Spin Ice and Quantum Spin Liquid in Geometrically Frustrated Magnets

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Outline:

1. Introduction of Geometrically Frustrated Magnets (GFM)

   What? & How? & Why?

2. Spin Ice

   1) Structure, Residual entropy

   2) "Dipolar Spin Ice" model

   3) Magnetic monopole

   4) Dynamic spin ice: $Pr_2Sn_2O_7$

   5) Monopole dimers in $Dy_2Ge_2O_7$

3. Quantum Spin Liquid (QSL)

   1) Resonating Valence Bond state, Spinon

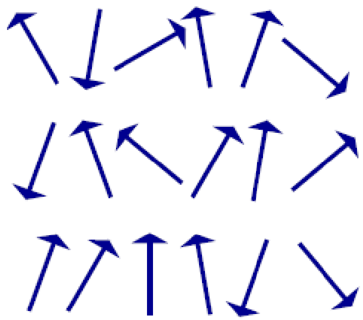
   2) Fermionic-like excitations in insulating QSL

   3) QSL in the $S = 1/2$ triangular lattice $Ba_3CuSb_2O_9$

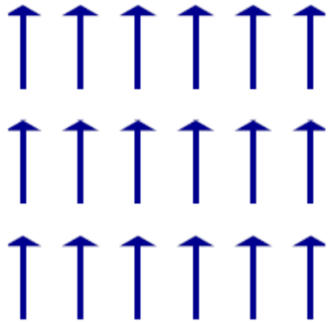
   3) QSL in the $S = 1$ triangular lattice $Ba_3NiSb_2O_9$

4. Summary & Outlook

Non-frustrated magnets

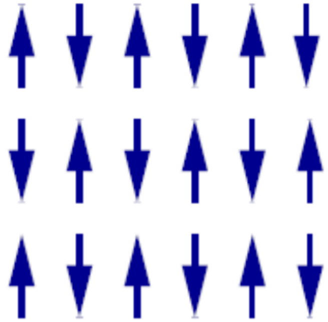


Paramganetism



Ferromagnetism
$T < T_c$

Curie



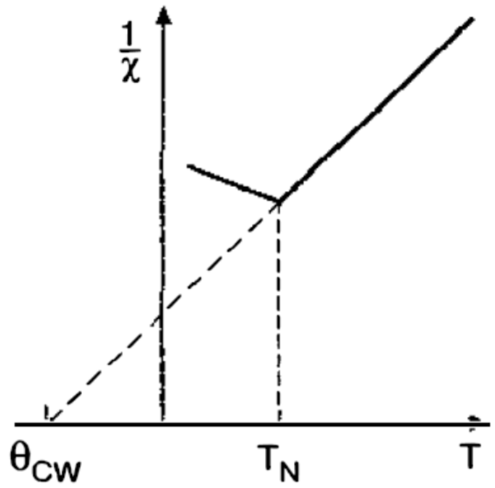
Antiferromagnetism
$T < T_N$

Néel

$$H = -\sum_{ij} J_{ij} S_i \cdot S_j$$

$$T_N = \frac{2}{3} z S(S+1) k_B |J|$$

$$\chi = \frac{C}{T - \theta_{CW}}$$



Non-frustrated $T_N \sim \theta_{CW}$

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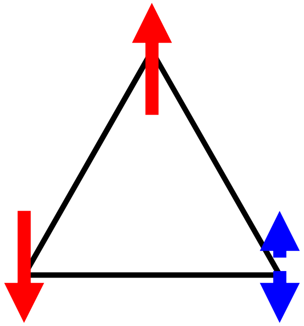
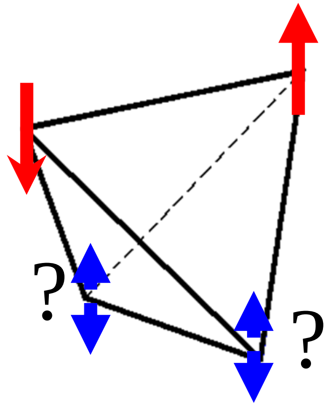
Geometrically Frustrated Lattice

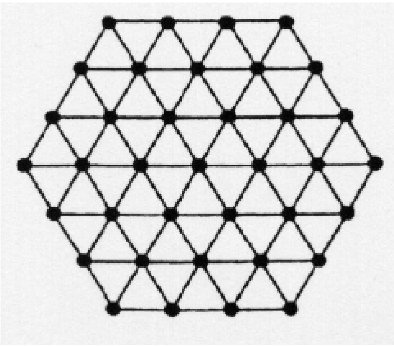




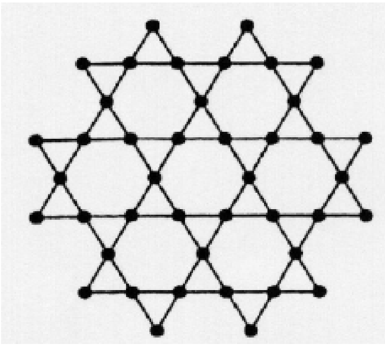
Interactions between magnetic degree of freedom in a lattice are incompatible with the underling crystal geometry ------Frustration

2D

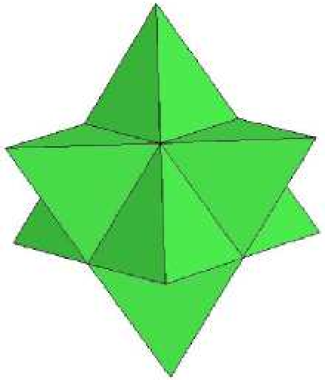
3D



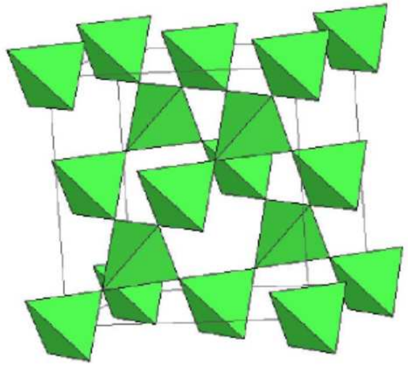
Triangular



Kagome

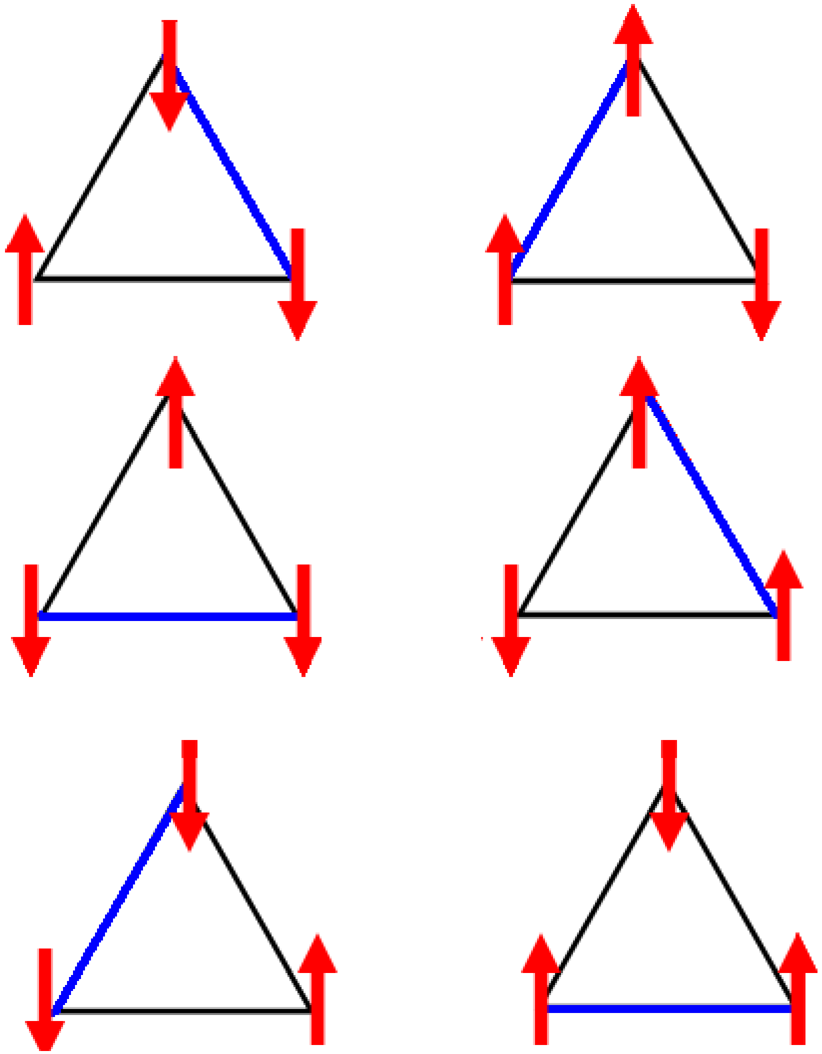


Face centered cubic

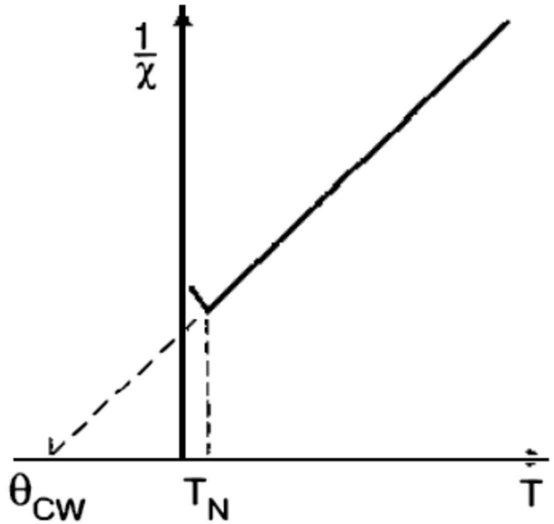


Pyrochlore

Frustration leads to degeneracy



Degeneracies can persist.
When they do:
1. spin fluctuations are enhanced.
2. magnetic ordering is suppressed.



Frustrated $T_N << \theta_{CW}$

Ramirez introduced $f = |\theta_{CW}|/T_N > 10$

The history of “frustration”

*“**Frustration is the name of the game.**” Anderson P. W., Aspen 1976*

MAGNETIC FRUSTRATION AND LATTICE DIMENSIONALITY

RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR ?*

P. W. Anderson
Bell Laboratories, Murray Hill, New Jersey 07974
and
Cavendish Laboratory, Cambridge, England

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(Received December 5, 1972; Invited**)

ABSTRACT

The possibility of a new kind of electronic state is pointed out, corresponding roughly to Pauling's idea of "resonating valence bonds" in metals. As observed by Pauling, a pure state of this type would be insulating; it would represent an alternative state to the Néel antiferromagnetic state for S = 1/2. An estimate of its energy is made in one case.

The s

Department of Physics, Brock University St. Catharines, Ontario L2S 3A1 Canada

(*Received* 1 *April* 1986 *by M.F. Collins*)

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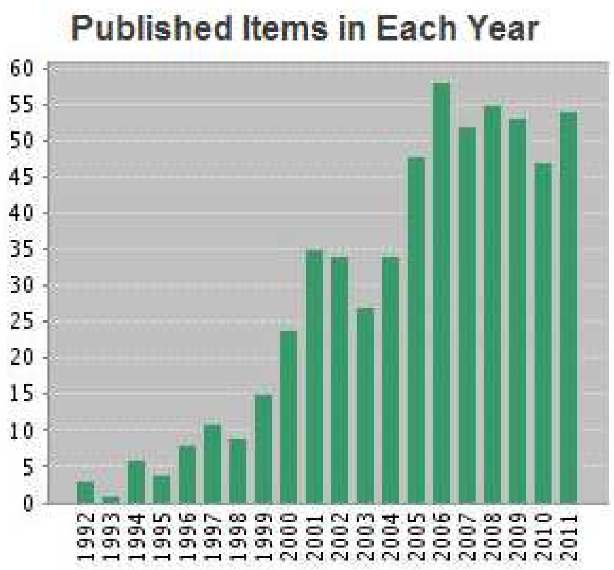
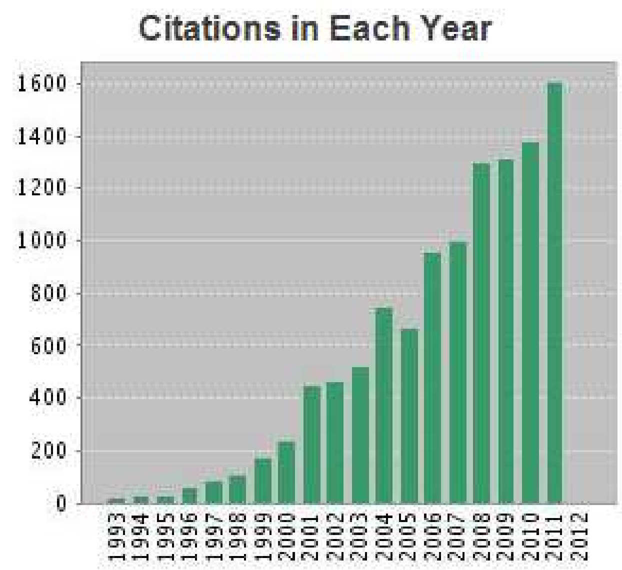
“Geometrically Frustrated” on Web of Science

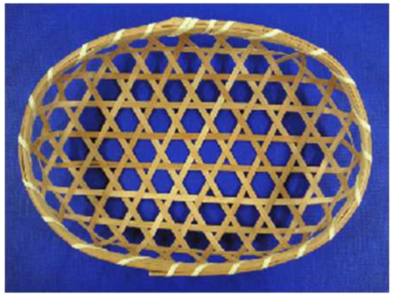




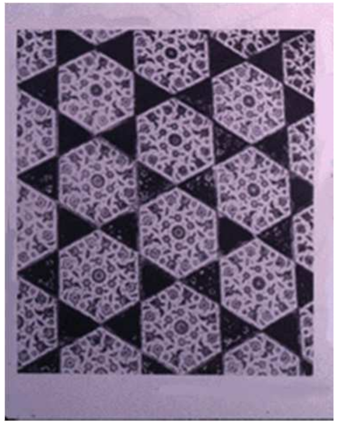
Beyond physics

"Let no one destitute of geometry enter my doors."

