

Mainz, Germany: 13 Nov. 2019

Novel Electronic and Magnetic Phases in Correlated Spin-Orbit Coupled Oxides

Importance of the quantification of Coulomb interaction in 5d oxides

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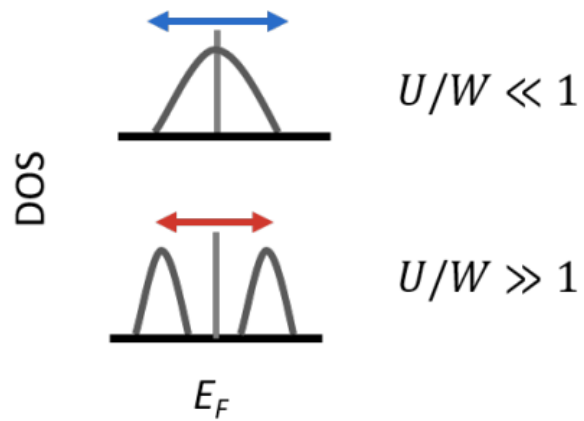
Abstract

- **Introduction & Motivation**
- **iridates**
- **osmates**
- **Summary**

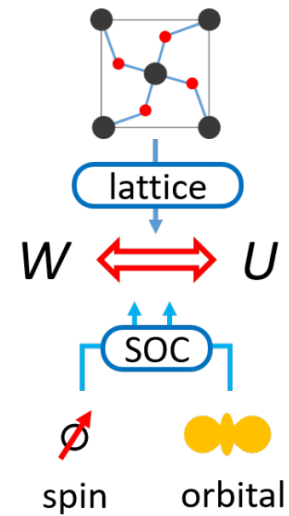
Transition metal oxides

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|--|--|--|---|--|--|---|---|---|--|---|---------------------------------------|---|---|---|---------------------------------------|--------------------------------------|--------------------------------------|---|---------------------------------------|--|--|---|---|---------------------------------------|--|---|--|--|--|---------------------------------------|--|--|--|---|---|--------------------------------------|--|---------------------------------------|---|
| 1 H Hydrogen 1.008 | | | | | | | | | | | | | | | | | 2 He Helium 4.002602 | | | | | | | | | | | | | | | | | | | | | | |
| 3 Li Lithium 6.94 | 4 Be Beryllium 9.0121831 | | | | | | | | | | | | | | | | | 5 B Boron 10.81 | 6 C Carbon 12.011 | 7 N Nitrogen 14.007 | 8 O Oxygen 15.999 | 9 F Fluorine 18.998403163 | 10 Ne Neon 20.1797 | | | | | | | | | | | | | | | | |
| 11 Na Sodium 22.98976928 | 12 Mg Magnesium 24.305 | | | | | | | | | | | | | | | | | 13 Al Aluminum 26.9815385 | 14 Si Silicon 28.0855 | 15 P Phosphorus 30.973761998 | 16 S Sulfur 32.06 | 17 Cl Chlorine 35.45 | 18 Ar Argon 39.948 | | | | | | | | | | | | | | | | |
| 19 K Potassium 39.0983 | 20 Ca Calcium 40.078 | 21 Sc Scandium 44.955909 | 22 Ti Titanium 47.867 | 23 V Vanadium 50.9415 | 24 Cr Chromium 51.9961 | 25 Mn Manganese 54.938044 | 26 Fe Iron 55.845 | 27 Co Cobalt 58.933194 | 28 Ni Nickel 58.6934 | 29 Cu Copper 63.546 | 30 Zn Zinc 65.38 | 31 Ga Gallium 69.723 | 32 Ge Germanium 72.630 | 33 As Arsenic 74.921595 | 34 Se Selenium 78.971 | 35 Br Bromine 79.904 | 36 Kr Krypton 83.798 | 37 Rb Rubidium 85.4678 | 38 Sr Strontium 87.62 | 39 Y Yttrium 88.90584 | 40 Zr Zirconium 91.224 | 41 Nb Niobium 92.90637 | 42 Mo Molybdenum 95.95 | 43 Tc Technetium (98) | 44 Ru Ruthenium 101.07 | 45 Rh Rhodium 102.90550 | 46 Pd Palladium 106.42 | 47 Ag Silver 107.8682 | 48 Cd Cadmium 112.411 | 49 In Indium 114.818 | 50 Sn Tin 118.710 | 51 Sb Antimony 121.757 | 52 Te Tellurium 127.60 | 53 I Iodine 126.90447 | 54 Xe Xenon 131.293 | | | | |
| 55 Cs Caesium 132.90545196 | 56 Ba Barium 137.327 | 57 - 71 Lanthanoids | 72 Hf Hafnium 178.49 | 73 Ta Tantalum 180.94788 | 74 W Tungsten 183.84 | 75 Re Rhenium 186.207 | 76 Os Osmium 190.23 | 77 Ir Iridium 192.222 | 78 Pt Platinum 195.084 | 79 Au Gold 196.966569 | 80 Hg Mercury 200.592 | 81 Tl Thallium 204.38 | 82 Pb Lead 207.2 | 83 Bi Bismuth 208.98040 | 84 Po Polonium (209) | 85 At Astatine (210) | 86 Rn Radon (222) | 87 Fr Francium (223) | 88 Ra Radium (226) | 89 - 103 Actinoids | 104 Rf Rutherfordium (261) | 105 Db Dubnium (268) | 106 Sg Seaborgium (269) | 107 Bh Bohrium (270) | 108 Hs Hassium (277) | 109 Mt Meitnerium (278) | 110 Ds Darmstadtium (281) | 111 Rg Roentgenium (282) | 112 Cn Copernicium (285) | 113 Nh Nihonium (286) | 114 Fl Flerovium (289) | 115 Mc Moscovium (288) | 116 Lv Livermorium (293) | 117 Ts Tennessine (294) | 118 Og Oganesson (294) | | | | |
| 57 La Lanthanum 138.90547 | 58 Ce Cerium 140.16 | 59 Pr Praseodymium 140.90766 | 60 Nd Neodymium 144.242 | 61 Pm Promethium (145) | 62 Sm Samarium 150.36 | 63 Eu Europium 151.964 | 64 Gd Gadolinium 157.25 | 65 Tb Terbium 158.92535 | 66 Dy Dysprosium 162.502 | 67 Ho Holmium 164.93033 | 68 Er Erbium 167.259 | 69 Tm Thulium 168.93432 | 70 Yb Ytterbium 173.045 | 71 Lu Lutetium 174.967 | | | | | | | | | | | 89 Ac Actinium (227) | 90 Th Thorium 232.0377 | 91 Pa Protactinium 231.03688 | 92 U Uranium 238.02891 | 93 Np Neptunium (237) | 94 Pu Plutonium (244) | 95 Am Americium (243) | 96 Cm Curium (247) | 97 Bk Berkelium (247) | 98 Cf Californium (251) | 99 Es Einsteinium (252) | 100 Fm Fermium (257) | 101 Md Mendelevium (258) | 102 No Nobelium (259) | 103 Lr Lawrencium (260) |

- Transition metal oxides

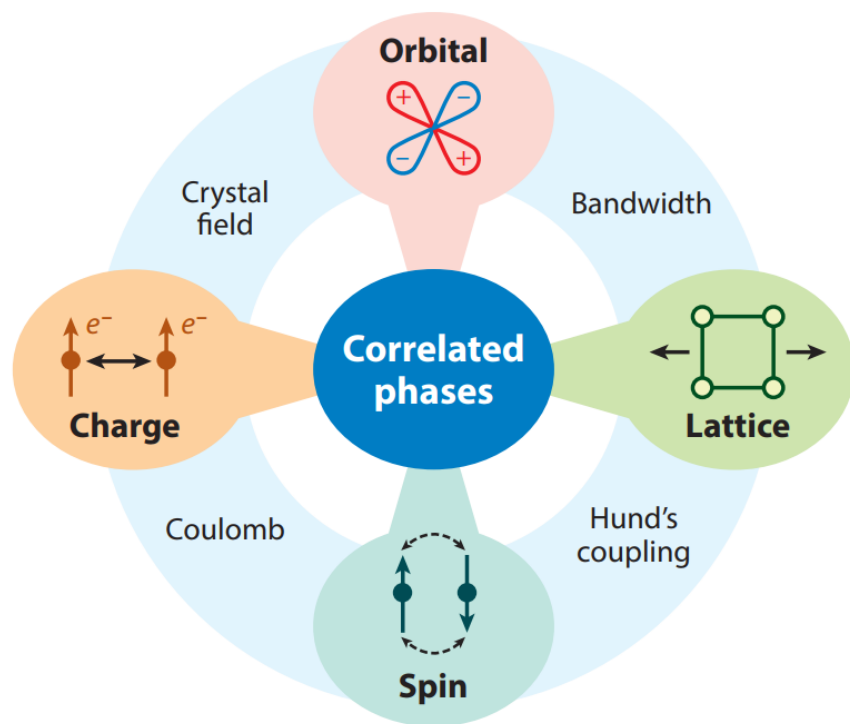


- Competition between U and W .

