5. Spin ice

5.1. Pyrochlore Ising model and ice rules

Pyrochlore lattice $\hat{=}$ fcc lattice with 4 atoms per unit cell

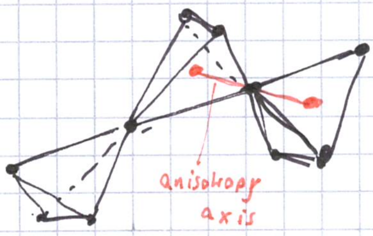
$\hat{=}$ lattice of corner-sharing tetrahedra (2 tetrahedra per unit cell)

Crystal field follow local symmetry

↝ defines local anisotropy axes which connect centers of neighboring tetrahedra

∃ pyrochlore magnets with easy-axis anisotropy ↝ „spin ice"

with easy-plane anisotropy ↝ „pyrochlore XY"



„Classical" spin-ice compounds: $Dy_2Ti_2O_7$, $Ho_2Ti_2O_7$

$J = 15/2$ $\qquad J = 8$

have large spins and $D < 0$ anisotropies.

DS_z^2, S_z in local axis

↝ atomic ground state is Ising doublet.

Exchange interaction J is typically ferromagnetic,

but easy axes of neighboring moments are not parallel!

$(\hat{z}_1^{out} \cdot \hat{z}_2^{out} = -\frac{1}{3})$

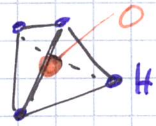
↝ ferromagnetic interaction is frustrated (!),

energy is minimized by all configurations where 2 spins point in to and 2 spins point out of a tetrahedron.

antiferromagnetic interaction is unfrustrated and yields all-in-all-out state.

Local configuration „2 in, 2 out" is called ice rule.

Similar physics is realized in water ice (H_2O), where heavy oxygen atoms sit in centers of tetrahedra, and each hydrogen (proton) at a corner, shared by two oxygens. Energy minimum is reached if 2 out of 4 hydrogens are closed to one oxygen.



Ice rule is satisfied by 6 of $2^4 = 16$ states of single tetrahedron.

↷ Classical ground-state manifold is highly degenerate.

Estimate of residual entropy (Pauling 1950):

total number of states

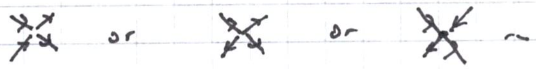
$$S/N_s = k_B \ln 2^{N_s} \left(\frac{6}{16}\right)^{N_t} \underset{N_s = 2N_t}{=} k_B \ln \sqrt{\frac{3}{2}} = k_B \frac{1}{2} \ln \frac{3}{2}$$

2^{N_s}: # of spins; N_t: # of tetrahedra

This degenerate ground-state manifold defines a classical spin liquid.

5.2. Artificial magnetostatics & spin correlations

Ice rule „two-in, two-out" can be re-interpreted:

If spins are regarded as fluxes of a vector field, then this must be divergence-free in each tetrahedron: 

Formally, define magnetisation per tetrahedron α:

$$\vec{M}(\vec{r}_\alpha) = \sum_{i\in\alpha} \vec{S}_i$$

Microscopically and with ice rules obeyed, $\vec{M}$ can take 6 values, proportional to $\pm(1,0,0)$, $\pm(0,1,0)$, $\pm(0,0,1)$.

Now perform coarse graining $\vec{M}(\vec{r}_\alpha) \to \vec{M}(\vec{r})$ $\underbrace{\text{smooth}}$.

Ice rule then implies

$$\boxed{\vec{\nabla}\cdot\vec{M} = 0}$$

„Emergent magnetostatics" ($\rightsquigarrow \vec{M} = \vec{\nabla}\times\vec{A}$)

Ice rule, and thus $\vec{\nabla}\cdot\vec{M} = 0$, will be violated by monopole defects, see below.

At finite temperatures, not all types of states from spin-ice manifold are equally probable $\curvearrowright$ „entropic" selection.

