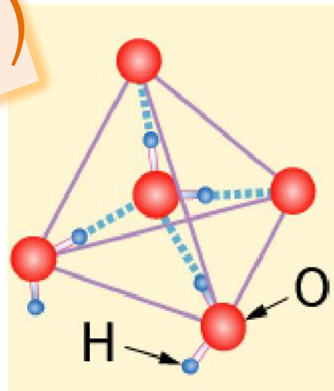
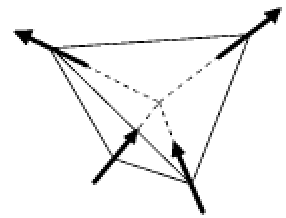
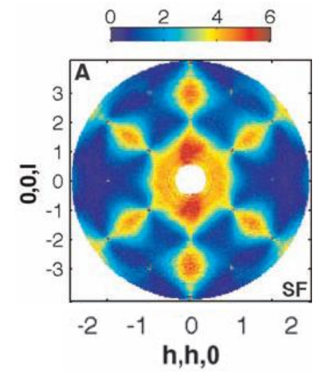
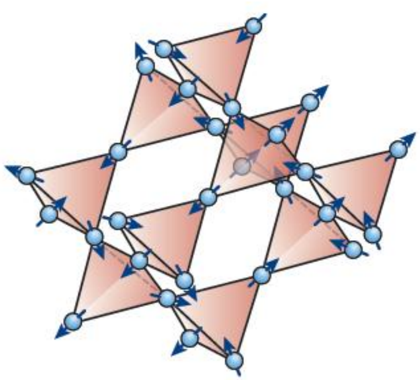
R/2 ln(3/2)

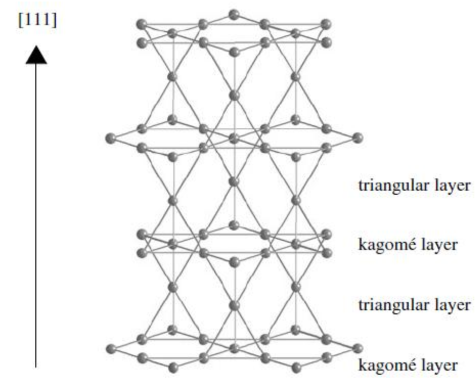






Spin Ice review

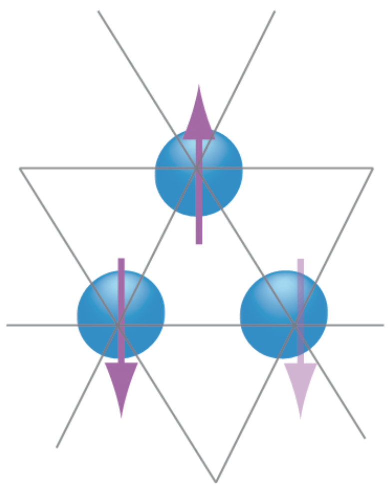




R/4 ln(4/3)

Geometrical frustration

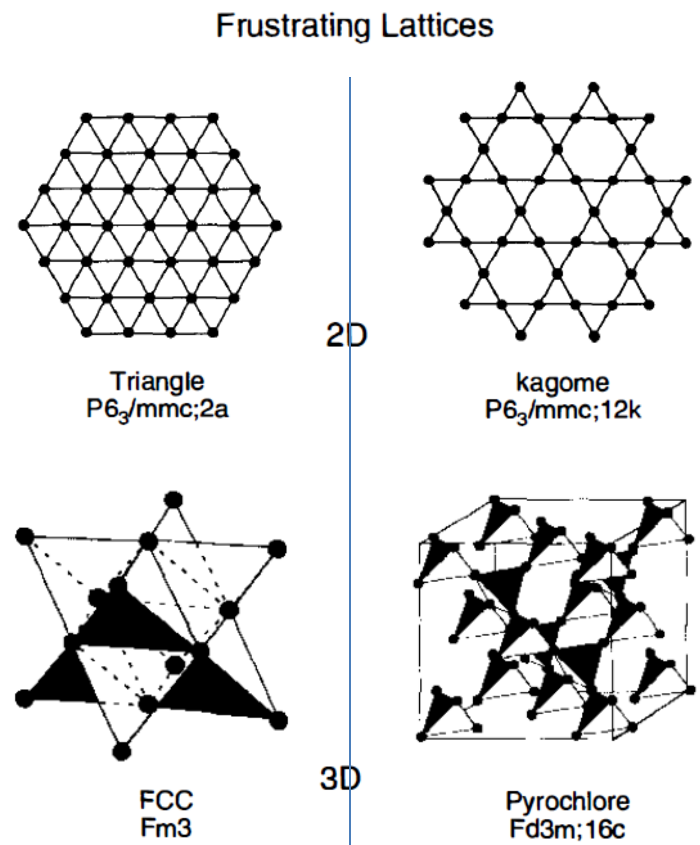
Antiferromagnets on triangular lattice



Ising spin	Zero-point entropy
Heisenberg spin	Néel LRO (120-deg structure)

Frustration parameter

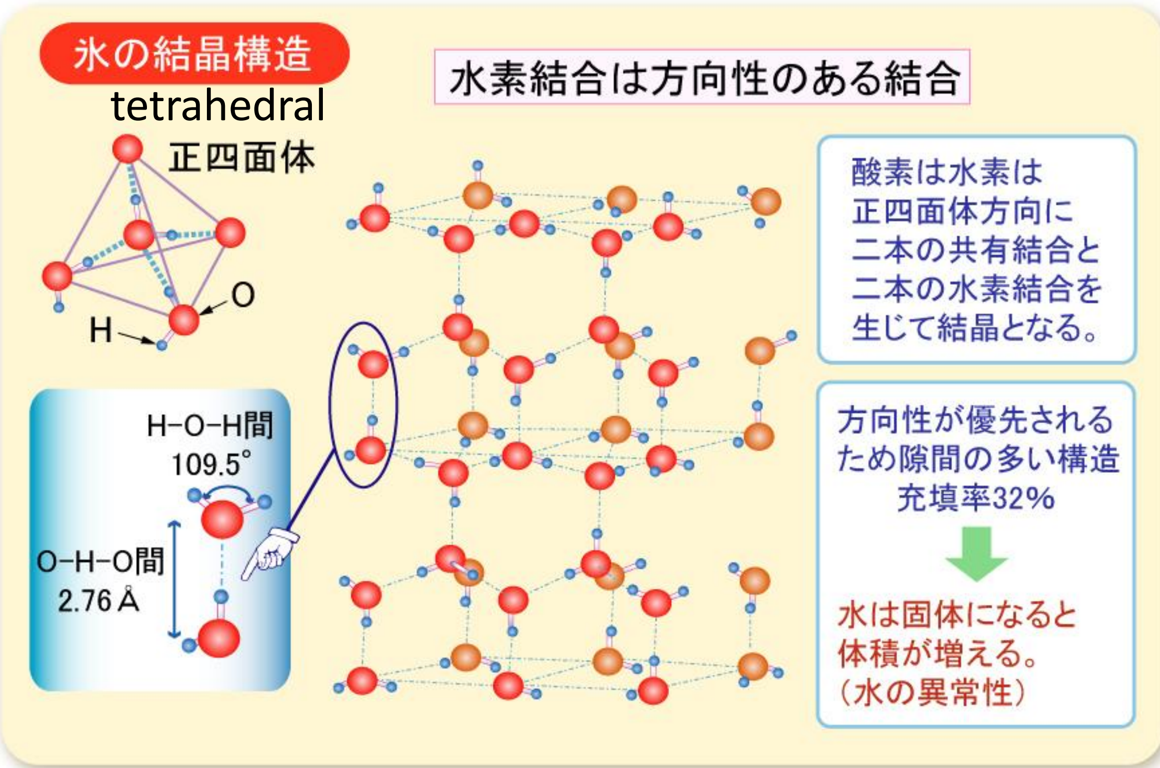
$$f = \theta_{cw} / T_c >> 1$$



Edge-sharing

Corner-sharing

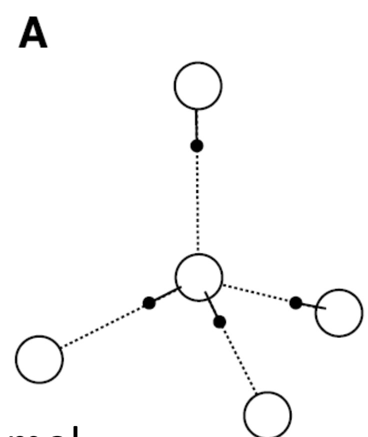
Residual entropy in water ice



O-H-O 2.76 Å
O-H distance (gas) 0.95 Å

O-H bonding energy (221 kCal/mol) is so strong that the molecule structure is left unchanged by forming ice from vapor.

2-near 2-far configuration



2 positions of 2 H for N oxygen — $2^{2N}=4^N$

2-near 2-far configuration — $({}_4C_2 / 2^4)^N=(3/8)^N$

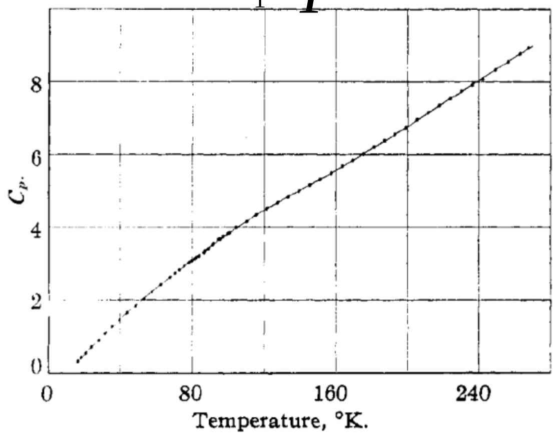
Residual entropy ($S = k_B \ln W$) — **R ln(3/2)**

Linus Pauling (1935) JACS 57, 2680

$=0.405R = 3.371$ J/K mol

Heat capacity measurement of Ice

$$\Delta S = \int_{T_1}^{T_2} \frac{C}{T} dT$$



Giauque & Stout (1936) JACS 58, 1144

CALCULATION OF ENTROPY OF WATER

0–10°K., Debye function $h\nu/k$ = 192	0.022
10–273.10°K., graphical	9.081
Fusion 1435.7/273.10	5.257
273.10–298.10°K., graphical	1.580
Vaporization 10499/298.10	35.220
Correction for gas imperfection	0.002
Compression R ln 2.3756/760	−6.886
Cal./deg./mole	44.28 ± 0.05

(Huge latent entropy)

T°K	$-(F°-E_0°)/T$	$S°$	$C°_P$
298.1	37.179	45.101	8.000
300	37.230	45.151	8.002
350	38.452	46.389	8.066
400	39.513	47.472	8.155
450	40.452	48.439	8.260
500	41.296	49.315	8.379
550	42.062	50.119	8.504
600	42.765	50.864	8.635
650	43.415	51.561	8.771
700	44.020	52.216	8.910
750	44.587	52.836	9.053
800	45.121	53.425	9.199

