Santa Barbara, 2004

Spin and Charge Frustration in Spinel Oxides

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Collaborators
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Exotic phases produced by geometrical frustration on pyrochlore lattice

..Introduction

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

spin JT phase and its magnetic field control

..Charge frustration in AlV_2O_4

.....3-1 charge ordering .valence skipping)

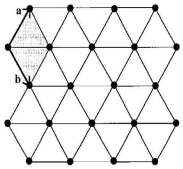
..Charge & Spin Liquid State

.... .Heavy Fermion Oxides LiV_2O_4

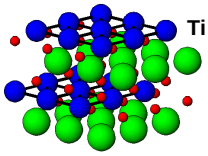
5. Comment on CO in pseudo gap phase of cuprates

Yazdani

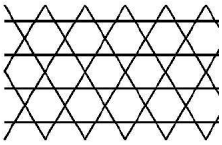
Geometrically Frustrated Lattices



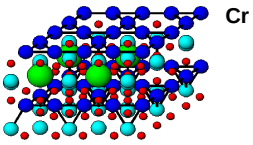
Triangular lattice



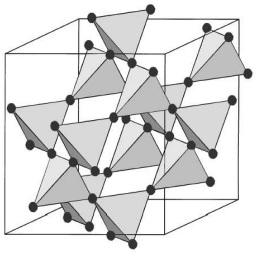
$NaTiO_2$, $LiVO_2$, ...



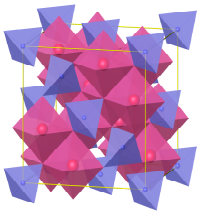
Kagome lattice



$SrCr_9Ga_3O_{19}$

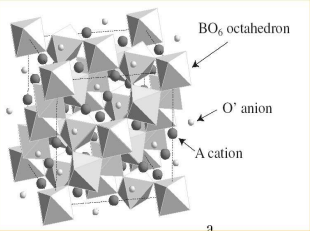


Pyrochlore lattice



Spinel (AB_2O_4)

$Fe_3O_4=FeFe_2O_4$



Pyrochlore($A_2B_2O_7$)

$Y_2Mo_2O_7$

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

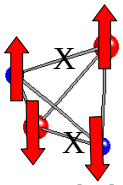
Orbital Frustration?

Exotic Phase (transition) ?

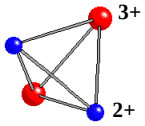
-Nature always tries to reduce the degeneracy

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

Frustrated AF magnet

Spin driven structural phase transition – spin JT
Its magnetic field control
H.Ueda & H.T et al. PRL submitted

