Russian Science Foundation

Спин-орбитальное взаимодействие, как источник новых эффектов в магнитных системах

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Introduction: Spin-orbit coupling (SOC) in transition metal compounds

Spin-orbit coupling: $\hat{H}_{SOC} = \sum_i \zeta \vec{\hat{l}}_i \vec{\hat{s}}_i \rightarrow \lambda \vec{\hat{L}} \vec{\hat{S}}$

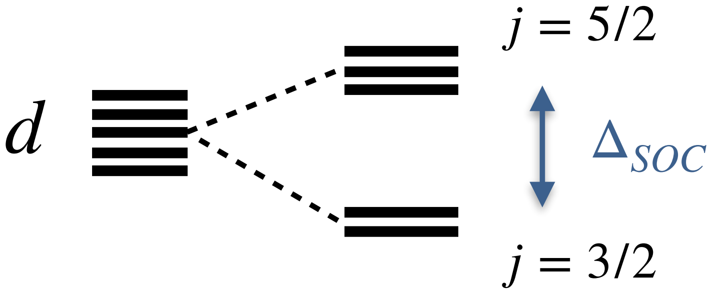
SOC parameter $\zeta \sim \left(\frac{Ze^2}{\hbar c}\right)^2 \frac{m_e e^4}{\hbar^2}$ is large for heavy elements;

SOC for a single electron:

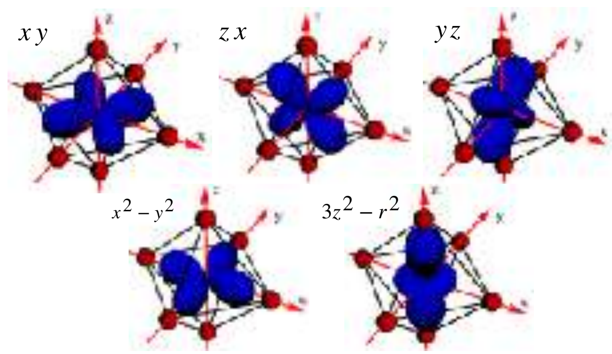
$$\vec{j} = \vec{l} + \vec{s}$$

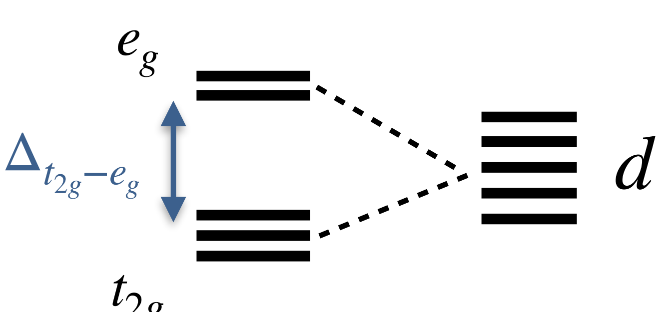
$$\hat{H}_{SOC} = \zeta \vec{\hat{l}} \vec{\hat{s}} = \zeta \left(\hat{j}^2 - \hat{l}^2 - \hat{s}^2\right)/2$$

Fixed s and l; $j=l+s$ or $j=l-s$



Crystal field splitting (CFS)

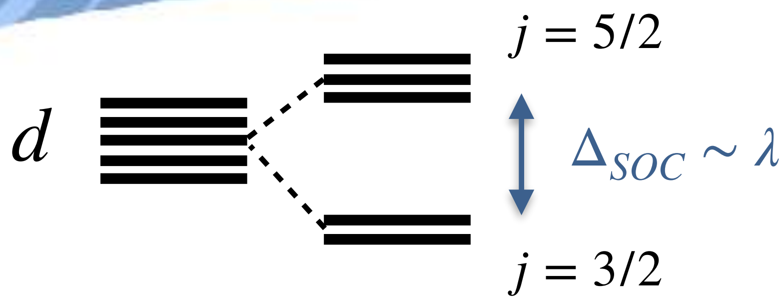




SOC + CFS

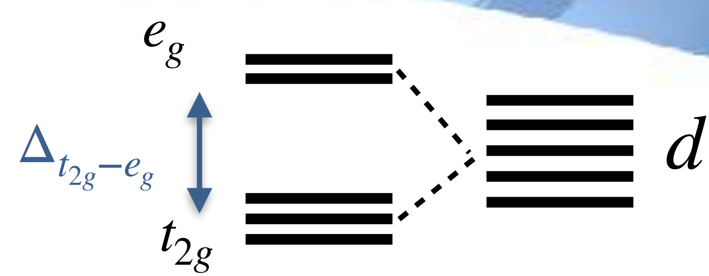
?

Introduction:
Various energy scales



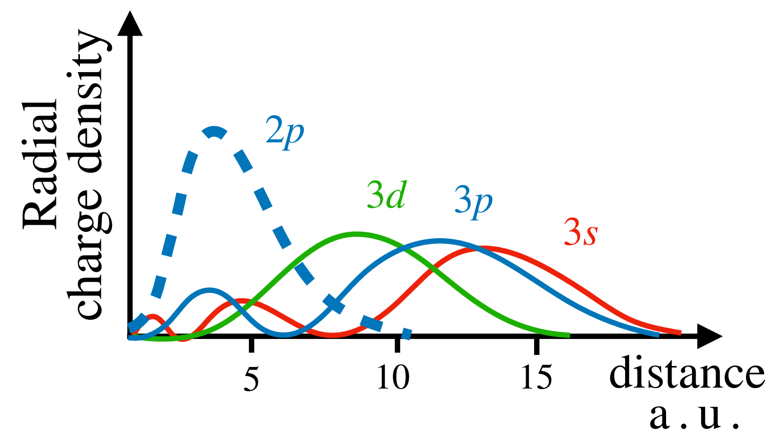
SOC + CFS

?

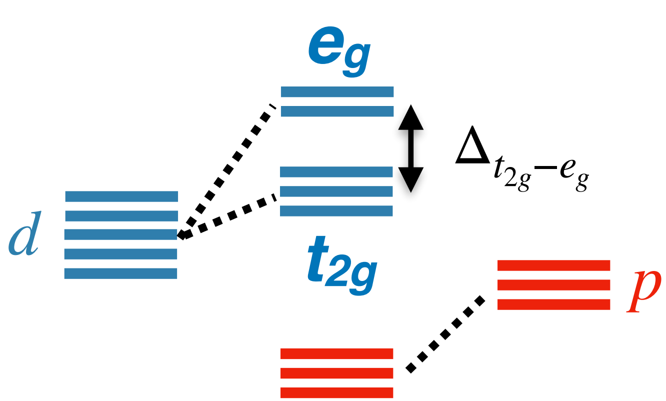


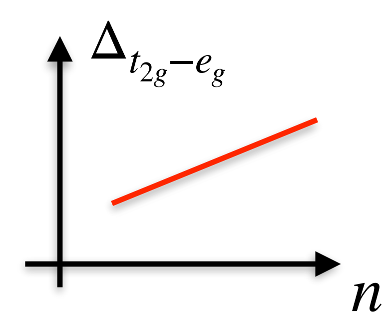
$$\lambda \sim \left(\frac{Ze^2}{\hbar c}\right)^2 \frac{m_e e^4}{\hbar^2}$$

SOC is large in heavy metals: Au, Ir, …,
but they have a larger principle number, n

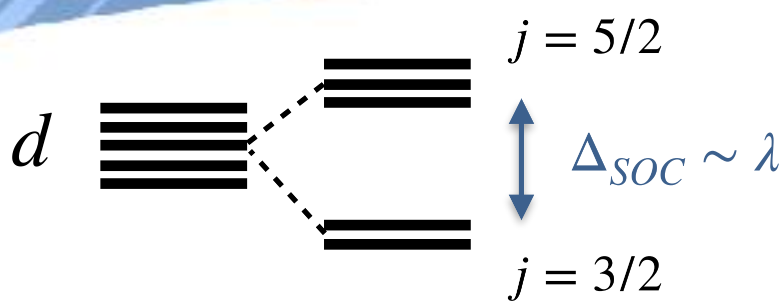


Larger $n \Rightarrow$ stronger hybridization $\Rightarrow$ larger the crystal-field field



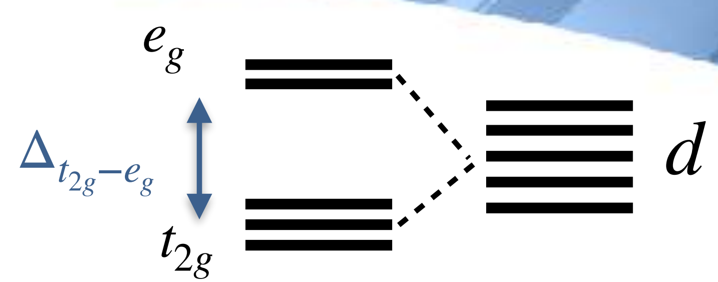


Introduction:
Various energy scales

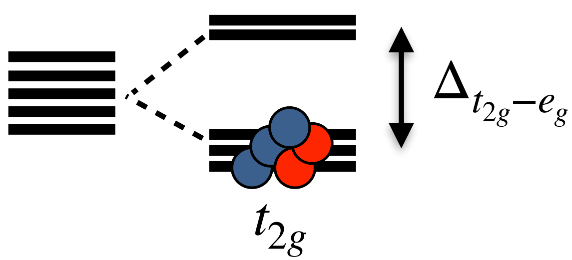


SOC + CFS

?



- Typically all *4d* and *5d* metals are in the **low spin** state (we first fill t_{2g} states)



Typical parameters for transition metals

	$\Delta_{t_{2g}-e_g}$	λ	***Hund's J_H***	***Hubbard U***
3d	*1-2 eV*	*20-100 meV*	*0.7-1 eV*	*3-10 eV*
4d	*3-4 eV*	*0.1-0.3 eV*	*0.5-0.8 eV*	*2-5 eV*
5d	*4-4.5 eV*	*0.3-0.5 eV*	*0.3-0.5 eV*	*1-2 eV*

see e.g.
Abragam and Bleaney
"EPR of transition ions",

- Since $\Delta_{t_{2g}-e_g} \gg \lambda$ we can restrict ourselves to consideration of **SOC for the t_{2g} states only**

Introduction:
Spin-orbit coupling (SOC) for t_{2g} - states

$$\hat{H}_{SOC} = \lambda \hat{\vec{l}}\hat{\vec{s}} = \lambda(\hat{l}_x\hat{s}_x + \hat{l}_y\hat{s}_y + \hat{l}_z\hat{s}_z)$$

Let's calculate this operator! We know how it works with Y_{l,m_l} and transformation rules:

$$\hat{l}_z Y_{l,m_l} = m_l Y_{l,m_l}$$

$$\hat{l}^- = \hat{l}^x - i\hat{l}^y \quad \hat{l}^+ = \hat{l}^x + i\hat{l}^y$$

$$\hat{l}^\pm Y_{l,m_l} = \sqrt{(l \pm m_l + 1)(l \mp m_l)}\, Y_{l,m_l \pm 1}$$

$$D_x = \frac{1}{\sqrt{2}}(Y_{1,-1} - Y_{1,1}) \quad D_{xy} = \frac{i}{\sqrt{2}}(Y_{2,-2} - Y_{2,2})$$

$$D_y = \frac{i}{\sqrt{2}}(Y_{1,-1} + Y_{1,1}) \quad D_{yz} = \frac{i}{\sqrt{2}}(Y_{2,1} + Y_{2,-1})$$

$$D_z = Y_{1,0} \quad D_{xz} = \frac{1}{\sqrt{2}}(Y_{2,-1} - Y_{2,1})$$

$$D_{3z^2-r^2} = Y_{2,0}$$

$$D_{x^2-y^2} = \frac{1}{\sqrt{2}}(Y_{2,2} + Y_{2,-2})$$

Finally one obtains

$\hat{L}_x D_{xz} = -iD_{xy}$	$\hat{L}_y D_{xz} = iD_{x^2-y^2} - i\sqrt{3}D_{3z^2-r^2}$	$\hat{L}_z D_{xz} = iD_{yz}$
$\hat{L}_x D_{yz} = i\sqrt{3}D_{3z^2-r^2} + iD_{x^2-y^2}$	$\hat{L}_y D_{yz} = iD_{xy}$	$\hat{L}_z D_{yz} = -iD_{xz}$
$\hat{L}_x D_{xy} = iD_{xz}$	$\hat{L}_y D_{xy} = -iD_{yz}$	$\hat{L}_z D_{xy} = -2iD_{x^2-y^2}$
$\hat{L}_x D_{x^2-y^2} = -iD_{yz}$	$\hat{L}_y D_{x^2-y^2} = -iD_{xz}$	$\hat{L}_z D_{x^2-y^2} = 2iD_{xy}$
$\hat{L}_x D_{3z^2-r^2} = -i\sqrt{3}D_{yz}$	$\hat{L}_y D_{3z^2-r^2} = i\sqrt{3}D_{xz}$	$\hat{L}_z D_{3z^2-r^2} = 0$

Spin operators are even simpler (just use s^+ and s^-)…

Introduction:
Spin-orbit coupling (SOC) for t_{2g} - states

$$\hat{H}_{SOC} = \lambda \hat{\vec{l}}\,\hat{\vec{s}}$$

_p_-orbitals

$$\begin{array}{cccccc}
x\uparrow & y\uparrow & z\uparrow & x\downarrow & y\downarrow & z\downarrow
\end{array}$$
$$\left(\begin{array}{ccc|ccc}
0 & -\frac{i\lambda}{2} & 0 & 0 & 0 & \frac{\lambda}{2} \\
\frac{i\lambda}{2} & 0 & 0 & 0 & 0 & -\frac{i\lambda}{2} \\
0 & 0 & 0 & -\frac{\lambda}{2} & \frac{i\lambda}{2} & 0 \\
\hline
0 & 0 & -\frac{\lambda}{2} & 0 & \frac{i\lambda}{2} & 0 \\
0 & 0 & -\frac{i\lambda}{2} & -\frac{i\lambda}{2} & 0 & 0 \\
\frac{\lambda}{2} & \frac{i\lambda}{2} & 0 & 0 & 0 & 0
\end{array}\right)$$

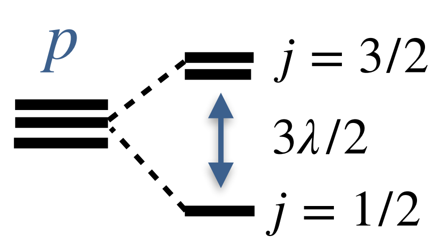
_d_-orbitals

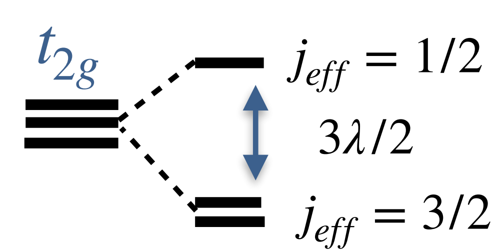
$$\begin{array}{cccccccccc}
yz\uparrow & zx\uparrow & xy\uparrow & 3z^2\uparrow & x^2\text{-}y^2\uparrow & yz\downarrow & zx\downarrow & xy\downarrow & 3z^2\downarrow & x^2\text{-}y^2\downarrow
\end{array}$$
$$\left(\begin{array}{ccccc|ccccc}
0 & \frac{i\lambda}{2} & 0 & 0 & 0 & 0 & 0 & -\frac{\lambda}{2} & -\frac{1}{2}i\sqrt{3}\lambda & -\frac{i\lambda}{2} \\
-\frac{i\lambda}{2} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i\lambda}{2} & \frac{\sqrt{3}\lambda}{2} & -\frac{\lambda}{2} \\
0 & 0 & 0 & 0 & i\lambda & \frac{\lambda}{2} & -\frac{i\lambda}{2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{1}{2}i\sqrt{3}\lambda & -\frac{\sqrt{3}\lambda}{2} & 0 & 0 & 0 \\
0 & 0 & -i\lambda & 0 & 0 & \frac{i\lambda}{2} & \frac{\lambda}{2} & 0 & 0 & 0 \\
\hline
0 & 0 & \frac{\lambda}{2} & -\frac{1}{2}i\sqrt{3}\lambda & -\frac{i\lambda}{2} & 0 & -\frac{i\lambda}{2} & 0 & 0 & 0 \\
0 & 0 & \frac{i\lambda}{2} & -\frac{\sqrt{3}\lambda}{2} & \frac{\lambda}{2} & \frac{i\lambda}{2} & 0 & 0 & 0 & 0 \\
-\frac{\lambda}{2} & -\frac{i\lambda}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i\lambda \\
\frac{1}{2}i\sqrt{3}\lambda & \frac{\sqrt{3}\lambda}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{i\lambda}{2} & -\frac{\lambda}{2} & 0 & 0 & 0 & 0 & 0 & i\lambda & 0 & 0
\end{array}\right)$$

