# Exotic Metals from Geometrical Frustration

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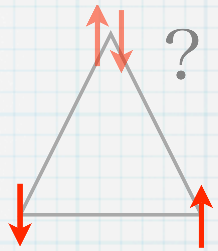
Department of Physics, Okayama University

# Topics




## (1) Pseudogap Metal in $LiVS_2$

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JAEA

## (2) High-Entropy Metal in $CuRhO_2$

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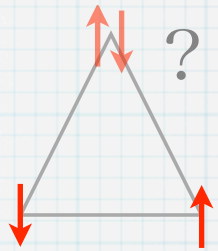


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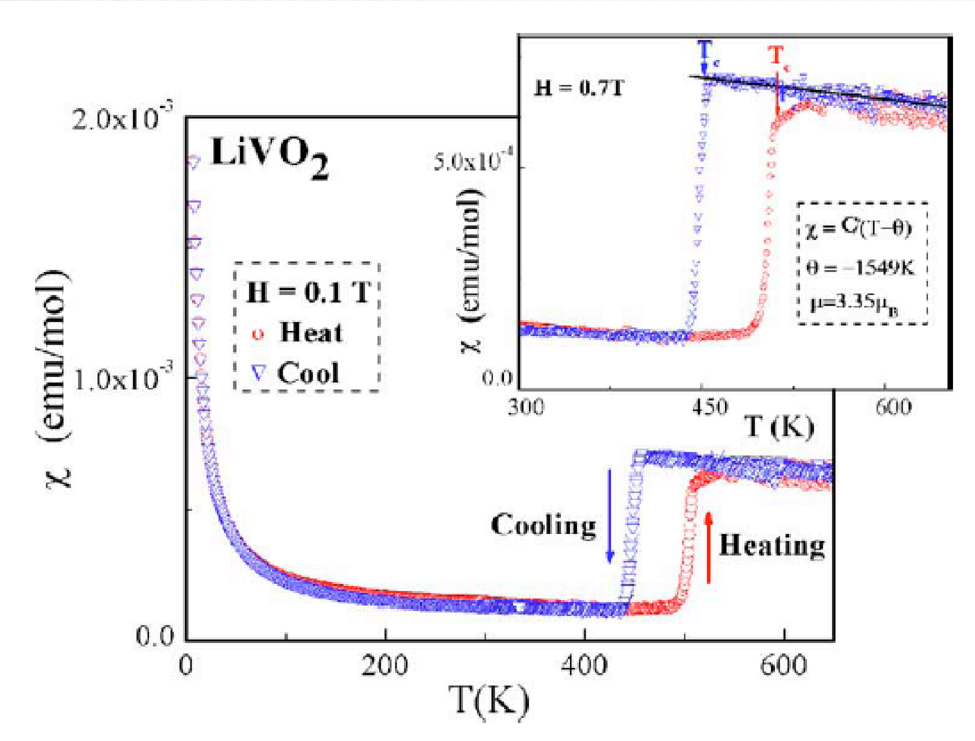
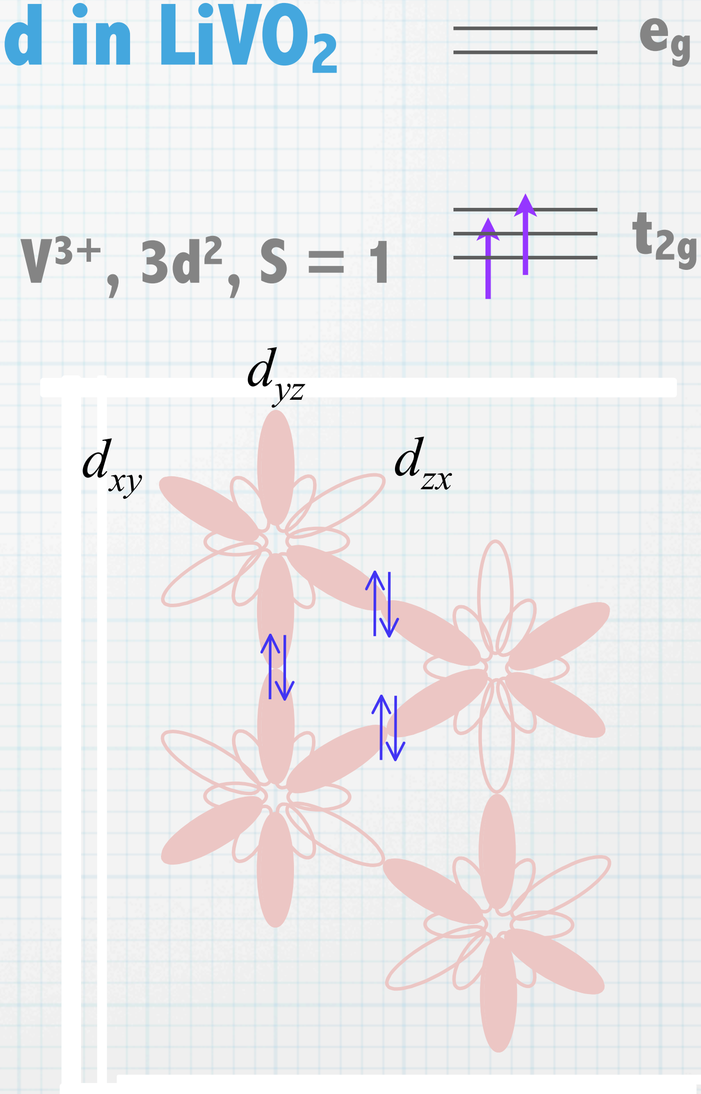
# Valence Bond Solid in $LiVO_2$




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

Weiss T = - 1500 K (AF), indicating strong frustration.

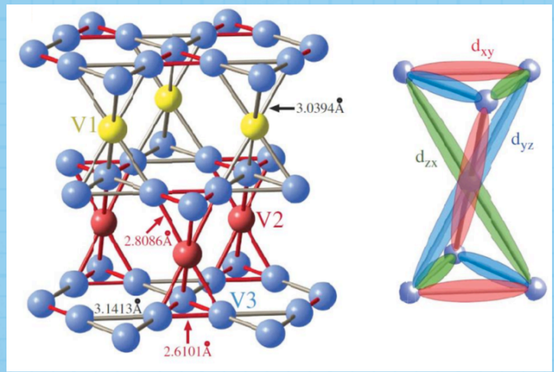
1st order transition from CW insulator to non-magnetic insulator at ~ 500 K.



