Toward Microscopic Understanding of Two Frustrated Antiferromagnets

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Outline

- **Motivation: Quantum spin liquid states**
- **Quantum spin states in $Zn_xCu_{4-x}(OD)_6Cl_2$**
- **Frustrated minority spins in $GeNi_2O_4$**
- **Summary**

Collaborators

$Zn_xCu_{4-x}(OD)_6Cl_2$

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$GeNi_2O_4$

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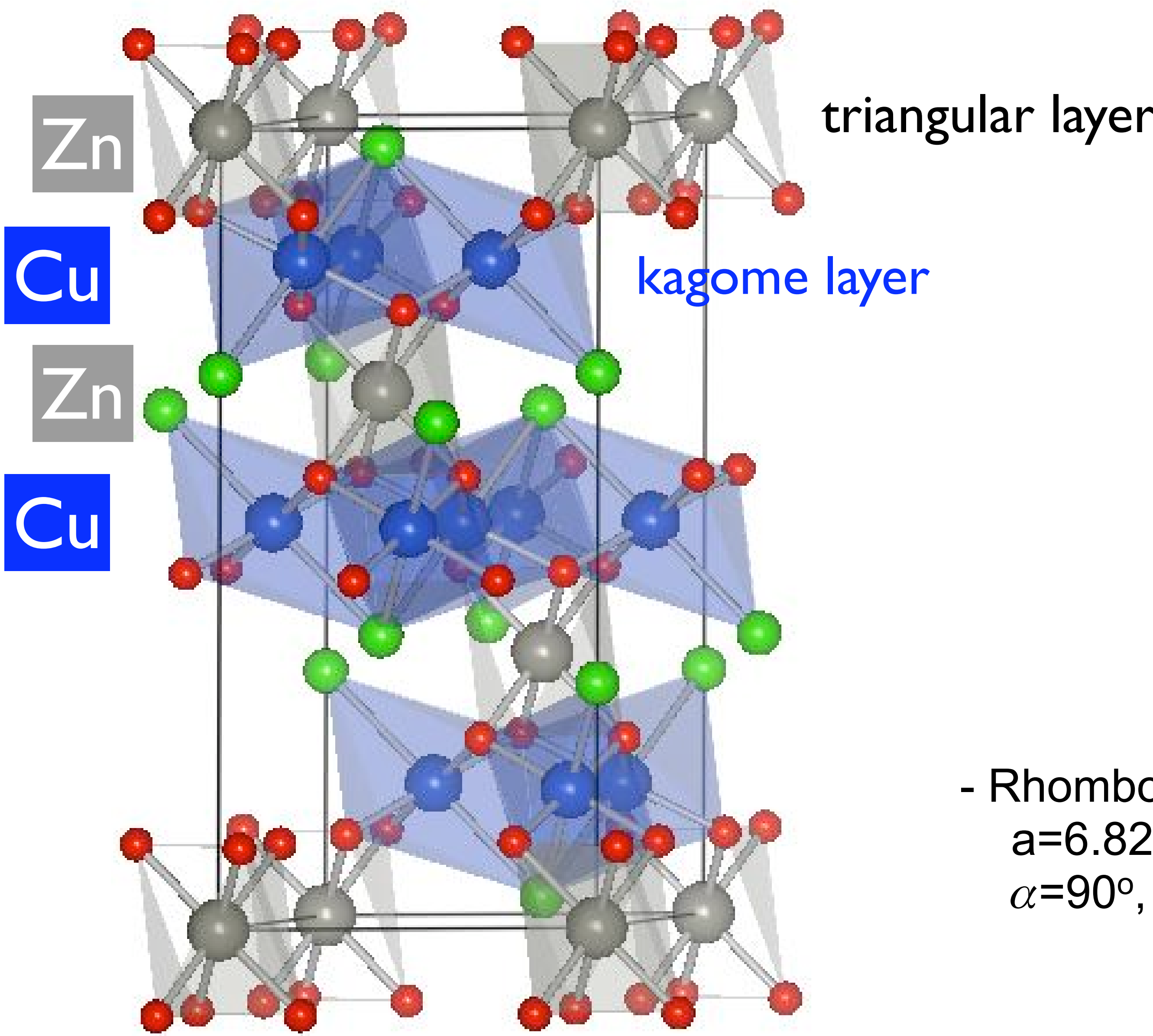
Quantum kagome antiferromagnet

$Zn_xCu_{4-x}(OD)_6Cl_2$ (S=1/2)

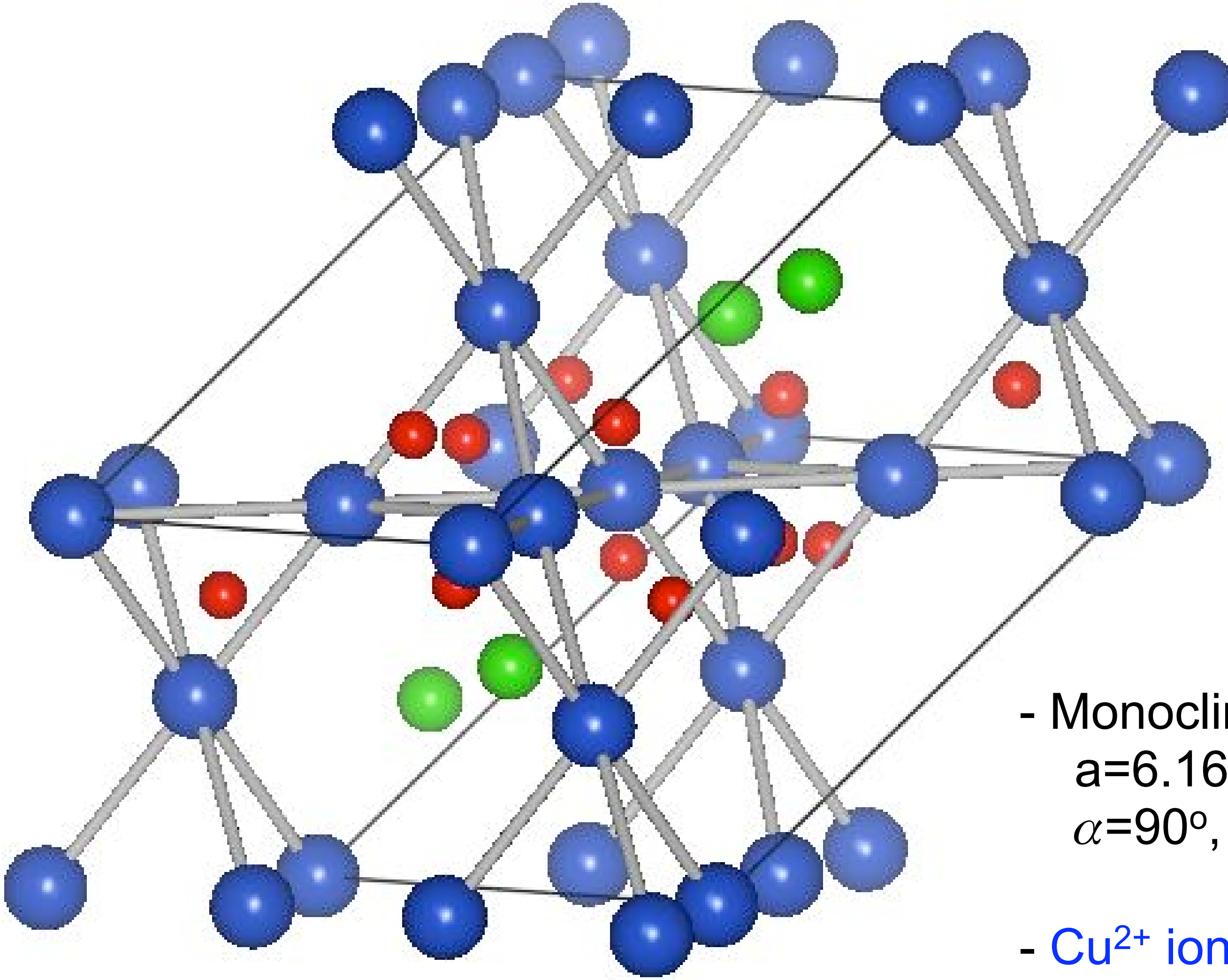
$ZnCu_3(OD)_6Cl_2$: A perfect kagome system???

M.P. Shores/G. Nocera *et al.*, JACS (2005)



- Rhombohedral, R-3m (#166),
  a=6.8293A, b=6.8293, c=14.024A
  α=90°, β=90°, γ=120°

$Cu_4(OD)_6Cl_2$: a pyrochlore system?



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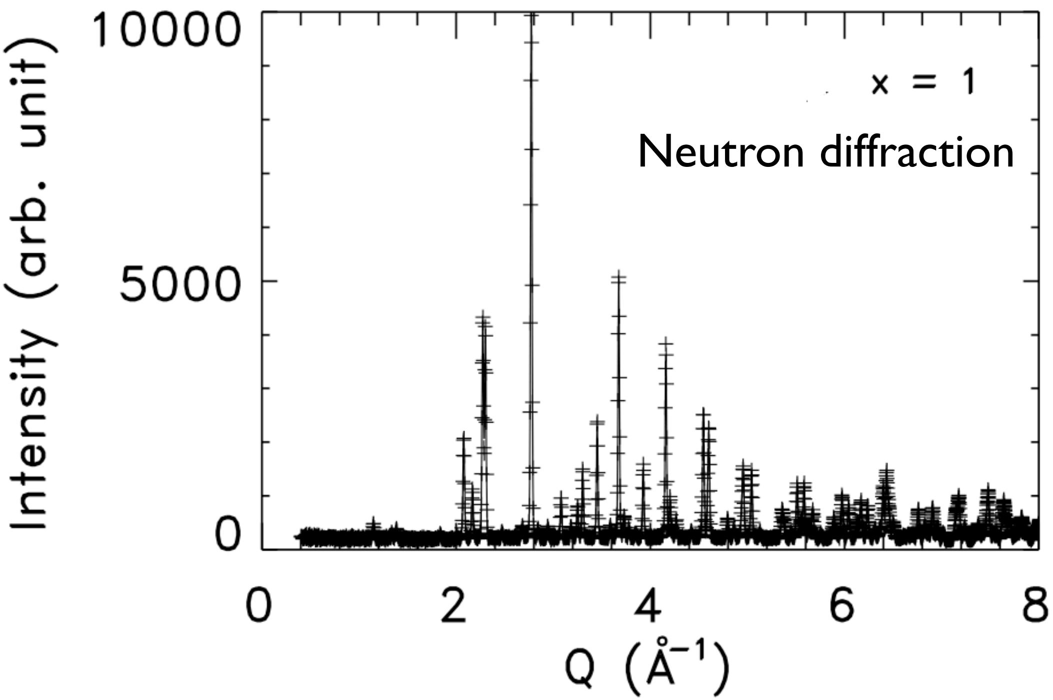
e layer

- Monoclinic, $P2_1/n$ (#14), a=6.1637A, b=6.8166, c=9.114A α=90^o, β=99.6515^o, γ=90^o

- Cu^{2+} ions form the pyrochlore lattice.

$ZnCu_4(OD)_6Cl_2$: Crystal Structure

S.-H. Lee *et al.*, Nature Materials (2007)
supplementary information

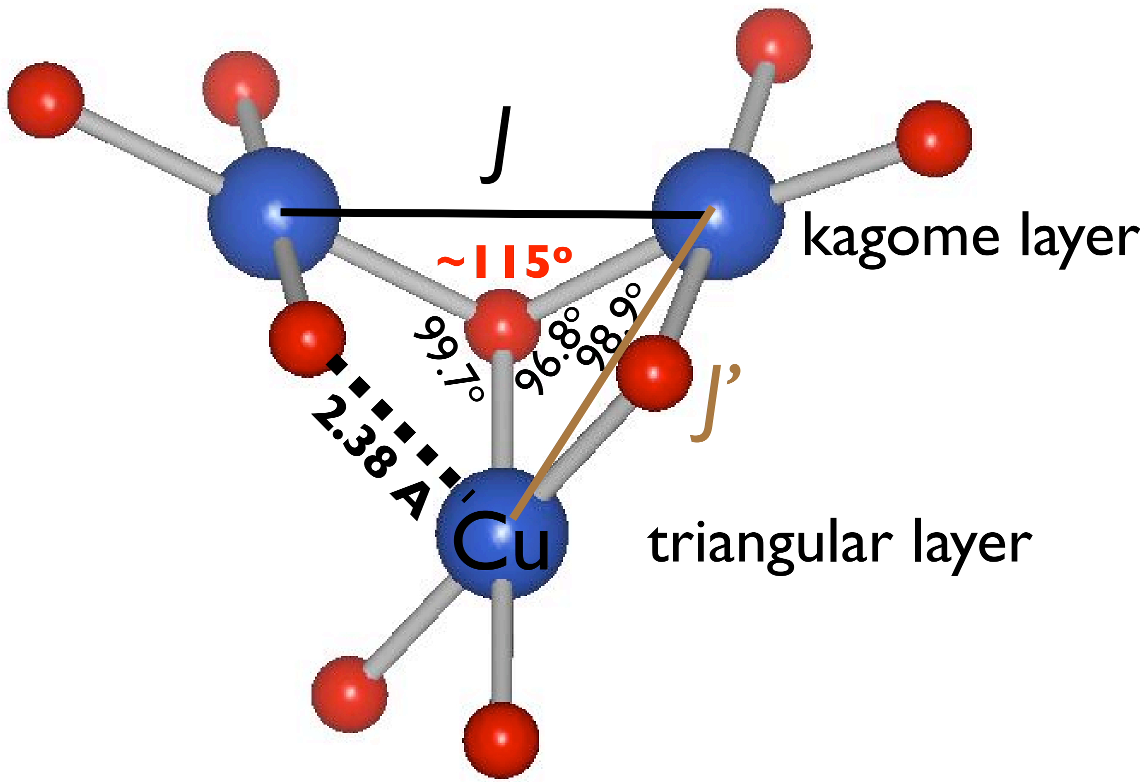


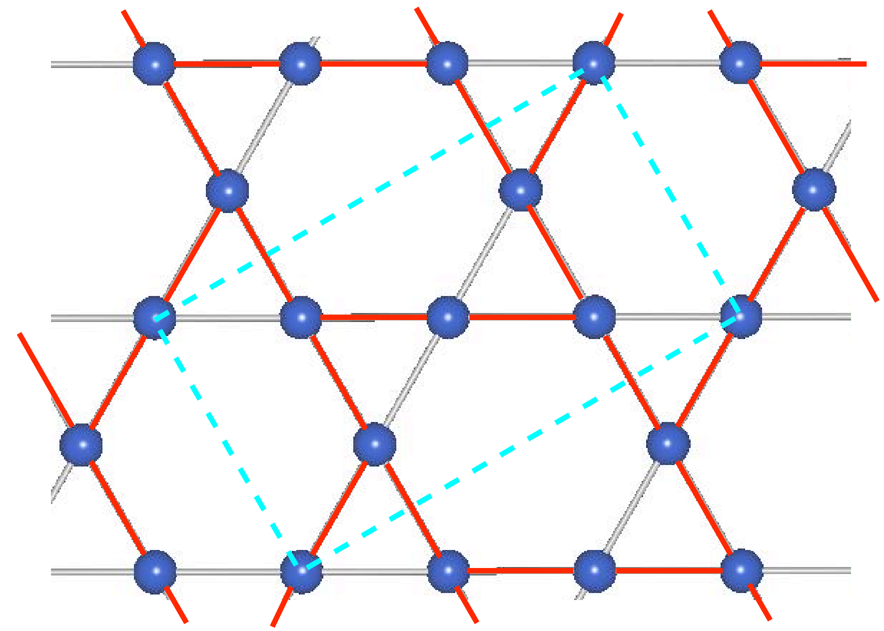
Rhombohedral, R-3m

Atom	Site	fraction	x	y	z
Cu1	3b	0.3723	0	0	1/2
Cu2	9e	0.8927			
Zn1	3b	0.6277			
Zn2	9e	0.1073			
Cl	6c	1	0	0	0.195773
O	36i	1	0.206226	0.412451	0.061618
D	36i	0.9935	0.131562	0.263119	0.090799

