Кластерные моттовские магнетики.

Эффект Яна-Теллера или спин-орбитальное взаимодействие: кто кого?

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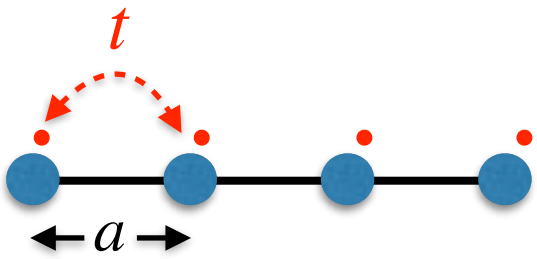
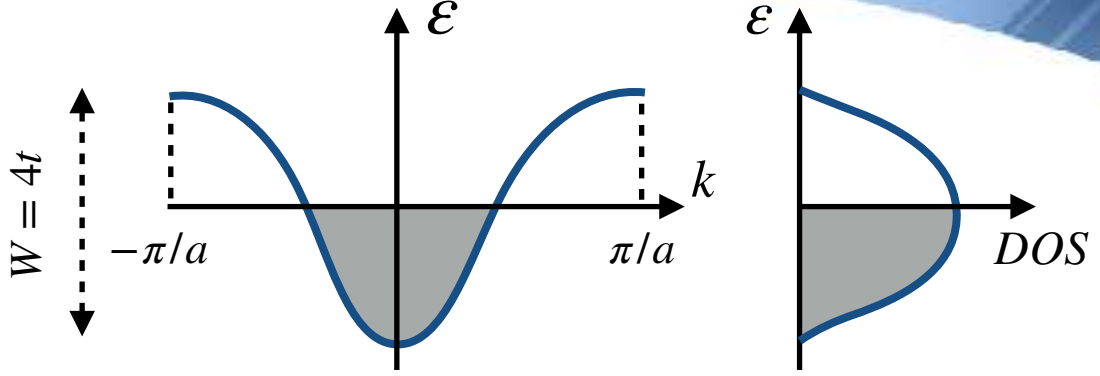
Часть I

Кластерные моттовские магнетики

Account of strong electronic correlations





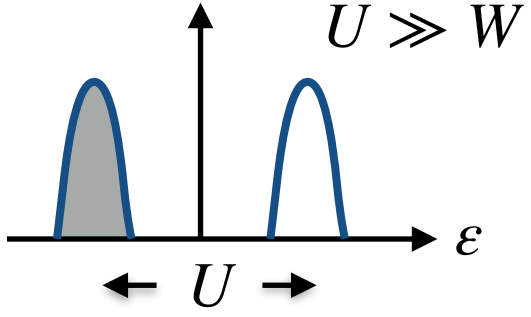
$$H_{kin} = -t \sum_{\langle ij \rangle \sigma} c^{\dagger}_{i\sigma} c_{j\sigma} \xrightarrow{\text{Fourier}} H_{kin} = \sum_{\mathbf{k}\sigma} \varepsilon(\mathbf{k}) c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}$$

Half-filling (1 electron/site) ⟶ Metal

Hubbard model

$$H = -t \sum_{\langle ij \rangle \sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

U - on-site Coulomb repulsion



Multi-orbital Hubbard model

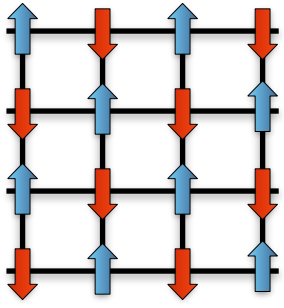
$$H = -\sum_{ij\sigma}\sum_{ab} t_{ij} c^{\dagger}_{ia\sigma} c_{jb\sigma} + \frac{1}{2}\sum_{i\sigma\sigma' abcd} U_i^{abcd} c^{\dagger}_{ia\sigma} c^{\dagger}_{ic\sigma'} c_{ib\sigma} c_{id\sigma'}$$

i - sites
$abcd$ - orbital index
σ, σ' - spins

Spin ordering (magnetism)

$$H_{Hub} = -t\sum_{\langle ij\rangle\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + U\sum_i n_{i\uparrow} n_{i\downarrow}$$

$$\rightarrow \; J\sum_{\langle ij\rangle} \mathbf{S}_i \mathbf{S}_j$$

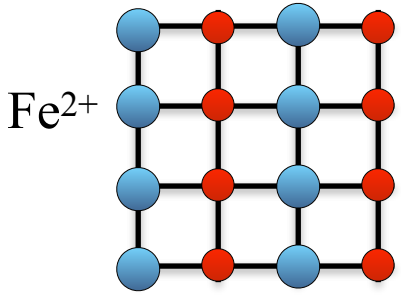


$$J = \frac{2t^2}{U}$$

Charge ordering

$$H = H_{Hub} + V\sum_{\langle ij\rangle\sigma\sigma'} n_{i\sigma} n_{j\sigma'}$$

V - intersite Coulomb repulsion



Multi-orbital Hubbard model

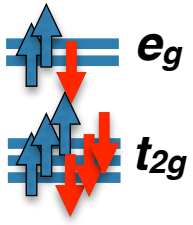
$$H = -\sum_{ij\sigma}\sum_{ab} t_{ij} c^{\dagger}_{ia\sigma} c_{jb\sigma} + \frac{1}{2}\sum_{i\sigma\sigma' abcd} U_i^{abcd} c^{\dagger}_{ia\sigma} c^{\dagger}_{ic\sigma'} c_{ib\sigma} c_{id\sigma'}$$

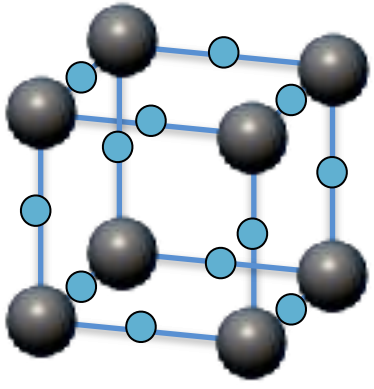
i - sites
$abcd$ - orbital index
σ, σ' - spins

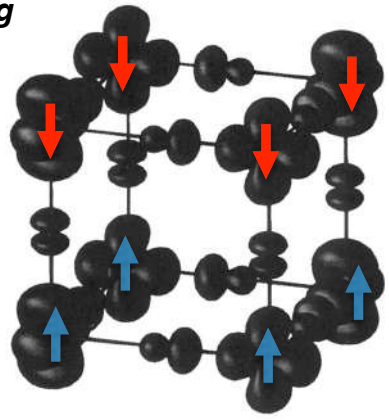
Orbital ordering

$KCuF_3$

Cu^{2+} ($3d^9$)







$KCuF_3$: AFM S=1/2 chains!

K. Kugel, D. Khomskii, JETP 37, 725 (1973)

A. Liechtenstein et al, PRB 52, 5467 (1995)

I. Leonov et al., PRL 101, 096405 (2008)

Multi-orbital Hubbard model

$$H = -\sum_{ij\sigma}\sum_{ab} t_{ij} c^{\dagger}_{ia\sigma} c_{jb\sigma} + \frac{1}{2}\sum_{i\sigma\sigma' abcd} U_i^{abcd} c^{\dagger}_{ia\sigma} c^{\dagger}_{ic\sigma'} c_{ib\sigma} c_{id\sigma'}$$

i - sites
$abcd$ - orbital index
σ, σ' - spins

"Mott materials"

Mott insulators,
Hund's metals, …

Impurity center: a single ion

Degrees of freedom:

- charge
- spin
- orbital

+ site

Cluster Mott magnets

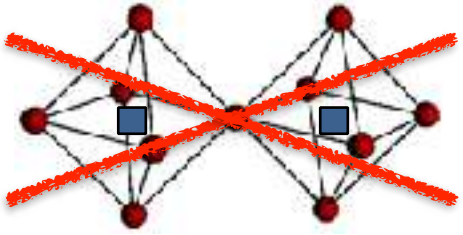
Impurity center: **a cluster** of ions

$abcd$ - {orbitals, sites} index

Typical geometries of cluster magnets (on examples of MeL_6 octahedra)

Geometry

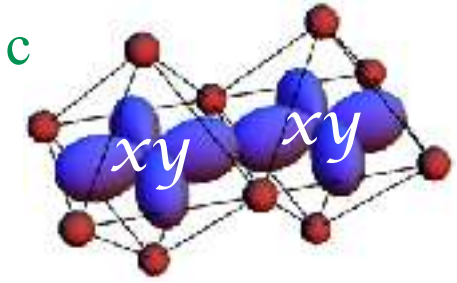
Common corner

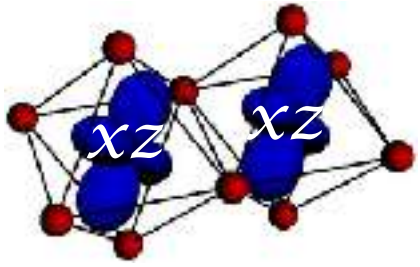


Electrons are localized at sites

No cluster magnets with this geometry

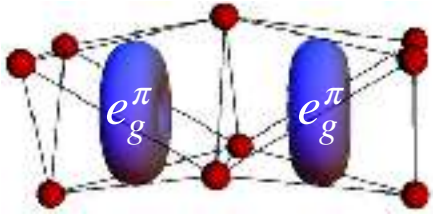
Common edge



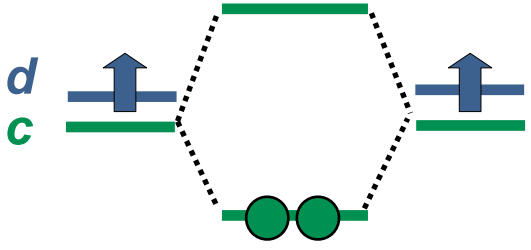


$d = xz/yz$

Common face



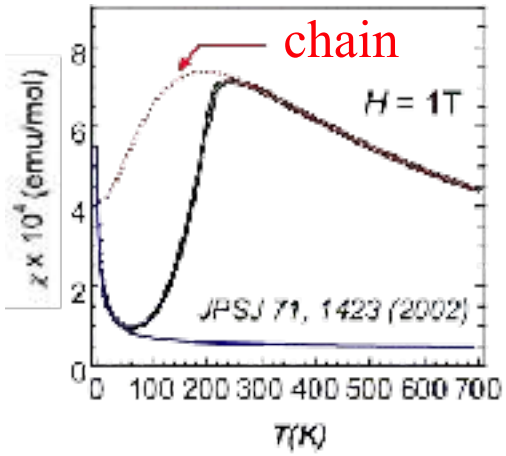
$d = e_g^\pi$

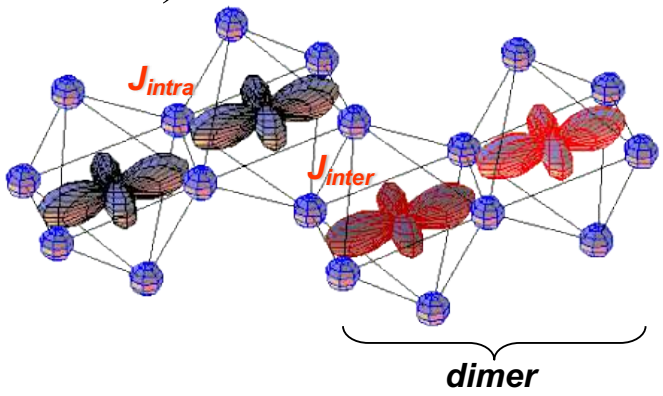


Typically there are two types of orbitals: molecular orbitals and site-localized

Examples of cluster Mott magnets
N=2 (Dimers)

$NaTiSi_2O_6$ Ti^{3+} ($3d^1$, $S=1/2$)

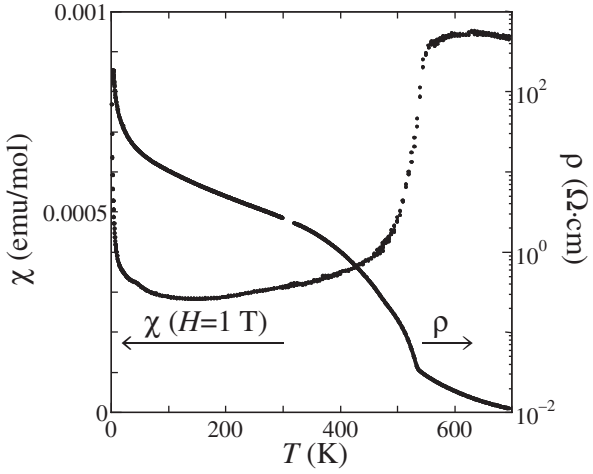




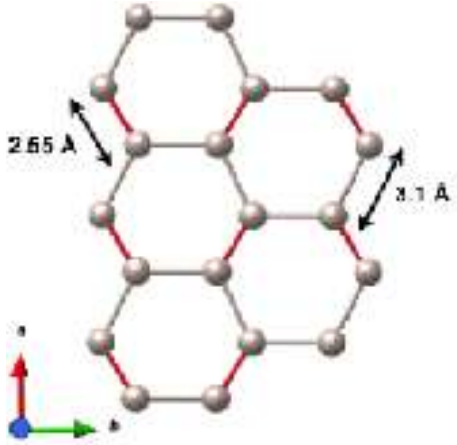
Streltsov et al.,
PRL 96, 249701 (2006)

Van Wezel, Van den Brink,
EPL 75, 957 (2006)

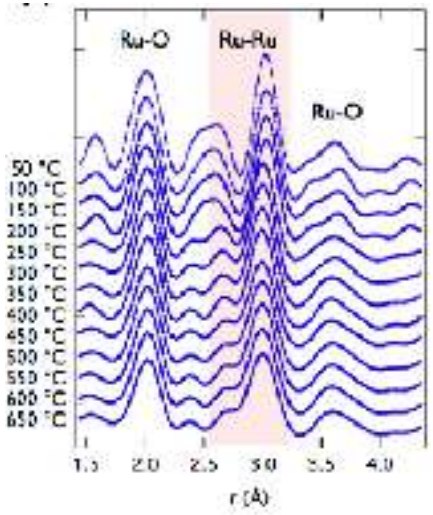
Li_2RuO_3 Ru^{4+} ($S=1$)



