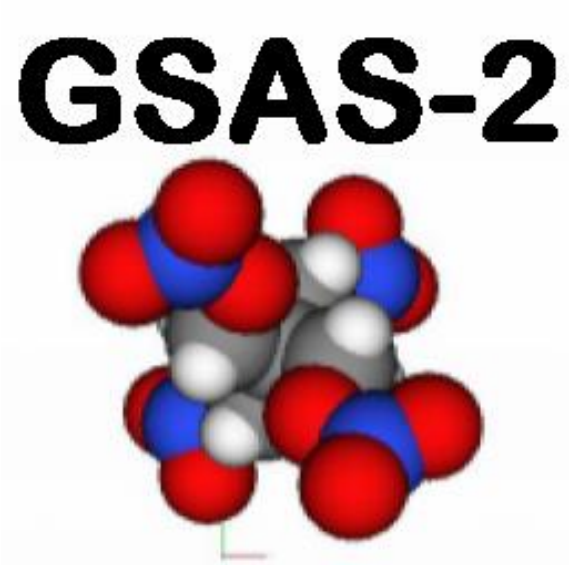
SYSTEMATIC DETERMINATION OF MAGNETIC STRUCTURES DRIVEN BY SPACE GROUPS IN GSAS-II



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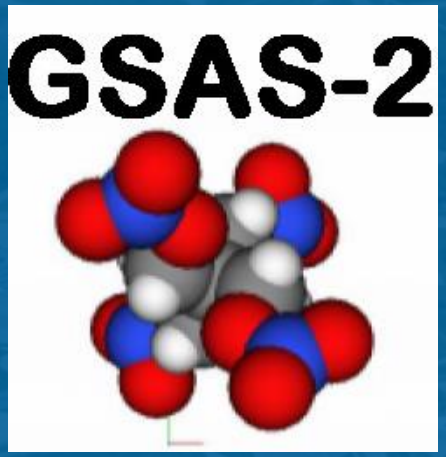
THANKS TO: BRIAN TOBY, J.M. PEREZ-MATO & COWORKERS

Oak Ridge, June 5, 2023

GSAS-II



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

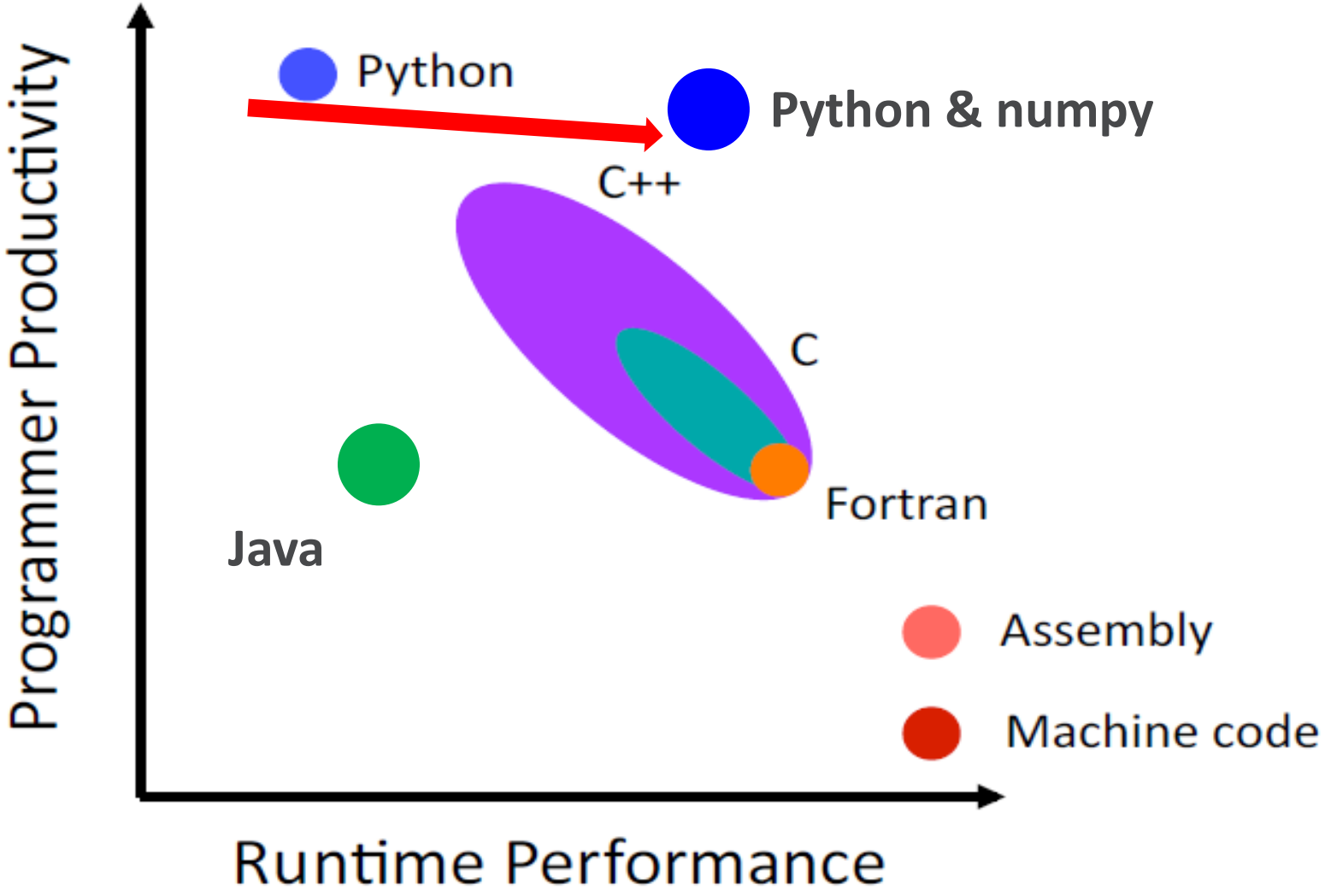
GSAS-II is intended to more than replace GSAS & EXPGUI with a new, modern, extensible, and *open-source* crystallographic analysis code

- 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
```

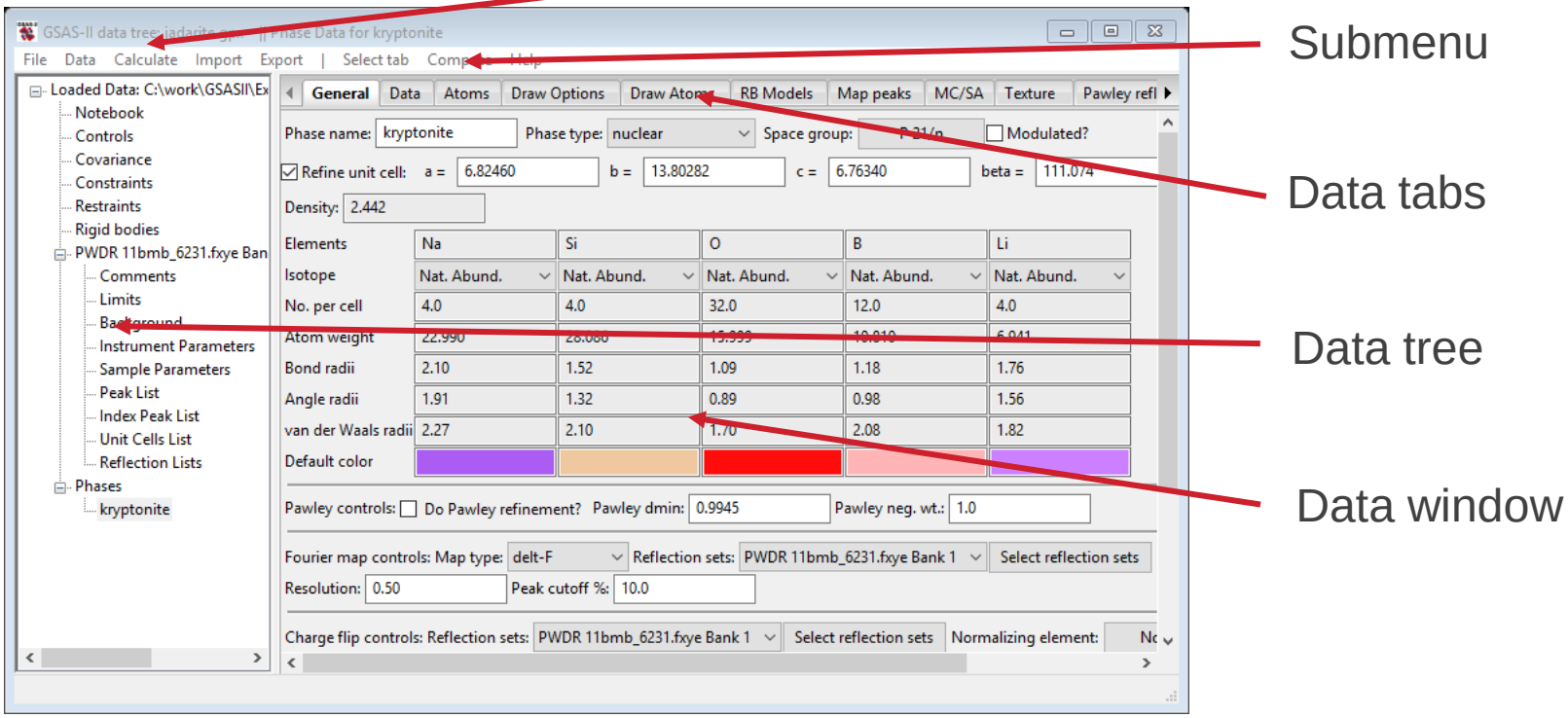
NB: the 4D version is almost identical except that F_{hklm} is used

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

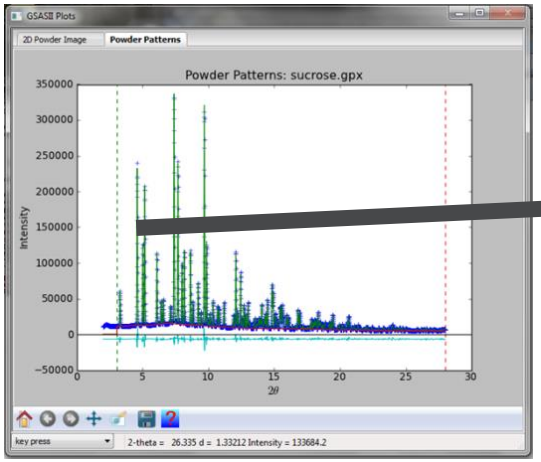
GSAS-II: modern GUI – 2 frames + console

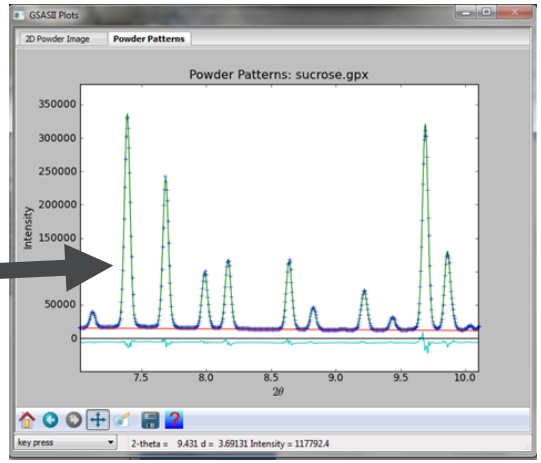


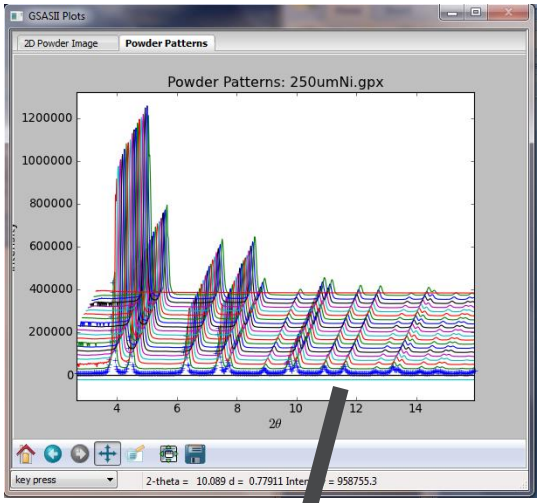
Plot & console in separate frames

THE PLOTS - ADVANCED VISUALIZATION

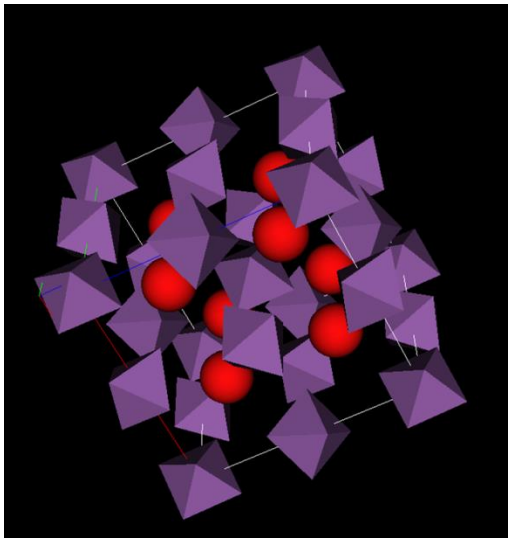
Powder profile – easy zoom



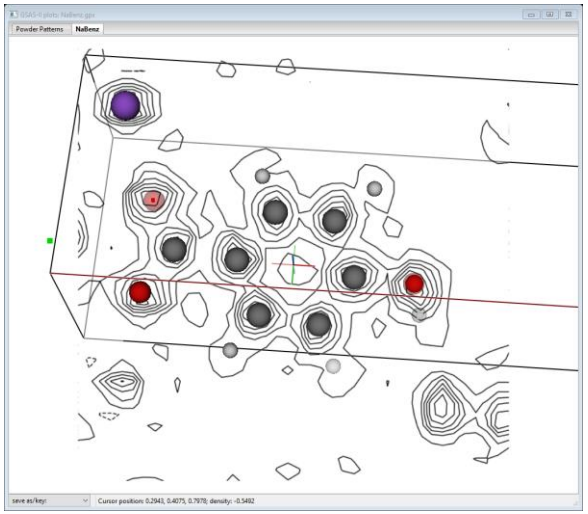




