COLLÈGE DE FRANCE
1530

Chaire de Physique de la Matière Condensée
Antoine Georges

Cycle 2016-2017
16 mai 2017

Contrôle des fonctionnalités des oxydes

Hétéro-structures, Impulsions Lumineuses

Cours 4

Les Nickelates $RNiO_3$:

- *Une transition métal-isolant contrôlable au mécanisme original*
- *« Ingénierie orbitale »: vers un supraconducteur synthétique ?*

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Control of Oxide Functionalities

Heterostructures, Light pulses

Lecture 4

Nickelates $RNiO_3$:

- A controlable metal-insulator transition

- « Orbital engineering »: towards a synthetic superconductor ?

Today's seminar – May 16

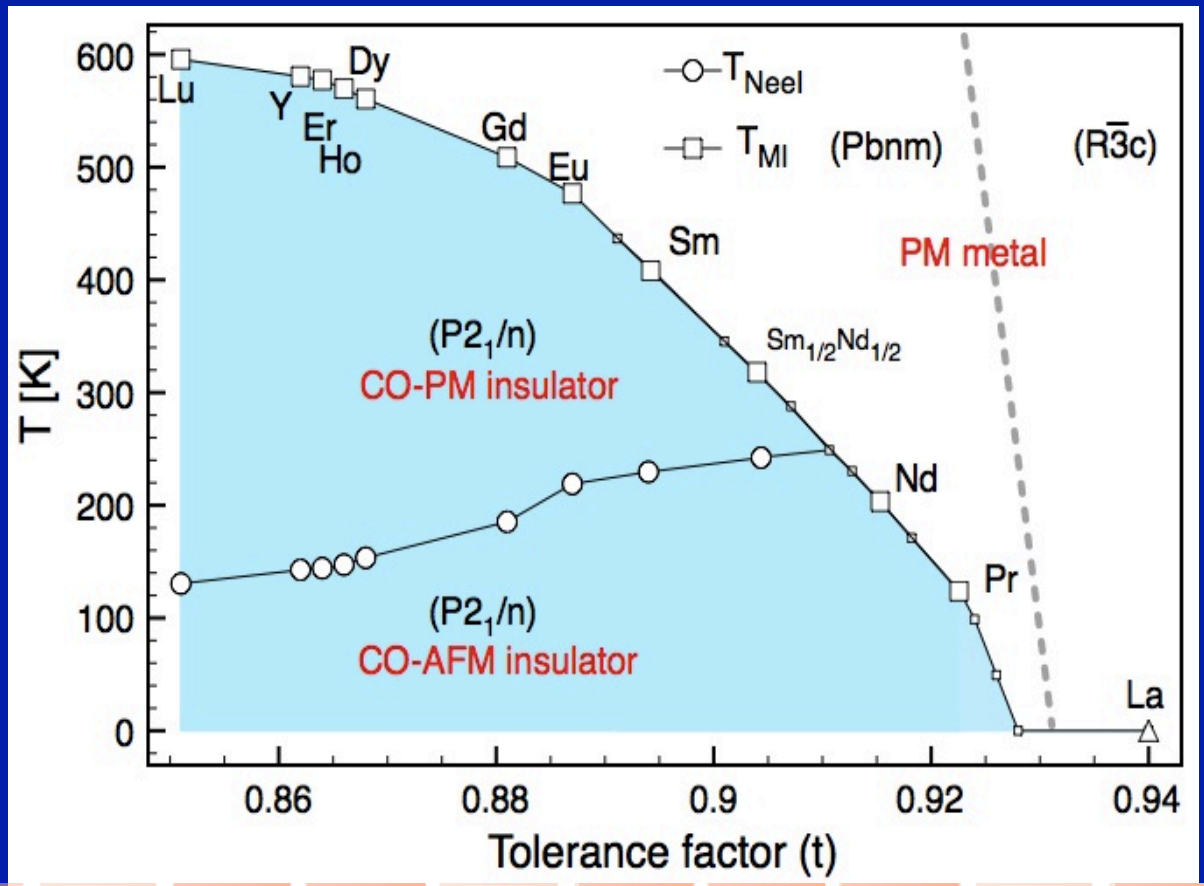
Andres Santander-Syro

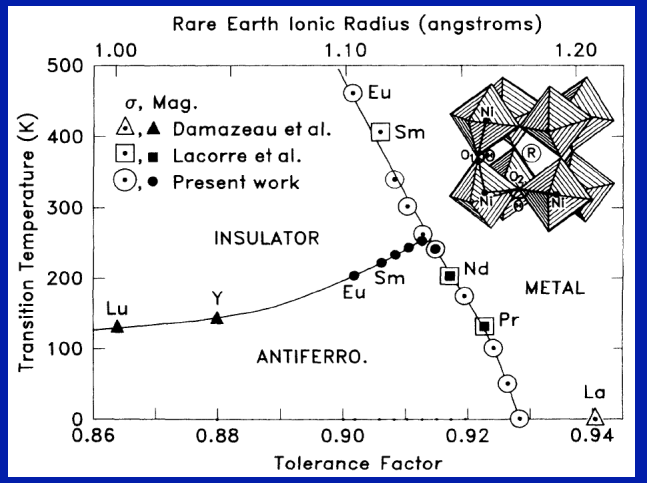
CSNSM-Orsay

Novel two-dimensional electron systems at the surface of transition-metal oxides

Image: Synchrotron Radiation Center, Madison, Wisconsin

MIT in Nickelates $RNiO_3$





$$t = \frac{d_{R-O}}{\sqrt{2}d_{Ni-O}}$$

Tolerance factor:
smaller t
= Larger distortion

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

R.Sherwitzl, PhD thesis, Geneva 2012 Adapted from Catalan, *Phase Transitions*, (2008)

Early work: Demazeau et al. (Bordeaux, Hagenmuller's group 1971) Lacorre, Torrance et al. 1992 (IBM San Jose & Le Mans)

Acknowledgements:

MARVEL
NATIONAL CENTRE OF COMPETENCE IN RESEARCH

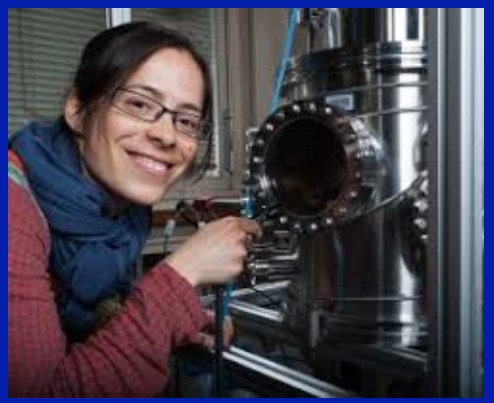
erc
European Research Council

THEORY:

Alaska Subedi
Paris

Oleg Peil
Geneva/Paris
now in Leoben, Austria

EXPERIMENTS:



Dirk van der Marel, Jean-Marc Triscone

Marta Gibert, Sara Catalano

University of Geneva - DQMP

Many Figures below are from the following publications:

MARVEL
NATIONAL CENTRE OF COMPETENCE IN RESEARCH

PHYSICAL REVIEW B **90**, 045128 (2014)

European Research Council

Orbital polarization in strained $LaNiO_3$: Structural distortions and correlation effects

Oleg E. Peil,[1,2,*] Michel Ferrero,[2] and Antoine Georges[1,2,3]

PHYSICAL REVIEW B **91**, 075128 (2015)

Low-energy description of the metal-insulator transition in the rare-earth nickelates

Alaska Subedi,[1,2] Oleg E. Peil,[2,3] and Antoine Georges[2,3,4]

PHYSICAL REVIEW B **92**, 155145 (2015)

Optical spectroscopy and the nature of the insulating state of rare-earth nickelates

J. Ruppen,[1] J. Teyssier,[1] O. E. Peil,[1,2] S. Catalano,[1] M. Gibert,[1] J. Mravlje,[3] J.-M. Triscone,[1] A. Georges,[1,2,4] and D. van der Marel[1]

Impact of antiferromagnetism on the optical properties of rare earth nickelates

arXiv:1702.0060

J. Ruppen,[1] J. Teyssier,[1] I. Ardizzone,[1] O. E. Peil,[1,2] S. Catalano, M. Gibert,[1] J.-M. Triscone,[1] A. Georges,[1,2,3] and D. van der Marel[1,*]

Why are Nickelates interesting ? Why renewal of interest in recent years ?

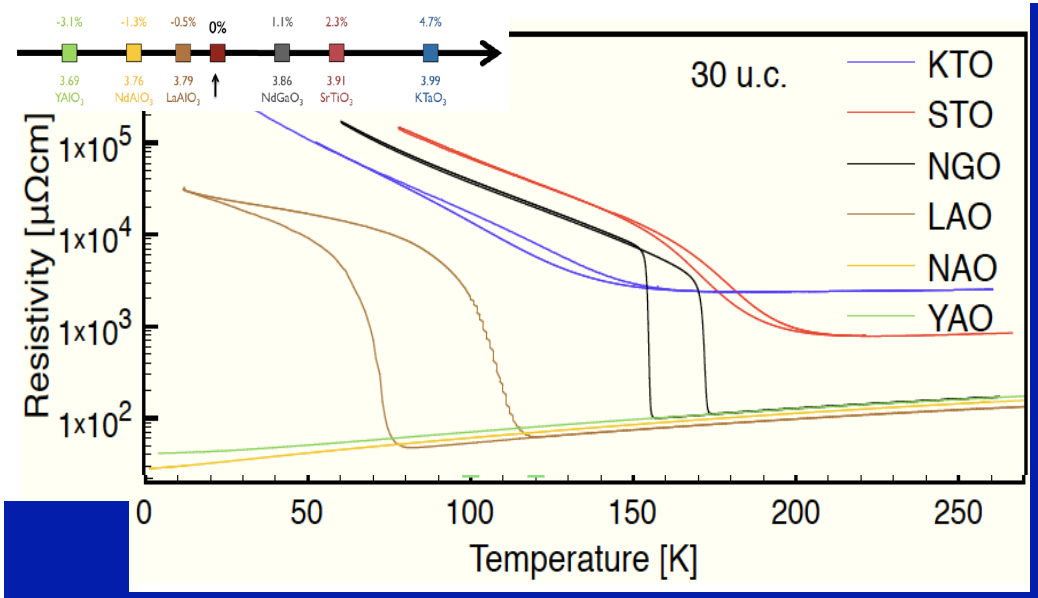
- Controllability / Tunability !
- Thin films and heterostructures open new avenues for these materials.
- *Have been proposed as a way to engineer a synthetic superconductor through control of orbital degeneracy*

CONTROL: Traditional and Novel routes

Bandwidth	Pressure Size of rare-earth Distortion Tolerance factor 3d,4d,5d metal	Strained thin films and heterostructures Control by Light pulses /`non-linear phononics'
Crystal field, Orbital degeneracy	Size of rare-earth Distortion Tolerance factor	- Same -
Filling of shell, Electron density Doping	Chemistry	Ionic liquids Gating
	$Sr,Ca^{2+} \rightarrow La, R^{3+}$	
Interaction strength	3d,4d,5d metal	Tunable dielectric gating ? Light ?
Charge-Transfer	Change apical oxygen distance Change ligand: O→ S, Se…	Light ?

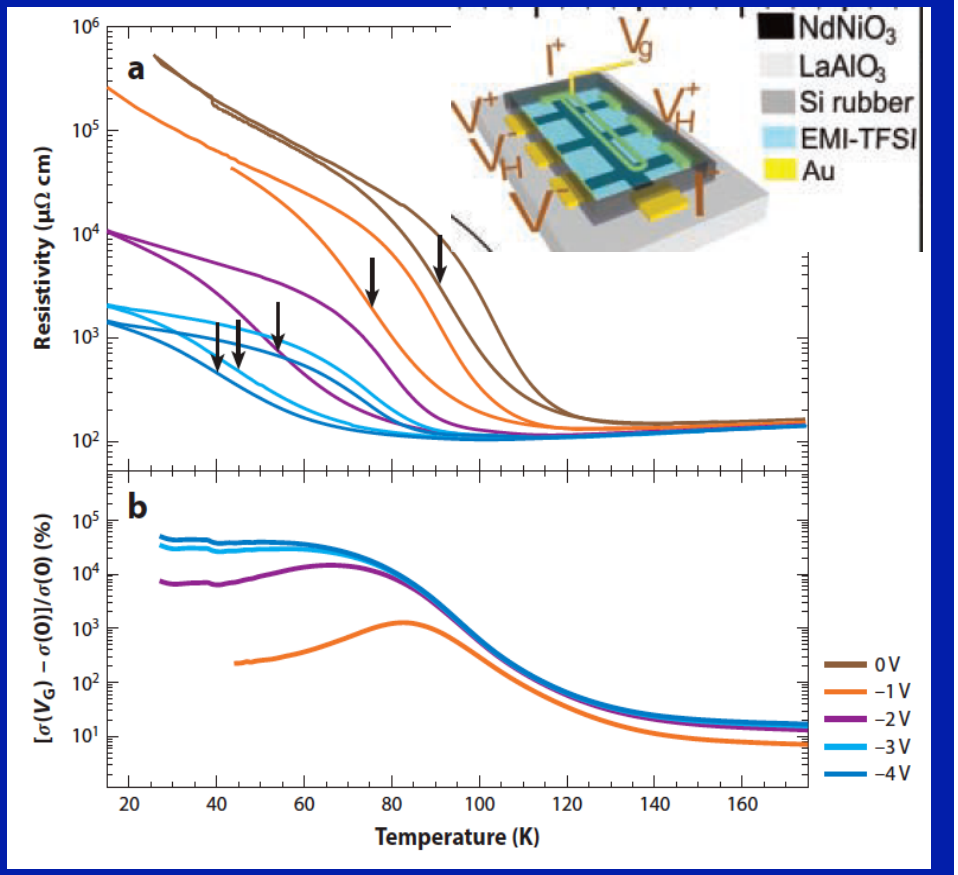
Controllability by: Strain, Gating, Light… Nickelates have it all !

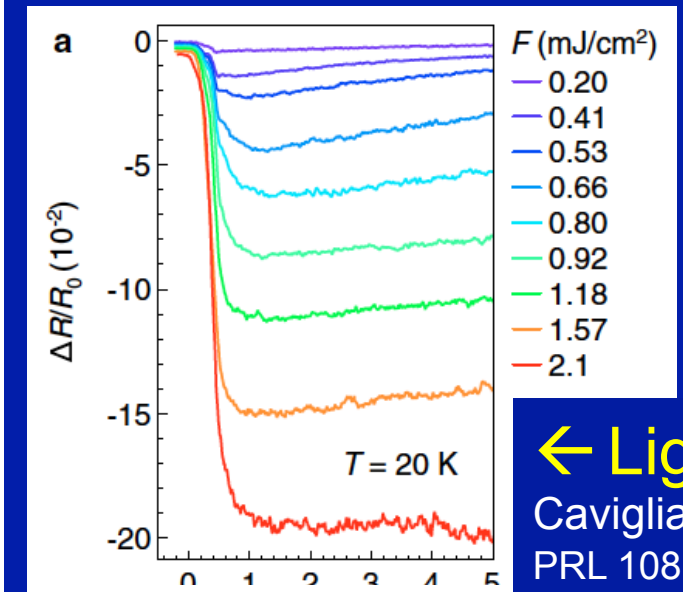
- Beautiful work by several groups over recent years, e.g:
- Triscone et al. - Geneva
- Keimer et al. – Stuttgart
- Cavalleri - Caviglia et al. – Hamburg
- Ahn et al. – Yale
- Stemmer et al. – Santa Barbara
- Chakhalian et al. - Arkansas
- Hwang et al. – Stanford
- Bibes, Barthelemy et al. – Thales/Palaiseau
- Stephan, Gloter et al. – LPS-Orsay
- and several others…



$NdNiO_3$
← Strain control

Scherwitzl et al.
PRL 106, 246403 (2012)





← Light control

Caviglia et al.
PRL 108, 136801 (2012)

Ionic liquid gating control

R.Scherwitzl et al.
Adv. Mat. 22, 5517 (2010)

Sensitivity to pressure in bulk
→ Sensitivity to Strain
in Thin-films/Heterostructures

e.g. Nickelates:

RAPID COMMUNICATIONS

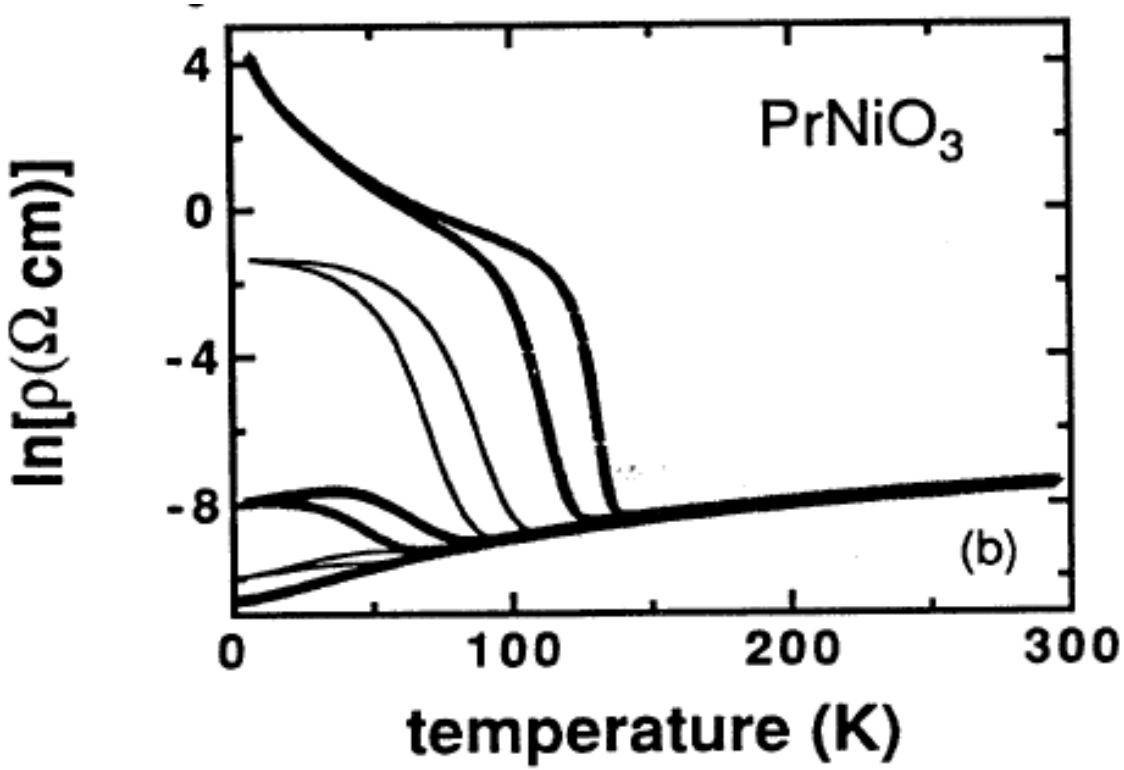
PHYSICAL REVIEW B VOLUME 47, NUMBER 18 1 MAY 1993-II

