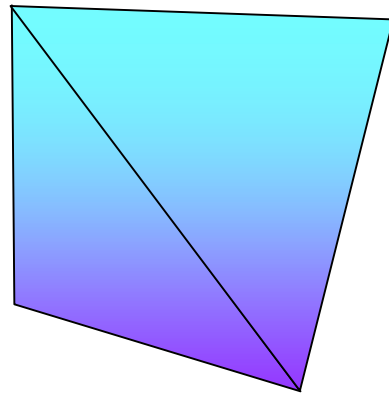


# Geometrical Correlation of Itinerant Electrons Probed by Muons and Neutrons



## Plan:

- Introduction
- $\text{LiV}_2\text{O}_4$ -a model case
- Other pyrochlores
- Summary

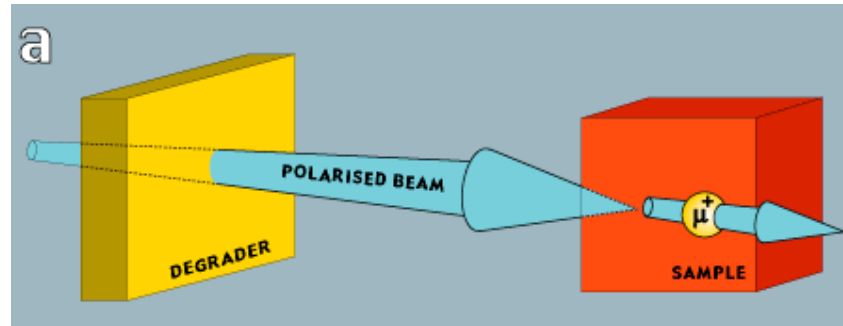
Ryosuke Kadono

*Institute for Materials Structure Science,  
High Energy Accelerator Research Organization (KEK),  
and*

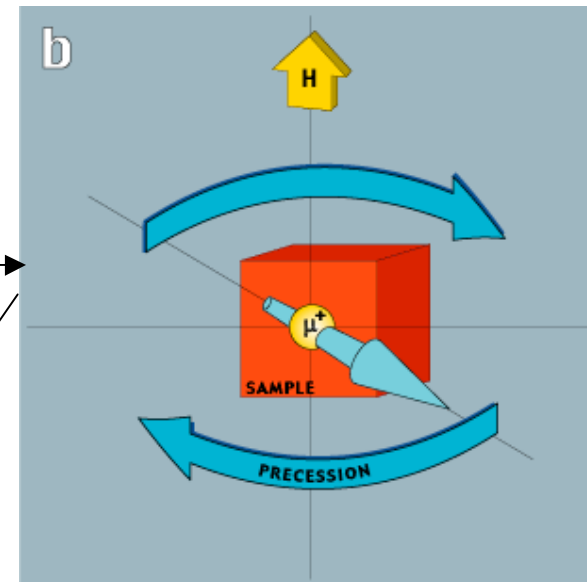
*Department of Materials Structure Science,  
The Graduate University for Advanced Studies*

## Method:

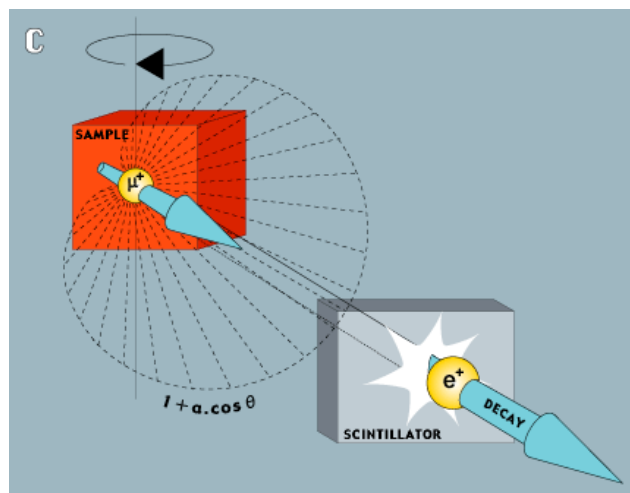
# Muon Spin Rotation ( $\mu$ SR)



a) Muons are produced with 100% spin polarization and transported by a beamline for implantation to sample.



b) The implanted muons stop between atoms, where they start Larmor precession according to the local magnetic fields.



c) Muons emit positrons to the direction when their spins were pointing upon decay, which are detected by scintillation counters.

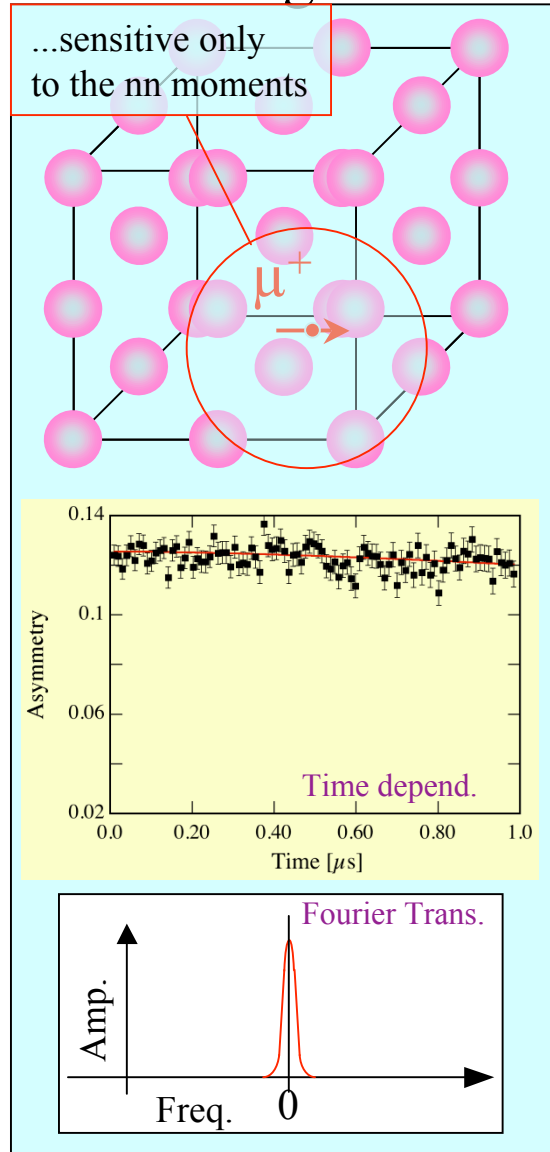
→ The signal of scintillation counters oscillates periodically due to the Larmor precession of muons.

# Method:

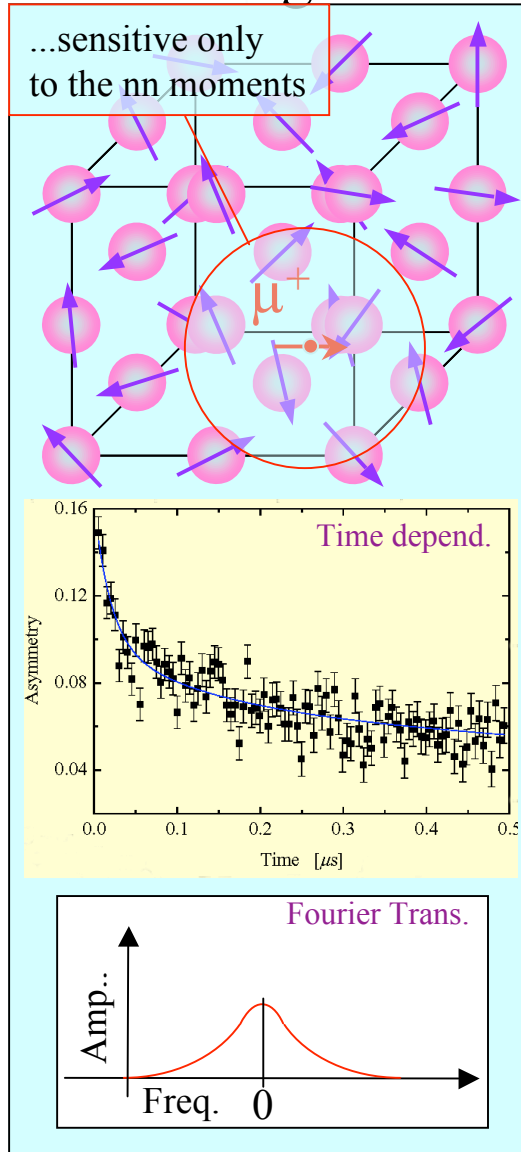
# Muon Spin Rotation ( $\mu$ SR)

...How muons probe magnetic state of matter?