Thus, if $\Delta_{t_{2g}-e_g}$ large enough

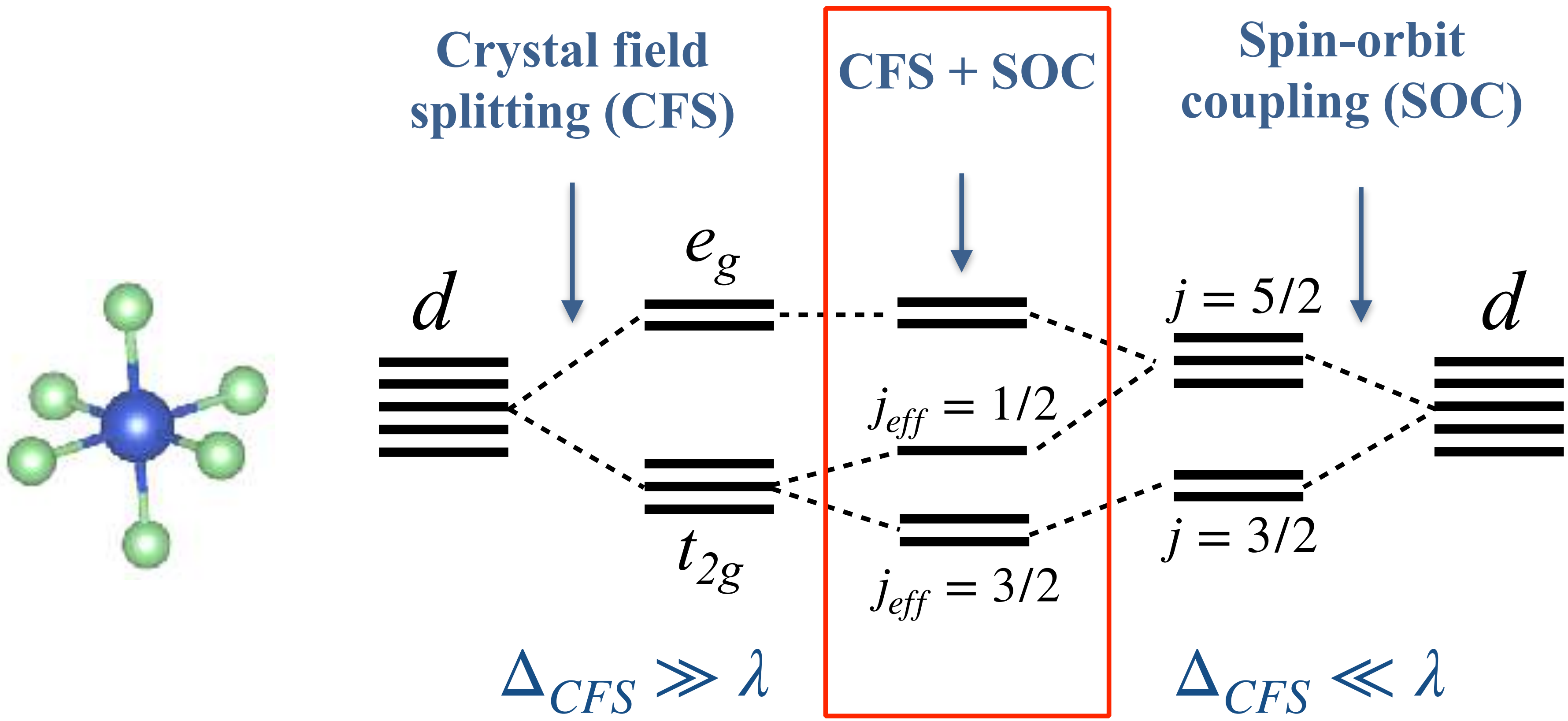
$$\left\{\begin{array}{l} t_{2g} \rightarrow p \\ \lambda \rightarrow \lambda \\ l \rightarrow -l_{eff} \end{array}\right.$$

Heavy transition metals can be described by $l_{eff} = 1$





Introduction:
Spin-orbit coupling and crystal-field splitting



4d-5d **transition metal compounds**

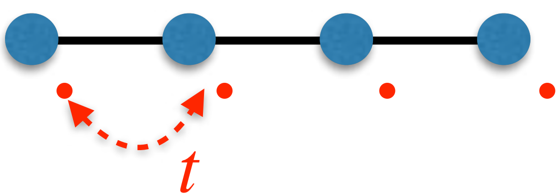
$$l_{eff} = -1 \quad j_{eff} = \{1/2, 3/2\}$$

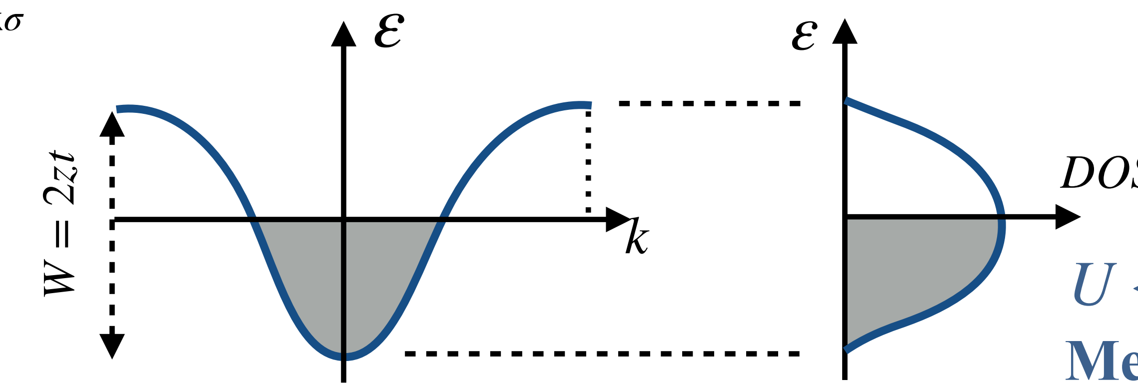
Electronic properties:

Spin-orbit assisted
Mott transition

Mott-Hubbard transition in a nutshell

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

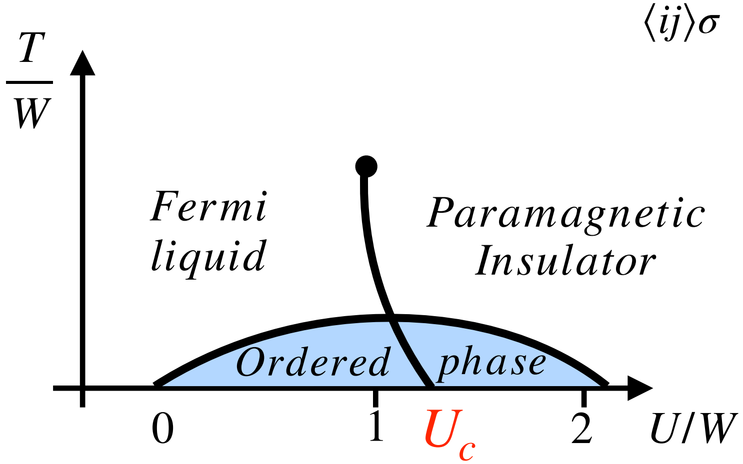




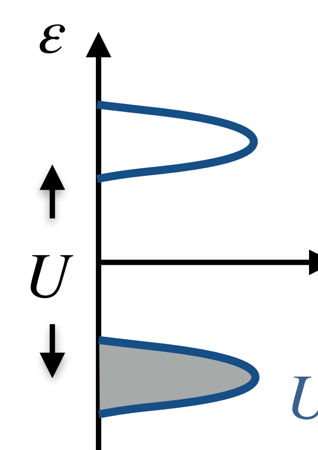
$U \ll W$

Metal

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



Metal-Insulator (Mott-Hubbard) transition!



$U \gg W$

Insulator

U - on-site Coulomb repulsion

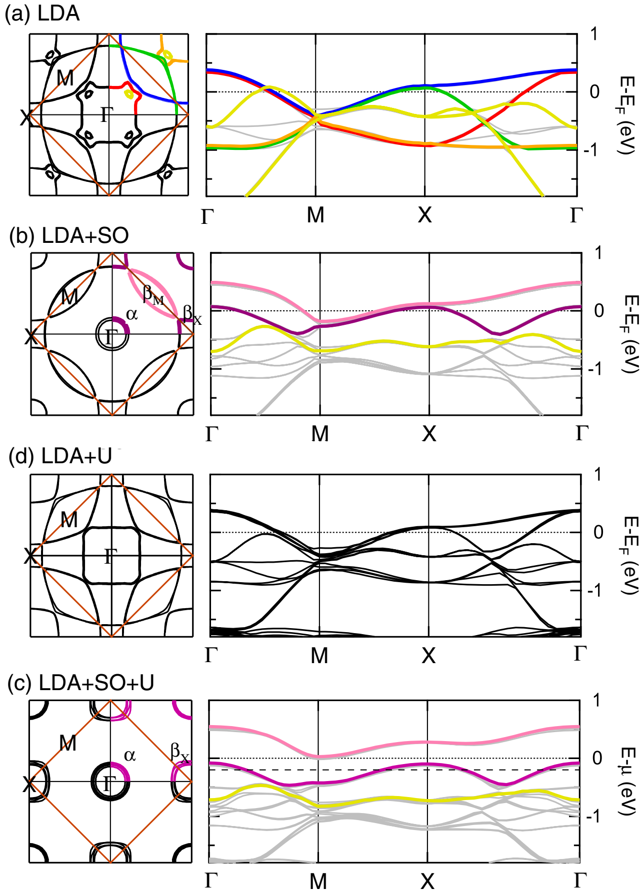
Spin-orbit assisted Mott insulator

U

W, bandwidth

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

Sr_2IrO_4



PRL 101, 76402 (2008)

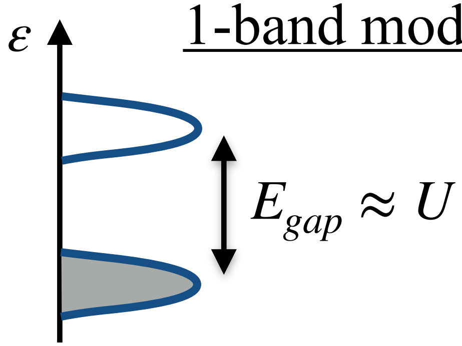
Spin-orbit assisted Mott state!

Other SO-assisted Mott insulators: $\alpha-RuCl_3$, Ba_2NaOsO_6, Ca_2MnReO_6 etc.

Spin-orbit assisted Mott state: What exactly SOC does

1. SOC lifts orbital degeneracy / induces additional splitting

1-band model

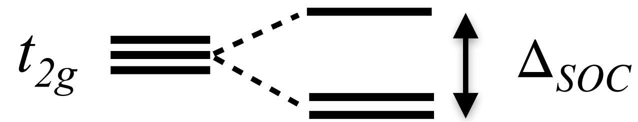


N-band model

$$E_{gap} \approx U - W\sqrt{N}$$

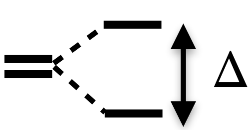
$$U_{c1} \sim \sqrt{N}$$

PRB 54, R11026 (1996)



and thus stimulates metal-insulator transition

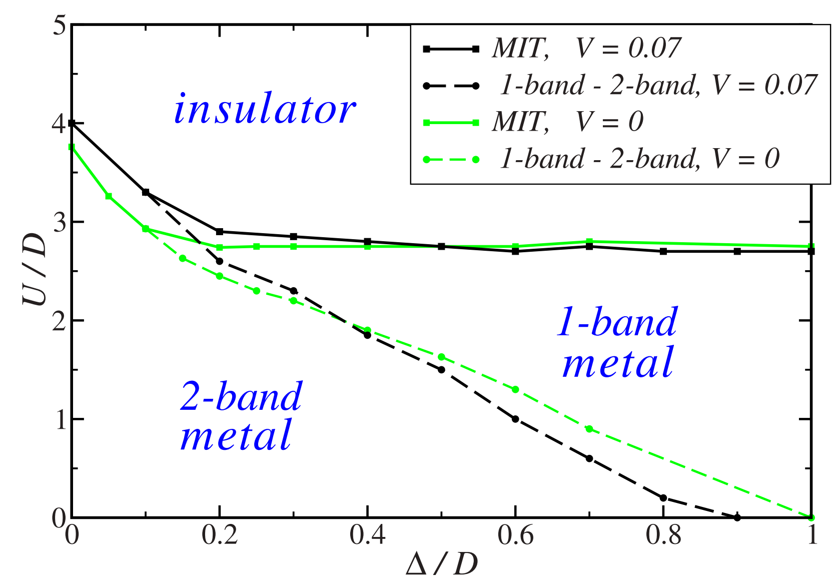
Compare with the crystal-field splitting (Δ):



Crystal-field splitting (Δ) helps metal-insulator transition!

Poteryaev et al., PRB 78, 045115 (2008)

1/4-filled two-band Hubbard model on square lattice

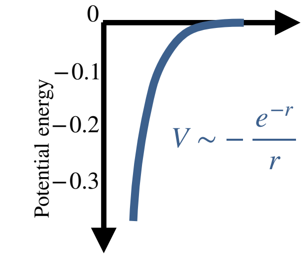


Spin-orbit assisted Mott state:
What exactly SOC does

2. Coulomb correlations effectively increase SOC

Correlation effects make electrons more localized, atomic-like; this is good for SOC

$$\lambda(r) \sim -\frac{1}{r}\frac{\partial V}{\partial r}$$



Sr_2RhO_4: $\lambda = 0.13\, eV$

$$\lambda_{eff} = 2.15\lambda = 0.28\, eV$$

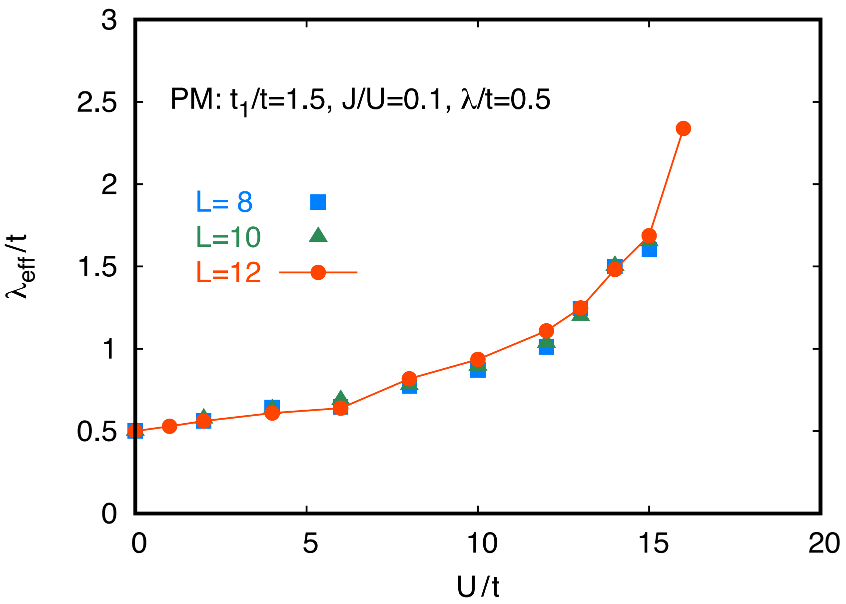
G. Liu et al., PRL 101, 26408 (2008)

<u>Variational Monte Carlo (VMC)</u>

- Two-orbital model (*yz/zx*)
- Square lattice
- quater filling ($n = 1$)

L - square width; $t_1 = dd\pi$

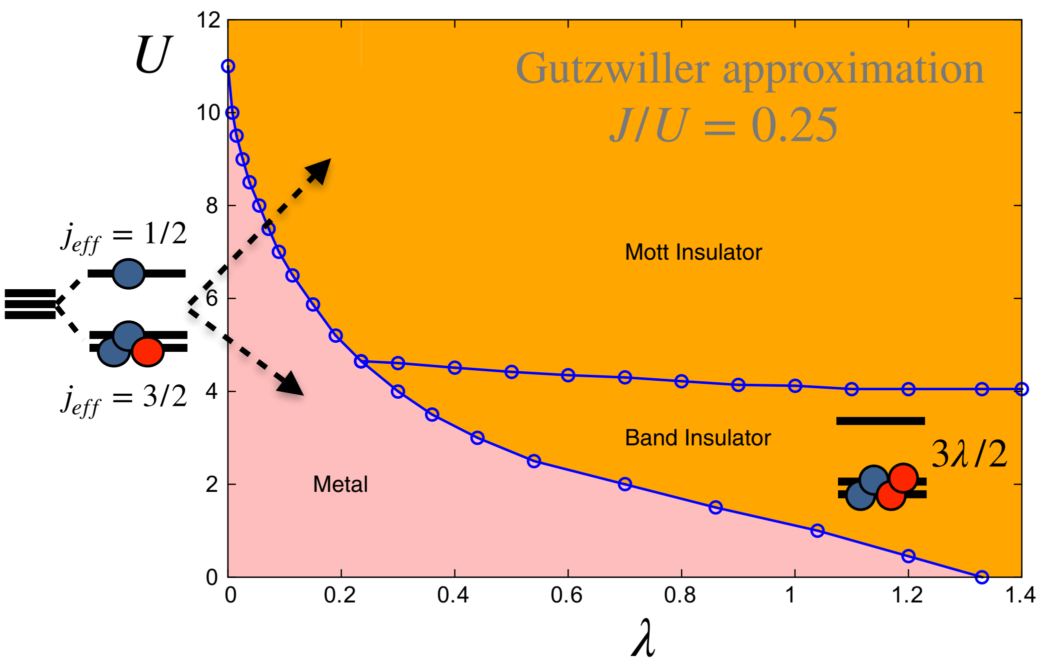
K. Kubo J. Phys. Soc. Jpn. 91, 124707 (2022)



