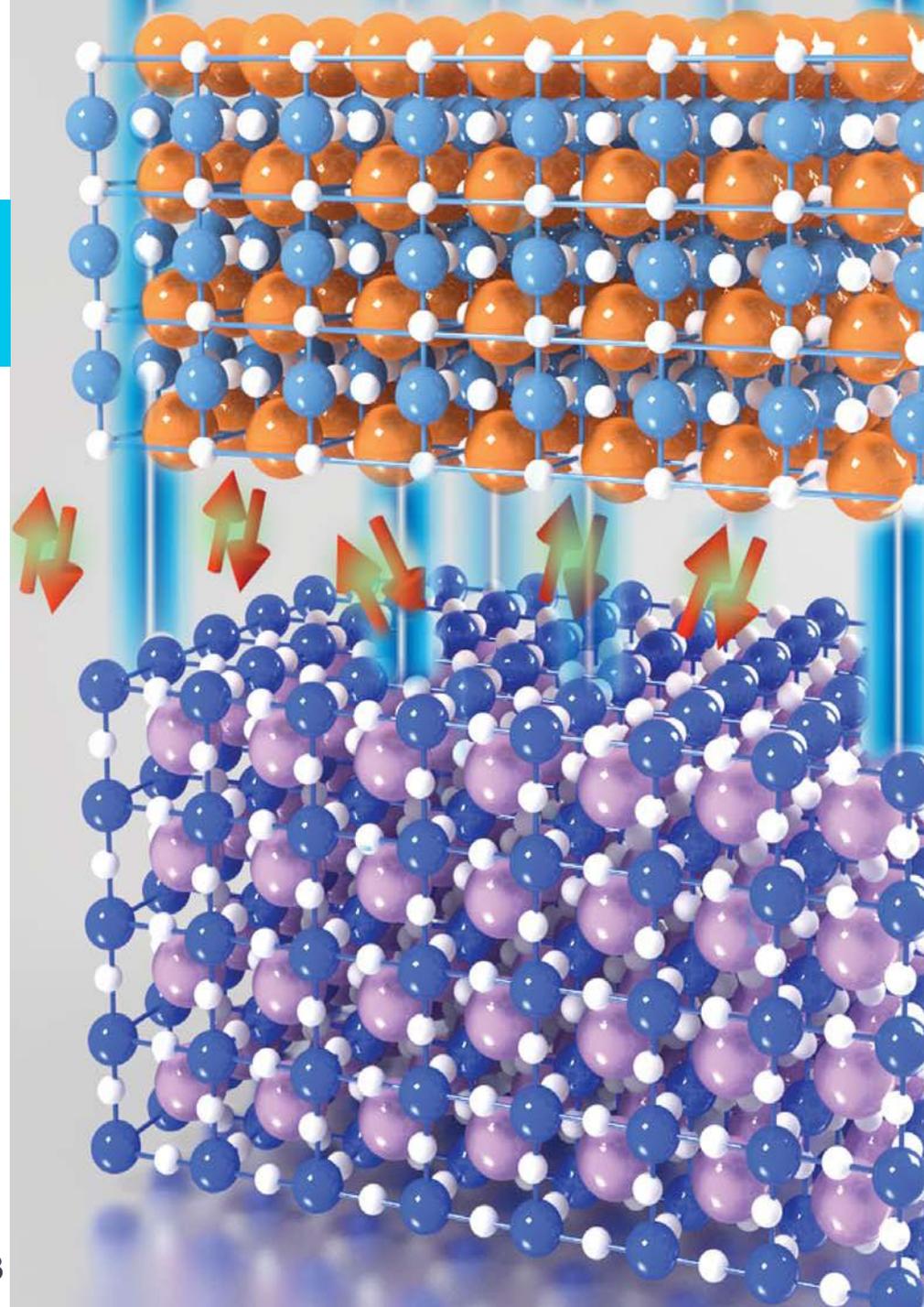


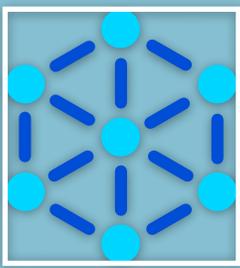
Strong Correlations at Oxide Interfaces: What is hidden in a plane view?