Plato (c. 427 - 347 B.C.E.)



Kagome: eyes in the basket



Islamic tiling pattern

Why GFM

Magnetism and Magnetic materials in every day life

New physics

1. Exotic ground states with no magnetic ordering
   show residual entropy and abnormal thermodynamics
   spin ice and quantum spin liquid

2. Suppressed long range ordered state provide abnormal phenomena
   multiferrocity, quantum phase transition, spin lattice coupling

Spin Ice

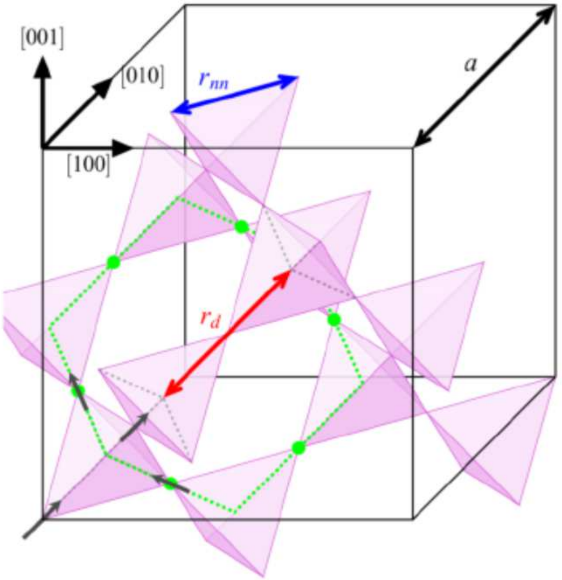
VOLUME 79, NUMBER 13 PHYSICAL REVIEW LETTERS 29 SEPTEMBER 1997

Geometrical Frustration in the Ferromagnetic Pyrochlore $Ho_2Ti_2O_7$

M. J. Harris,[1] S. T. Bramwell,[2] D. F. McMorrow,[3] T. Zeiske,[4] and K. W. Godfrey[5]

$Ho_2Ti_2O_7$, $\theta_{CW} \sim 1.9$ K, no ordering down to 50 mK.

Pyrochlore



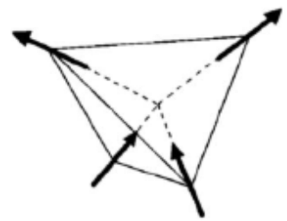
Doublet

	[R]	[R^{3+}]	S	L	J
Dy	[Xe] $4f^{10}$ $6s^2$	[Xe] $4f^9$	5/2	5	15/2
Ho	[Xe] $4f^{11}$ $6s^2$	[Xe] $4f^{10}$	2	6	8

	GS	g_J	μ	Δ (meV)	Δ (K)
Dy	$\lvert 15/2, \pm 15/2 \rangle$	4/3	$\approx 10\ \mu_B$	~ 0.033	~ 380
Ho	$\lvert 8, \pm 8 \rangle$	5/4	$\approx 10\ \mu_B$	~ 0.020	~ 240

Jaubert & Holdsworth, JPCM (2011)

Ising axis <111>
Two in two out



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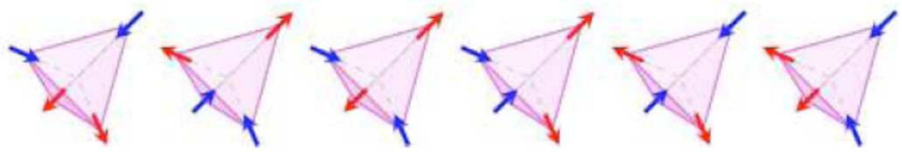
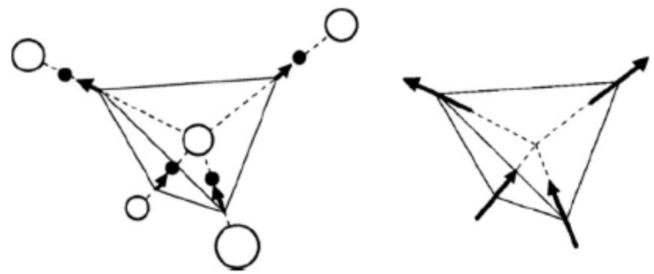
Pauling's water ice entropy



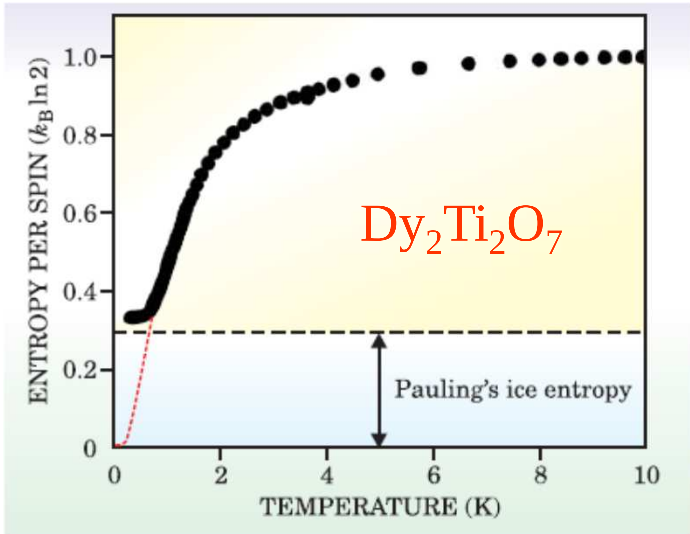


One tetrahedron:
Total number of states: $2^4 = 16$
Total magnetism zero: 6 ground states, fraction 6/16

Pyrochlore lattice, N spins:
Total number of states 2^N
Number of tetrahedra N/2
Total number of ground states: $W = 2^N*(6/16)^{N/2}$

Entropy per spin:
$S_0/k_BN = (1/N)\ln W = 1/2\ln 3/2$
Pauling's entropy for water ice

$$S_0 = S_f - \Delta S = R\ln 2 - \Delta S$$



Ramirez et al., Nature (1999)

Dipolar Spin Ice Model (DSM)

$Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$

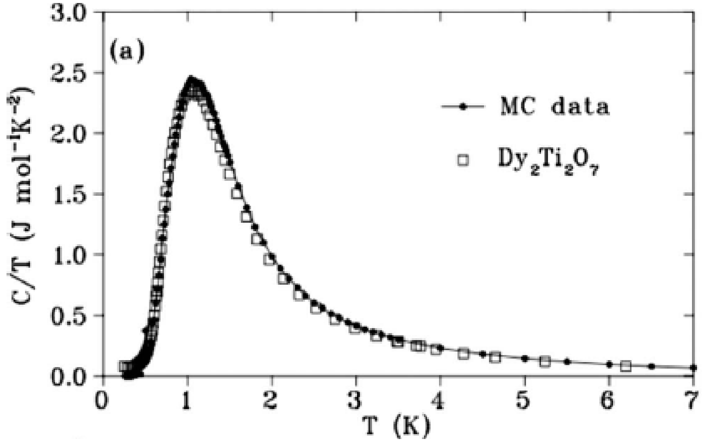
Shielded 4*f* electrons: weak $J_{nn} \sim 1$ K

$$D_{nn} = \frac{5}{3}\left(\frac{\mu_0}{4\pi}\right)\frac{\mu^2}{r_{nn}^3} \sim 2.35\text{K}$$

$$r_{nn} = (a/4)\sqrt{2}$$

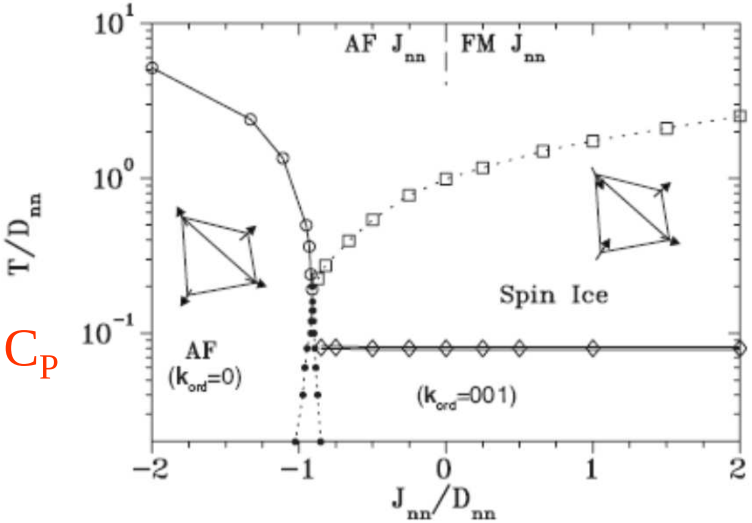
J_{nn}: antiferromagnetic
D_{nn}: ferromagnetic
$J_{eff} = J_{nn} + D_{nn}$

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



Hertog & Gingras, PRL (2000)

T_{peak} of C_P



Melko & Gingras, JPCM (2004)

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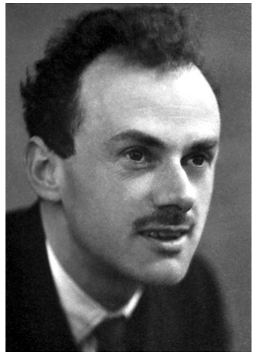
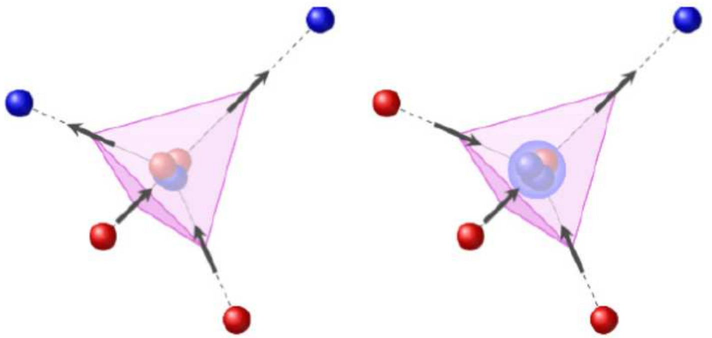
Magnetic monopole

"A magnetic monopole is an isolated particle that acts as a source of a magnetic field" *Paul Dirac , 1931*



Dumbbell model



Magnetic monopole

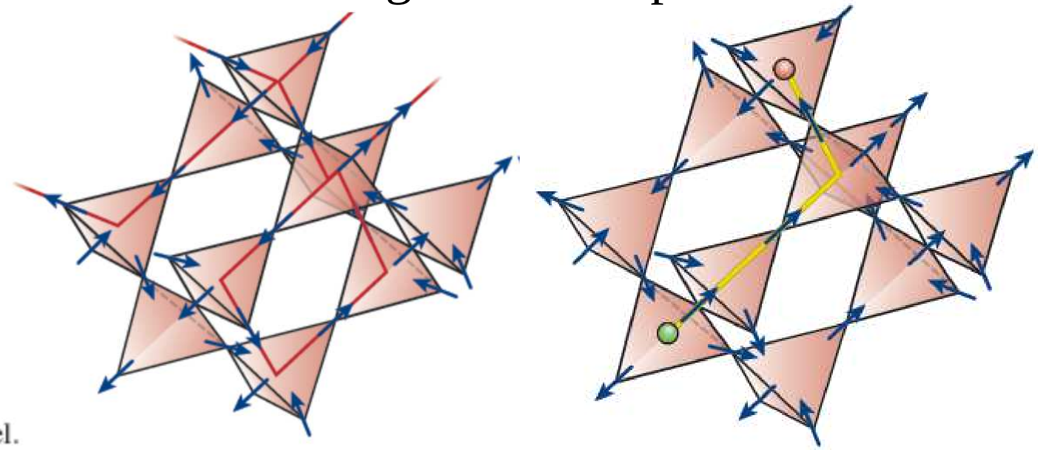


Table 4. Mapping from the dipolar spin ice to the dumbbell model.

Dipolar spin ice	Dumbbell/monopoles
2 in–2 out ground state	Vacuum
3 in–1 out defects (local excitations)	Quasi-particles (monopoles)
Dipolar interactions between magnetic dipoles	Coulomb interactions between magnetic monopoles
Pyrochlore lattice	Diamond lattice
Canonical ensemble	Grand canonical ensemble

$$Q = \frac{2\mu}{r_d} \qquad v_{\min} = -\frac{\mu_0}{4\pi}\frac{Q^2}{r_d} \approx -3\mathrm{K}$$

3 K, create monopole dimers

Jaubert & Holdsworth, JPCM (2011)

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“Popular” monopole

Not fundamental particles but emergent quasi-particles or excitations

Have many characteristics of isolated magnetic charges

Relaxation rate, μ_{SR}, neutron

Castelnovo et al., Nature (2008)
Brawell et al., Nature (2009)
Jaubert & Holdsworth, Nature Phys. (2009)
Fennell et al., Science (2009)
Morris et al., Science (2009)
Giblin et al., Nature Phys. (2011)

#1 sitcom “The big bang theory”
Episode “Monopole expedition”

Sheldon tried his best to find magnetic monopole!

