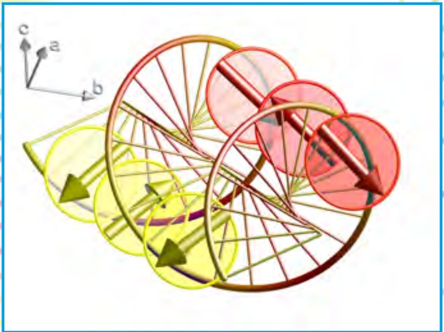
Magnetic structure refinement

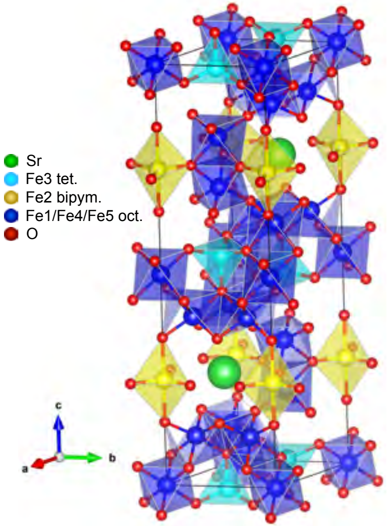


Navid Qureshi

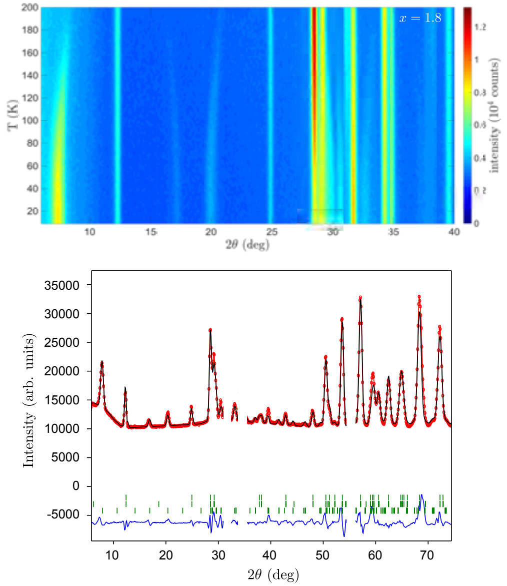
Motivation

How to make a complex problem *simple*?

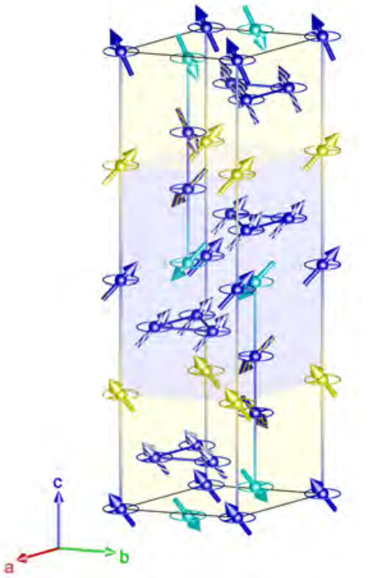
Complex crystal structure
(24 magnetic ions in unit cell)



Limited observations



Even more complex
magnetic structure

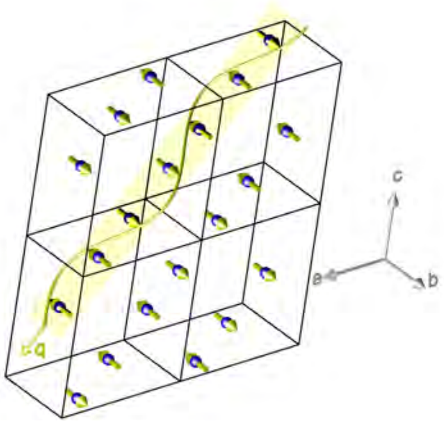


Motivation

How to benefit from macroscopic properties?

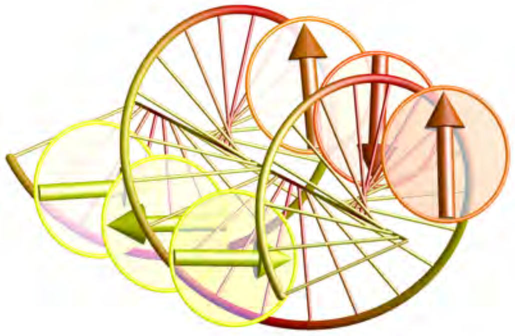
CuO (multiferroic)

collinear AF

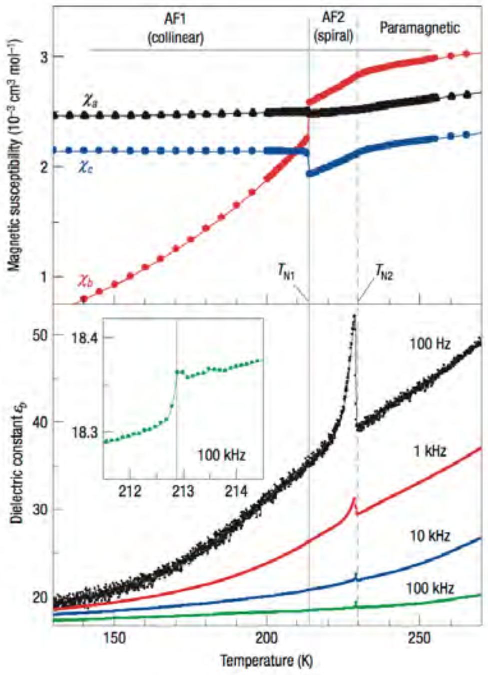


Cannot induce P!

magnetic spiral



Can induce P!



Kimura et al. (2008) *Nat. Mater.* **7** 291

Motivation

How to benefit from macroscopic properties?

SYMMETRY

SYMMETRY

Outline

- Magnetic symmetry

  symmetry operators, time inversion

- Group theory

  irreducible representations

- Magnetic structure refinement

  single irrep, mixed irrep, SDW, cycloid, ...

- Conclusion

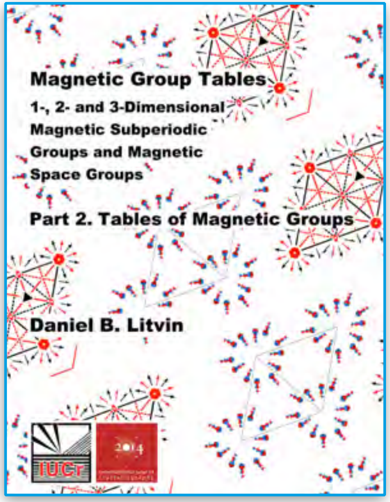
Magnetic symmetry

Crystallographic and magnetic space groups

230 crystallographic space groups

it.iucr.org

1651 magnetic space groups



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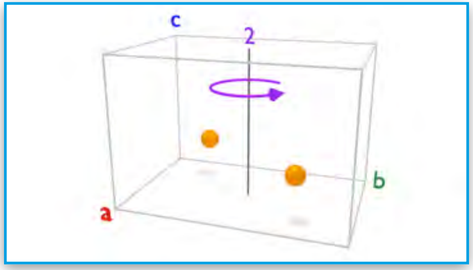
space groups are groups in the mathematical sense → group theory