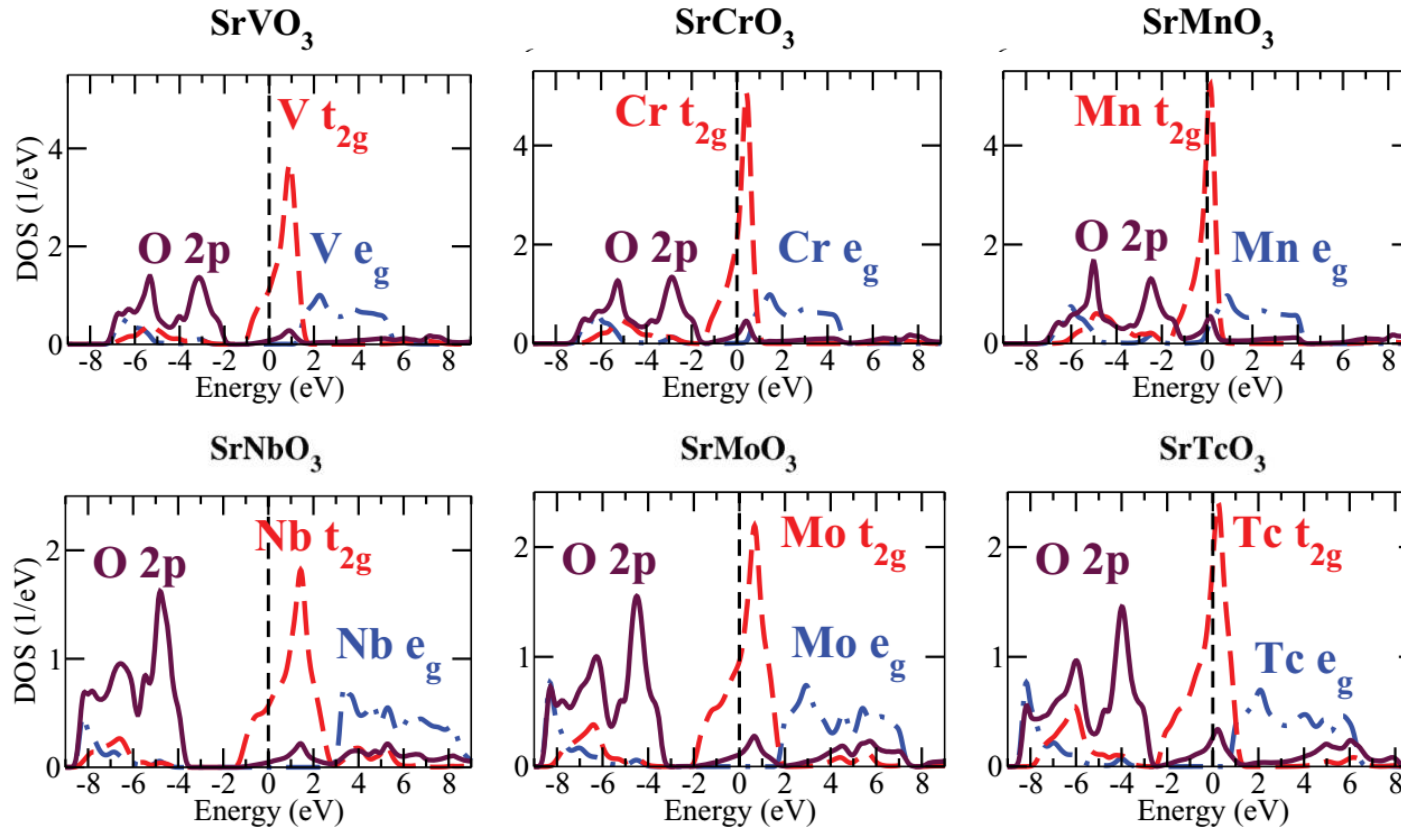


- Many degrees of freedoms.

■ Transition metal oxides



- High- T_C superconductors
- Colossal magnetoresistance (CMR)
- Unconventional magnetism
- (Multi)ferroicity
- Charge/spin/orbital order



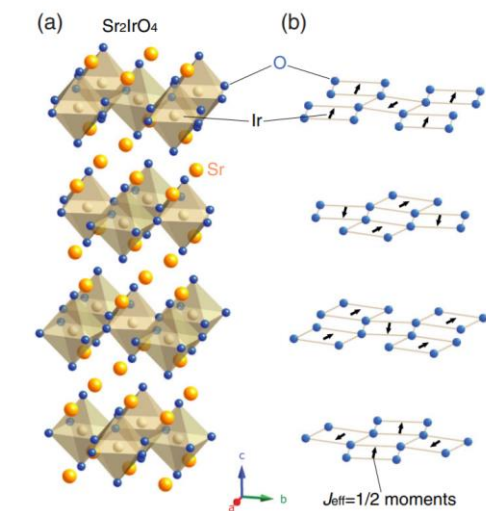
Vaugier *et al.*, PRB **86** 165105 (12)

- 3d oxides
 - Narrow bands
 - Strong correlation governs the physics
 - Role of SOC is minimal

| | 3d oxides | 5d oxides |
|-----|--------------------------|------------------------|
| | Cuprates, Manganites, .. | Iridates, Osmates, ... |
| U | 5-10 eV | 1-2 eV |
| W | a few eV | a few eV |
| SOC | minimal | ~0.5 eV |

- In 5d oxides..
 - ✓ energy scales of associated physical parameters are similar.
 - ✓ small tuning of specific parameter can change the essential physics.
 - ✓ recent experimental findings show physics in small energy scales.
 - ✓ correct quantification of parameters are important.

■ Sr2IrO4: cuprate analogue



$$J_{ij} = \frac{t_{ij}t_{ji}}{U}$$

- ✓ Heisenberg interaction scale of 60-100 meV

Resolution of RIXS energy scale:

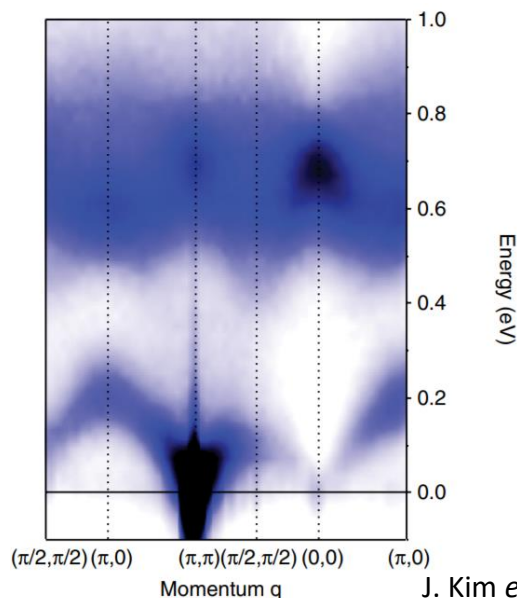
2000: 1500 meV

2010: 140 meV

2016: 8 meV

$$J=60 \text{ meV}, J'=-20 \text{ meV}, J''=15 \text{ meV}, \dots$$

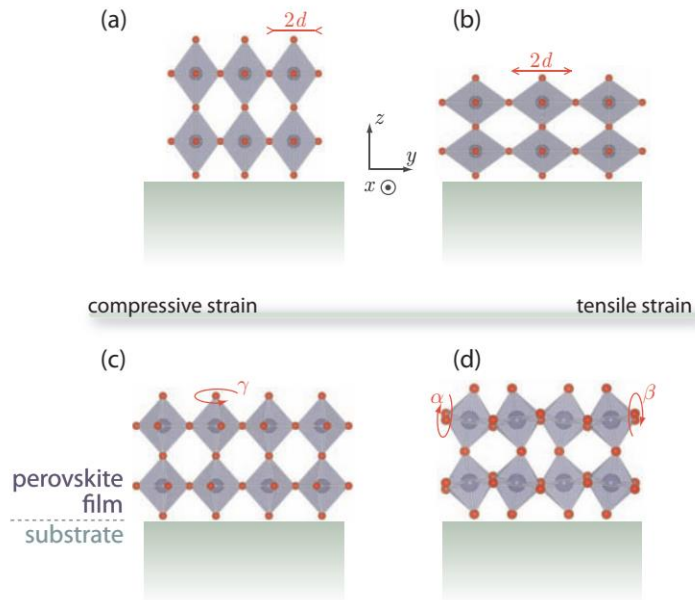
- ✓ Small scale of physical parameters < eV are at play
: U , t , J , SOC, .. etc



- Correct quantification of parameters are important.

