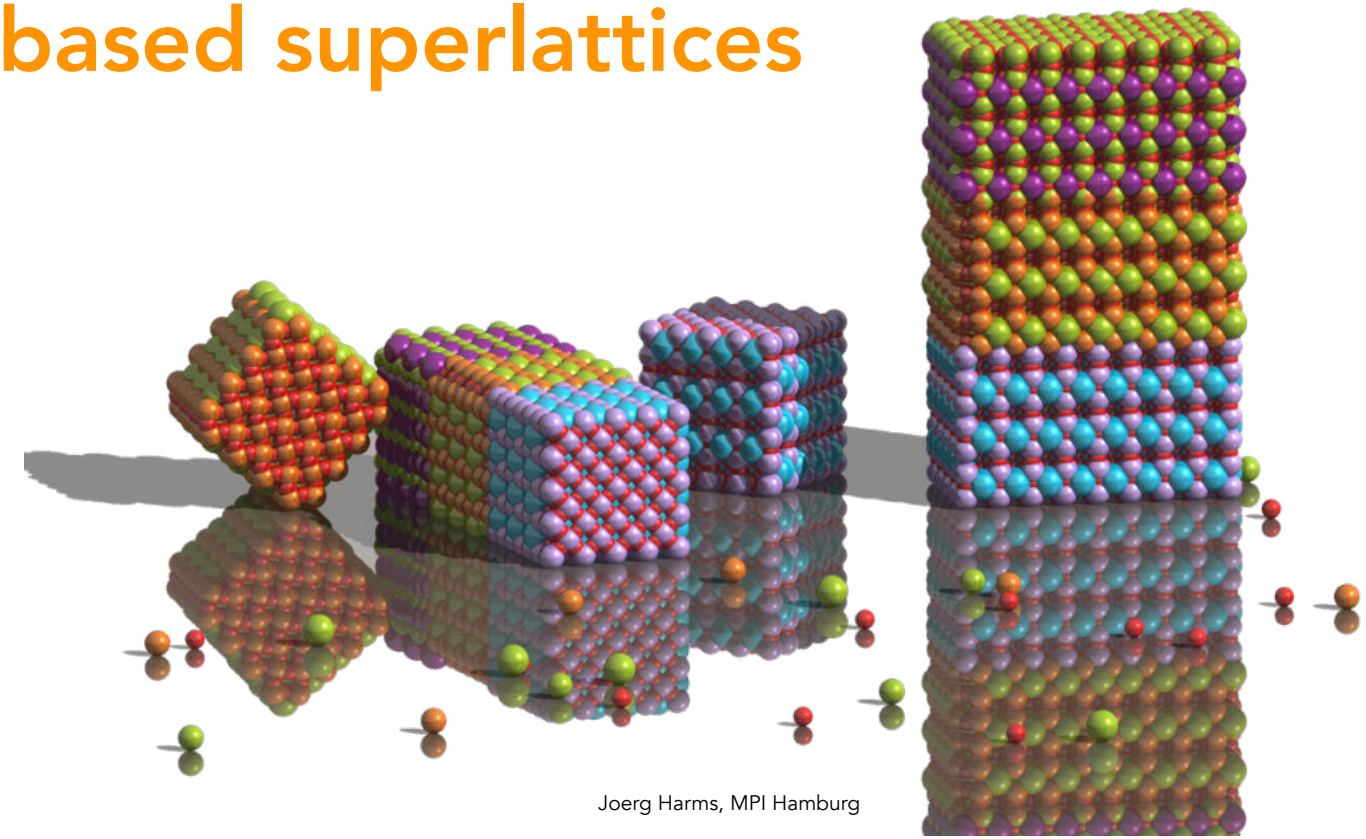
Metal-insulator transition in nickelates and nickelate based superlattices

Jean-Marc Triscone
University of Geneva



Joerg Harms, MPI Hamburg

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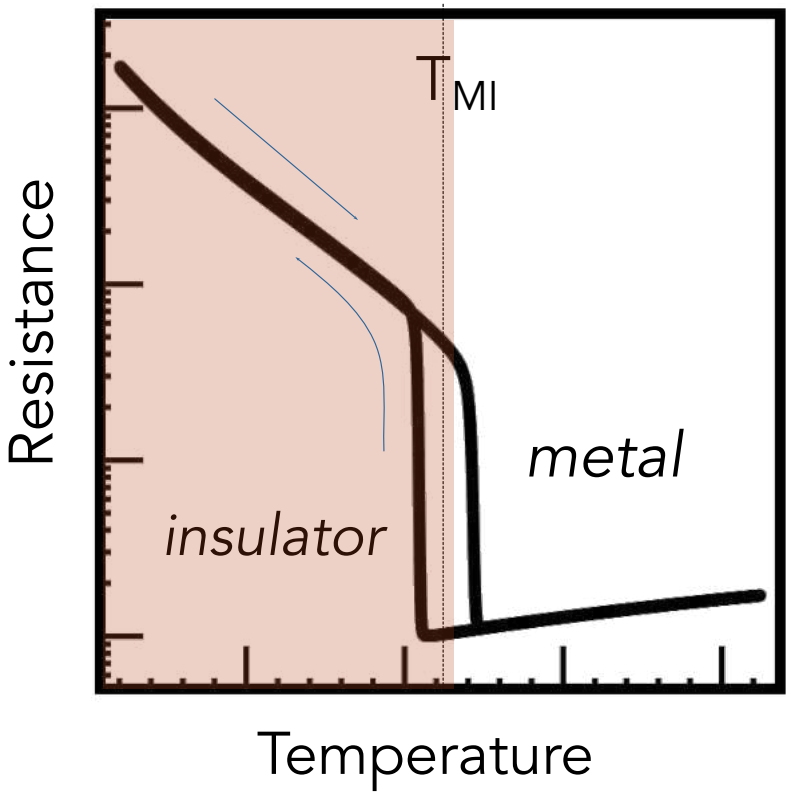
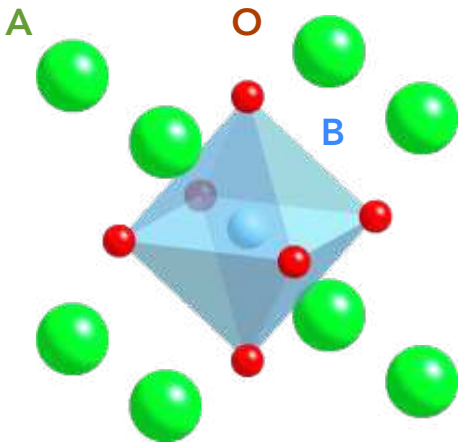
Metal-insulator transition



Transition metal oxides and perovskites ABO_3



ABO_3

Perovskite - $CaTiO_3$

Perovskite structure - a very common structure on Earth

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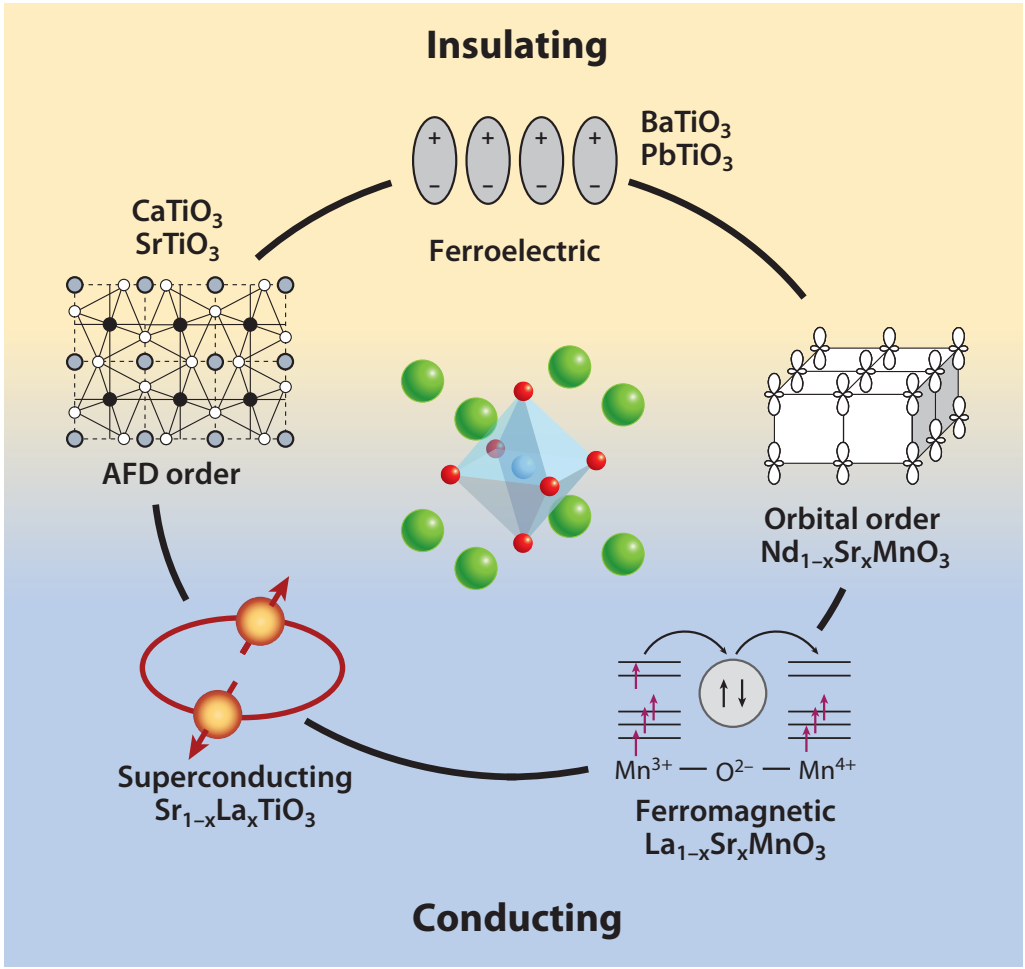
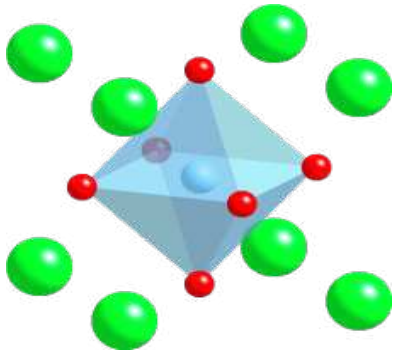
TMO's display a variety of properties

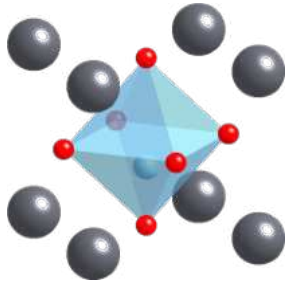




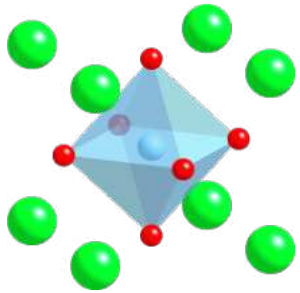
ABO_3

P. Zubko et al., *Ann. Rev. Cond. Matter Phys.* **2**, 141 (2011)

TM-oxides - Lego bricks



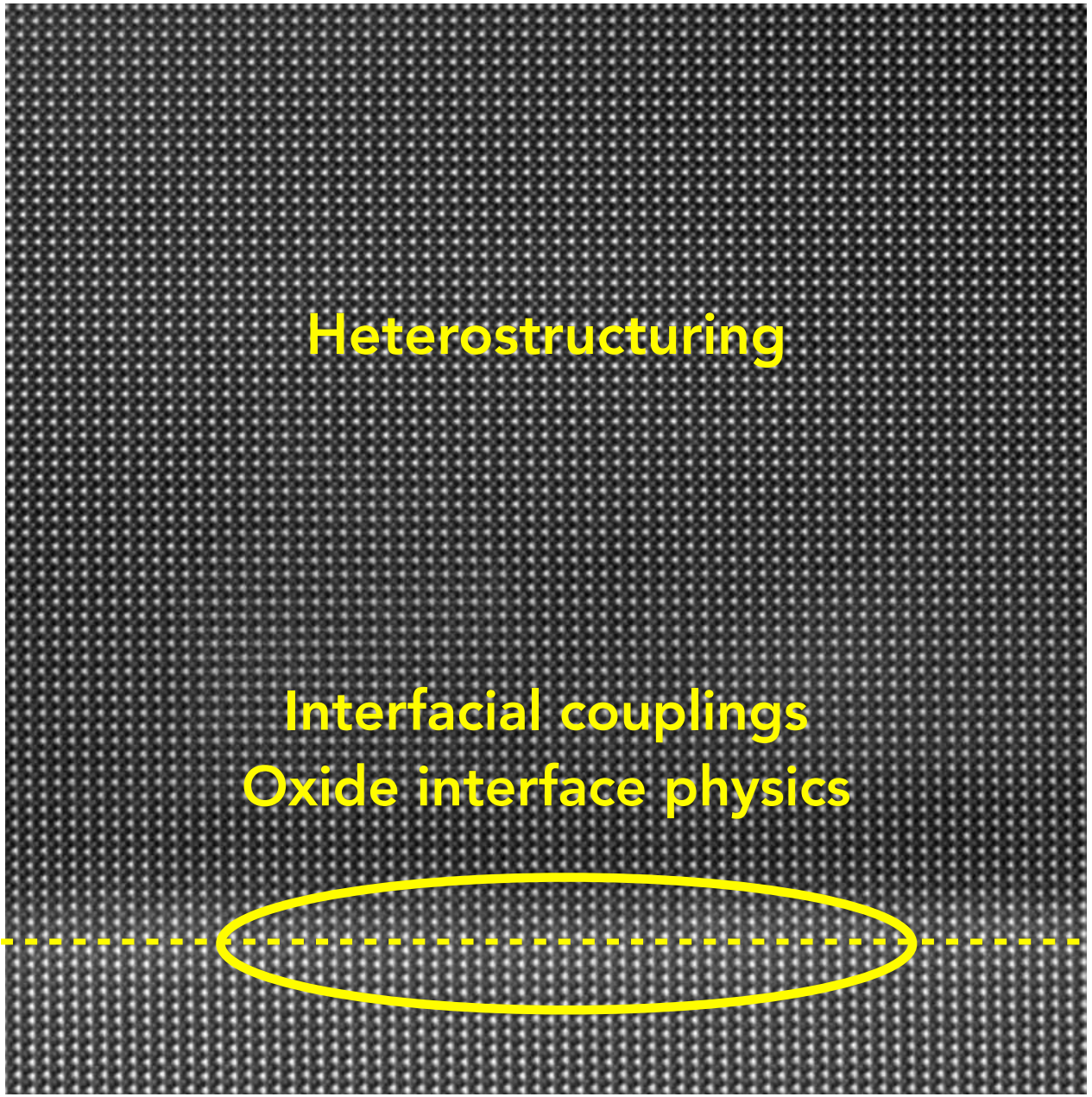
$PbTiO_3$ ferroelectric $T<T_C$
Tetragonal and ferroelectric
(a=b=**3.904Å**, c=4.152Å)



$SrTiO_3$ paraelectric at all temperatures
(a=b=c=**3.905Å**)

Very perfect structures can be realised

Novel properties / functionalities



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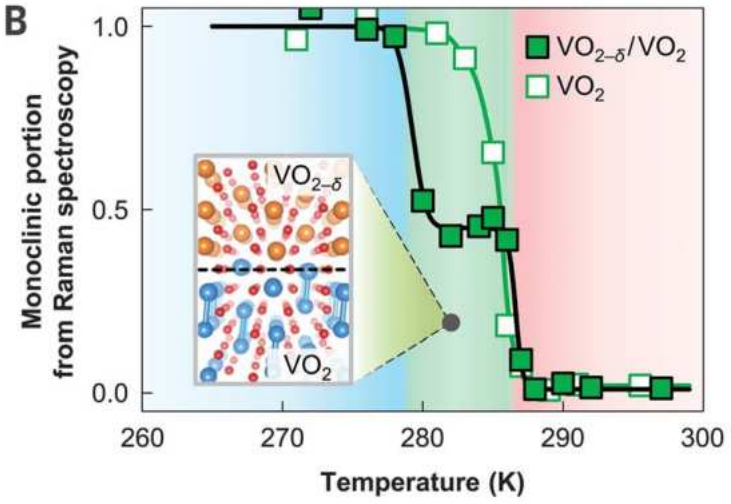
Metal-to-insulator transition in VO_2

Isostructural metal-insulator transition in VO_2

D. Lee[1], B. Chung[2], Y. Shi[3], G.-Y. Kim[4]*, N. Campbell[5], F. Xue[3], K. Song[4], S.-Y. Choi[4]*, J. P. Podkaminer[1], T. H. Kim[1], P. J. Ryan[6,7], J.-W. Kim[6], T. R. Paudel[8], J.-H. Kang[1], J. W. Spinuzzi[9], D. A. Tenne[9], E. Y. Tsymbal[8], M. S. Rzchowski[5], L. Q. Chen[3], J. Lee[2]†, C. B. Eom[1]†



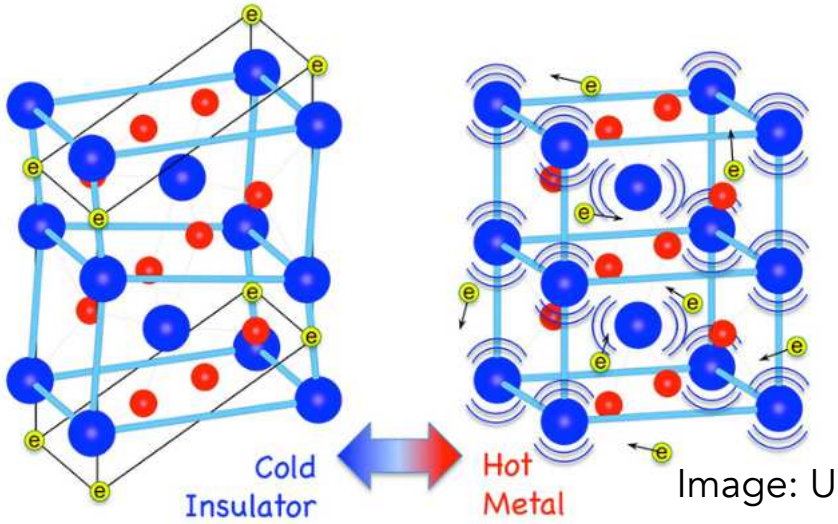


Image: US-DOE

monoclinic rutile

Electronic and structural phase transitions

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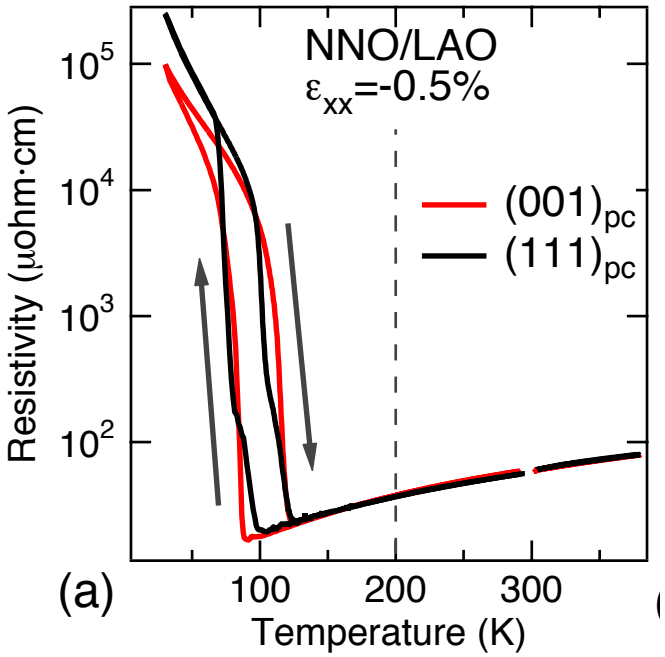
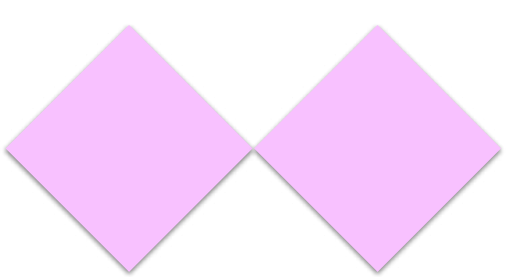
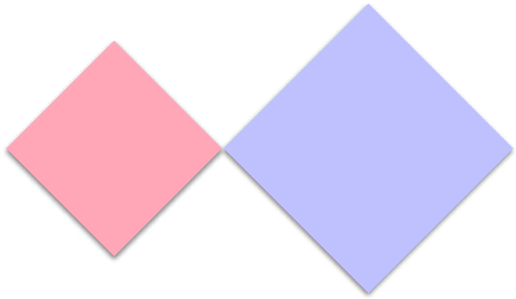
Metal-to-insulator transition in nickelates



$NdNiO_3$



metallic orthorhombic



insulating monoclinic

Electronic and structural phase transitions

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Why studying the M-I transition systems?

Fundamental interest : why a MIT?

Possible applications:

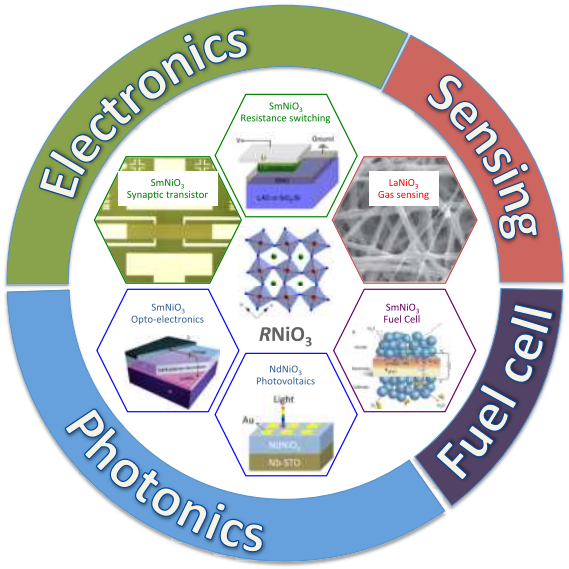

Table 1. Overview of applications proposed in literature for rare earth nickelates, RNiO$_3$.

Application field	Application	Investigated material	References
Electrode material	Anode	$LaNiO_{3-\delta}$	[181]
	Supercapacitor	$LaNiO_3$/NiO	[182–184]
	In heterostructures	$LaNiO_3$	[185–196]
	Buffer layer in HTS	$LaNiO_3$	[197–200]
Opto-electronics	Tunable photonics	$SmNiO_3$	[125, 201, 202]
	Photodetection	$GdNiO_3$	[203]
	Thermochromism	$SmNiO_3$, $NdNiO_3$	[204–206]
	Photovoltaics	$NdNiO_3$	[207, 208]
Ion-conduction/catalysis	Fuel cell, SOFC	$SmNiO_3$	[126, 209]
	Oxygen reduction	$LaNiO_3$	[210–213]
Resistance switching	Neuromorphic device	$SmNiO_3$, $NdNiO_3$	[124, 214–216]
	Neuromimetic circuits	$SmNiO_3$	[217]
	Synaptic transistor	$SmNiO_3$	[124]
	Transistor	$LaNiO_3$/Si	[128]
	Mott transistor	$NdNiO_3$	[129, 218]
	Proton-gated transistor	$SmNiO_3$	[125]
Sensing	Gas sensing	$LaNiO_3$	[184, 219–220]
Magnetism	Magnetotransport	$SmNiO_3$	[230]
	Multiferrocity	$SmNiO_3$, $NdNiO_3$	[6, 231, 232]

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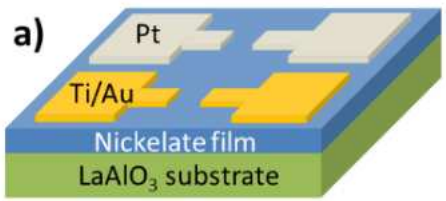
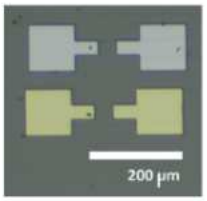
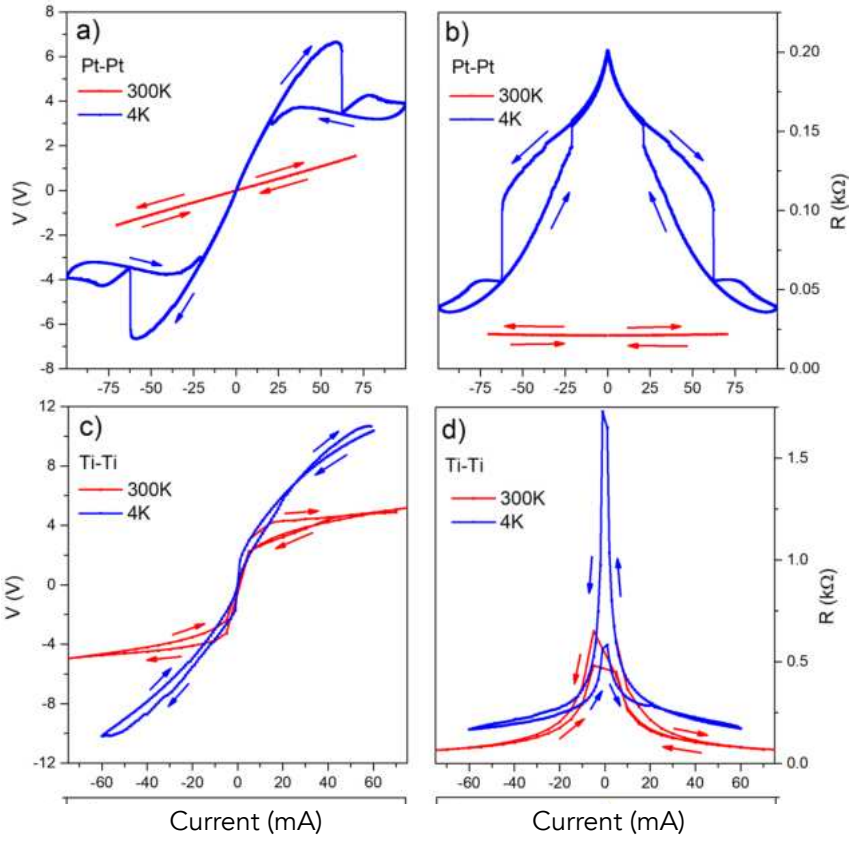
Sara Catalano et al. Rep. Prog. Phys. **81**, 046501 (2018)

Volatile and non-volatile switching





Pt and Ti electrodes



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C. W. Rischau et al. preprint.

Outline

Part 1: MIT and nickelates

-Things to know / understand

-Some examples of MIT's

-Nickelates: basic properties, phase diagram

-Electronic structure and origin of the transition

Part 2: Heterostructures based on nickelates - recent work

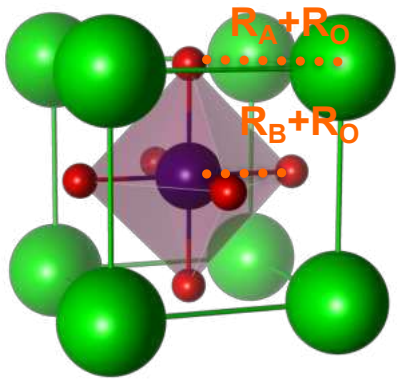
-$NdNiO_3/SmNiO_3$ phase boundary cost

-Coupling - decoupling of the transition

-Turning a metal into an insulator

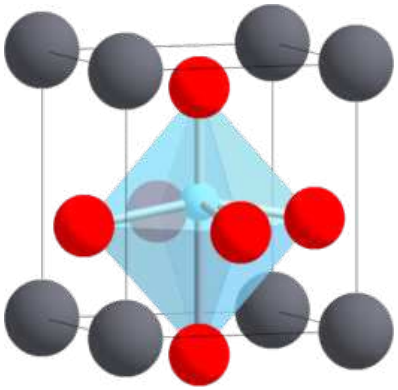
Things to know / understand

Structural instabilities in ABO_3 perovskites

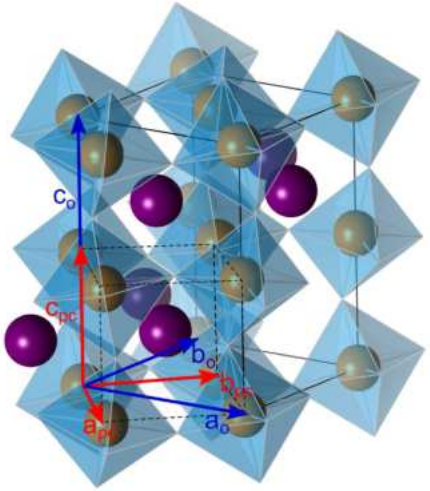


Ideally : $R_A + R_O = \sqrt{2}(R_B + R_O)$

Tolerance factor t: $t=\frac{R_A+R_O}{\sqrt{2}(R_B+R_O)}$



t>1 - $PbTiO_3$
Displacement of the B cation



t<1 - $NdNiO_3$
Oxygen octahedra rotations

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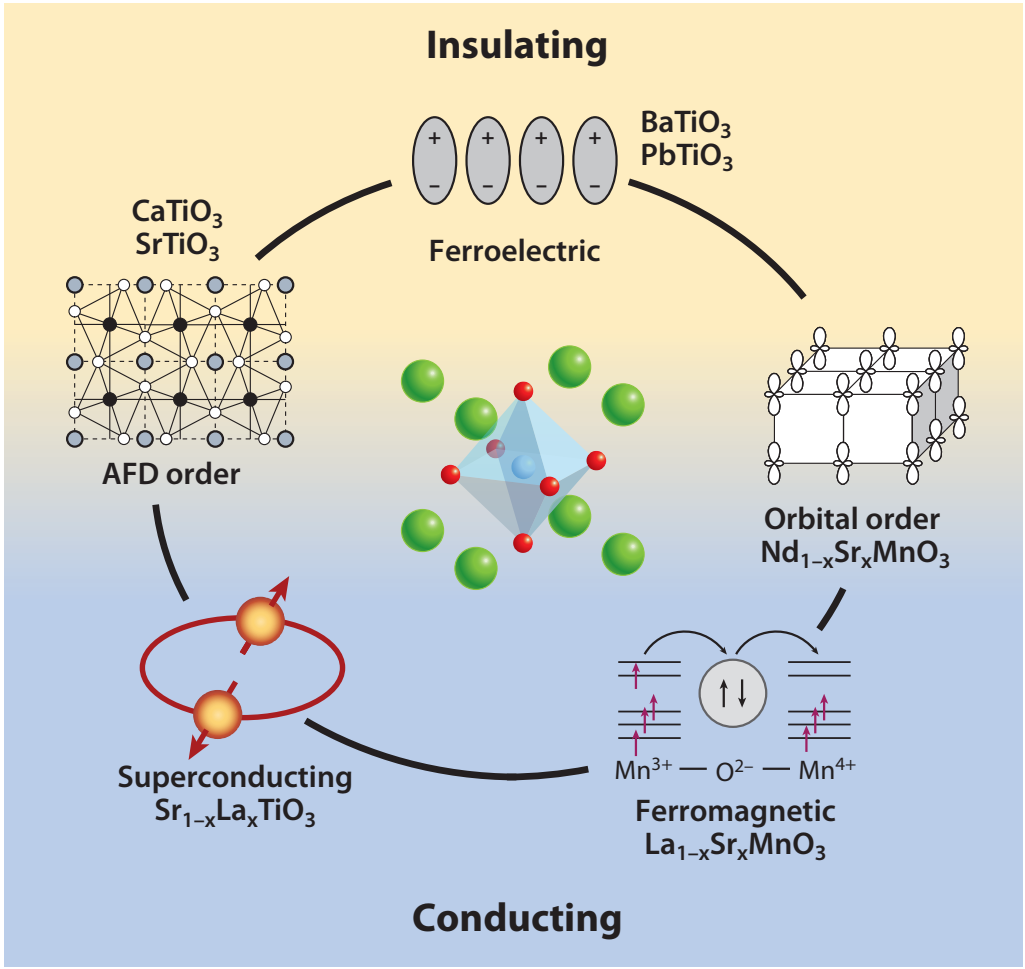
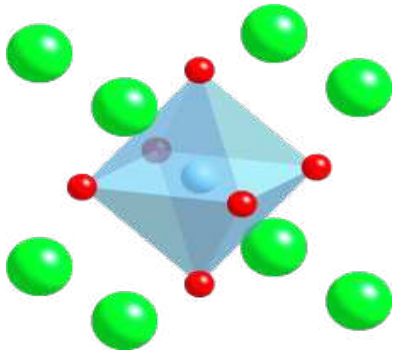
TMO's display a variety of properties

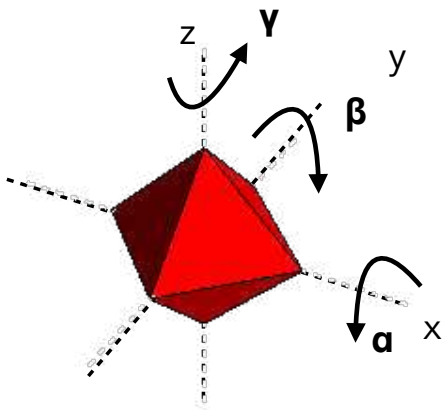


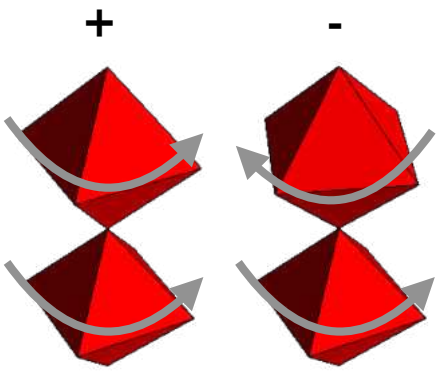


ABO_3

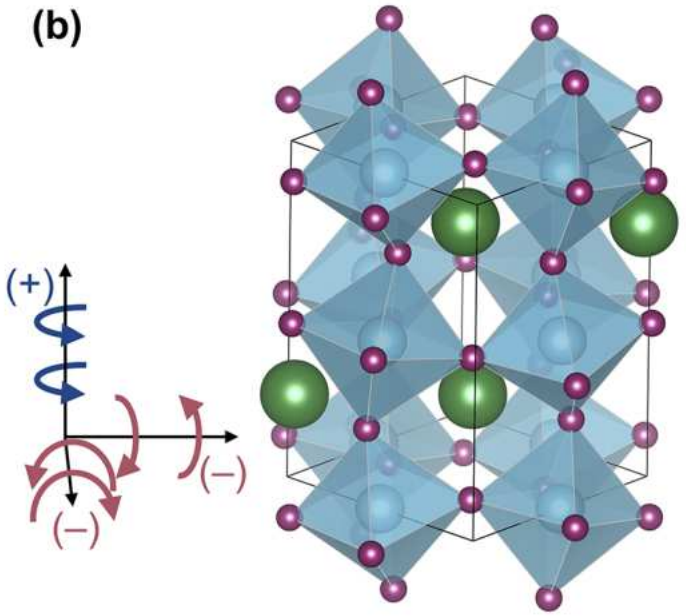
P. Zubko et al., *Ann. Rev. Cond. Matter Phys.* **2**, 141 (2011)

