Spin exchange interactions and magnetic properties

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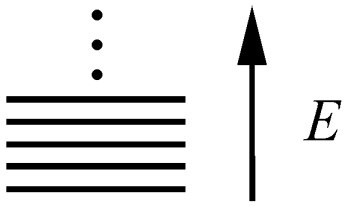
$Na_3Cu_2SbO_6$	AF-F vs. AF-AF chain?
Ca_3CoMnO_6	Ising magnetism vs. JT distortion
$Sr_3Fe_2O_5$	Magnetic dipole-dipole & 3D order
Cs_2CuCl_4	Cause for 2D spin lattice
$Bi_4Cu_3V_2O_{14}$	Diamond chain?
$Cu_3(CO_3)_2(OH)_2$	Diamond chain?
$YbAl_3C_3$	Phase transition & spin gap
$[Cu(HF_2)(pyz)_2]BF_4$	Magnetoelastic interaction

Magnetic solids:

Low-energy excitations



$$\hat{H}_{spin} = \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j$$ **Pair-wise spin exchange**

Spin exchange parameter J_{ij}

- **Experiment:** Fitting with spin-lattice models, unique?
- **Theory**
  - **Formal:** Excitation spectrum in terms of J's
  - **Computational:** Numerical values of J's
    - Ordered spin states
    - ΔE (spin $\hat{H}$): J's $\leftrightarrow$ ΔE (electronic $\hat{H}$): DFT+U calc.
- **New physics?**

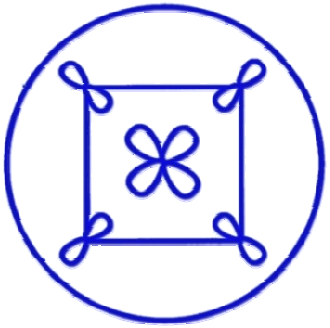
Magnetic orbitals & spin exchange

V^{4+} (d^1)

xy

Cu^{2+} (d^9)

$x^2–y^2$

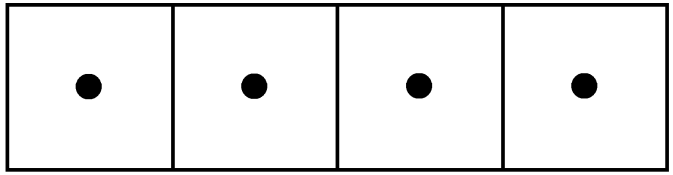


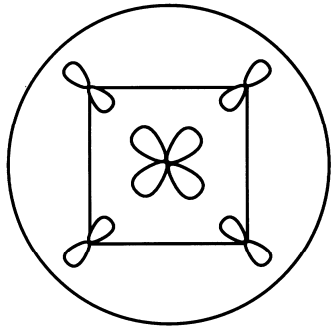
Local bonding: d-orbital with p-orbital tails

Spin exchange: Governed by the p-orbital tails

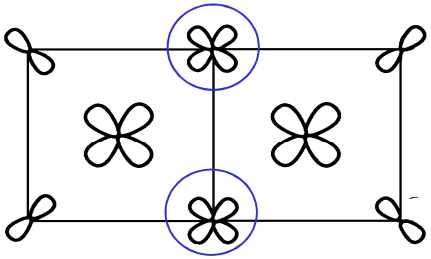
→ Pair-wise interactions

CuO_2 chain





J_{nn}

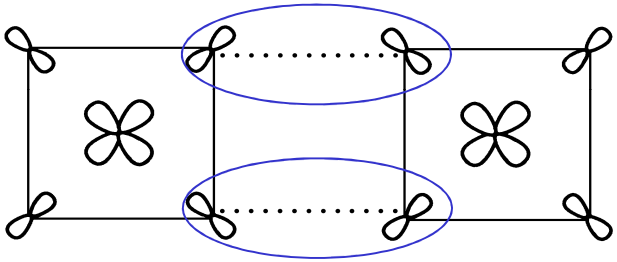


Superexchange

$$S_{ij} = \langle \phi_i | \phi_j \rangle \approx 0, \ \rho_{ij} = \phi_i \phi_j \neq 0$$

$J_{nn} > 0$

J_{nnn}



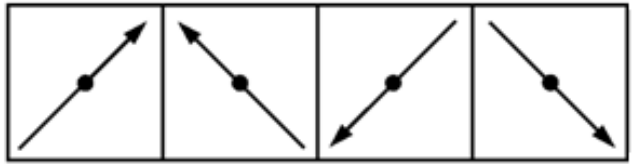
Super-superexchange

$$S_{ij} = \langle \phi_i | \phi_j \rangle \neq 0, \ \rho_{ij} = \phi_i \phi_j \approx 0$$

$J_{nnn} < 0$

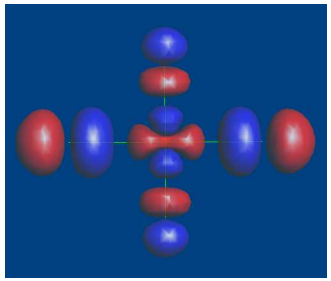
Geometric spin frustration

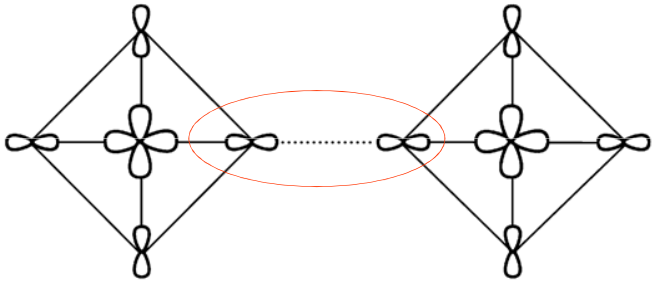
$\rightarrow$ Non-collinear spin

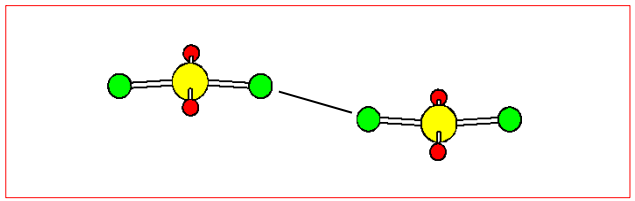


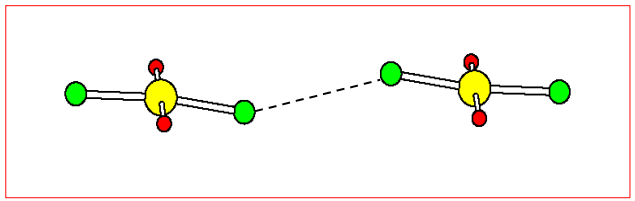
$(CuCl)LaNb_2O_7$

$CuCl_2O_2$

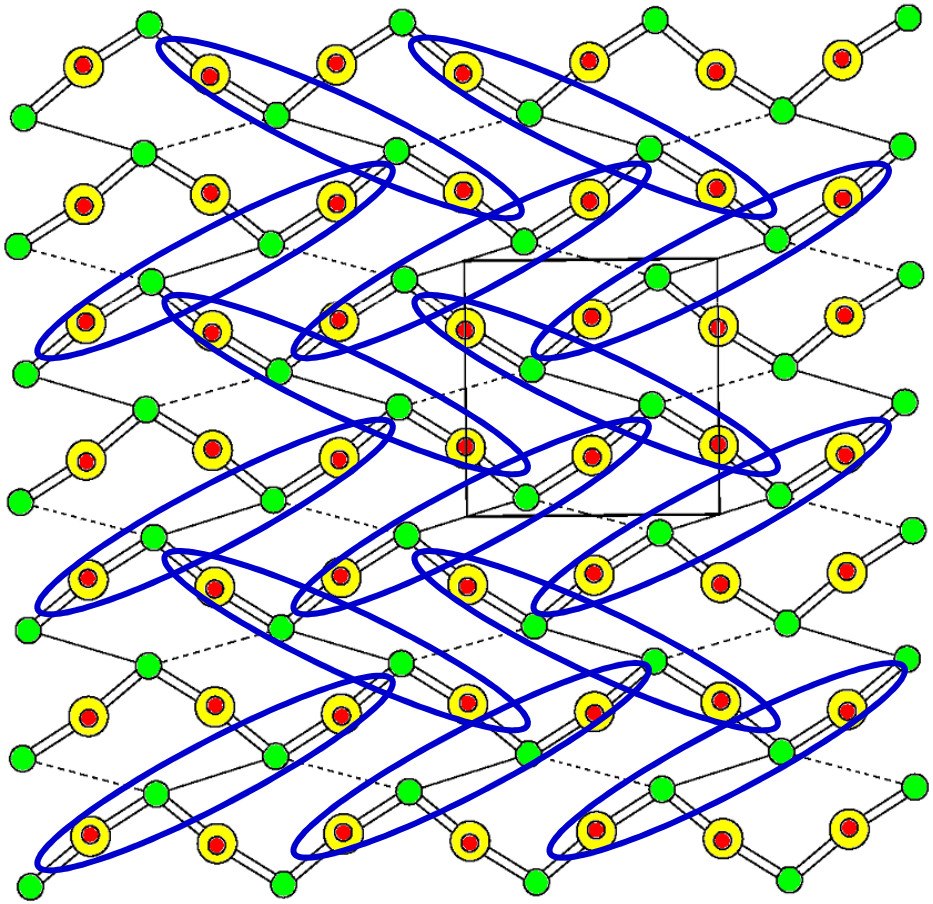






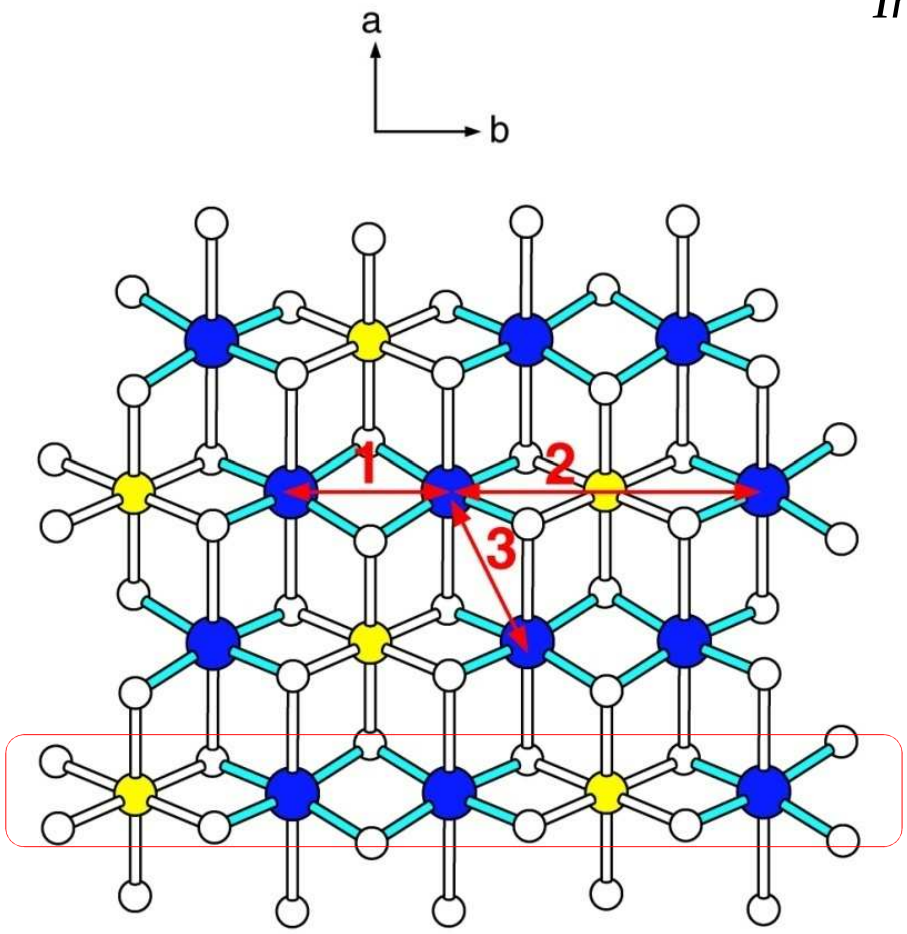


$CuClO_2$ layer: spin dimer



$Na_3Cu_2SbO_6$ & $Na_2Cu_2TeO_6$: AF-F or AF-AF chain?