Extraordinary pressure dependence of the metal-to-insulator transition in the charge-transfer compounds $NdNiO_3$ and $PrNiO_3$

P. C. Canfield and J. D. Thompson
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

S-W. Cheong and L. W. Rupp
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

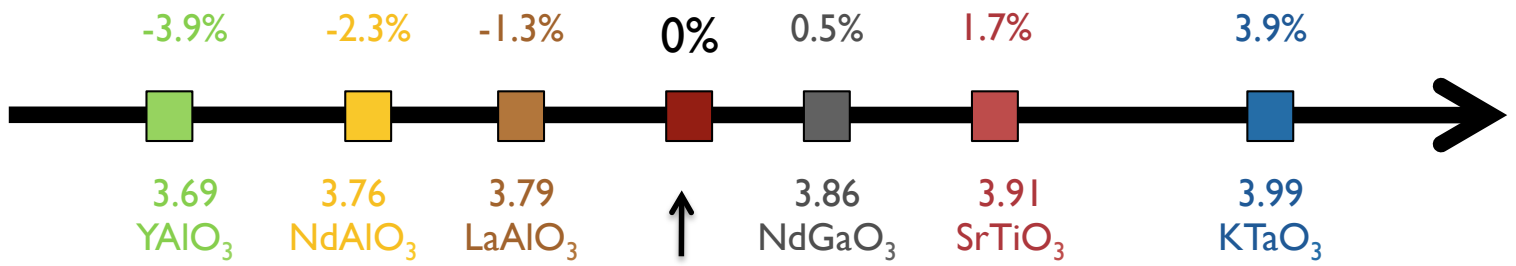
(Received 4 September 1992)



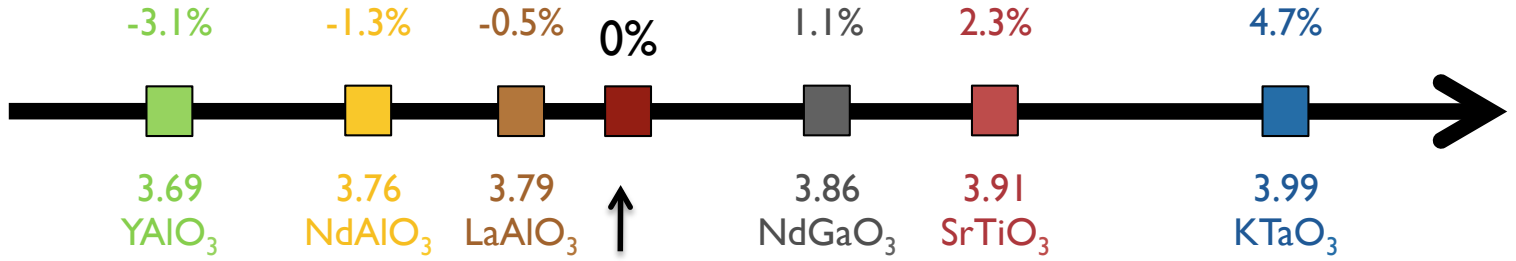
Canfield et al.
PRB 1993

FIG. 2. (a) Temperature-dependent resistivity of $PrNiO_3$ for applied pressures of 1 bar, 5.2 kbar, 9.0 kbar, 10.8 kbar, and 14.1 kbar. Data sets for each pressure are shown alternately as solid lines and crosses. The furthest right data set (crosses) is 1 bar data and the furthest left data set (crosses) is 14.1 kbar data. For each data set the further right curve is the warming data. (Note: for the 14.1 kbar data set there is no hysteresis and therefore no difference between warming and cooling data.) (b) Temperature dependence of the natural log of the resistivity of $PrNiO_3$ at the same pressures.

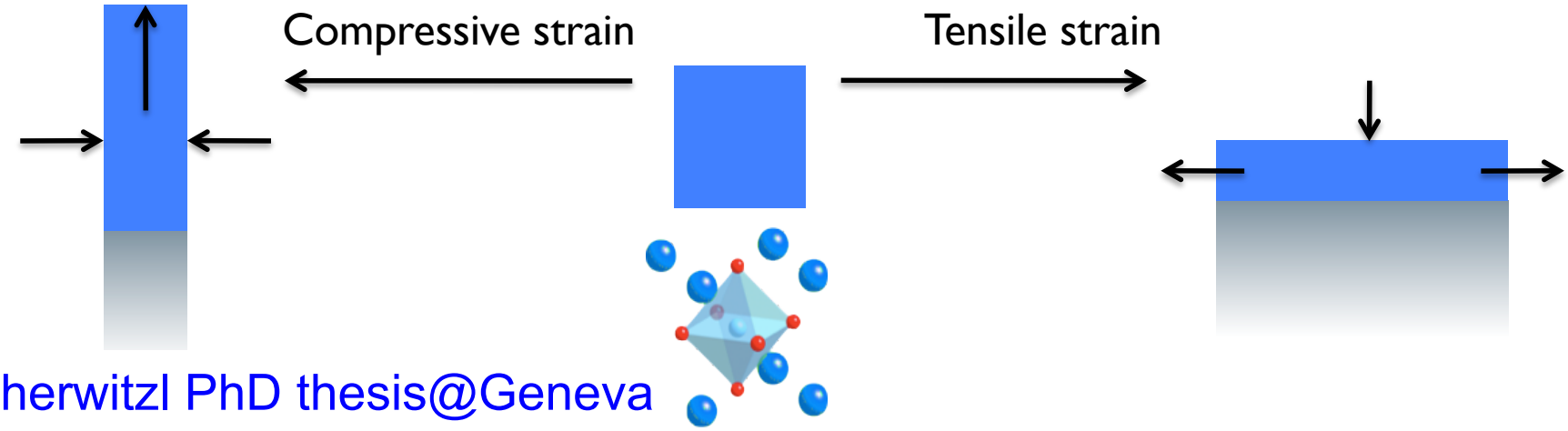
Strain-Control by growth on different substrates: $RNiO_3$



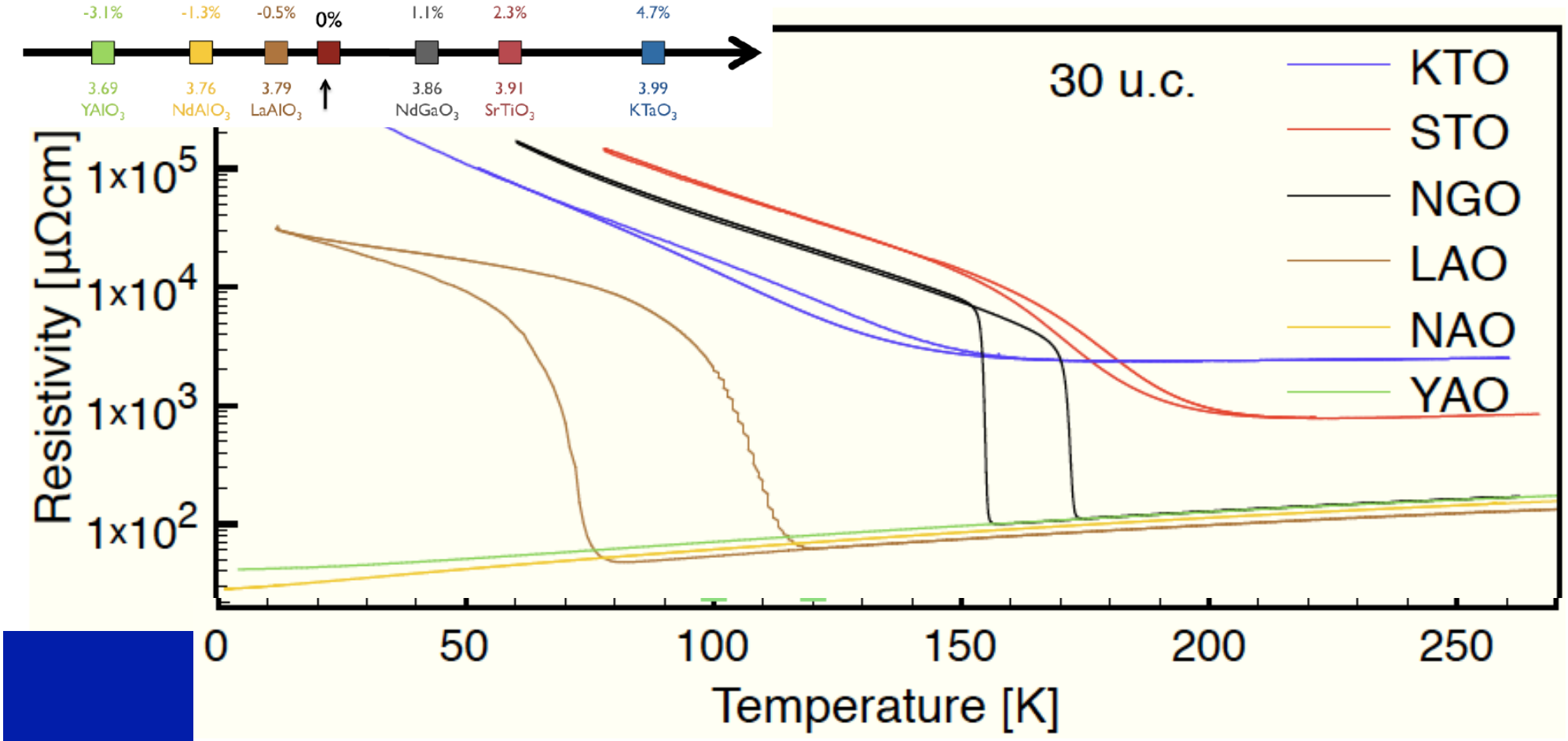
$LaNiO_3$: 3.84 Å pc



$NdNiO_3$: 3.81 Å pc



R.Scherwitzl PhD thesis@Geneva



Compressive strain:

- Does not change much resistivity in metallic state (~ 50%)
- Efficiently shifts MIT to lower T, even complete suppression: → NNO ~ LAO

Tensile strain:

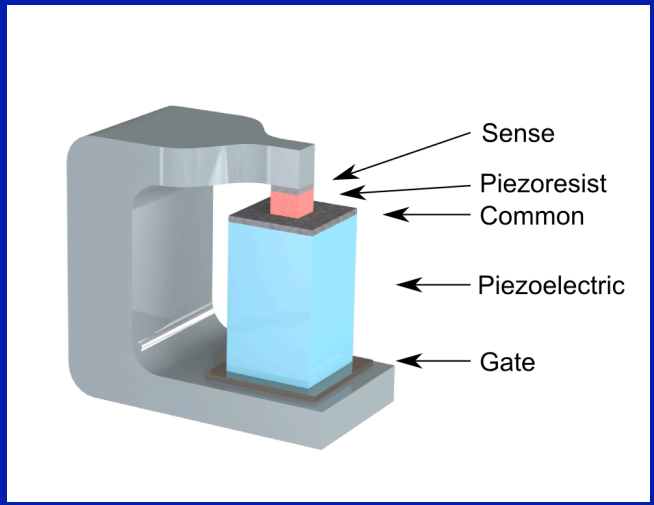
- Increases resist in metallic phae
- Smaller shift of MIT to higher T (except KTO: disorder ?)

R.Scherwitzl PhD thesis@Geneva

Possible applications ?

- Bolometers
- `Piezoelectronic' transistor (PET)
- ``Synaptic'' devices (e.g. Ha et al. Phys Rev Applied 2, 064003, 2014)
- `Control of MIT by voltage pulses

→Resistive RAMs

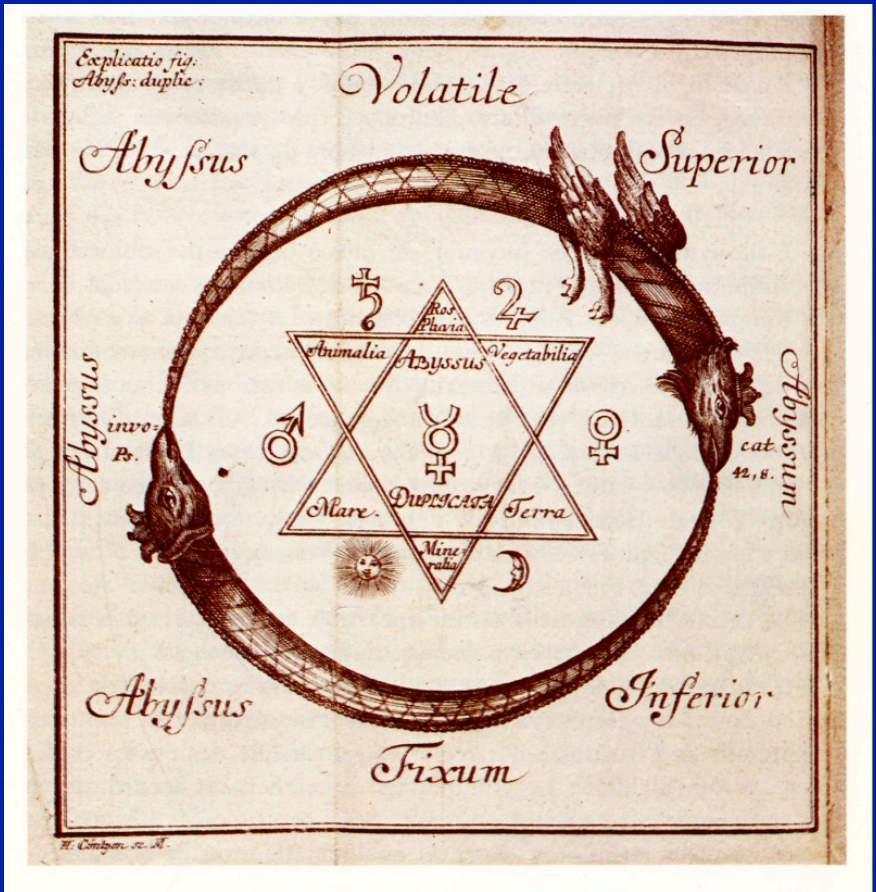


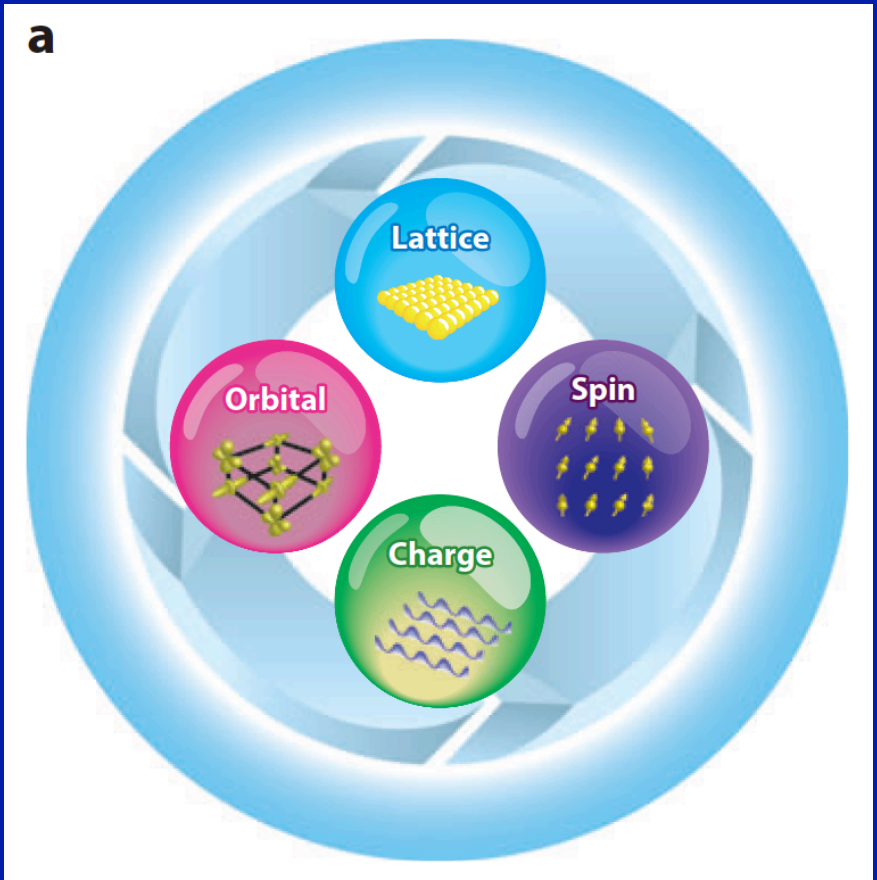
Schematic design of a piezoelectric transistor (IBM)

A creative proposal: turning a nickelate into a superconducting cuprate-like material by strain-engineering ?

Modern alchemy… ?

Chaloupka and Khaliullin, PRL 2008
Hansmann et al., PRL 2010





Orbital Order and Possible Superconductivity in $LaNiO_3/LaMO_3$ Superlattices

Jiří Chaloupka[1,2] and Giniyat Khaliullin[1]

[1]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*
[2]*Institute of Condensed Matter Physics, Masaryk University, Kotlářská 2, 61137 Brno, Czech Republic*
(Received 3 July 2007; published 10 January 2008)

A hypothetical layered oxide La_2NiMO_6 where NiO_2 and MO_2 planes alternate along the c axis of ABO_3 perovskite lattice is considered theoretically. Here, M denotes a trivalent cation Al, Ga,... such that MO_2 planes are insulating and suppress the c-axis charge transfer. We predict that correlated e_g electrons in the NiO_2 planes develop a planar x^2-y^2 orbital order driven by the reduced dimensionality and further supported by epitaxial strain from the substrate. Low-energy electronic states can be mapped to a single-band $t - t' - J$ model, suggesting favorable conditions for high-T_c superconductivity.