Oxygen octahedra rotations - the Glazer notation





For instance: $a^+b^-c^0$



The orthorhombic structure (Pnma) $a^-b^+c^-$

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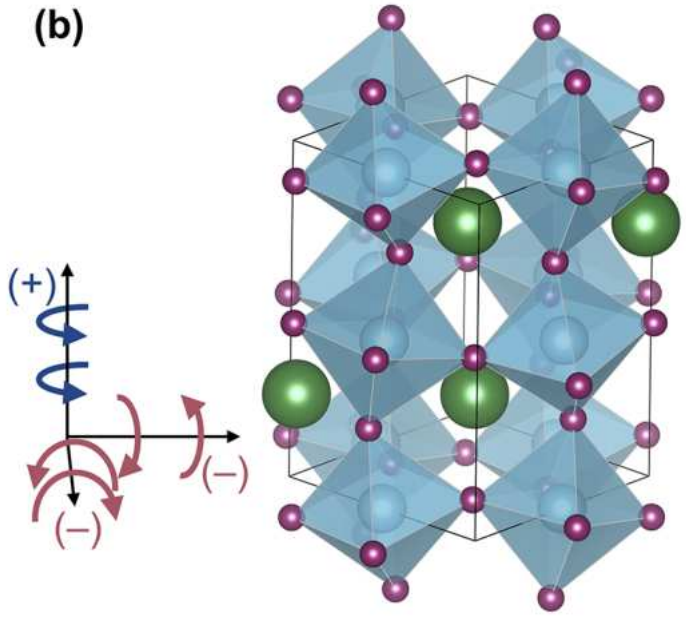
The orthorhombic structure - $LaVO_3$

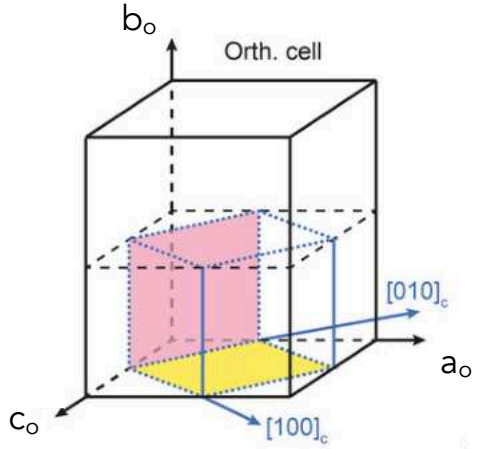


$LaVO_3$
a_o=5.555Å
b_o=7.849Å - in phase rotations
c_o=5.553Å

b_o is the orthorhombic « long-axis »

The orthorhombic structure (Pnma) $a^-b^+c^-$

Link to the pseudocubic unit cell



$$a_{pc} \approx b_o/2 \approx a_o/\sqrt{2}$$

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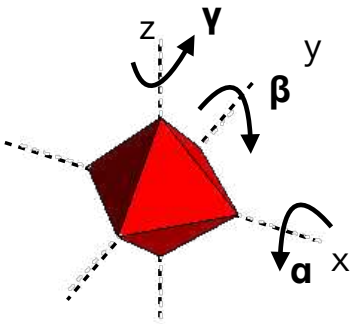
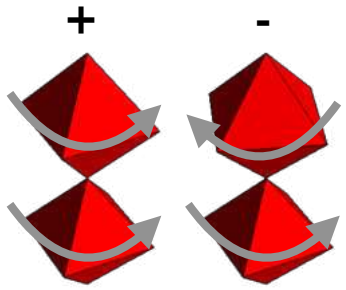
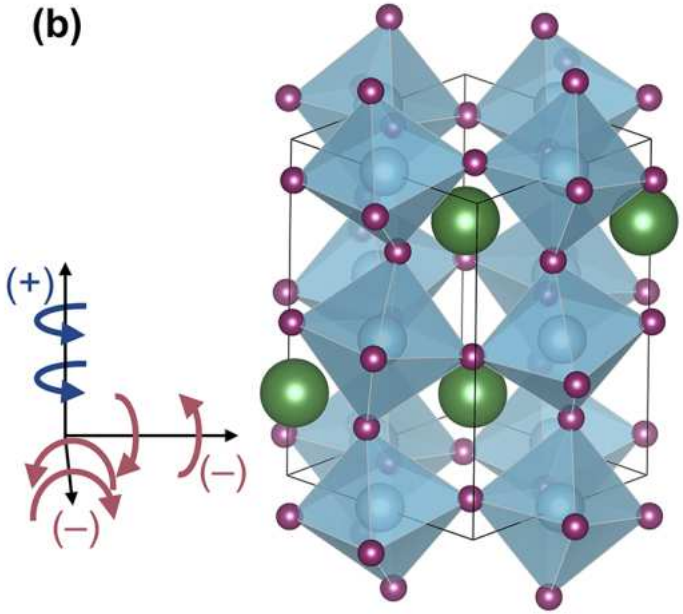
Antipolar motion in orthorhombic perovskites

Orthorhombic structure at RT as many perovskites - Pnma with a tilt pattern $a^-b^+c^-$





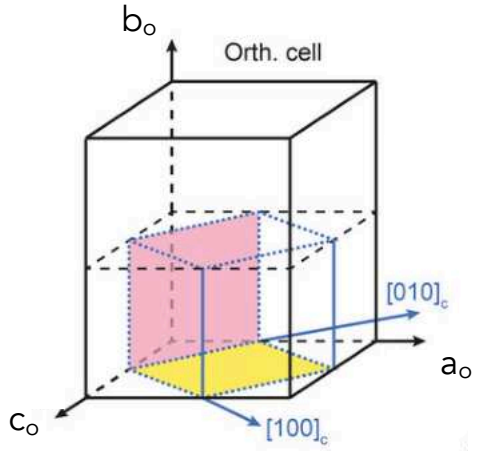
$a^-b^+c^-$



Orthorhombic structure $a^-b^+c^-$

$LaVO_3$
a_o=5.555Å
b_o=7.849Å - in phase rotations
c_o=5.553Å

b_o is the orthorhombic « long-axis »

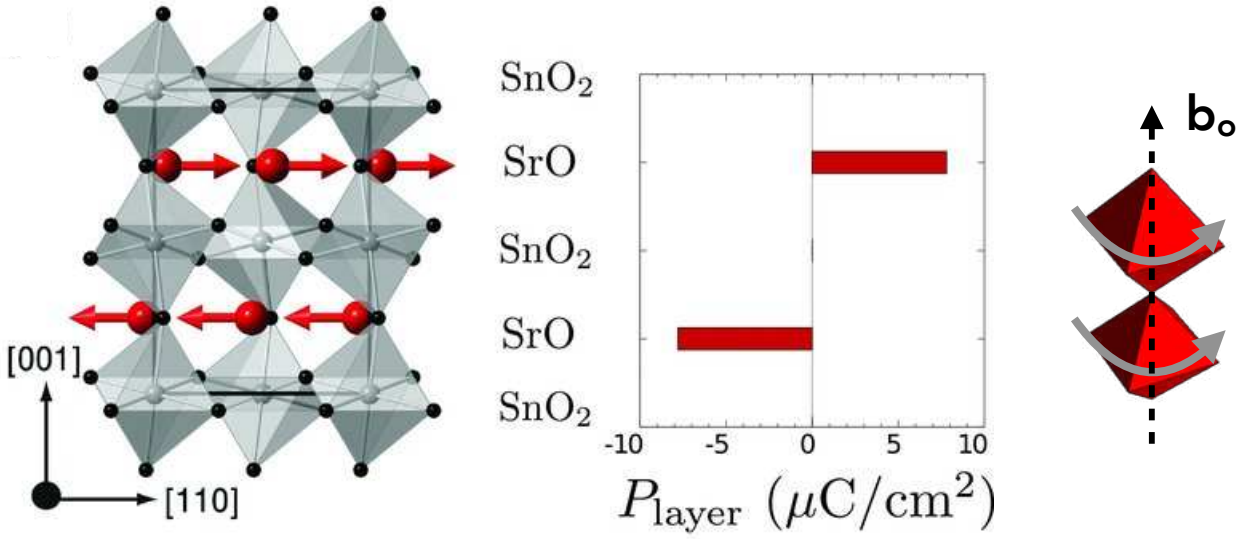


Perovskite vanadates RVO_3

These instabilities couple to an anti-polar mode (AM) X_5^-

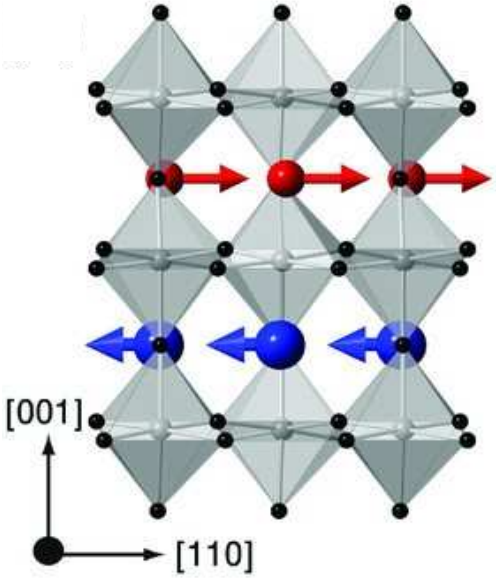
$$F \sim \phi_{xy}^- \phi_z^+ X_5^-$$

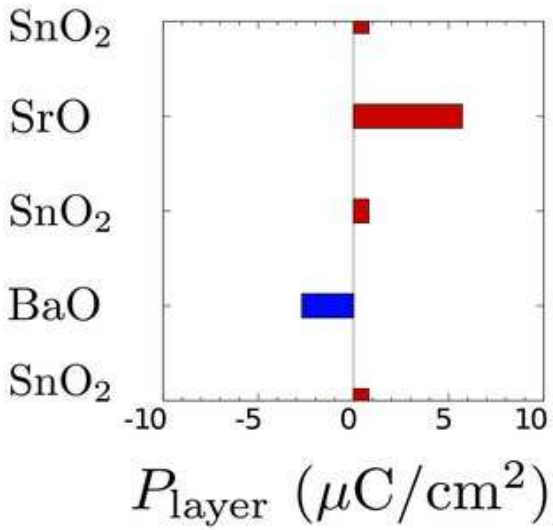
AM - cation displacements in the [110] pseudocubic direction

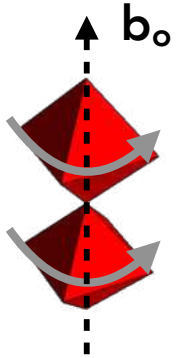


J. Rondinelli and C. Fennie Adv. Func. Mat. **23**, 4810 (2013)

Synthetic ferroelectric
1u.c./1u.c. (odd) $ABO_3/A'BO_3$ superlattices







The long orthorhombic axis - in-phase rotations has to be out of plane

J. Rondinelli and C. Fennie Adv. Func. Mat. **23**, 4810 (2013)
M.J. Pitcher et al. Science **347**, 420 (2015)

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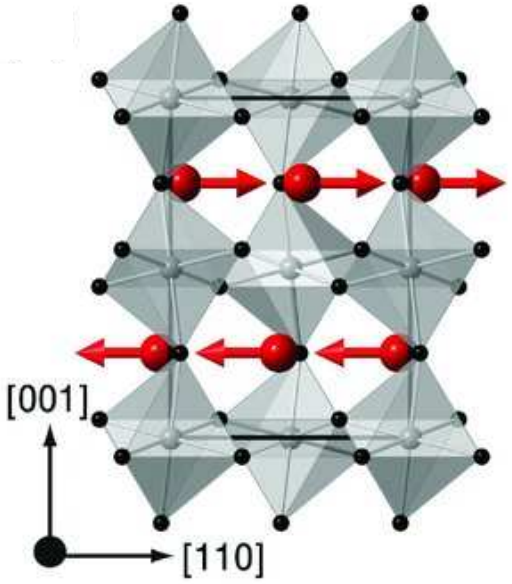
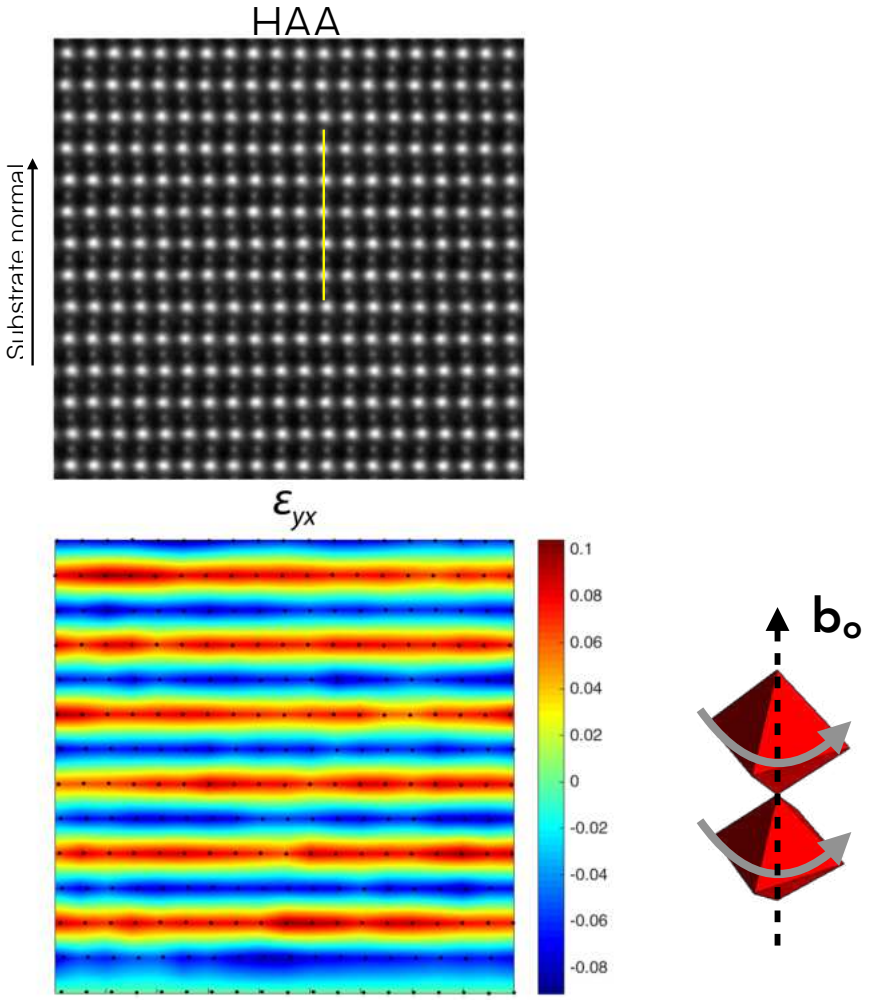
AM seen using adapted GPA





GPA (Geometrical phase analysis) allows the anti-polar modes to be visualised and the long axis direction to be determined

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H. Meley et al. APL Mat. **6**, 046102 (2018)

Metal insulator transitions

Band theory

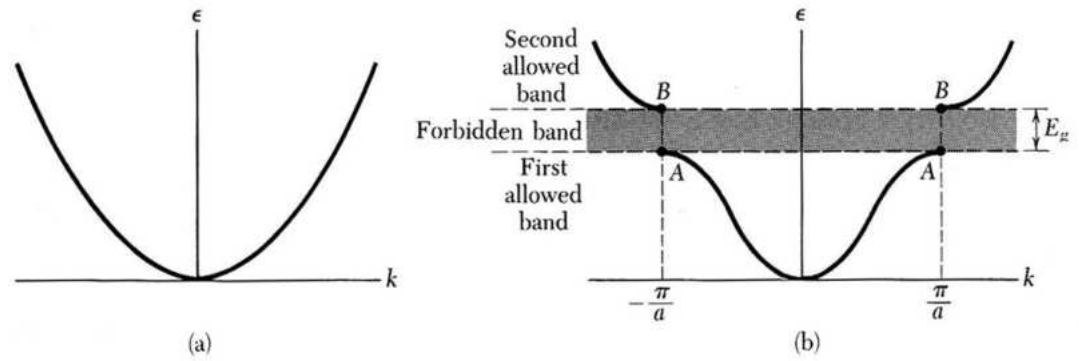


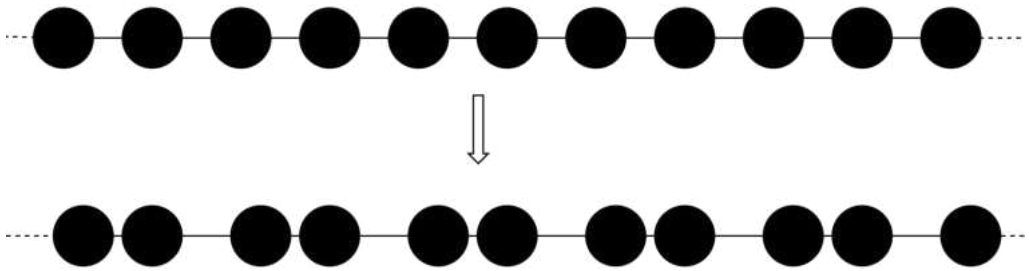
Figure 2 (a) Plot of energy ϵ versus wavevector k for a free electron. (b) Plot of energy versus wavevector for an electron in a monatomic linear lattice of lattice constant a. The energy gap E_g shown is associated with the first Bragg reflection at $k = \pm\pi/a$; other gaps are found at $\pm n\pi/a$, for integral values of n.

Source: "Intro. to Solid State Physics, 7th Ed.", C. Kittel, John Wiley & Sons, Inc., N.Y., 1996.

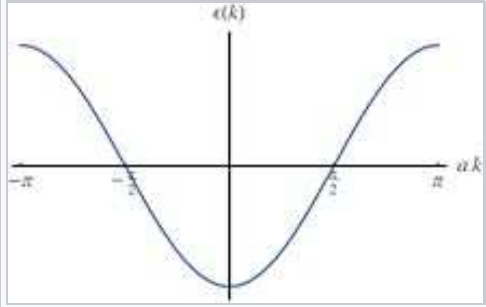
We know from band theory that a half filled band system should be metallic - but some half filled « systems » are insulating - why?

Peierls transition in 1D

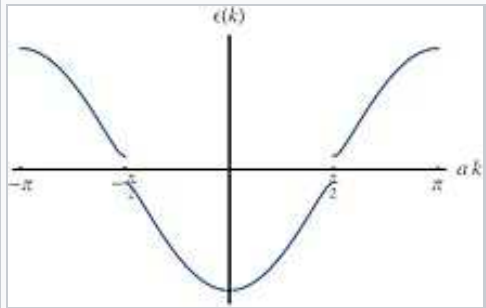
1D chain
undistorted



1D chain
with a distortion



The lowest Bloch band of an undistorted 1D lattice.

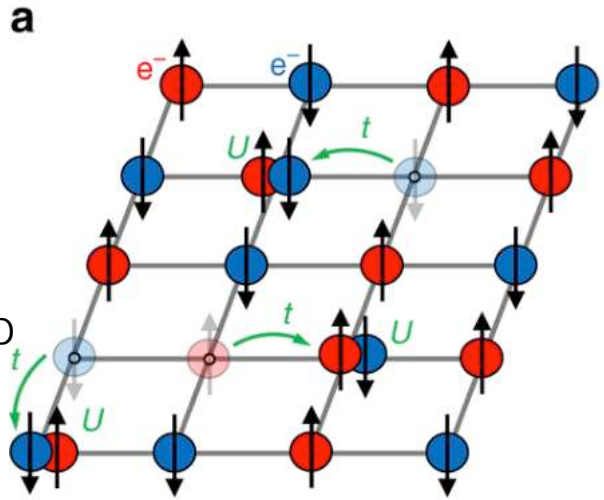


The lowest Bloch bands of a distorted 1D lattice. Energy gaps appear in $ka = \pm\pi/2$ as a result of the Peierls' instability.

Wikipedia

The Mott transition

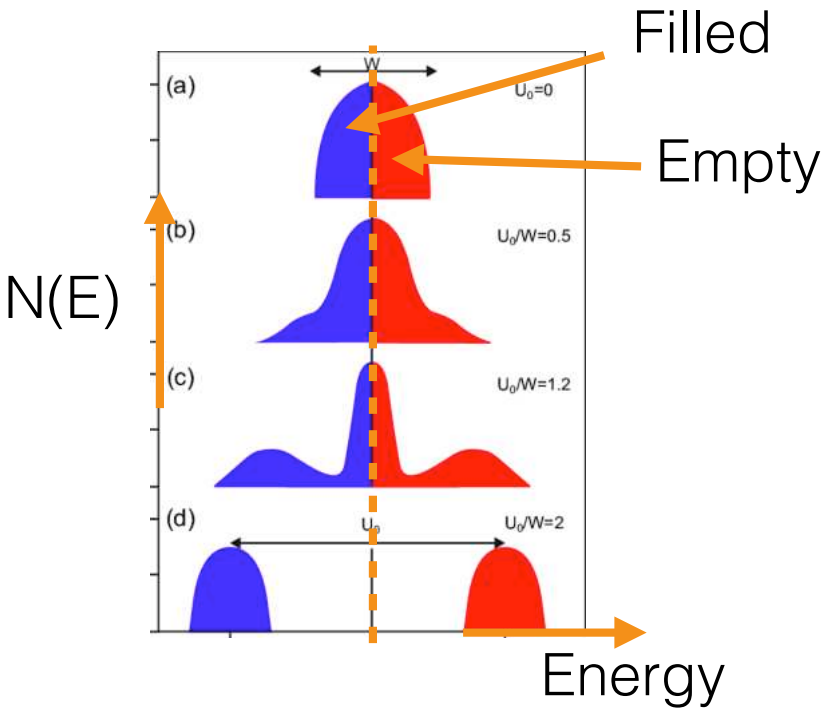
Site model



Here, one has the bandwidth W (linked to t) and the (on site) Coulomb repulsion U

$$H = -t \sum_{\langle i,j \rangle, s} \left\{ c_{is}^{\dagger} c_{js} + c_{js}^{\dagger} c_{is} \right\} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} =$$

n.n. hopping — onsite repulsion



At 1/2 filling, 1 electron per unit cell, the system goes to an insulating state if U>>W

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Photoemission on $SrVO_3$ films

PRL **104,** 147601 (2010) PHYSICAL REVIEW LETTERS week ending 9 APRIL 2010

Dimensional-Crossover-Driven Metal-Insulator Transition in $SrVO_3$ Ultrathin Films

K. Yoshimatsu,[1] T. Okabe,[1] H. Kumigashira,[1,2,3,*] S. Okamoto,[4] S. Aizaki,[5] A. Fujimori,[5] and M. Oshima[1,3,6]

[1]*Department of Applied Chemistry, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan*
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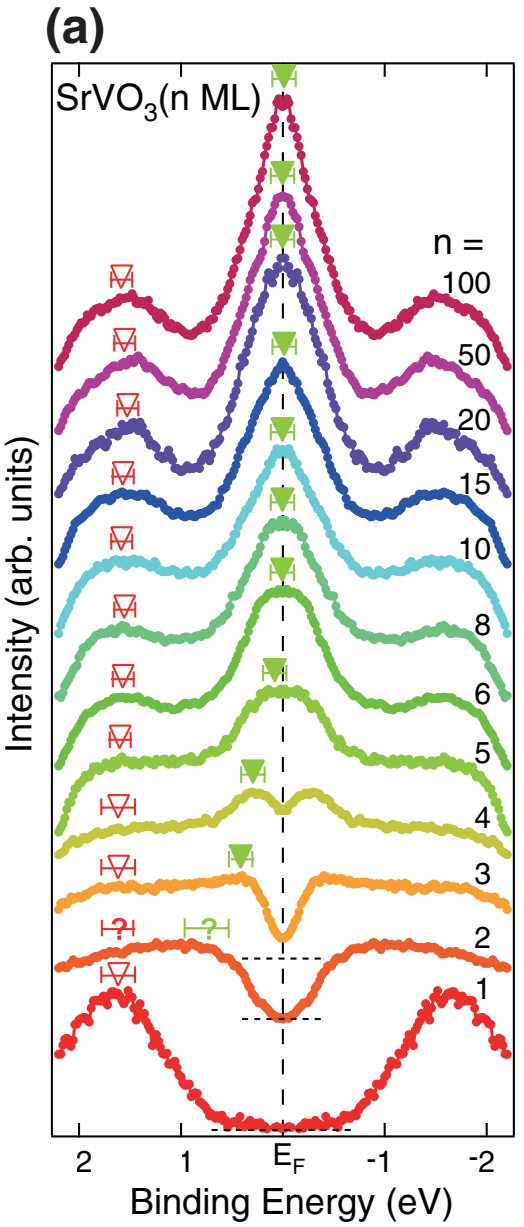
(Received 12 November 2009; published 9 April 2010)



$SrVO_3$ thickness: 100 to 1 unit cell

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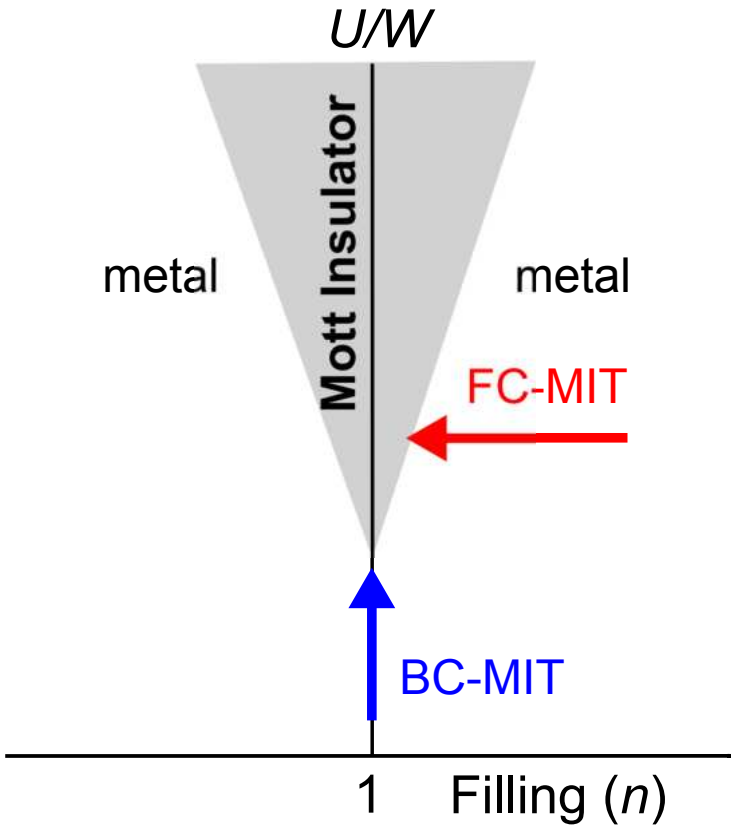
The Mott insulating state



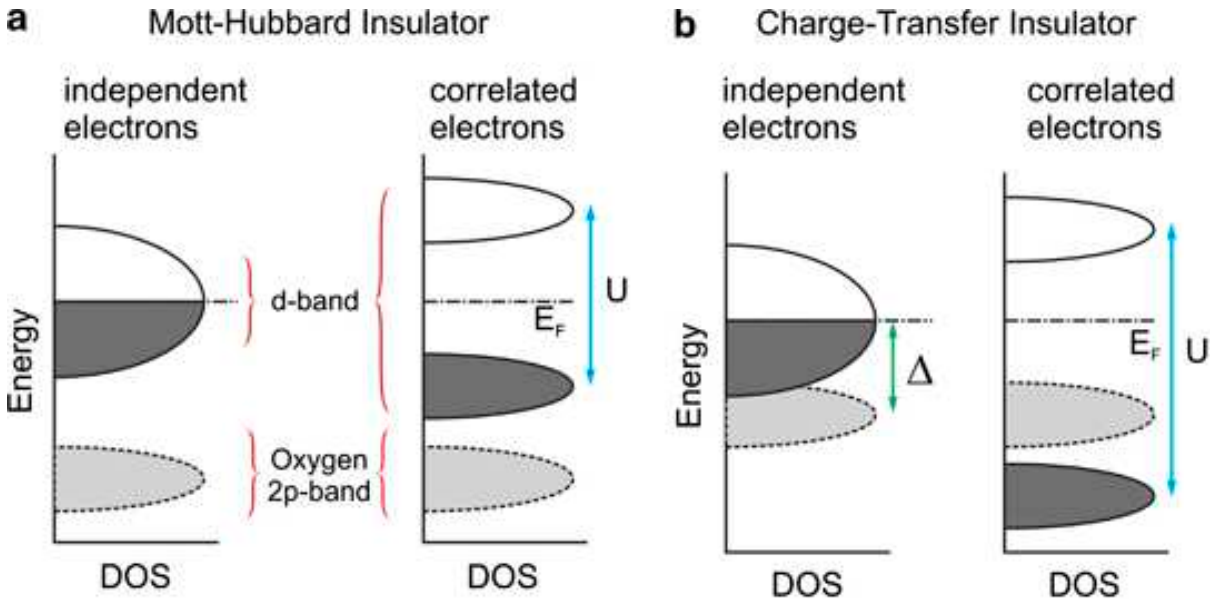
You can control the transition by changing W (or t) - bandwidth control or

by changing the filling - the idea of the Mott transistor

Mott insulators - charge transfer insulators

Role of the oxygen p-band

The distance in energy between the d-band of the transition metal et p-band of oxygen, Δ, is the charge transfer gap



VOLUME 55, NUMBER 4 PHYSICAL REVIEW LETTERS 22 JULY 1985

Band Gaps and Electronic Structure of Transition-Metal Compounds

J. Zaanen and G. A. Sawatzky
Physical Chemistry Department, Material Science Center, University of Groningen, 9747 AG Groningen, The Netherlands

and

J. W. Allen
Xerox Palo Alto Research Center, Palo Alto, California 94304

(Received 22 January 1985)

Δ controls the hopping

Electronic structure in perovskites and electronic degeneracy

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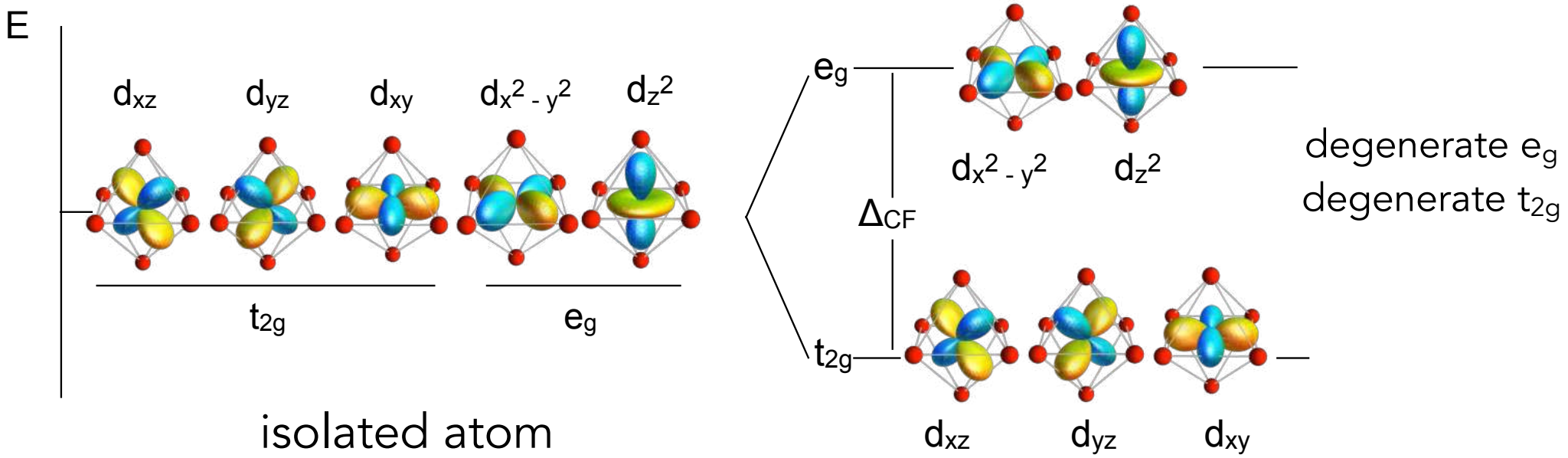
Electronic structure, orbitals and crystal field splitting