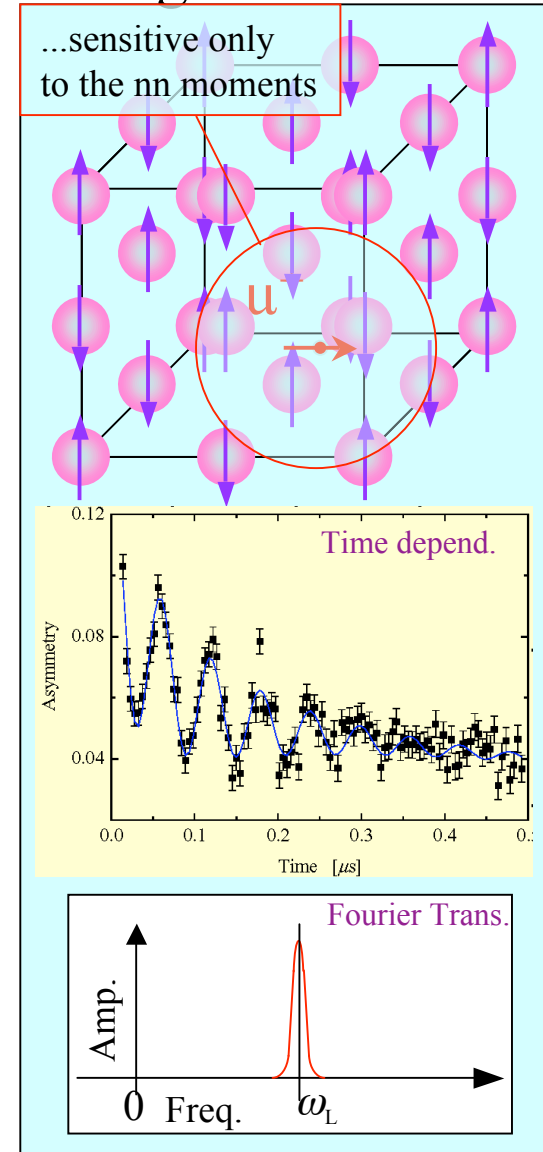
## Diamagnetic



## Paramagnetic



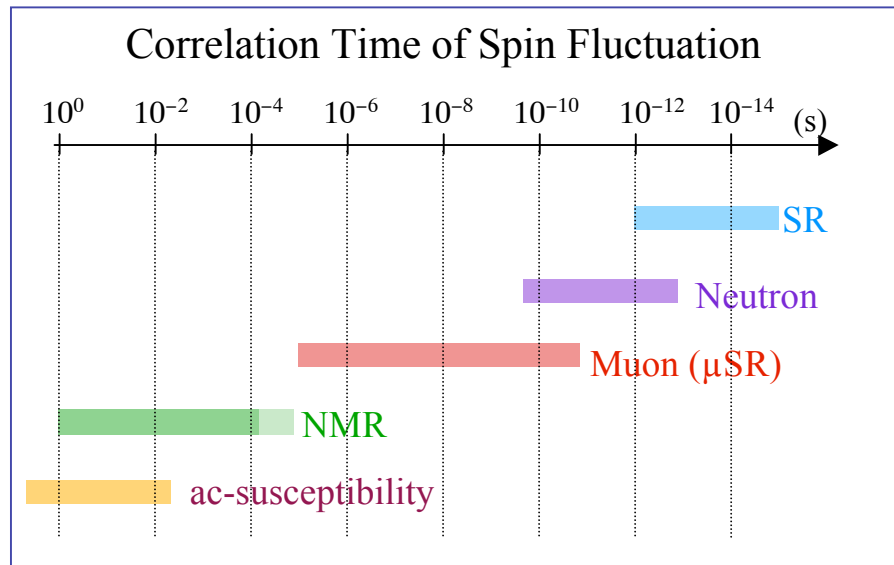
## Magnetic Order



Method:

# Muon Spin Rotation ( $\mu$ SR)

...Unique time window for the spin dynamics

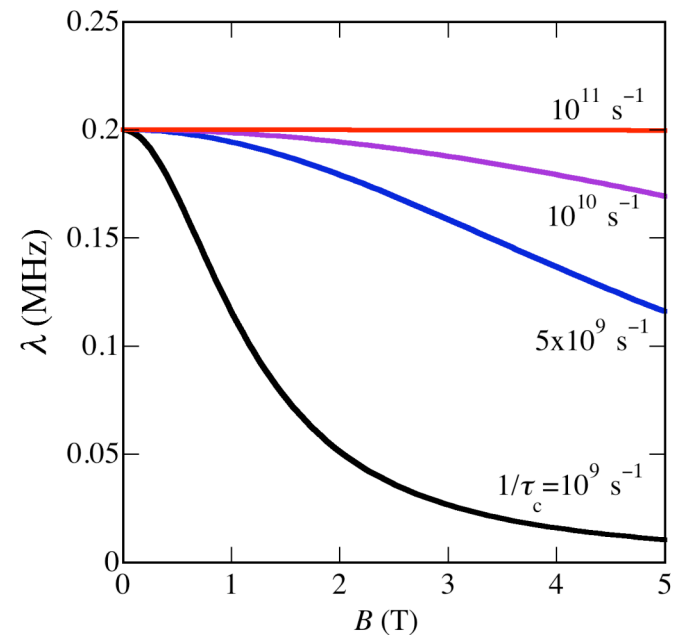


A unique “niche”  
between NMR and neutron

Spin relaxation rate:

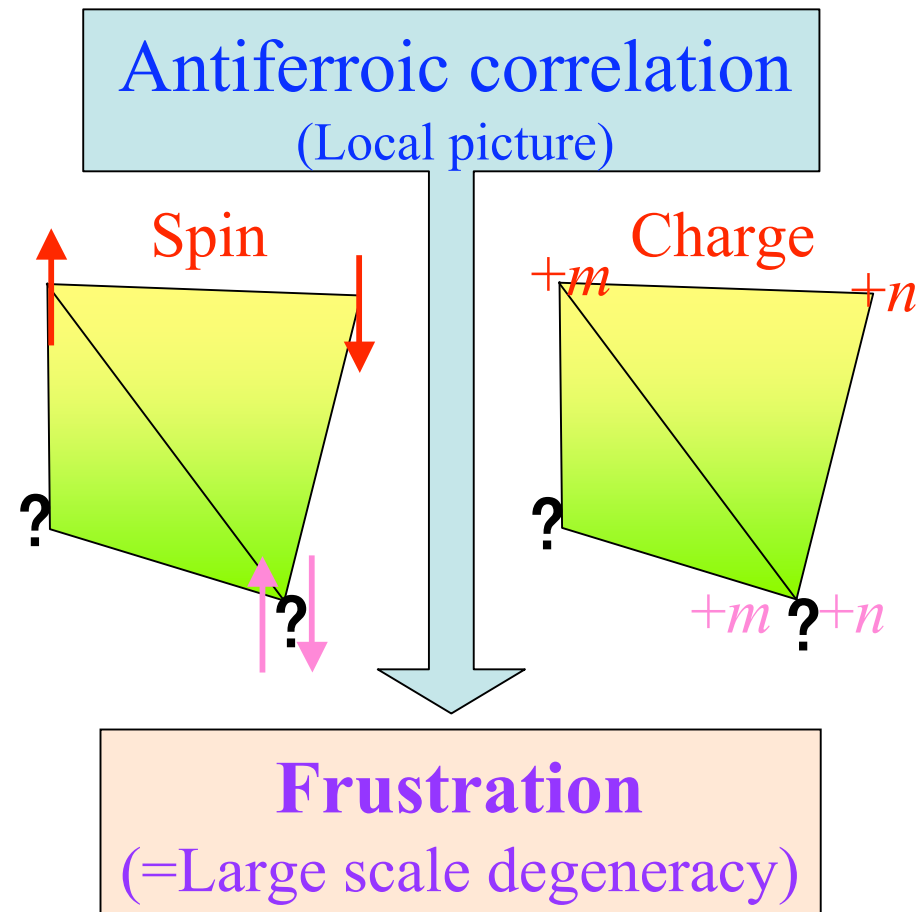
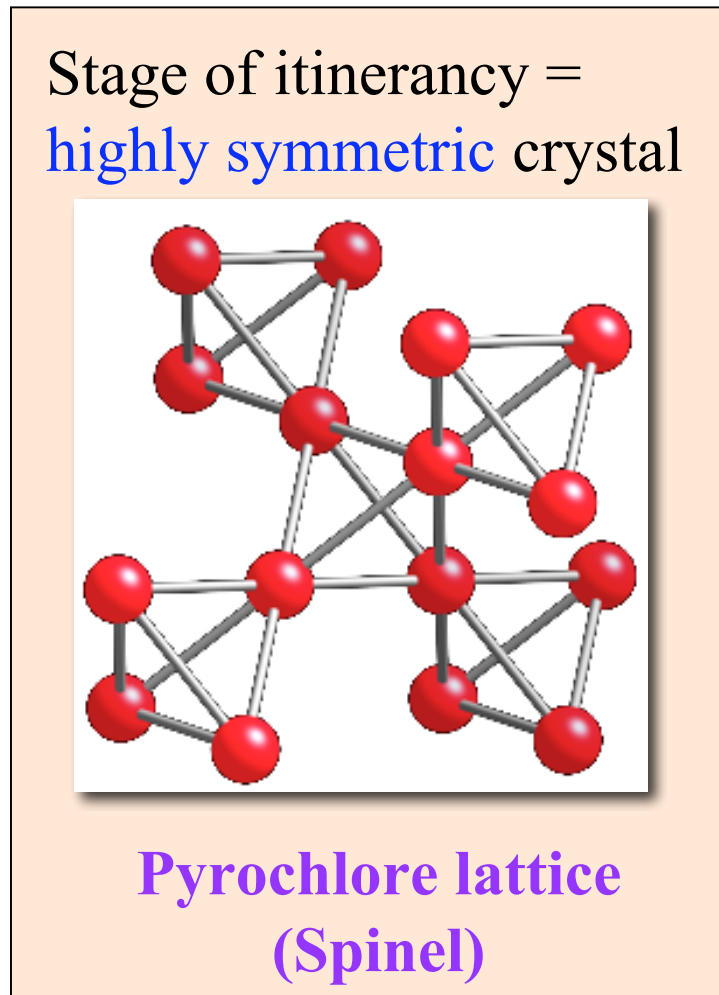
$$\lambda \approx \frac{2\delta^2\nu}{\omega_\mu^2 + \nu^2}$$

$$\nu = \frac{1}{\tau_c}, \quad \omega_\mu = \gamma_\mu B$$



# Issue: Geometrical Correlation of Itinerant Electrons

What would happen when frustration acts on metallic conduction?

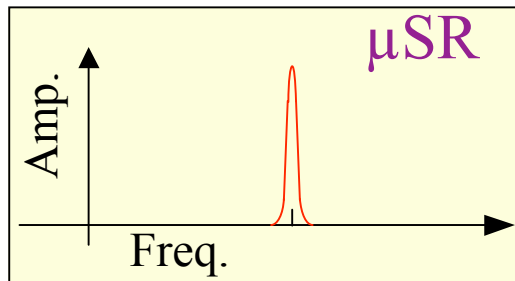
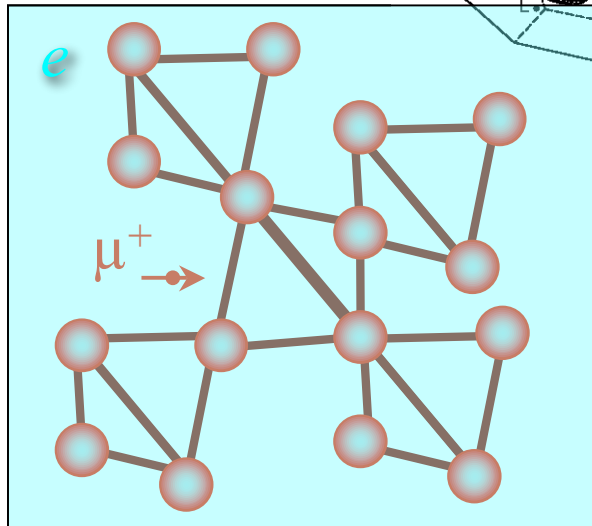
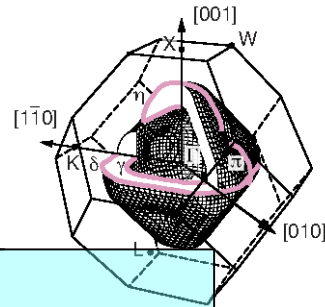


...so far extensively studied on local spin/charge systems.