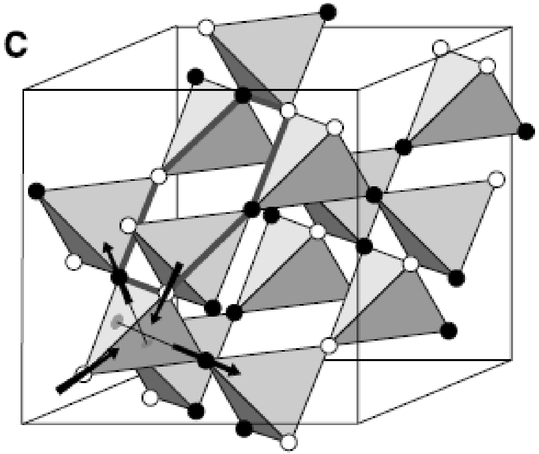
Gordon (1934) J. Chem. Phys. 2, 65

Molecular band calculation of steam

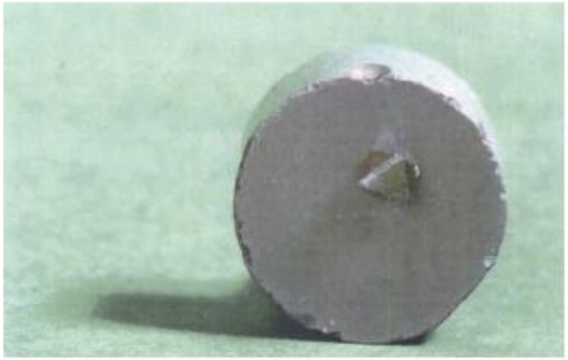
$S_{298.1°}$ = 45.1 cal/K mol

ΔS = 0.82 cal/K mol
= 3.43 J/K mol
~ R ln(3/2) = 3.37 J/K mol

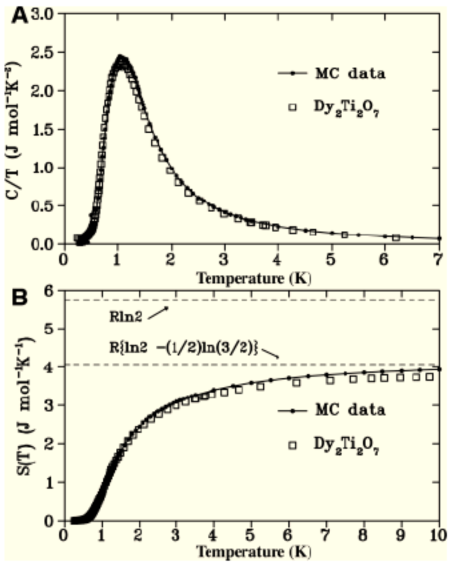
Agreement might be fortuitous.
Very complicate due to vapour-liquid, liquid-ice transition

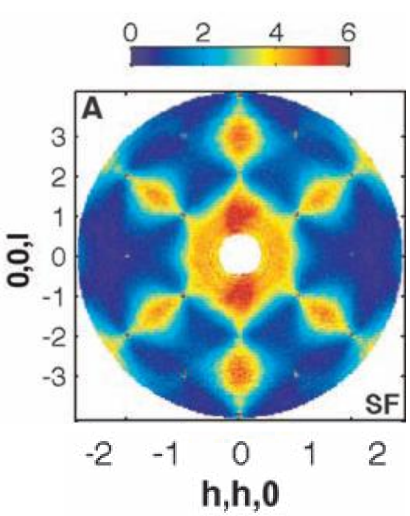


R/2 ln(3/2)

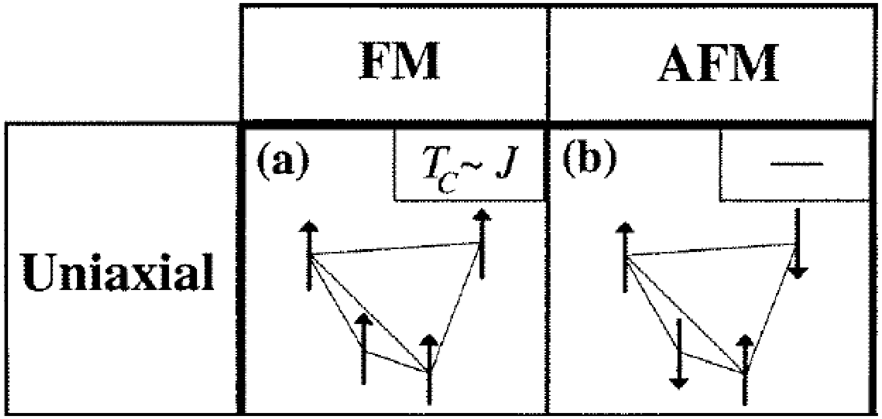


SPIN ICE





Ising Antiferromagnets on Pyrochlore



At first glance, there is *frustration* only for *antiferromagnets*, and *no-frustration for ferromagnets*.

(Ising in cubic pyrochlore is *unphysical*).

VOLUME 79, NUMBER 13 PHYSICAL REVIEW LETTERS 29 SEPTEMBER 1997

Geometrical Frustration in the Ferromagnetic Pyrochlore $Ho_2Ti_2O_7$

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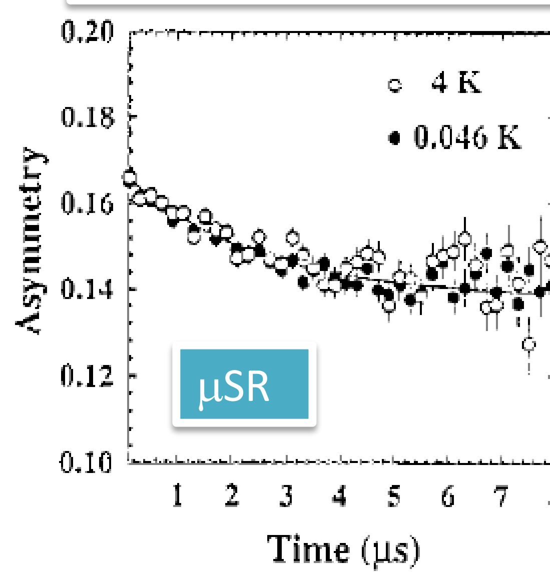
[2] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom
[3] Department of Solid State Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark
[4] Institut für Kristallographie, Universität Tübingen, c.o. Hahn-Meitner-Institut, Glienickerstrasse 100, D-14109, Berlin, Germany
[5] Oxford Physics, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, United Kingdom
(Received 19 May 1997)

We report a detailed study of the pyrochlore $Ho_2Ti_2O_7$, in which the magnetic ions (Ho^{3+}) are ferromagnetically coupled with $J \sim 1$ K. We show that the presence of local Ising anisotropy leads to a geometrically frustrated ground state, preventing long-range magnetic order down to at least 0.05 K. However, unlike in the case of a frustrated *antiferromagnet*, this disorder is principally static. In a magnetic field, the ground-state degeneracy is broken and ordered magnetic phases are formed which display an unusual history dependence due to the slow dynamics of the system. These results represent the first experimental evidence for geometrical frustration in a *ferromagnetic* system. [S0031-9007(97)04147-1]

PACS numbers: 75.50.Lk, 75.25.+z, 75.40.Gb

No LRO down to 0.046 K
(J. Magn. Magn. Matter 177-184, 757)



Cubic Pyrochlore $A_2B_2C_7$

Insulator

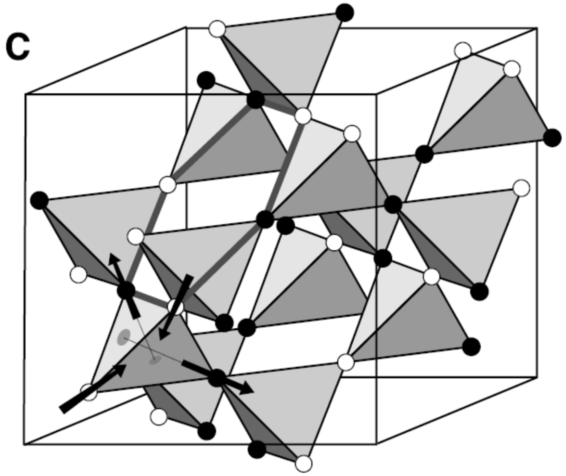
A: rare-earth (Ho, Dy)

Ho^{3+} ($4f^{10}$)

Dy^{3+} ($4f^{9}$)

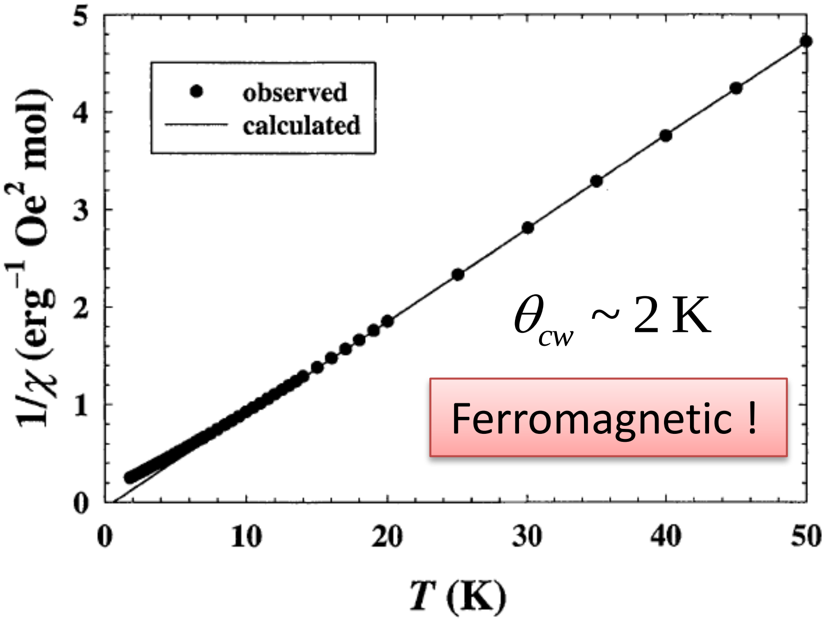
B: Ti/Sn (non-magnetic)

C: O (center of tetrahedra)



Local easy axis: <111>

$Ho_2Ti_2O_7$



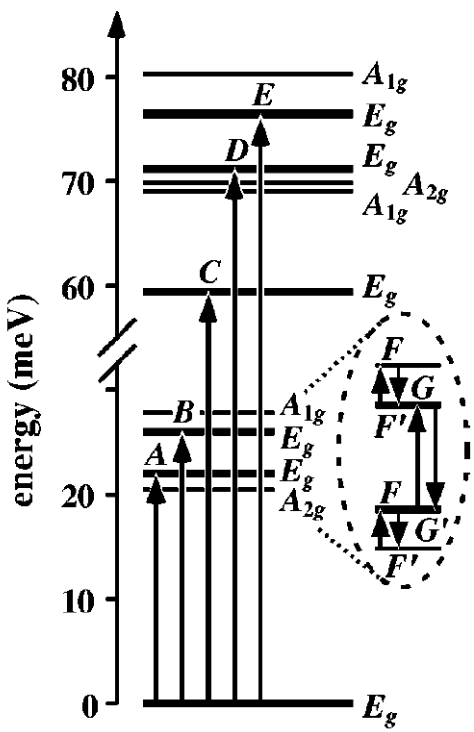
$\theta_{cw} \sim 2\,\mathrm{K}$

Ferromagnetic !