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

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

θ_{CW} = –90K, T_N = 7K

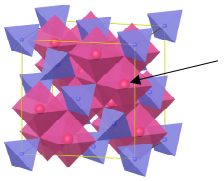
$T_N/|\theta_{CW}|$ = 0.08

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

θ_{CW} = –350K, T_N = 13K

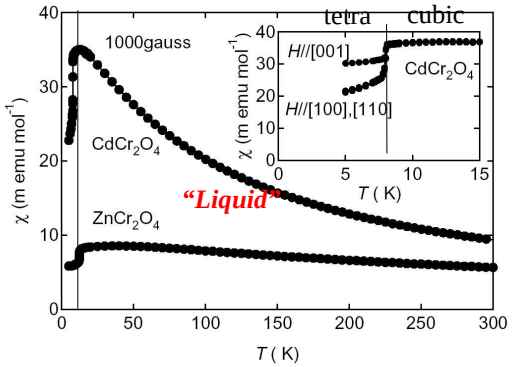
$T_N/|\theta_{CW}|$ = 0.04

Geometrical frustration evident



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

t_{2g}



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

Emergent excitations in a geometrically frustrated magnet

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T. H. Kim‡§ & S.-W. Cheong‡

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† Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218, USA
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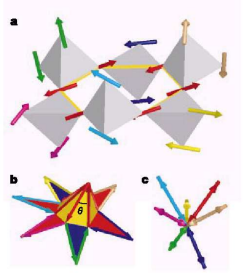
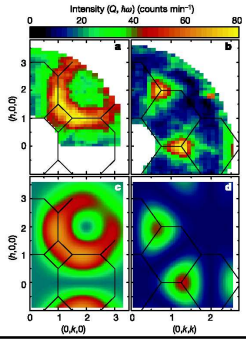
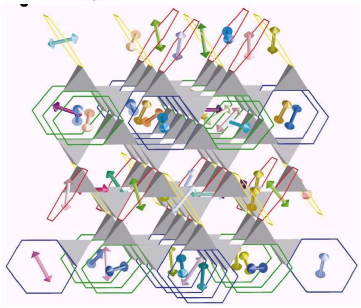






Spin JT transition in $CdCr_2O_4$ and $ZnCr_2O_4$ spinels

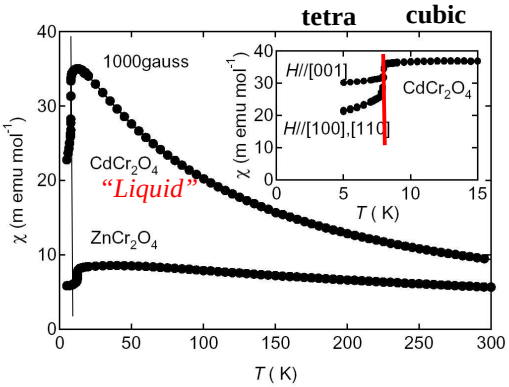
Cr^{3+}·(d^3; S=3/2)

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

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

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

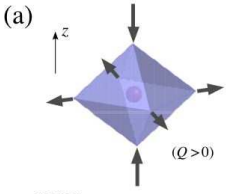
$T_N = T_S = 13K << \theta_{CW}$



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

accompanied with 1st order

Cubic to Tetragonal transition



no orbital degree of freedom

▼

Spin- JT transition

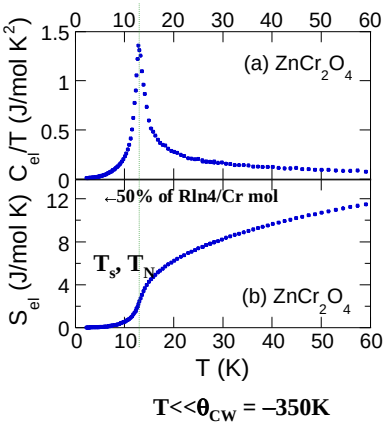
remove "spin degeneracy" by lattice distortion

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

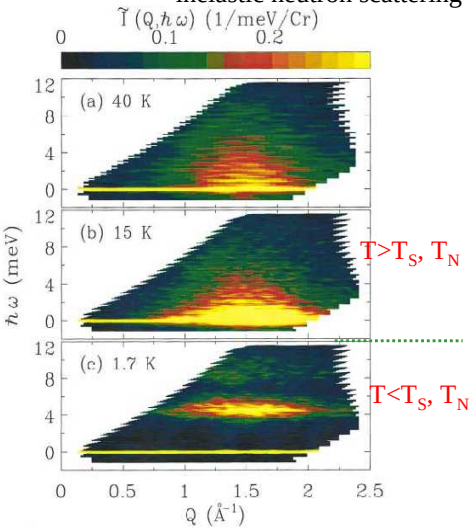
Gigantic entropy at low T – support for spin-JT

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

inelastic neutron scattering



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



$T > T_S, T_N$

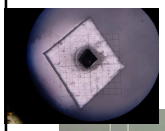
$T < T_S, T_N$

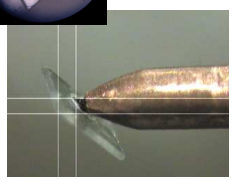
Complicated lattice distortion below T_N – support for spin-JT

Low T structure more complicated than the simple elongation of cubic <001> (orbital JT) should be compatible with non-colinear Neel state with 2 x 2 x2 magnetic unit cell

O.Tchernyshyov PRL (03)