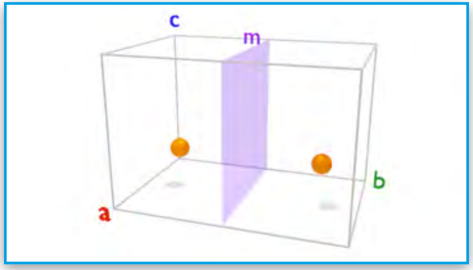
Magnetic symmetry

Conventional symmetry operators

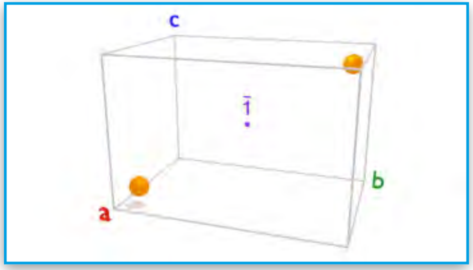
Rotations (order n: $2\pi/n$)



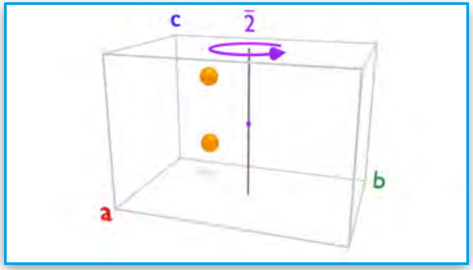
Mirror planes (m)



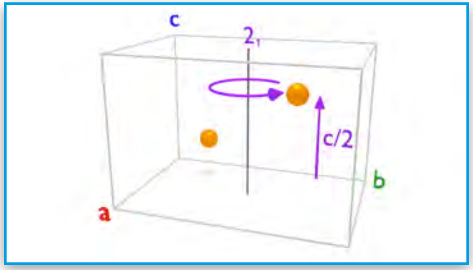
Inversion ($\bar{1}$)



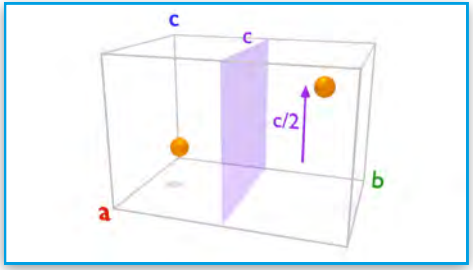
Roto-inversion ($\bar{n}$)



Screw axes (rot + trans)



Glide planes (mirror + trans)

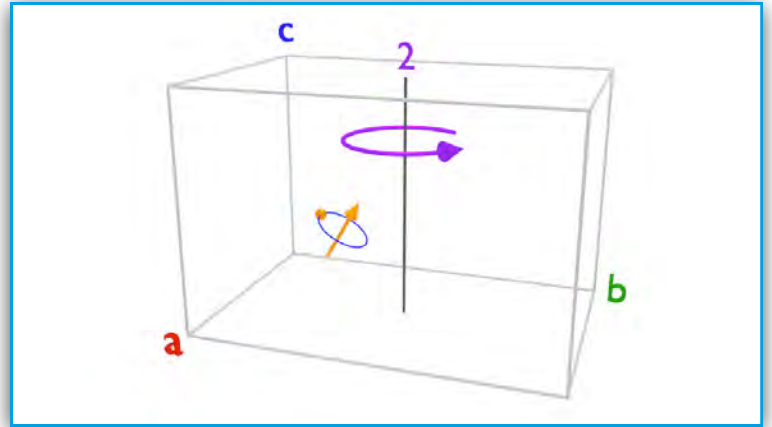


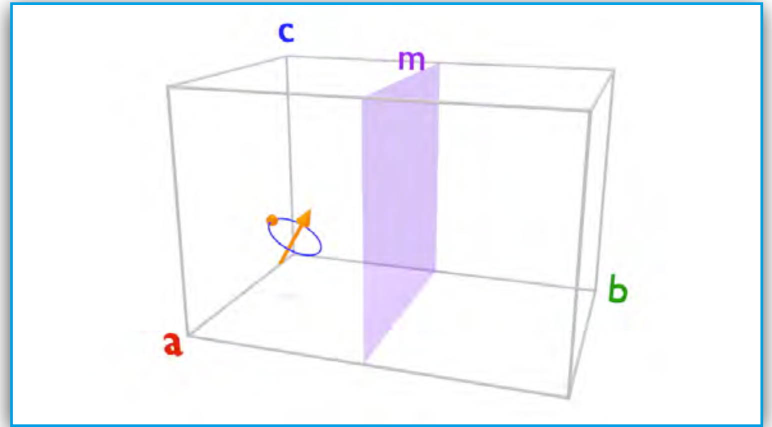
Magnetic symmetry

Magnetic symmetry operators

Magnetic symmetry operations = “usual” crystallographic symmetries + time inversion

A magnetic moment transforms like an axial or pseudo vector





2: $\mu_\alpha \parallel 2$ conserved, $\mu_\alpha \perp 2$ inverted

2’: $\mu_\alpha \parallel 2'$ inverted, $\mu_\alpha \perp 2'$ conserved

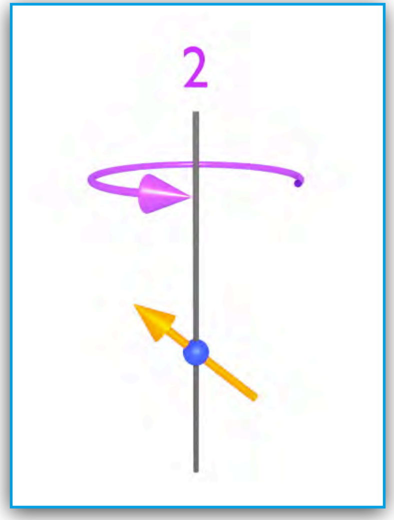
m: $\mu_\alpha \parallel m$ inverted, $\mu_\alpha \perp m$ conserved

m’: $\mu_\alpha \parallel m'$ conserved, $\mu_\alpha \perp m'$ inverted

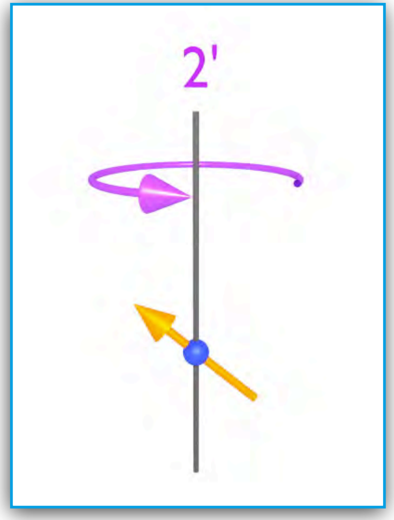
Magnetic symmetry

Magnetic symmetry operators

Magnetic moments on special Wyckoff positions have less degrees of freedom.



