DFT+DMFT, oxide superlattices and the metal-insulator transition: the good, the bad and the ugly

A. J. Millis

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Support:
US-DOE-ER-046169
US-NSF-DMR-1006282

Hyowon Park, Andrew J. Millis, and Chris A. Marianetti, PRL 109, 156402 (2012)
E. Gull, O. Parcollet and A. J. Millis, PRL 110 216406 (2013)
H. T. Dang, A. J. Millis and C. Marianetti, arXiv:1309.2995

Bangalore 2014

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Collaborators

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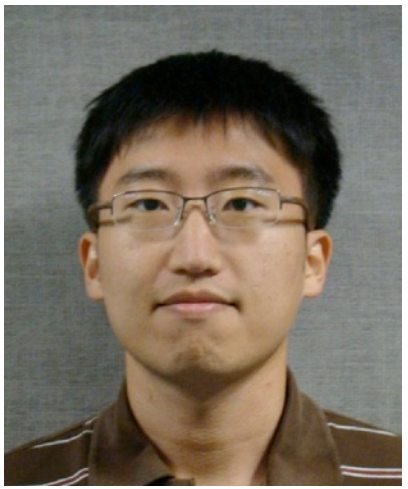
***Hyowon Park**



M-J. Han (CU->ANL->KAIST)
X. Wang (CU->U-Md)
L. deMedici (ESPCI)

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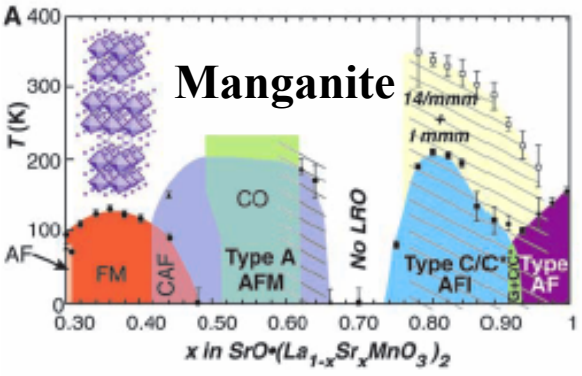
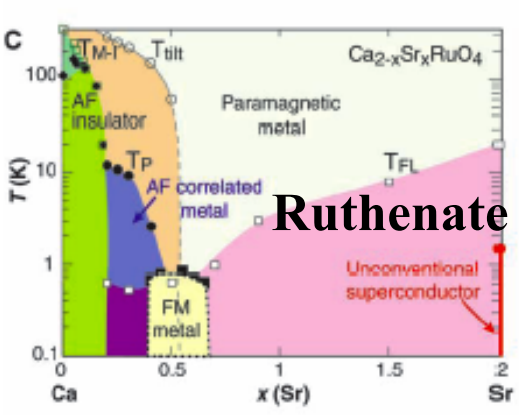
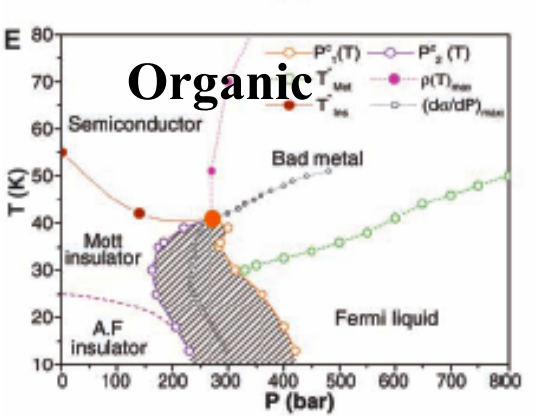
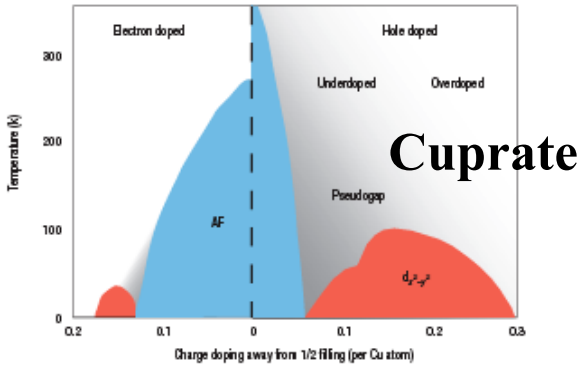
Materials with Strongly Correlated Electrons Do Interesting Things









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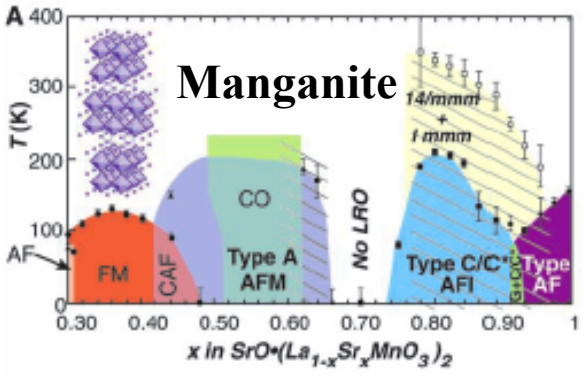
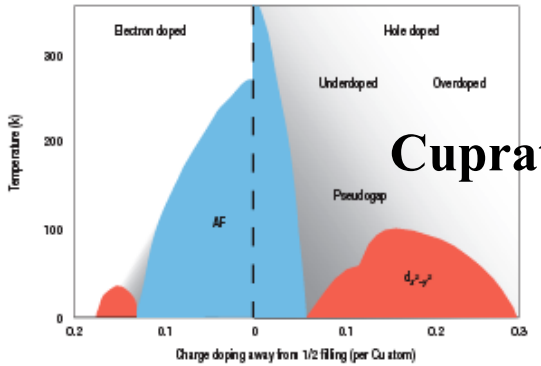
One would like to



Manganite



Cuprate

- **Design materials with desired behavior**
- **Control the phases with external fields**

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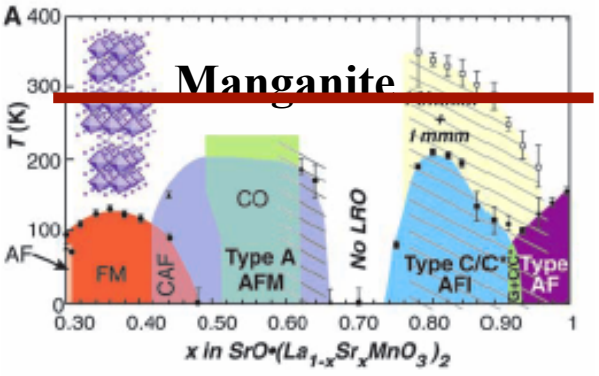
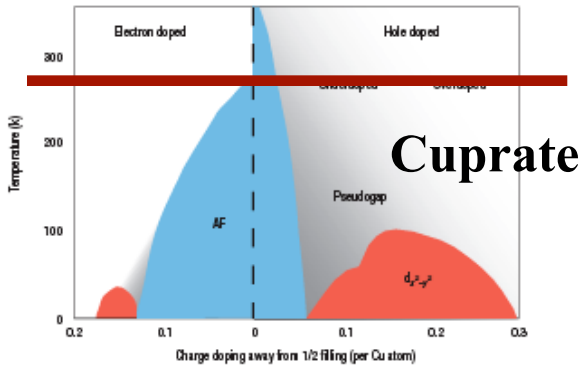
One would like to





- Design materials with desired behavior
- Control the phases with external fields
- Move the interesting behavior closer to (or above) room temperature

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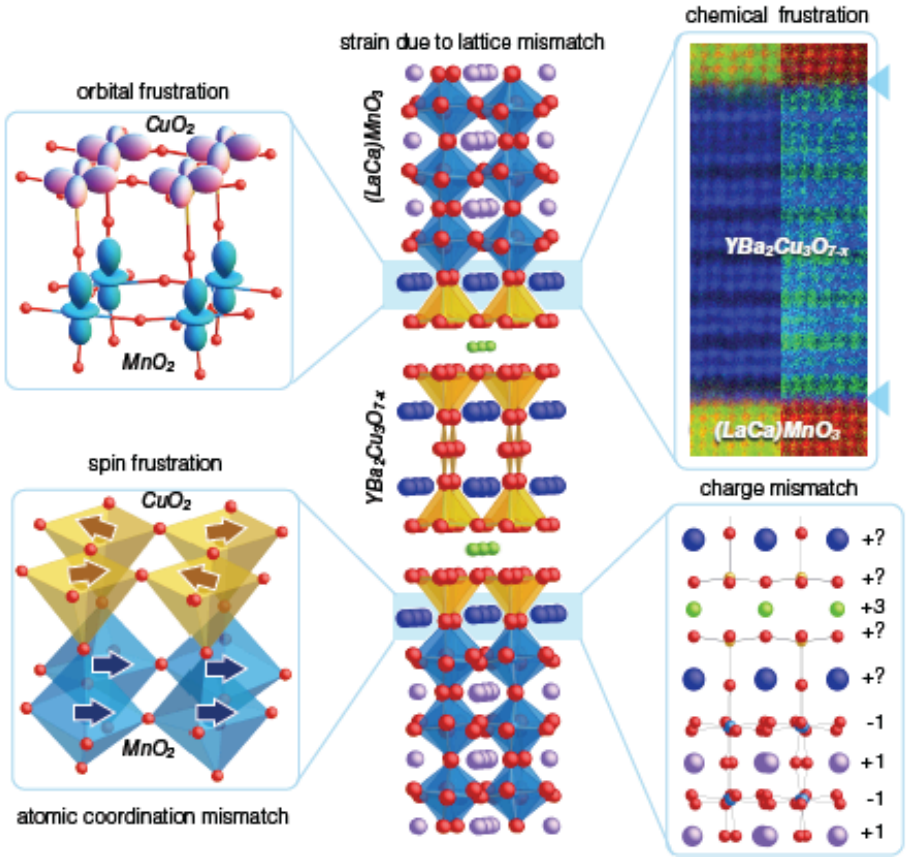
Oxide epitaxy: Can now combine ‘interesting’ materials on atomic scale



Control (in principle)

- Charge density
- Strain
- Local geometry (coordination/bond angles)
- Proximity (of different kinds of orders)

=>Access (in principle) new physics

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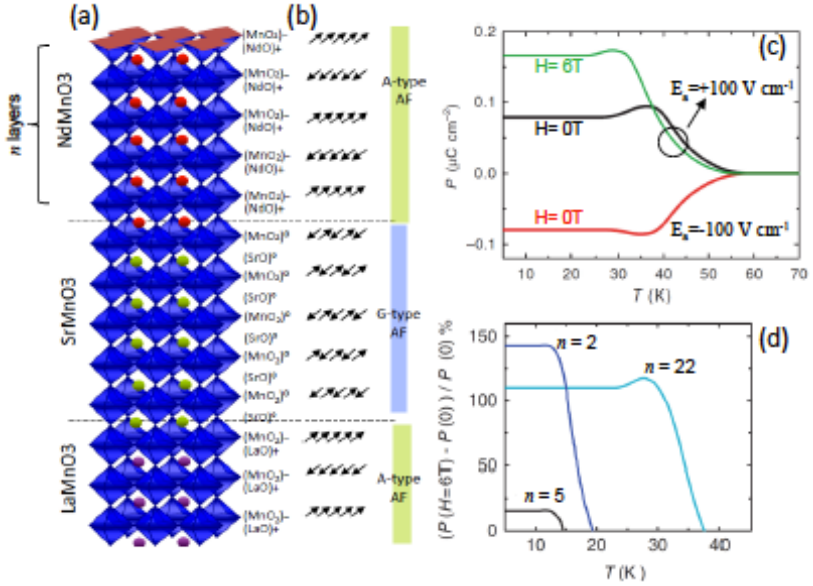
Examples

