

APS March Meeting 2020, F46 Pyrochlores I

Magnetism of classical pyrochlore antiferromagnet $\text{Na}_3\text{Mn}(\text{CO}_3)_2\text{Cl}$

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K. Nawa et al., Phys. Rev. B, 98, 144426 (2018).

Ground state of pyrochlore antiferromagnet

Classical pyrochlore antiferromagnet

An extensive degeneracy in ground states

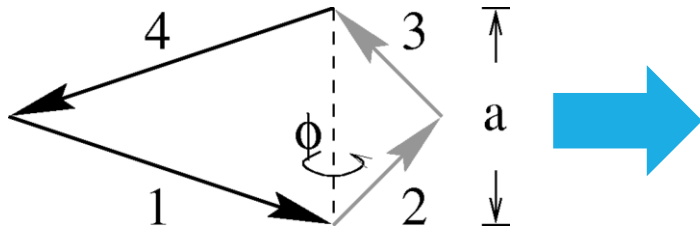


exhibit neither long-range magnetic order nor a spin-glass transition

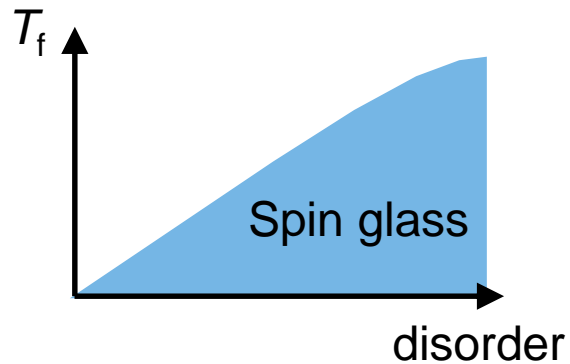
J. N. Reimers, PRB, **45**, 7287 (1992).

R. Moessner and J. T. Chalker, PRL, **80**, 2929 (1998);

PRB, **58**, 12049 (1998).

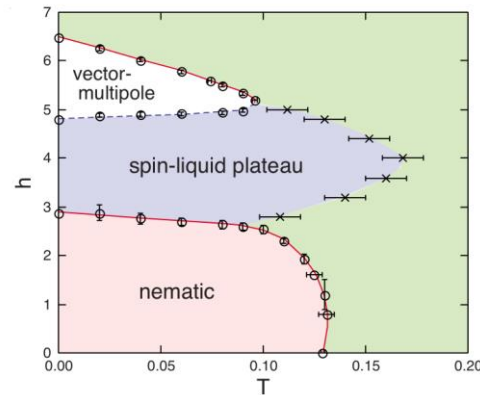
Macroscopic degeneracy can be lifted by...

Bond disorder



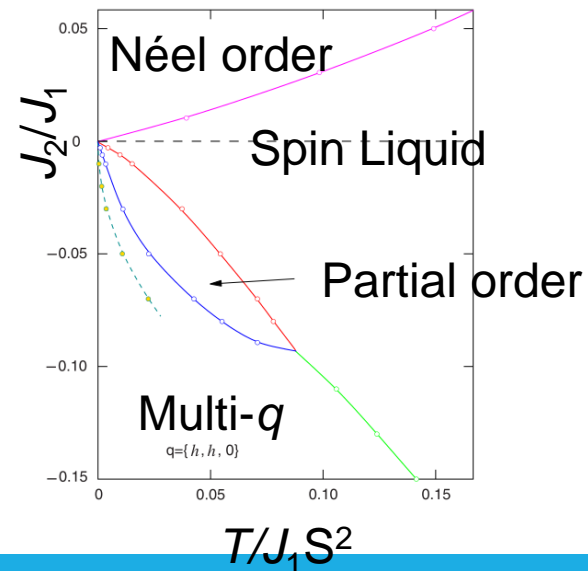
T. E. Saunders and J. T. Chalker, PRL **98**, 157201 (2007).

Biquadratic interactions

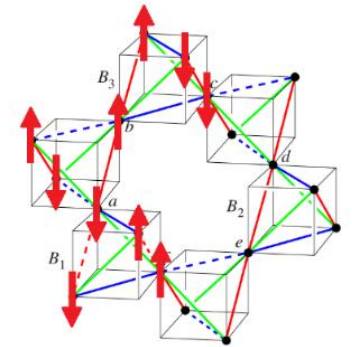


N. Shannon et al, PRB **81**, 184409 (2010).

Second/third neighbor interactions



Partial order: 2-up-2-down in a single tetrahedron



G. -W. Chern et al, PRB **78**, 144418 (2008).
T. Okubo et al., PRB **84**, 144432 (2011).

Pyrochlore network in $\text{Na}_3 T(\text{CO}_3)_2\text{Cl}$

Classical pyrochlore antiferromagnet

cf. $3d^5$, $S = 5/2$

FeF_3 : all-in-all-out order ($T_N \sim 15$ K)

$\text{Mn}_2\text{Sb}_2\text{O}_7$: spin glass ($T_f \sim 6$ K/41 K)

ZnFe_2O_4 : AF Order+SRO ($T_N = 11$ K)/SRO

$\text{NaSrMn}_2\text{F}_7$: spin glass ($T_f \sim 2.7$ K)



$\text{Na}_3 T(\text{CO}_3)_2\text{Cl}$ ($T = \text{Co}, \text{Mn}$)

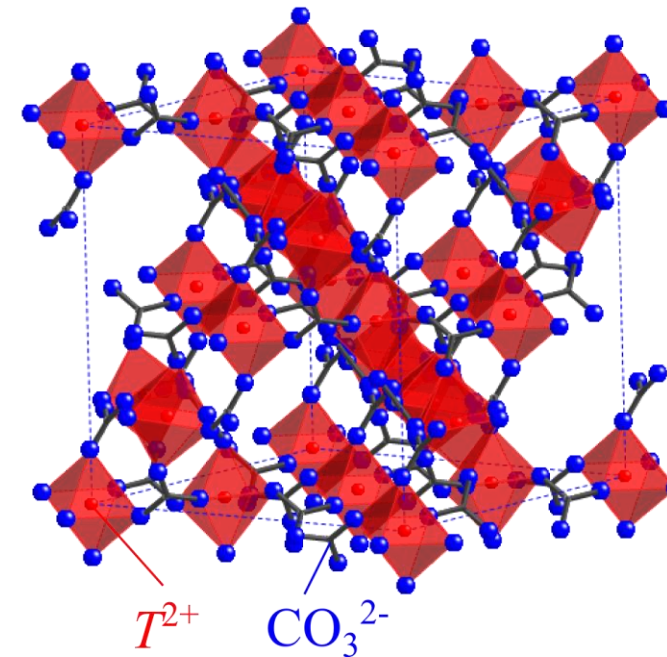
TO_6 octahedra are connected by CO_3^{2-} ions, forming pyrochlore lattice.

