Structural and magnetic disorder in defect spin ice $Ho_2Ti_{1.5}Sc_{0.5}O_{6.75}$

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ADD 2022-21/10/22

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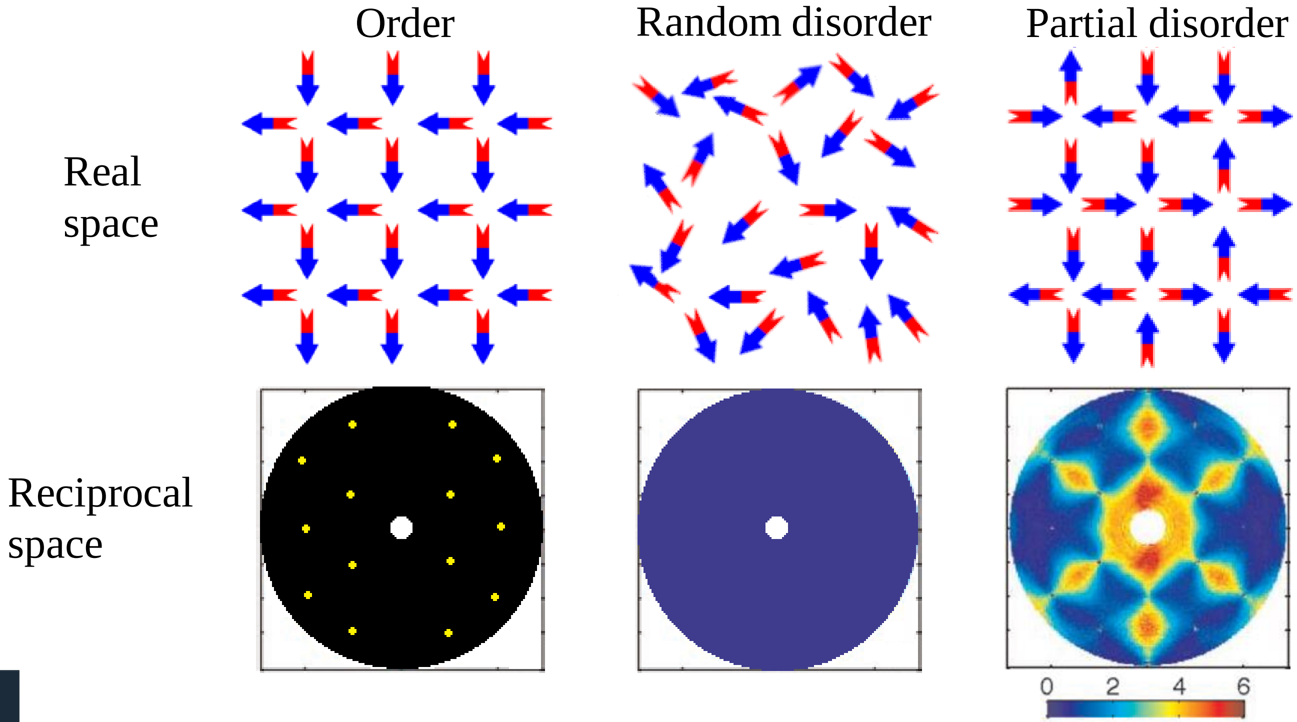
Content

- Diffuse scattering
- Frustration in magnetism
  - Spin liquids
  - Spin ice
- Polarisation analysis
  - D7
- $Ho_2Ti_2O_7$
- $Ho_2Ti_{1.5}Sc_{0.5}O_{6.75}$
  - Nuclear
  - CEF
  - Magnetism

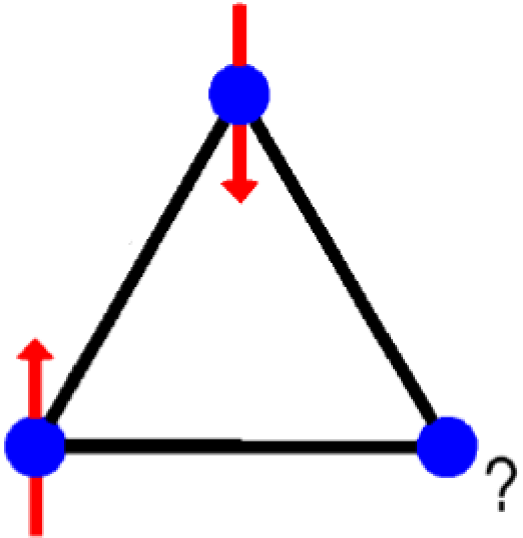
Diffuse scattering

-Example: Magnetic only



Frustration in magnetism

2D triangular antiferromagnet

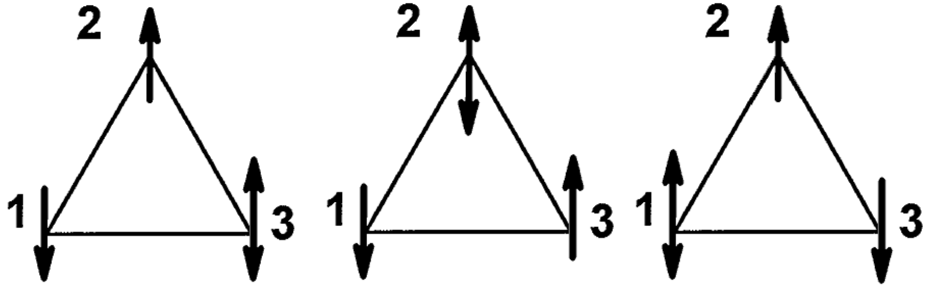


- Local pair particle-particle interactions are in a conflict.
- Highly degenerate ground state.
- Example: Spin liquids.

A.A. Zvyagin, Low Temp. Phys. 39, 901-22 (2013).

Frustration in magnetism

2D triangular antiferromagnet



- Local pair particle-particle interactions are in a conflict.

- Highly degenerate ground state.

- Example: Spin liquids.

M. F. Collins et al., *Can. J. Phys.* 75 (1997) 605

Spin liquid phase

Spin liquids: Spins do not exhibit long range order.

Quantum spin liquid (QSL):

- Small spin (S~1/2).
- Spin fluctuate even at T=0K.
- Long range entanglement.

Classical spin liquid (CSL):

- Large spin (S>>1/2).
- Spin freeze at low T.
- Particles in localised states.

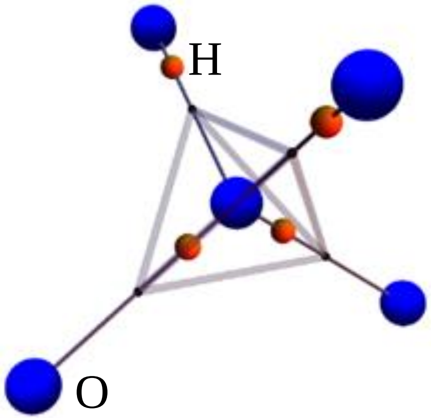
Sub-family: Spin ice

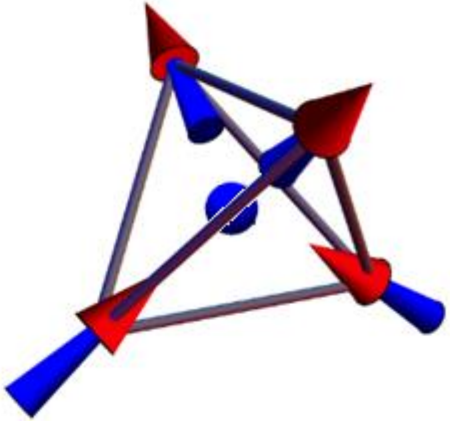
Balents, L,. *Nature* **464,** 199–208 (2010).