Kagome lattice, magnetically 90% filled

$Cu_4(OD)_6Cl_2$: superexchange paths

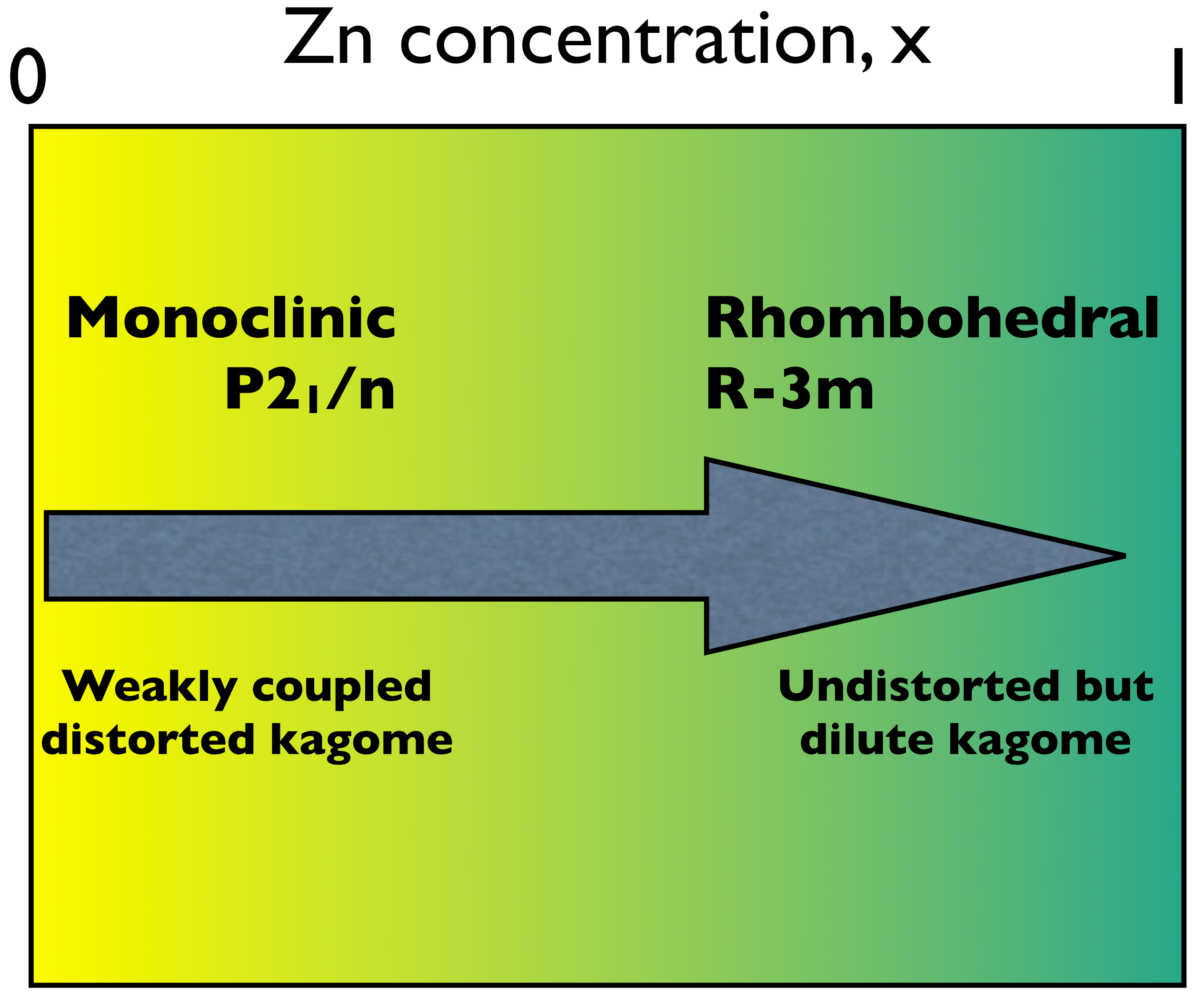




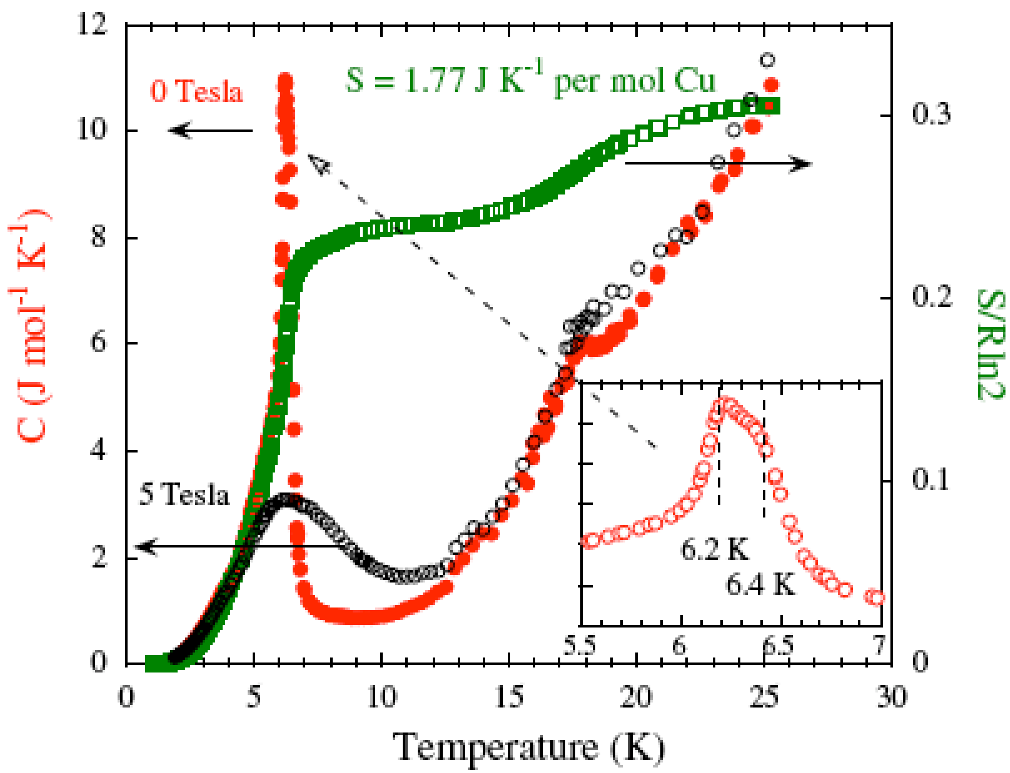
- Jahn-Teller distortion around the doped Cu^{2+} ion
- Bond angle of Cu^{2+}-O^{2-}-Cu^{2+} > 110° between kagome spins:
  strong AFM *J* in the kagome layer
- Bond angles of Cu^{2+}-O^{2-}-Cu^{2+} < 100° between kagome and triangular spins:
  weak coupling between kagome and triangular layers
- In kagome layer, two bonds with different bond angles and lengths

Weakly coupled **distorted** kagome system

Phase Diagram of $Zn_xCu_{4-x}(OD)_6Cl_2$



$Cu_4(OD)_6Cl_2$: Phase Transitions at Low Temperatures



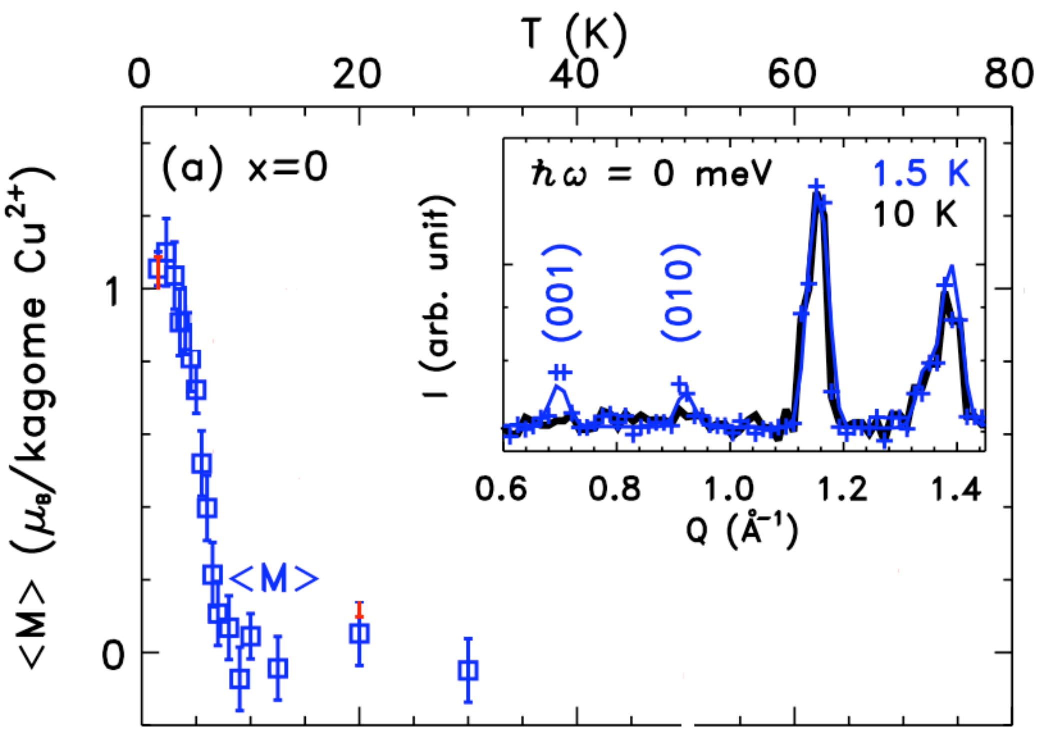
Zheng *et al.*, PRL (2005)

- Two transitions at ~ 18 K and ~ 6 K.
- From μSR data, they interpreted the 18K transition involves a long range order.
- At 6K, it transits to a metastable state with strong fluctuations.

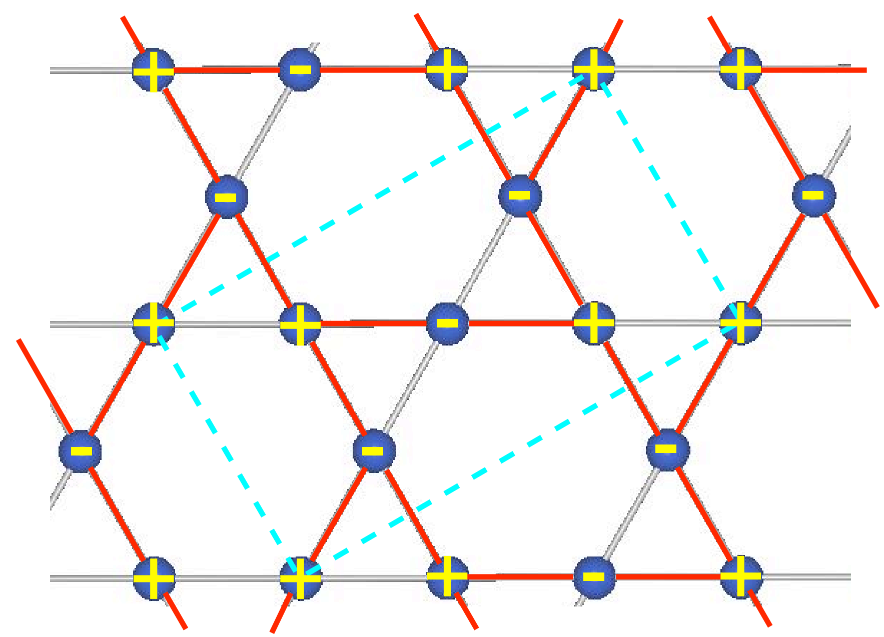
- But.. the entropy released at 18 K is only 0.05 Rln2/Cu, surprisingly small for a Neel ordering (SRln2/Cu).
- The large amount of entropy is released at 6 K.