Multiferroicity

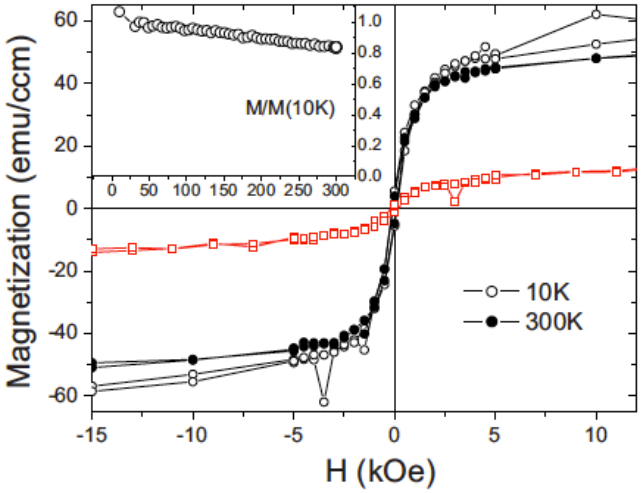
$(LaMnO_3)_n(SrMnO_3)_m\ (NdMnO_3)_l$



Rogdakis...Panagopolous, Nat. Comm 3 1064 (12)

?Room Temperature Ferromagnetism?

$(LaVO_3)_6/(SrVO_3)_1$



Luders et al Phys Rev B80 241102 (2009)

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Challenge for Theory

The Stuart Parkin question: What do I have to grow to get a room temperature superconductor??

More prosaically: need theory to

(a) determine electronic properties of model systems
(b) predict structures (esp oxygen positions)
(c) connect physical and chemical structure to properties

=> DFT+DMFT

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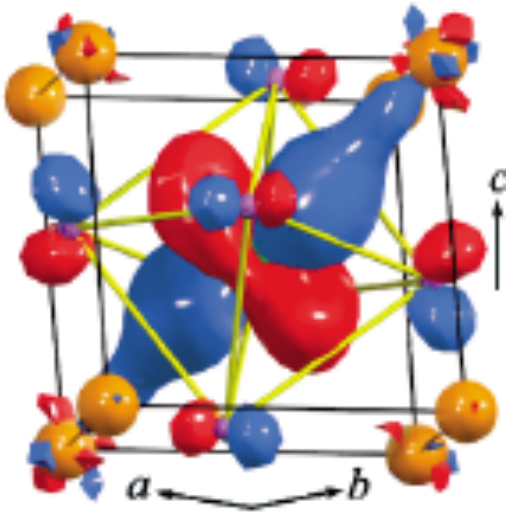
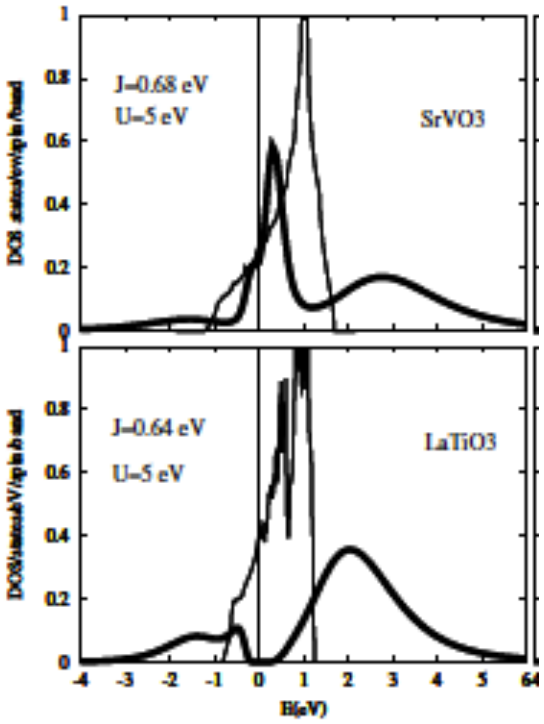
structure and properties (1a): local crystal structure

example: d^1 perovskites





Pavarini//Georges 2004: $GdFeO_3$ rotational distortion essential to insulating phase of $LaTiO_3$

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To understand metal-insulator transition

incorporate physics of crystal structure (esp.octahedral rotations) on equal footing with many-body effects

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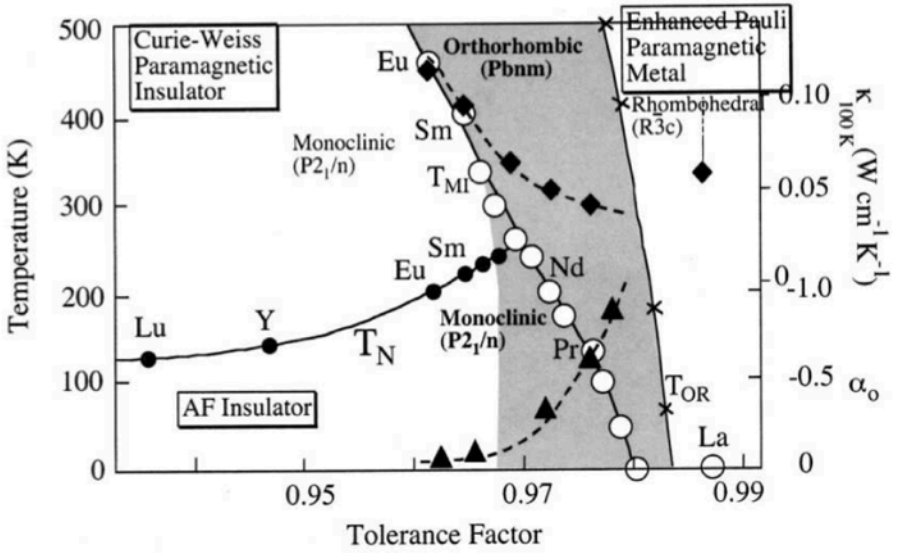
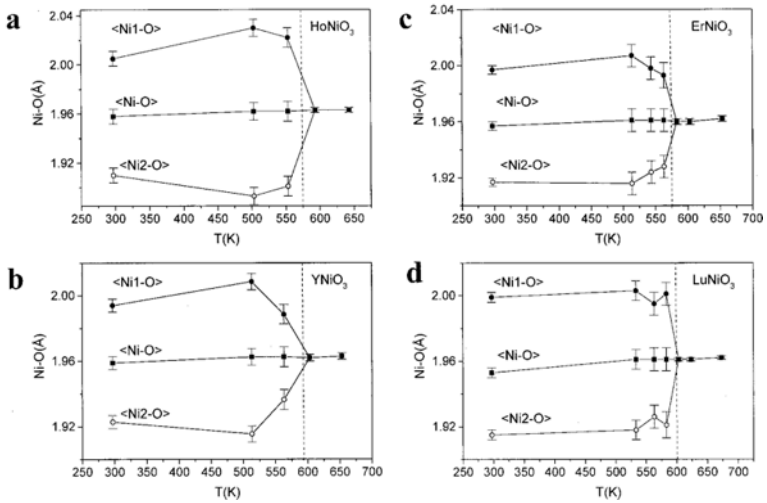
structure and properties (1b): oxygen displacements

example: rare earth nickelates





Metal-insulator transition coincident with change in Ni-O bond-length.

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To understand metal-insulator transition in nickelates

incorporate physics of changes in transition metal-oxygen bond lengths on equal footing with many-body effects

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Structure and properties (2): Charge transfer

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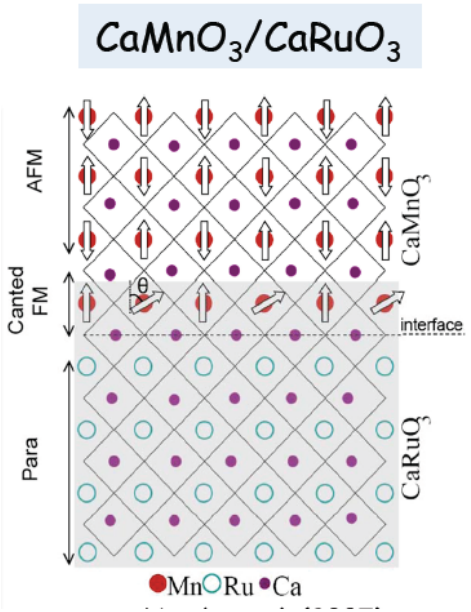
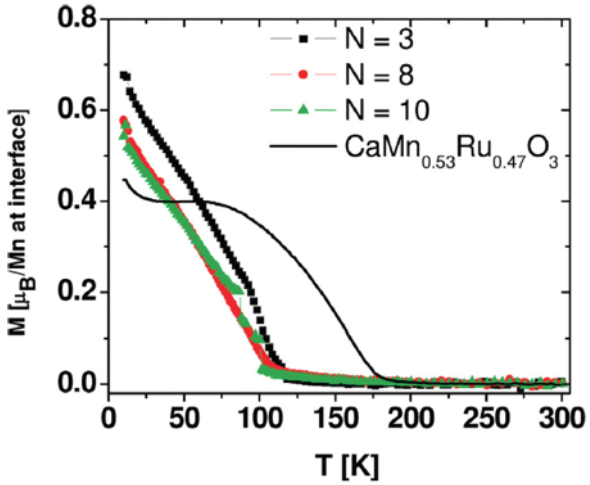
Ferromagnetism at interface between paramagnet, antiferromagnet





He et al JAP 109 07D729 (2011)
(see also Takahashi, Kawasaki and Tokura APL 79 1324 (2001)

Idea: charge flow across interface dopes $CaMnO_3$
?how much charge moves? ?in which direction?

