The Abdus Salam International Centre for Theoretical Physics

2357-16

Innovations in Strongly Correlated Electronic Systems: School and Workshop

6 - 17 August 2012

Overview of quantum spin liquid from toy of theorists to reality

Hide TAKAGI

Department of Physics, University of Tokyo/RIKEN, Kashiwa
Chiba
JAPAN

Overview of quantum spin liquid from toy of theorists to reality

Hide TAKAGI

Department of Physics, University of Tokyo

東京大学
THE UNIVERSITY OF TOKYO

Outline

1. Introduction, what is the holy grail?

2. How to realize frustrated
lattice in real materials?

3. Emergent quantum spin liquid candidates
2D triangular, Kagome and 3D hyperkagome

4. Related topics
Kitaev liquid, Spin ice, Charge analogue,
spin-lattice-orbital coupling

NATURE|Vol 464|11 March 2010|doi:10.1038/nature08917
REVIEW INSIGHT

Spin liquids in frustrated magnets

Leon Balents[1]

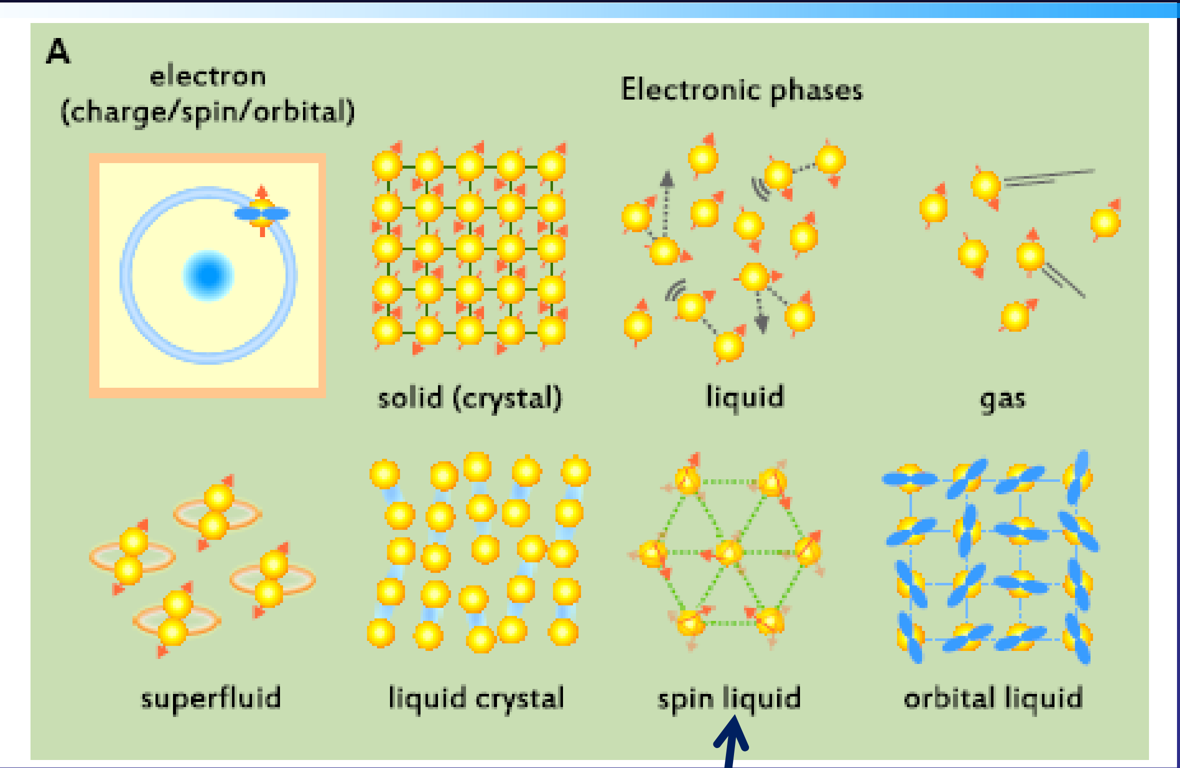
Frustrated magnets are materials in which localized magnetic moments, or spins, interact through competing exchange interactions that cannot be simultaneously satisfied, giving rise to a large degeneracy of the system ground state. Under certain conditions, this can lead to the formation of fluid-like states of matter, so-called spin liquids, in which the constituent spins are highly correlated but still fluctuate strongly down to a temperature of absolute zero. The fluctuations of the spins in a spin liquid can be classical or quantum and show remarkable collective phenomena such as emergent gauge fields and fractional particle excitations. This exotic behaviour is now being uncovered in the laboratory, providing insight into the properties of spin liquids and challenges to the theoretical description of these materials.

good review
for new comers

Leo Balents Nature (10)

concept of electronic phase

"Electronic matters" in TMO: a rich variety of phases associated with multiple degrees of freedom



H.Takagi & H.Y.Hwang Science 327 (2010) 1601

charge/spin/orital almost independent
charge:solid/spin:liquid

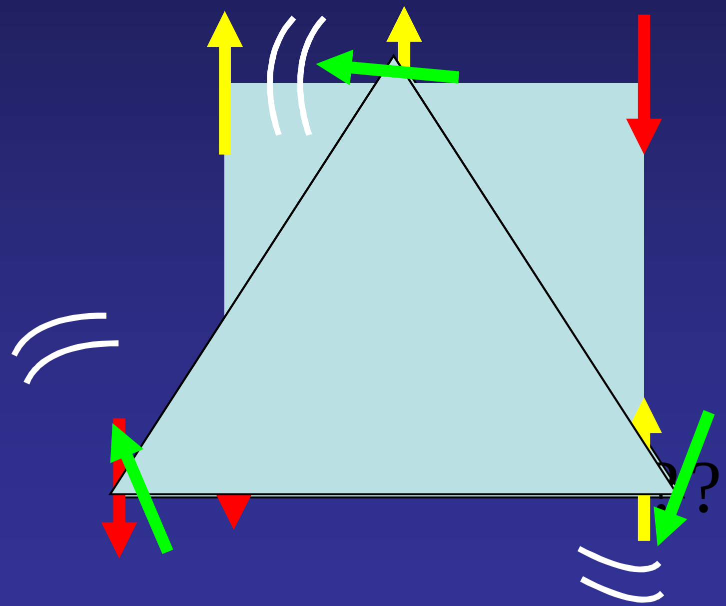
coupling of spin-charge-orbital
even more complicated
self organized pattern of charge/spin/orital

Quantum Spin Liquid: One of the biggest dreams of Materials Physicists

RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR ?*

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

(Received December 5, 1972; Invited**)



P.W.Anderson
1972

1979 nobel prize in physics

Look for
triangular based
S=1/2 Heisenberg
antiferrognet!

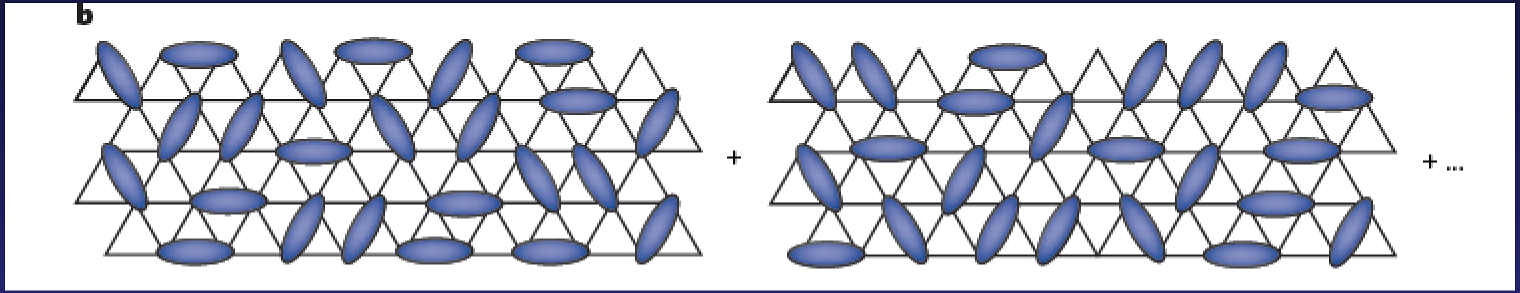
Antiferromagnetically coupled spins
on square lattice => spin solid

Antiferromagnetically coupled spins on triangular lattice
Frustration + quantum effect => Quantum Spin Liquid

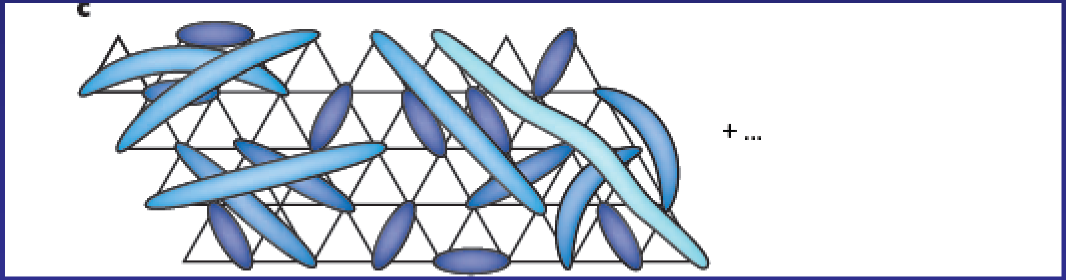
Quantum Spin Liquid: The Zoo

L.Balents
Nature(10)

superposition of spin singlet pairs



short range RVB



long range RVB

gapless

spin Fermi surface

chirality ordering

PHYSICS

An End to the Drought of Quantum Spin Liquids

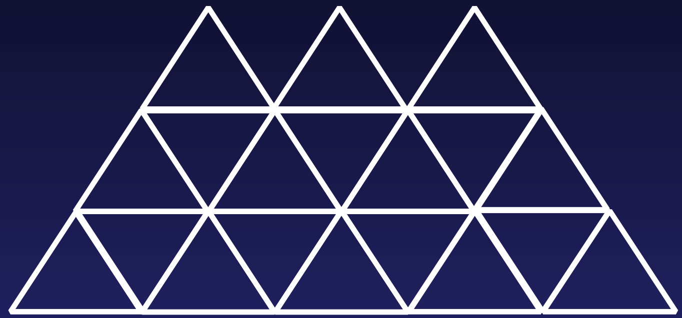
Patrick A. Lee

After decades of searching, several promising examples of a new quantum state of matter have now emerged.

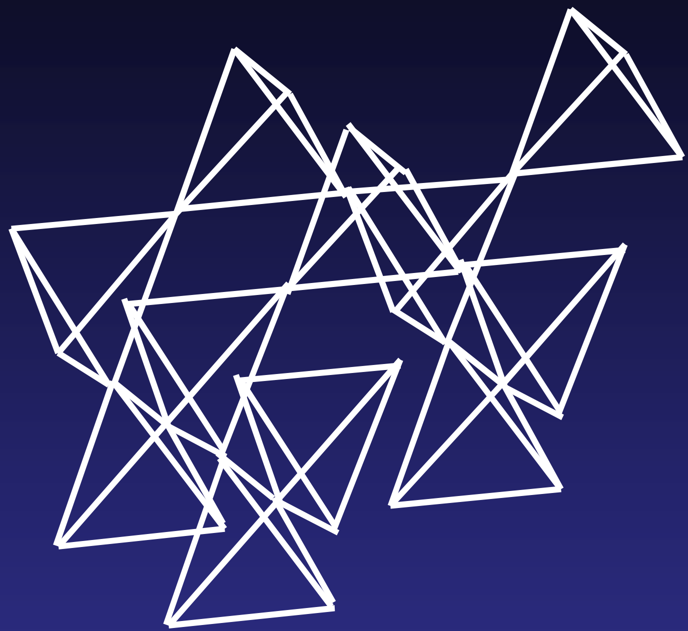
Electrons possess magnetic behavior through the quantum mechanical property of spin. The magnetic properties of materials then arise from the collective interac-

From toy of theorists to reality

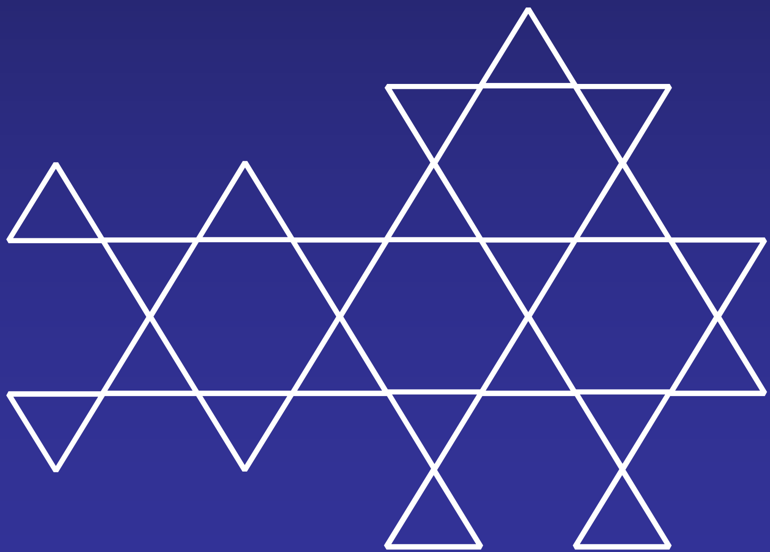
Frustrated Lattice



2D triangular lattice



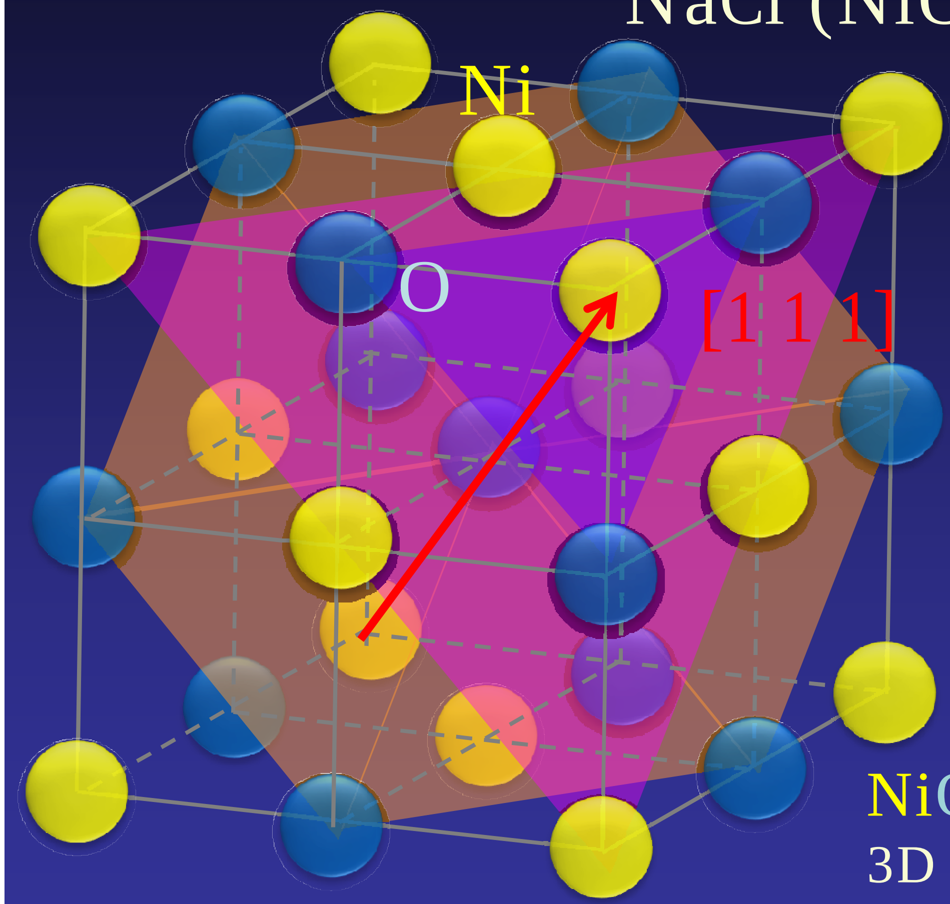
3D Pyrochlore lattice

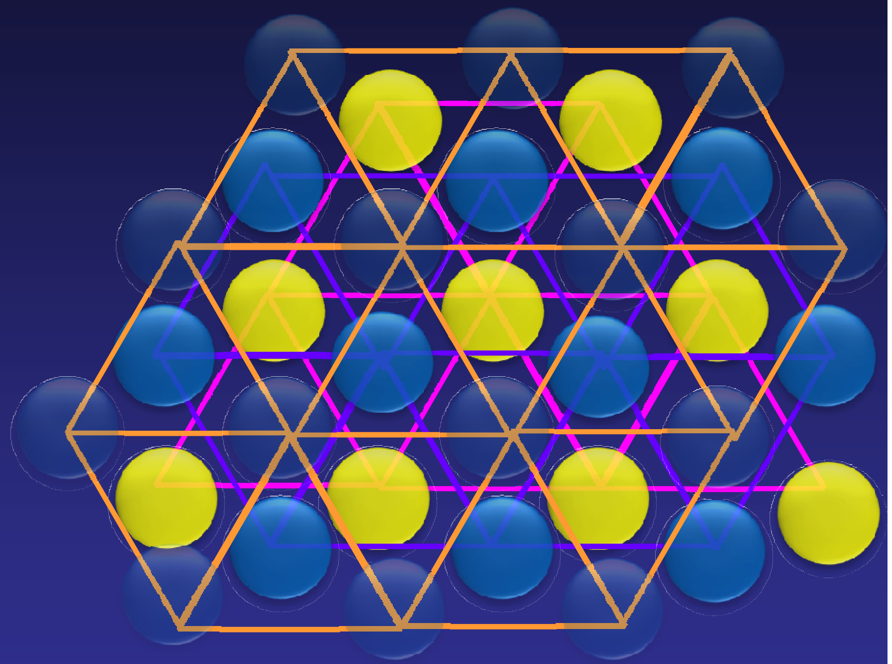


2D Kagome lattice

triangular plane in simple cubic structure

NaCl (NiO)





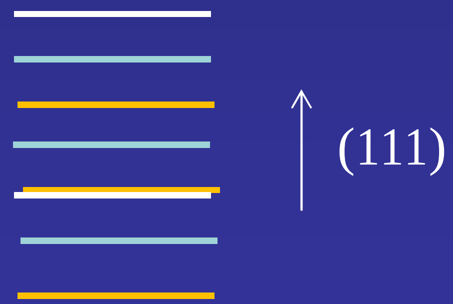
NiO , Ni fcc

3D

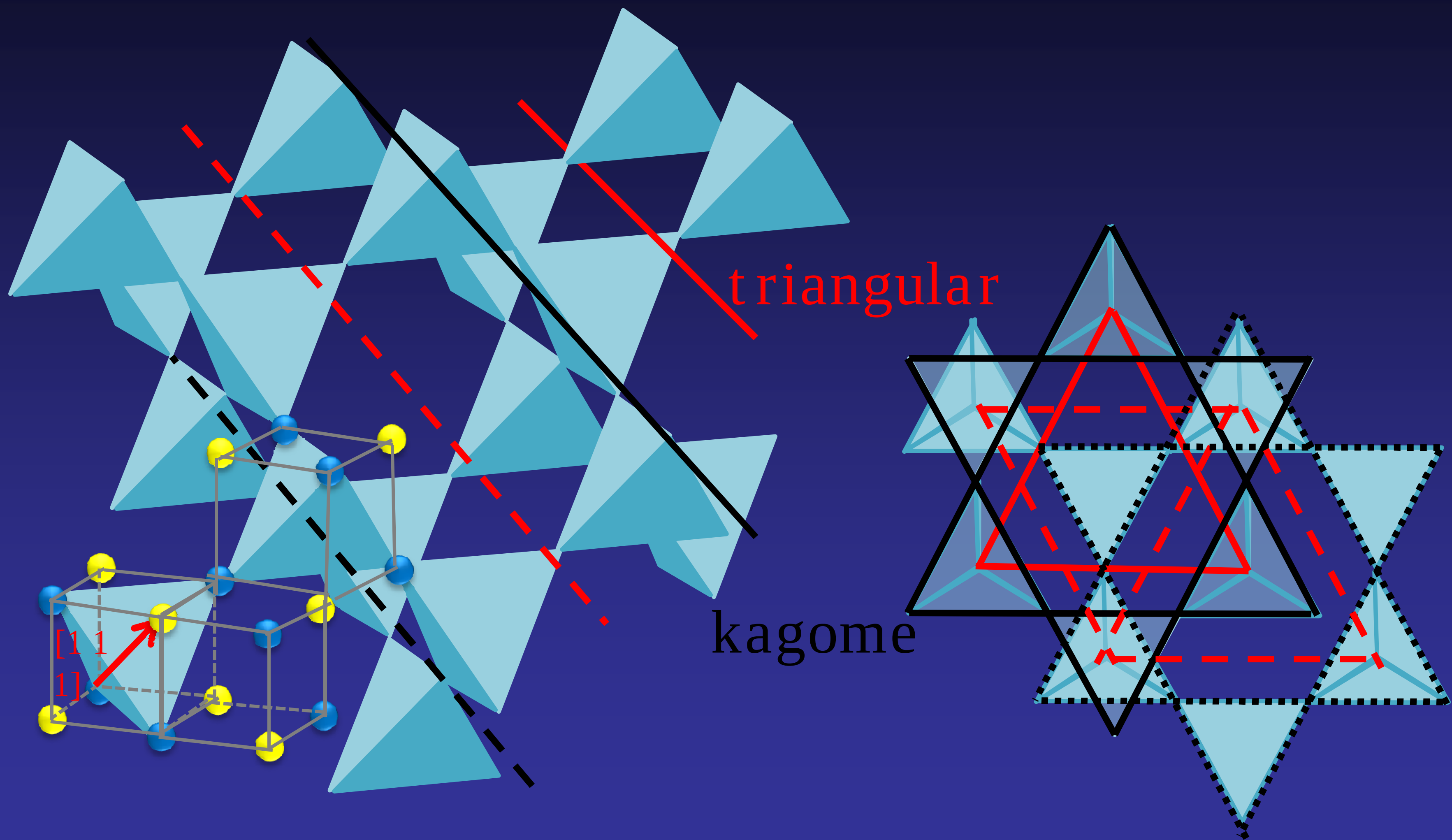
↓

$(Li_{1/2}Ni_{1/2})O$

$=(1/2LiNiO_2)$ 2D

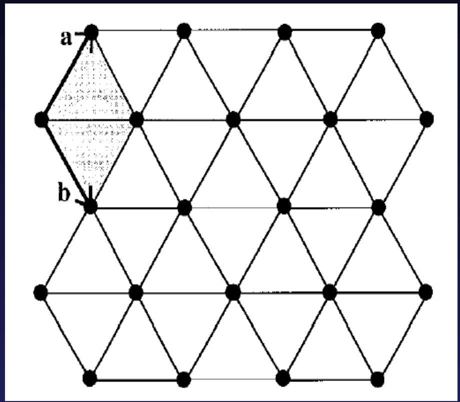


Pyrochlore structure from NaCl
Kagome plane from Pyrochlore

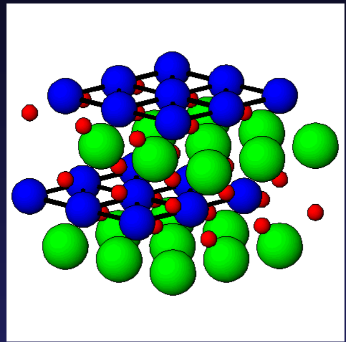


exploring exotic electronic phases: spin liquid

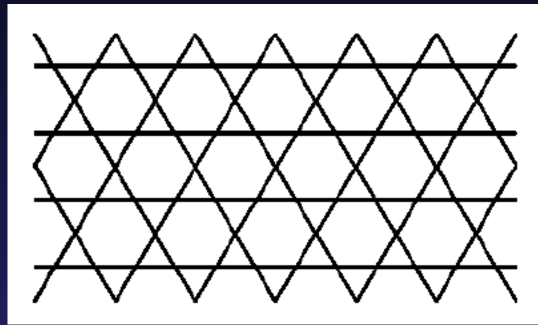
Geometrically Frustrated Lattices



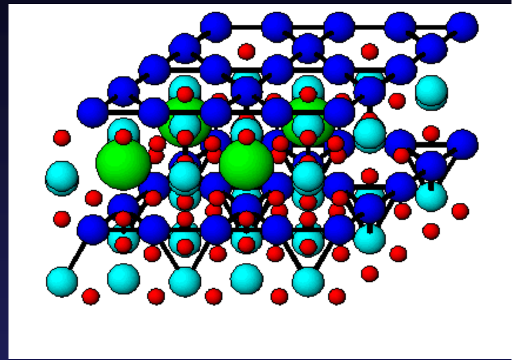
2D Triangular lattice



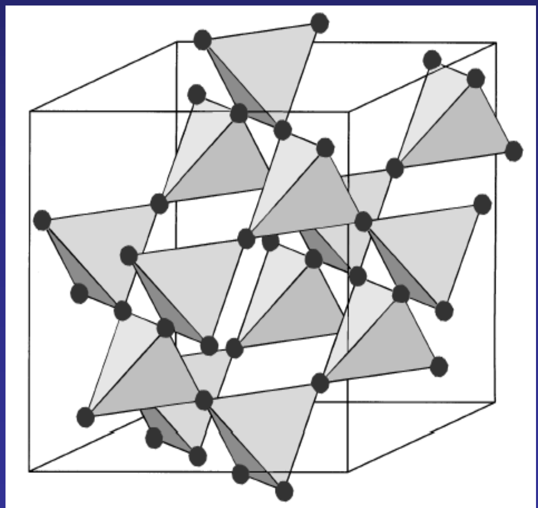
$NiGa_2S_4$, BEDT-TTFCu(NCS) , $NaTiO_2$



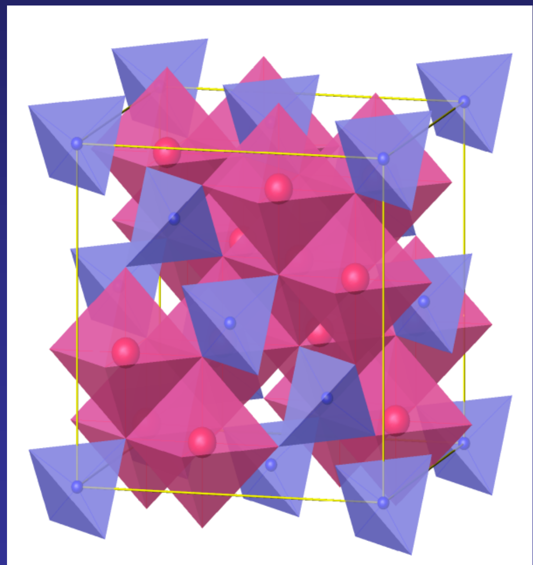
2D Kagome lattice



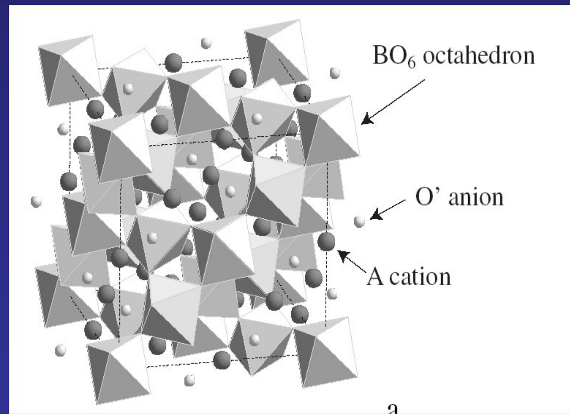
$ZnCu_3(OH)_6Cl_2$
$SrCr_9Ga_3O_{19}$,



3D Pyrochlore lattice



Spinel (AB_2O_4)
$Fe_3O_4=FeFe_2O_4$



Pyrochlore($A_2B_2O_7$)
$Y_2Mo_2O_7$

S=1/2!