Inorg. Chem. **47**, 128 (2008)



J_1, J_3: Cu-O-Cu

J_2: Cu-O…O-Cu

J_1-J_2 chain

k_BK

$Na_3Cu_2SbO_6$

	Calc.		χ-fitting	
	U = 4 eV	U = 5 eV	AF-F	AF-AF
J_1	-179	-166	-209	62
J_2	379	345	165	160
J_3	21	19	-	-

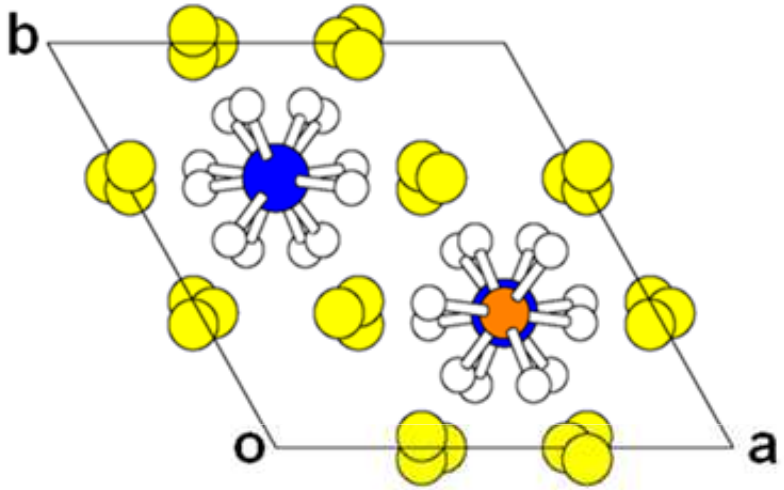
$Na_2Cu_2TeO_6$

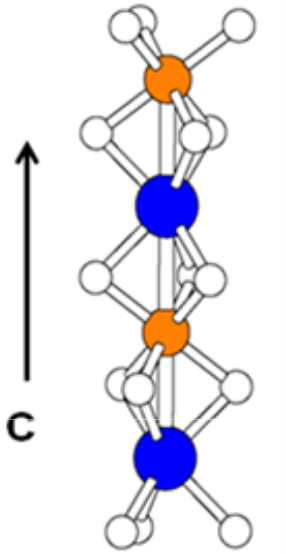
	Calc.		χ-fitting	
	U = 4 eV	U = 5 eV	AF-F	AF-AF
J_1	-190	-175	-215	28
J_2	733	617	272	270
J_3	32	19	-	-

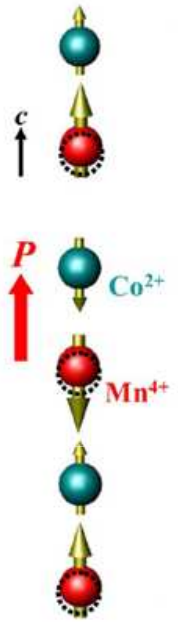
Neutron scattering: AF-F model!

Ca_3CoMnO_6: Ising magnetism vs. JT distortion

Phys. Rev. B **79**, 054432 (2009)







CoO_6 TP : **Co^{2+} (HS, d^7) at high T**

MnO_6 OCT: **Mn^{4+} (HS, d^3)**

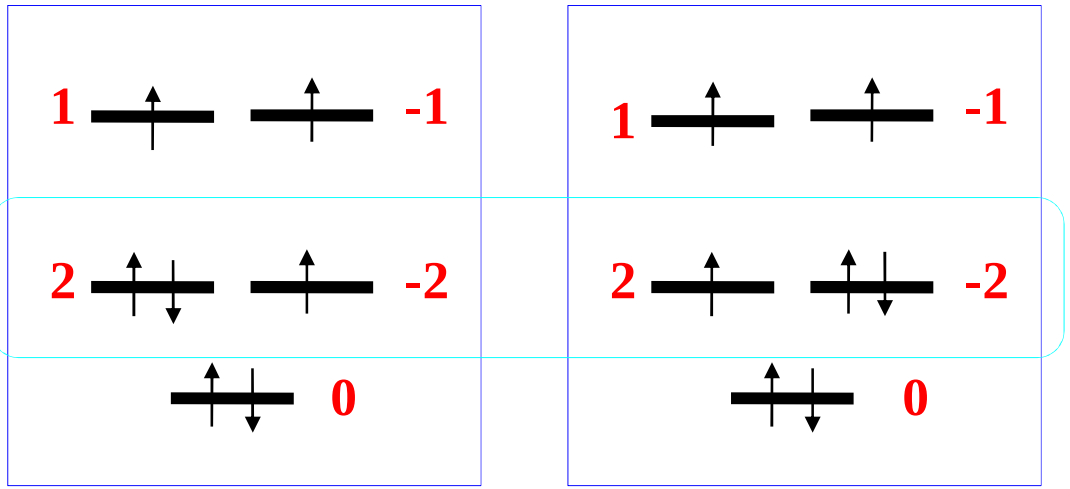
↑↑↓↓

Collinear ↑↑↓↓ :

No inversion symmetry → ferroelectric polarization

Ising magnetism?

High spin Co^{2+} (d^7, L = 2, S = 3/2) at TP



$(2, -2) \leftrightarrow (x^2-y^2, xy)$

$(1, -1) \leftrightarrow (xz, yz)$

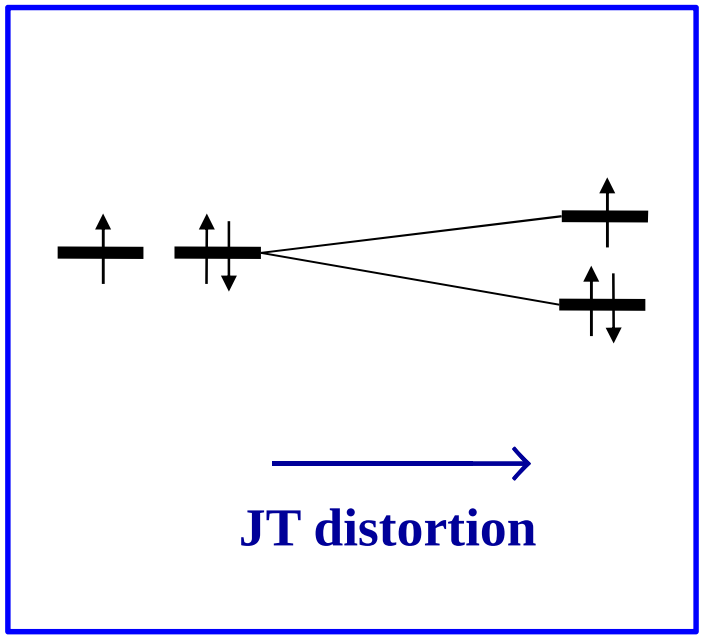
$0 \leftrightarrow z^2$

z-axis
// the 3-fold rotational axis

Unevenly filled degenerate level
Ising magnetism

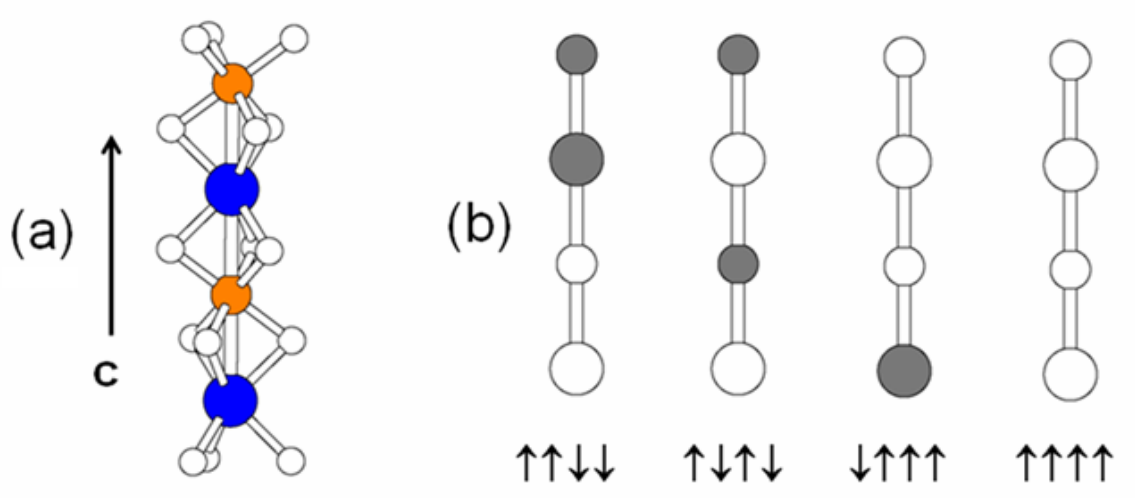
$$\hat{\mathbf{H}}_{SOC} = \lambda \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \rightarrow \quad J = 7/2, \quad J_z = \pm 7/2, \quad \Delta J_z = 7 > 1$$

Jahn-Teller (JT) instability:
Unevenly filled degenerate level



JT distortion → Removal of Ising magnetism?

DFT+U+SOC calculations



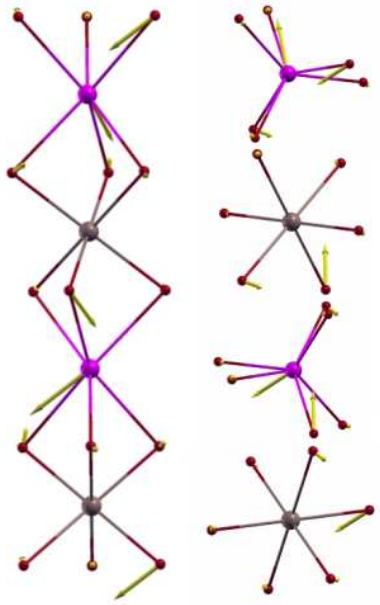
meV/ FU

Structure used	↑↑↓↓	↑↓↑↓	↑↑↑↓	↑↑↑↑
Experimental with C_3 symmetry (293 K)	0.00 (59.2)[a]	1.69	9.41	31.75
Optimized with C_3 symmetry	0.00 (31.3)[a]	14.38	21.87	53.12
Optimized without C_3 symmetry	0.00 (0.00)[a]	11.89	21.26	52.93

The ↑↑↓↓ state undergoes a JT distortion.

Ca_3CoMnO_6

JT distortion



↑↑↓↓

Loss of the C_3 symmetry

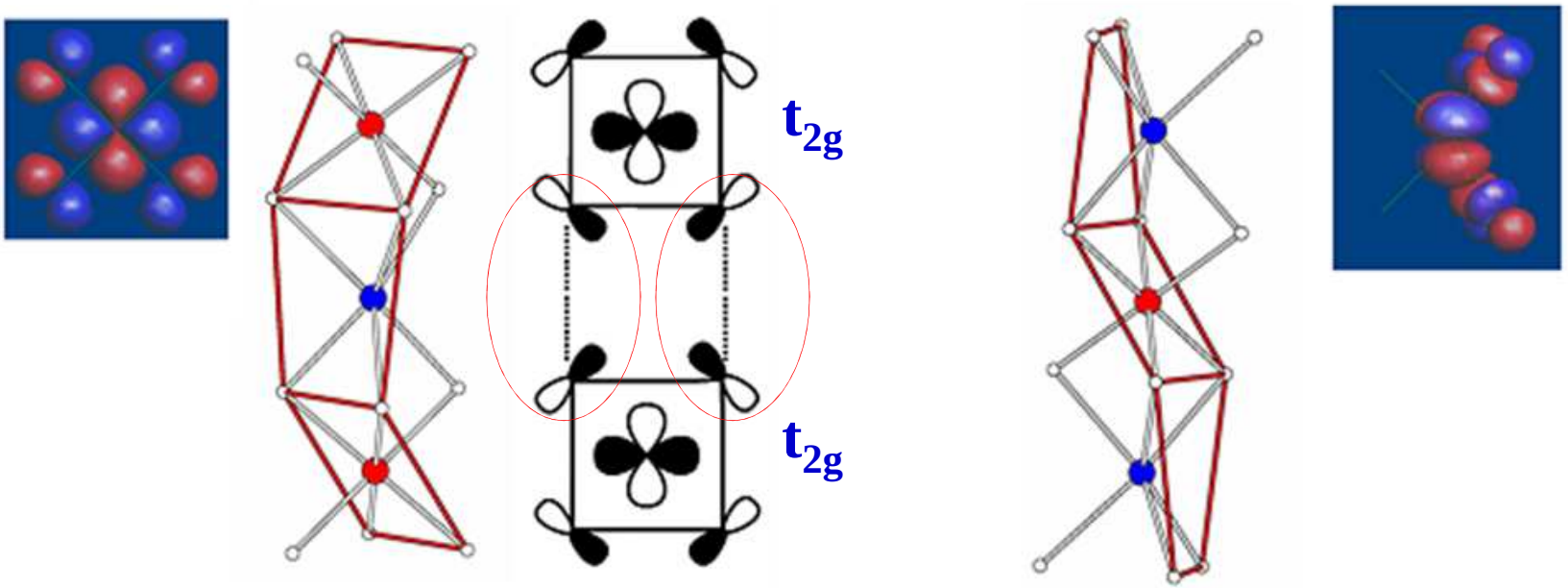
$\|\uparrow\uparrow\downarrow\downarrow\rangle$	Spin Moment		Orbital Moment (μ_L)	
	Co^{2+}	Mn^{4+}	Co^{2+}	Mn^{4+}
Experimental with C_3 symmetry	2.48	2.61	1.50	-0.02
Optimized with C_3 symmetry	2.49	2.59	1.50	-0.02
Optimized without C_3 symmetry	2.49	2.59	0.56	-0.02