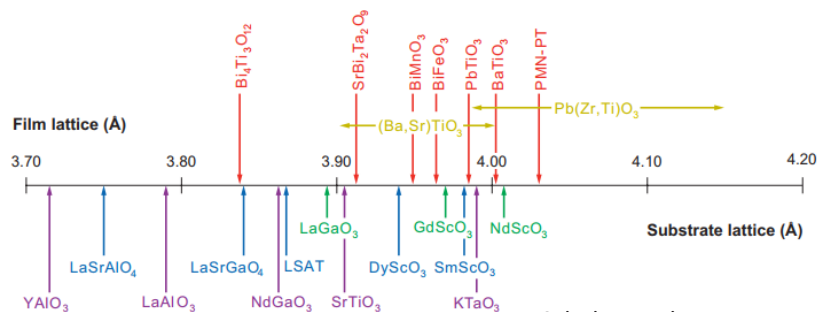
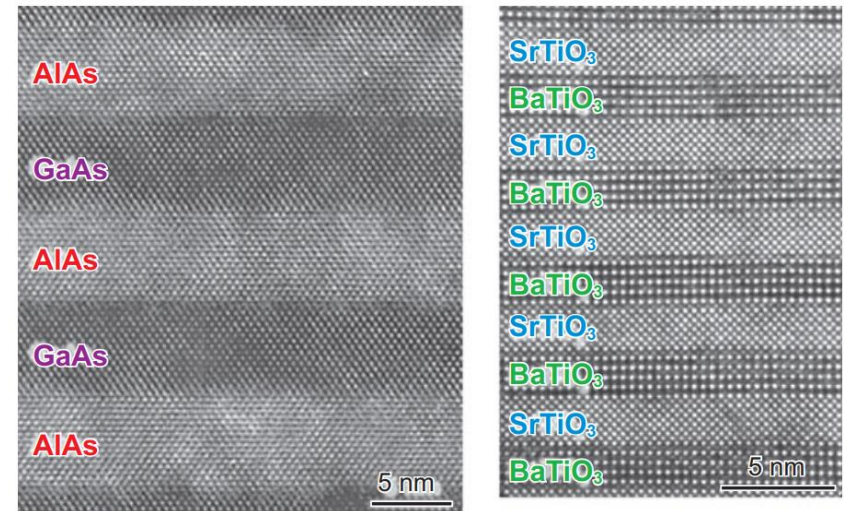
■ Material tuning

■ Epitaxial strain engineering



Rondinelli & Spaldin, Adv. Mater. **23** 3363 (2011)

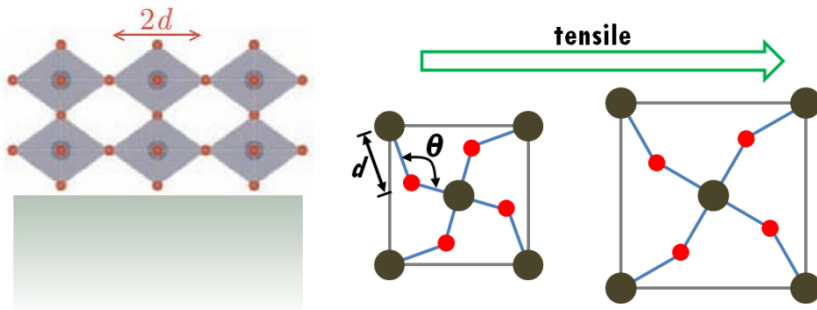
■ Heterostructuring



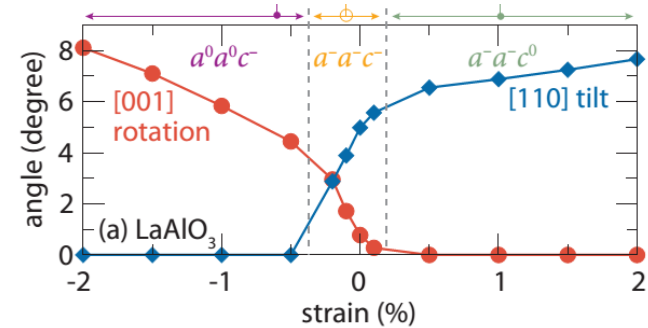
Scholm *et al.*, Annu. Rev. Mater. Res. **37** 589 (2007)

■ Material tuning

Strain

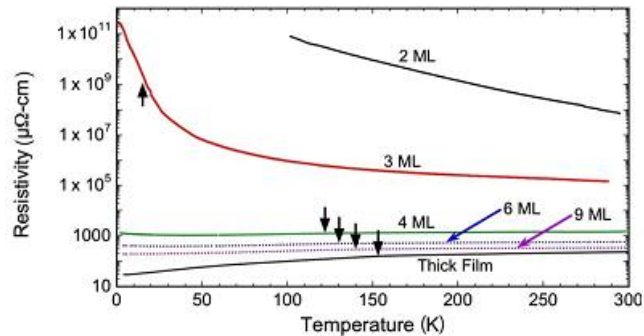


Symmetry



Rondinelli *et al.*, Adv. Mater. (2011)

Dimensionality

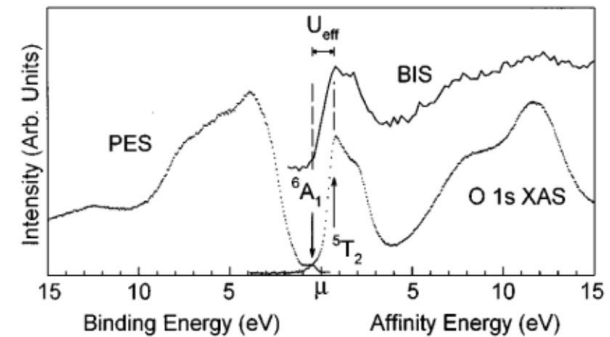


Xia *et al.*, PRB(R) **79** 040407 (2009)

- Tuning of bandwidth, hopping, crystal field splitting, symmetry, *etc*

“what about U ?”

- In DFT-based studies, strong correlation is treated with adding Hubbard-type parameter U
 - DFT+ U
 - DFT+DMFT
- The size of U is decided to fit experimental results
 - gap size
 - moment size
 - PES/IPES
- In practice for DFT studies, constant U has been employed upon structural modification.
 - strain, dimensional changes, etc.



“Is U parameter varies upon structural modification?”

■ cRPA (constrained random phase approximation)

- Exclude all the screening channels within the target correlated subspace (d orbitals for TMOs) from the total polarizability:

$$P^r = P - P^c$$

- Partially screened Coulomb interaction can be obtained by solving following Bethe-Salpeter equation:

$$\mathbf{U}^{-1} = [\mathbf{U}^{bare}]^{-1} - P^r$$

, where the correlated subspace is constructed by means of MLWF.

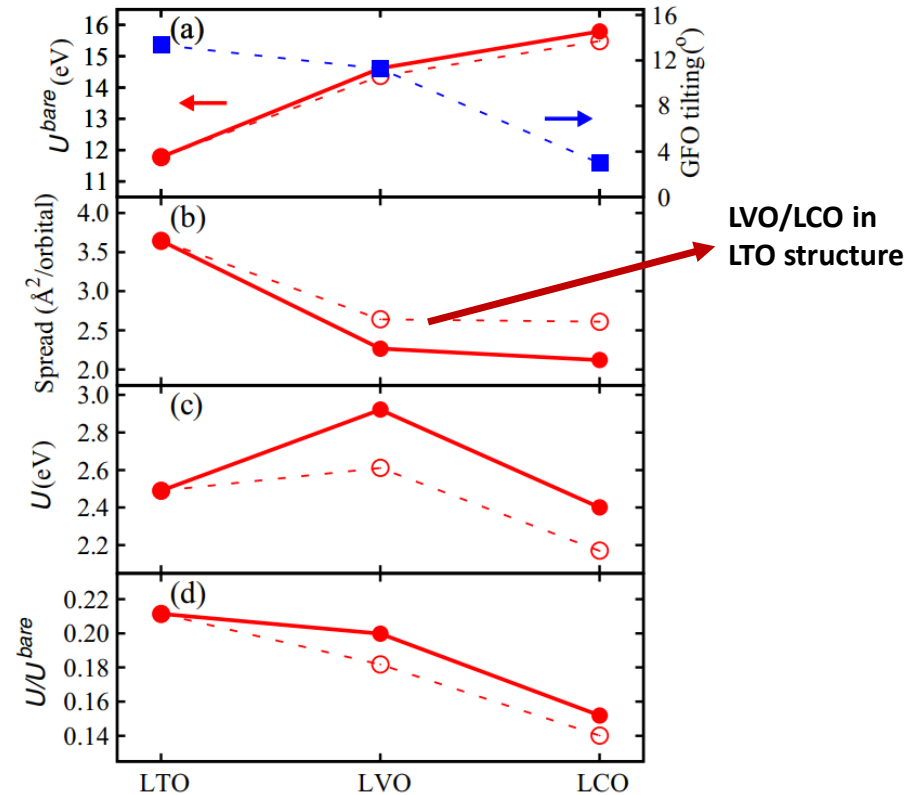
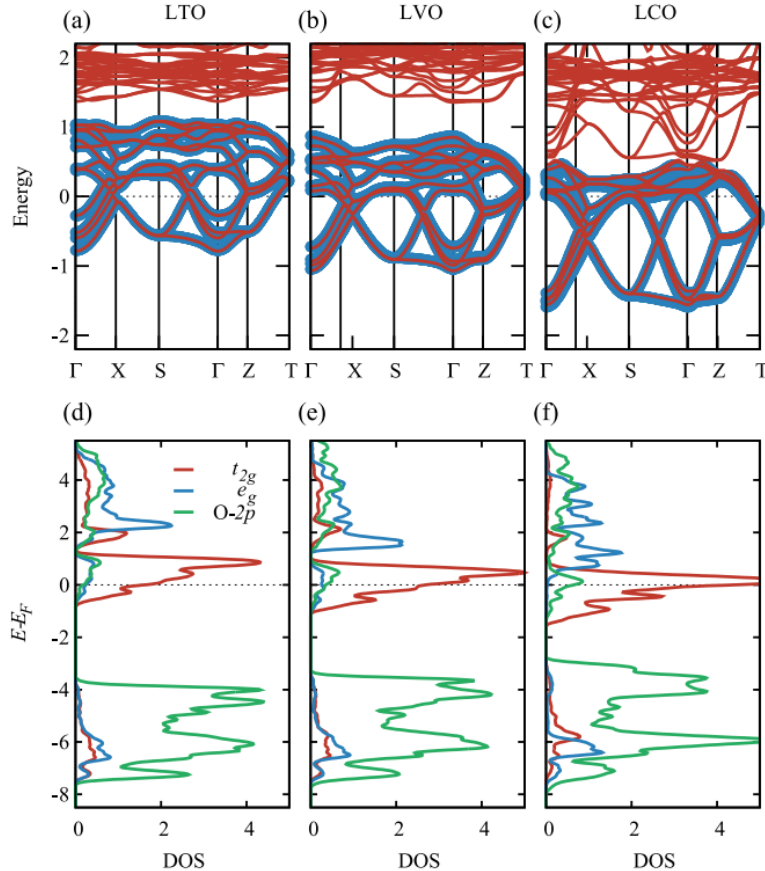
- Interaction parameters are calculated from

$$\mathbf{U}_{ijkl} = \lim_{\omega \rightarrow 0} \iint d^3r d^3r' w_i^*(\mathbf{r}) w_k^*(\mathbf{r}') \mathbf{U}(\mathbf{r}, \mathbf{r}', \omega) w_j(\mathbf{r}) w_l(\mathbf{r}'),$$