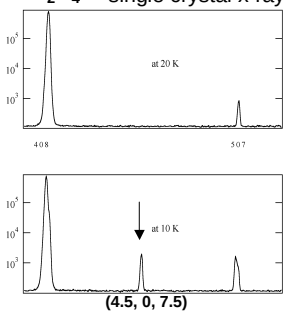
→.Revisit to low-T crystal structure of $ZnCr_2O_4$





Domains removed by applying uniaxial pressure

$ZnCr_2O_4$ single crystal x-ray

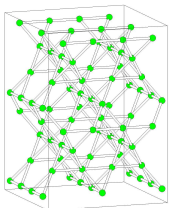


2x2x2 superlattice

$I_{4\bar{3}2}$

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

associated with large spin-lattice coupling ?

eventually cubic ?

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

Ordered local spin excitations coupled strongly with lattice

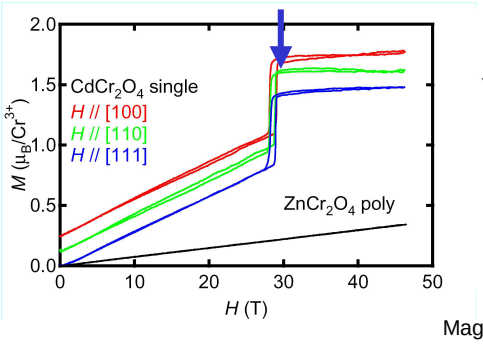
Magnetic field control of frustration – M–H curve of $CdCr_2O_4$ at 1.8 K

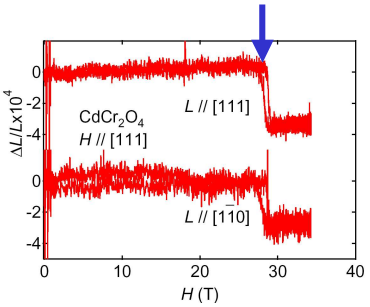
- **metamagnetic transition to a plateau state at 28 T (first order)**

plateau at M=1.5μ_B 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





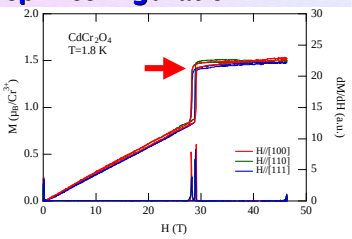
Magnetostriction comparable magnitude with to tetragonal ditortion
evidence for spin JT

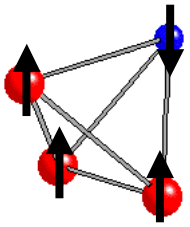
1/2 magnetization plateau in $CdCr_2O_4$

ferrimagnetic state with 3 up–1 down spin configuration

Plateau state

M=1.5μ_B=1/2 x3μ_B (full moment of Cr^{3+} S=3/2)



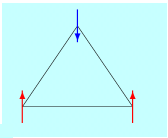


3↑□□□↓□□□↑□

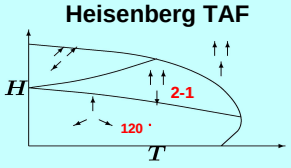
2/(1+3) = 1 / 2

three-up & one-down in each tetrahedron

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



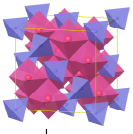
Heisenberg TAF

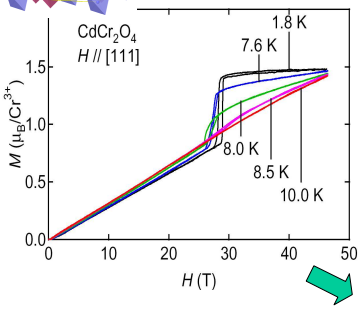


S. Miyashita, JPSJ (1986)

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

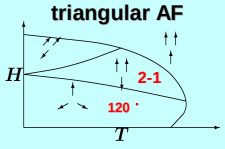
H–T phase diagram of $CdCr_2O_4$





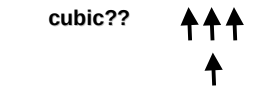
Coupling with lattice plays an important role

triangular AF

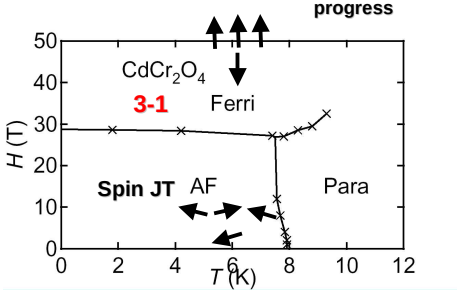


S. Miyashita, JPSJ (1986)

cubic??



