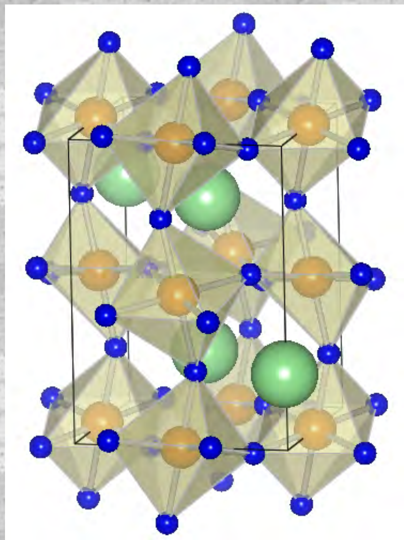
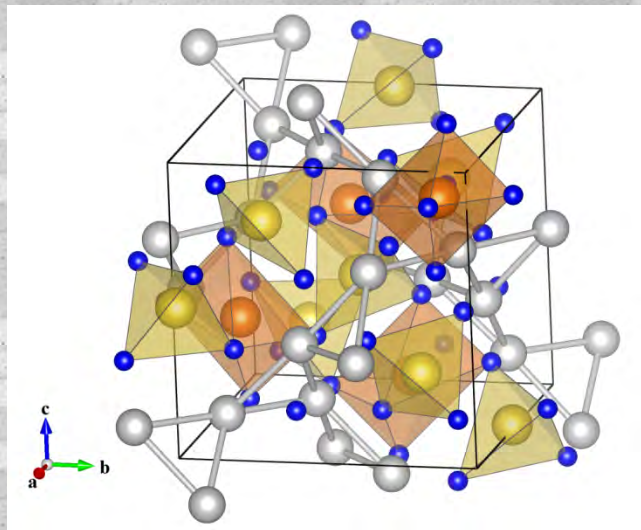
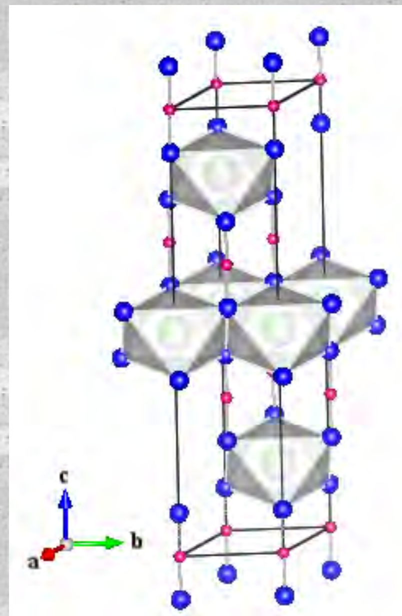
# Exotic electronic states produced by strong spin-orbit coupling in complex Ir oxides



$SrIrO_3$




$Na_3Ir_3O_8$




H-$Li_2IrO_3$

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Max Planck Institute for Solid State Research

# Collaborators

Synthesis, characterization, physical properties

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Resonant inelastic x-ray scattering (RIXS)

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SPring-8

Theory

A. Yaresko, G. Jackeli (MPI Stuttgart)

# Outline

## 1. Spin-orbital Mott insulators

Spin-orbit coupling leads to $J_{eff} = 1/2$ state
Weak Mott insulator produced by modest Coulomb $U$

## 2. Metallic iridates close to MIT

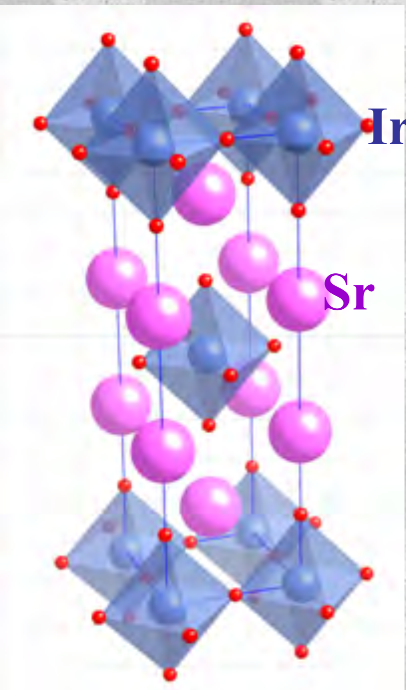
Spin-orbit coupling induced semi-metals
1. Semi-metal protected by Dirac node
2. Competition between molecular orbital formation and SOC

## 3. New "honeycomb" spin liquid near MIT

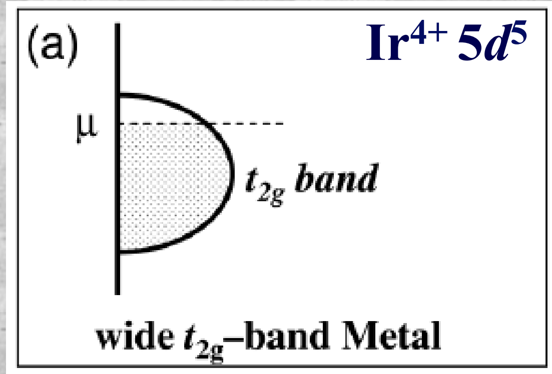
Honeycomb iridates... Possible playground for Kitaev spin liquid
Spin liquid behavior likely originating from weak Mottness

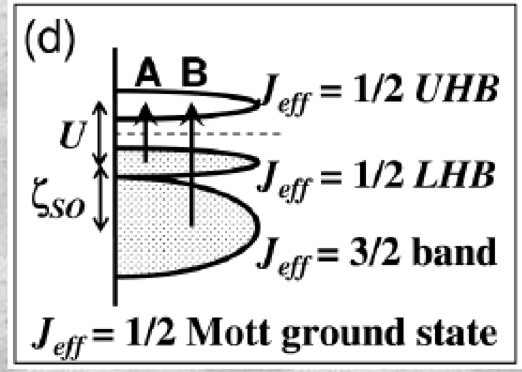
# Spin-orbital Mott insulator $Sr_2IrO_4$ … $J_{eff}$ = 1/2 state

B. J. Kim et al., PRL(08), Science (09)




$K_2NiF_4$-type structure



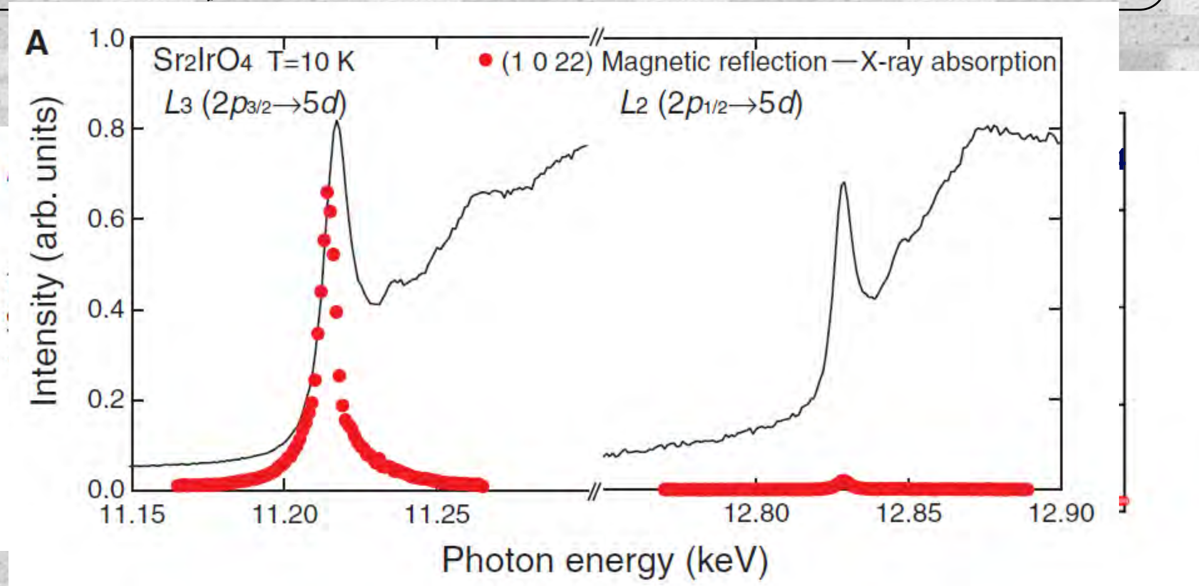

$$J_{eff\,1/2} = \frac{1}{\sqrt{3}}\left( \left| d_{xy}, \pm 1/2 \right\rangle \pm \left| d_{yz}, \mp 1/2 \right\rangle + \underline{i} \left| d_{zx}, \mp 1/2 \right\rangle \right)$$