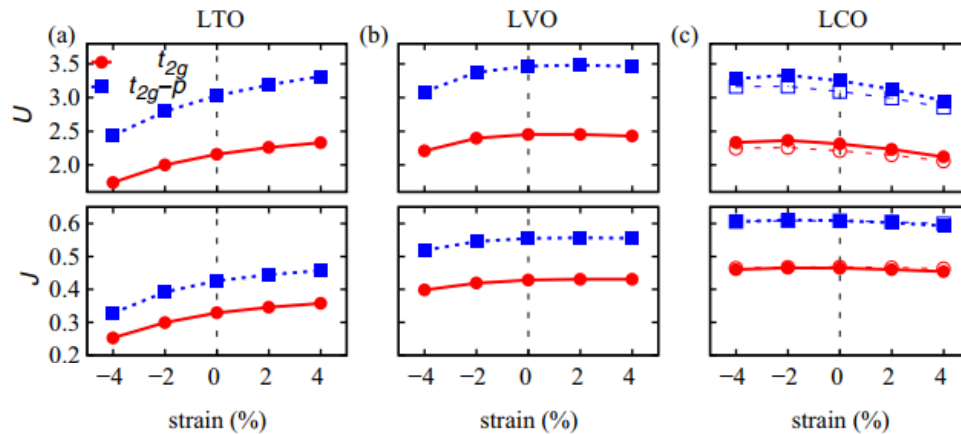
- U and J are obtained by averaging \mathbf{U}_{ijij} and $\mathbf{U}_{ijji}(i \neq j)$ matrix elements.
- We employed both $t2g/t2g$ and $t2g/t2g-p$ models.

3d oxides

BK et al., PRB 98 075130 (2018)



- Typical transition metal oxide perovskites chosen with varying occupancies:
 - LaTiO₃ (LTO, d^1), LaVO₃ (LVO, d^2) and LaCrO₃ (LCO, d^3)
 - t_{2g} - e_g levels are well-separated
 - d - p hybridization changes upon occupation
- Increase of U^{bare}
 - not from tilting but from occupation
- U does not follow trend of U^{bare}
- Strongly **enhanced screening** upon occupancy
- Competition between localization and screening

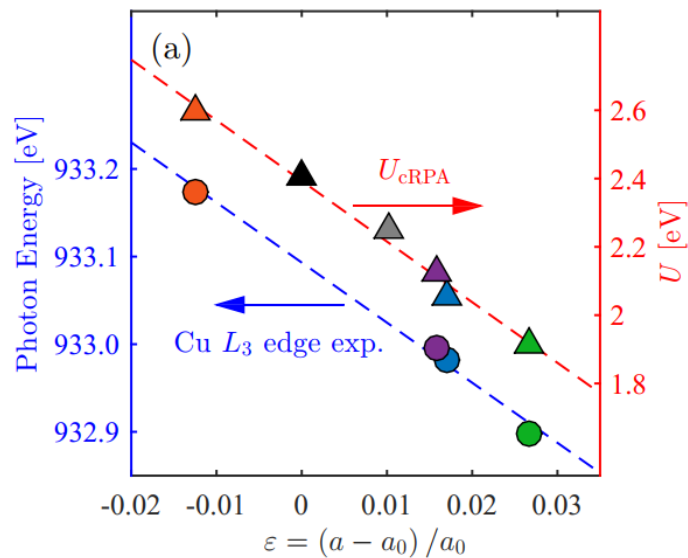


- Different strain dependence upon system.
 - LTO: U increase upon tensile strain
 - LCO: U decrease upon tensile strain

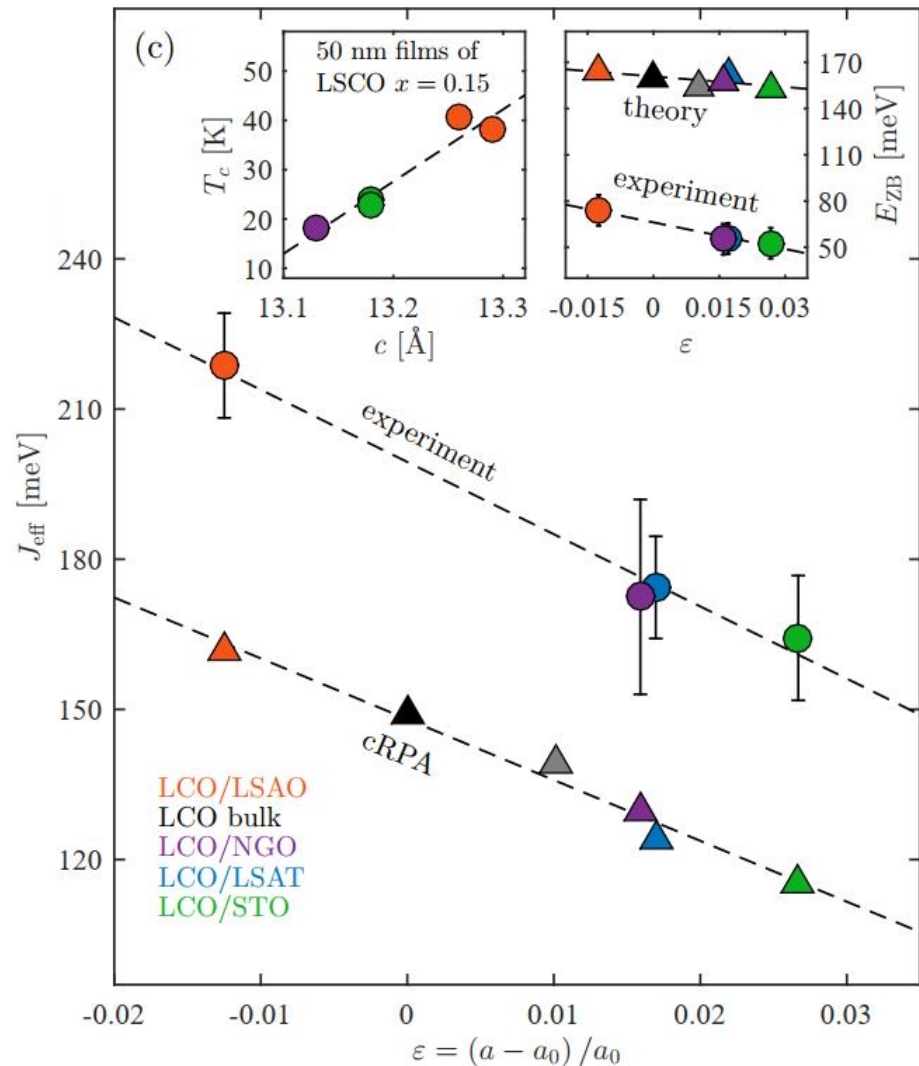
- Physics from localization, hybridization, and screening.
 - Wannier localization: effective in LTO
 - screening: more effective for LCO
 - Enhanced d - p overlap for LCO

La2CuO4

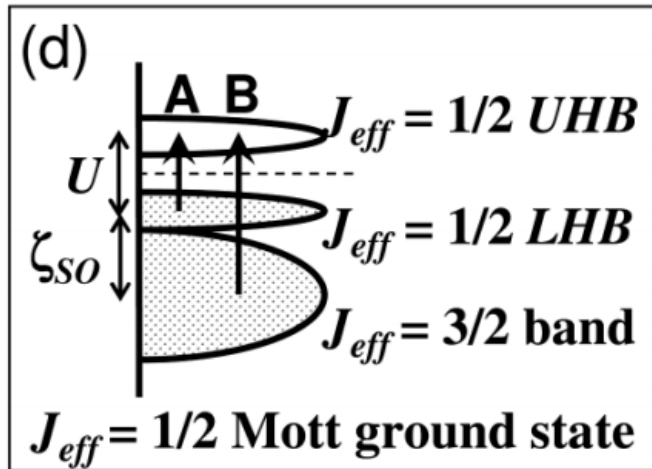
Ivashko *et al.*, Nature Comm. 10 786 (2019)



- Clear indication of change of U upon epitaxial strain.
- Clue to find the optimal condition for highest T_c .
 - enhancing Coulomb interaction & magnetic exchange interactions