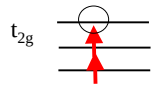
Measurement up to 100T now in progress



More fun out of $CdCr_2O_4$

ZnV_2O_4 , CdV_2O_4 S=1 pyrochlore AF

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



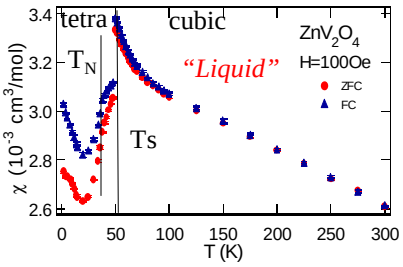
T_{st} = 50K
> T_N = 40K
θ_{CW} = −420K

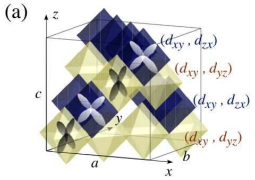
$T_N / |\theta_{CW}|$ = 0.095

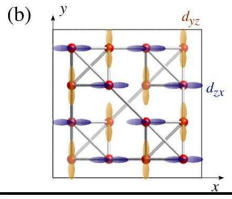
Additional ingredient: orbital degrees of freedom

Suppression of spin frustration by ..... ordering → AF ordering

$T_N \neq T_S$







d_{yz}, d_{zx} ordering
Motome

$d_{yz} \pm i\, d_{zx}$
O.Tchernyshyov

$LiVO_2$ (triangular)
orbital ordering & formation of spin singlet

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

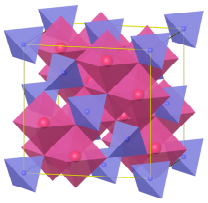
M=	Ti	V	Cr	Mn
$Li^{1+} M_2^{3.5+} O_4$ (Al^{3+}) "**Charge**" frustration 1 : 1 3+ & 4+, mixed valent	$d^{0.5}$ $LiTi_2O_4$ BCS SC	$d^{1.5}$ LiV_2O_4	$d^{2.5}$ $(LiCr_2O_4)$ ‖ AlV_2O_4	$d^{3.5}$ $LiMn_2O_4$
$Zn^{2+} M^{3+}_2 O_4$ (Mg^{2+}, Cd^{2+}) "**Spin**" frustration all 3+, AF Ins.	d^1 $(ZnTi_2O)$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

Charge frustration on pyrochlore lattice

coupling with lattice and orbitals to remove degeneracy – Fe_3O_4



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

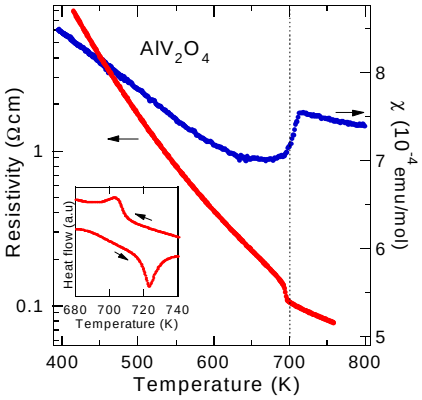
Mixed valent At first glance,
with 1:1 mixture of $V^{2+}(d^3, s=3/2)$ &$V^{3+}(d^2, s=1)$

Verway problem

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

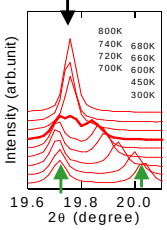
700 K anomaly in χ&ρ accompanied with structural phase transition from Cubic to Rhombhedral



- Resistivity insulating even above RT

Charge ordered? '

Cubic ($Fd\bar{3}m$)

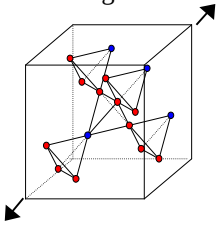


Matsuno et al.

