Orbital physics in transition metal compounds: new trends

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REVIEWS OF TOPICAL PROBLEMS

PACS numbers: 71.20.Be, **71.70.–d**, **75.10.–b**

Orbital physics in transition metal compounds: new trends

S V Streltsov, D I Khomskii

Contents

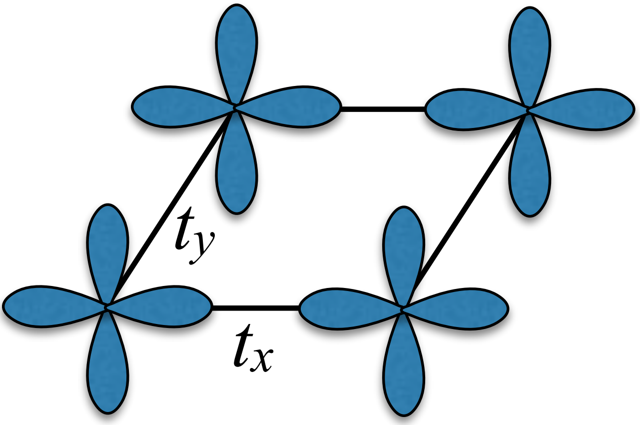
Three main roles of orbitals

Additional degree of freedom

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

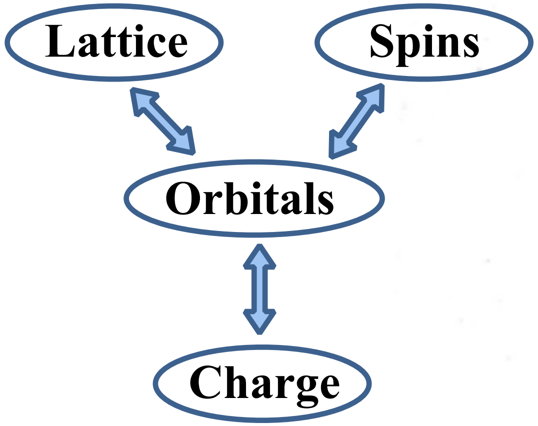
$$H = -\sum_{\langle ij\rangle mm'\sigma} t_{mm'} c^{\dagger}_{im'\sigma} c_{jm\sigma} + U \sum_{im} n_{im\uparrow} n_{im\downarrow} + U' \sum_{\substack{i,m\neq m' \\ \sigma\sigma'}} n_{im\sigma} n_{im'\sigma'} - J_H \sum_{\substack{i,m\neq m' \\ \sigma\sigma'}} c^{\dagger}_{im\sigma} c_{im\sigma'} c^{\dagger}_{im'\sigma'} c_{im'\sigma}$$

Directional character



$t_x >> t_y$

“Glue” for different degrees of freedom



Lattice

Spins

Orbitals

Charge

Effective reduction of dimensionality due to orbital degrees of freedom

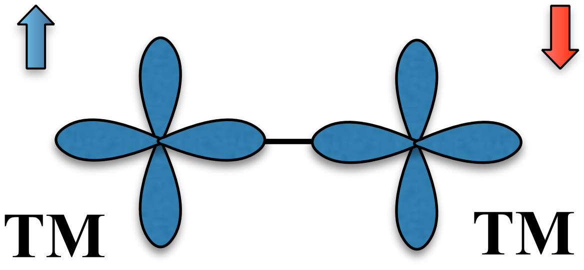
- Formation of low-dimensional magnetic systems due to orbital ordering
- "1D-zation" of electron spectrum and orbitally driven Peierls state
- Novel states close to the Mott transition: "molecules" in solids

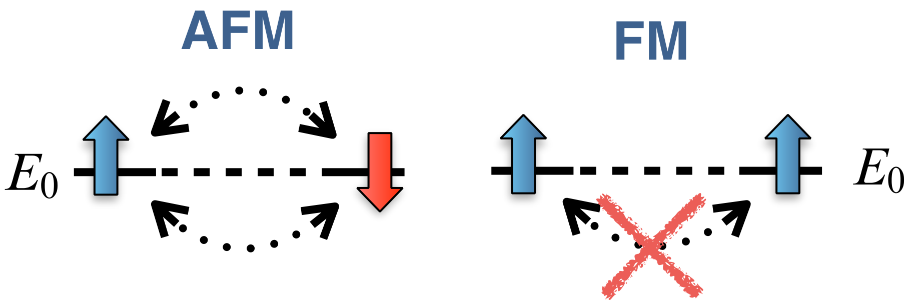
1. Effective reduction of dimensionality

Introduction: orbitals and magnetism

Heisenberg model

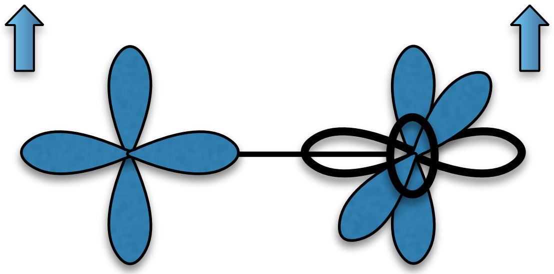
$$H = J \sum_{ij} \mathbf{S}_i \mathbf{S}_j$$

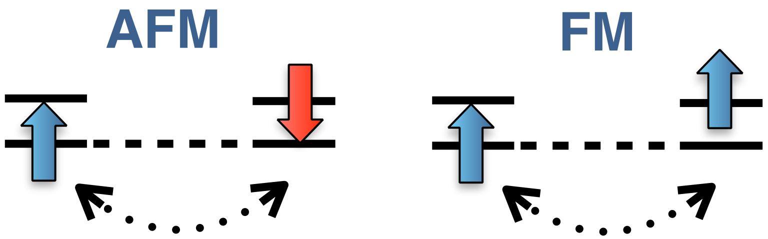




strong

$$J_1 = E_{\mathrm{FM}} - E_{\mathrm{AFM}} = E_0 - \left(E_0 - \frac{2t^2}{U} \right) = \boxed{\frac{2t^2}{U}}$$



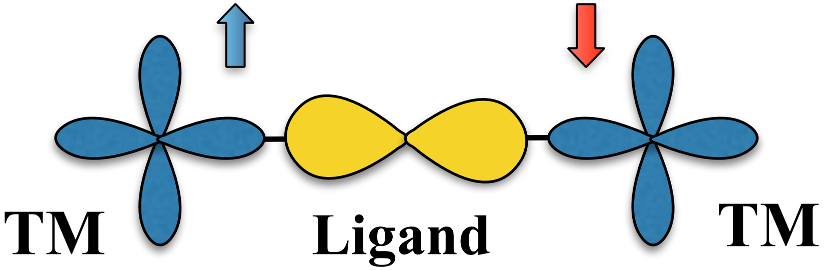


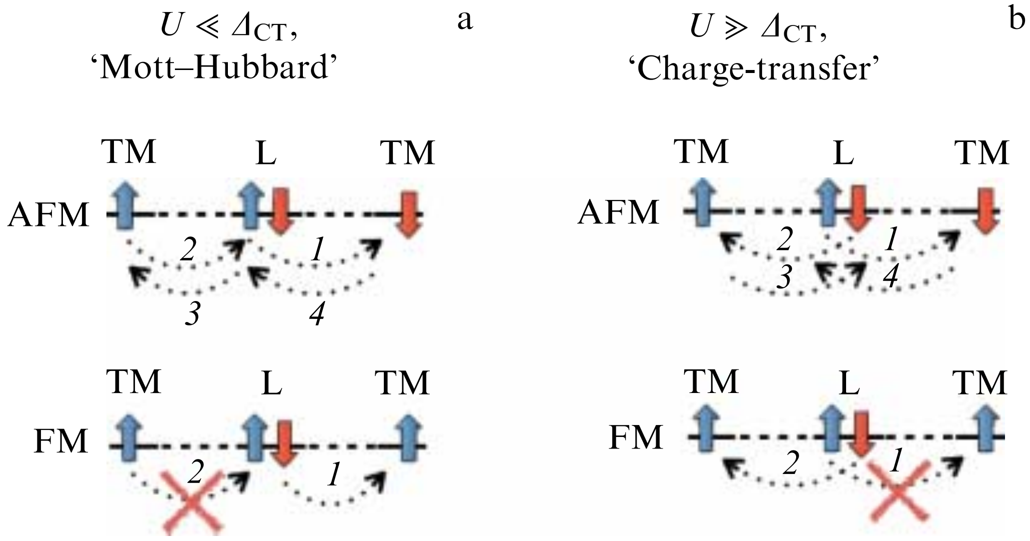
weak

$$J_2 = E_{\mathrm{FM}} - E_{\mathrm{AFM}} = E_0 - \frac{t^2}{U - J_{\mathrm{H}}} - E_0 + \frac{t^2}{U} \sim \boxed{-\frac{t^2 J_{\mathrm{H}}}{U^2}}$$

1. Effective reduction of dimensionality

Introduction: superexchange



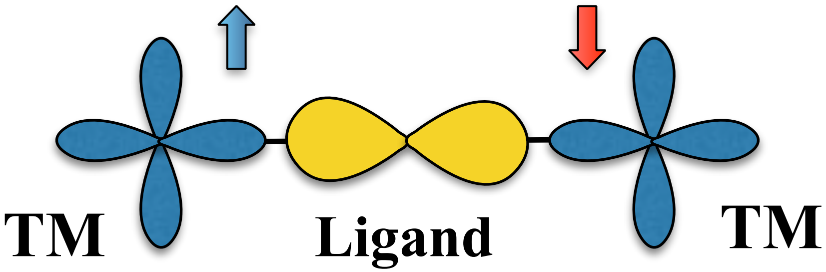


$$\boxed{J \sim \left(t_{\mathrm{dd}}^{\mathrm{eff}}\right)^2 \left(\frac{1}{U} + \frac{1}{\varDelta_{\mathrm{CT}} + U_{\mathrm{pp}}/2}\right)}$$

$$J \sim \frac{t_{\mathrm{pd}}^4}{\varDelta_{\mathrm{CT}} U \varDelta_{\mathrm{CT}}} = \frac{\left(t_{\mathrm{dd}}^{\mathrm{eff}}\right)^2}{U} \qquad J \sim \frac{t_{\mathrm{pd}}^4}{\varDelta_{\mathrm{CT}}(\varDelta_{\mathrm{CT}} + U_{\mathrm{pp}}/2)\, \varDelta_{\mathrm{CT}}} = \frac{\left(t_{\mathrm{dd}}^{\mathrm{eff}}\right)^2}{\varDelta_{\mathrm{CT}} + U_{\mathrm{pp}}/2}$$

1. Effective reduction of dimensionality

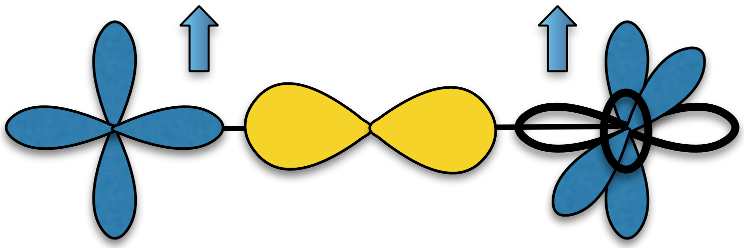
Introduction: GKA rules



strong

AFM

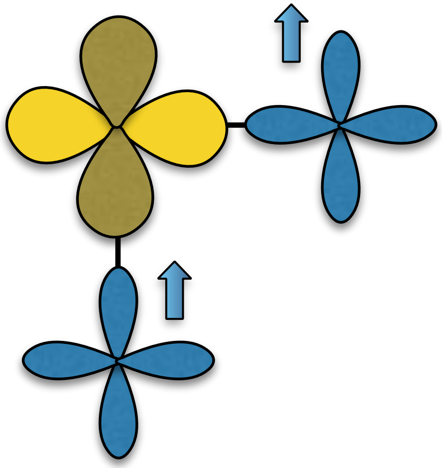
$$J \sim \left(t_{\mathrm{dd}}^{\mathrm{eff}}\right)^2\left(\frac{1}{U}+\frac{1}{\Delta_{\mathrm{CT}}+U_{\mathrm{pp}}/2}\right)$$



weak

FM

$$J \sim -\left(t_{\mathrm{dd}}^{\mathrm{eff}}\right)^2\left(\frac{J_{\mathrm{H}}}{U^2}+\frac{J_{\mathrm{H}}}{\left(\Delta_{\mathrm{CT}}+U_{\mathrm{pp}}/2\right)\Delta_{\mathrm{CT}}}\right)$$



weak

FM

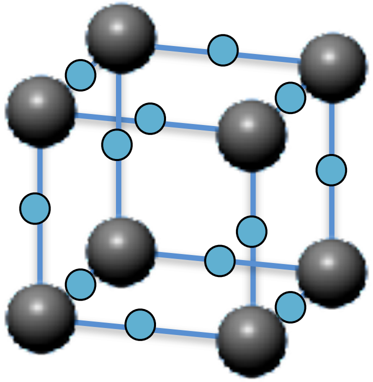
$$J \sim -\frac{\left(t_{\mathrm{dd}}^{\mathrm{eff}}\right)^2 J_{\mathrm{H}}^{\mathrm{p}}}{\left(\Delta_{\mathrm{CT}}+U_{\mathrm{pp}}/2\right)\Delta_{\mathrm{CT}}}$$

1. Effective reduction of dimensionality

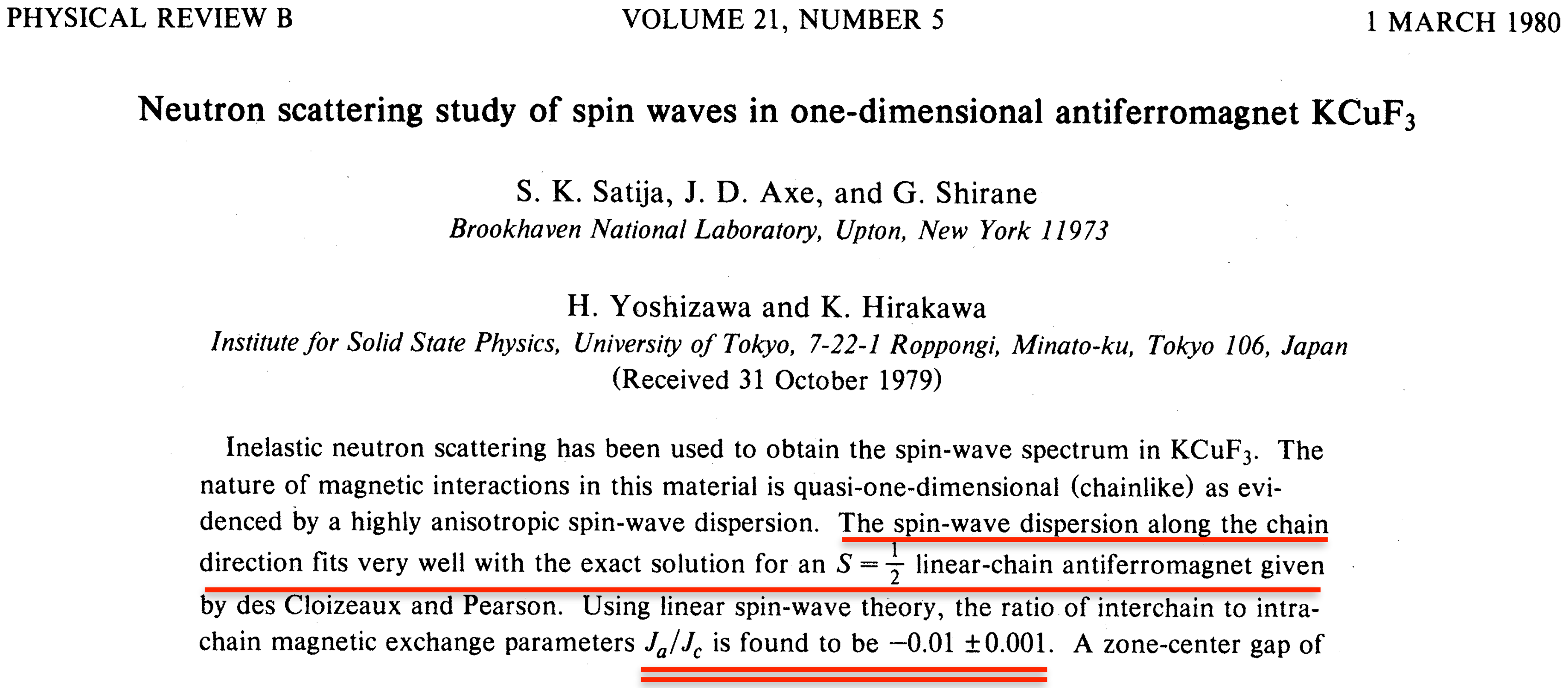
1.1 Low-dimensional magnetism due to orbital ordering

$KCuF_3$

Crystal structure:
perovskite (3D)



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



PHYSICAL REVIEW B VOLUME 21, NUMBER 5 1 MARCH 1980

Neutron scattering study of spin waves in one-dimensional antiferromagnet $KCuF_3$

S. K. Satija, J. D. Axe, and G. Shirane
Brookhaven National Laboratory, Upton, New York 11973

H. Yoshizawa and K. Hirakawa
Institute for Solid State Physics, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan

(Received 31 October 1979)

Inelastic neutron scattering has been used to obtain the spin-wave spectrum in $KCuF_3$. The nature of magnetic interactions in this material is quasi-one-dimensional (chainlike) as evidenced by a highly anisotropic spin-wave dispersion. The spin-wave dispersion along the chain direction fits very well with the exact solution for an $S = \frac{1}{2}$ linear-chain antiferromagnet given by des Cloizeaux and Pearson. Using linear spin-wave theory, the ratio of interchain to intrachain magnetic exchange parameters J_a/J_c is found to be -0.01 ± 0.001. A zone-center gap of

1. Effective reduction of dimensionality

1.1 Low-dimensional magnetism due to orbital ordering

$KCuF_3$

Crystal structure:
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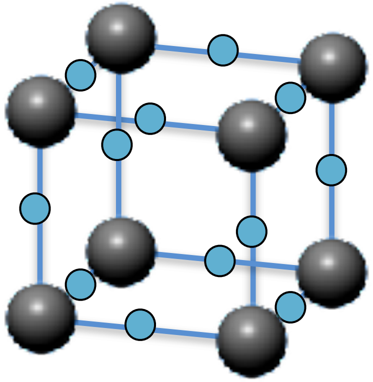
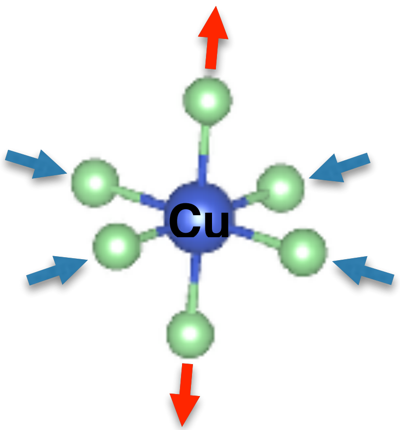
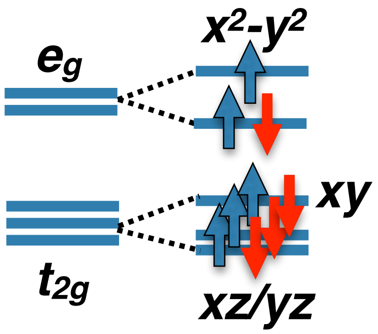


Cu^{3+} $(3d^9)$

Jahn-Teller distortions:

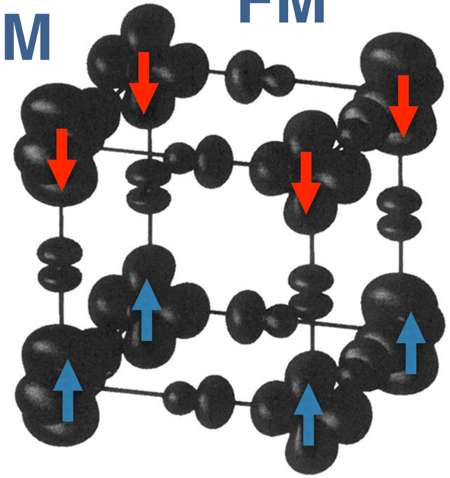




week
FM

week
FM

strong
AFM



AFM
S=1/2
chains!

