

# Science highlights from polarized neutron diffraction at HB-2A (POWDER) instrument

Stuart Calder

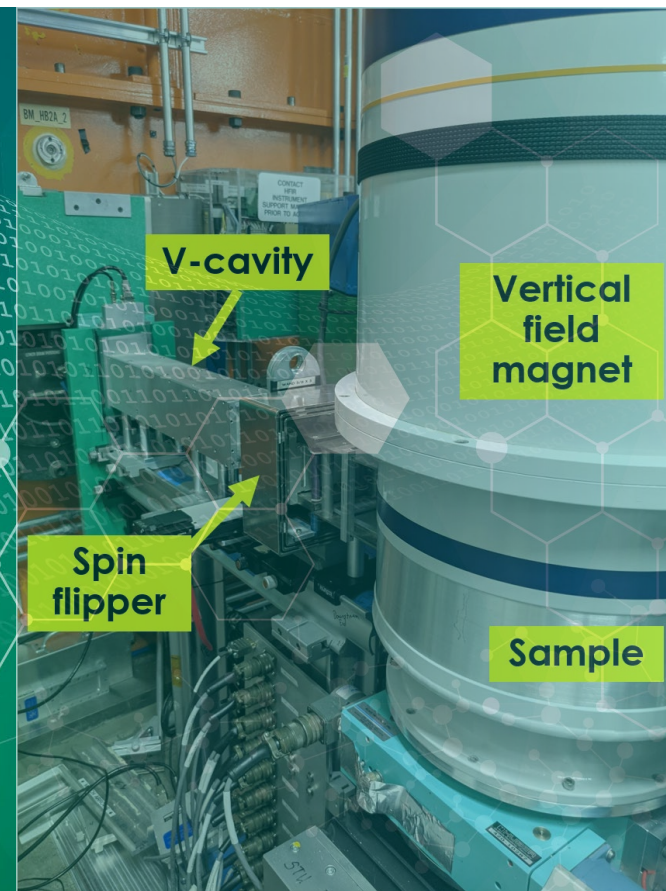
Neutron Scattering Division

Oak Ridge National Laboratory

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

Monday March 30<sup>th</sup>, 2026

13:00 – 13:45



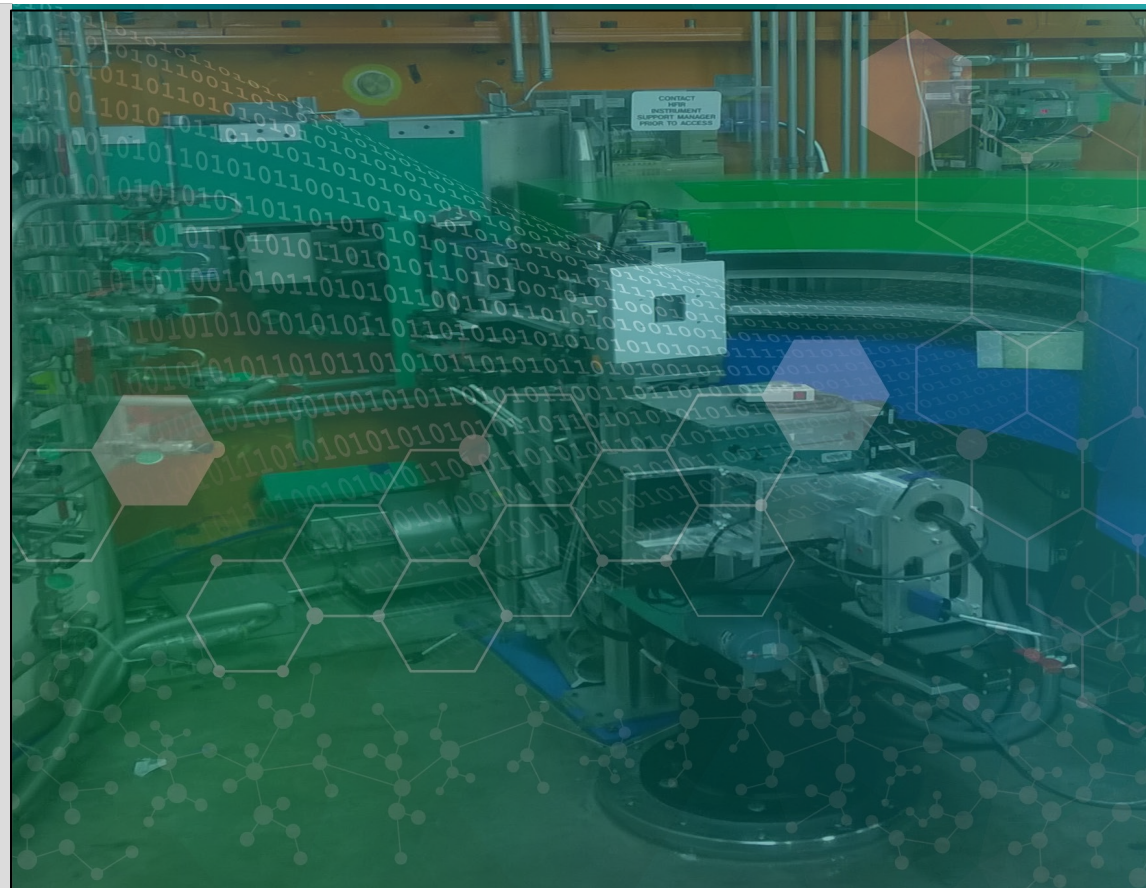
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**ENERGY**

# Overview of talk

- Overview of the HB-2A Instrument
- Development of half polarized neutron diffraction on HB-2A
- Science highlights on HB-2A
  - Single Molecular Magnets
  - Rare earth based frustrated magnets
  - Anisotropy, g-tensor and exchange interactions
  - Weak moments. 0.2  $\mu\text{B}$  observed, lower possible.
  - $S=1/2$  is “easy”
  - Weak ferromagnetic signals
  - Hydrogen containing materials measured
  - Small samples

# HB-2A: POWDER

- ORNL's high flux, constant wavelength, extreme sample environment powder diffractometer



# HB-2A: Team

## Malcolm Cochran (SA)

- Ultra-low temperature sample changers
- MIDAS concept
- Everything else

## Stuart Calder (IS)

- Layered and van der Waals materials
- 5d-based strong spin-orbit compounds
- Geometric frustration

## Clarina dela Cruz (GL)

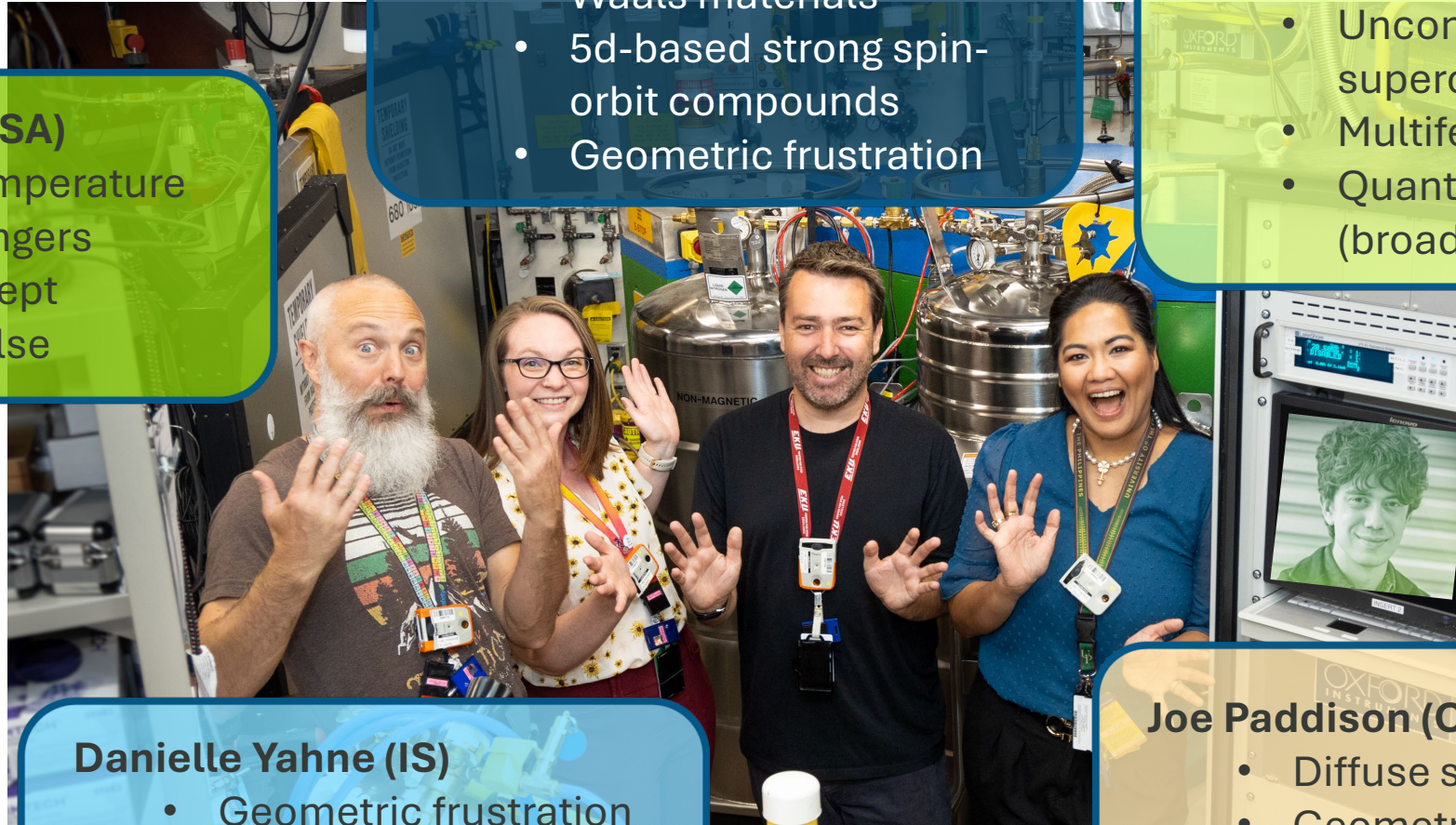
- Unconventional superconductors
- Multiferroics
- Quantum materials (broadly)

## Danielle Yahne (IS)

- Geometric frustration
- Skyrmions
- Gas loading for CO<sub>2</sub> capture materials

## Joe Paddison (CIS)

- Diffuse scattering
- Geometric frustration
- Spinteract/Spinvert

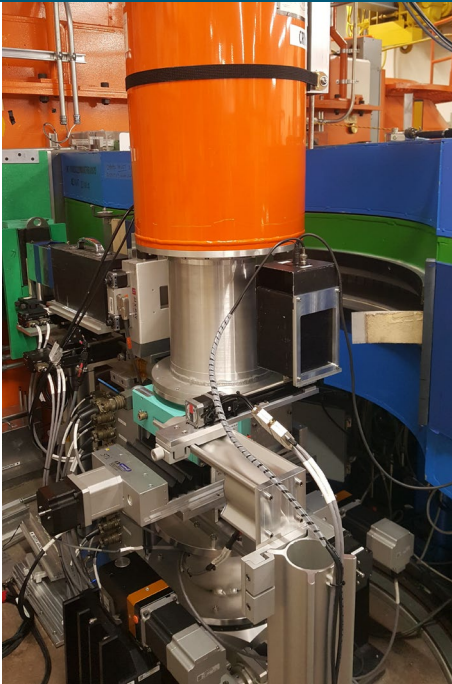


Former: Ovi Garlea (now HYSPEC)

Keith Taddei (now APS)

# HB-2A Neutron Powder Diffractometer at HFIR, ORNL

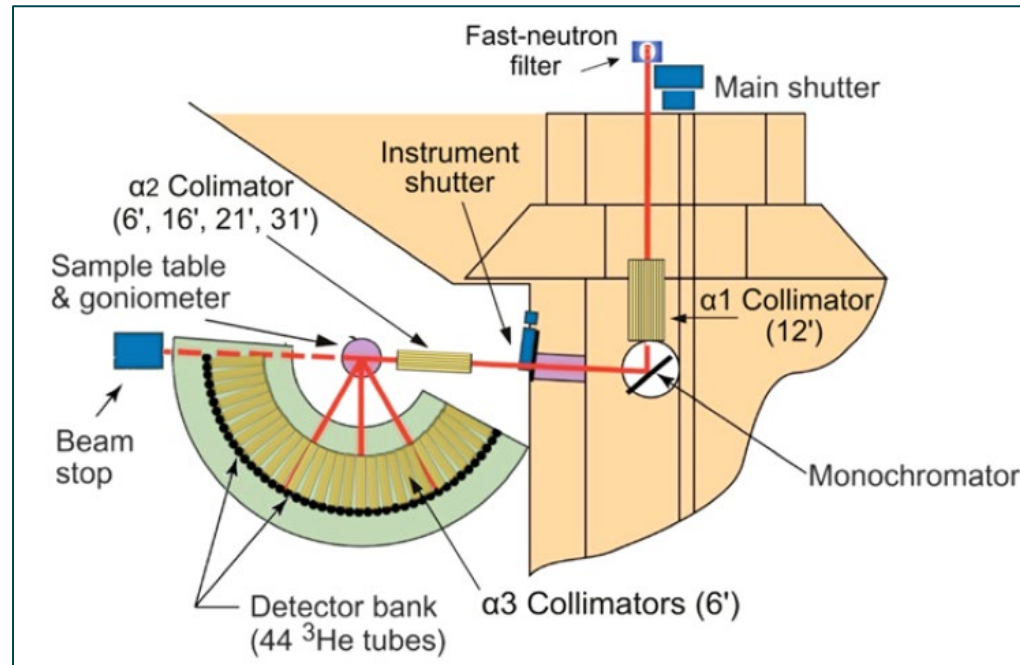
## Neutron Powder Diffraction



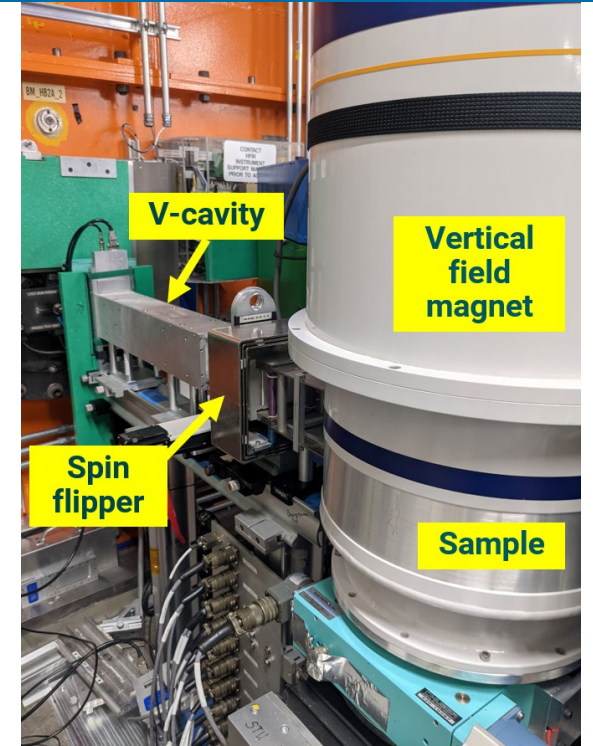
HB-2A unpolarized mode is used for magnetic structure determination.

<https://neutrons.ornl.gov/powder>

Ge(hkl)	$\lambda$ (Å)	Q (Å <sup>-1</sup> )	Flux (n/cm <sup>2</sup> s)
(113)	2.41	0.2 - 5.1	5 x 10 <sup>6</sup>
(115)	1.54	0.35 - 7.9	1 x 10 <sup>7</sup>
(117)	1.12	0.5 - 10.9	4 x 10 <sup>6</sup>



## Half-polarized Neutron Powder Diffraction (pNPD)



V-cavity used for  $\lambda = 2.41$  Å



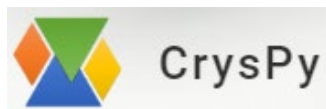
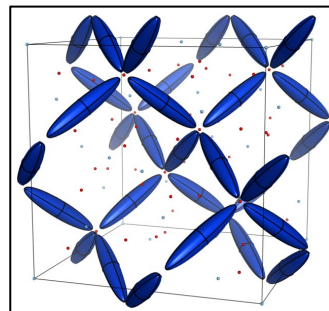
# HB2A: Half-Polarized neutron powder diffraction (pNPD)

ONLY sensitive to net ferro-magnetic signals

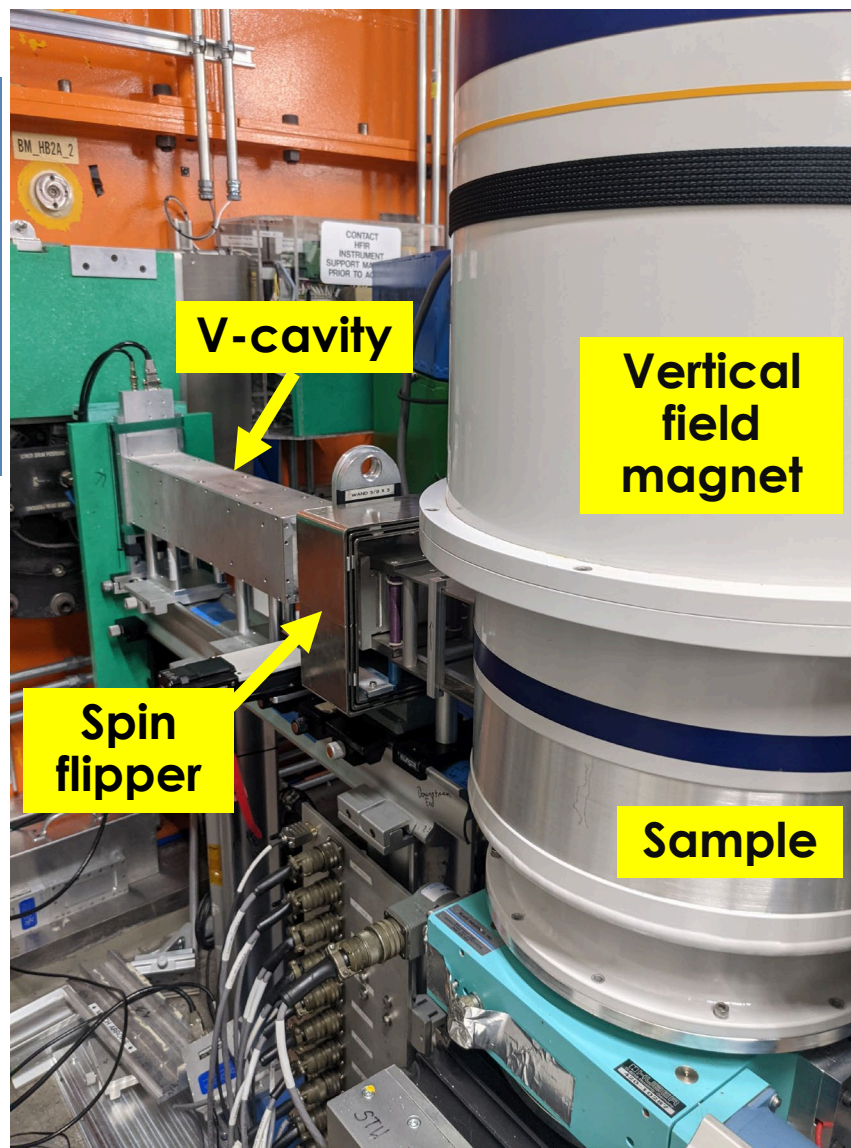
Probe order in weak ferromagnets or ferrimagnets

Measure local site susceptibility tensor in any material

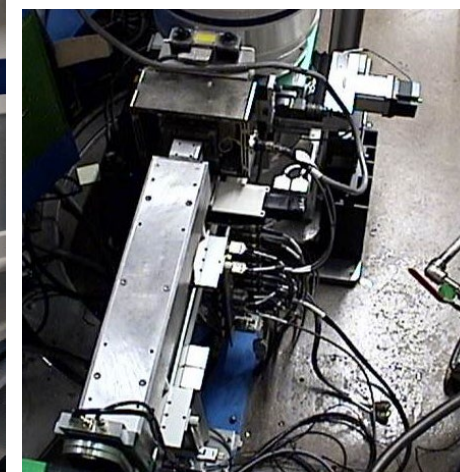
$$\chi = \frac{m_i}{H} = \begin{pmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{12} & \chi_{23} & \chi_{23} \\ \chi_{13} & \chi_{23} & \chi_{33} \end{pmatrix}$$



<https://sites.google.com/view/cryspy/main>



V-cavity used for  $\lambda = 2.41 \text{ \AA}$



# Recent review article for pNPD on HB-2A

<https://doi-org.ornl.idm.oclc.org/10.1016/j.jmmm.2025.173342>

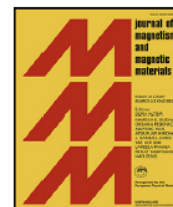
Journal of Magnetism and Magnetic Materials 630 (2025) 173342



Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: [www.elsevier.com/locate/jmmm](http://www.elsevier.com/locate/jmmm)



Review article

## Magnetic pair distribution function and half polarized neutron powder diffraction at the HB-2A powder diffractometer<sup>☆</sup>

Raju Baral<sup>a</sup>, Danielle R. Yahne<sup>a</sup>, Malcolm J. Cochran<sup>a</sup>, Matthew Powell<sup>b</sup>, Joseph W. Kolis<sup>b</sup>, Haidong Zhou<sup>c</sup>, Stuart Calder<sup>a</sup>

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<sup>c</sup> Department of Physics and Astronomy, University of Tennessee, Knoxville, 37996, TN, USA

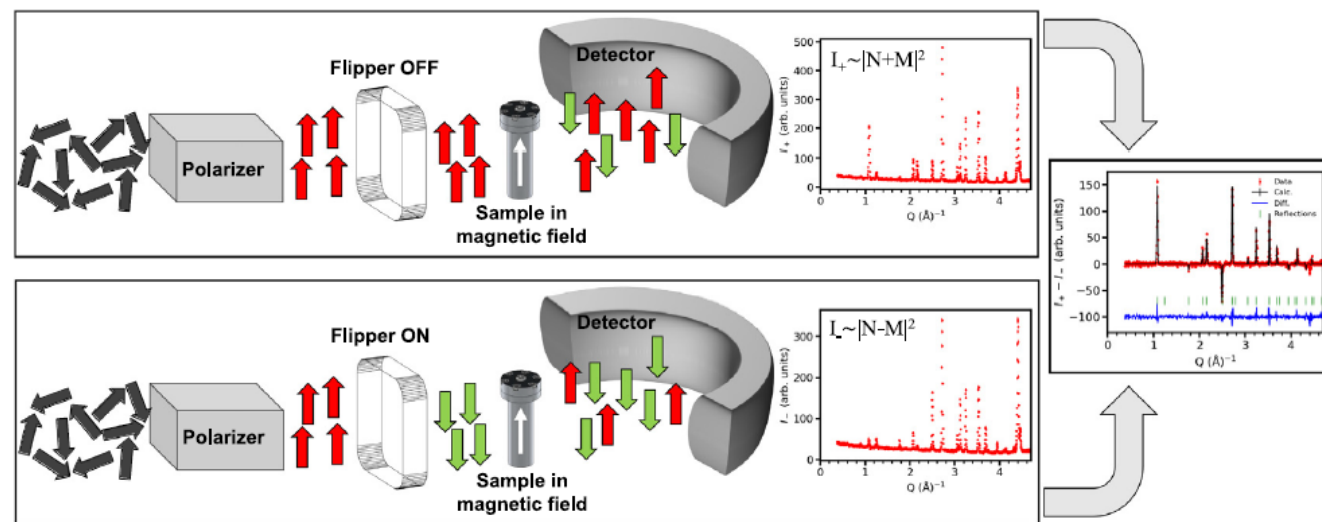
### ARTICLE INFO

#### Keywords:

Magnetic pair distribution function  
Half polarized neutron scattering  
Local magnetic structure  
Short range order

### ABSTRACT

Local magnetic order and anisotropy are often central for understanding functional properties in quantum materials and beyond. Advances in neutron scattering and analysis tools now allow for quantitative determination. We demonstrate total neutron scattering and polarized neutron measurements on the HB-2A powder diffractometer at the High Flux Isotope Reactor (HFIR). In recent years, magnetic pair distribution function (mPDF) has emerged as a powerful technique for probing local magnetic spin order. The method can be broadly applied to any magnetic material but is particularly powerful with short-range magnetic order, such as materials with reduced dimer magnets, thermoelectrics, multiferroics, and correlated paramagnets. The method is particularly powerful when the short-range order is adopted. Half-polarized neutron powder diffraction (HPNPD) is a technique that combines the local susceptibility tensor on the magnetic sites to quantify the magnetic pair distribution function (mPDF) and pNPD can therefore provide valuable insights into the local magnetic structure. Measurements optimized for these techniques are presented as exemplars where short-range order dominates, these include measurements to ultra-high resolution typically accessible for such experiments.