JPSJ (01), PRL (93)

Rhomb ($R\bar{3}m$)

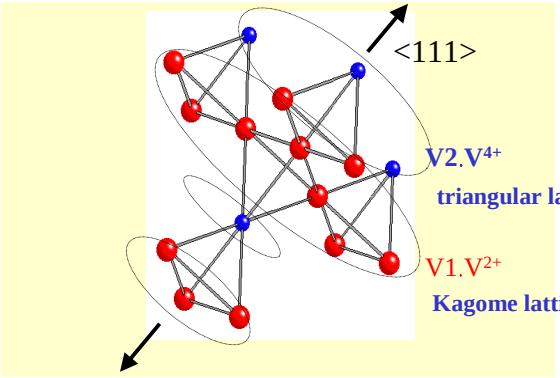
elongation along <1 1 1>



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)**

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

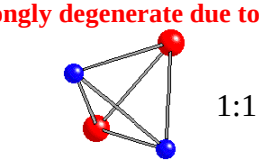
(2.5-δ(V1). 2.5+3δ (V2) ,δ=0.5 ionic limit)

Geometrical frustration &charge ordering

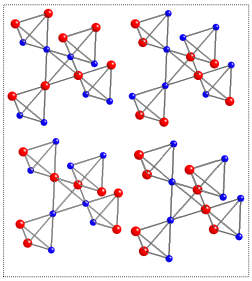
Anderson(56)

1-1 order. Fe_3O_4 (Verway)

strongly degenerate due to geomery



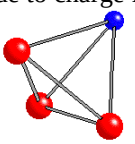
1:1 2+&3+



3-1 order. AlV_2O_4

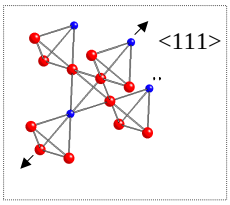
degeneracy suppressed

unique to charge frustration!



3:1 2+&4+

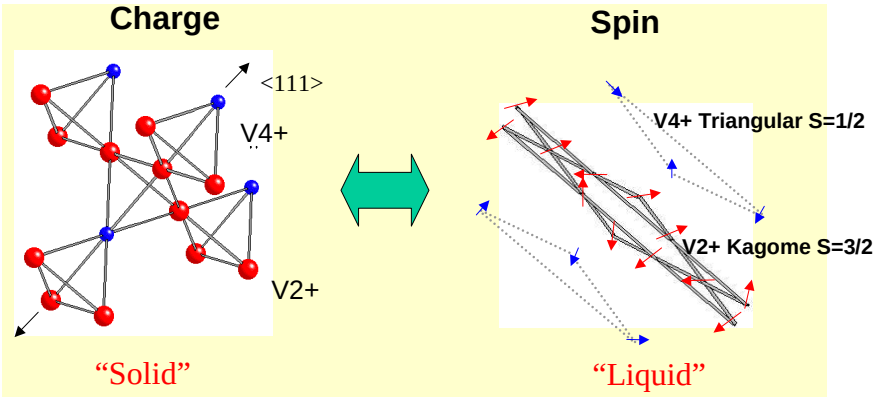
Valence skipping



& 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



3-1 order at 700 K

flexible

No long range order detected

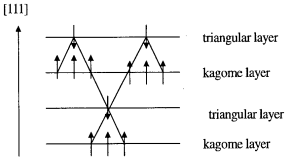
Not flexible always 1:1 up & down

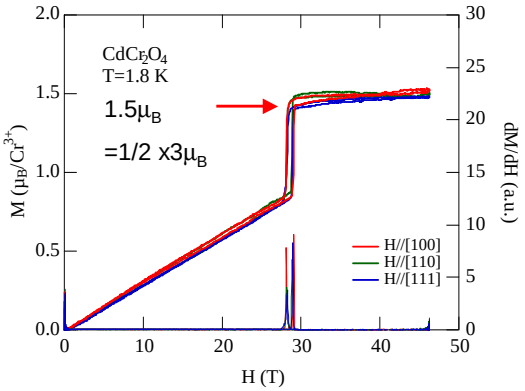
1/2 magnetization plateau in $CdCr_2O_4$ – spin version of 3-1 ordering in AlV_2O_4

