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Workshop on Novel States and Phase Transitions in Highly Correlated Matter

12 - 23 July 2004

Spin and charge frustration in Spinel oxides

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ICTP Trieste, 2004

Spin and Charge Frustration in Spinel Oxides

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Collaborators
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H. Mitamura and T. Goto (ISSP)
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Exotic phases produced by geometrical frustration on pyrochlore lattice

1. Introduction

2. Spin frustration in $Zn(Cd)Cr_2O_4$

spin JT phase and its magnetic field control

[1] magnetization plateau state with ***3-1*** spin ordering

3. Charge frustration in AlV_2O_4

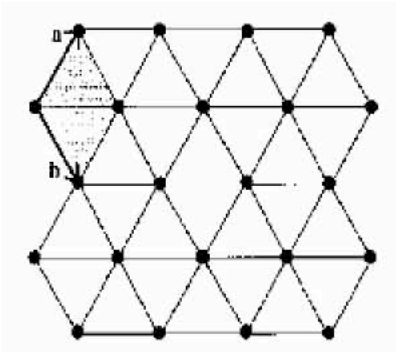
3-1 charge ordering (valence skipping)

4. Charge & Spin Liquid State

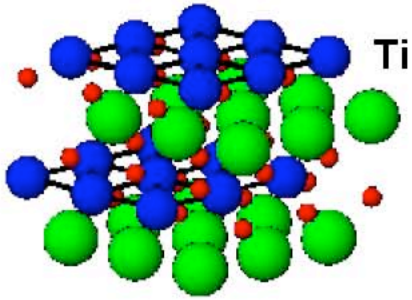
Heavy Fermion Oxides LiV_2O_4

close proximity to ***3-1*** charge ordering

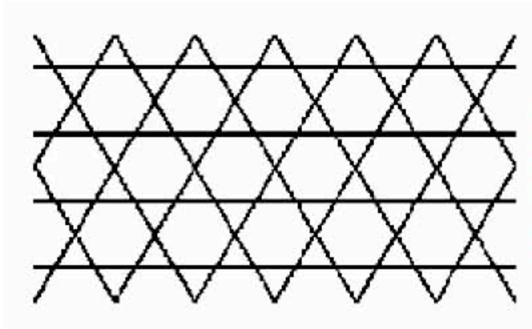
Geometrically Frustrated Lattices



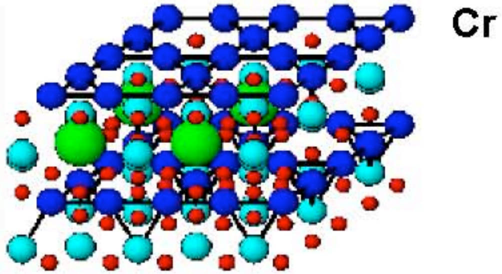
2D Triangular lattice



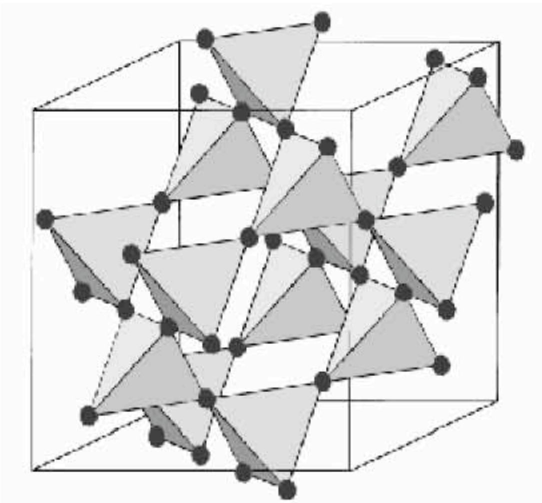
$NaTiO_2$, $LiVO_2$,
$LiNiO_2$, Na_xCoO2



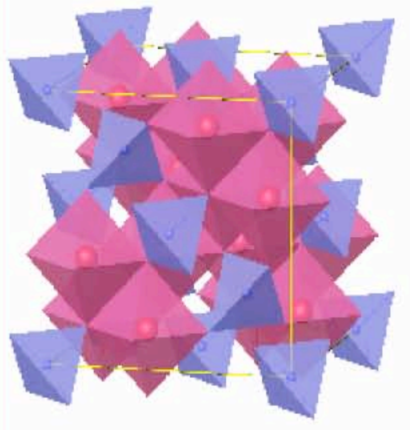
2D Kagome lattice



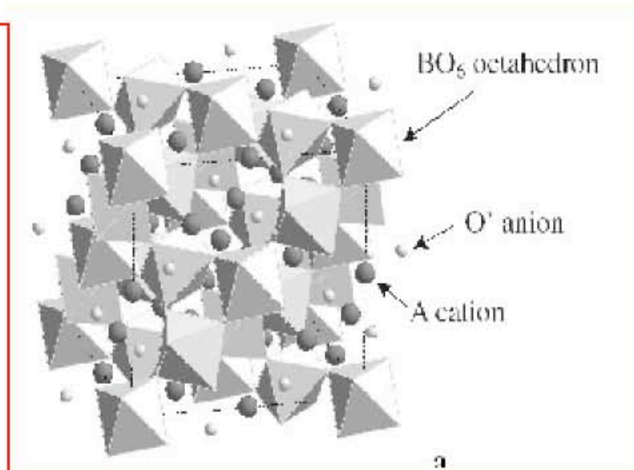
$SrCr_9Ga_3O_{19}$



3D Pyrochlore lattice



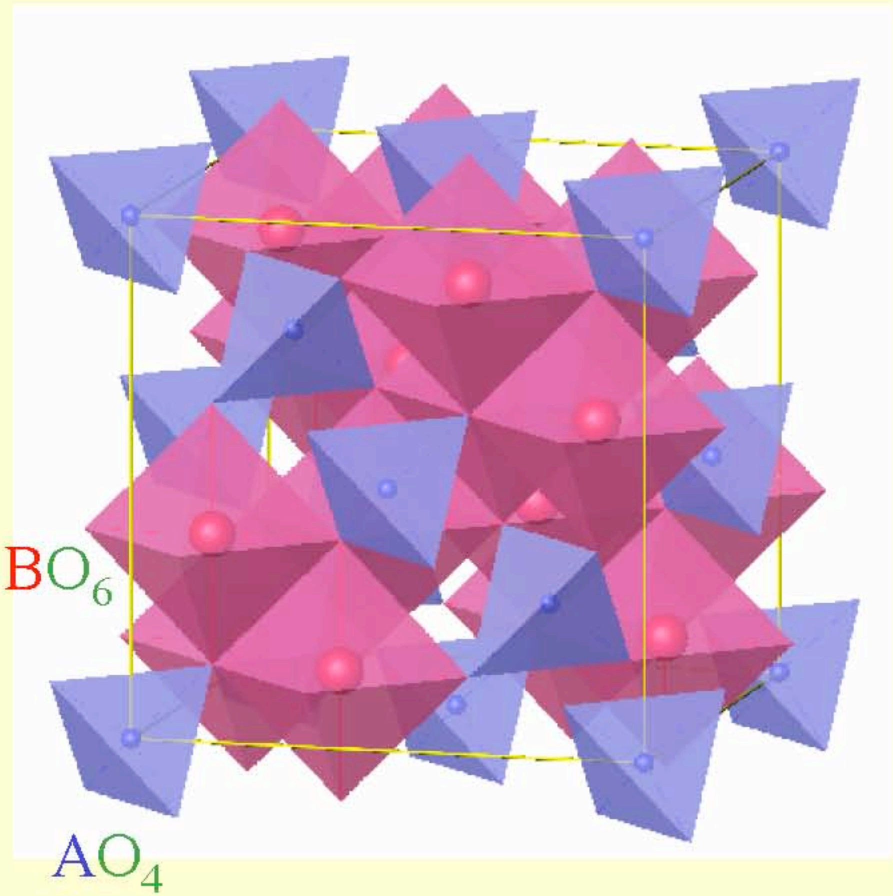
Spinel (AB_2O_4)
$Fe_3O_4=FeFe_2O_4$



Pyrochlore($A_2B_2O_7$)
$Y_2Mo_2O_7$

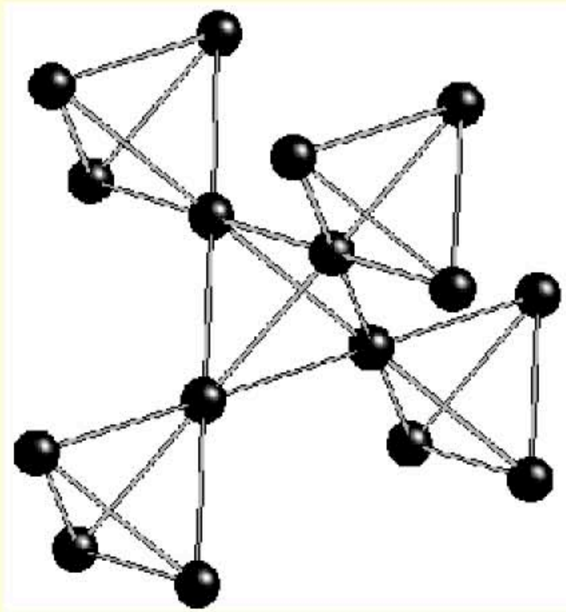
Spinel Structure: AB_2O_4

(cubic: *Fd3m*)



"B-sublattice"

corner-shared tetrahedra



"Pyrochlore" Lattice

What do we expect ?

Spin Frustration (when AF)

- Strongly degenerate low lying spin excitations

Prevents long range order 3D spin liquid

Charge Frustration (when mixed valent)

Verway problem

$Fe_3O_4=Fe^{3+}Fe_2^{2.5+}O_4$ 1:1 Fe2+ & Fe3+

- Strongly degenerate low lying charge excitations

Prevents long range order charge liquid

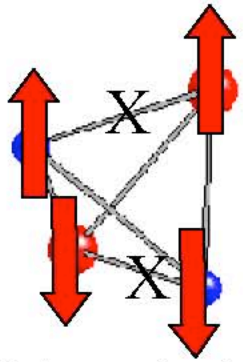
Orbital Frustration?

Exotic Phase (transition) ?

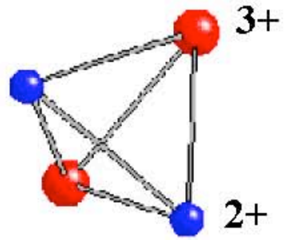
-Nature always tries to reduce the degeneracy

couple with lattice, orbital, itinerant carriers

Anderson 1956



S=0 / tetrahedron



charge / tetrahedron=const
Anderson condition

Guide map of "simple" spinel oxides

Heavy Fermion charge & spin liquid
C.Urano, S.Kondo and H.T et. al PRL(00)

Frustrated charge ordered insulator
3-1 type CO "valence skipping"
K.Matsuno, H.T et al PRL(03)

ionic & nonmagnetic ↓ transition metal ↓

	M= Ti	V	Cr	Mn
$Li^{1+} M_2^{3.5+} O_4$ (Al^{3+}) "**Charge**" frustration 1 : 1 3+ & 4+, mixed valent	$d^{0.5}$ $LiTi_2O_4$ BCS SC	$d^{1.5}$ LiV_2O_4 ←	$d^{2.5}$ ($LiCr_2O_4$) = AlV_2O_4	$d^{3.5}$ $LiMn_2O_4$
$Zn^{2+} M^{3+}_2 O_4$ (Mg^{2+}, Cd^{2+}) "**Spin**" frustration all 3+, AF Ins.	d^1 ($ZnTi_2O$) $MgTi_2O_4$	d^2 ZnV_2O_4 MgV_2O_4 CdV_2O_4	d^3 ***$ZnCr_2O_4$*** $MgCr_2O_4$ ***$CdCr_2O_4$***	d^4 $ZnMn_2O_4$

Frustrated AF magnet

Spin driven structural phase transition – spin JT
½ magnetization plateau state

H.Ueda & H.T et al. PRL submitted

S=3/2 pyrochlore Heisenberg AF without orbital degrees of freedom: $CdCr_2O_4$ and $ZnCr_2O_4$