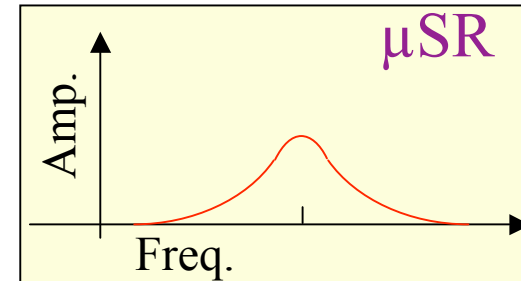
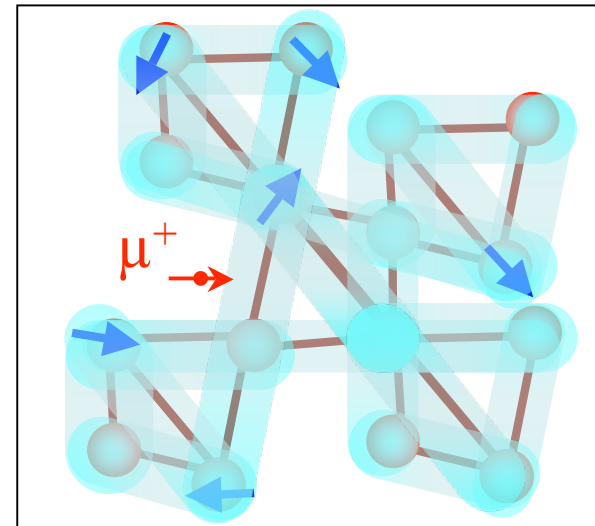
# Muon Spin Rotation ( $\mu$ SR): ...One of the most sensitive probes for frustration

## Electronic state of...

Normal metal  
...only reflecting  
crystal symmetry  
(Single electron)



Poor metal  
Geometrical Correlation  
...inhomogeneous spin/charge flow

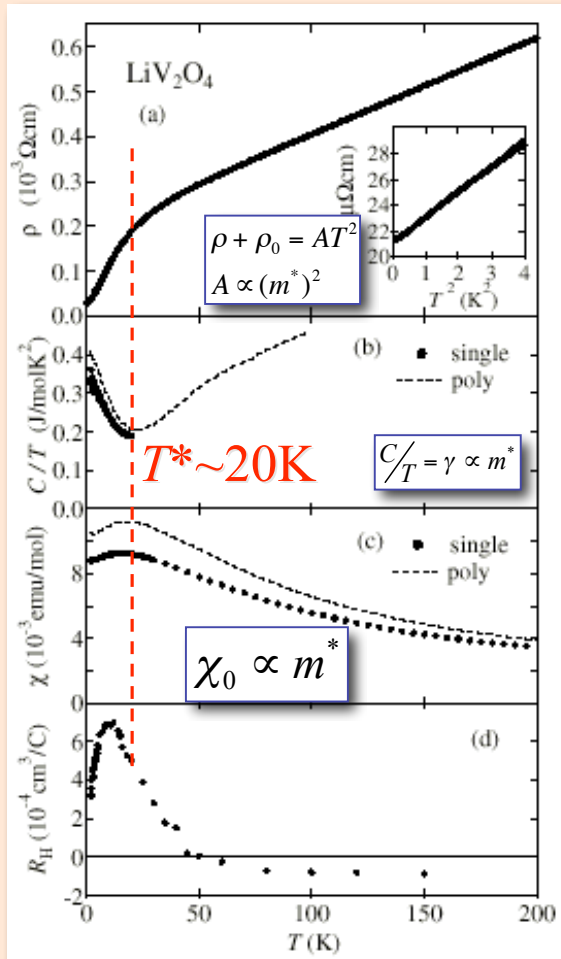


Example:

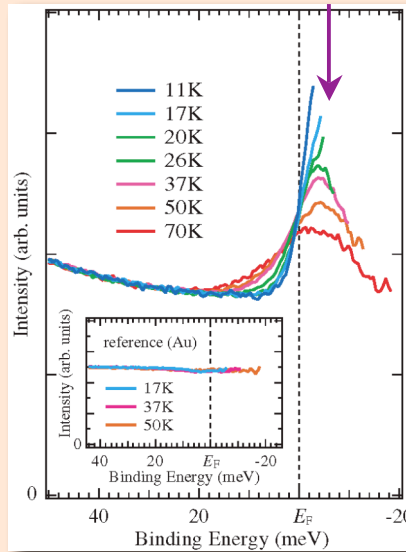
# “Heavy Fermion” State in Metallic Spinels

YMn<sub>2</sub>(‘89), **LiV<sub>2</sub>O<sub>4</sub>**(‘97)

LiV<sub>2</sub>O<sub>4</sub>



[*sc*-LiV<sub>2</sub>O<sub>4</sub>, Urano *et al.* '00]

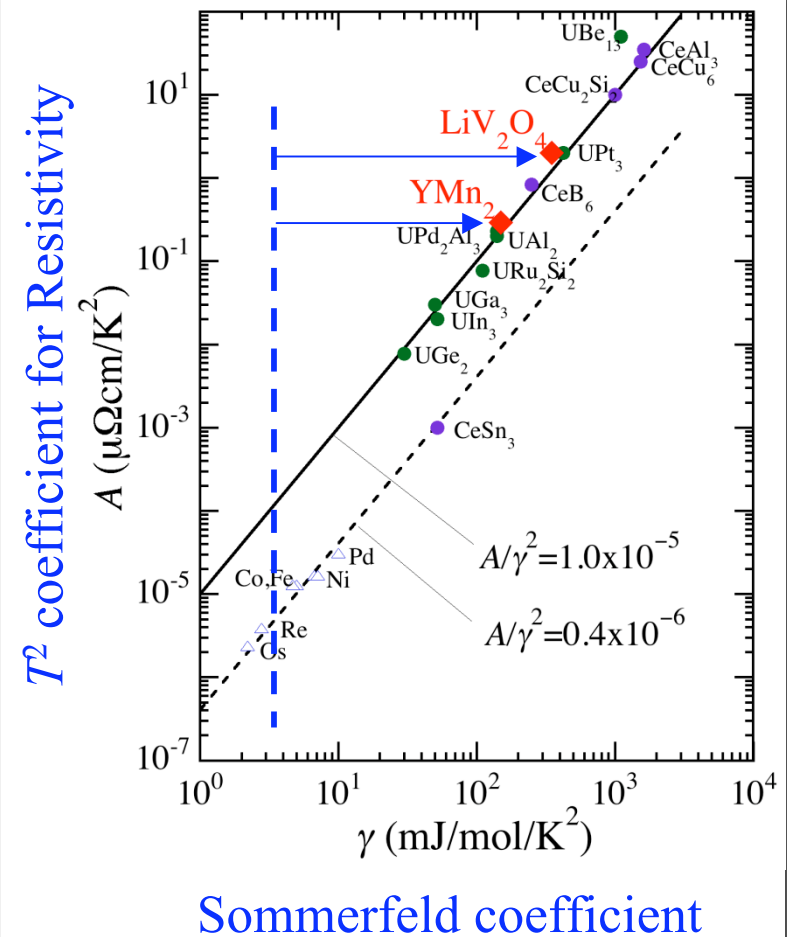


Quasiparticle peak in photo-emission spectra

[Shimoyamada *et al.* '06]

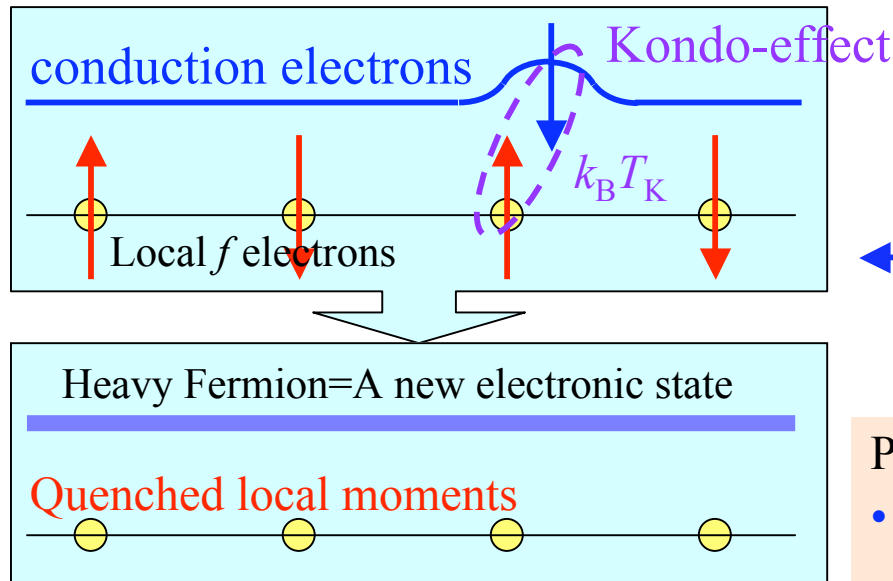
Mass enhancement  $\sim 10^2!$

(according to specific heat, etc.)

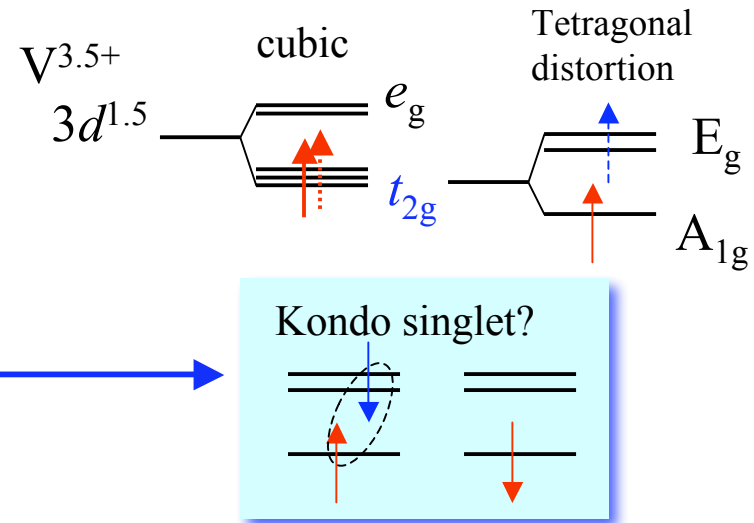
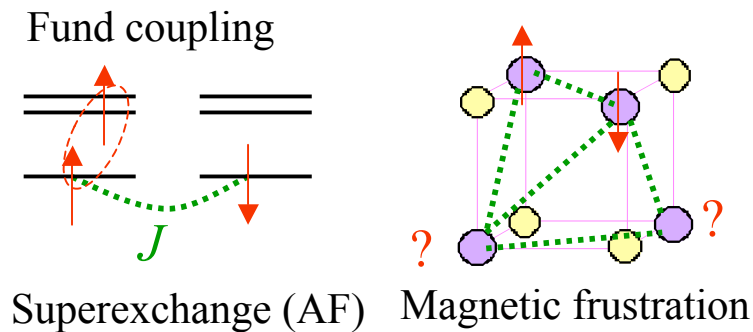


# LiV<sub>2</sub>O<sub>4</sub>: What is the origin of the HF-like behavior?

## • Conventional Heavy Fermion systems



...competing interactions



## Proposed Theoretical Models

### • Kondo scenario for $3d$ metals:

Anisimov *et al.*, PRL **83** (1999) 364.