A partial quenching of μ_L by JT distortion $\rightarrow$ a weak JT distortion

Why ↑↑↓↓ ? J_{NNN} , strongly AFM

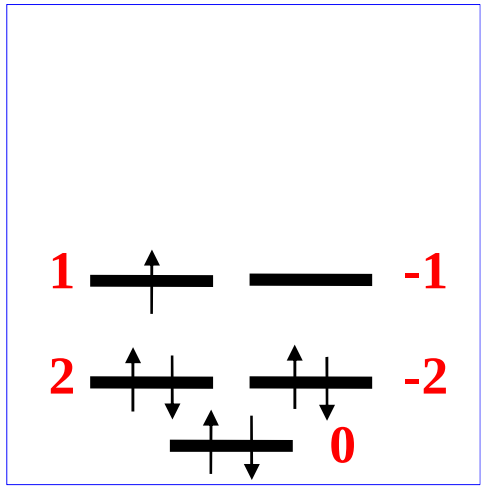
meV

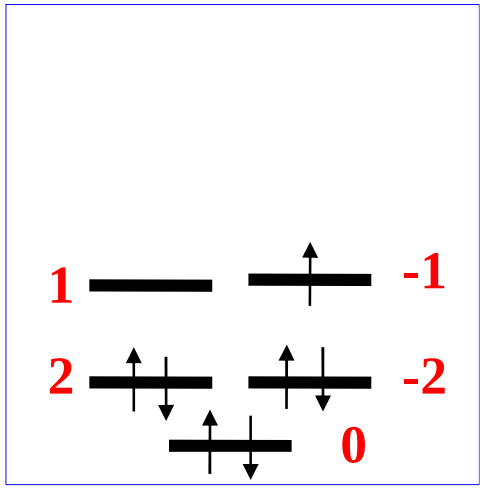
Geometry	$J_{Co\text{-}Mn}$	$J_{Mn\text{-}Mn}$	$J_{Co\text{-}Co}$
Experimental	3.34	2.09	1.63
Optimized with high μ_L	4.31	4.89	2.64
Optimized with low μ_L	4.56	4.72	2.47

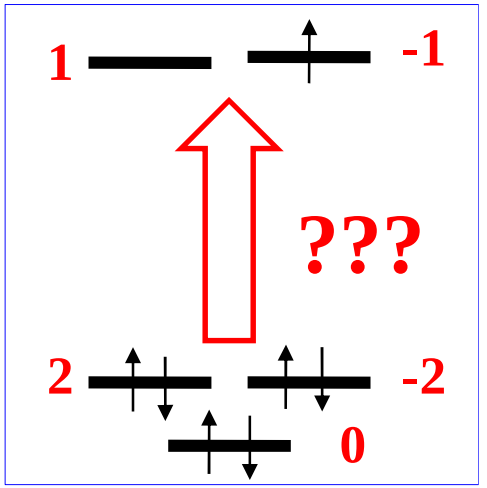


Neutron diffraction at low T

Low spin Co^{2+} (d^7, L = 1, S = 1/2) at TP?







Ising magnetism:

$J = 3/2, \quad J_z = \pm 3/2, \quad \Delta J_z = 3 > 1$

DFT+U calc: High-spin << Low-spin !

Spin orientation & 3D order

$$\textbf{SOC}: \quad \lambda \vec{S} \cdot \vec{L}$$

$$\textbf{SE}: \quad -\sum_{i<j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

$$\textbf{AS}: \quad \vec{D} \cdot (\vec{S}_i \times \vec{S}_j)$$

$$\textbf{MDD}: \quad \left(\frac{g^2 \mu_B^2}{a_0^3} \right) \left(\frac{a_0}{r_{ij}} \right)^3 \left[-3(\vec{S}_i \cdot \vec{e}_{ij})(\vec{S}_j \cdot \vec{e}_{ij}) + (\vec{S}_i \cdot \vec{S}_j) \right]$$

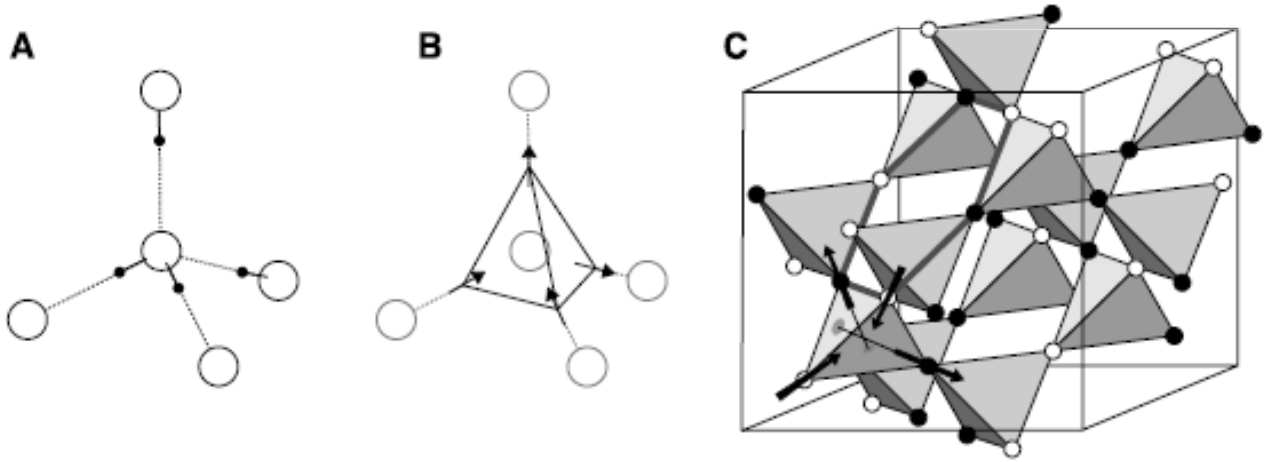
MDD interactions

Cause for spin orientation & 3D magnetic order

$$\text{MDD} \propto S^2$$

Spin ice systems: $Dy_2Ti_2O_7 \rightarrow Dy^{3+}\ (f^9)$

$Ho_2Ti_2O_7 \rightarrow Ho^{3+}\ (f^{10})$

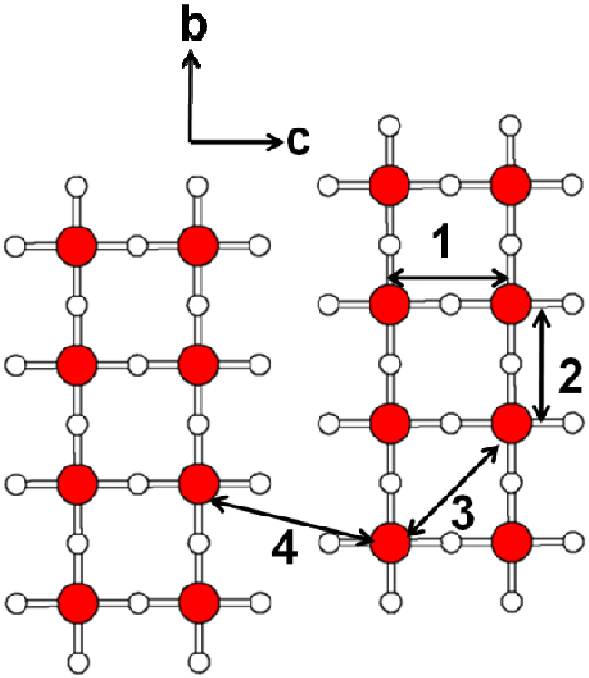


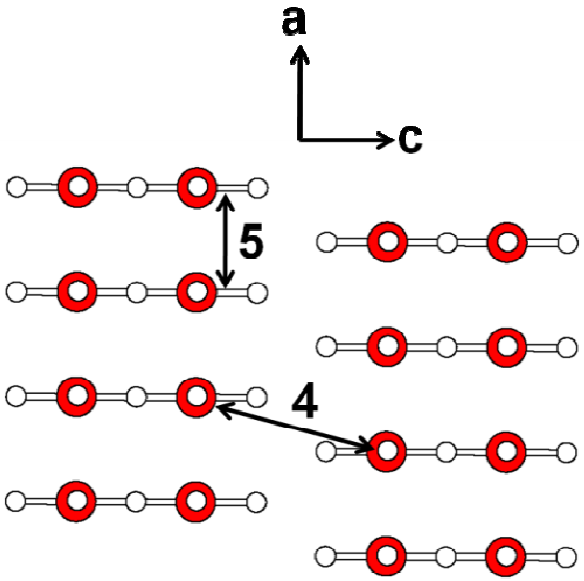
Transition-metal analog?

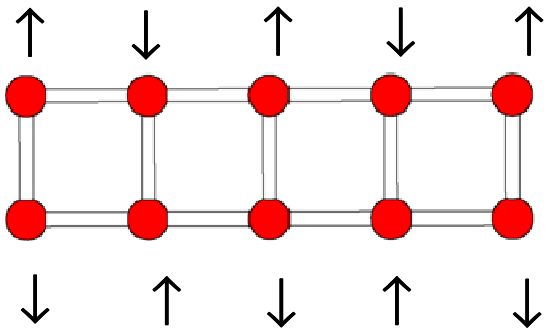
$Sr_3Fe_2O_5$: MDD & 3D order?

Fe^{2+} (S = 2, d^6)

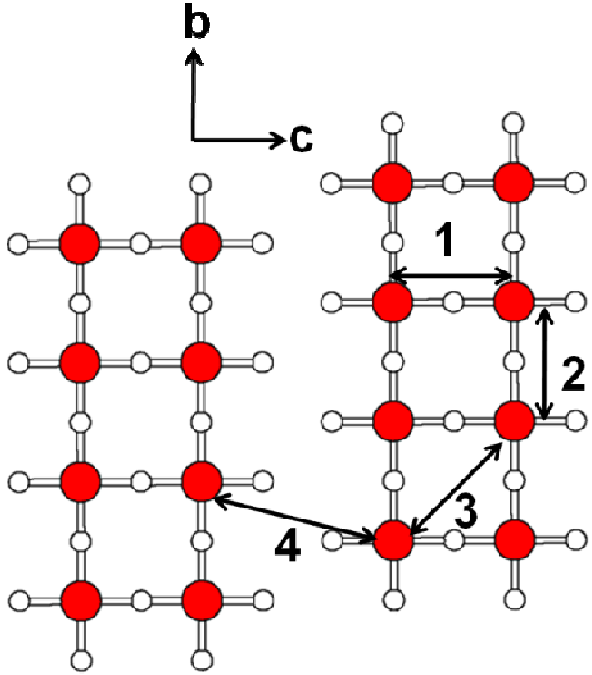
Inorg. Chem. **48**, 9051 (2009)

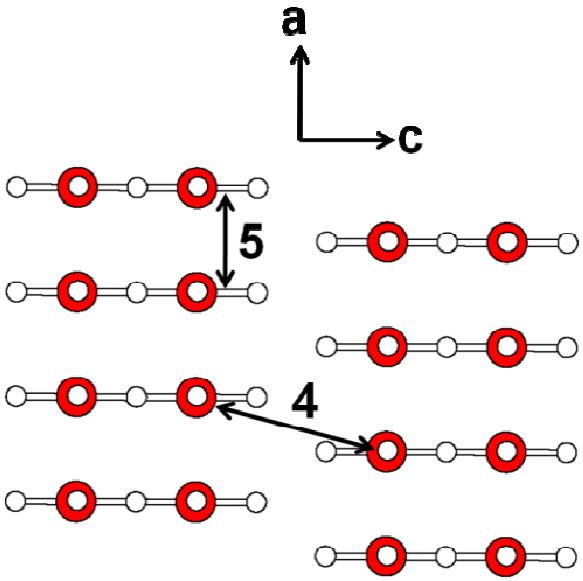






3D AFM structure
(2a, 2b, c) supercell





$k_B K$

J_1	73.9
J_2	70.4
J_3	4.6
J_4	-0.06
J_5	17.2

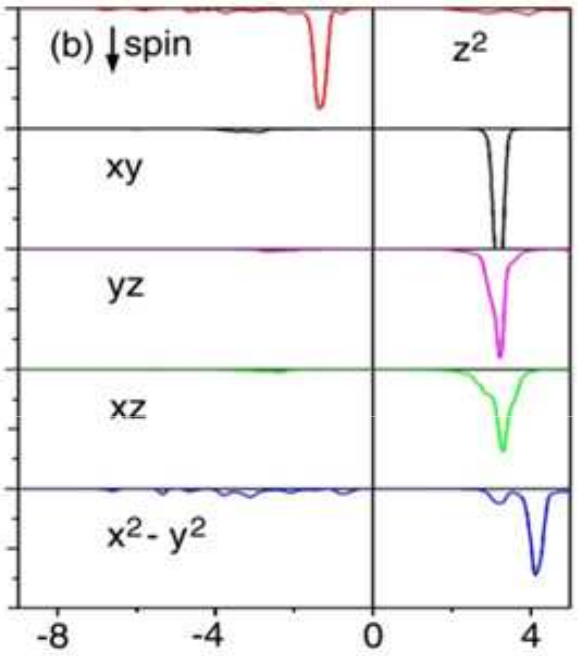
$J_1, J_2, J_5 \rightarrow$ (2a, 2b, c)
//ab AFM slab

Inter-slab $\rightarrow$ $(J_2, J_4, J_4), (J_5, J_4, J_4)$
frustrated

Monte Carlo $\rightarrow$ No 3D order

$T_N \approx 280$ K !

$$\hat{H}_{SOC} = \lambda \hat{S} \cdot \hat{L} \approx \lambda \hat{S}_{z'} \left(\hat{L}_z \cos\theta + \frac{1}{2} \hat{L}_+ e^{-i\phi} \sin\theta + \frac{1}{2} \hat{L}_- e^{i\phi} \sin\theta \right) + \ldots$$



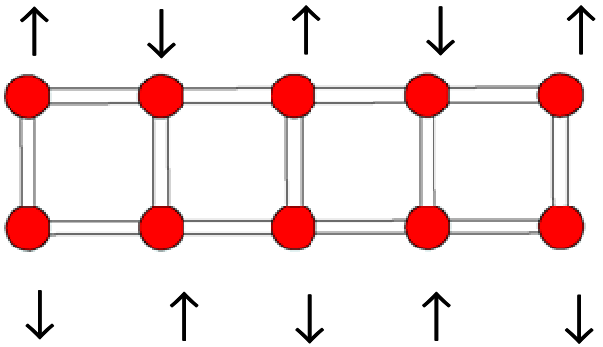
$$-\frac{\left\langle \phi_{occ} \left| \hat{H}_{SOC} \right| \phi_{unocc} \right\rangle^2}{\Delta E}$$