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To understand oxide superlattices

understand charge flow between different materials =>work functions, atomic physics contribution to electronegativity and long-ranged Coulomb interaction (charge balance) on equal footing with many-body energetics

=>DFT+DMFT with full charge self consistency

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Important point

the many body physics of the metal-insulator transition and the charge flow in superlattices are intimately related

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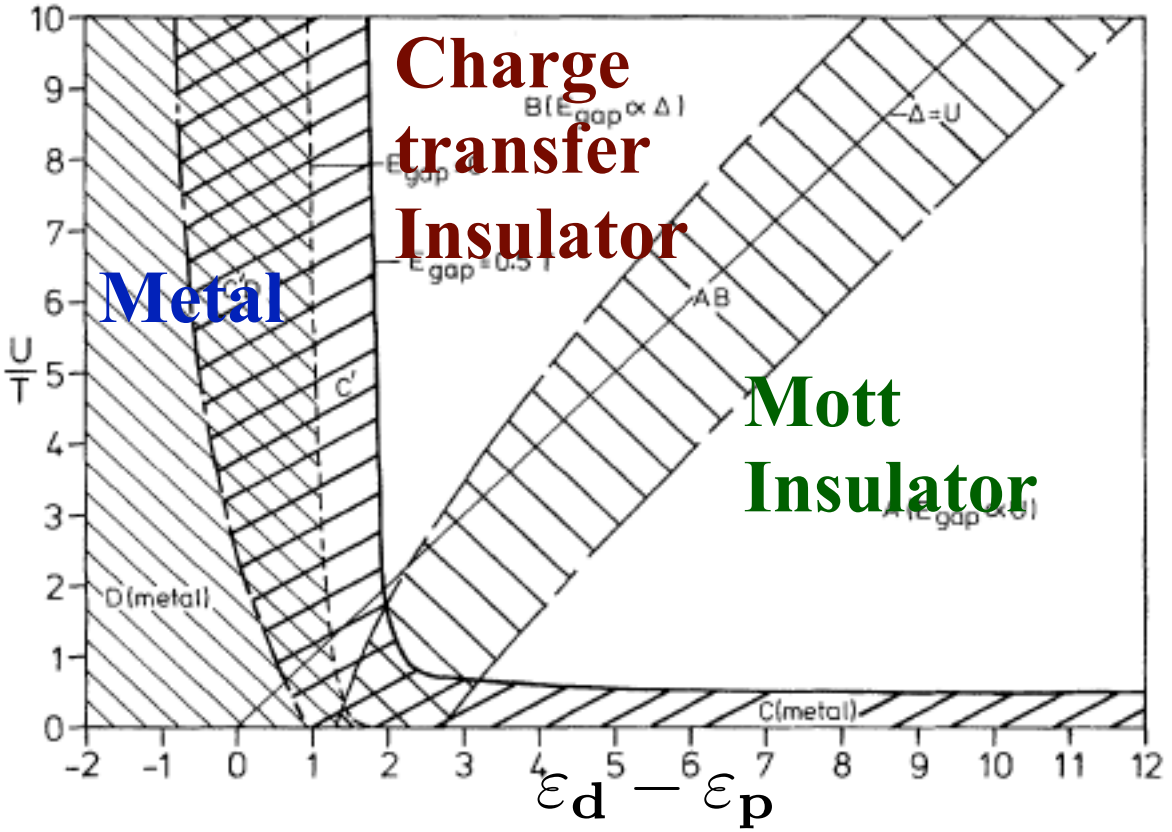
p-d splitting governs both metal-insulator transition and superlattice charge flow.



Conventional Wisdom

Oxygen energy: DFT band theory

d-level energy: correlation physics

VOLUME 55, NUMBER 4 PHYSICAL REVIEW LETTERS 22 JULY 1985

Band Gaps and Electronic Structure of Transition-Metal Compounds

Zaanen Sawatzky Allen

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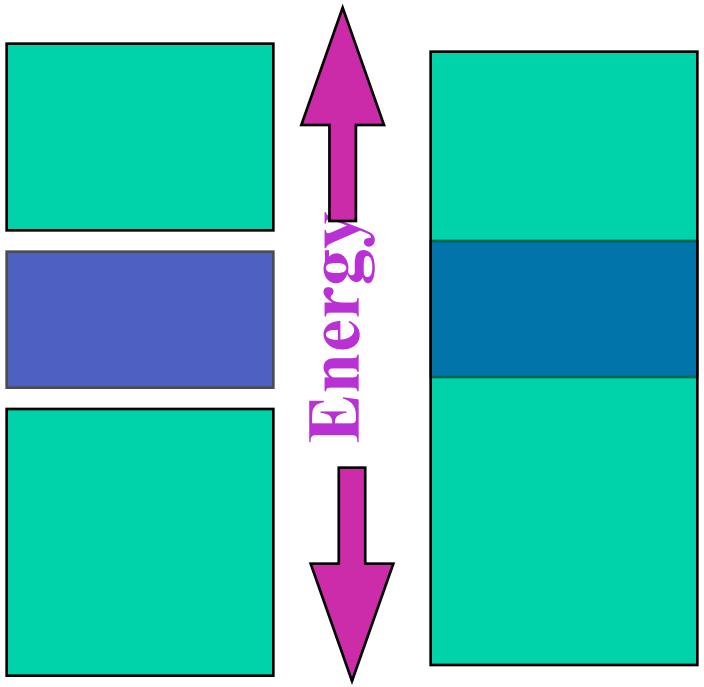
General Approach to Many-Body Electronic Structure

- =>partition d.o.f. into ``correlated subspace'' (active space) (atomic-like d orbitals) and ``background''

- treat correlated subspace by many-body method (DMFT); treat background by mean field method (DFT)

- embed active space into background (DMFT self-consistency+double counting +charge self consistency)



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Correlated subspace: transition metal d orbitals

Interaction: **Full multiplet structure of d-shell (here written for t_{2g} or e_g)**

$$
\begin{aligned}
H &= U\sum_{a} n_{a\uparrow}n_{a\downarrow} + (U-2J)\sum_{a>b,\sigma=\uparrow,\downarrow} n_{a\sigma}n_{b\sigma} \\
&\quad +(U-3J)\sum_{a\neq b\sigma} n_{a\sigma}n_{b\bar{\sigma}} - J\sum_{a\neq b} c^{\dagger}_{a\uparrow}c^{\dagger}_{a\downarrow}c_{b\uparrow}c_{b\downarrow} + c^{\dagger}_{a\uparrow}c^{\dagger}_{b\downarrow}c_{b\uparrow}c_{a\downarrow}
\end{aligned}
$$

U: screened in solid--phenomenological or 'c-RPA' calculations.

J: close to atomic limit value

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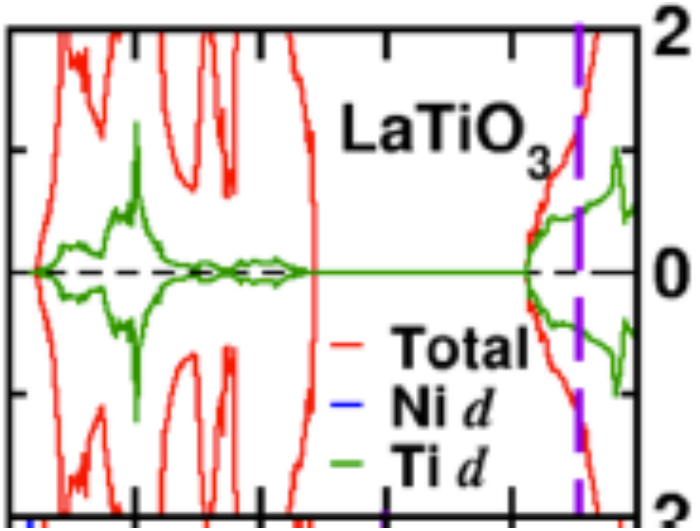
DFT+DMFT

$$\mathbf{G}^{-1} = \left[\omega\hat{\mathbf{1}} - \hat{\mathbf{H}}_{\mathbf{DFT}} - \hat{\mathbf{P}}_{\mathbf{d}}\left(\hat{\boldsymbol{\Sigma}}_{\mathbf{d}}(\omega) - \hat{\boldsymbol{\Sigma}}_{\mathbf{dc}}\right)\hat{\mathbf{P}}_{\mathbf{d}}\right]$$

Defines p and (bare) d level energies, and (via Wannier or projector method) d-orbital wave function



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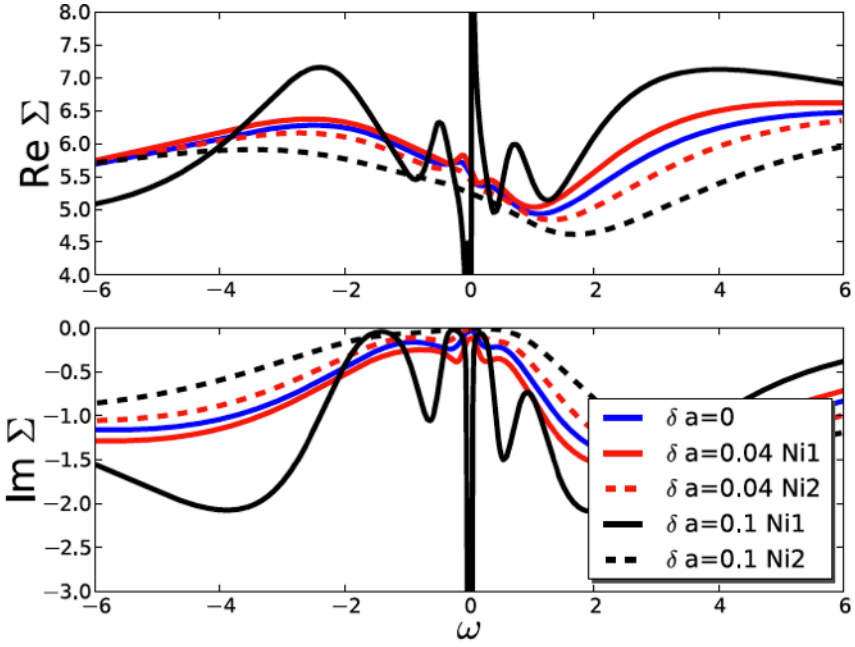
DFT+DMFT

$$\mathbf{G}^{-1} = \left[\omega\hat{\mathbf{1}} - \hat{\mathbf{H}}_{\mathbf{DFT}} - \hat{\mathbf{P}}_{\mathbf{d}}\left(\hat{\boldsymbol{\Sigma}}_{\mathbf{d}}(\omega) - \hat{\boldsymbol{\Sigma}}_{\mathbf{dc}}\right)\hat{\mathbf{P}}_{\mathbf{d}}\right]$$

Many-body physics of d-level: real part implies Hartree shift of d-states relative to DFT

DFT+U: static Hartree approx



(H. Park: LaNiO3 in ideal and disproportionated state)

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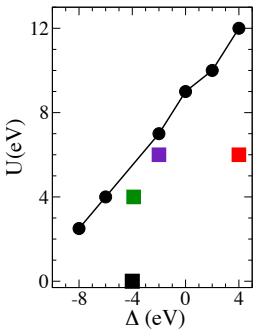
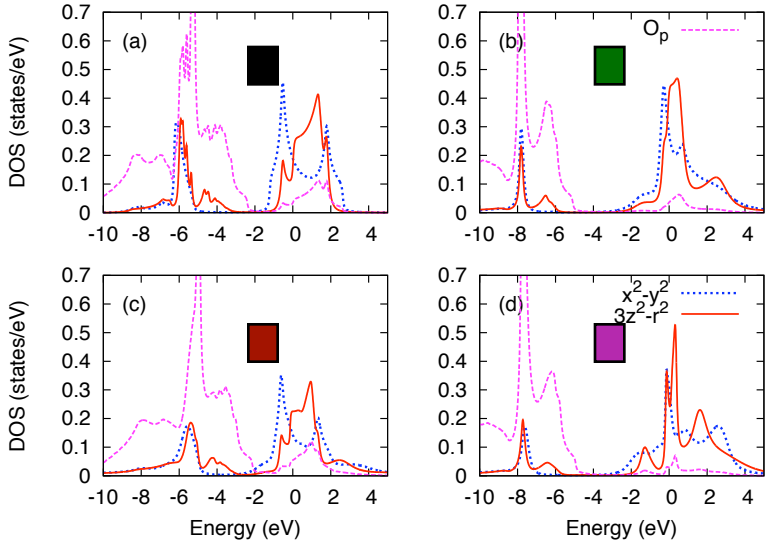
DFT+DMFT

$$\mathbf{G}^{-1} = \left[\omega\hat{\mathbf{1}} - \hat{\mathbf{H}}_{\mathbf{DFT}} - \hat{\mathbf{P}}_{\mathbf{d}}\left(\hat{\boldsymbol{\Sigma}}_{\mathbf{d}}(\omega) - \hat{\boldsymbol{\Sigma}}_{\mathbf{dc}}\right)\hat{\mathbf{P}}_{\mathbf{d}}\right]$$

Double counting correction: cancels portion of Hartree shift: controls physical p-d splitting.