# HB-2A: Sample Environments

Low and ultra-low temperature: 300 to 0.06 K  
Up to 14 Samples



Cryo Magnets:  
6 T, 300 to 0.06 K  
Up to 3 Samples



High Pressure:  
Gas up to 0.7 GPa  
Clamp up to 2 GPa



High temperature:  
Up to 1700 K

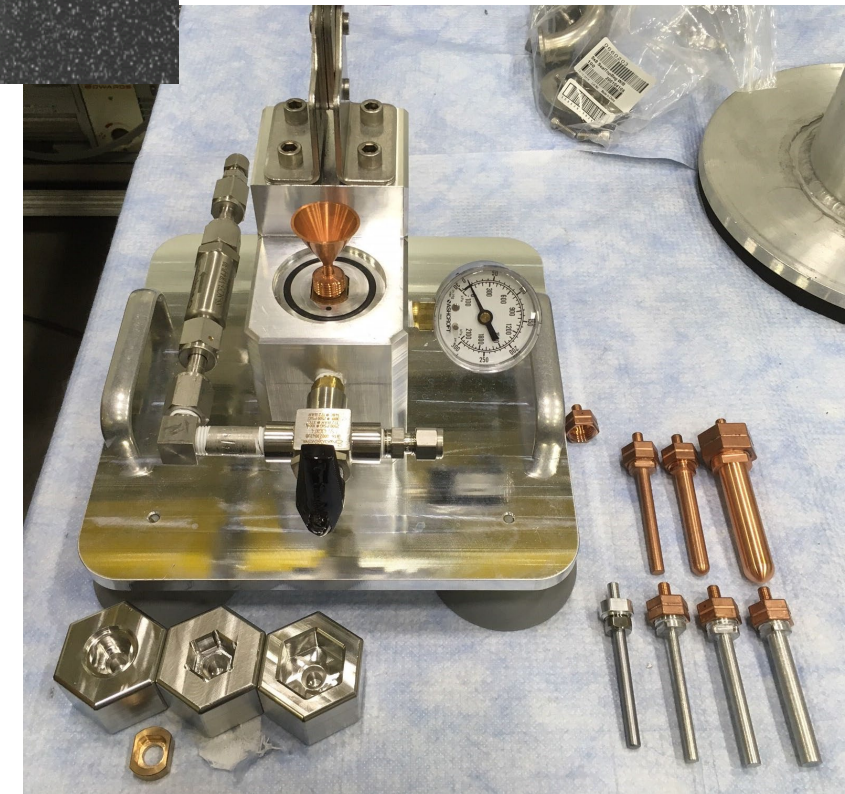
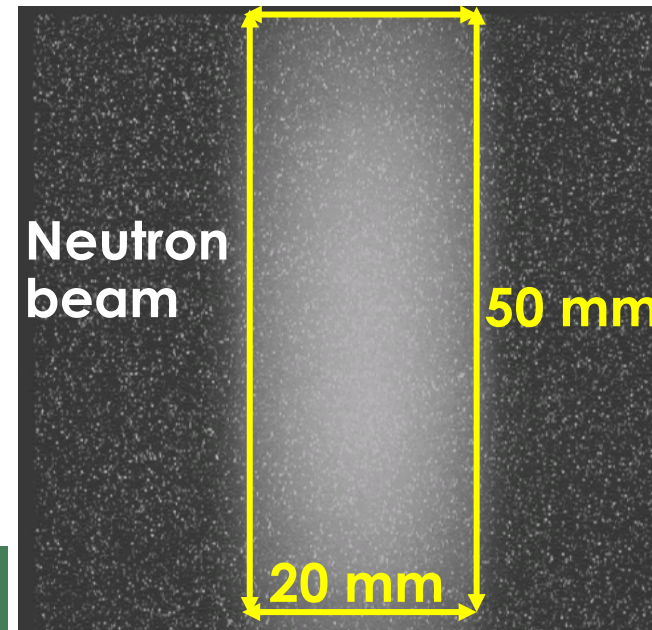


# HB-2A: Sample Cans

HB-2A beam is large  
→ typically the more mass  
the better!

$\rho$ NPD sample preparation:

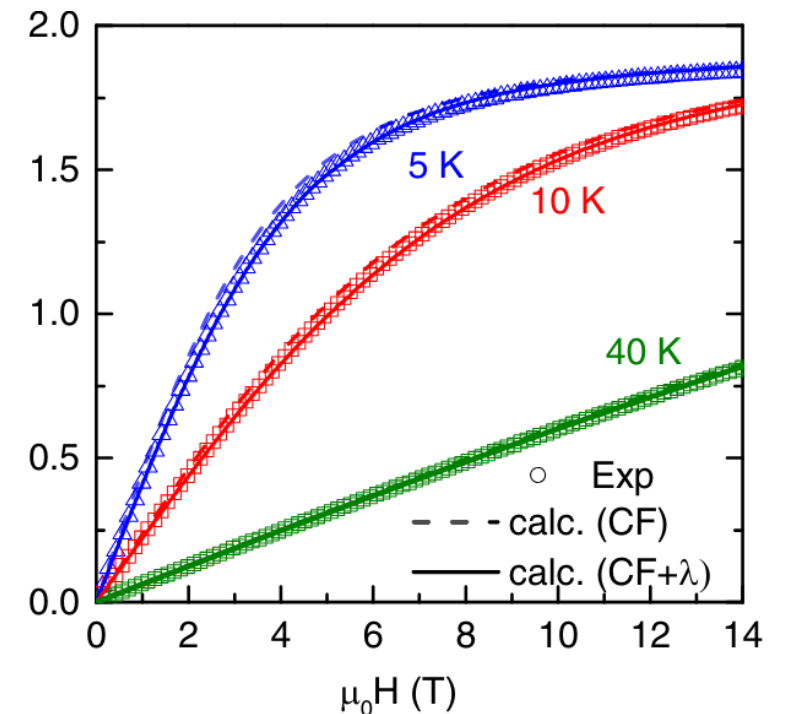
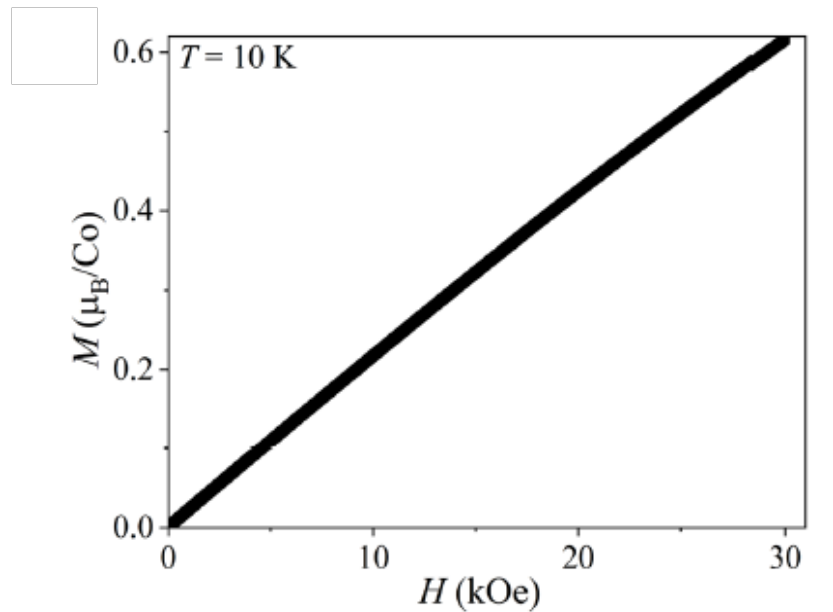
- Need net ferromagnetic moment.
- Apply a magnetic field
- Want to avoid grain rotation
  - Press sample into pellet
  - Use Flourinert, methanol-ethanol



# What magnetic fields and temperatures to measure for pNPD?

- Measure in the linear  $M/H$  paramagnetic regime
- Can directly know magnitude of pNPD signal to expect and choose optimal field, temperature.

- HB-2A available field range is 1 T – 3.5 T
  - Higher or lower fields see significant drop in flipping ratio
  - Ranges will increase with upgrades



# HB-2A: Polarization

- The polarization capability is fully available to users through the normal beamtime proposal calls.



# The beginnings of polarization on HB-2A: 2009-2015

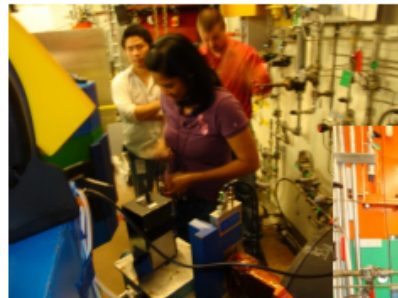
- Initially  $^3\text{He}$  polarizer cell used for  $\lambda=1.54 \text{ \AA}$ .
- First powder diffractometer in US capable of performing polarized studies.

## HB-2A

### Polarized neutron diffraction experiments now possible at the HB2A Powder diffractometer

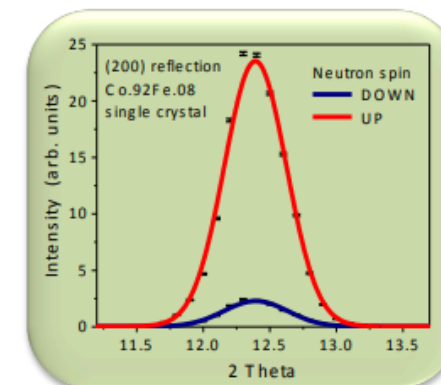
Polarized neutron diffraction is one of the most powerful technique in studying magnetism, since it allows to reach high precision in measuring weak magnetic moments.

The HB2A instrument scientists in collaboration with NFDD instrument development team have successfully installed and tested a  $^3\text{He}$  polarizer cell that provides a unique capability to the powder diffractometer. This makes **HB2A the first powder diffractometer in US capable of performing polarized studies** for high sensitivity to weak ferromagnetism.



Pictures display Clarina de la Cruz, Ovi Garlea, Tony Tong and Daniel Brown performing the polarized neutron diffraction experiment at the HB2A instrument.

Polarization efficiency has first been evaluated using a  $\text{Co}_{0.92}\text{Fe}_{0.8}$  single crystal. Figure below shows the intensity of (200) Bragg reflection measured with neutrons polarized UP or DOWN, perpendicular to the scattering plane.



# The beginnings of polarization on HB-2A: 2009-2015

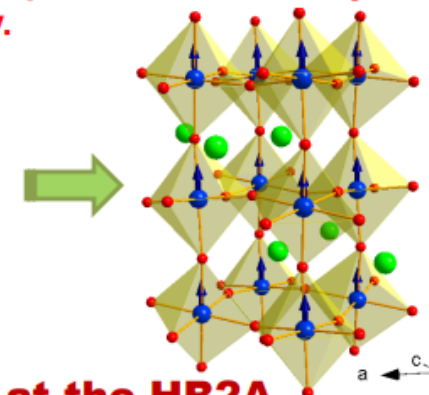
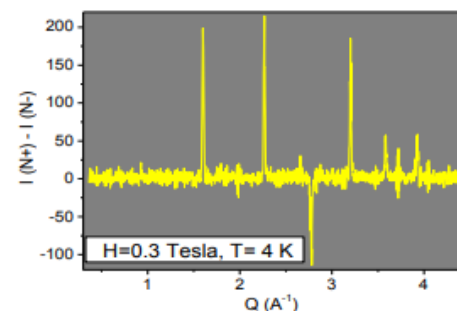
- **2012:** First polarized paper published.

**HB-2A**

## Polarized neutron diffraction at HB2A



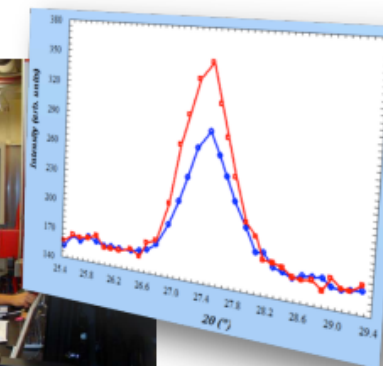
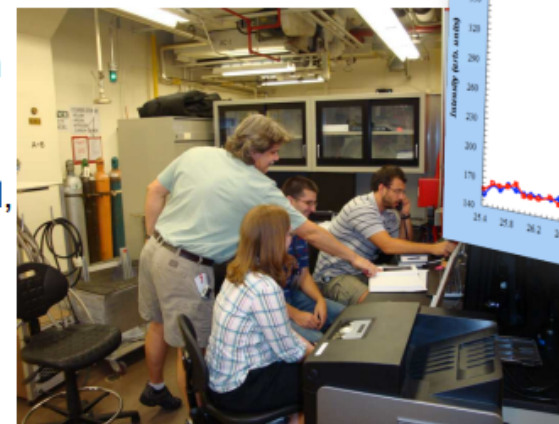
Polarized neutrons were further used to precisely measure the magnitude of the ordered magnetic moment in an **itinerant ferromagnet**. The difference scattering from neutron beam polarized parallel and antiparallel to the applied magnetic field gives an **improvement of nearly one order of magnitude in detection sensitivity**.



## Fist user experiment using polarized neutrons at the HB2A

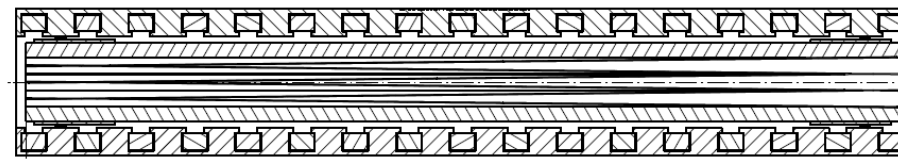
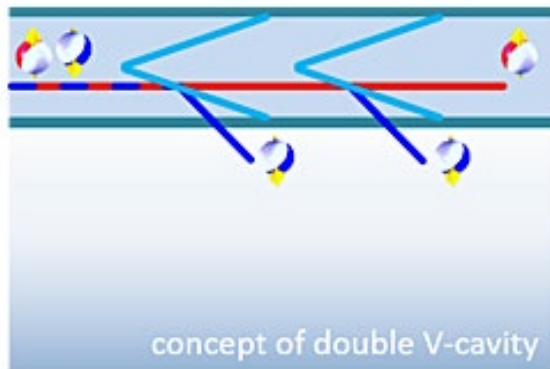
A group led by Prof. Mark Meisel of Univ of Florida have used the polarization capability to explore the magnetization density distribution in a Co-Fe Prussian Blue analog.

Picture displays Daniel Pajerowski, Mark Meisel, Elisabeth Knowles conducting the polarized experiment at the Hb2A. The insert plot shows the diffraction intensity obtained from two neutron spin states.

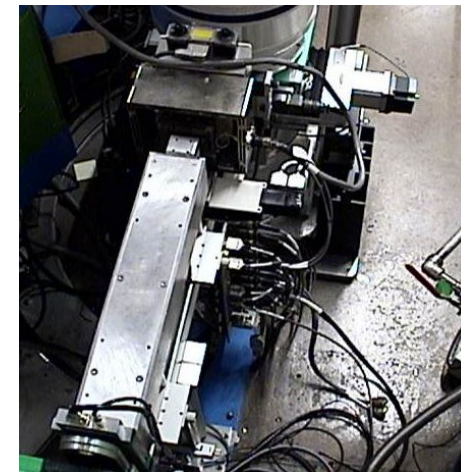


# The beginnings of polarization on HB-2A: 2015-present V-cavity

- **2015:** Initial successful tests using V-cavity for  $\lambda = 2.41 \text{ \AA}$
- **V-cavity**
  - Fe/Si supermirror wafers arranged in a V-shape
  - Spin-dependent transmission (Flux cut by at least 50%): One spin transmitted, one reflected/absorbed
  - V-shape allows for shorter device to fit beamlines
  - Typically better for longer ( $>2 \text{ \AA}$ ) wavelengths



BEAM →

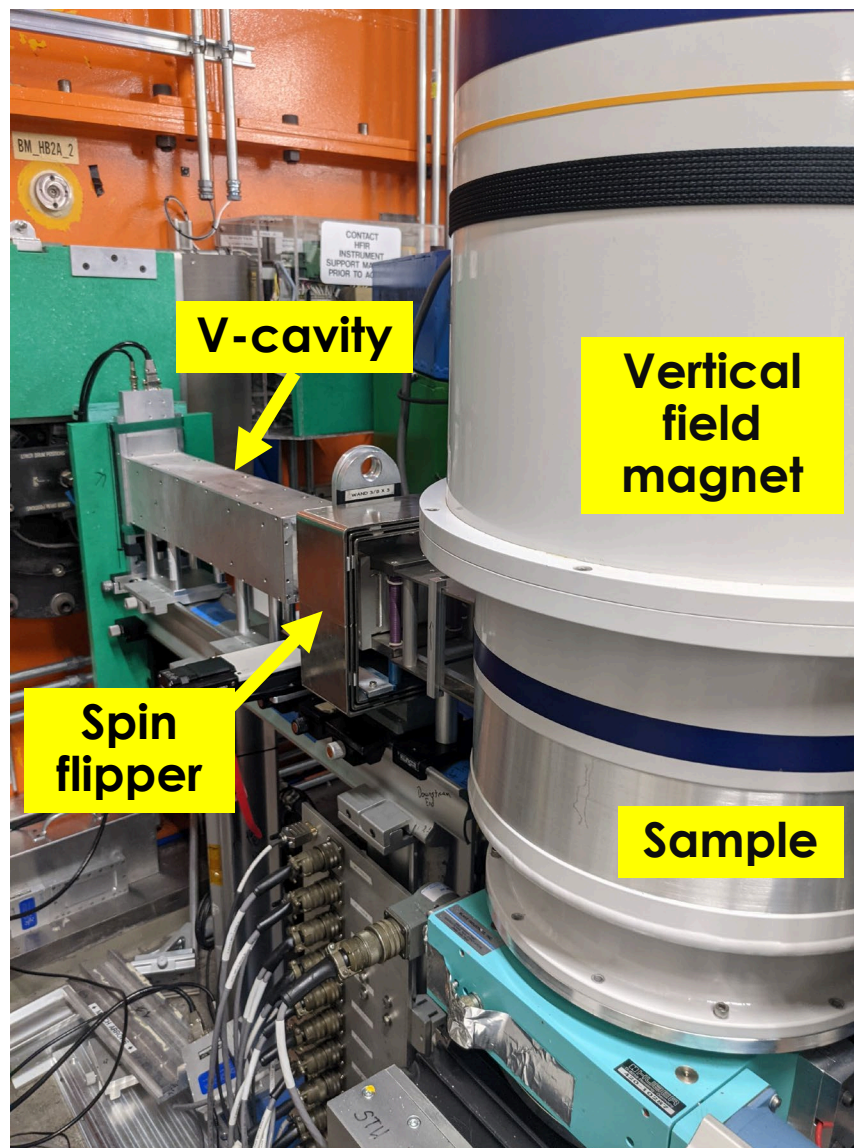


<https://www.swissneutronics.ch/products/polarizing-devices/polarizing-v-cavities/>

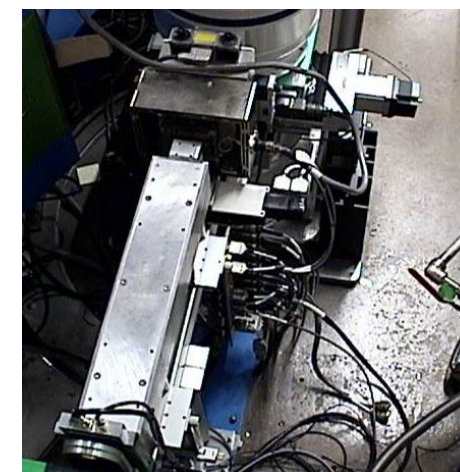
# The beginnings of polarization on HB-2A: 2015-present

- **2018:** polarized set-up was on HB-2A when reactor went down for one year.
- **2020-present:** Several successful experiments
- **2022:** Installed new V-cavity and motorized stage
- **2026:** Plan to test and install analyzer in direct beam to quantify beam depolarization

**Half-Polarization for HB-2A is fully in the user program**

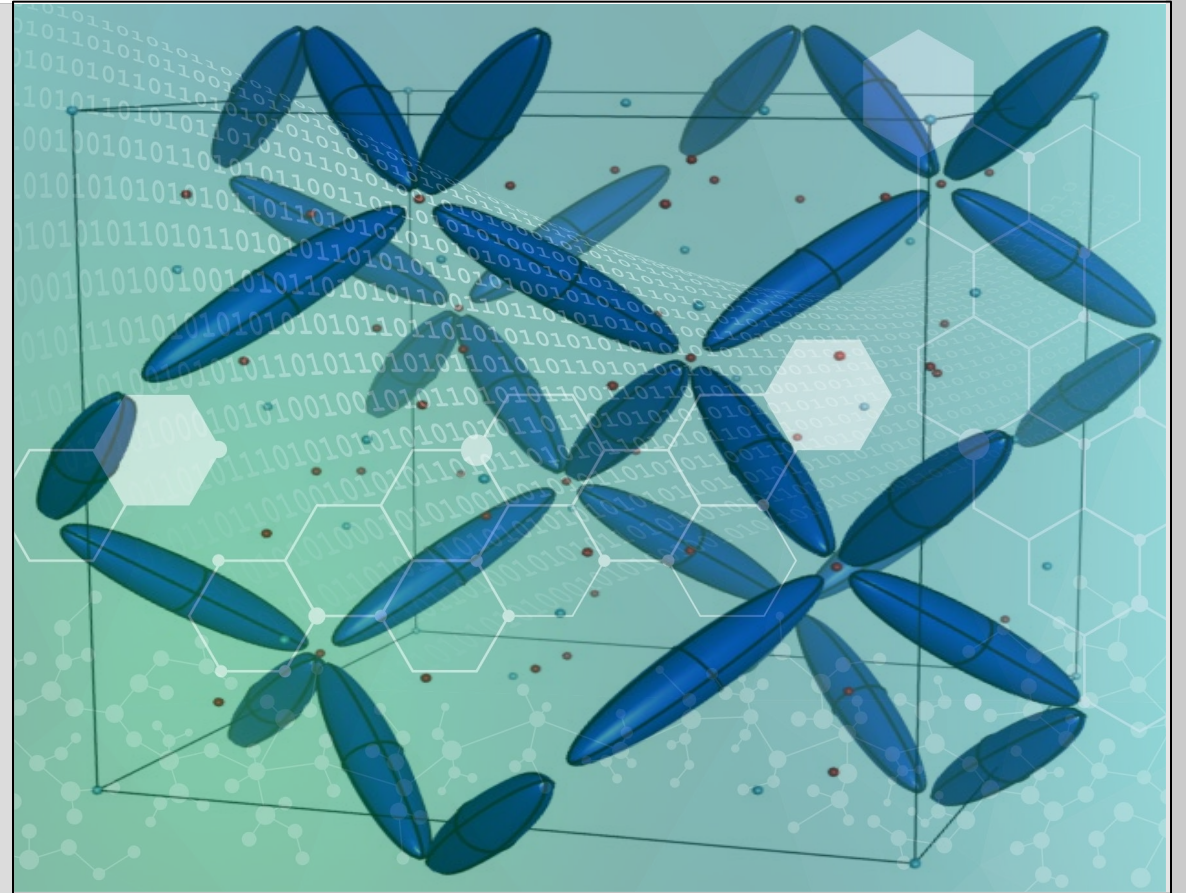


V-cavity used for  $\lambda = 2.41 \text{ \AA}$



# HB-2A: Science Highlights

- Successful measurements on a variety of science cases:
  - Single Molecular Magnets
  - Rare earth based frustrated magnets
  - Anisotropy, g-tensor and exchange interactions
  - Weak moments.  $0.2 \mu_B$  observed, lower possible.
  - $S=1/2$  is “easy”
  - Weak ferromagnetic signals
  - Hydrogen containing materials measured
  - Small samples