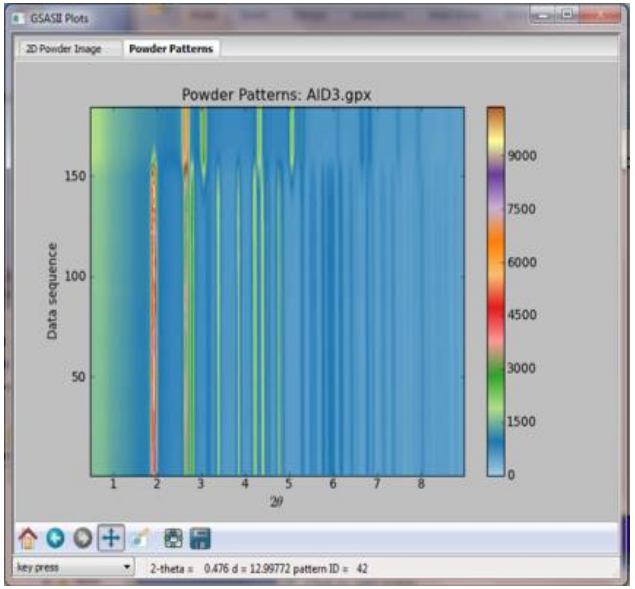
Waterfall plot



Structure drawing



contoured density thru any plane



Contour plot

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INTRODUCTION TO MAGNETISM IN GSAS-II

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MAGNETISM – SOME BASICS

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

Nuclear structure factor Magnetic structure factor

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

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

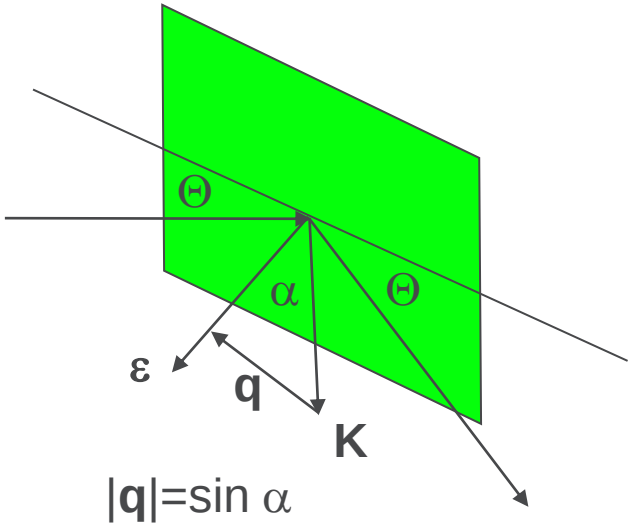
The p's & q's? (after Bacon, 1975)

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

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

$\boldsymbol{\varepsilon}_\mathbf{h}$ – *unit vector* || **h** – diffraction vector
$\mathbf{K}_m$ – *unit vector* || *magnetic moment on atom m*
$\therefore$ **q** *small for* **h** || ***K*** *& large for* **h** $\perp$ **K**

0.539x10^{-12}cm – similar to b_n
e – electron charge
γ *– neutron magnetic moment*
m_N *– neutron mass*
c – speed of light



|**q**|=sin α

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.)