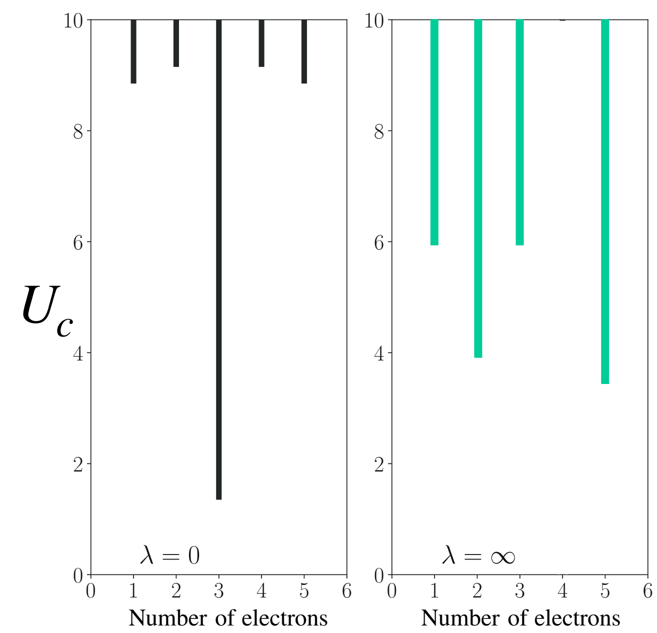
Spin-orbit assisted Mott state:
Model results

Model calculations:
3-bands Hubbard model, Bethe lattice ($D = 1$)

Phase diagram: t_{2g}^4



Critical U_c for
metal-insulator transition



DMFT ($J/U = 0.2$)

L. Du et al., Eur. Phys. J. B. 86, 94 (2013)

R. Triebl et al., PRB 98, 205128 (2018)

Structural properties:

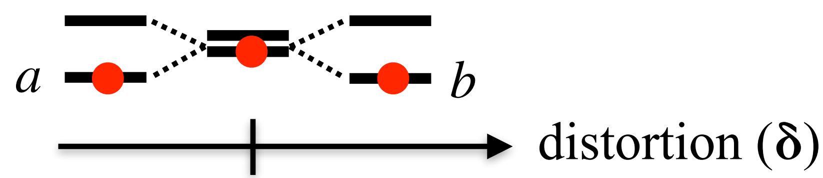
Jahn-Teller effect and

Spin-orbit coupling

Jahn-Teller effect in a nutshell

Idea

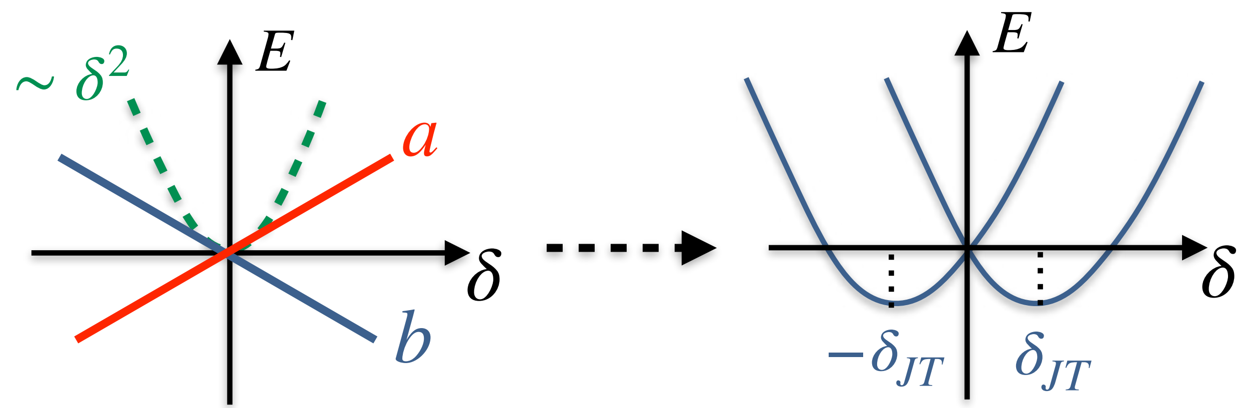
Let's consider a model two-levels (a & b) system in a certain surrounding



$$E_{JT} = \pm g|\delta| + \frac{B\delta^2}{2}$$

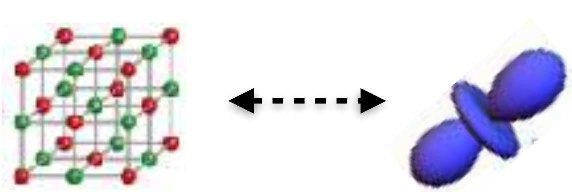
Coupling with lattice

Elastic energy



Thus, a system aims to lift orbital degeneracy by distorting surrounding

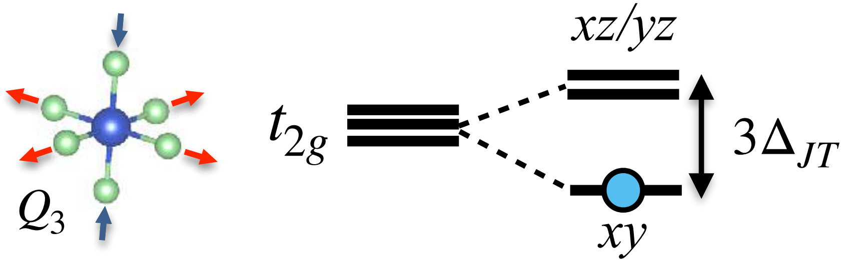
"Orbital-lattice" coupling



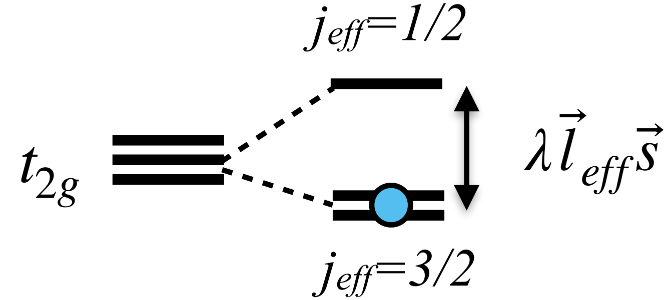
Jahn-Teller effect vs. Spin-orbit coupling

general idea (on example of t_{2g}^1 configuration)

Jahn-Teller effect



Spin-orbit coupling



Wavefunction: $|xy\rangle$

e.g. $\sqrt{\frac{2}{3}}|xy\uparrow\rangle - \frac{1}{\sqrt{6}}i|xz\downarrow\rangle - \frac{1}{\sqrt{6}}|yz\downarrow\rangle$

1. Electrons are on **cubic (real)** harmonics — Electrons are on **spherical** harmonics
2. **Spin-orbit coupling generally counteracts to the Hund's exchange!**

The Jahn-Teller effect and Spin-orbit coupling may compete!
But… Hund's exchange also compete with spin-orbit coupling!

How to solve the Jahn-Teller problem in practice?

$$\hat{H} = \hat{H}_{SOC} + \hat{H}_{elast} + \hat{H}_{JT} + \hat{H}_U$$

Spin-orbit coupling

$$\hat{H}_{SOC} = -\zeta \sum_i \hat{\vec{l}}_i \hat{\vec{s}}_i$$

Interaction between electrons

$$\hat{H}_U = (U - 3J_H)\frac{\hat{N}(\hat{N}-1)}{2} - 2J_H \hat{\mathbf{S}}^2 - \frac{J_H}{2}\hat{\mathbf{L}}^2 + \frac{5}{2}\hat{N}$$

Elastic term classical vibrations

$$\hat{H}_{elast} = \frac{B}{2}\sum_j Q_j^2$$

dynamic+quantum: $\hat{H}_{elast} = \sum_j \hbar\omega_j (a_j^\dagger a_j + \frac{1}{2})$

Coupling to lattice static + classics

$$\hat{H}_{JT}^{t\otimes E} = -g\left(\hat{l}_x^2 - \hat{l}_y^2\right)Q_2 - g\left(\hat{l}_z^2 - 2/3\right)Q_3$$

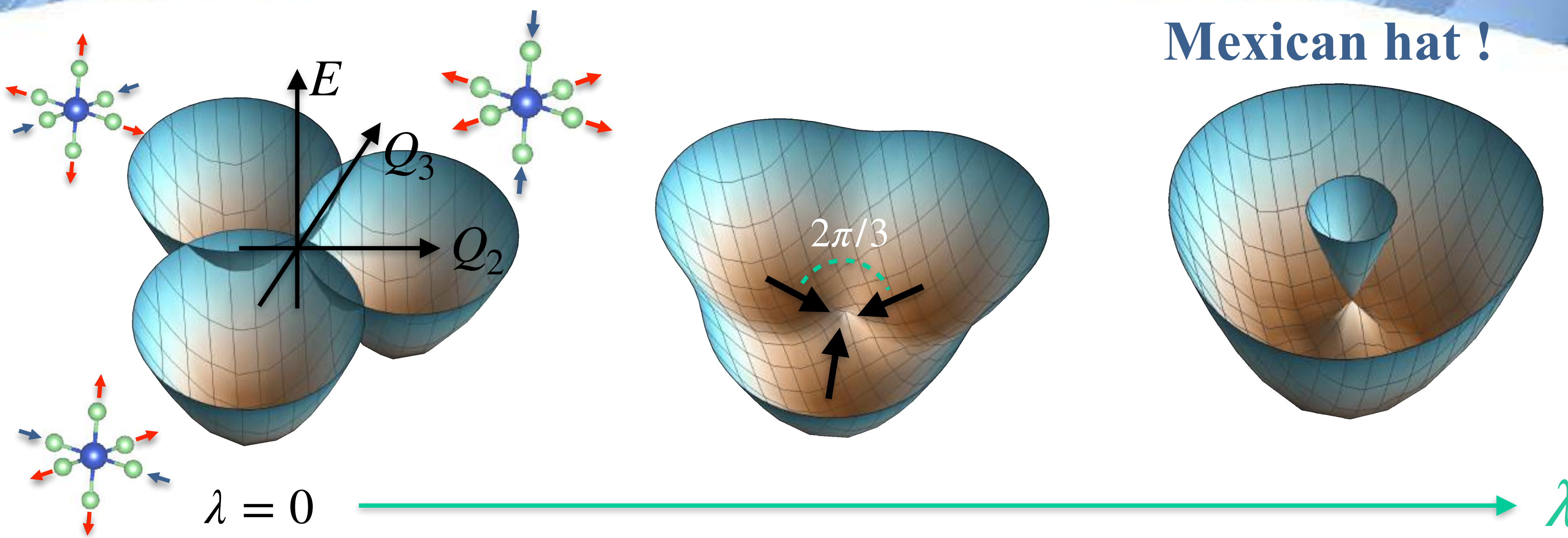
dynamic+quantum

$$\hat{H}_{JT}^{t\otimes E} = -\frac{g}{\sqrt{2\hbar\omega}}\left(\hat{l}_x^2 - \hat{l}_y^2\right)(a_2 + a_2^\dagger) - \frac{g}{\sqrt{2\hbar\omega}}\left(\hat{l}_z^2 - 2/3\right)(a_3 + a_3^\dagger)$$

Technique: **Exact diagonalization**

The Jahn-Teller effect vs. SOC: *d^1*

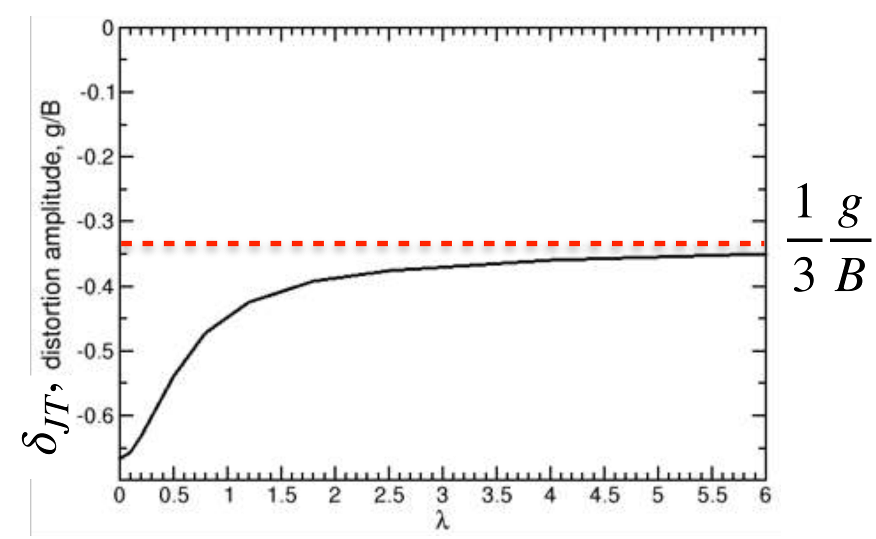
suppression of JT distortions



Details: Exact diagonalization, $T \otimes e$ problem (no dynamic effects)

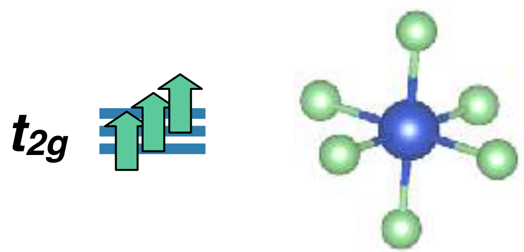
Examples: <u>Compression is tiny:</u> Cs_2TaCl_6, Rb_2TaCl_6 etc.

<u>Seems undistorted:</u> Ba_2NaOsO_6, Ba_2MgReO_6 etc



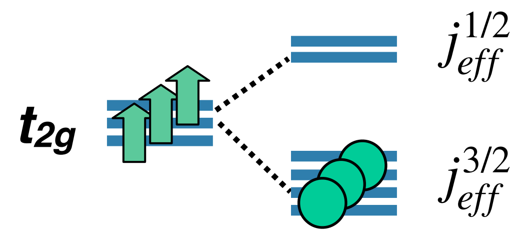
The Jahn-Teller effect vs. SOC: d^3
increase of JT distortions

JT effect ($\lambda = 0$)

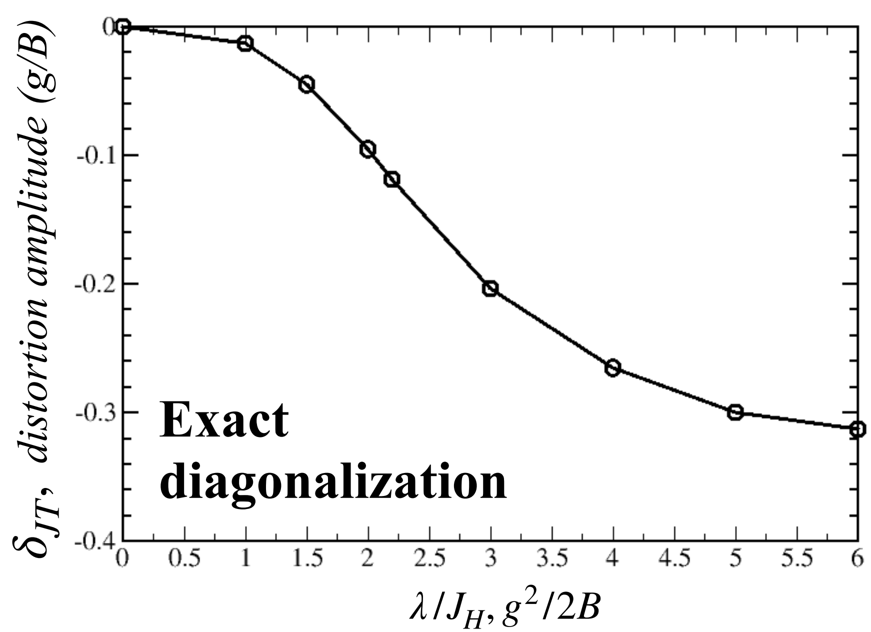


No Jahn-Teller distortions

SOC ($\lambda \rightarrow \infty$)

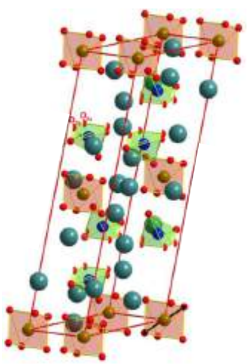


Jahn-Teller active!

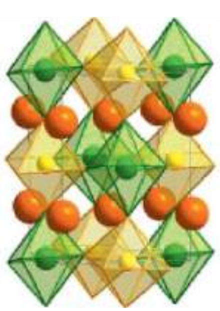


Spin-orbit coupling induces Jahn-Teller distortions (compression)!