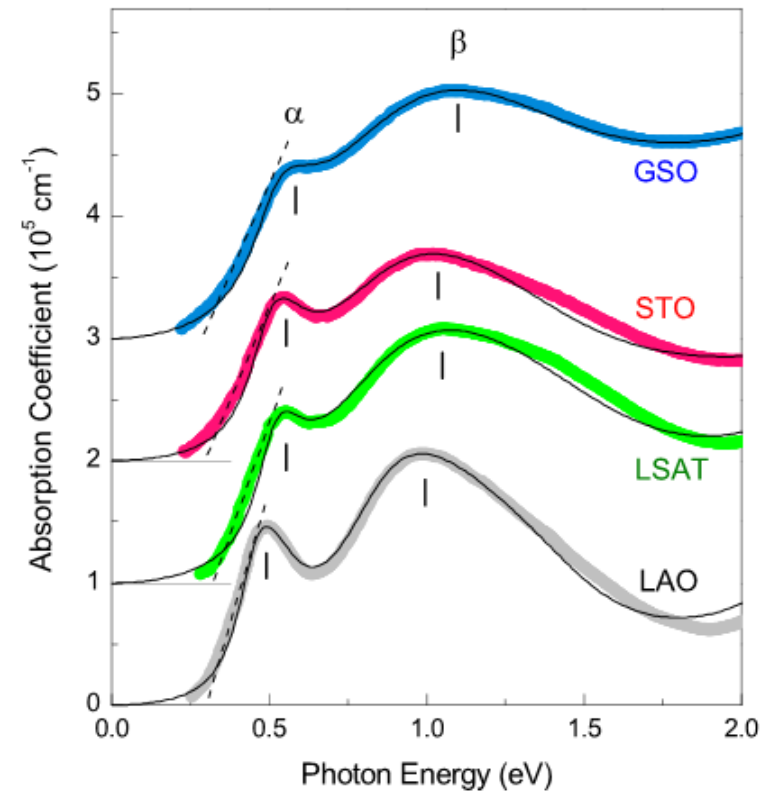


Sr2IrO4



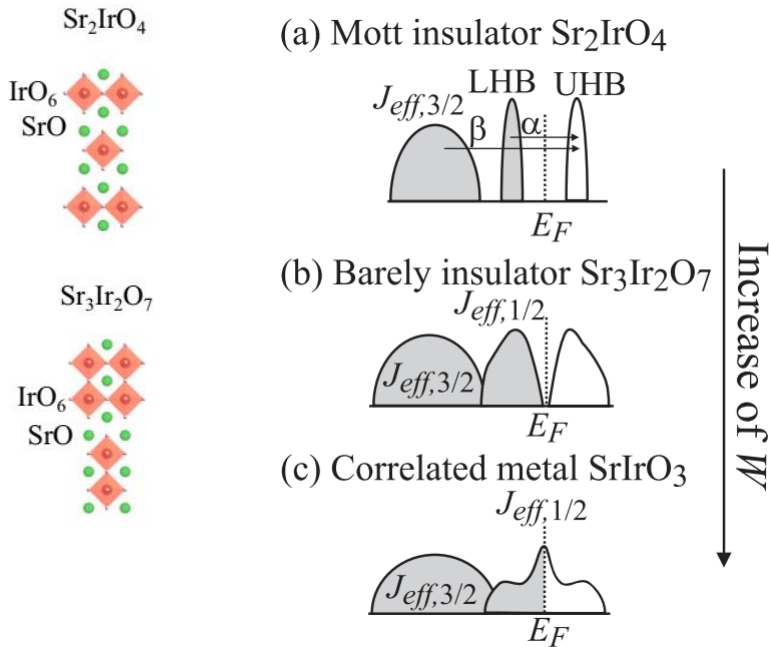
B.J.Kim *et al.*, PRL **101** 076402 (2008)

- Shift of α -peak: suggestive of U variations.



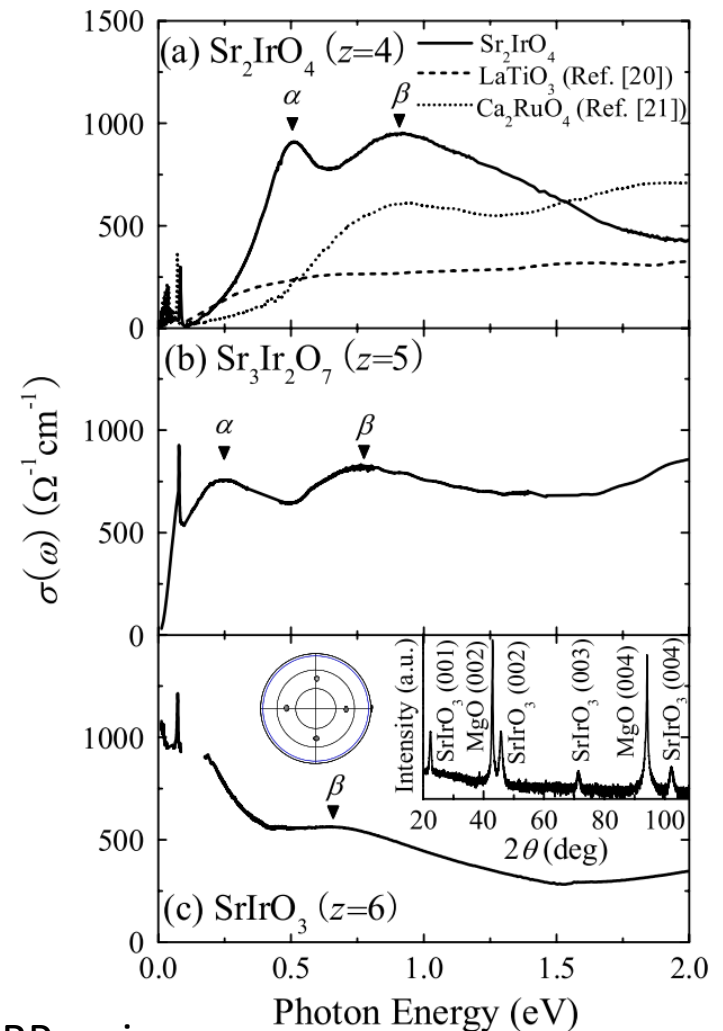
Nichols *et al.*, APL **102** 141908 (2013)

Ruddlesden-Popper series

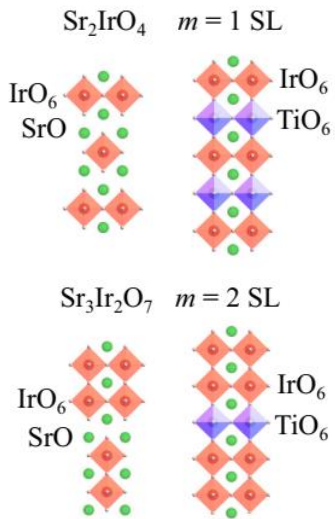


B.J.Kim *et al.*, PRL **101** 076402 (2008)

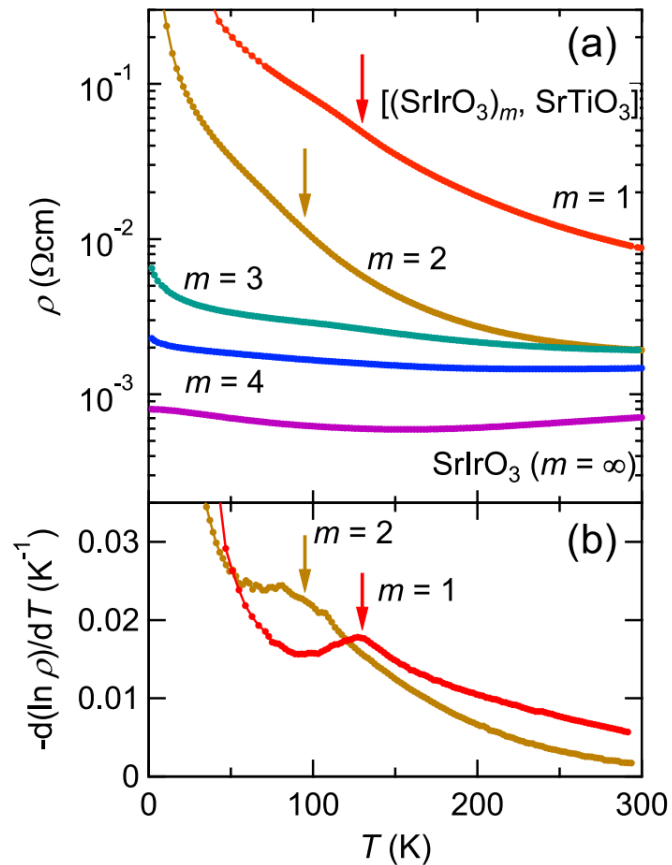
- Dimensional insulator-to-metal transition among RP series.
- Previously interpreted as increase of W upon dimensionality.
- Effective increase of U can be identified from optics.