# Molecule based magnets



Daniel Pajeroski



Ovi Garlea

# Molecule based magnets

PHYSICAL REVIEW B 86, 054431 (2012)

## Magnetic neutron scattering of thermally quenched K-Co-Fe Prussian blue analog photomagnet

Daniel M. Pajerowski,<sup>1,2</sup> V. Ovidiu Garlea,<sup>3</sup> Elisabeth S. Knowles,<sup>2</sup> Matthew J. Andrus,<sup>4</sup> Matthieu F. Dumont,<sup>2,4</sup> Yitzi M. Calm,<sup>2</sup> Stephen E. Nagler,<sup>3</sup> Xin Tong,<sup>5</sup> Daniel R. Talham,<sup>4</sup> and Mark W. Meisel<sup>2</sup>

<sup>1</sup>NIST Center for Neutron Research, Gaithersburg, Maryland 20899-6012, USA

<sup>2</sup>Department of Physics and National High Magnetic Field Laboratory, University of Florida, Gainesville, Florida 32611-8440, USA

<sup>3</sup>Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6393, USA

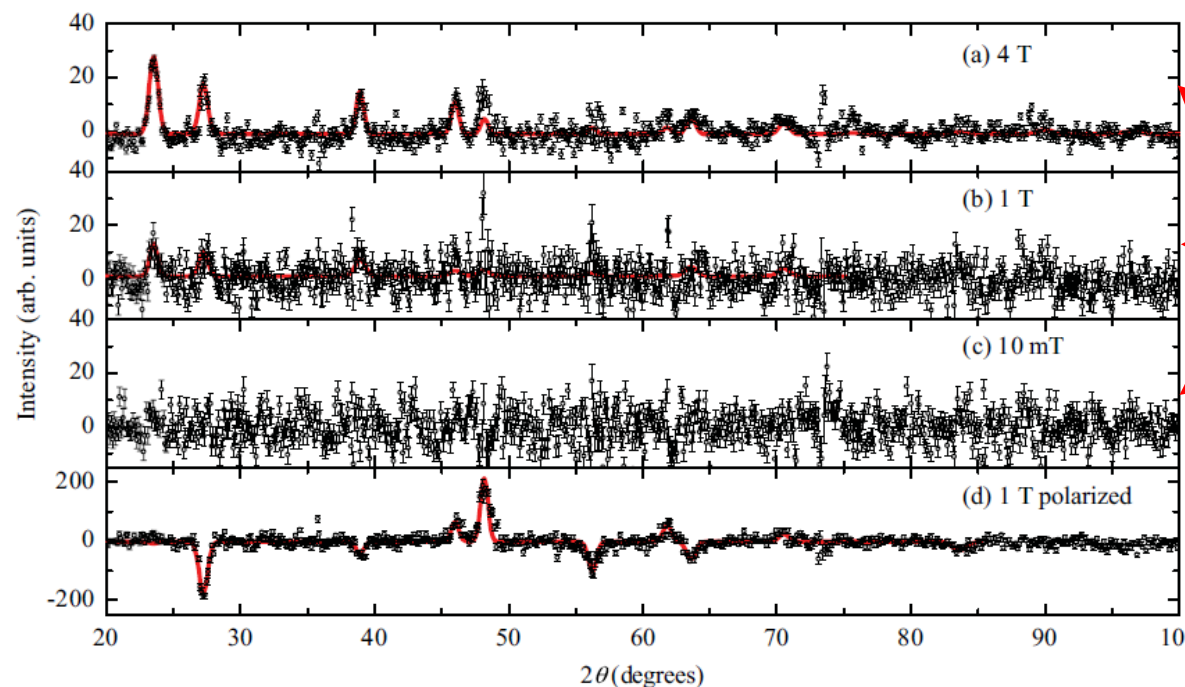
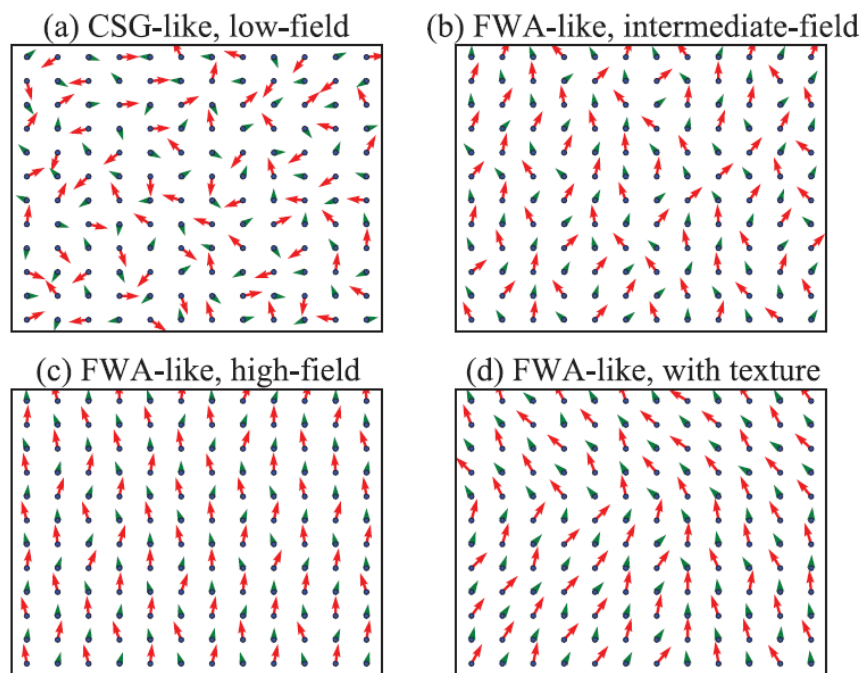
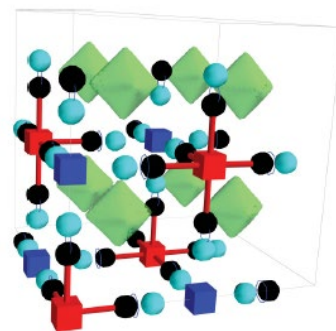
<sup>4</sup>Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, USA

<sup>5</sup>Instrument and Source Design Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6393, USA

(Received 7 June 2012; published 20 August 2012)

DOI: [10.1103/PhysRevB.86.054431](https://doi.org/10.1103/PhysRevB.86.054431)

- Photomagnetic coordination polymer  
Prussian blue analog  
 $\text{K}_{0.27}\text{Co}[\text{Fe}(\text{CN})_6]_{0.73}[\text{D}_2\text{O}_6]_{0.27} \cdot 1.42\text{D}_2\text{O}$
- Field induced behavior
- Ferromagnetic wandering access



Temperature subtracted data: 4K - 40K

4 K polarized data: spin up - spin down

# Experimental determination of the magnetic anisotropy in single molecule magnets

Hannah H. Slavensky

Bo Iverson

Aarhus

DOI: [10.1039/d5sc03103f](https://doi.org/10.1039/d5sc03103f)

# Magnetic anisotropy in single molecule magnets (SMMs)

- SMMs exhibit slow relaxation of magnetization thereby possessing an energy barrier for magnetic reversal.
  - potential applications in molecular spintronics and quantum computing.
- Magnetic anisotropy is a crucial property of SMMs.
  - Small structural changes can alter the magnetic properties
  - accurate experimental methods to investigate magnetic anisotropy are critical.

Large hydrogen content in sample, but still obtained multiple reflections to refine due to sensitivity of pNPD.

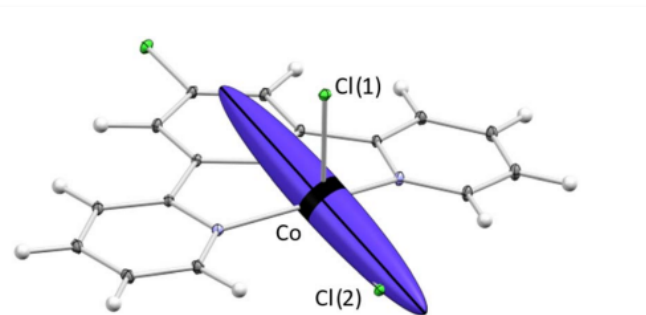
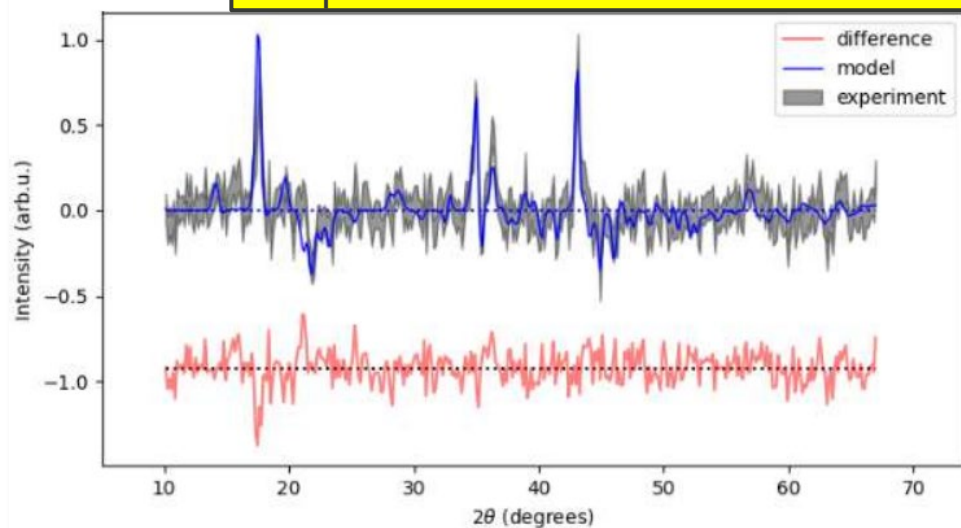


Fig. 8 Experimental magnetic susceptibility tensor obtained from pNPD. The ellipsoid of the tensor is scaled arbitrarily with relative magnitudes corresponding to the relative eigenvalues in  $\mu_B T^{-1}$ .

$$\hat{\chi} = \begin{pmatrix} 0.23(20) & -0.16(16) & -0.69(60) \\ -0.16(16) & 0.33(14) & 1.10(38) \\ -0.69(60) & 1.10(38) & 4.88(52) \end{pmatrix} \mu_B \cdot T^{-1}$$

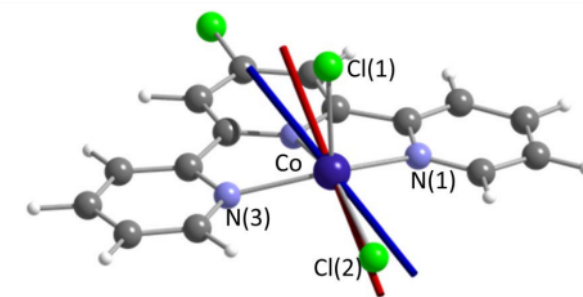


Fig. 9 Visualization of the magnetic easy axis of 1 from theoretical calculations (red) and PPND (blue).

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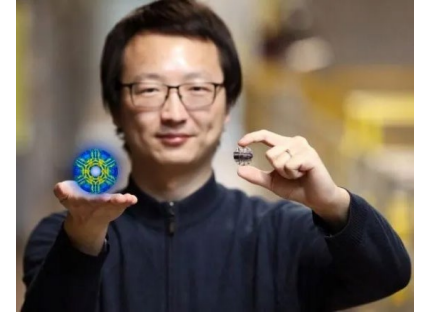
Cite this: *Chem. Sci.*, 2025, 16, 16610

All publication charges for this article have been paid for by the Royal Society of Chemistry

## Experimental determination of the magnetic anisotropy in five-coordinated Co(II) field-induced single molecule magnets

Hannah H. Slavensky,<sup>a</sup> Vijay S. Parmar,<sup>a\*</sup> Sofie S. Leiszner,<sup>a</sup> Andreas M. Thiel,<sup>a</sup> Helene Lassen,<sup>a</sup> Stuart Calder,<sup>b</sup> Iurii Kibalin,<sup>c</sup> and Bo B. Iversen<sup>a\*</sup>

# Anisotropy and crystal fields: tripod magnet



**Xiaojian Bai**

- ORNL Postdoc (2019-2022)

- LSU Assistant Prof.  
(August 2022 - present)

**S. Calder, H. Cao, I Kibalin, A Gukasov**

# Anisotropy and crystal fields: tripod magnet

- Anisotropic single-ion properties from SOC and CEF are crucial to understand the resultant collective magnetic phenomena.
- Inelastic neutron scattering can provide this information, but finding a unique model can be challenging
  - Limited number of excitations
  - Large number of variables

## Using pNPD can provide an alternative route

- Rietveld refinement method used on multiple reflections
- Better statistical analysis
- Often faster data collection (single temperature).

PHYSICAL REVIEW RESEARCH 3, 023012 (2021)

### Effective point-charge analysis of crystal fields: Application to rare-earth pyrochlores and tripod kagome magnets $R_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$

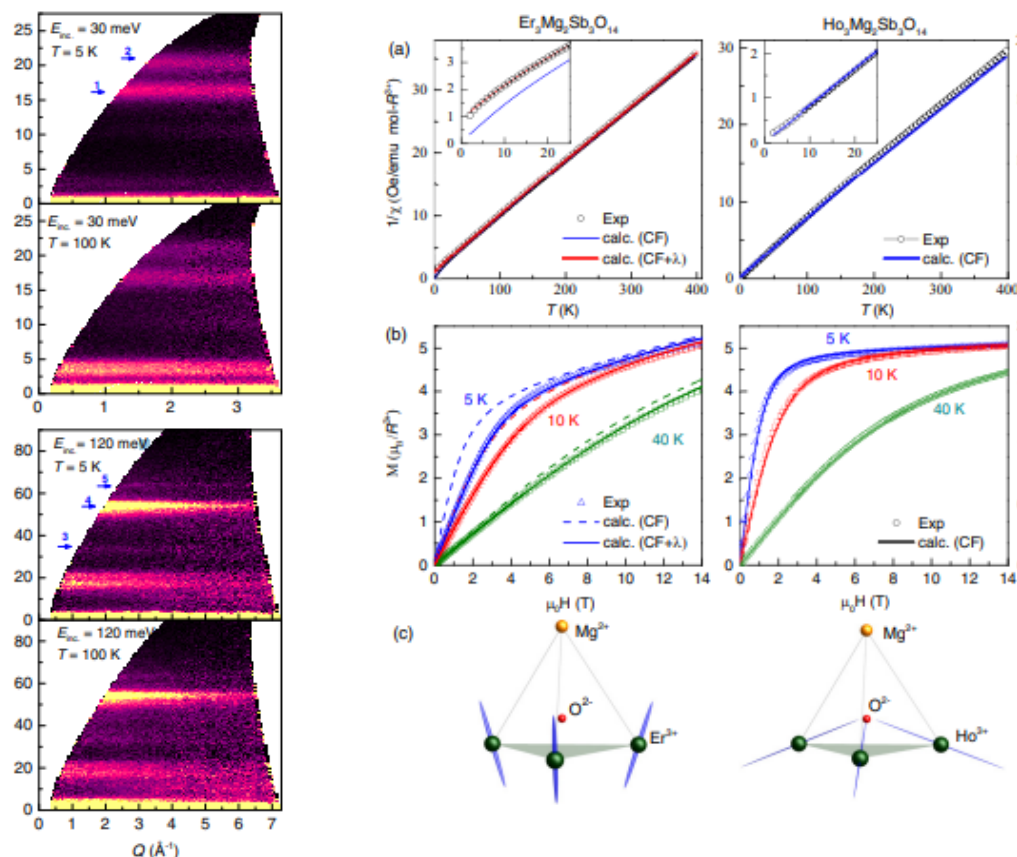
Zhiling Dun<sup>1</sup>, Xiaojian Bai<sup>1</sup>, Matthew B. Stone<sup>2</sup>, Haidong Zhou<sup>3</sup>, and Martin Mourigal<sup>1</sup>

<sup>1</sup>School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

<sup>2</sup>Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

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(Received 5 May 2020; revised 22 February 2021; accepted 16 March 2021; published 2 April 2021)



# Anisotropy and crystal fields: tripod magnet $\rightarrow$ Ho

Ho: Quantum tunnelling and spin fragmentation behavior at low temperatures, driven by CEF.

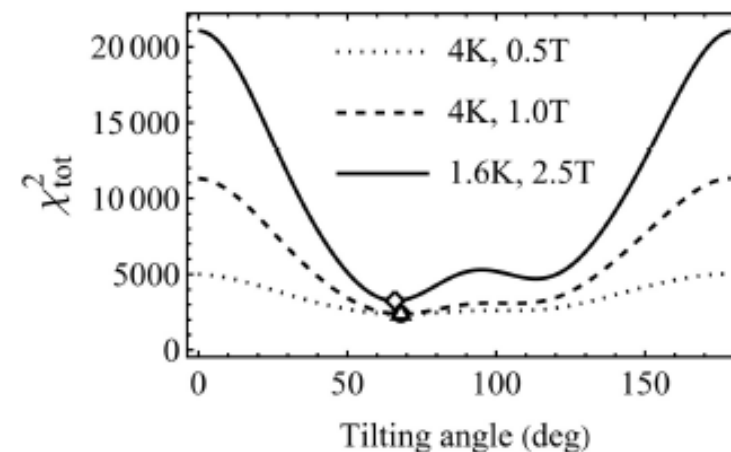
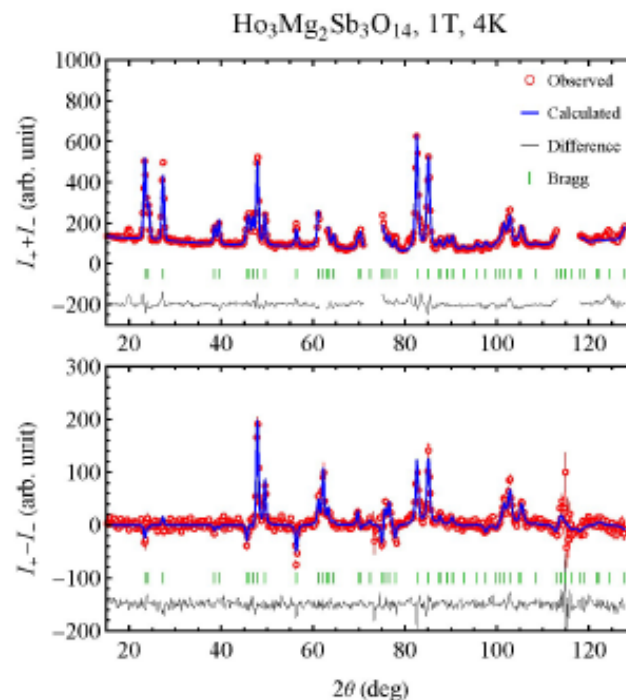
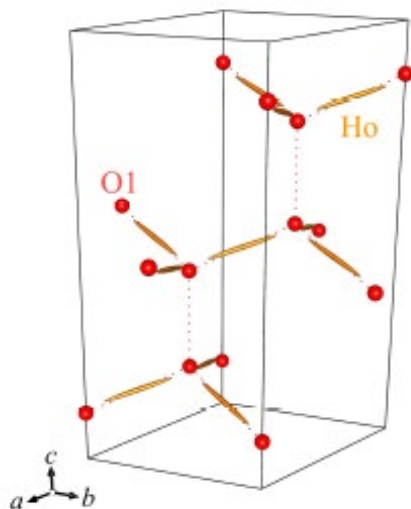
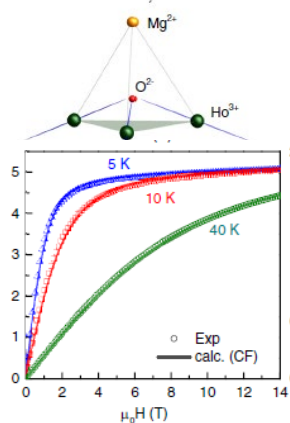
Ho: Ising moment with axis pointing to the center of local tetrahedron.