### • Magnetic frustration:

Eyert *et al.*, Europhys. Lett. **46** (1999) 762.

### • Low-dimensional magnet:

Fulde *et al.*, Europhys.Lett. **54** (2001) 779.

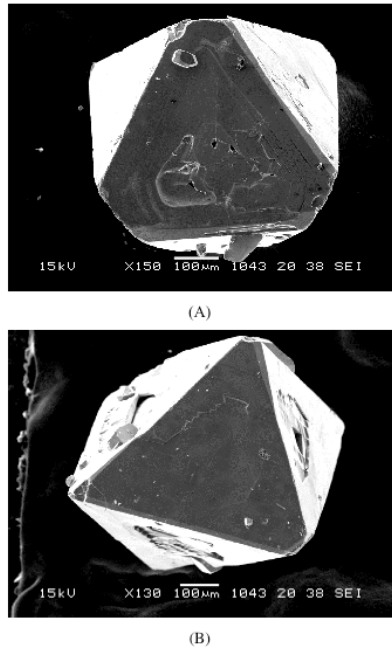
### • Proximity to Mott Insulator:

Arita *et al.*, PRL 98 (2007) 16402.

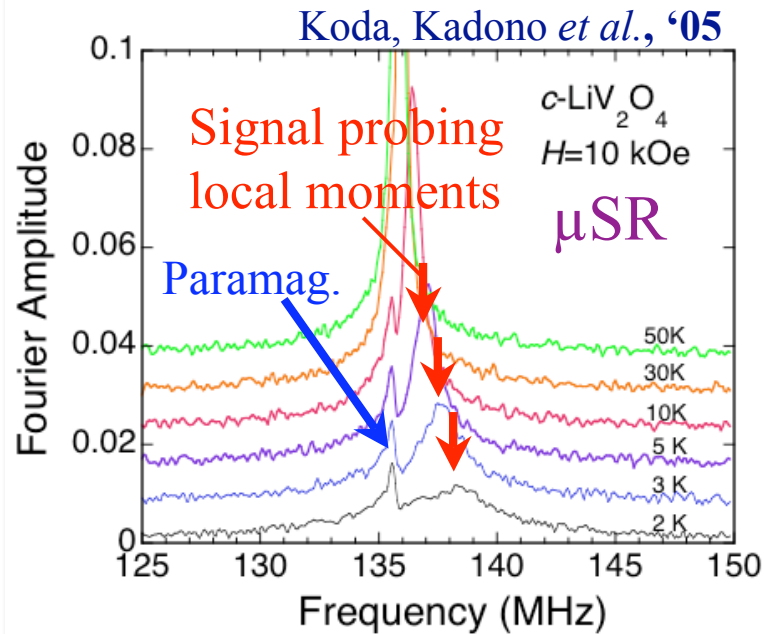
...



# LiV<sub>2</sub>O<sub>4</sub>: Local moments develop below $T^*$ ! ... $\mu$ SR



single-crystal  
(Matsushita *et al.*)  
~ 0.1g  
 $\mu$ SR measured at  
TRIUMF M15.



Analysis: Fits in time domain by

$$A_0 G_{xy}(t) = A_0 e^{-i\phi} \sum_i f_i \exp(i\omega_i t) \exp(-\Lambda_i t)$$

$A_0$ : instrumental asymmetry

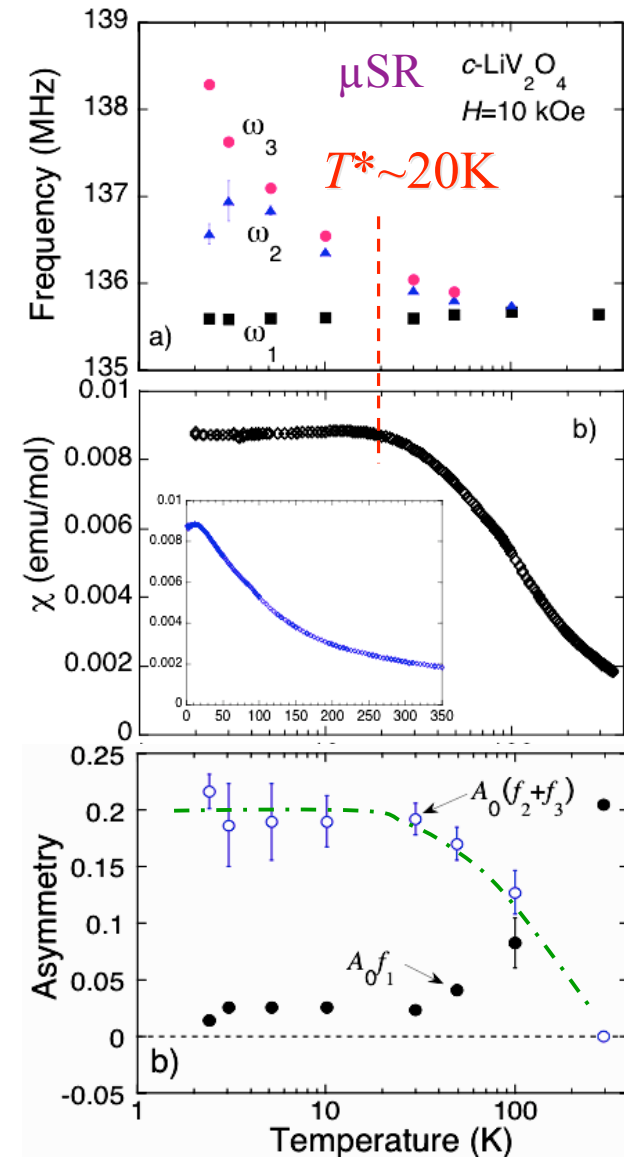
$e^{-i\phi}$ : initial phase

$f_i$ : fractional yield of  $i$ -th component

$\omega_i$ : precession frequency

$\Lambda_i$ : relaxation rate

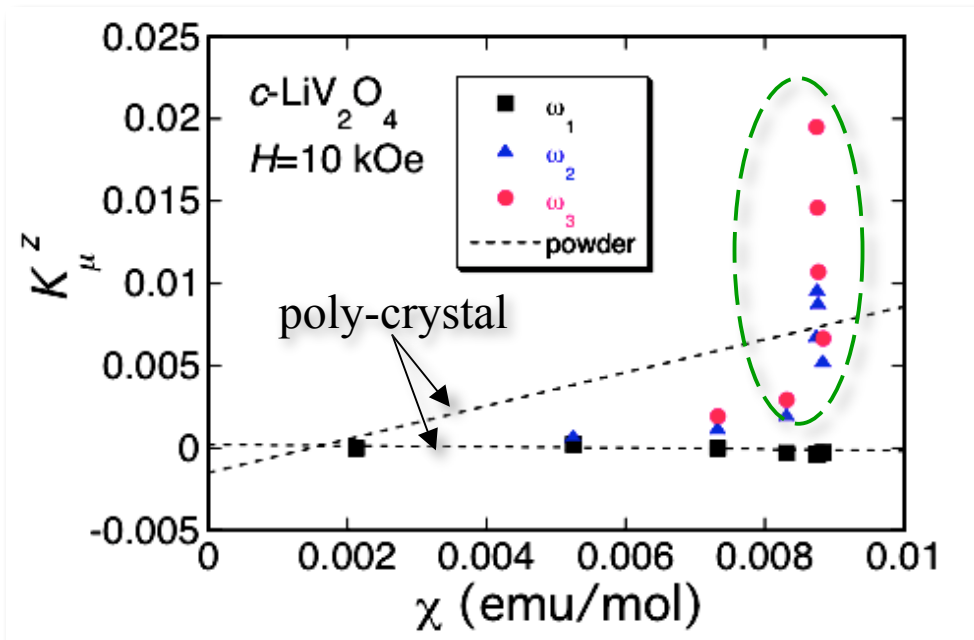
...three components ( $i=1-3$ ) are  
enough to reproduce data.



# LiV<sub>2</sub>O<sub>4</sub>: Local inhomogeneity probed by $\mu^+$ Knight shift

$K$ - $\chi$  plot:

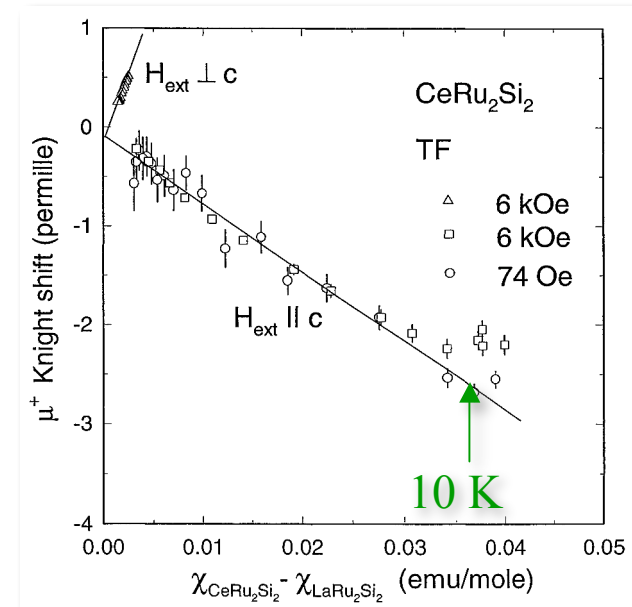
The Knight shift vs bulk susceptibility  
...must be linear in normal metals.



↑ The broad lines exhibit highly non-linear behavior below  $\sim T^*$ .