Valence bond solid:
T < 540 K



Valence bond liquid:
T > 540 K



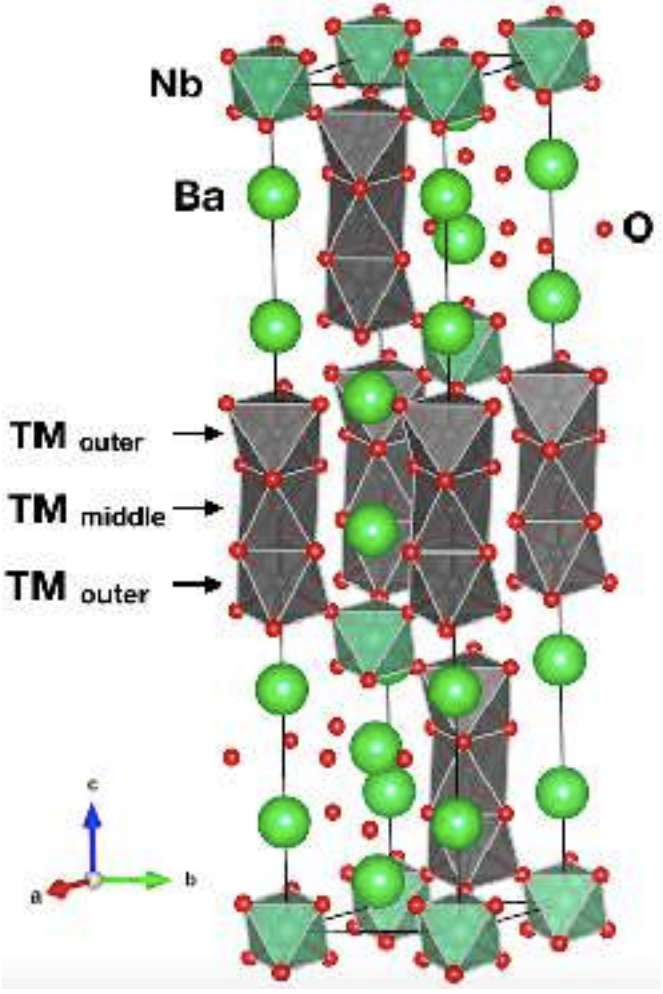
Dimers flow over the lattice

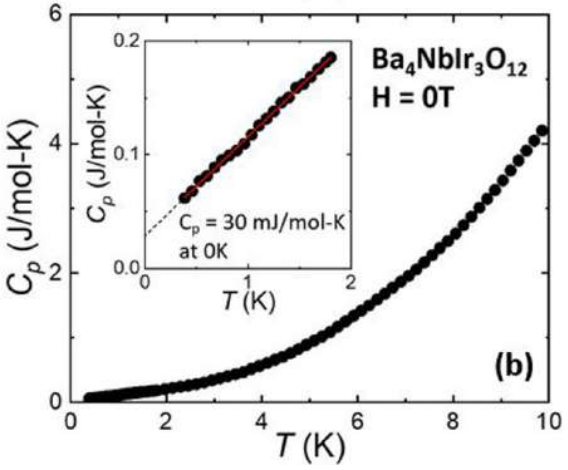
Kimber et al.,
PRB 89, 081408 (2014)

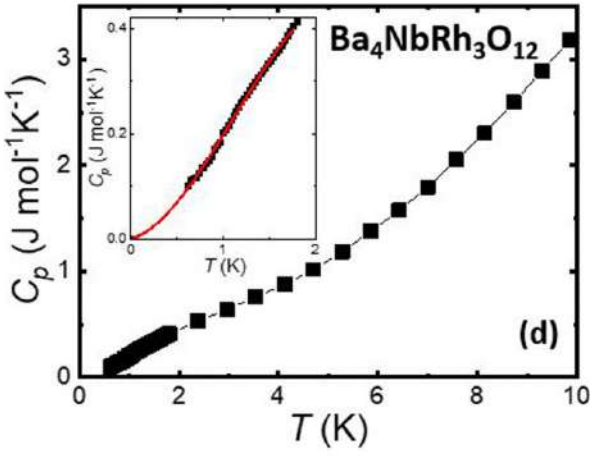
Examples of cluster Mott magnets
N=3 (Trimers)

Linear trimers: e.g. $Ba_4Nb(Rh,Ir)_3O_{12}$ $Ir^{3.66+}/Rh^{3.66+}$ $t_{2g}^{5.33}$

$$\mu_{eff}^{ionic} = 2.48\mu_B/f.u.$$







$$\mu_{eff} = 0.8\mu_B/f.u. \qquad \mu_{eff} = 1.5\mu_B/f.u.$$

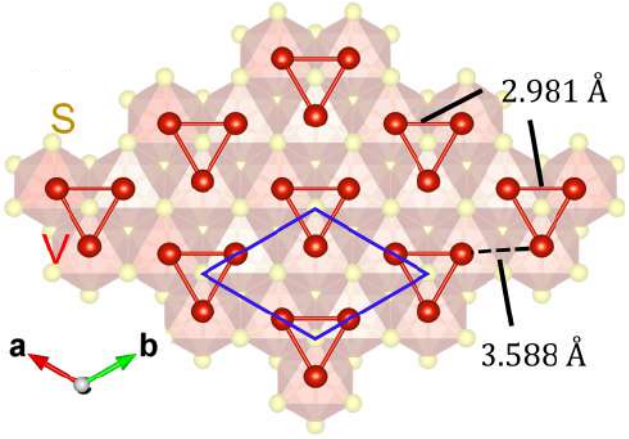
Spin liquid?

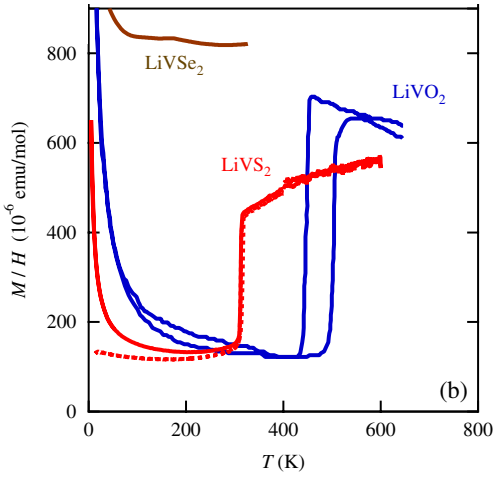
Nguyen, Cava, PRM 3, 014412 (2019)

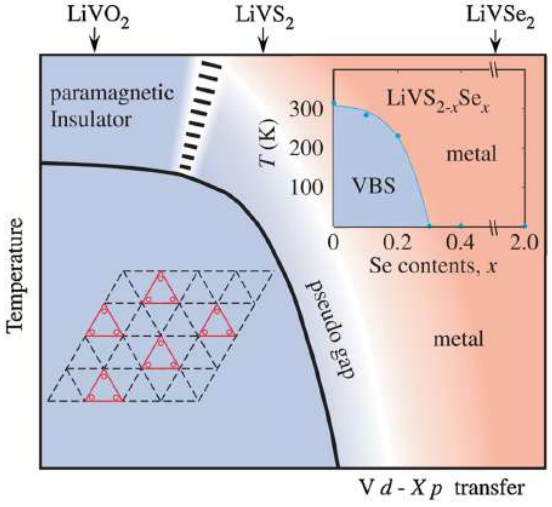
Examples of cluster Mott magnets
N=3 (Trimers)

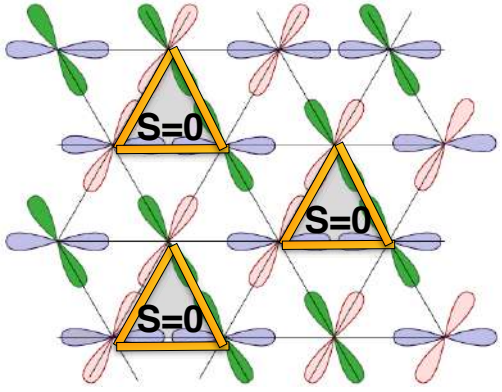
Triangles: LiV(O,S,Se)$_2$, $LiZn_2Mo_3O_8$, Nb_3Cl_8

$LiV(S,O,Se)_2$ V^{2+} ($3d^2$) or 6 electrons per V_3









antibonding

nonbonding

bonding

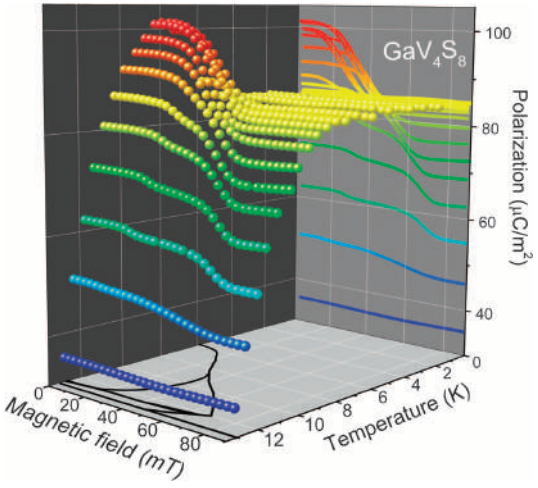
Pen et al.,
PRL 78, 1323 (1997)

Katayama et al.,
PRL 103, 146405 (2009)

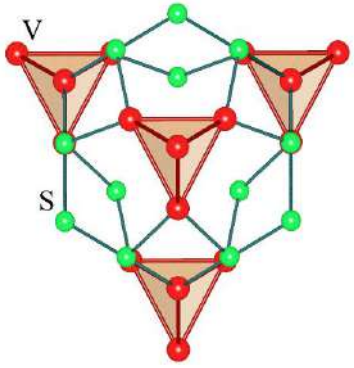
Kojima et al.,
PRB 100, 235120 (2019)

Examples of cluster Mott magnets
N=4 (Tetramers)

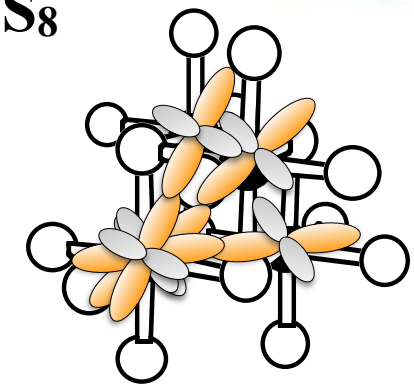
Tetramers: GaV_4S_8

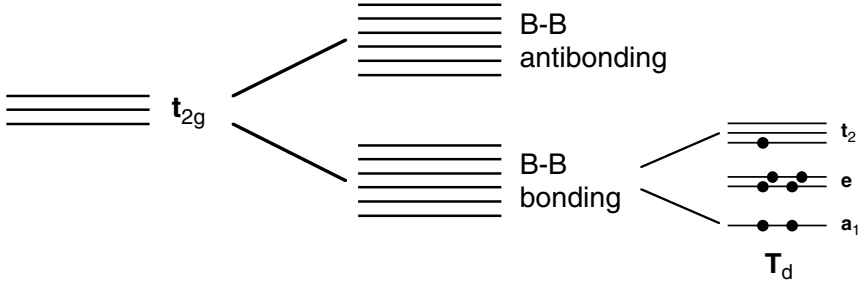


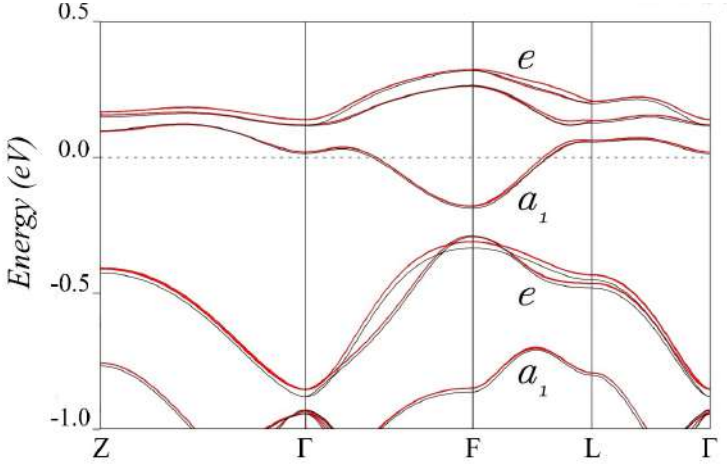
Ruff et al., Sci. Adv. 1, e1500916 (2015)

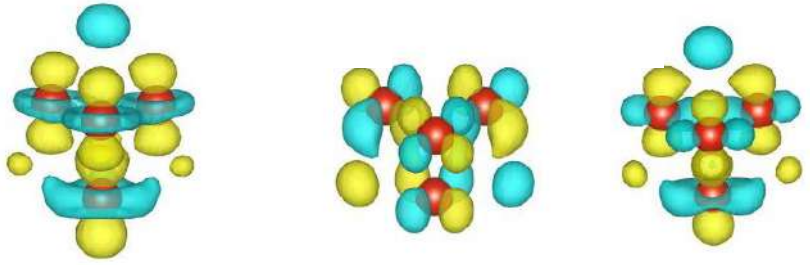


Cluster V_4S_8





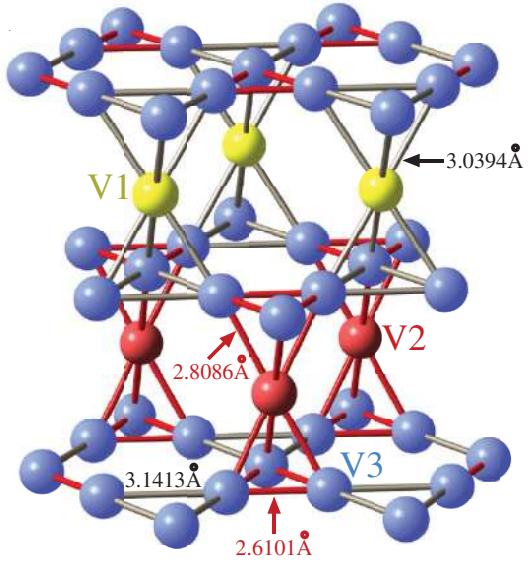


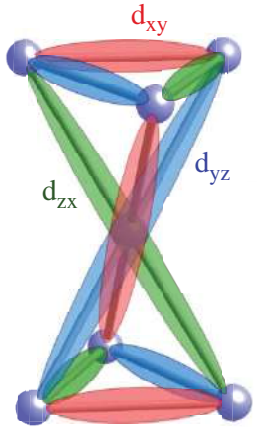


*Nikolaev, Solovyev PRB **99**, 100401 (2019)*

Examples of cluster Mott magnets
N=7 (Heptamers?)

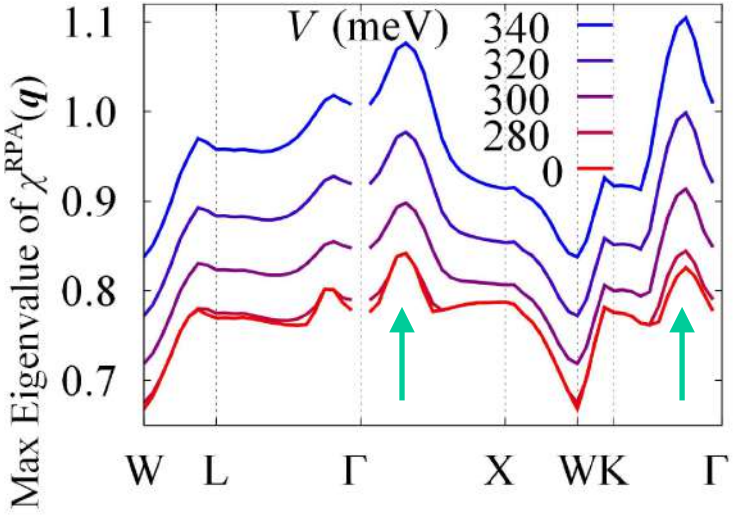
Spinel AlV_2O_4





Y. Horibe et al
Phys. Rev. Lett. 96, 86406 (2006).

Mechanism:
Peierls-like transition

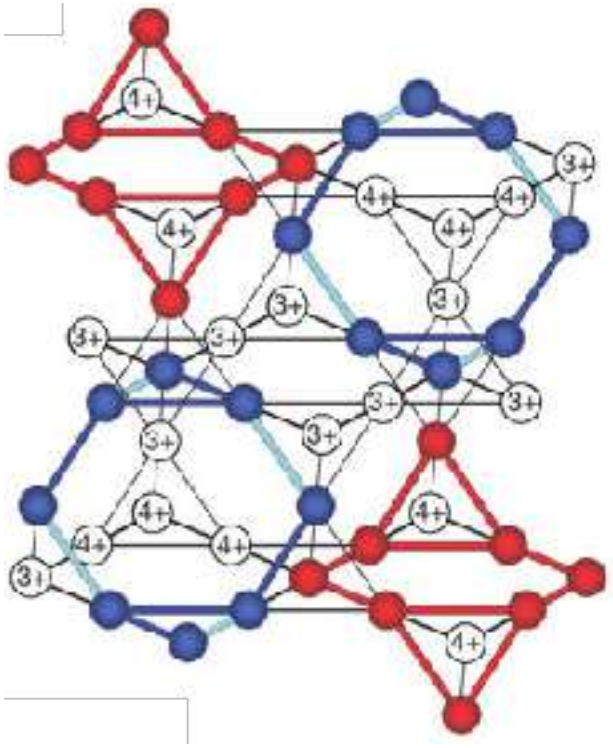


A. Uehara, H. Shinaoka, and Y. Motome,
Phys. Rev. B 92, 195150 (2015).

Orbitals reduce dimensionality: 3D → 0D

Examples of cluster Mott magnets
N=8 (Octamers)

$CuIr_2S_4$: spinel



Nominally: $Ir^{3.5+}$ ($t_{2g}^{5.5}$)

T<230 K:

1) charge ordering
Ir^{3+} (t_{2g}^{6}) and Ir^{4+} (t_{2g}^{5})

2) tetragonal elongation
c/a>1

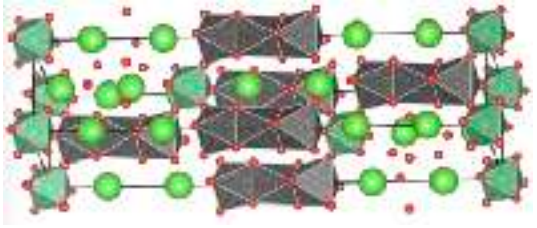
3) dimerization
Ir^{4+} — Ir^{4+} dimers

Radaelli et al., Nature 416, 155 (2002)

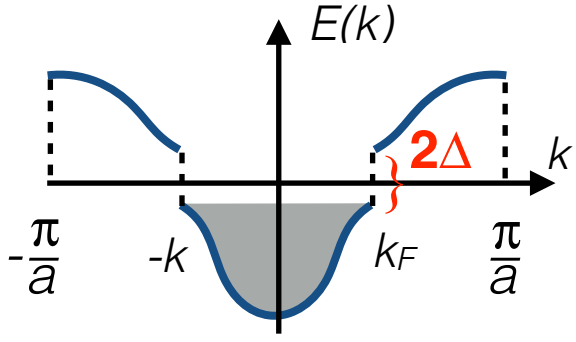
What is the reason for such complex distortions?

