KITP UCSB 11/19/07

Quantum Liquid Produced by Geometrical Frustration in Spinel Oxides

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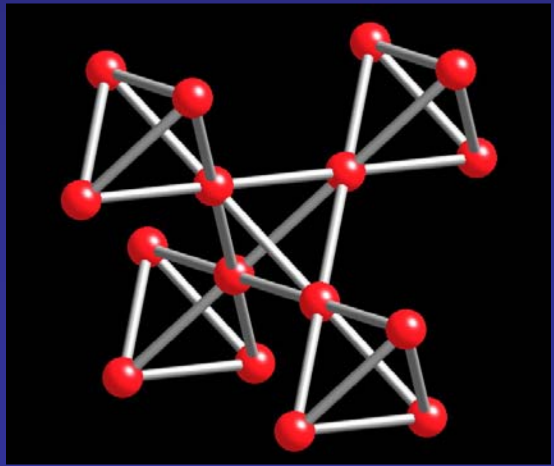


Collaborators

Y.Okamoto, N,Katayama, M.Nohara (U-Tokyo)

S.Niitaka, P.Jonson, H.Katori, A.Yamamoto (RIKEN)

Pressure:N.Takeshita (CERC-AIST)

NMR: S.Fujiyama, K.Kanoda, M.Takigawa (U. Tokyo)

Neutron: S.Shamoto (JAERI)

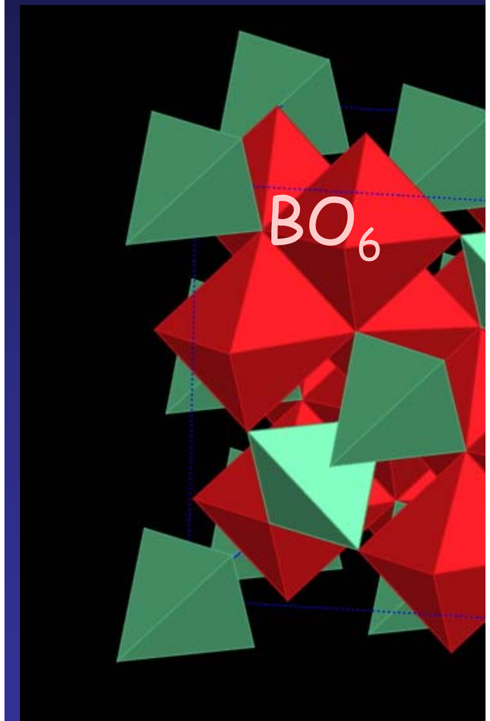
Discussion D. Khomskii (Koln), R.Arita (RIKEN)

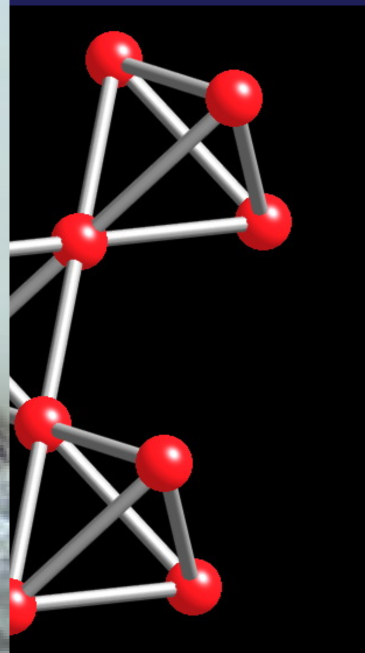
Spinel oxide: AB_2O_4

(cubic: Fd3m)

"B-sublattice"

etrahedra





Lattice

→ *geometrical frustration*

Geometrical frustration in ice

O - H - O

O - H - O

H:
pyrochlore lattice

O:
Inside H tetrahedron

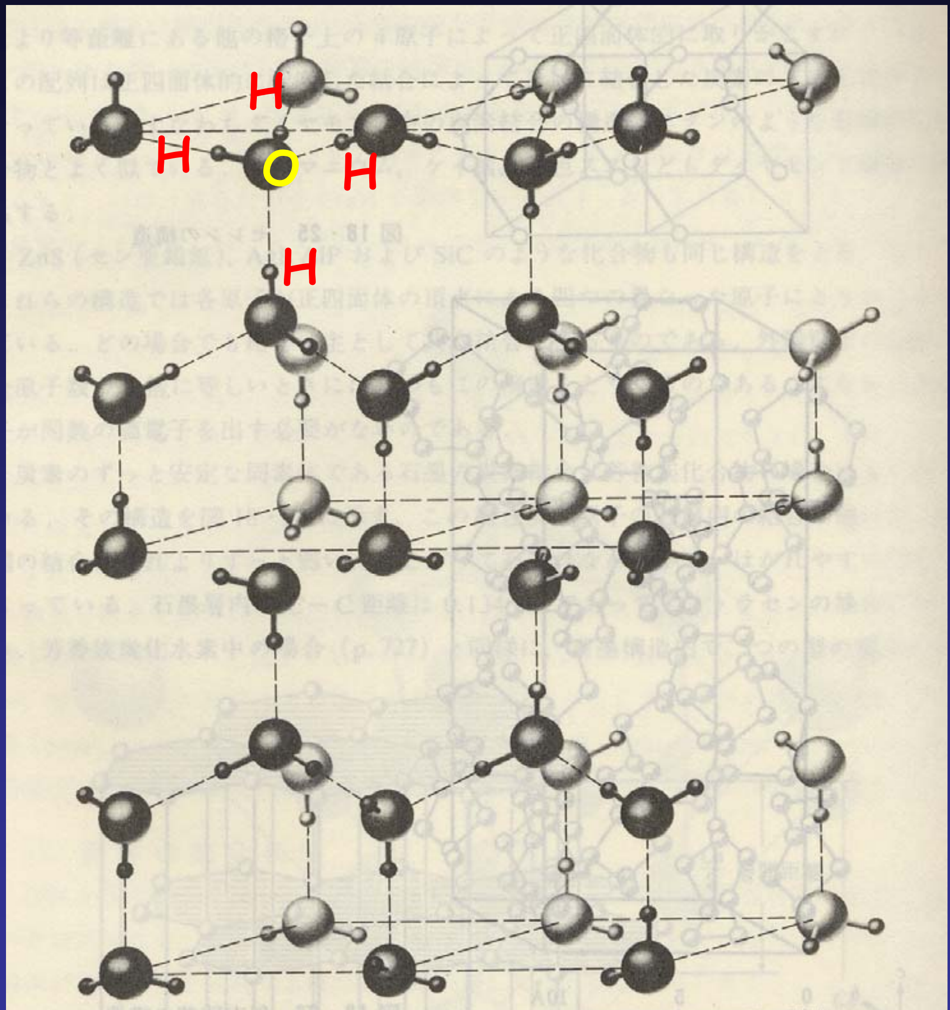


図 18・27 氷の結晶中の分子の配列．図に表わされる水分子の配向には任意性がある．各酸素-酸素軸上に陽子が一つあり，二つの酸素のいずれか一つに近くなっている［Linus Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca (1960)］

two short & two long for O
⇒Up spin & down spin

Macroscopic degeneracy remains

$S = 1/2 \ln 3/2$

per hydrogen

Pauling

What do we expect for spinel related oxides?

Strongly degenerate low lying excitations originating from geometrical frustration

- **liquid state of spin, charge and (perhaps) orbital**
  (liquid crystal?)

Nature always tries to suppress the degeneracy

couple with lattice, orbital, itinerant carriers

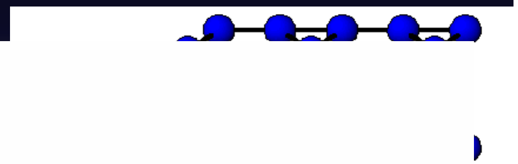
- **Exotic Phase (transition)?**

how to lift the degeneracy

self organization of spins, charges, orbitals

sensitive to perturbation: gigantic response

Geometrically Frustrated Lattices



2D

Physics Today Feb 2007

search & discovery

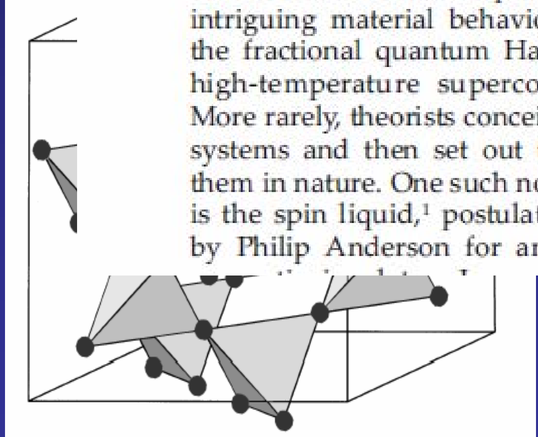
New candidate emerges for a quantum spin liquid

A newly synthesized mineral is perhaps the most promising material yet to realize a hypothetical state with exotic behavior.

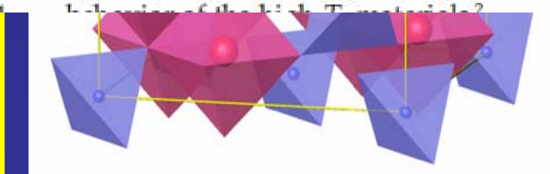
Nature sometimes surprises us with intriguing material behavior. Witness the fractional quantum Hall effect or high-temperature superconductivity. More rarely, theorists conceive of novel systems and then set out to look for them in nature. One such novel system is the spin liquid,[1] postulated in 1973 by Philip Anderson for an antiferro-

The discovery of high-T_c superconductivity renewed interest in spin liquids because copper oxide materials are antiferromagnetic insulators before they are doped to become superconductors. Anderson and others have used the concept of a resonating-valence-bond, which underlies the prediction of a spin-liquid state, to try to explain the

at MIT were able to synthesize a rare mineral known as herbertsmithite.[3] (The small amounts found in nature are not sufficiently pure.) It's a member of the paratacamite family characterized by the formula $Zn_xCu_{4-x}(OH)_6Cl_2$, where $x = 1$ for herbertsmithite. As pictured in figure 2 and confirmed by crystallography, the spin-½ copper atoms



3D Pyrochlore lattice



Spinel (AB_2O_4)

$Fe_3O_4 = FeFe_2O_4$

Pyrochlore($A_2B_2O_7$)

$Y_2Mo_2O_7$

a wide variety of materials, most popular oxide structure

Progress in searching for new spinel oxides and exotic spin, charge orbital states at RIKEN/Tokyo

Spin liquid ground state in $Na_4Ir_3O_8$ with hyper-Kagome lattice (ordered spinel)

new compound PRL 99 137207 (07)

Charge frustration & heavy fermion formation in mixed valent LiV_2O_4 (1:1 V3+ & 4+) spinel

charge analogue of spin liquid

strong electron correlations in the presence of frustration

PRL99 167402 (07)

Orbital & charge ordering in mixed valent spinel $LiRh_2O_4$

new compound

And more ,,,,,

$LiVS_2$, $Hg_2Ru_2O_7$

Spin liquid ground state in $Na_4Ir_3O_8$ with hyper-Kagome (ordered spinel) lattice

Okamoto, Nohara, Katori & Takagi PRL 99 137207 (07)

Searched for Ir spinel
After struggle, by chance found $Na_4Ir_3O_8$ closely related to spinel

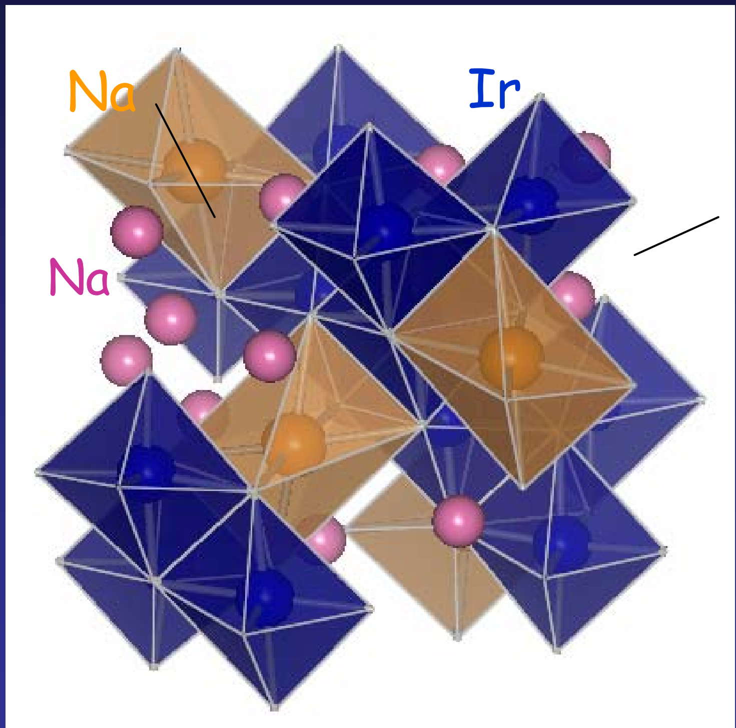
$Na_4Ir_3O_8$: cubic $P4_132$, a = 8.985 Å

		x	y	z	g	B(Å)
Ir	12d	0.61456(7)	x + 1/4	5/8	1.00	0.15
Na1	4b	7/8	7/8	7/8	1.00	2.6
Na2	4a	3/8	3/8	3/8	0.75	2.6
Na3	12d	0.3581(8)	x + 1/4	5/8	0.75	2.6
O1	8c	0.118(11)	x	x	1.00	0.6
O2	24e	0.1348(9)	0.8988(8)	0.908(11)	1.00	0.6