(X Wang PRL 2011 LaNiO3 with different U and double counting)

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Crucial question for superlattice and metal-insulator transition in bulk materials

??What is the double counting??

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Accepted choice: `FLL'

Added interaction:

$$H_{\text{int}} = \frac{1}{2}\sum_{m,m',\sigma} U_{mm'} n_{m\sigma} n_{m'-\sigma} + \frac{1}{2}\sum_{m,m',m\neq m',\sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}$$

Atomic limit exp. val.

$$E^{\text{at lim}} = \frac{1}{2}UN(N-1) - \frac{1}{2}JN_{\uparrow}(N_{\uparrow}-1) - \frac{1}{2}JN_{\downarrow}(N_{\downarrow}-1)$$

$$\mathbf{E = E_{DFT} + \langle H_{int} \rangle - E_{at}}$$

=>hartree contribution to d-level self energy

$$\hat{\Sigma}^{\mathbf{dc}}_{\sigma} = \mathbf{U \langle N \rangle - J \langle N_{\sigma} \rangle}$$

Czyzyk and Sawatzky, PRB49 14211 (1994)
M. Karolak et al, J Elect Spectr.181 p. 11 (2010)

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Note 1/2 in energy

Added interaction:

$$H_{\text{int}} = \frac{1}{2}\sum_{m,m',\sigma} U_{mm'} n_{m\sigma} n_{m'-\sigma} + \frac{1}{2}\sum_{m,m',m\neq m',\sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}$$

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Czyzyk and Sawatzky, PRB49 14211 (1994)
M. Karolak et al, J Elect Spectr.181 p. 11 (2010)

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Charge flow

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To understand charge transfer across oxide interface

1. correctly place oxygen states on each side of interface

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To understand charge transfer across oxide interface

1. correctly place oxygen states on each side of interface

2. determine p-d gap

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To understand charge transfer across oxide interface

1. energy of oxygen states on each side of interface

2. determine p-d gap

3. account for effects of charge flow

Conventional wisdom

Basic (uncorrelated) electronic structure

Many body physics of transition metal d-orbital

Full charge self-consistency

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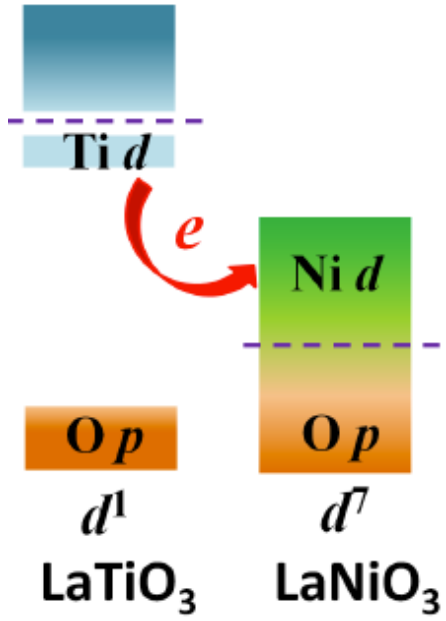
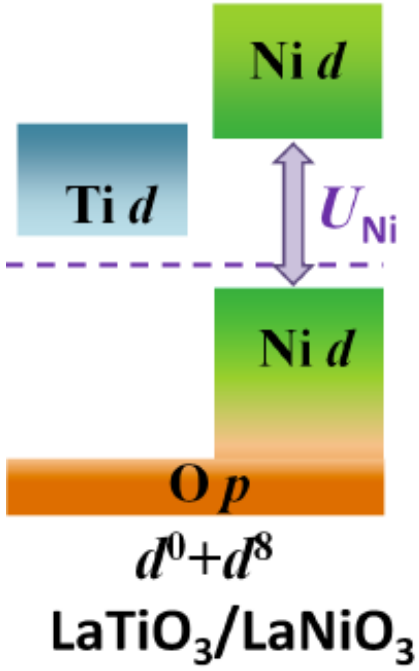
$LaTiO_3/LaNiO_3$ (001)

$LaTiO_3$: d^1 `Mott' insulator $LaNiO_3$: d^7 correlated metal

Idea: if put them together, complete charge transfer Ti->Ni =>S=1 (Ti d^0 Ni d^8) Insulator





H. Chen, AJM and C. Marianetti
Phys. Rev. Lett. 111, 116403 (2013)

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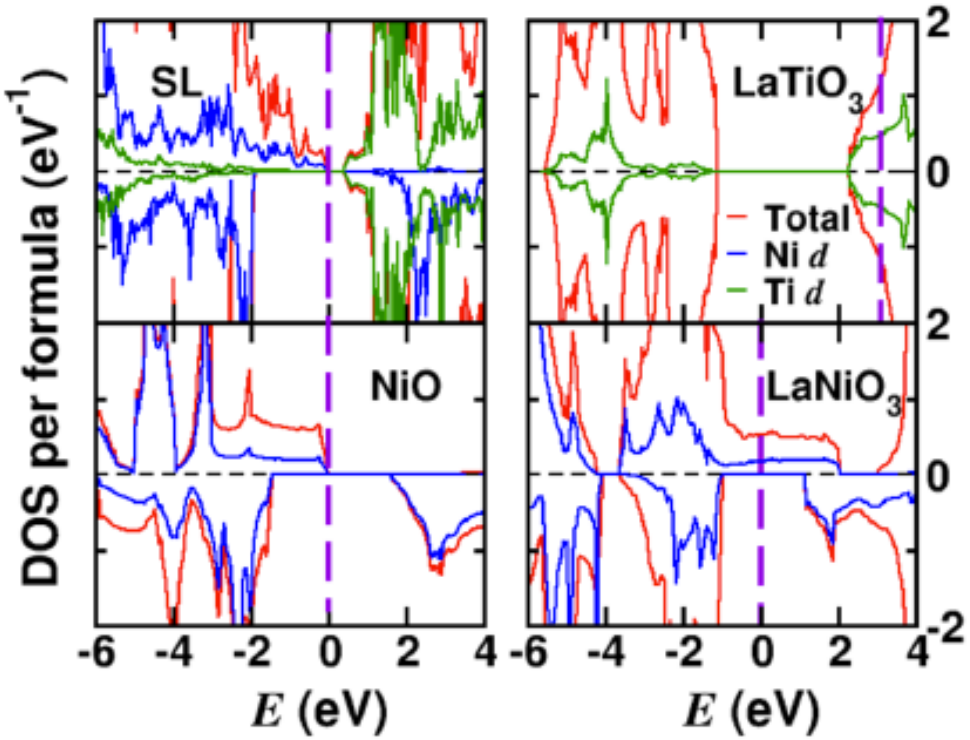
Calculation: DFT+U (FLL double counting)



(FLL double counting)

*oxygen bands line up (approximately)

*local physics fixes d level energy relative to O

*d-level energy difference drives complete charge transfer

H. Chen, AJM and C. Marianetti, Phys. Rev. Lett. 111, 116403 (2013)

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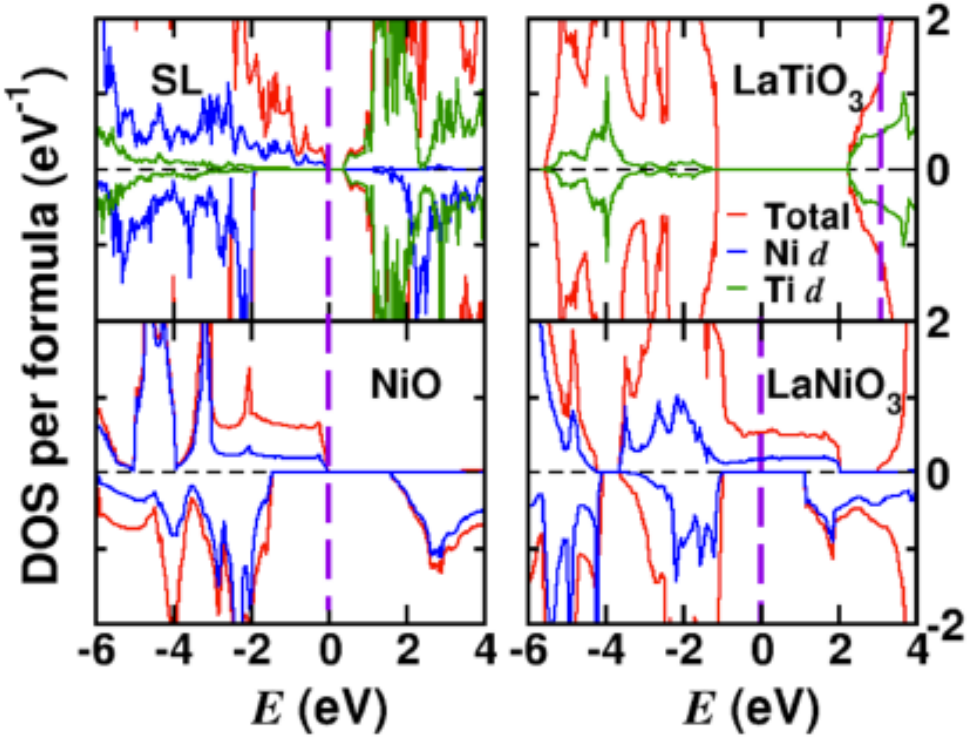
Side remark:
actual charge density almost unchanged



`rehybridization': degree of mixing of other (uninteresting) states changes to compensate transfer of near fermi surface charge

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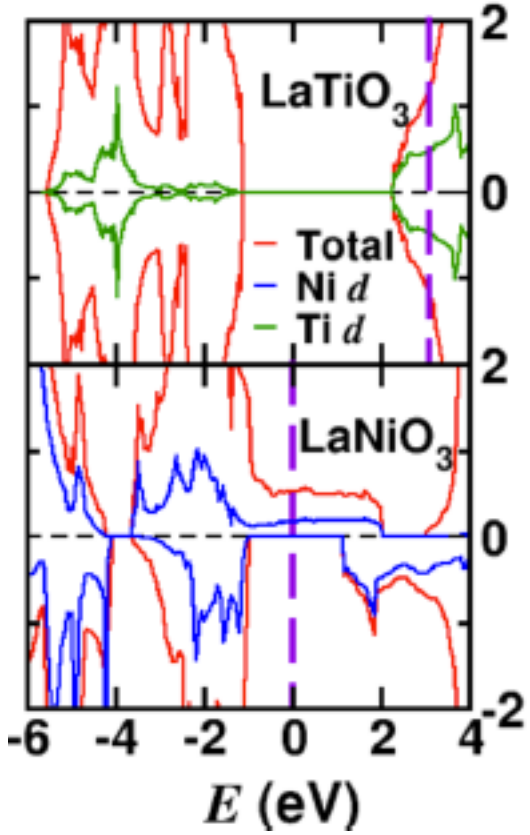
Rough physical picture:
oxygen states line up.
Charge transfer controlled by energy of d band relative to p-levels