Spin ice phase

Spin ice:

- Obey ice rule (two-in-two-out).
- Magnetic ions have doublet ground state.
- Pinch points.





C. Castelnovo, et al., *Annu. Rev. Conden. Ma. P.*, **3** 35-55 (2012).

Spin ice phase

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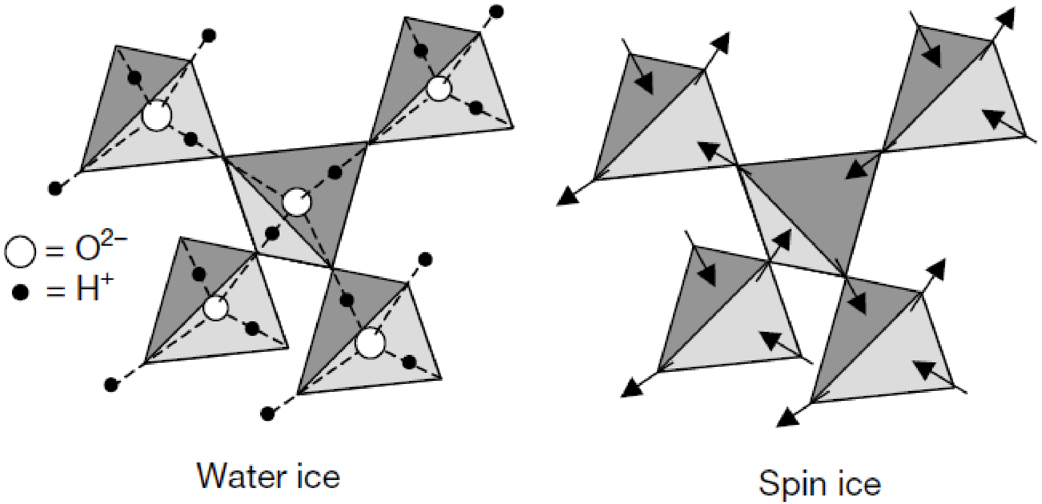
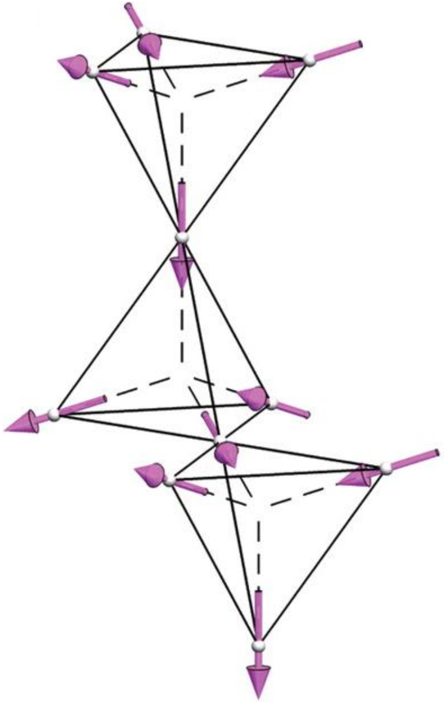
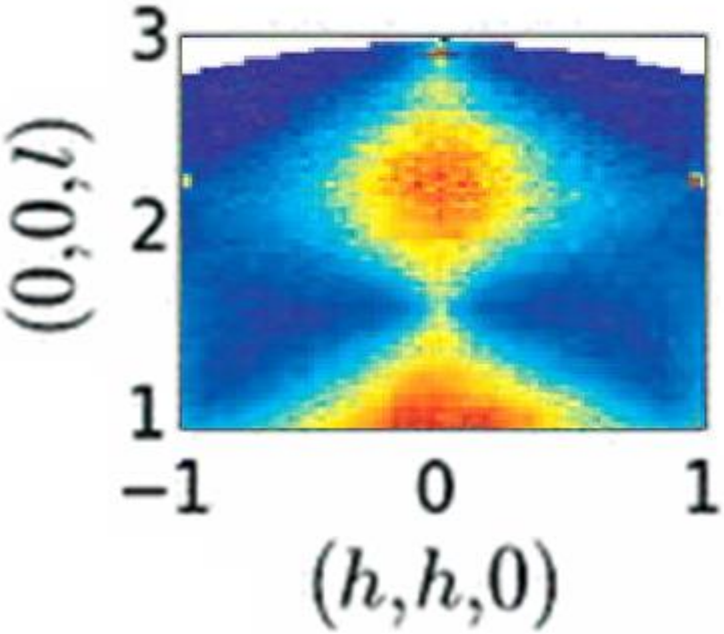