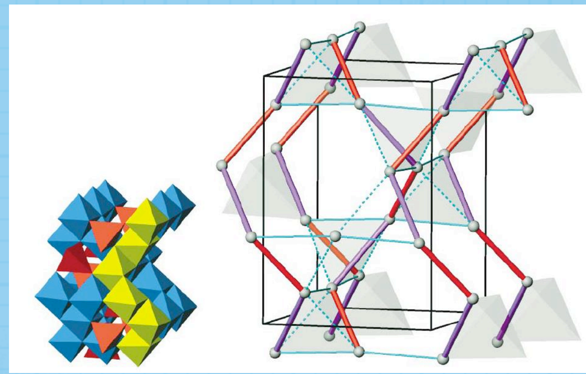

Vanadium trimers

# Valence Bond Solids are ubiquitous

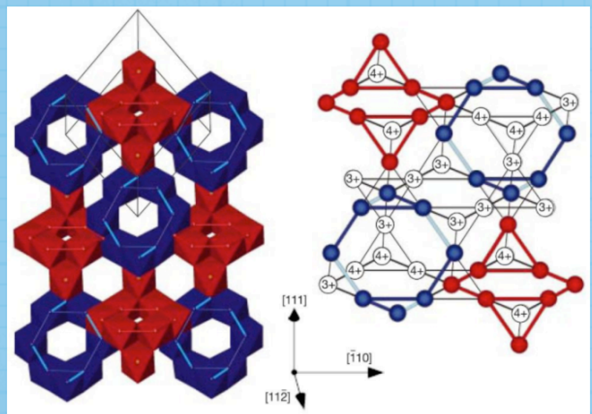
## Pyrochlore Lattice




heptmer in $AlV_2O_4$

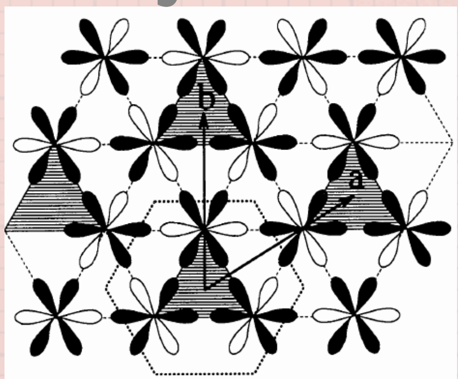


Helical dimer in $MgTi_2O_4$




Octermer in $CuIr_2S_4$

## Triangular Lattice

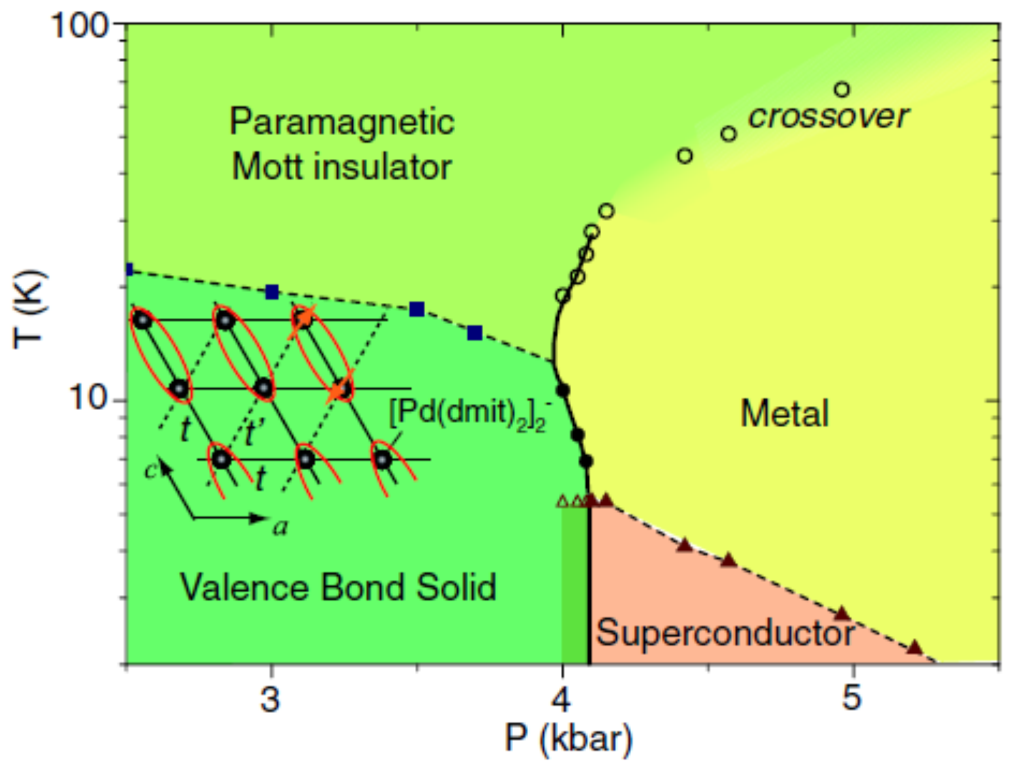



$$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

Trimer in $LiVO_2$

# What kind of metal do we expect if VBS melts ?

$EtMe_3P[Pd(dmit)_2]_2$



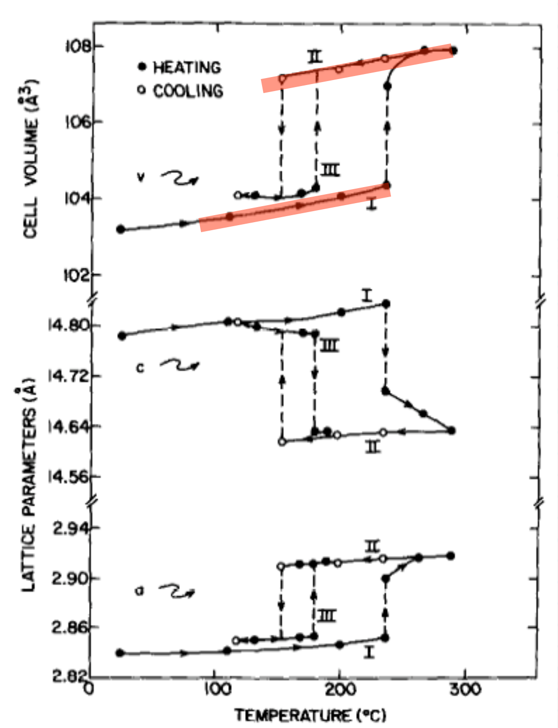

Shimizu *et al*., PRL **99**, 256403 (2007).

**In organic systems, BVS melts under pressure and superconductivity emerges.**

**Spin singlet in real space turns into spin singlet in k-space.**

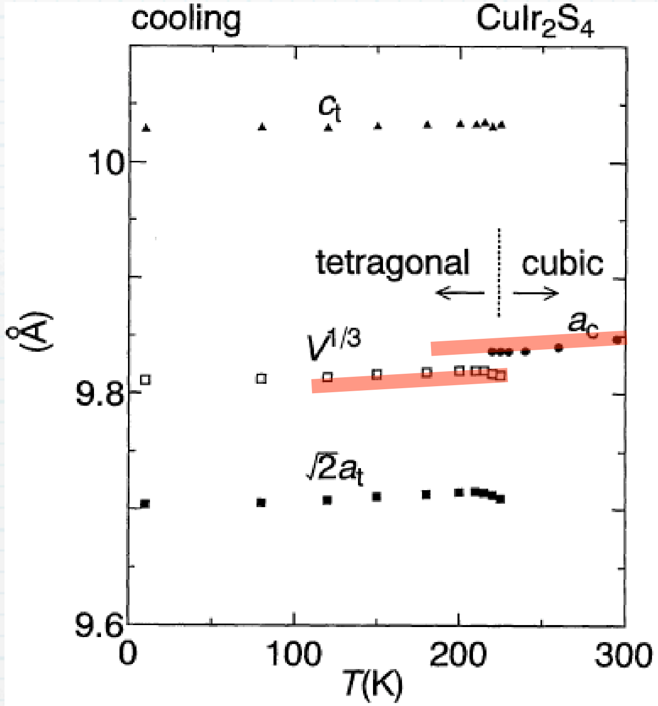
# Inorganic Systems: VBS is stabilized by Pressure

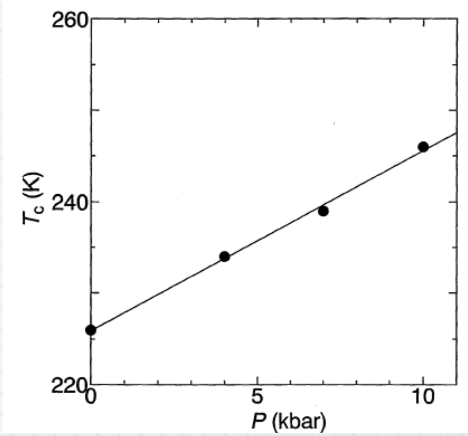
Trimer in $Li_{0.8}VO_2$




Cardoso *et al*., J. Solid State Chem. **72**, 234 (1988).

Octermer in $CuIr_2S_4$



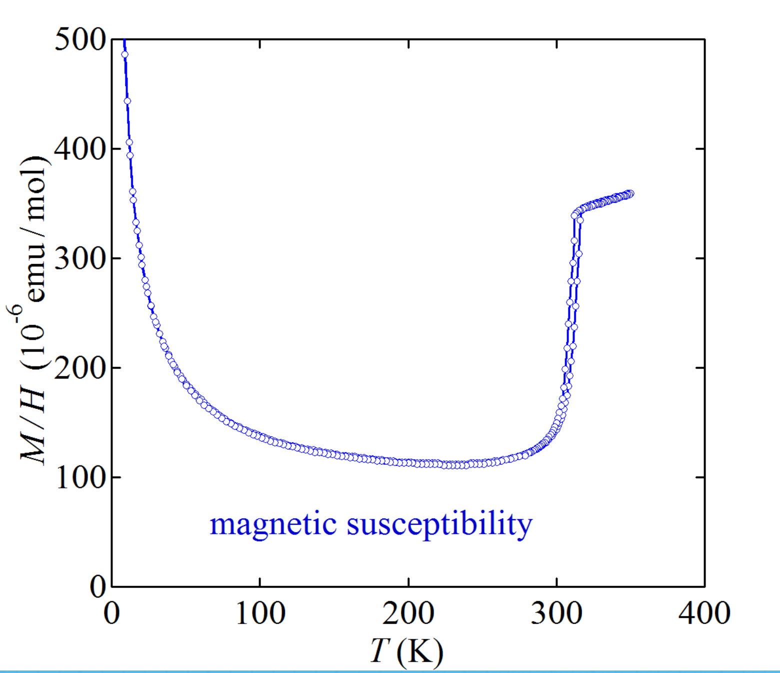




Furubayashi *et al*., JPSJ **63**, 3333 (1994).

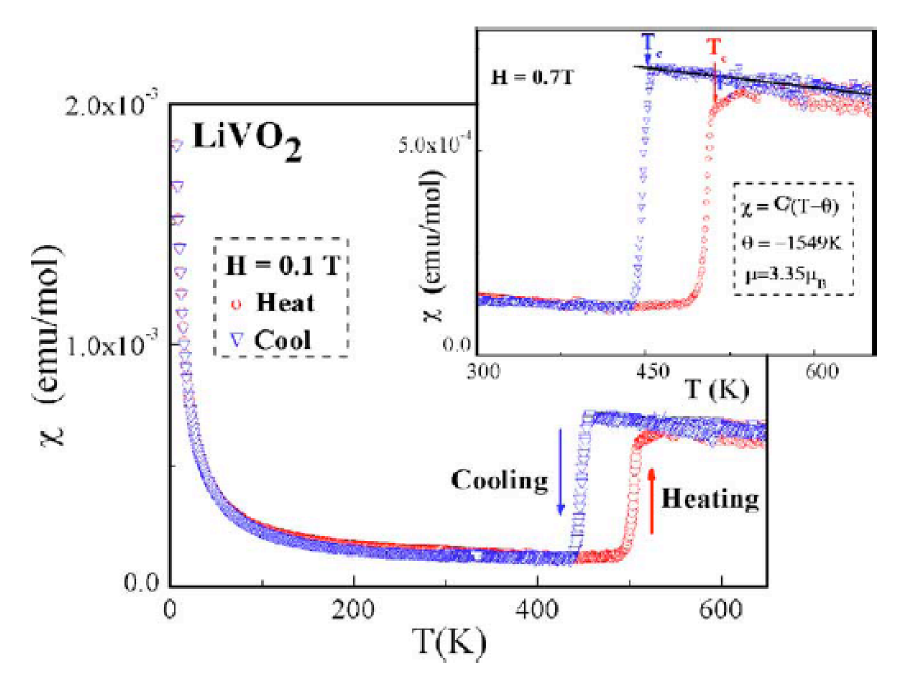
**Cell volume decreases at the VBS transition.**