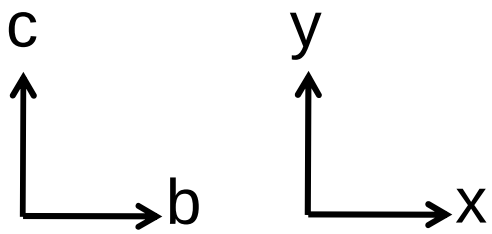
$z^2 \leftrightarrow$ xz, yz

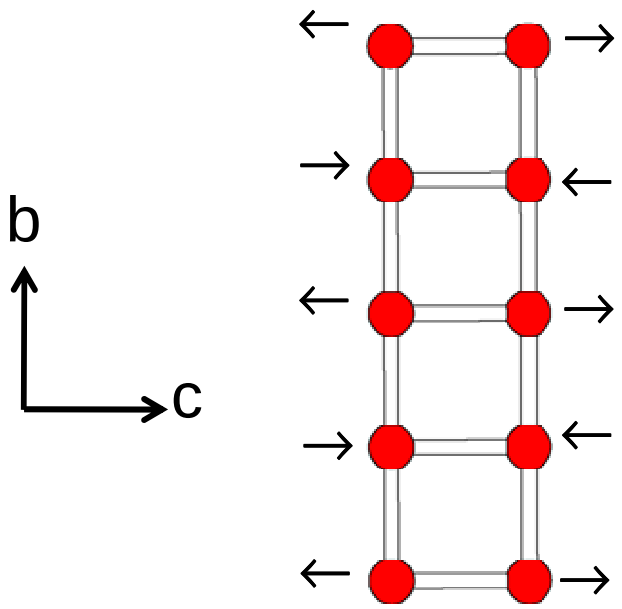
$\theta = 90°$

Spin: $\perp$a

//c or //b?







meV/ 8 FUs

	SOC	MDD
//a	1.843	0.258
//b	0.217	0.102
//c	0.000	0.000

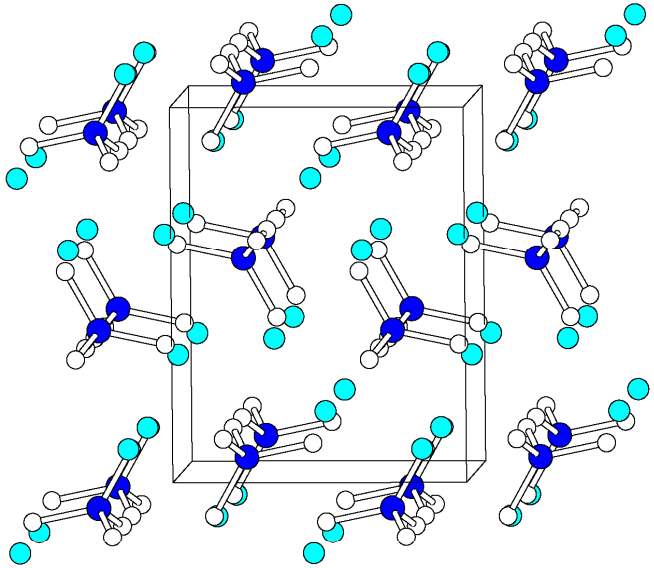
SOC: Local interaction
Cannot remove the inter-slab spin frustration

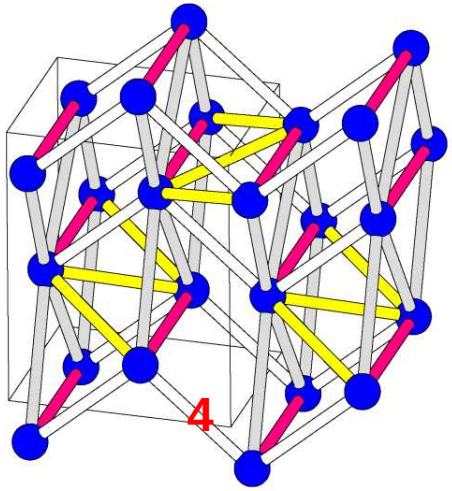
MDD : Long-range interaction
Removes the inter-slab spin frustration
3D AFM ordering

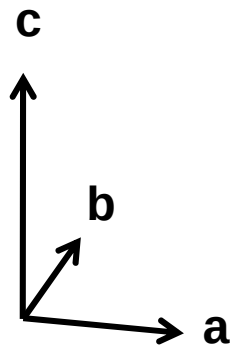
Cs_2CuCl_4: Cause for 2D spi lattice

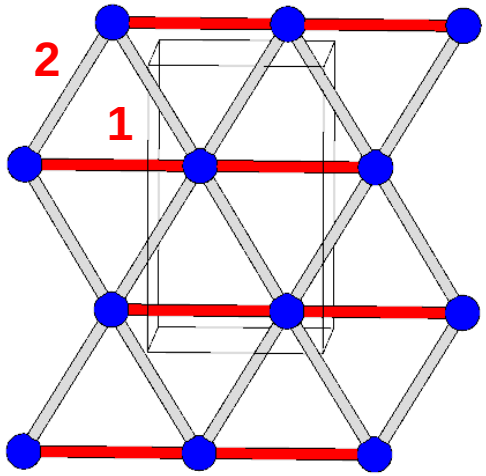
Isolated $(CuCl_4)^{2-}$ ions

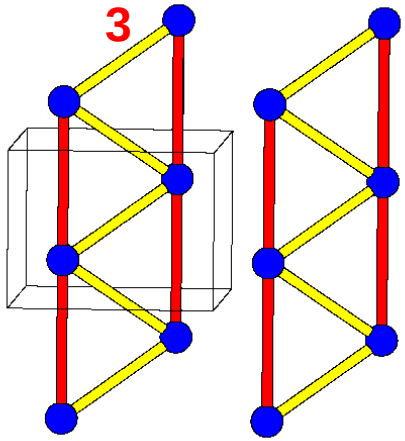
Inorg. Chem. **48**, 4185 (2009)









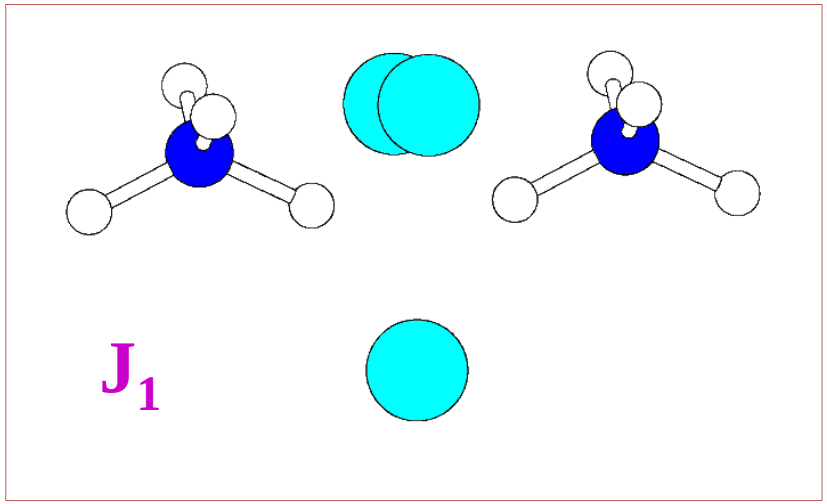


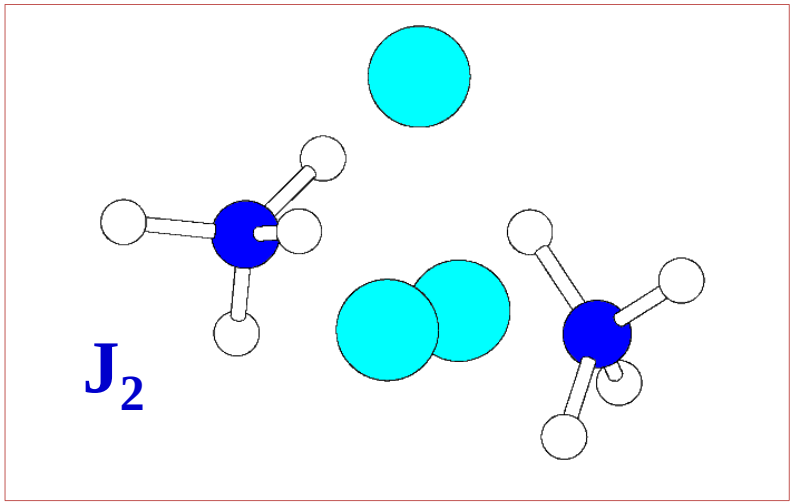
2D triangular antiferromagnet //bc: $J_2/J_1 \approx 1/3$

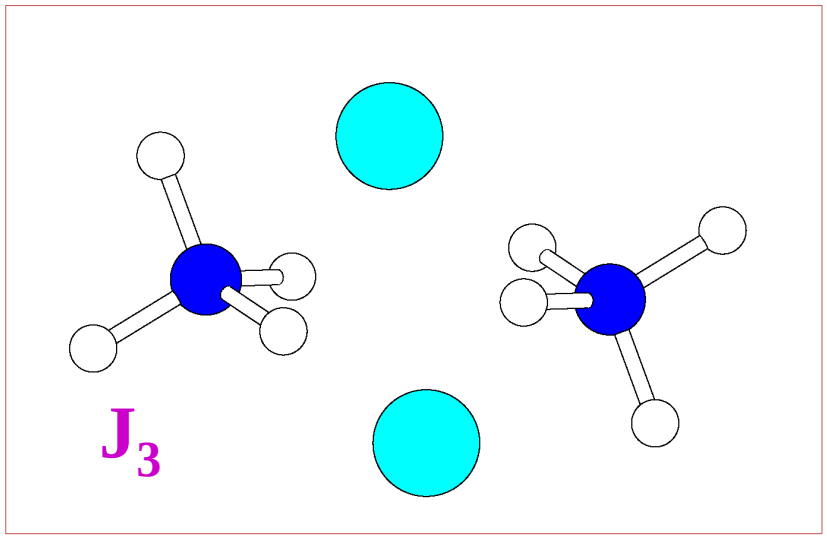
$k_B K$

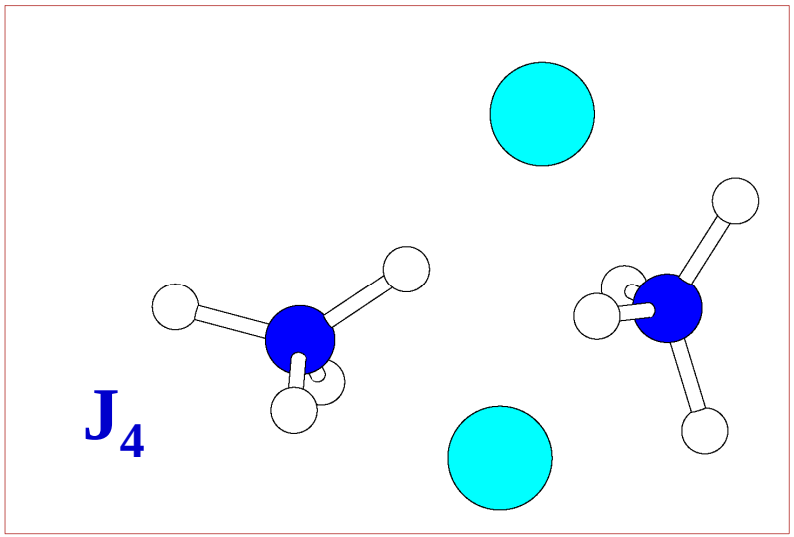
	A_2CuCl_4				$(CuCl_4)_2$
	A = Cs	A = Rb	A = K	A = Na	
J_1	8.5	14.0	16.6	21.2	36.2
J_2	4.8	4.8	4.8	4.5	4.3
J_3	0.0	3.6	6.2	12.6	12.8
J_4	-0.3	-0.2	-0.3	-0.7	-0.3