A broad distribution of hyperfine parameter  
 $A_\mu \sim 6 \pm 3 \text{ kOe}/\mu_B$

cf. Typical example of HF metal:  
CeRu<sub>2</sub>Si<sub>2</sub> ( $T_K \sim 10\text{-}20 \text{ K}$ )

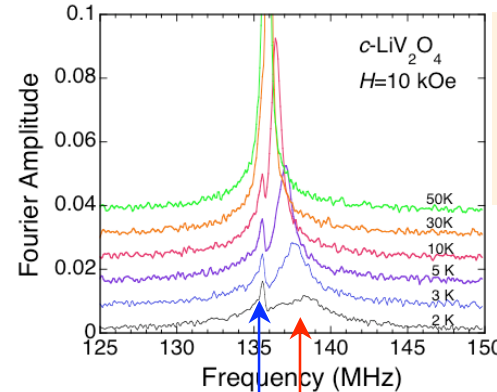


↑ no such anomaly  
(homogeneous metal)

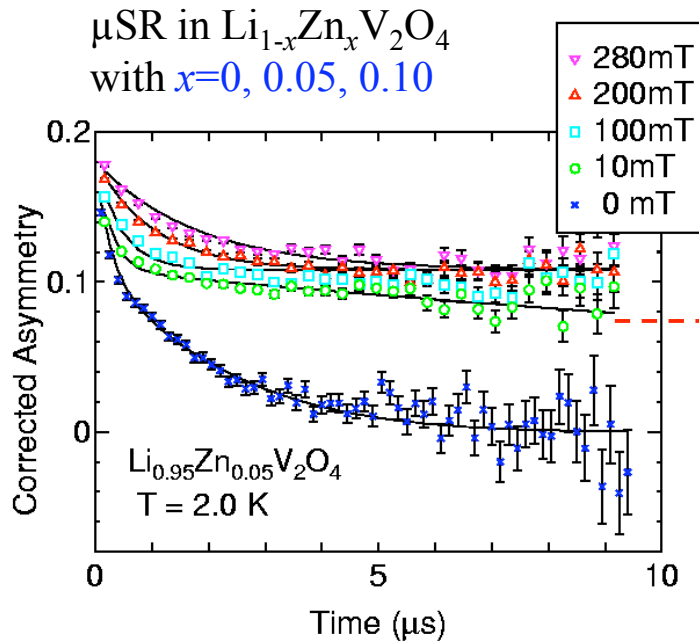
# LiV<sub>2</sub>O<sub>4</sub>: Spin fluctuation probed by LF-μSR

Spin-lattice relaxation: response to a longitudinal field (LF)

↓ There are two components with their fluctuation rate much different with each other as inferred from the response to LF.

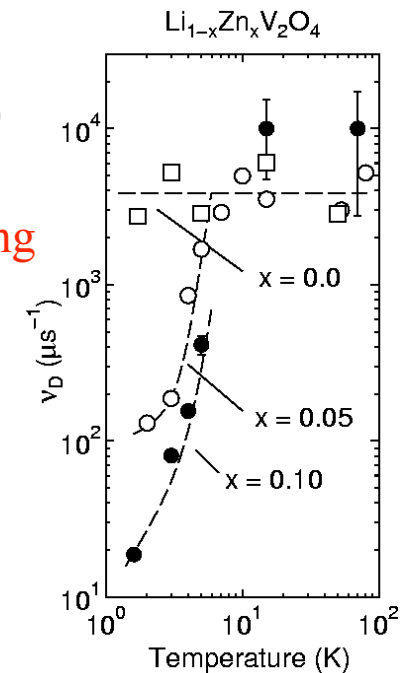
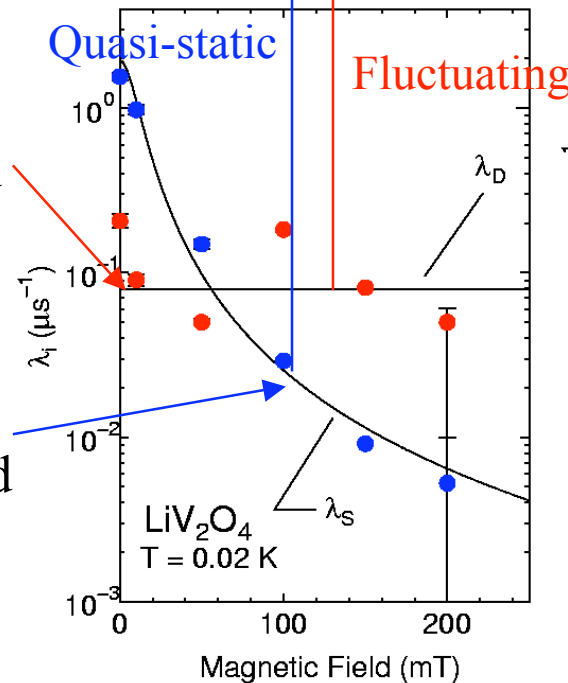


...corresponding to the components observed in TF.



Koda, Kadono *et al.*, '04

...hardly quenched  
↑  
...easily quenched



...fluctuation is suppressed for  $x > 0$  at low  $T$ .

# LiV<sub>2</sub>O<sub>4</sub>: The ground state suggested from $\mu$ SR

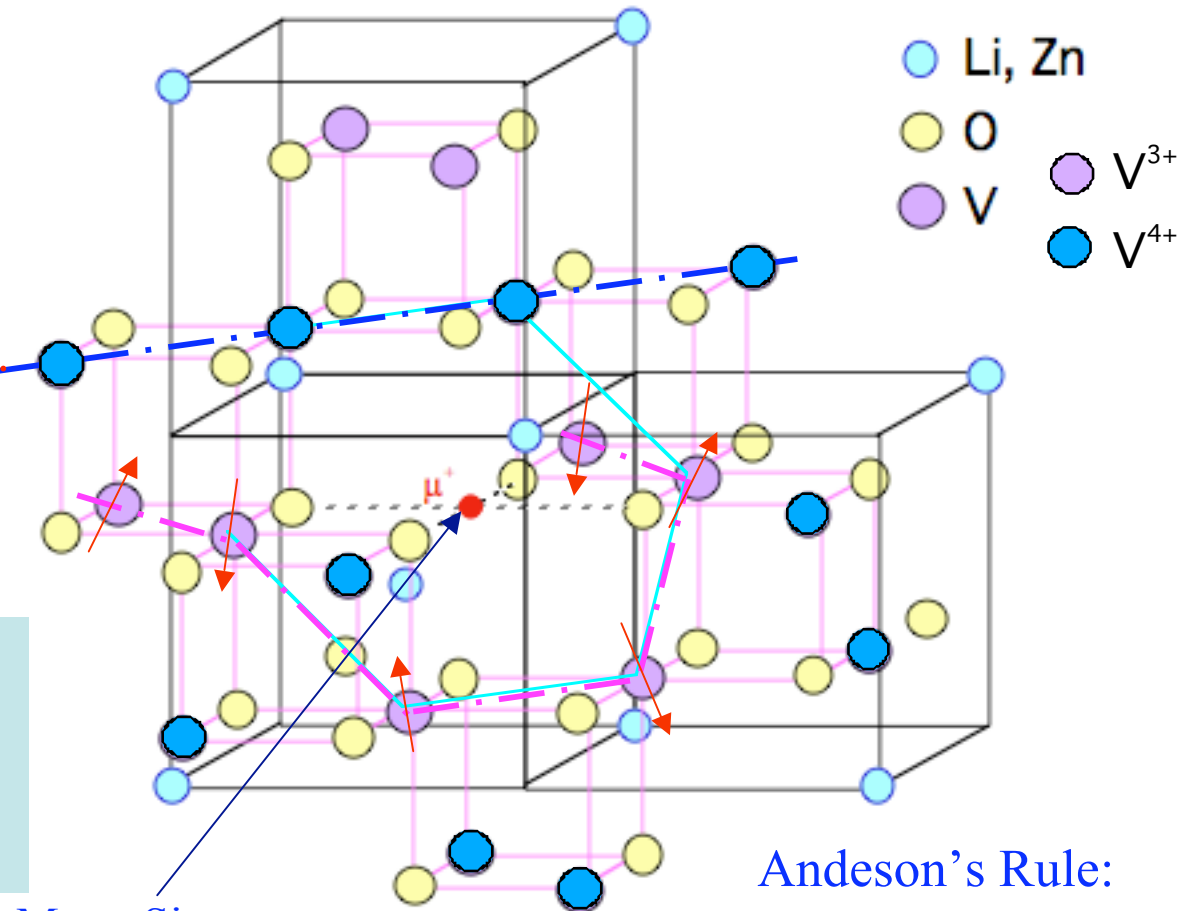
Two kinds of signals in  $\mu$ SR suggests development of  
 (a) weakly magnetic ( $\sim$ or non-magnetic) state, and  
 (b) **inhomogeneous paramagnetic state fluctuating over a frequency range of  $\nu \sim 10^6$ - $10^9$ /s.**

$\nu < k_B T^* \sim 10^{11}$ /s  
 ...not like Kondo fluctuation

One possibility:  
 quasi-1D chain correlations for V<sup>3+</sup> (S=1, Haldane?) and V<sup>4+</sup> (S=1/2, Heisenberg) ions,

[...a model suggested by Fulde *et al.*, '01]

...A snap shot



**Muon Site:**  
 ...Center of O-octahedron, with  
 six V ions forming a hexagon ring.

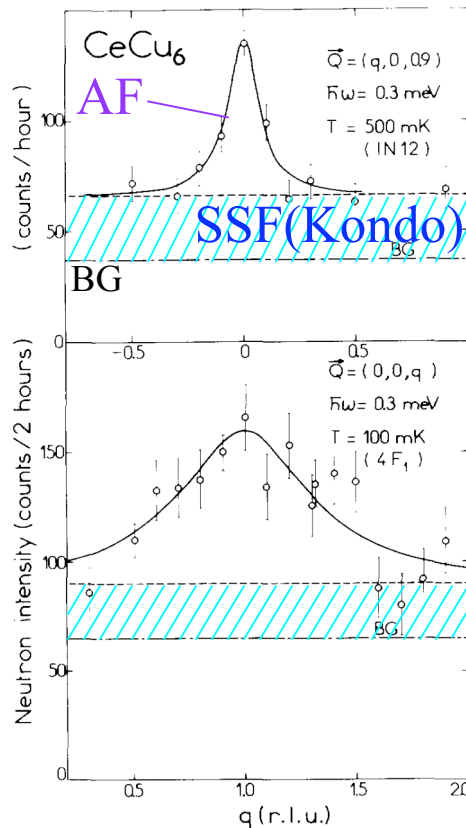
**Anderson's Rule:**  
 Each tetrahedron is  
 occupied by two  
 V<sup>3+</sup> and V<sup>4+</sup> ions.