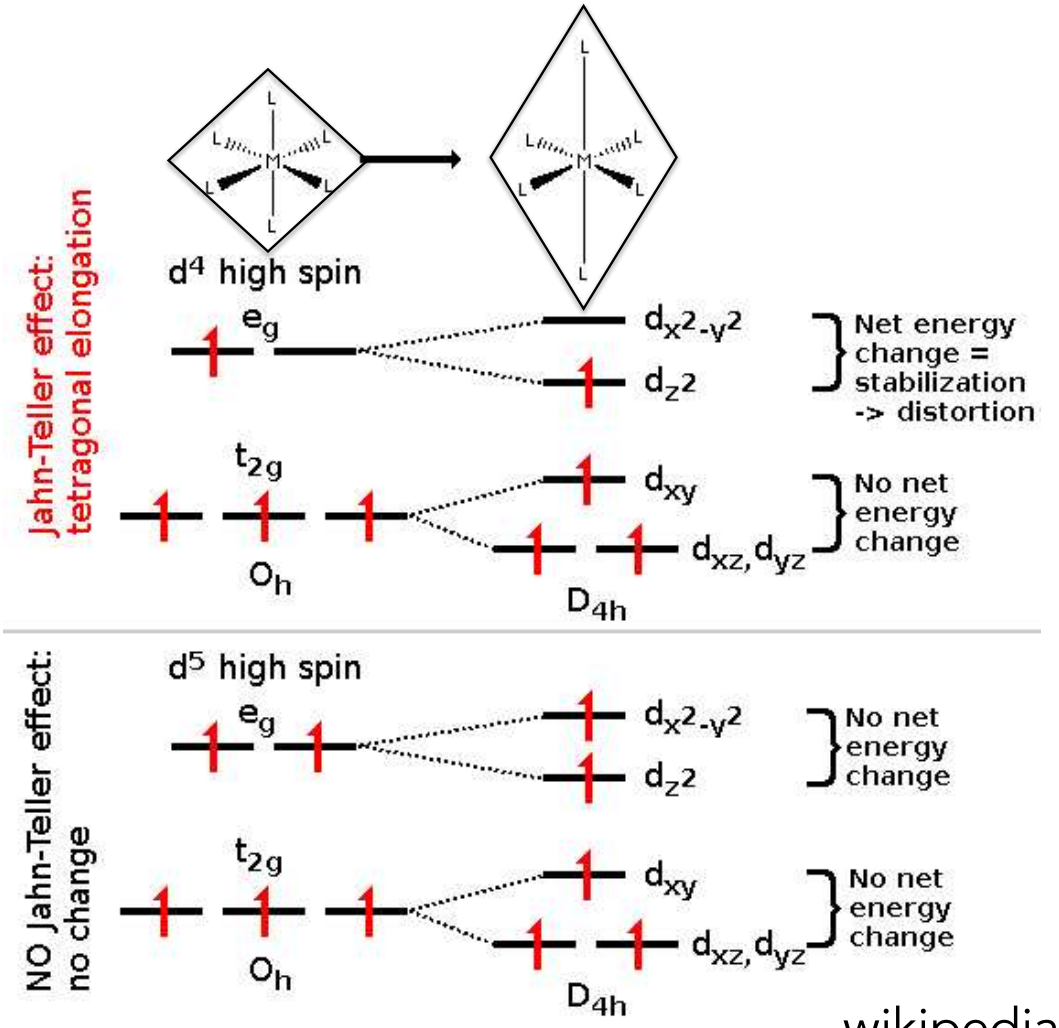
Transition metal oxides, d-orbitals, t_{2g} and e_g



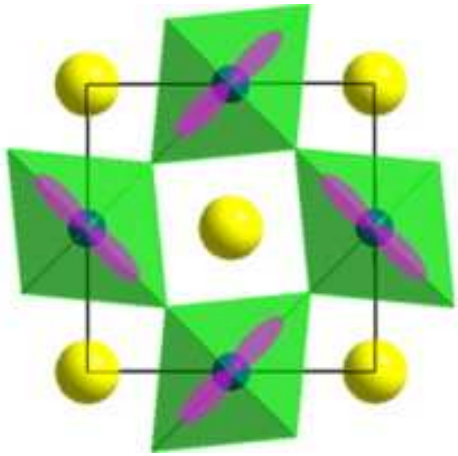
in the perovskite structure with the crystal fied

Degenerate energy levels - Jahn-Teller distortion

In the case of degenerate energy levels, a distortion can lift the degeneracy and lower the energy of the system



wikipedia



in a crystal

The lifting of degeneracy can lead to a Mott insulating state

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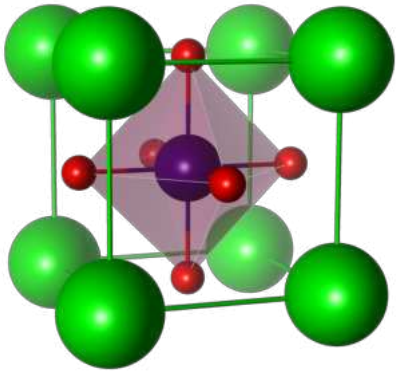
As we will see, the nickelates are in a rather similar situation but find another way to lift the orbital degeneracy

The rare earth nickelates $RENiO_3$



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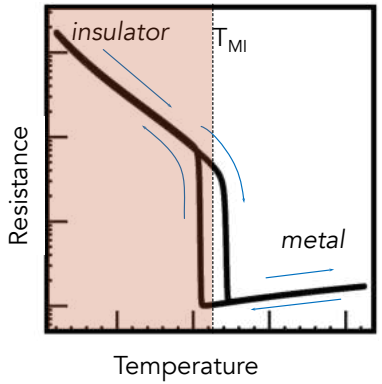
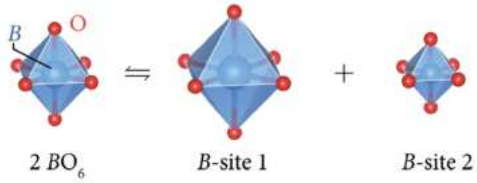
Perovskite nickelates $RNiO_3$

Metal-Insulator Transition



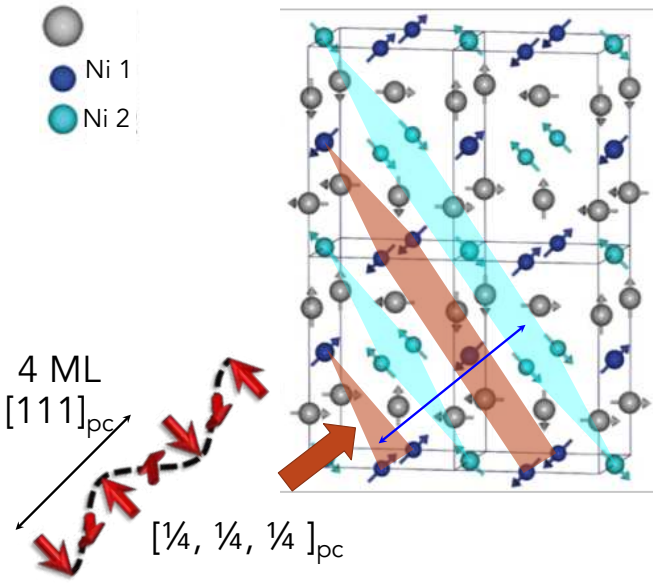
- Structural Transition: orthorhombic to monoclinic
- Bond Length Disproportionation



Alonso *PRL* (1999) - Mizokawa *PRB* (2000) - Park *PRL* (2012) - Johnston *PRL* (2014) - Subedi *PRB* (2015)

Antiferromagnetic ordering

in insulating phase



Garcia-Muñoz *et al.*, *Phys. Rev. B* 50, 978 (1994)
Scagnoli *et al.*, *Phys. Rev. B* 73, 100409 (2006)

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A lot of work on nickelates

Quantifying octahedral rotations

PHYSICAL REVIEW LETTERS

9 SEPTEMBER 2011

PRL 107, 116805 (2011)

Asymmetric Orbital-Lattice Interactions in Ultrathin Correlated Oxide Films

PHYSICAL REVIEW B 82, 165112 (2010)

tivity of $LaNiO_3$: Coherent transport and correlation driven mass enhancement

nature nanotechnology

LETTERS

PUBLISHED ONLINE: 6 APRIL 2014 | DOI: 10.1038/NNANO.2014.59

Atomic-scale control of competing electronic

Polarity compensation in ultra-thin films of complex oxides: The case of nickelate

Structure of Nickelates to Achieve Two-

al Electron Conduction

ADVANCED MATERIALS

www.advmat.de

Materials Views

www.MaterialsViews.com

Electric-Field Control of the Metal-Insulator Transition in

APL MATERIALS 1, 032110 (2013)

se diagram of compressively strained nickelate films

APPLIED PHYSICS LETTERS 96, 233110 (2010)

L 107, 176401 (2011)

PHYSICAL REVIEW LETTERS

week ending 21 OCTOBER 2011

Strain-mediated metal-insulator tra

of NdNiO

Selected for a Viewpoint in *Physics*

PHYSICAL REVIEW LETTERS

week ending 30 MARCH 2012

PRL 108, 136801 (2012)

Ultrafast Str

APPLIED PHYSICS LETTERS 1

Mott Physics near the Insulator-To-Metal Transition in $NdNiO_3$

PHYSICAL REVIEW B 86, 195147 (2012)

Tailoring the electro

(111)

APL MATERIALS 3, 062506 (2015)

ight near the Fermi level of $NdNiO_3$ thin films

Zubko,[2]

ARTICLE

Received 6 Apr 2013 | Accepted 4 Oct 2013 | Published 6 Nov 2013

DOI: 10.1038/ncomms3714

Heterointerface engineered electronic and magnetic phases of

nature materials

LETTERS

PUBLISHED ONLINE: 6 FEBRUARY 2011 | DOI: 10.1038/NMAT2958

ns of $NdNiO_3$ films th

Dimensionality Control of Electronic Phase Transitions in Nickel-Oxide Superlatti

ital reflectometry of oxi

nature materials

LETTERS

PUBLISHED ONLINE: 22 JANUARY 2012 | DOI: 10.1038/NMAT3224

kiser[1], Maurits W. Haverkort[1], Sebastian Brück

PRL 109, 156402 (2012)

PHYSICAL REVIEW LETTERS

week ending 12 OCTOBER 2012

83, 153411 (2011)

PRL 114, 026801 (2015)

week ending 7 JANUARY 2011

Selected for a Viewpoint in *Physics*

PHYSICAL REVIEW LETTERS

week ending 16 JANUARY 2015

$LaMnO_3$ superlattices

ormal

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

PHYSICAL REVIEW LETTERS

W B 90, 045128 (2014)

ARTICLES

PUBLISHED ONLINE: 25 JANUARY 2016 | DOI:

nature physics

e and Spin Or

PRL 112, 106404 (2014)

PHYSICAL REVIEW LETTERS

in the Nickelates

LETTER

doi:10.1038/nature17628

Hybridization-co

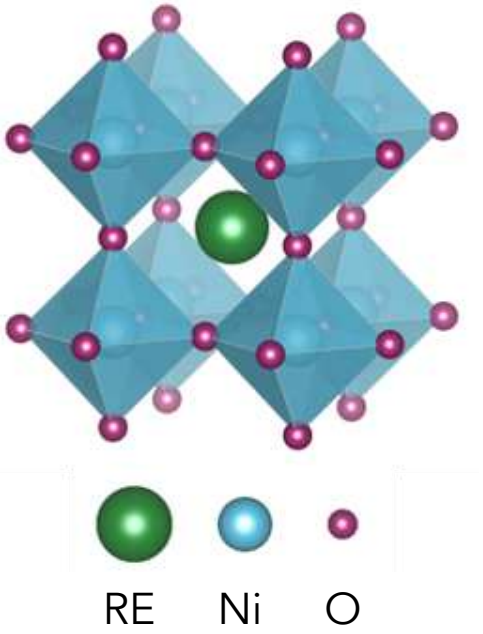
induced magneti

Charge Disproportionation without Charge Transfer in t

Nickelates as a Possible Mechanism for the Metal-In

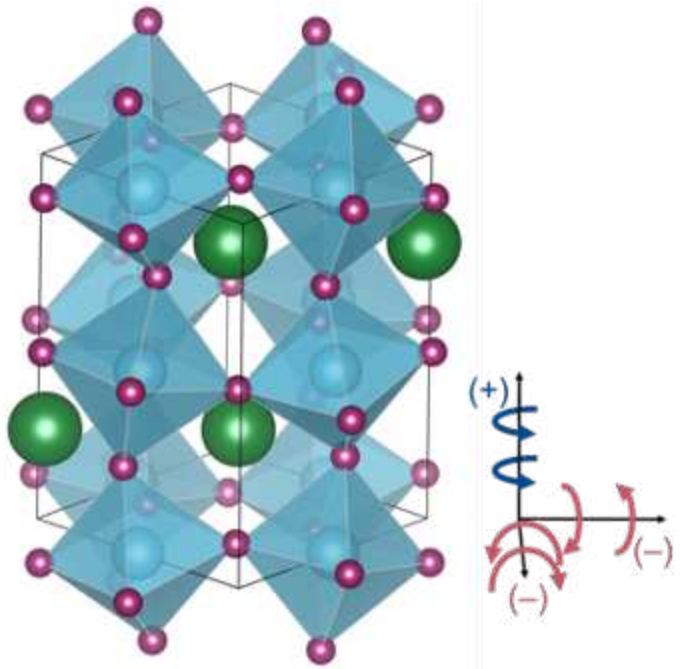
Polar metals by geometric design

Perovskite nickelates $RNiO_3$



Structural distortions

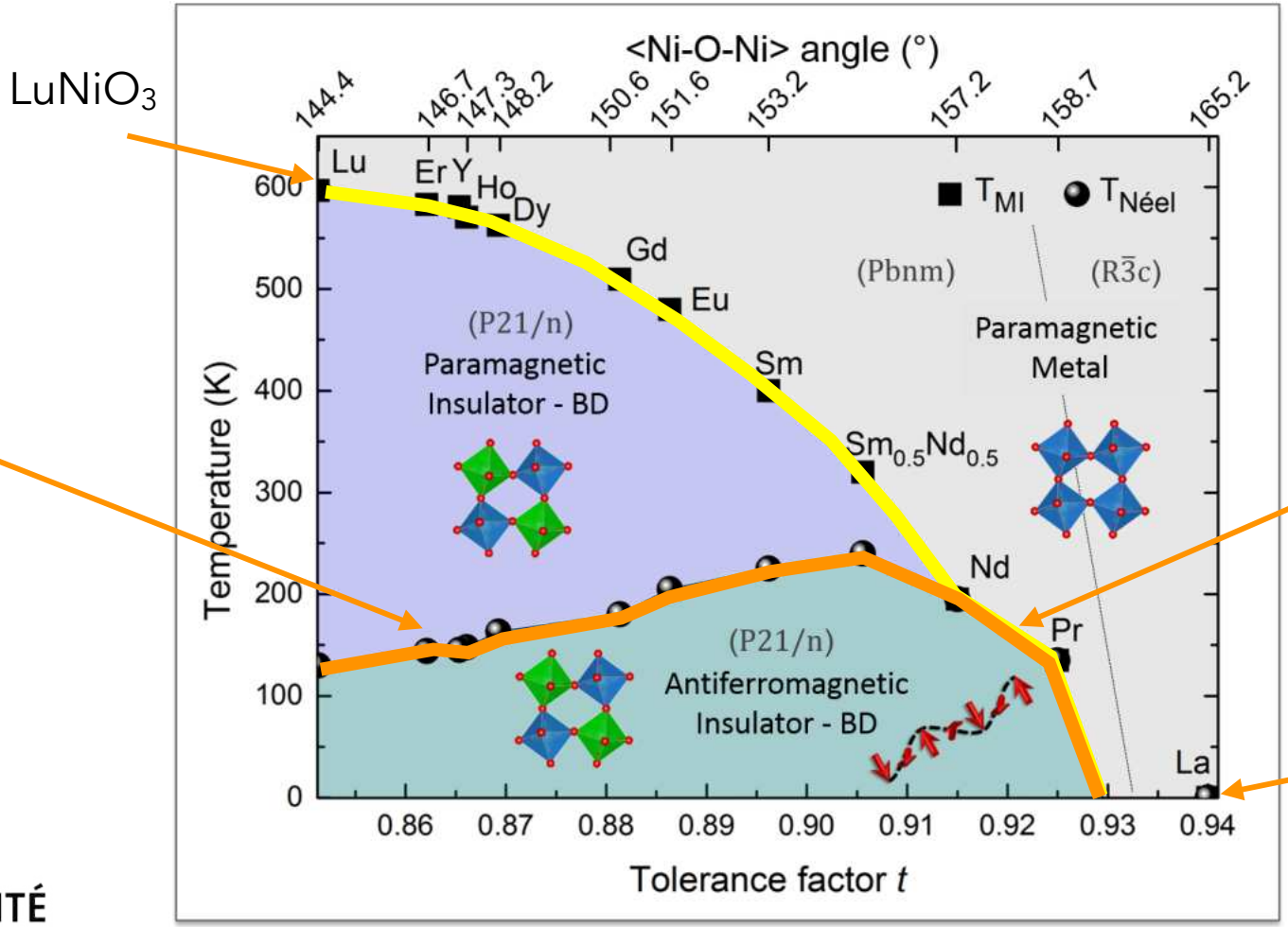
$a^-b^+c^-$



t=1 - cubic $a^0a^0a^0$

t<1 - orthorhombic $a^-b^+c^-$

$RNiO_3$ - phase diagram



$LuNiO_3$

T_N

T_{MI}

$LaNiO_3$

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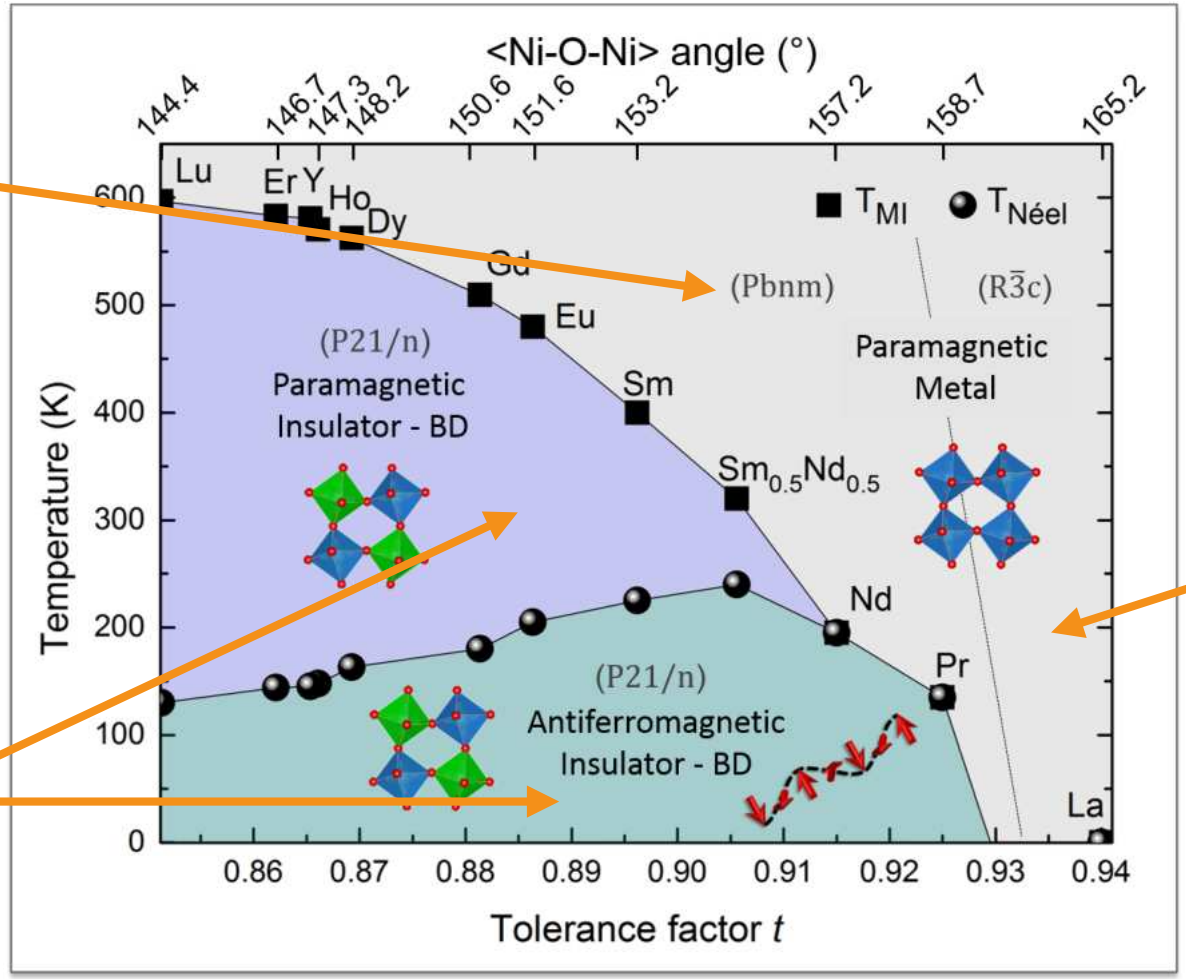
$RNiO_3$ - phase diagram

Orthorhombic
$a^-b^+c^-$

Monoclinic
$a^-b^+c^-$



Rhombohedral
$a^-a^-a^-$

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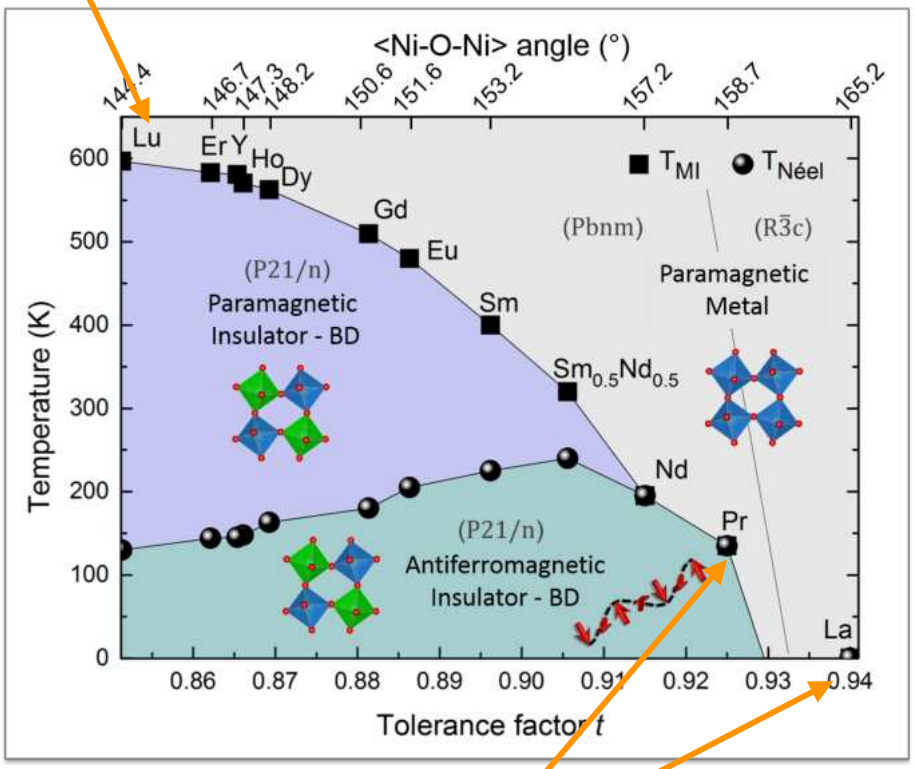
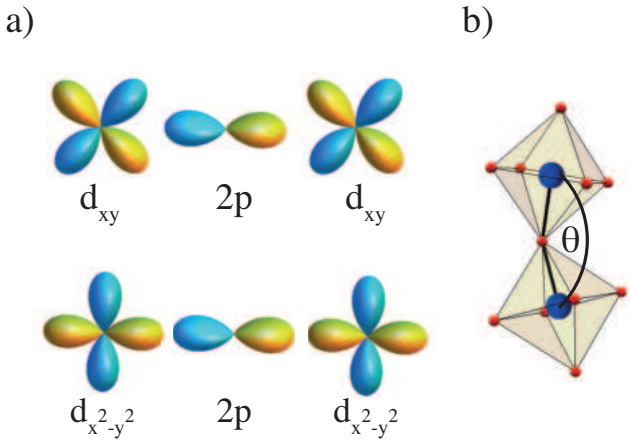
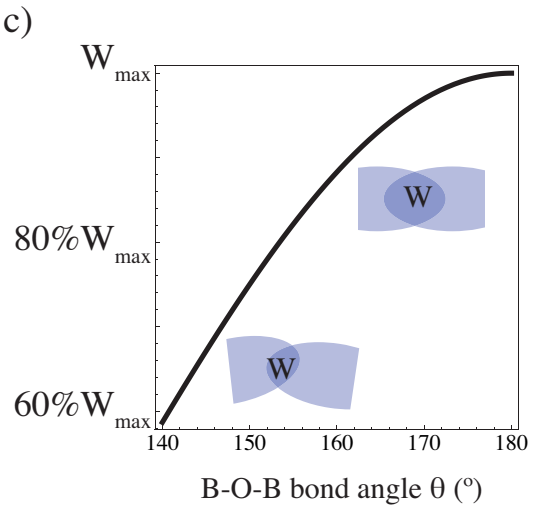
Distortions and Ni-O-Ni bond angle

$LuNiO_3$ - large distortions, small W







The Ni-O-Ni bond angle controls the orbital overlap and bandwidth of the system - and the metal to insulator transition

$PrNiO_3$ or $LaNiO_3$ - small distortions, large W - the metallic state is favoured

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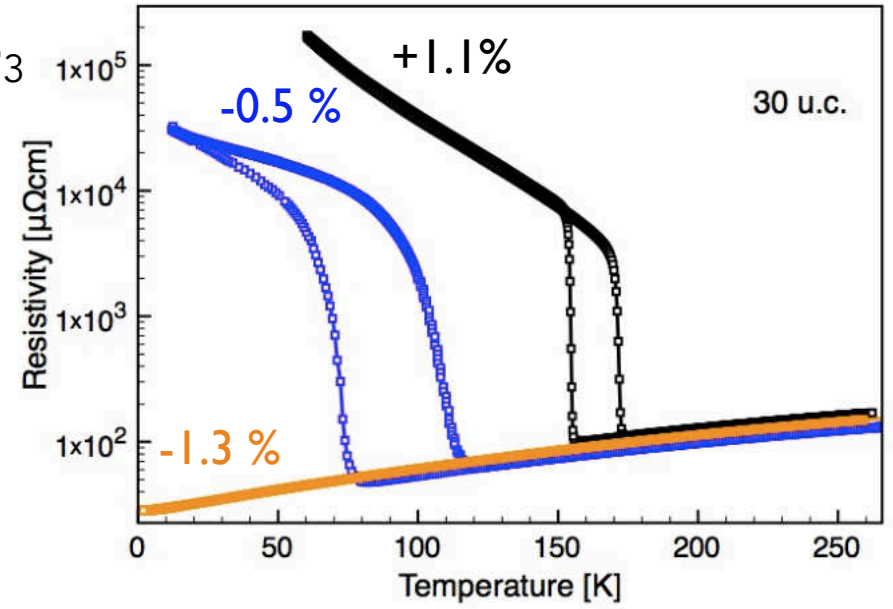
Effect of strain on the MIT

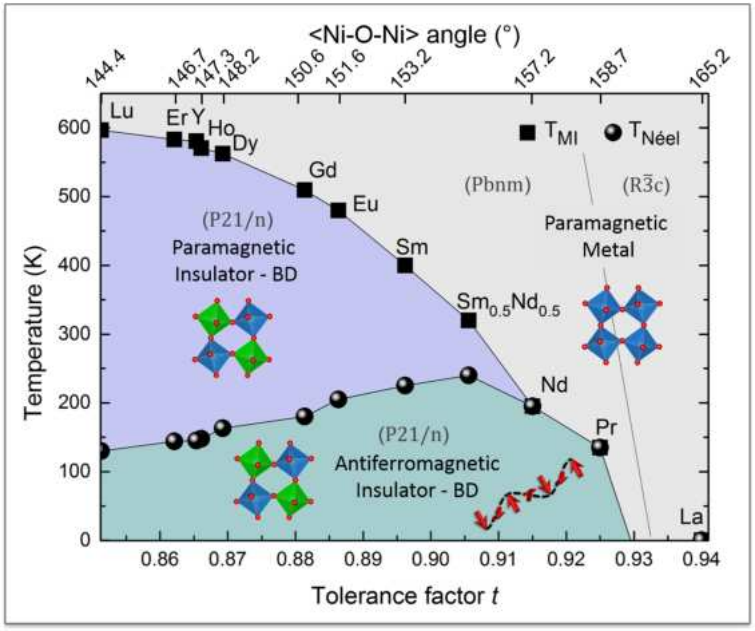
$NdNiO_3$

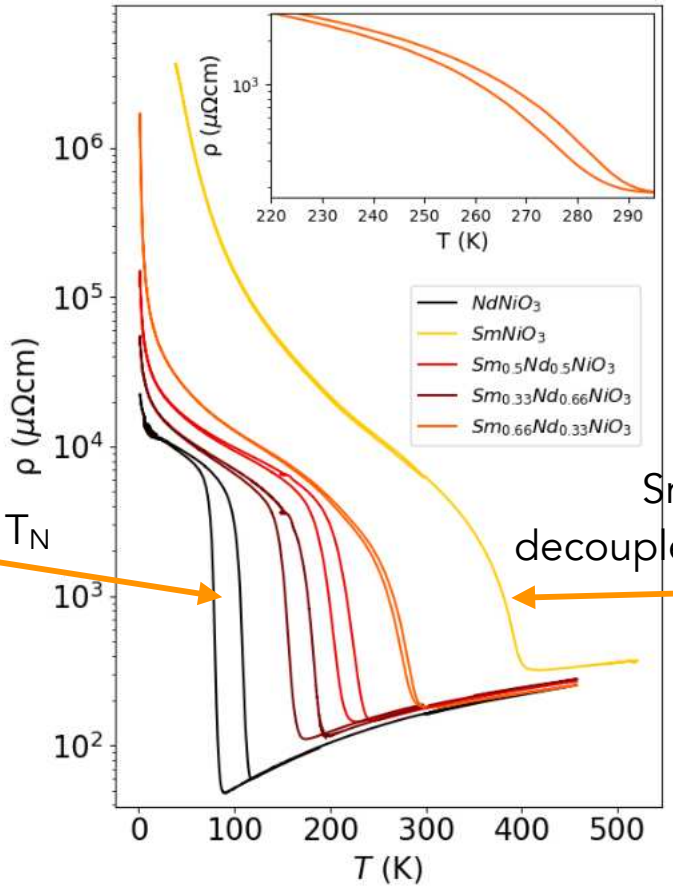


If you strain a nickelate film on a substrate, you modify the rotations pattern, Ni-O-Ni bond angles and band width of the system

R. Scherwitzl et al., Adv. Mater., (2010)
J. Liu et al. Nat. Comm. **4**, 3714 (2013)
S. Catalano et al., APL Materials **2**, 116110 (2014)
A. Caviglia et al., PRL **108**, 136801 (2012)

Order of the transition





$NdNiO_3$
coupled T_{MI} and T_N

$SmNiO_3$
decoupled T_{MI} and T_N

Series of thin film samples between $NdNiO_3$ and $SmNiO_3$ - $(Sm_{1-x}Nd_x)NiO_3$

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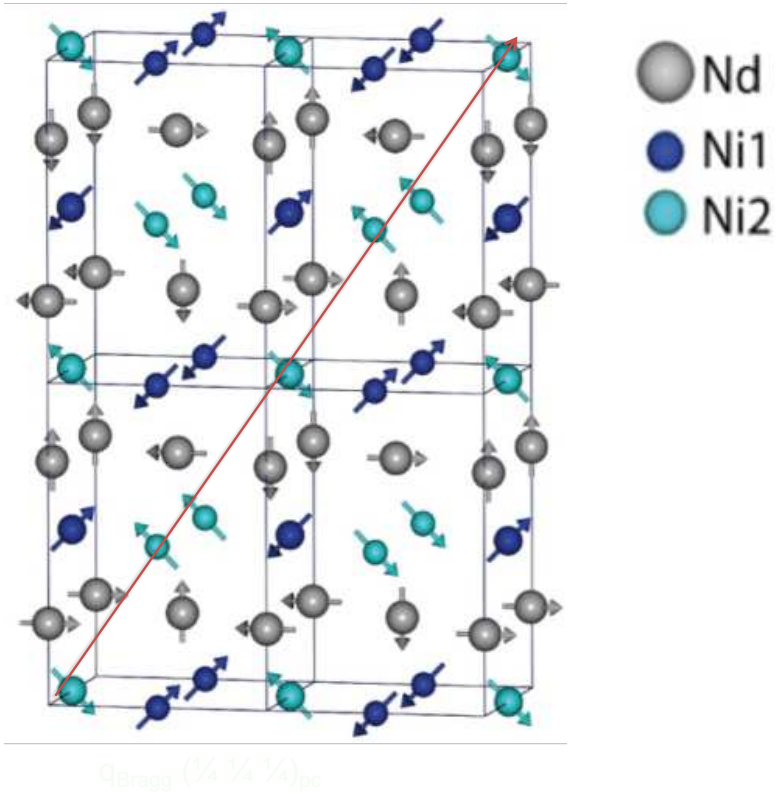
Coupled: 1st order - decoupled: 2nd order?

How to measure the Néel transition?

- Néel transition to AFM ground state
- $q_{Bragg}=(¼\ ¼\ ¼)_{pc}$
- $T_{Néel} \leq T_{MI}$

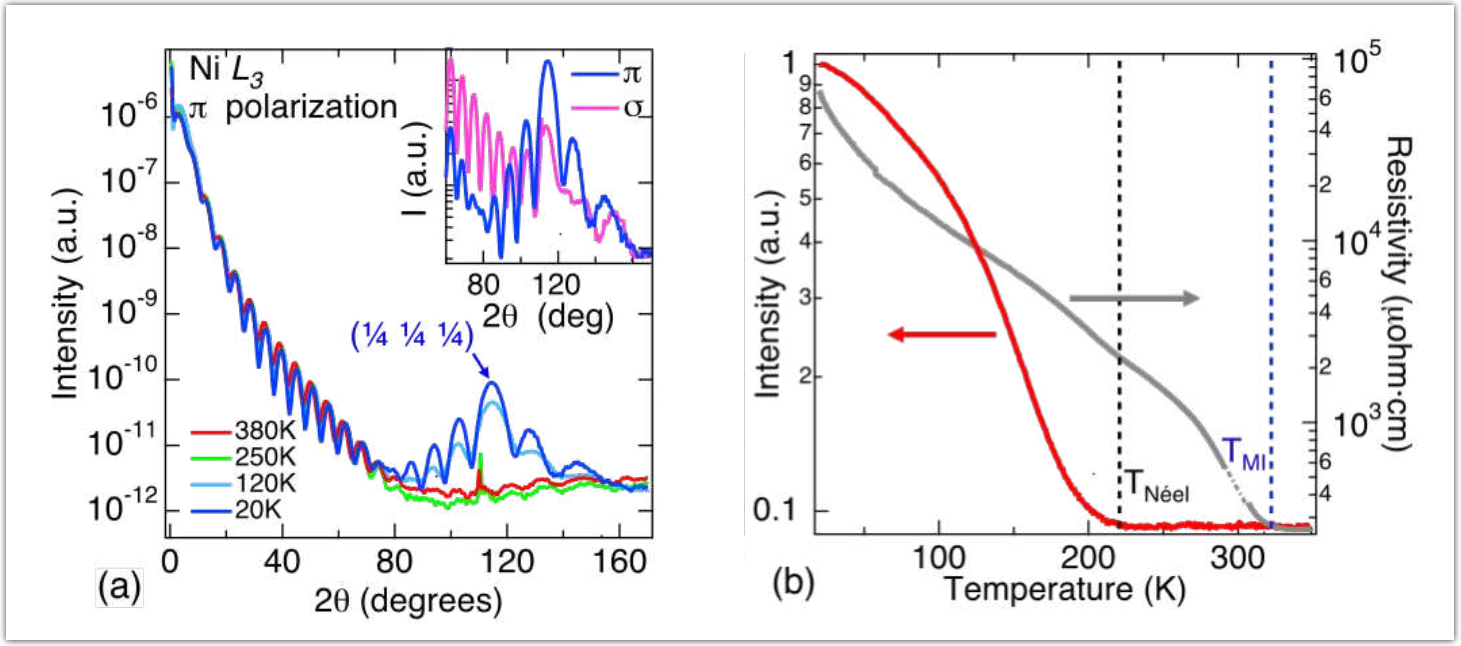
📖 Garcia Munoz *et al.*, *PRB*, (1994)
📖 Scagnoli *et al.*, *PRB*, (2006)
📖 Caviglia *et al.*, *PRB*, (2013)



- In thin films can be identified by Resonant Soft X-Ray Diffraction

How to measure the Néel transition?