# Negative pressure by chemical substitution

LiVS$_2$




LiVO$_2$

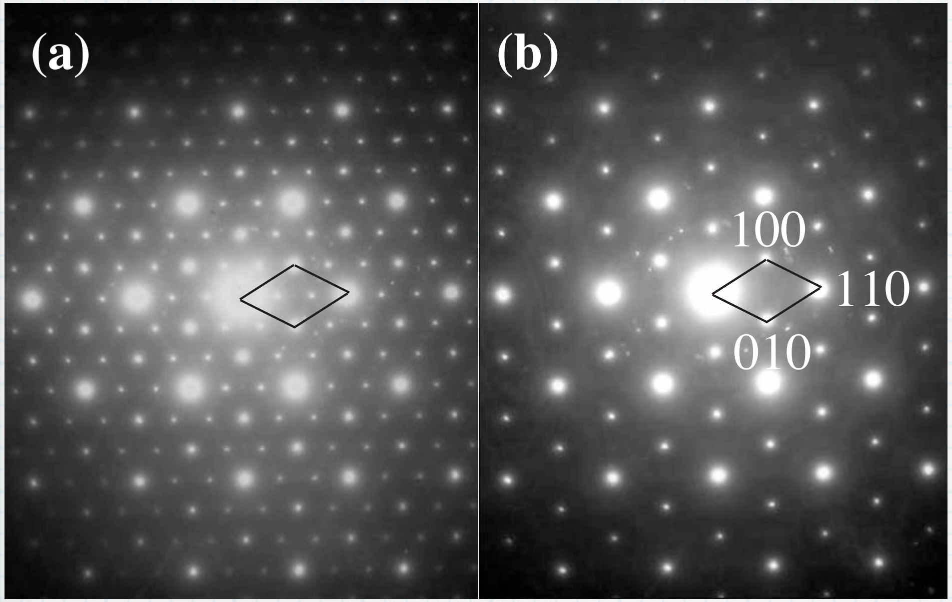



W. Tian *et al.*, Mater. Res. Bull. **39** (2004) 1319 .

**Transition Temperature is reduced by replacing O to S.**

# Trimer at low temperatures in $LiVS_2$

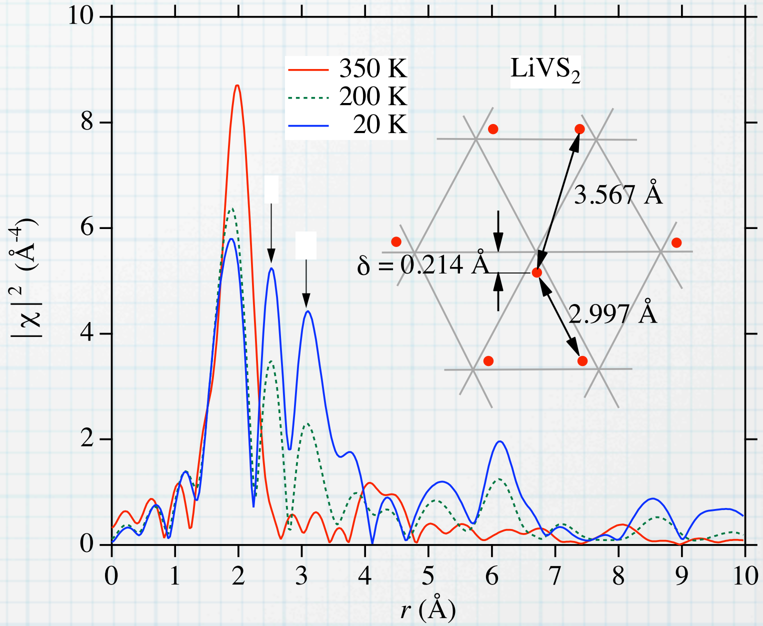
Electron Diffraction




295 K (< $T_c$ )
{1/3, 1/3, 0}
superlattice

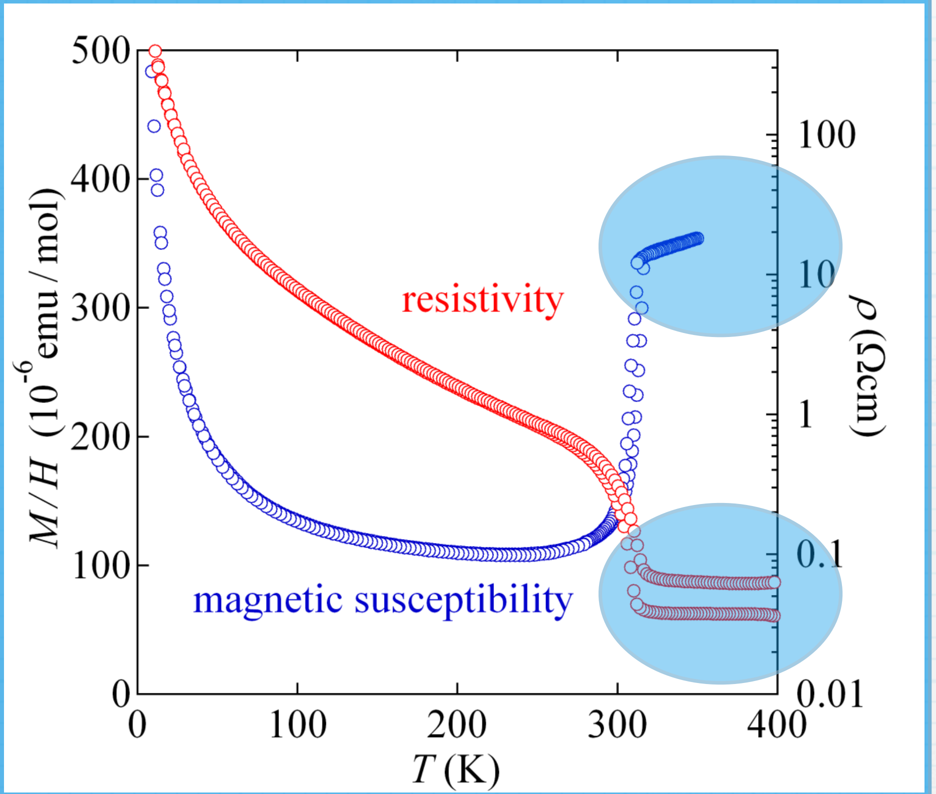
350 K

EXAFS, BL14B1, SPring-8

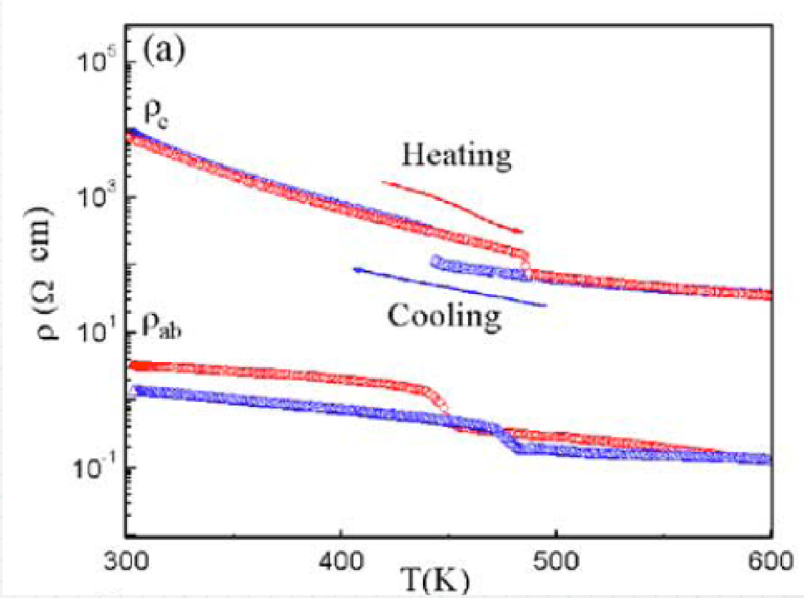


# Metal-Insulator Transition in $LiVS_2$

$LiVS_2$



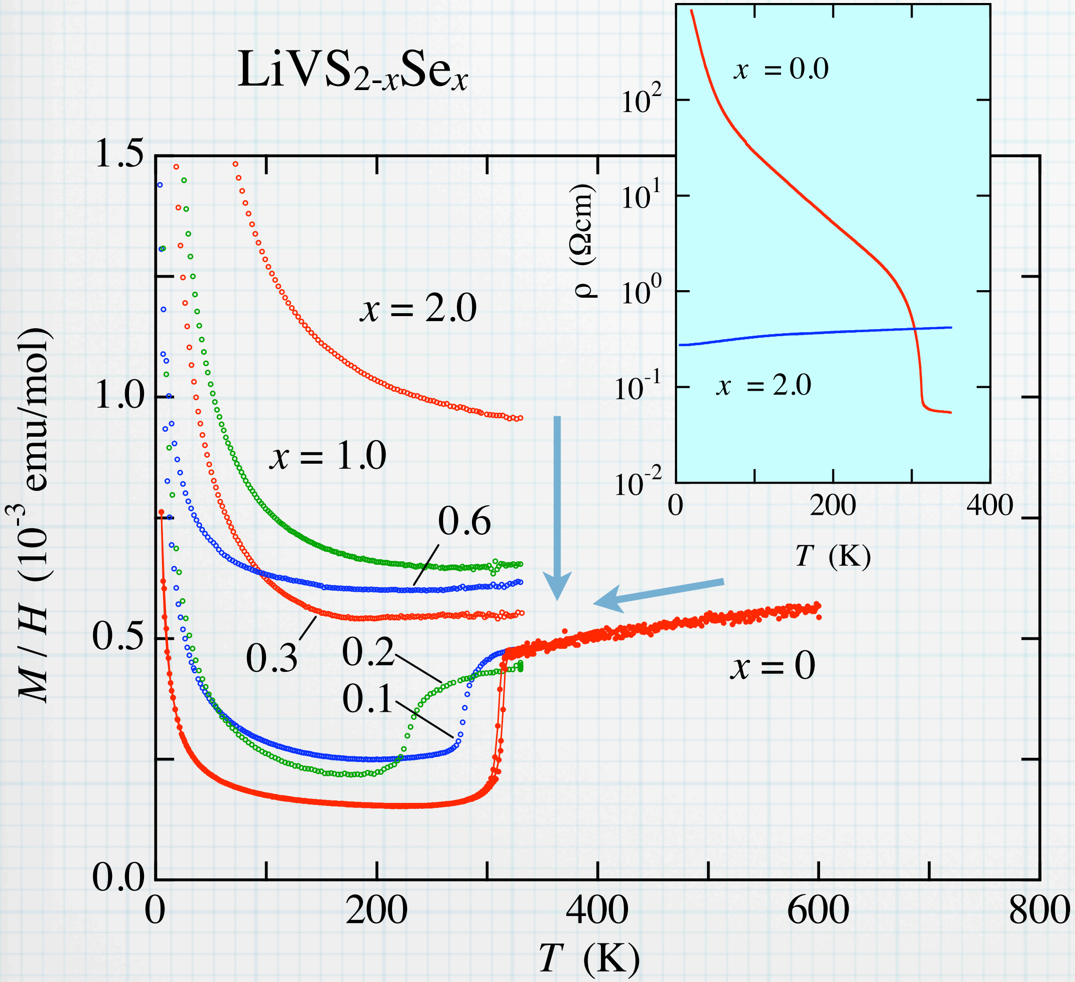

$LiVO_2$

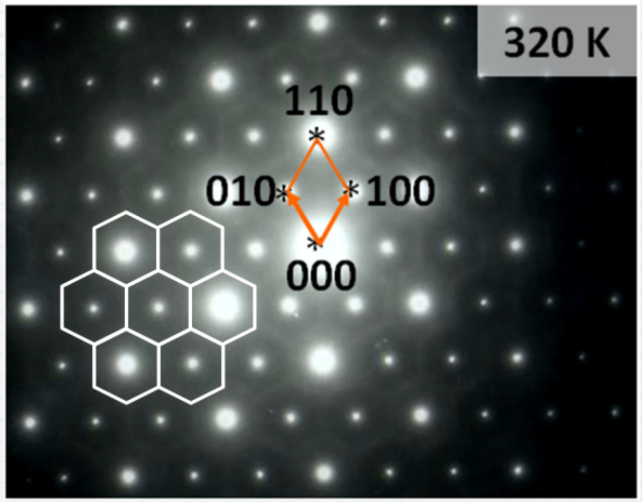



W. Tian *et al.*, Mater. Res. Bull. **39** (2004) 1319 .

