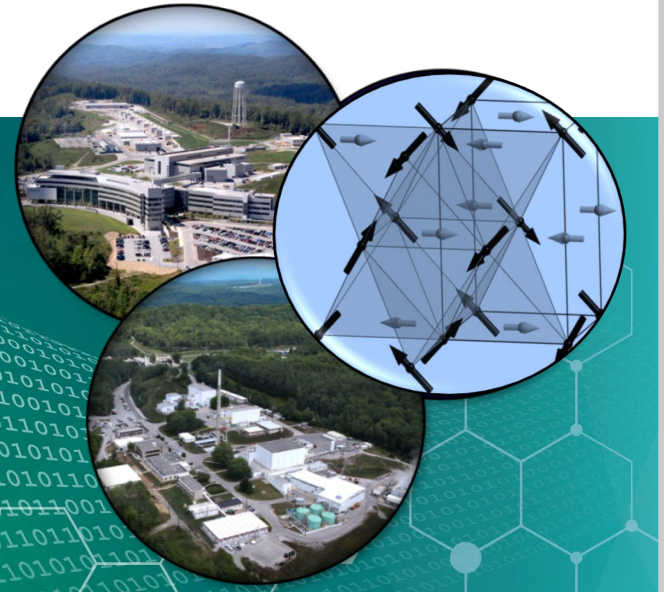
OAK RIDGE National Laboratory

A Hierarchy of Magnetic Structures based on Lattice Dimensionality

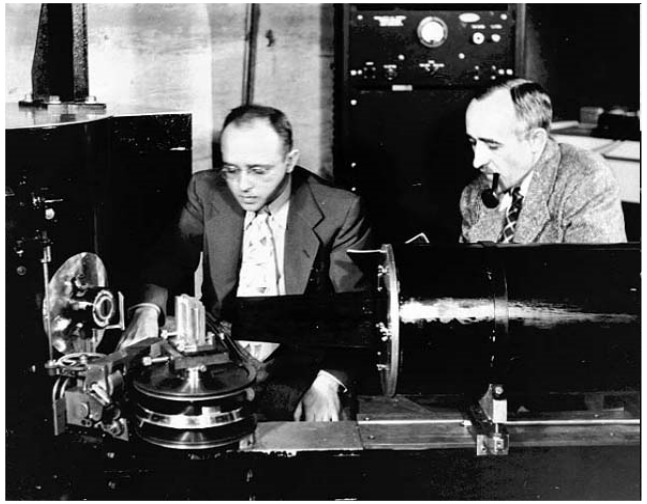


V. Ovidiu Garlea
Neutron Scattering Division,
Oak Ridge National Laboratory

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

U.S. DEPARTMENT OF ENERGY

The beginnings of Magnetic Structure Analysis

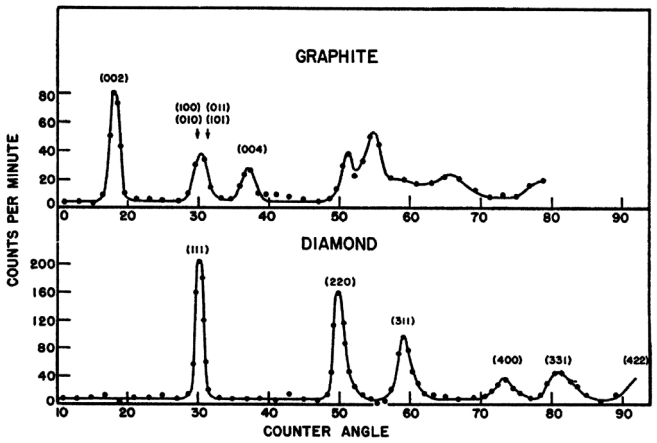


1948: First demonstration of the neutron diffraction

REVIEW VOLUME 73, NUMBER 8

The Diffraction of Neutrons by Crystalline Powders

E. O. WOLLAN AND C. G. SHULL
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received January 5, 1948)

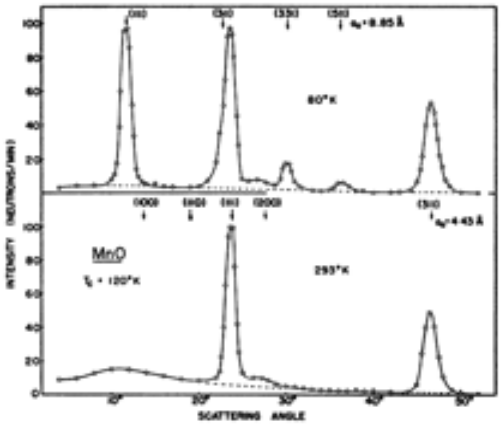


1949: the first direct evidence of Antiferromagnetism (in MnO)

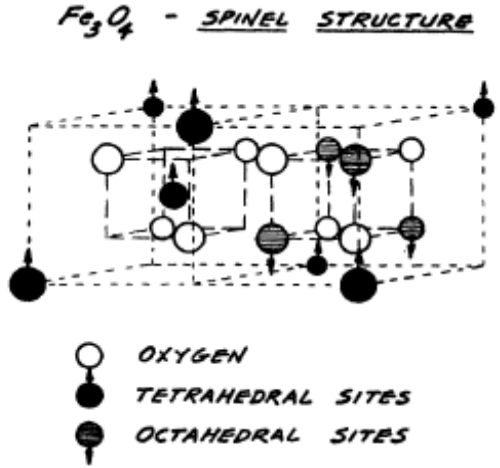
Detection of Antiferromagnetism by Neutron Diffraction*

C. G. SHULL
Oak Ridge National Laboratory, Oak Ridge, Tennessee
AND
J. SAMUEL SMART
Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland
August 29, 1949

AFM: Louis Néel – 1930



1951: the Néel model of ferrimagnetism was confirmed (magnetite Fe3O4)



The beginnings of Magnetic Structure Analysis

1953: Review articles on magnetic structures began appearing

REVIEWS OF MODERN PHYSICS VOLUME 25, NUMBER 1 JANUARY, 1953

Neutron Diffraction Studies of Various Transition Elements

C. G. SHULL AND M. K. WILKINSON
Oak Ridge National Laboratory, Oak Ridge, Tennessee

Fe_3O_4, MnO, FeO, CoO, NiO, Cr, a-Mn, Ni, Fe
(powder and single crystal data /
unpolarized and polarized neutrons)

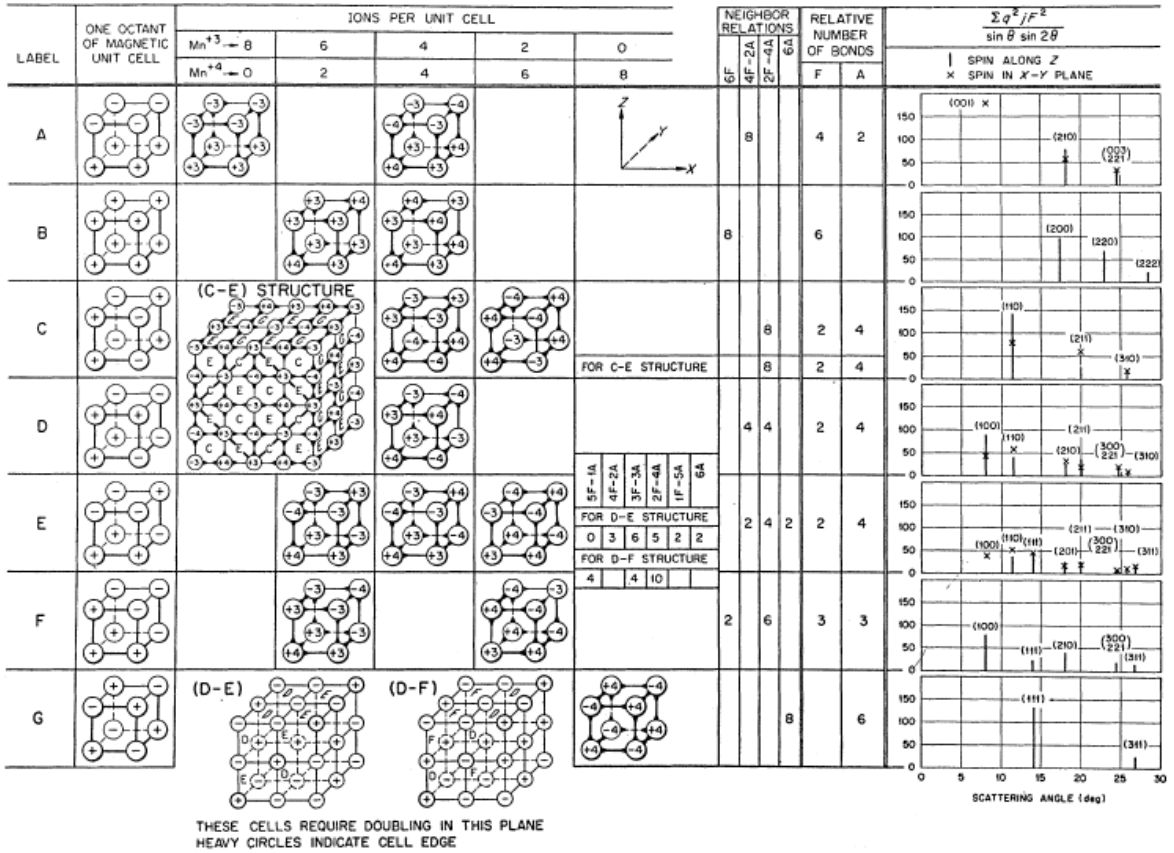
1955: Scheme of magnetic structures of the perovskite $La_{1-x}Ca_xMnO_3$

PHYSICAL REVIEW VOLUME 100, NUMBER 2 OCTOBER

Neutron Diffraction Study of the Magnetic Properties of the Series of Perovskite-Type Compounds $[(1-x)La, xCa]MnO_3$†

E. O. WOLLAN AND W. C. KOEHLER
Oak Ridge National Laboratory, Oak Ridge, Tennessee

cited over 2,300 times (to date)