- Néel transition to AFM ground state
- $q_{Bragg}=(¼\ ¼\ ¼)_{pc}$
- $T_{Néel} \leq T_{MI}$



📖 S. Catalano *et al.*, *APL Materials* ***3***, *062506* (2015)

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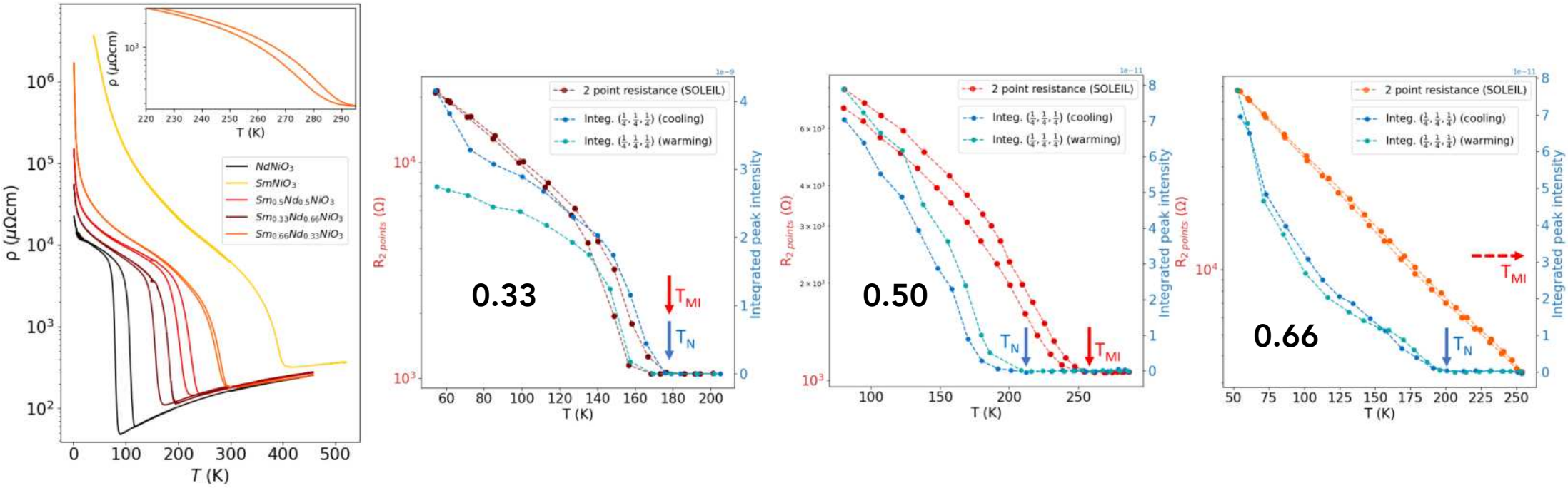
Coupled or decoupled Néel and MIT transitions



The series of thin film samples between $NdNiO_3$ and $SmNiO_3$ - $(Sm_{1-x}Nd_x)NiO_3$ show that one can have decoupled transitions and a first order MIT

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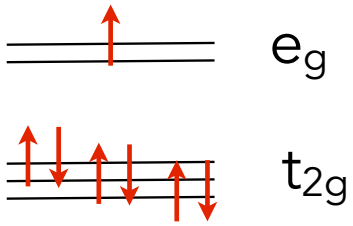
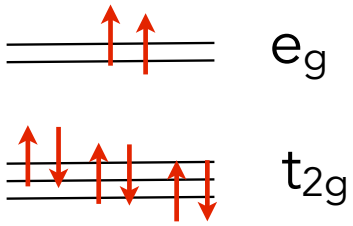
Lucia Varbaro et al. APL Mat. (2024)

Electronic structure and origin of the transition



Ni^{3+}: d^7 $t_{2g}^6 e_g^1$

Ni does not like the 3^+ state



Ni^{2+}: $d^8\underline{L}$ $t_{2g}^6 e_g^2$

3^+ to 2^+ d^7 to $d^8\underline{L}$
with a oxygen ligand hole

Origin of the transition - bond and charge disproportionation

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]

[1]*Code 6391, Naval Research Laboratory, Washington, D.C. 20375, USA*
[2]*II. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, 50937 Köln, Germany*
[3]*Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, 28049 Madrid, Spain*
[4]*ISIS Neutron Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, United Kingdom*
[5]*Hahn-Meitner-Institut Berlin Abteilung, SF-2 Glienicker Strasse 100 14109 Berlin, Germany*

(Received 12 February 2007; published 26 April 2007)

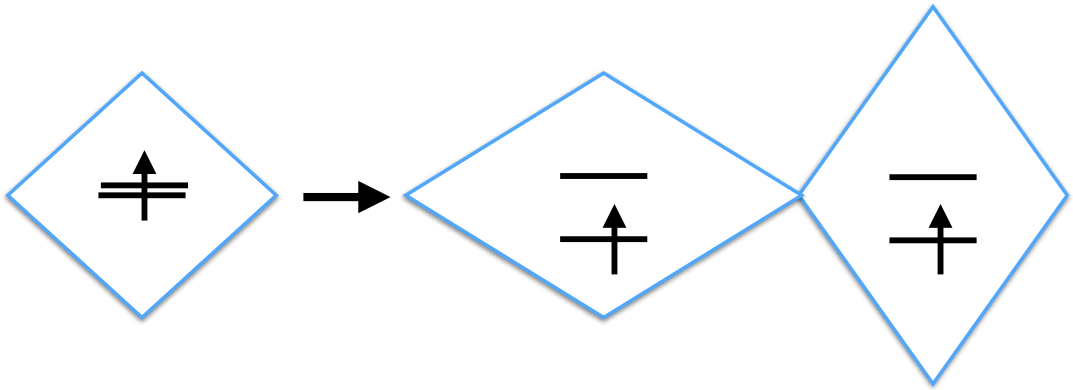
We show that the Mott transition in orbitally degenerate systems can, and often does, proceed not in the standard ''Mott insulator—weakly correlated metal'' sequence, but via a novel intermediate phase with a charge (rather than orbital) ordering. Lifting an orbital degeneracy this way can be viewed as an alternative to a Jahn-Teller distortion. This may occur in a crossover between localized and itinerant regimes, if Hund's rule coupling overcomes the on site Coulomb repulsion. We show both by calculations and by experiment that this scenario is realized in rare-earth nickelates, and argue that the same phenomenon takes place in many other systems.

DOI: 10.1103/PhysRevLett.98.176406 PACS numbers: 71.30.+h, 64.70.Kb, 71.15.Mb, 71.20.−b

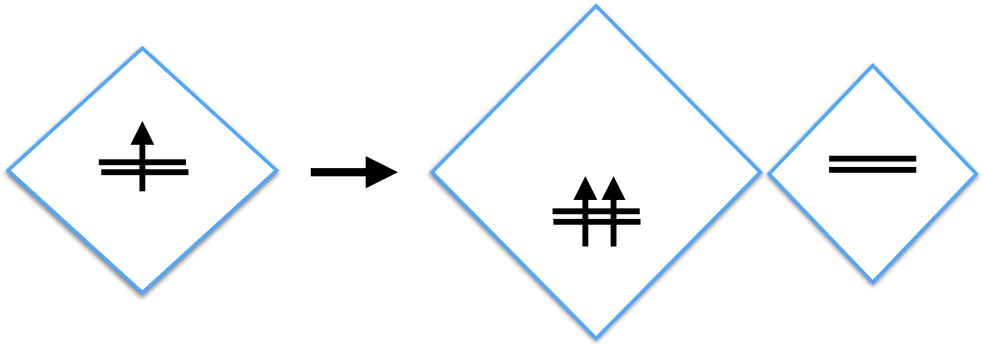
Bond and charge disproportionation

PRL Mazin « Nature abhors an orbital degeneracy. A solution is to develop a Jahn-Teller distortion »

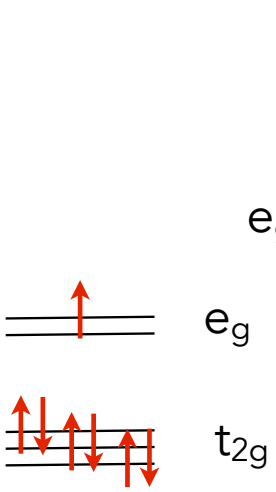
Narrow bands are however required - for broad bands the kinetic energy dominates and the Jahn-Teller instability is suppressed



When U is of the order of W and J, the system finds another trick to lift the orbital degeneracy - a bond and electronic disproportionation

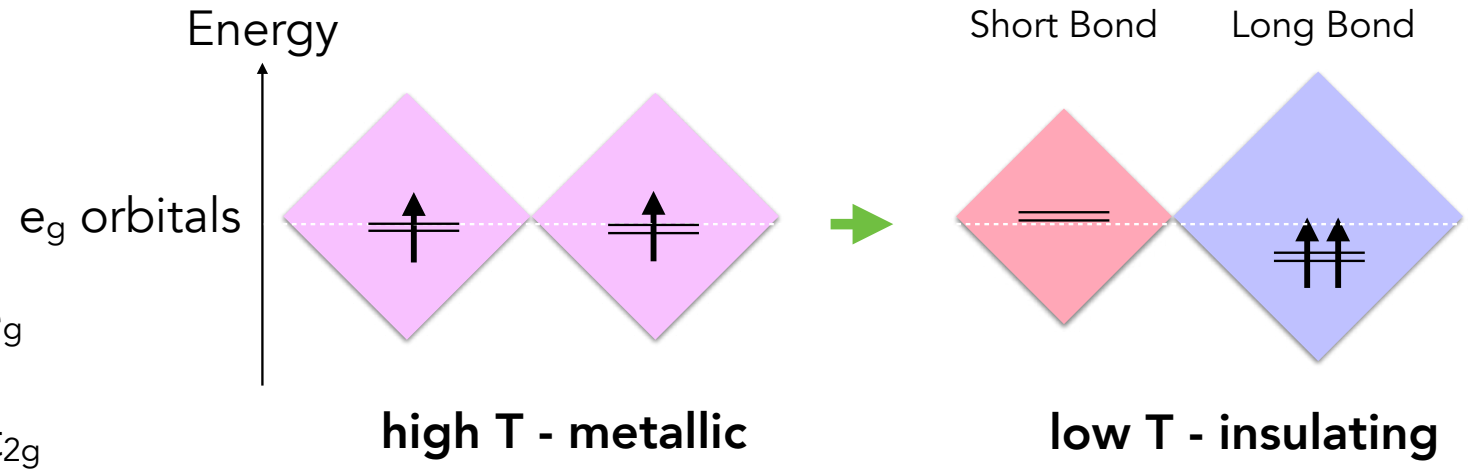


Mechanism of the MIT - $RNiO_3$



Ni^{3+}: d^7 $t_{2g}^6 e_g^1$

Low energy picture



high T - metallic

Electronically-degenerate
Bond-proportionate

low T - insulating

Electronically-non-degenerate
Bond-disproportionate

A site selective Mott insulating state

I. Mazin et al. PRL 98, 176406 (2007)
H. Park, A.J. Millis, C.A. Marianetti, PRL 109, 156402 (2012)
A. Subedi, O.E. Peil, A. Georges, PRB 91, 075128 (2015)
R.J. Green, M.W. Haverkort and G.A. Sawatzky, PRB 94, 195127 (2016)
A. Mercy, J. Bieder, J. Iniguez, Ph. Ghosez, Nat. Comm. 8, 1677 (2017)
O. E. Peil, A. Hampel, C. Ederer, A. Georges PRB, 99, 245127 (2019)

Order parameters describing the transition

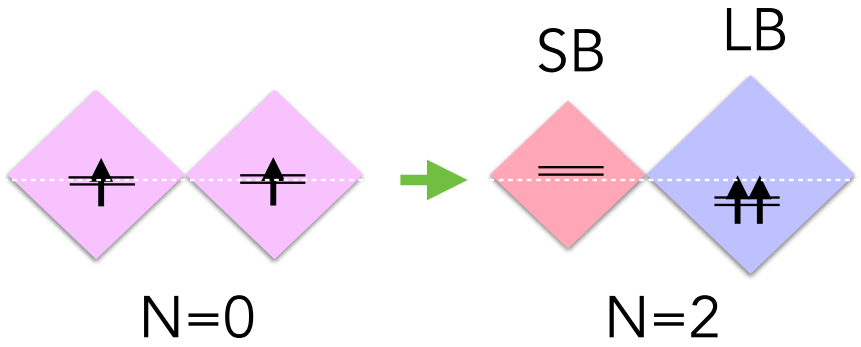
N- the electronic disproportionation

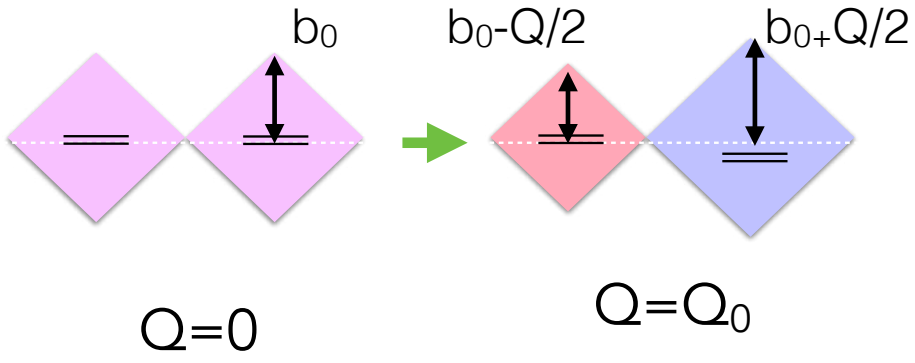
$$\mathbf{N} = n_{LB} - n_{SB}$$

Q is the amplitude of the BD defined as the difference in bond length (b_0 metallic phase)

LB - $b = b_0 + \mathbf{Q}/2$

SB - $b = b_0 - \mathbf{Q}/2$

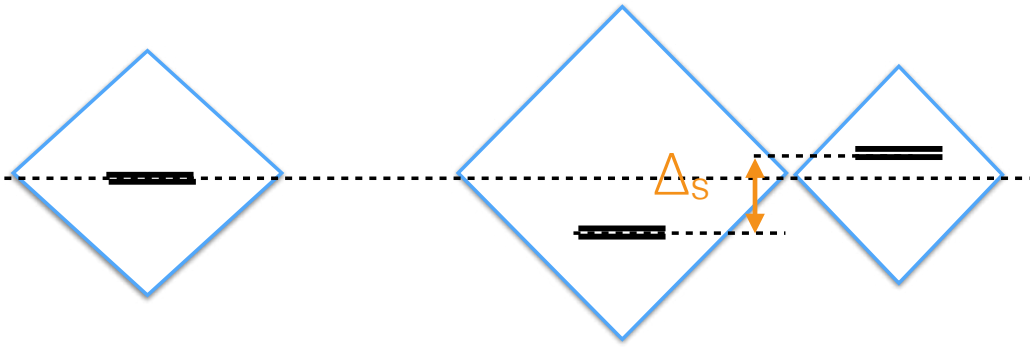




The low energy picture

Only Ni 3d e_g orbitals - breathing distortion assumed at this stage

e_g energy levels for the undeformed octahedron



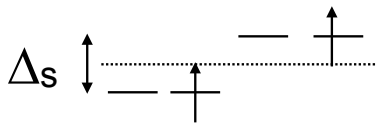
above T_{MI} - no BD

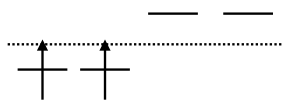
Below T_{MI} - BD

When does the system transition?

Orthorhombic equivalent sites		Monoclinic inequivalent sites
$e_g^1 + e_g^1$	⟶	$e_g^2 + e_g^0$
$(d^8L + d^8L)$		$(d^8 + d^8L^2)$

Energy at which one is getting charge disproportionation:

Monoclinic 



here Δ_s « without » U and J

$\Delta_s/2-\Delta_s/2$ $\quad -\Delta_s/2-\Delta_s/2+U-3J$ ⟶ $U-3J-\Delta_s=0$

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A. Subedi, O.E. Peil, A. Georges, PRB **91**, 075128 (2015)

Going further and taking into account the BD « cost »

PHYSICAL REVIEW B **99**, 245127 (2019)

Mechanism and control parameters of the coupled structural and metal-insulator transition in nickelates

Oleg E. Peil,[1,2] Alexander Hampel,[3] Claude Ederer,[3] and Antoine Georges[2,4,5,6]

[1]*Materials Center Leoben Forschung GmbH, Roseggerstraße 12, 8700 Leoben, Austria*

[2]*DQMP, Université de Genève, 24 quai Ernest Ansermet, 1211 Genève, Switzerland*

[3]*Materials Theory, ETH Zürich, Wolfgang-Pauli-Strasse 27, 8093 Zürich, Switzerland*

[4]*Collège de France, 11 place Marcelin Berthelot, 75005 Paris, France*

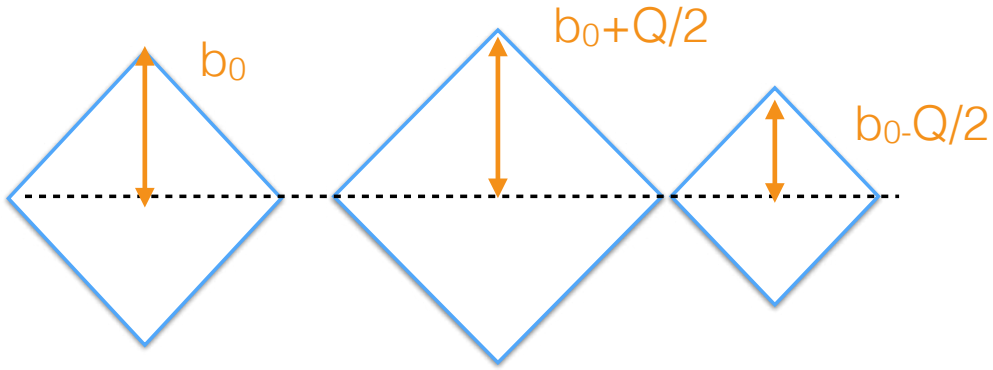
[5]*Center for Computational Quantum Physics, Flatiron Institute, 162 Fifth Avenue, New York, New York 10010, USA*

[6]*CPHT, Ecole Polytechnique, CNRS, Université Paris-Saclay, 91128 Palaiseau, France*

(Received 19 September 2018; revised manuscript received 12 February 2019; published 12 June 2019)

The path followed in Oleg Peil et al.

The BD is costing an elastic energy:
$KQ^2/2$ - Q is the amplitude of the BD defined as the disproportionation in bond length (b_0 metallic phase)



The gain in energy is due to the lifting of the degeneracy: -gQv/2 - where v (N in our previous notation) depends on Q and
$v(Q) = n_{LB}-n_{SB}$ - the electronic disproportionation

The difference of the on-site energies between the LB and SB (Δ_s) is gQ where g is the electron-lattice coupling parameter (here taking into account U and J)

One then minimise the energy with respect to Q

Minimizing the total energy,

$$E = \langle H \rangle \equiv E_{\mathrm{el}}[\nu] - \frac{gQ\nu}{2} + \frac{KQ^2}{2}, \tag{4}$$

with respect to Q (using the Hellman-Feynman theorem) yields

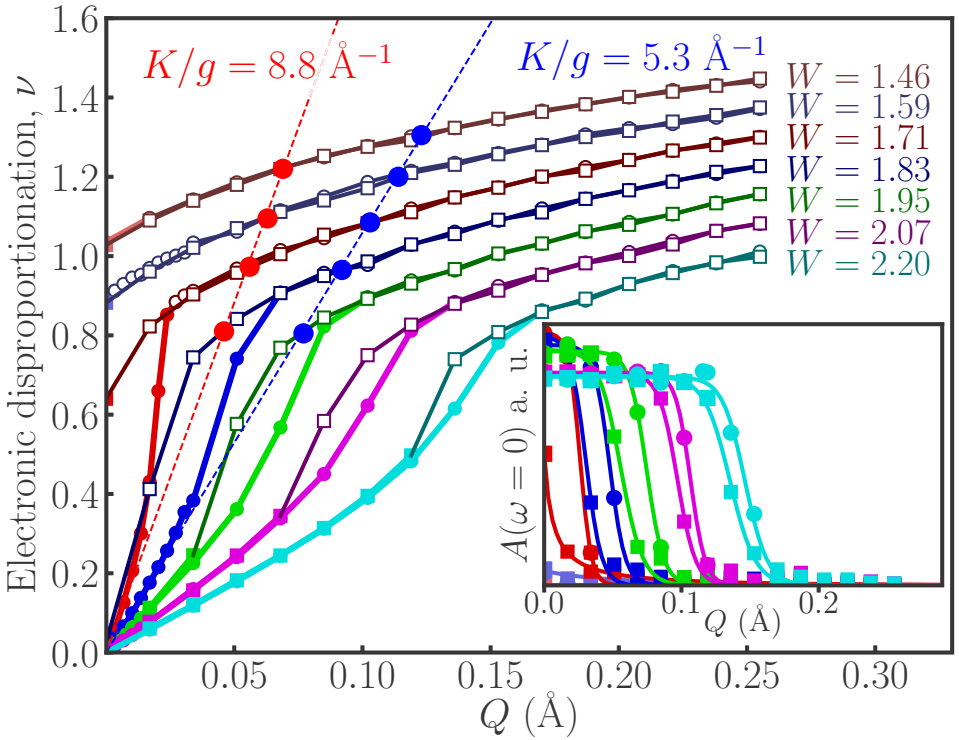
$$\frac{2K}{g}\bar{Q} = \nu[\bar{Q}], \tag{5}$$

highly non-linear obtained by DMFT

O. Peil et al. PRB **99**, 245127 (2019)

ν versus Q

at 120K



For a given K/g - say 5.3A^{-1}

1) Large W (say 2.20) - only one solution Q=0, ν=0 - metallic state
2) Small W (say 1.46) - only one solution ν=1.3 - insulating
3) Intermediate W (1.83) - two crossings at Q=0, ν=0 and ν=1 - phase coexistence

First order phase transition

Part 2 : Heterostructures based on nickelates

$SmNiO_3/NdNiO_3$ superlattices

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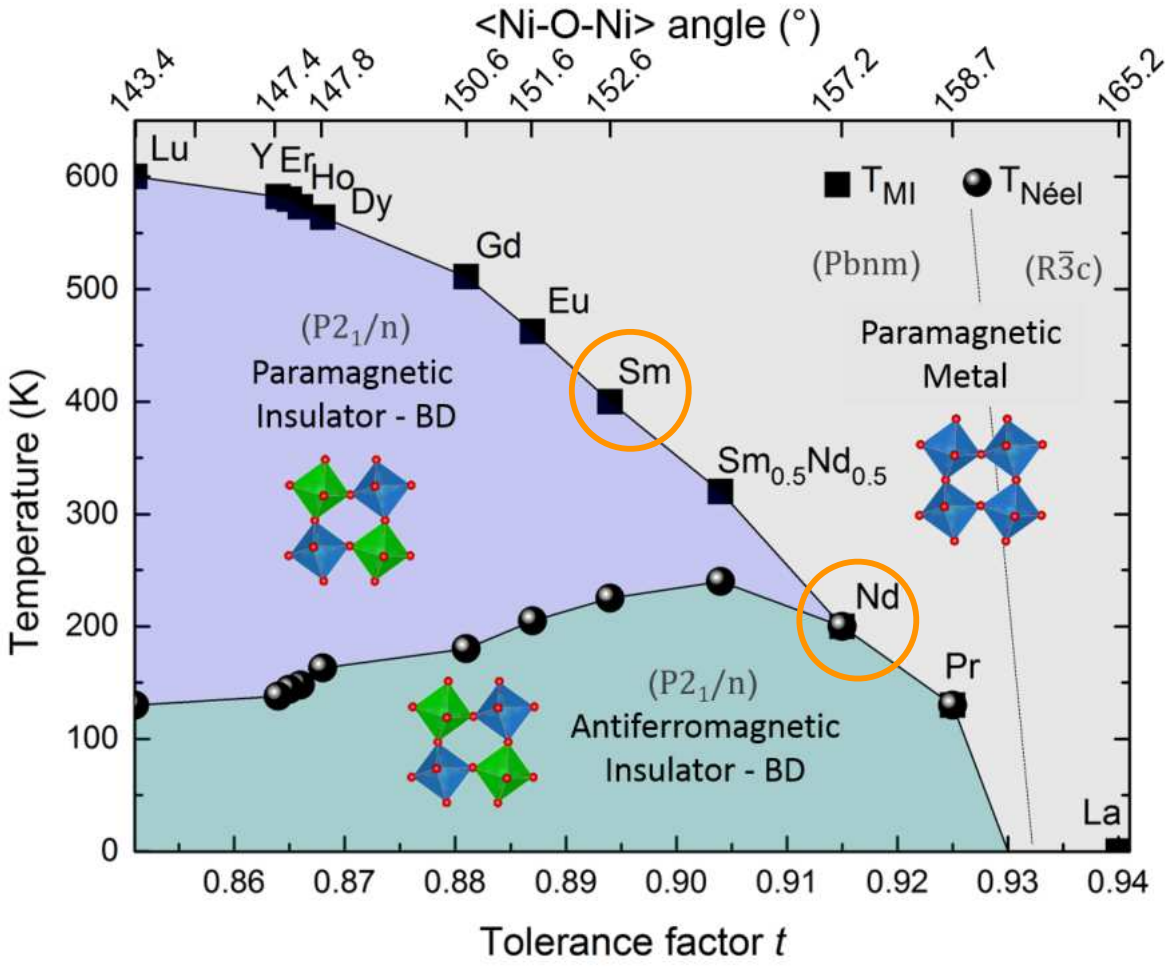
$SmNiO_3/NdNiO_3$ superlattices



$SmNiO_3$
T_{MI}=400K
$T_{Néel}$=230K

$NdNiO_3$
T_{MI}=200K
$T_{Néel}$=200K

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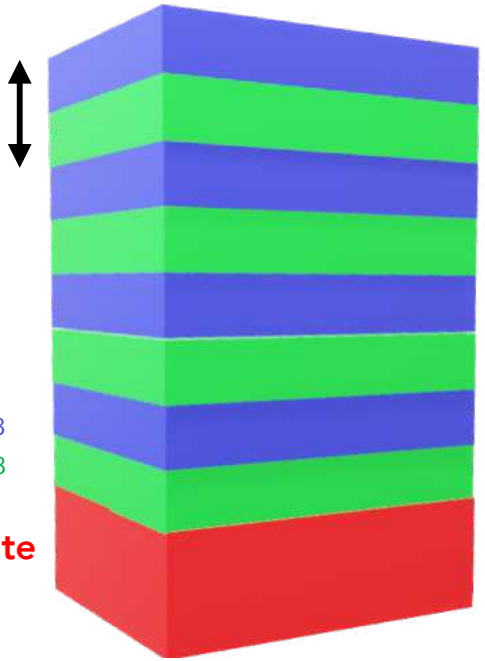
(001) (m $SmNiO_3$/n $NdNiO_3$) superlattices

Superlattice wavelength Λ

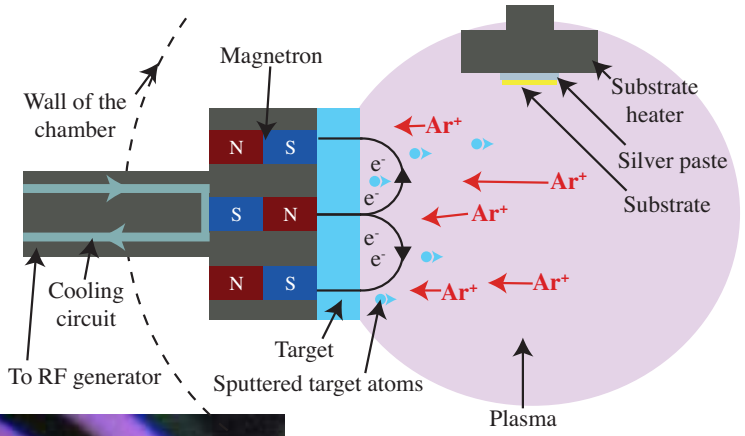


m=n

(m $NdNiO_3$ / m $SmNiO_3$)$_L$

We use T_{MI} as a probe of the interfacial coupling

Growth of the nickelate structures



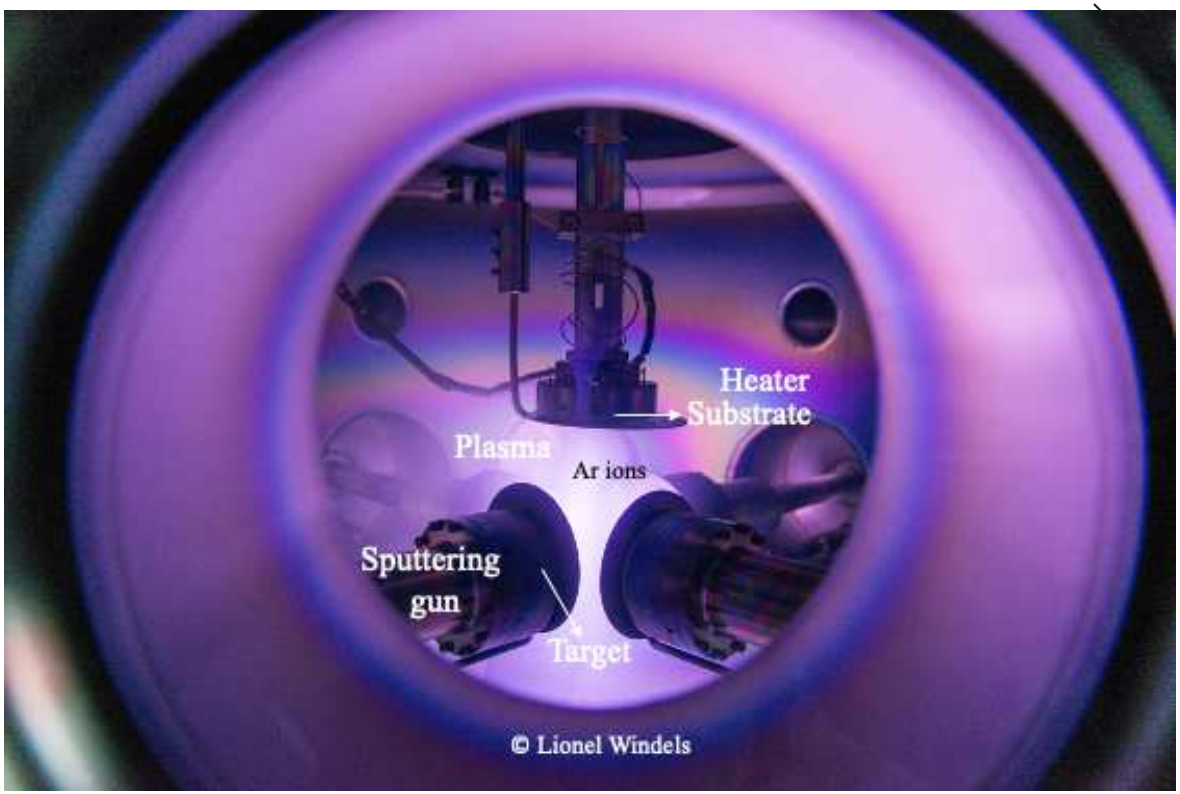
Off-axis RF magnetron sputtering

high pressure

O_2/Ar - 180mTorr

T_s=460°C

Substrate: (001) $LaAlO_3$



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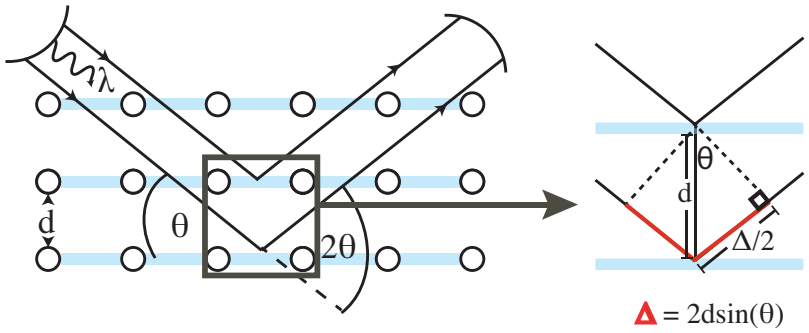
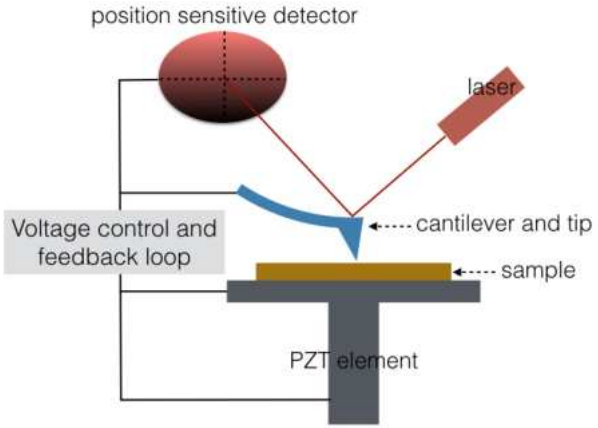
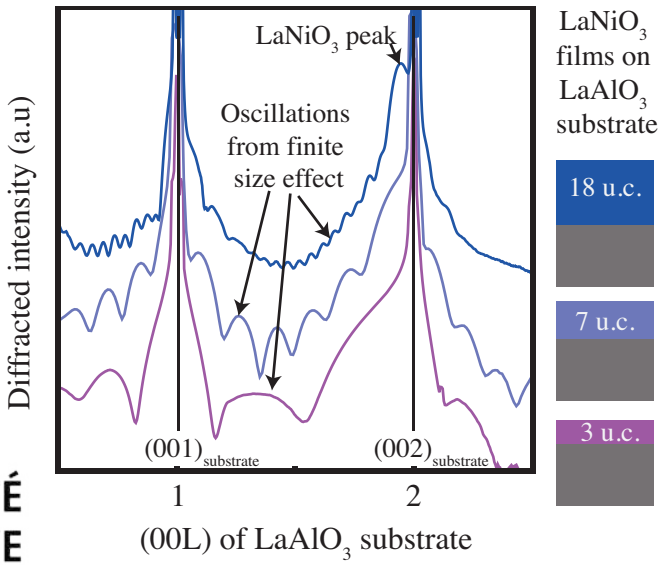
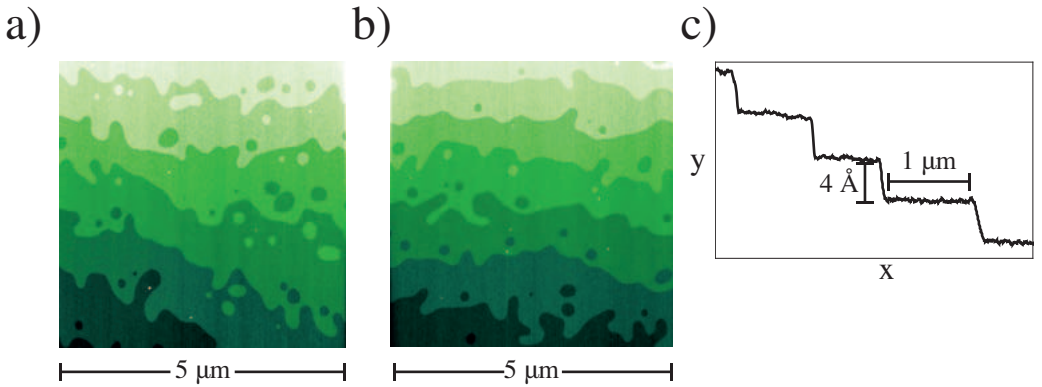
X-ray diffraction and AFM topographies