μ on 2 $\longrightarrow$ only $\mu_{||}$



μ on 2' $\longrightarrow$ only $\mu_{\perp}$

Not using the magnetic symmetry is like treating the crystal structure in *P1*!

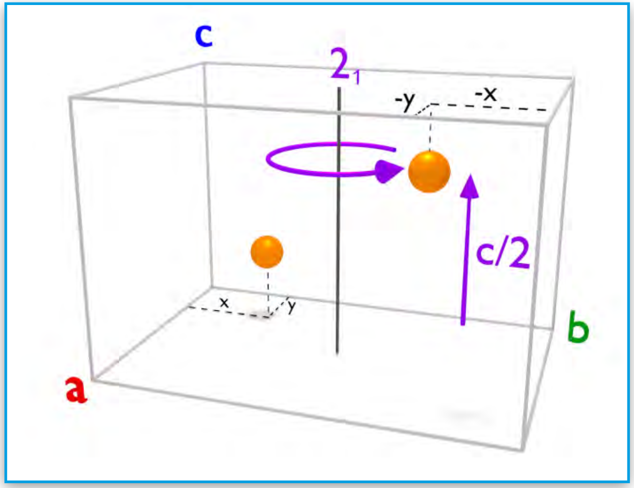
Magnetic symmetry

Magnetic symmetry operators

Mathematical description (polar vectors):

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \cdot \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix}$$

Seitz notation: (R|t)



Symmetry contained in the coordination triplet:
e.g. 2_1 screw axis along c: -x, -y, z+1/2

Axial vectors: $$\begin{pmatrix} u' \\ v' \\ w' \end{pmatrix} = \det(\mathbf{R}) \cdot T \cdot \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \cdot \begin{pmatrix} u \\ v \\ w \end{pmatrix}$$

Group theory

Definitions

Physical systems (crystals and magnetic structures) are provided with a certain symmetry, which needs to be reflected correctly in a mathematical way.

Definition of a group:

A group G of order n is a set of distinct elements $g_1, g_2, \ldots, g_n$. Any two elements g_i and g_j combined by an operation called the group multiplication (○) should satisfy the following four axioms:

- closed under multiplication: the unique product $g_i \circ g_j$ also belongs to G
- the associative law holds: $g_k \circ (g_j \circ gi) = (g_k \circ g_j) \circ g_i$
- there exists an identity element: $E \circ g = g \circ E = g$
- there exists an inverse element: $g^{-1} \circ g = g \circ g^{-1} = E$

Space groups fulfil those four axioms!

If any two elements commute, then the group is Abelian: $g_j \circ g_i = g_i \circ g_j$

Group theory

Definitions

Physical systems (crystals and magnetic structures) are provided with a certain symmetry, which needs to be reflected correctly in a mathematical way.

Definition of a subgroup:

H is a subgroup of *G*, if it is a group itself (fulfils the 4 axioms) and if all elements h_i are elements of *G*.

Definition of a class:

Group elements which are conjugate to each other can be classified into classes.
An element *b* is conjugate to *a* if there is a group element *g* so that $b = gag^{-1}$.

In Abelian groups every group element builds a class of its own:

$$gag^{-1} = gg^{-1}a = Ea = a$$

Group theory

Example - $Ni_3V_2O_8$

Space group *Cmce*, magnetic Ni ions on Wyckoff sites 4a (0,0,0) and 8e (1/4,*y*,1/4)

Symmetry operators:

$(1)\ 1$

$(2)\ 2(0,\,0,\,1/2)\ \ 0,\,1/4,\,z$

$(3)\ 2(0,\,1/2,\,0)\ \ 0,\,y,\,1/4$

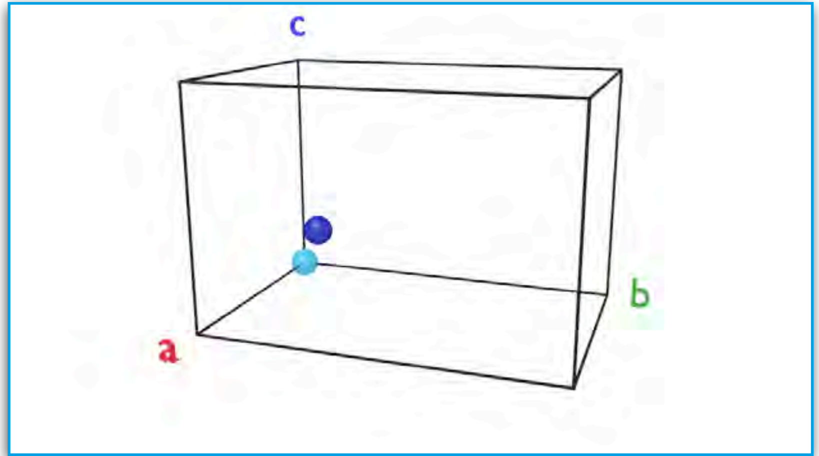
$(4)\ 2\ \ x,\,0,\,0$

$(5)\ \text{-}1\ \ 0,\,0,\,0$

$(6)\ b\ \ x,\,y,\,1/4$

$(7)\ c\ \ x,\,1/4,\,z$

$(8)\ m\ \ 0,\,y,\,z$



Generators selected:

$t(1/2,\,1/2,\,0),\ (2),\ (3),\ (5)$

$t(1,\,0,\,0),\ t(0,\,1,\,0),\ t(0,\,0,\,1)$

Group theory

Example - $Ni_3V_2O_8$

identify the symmetry operators of the space group which are compatible with the magnetic translation symmetry ⟶ **little group (subgroup)**

$$\mathbf{R}\cdot\mathbf{q}=\mathbf{q}+\mathbf{G}$$

Propagation vector **q** = (0.5 0 0)

Symmetry operators:

(1) 1

(2) $\cancel{2(0,\,0,\,1/2)\;\;0,\,1/4,\,z}$

(3) $\cancel{2(0,\,1/2,\,0)\;\;0,\,y,\,1/4}$

(4) $2\;\;x,\,0,\,0$

(5) $\cancel{\text{-}1\;\;0,\,0,\,0}$

(6) $b\;\;x,\,y,\,1/4$

(7) $c\;\;x,\,1/4,\,z$

(8) $\cancel{m\;\;0,\,y,\,z}$

$$\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}\cdot\begin{pmatrix}0.5\\0\\0\end{pmatrix}=\begin{pmatrix}-0.5\\0\\0\end{pmatrix}=\underbrace{\begin{pmatrix}0.5\\0\\0\end{pmatrix}}_{=\mathbf{q}}-\underbrace{\begin{pmatrix}1\\0\\0\end{pmatrix}}_{=\mathbf{G}?}$$

not with C centring!