Successive phase transitions in $T = \text{Co}$

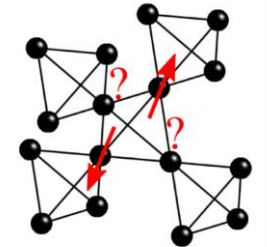
$T_a \sim 4.5$ K : spin-glass like transition

$T_N \sim 1.5$ K : all-in-all-out magnetic order

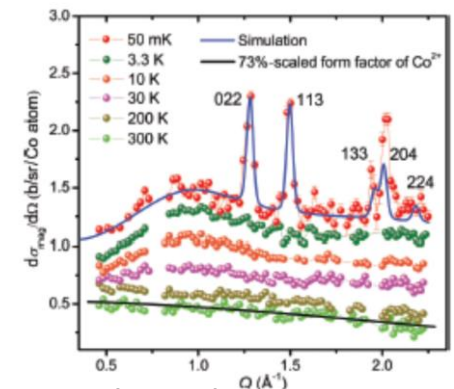
Any uniqueness from the crystal structure?



M. Leblanc et al., Rev. Chim. Miner. **22**, 107 (1985).
H. D. Zhou et al., JPCM **20**, 325201 (2008).
D. C. Peets et al., PRB, **94**, 174431 (2016).
W. Schiessl et al., PRB, **53**, 9143 (1996).
K. Kamazawa et al., PRB, **68**, 024412 (2003).
M. B. Sanders et al., JPCM, **29**, 045801 (2017).



Neutron diffraction for $T = \text{Co}$



Y. Zheng et al., Acta Cryst. **C67z**, i56 (2011).
F. Zhendong et al., Phys. Rev. B, **87**, 214406 (2013).

Experiments

- Sample synthesis

Solvothermal method

- Single crystal XRD experiments

Performed at KEK, BL-8A, $\lambda = 0.9999 \text{ \AA}$

- Magnetization measurements

MPMS (Quantum Design)

Low-temperature probe[†]

(adiabatic-demagnetization refrigerator)

Pulse-field magnetization at IMR

- Heat capacity measurements

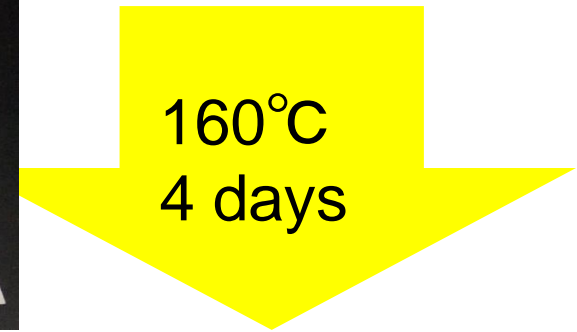
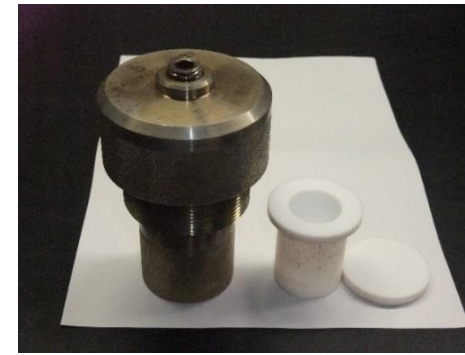
PPMS (Quantum Design)

- Powder neutron diffraction experiments

Performed at ANSTO, ECHIDNA

$\lambda = 2.4395 \text{ \AA}$

- $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$
- Na_2CO_3 , NaHCO_3
- 1,10-phenanthroline monohydrate
- Ethanol, pure water