Bramwell (2000) J. Phys. Condens. Matter 12, 483

Ising spin in Pyrochlore

Crystal field splitting



ground state
pure doublet

	Ho^{3+}	Dy^{3+}
electron configuration	$4f^{10}$	$4f^{9}$
S	2	5/2
L	6	5
J	8	15/2
Ground state	$\left\|8, M_J\right\rangle = \left\|8, \pm 8\right\rangle$	$\left\|\frac{15}{2}, M_J\right\rangle = \left\|\frac{15}{2}, \pm\frac{15}{2}\right\rangle$

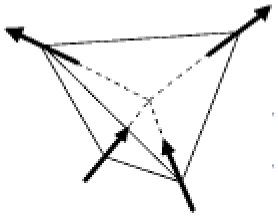
Next excitation level is separated ~ 200 K

Ising spin system

Anisotropic Ising Magnet

Heisenberg Hamiltonian with easy axis anisotropy

$$H=\frac{D}{2}\sum_{K,\kappa}(\hat{\mathbf{d}}_\kappa\cdot\mathbf{S}_{K,\kappa})^2+J\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j\,.$$



$\hat{\mathbf{d}}_\kappa$ local easy axis

$|J/D|<<1$

$D\sim$ -50 K

$J\sim$ 1K

$$\vec{S}_i=T_i\cdot\hat{d}_i$$

$T_i=1$: spin pointing out of a "up" tetrahedron

$T_i=-1$: spin pointing in of a "up" tetrahedron

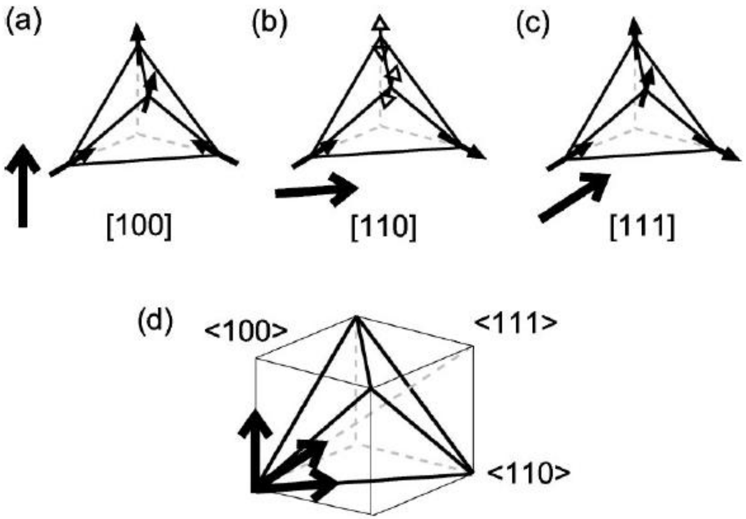
$$H=DN-\frac{J}{3}\sum_{\langle i,j\rangle}T_iT_j\,.$$

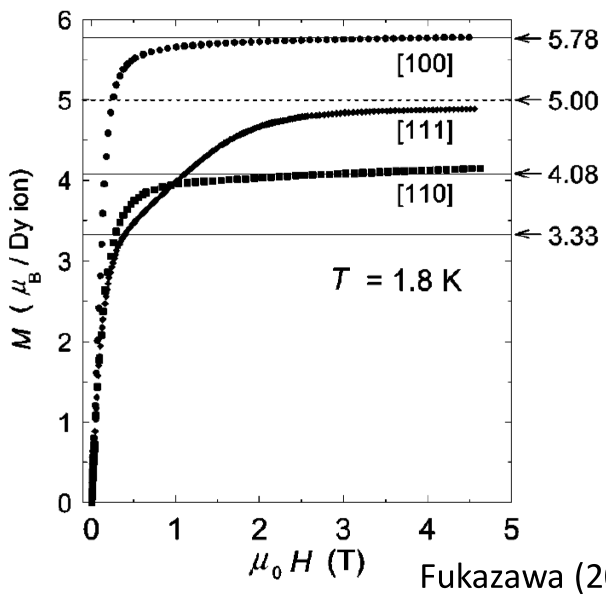
*"Heisenberg magnet on the pyrochlore lattice can be mapped on to an Ising model with an exchange constant of **the opposite sign**"* R. Moessner (1998) PRB **57**, R5587

For J > 0 (AFM), choose all spin "IN" or "OUT" → NO FRUSTRATION

For J < 0 (FM), maximize the number of pair of IN & OUT → Macroscopically degenerated states
Frustrated in ferromagnets

Magnetization in $(Dy,Ho)_2Ti_2O_7$

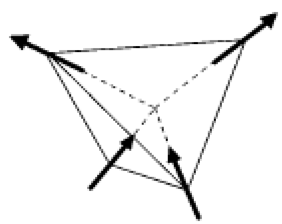




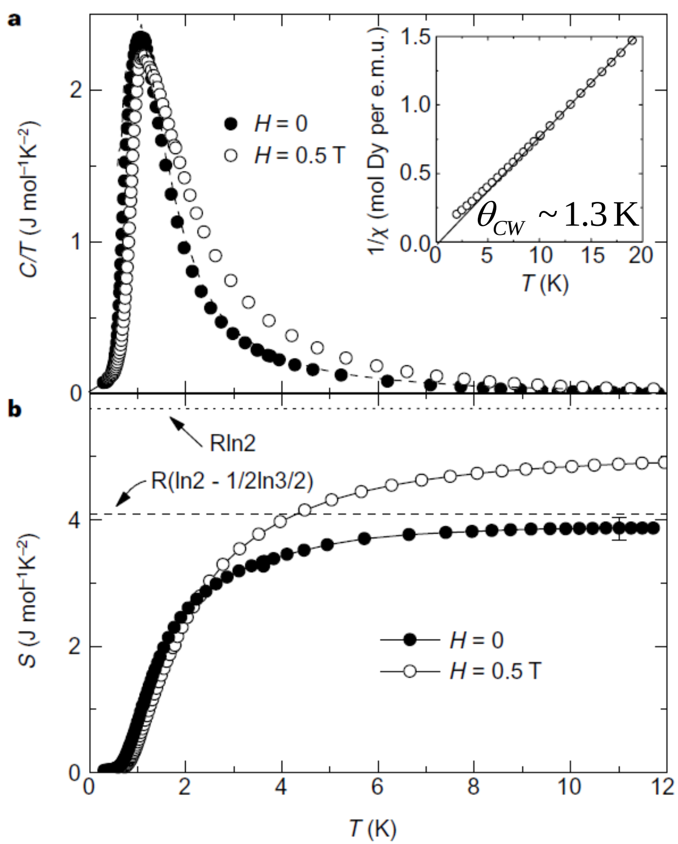
Fukazawa (2002) PRB 65, 054410

H // [100]	All spins couple to field with ice-rule. Unique configuration preferred.	$M_{sat} = p_{eff} / \sqrt{3}$
H // [110]	2 spins couple (α chain), 2 spins free (β chain) IN-OUT for both chains.	$M_{sat} = p_{eff} / \sqrt{6}$
H // [111]	Small H: Field // one easy axis the other 3 form in-in-out / out-out-in Large H: Ice rule broken. 1-in 3-out/3-in 1-out	$M_{sat} = p_{eff} / 3$ $M_{sat} = p_{eff} / 2$

Residual entropy in Spin Ice



For N spins, possible configurations	2^N
Number of tetrahedron	N/2
2-IN 2-OUT configurations	$({}_4C_2 / 2^4)^{N/2} = (3/8)^{N/2}$
Residual entropy	$\frac{R}{2}\ln\left(\frac{3}{2}\right) \approx 0.2027R$ $= 1.68\ \mathrm{J/K \cdot mol}$



Zero-point entropy in 'spin ice'

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* *Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974, USA*

† *Chemistry Department, Princeton University, Princeton, New Jersey 08540, USA*

‡ *Department of Physics, Indian Institute of Science, Bangalore 560012, India*

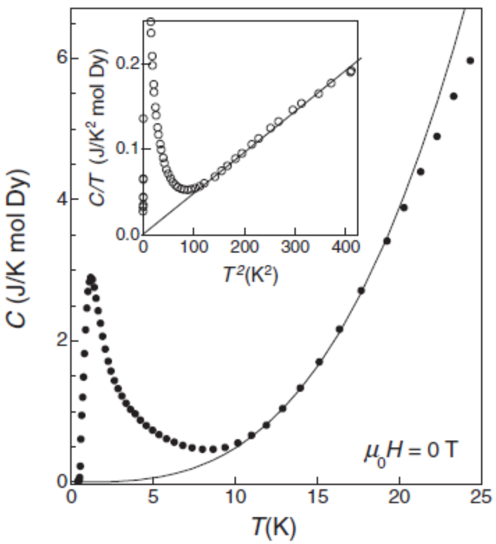
Heat capacity of single crystal $Dy_2Ti_2O_7$

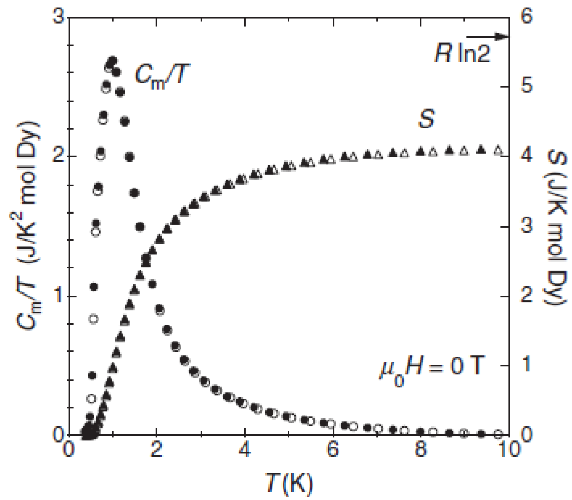
Nature (1999) **399**, 333-335

Specific Heat of $Dy_2Ti_2O_7$

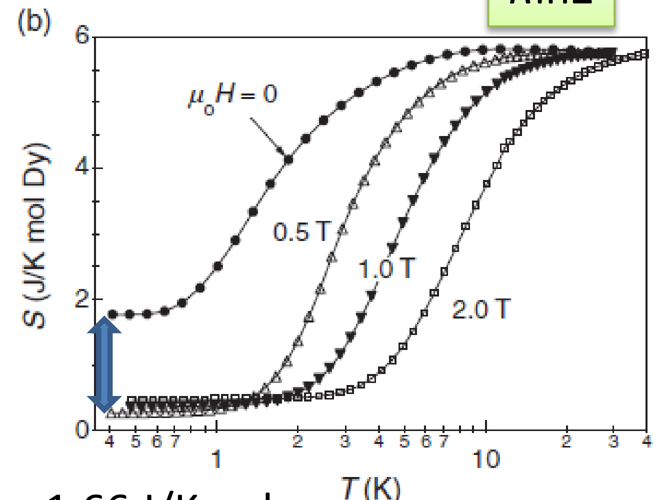
Hiroi (2003) JPSJ 72, 411-418

raw data





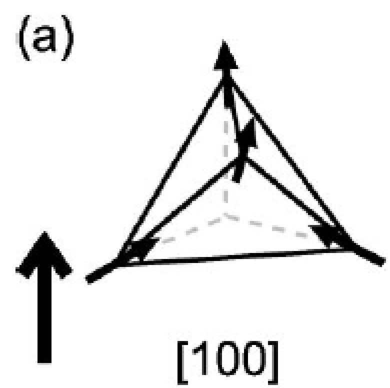
*R*ln2



1.66 J/Kmol

Lattice contribution is negligible below 10 K

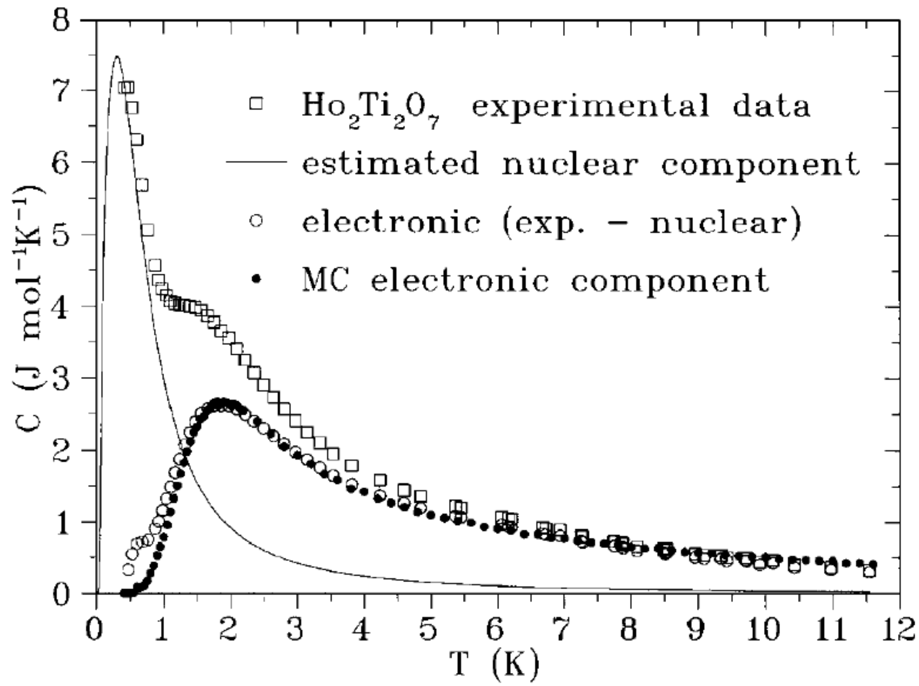
Very simple.
Total entropy R ln2
Magnetic entropy dominant