PHYSICAL REVIEW X **10**, 031069 (2020)

## Quantum Versus Classical Spin Fragmentation in Dipolar Kagome Ice $\text{Ho}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$

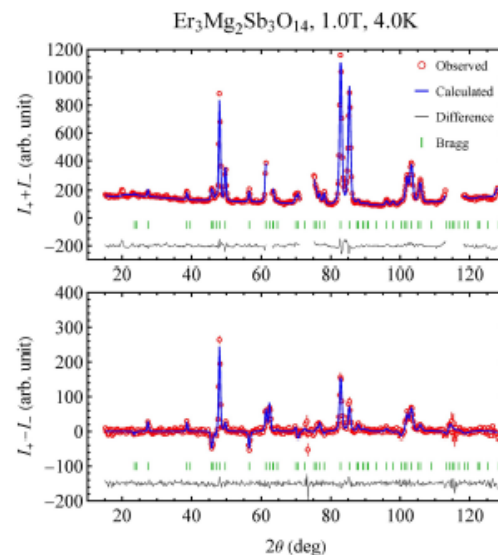
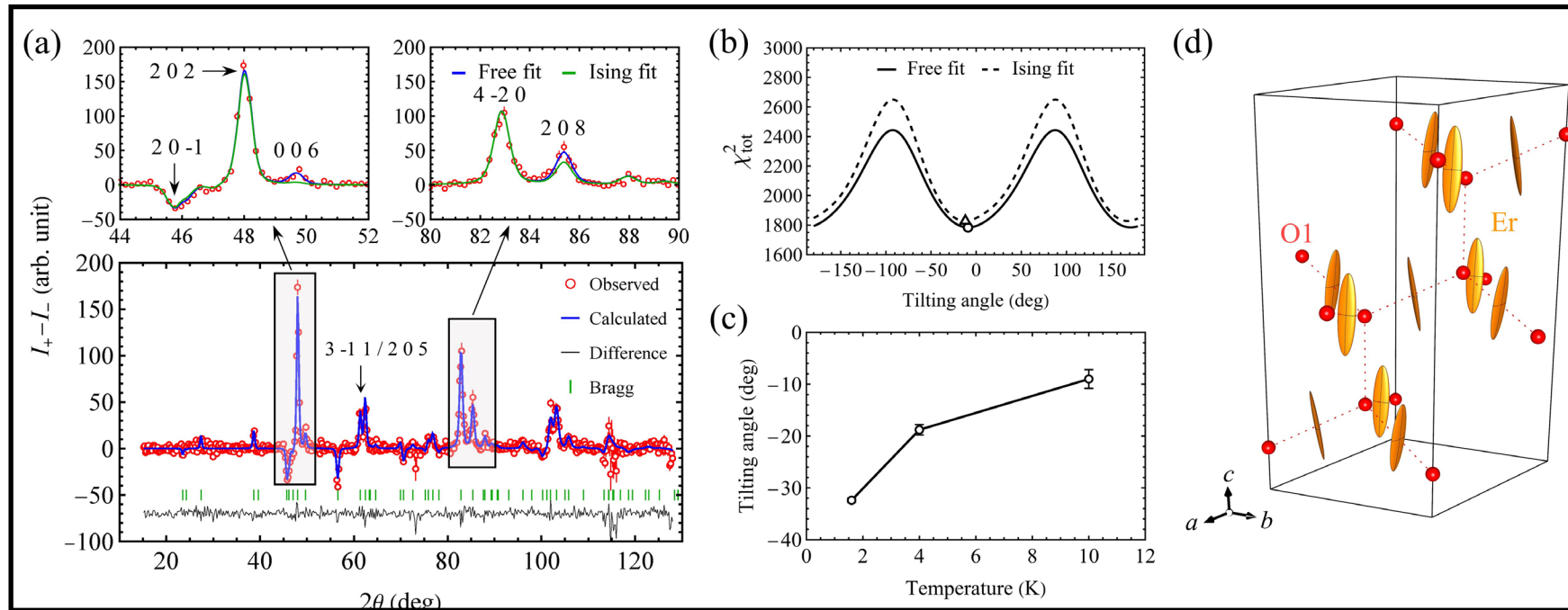
Zhiling Dun<sup>1,2,4,†</sup>, Xiaojian Bai,<sup>1,4</sup> Joseph A. M. Paddison,<sup>1,3,4,†</sup> Emily Hollingworth,<sup>1</sup> Nicholas P. Butch,<sup>5</sup> Clarina D. Cruz,<sup>6</sup> Matthew B. Stone,<sup>9</sup> Tao Hong,<sup>9</sup> Franz Demmel,<sup>7</sup> Martin Mourigal,<sup>1,4</sup> and Haidong Zhou<sup>2,8</sup>

### Point charge model with INS



# Anisotropy and crystal fields: tripod magnet $\rightarrow$ Er

- Potential quantum spin-liquid.
- XY anisotropic model previously assumed
- Strong uniaxial behavior that is pseudo-Ising like for Er from PC model
- Confirmed with polarized neutrons



$$g_{\bar{x}} = \sqrt{\chi_{\bar{x}} \times 3T / S(S+1) / \mu_B} \approx 17.9(3) \text{ vs CEF fit } \sim 19$$

# Dimer state in the Shastry-Sutherland magnet $\text{Yb}_2\text{Be}_2\text{SiO}_7$

<https://doi.org/10.1038/s41467-026-69258-7>



Alexander Brassington  
University of Tennessee

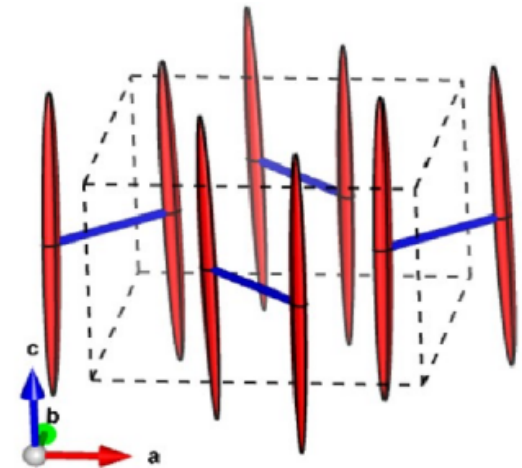
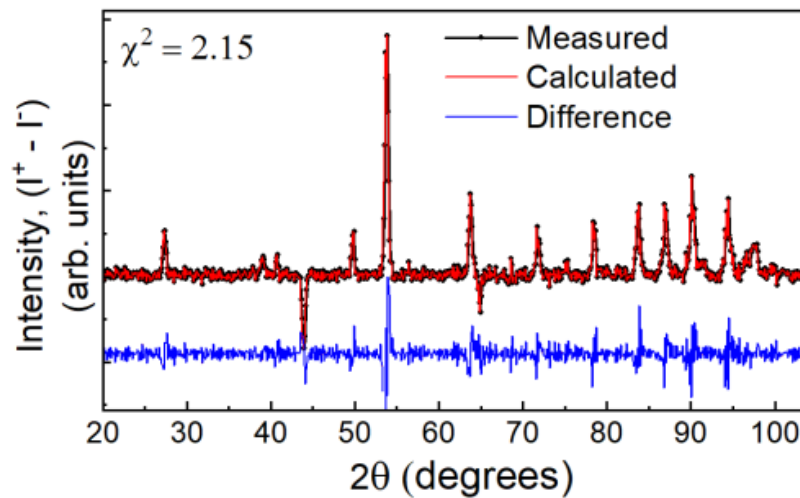
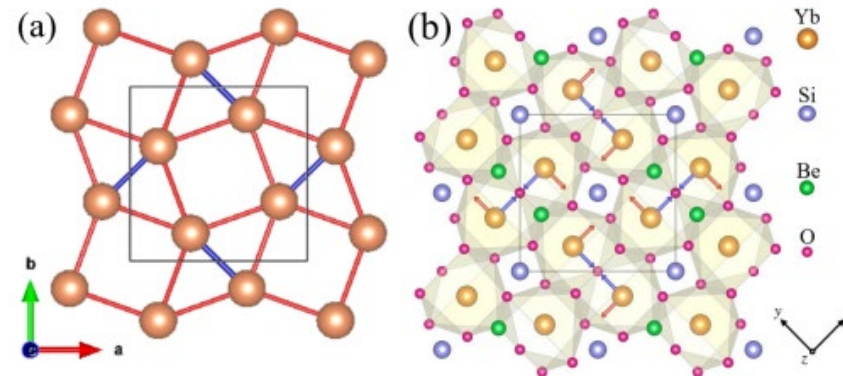
# Dimer state in the Shastry-Sutherland magnet $\text{Yb}_2\text{Be}_2\text{SiO}_7$

The Shastry-Sutherland lattice (SSL) consists of a plane of orthogonal dimers  
→ canonical 2D models that can host entangled spin states.

No long range magnetic order down to 50 mK.

Low Yb point symmetry.

pNPD shows Ising-like anisotropy along c-axis



Brassington, SC *et. al*, Nature Communications 17:2751 (2026)  
<https://doi.org/10.1038/s41467-026-69258-7>

# Unconventional colossal magnetoresistance (CMR) in $\text{Mn}_3\text{Si}_2\text{Te}_6$



Raju Baral  
ORNL

<https://doi.org/10.1103/9pq7-5svy>

# Unconventional colossal magnetoresistance (CMR) in $\text{Mn}_3\text{Si}_2\text{Te}_6$ linked to out of plane spin angle

## Article


### Control of chiral orbital currents in a colossal magnetoresistance material

<https://doi.org/10.1038/s41586-022-05262-3>

Received: 8 June 2022

Accepted: 22 August 2022

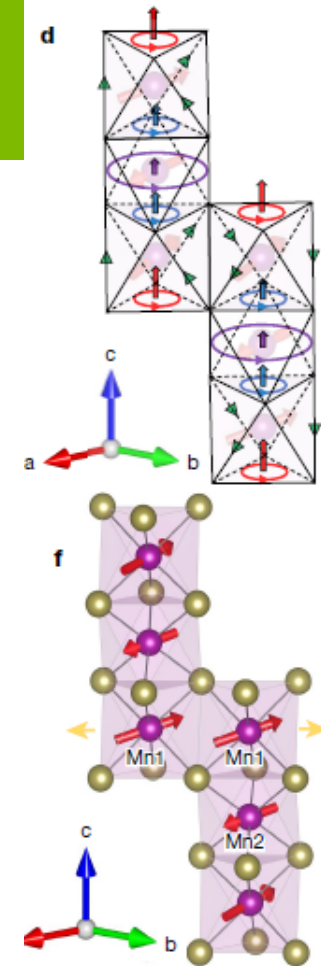
Published online: 12 October 2022

 Check for updates

Nature

Yu Zhang<sup>1</sup>, Yifei Ni<sup>1</sup>, Hengdi Zhao<sup>1</sup>, Sami Hakani<sup>2</sup>, Feng Ye<sup>3</sup>, Lance DeLong<sup>4</sup>, Itamar Kimchi<sup>2,5</sup> & Gang Cao<sup>1,5</sup>

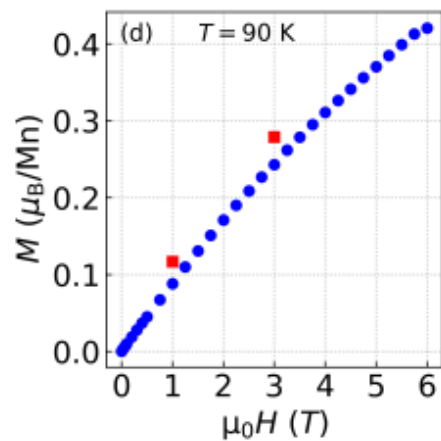
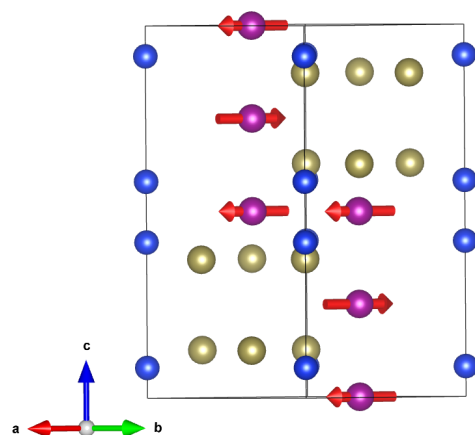
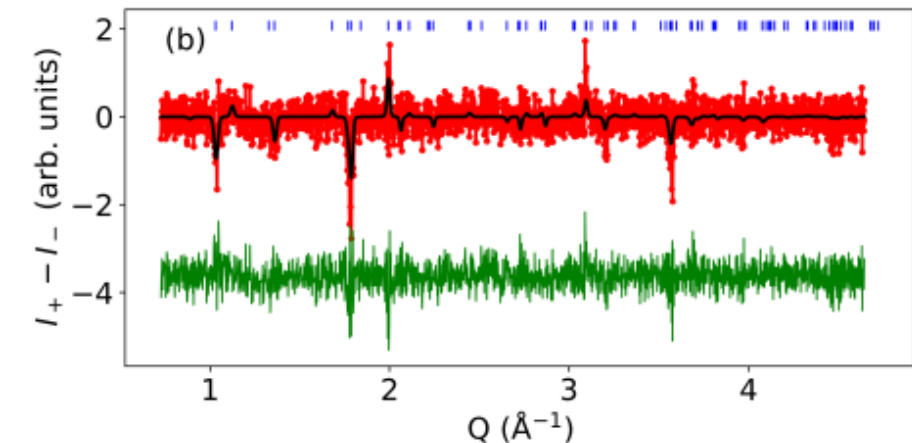
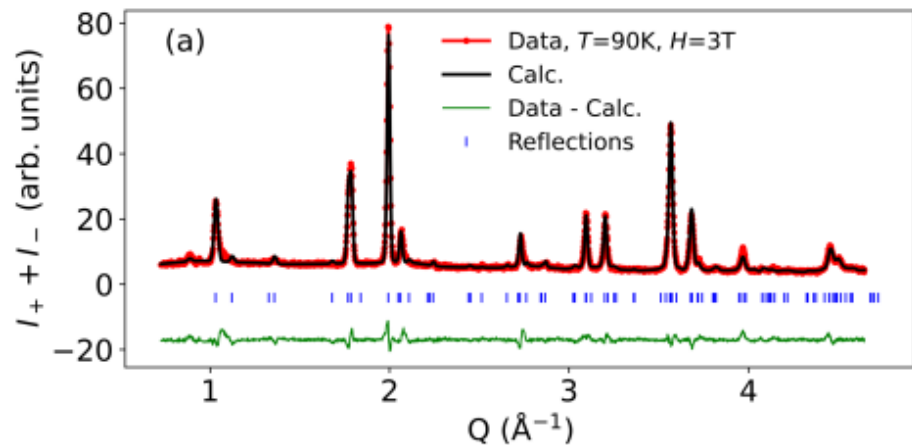
Colossal magnetoresistance (CMR) is an extraordinary enhancement of the electrical conductivity in the presence of a magnetic field. It is conventionally associated with a field-induced spin polarization that drastically reduces spin scattering and electric resistance. Ferrimagnetic  $\text{Mn}_3\text{Si}_2\text{Te}_6$  is an intriguing exception to this rule: it exhibits a seven-order-of-magnitude reduction in  $ab$  plane resistivity that occurs only when a magnetic polarization is avoided<sup>1–3</sup>. Here, we report an exotic quantum state that is driven by  $ab$  plane chiral orbital currents (COC) flowing along edges of  $\text{MnTe}_6$  octahedra. The  $c$  axis orbital moments of  $ab$  plane COC couple to the ferrimagnetic Mn spins to drastically increase the  $ab$  plane conductivity (CMR) when an external magnetic field is aligned along the magnetic hard  $c$  axis. Consequently, COC-driven CMR is highly susceptible to small direct currents exceeding a critical threshold, and can induce a time-dependent, bistable switching that mimics a first-order ‘melting transition’ that is a hallmark of the COC state. The demonstrated current-control of COC-enabled CMR offers a new paradigm for quantum technologies.



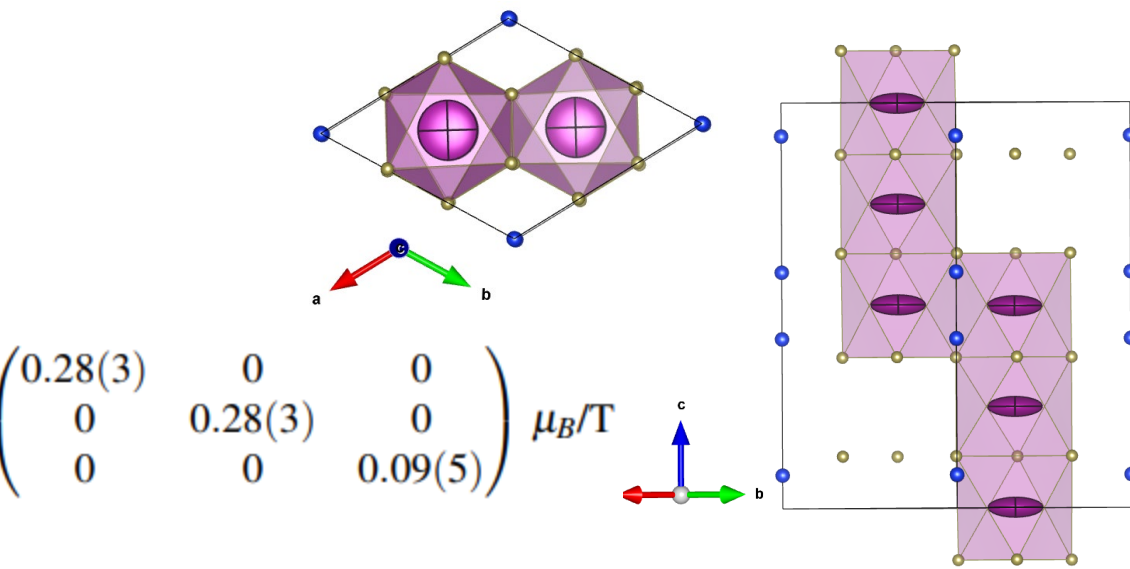
# Polarization on HB-2A: Planar anisotropy in the topological ferrimagnet $\text{Mn}_3\text{Si}_2\text{Te}_6$

Unconventional colossal magnetoresistance (CMR) behavior below  $T_c = 78$  K

XY anisotropy, CMR induced by out of plane spins



$$\begin{pmatrix} 0.28(3) & 0 & 0 \\ 0 & 0.28(3) & 0 \\ 0 & 0 & 0.09(5) \end{pmatrix} \mu_B/T$$



PHYSICAL REVIEW B **112**, 024405 (2025)

Short-range magnetic order and planar anisotropy in the topological ferrimagnet  $\text{Mn}_3\text{Si}_2\text{Te}_6$

Raju Baral<sup>1,\*</sup>, Andrew F. May<sup>2</sup>, and Stuart Calder<sup>1,†</sup>

<sup>1</sup>Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

<sup>2</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

(Received 2 May 2025; accepted 3 June 2025; published 2 July 2025)

$\text{Mn}_3\text{Si}_2\text{Te}_6$  is a ferrimagnetic topological nodal-line semiconductor that exhibits unconventional colossal magnetoresistance behavior, with short-range spin fluctuations being potentially intimately linked to the emergent properties. Here we determine the short-range magnetic order and anisotropy through total neutron scattering and polarized neutron powder diffraction measurements on polycrystalline  $\text{Mn}_3\text{Si}_2\text{Te}_6$ . Strong in-plane anisotropy is quantified on the Mn ions through extraction of the local site susceptibility tensor. The real-space local spin structure is determined through the application of magnetic pair distribution function analysis covering a wide temperature range. Short-range order over a locally frustrated trimer of three nearest neighbors is found to exist well above the long-range ferrimagnetic transition.

DOI: 10.1103/9pq7-5svy

# Investigating the origin of zero moment layers in $K_3Er(VO_4)_2$

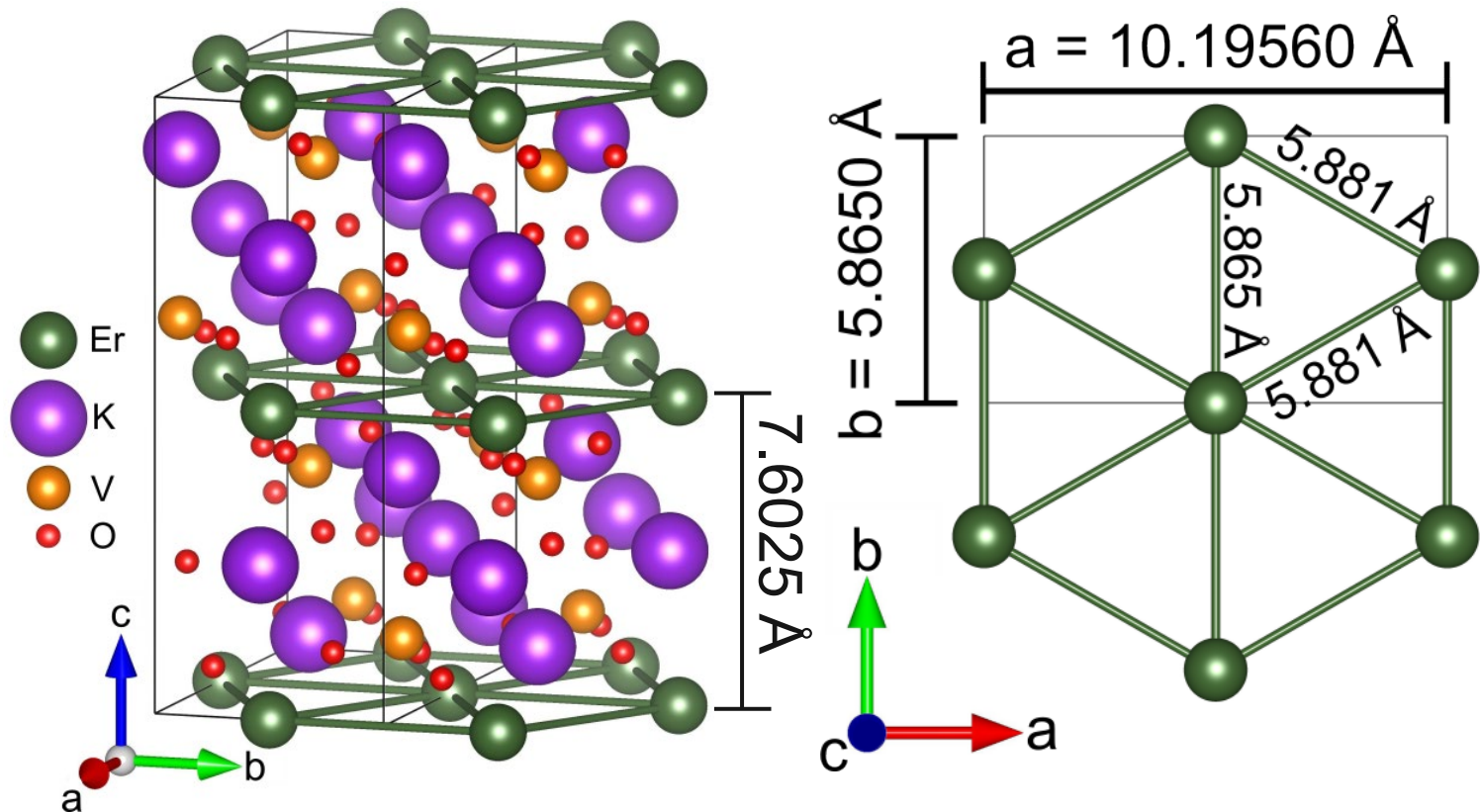


Danielle Yahne

# Distorted 2D triangular lattice $K_3Er(VO_4)_2$

Investigating geometric frustration in 2D triangular materials:  
search for spin liquid phases

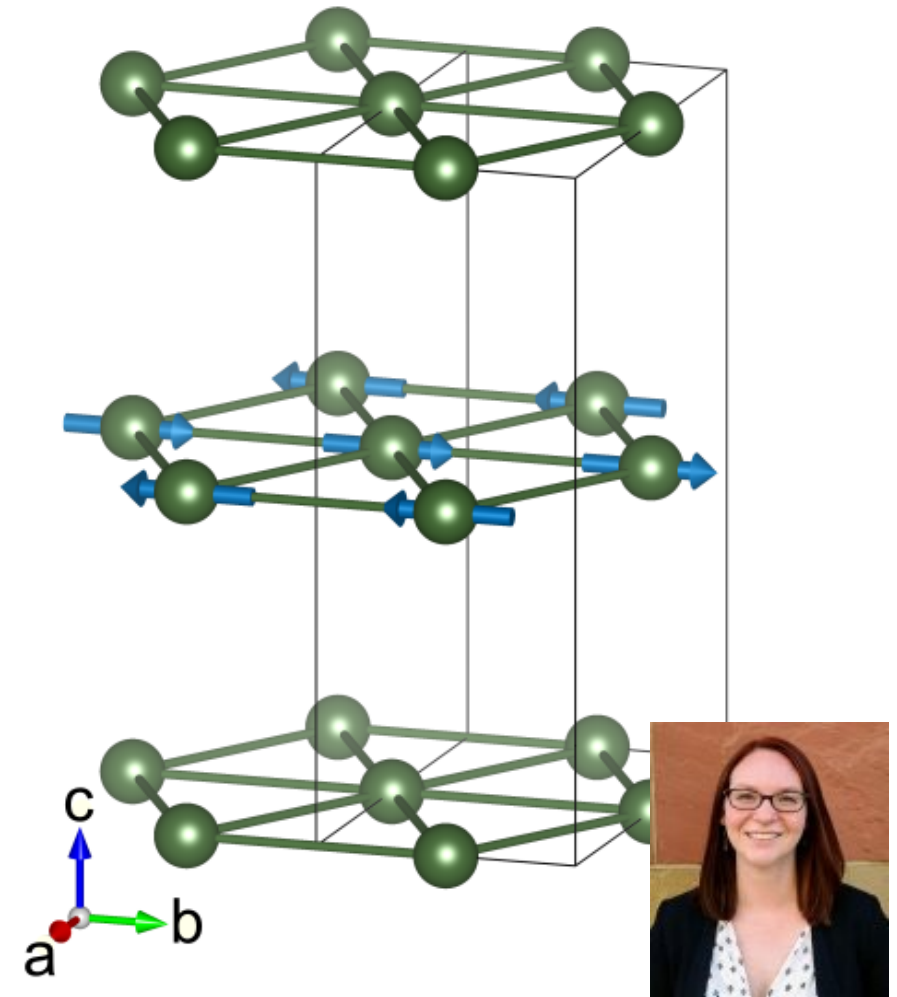
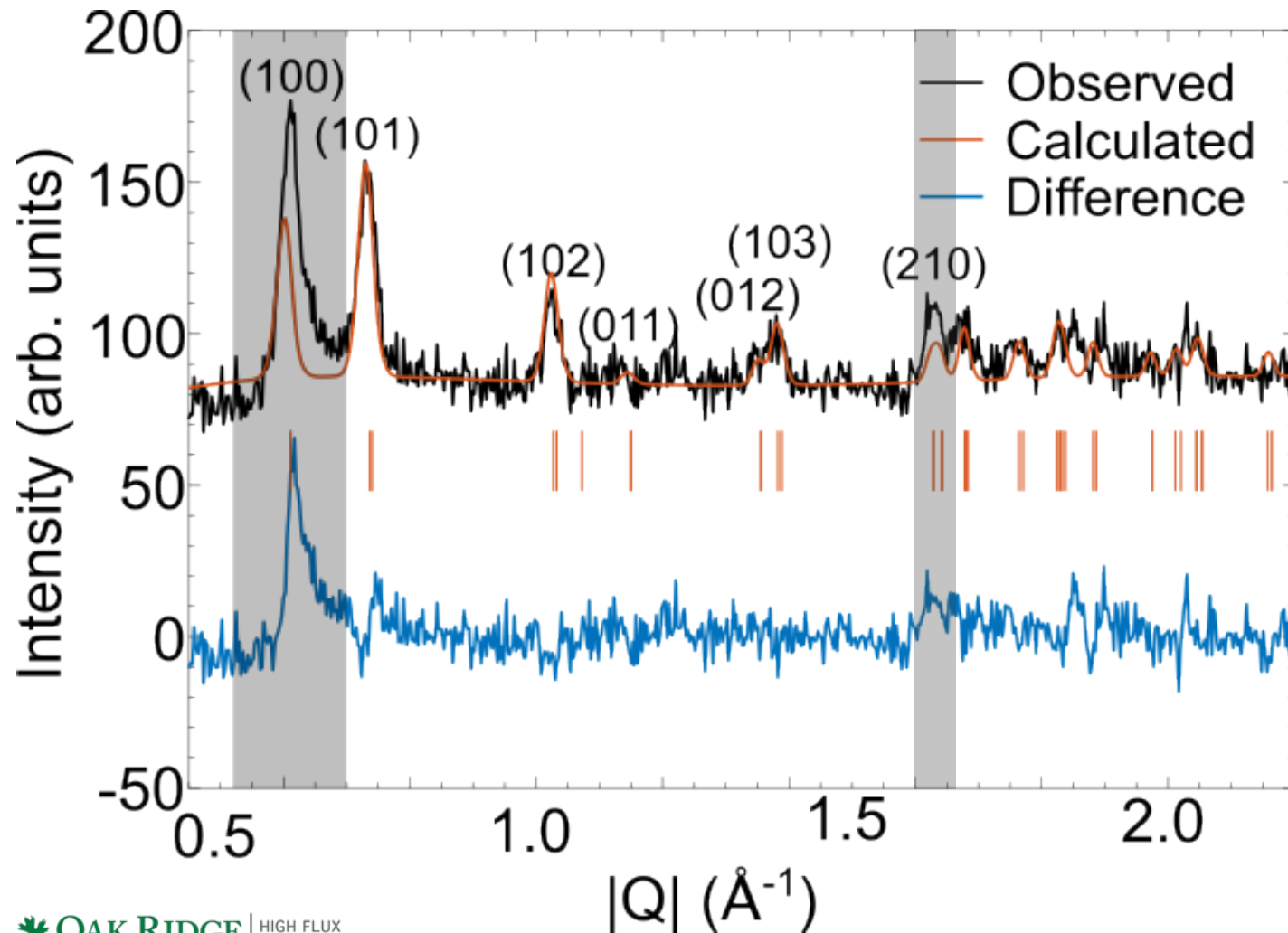
Heat capacity,  
susceptibility, and  
magnetization find  
evidence of short-range  
correlations and XY  
anisotropy



