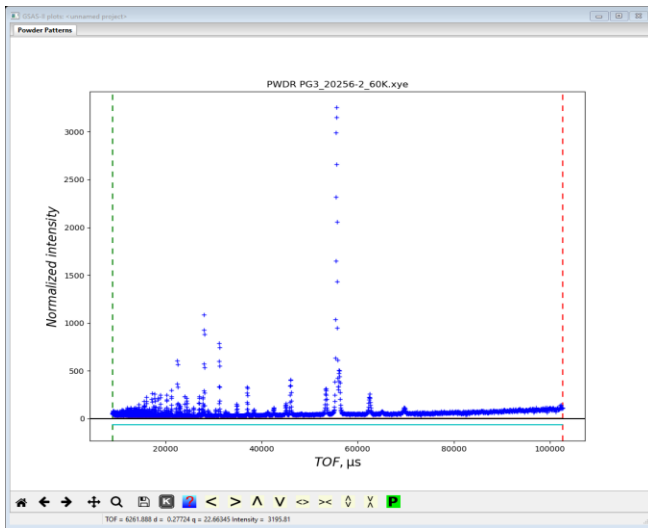
NB: something odd about POWGEN wts?
Similar in LaB_6 fit (V normalization issue)

MAGNETIC STRUCTURE DETERMINATION IN GSAS-II: PRELIMINARIES

START: DATA & CHEMICAL STRUCTURE

Tutorial: Magnetic Structures in GSAS-II – V (most complex case) Mn_3O_4 – hausmannite – POWGEN data

Import data (as topas file; x,y,e table @60K) & import chemical structure (cif file)



Elements	Mn	O
Isotope	Nat. Abund.	Nat. Abund.
No. per cell	12.0	16.0
Atom weight	54.938	15.999
Bond radii	1.54	1.09
Angle radii	1.30	0.89
van der Waals radii	1.70	1.70

not magnetic – do structure refinement 1st → LT chemical structure

NB: cif files sometimes in 1st setting; GSAS-II wants 2nd setting

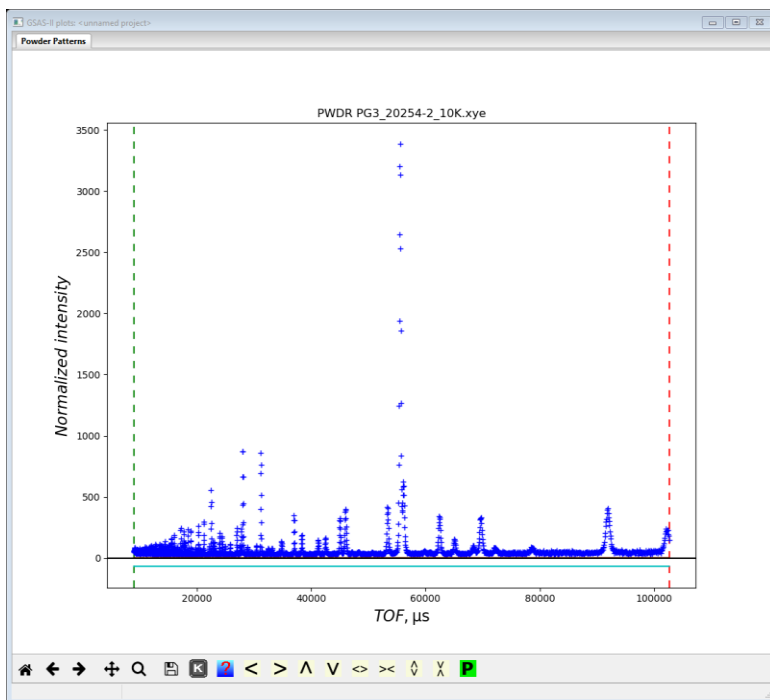
Transformation tool: in menu

Result: in GSAS-II project file *.gpx – use for input to magnetic structure determination

MAGNETIC STRUCTURE OF Mn_3O_4 AT 10K

New GSAS-II project: read in data & chemical structure

POWGEN data & phase from 60K result



Elements	Mn	O
Isotope	Nat. Abund.	Nat. Abund.
No. per cell	12.0	16.0
Atom weight	54.938	15.999
Bond radii	1.54	1.09
Angle radii	1.30	0.89
van der Waals radii	1.70	1.70
Default color		