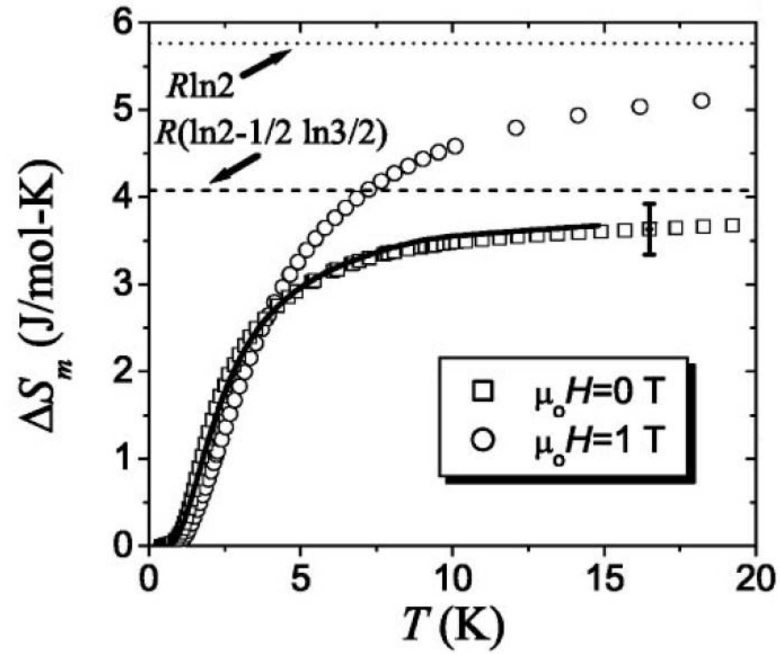
H // [100]

All spins couple to field
Aligned to unique configuration with keeping ice-rule.

Specific Heat of $Ho_2Ti_2O_7$



Bramwell (2001) PRL 87, 047205



Cornelius & Gardner (2001) PRB 64, 060406(R)

Nuclear hyperfine coupling causes a Schottky anomaly.
Estimation of the nuclear component was done by C meas. of isostructual Ho_2GaSbO_7.

Large magnetic moment in Pyrochlore $R_2B_2C_7$

Large magnetic moment

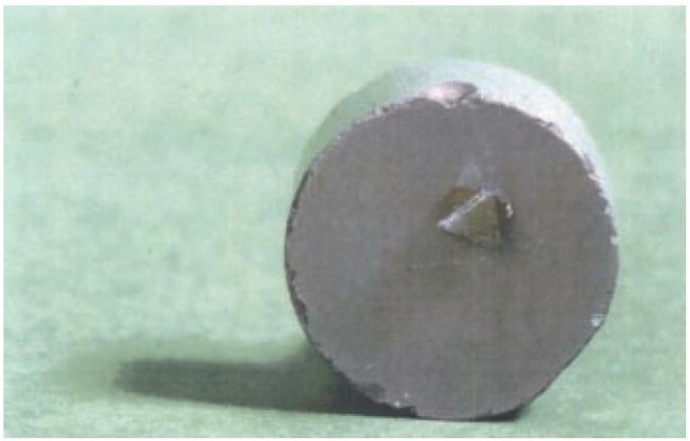
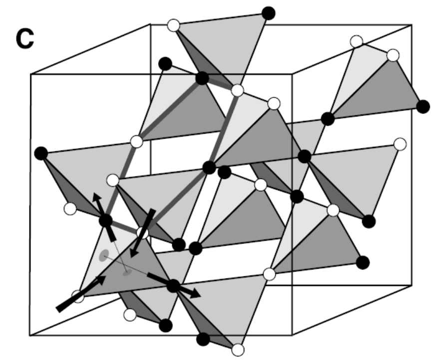


Fig. 2. Flux-grown octahedral crystal of $Ho_2Ti_2O_7$ stuck to a NdFeB permanent magnet at room temperature. The strong paramagnetism reflects the large magnetic moment of Ho^{3+}.



	Ho^{3+}	Dy^{3+}
electron configuration	$4f^{10}$	$4f^{9}$
g_J	5/4	4/3
J	8	15/2
$p_{eff}=g_J(J(J+1))^{1/2}$	10.61	10.65

Bramwell (2001) Science 294, 1495

Dipolar spin ice model

Large magnetic moment

	Ho^{3+}	Dy^{3+}
μ/μ_B	10.61	10.65

Dipolar spin ice model

$$H = -J\sum_{\langle ij\rangle}\mathbf{S}_i^{z_i}\cdot\mathbf{S}_j^{z_j} + Dr_{\rm nn}^3\sum_{j>i}\frac{\mathbf{S}_i^{z_i}\cdot\mathbf{S}_j^{z_j}}{|\mathbf{r}_{ij}|^3} - \frac{3(\mathbf{S}_i^{z_i}\cdot\mathbf{r}_{ij})(\mathbf{S}_j^{z_j}\cdot\mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5}$$

For nearest-neighbor

$$S_i\cdot S_j = -\frac{1}{3}\sigma_i\cdot\sigma_j$$

$$(S_i\cdot r_{ij})\cdot(S_j\cdot r_{ij}) = -\frac{2}{3}\sigma_i\cdot\sigma_j$$

$$H = \sum\left(\frac{J}{3}+\frac{5D}{3}\right)\sigma_i\cdot\sigma_j$$

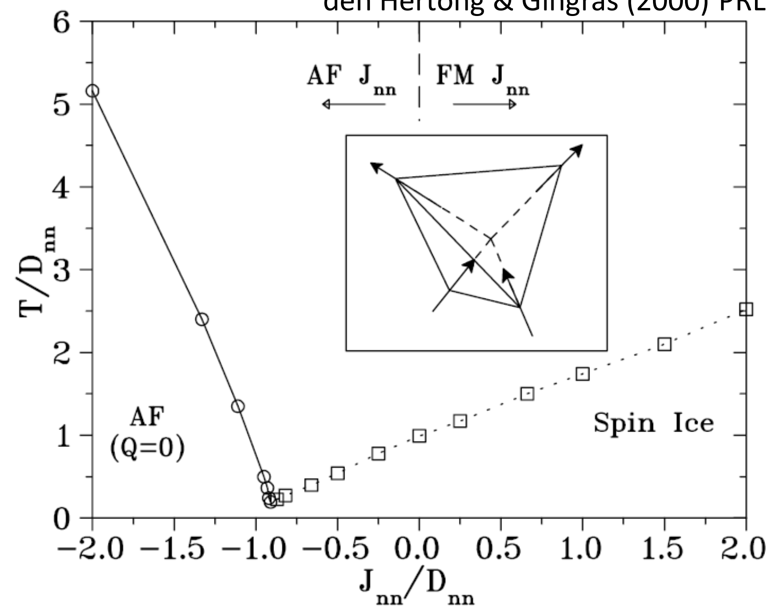
$$\equiv\sum(J_{nn}+D_{nn})\sigma_i\cdot\sigma_j \equiv \sum J_{eff}\sigma_i\cdot\sigma_j$$

Dipole-dipole energy for nearest-neighbor

$$D = \frac{\mu_0}{4\pi}\frac{\mu^2}{r_{nn}^3} \sim 1.4\ \mathrm{K}$$

$$r_{nn} = a\frac{\sqrt{2}}{4},\ a \sim 10\ \mathring{A}$$

den Hertong & Gingras (2000) PRL 84, 3430



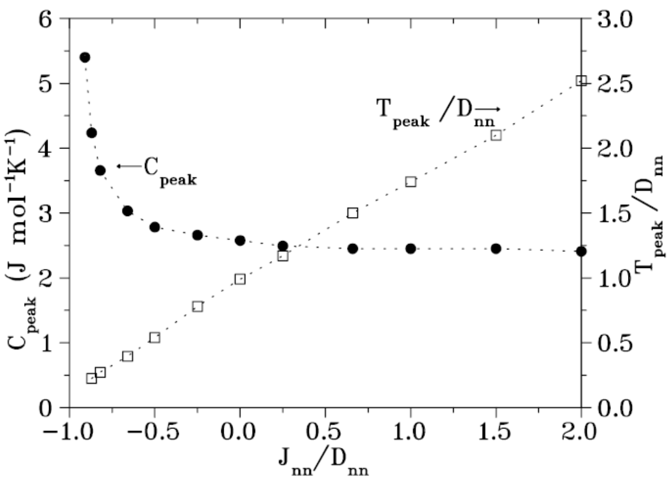
$J_{nn}+D_{nn}<0$ No frustration: All-in/All-out

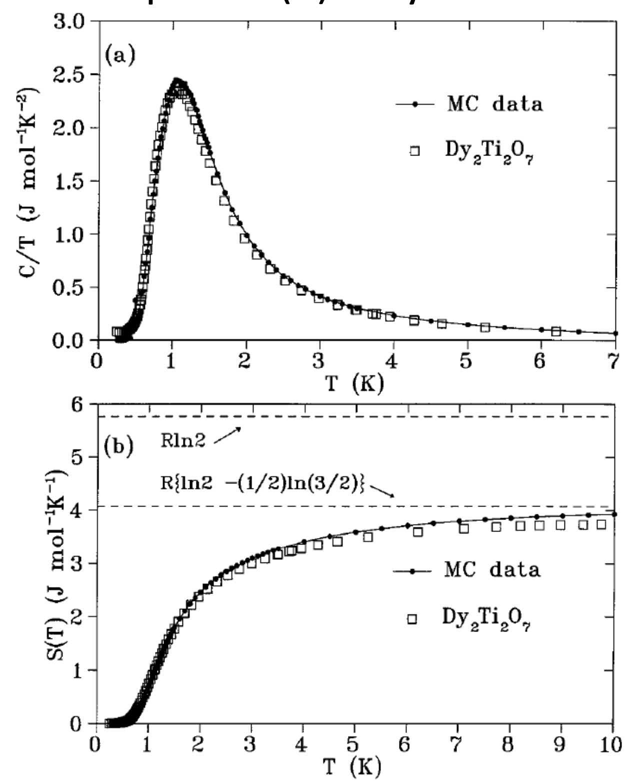
$J_{nn}+D_{nn}>0$ Spin ice

Monte-Carlo Simulation in Dipolar spin ice model

den Hertong & Gingras (2000) PRL 84, 3430

MC simulation based on dipolar spin ice model can explain $C(T)$ very well.