Monoclinic polymorph of  
 $K_3Er(VO_4)_2$  consists of  
layers of 2D *isosceles*  
triangular lattices

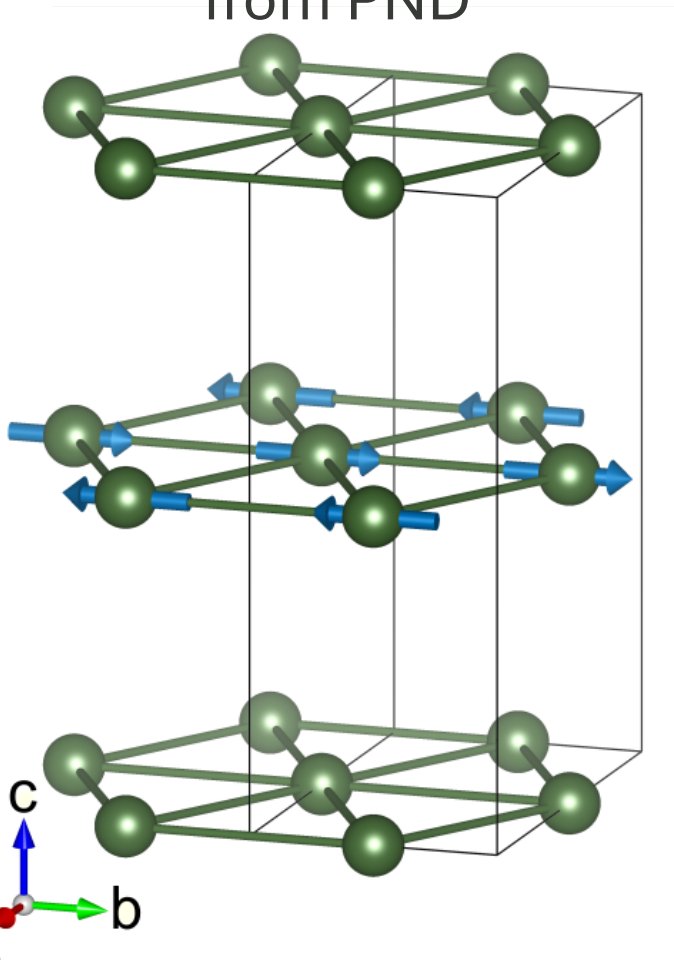


# Unpolarized Powder neutron diffraction shows long-range order on top of diffuse Warren-like scattering



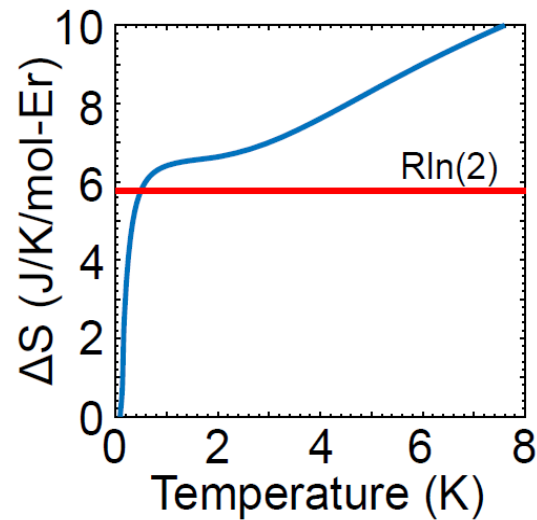
# Where did the moment go?

Magnetic structure  
from PND

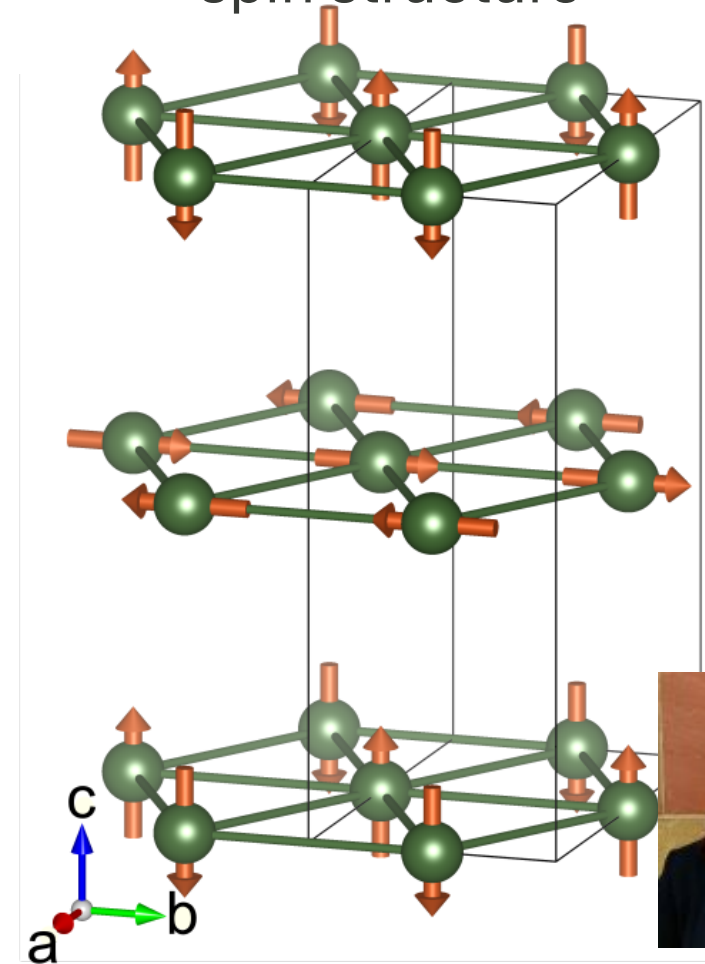


$$\mu_{ii} = g_{ii} S_i$$
$$g_z \sim 0$$
$$\mu_z \sim 0$$

Fully ordered?

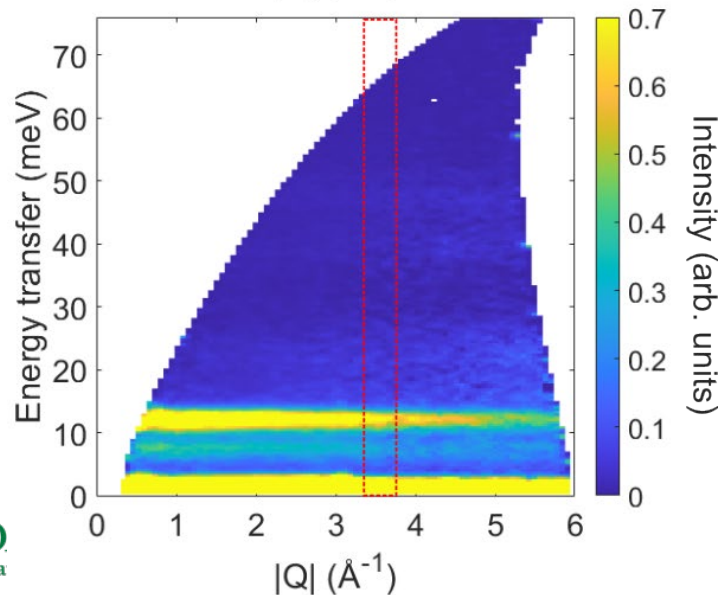
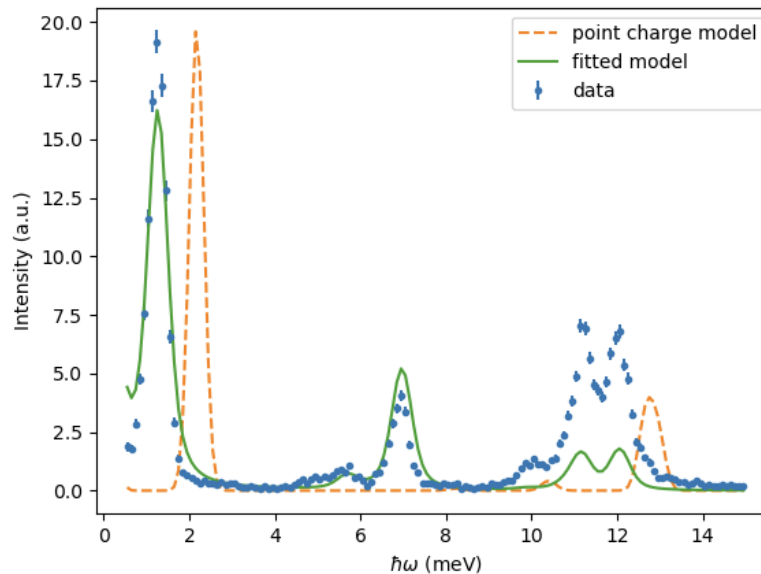
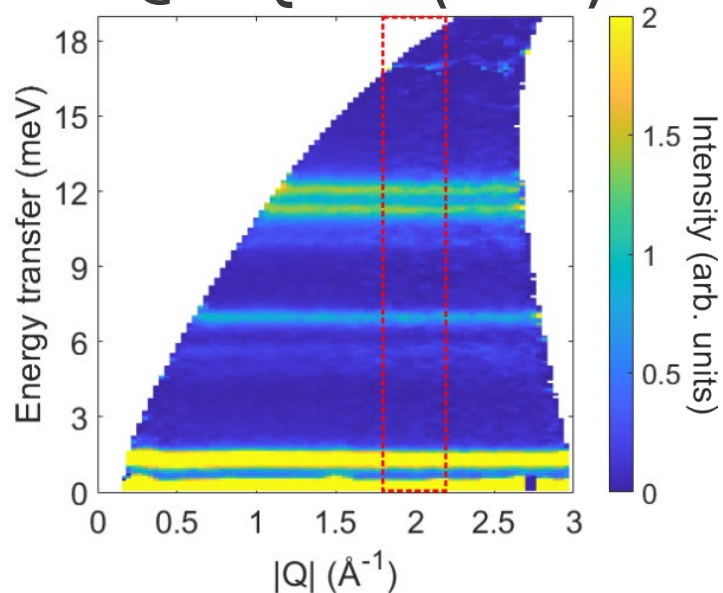


Possible pseudo-  
spin structure

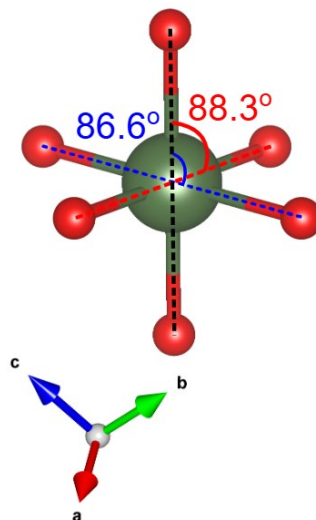


# Crystal field analysis under-constrained

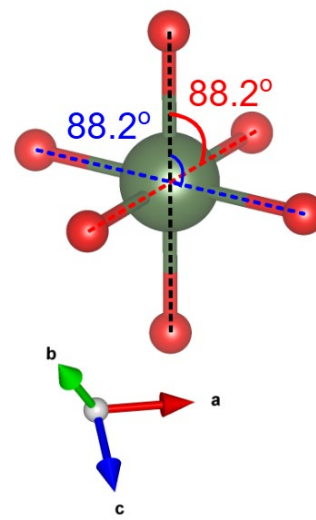
INS @ SEQUOIA (ORNL)



Monoclinic



Trigonal



$$g = \begin{pmatrix} 8.43 & 0 & 0 \\ 0 & 8.43 & 0 \\ 0 & 0 & 3.30 \end{pmatrix}$$

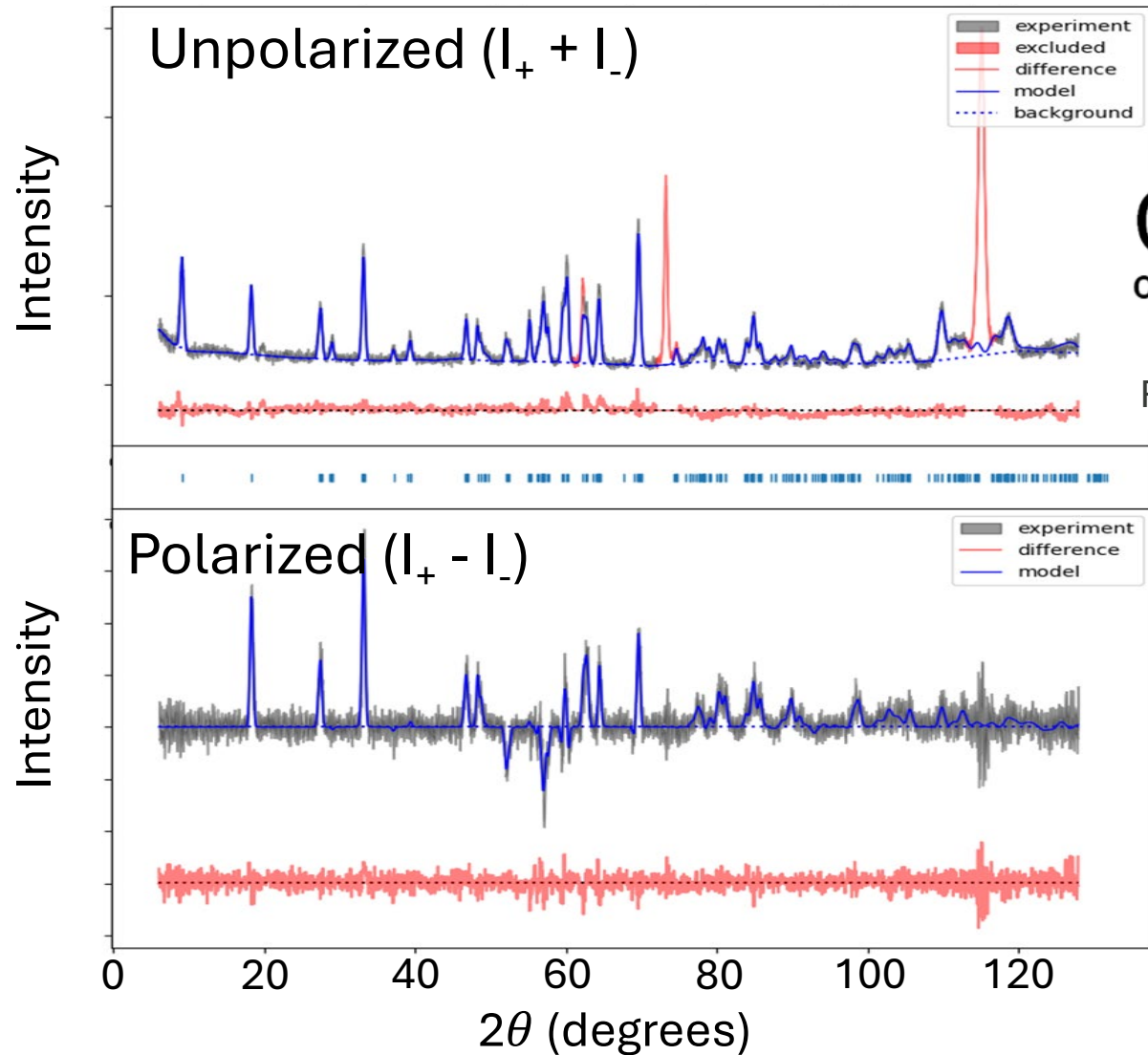
$E_{\text{calc}}$ (meV)	$E_{\text{obs}}$ (meV)
0	0
1.27	1.23
6.97	6.89
11.16	11.19
12.06	12.06
36.83	-
37.49	-
38.02	-

*PyCrystalField*: A. Scheie, J. Appl. Cryst. 54, 356 (2021)

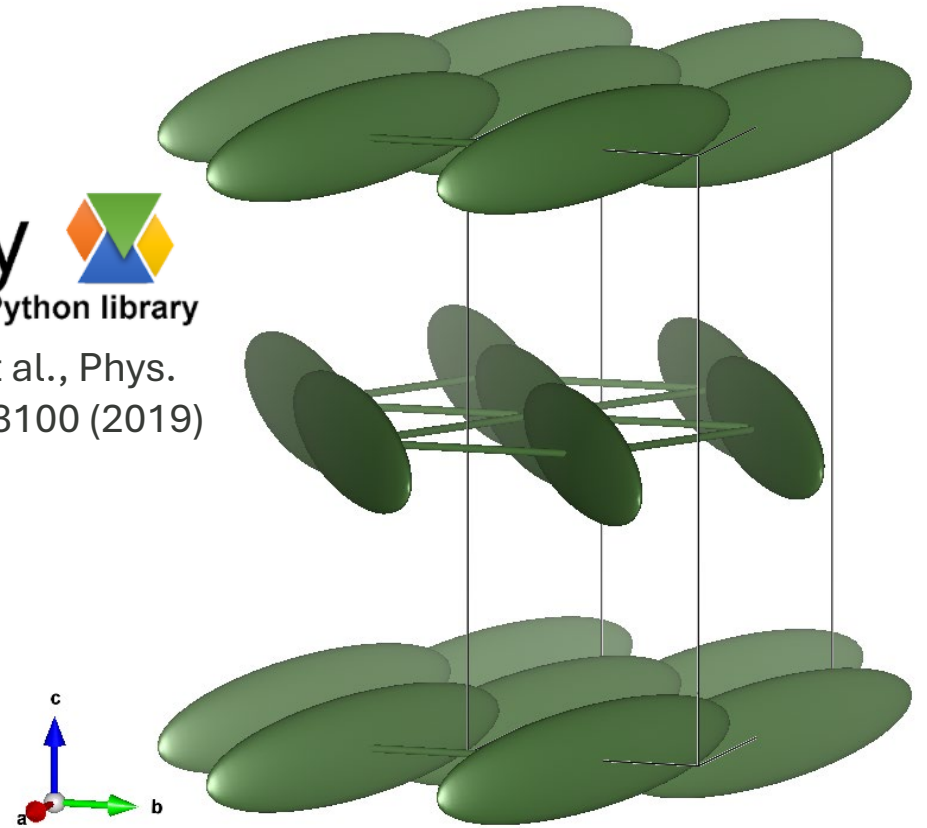


# Magnetization ellipsoids Ising-like in AB-plane

H = 1 T, T = 2 K



**CrysPy**   
 Crystallographic Python library  
 I. A. Kibalin et al., Phys.  
 Rev. Res. 1, 033100 (2019)



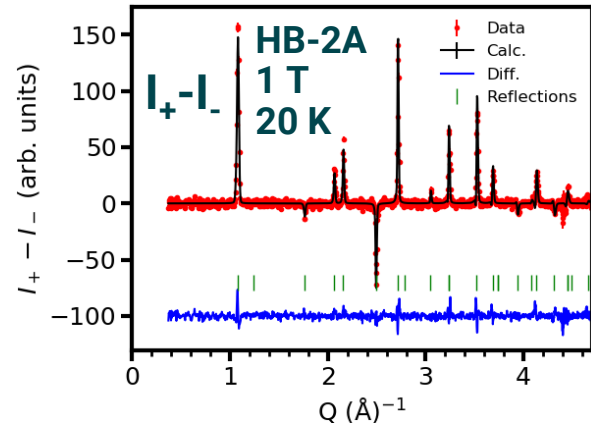
$$\chi_{ij} = \begin{pmatrix} 5.92 & 3.78 & -1.01 \\ 3.78 & 3.79 & -0.26 \\ -1.01 & -0.26 & 2.66 \end{pmatrix}$$