J. Snyder et al., *Nature* **413**, 48-51 (2001)

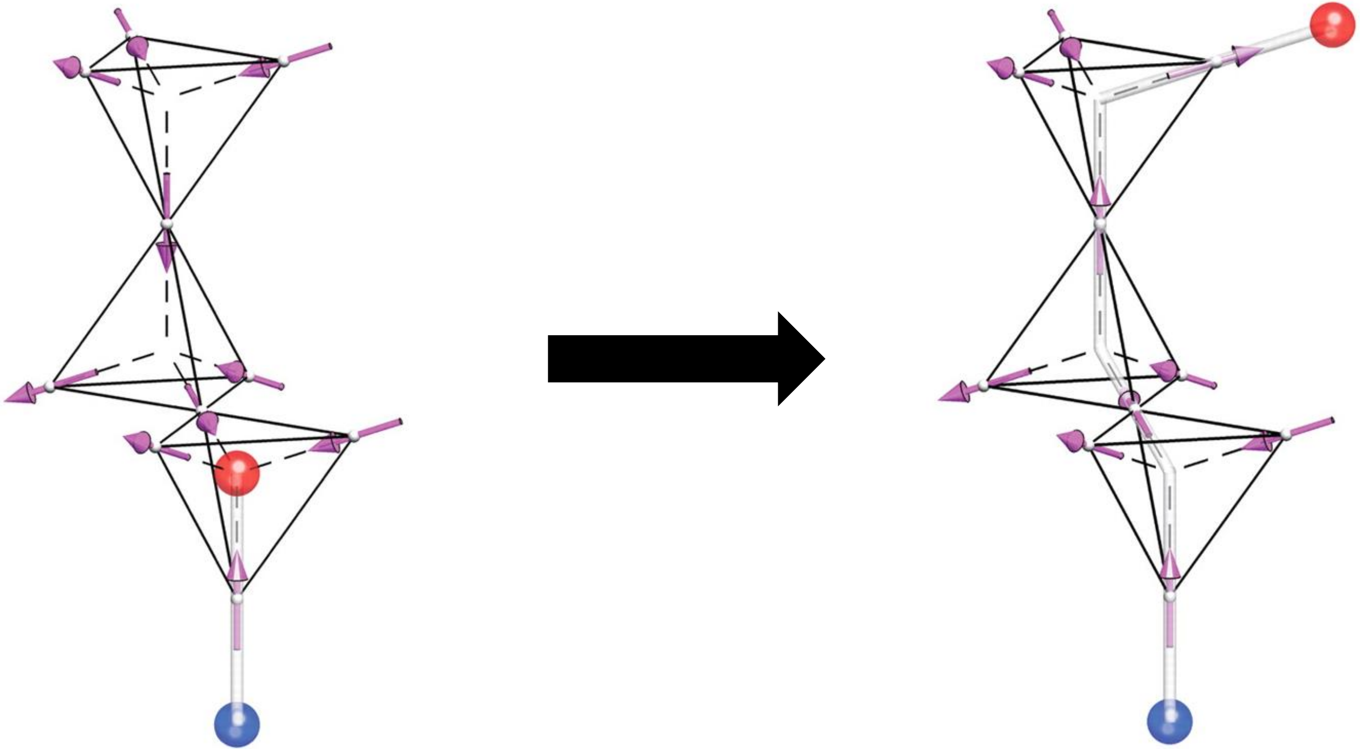
Spin ice phase





T. Fennell, et al. *Science* **326**, 5951 (2009)

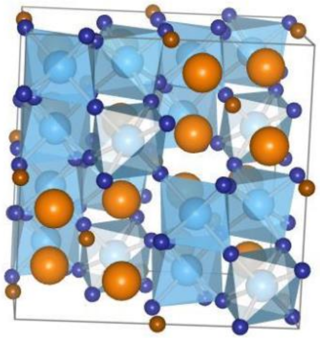
Spin ice phase



T. Fennell, et al. *Science* **326**, 5951 (2009)

Spin ice in pyrochlores

Pyrochlores $A_2B_2O_7$



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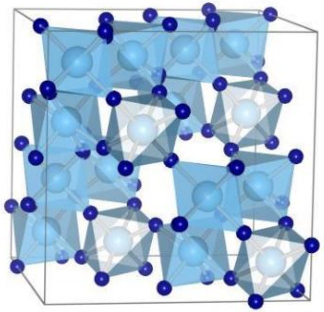

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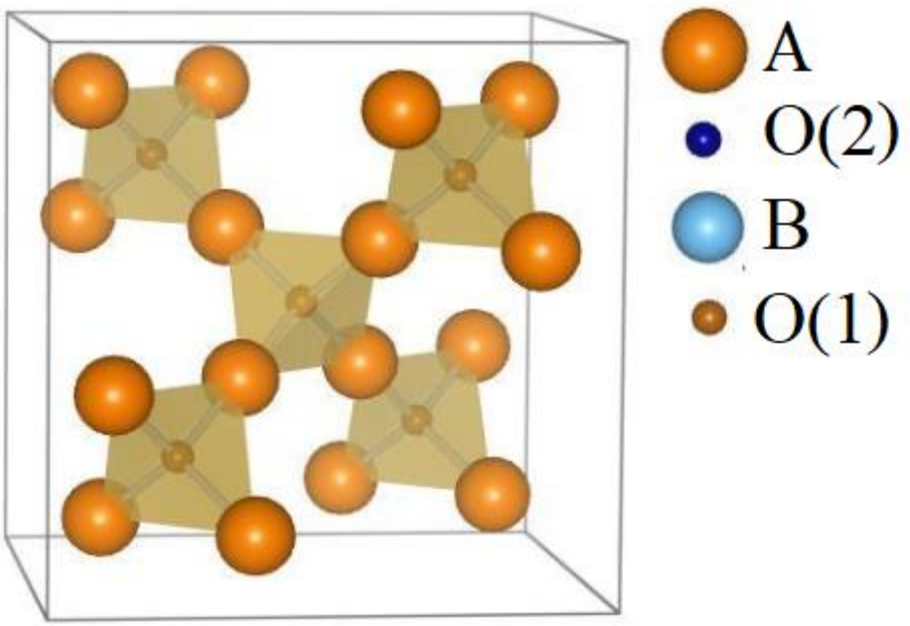
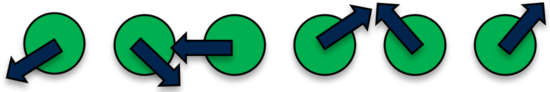


Subramanian, M.A.; Aravamudan, G.; Subba Rao, G.V..
Prog. Solid St. Chem. 1983, 15, 55–143

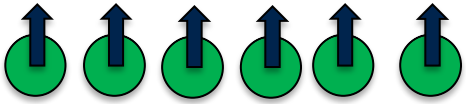
Polarisation analysis

Unpolarised



Nuclear + Magnetic

Polarised



Nuclear

Magnetic

$|\uparrow\rangle \longrightarrow |\uparrow\rangle$ Non-spin-flip

$|\downarrow\rangle \longrightarrow |\uparrow\rangle$ Spin-flip

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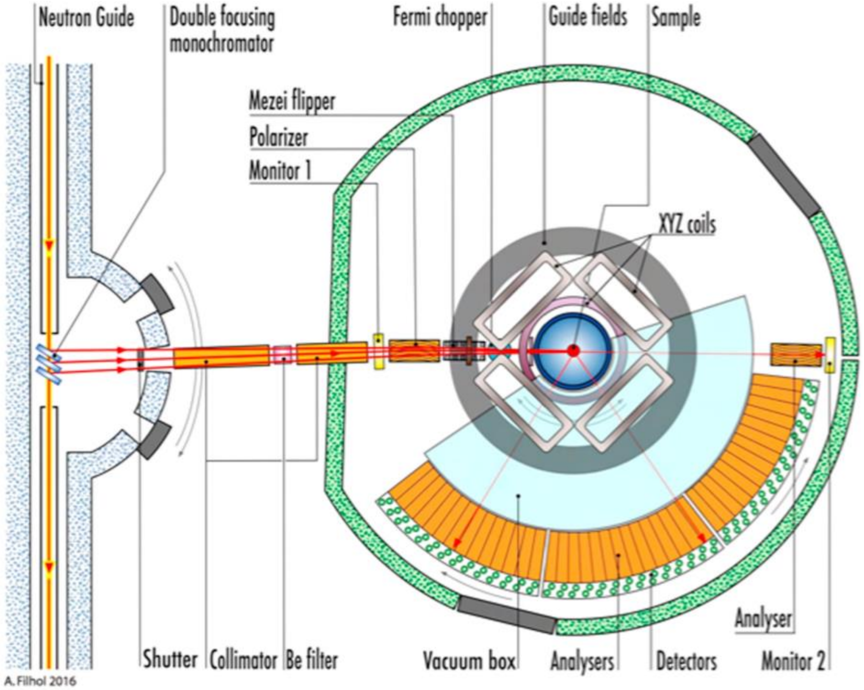
D7

- Diffuse scattering diffractometer.

- Neutrons are polarised (SF and NSF in each XYZ-direction).