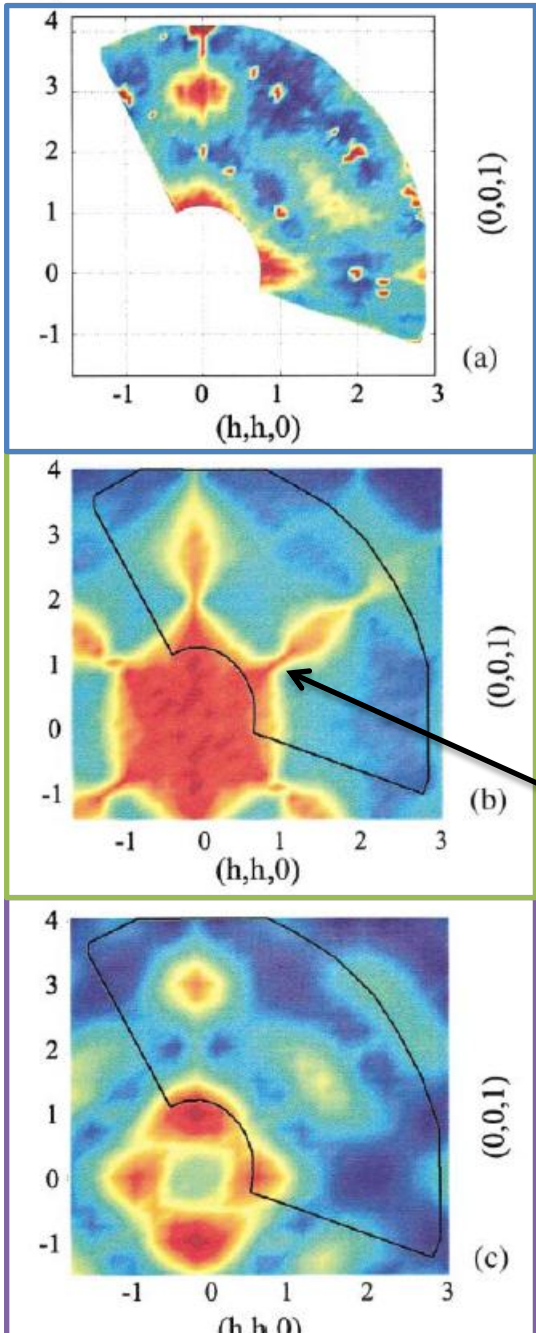




	$Ho_2Ti_2O_7$	$Dy_2Ti_2O_7$
D (K)	1.41	1.41
D_{nn} (K)	2.35	2.35
J (K)	-1.65	-3.72
J_{nn} (K)	-0.55	-1.24
J_{eff}(K)	+1.8	+1.1

D is calculated by the moment μ and the distance, a.
Fitting to the C measurement gives J and J_{eff}.

Neutron scattering



< Experiment>
$Ho_2Ti_2O_7$, T = 50 mK

<Monte-Carlo simulation>
Nearest neighbor spin ice model
D = 0, *J* > 0

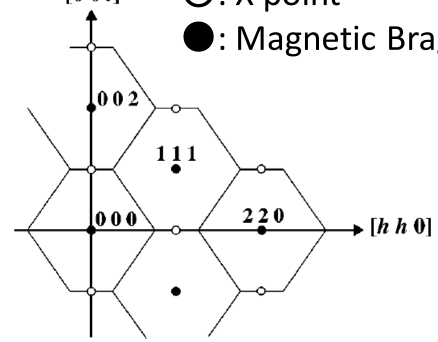
"Pinch-point"
Clear feature of spin ice

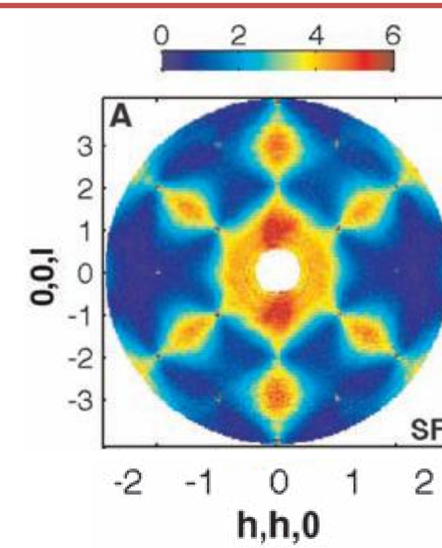
<Monte-Carlo simulation>
Dipolar spin ice model
D_{nn} = 2.35 K, J_{nn} = -0.52 K (AF)

This model captures exp well
(0,0,3) (3/2, 3/2, 3/2)

Bramwell (2001) PRL 87, 047205

Zone boundary
○: X point
●: Magnetic Bragg peak





Lately, confirmed by polarized neutron scattering

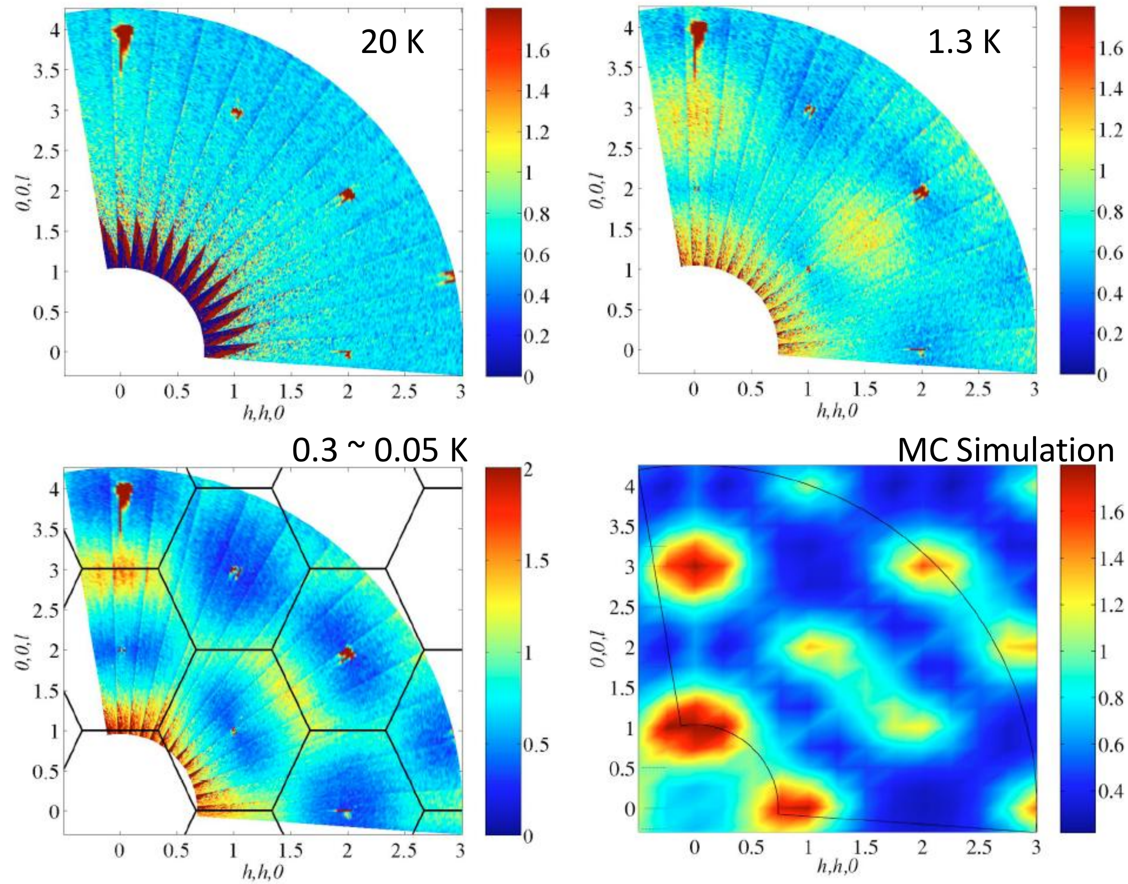
Fennel et al (2009), Science 326, 415

Neutron scattering in $^{162}Dy_2Ti_2O_7$

Dy naturally contains several isotopes and some of them are strong neutron absorber.

TABLE I. Isotopic abundances and absorption cross sections (σ_a) of natural dysprosium and the enriched sample used in these experiments (Ref. 32).

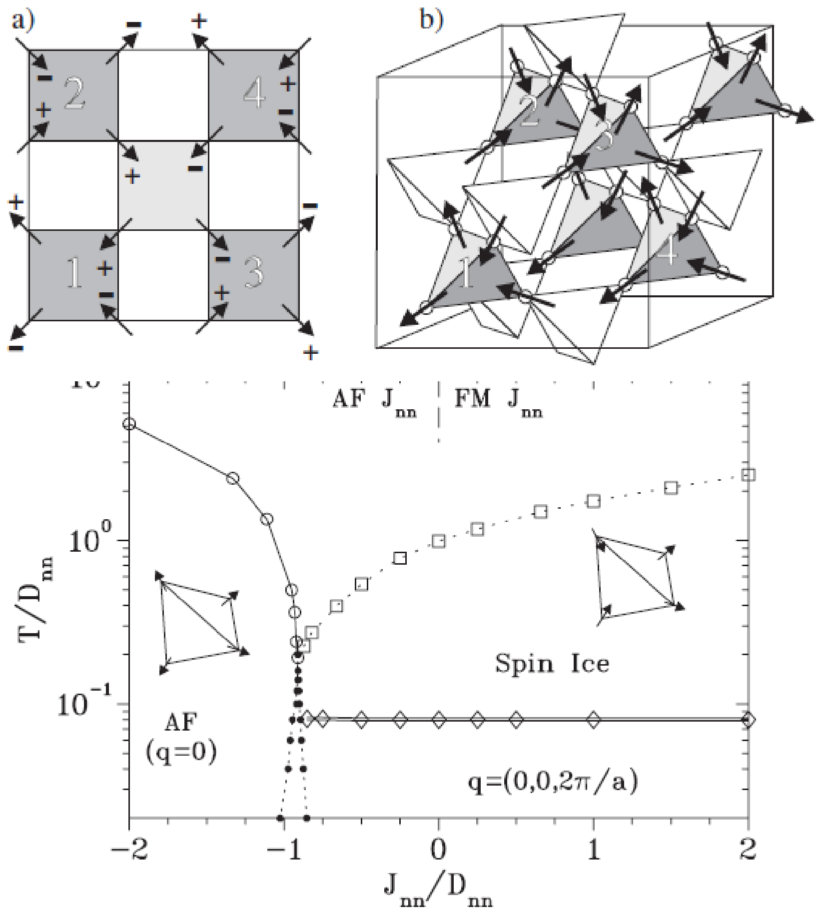
Isotope	Natural Abundance (%)	Sample Content (%)	σ_a (barn)
Natural			994.(13.)
^{156}Dy	0.06	<0.01	33.(3.)
^{158}Dy	0.1	<0.01	43.(6.)
^{160}Dy	2.34	0.02	56.(5.)
^{161}Dy	19	0.47	600.(25.)
^{162}Dy	25.5	96.8	194.(10.)
^{163}Dy	24.9	2.21	124.(7.)
^{164}Dy	28.1	0.5	2840.(40.)
Sample			207.6



Spin ice correlation develops below 1.3 K

Long-range order in Dipolar Spin Ice

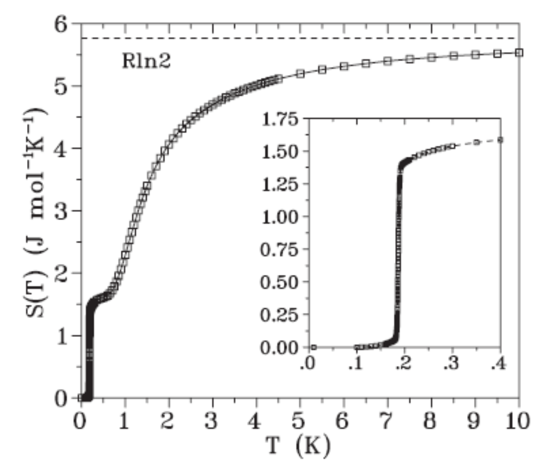
(0, 0, 2π/a) Phase



Dipole type interaction is "complicated".