(SrIrO₃)_m/(SrTiO₃)



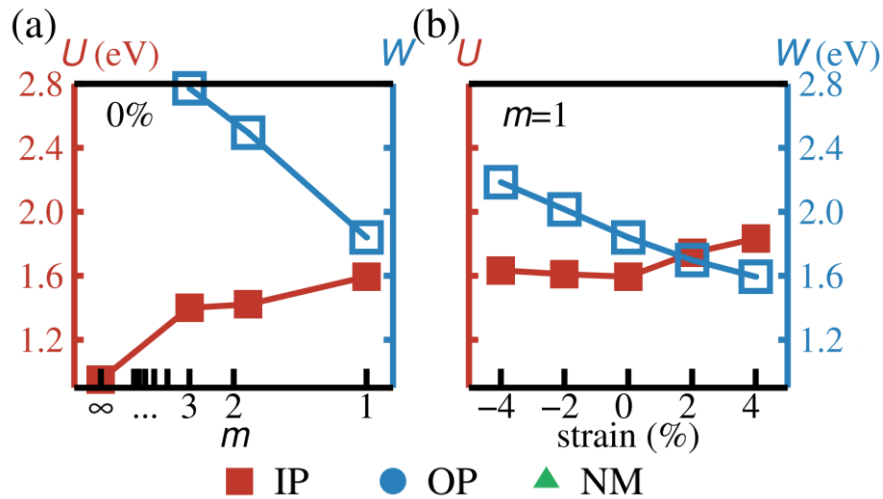
Matsuno *et al.*, PRL **114** 247209 (2015)



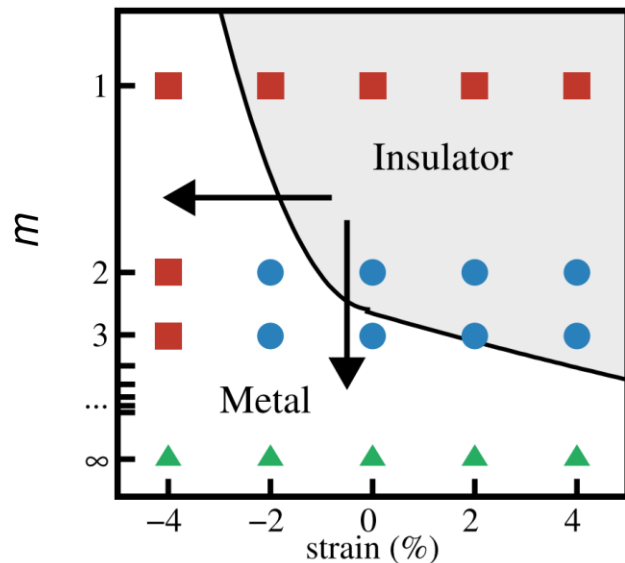
- Systematic study of dimensional effect using superlattice.
- Insulator-metal transition as well as magnetic transition observed.

$(\text{SrIrO}_3)_m/(\text{SrTiO}_3)$

BK *et al.*, PRB **95** 115111 (2017)



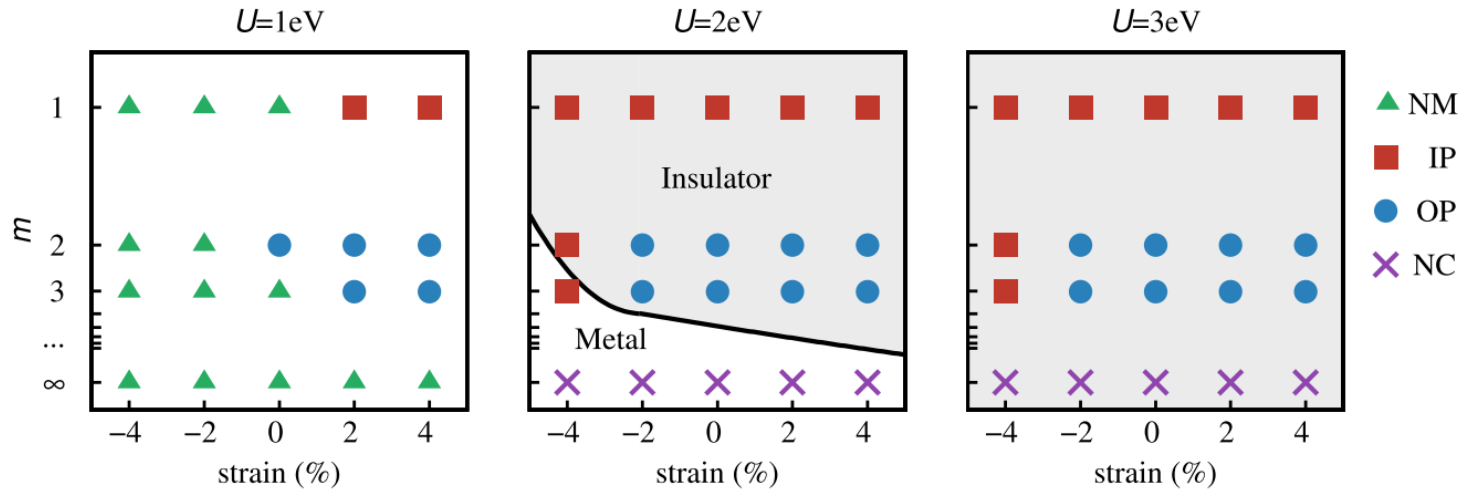
- Dimensional change of U & W can be quantified.
- Strain-dependence is not pronounced.



- Dimensionality-strain phase diagram
 - DFT+SOC+ U with calculated U value.
 - Correct electronic and magnetic phase obtained.
 - Reproduces experimental findings.

$(\text{SrIrO}_3)_m/(\text{SrTiO}_3)$

BK *et al.*, PRB **95** 115111 (2017)



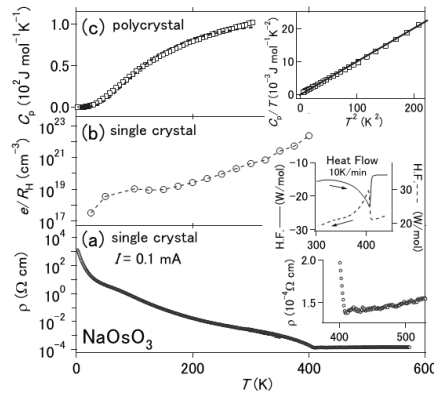
- Employing the same U value for different structures results in wrong phase diagram.
- One need to take account of the varying U !

NaOsO₃ and LiOsO₃

RAPID COMMUNICATIONS

PHYSICAL REVIEW B **80**, 161104(R) (2009)**Continuous metal-insulator transition of the antiferromagnetic perovskite NaOsO₃**

Y. G. Shi,^{1,2} Y. F. Guo,^{1,2} S. Yu,³ M. Arai,⁴ A. A. Belik,^{1,2} A. Sato,⁵ K. Yamaura,^{2,3,*} E. Takayama-Muromachi,^{1,2,3}
 H. F. Tian,⁶ H. X. Yang,⁶ J. Q. Li,⁶ T. Varga,⁷ J. F. Mitchell,⁷ and S. Okamoto⁸



- **Continuous MIT**
 - Cooling and warming curve follows the same trace.
 - Continuous change in carrier density

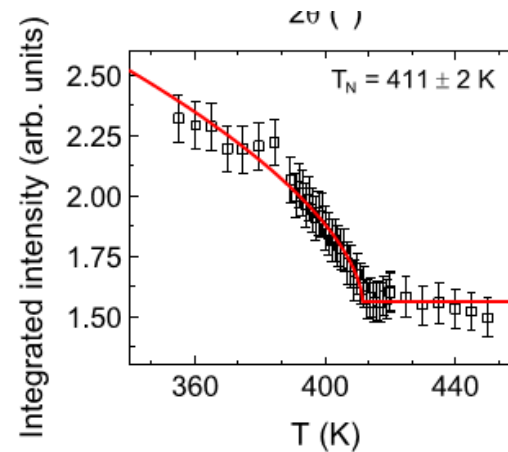
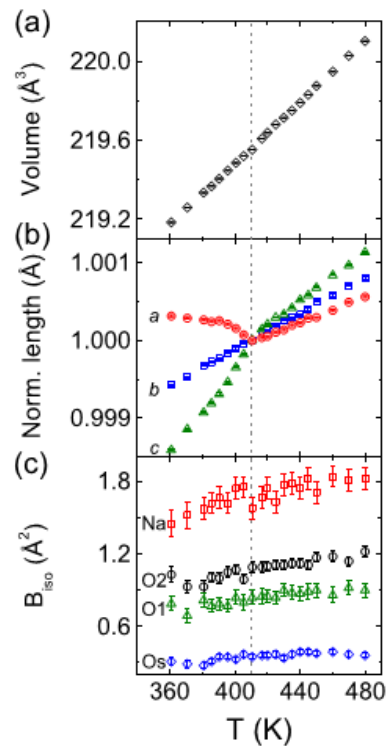
- **Ground state: G-type antiferromagnetic insulator**

NaOsO₃ and LiOsO₃PRL **108**, 257209 (2012)