Initial probe to capture QSL signature?

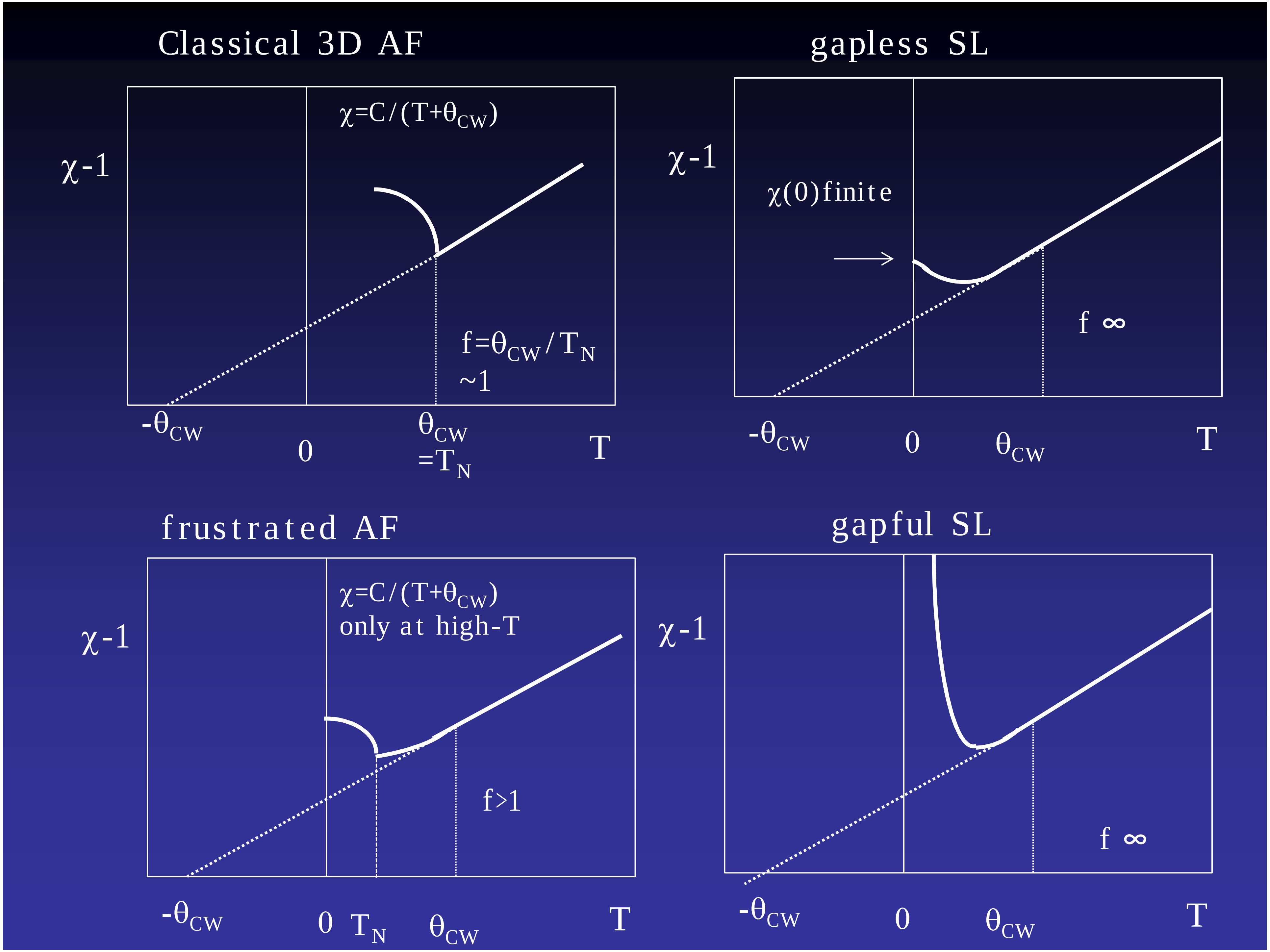
Magnetic susceptibility $\chi(T)$
Curie-Weiss at high-T presence of localized moment
No order absence of kink associated with AF
(frustration $T_N < \theta_{CW}$ $f = \theta_{CW}/T_N$)

Confirm absence of ordering
by NMR, bneutron, x-ray, mSR

T->0 $\chi(T)$ finite (gapless) or exponential suppression (gapful)

T->0 specific heat C(T)/T finite (gapless) or zero (T-dep.?)

T->0 thermal conductivity $\kappa(T)/T$ finite (gapless) or zero


Classical 3D AF
χ-1
χ=C/(T+θCW)
f=θCW/TN
~1
-θCW
0
θCW
=TN
T
gapless SL
χ-1
χ(0)finite
f ∞
-θCW
0
θCW
T
frustrated AF
χ-1
χ=C/(T+θCW)
only at high-T
f>1
-θCW
0 TN
θCW
T
gapful SL
χ-1
f ∞
-θCW
0
θCW
T

Initial probe to capture QSL signature?

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Curie-Weiss at high-T presence of localized moment
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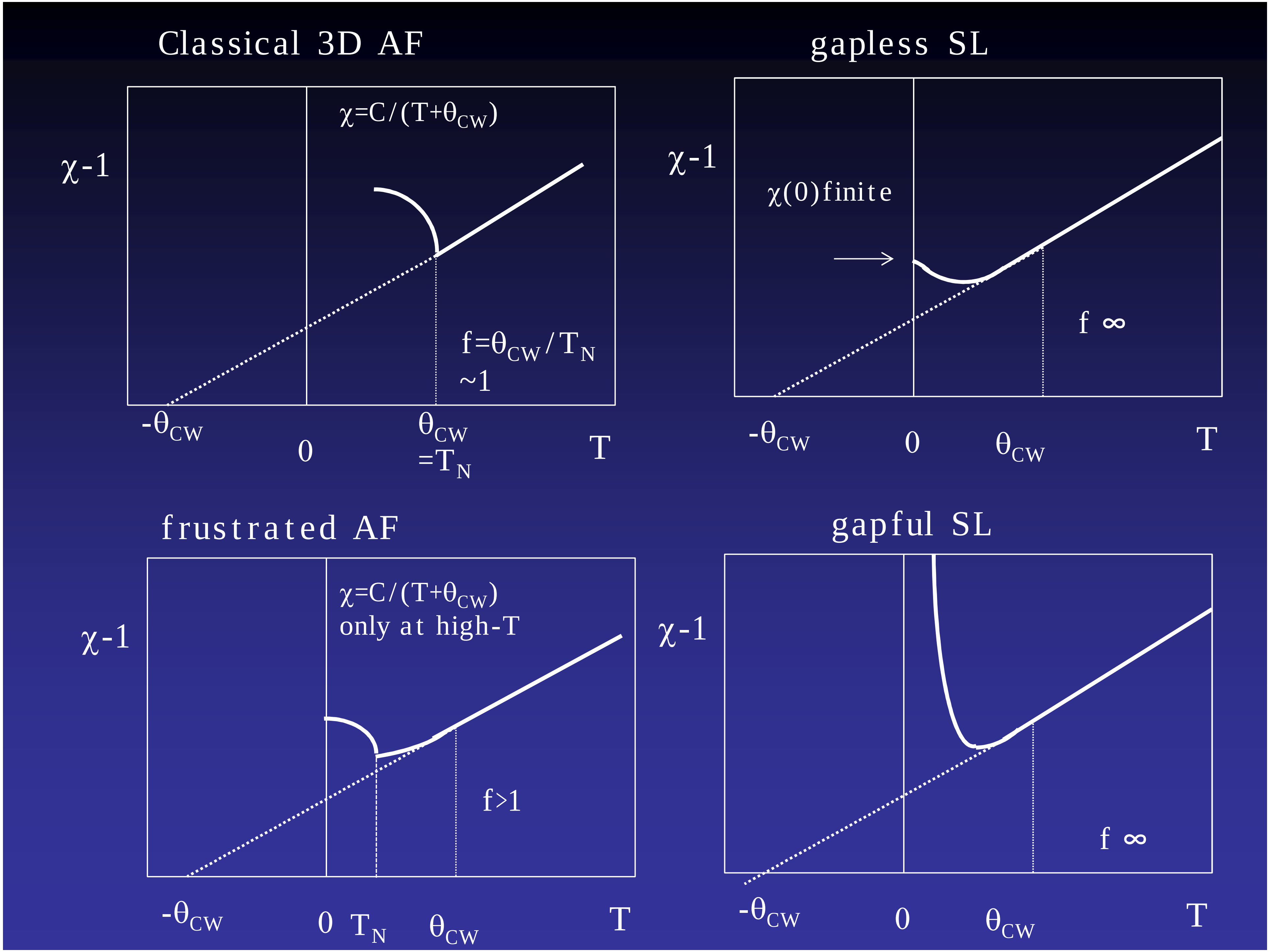
Classical 3D AF
χ-1
χ=C/(T+θCW)
f=θCW/TN
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θCW
=TN
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gapless SL
χ-1
χ(0)finite
f ∞
-θCW
0
θCW
T
frustrated AF
χ-1
χ=C/(T+θCW)
only at high-T
f>1
-θCW
0
TN
θCW
T
gapful SL
χ-1
f ∞
-θCW
0
θCW
T

Emergent spin liquid candidate

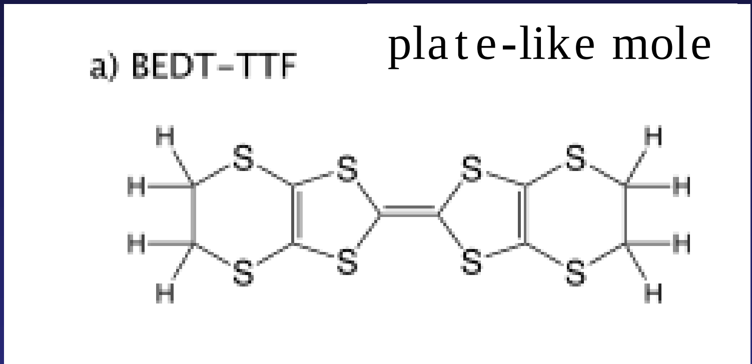
Two dimensional triangular spin systems

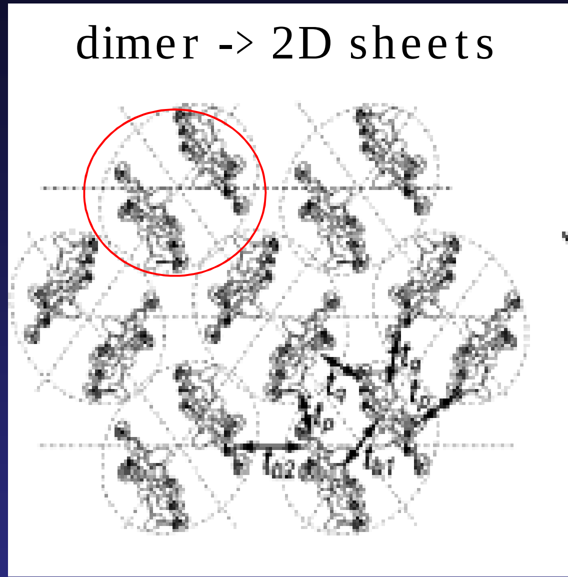
κ-(BEDT-TTF)$_2$-$Cu_2(CN)_3$

$EtMe_3Sb[Pd(dmit)_2]_2$

Organic S=1/2 2D triangular Heisenberg AF

κ-(BEDT-TTF)$_2$-Cu$_2$(CN)$_3$ K.Kanoda





layered stacking

donor

(BEDT-TTF)$_2^+$

X$^-$

accepter

(BEDT-TTF)$_2^+$

X$^-$

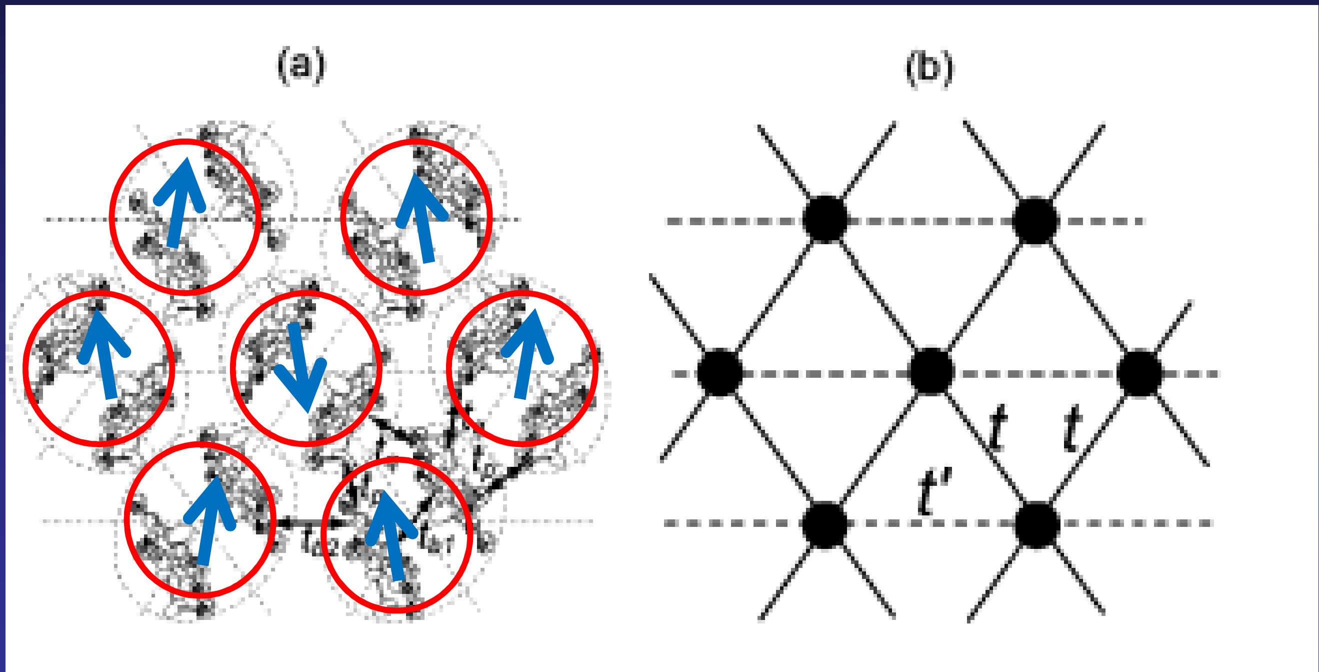
κ-(BEDT-TTF)$_2^+$ X$^-$

1 electron / dimer
intra-dimer coupling strong

-> 1 ele. per bonding orbital
half filled

-> S=1/2 2D Mott ins.

2D S=1/2 trianglar AF κ-(BEDT-TTF)$_2$-Cu$_2$(CN)$_3$

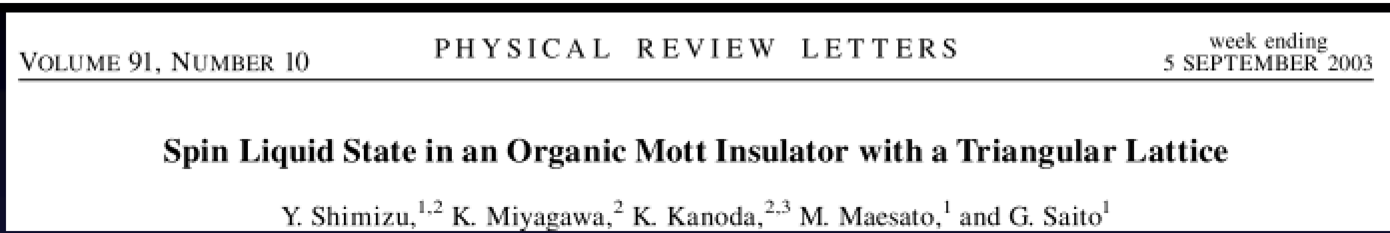


ET$_2$-Cu$_2$(CN)$_3$

t~t'

->

effectively triangular



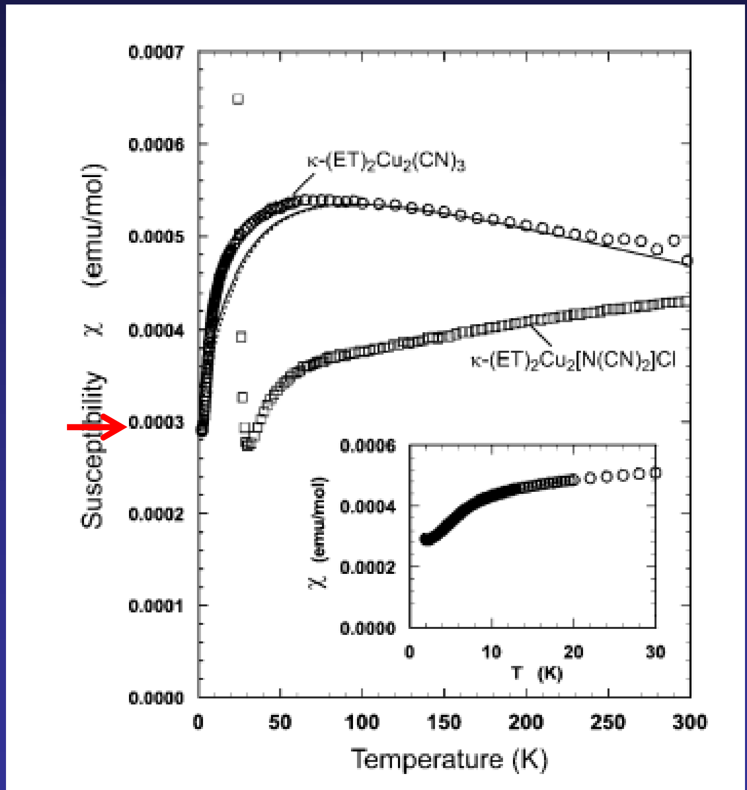
VOLUME 91, NUMBER 10 PHYSICAL REVIEW LETTERS week ending 5 SEPTEMBER 2003

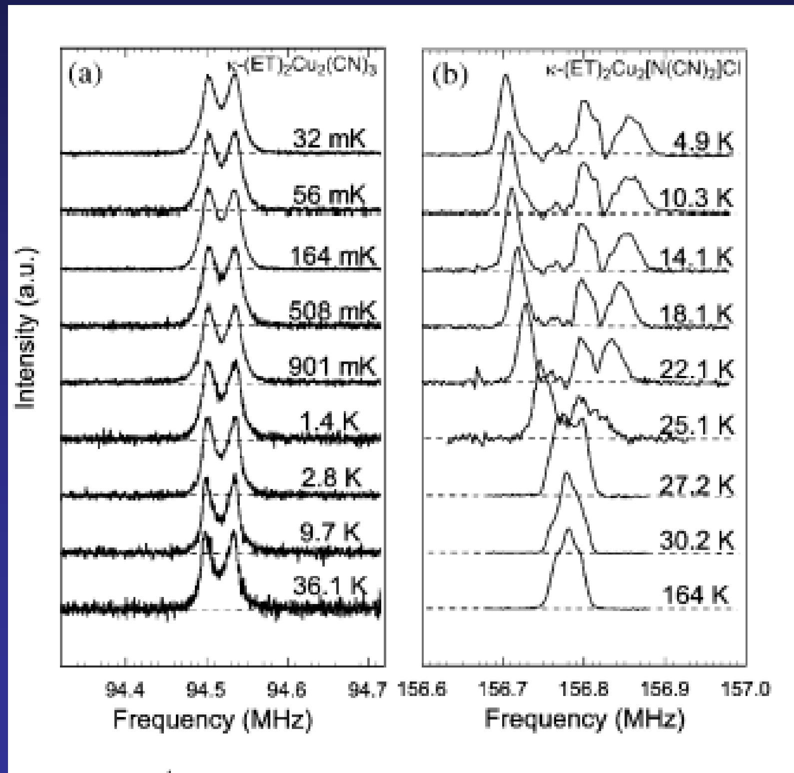
Spin Liquid State in an Organic Mott Insulator with a Triangular Lattice

Y. Shimizu,[1,2] K. Miyagawa,[2] K. Kanoda,[2,3] M. Maesato,[1] and G. Saito[1]

$t=t'$ $t \neq t'$

κ-(BEDT-TTF)$_2$-Cu$_2$(CN)$_3$ κ-(BEDT-TTF)$_2$-Cu$_2$[N(CN)$_2$]Cl





$\chi(0)=2.9\text{x}10^{-4}$ emu/mol

non zero!

gapless

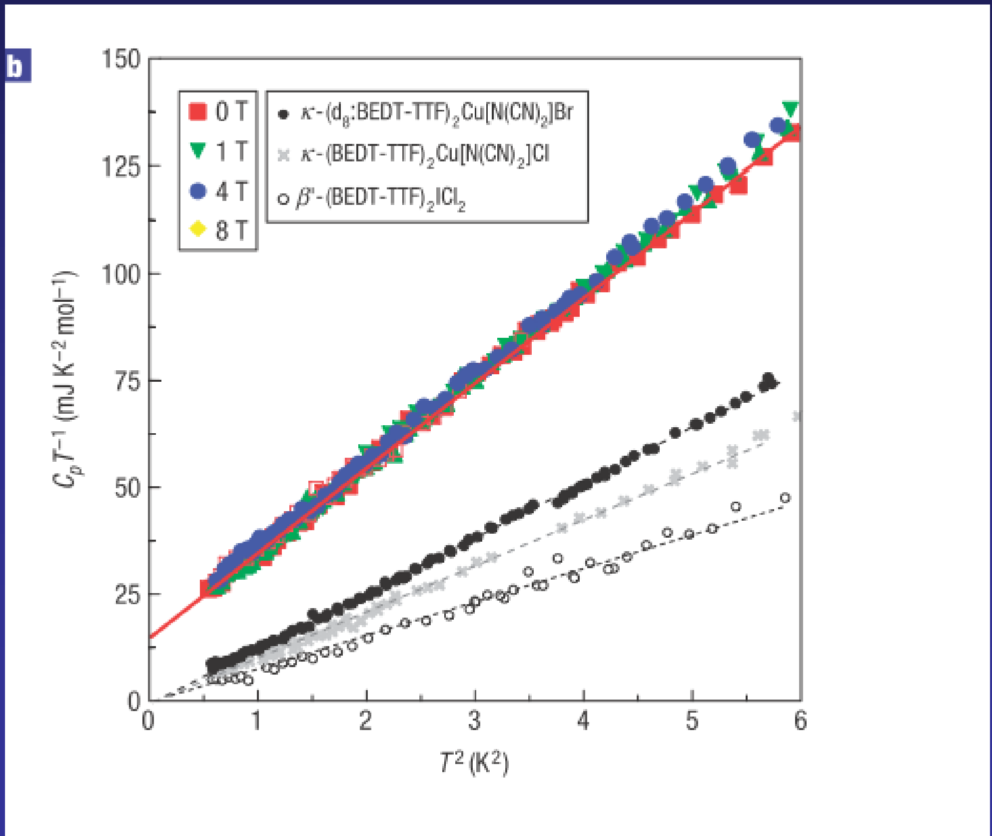
NMR no order

AF

LETTERS

Thermodynamic properties of a spin-1/2 spin-liquid state in a κ-type organic salt

SATOSHI YAMASHITA[1], YASUHIRO NAKAZAWA[1,2]*, MASAHARU OGUNI[3], YUGO OSHIMA[2,4], HIROYUKI NOJIRI[2,4], YASUHIRO SHIMIZU[5], KAZUYA MIYAGAWA[2,6] AND KAZUSHI KANODA[2,6]



$\chi(0)=2.9\times10^{-4}$ emu/mol

$\gamma(0)=13$ mJ/mol K^2

Wilson ratio

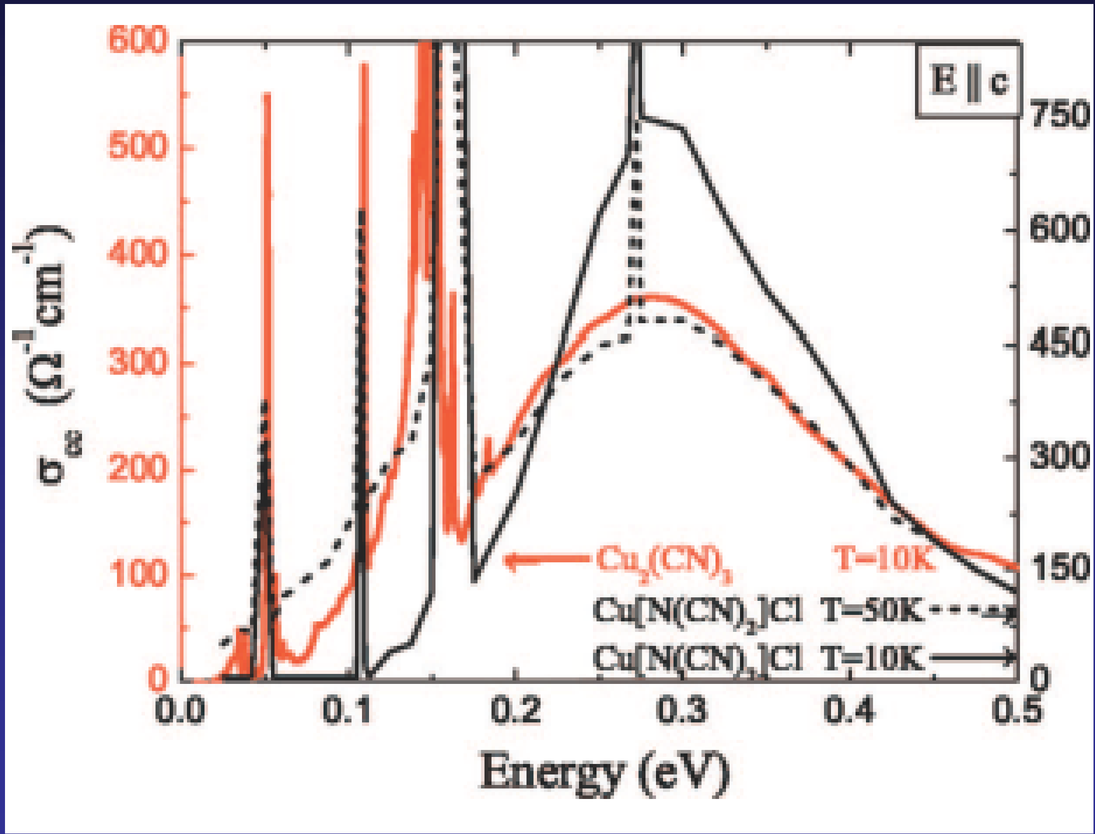
$R_W=[\pi^2 k_B^2/3\mu_B^2]\,\chi(0)/\gamma(0)$

~1 !

like free electron!