$Cu_4(OD)_6Cl_2$: Elastic neutron scattering and Neel state

S.-H. Lee *et al.*, Nature Materials (2007)

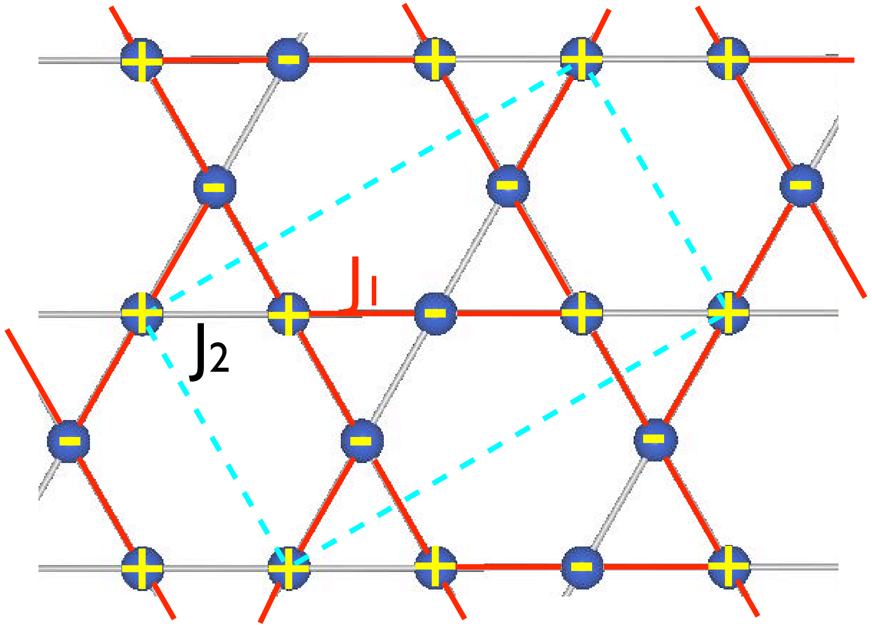


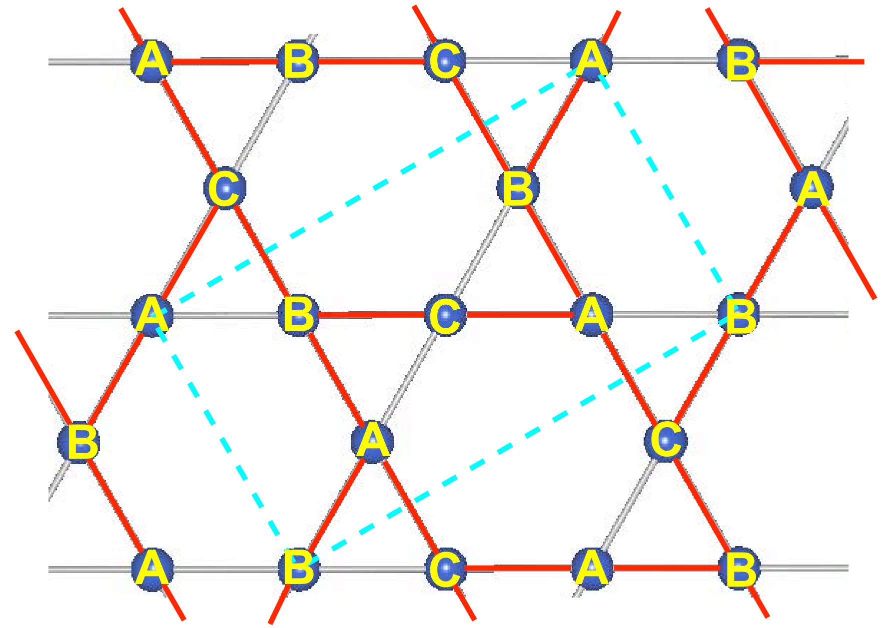
- Neel ordering occurs at ~ 7 K.
- Q_M = (001).
- consistent with the specific heat data that showed the large amount of entropy was released around 6K.



- The Neel state is collinear, rather than 120 degree configuration.

Collinear vs 120° configuration





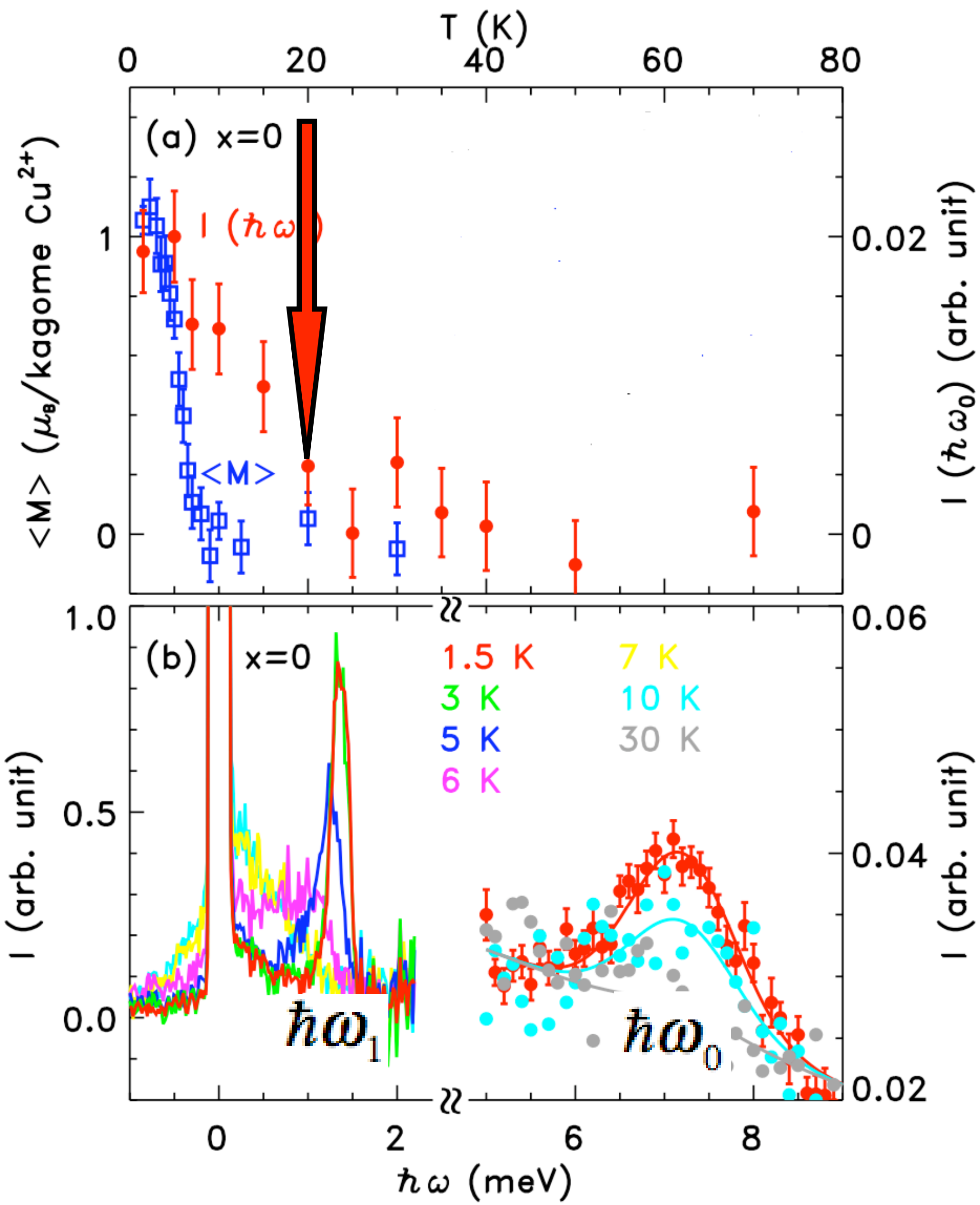
$E\ (\text{coll}) = 4\ J_2 - 8\ J_1$

$E\ (120°) = -2\ J_2 - 4\ J_1$

$E\ (\text{coll}) < E\ (120°) \Rightarrow J_2 < 2/3\ J_1$

- If we take Goodenough's prediction, $J \sim \cos^4\theta/d^7$, $J_2 \sim 1/3\ J_1$ for $Cu_4(OD)_6Cl_2$.

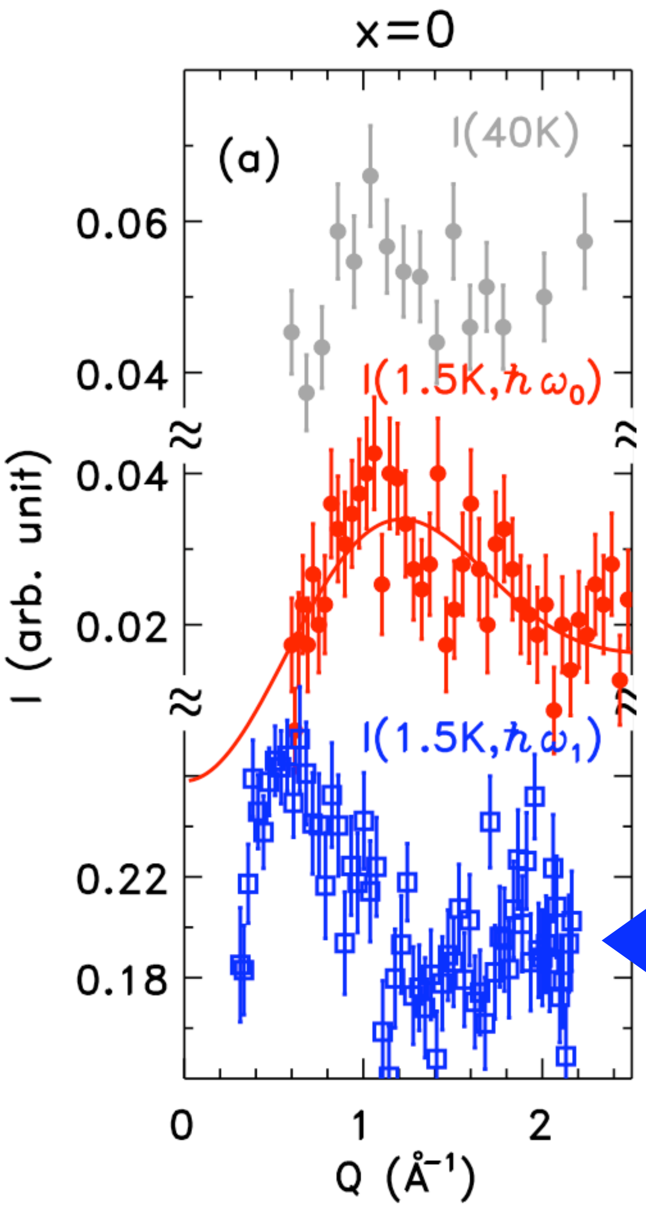
$Cu_4(OD)_6Cl_2$: Phase Transitions at Low Temperatures



- The 7 meV mode survives well above 7K, gradually diminishes around 20K, coincides with the 18K transition in the Cv.
- The energy of the 7 meV mode does not change with T

- Two excitations at 1.5K at 1.3 meV and 7 meV.
- With warming, the 1.3meV mode shifts to lower energies and above the Neel transition, it becomes quasielastic continuum.

$Cu_4(OD)_6Cl_2$: Q-dependence of the magnetic fluctuations



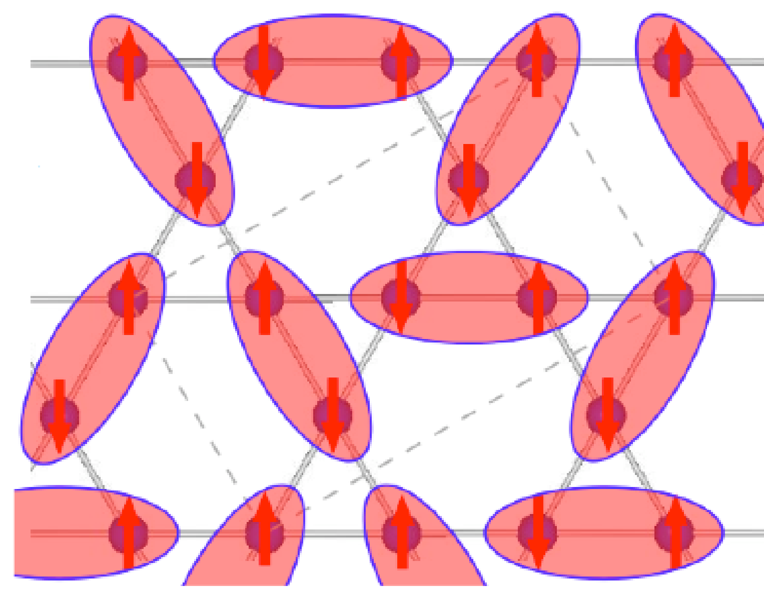
- The two excitations also have different Q dependence

$\hbar\omega_0$ mode

Spin dimers: $1-\frac{\sin(Qr_0)}{Qr_0}$ with $r_0 = 3.41$ Å

$\hbar\omega_1$ mode

Spin waves

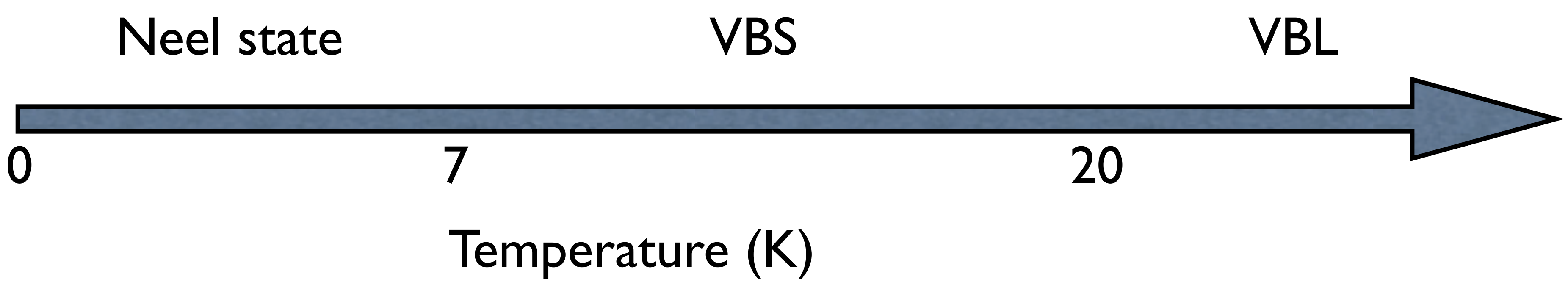


Summary on $Cu_4(OD)_6Cl_2$

- Specific heat: two transitions at ~ 18 K and ~ 6 K.
- Their interpretation of the μSR data:
  - The 18K transition: LRO
  - The 6K transition is to a metastable state with strong fluctuations.
- But.. the entropy released at 18 K is only 0.05 Rln2/Cu << SRln2/Cu.
- The large amount of entropy is released at 6 K.

- Elastic neutron scattering:
  - LRO occurs below T_N ~ 7K.
  - No evidence for another LRO above T_N.
- Inelastic neutron scattering:
  - The energy of spin waves shifts from 1.3 meV at 1.5K to lower energies as T increases to T_N, and it becomes a gapless continuum.
  - The 2nd excitation mode at 7 meV gradually weakens and disappears ~20K.
  - The energy of the 7 meV mode does not shift with increasing T.
  - S(Q,hw=7meV) resembles that of spin dimers.
  - Above 20K, S(Q) at low energies resembles that of spin dimers.