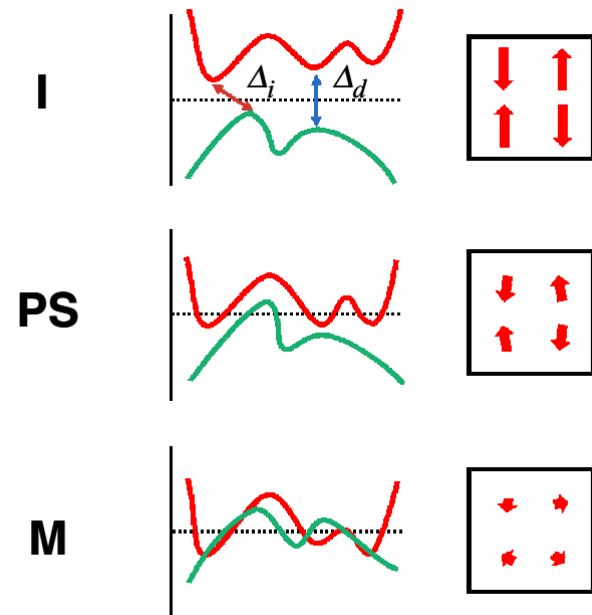
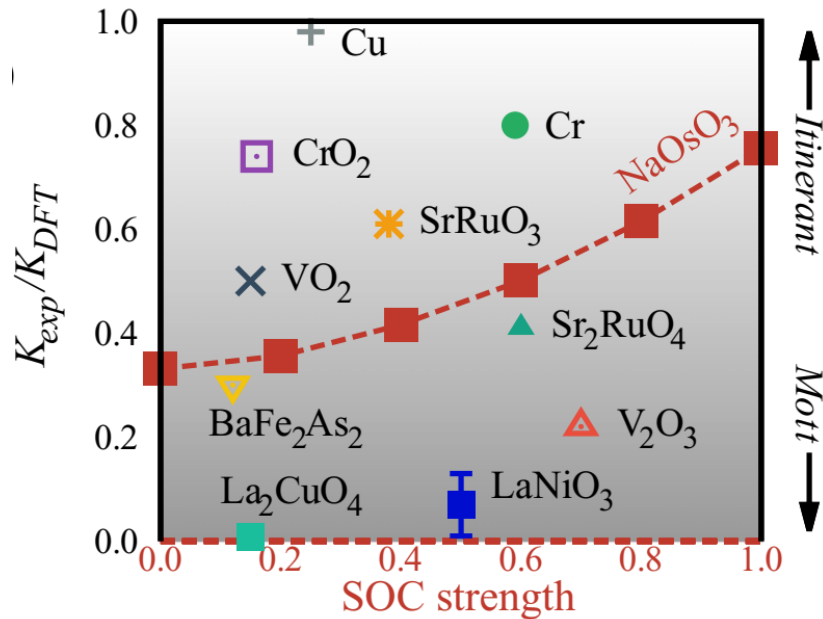
PHYSICAL REVIEW LETTERS

week ending
22 JUNE 2012**Magnetically Driven Metal-Insulator Transition in NaOsO₃**

S. Calder,^{1,*} V. O. Garlea,¹ D. F. McMorrow,² M. D. Lumsden,¹ M. B. Stone,¹ J. C. Lang,³ J.-W. Kim,³ J. A. Schlueter,⁴
Y. G. Shi,^{5,6} K. Yamaura,⁶ Y. S. Sun,⁷ Y. Tsumimoto,⁷ and A. D. Christianson¹



- limited structural effect.
- $T_{MIT} = T_N$.
- magnetism-driven.

NaOsO₃ and LiOsO₃BK *et al.*, PRB **94** 241113R (2016)

- SOC-induced renormalization of U .
- T-dep. spin-fluctuation drives the MIT of the system.

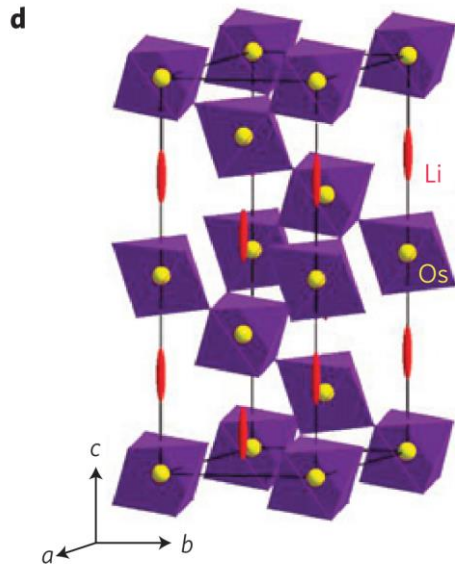
LETTERS

PUBLISHED ONLINE: 22 SEPTEMBER 2013 | DOI: 10.1038/NMAT3754

nature
materials

A ferroelectric-like structural transition in a metal

Youguo Shi^{1,2†}, Yanfeng Guo^{1,3†}, Xia Wang¹, Andrew J. Princep³, Dmitry Khalyavin⁴, Pascal Manuel⁴, Yuichi Michiue⁵, Akira Sato⁶, Kenji Tsuda⁷, Shan Yu¹, Masao Arai⁸, Yuichi Shirako⁹, Masaki Akaogi⁹, Nanlin Wang², Kazunari Yamaura^{1★} and Andrew T. Boothroyd^{3★}



- First example of polar metal
- $R-3c$ to $R3c$ transition
- Ground state: paramagnetic metal

NaOsO₃ and LiOsO₃

- Low- T

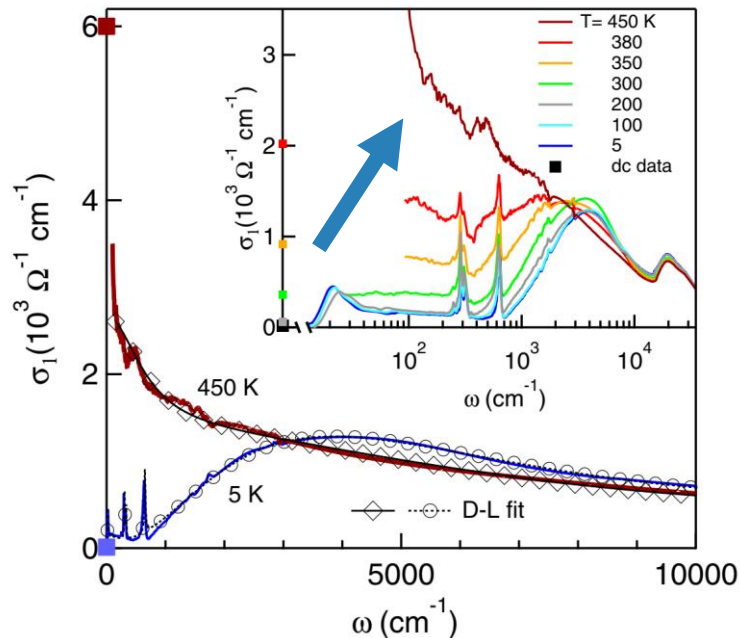
| | NaOsO ₃ | LiOsO ₃ |
|------------|--------------------|--------------------|
| Symmetry | <i>Pnma</i> | <i>R3c</i> |
| magnetism | G-AFM | paramagnetic |
| electronic | insulator | metal |

- Similar electronic structure expected but very different ground state.

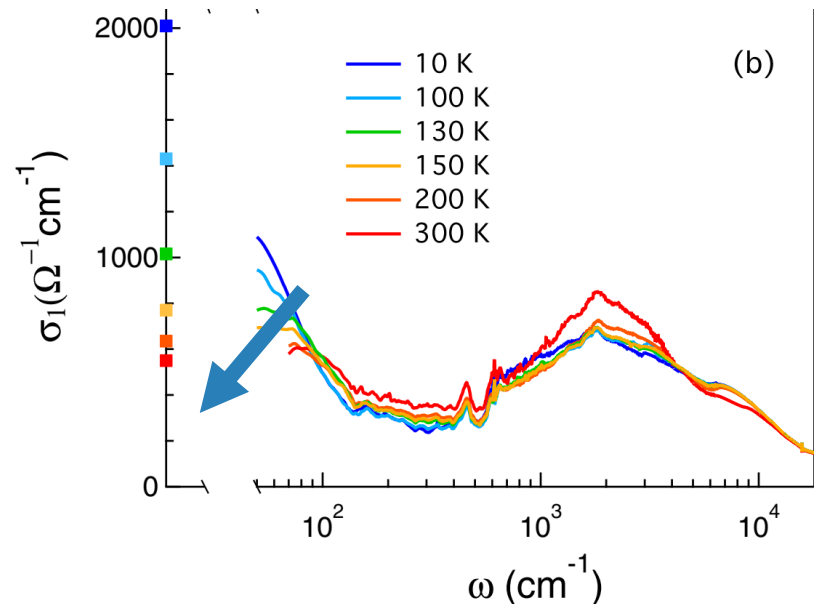
NaOsO₃ and LiOsO₃

- High-T: optical conductivity

Lo Vecchio *et al.*, Sci. Rep **3** 2990 (2013)



Lo Vecchio *et al.*, PRB **93** 161113R (2016)