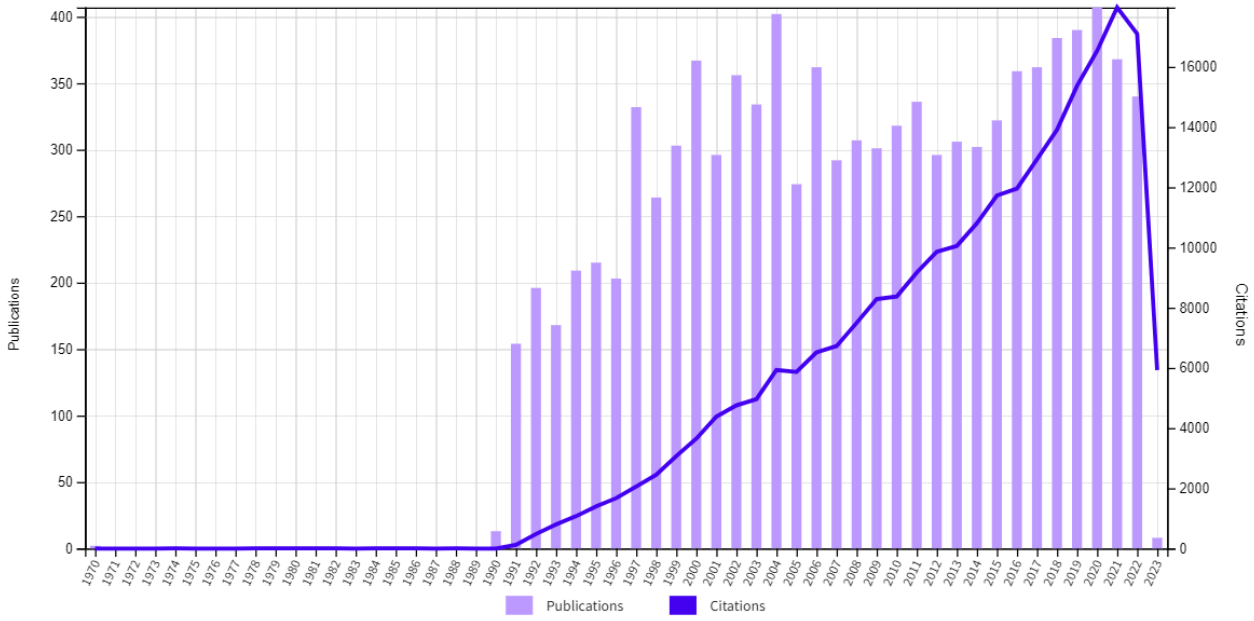


OAK RIDGE National Laboratory | HIGH FLUX ISOTOPE REACTOR | SPALLATION NEUTRON SOURCE

Evolution in time of the number of magnetic structure entries

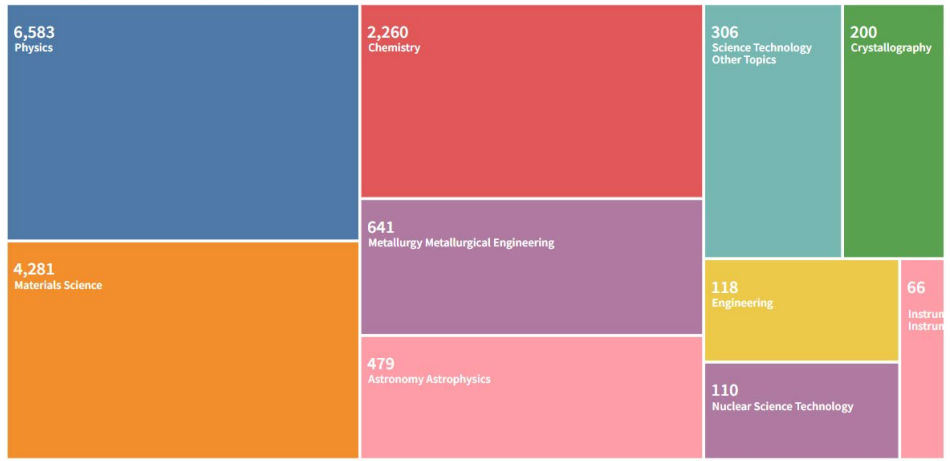
marked increases in ~ 1990s likely associated with introduction of computational tools and the discovery of high-Tc superconductors and colossal magnetoresistance (CMR)

Web of Science citation report
(*magnetic structure + neutron diffraction*)



References: 9,849
Times Cited: 243,394 ; Average: 24.7/item

Research areas:

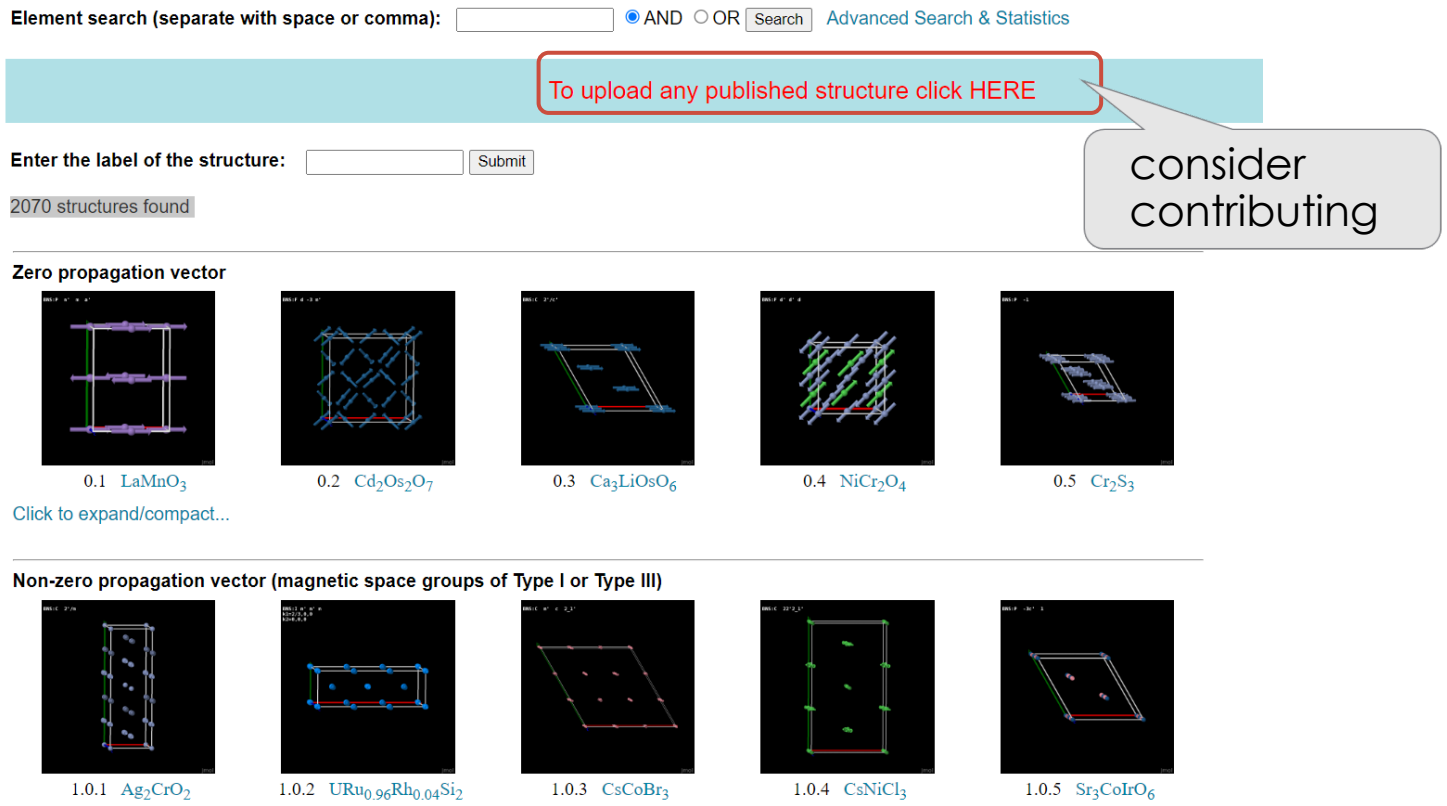


The discovery of novel magnetic structures is unceasing, driven by their relationships to ferroelectricity, thermo-electricity, superconductivity, improved permanent magnets, and spintronic technologies

Standard description of magnetic structures

- ✓ IUCr Commission on Magnetic Structures formed in 2011 (https://magcryst.org)
- ✓ **MagneticCIF or MCIF:** Standard format for magnetic structures
- ✓ MAGNDATA: A Collection of magnetic structures with portable mcif-type files

  at Bilbao Crystallographic Server: http://www.cryst.ehu.es/ (~ 2070 structures in June 2023)




```
_space_group.magn_number_BNS 58.395
_space_group.magn_name_BNS "P n 'n m"
_cell_length_a                4.57100
_cell_length_b                4.57100
_cell_length_c                8.85300
_cell_angle_alpha             90.00
_cell_angle_beta              90.00
_cell_angle_gamma             90.00

loop_
_space_group_symop.magn_id
_space_group_symop.magn_operation_xyz
_space_group_symop.magn_operation_mxmymz
1 x,y,z,+1 mx,my,mz
2 x+1/2,-y+1/2,-z+1/2,+1 mx,-my,-mz
3 x+1/2,-y+1/2,z+1/2,+1 -mx,my,-mz
4 x,y,-z,+1 -mx,-my,mz
5 -x+1/2,y+1/2,-z+1/2,-1 mx,-my,mz
6 -x,-y,z,-1 mx,my,-mz
7 -x,-y,-z,-1 -mx,-my,-mz
8 -x+1/2,y+1/2,z+1/2,-1 -mx,my,mz

loop_
_space_group_symop.magn_centering_id
_space_group_symop.magn_centering_xyz
_space_group_symop.magn_centering_mxmymz
1 x,y,z,+1 mx,my,mz

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
W1 W 0.00000 0.00000 0.00000
Cr1 Cr 0.00000 0.00000 0.33300
O1 O 0.30800 0.30800 0.00000
O2 O 0.30800 0.30800 0.33300
```

Magnetic structure determination with GSAS-II, ORNL, Jun

Standard description of magnetic structures

IUCr Commission on Magnetic Structures

Guidelines for communicating commensurate magnetic structures (Prof. Manuel Perez-Mato):