Kugel & Khomskii, JETP 37, 725 (1973)

Orbitals reduce dimension: 3D → 1D

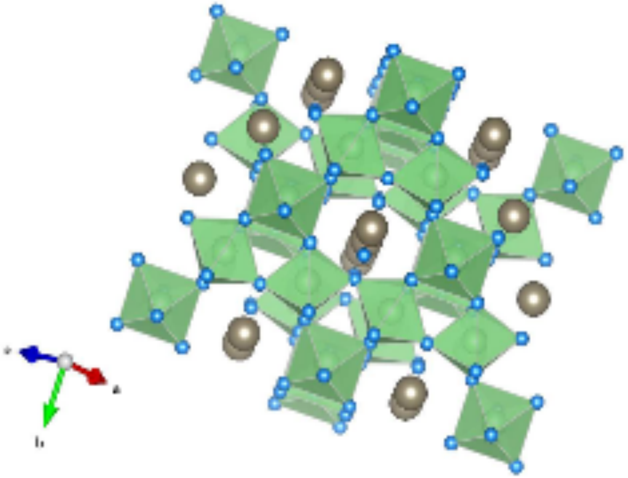
1. Effective reduction of dimensionality

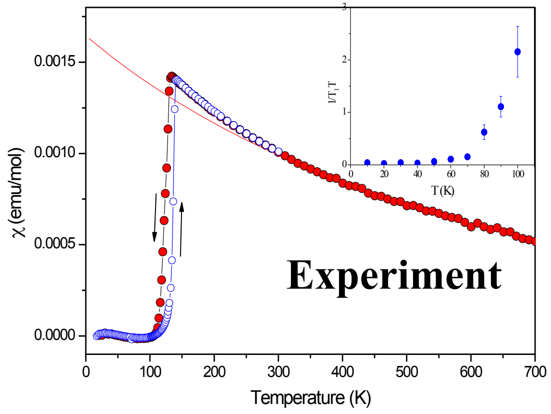
1.1 Low-dimensional magnetism due to orbital ordering

$Tl_2Ru_2O_7$

Crystal structure:
pyrochlore (3D)

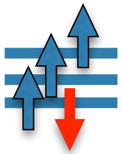
Ru^{4+} ($4d^4$, S=1)

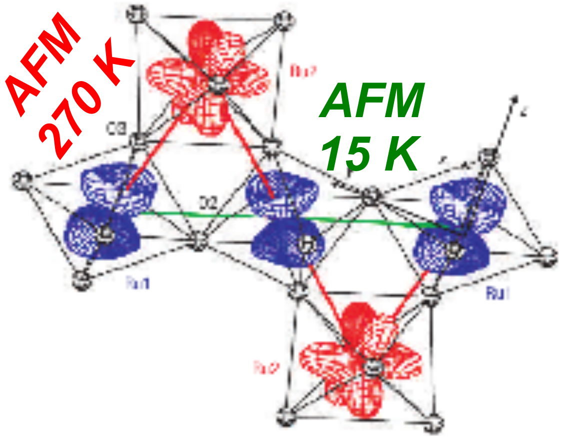




Orbital
ordering:
(LDA+U)

Ru^{4+}





AFM chain S=1: Haldane chains

S. Lee et al., Nat. Mater. ***5****, 471 (2006)*

Orbitals reduce dimensionality: 3D → 1D

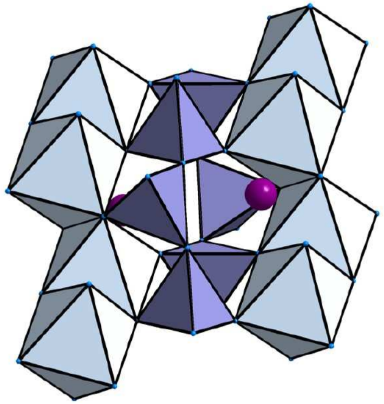
1. Effective reduction of dimensionality

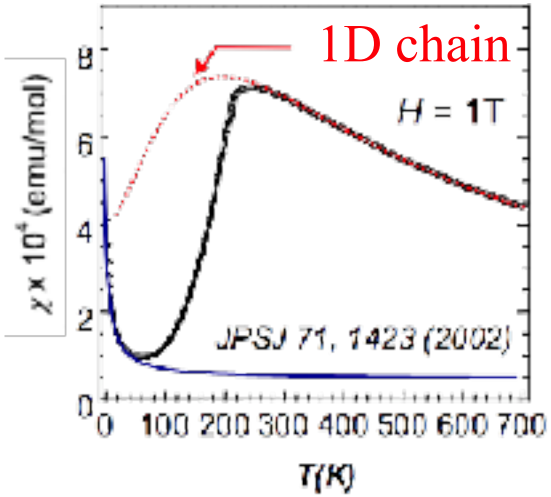
1.1 Low-dimensional magnetism due to orbital ordering

$NaTiSi_2O_6$

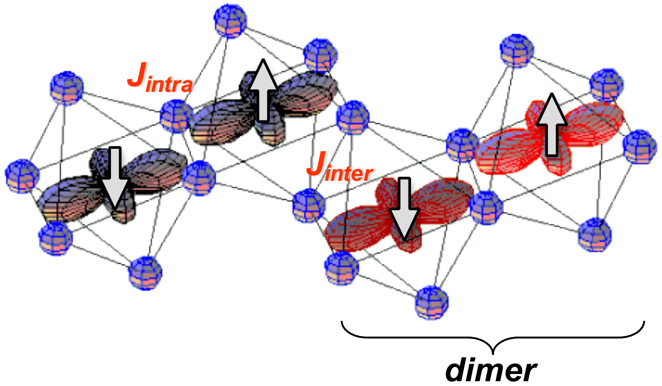
Crystal structure:
pyroxene (1D)

Ti^{3+} ($3d^1$, S=1/2) →





Orbital
ordering:
(LDA+U)



Exchange constants:

In dimer: J_{intra} = 396 K (AFM)
inter-dimer: J_{inter} = -5 K (FM)

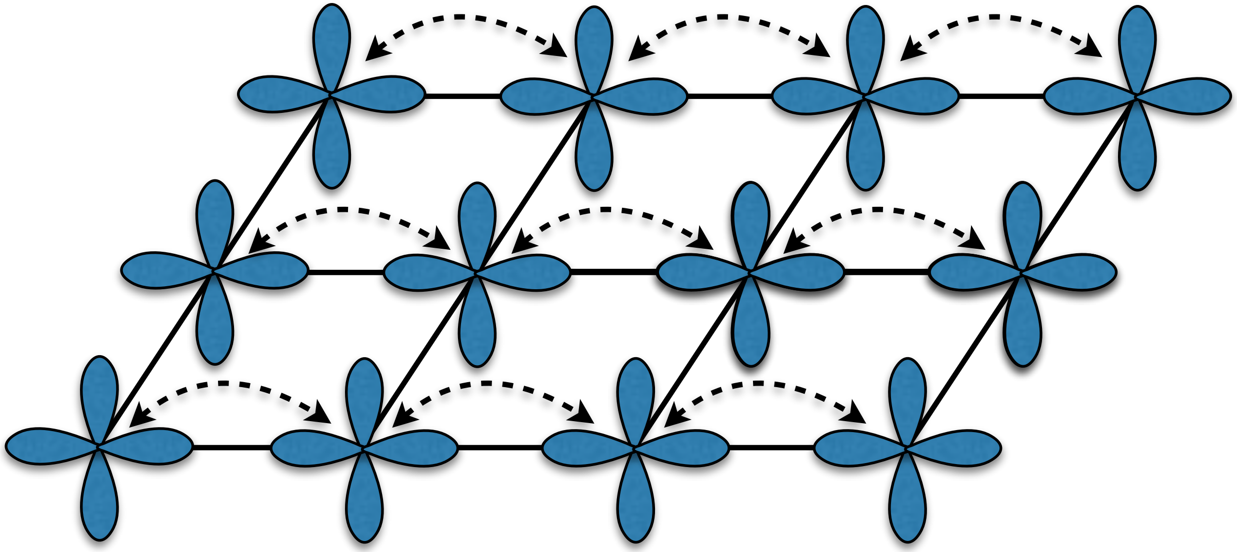
Streltsov et al., PRL 96, 249701 (2006)

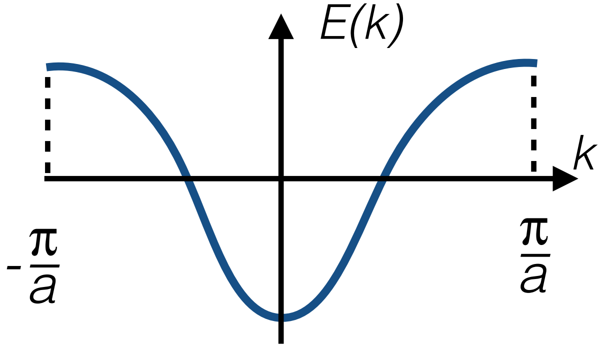
Orbitals reduce dimensionality: 1D ⟶ 0D

1. Effective reduction of dimensionality

1.2 “1D-zation” of electron spectrum

Directional character of orbitals



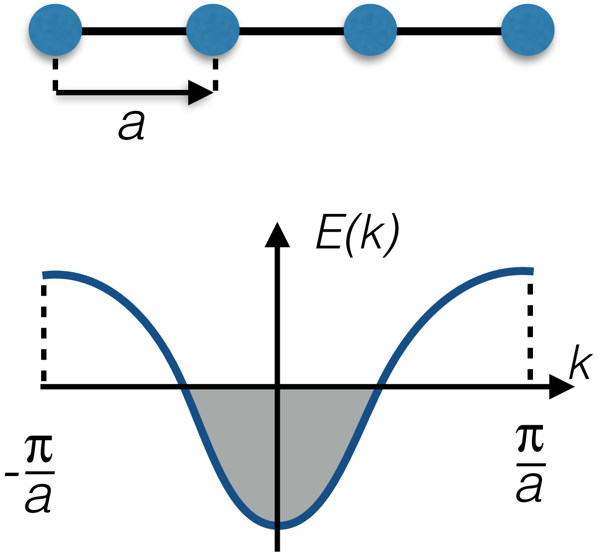


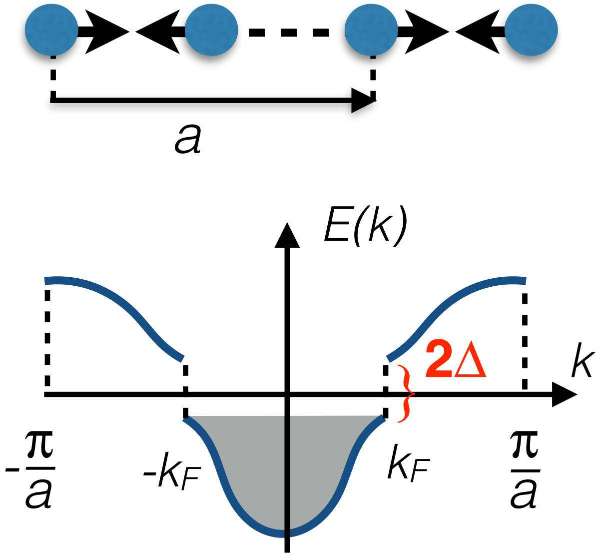
1. Effective reduction of dimensionality
1.2 “1D-zation” of electron spectrum

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!

1. Effective reduction of dimensionality

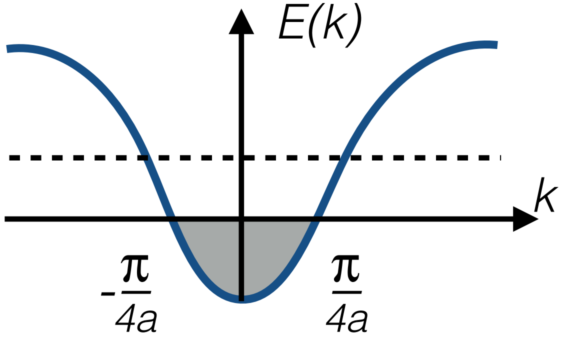
1.2 “1D-zation” of electron spectrum

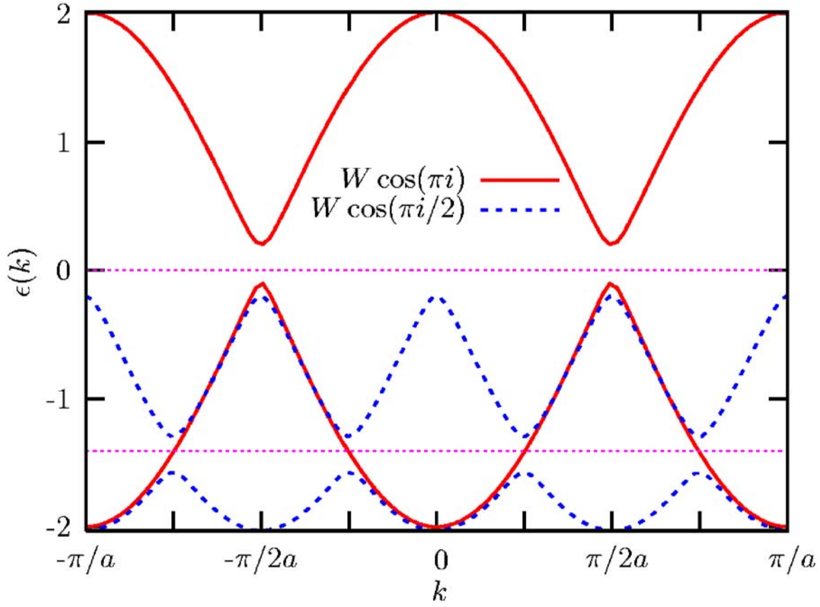
Peierls transition: 1D chain

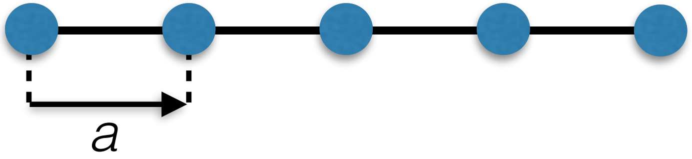
Instability at $|q| = 2k_F$

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

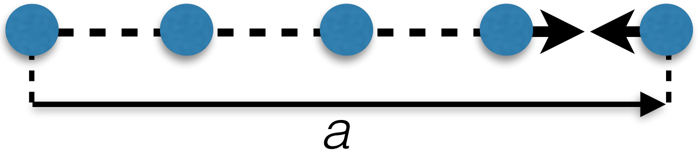
$$|k_F| = \frac{\pi}{4a} \quad |q| = \frac{\pi}{2a}$$







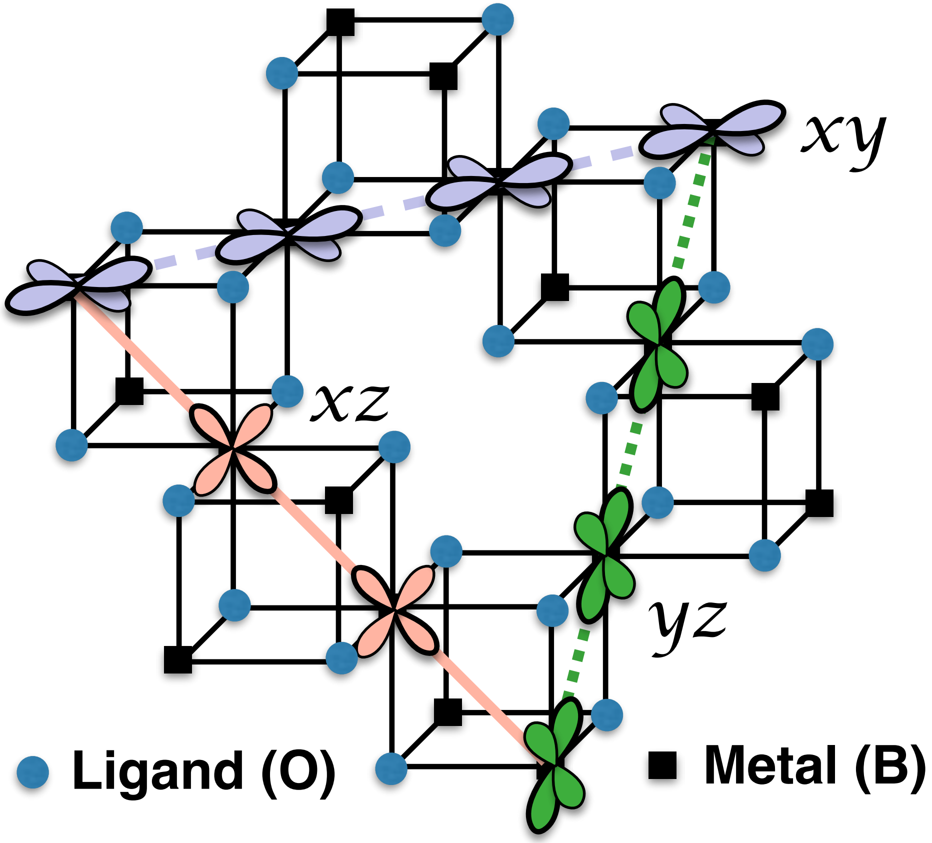
quadrupling of the u.c.!



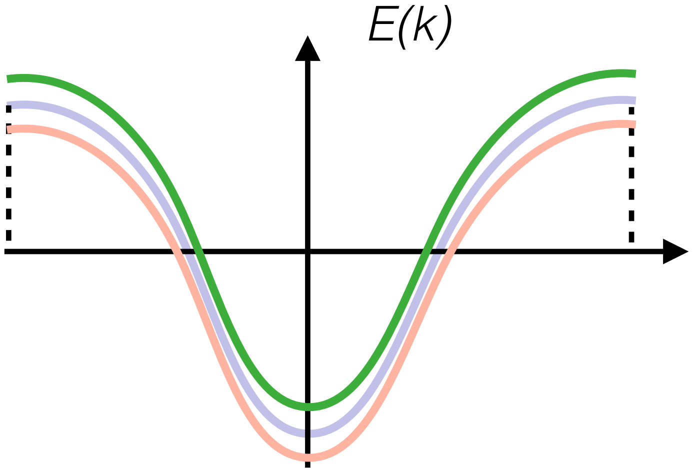
1. Effective reduction of dimensionality

1.2 “1D-zation” of electron spectrum

Spinels: AB_2O_4



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



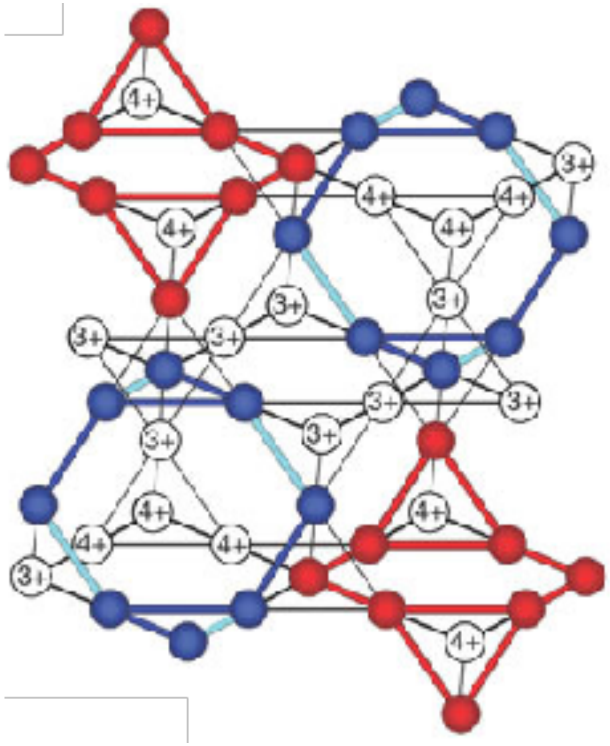
Natural formation of 1D bands due to orbitals…

1. Effective reduction of dimensionality

1.2 “1D-zation” of electron spectrum

CuIr$_2$S$_4$: 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

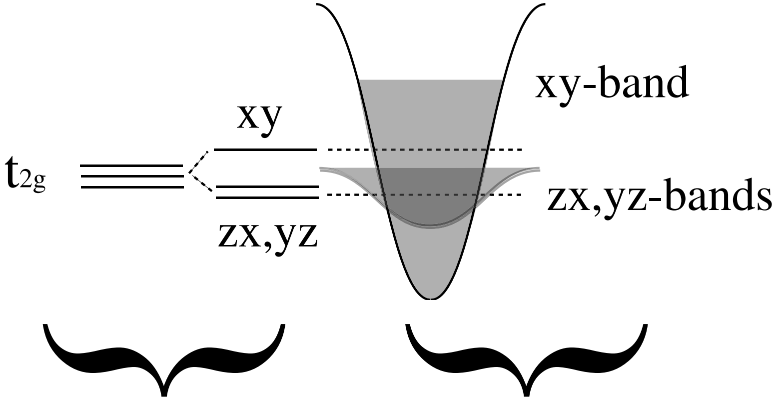
Radaelli et al., Nature 416, 155 (2002)

What is the reason for such complex distortions?

1. Effective reduction of dimensionality

1.2 “1D-zation” of electron spectrum

$CuIr_2S_4$: spinel

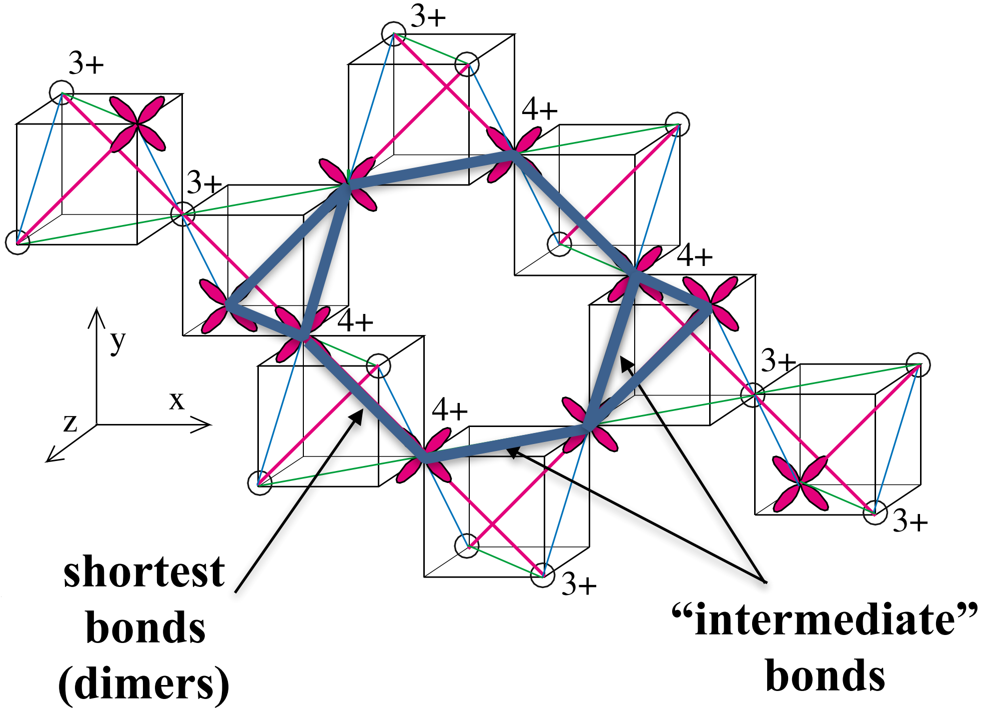


tetragonal elongation

xy-band is 3/4 filled

⇩

Tetramerization?