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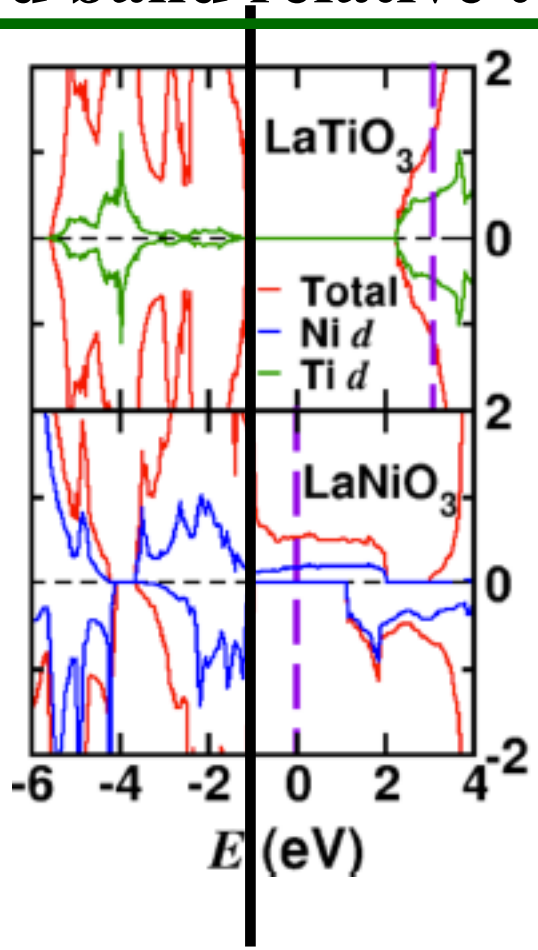

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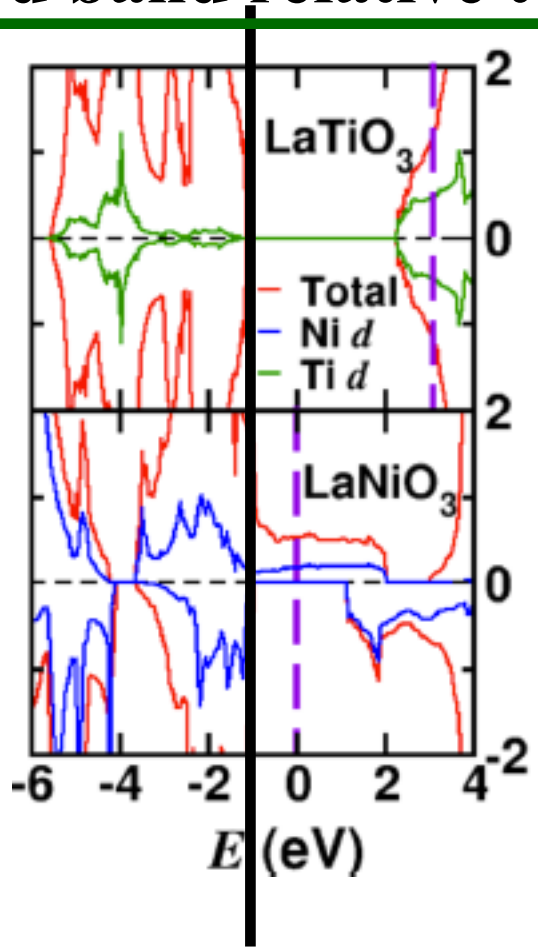

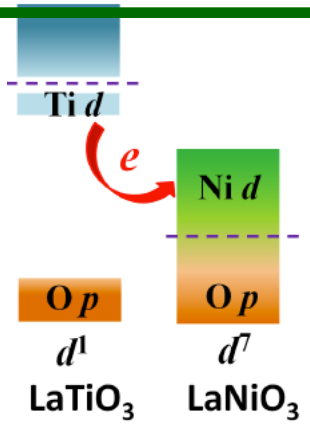

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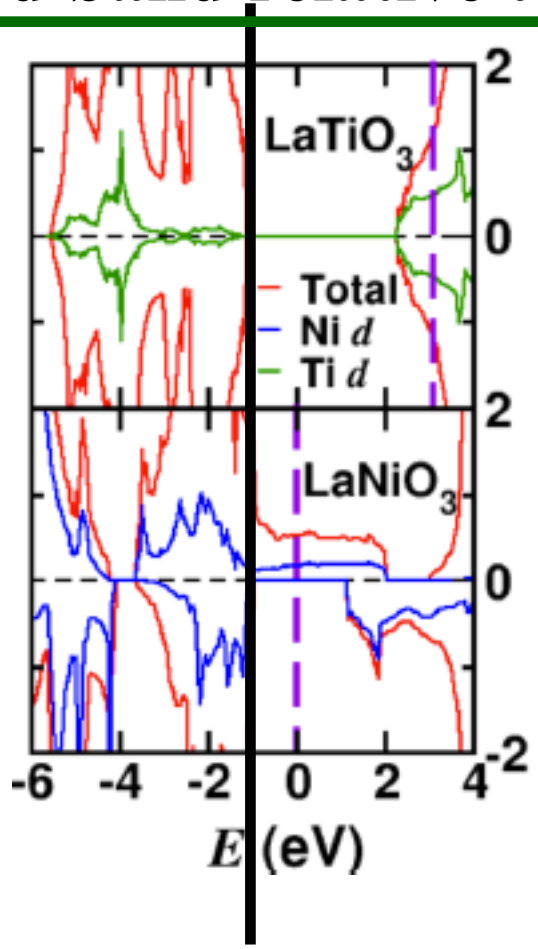

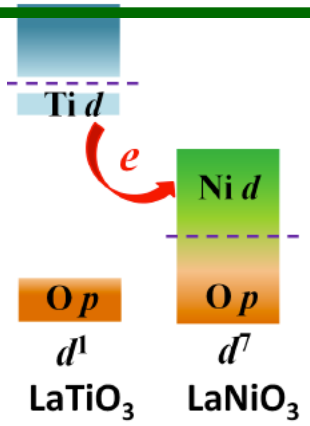

(Note: thicker interface =>Schottky barrier effects.)

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?Are the estimates right?

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Two examples

NiO

$LaTiO_3$

Experimentally:
both charge transfer insulators

Theory: DFT+DMFT, defining d orbitals from MLWF defined over energy range of p-d manifold

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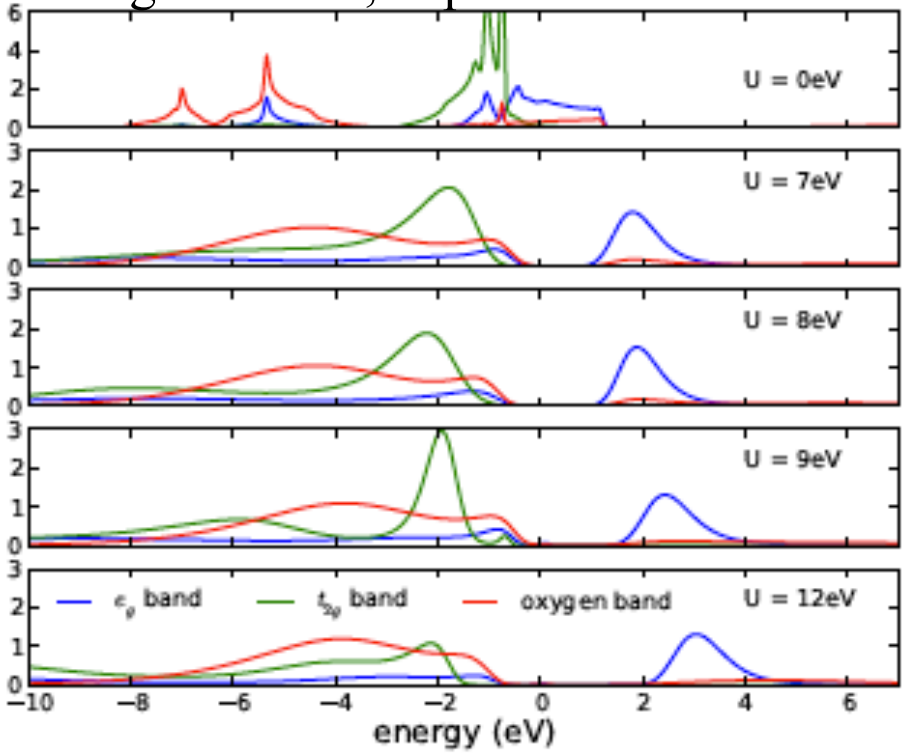
NiO: Full charge sc +FLL double counting produces insulator

H. T. Dang and AJM, unpublished



- insulator
- gap (3eV)<expt (4eV)
- p-d splitting only weakly U-dependent
- p bands too close to d-bands

FLL double counting for NiO also discussed in M. Karolak et al, J Elect Spectr.181 p. 11 (2010)

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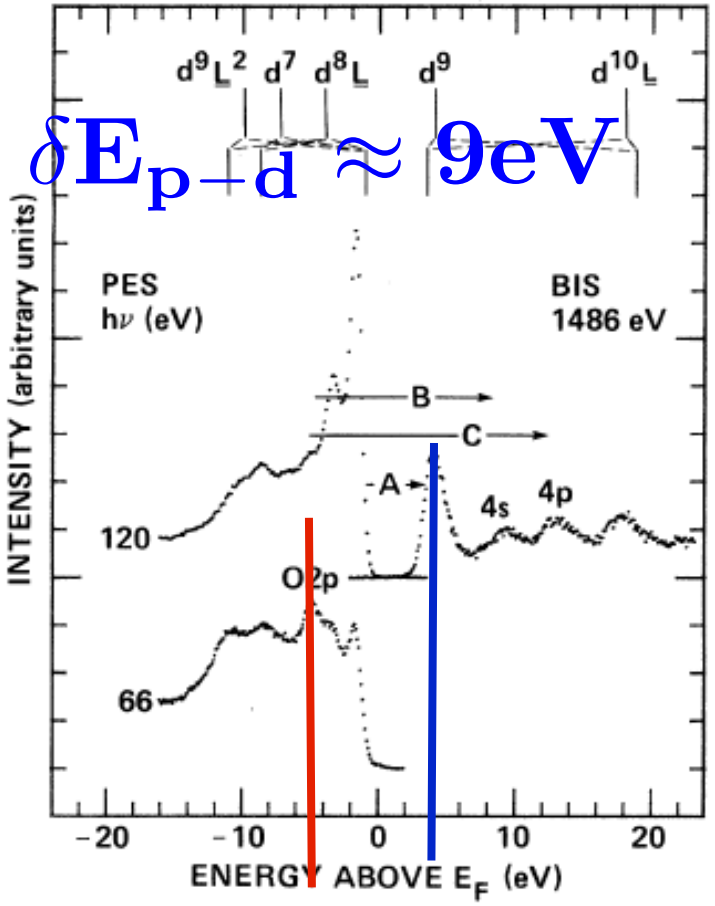
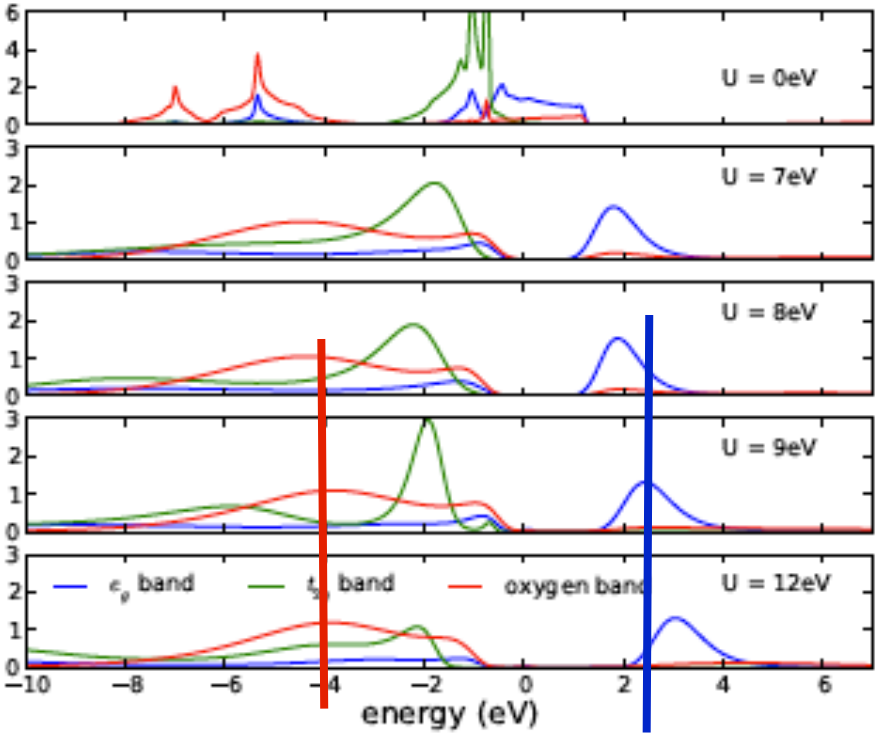
p-d splitting: DFT/DMFT vs Expt