Spinon FS?

Why not 120 ° structure?



Close proximity
to metal
U/t not so small

higher order
interaction stabilize
spin liquid?

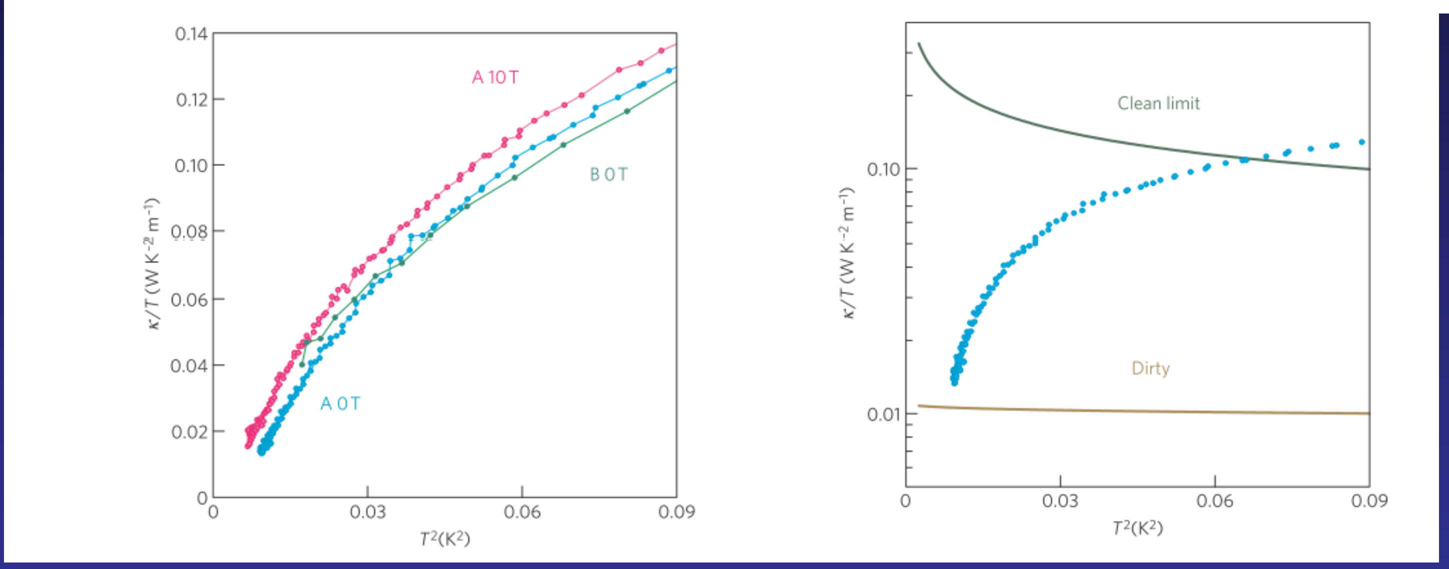
Charge gap very small
Kezsmarki et al PRB

Issues and Challenges: why κ/T ->0?

Absence of gapless excitation?

Thermal-transport measurements in a quantum spin-liquid state of the frustrated triangular magnet κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

Minoru Yamashita[1]★, Norihito Nakata[1], Yuichi Kasahara[1,2], Takahiko Sasaki[2], Naoki Yoneyama[2], Norio Kobayashi[2], Satoshi Fujimoto[1], Takasada Shibauchi[1] and Yuji Matsuda[1]



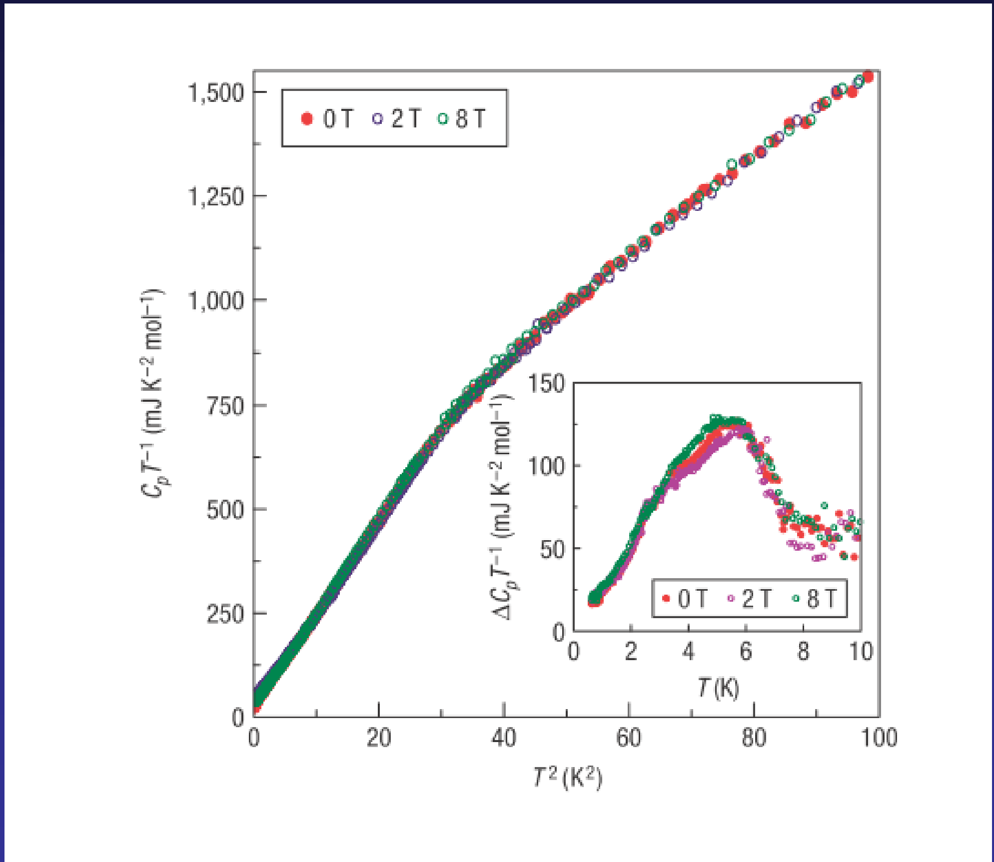
l=3a

thermal conductivity κ

sensitive to chargeless excitation $\kappa = 1/3\ C\ v\ l$

If finite DOS, κ/T should be nonzero

Issues and Challenges: What is 6K anomaly?

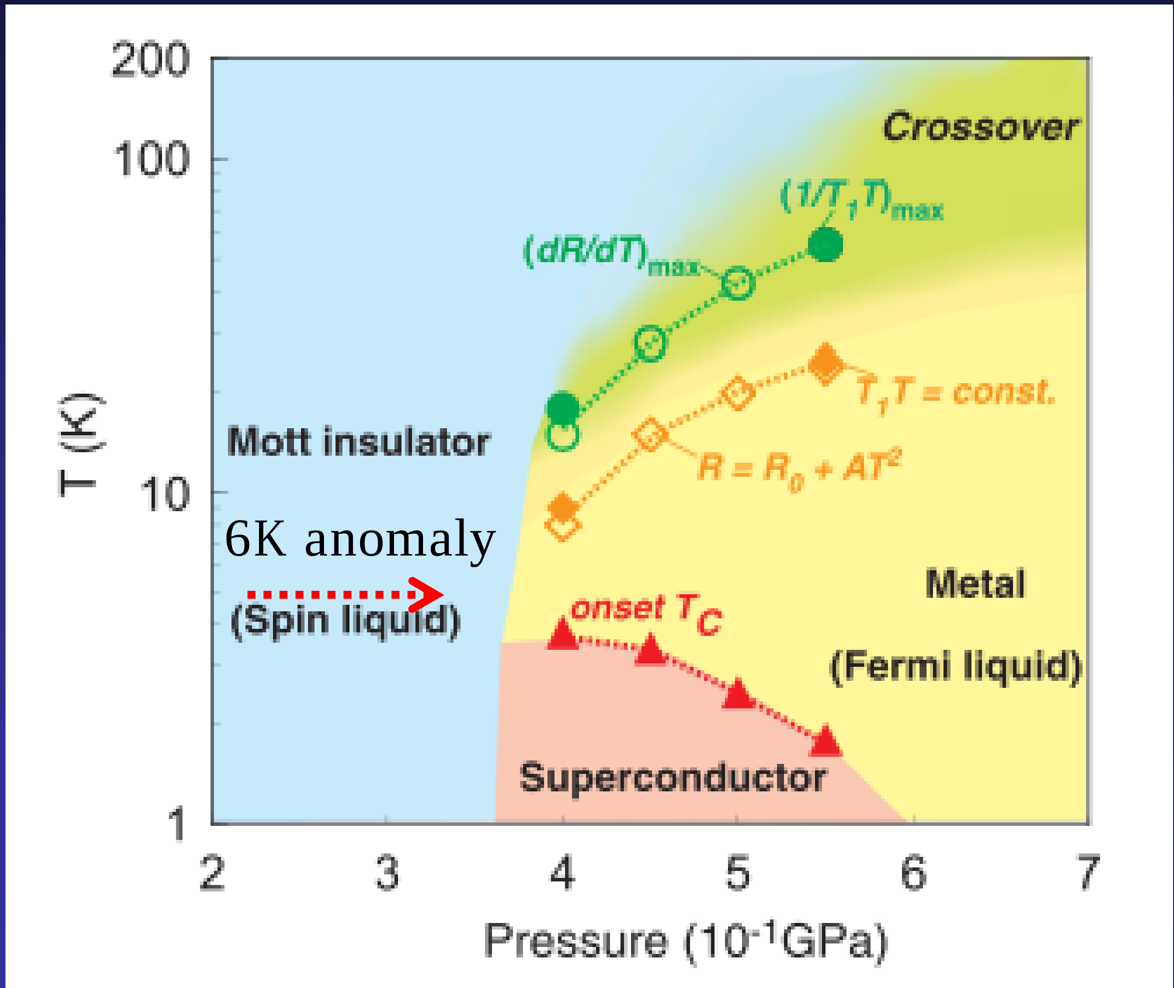


also in NMR
nuclear M decay
shows anomaly
(non single exp)
below 6K

anomaly in thermal
expansion

phase transition of
spinon FS?
P.A.Lee

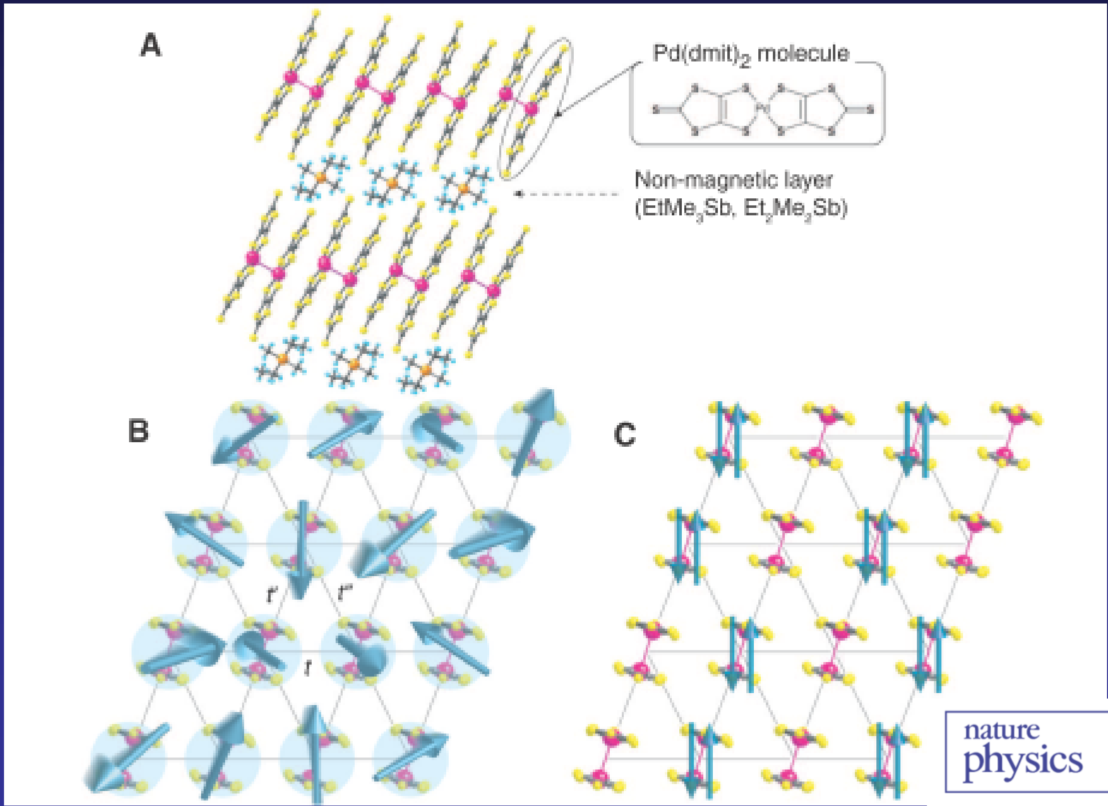
6K anomaly and pressure induced SC

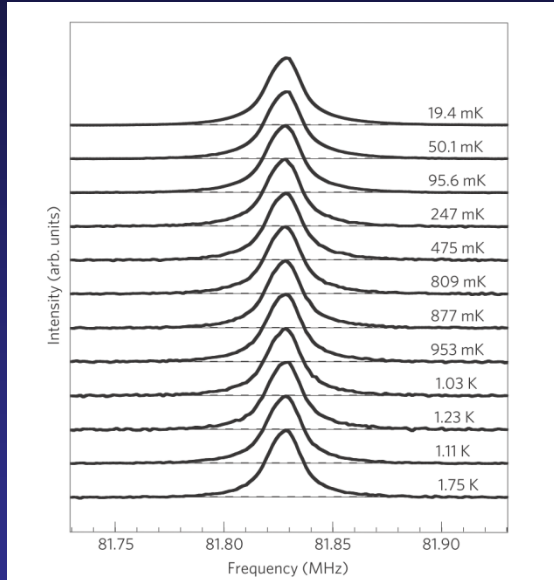


$EtMe_3Sb[Pd(dmit)_2]_2$
A new generation of spin liquid candidates

S=1/2 Mott ins. on 2D triangular lattice R.Kato

$[Pd(dmit)_2]_2$ 1 el/dimer



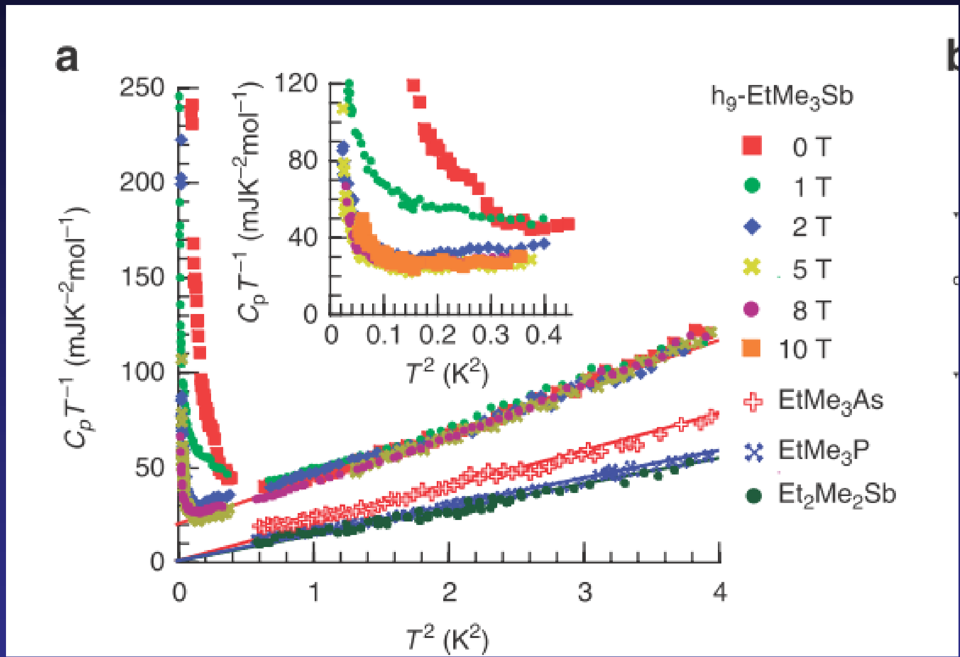


nature physics LETTERS
PUBLISHED ONLINE: 11 JULY 2010 | DOI: 10.1038/NPHYS1715

Instability of a quantum spin liquid in an organic triangular-lattice antiferromagnet

T. Itou[1]*, A. Oyamada[1], S. Maegawa[1] and R. Kato[2]

$EtMe_3Sb[Pd(dmit)_2]_2$ Wison ratio again close to 1



$\chi(0)$=4.4x10^{-4} emu/mol

$\gamma(0)$=19.9 mJ/mol K^2

Wilson ratio

$RW=[(2/3)\pi^2 k_B{}^2/\mu_B{}^2]\,\chi(0)/\gamma(0)$

~1 !

like free electron!

Spinon FS?

ARTICLE

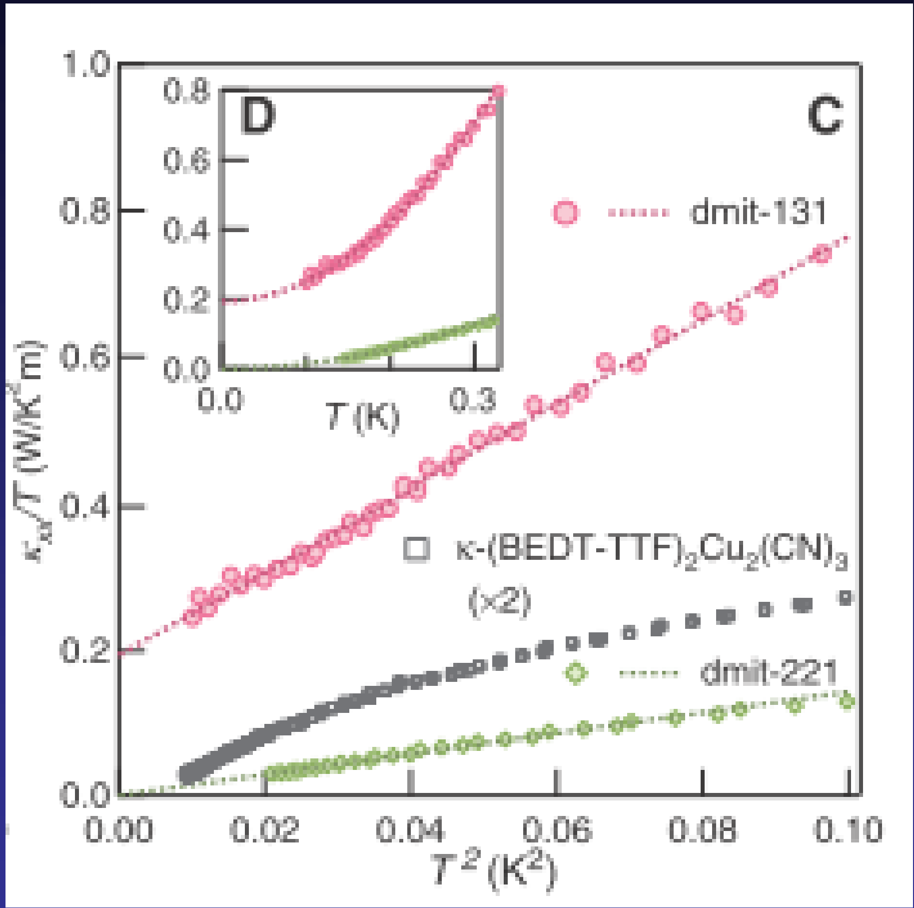
Received 31 Aug 2010 | Accepted 14 Mar 2011 | Published 12 Apr 2011 DOI: 10.1038/ncomms1274

Gapless spin liquid of an organic triangular compound evidenced by thermodynamic measurements

Satoshi Yamashita[1,2], Takashi Yamamoto[1], Yasuhiro Nakazawa[1,3], Masafumi Tamura[4] & Reizo Kato[2]

A finite κ/T observed for $EtMe_3Sb[Pd(dmit)_2]_2$

gapless excitation is there



$\kappa/T = 1/3\ C\ v\ l$

$l = 1\ \mu m$!

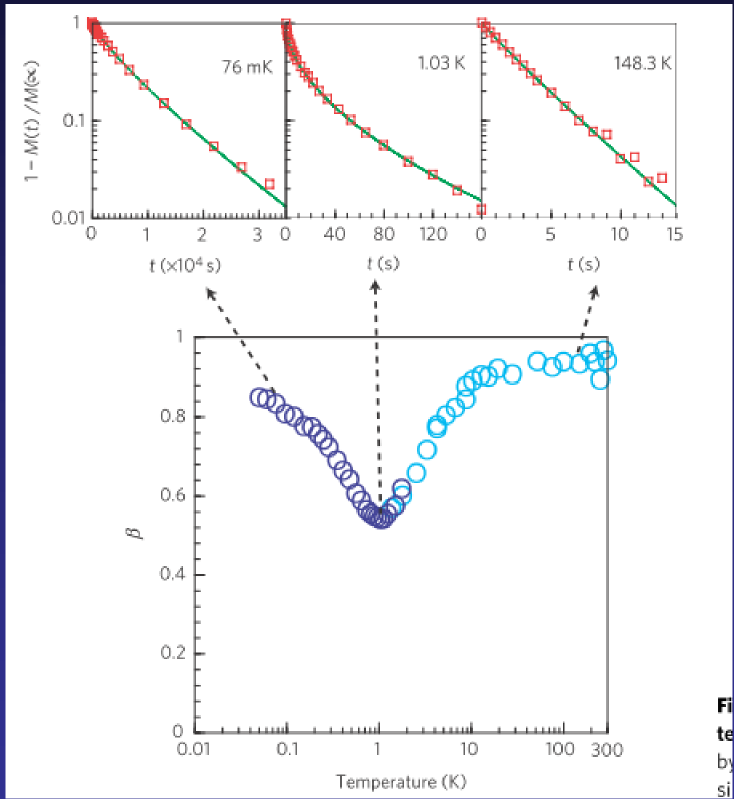
excitation highly mobile

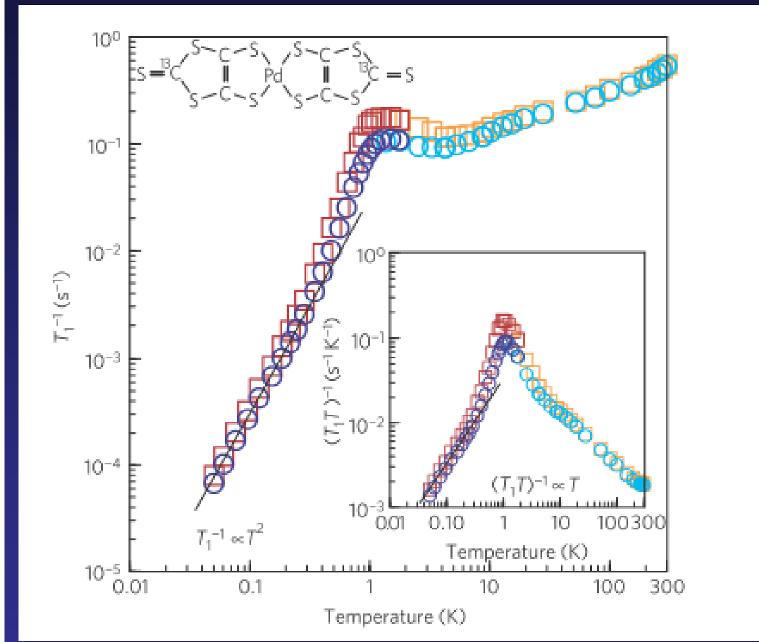
Highly Mobile Gapless Excitations in a Two-Dimensional Candidate Quantum Spin Liquid

Minoru Yamashita,[1*] Norihito Nakata,[1] Yoshinori Senshu,[1] Masaki Nagata,[1] Hiroshi M. Yamamoto,[2,3] Reizo Kato,[2] Takasada Shibauchi,[1] Yuji Matsuda[1*]

Yamashita, Kato, Matsuda, Science (10)

Issues and Challenges:
$EtMe_3Sb[Pd(dmit)_2]_2$ 1K anomaly in T_1^{-1}

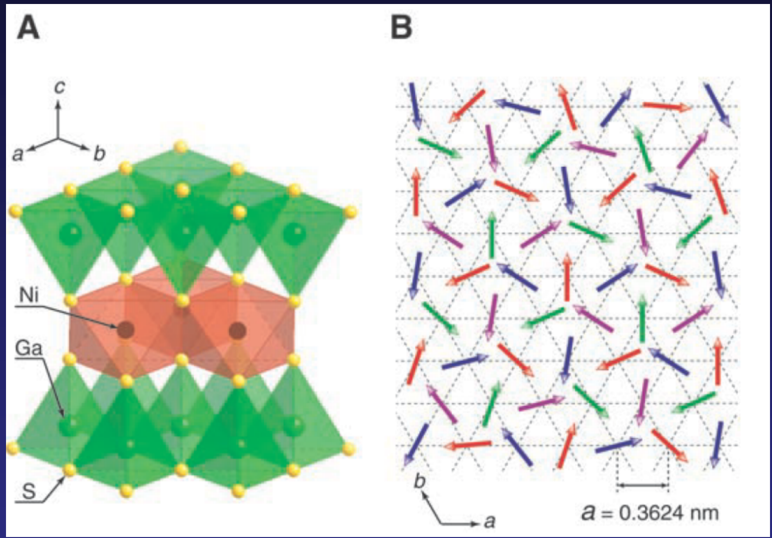


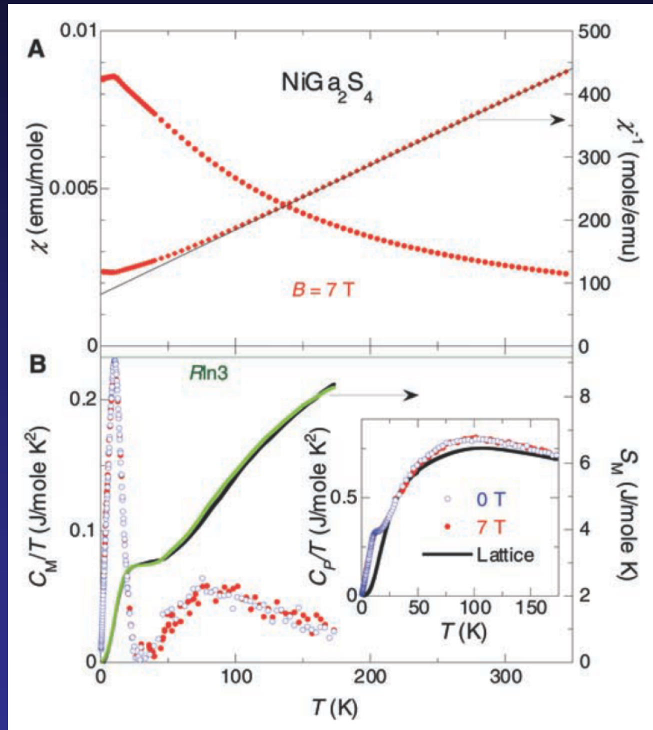


Itou Nature Phys.