# LiV<sub>2</sub>O<sub>4</sub>: Inelastic Neutron Scattering ( $T < T^*$ )

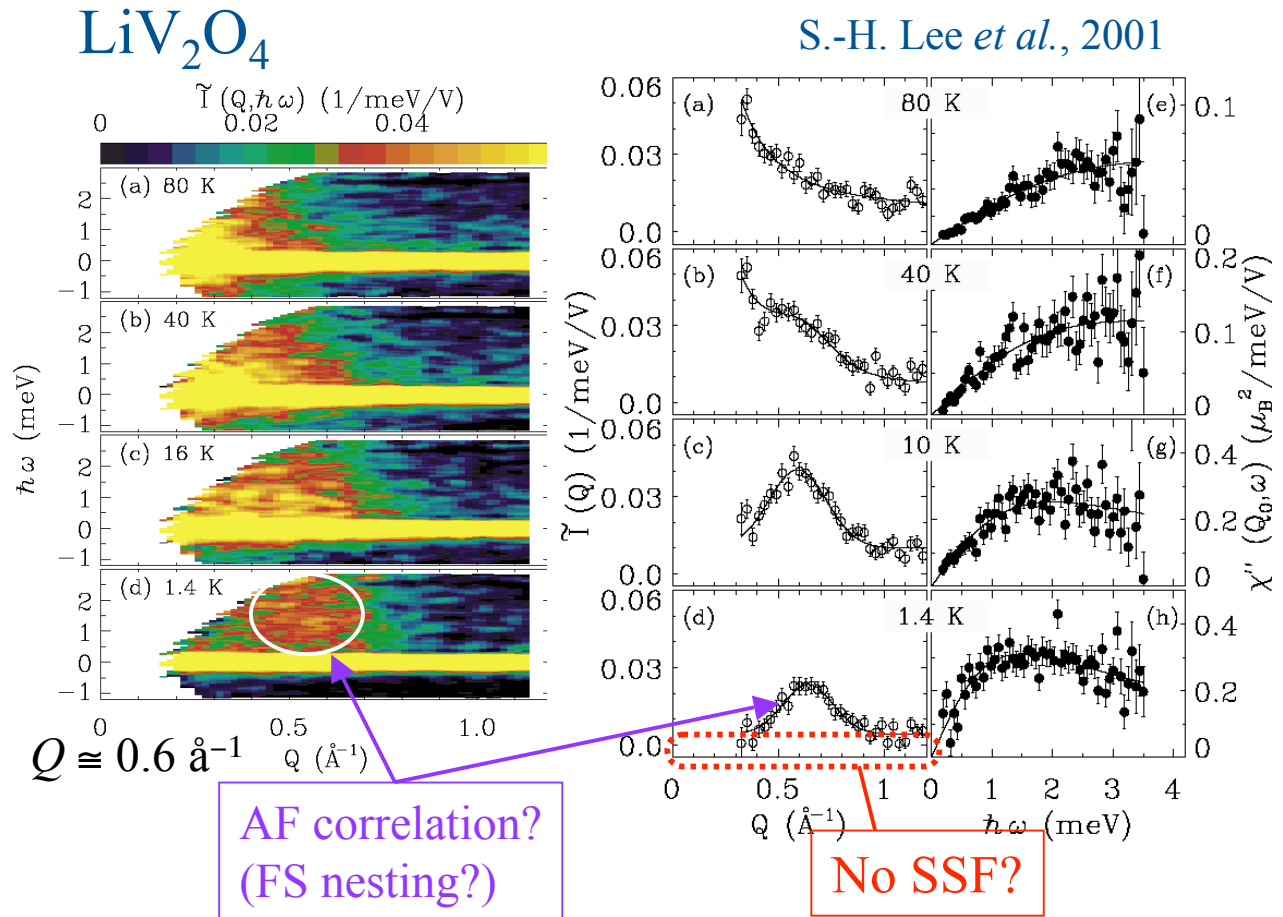
Antiferromagnetic correlation vs single-site fluctuation (SSF)

SSF...due to the Kondo coupling to conduction electrons

HF-system



$$k_B T_K \sim 10^0 \text{ meV} (\sim 10^{11}/\text{s})$$

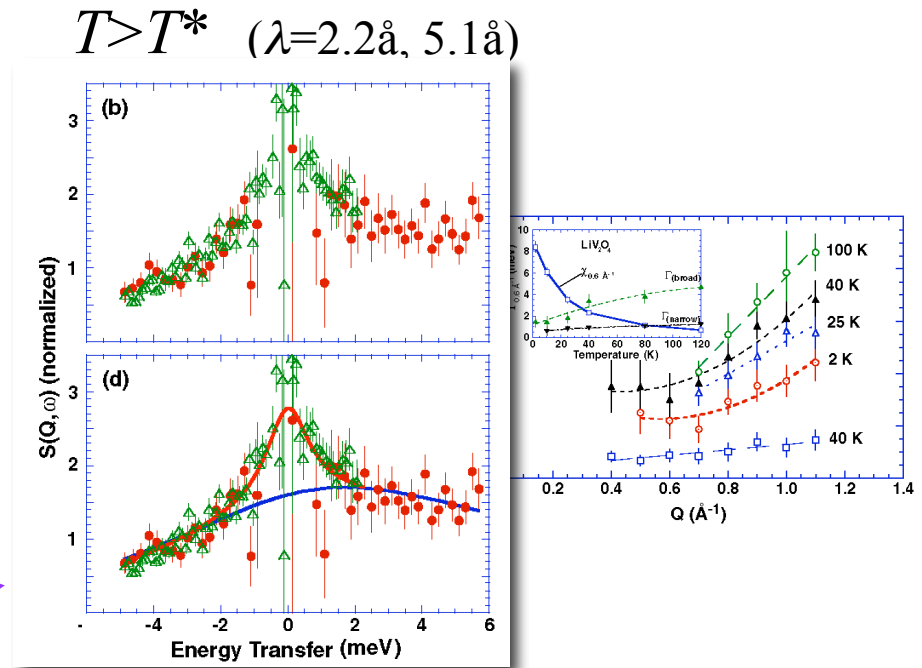
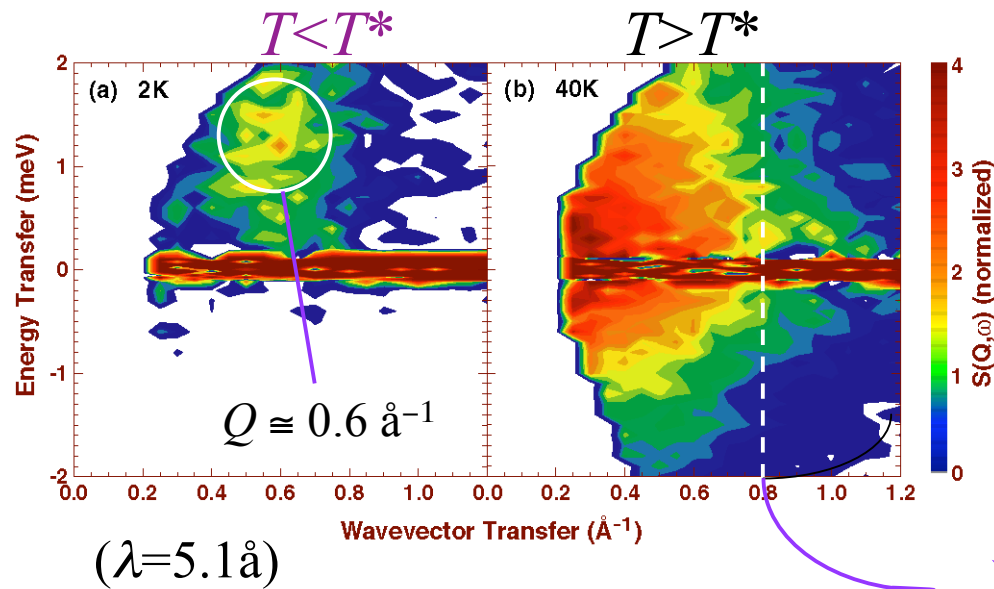


(NB: phonon parts subtracted using LiTi<sub>2</sub>O<sub>4</sub> data)

# LiV<sub>2</sub>O<sub>4</sub>: Inelastic Neutron Scattering ( $T > T^*$ )

Paramagnetic response: observation of two components

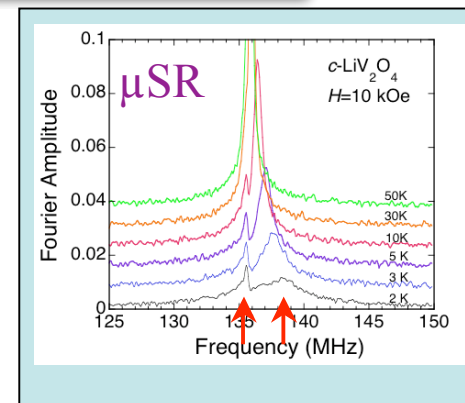
A. P. Murani *et al.*, 2004



Imaginary part of  $\chi$  for “spin glass”

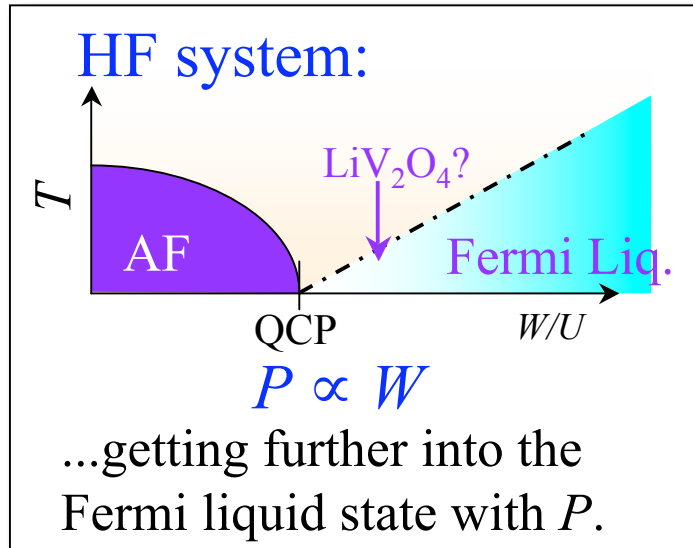
$$\chi''(Q, \omega) = \omega \sum_i \frac{\chi_i^Q \Gamma_i^Q}{(\Gamma_i^Q)^2 + \omega^2}$$

$i=2$  seems to be needed to reproduce data. → ...in good accord with  $\mu$ SR.