1. Anisotropic $(S_i \cdot r_{ij}) \cdot (S_j \cdot r_{ij})$
2. Long ranged (~ $1/r^3$, D_{nnn} ~ 0.2 D_{nn})

Loop Monte Carlo simulation shows the long-range ordered state



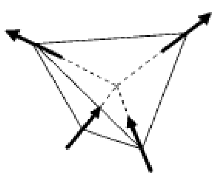
No experimental evidence down to 50 mK.
(Due to the 1st order phase transition nature?)

Melko et al. (2001) PRL 87, 067203
Melko (2004) J. Phys. Condens. Matter 16, R1277

“Dipolar Spin Ice” and/or “Nearest-neighbor model”

“Ice rule”

Local constraint from nearest-neighbor interaction in a tetrahedra



Rare earth (Ho, Dy) contains large magnetic moment $10\mu_B$

“Dipole spin ice”

$$H = -J \sum_{\langle ij \rangle} \mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j} + D r_{\text{nn}}^3 \sum_{j>i} \frac{\mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j}}{|\mathbf{r}_{ij}|^3} - \frac{3(\mathbf{S}_i^{z_i} \cdot \mathbf{r}_{ij})(\mathbf{S}_j^{z_j} \cdot \mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5}$$

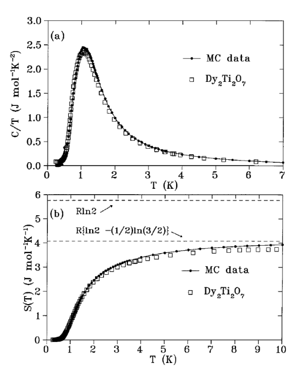
Long-ranged interaction

Ewald method
(Loop MC)
Infinite distance

Truncation of dipole interaction by 5^{th} or 12^{th} NN.

Partial LRO, no ice rule

Ice rule preserved
Heat capacity data OK.



Why does the infinite distance result resemble the nearest-neighbor interaction more than a truncated interaction?

"Projective equivalence"

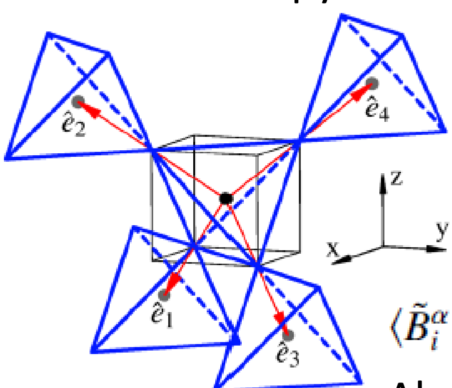
Start from NN Heisenberg

$$H = \sum_{(i,j)} \vec{S}_i \cdot \vec{S}_j$$

With local constraint

$$\sum_{i \in \otimes} S_i^{\alpha} = 0$$

Define artificial vector field from spin on vertex of pyrochlore lattice



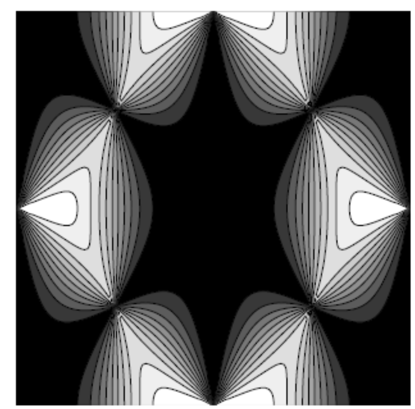
$$\vec{B}_i = \vec{S}_i^{\alpha} \hat{e}_i$$

$$\langle \tilde{B}_i^{\alpha}(\mathbf{x}) \tilde{B}_j^{\beta}(0) \rangle \propto \delta_{\alpha\beta} \frac{3x_i x_j - r^2 \delta_{ij}}{r^5},$$

Algebraic long-distance behavior!

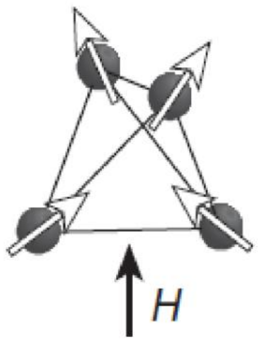
"one can construct a model dipole interaction, by adding terms of shorter range, which yields *precisely the same ground states, and hence T =0 entropy, as the nearest-neighbor interaction.*"

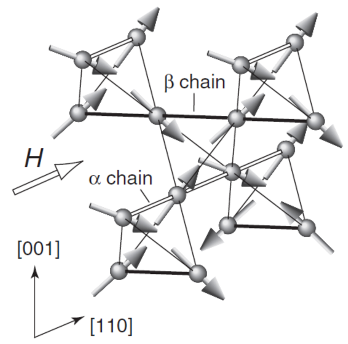
Pinch-point in S[hhk]



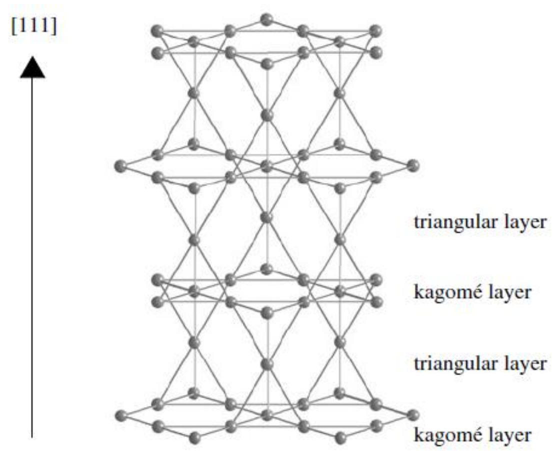
"In short, dipolar spins are ice because ice is dipolar."

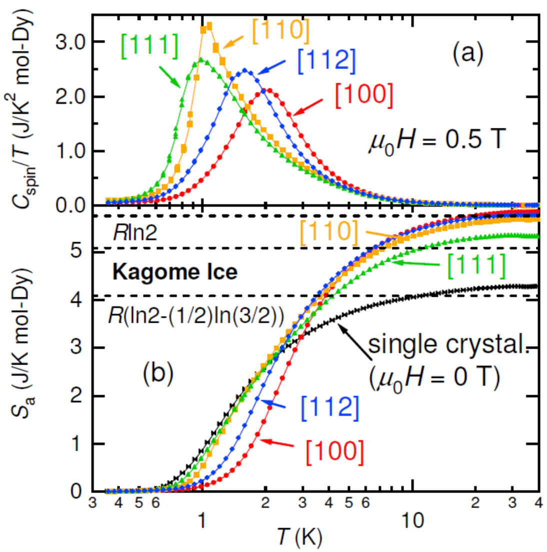
S.V. Isakov, R. Moessner and S.L. Sondhi, PRL 93, 167204 (2004) ; PRL 95, 217201 (2005)





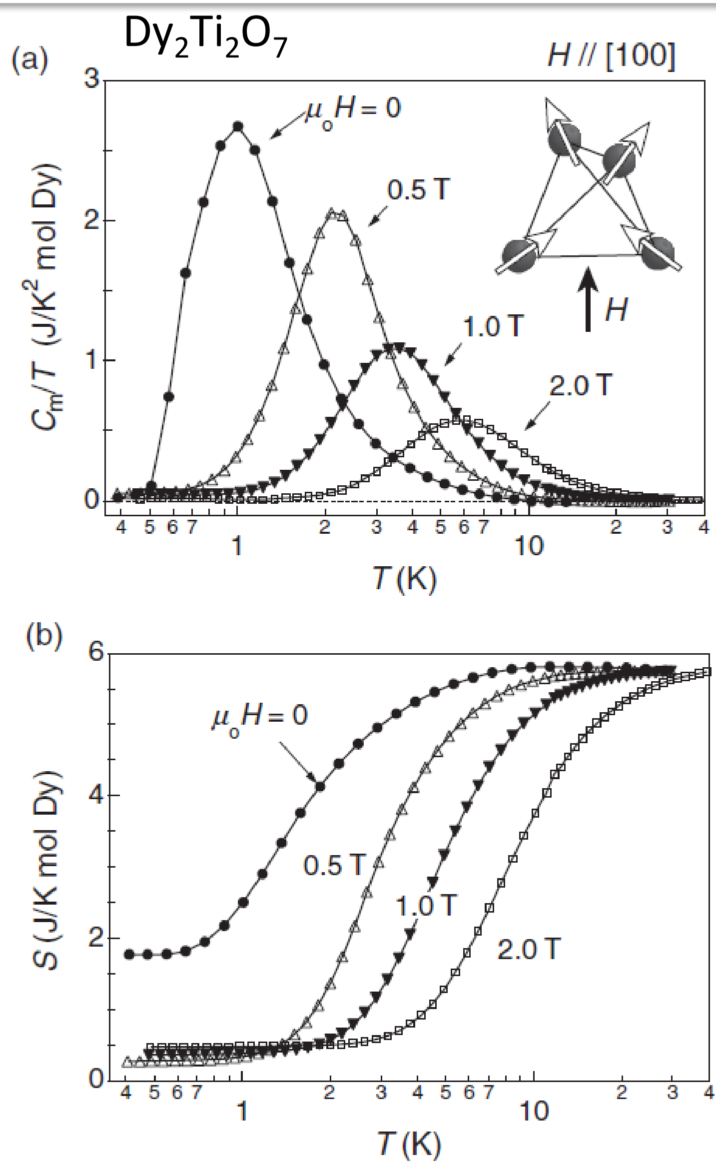
SPIN ICE UNDER MAGNETIC FIELD



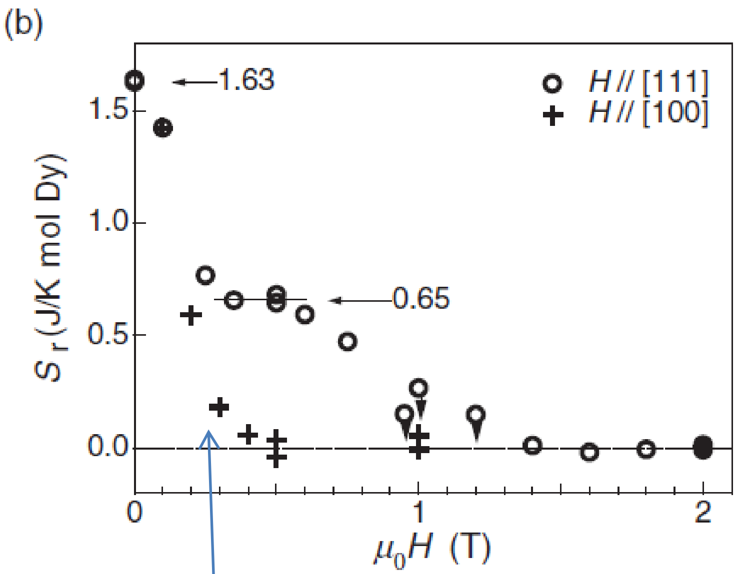


Spin Ice: H // [100]

Hiroi (2003) JPSJ 72, 411-418



Only one configuration preferred without breaking ice rule.