Khomskii & Mizokawa, PRL 94, 156402 (2005)

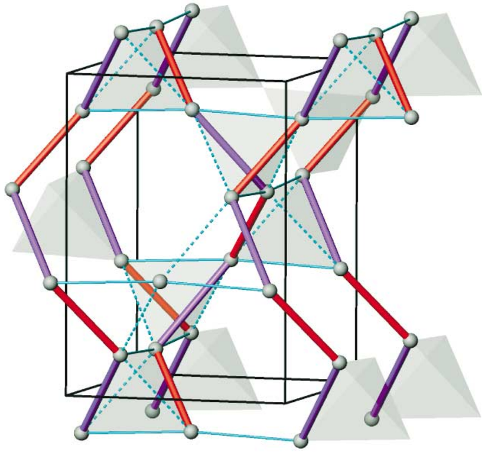
Orbitals reduce dimensionality: 3D → 0D

1. Effective reduction of dimensionality

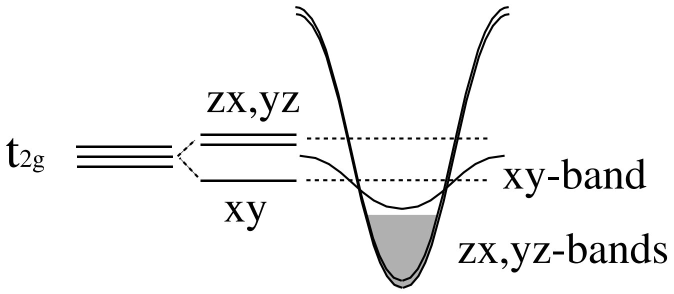
1.2 “1D-zation” of electron spectrum

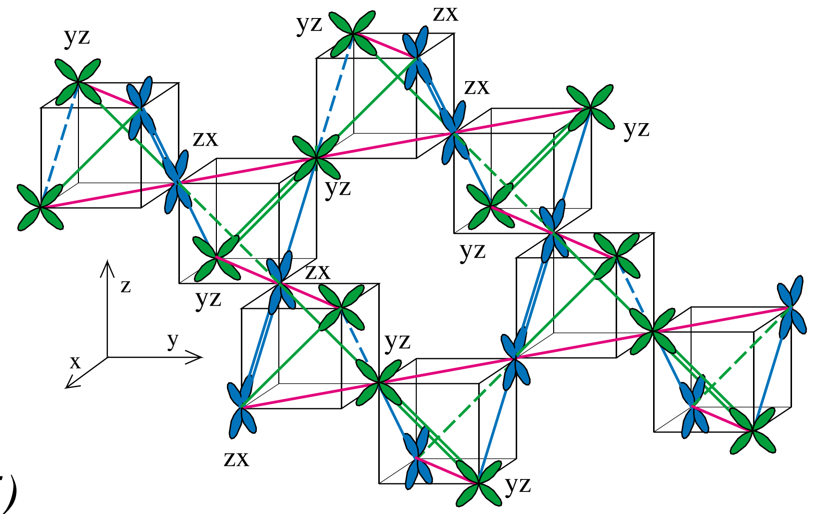
$MgTi_2O_4$: spinel

T<260 K:
Superstructure



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





Khomskii & Mizokawa, PRL 94, 156402 (2005)

Orbitals reduce dimensionality: 3D → 1D

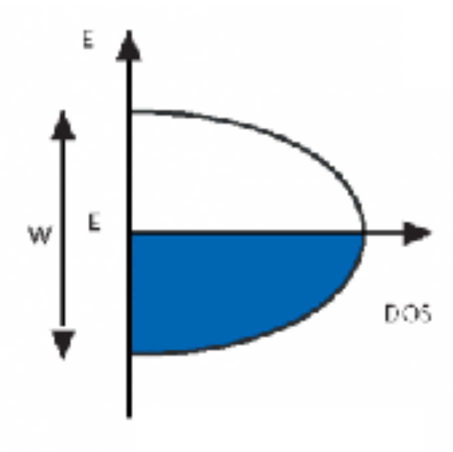
1. Effective reduction of dimensionality

1.3 Novel states near Mott transition “Molecules-in-solids”

Hubbard model: $$H = -t \sum_{\langle ij \rangle \sigma} c^\dagger_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

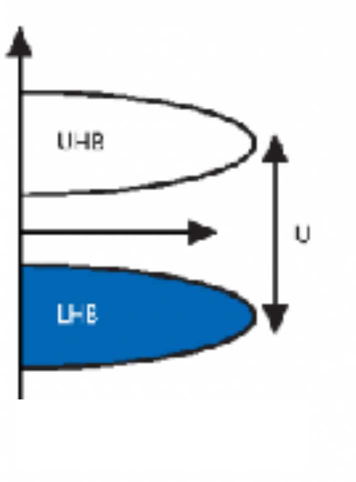
In solids:

$U/t \ll 1$



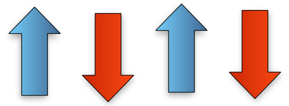
Metal

$U/t \gg 1$



Mott insulator

AFM Ground state

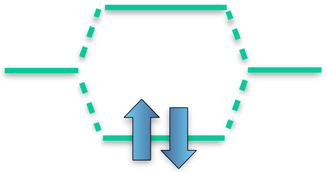


1. Effective reduction of dimensionality
1.3 “Molecules-in-solids”

Hubbard model: $$H = -t \sum_{\langle ij \rangle \sigma} c^\dagger_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

Molecules:

$U/t \ll 1$



$$|MO\rangle = \frac{1}{2} |(c^\dagger_{1\uparrow} + c^\dagger_{2\uparrow})(c^\dagger_{1\downarrow} + c^\dagger_{2\downarrow})\rangle$$

Molecular orbitals

↕

Metal

$U \sim t$

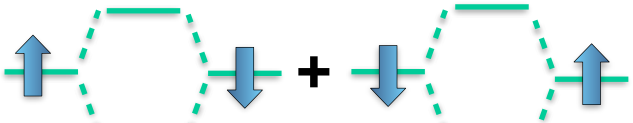
$$\Psi_{CF} = \frac{\sin\theta}{\sqrt{2}} \left(c^\dagger_{1\uparrow} c^\dagger_{2\downarrow} - c^\dagger_{1\downarrow} c^\dagger_{2\uparrow} \right) + \frac{\cos\theta}{\sqrt{2}} \left(c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} + c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} \right)$$

Coulson-Fisher

↕

?

$U/t \gg 1$



$$|HL\rangle = \frac{1}{\sqrt{2}} |c^\dagger_{1\uparrow} c^\dagger_{2\downarrow} - c^\dagger_{1\downarrow} c^\dagger_{2\uparrow}\rangle$$

Heitler-London

↕

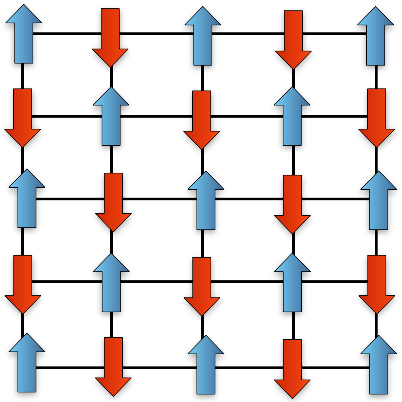
Insulator

Solids:

1. Effective reduction of dimensionality

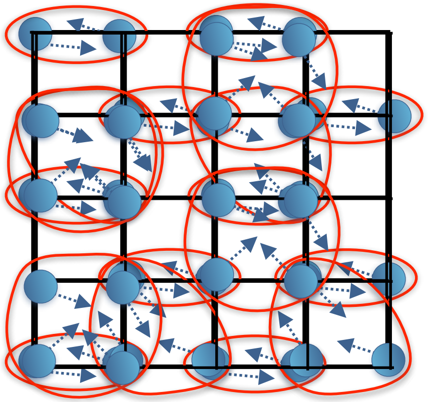
1.3 “Molecules-in-solids”

Insulator

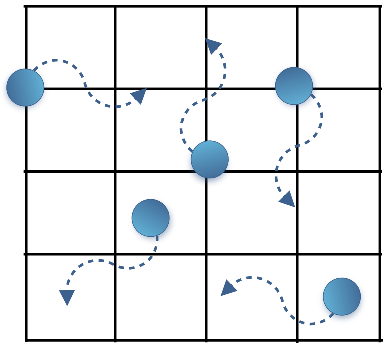


$U/t \gg 1$

Intermediate situation



Metal



$U/t \ll 1$

“Molecules-in-solids”: Metallic drops in an insulating media

Plenty of mechanisms of spontaneous formation of “molecules”:
Peierls effect, CDW instability, <u>orbital ordering</u>.

1. Effective reduction of dimensionality

1.3 “Molecules-in-solids”

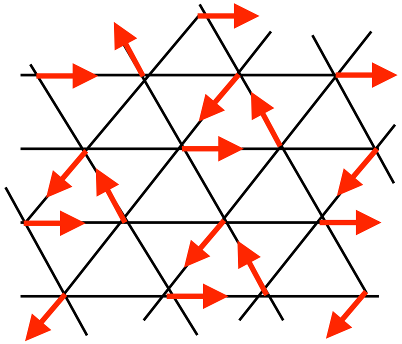
$LiCrO_2$ (Cr^{3+} d^3)

Exp: Insulator

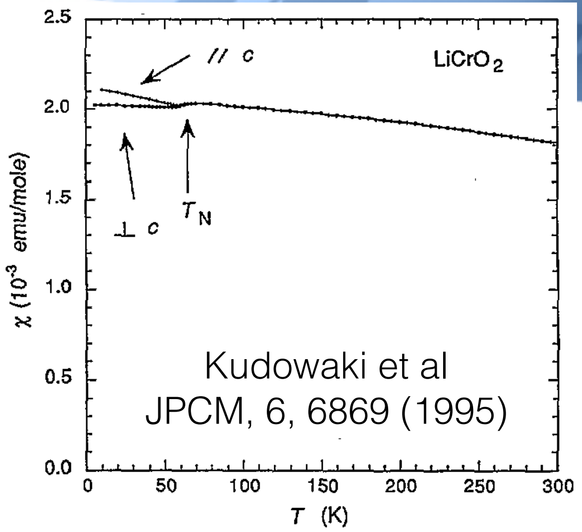
W~1 eV,   U~4 eV

U >> W

Mazin PRB 75, 094407 (2007)



Soubeyroux et al
PSS, 67, 633 (1981)

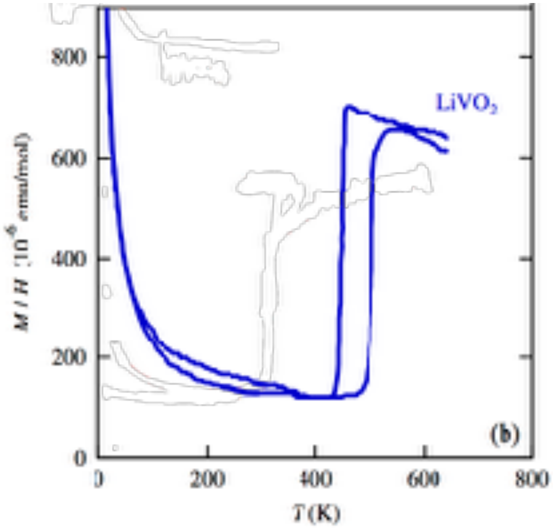


Kudowaki et al
JPCM, 6, 6869 (1995)

$LiVO_2$ (V^{3+} d^2)

Exp: Insulator

Kobayashi et al,
Mater. Res. Bull. 4, 95 (1969).



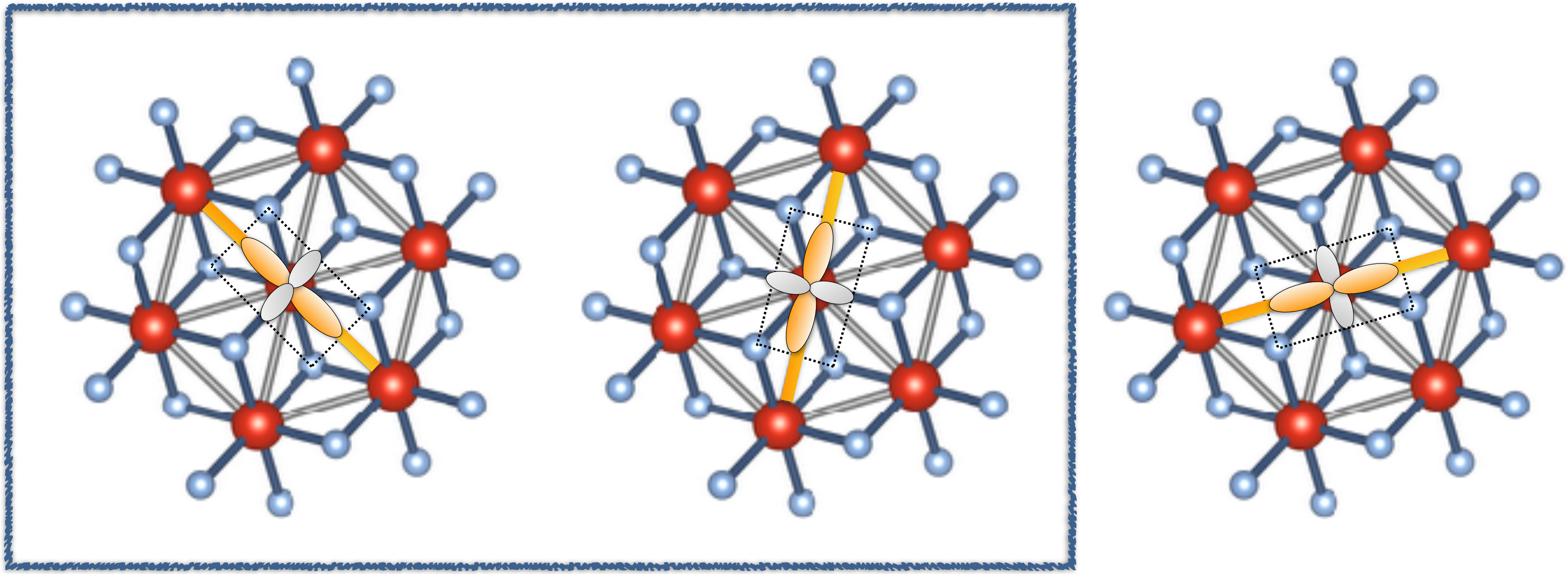
What is the difference between $LiCrO_2$ and $LiVO_2$?

Active orbital degrees of freedom!

1. Effective reduction of dimensionality

1.3 “Molecules-in-solids”

t_{2g} orbitals on triangular lattice



(1) **Configuration d^3 (S=3/2)**- leaves frustration

Configuration d^2 (S=1) - relieves frustration: makes 2 out of 3 Me-Me bonds inequivalent

(2) **One of the lobes takes part in direct Me-Me exchange**

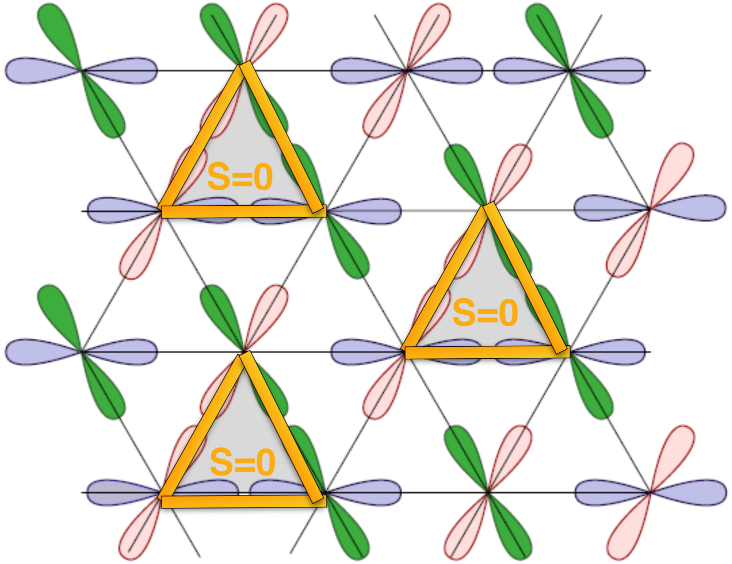
1. Effective reduction of dimensionality

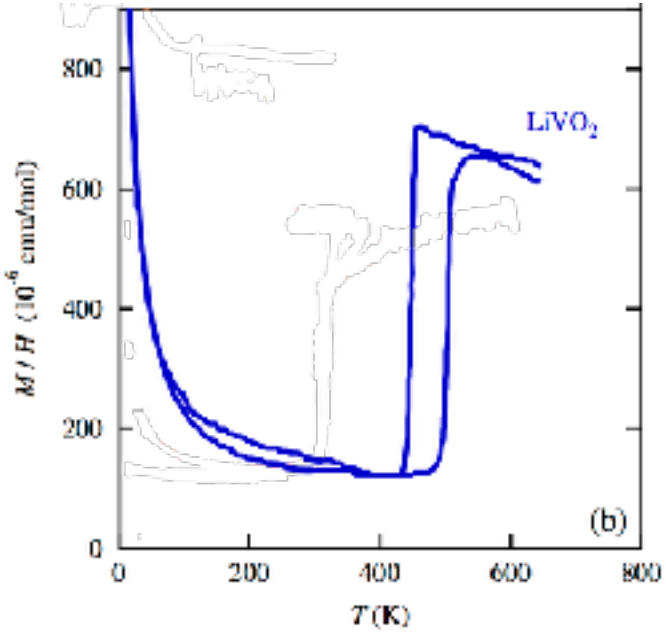
1.3 “Molecules-in-solids”

LiVO$_2$

Orbitally induced trimerization → **Spin gap**

H. F. Pen, J. van den Brink, D. I. Khomskii, G. A. Sawatzky,
Phys. Rev. Lett. 78, 1323 (1997).





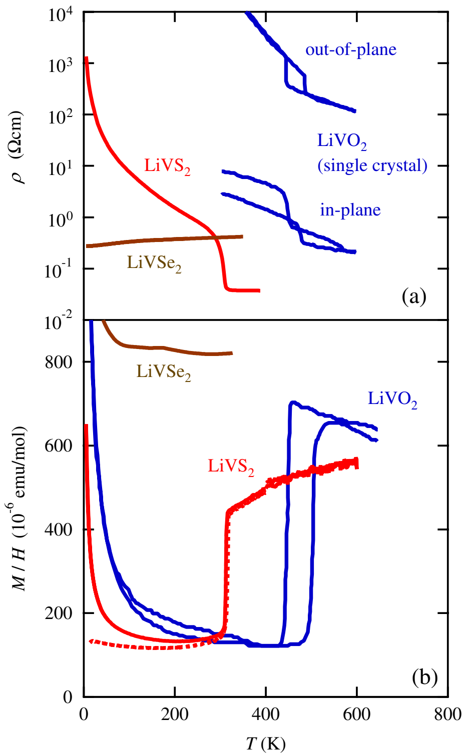
“Molecules” in solids!
(Valence bond solid)

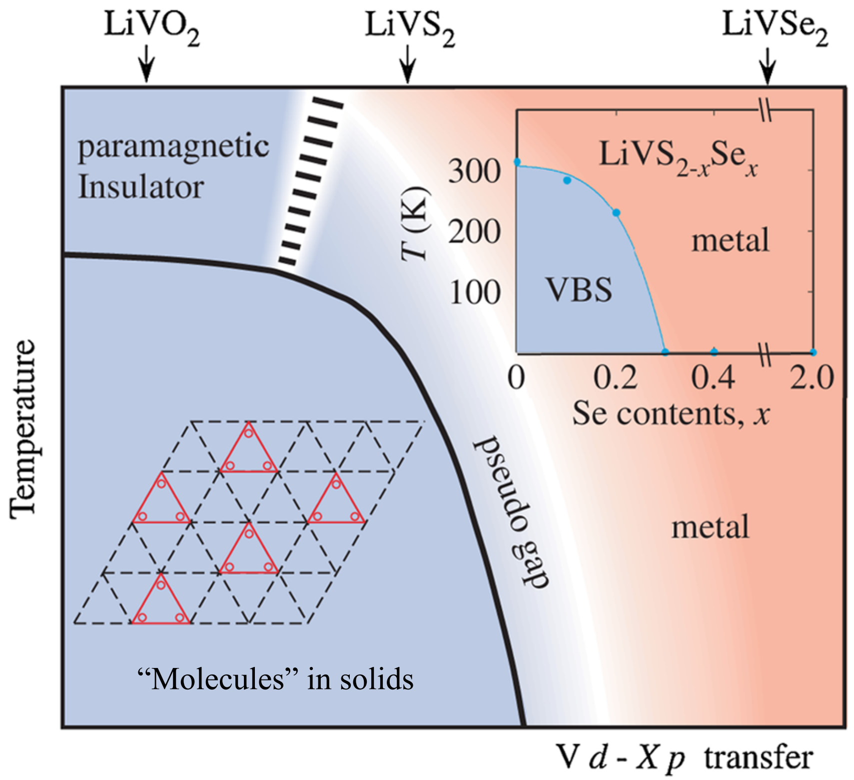
Trimerization: J. Solid State Chem. 72, 234 (1988).

1. Effective reduction of dimensionality

1.3 “Molecules-in-solids”

LiVL_2 L: $O \to S \to Se$ increase metallization!





Phys. Rev. Lett. 103, 146405 (2009)

“Molecules” do not appear, when we are far from the insulating regime

Orbitals reduce dimensionality: 2D → 0D

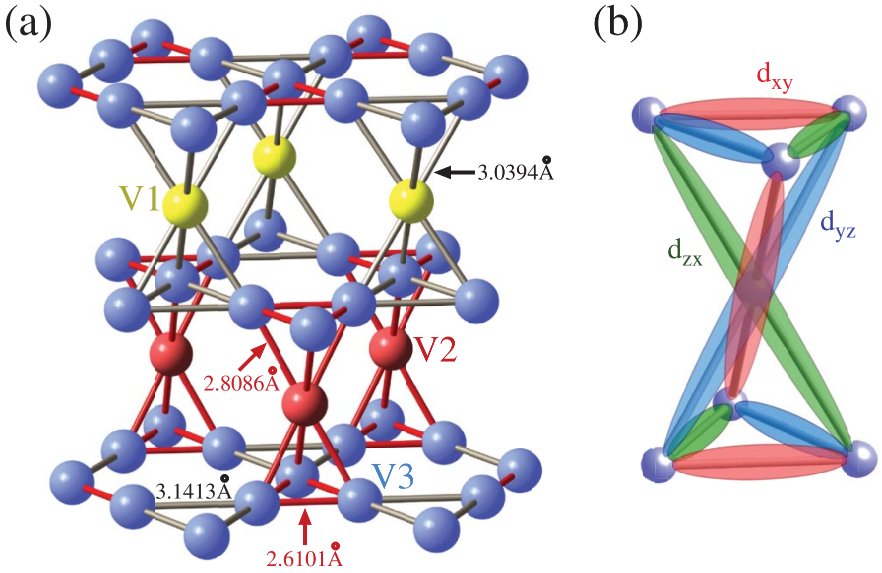
1. Effective reduction of dimensionality

1.3 “Molecules-in-solids”

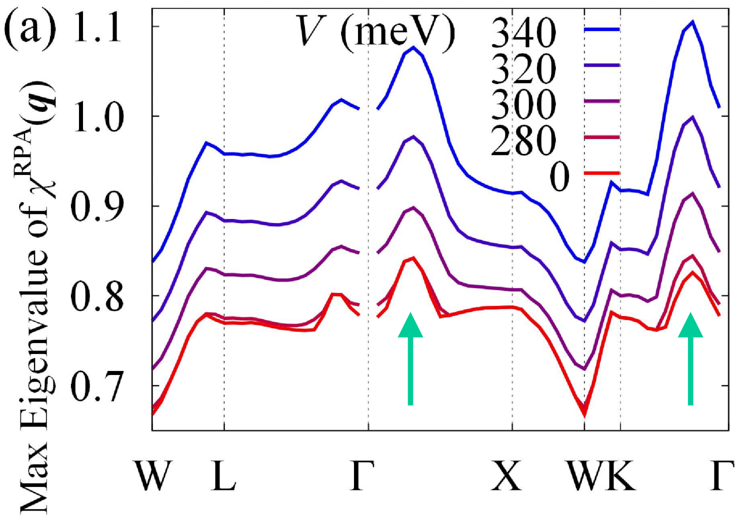
Spinel $\mathbf{AlV_2O_4}$

Clusters: Heptamers

Mechanism:
Peierls-like transition



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



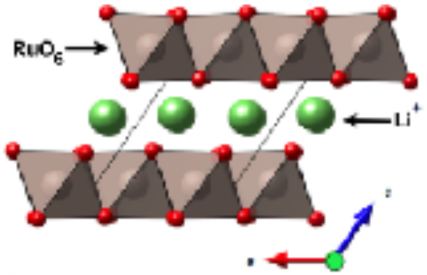
A. Uehara, H. Shinaoka, and Y. Motome,
Phys. Rev. B 92, 195150 (2015).

Orbitals reduce dimensionality: 3D → 0D

1. Effective reduction of dimensionality

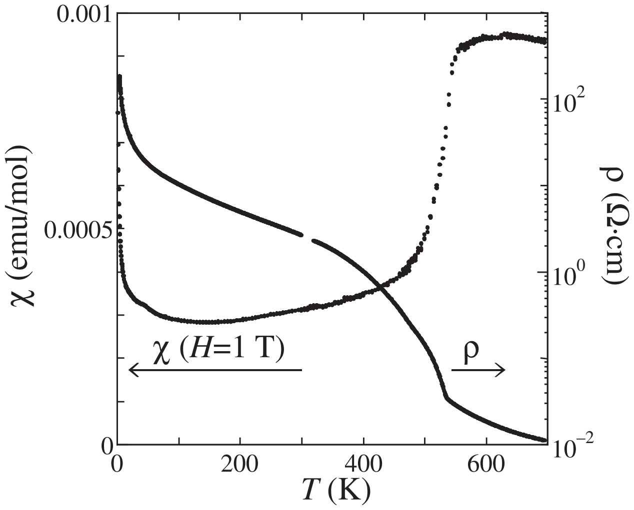
1.3 “Molecules-in-solids”

Li_2RuO_3



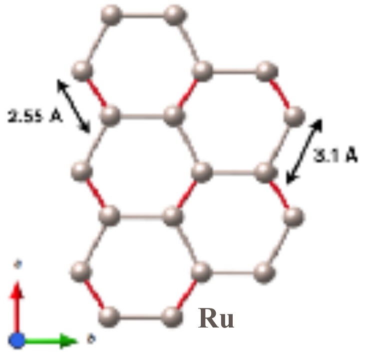
Ru^{4+}: $4d^4$ *(S=1)*

“Metal-insulator-like” (?) and, magnetic transitions at 540K

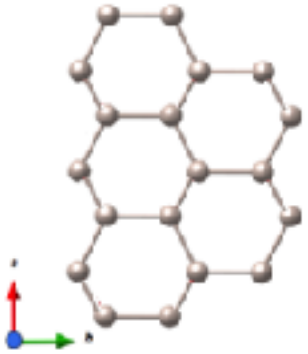


X-ray powder diffraction:
Structural transition (?)