Large $\vec{M}(\vec{r})$ corresponds to few configurations (all spins must align in similar fashion on neighboring tetrahedra); small $\vec{M}(\vec{r})$ corresponds to many configurations. Gibbs free energy is entropic:

$$G[M(\vec{r})] = \frac{T}{V}\int d^3r \, \frac{K}{2}\,|M(\vec{r})|^2$$

const parameter (K)

„Coulomb phase"

This alone would give (via $G = T\sum_k \frac{K}{2}|M(\vec{k})|^2$)

$$\langle M_\mu(\vec{k})\, M_\nu(-\vec{k})\rangle = \int \mathcal{D}M\, e^{-G/T} M_\mu M_\nu = \frac{\delta_{\mu\nu}}{K}$$

However, $\vec{\nabla}\cdot\vec{M}=0$ implies $\vec{k}\cdot\vec{M}(\vec{k})=0$, and hence forces $\vec{M}$ to be orthogonal to $\vec{k}$:

$$\langle M_\mu(\vec{k})\; M_\nu(-\vec{k})\rangle = \frac{1}{K}\left(\delta_{\mu\nu}-\frac{k_\mu k_\nu}{|\vec{k}|^2}\right)$$

Fourier transform back to real space:

$$\underline{\langle M_\mu(0)\; M_\nu(\vec{r})\rangle \propto \frac{1}{K}\,\frac{\delta_{\mu\nu}-3\hat{r}_\mu\hat{r}_\nu}{r^3}} \qquad \hat{r}_\mu=\frac{r_\mu}{|\vec{r}|}$$

This looks like <u>dipolar</u> correlations (!).

<u>Remarks</u>

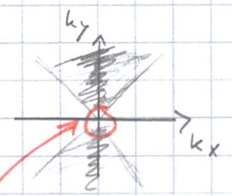
- Spin correlations are <u>long-ranged</u> ! in real space (power-law decay), despite spin-liquid nature of state.

- Momentum-space structure implies singular points:

  E.g. $\mu=\nu=1$

$$\langle M_1(\vec{k})\; M_1(-\vec{k})\rangle \propto \left(1-\frac{k_x^2}{k_x^2+k_y^2+k_z^2}\right)$$

Focus on xy plane $\quad \propto \dfrac{k_y^2}{k_x^2+k_y^2}$



pinch point

$$\lim_{k_x\to 0}\lim_{k_y\to 0} \neq \lim_{k_y\to 0}\lim_{k_x\to 0}$$

5.3. Monopole excitations

[001] field

2in - 2out states form ground-state manifold of spin ice.

Excited states arise from violations of ice rule.

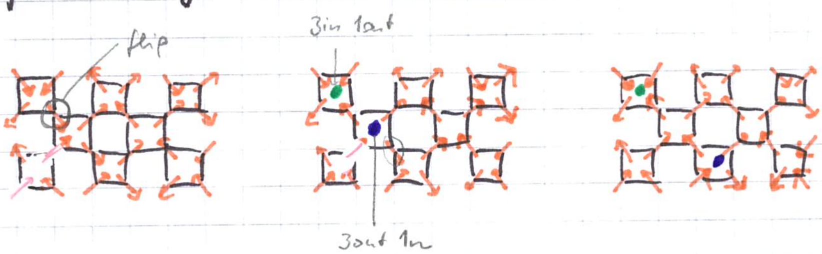
Single tetrahedron : 3in - 1out , 3out - 1in $\hat{=}$ lowest excitations

all in , all out $\hat{=}$ higher excitations

Flipping one spin in spin-ice state involves two tetrahedra and creates 3in - 1out + 3out - 1in state. Further spin flips can separate these two point defects.

→ Dipole excitation (spin flip) fractionalizes into monopole + antimonopole.

Projected config:



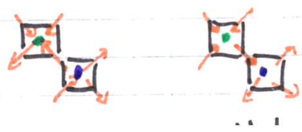
spin-ice config — monopole-antimonopole pair after one spin flip — two spin flips

Classical spin ice is simple (simplest?) example for fractionalization in three space dimensions.

Monopoles are sources and sinks of emergent magnetic field $\vec{M}$.