Spin dimers $(CuCl_4)_2$



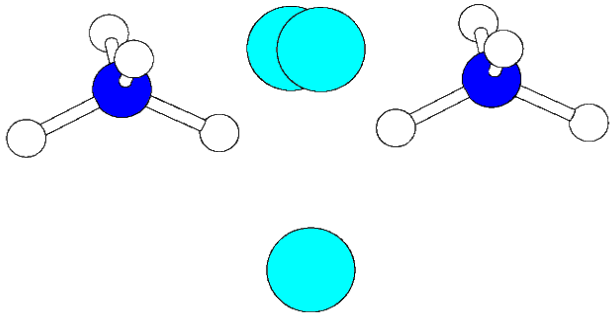


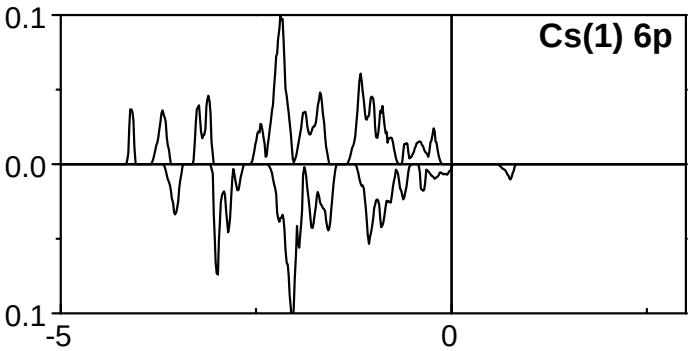


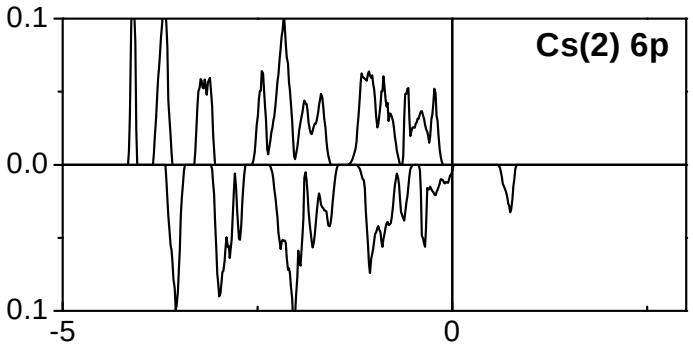


Symmetrical

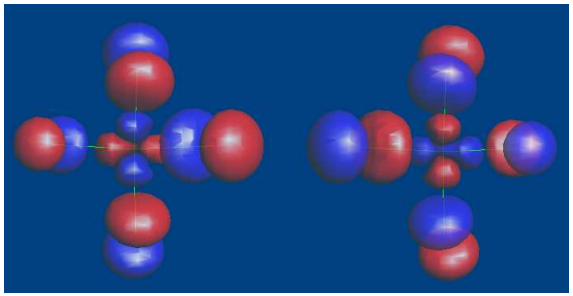
Asymmetrical



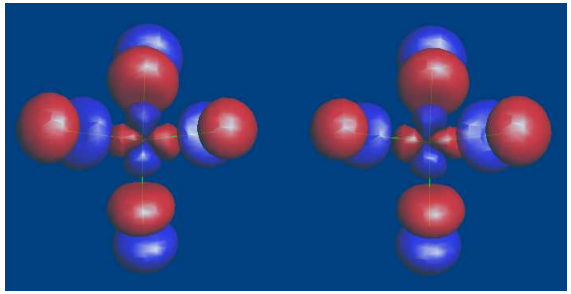


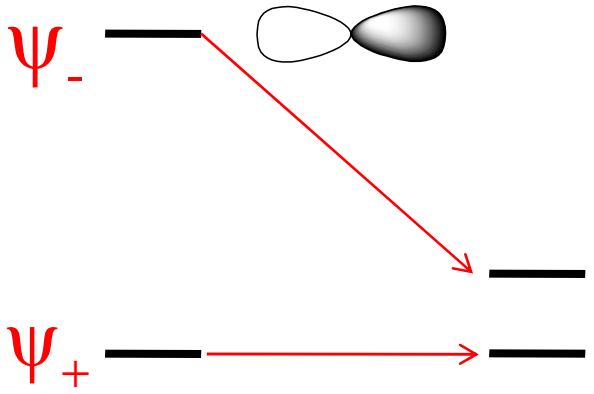


ψ_-



ψ_+





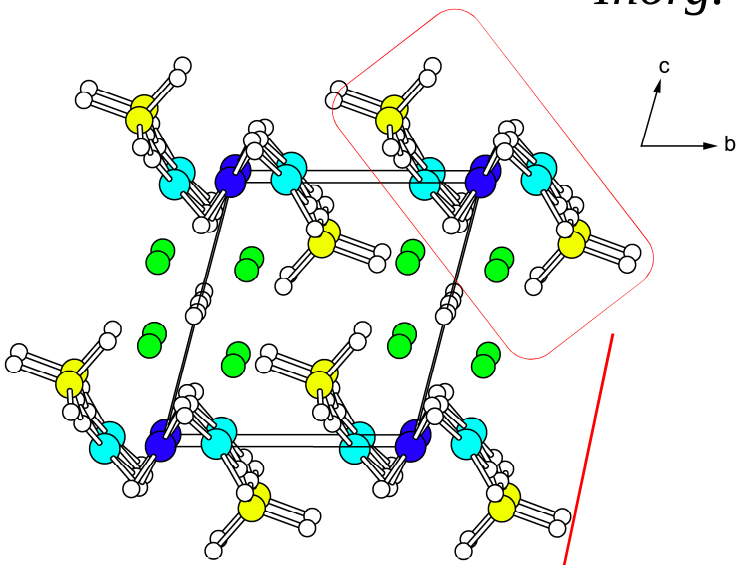
without Cs 6p

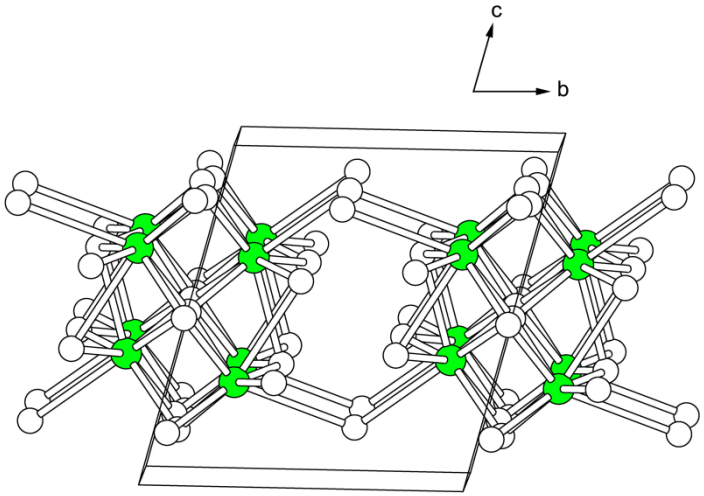
with Cs 6p

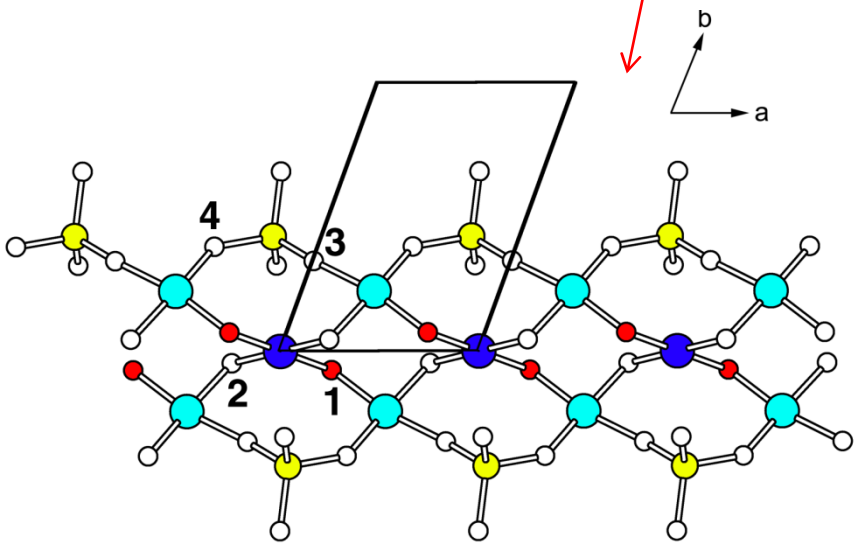
Selective participation of the Cs^+ 6p orbitals

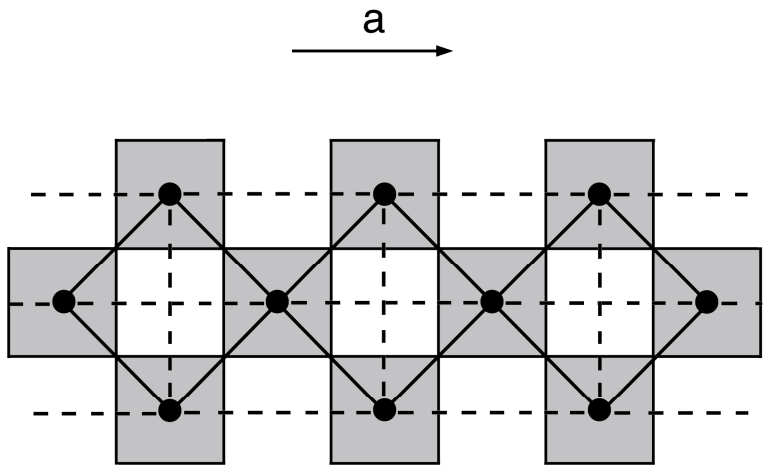
$Bi_4Cu_3V_2O_{14}$: Diamond chain?

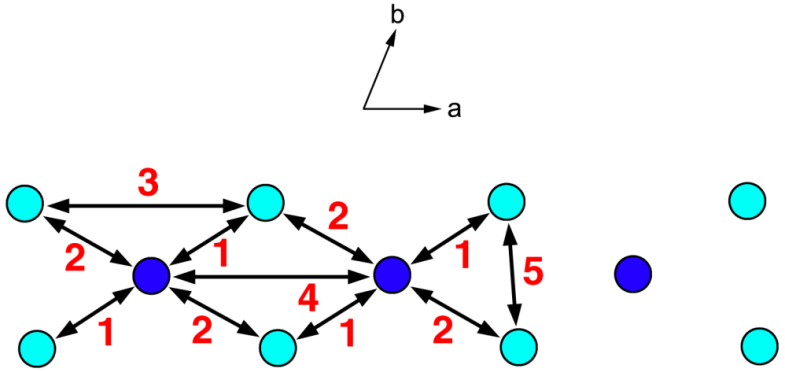
Inorg. Chem. **47**, 4779 (2008)

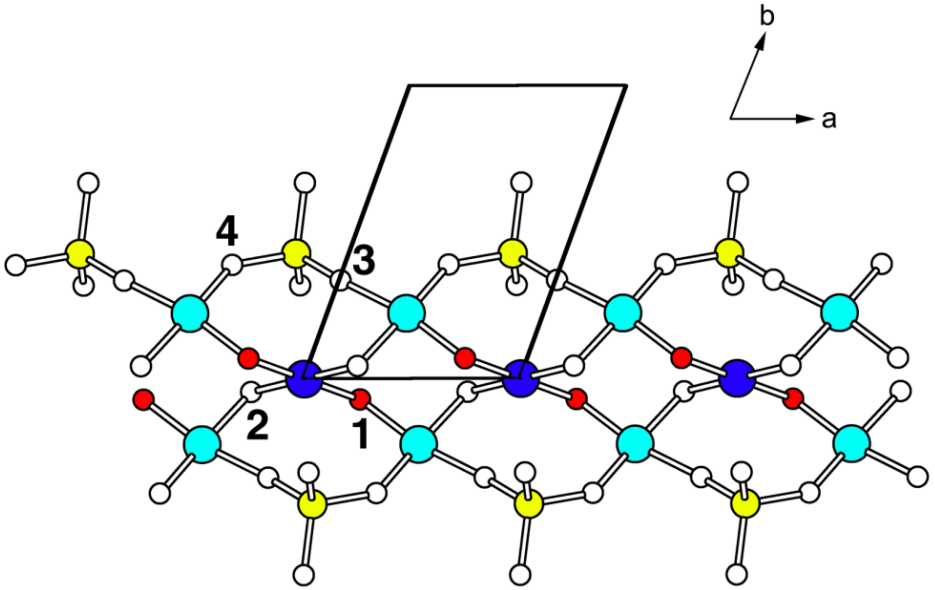






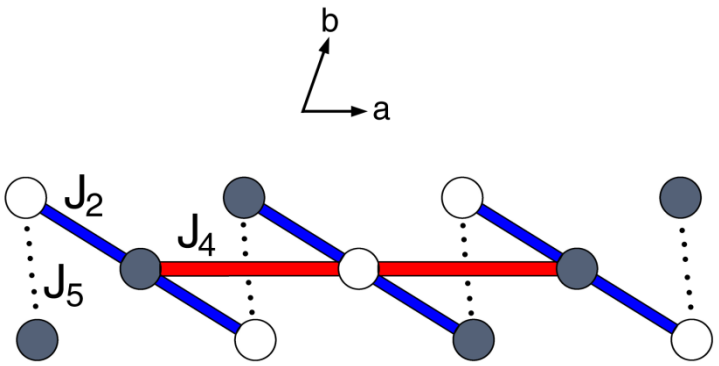






J_1	∠Cu-O-Cu = 103.4
J_2	∠Cu-O-Cu = 114.5

J_3	O…O = 2.729 O…O = 2.687	∠Cu-O…O = 159.2, 109.7 ∠Cu-O…O = 142.6, 124.0
J_4	O…O = 2.646 O…O = 2.646	∠Cu-O…O = 133.4, 130.8 ∠Cu-O…O = 133.4, 130.8
J_5	O…O = 2.906 O…O = 2.906	∠Cu-O…O = 78.4, 80.1 ∠Cu-O…O = 78.4, 80.1