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

$\theta_{CW} = -90K, \ T_N = 7K$

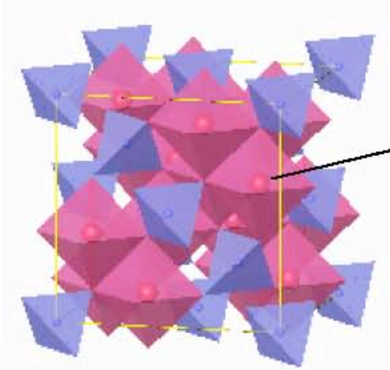
$T_N / |\theta_{CW}| = 0.08$

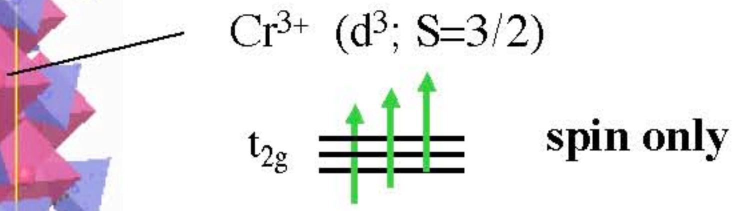
$Zn^{2+}Cr^{3+}{}_2O_4$

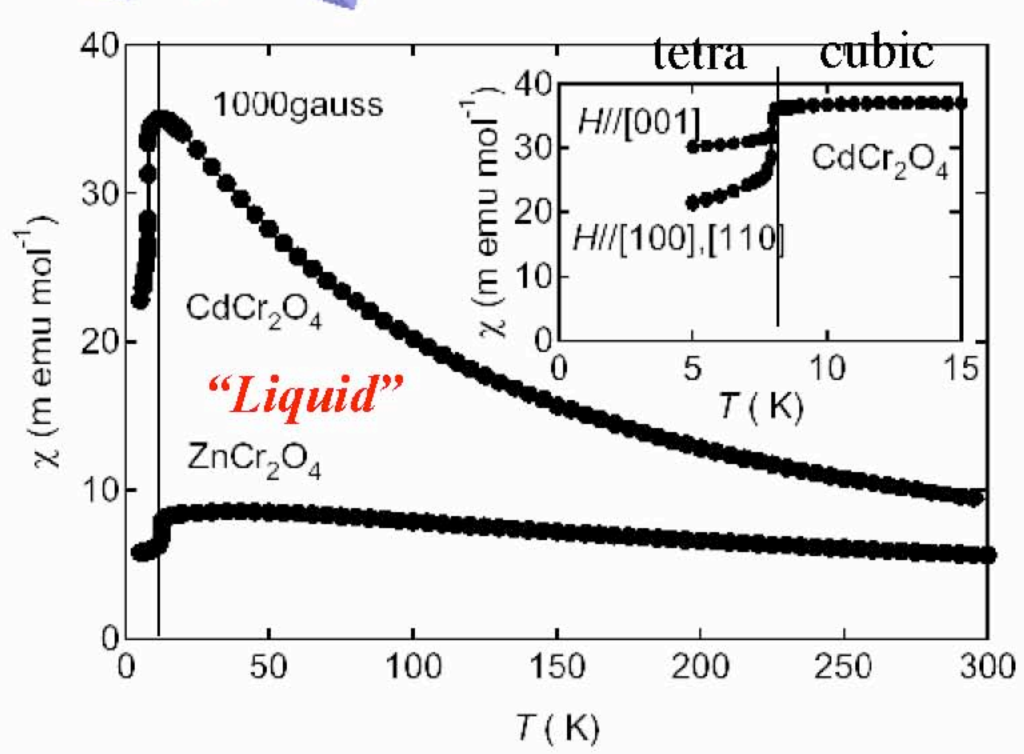
$\theta_{CW} = -350K, \ T_N = 13K$

$T_N / |\theta_{CW}| = 0.04$

Geometrical frustration evident





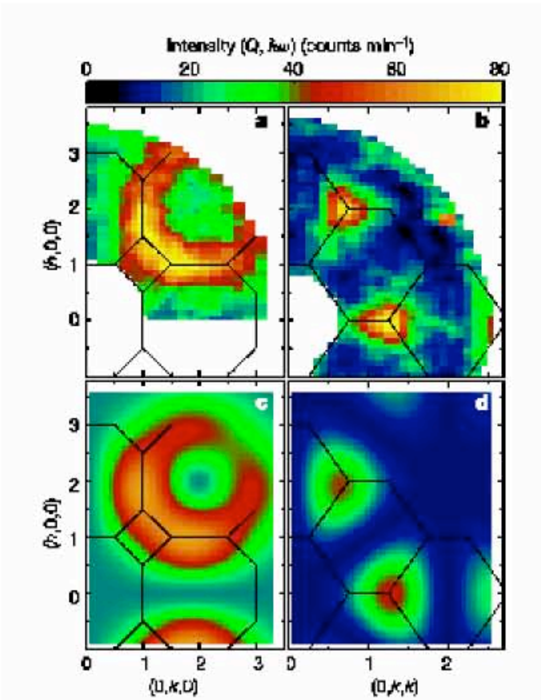


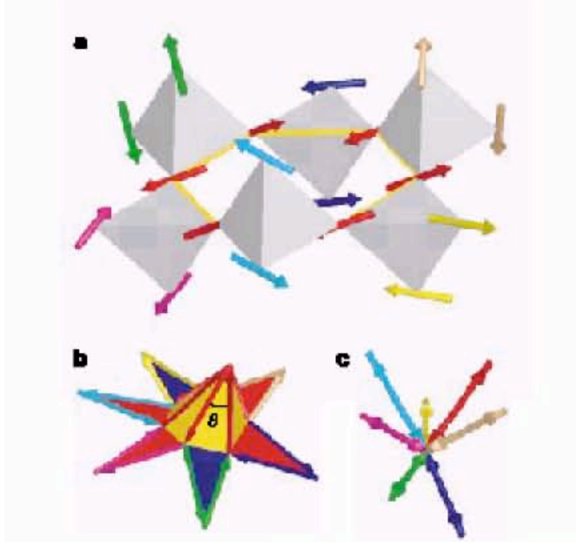
Hexagonal spin cluster formation in the spin liquid phase above $T_s = T_N$

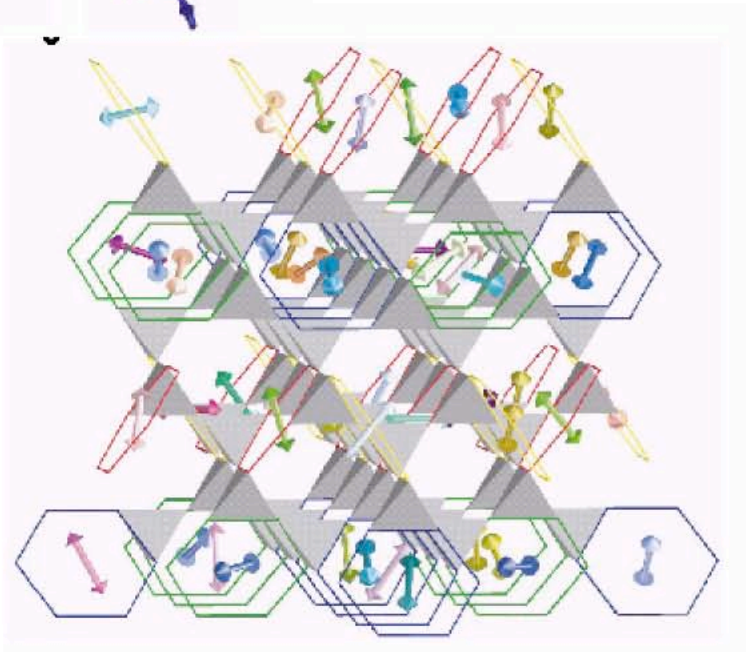
Emergent excitations in a geometrically frustrated magnet

S.-H. Lee*, C. Broholm*†, W. Ratcliff‡, G. Gasparovic†, Q. Huang*
T. H. Kim‡§ & S.-W. Cheong‡

* *NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*
† *Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218, USA*
‡ *Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA*

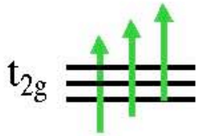






Spin JT transition in $CdCr_2O_4$ and $ZnCr_2O_4$ spinels

Cr^{3+} (d^3; S=3/2)



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

$T_N = T_S = 7K << \theta_{CW}$

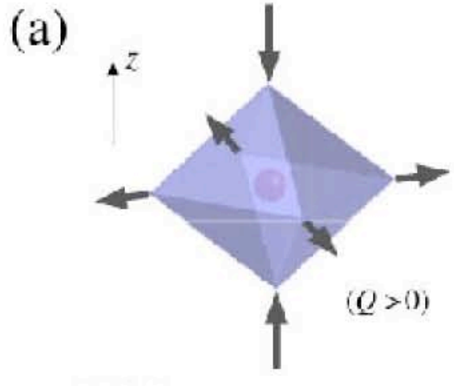
$Zn^{2+}Cr^{3+}{}_2O_4$

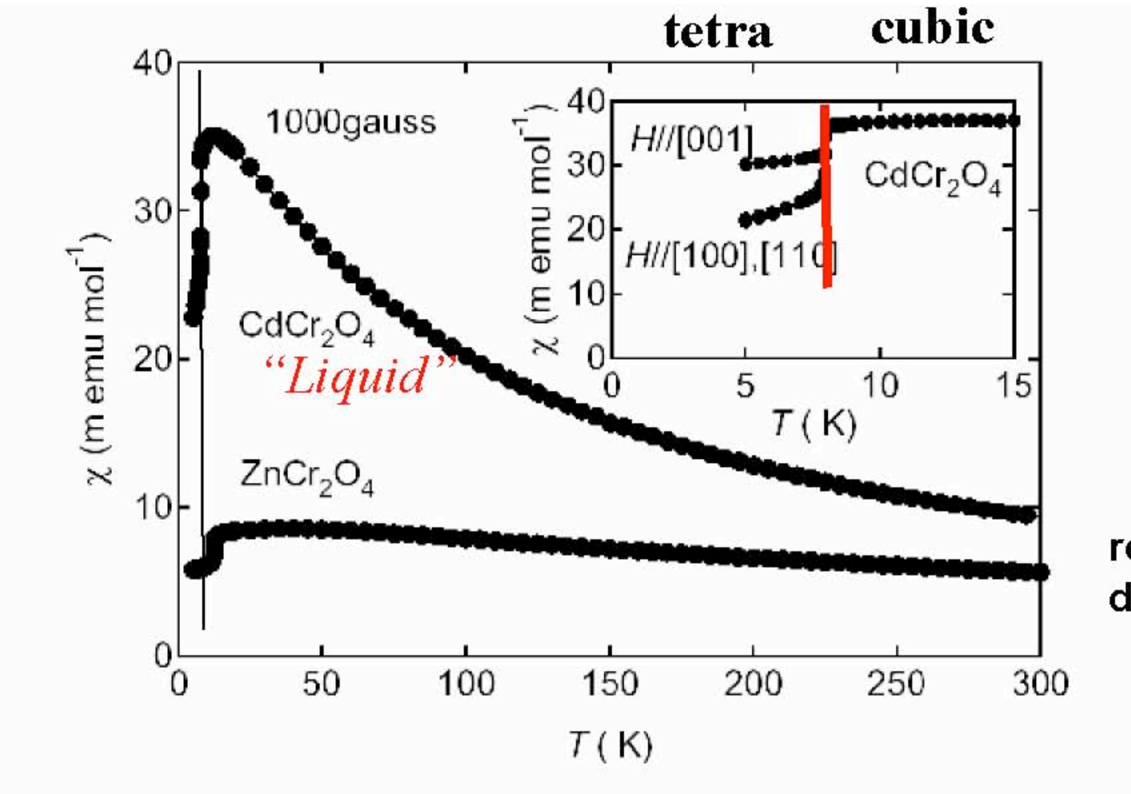
$T_N = T_S = 13K << \theta_{CW}$

AF ordering (easy plane type & complicated non-colinear)

accompanied with 1st order

Cubic to Tetragonal transition





no orbital degree of freedom

↓

Spin- JT transition

remove "spin degeneracy" by lattice distortion

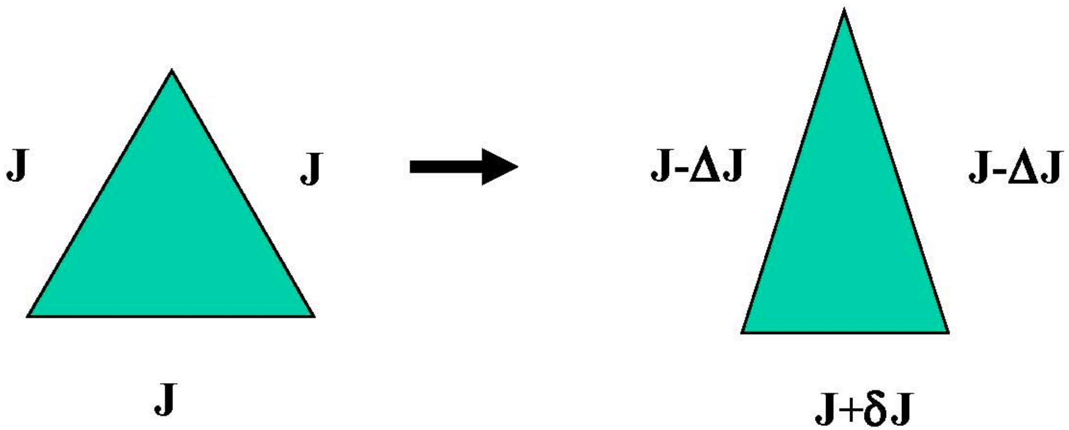
Yamashita and K.Ueda, PRL(01)
O.Tchernyshyov PRL &PRB (02)