**Jak
Chakhalian**

*Laboratory for Artificial
Quantum Materials*

Rutgers University





LABORATORY FOR ARTIFICIAL QUANTUM MATTER AT RUTGERS

FORMED IN 2016

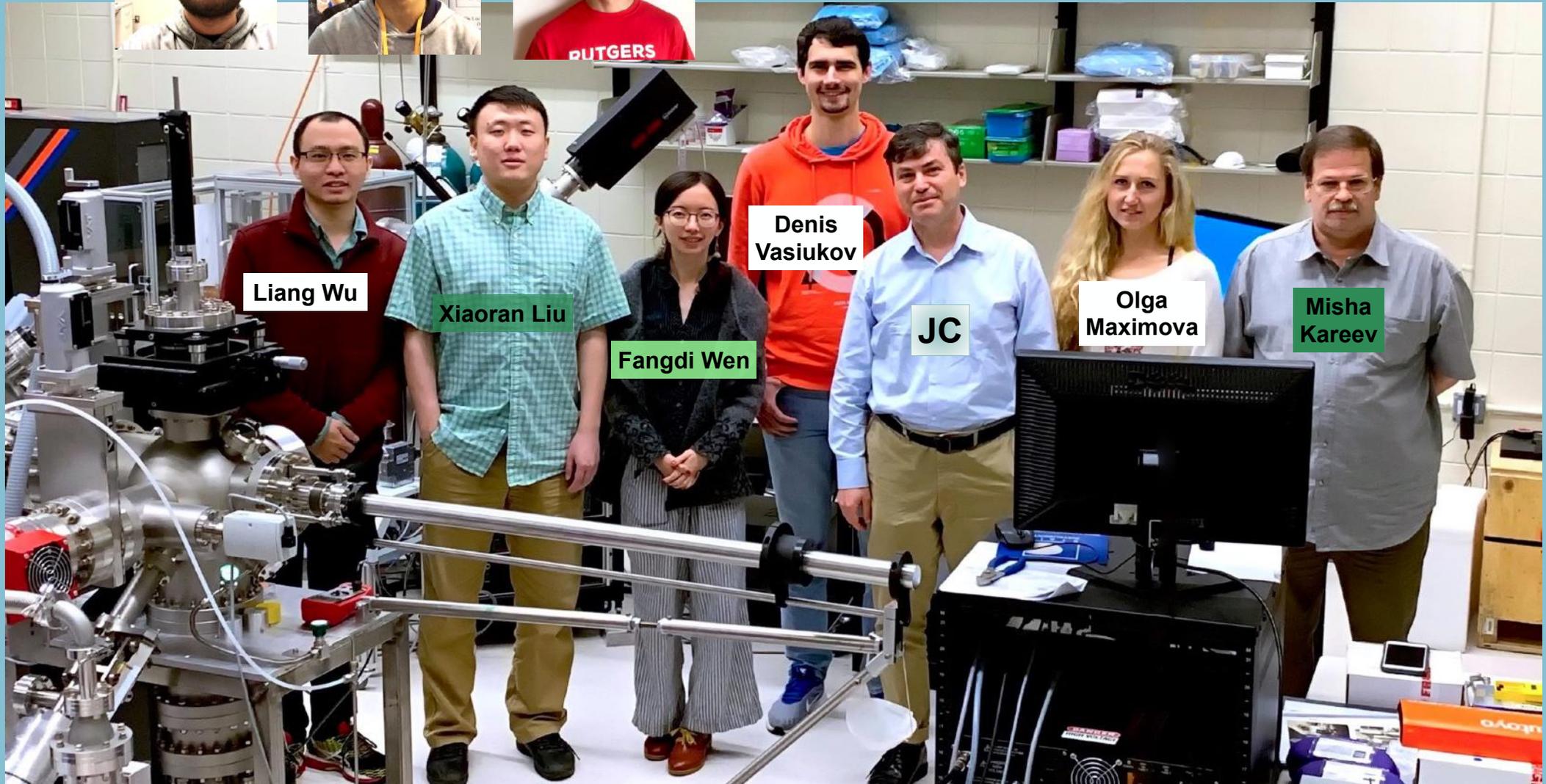
Michael Terilli



Tsung-Chi Wu



Chong Chia



Liang Wu

Xiaoran Liu