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

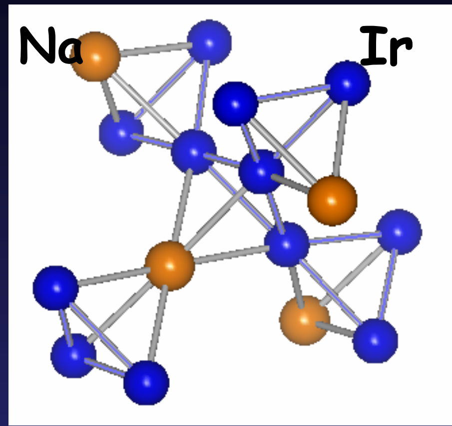
B-cation ordered spinel

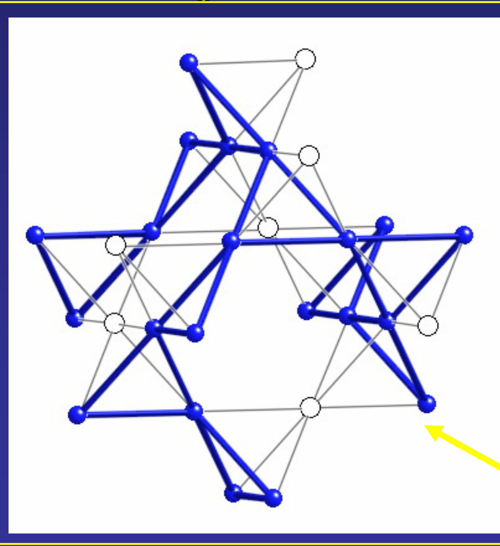
$2\ (Na_{3/2})_1\ (Ir_{3/4}, Na_{1/4})_2 O_4$



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

Isostructural to $Na_4Sn_3O_8$



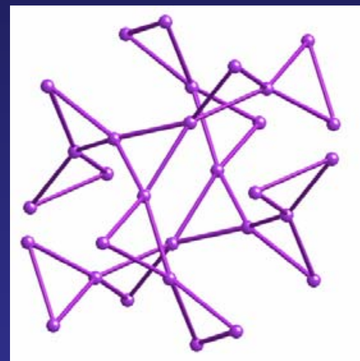


"hyper-Kagome" frustration

B-site

$\frac{3}{4}$: Ir, $\frac{1}{4}$: Na

Cation ordering

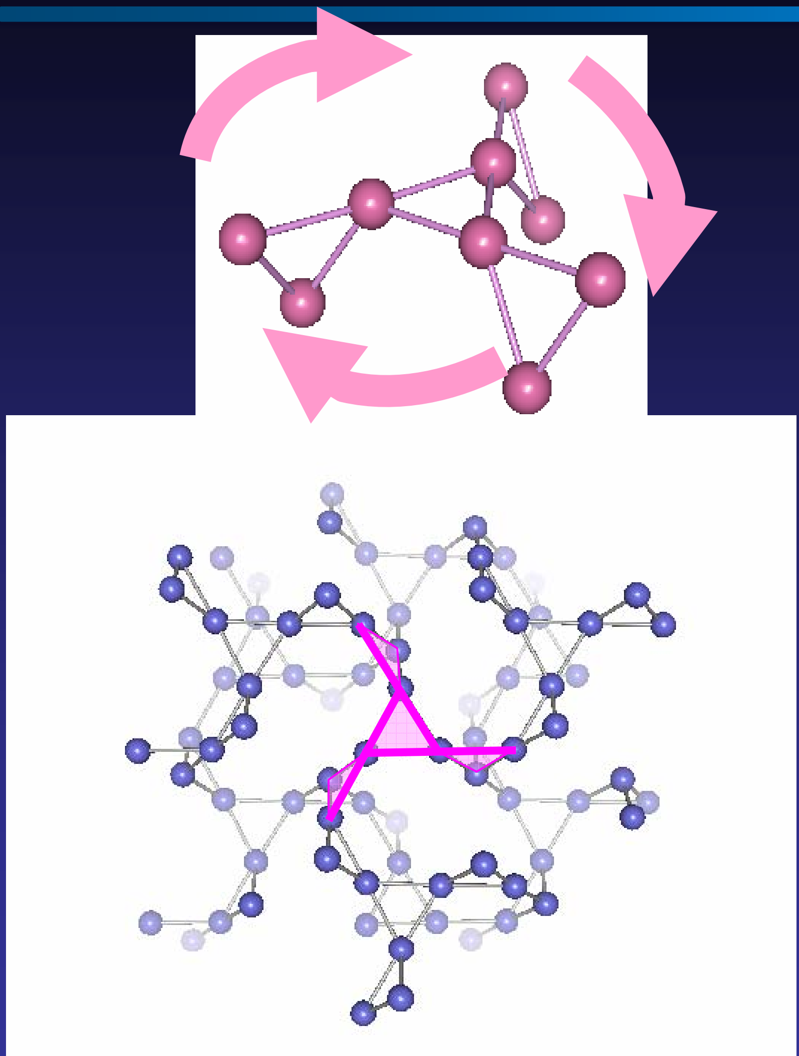


Closely related to garnet

Ir^{4+}

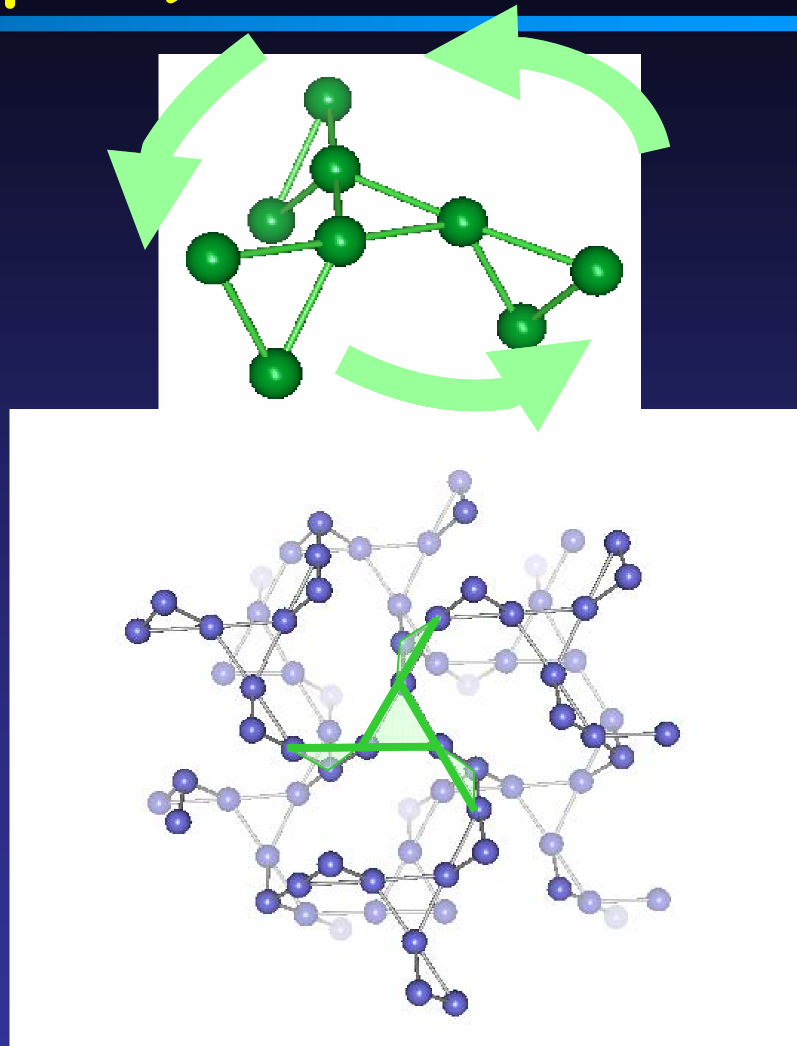
$5d^5$; S = 1/2

Hyperkagome (ordered spinel) lattice has "chirality"



$P4_132$

L



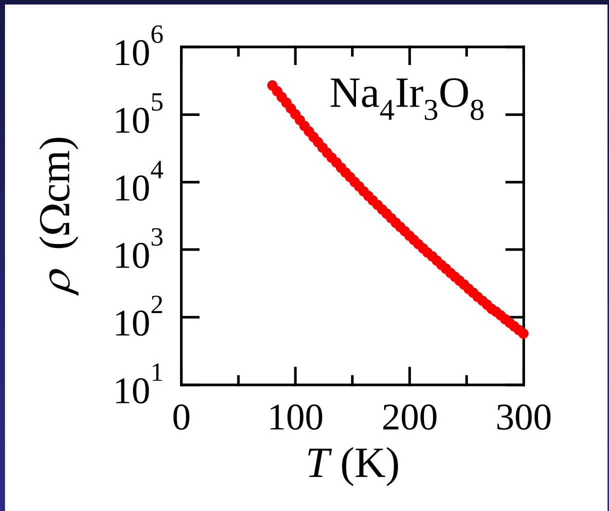
$P4_332$

R

$Na_4Ir_3O_8$ S=1/2 Mott Insulator with AF interaction

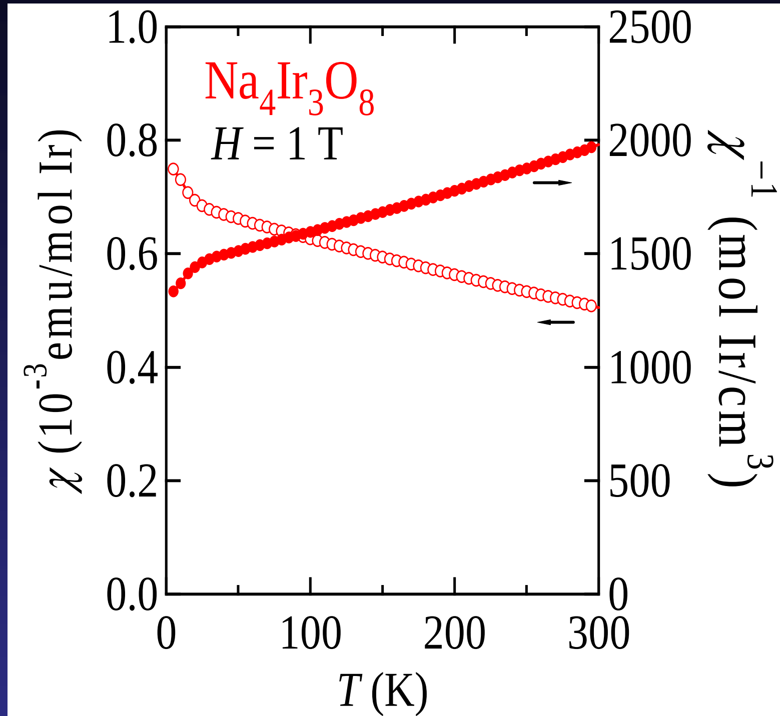
$5d^5$

S = 1/2



Mott insulator

S=1/2 hyper-Kagome



θ_W = -650 K

strong AF int.

J ~ 400K estimated

μ_{eff} = 1.96 μ_B / Ir

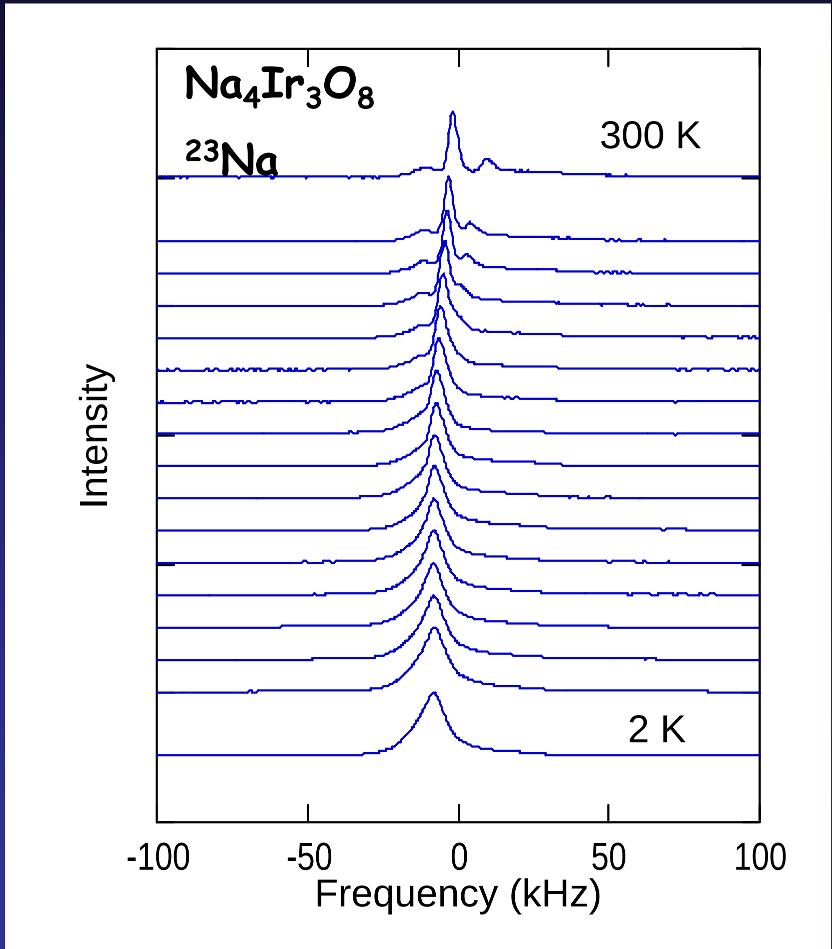
(S = 1/2 → 1.73 μ_B)

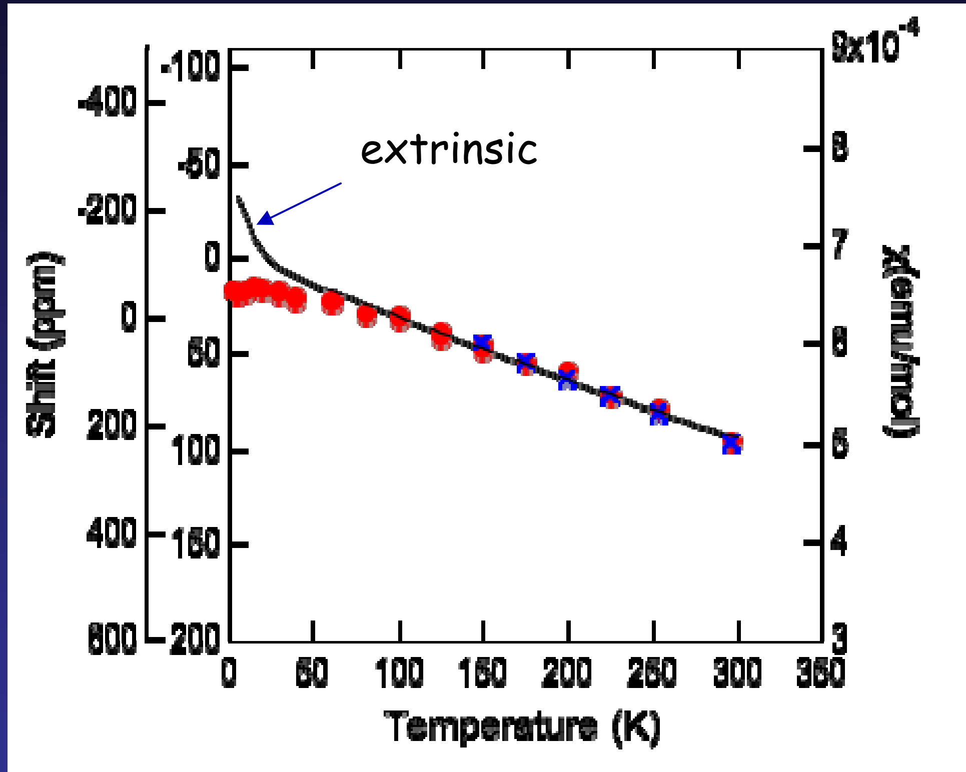
No ordering in χ down to 1.8 K << θ_{cw}= 650K

Strong frustration

Spin liauid?