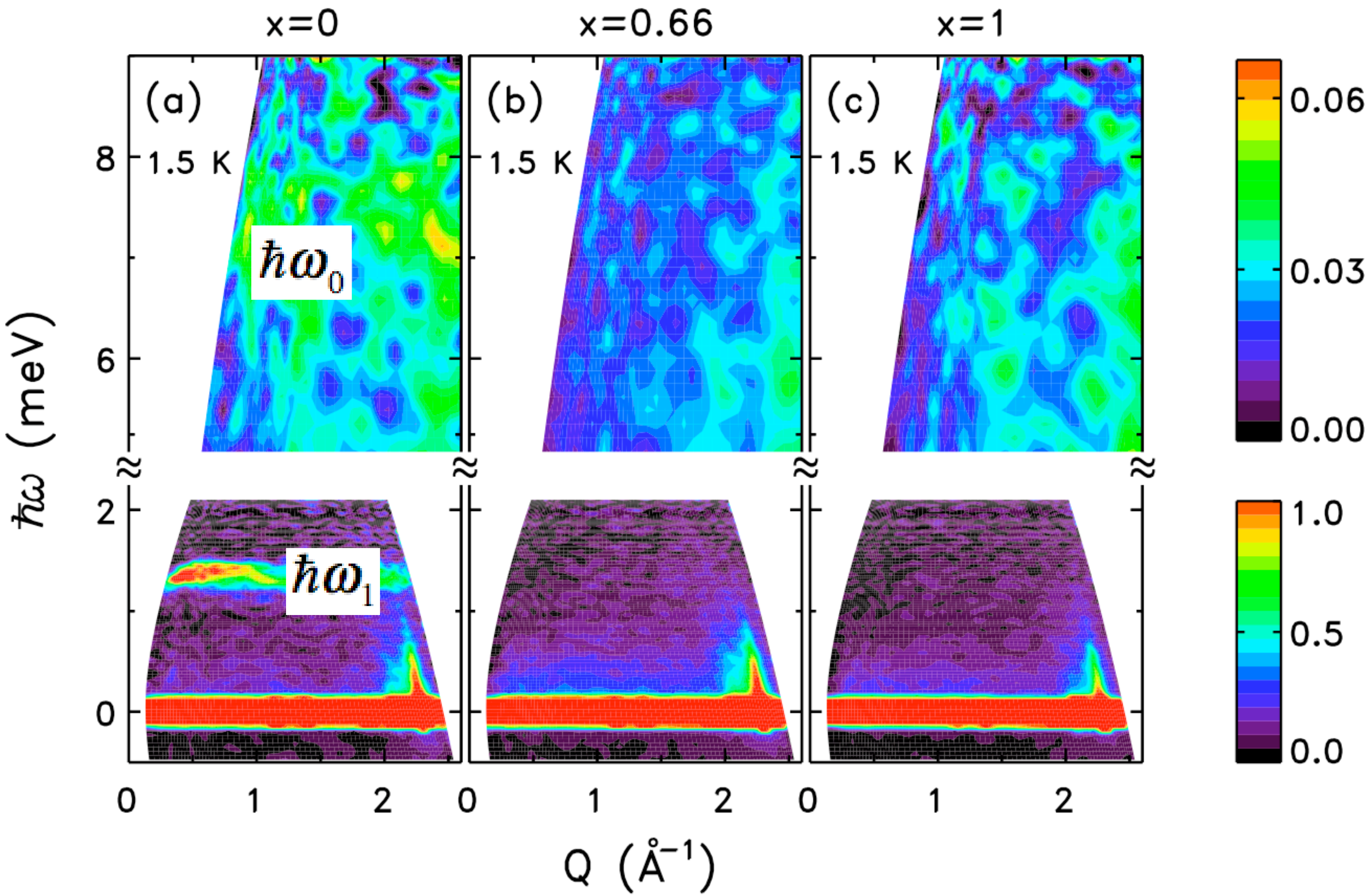
$Cu_4(OD)_6Cl_2$



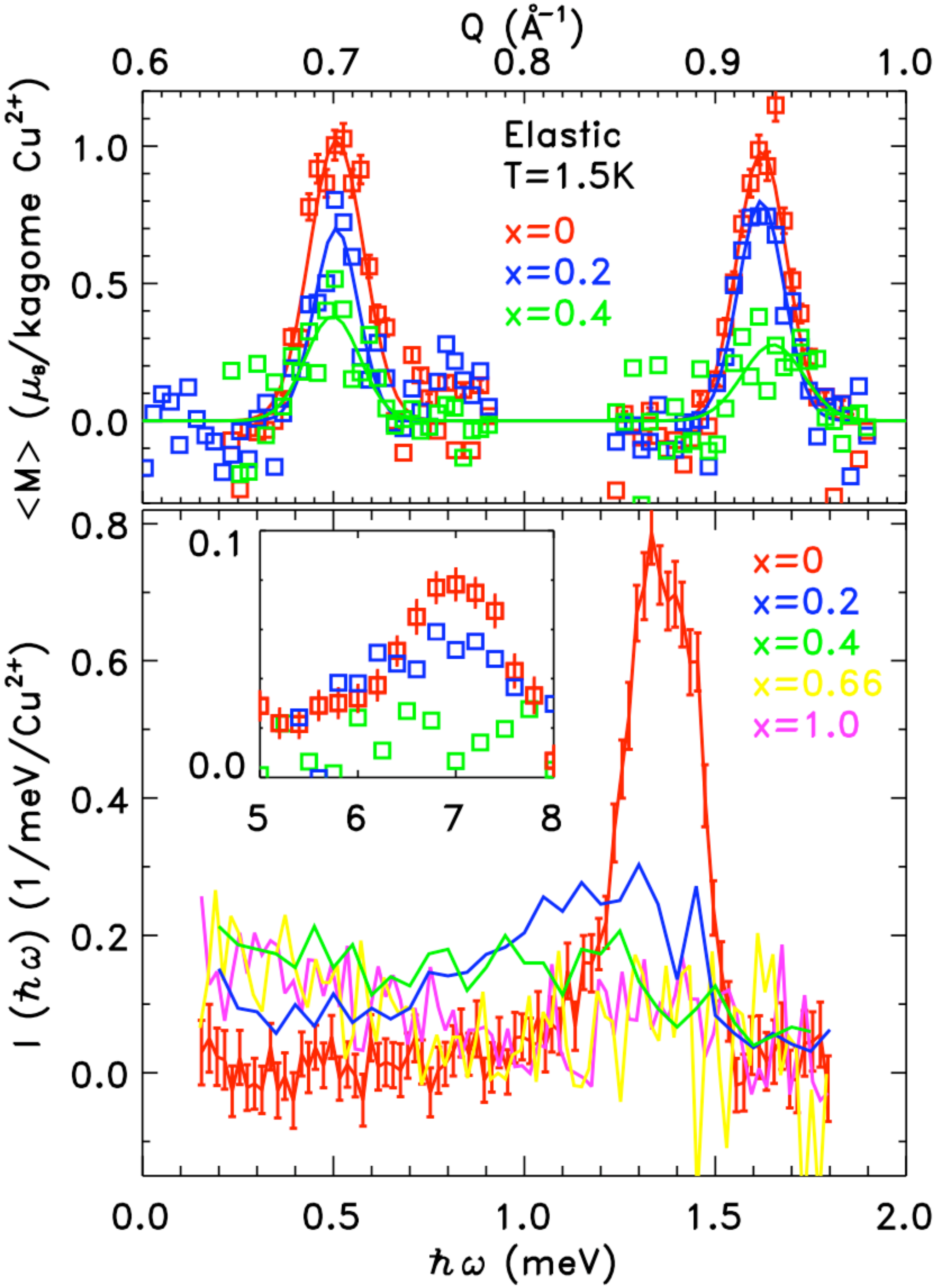
Zn doping effects on

$Zn_xCu_{4-x}(OD)_6Cl_2$

$Zn_xCu_{4-x}(OD)_6Cl_2$: Spin Fluctuations with x



$Zn_xCu_{4-x}(OD)_6Cl_2$: Spin correlations vs x



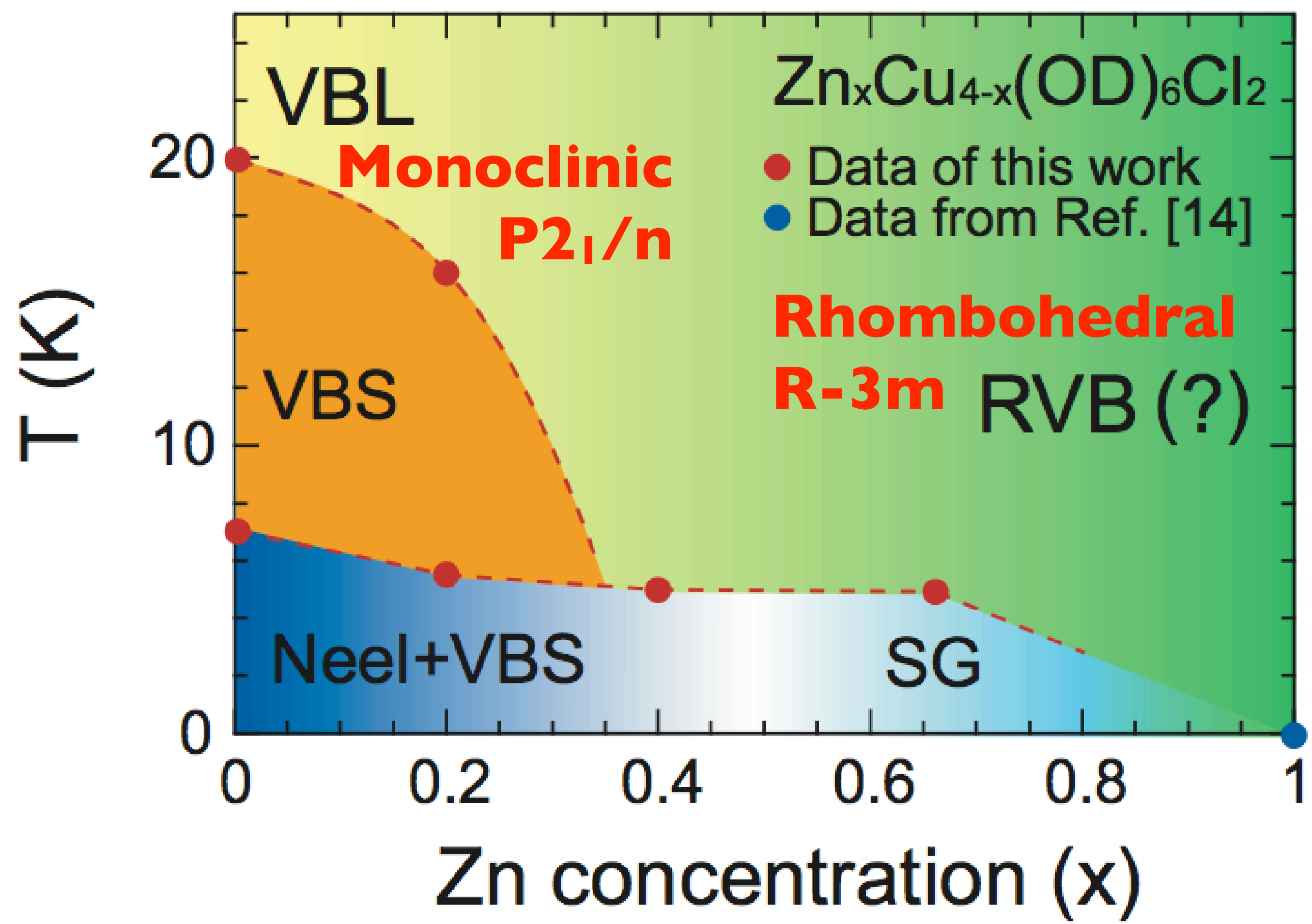
Elastic scattering at 1.5 K

- The Neel state weakens upon Zn doping.
- It disappears just above x = 0.4.

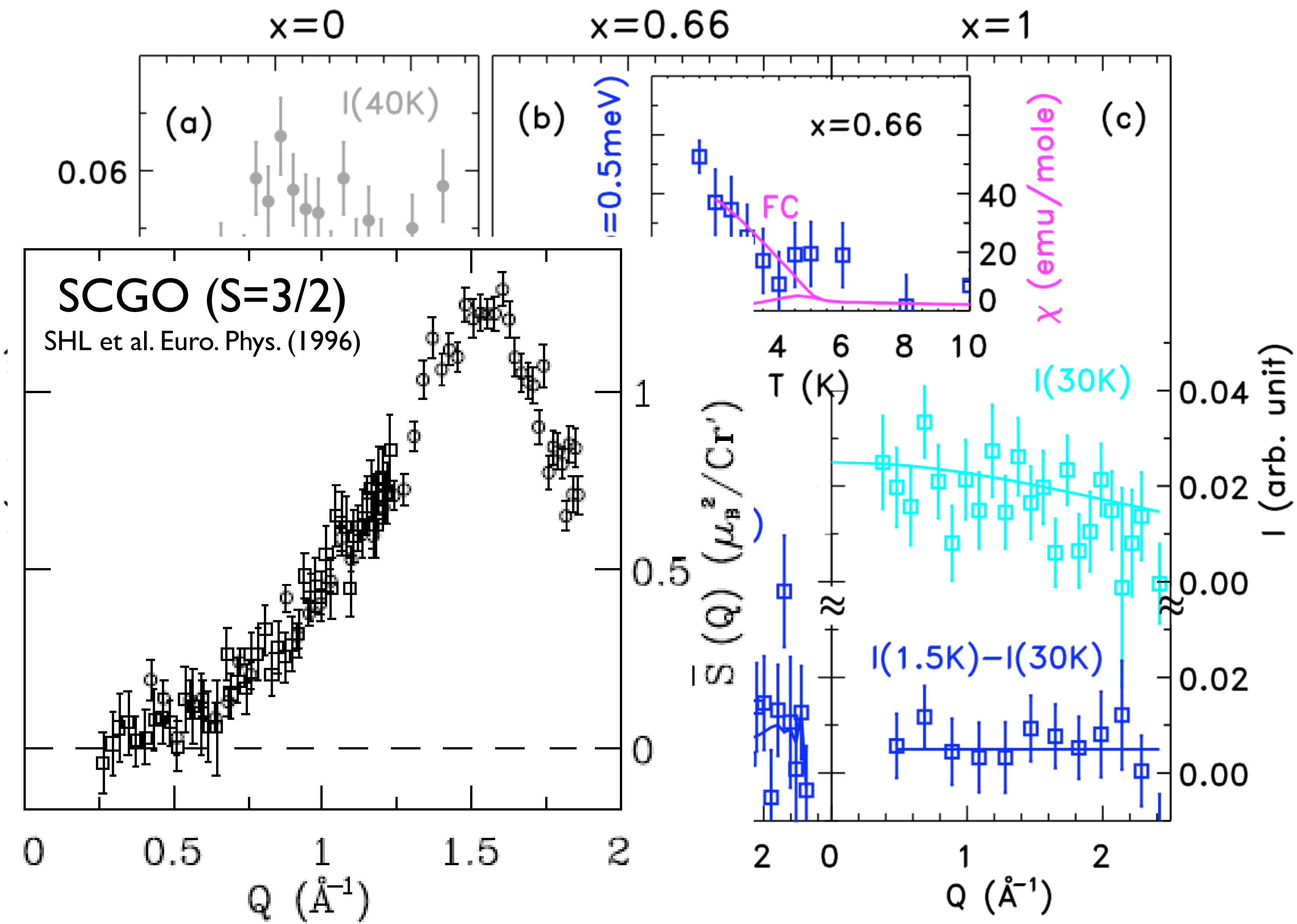
Inelastic scattering at 1.5 K

- The $h\omega_0$ = 7 meV mode disappears at x ~ 0.4.
- The $h\omega_1$ = 1.3 meV mode weakens and shifts to low energies with x.
- The energy excitation spectrum becomes a featureless continuum for x > 0.4.