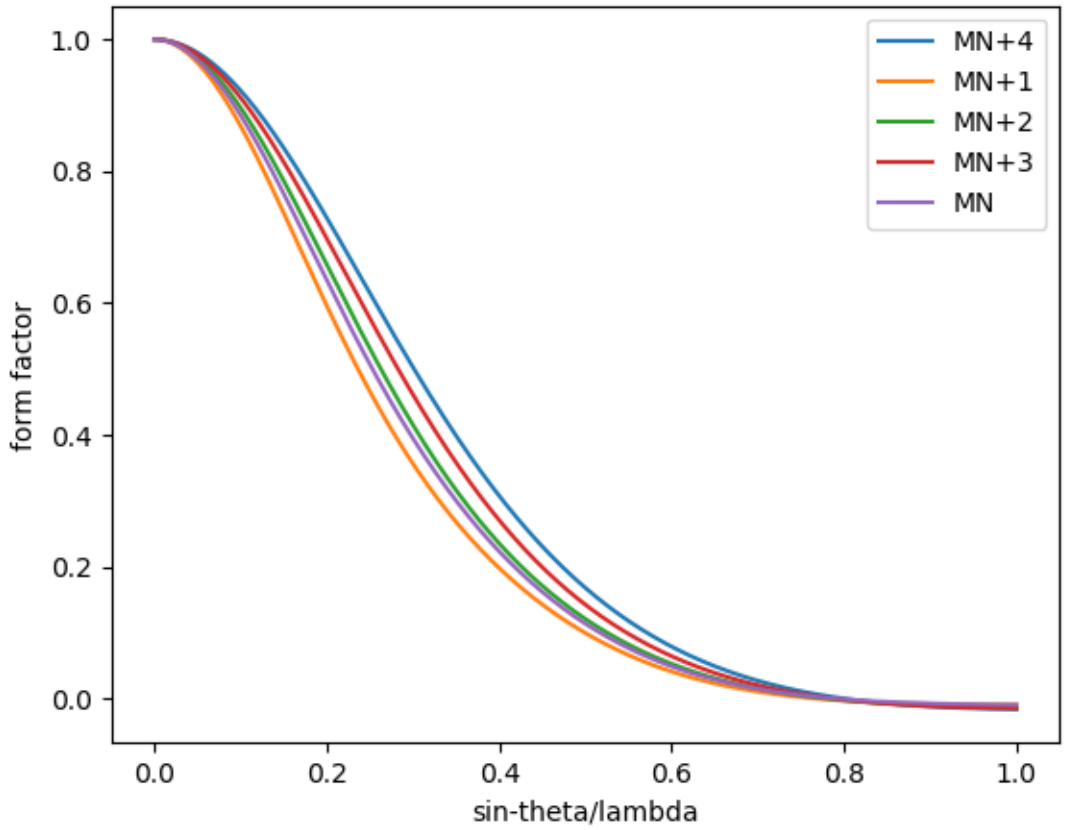
In GSAS-II:
Form factor coefficients <j_0> and <j_2> (higher terms ignored)

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

Landé g factor = 2 for 1st row transition elements:
quenched orbital contribution
In general f_m → 0 for sinΘ/λ > 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:

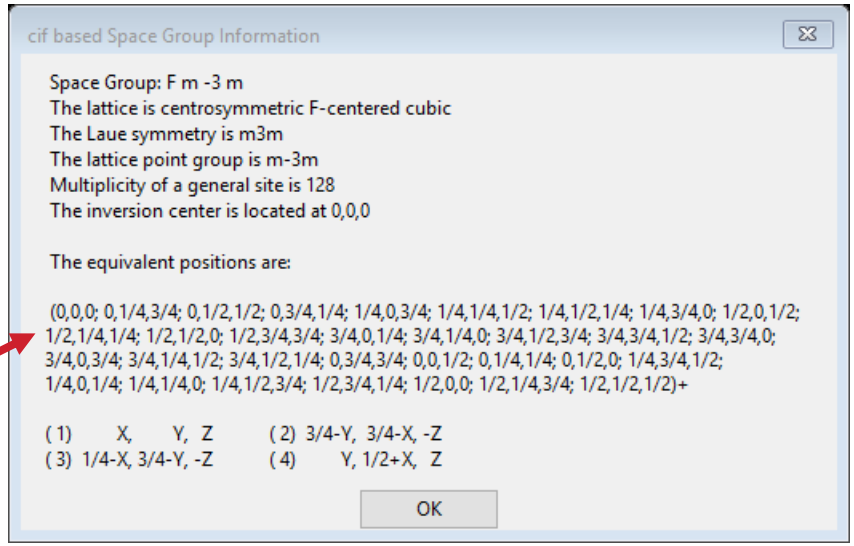
Import Bilbao magnetic cif files:

operators from mcif file

(fixed – can't change 'em)

Occasionally peculiar:

NiO mcif has 32 centering ops!



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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 hkls 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

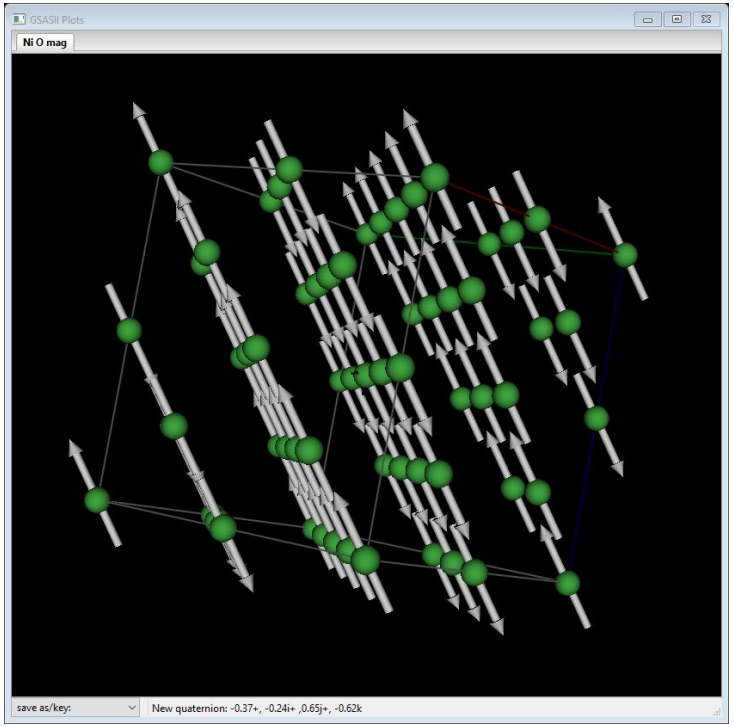
  Pnma: $P_a$nma, $P_b$nma, $P_C$nma, etc.

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.

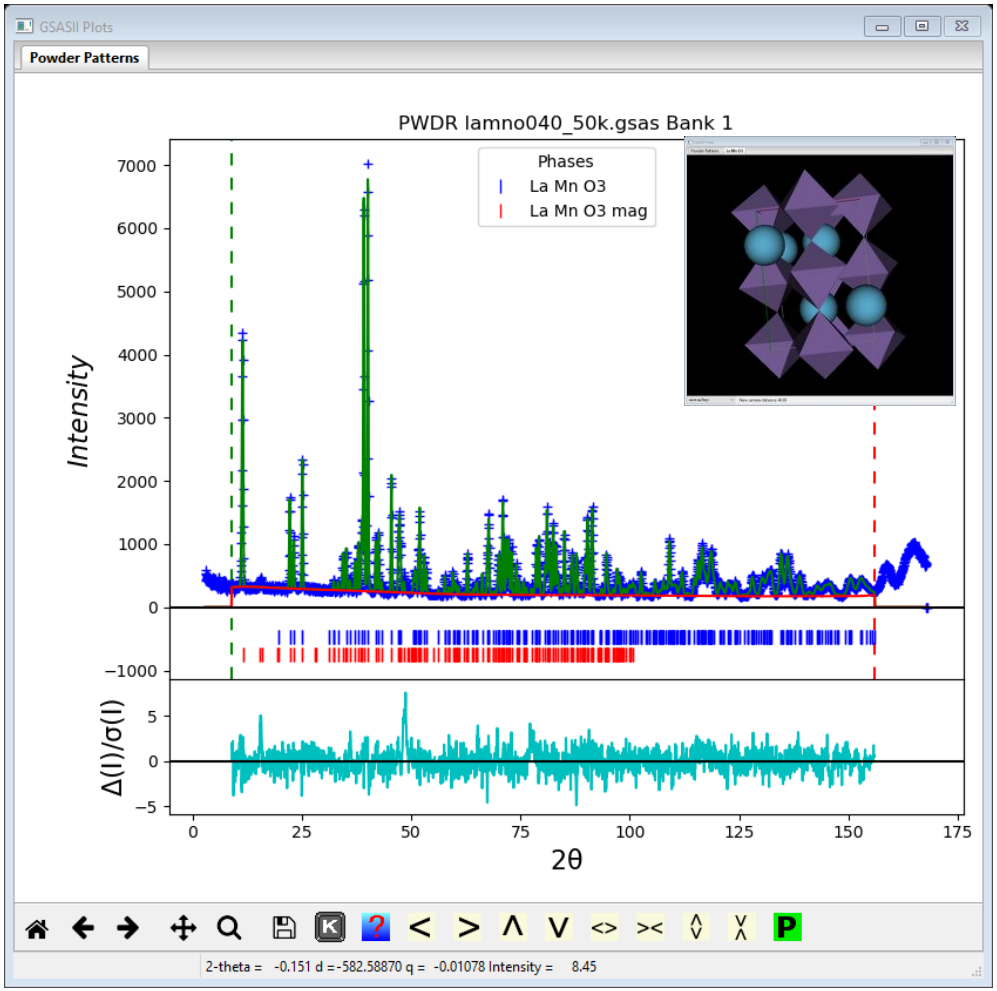
NB: old GSAS used Cartesian magnetic moment components