$Sr_2CoO_4$… FM metal

$Sr_2RhO_4$… Para metal

$Sr_2IrO_4$… AF insulator

($T_N$ ~ 240 K)



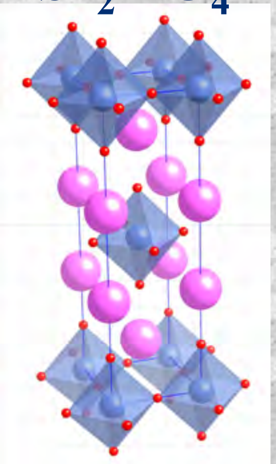

**Contrasted RXS scattering → $J_{eff}$ = 1/2 state**

# 2D Heisenberg antiferromagnetism in $Sr_2IrO_4$

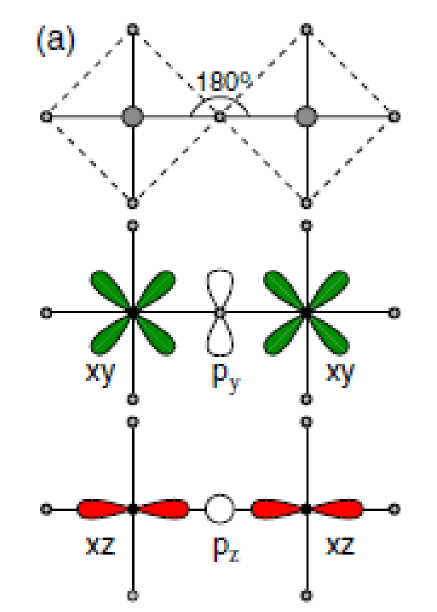
## Unique magnetic coupling between $J_{eff}$ = 1/2 moments

**180° Ir-O-Ir bond**
**(corner-sharing $IrO_6$)**

$Sr_2IrO_4$



$T_N$ ~ 240 K

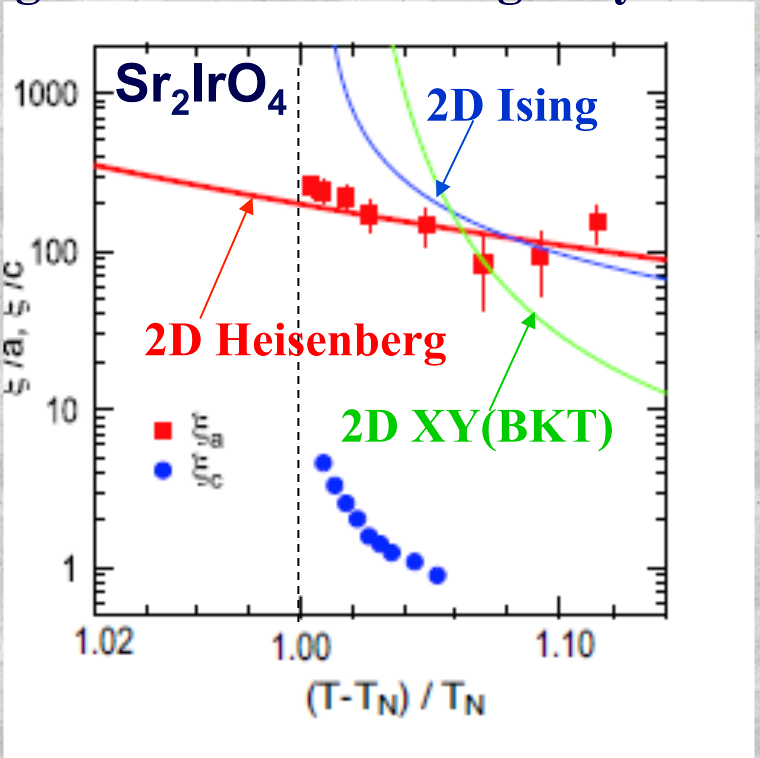



$$H_{ij} = J_1 S_i \cdot S_j + J_2 (S_i \cdot r_{ij})(r_{ij} \cdot S_j)$$

**Heisenberg** (+ weak anisotropy term)

G. Jackeli and G. Khaliullin, PRL 102, 017205 (2009)

**Magnetic correlation length by RXS**

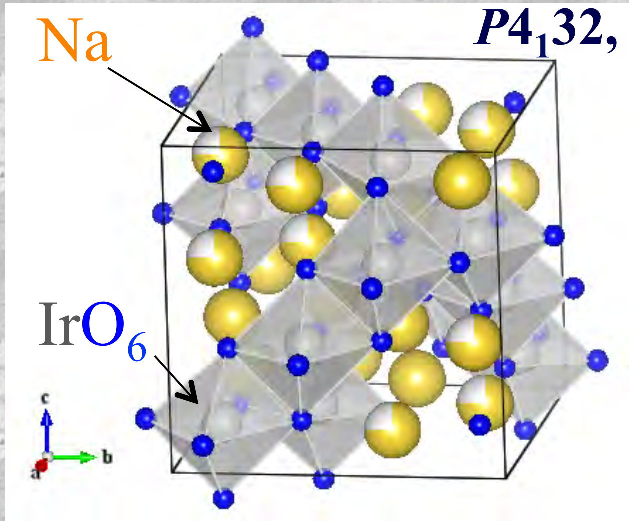



S. Fujiyama et al., PRL 108 (2012)

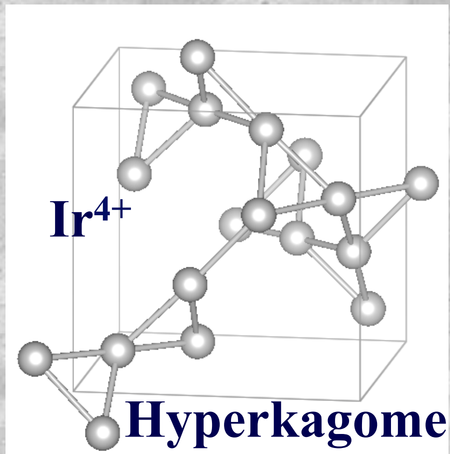
***S*** **= 1/2 Heisenberg AF, *J* ~ 0.1 eV**