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

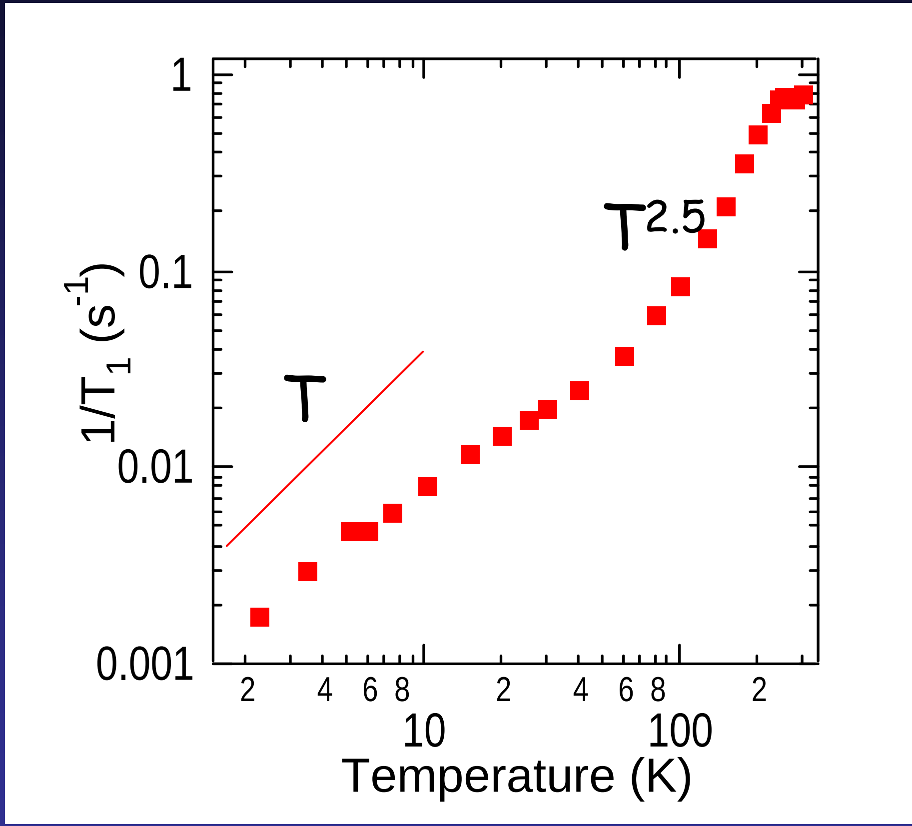




$\chi(T) \rightarrow$ constant at T=0 limit
gapless

Fujiyama, Kanoda

Power law decay of nuclear spin-lattice relaxation rate



S. Fujiyama, K. Kanoda

No $1/T_1$ divergence down to 2K
no ordering and freezing!

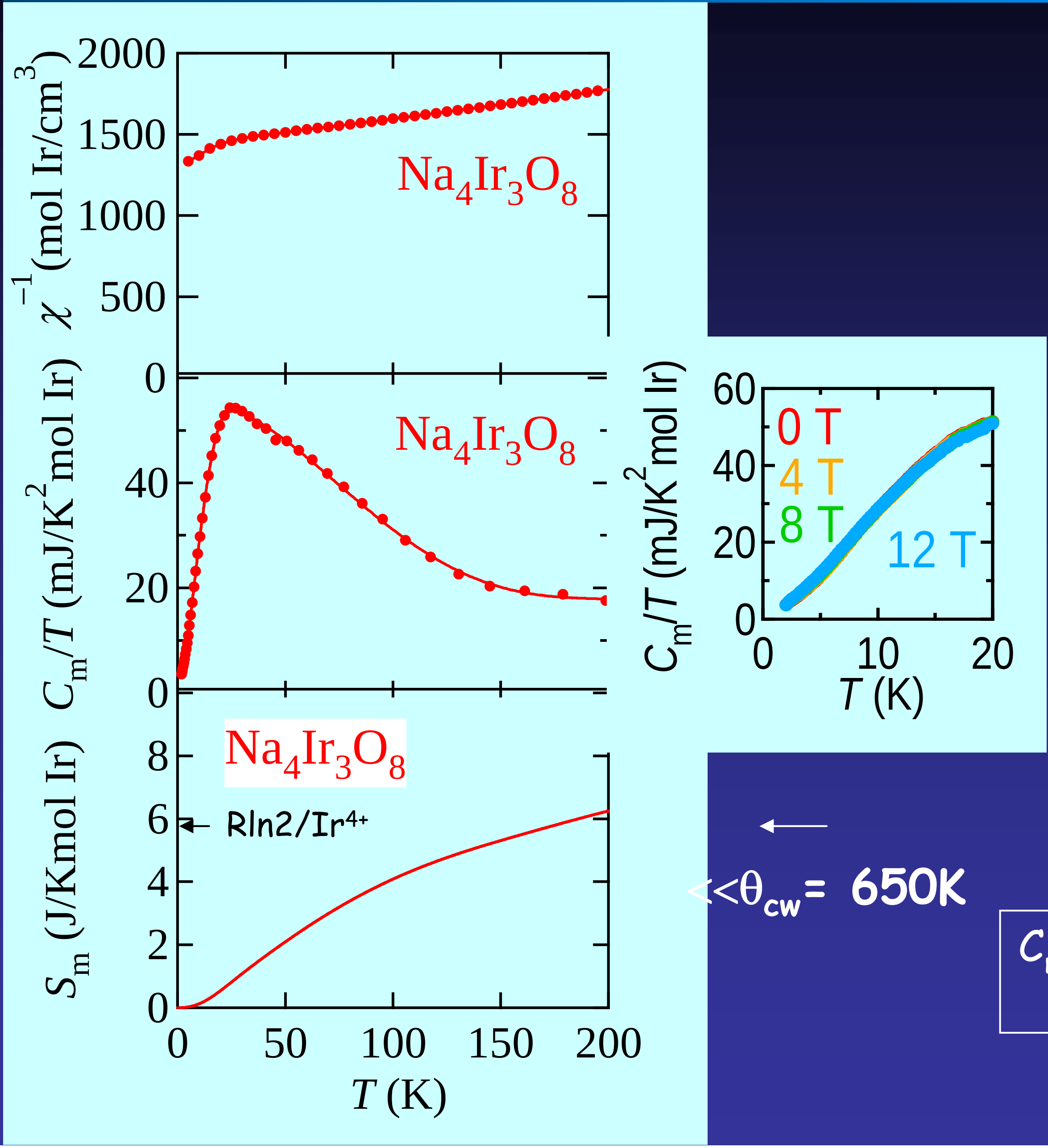
$1/T_1$ constant above
T~ 200K (~J/2)

Consistent with a large J~400K

Power low decay below 200 K

~T-linear below 10 K??
$1/T_1T$ const
low lying spin excitaion??

C(T) supports for spin liquid ground state



-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

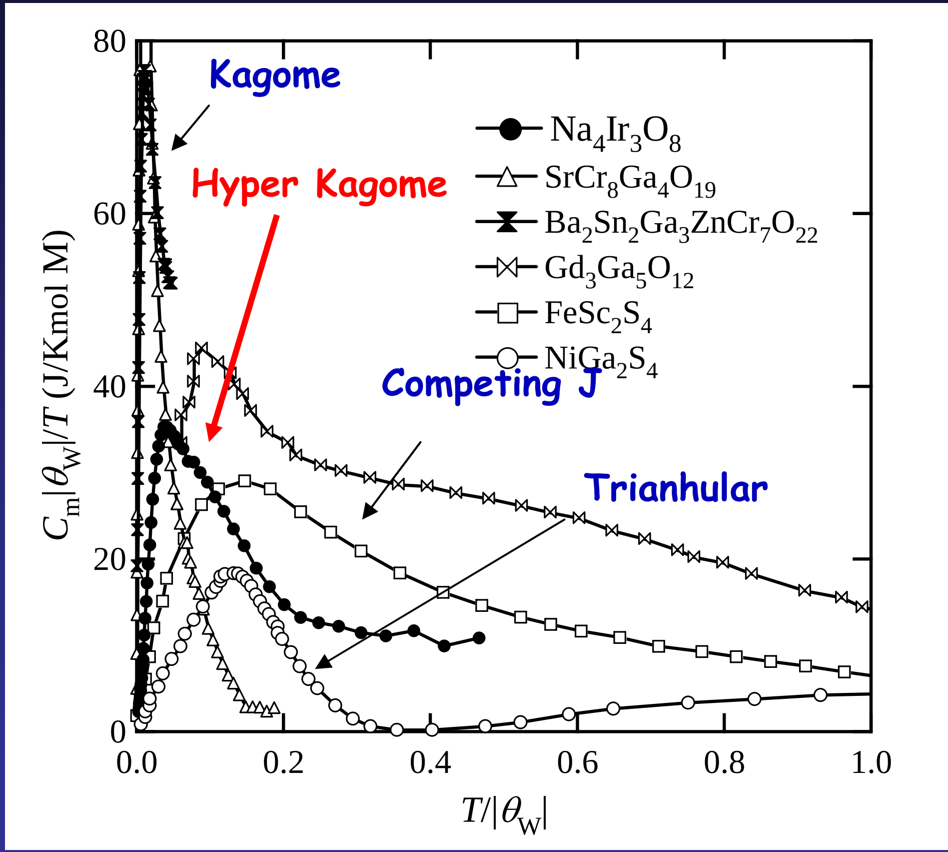
low E excitation originates from (large) J scale

strongly degenerate low lying spin excitation created by J

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

$C_m(T) \propto T^2$ down to 2K
E linear DOS (gap node)

Comparison with other geometrically frustrated magnet - entropy weight down shift



Issues:

- T^2 specific heat in 3D?

-$(T_1T)^{-1}$ constant?

very small γT term observed below 1 K

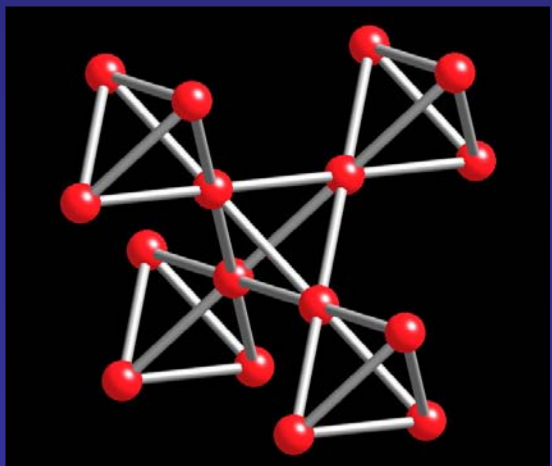
likely disorder (imp.)?