# Frustrated magnetism on the pyrochlore lattice

# Pyrochlores: classic spin ice $\text{Ho}_2\text{Ti}_2\text{O}_7$

Monopoles in  $\text{Ho}_2\text{Ti}_2\text{O}_7$

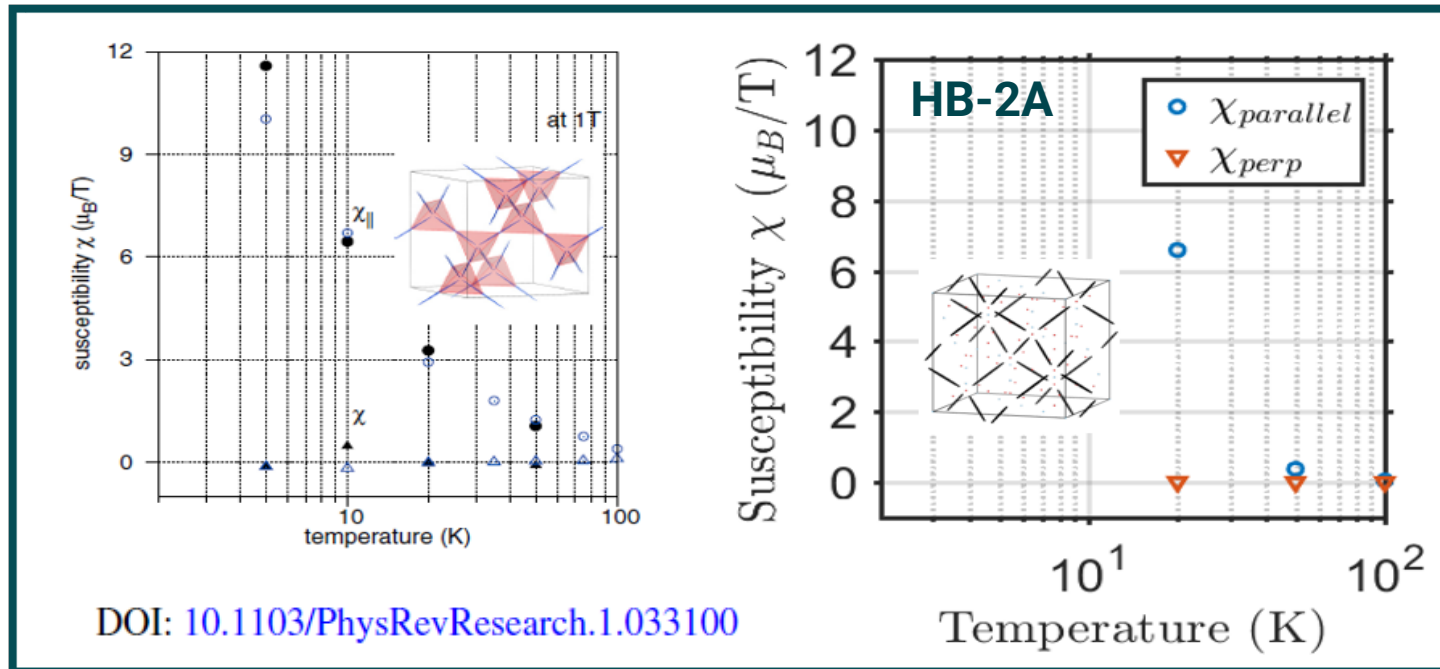
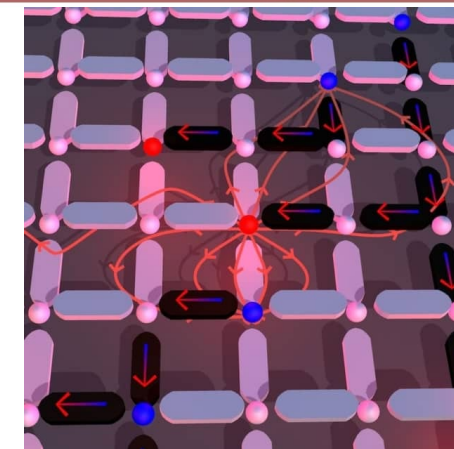
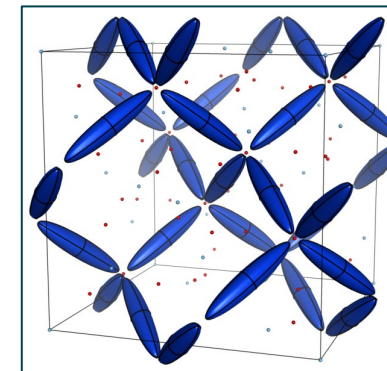
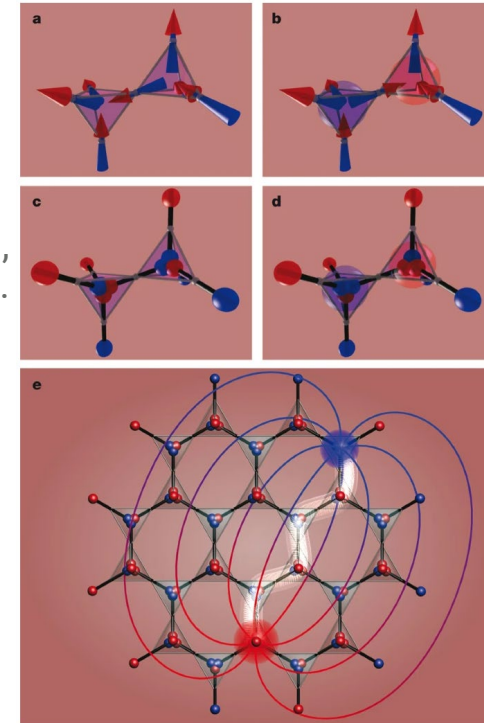


- Benchmarking HB-2A with a “standard”  $\text{Ho}_2\text{Ti}_2\text{O}_7$

- Highlights spin ice rules

- Powders and single crystal give the same information here.

Castelnovo et al,  
Nature.

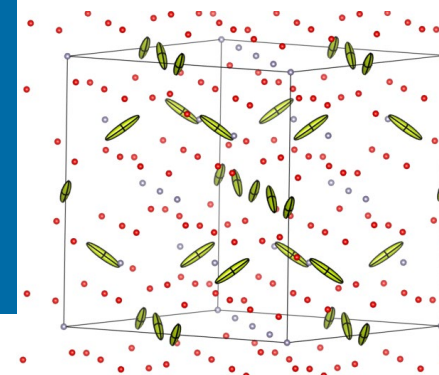
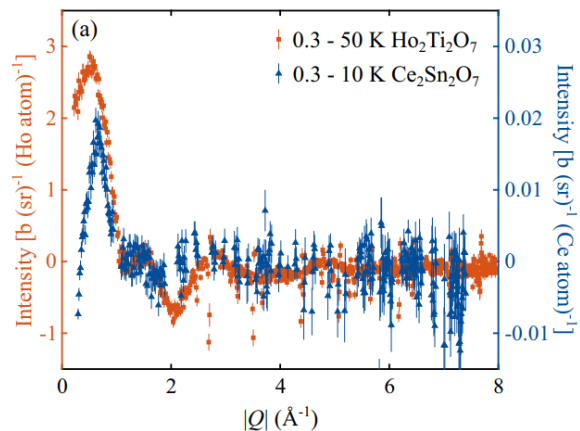


# Pyrochlores: Dipolar-octupolar ordering in $\text{Ce}_2\text{Sn}_2\text{O}_7$

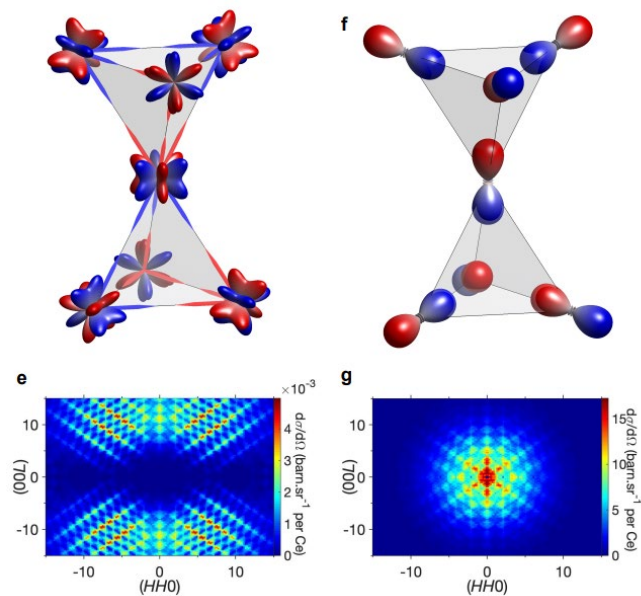


Yahne, SC, *et al.*, PRX 14, 011005 (2024)

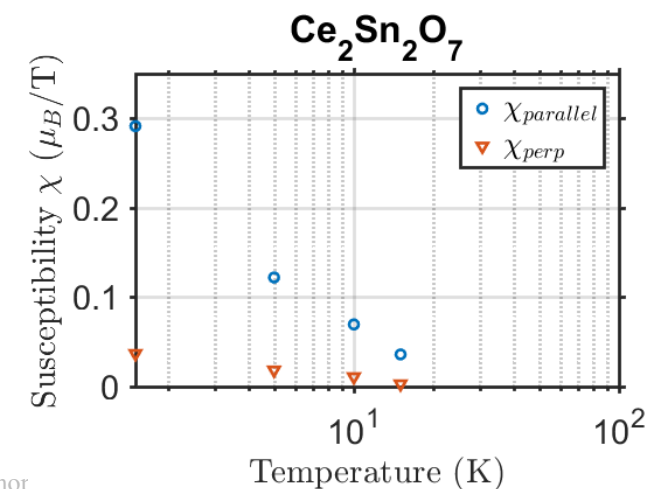
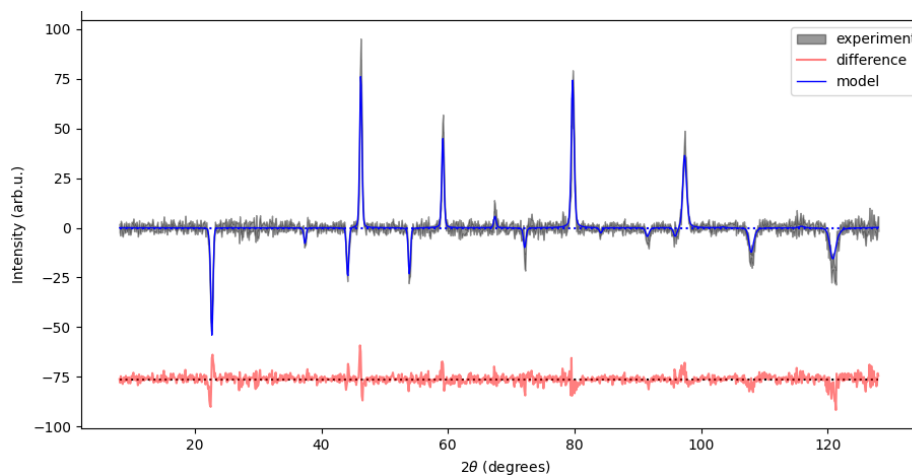
- Half-polarized powder diffraction on HB-2A probed dipolar ordering
- Behavior similar to classic spin ice
- Absence of proposed octupolar phase?



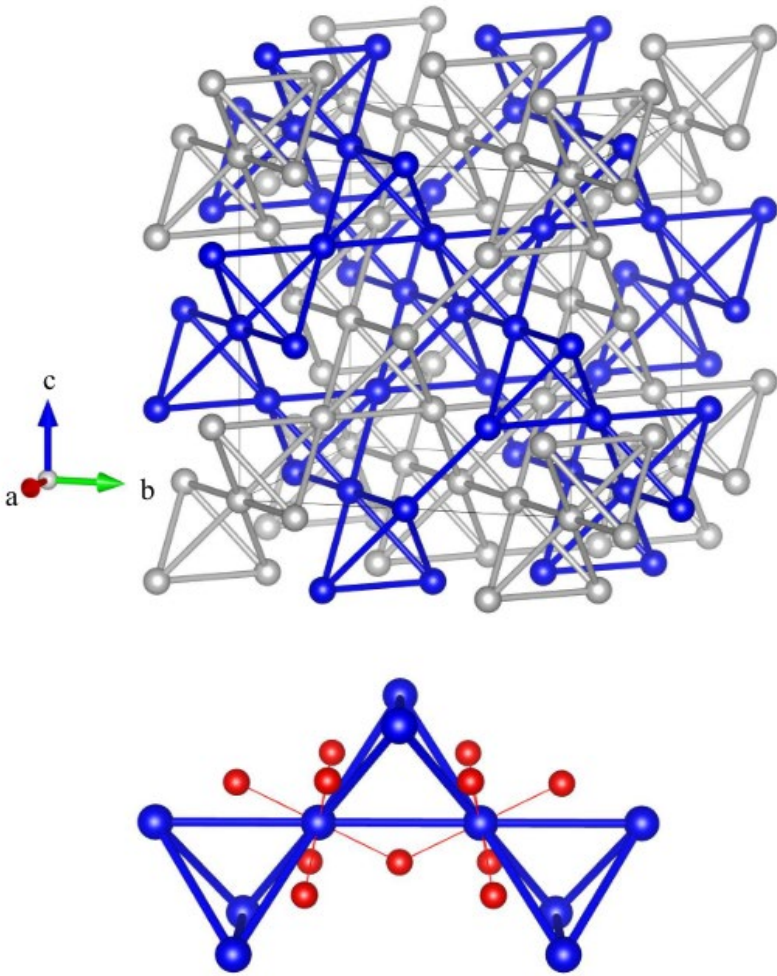
HB-2A data



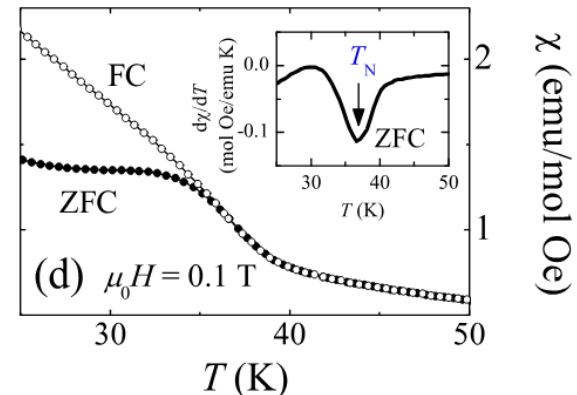
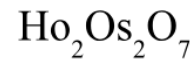
Sibille *et al.*, Nature Physics (2020)



# Ho<sub>2</sub>Os<sub>2</sub>O<sub>7</sub> with Ho<sup>3+</sup> and Os<sup>4+</sup> ions: J=0 and spin-ice?



- Pyrochlore lattice with magnetic ions on A and B site
- Induced magnetism from J=0 state
  - singlet-triplet excitations where the ions develop collective magnetism due to interaction effects
- Spin ice behavior?
- Signs of long range order at 36K, short range order to <1 K.



Phys. Rev. B **93**, 134426 (2016)

<https://doi.org/10.1103/PhysRevB.109.054408>

PHYSICAL REVIEW B **109**, 054408 (2024)

## Local site behavior of the 5d and 4f ions in the frustrated pyrochlore Ho<sub>2</sub>Os<sub>2</sub>O<sub>7</sub>

S. Calder<sup>1,\*</sup>, Z. Y. Zhao<sup>2</sup>, M. H. Upton<sup>3</sup>, and J.-Q. Yan<sup>2</sup>

<sup>1</sup>Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

<sup>2</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

<sup>3</sup>Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

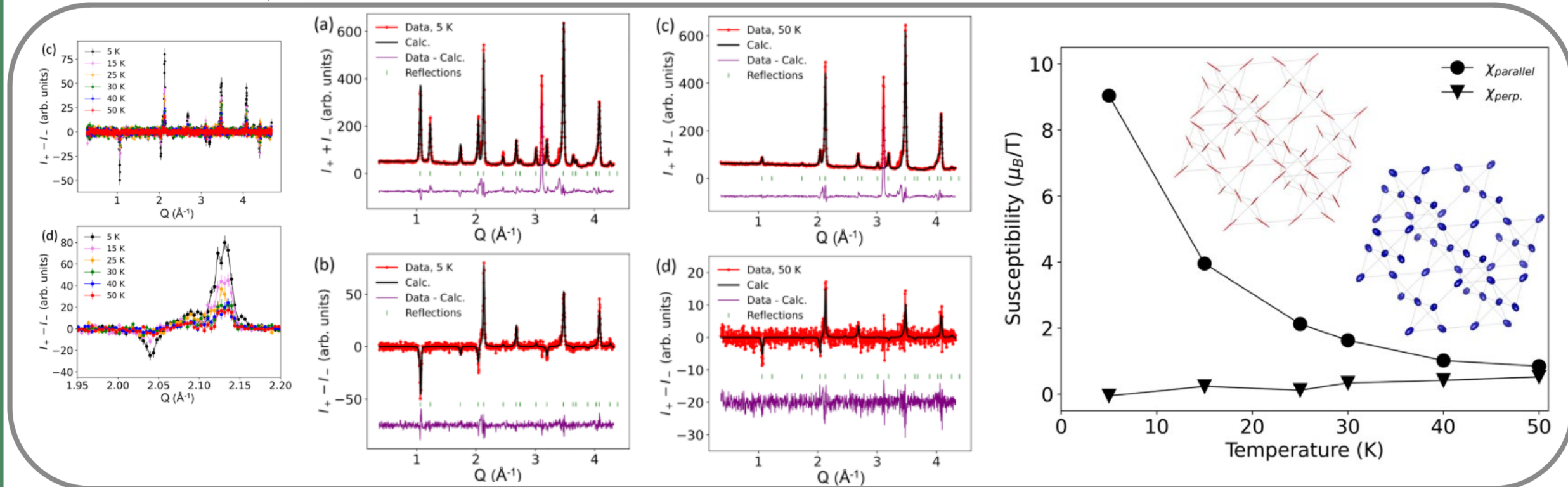
(Received 17 July 2023; accepted 11 January 2024; published 8 February 2024)

The pyrochlore osmate Ho<sub>2</sub>Os<sub>2</sub>O<sub>7</sub> is a candidate material for a fragile  $J = 0$  local singlet ground state; however little is known regarding the single-ion behavior of either the Os or Ho ions. To address this we present polarized neutron powder diffraction (PNPD) and RIXS measurements that separately probe the local site behavior of the Os and Ho ions. The PNPD results are dominated by Ho<sup>3+</sup> scattering and the analysis reveals local site susceptibility behavior consistent with spin-ice materials. Complementary unpolarized neutron powder diffraction shows an ordered spin-ice ground state in an applied magnetic field. To isolate the Os<sup>4+</sup> single-ion behavior we present resonant inelastic x-ray scattering (RIXS) measurements at the osmium  $L$  edge. Analysis of the RIXS spectra parametrizes the spin-orbit coupling (0.35 eV), Hund's coupling (0.27 eV), and trigonal site distortion (−0.17 eV). The results are considered within the context of a  $J = 0$  model and possible departures from this through structural distortions, excitonic interactions, and  $5d$ - $4f$  interactions between the Os ion and the surrounding Ho lattice. The experimental methodology employed highlights the complementary information available in rare-earth-based  $5d$  pyrochlores from distinct neutron and x-ray scattering techniques that allow for the isolation and determination of the behavior of the different ions.

DOI: 10.1103/PhysRevB.109.054408

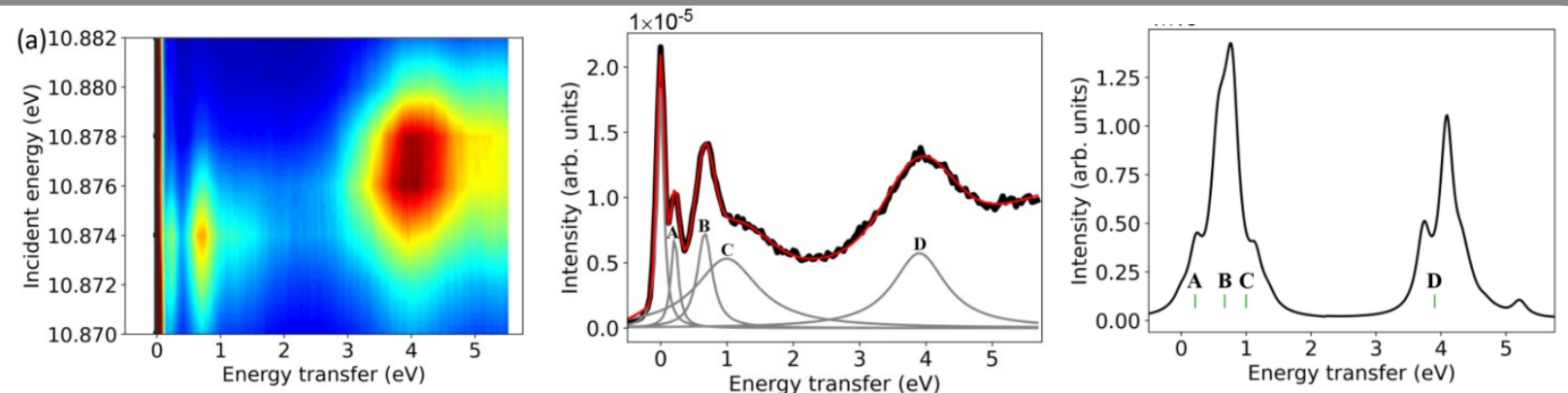
S. Calder, ORNL, Polarized workshop 2026, POWDER (HB-2A) instrument: Science Highlights

# Ho<sub>2</sub>Os<sub>2</sub>O<sub>7</sub> with Ho<sup>3+</sup> and Os<sup>4+</sup> ions: J=0 and spin-ice?



<https://doi.org/10.1103/PhysRevB.109.054408> Calder *et al.*, Rev. B **109**, 054408 (2024)

- PNPD dominated by Ho signal
  - Spin ice like behavior
- RIXS access ONLY Os ion
  - J=0 ground state, but with trigonal distortion



# Ferromagnetism in Heuslers



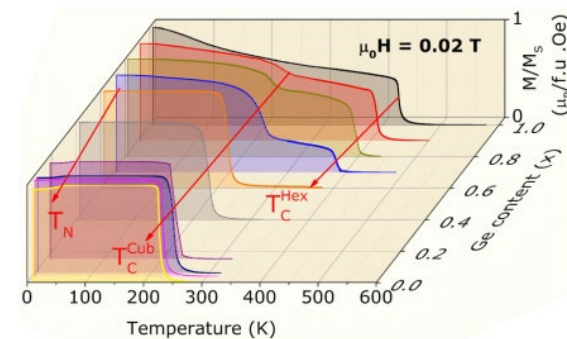
Keith Taddei



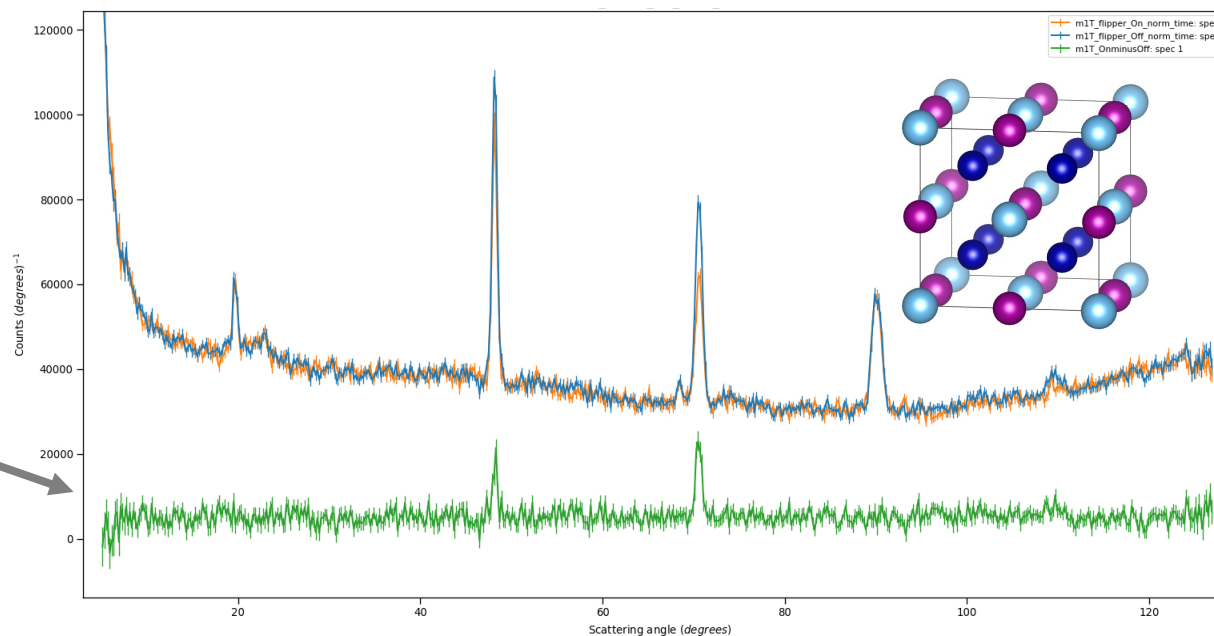
Antonio dos Santos

# Half Polarization on HB-2A studying Ferromagnetic Heusler

- Heuslers alloys are multifunctional materials with strong magnetostructural coupling.  $T_C \gg 300$  K
- No magnetic signal observed on traditional diffractometers
- Polarization study on small (0.6g) sample of absorbing Heusler compound
- Use polarization to study Ferromagnetism and isolate nuclear scattering for site ordering.