**VBS is robust irrespective of high temperature phases, metallic in $LiVS_2$ and semiconducting in $LiVO_2$.**

# Pseudogap behavior in the metallic phase



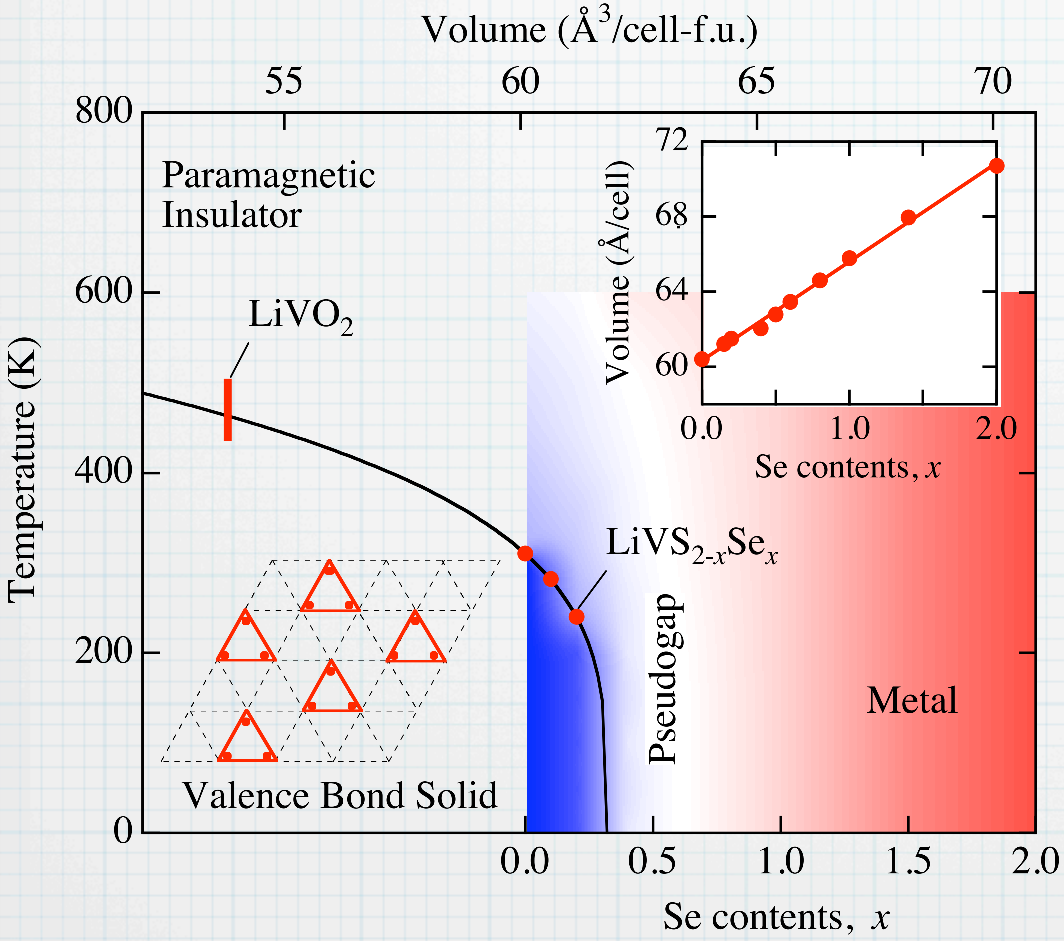




Diffuse scattering due to local trimer formation.

VBS state is suppressed by Se doping.

Gradual decrease in susceptibility by approaching VBS phase, indicative local singlet.

# Conclusion



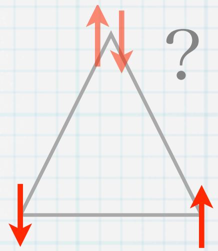

VBS can be melted by negative pressure.

VBS is robust from insulating to metallic side.

No superconductivity when VBS melts.

Short range correlation, or pseudogap, at the vicinity of phase boundary.

# Topics

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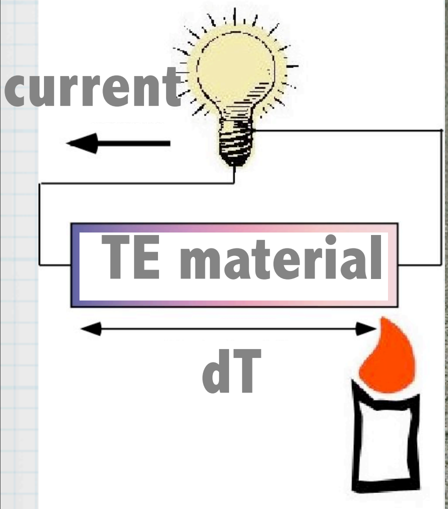
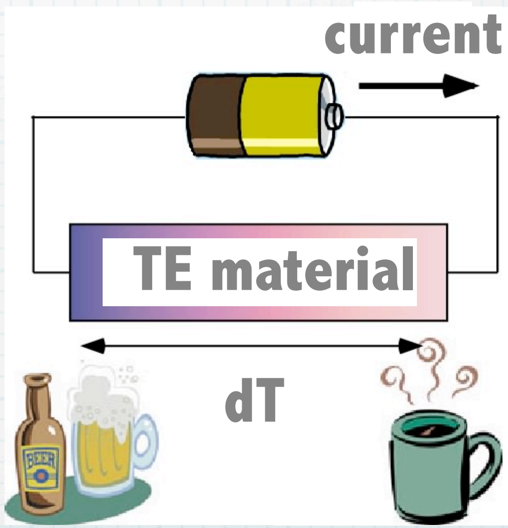
# Frustration can be a new route to thermoelectric materials