**Similar with $La_2CuO_4$?**

# Hyperkagome $Na_4Ir_3O_8$ … 3D quantum spin liquid

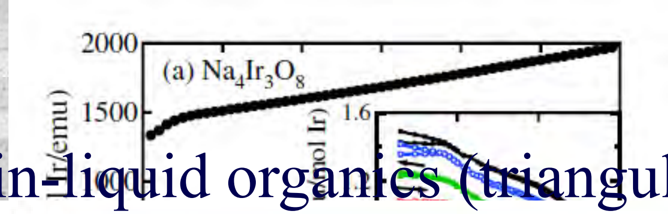



$P4_132$, $a$ = 8.985 Å

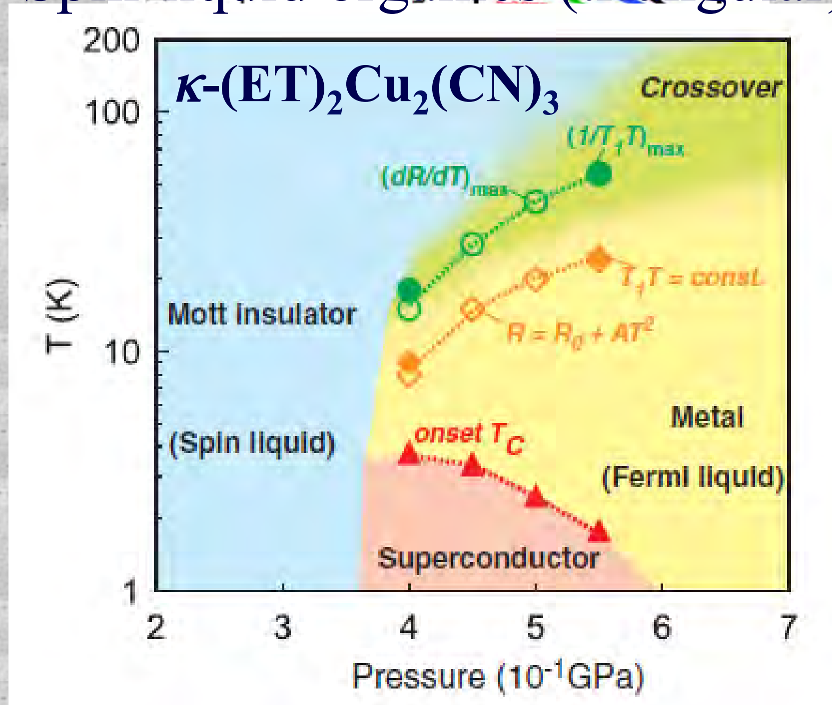



Hyperkagome lattice

3D network of corner-sharing triangle
Geometrically frustrated lattice




Spin-liquid organics (triangular)




Y. Kurosaki et al., PRL 95, 177001 (2005)
Y. Okamoto et al., PRL 99, 137207 (2007)

No magnetic order down to 2 K
despite $\theta_W$ = -650 K

**Candidate of 3D spin liquid... unconventional SC upon doping?**

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Spin liquid behavior likely originating from weak Mottness

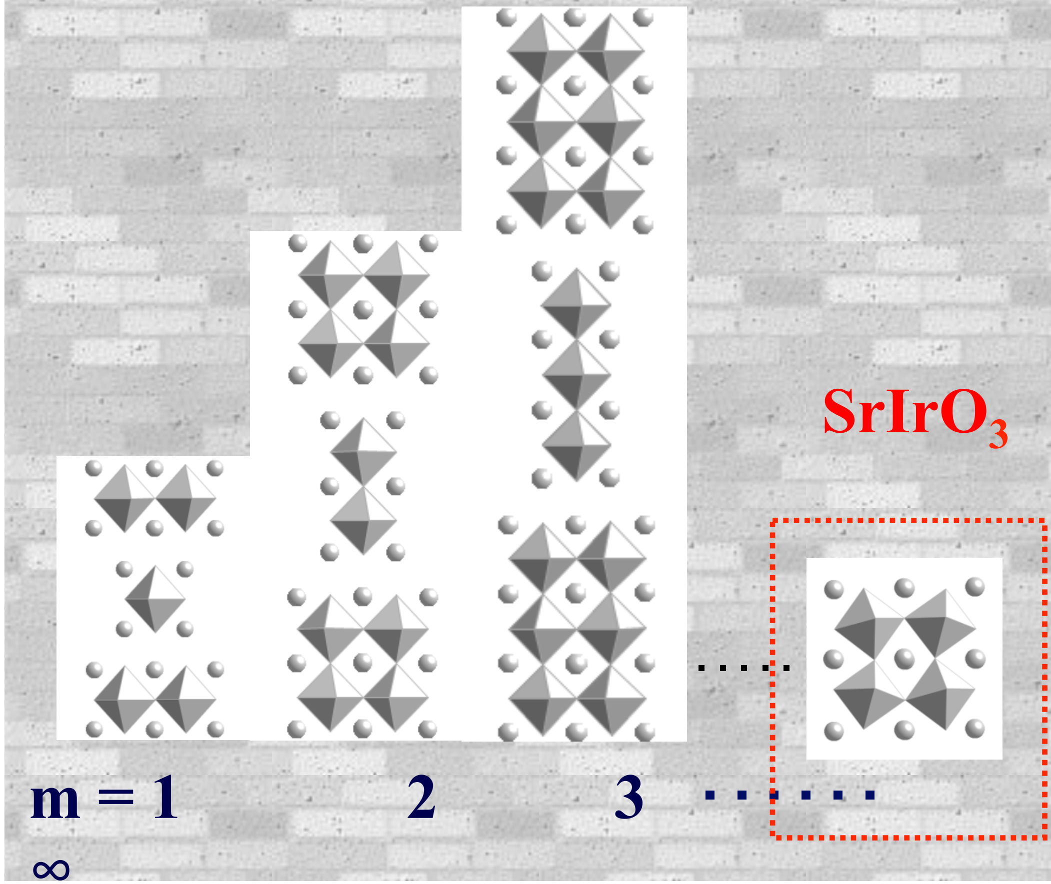
# 1. Metal produced from $Sr_2IrO_4$

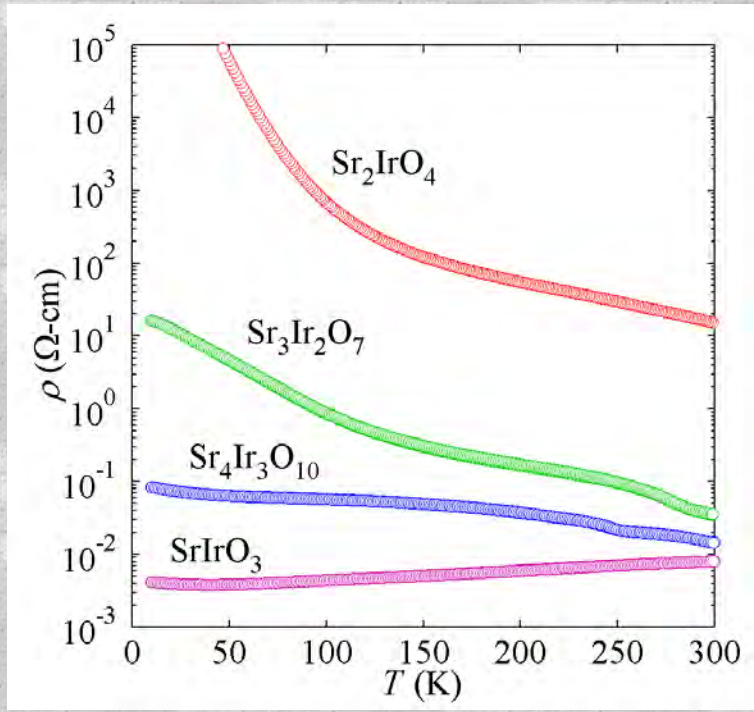
## I. Doping onto weak Mott insulator $Sr_2IrO_4$

$Sr_{2-x}La_xIrO_4$ … no metallic state — Y. Klein et al., J. Phys. 20 (2008)

$Sr_2Ir_{1-x}Rh_xO_4$… metal? $x > 0.2$ required… — T. F. Qi et al., PRB 86, (2012)