Turning a Nickelate Fermi Surface into a Cupratelike One through Heterostructuring

P. Hansmann,[1,2] Xiaoping Yang,[1] A. Toschi,[1,2] G. Khaliullin,[1] O. K. Andersen,[1] and K. Held[2]

[1]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*
[2]*Institute for Solid State Physics, Vienna University of Technology, 1040 Vienna, Austria*
(Received 2 July 2008; published 29 June 2009)

Using the local density approximation and its combination with dynamical mean-field theory, we show that electronic correlations induce a single-sheet, cupratelike Fermi surface for hole-doped 1/1 $LaNiO_3/LaAlO_3$ heterostructures, even though both e_g orbitals contribute to it. The Ni $3d_{3z^2-1}$ orbital plays the role of the axial Cu 4s-like orbital in the cuprates. These two results indicate that "orbital engineering" by means of heterostructuring should be possible. As we also find strong antiferromagnetic correlations, the low-energy electronic and spin excitations in nickelate heterostructures resemble those of high-temperature cuprate superconductors.

``Orbital engineering'' in oxides

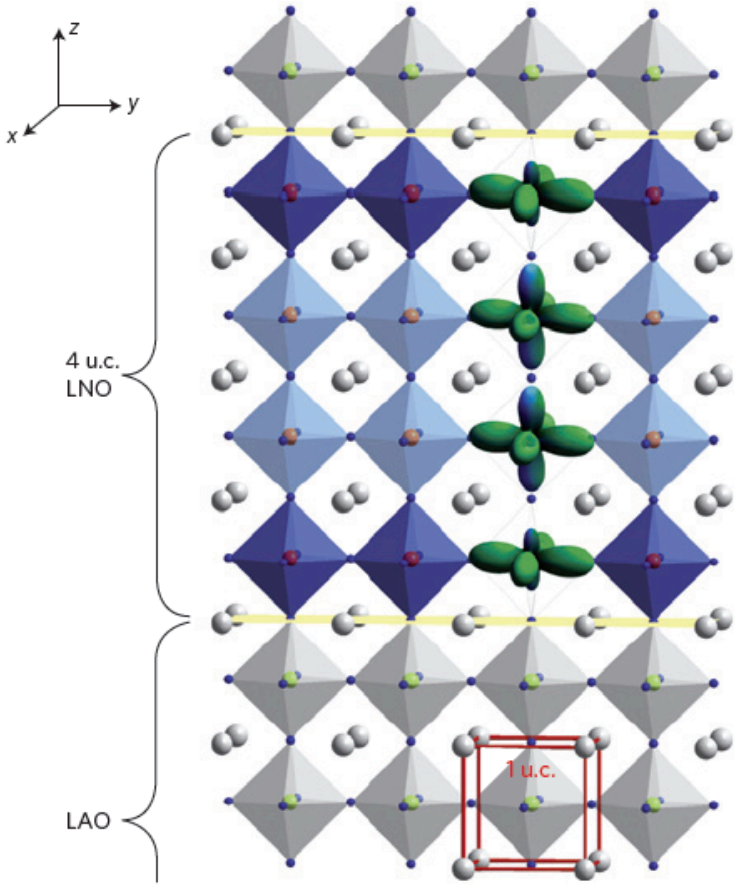


Figure 5 | Heterostructure of metallic $LaNiO_3$ with partially occupied Ni e_g orbitals (LNO, blue) and insulating $LaAlO_3$ (LAO, white)[46]. The orbital polarization at the interface (x^2-y^2 shown in green and $3z^2-r^2$ shown in dark blue) is exaggerated for clarity. Figure reproduced from ref. 46, © 2011 NPG.

$LaNiO_3$

Naïve ionic counting: $Ni^{3+} \rightarrow d^7$

Low-spin configuration:

6 electrons in filled t_{2g}

1 electron in e_g doublet

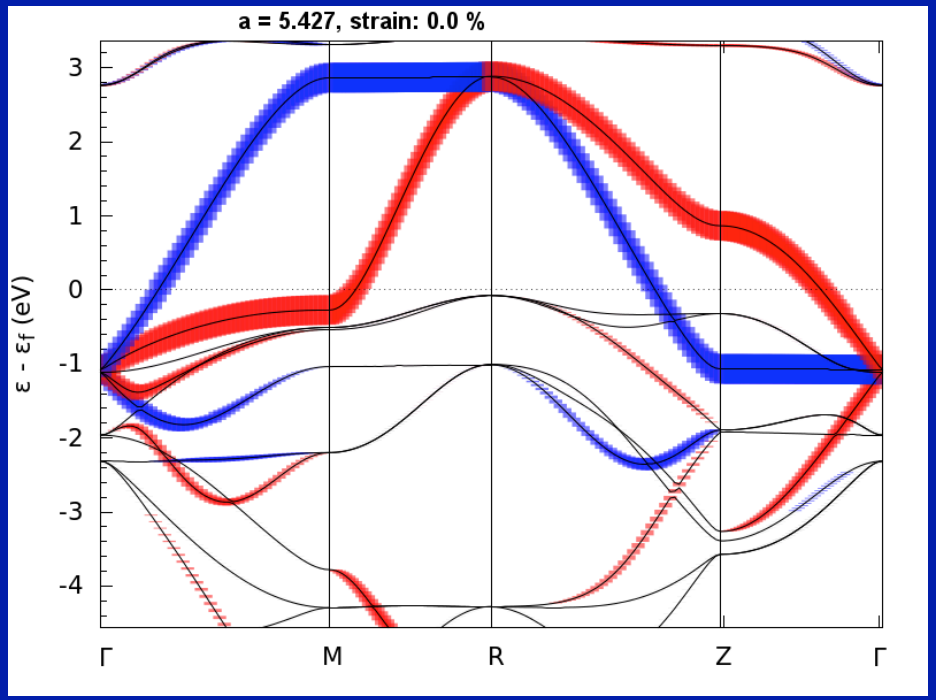
(1/4-filled band)

Can we split apart the d_{x2-y2} and the d_{3z2-r2} orbitals by tensile strain (contracting c-axis) or heterostructuring ?

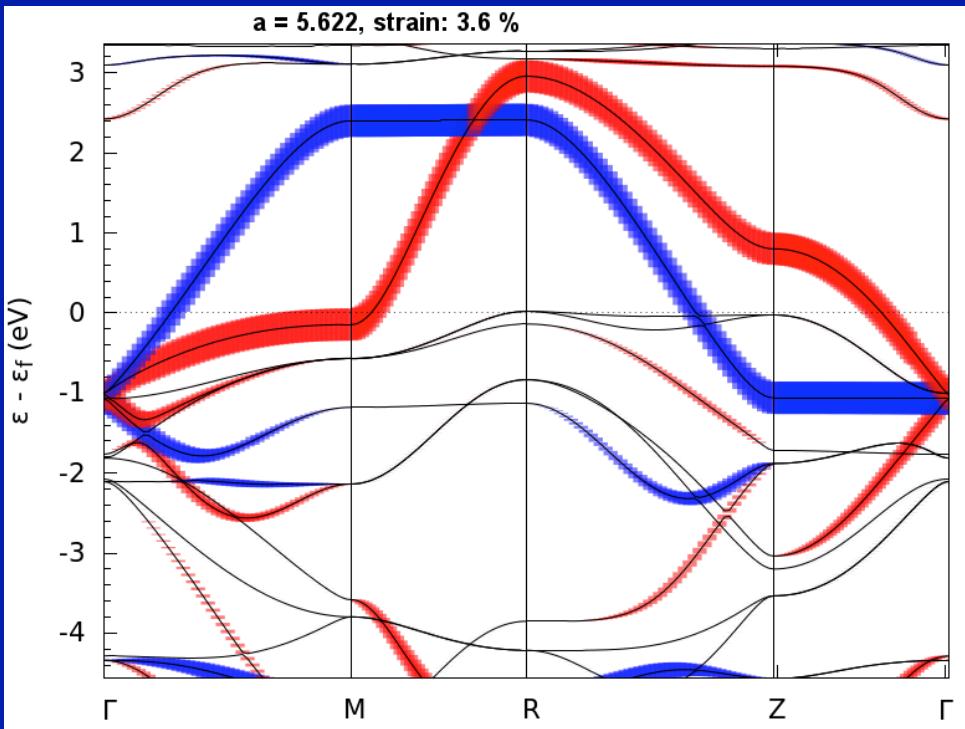
Analogy with the electronic structure of cuprate hi-Tc superconductors

- La_2CuO_4: Cu^{2+} d^9 shell
- t_{2g} filled (6 electrons)
- Large Jahn-Teller deformation of octahedra with c>a: $3z^2-r^2$ is favored, fully split and hence filled by 2 electrons
- Remaining: 1 electron in x^2-y^2 band (1/2-filled)
- Nickelates: By splitting e_g shell: empty $3z^2-r^2$ and ½-filled x^2-y^2 ?

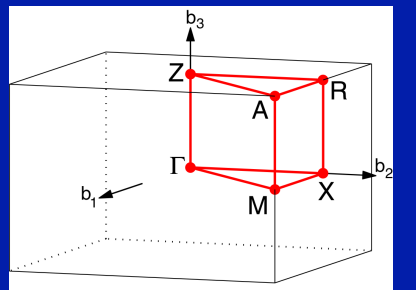
Band-structure of $LaNiO_3$ in idealized tetragonal structure



← Unstrained
Bottom: 3.6% tensile strain

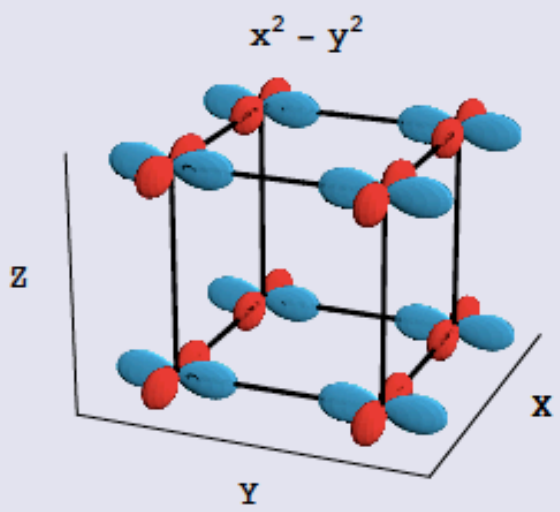


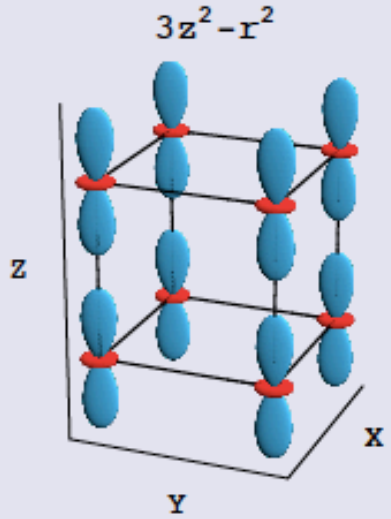
Fat bands:
Red – z^2
Blue – x^2-y^2
Peil et al. PRB 2014



TET path: Γ-X-M-Γ-Z-R-A-Z|X-R|M-A
[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

e_g eigenstates of the cubic system:





Overlap Integrals (Slater & Koster)

$$t^x = t_0 \begin{pmatrix} \frac{3}{4} & -\frac{\sqrt{3}}{4} \\ -\frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix} \quad t^y = t_0 \begin{pmatrix} \frac{3}{4} & \frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix} \quad t^z = t_0 \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

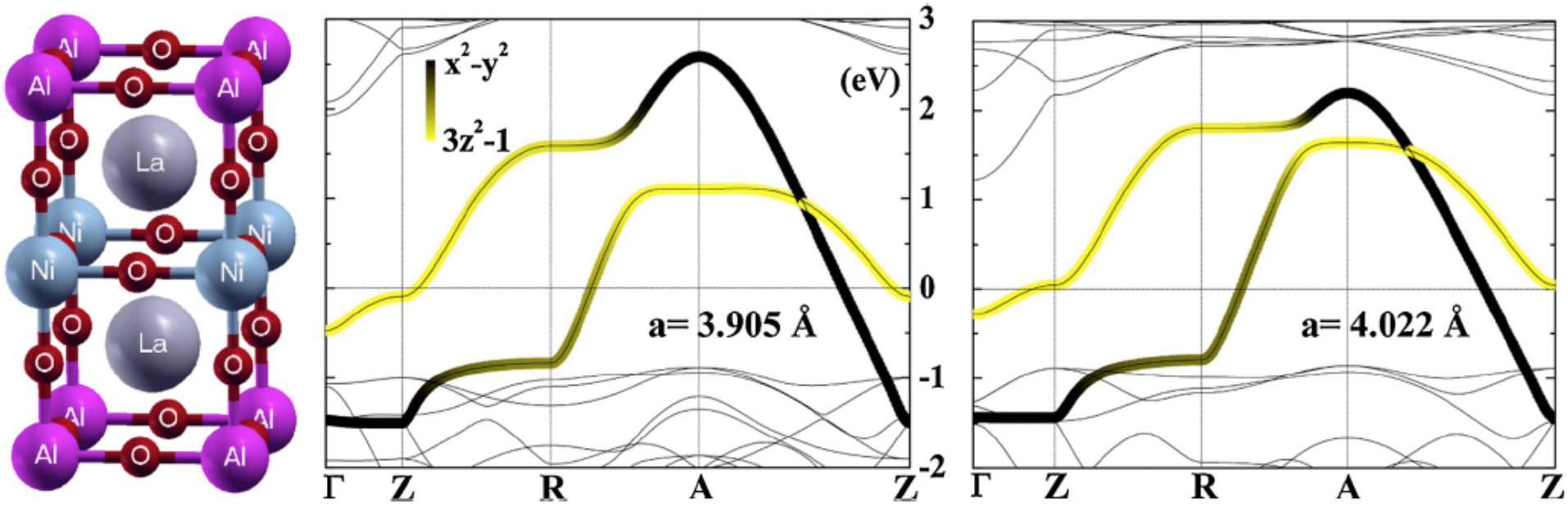


FIG. 1 (color online). The 1/1 $LaNiO_3/LaAlO_3$ heterostructure (left) and its LDA (*N*MTO) band structures without (center) and with (right) strain. The Bloch vector is along the lines $\Gamma(0,0,0) - Z(0,0,\frac{\pi}{c}) - R(0,\frac{\pi}{a},\frac{\pi}{c}) - A(\frac{\pi}{a},\frac{\pi}{a},\frac{\pi}{c}) - Z(0,0,\frac{\pi}{c})$. The shading gives the $x^2 - y^2$ vs $3z^2 - 1e_g$ Wannier-function character.

1/1 $LaNiO_3/LaAlO_3$ Heterostructure

Band-structure (LDA):

Stabilisation of the x^2-y^2 orbital under tensile strain

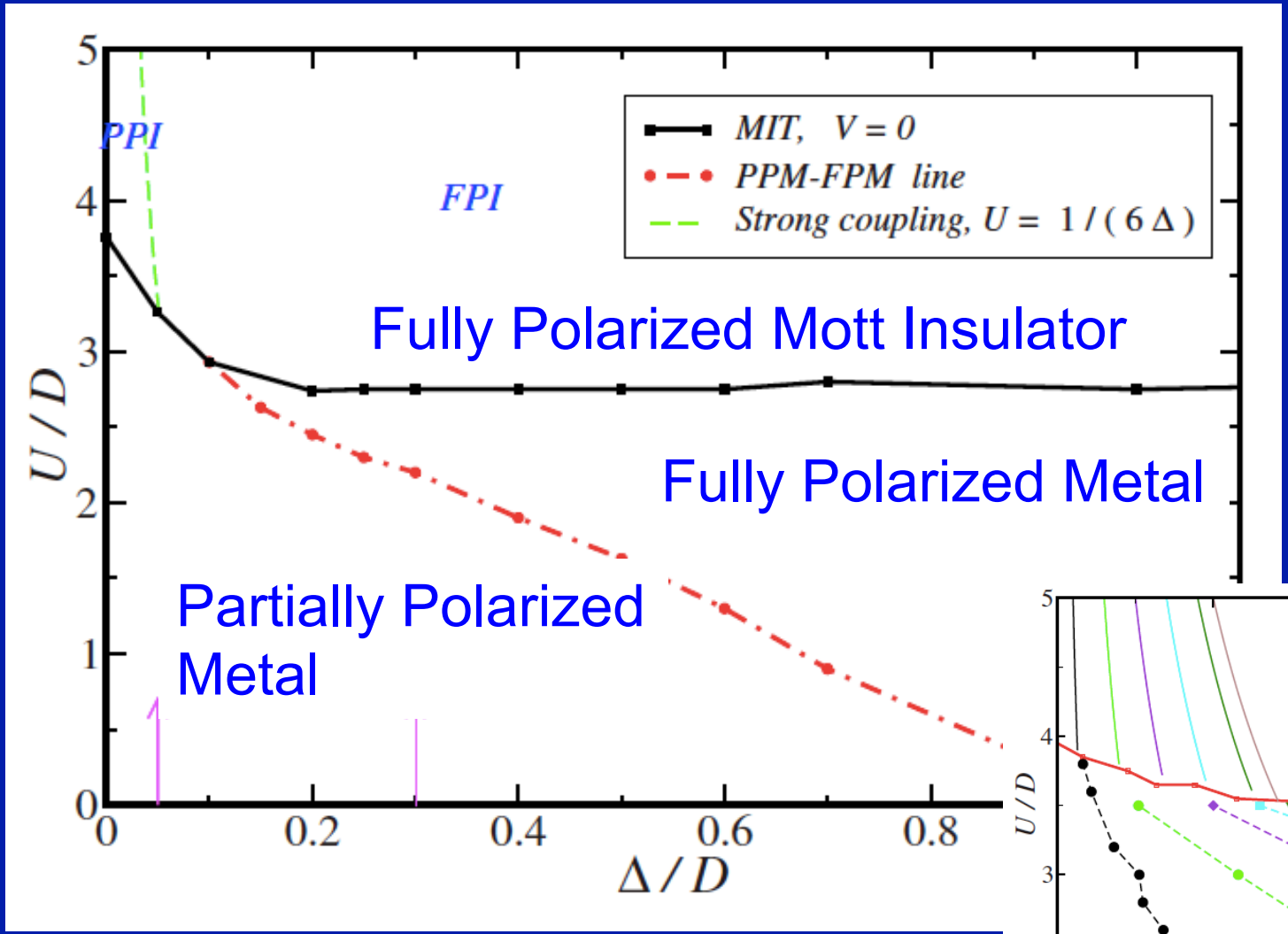
Destabilisation of the $3z^2$-r^2 orbital