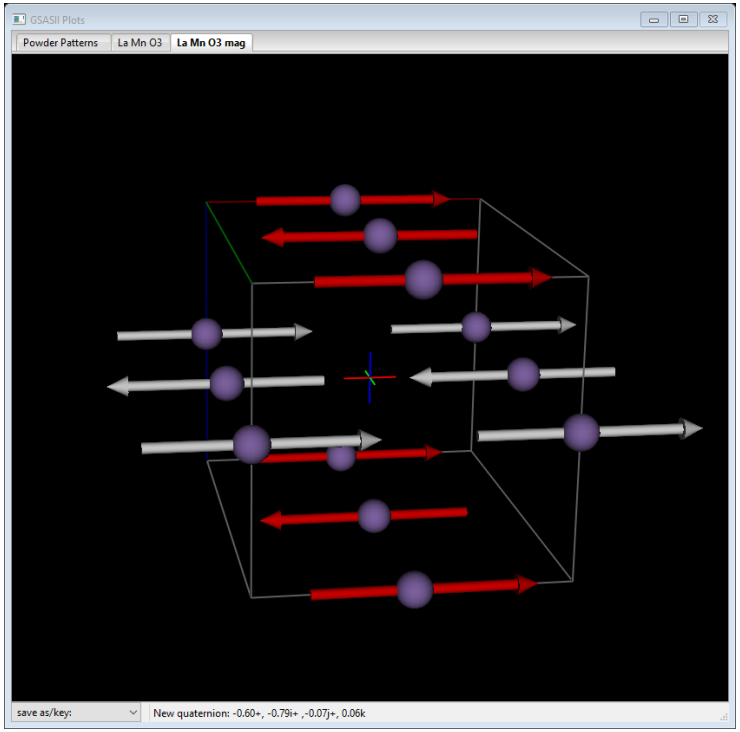
MAGNETIC STRUCTURE ANALYSIS IN GSAS-II

Magnetic Rietveld refinement – 2 phase

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



Antiferromagnet Pn'ma'
Fe @ 0,0,1/2 Mx,My,Mz
allowed but only Mx >0
Mx=3.678(19)μ_B



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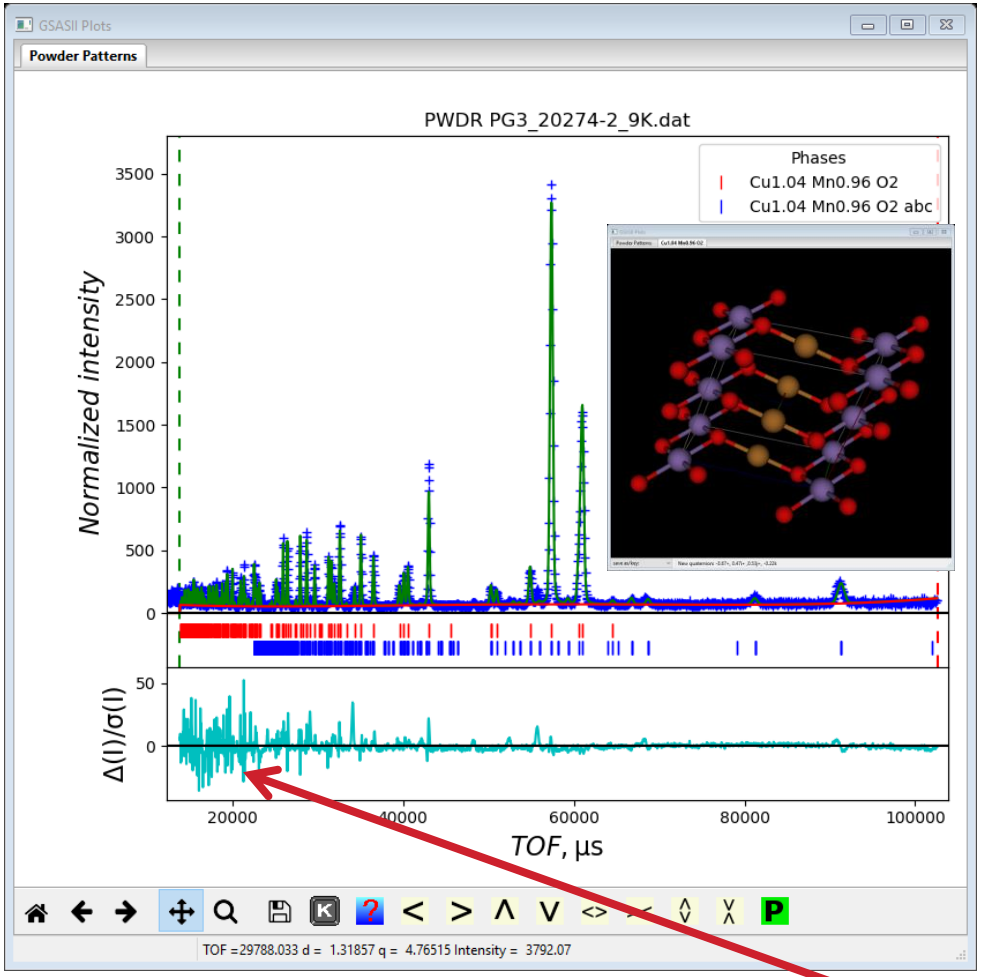
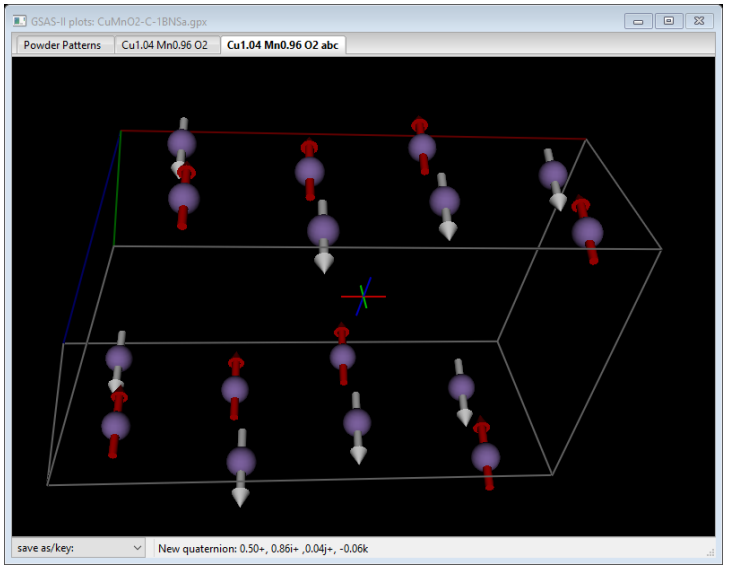
POWGEN DATA EXAMPLE

$Cu_{1.04}Mn_{0.96}O_2$ Type IV antiferromagnet (Bilbao 1.178 similar)



C2/m (Mn @ 0,0,0)
5.554,2.885,5.902,104.354→
$C_a\bar{1}$' (non-std! not grey!)
11.0866,5.7707,5.902, 90,104.354,90



Shifted Mn atom: @ 1/8,1/8,0:
Mx,My,Mz=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

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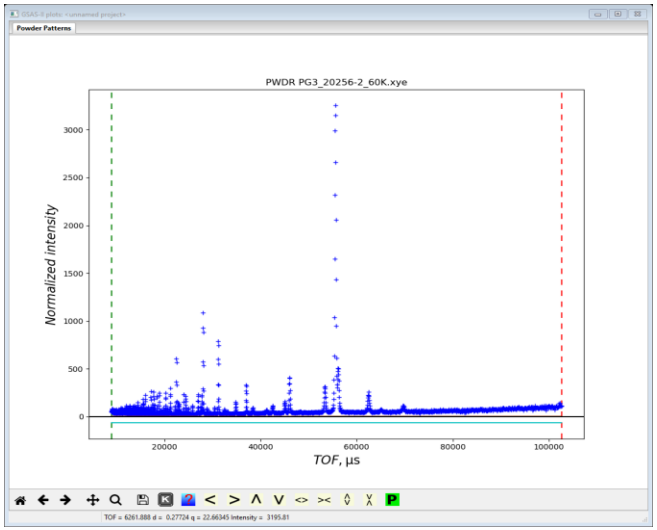
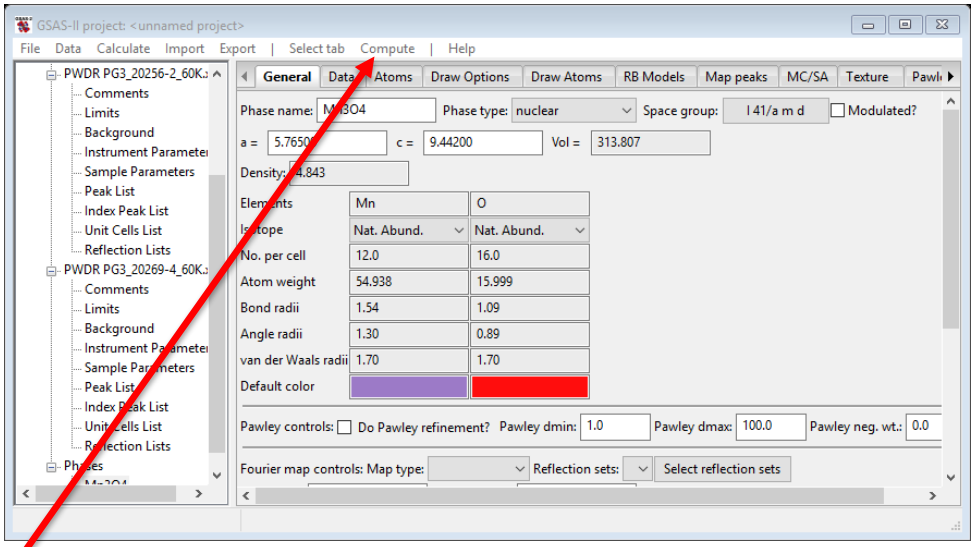
START: DATA & CHEMICAL STRUCTURE

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)



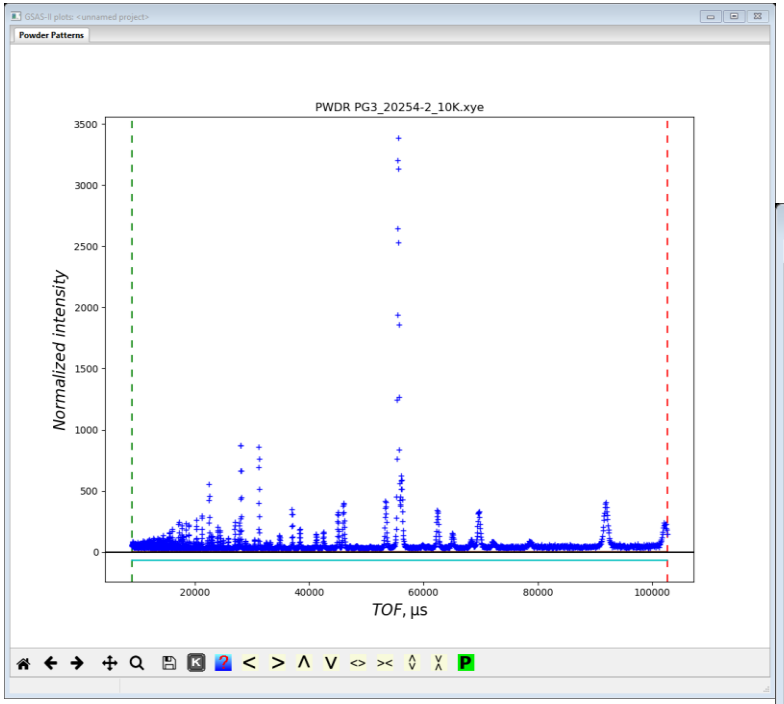