Group theory

Example - $Ni_3V_2O_8$

identify the symmetry operators of the space group which are compatible with the magnetic translation symmetry ⟶ **little group (subgroup)**

$$\mathbf{R} \cdot \mathbf{q} = \mathbf{q} + \mathbf{G}$$

Propagation vector **q** = (0.5 0 0)

Symmetry operators:

(1) 1	$\cancel{(2)\ 2(0,\ 0,\ 1/2)\ \ 0,\ 1/4,\ z}$
$\cancel{(3)\ 2(0,\ 1/2,\ 0)\ \ 0,\ y,\ 1/4}$	(4) $2\ \ x,\ 0,\ 0$
$\cancel{(5)\ \text{-}1\ \ 0,\ 0,\ 0}$	(6) $b\ \ x,\ y,\ 1/4$
(7) $c\ \ x,\ 1/4,\ z$	$\cancel{(8)\ m\ \ 0,\ y,\ z}$

Representative elements of the little group:

- (1) identity
- (4) 2-fold rotation axis along *x*
- (6) glide plane within *xy* plane
- (7) glide plane within *xz* plane

Group theory

Definitions

Definition of a representation:

If the square matrices $\mathbf{\Gamma}(g_i)$ associated with each element g_i of group G of order n satisfy the homomorphism rule

$$\mathbf{\Gamma}(g_j)\mathbf{\Gamma}(g_i) = \mathbf{\Gamma}(g_k)$$

for the corresponding relation of the group elements

$$g_j g_i = g_k$$

then the set of matrices $\mathbf{\Gamma}(g_i)$, $\mathbf{\Gamma}(g_i)$, ..., $\mathbf{\Gamma}(g_i)$ is called a *representation* of the group G.

The size of the matrices is the *dimension d* of the representation.

Every representation $\mathbf{\Gamma}(g_i)$ has an equivalent representation: $\mathbf{\Omega}(g) = \mathbf{P}^{-1}\mathbf{\Gamma}(g)\mathbf{P}$

Group theory

Definitions

Reducible and irreducible representations:

If a representation $\mathbf{\Gamma}(g)$ can be block-diagonalized according to

$$\mathbf{\Gamma}(g) = \begin{pmatrix} \mathbf{\Gamma}^1(g) & 0 \\ 0 & \mathbf{\Gamma}^2(g) \end{pmatrix}$$

with the dimension being $d_{\mathbf{\Gamma}} = d_{\mathbf{\Gamma}1} + d_{\mathbf{\Gamma}2}$, then $\mathbf{\Gamma}(g)$ is called *reducible*.

If no equivalence transformation ($\mathbf{P}^{-1}\mathbf{\Gamma}(g)\mathbf{P}$) can achieve such a block-diagonalization, then the presentation is called *irreducible*.

Group theory

Definitions

Character of a representation:

The character of a matrix representation $\mathbf{\Gamma}(g)$ is its trace:

$$\chi(g) = \mathrm{Tr}[\mathbf{\Gamma}(g)] = \sum_i \Gamma_{i,i}(g)$$

The trace is invariant under equivalence transformations.

$$\mathrm{Tr}[\mathbf{P}^{-1}\mathbf{\Gamma}(g)\mathbf{P}] = \mathrm{Tr}[\mathbf{\Gamma}(g)\mathbf{P}\mathbf{P}^{-1}] = \mathrm{Tr}[\mathbf{\Gamma}(g)]$$

→ The character is suited to show the equivalence between matrix representations.

Group theory

The orthogonality theorem

An outcome of the Schür lemmas is the *orthogonality theorem*

$$\sum_{g\in G} \mathbf{\Gamma}^{U}_{j,l}(g) \left[\mathbf{\Gamma}^{V}_{n,m}(g)\right]^* = \frac{n_G}{d_U}\delta_{UV}\delta_{jn}\delta_{lm}$$

The orthogonality theorem together with the properties of characters yield fundamental relations from which the *character table* of a group can be constructed.

Group theory

Character tables

- The number of inequivalent irreducible representations n_r is equal to the number of classes n_{cl}.

$$n_r = n_{cl}$$

- The sum of squares of the dimensions of inequivalent irreducible representations is equal to the order n_G of the group.

$$\sum d_U^2 = n_G$$

- First orthogonality of characters

$$\sum_{g\in G} \chi^U(g)\left[\chi^V(g)\right]^* = n_G \delta_{UV}$$

- Second orthogonality of characters

$$\sum_U \chi_e^U \left[\chi_f^U\right] = \frac{n_G}{n(C_e)}\delta_{ef}$$

- Relation for characters resulting from class multiplication

$$n(C_e)n(C_f)\chi_e^U(g)\chi_f^U(g) = d_U \sum_w c_{ef}^w n(C_w)\chi_w^U(g)$$

Group theory

Character tables - *Example*

- The number of inequivalent irreducible representations n_r is equal to the number of classes n_{cl}.

$$n_r = n_{cl}$$

Little group contains 4 elements (n_G=4). Using $b = gag^{-1}$ shows that each of the elements builds a class.

$$G = \{E,\, 2_x,\, b,\, c\}$$

	E	2_x	b	c
Γ_1				
Γ_2				
Γ_3				
Γ_4				

→ **4 inequivalent irreducible representations**

Group theory

Character tables - *Example*

- The sum of squares of the dimensions of inequivalent irreducible representations is equal to the order n_G of the group.

$$\sum d_U^2 = n_G$$

	E	2_x	b	c
Γ_1	1	1	1	1
Γ_2	1			
Γ_3	1			
Γ_4	1			

→ 4 one-dimensional representations including the identity representation $\chi^1(g) = 1$

→ the identity E is necessarily represented by $\chi^U(E) = 1$

Group theory

Character tables - *Example*

- First orthogonality of characters

$$\sum_{g \in G} \chi^U(g) \left[\chi^V(g)\right]^* = n_G \delta_{UV}$$

	E	2_x	b	c
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

$U = V = 2$: $\quad 1 \cdot 1 + 1 \cdot 1 + (-1) \cdot (-1) + (-1) \cdot (-1) = 4$

$U = 1, V = 2$: $\quad 1 \cdot 1 + 1 \cdot 1 + 1 \cdot (-1) + 1 \cdot (-1) = 0$

Group theory

Basis functions

A set of functions $\{\psi_1, \psi_2, \dots \psi_{d^U}\}$ is called a basis for a representation Γ^U, if

$$g_k \psi_j^U = \sum_{i=1}^{d_U} \psi_i^U \Gamma_{i,j}^U(g_k)$$

e.g: {(a,0,0), (0,b,0), (0,0,c)}
{(a,a,0), (0,0,c)}
{(a,a,a)}

i.e. if the basis is closed within itself under operations $g \in G$

An arbitrary function f contains, in general, components of various irreducible representations:

$$f = \sum_U \sum_j c_j^U \psi_j^U$$

When the projection operator O_U is applied to the function f, it picks up the symmetry-adapted function ψ_j^U

$$O_U = \frac{d_U}{n_G} \sum_{g \in G} \left[\Gamma_{i,j}^U(g)\right]^* g \qquad O_U f = c_j^U \psi_j^U$$

Group theory

Basis functions - *Example*

We are interested in the spin orientation → $f = \mathbf{S} = \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}$