T < 540 K



T > 540 K



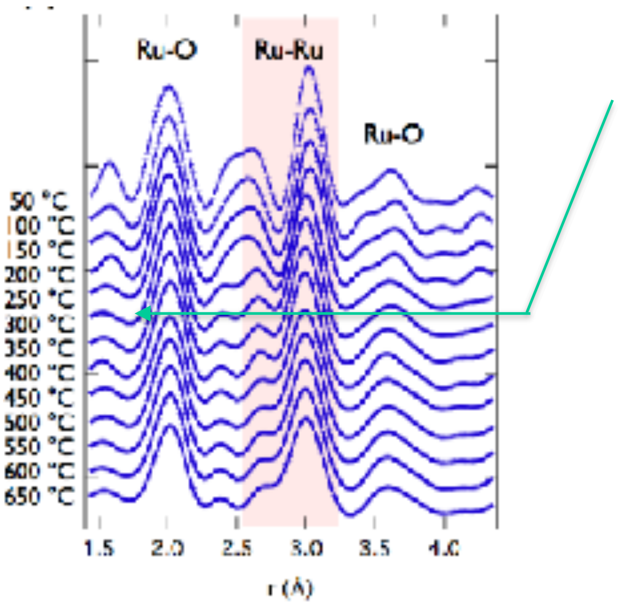
Formation of dimers and that’s it?

Y. Miura et al., JPSJ 76, 033705 (2007)

1. Effective reduction of dimensionality

1.3 “Molecules-in-solids”

Li_2RuO_3: New twist of the story



<u>X-Ray diffraction</u>: dimers exist $T < T_s$=540 K

Y. Miura, Y. Yasui, M. Sato, N. Igawa, K. Kakurai,
J. Phys. Soc. Japan 76, 033705 (2007)

<u>X-Ray diffraction, pair distribution function analysis</u>: dimers exist even for $T > T_s$=540 K

S. Kimber, I. Mazin, J. Shen, H. Jeschke, S. Streltsov,
D. Argyriou, R. Valenti, D. Khomskii,
PRB 89, 081408 (2014)

Li_2RuO_3

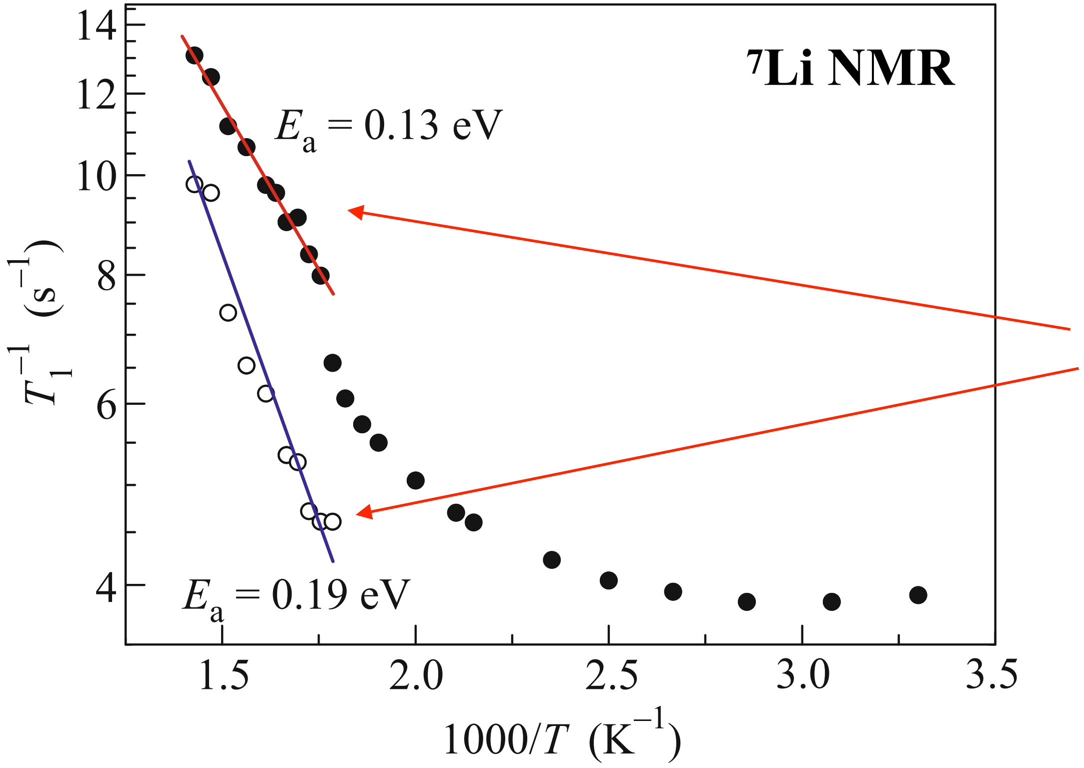
T < 540 K: Valence bond solid (dimers are ordered)

T > 540 K: Valence bond liquid (dimers flow over the lattice)

1. Effective reduction of dimensionality

1.3 "Molecules-in-solids"

Li_2RuO_3: any other experimental evidences of valence bond liquid besides PDF?



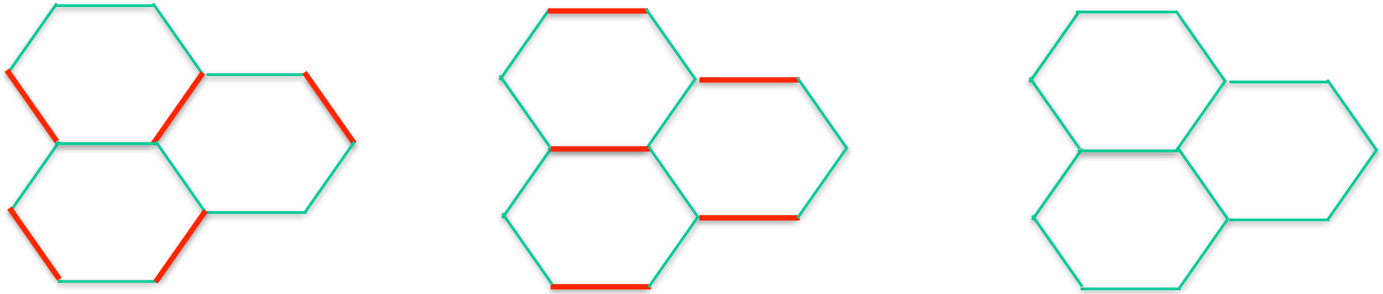
Activation processes in the HT phase!

Y. Arapova, A. Buzlukov, A. Germov, K. Mikhalev, T. Tan, J. Park, S. Streltsov, JETP Lett. 105, 375 (2017).

1. Effective reduction of dimensionality

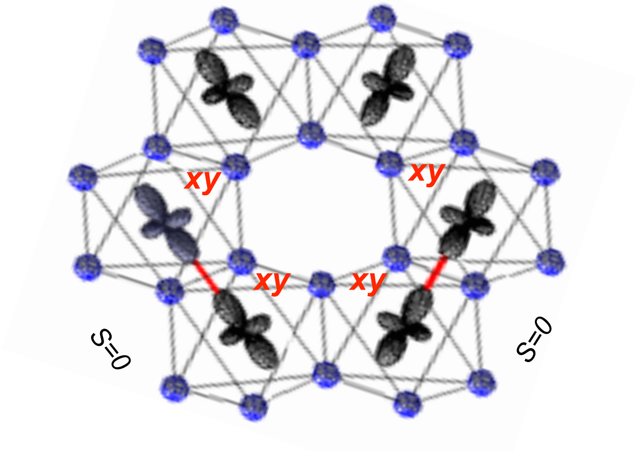
1.3 “Molecules-in-solids”

Valence bond liquid in Li_2RuO_3: what theory says



	Armchair	Parallel dimers	Uniform
NM GGA total energy (meV/f.u.)	**0**	$T_s \sim$ **500 K**	$T_s \ll$ **1700 K**

PRB 89, 081408 (2014)



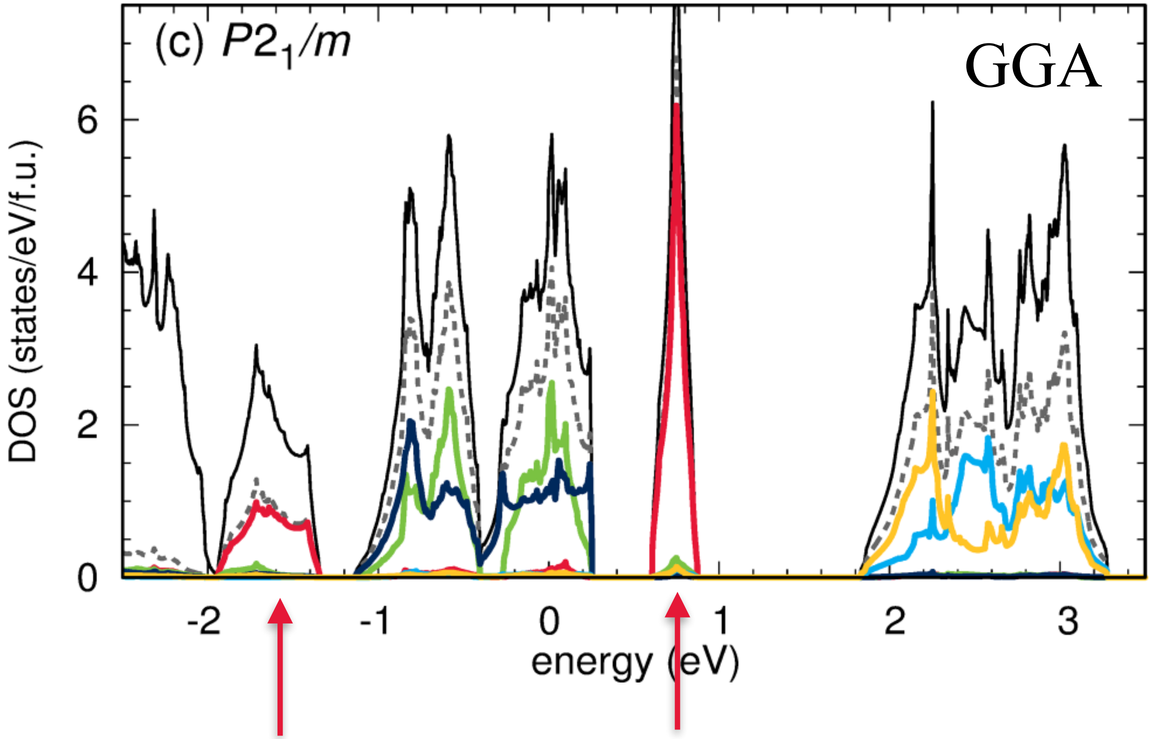
Uniform metallic solution is highly unfavourable!

We gain a lot of energy by the direct xy/xy exchange

1. Effective reduction of dimensionality

1.3 “Molecules-in-solids”

DFT: Formation of molecular orbitals in dimers in Li_2RuO_3 significantly reduces total energy



Bonding xy-xy

Antibonding xy-xy

1. Effective reduction of dimensionality.
“Molecules-in-solids”

Examples of “Molecules-in-solids”

$LiVO_2$: formation of trimers

AlV_2O_4: formation of heptameters

Li_2RuO_3: formation of very stable dimers

Can we have these “Molecules” without structurally isolated clusters?

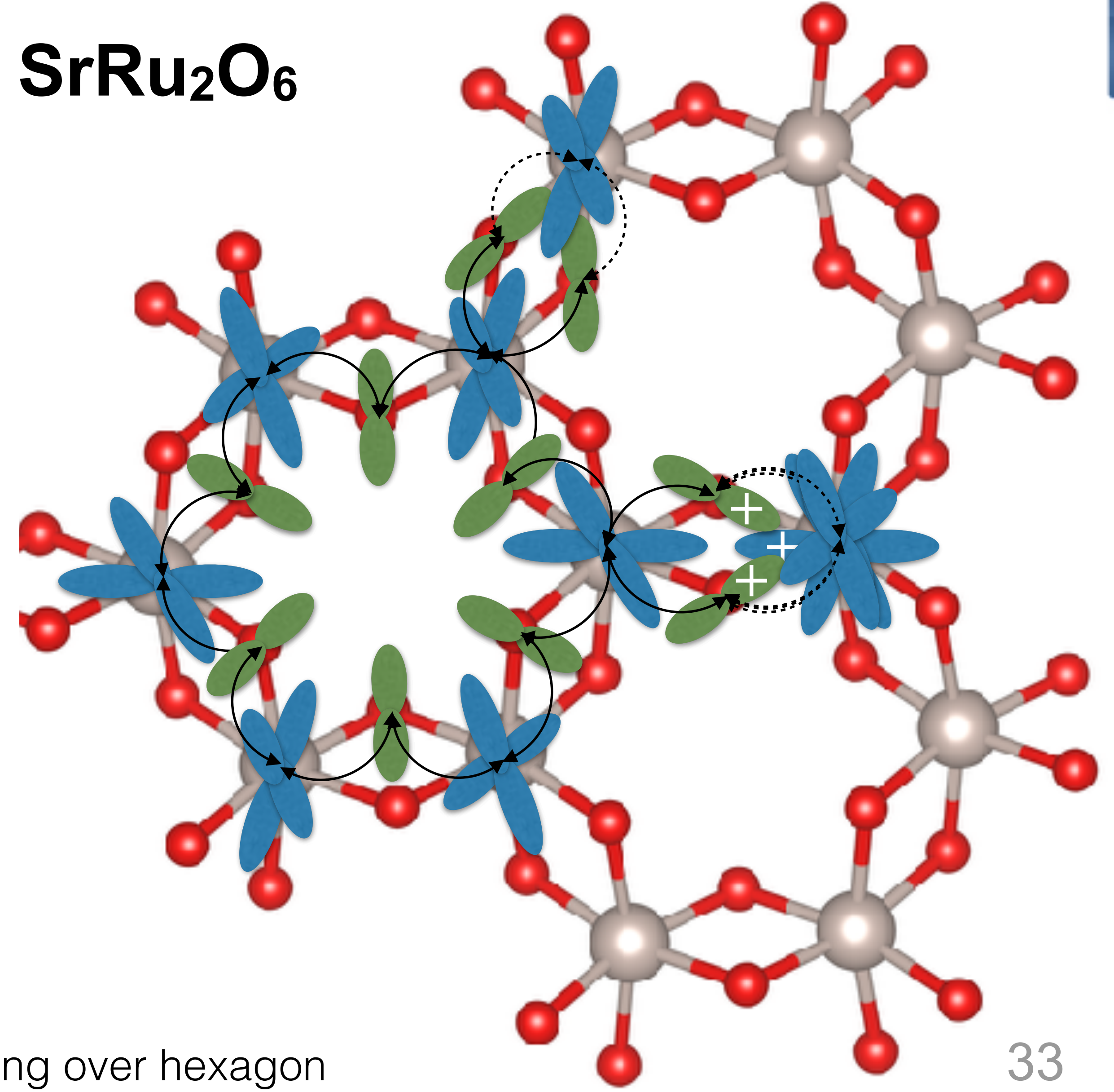
1. Effective reduction of dimensionality

1.3 “Molecules-in-solids”

Let’s consider

1) Honeycomb lattice
2) Transition metals: t_{2g} ions
3) Hopping only via ligand p-orbitals

SrRu$_2$O$_6$



Molecules = TM$_6$ hexagons
(no clusters; all TM-TM bonds are the same)

Twofold nature of electrons:

(1) **electrons are confined** in hexagons

(2) **electrons are delocalized** moving over hexagon

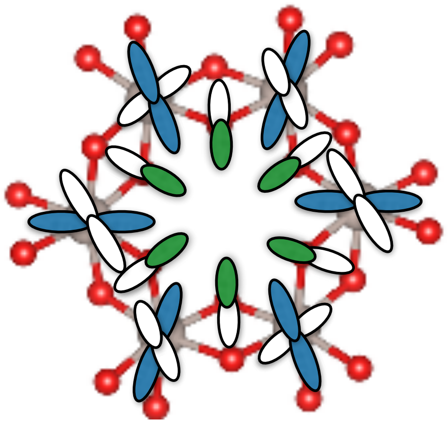
1. Effective reduction of dimensionality

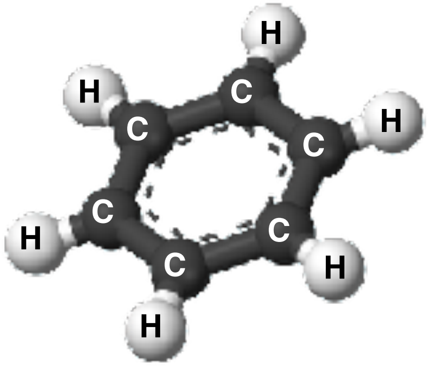
1.3 “Molecules-in-solids”

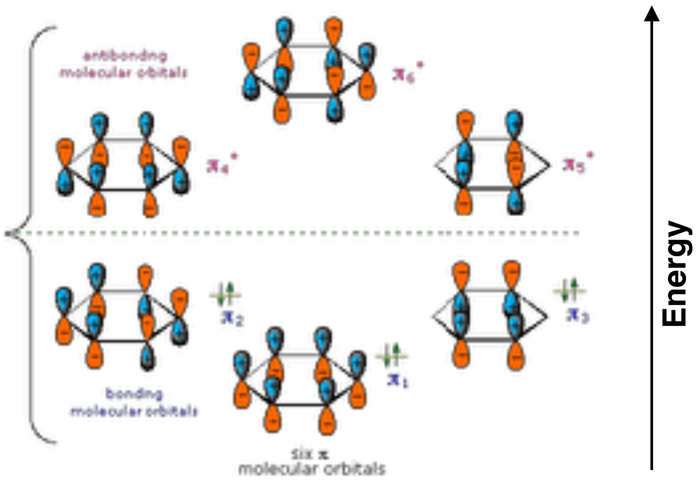
SrRu$_2$O$_6$: (4d) electronic analog of benzene!

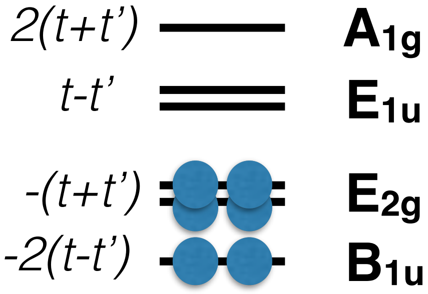
SrRu$_2$O$_6$: Ru - 4d^3
six d-electons/u.c.

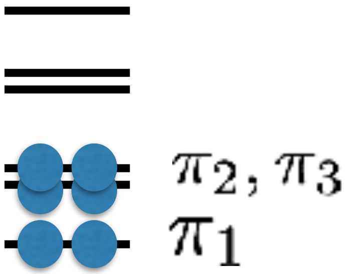
Benzene C$_6$H$_6$: three sp^2-electrons/C
six p-electons/u.c.











1. Effective reduction of dimensionality

1.3 “Molecules-in-solids”

Examples: **Na_2IrO_3, Li_2IrO_3, Na_2RuO_3**

PRL 109, 197201 (2012)

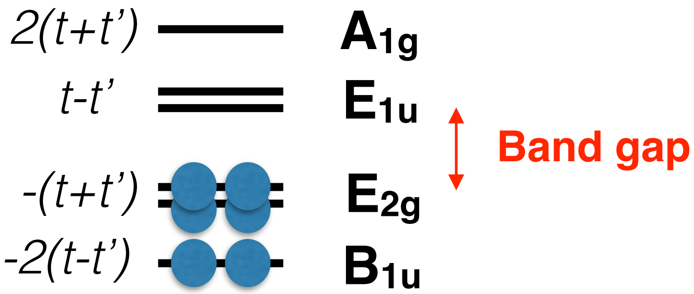
PRB 90, 161110 (2014)

Strong direct d-d hopping and spin-orbit coupling spoils MOs on hexagons

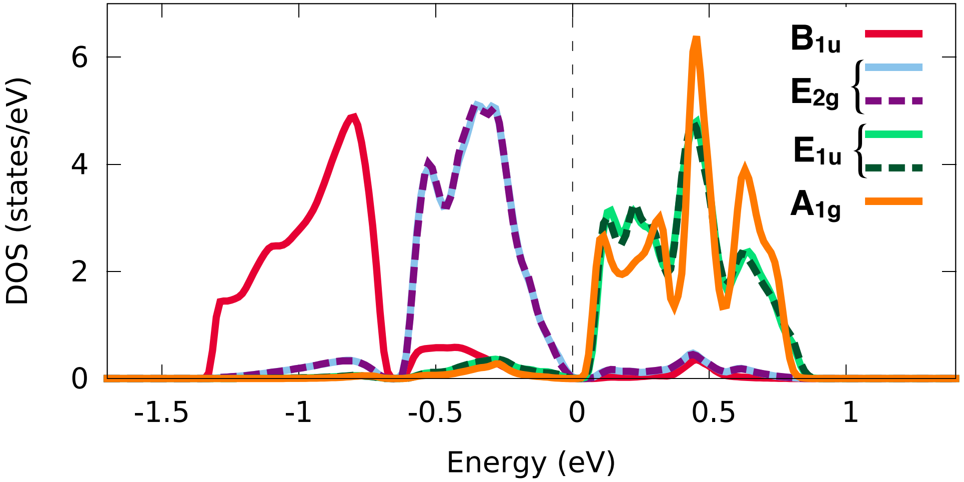
$SrRu_2O_6$, $AgRuO_3$ perfect hexagonal lattice (no dimerization!) with MO!