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

3↑□□□↓□□□↑□

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
	$d^{0.5}$	$d^{1.5}$	$d^{2.5}$	$d^{3.5}$
$Li^{1+} M_2^{3.5+} O_4$ (Al^{3+}) "**Charge**" frustration 1 : 1 3+ & 4+, mixed valent	$LiTi_2O_4$ BCS SC	***LiV_2O_4***	$(LiCr_2O_4)$ || AlV_2O_4	$LiMn_2O_4$
$Zn^{2+} M^{3+}_2 O_4$ (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

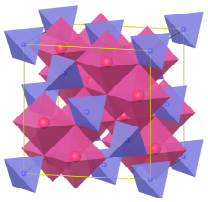
But, at glance, do nothing to suppress the degeneracy

- Cubic to 4K - All V crystallographically equivalent

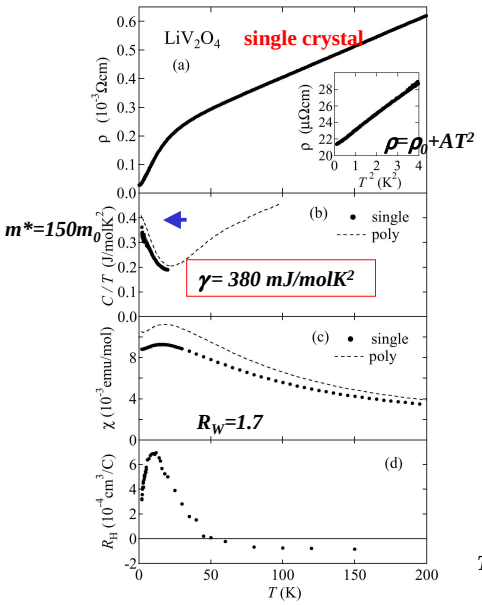
No charge ordering

- No magnetic ordering to 20mK

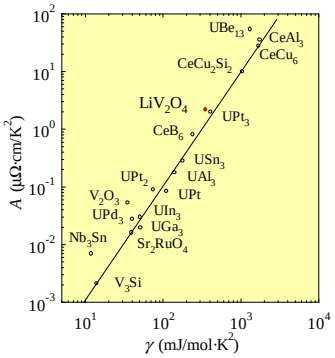
→ The first heavy fermion oxides



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?
1.5 d-electron — LDA+U (Anisimov *et al.*)
0.5 e_g (itinerant)+ 1 a_{1g} (localized)
trigonal field splitting

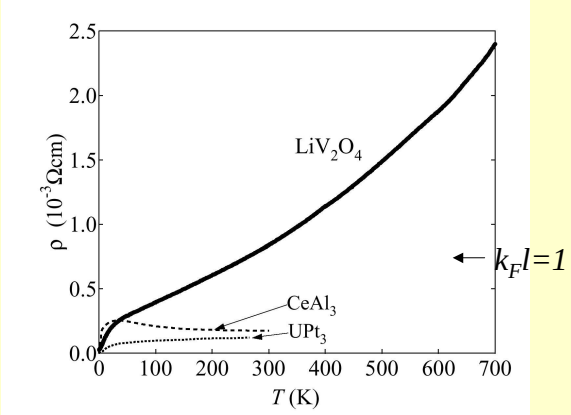
-Geometrical frustration?

A.George
P.Coleman
P.Fulde

HF state in LiV_2O_4 is located at the critical vicinity to CO state,
Where geometrical frustration plays a vital role.