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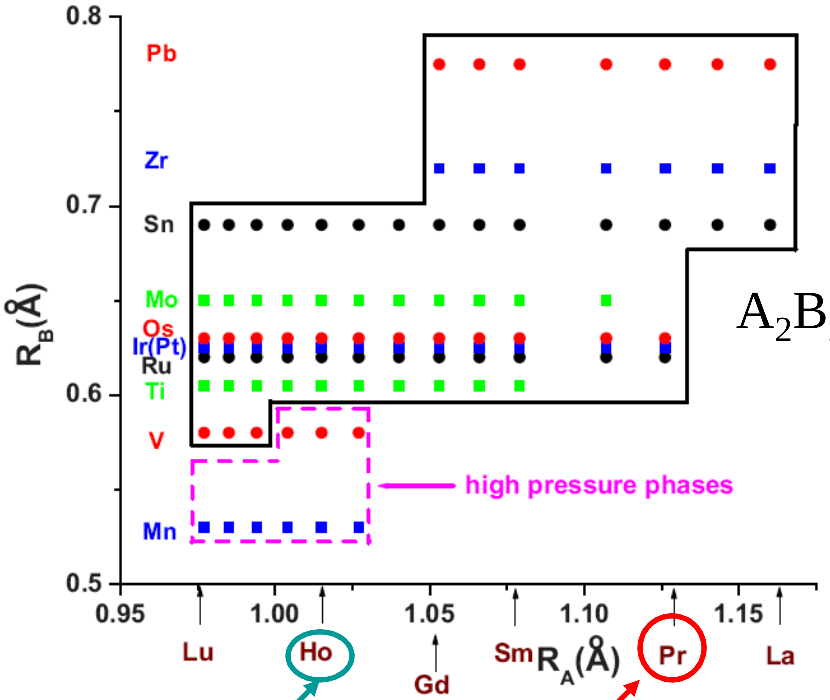
$Pr_2Sn_2O_7$: dynamic spin ice

Zhou et al., PRL (2008)

Change J_{nn}/D_{nn}

Change D_{nn}?



$A_2B_2O_7$ pyrochlore

Gardner et al., Rev. Mod. Phys. (2010)

$\mu_{eff} = 10.6\ \mu_B$ $\mu_{eff} = 3.6\ \mu_B$, $D_{nn} \propto \mu^2$

$Pr_2Sn_2O_7$: No ordering down to 90 mK, doublet ground state
Ising axis along <111>

Matsuhira et al., JPSJ (2002)

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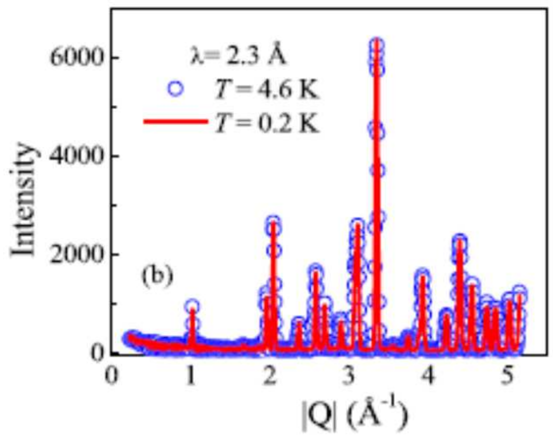
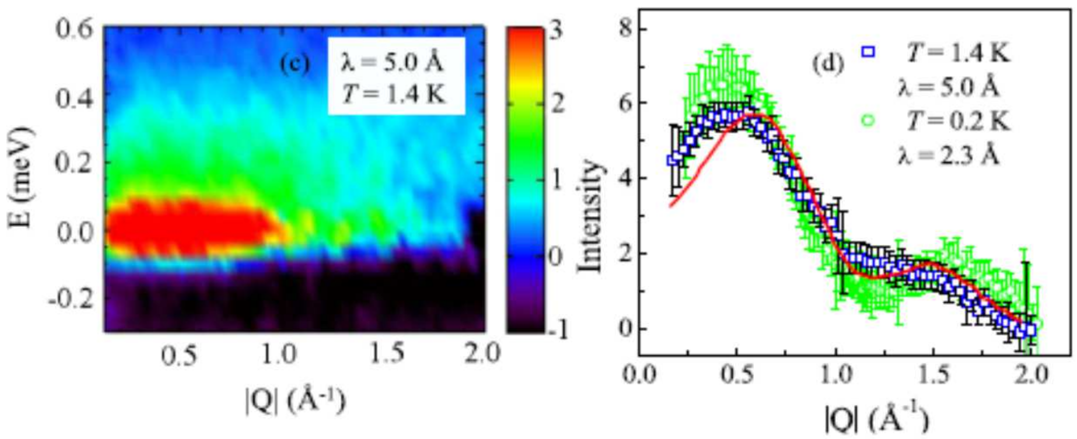
Evidence for dipolar spin ice



Elastic diffuse scattering:
typical dipolar spin ice form

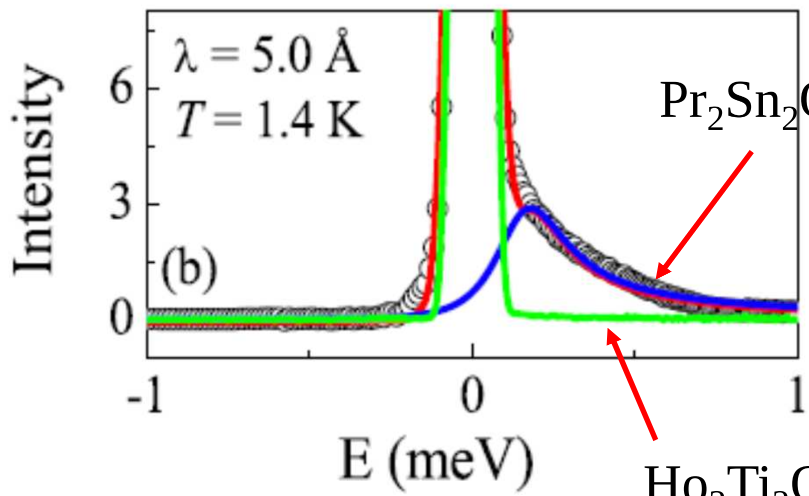
D_{nn} = 0.13 K
T_{peak} = 1.25 K
J_{nn}/D_{nn} ~ 10.9

Spin ice with Weak D_{nn} and FM J_{nn} different from $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$ with AFM Jnn



$Ho_2Ti_2O_7$ J_{nn}/D_{nn} ~ -0.27
$Dy_2Ti_2O_7$ J_{nn}/D_{nn} ~ -0.49

Evidence for dynamic ground state

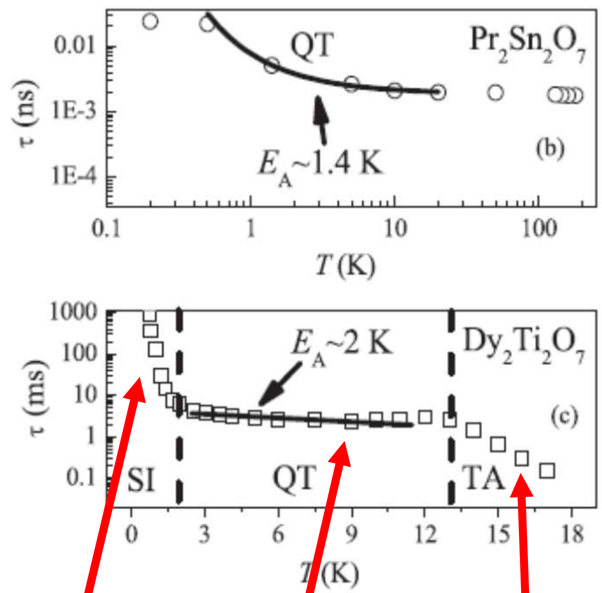


$Pr_2Sn_2O_7$

$Ho_2Ti_2O_7$

Quasielastic neutron scattering: dynamic spins

Quantum tunneling: dynamic spin ice



5 K ~ 10 K
T-independent τ
Quantum tunneling

$T < 5$ K
spin ice region

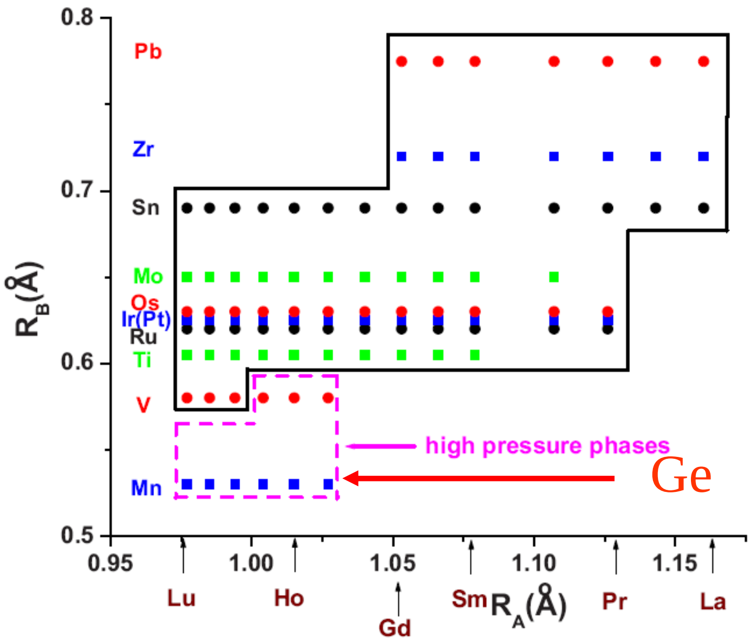
At HT $E_a \sim 220$ K
transition between doublets

"Quantum melting of spin ice"

Onoda & Tanaka, PRL (2010)

Exploration for new spin ices

Change J_{nn}?
J_{nn} is sensitive to lattice parameter changes



$1.36 < R_A/R_B < 1.71$

$R_2Ge_2O_7$ (R = Ho, Dy)
Pyrochlore structure under high pressure

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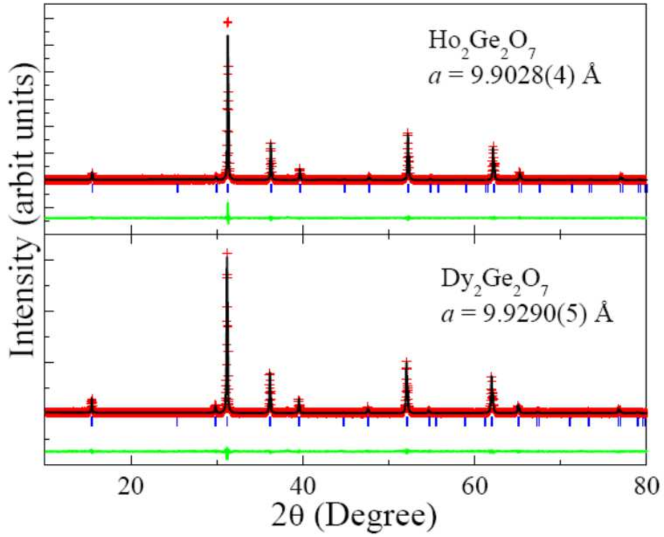
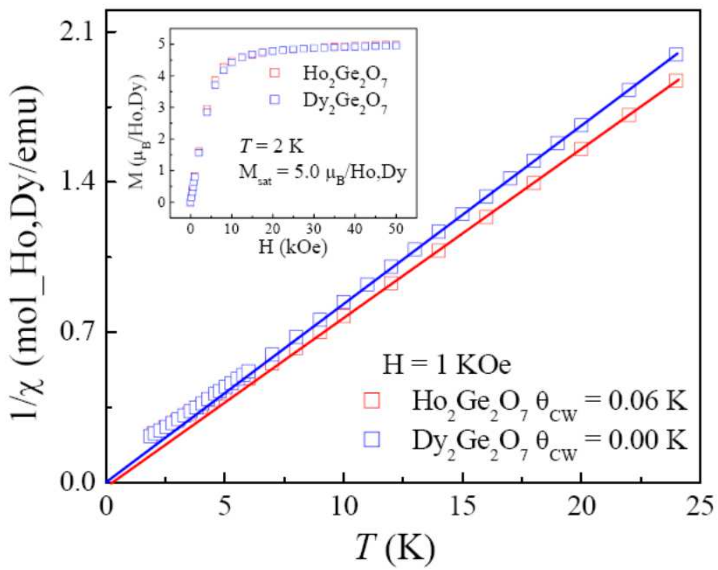
New spin ices: $Ho_2Ge_2O_7$, $Dy_2Ge_2O_7$