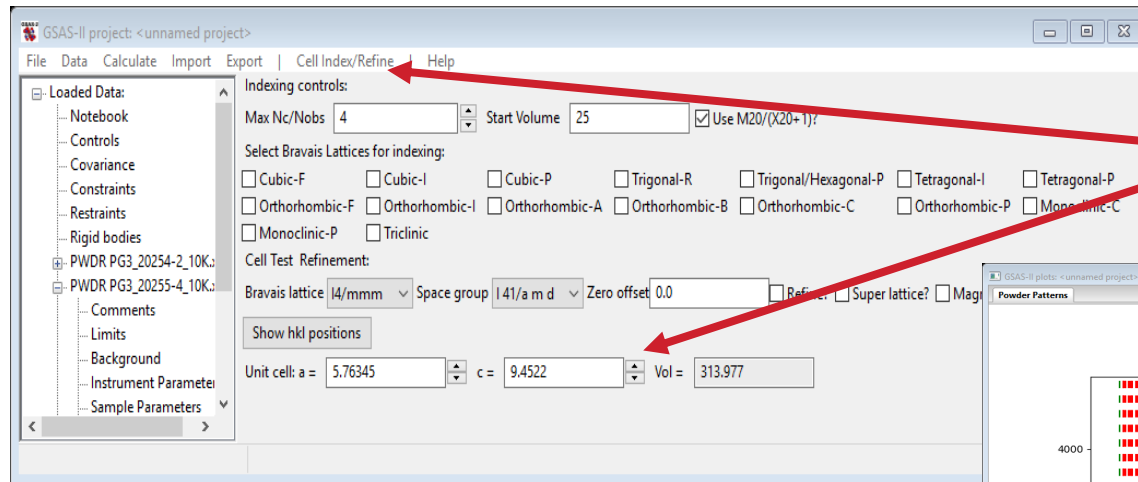
Pawley controls: Do Pawley refinement? Pawley dmin: 1.0 Pawley dmax: 100.0 Pawley neg. wt.: 0.0

NB: this is the chemical phase; magnetic phase added later (with Mn only)

MAGNETIC STRUCTURE PRELIMINARIES

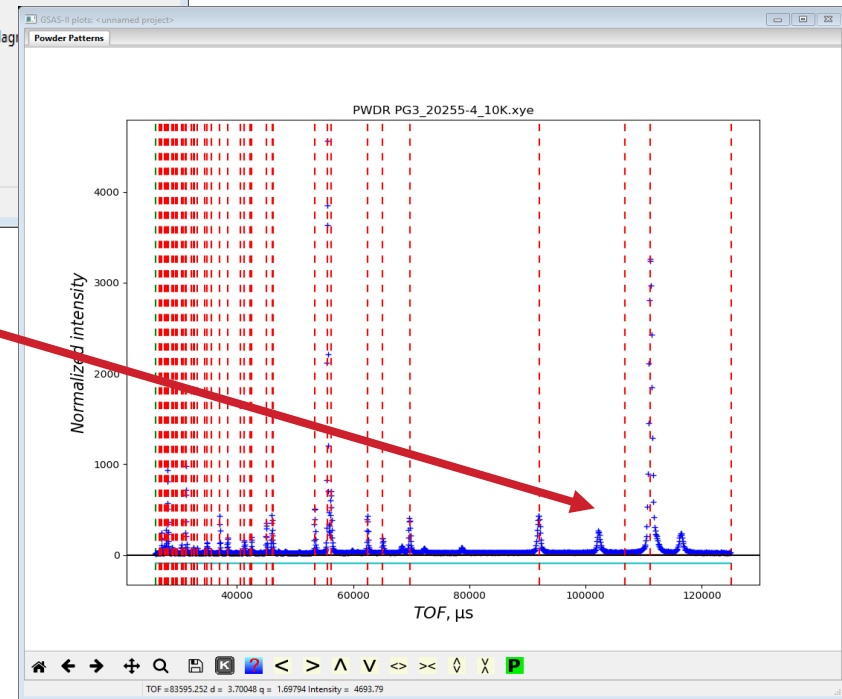
Magnetic lattice & propagation vectors – indexing pattern