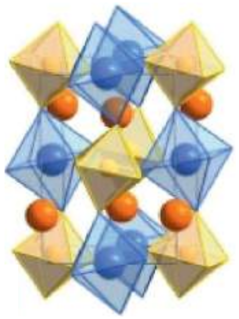
$Ba_8Al_2IrO_{14}$



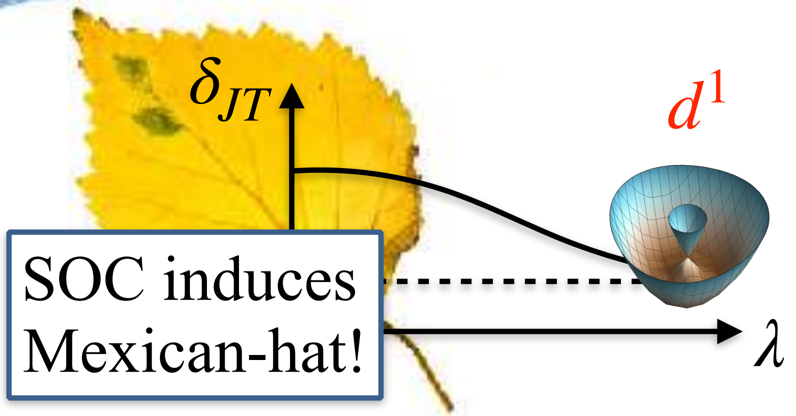
Sr_2MgIrO_6

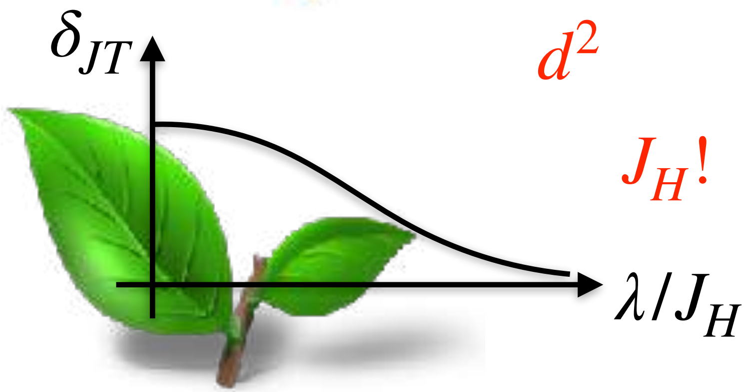


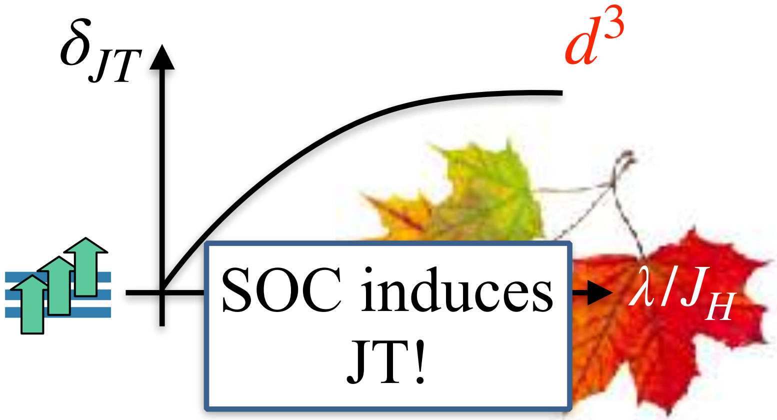
Sr_2CaIrO_6

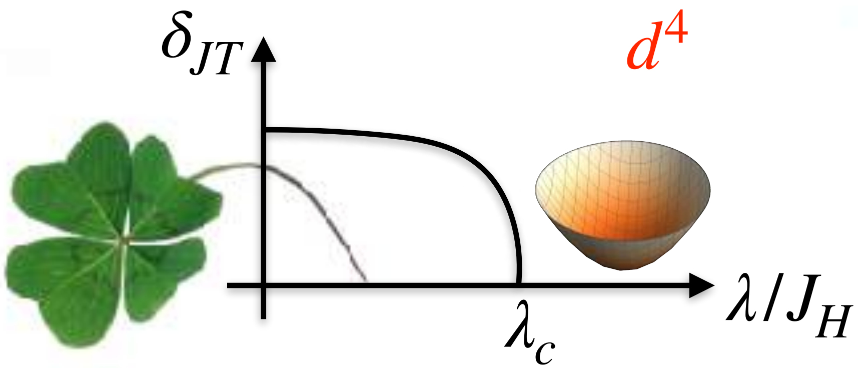


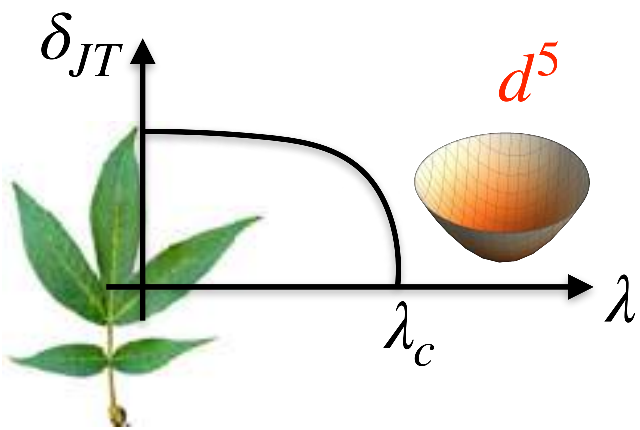
Botany of the Jahn-Teller effect











*S.S., Khomskii PRX **10**, 031043 (2020)*

*S.S., Temnikov, Kugel, Khomskii PRB **105**, 205142 (2022)*

*K. Warren Comp. Chem.: Structure and Bonding, **57**, 119 (1982)*

Magnetic properties:

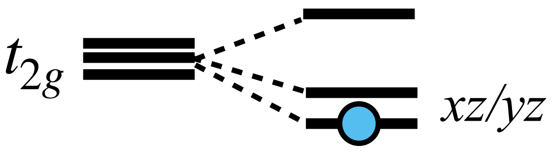
Higher order multipoles

Spin-orbit coupling and d^1 configuration

<u>Weak SOC</u>

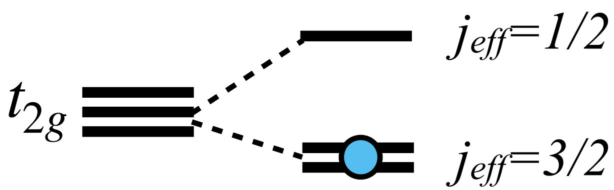
Orbital moment is quenched, $S = 1/2 \Longrightarrow M = 2S = 1\mu_B$

Example: $YTiO_3$ ($M = 0.84\mu_B$)



<u>Strong SOC (wrt non-cubic field)</u>

$p - t_{2g}$ equivalence: $p \rightarrow t_{2g}$, $l \rightarrow -l_{eff}$



Mag. mom: $M = 2S - l_{eff}$

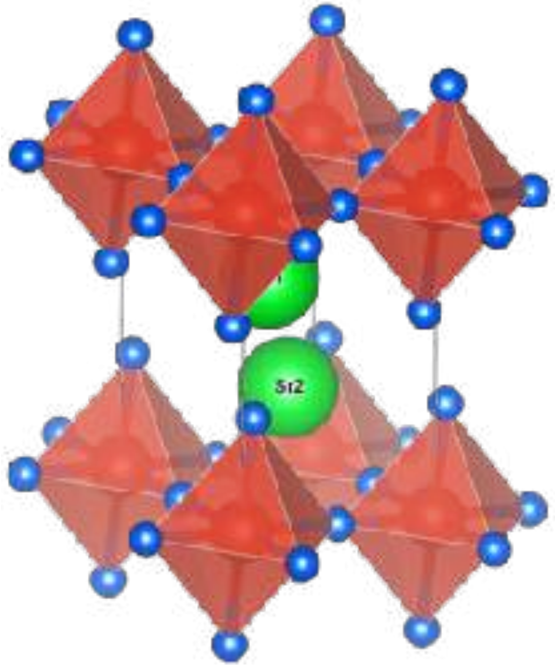
$S = 1/2, l_{eff} = 1 \Longrightarrow M = 0$

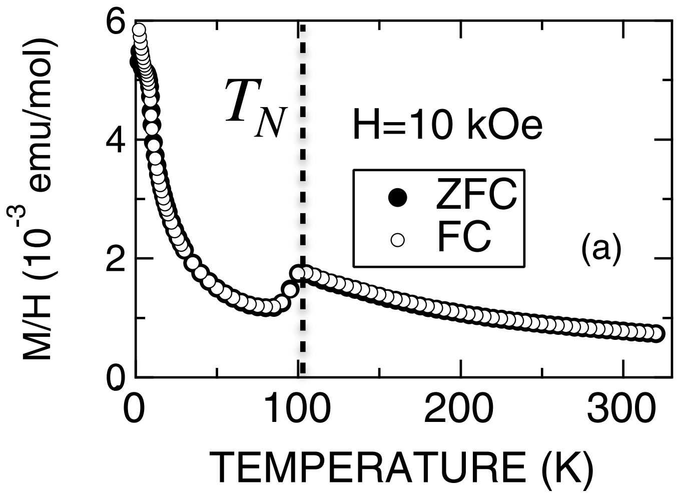
No local magnetic moment!

Any examples (materials)?

Strong spin-orbit coupling and d^1

Sr_2VO_4: V^{4+} ($3d^1$)





PRB 89, 020402 (2014)

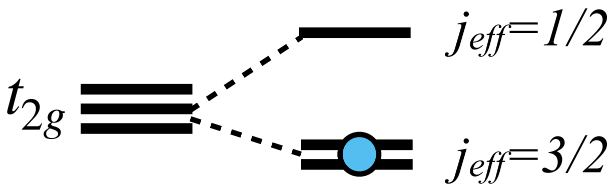
Jackeli and Khaliullin PRL 103, 067205 (2009)

Eremin et al., PRB 84, 212407 (2011)

<u>Neutrons:</u> did NOT find magnetic contributions for $T < T_N$ — *JSSC 85, 321 (1990)*

<u>μ^+SR:</u> some AFM for $T < 8K$ — *PRB 92, 064408 (2015)*

λ for *3d* ions is typically small…



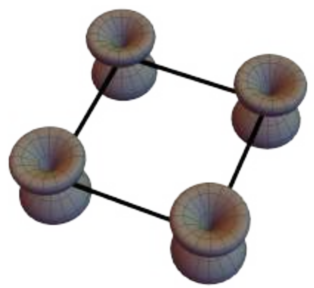
$M = 0$?

What is going on at 100K?
What is being ordered if magnetic moment is zero?

3-band Hubbard model with 1 electron on the square lattice (= Sr_2VO_4)

Dipoles

$$\langle S\rangle = \langle L\rangle = 0$$

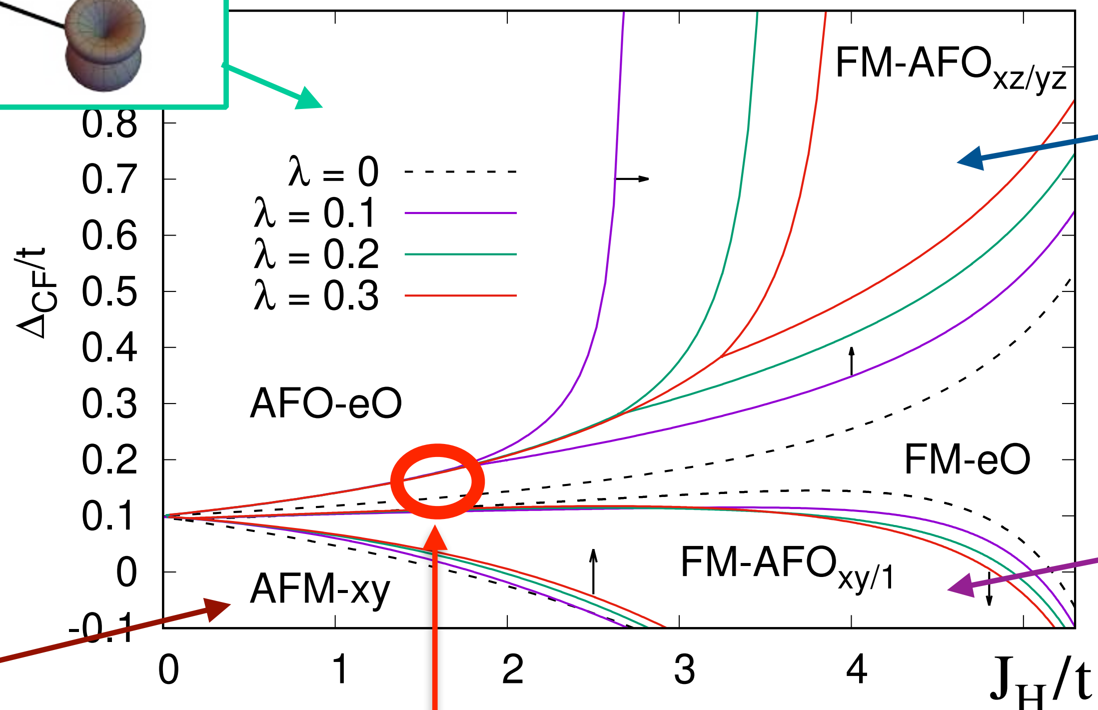


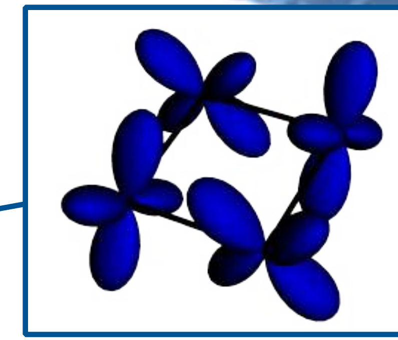
Octupoles

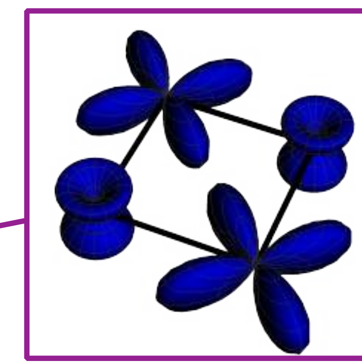
$$\langle T_x^\alpha\rangle \neq 0,\ \langle T_x^\beta\rangle \neq 0$$

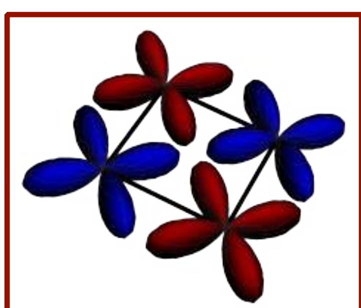
$$T_x^\alpha = J_x^3 - \frac{1}{2}(\overline{J_xJ_y^2} + \overline{J_z^2J_x})$$

$$T_x^\beta = \frac{\sqrt{15}}{6}(\overline{J_xJ_y^2} - \overline{J_z^2J_x})$$









Realistic parameters for Sr_2VO_4

Magnetic octupoles might order!!!

xy

$\Delta_{CF} > 0$

xz/yz

P. Igoshev, V. Irkhin, S.S. arXiv:2406.07386

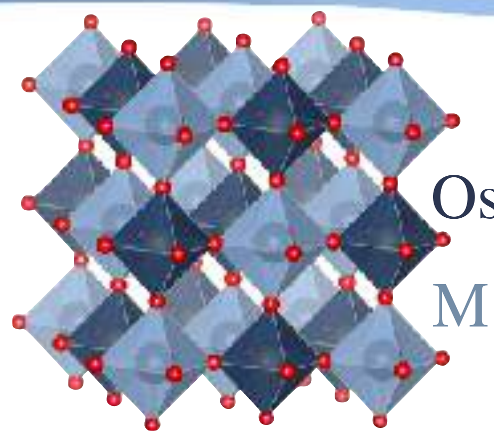
Strong spin-orbit coupling and d^2

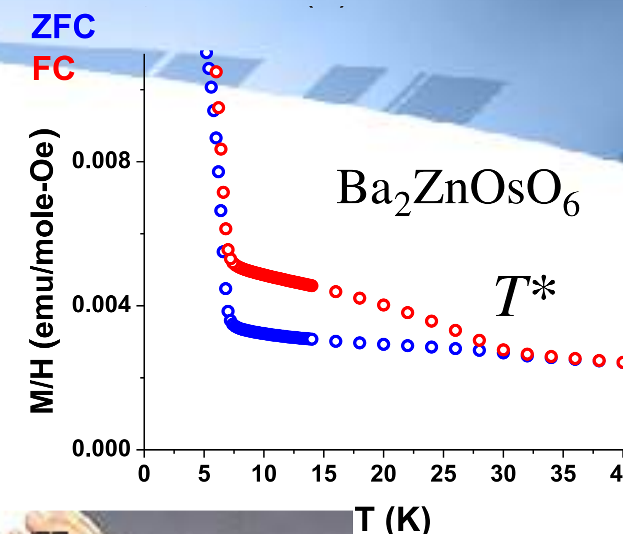
$Ba_2(Zn,Mg,Ca)OsO_6$

Naively $S = 1 \Longrightarrow M = 2\mu_B$

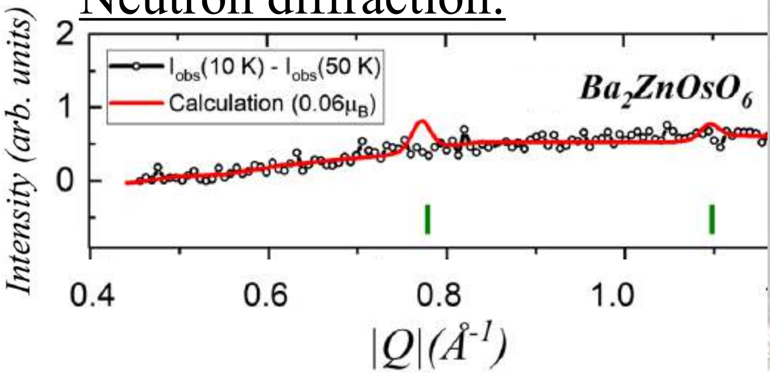
<u>Structure</u>: $Fm\bar{3}m$ (any T!)

