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Advocacy of the combined use of representation analysis and magnetic crystallographic symmetry for the magnetic structure determination

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Currently, there is a growing understanding of the fact that in many cases the use of representation analysis RA (decomposition of the magnetic representation into irreducible representations *irreps*) together with Shubnikov group symmetry or with magnetic superspace 3D+1 groups allows one to find a hidden symmetry, which is not evident from the RA alone. Certain additional constraints on the normal modes (symmetry adapted magnetic configurations) obtained from the RA can be imposed using crystallographic symmetry arguments [1,2,5]. The software tools [1,2] are now capable of doing the detailed symmetry analysis of the magnetic phase transitions that allows one fully explore possible maximally symmetric solutions and apply them in the analysis of magnetic neutron diffraction experiments. The examples that illustrate the advantages of the combined RA and magnetic symmetry analysis include full propagation-vector star antiferromagnetic order in quantum spin trimer system $Ca_3CuNi_2(PO_4)_4$ [3], antiferromagnetic canting and symmetry lowering in ferromagnetic pyrochlore $Tm_2Mn_2O_7$ [4] and many multiferroics. A collection of magnetic structures with symmetry descriptions is in [6].

[1]] B.J Campbell et al., J. Appl. Cryst., 39607 (2006); ISOTROPY Software Suite, http://iso.byu.edu
[2] M. Aroyo, et al., Bulg. Chem. Commun. 43, 183 (2011); Bilbao Crystallographic Server http://www.cryst.ehu.es
[3] V. Pomjakushin, J. Phys.: Condens. Matter 26 496002 (2014)
[4] E. Pomjakushina, V. Pomjakushin, K. Rolfs, J. Karpinski, and K. Conder, Inorg. Chem., 54 (18), 9092, (2015)
[5] IUCr Commission on Magnetic Structures http://magcryst.org ; http://magcryst.org/meetings/cmsworkshop2014/program/
[6] Bilbao database of more than 400 published commensurate and incommensurate magnetic structures - http://webbdcrista1.ehu.es/magndata/

"Usual" Representation Analysis RA in case of multidimensional irreps and/or multi-arm

case of >1D irreps

1. Only general direction of order parameter OPD in representation space is considered. For example for 3D irrep OPD=(a,b,c): no special (a,0,0), (a,a,0), (a,a,a) … ⇒ symmetry lost
   multi-*Arm* (multi-**k**) structure: postulated 1k is enough
2. Symmetry of propagation vector arm **k** group G_k can be lower than parent
3. A symmetry unique spin position can split up into orbits.
4. The spins on different orbits are uncoupled ⇒ symmetry lost
5. Decomposition of magnetic representation into *irreps* on different orbits can have no overlapping ⇒ some spins are forced to be zero by symmetry in one-**k** paradigm ⇒ symmetry lost
6. Solutions that are considered do not have maximal possible symmetry

what if several magnetic modes S_0^1, S_0^2, S_0^3… are possible in RA?

Two commensurate cases when k="rational fraction"

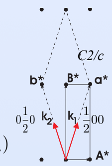
1. multi-dimentional (nD) irreducible representation generates *nD* magnetic modes $S_0^1, S_0^2, S_0^3 \dots S_0^{nD}$

$$\mathbf{S}(0) \sim \sum_{l=1}^{nD} C_l \mathbf{S}_0^l$$

2. multi-*Arm*/multi-**k** structure (non-equivalent $\mathbf{k}_1, \mathbf{k}_2, \dots \mathbf{k}_m$). *nA* magnetic modes $S_0^1, S_0^2, S_0^3 \dots S_0^{nA}$

$$\mathbf{S}(\mathbf{t}_n) \sim \sum_{m=1}^{nA} C_m' \mathbf{S}_0^m \cos(2\pi \mathbf{k}_m \mathbf{t}_n + \varphi_m)$$

RA: widespread unfavorable paradigm that one-**k** is enough…



Example of mutiarm, full star {$\mathbf{k}_1,\mathbf{k}_2$}: J. Phys.: Condens. Matter **26** 496002

any relations between mixing coefficients C_l or C_m' ?

for incommensurate structures:

any constraints on mixing coefficients ?
1. between atoms related by $\bar{1}$? 2. phases along x,y,z at $\bar{1}$?

$$\mathbf{S}_0 = |C_x| e^{i\phi_x}\mathbf{e}_x + |C_y|\mathbf{e}_y,\ \phi_x = 0, \frac{\pi}{2}, \dots ?$$

amplitude modulation for $\phi_x = 0$,
cycloid or helix for e.g. $\phi_x = \frac{\pi}{2}, \dots ?$ $\{\mathbf{k}, -\mathbf{k}\}$

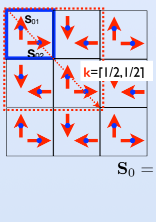
No from RA alone…

Yes from magnetic symmetry!