$|\uparrow\rangle \longrightarrow |\uparrow\rangle$ Non-spin-flip

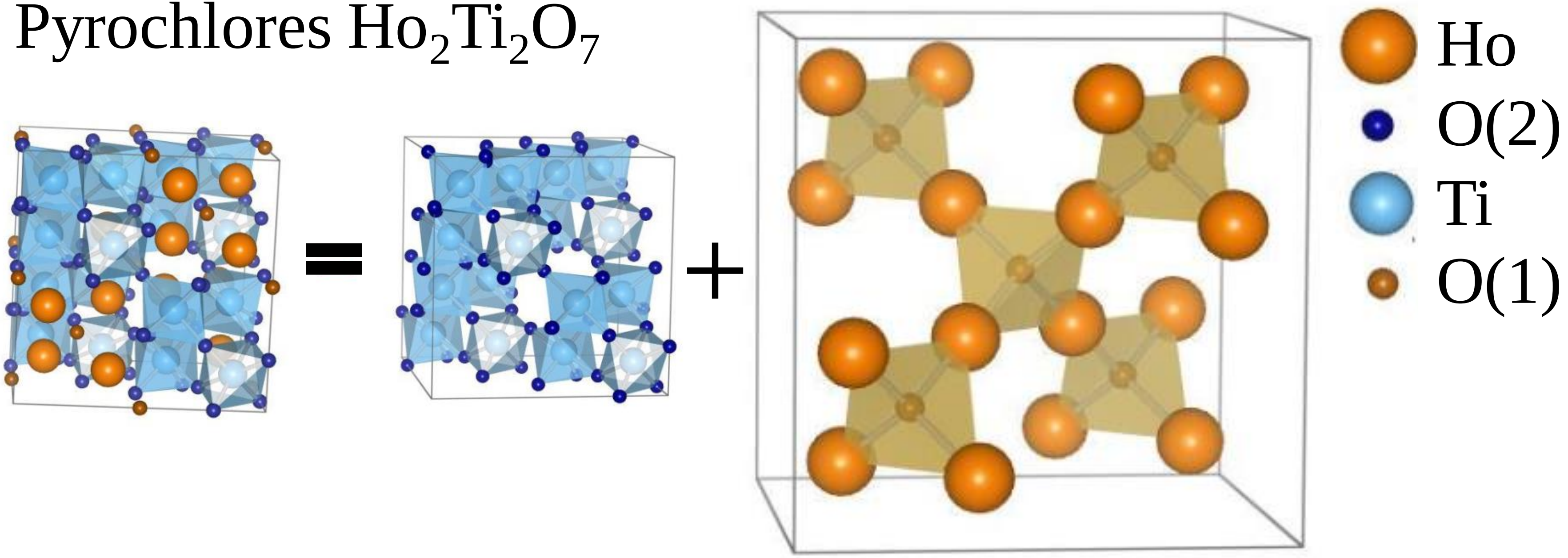
$|\downarrow\rangle \longrightarrow |\uparrow\rangle$ Spin-flip



T. Fennell et al., *Nucl. Inst. and Meth. Phys. Res. A* **857** 24 (2017)

$Ho_2Ti_2O_7$ as a spin ice

Pyrochlores $Ho_2Ti_2O_7$



$Ho_2Ti_{1.5}Sc_{0.5}O_{6.75}$

Ti charge = +4

Sc charge = +3

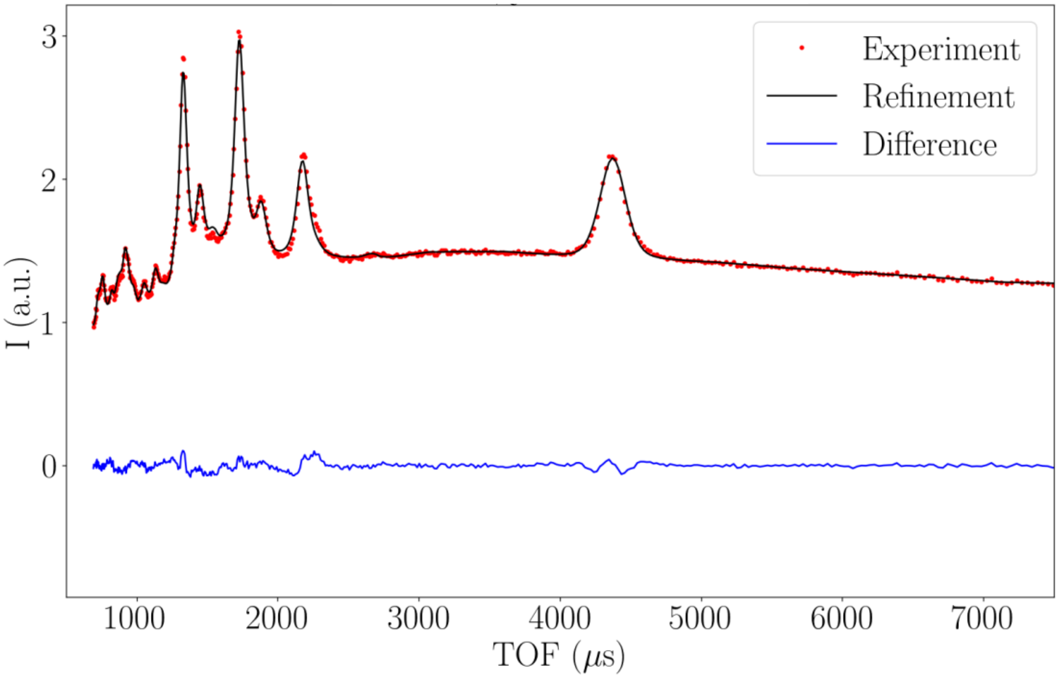
O charge = -2

Changing some Ti by Sc makes the sample more negative.

Charge compensating O vacancies.

Total scattering measurements on $Ho_2Ti_{1.5}Sc_{0.5}O_{6.75}$

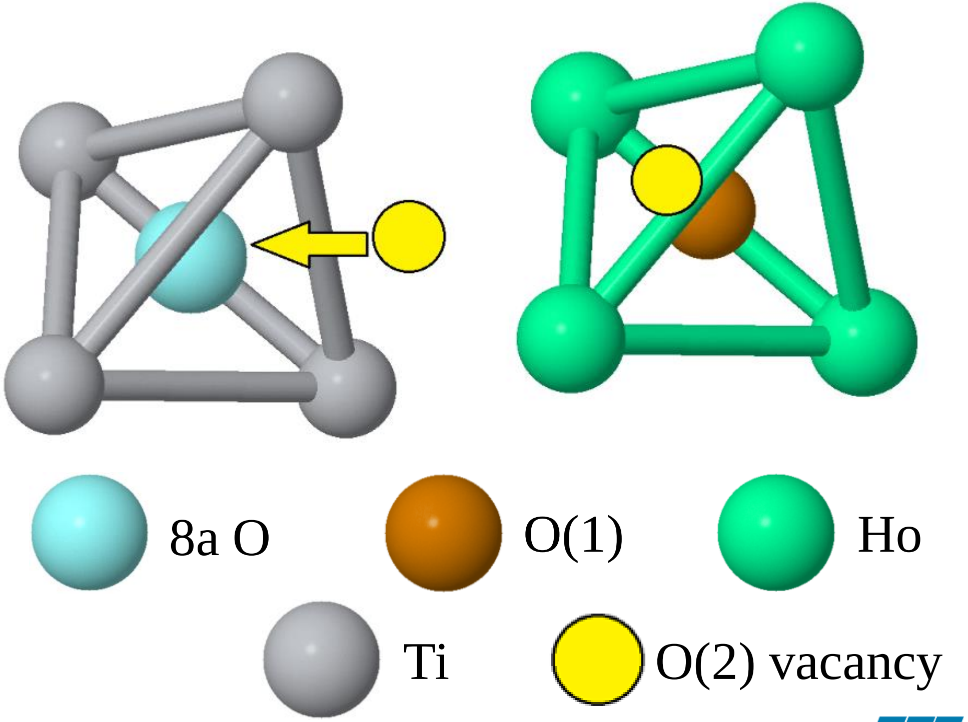
- Using POLARIS (ISIS)
- Bragg refinement
    - Pyrochlore structure
    - O(2) vacancies: 3.9±0.2%
    - O(2) displaced: 0.65±0.1%