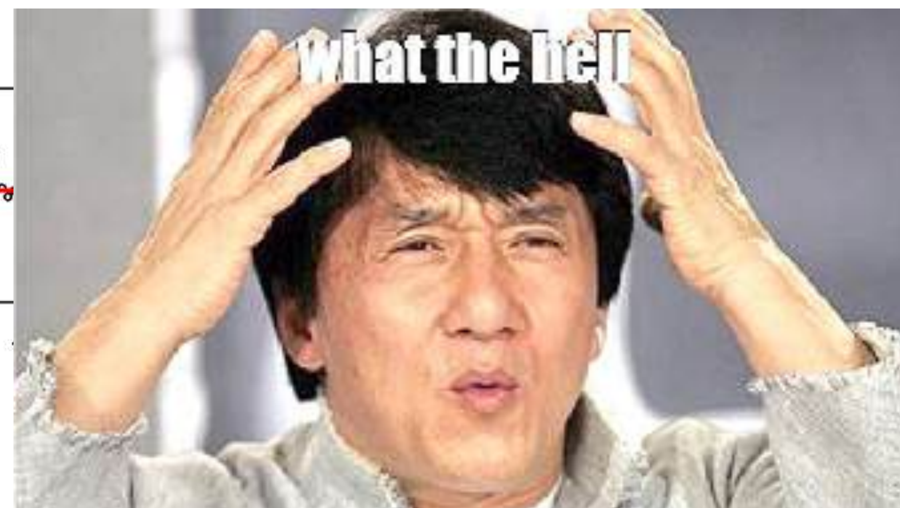
Jahn-Teller effect???

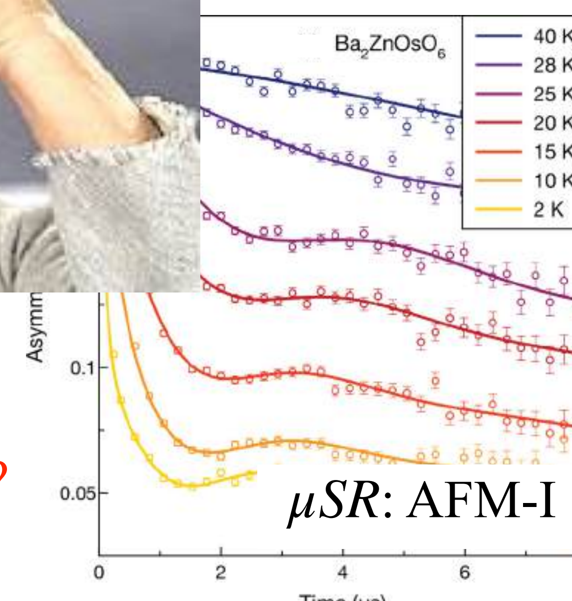




<u>Neutron diffraction:</u>







System	T^*	θ_{CW}	μ_{ord}
Ba_2CaOsO_6	49	$-156.2(3)$	$<0.13\ \mu_B$
Ba_2MgOsO_6	51	$-120(1)$	$<0.11\ \mu_B$
Ba_2ZnOsO_6	30	$-149.0(4)$	$<0.06\ \mu_B$

Magnetic moments???

No Bragg peaks for AFM-I ???

μSR: AFM-I

PRB 94, 134429 (2016), PRL 124, 087206 (2020)

Magnetic properties:
Kitaev model
and Kitaev materials

Kitaev interaction: all new is well-forgotten old

(simplified) Heisenberg model:

$$\hat{H} = \sum_{i>j} J_{ij} \hat{\vec{S}}_i \hat{\vec{S}}_j \longrightarrow$$

Heisenberg model:

$$\hat{H} = \sum_{i>j} \hat{\vec{S}}_i \begin{pmatrix} J^{xx} & J^{xy} & J^{xz} \\ J^{yx} & J^{yy} & J^{yz} \\ J^{zx} & J^{zy} & J^{zz} \end{pmatrix}_{ij} \hat{\vec{S}}_j$$

Spin-orbit coupling

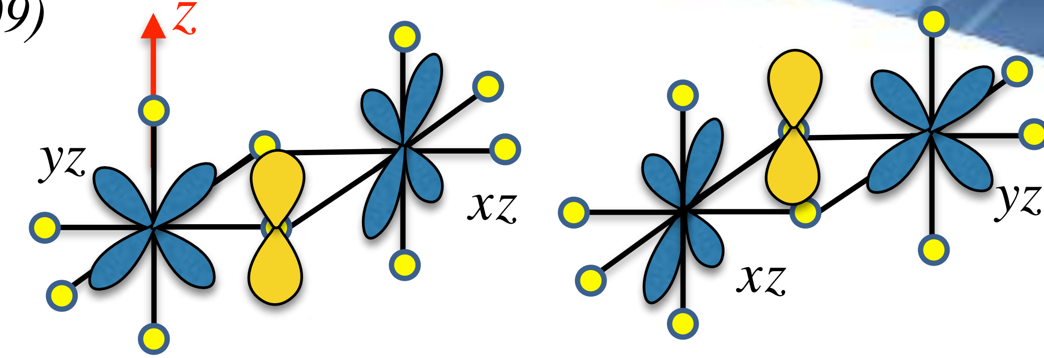
- Symmetric anisotropic exchange
- Dzyaloshinskii-Morya
- Single-ion anisotropy

Ising model, Kitaev model …

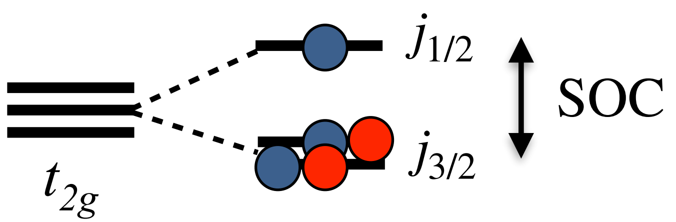
Alexei Kitaev = Алексей Китаев

$j_{eff} = 1/2$ + Common edge + ligand hopping = Kitaev exchange

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



Let
1) Configuration t_{2g}^5
2) SOC is strong
3) Common edge geometry
4) Ligand-assisted hoppings **<u>only</u>**



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

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

Superexchange: $$H = \sum_{i>j} J_{ij}\hat{\vec{S}}_i\hat{\vec{S}}_j \qquad J \sim \frac{t^2}{U}$$

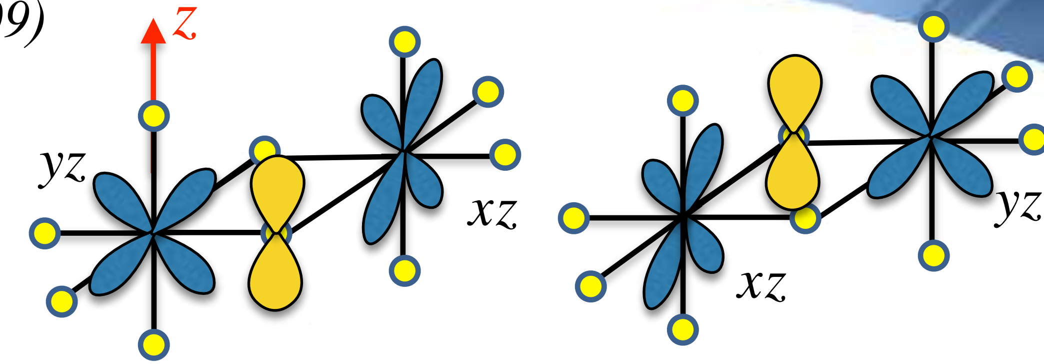
but $\langle j^z_{1/2,a}|\hat{t}|j^z_{-1/2,b}\rangle = \langle j^z_{-1/2,a}|\hat{t}|j^z_{1/2,b}\rangle = 0$

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

NO conventional AFM superexchange!

j_{eff} = 1/2 + Common edge + ligand hopping = Kitaev exchange

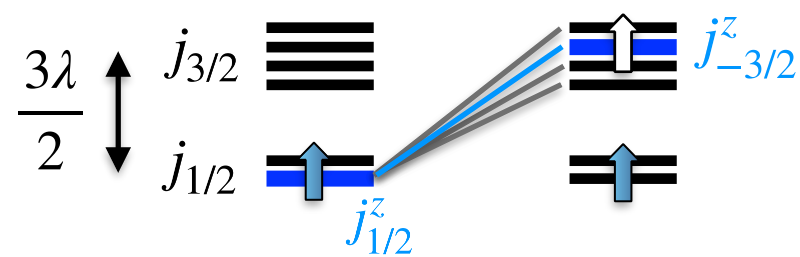
G. Jackeli, G. Khaliullin, PRL 102, 17205 (2009)



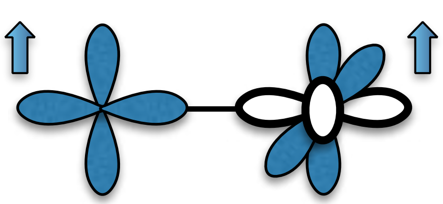
Let

1) Configuration t_{2g}^5
2) SOC is strong
3) Common edge geometry
4) Ligand-assisted hoppings **only**

Next order: Hoppings to empty orbitals
(in hole representation)



Analogue of



$$\boxed{\hat{H}_{ij} = KJ_i^zJ_j^z \rightarrow JS_i^zS_j^z}$$

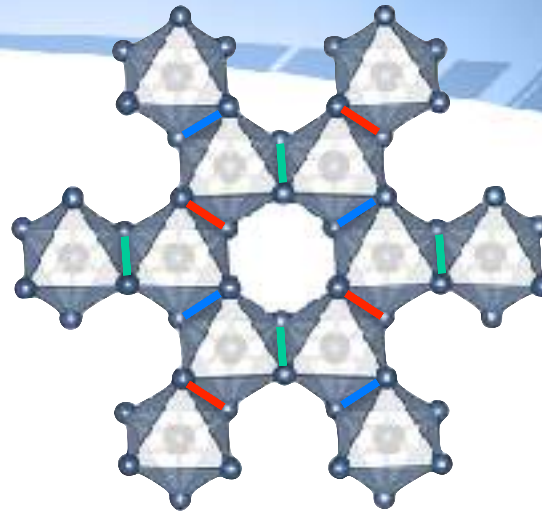
$z \perp$ basal plane

Exchange between
half-filled/empty orbitals

$$K \sim -\frac{\tilde{t}_{dd}^2 J_H}{U^2} < 0$$

Bond-dependended anisotropic exchange

Possible candidates for Kitaev physics (1st generation)



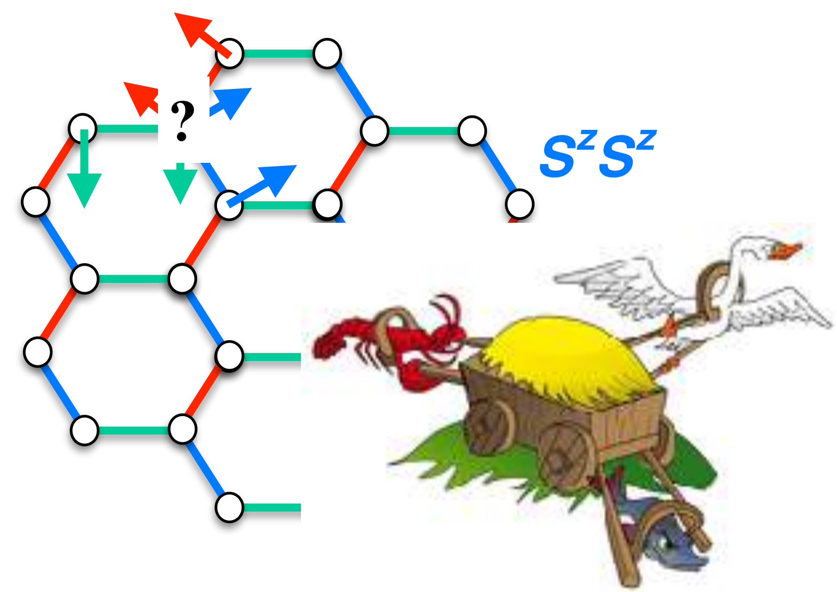
1) Configuration t_{2g}^5
2) Common edge geometry
3) Ligand-assisted hoppings
4) SOC is strong

Na_2IrO_3

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

Kitaev model $$\hat{H} = -\sum_{\langle ij\rangle_\gamma} K_\gamma \hat{S}_i^\gamma \hat{S}_j^\gamma$$

Kitaev Ann. Phys. 321, 2 (2006)



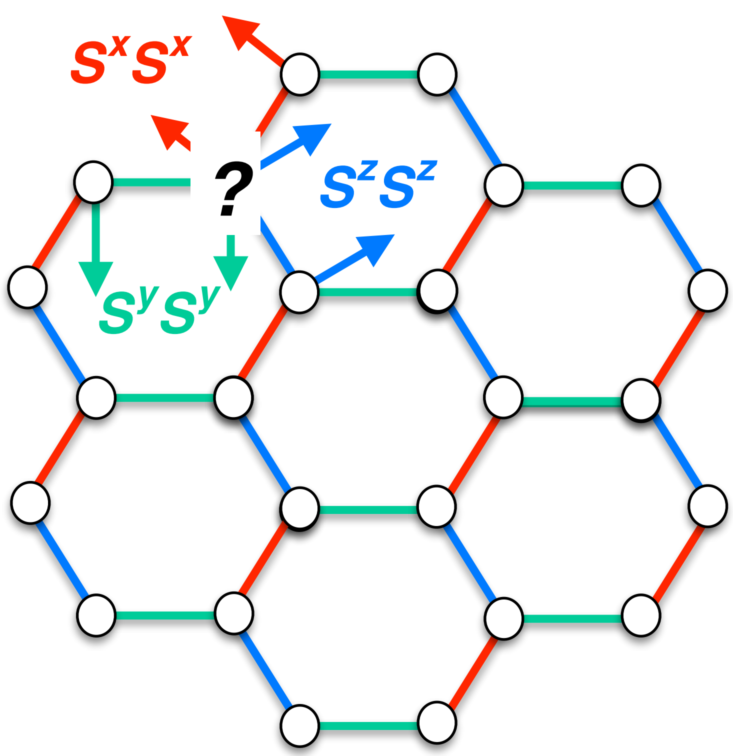
- **Exactly solvable**
- **Highly frustrated model**
- **Quantum spin-liquid (based on Ising model)**
- **Fractionalized excitations (Majoranas)**

Kitaev materials (1st generation): Na_2IrO_3 α-Li_2IrO_3 Li_2RhO_3 α-$RuCl_3$

Kitaev model: classical variant

$$H = -K_x \sum_{x\ \text{bonds}} S_i^x S_j^x - K_y \sum_{y\ \text{bonds}} S_i^y S_j^y - K_z \sum_{z\ \text{bonds}} S_i^z S_j^z = -\sum_{\langle ij \rangle_\gamma} K_\gamma S_i^\gamma S_j^\gamma$$

$$\gamma = \{x, y, z\}$$



Features of classical Kitaev model

- Spins are strongly frustrated
- Spins can't order even at $T = 0$

1982 г. Апрель Том 136, вып. 4

УСПЕХИ ФИЗИЧЕСКИХ НАУК

ЭФФЕКТ ЯНА—ТЕЛЛЕРА И МАГНЕТИЗМ: СОЕДИНЕНИЯ ПЕРЕХОДНЫХ МЕТАЛЛОВ

К. И. Кугель, Д. И. Хомский

$$H = J \Big(\sum_{\langle i,\, j \rangle_x} \tau_i^x \tau_j^x + \sum_{\langle i,\, j \rangle_x} \tau_i^y \tau_j^y + \sum_{\langle i,\, j \rangle_z} \tau_i^z \tau_j^z \Big), \qquad (34)$$

где символ $\langle i,\ j \rangle_{x,\ y,\ z}$ обозначает пары i, j, расположенные по осям x, y

Majorana fermions

(Dirac) fermions: a and $a^\dagger$

Majorana fermions (majoranas)

$$c_1 = a + a^\dagger \qquad c_2 = -i(a - a^\dagger) \longrightarrow c_1^\dagger = a^\dagger + a = c_1 \qquad c_2^\dagger = i\left(a - a^\dagger\right)^\dagger = -i\left(a - a^\dagger\right) = c_2$$