Spin Jahn-Teller transition

Yamashita and K.Ueda, PRL(01)

O.Tchernyshyov PRL &PRB (02)

remove “spin degeneracy” instead of orbital degeneracy by lattice ditortion

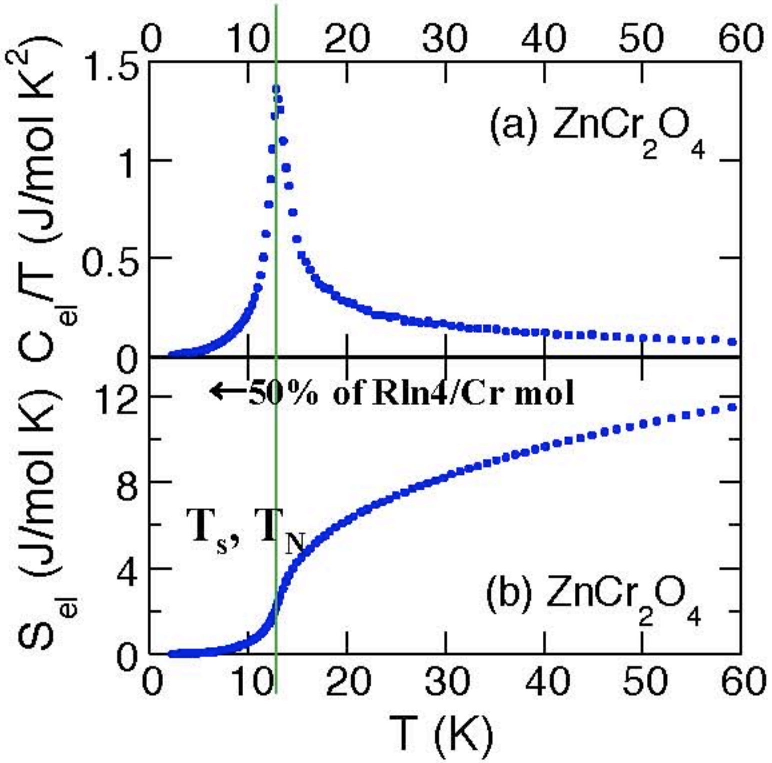


exchange-striction driven ordering

3D analogue of spin Peierls transition

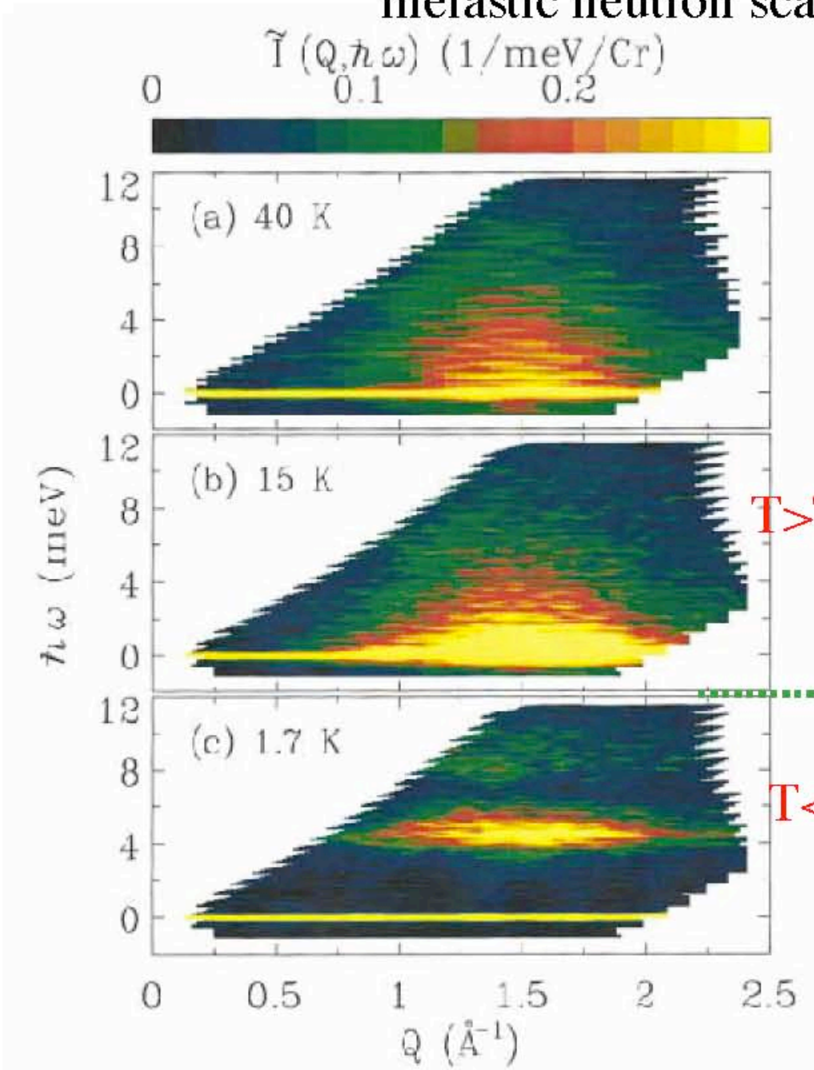
Gigantic entropy quenched at T_S (<< Θ_{CW})
- support for spin JT

S. –H. Lee, C. Broholm, *et al*. PRL **84**, 3718 (2000).



$T<<\theta_{CW} = -350K$

inelastic neutron scattering



$T>T_S$, T_N

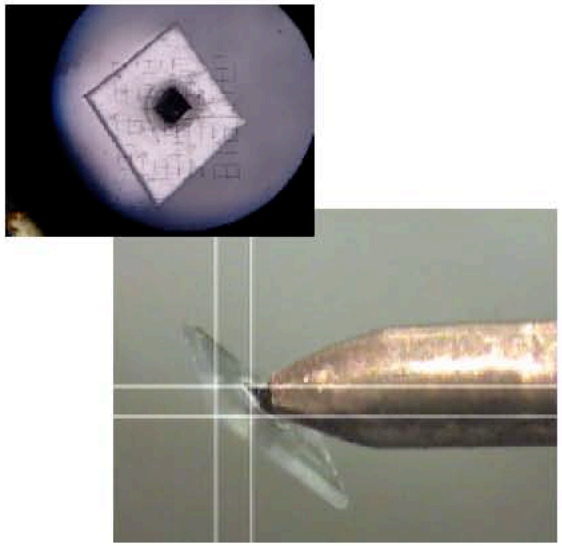
$T<T_S$, T_N

Complicated lattice distortion below T_N - support for spin-JT

O.Tchernyshyov PRL (03)

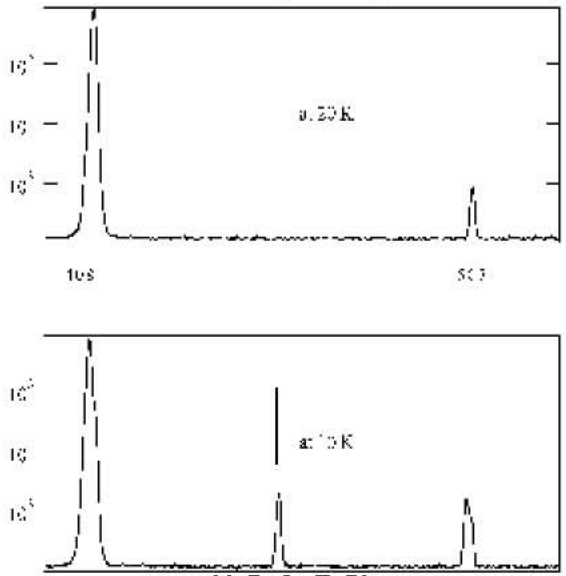
In spin JT phase, AF-bond shorter F-bond longer
Lattice distortion should be compatible with non-colinear Neel state with 2 x 2 x2 magnetic unit cell

Low T structure more complicated than the simple elongation of cubic <001> (orbital JT)
→ Revisit to low-T crystal structure of $ZnCr_2O_4$



Domains removed by applying uniaxial pressure

$ZnCr_2O_4$ single crystal x-ray

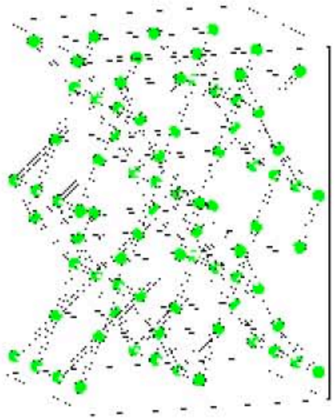


2x2x2 superlattice

$I\bar{4}m2$

Tetra

$T<T_N$



more fun out of $CdCr_2O_4$
- magnetic field control of frustration

- **When spins aligned by H, frustration will be reduced**

field induced structural phase transition?   eventually cubic ?

-**Magnetization plateau state as observed in other frustrated magnets?**

Crystallization of spin excitations

Perhaps, the ordering coupled strongly with lattice

Magnetic field control of frustration
- M-H curve of $CdCr_2O_4$ at 1.8 K

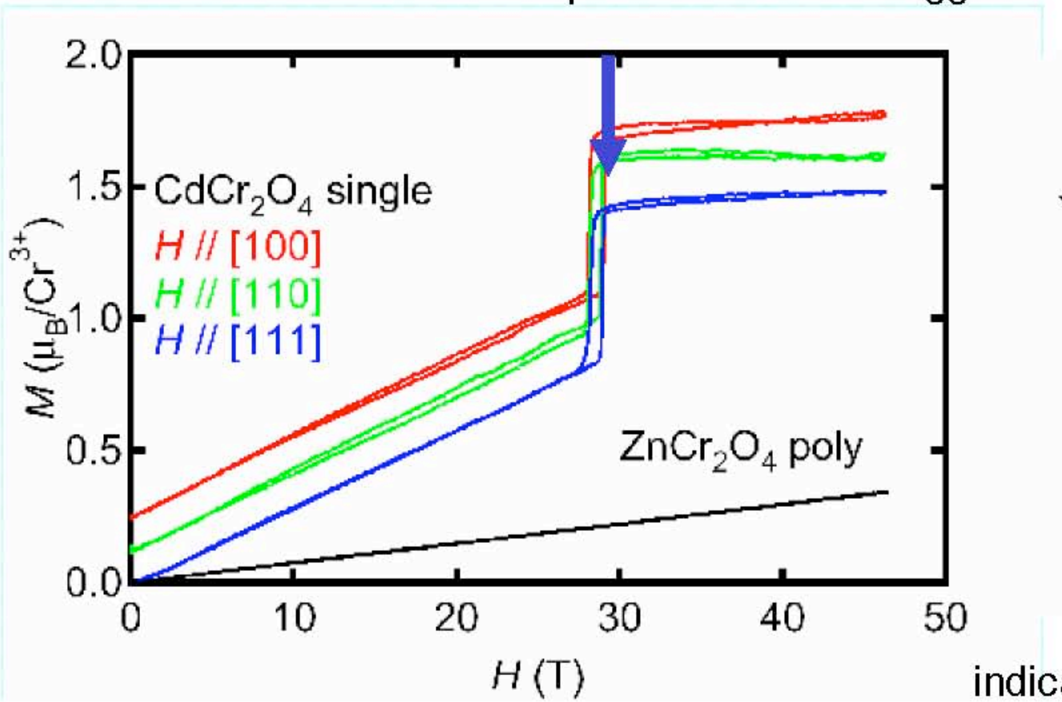
- **metamagnetic transition to a plateau state at 28 T (first order)**