Total scattering measurements on $Ho_2Ti_{1.5}Sc_{0.5}O_{6.75}$

Origin of disorder

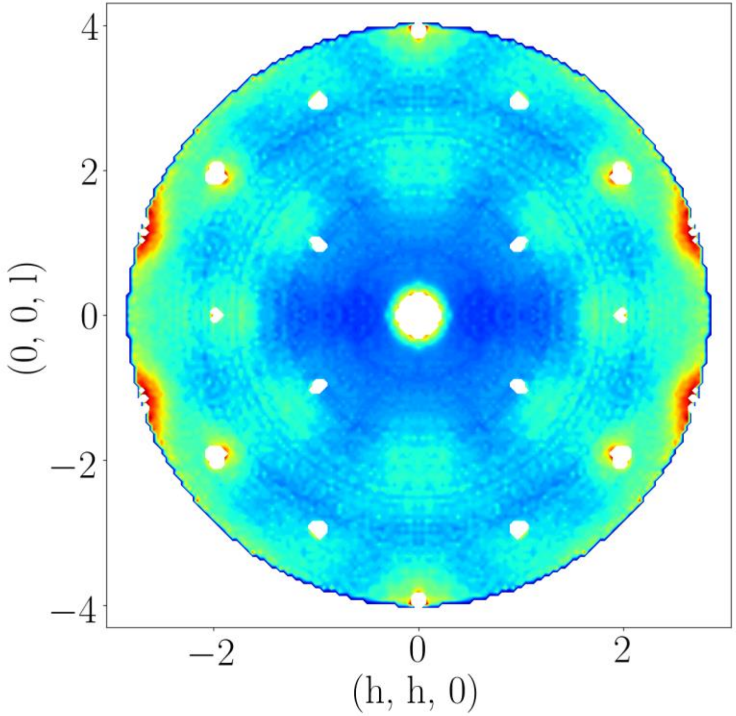
- O(2) vacancies 3.9±0.2%
- O(2) displaced: 0.65±0.1%



Diffuse scattering at low Q

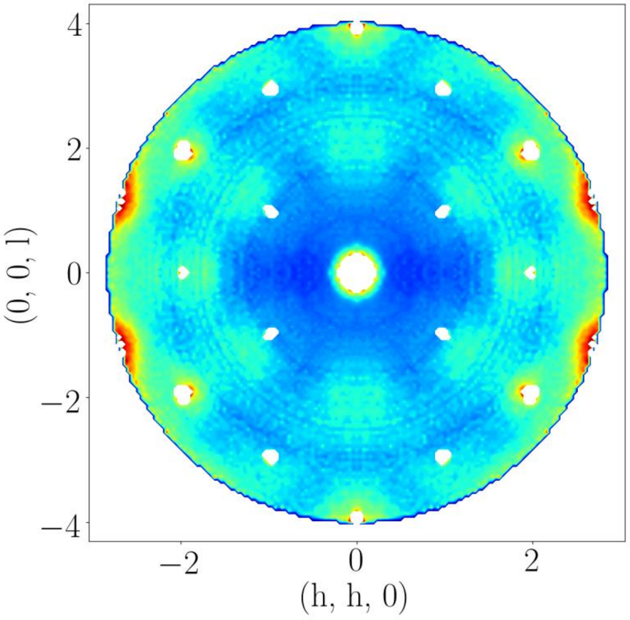
Results from D7 (ILL) – isolate structural diffuse using XYZ PA, access to low *Q*