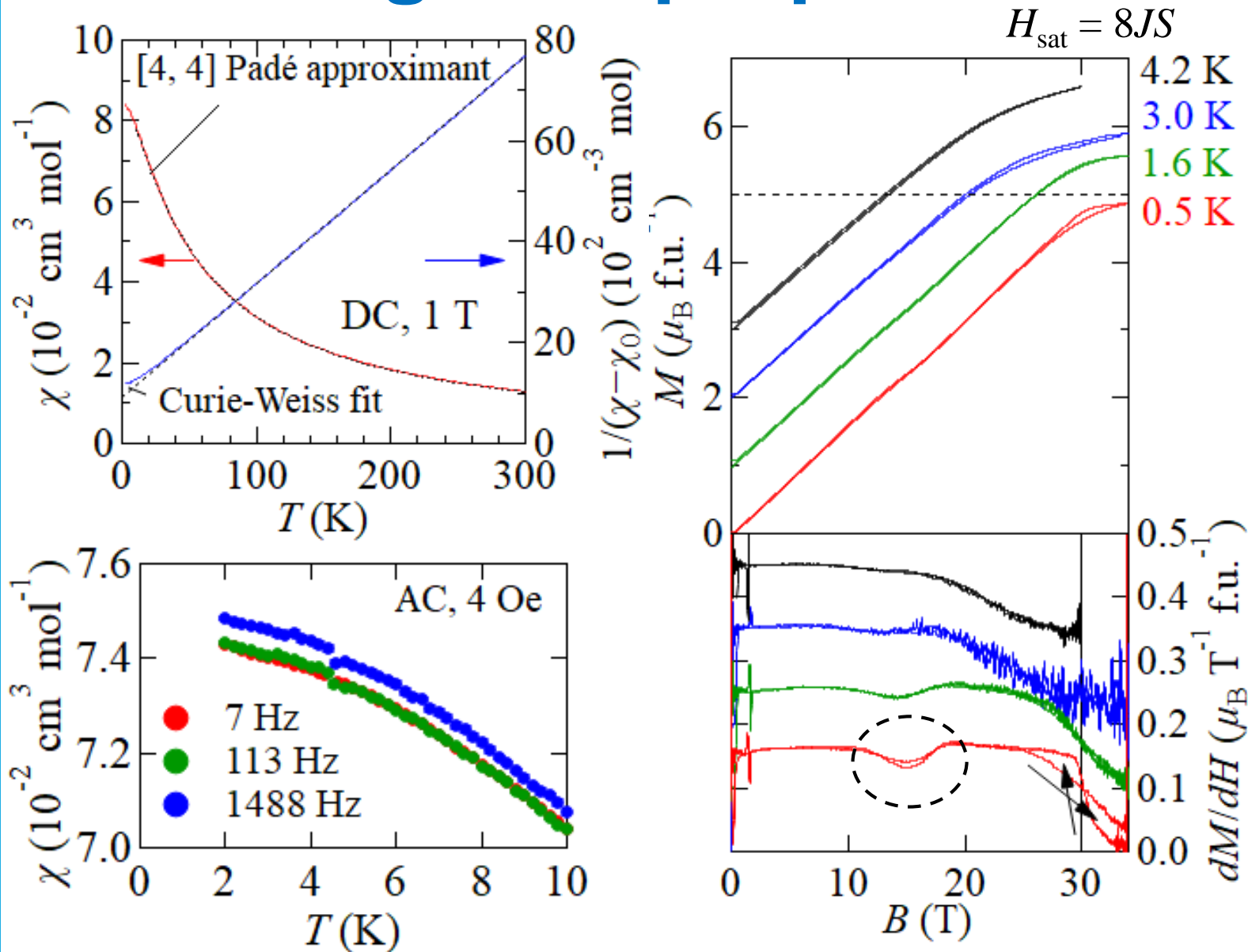


Poly
(Crystal size is small)



[†]T. J. Sato et al., Rev. Sci. Instrum., **87**, 123905 (2016).

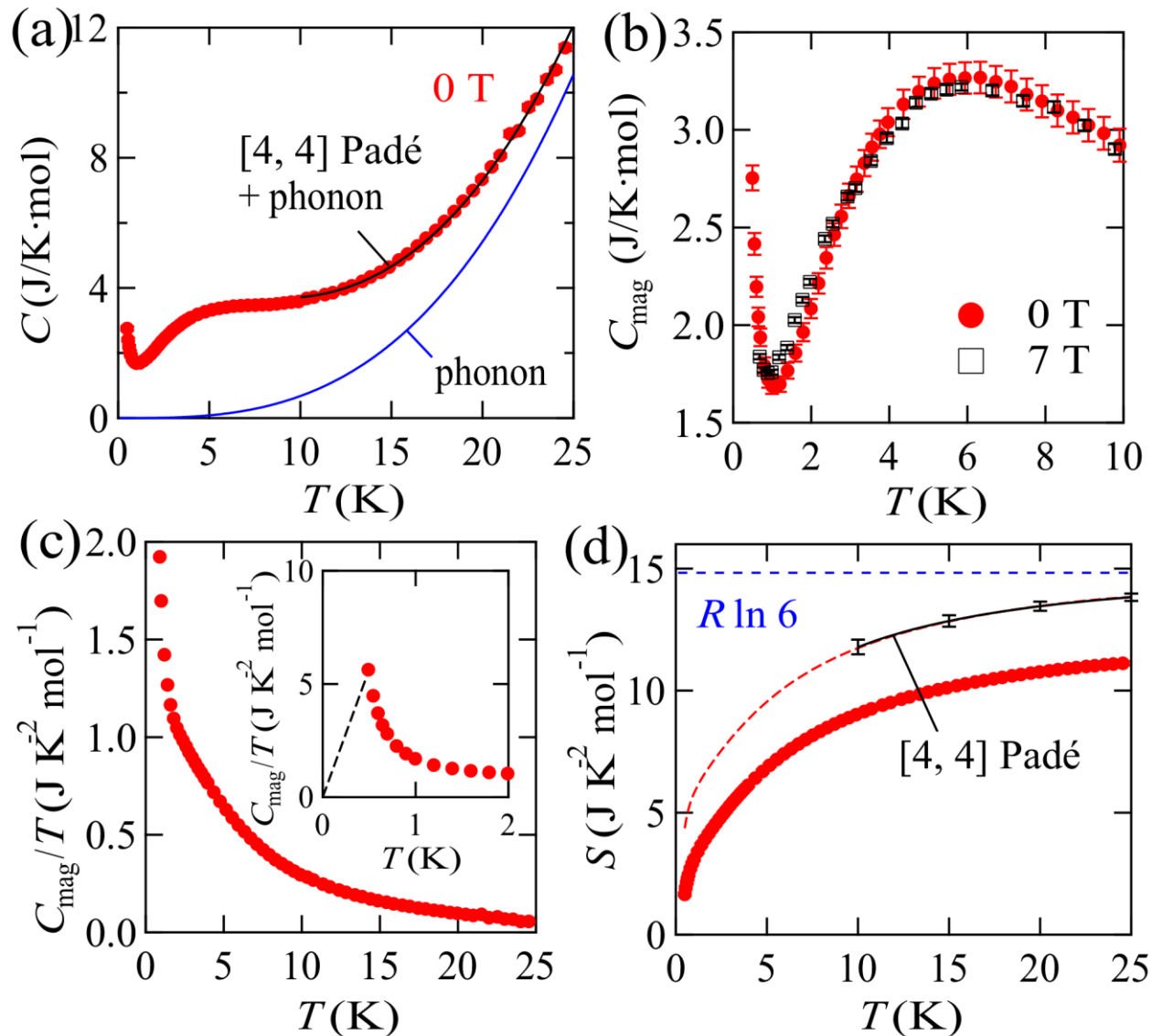
Bulk magnetic properties



- Follows a Curie-Weiss fit down to 50 K.
 $\mu_{\text{eff}}^2 = 35.6$ (35 for $S = 5/2$)
 $\theta = 40.9(1)$ K
- From fit to 10 – 300 K, (HTSE + [4,4] Padé†)
 $g = 1.99(1)$, $J = 2.03(1)$ K
- Linear increase of MH curve
- Saturation field of 30.6(3) T
 $S = 5/2$, $g = 1.99$: **$J = 2.0(1)$ K**

†A. Lohmann et al., PRB., **89**, 014415 (2014).