Isolate Ru_6 cluster:

2 Ru in the u.c. (6 electrons)



GGA calculation for $SrRu_2O_6$:

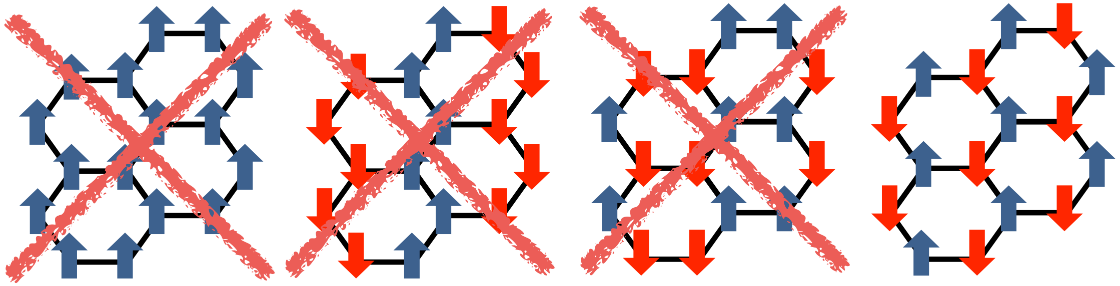


S.S., I. Mazin, K. Foyevtseva PRB 92, 134408 (2015)

1. Effective reduction of dimensionality

1.3 “Molecules-in-solids”

Anomalous properties, which MOs bring: Magnetism

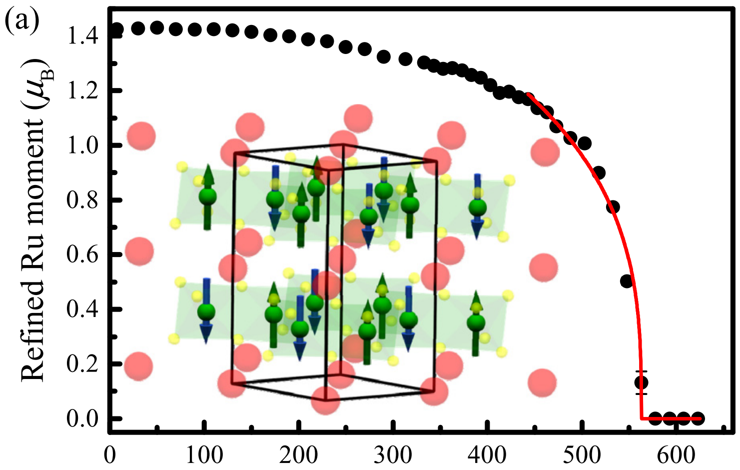


$SrRu_2O_6$ is an non-Heisenberg magnet!

Is this related with unusually high T_N for layered material?

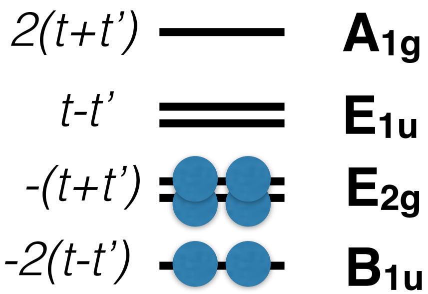
T_N = 560 K!

C. I. Hiley et al
PRB 92, 104413 (2015)



1. Effective reduction of dimensionality

1.3 “Molecules-in-solids”



Selection rule: parity

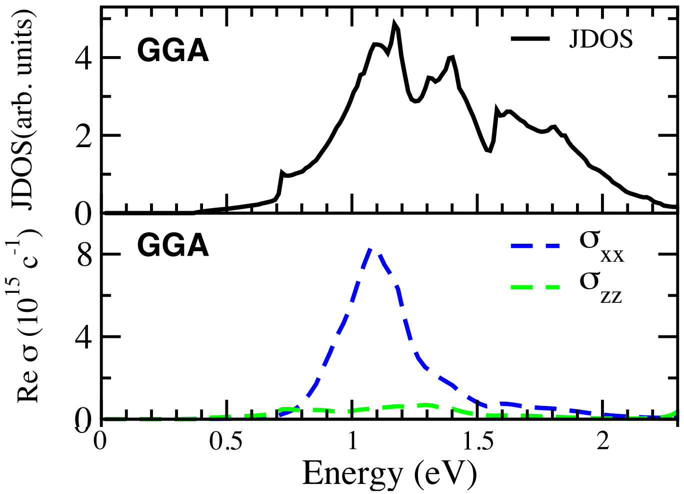
$$\cancel{\begin{matrix} B_{1u} \to E_{1u} \\ E_{2g} \to A_{1g} \end{matrix}}$$

p^x and p^y components of momentum operator transform according to E_{1u}

Selection rule: symmetry (*D_{6h}*)

$$\begin{aligned} B_{1u} \times A_{1g} &= B_{1u} \\ B_{1u} \times E_{2g} &= E_{1u} \\ E_{2g} \times E_{1u} &= B_{1u} + B_{2u} + E_{1u} \\ E_{1u} \times A_{1g} &= E_{1u} \end{aligned}$$

$$\begin{gathered} \cancel{B_{1u} \to A_{1g}} \\ \cancel{B_{1u} \to E_{2g}} \\ E_{2g} \to E_{1u} \\ \cancel{E_{1u} \to A_{1g}} \end{gathered}$$



Joint density of states (JDOS)

$$J(\omega) = \sum_{c,v} \int \delta(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \hbar\omega) d\mathbf{k}$$

Real part of optical conductivity

$$\mathrm{Im}\ \varepsilon_{\alpha\beta}(\omega) = \frac{e^2}{\pi m^2 \omega^2} \sum_{c,v} \int \langle c, \mathbf{k} | p^\alpha | v, \mathbf{k} \rangle \langle v, \mathbf{k} | p^\beta | c, \mathbf{k} \rangle \times \delta(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \hbar\omega) d\mathbf{k}. \qquad (5)$$

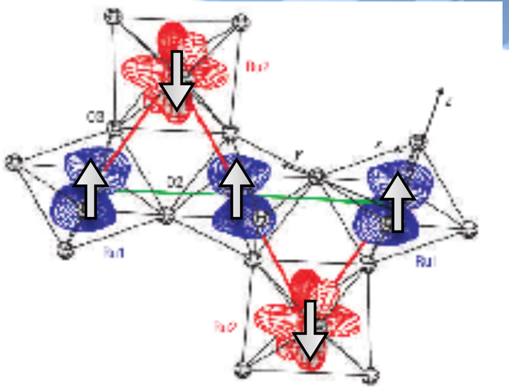
Formation of MOs suppresses optical transitions

*Z. Pchelkina, S.S., I. Mazin Phys. Rev. B **94**, 205148 (2016).*

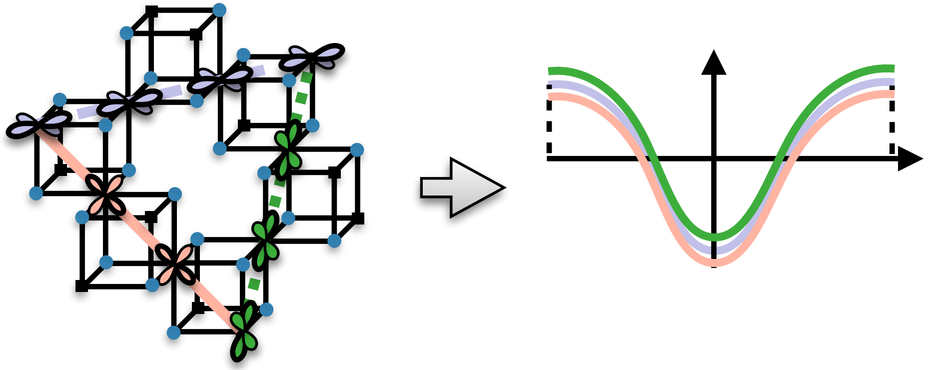
1. Effective reduction of dimensionality

Take-home messages

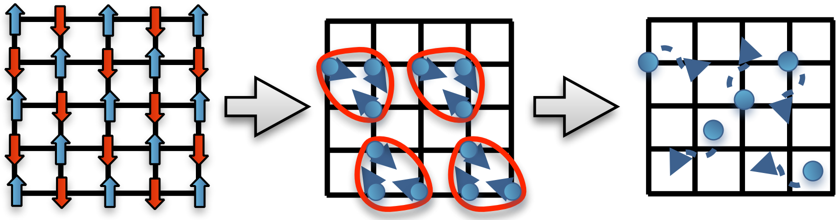
1. Orbitals may **reduce dimensionality** of a magnetic subsystem



2. Orbitals may **induce “1D-zation”** of electronic spectrum



3. There may appear an intermediate state - **“Molecules-in-solids”** on a verge of metal-insulator transition



Orbital-selective effects

- Orbital-selective Mott transition
- Orbital-selective behavior and (partial) suppression of magnetism

2. Orbital-selective effects
Orbital-selective Mott (OSM) transition

Starting point: Anisimov et al., Eur. Phys. J. B 25, 191 (2002)

see also Gorelov et al., PRL 104, 225401 (2010)

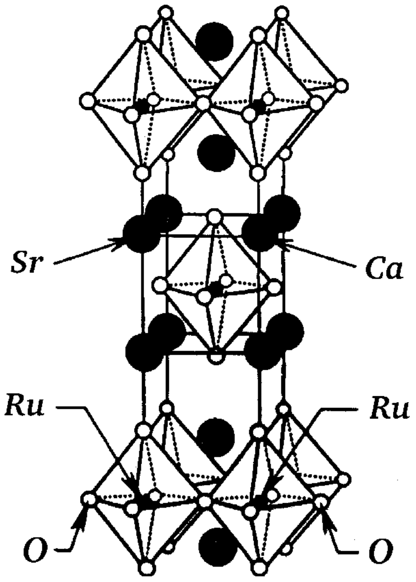


Fig. 1. Basic crystal structure of $Ca_{2-x}Sr_xRuO_4$.

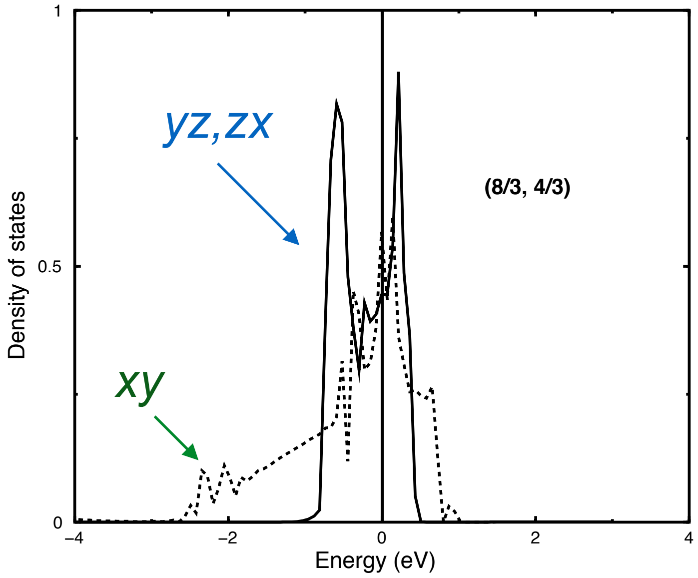


Fig. 3. Density of t_{2g} states for Sr_2RuO_4 obtained from LDA calculation. The solid line is the DOS for the (xz, yz)-orbitals and the dashed line for the xy-orbital. $(n_{(yz,zx)}, n_{xy})$ indicates

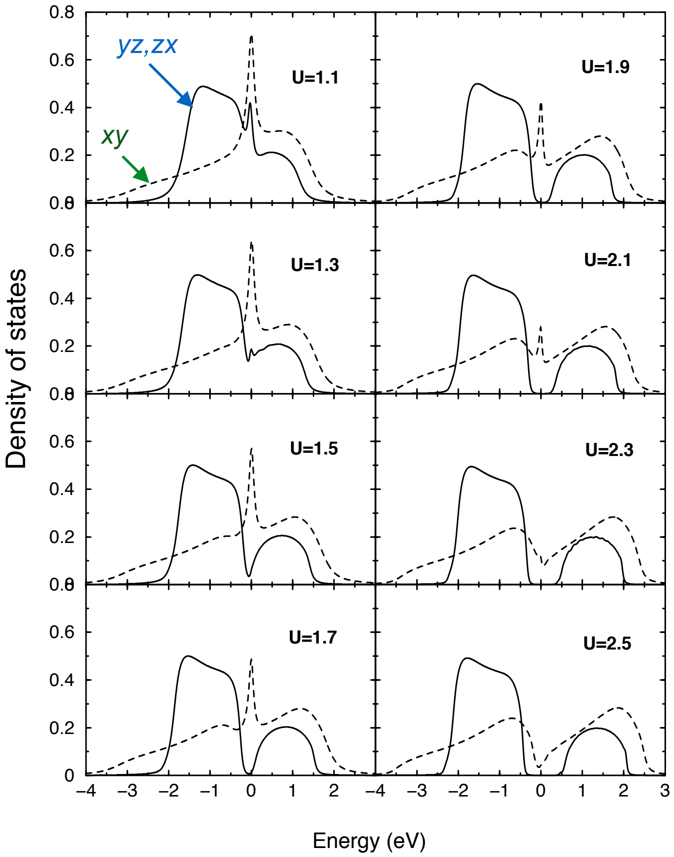


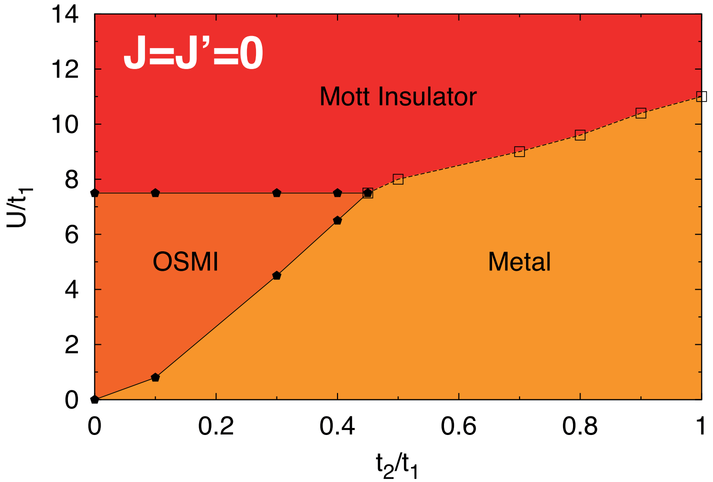
Fig. 6. Results of LDA+DMFT(NCA) calculations obtained within LDA DOS for Sr_2RuO_4. The solid line is the DOS for xz, yz-orbitals and the dashed line for (xy)-orbital. At $U =$

Geometry: layered structure, common corner sharing

Orbital-selectivity: Metal-insulator transition occurs first for the *xz/yz* orbitals (U_c=1.5 eV) and only then for the *xy* orbitals (U_c=2.5 eV)

2. Orbital-selective effects
Orbital-selective Mott (OSM) transition

2D Square lattice, two orbitals, half-filling (2 electrons/site)

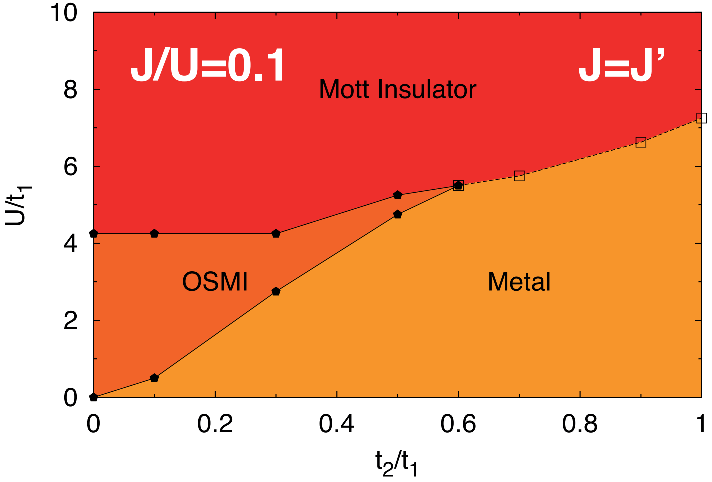


$$\mathcal{H} = \mathcal{H}_{\text{kin}} + \mathcal{H}_{\text{int}}$$

α - orbital index

$$\mathcal{H}_{\text{kin}} = -\sum_{\langle i,j\rangle,\alpha,\sigma} t_\alpha c^\dagger_{i,\alpha,\sigma} c_{j,\alpha,\sigma} + \text{h.c.},$$

$$\mathcal{H}_{\text{int}} = U\sum_{i,\alpha} n_{i,\alpha,\uparrow} n_{i,\alpha,\downarrow} + U' \sum_{i,\sigma,\sigma'} n_{i,1,\sigma} n_{i,2,\sigma'}$$
$$- J \sum_{i,\sigma,\sigma'} c^\dagger_{i,1,\sigma} c_{i,1,\sigma'} c^\dagger_{i,2,\sigma'} c_{i,2,\sigma} - J' \sum_i (c^\dagger_{i,1,\uparrow} c^\dagger_{i,1,\downarrow} c_{i,2,\uparrow} c_{i,2,\downarrow} + \text{h.c.})$$



Effect of orbital mixing ($t_{mm'} \neq 0$)

(1) Destabilization of the OSM state

Effect of the Hund's coupling:

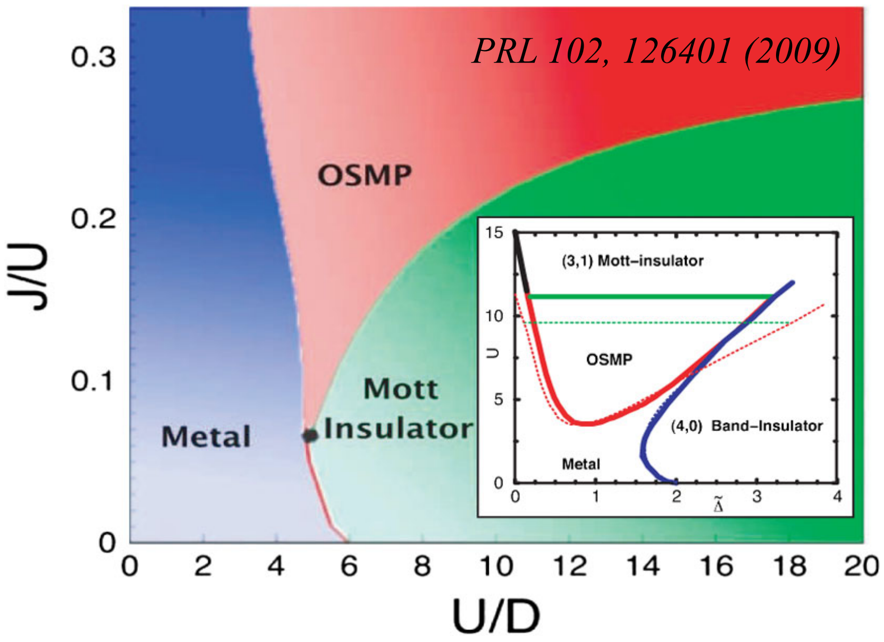
(1) Stabilization of Mott phase
(2) Stabilization of the OSM state

Tocchio et al., JPCM 28, 105602 (2016)

2. Orbital-selective effects

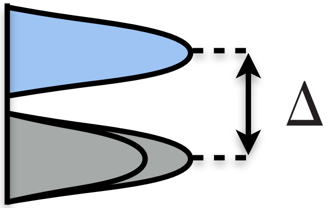
Orbital-selective Mott (OSM) transition

OSM transition is possible even in the case of the same bandwidths

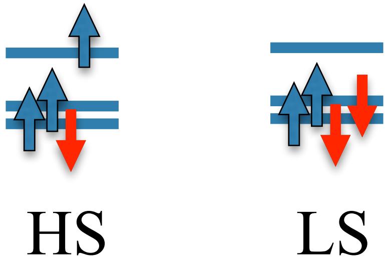

PRL 102, 126401 (2009)

$$H = -t \sum_{\langle ij\rangle, m\sigma} (d^\dagger_{im\sigma} d_{jm\sigma} + \text{H.c.}) + \sum_{i,m\sigma} \varepsilon_m d^\dagger_{im\sigma} d_{im\sigma}$$
$$+ U \sum_{i,m} n_{im\uparrow} n_{im\downarrow} + \left(U' - \frac{J}{2}\right) \sum_{i,m>m'} n_{im} n_{im'}$$
$$- J \sum_{i,m>m'} [2\mathbf{S}_{im} \cdot \mathbf{S}_{im'} + (d^\dagger_{im\uparrow} d^\dagger_{im\downarrow} d_{im'\uparrow} d_{im'\downarrow} + \text{H.c.})].$$

3 Band model with
crystal-field splitting
(4 electrons/site)



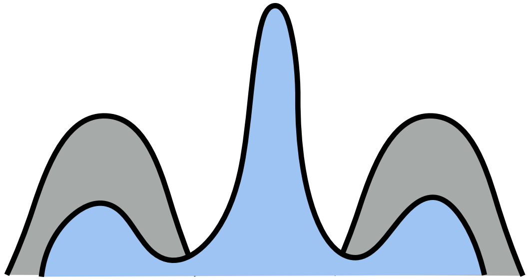
With J we increase energy difference between high-spin and low-spin configurations (and suppress orbital fluctuations)



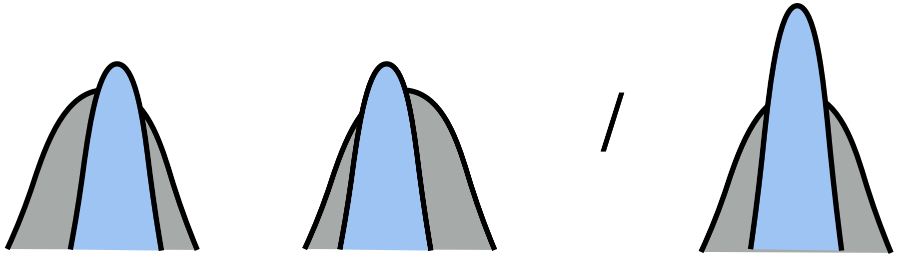
2. Orbital-selective effects

Orbital-selective Mott (OSM) transition

Orbital-selective Mott state



Mott state / Metal



(1) Makes orbitals different

Crystal-field splitting

(2) Suppress orbital fluctuations

J_H suppresses orbital fluctuations

(1) Makes orbitals "the same"

Crystal-field splitting

(2) Mixing orbitals

Typical for real materials

$t_{mm',ij}c^{\dagger}_{im\sigma}c_{jm\sigma}$ with $m \neq m'$

2. Orbital-selective effects
Orbital-selective Mott (OSM) transition

Double exchange is a natural realization of the orbital-selectivity

Let's consider (1) metallic system;
(2) noninteger number of electrons per site;
(3) there are two types carriers: itinerant and localized.

AFM **FM**

Itinerant electrons

Localized electrons

Examples:

CrO$_2$, CMR manganates etc.