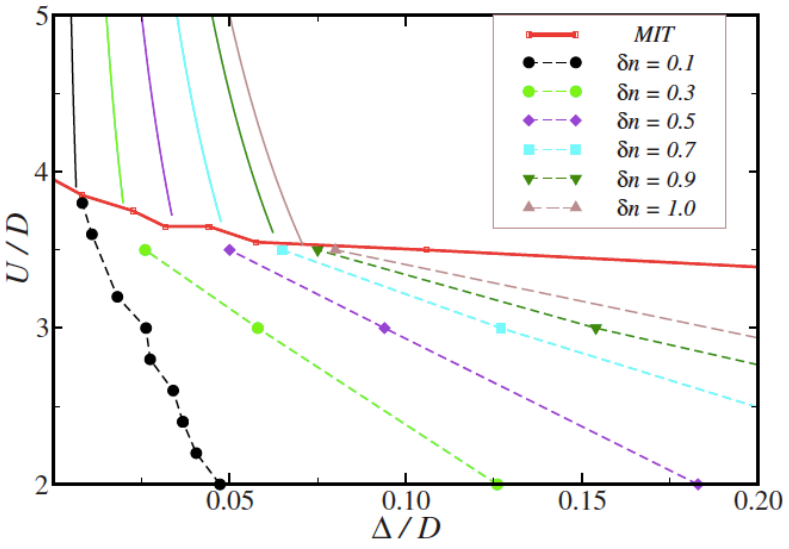
From Hansmann et al. PRL (2009)

Electronic correlations enhance orbital polarization in a d^1 2-orbital shell

- Atomic limit: Full polarization as soon as crystal-field splitting $\Delta_c > 0$
- ¼-filled Mott insulator: $\Delta_c > c\ t^2/U$
- Non-interacting limit: Full polarization for $\Delta_c > D$, ½-bandwidth
- Correlated metal: Effective bandwidth reduced by correlations (Brinkman-Rice): $\Delta_c > Z.D$

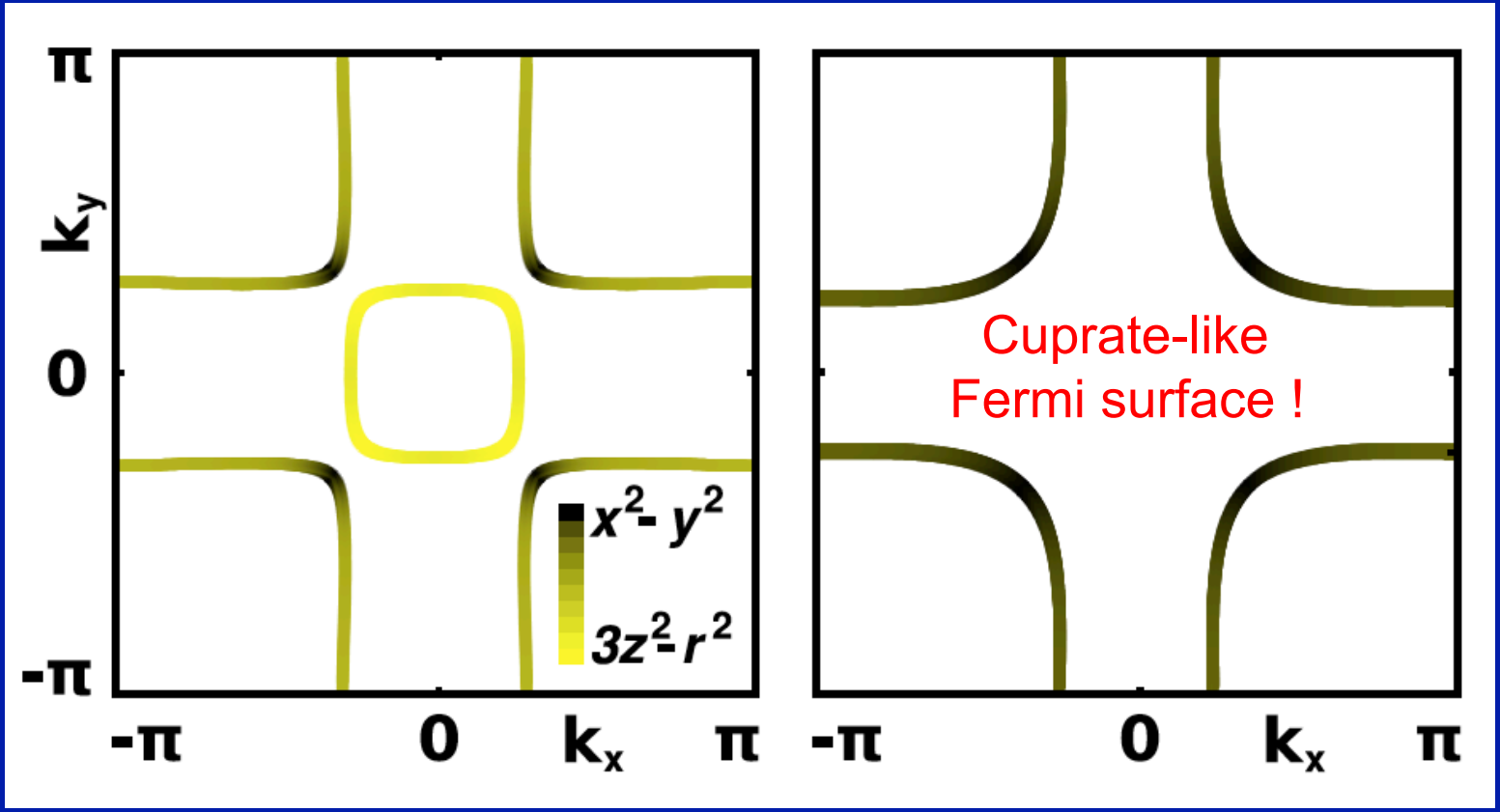
Orbital polarization in a ¼-filled 2-orbital Hubbard model: DMFT, from Poteryaev et al. PRB 78, 045115 (2008)





See also: Manini et al. PRB 66, 115107 (2002)

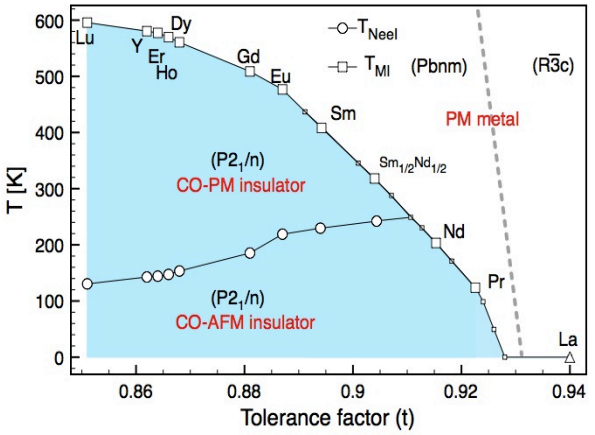
Hansmann et al. (PRL 2009, PRB 2010) performed DMFT calculations using a 2-orbital Hubbard-Kanamori model and predict a large orbital polarization due to the physics described in previous slide



Increasing U

Does this work in practice ?

→ You will know by the end of the lecture…



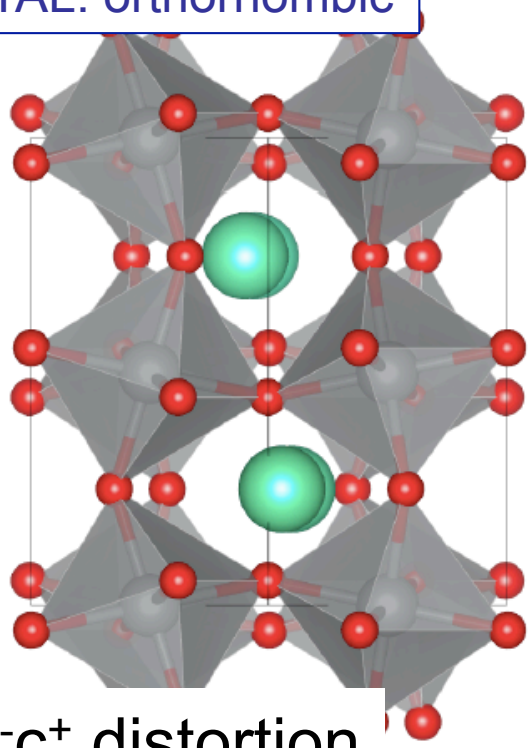
MIT of Nickelates: Puzzles

- Naive valence counting (ionic picture):
- $Ni^{3+} \rightarrow 3d^7 = t_{2g}^6 e_g^1$
- Orbital degeneracy (1 electron in e_g doublet) should lead to strong Jahn-Teller distortion → NOT observed !
- Indeed, Ni^{3+} rarely stabilized, Ni^{2+} (d^8) common (as in NiO)
- MIT comes with structural bond-disproportionation
- 1st order MIT
- MIT as Mott transition of ¼-filled e_g band NOT a tenable picture (fine-tuning required, structural transition and evolution over the RE series not accounted for, etc… - more below)

Bond Disproportionation

$LuNiO_3$, *Pbnm*, high-T

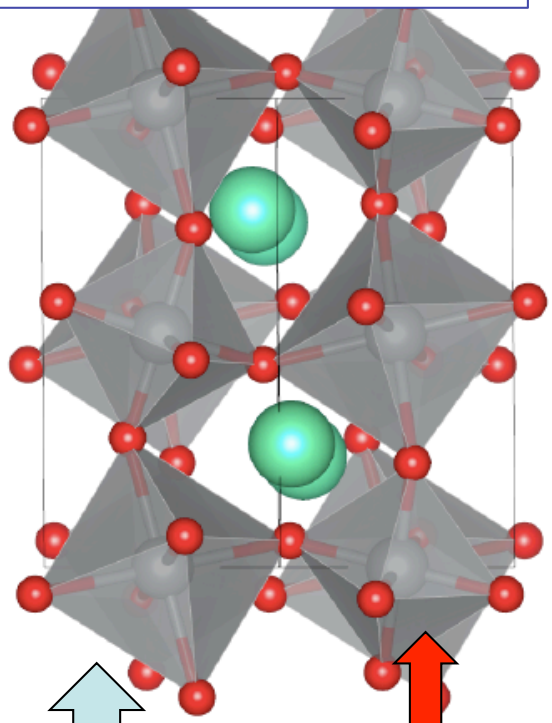
METAL: orthorhombic

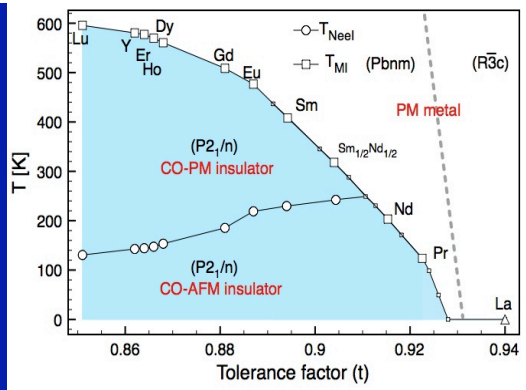


$a^-a^-c^+$ distortion

$LuNiO_3$, $P2_1/n$, low-T

INSULATOR: monoclinic





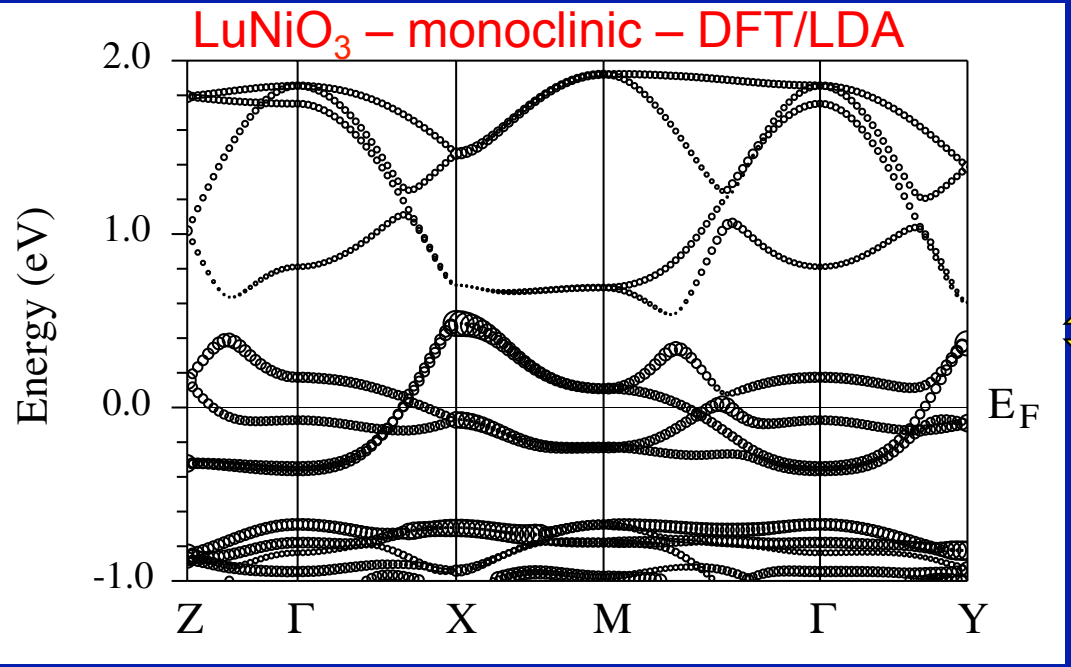
Long-bond (LB) Short-bond (SB)

NiO_6 octahedron

Low-T phase: two types of Ni-sites

Let us look at the DFT bandstructure of the low-T (monoclinic) phase:

8 =
= 2
× 4 atoms in cell
e_g bands
(Ni with strong admixing of oxygen)

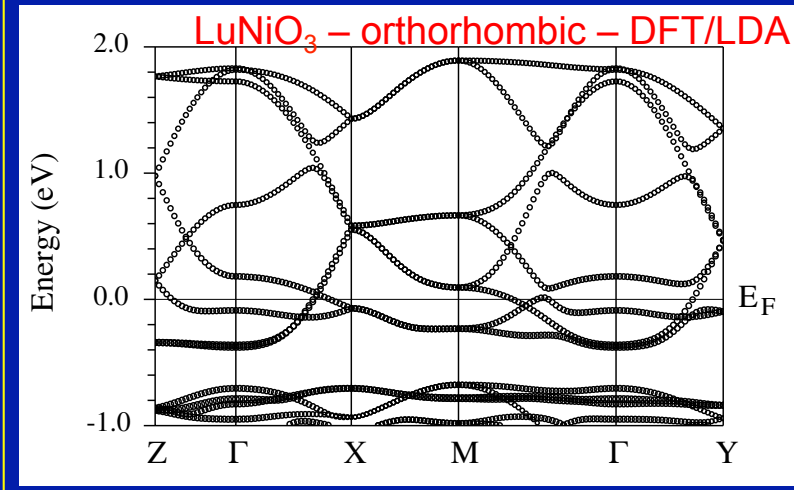


Separated into 2 manifolds (~ Peierls mechanism) by LB/SB disp.