Cluster Mott magnets: Mechanisms of formation

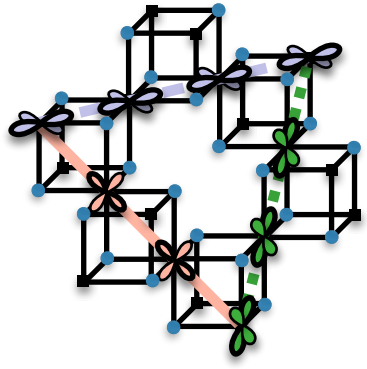
1. **There are structural clusters (dimers, trimers, …)**



2. **Charge density wave instabilities / Peierls transitions**



3. **Orbitally induced distortions / Peierls transitions**

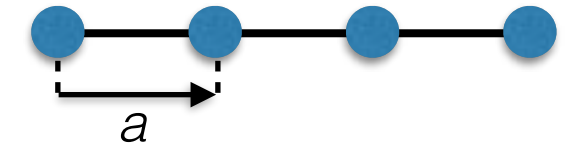


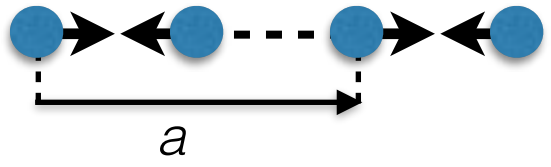
Cluster Mott magnets: Mechanisms of formation

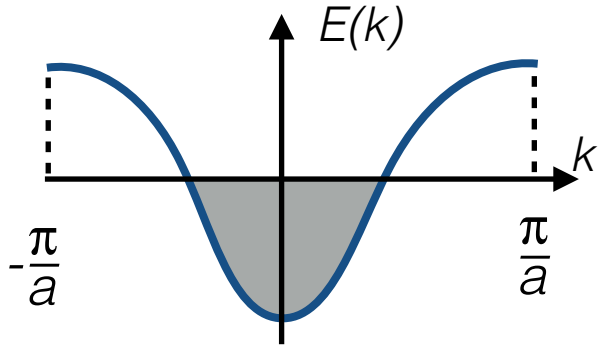
Peierls transition: 1D chain

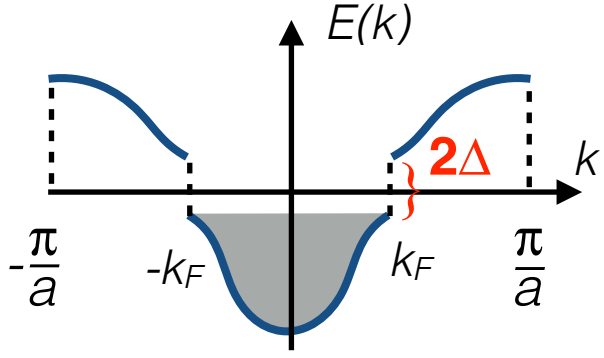
doubling of the u.c.!

Half-filling
(1 electron/site)









Instability at $|q| = 2k_F$

Half-filling (1 electron/site): $|k_F| = \frac{\pi}{2a}$, $|q| = \frac{\pi}{a}$

Gain in kinetic energy: $\sim -|\Delta|^2 \ln |\Delta|$

Loss in elastic energy: $\sim |\Delta|^2$

Lattice deformations are possible for other fillings!

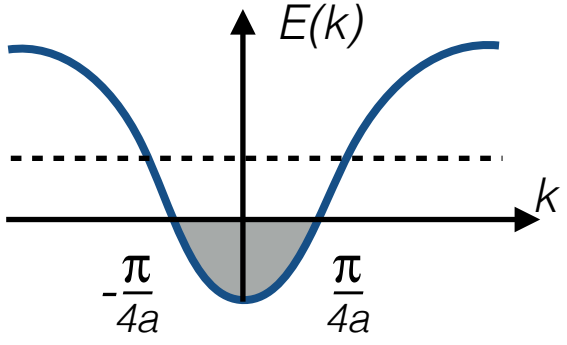
Cluster Mott magnets: Mechanisms of formation

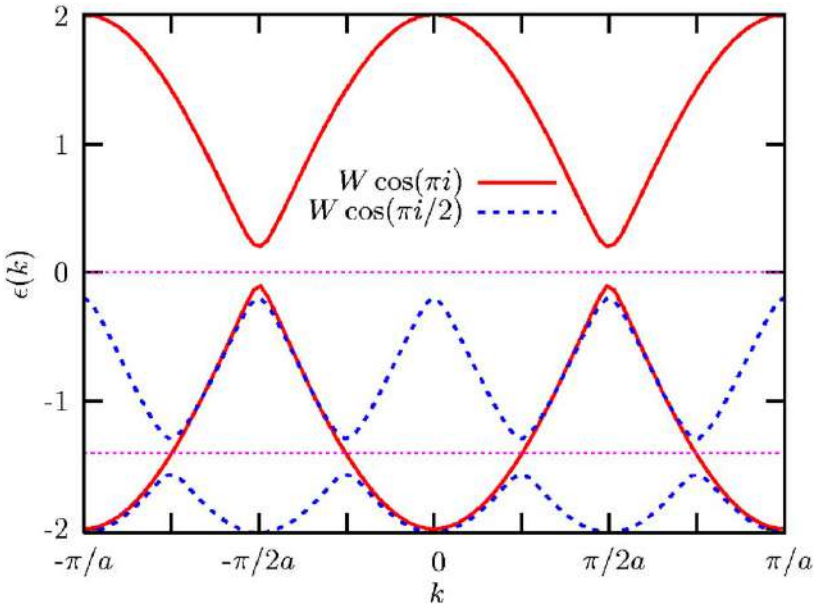
Peierls transition: 1D chain

Instability at $|q| = 2k_F$

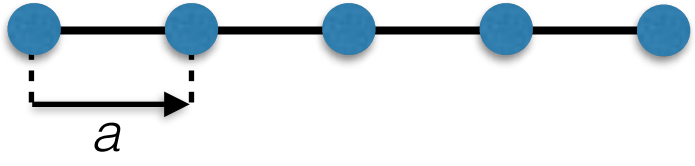
quarter-filling (1/2 electron/site):

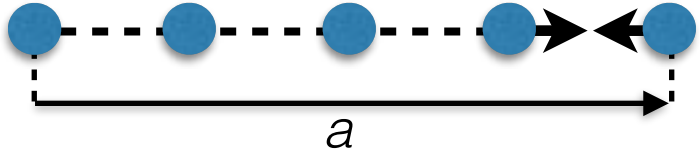
$$|k_F| = \frac{\pi}{4a} \quad |q| = \frac{\pi}{2a}$$





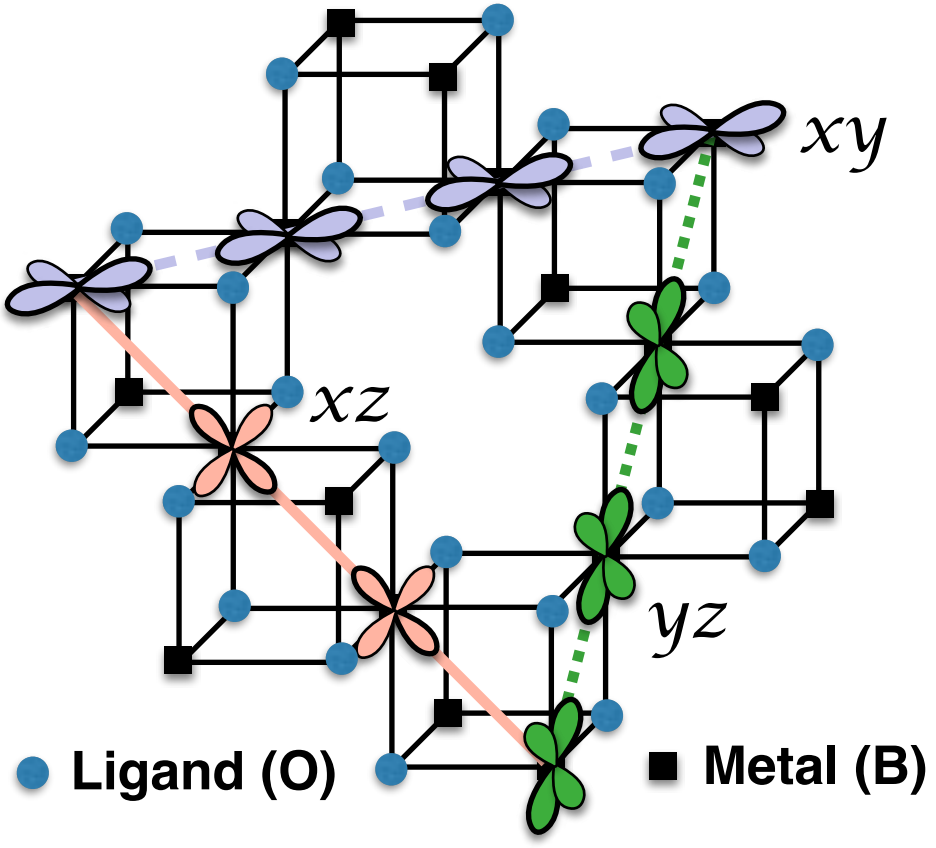
quadrupling of the u.c.!



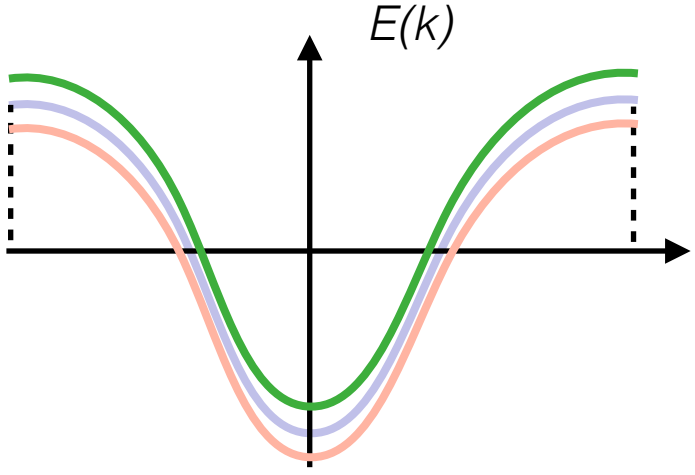


Cluster Mott magnets: Orbitally induced Peierls transition

Spinels: AB_2O_4



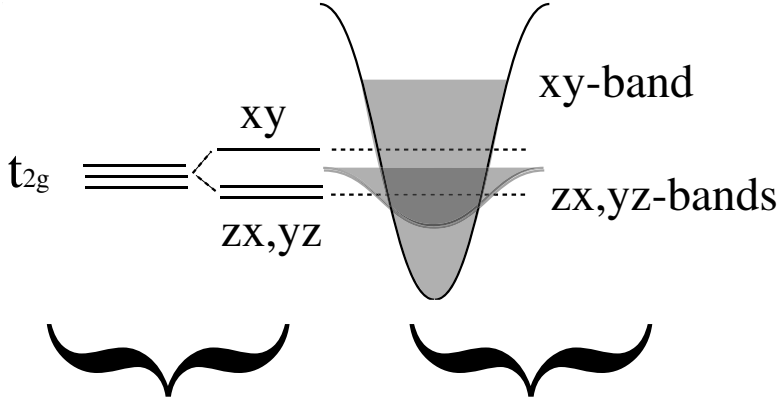
Assumption:
the most important is a direct overlap between *d*-orbitals



Natural formation of 1D bands due to orbitals…

Cluster Mott magnets: Orbitally induced Peierls transition

$CuIr_2S_4$: spinel

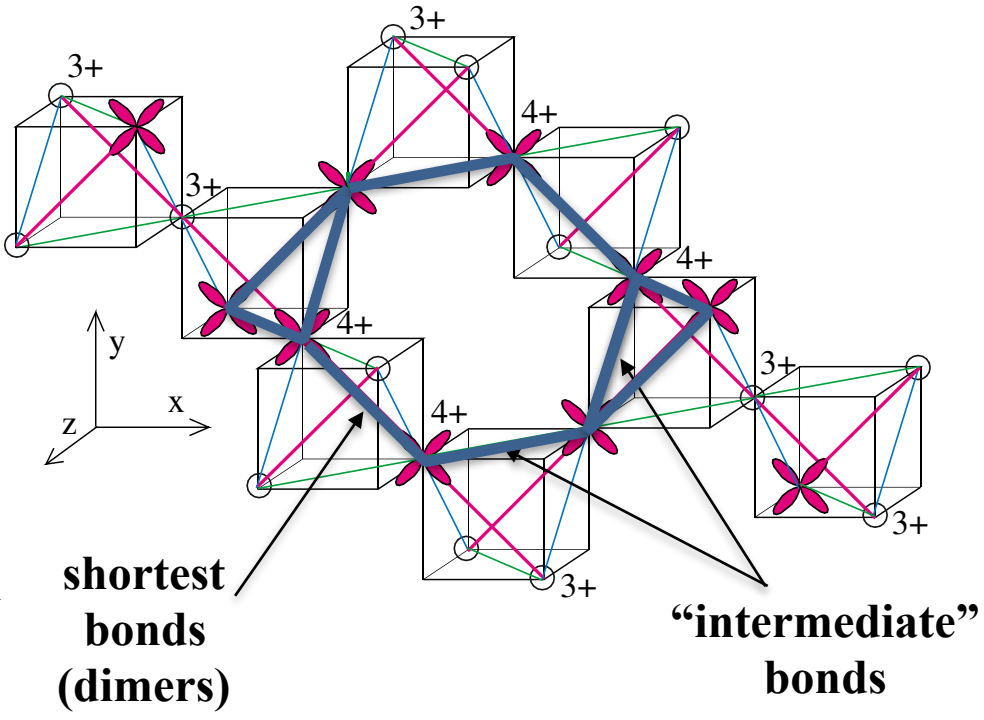


tetragonal elongation

xy-band is 3/4 filled

⇩

Tetramerization?