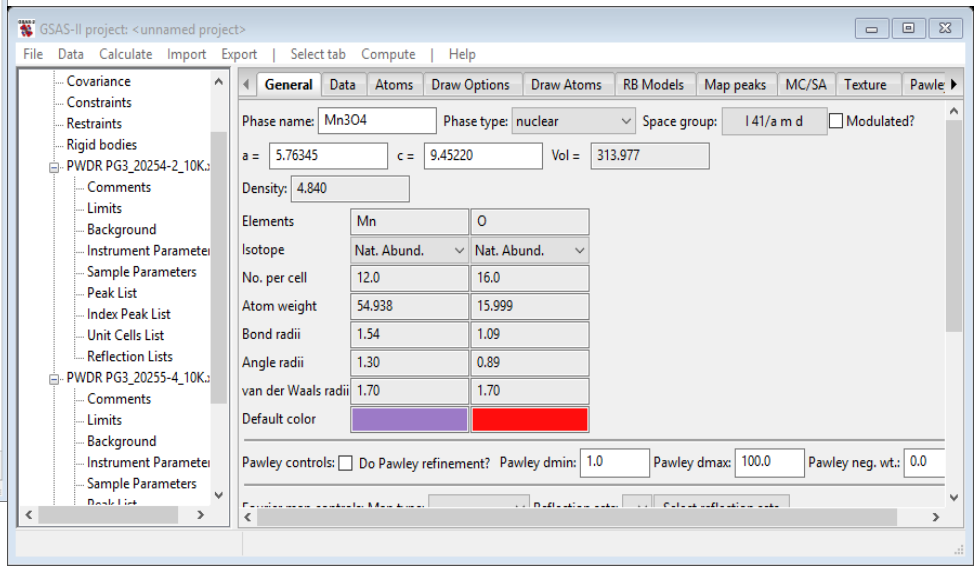
not magnetic – do structure refinement 1st → LT chemical structure
NB: cif files sometimes in 1st setting; GSAS-II wants 2nd setting
Transformation tool: in menu
Result: in GSAS-II project file *.gpx – use for input to magnetic structure determination

MAGNETIC STRUCTURE OF Mn_3O_4 AT 10K

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

POWGEN data & phase from 60K result



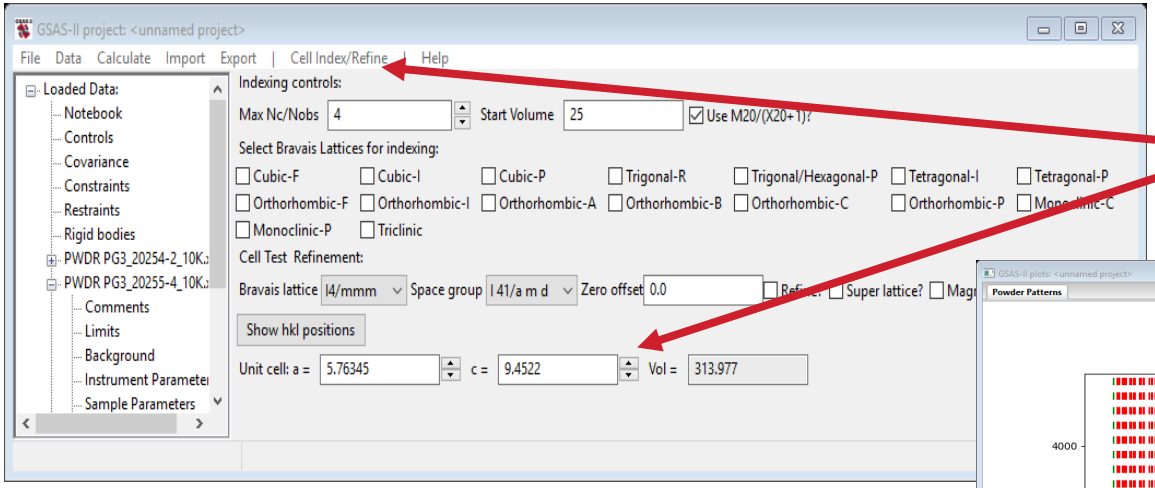


NB: this is the chemical phase; magnetic phase added later (with Mn only)

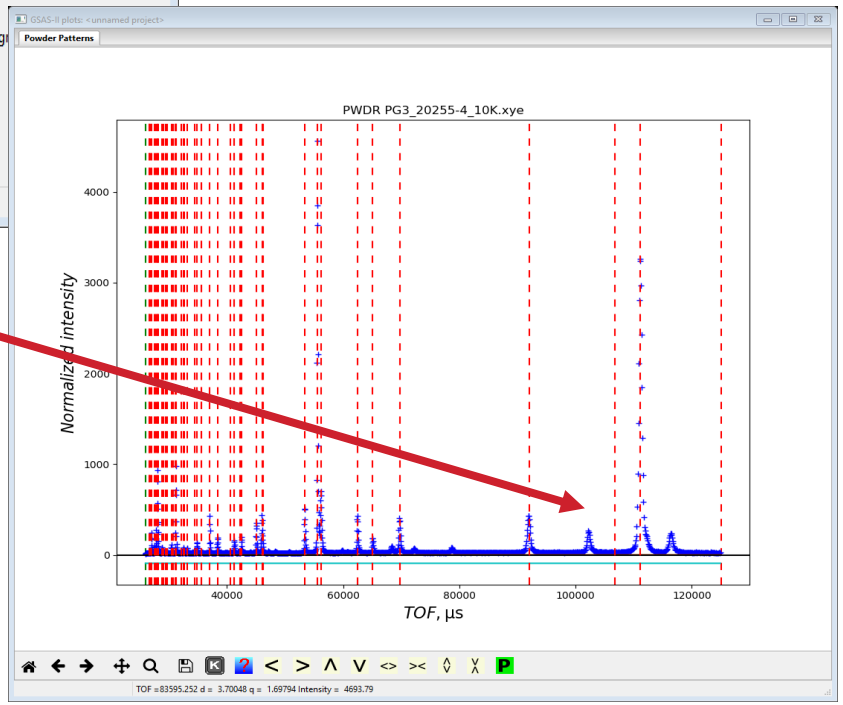
MAGNETIC STRUCTURE PRELIMINARIES

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 (0,½,0) & (0,0,1) –
double b & remove centering

MAGNETIC SPACE GROUP IDENTIFICATION

MAGNETIC SPACE GROUP SELECTION

Need exhaustive list that are subgroups of parent grey group

Magnetic space group is from loss of symmetry
Parent: I 4_1/amd1' → 128 operations!