## Power Generation




Candle Radio

## Peltier Cooling





Refrigerator

# Requirements for thermoelectric materials

## 1. Large “Power Factor” (PF)

$$PF = S^2\sigma$$

Large Seebeck $S = \Delta V / \Delta T$

High electrical conductivity $\sigma$

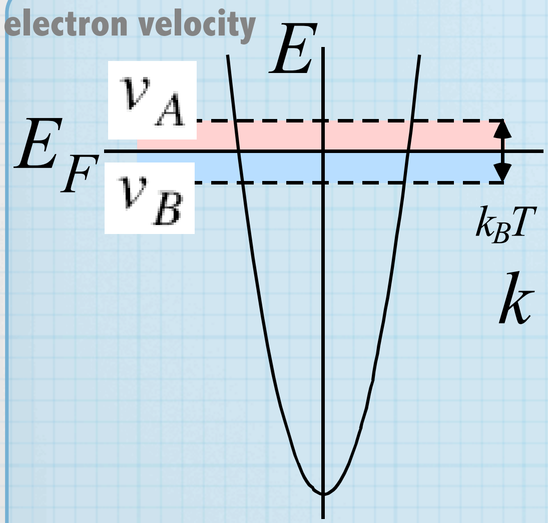
## 2. Large “Dimentionless Figure of Merit” (ZT)

$$ZT = \left(\frac{S^2\sigma}{\kappa}\right)T$$

Large PF $PF$

Low thermal conductivity $\kappa$

# Hard to realize both "large Seebeck" and "high




$$v_A^2 \sim v_B^2$$

**Large Fermi surface**

$$\sigma \propto v_A^2 + v_B^2$$ **Large**

**Symmetric band to $E_F$**

$$S \propto \frac{v_A^2 - v_B^2}{v_A^2 + v_B^2} \sim 0$$

Small $PF = S^2\sigma$

**Boltzmann's transport**

$$\sigma = e^2 K_0$$

$$S = \frac{1}{eT}\frac{K_1}{K_0}$$

$$K_n = \sum_k \tau(k)v(k)v(k)\left[-\frac{\partial f}{\partial E}\right](E_k - \mu)^n$$

$$K_0 \sim \left(v_A^2 + v_B^2\right)$$

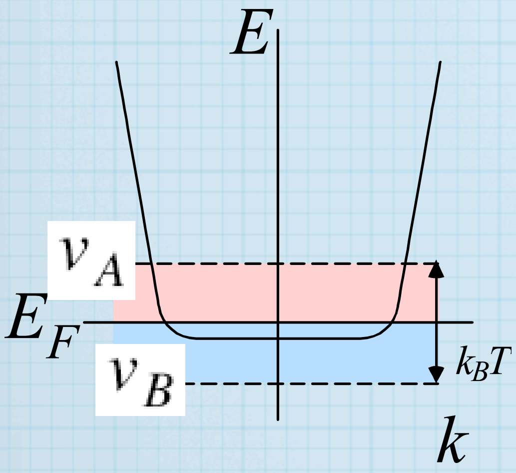
$$K_1 \sim k_B T\left(v_A^2 - v_B^2\right)$$

# "Pudding Mold" Band Drives Large Thermopower in $Na_xCoO_2$

triangular lattice

Kazuhiko KUROKI and Ryotaro ARITA[1]

Journal of the Physical Society of Japan
Vol. 76, No. 8, August, 2007, 083707




$$v_A^2 >> v_B^2 \sim 0$$

**Large Fermi surface**

$$\sigma \propto v_A^2 + v_B^2$$ large

**Highly asymmetric band**

$$S \propto \frac{v_A^2 - v_B^2}{v_A^2 + v_B^2}$$ large

$$PF = S^2\sigma$$ large

**Boltzmann's transport**

$$\sigma = e^2 K_0$$

$$S = \frac{1}{eT}\frac{K_1}{K_0}$$

$$K_n = \sum_k \tau(k)v(k)v(k)\left[-\frac{\partial f}{\partial E}\right](E_k - \mu)^n$$

$$K_0 \sim \left(v_A^2 + v_B^2\right)$$

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VOLUME 87, NUMBER 23 PHYSICAL REVIEW LETTERS 3 DECEMBER 2001

# Effects of Spin and Orbital Degeneracy on the Thermopower of Strongly Correlated Systems

W. Koshibae and S. Maekawa

$Co^{3+}$ $3d^6$ $Co^{4+}$ $3d^5$


$g_3 = 1$ $g_4 = 2 \times 3 = 6$

**hopping**

→

**charge current** $+e$

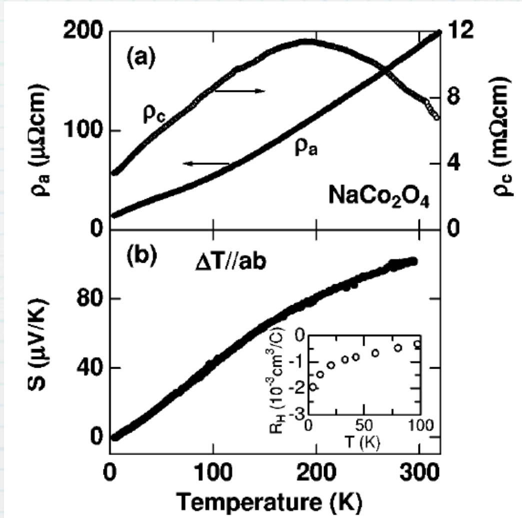
**entropy flow**

$k_B \ln g_4 - k_B \ln g_3$

## Extended Heikes eq.

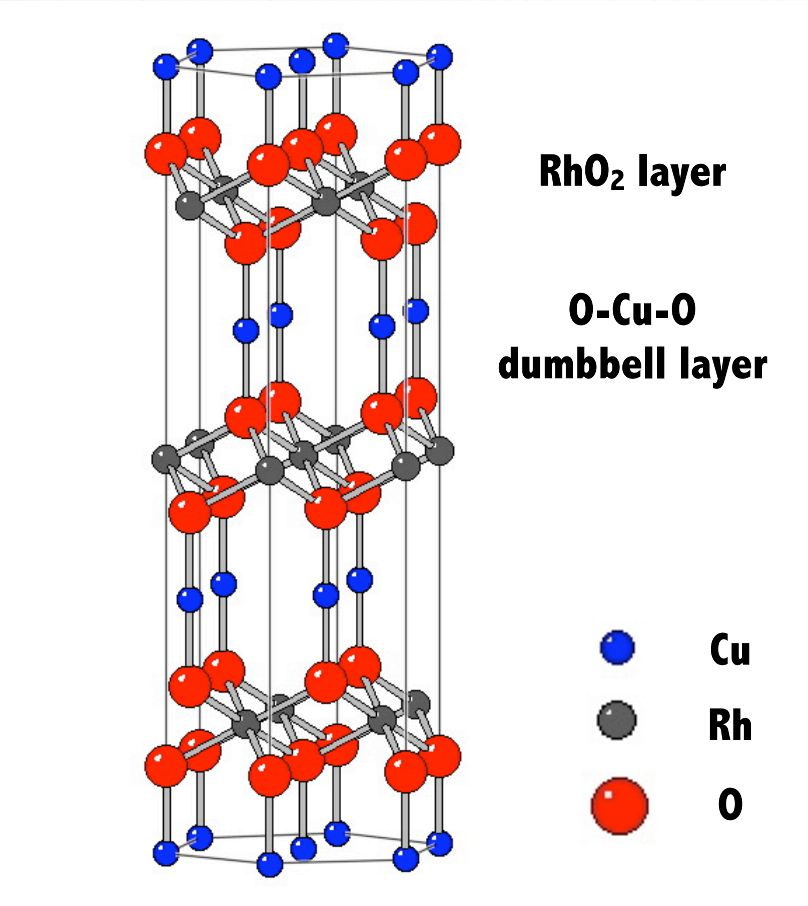
$$S = \frac{k_B}{e}\left(\ln g_4 - \ln g_3\right) = 154\ \mu\mathrm{V/K}$$

## High-T limit / hopping conduction



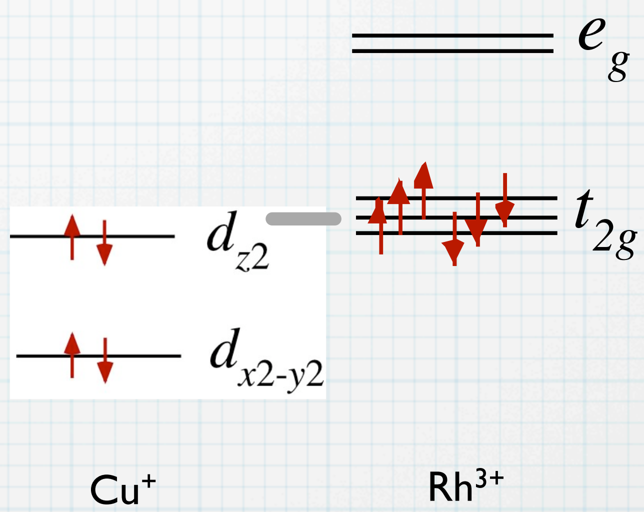
# Layered Rh oxides with $d^6$ low-spin state