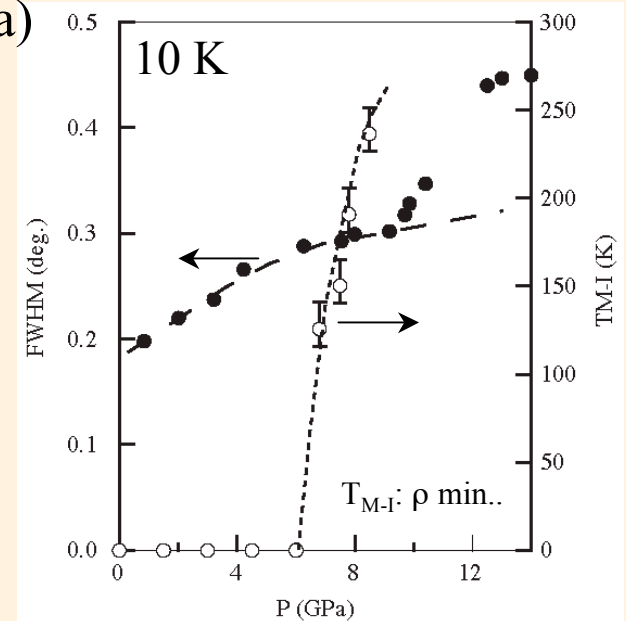
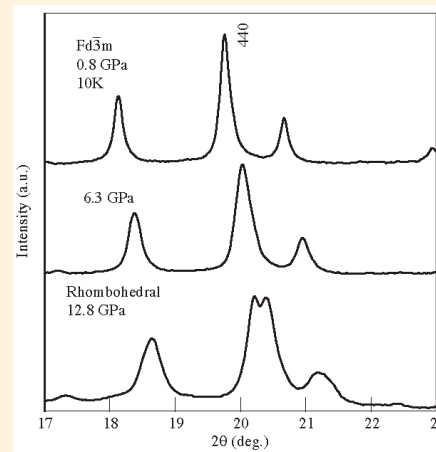
# LiV<sub>2</sub>O<sub>4</sub>: A New Class of Metal?

## Implications from other experiments: Effect of Pressure



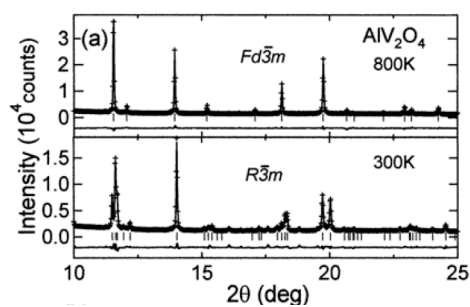
LiV<sub>2</sub>O<sub>4</sub>:  $P$ -induced MI transition and reduction of symmetry ( $P > 10$  GPa)

$Fd\bar{3}m \rightarrow R\bar{3}m$

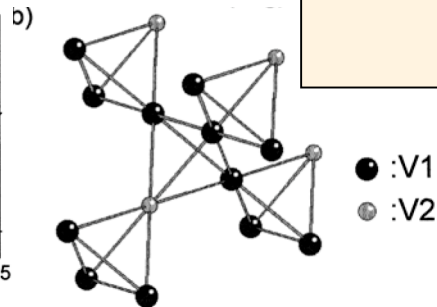


...not like a canonical HF system

cf. Charge order in AlV<sub>2</sub>O<sub>4</sub>



$Fd\bar{3}m \rightarrow R\bar{3}m$

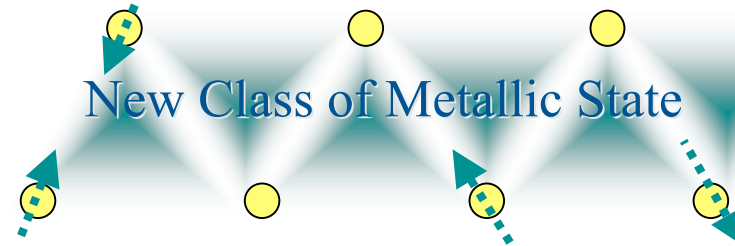


$V^{2.5+} \rightarrow V^{2.5 \pm \delta}$

Matsuo *et al.*, 01

Geometrical Correlation

New Class of Metallic State

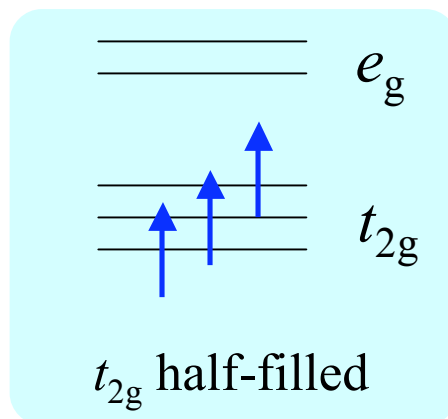


# Geometrical correlation: Other pyrochlore examples

Problem for  $A_2B_2O_7$ : Structural and associated MI transition

Q: How to preserve cubic symmetry?

A: Let the  $t_{2g}$  band half-filled (no orbital degeneracy).



Structural phase transition is suppressed by the lack of OD.

$Ru^{5+}$  ( $4d^3$ )  $S=3/2$

$Hg_2Ru_2O_7$  (MIT)

$Cd_2Ru_2O_7$  (CDW?)

$Ca_2Ru_2O_7$  (Metal?)

Ion Radius

$Ru^{5+} < Os^{5+}$

$Cd^{2+} < Ca^{2+} < Hg^{2+}$

$Os^{5+}$  ( $5d^3$ )  $S=3/2$

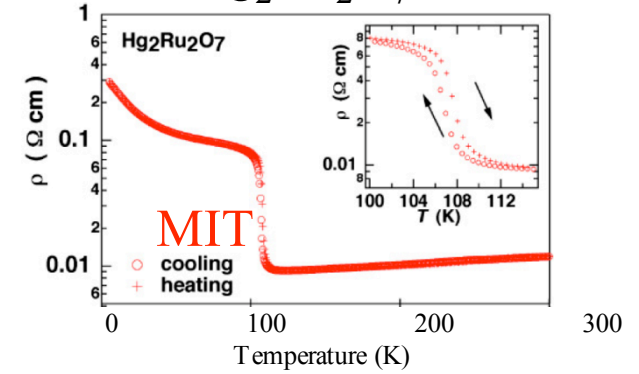
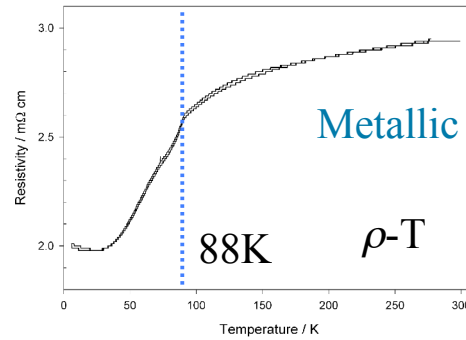
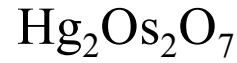
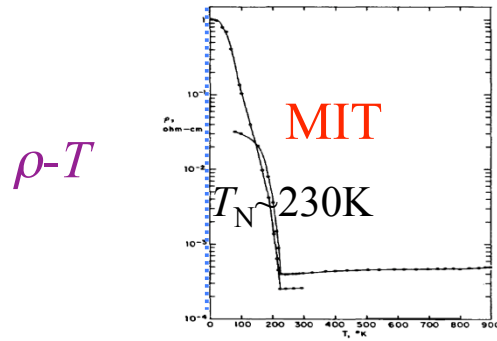
$Cd_2Os_2O_7$  (MIT)

$Hg_2Os_2O_7$  (Metal)

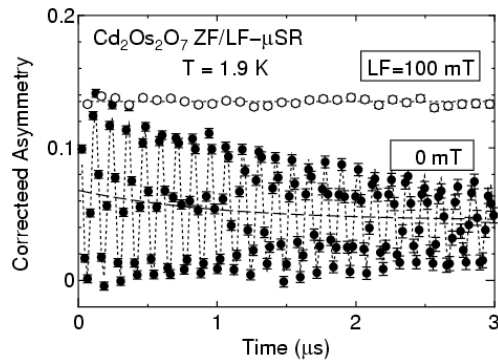
...It seems not trivial to obtain high quality specimens (some of them requires high pressure for synthesis).



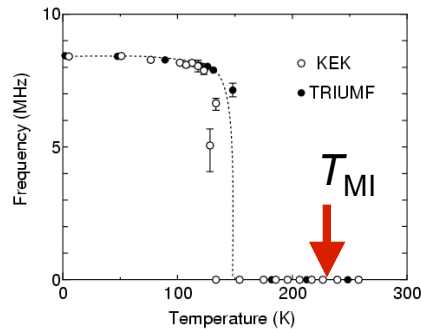
# Geometrical correlation: Other pyrochlore examples



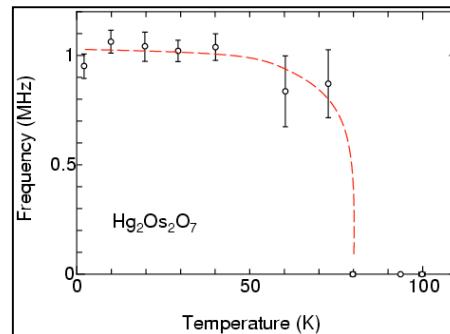
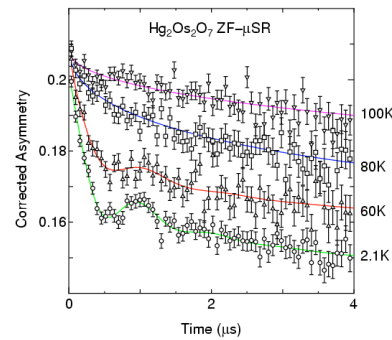
A.Koda *et al.*, '07



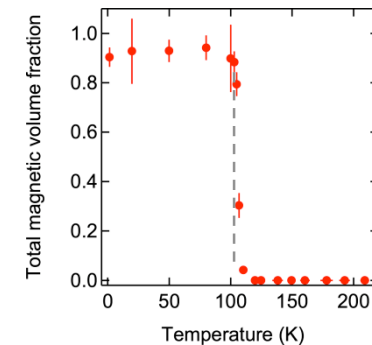
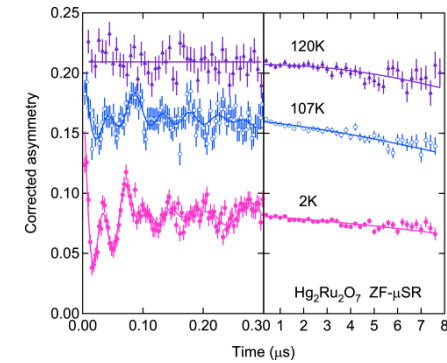
$\mu$ SR