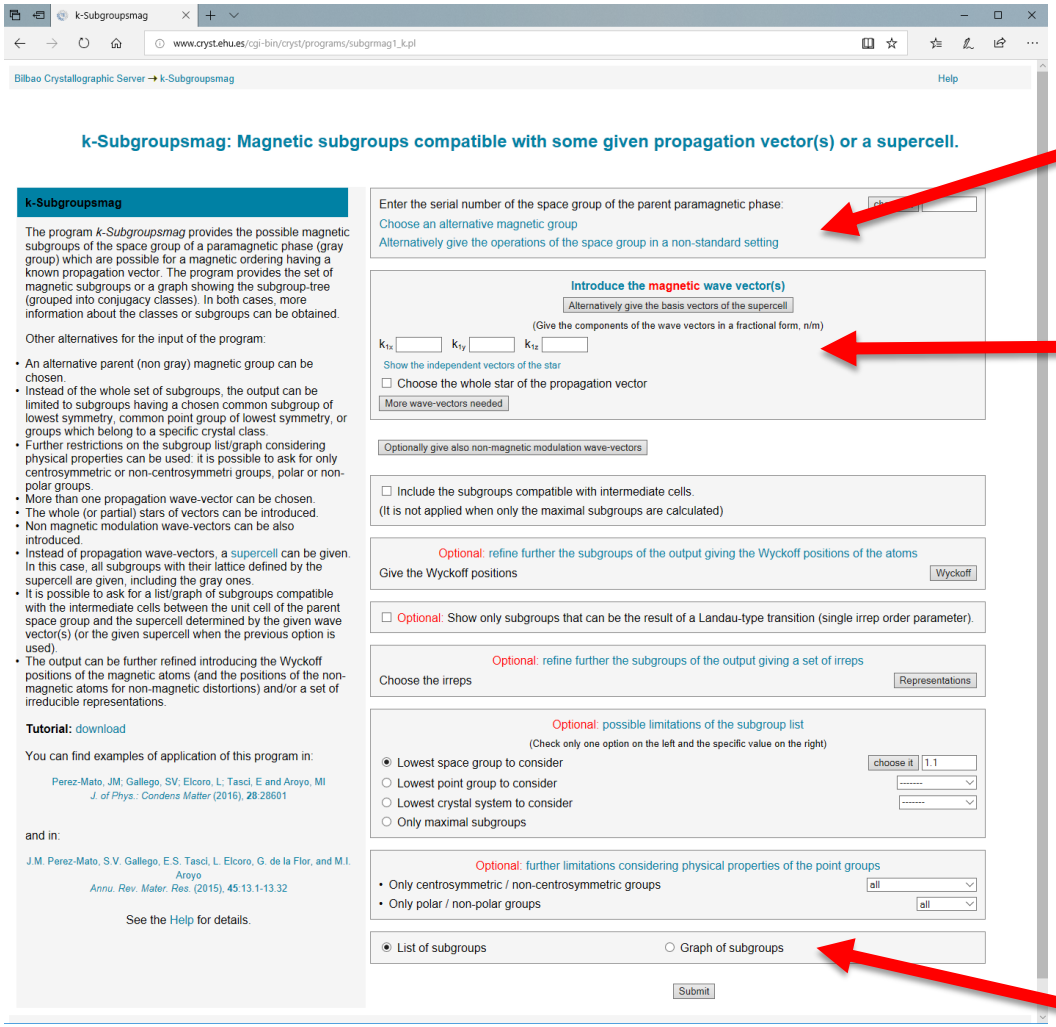
x,y,z	x+1/2,y+1/2,z+1/2	x,y,z	x+1/2,y+1/2,z+1/2
-y+1/4,x+3/4,z+1/4	-y+3/4,x+1/4,z+3/4	-y+1/4,x+3/4,z+1/4	-y+3/4,x+1/4,z+3/4
-x+1/2,-y,z+1/2	-x,-y+1/2,z	-x+1/2,-y,z+1/2	-x,-y+1/2,z
y+1/4,-x+1/4,z+3/4	y+3/4,-x+3/4,z+1/4	y+1/4,-x+1/4,z+3/4	y+3/4,-x+3/4,z+1/4
-x,y,z	-x+1/2,y+1/2,z+1/2	-x,y,z	-x+1/2,y+1/2,z+1/2
-y+1/4,-x+3/4,z+1/4	-y+3/4,-x+1/4,z+3/4	-y+1/4,-x+3/4,z+1/4	-y+3/4,-x+1/4,z+3/4
x+1/2,-y,z+1/2	x,-y+1/2,z	x+1/2,-y,z+1/2	x,-y+1/2,z
y+1/4,x+1/4,z+3/4	y+3/4,x+3/4,z+1/4	y+1/4,x+1/4,z+3/4	y+3/4,x+3/4,z+1/4
-x,-y,-z	-x+1/2,-y+1/2,-z+1/2	-x,-y,-z	-x+1/2,-y+1/2,-z+1/2
y+3/4,-x+1/4,-z+3/4	y+1/4,-x+3/4,-z+1/4	y+3/4,-x+1/4,-z+3/4	y+1/4,-x+3/4,-z+1/4
x+1/2,y,-z+1/2	x,y+1/2,-z	x+1/2,y,-z+1/2	x,y+1/2,-z
-y+3/4,x+3/4,-z+1/4	-y+1/4,x+1/4,-z+3/4	-y+3/4,x+3/4,-z+1/4	-y+1/4,x+1/4,-z+3/4
x,-y,-z	x+1/2,-y+1/2,-z+1/2	x,-y,-z	x+1/2,-y+1/2,-z+1/2
y+3/4,x+1/4,-z+3/4	y+1/4,x+3/4,-z+1/4	y+3/4,x+1/4,-z+3/4	y+1/4,x+3/4,-z+1/4
-x+1/2,y,-z+1/2	-x,y+1/2,-z	-x+1/2,y,-z+1/2	-x,y+1/2,-z
-y+3/4,-x+3/4,-z+1/4	-y+1/4,-x+1/4,-z+3/4	-y+3/4,-x+3/4,-z+1/4	-y+1/4,-x+1/4,-z+3/4
-x,-y,-z	-x+1/2,-y+1/2,-z+1/2	-x,-y,-z	-x+1/2,-y+1/2,-z+1/2
y+3/4,-x+1/4,-z+3/4	y+1/4,-x+3/4,-z+1/4	y+3/4,-x+1/4,-z+3/4	y+1/4,-x+3/4,-z+1/4
x+1/2,y,-z+1/2	x,y+1/2,-z	x+1/2,y,-z+1/2	x,y+1/2,-z
-y+3/4,x+3/4,-z+1/4	-y+1/4,x+1/4,-z+3/4	-y+3/4,x+3/4,-z+1/4	-y+1/4,x+1/4,-z+3/4
x,-y,-z	x+1/2,-y+1/2,-z+1/2	x,-y,-z	x+1/2,-y+1/2,-z+1/2
y+3/4,x+1/4,-z+3/4	y+1/4,x+3/4,-z+1/4	y+3/4,x+1/4,-z+3/4	y+1/4,x+3/4,-z+1/4
-x+1/2,y,-z+1/2	-x,y+1/2,-z	-x+1/2,y,-z+1/2	-x,y+1/2,-z
-y+3/4,-x+3/4,-z+1/4	-y+1/4,-x+1/4,-z+3/4	-y+3/4,-x+3/4,-z+1/4	-y+1/4,-x+1/4,-z+3/4
x,y,z	x+1/2,y+1/2,z+1/2	x,y,z	x+1/2,y+1/2,z+1/2
-y+1/4,x+3/4,z+1/4	-y+3/4,x+1/4,z+3/4	-y+1/4,x+3/4,z+1/4	-y+3/4,x+1/4,z+3/4
-x+1/2,-y,z+1/2	-x,-y+1/2,z	-x+1/2,-y,z+1/2	-x,-y+1/2,z
y+1/4,-x+1/4,z+3/4	y+3/4,-x+3/4,z+1/4	y+1/4,-x+1/4,z+3/4	y+3/4,-x+3/4,z+1/4
-x,y,z	-x+1/2,y+1/2,z+1/2	-x,y,z	-x+1/2,y+1/2,z+1/2
-y+1/4,-x+3/4,z+1/4	-y+3/4,-x+1/4,z+3/4	-y+1/4,-x+3/4,z+1/4	-y+3/4,-x+1/4,z+3/4
x+1/2,-y,z+1/2	x,-y+1/2,z	x+1/2,-y,z+1/2	x,-y+1/2,z
y+1/4,x+1/4,z+3/4	y+3/4,x+3/4,z+1/4	y+1/4,x+1/4,z+3/4	y+3/4,x+3/4,z+1/4

Actually, twice as many with 0,½,0 prop. vector!
Now start removing cycles of operations to give new space group (subgroup of parent)
NB: new origin might be different to match standard setting
Horrible job by hand!