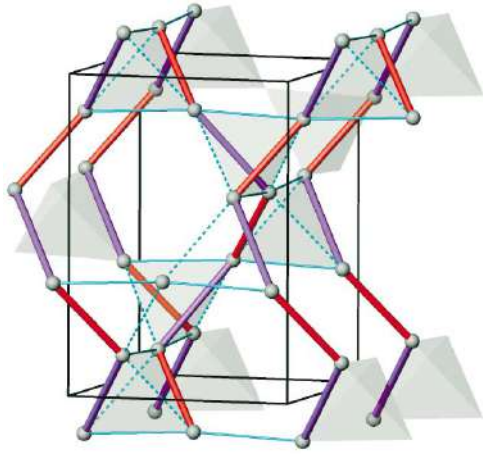
Khomskii & Mizokawa, PRL 94, 156402 (2005)

Orbitals reduce dimensionality: 3D → 0D

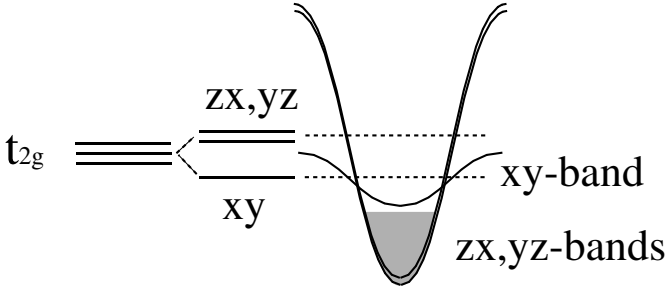
Cluster Mott magnets: Orbitally induced Peierls transition

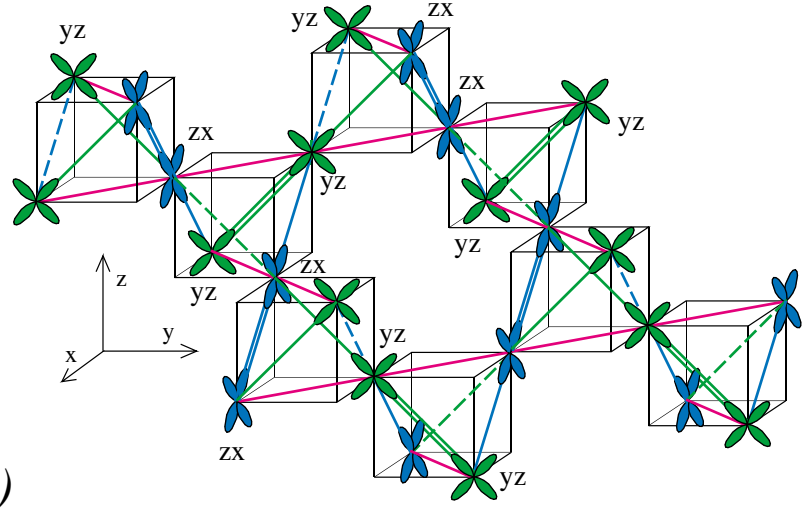
$MgTi_2O_4$: spinel

T<260 K:
Superstructure



Schmidt et al.,
PRL 92, 56402 (2004)



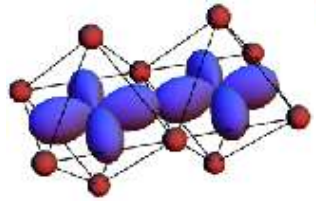


Khomskii & Mizokawa, PRL 94, 156402 (2005)

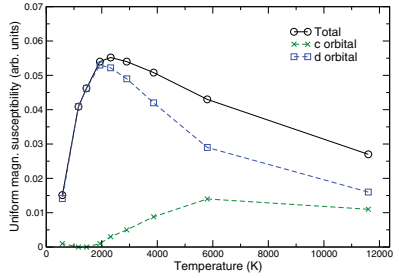
Orbitals reduce dimensionality: 3D → 1D

Some features of cluster Mott magnets

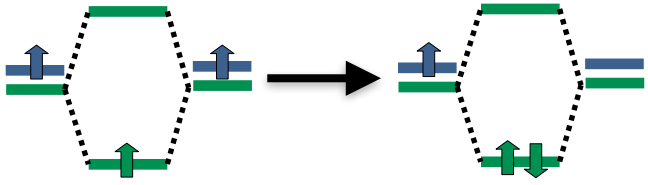
1. **Formation of molecular orbitals**



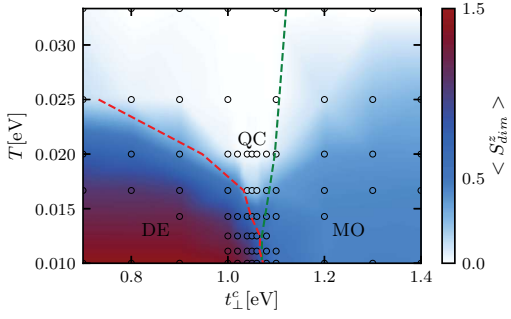
2. **Orbital-selective behaviour**



3. **(Cluster) spin-state transitions**

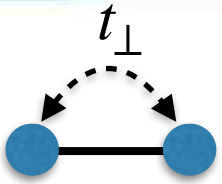


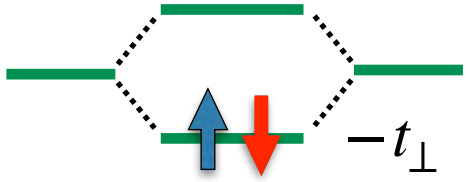
4. **Suppression of a long-range magnetic order**



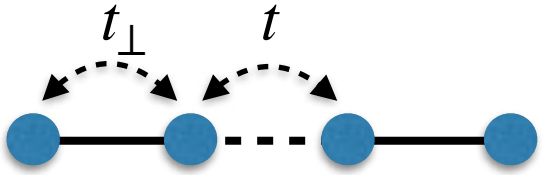
The simplest cluster: a dimer (one electron / site)

An isolated dimer





Dimerized chain



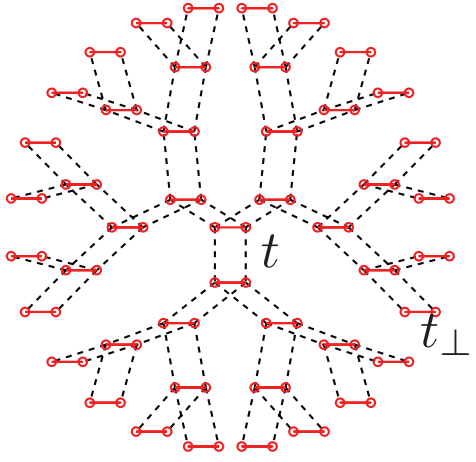
$t_\perp \gg \{t, U\}$ *S=0* dimers

$t_\perp \sim t \sim U$???

$U \gg t \sim t_\perp$ AFM Bonner-Fisher chain (insulator)

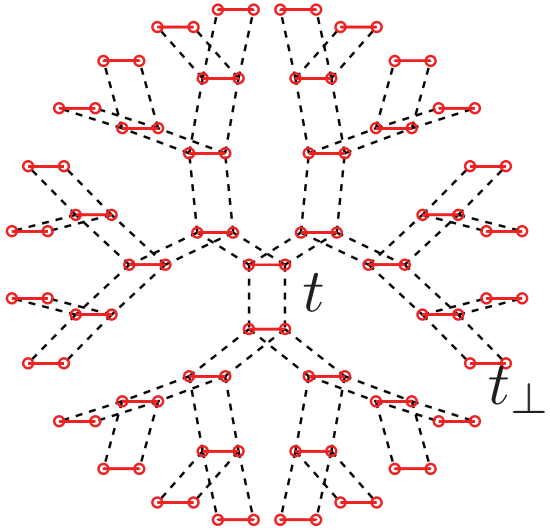
Dynamical Mean Field Theory (DMFT)

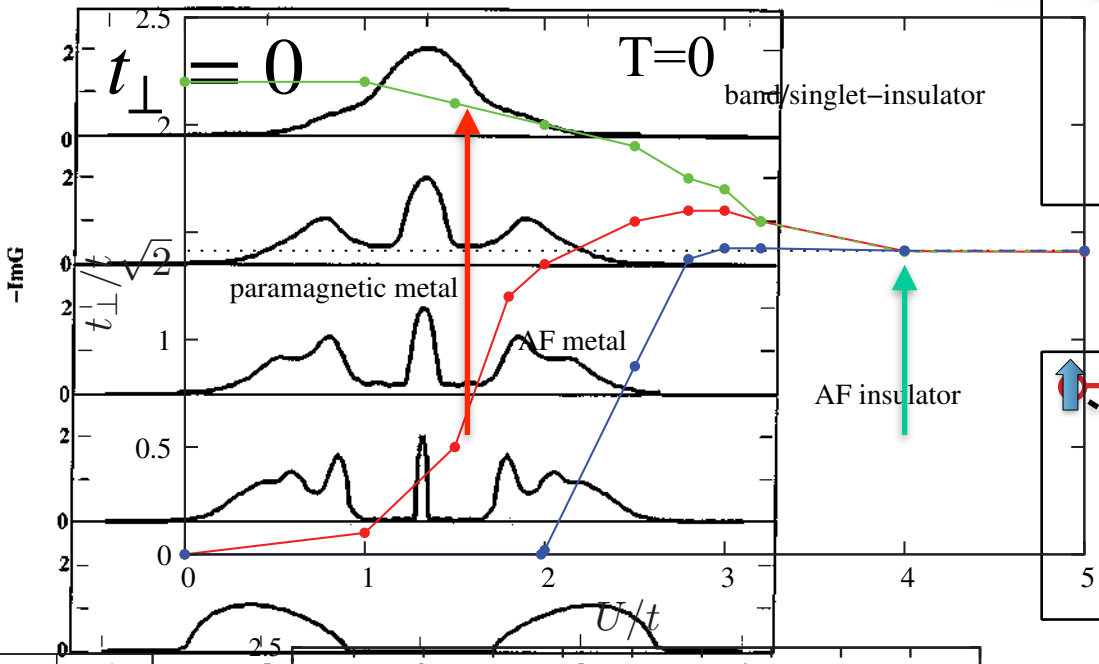
Bethe lattice

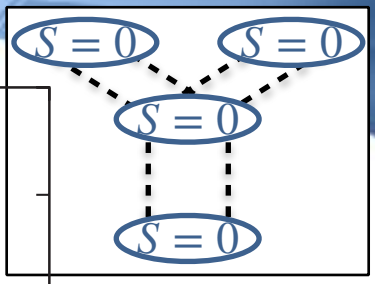


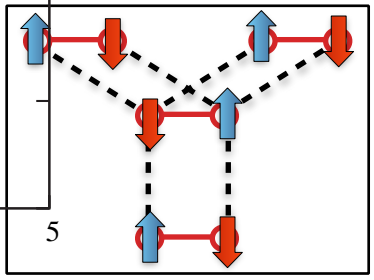
$$H = -t \sum_{\langle ij \rangle, \sigma} (a^\dagger_{i\sigma} a_{j\sigma} + b^\dagger_{i\sigma} b_{j\sigma}) - t_\perp \sum_{i\sigma} (a^\dagger_{i\sigma} b_{i\sigma} + b^\dagger_{i\sigma} a_{i\sigma})$$
$$+U \sum_{i\sigma} (n_{ai\uparrow} n_{ai\downarrow} + n_{bi\uparrow} n_{bi\downarrow})$$

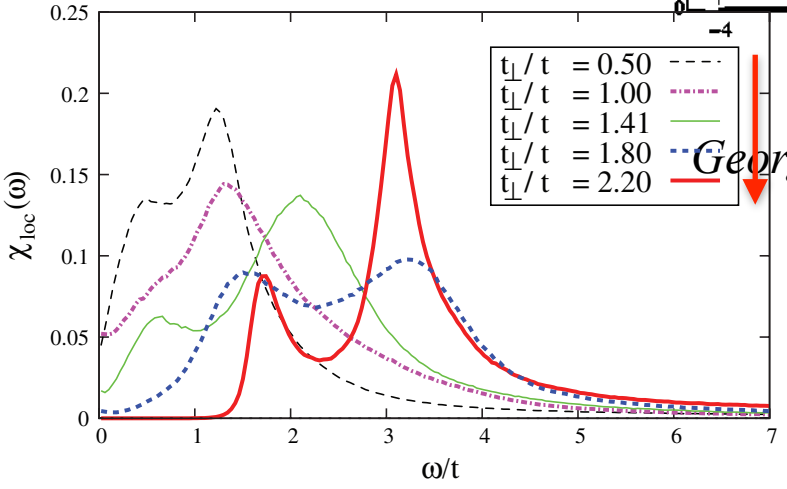
The simplest case: Bethe lattice of dimers (one electron/site)

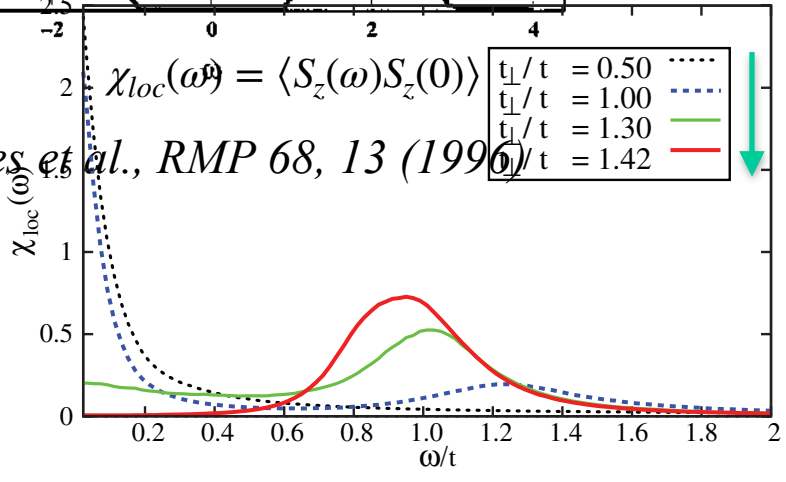










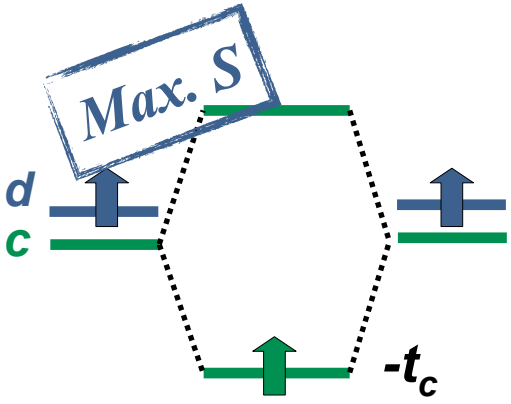


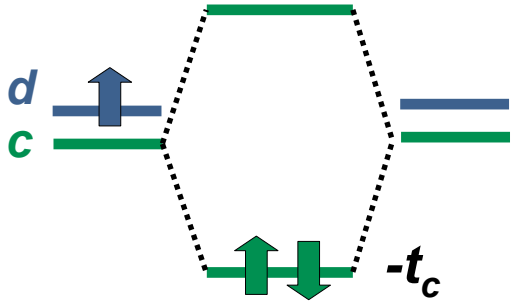
Georges et al., RMP 68, 13 (1996).