* Peierls-like mechanism induces a modulation of on-site energies:
LB sites are lower by Δ/2, SB sites higher by Δ/2
Δ ~ 0.25 eV

- Within LDA, the phase is metallic (Peierls gap opens at nominal ½-filling position

→ Correlation effects are crucial to account for insulating nature



Long-bond/Short-bond character

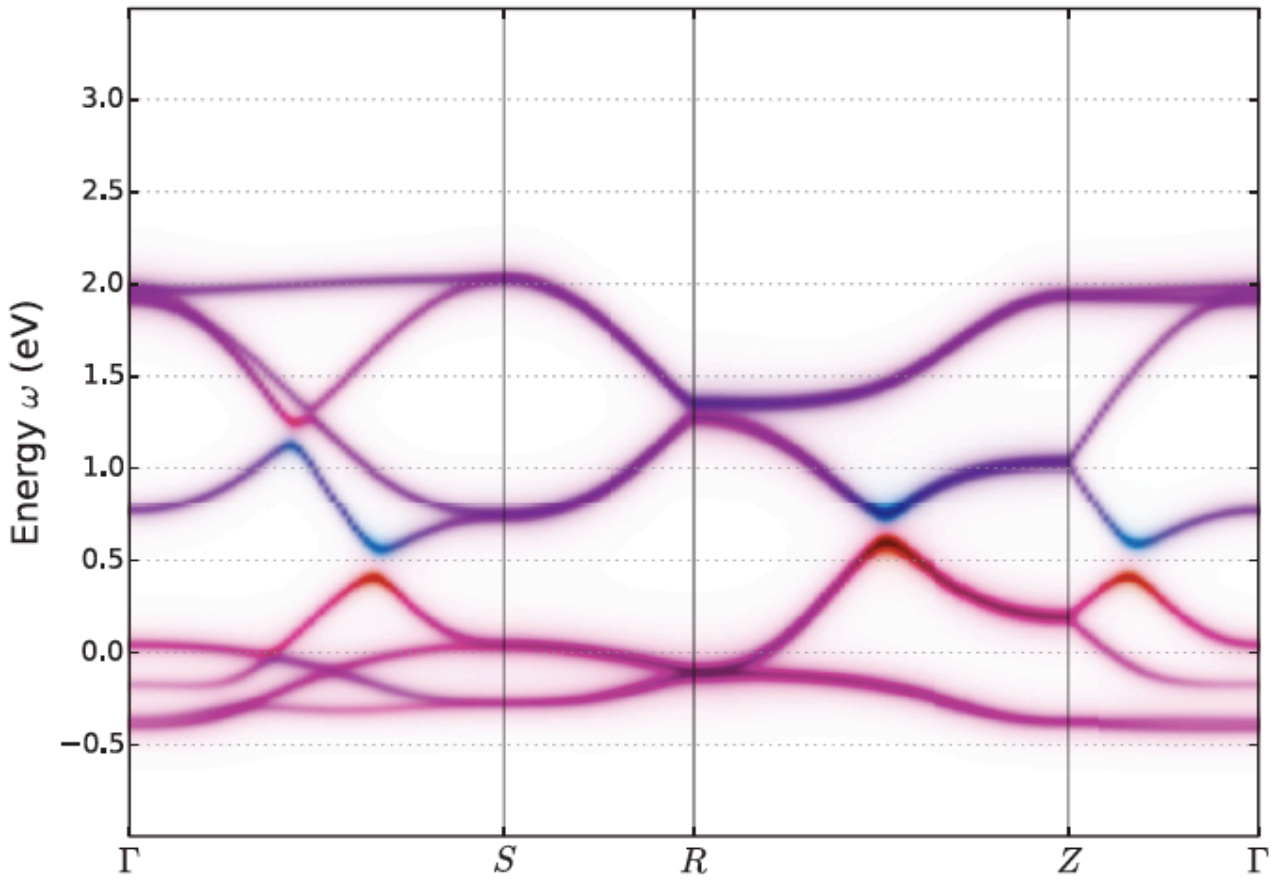
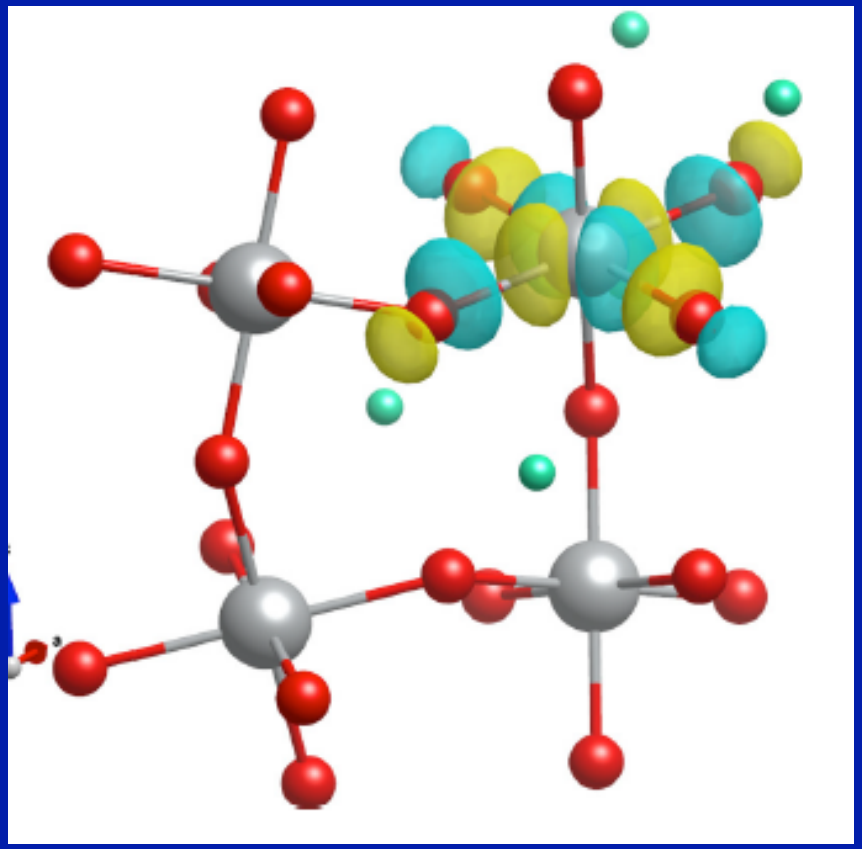
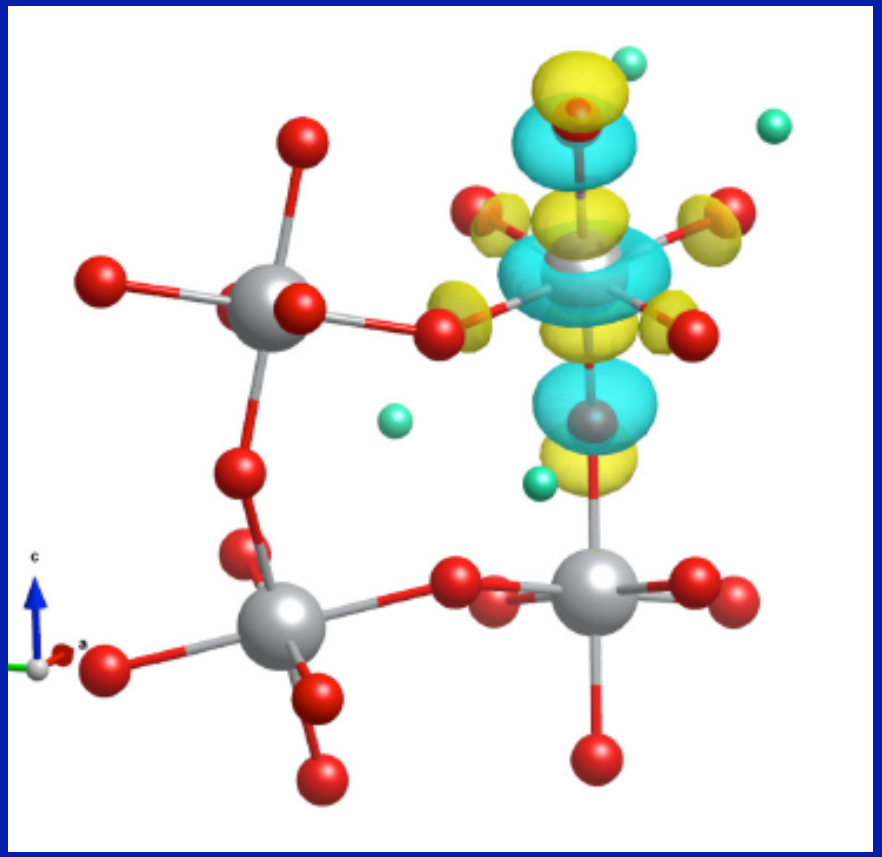


FIG. 3. (Color online) The bare (GGA) band structure of the monoclinic phase of $SmNiO_3$. The color represents the site character of the states: LB (red) and SB (blue). Note the Peierls splitting at an energy +0.5–0.7 eV. The position of the Fermi level is $\varepsilon = 0$.

Strong O-Ni covalency

e_g Wannier functions have strongly mixed Ni-O character





Subedi et al. PRB (2015).

See also recent work by J.Varignon et al. arXiv:1603.05480

Some key insights…

Insight 1:
Strong covalency of Ni-O bond
→ Formation of "Ligand holes"

Additional Oxygen Ordering in "$La_2NiO_{4.25}$" ($La_8Ni_4O_{17}$). II. Structural Features

J. Sol. State Chem. 106, 330 (1993)
Thanks to: J-M Tarascon

A. DEMOURGUES, F. WEILL, B. DARRIET, A. WATTIAUX, J. C. GRENIER, P. GRAVEREAU, AND M. POUCHARD

Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351, Cours de la Libération, 33405 Talence Cedex, France

Received January 11, 1993; in revised form March 25, 1993; accepted March 29, 1993

On the basis of data obtained from the refinement of neutron diffraction experiments, the structural features of $La_8Ni_4O_{17}$ ("$LaNiO_{4.25}$") are discussed. It is shown that the additional oxygen atoms in the La_2O_2 layers form (O_3^{5-}) polyoxides including one delocalized hole. In the NiO_2 planes, a periodic modulation of the equatorial Ni–O distances characterizes various electronic configurations of the nickel cations and a 2D charge density wave occurs, which is more pronounced at low temperature than at room temperature. A strong coupling between the (O_3^{5-}) polyoxides and the NiO_2 planes results from charge transfer mechanisms, which also account for the stabilization of monovalent nickel (Ni^+) in this compound. The formation of —Ni^+–(O_3^{5-})–Ni^+–(O_3^{5-})— chains along given $\langle 111 \rangle_T$ directions is correlated to the interstitial oxygen ordering previously evidenced.

Extreme picture: $d^8\underline{L}$ (= e_g^2) rather than d^7 "Negative charge-transfer insulator" (Mizokawa, Sawatzky et al.)

VOLUME 67, NUMBER 12 PHYSICAL REVIEW LETTERS 16 SEPTEMBER 1991

Origin of the Band Gap in the Negative Charge-Transfer-Energy Compound $NaCuO_2$

T. Mizokawa, H. Namatame, and A. Fujimori
Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

K. Akeyama, H. Kondoh,[(a)] and H. Kuroda
Department of Chemistry, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

N. Kosugi
Division of Molecular Engineering, Kyoto University, Yoshida, Kyoto 606, Japan
(Received 19 April 1991)

See also: PRB 49, 7193 (1994) mentioning Nickelates

PHYSICAL REVIEW B VOLUME 61, NUMBER 17 1 MAY 2000-I

Spin and charge ordering in self-doped Mott insulators

T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky
Solid State Physics Laboratory, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
(Received 20 January 2000)

Insight 2

LB/SB site disproportionation
is an alternative route to JT
in order to lift orbital degeneracy
and is promoted by Hund's coupling
(Mazin et al.)

PRL **98,** 176406 (2007) PHYSICAL REVIEW LETTERS week ending 27 APRIL 2007

Charge Ordering as Alternative to Jahn-Teller Distortion

I. I. Mazin,[1,2] D. I. Khomskii,[2,*] R. Lengsdorf,[2] J. A. Alonso,[3] W. G. Marshall,[4] R. M. Ibberson,[4] A. Podlesnyak,[5] M. J. Martínez-Lope,[3] and M. M. Abd-Elmeguid[2]

Insight 3 - Millis et al.

Insulating nature of the disproportionated phase involves:

- Mott mechanism on LB sites

(leaving a large magnetic moment)

- Screening of moment on SB sites by ligand holes on neighbouring oxygens

PRL **109,** 156402 (2012) PHYSICAL REVIEW LETTERS week ending 12 OCTOBER 2012

Site-Selective Mott Transition in Rare-Earth-Element Nickelates

Hyowon Park,[1,2] Andrew J. Millis,[1] and Chris A. Marianetti[2]

[1]*Department of Physics, Columbia University, New York, New York 10027, USA*

[2]*Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, USA*

(Received 13 June 2012; published 9 October 2012)

Based on DMFT calculation involving all Ni and O states

(Too) Extreme, but simple, picture:

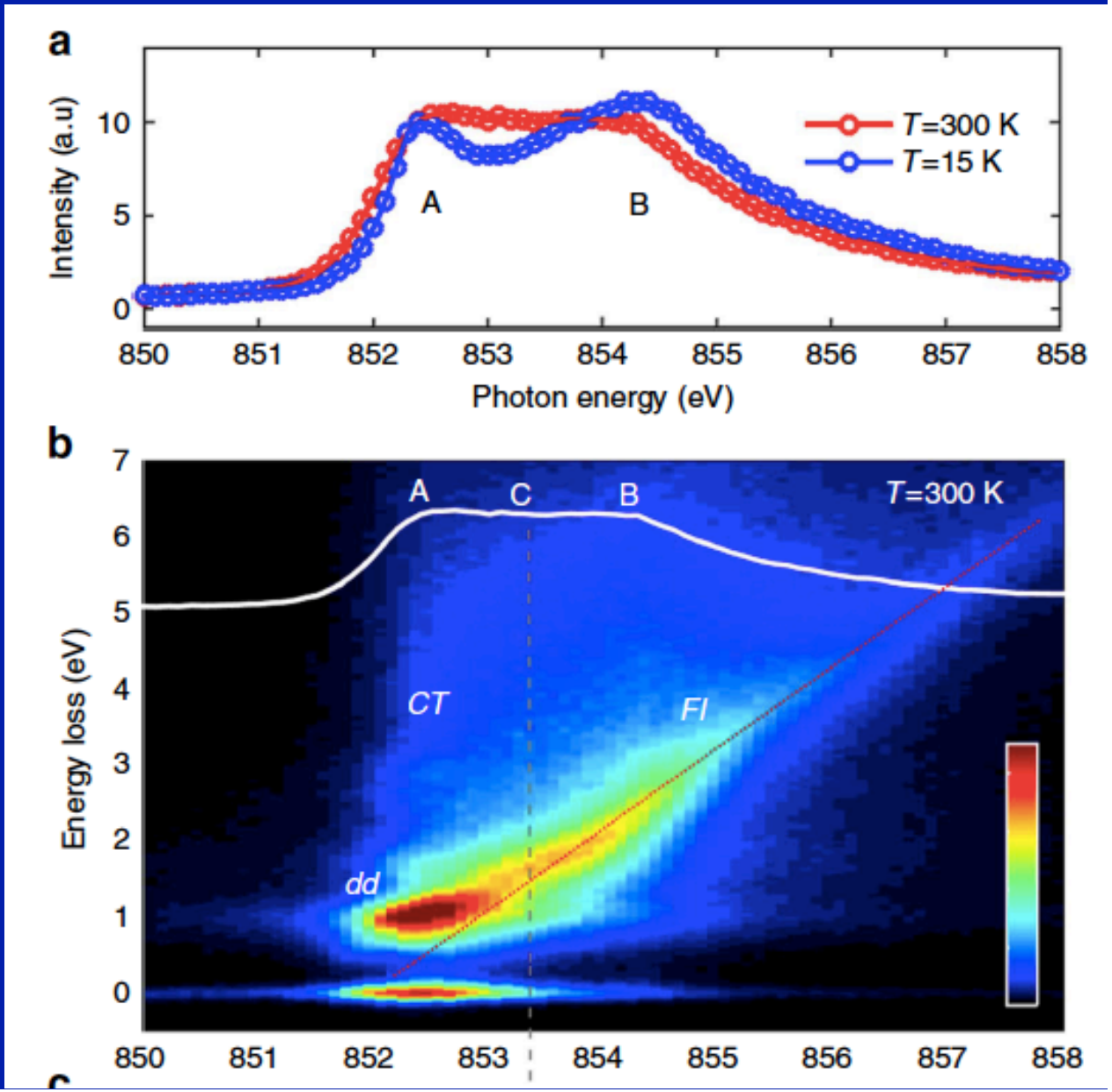
$$d^7 + d^7 \rightarrow d^8\,(\mathrm{LB}) \quad + \quad d^8\,\underline{L}^2\,(\mathrm{SB})$$

S=1
localized
moment
→Mott
insulator

S=1 moment
screened
by two ligand
holes
shared by 6 oxygens
cf. `Kondo insulator'

Park, Millis and Marianetti PRL 109, 156402 (2012)
Johnston et al. PRL 112, 106404 (2014)

Direct experimental evidence for Ligand Holes: XAS - RIXS



Bisogni et al.
Nature Comm.
7.13017

Relevance of ligand holes to cathode materials for batteries

CHEMISTRY OF MATERIALS

Article

pubs.acs.org/cm

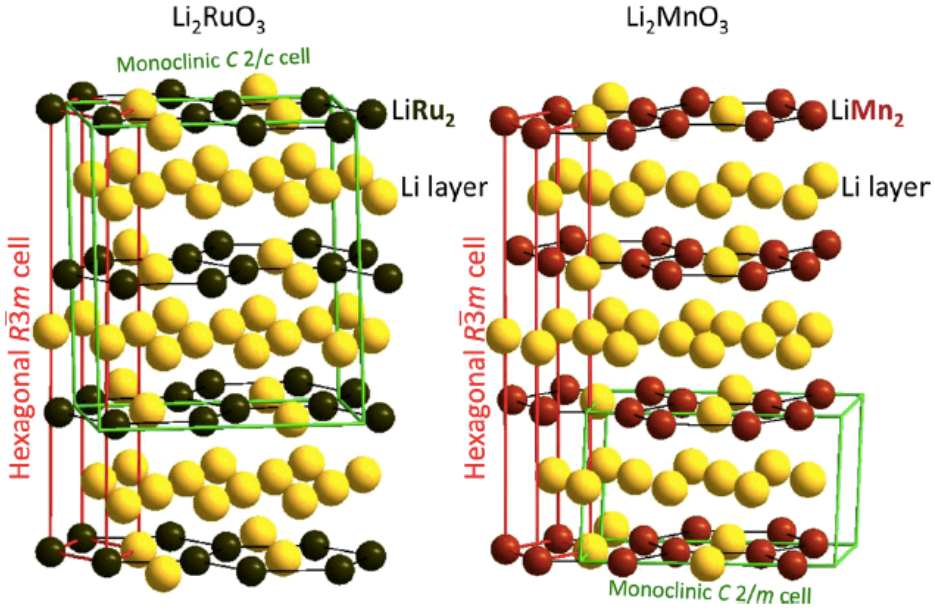
ACS Publications

1121

dx.doi.org/10.1021/cm400193m | *Chem. Mater.* 2013, 25, 1121−1131

High Performance $Li_2Ru_{1-y}Mn_yO_3$ ($0.2 \leq y \leq 0.8$) Cathode Materials for Rechargeable Lithium-Ion Batteries: Their Understanding

M. Sathiya,[†,‡] K. Ramesha,[*,§] G. Rousse,[∥] D. Foix,[⊥] D. Gonbeau,[⊥] A. S. Prakash,[§] M. L. Doublet,[#] K. Hemalatha,[§] and J.-M. Tarascon[*,†,‡]



subsequent discharge. One then believes that the missing reversible process accounting for 0.6 electrons is most likely nested in the reversible oxidation of O^{2-} to O^{-} which necessitates the creation of a hole on oxygen. Such a process does not come as a total surprise as it was proposed by our group back in 1999 to explain the full deinsertion of Li^{+} into $LiCoO_2$.[52] Moreover, physicists are frequently dealing with this redox aspect by talking about holes on oxygen, and the most

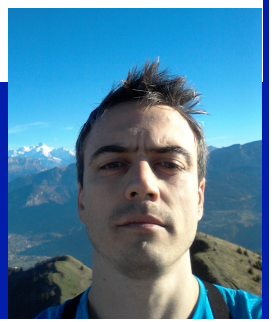
dx.doi.org/10.1021/cm400193m | *Chem. Mater.* 2013, 25, 1121−1131

How can one build
a simple picture
taking this physics into account
and involving only
the `low-energy' e_g states ?