Unit Cells List (for the PWDR data set)



Menu:
Load unit cell from phase
& index pattern (I 4/m m m)

Unindexed lines: cell doubling needed
Easily explored here:
Set P4/mmm & double a or b →
Every line indexed
→ 2 propagation vectors suggested
by 2 phase changes from 60K to 10K:
I chose $(0, \frac{1}{2}, 0)$ & $(0, 0, 1)$ –
double b & remove centering



MAGNETIC SPACE GROUP IDENTIFICATION

MAGNETIC SPACE GROUP IDENTIFICATION

Bilbao Crystallographic Server – k-SUBGROUPSMAG

A subgroup of the parent chemical space group as a gray group

k-Subgroupsmag

The program *k-Subgroupsmag* provides the possible magnetic subgroups of the space group of a paramagnetic phase (gray group) which are possible for a magnetic ordering having a known propagation vector. The program provides the set of magnetic subgroups or a graph showing the subgroup-tree (grouped into conjugacy classes). In both cases, more information about the classes or subgroups can be obtained.

Other alternatives for the input of the program:

- An alternative parent (non gray) magnetic group can be chosen.
- Instead of the whole set of subgroups, the output can be limited to subgroups having a chosen common subgroup of lowest symmetry, common point group of lowest symmetry, or groups which belong to a specific crystal class.
- Further restrictions on the subgroup list/graph considering physical properties can be used: it is possible to ask for only centrosymmetric or non-centrosymmetric groups, polar or non-polar groups.
- More than one propagation wave-vector can be chosen.
- The whole (or partial) stars of vectors can be introduced.
- Non magnetic modulation wave-vectors can be also introduced.
- Instead of propagation wave-vectors, a **supercell** can be given. In this case, all subgroups with their lattice defined by the supercell are given, including the gray ones.
- It is possible to ask for a list/graph of subgroups compatible with the intermediate cells between the unit cell of the parent space group and the supercell determined by the given wave vector(s) (or the given supercell when the previous option is used).
- The output can be further refined introducing the Wyckoff positions of the magnetic atoms (and the positions of the non-magnetic atoms for non-magnetic distortions) and/or a set of irreducible representations.

Tutorial: [download](#)

You can find examples of application of this program in:

Perez-Mato, J.M., Gallego, S.V., Elcoro, L., Tasci, E. and Arayo, M.I. *J. of Phys.: Condens Matter* (2016), 28:28601

and in:

J.M. Perez-Mato, S.V. Gallego, E.S. Tasci, L. Elcoro, G. de la Flor, and M.I. Arayo *Annu. Rev. Mater. Res.* (2015), 45:13.1-13.32

See the [Help](#) for details.

Enter the serial number of the space group of the parent paramagnetic phase:

Choose an alternative magnetic group

Alternatively give the operations of the space group in a non-standard setting

Introduce the magnetic wave vector(s)

Alternatively give the basis vectors of the supercell

(Give the components of the wave vectors in a fractional form, n/m)

k_x k_y k_z

Show the independent vectors of the star

Choose the whole star of the propagation vector

Include the subgroups compatible with intermediate cells.
(It is not applied when only the maximal subgroups are calculated)

Optional: refine further the subgroups of the output giving the Wyckoff positions of the atoms

Give the Wyckoff positions

Optional: Show only subgroups that can be the result of a Landau-type transition (single irrep order parameter).

Optional: refine further the subgroups of the output giving a set of irreps

Choose the irreps

Optional: possible limitations of the subgroup list
(Check only one option on the left and the specific value on the right)

Lowest space group to consider

Lowest point group to consider

Lowest crystal system to consider

Only maximal subgroups

Optional: further limitations considering physical properties of the point groups

Only centrosymmetric / non-centrosymmetric groups

Only polar / non-polar groups

List of subgroups Graph of subgroups

Space group number
Alternatively – input operators
Allows nonstd space groups.