Fangdi Wen

Denis
Vasiukov

JC

Olga
Maximova

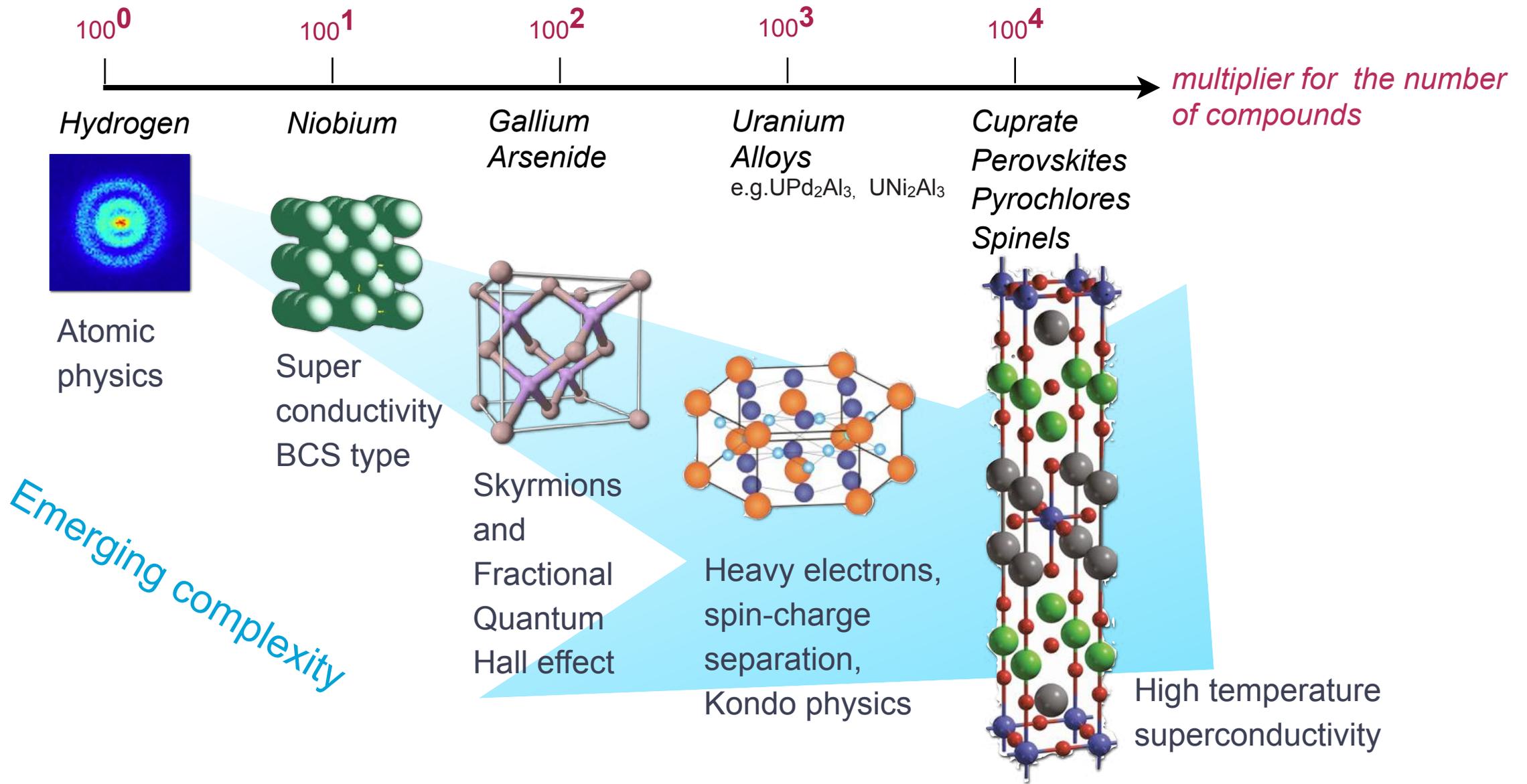
Misha
Kareev

Topics I plan to covered

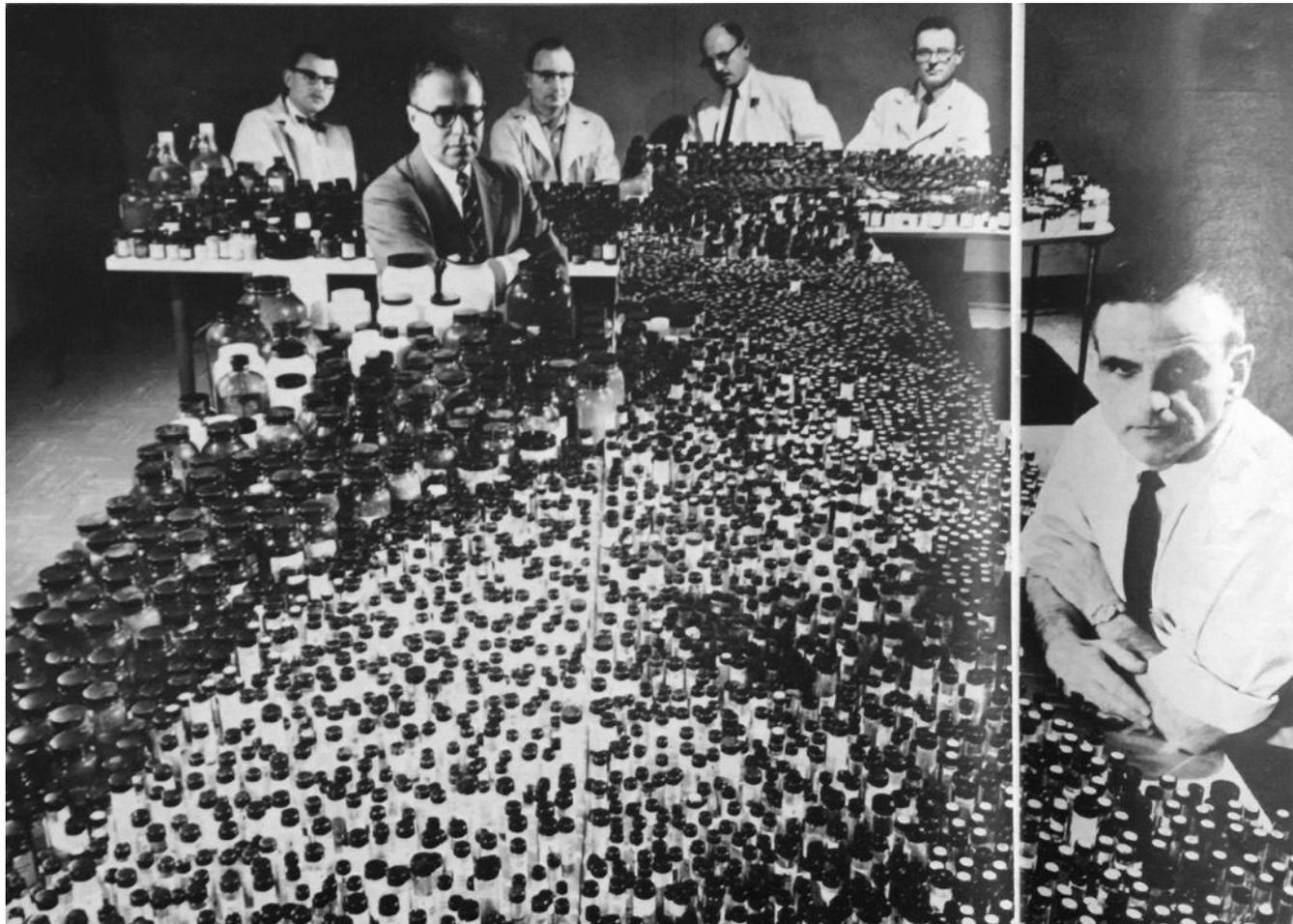
- What are quantum materials (QMs) ?
- What “knobs” do we have for controlling synthetic quantum matter (SQM) ?
- **QMs designer toolkit:**
 - Epitaxial stabilization
 - Solid Phase Epitaxy (SPE)
 - Defects
 - Polarity and ways to compensation it
 - Geometrical lattice engineering
 - Strain
- **Selected examples** - 2D spin and orbit polarized metal and synthetic Quantum Spin Liquid