PHYSICAL REVIEW B **91**, 075128 (2015)

Low-energy description of the metal-insulator transition in the rare-earth nickelates

Alaska Subedi,[1,2] Oleg E. Peil,[2,3] and Antoine Georges[2,3,4]



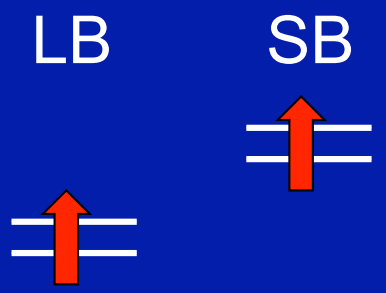
Simple energetics

Compare two (extreme) configurations:

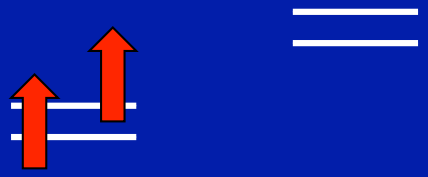
e_g^1(LB) + e_g^1 (SB) *vs.* e_g^2(LB) + e_g^0 (SB)

corresponding to $d^7 + d^7 \rightarrow d^8$ (LB) + $d^8 \underline{L}^2$ (SB) !

S=1/2 on each site
Orbital degeneracy
No electronic disproportionation



$-\Delta/2 + \Delta/2 = 0$



S=1 on LB sites,
S=0 on SB
Disproportionation of e_g occupancy

$-\Delta/2 - \Delta/2 + U-3J = U-3J-\Delta$

→ Consider the (unusual) regime

$$U - 3J < \Delta \lesssim 0 \text{ !}$$

In which the disproportionated configuration is favorable

Simplest Model

Simplify to 2 atoms (LB,SB) per unit cell, 2 orbitals per site

$$H = -t \sum_{m=1}^{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{\langle ij \rangle} (d^{\dagger}_{m\sigma i} d_{m\sigma j} + h.c.) + H_{\text{int}}$$

$$- \frac{\Delta}{2} \sum_{m\sigma, i\in A} d^{\dagger}_{m\sigma i} d_{m\sigma i} + \frac{\Delta}{2} \sum_{m\sigma, j\in B} d^{\dagger}_{m\sigma j} d_{m\sigma j},$$

n.n hopping

Peierls modulation

$$H_{\text{int}} = U \sum_{m} \hat{n}_{m\uparrow} \hat{n}_{m\downarrow} + (U - 2J) \sum_{m\neq m'} \hat{n}_{m\uparrow} \hat{n}_{m'\downarrow} +$$

$$+ (U - 3J) \sum_{m<m',\sigma} \hat{n}_{m\sigma} \hat{n}_{m'\sigma} +$$

Kanamori interactions for e_g shell

U: on-site Coulomb

J: Hund's coupling

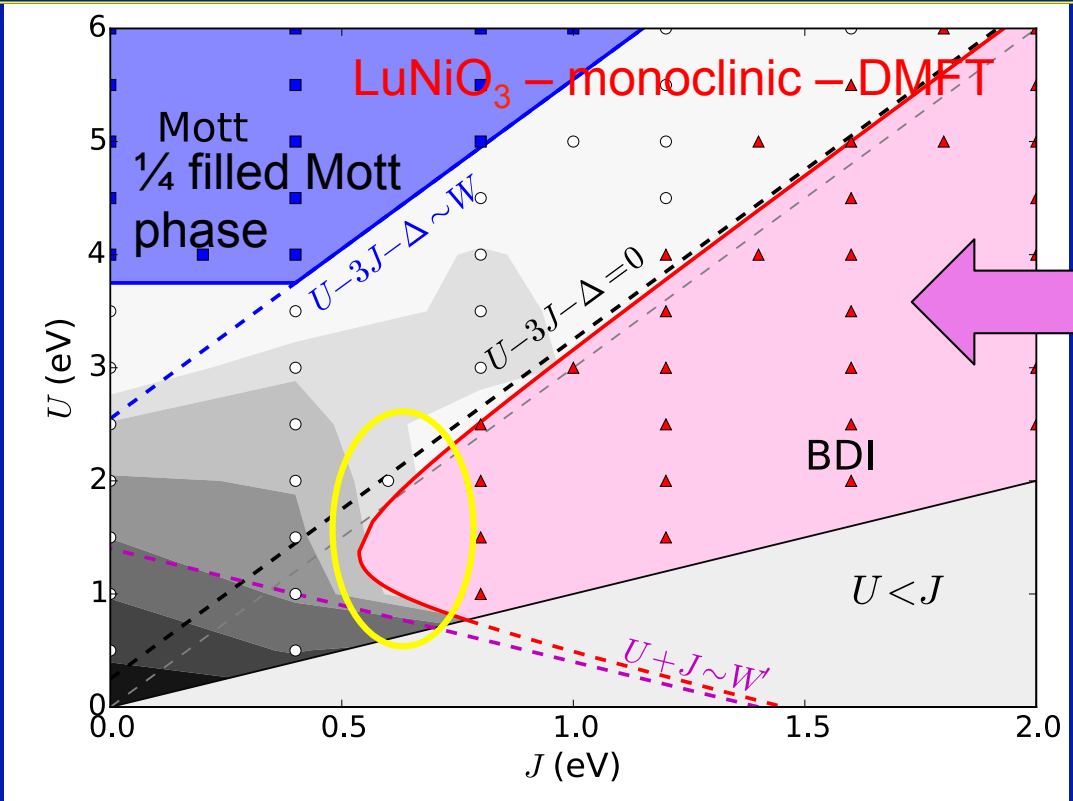
(+ possibly spin-flip, pair-hopping)

Two types of calculations

- Realistic electronic structure of each phase using LDA+DMFT (Dynamical Mean-Field Theory) based on e_g Wannier functions + many-body interactions (U,J)
- Calculations with simple model above (also solved with DMFT)
- Complementary (model+material-realistic) approaches help understanding

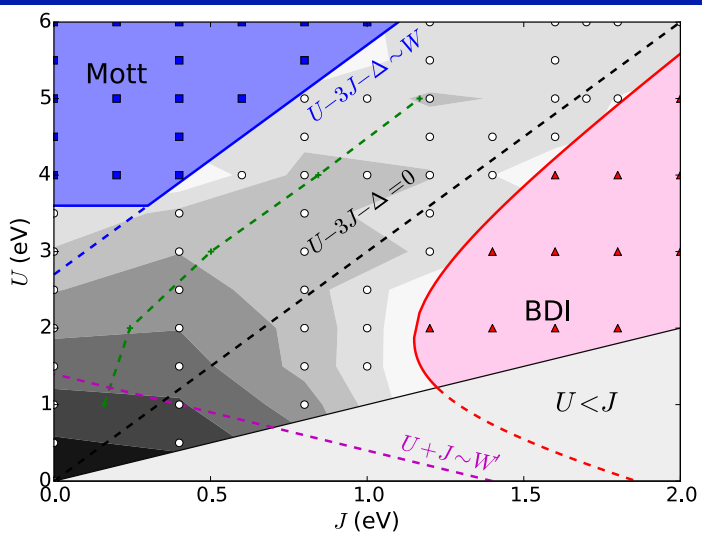
LDA+DMFT (e_g states only), low-T structure $LuNiO_3$

Investigation of phases as a function of U,J



Mott+Peierls
bond disproportionate
insulator
(Selective Mott
on LB sites)

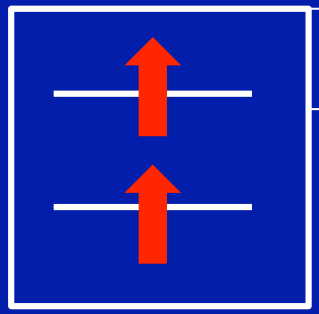
$LuNiO_3$ – orthorombic – DMFT



Note: Location of BDI phase boundary
is extremely sensitive to value of Δ
while ¼ filled Mott is NOT
(hence would require fine-tuning to
account for ortho metallic vs. mono insulating)

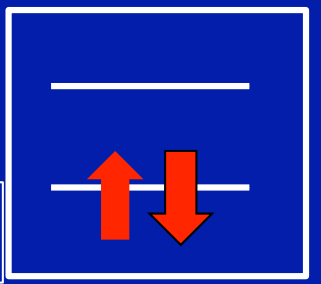
What are the implications for Orbital Polarisability ?

- Obviously a d^8 (e_g^2) Ni^{2+} configuration is not very favorable…
- Two orbitals split by Δ_c :



S=1 (HS) configuration: energy U-3J

S=0 (LS) configuration: energy U-Δ_c



→ Orbital polarisation requires $\Delta_c > 3J$!
(atomic limit estimate)

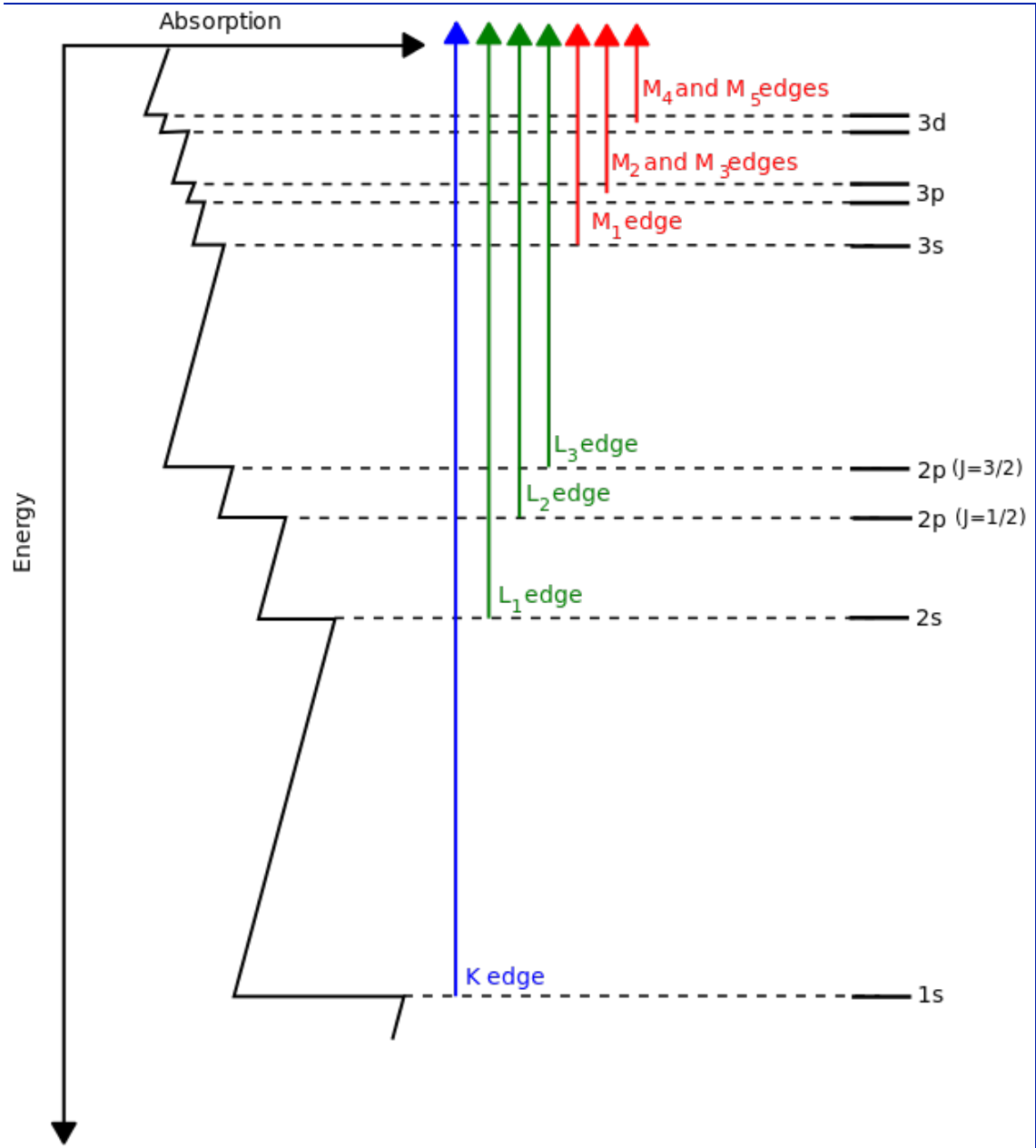
And indeed, experiments reveal some orbital polarization under tensile strain…
but a rather modest one.

PHYSICAL REVIEW B 88, 125124 (2013)

Strain and composition dependence of orbital polarization in nickel oxide superlattices

M. Wu,[1] E. Benckiser,[1,*] M. W. Haverkort,[1,2] A. Frano,[1,3] Y. Lu,[1] U. Nwankwo,[1] S. Brück,[4,5] P. Audehm,[4] E. Goering,[4] S. Macke,[2] V. Hinkov,[2] P. Wochner,[4] G. Christiani,[1] S. Heinze,[1] G. Logvenov,[1] H.-U. Habermeier,[1] and B. Keimer[1,†]

A combined analysis of x-ray absorption and resonant reflectivity data was used to obtain the orbital polarization profiles of superlattices composed of four-unit-cell-thick layers of metallic $LaNiO_3$ and layers of insulating RXO_3 (R = La, Gd, Dy and X = Al, Ga, Sc), grown on substrates that impose either compressive or tensile strain. This superlattice geometry allowed us to partly separate the influence of epitaxial strain from interfacial effects controlled by the chemical composition of the insulating blocking layers. Our quantitative analysis reveals orbital polarizations up to 25%. We further show that strain is the most effective control parameter, whereas the influence of the chemical composition of the blocking layers is comparatively small.



X-ray Absorption Spectroscopy (XAS)

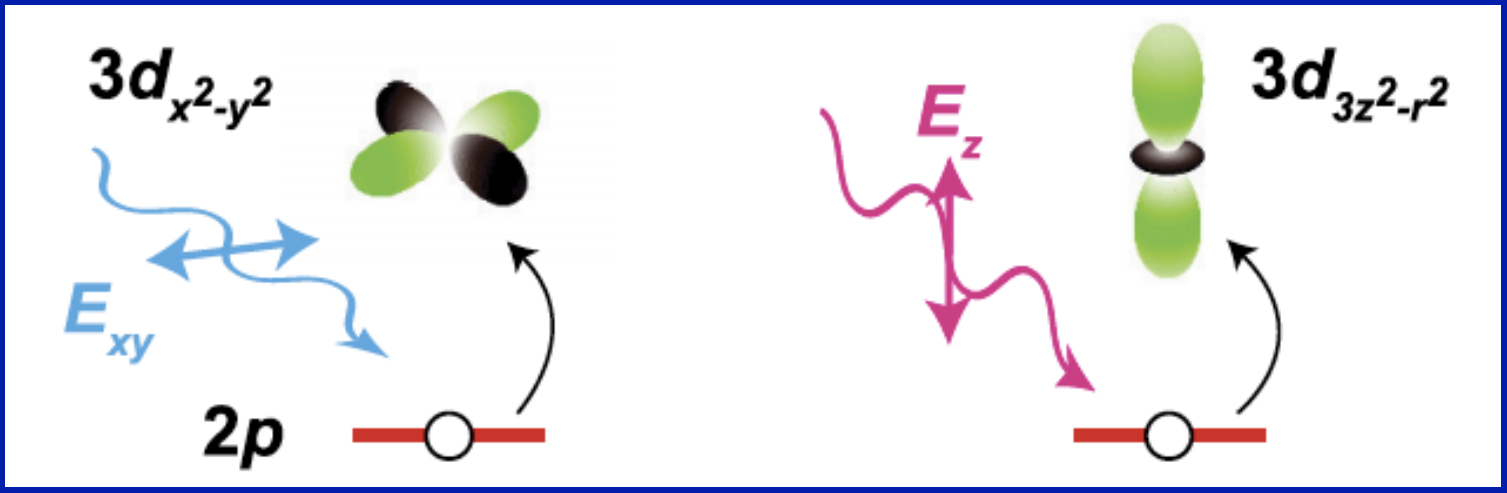
Send an X-photon
Kick an electron from
a core state
into the available (empty)
valence states close to
Fermi level.
Using polarized X-rays,
orbital-resolved
information can be
obtained