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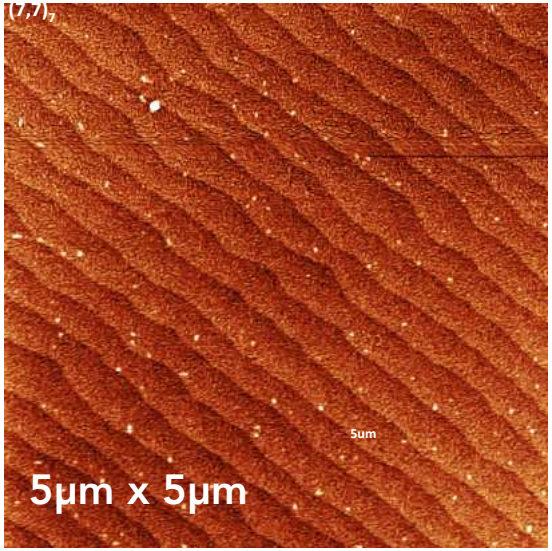
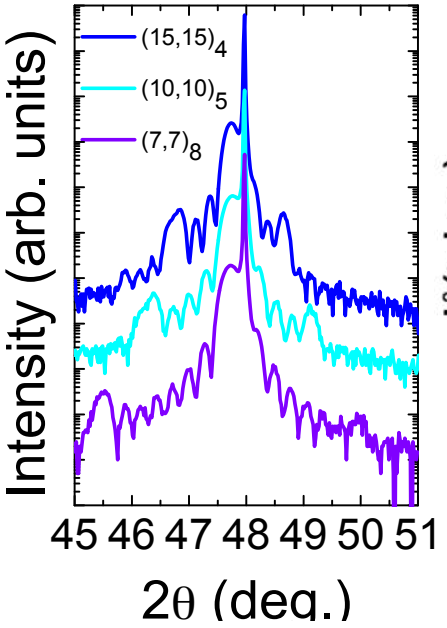
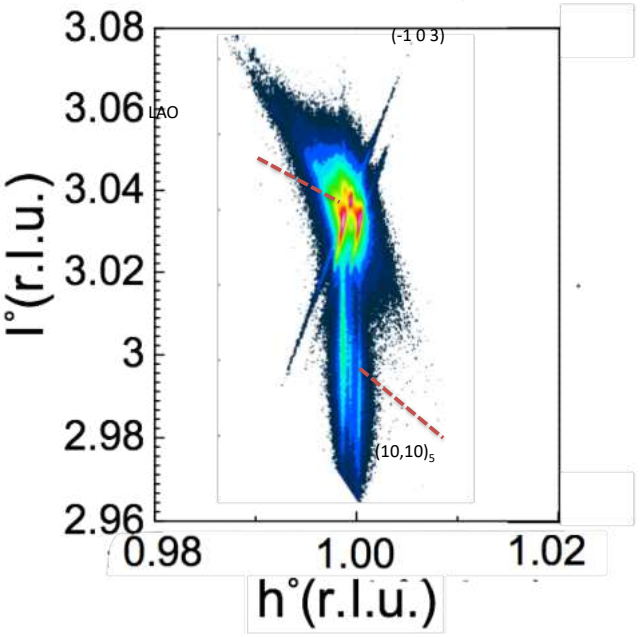
(001) (m $SmNiO_3$/m $NdNiO_3$) SL







Total superlattice thickness 40nm

All SL coherently strained

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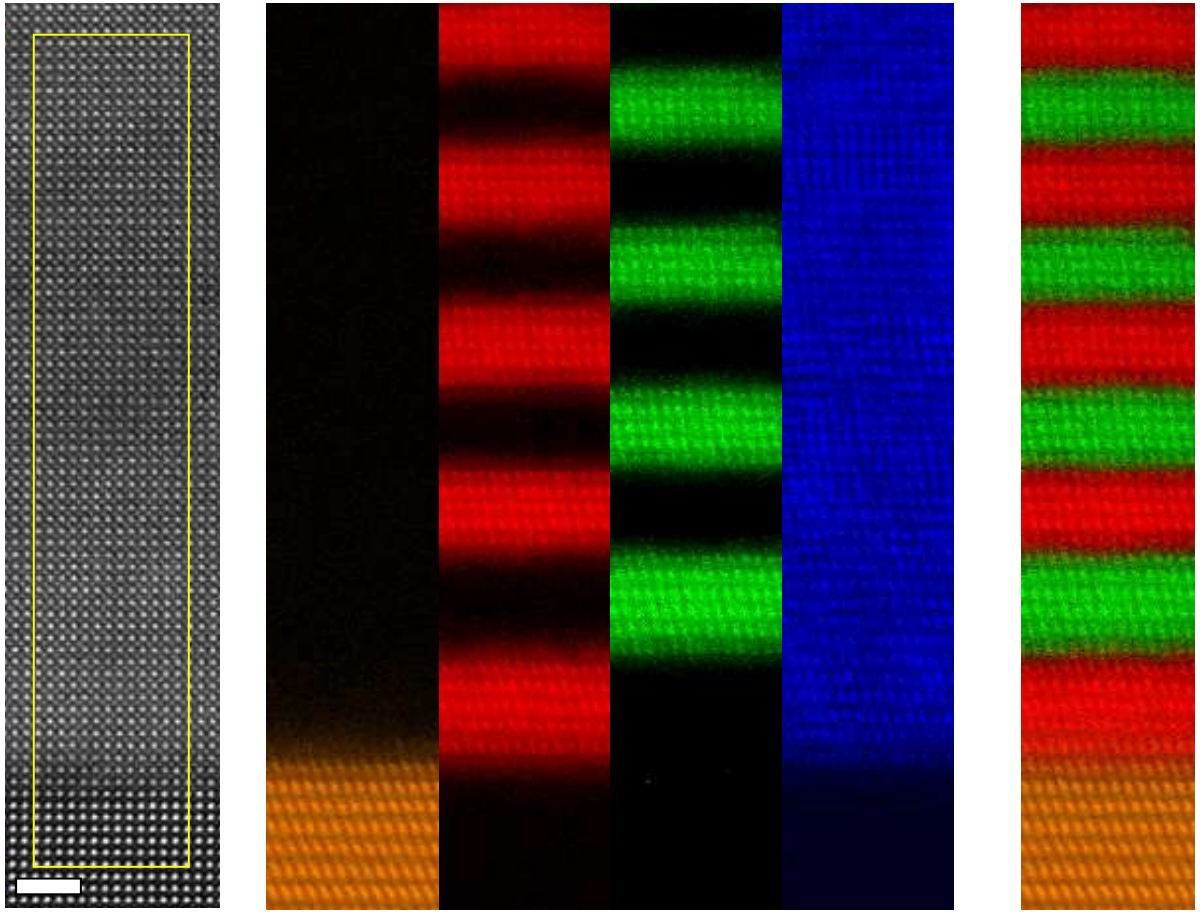
Scanning transmission electron microscopy

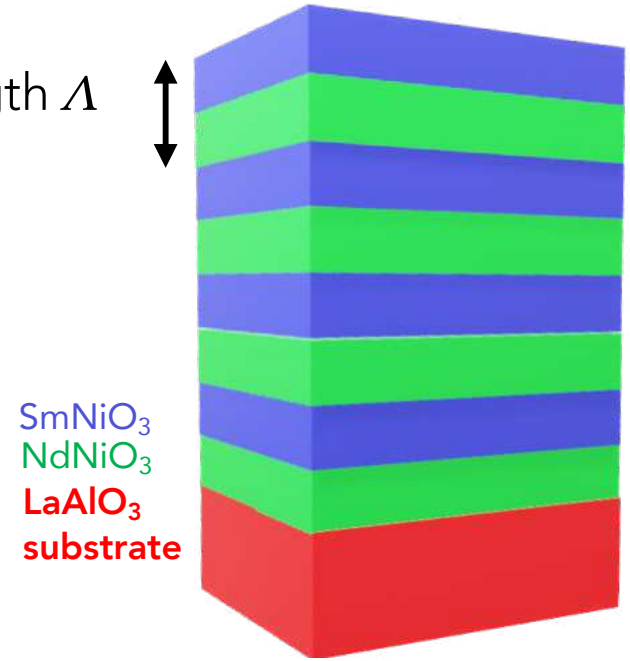


HAADF La Nd Sm Ni Superlattice

$SmNiO_3/NdNiO_3$ superlattices

Transport properties

Superlattice wavelength Λ



m=n

(m $NdNiO_3$ / m $SmNiO_3$)$_L$

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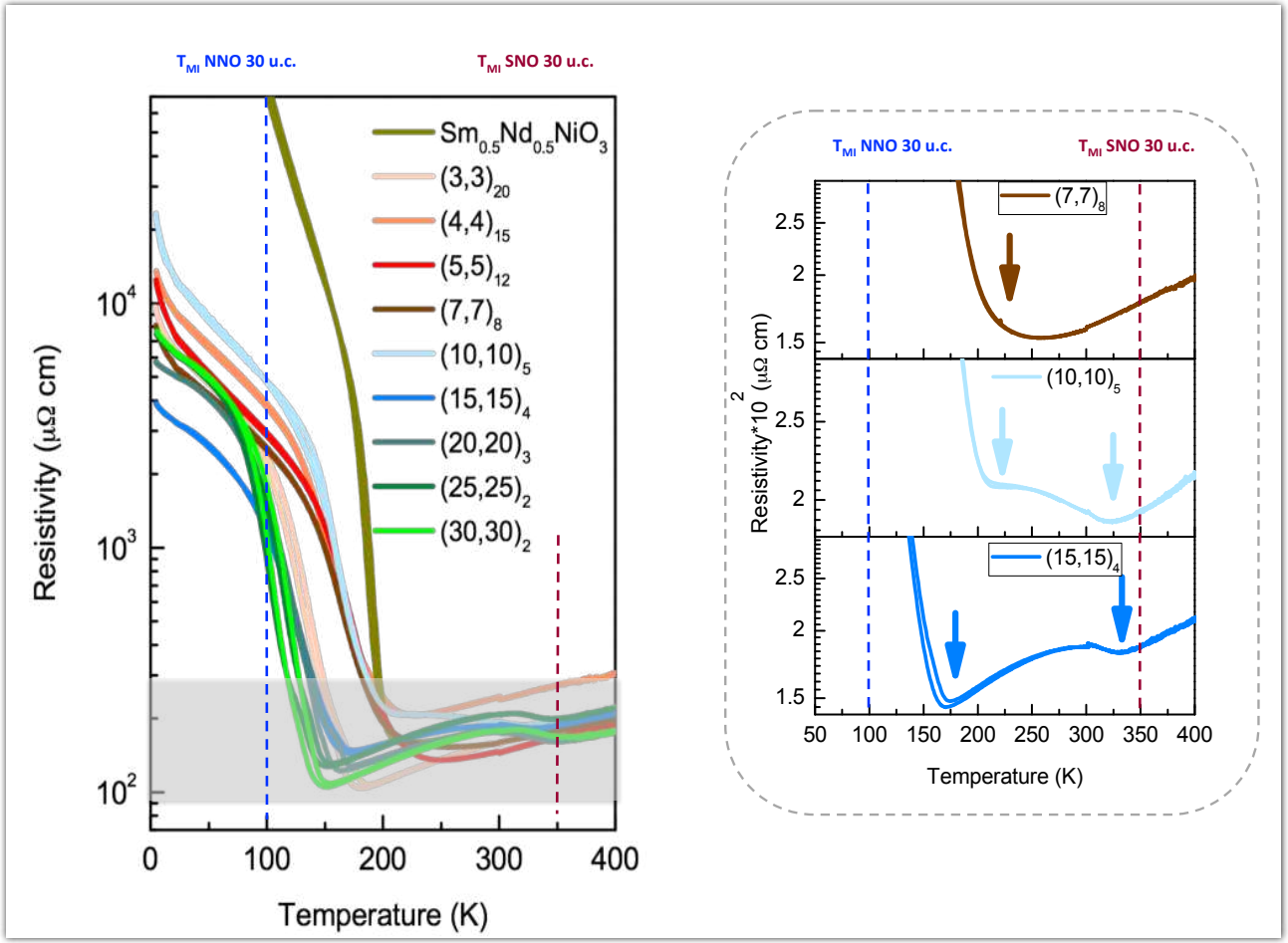
T_{MI} versus wavelength



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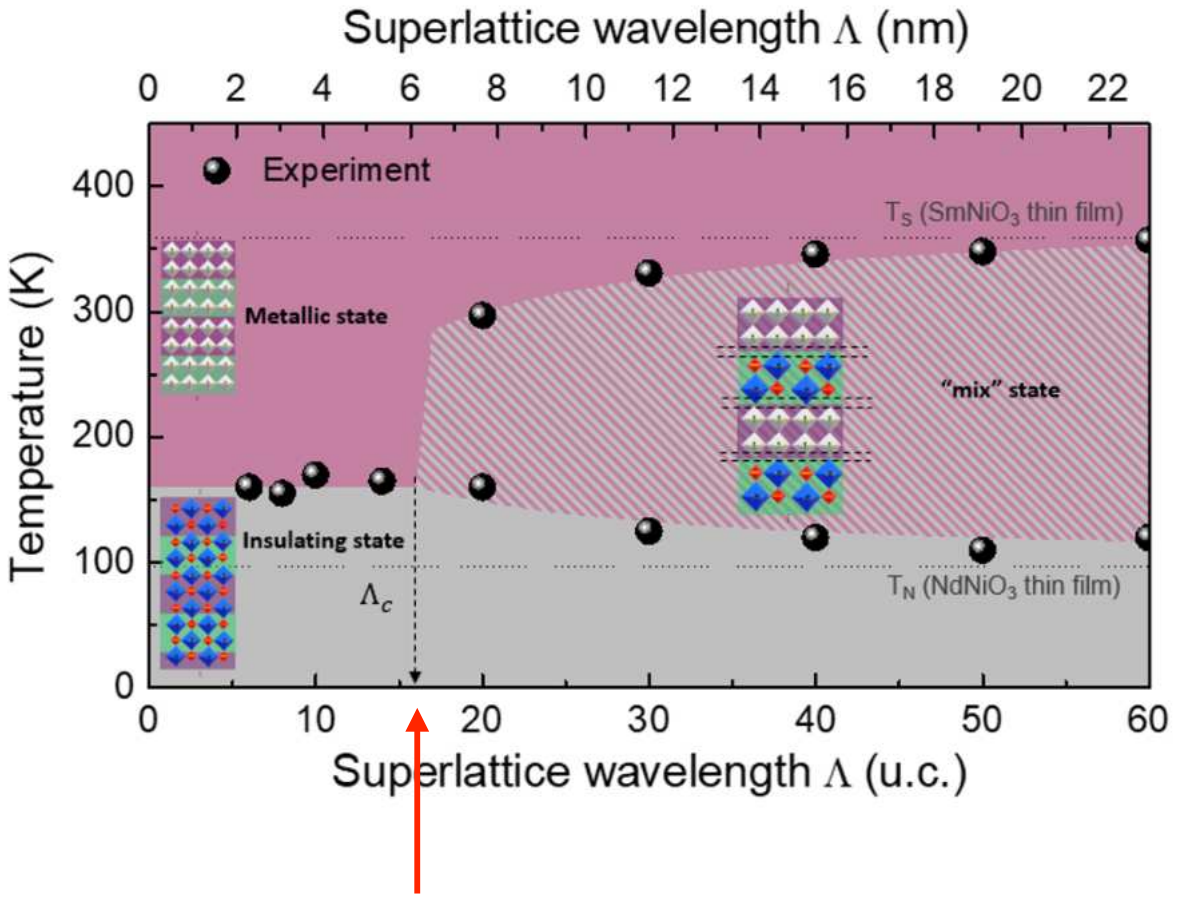
T_{MI} versus wavelength

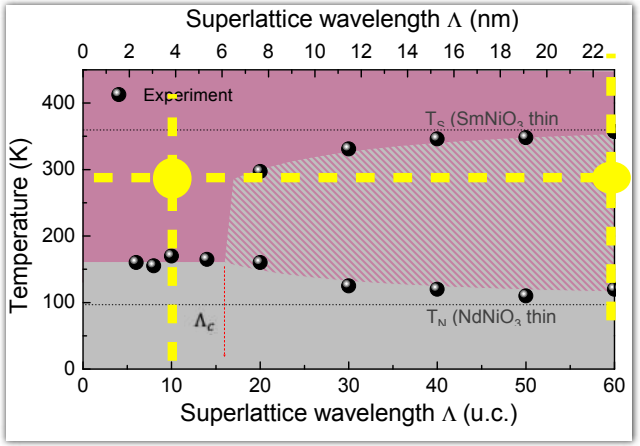


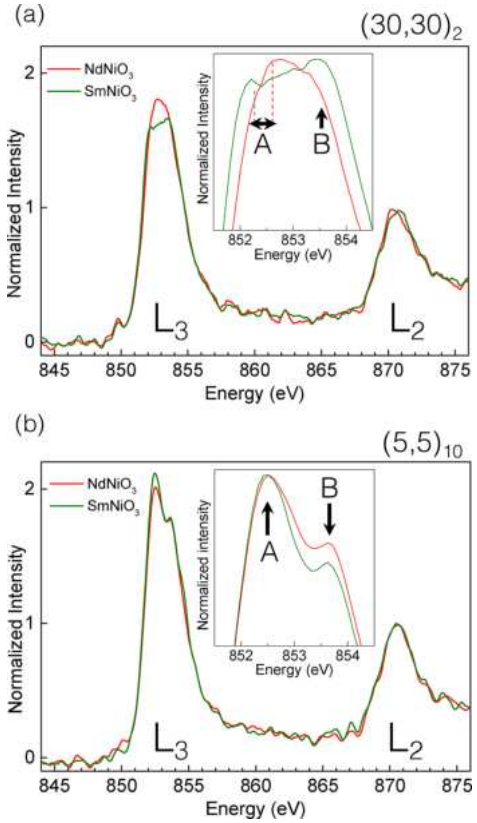
C. Dominguez et al. Nature Materials **19**, 1182 (2020)

Critical wavelength Λ_c

Behaviour confirmed at the u.c. level using STEM

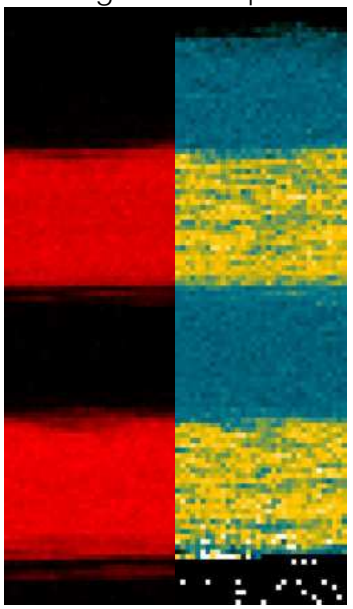
EELS spectra allow the insulating and metallic states to be differentiated at the unit cell scale





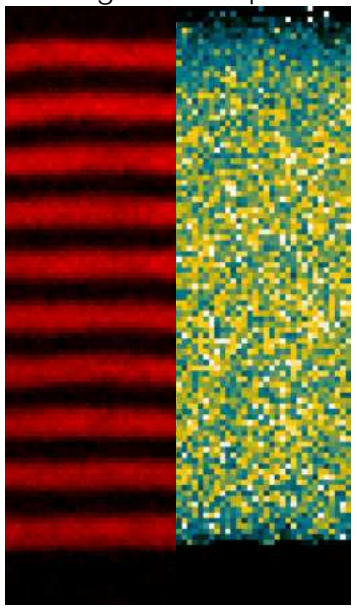
$(30,30)_2$

Nd signal Peak position



$(5,5)_{10}$

Nd signal Peak position



Pixel size: 1 p.c. unit cell

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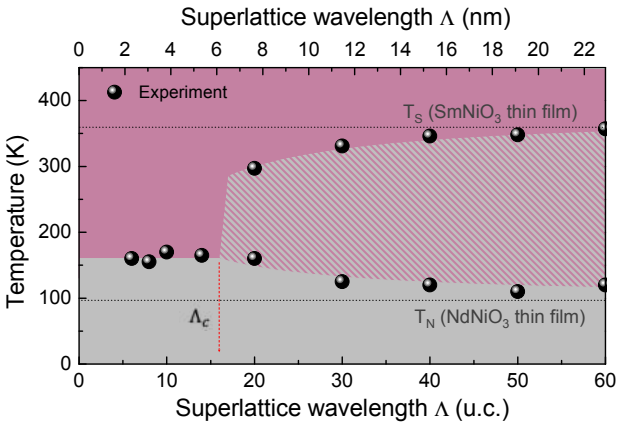
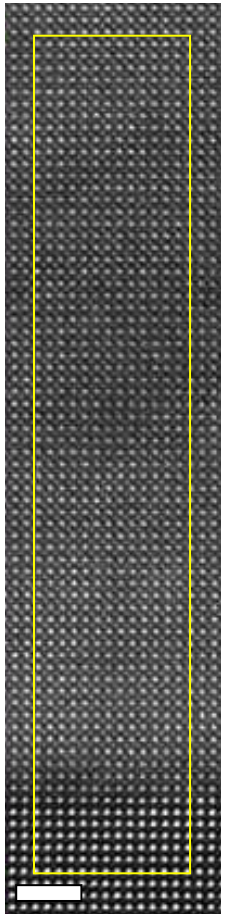
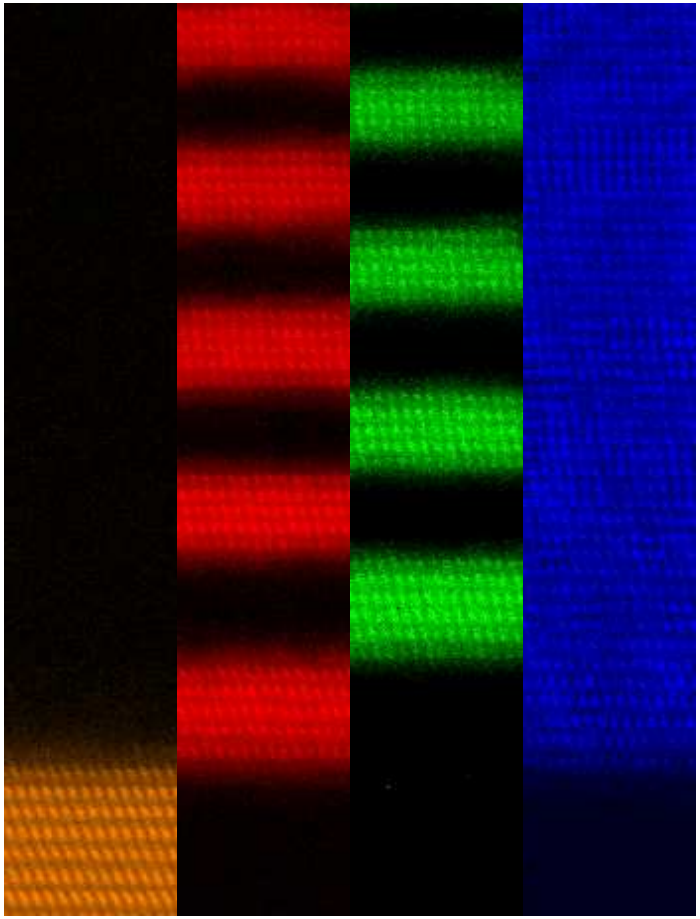
B. Mundet et al., Nano Letters 21(6), 2021

Origin of the coupling - intermixing?

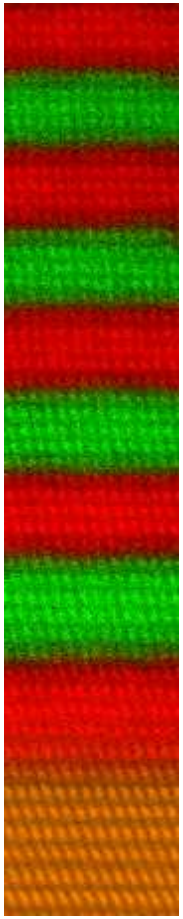




HAADF



La Nd Sm Ni



Superlattice

A 5/5 SL

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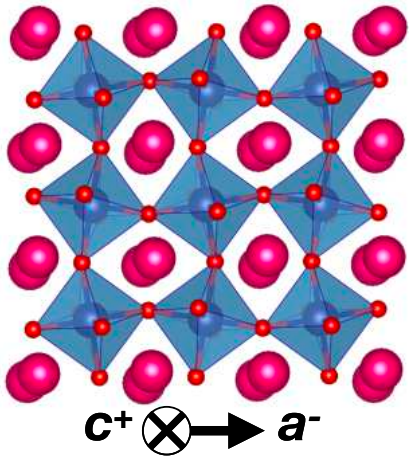
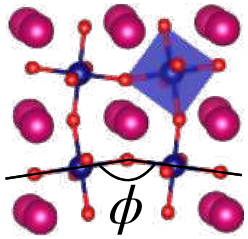
Origin of the coupling - structural coupling?

$[001]_{PC}$ zone axis (top view)



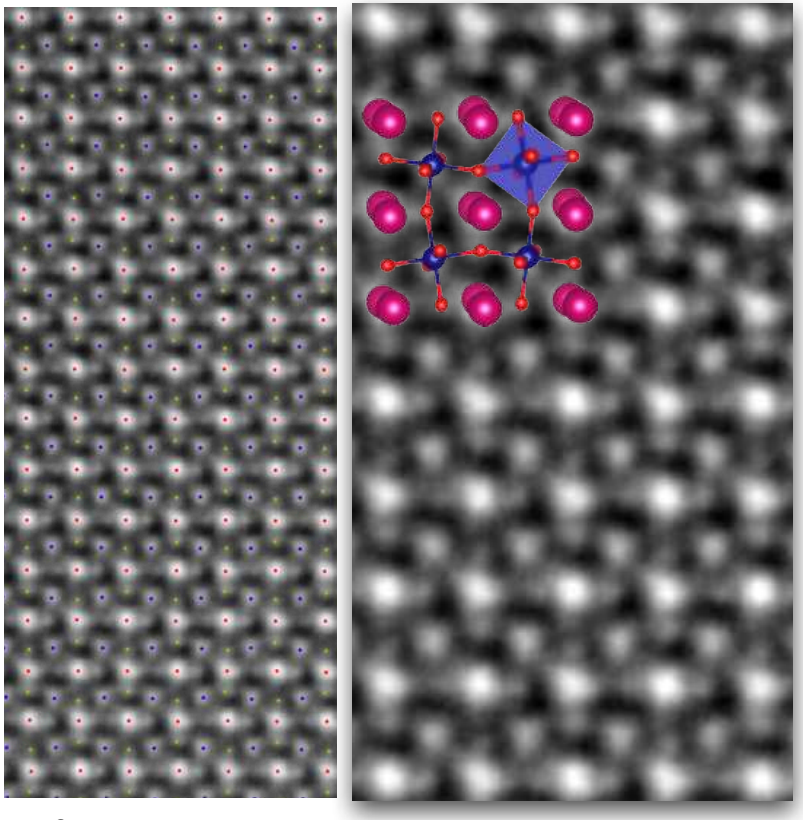
In-phase rotations along zone axis



Rare-earth

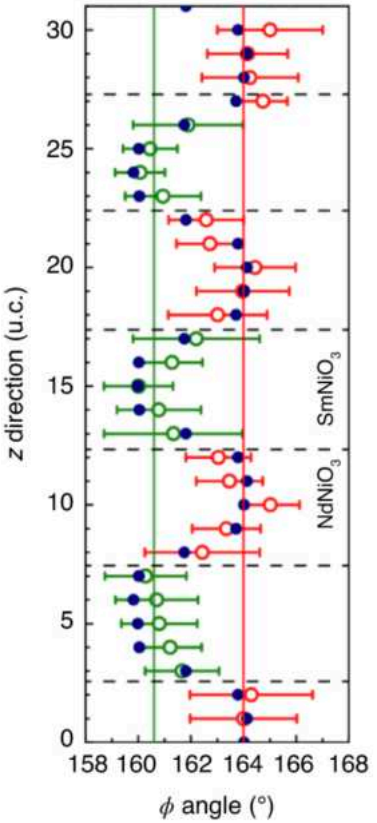
Nickel

Oxygen



2D Gaussian fitting using Atomap documentation in Python

Depth profile



● DFT calculations

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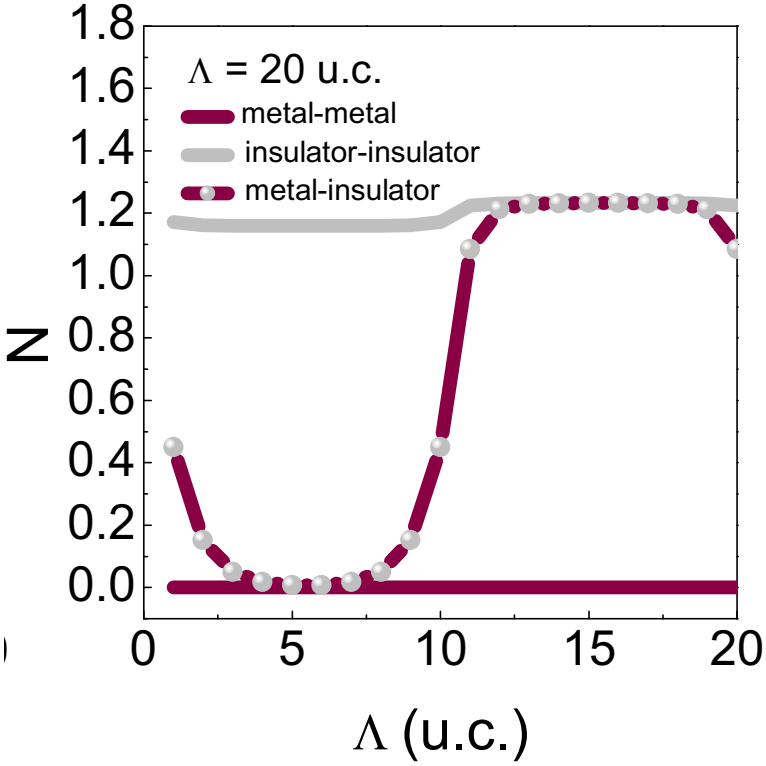
LIÈGE université

Origin of the coupling - cost of having a M-I phase boundary



Metallic- Metallic : $E_{m1}+E_{m2}$

Insulating-Insulating : $E_{i1}+E_{i2}$

Metallic-Insulating : $E_{m1}+E_{i2}+E_{PB}$

$$F(N) = \alpha N^2 + \beta N^4 + \gamma N^6 + \frac{1}{2}\xi_I^2(\nabla N)^2$$

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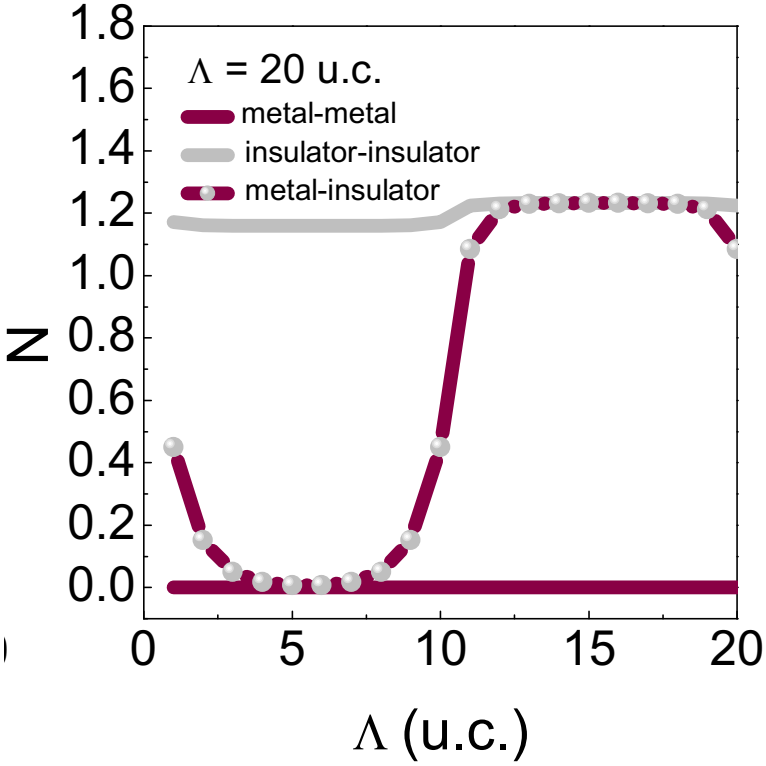
CCQ: Alexandru B. Georgescu, Antoine Georges and Andrew J. Millis