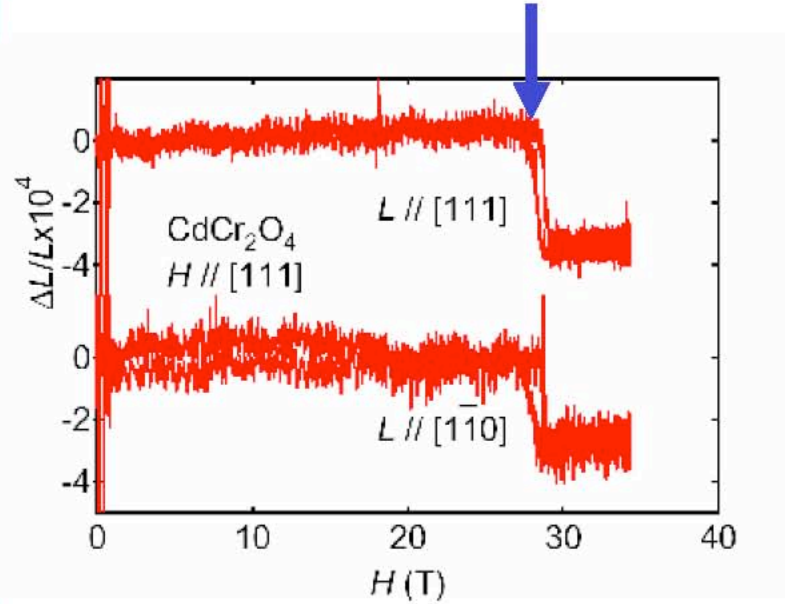
plateau at M=1.5μ_B, *stable* over at least 20T

no anisotropy (*Heisenberg*)

- **magnetostriction as large as ~10^{-3} though spin-orbit negligible**

Magnetostriction normally of the order of 10^{-5} even with spin-orbit
structural phase transition suggested from ESR





indicative of strong spin – lattice coupling

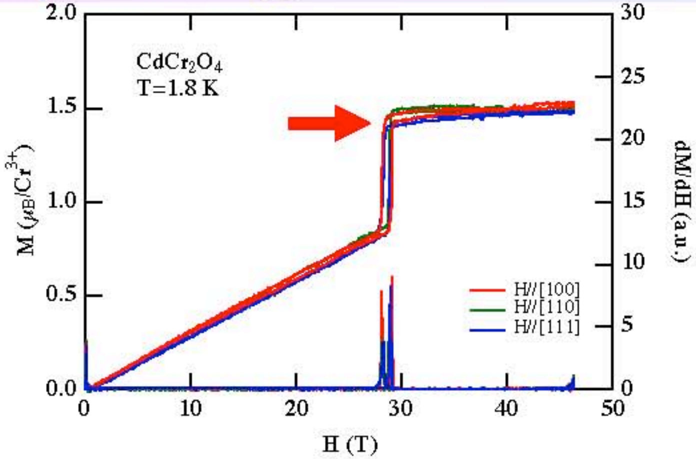
Magnetostriction comparable magnitude with
to tetragonal ditortion

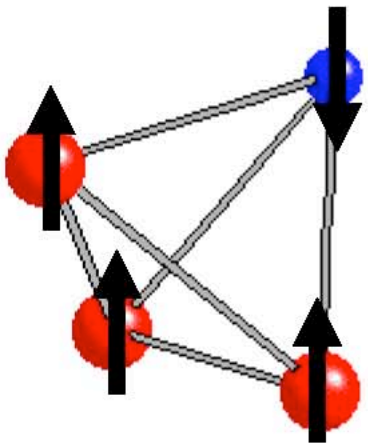
1/2 magnetization plateau in $CdCr_2O_4$

ferrimagnetic state with 3 up-1 down spin configuration

Plateau state

$M=1.5\mu_B=1/2 \times 3\mu_B$ (full moment of Cr^{3+} $S=3/2$)



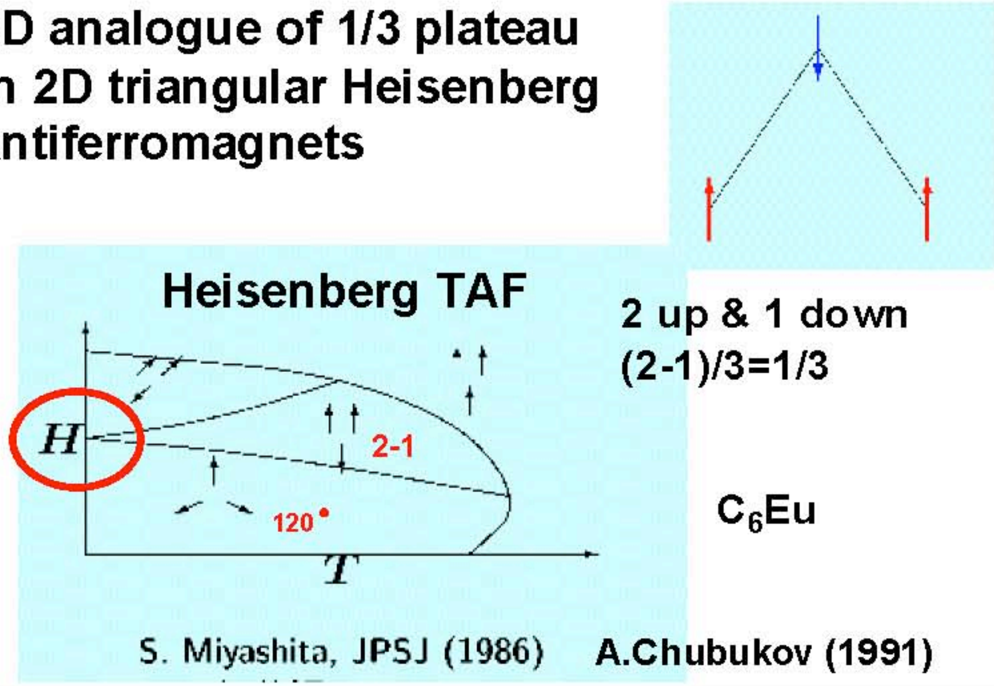


3↑ − 1↓ = 2↑

$2/(1+3) = 1/2$

three-up & one-down in each tetrahedron

3D analogue of 1/3 plateau in 2D triangular Heisenberg antiferromagnets



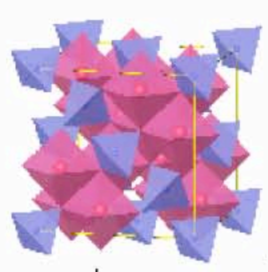
2 up & 1 down
(2-1)/3=1/3

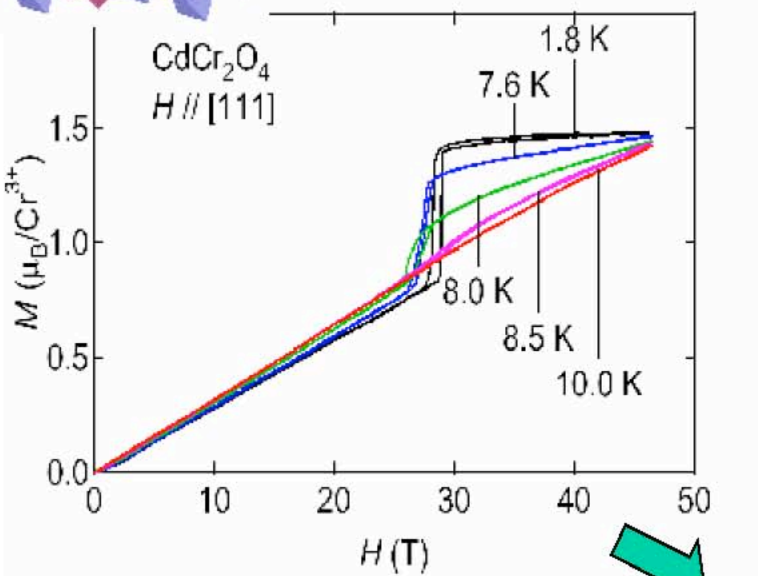
C_6Eu

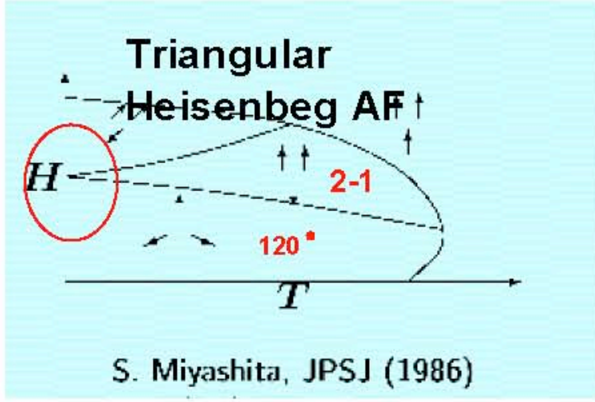
S. Miyashita, JPSJ (1986)

A.Chubukov (1991)

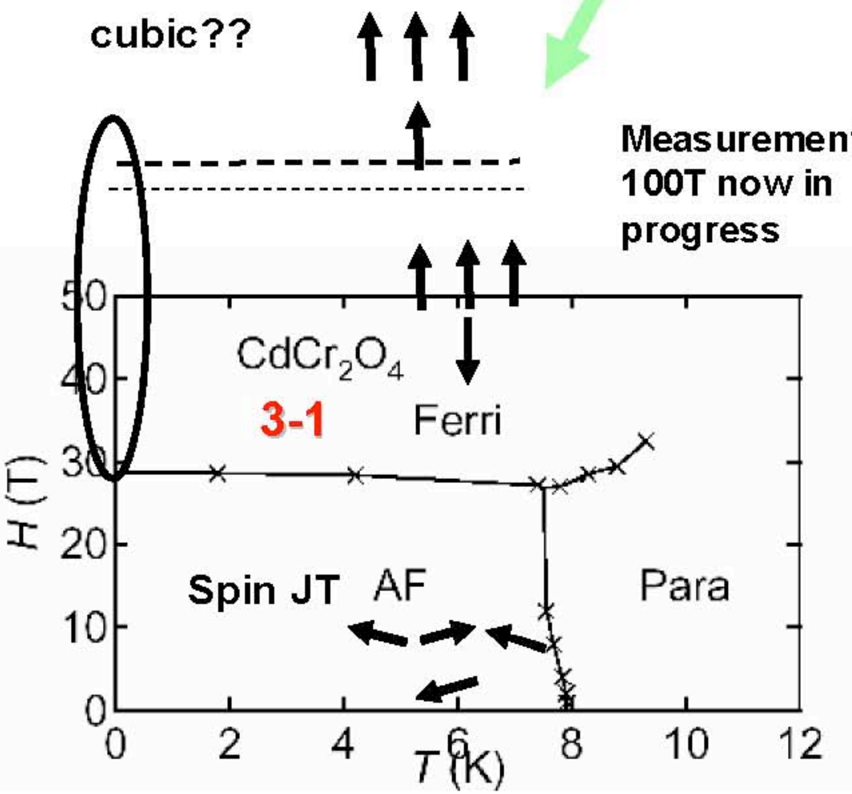
H-T phase diagram of $CdCr_2O_4$







A.Chubukov (1991)



Measurement up to 100T now in progress

Stability of ½ plateau state over 20 T remarkable

coupling with lattice **plays an important role**

Need for spin-lattice coupling to get stable plateau

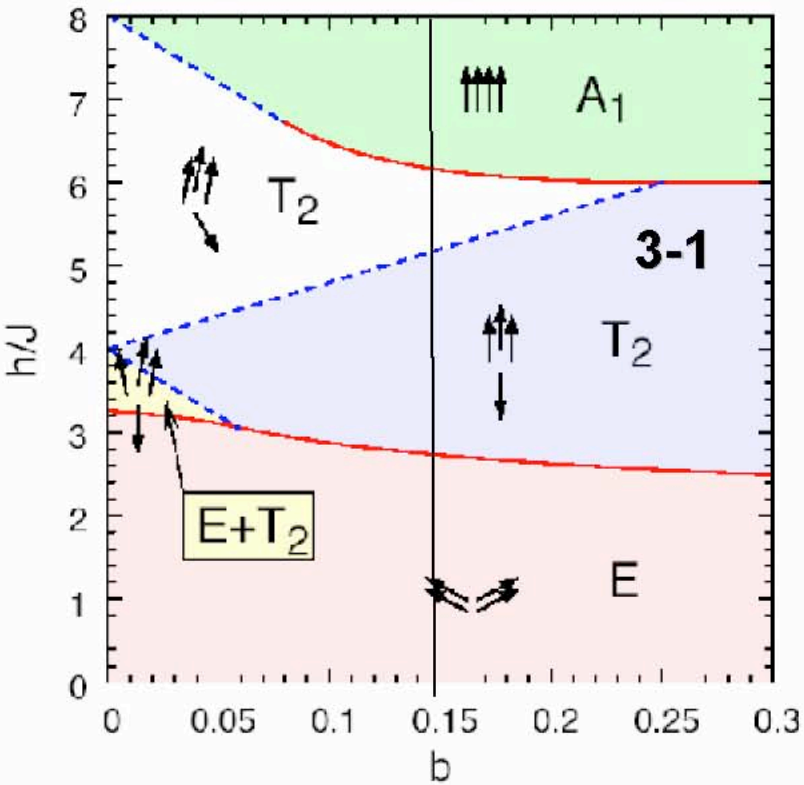
K.Penc, N.Shannon and
H.Shiba, submitted