Uniqueness: 3D S=1/2

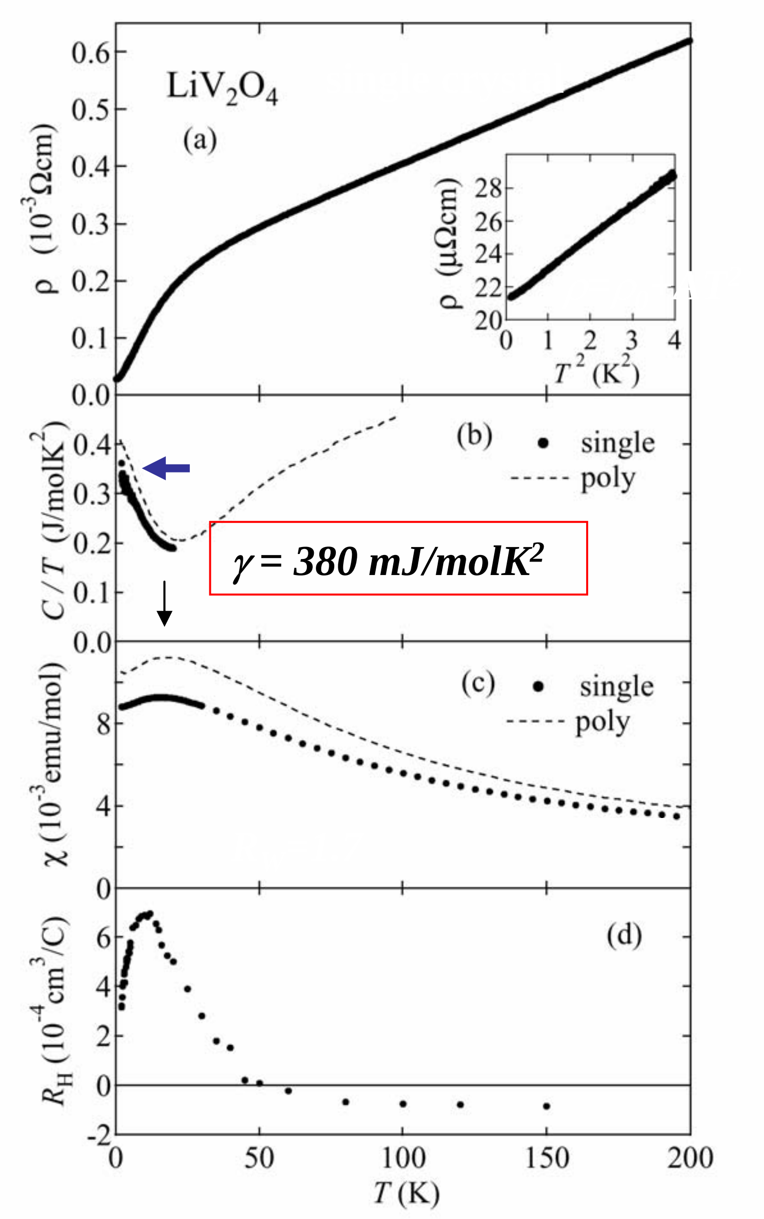
- Much cleaner, no evidence for freezing

Charge frustration & heavy fermion formation in LiV_2O_4 spinel probed by optical response

Jonson, Takenaka, Niitaka, Takagi, PRL99 167402 (07)



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



C.Urano, H.T et al PRL 85, 1052 (00)
H.T et al. Mat.Sci. Eng. B63, 147 (99)

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

"charge" frustration

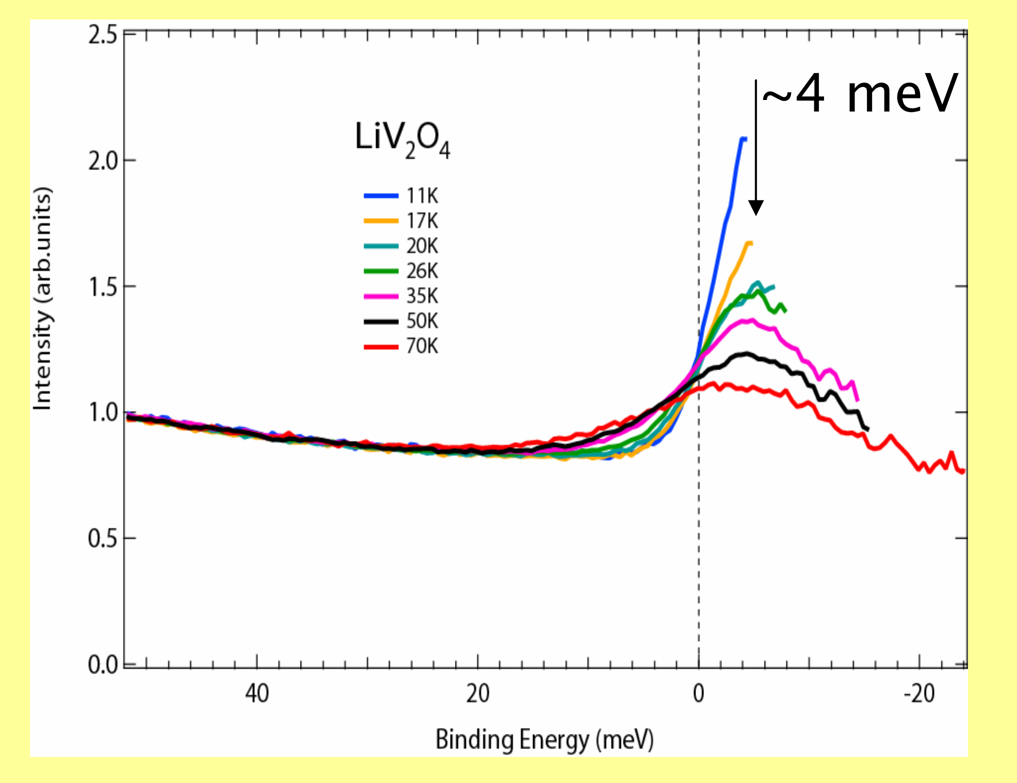
1:1 V3+ & V4+ on pyrochlore lattice

want to order but cannot show any charge & spin ordering due to strong frustration

Charge analogue of spin liquid

Heavy fermion ground state results!

Evolution of quasi-particle DOS peak 4 meVabove E_F



Only t_{2g} electrons involved

A new route to heavy fermion by frustration

not Kondo

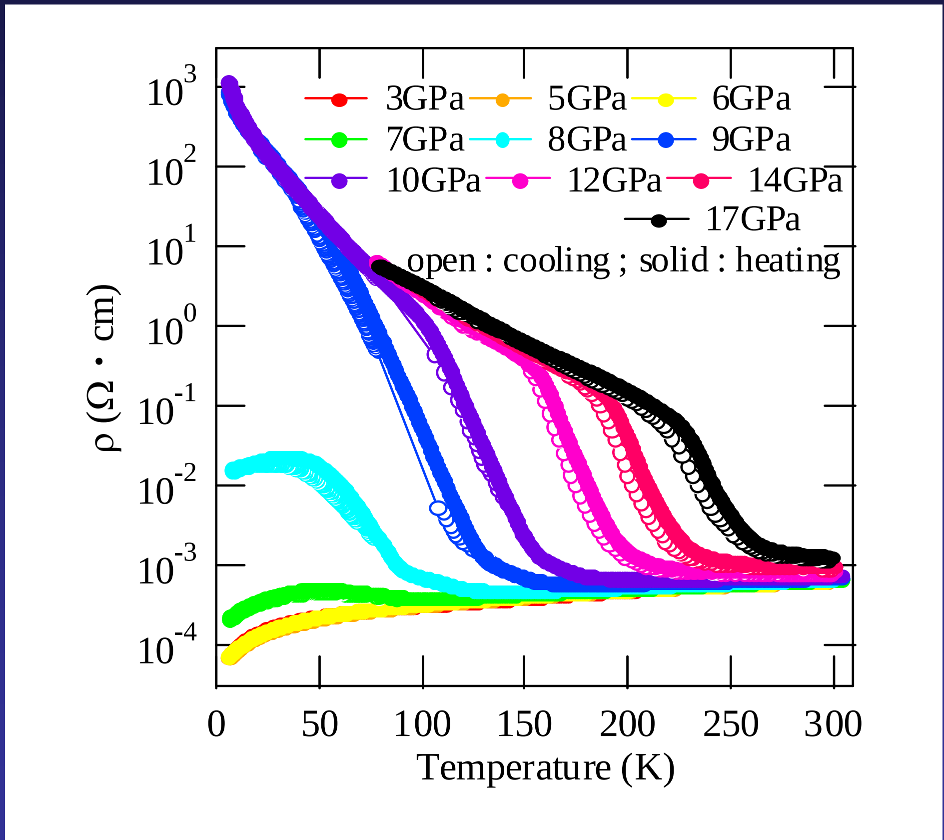
Shin, PRL

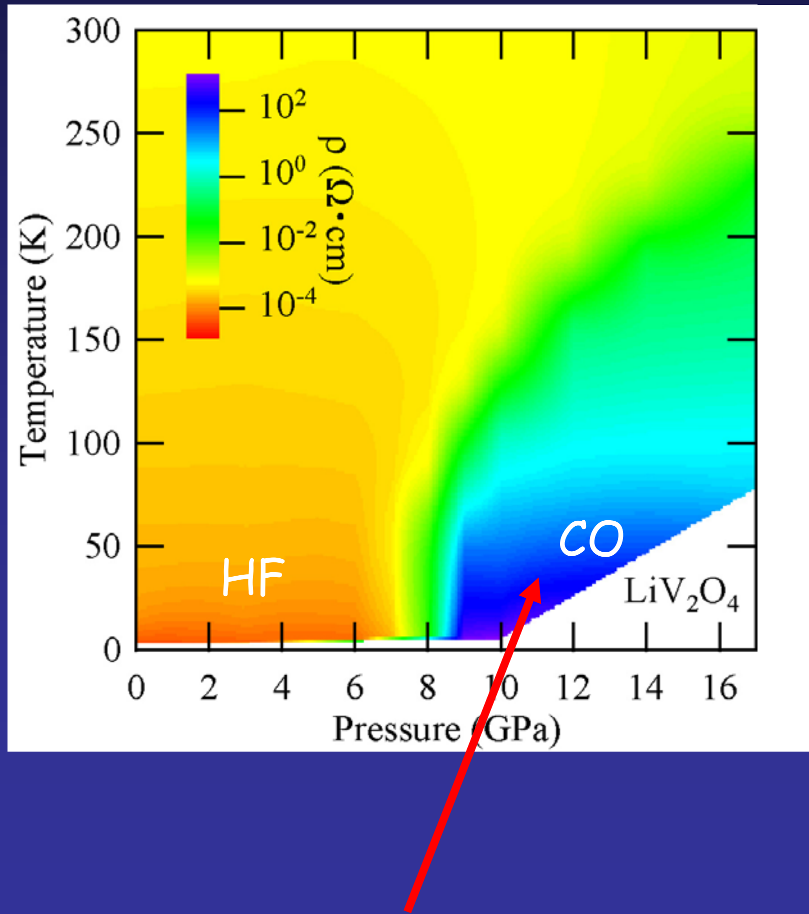
Key ingredients: close proximity to charge ordered insulator without charge/magnetic ordering due to geometrical frustration

Crystallization of heavy fermions under pressure in LiV_2O_4

HF state of LiV_2O_4 close proximity to CO

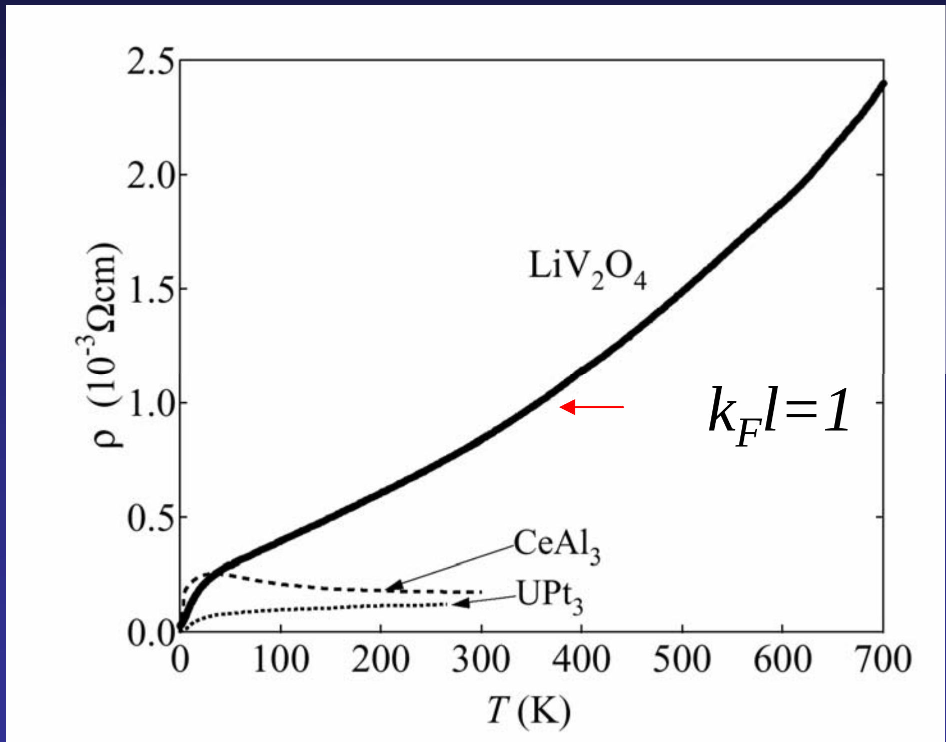
S. Niitaka, N. Takeshita





Contrast between LiV_2O_4 and Kondo intermetallics

absence of
resistivity saturation (bad metal), logT



analogous to TMOs near Mott(CO) transition, indicative of close proximity to CO : Mott-Hubbard physics rather than Kondo physics?