What are **quantum materials ?**

Emerging phenomena in quantum matter



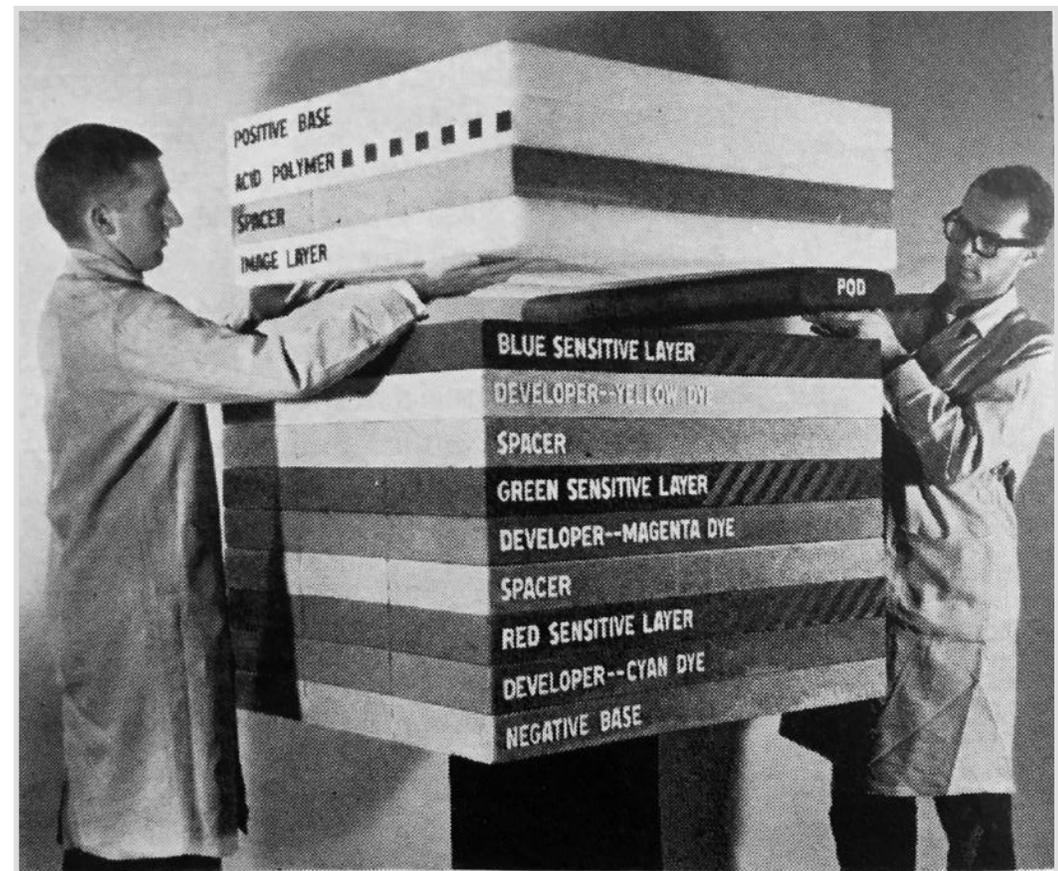
Irrational approach to materials design



5,000 Tries for the Key Chemicals



JANUARY 25 · 1963 · 20¢



POLAROID HOW THE FILM WORKS

POSITIVE BASE
ACID POLYMER
SPACER
IMAGE LAYER

POD
BLUE SENSITIVE LAYER
DEVELOPER--YELLOW DYE
SPACER
GREEN SENSITIVE LAYER
DEVELOPER--MAGENTA DYE
SPACER
RED SENSITIVE LAYER
DEVELOPER--CYAN DYE
NEGATIVE BASE