Large degeneracy near the ground state



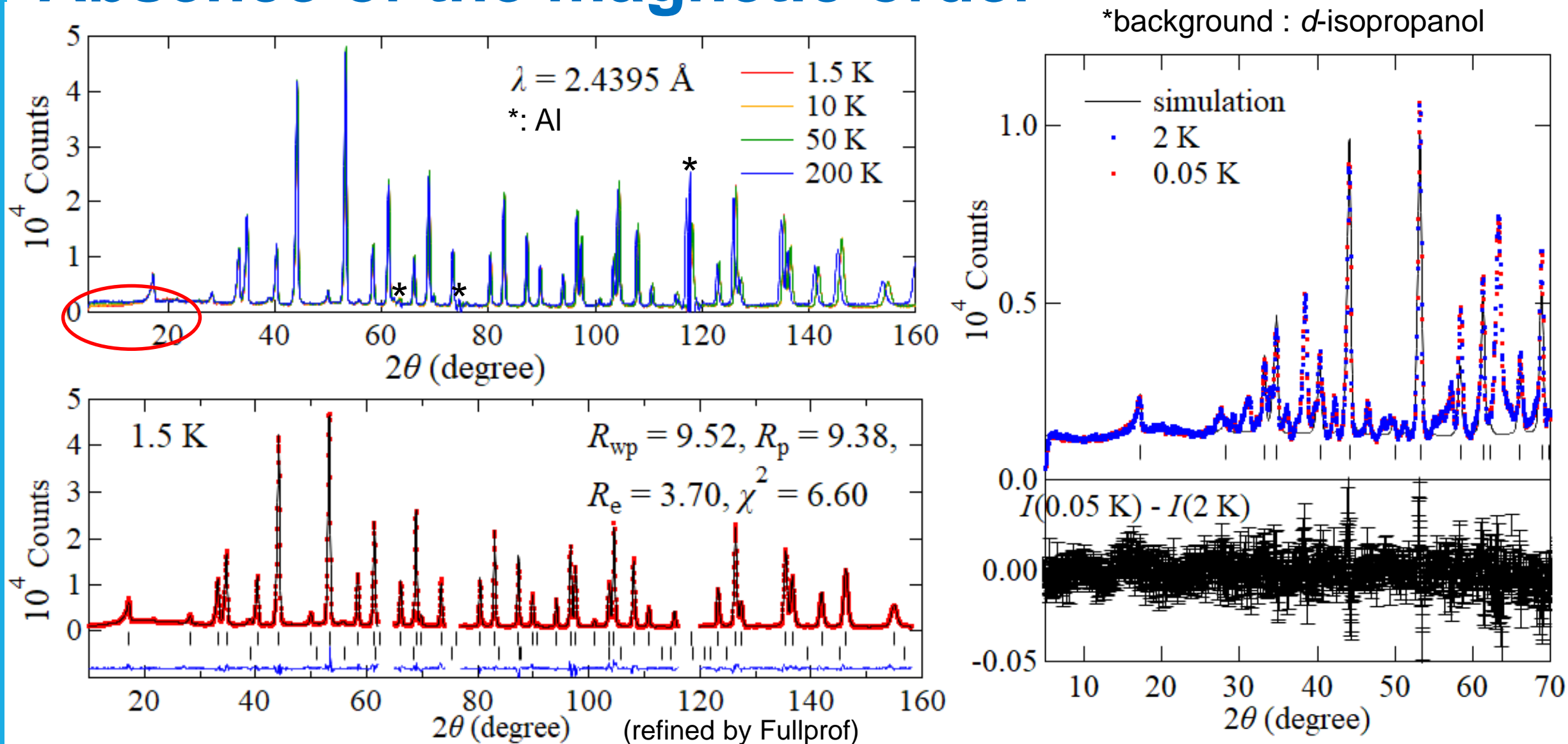
- Broad peak of C around 5 K.
→ antiferromagnetic short range order
- Fitting (10 - 25 K)
[4,4] Padé[†] + Debye model
 $J = 1.9(1)$ K, $\theta_D = 333(6)$ K
- Estimation of magnetic entropy
 $S_{\text{mag}} \sim 4$ J K⁻² mol⁻¹ (almost 1/4 of the total) is still unreleased at 0.5 K.



Supports highly degenerated ground state in $\text{Na}_3\text{Mn}(\text{CO}_3)_2\text{Cl}$.