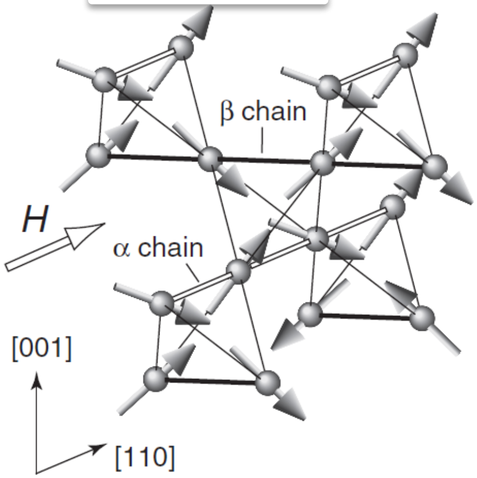


Release of residual entropy by applying field

Spin Ice: H // [110]

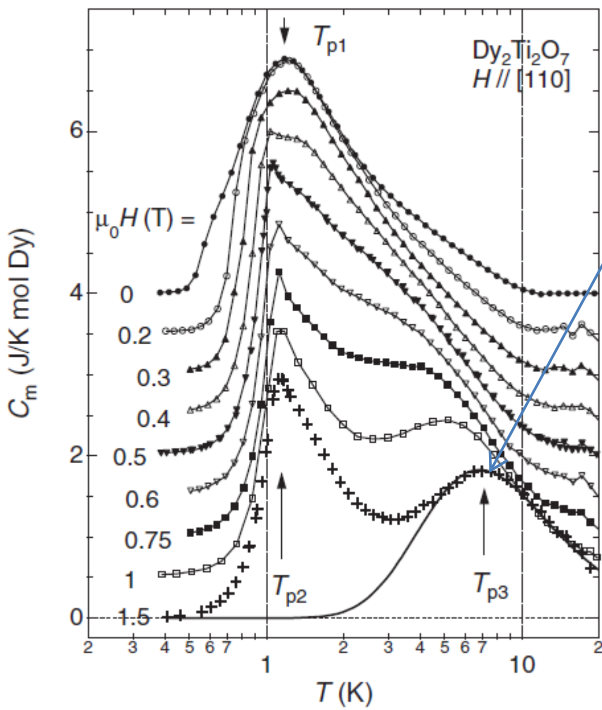
Hiroi (2003) JPSJ 72,3045-3048

H // [110]



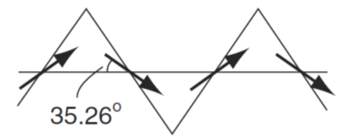
2 spins couple (α chain)
2 spins free (β chain)

$Dy_2Ti_2O_7$



Heat capacity of α chain
(Schottky-type)

$$C_\alpha = \frac{R(\Delta/2k_BT)^2}{2\cosh^2(\Delta/2k_BT)}, \Delta = 2p_{eff}\mu_B H\cos\theta$$



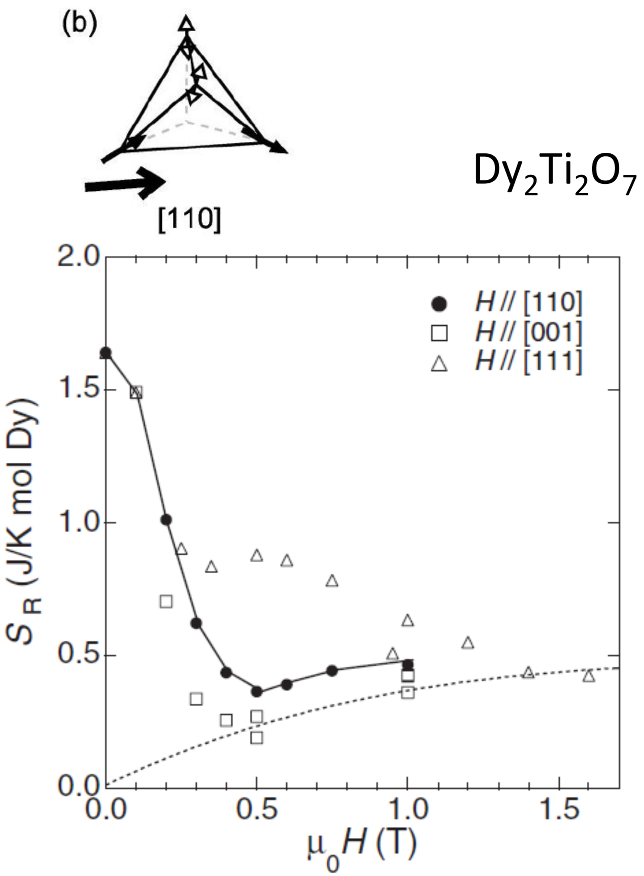
θ = 35.26°

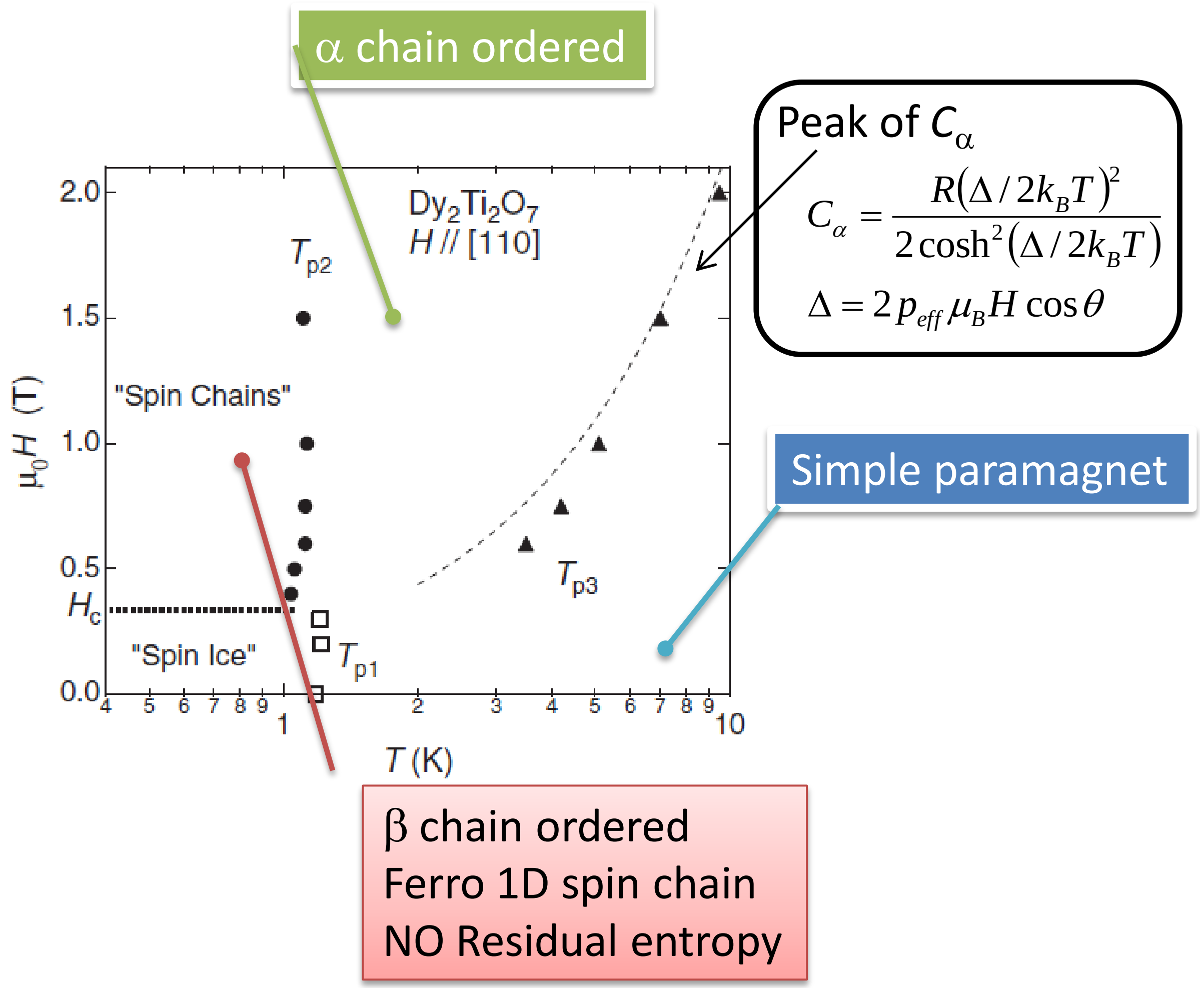
Fitting works very well without any adjustable parameters.

Higher temperature peak comes from α chain.
In turn, lower one from β chain.

Spin Ice: H // [110]

Hiroi (2003) JPSJ 72,3045-3048

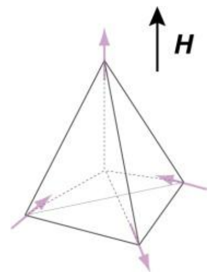




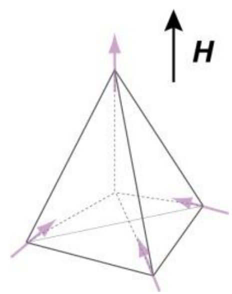
Residual entropy is released by field.
No macroscopic degenecy in "spin chains" phase.

Spin Ice: H // [111]

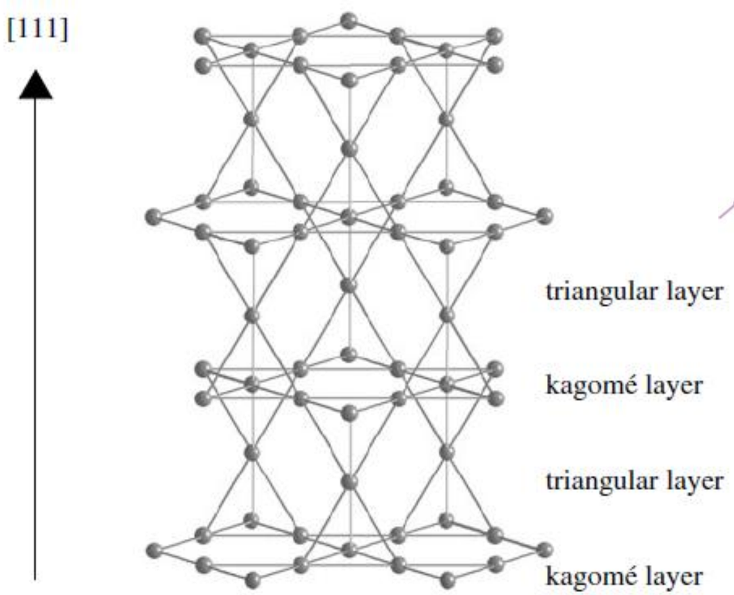
Along [111], Pyrochlore lattice consists alternating triangular and kagomé layers.

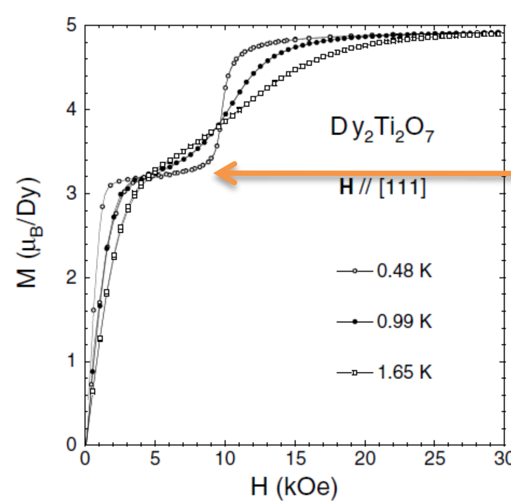


Spins on triangular layer are fixed to [111]. Others on kagomé layer form 2-in 1-out/1-in 2-out
(up spins are preferred).