Magnetic signal from 0.6 g of an absorbing Ferromagnet



# Low dimensional metal-organic frameworks (MOFs)

research papers



STRUCTURAL SCIENCE  
CRYSTAL ENGINEERING  
MATERIALS

ISSN 2052-5206

## Low-dimensional metal–organic frameworks: a pathway to design, explore and tune magnetic structures

Stuart Calder,<sup>a\*</sup> Raju Baral,<sup>a</sup> C. Charlotte Buchanan,<sup>b</sup> Dustin A. Gilbert,<sup>b,c</sup> Rylan J. Terry,<sup>d</sup> Joseph W. Kolis<sup>d</sup> and Liurukara D. Sanjeewa<sup>e</sup>

Received 15 May 2024  
Accepted 15 August 2024

<https://doi.org/10.1107/S2052520624008023>

PHYSICAL REVIEW MATERIALS 6, 124407 (2022)

## Magnetic interactions in the one-dimensional spin-chain metal-organic compounds $M(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2$ ( $M = \text{Cu}, \text{Co}, \text{Mn}$ )

S. Calder<sup>1,\*</sup>, L. D. Sanjeewa,<sup>2,3</sup> V. O. Garlea,<sup>1</sup> J. Xing,<sup>4</sup> R. J. Terry<sup>5</sup> and J. W. Kolis<sup>5</sup>

<sup>1</sup>Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

<sup>2</sup>University of Missouri Research Reactor (MURR), Columbia, Missouri 65211, USA

<sup>3</sup>Department of Chemistry, University of Missouri, Columbia, Missouri 65211, USA

<sup>4</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

<sup>5</sup>Department of Chemistry and Center for Optical Materials Science and Engineering Technologies, Clemson University, Clemson, South Carolina 29634, USA



(Received 13 June 2022; accepted 2 December 2022; published 19 December 2022)

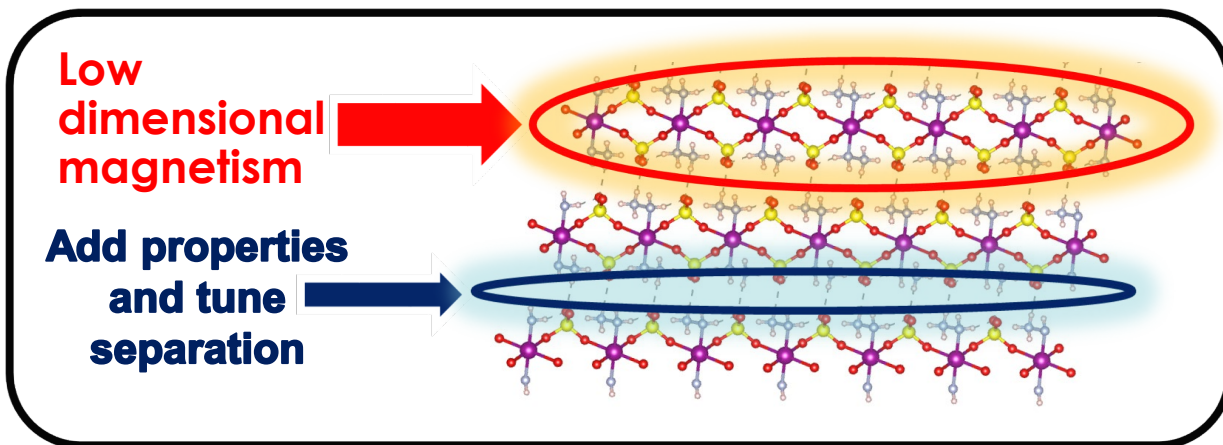
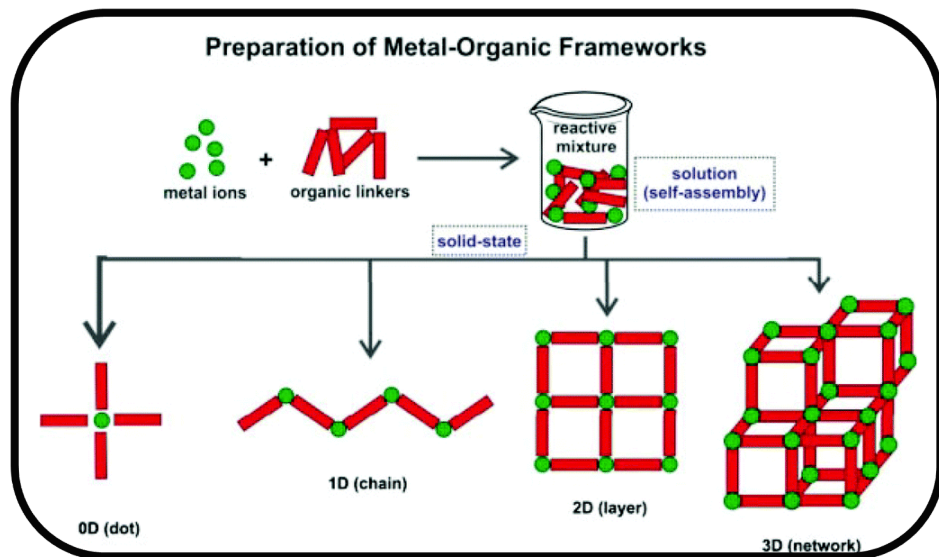
<https://doi.org/10.1103/PhysRevMaterials.6.124407>

# 1D spin-chains in MOFs

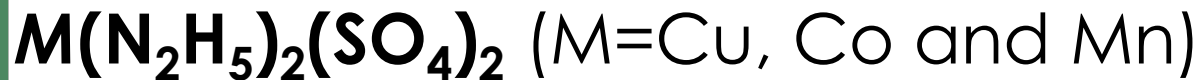
# 1D spin-chains in MOFs

## General Motivation: Quantum behavior by design in low dimensional Magnetic MOFs

- **Magnetism largely unexplored**
- **Straightforward synthesis to tune low dimensional behavior and further coupled properties.**



# 1D spin-chains in metal-organic frameworks



- Metal hydrazinium sulfates.
- Initially synthesized in the 1800s!
- 1D chains have provided main interest
  - 1D AFM Heisenberg model

Curtius and Schrader, *J. prakt. Chem.*, 1894, **50**, 311.  
Traube and Passage, *Ber.*, 1913, **46**, 1505.

1961

817. *Hydrazinium(1+) as a Ligand.*

By C. K. PROUT and H. M. POWELL

The crystal structure of hydrazinium(1+) zinc sulphate,  $(N_2H_5)_2Zn(SO_4)_2$ , has been determined. It contains infinitely extended, essentially one-dimensional complexes of the same overall composition. These consist of zinc ions octahedrally surrounded by four oxygen and two nitrogen atoms. The oxygen atoms belong to sulphate groups which bridge to neighbouring zinc ions. Each co-ordinated nitrogen atom forms one end of a hydrazinium group, which is not co-ordinated to zinc through its other nitrogen atom. There is a system of hydrogen bonding between oxygen atoms and nitrogen atoms of both sorts. These bonds are formed both within the linear complex and between neighbouring complexes, so that the crystal as a whole is a three-dimensionally bonded structure.

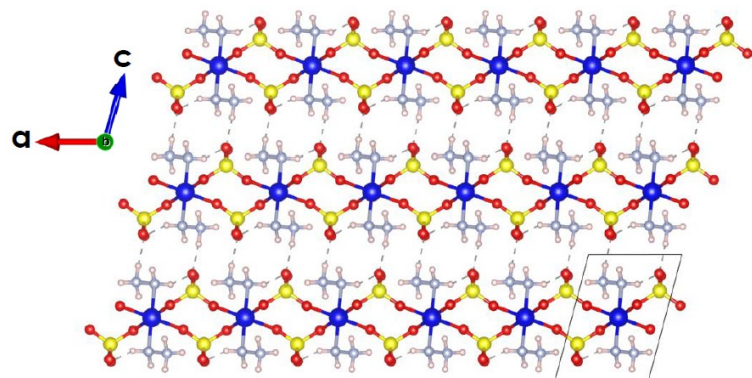
1505

82. **Wilhelm Traube und W. Passage. Über luftbeständige Chromoxydul-Verbindungen.**

[Aus dem Chemischen Institut der Universität Berlin.]

(Eingegangen am 12. April 1913)

Gelegentlich einiger mit Verbindungen des zweiwertigen Chroms geführter Versuche haben wir die Beobachtung gemacht, daß diese Chromoxydul-Salze mit freiem Hydrazin bzw. mit Salzen des Hydrazins zu Verbindungen zusammentreten, die ohne Sauerstoff noch zweiwertiges Chrom enthalten, die aber im Vergleich mit den gewöhnlichen Chromoxydul-Verbindungen der großen Veränderlichkeit und Empfindlichkeit der bisher beobachteten gegenüber eine auffallende Beständigkeit zeigen.



IOP Publishing

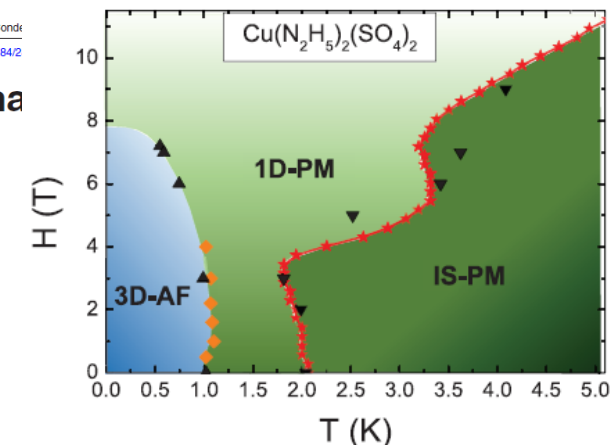
*J. Phys.: Condens. Matter* **28** (2016) 506004 (6pp)

Journal of Physics: Condens.

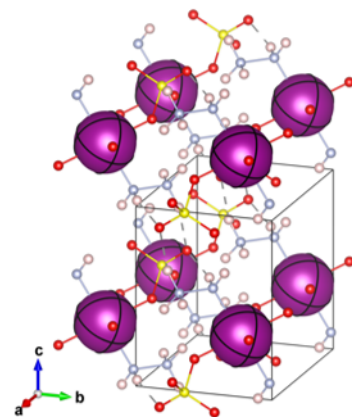
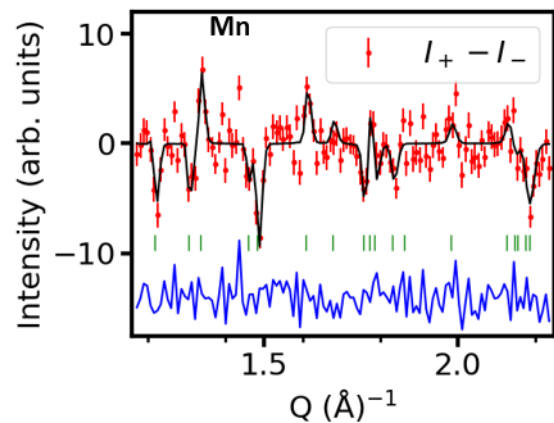
doi:10.1088/0953-8984/28

## Crossover from one- to three-dimensional behavior in the $S = 1/2$ Heisenberg antiferromagnet $Cu(N_2H_5)_2(SO_4)_2$

A Paduan-Filho, A P Vieira, J G A Ramon and R S Freitas

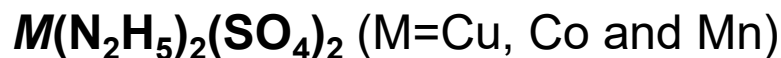


# 1D spin-chains in metal-organic frameworks



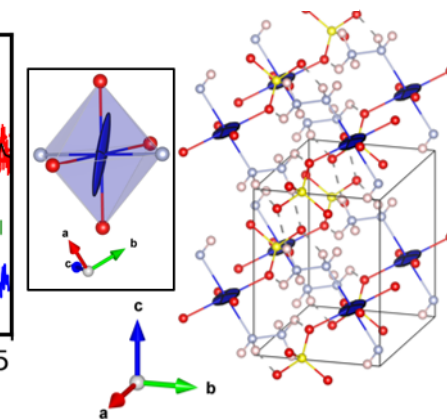
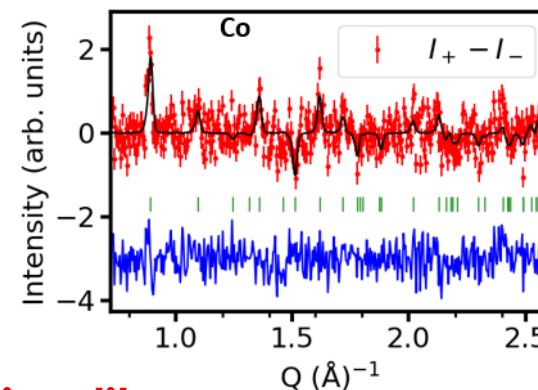
**Heisenberg**

$$\chi_{\text{Mn}} = \begin{pmatrix} 0.25(3) & 0 & 0 \\ 0 & 0.25(3) & 0 \\ 0 & 0 & 0.25(3) \end{pmatrix} \mu_B \text{T}^{-1}$$



- Mn and Co not deuterated
- Cu deuterated

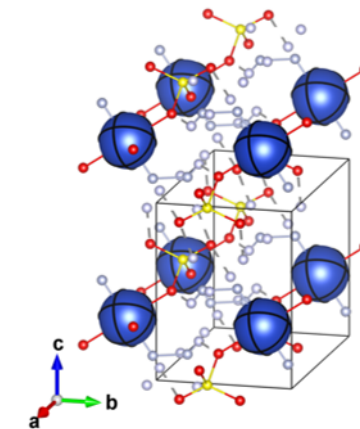
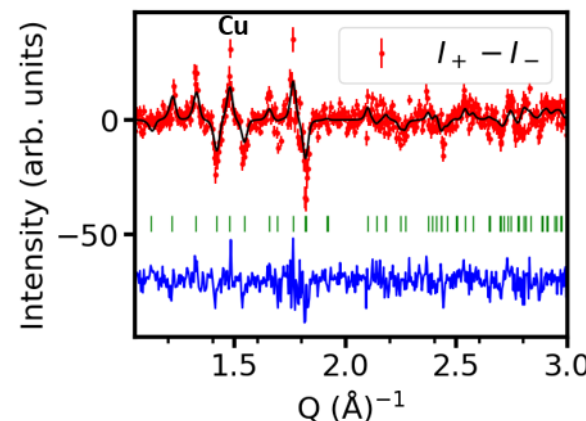
$$\chi_{\text{Co}} = \begin{pmatrix} 0.183(28) & 0.135(20) & -0.067(58) \\ 0.135(20) & 0.0999(65) & 0.015(28) \\ -0.067(58) & 0.015(28) & 0.068(31) \end{pmatrix} \mu_B \text{T}^{-1}$$



**Ising-like**

$$\chi_{\text{Cu}} = \begin{pmatrix} 0.0364(36) & 0 & 0 \\ 0 & 0.0364(36) & 0 \\ 0 & 0 & 0.0364(36) \end{pmatrix} \mu_B \text{T}^{-1}$$

**Heisenberg**

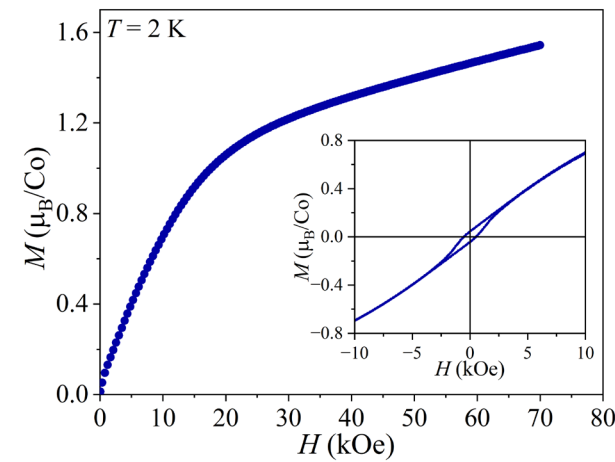
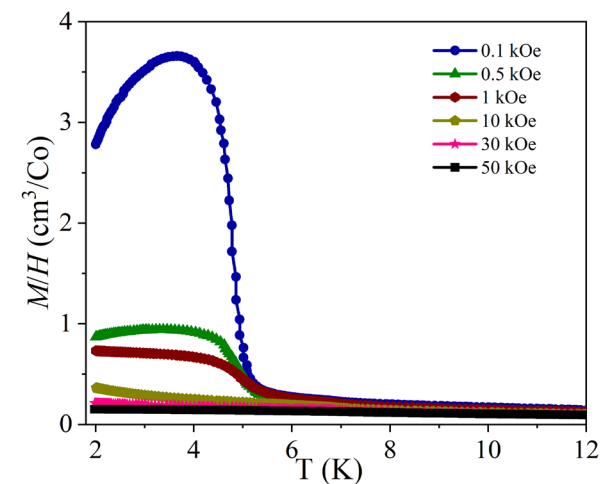
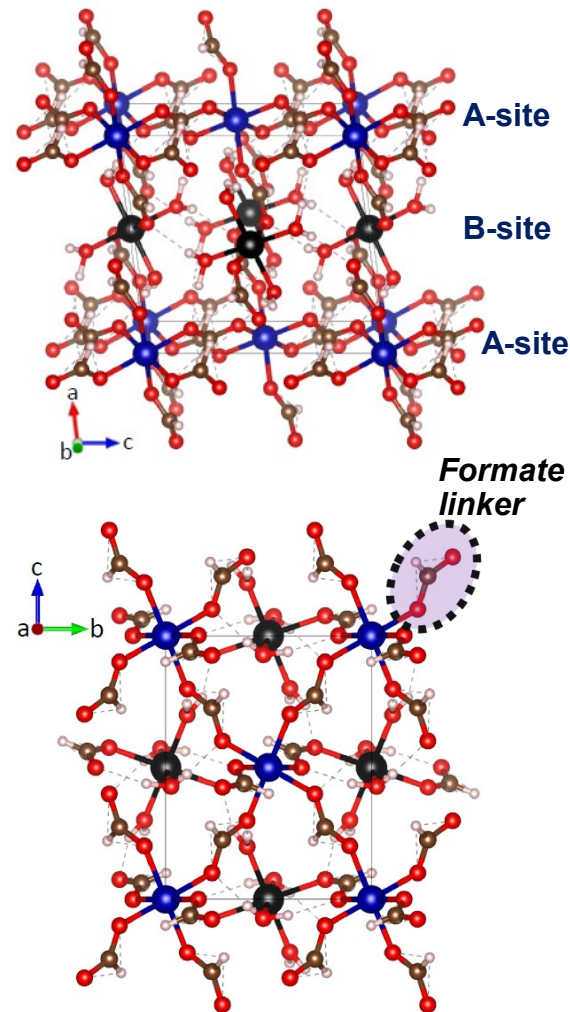
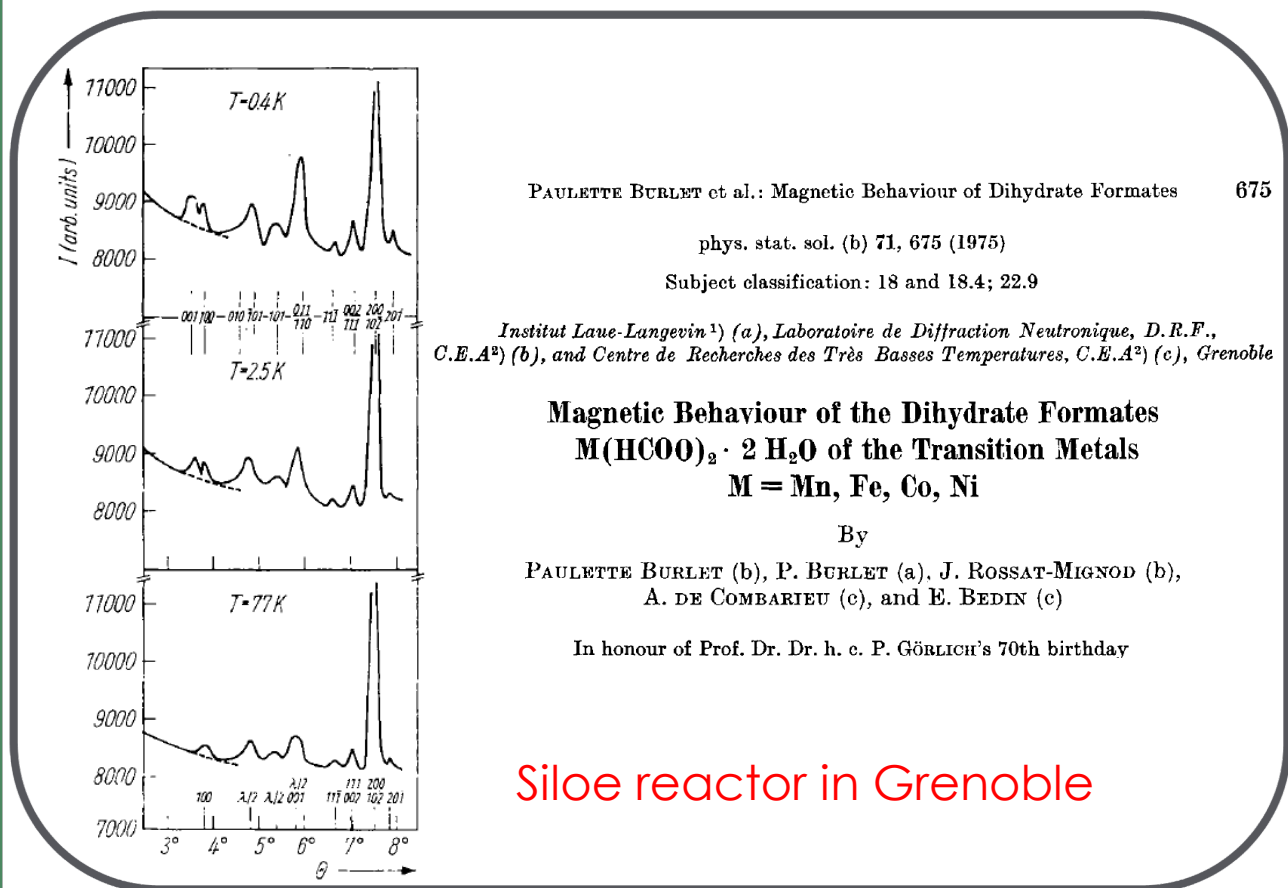


# 2D layered metal-organic framework

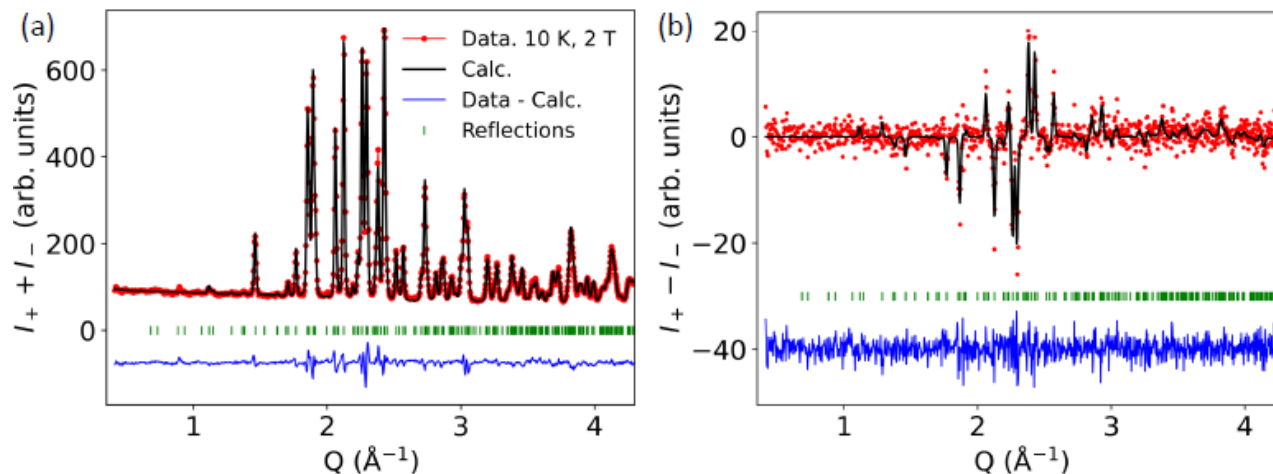
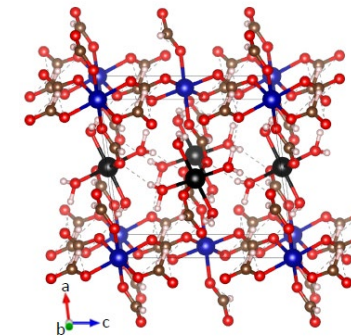
**S. Calder, Sanjeewa et al.,  
PRM,**

# Revisiting $\text{Co}(\text{DCOO})_2 \cdot 2\text{D}_2\text{O}$

- First neutron diffraction study on a MOF: hydrated formate  $\text{M}(\text{DCOO})_2 \cdot 2\text{D}_2\text{O}$  ( $\text{M}=\text{Co}, \text{Ni}$ )
- Formate offers a small bridging ligand to support magnetic interactions.