Summary: Phase Diagram of $Zn_xCu_{4-x}(OD)_6Cl_2$

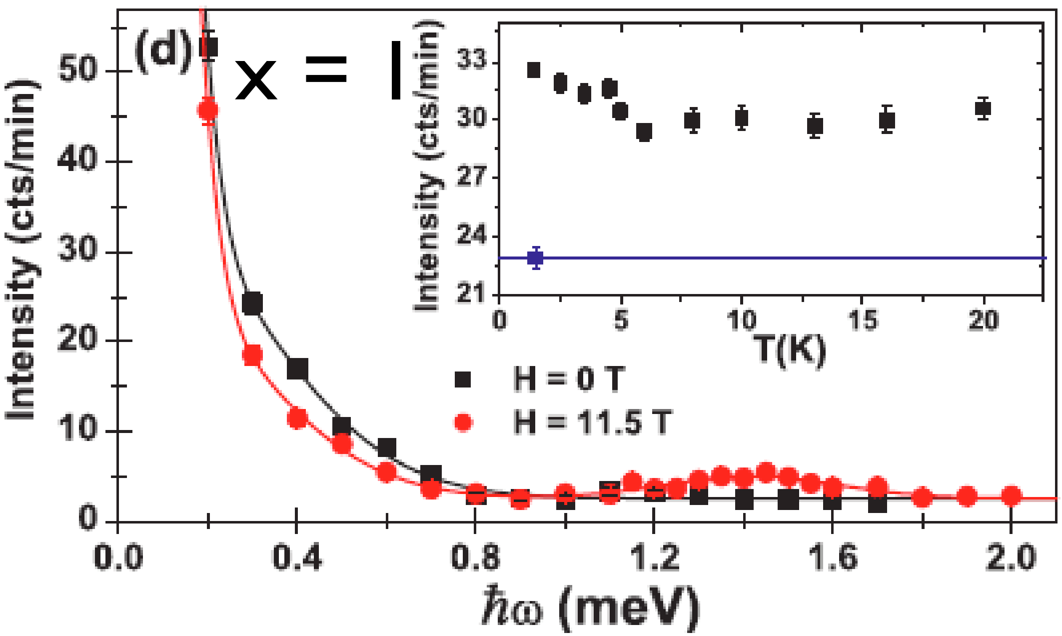


$Zn_xCu_{4-x}(OD)_6Cl_2$: Spin Fluctuations vs x

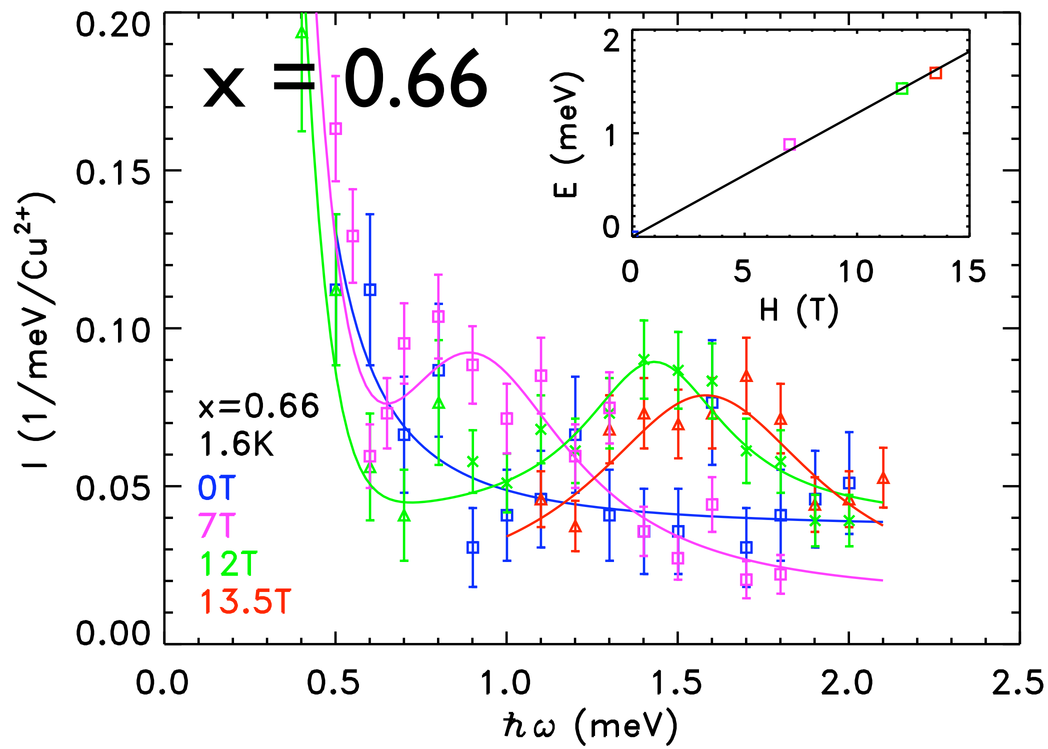


$Zn_xCu_{4-x}(OD)_6Cl_2$ (x > 0.66): Magnetic field effects on spin fluctuations

J.S. Helton/Y. Lee *et al.*, PRL (2007)



S.-H. Lee *et al.*, Nature Materials (2007)



$$E \text{ (meV)} = 0.12(3) H \text{ (T)} \approx g\mu_B H$$

No evidence for any field induced static ordering.

$ZnCu_3(OD)_6Cl_2$: Characteristics of Spin Fluctuations

- Featureless in energy and in momentum
- Under H, E (meV) = $g\mu_B H$

- For x = 1, 10% of Cu^{2+} ions at triangular sites.
- Are those free spins responsible for the spin fluctuations in the x = 1 system?

- Assuming that all Cu^{2+} ions contribute to the observed intensity,

$$\int_{0.2\,meV}^{1.7\,meV} I(\hbar\omega)d(\hbar\omega) = 0.11(3)\,/\,Cu^{2+}$$

whereas if only the 10% free spins contribute,

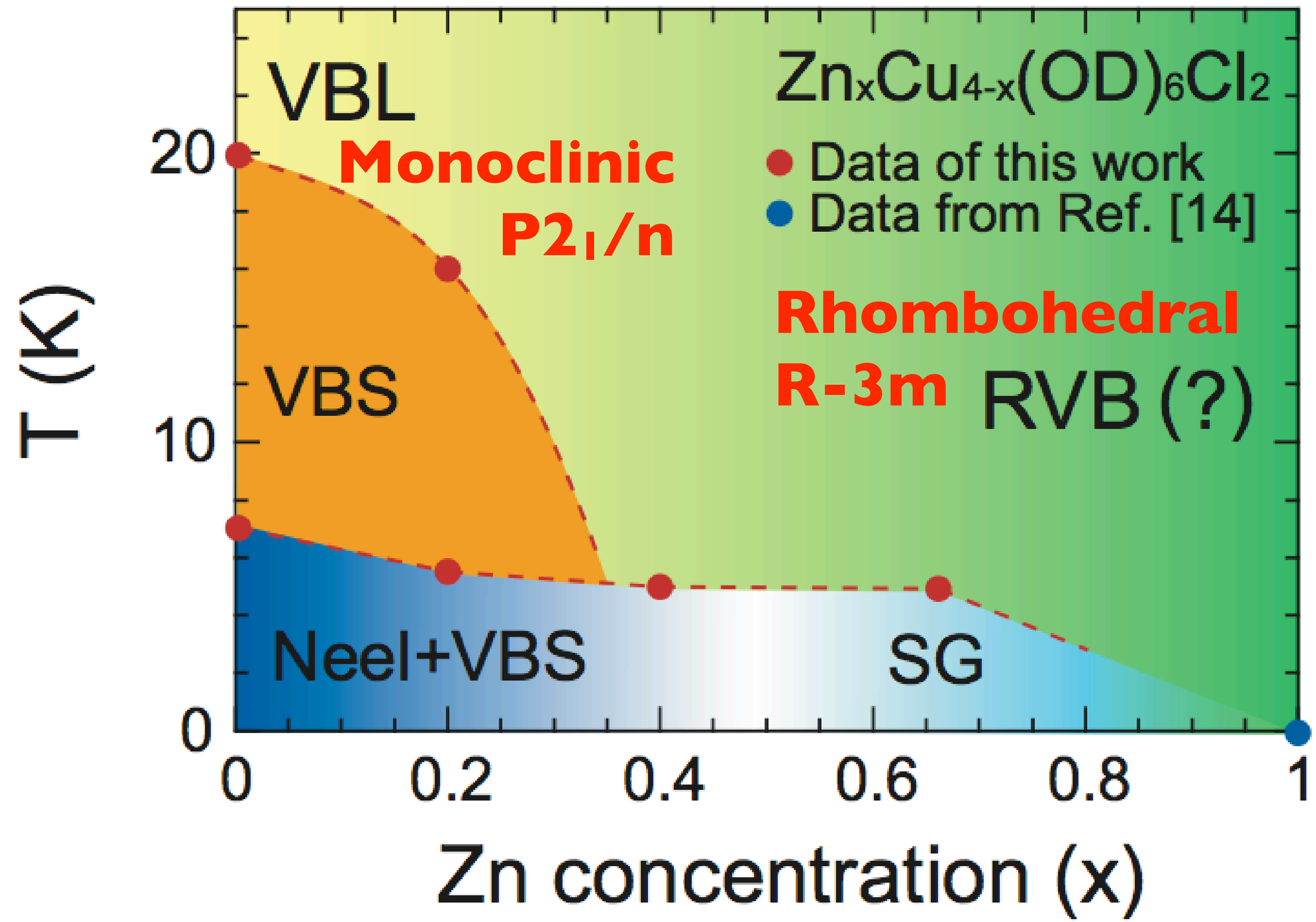
$$\int_{0.2\,meV}^{1.7\,meV} I(\hbar\omega)d(\hbar\omega) = 1.1(3)\,/\,Cu^{2+}$$

$$> S(S+1)\,/\,Cu^{2+} = 0.75\,/\,Cu^{2+}$$

- As x increases, the spin fluctuations gradually shifts from the collective spin waves of x = 1 to the low energy continuum of x = 0.

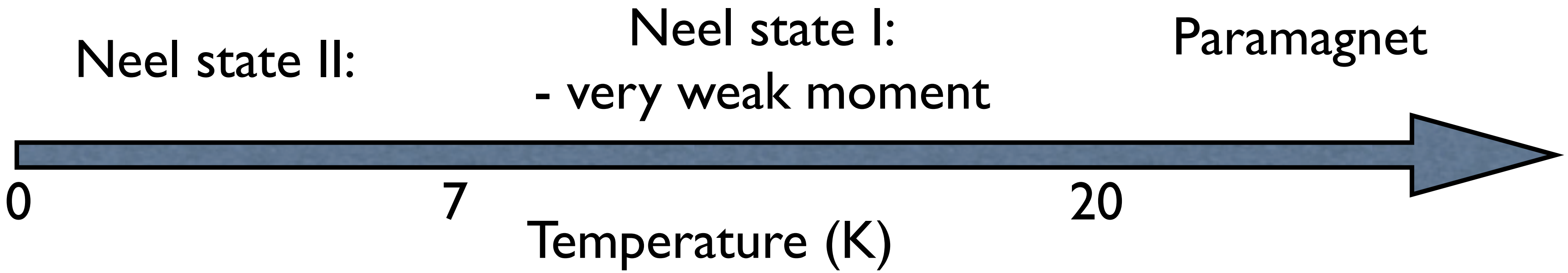
We conclude that the low energy continuum of $ZnCu_3(OD)_6Cl_2$ is due to collective excitations of kagome Cu^{2+} ions.

Summary: Phase Diagram of $Zn_xCu_{4-x}(OD)_6Cl_2$



Scenarios for $Cu_4(OD)_6Cl_2$

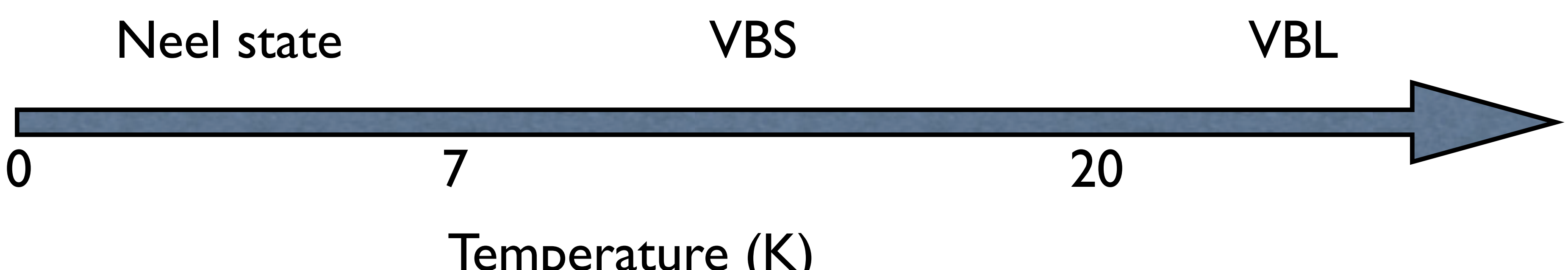
- Scenario I



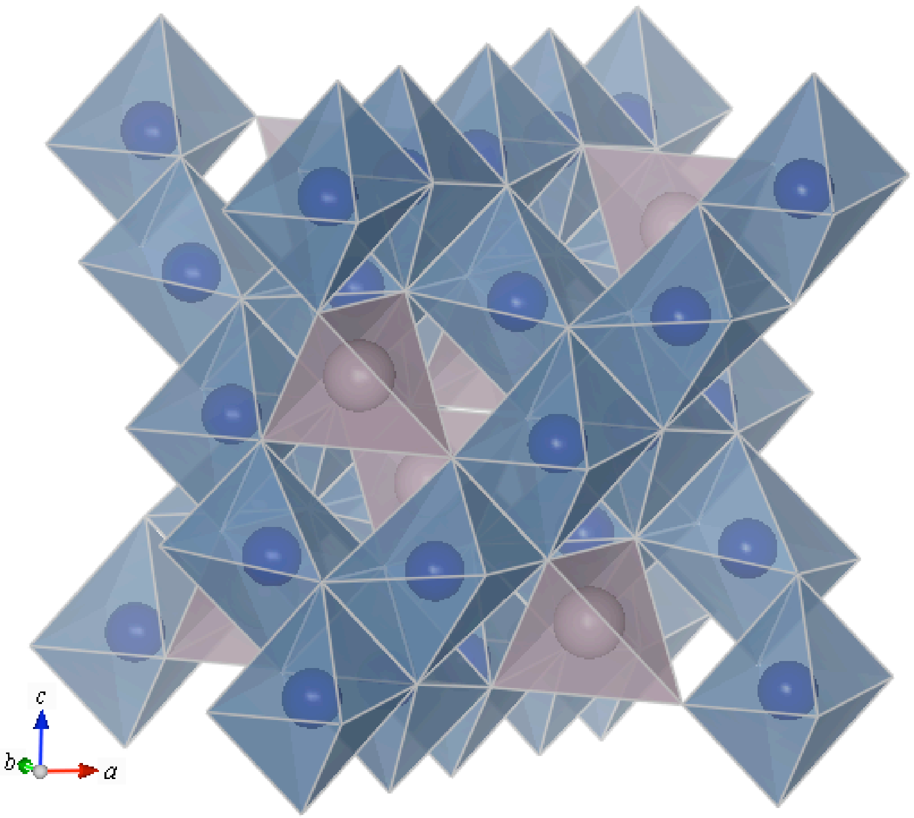
but..