**Delafossite $CuRhO_2$**




**Band insulator**

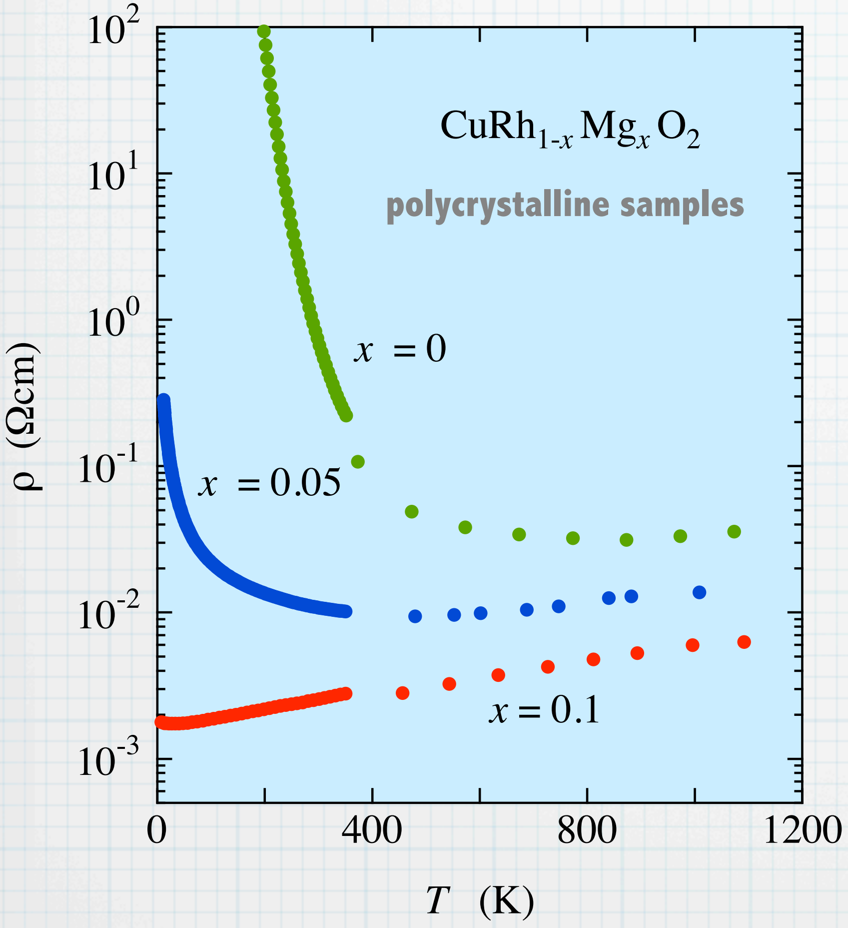
* $d^6$ low-spin state

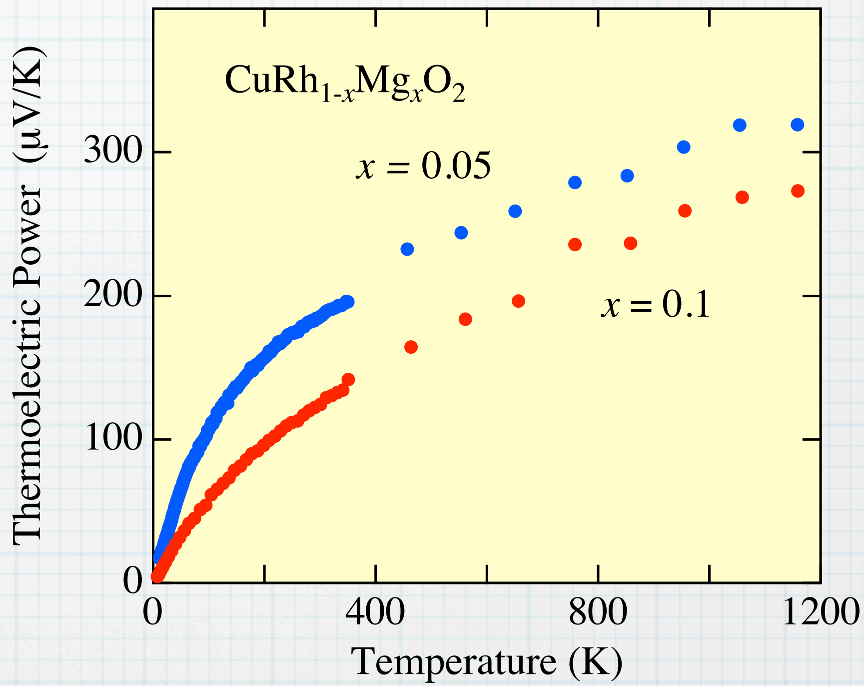



**Hole doping by substituting $Mg^{2+}$ for $Rh^{3+}$**

**$CuRh_{1-x}Mg_xO_2$**

# Large Seebeck and Metallic Conductivity Realized

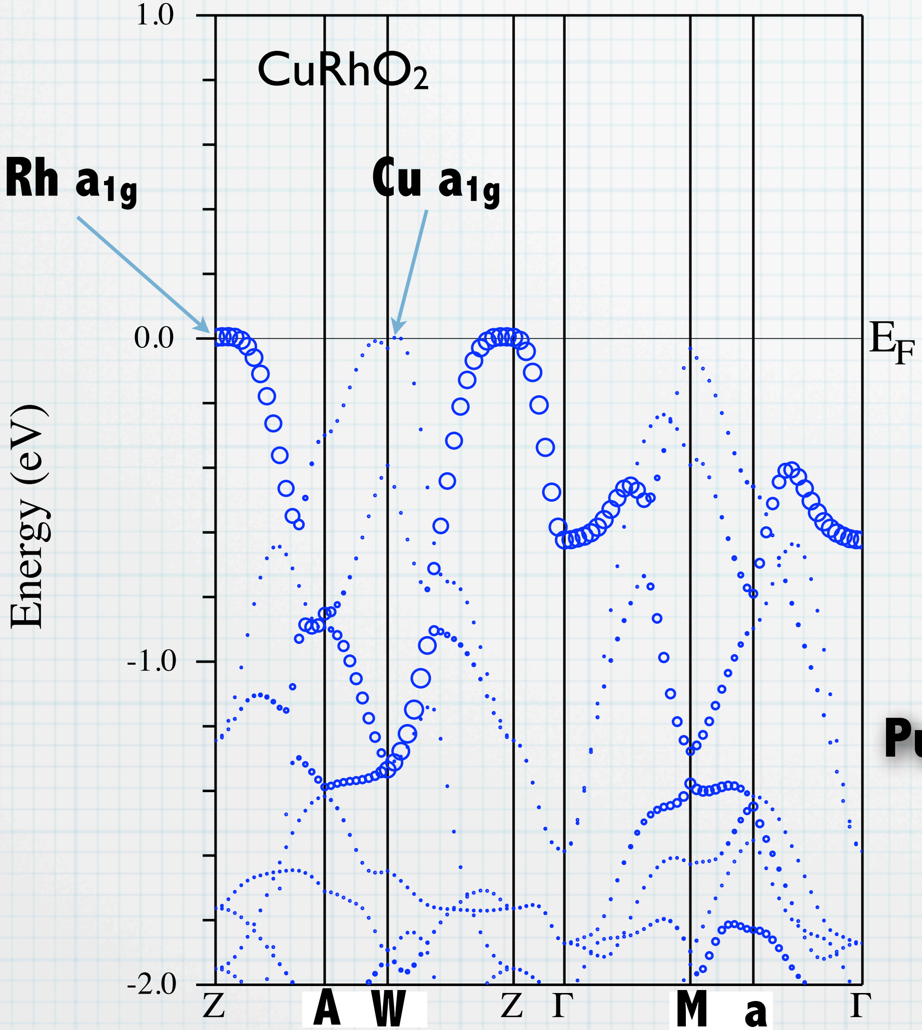


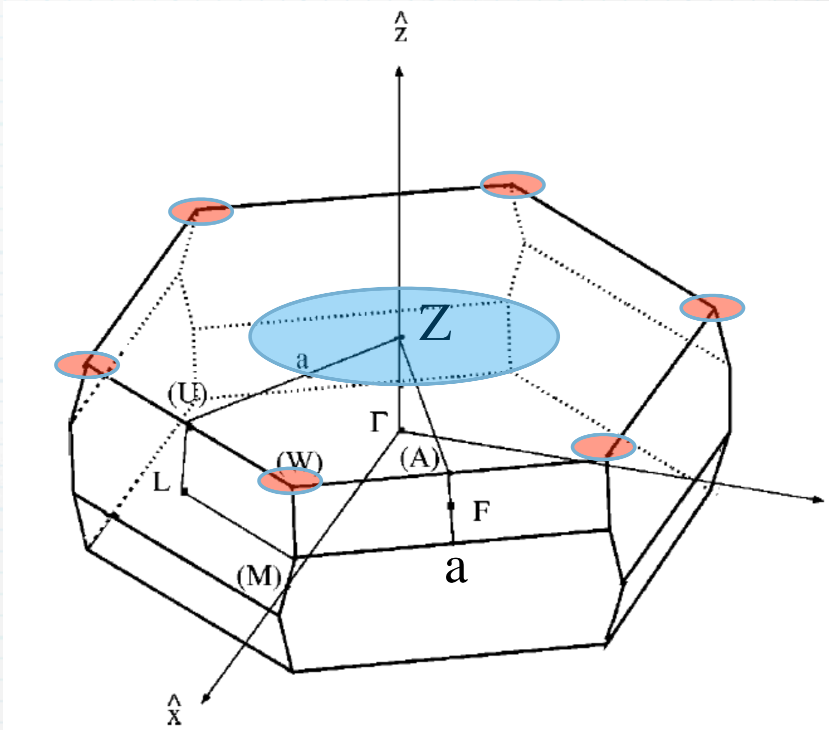




**Large Mg solubility of x = 0.1.**

**Large mobility of ~ 1 $cm^2/Vs$.