Experimental

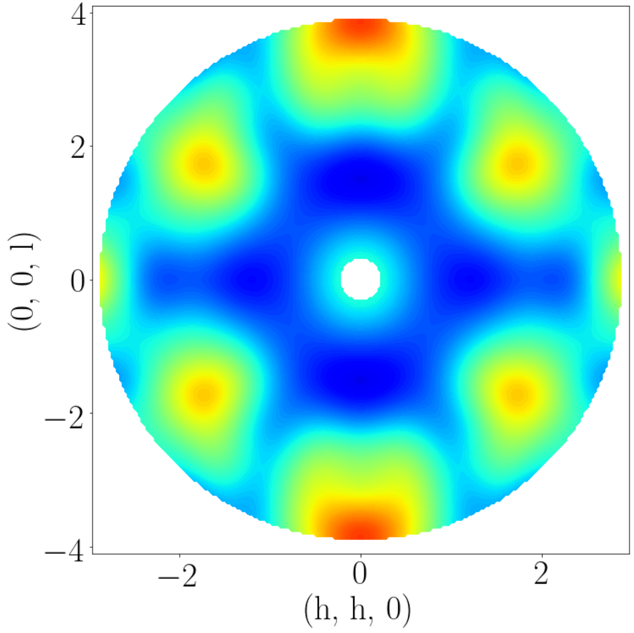


DFT calculations

Experimental

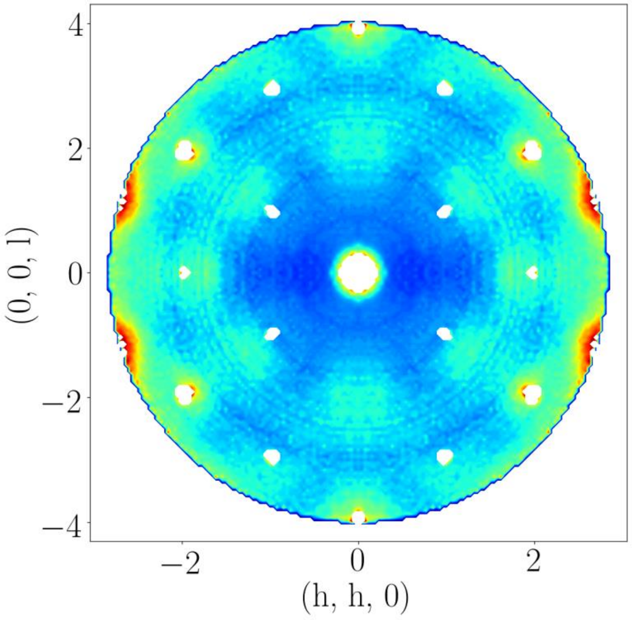


DFT with O(2) vacancy only

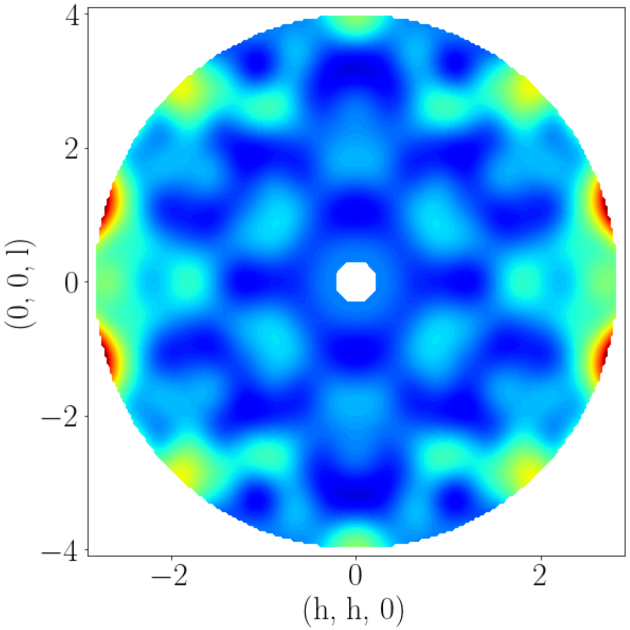


DFT calculations

Experimental

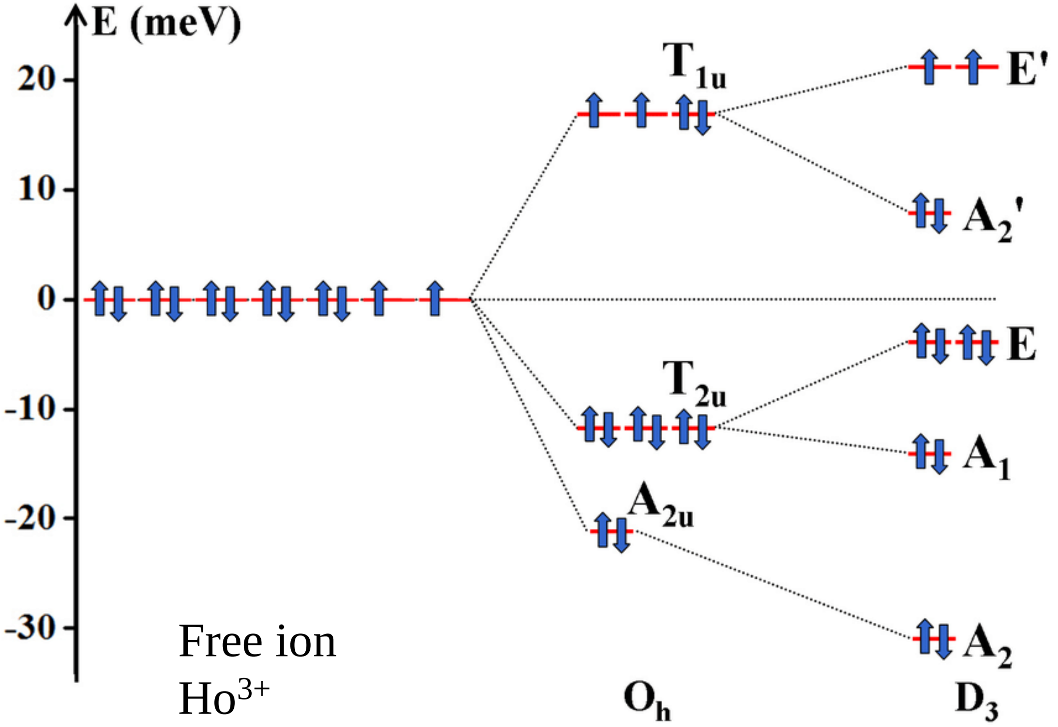


DFT with O(2) vacancy and O(2) displacement



Crystal Electric Field levels

- Further energy splitting
  - Caused by interactions between sites
  - Change the ground state of magnetic ions
  - Affects the spin direction

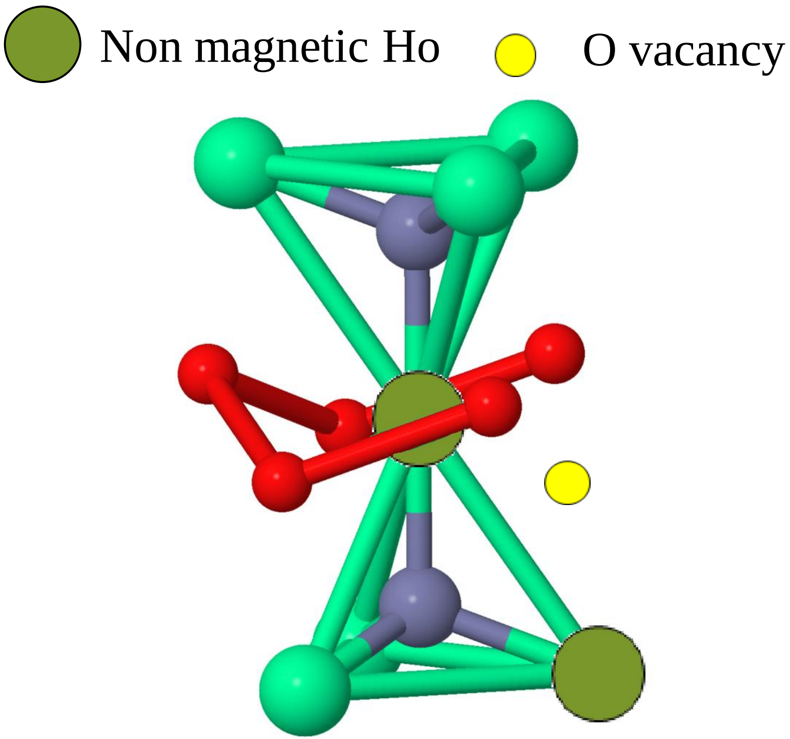


Ju, Meng et al. *J. Mater. Chem. C.*, 4 (2016)

Crystal Electric Field levels

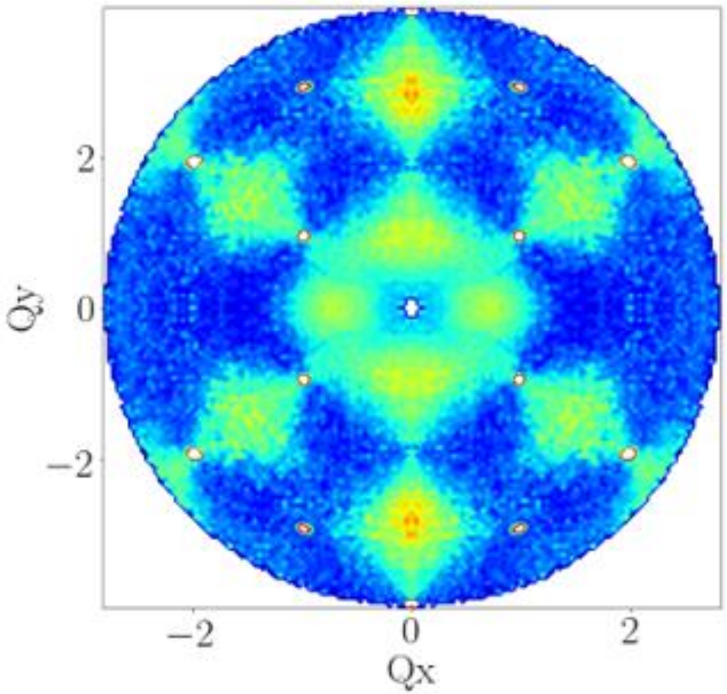
4.55% of O(2) ions removed.