Phase transition of spinon FS?

S=1 triangular AF magnet $NiGa_2S_4$





Spin Disorder on a Triangular Lattice

Satoru Nakatsuji,[1*] Yusuke Nambu,[1] Hiroshi Tonomura,[1] Osamu Sakai,[1] Seth Jonas,[3] Collin Broholm,[3,4] Hirokazu Tsunetsugu,[2] Yiming Qiu,[4,5] Yoshiteru Maeno[1,6]

Spin freezing at 8.5 K

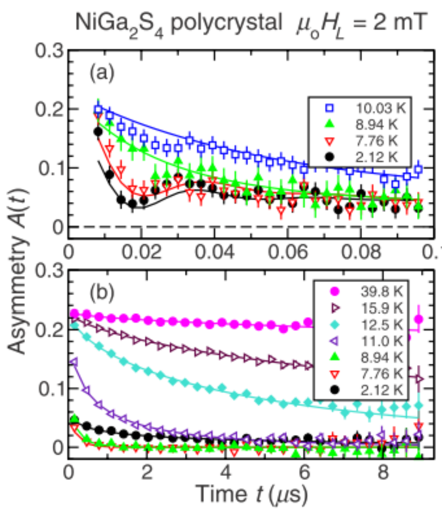
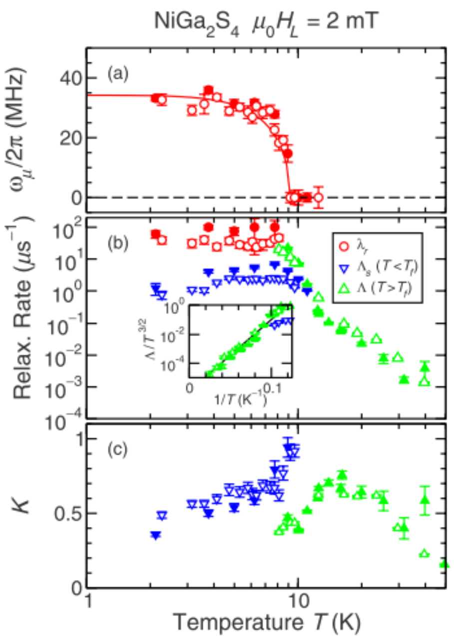


FIG. 1. (Color online) Representative (a) early- and (b) late-time LF-μSR asymmetry data in polycrystalline NiGa$_2$S$_4$; applied longitudinal field $\mu_0 H_L$=2 mT. Curves: fits to Eqs. (1)–(3).



Maclaughlin et al. PRB

Organics

Likely, closest to holly grail.
But, there remains many issues yet to be tackled.

Nature of low T anomaly 6K, 1K?
Intrinsic? Related to instability of spinon FS

BEDT thermal conductivity can be understood localized excitation?

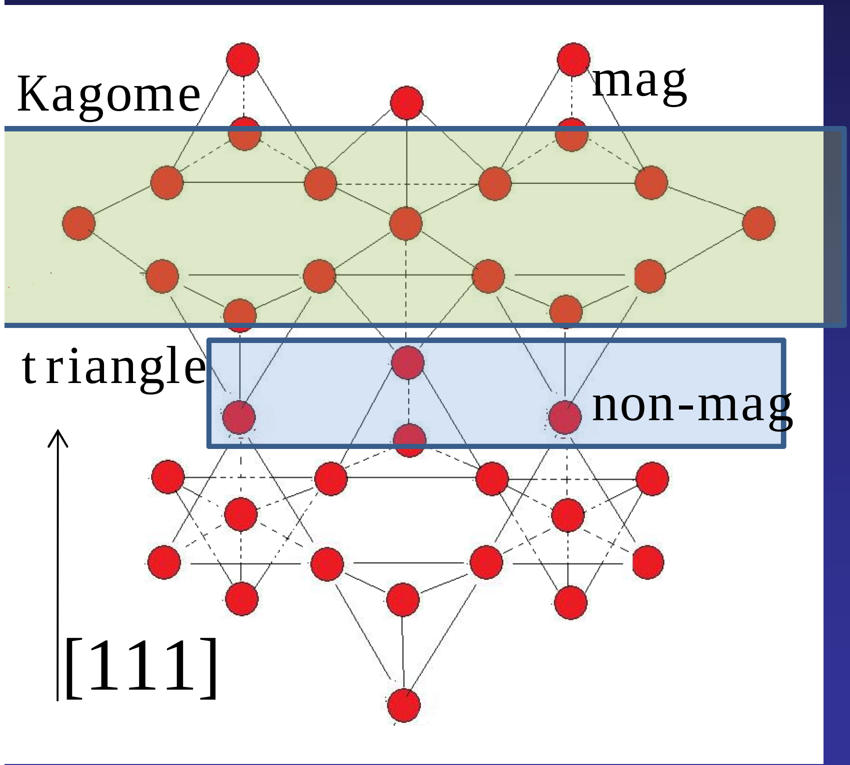
How to establish the presence of spinon FS?

Emergent quantum spin liquid:

S=1/2 2D Kagome

Perfect S=1/2 Kagome

Hybertsmithite $ZnCu_3(OH)_6Cl_2$

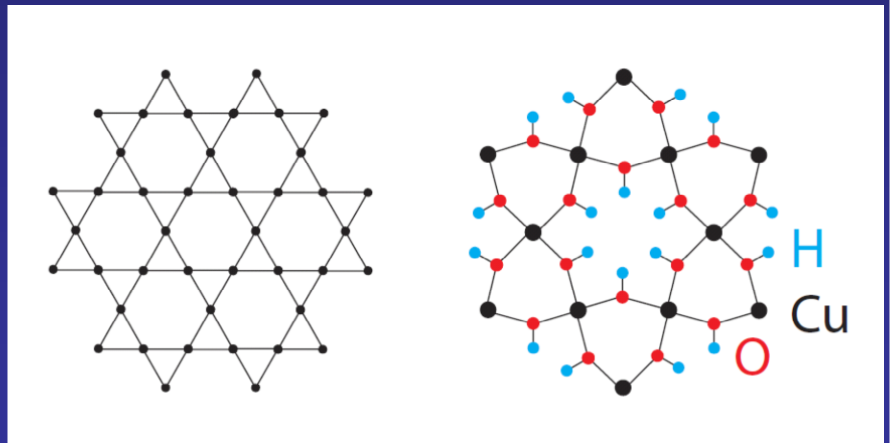


$ZnCu_3(OH)_6Cl_2$

Cu^{2+}

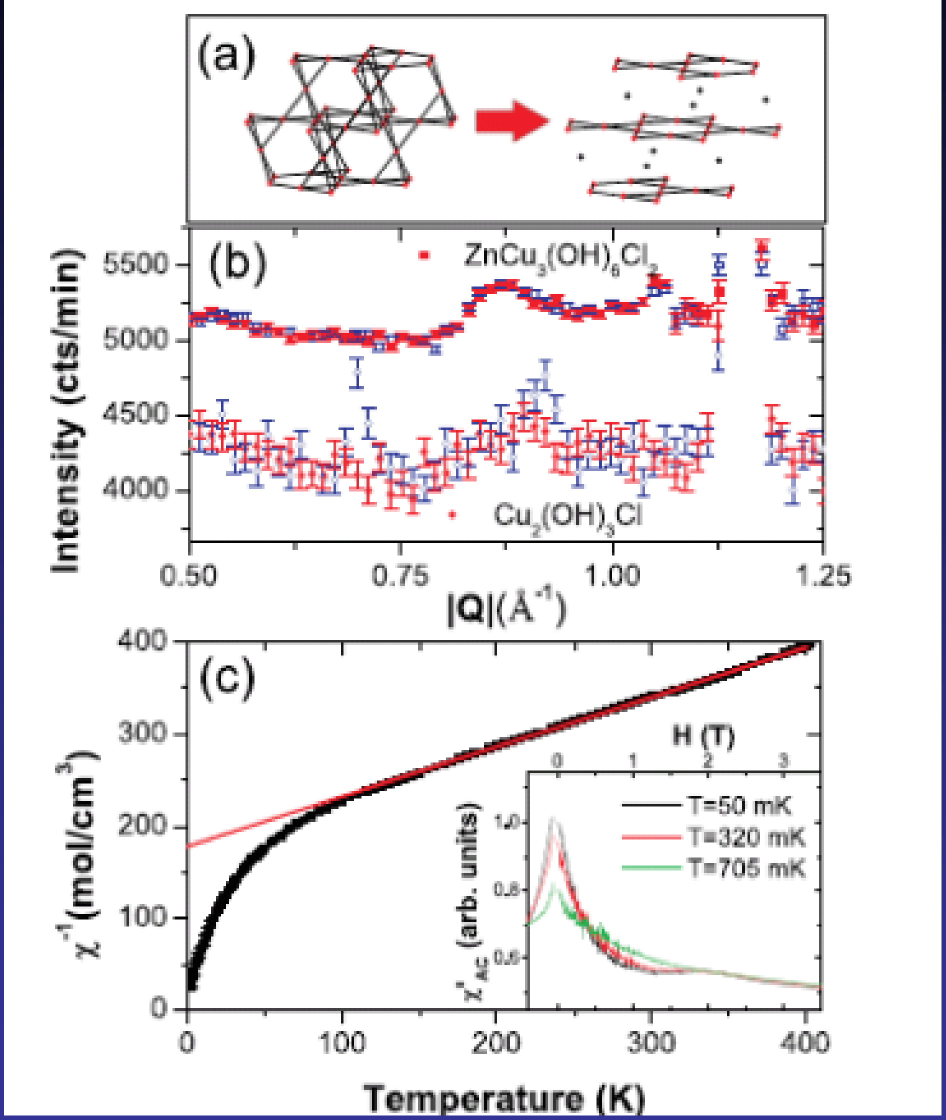
Zn^{2+}

R3m



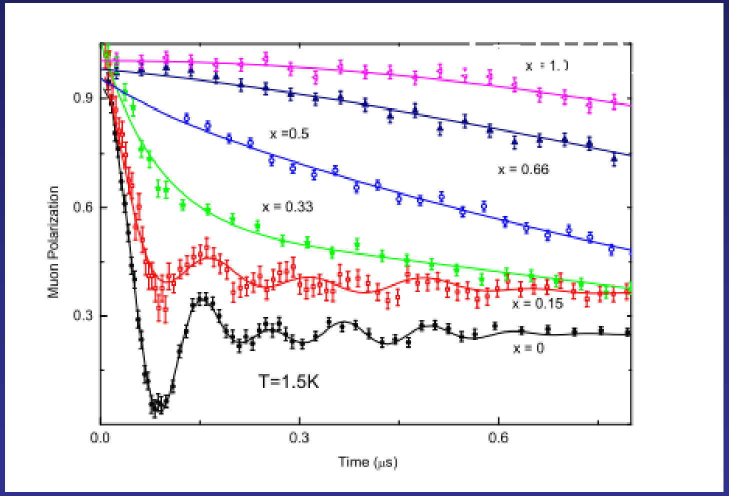
M.P. Shores, E.A. Nytko, B.M. Barlett and D.G. Nocera, J. A. Chem. Soc., **127**, 13462 (2005)

Spin liquid behavior of $ZnCu_3(OH)_6Cl_2$



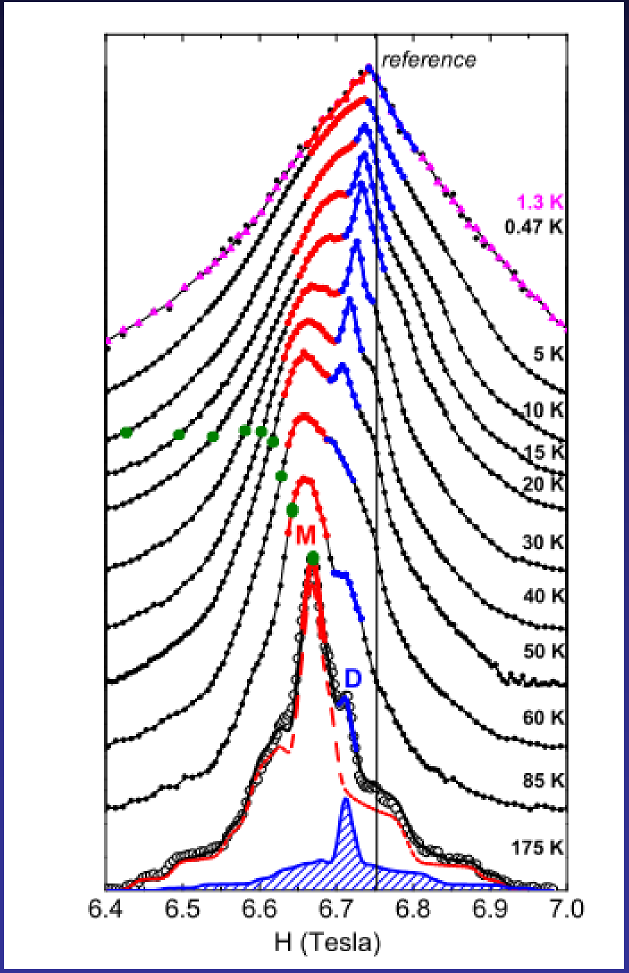
J=180K

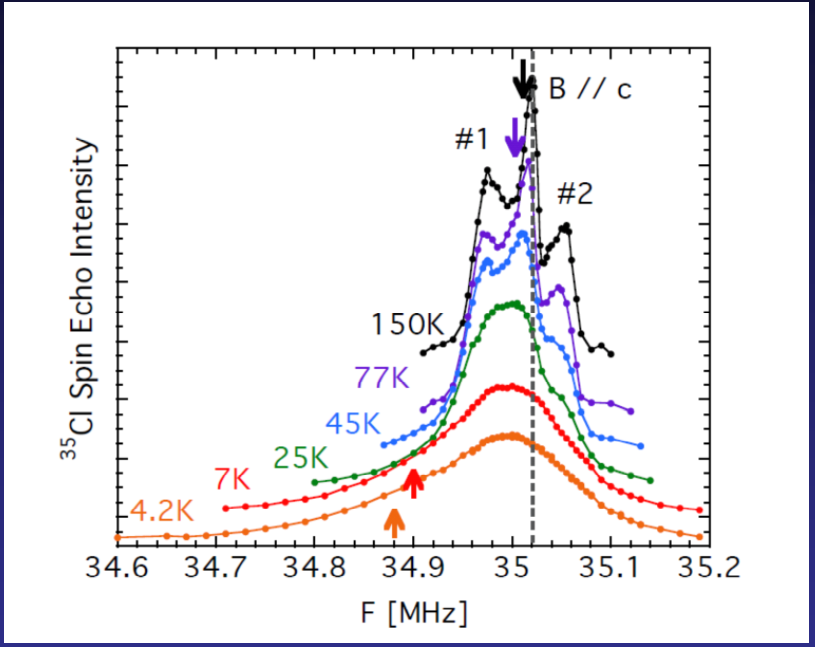
No siganture of ordering
Y.S.Lee PRL, Medels PRL



NMR

broad (in particular at low T) but no clear evidence for or





Imai

Cl

Zn and Cu exchange
indicated from neutron
Lee

Disorder effect subject of
debate

Mendels

Cu

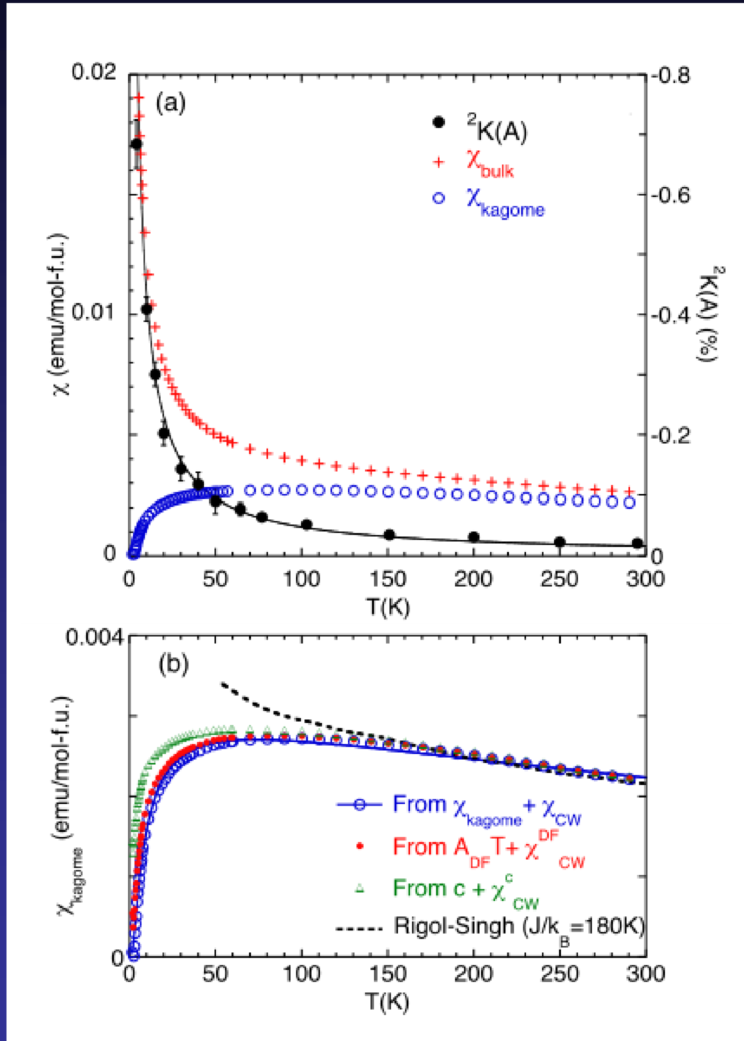
Small but finite spin gap?

Small spin gap
~J/4-J/20
predicted
Lhuillier
Huse...

But,
experimentally
cannot distinguish

$\chi(0)$ finite

$\chi(0)$ zero
exponential
decay
power law decay

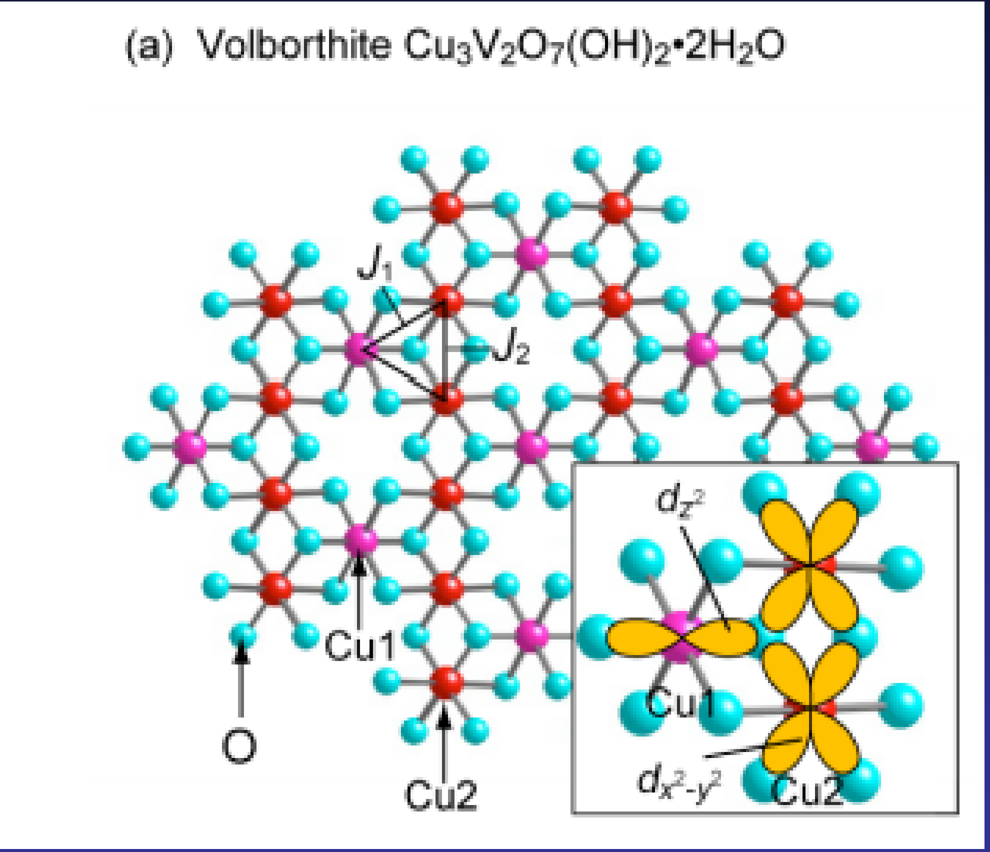


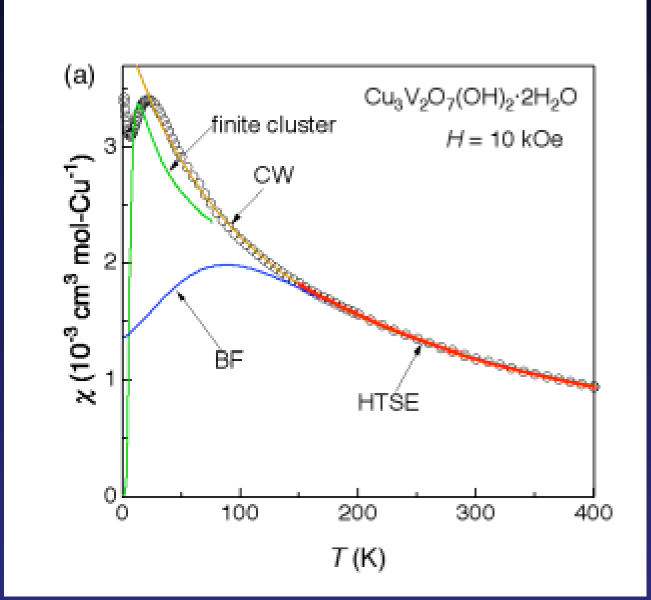
Local Spin Susceptibility of the $S = 1/2$ Kagome Lattice in $ZnCu_3(OD)_6Cl_2$

T. Imai,[1,2] M. Fu,[1] T. H. Han,[3] and Y. S. Lee[3]

Volborthite $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$

two Cu sites but very clean





finite susceptibility
gapless spin liquid?