Propagation vector(s)

Optional controls –
Limit results

Result as list (or graph)

k-SUBGROUPSMAG RESULT

Full list of possible magnetic space groups – by elimination of operators from parent gray group

E.g. start: $I4_1/amd1'$; $k=(0, \frac{1}{2}, \frac{1}{2})$

Input data

Subgroups of the paramagnetic space group : $I4_1/amd1'$ (N. 141)
 Lowest magnetic space group to consider: $P1$ (N. 1.1)
 Magnetic propagation wave-vectors: (0, 5, 5)

List of subgroups that fulfill the given conditions

Get the subgroup-graph

N	Group Symbol	Transformation matrix	Group-Subgroup index	Other members of the Conjugacy Class	irreps	Magnetic structure models (MAGMODELIZE)
1	C_2/c (No. 15.90)	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 1 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	<input type="checkbox"/>
2	C_2/c (No. 15.90)	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 1 & 0 & 2 & 1/2 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	<input type="checkbox"/>
3	C_2/m (No. 12.63)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 1/2 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	<input type="checkbox"/>
4	C_2/m (No. 12.63)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	<input type="checkbox"/>
5	C_2c (No. 9.40)	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 1 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	<input type="checkbox"/>
6	C_2m (No. 8.35)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	<input type="checkbox"/>
7	C_2 (No. 5.16)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 1/2 \\ -1 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	<input type="checkbox"/>
8	C_2 (No. 5.16)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	<input type="checkbox"/>
9	P_21 (No. 2.7)	$\begin{pmatrix} 1/2 & -1/2 & 1 & 0 \\ 1/2 & 1/2 & 1 & 0 \\ -1/2 & -1/2 & 1 & 1/2 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	<input type="checkbox"/>
10	P_21 (No. 2.7)	$\begin{pmatrix} 1/2 & -1/2 & 1 & 0 \\ 1/2 & 1/2 & 1 & 0 \\ -1/2 & -1/2 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	<input type="checkbox"/>
11	P_21 (No. 1.3)	$\begin{pmatrix} 1/2 & -1/2 & 1 & 0 \\ 1/2 & 1/2 & 1 & 0 \\ -1/2 & -1/2 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	32=2x16	Conjugacy Class	Get irreps	<input type="checkbox"/>

Select/Deselect all subgroups
 Include structure data of the parent phase

Submit selected subgroups to MAGMODELIZE:

**Hint: Submit many subgroups to MAGMODELIZE, when the 'include structure' option is selected, may take too long*

Input data

Subgroups of the paramagnetic space group : $I4_1/amd1'$ (N. 141)
 Lowest magnetic space group to consider: $P1$ (N. 1.1)
 Magnetic propagation wave-vectors: (0, 5, 5)

4 Maximal subgroups

Graph of subgroups that fulfill the given conditions

Get the full list of subgroups

More options

Graph made using Graphviz
 Download a postscript file

Get information about the groups of the conjugacy class with label

Get the subgraph between the group (or conjugacy class) with label and the group (or conjugacy class) with label according to these rules

Bilbao Crystallographic Server
<http://www.cryst.ehu.es>

For comments, please mail to administrador.bcs@ehu.es

Intended process: use symbol (or operators) & transformation matrix/vector & try against data. Tools for structure input → test for allowed mag. moments

GSAS-II \leftrightarrow k-SUBGROUPSMAG

Direct call & data retrieval from web page table in Python
 Example: Mn_3O_4 “hausmannite” at 10K – Type IV magnetic structure

GSAS-II + I4₁/amd

k-SUBGROUPSMAG options

k-vector 1: 0 1/2 0
 k-vector 2: 0 0 1
 k-vector 3: [] [] []

Use whole star:

Filter by: []

preserve axes:

test for mag. atoms: Mn

all have moment:

max unique: 100

Ok Cancel



Send request

Bilbao site
www.cryst.ehu.es/cgi-bin/programs/subgmag1_general_GSAS.pl

Makes html table of magnetic space subgroups, etc.

GSAS-II project: Mn3O4 10K - Copy.gpx

Project: Mn3O4 10K - Copy.gpx

Indexing controls: Max Nc/Nobs: 4 Start Volume: 25 Use M20(020-1)?