25% of Ho ions non-magnetic.



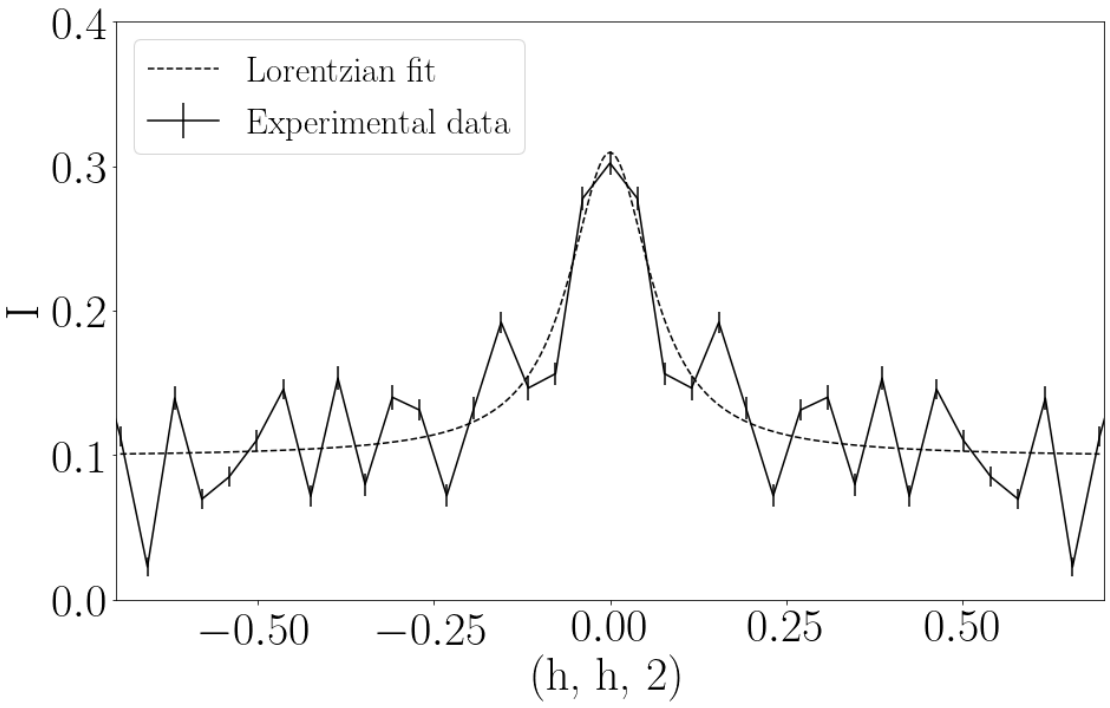
$Ho_2Ti_{1.5}Sc_{0.5}O_{6.75}$: Magnetic at 50mK

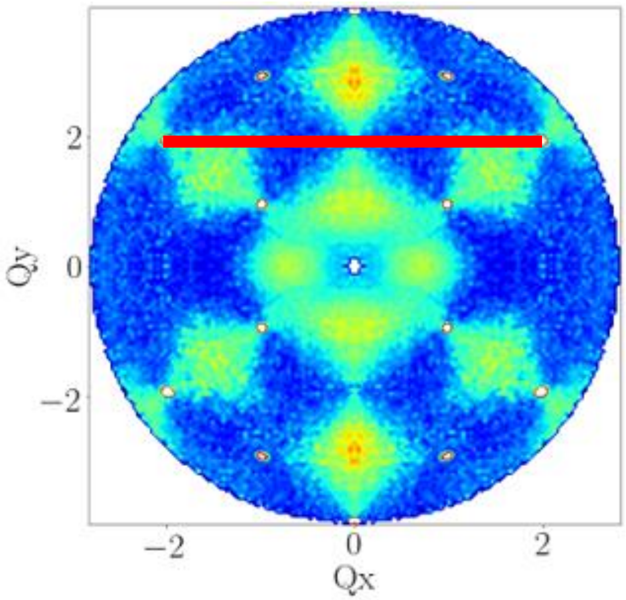
Experimental



Sen, A. & Moessner, R. Phys. Rev. Lett. 114, 247207 (2015)

$Ho_2Ti_{1.5}Sc_{0.5}O_{6.75}$ pinch point along (hh2)





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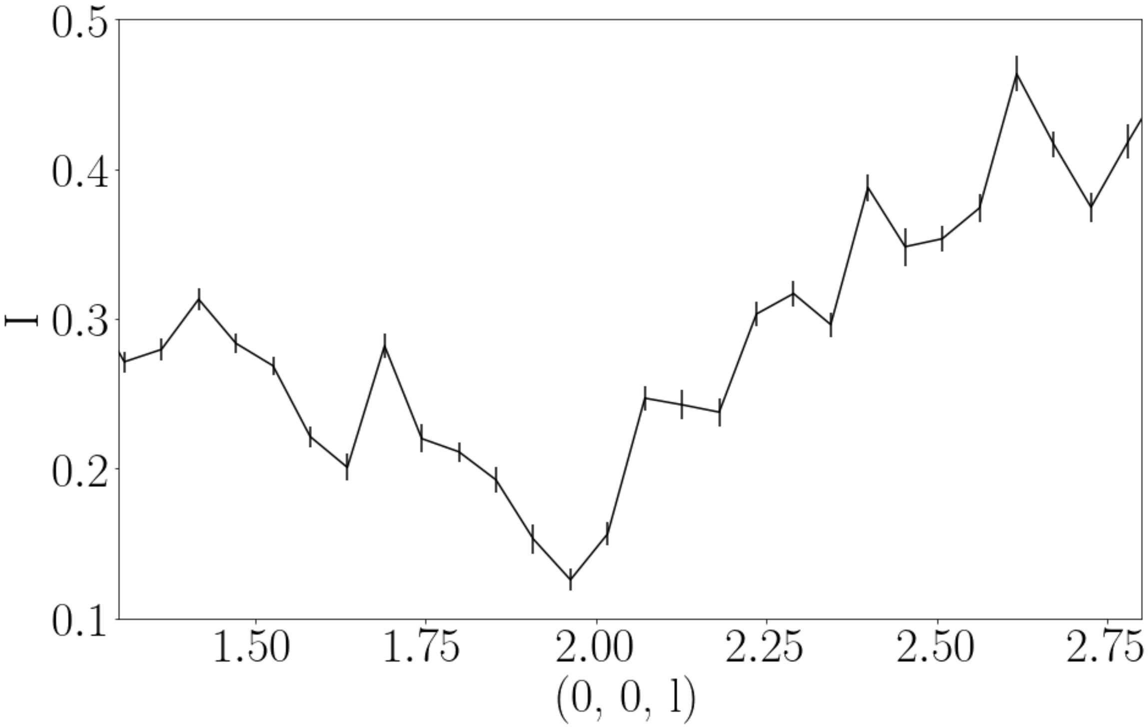