Heisenberg pyrochlore AF

$$\mathcal{H} = \sum_{\langle i,j \rangle} J \left[\mathbf{S}_i \mathbf{S}_j - b(\mathbf{S}_i \mathbf{S}_j)^2 \right] - \mathrm{h} \sum_i \mathbf{S}_i \ .$$

biquadratic term represents spin-lattice coupling

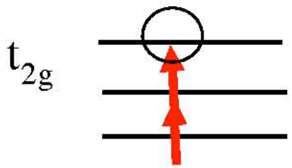
b: dimensionless coupling constant



ZnV_2O_4 , CdV_2O_4 S=1 pyrochlore AF

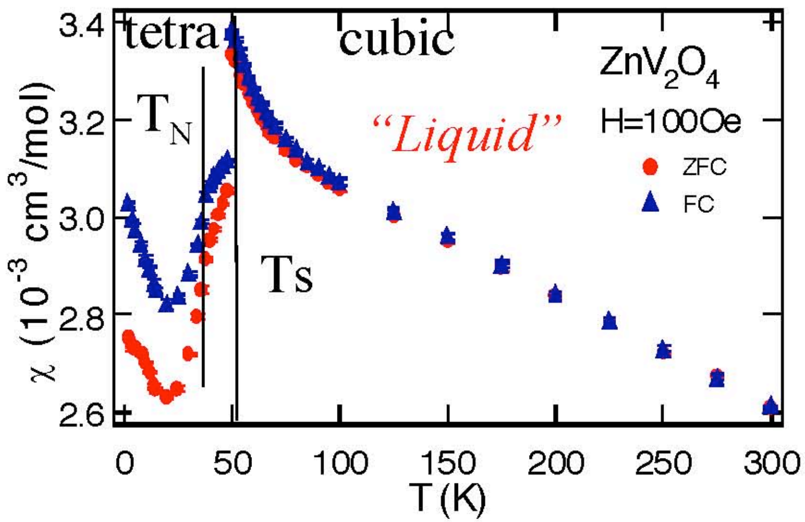
More fun out of $CdCr_2O_4$

V^{3+} (d^2, S=1)



T_{st} = 50K
> T_N = 40K
θ_{CW} = -420K

$T_N/\ |\theta_{CW}|$ = 0.095



Additional ingredient:
orbital degrees of freedom

Cubic-Tetragonal phase transition occurs first

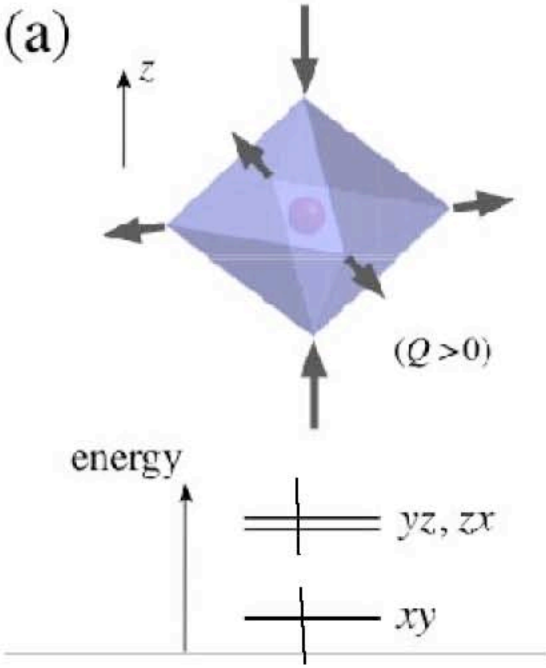
$T_N \neq T_S$

Suppression of spin frustration by orbital ordering → AF ordering

Simple orbital JT at Ts?? no

Stabilization of AF ordering by orbital ordering in ZnV_2O_4

$T<T_S$



compression along c-axis

Not simple JT

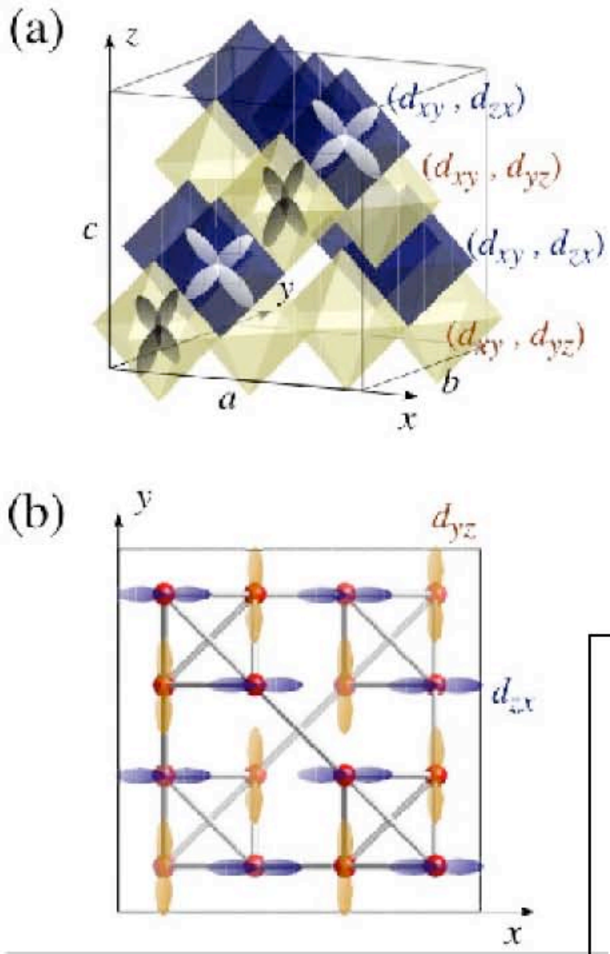
Orbital degeneracy remains

d_{yz}, d_{zx} orbital ordering

→ anisotropic spin coupling, stabilizing AF

gain magnetic E

Motome



Recent structural analysis support for the Motome picture

$LiVO_2$ (triangular)

orbital ordering & formation of spin singlet

Guide map of "simple" spinel oxides

Heavy Fermion charge & spin liquid (points to LiV_2O_4)
C.Urano, S.Kondo and H.T et. al PRL(00)

Frustrated charge ordered insulator
3-1 type CO "valence skipping" (points to AlV_2O_4)
K.Matsuno, H.T et al PRL(03)

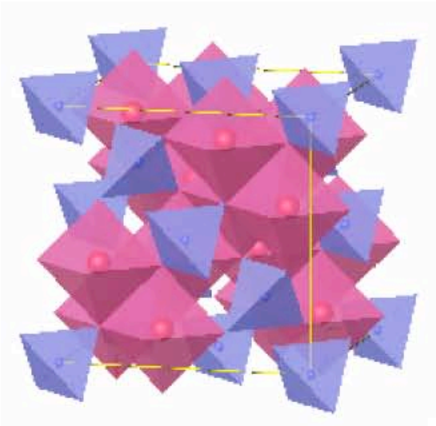
ionic & nonmagnetic ↓ / transition metal ↓

	M= Ti	V	Cr	Mn
$Li^{1+} M_2^{3.5+} O_4$ (Al^{3+}) "**Charge**" frustration 1 : 1 3+ & 4+, mixed valent	$d^{0.5}$ $LiTi_2O_4$ BCS SC	$d^{1.5}$ LiV_2O_4 ←	$d^{2.5}$ ($LiCr_2O_4$) ‖ ***AlV_2O_4***	$d^{3.5}$ $LiMn_2O_4$
$Zn^{2+} M^{3+}_2 O_4$ (Mg^{2+}, Cd^{2+}) "**Spin**" frustration all 3+, AF Ins.	d^1 ($ZnTi_2O$) $MgTi_2O_4$	d^2 ZnV_2O_4 MgV_2O_4 CdV_2O_4	d^3 $ZnCr_2O_4$ $MgCr_2O_4$ $CdCr_2O_4$	d^4 $ZnMn_2O_4$

Frustrated AF magnet
H.Ueda & H.T et al. PRL submitted

Suppression of frustration by coupling with lattice

Charge frustration on pyrochlore lattice



$Al^{3+}V_2^{2.5+}O_4$ spinel

Mixed valent At first glance,
with 1:1 mixture of V^{2+}(d^3, s=3/2) & V^{3+}(d^2, s=1)

Verway problem?

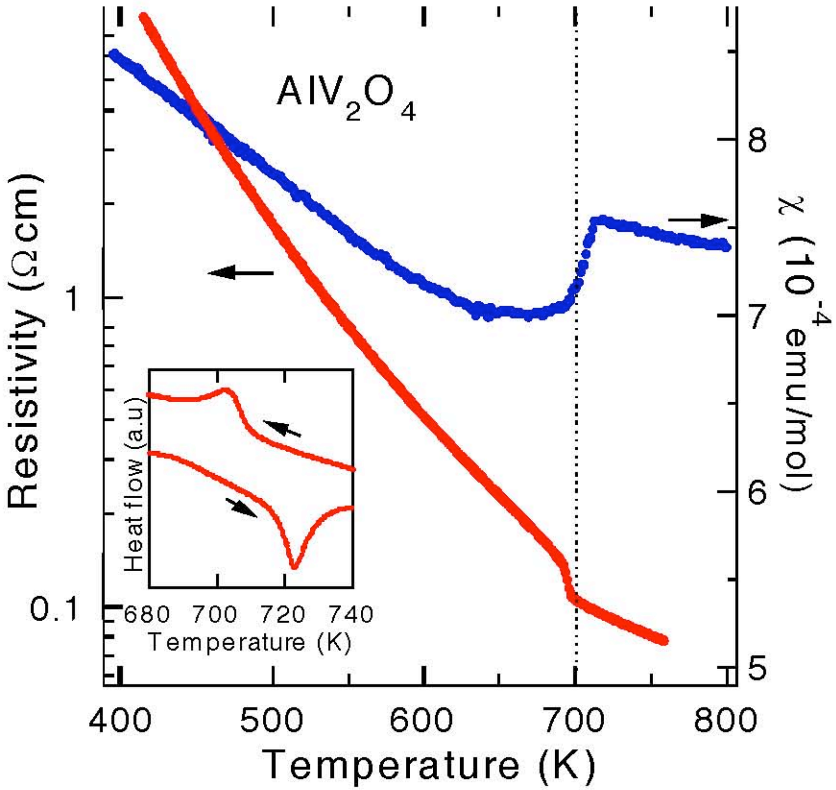
CO(OO) hard to achieve due to frustration – Fe_3O_4

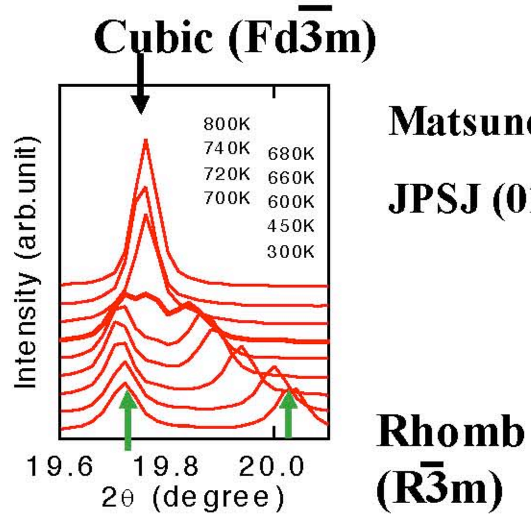
Unexpectedly, very stable CO observed

Overcoming the frustration (degeneracy) by having valence skipping configuration, V^{2+}- V^{4+}, with 3:1 ratio

One of the first pyrochlore systems with CO pattern identified

700 K anomaly in χ & ρ accompanied with structural phase transition from Cubic to Rhombhedral

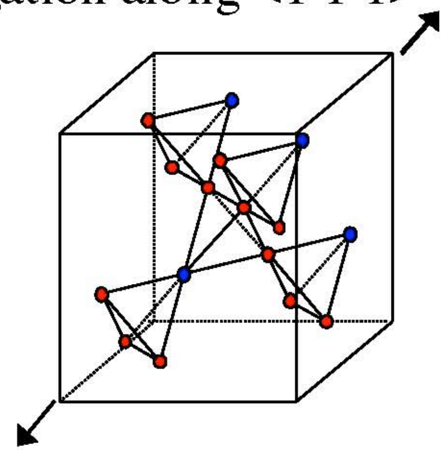




Matsuno et al.