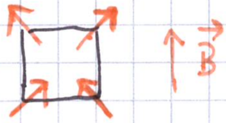
Remarks

- Monopole and antimonopole can seperate, but remain connected by chain (or „string") of flipped spins.
- Neighboring pair of monopole + antimonopole cannot



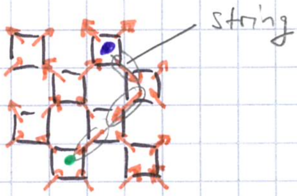
Magnetic-field „tuning" of monopoles

Field ∥ [001] and equivalent directions



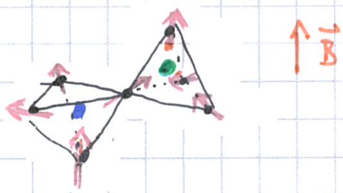
↝ polarizes spins compatible with ice rules

↝ ground state is given by single ice state (w/o monopoles)



In this background, monopole-antimonopole pairs are connected by directed strings. Their entropic formation can be detected in spin correlations.

Field ∥ [111] and equivalent directions

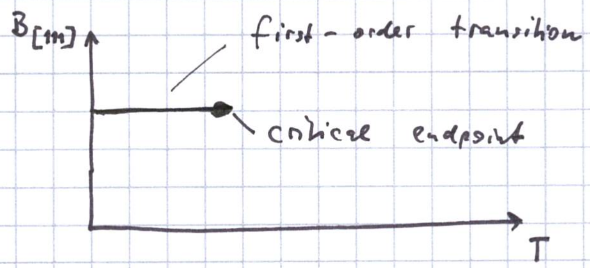


↝ polarizes spins such that field-dominated state has half of all tetrahedra w/ monopole and —//— w/ antimonopole

↝ field acts like (staggered) chemical potential for monopoles

↝ exchange interaction (wants ice rule obeyed) and field (want staggered monopole config) compete!

↝ phase transition as function of [111] field (no symmetry breaking!)



$\hat{=}$ $\boxed{\text{liquid-gas transition of monopoles}}$!!

(this requires interaction between monopoles, comes partially from dipolar interactions, see 5.4.)

5.4. Dipolar spin ice

In many spin-ice compounds, moments are large and exchange interaction is small $\curvearrowright$ dipolar interaction NOT negligible.

$Dy_2Ti_2O_7$ $(Dy: J = 15/2)$, $Ho_2Ti_2O_7$ $(Ho: J = 8)$

Hamiltonian:

$$\boxed{H = -J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + D r_{nn}^3 \sum_{i>j} \frac{\vec{S}_i \cdot \vec{S}_j - 3(\vec{S}_i \cdot \hat{r}_{ij})(\vec{S}_j \cdot \hat{r}_{ij})}{|r_{ij}|^3}}$$

where local Ising moment is $\vec{S}_i = \underset{\pm 1}{\sigma_i} \; \underset{\text{local axis}}{\hat{z}_i}$,

$\hat{r}_{ij} = \vec{r}_{ij} / |\vec{r}_{ij}|$, and r_{nn} is nearest-neighbor distance,

$D = \frac{\mu_0}{4\pi} \frac{\mu^2}{r_{nn}^3}$, $\mu \approx 10 \mu_B$

Numbers for $Dy_2Ti_2O_7$:

Dipolar coupling at nearest-neighbor sites: $D_{nn} = \frac{5D}{3} \simeq 2.35$ K