A.Koda *et al.*, '06

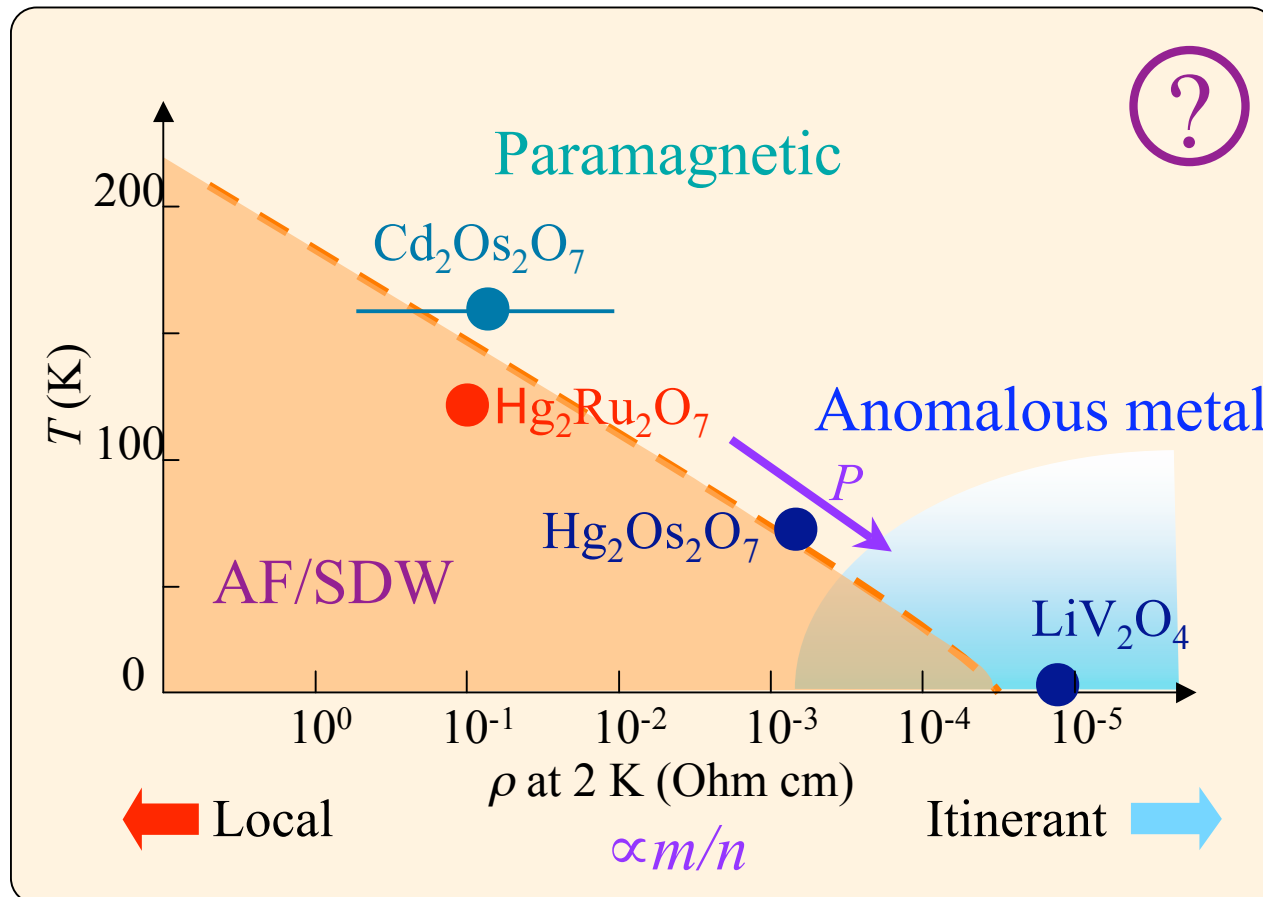


K.H. Satoh *et al.*, '08



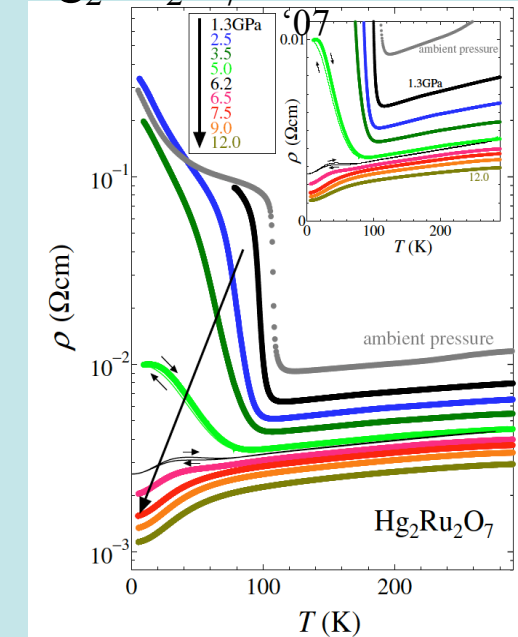
# Geometrical correlation: Other pyrochlore examples

“Metal”ness vs Frustration



Heavy Fermion state

$\text{Hg}_2\text{Ru}_2\text{O}_7$  Takeshita *et al.*,

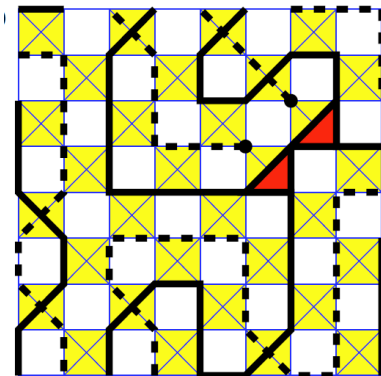
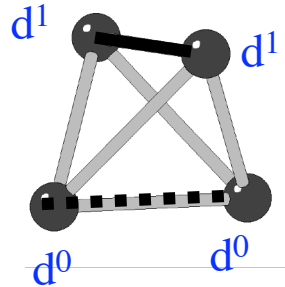


...suppression of MI transition (by pressure) leads to HF-like behavior similar to  $\text{LiV}_2\text{O}_4$ .

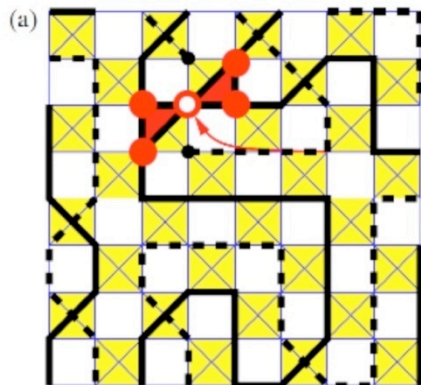
# Geometrical correlation: Other pyrochlore examples

## Other exotic ground states:

### Fractional Charge State

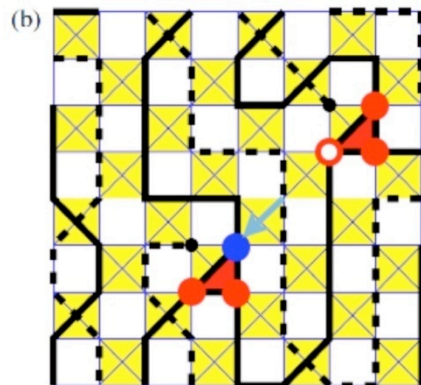


Distribute charges according to the Anderson's rule....then put one electron into the lattice:



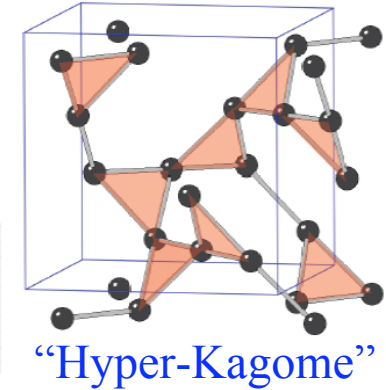
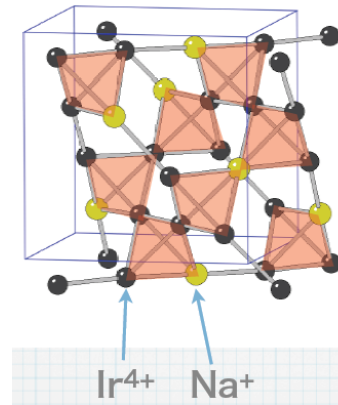
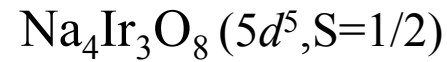
Migration of a doped electron:

(Fulde *et al.*, '02)

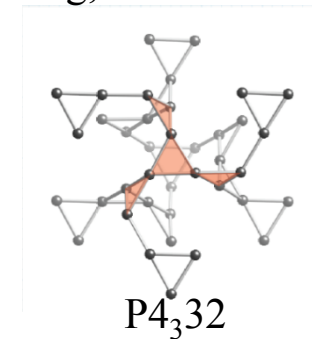
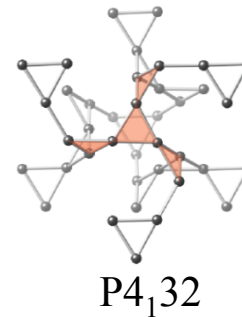


Migration of host electron:  
5 electrons split into  
effectively 2.5 e charges.

### Chiral metal



...If one can get it carrier-doped, and even get superconducting, then...



Exotic superconductivity due to the lack of inversion symmetry?

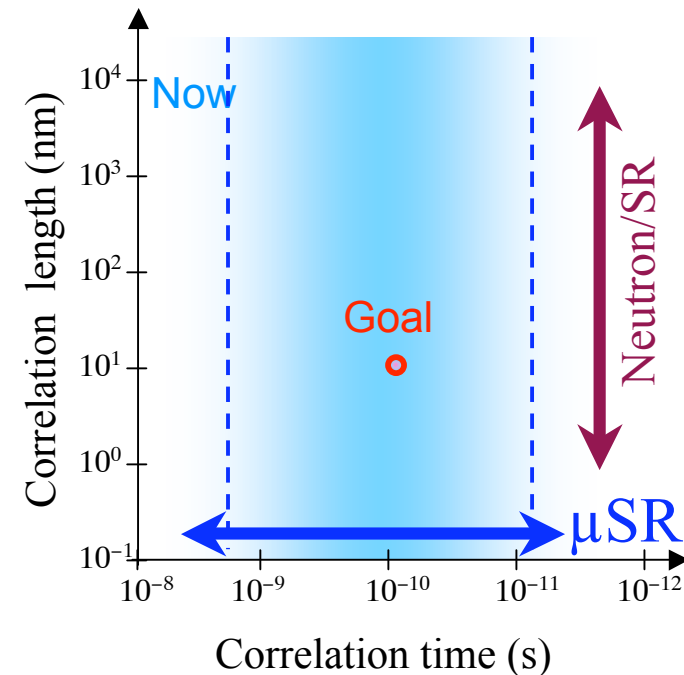
(Nohara)

# Summary

- Geometrically antiferroic correlation (GAC) between electrons conducting on highly symmetric orbits might give rise to **new class of metallic state**, where the HF behavior in cubic spinels/pyrochlores might be one such manifestation.
- Both  $\mu$ SR, neutron scattering, and SR should work together to elucidate the microscopic details of the new metallic ground state observed in cubic spinels/pyrochlores.
- Now it seems that time is mature to launch an in-depth studies of GAC in combination with a systematic and large-scale search for new candidates for “frustrated metals”.

## Our Goal:

...to pin down the characteristic scales of time/length with unprecedented precision.



# Collaborators (past, present, and future):

## Material synthesis

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JAEA-ASRC

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