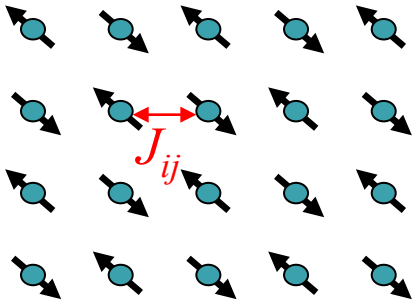
- Parent space group
- Propagation vector(s)
- MSG symbol and numerical index
- Transformation from the parent basis to the one used for magnetic structure

  e.g.: (a,b,2c; 0, 0, 0), i. e. the origin and orientation of the cell parameters
- Transformation to standard setting of MSG (e.g.: (c, a, b; 0, 0,-1/8))
- MSG symmetry operations
- Positions of magnetic and non-magnetic atoms
- Magnetic moments and their MSG constraints
- Description of primary and, eventually, secondary irreps

M1	1.34(2)	8.35(2)	0.0	(m_x, m_y, 0)	8.46(2)
M2	0.0	0.0	1.38(1)	(0, 0, m_z)	1.38(1)

A Hierarchy of Magnetic Structures based on Lattice Dimensionality

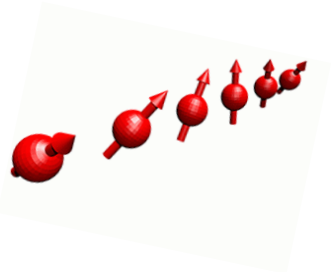
A magnetic state in a solid is the net result of the competing influences, thermal energy tending to randomize moments versus some quantum mechanical coupling tending to order moments



Spin-Hamiltonian:

isotropic or anisotropic exchange interactions

$$\mathcal{H}_{ex} = -\sum_{ij} J_{ij}^{xy}(\mathbf{S}_{ix}\cdot\mathbf{S}_{jx} + \mathbf{S}_{iy}\cdot\mathbf{S}_{jy}) + J_{ij}^{z}(\mathbf{S}_{iz}\cdot\mathbf{S}_{jz})$$



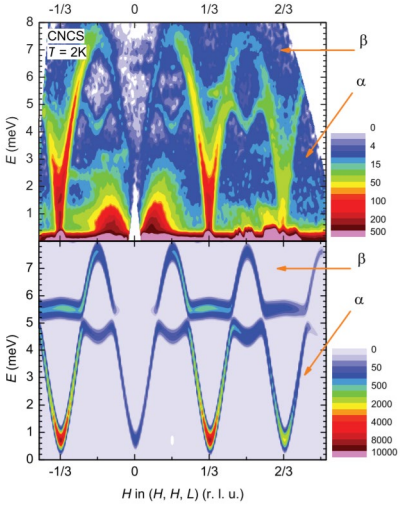
antisymmetric Dzyaloshinskii-Moriya $\mathcal{H}_{DM} = -\sum_{ij} D_{ij}\mathbf{S}_i \times \mathbf{S}_j$

dipolar interactions $\mathcal{H}_{dip} = \sum_{ij} \frac{(g\mu_B)^2}{r_{ij}^3}[3(\mathbf{r}_{ij}\cdot\mathbf{S}_i)(\mathbf{r}_{ij}\cdot\mathbf{S}_j) - \mathbf{S}_i\cdot\mathbf{S}_j]$

single-ion anisotropy $\mathcal{H}_{ani} = -\frac{1}{2}\sum_i D\mathbf{S}_{iz}^2 + \frac{1}{2}\sum_i D'(\mathbf{S}_{ix}^2 - \mathbf{S}_{iy}^2)$

field coupling $\mathcal{H}_H = -\mathbf{H}\sum_i g_i\mu_B\mathbf{S}_i$

- **Static order:**
  Neutron diffraction (elastic scattering)
- **Spin dynamics:**
  Inelastic neutron scattering

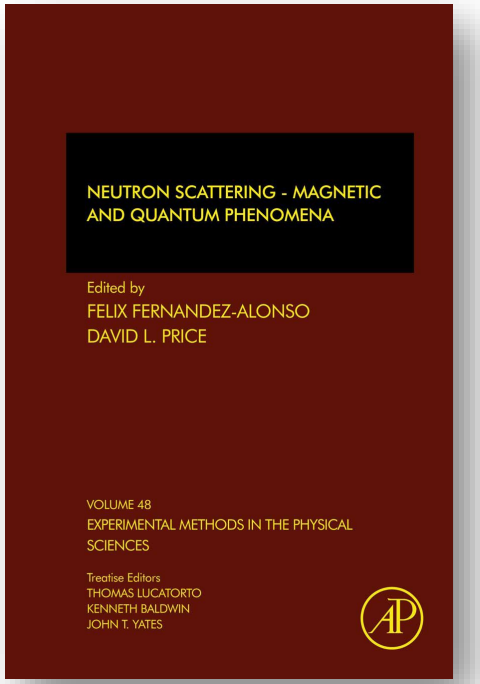


A Hierarchy of Magnetic Structures based on Lattice Dimensionality

most of magnetic ground states being realized primarily through the competition between *exchange interactions* $\left(\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \right)$

→ the effective dimensionality of the lattice plays an important role in the magnetic behavior and selection of magnetic structure

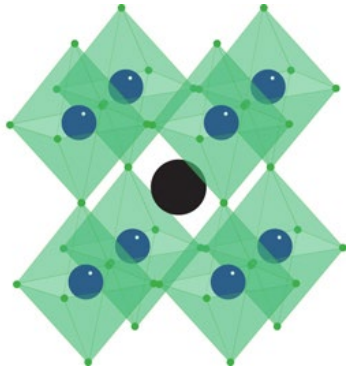
- ❑ 3D - networks
  perovskite, pyrochlore - corner-sharing tetrahedral, spinels with pyrochlore and diamond lattices, edge-sharing tetrahedra, …
- ❑ Layered structures
  square-planar, edge-sharing triangles, kagomé, honeycomb lattices, striped-kagomé …
- ❑ Quasi-one-dimensional lattices
  simple-chain, ladders, sawtooth chains,…



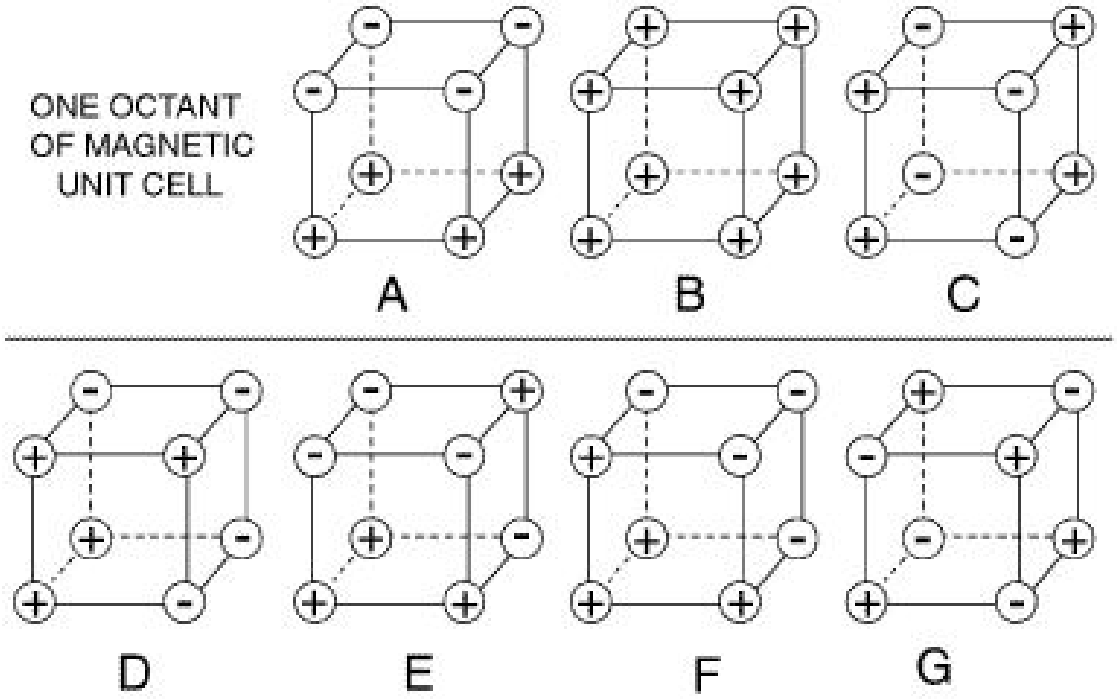
Magnetic Structures chapter in Experimental Methods in the Physical Sciences: Neutron Scattering - Magnetic and Quantum Phenomena

3D - networks : Perovskites

ABO_3



Ordering scheme proposed by:
E. Wollan and W. Koehler, Phys. Rev., 100, 545 (1955)



A-type : antiferro- coupled ferromagnetic planes

B-type: ferromagnetic order (also called **F**)

C-type: ferromagnetic coupled antiferromagnetic planes

D-type: criss-crossed stripes

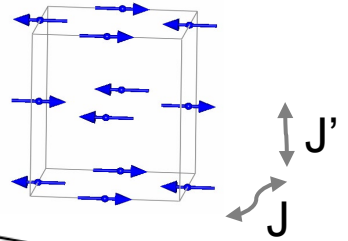
E and F-type: antiferromagnetism with ferrimagnetic planes

G-type: antiferromagnetically coupled spins in all directions

3D - networks : Perovskites

Moussa et al., *Phys. Rev. B* 54 15149 (1995)