JPSJ (01), PRL (93)

elongation along <1 1 1>



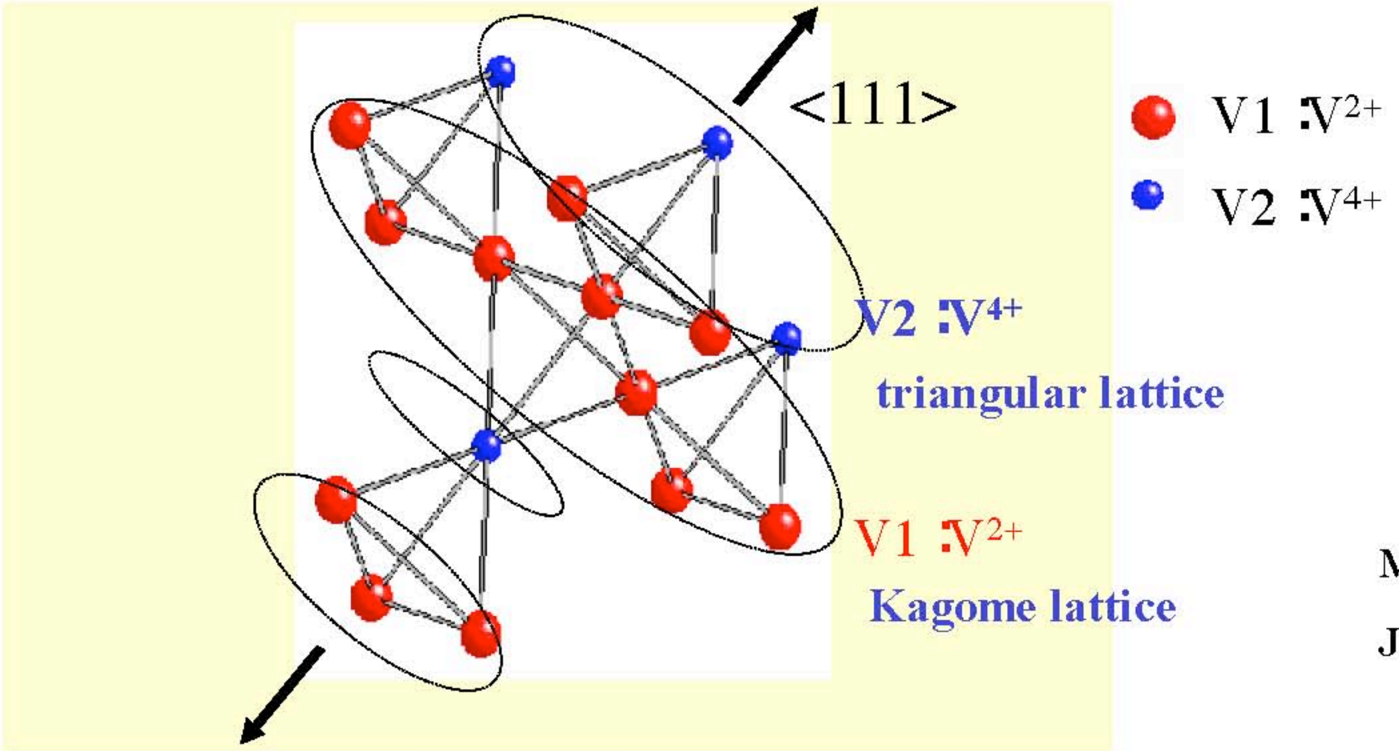
- Resistivity insulating even above RT

Charge ordered? ‘

3-1charge ordering (V^{2+} - V^{4+}) below 700 K in AlV_2O_4

Rhombhedral phase - elongated along <111>

V1、V2 inequivalent (**V1:V2=3:1**)



Matsuno et al.

JPSJ (01), PRL (93)

- Not compatible with 1:1 2+, 3+
- Valence skipping configuration, 3:1 **2+(V1), 4+(V2)**

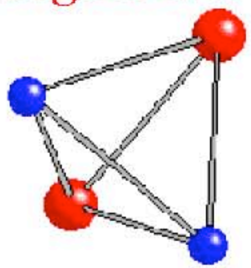
$$Al_4^{3+}V_3^{2+}V_1^{4+}O_{16}$$

(2.5-δ (V1)、 2.5+3δ (V2) , δ =0.5 ionic limit)

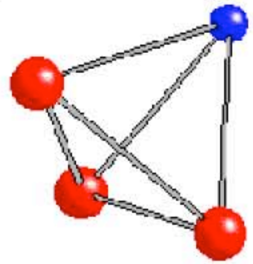
Geometrical frustration &charge ordering

Anderson(56)

1-1 order ：Fe_3O_4 (Verway)	**3-1 order ：AlV_2O_4**
strongly degenerate due to geomery	**degeneracy suppressed** unique to charge frustration!

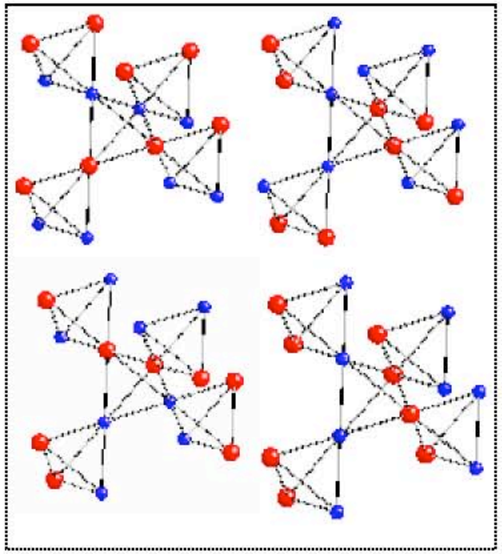


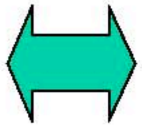
1:1 2+&3+

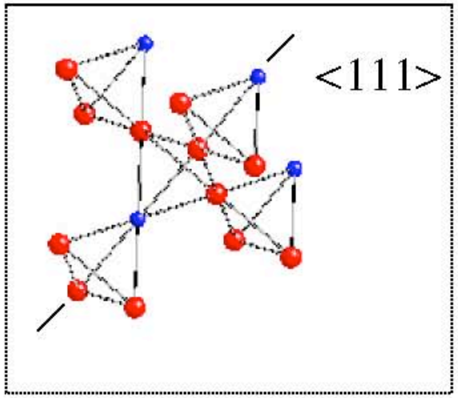


3:1 2+&4+

Valence skipping





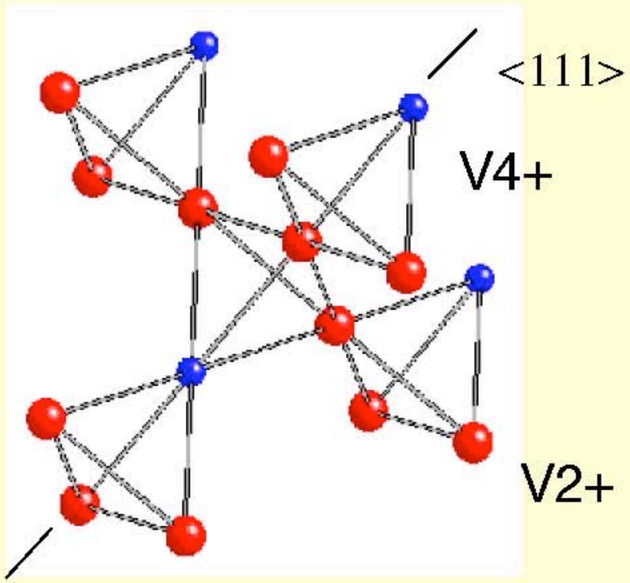


& coupled with Rhomb distortion

Fe_3O_4(1-1order)		AlV_2O_4(3-1order)
T_{CO} :120K orbital ordering?	<	T_{CO}:700K Stable!

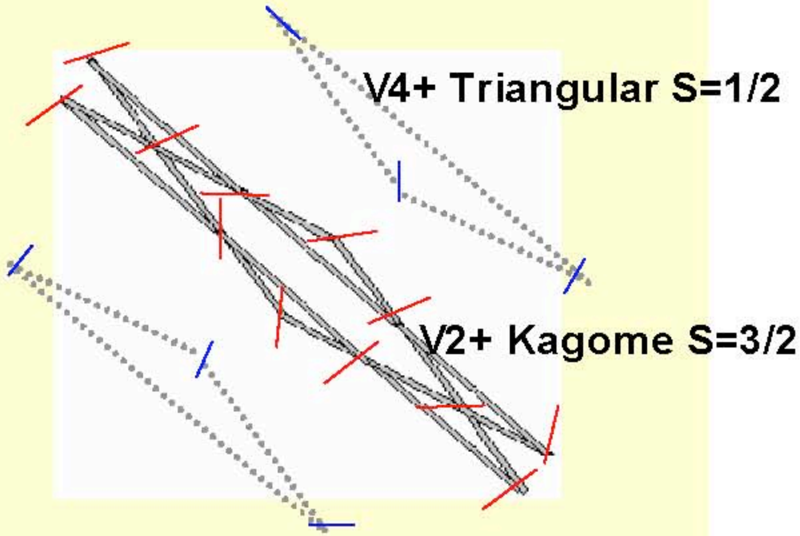
Charge ordering in geometrically frustrated AlV_2O_4 — Contrast between spin & charge

Charge



"Solid"

Spin



"Liquid"

3-1 order at 700 K

flexible

No long range order detected

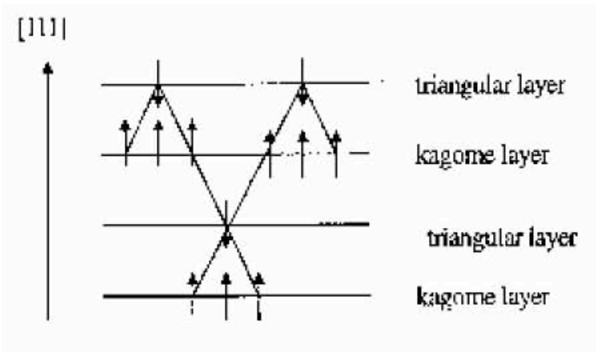
Not flexible always 1:1 up & down

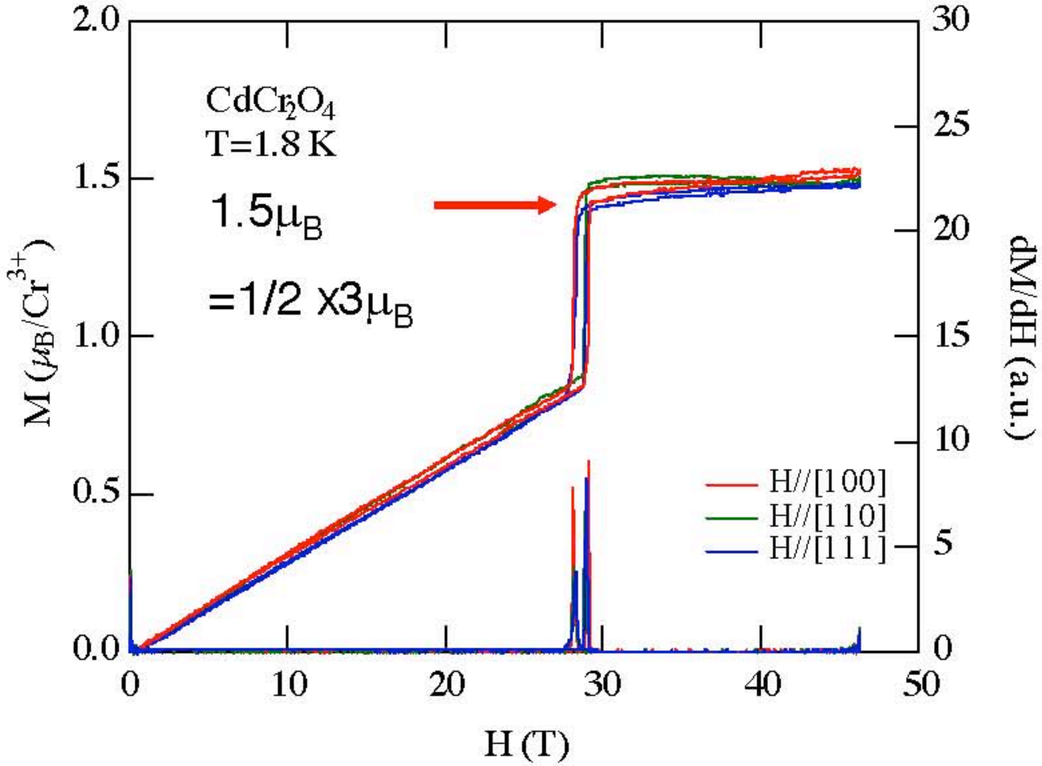
1/2 magnetization plateau in $CdCr_2O_4$ – spin version of 3-1 ordering in AlV_2O_4

3-1 spin ordering in $CdCr_2O_4$ three-up & one-down

$3\uparrow - 1\downarrow = 2\uparrow$

$2/(1+3) = ½$





couple with Rhombhedral distortion ??

