Computer determination of Systematic Extinction Rules for Magnetic Space Groups

MAGNEXT

Universidad del País Vasco / Euskal Herriko Unibertsitatea — ZTF-FCT Zientzia eta Teknologia Fakultatea / Facultad de Ciencia y Tecnología

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BILBAO CRYSTALLOGRAPHIC SERVER

The Bilbao Crystallographic Server is a free access website with crystallographic databases and programs. The server gives access to the databases containing the data from the International Tables of Crystallography vol. A, Space Group Symmetry, and vol. A1, Symmetry Relations between Space Groups, providing very useful information for studies related with crystal-structure symmetry, phase transitions and solid state problems. The available software is divided in several shells according to different topics.

NEW SHELL:

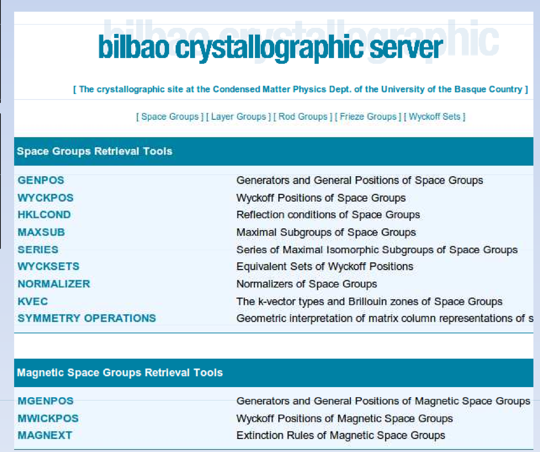
'MAGNETIC SPACE GROUPS'

NEW TOOLS:

MGENPOS Tables of Magnetic Space Groups General Positions

MWYCKPOS Tables of Magnetic Space Groups Wyckoff Positions

MAGNEXT: Extinction Rules for Magnetic Space Groups



MAGNETIC SPACE GROUPS

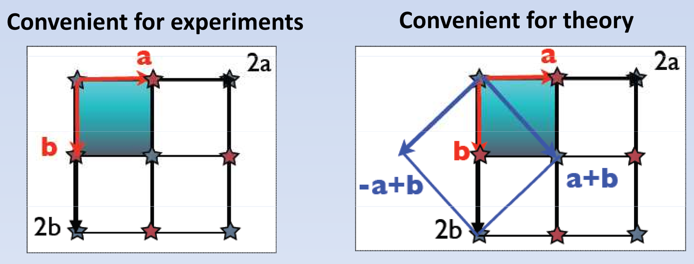
Time-inversion symmetry + 230 Space Groups:
1651 Magnetic Space Groups
36 Bravais Lattices

FOUR TYPES of Magnetic Space Groups

TYPE 1: White groups	**TYPE 2**: Grey groups
Fedorov Space Groups	Fedorov Space Groups + 1'
Ferromagnetic Phases	Paramagnetic Phases
TYPE 3: Black-and-white groups	**TYPE 4**: Black-and-white groups
t-subgroups of Grey Groups	k-subgroups of Grey Groups
Ferrimagnetic Phases Antiferromagnetic Phases Complex Magnetic Structures	Antiferromagnetic Phases (propagation vector k ≠ 0)

TYPE 4: Two settings in use:

OG setting	BNS setting
Paramagnetic unit cell	Different and bigger unit cell than the paramagnetic one
Convenient for experiments	Convenient for theory