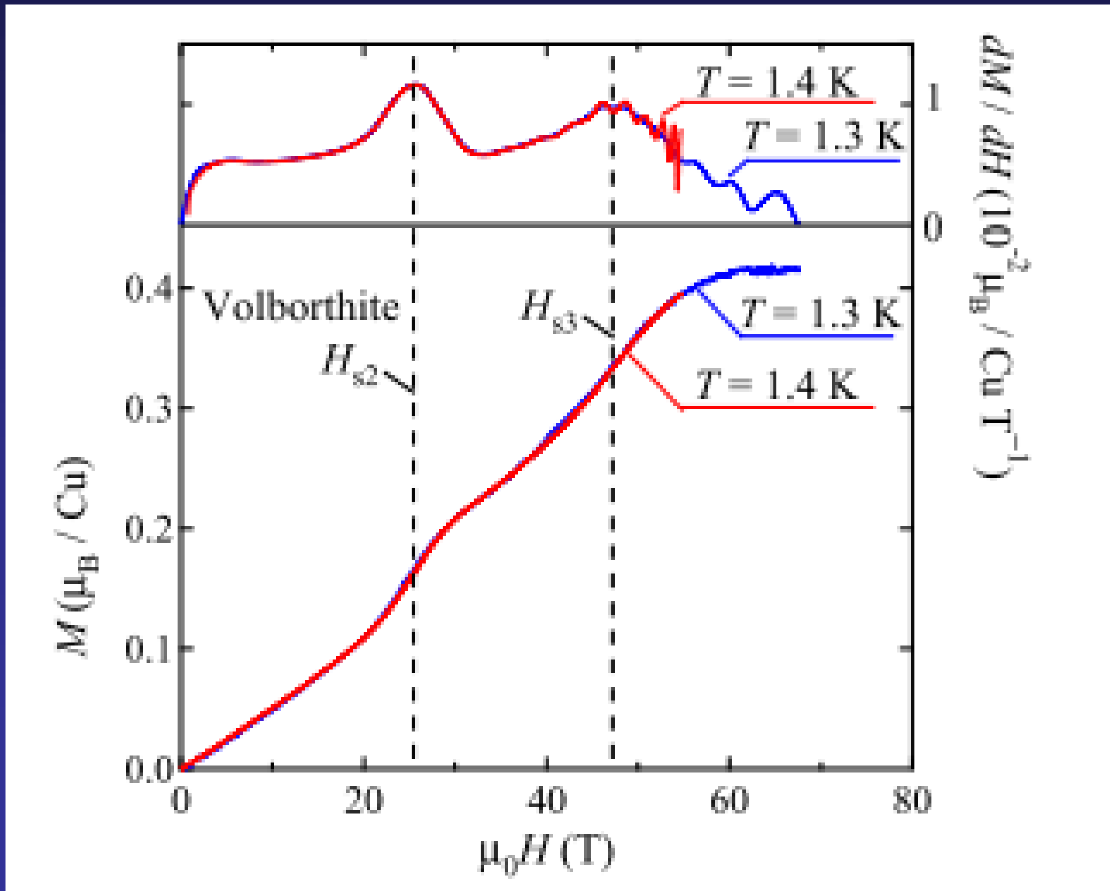
[6] Lafontaine M A, Bail A L and Férey G 1990 *J. Solid State Chem.* **85** 220
[7] Hiroi Z, Kobayashi N, Hanawa M, Nohara M, Takagi H, Kato Y and Takigawa M 2001 *J. Phys. Soc. Jpn.* **70** 3377

Anomalous magnetization plateaus in Volborthite

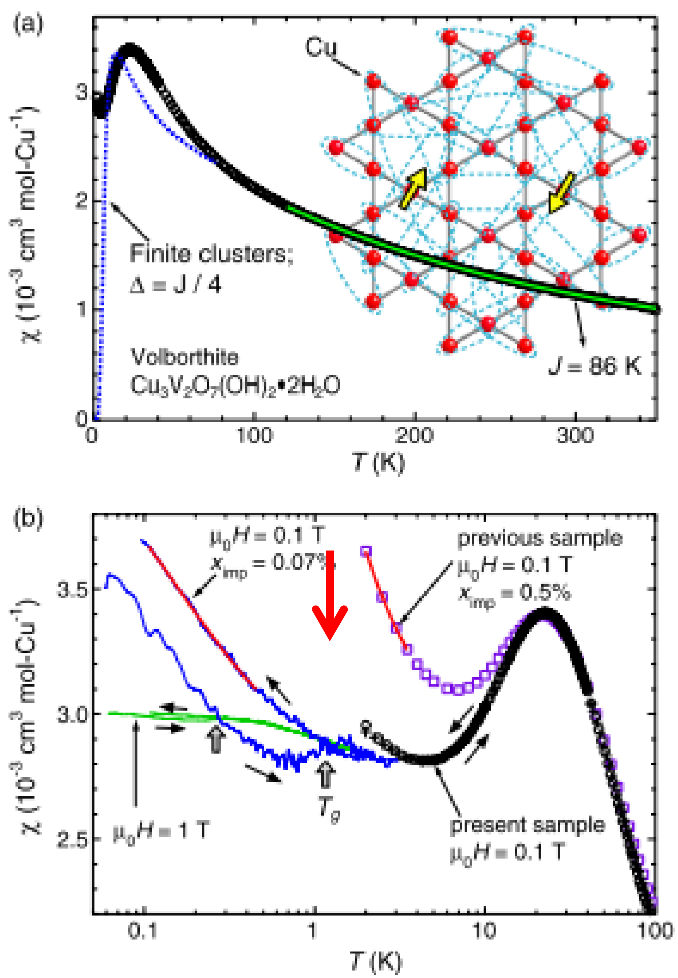
Magnetization "Steps" on a Kagome Lattice in Volborthite

Hiroyuki YOSHIDA, Yoshihiko OKAMOTO, Takashi TAYAMA, Toshiro SAKAKIBARA, Masashi TOKUNAGA, Akira MATSUO, Yasuo NARUMI, Koichi KINDO, Makoto YOSHIDA, Masashi TAKIGAWA, and Zenji HIROI*

not plateau



1 K transition in Volborthite



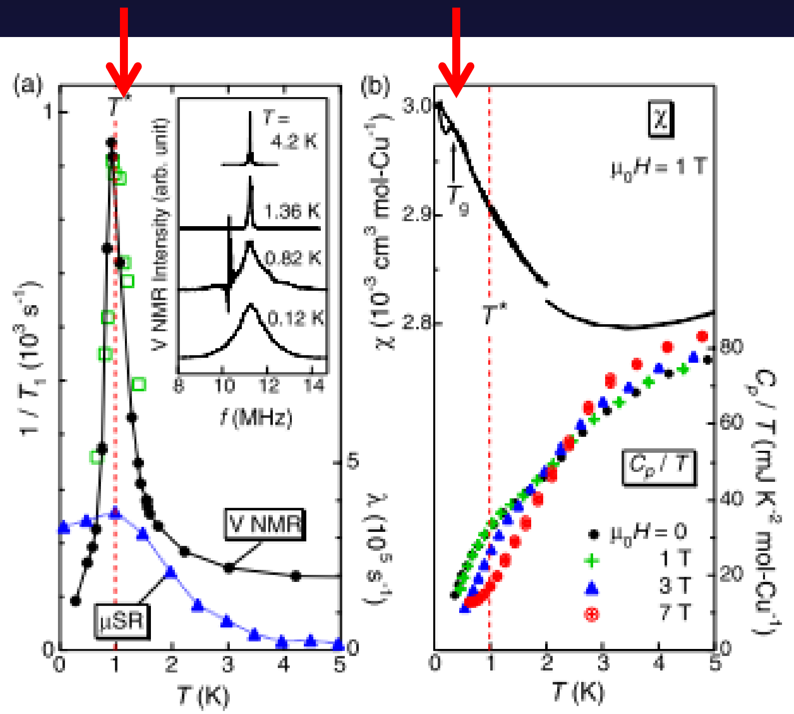
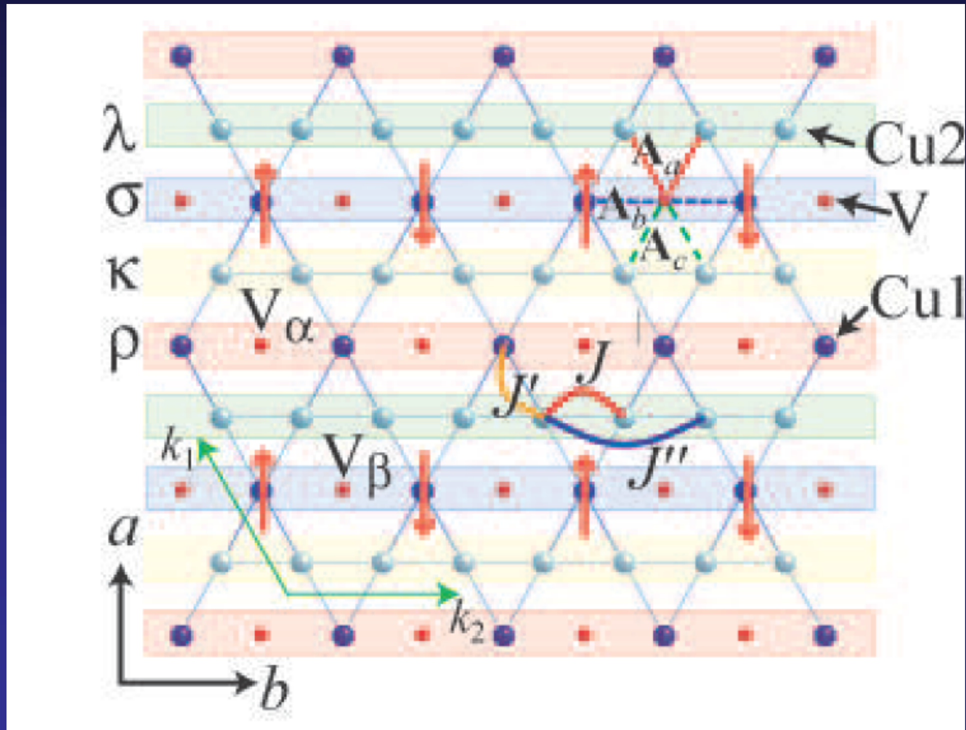


Fig. 2. (Color online) (a) Relaxation rates λ (triangles) from previous μSR measurements[21] at $\mu_0 H = 0.01$ T and $1/T_1$ from the present ^{51}V NMR experiments at $\mu_0 H = 1$ (circles) and 4 (squares) T. The inset shows the temperature evolution of the NMR spectra taken at $\mu_0 H = 1$ T at frequencies between 8 and 14.5 MHz. (b) Magnetic susceptibility χ measured at $\mu_0 H = 1$ T [the same data given in Fig. 1(a)] and heat capacity divided by temperature C_p/T at $\mu_0 H = 0$, 1, 3, and 7 T obtained in a Quantum Design PPMS system.

Volborthite: distorted kagome: 1D chain + bridge

1D physics?



A Heterogeneous Spin State in the Field-Induced Phase of Volborthite

M. Yoshida,[1] M. Takigawa,[1] H. Yoshida,[2] Y. Okamoto,[1] and Z. Hiroi[1]

[1]*Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan*

[2]*Superconducting Materials Center, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan*

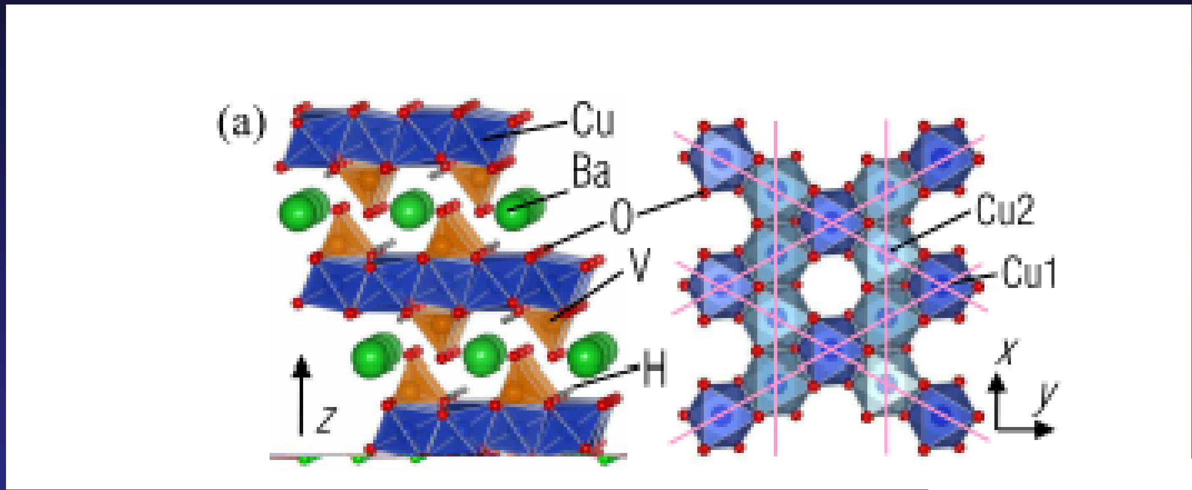
(Dated: April 1, 2011)

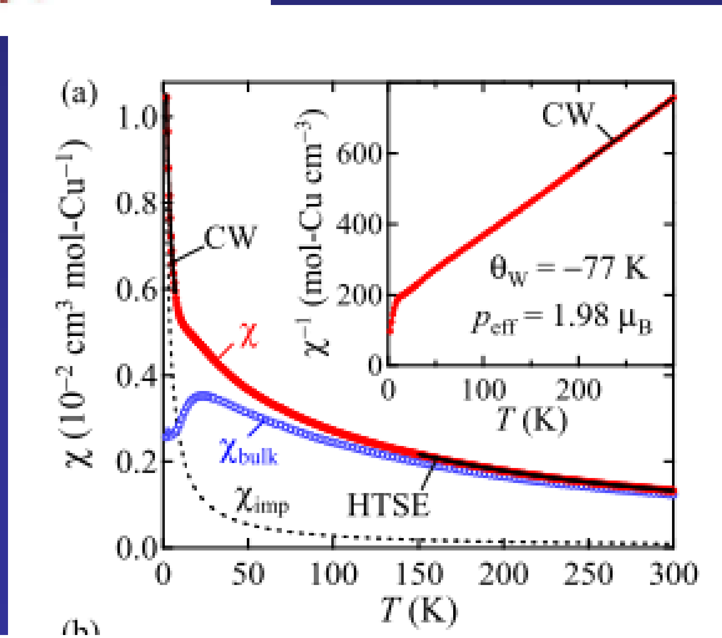
Journal of the Physical Society of Japan
Vol. 78, No. 3, March, 2009, 033701

LETTERS

Vesignieite $BaCu_3V_2O_8(OH)_2$ as a Candidate Spin-1/2 Kagome Antiferromagnet

Yoshihiko OKAMOTO*, Hiroyuki YOSHIDA, and Zenji HIROI





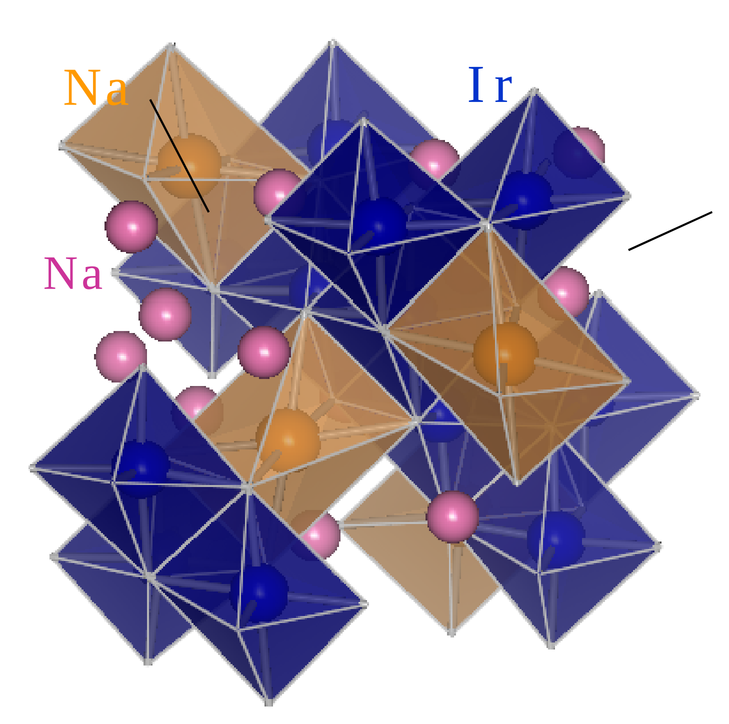
Emergent quantum spin liquid

3D Hyperkagome

$Na_4Ir_3O_8$: Ir^{4+} oxide with hyper-kagome structure

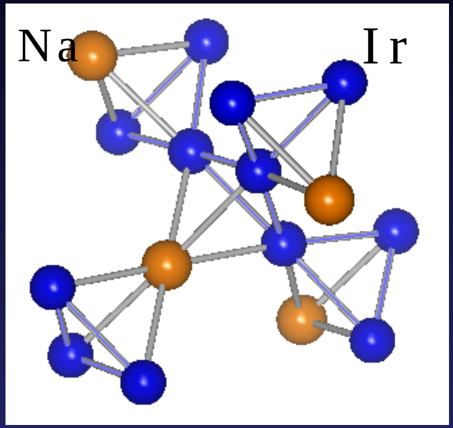
B-cation ordered spinel

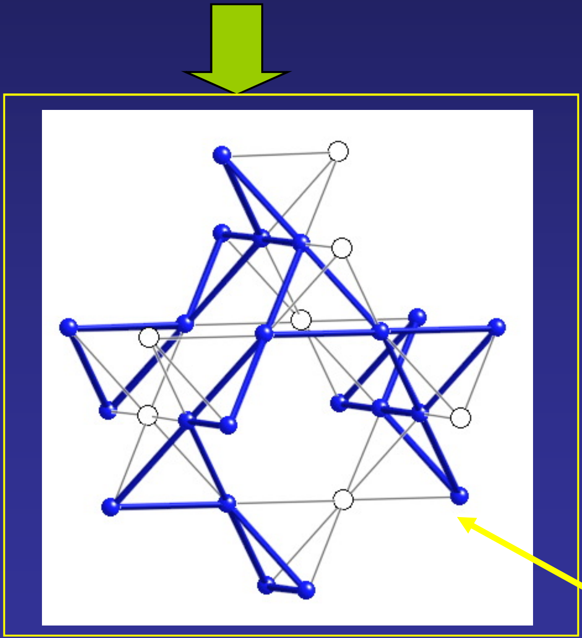
2 $(Na_{3/2})_1\ (Ir_{3/4}, Na_{1/4})_2O_4$



$Na_4Ir_3O_8$: cubic $P4_132$, a = 8.985 Å

Isostructural to $Na_4Sn_3O_8$

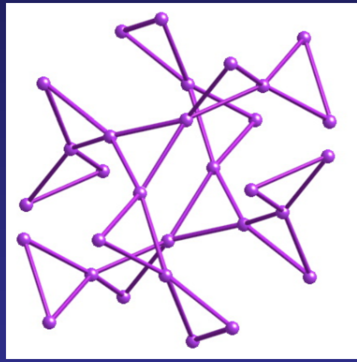




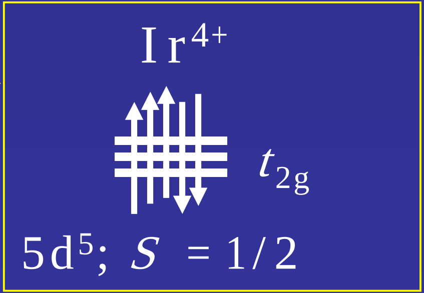
"hyper-Kagome" frustration

B-site

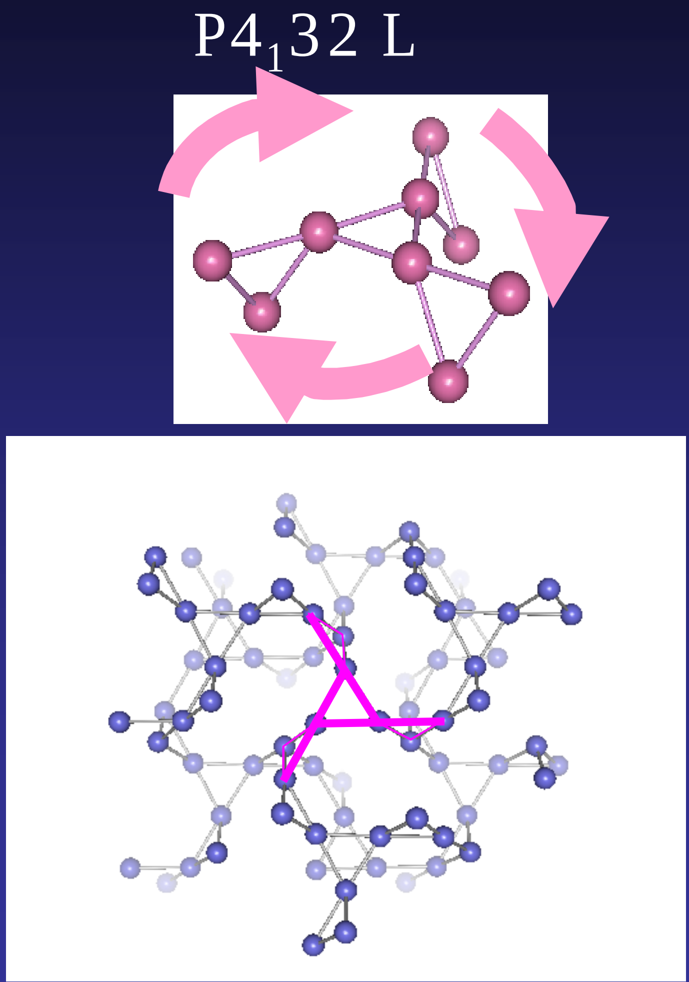
¾ : Ir, ¼ : Na
Cation ordering

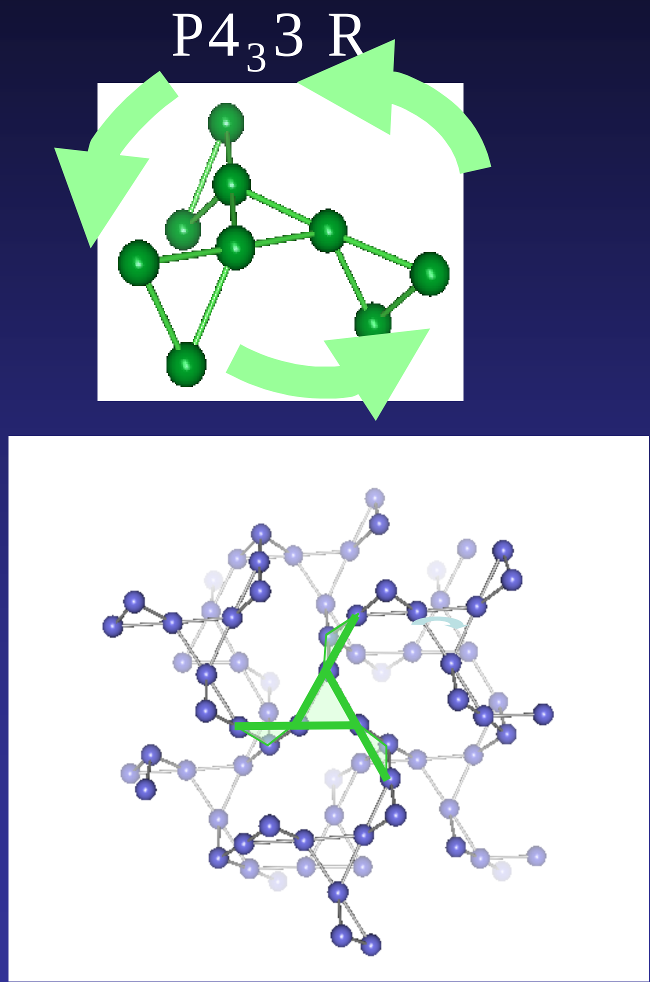


Closely related to garnet



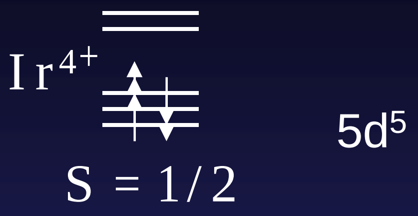
Hyperkagome (ordered spinel) lattice has "chirality"

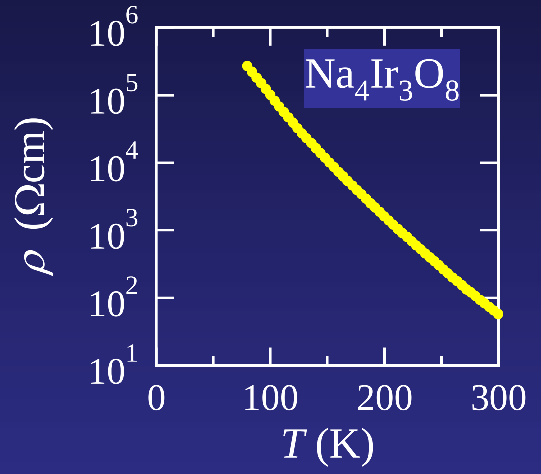


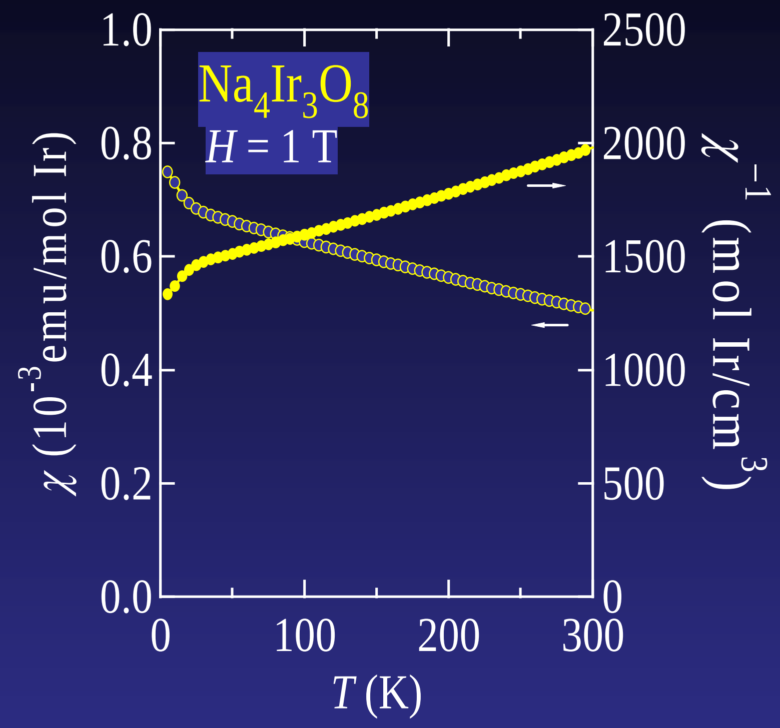


Spin liquid formed on lattice with chirality!
(+ strong spin orbit coupling)

$Na_4Ir_3O_8$ S=1/2 Mott Ins. with AF interaction







Mott insulator

S=1/2 hyper-Kagome

θ_W = -650 K μ_{eff} = 1.96 μ_B / Ir

strong AF int.   (S = 1/2 → 1.73 μ_B)