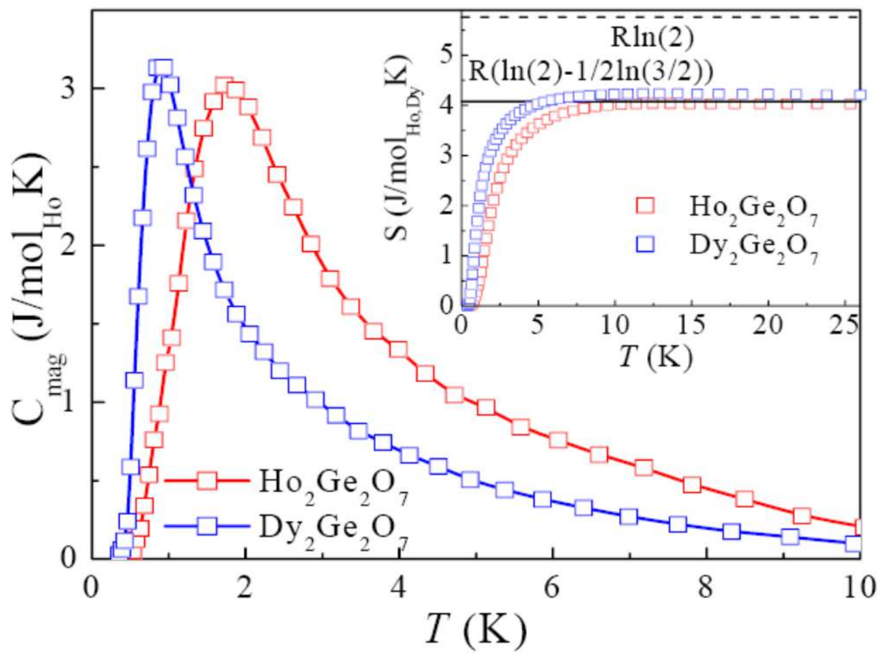
Zhou et al., Nature Commun. (2011)



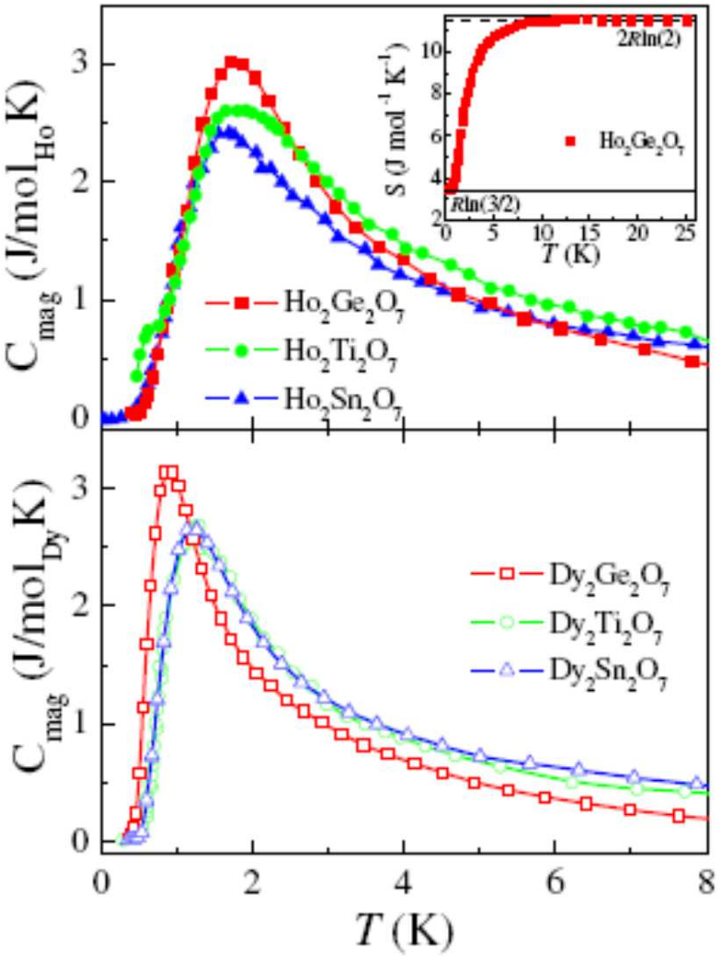
$a < 10.0$ Å

9 GPa 1000 °C



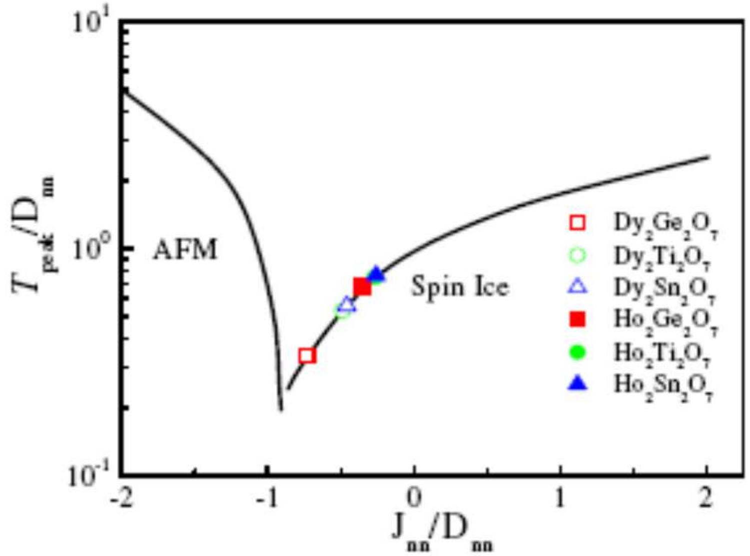


Chemical pressure effects on spin ice



	a	θ_{CW}	D_{nn}	T_{peak}	J_{nn}/D_{nn}
	Å	K	K		
$Ho_2Sn_2O_7$	10.37	1.8	2.17	1.65	-0.26
$Ho_2Ti_2O_7$	10.10	1.9	2.35	1.75	-0.27
$Ho_2Ge_2O_7$	9.90	0.06	2.50	1.70	-0.35
$Dy_2Sn_2O_7$	10.40	1.7	2.15	1.20	-0.46
$Dy_2Ti_2O_7$	10.10	0.5	2.35	1.25	-0.49
$Dy_2Ge_2O_7$	9.90	0.0	2.50	0.828	-0.73

$$\theta_{CW} \sim J_{eff} = J_{nn} + D_{nn}$$



Dense monopole dimers in $Dy_2Ge_2O_7$

Magnetic charges move in the lattice

Magnetic electrolyte "magnetolyte"

↔

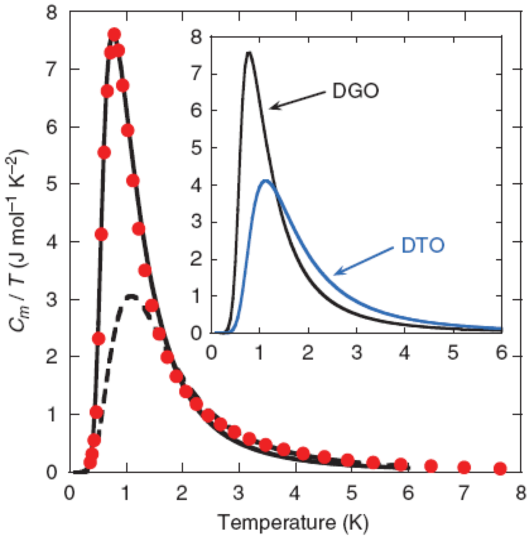
Charged ions move in the solution

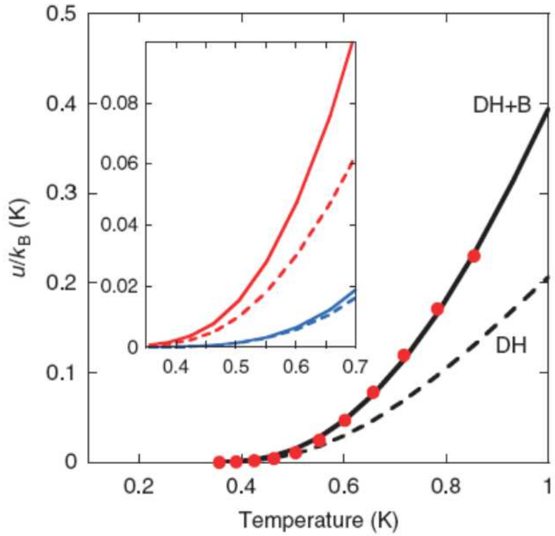
Electrolyte

Debye-Hückel theory describes how charged ions move in a solution (electrolyte).

Peter Debye   Erich Hückel

By using DH equation





$Dy_2Ge_2O_7$ chemical potential

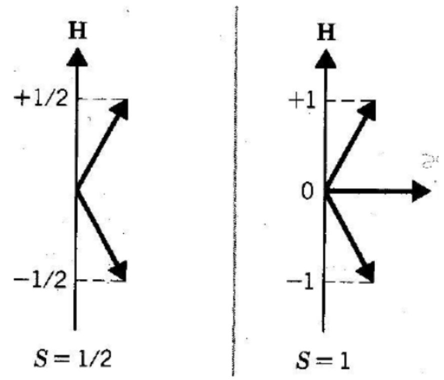
ν = -3.35 K ν_{min} = -3 K approaching the strongly correlated monopole region

For a dense electrolyte, a correction has to be made for the paring of charges (Bjerrum pairs)

$Dy_2Ge_2O_7$ 50% monopoles dimerized,

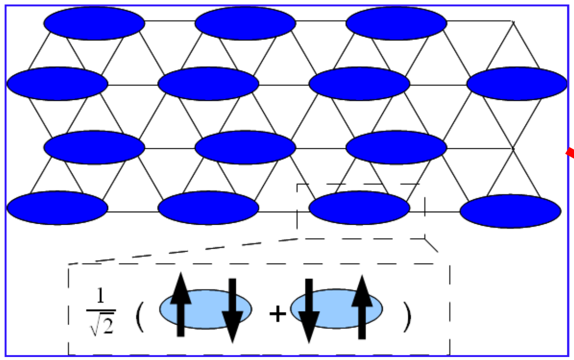
Quantum Spin Liquid (QSL)

Quantum fluctuations destabilize the ordered state



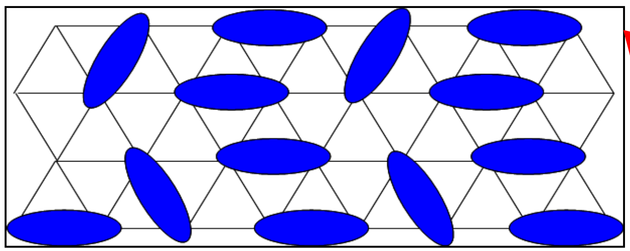
Resonating valence bond (RVB) state

Anderson Mater. Res. Bull. (1973)

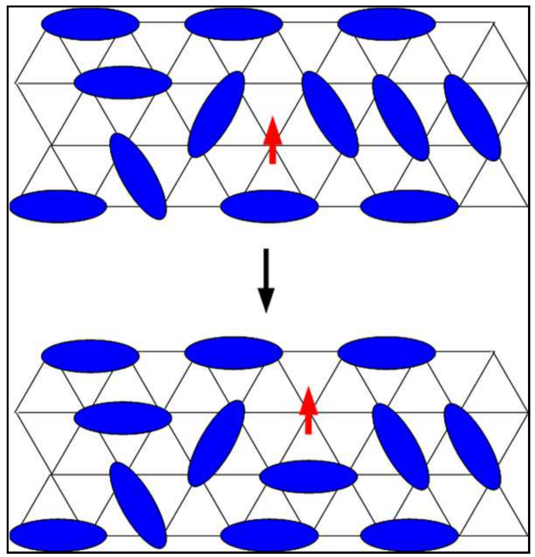


Valence bond solid

Quantum fluctuation



Valence bond liquid (RVB)

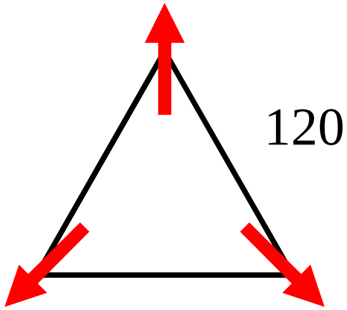


Exotic excitation: spinon

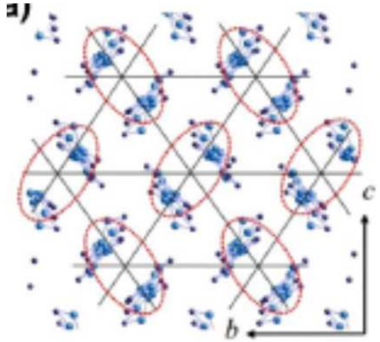
Balents, Nature (2010)

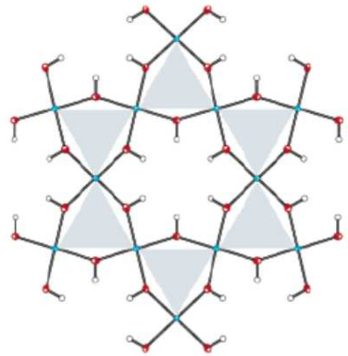
QSL candidates

Neel states always win!