Origin of the coupling - cost of having a M-I phase boundary



Metallic- Metallic : $E_{m1}+E_{m2}$

Insulating-Insulating : $E_{i1}+E_{i2}$

Metallic-Insulating : $E_{m1}+E_{i2}+E_{PB}$

$$F(N) = \alpha N^2 + \beta N^4 + \gamma N^6 + \frac{1}{2}\xi_I^2(\nabla N)^2$$

E_b = phase boundary cost goes as $(\nabla N)^2$ (or $(\nabla Q)^2$)

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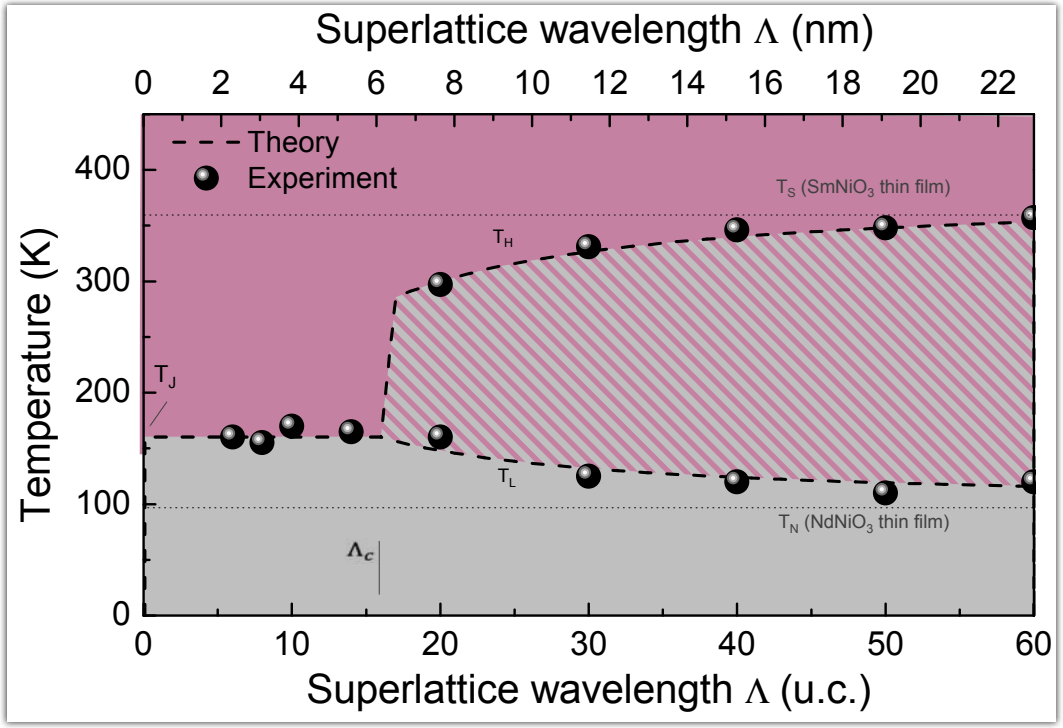
CCQ: Alexandru B. Georgescu, Antoine Georges and Andrew J. Millis

Experimental phase diagram and modelling



$$\Lambda_C = 2m_C$$
when $T_H(m) = T_L(m)$

$$\Lambda_c = 4E_{PB}\frac{K_S T_N + K_N T_S}{K_S K_N (T_S - T_N)}$$

$$T_J = T_L(m_c) = T_H(m_c)$$

$$T_J = \frac{T_N T_S (K_s + K_N)}{K_N T_S + K_S T_N}$$

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C. Dominguez et al. Nature Materials **19**, 1182 (2020)

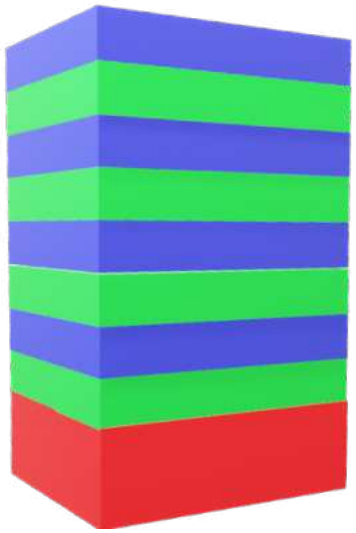
The phase boundary cost E_b is responsible for the coupling of the MI transitions

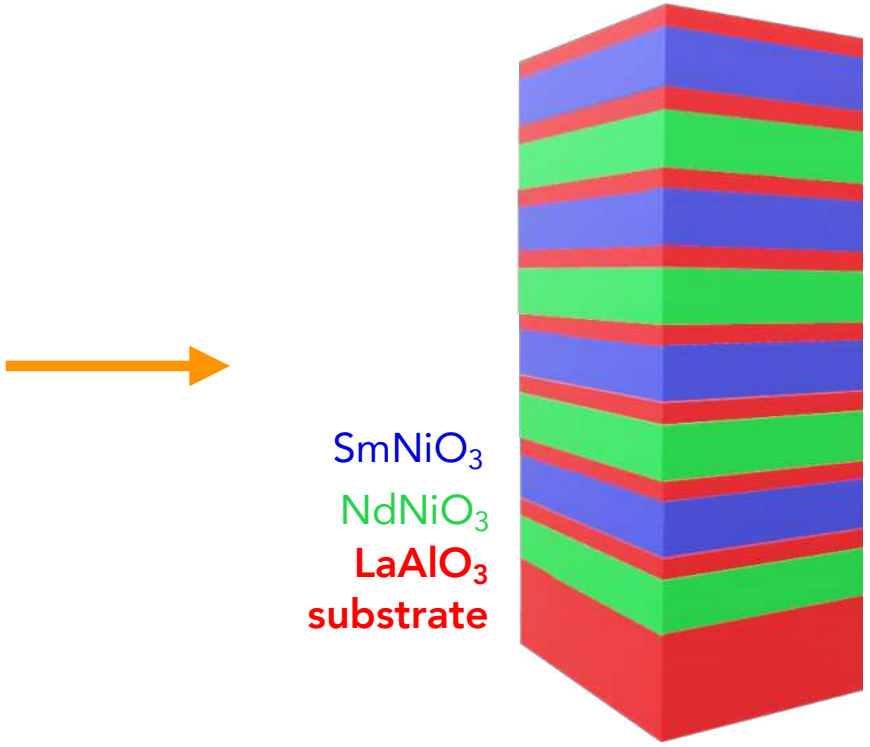
Can one tune this coupling inserting between the $SmNiO_3$ and $NdNiO_3$ layers a simple insulator?

How to control / tune the coupling?

(m $NdNiO_3$/ d $LaAlO_3$/ m $SmNiO_3$/ d $LaAlO_3$)$_L$

(m $NdNiO_3$ / m $SmNiO_3$)$_L$





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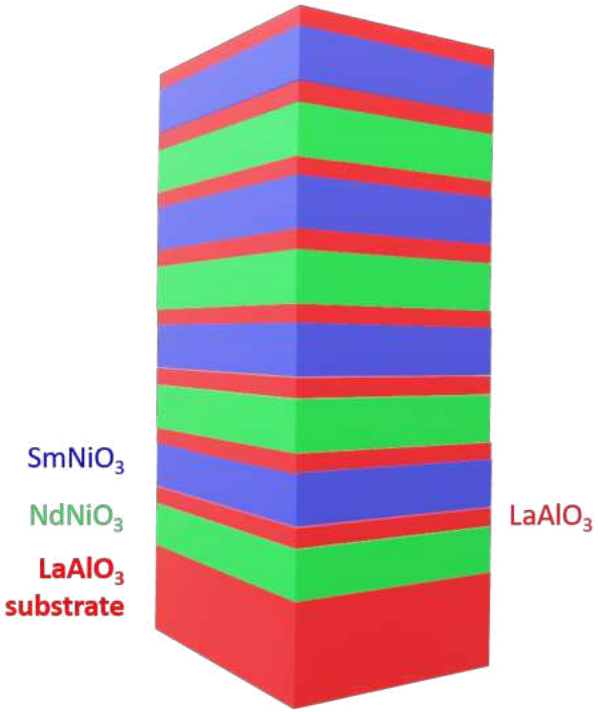
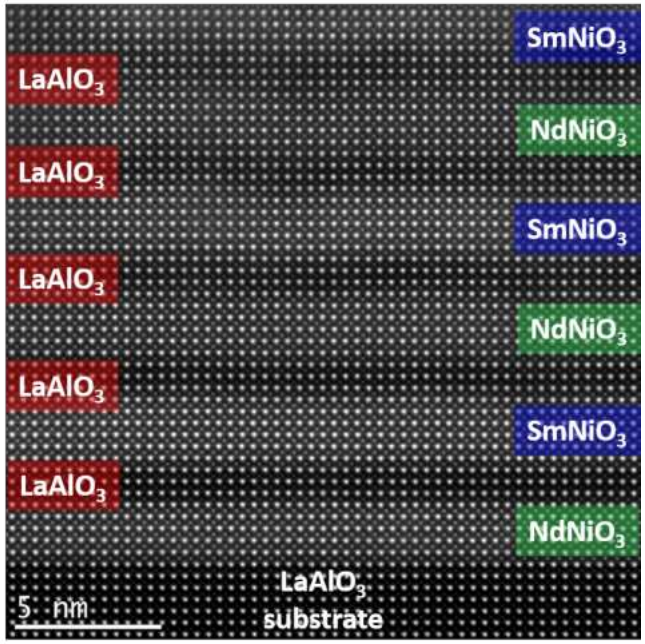
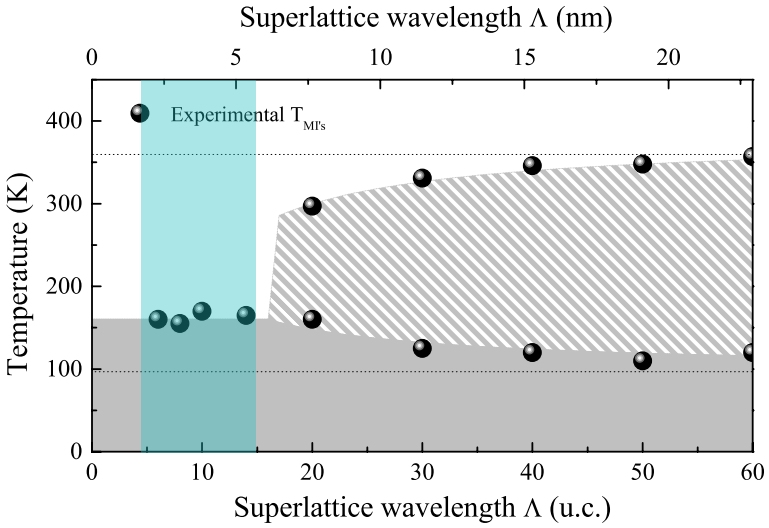
Introducing $LaAlO_3$ layers between the $ReNiO_3$ ones

$SmNiO_3/NdNiO_3$ superlattices with $LaAlO_3$ spacers







Idea: choose a wavelength below Λ_c - m=6

$LaAlO_3$ thickness d, d=0,1,2,3,4 unit cells

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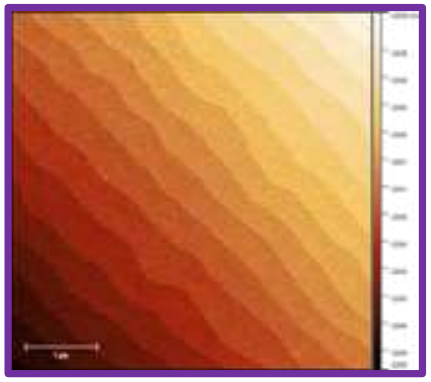
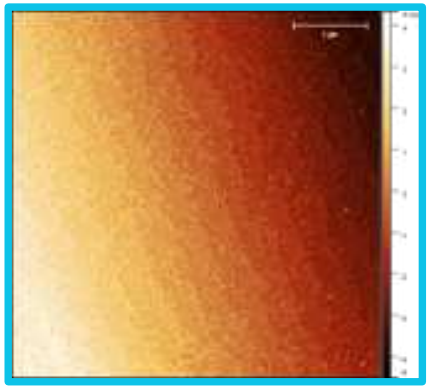
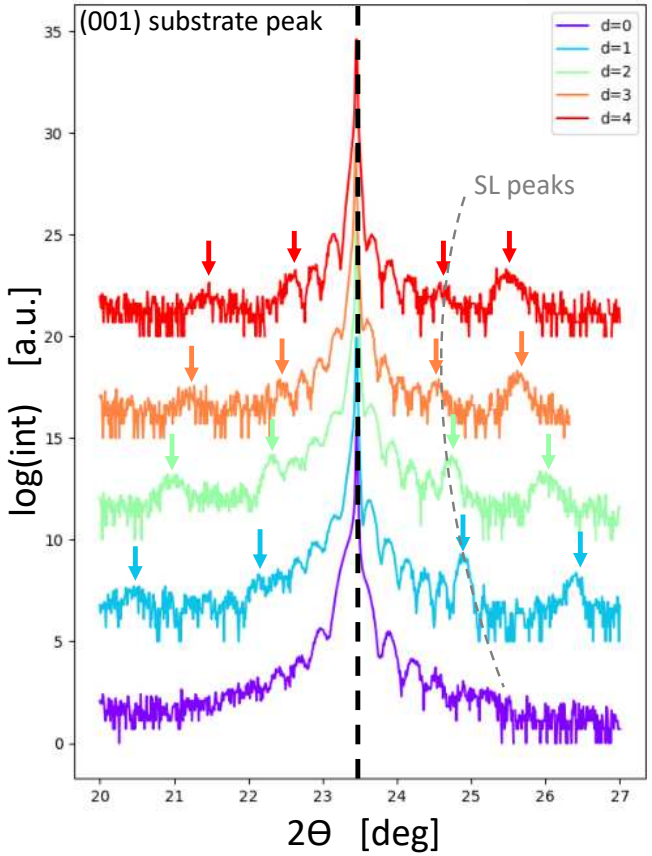
Structural characterization

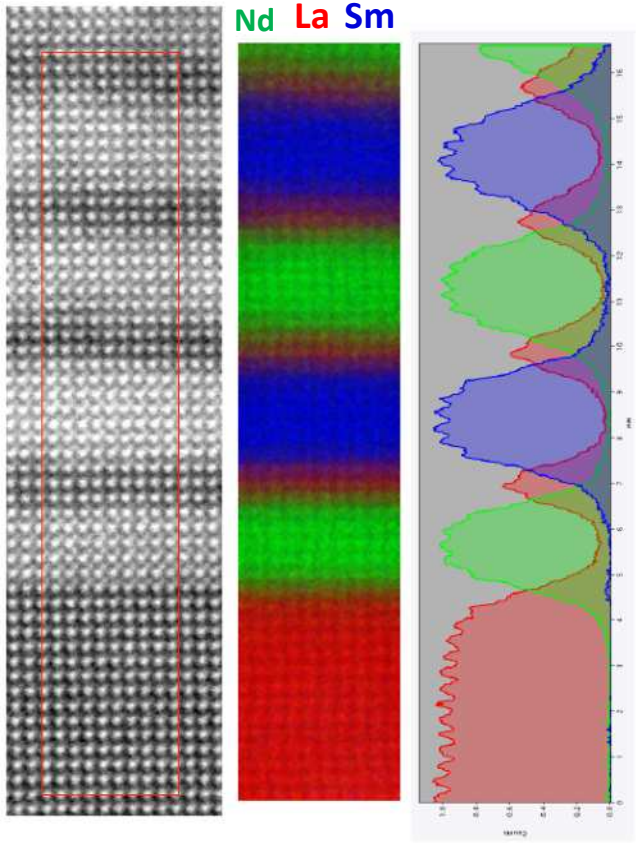
Without $LaAlO_3$ spacer



With $LaAlO_3$ spacer





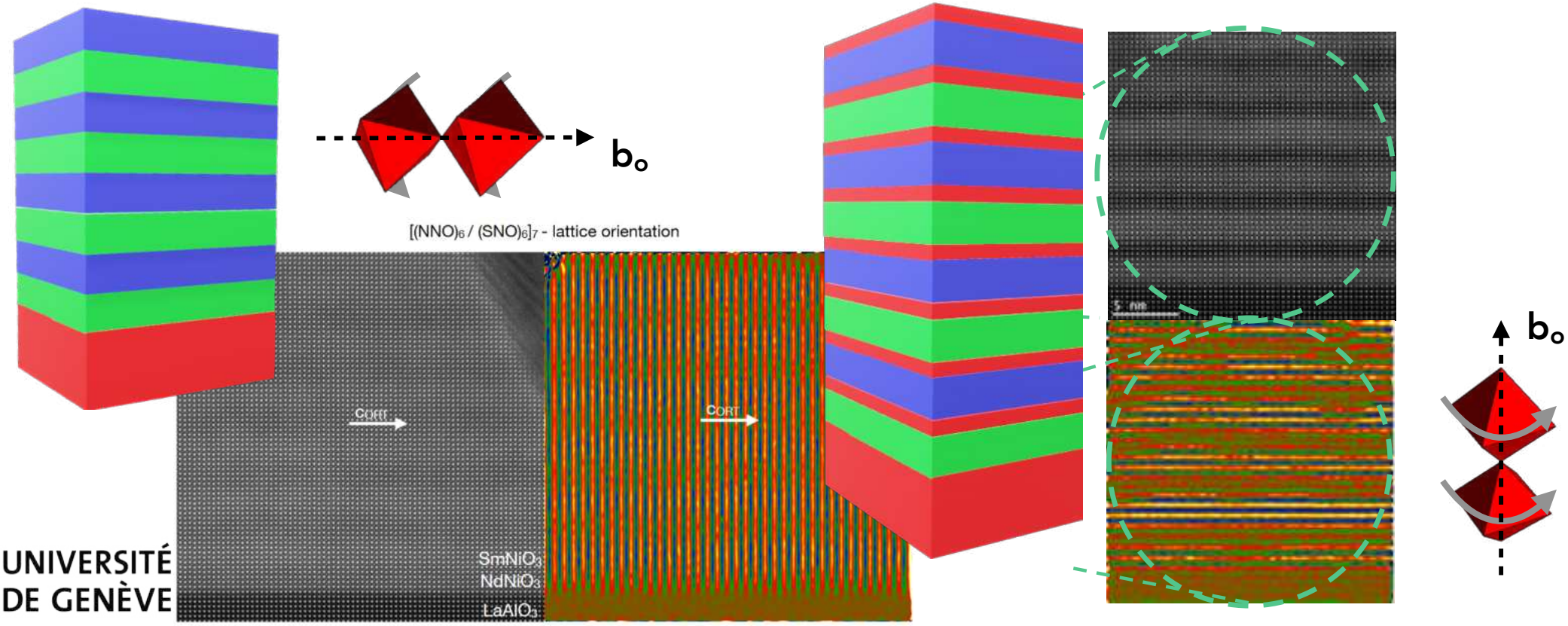


STEM/EELS analyses

Long orthorhombic axis orientation

(m $NdNiO_3$ / m $SmNiO_3$)$_L$

(m $NdNiO_3$/ d $LaAlO_3$/ m $SmNiO_3$/ d $LaAlO_3$)$_L$



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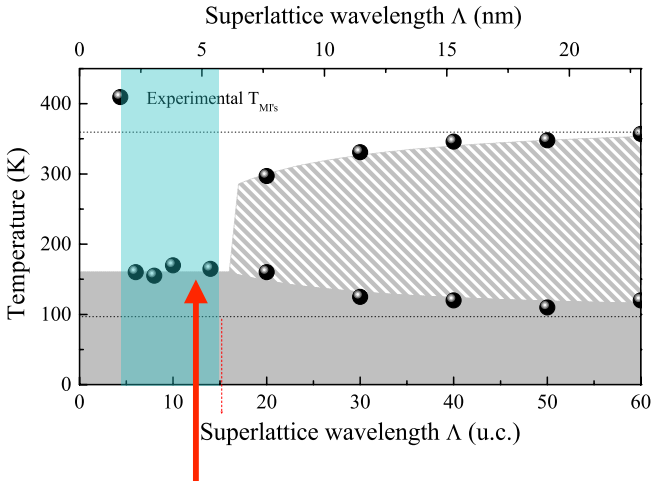
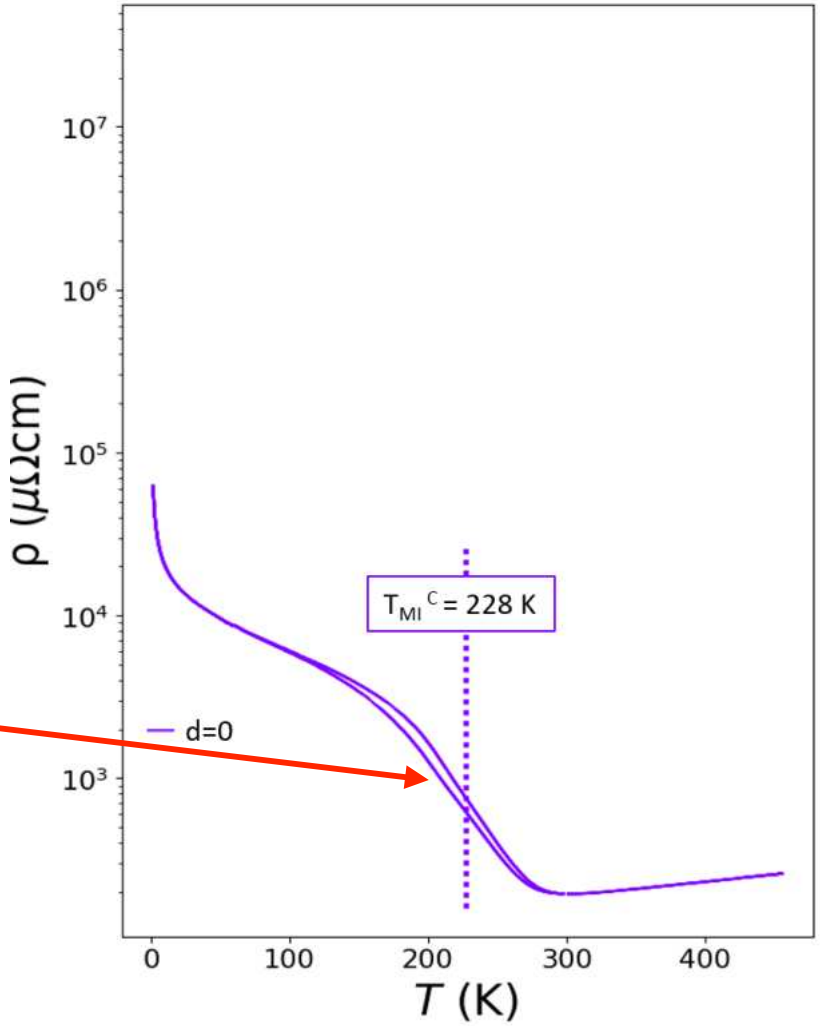
6u.c. $SmNiO_3$/6u.c $NdNiO_3$ superlattices with d-u.c. $LaAlO_3$ spacers



SL without $LaAlO_3$



A single unit cell of $LaAlO_3$ decouples the transitions

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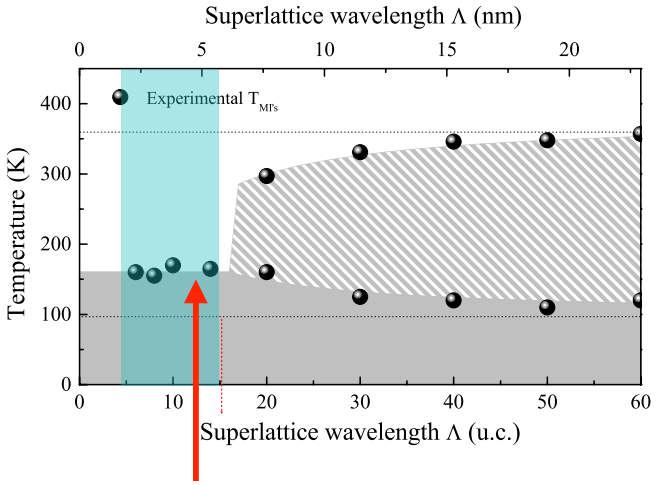
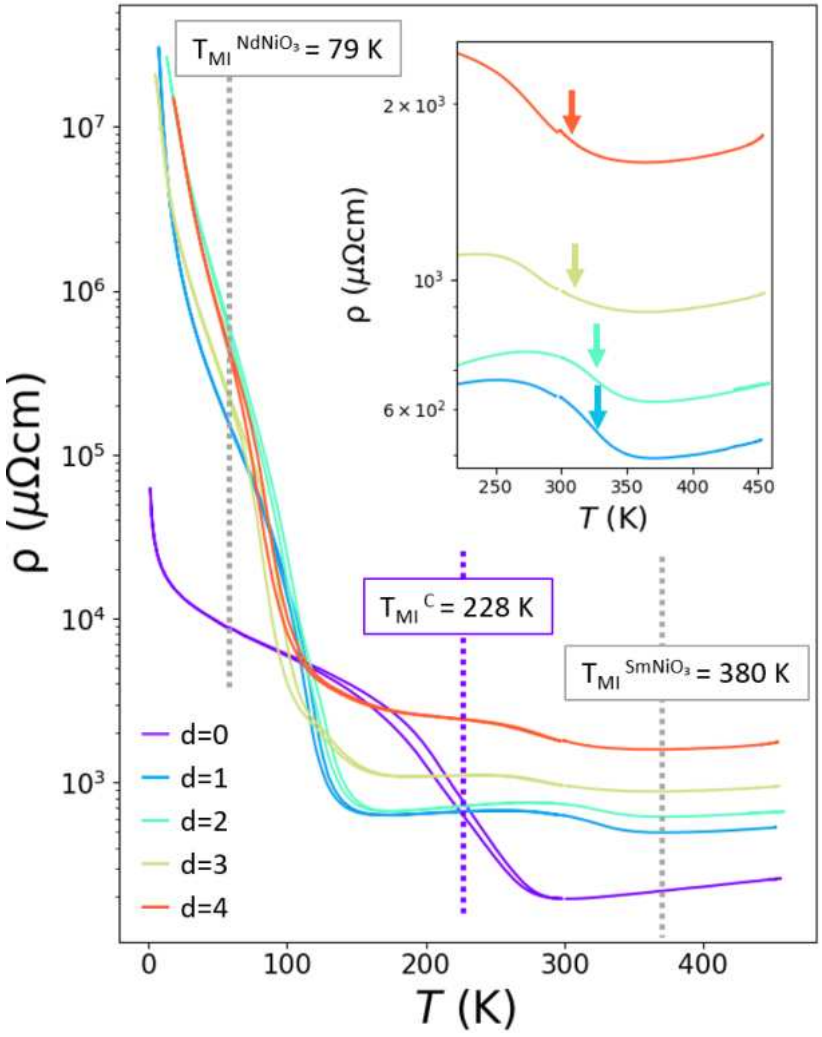
6u.c. $SmNiO_3$/6u.c $NdNiO_3$ superlattices with d-u.c. $LaAlO_3$ spacers



SL without $LaAlO_3$



A single unit cell of $LaAlO_3$ decouples the transitions

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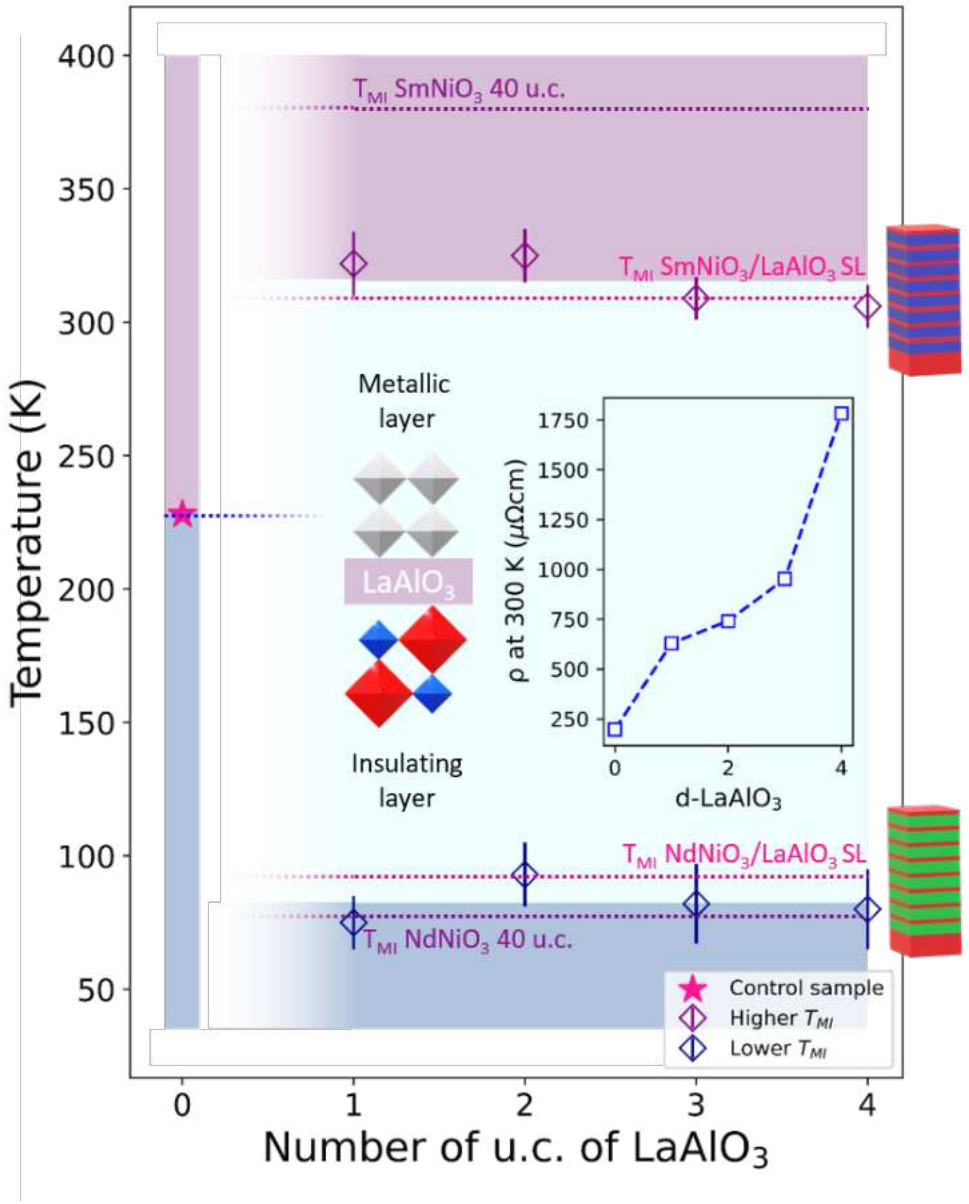
Phase diagram

Lucia Varbaro et al.
Advanced Electronic
Materials 2201291 (2023)



$SmNiO_3/LaAlO_3$

$NdNiO_3/LaAlO_3$

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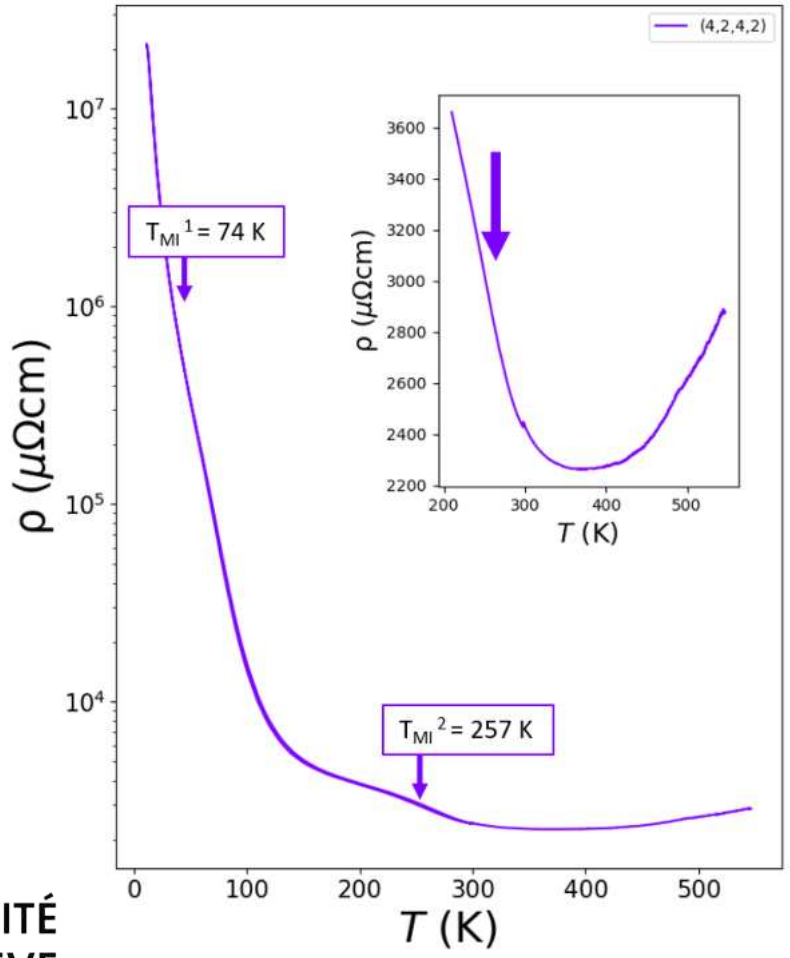
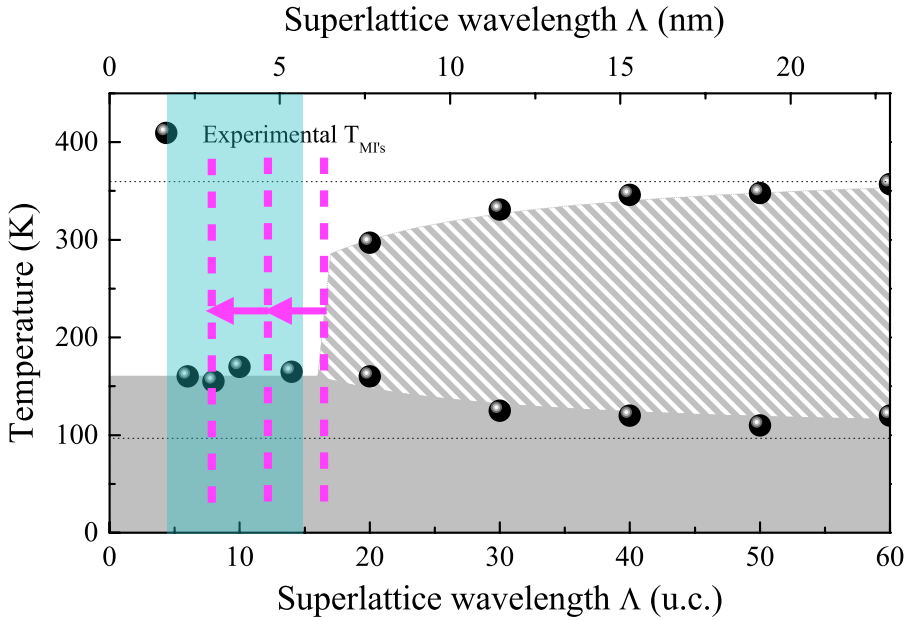
Similar behaviour for a 4u.c. $SmNiO_3$/4u.c $NdNiO_3$ SL with 2-u.c. $LaAlO_3$