meV

	U = 5 eV	U = 6 eV
J_1	1.9	1.3
J_2	15.7	13.1
J_3	-0.9	-0.8
J_4	18.7	16.5
J_5	3.6	2.9

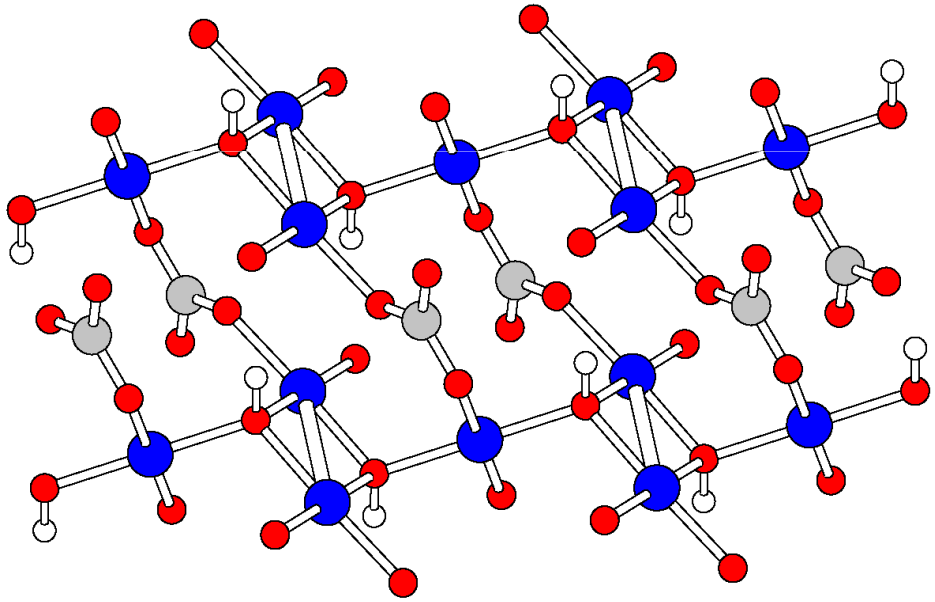
Not a diamond chain

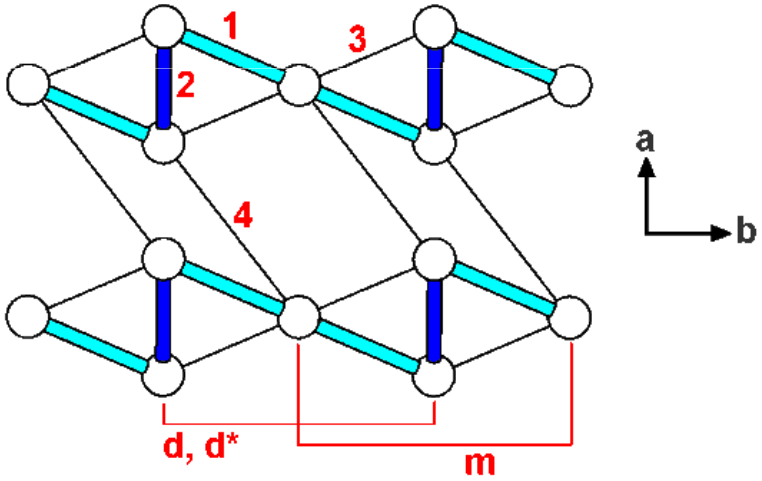
An AFM chain made up of AFM trimers

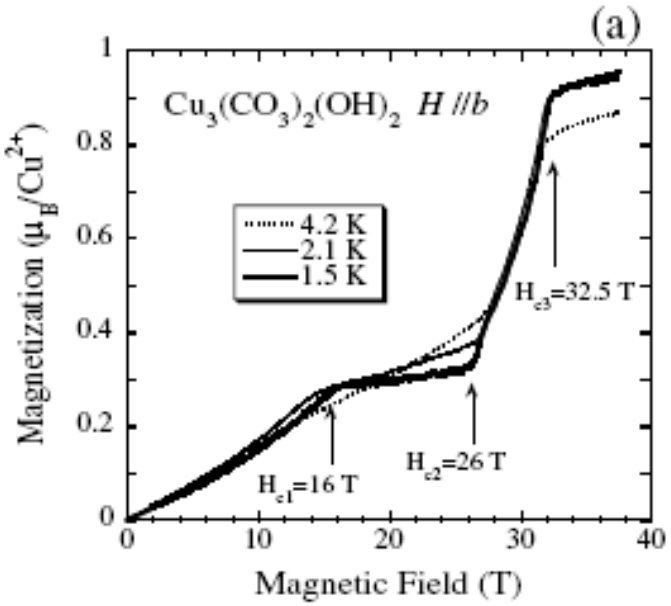
Azurite, $Cu_3(CO_3)_2(OH)_2$

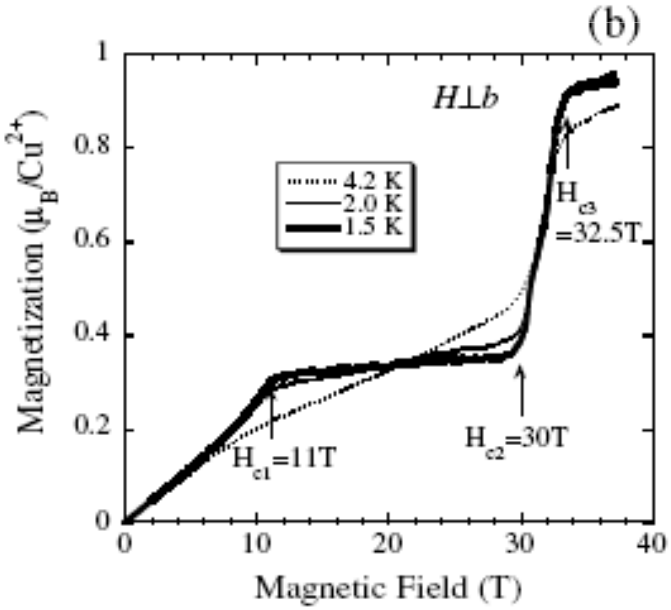
Frustrated or unfrustrated diamond chain?

J. Phys.:Condens. Matter, **21**, 392201 (2009)

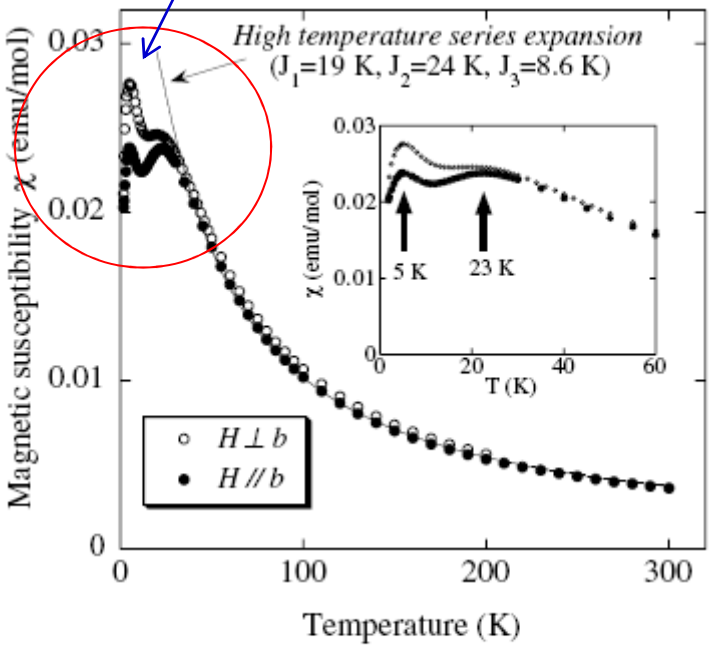


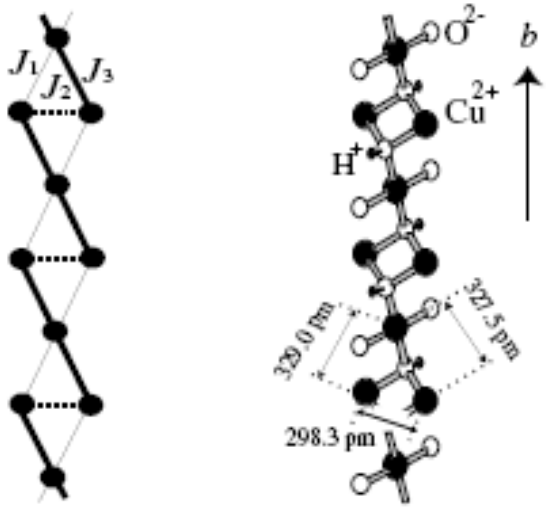






Double peaks!





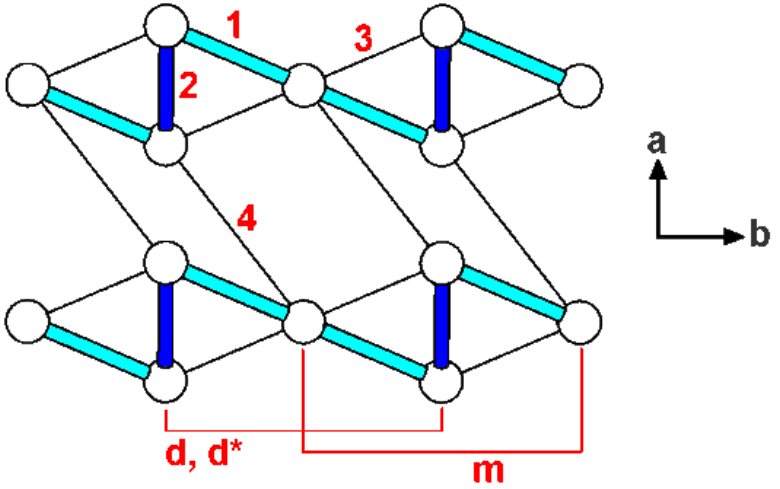
$J_2, J_1, J_3 > 0$:

Frustrated diamond

$J_2, J_1 > 0, J_3 < 0$:

Unfrustrated diamond

Double peaks in χ vs T

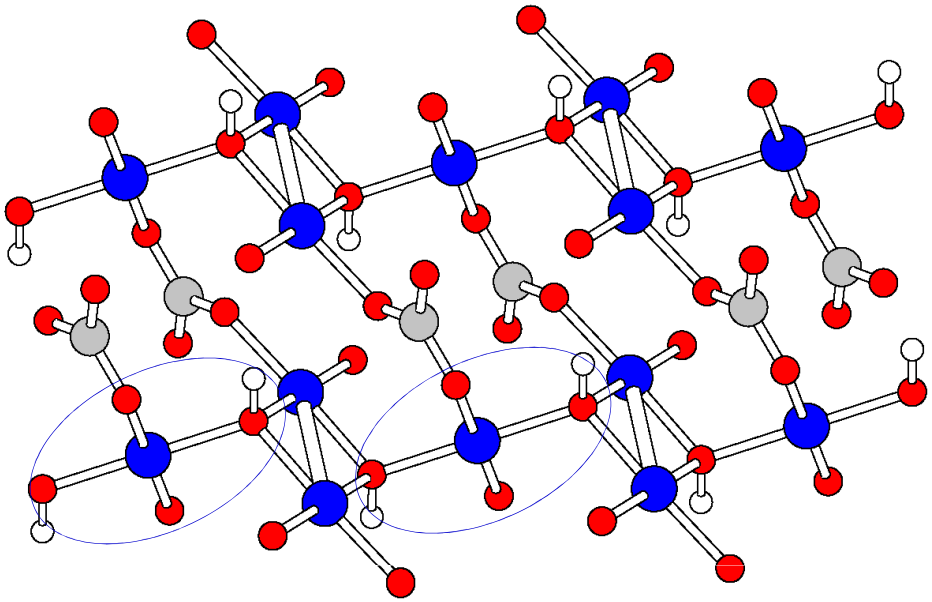


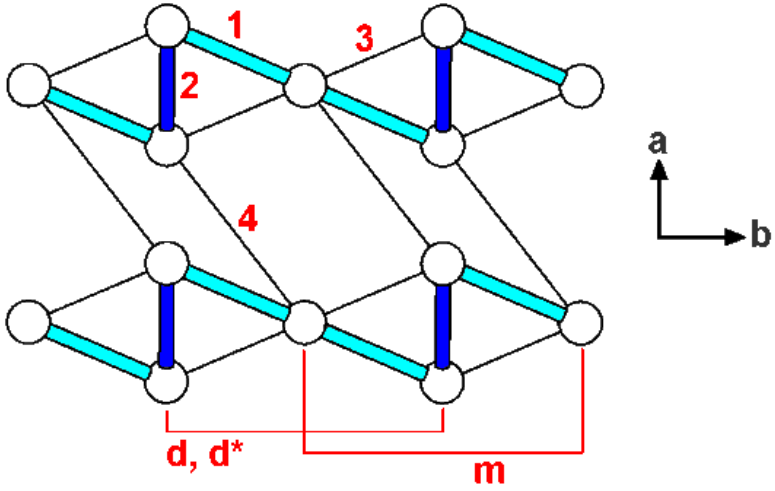
Neutron scattering

Phys. Rev. Lett. **100**, 117202

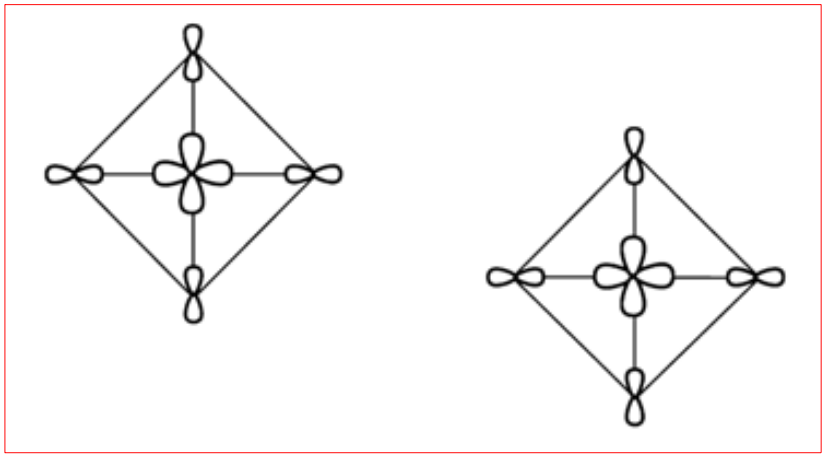
	$k_B K$
J_2	55
J_1	1
J_3	-20
J_m	10.1
J_d, J_{d*}	1.8
J_4	0