120° order





"An end to the drought of QSL"

Patrick A. Lee Science (2008)

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

ZnCu$_3$(OH)$_6$Cl$_2$

Table 1 | Some experimental materials studied in the search for QSLs

Material	Lattice	S	Θ_{cw} (K)	R*	Status or explanation
κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$	Triangular†	½	−375‡	1.8	Possible QSL
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$	Triangular†	½	−(375–325)‡	?	Possible QSL
Cu$_3$V$_2$O$_7$(OH)$_2$•2H$_2$O (volborthite)	Kagomé†	½	−115	6	Magnetic
ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite)	Kagomé	½	−241	?	Possible QSL
BaCu$_3$V$_2$O$_8$(OH)$_2$ (vesignieite)	Kagomé†	½	−77	4	Possible QSL
Na$_4$Ir$_3$O$_8$	Hyperkagomé	½	−650	70	Possible QSL
Cs$_2$CuCl$_4$	Triangular†	½	−4	0	Dimensional reduction
FeSc$_2$S$_4$	Diamond	2	−45	230	Quantum criticality

Balents Nature (2010)

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Fermionic-like excitations in insulating QSL

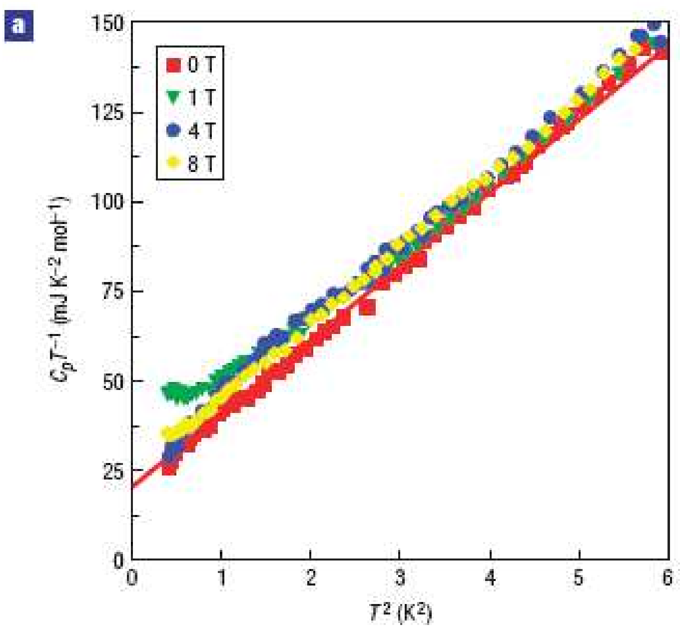
Excitations at low temperatures in insulating QSL:
large χ_0
$C_{mag} \sim \gamma T$ with large γ
Wilson ratio R: $10^0 \sim 10^1$

$$R = \frac{4\pi^2 k_B{}^2 \chi_0}{3(g\mu_B)^2 \gamma}$$

Similar to Fermi-liquid behavior in metal

"Spinon Fermi surface" theory

Motrunich, PRB (2005)
Lee S. S. & Lee P. A., PRL (2005)
Ran et al., PRL (2007)
Lee S. S. et al., PRL (2007)
Lawler et al., PRL (2008)
Zhou Yi & Lee P. A., PRL (2011)

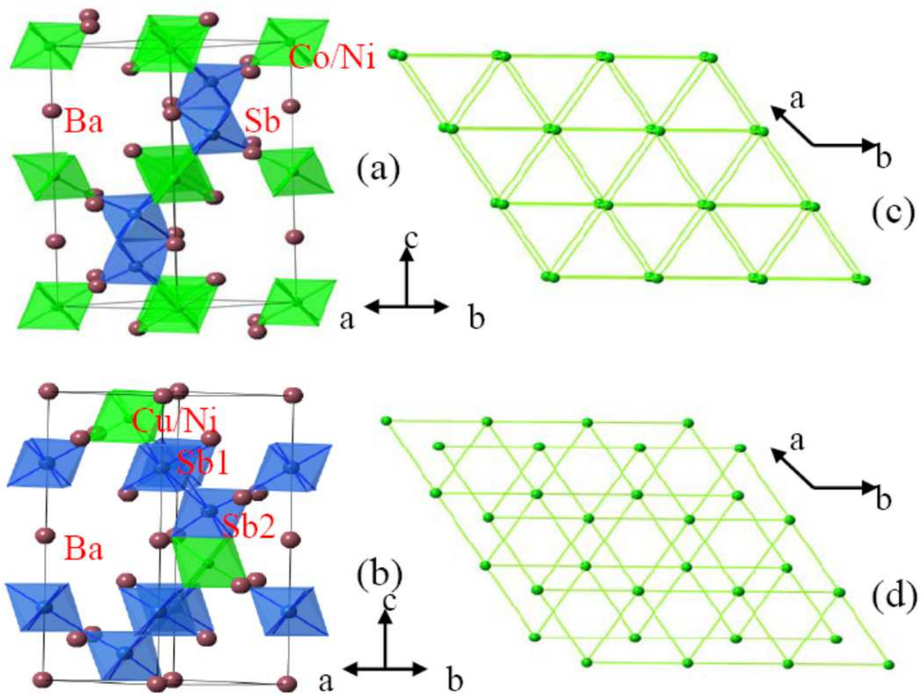


κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$
$C_p/T = \gamma + \beta T^2$
γ= 12 mJ/molK^2
R = 1.8

Yamashita et al., Nature Phys. (2008)

Triangular lattice in $Ba_3MSb_2O_9$

No inorganic QSL with triangular lattice
Organic, H, Ir: bad for neutron

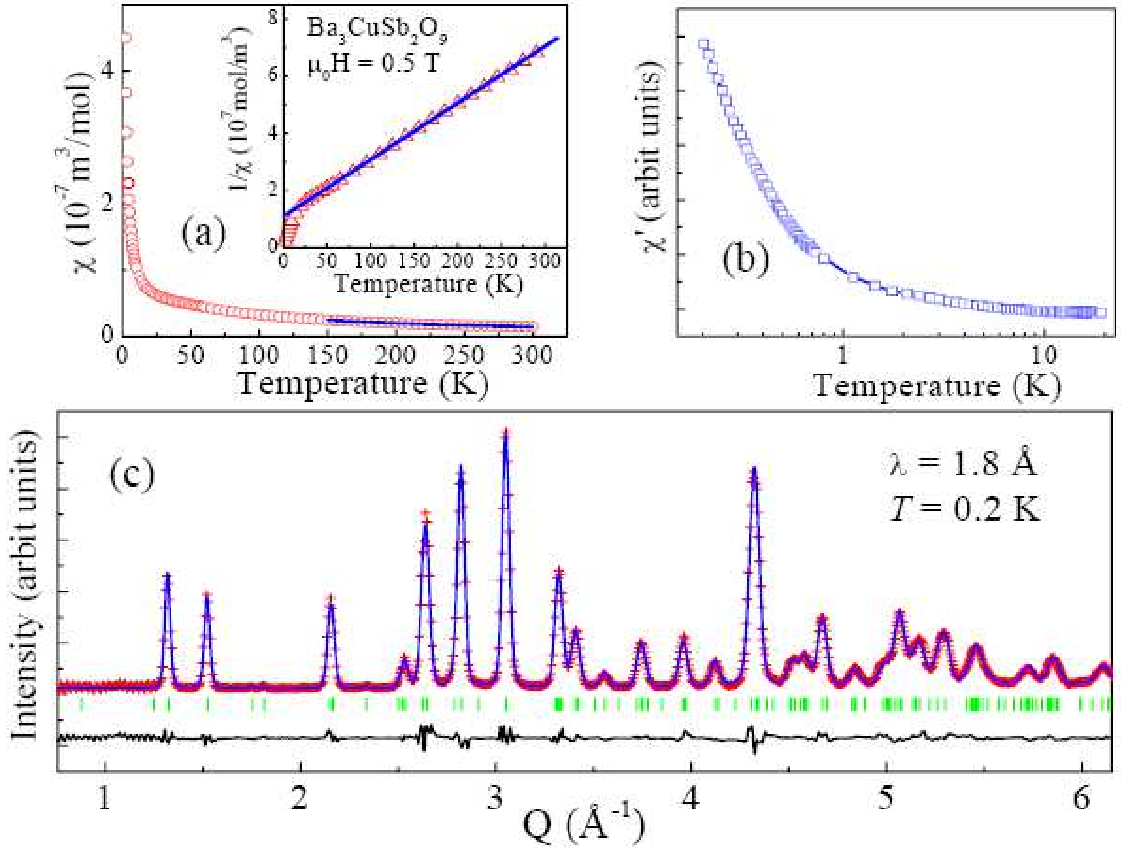


6H-A *P*6_3*/mmc*
$Ba_3CoSb_2O_9$ $T_N = 3.5$ K
$Ba_3NiSb_2O_9$ $T_N = 13$ K

Doi et al., JPCM. (2004)

6H-B *P*6_3*mc*
$Ba_3CuSb_2O_9$?
$Ba_3NiSb_2O_9$ HP phase ?

Large frustration in $Ba_3CuSb_2O_9$ *Zhou et al., PRL (2011)*



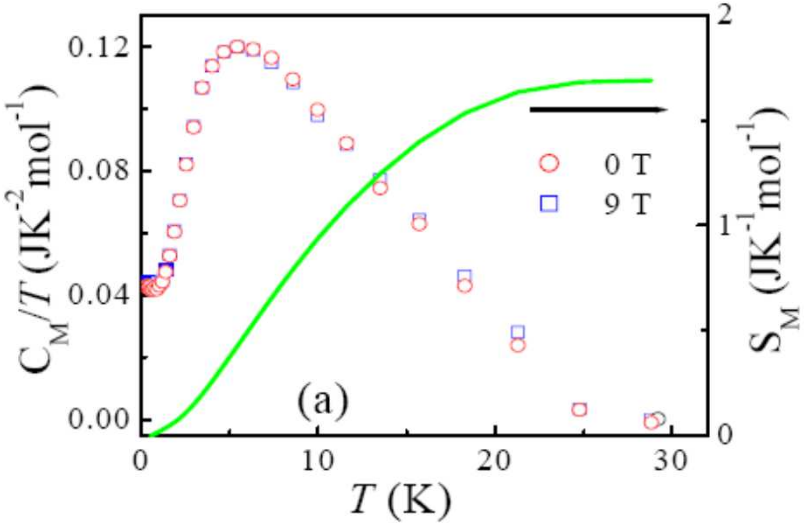
Insulator

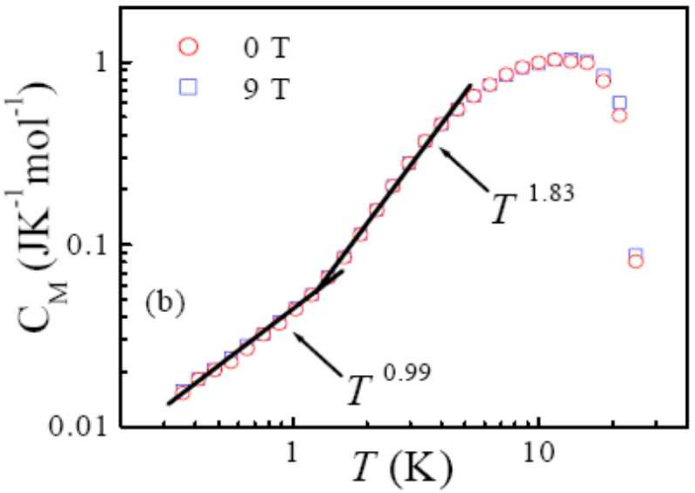
No ordering down to 0.2 K

θ_{CW} = -55 K, f > 275

J ~ -32 K

Fermionic-like excitations in $Ba_3CuSb_2O_9$





$T < 30$ K, spin fluctuations
$\Delta S = 1.7$ J/molK, 30% of Rln(2)

$T < 5$ K, thermally disordered SL state
$C_M \sim T^{1.83}$, $\alpha \approx 2$
Spin waves for a 2D AFM

$T < 1.4$ K, QSL
$C_M \sim \gamma T^{0.99}$, $\alpha \approx 1$
$\gamma = 43.4 \text{mJ/molK}^2$

Spinon-like Fermi surfaces at finite temperatures

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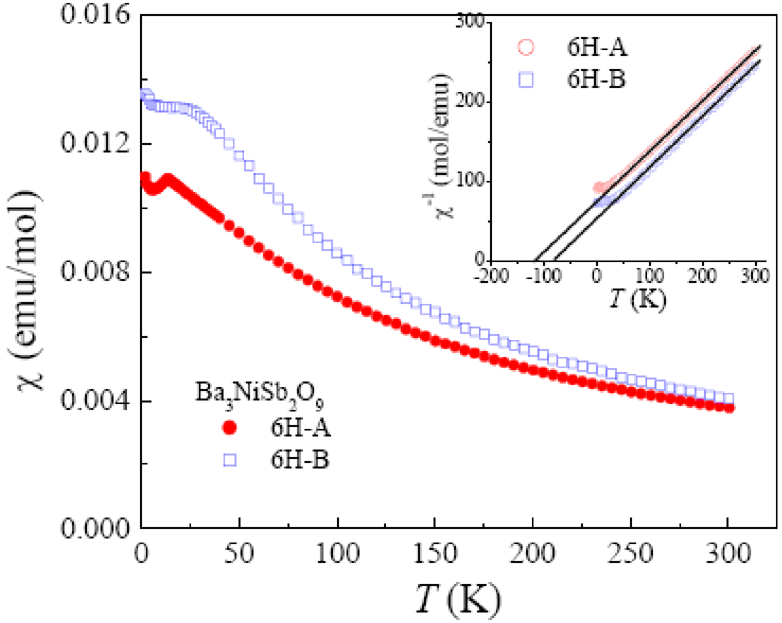
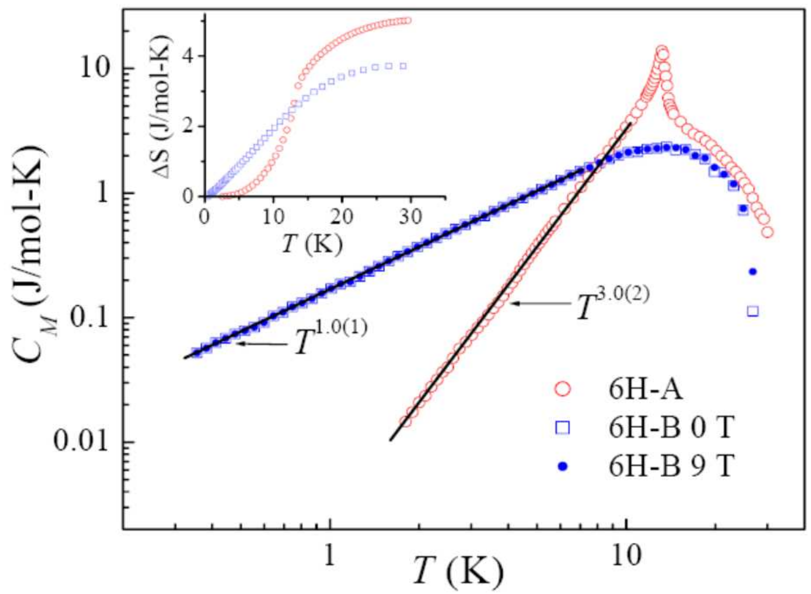
Fermionic-like excitations in $Ba_3NiSb_2O_9$ with S = 1