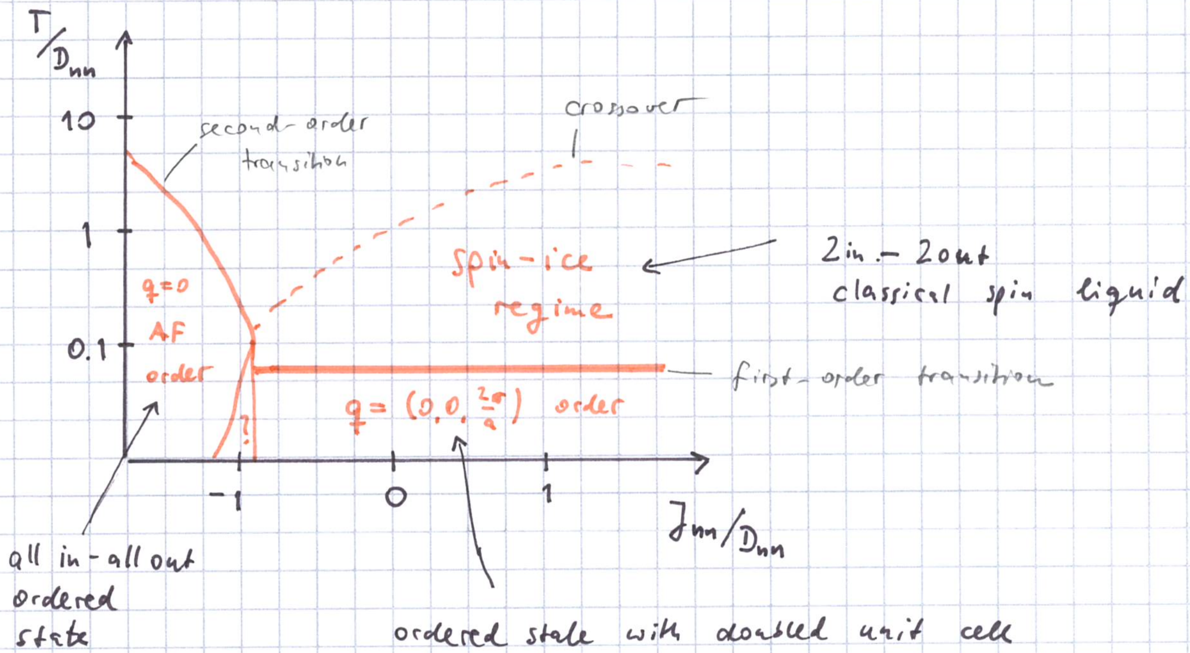
Nearest-neighbor exchange coupling $J_{nn} = J/3 \simeq -1.24$ K (antiferro!)

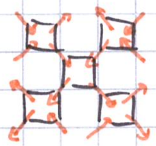
$\hat{z}^a \cdot \hat{z}^b = -1/3$

$\curvearrowright$ Effective nearest-neighbor coupling $J_{eff} = D_{nn} + J_{nn} \simeq +1.1$ K (ferro)

Dipolar spin-ice model has physics beyond the nearest-neighbor ice model (which is a classical spin liquid).

Phase diagram of dipolar spin-ice model (from Monte-Carlo)





(crystallographic unit cell has one up and one down tetrahedron; this phase has two different up tetrahedra)

Ratio J_{nn}/D_{nn} is -0.49 in $Dy_2Ti_2O_7$
-0.27 in $Ho_2Ti_2O_7$

and decreases with smaller lattice constant. (or pressure)

Monopole interactions

In nearest-neighbor spin-ice model, monopole excitations do NOT interact apart from „contact interaction" (creation energy).

In dipolar spin-ice model, the dipolar spin-spin interaction leads to a long-range interaction of monopole excitations which is of $1/r$ form (!), i.e. monopoles behave as magnetic point charges!

Plausibility argument:

$$H_{dip} = D\, r_{nn}^3 \sum_{i>j} \frac{\vec{S}_i \cdot \vec{S}_j - 3(\vec{S}_i \cdot \hat{r}_{ij})(\vec{S}_j \cdot \hat{r}_{ij})}{|r_{ij}|^3}$$

Now replace each spin by pair of „charges" , with charges located in tetrahedra. The above energy is then given by pairwise Coulomb interaction of these charges:

$$\boxed{V(r_{\alpha\beta}) = \begin{cases} \dfrac{\mu_0}{2\pi} \dfrac{Q_\alpha Q_\beta}{r_{\alpha\beta}} & \alpha \neq \beta \\ \dfrac{1}{2} v_0 Q_\alpha^2 & \alpha = \beta \end{cases}}$$

with „self-energy" $v_0 \left(\frac{\mu}{r_{nn}}\right)^2 = \frac{J}{3} + \frac{4}{3}\left(1 + \sqrt{\frac{2}{3}}\right) D$

Apparently, this replacement dipole $\longleftrightarrow$ pair of monopoles is exact in limit „monopole distance $\to 0$"; here it is approximate and holds at long distances.