Rational approach to materials design



Marcel Proust

'The real voyage of discovery consists of not in seeking new landscapes but in having new eyes.'

In Search of Lost Time

Broken symmetry and order parameter

Temperature or control parameter



liquid



metal



magnetic insulator



critical temperature T_c



solid



insulator



superconductor

disordered phase

higher symmetry

ordered phase

lower symmetry

Broken symmetry means the appearance of an ordered phase with a **non-zero order parameter**

Interfaces as new phases of quantum matter ?



Lev Landau

Nobel prize 1962

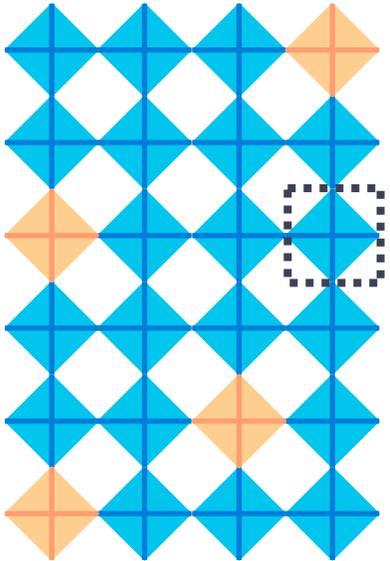
Landau `recipe' of getting
new collective phases and states →

The sudden disappearance of an element(s) of symmetry in one phase leads to the occurrence of a phase transition into a new phase of lower symmetry.

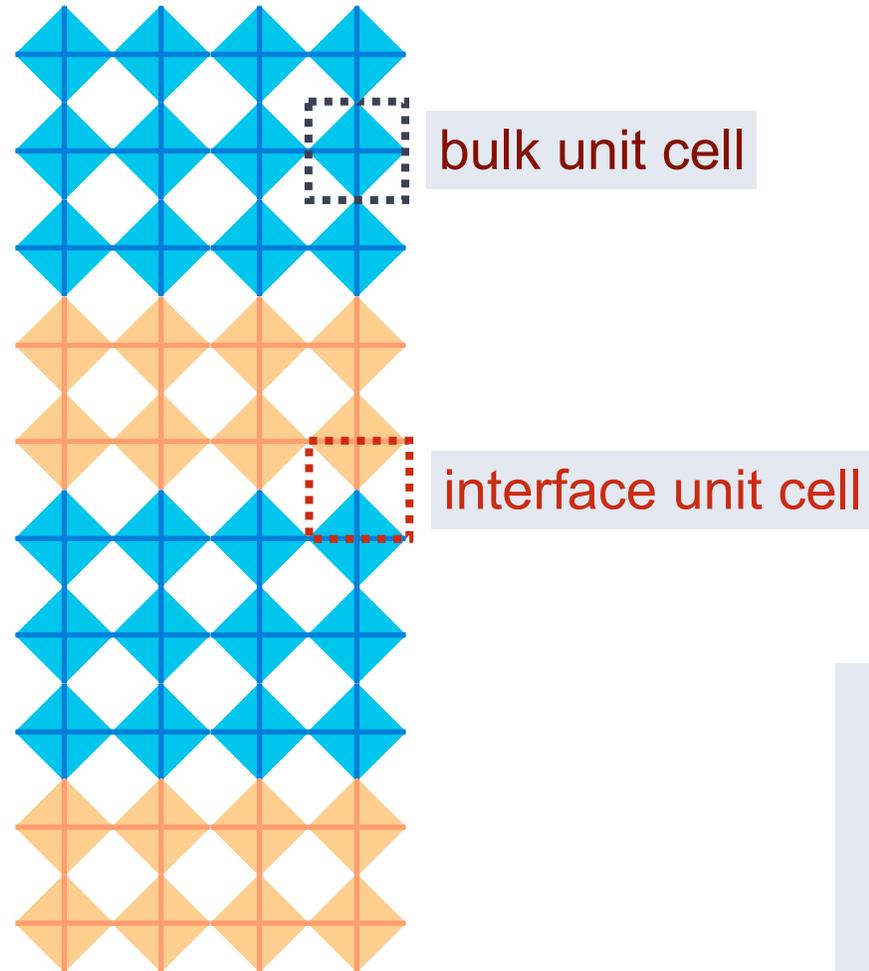
Goal: Assume control over symmetry breaking \equiv Devise new designer phases