Λ_c is going down

E_b is going down

$E_b \sim (\nabla N)^2$

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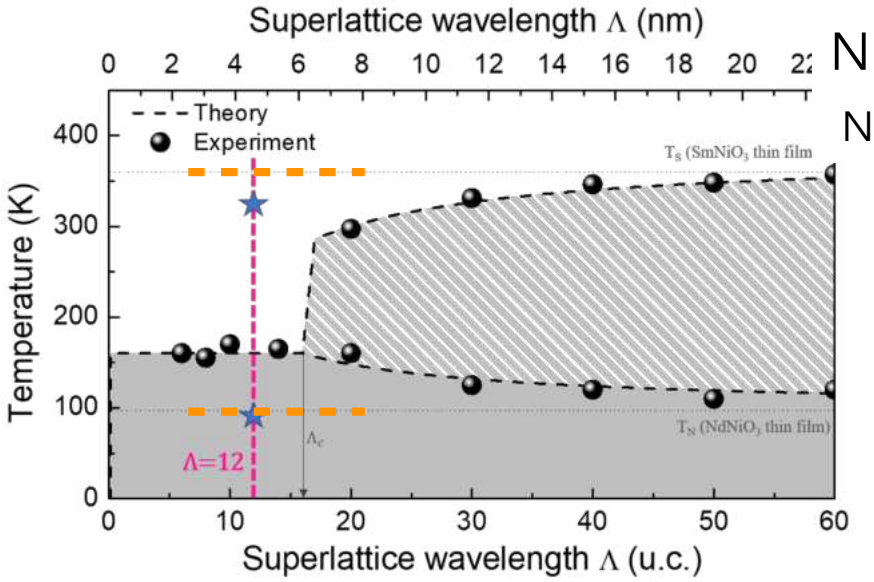
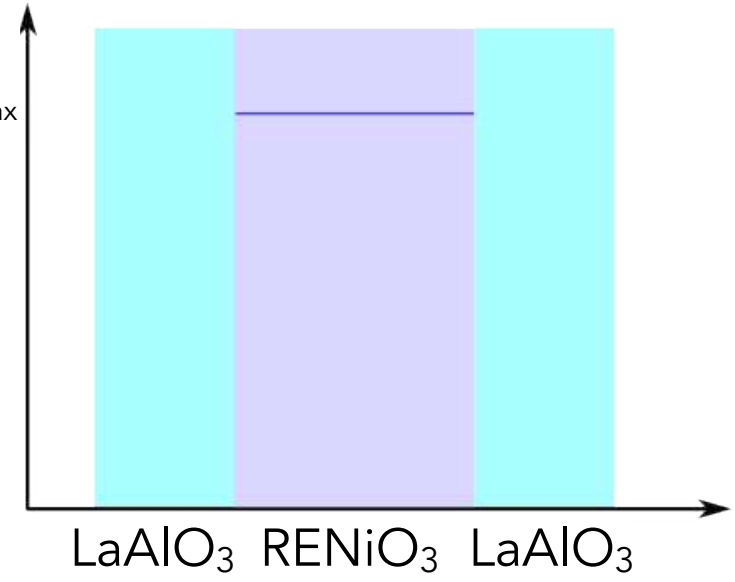
Behavior of N in the new SL

Λ_c is going down
E_b is going down
$E_b \sim (\nabla N)^2$

N undefined in $LaAlO_3$





The observed T_{MI}'s are similar to the ones of large wavelengths SL

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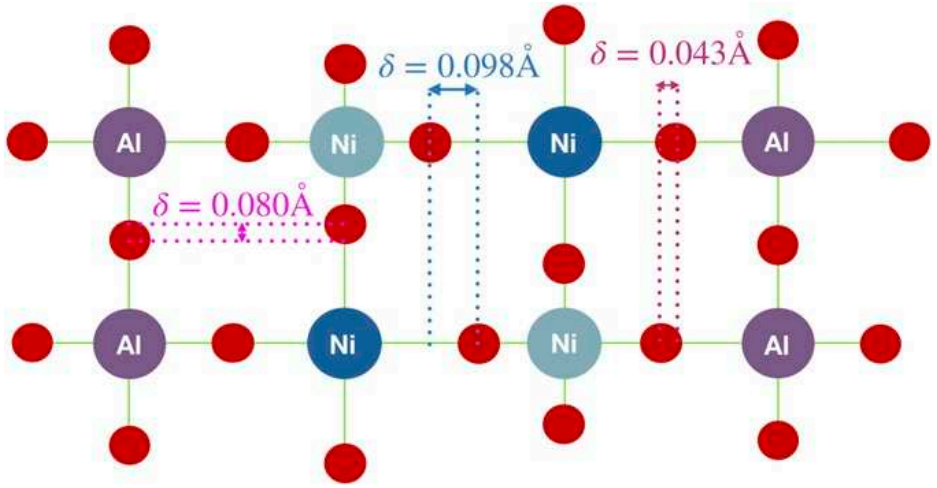
Behavior of Q in the new SL

Q - structural - « can be defined » in $LaAlO_3$ - has to be continuous

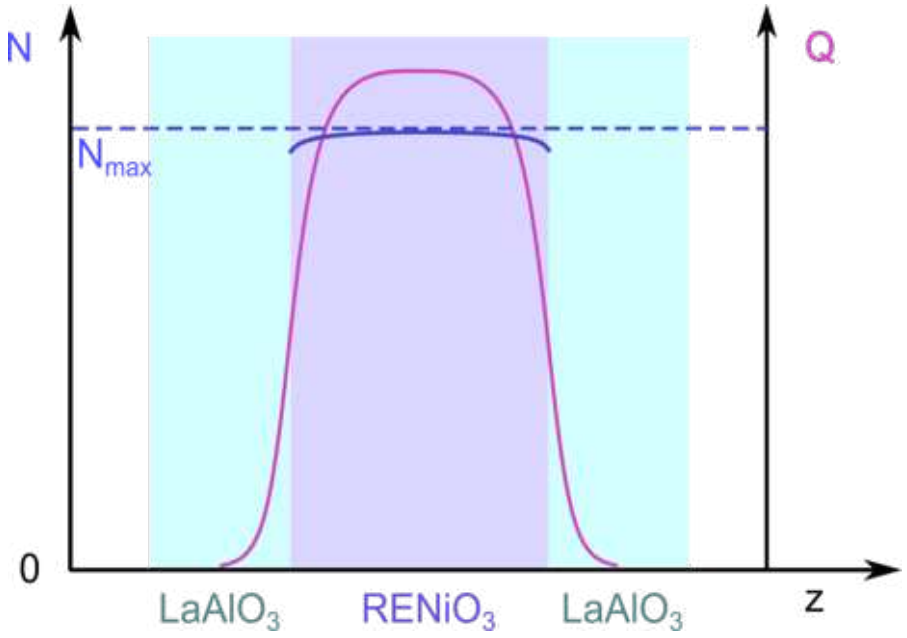
Evolves very sharply at the interfaces - « propagates » into $LaAlO_3$



$NdNiO_3/NdAlO_3$

A.B. Georgescu et al. PNAS **116**, 14434 (2019)
See also A.S. Disa et al. PRM **1**, 024410 (2017)

Q and N



What can one conclude?

$(\nabla Q)^2$ does not cost much energy since the MIT's are not affected

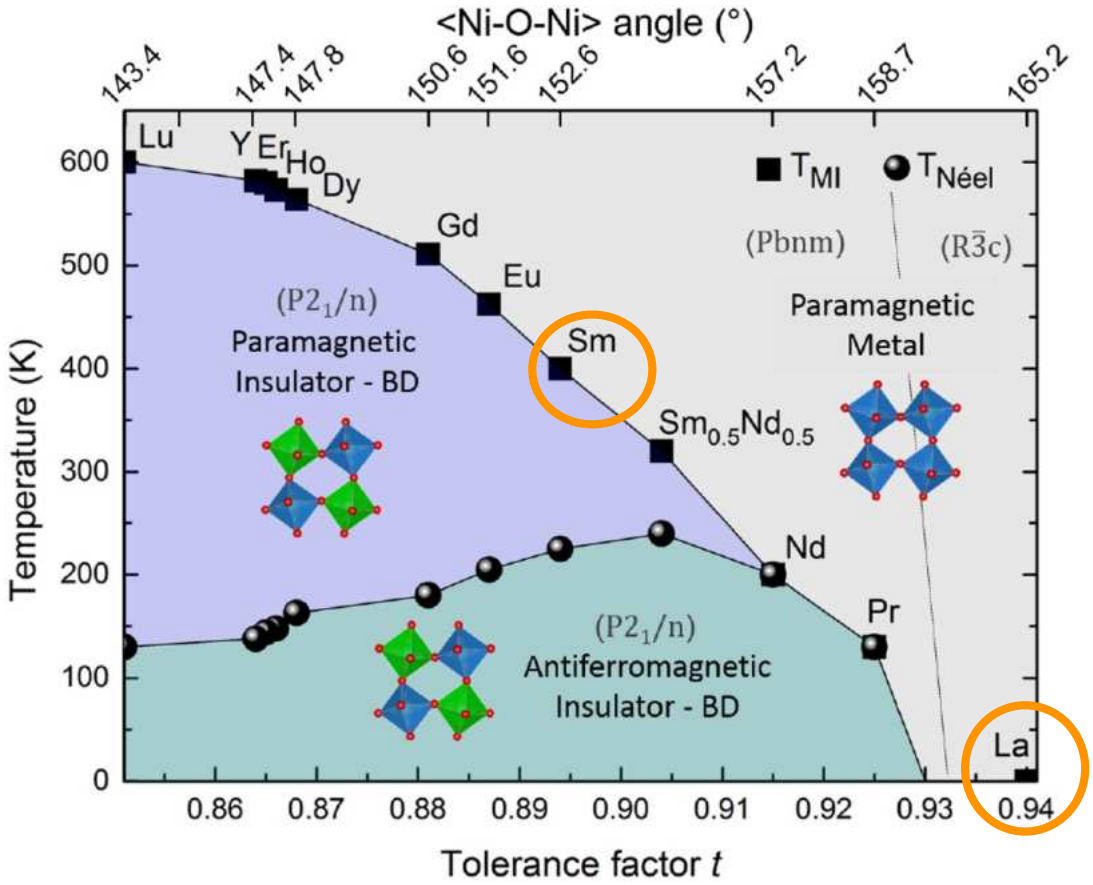
N is the leading order parameter controlling E_b and the coupling

Lucia Varbaro et al. Advanced Electronic Materials 2201291 (2023)

The phase boundary cost E_b is responsible for the coupling of the MI transitions

Can one use the phase boundary cost E_b to turn a metal into an insulator?

Possible choice for the constituent materials



Possible difficulties:

$LaNiO_3$ - rhombohedral and « very » metallic

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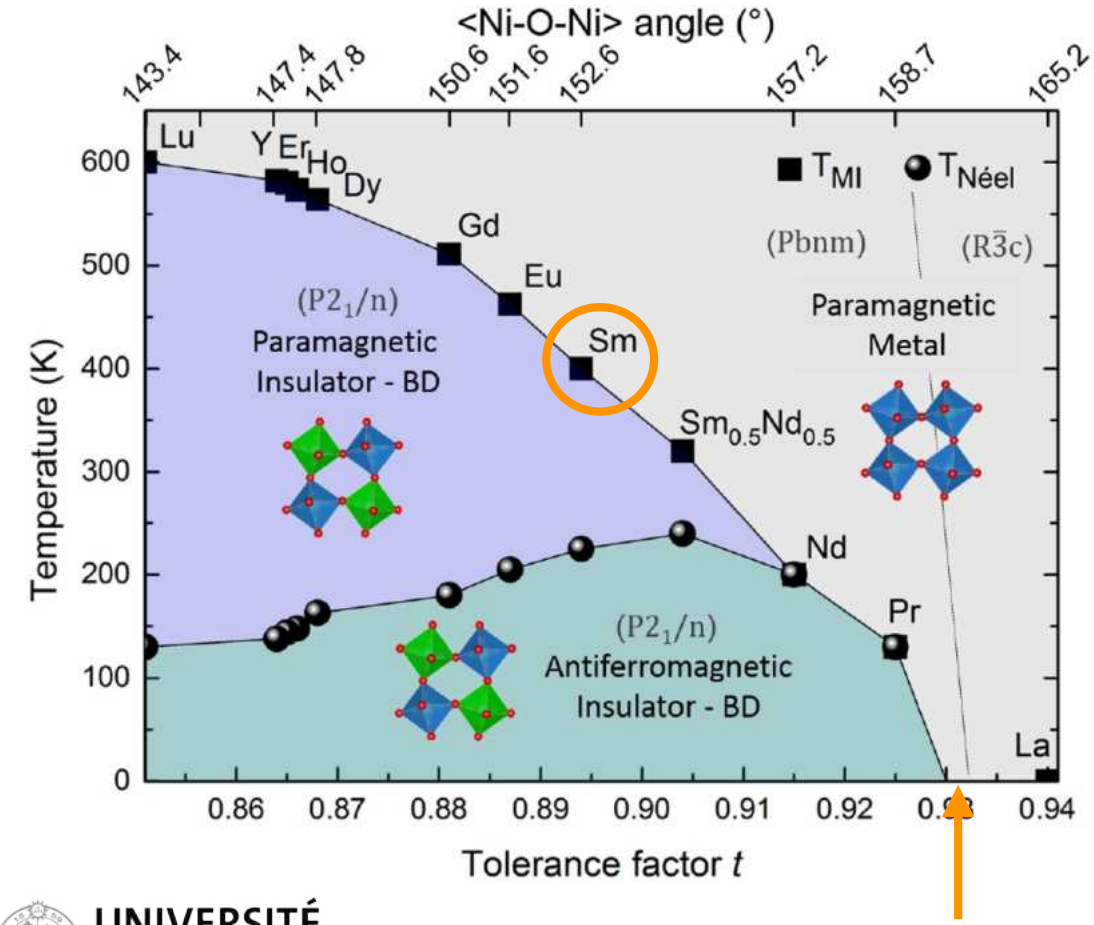
Possible choice for the constituent materials



Possible difficulties:

$LaNiO_3$ - rhombohedral and
« very » metallic

A better choice (?):

An orthorhombic solid solution of $LaNiO_3$ and $NdNiO_3$

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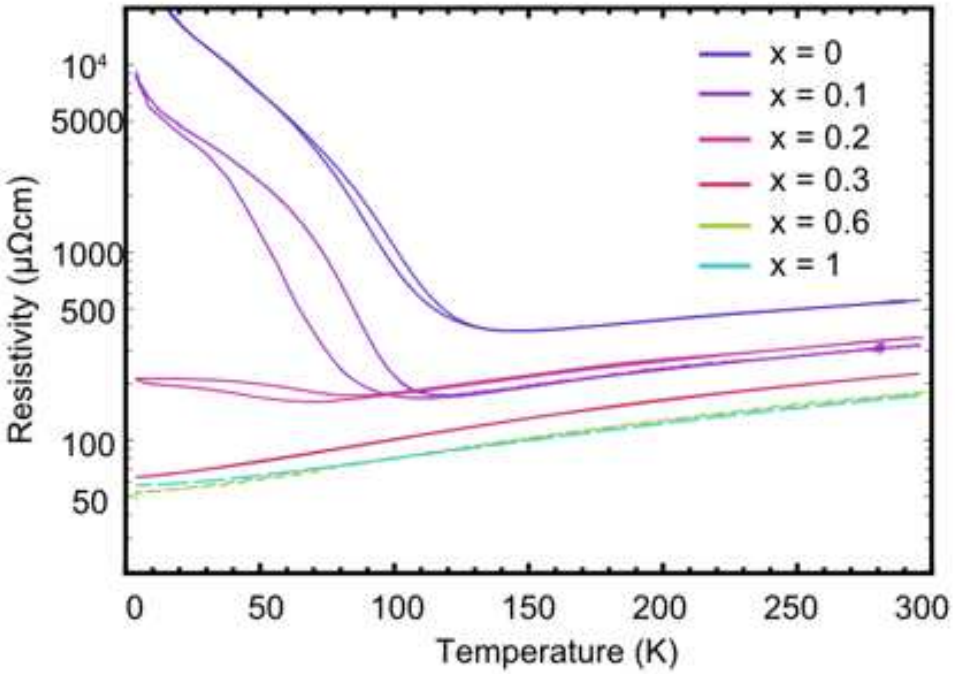
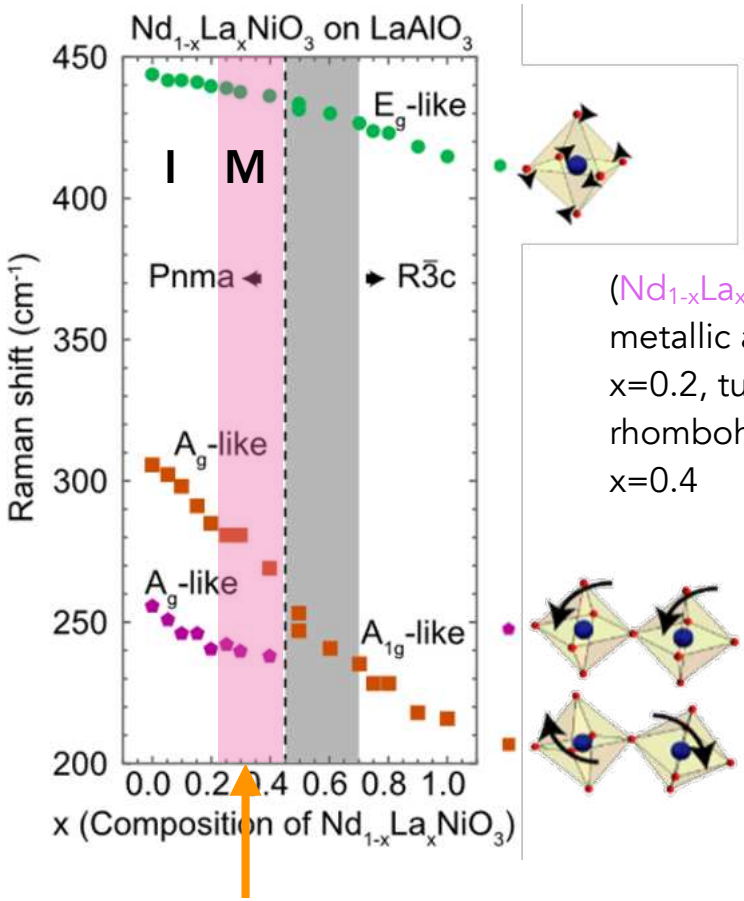
Solid solutions $(Nd_{1-x}La_x)NiO_3$



J. Fowlie et al. APL Mater. **9**, 081119 (2021)



$(Nd_{1-x}La_x)NiO_3$: fully metallic above x=0.2, turns rhombohedral at x=0.4

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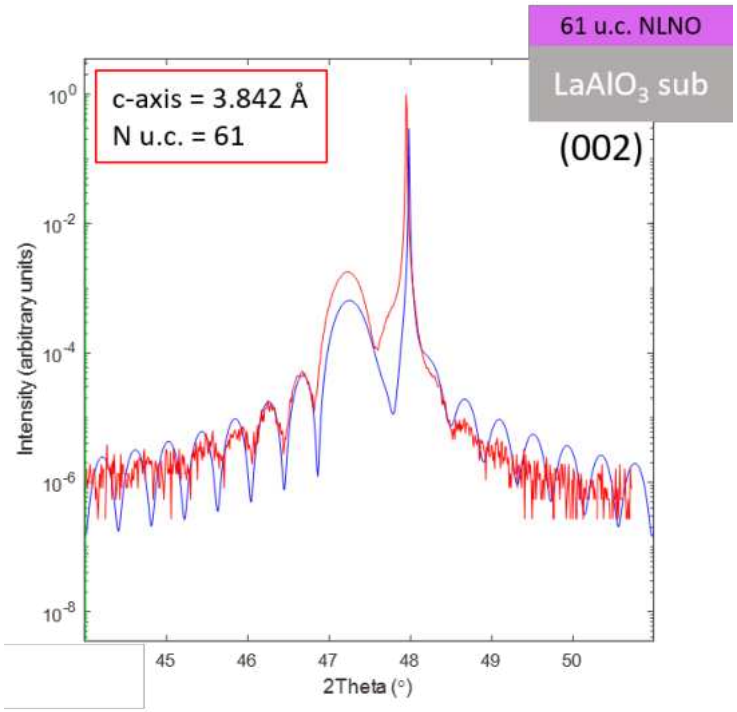
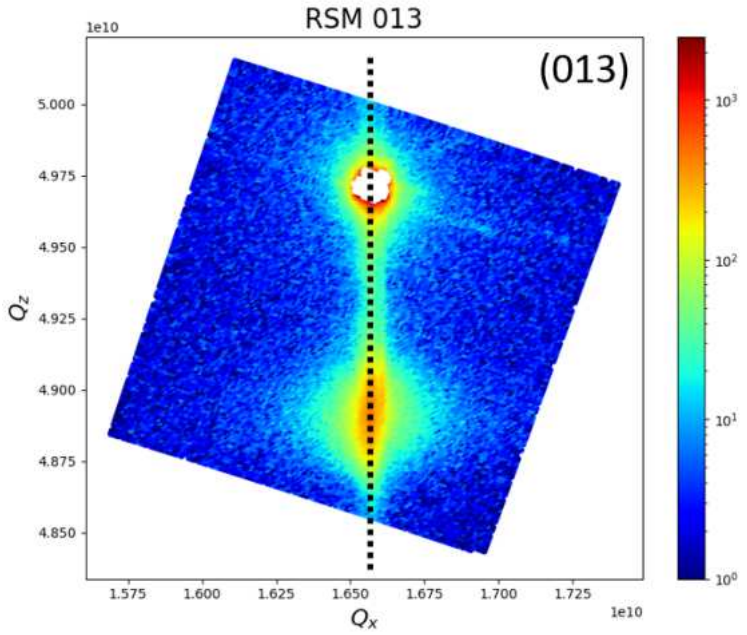
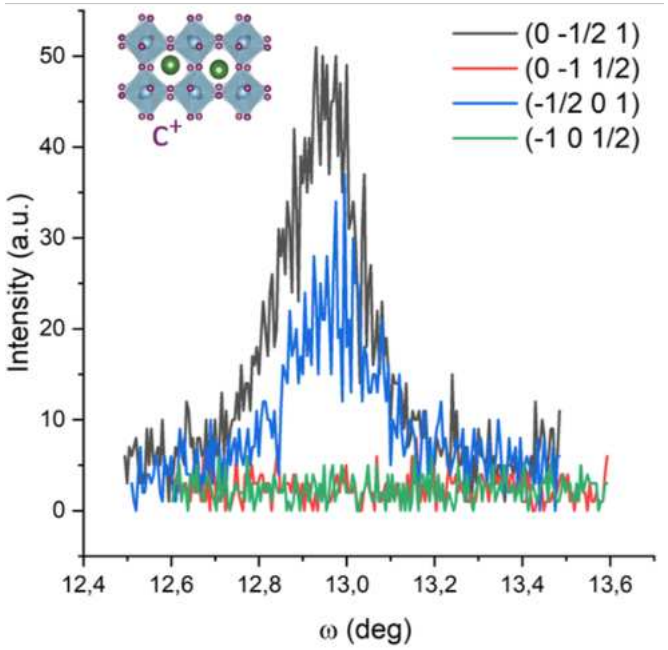
$(Nd_{0.7}La_{0.3})NiO_3$ on (001) $LaAlO_3$ - XRD



θ-2θ scan





Reciprocal space map

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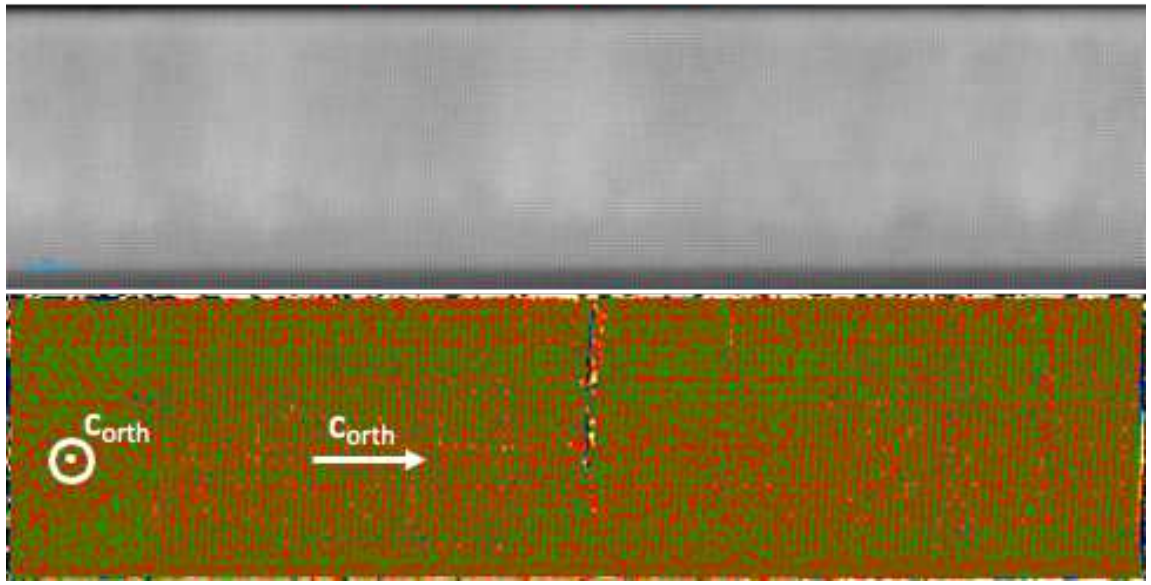
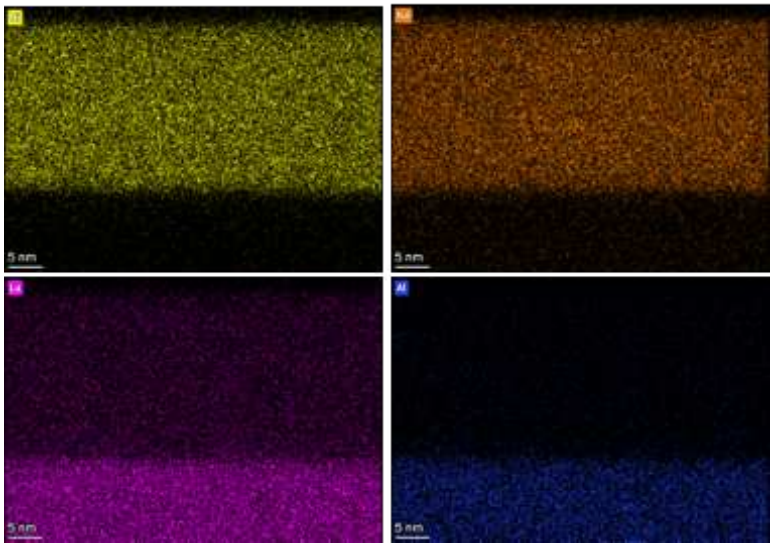
$(Nd_{0.7}La_{0.3})NiO_3$ on (001) $LaAlO_3$ - STEM/EDX

HAADF STEM image + GPA



- EDX composition ratio: La/Nd ~ 0.3/0.7
- Homogeneous distribution



Bernat Mundet et al. APL Materials 12, 031124 (2024)

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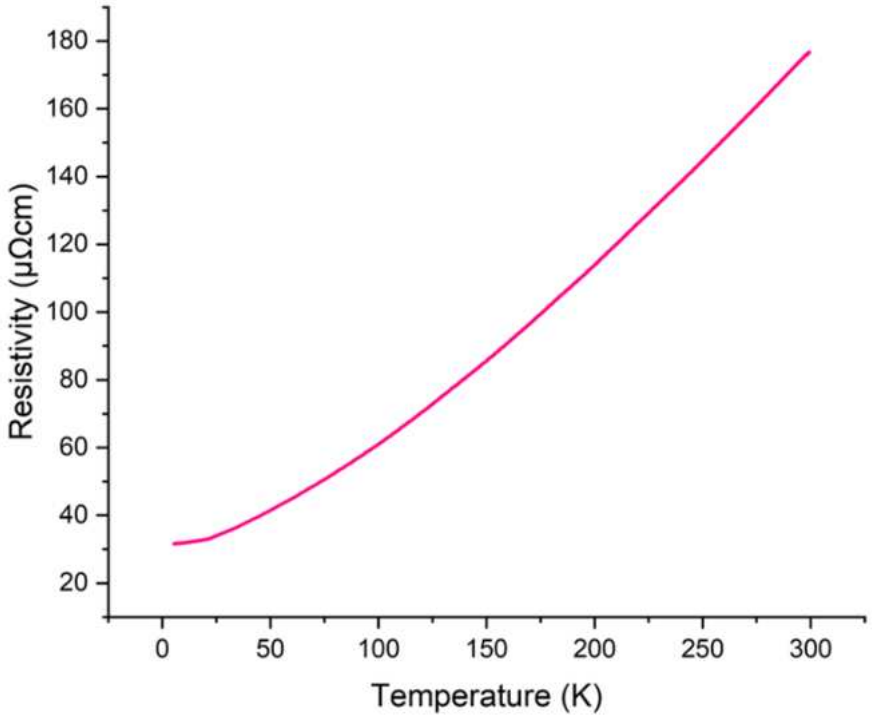
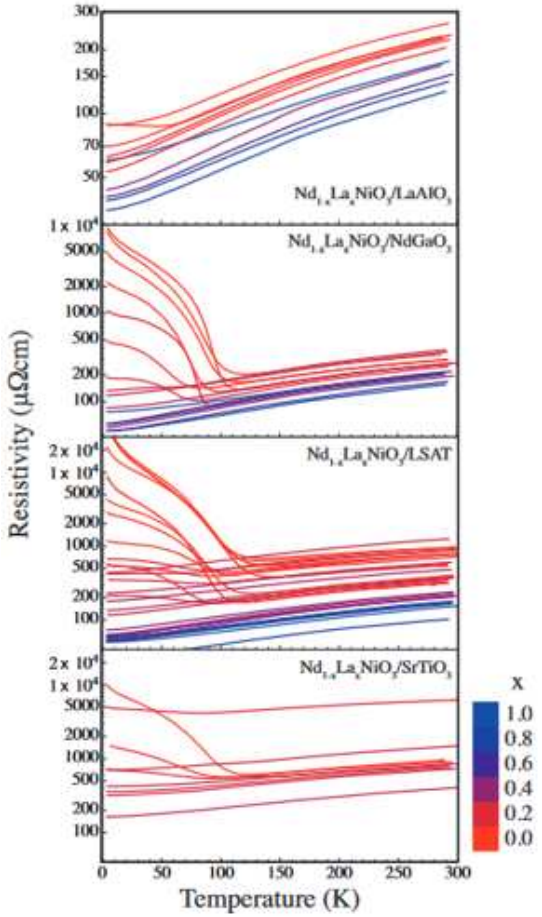
$(Nd_{0.7}La_{0.3})NiO_3$ on (001) $LaAlO_3$ - transport