Guide map of “simple” spinel oxides

Heavy Fermion charge & spin liquid
C.Urano, S.Kondo and H.T et. al PRL(00)

Frustrated charge ordered insulator
3-1 type CO “valence skipping”
K.Matsuno, H.T et al PRL(03)

ionic & nonmagnetic ↓ transition metal ↓

	M= Ti	V	Cr	Mn
$Li^{1+} M_2^{3.5+} O_4$ (Al^{3+}) “**Charge**” frustration 1 : 1 3+ & 4+, mixed valent	$d^{0.5}$ $LiTi_2O_4$ BCS SC	$d^{1.5}$ ***LiV_2O_4***	$d^{2.5}$ ($LiCr_2O_4$) = AlV_2O_4	$d^{3.5}$ $LiMn_2O_4$
$Zn^{2+} M^{3+}_2 O_4$ (Mg^{2+}, Cd^{2+}) “**Spin**” frustration all 3+, AF Ins.	d^1 ($ZnTi_2O$) $MgTi_2O_4$	d^2 ZnV_2O_4 MgV_2O_4 CdV_2O_4	d^3 $ZnCr_2O_4$ $MgCr_2O_4$ $CdCr_2O_4$	d^4 $ZnMn_2O_4$

Frustrated AF magnet
H.Ueda & H.T et al. PRL submitted

Suppression of frustration by coupling with lattice

Verway system without charge ordering –heavy fermion oxide LiV_2O_4

•$V^{3.5+}$ mixed valent 1:1 V^{3+} & V^{4+}
$3d^{1.5}$ 1.5 electron /V → t_{2g}

•Situation analogous to AlV_2O_4

But, at glance, do nothing to suppress the degeneracy

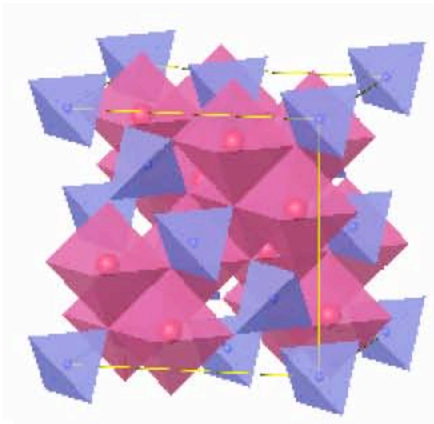
•Cubic to 4K - All V crystallographically equivalent

No charge ordering

•No magnetic ordering to 20mK

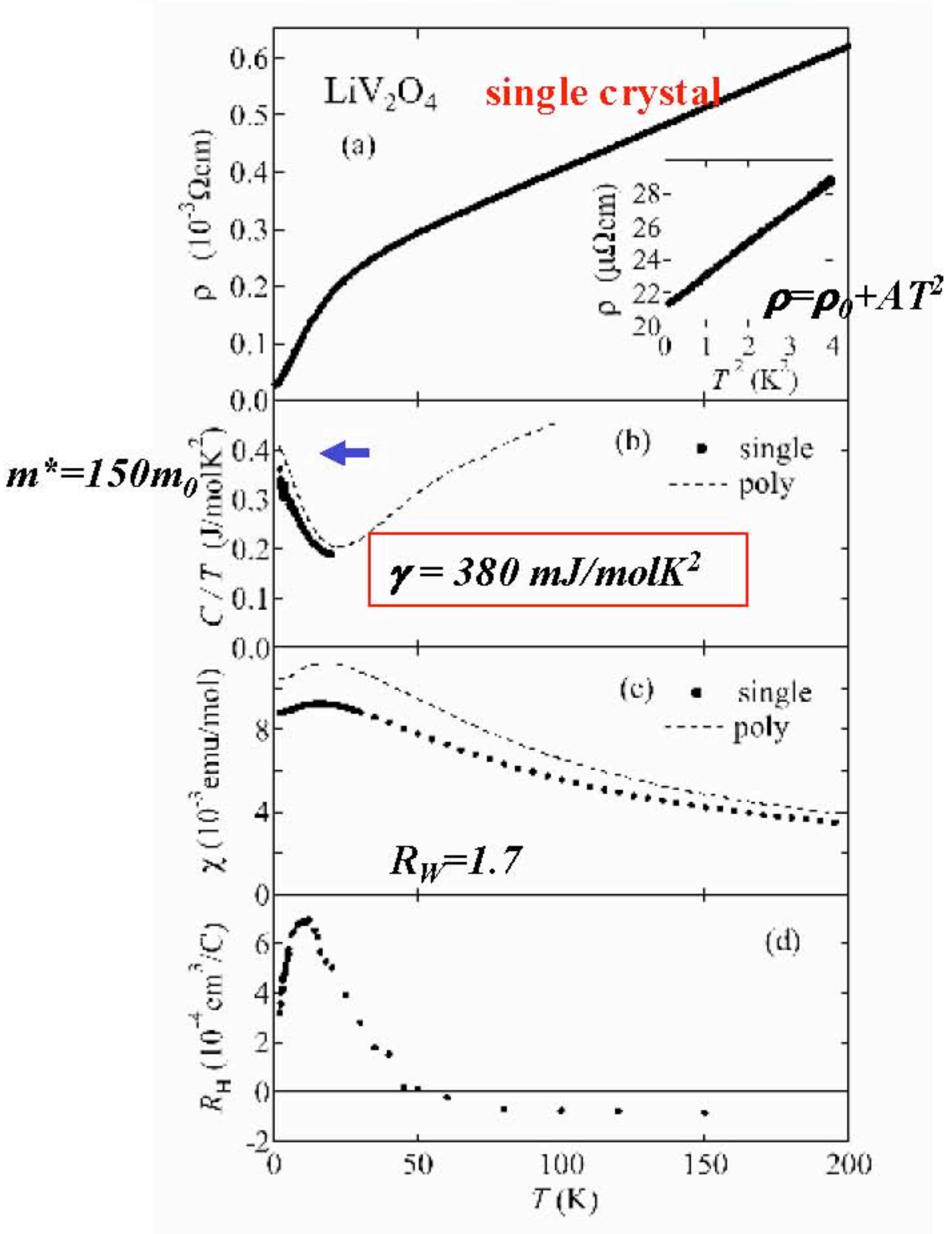
——— The first heavy fermion oxides

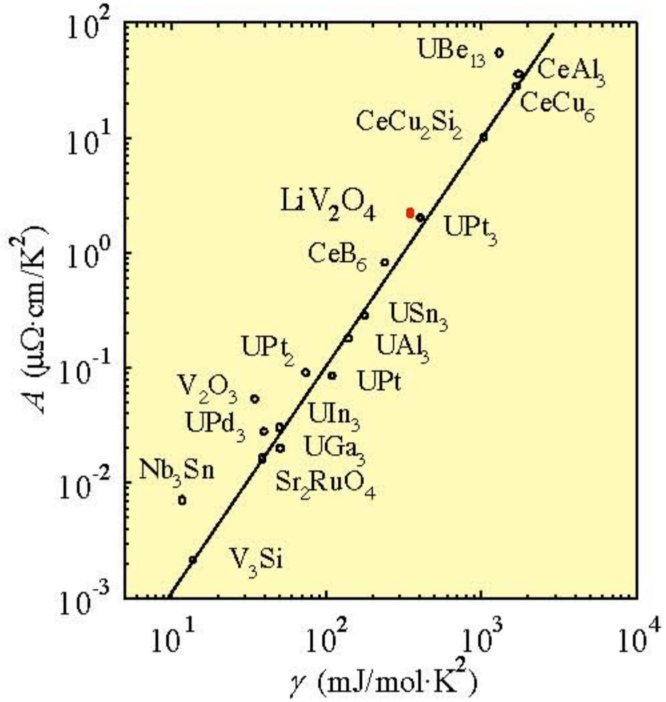
S.Kondo et al.



Heavy Fermion oxide LiV_2O_4

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





Kadowaki-Woods

T^*=20-30 K

Origin of the heavy quasiparticle mass?

Only t_{2g} electrons involved

-Kondo Scenario? LDA+U (Anisimov *et al.*)

1.5 d-electron 0.5 e_g (itinerant)+ 1 a_{1g} (localized)

trigonal field splitting

-Geometrical frustration?

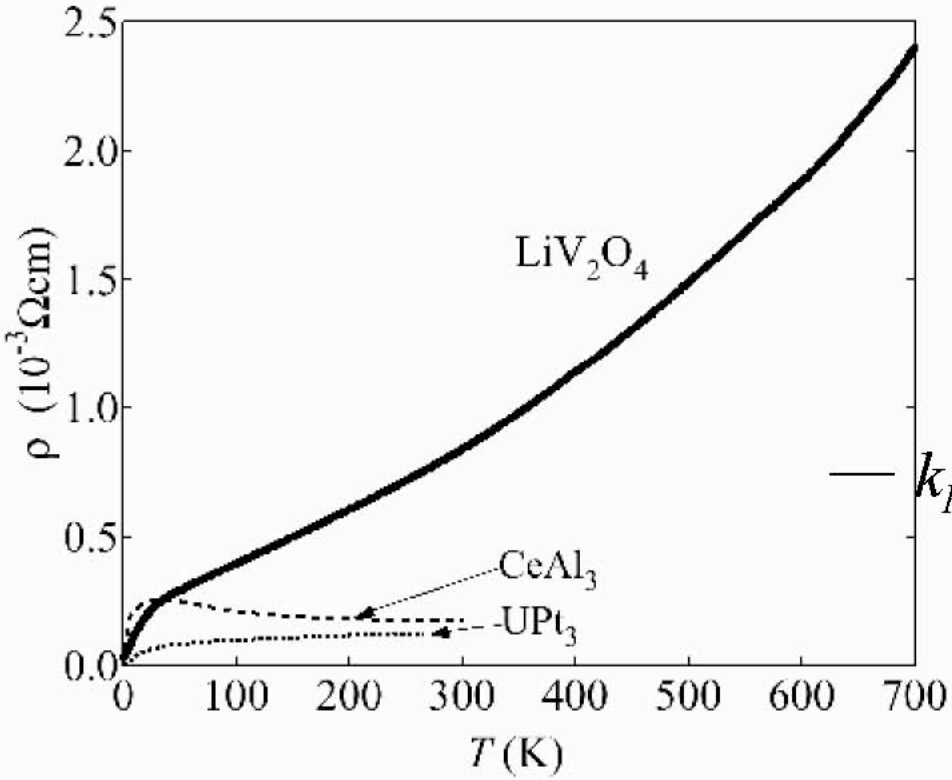
A. George
P.Coleman
P.Fulde

A Fermi liquid critically close to charge ordered insulating state but without magnetic ordering, which is realized by charge & spin frustration