$\delta E_{p-d} \approx 9eV$





$\delta E_{p-d} \approx 7eV$

VOLUME 53, NUMBER 24 PHYSICAL REVIEW LETTERS 10 DECEMBER 1984

Magnitude and Origin of the Band Gap in NiO

G. A. Sawatzky[(a)] and J. W. Allen

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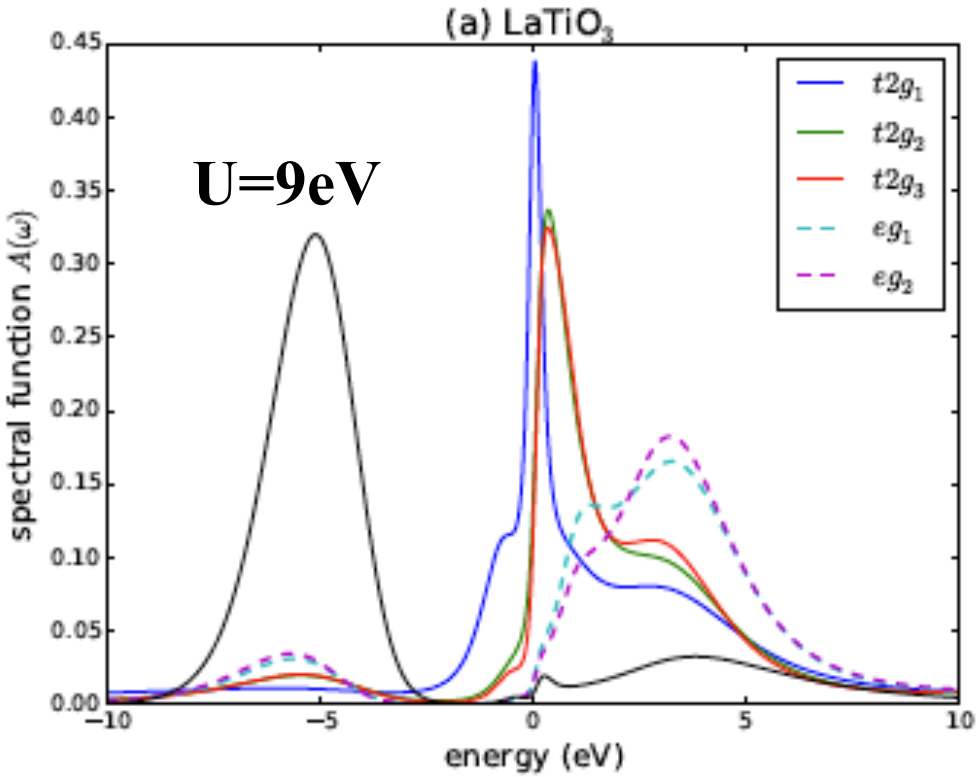
$LaTiO_3$: Full charge sc +FLL double counting produces metal



Experimental structure

H. T. Dang, C. Marianetti and AJM, unpublished

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?What is going on?

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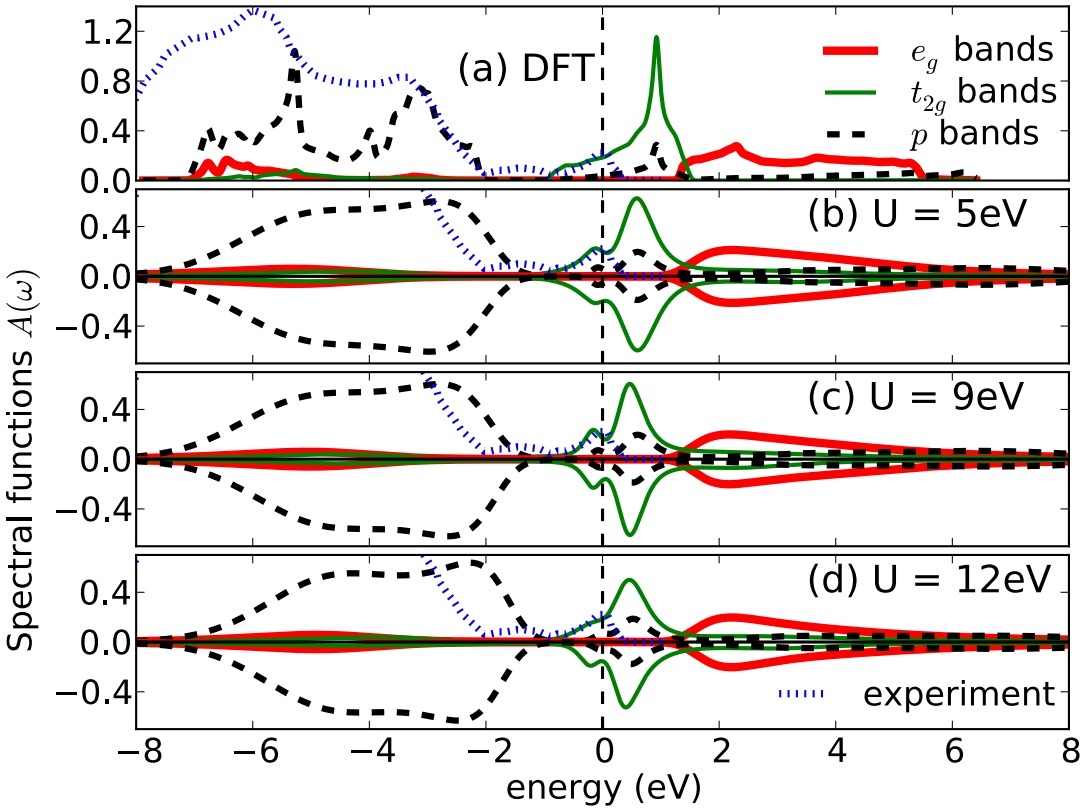
$SrVO_3$: an instructive example

Cubic, moderately correlated metal

DFT+DMFT TRIQS Code



FLL+ full charge self consistency keeps relative separation of p and d bands ~constant and ~1eV smaller than exptvalue for all U

Without charge self consistency, p-bands stay at DFT position

H. T. Dang, AJM and C. Marianetti
arXiv:1309.2995

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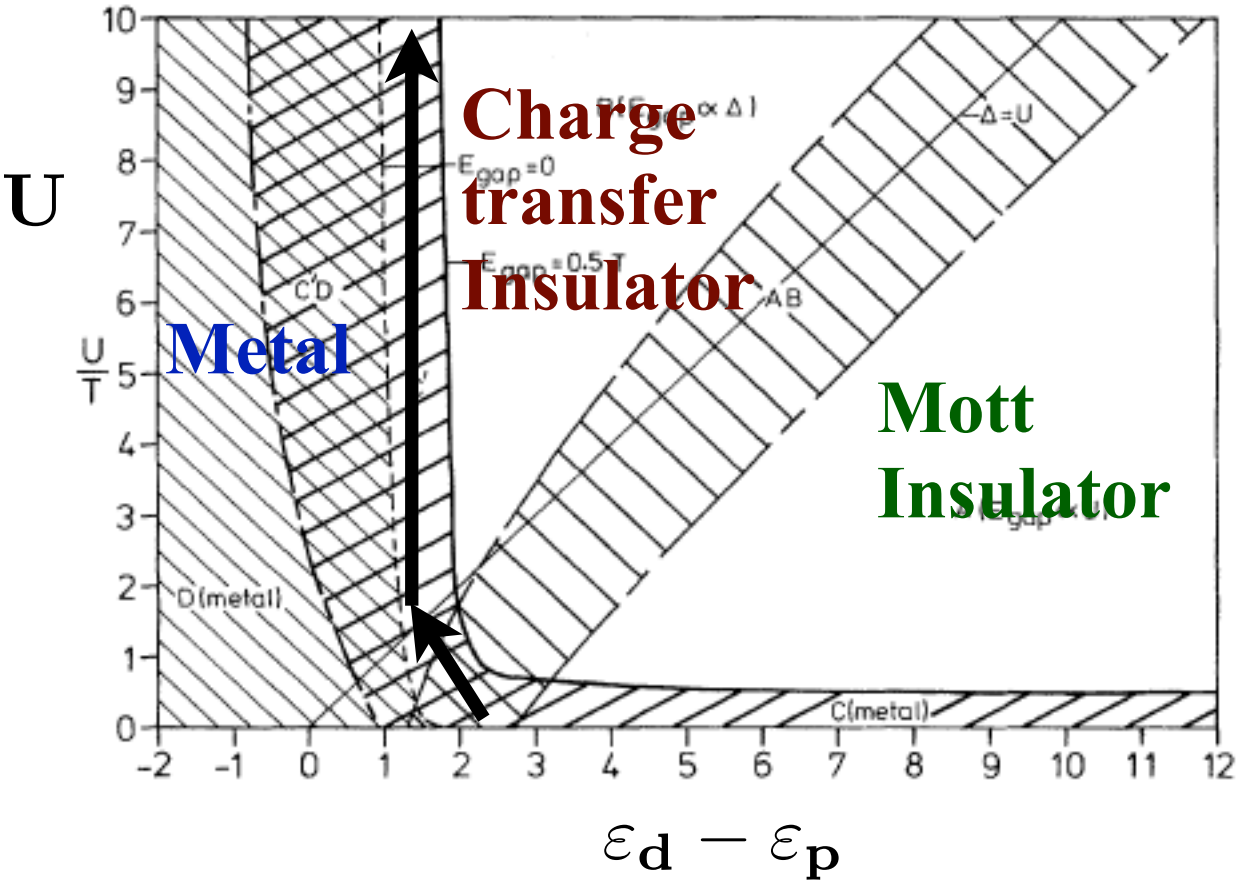
DFT+DMFT: increasing U moves you more or less vertically in the ZSA phase diagram.