## II. Bandwidth control in Ruddlesden Popper Series $Sr_{m+1}Ir_mO_{3m+1}$



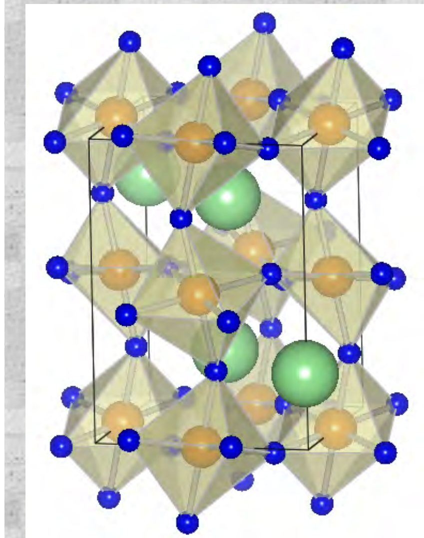




**Insulator to metal by increasing number of $IrO_2$ plane**

# $SrIrO_3$: not half-filled metal, but semi-metal

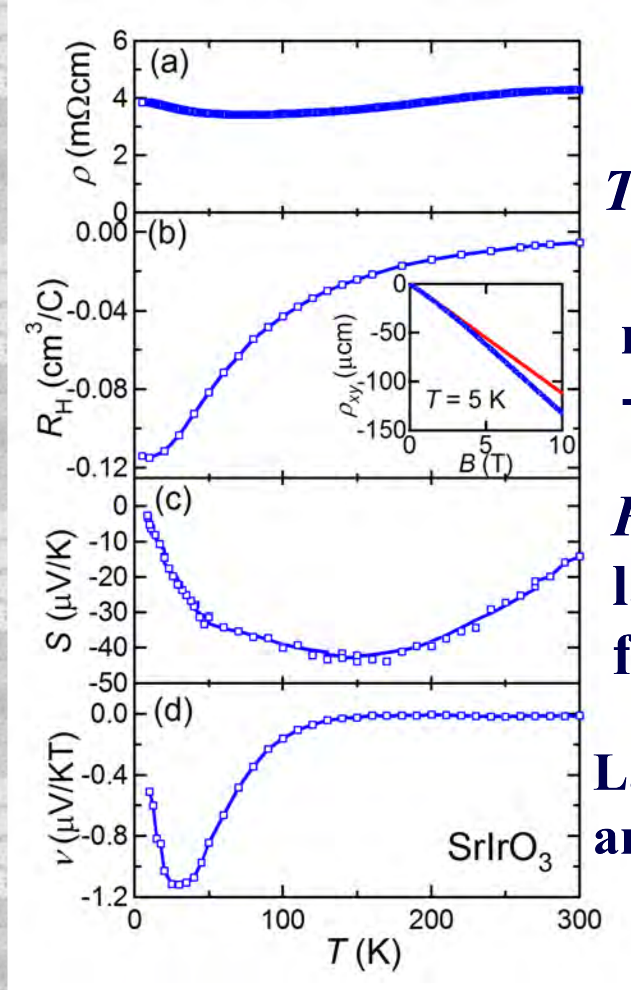
## Perovskite $SrIrO_3$

**(synthesized under high pressure)**



**$GdFeO_3$-type**
**Orthorhombic, *Pbnm***
**$IrO_6$ rotation & tilt**

**$\sqrt{2}a_c \times \sqrt{2}a_c \times 2a_c$**
**($a_c$: cubic unit cell)**



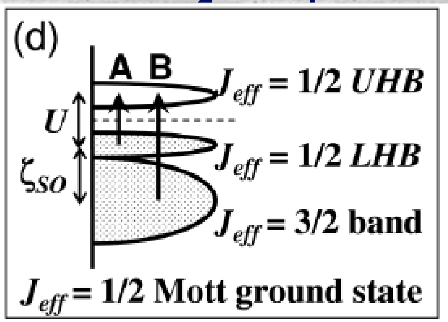

**$T$-dependent $R_H$**

**non-linear $\rho_{xy}$**
**→ two carrier**

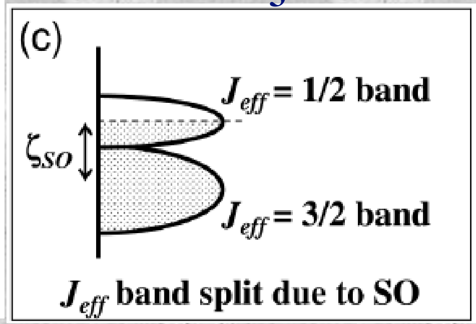
**$R_H$, $S < 0$**
**larger mobility for electrons**

**Large Nernst ambipolar effect**

**$Sr_2IrO_4$**




**$SrIrO_3$?**



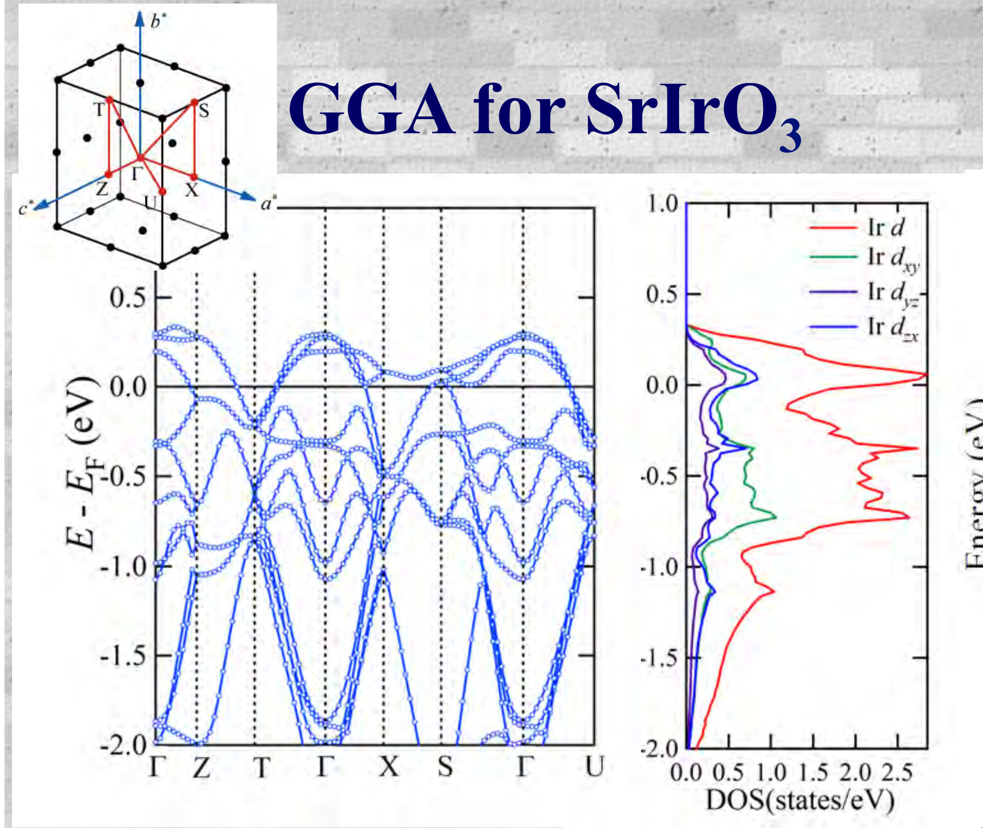

**Semi-metal, $n \sim 5 \times 10^{19}$ cm$^{-3}$**

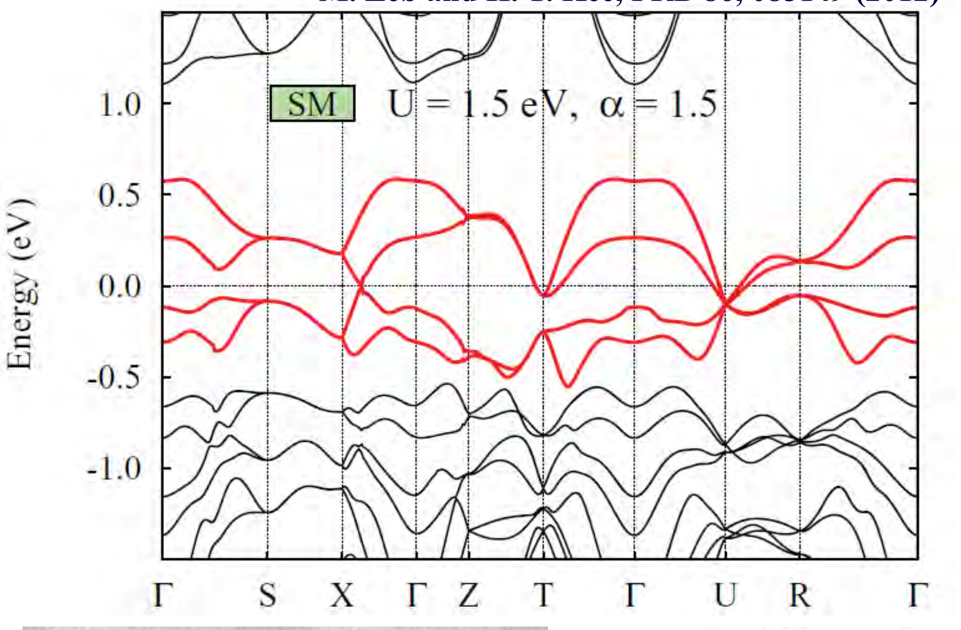
# Semi-metal by band crossing and spin-orbit coupling