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

Coherent - incoherent crossover seen in optical conductivity $\sigma(\omega)$

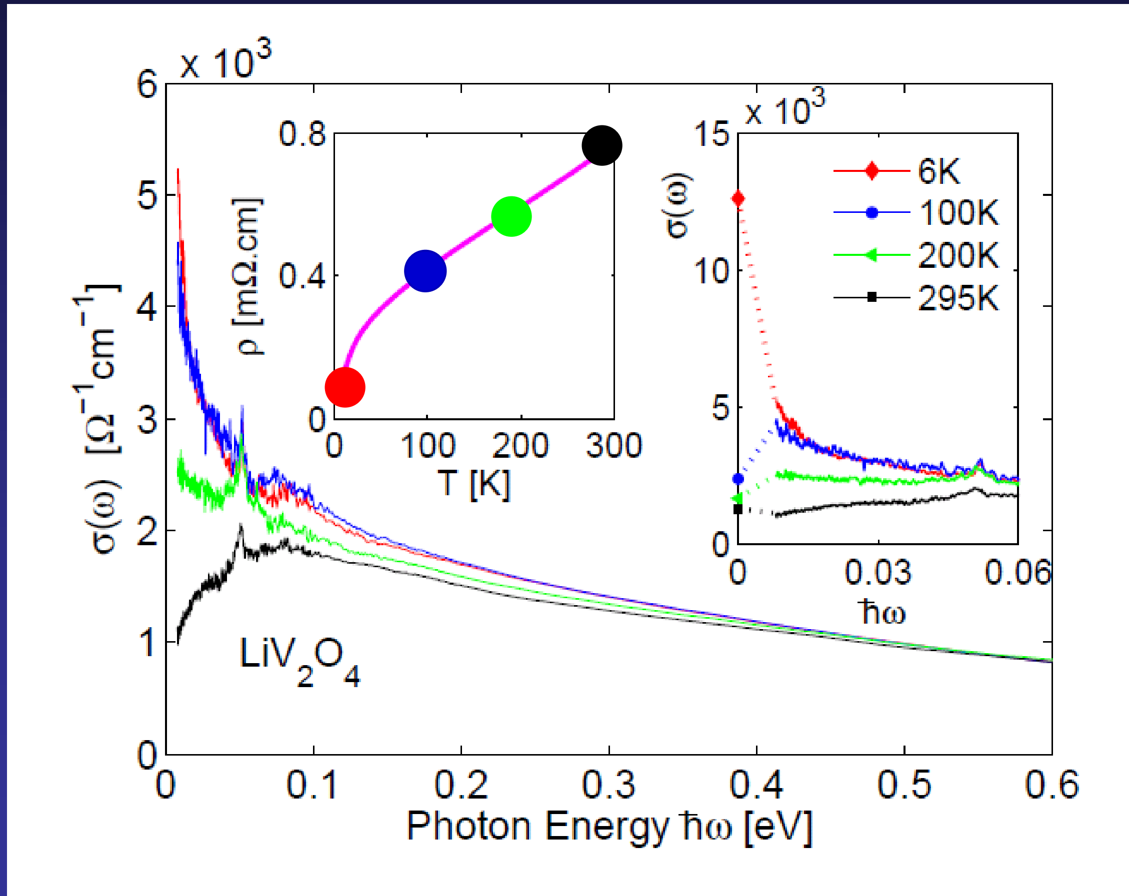
PRL99 167402 (07)

E scale of

Spectral weight transfer ?

Not J_k ~20 K

But much larger



Coherent Drude marginally formed only at low T

Spectral weight transfer over eV-scale to establish coherent QP states

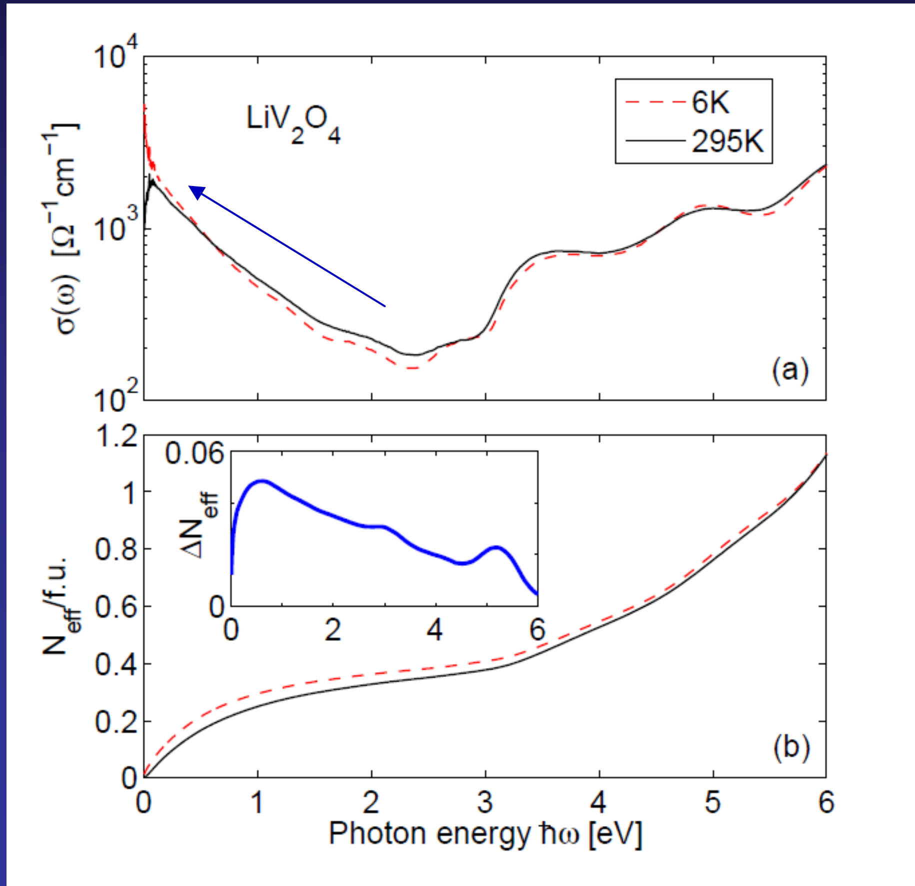
PRL99 167402 (07)

optical conductivity $\sigma(\omega)$

Mott physics dominates the QP state rather than low E Kondo physics

Close proximity
to Correlation driven COstate
in the presence of Frustration

"Charge" analogue of spin liquid



Orbital & Charge Ordering in Geometrically Frustrated $LiRh_2O_4$

4d 5d anlogue of LiV_2O_4??

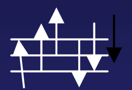
Discovered as a new compound

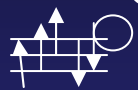
Two transitions to lift the degeneracy

Band JT + dimerization

New mixed valent spinel $LiRh_2O_4$

- $Rh^{3.5+}$: $4d^{5.5}$ LS 0.5 hole in t_{2g}
  - 1:1 Rh3+ ($4d^6$) & Rh4+ ($4d^5$)





t_{2g}

non-magnetic S=1/2

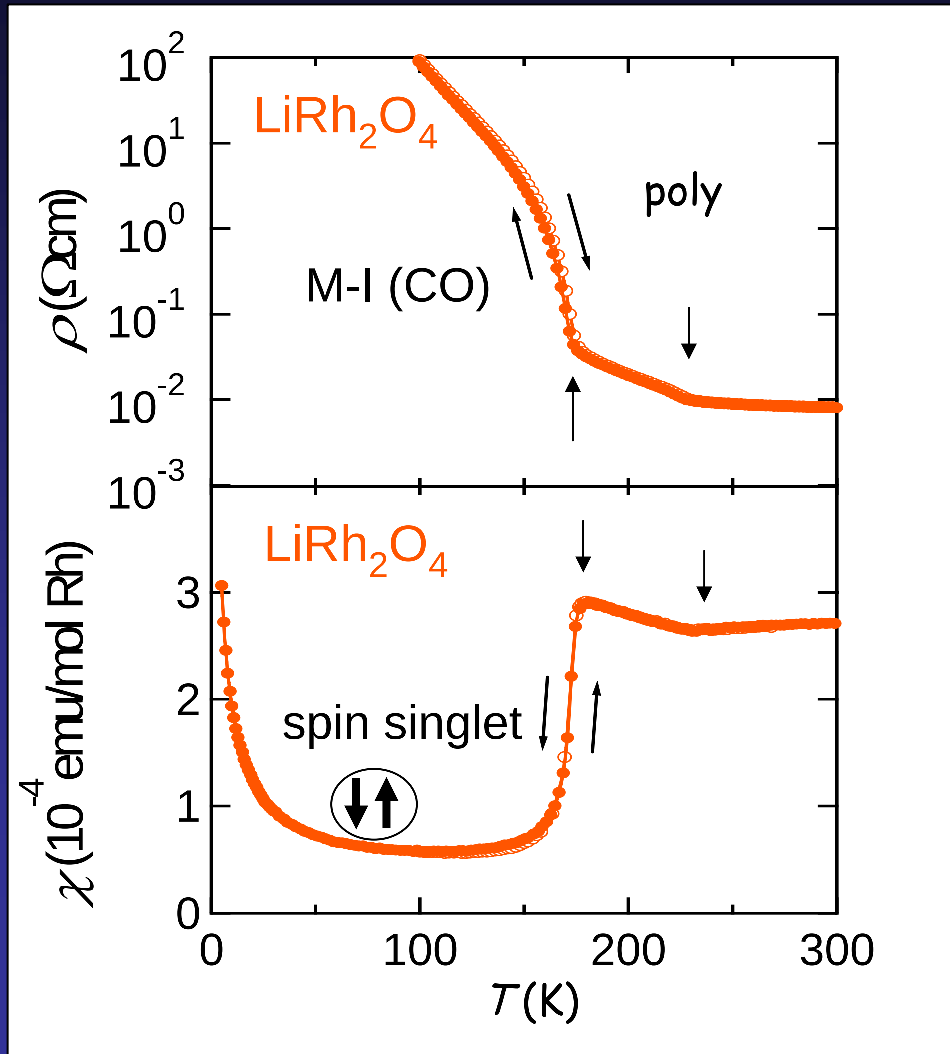
- charge ordering (1^{st} order M-I) at 170 K: Contrast to LiV_2O_4!

"singlet molecules" in solid

to suppress frustration

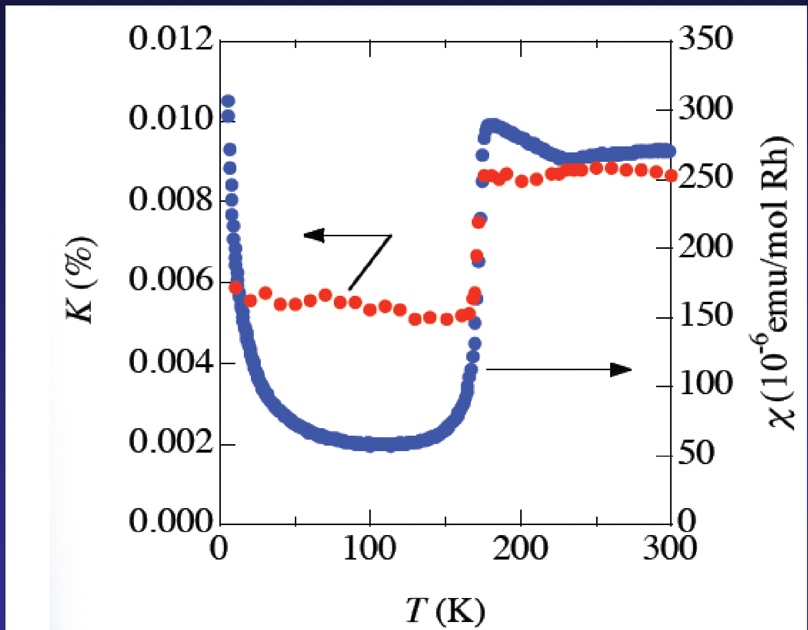
-Additional anomaly at 230 K

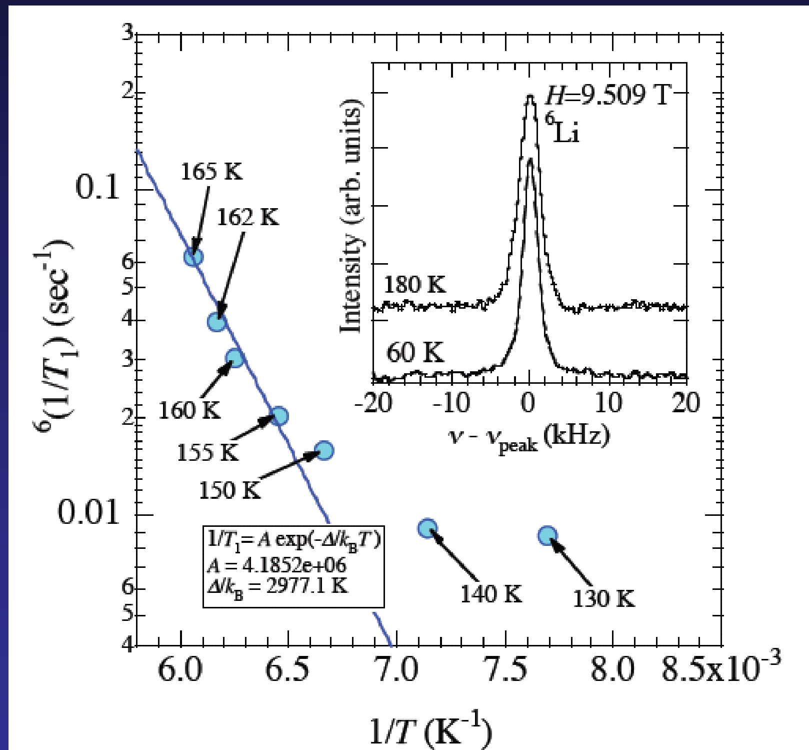
(M-M)



Robust spin singlet formation indicated by Li-NMR

Waki, Takigawa



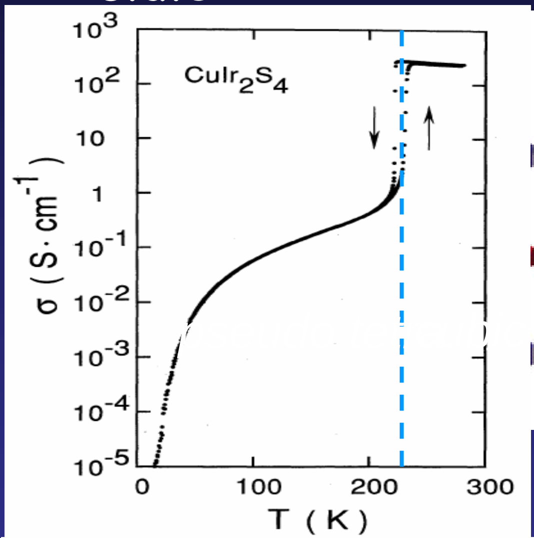


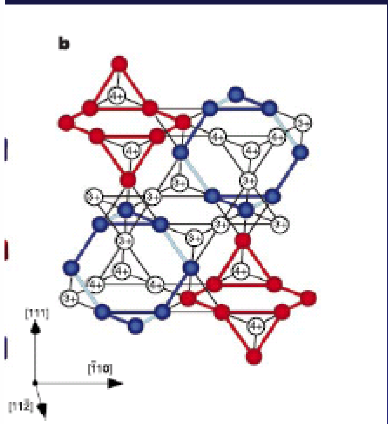
Activation energy ~ 3000K
Robust singlet

Valence bond solid (spin singlet insulator) ubiquitous in mixed valent spinel?