All spins point to upward.
Ice-rule broken state.
3-in 1-out / 1-in 3-out





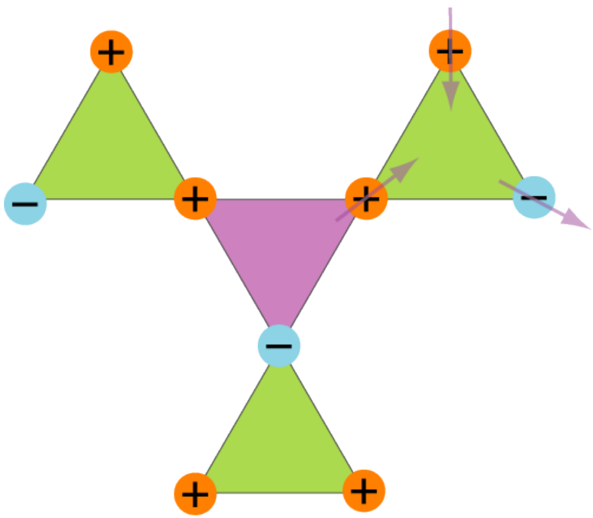
$M_{sat}/2$: 3-in 1-out

$M_{sat}/3$: kagomé ice

Matsuhira (2002) J. Phys.: Condens. Matter 14 L559

Residual entropy in kagomé ice

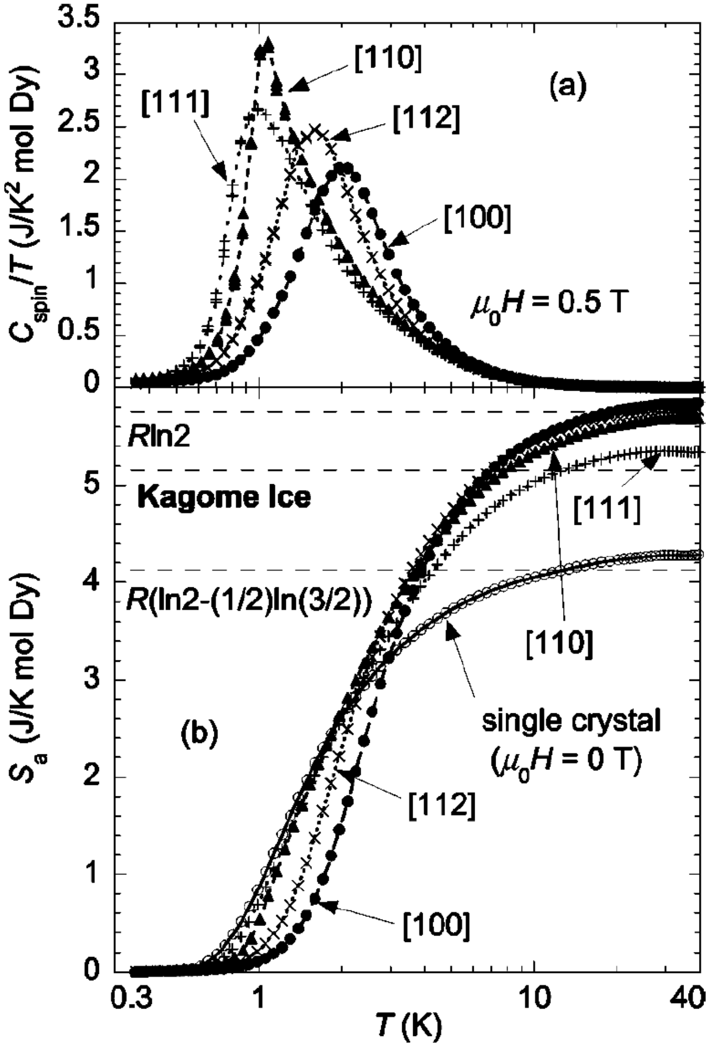
Rough estimation for 4 triangles

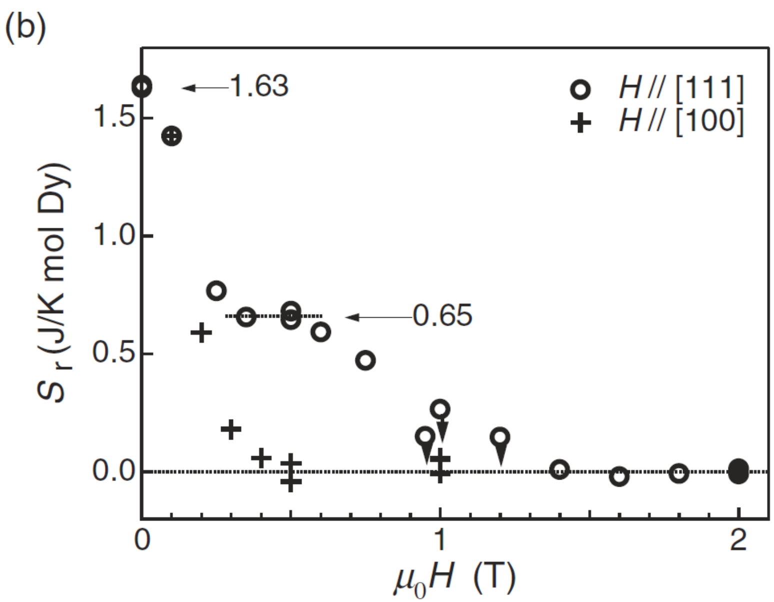


Number of spins	*N*
Number of triangle (3/2 spins/triangle)	Up *N*/3 : Down *N*/3
Spin configurations for up triangles	$3^{N/3}$
Allowed state for down triangle	$\left(\frac{3\times2\times2}{27}\right)^{N/3}=\left(\frac{4}{9}\right)^{N/3}$
Number of spins on kagomé plane	3/4
$S=k_B \ln W$ per Dy-mol	$\frac{3}{4}k_B\ln 3^{N/3}\left(\frac{4}{9}\right)^{N/3}=0.0719R=0.598\frac{\mathrm{J}}{\mathrm{K\cdot Dy\text{-}mol}}$
Exact (dimer model on honeycome) R. Moessner and S.L. Sondhi (2001) PRB 63, 224401 M. Udagawa, M. Ogata and Z. Hiroi (2002) JPSJ 71, 2365	0.0808 *R* = 0.672 J/K Dy-mol

Kagomé Ice

$Dy_2Ti_2O_7$, H = 0.5 T





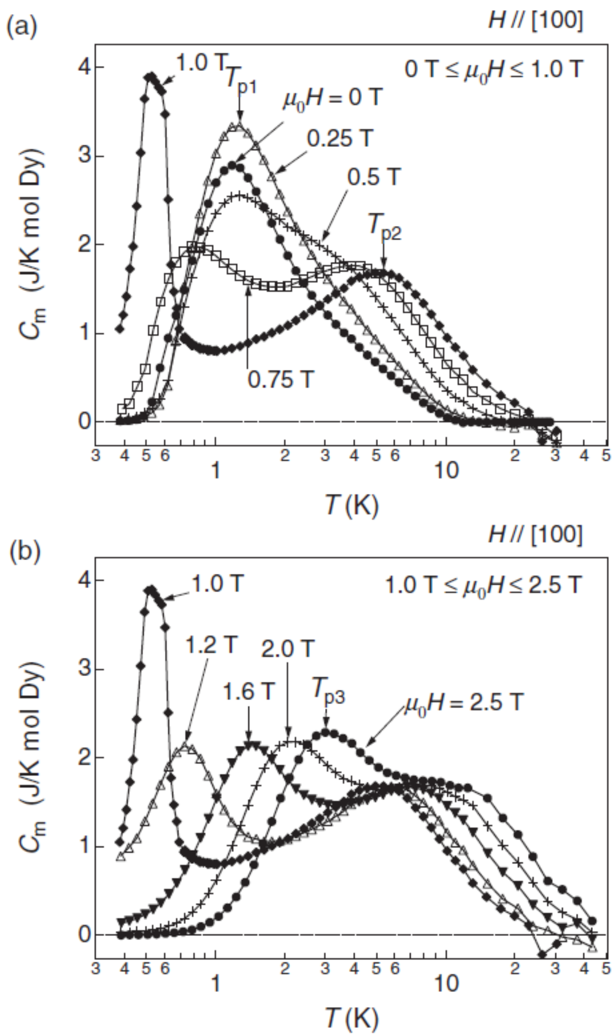
Residual entropy of spin ice is confirmed.
0.65 J/K Dy-mol ~ $S_{kagomé\ ice}$0.67 J/K Dy-mol

Higashinaka (2003) PRB 68, 014415

Hiroi (2003) JPSJ 72, 411-418

Phase diagram: H [111]

Heat capacity measurement of $Dy_2Ti_2O_7$



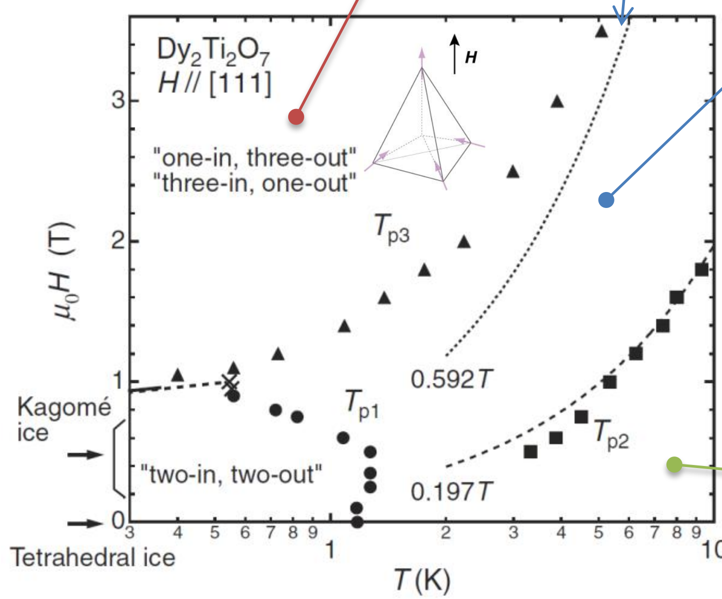
All spin up

$$k_B T_{p3} = 0.38 \times (2 p_{eff} \mu_B H)/3$$

1 UP
3 free

Zeeman splitting of apical spin on triangular plane

$$k_B T_{p2} = 0.38 \times (2 p_{eff} \mu_B H)$$



Paramagnetic

Hiroi (2003) JPSJ 72, 411-418

Résumé

➢Ferromagnetic Heisenberg model with easy axis on pyrochlore turns to AF Ising spin requiring ice-rule.

$$H=\frac{D}{2}\sum_{K,\kappa}(\hat{\mathbf{d}}_\kappa\cdot\mathbf{S}_{K,\kappa})^2+J\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j=DN-\frac{J}{3}\sum_{\langle i,j\rangle}T_iT_j$$

➢Pyrochlore oxides, $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ are the best two materials hosting spin-ice state.

➢Residual entropy of ice Rln(3/2)/2 = 1.68 J/K Dy-mol is fairly confirmed in spin ice.

- Pylochlore spin ice system is much simpler than water ice.
- Total entropy Rln(2), magnetic entropy dominant below $k_B T < 10\,J$

➢Neutron scattering experiments show evidence of long-ranged dipole interaction

"Spin ices are dipolar"

➢Anisotropic behavior of *M* and *C* under magnetic field along [100], [110], [111] can be well understood by the spin-ice model

➢Another frustrated state with residual entropy, kagomé ice state, is found under H // [111]