## GGA for $SrIrO_3$

## GGA+SOC for $SrIrO_3$

M. Zeb and H. Y. Kee, PRB 86, 085149 (2012)



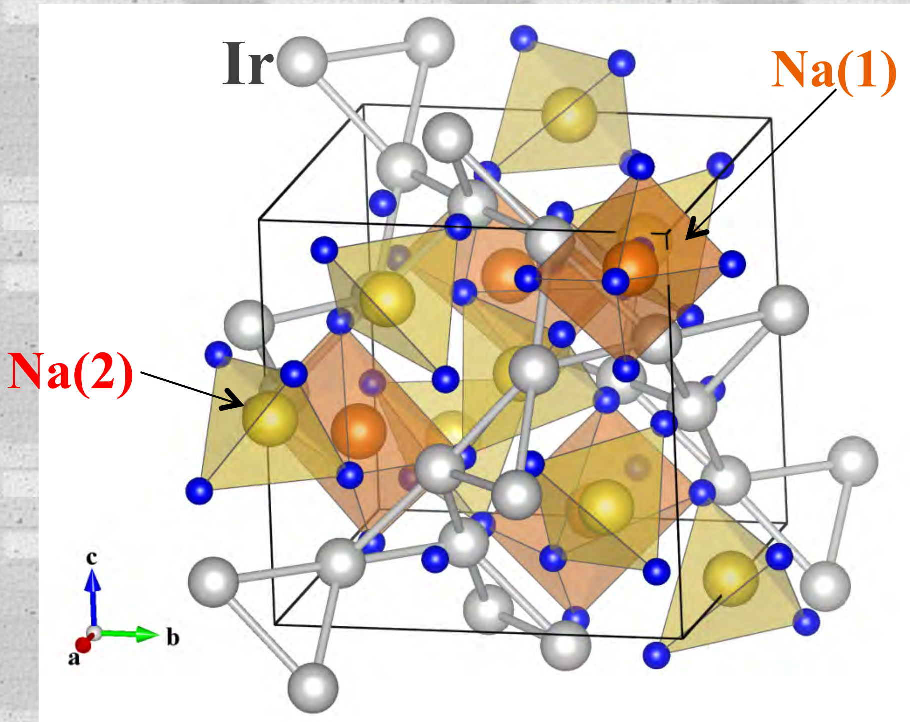

**Band crossing around $E_F$ due to BZ folding**

**Band splitting at the crossing points by SOC**
**→ $J_{eff}$ = 1/2 semi-metal**

**Semi-metal protected by the Dirac node**
**"Topological crystalline metal"** ...Y. Chen et al, Nature Com. 6, 6593 (2015)

# 2. Carrier doping to hyperkagome iridate

**New phase, $Na_3Ir_3O_8$(338), not 438!**




Grown by flux method

**Single crystal x-ray analysis**

$P4_132$, $a$ = 8.9857 Å (293 K), $Z$ = 4

| | site | $x$ | $y$ | $z$ | $g$ |
|---|---|---|---|---|---|
| Ir | 12$d$ | 0.61264 | 0.86264 | 0.62500 | 1 |
| Na1 | 4$b$ | 0.87500 | 0.87500 | 0.87500 | 1 |
| Na2 | 8$c$ | 0.25704 | 0.25704 | 0.25704 | 1 |
| O1 | 8$c$ | 0.1144 | 0.1144 | 0.1144 | 1 |
| O2 | 24$e$ | 0.1364 | 0.9071 | 0.9186 | 1 |

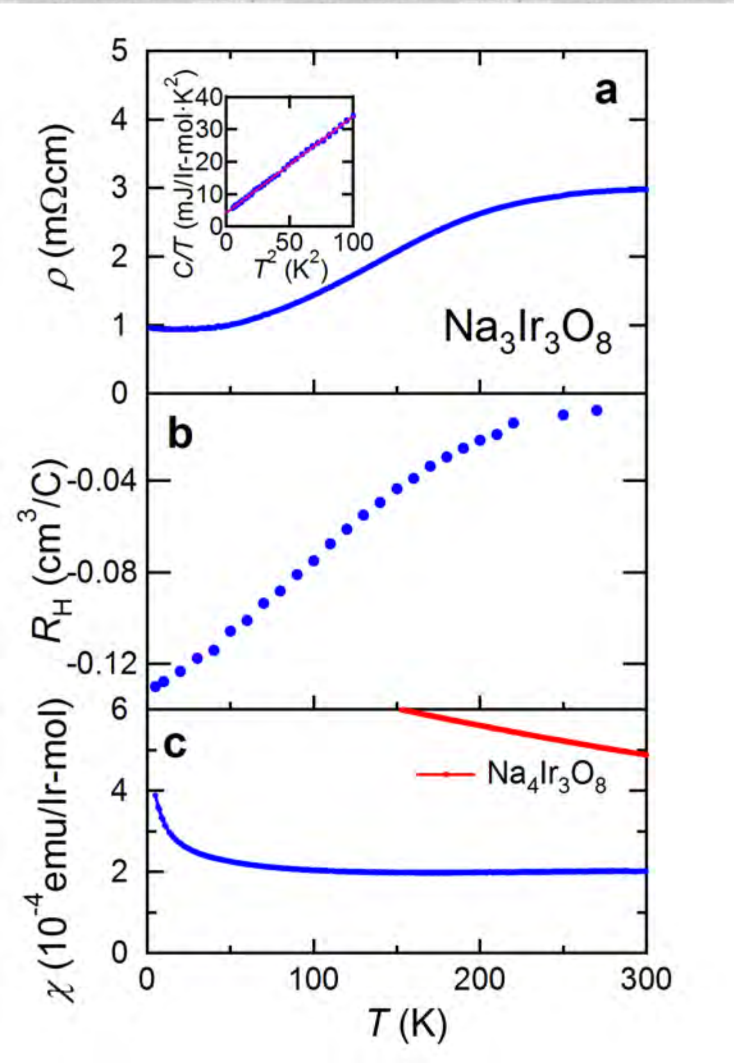
**Stoichiometric compounds!**

Na(1): Octahedral site in the pyrochlore
Na(2): Tetrahedral site like in a spinel