	E	2_x	b	c
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

Projection operator: $O_U = \frac{d_U}{n_G} \sum_{g \in G} \left[\Gamma^U_{i,j}(g)\right]^* g \qquad O_U f = c^U_j \psi^U_j$

$$\psi^1_1 = \frac{1}{4}\left[1 \cdot \begin{pmatrix} S_{1x} \\ S_{1y} \\ S_{1z} \end{pmatrix}\right.$$

Group theory

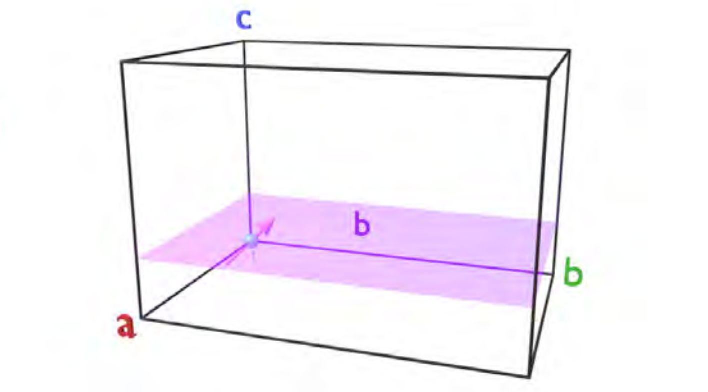
Basis functions - *Example*

We are interested in the spin orientation → $f = \mathbf{S} = \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}$

Projection operator: $O_U = \frac{d_U}{n_G} \sum_{g \in G} \left[\Gamma^U_{i,j}(g)\right]^* g \qquad O_U f = c^U_j \psi^U_j$

$$\psi^1_1 = \frac{1}{4}\left[1 \cdot \begin{pmatrix} S_{1x} \\ S_{1y} \\ S_{1z} \end{pmatrix} + 1 \cdot \begin{pmatrix} S_{1x} \\ -S_{1y} \\ -S_{1z} \end{pmatrix}\right.$$

	E	2_x	b	c
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1



Group theory

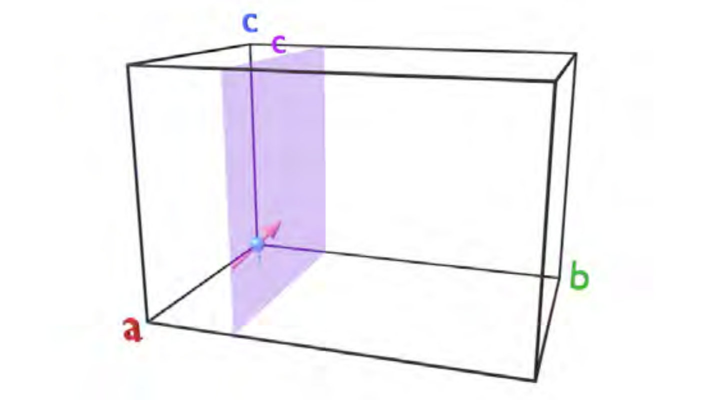
Basis functions - *Example*

We are interested in the spin orientation → $f = \mathbf{S} = \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}$

	E	2_x	b	c
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

Projection operator: $O_U = \frac{d_U}{n_G} \sum_{g \in G} \left[\Gamma^U_{i,j}(g)\right]^* g \qquad O_U f = c^U_j \psi^U_j$

$$\psi^1_1 = \frac{1}{4}\left[1 \cdot \begin{pmatrix} S_{1x} \\ S_{1y} \\ S_{1z} \end{pmatrix} + 1 \cdot \begin{pmatrix} S_{1x} \\ -S_{1y} \\ -S_{1z} \end{pmatrix} + 1 \cdot \begin{pmatrix} -S_{2x} \\ -S_{2y} \\ S_{2z} \end{pmatrix}\right.$$



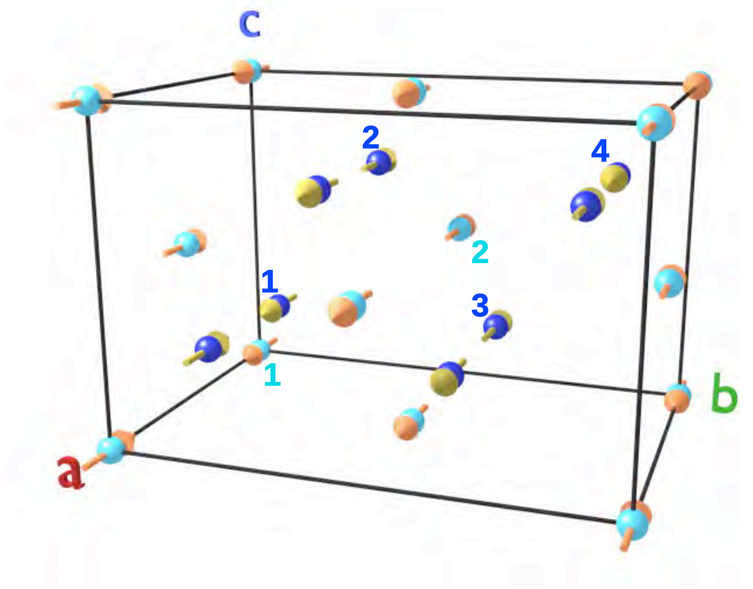
→ only x-component of spin (antiferromagnetically coupled)