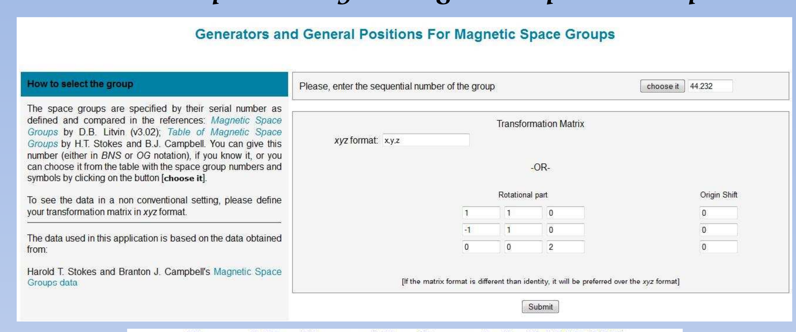


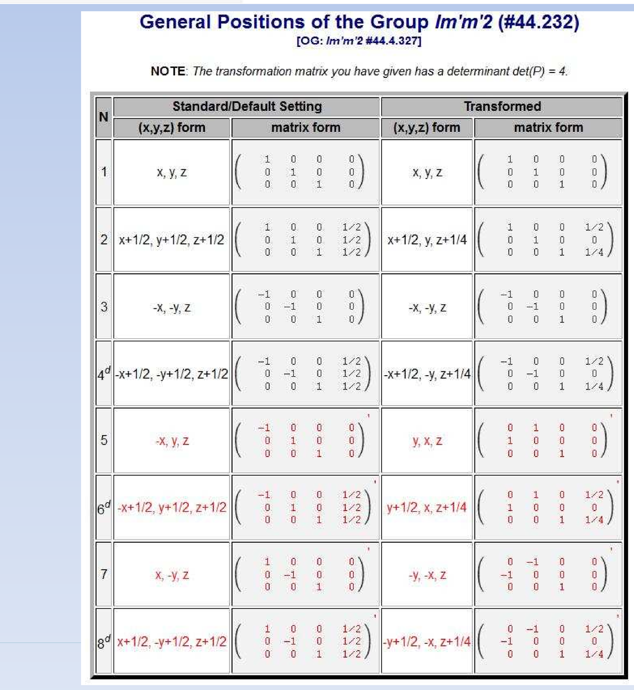
OG: *W. Opechowski, R. Guccione* BNS: *N.V. Belov, N. N. Neronova, T. S. Smirnova*

Different indexation and extinction rules

MGENPOS

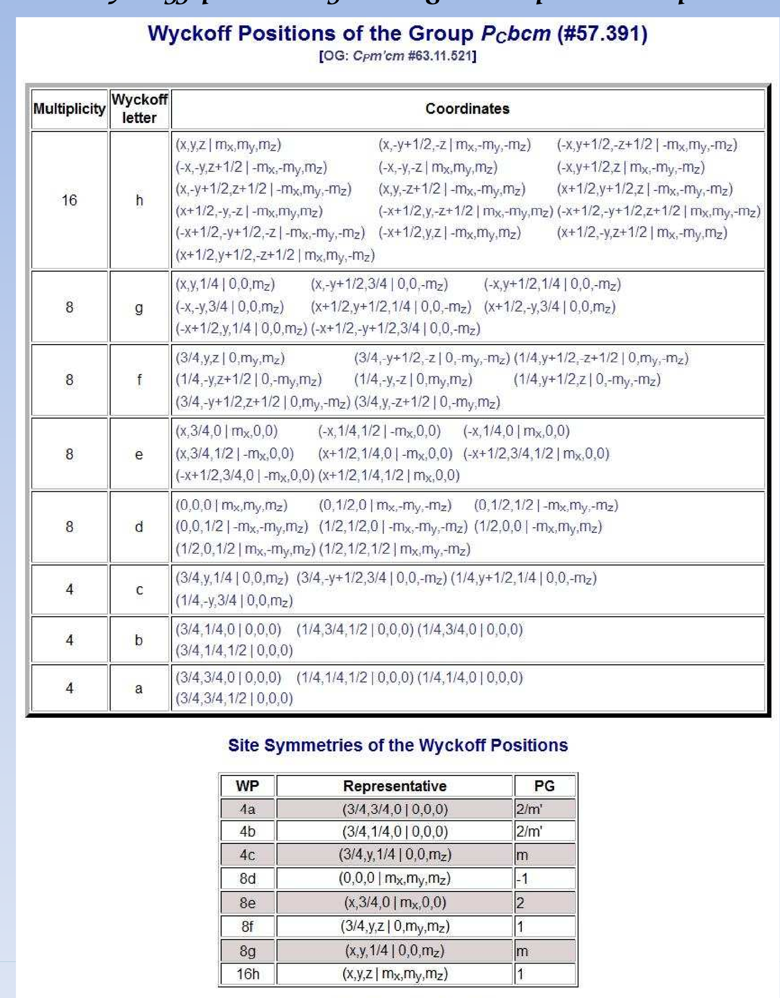
General positions for Magnetic Space Groups