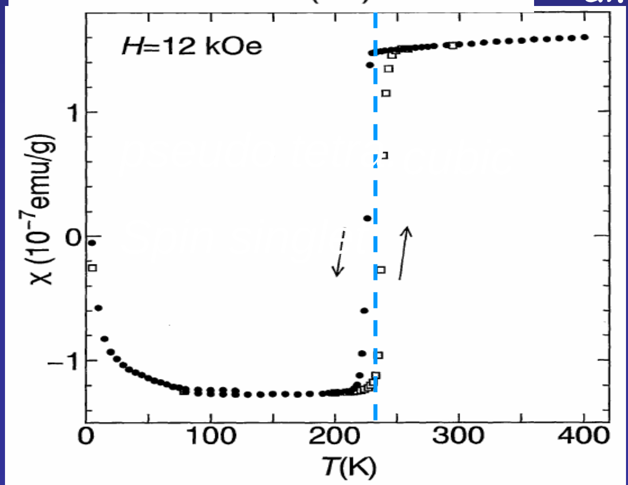
$CuIr_2S_4$ 1:1 Ir 3+ and Ir 4+

Spin singlet octomer of Ir 4+ in CO state





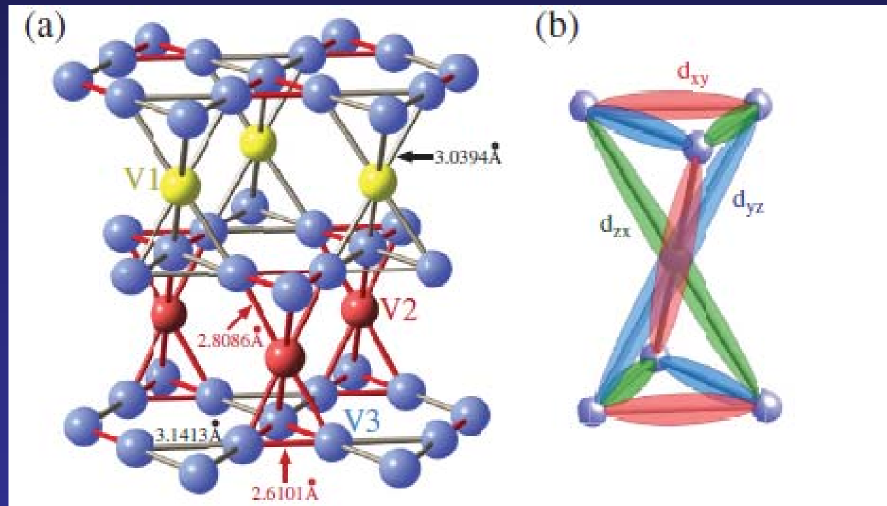
P. G. Radaelli *et al.*,



Furubayashi *et al.*,

AlV_2O_4 1:1 V 2+ and V 3+

spin singlet heptamer formation in CO state



Y.Horibe, T.Katsufuji et al. PRL 96 084606 (06)

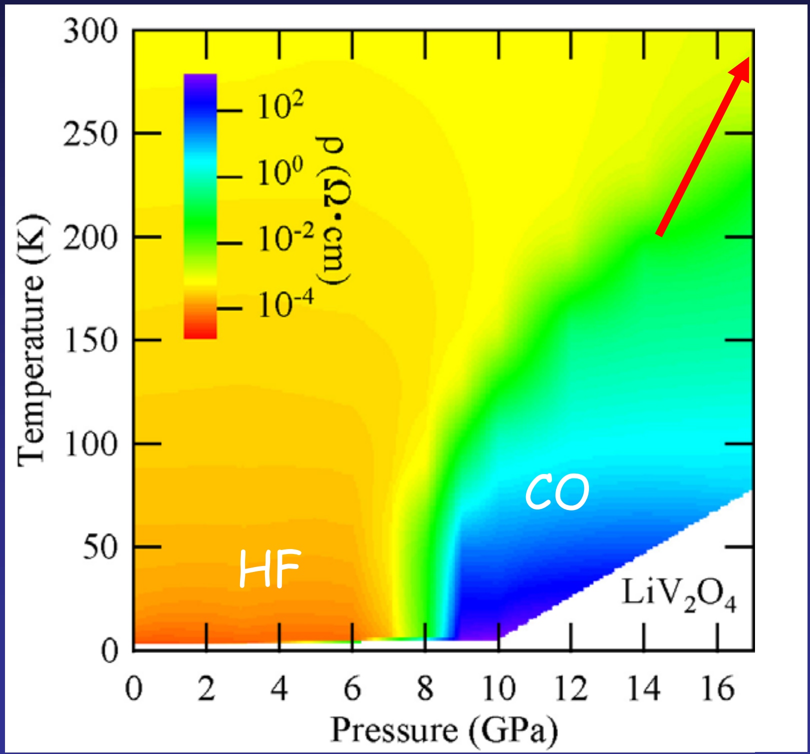
Very large distorion of metal-metal distance ~10% to form singlet molecule

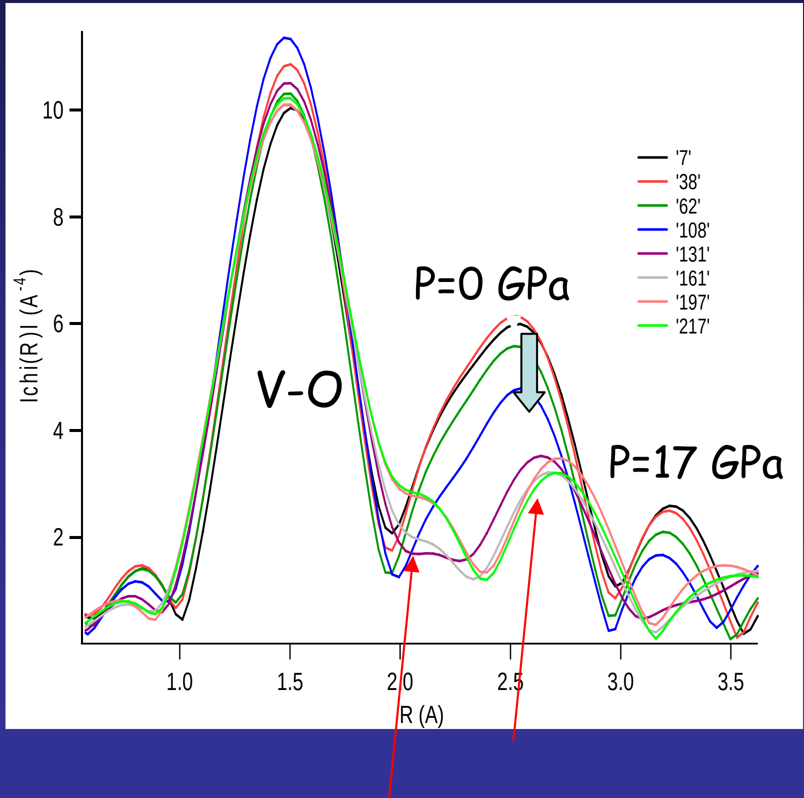
$LiRh_2O_4$ NMR suggests singlet stabilized 3000K

Valence bond solid formation also in charge ordered state of LiV_2O_4 ?

With N,Dragoe (Orsay)

EXAFS, large V-V modulation P>Pc
valence bond crystal with orbital ordering



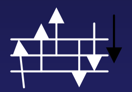


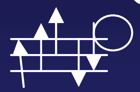
Pressure induced
metal-insulator transition

PRB

How does system evolve into spin singlet insulator?

- $Rh^{3.5+}$: $4d^{5.5}$ LS 0.5 hole in t_{2g}
  - 1:1 Rh3+ ($4d^6$) & Rh4+ ($4d^5$)





t_{2g}

non-magnetic   S=1/2

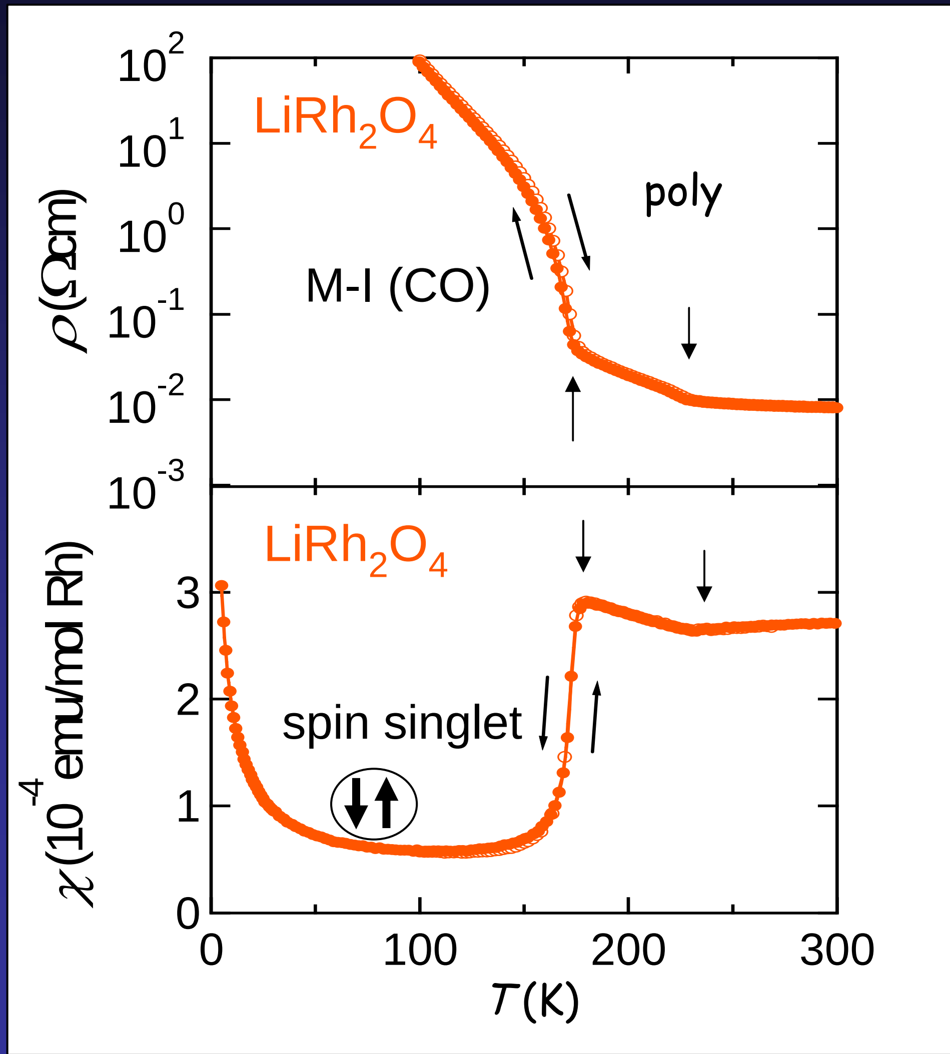
- charge ordering (1^{st} order M-I) at 170 K:

"singlet molecules" in solid

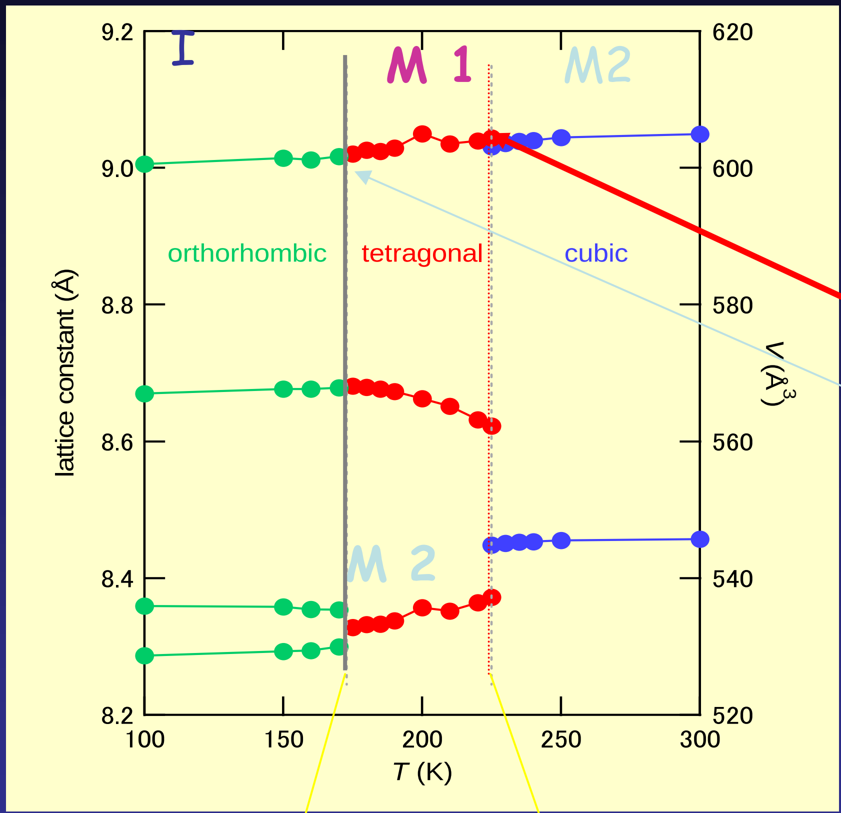
to suppress frustration

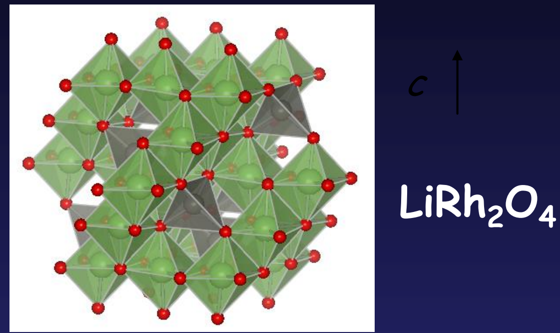
-Additional anomaly at 230 K

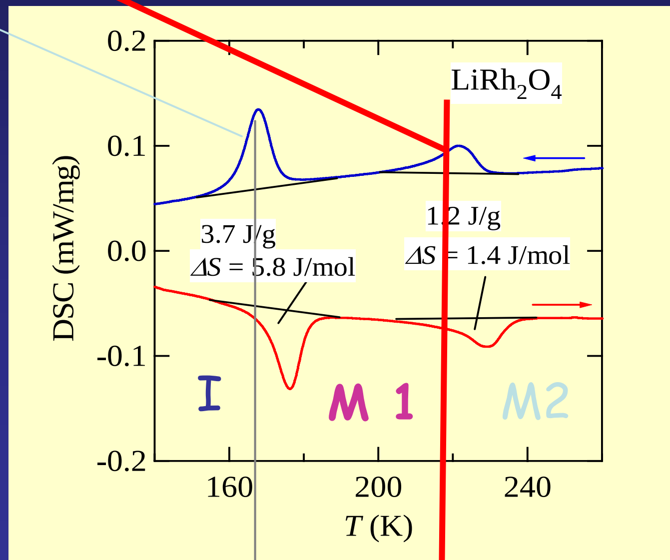
(M-M)