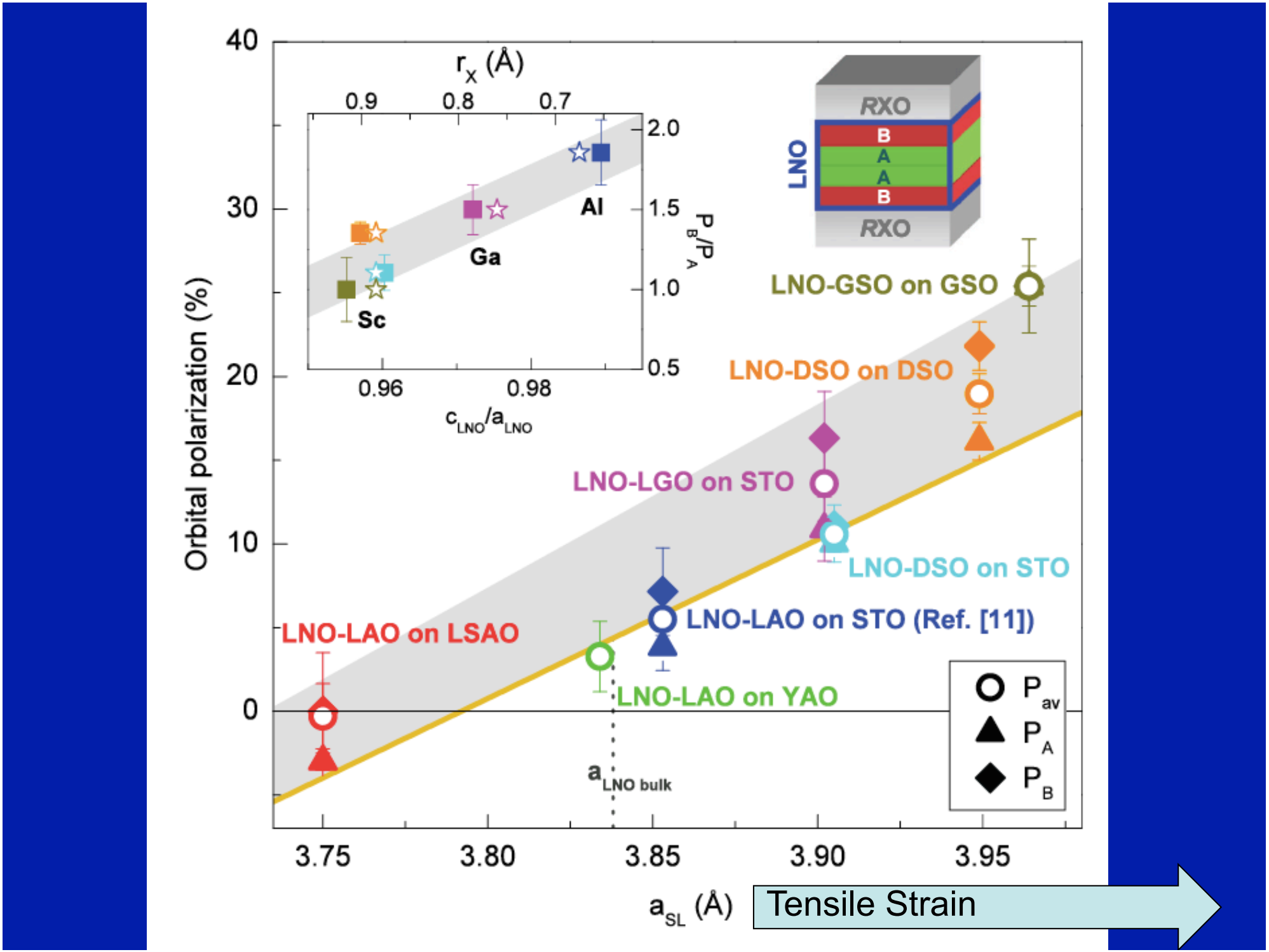
(In Wu et al, experiments:
Ni-L edges)

In order to quantitatively analyze the observed dichroism, we applied the sum rule for linear dichroism,[9,21] which relates the ratio of holes in the Ni e_g orbitals to the energy-integrated XAS intensities across the Ni L edge $I_{x,z} = \int_{L_{3,2}} I_{x,z}(E)dE$ for in-plane (x) and out-of-plane (z) polarization, respectively:

$$X = \frac{h_{3z^2-r^2}}{h_{x^2-y^2}} = \frac{3I_z}{4I_x - I_z}. \quad (1)$$

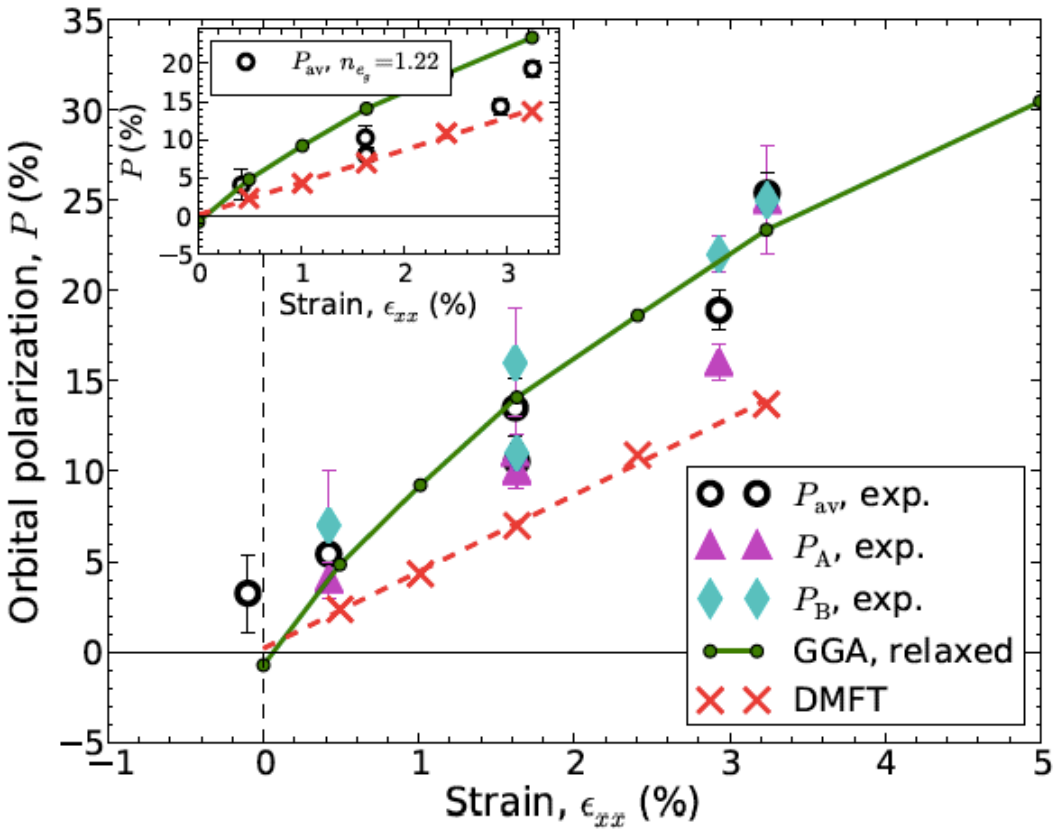
Here, $h_{x^2-y^2}$ and $h_{3z^2-r^2}$ are the hole occupation numbers of orbitals with $x^2 - y^2$ and $3z^2 - r^2$ symmetries.




Orbital polarization (%)
40
30
20
10
0
3.75
3.80
3.85
3.90
3.95
a_{SL} (Å)
$a_{LNO\ bulk}$
LNO-LAO on LSAO
LNO-LAO on YAO
LNO-LAO on STO (Ref. [11])
LNO-LGO on STO
LNO-DSO on STO
LNO-DSO on DSO
LNO-GSO on GSO
P_{av}
P_A
P_B
r_X (Å)
0.9
0.8
0.7
Sc
Ga
Al
0.96
0.98
c_{LNO}/a_{LNO}
2.0
1.5
1.0
0.5
P_B/P_A
RXO
B
A
A
B
RXO
LNO
Tensile Strain

(LDA+) DMFT calculations
yield good agreement with experiments,
provided:

- Either calculation is done by including all Ni-3d and O-2p states, with fairly standard values of U,J
- Or, alternatively, above low-energy 2-orbital e_g description is used, BUT with values of U-3J small or negative (that was the problem with previous predictions of large orbital polarization, quoted above)



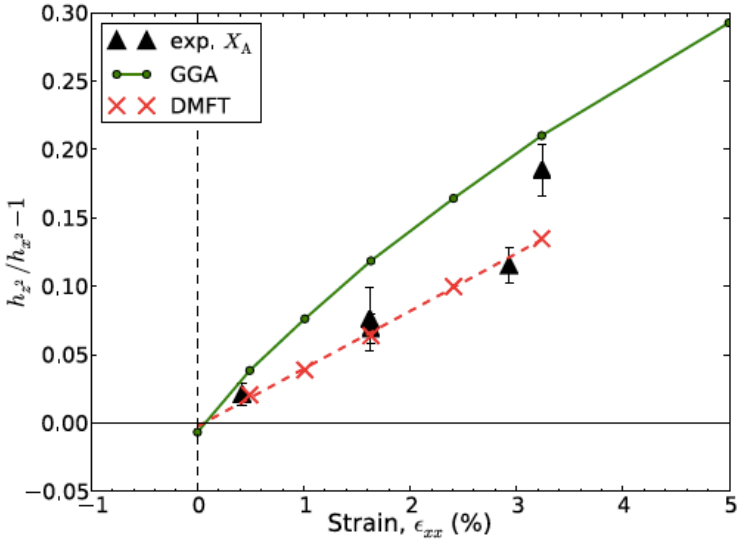


FIG. 12. (Color online) The ratio of the hole occupancies, X, as a function of strain (for experimental points the value for the inner layers, X_A, is used).

In order to quantitatively analyze the observed dichroism, we applied the sum rule for linear dichroism,[9,21] which relates the ratio of holes in the Ni e_g orbitals to the energy-integrated XAS intensities across the Ni L edge $I_{x,z} = \int_{L_{3,2}} I_{x,z}(E)dE$ for in-plane (x) and out-of-plane (z) polarization, respectively:

$$X = \frac{h_{3z^2-r^2}}{h_{x^2-y^2}} = \frac{3I_z}{4I_x - I_z}. \quad (1)$$

Here, $h_{x^2-y^2}$ and $h_{3z^2-r^2}$ are the hole occupation numbers of orbitals with $x^2 - y^2$ and $3z^2 - r^2$ symmetries.

LDA+DMFT calculations including all Ni and O states are in good quantitative agreement with this finding

Peil, Ferrero &AG PRB 90, 045128 (2014)

Han, Wang, Marianetti, Millis. 107, 206804 (2011)

Park, Millis and Marianetti PRB 93, 235109 (2016)

Distortions and c-axis changes induced by strain (cf. lecture 2) - Theory (DFT-GGA) -

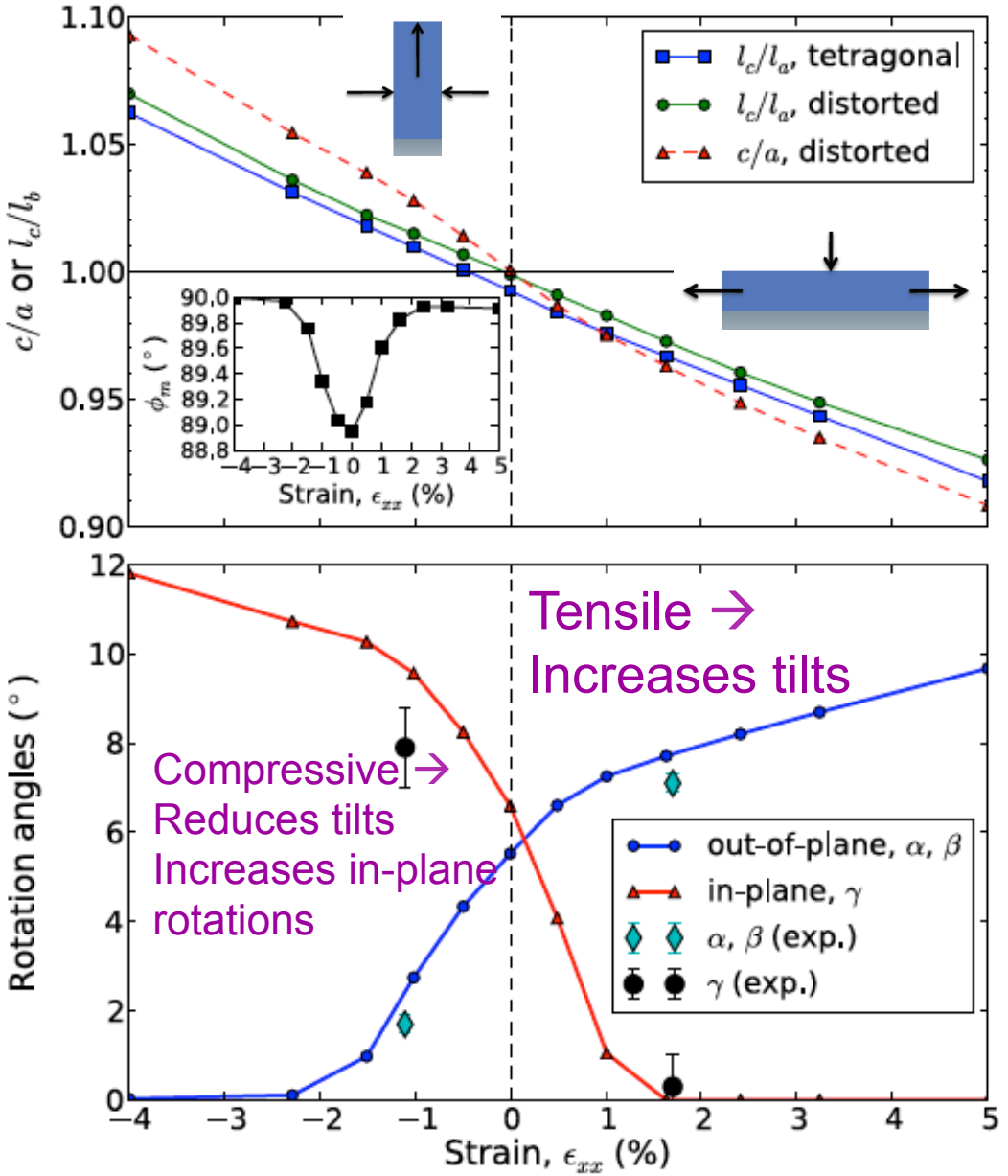
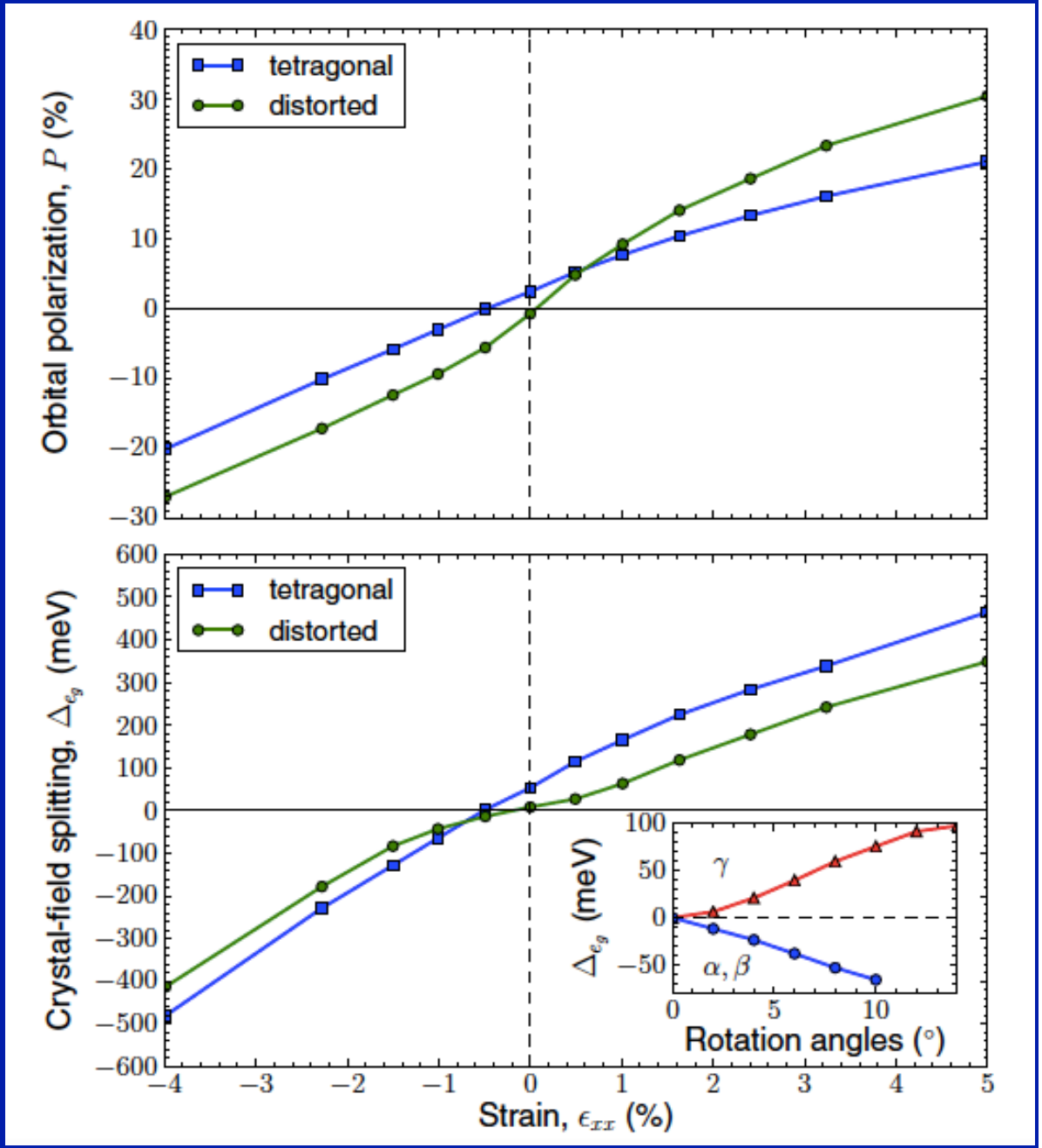


FIG. 1. (Color online) Top: Bond-length ratio, l_c/l_a, for the distorted (solid green) and tetragonal (solid blue) structures under strain. The broken line displays the c/a ratio for the distorted structure (for the tetragonal structure it is identical to the bond-length ratio). In both cases, the strain is defined with respect to $a_{p,\mathrm{eq}}$ of bulk LNO; the shift of the zero-strain point in the tetragonal case reflects thus the difference in the lattice constants of the two types of structures. Bottom: Dependence of the octahedral in-plane rotations (γ) and out-of-plane tilts ($\alpha = \beta$) on strain for the fully relaxed distorted structure. Also, structural refinement data from Ref. [46] are shown with diamonds for $\alpha = \beta$ and with circles for γ. Inset: Inclination angle ϕ_m of the pseudocubic axis c_p with respect to the ab plane.

O.Peil, M.Ferrero & A.G. PRB 2014
cf. also May et al PRB 2010

- Large crystal-fields are needed

- Distortions increase orbital polarisation



Peil et al. PRB 2014

How to reach larger orbital polarisations ?