Cheng, H. D. Zhou et al., PRL (2011)

QSL S =1? 3GPa 600 °C 6H-B phase $Ba_3NiSb_2O_9$





6H-A

T_N = 13 K

θ_{CW} = -117 K, f = 9

$C_M \sim T^3$, 3D AFM

6H-B

No ordering down to 0.35 K

θ_{CW} = -76 K, f > 217

χ_0 = 0.013 emu/mol

$C_M \sim \gamma T$, γ = 168 mJ/molK^2

R = 5.6

Theories for $Ba_3NiSb_2O_9$

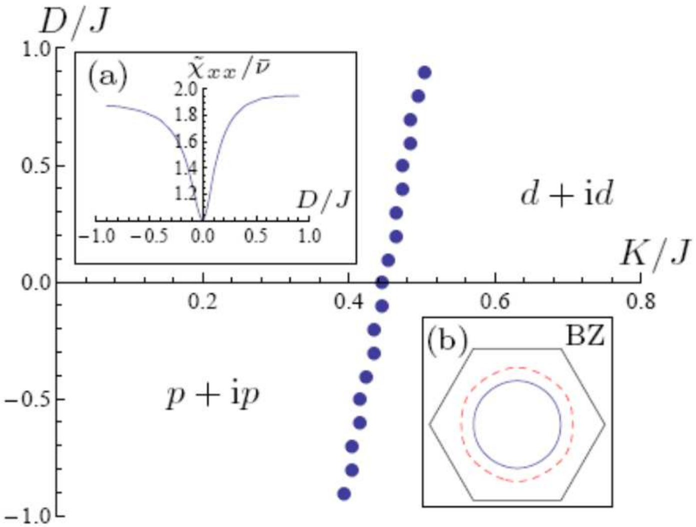


FIG. 2. The phase boundary between SL GS's with $p+\mathrm{i}p$ and $d+\mathrm{i}d$ pairing. (a) The spin susceptibility $\tilde{\chi}_{xx}$ in the $d+\mathrm{i}d$ phase as a function of D/J for $K/J = 0.55$. The susceptibility is normalized by the average density of states, $\bar{\nu} = (\nu_x + \nu_z)/2$, where ν_x is calculated without the gap. (b) Gapped (dashed red line) and ungapped (blue line) Fermi surfaces of x, y, and z-fermions for $K/J = 0.55$, $D/J = 0.8$.

Serbyn et al., PRB (2011)

Gapless excitation with d + id topological pairing

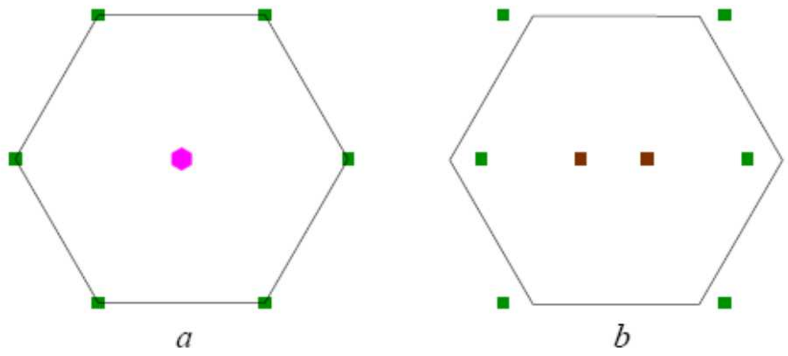


FIG. 1: a, The spin liquid we are considering contains a quadratic band touching at $\vec{k} = 0$ (hexagon), and Dirac points (squares) at the corners of the Brillouin zone. b, with a nonzero and small nematic order $N_1 > 0$, the quadratic band touching is split into two Dirac points, and the locations of the other Dirac points are shifted.

Xu et al., arXiv:1110.3328 (2011) PRL accepted

Gapless fermionic spinon excitations wit quadratic band touching

Summary & Outlook

- $Pr_2Sn_2O_7$: dynamic spin ice with weak D_{nn}
- Chemical pressure drives the spin ice towards the AFM phase boundary
- $Dy_2Ge_2O_7$ with ν = -3.35 K is the most strongly correlated spin ice so far
- New QSLs, $Ba_3CuSb_2O_9$ (S = 1/2) & $Ba_3NiSb_2O_9$ (S =1) with triangular lattice, show fermionic-like thermodynamics

*H. D. Zhou et al., PRL **101**, 227204 (2007)*
*H. D. Zhou et al., Nature Commun. **2:478** (2011)*
*H. D. Zhou et al., PRL **106**, 147204 (2011)*
*Cheng, H. D. Zhou et al., PRL **107**, 197204 (2011)*

- Single crystals
- Lower temperatures ~ 20 mK
- Perturbations (high pressure, high magnetic field)

Physics & Materials

Geometrically frustrated magnets

Exotic ground state: spin glass,
spin liquid, spin ice, frustrated odering

Spin/orbital/ lattice coupling systems

Orbital odering, structural distortion,
metal-insulator transition

Multiferroics

Strong correlation between
magnetism and ferroelectricity

Low demisinonal magnets:

Topological insulator

Acknowledgements:

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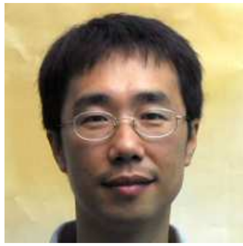
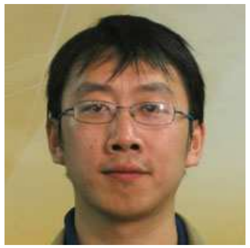
L. Balicas



E. S. Choi



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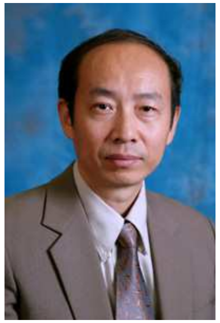
J. B. Goodenough



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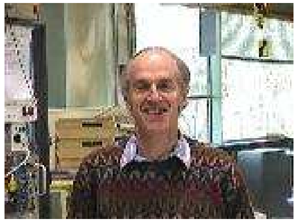

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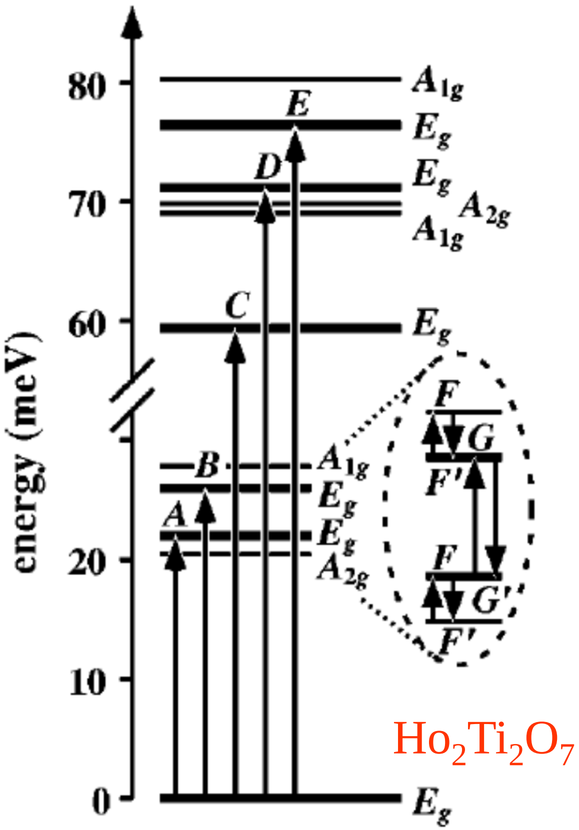
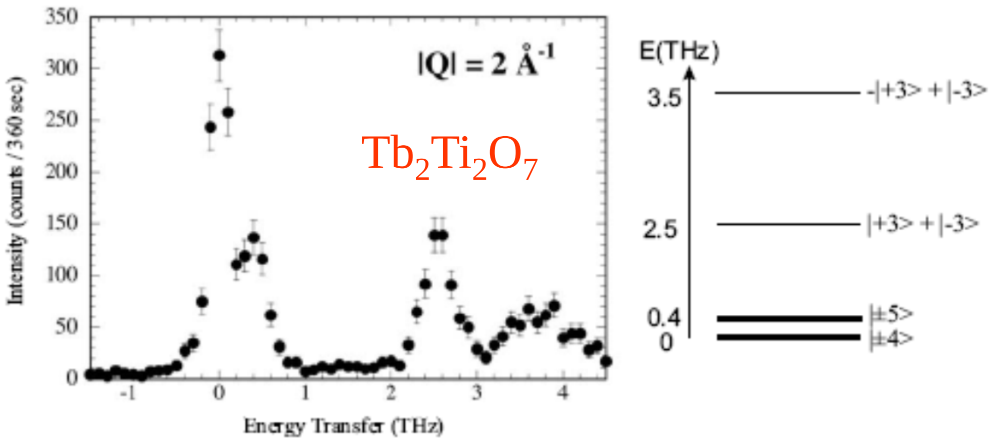
NSF

Crystal field in $Ho_2Ti_2O_7$

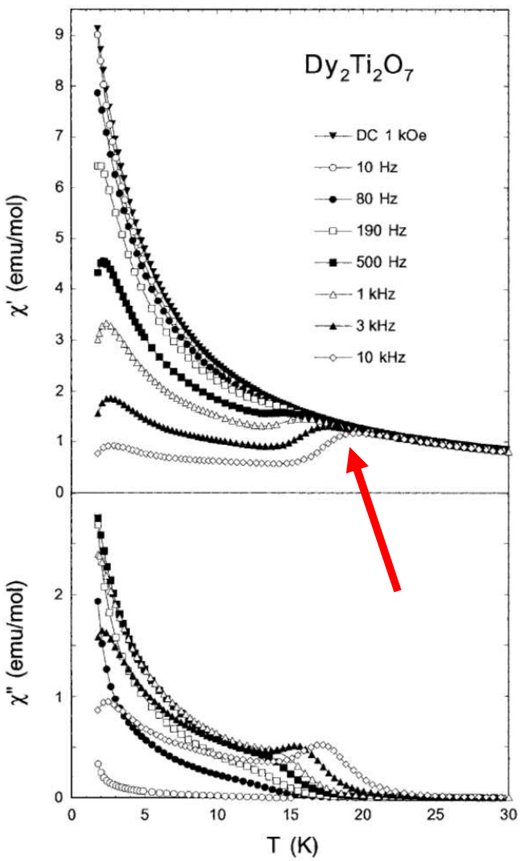


Rosenkranz et al, J. Appl. Phys. (2000)

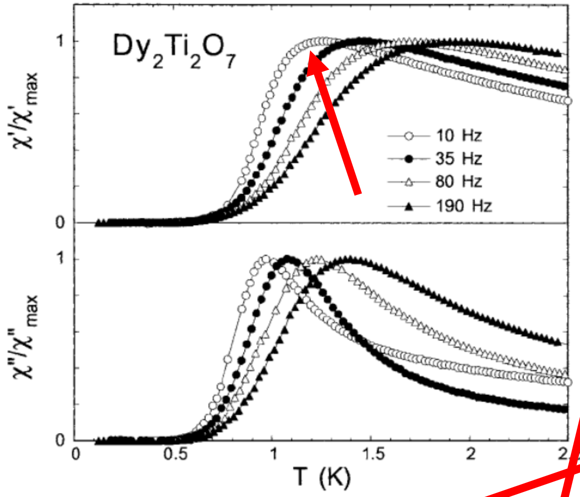


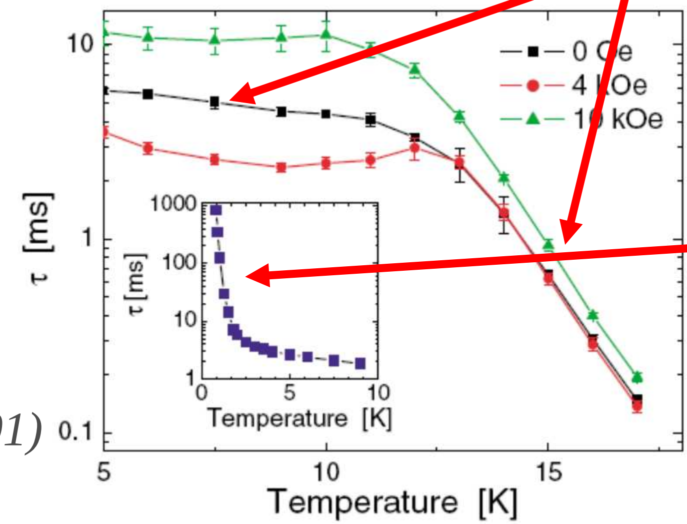
Gingras et al., PRB (2000)