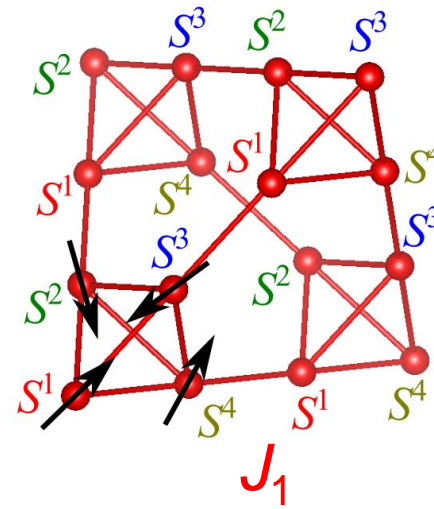
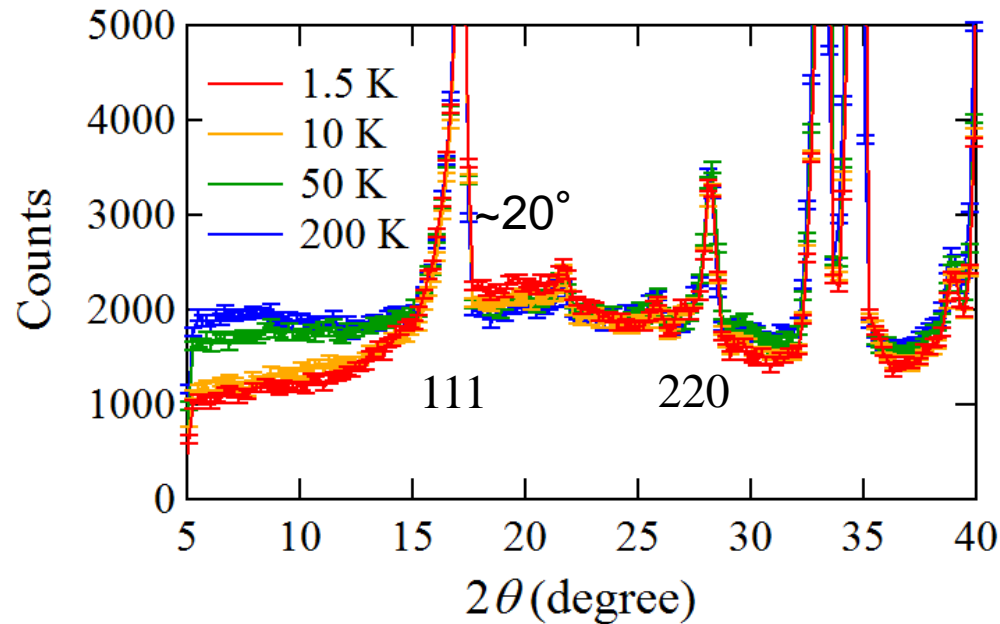
[†]A. Lohmann et al., PRB., **89**, 014415 (2014).

Absence of the magnetic order



Magnetic order is not detected even down to 0.05 K.

Development of magnetic diffuse scattering



Analyzed by mean-field theory calculations[†].

a, b : sublattice 1,2,3,4
μ, ν : x,y,z component

[†]M. Enjalran and M. J. G. Gingras, Phys. Rev. B, **70**, 174426 (2004).

1. Estimating $J(\mathbf{q})$

$$J_{\mu\nu}^{ab}(\mathbf{q}) = - \sum_i J_1 \delta_{ab:NN} (\mathbf{n}^\mu \cdot \mathbf{n}^\nu) e^{-i\mathbf{q} \cdot \mathbf{R}_{ij}^{ab}}$$

Nearest neighbor

$$+ J_d R N_N^3 \sum_i \left(\frac{\mathbf{n}^\mu \cdot \mathbf{n}^\nu}{|\mathbf{R}_{ij}^{ab}|^3} - \frac{3(\mathbf{n}^\mu \cdot \mathbf{R}_{ij}^{ab})(\mathbf{n}^\nu \cdot \mathbf{R}_{ij}^{ab})}{|\mathbf{R}_{ij}^{ab}|^5} \right) e^{-i\mathbf{q} \cdot \mathbf{R}_{ij}^{ab}}$$

Dipole-dipole interactions

$$J(\mathbf{q}) \mathbf{U}_\mu^\alpha(\mathbf{q}) = \lambda_\mu^\alpha(\mathbf{q}) \mathbf{U}_\mu^\alpha(\mathbf{q}) \text{ (12} \times \text{12 matrix)}$$

2. Estimating scattering cross-sections

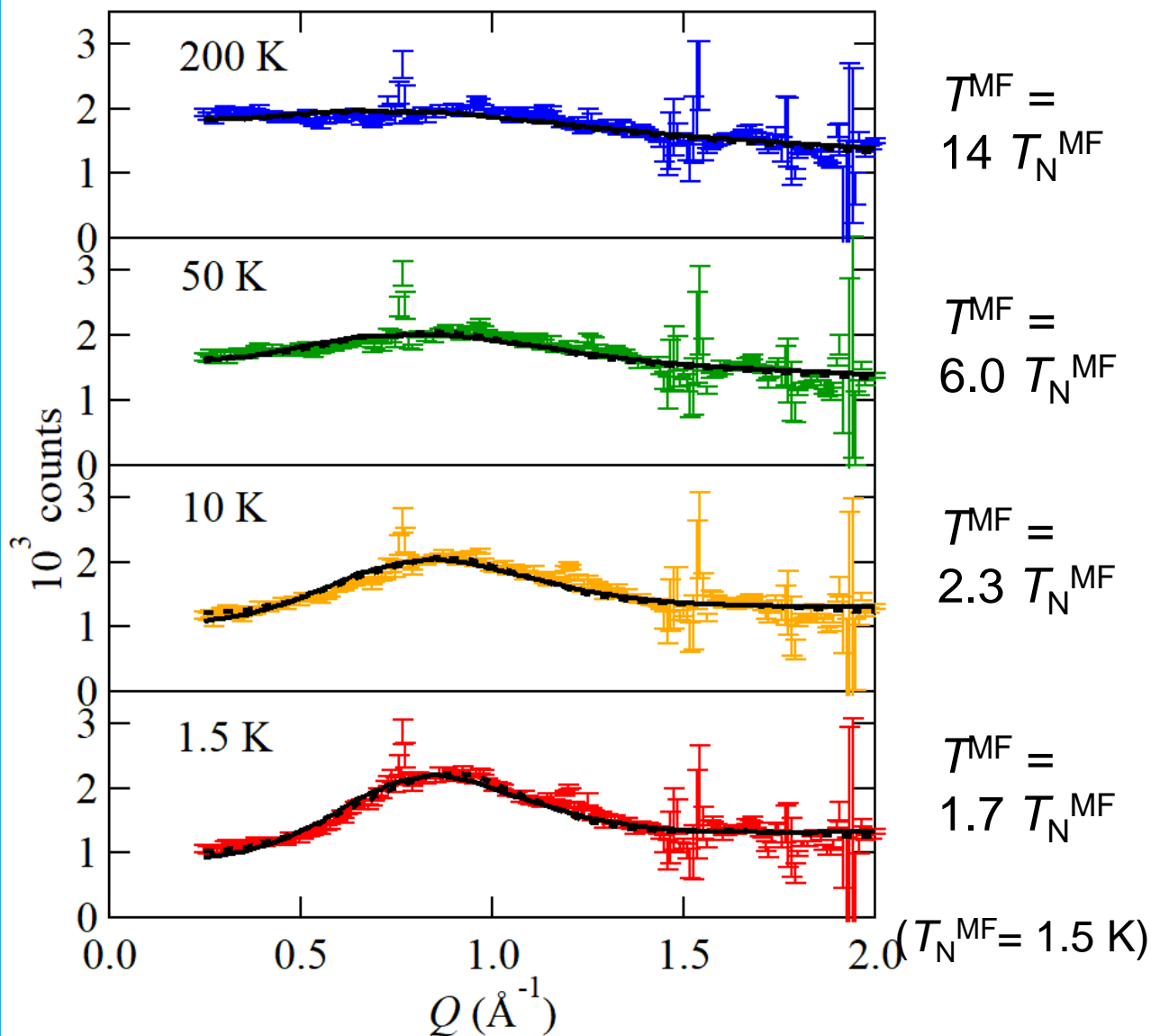
$$\langle S_i^{a,\mu} S_j^{b,\nu} \rangle \sim \frac{1}{3} \left(\delta_{ij} \delta_{ab} \delta_{\mu\nu} + \frac{\beta}{3} J_{\mu\nu}^{ab}(i,j) \right)$$