- Concepts for materials design by the Yale group (C.Ahn, S.Ismail-Beigi et al.)
- Brief review: APL Materials 3, 062303 (2015)
- Chen et al. PRL 110, 186402 (2013)
- Disa et al. PRL 114, 026801 (2015)
- Seminar by Charles Ahn @ CdF, 2016

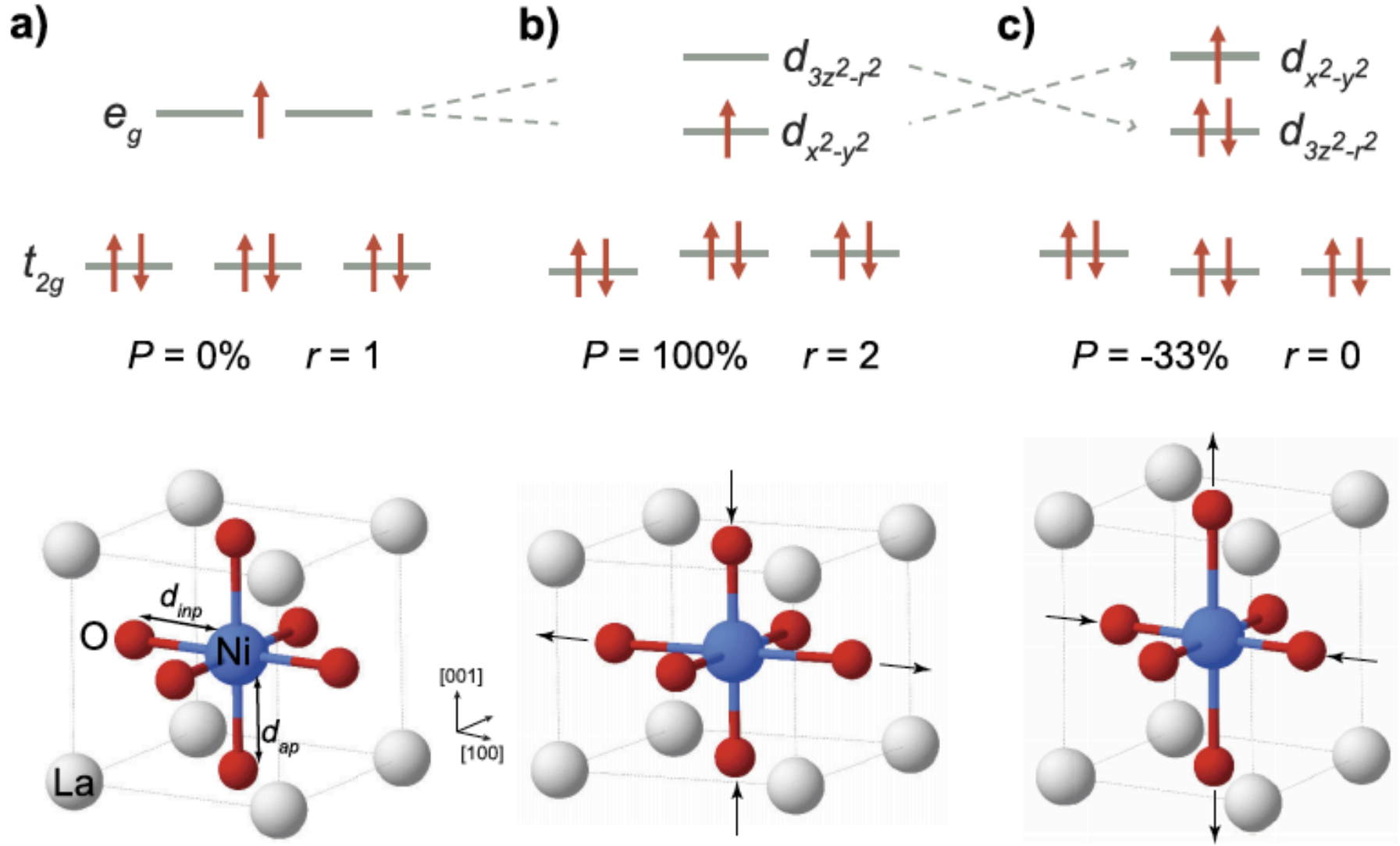


FIG. 1. $3d$ ionic configuration and structure of (a) bulk RNiO$_3$, (b) proposed orbitally polarized two-component nickelate heterostructures, and (c) high-temperature superconducting cuprates (and three-component nickelate heterostructures).

Disa et al.,APL Materials 2015

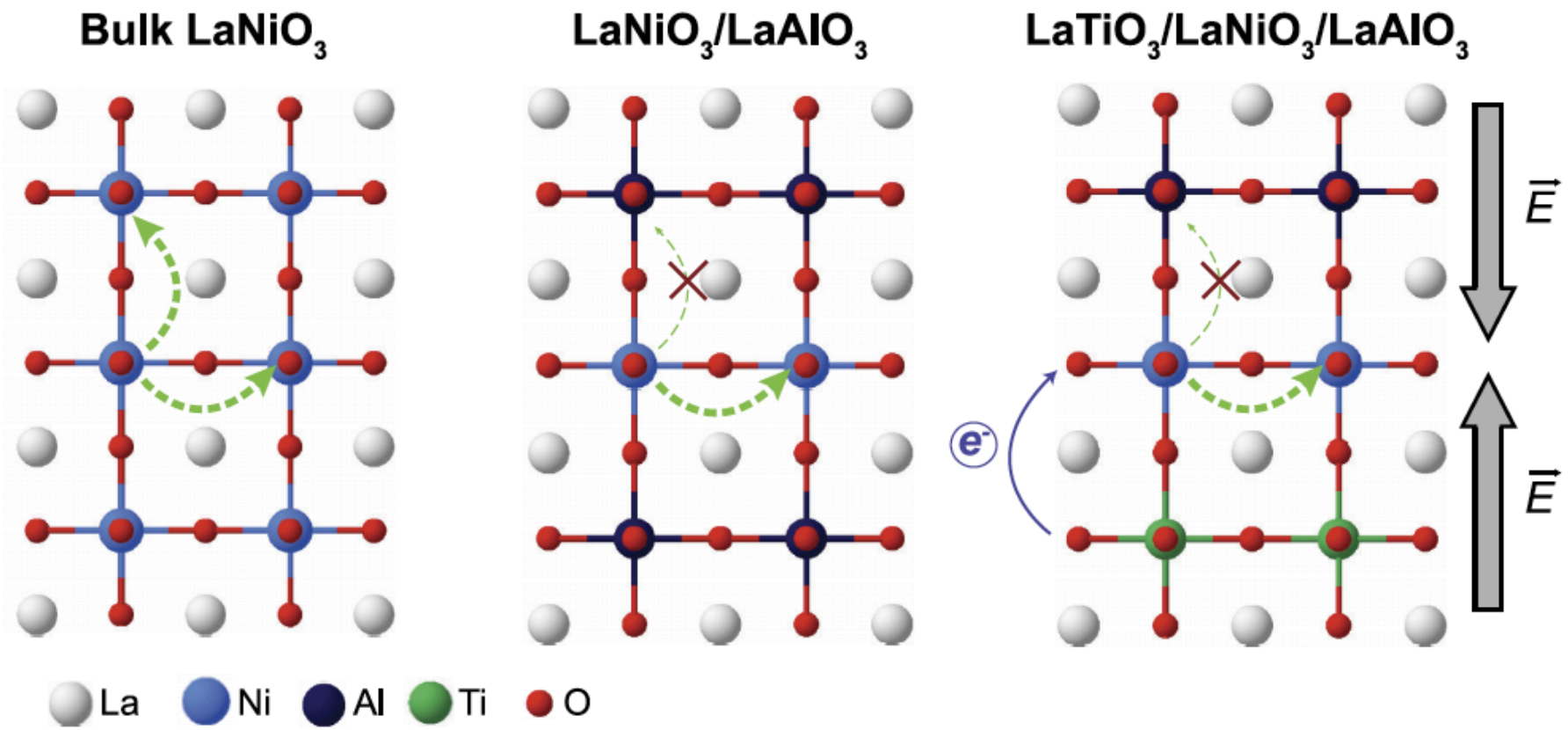


FIG. 2. Schematic structures of nickelate systems discussed in this review, including a depiction of in-plane and out-of-plane hopping amplitudes and an illustration of electron transfer and polar fields in three-component heterostructures.

Disa et al.,APL Materials 2015

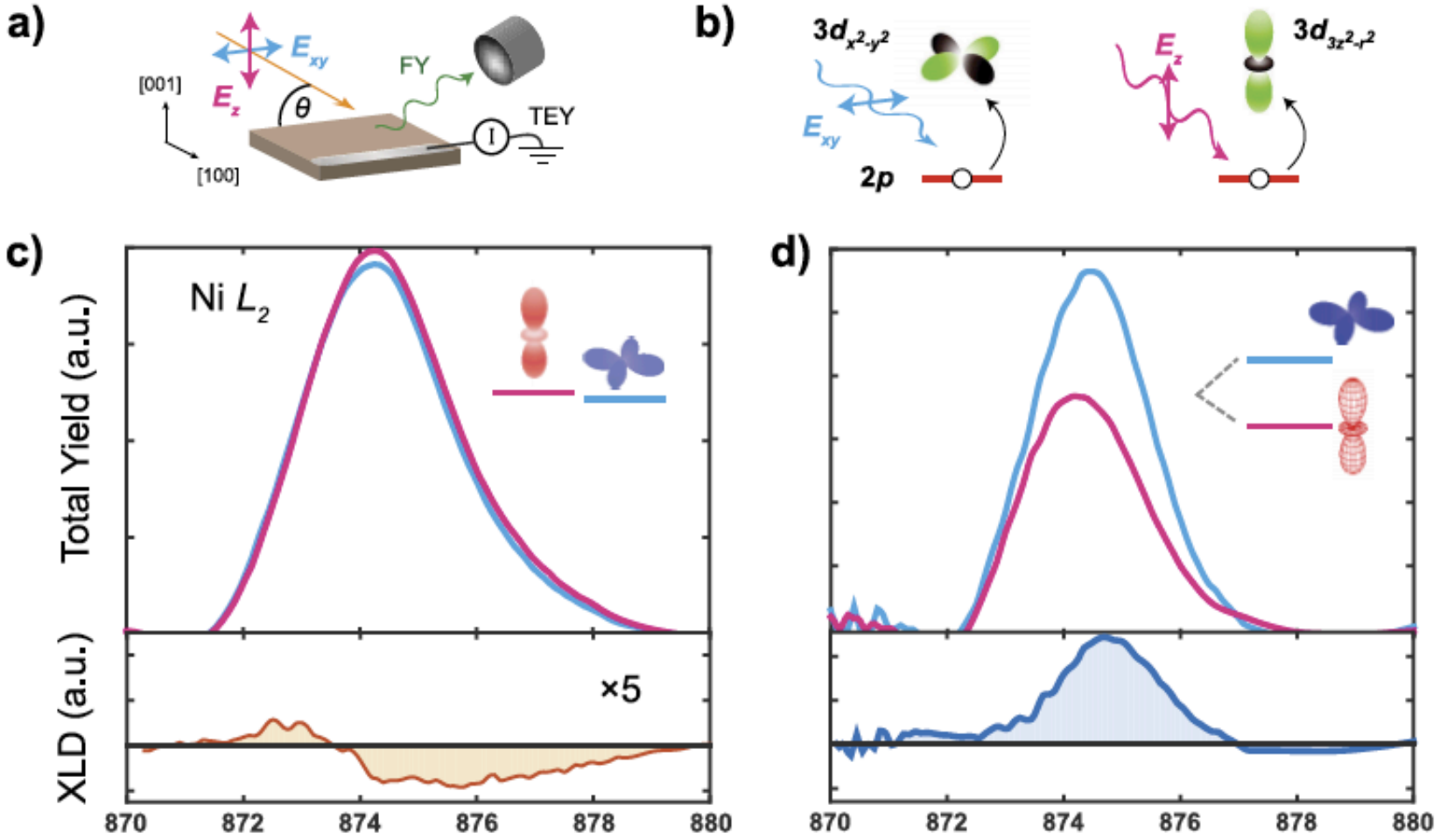


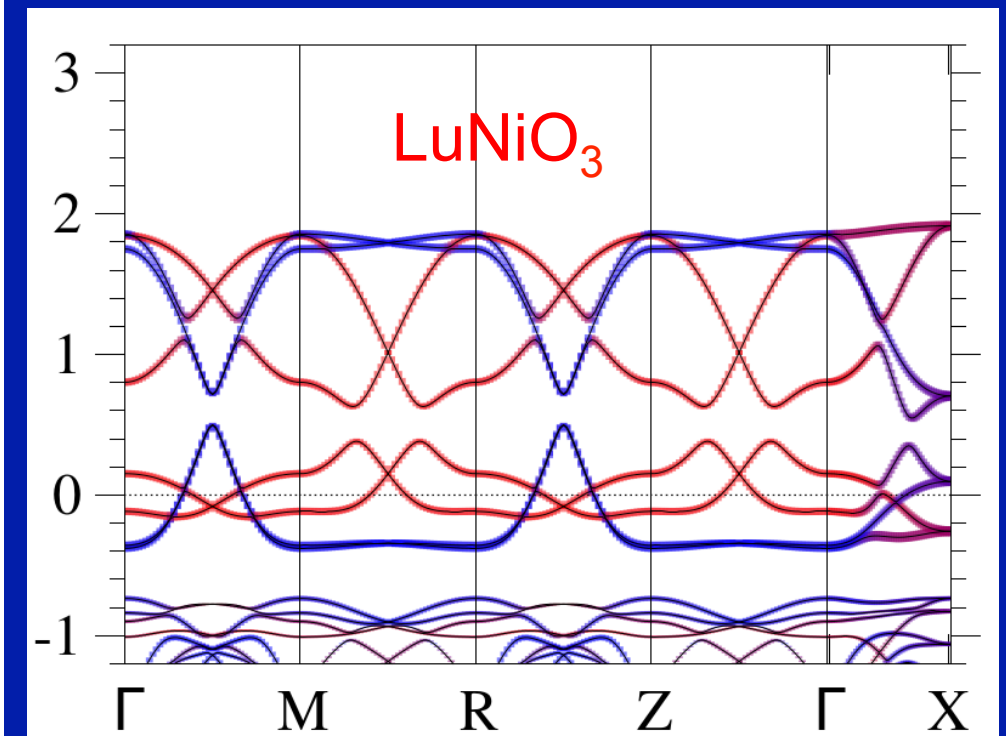
FIG. 3. (a) Schematic of XLD/orbital reflectometry measurement geometry and (b) orbitals probed by incident x-ray polarization. XAS spectra for each polarization may be obtained in fluorescence yield (FY) or total electron yield (TEY) modes. (c) TEY spectra and normalized linear dichroism ($I_{Exy} - I_{Ez}$) for a two-component ($LaNiO_3/LaAlO_3$) superlattice and (d) three-component ($LaTiO_3/LaNiO_3/LaAlO_3$) superlattice, showing large difference in effect on e_g orbitals (from Ref. 30 with permission).

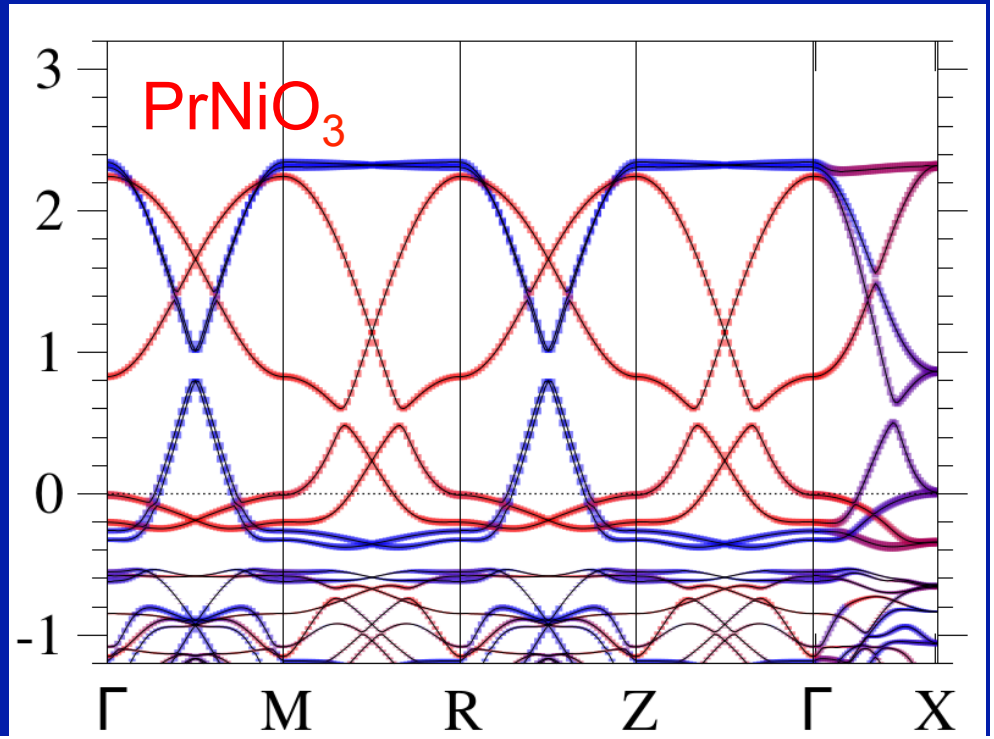
Disa et al.,APL Materials 2015

Trends over the RE series

As size of RE decreases (distortion increases):

- The two manifolds of Peierls-split bands split more and more
- Bandwidth of each manifold decreases
- Susceptibility to electronic disproportionation increases and couples to breathing mode.





Take-home and Perspectives

- Consistent picture of insulating phase has now emerged
- Quantitative DMFT calculations and simple model, key parameters identified
- Role of breathing phonon to be taken into account explicitly and trends over the RE series to be understood better: in progress
- Orbital polarization: tricolor heterostructures (cf. Ahn et al.) or other materials (early TMOs t_{2g}'s) with less hybridization to ligands – avoiding `negative charge transfer/ligand holes'