**Hyperkagome network is identical with 438**

**$Ir^{4.33+}$, 1/3 hole doping onto $Na_4Ir_3O_8$**

# Semi-metallic state in 338 hyper-kagome




**Metallic as expected from 1/3 hole doping**
**poor metal $\rho \sim 1$ mΩcm at 5 K**

**Temperature dependent $R_H$**
**$R_H < 0$, electron dominant**
**Small carrier number $n \sim 10^{19}$ $cm^3$**

**…Semi-metal**

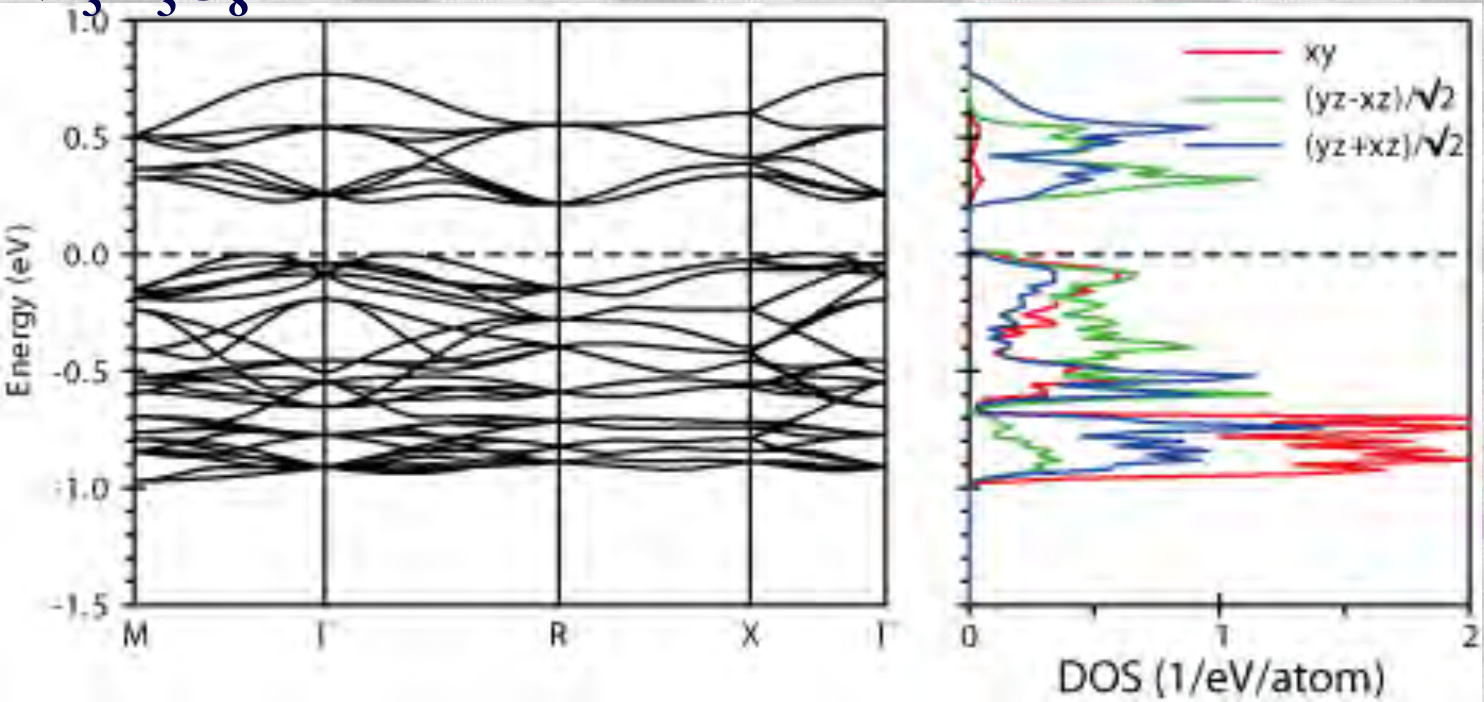
**Seemingly incompatible with 1/3 doped Mott insulator**