Note: large v_0 ($\hat{=}$ large J, D) enforces $Q_\alpha = 0$ $\hat{=}$ ice rule!

The above argument implies that monopole excitations in dipolar spin ice act like magnetic point charges, with Coulomb-type interaction.

Recall Maxwell $\operatorname{div} \vec{B} = 0$ — remains true (must!)

but $\boxed{\operatorname{div} \mu_0 \vec{H} = Q}$ is not forbidden

Spin-ice monopole are sources and sinks of $\vec{H}$.

ATTN: Charge Q is not quantized, but depends on microscopics.

Further remarks:

- System with finite density of monopoles and antimonopoles behaves approximately like ionic liquid ($\rightsquigarrow$ magnetolyte).

- Monopole picture is not fully accurate, because it neglects background spin configuration ($\rightarrow$ strings of spin flips) and short-range effects (monopole & anti-monopole cannot always annihilate)

5.5. Experimental situation

$Dy_2Ti_2O_7$ (also $Ho_2Ti_2O_7$, but non-Kramers doublet)

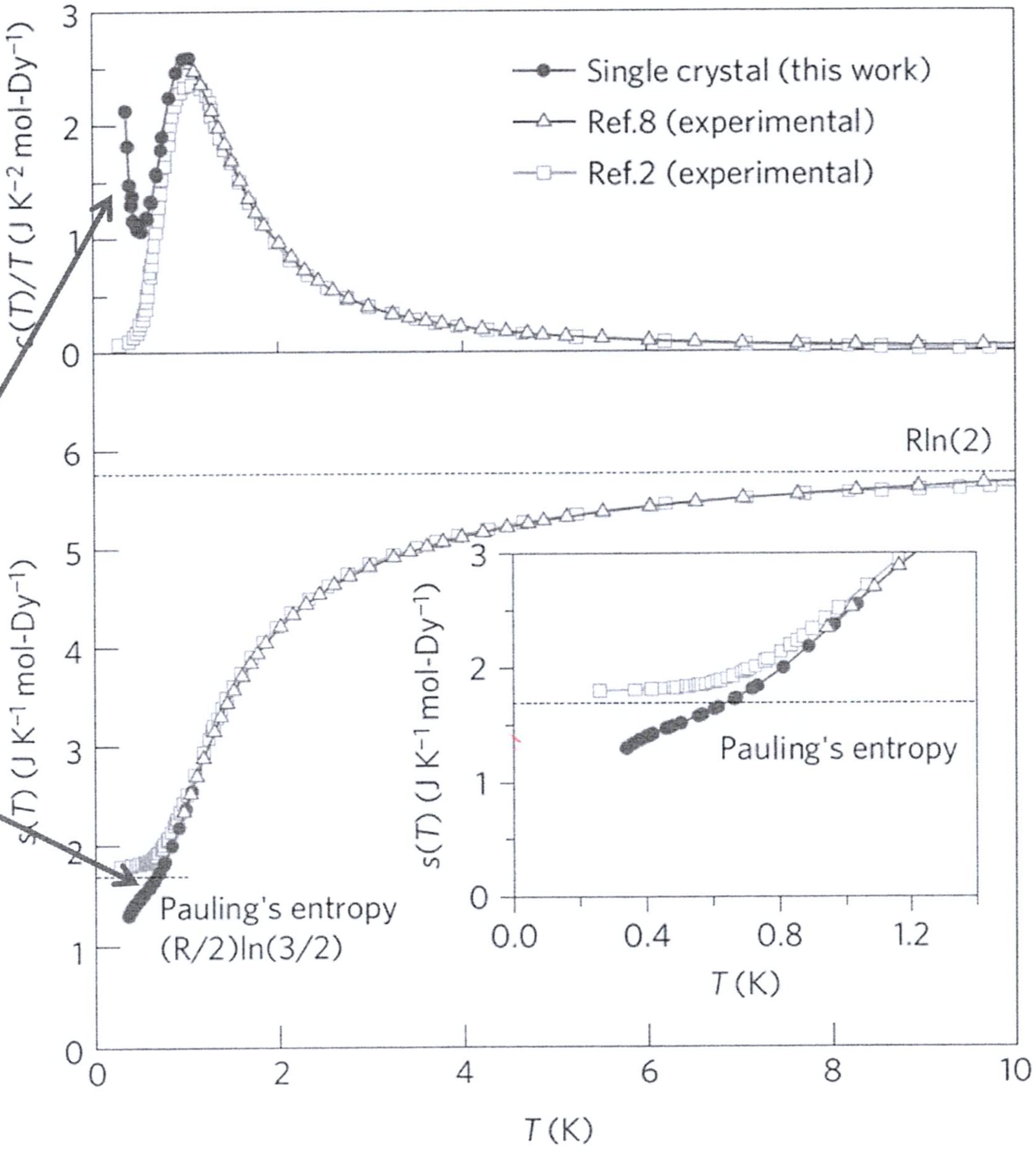
- Pauling entropy seen (?)
- Liquid-gas transition in [111] field seen
- Pinch points seen
- Entropic strings in [100] field "seen"
- Equilibration difficult below 0.5 K (T_{ice} ~ 1K) because monopole annihilation difficult