Some definitions/details

magnetic mode $\mathbf{S}_0$ for chosen irrep* specifies magnetic configuration of all spins in zeroth cell

$$\mathbf{S}_0 = (s_{x1}, s_{y1}, s_{z1}, s_{x2}, s_{y2}, s_{z2}, \dots, s_{xN}, s_{yN}, s_{zN})$$



$$\mathbf{S}_0 = (0,1,0,1,0,0)$$

Find symmetry breaking for *Pnma* at X-point [1/2,0,0] of BZ for irrep mX1

g: Group elements, G: matrices or irreducible representation *irrep*, 1': time inversion

g =	1	2_x	2_y	2_z	-1	n	m	a
G =	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&-1\\-1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&-1\\-1&0\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$
g' =	g · 1'							
G' =	G·(-1)							

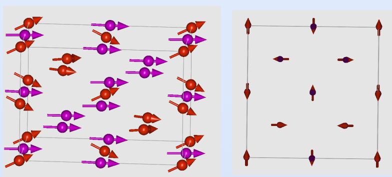
Find group elements *g* whose G leave two dimensional vector - order parameter OP=$\begin{pmatrix}a\\b\end{pmatrix}$ invariant → resulting symmetry → Isotropy subgroup

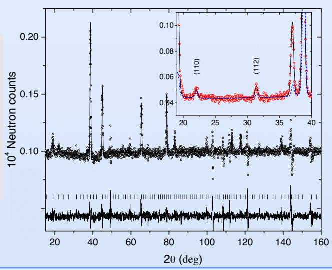
OP										resulting symmetry
OP=$\begin{pmatrix}a\\a\end{pmatrix}$		1			2_z		n	m		
	g =	✓						✓		P_bmn2_1
	g' =				✓		✓			
OP=$\begin{pmatrix}a\\0\end{pmatrix}$		1	2_x					m		
	g =	✓						✓		$P_a1\ 2_1/m\ 1$
	g' =		✓			✓				
OP=$\begin{pmatrix}a\\b\end{pmatrix}$		1	2_x					m		
	g =	✓								$P_a1\ m\ 1$

Magnetic structure of Pyrochlore $Tm_2Mn_2O_7$ at Γ-point k=0 (Fd-3m)

$$\Gamma_{mag} = \Gamma_2^+(1D) \oplus \Gamma_3^+(2D) \oplus \Gamma_5^+(3D) \oplus \boxed{2\Gamma_4^+(3D)}$$

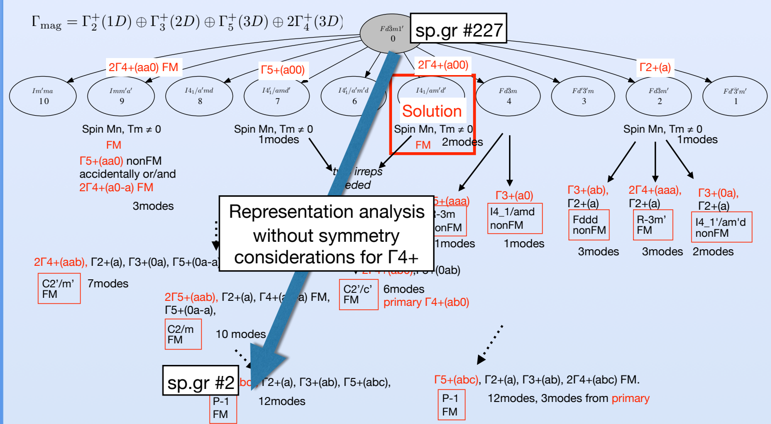
141.557 I4_1/am'd'





HRPT/SINQ Magnetic neutron diffraction

Maximal and non-maximal MG for the parent SG 227 (*Fd-3m*) at gamma point k = (0, 0, 0) generated by *one irrep* for 16d (1/2,1/2,1/2), 16c (0,0,0) position



Antiferromagnetic order in orthorhombic multiferroic $TmMnO_3$

Pnma k=[1/2,0,0], *irrep*: **2D** mX1(τ_1)

Order parameter direction | Magnetic Shubnikov Space group

ISODISTORT
Version 6.1.8, November 2014
Harold T. Stokes, Branton J. Campbell, and Dorian M. Hatch,
http://stokes.byu.edu/iso/

P1 (a,0) 11.55 P_a2_1/m, basis={(2,0,0),(0,1,0),(0,0,1)}, origin=(1/2,0,0), s=2, i=4, k-active= (1/2,0,0)

Maximal symmetry solution!

P3 (a,a) 31.129 P_bmn2_1, basis={(0,1,0),(2,0,0),(0,0,-1)}, origin=(3/4,1/4,0), s=2, i=4, k-active= (1/2,0,0)

C1 (a,b) 6.21 P_am, basis={(2,0,0),(0,1,0),(0,0,1)}, origin=(0,1/4,0), s=2, i=8, k-active= (1/2,0,0)

conventional general solution in RA: lowest symmetry for the given irrep: two independent Mn-spins