**T. Takayama et al., Scientific Reports 4, 6818 (2014)**

# If no SOC, band insulator even with $Ir^{4.33+}$

**LDA without SOC** **Calculation by A. Yaresko**

$Na_3Ir_3O_8$

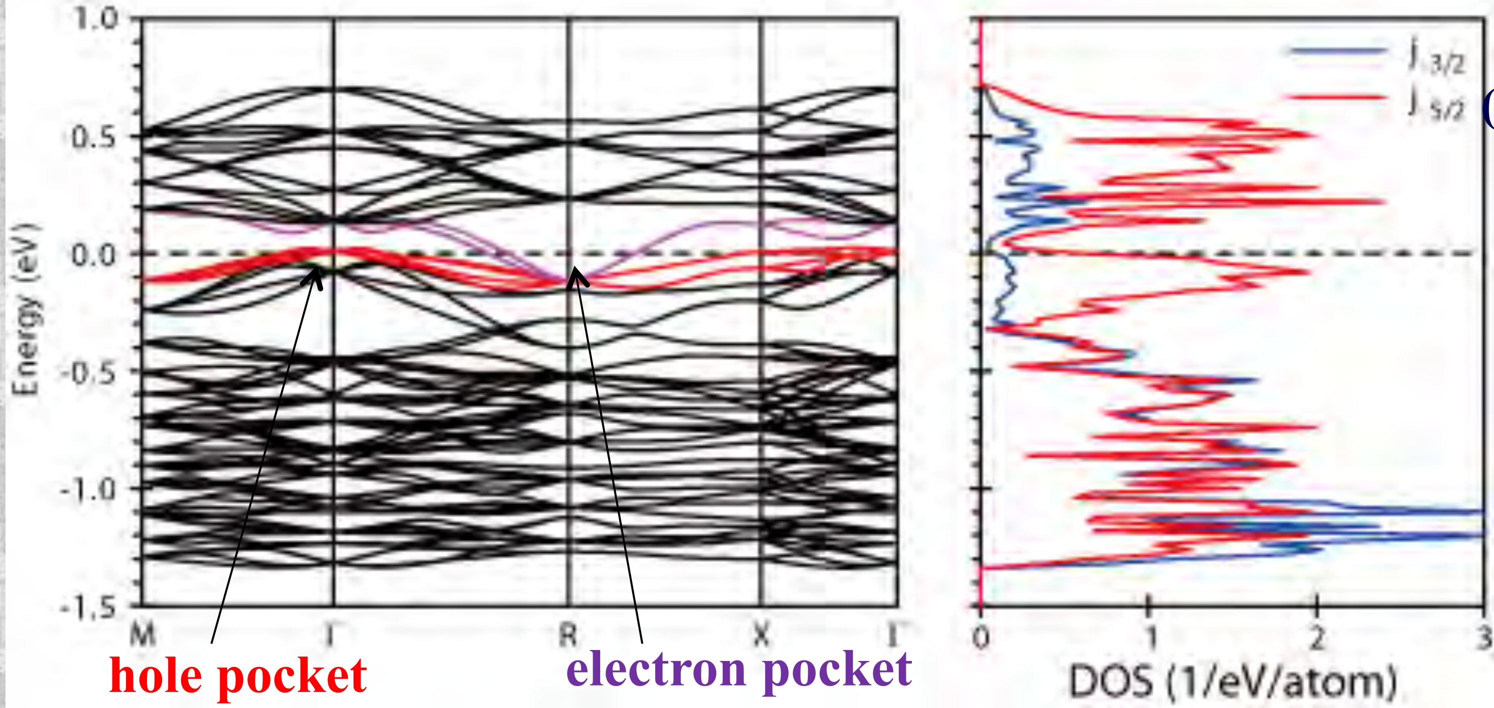



**Band insulator despite with non-integer valence state $Ir^{4.33+}$ ($5d^{4.67}$)**

**One of $t_{2g}$ orbitals is fully filled, but others are not.**
**Orbital ordering?**

# With SOC, a semi-metal is produced

$Na_3Ir_3O_8$ LDA with SOC Calculation by A. Yaresko



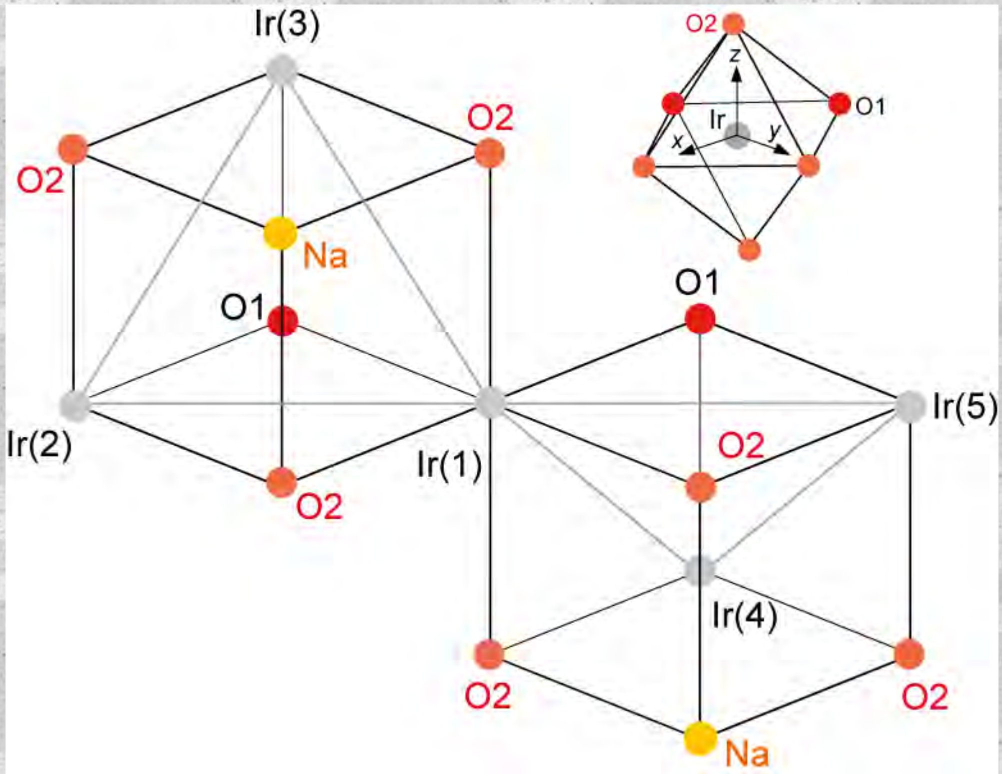

Splitting of Kramers degeneracy due to SOC and chirality
Larger dispersion in electron bands → $R_H < 0$

$J_{eff}$ = 1/2-like character by SOC

$SrIrO_3$: half-filled metal —SOC→ semi-metal
$Na_3Ir_3O_8$: Band insulator —SOC→ semi-metal?

# Band insulator with molecular orbital formation

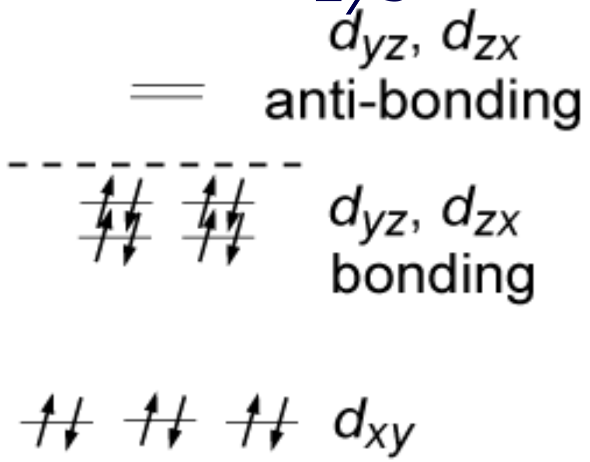
## $Na_3Ir_3O_8$: Assume no spin-orbit coupling...




Bond length... Ir-O1 >> Ir-O2
Hopping via O2 dominant

$Ir^{4.33+}$ $5d^{4\,2/3}$

14 electron per $Ir_3$

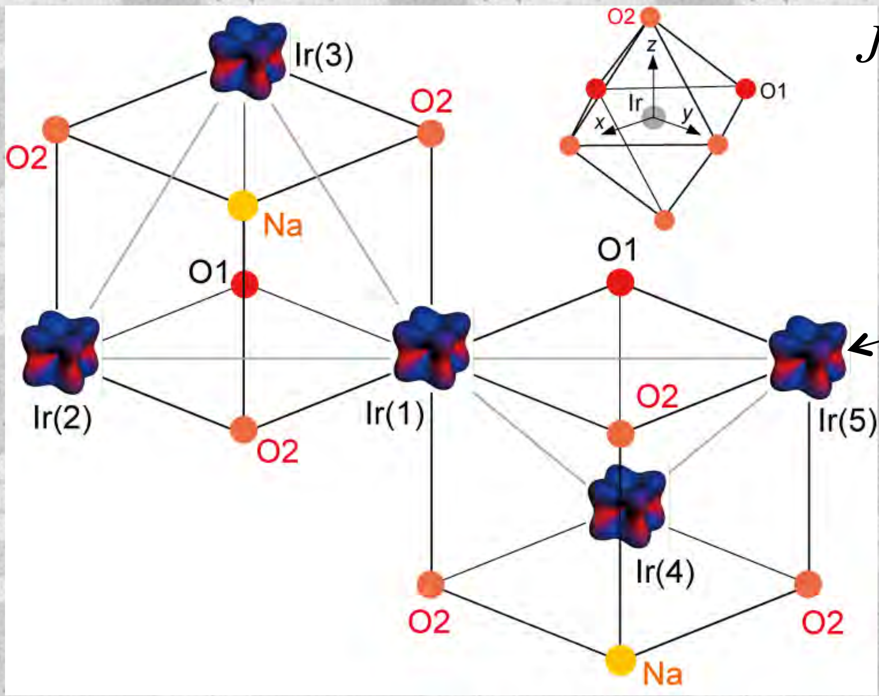


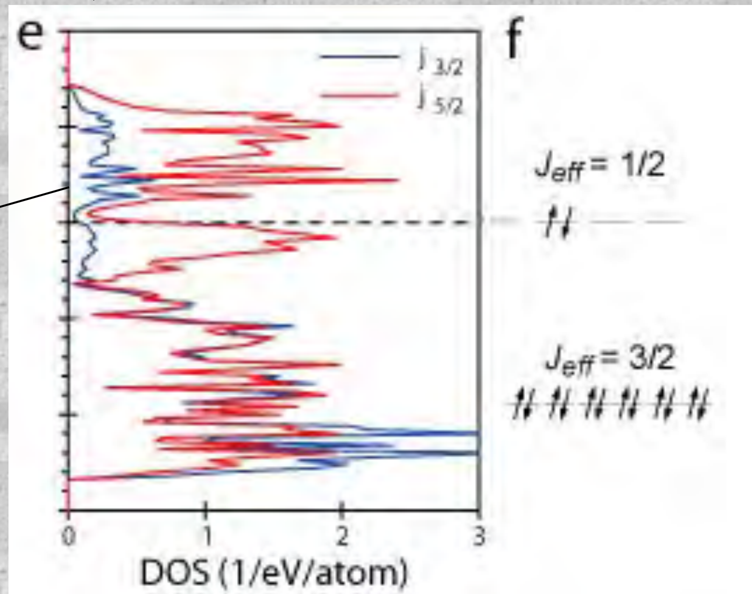

**Ir *d* – O2 *p* – Ir *d* hopping creates molecular orbital on each triangle**
**"$Ir_3$ molecule"...14 electrons fulfill the orbitals right below the gap**
**→ Band insulator**

# SOC destroy Molecular orbital to form $J_{eff} = 1/2$

**With SOC, Ir $t_{2g}$ orbitals form $J_{eff} = 1/2$ state**

$$J_{eff\,1/2} = \frac{1}{\sqrt{3}}\left( |xy,\pm\sigma\rangle \pm |yz,\mp\sigma\rangle + i|zx,\mp\sigma\rangle \right)$$




**By SOC, $d_{xy}$, $d_{yz}$, $d_{zx}$ entangled to form $J_{eff} = 1/2$-like state**
**$t_{2g}$ electrons delocalize out of "$Ir_3$ molecules"**

**Turn on SOC, molecular orbital destroyed and semi-metal appears**

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Honeycomb iridates... Possible playground for Kitaev spin liquid
Spin liquid behavior likely originating from weak Mottness