Large (hidden) entropy change and Cubic-Tetragonal transition at M2-M1 transition







orthorhombic

a = 8.29 Å
b = 8.36 Å
(b/a ~ 1.01)
c = 8.67 Å

tetragonal

a = 5.89 Å
($\sqrt{2}a$ = 8.34 Å)
c = 8.67 Å
(c/a ~ 1.04)

cubic

a = 8.46 Å

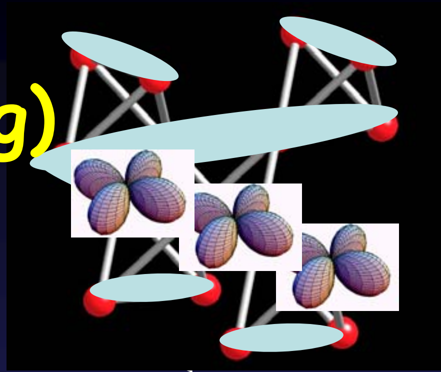
~70% of R/Rh4+

ΔS ~20%of R/Rh4+

superstructure **No-superstructure in ED**

→ Likely (band) JT transition

Band JT (orbital ordering) + dimerization in $LiRh_2O_4$

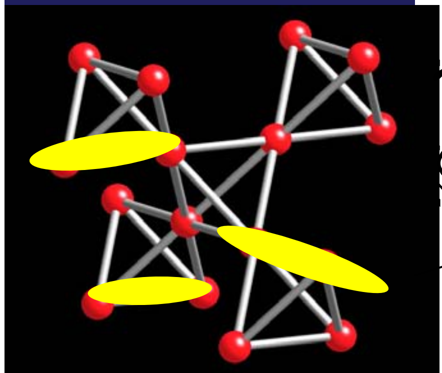


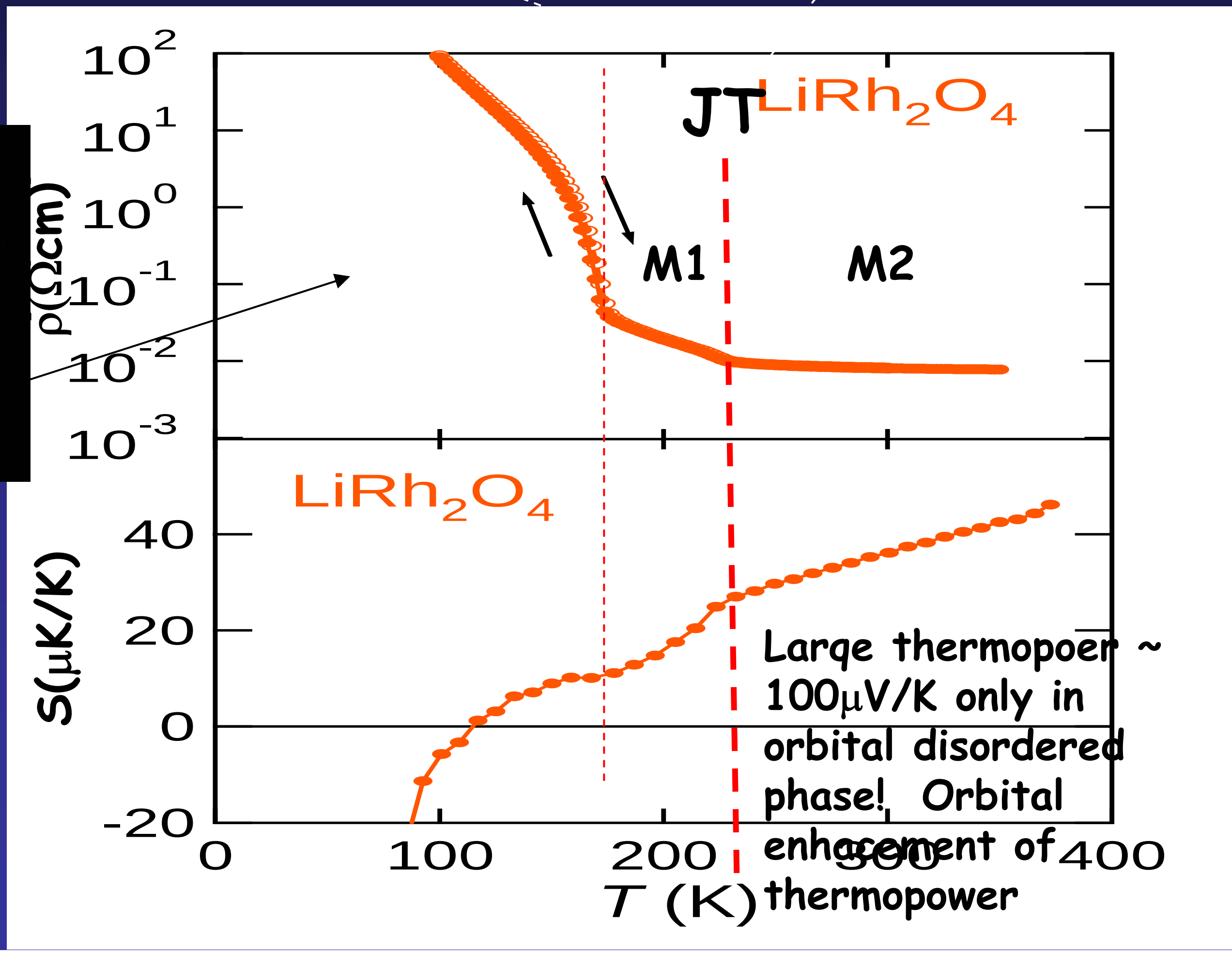
orbital ordered metal
1D xy

orbital disordered metal

Tetra
small S

Cubic
large S (like Co-oxide)





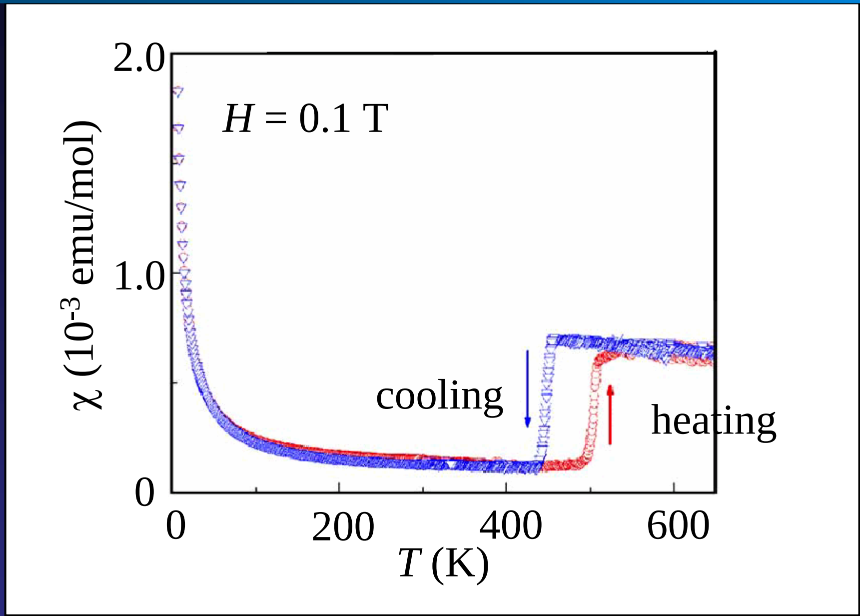
Large thermopoer ~ 100μV/K only in orbital disordered phase! Orbital enhacement of thermopower

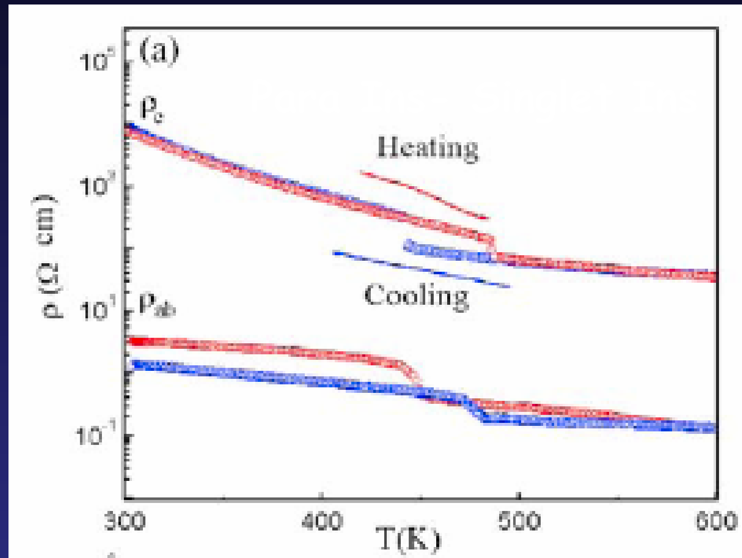
Charge ordering - dimerization within xy chain band?

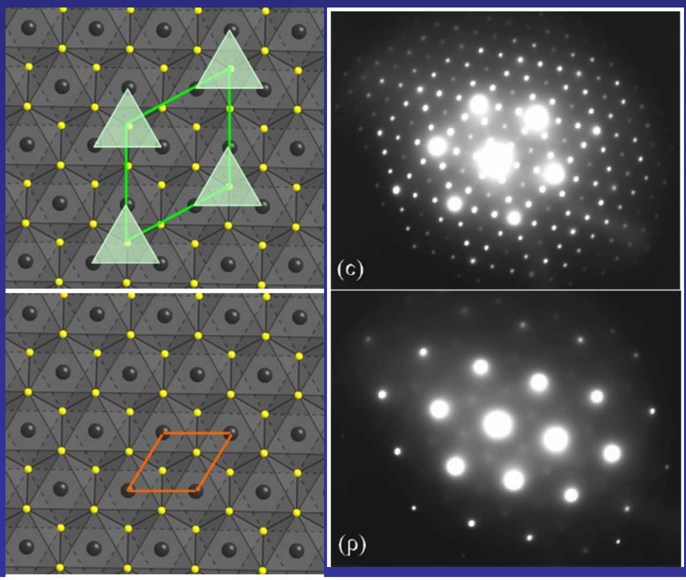
Other related new compound

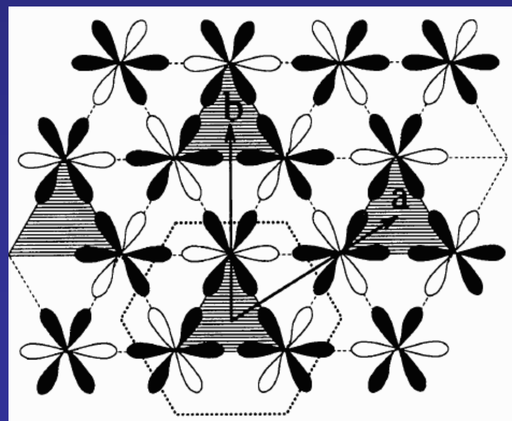
Mott transition on frustrated lattices

Spin singlet ground state in S=1 Mott insulator with frustrated triangular lattice: $LiVO_2$