Expansion of correlation function

$$\frac{d\sigma}{d\Omega}(\mathbf{Q}) = \frac{C}{3} \{f(\mathbf{Q})\}^2 \sum_{\alpha,\mu} \frac{|\mathbf{F}_{\mu\perp}^\alpha(\mathbf{q})|^2}{1 - \frac{\lambda_\mu^\alpha(\mathbf{q})}{3T^{\text{MF}}}}$$

$$\mathbf{F}_{\mu\perp}^\alpha(\mathbf{q}) = \sum_a \{ \mathbf{U}_u^{\alpha,a}(\mathbf{q}) - (\mathbf{U}_u^{\alpha,a}(\mathbf{q}) \cdot \mathbf{Q}) \mathbf{Q} \} e^{i\mathbf{G} \cdot \mathbf{r}_a}$$

Diffuse scattering induced from magnetic frustration



Solid : $J-J_d$

Dashed : $J-J'-J_d$ (J' : weakly FM, -0.4 K)

The simulation using

$J_1 = 2 \text{ K}$ (χT , C , MH),

$J_d = 0.125 \text{ K}$ (from R_{NN})

well reproduces

the Q -dependence.



Dominant J_1 should lead to degenerate ground state.

$\text{Na}_3\text{Mn}(\text{CO}_3)_2\text{Cl}$ compared with $\text{Na}_3\text{Co}(\text{CO}_3)_2\text{Cl}$

| Material | $\text{Na}_3\text{Mn}(\text{CO}_3)_2\text{Cl}$ | cf. $\text{Na}_3\text{Co}(\text{CO}_3)_2\text{Cl}^*$ |
|---------------------|--|---|
| spin S | spin 5/2 (nearly classical) | Pseudo-spin 1/2 |
| g and J | $g = 1.99$, $J_1 \sim 2$ K (Heisenberg) | $g = 4.04$, $J_1 \sim 9$ K, $J_2 \sim$ weak FM? |
| Magnetic Transition | Absence of spin glass transition above 2 K Absence of magnetic order above 0.05 K | spin glass transition at 4.5 K? Order at $T_N = 1.5$ K (all-in-all-out) |

Single-ion anisotropy/anisotropic exchange interactions

→ All-in-all-out order (**Co**)

Highly isotropic exchange interactions

→ Degenerate ground state (**Mn**)

*K. Nawa et al., unpublished.
F. Zhendong et al., Phys. Rev. B, **87**, 214406 (2013).

Summary

Magnetic properties of $\text{Na}_3\text{Mn}(\text{CO}_3)_2\text{Cl}$ well explained as a classical pyrochlore antiferromagnet:

- Mn atoms form a pyrochlore lattice.
- Nearest neighbor interactions are estimated as $J = 2$ K.
- Antiferromagnetic short range order develops below 50 K.
- On the other hand, no apparent signature of a spin-glass transition (>2 K) and a magnetic order (>0.05 K) is detected.

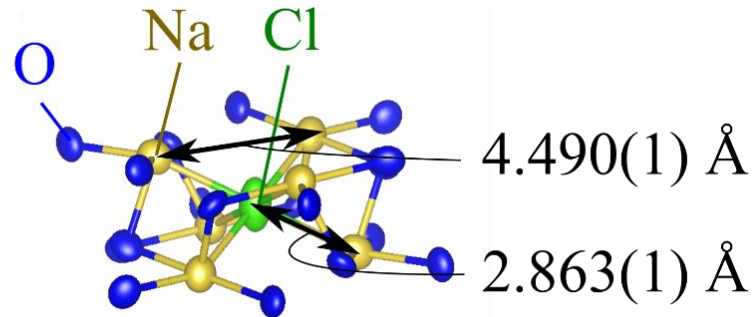
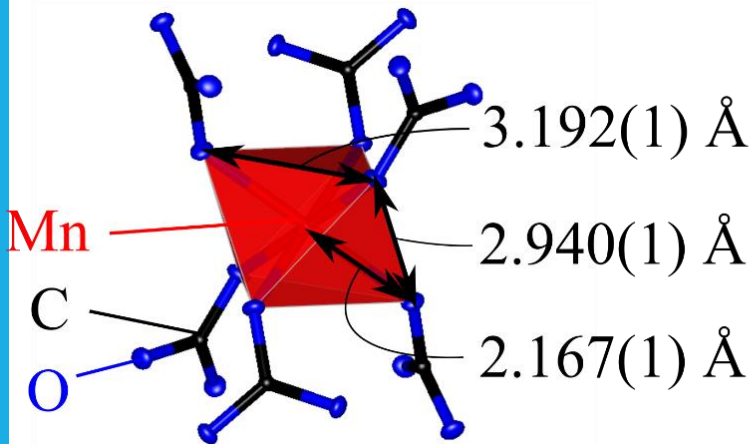
→ **A large degeneracy remains near the ground state.**

Low-energy spin dynamics should be further examined.