Spin dynamics



Matsuhira et al., JPCM (2001)





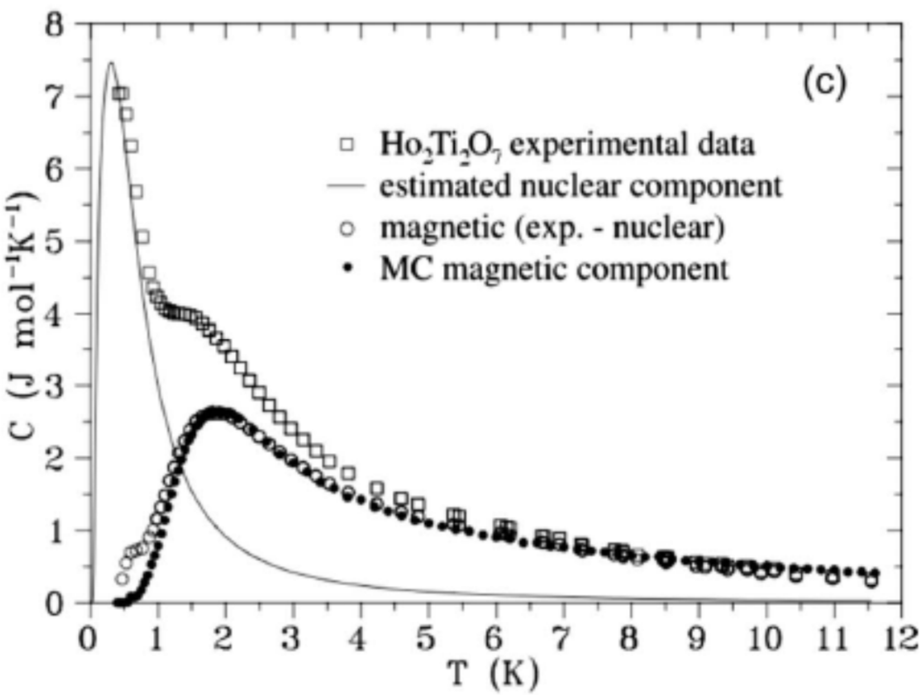
Snyder et al., PRL (2003)

At HT E_a ~ 220 K
transition between doublets

5 K ~ 10 K
T-independent τ
Quantum tunneling

T < 5 K
spin ice region

C_P of $Ho_2Ti_2O_7$



Spinel structure

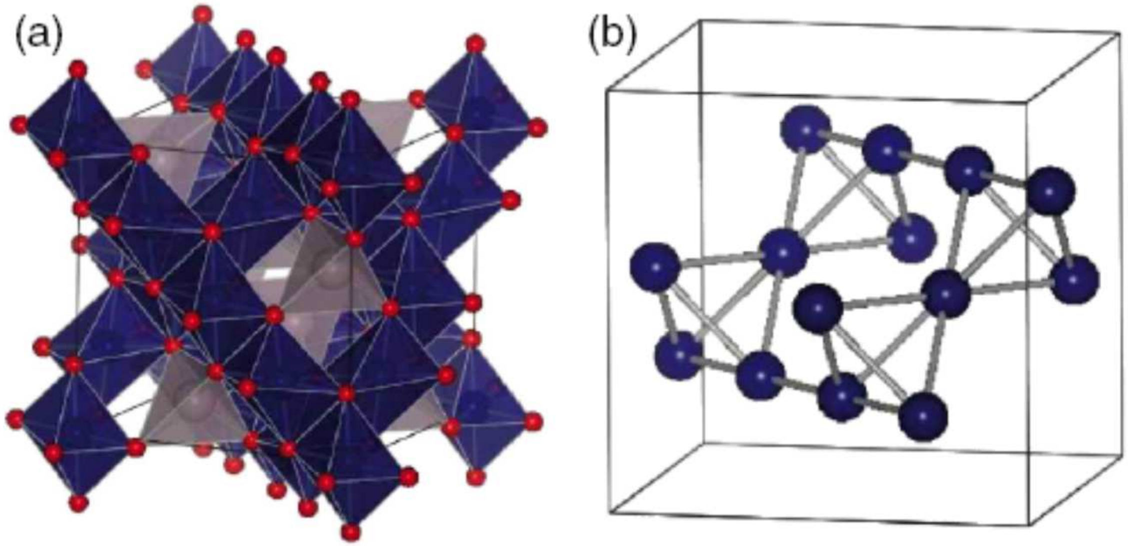
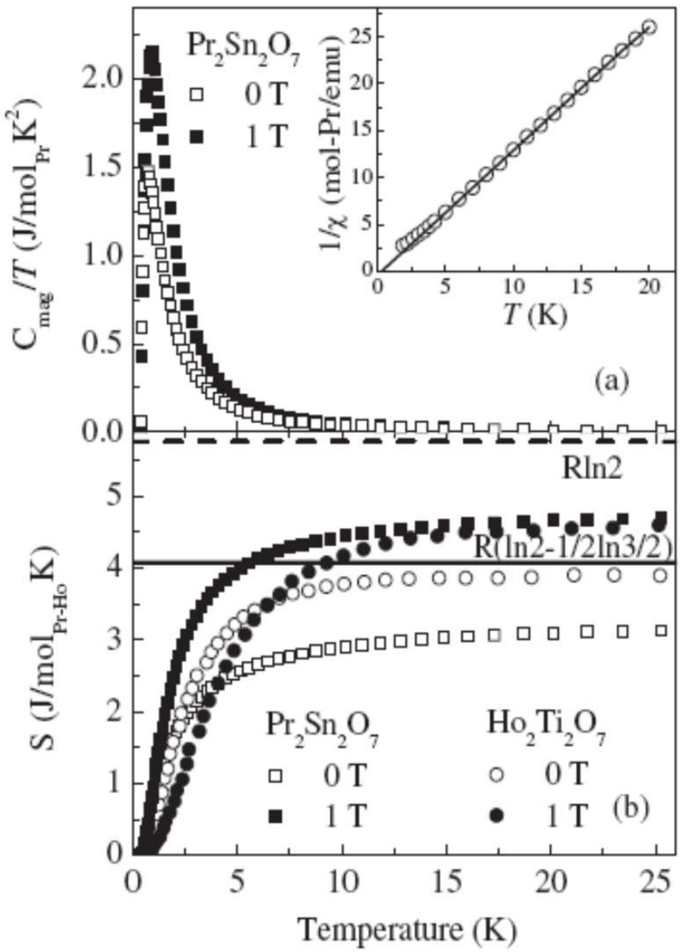


Fig. 1. (Color online) (a) Crystal structure of spnel AB_2O_4. The blue (grey) polygon represents BO_6 octahedron (AO_4 tetrahedron). The neighboring BO_6 octahedra share an edge. (b) The B ions form the three-dimensional network of corner-sharing tetrahedra.

Spin ice with weak D_{nn}

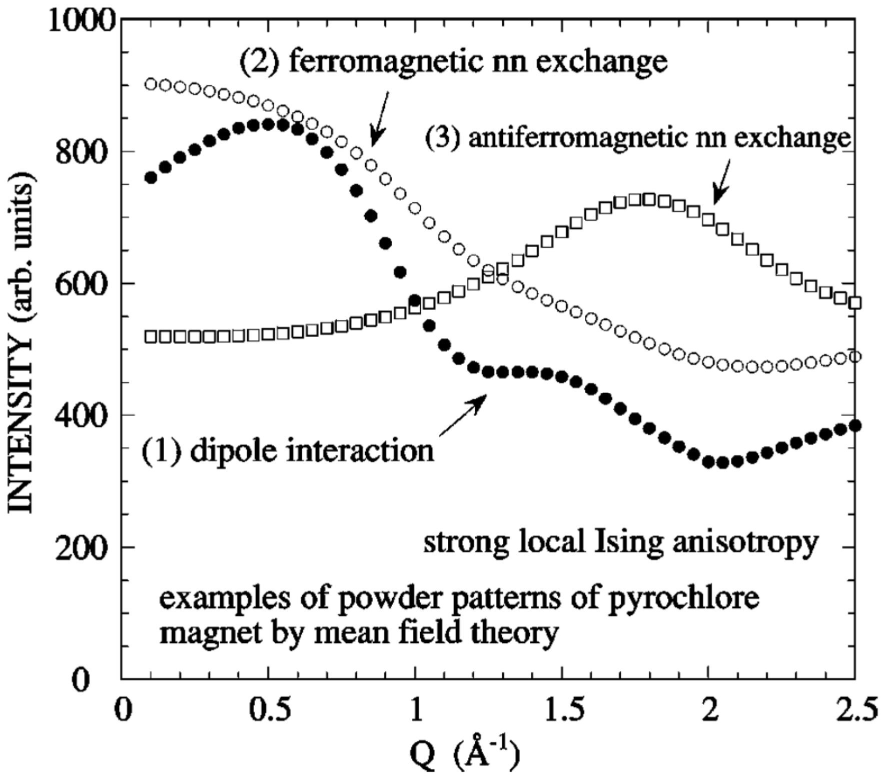


D_{nn} = 0.13 K
T_{peak} = 1.25 K
J_{nn}/D_{nn} ~ 10.9

Spin ice with Weak D_{nn} and FM J_{nn}

ΔS = 3.1 J/molK
< ΔS = 4.1J/molK for $Ho_2Ti_2O_7$ $Dy_2Ti_2O_7$

Diffuse scattering for spin ice



H. Kadowaki et al., PRB (2002)

High pressure synthesis

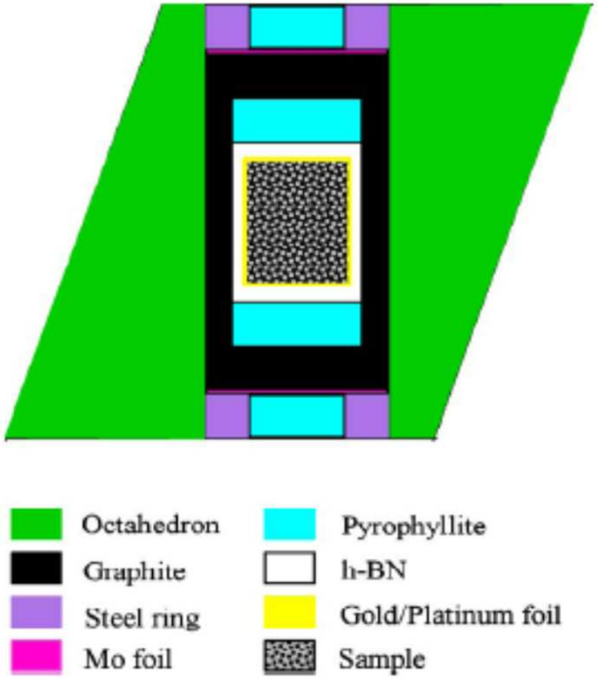
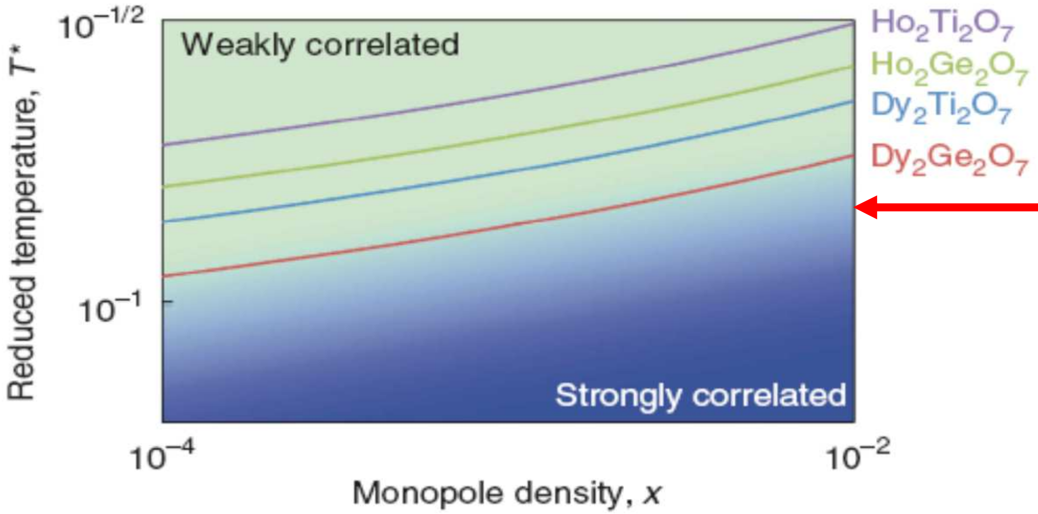


FIG. 1. (Color online) The assembly for high-pressure synthesis in a Walker multianvil press.