- The spin wave gap is proportional to the frozen moment.
- The 7 meV energy does not shift with increasing T.

- Scenario II



Spinel AB_2O_4: Crystal Structure



- At high temperature,
  Fd3m, cubic
  a=6.1637A, b=6.8166, c=9.114A
  $\alpha=\beta=\gamma=90^o$

- AO_4 tetrahedra

- BO_6 Octahedra

- The octahedra are edge sharing

- B ions form a pyrochlore lattice

Guide map of "simple" spinel oxides

From Takagi's talk '06

Transition Metal **M** =	**Ti**	**V**	**Cr**	**Mn**
$Li^{1+}M_2^{3.5+}O_4$ "**Charge**" **frustration** 1:1 3+ & 4+, mixed valent	**$d^{0.5}$** **$LiTi_2O_4$** BCS SC	**$d^{1.5}$** **LiV_2O_4** Heavy Fermion	**$d^{2.5}$** **($LiCr_2O_4$)**	**$d^{3.5}$** **$LiMn_2O_4$**
$Zn^{2+}M_2^{3+}O_4$ **(Mg^{2+}, Cd^{2+}, Hg^{2+})** Mott insulator "**Spin**" **frustration** all 3+, AF interactions	**d^1** **$MgTi_2O_4$**	**d^2** **ZnV_2O_4** **MgV_2O_4** **CdV_2O_4** **MnV_2O_4**	**d^3** **$ZnCr_2O_4$** **$CdCr_2O_4$** **$HgCr_2O_4$** **$CoCr_2O_4$**	**d^4** **$ZnMn_2O_4$** **$MnMn_2O_4$**

orbital degeneracy
spin-orbit-lattice coupling
effective 1D physics

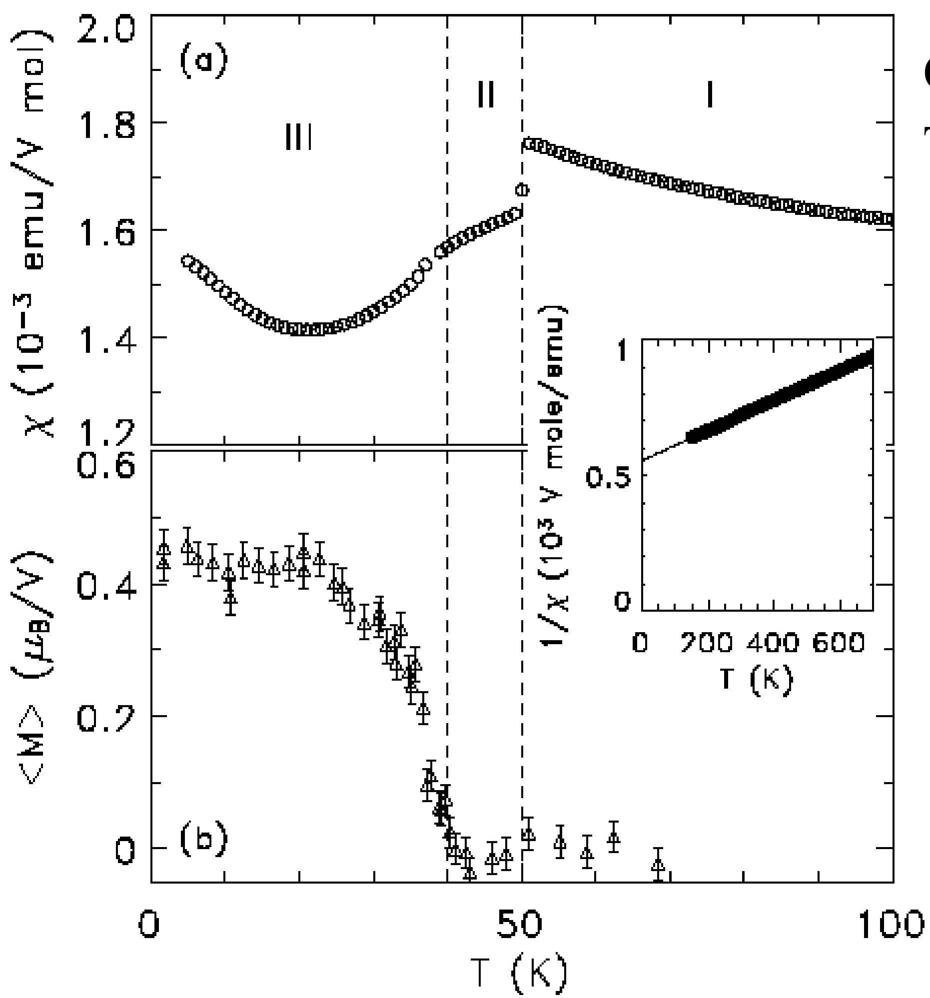
Spin liquid
3D spin-Peierls transition
Field-induced plateau states
Multiferroic behaviors

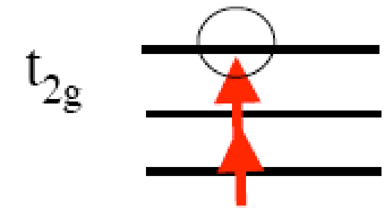
S = 1 pyrochlore AFM with orbital degrees of freedom: AV_2O_4 (A = Zn, Cd)

Additional ingredient: orbital degrees of freedom

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

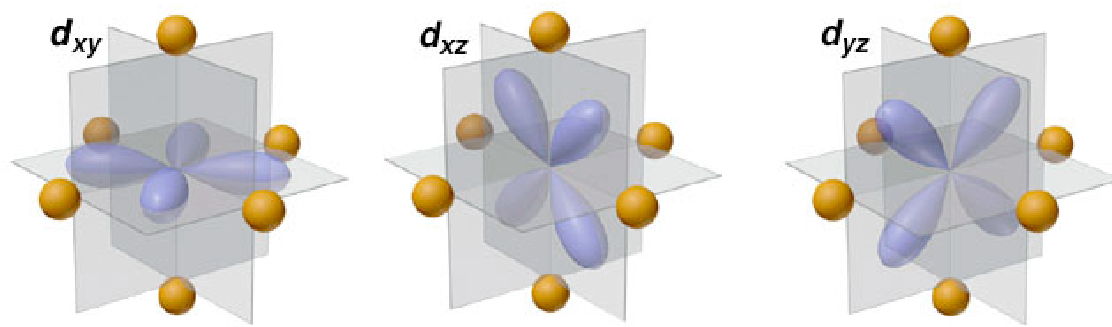
Y. Ueda et al., (1997)





Θ_{CW} = -1000 K

T_N = 40 K



Two transitions

$T_N \neq T_S$

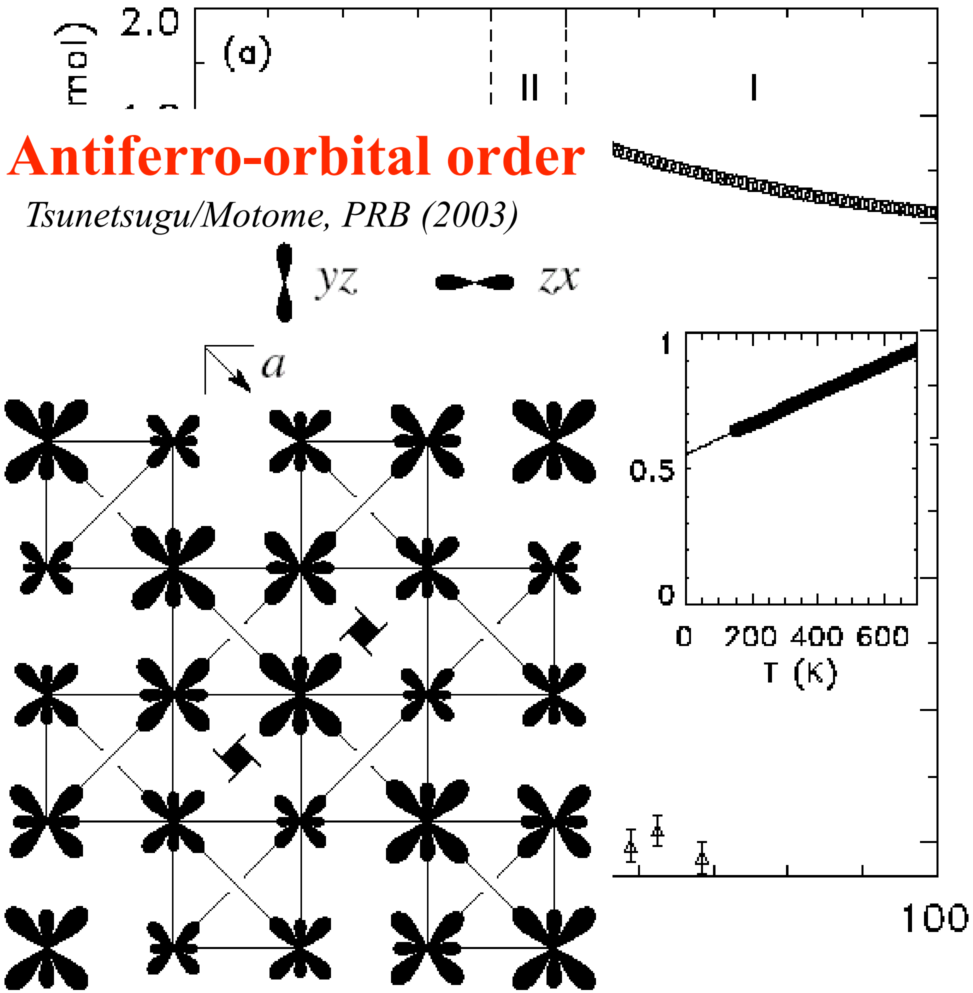
Effect of the A^{2+}-ion on orbital ordering in AV_2O_4

SHL et al., PRL (2004)
Zhang/Louca/SHL et al., PRB (2006)

ZnV_2O_4

Antiferro-orbital order

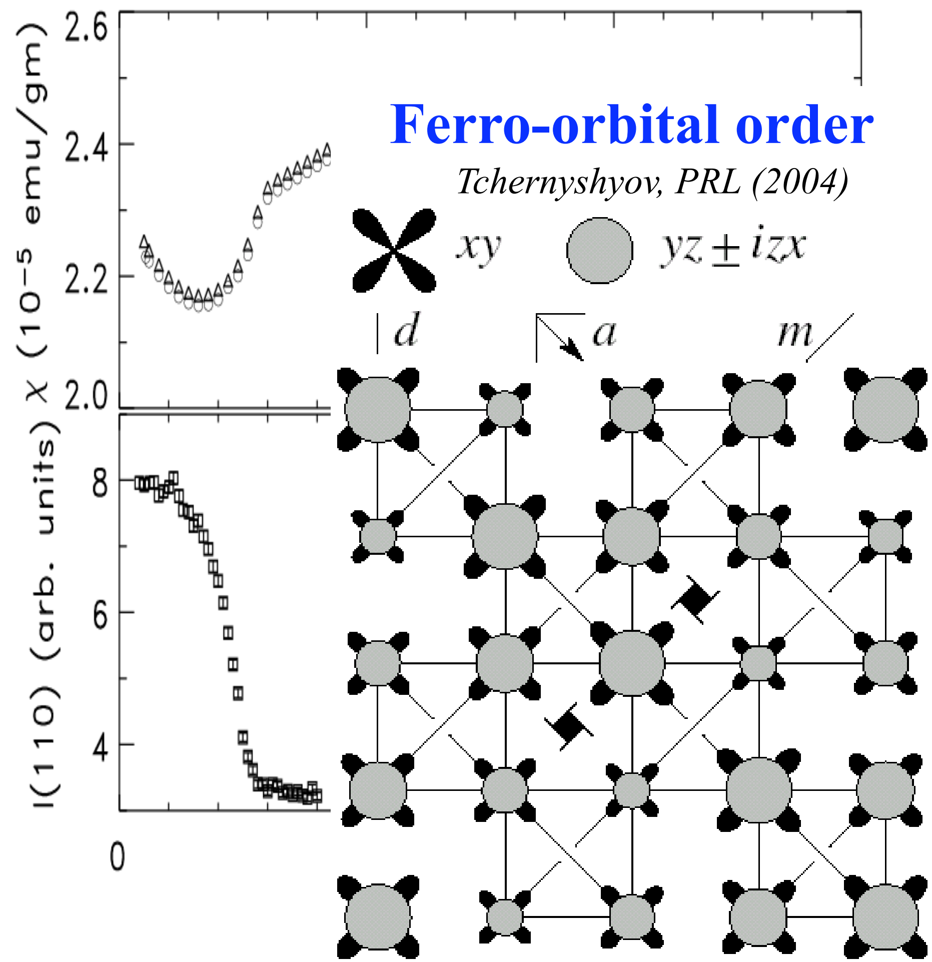
Tsunetsugu/Motome, PRB (2003)



CdV_2O_4

Ferro-orbital order

Tchernyshyov, PRL (2004)