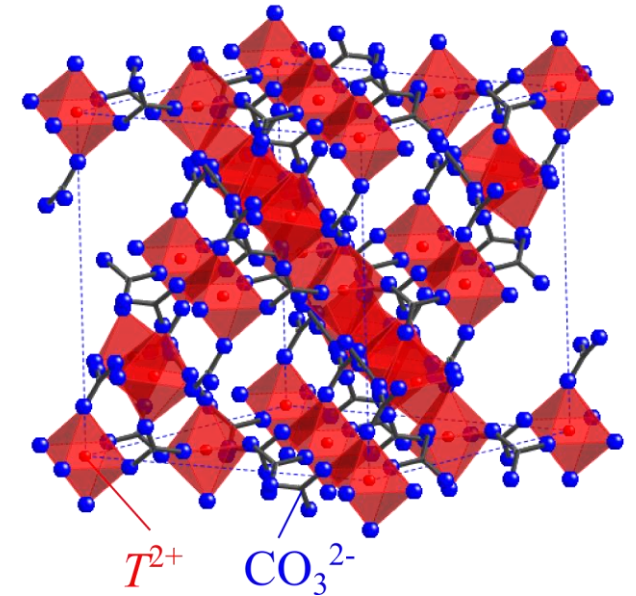
Crystal structure

| | site | x | y | z | B_{eq} |
|----|------|-------------|------------|------------|-----------------|
| Na | 48f | 1/8 | 0.34864(2) | 5/8 | 1.410(4) |
| Mn | 16c | 0 | 1/2 | 1/2 | 0.752(1) |
| C | 32e | 0.03054(2) | 0.71946(2) | 0.53054(2) | 0.682(2) |
| O | 96g | -0.02533(2) | 0.51505(2) | 0.51505(2) | 1.108(3) |
| Cl | 16d | 1/4 | 1/2 | 1/2 | 2.032(2) |

(B_{eq} from $8\pi^2/3 (U_{11} + U_{22} + U_{33})$ in units of \AA^2)



$Fd\bar{3}$ (cubic), $a = 14.1942 \text{ \AA}$

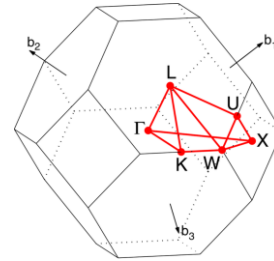
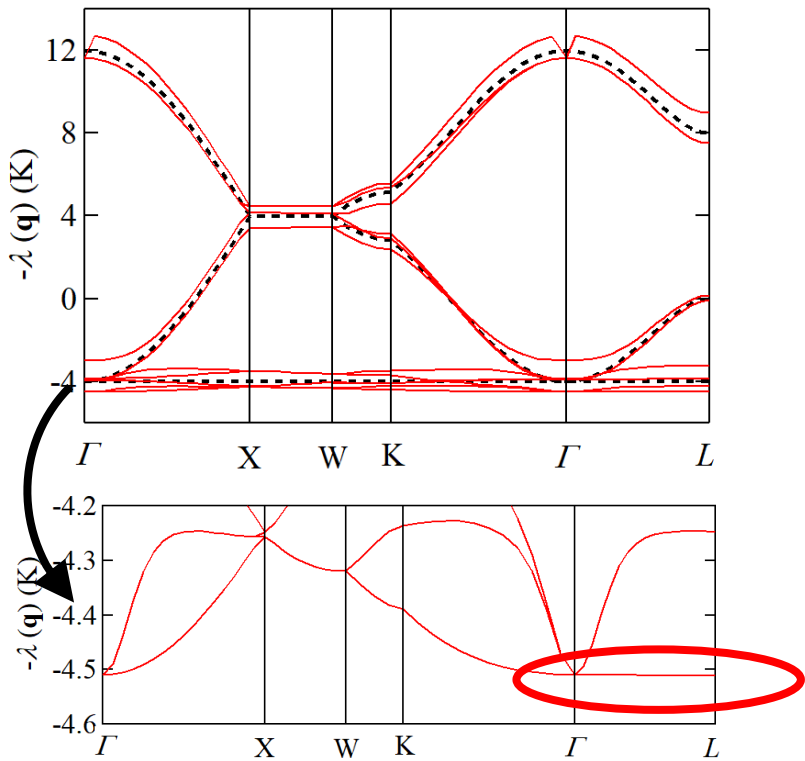


MnO_6 octahedra
suppressed along [111]
cf. Mn-O : 2.190 \AA (MnCO_3)

ClNa_6 octahedra
suppressed along [111]
cf. Na-Cl : 2.820 \AA (NaCl)

Energy spectrum and $S(q)$ map

(Simulation from MFT)



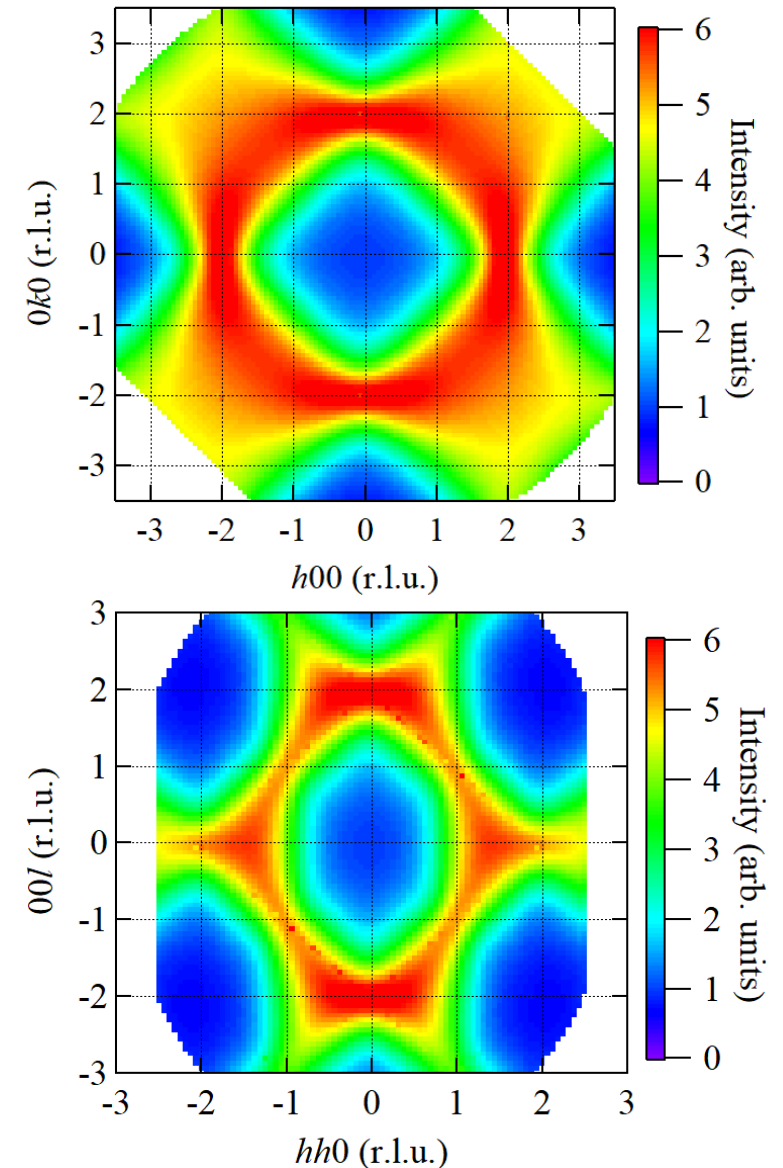
Dashed curves:
 $J = 2 \text{ K}, J_{\text{dd}} = 0 \text{ K}$
 Solid curves:
 $J = 2 \text{ K}, J_{\text{dd}} = 0.125 \text{ K}$