From thin films to ultra - quantum materials

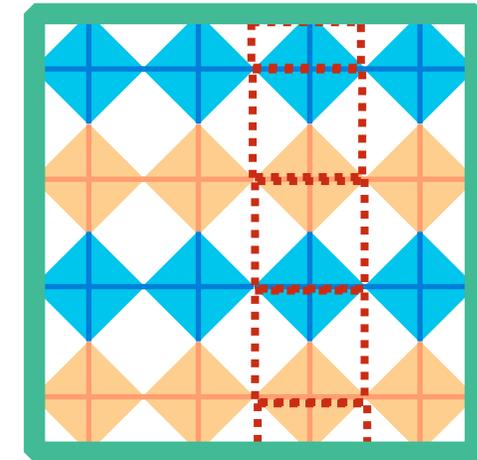
Randomly doped
bulk crystal



Ultra-thin superlattice



Interface Controlled Quantum Material
(ICQM)



ICQM is

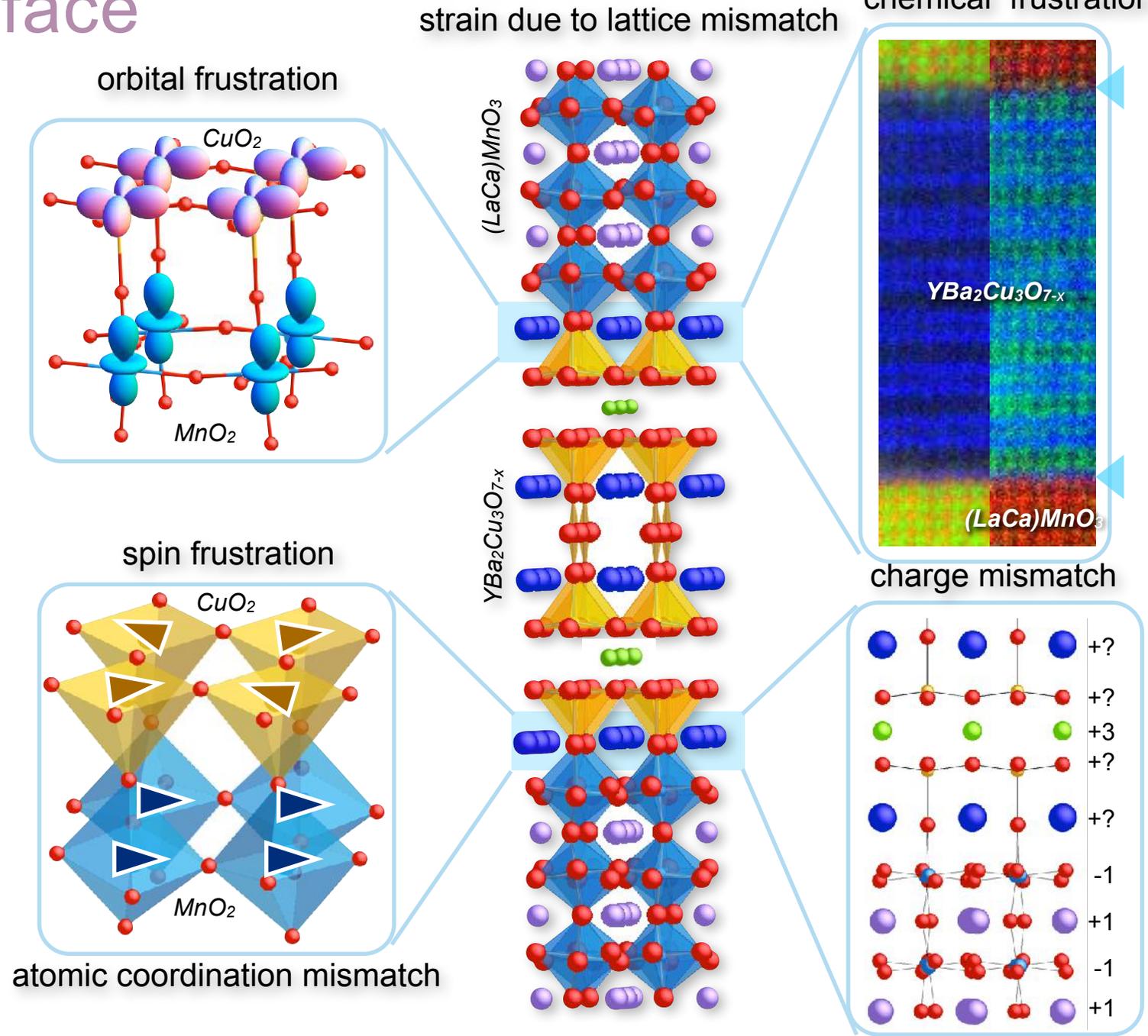
A material that has **no bulk unit cells**
 Properties defined by interface/surface
 Possess emerging quantum state