"Bad metal" behavior in LiV_2O_4

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



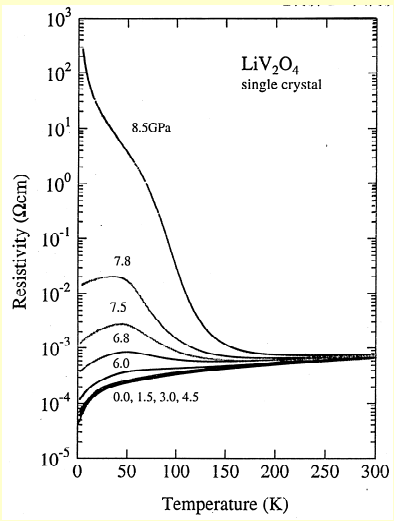
Distinct from conventional HFs

absence of resistivity saturation

Metallic behavior above IR limit

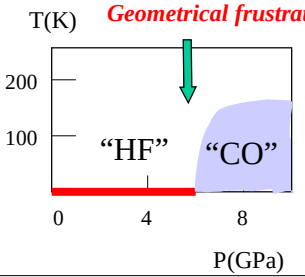
C.Urano, H.T et al PRL 85, 1052 (00)

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+})

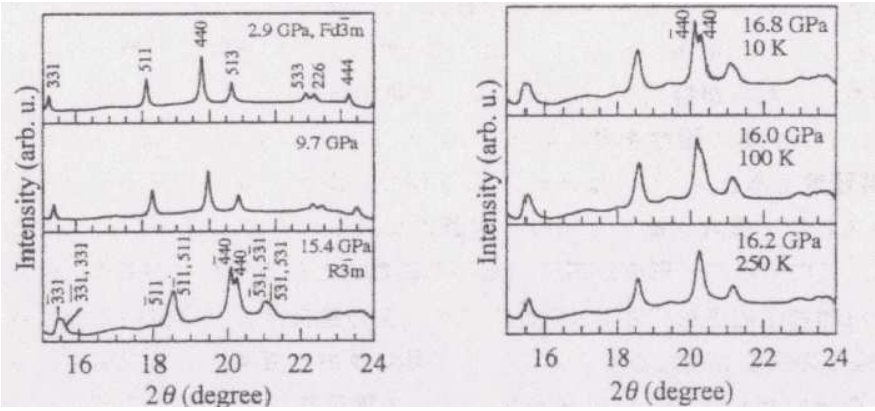


charge liquid critically close to COI but no magnetic ordering due to spin frustration

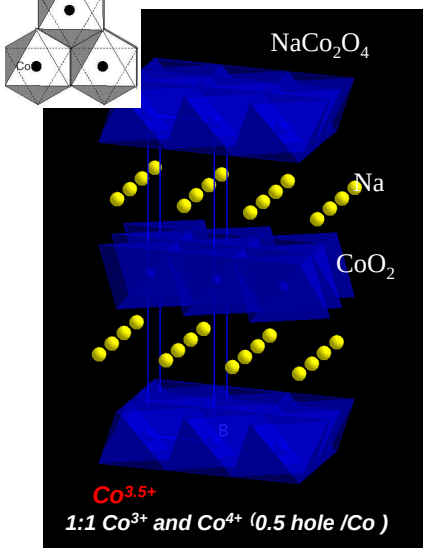
Pressure induced Cubic-Rhombhedral transition

Osaka G

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



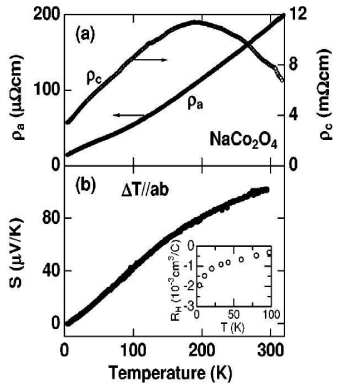
Thermoelectric material on triangular lattice



A large γ=60mJ/molK²
carry large entropy

S^2/ρ = 40 mW/K²cm, ZT = 0.1 (RT)

Melted COI ?



Terasaki *et al.*, Phys. Rev. B **56** 12685

2D Co layer :triangular lattice

- Closely related to Watery SC

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