“Degeneration lines”
 along Γ -L

Although degeneracy near the ground state is lifted by J_{dd} , its magnitude is not so large compared to J .

N. P. Raju *et al.*, Phys. Rev. B, **59**, 14489 (1999).

W. Setyawan and S. Curtarolo, Comp. Mater. Sci. **49**, 299 (2010).

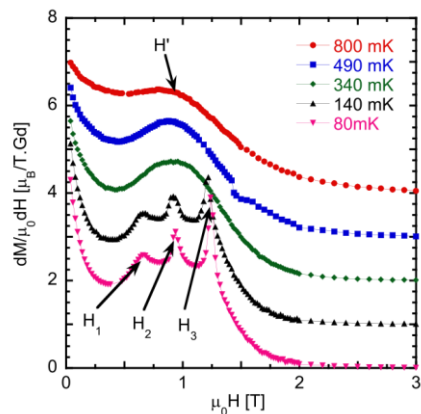
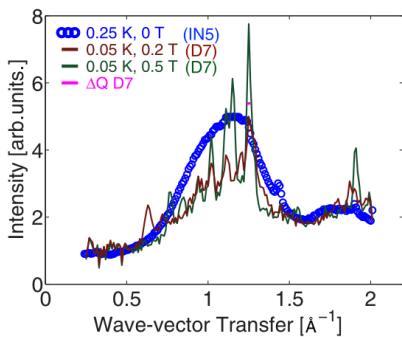
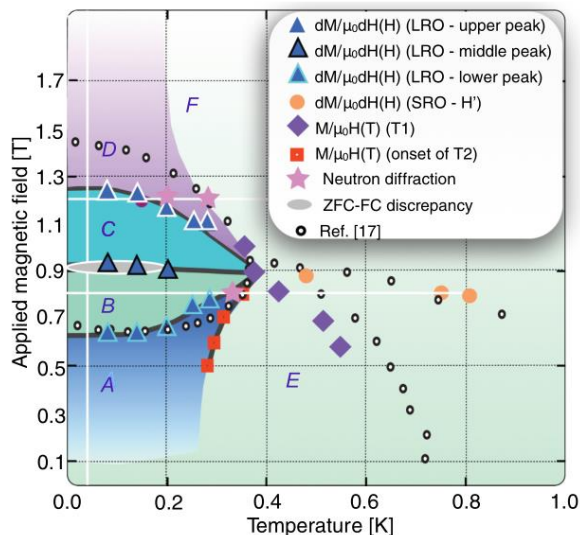


Origin of the field-induced anomaly

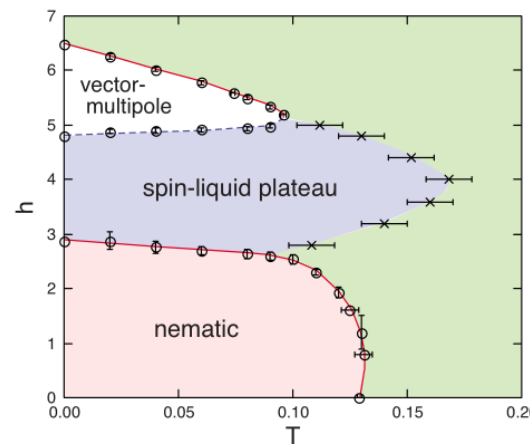
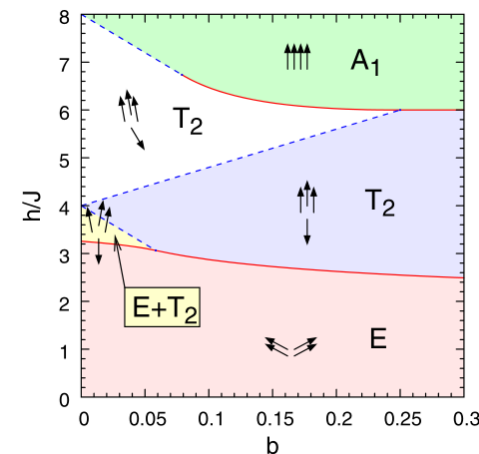
Dipole-dipole interaction?

Spin-lattice coupling?

Ex. $\text{Gd}_3\text{Ga}_5\text{O}_{12}$



K. Penc *et al.*,
Phys. Rev. Lett.
93, 197203 (2004).



N. Shannon *et al.*,
Phys. Rev. B, **81**,
184409 (2010).

(for $b = 0.1, J_3 = 0$)

P. Schiffer *et al.*, Phys. Rev. B, **73**, 2500 (1994).

P. P. Deen *et al.*, Phys. Rev. B, **91**, 014419 (2015).