Hafermann, Katsnelson, Lichtenstein, Europhys. Lett. 85, 37006 (2009).

More complicated situation: a dimer with two different orbitals

Isolated dimer
(e.g. 1.5 e/site)





"Double exchange"

"Molecular-Orbital state"

$S_{tot}=3/2$

3d transition metal oxides

Competition

$J_H \not\to \infty$

$S_{tot}=1/2$

4d-5d transition metal oxides

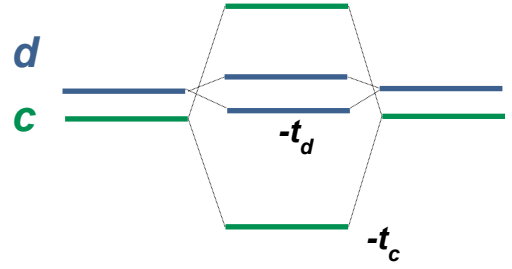
$$E_{DE} = -t_c - J_H$$

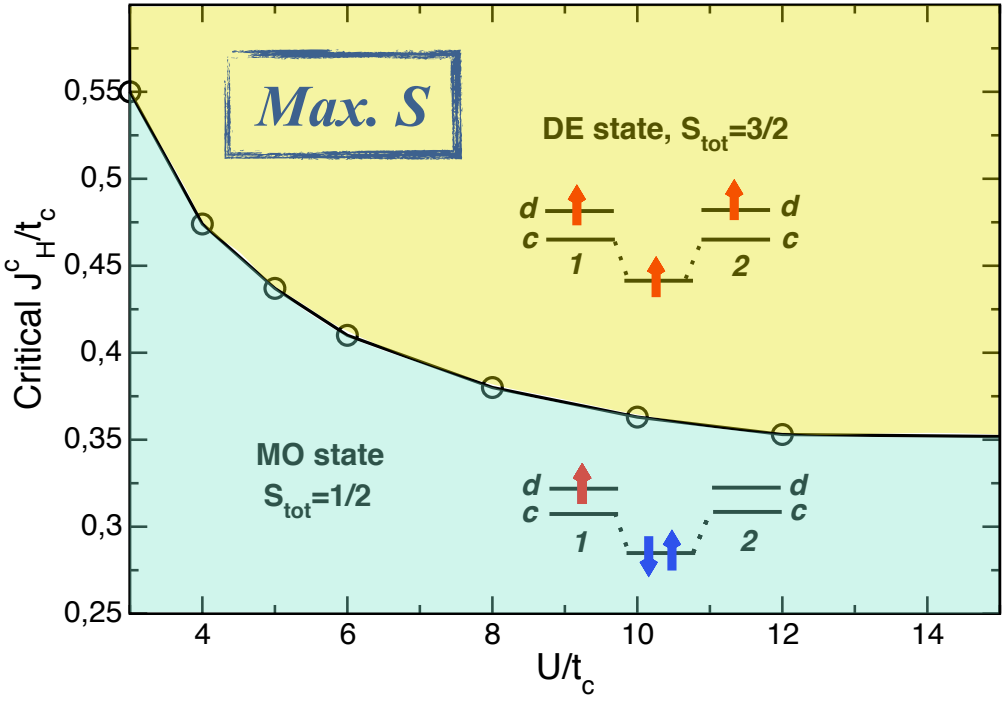
$$E_{MO} = -2t_c - t_d - \frac{J_H}{2}$$

The double exchange (maximum S_{tot}) state can be suppressed!

More complicated situation: a dimer with two different orbitals

Exact diag. (T=0) for a dimer





Dimer: 2 orbitals/site;
1.5 electrons/site

Model: $H = H_0 + H_U$

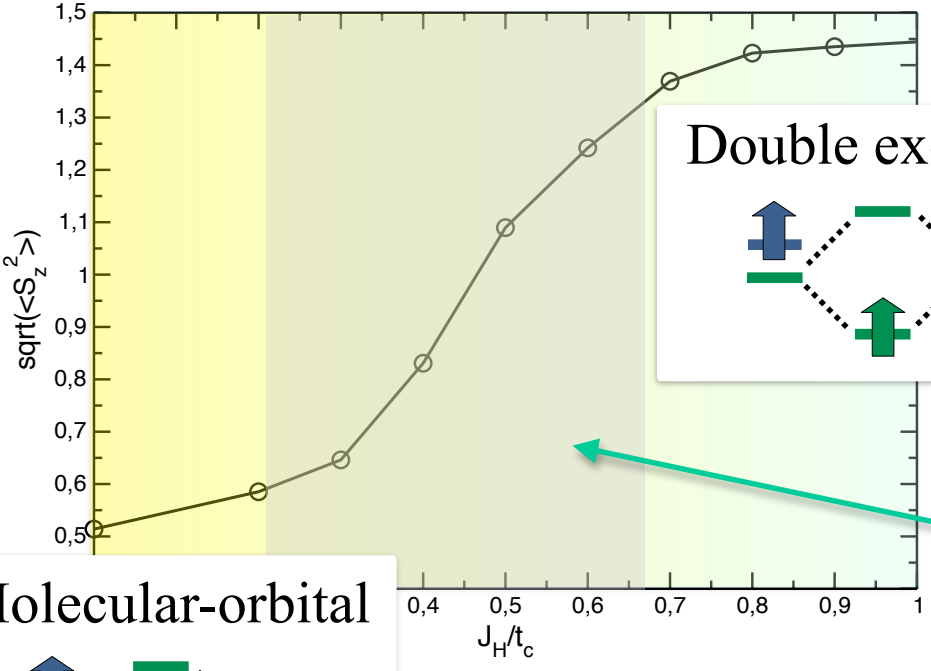
$$H_0 = t_c c_2^\dagger c_1 + t_d d_2^\dagger d_1 + H.c.$$

$$H_U = \frac{1}{2} \sum_{\substack{j \\ mm'\sigma}} U^{mm'} n_{j,m}^{\sigma} n_{j,m'}^{-\sigma} + \frac{1}{2} \sum_{\substack{j \\ \langle mm' \rangle \sigma}} (U^{mm'} - J_H^{mm'}) n_{j,m}^{\sigma} n_{j,m'}^{\sigma}$$

Transition from molecular-orbital to double exchange regime is discontinues

Dimerized chain: Orbital-selective effects

Dimerized chain: cluster-DMFT results



Technical details:

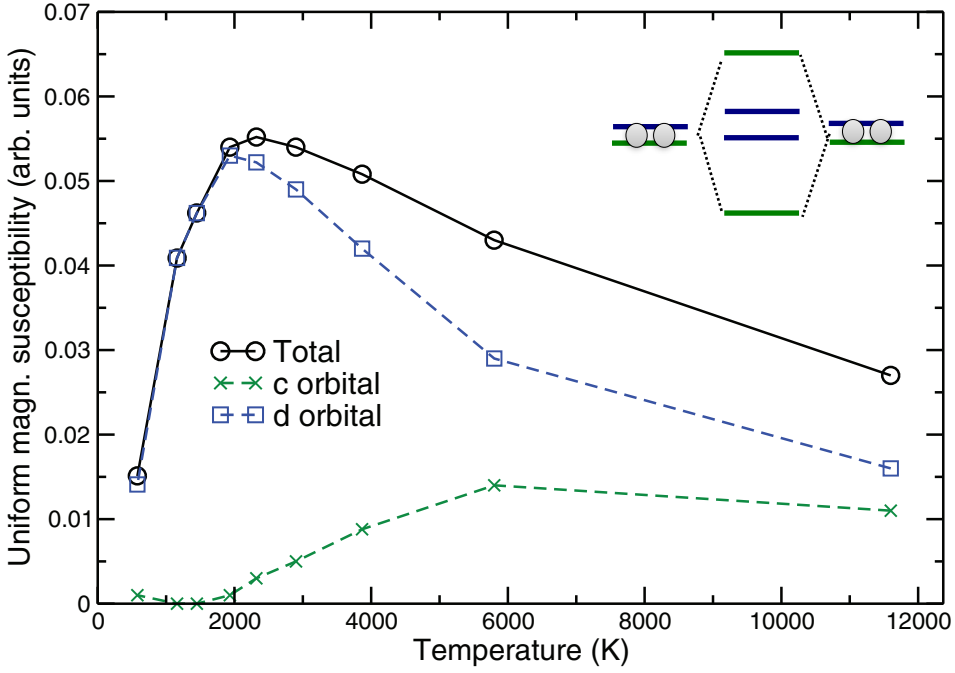
- HF-QMC, T= 1100 K
- 2 bands; 1.5 electrons/site;
- Realistic values for 4*d*/5*d* TMO
  t_d=0.1eV, t_c=0.6eV, U=5eV, t'=0.5t_d

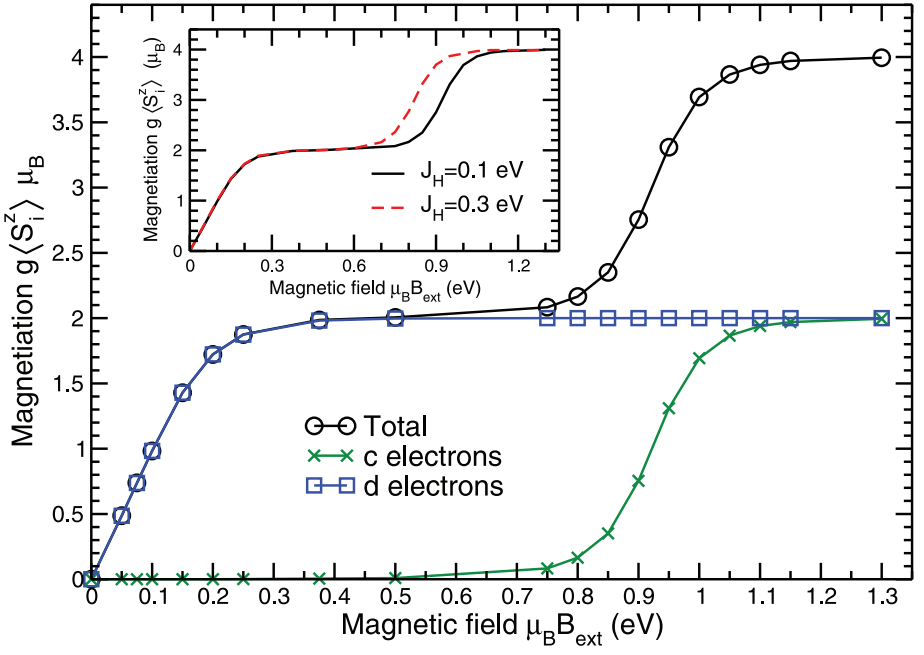
Molecular-orbital/Double exchange transition: smooth crossover

Streltsov & Khomskii PNAS ***113****, 10491 (2016)*

Dimerized chain: Orbital-selective effects

Dimerized chain:





c and *d* orbitals "work" at different ***T***

Orbital-selective behaviour!

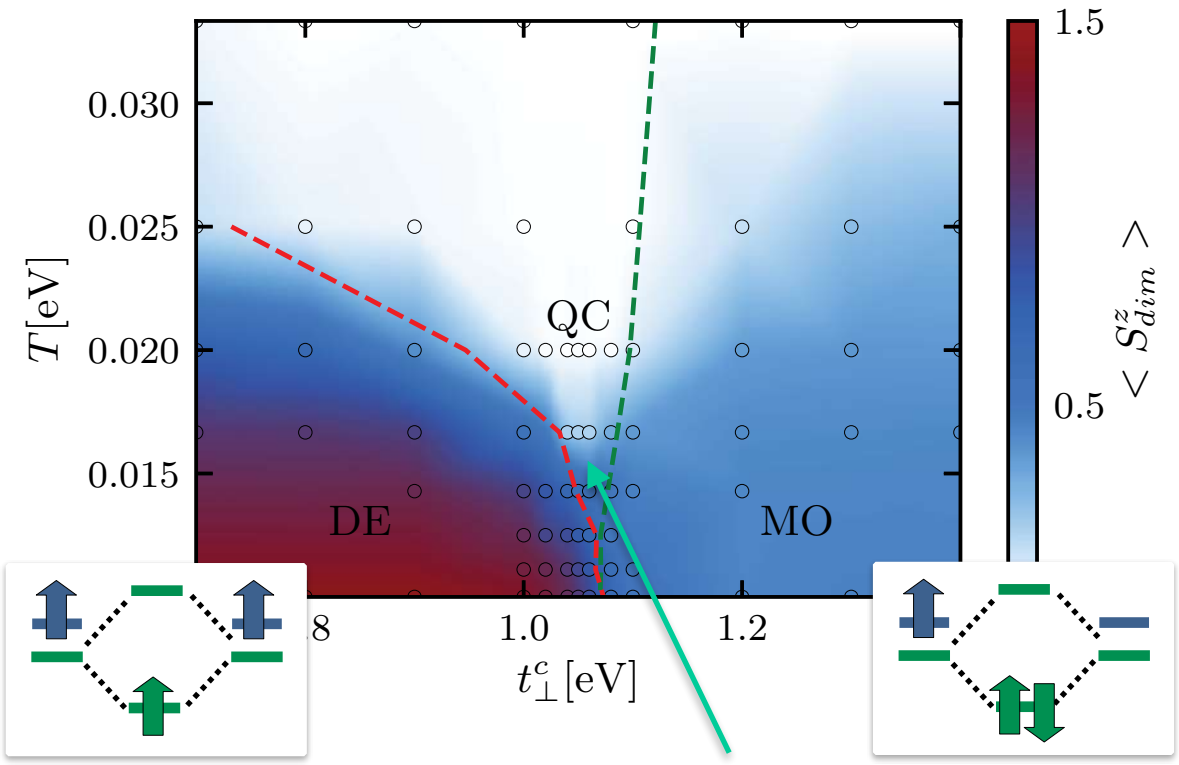
c and *d* orbitals "work" at different ***B***

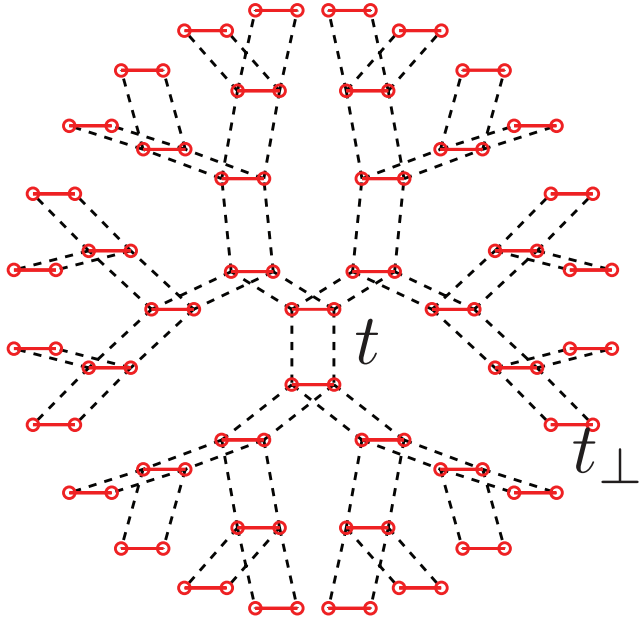
Orbital-selective behaviour!

Streltsov and Khomskii, Physics-Uspekhi 60, 1121 (2017).