Majoranas:

(1) $c^\dagger = c$

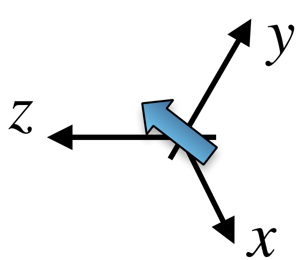
(2) $c^2 = 1$

(3) $c_j c_i = -c_i c_j$ if $j \neq i$

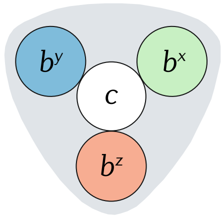
Spins can be expressed be expressed via two (conventional) fermions: $a, a^\dagger$

$$\hat{\vec{S}}_i = \frac{1}{2} \sum_{\sigma\sigma'} a_{i\sigma}^\dagger \vec{\sigma}_{\sigma\sigma'} a_{i\sigma'}, \qquad \sigma, \sigma' = \uparrow, \downarrow$$

Spin operators can be expressed* via four majoranas: b^x, b^y, b^z, c



$$\xrightarrow{S_i^\gamma = \frac{i}{2} b_i^\gamma c_i}$$



*commutation relations for Pauli matrixes are conserved, if additional constraint $b^x b^y b^z c = 1$ is applied

Kitaev model: quantum case

Kitaev model via majoranas
$$\hat{H} = -\sum_{\langle ij\rangle_\gamma} K_\gamma \hat{S}_i^\gamma \hat{S}_j^\gamma = \frac{1}{4}\sum_{\langle ij\rangle_\gamma} K_\gamma \overbrace{b_i^\gamma b_j^\gamma}^{u_{ij}} c_i c_j = \frac{1}{4}\sum_{\langle ij\rangle_\gamma} K_\gamma u_{ij}^\gamma c_i c_j,$$

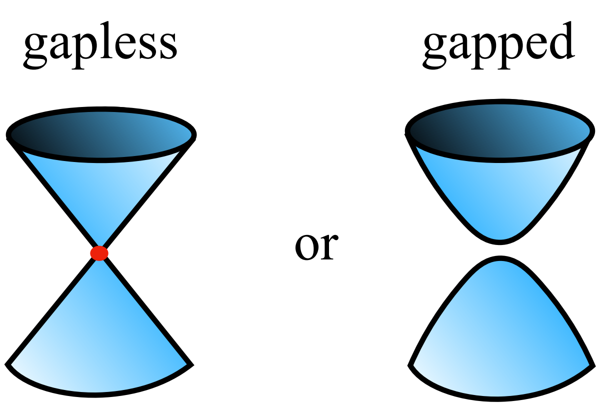
Quadratic form! Readily diagonizable if u_{ij}^γ were numbers. Non-interacting c majoranas?

$$u_{ij}^\gamma u_{ij}^\gamma = b_i^\gamma b_j^\gamma b_i^\gamma b_j^\gamma = -1 \Rightarrow \quad u_{ij}^\gamma = \pm i$$

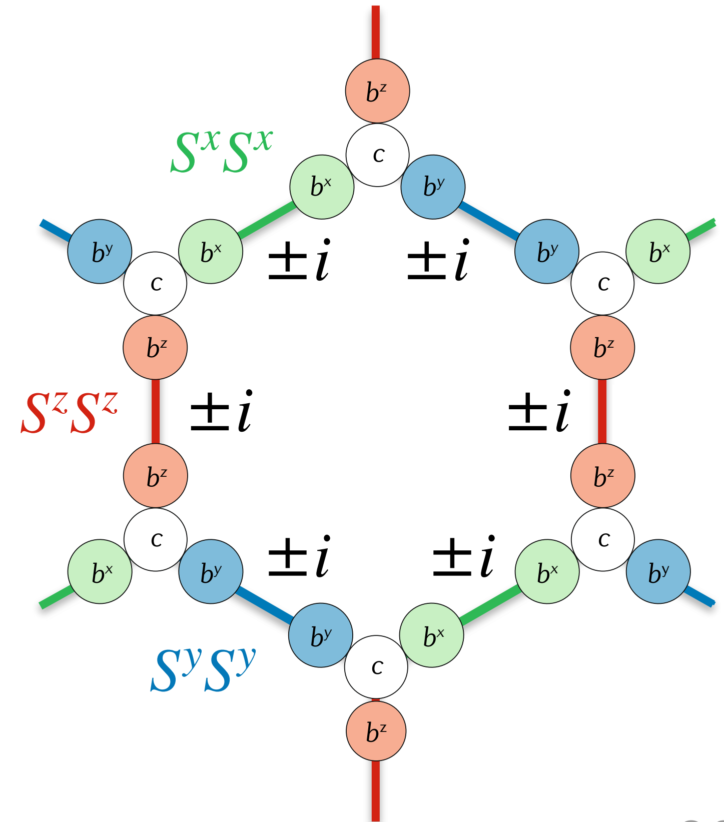
Flux: $W_p = u_{12}u_{23}u_{34}u_{45}u_{56}u_{61} = \pm 1$

One can show numerically or analytically that the ground state corresponds to $W_p = +1$ on all hexagons

Spectrum:



Kitaev Ann. Phys. 321, 2 (2006)

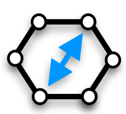


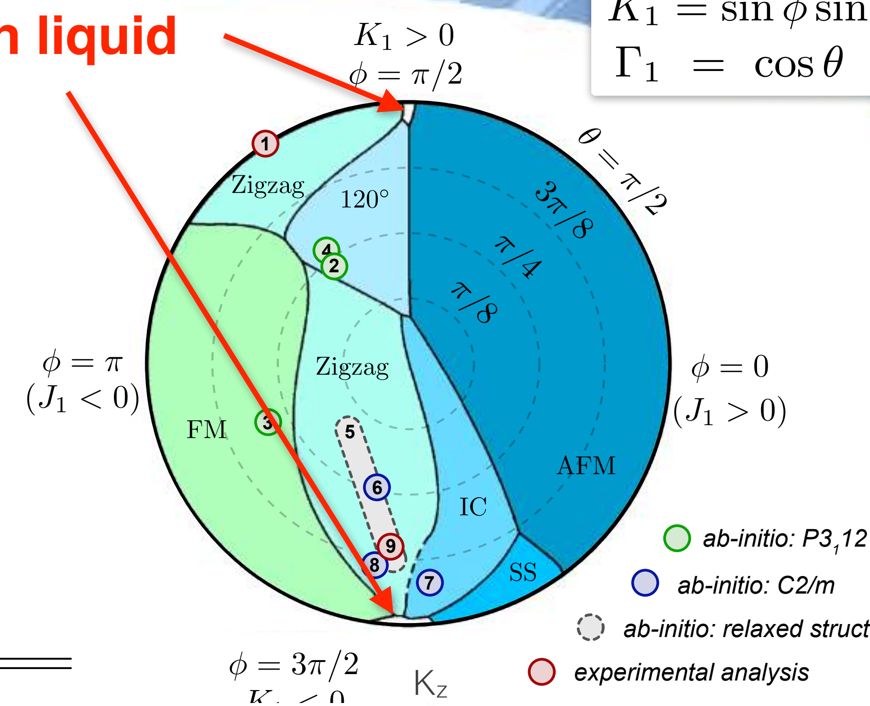
Possible candidates for Kitaev physics
(1^{st} generation)

$$
\begin{aligned}
J_1 &= \cos\phi \sin\theta \\
K_1 &= \sin\phi \sin\theta \\
\Gamma_1 &= \cos\theta
\end{aligned}
$$

Kitaev-Heisenberg model

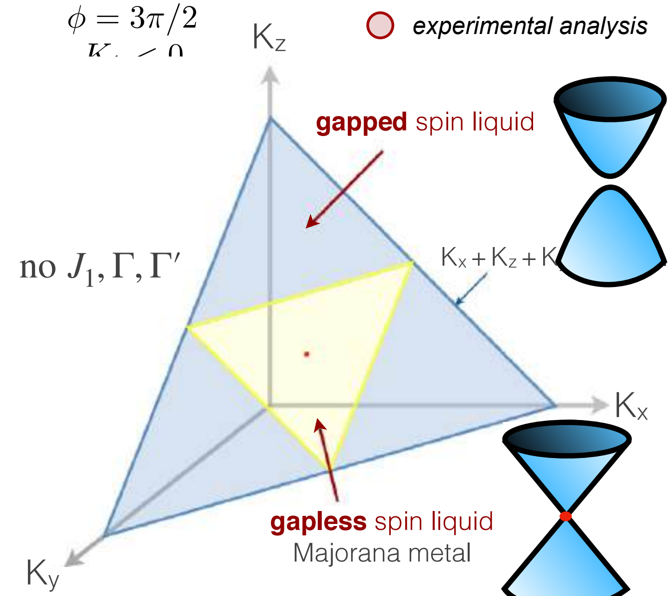
$$\mathcal{H}_{ij} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + K_{ij}\ S_i^\gamma S_j^\gamma + \Gamma_{ij}\left(S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha\right)$$
$$+\Gamma'_{ij}\left(S_i^\gamma S_j^\alpha + S_i^\gamma S_j^\beta + S_i^\alpha S_j^\gamma + S_i^\beta S_j^\gamma\right)$$

What about J_3? 



Experimental results

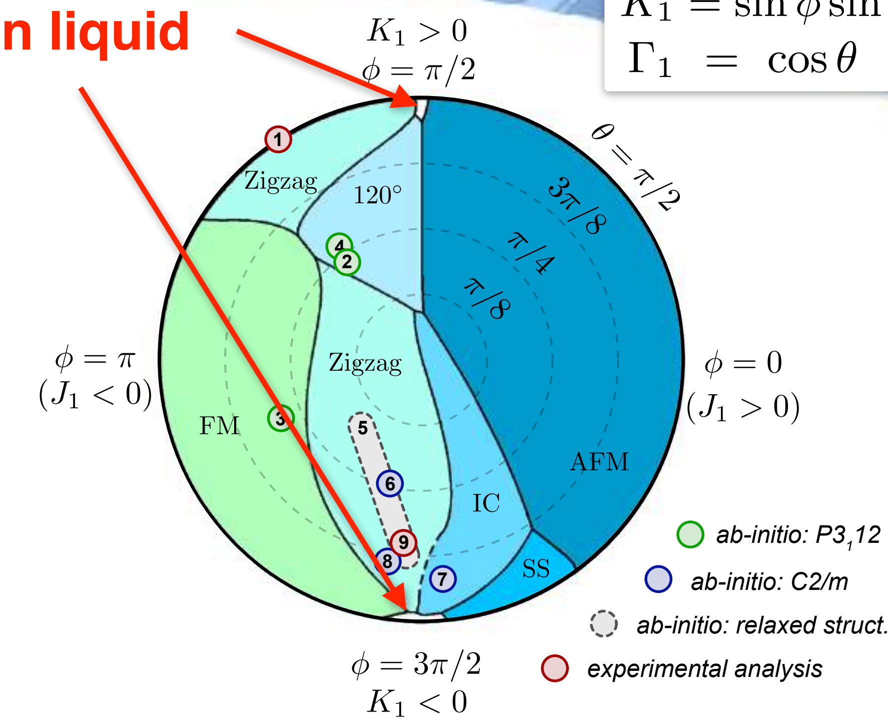
Property	Na_2IrO_3	α-Li_2IrO_3	Li_2RhO_3	α-$RuCl_3$
$\mu_{\text{eff}}\ (\mu_B)$	1.79	1.83	2.03	2.0 to 2.7
Θ_{iso} (K)	~ -120	-33 to -100	~ -50	$\sim +40$
Θ_{ab} (K)	-176	$\Theta_{ab} > \Theta_c$	–	+38 to +68
Θ_c (K)	-40	–	–	-100 to -150
T_N (K)	$13-18$	~ 15	(6)	7 to 14
Order	Zigzag	Spiral	Glassy	Zigzag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



Possible candidates for Kitaev physics
(1st generation)

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

Spin liquid



Kitaev-Heisenberg model

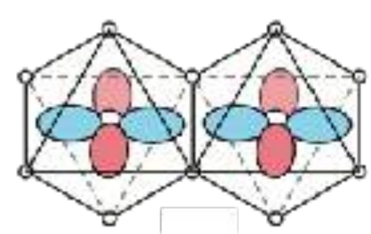
$$\mathcal{H}_{ij} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + K_{ij}\ S_i^\gamma S_j^\gamma + \Gamma_{ij}\left(S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha\right)$$
$$+ \Gamma'_{ij}\left(S_i^\gamma S_j^\alpha + S_i^\gamma S_j^\beta + S_i^\alpha S_j^\gamma + S_i^\beta S_j^\gamma\right)$$

$$H_{ij} = \vec{S}_i \begin{array}{c} \begin{array}{ccc} x & y & z \end{array} \\ \begin{pmatrix} J & \Gamma & \Gamma' \\ \Gamma & J & \Gamma' \\ \Gamma' & \Gamma' & J+K \end{pmatrix}_{ij} \end{array} \vec{S}_j$$

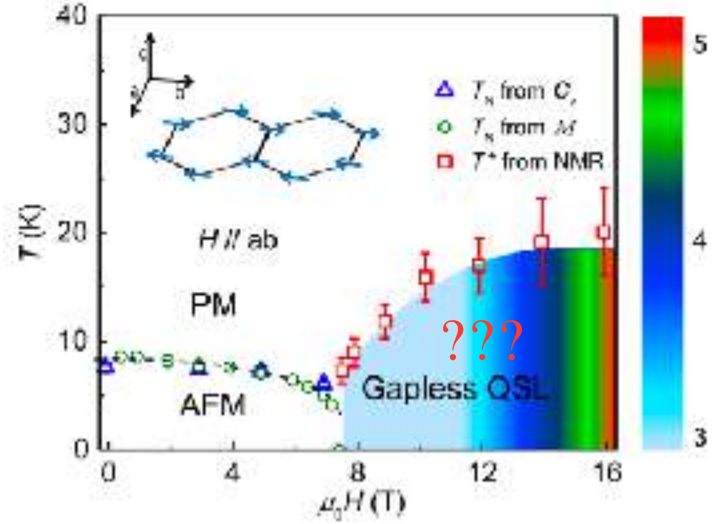
α-$RuCl_3$ $\quad T_N = 7K$

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

Why is Heisenberg J_1 (isotropic exchange with nearest neighbors) so large?



Field-induced phenomena in α-RuCl$_3$



AFM is destroyed by in-plane magnetic field

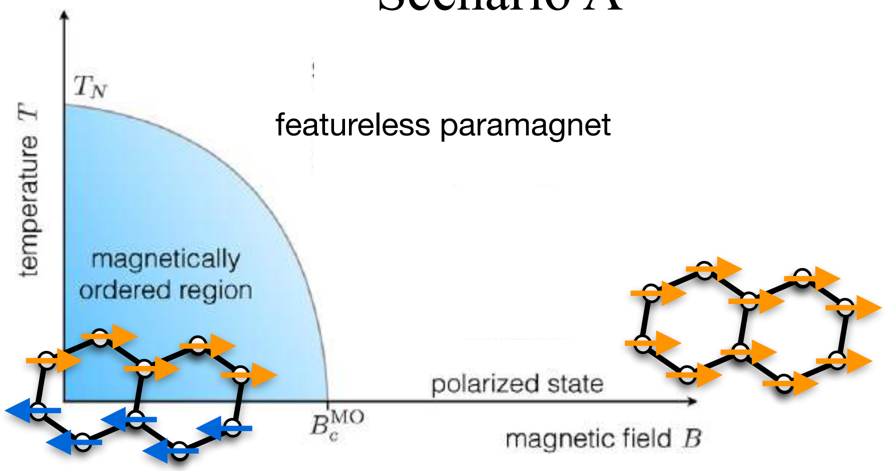
*J. Zheng et al., PRL **119**, 227208 (2017)*

*S.-H. Baek et al., PRL **119**, 37201 (2017)*

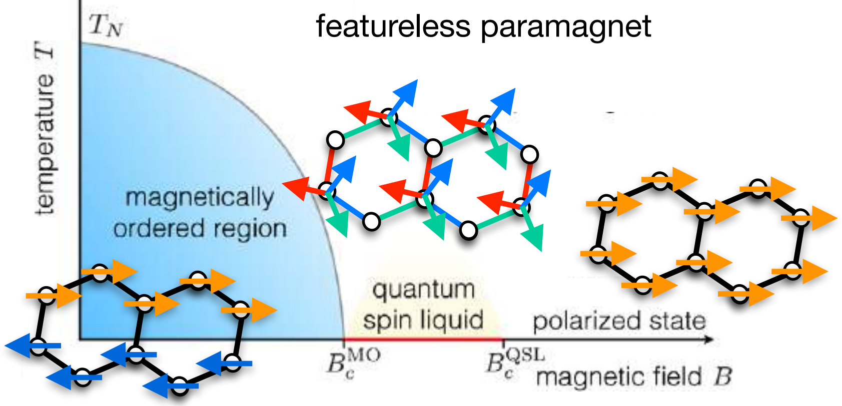
*A. Banerjee et al., NPJ Quantum Mater. **3**, 8 (2018)*