Group theory

Magnetic models - Γ_1

	1	2
S_x	+	-
S_y	0	0
S_z	0	0

	1	2	3	4
S_x	+	-	-	+
S_y	+	+	-	-
S_z	+	-	+	-



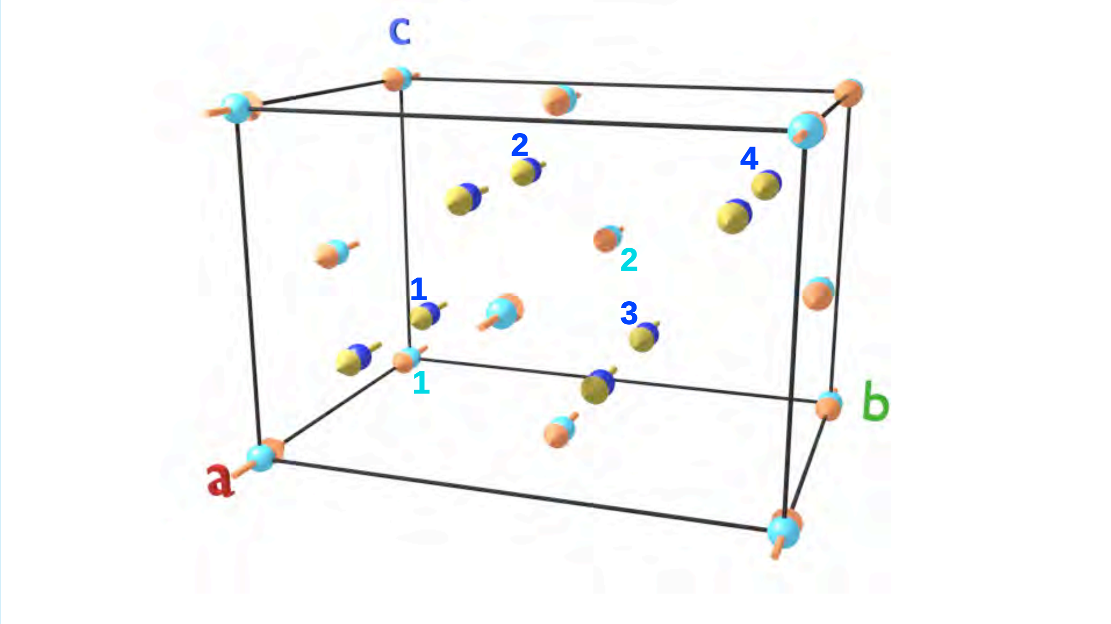
4 refinable coefficients instead of 36

Group theory

Magnetic models - Γ_2

	1	2
S_x	+	+
S_y	0	0
S_z	0	0

	1	2	3	4
S_x	+	+	+	+
S_y	+	-	+	-
S_z	+	+	-	-



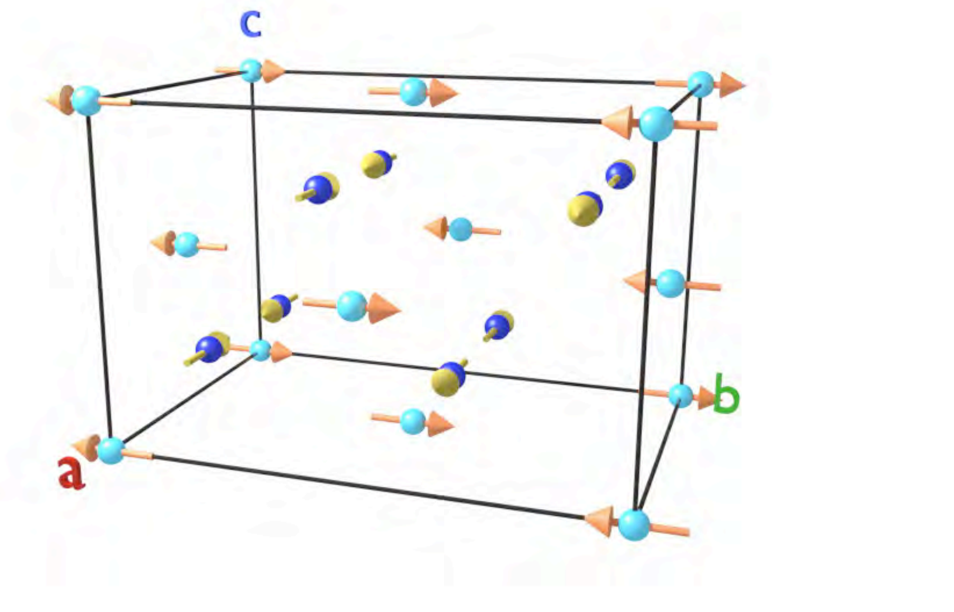
4 refinable coefficients instead of 36

Group theory

Magnetic models - Γ_3

	1	2
S_x	0	0
S_y	+	-
S_z	+	+

	1	2	3	4
S_x	+	+	-	-
S_y	+	-	-	+
S_z	+	+	+	+



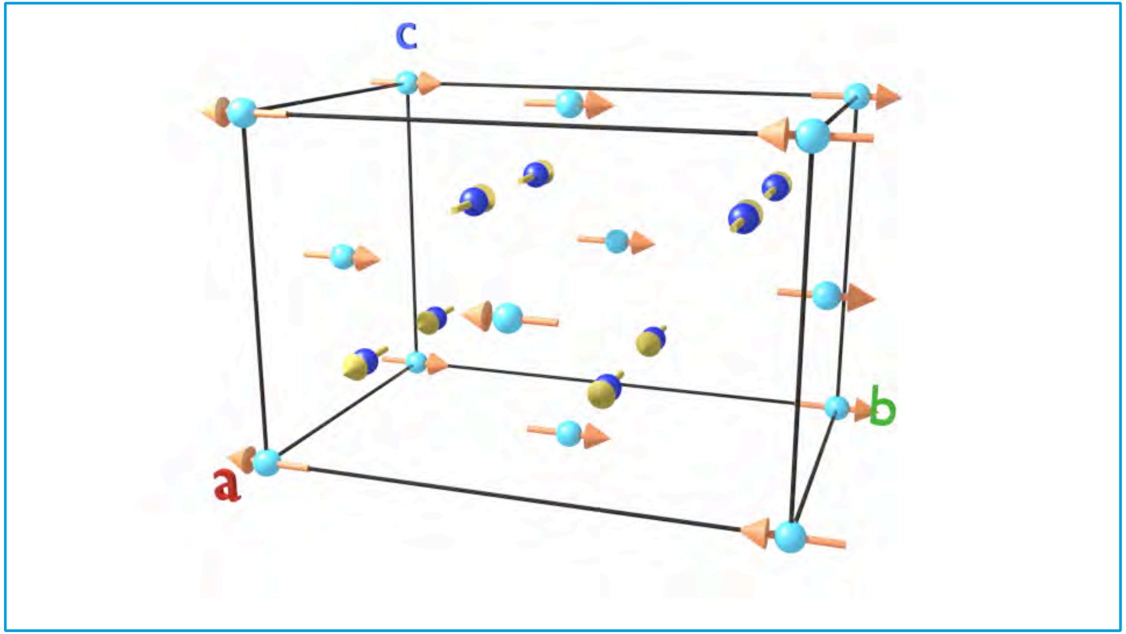
5 refinable coefficients instead of 36

Group theory

Magnetic models - Γ_4

	1	2
S_x	0	0
S_y	+	+
S_z	+	-

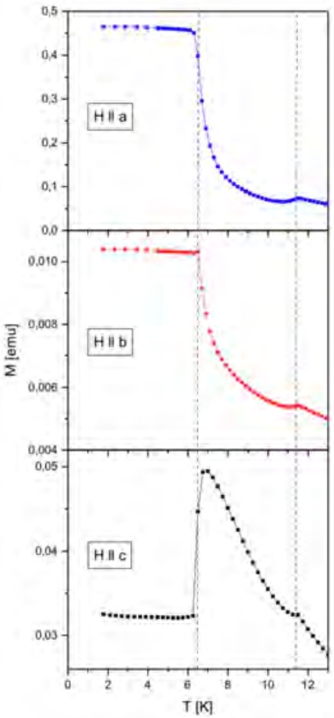
	1	2	3	4
S_x	+	-	+	-
S_y	+	+	+	+
S_z	+	-	-	+