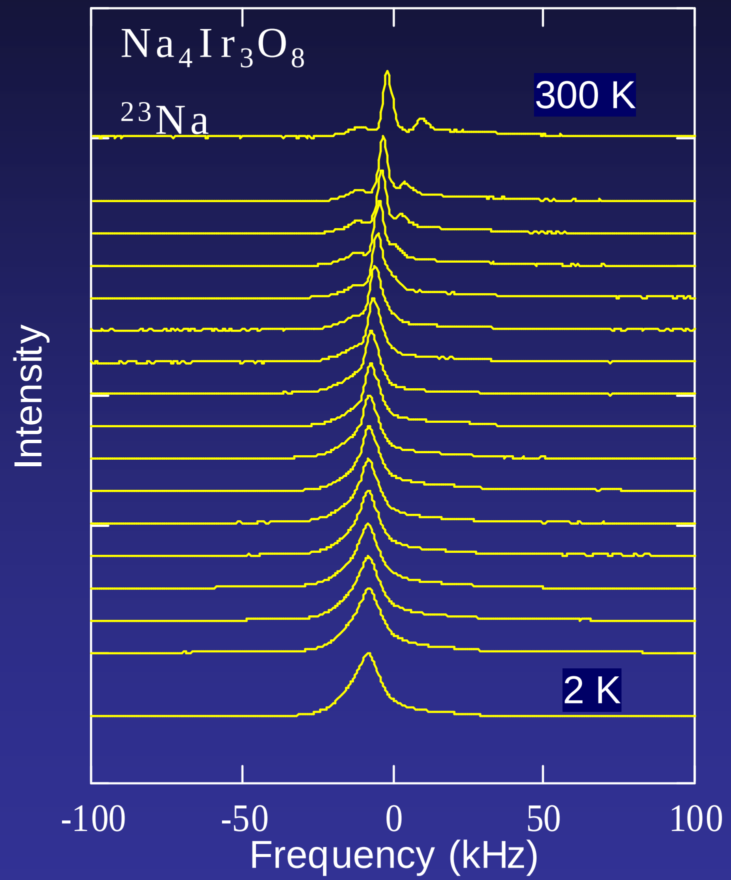
J=650 K estimated

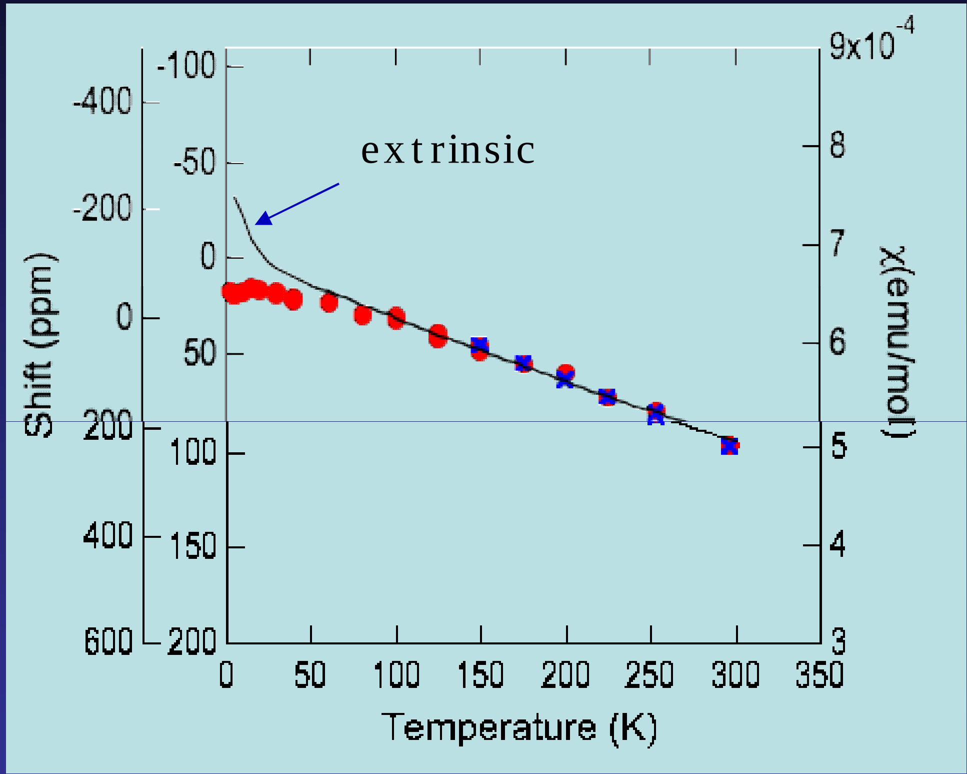
(comment: J~350 K Y.B.Kim analysis)

No ordering in χ down to 1.8 K << θ_{cw}= 650K   Strong frustration

No long range ordering detected by neutron down to 4K

^{23}Na NMR indicates absence of magnetic ordering down to 2 K (J=650 K) - evidence for spin liquid





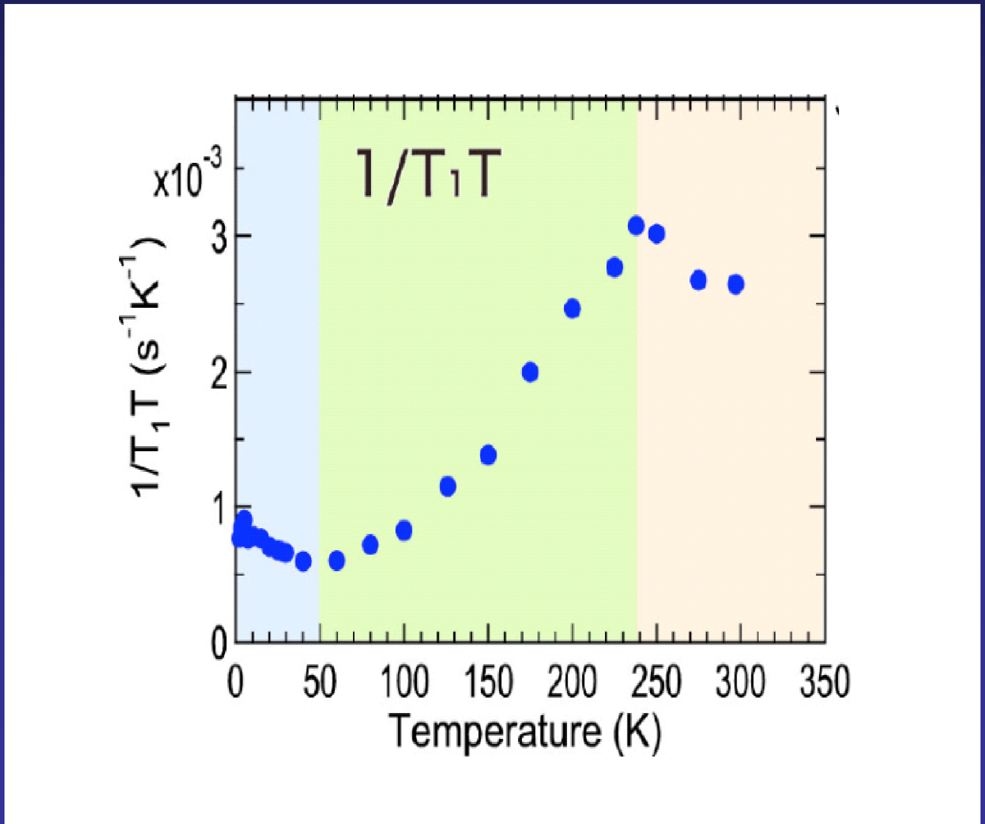
$\chi(T) \rightarrow$ constant at T=0 limit

gapless

Fujiyama, Kanoda

nuclear spin-lattice relaxation rate
No $1/T_1$ (and $1/T_1T$) divergence down to 2K
no ordering and freezing!

Marked contrast with the other Quantum spin liquid candidates



$1/T_1$ constant above
T~ 200K (~J/2)

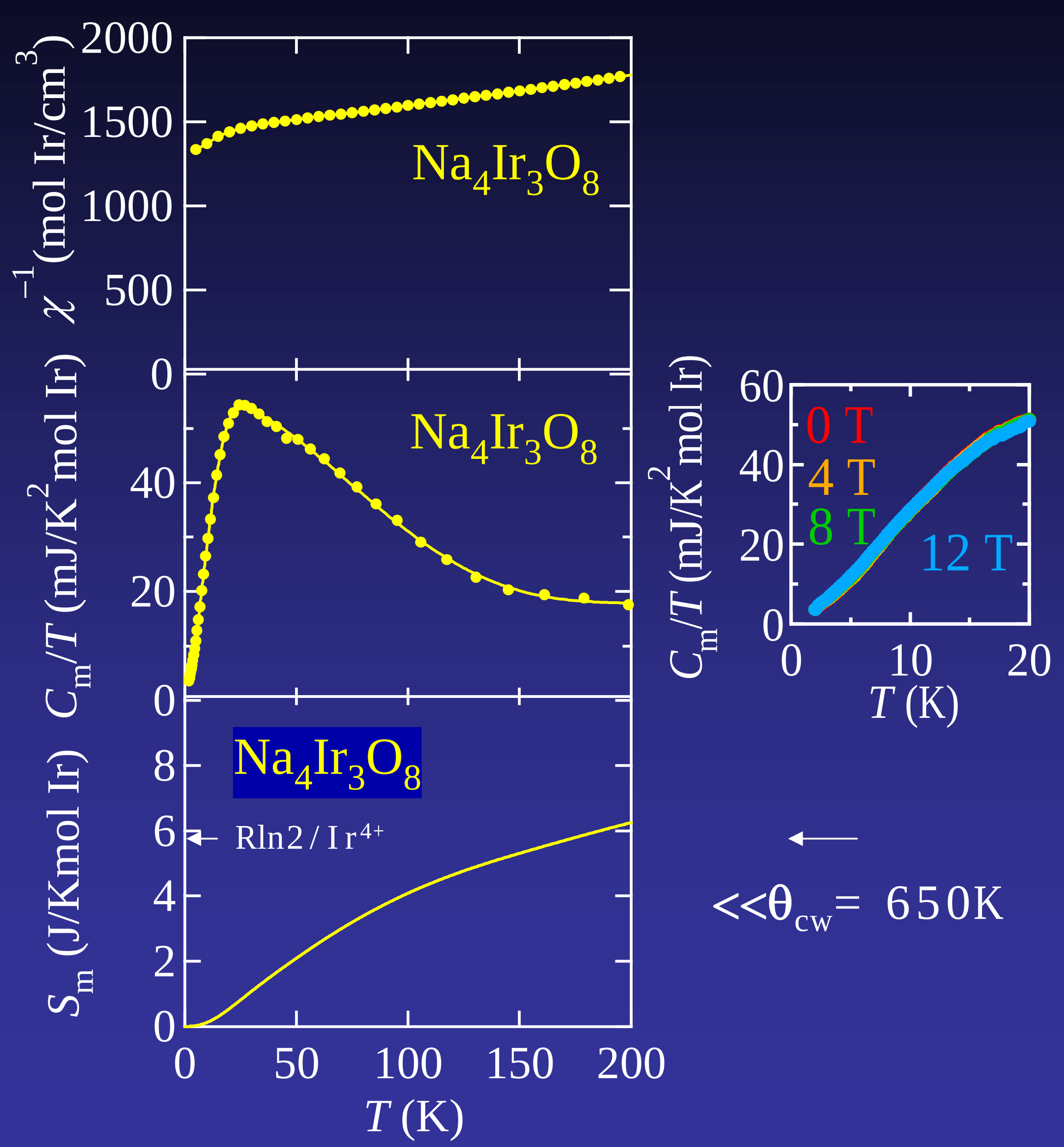
Consistent with a large J~650K
& S=1/2

Power low decay below 200 K
Pseudo-gap feature
in spin excitation?

$1/T_1T$ const below 10 K
finite DOS?

S. Fujiyama, K. Kanoda

C(T) supports for spin liquid ground state



$<<\theta_{cw}=$ 650K

- -No evidence for long range ordering in C(T) :only broad peak
- -Large entropy remains even at low T
- -Magnetic field independent up to 12 T

strongly degenerate low lying spin excitation created by a large AF J

$C_m(T) \propto T^2$ down to 2K
E linear DOS
Pseudo gap?
conected to finite γ?

Points to checked raised by theorists

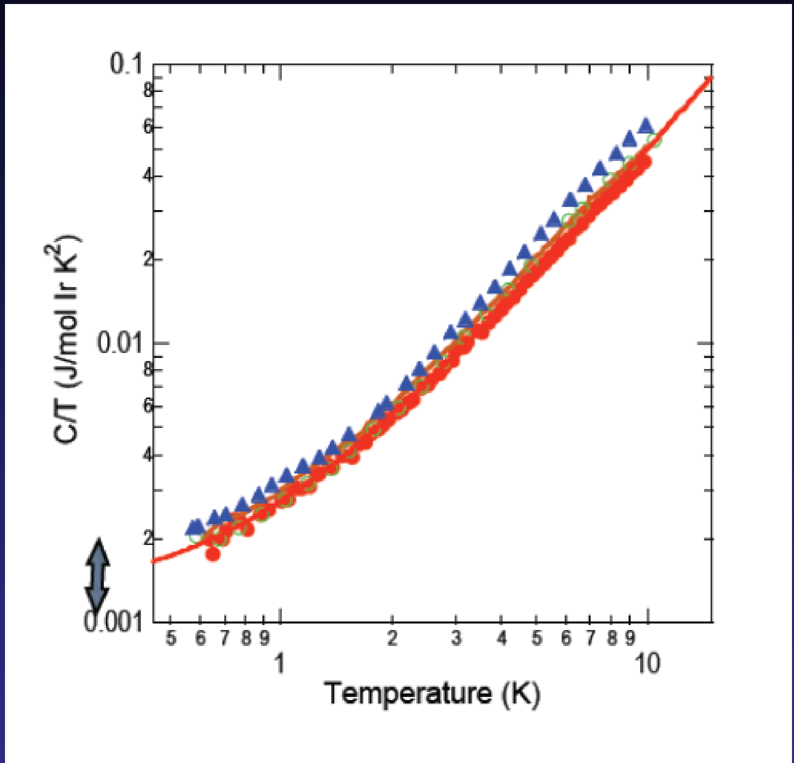
Y.B.Kim (Toronto), L.Balents (UCSB), P.A.Lee & Senthil (MIT)

1. What kind of QSL?
   a Finite DOS at E=0? (spinon FS?)

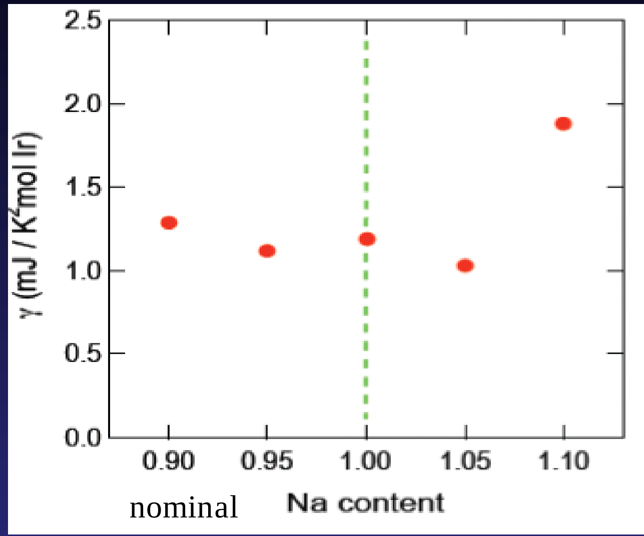
2. Orbital state: strong SO coupling anticipated
   5d relativistic effect strong
   S=1/2 or J_{eff}=1/2?

3. Spin Liquid Insulator-Metal transition?
   SC???

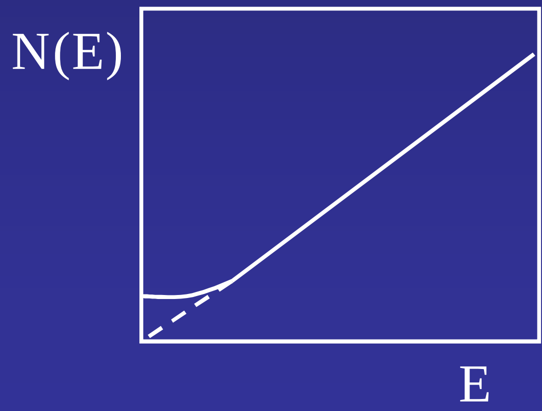
Small but finite γ in C(T) at low T: spin FS?



$C_m(T) \propto T^2$ at high T down to 2K
E linear DOS at high E??



5 samples with different nominal Na composition



-Below 1K

a small γ / ~ 1 mJ mol Ir

independent of synthesis condition

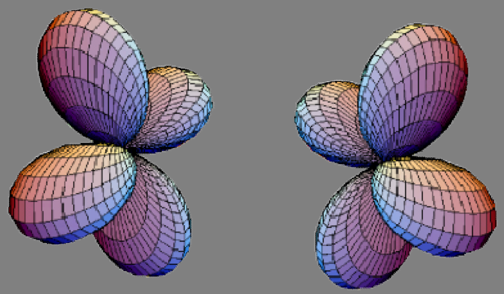
Wilson ratio R_W~ 40 !!? (Kanoda BEDT R_W=1)

Alternative route to quantum spin liquid

Kitaev magnet

Spin-orbit coupling & “electronic matter”

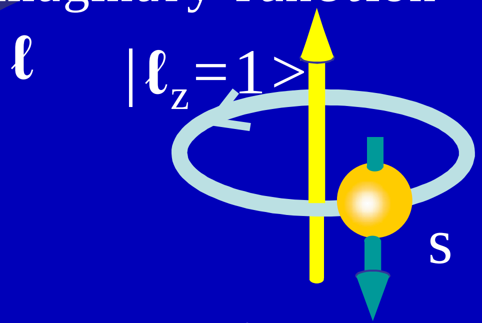
real function



$d_{yz,zx} = |\ell_z = 1\rangle \pm |\ell_z = -1\rangle$

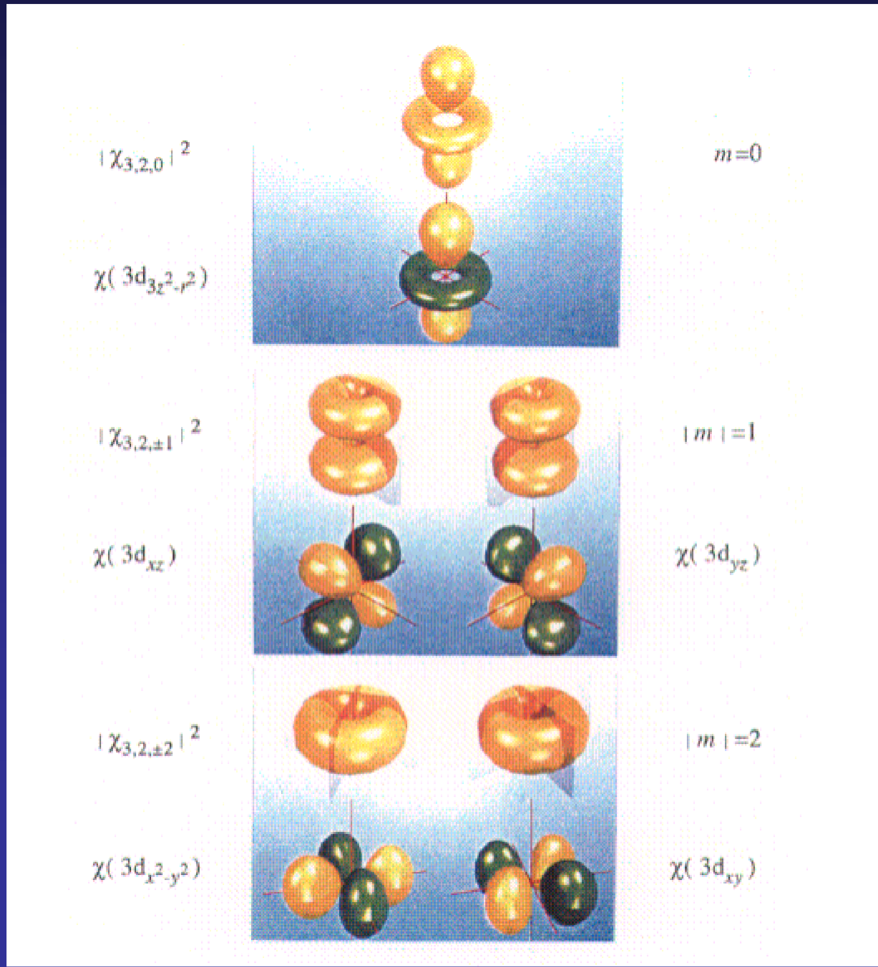
orbital moment quenched
anisotropic, chemical bonds

imaginary function



isotropic
quantum phase e(iφ)

orbital 5-fold degenerate
$L_Z = 2, 1, 0, -1, -2$
$dx_2\text{-}y_2$, dz_2, dyz, dzx, dyz



5d transition metal (Ir) oxides : novel playground for spin-orbit coupling induced electronic matter

Energy(K)

10^5
10^4
10^3
10^2
10^1

3d TM (Fe,Co,Ni, Cu..)

Coulomb U

Crystal field D

Spin-orbit coupling λ

4d TM (Mo, Ru...)

Coulomb U

Crystal field D

Spin-orbit coupling λ

5d TM (Re, Os, Ir, Pt...)

Coulomb U

Crystal field D

Spin-orbit coupling λ

Traditional playground for correlated electron physics

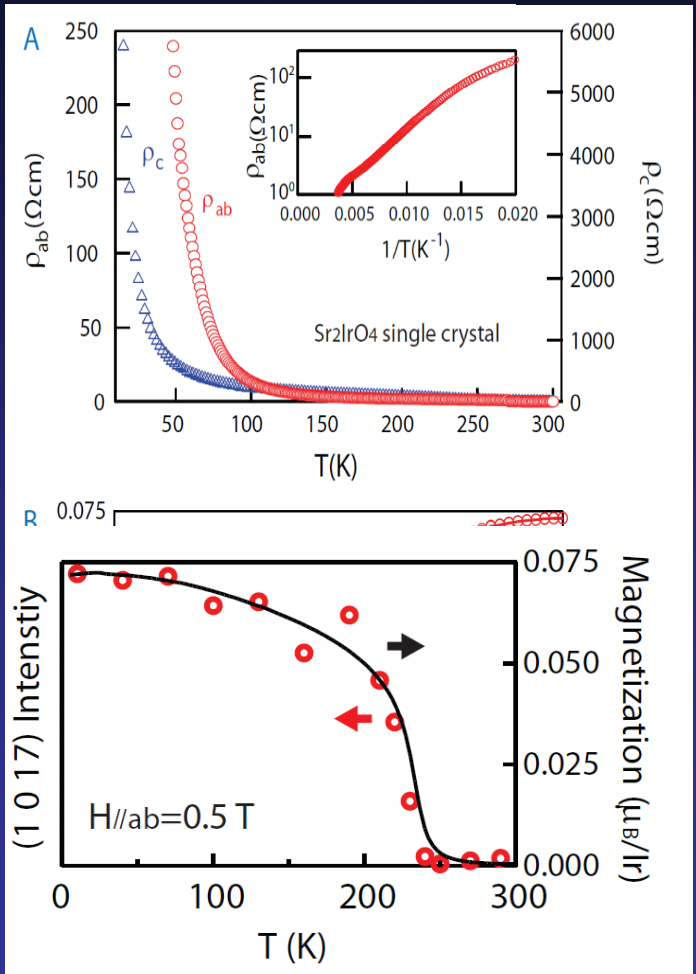
SO not small perturbation

can change the landscape of electronic structure

hierarchy of E-scale

Mystery of Sr_2IrO_4 : why insulating?

K_2NiF_4 structure



Insulator
Meta-magnetism Hc~0.2T
M_S~0.1μ_B below T_C~240 K

Group 9 $Sr_2M^{4+}O_4$ — B.J.Kim , PRL (08)
all d^5, the same structure

3d Sr_2CoO_4 Ferromagnetic metal
4d Sr_2RhO_4 Paramagnetic metal
5d Sr_2IrO_4 Boring metal? Magnetic Insulator

Transfer increase, naively should be more metallic

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

C.Cao PRB(98)

Sr_2IrO_4: Spin-orbit coupling induced Mott insulator?

B.J.KIM, PRL (08)

Ir 4+ ($5d^5$), low spin config.

~4 eV

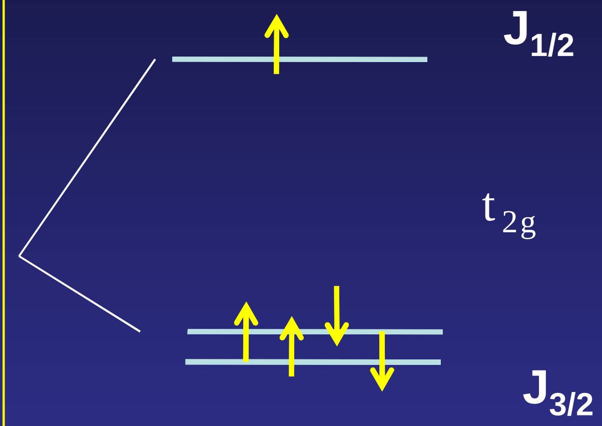
$|xy\rangle=|2\rangle-|-2\rangle=|0\rangle_{eff}$

$|yz\rangle=|1\rangle+|-1\rangle$

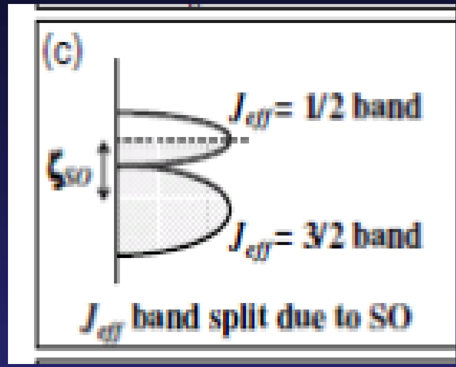
$|zx\rangle=-|1\rangle-|-1\rangle$

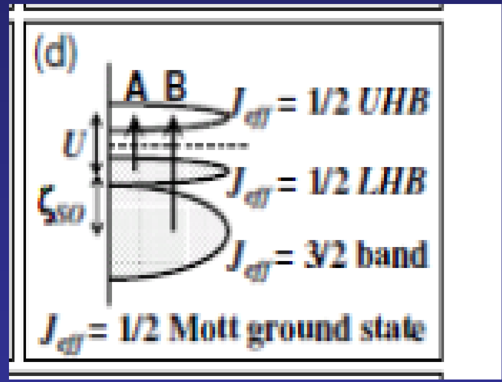
$L_{eff}=1$

Magnetic Insulator
with J=1/2 moment



spin-orbit coupling ~0.6 eV
Crystal field in t_{2g}~0.2eV
U~2 eV?