Use Bilbao tools: k-SUBGROUPSMAG

MAGNETIC SPACE GROUP IDENTIFICATION

Bilbao Crystallographic Server – k-SUBGROUPSMAG

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



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

Propagation vector(s)

Optional controls –
Limit results

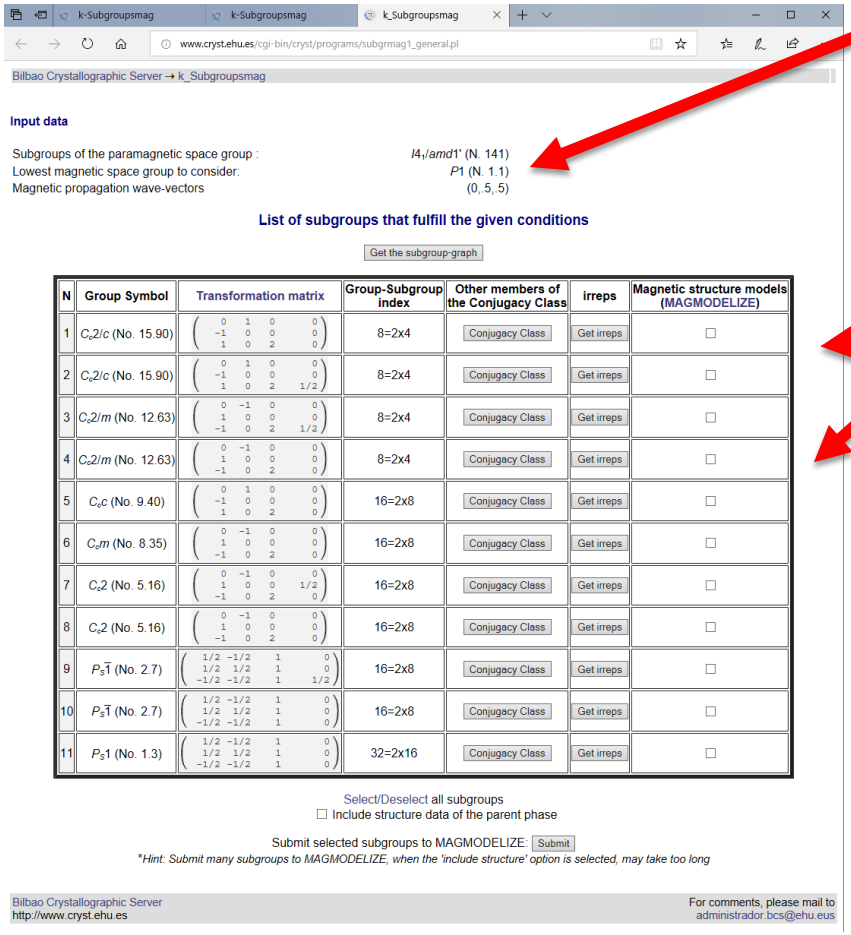
Result as list (or graph)

Argonne NATIONAL LABORATORY

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=(0,½, ½)



Bilbao Crystallographic Server → k_Subgroupsmag

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

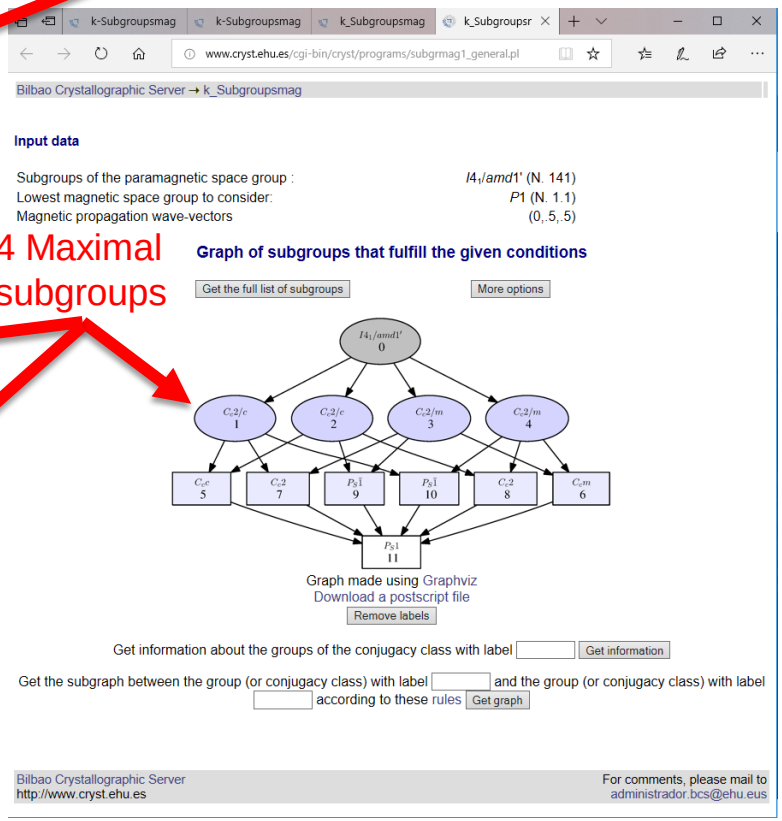
N	Group Symbol	Transformation matrix	Group-Subgroup index	Other members of the Conjugacy Class	irreps	Magnetic structure models (MAGMODELIZE)
1	C_c2/c (No. 15.90)	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 1 & 0 & 2 & 0 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	☐
2	C_c2/c (No. 15.90)	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 1 & 0 & 2 & 1/2 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	☐
3	C_c2/m (No. 12.63)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 1/2 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	☐
4	C_c2/m (No. 12.63)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 0 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	☐
5	C_cc (No. 9.40)	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 1 & 0 & 2 & 0 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
6	C_cm (No. 8.35)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 0 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
7	C_c2 (No. 5.16)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 1/2 \\ -1 & 0 & 2 & 0 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
8	C_c2 (No. 5.16)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 0 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
9	$P_s\bar{1}$ (No. 2.7)	$\begin{pmatrix} 1/2 & -1/2 & 1 & 0 \\ 1/2 & 1/2 & 1 & 0 \\ -1/2 & -1/2 & 1 & 1/2 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
10	$P_s\bar{1}$ (No. 2.7)	$\begin{pmatrix} 1/2 & -1/2 & 1 & 0 \\ 1/2 & 1/2 & 1 & 0 \\ -1/2 & -1/2 & 1 & 0 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
11	P_s1 (No. 1.3)	$\begin{pmatrix} 1/2 & -1/2 & 1 & 0 \\ 1/2 & 1/2 & 1 & 0 \\ -1/2 & -1/2 & 1 & 0 \end{pmatrix}$	32=2x16	Conjugacy Class	Get irreps	☐

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

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

Bilbao Crystallographic Server
http://www.cryst.ehu.es
For comments, please mail to
administrador.bcs@ehu.eus

4 Maximal subgroups



Bilbao Crystallographic Server → k_Subgroupsmag

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)

Graph of subgroups that fulfill the given conditions

Get the full list of subgroups | More options

Graph made using Graphviz
Download a postscript file
Remove labels

Get information about the groups of the conjugacy class with label [ ] Get information

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

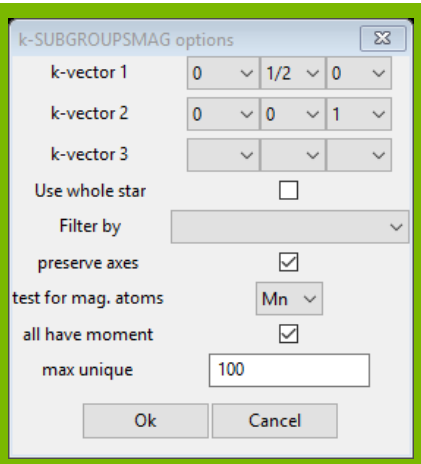
Bilbao Crystallographic Server
http://www.cryst.ehu.es
For comments, please mail to
administrador.bcs@ehu.eus

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

GSAS-II ← → k-SUBGROUPSMAG

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

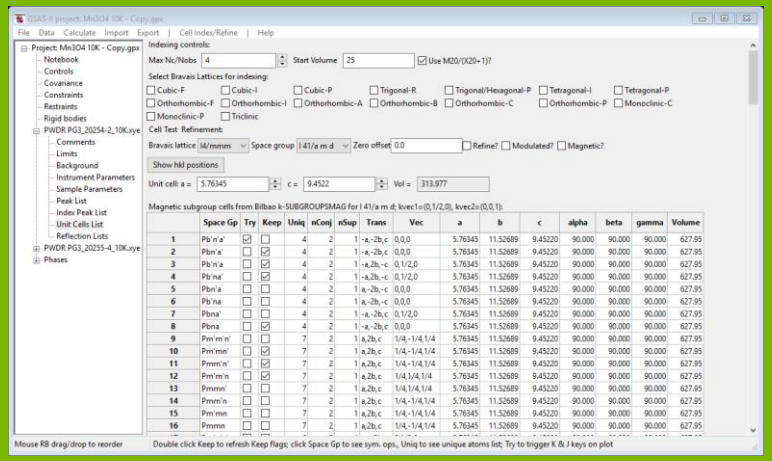
GSAS-II + $I4_1/amd$



Send request

Bilbao site
www.cryst.ehu.es/cgi-bin/programs/subgrmag1_general_GSAS.pl

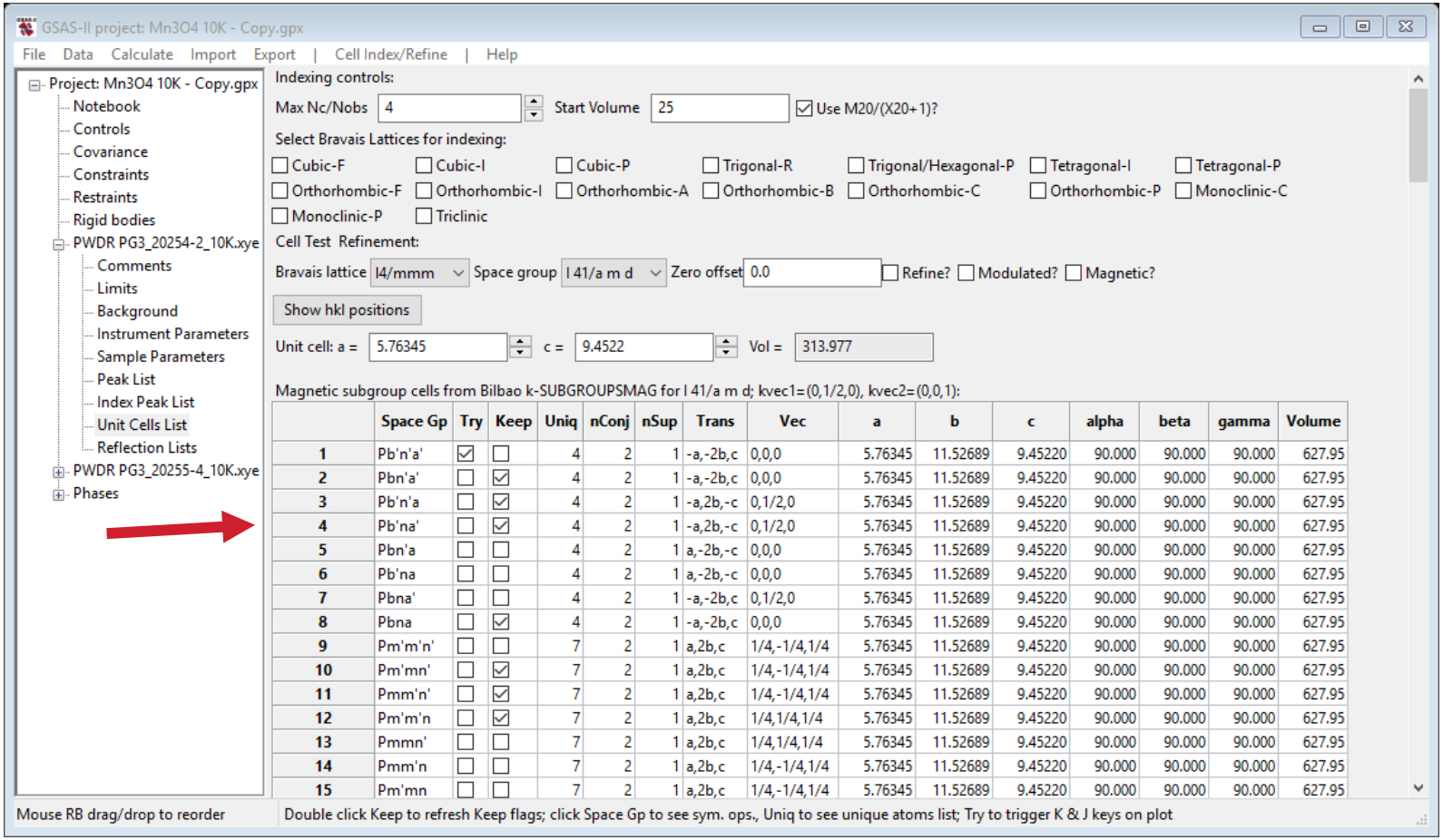
Makes html table of magnetic space subgroups, etc.