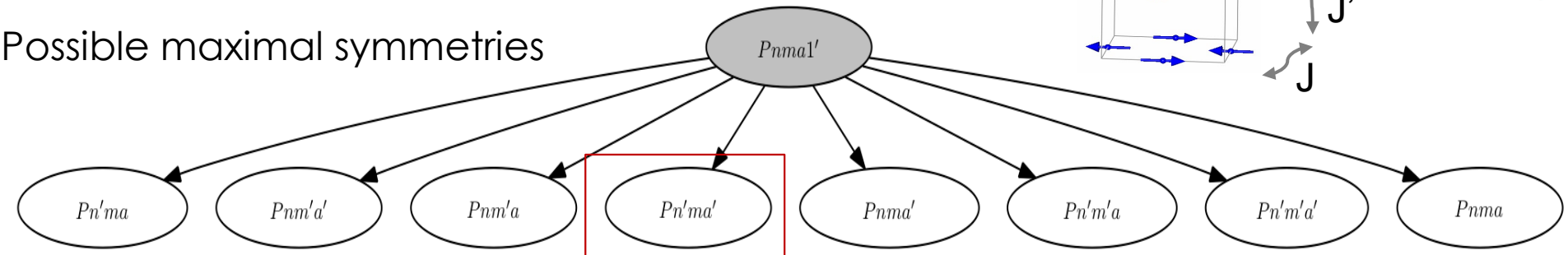
$LaMnO_3$ *Pnma*, **k**= (0,0,0), Mn in 4b: (0,0,1/2)



$$\mathcal{H} = -\sum_{i,j} J_{ij}(S_i \cdot S_j) - D\sum_i S_i^{z2}$$

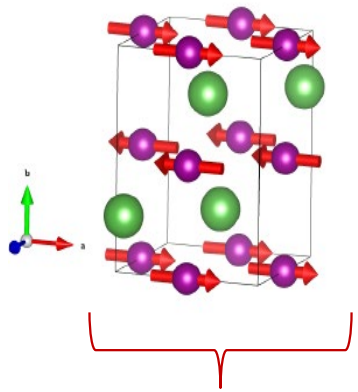
J ~ 9.6 K,
J' ~ - 6.7 K
D = 1.92 K

Possible maximal symmetries

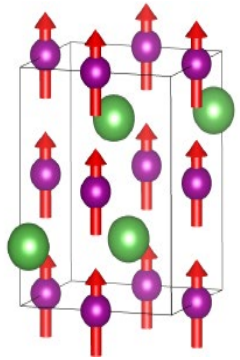


Multiplicity	Wyckoff letter	Coordinates
8	d	(x,y,z | m_x,m_y,m_z) (x+1/2,-y+1/2,-z+1/2 | -m_x,m_y,m_z) (-x,y+1/2,-z | -m_x,m_y,-m_z) (-x+1/2,-y,z+1/2 | m_x,m_y,-m_z) (-x,-y,-z | m_x,m_y,m_z) (-x+1/2,y+1/2,z+1/2 | -m_x,m_y,m_z) (x,-y+1/2,z | -m_x,m_y,-m_z) (x+1/2,y,-z+1/2 | m_x,m_y,-m_z)
4	c	(x,1/4,z | 0,m_y,0) (x+1/2,1/4,-z+1/2 | 0,m_y,0) (-x,3/4,-z | 0,m_y,0) (-x+1/2,3/4,z+1/2 | 0,m_y,0)
4	b	(0,0,1/2 | m_x,m_y,m_z) (1/2,1/2,0 | -m_x,m_y,m_z) (0,1/2,1/2 | -m_x,m_y,-m_z) (1/2,0,0 | m_x,m_y,-m_z)
4	a	(0,0,0 | m_x,m_y,m_z) (1/2,1/2,1/2 | -m_x,m_y,m_z) (0,1/2,0 | -m_x,m_y,-m_z) (1/2,0,1/2 | m_x,m_y,-m_z)

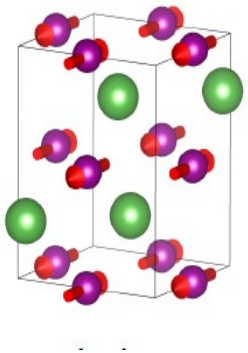
Ax



By



Gz



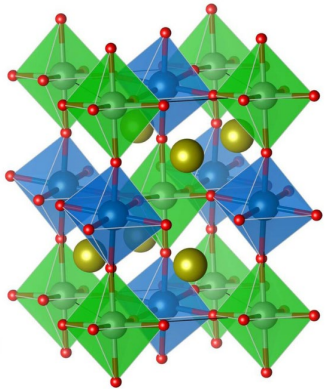
$LaMnO_3$

$m(Mn^{3+}) \approx 3.87\mu_B$

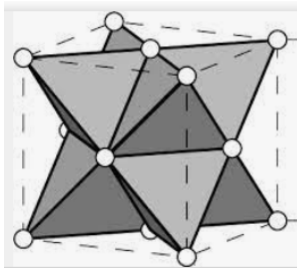
small ferromagnetic component possible due to D-M → AxBy

3D - networks : Double Perovskites of alternating octahedra

$A_2BB'O_6$

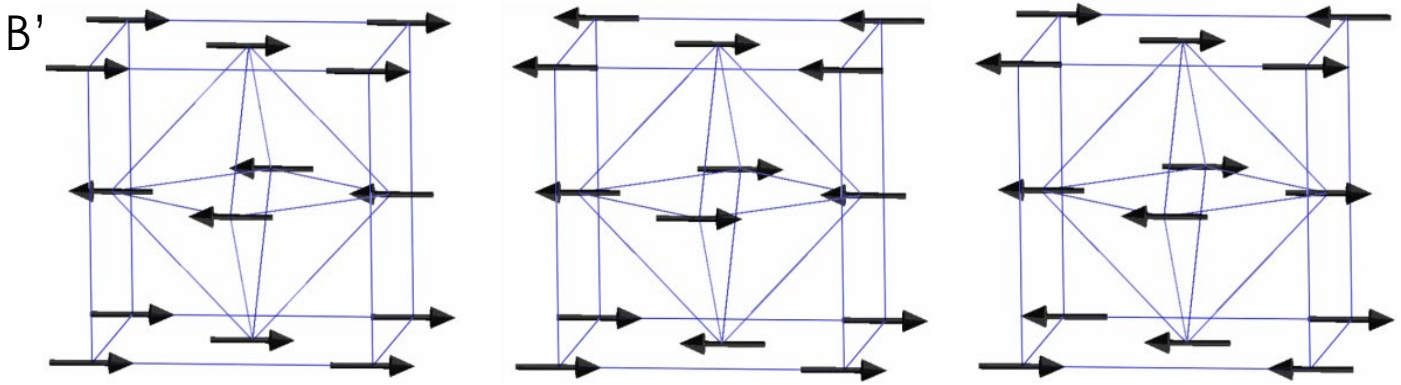


B' magnetic site = frustrated FCC lattice with edge-sharing tetrahedra
A = diamagnetic alkaline earth or lanthanide cation



C. Jones and P. D. Battle, J. Solid State Chem. 78, 108, 1989

- Type I: dominant (B'-O-O-B') NN interactions → AFM order between successive (001) Ferro planes ; **k** = (0, 0, 1)
- Type II: dominant (B'-O-A-O-B') NNN exchange interactions → spins alternate along two directions
- Type III: comparable NN and NNN ; **k** = (½, ½, ½)



AFM I
Sr_2LuRuO_6
Ba_2YRuO_6

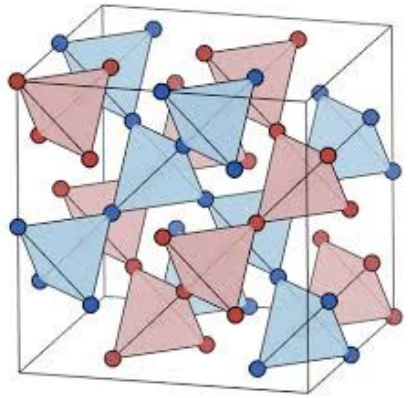
AFM II
Ca_2WMnO_6
Sr_2MoMnO_6

AFM III
Ba_2LaRuO_6

- when B, B' or A, B' are magnetic: the interplay between intra-lattice and inter-lattice interactions can lead to a large variety of magnetic states

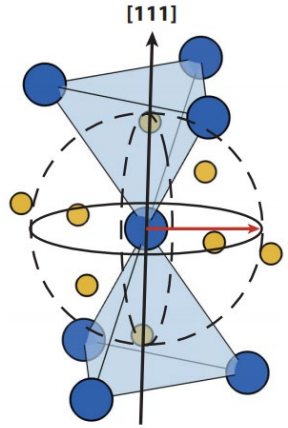
3D - networks : Pyrochlore: Corner-sharing tetrahedral lattices

$A^{3+}_2B^{4+}_2O_7$

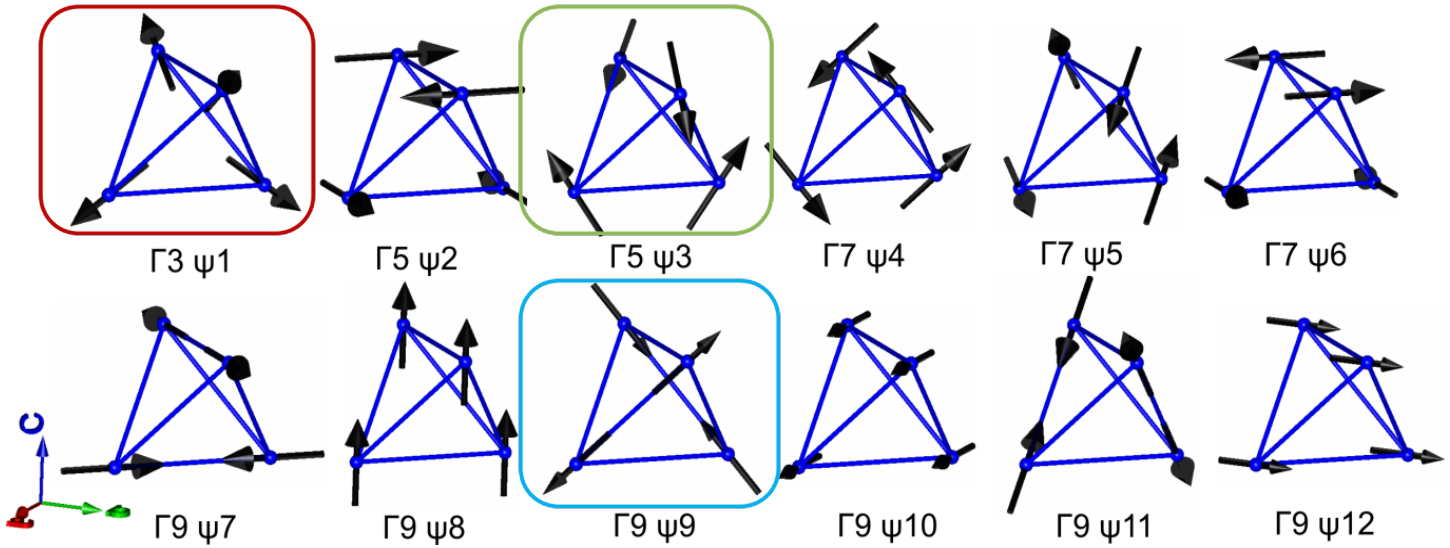


- two interpenetrating lattices (A, B) of corner-sharing tetrahedra ($Fd\bar{3}m$, sites 16c and 16d)
- strong geometrically frustrated NN AFM interactions
  → single-ion anisotropy, dipolar interactions, antisymmetric D-M are relevant