**

# "Pudding Mold Band" is present at Z point



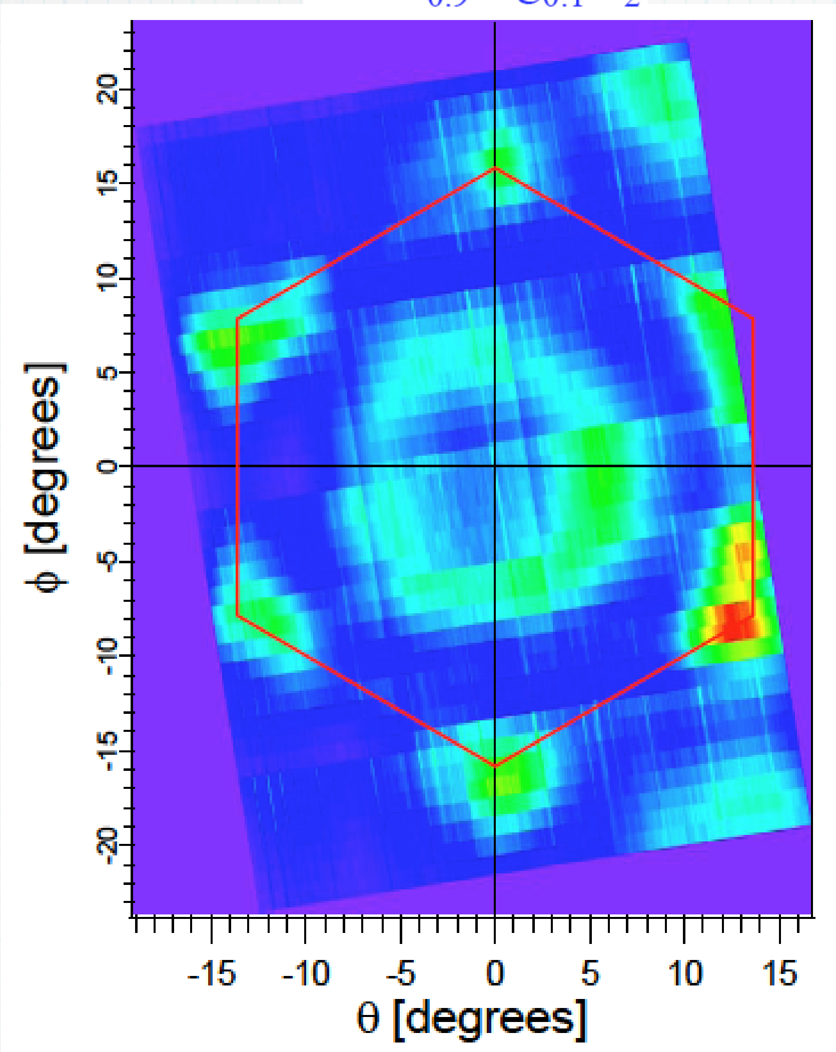



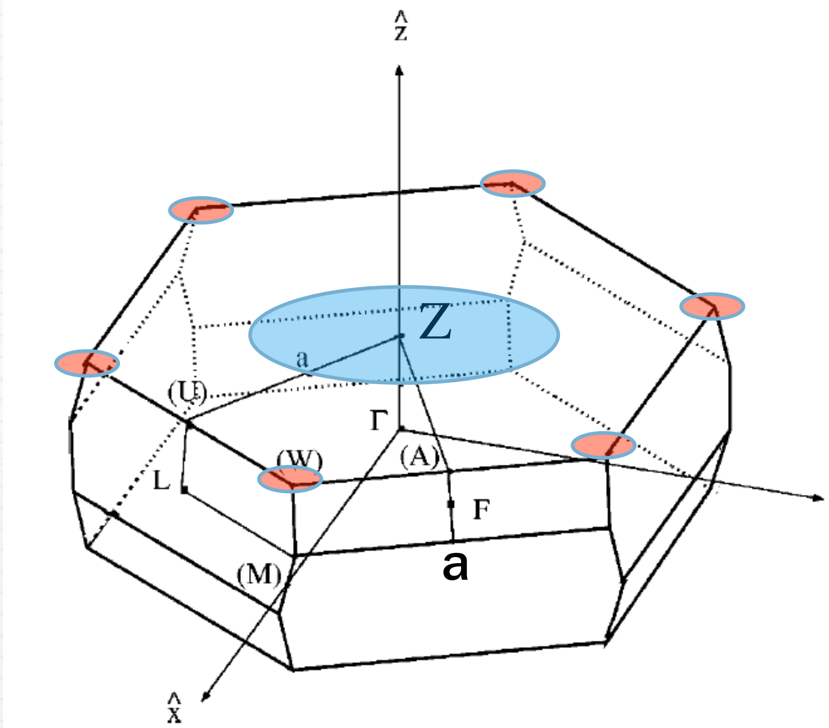

**Pudding Mold Band of Rh $a_{1g}$ centered at Z**

Pocket of Cu $a_{1g}$ centered at W

# “Pudding Mold Band” is present at Z point

$CuRh_{0.9}Mg_{0.1}O_2$



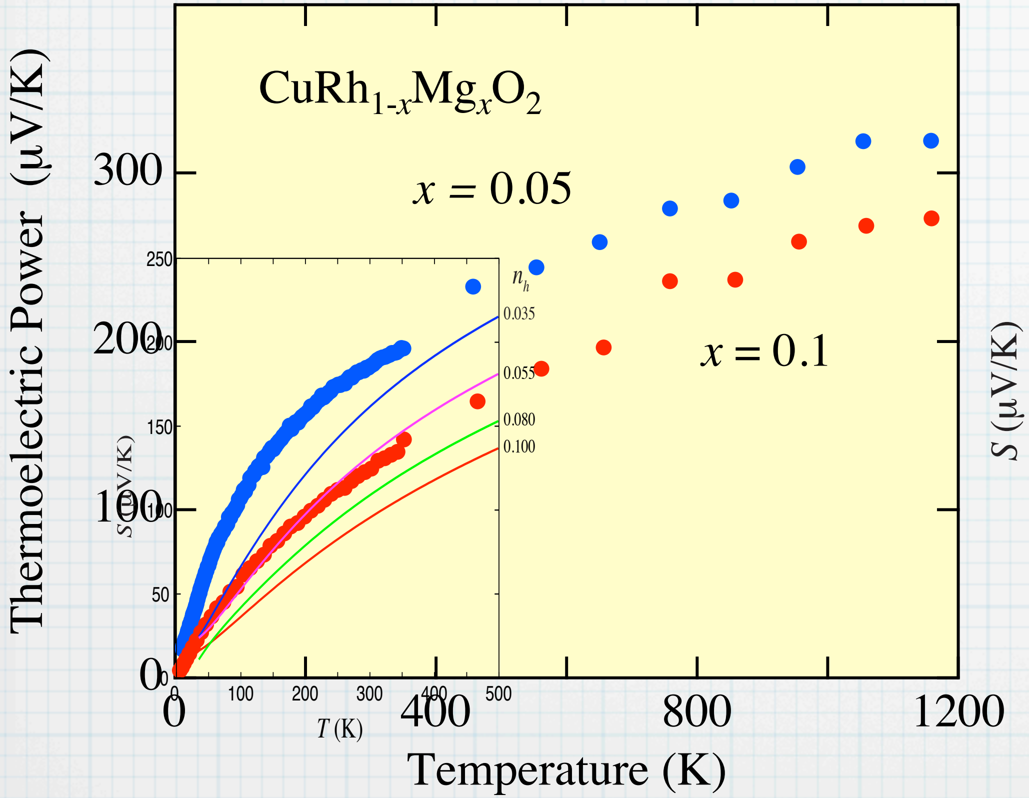




hν = 100 eV
T = 18K

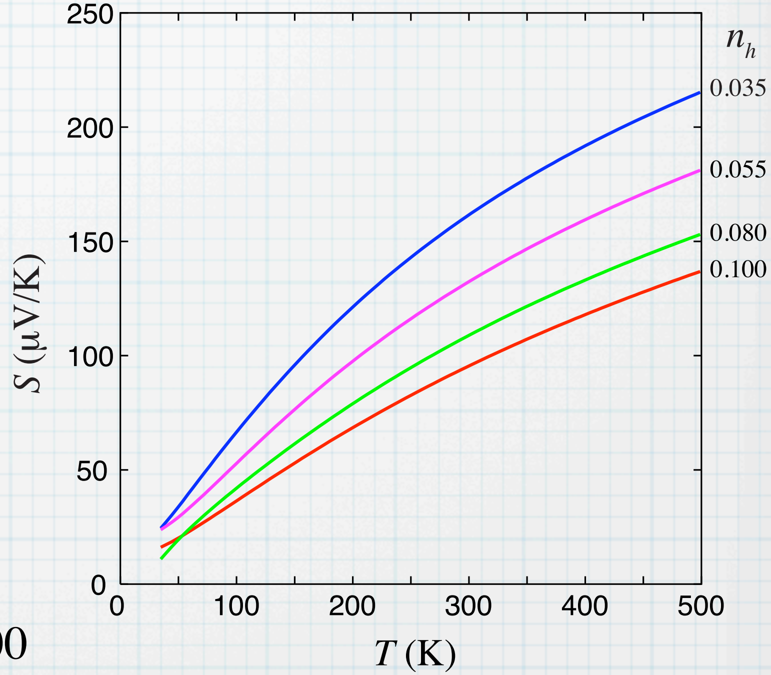
SRC-Wisconsin
collaboration with N. Bontemps (Paris)