Two orbitals, two planes Bethe lattice: Orbital-selective effects

Cluster-DMFT



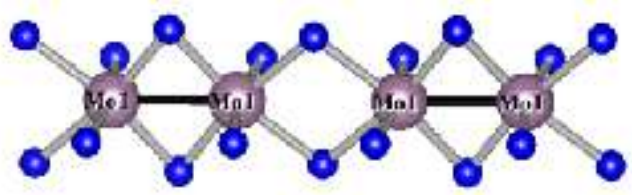


Suppression of a long-range magnetic order in the transition region!

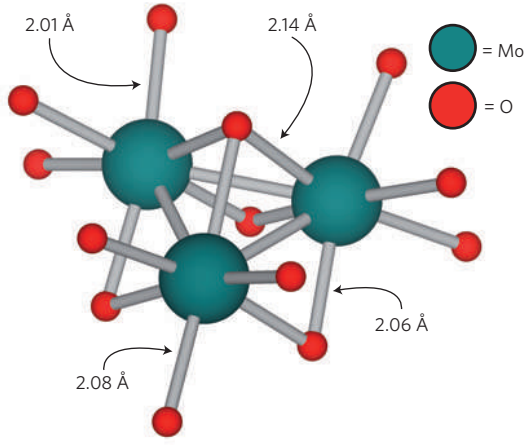
Harland, Poteryaev, Streltsov, Lichtenstein, PRB 99, 045115 (2019)

Examples of cluster Mott magnets

1. **Orbital selective behaviour in $Y_5Mo_2O_{12}$**



2. **"Mo_3O_8" cluster magnets: quantum spin liquids, quantum paramagnets, 120^0 AFM, ferromagnets, diamagnets**

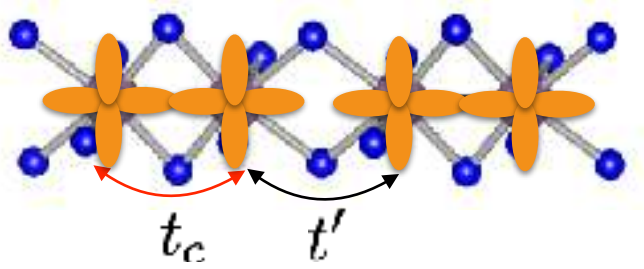


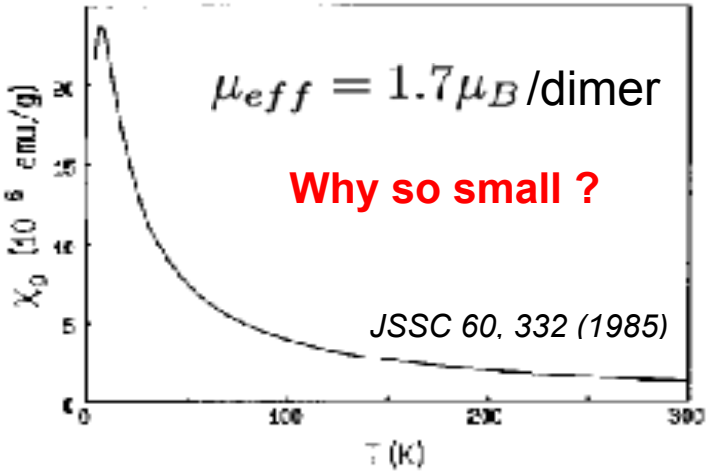
Orbital-selective effects: example of real materials

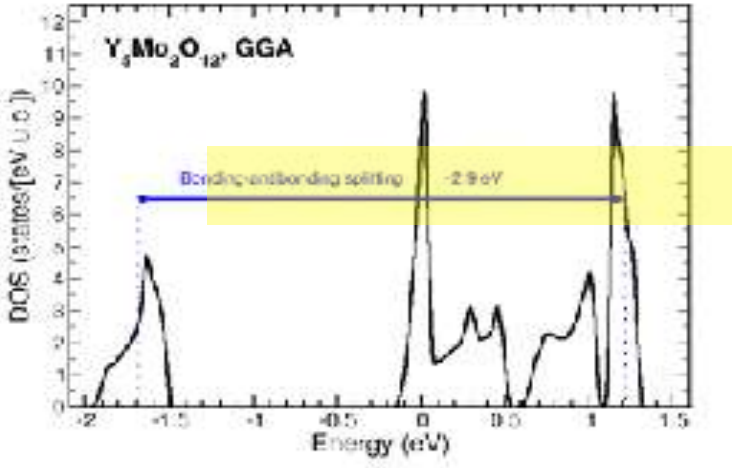
Suppression of magnetic moments in $Y_5Mo_2O_{12}$

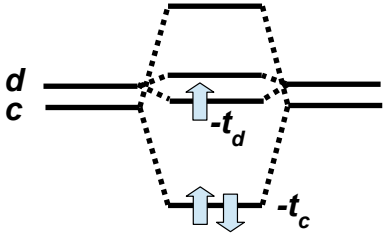
$Mo^{4.5+}$: $4d^{1.5}$ $\mu_{eff} = 3.24\mu_B$ /dimer

Crystal structure: dimerized chains









S=1/2 per dimer

$\mu_{eff} = 1.73\mu_B$ /dimer

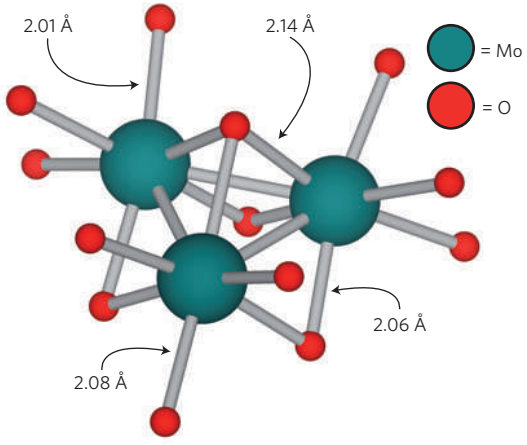
Other examples: $Ba_3YRu_2O_9$, CdV_2O_4, MoO_2, $Nb_2O_2F_3$

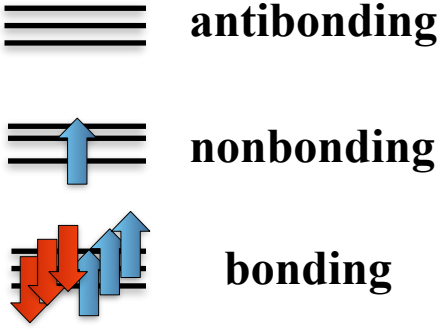
A very important examples of cluster Mott magnets

General formula: $[A_xB_y]^{5+}Mo_3O_8$ $[Mo_3]^{11+} \longrightarrow d^7$

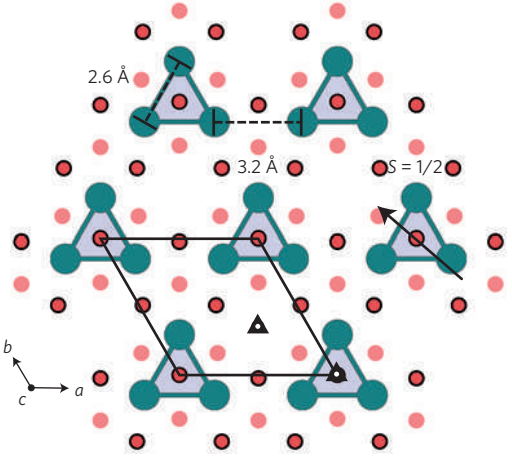
$LiZn_2Mo_3O_8$, $Li_2(Sc,In)Mo_3O_8$, Nb_3Cl_8

Main structural unit: Mo_3 trimer





Trimers form 2D triangular lattice



Triangular lattice (highly frustrated!) of triangles with a single electron per triangle

Valence-bond condensation in $LiZn_2Mo_3O_8$?

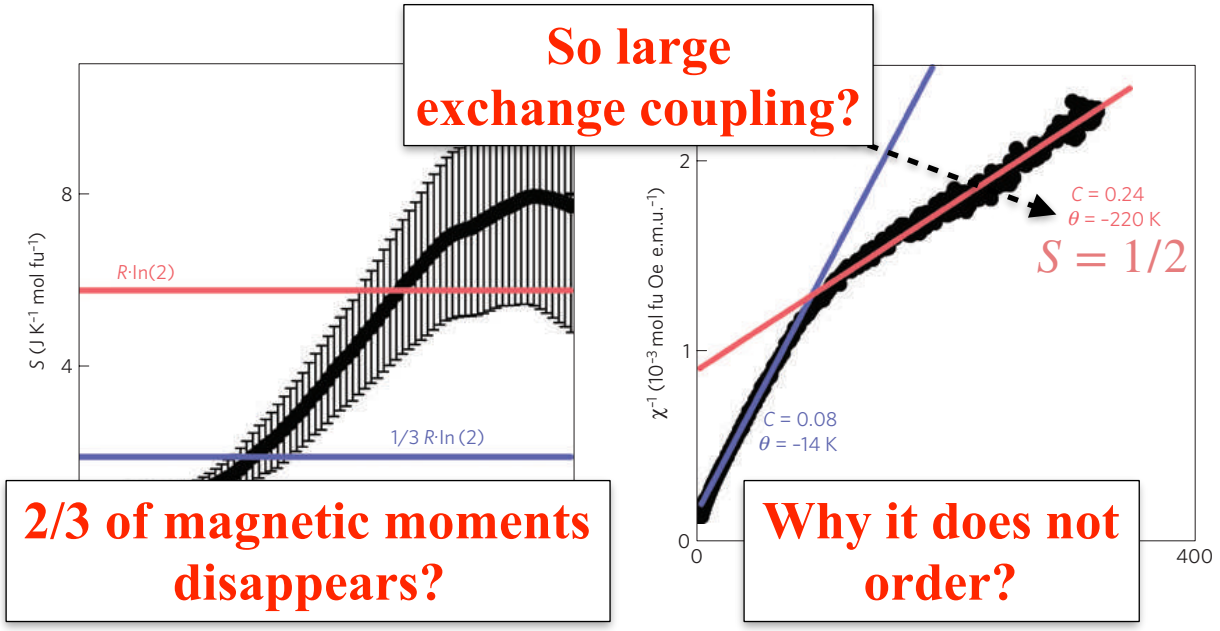
nature materials

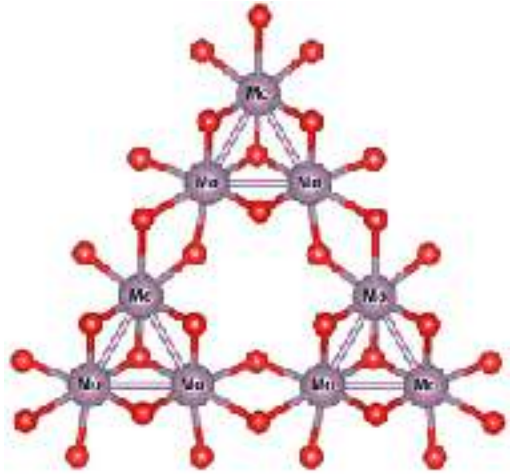
LETTERS

PUBLISHED ONLINE: 6 MAY 2012 | DOI: 10.1038/NMAT3329

Possible valence-bond condensation in the frustrated cluster magnet $LiZn_2Mo_3O_8$

J. P. Sheckelton, J. R. Neilson, D. G. Soltan and T. M. McQueen*

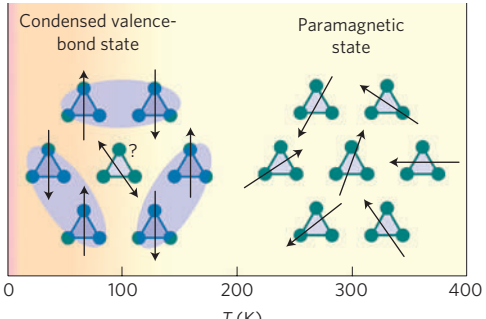




see also

Mourigal et al., PRL 112, 027202 (2014)

Possible model



Quantum spin-liquid in $LiIn_{1-x}Sc_xMo_3O_8$

Haraguchi et al., PRB 92, 011409 (2015)

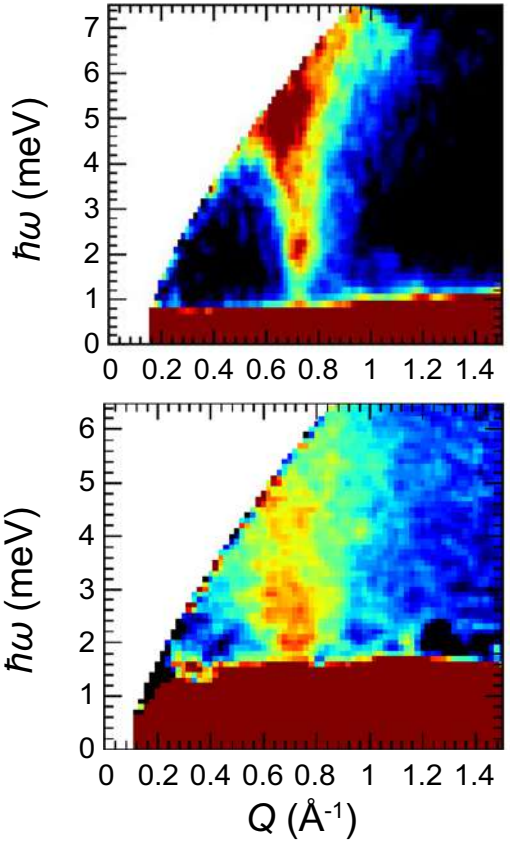
$Li_2InMo_3O_8$
120^0 AFM
(T_N=12 K)

$\mu_{eff} = 1.61\mu_B$
$\Theta_{CW} = -242K$
$J_\Delta = 112\ K$

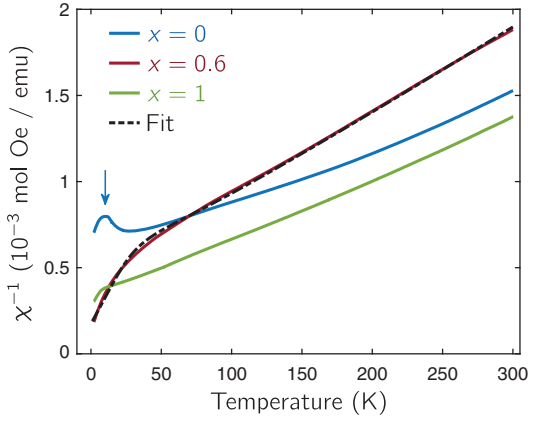
$Li_2ScMo_3O_8$
QSL

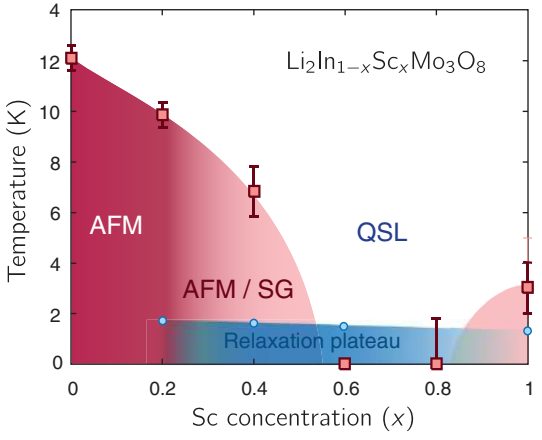
$\mu_{eff}^{HT} = 1.65\mu_B$
$\Theta_{CW} = -127K$
$J_\Delta = 67\ K$

Iida et al., Sci. Rep. 9, 1826 (2019)