$Fd\bar{3}m$, **k** = (0, 0, 0)



$\Gamma_{mag}(A) = 1\,\Gamma_3^{(1)} + 2\,\Gamma_5^{(1)} + 3\,\Gamma_7^{(1)} + 3\,\Gamma_9^{(2)}$



$Sm_2Ti_2O_7$: Ising all-in/all-out

$\Gamma_3\psi_1$ (*Fd-3m'*)

$Er_2Ti_2O_7$: AFM- XY pyrochlore

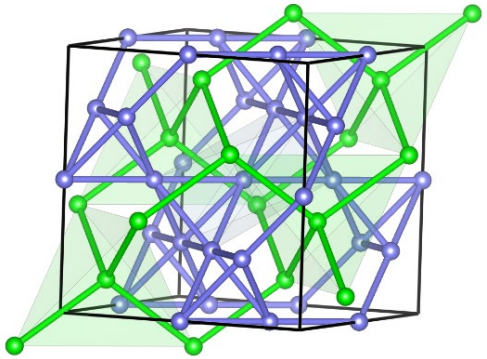
$\Gamma_5\psi_3$ ($I4_1'/am'd$)

$Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$: Ising two-in/two-out, spin ice

$\Gamma_9\psi_9$ ($I4_1/am'd'$)

3D - networks : Spinel

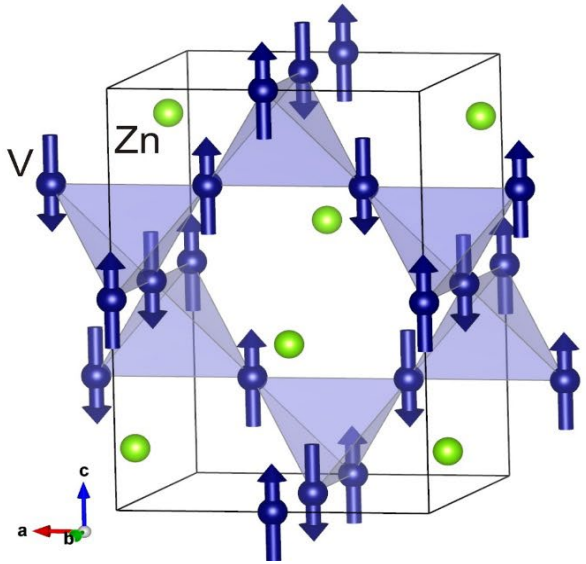
$A^{2+}B^{3+}_2X_4$ corner-sharing tetrahedra (B) and diamond (FCC) lattice (A)



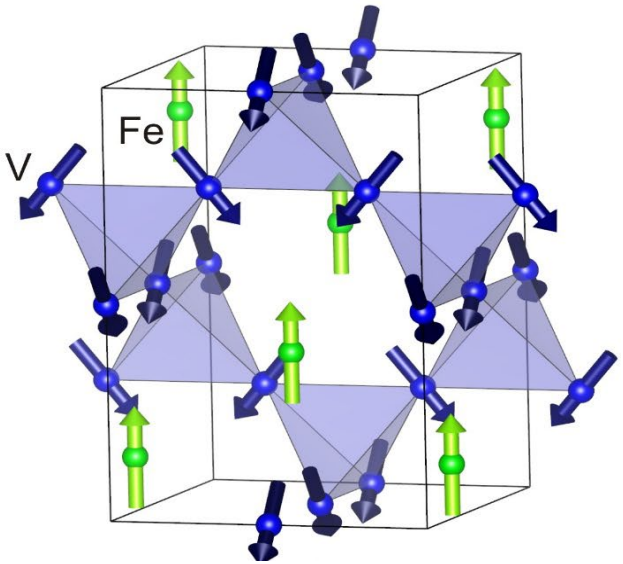
chemically versatile: transition metal Oxides, Sulfides and Selenides

- AV_2O_4, with V^{3+} ($3d^2$) - model systems for studying orbital order
- Sequence of phase transitions: structural distortion followed by a magnetic transition.

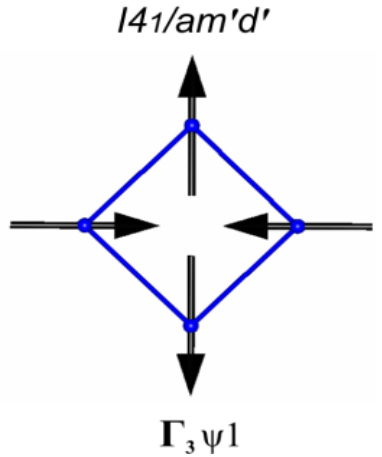
ZnV_2O_4 $Fd\bar{3}m \rightarrow I4_1/amd$ (T_S=50K)
k = (0, 0,1), *AFM* (T_N=40K)



FeV_2O_4 (A = Fe^{2+} ($3d^6$) S=2)
$Fd\bar{3}m \rightarrow I4_1/amd \rightarrow Fddd \rightarrow I4_1/amd$.
collinear FerriM (T_{N1}= 110K) → canted FerriM (60K)



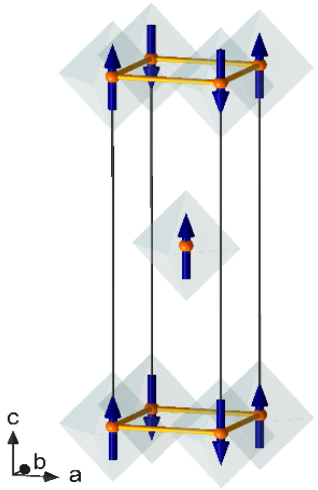
"two-in/two-out"



2D structures: Square-planar metal-oxygen/halogen

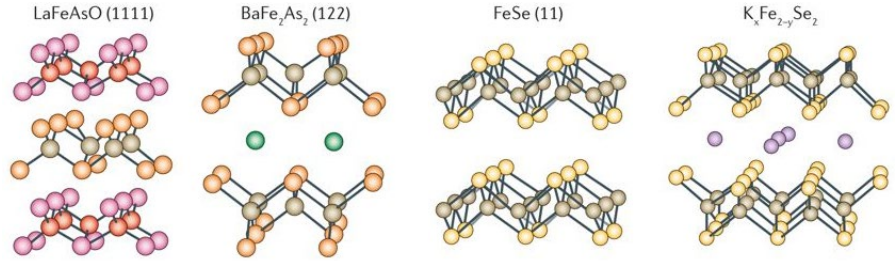
K_2NiF_4

R. Plumier and E. Legrand, *J. Phys. Radium,* 24, 741 (1963)
R. J. Birgeneau, H. J. Guggenheim, and G. Shirane, *PRL* 22, 720 (1969)



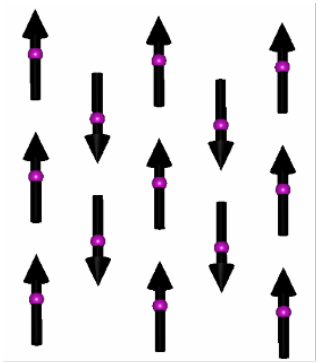
Inter-layer exchange smaller than the intra-plane exchange by at least three orders of magnitude → 2D Heisenberg antiferromagnet. ("Bragg ridges" rather than Bragg peaks)

Layered perovskite - high-Tc Cuprates
Fe - pnictides: ZrCuSiAs–type (1111)
or $ThCr_2Si_2$-type (122), Fe(Se,Te) (11)



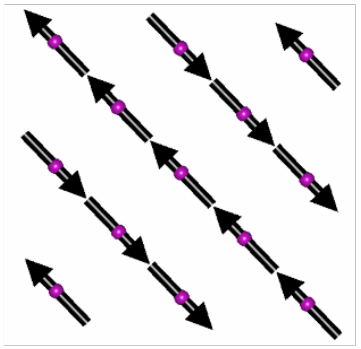
structure distorts at T_N

NN AFM



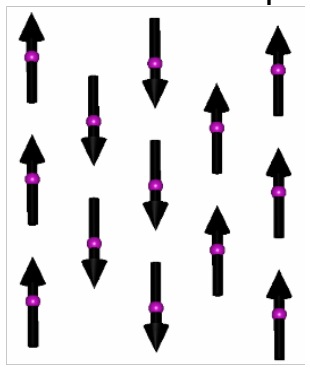
Cuprates

stripe order



LaFeAsO, $BaFe_2As_2$

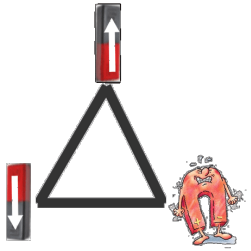
double-stripe



$Fe_{1+\delta}Te$

D. J. Singh, *Sci. Technol. Adv. Mater.,* 13, 054304 (2012)

2D structure: edge-sharing equilateral triangles



- simplest geometrical frustrated lattice

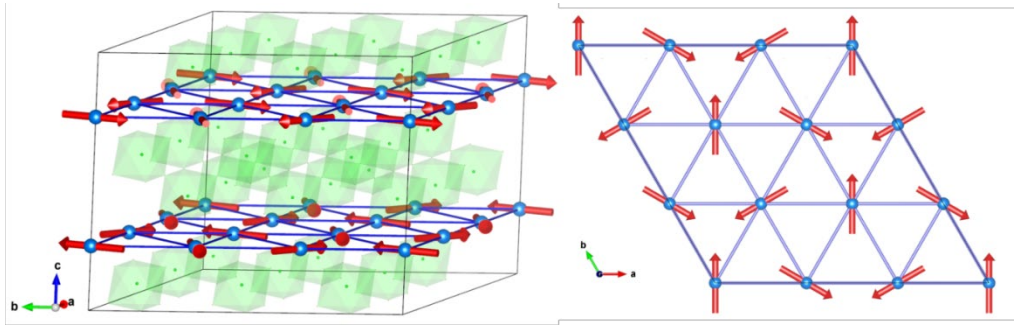
→ planar 120° spin structure or "three-sublattice $\sqrt{3} \times \sqrt{3}$ state"

→ other ordered states can be stabilized by NNN interactions, anisotropy of the orbital configuration, or magnetoelastic coupling.