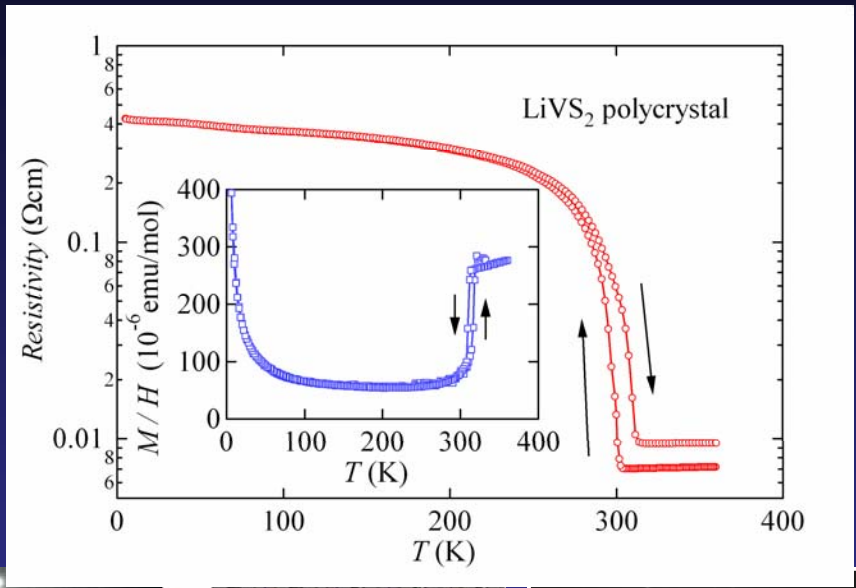
Penc, Khomskii, Sawatzky・・・

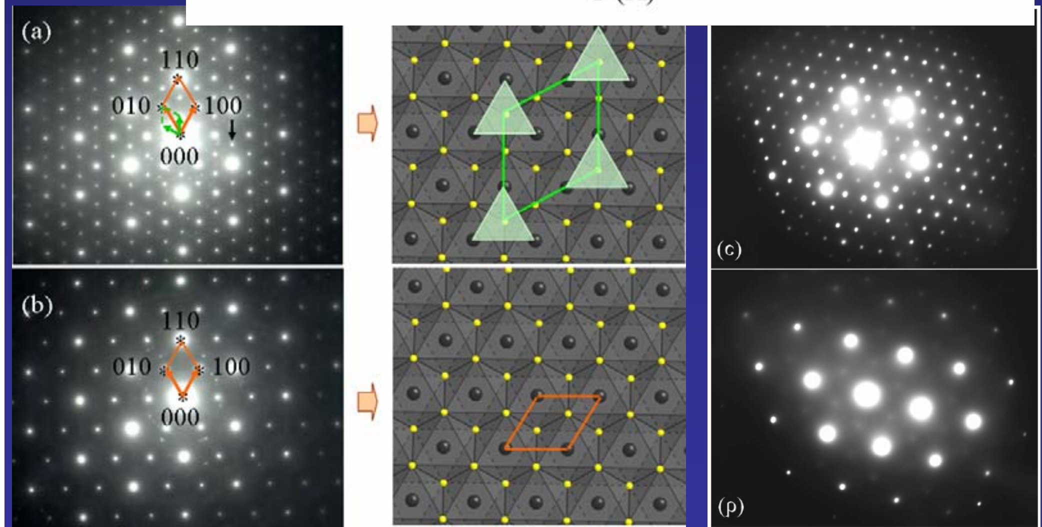
Suppression of spin frustration by orbital ordering

Trimer formation observed in ED

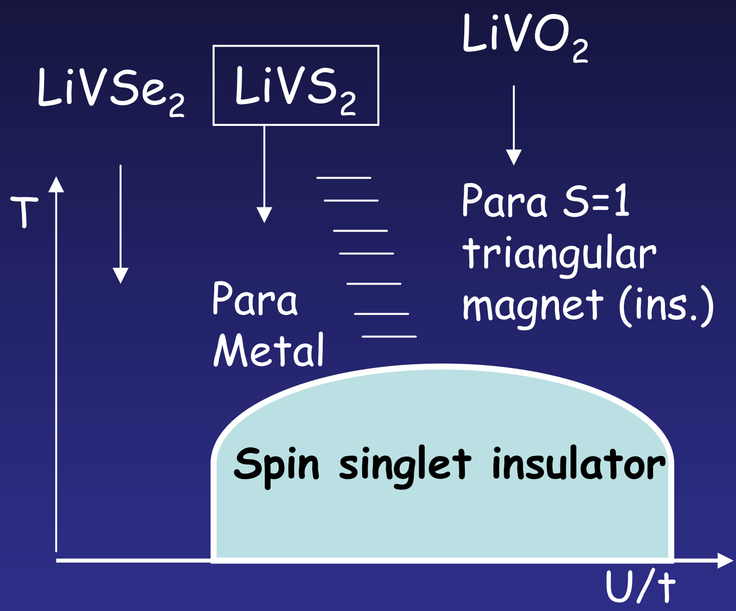
$LiVS_2$: itinerant analogue of $LiVO_2$
Metal to (trimer) singlet insulator transition
spin + orbital may not be enough for $LiVO_2$

Not “new” but first investigated





LiVS$_2$ LiVO$_2$

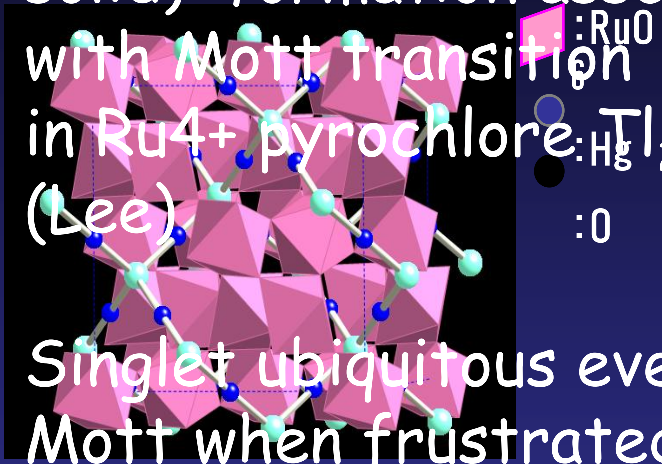


Spin singlet (trimer) state are so robust in the vicinity of M-I

trimer formation just like $LiVO_2$
indicated by ED in ins, phase

Metal-Insulator Transition in New Pyrochlore $Hg_2Ru^{5+}{}_2O_7$

spin singlet (valence bond solid) formation assciated with Mott transition in Ru4+ pyrochlore $Tl_2Ru_2O_7$ (Lee)



Singlet ubiquitous even in Mott when frustrated

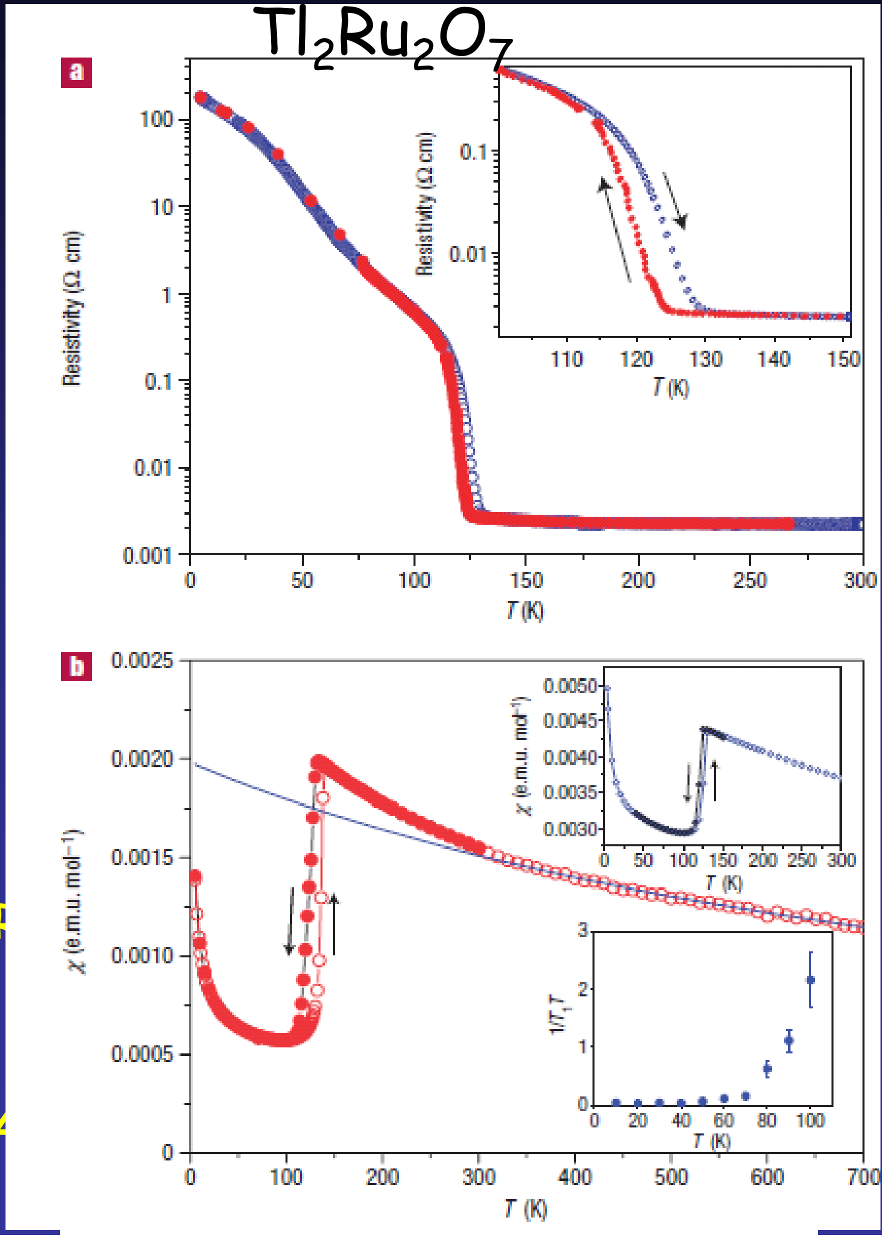
- Unique system

Ru 5+ system not Ru 4+ $t_{2g}{}^3$

no orbital degrees of freedom

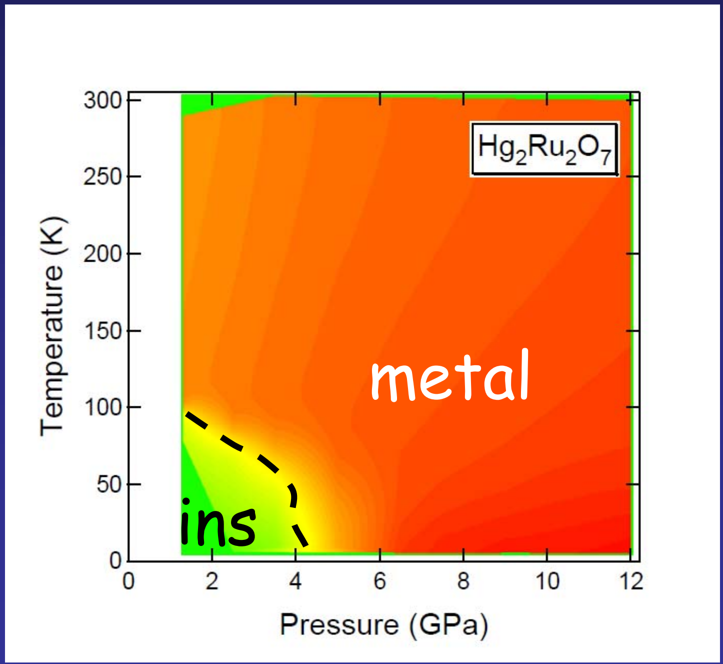
AF ordering found in ins. phase by Hg NMR (Takigawa) + small distortion

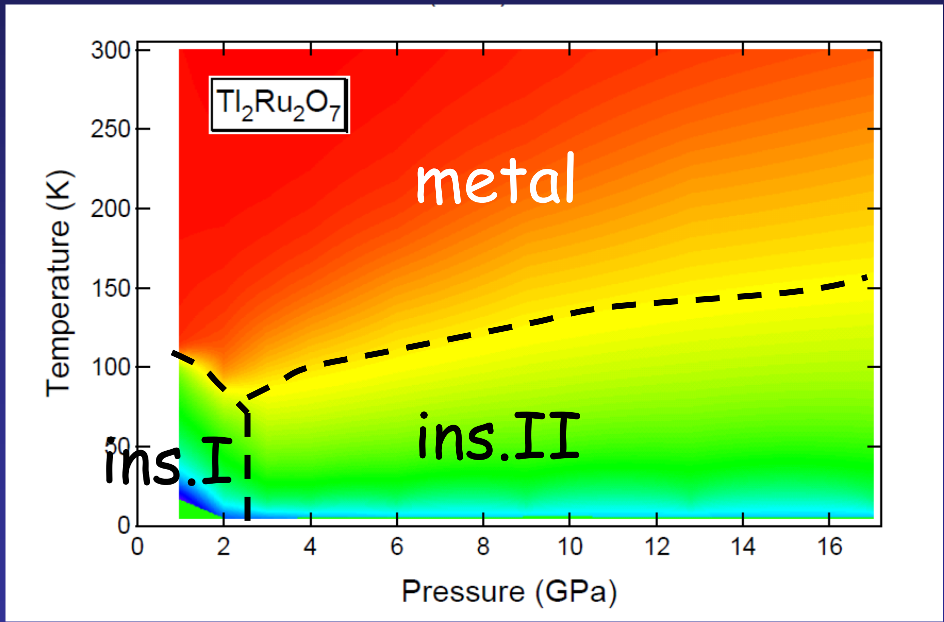
Itinerant analogue of $ZnCr_2O_4$ (spin-JT)



$Hg_2Ru_2O_7$ vs. $Tl_2Ru_2O_7$

No orbital	Orbital
$Hg_2Ru^{5+}{}_2O_7$  $t_{2g}{}^3$	$Tl_2Ru^{4+}{}_2O_7$  $t_{2g}{}^4$
AF ins. (spin JT)	Singlet ins.





Orbitals play a vital role in forming singlet

Summary

$Na_4Ir_3O_8$

Spin liquid ground state on hyper-Kagome lattice
V shaped excitation spectrum?

LiV_2O_4

HF state realized by correlation + frustration ?

$LiRh_2O_4$

VBS ubiquitus in mixed valent system
Band JT (orbital ordering) + dimerization
Orbital important for VBS formation

More······