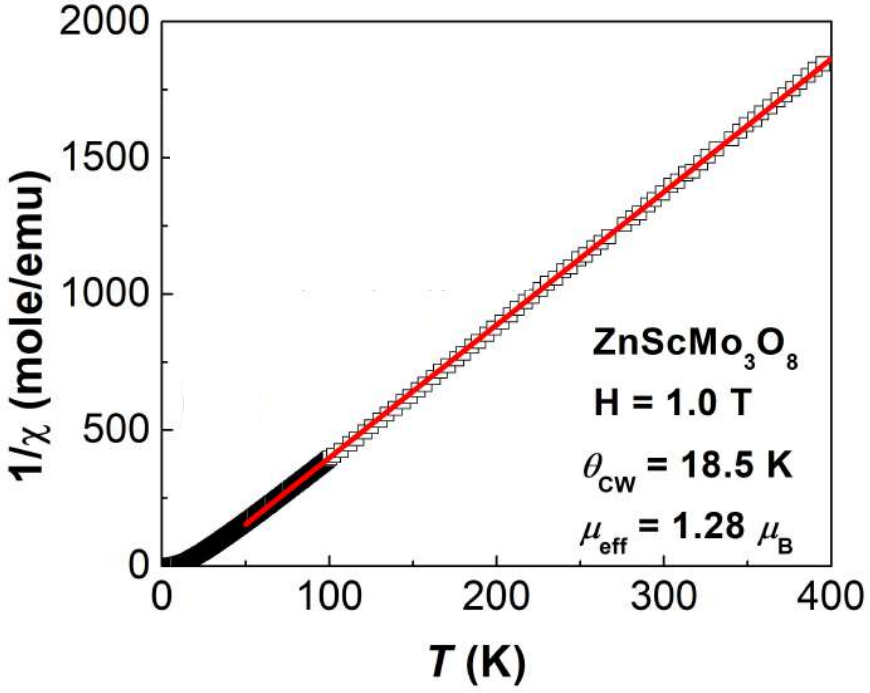
Akbari-Sharbaf et al., PRL 120, 227201 (2018)

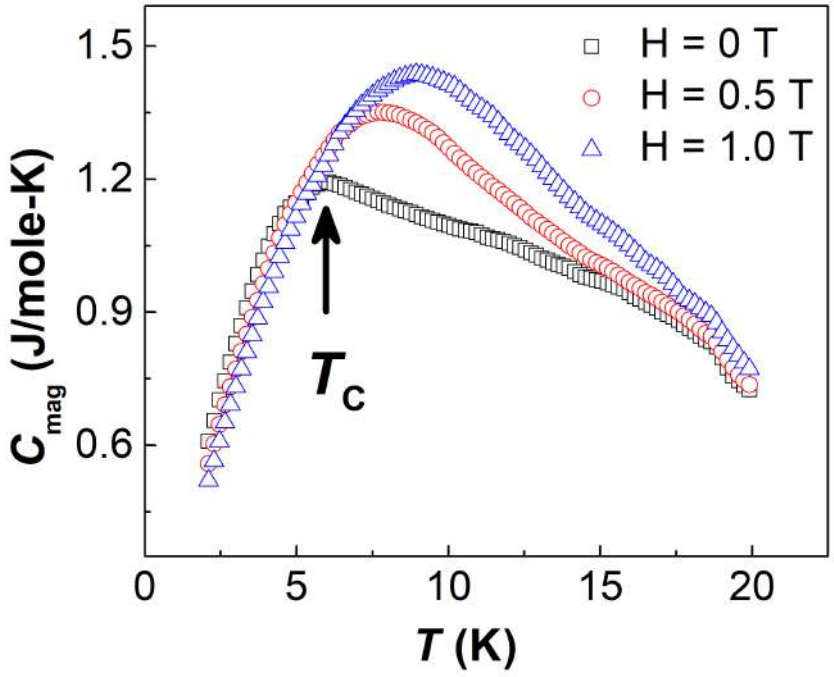




$Li_2ScMo_3O_8$ (or $Li_2In_{0.4}Sc_{0.6}Mo_3O_8$) show a spin-liquid behaviour!

Ferromagnetism in $ZnScMo_3O_8$





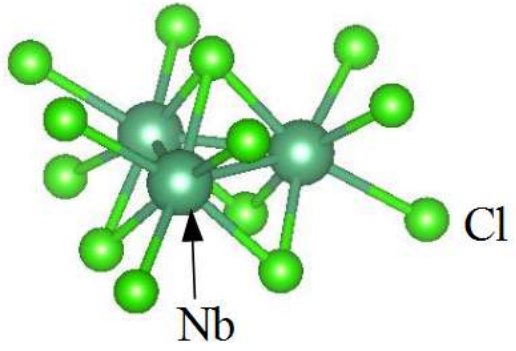
What? Ferromagnetic insulating oxide?

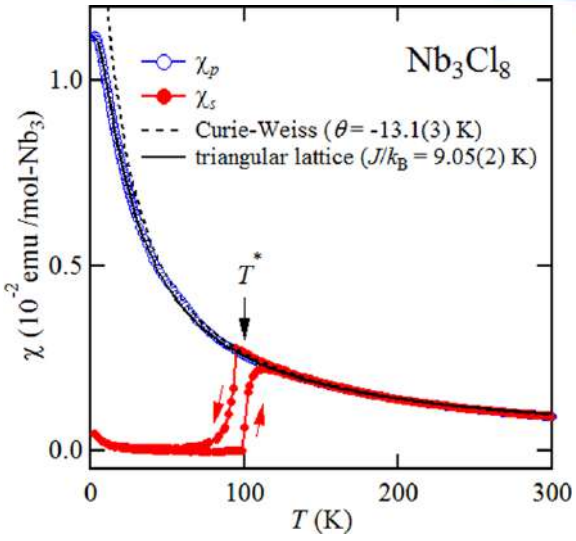
Q. Chen et al., private communication

$MgScMo_3O_8$ also shows FM behavior at HT…

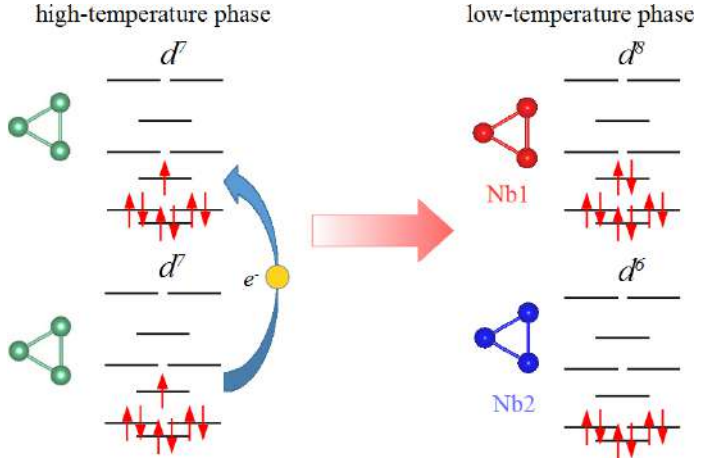
Diamagnetism in Nb_3Cl_8

$[Nb_3]^{8+} \longrightarrow d^7$

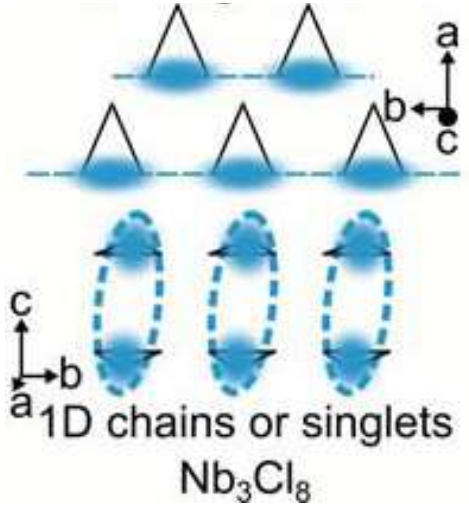




Haraguchi et al., Inorg. Chem. 56, 3483 (2017)



Sheckelton et al., Inorg. Chem. Front. 4, 481 (2017)



Summary on Mo_3O_8 (Nb_3Cl_8) systems

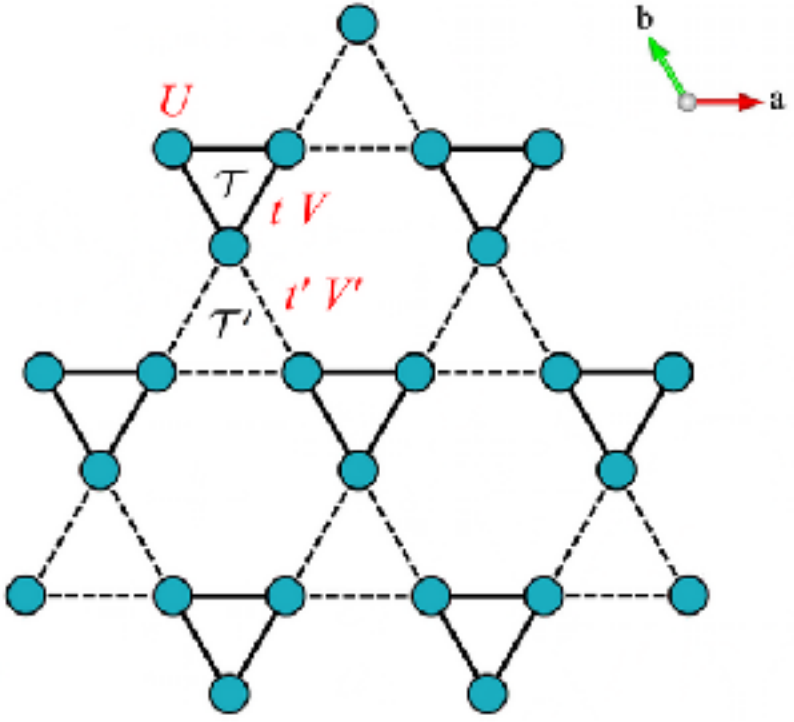
$LiZn_2Mo_3O_8$	Valence bond condensation	T*=96 K
$Li_2InMo_3O_8$	120^0 AFM	T_N=12 K
$Li_2ScMo_3O_8$	Quantum spin liquid?	T*~40 K
$ZnScMo_3O_8$	Ferromagnet	T_C=6 K
Nb_3Cl_8	Diamagnetic	T_D=100 K

T* - temperature of 2/3 spins “freezing”

T_D - temperature of transition to diamagnetic state

Mo_3O_8 systems: Model treatment

$\mathcal{T}$ - trimers



Filling: 1 electrons per Mo_3

Model: 1/6-filled extended Hubbard model on Kagome lattice

$$\mathcal{H} = \sum_{\substack{\langle mm' \rangle \in \mathcal{T} \\ \sigma}} t\left(c_m^{\dagger\sigma} c_{m'}^{\sigma} + \mathrm{H.c.}\right) + V n_m n_{m'}$$

$$+ \sum_{\substack{\langle mm' \rangle \in \mathcal{T}' \\ \sigma'}} t'\left(c_m^{\dagger\sigma} c_{m'}^{\sigma} + \mathrm{H.c.}\right) + V' n_m n_{m'} + U \sum_m n_m^{\uparrow} n_m^{\downarrow}$$

Filling 1/6 => ***U*** is **NOT** operative

Electrons can be localized by **intersite Coulomb interaction (*V,V'*)**

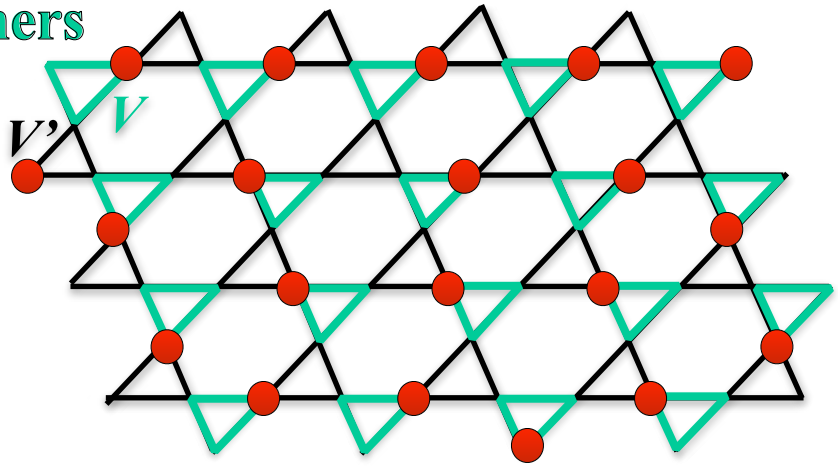
Chen, Kee, Kim, PRL 113, 197202 (2014)

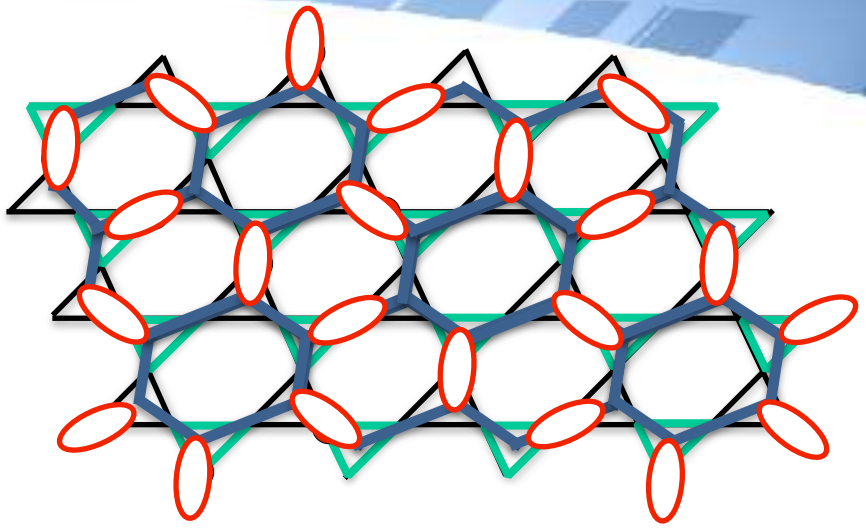
Chen, Kee, Kim, PRB 93, 245134 (2016)

Chen, Lee, PRB 97, 035124 (2018)

Quantum dimer model on honeycomb lattice

Trimers

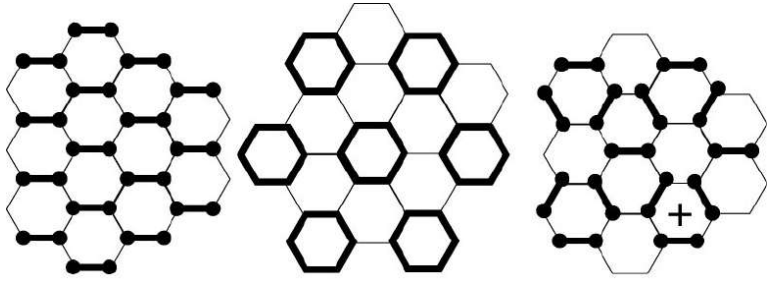




***V,V'*: Massive ground state degeneracy, which covering is better?**

Quantum dimer model

$$H_{QDM} = -t\hat{T} + v\hat{V}$$

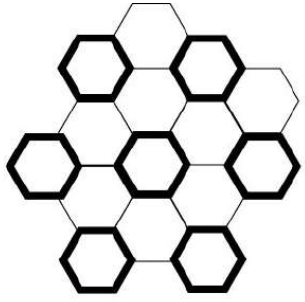


Moessner et al., PRB 64, 144416 (2001)

Chen, Kee, Kim, PRB 93, 245134 (2016)