- ✓ VX_2 and AMX_3, where A = Cs, Rb, X = Cl, Br, I, S, Se, Te
- ✓ $A^+M^{3+}O_2$ series with delafossite or a-$NaFeO_2$ structures
- ✓ 6H-perovskites $Ba_3M'M''_2O_9$ with M' = Ni, Co, Mn, and M''= Nb or Sb
- ✓ tetrahedral oxoanions: $RbFe(MoO_4)_2$, $K_2M^{2+}{}_3(VO_4)_2CO_3$, $Na_2BaM^{2+}(VO_4)_2$, $K_3RE^{3+}(VO_4)_2$ …

XY -type anisotropy (D ≤ 0)

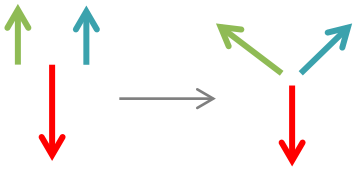
- one magnetic transition to 120° spin structure in *ab plane*

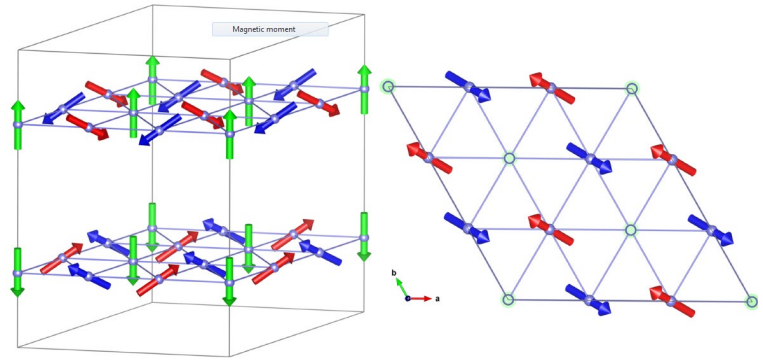


$Ba_3NiNb_2O_9$, k = (⅓, ⅓, ½)

Easy-axis anisotropy (D > 0)

- successive transitions: colinear and canted "Y"

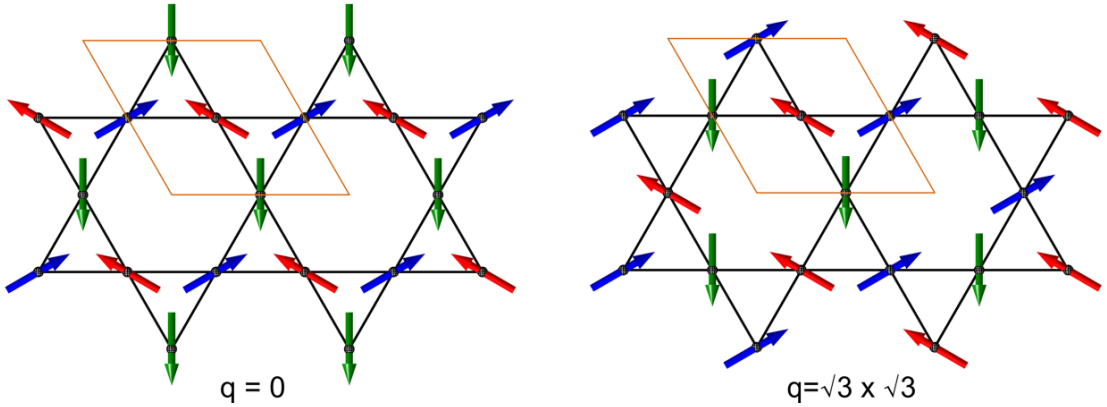




$K_2Mn_3(VO_4)_2CO_3$, k = (⅓, ⅓, 0)

2D structure: Kagomé (corner-shared triangular) lattice

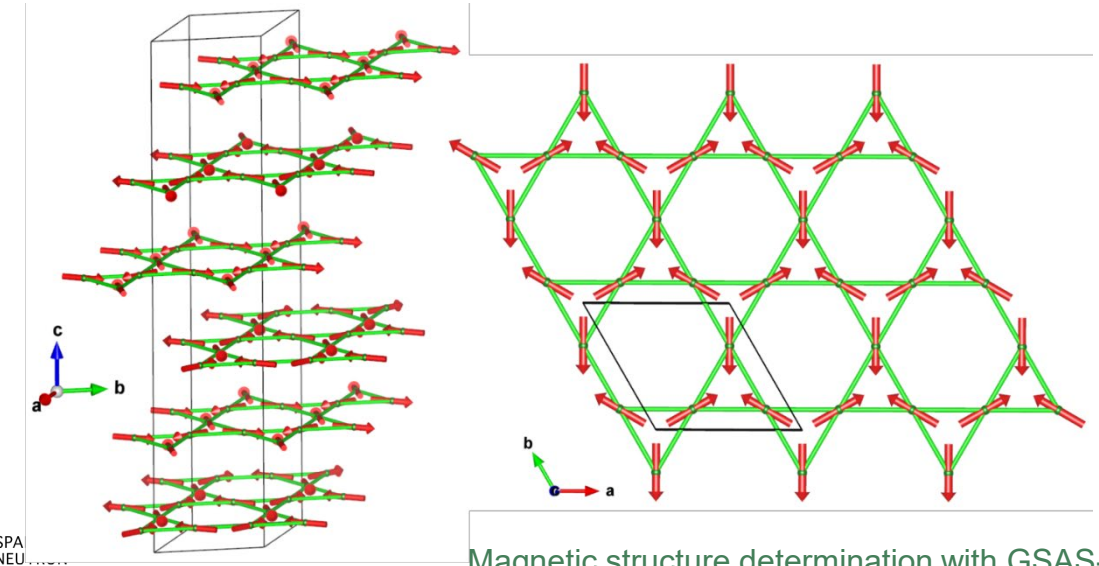
- variety of ground states: spin liquid, short-range order, or long-range order that can be stabilized by further-neighbor and D-M interactions
  - classical kagomé lattice orders with planar *120°* between *NN* spins



***q* = 0** : spin arrangement with uniform vector chirality

***q* = √3 x √3** : alternative spin arrangement with staggered vector chirality

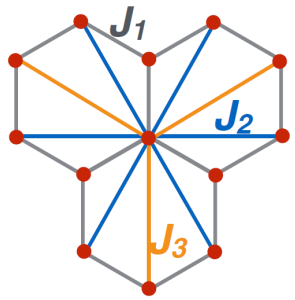
  - Jarosite, volborthite, herbertsmithite, and kapellasite series

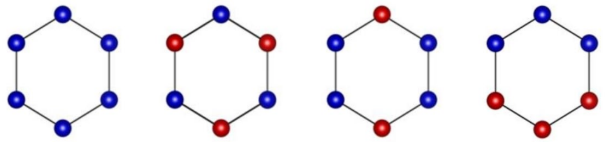


Fe-based jarosites $AFe_3(SO_4)_2(OH)_6$, with A = K, Na, Ag, (*R-3m* symmetry)
k = (0, 0, 3/2) order into planar "**q = 0**" type with AFM stacking of the layers)

A. Wills, PRB , 63, 064430 (2001)

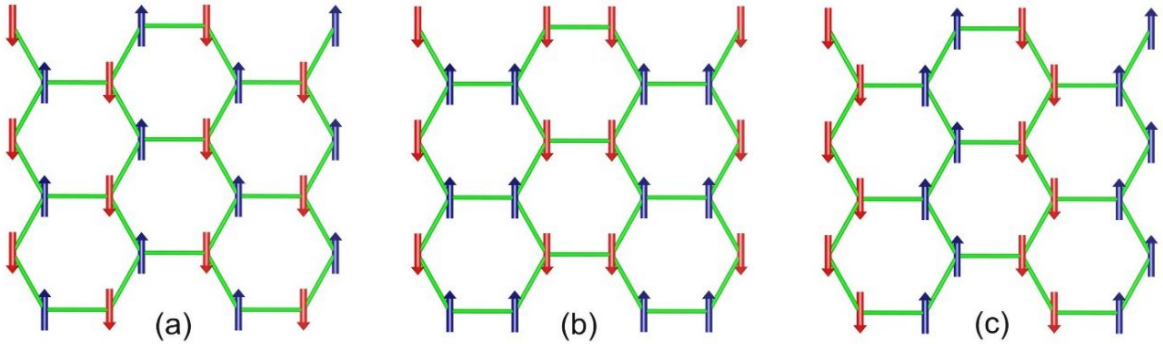
2D structure: honeycomb lattices





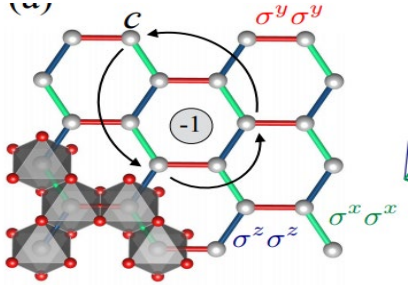
$$H = J_1 \sum_{n} S_i \cdot S_j + J_2 \sum_{nn} S_i \cdot S_j + J_3 \sum_{nnn} S_i \cdot S_j + Jz \sum_{nn} S_i \cdot S_j$$

Néel Stripe Zigzag

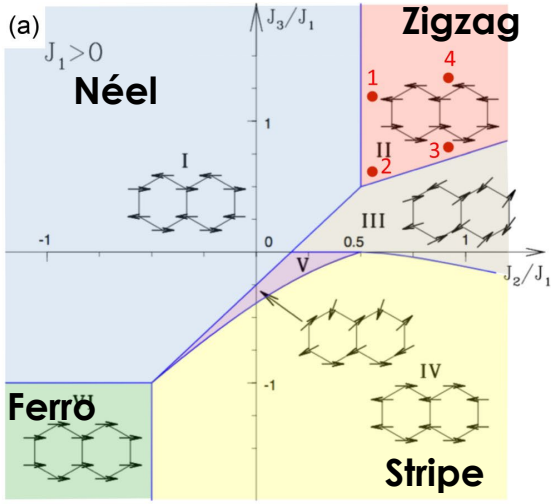


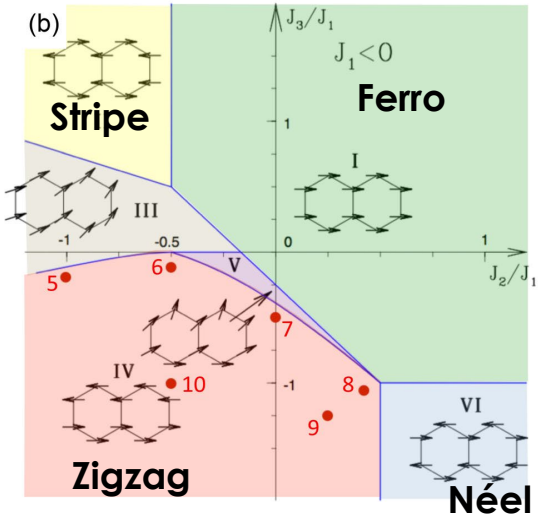
the Heisenber-Kitaev model (S=1/2 interacting via anisotropic bond-dependent coupling → Majorana-like excitations (a-$RuCl_3$, Na_2IrO_3, …)