Open issues:

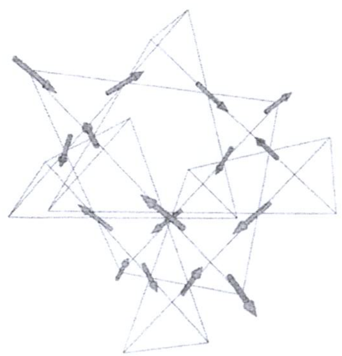
- Role of defects (not fully clear)
- Missing Pauling entropy (2013 paper)
- Low-T order (not seen so far)

Absence of Pauling plateau in $Dy_2Ti_2O_7$?

Specific-heat measurement
with careful equilibration



Defect physics?
Signature of ordering?



$\mathbf{q} = (0, 0, 2\pi/a)$

Pomaranski *et al.*, Nat. Phys. **9**, 353 (2013)

5.6. Quantum spin ice

Classical spin ice: Ising moments on pyrochlore, no spin flips in Hamiltonian
(good approx for large moments with anisotropy $D < 0$)

Quantum spin ice: Moments small (often $J = \frac{1}{2}$), spin-flip terms allowed

Generic nearest-neighbor Hamiltonian: (in rotated $\hat{=}$ local spin basis!)

$$\boxed{\begin{aligned} H = \sum_{\langle ij \rangle}{}' \Big[& J_{zz} S_i^z S_j^z - J_\pm \left(S_i^+ S_j^- + S_i^- S_j^+ \right) \\ & + J_{\pm\pm} \left(\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^- \right) \\ & + J_{z\pm} \left(S_i^z \left(\zeta_{ij} S_j^+ + \zeta_{ij}^* S_j^- \right) + \left(\zeta_{ij} S_i^+ + \zeta_{ij}^* S_i^- \right) S_j^z \right) \Big] \end{aligned}}$$

(includes all symmetry-allowed nearest-neighbor interactions; γ_{ij}, ζ_{ij} are phase factors $1, e^{\pm i 2/3 \pi}$ depending on basis choice)

$J_{zz} \;\hat{=}\;$ classical spin ice

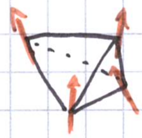
($J_\pm$, $J_{\pm\pm} \;\hat{=}\;$ pyrochlore XY model)

Generically, spin-flip terms connect states from degenerate spin-ice manifold and eliminate residual (Pauling) entropy.

Depending on parameters, various states can emerge.

a) Splayed ferromagnet:

Ferromagnet w/ non-coplanar moments



b) XY-type states „ψ_2", „ψ_3"

Spins oriented in local XY plane

⋮

c) U(1) quantum spin liquid

(Tetrahedron states 3in, 1out, 1in 3out become creation/annihilation operators

Operators for) for spinons, coupled to U(1) gauge field