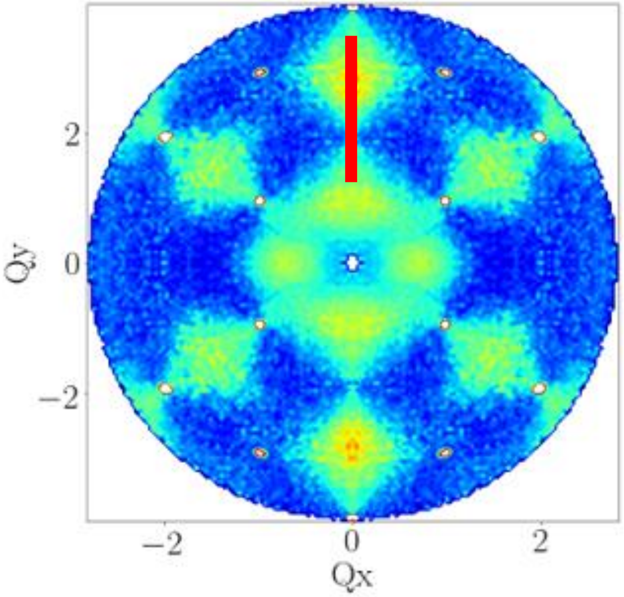

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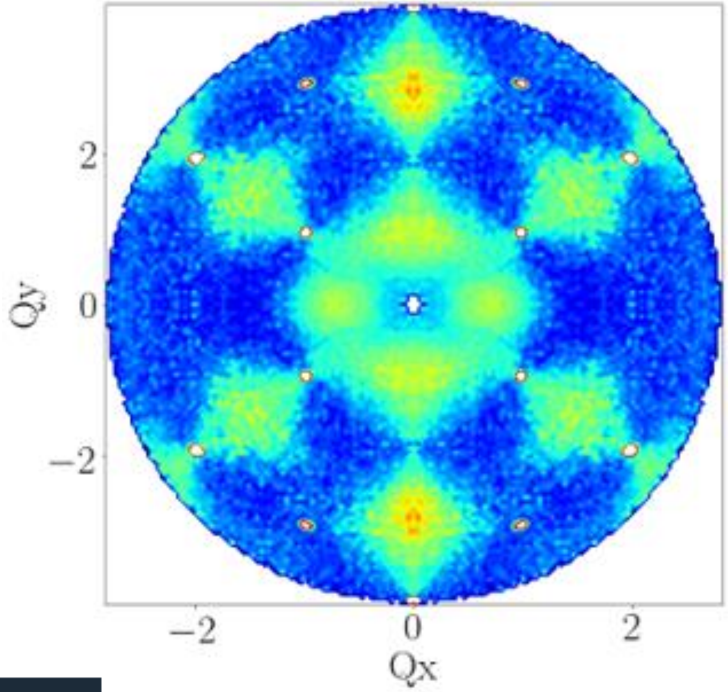
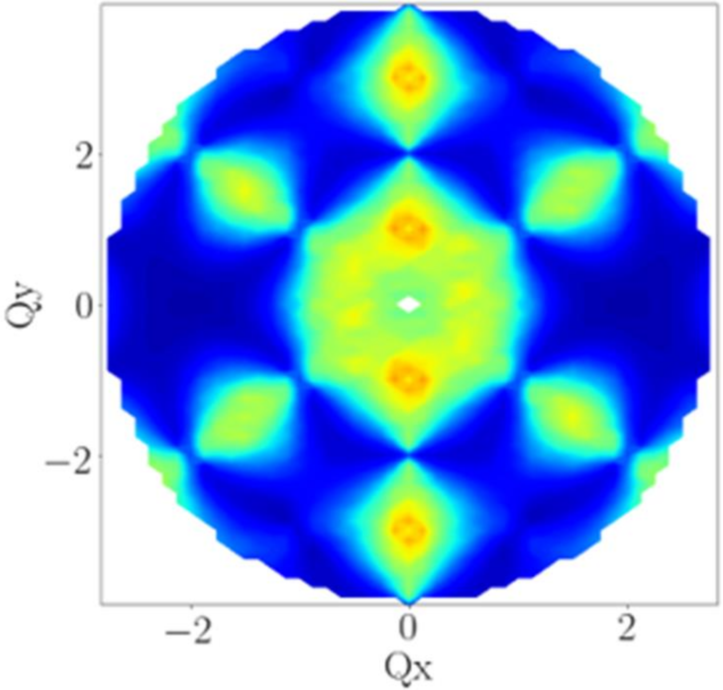


Theory



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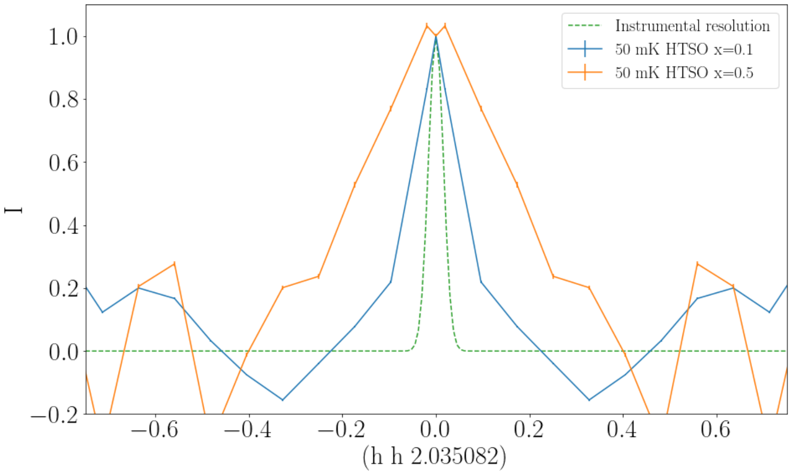

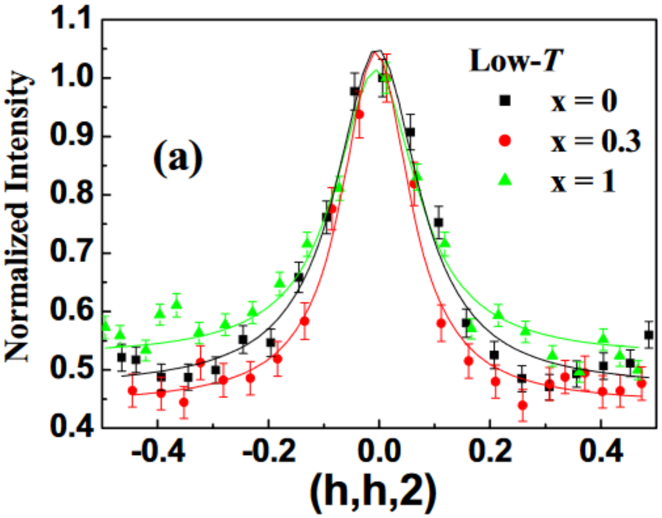

Sen, A. & Moessner, R. Phys. Rev. Lett. 114, 247207 (2015)

Conclusion

- XYZ-PA is essential to separate the structural and magnetic diffuse scattering.
- O(2) oxygen vacancies are the dominant defects $Ho_2Ti_{1.5}Sc_{0.5}O_{6.75}$.
- Find singlet ground states of Ho next to vacancies.
- Pinch points present with ghost spins.

Future outlook

- Broadening of pinch points

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