Cheng et al., PRB (2010)

$Dy_2Ge_2O_7$:approaching the strongly correlated monopole region

ν: the chemical potential for monopole pair creation



$Dy_2Ti_2O_7$ ν = -4.35 K

$Dy_2Ge_2O_7$ ν = -3.35 K

ν_{min} = -3 K

$$T^* = 4\pi k_B Ta / \mu_0 Q^2$$

Heat capacity analysis

$$u = |\nu| x$$

$$x = \frac{e^{(\nu_{DH} - |\nu|)/k_B T}}{1 + e^{(\nu_{DH} - |\nu|)/k_B T}}$$

$$\frac{\nu_{DH}}{k_B T} = \frac{l_T}{l_D + a}$$

$$l_T = \frac{\mu_0 Q^2}{8\pi k_B T}$$

$$l_D^{-1} = \sqrt{\frac{\mu_0 Q^2 x}{k_B T V_d}}$$

Dimer correction

$$\nu_d = 2|\nu| - \mu_0 Q^2 /(4\pi a)$$

$$x_B \approx 2\exp\left(\frac{\nu_d}{k_B T}\right)$$

$$\frac{\nu_{DH}}{k_B T} = \frac{l_T}{l_D + 2a}$$

$$u = |\nu_d| x_B + |\nu| x$$

u: energy
x: # of monopoles per latt.
l_T: Bjerrum length
l_D: Debye length
V_d: volume per diamond latt.
ν_d: dimer chemical potential
x_B: # of pairs per diamond

Spionon excitations: gap or gapless?

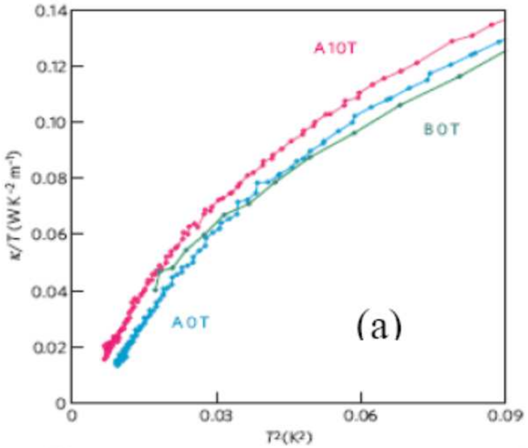
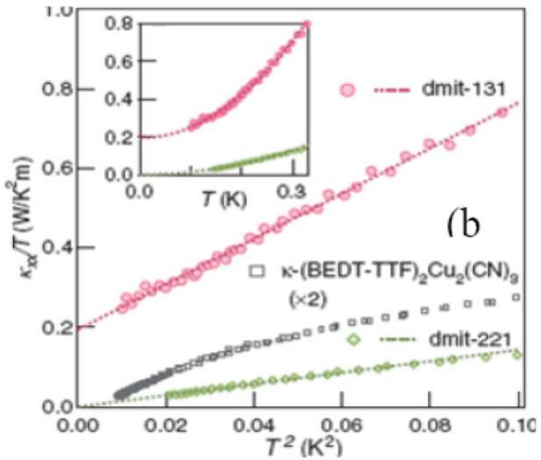
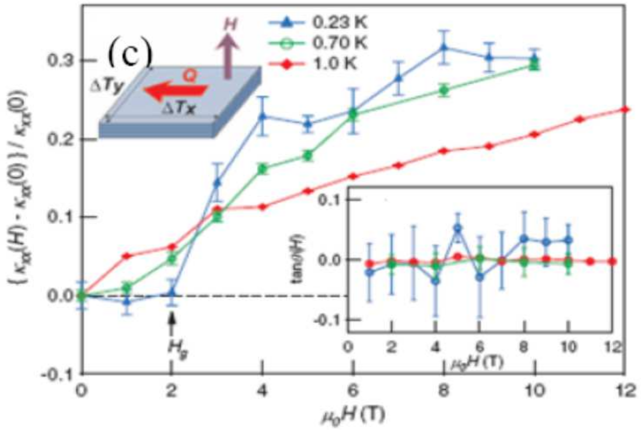


Fig. 5 Thermal conductivity for (a) κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ (After Ref.[5]). (b) Et$_2$Me$_2$Sb[Pd(dmit)$_2$]$_2$, labeled as dmit-131. (c) Field dependence of thermal conductivity for dmit-131, (After Ref.[8]). Here dmit-131 is the same compound we mentioned as dmit in the main text.





Yamashita et al., Nature Phys. (2009), Science (2010)

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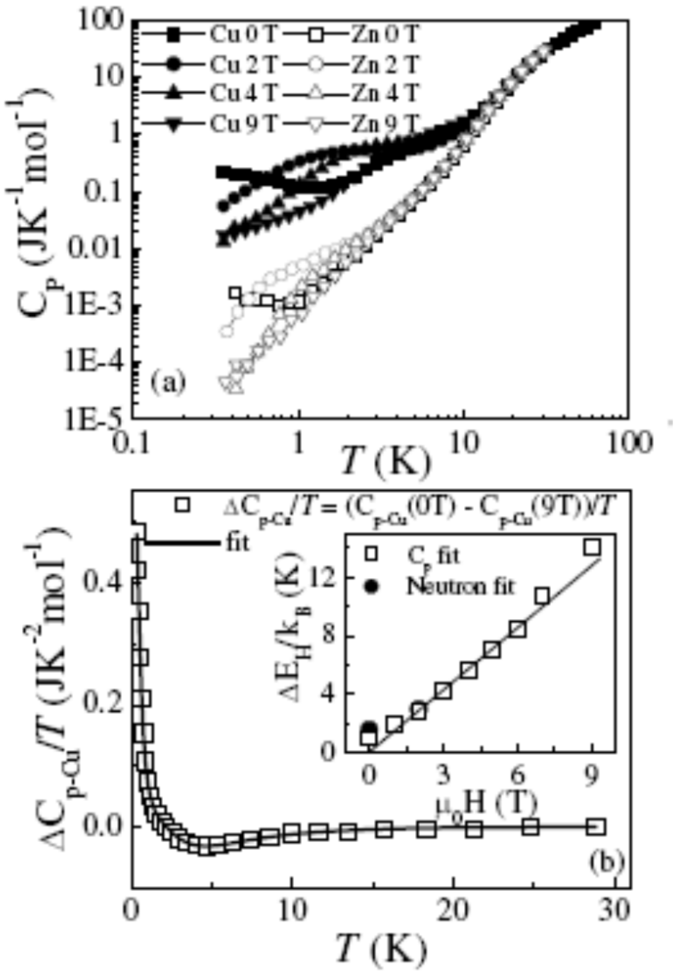
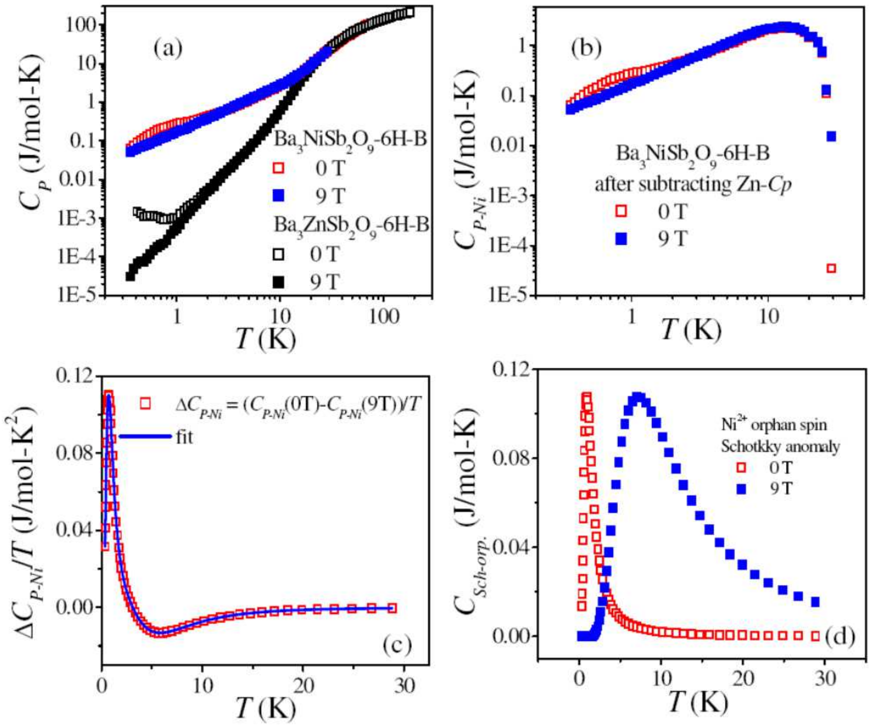
Specific heat for $Ba_3CuSb_2O_9$

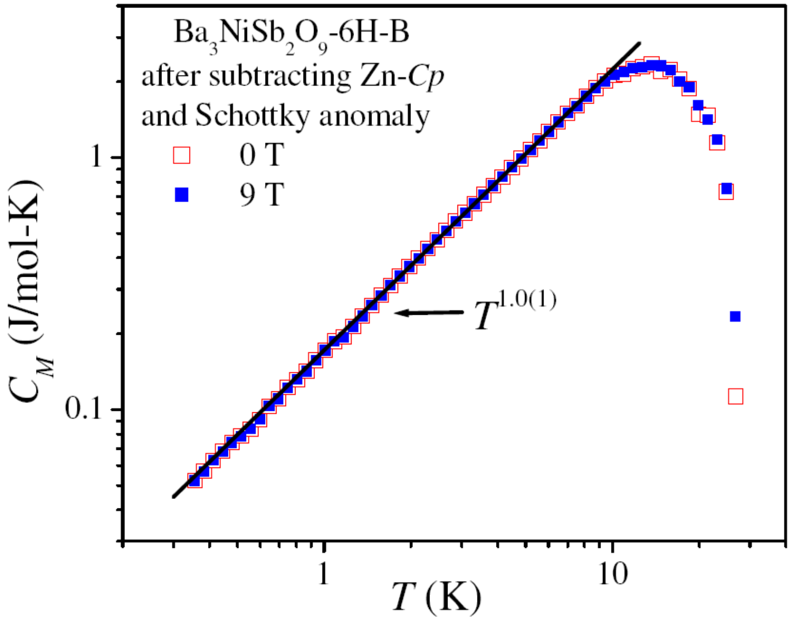


Zhou et al., PRL (2011)

NHMFL

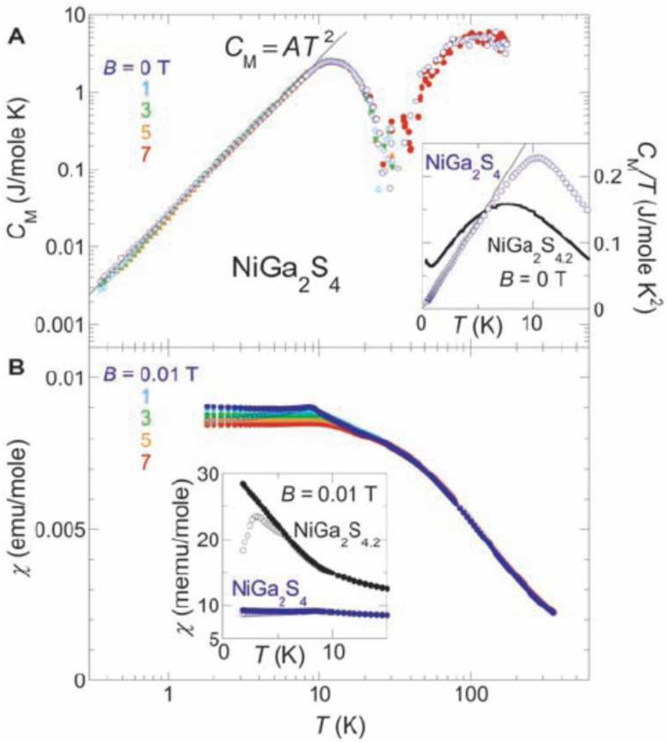
Specific heat for $Ba_3NiSb_2O_9$





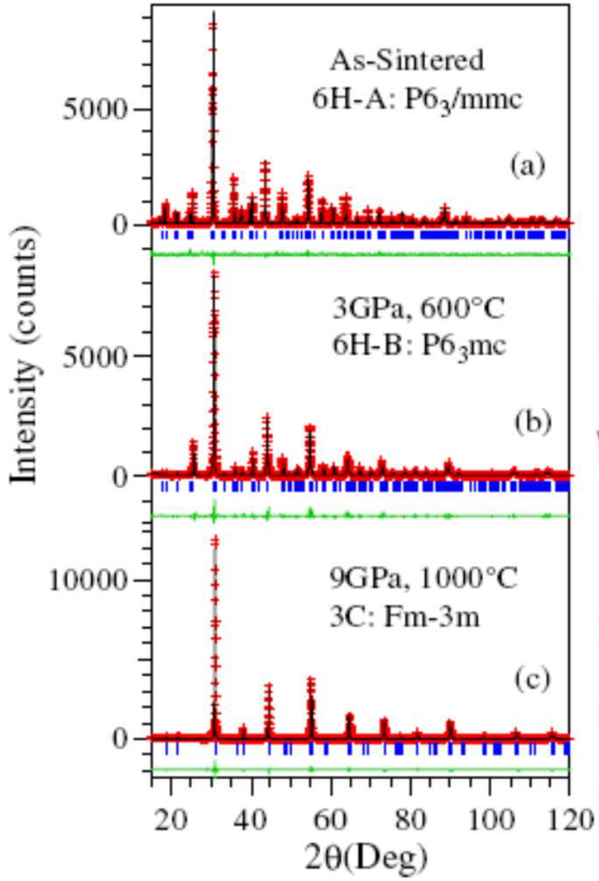
Cheng et al., PRL (2011)

QSL with S = 1?



Nakatsuji et al., Science (2005)

$NiGa_2S_4$
Ni^{2+} S =1 triangular lattice
$C_M \sim T^2$
Quadrupolar order



$Ba_3NiSb_2O_9$ 6H-B
Ni^{2+} S =1 triangular lattice