No energy gain due to hoppings!

$$\delta E_{DE} \sim -Wx$$

Proposed:

C. Zener on examples of Mn-Mn dimer

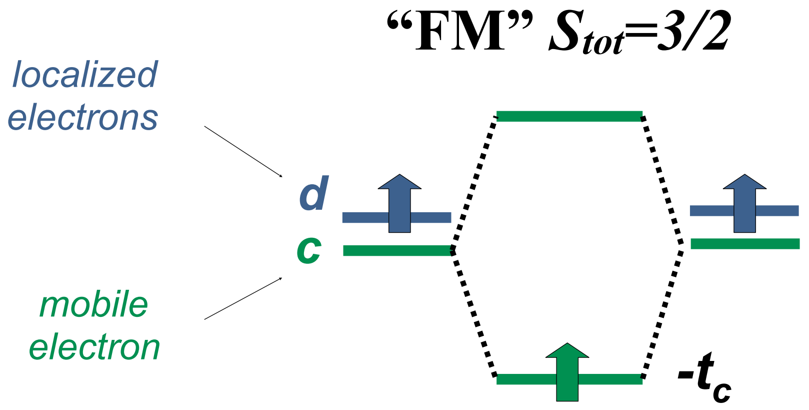
C. Zener, Phys. Rev. 82, 403 (1951)

2. Orbital-selective effects

Orbital-selective behavior and suppression of magnetism

E.g. 1.5 electron per site

Double exchange in case of an <u>isolated dimer</u>



Maximum gain in Hund's energy, J_H

For an isolated dimer: "double exchange" = maximum S_{tot} state

Important ingredients:

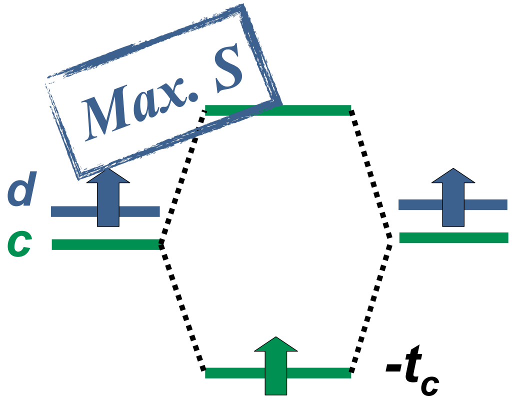
- two sets of orbitals - localized "***d*** " and molecular "***c***"
- $J_H \to \infty$

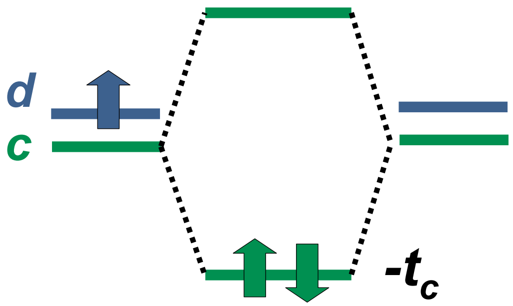
2. Orbital-selective effects

Orbital-selective behavior and suppression of magnetism

Isolated dimer

(e.g. 1.5 e/site)





“Double exchange”

“Molecular-Orbital state”

$S_{tot}=3/2$

3d transition metal oxides

Competition

$\xcancel{J_H \to \infty}$

$S_{tot}=1/2$

4d-5d transition metal oxides

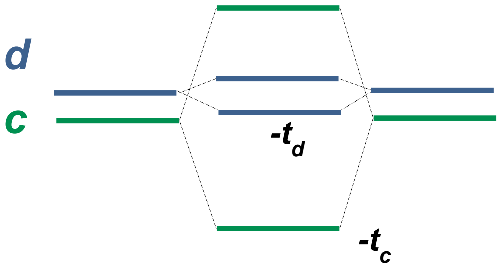
$$E_{DE} = -t_c \underline{- J_H}$$

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

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

2. Orbital-selective effects
Orbital-selective behavior and suppression of magnetism

Exact diag. (T=0) for a dimer

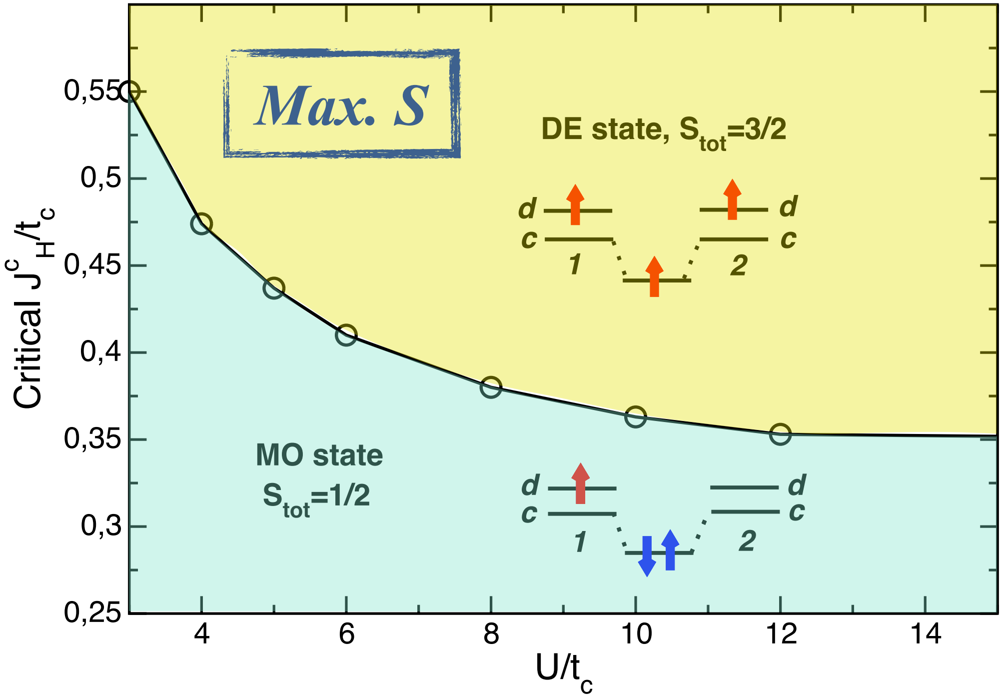


Dimer: 2 orbitals/site;
1.5 electrons/site

Model: $H = H_0 + H_U$

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

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

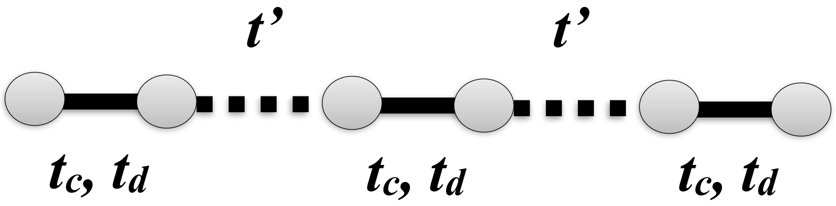


Transition from molecular-orbital to double exchange regime is discontinues

2. Orbital-selective effects

Orbital-selective behavior and suppression of magnetism

Dimerized chain:



Each site has two orbitals: "c" electrons are "hopping"

"d" electrons are "localized"

Model: Hubbard model $H = H_0 + H_{inter} + H_U$

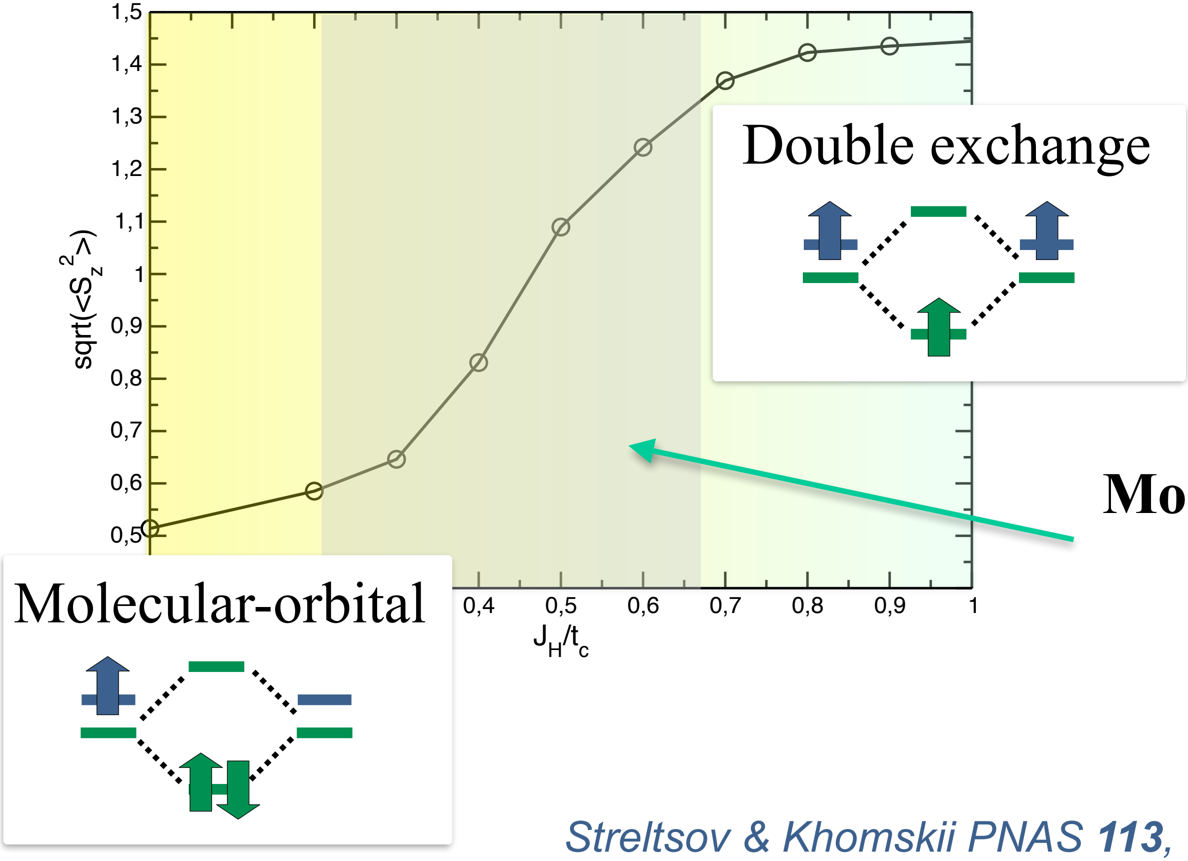
$$\begin{aligned} H_0 &= \sum_i \left(t_c c^\dagger_{i,2} c_{i,1} + t_d d^\dagger_{i,2} d_{i,1} + H.c. \right), \\ H_{inter} &= \sum_i \left(t'_c c^\dagger_{i,2} c_{(i+1),1} + t'_d d^\dagger_{i,2} d_{(i+1),1} + H.c. \right), \\ H_U &= \frac{1}{2} \sum_{\substack{j \\ mm'\sigma}} U^{mm'} n^\sigma_{j,m} n^{-\sigma}_{j,m'} + \frac{1}{2} \sum_{\substack{j \\ \langle mm' \rangle \sigma}} (U^{mm'} - J_H^{mm'}) n^\sigma_{j,m} n^\sigma_{j,m'} . \end{aligned}$$

Solver: Dynamical mean field theory (DMFT)

2. Orbital-selective effects

Orbital-selective behavior and suppression of magnetism

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)*

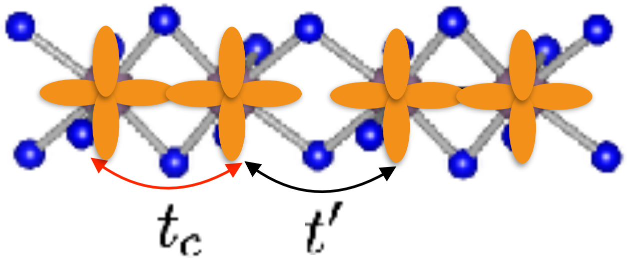
2. Orbital-selective effects

Orbital-selective behavior and suppression of magnetism

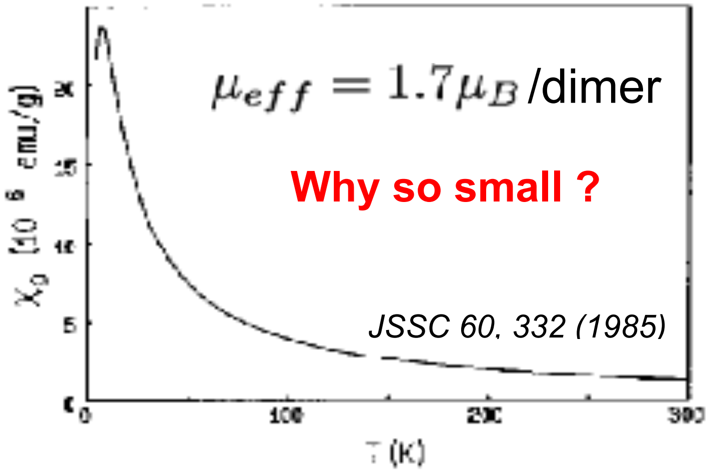
Suppression of magnetic moments in $Y_5Mo_2O_{12}$

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

Crystal structure: dimerized chains



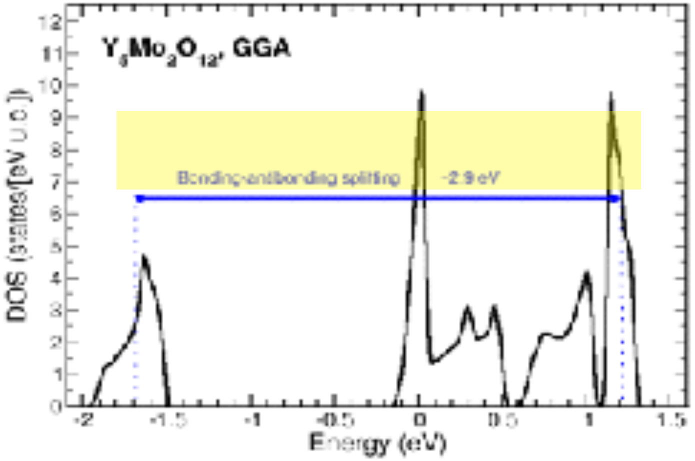
$t'/t_c \sim 5\%$

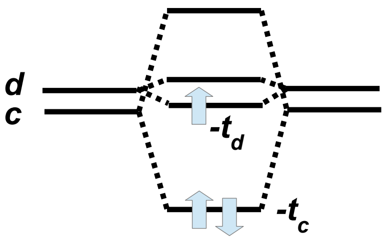


$\mu_{eff} = 1.7\mu_B$ /dimer

Why so small ?

JSSC 60, 332 (1985)





S=1/2 per dimer

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

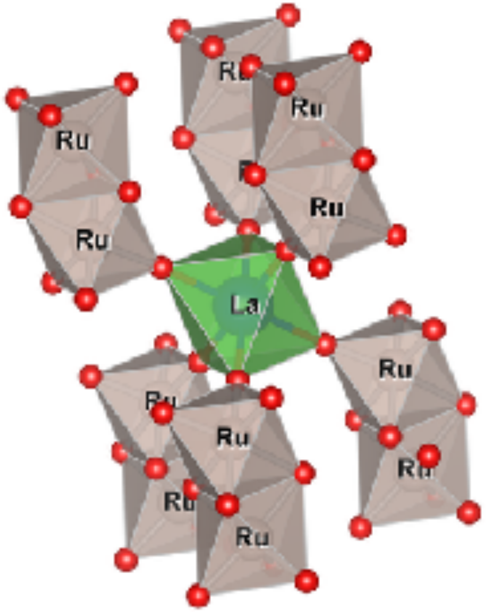
Molecular-orbital state is realized !

"*c*" electrons (*xy* orbitals) form MO
"*d*" (*xz*/*yz* orbitals) retain local moments

2. Orbital-selective effects

Orbital-selective behavior and suppression of magnetism

	Elec. conf.	Theoretical (basing on ionic conf.)	Experimental
$Ba_3\mathbf{Nd}Ru_2O_9$	$4d^{3.5}$	$\mu = 2.5\mu_B$ /Ru	$\mu = 1.6\mu_B$ /Ru
$Ba_3\mathbf{La}Ru_2O_9$	$4d^{3.5}$	$\mu = 2.5\mu_B$ /Ru	$\mu = 1.2\mu_B$ /Ru
$Ba_3\mathbf{Y}Ru_2O_9$	$4d^{3.5}$	$\mu = 2.5\mu_B$ /Ru	$\mu = 0.56\mu_B$ /Ru



Dimers made of the edge sharing RuO_6 octahedra

$$t'/t_c \sim 40 - 50\%$$

Dimers are not "well isolated"
("strongly coupled dimers")

2. Orbital-selective effects

Orbital-selective behavior and suppression of magnetism

	Elec. conf.	**Theoretical (basing on ionic conf.)**	**Experimental**
$Ba_3\mathbf{Nd}Ru_2O_9$	$4d^{3.5}$	$\mu = \underline{2.5\mu_B \text{ /Ru}}$	$\mu = \underline{1.6\mu_B \text{ /Ru}}$
$Ba_3\mathbf{La}Ru_2O_9$	$4d^{3.5}$	$\mu = \underline{2.5\mu_B \text{ /Ru}}$	$\mu = \underline{1.2\mu_B \text{ /Ru}}$
$Ba_3\mathbf{Y}Ru_2O_9$	$4d^{3.5}$	$\mu = \underline{2.5\mu_B \text{ /Ru}}$	$\mu = \underline{0.56\mu_B \text{ /Ru}}$

Standard explanations

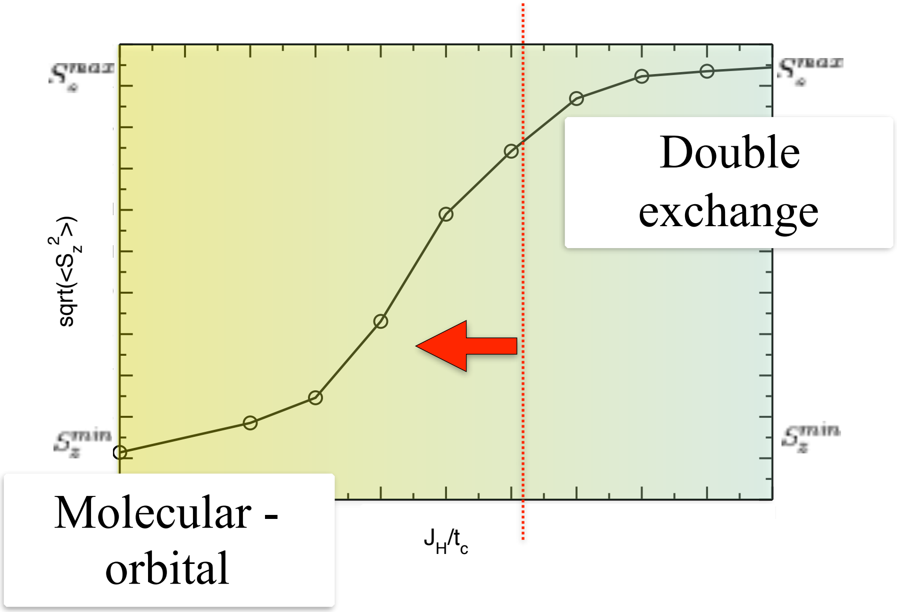
1. Hybridization effects - oxidation state of Ru is the same;
2. Spin-orbit coupling - (1) RuO_6 octahedra are strongly distorted;
   (2) GGA+SOC shows no orbital moment;

does NOT work!

2. Orbital-selective effects

Orbital-selective behavior and suppression of magnetism

	Elec. conf.	Theoretical (basing on ionic conf.)	Experimental
Ba_3**Nd**Ru_2O_9	$4d^{3.5}$	$\mu = 2.5\mu_B$ /Ru	$\mu = 1.6\mu_B$ /Ru
Ba_3**La**Ru_2O_9	$4d^{3.5}$	$\mu = 2.5\mu_B$ /Ru	$\mu = 1.2\mu_B$ /Ru
Ba_3**Y**Ru_2O_9	$4d^{3.5}$	$\mu = 2.5\mu_B$ /Ru	$\mu = 0.56\mu_B$ /Ru



Double exchange

Molecular - orbital

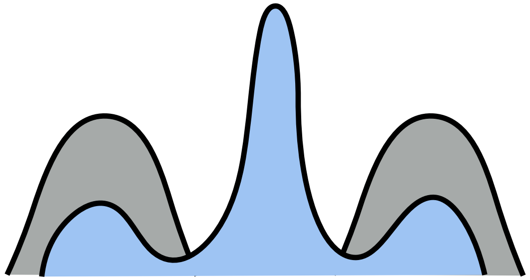
Are we in the crossover MO/DE regime?

Details of the crystal structure defines $t_c/t_d/t'/J_H$ and what portion of magnetic moment is suppressed.

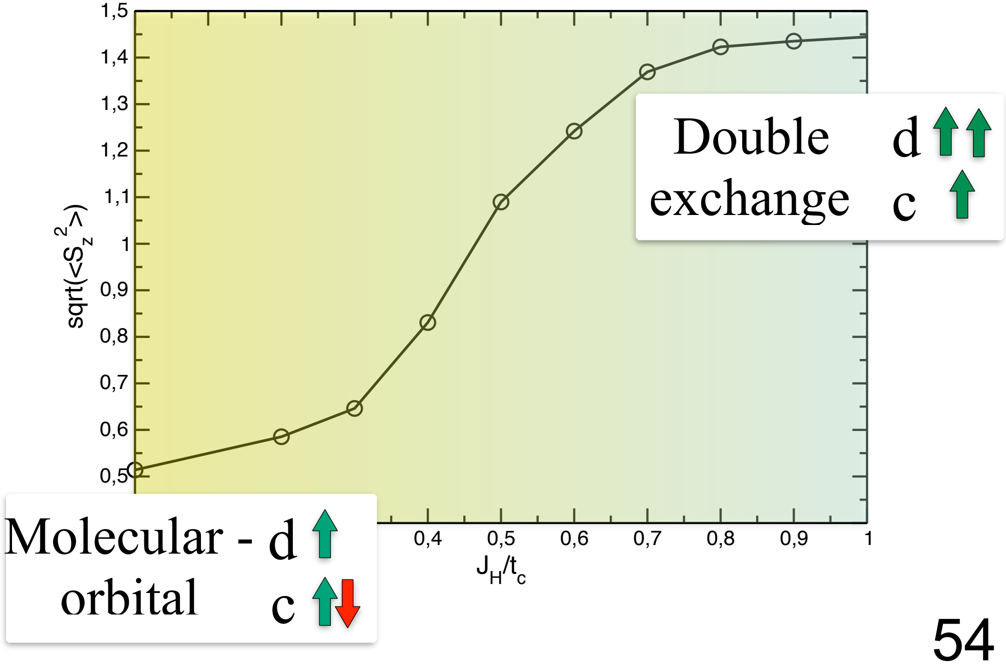
2. Orbital-selective effects

Take-home messages

1. Directional character of orbitals may result in a very different bandwidths (for different orbitals) and as a result to the **orbital-selective Mott transition**



2. Orbital-selective effects may strongly **suppress magnetism** (especially in dimerized systems)



Double exchange d ↑↑ c ↑

Molecular orbital - d ↑ c ↑↓

Spin-orbit related effects

- j_{eff} =1/2 and the spin-orbit-assisted Mott state
- Spin-orbit coupling versus Jahn-Teller effect
- Kitaev exchange