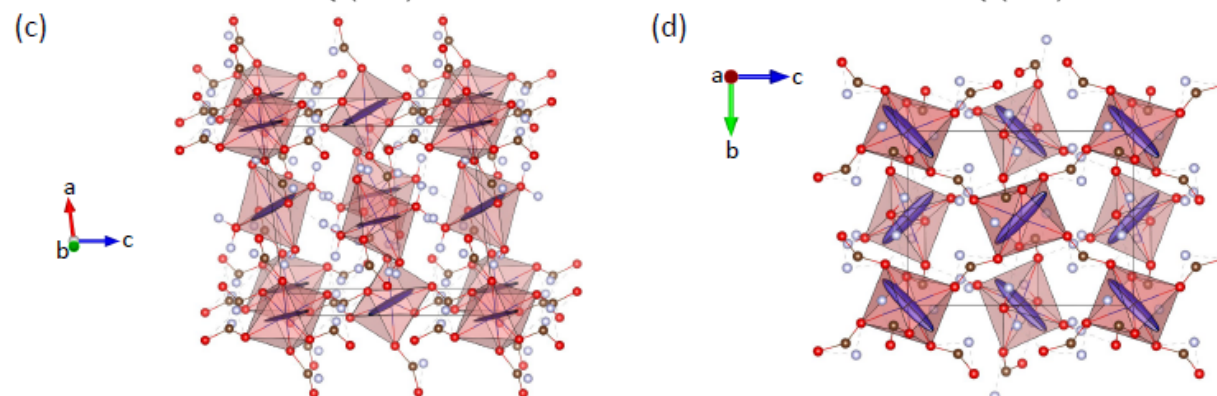


# Local susceptibility in 2D MOF $\text{Co}(\text{DCOO})_2 \cdot 2\text{D}_2\text{O}$

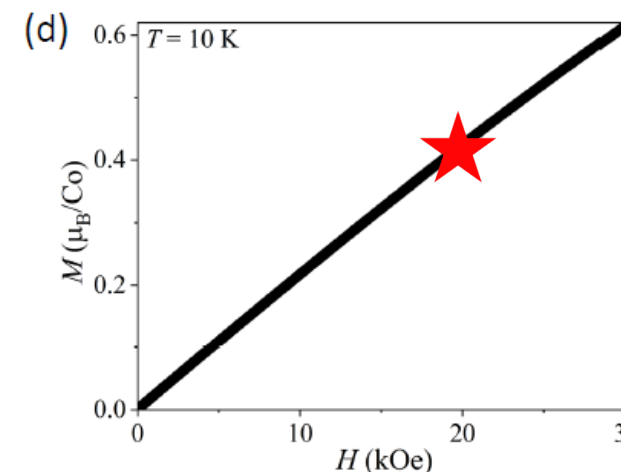


Flipping difference (ON-OFF)

$$\Delta = I_+ - I_- = 4\mathbf{P}_i \cdot (\mathbf{F}_N * \mathbf{F}_{M\perp})$$



$$\begin{pmatrix} 0.053(35) & 0.088(48) & 0.071(34) \\ 0.088(48) & 0.257(34) & 0.165(36) \\ 0.071(34) & 0.165(36) & 0.237(33) \end{pmatrix} \mu_B/\text{Co}$$



- Averaged Magnetization from PNPD at 10K, 2 T is  $0.36\mu_B$

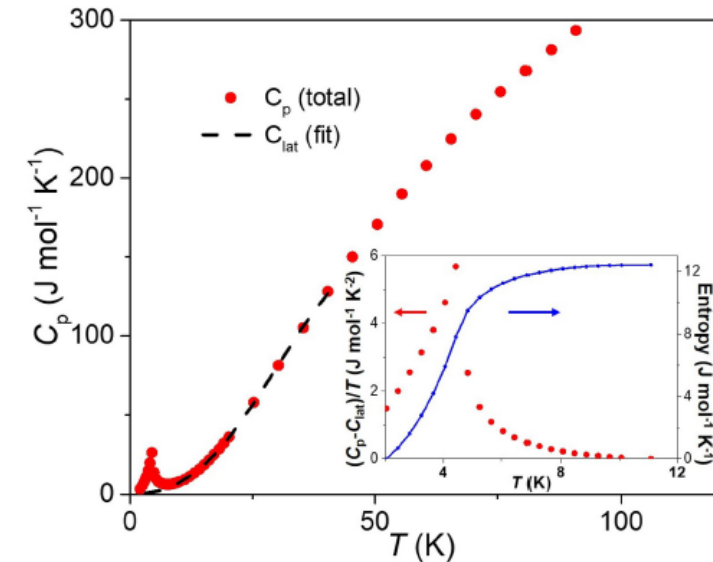
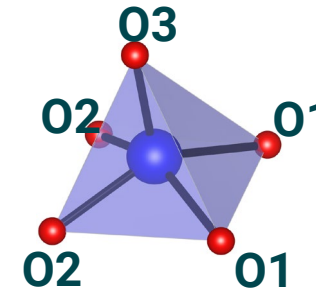
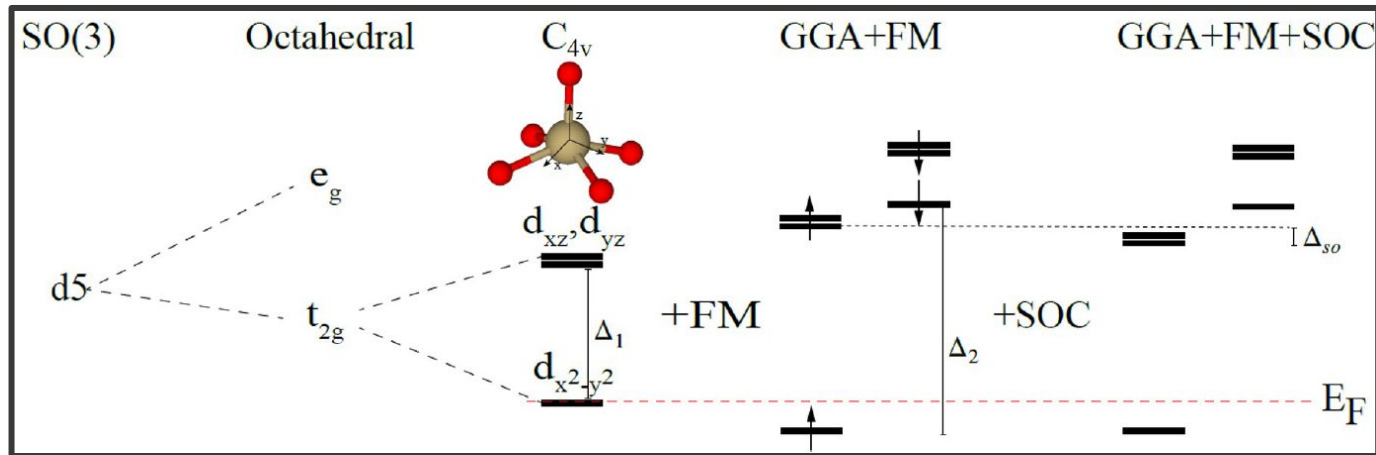
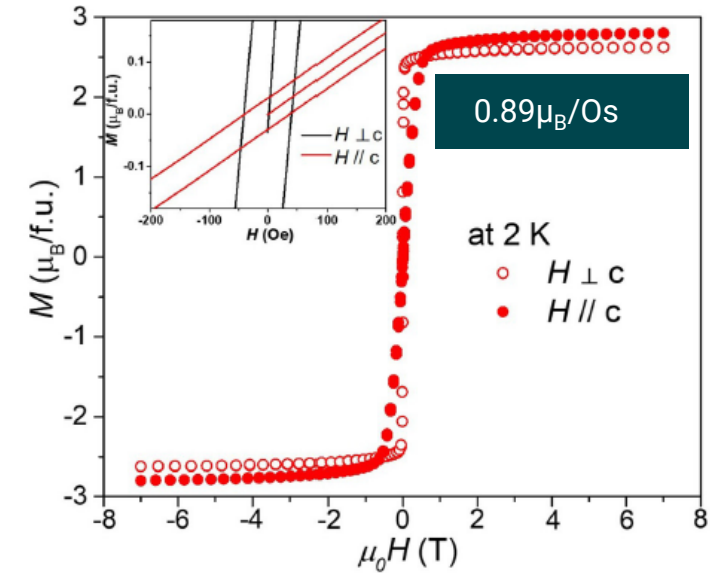
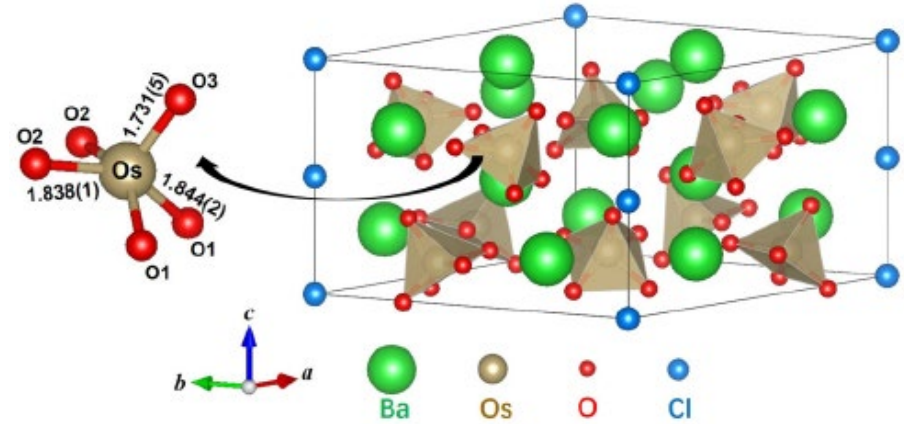
# Low moment magnetism in $5d^1$ osmate material

# Ba<sub>5</sub>(OsO<sub>5</sub>)<sub>3</sub>Cl: 5d<sup>1</sup> apatite

- Space group  $P6_3cm$  (#185)
- OsO<sub>5</sub> tetragonal pyramids
- $T_c = 5$  K
- $\Theta_W = 8$  K (FM)
- Ferroelectric order below 150 K

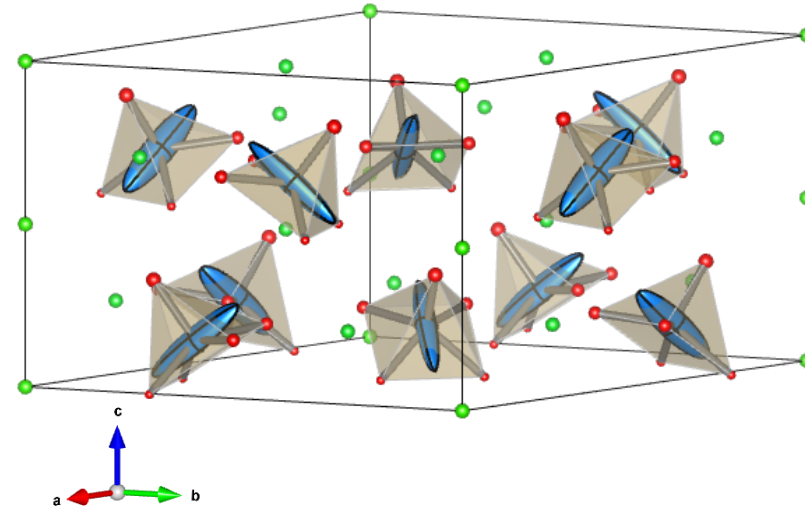
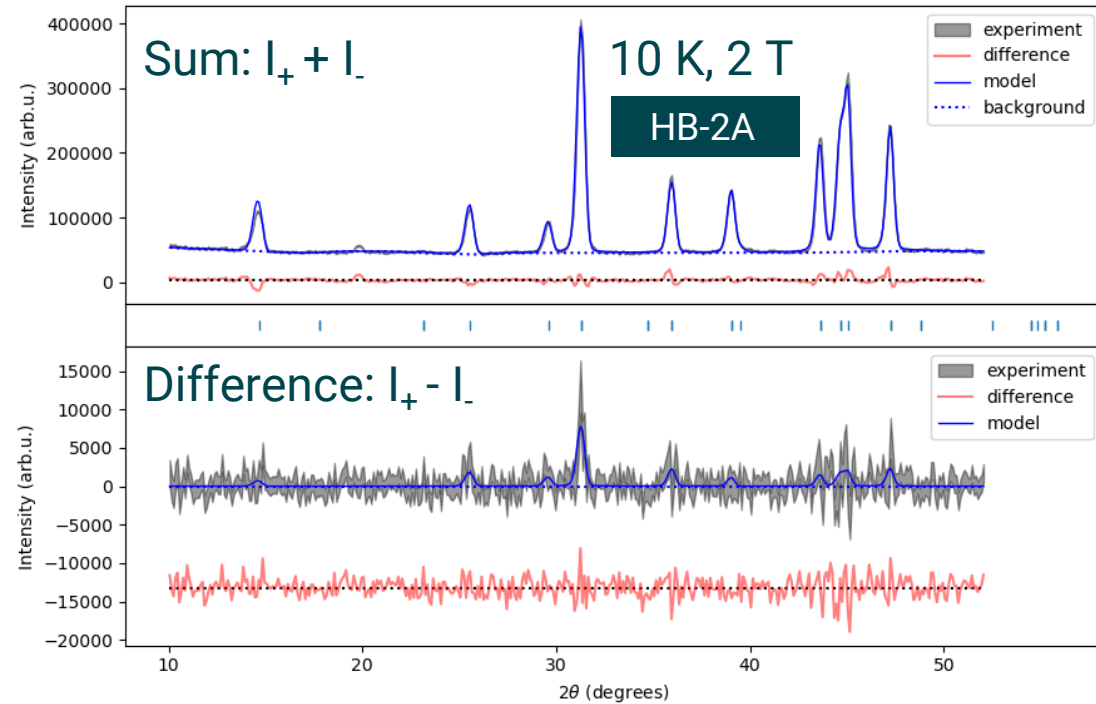
C. Tian *et al.*, Physical Review Materials 5, 114402 (2021)

- $S=1/2$  moment of  $1\mu_B/\text{Os}^{7+}$
- Reduced role of SOC

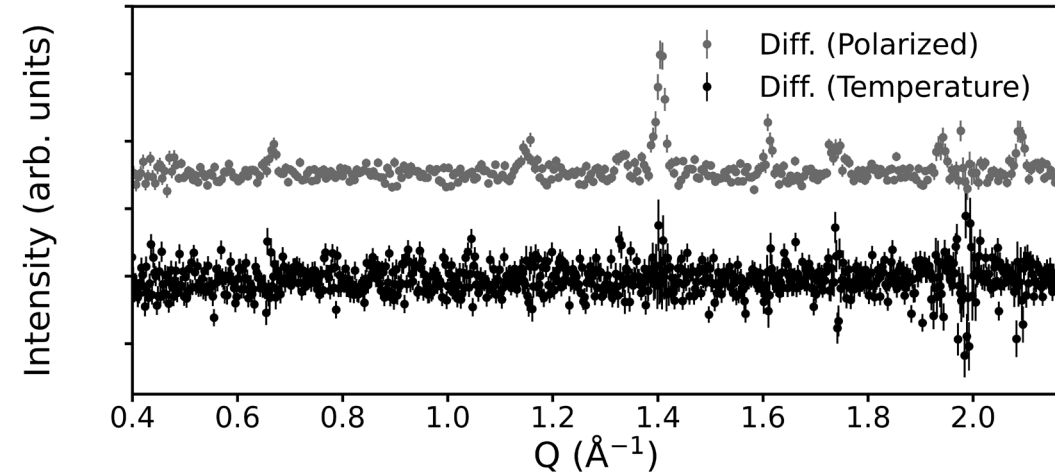


# Half-polarized Neutron Powder Diffraction (pNPD): $\text{Ba}_5(\text{OsO}_5)_3\text{Cl}$

No signal with standard unpolarized neutron diffraction



$$\chi = \begin{pmatrix} 0.14(4) & -0.021 & 0.26(3) \\ -0.021 & 0.12(3) & -0.148 \\ 0.26(3) & 0.148 & 0.05(3) \end{pmatrix}$$



Data analysis with CrysPy

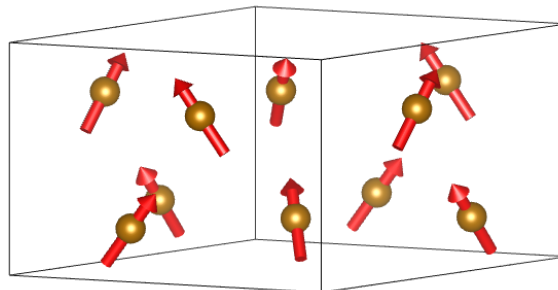
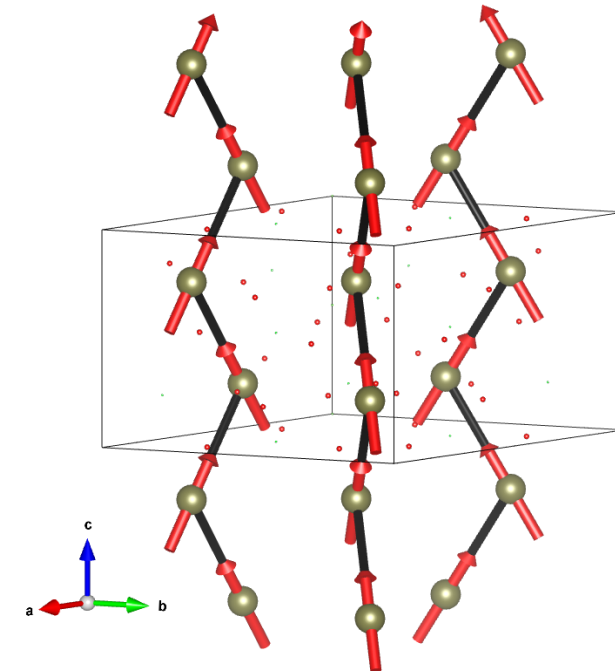
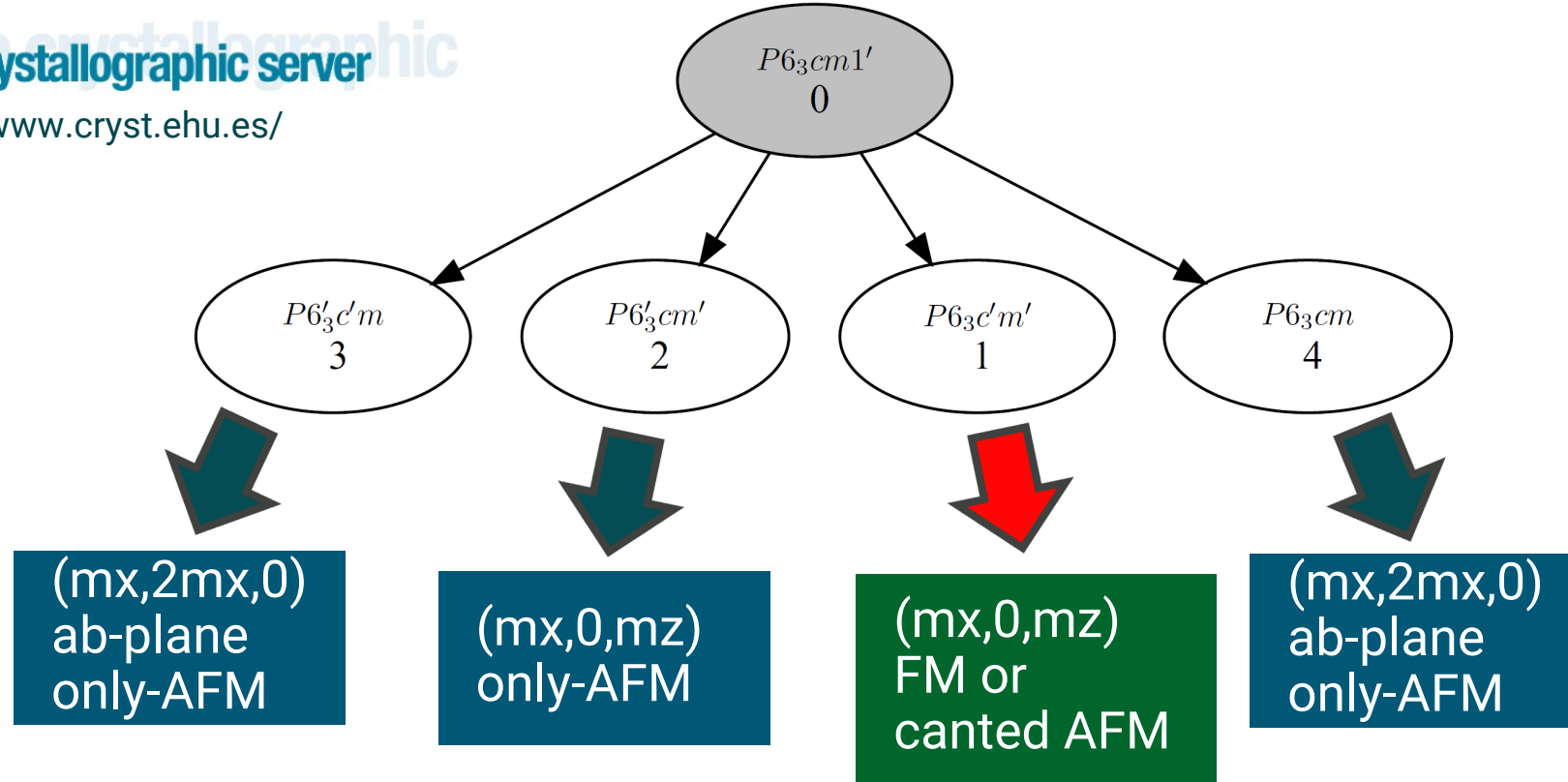


<https://sites.google.com/view/crspy>

# Symmetry allowed magnetic structures for $\text{Ba}_5(\text{OsO}_5)_3\text{Cl}$

bilbao crystallographic server

<https://www.cryst.ehu.es/>



$P6_3c'm'$   
FM for moments along **c**-axis.  
**a**-direction is AFM.  
→ Either FM or canted FM (with net moment)

# Conclusion

- HB-2A (POWDER) is fully available for polarized experiments to users.
  - Offers high resolution and flux on powder samples.
- Successful measurements on a variety of science cases:
  - Rare earth based frustrated magnets
  - Anisotropy, g-tensor and exchange interactions
  - Weak moments.  $0.2 \mu_B$  observed, lower possible.
  - $S=1/2$  is “easy”
  - Weak ferromagnetic signals
  - Hydrogen containing materials measured
  - Small samples