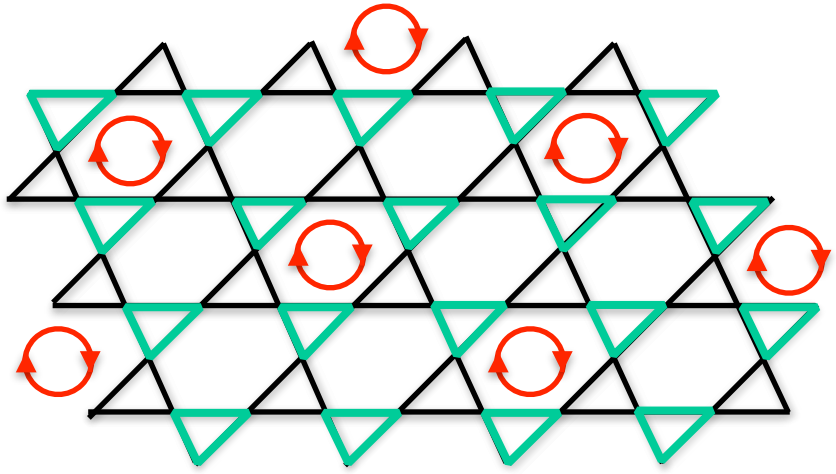
$t/V' \ll 1,\ t'/V \ll 1,\ t \sim t'$

Ground state:



Plaquette charge order explains freezing of 2/3 of spins

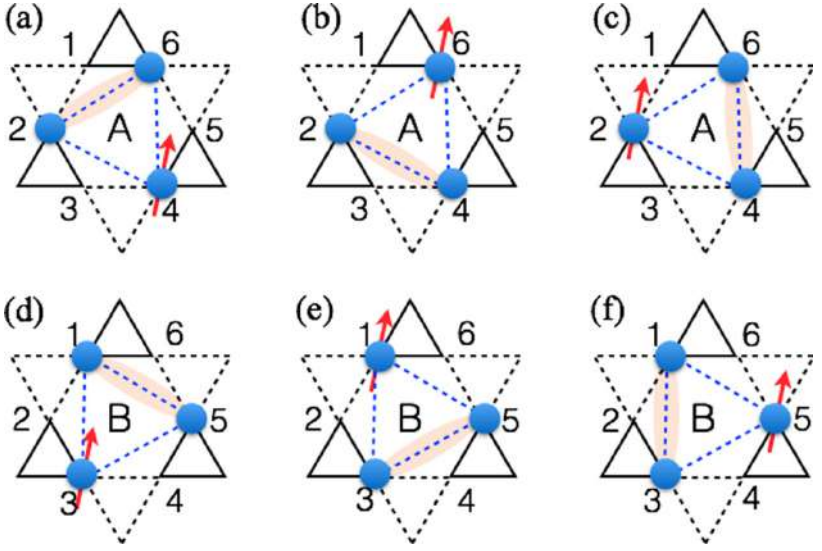
Ground state: Plaquette charge order (PCO)



$$= \frac{1}{\sqrt{2}}\left(\mathbb{A} + \mathbb{B} \right)$$

$$|\Psi\rangle_c = \prod_{\boldsymbol{R}} \frac{1}{\sqrt{2}} [|\hexagon_{\boldsymbol{R}}\rangle_A + |\hexagon_{\boldsymbol{R}}\rangle_B]$$

Feature of plaquette charge order state



Chen, Kee, Kim, PRB 93, 245134 (2016)

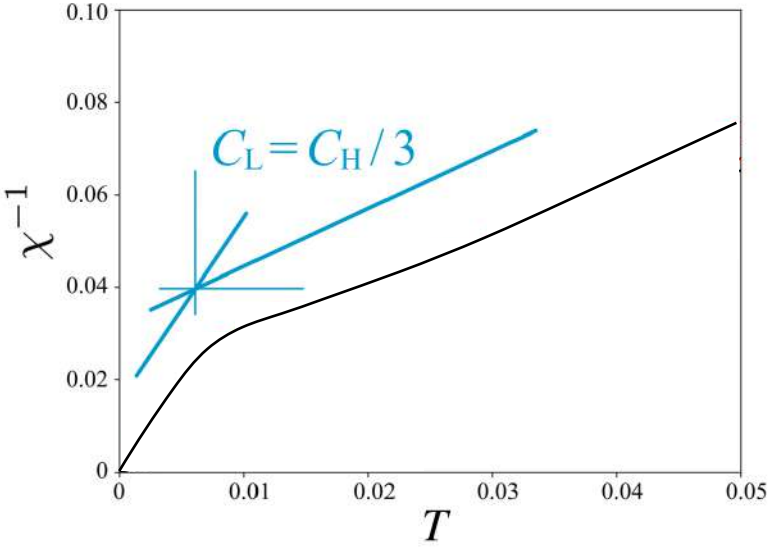
2/3 spins form *S=0* !

Nikolaev, Solovyev, Streltsov arXiv:2001.0747

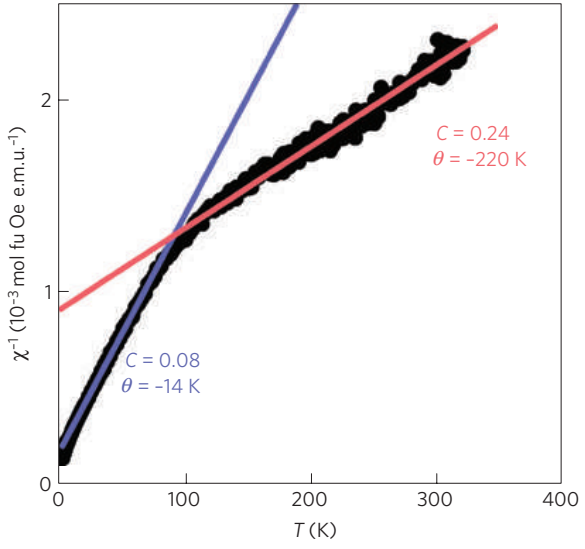
Does it work for $LiZn_2Mo_3O_8$?

Hubbard model
12 sites, 1 electron/site,
Breathing Kagome lattice
by exact diagonalization

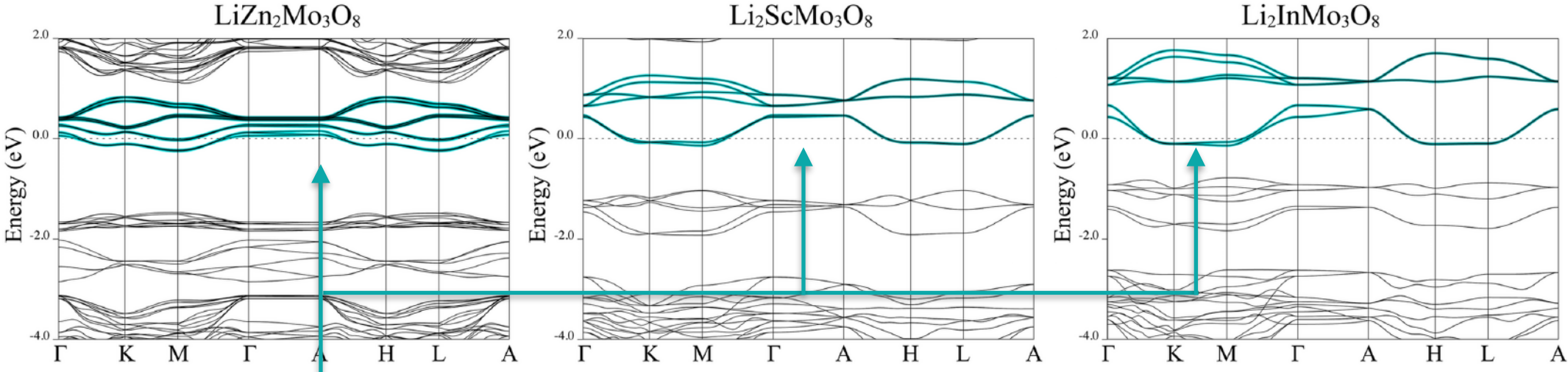
Nikolaev, Solovyev, Streltsov
arXiv:2001.0747

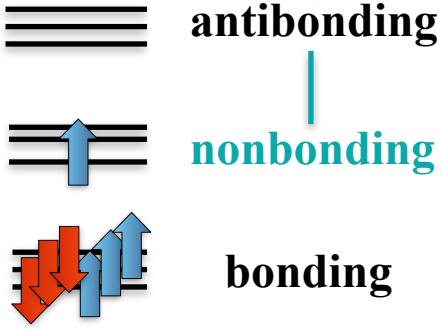


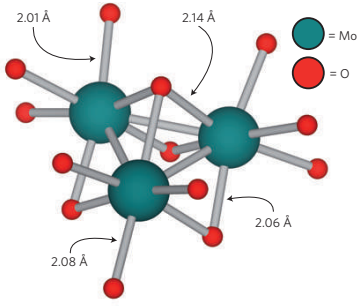
Experiment:
$LiZn_2Mo_3O_8$



What about real materials?







Hoppings: Wannier90
U,V,V': cRPA

DFT results

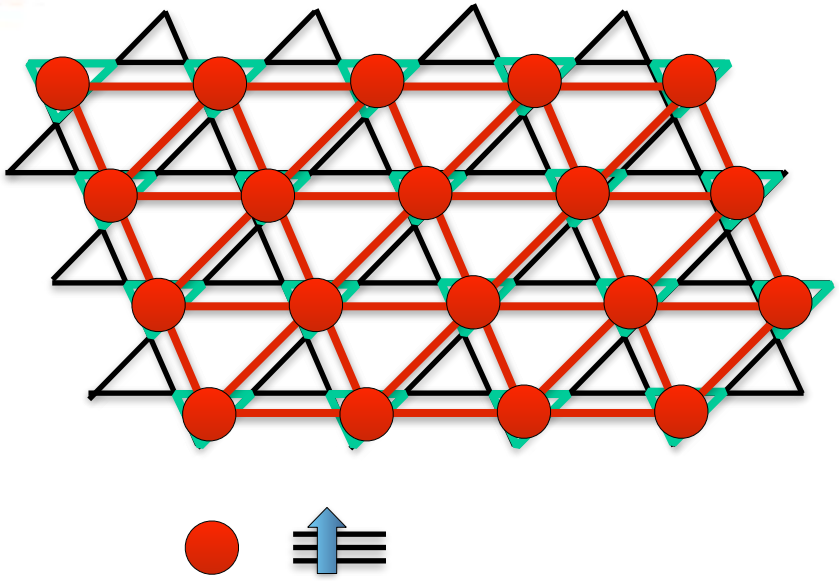
	U	t	V	t'	V'	$\lvert t\rvert/V'$	t'/V	t_{nn}
$LiZn_2Mo_3O_8$	2.0	−0.134	0.8	0.113	0.6	0.22	0.14	0.026

$LiZn_2Mo_3O_8$ Theory: $T^*=92$ K Experiment: $T^*=96$ K

$LiSc_2Mo_3O_8$, $LiIn_2Mo_3O_8$ } **Perturbation theory *t/V'*?**

$t \gg t'$ **Electrons localized on trimers?**

$Li(InSc)_2Mo_3O_8$: Heisenberg model on triangular lattice

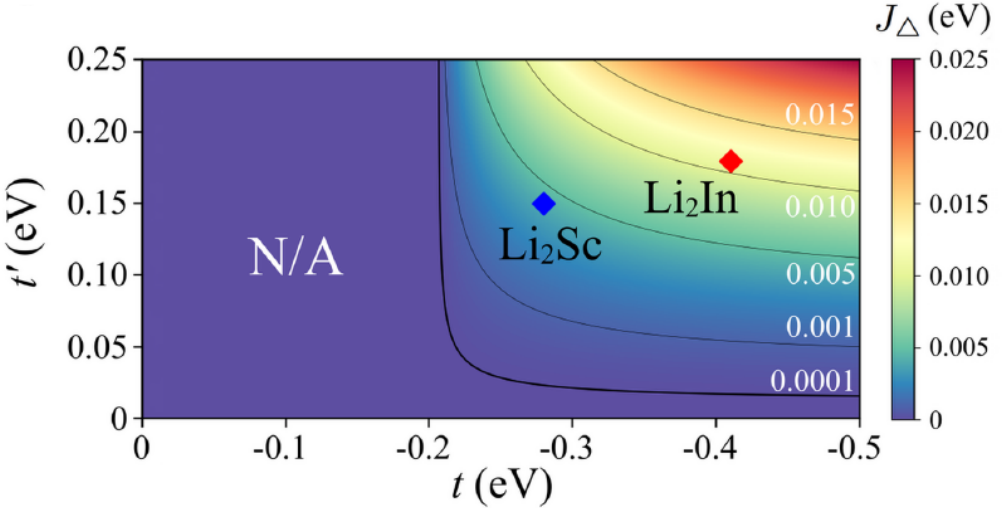


3 orbital Hubbard model on triangular lattice → **Heisenberg model on triangular lattice**

$$J_{\triangle} = -\frac{8t'^2}{3(2V+3|\Delta|-2V')} + \frac{4t'^2}{3(U+2V-2V')}$$

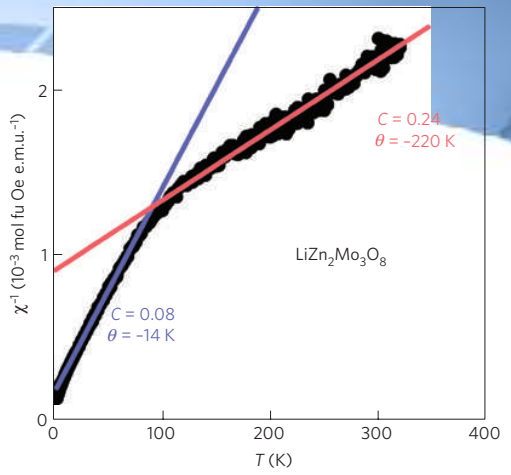
$$+\frac{8t'^2}{3(U+2V+3|\Delta|-2V')}, \text{ where } \Delta = 3t$$

- **$Li_2InMo_3O_8$** strong AFM coupling ($J_{\triangle} = 110K$) results in 120^0 AFM;
- **$Li_2ScMo_3O_8$**: exchange coupling is suppressed and quantum fluctuations may result in QSL formation;
- This explains how **$ZnScMo_3O_8$** may appear to be FM;

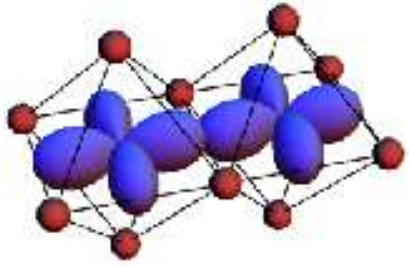


Take-home messages

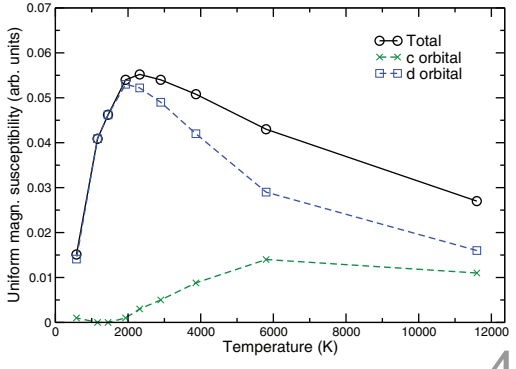
- Cluster Mott magnets often can be spontaneously formed by (orbitally) induced Peierls transitions;



- Physical properties of cluster Mott magnets can be very different from their conventional counters;



- There are typically two types of orbitals: molecular and site-localized. These orbitals can behave very differently: **Orbital-selective behaviour**;



Часть II

Эффект Яна-Теллера или спин-орбитальное взаимодействие: кто кого?

The End

Спасибо за внимание !