3. Spin-orbit related effects
Introduction: SOC for d-orbitals, basics

Spin-orbit coupling (SOC): $H_{SOC} = \lambda \mathbf{l}\mathbf{s}$

Orbital moment for e_g is quenched => we consider t_{2g}-ions

***d*-orb.**

$$H_{SOC}^{mm'} = \begin{array}{ccccc|ccccc}
yz_\uparrow & zx_\uparrow & xy_\uparrow & 3z^2_\uparrow & x^2\text{-}y^2_\uparrow & yz_\downarrow & zx_\downarrow & xy_\downarrow & 3z^2_\downarrow & x^2\text{-}y^2_\downarrow \\
0 & \frac{i\lambda}{2} & 0 & 0 & 0 & 0 & 0 & -\frac{\lambda}{2} & -\frac{1}{2}i\sqrt{3}\lambda & -\frac{i\lambda}{2} \\
-\frac{i\lambda}{2} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i\lambda}{2} & \frac{\sqrt{3}\lambda}{2} & -\frac{\lambda}{2} \\
0 & 0 & 0 & 0 & i\lambda & \frac{\lambda}{2} & -\frac{i\lambda}{2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{1}{2}i\sqrt{3}\lambda & -\frac{\sqrt{3}\lambda}{2} & 0 & 0 & 0 \\
0 & 0 & -i\lambda & 0 & 0 & \frac{i\lambda}{2} & \frac{\lambda}{2} & 0 & 0 & 0 \\
\hline
0 & 0 & \frac{\lambda}{2} & -\frac{1}{2}i\sqrt{3}\lambda & -\frac{i\lambda}{2} & 0 & -\frac{i\lambda}{2} & 0 & 0 & 0 \\
0 & 0 & \frac{i\lambda}{2} & -\frac{\sqrt{3}\lambda}{2} & \frac{\lambda}{2} & \frac{i\lambda}{2} & 0 & 0 & 0 & 0 \\
-\frac{\lambda}{2} & -\frac{i\lambda}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i\lambda \\
\frac{1}{2}i\sqrt{3}\lambda & \frac{\sqrt{3}\lambda}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{i\lambda}{2} & -\frac{\lambda}{2} & 0 & 0 & 0 & 0 & 0 & i\lambda & 0 & 0
\end{array}$$

***p*-orb.**

$$H_{SOC}^{mm'} = \begin{array}{ccc|ccc}
x_\uparrow & y_\uparrow & z_\uparrow & x_\downarrow & y_\downarrow & z_\downarrow \\
0 & -\frac{i\lambda}{2} & 0 & 0 & 0 & \frac{\lambda}{2} \\
\frac{i\lambda}{2} & 0 & 0 & 0 & 0 & -\frac{i\lambda}{2} \\
0 & 0 & 0 & -\frac{\lambda}{2} & \frac{i\lambda}{2} & 0 \\
\hline
0 & 0 & -\frac{\lambda}{2} & 0 & \frac{i\lambda}{2} & 0 \\
0 & 0 & -\frac{i\lambda}{2} & -\frac{i\lambda}{2} & 0 & 0 \\
\frac{\lambda}{2} & \frac{i\lambda}{2} & 0 & 0 & 0 & 0
\end{array}$$

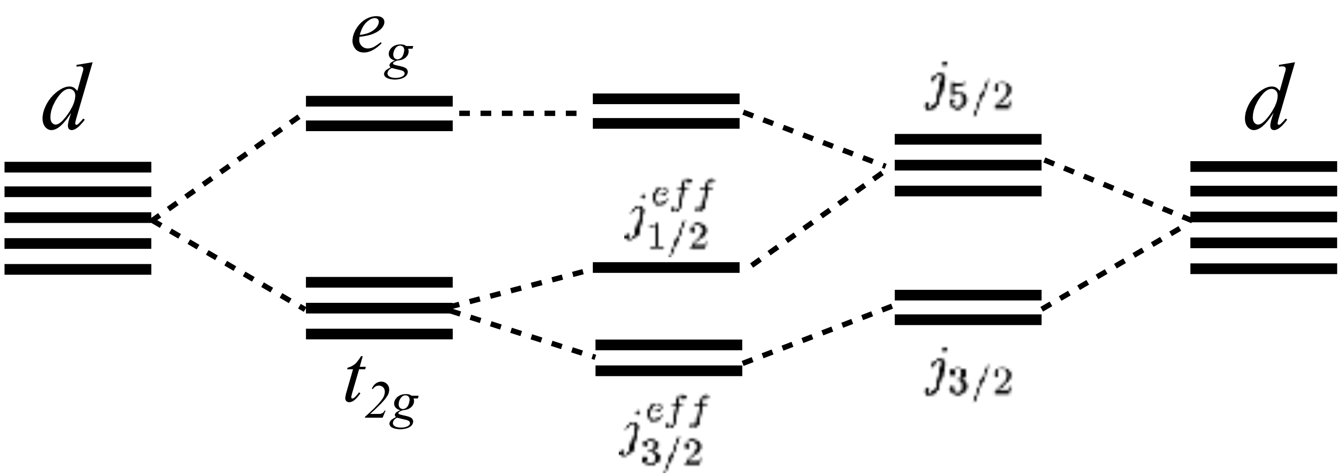
Thus, if $\Delta_{t_{2g}-e_g}$ large enough $\begin{cases} t_{2g} \rightarrow p \\ l \rightarrow l_{eff} = 1 \\ \lambda \rightarrow -\lambda \end{cases}$

	$\Delta_{t_{2g}-e_g}$	***U***
3d	*1-2 eV*	*3-10 eV*
4d	*3-4 eV*	*2-5 eV*
5d	*4-4.5 eV*	*1-3 eV*

At least 5d transition metals can be described with $l_{eff} = 1$ ($j_{eff}=1/2$ and $3/2$)

3. Spin-orbit related effects

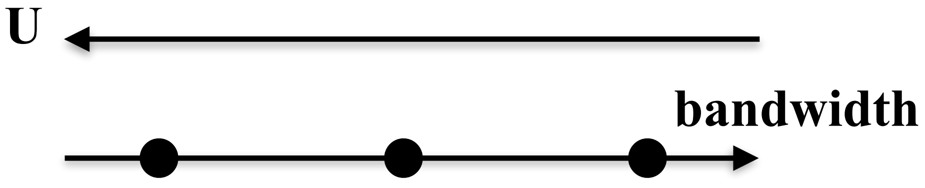
Introduction: one electron scheme of d-levels splitting



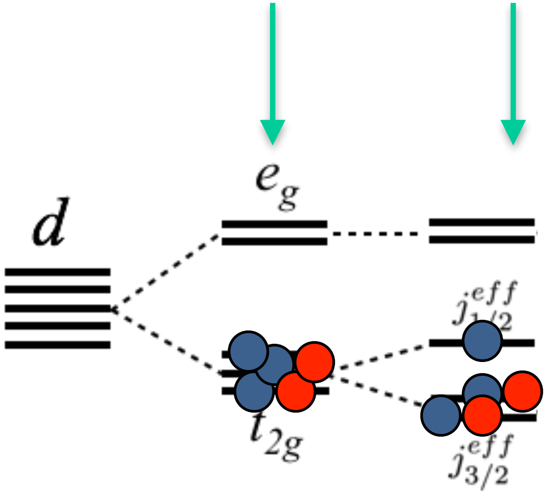
$\Delta_{CFS} \gg \lambda$ $\Delta_{CFS} \ll \lambda$

3. Spin-orbit related effects

Spin-orbit-assisted Mott state

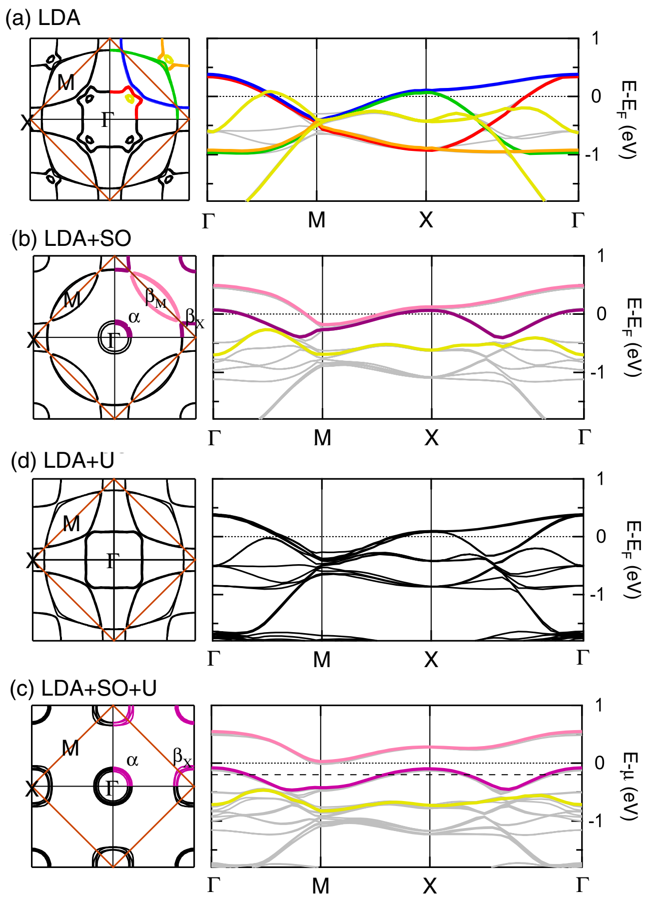


Co($3d^5$)	Rh($4d^5$)	Ir ($5d^5$)
Sr_2CoO_4	Sr_2RhO_4	Sr_2IrO_4
metal	metal	**insulator**



$n_{t_{2g}} = 5/3 \quad n_{j_{eff}=1/2} = 1$

Sr_2IrO_4



Kim et al., PRL 101, 76402 (2008)

Spin-orbit-assisted Mott state!

3. Spin-orbit related effects
Spin-orbit and Kitaev exchange

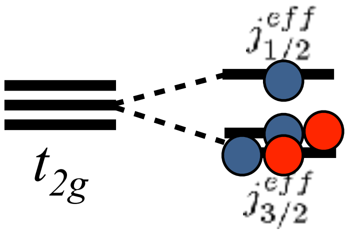
Let's consider

1) Hopping **<u>only</u>** via ligand p-orbitals
2) SOC is the strongest coupling
3) Conf: d^5 (j_{eff}=1/2 is half-filled)

$t_{xy/xy}=0;$

$(t_{xy/xz}=0;\ \ t_{xy/yz}=0;\ t_{yz/yz}=0;\ t_{xz/xz}=0;)$

$\boldsymbol{t_{yz/xz}=t;\ t_{yz/xz}=t;}$

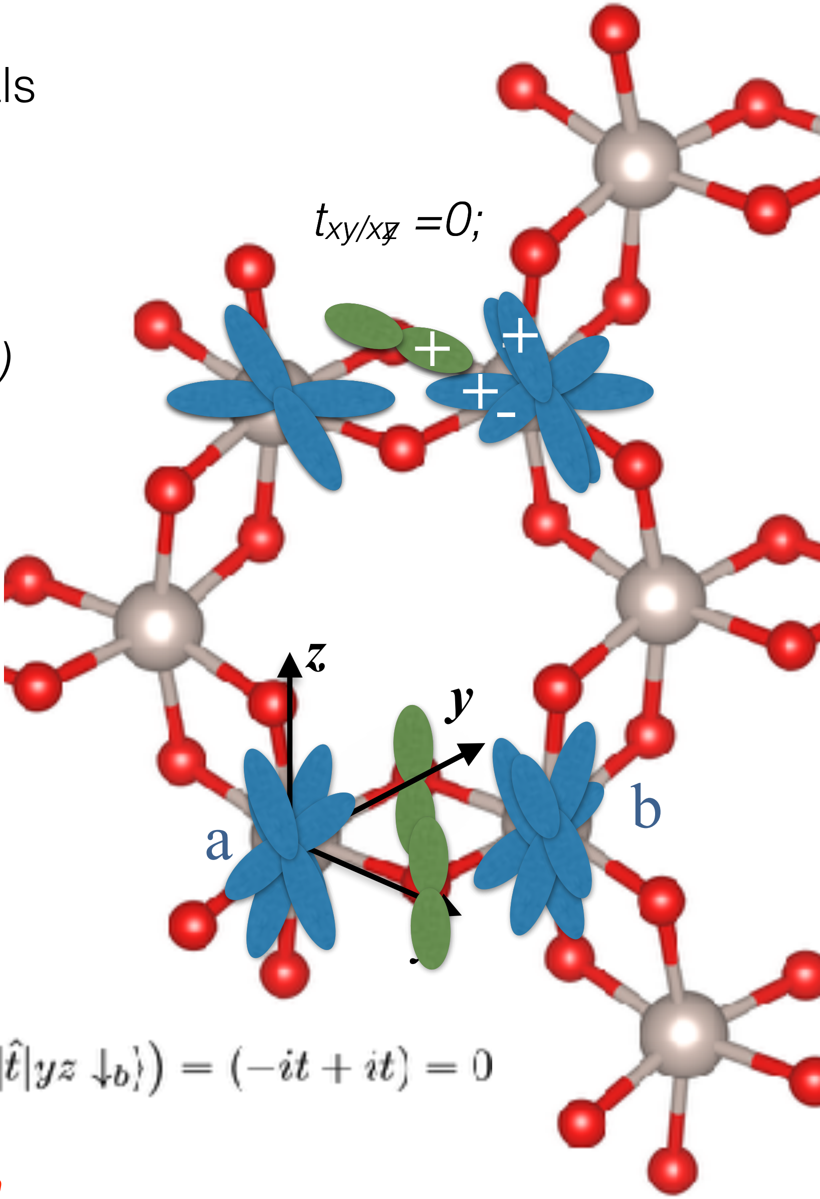


$$|J^z_{1/2}\rangle = \frac{1}{\sqrt{3}}\left(|xy\uparrow\rangle + |(ixz+yz)\downarrow\rangle\right),$$
$$|J^z_{-1/2}\rangle = \frac{1}{\sqrt{3}}\left(|xy\downarrow\rangle + |(ixz-yz)\uparrow\rangle\right),$$

Superexchange: $J \sim \dfrac{t^2_{dd,eff}}{U}$

but $\langle J^z_{1/2,a}|\hat{t}|J^z_{-1/2,b}\rangle = \langle J^z_{-1/2,a}|\hat{t}|J^z_{1/2,b}\rangle = 0$

$$\langle J^z_{1/2,a}|\hat{t}|J^z_{1/2,b}\rangle = \frac{1}{3}\left(-i\langle yz\downarrow_a|\hat{t}|xz\downarrow_b\rangle + i\langle xz\downarrow_a|\hat{t}|yz\downarrow_b\rangle\right) = (-it+it) = 0$$



NO AFM superexchange!

3. Spin-orbit related effects
Spin-orbit and Kitaev exchange

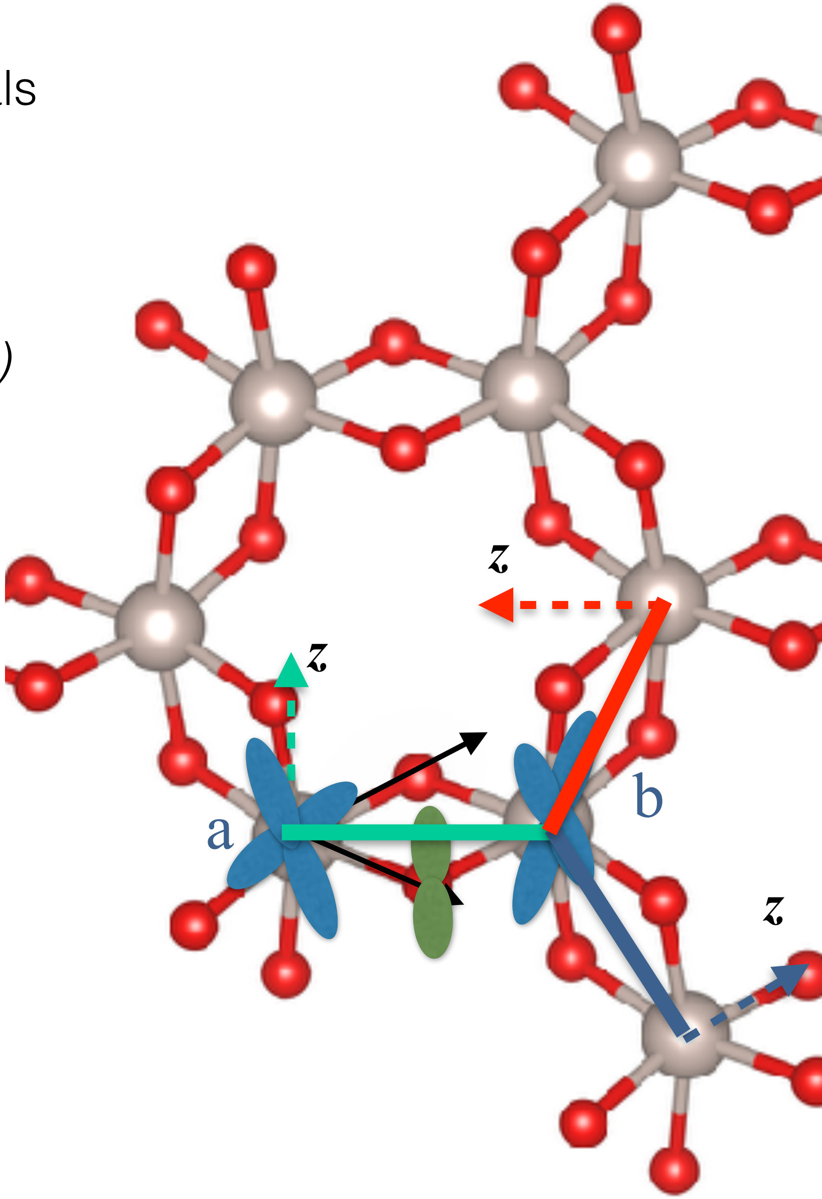
Let's consider

1) Hopping **only** via ligand p-orbitals
2) SOC is the strongest coupling
3) Conf: d^5 (j_{eff}=1/2 is half-filled)

$t_{xy/xy} = 0;$

$(t_{xy/xz} = 0; \; t_{xy/yz} = 0; \; t_{yz/yz} = 0; \; t_{xz/xz} = 0;)$

$\boldsymbol{t_{yz/xz} = t; \; t_{yz/xz} = t;}$



There will be only higher order (FM) terms!

$$K \sim -\frac{t_{pd}^4}{\Delta_{CT} U} \frac{J_H}{U}$$

Strong SOC => $$\langle J^z_{1/2} | \hat{l}_z | J^z_{1/2} \rangle = \frac{2}{3}$$

with $K < 0$ (FM)

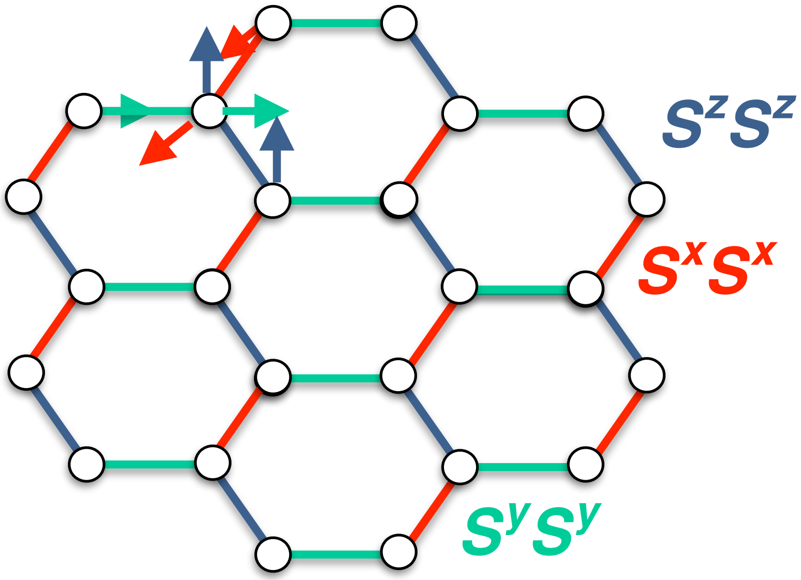
3. Spin-orbit related effects
Spin-orbit and Kitaev exchange

Kitaev model $H = \sum_{ij} K_{ij} S_i^\gamma S_j^\gamma$

Kitaev Ann. Phys. 321, 2 (2006)

Highly frustrated model (spin liquid GS)

Exactly solvable



Jackeli-Khaliullin: d^5 systems on honeycomb lattice can be a realization of the Kitaev model

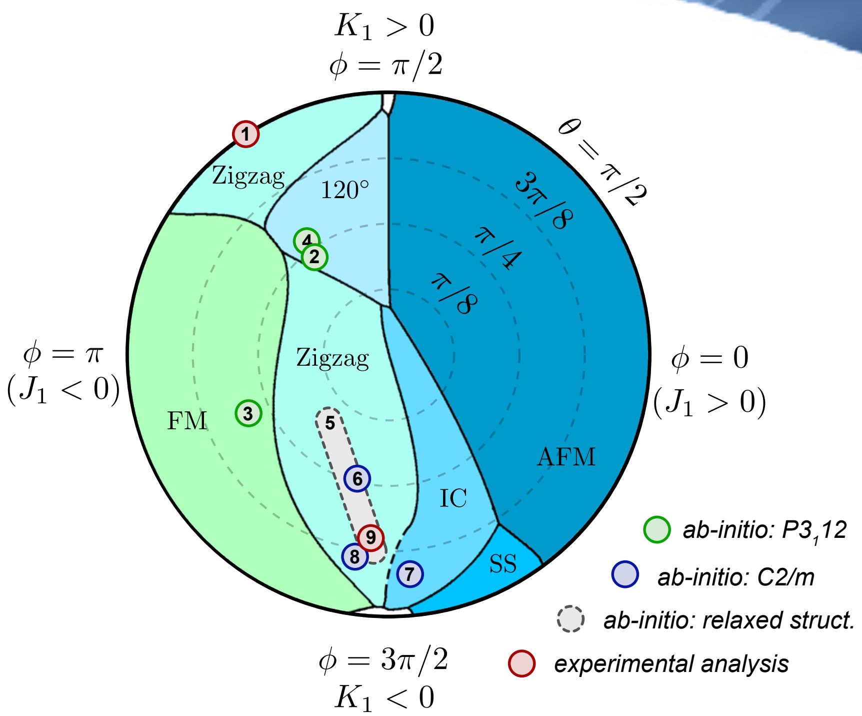
G. Jackeli and G. Khaliullin, PRL 102, 17205 (2009).