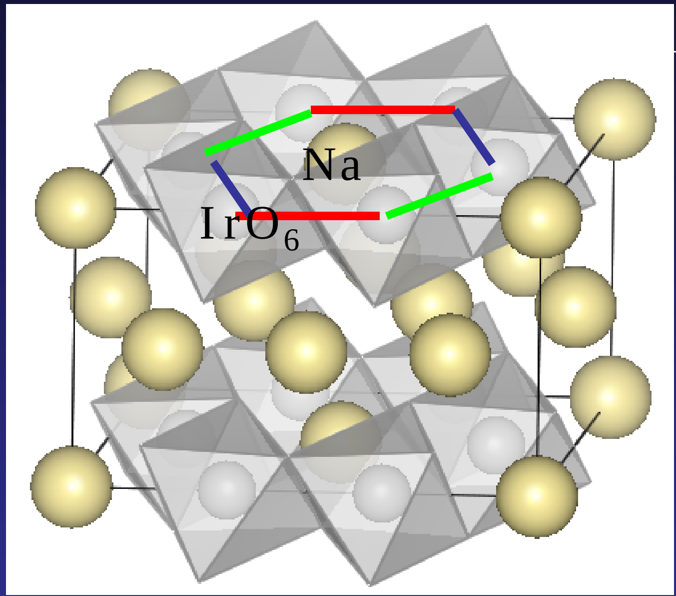
Orbital-spin complex

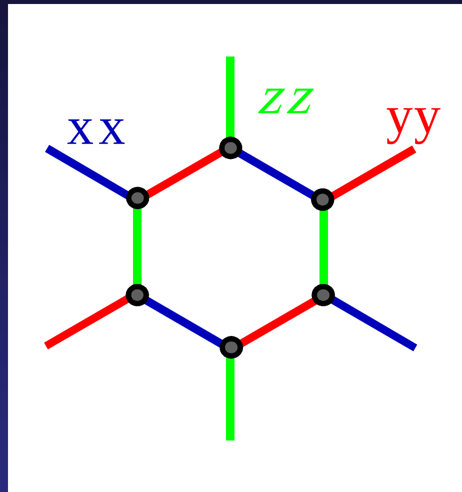
$$J_{eff\,1/2}=\frac{1}{\sqrt{3}}\left(|xy,\pm 1/2\rangle \pm |yz,\mp 1/2\rangle + i|zx,\mp 1/2\rangle\right)$$

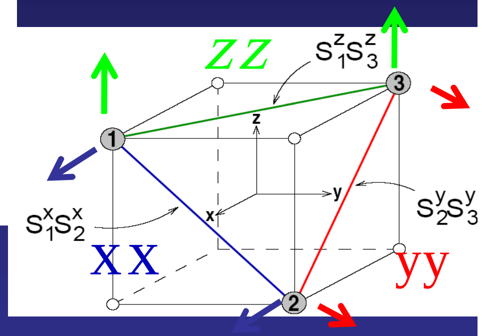
Unique exchange interactions in $J_{1/2}$ magnet

Jackeli PRL (09)

$$J_{eff\,1/2} = \frac{1}{\sqrt{3}}\left(|xy,\pm 1/2\rangle \pm |yz,\mp 1/2\rangle + i|zx,\mp 1/2\rangle\right)$$







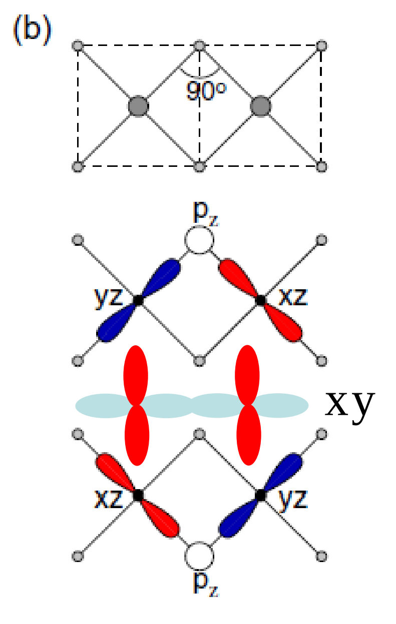
$$\mathcal{H}_{ij}^{(\gamma)} = -J S_i^\gamma S_j^\gamma$$

interference between exchange paths
Bond dependent anisotropic coupling
- compass model

compass on honeycomb

Kitaev system
Spin liquid with
fractional excitation
Jackeli & Kaliulin

Na_2IrO_3 Reality: Kitaev-Heisenberg Model



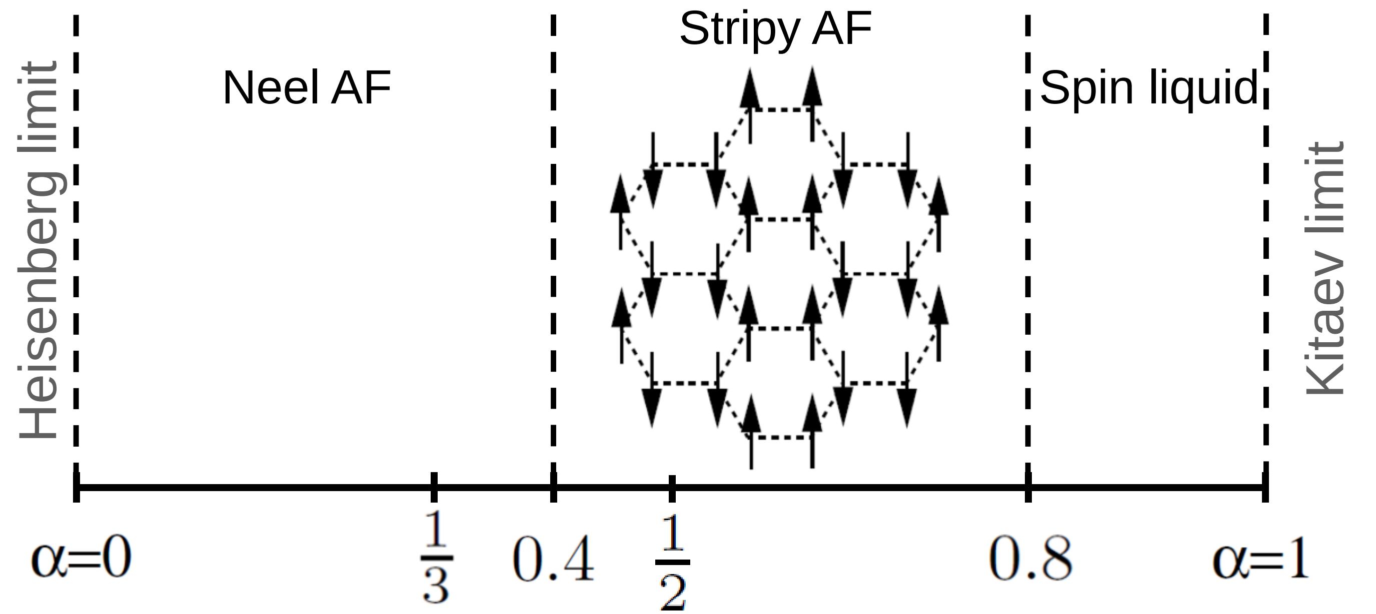
direct exchange cannot be ignored

Jackeli

$$\mathcal{H}_{ij}^{(\gamma)} = -J_1 \; S_i^{\gamma} S_j^{\gamma} + J_2 \; \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

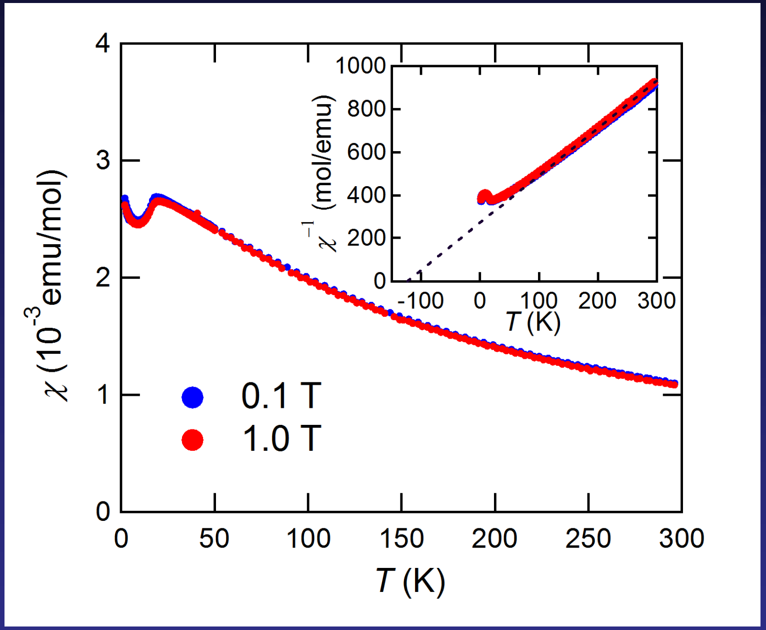
Kitaev　　Heisenberg

$$J_1 = 2\alpha \; , \quad J_2 = 1 - \alpha$$



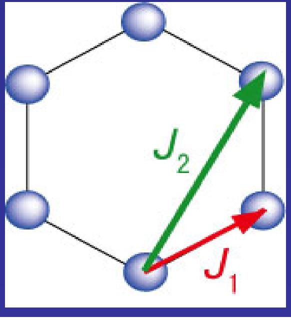
Honeycomb Iridate :Kitaev-Heisenberg system?

Na_2IrO_3 (AF dominant)



Θ_W ~ -125 K, μ_{eff} ~ 1.91 μ_B

T_N ~17 K, $f = |\Theta_W| / T_N$ ~ 7

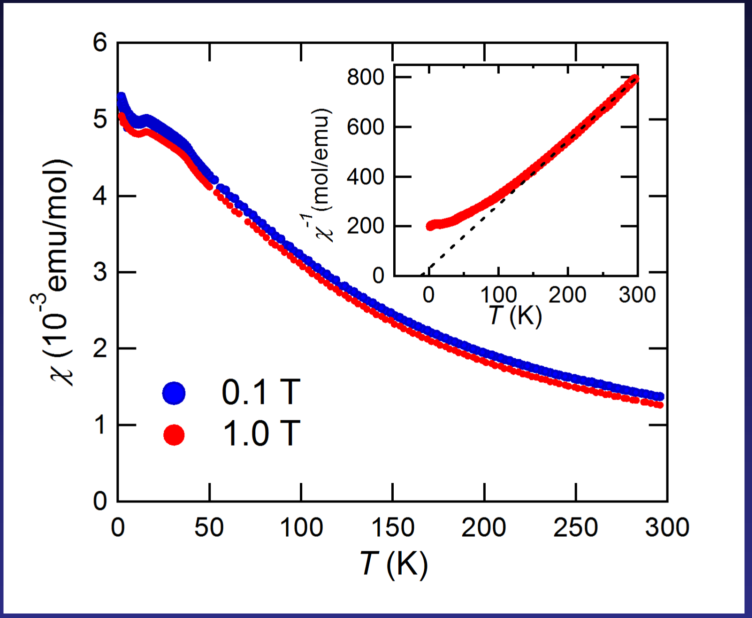


J_1, J_2 frustration?

frustrated

AF Honeycomb?

Li_2IrO_3 (AF+F)



Θ_W ~ -12 K, μ_{eff} ~ 1.76 μ_B

three anomalies

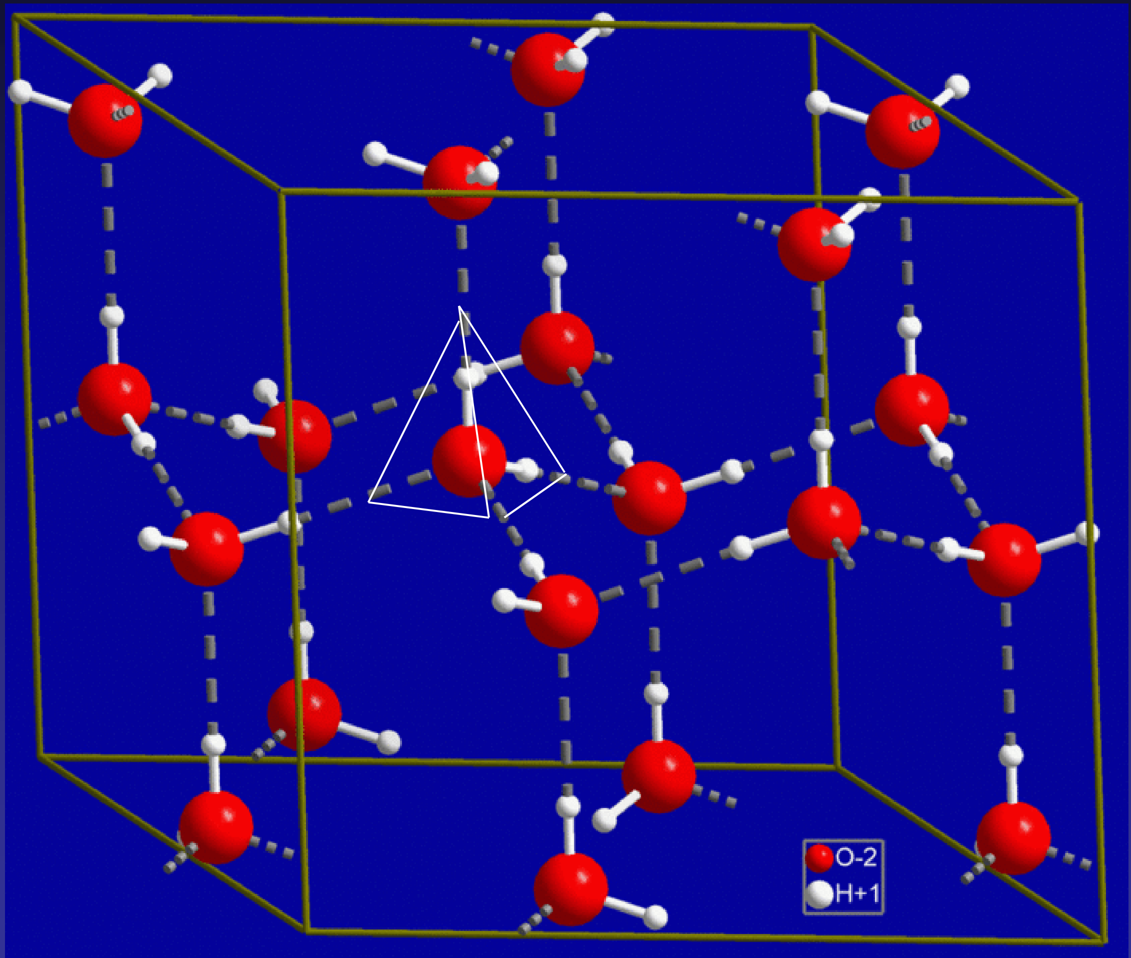
T_{c1}=40 K, T_{c2}=15 K, T_{c3}=5K

More ferromagnetic

compass

Classical spin liquid: Spin Ice

Pauling Ice rule



H :
pseudo pyrochlore

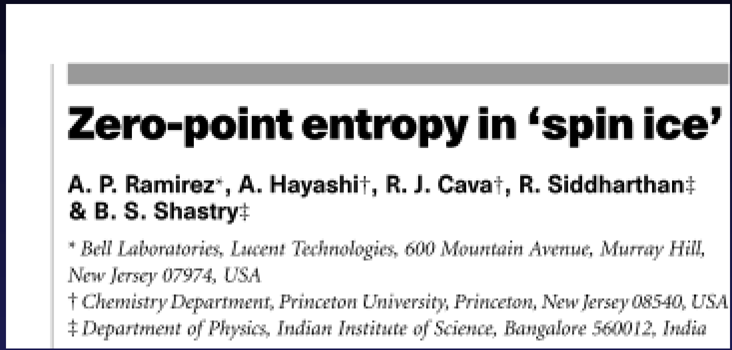
O:
at the center of
tetrahedron

O bonded
with two H atoms

two bonded
two not bonded

many configurations

Sres= 1/2R ln(3/2)
1.68 J /molK



Zero-point entropy in 'spin ice'

A. P. Ramirez*, A. Hayashi†, R. J. Cava†, R. Siddharthan‡ & B. S. Shastry‡

* 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

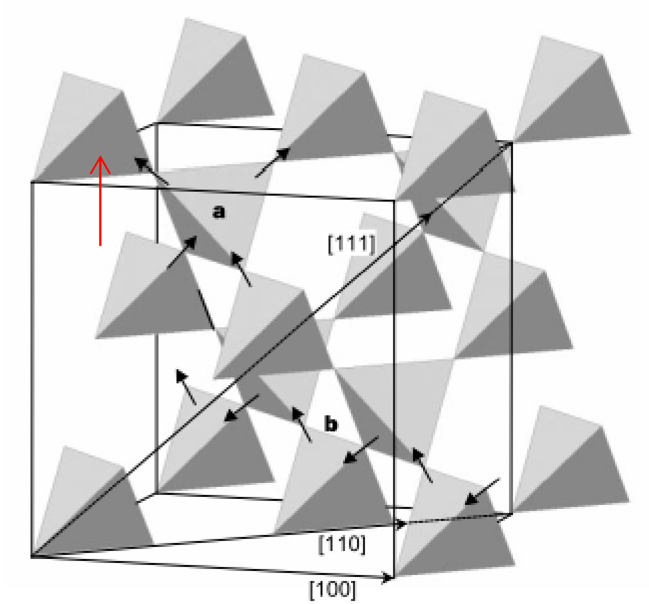


Figure 1 A section of the pyrochlore lattice, with the unit cell shown. Also shown are the principal crystal axes and two different spin configurations, discussed in the text, for Dy spins which lie on the vertices of the tetrahedra. Panel **a** shows the ground-state configuration of ferromagnetically interacting Ising spins on a tetrahedron. Panel **b** shows part of the subfamily of spins which do not couple to a field along (110).

Dy_2Ti_2O7

pyrochlore structure
Dy form pyrochlore lattice

Strong Ising anisotropy
point
to the center of tetrahedron
"In" or "Out"

Ferromagnetic interaction
(exchange + dipolar)

2 in 2 out per tetrahedron

letters to nature

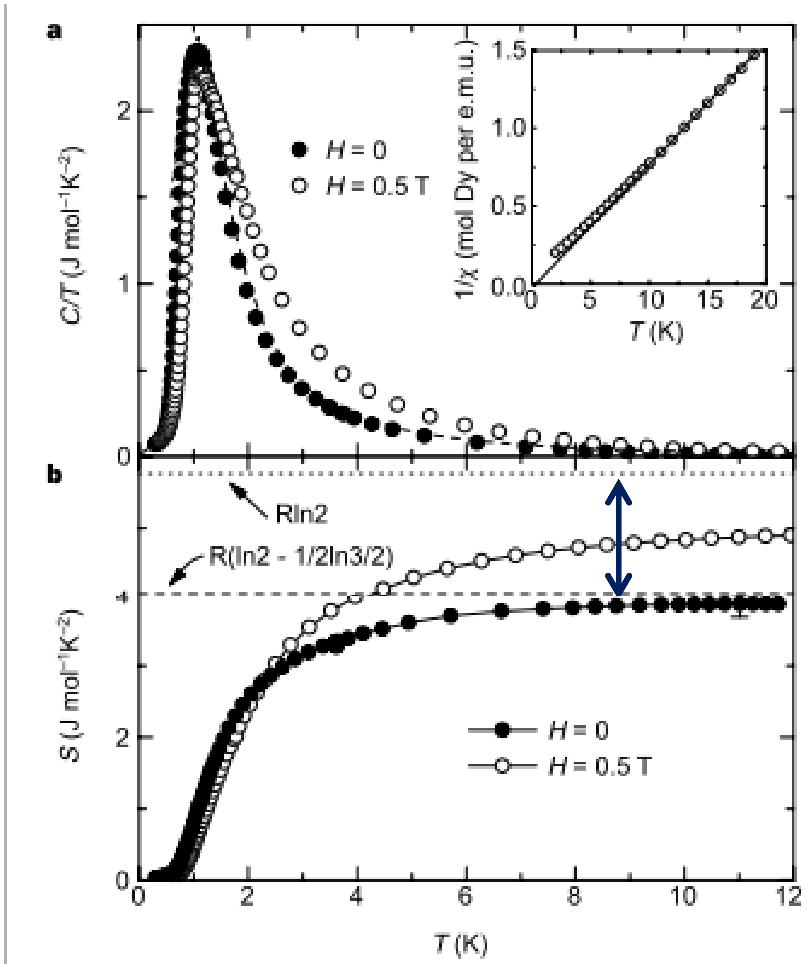


Figure 2 Specific heat and entropy of the spin-ice compound $Dy_2Ti_2O_7$ showing agreement with Pauling's prediction for the entropy of water ice I_h, $R(\ln 2 - (1/2)\ln(3/2))$. **a**, Specific heat divided by temperature of $Dy_2Ti_2O_7$ in $H = 0$ and 0.5 T. The dashed line is a Monte Carlo simulation of the zero-field $C(T)/T$, as discussed in the text. **b**, Entropy of $Dy_2Ti_2O_7$ found by integrating C/T from 0.2 to 14 K. The value of $R(\ln 2 - (1/2)\ln(3/2))$ is that found for ice I_h and $R\ln 2$ is the full spin entropy. Inset, susceptibility (M/H) of $Dy_2Ti_2O_7$ in a field of 0.02 T.

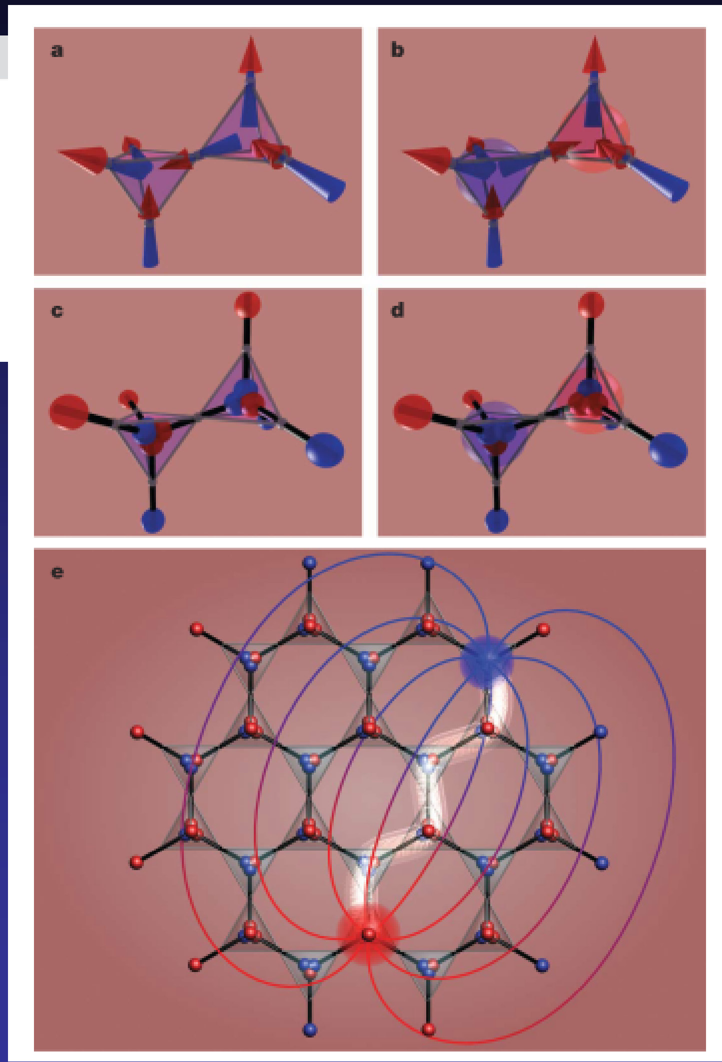
hidden ice entropy
1/2ln(3/2)


nature Vol 451|3 January 2008|doi:10.1038/nature06433

LETTERS

Magnetic monopoles in spin ice

C. Castelnovo[1], R. Moessner[1,2] & S. L. Sondhi[3]



spin ice state
two-in two-out
ensemble of loops

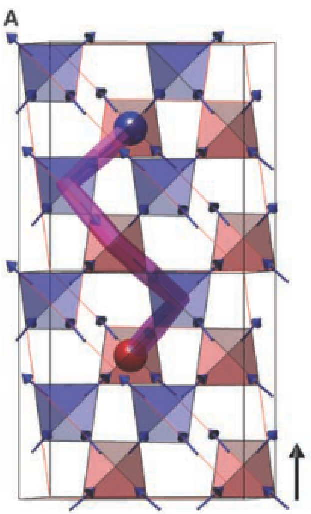
loop cut:
magnetic charges
at the ends

Dirac Strings and Magnetic Monopoles in the Spin Ice $Dy_2Ti_2O_7$

D. J. P. Morris,[1*] D. A. Tennant,[1,2*] S. A. Grigera,[3,4*] B. Klemke,[1,2] C. Castelnovo,[5] R. Moessner,[6] C. Czternasty,[1] M. Meissner,[1] K. C. Rule,[1] J.-U. Hoffmann,[1] K. Kiefer,[1] S. Gerischer,[1] D. Slobinsky,[3] R. S. Perry[7]

Magnetic Coulomb Phase in the Spin Ice $Ho_2Ti_2O_7$

T. Fennell,[1*] P. P. Deen,[1] A. R. Wildes,[1] K. Schmalzl,[2] D. Prabhakaran,[3] A. T. Boothroyd,[3] R. J. Aldus,[4] D. F. McMorrow,[4] S. T. Bramwell[4]



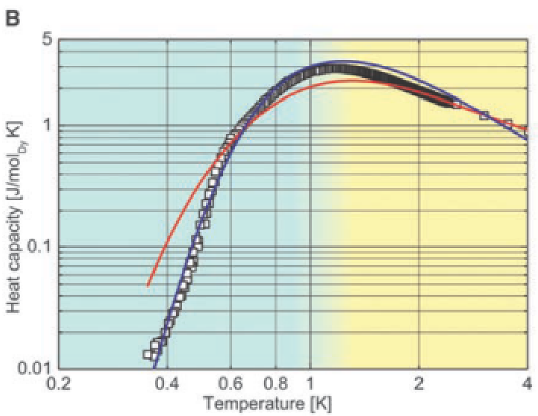


Fig. 1. Gas of deconfined magnetic monopoles. (**A**) The Ising spins are constrained to point along the direction connecting the centers of the two tetrahedra they belong to. The lowest energy for a tetrahedron is obtained for a two-in-two-out configuration, as illustrated. There are six such configurations with net ferromagnetic moments along one of the six equivalent ⟨100⟩ directions. The noncollinearity of the Ising axes is the source of the frustration in spin ice. In $Dy_2Ti_2O_7$ the "Ising" crystal field doublet is separated from other levels by more than 100 K. Applying a field, **B** || [001], results in a preference for aligning the tetrahedral magnetization with the applied field direction (arrow). In the 3D pyrochlore lattice, Dirac strings of flipped spins terminate on tetrahedra where magnetic monopoles reside. (**B**) The measured heat capacity per mole of $Dy_2Ti_2O_7$ at zero field (open squares) is compared with a Debye-Hückel theory for the monopoles (blue line) and the best fit to a single-tetrahedron (Bethe lattice) approximation (red line). The ice-blue background indicates the spin-ice regime; the yellow background indicates the paramagnetic regime.