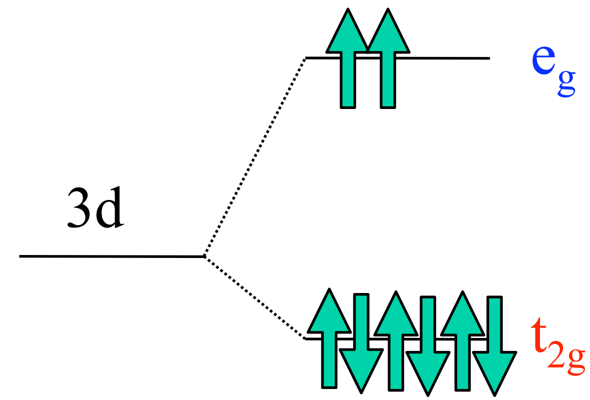


A Spinel with e_g electrons

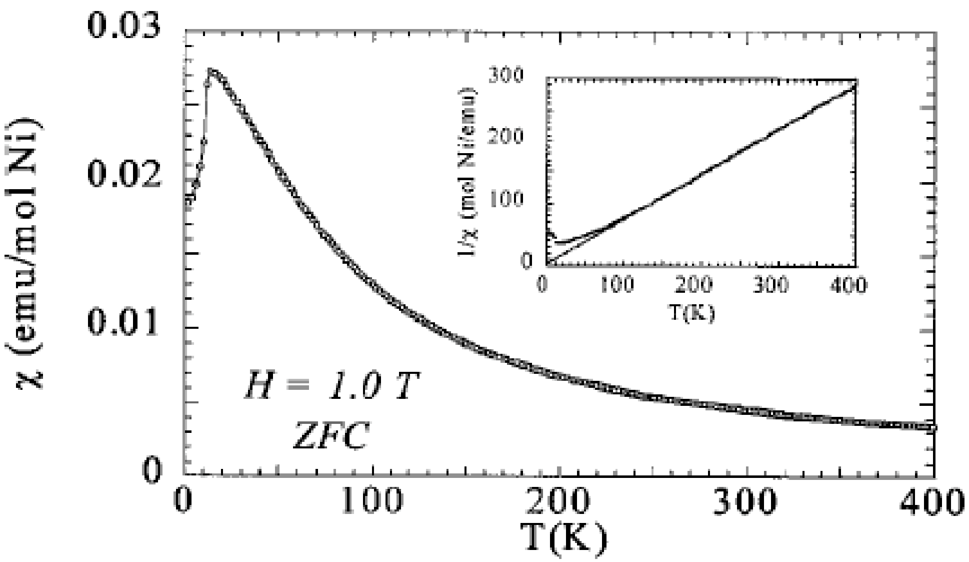
$GeNi_2O_4$ (S=1)

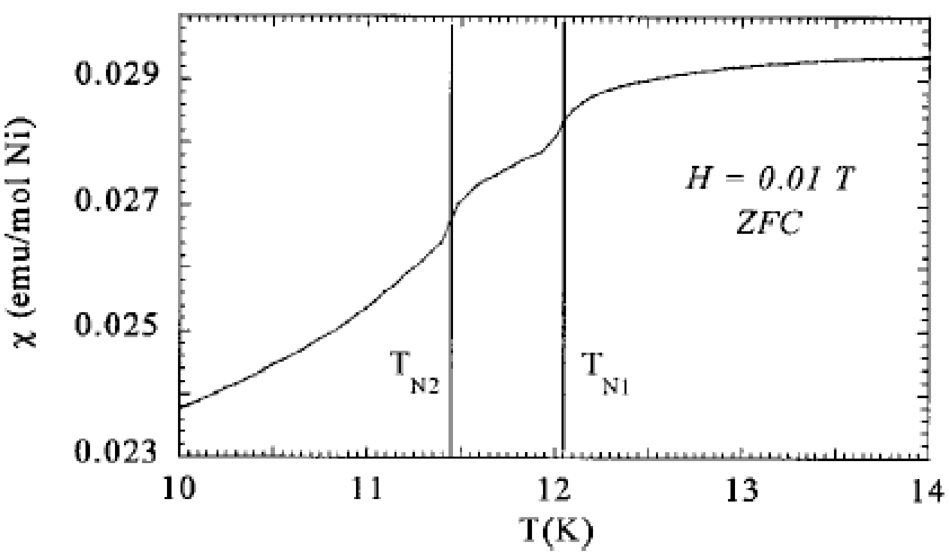
$GeNi_2O_4$: An S=1 spinel

Ni^{2+} ($3d^8$): no orbital degeneracy



Takagi's group, unpublished (2002)
M.K. Crawford *et al.*, PRB (2003)



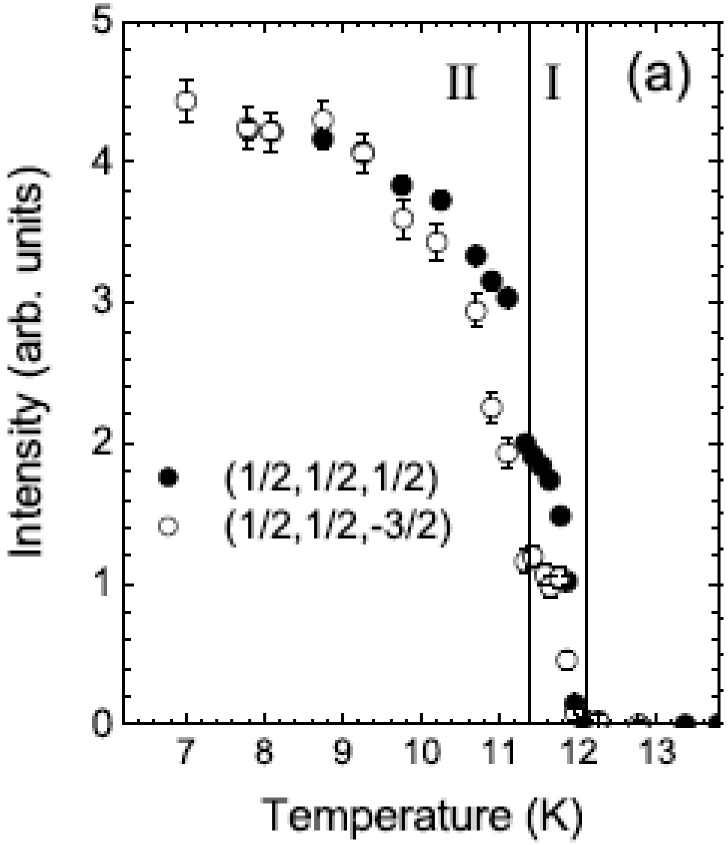


- Θ_{CW} = -4.4 K
- Two transitions at 12.1 K and 11.4 K
- No structural transition
- The two transitions are purely magnetic

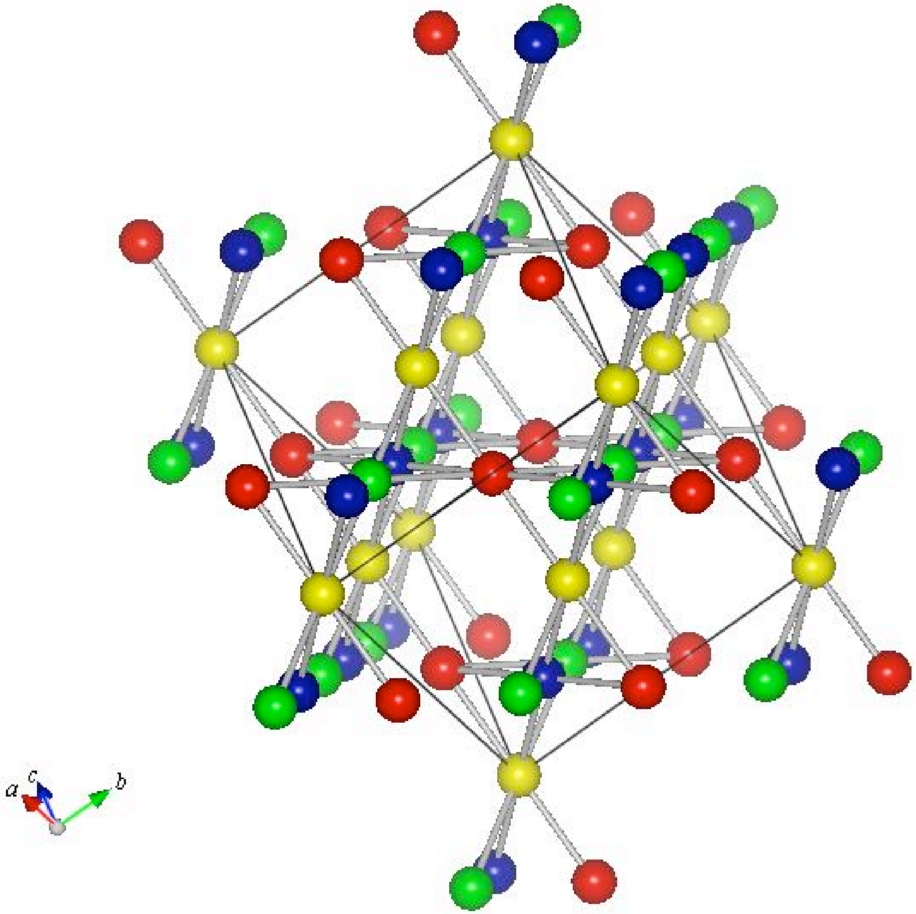
- $T_N > |\Theta_{CW}|$: AFM and FM Js

$GeNi_2O_4$: Neutron diffraction from a single crystal

M. Matsuda *et al.*, cond-mat/0708.3162 (2007)



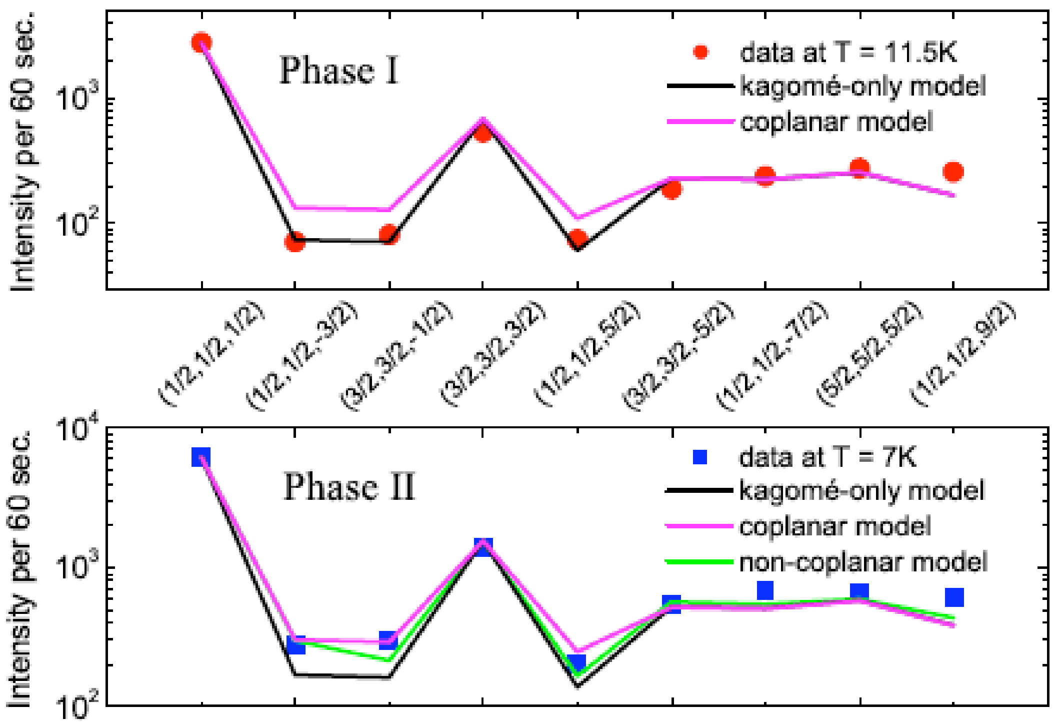
- I(1/2,1/2,1/2) / I(1/2,1/2,-3/2) is different in the two phases
- The two phases have different magnetic structures

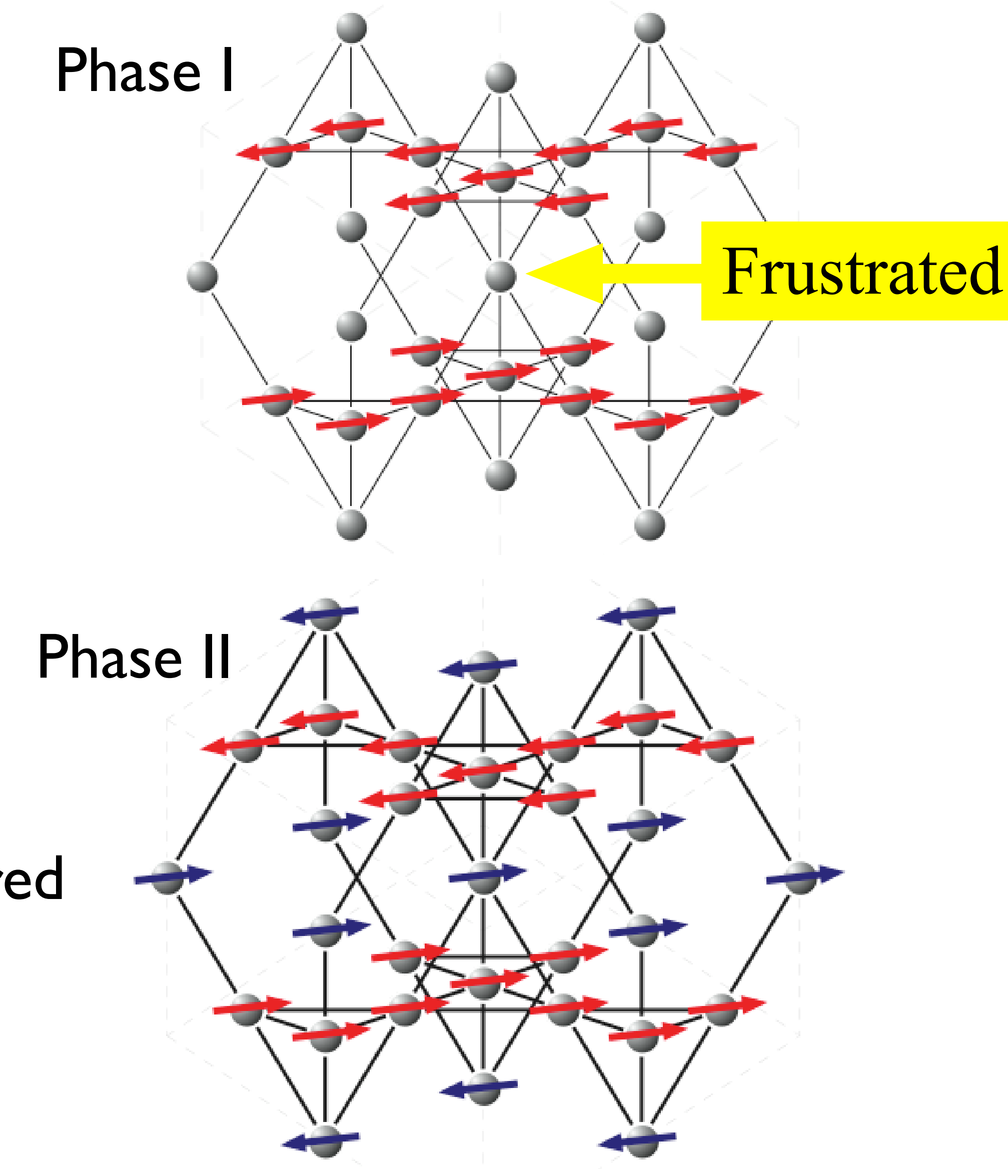


- Four sublattices each of which forms an FCC lattice
- Along <111>, three sublattices form kagome planes and one forms triangular planes