# “Pudding Mold Band” scenario looks OK

## Observation



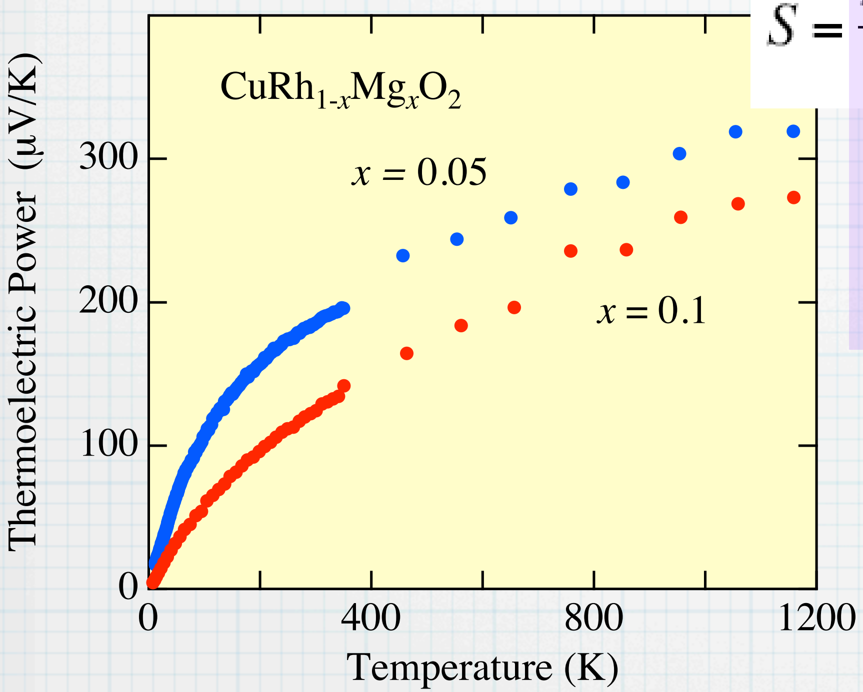

## calculation




Kuroki & Arita

# Spin & Orbital Scenario predicts High-T value of S

(Heikes)



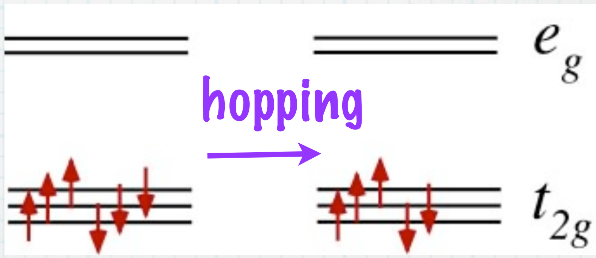

$$S = \frac{k_B}{e}(\ln g_4 - \ln g_3) - \frac{k_B}{e}\ln\frac{x}{1-x}$$

| Spin & Orbital entropy | Charge configuration entropy |
|---|---|
| $+154\ \mu$V/K | $+190\ \mu$V/K for $x = 0.1$ |

**High T limit**

$$S \to 344\ \mu\text{V/K}$$

d⁶ LS　　d⁵ LS



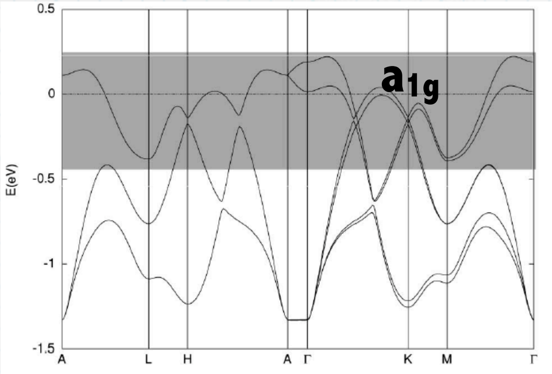

$g_3 = 0$　　$g_4 = 2 \times 3 = 6$

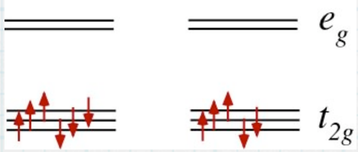
Koshibae et al. Phys. Rev. Lett. 87 (2001) 236603.

# "In-between-state" is ubiquitous theme in strongly correlated systems

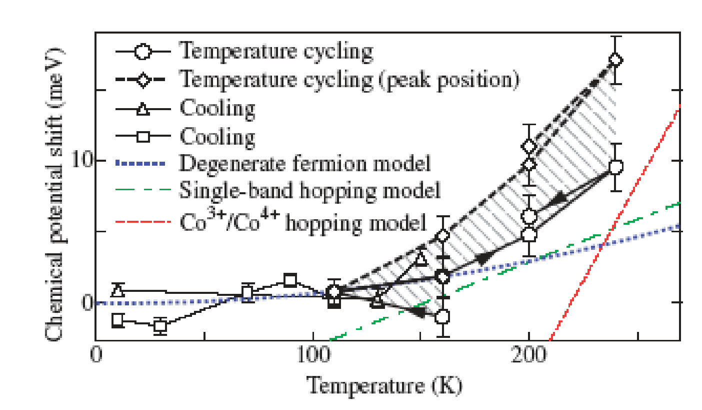
$$S = \frac{1}{eT}\frac{K_0}{K_1} + \frac{\mu}{eT}$$

| kinetic term | entropy term |
| --- | --- |
| Band limit | Atomic limit |
| QP band better described in k space | Hubberd band better described in real space |




$Na_xCoO_2$

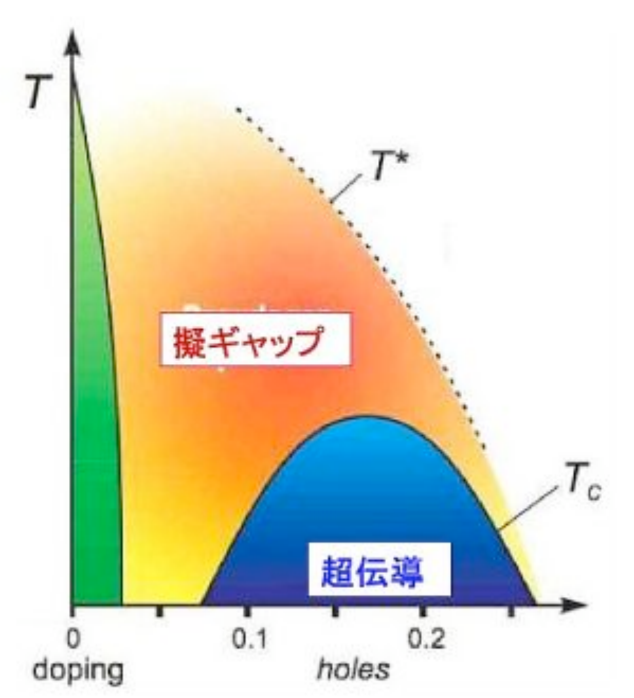



**Crossover between band limit & Atomic limit by PES**

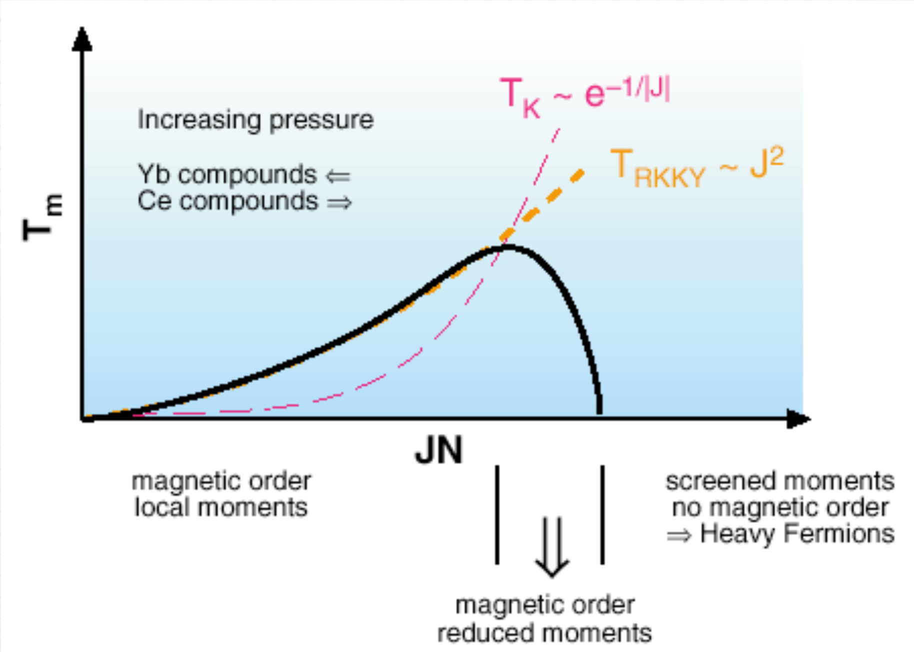
Isida & Fujimori, JPSJ 76, 103709 (2007).

# "In-between-state" is ubiquitous theme in strongly correlated systems

**d-electron system: high-Tc**




**f-electron systems: heavy fermion**




**Atomic limit** — **Band limit** (d-electron)

**Mott Physics** — **Fermi Liq. & SCR**

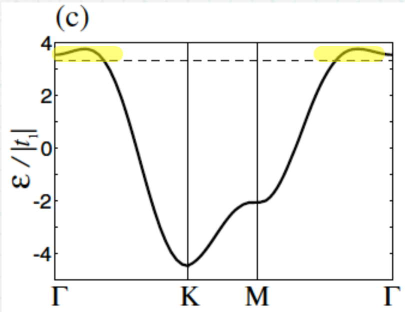
**Atomic limit** — **Band limit** (f-electron)

**localized f** — **delocalized f**

# Conclusion

Geometrical Frustration

**Band limit**

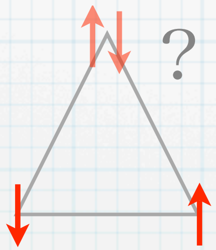



"pudding-mold band"

single band tight binding model

Kuroki & Arita, JPSJ 76, 083707 (2007).

**Atomic limit**




spin/orbital degeneracy

High-entropy metal (thermoelectric materials)

* physics of "in-between-state"
* material design from geometrical frustration