If the calculation starts with too small a p-d energy splitting, it remains in the metallic regime as U increases

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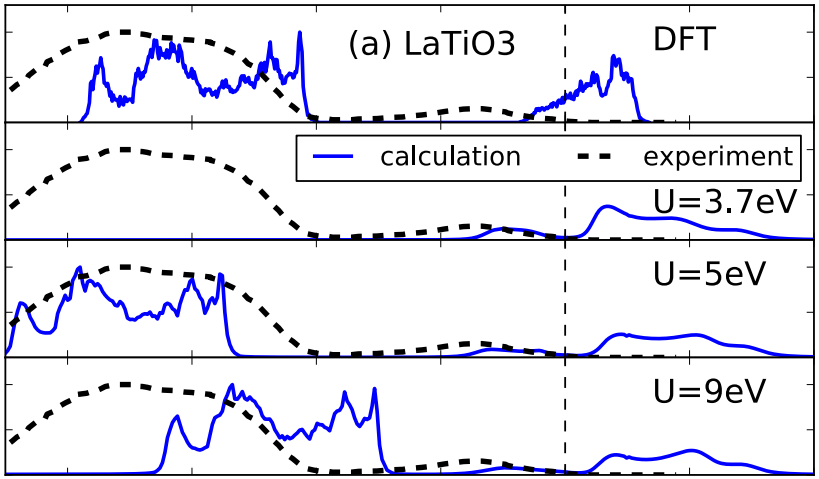
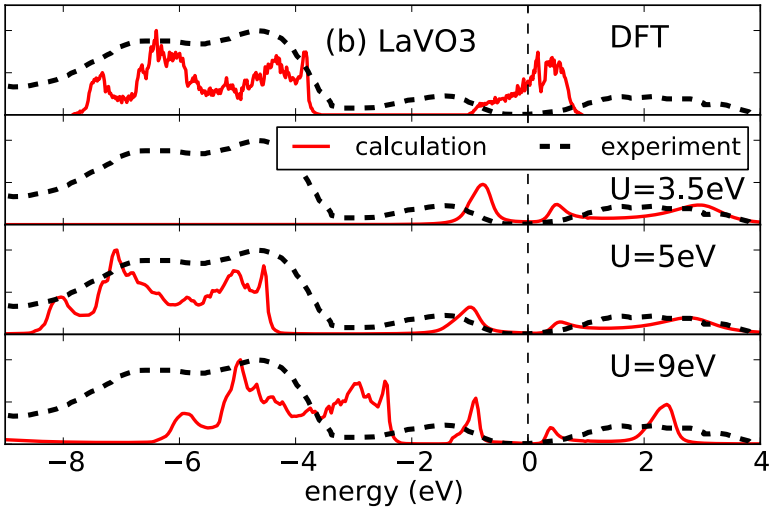
Titanates/Vanadates

For each U, adjust E_{dc} by hand so calc gives insulating gap of size found in experiment. Compute oxygen bands. Relatively narrow U-range consistent with expt

U~5-6eV is found in c-RPA calculations





Single-site DMFT +DFT ``works" *provided* oxygen levels are correctly positioned and reasonable U chosen

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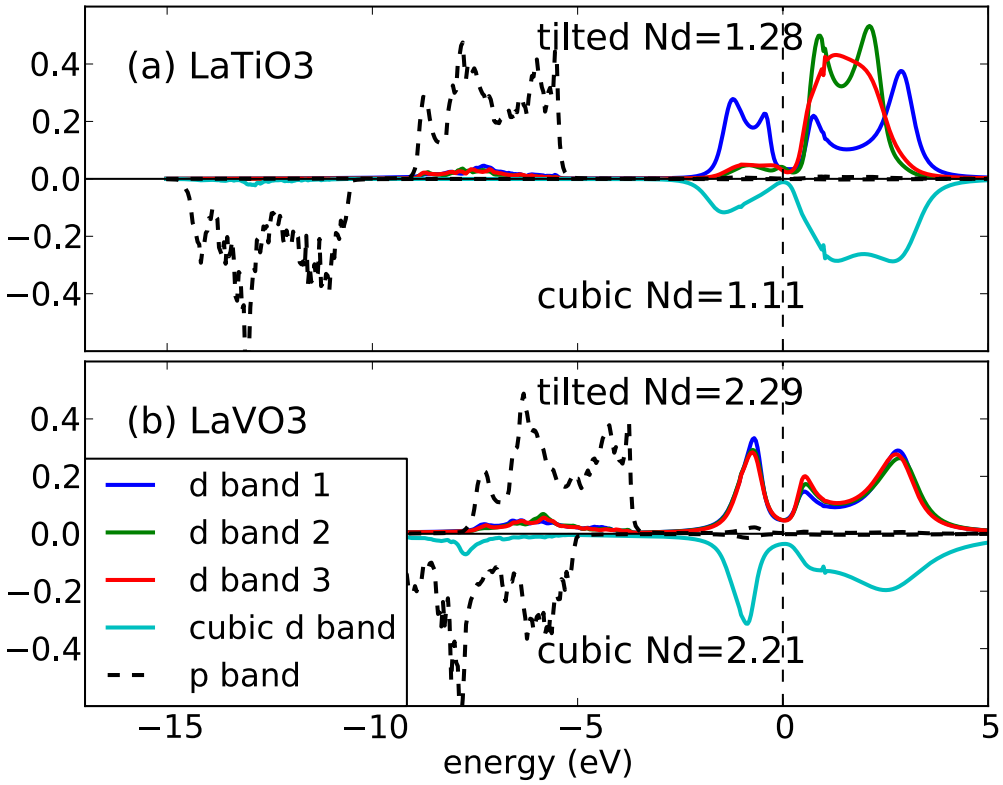
Aside: $GdFeO_3$-distorted (tilted) structure essential for insulator



$GdFeO_3$ structural distortion (and associated level splitting) essential for insulating behavior of $LaTiO_3$ (as previously found by Pavarini, Georges et al); much less so for $LaVO_3$

H. T. Dang, C. Marianetti and AJM, unpublished

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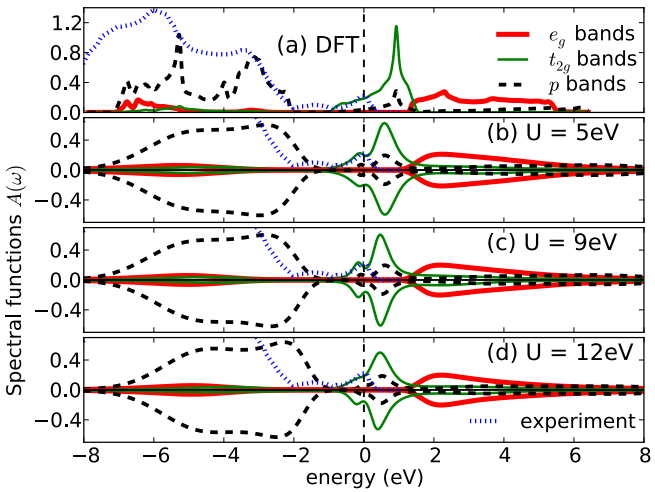
?How to position oxygen levels?



Fully charge self consistent DFT +DMFT pins p-d splitting to value (slightly) smaller than DFT value.

=>2 options

Modify band theory

***Better approx than DFT (?GW?)**

Modify E_{DC}

***Haule/Kotliar**
***Park/Marianetti**

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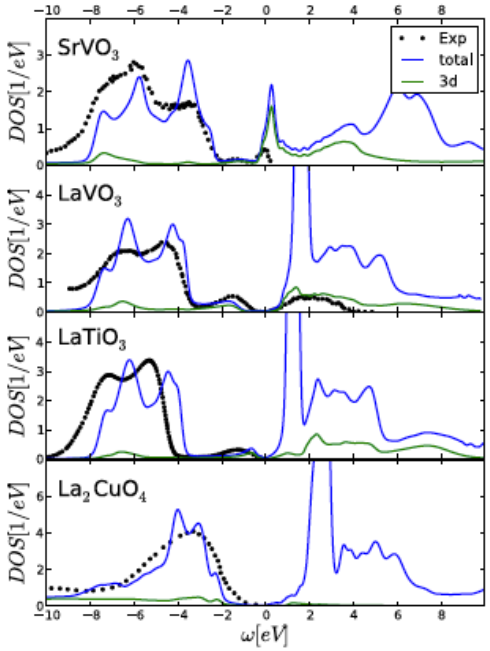
Modify E_{DC} (1)

Haule et al arXiv:1310.1158

$$E_{DC} = N_d \left(U - \frac{J}{2} \right) \left(N_d^0 - \frac{1}{2} \right)$$

N_d^0: formal valence



U=10eV

Good agreement with data

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But: big problem with energetics

FLL double counting

$$E^{\text{at lim}} = \frac{1}{2}UN(N-1) - \frac{1}{2}JN_{\uparrow}(N_{\uparrow}-1) - \frac{1}{2}JN_{\downarrow}(N_{\downarrow}-1)$$

Haule double counting

$$E_{DC} = N_d\left(U - \frac{J}{2}\right)\left(N_d^0 - \frac{1}{2}\right)$$

Haule double counting is level shift, not interaction energy=>no factor of 1/2 => problem for energetics

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Alternative (ad hoc)

Park, AJM, Marianetti arXiv:1310.5772

$$\mathbf{E_{DC}} = \frac{\mathbf{1}}{\mathbf{2}}\mathbf{U'N_d\left(N_d - 1\right)} - \frac{\mathbf{1}}{\mathbf{2}}\mathbf{J}\sum_{\sigma}\mathbf{N}_{\sigma}\left(\mathbf{N}_{\sigma} - \mathbf{1}\right)$$