Two possible scenarios: highly debated; no final answer yet

Scenario A

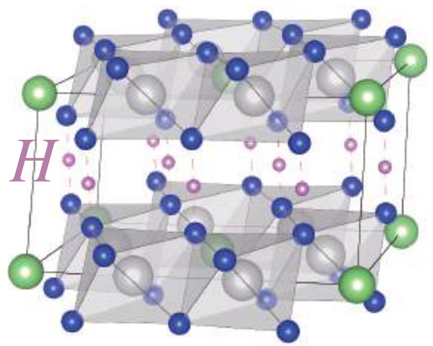


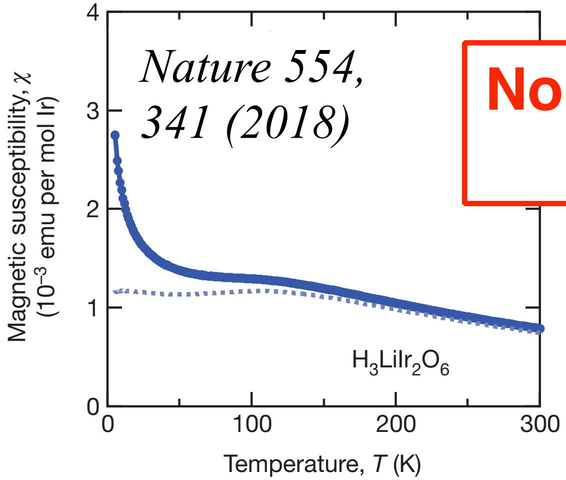
Scenario B

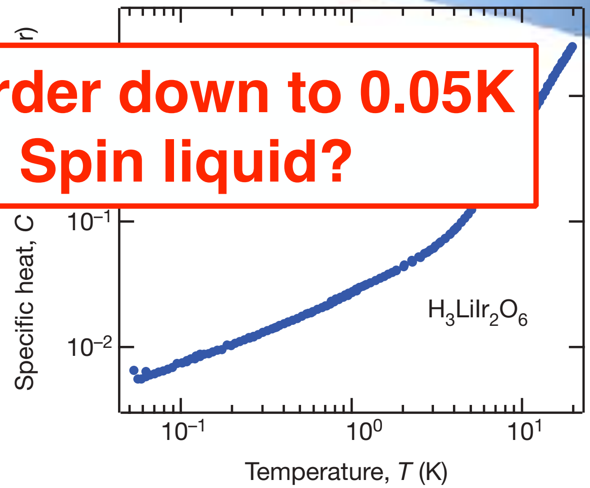


2^{nd} generation of Kitaev materials: defeat of hopes

$H_3LiIr_2O_6$





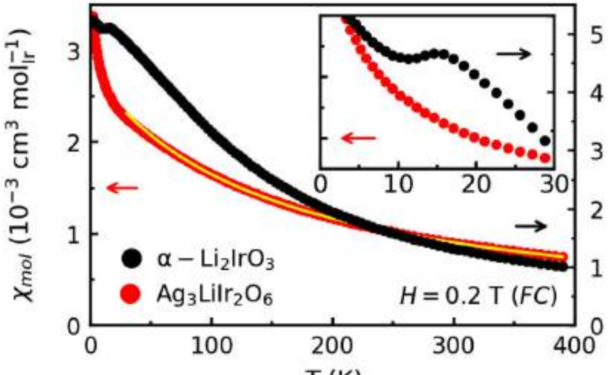


NO <u>magnetic</u> order due to H zero-point motion
(**dynamic disorder**)

Y. Li et al., PRL 121, 247202 (2018)

$Ag_3LiIr_2O_6$
$Na_3NaIr_2O_6$
$Cu_3LiIr_2O_6$
Cu_2IrO_3

Reported to have NO long-ranged magnetic order

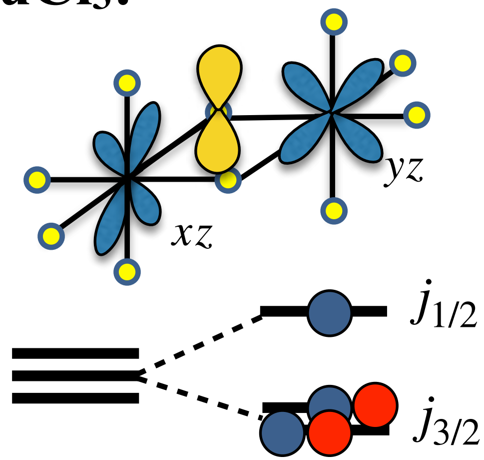


Most probably: a **static disorder**

PRL 123, 237203 (2019), PRB 103, 094427 (2021), JACS 139, 15371 (2017)

What about other geometries?
or anisotropic exchange on FCC lattice

α- RuCl$_3$:



$\langle xz|\hat{t}|yz\rangle = t, \quad \langle xy|\hat{t}|xy\rangle = 0$

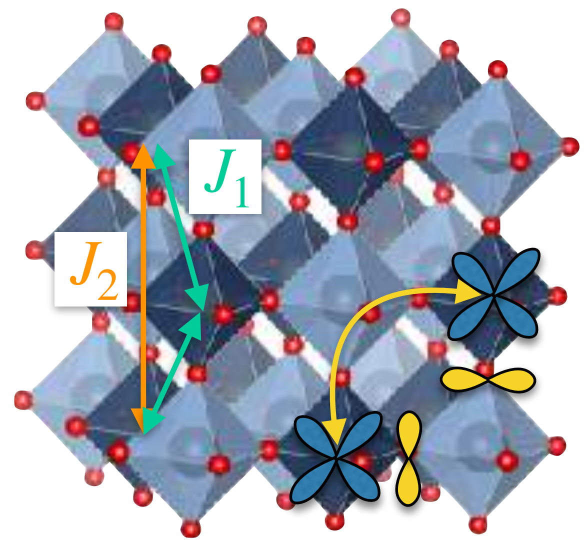
↓

No overlap between half-filled orbitals

NO AFM superexchange!

Kitaev is FM: $K \sim -\frac{\tilde{t}_{dd}^2 J_H}{U^2} < 0$

Double perovskites: 2x ABO$_3$ → A$_2$BB'O$_6$



FCC: large frustration

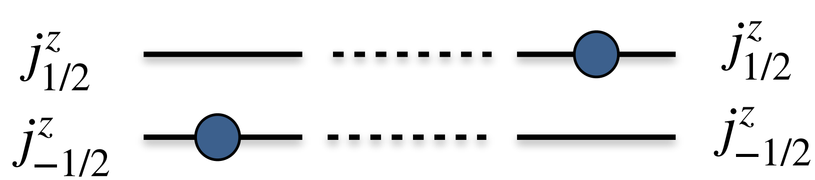
Path: TM-O-O-TM

$\langle xy_a|\hat{t}|xy_b\rangle = t$

↓

$\langle j^z_{\pm 1/2,a}|\hat{t}|j^z_{\pm 1/2,b}\rangle = t/3$

Overlap between half-filled orbitals

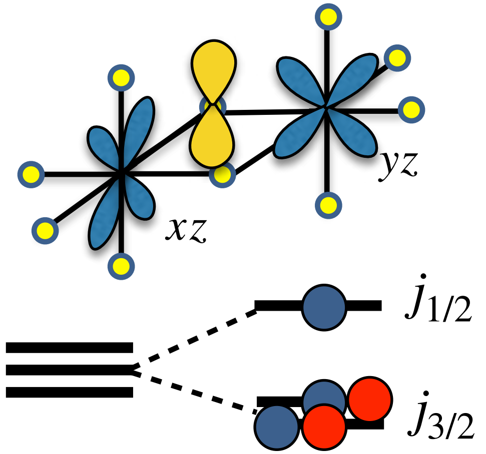


Kitaev is AFM: $K \sim +J\frac{J_H}{U}$

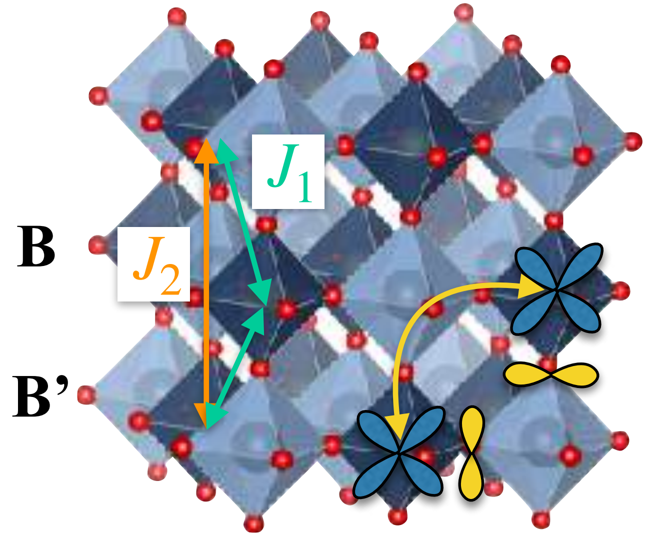
J is isotropic exchange

What about other geometries? or anisotropic exchange on FCC lattice

$RuCl_3$: Path: TM-O-TM



Double perovskites: 2x ABO_3 → $A_2BB'O_6$



FCC: large frustration

Path: TM-O-O-TM

Kitaev is AFM: $K \sim +J\frac{J_H}{U}$

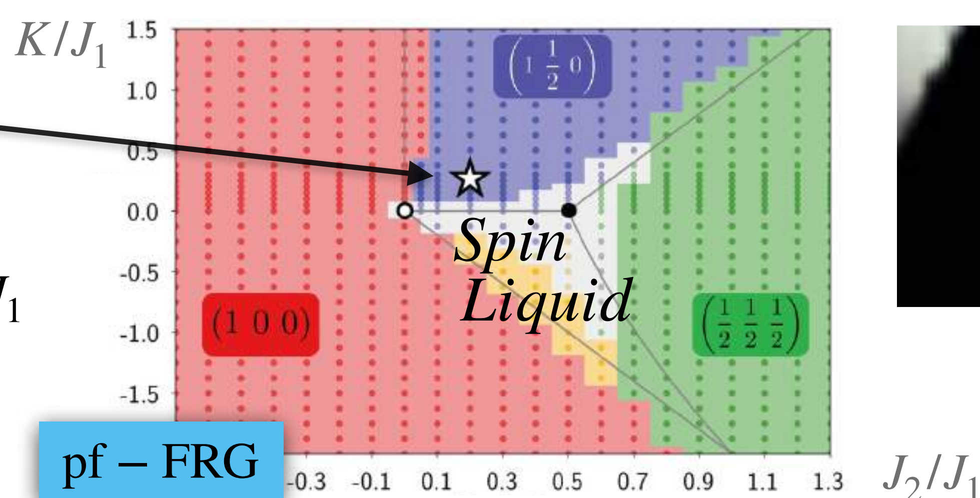
J is isotropic exchange

Ba_2CeIrO_6

DFT: $J_1 \sim 5$ meV

$K_1 \approx J_2 \approx 0.2 J_1$

A. Revelli et al., PRB 100, 085139 (2019)



Other materials with Kitaev-like interactions: $Ba_3IrTi_2O_9$ (triangular), $Na_4Ir_3O_8$ (hyperkagome)

Kitaev materials, 3rd generation: Cobaltites ???

PHYSICAL REVIEW B **97**, 014407 (2018)

Pseudospin exchange interactions in d^7 cobalt compounds: Possib

Huimei Liu and Giniyat Khaliullin
Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-

PHYSICAL REVIEW B **97**, 014408 (2018)

Kitaev-Heisenberg Hamiltonian for high-spin d^7 Mott insulators

Ryoya Sano, Yasuyuki Kato, and Yukitoshi Motome
Department of Applied Physics, The University of Tokyo, Tokyo 113-8656, Japan

PHYSICAL REVIEW B **102**, 224429 (2020)

Kitaev interactions in the Co honeycomb antiferromagnets $Na_3Co_2SbO_6$ and $Na_2Co_2TeO_6$

M. Songvilay,[1,2] J. Robert,[3] S. Petit,[3] J. A. Rodriguez Rivera,[4,5] W. D. Ratcliff,[4] F. Damay,[3] V. Balédent,[6] M. Jiménez-Ruiz,[7] P. Lejay,[2] E. Pachoud,[2] A. Hadj-Azzem,[2] V. Simonet,[2] and C. Stock[1]

Antiferromagnetic Kitaev interaction in J_{eff} = 1/2 cobalt honeycomb materials $Na_3Co_2SbO_6$ and $Na_2Co_2TeO_6$

Chaebin Kim[1,2], Jaehong Jeong[10,2,3], Gaoting Lin[4], Pyeongjae Park[1,2], Takatsu... Shinichiro Asai[5], Shinichi Itoh[6], Heung-Sik Kim[7], Haidong Zhou[8], Jie Ma[10,4,9] + S...

Published 11 November 2021 • © 2021 IOP Publishing Ltd
Journal of Physics: Condensed Matter, Volume 34, Number 4
Citation Chaebin Kim *et al* 2022 *J. Phys.: Condens. Matter* **34** 045802

nature COMMUNICATIONS

https://doi.org/10.1038/s41467-021-25567-7 OPEN

Field-induced quantum spin disordered state in spin-1/2 honeycomb magnet $Na_2Co_2TeO_6$

Spin interaction and magnetism in cobaltate Kitaev candidate materials: and model Hamiltonian approach

Shishir Kumar Pandey[1] and Ji Feng[1,2,3,*]

SCIENCE ADVANCES | RESEARCH ARTICLE

PHYSICS

Weak-field induced nonmagnetic state in a Co-based honeycomb

Ruidan Zhong[1], Tong Gao[2], Nai Phuan Ong[2], Robert J. Cava[1]*

PHYSICAL REVIEW B **106**, 014413 (2022)

Dominant Kitaev interactions in the honeycomb materials $Na_3Co_2SbO_6$ and $Na_2Co_2TeO_6$

Alaric L. Sanders,[1] Richard A. Mole,[2] Jiatu Liu,[3] Alex J. Brown,[1] Dehong Yu,[2] Chris D. Ling,[3] and Stephan Rachel[1,*]

Kitaev materials, 3rd generation: Cobaltites ???

Strong anisotropy of exchange interaction or $j_{eff}=1/2$ physics is important not only for t_{2g}^5configuration (i.e. Ru^{3+}, Ir^{4+} ions) and honeycomb geometry

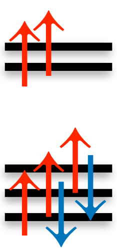
Isolated Co^{2+}:

-2	-1	0	1	2
↑↓	↑↓	↑	↑	↑

$L = 3, S = 3/2$

(^4F)

Co^{2+} in octahedra:

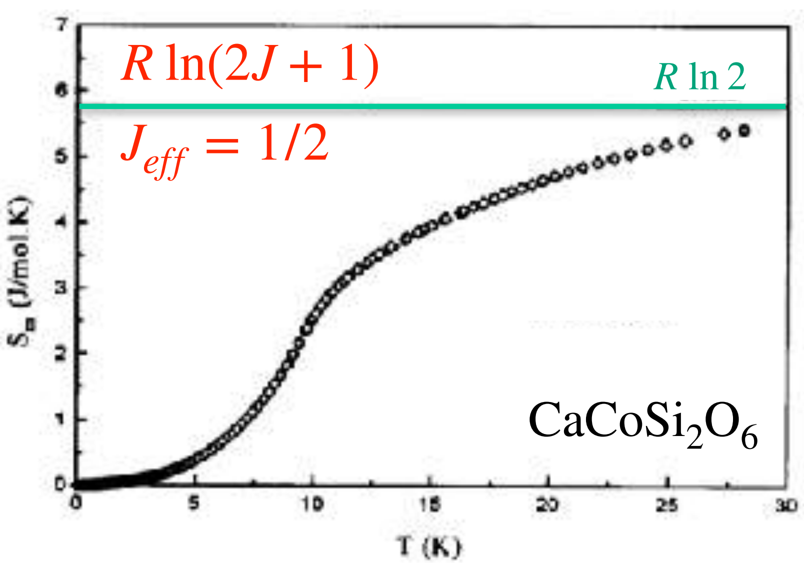


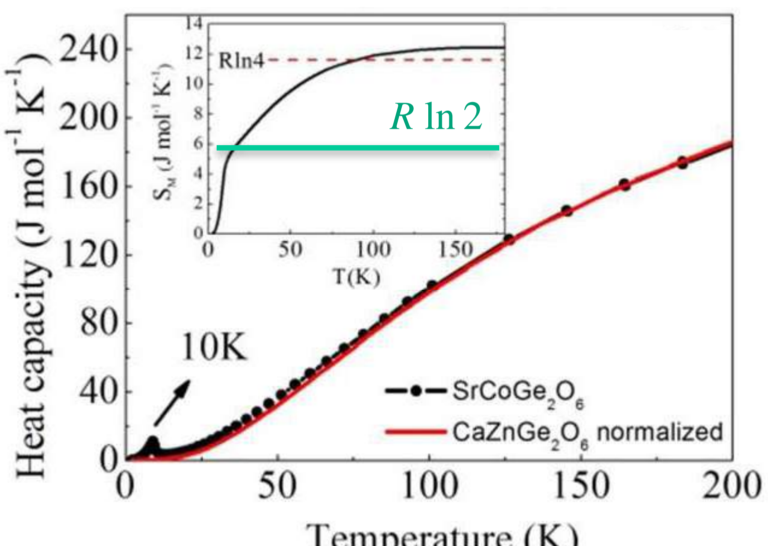
$L_{eff} = 1, S = 3/2$

$n > N/2 \Rightarrow$

$J_{eff} = |L_{eff} - S| = 1/2$

$$\underbrace{\begin{array}{ccc} -1 & 0 & 1 \\ \uparrow\downarrow & \uparrow\downarrow & \uparrow \end{array}}_{t_{2g}}$$