Return result
205 subgroups!
64 maximal subgroups!

RESULT FROM k-SUBGROUPSMAG (GSAS)

205 possible magnetic space subgroups (64 maximal) for $I4_1/amd$ & k=(0,½,0) +(0,0,1)

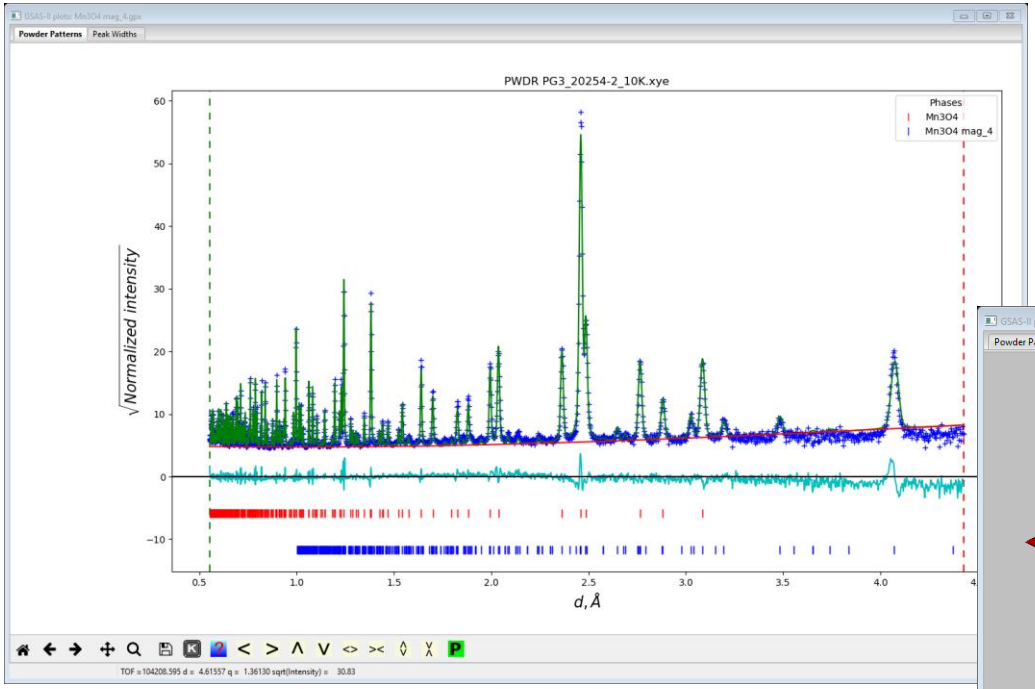


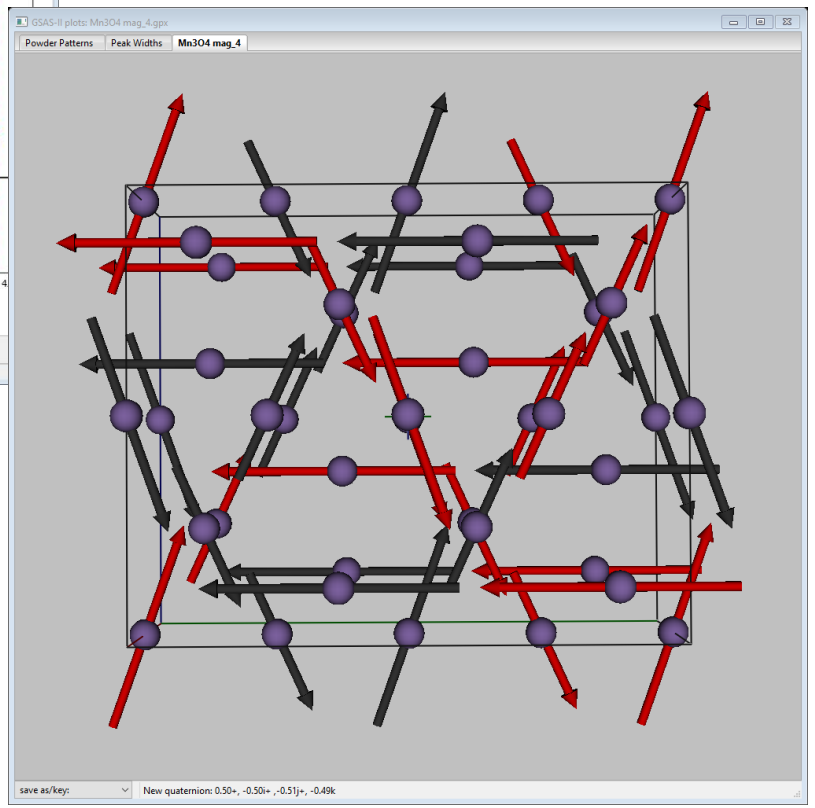
	Space Gp	Try	Keep	Uniq	nConj	nSup	Trans	Vec	a	b	c	alpha	beta	gamma	Volume
1	Pb'n'a'	☑	☐	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
2	Pbn'a'	☐	☑	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
3	Pb'n'a	☐	☑	4	2	1	-a,2b,-c	0,1/2,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
4	Pb'na'	☐	☑	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	☐	☐	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	☐	☐	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'	☐	☐	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	☐	☑	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'	☐	☐	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'	☐	☑	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'	☐	☑	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	☐	☑	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'	☐	☐	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	☐	☐	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	☐	☐	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

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} ~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 Pb'na' .

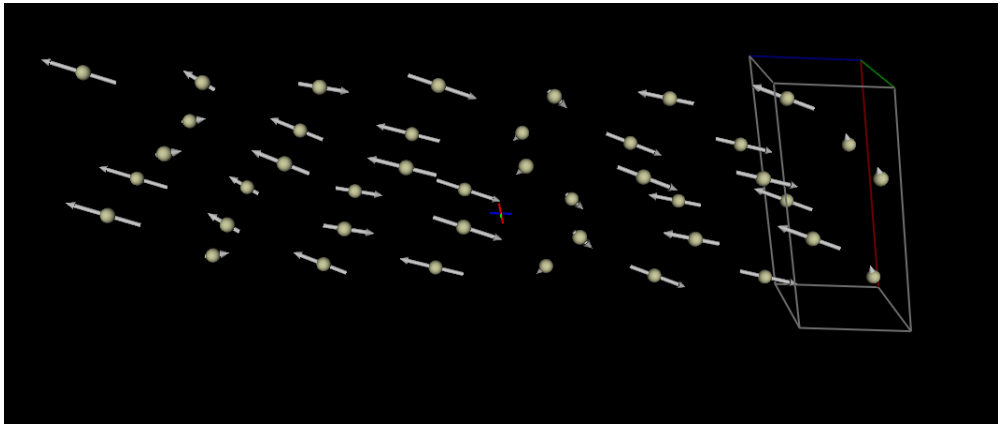
CONCLUSION

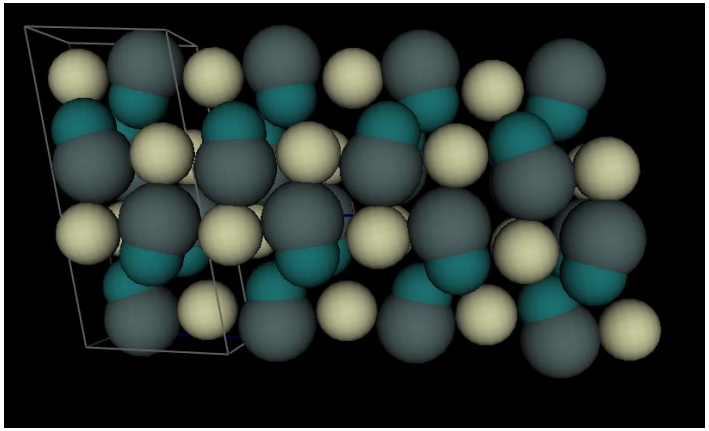
LINK: GSAS-II ← → k-SUBGROUPSMAG

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