5 refinable coefficients instead of 36

Group theory

Magnetic models



Γ_1	1	2		1	2	3	4
S_x	+	-	S_x	+	-	-	+
S_y	0	0	S_y	+	+	-	-
S_z	0	0	S_z	+	-	+	-

Γ_3	1	2		1	2	3	4
S_x	0	0	S_x	+	+	-	-
S_y	+	-	S_y	+	-	-	+
S_z	+	+	S_z	+	+	+	+

Γ_2	1	2		1	2	3	4
S_x	+	+	S_x	+	+	+	+
S_y	0	0	S_y	+	-	+	-
S_z	0	0	S_z	+	+	-	-

Γ_4	1	2		1	2	3	4
S_x	0	0	S_x	+	-	+	-
S_y	+	+	S_y	+	+	+	+
S_z	+	-	S_z	+	-	-	+

Group theory

Literature

T. Inui, Y. Tanaba and Y. Onodera.
Group Theory and Its Applications in Physics
Springer-Verlag (1990)

R. Ballou and B. Ouladdiaf
Representation Analysis of Magnetic Structures
in *Neutron Scattering from Magnetic Materials*
ed. by T. Chatterji, Elsevier (2006)

N. Qureshi
Magnetic properties of the kagome staircase mixed system $(Co_xNi_{1-x})_3V_2O_8$
PhD thesis
http://tuprints.ulb.tu-darmstadt.de/1402/

Data analysis

Freely available programs

The symmetry-adapted magnetic model (least possible coefficients) has to be refined using e.g. a least-squares algorithm.

We measure $I \sim F^2$ i.e. we loose the information about the phase.

FullProf Suite (including BasIreps for calculation of irreducible representations)
https://www.ill.eu/sites/fullprof/

Cambridge Crystallographic Subroutine Library
https://www.ill.eu/sites/ccsl/html/ccsldoc.html

Jana http://jana.fzu.cz

GSAS-II https://subversion.xray.aps.anl.gov/trac/pyGSAS

Mag2Pol https://www.ill.eu/instruments-support/instruments-groups/instruments/d3/software/

Data analysis

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FullPr… … of irreducible representations)

Cambrid… …rary
…ccsl/html/ccsldoc.html

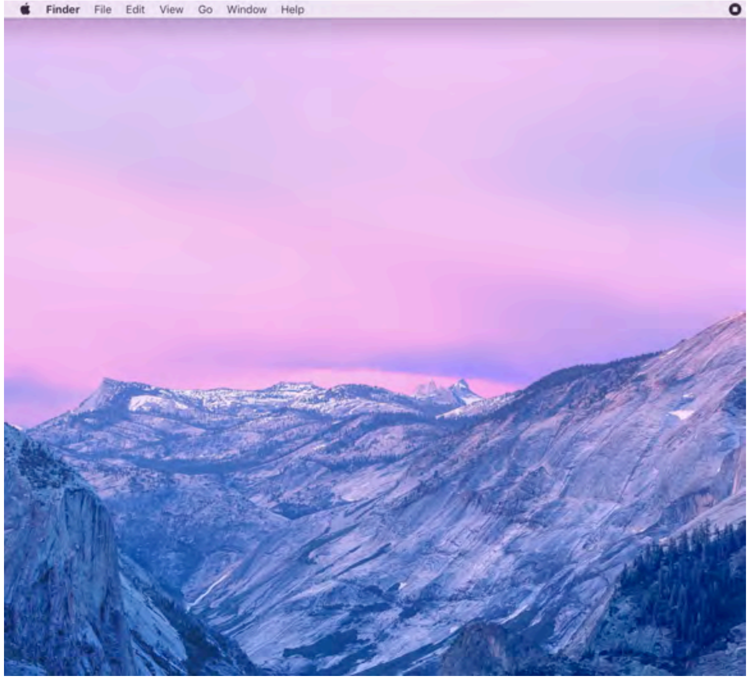
Qureshi (2019) *J. Appl. Cryst.* **52** 175

Jana http://jana.fzu.cz **GSAS-II** https://subversion.xray.aps.anl.gov/trac/pyGSAS

Mag2Pol https://www.ill.eu/instruments-support/instruments-groups/instruments/d3/software/

Magnetic structure refinement

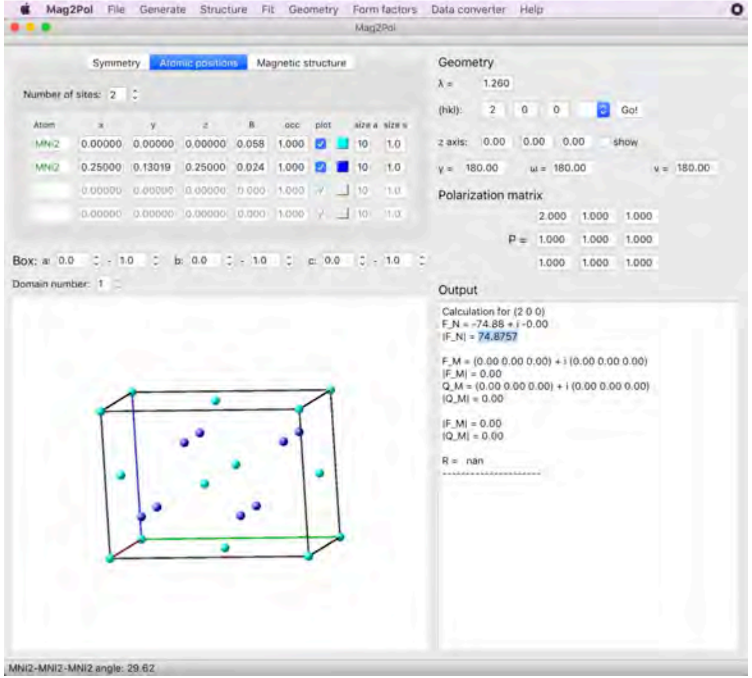
Set up nuclear structure



- atomic positions etc. usually are determined during the experiment
- extinction coefficients depend on sample
- Scale factor is important to determine size of magnetic moment

Magnetic structure refinement

Set up magnetic symmetry



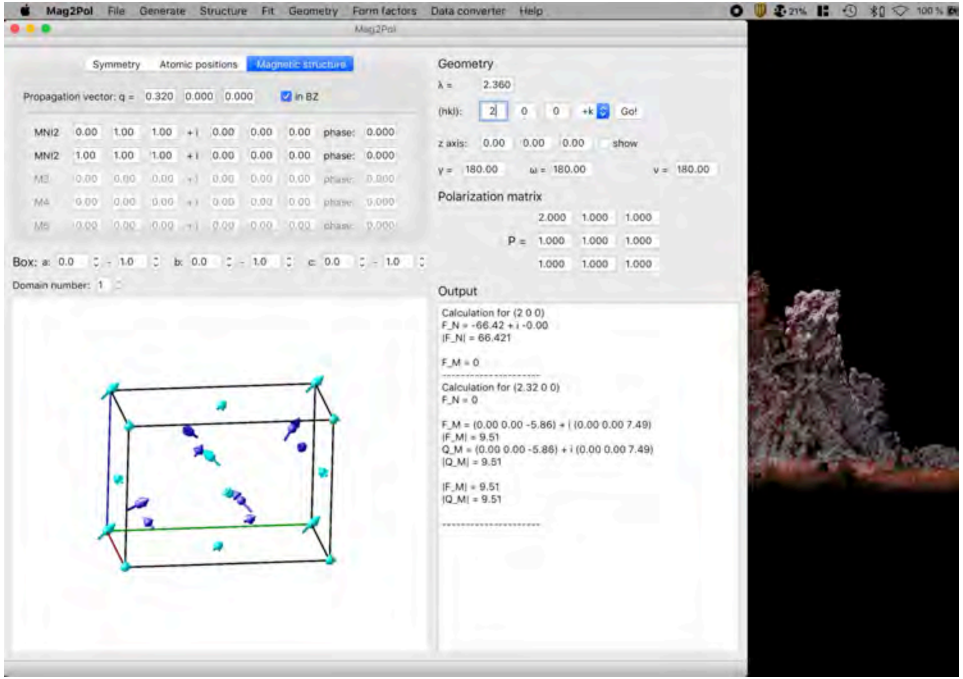
	E	2_x	b	c
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