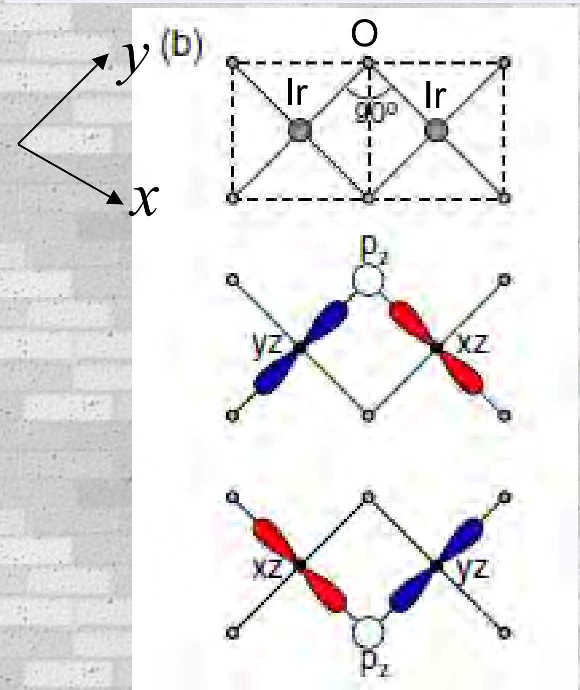
# Honeycomb iridate $\alpha$-$A_2IrO_3$ : Candidate for Kitaev spin liquid

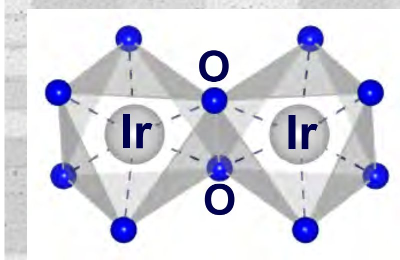
G. Jackeli and G. Khaliullin, PRL 102, 017205 (2009)

**Magnetic coupling in Ir-O-Ir bond with $J_{eff}$ = 1/2 state**

$$J_{eff\,1/2} = \frac{1}{\sqrt{3}}\left( \left| d_{xy}, \pm 1/2 \right\rangle \pm \left| d_{yz}, \mp 1/2 \right\rangle + i \left| d_{zx}, \mp 1/2 \right\rangle \right)$$

**90° bond (edge-sharing $IrO_6$)**



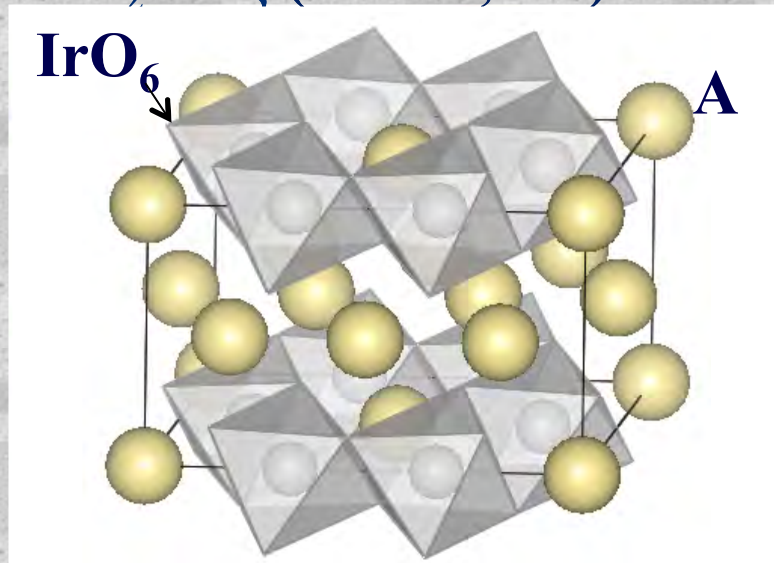




**Destructive interference between two paths**

$$H_{ij}^{(\gamma)} = -JS_i^\gamma S_j^\gamma \text{ (in } \alpha\beta \text{ plane)}$$

**- bond-dependent FM**

**$\alpha$-$A_2IrO_3$ (A = Li, Na)**

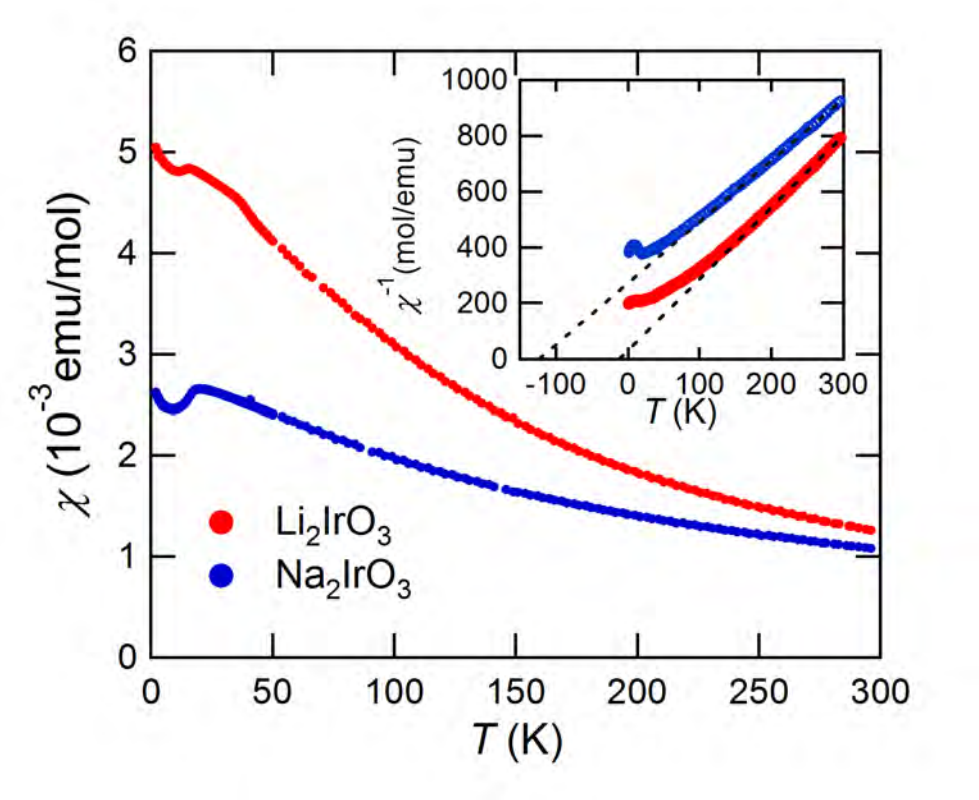



**Kitaev spin liquid??**

**<u>In real materials,</u>**

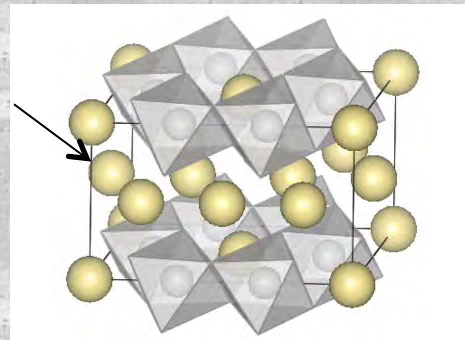
- **Other interactions ($J_{AF}$, $J_2$, )**
- **Distortion in $IrO_6$ octahedra**

# Antiferromagnetic ordering in $\alpha$-$A_2IrO_3$ (Na, Li)




Also by Y. Singh, P. Gegenwart et al, PRL (12)

$\alpha$-$A_2IrO_3$
A = Na or Li
*C2/m*



- $\alpha$-$Na_2IrO_3$
  $T_N \sim 17$ K, $\theta_W \sim -125$ K
- $\alpha$-$Li_2IrO_3$
  $T_N \sim 15$ K, $\theta_W \sim -12$ K

- **Large difference of $\theta_W$ between $\alpha$-$Li_2IrO_3$ and $\alpha$-$Na_2IrO_3$**
- **Kitaev-type (ferro) interaction seems secondary...**

**Enhance Kitaev... Hyperhoneycomb $\beta$-$Li_2IrO_3$** T. Takayama et al., PRL (2015)

**Go opposite way... New spin-liquid H-$Li_2IrO_3$**

# Summary

**Spin-orbital Mott insulators in iridates**

**...Produced by weak *U*, assisted by strong spin-orbit coupling**

**1. Metallic iridates close to MIT**

Semi-metals produced by spin-orbit coupling
The nature of metallic state is critically influenced by SOC.

**2. Weak Mott iridium magnets**

Sizable charge fluctuation, long-range hopping
May stabilize spin-liquid ground state.

**Novel metal-insulator transition under the influence of SOC**