$GeNi_2O_4$: Magnetic structures of the two phases

M. Matsuda *et al.*, cond-mat/0708.3162 (2007)



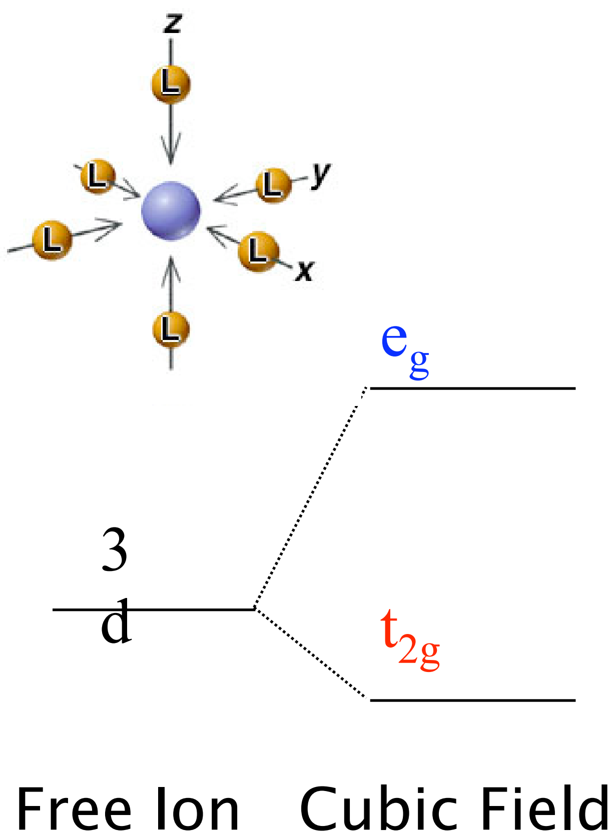


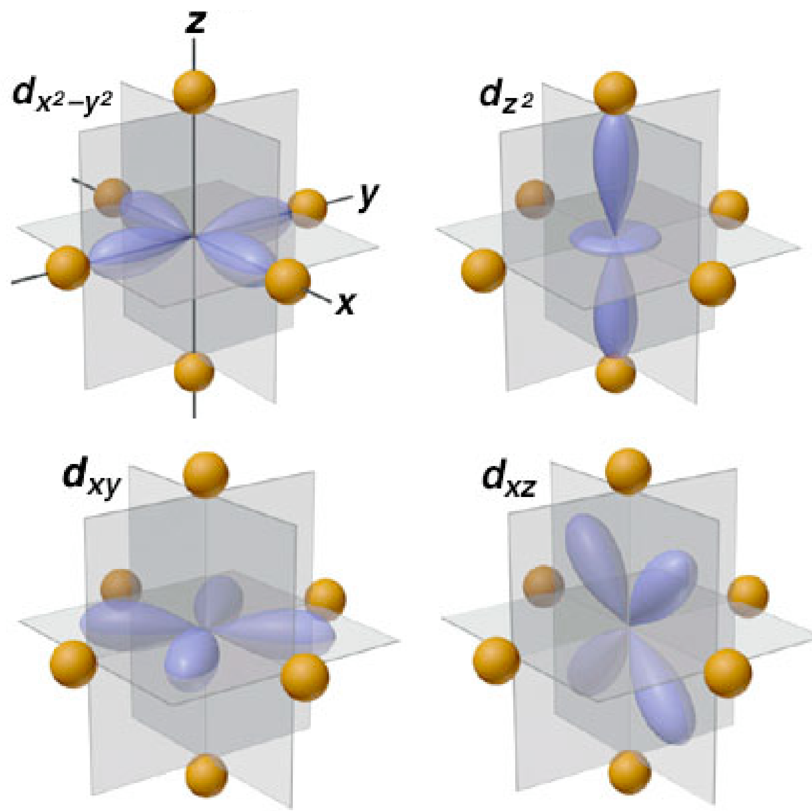
- In phase I, only kagome spins are ordered with <M> = 1.3 μ_B

- In phase II, kagome and triangular spins are ordered with <M> = 1.8 μ_B
- kagome and triangular spins lie on the <111> plane

Spinels AB_2O_4 with B = 3d transition metal ions

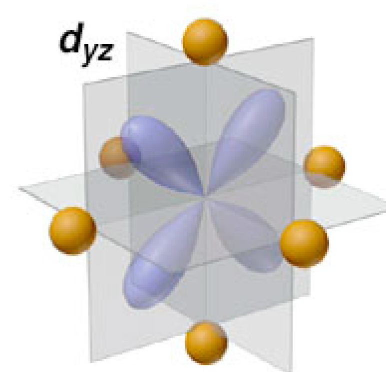
Electronic states vs Magnetism





lie along the ligand axes

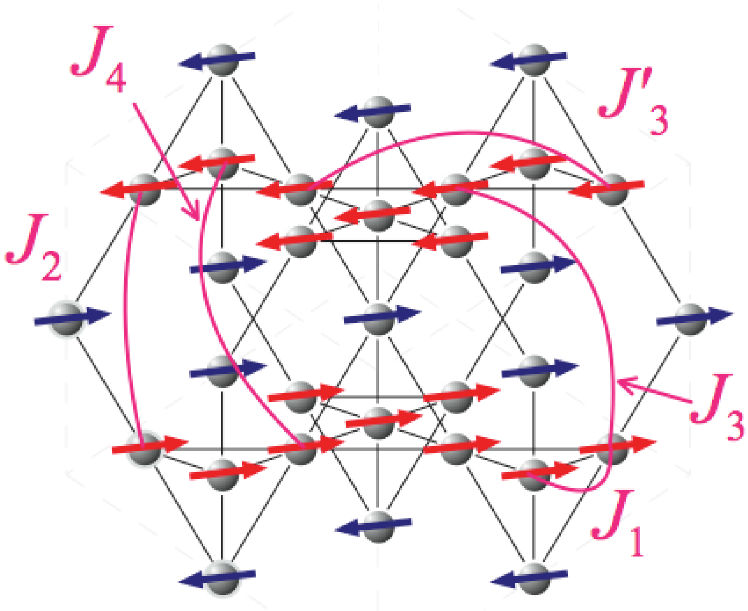
B-O-B superexchange
--> 2nd or 3rd neighbor Js



lie between the ligand axes

B-B direct overlap
--> AFM NN J

$GeNi_2O_4$: The origin of the two magnetic phase transitions



Superexchange interactions that involve one to two superexchange steps

J	d	Path	θ	n_B	Z_K	Z_T
J_1	$\sqrt{2}$	BOB	90°	2	4 (I), 2 (T)	6 (K)
J_2	$\sqrt{6}$	$BOAOB$	125°, 125°	1	4 (I), 4 (K), 4 (T)	12 (K)
		$BOBOB$	90°, 90°	4		
J_3	$\sqrt{8}$	$BOAOB$	125°, 125°	2	2 (I), 4 (K)	6 (I)
J'_3	$\sqrt{8}$	$BOBOB$	90°, 90°	4	4 (I), 2 (K)	6 (T)
J_4	$\sqrt{10}$	$BOAOB$	125°, 125°	1	8 (K), 4 (T)	12 (K)

Mean-field energy for the observed (1/2,1/2,1/2) structure

$$E_{\rm kag} = 2J_1 - J_3 + J'_3 - 4J_4;$$
$$E_{\rm tri} = 3J_3 - 3J'_3,$$

$$E_{\rm tot} = \tfrac{3}{4}E_{\rm kag} + \tfrac{1}{4}E_{\rm tri} = \tfrac{3}{2}J_1 - 3J_4$$

Mean-field energy for (1,0,0) and (1,1,0) structures

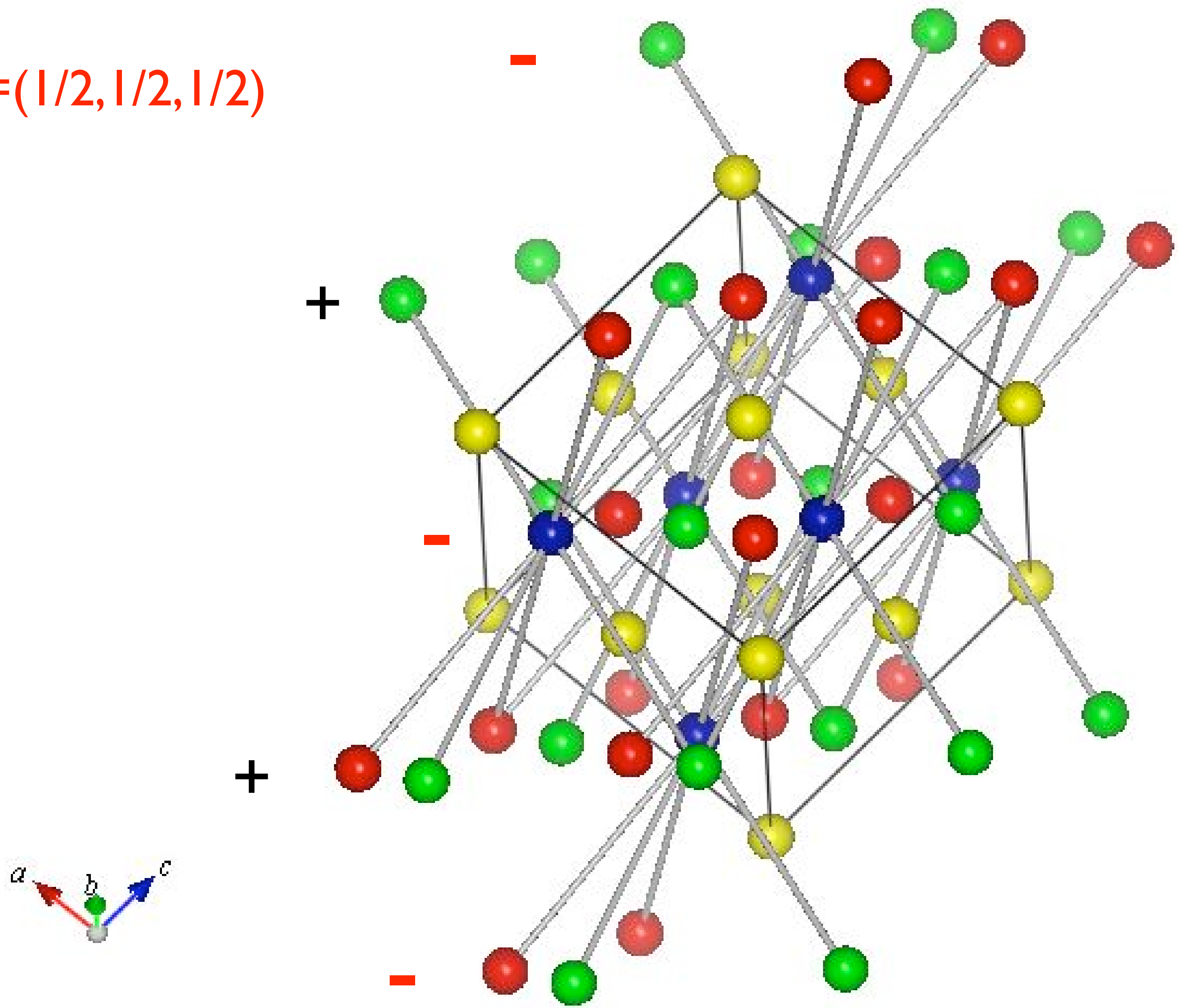
$$E^*_{\rm tot} = -J_3 - J'_3 + 3J_6 \pm |J_1 - 2J_2 + 2J_4|$$

$$E_{\rm tot} < E^*_{\rm tot} \quad \Rightarrow \quad \boxed{J_4 > \frac{5}{2}J_1 - 2J_2 + J_3 + J'_3}$$

:AFM J_4, FM J_1

Consistent with the Goodenough-Kanamori rules for $GeNi_2O_4$

J_4 bondings among kagome spins



-8 J_4

Average total E due to J_4 per spin
$= 3*(-8 J_4) /4 = -6 J_4$

$GeNi_2O_4$: The origin of the two magnetic phase transitions

Mean-field energy for kagome and triangular spins

$$\begin{aligned} E_{\rm kag} &= 2J_1 - J_3 + J_3' - 4J_4; \\ E_{\rm tri} &= 3J_3 - 3J_3', \end{aligned} \quad \Rightarrow \quad \begin{aligned} k_B T_{N1} &= \tfrac{2}{3}|E_{\rm kag}| \\ k_B T_{N2} &= \tfrac{2}{3}|E_{\rm tri}| \end{aligned}$$

$$k_B T_{N2} \lesssim k_B T_{N1} \quad \Rightarrow \quad J_4 - J_1/2 \gtrsim J_3' - J_3$$

$J_3' > J_3$; J_3' may be antiferromagnetic and J_3 ferromagnetic

consistent with the Goodenough-Kanamori rules?

J	d	Path	θ	n_B	Z_K	Z_T
J_1	$\sqrt{2}$	BOB	90°	2	4 (I), 2 (T)	6 (K)
J_2	$\sqrt{6}$	$BOAOB$	125°, 125°	1	4 (I), 4 (K), 4 (T)	12 (K)
		$BOBOB$	90°, 90°	4		
J_3	$\sqrt{8}$	$BOAOB$	125°, 125°	2	2 (I), 4 (K)	6 (I)
J_3'	$\sqrt{8}$	$BOBOB$	90°, 90°	4	4 (I), 2 (K)	6 (T)
J_4	$\sqrt{10}$	$BOAOB$	125°, 125°	1	8 (K), 4 (T)	12 (K)

Summary

$GeNi_2O_4$

- The two magnetic phase transitions are due to the existence of two types of spins for a given k: majority kagome and minority triangular spins.
- At 12.1K, kagome spins order due to AFM J_4 interactions.
- At 11.4K, triangular spins order. Exchange theory containing only *J*s calls for AFM J_3' and FM J_3, which is not consistent with the Goodenough-Kanamori rules.