Hermanns, et al., Annu. Rev. Cond. Matter 9, 17 (2018)



$J_2/J_1 – J_3/J_1$ phase diagrams for AF $J_1 > 0$ and for FM $J_1 < 0$





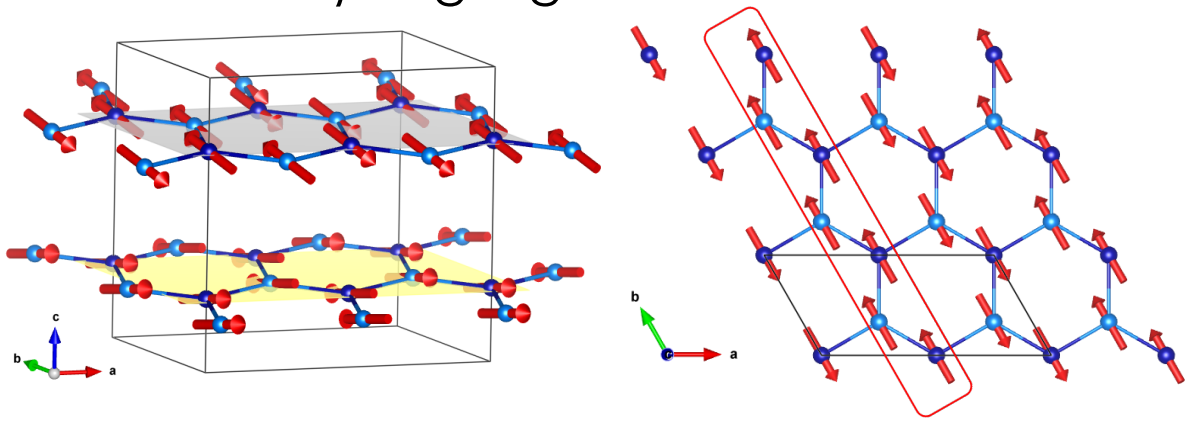
Lefrancois, PRB B 94, 214416 (2016)
Fouet, Eur. Phys.J. B 20, 241 (2001)

2D structure: honeycomb lattices

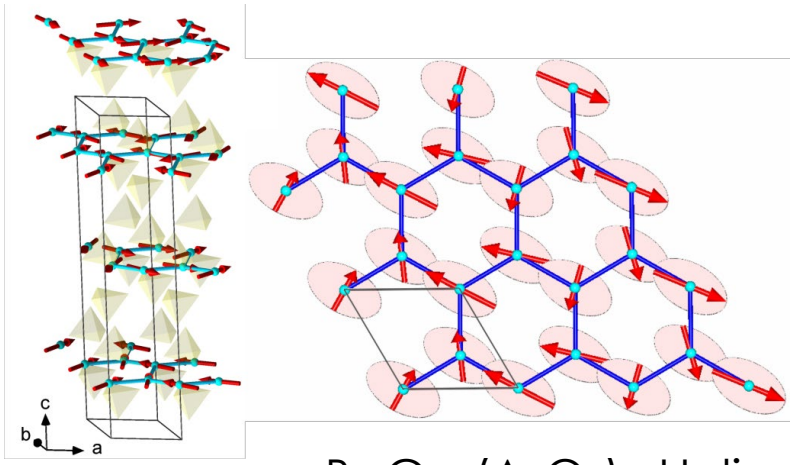
Examples of honeycomb lattice compounds:

- MnTiO3, - Néel order,
- $Cu_3M_2SbO_6$, $Na_3M_2SbO_6$ (M=Cu, Mn, Co, Ni) - zigzag order

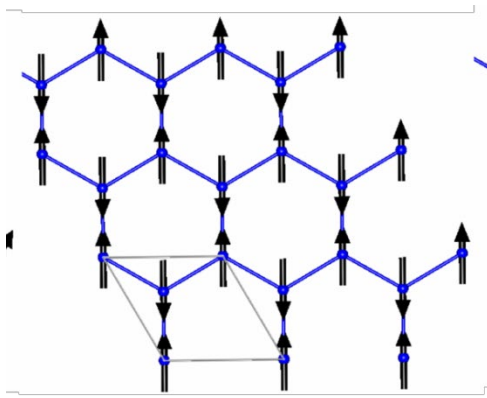
- $Na_2Co_2TeO_6$, Zigzag
  k = (1/2, 0, 0), $P_C2_12_12_1$



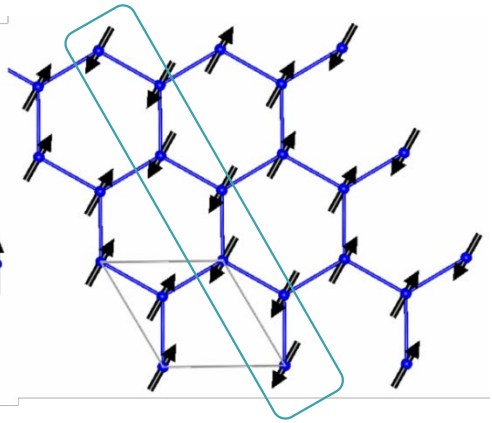
- $BaM_2(XO_4)_2$
  (M = Co, Ni, and X = P, As, V),



$BaCo_2(AsO_4)_2$, Helical
k = (0.261, 0, -4/3)



$BaNi_2(PO_4)_2$, Néel
k = (0, 0, 0)

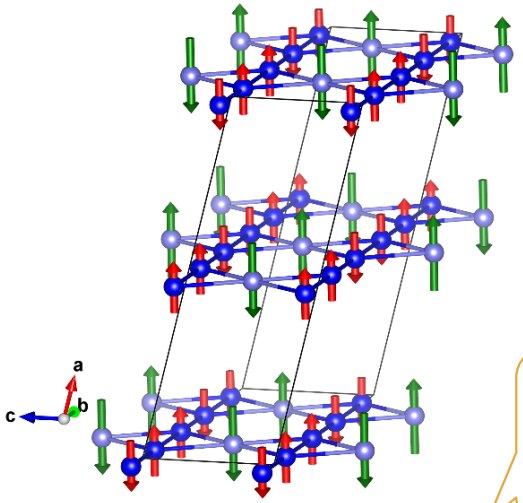


$BaNi_2(AsO_4)_2$, Zigzag
k = (½, 0, ½)

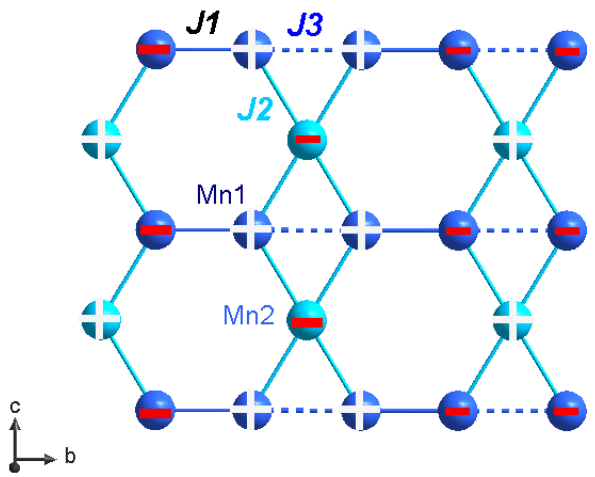
2D structure: frustrated "bow-tie" lattices