Possible physical
realizationes of Kitaev model: Na_2IrO_3 α-Li_2IrO_3 Li_2RhO_3 α-$RuCl_3$

3. Spin-orbit related effects
Spin-orbit and Kitaev exchange

Kitaev-Heisenberg model

$$\mathcal{H}_{ij} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + K_{ij}\ S_i^\gamma S_j^\gamma + \Gamma_{ij}\left(S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha\right) + \Gamma'_{ij}\left(S_i^\gamma S_j^\alpha + S_i^\gamma S_j^\beta + S_i^\alpha S_j^\gamma + S_i^\beta S_j^\gamma\right)$$



$$J_1 = \cos\phi \sin\theta$$
$$K_1 = \sin\phi \sin\theta$$
$$\Gamma_1 = \cos\theta$$

Experimental results

Property	Na_2IrO_3	α-Li_2IrO_3	Li_2RhO_3	α-$RuCl_3$
μ_{eff} (μ_B)	1.79	1.83	2.03	2.0 to 2.7
Θ_{iso} (K)	~ -120	-33 to -100	~ -50	$\sim +40$
Θ_{ab} (K)	-176	$\Theta_{ab} > \Theta_c$	–	+38 to +68
Θ_c (K)	-40	–	–	-100 to -150
T_N (K)	$13-18$	~ 15	(6)	7 to 14
Order	Zigzag	Spiral	Glassy	Zigzag
k-vector	$(0, 1, \frac{1}{2})$	$(0.32, 0, 0)$	–	$(0, 1, \frac{1}{2})$

3. Spin-orbit related effects

Spin-orbit and Kitaev exchange

Kitaev-Heisenberg model

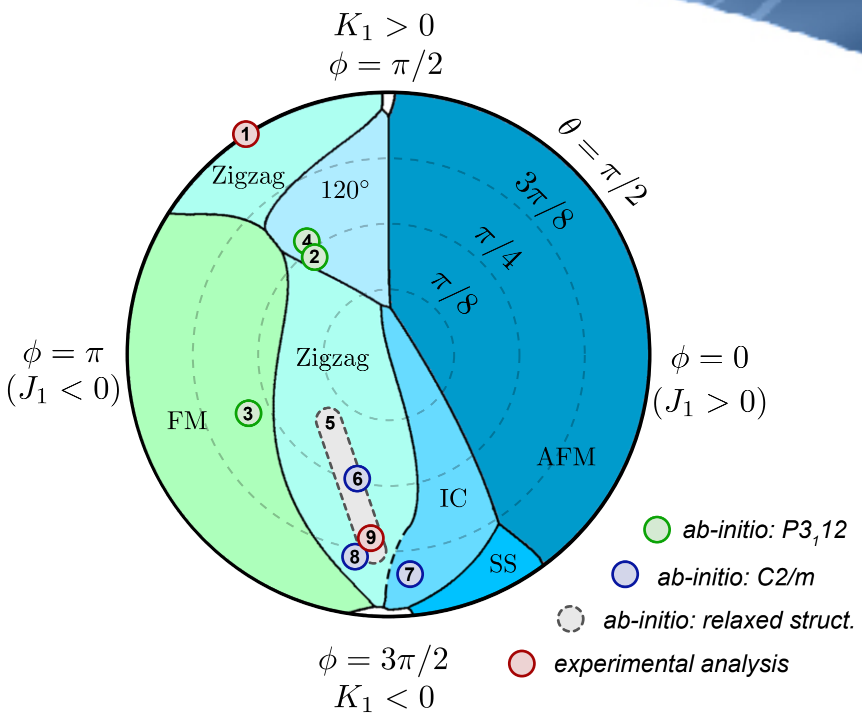
$$\mathcal{H}_{ij} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + K_{ij}\ S_i^\gamma S_j^\gamma + \Gamma_{ij}\left(S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha\right)$$
$$+\,\Gamma'_{ij}\left(S_i^\gamma S_j^\alpha + S_i^\gamma S_j^\beta + S_i^\alpha S_j^\gamma + S_i^\beta S_j^\gamma\right)$$

Na_2IrO_3

Method	J_1	K_1	Γ_1	Γ'_1	K_2	J_3
Pert. Theo.[42]	$+3.2$	-29.4	$+1.1$	-3.5	-0.4	$+1.7$
QC (2-site)[41]	$+2.7$	-16.9	$+1.0$	–	–	–
ED (6-site)[43]	$+0.5$	-16.8	$+1.4$	-2.1	-1.4	$+6.7$

α-$RuCl_3$

Method	Structure	J_1	K_1	Γ_1	J_3
Exp. An.[161]	–	-4.6	$+7.0$	–	–
Pert. Theo.[146]	$P3_112$	-3.5	$+4.6$	$+6.4$	–
QC (2-site)[39]	$P3_112$	-1.2	-0.5	$+1.0$	–
ED (6-site)[43]	$P3_112$	-5.5	$+7.6$	$+8.4$	$+2.3$
Pert. Theo.[146]	Relaxed	$-2.8/-0.7$	$-9.1/-3.0$	$+3.7/+7.3$	–
ED (6-site)[43]	$C2/m$	-1.7	-6.7	$+6.6$	$+2.7$
QC (2-site)[39]	$C2/m$	$+0.7$	-5.1	$+1.2$	–
DFT[175]	$C2/m$	-1.8	-10.6	$+3.8$	$+1.3$
Exp. An.[176]	–	-0.5	-5.0	$+2.5$	$+0.5$



$$J_1 = \cos\phi\sin\theta$$
$$K_1 = \sin\phi\sin\theta$$
$$\Gamma_1 = \cos\theta$$

3. Spin-orbit related effects
Spin-orbit and Kitaev exchange

LETTER

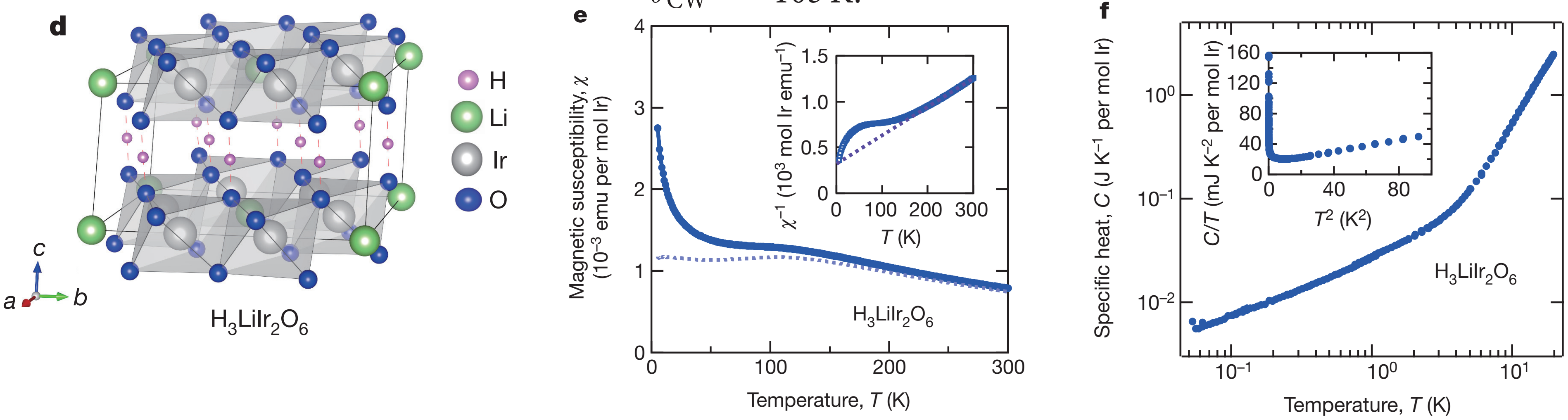
15 FEBRUARY 2018 | VOL 554 | NATURE | 343

A spin–orbital-entangled quantum liquid on a honeycomb lattice

K. Kitagawa[1]*, T. Takayama[2]*, Y. Matsumoto[2], A. Kato[1], R. Takano[1], Y. Kishimoto[3], S. Bette[2], R. Dinnebier[2], G. Jackeli[2,4]
H. Takagi[1,2,4]

$H_3LiIr_2O_6$

$\theta_{CW} = -105\,K.$



χ(T): no long-range magnetic order down to 2 K

C(T): no long-range magnetic order down to 0.05 K

3. Spin-orbit related effects
Spin-orbit coupling vs. Jahn-Teller effect

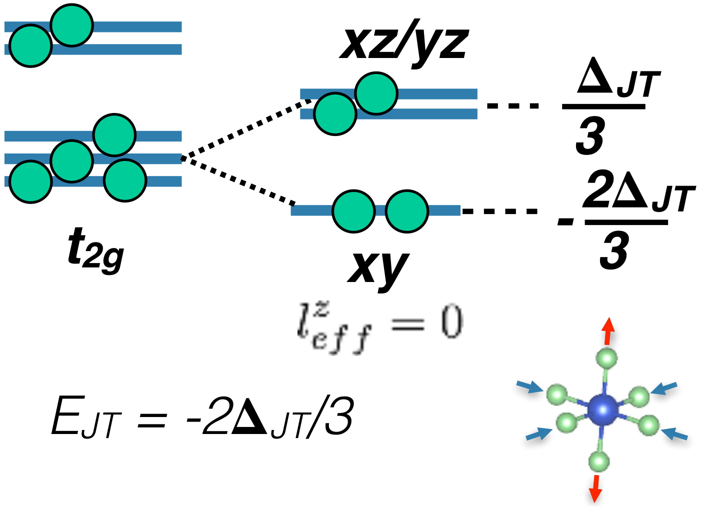
Weak spin-orbit coupling (3d) and large spins

Fe^{2+} $(\mathrm{t}_{2g}^4 \mathrm{e}_g^2,\ S=2)$ Co^{2+} $(\mathrm{t}_{2g}^5 \mathrm{e}_g^2,\ S=3/2)$

Mean-field approximation for the SOC $\lambda \vec{l}\vec{s} \rightarrow \lambda l^z s^z$

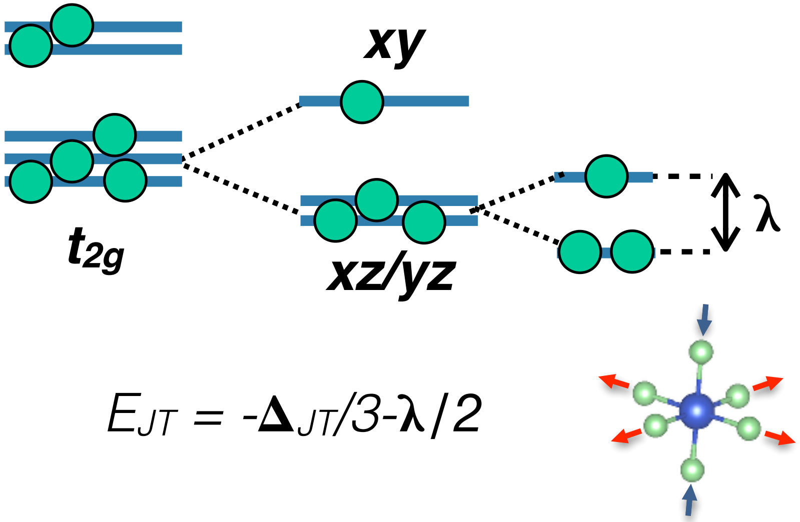
E.g. for Fe^{2+}, tetragonal distortions

Jahn-Teller scenario



$E_{JT} = -2\Delta_{JT}/3$

Spin-orbit scenario



$E_{JT} = -\Delta_{JT}/3 - \lambda/2$

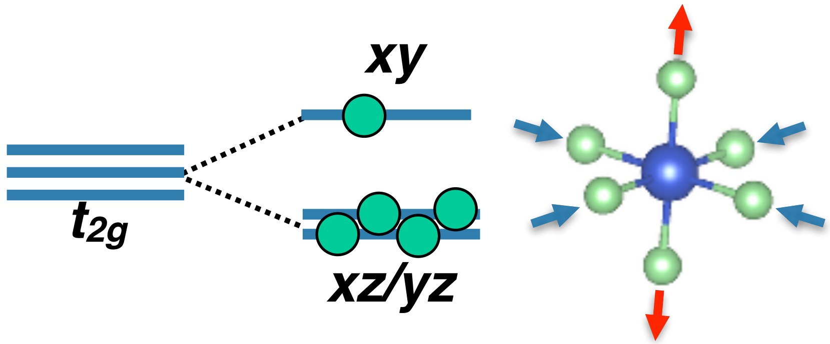
Spin-orbit coupling **competes** with the Jahn-Teller effect!

3. Spin-orbit related effects
Spin-orbit coupling vs. Jahn-Teller effect

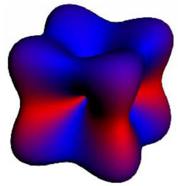
Strong spin-orbit coupling and small spins: d^5

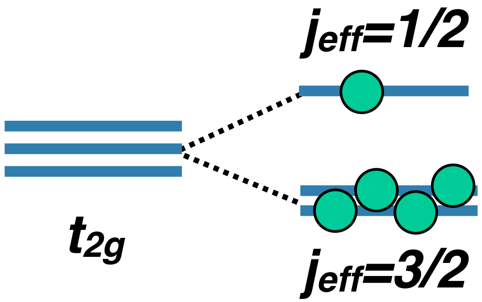
Ir^{4+} in octahedra (t_{2g}^5), or Cu^{2+} in tetrahedra (t_{2g}^5)

Jahn-Teller scenario



Spin-orbit scenario





$$|J^z_{1/2}\rangle = \frac{1}{\sqrt{3}}\left(|xy\uparrow\rangle + |(ixz + yz)\downarrow\rangle\right),$$

$$|J^z_{-1/2}\rangle = \frac{1}{\sqrt{3}}\left(|xy\downarrow\rangle + |(ixz - yz)\uparrow\rangle\right),$$

All components have the same weights
=> No distortions

Spin-orbit coupling suppresses the Jahn-Teller effect!

Is this what goes in $CuAl_2O_4$?

2. Spin-orbit related effects

Spin-orbit coupling vs. Jahn-Teller effect

Letters

IOP Publishing

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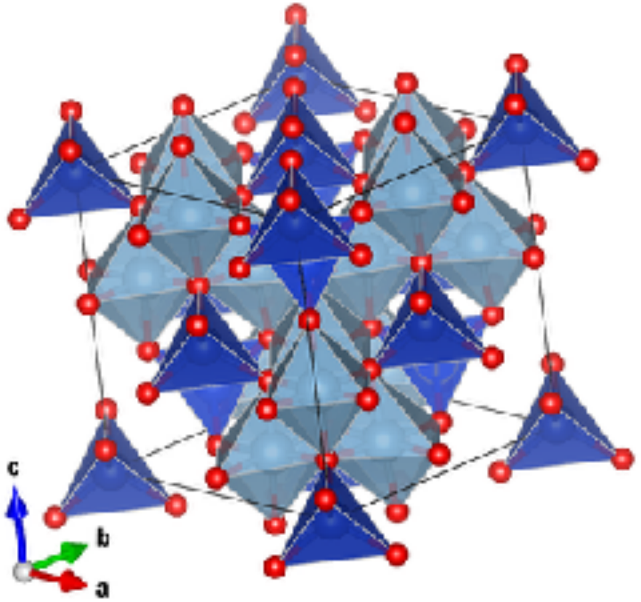
doi:10.1088/1361-648X/aa5c72

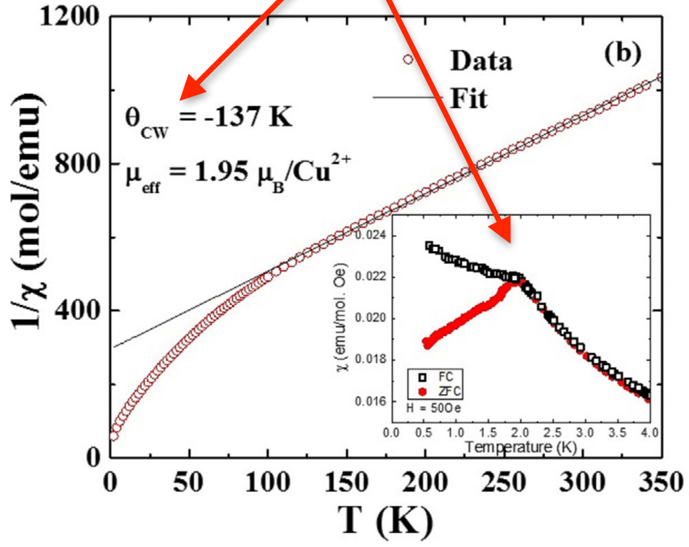
Spin glass behavior in frustrated quantum spin system $CuAl_2O_4$ with a possible orbital liquid state

R Nirmala[1,2,3], Kwang-Hyun Jang[1,3], Hasung Sim[4,5], Hwanbeom Cho[4,5],
Junghwan Lee[1,3], Nam-Geun Yang[1,3], Seongsu Lee[6,7], R M Ibberson[8,9],
K Kakurai[10,14], M Matsuda[10,11], S-W Cheong[7], V V Gapontsev[12]
S V Streltsov[12,13] and Je-Geun Park[1,3,4,5]

Cu^{2+}, but stays cubic at any temperature



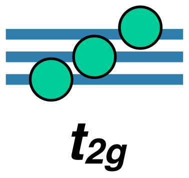
Strong magnetic frustrations



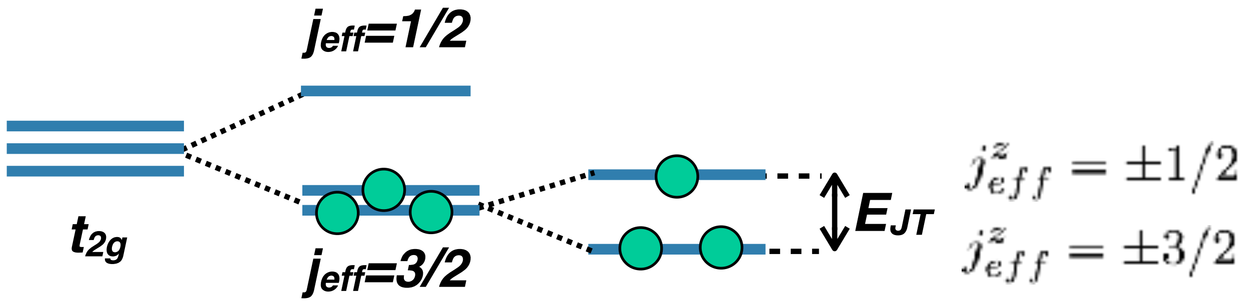
3. Spin-orbit related effects

Spin-orbit coupling vs. Jahn-Teller effect

Strong spin-orbit coupling: d^3



No need in JT

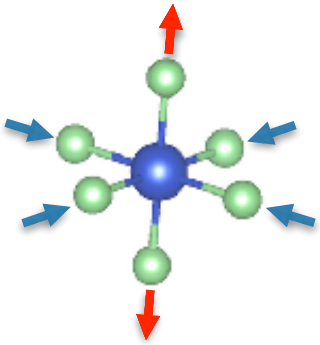


$$|J_{3/2}, J^z_{3/2}\rangle = -\frac{1}{\sqrt{2}}(|yz,\uparrow\rangle + i|xz,\uparrow\rangle),$$

$$|J_{3/2}, J^z_{-3/2}\rangle = \frac{1}{\sqrt{2}}(|yz,\downarrow\rangle - i|xz,\downarrow\rangle),$$

$$|J_{3/2}, J^z_{1/2}\rangle = \sqrt{\frac{2}{3}}\underline{|xy,\uparrow\rangle} - \frac{1}{\sqrt{3}}|\frac{1}{\sqrt{2}}(yz + ixz),\downarrow\rangle,$$

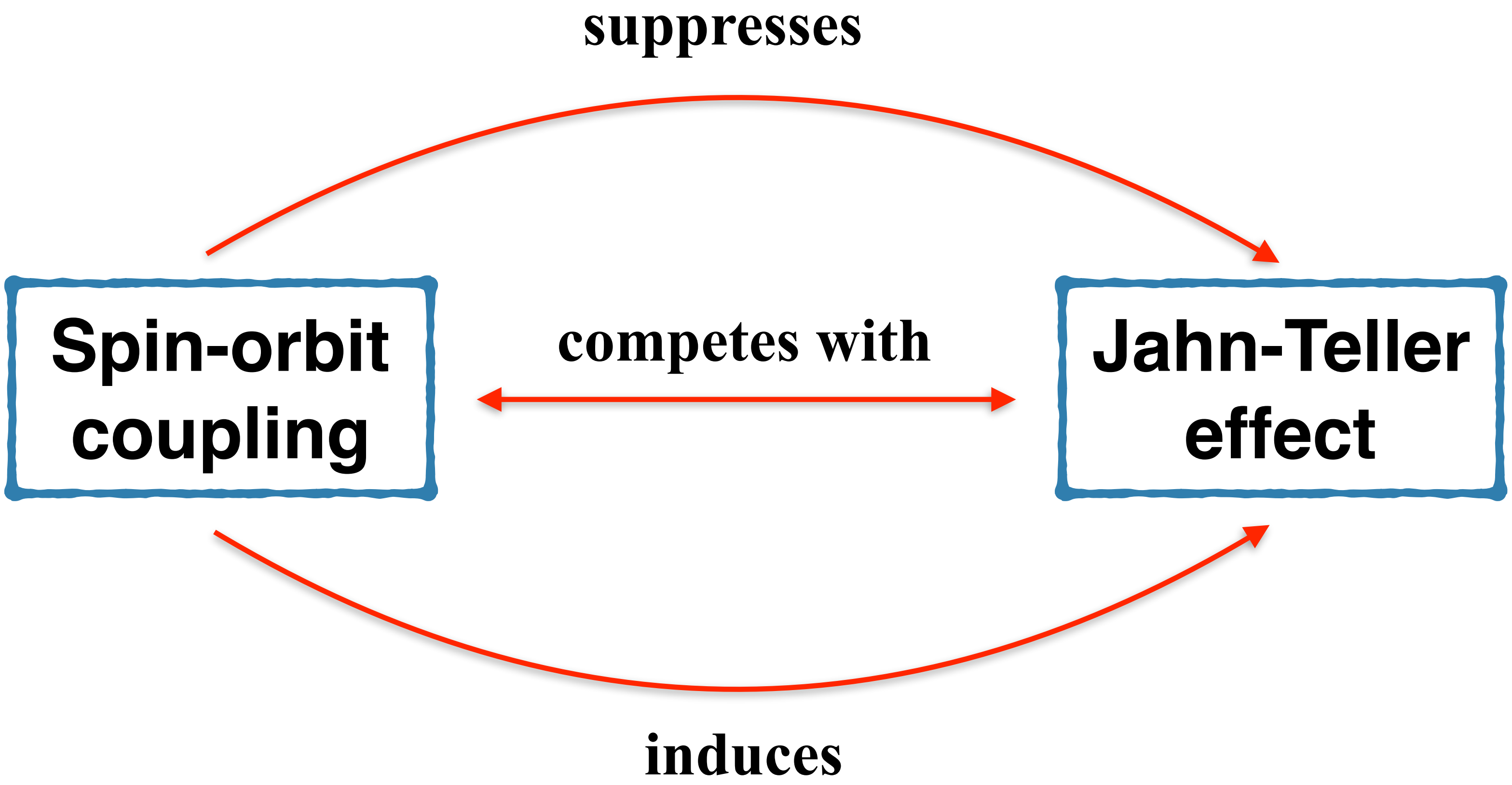
$$|J_{3/2}, J^z_{-1/2}\rangle = \sqrt{\frac{2}{3}}\underline{|xy,\downarrow\rangle} + \frac{1}{\sqrt{3}}|\frac{1}{\sqrt{2}}(yz - ixz),\uparrow\rangle.$$



Spin-orbit coupling **induces** the Jahn-Teller effect!

3. Spin-orbit related effects

Spin-orbit coupling vs. Jahn-Teller effect



suppresses

Spin-orbit coupling

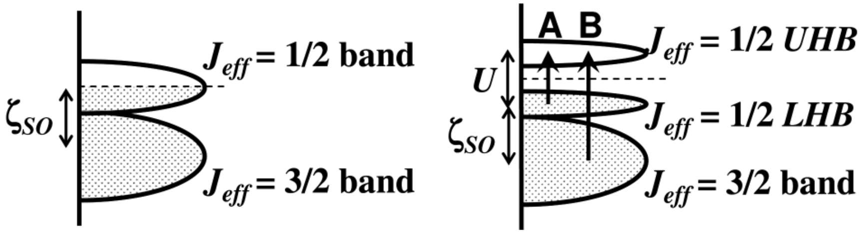
competes with

Jahn-Teller effect

induces

3. Spin-orbit related effects
Take-home messages

1. Spin-orbit coupling may **induce Mott transition**



2. Spin-orbit coupling **may induce strong anisotropy of exchange interaction**

$$H = \sum_{ij} K_{ij} S_i^{\gamma} S_j^{\gamma}$$

3. Spin-orbit coupling may **help to, compete with or completely suppress** the Jahn-Teller effect