MWYCKPOS

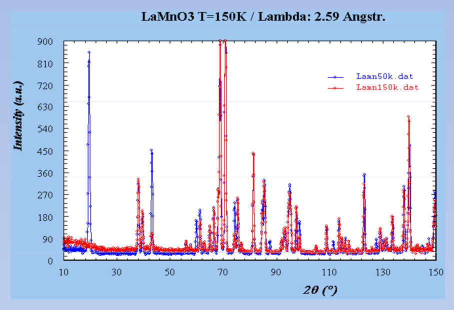
Wyckoff positions for Magnetic Space Groups



Tables of Magnetic Space Groups of Stokes used as source for the development of MGENPOS and MWYCKPOS: http://stokes.byu.edu/magneticspacegroups.html

MAGNETIC DIFFRACTION

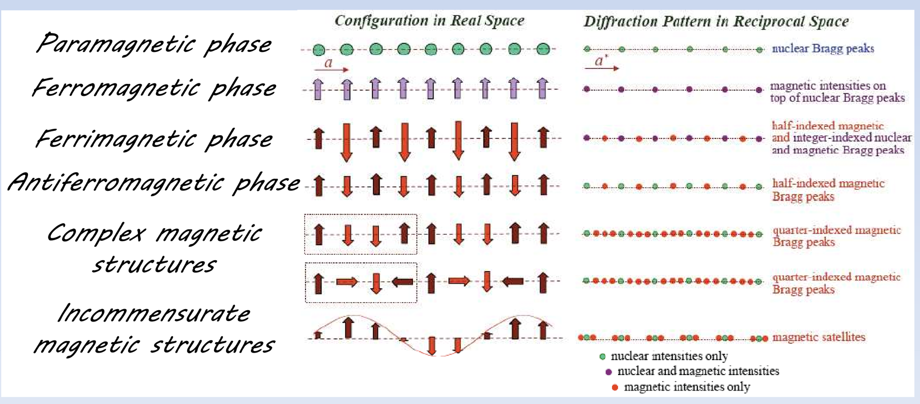
Diffraction patterns for magnetic unpolarised neutron diffraction: NUCLEAR and MAGNETIC contributions superposed at low-T



$LaMnO_3$ above T_N (T = 150 K)
$LaMnO_3$ below T_N (T = 50 K)
T_N = 139.5 K

MAGNETIC SYMMETRY → NEW EXTINCTION RULES → OVERLAP OF NUCLEAR AND MAGNETIC PEAKS

PREVIOUSLY FORBIDDEN PEAKS EMERGE → MAGNETIC SATELLITES



GETTING EXTINCTION RULES

Magnetic Structure Factor is an **axial vector** defined by the **Magnetic Moment density** inside the unit cell:

$$\vec{F}(\vec{H}) = \int \vec{M}(\vec{r}) e^{i2\pi\vec{H}\cdot\vec{r}} d\vec{r}$$

Crystal symmetry restriction:

$$\vec{F}(R\vec{H}) = m\cdot\det(R)\cdot e^{i2\pi\vec{H}\cdot\vec{t}}\cdot R\cdot\vec{F}(\vec{H}) = \vec{F}(\vec{H})$$

Extinctions restricted to **subspaces of reciprocal space**

Diffracted intensities dependence on structure factor

$$I(\vec{H}) \propto |\vec{F}(\vec{H})|^2 - \left|\frac{\vec{H}}{H}\cdot\vec{F}(\vec{H})\right|^2$$

EXTINCTION FOR $\vec{F} = 0$, $\vec{F} \parallel \vec{H}$

Through this method some different but redundant extinction rules are obtained for a single (h k l) restricted form

More Elegant and Direct Method:

New representation of the group:

$$T(R,m) = m\cdot\det(R)\cdot e^{i2\pi\vec{H}\cdot\vec{t}}\cdot R$$

Projecting this representation onto the Structure Factor Vector leaves it to a **restricted by symmetry form:**

$$P_1 = \frac{1}{|P_H|}\sum_{R\in P_H} T(R)$$

$$P_1\vec{F}(\vec{H}) = \vec{F}(\vec{H})_{\text{restricted by symmetry}}$$

Unique and global extinction rule for the given H-restricted form

EXAMPLE: P42'/m'nm'

$\vec{F}(R\vec{H}) = \vec{F}(\vec{H})$
Collect all $R_i\vec{H} = \vec{H}$

(h k l) forms	Different (h k l) restricted forms	Extinction
(h 0 0)	(h 0 0)	Extinction: h = 2n + 1
(0 k 0)	(0 k 0)	Extinction: k = 2n + 1
(0 0 l)	(0 0 l)	Extinction: l any
(h h 0)	(h h 0)	Extinction: h any
(-h h 0)	(-h h 0)	Extinction: h any

NEW TOOL IMPLEMENTED: MAGNEXT

MAGNEXT provides Extinction Rules for Magnetic Space Groups, as well as additional information such as Structure Factors and Propagation Vectors

FUTURE DEVELOPMENTS ON MAGNEXT

EXTINCTION RULES IN ANY SETTING

New Option: user-given Magnetic Space Group Generators (or General Positions) to obtain Extintion Rules at any setting

INCOMMENSURATE STRUCTURES

Extinction Rules for Magnetic Superspace Groups (Incommensurate Structures) given by user

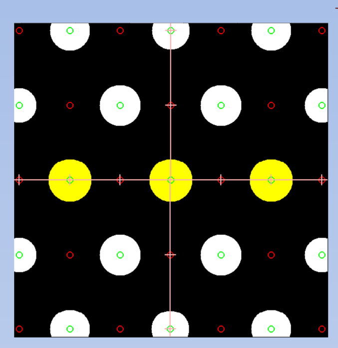
MAGNETIC SPACE GROUP FINDER

Lists of all COMPATIBLE MAGNETIC SPACE GROUPS with a set of Extinction Rules or a diffraction pattern given by user

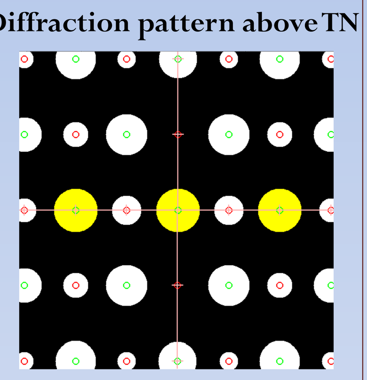
SYSTEMATIC EXTINCTIONS ANALYSIS IS HELPFUL TO SOLVE MAGNETIC STRUCTURES

Magnetic Structures Partially Solved by Extinction Rules Analysis

MnF_2 – $P4_2/mnm$



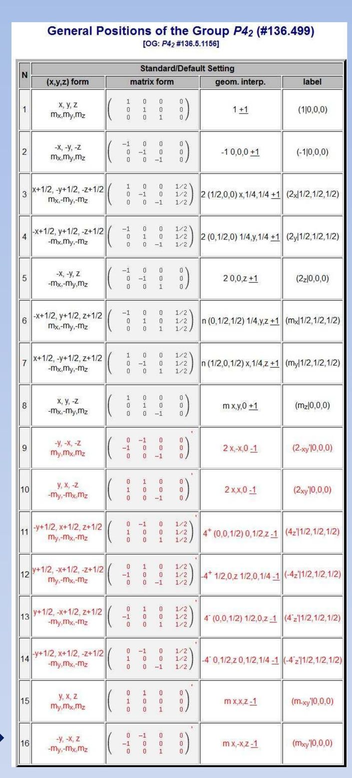
Diffraction pattern above TN

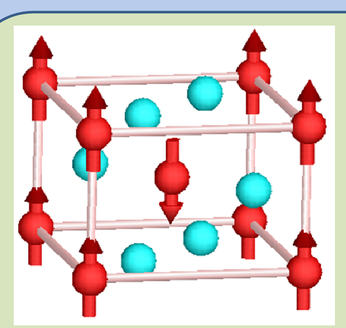


Diffraction pattern below TN

Magnetic Extinction rules from experiment:
(h 0 0) → h = 2n
(h 0 0) → k = 2n
(h 0 0) → l any