Representative elements of the little group:

- (1) identity
- (4) 2-fold rotation axis along *x*
- (6) glide plane within *xy* plane
- (7) glide plane within *xz* plane

Magnetic structure refinement

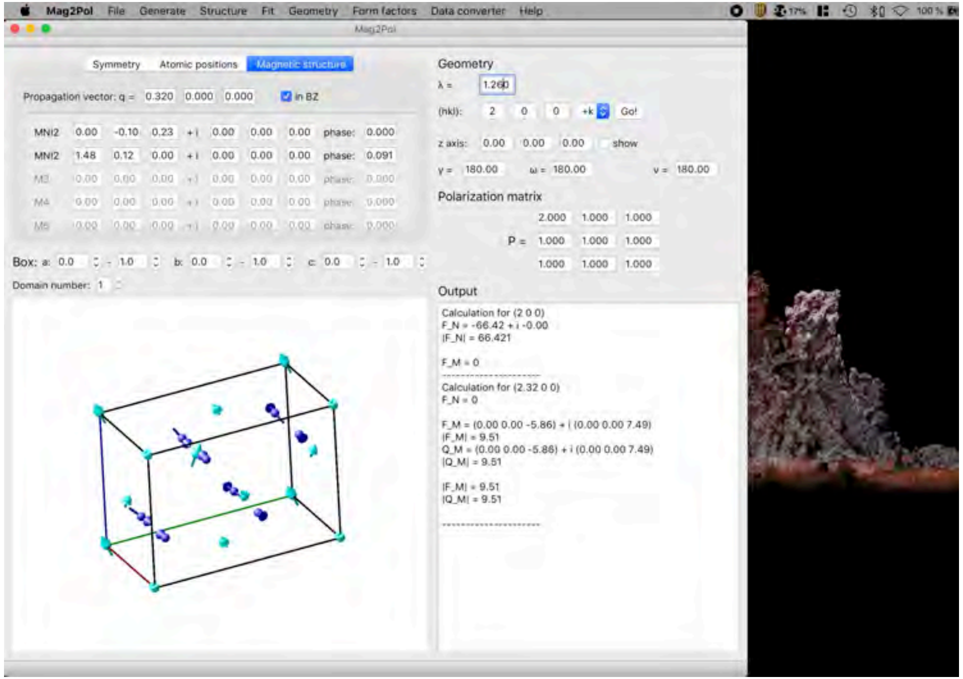
Load data and refine structure



- data are (hkl) vs intensity and sigmas
- eventually apply absorption correction
- equivalent reflections should be merged
- however, true magnetic symmetry not known at beginning of analysis —> treat in P1
- refine allowed and *reasonable* components

Magnetic structure refinement

Mixed representations



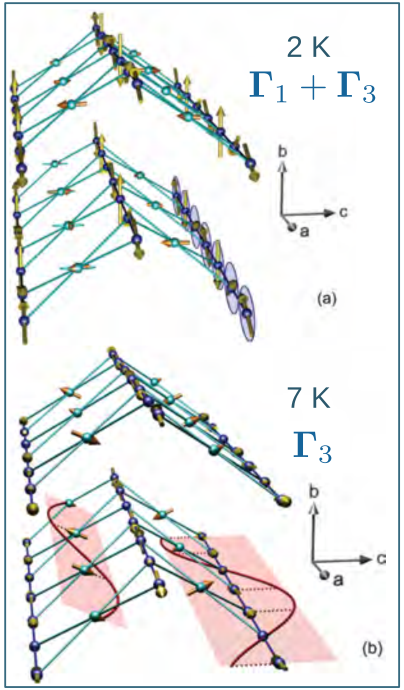
	E	2_x	b	c
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

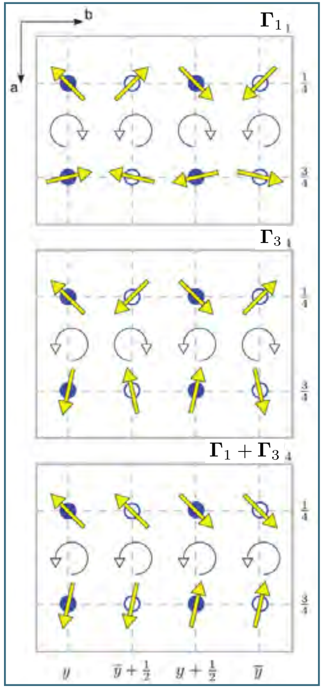
- two irreps can be combined -> symmetry reduction
- cycloids/helixes are usually explained with two irreducible representations
- e.g.: one real Fourier coefficient modulated by Γ3 and one imaginary Fourier coefficient modulated by Γ1

Magnetic structure refinement

Magnetic symmetry induces electric polarization

Qureshi et al., PRB **88** 174412 (2013)





HTI: sinusoidal modulation

LTI: cycloidal modulation

→ Mixed representation: reduction of symmetry

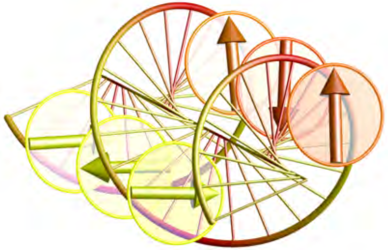
4 cycloid chains with same handedness

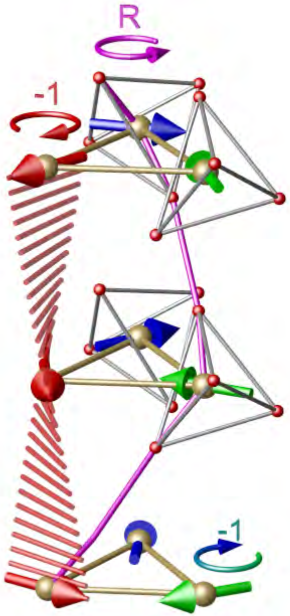
such a magnetic structure can induce a ferroelectric polarization due to the absence of inversion symmetry

Conclusions

Symmetry, symmetry, symmetry …

- refinement of complex magnetic structures without considering symmetry is hopeless
- magnetic symmetry = nuclear symmetry + propagation vector + time inversion
- group theory yields all necessary tools
- use macroscopic knowledge to facilitate analysis
- trial and error





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