	Cu…Cu	∠Cu-O-Cu	O…O
J_2	2.983	97.9	-
J_1	3.275	113.7	-
J_3	3.290	113.4	-
J_m	5.849	-	2.597
J_d, J_{d*}	5.849	-	3.893
J_4	4.872	-	2.219



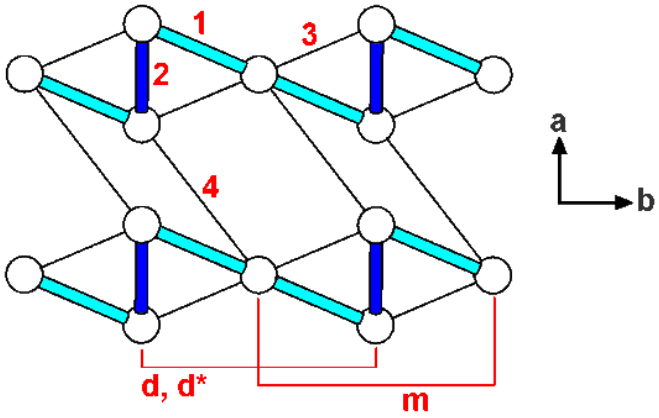


J_m



	U = 4 eV	U = 6 eV
J_2	363.3 (1.00)	221.7 (1.00)
J_1	89.4 (0.25)	52.6 (0.24)
J_3	86.1 (0.24)	46.3 (0.21)
J_m	0.1 (0.00)	1.2 (0.01)
J_d	-6.7 (-0.02)	0.15 (0.00)
J_{d^*}	-3.0 (-0.01)	-6.1 (-0.03)
J_4	46.3 (0.13)	27.9 (0.13)

$k_B K$



$J_1 \approx J_3$: frustration within a diamond chain

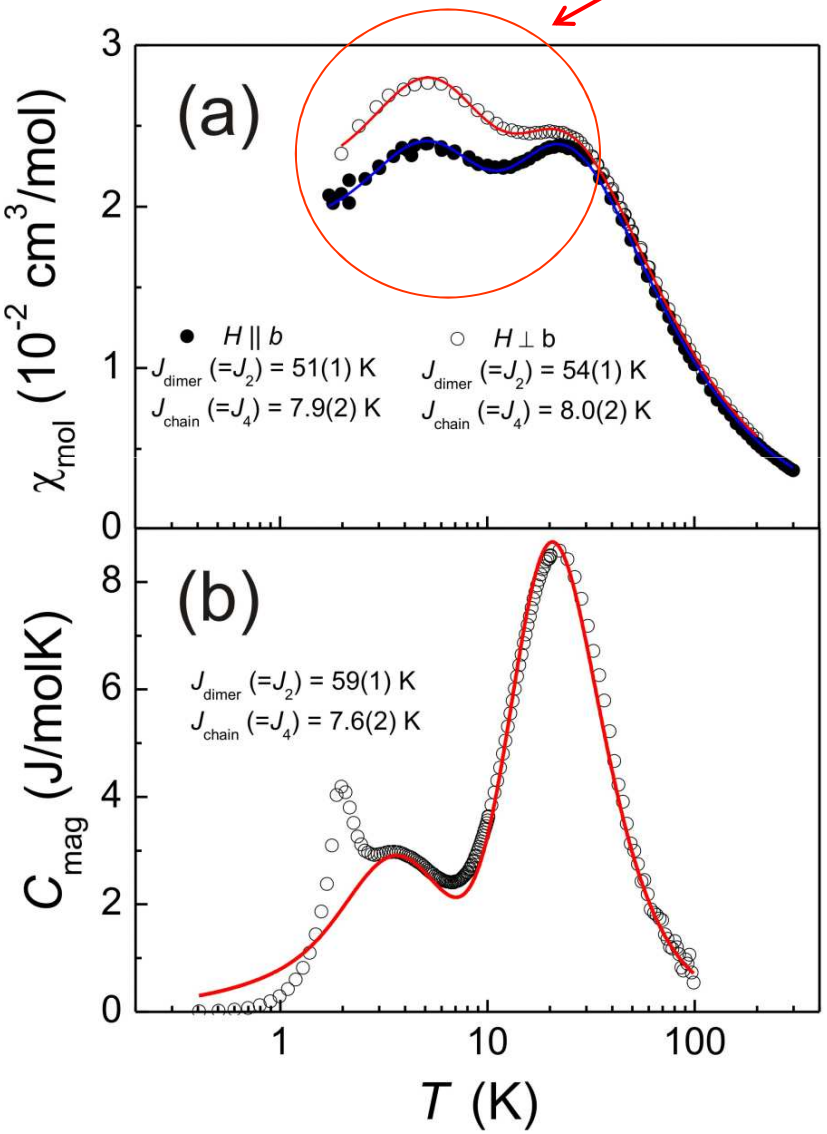
J_2 dimer & $(-J_2-J_4-)_\infty$ chain $\rightarrow$ J_2 dimer & $(-J_4-)_\infty$ chain?

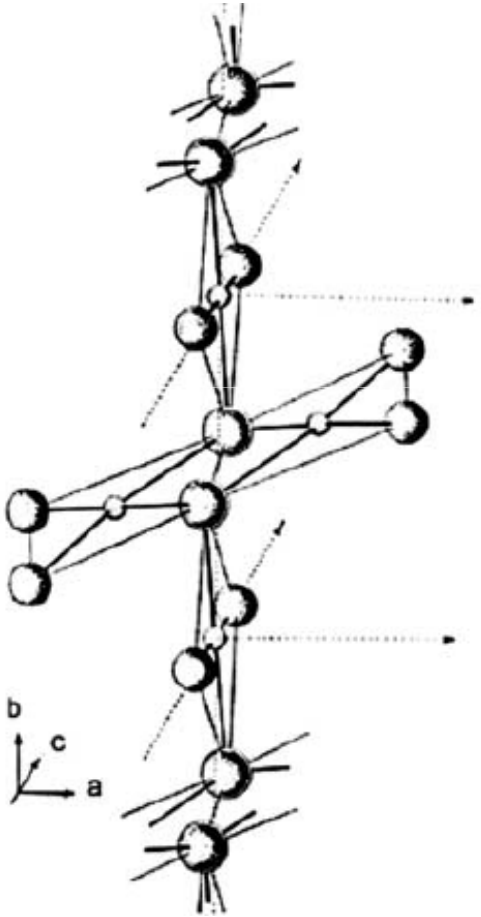
↑–(↓↑)– ↓–(↑↓)– ↑–(↓↑)– ↓–(↑↓)–
↑–( )– ↓–( )– ↑–( )– ↓–( )–

g-factor anisotropy

H⊥b: 2.02, 2.12

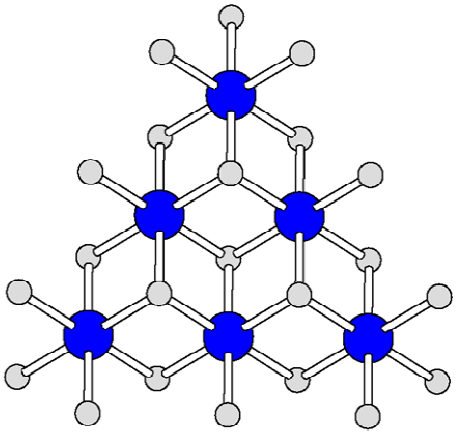
H//b: 1.86, 2.14



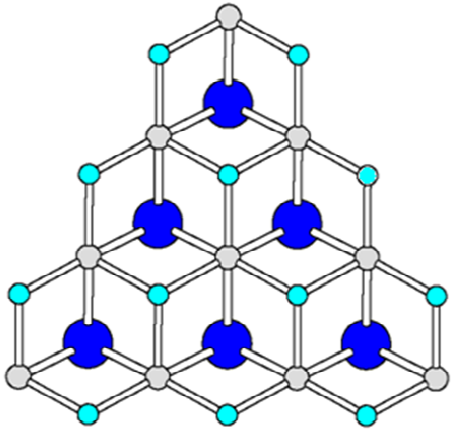


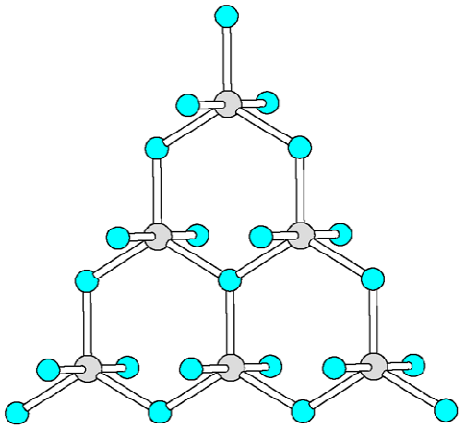
$YbAl_3C_3$: phase transition & spin gap

Yb^{3+} (f^{13}), Al^{3+}, C^{4-}

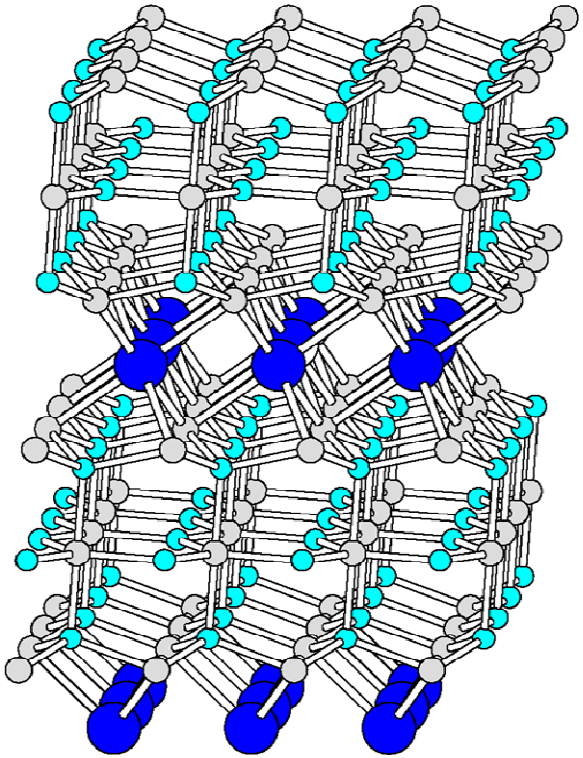


YbC_6 octahedra



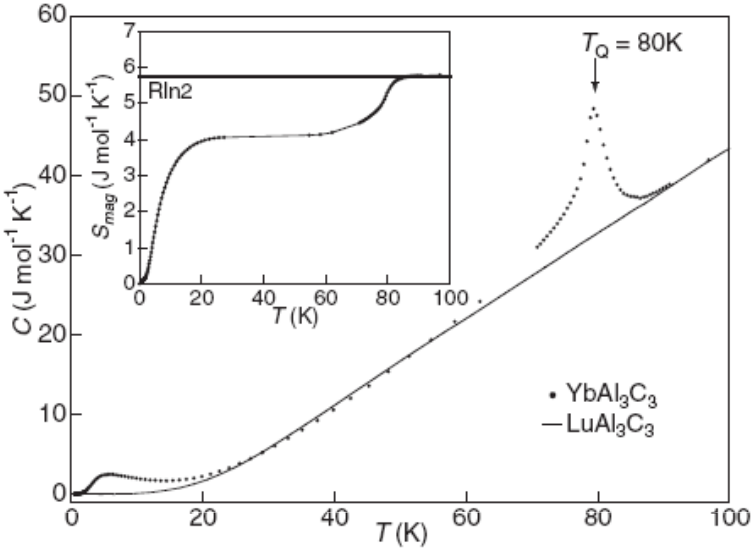


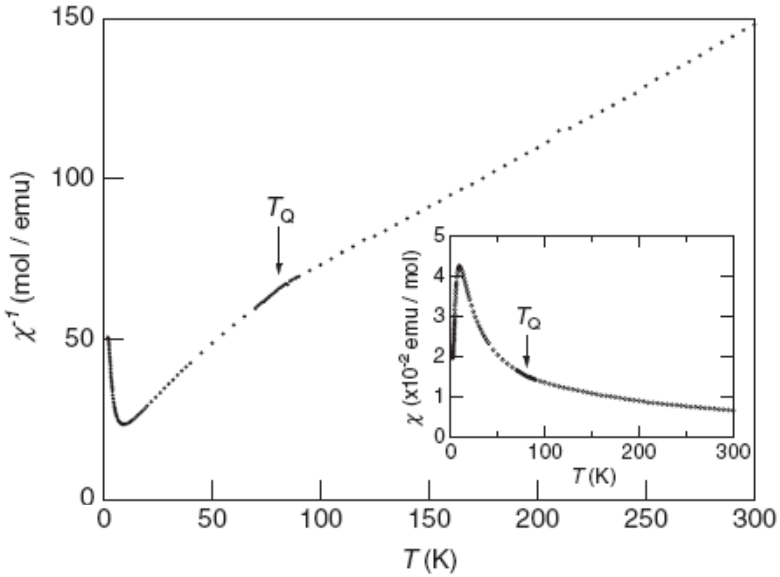
CAl_5 trigonal bipyramids



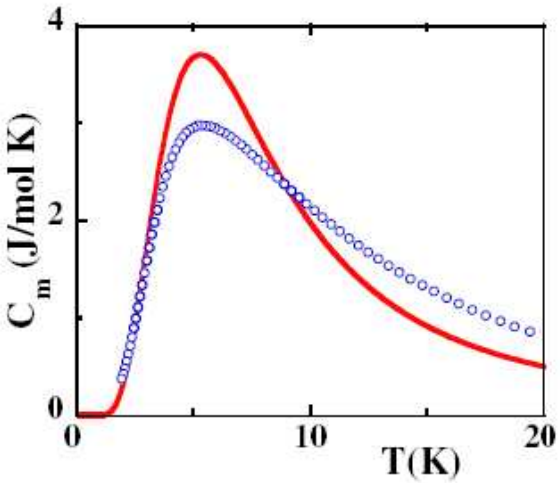
T* = 77 K: Antiferroquadrupolar order?