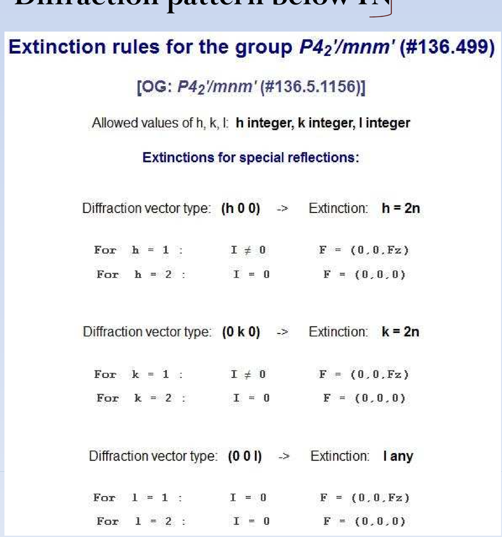
Possible groups:
$P4_2'/mnm'$
$P4_2'/m'n'm$

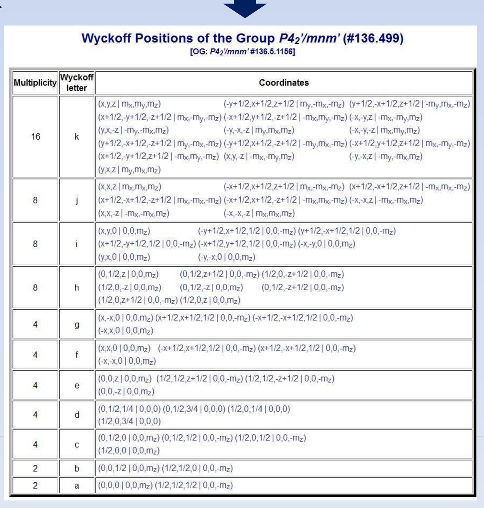




Atomic Positions:
Mn: 2a (0,0,0)
F: 4f (x = 0.31)

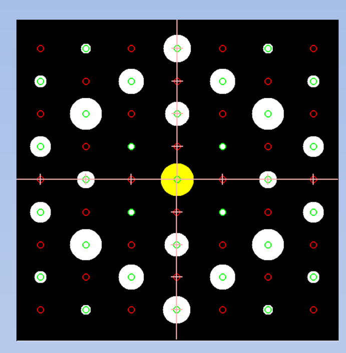
Possible structure of MnF2 (P42'/mnm')



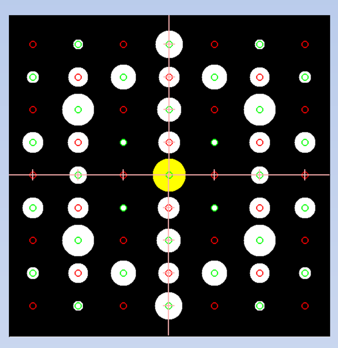


MnF_2 data: "Magnetism in Crystalline Materials – Application of the Theory of Groups of Cambiant Symmetry", A. P. Cracknell