Select Bravais Lattices for indexing: Cubic-F Cubic-I Cubic-P Trigonal-R Trigonal/Hexagonal-P Tetragonal-I Tetragonal-P Orthorhombic-F Orthorhombic-I Orthorhombic-A Orthorhombic-B Orthorhombic-C Orthorhombic-P Monoclinic-P Monoclinic-C Triclinic

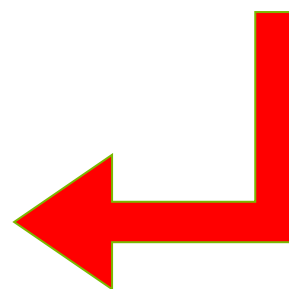
Rigid bodies: Monoclinic-P Triclinic

Cell Test Refinement: Bravais lattice: I4₁/mnm Space group: I4₁/a m d Zero offset: 0.0 Refine? Modulated? Magnetic?

Show hkl positions: Unit cell a = 5.76345 c = 1.4532 Vol = 313.977

Magnetic subgroup cells from Bilbao k-SUBGROUPSMAG for I4₁/a m d, kvec1=(0,1/2,0), kvec2=(0,0,1):

	Space Grp	Try	Keep	Uniq	nCons	nSnp	Trans	Vec	a	b	c	alpha	beta	gamma	Volume
1	Pbn'a'	<input checked="" type="checkbox"/>	<input type="checkbox"/>	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
2	Pbn'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
3	Pbn'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4	2	1	-a,-2b,c	0,1/2,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
4	Pbn'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4	2	1	-a,-2b,c	0,1/2,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
5	Pbn'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
6	Pbn'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
7	Pbn'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4	2	1	-a,-2b,c	0,1/2,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
8	Pbn'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
9	Pm'm'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
10	Pm'm'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
11	Pm'm'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
12	Pm'm'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
13	Pm'm'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
14	Pm'm'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
15	Pm'm'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
16	Pm'm'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95



Return result
 205 subgroups!
 64 maximal subgroups!

RESULT FROM k-SUBGROUPSMAG (GSAS)

205 possible magnetic space subgroups (64 maximal) for $I4_1/amd$ & $k=(0, \frac{1}{2}, 0) + (0, 0, 1)$

GSAS-II project: Mn3O4 10K - Copy.gpx

File Data Calculate Import Export Cell Index/Refine Help

Project: Mn3O4 10K - Copy.gpx

Indexing controls:
Max Nc/Nobs: 4 Start Volume: 25 Use M20/(X20+1)?

Select Bravais Lattices for indexing:
 Cubic-F Cubic-I Cubic-P Trigonal-R Trigonal/Hexagonal-P Tetragonal-I Tetragonal-P
 Orthorhombic-F Orthorhombic-I Orthorhombic-A Orthorhombic-B Orthorhombic-C Orthorhombic-P Monoclinic-C
 Monoclinic-P Triclinic

Cell Test Refinement:
Bravais lattice: $I4_1/mmd$ Space group: $I4_1/amd$ Zero offset: 0.0 Refine? Modulated? Magnetic?

Show hkl positions

Unit cell: a = 5.76345 c = 9.4522 Vol = 313.977

Magnetic subgroup cells from Bilbao k-SUBGROUPSMAG for $I4_1/amd$; $kvec1=(0, 1/2, 0)$, $kvec2=(0, 0, 1)$:

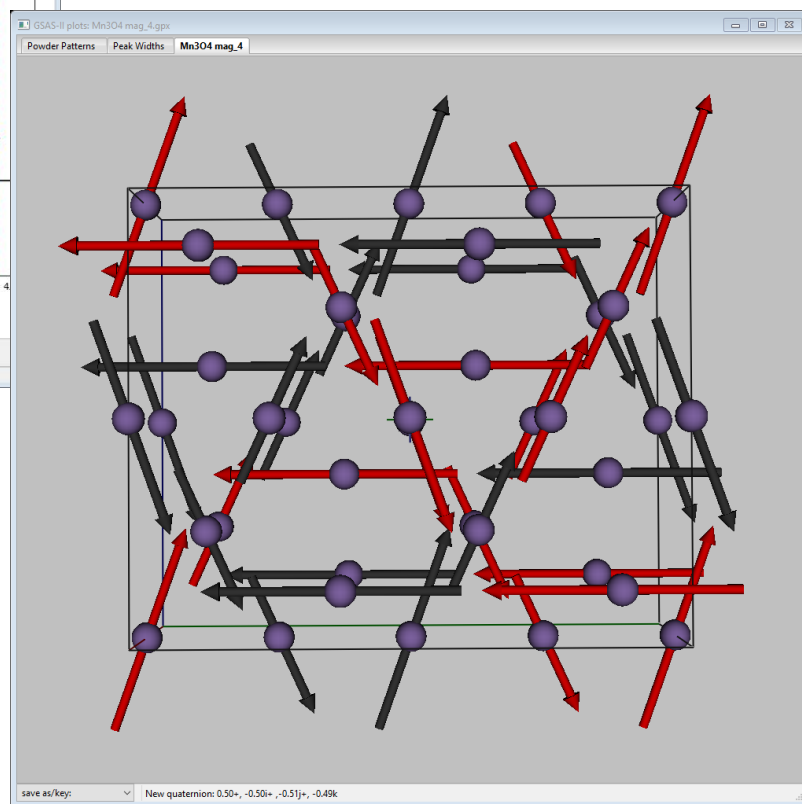
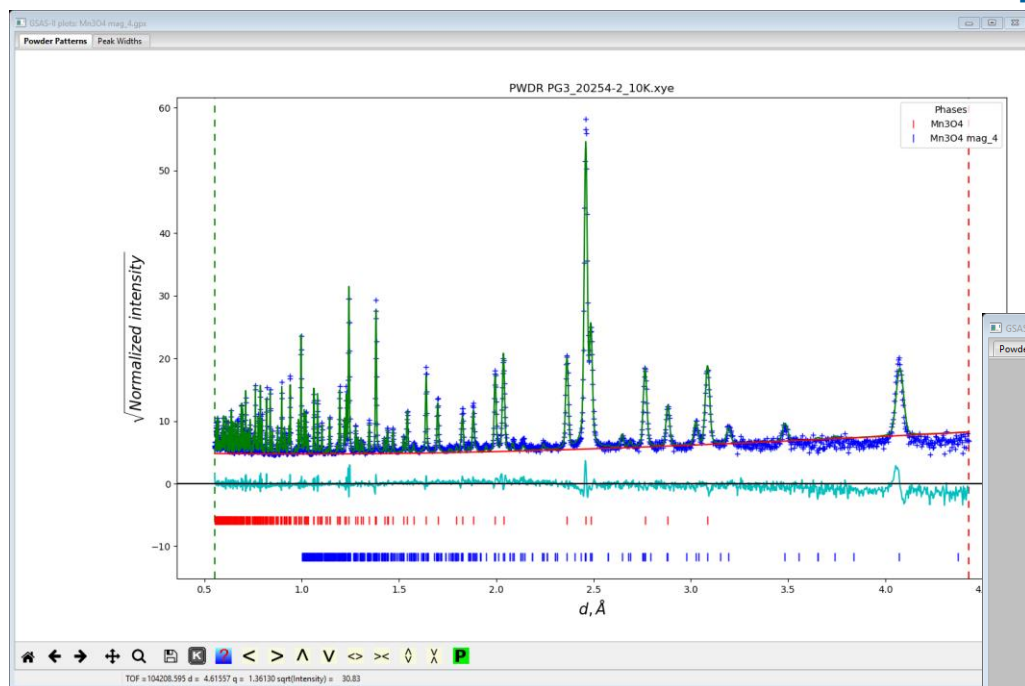
	Space Gp	Try	Keep	Uniq	nConj	nSup	Trans	Vec	a	b	c	alpha	beta	gamma	Volume
1	Pb'n'a'	<input checked="" type="checkbox"/>	<input type="checkbox"/>	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
2	Pbn'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
3	Pb'n'a	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4	2	1	-a,2b,-c	0,1/2,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
4	Pb'na'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4	2	1	-a,2b,-c	0,1/2,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
5	Pbn'a	<input type="checkbox"/>	<input type="checkbox"/>	4	2	1	a,-2b,-c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
6	Pb'na	<input type="checkbox"/>	<input type="checkbox"/>	4	2	1	a,-2b,-c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
7	Pbna'	<input type="checkbox"/>	<input type="checkbox"/>	4	2	1	-a,-2b,c	0,1/2,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
8	Pbna	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
9	Pm'm'n'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
10	Pm'mn'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
11	Pmm'n'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
12	Pm'm'n	<input type="checkbox"/>	<input checked="" type="checkbox"/>	7	2	1	a,2b,c	1/4,1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
13	Pmmn'	<input type="checkbox"/>	<input type="checkbox"/>	7	2	1	a,2b,c	1/4,1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
14	Pmm'n	<input type="checkbox"/>	<input type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
15	Pm'mn	<input type="checkbox"/>	<input type="checkbox"/>	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95