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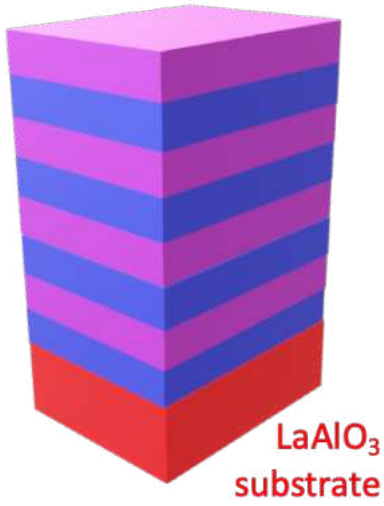
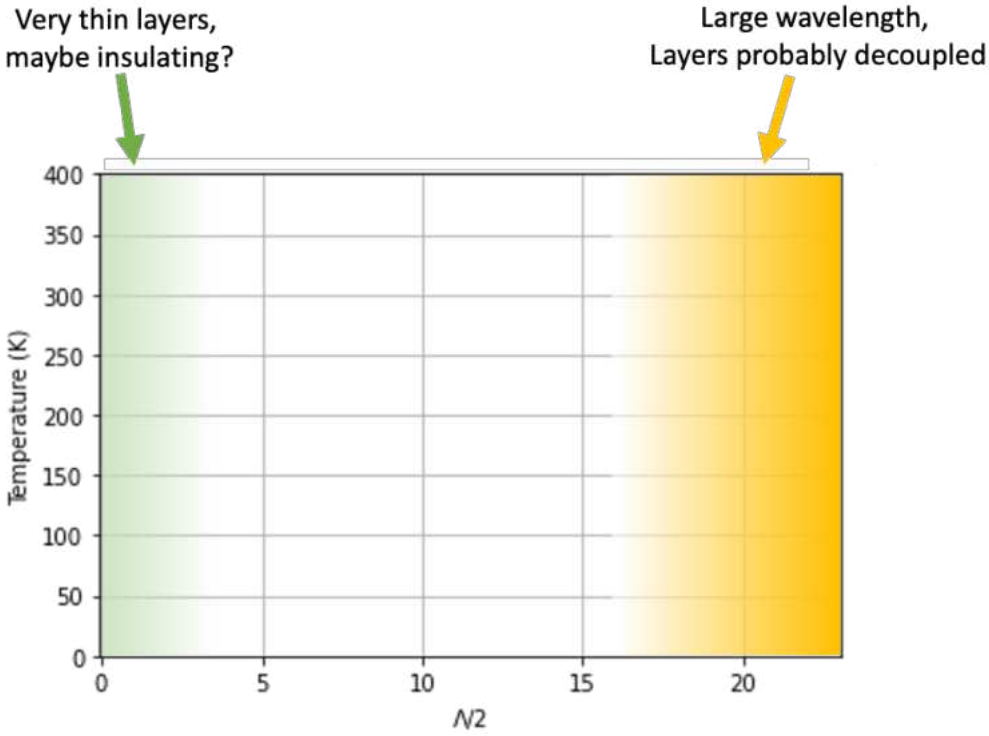
Jennifer Fowlie, PhD thesis, Geneva (2018)

m-$(Nd_{0.7}La_{0.3})NiO_3$/m-$SmNiO_3$ SL

$(m\ SmNiO_3\ /\ m\ Nd_{1-x}La_xNiO_3)_L$





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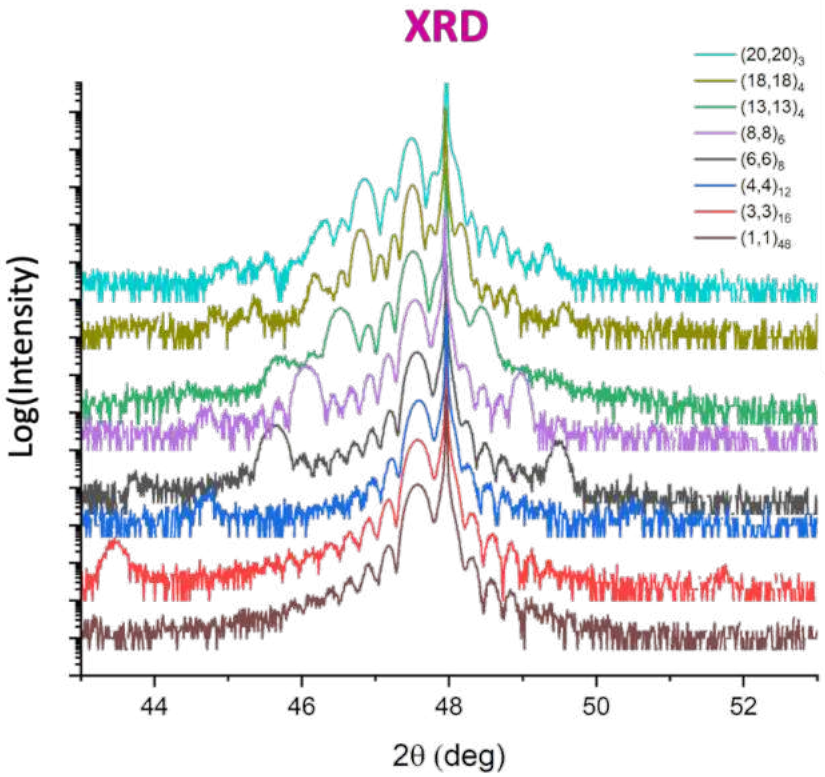
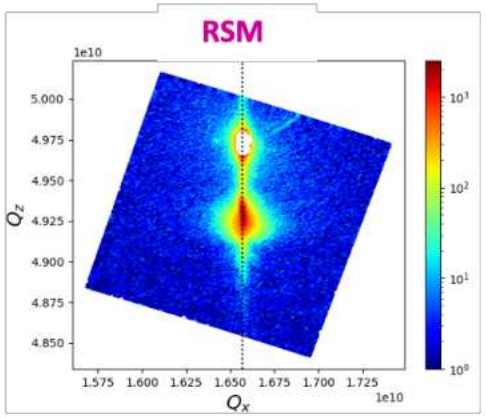
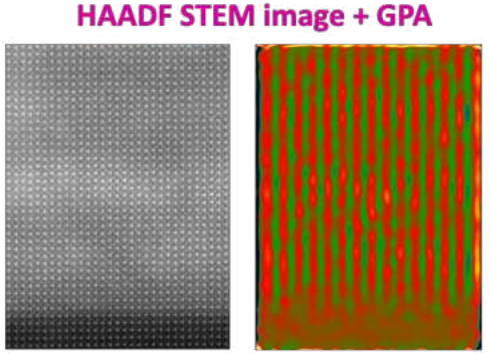
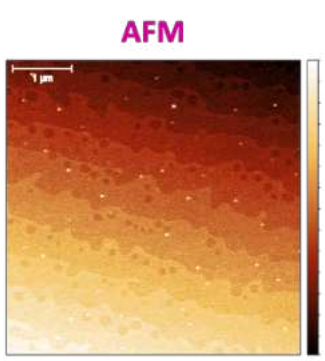
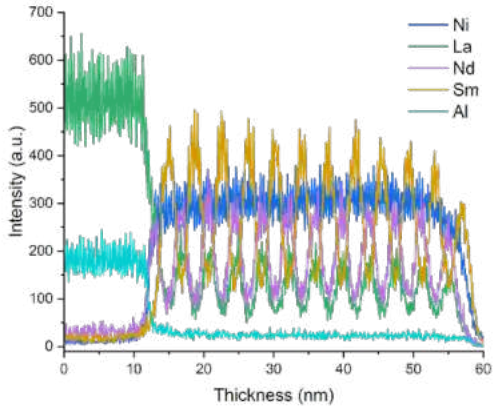
m-$(Nd_{0.7}La_{0.3})NiO_3$/m-$SmNiO_3$ SL - characterisation











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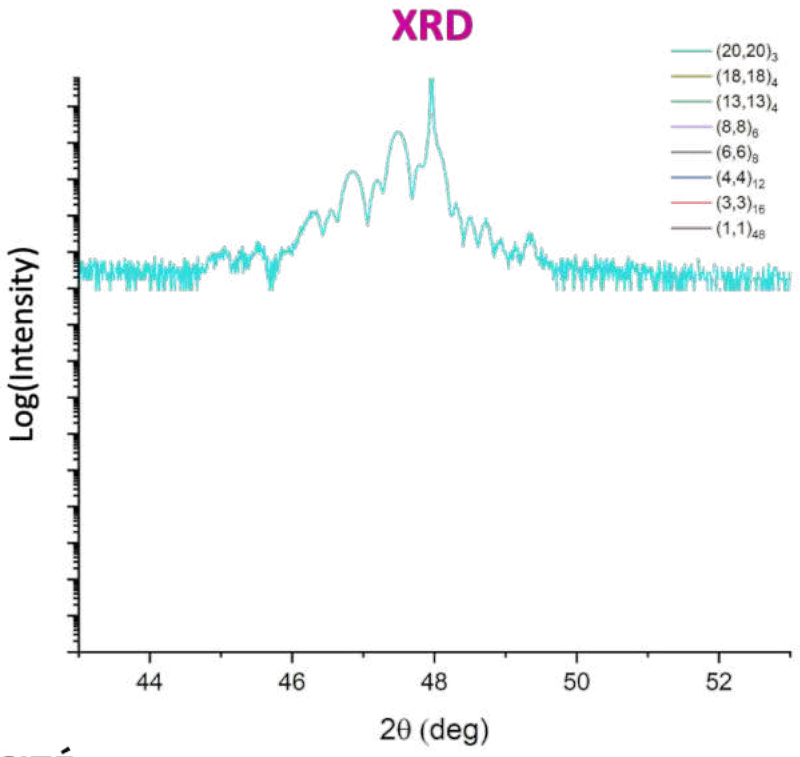
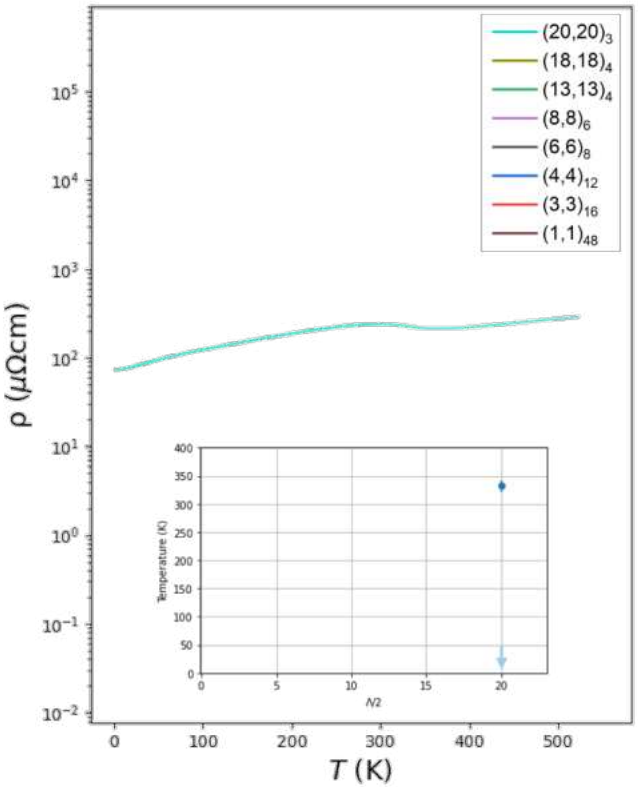
m-$(Nd_{0.7}La_{0.3})NiO_3$/m-$SmNiO_3$ SL - transport data



20/20



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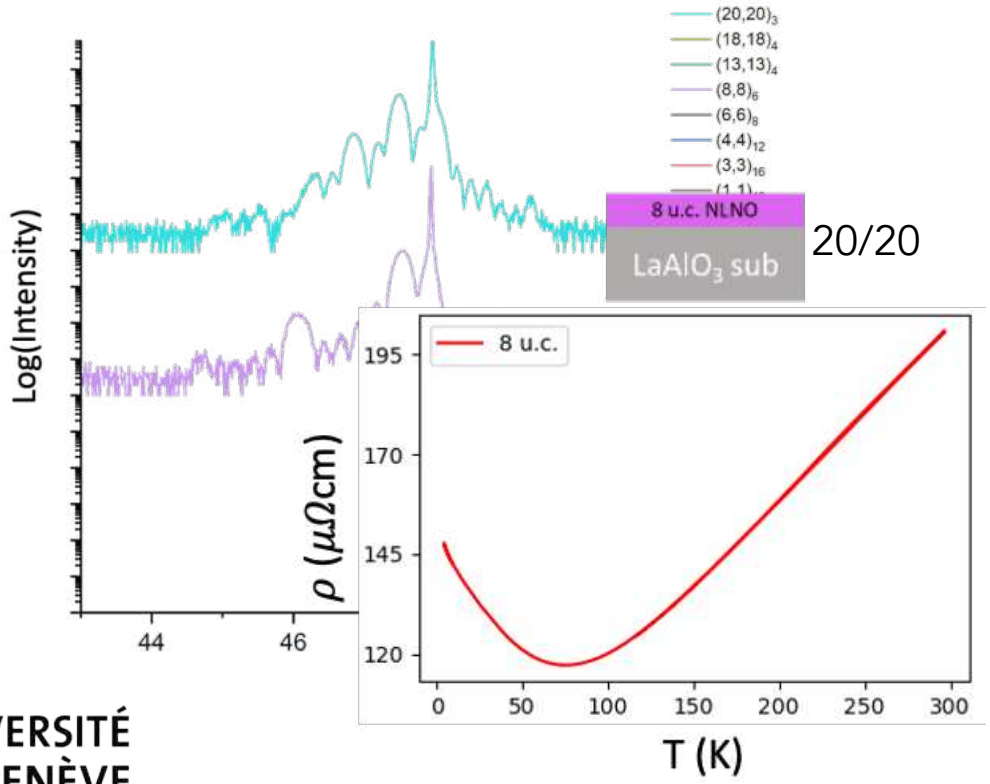
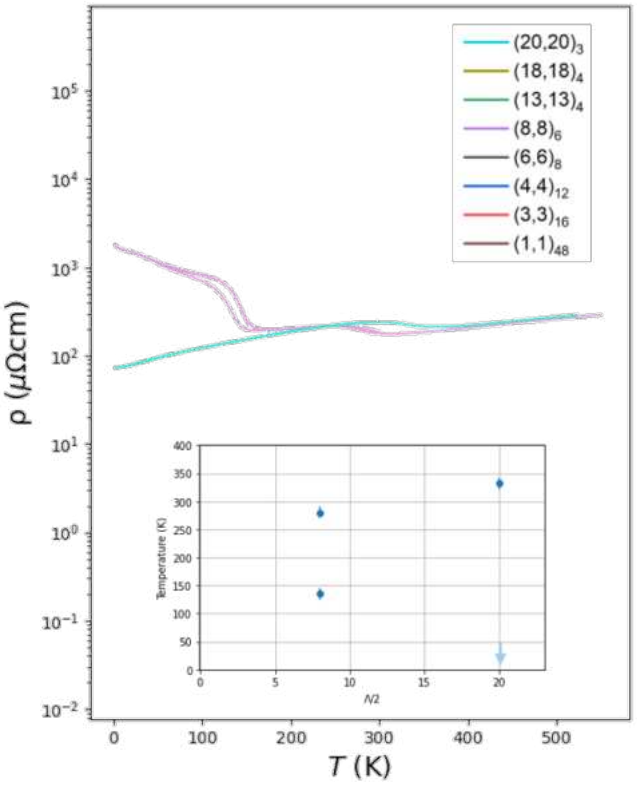
m-$(Nd_{0.7}La_{0.3})NiO_3$/m-$SmNiO_3$ SL - transport





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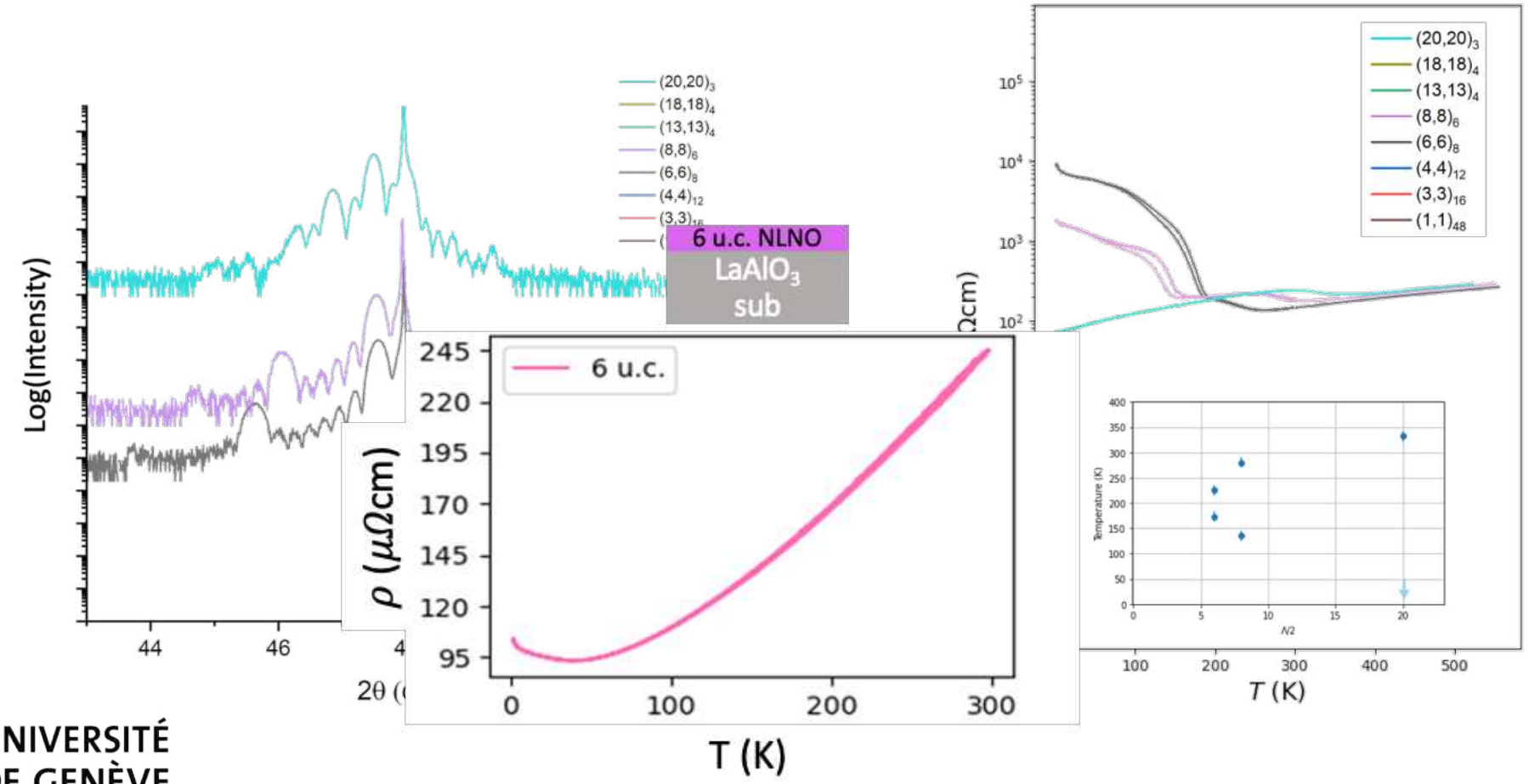
m-$(Nd_{0.7}La_{0.3})NiO_3$/m-$SmNiO_3$ SL - transport



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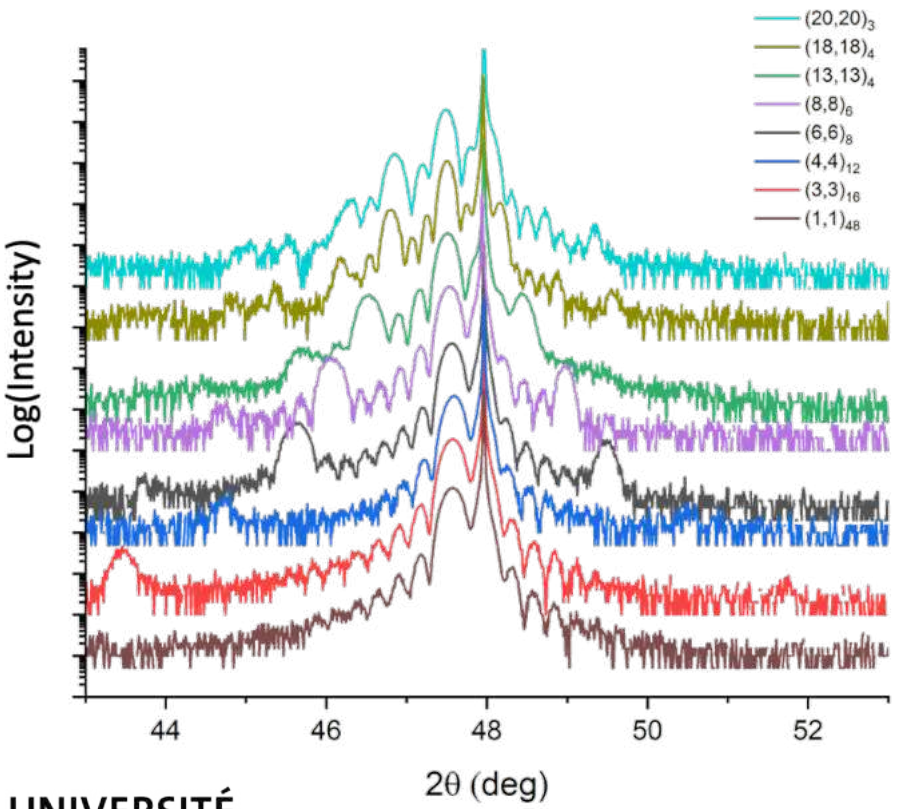
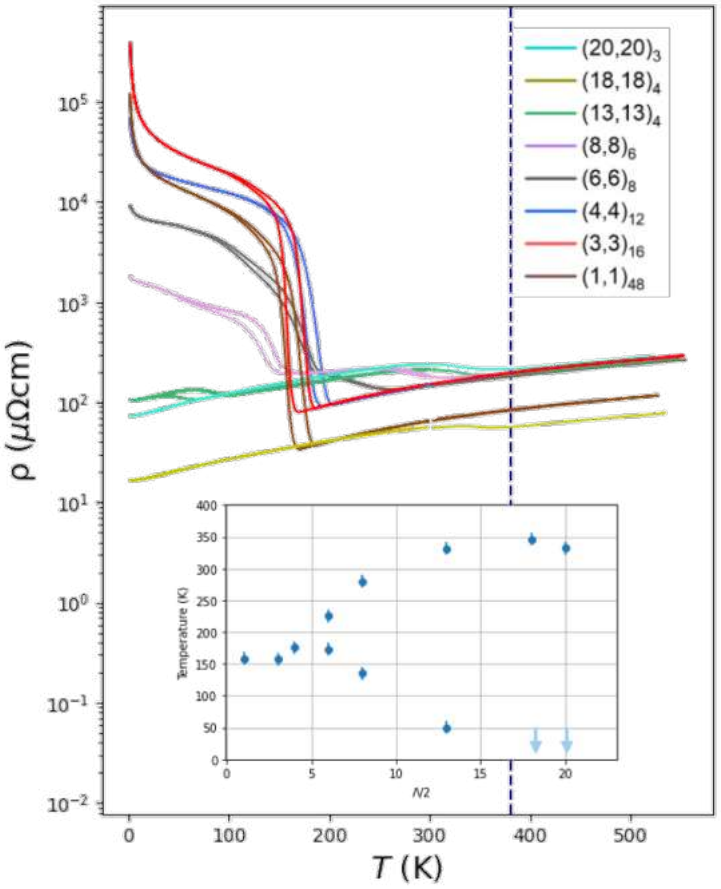
m-$(Nd_{0.7}La_{0.3})NiO_3$/m-$SmNiO_3$ SL - the full series





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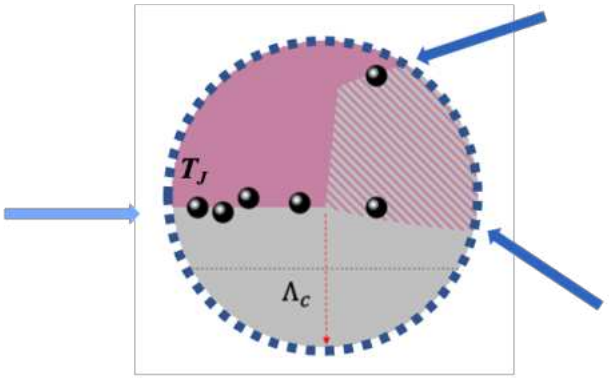
m-$(Nd_{0.7}La_{0.3})NiO_3$/m-$SmNiO_3$ SL - the full series

Joint temperature

$$T_J = \frac{T_N T_S (K_s + K_N)}{K_N T_S + K_S T_N}$$



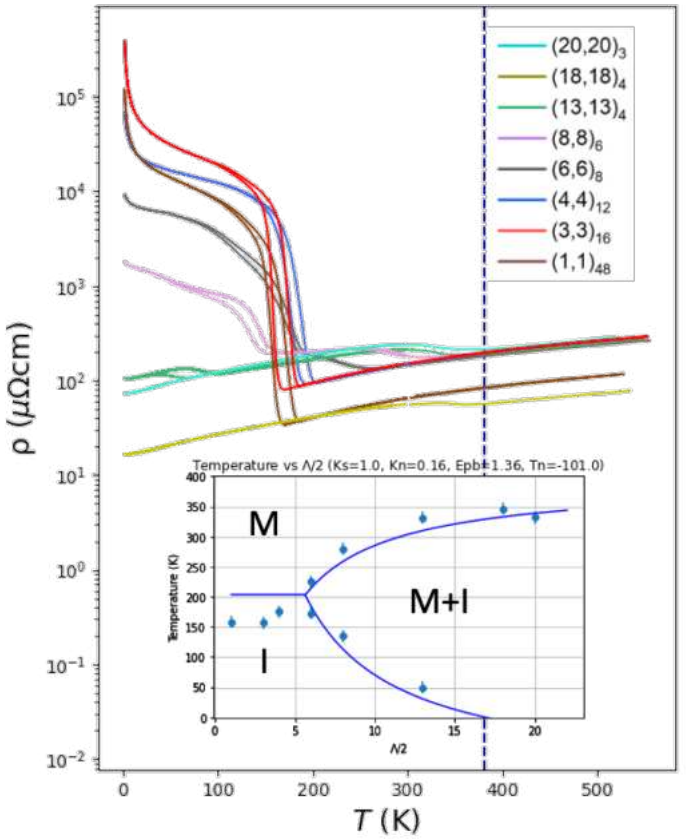
Upper branch:

$$T_H = T_N \left(1 - \frac{2E_{PB}}{K_S m}\right)$$

Lower branch:

$$T_L = T_N \left(1 + \frac{2E_{PB}}{K_N m}\right)$$

K_N/K_S =0.16
E_{PB} = 1.36
T_{NLNO} ∽ -100 K
T_{SNO}= 392 K



Claribel Domínguez et al., Nat. Mater. 19, 1182–1187 (2020)

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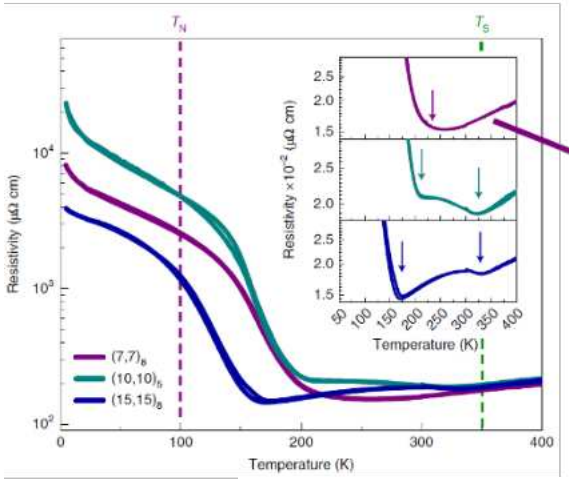
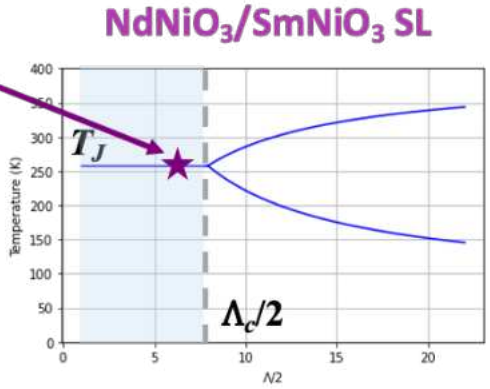
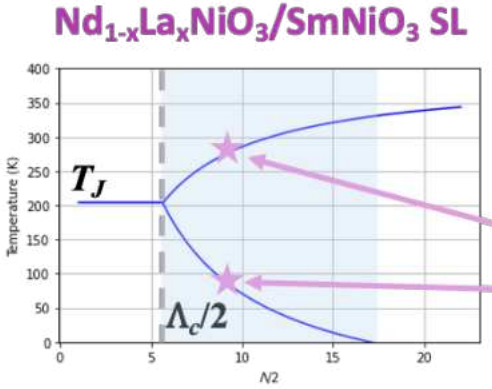
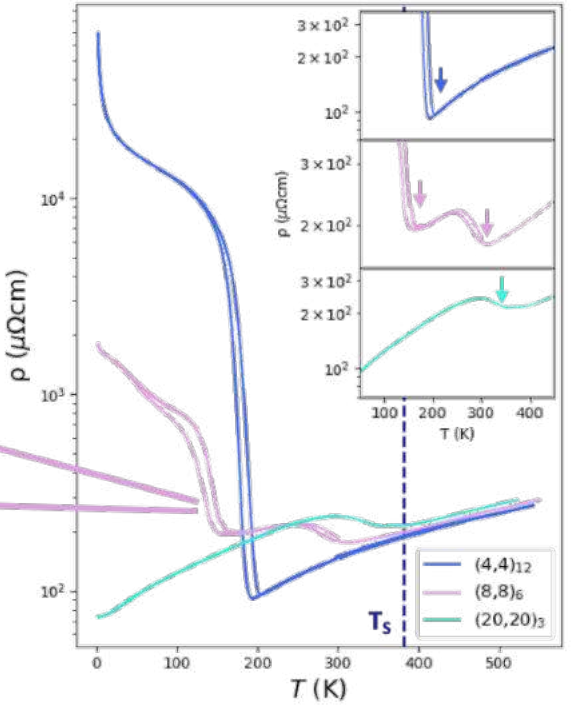
Summary of the findings









Claribel Dominguez et al. Nature Materials **19**, 1182 (2020)

Lucia Varbaro et al. manuscript in preparation

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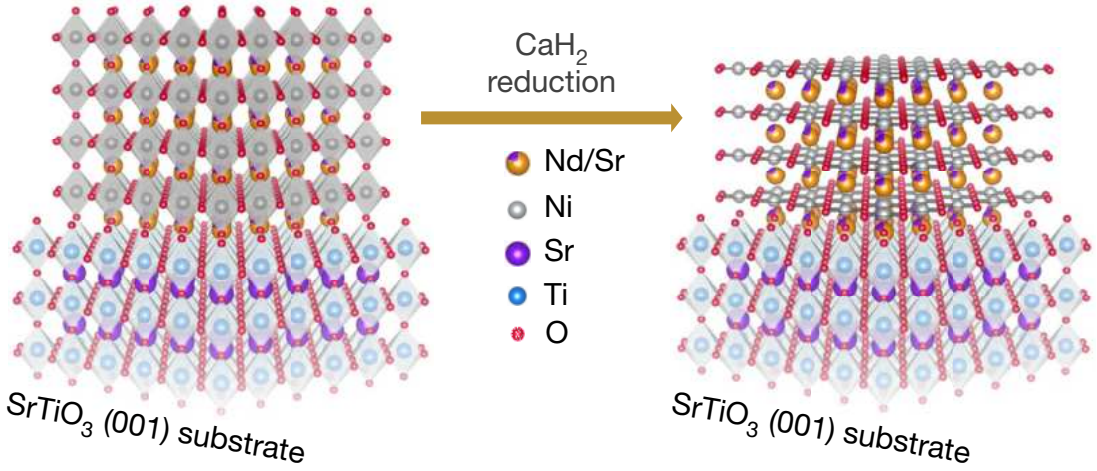
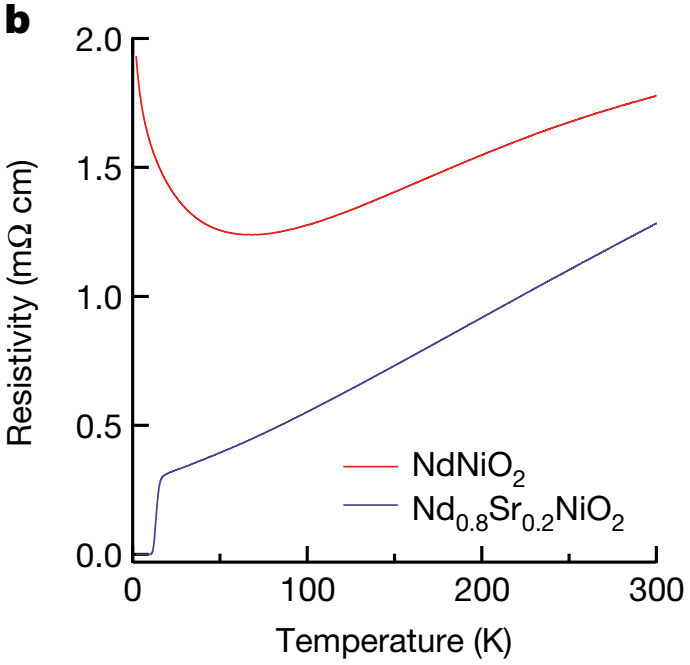
Much more to do and very exciting developments

Oxygen control in oxide structures



Topotactic reduction - « 113 » to « 112 » phase

Superconductivity in the infinite layer doped $NdNiO_2$ phase



D. Li et al. Nature **572**, 624 (2019)

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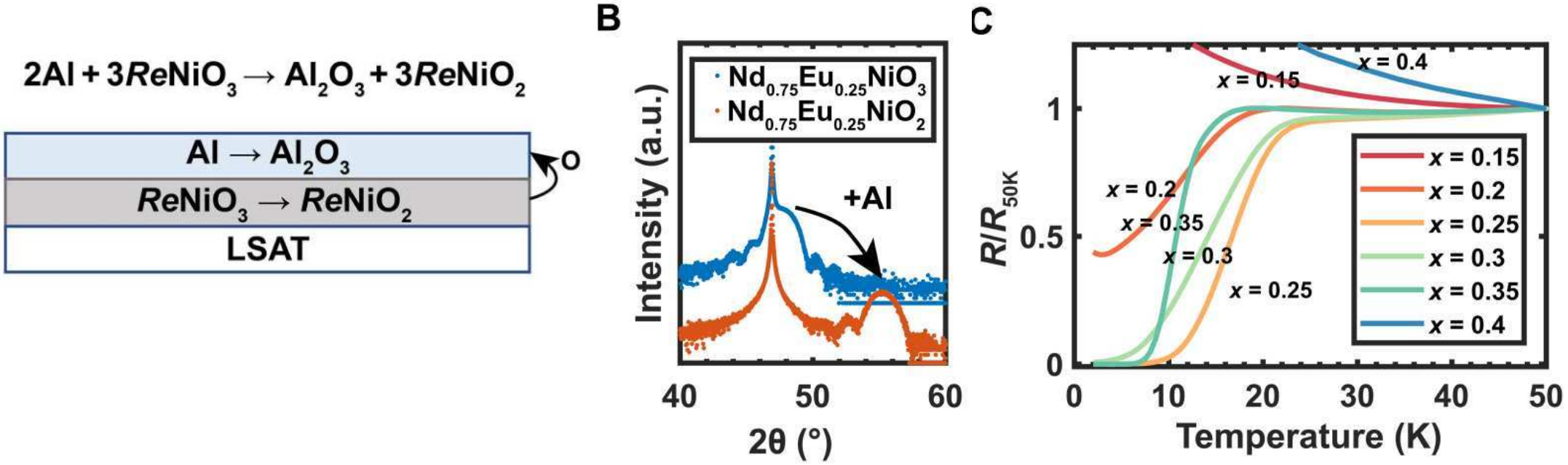
Solid state reduction

SCIENCE ADVANCES | RESEARCH ARTICLE

MATERIALS SCIENCE

Superconducting $Nd_{1-x}Eu_xNiO_2$ thin films using in situ synthesis

Wenzheng Wei[1]*, Dung Vu[1], Zhan Zhang[2], Frederick J. Walker[1], Charles H. Ahn[1,3,4]*



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