$LaMnO_3$ – Pnma



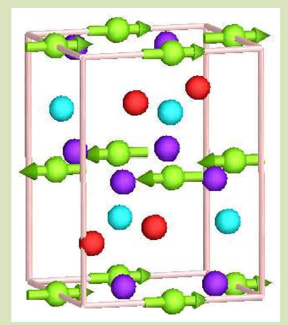
Diffraction pattern above T_N



Diffraction pattern below T_N

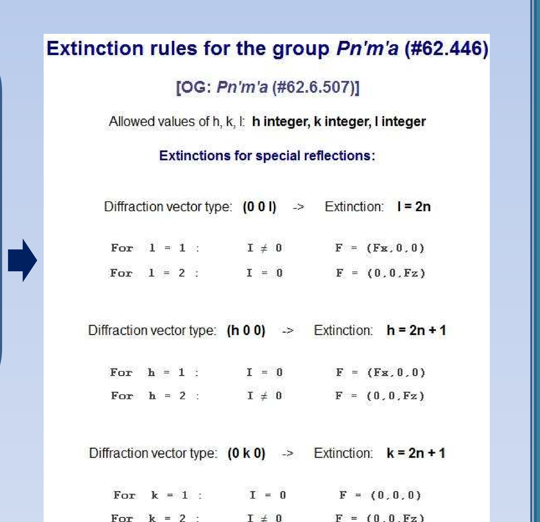
Magnetic Extinction Rules from experiment:
(h 0 0) → h = 2n + 1
(0 k 0) → k = 2n + 1
(0 0 l) → l = 2n

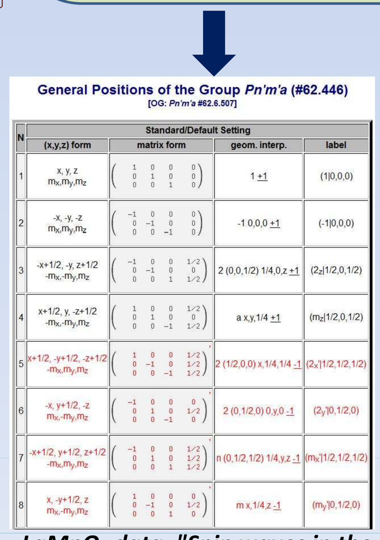
Possible groups:
Pnma'
Pn'ma

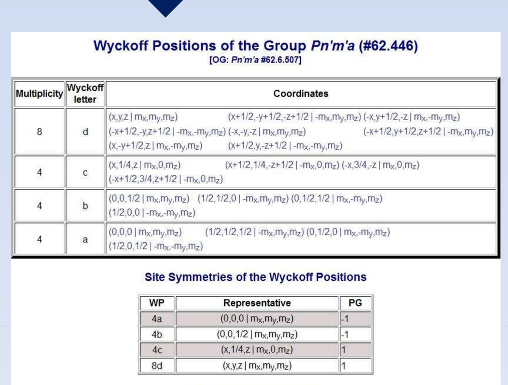


Atomic Positions
Mn: 4c (x = -0.0095, z = 0.0513)
La: 4b
O(1): 4c (x = 0.0777, z = 0.48493)
O(2): 8d (x = 0.7227, y = 0.0408, z = 0.3085)

Possible structure of $LaMnO_3$ (Pn'ma)



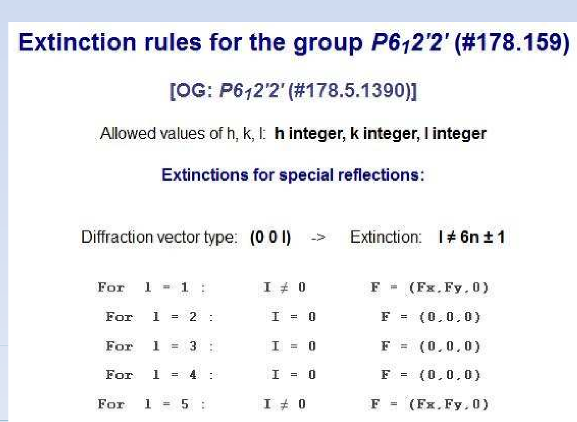




Extinction Rule Example: Group $P6_12'2'$

CURIOUS AND UNEXPECTED EXTINCTION RULE

Caused by the strange symmetry restriction on Structure Factor caused by $6_{1,5}$-fold hellicoidal axes



Diffraction patterns and structures pictures obtained with ISODISTORT
http://stokes.byu.edu/isodistort.html

$LaMnO_3$ data: "Spin waves in the antiferromagnet perovskite LaMnO3: a neutron scattering study", F.Moussa, M. Hennion, J.Rodríguez-Carvajal, L. Pinsard and A. Revcolevschi, Physical Review B 54 (21), 15149 (1996).