J. Phys. Soc. Jpn. 74, 2413 (2005)





Spin gap, dimer-like



$LuAl_3C_3$: Lu^{3+} (f^{14})

C_p anomaly at 110 K!

Phase transition at T*:

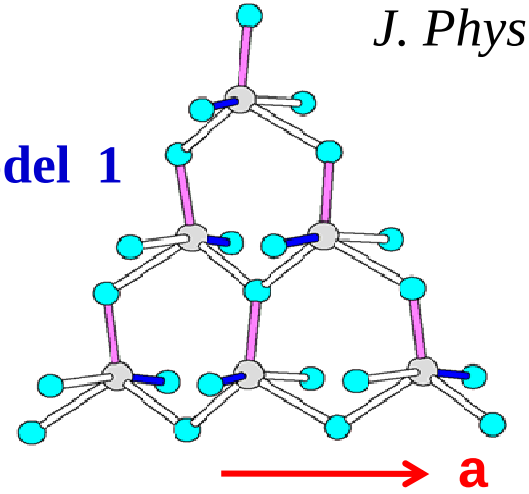
structural in origin?

J. Phys. Soc. Jpn. 76, 123703 (2007)

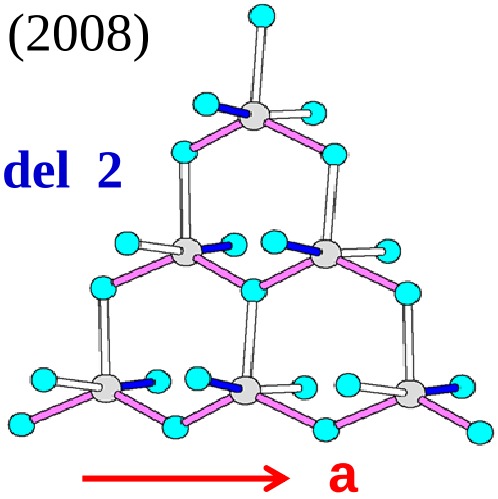
Below T*: Orthorhombic (Pbca)

J. Phys. Soc. Jpn. 77, 103601 (2008)

Model 1



Model 2

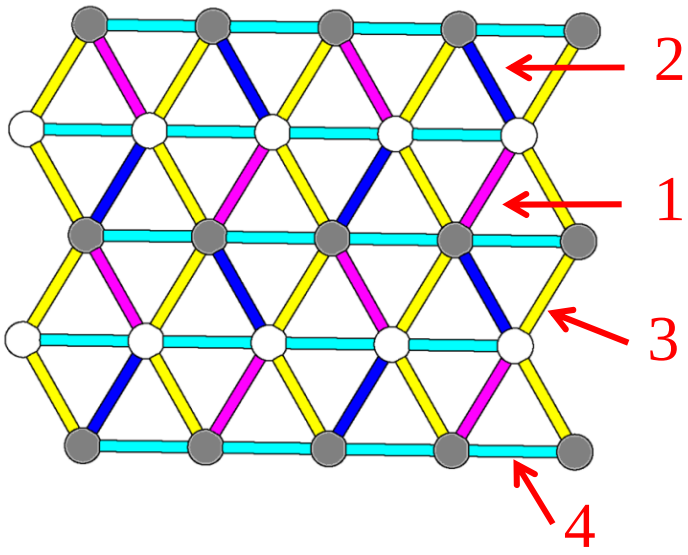


		C-Al_{ax}	C-Al_{eq}
$P6_3/mmc$	Exptl.	2.066, 2.066	1.962, 1.962, 1.962
Pbca	Model 1: Exptl.	1.391, 2.737	1.809, 2.182, 2.183
	Model 1: Optimized	1.750, 2.531	1.819, 2.087, 2.117
Pbca	Model 2: Exptl.	1.578, 2.552	1.868, 1.922, 2.266
	Model 2: Optimized	1.909, 2.323	1.897, 1.897, 2.146

Cooperative second-order Jahn-Teller distortion?

	eV/FU
Model 1: Exptl.	4.15
Model 1: Optimized	0.98
Model 2: Exptl.	1.36
Model 2: Optimized	0.00

	$k_B K$
J_1	17.9 (0.50)
J_2	35.6 (1.00)
J_3	19.6 (0.55)
J_4	-1.6 (0.04)



J_2-J_1 AFM chains, AFM coupled via J_3

→ AFM-coupling of FM chains

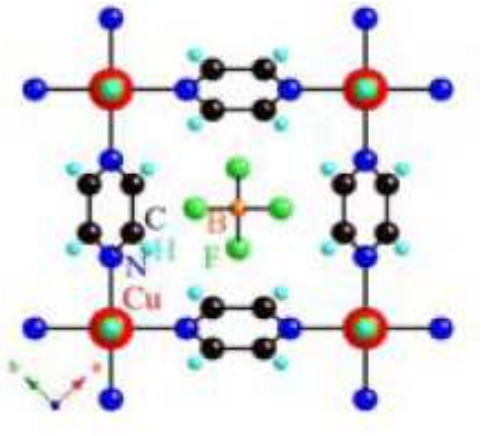
Effect of magnetic field

J. Phys. Soc. Jpn. 78, 014709 (2009)

- **T*= 110 K at 30 T:**
  Field → reduction of spin frustration
  AFM-coupling of FM chains?
- **^{27}Al NMR line broadening below T*:**
  More different Al-environments below T*

$[Cu(HF_2)(pyz)_2]BF_4$: Magnetoelastic interaction
IR spectra under magnetic field

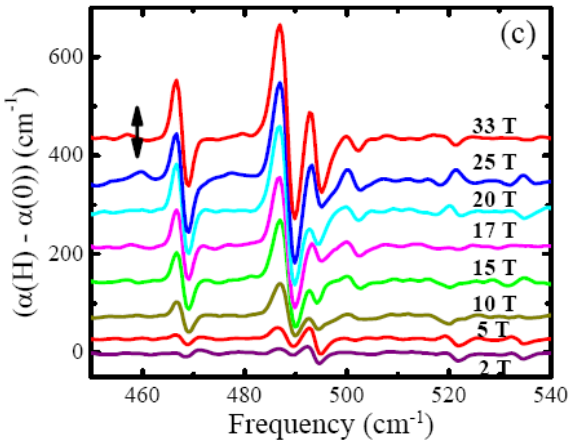
Phys. Rev. Lett. **103**, 157301 (2009)

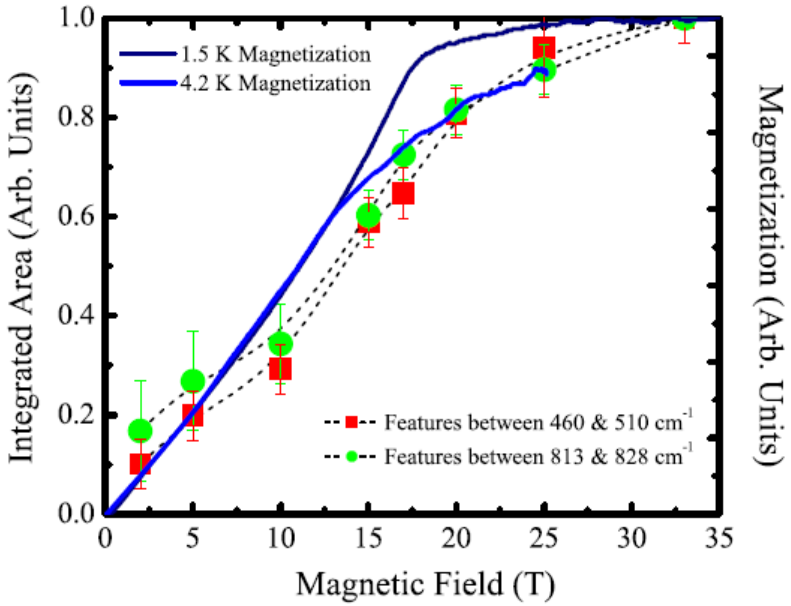


J/k_B = 6.1 K

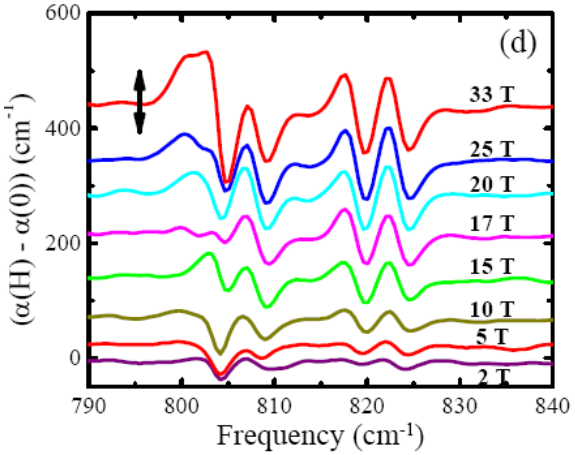
$\Delta E = 4J$

Out-of-plane pyz ring bend

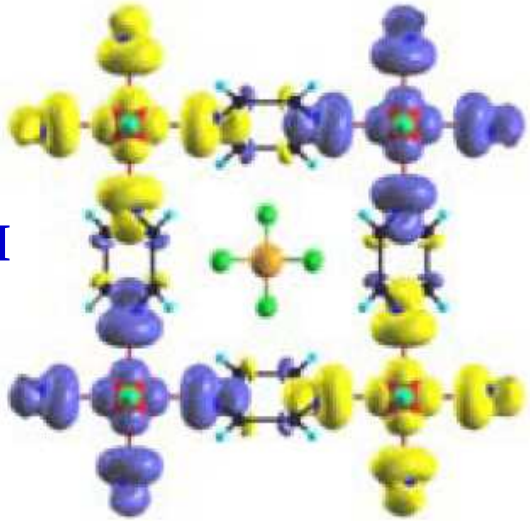




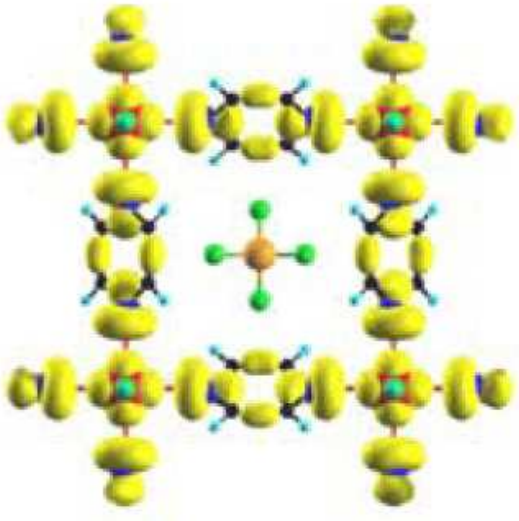
Out-of-plane pyz C-H bend

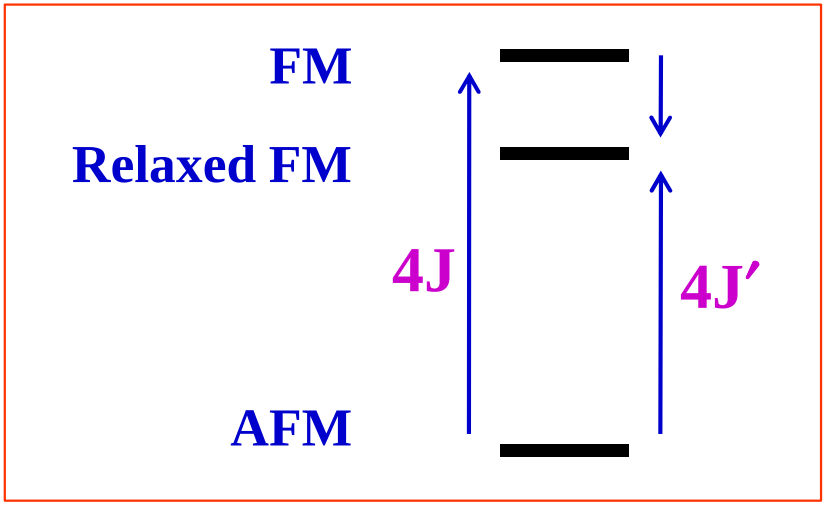


AFM



FM





$J \approx 4t^2/U$

Reduction of t?

pyz: Out-of-plane bending

How constant are J's? J(H)?