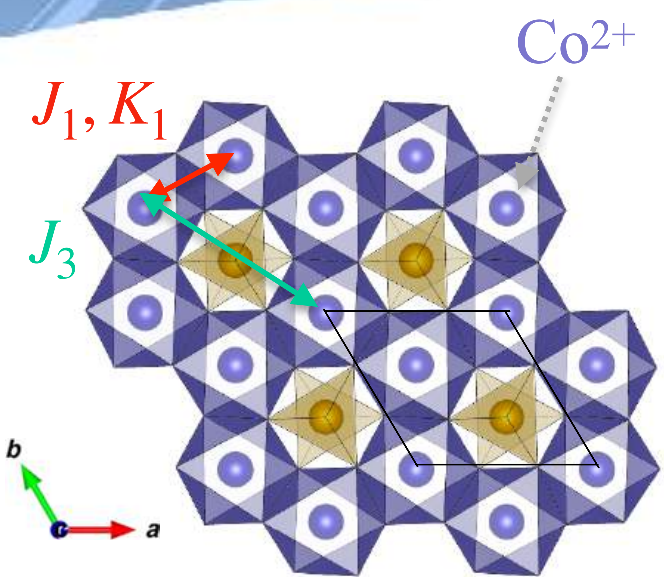


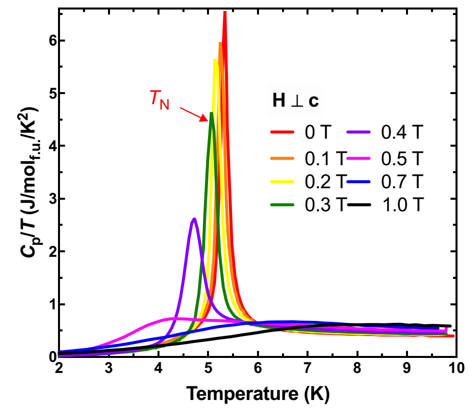


Durand et al., J. Solid State Chem. 124, 374 (1996)

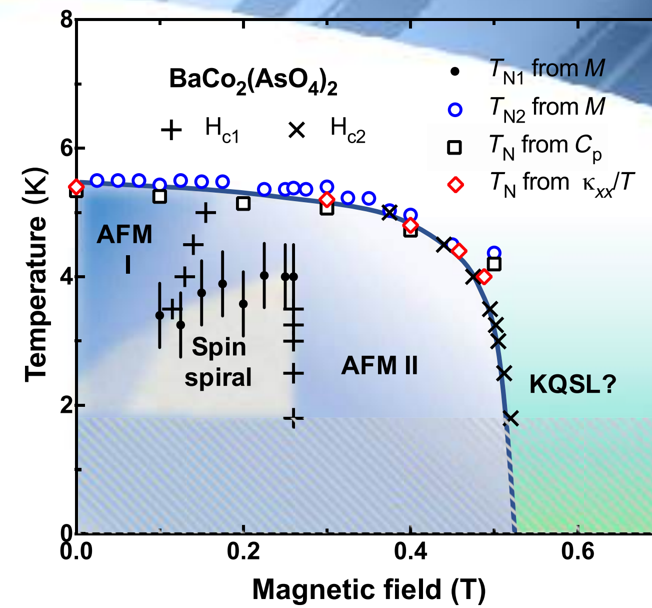
Ding et al., J. Mater. Chem. C 4, 4236 (2016)

Spin liquid in $BaCo_2(AsO_4)_2$?



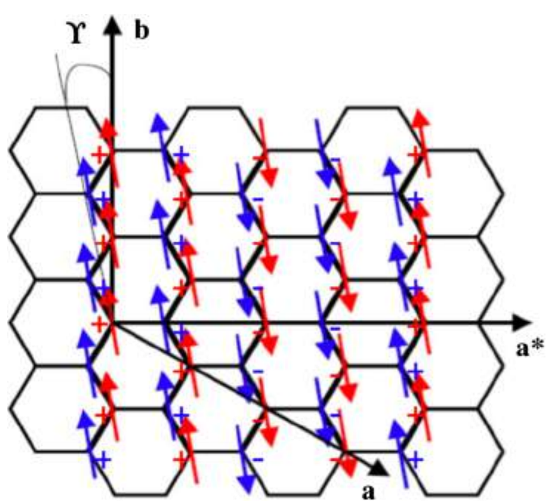


*R. Zhong et al., Science Advances **6**, eaay6953 (2020)*



Experimental magnetic structure

*L. Regnault et al, Hellyon **4**, e00507 (2018)*



$$J_{ij} = \begin{pmatrix} J & \Gamma & \Gamma' \\ \Gamma & J & \Gamma' \\ \Gamma' & \Gamma' & J+K \end{pmatrix}_{ij}$$

Kitaev, if $|K_1| \gg |J_1|$ and all the rest is small

Spin liquid?

Anisotropic exchange?

Kitaev?

$BaCo_2(AsO_4)_2$ is not Kitaev material
(but still extremely interesting)

Exchange tensor

$$\begin{pmatrix} J & \Gamma & \Gamma' \\ \Gamma & J & \Gamma' \\ \Gamma' & \Gamma' & J+K \end{pmatrix}_{ij}$$

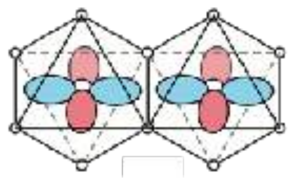
DFT+U+SOC
(U=6 eV)

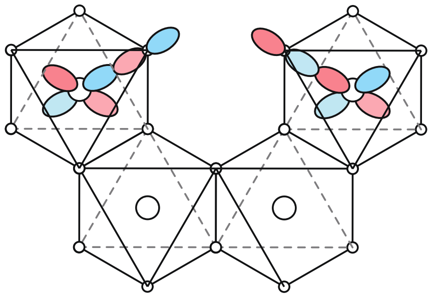
J_1	-40.9 K	J_3	24.6 K
K_1	2.2 K	K_3	0.2 K
Γ_1	-1.7 K	Γ_3	-6.0 K
Γ'_1	4.0 K	Γ'_3	-2.3 K

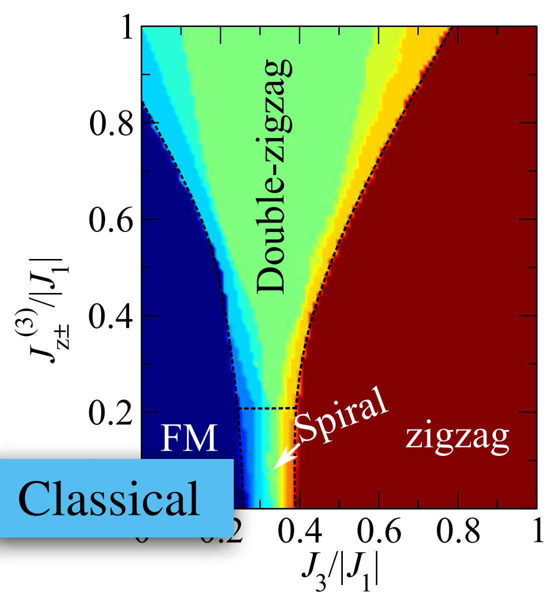
Why there is no a spin liquid

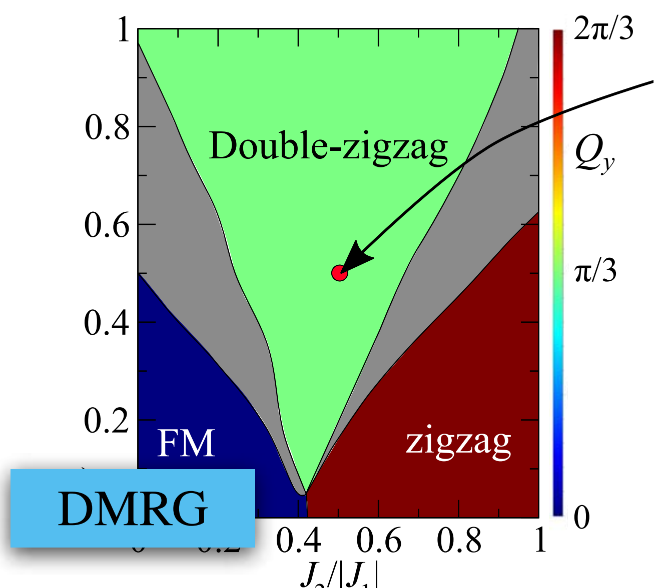
1. Isotropic exchange (J_1) much larger than Kitaev (K_1)

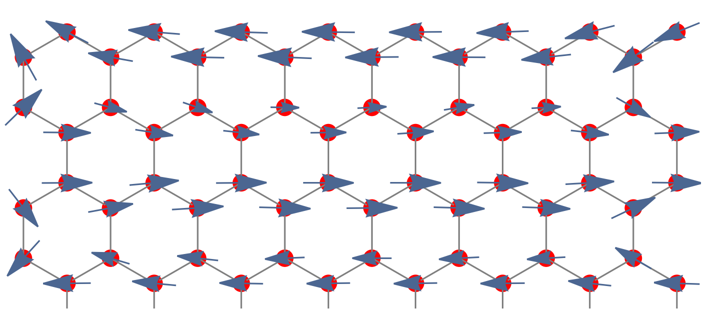
2. 3rd nn exchange (J_3) is very efficient







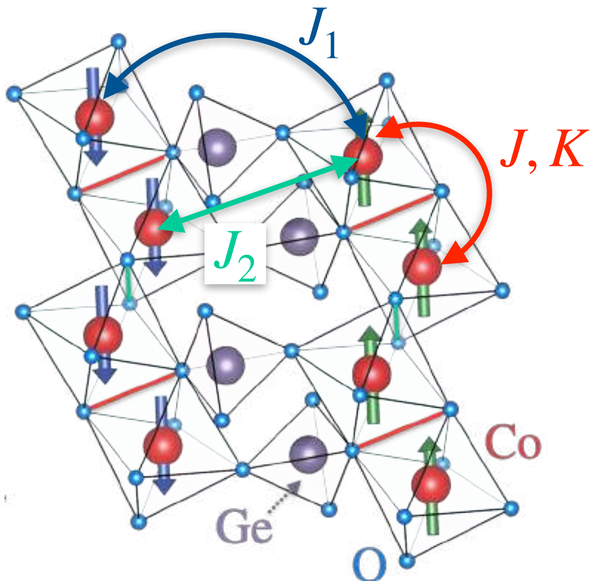




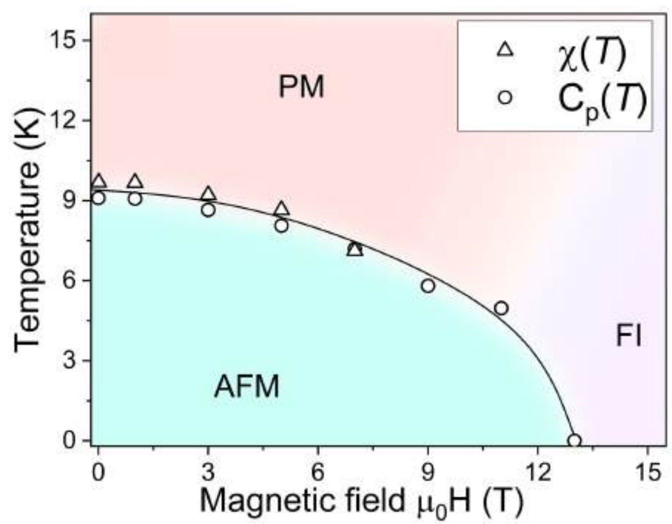
P. Maksimov et al, PRB 106, 165131 (2022)

Co-based pyroxenes $ABCo_2O_6$: novel (1D?) materials with strong Kitaev

$SrCoGe_2O_6$



Orders magnetically, but transition is suppressed by *H*



Inelastic neutrons

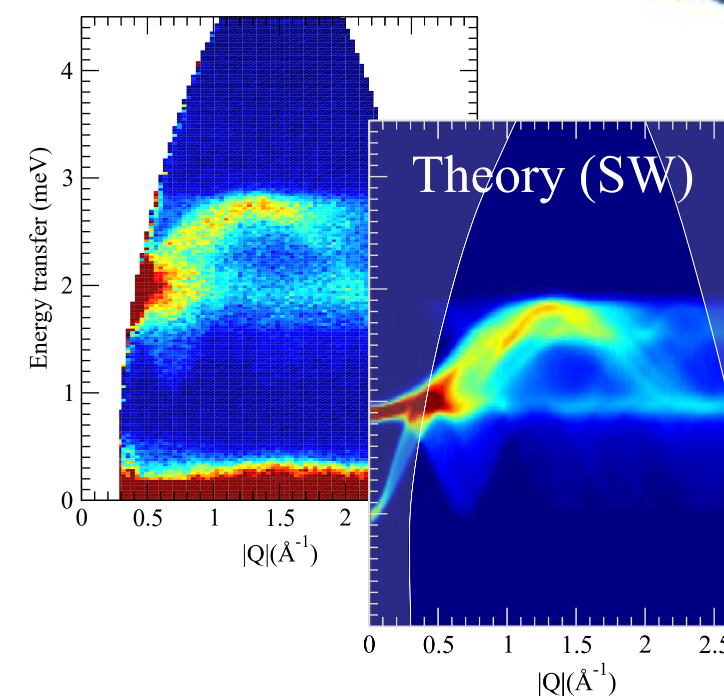


Table 1. Comparison of the exchanges from ab initio (GGA+U+SOC) calculations and neutron scattering fit (LSWT).

Method	J	K	$\|K/J\|$	Γ	Γ'	J_1	J_2
GGA+U+SOC	-1.20	1.12	0.93	-	-	0.74	1.06
LSWT	-0.87	0.83	0.96	0.43	-0.26	0.40	0.60

The exchanges are in units of meV.

Kitaev is large, $K/|J| = 0.96$!
The system is not 1D!

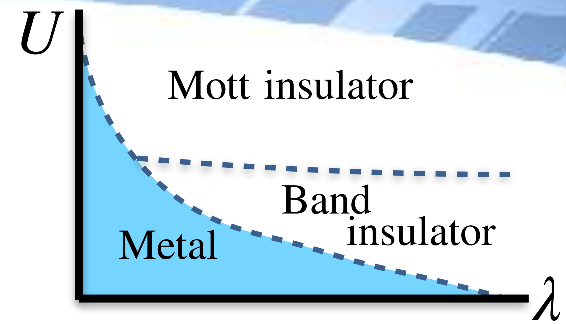
What about $ACoSi_2O_6$?

Maksimov et al., arXiv:2401.13550

Take-home messages

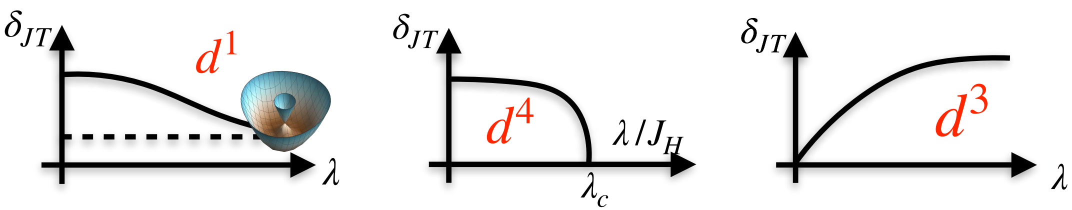
E

- Mott-Hubbard transition is affected by spin-orbit coupling (U_c is typically decreased)



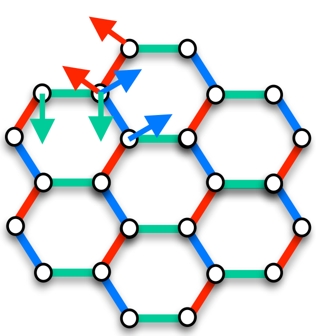
S

- Spin-orbit coupling strongly affects the Jahn-Teller effect (result depends on elec. number)



M

- There can hidden (magnetic) orders in spin-orbit materials



- Kitaev materials:
  <u>Iridates/ruthenates</u>: Kitaev can be large; Field-dependence?
  <u>Cobaltites</u> no solid evidence for Kitaev physics yet

D. Khomskii, S. Streltsov Chem. Rev. ***121****, 2992 (2021)*
T. Takayama et al., JPSJ ***90****, 062001 (2021)*