HF state in LiV_2O_4 is located at the critical vicinity to CO state,

"Bad metal" behavior in LiV_2O_4

analogous to TMOs near Mott(CO) transition, indicative of close proximity to CO



— $k_F l = 1$

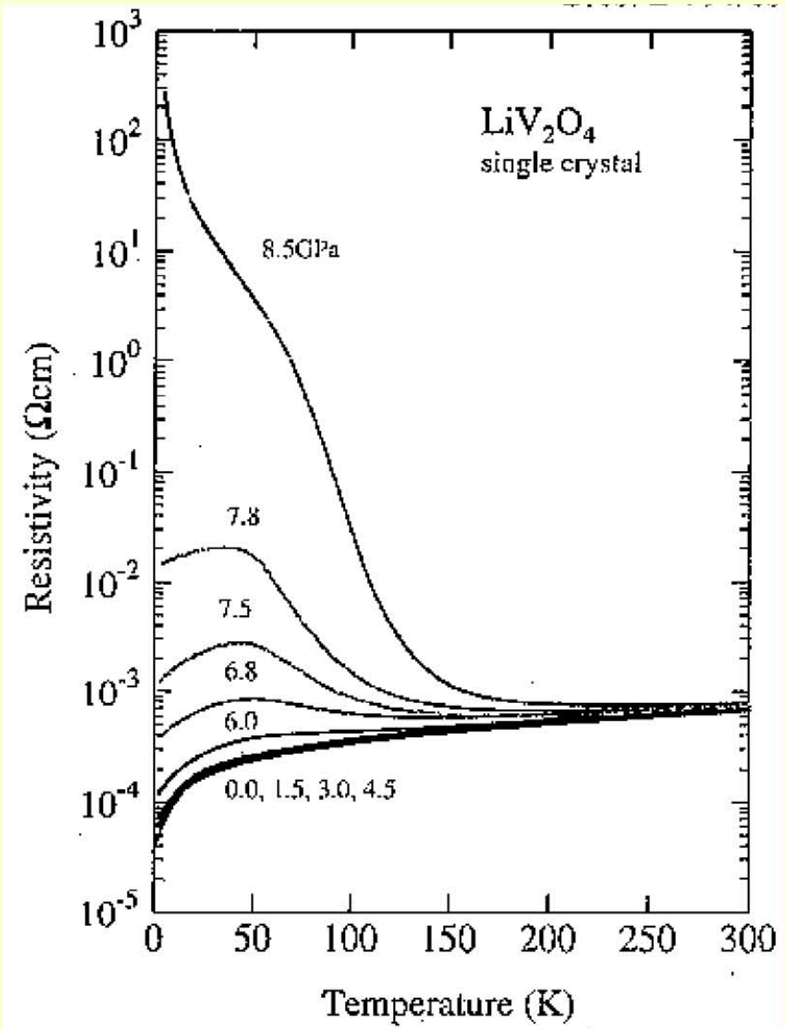
Distinct from conventional HFs

absence of resistivity saturation

Metallic behavior above IR limit

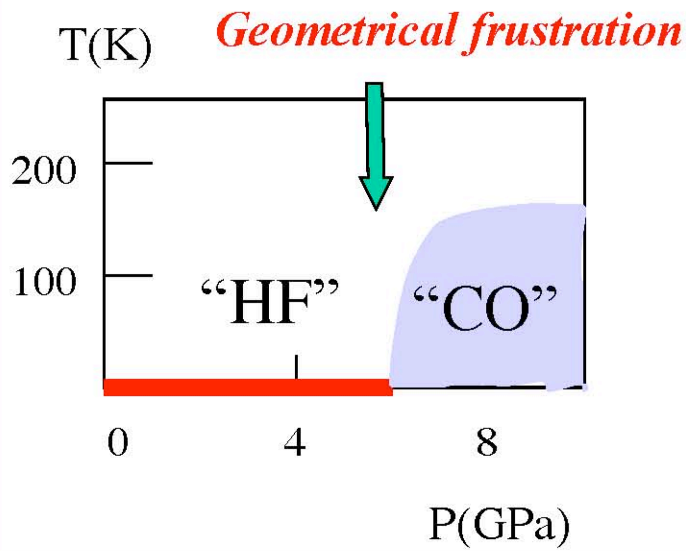
C.Urano, H.T et al PRL 85, 1052 (00)

Switching from HF metal to Charge Ordered Insulator – HF is a melted COI



Pressure induced metal-insulator transition

Very likely CO transition because of the mixed valent nature (formally 1:1 V^{3+}, V^{4+})

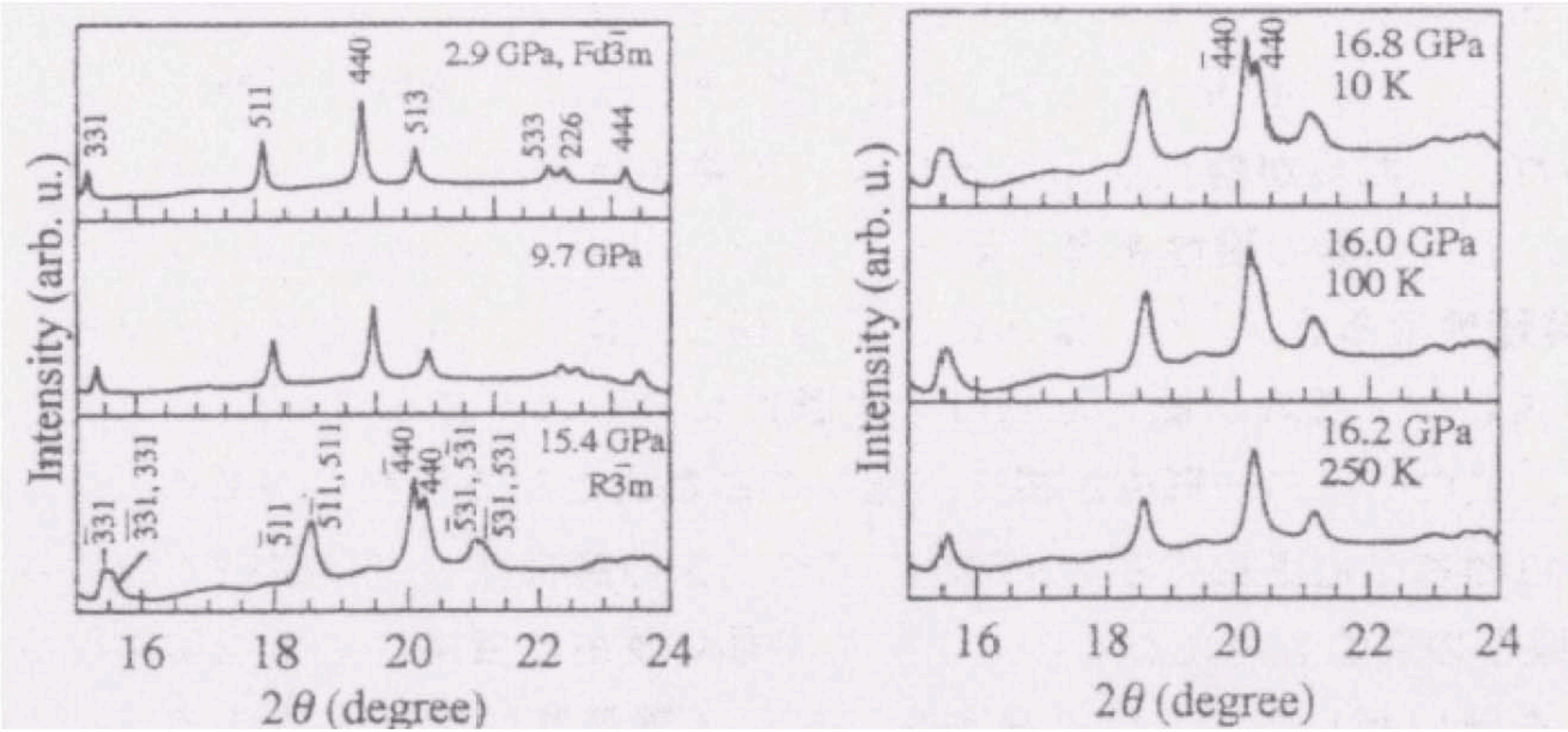


charge liquid critically close to COI but no magnetic ordering due to spin frustration

Pressure induced Cubic-Rhombhedral transition

Osaka G

HP Ins phase, possibly the same CO pattern as AlV_2O_4
$V4+$-$V2+$ or $V3+$-$V5+$?



Summary

Geometrical frustration dominates the physics of spinel oxides

AlV_2O_4 — **Lift charge degeneracy: 3-1 ordering, a text book example of CO on the spinel (pyrochlore) lattice**

$CdCr_2O_4$ — **Lift spin degeneracy: Spin JT system**

spin version of 3-1 ordering realized in magnetic fields as a magnetization plateau

3-1 ordering, a common way to suppress frustration

LiV_2O_4 — ***heavy fermion ground state realized in the presence of CO instability (3-1 ordering??)***

HF formation is linked with the physics of CO on the frustrated lattice

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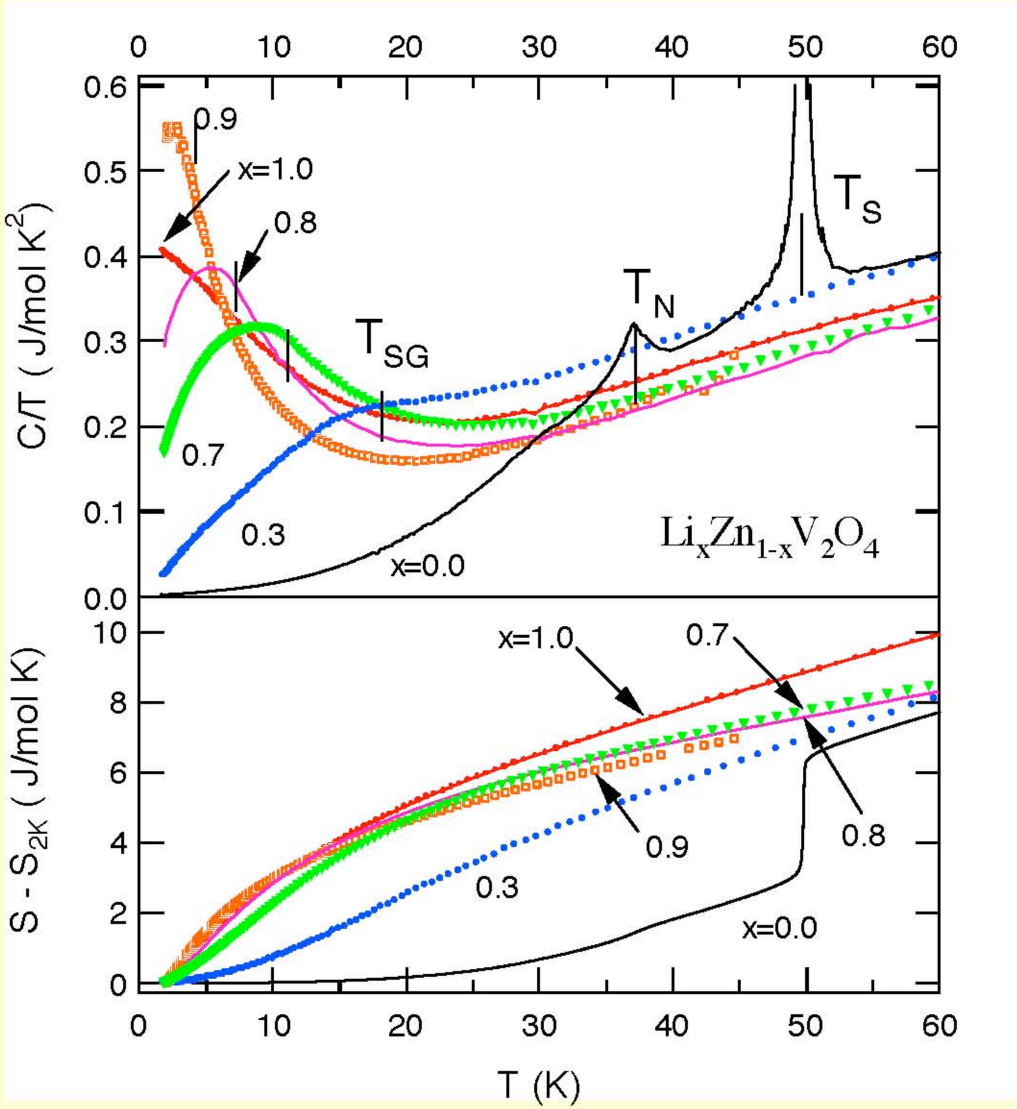
Evolution of C(T) from frustrated magnet to HF



x-independent large entropy S(50K)~50%Rln3/V

Critically close to CO Ins.
(charge frustration)

But can not quench spin degree of freedom due to spin frustration

Hole Doping

ZnV_2O_4 + 1/2 hole/V = LiV_2O_4