Mouse RB drag/drop to reorder Double click Keep to refresh Keep flags; click Space Gp to see sym. ops, Uniq to see unique atoms list; Try to trigger K & J keys on plot

Only 4 have all Mn with moment & minimal no. of Mn sites(4) – try each one
Selection creates magnetic phase; refine moments: best is Pb'na' (#4)

MAGNETIC STRUCTURE OF Mn_3O_4 AT 4K

Data from SNS/POWGEN – 2 frames; $R_{wp} \sim 15\%$



3 intersecting ferromagnetically coupled sets of moments – overall antiferromagnet
Agrees with Jensen, J.B. & Nielsen, O.V. J. Phys. C: Solid State Phys. (1974), 7, 409-424 except that mag space group is now identified as $\text{Pb}'na'$.

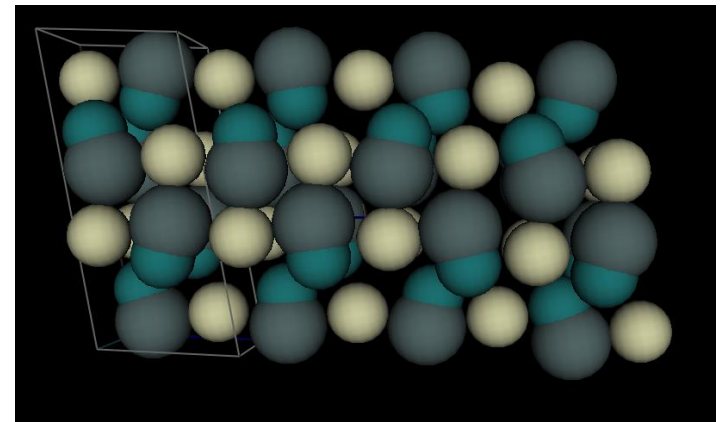
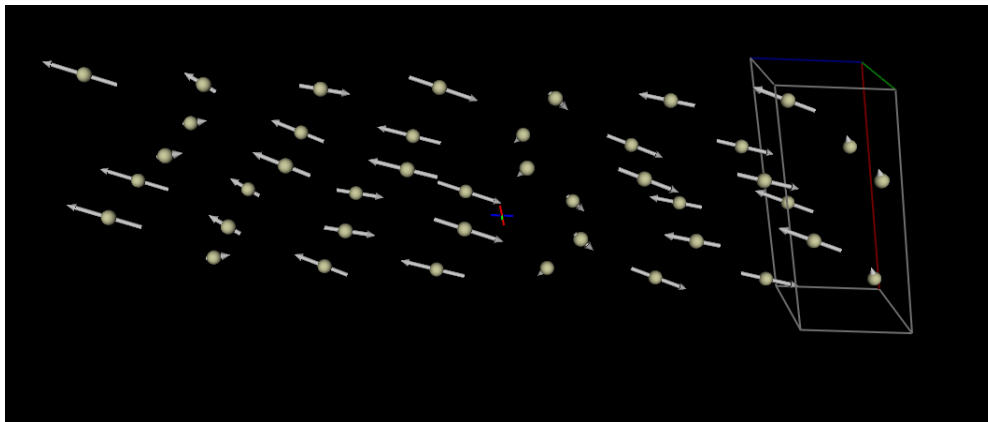
CONCLUSION

LINK: GSAS-II \leftrightarrow k-SUBGROUPSMAG

Magnetic structure solution made easy

- Process now in a few minutes
- No mystery (no irreps)
- Gives optimal result with correct magnetic space group
- Internet access required – connect to Bilbao Crystallographic Server
- Similar approach for structural phase transitions (NB: 2nd order) also now in GSAS-II
- Under construction: incommensurate structure analysis

E.g. CeRuSn – Ce moment & structure modulation – movies by GSAS-II



THANK YOU