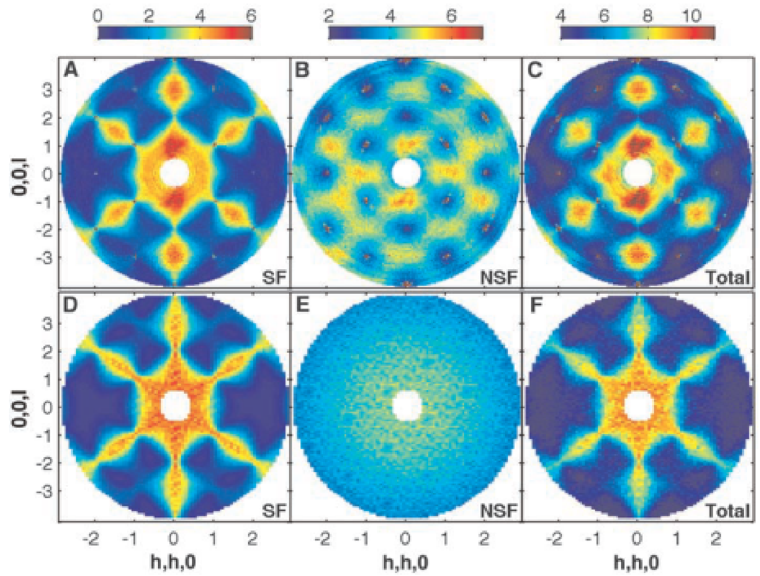
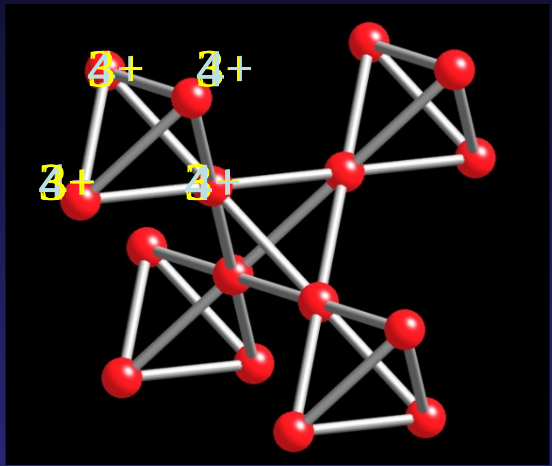


Fig. 2. Diffuse scattering maps from spin ice, $Ho_2Ti_2O_7$. Experiment [(**A**) to (**C**)] versus theory [(**D**) to (**F**)]. (A) Experimental SF scattering at $T = 1.7$ K with pinch points at (0, 0, 2), (1, 1, 1), (2, 2, 2), and so on. (B) The NSF scattering. (C) The sum, as would be observed in an unpolarized experiment (*20*, *22*). (D) The SF scattering obtained from Monte Carlo simulations of the near-neighbor model, scaled to match the experimental data. (E) The calculated NSF scattering. (F) The total scattering of the near-neighbor spin ice model.

Charge analog of quantum spin liquid

Charge analogue of spin liquid - LiV_2O_4 spinel

C.Urano, H.T et al PRL 85, 1052 (00)
Jonson, Niitaka, H.T et al., PRL99 167402 (07)



$Li^{1+}V^{3.5+}{}_2O^{2-}{}_4$

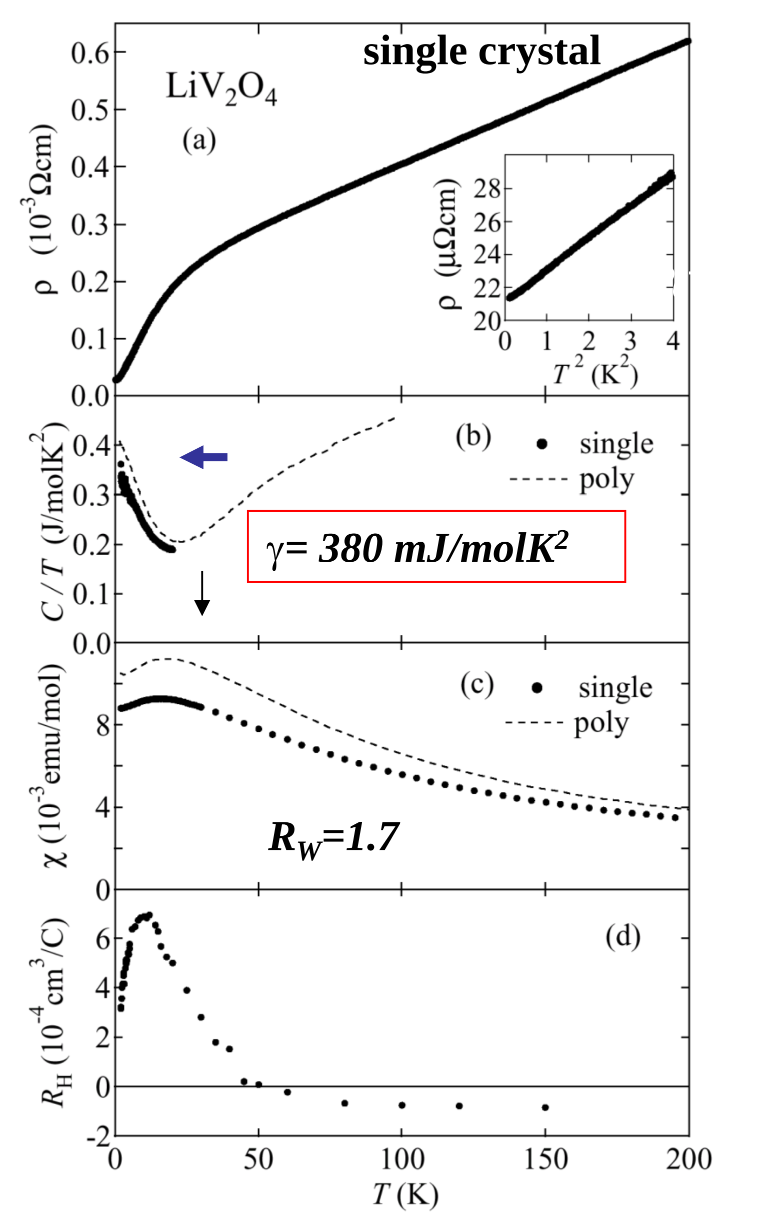
V: pyrochlore lattice

mixed valent
1:1 V3+ and V4+
equivalent to 1:1 ↑↓ spins

frustration : 3+-4+ ordering
(charge solid) suppressed
“charge liquid”

Heavy Fermion behavior in mixed valent (3+, 4+) spinel oxide LiV_2O_4

C.Urano, H.T et al PRL 85, 1052 (00)



specific heat coefficient
$\gamma \sim 400$ mJ/mol K^2
>>~1mJ/molK^2 (ordinary metal)

Electron mass >> $100m_e$ ($\gamma \propto m^*$)

first and perhaps only
Heavy fermion oxides

Only d-electrons involved
not conventional “Kondo” (Ce, U)
with conduction electrons and f-moments

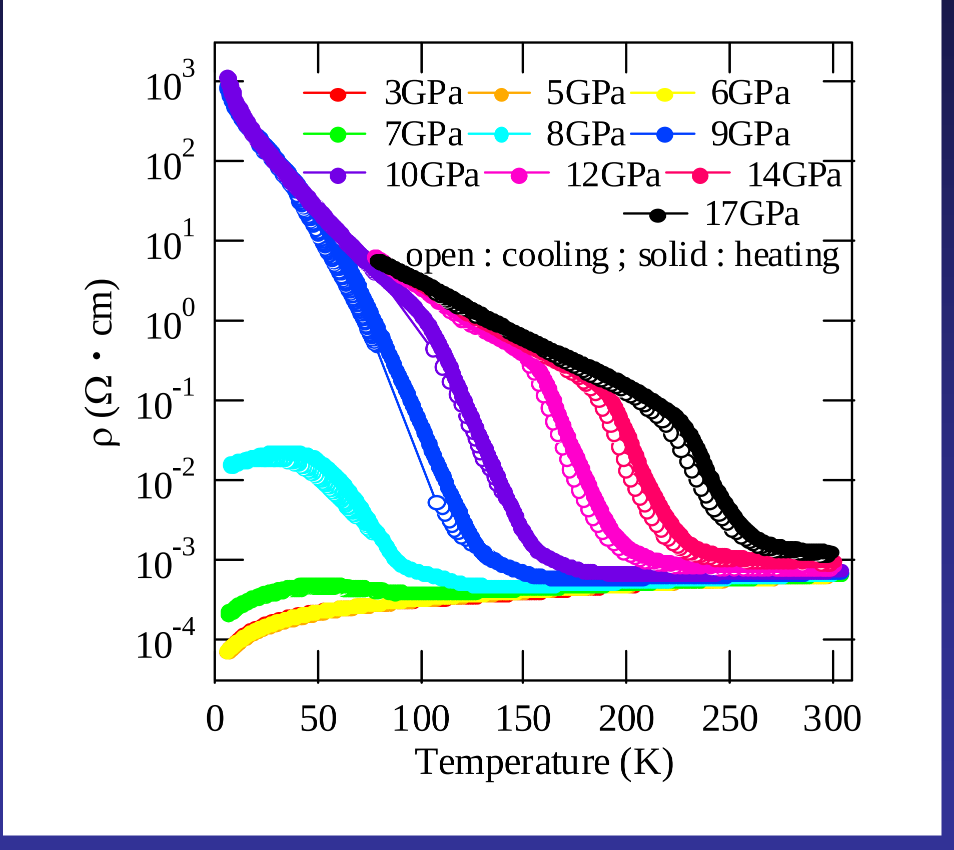
A new route to heavy fermion?

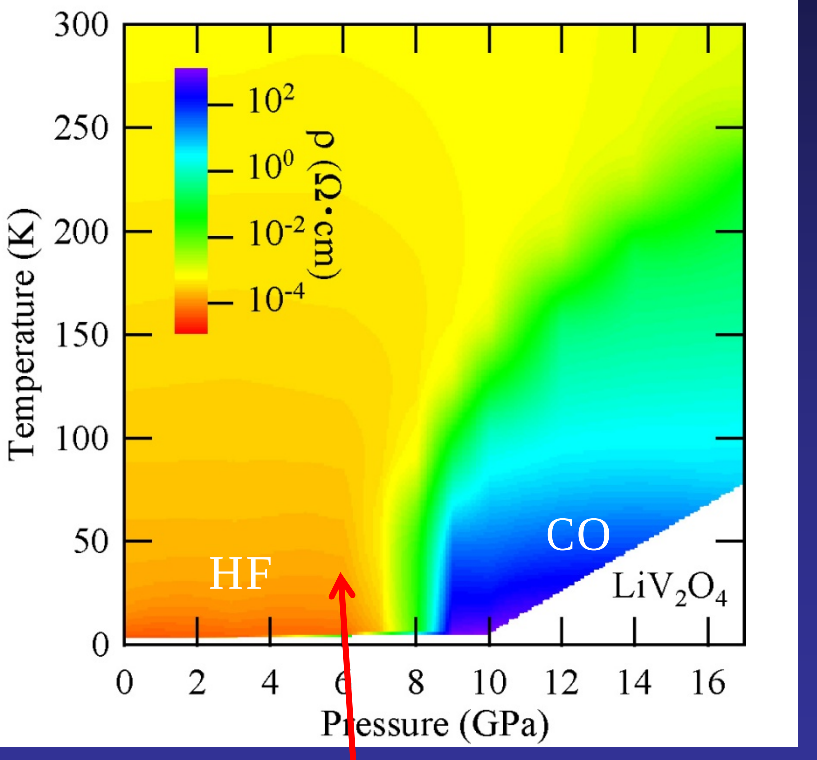
Marginally melted charge crystal?
Examine experimentally

Crystallization of heavy fermions under pressure in LiV_2O_4

HF state of LiV_2O_4 close proximity to CO
Melted charge crystal due to frustration!

S. Niitaka, N. Takeshita





Marginally melted!!

Close proximity to charge ordering gives rise to Heavy fermions
- Optical Conductivity -

Jonsson, Takenaka, Niitaka PRL99 167402 (07)

E scale of spectral weight transfer ?

meV scale

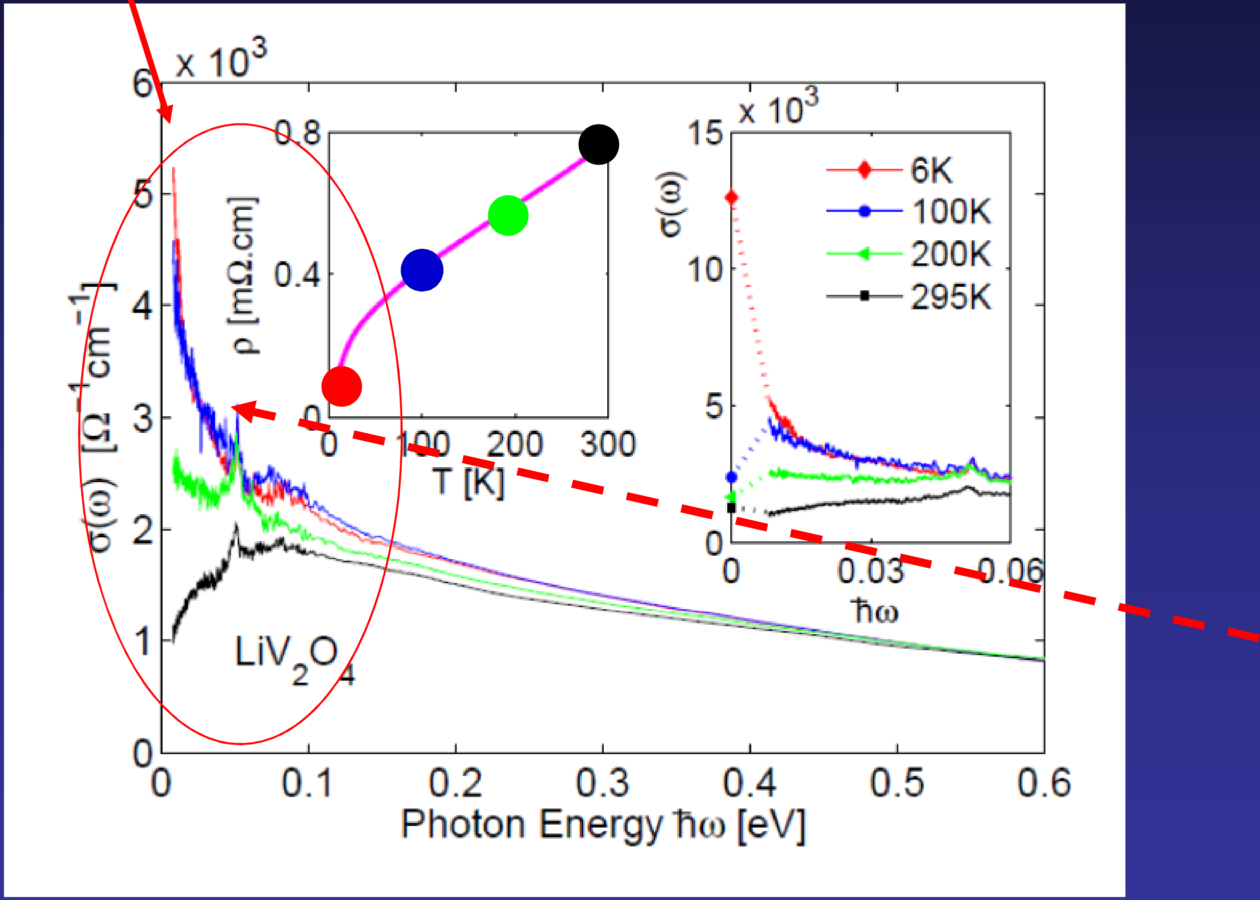
Kondo J_k ~20 K

No!!

eV scale

Coulomb physics (charge ordering)

Heavy quasi-particles



Coherent quasi-particles created by spectral weigh transfer over ~eV

Spin-orbital-lattice coupled phenomena
- lifting the degeneracy of spin liquid

Suppression of Frustration to lift the degeneracy inherent to spin liquid state:
emergent spin-charge-orbital complex state

Nature does not like degeneracy!

Couple with lattice and make the bonds anisotropic
→ Spin Jahn -Teller transition

Couple with orbitals and make the bonds anisotropic
→ Frustration driven orbital ordering

Lifting spin degeneracy by coupling with lattice

$Cd^{2+}Cr^{3+}{}_2O_4$

$T_N = T_S = 7K \ll \theta_{CW} = 70K$

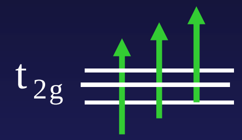
$Zn^{2+}Cr^{3+}{}_2O_4$

$T_N = T_S = 13K \ll \theta_{CW} = 390K$

$|T_N/\Theta_{CW}| < 0.1$

“spin only”

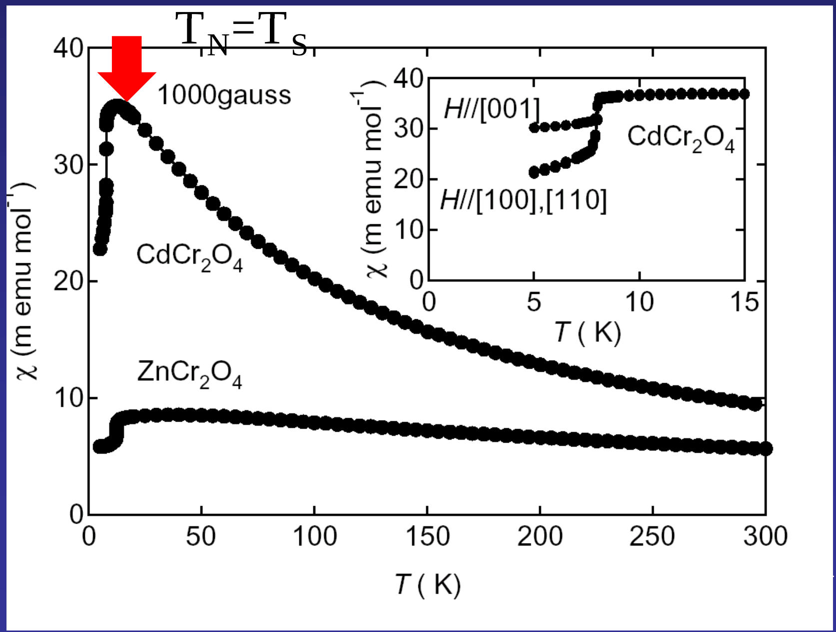
$Cr3+$ (d3; S=3/2)



xy, yz, zx

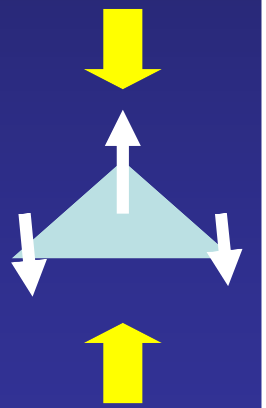
AF ordering marginally achieved

with Cubic -Tetragonal transition



Distort the lattice &
lift “spin degeneracy”
by making J anisotropic

Spin- JT transition



Yamashita and K.Ueda, PRL(01)
O.Tchernyshyov PRL &PRB (02)

S. –H. Lee, C. Broholm, *et al.*
PRL (00).

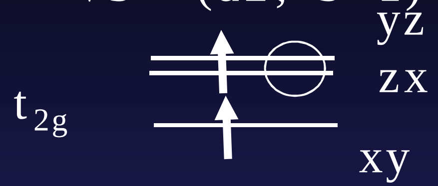
Lifting spin degeneracy by coupling with orbitals

$Mg^{2+}V^{3+}{}_2O_4$

T_N = 42 K < T_{OO}=62K

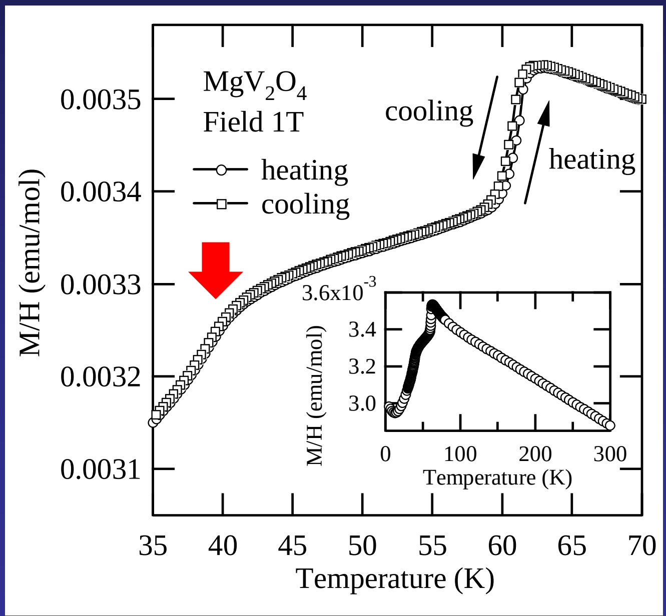
<< θ_{CW} =450K

V3+ (d2, S=1)



"choice of orbital"

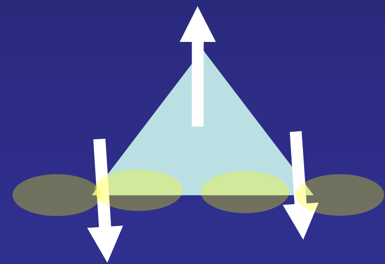
T_N T_S=T_{OO}



AF ordering marginally achieved by orbital ordering

Choose two orbitals out of three & lift spin degeneracy by making J anisotropic!

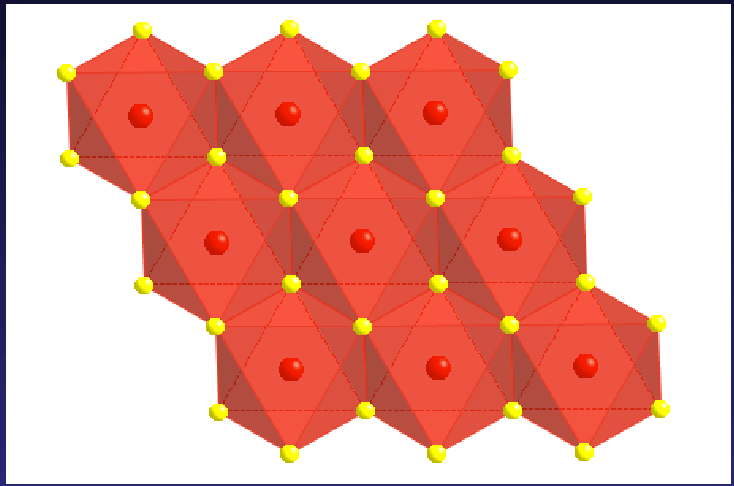
(110) spinel chains
orbital-F
spin-AF



ordered moment
~0.6-1 μ_B < 2 μ_B
why small?

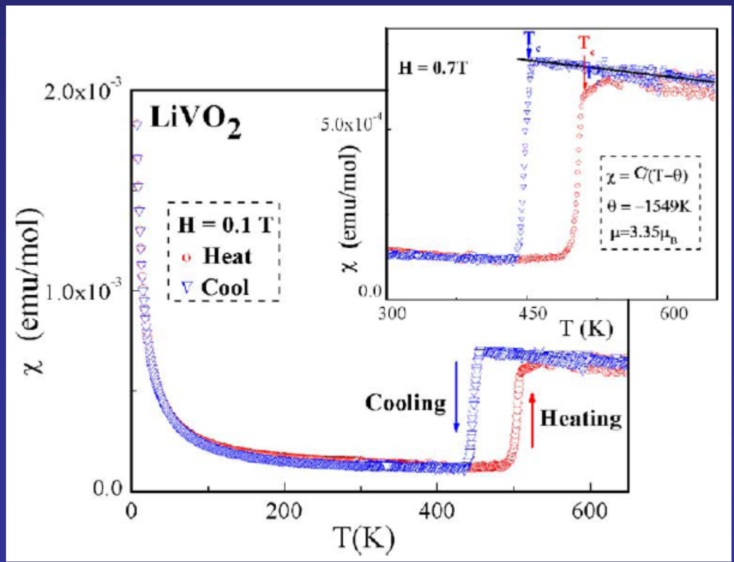
Motome (04)

$LiVO_2$: V_3 molecules inside the crystal

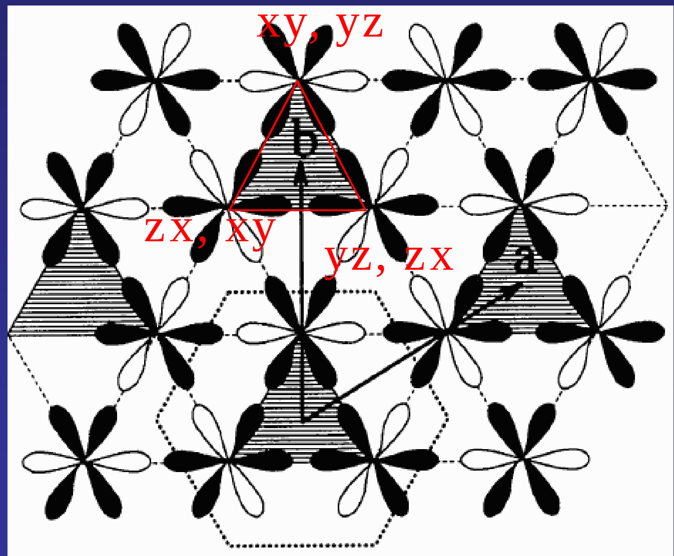


S=1 triangular magnet t_{2g}^2
with orbital degrees of freedom

⇒trimer singlet
with orbital ordering



3 V3+ ->2x3=6 electrons/trimes
3 bonds x 2 electrons = 6



W. Tian *et al.*, Mater. Res. Bull. **39** (2004) 1319 .

H.F. Pen *et al.*, Phys. Rev. Lett. **78** (1997) 1323.

Summary: Towards Quantum Spin Liquid

Organics,
perhaps closest to holly grail.
though, there remains many issues yet to be tackled.
Chemical flexibility of organics may
allow us to increase number of candidates

Inorganics,
many interesting candidates emerged in the last 5 years.
Need for new materials. Well ordeed.

How to probe microscopic properties of QSL, such as
spin FS?

There are more than one kinds of QSL (as s- p- d- wavaes in SC)
Needs more to enjoy the physics

Key for materials: as clean as possible, close to a metal!