NaOsO₃

- Increase of Drude part
- Metallic behavior as T increases

LiOsO₃

- Decrease of Drude part
- Insulating behavior as T decreases

NaOsO₃ and LiOsO₃

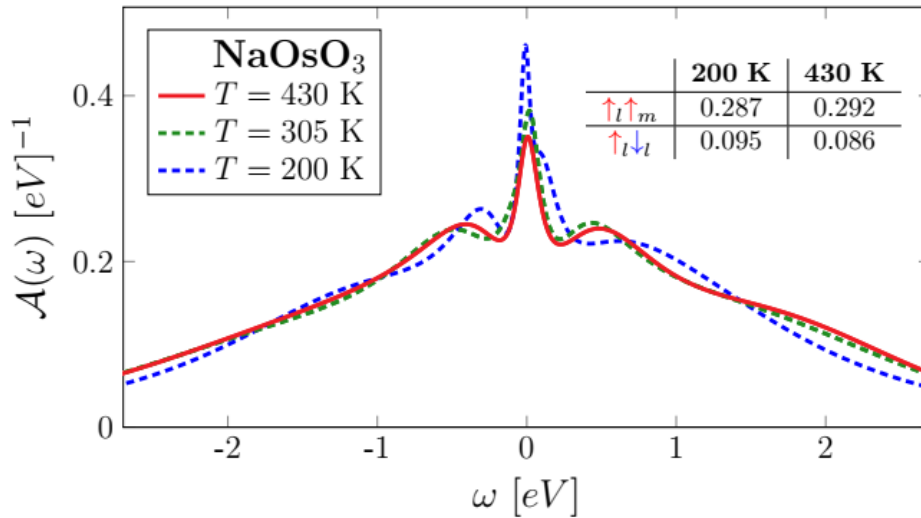
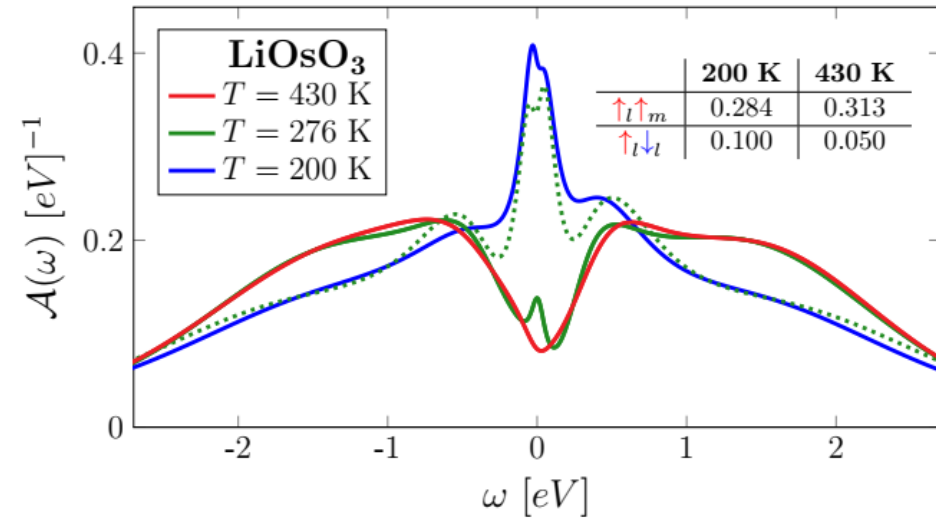
DFT+DMFT

- Wannier-projected t_{2g} orbitals.
- *w2dynamics* implementation.
- CTQMC

Physical parameters

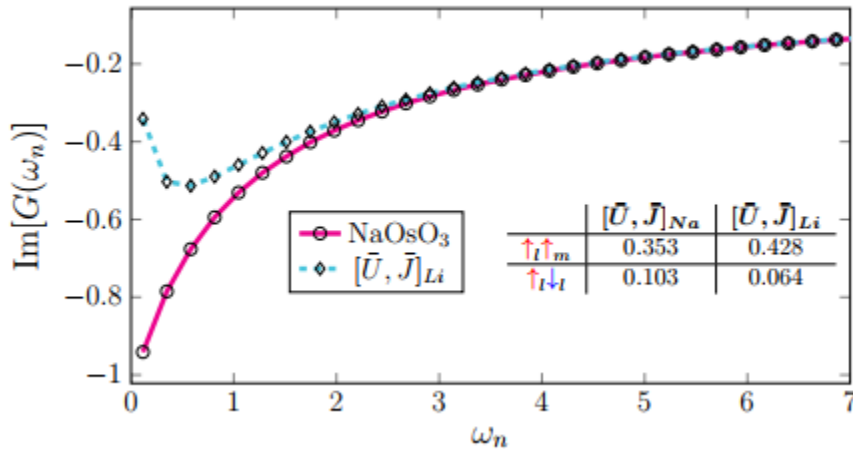
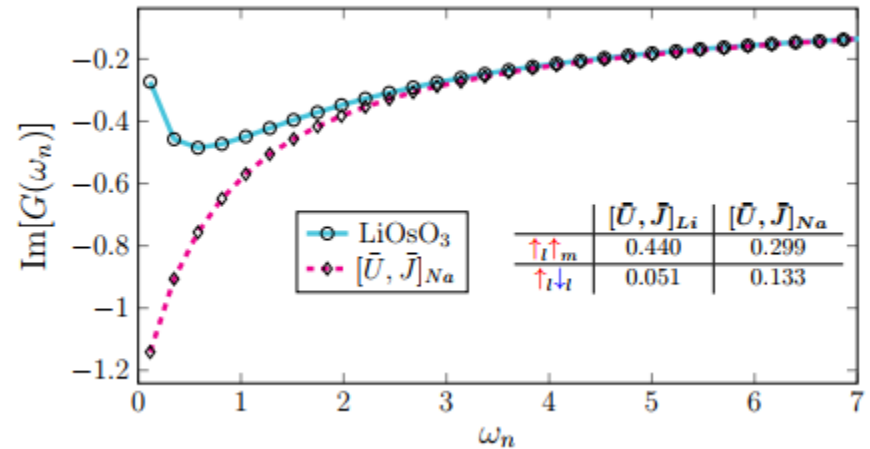
| | NaOsO ₃ | LiOsO ₃ |
|---------------------------------------|--------------------|--------------------|
| <i>U</i> | 2.25 eV | 2.35 eV |
| <i>J</i> | 0.24 eV | 0.25 eV |
| <i>W</i> | 3.9 eV | 3.5 eV |
| <i>intra t_{2g} splitting</i> | 150 meV | 250 meV |
| SOC | 0.3 eV | 0.3 eV |

On-site spectral function

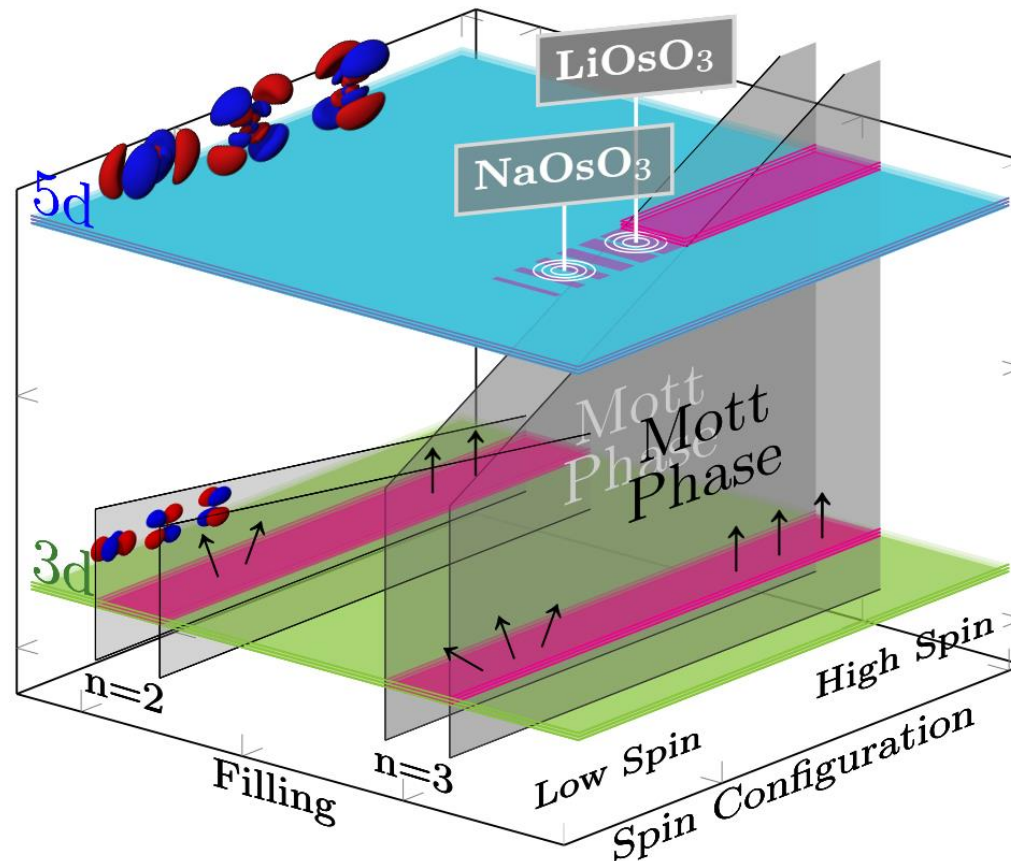
NaOsO₃LiOsO₃Springer, BK, *et al.*, arXiv:1910.05151

- Constructed from analytic continuation of on-site Green's function.
- Overall T-dep. behavior well-captured.
- Disappearance of metallic coherence for LiOsO₃ as T increase.
- Increase of interorbital spin alignment & decrease of intraorbital double occupancy.

Local Green's function

NaOsO₃LiOsO₃

- At high- T , metallic and insulating properties of NaOsO₃ and LiOsO₃ are well-described.
- Hund-Mott nature of insulating phase in LiOsO₃.
 - Enhanced interorbital spin alignment: large local moment.
 - Suppression of intraorbital occupation.
- Interchange of Coulomb parameters, U & J , produces perfect mirroring of Green's function.
- Small details in the interaction parameters are responsible for the stark difference in two systems.



- Two systems are located at the proximity to the $n=3$ Hund-Mott transition.
- In 5d systems, better description of related physical parameters are important.

Summary

- U is not a fixed parameter – strongly dependent on the electronic structure and structural details.
- When employing DFT+manybody approaches (+ U , +DMFT, etc), better quantification of Coulomb parameters are important – especially for 5d oxides.
- Implications for the TMO-based materials design.

BK, et. al, PRB **94** 241113 (2016)

BK, et. al, PRB **95** 115111 (2017)

BK, et. al, PRB **98** 075130 (2018)

Springer, **BK**, et. al, arXiv: 1910.05151

Liu, He, **BK**, et. al, to be submitted

Thank you