"bow-tie" or striped kagomé

$Ca_2Mn^{4+}{}_3O_8$, $K_2Mn^{2+}{}_3(VO_4)_2(OH)_2$



k = (0, ½ , 0)
m(Mn1) ≈ 1.7 μ_B
m(Mn2) ≈ 2.5 μ_B



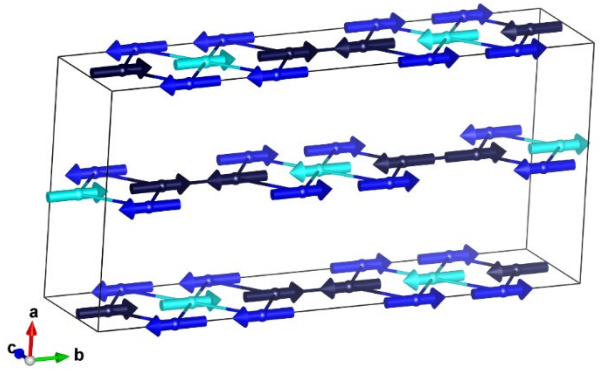
AFM - NN

Mn1, 3 NN

Mn2, 4 NN

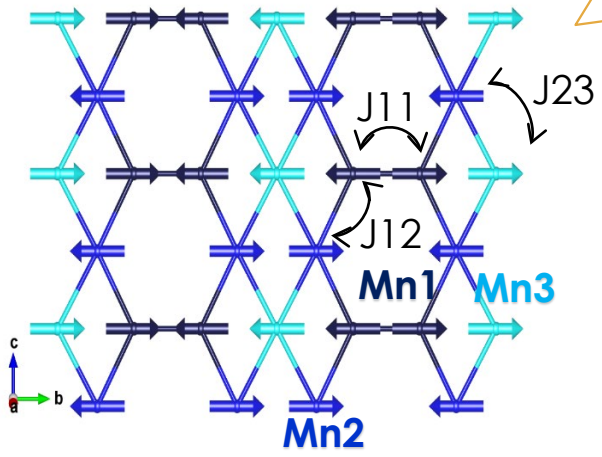
striped triangular lattice

$Mn^{2+}{}_5(VO_4)_2(OH)_4$



P_b2/c

k = (0, ½ , 0)
m(Mn1) ≈ 1.98 μ_B
m(Mn2) ≈ 2.43 μ_B
m(Mn3) ≈ 2.48 μ_B



AFM - NN

Mn1 , 3 NN

Mn2 , 4 NN

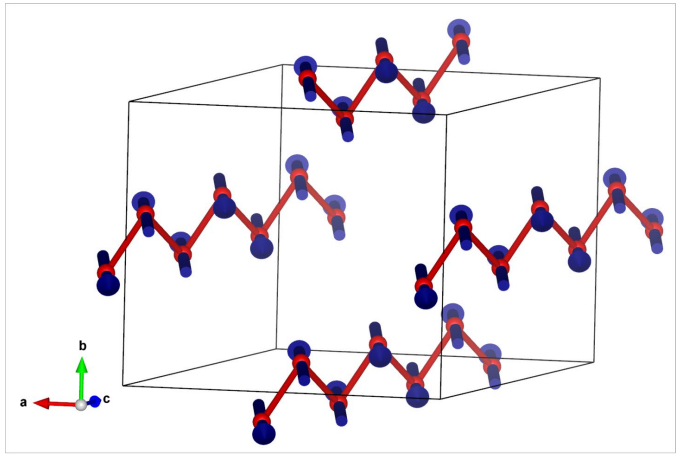
Mn1 , 4 NN

Quasi-1D structures

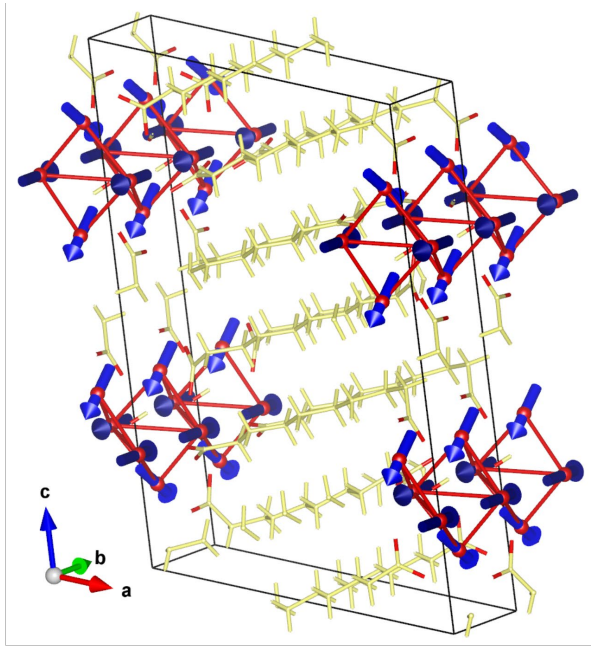
strong exchange coupling between magnetic ions only along one direction

- metal-organic frameworks (MOFs): connected low-dimensional inorganic subnetworks through non-magnetic molecules
- alkali-metal pyroxenes AMX_2O_6 , A = Li^+, Na^+; M = Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, and Fe^{3+}; X = Si^{4+}, Ge^{4+}
- brackebuschite $Ba_2M^{3+}(VO_4)_2(OH)$ and descloizite $SrM^{2+}(VO_4)(OH)$ transition metal vanadate

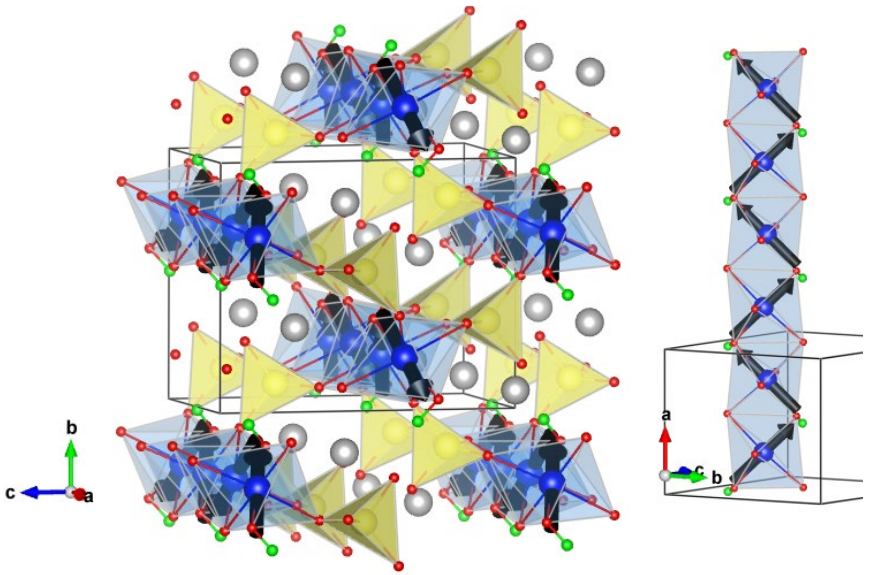
$NaMnGe_2O_6$ pyroxene
k = (0, 0, ½)



$Co_4(OH)_2(C_{10}H_{16}O_4)_3$
k = (0, 0, 0), interchain ~ 12A



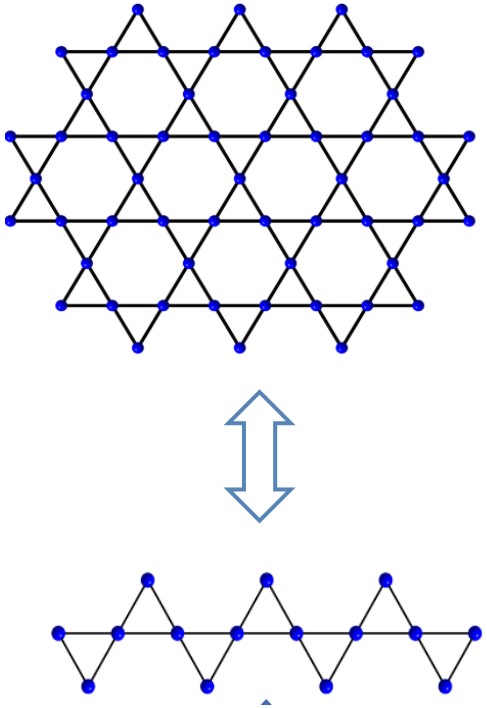
$SrCo^{2+}(VO_4)(OH)$
k = (0, 0, 0)



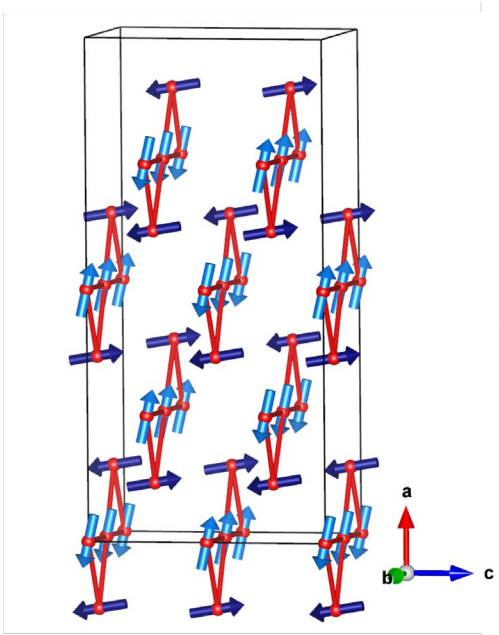
Quasi-1D structures : Delta or "sawtooth" chains

highly frustrated lattices derived from a kagomé lattice

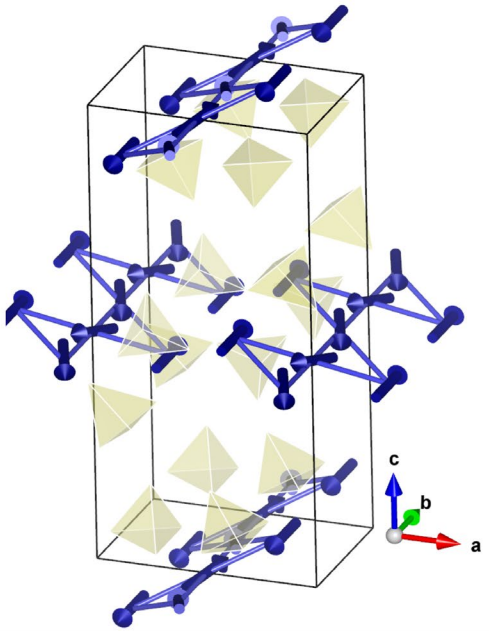
- olivines (M_2XO_4, X = Si , Ge) , oxy-arsenates $A_2Fe_2O(AsO_4)_2$, and alkali Transition Metal Molybdates $CsM_2(MoO_4)_2(OH)$ (M = Mn, Fe, Co, Zn), $Rb_2M_3(MoO_4)_3(OH)_2$ (A = K, Rb; M = Mn, Co),



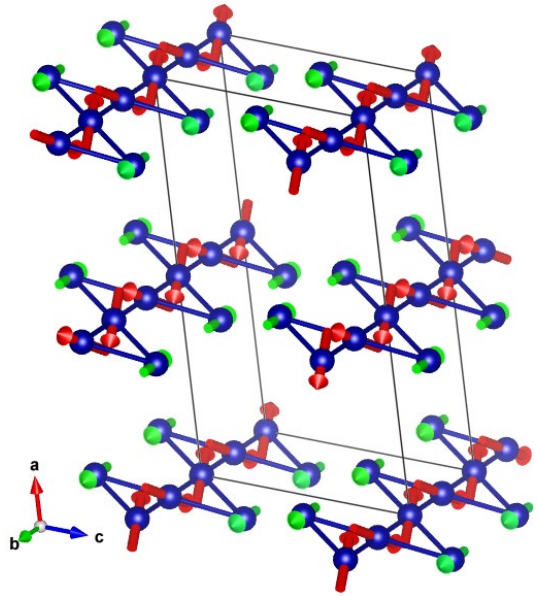
Ni_2SiO_4
k = (½, 0, ½);



$Rb_2Fe_2O(AsO_4)_2$
k = (0, 0, 0)



$CsM_2(MoO_4)_2(OH)$
k = (½, 0, 0)



Take home messages

Magnetic structure determination is an important step in understanding materials. A clear communication of the structure is extremely important.

The effective dimensionality & topology of the crystal lattice plays an important role in defining the magnetic ordered state. A hierarchy of magnetic structures based on lattice dimensionality can be established.

Think of the mechanisms that are responsible for the static magnetic order. Consider complementing your findings with spin dynamics studies to better understand your systems.

Thank you !