$\mathbf{U' < U}$ **increases p-d splitting**

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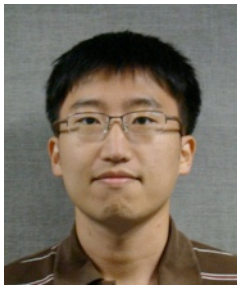
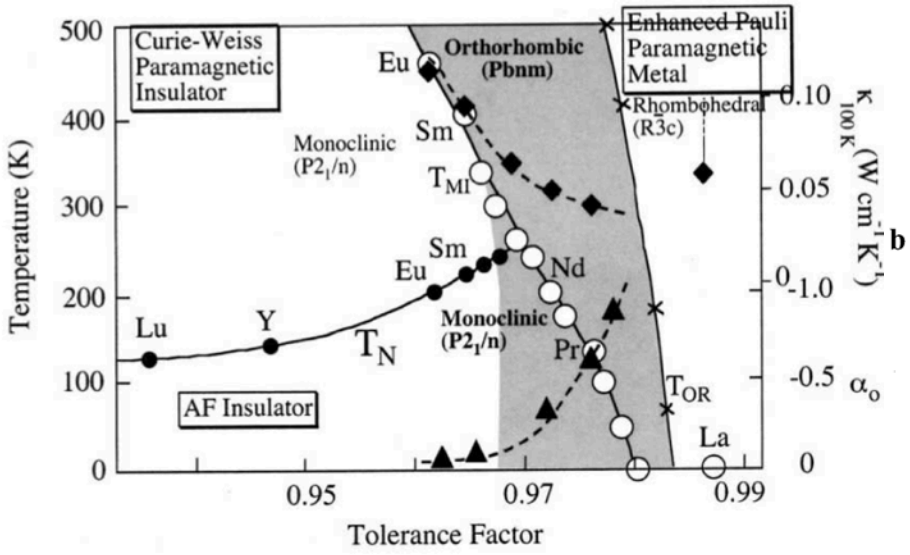
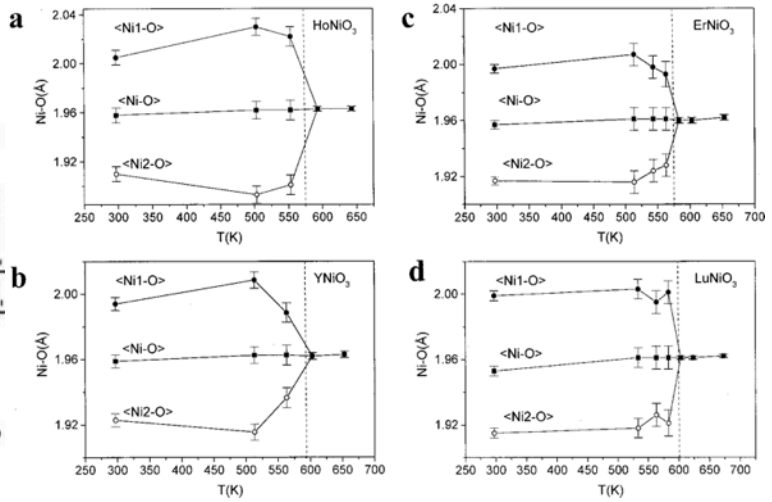
Total energy within DFt+DMFT: Application to rare earth nickelates



*Hyowon Park

PRL 109, 156402 (2012)
arXiv:1310.5772





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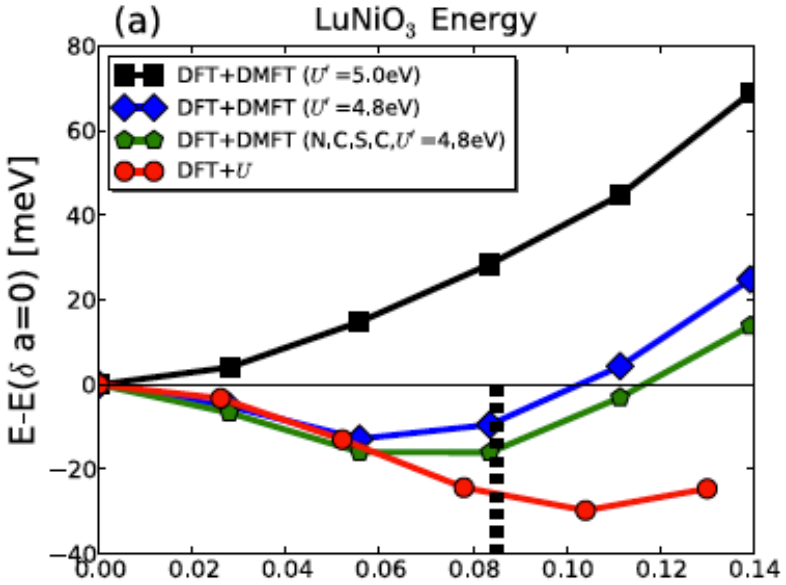
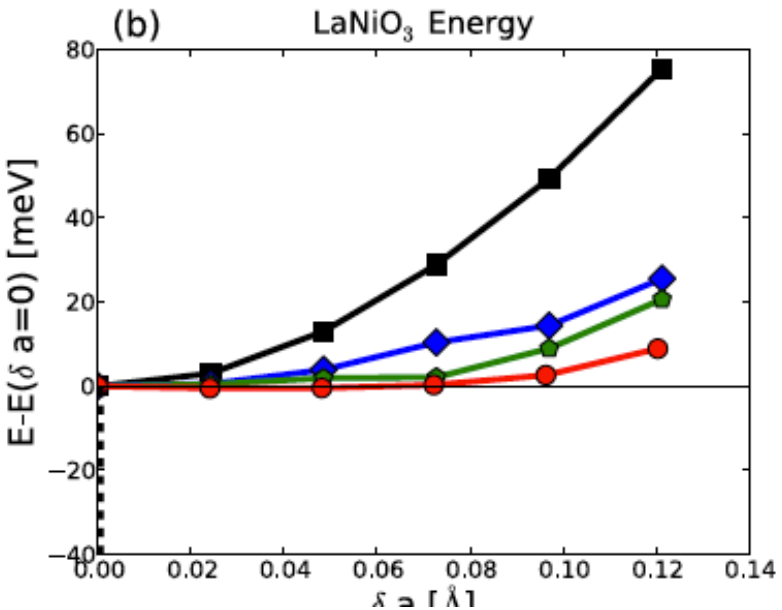
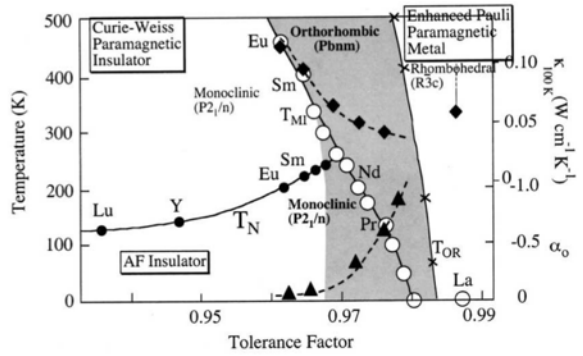
Energy as function of distortion







$\mathbf{U' = U}$ **No distortion**

$\mathbf{U' = 0.96U}$ **correct distortion**

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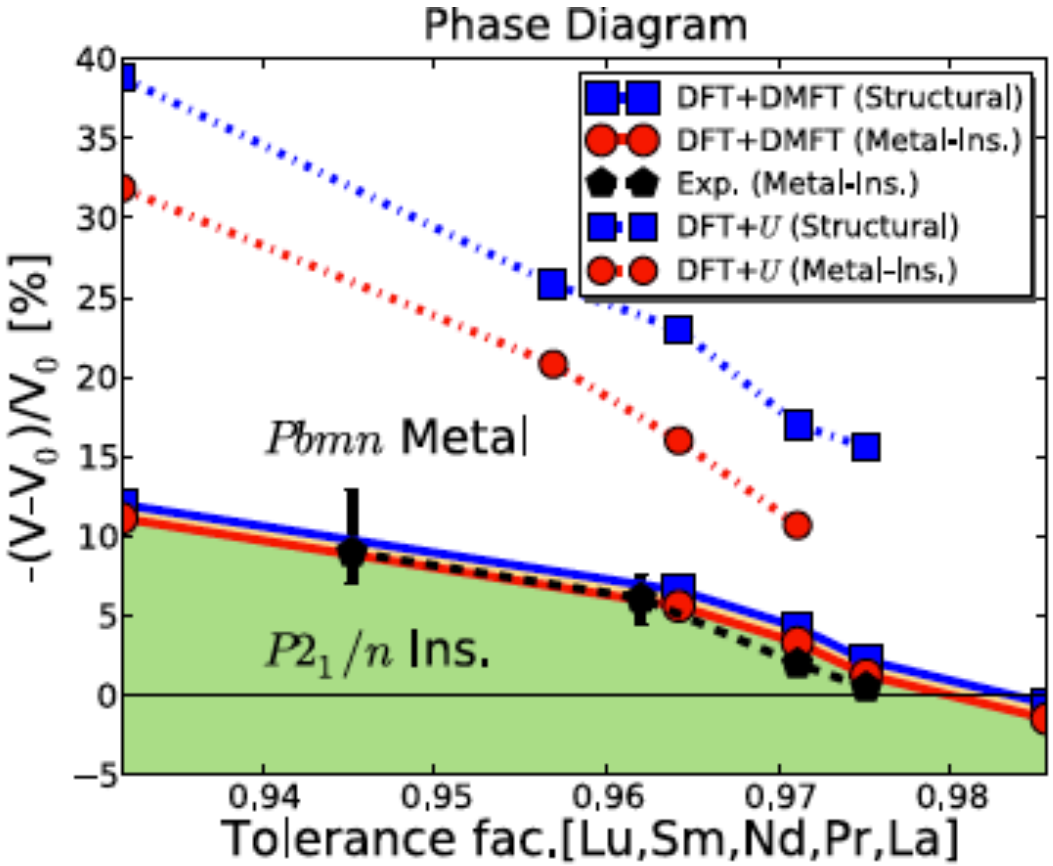
Entire pressure-rare earth phase diagram given correctly



$$U' = 0.96U = 4.8eV$$

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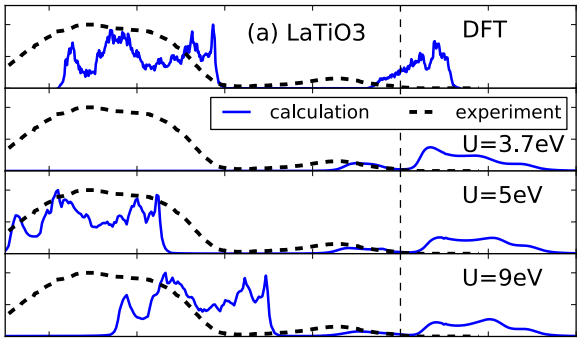
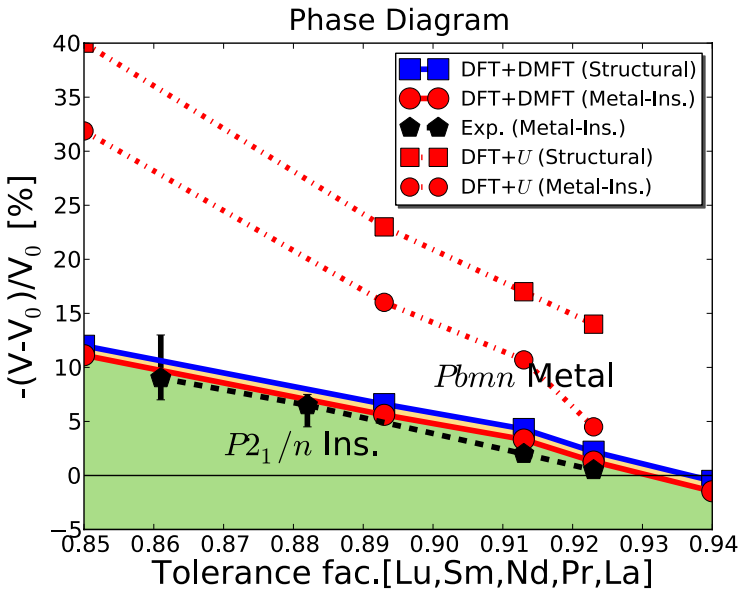
Conclusion





Key issue for DFT+DMFT: proper p-d energy splitting.

Is this a problem of double counting or band theory

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