Anatomy of an interface

Interface is a tool for breaking symmetries

↓

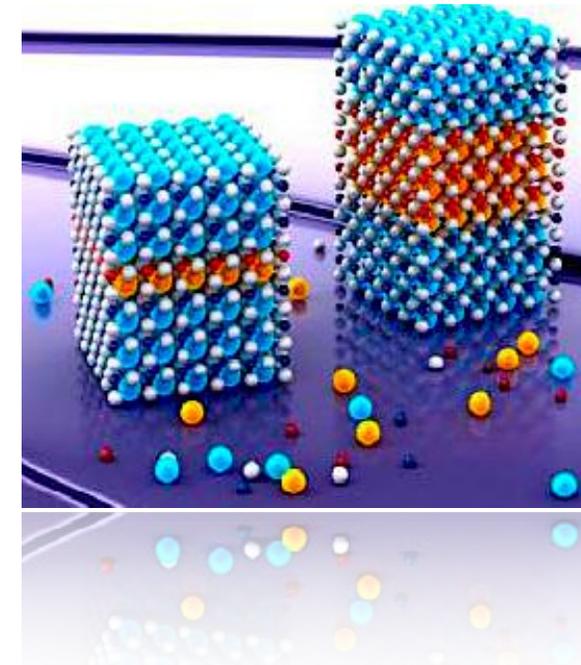
Emergent quantum states
energy scales
length scales



Control of quantum phases: bulk vs. heterostructures



Bulk crystals



Interface controlled quantum materials

Doping
Pressure
Magnetic Field
Polymorphs



Charge transfer and **Electrostatic gating**
Strain
Magnetic field

Designer lattice symmetry
Quantum confinement
Interface
Enables latent interactions

Why creating new quantum materials is hard ?

- Growth of complex materials is still poorly understood on the atomic level → The existing knowledge is largely phenomenological, often intuition based.
- Modern day `quantum alchemy`.
- For complex matter atomic theory of nucleation and growth does not exist and unlikely (?) feasible in the near future.
- *Corollary* → Every non-trivial new quantum material (bulk and film) often requires months or years of “alchemy” work. This work more often than not is based on experience and luck.

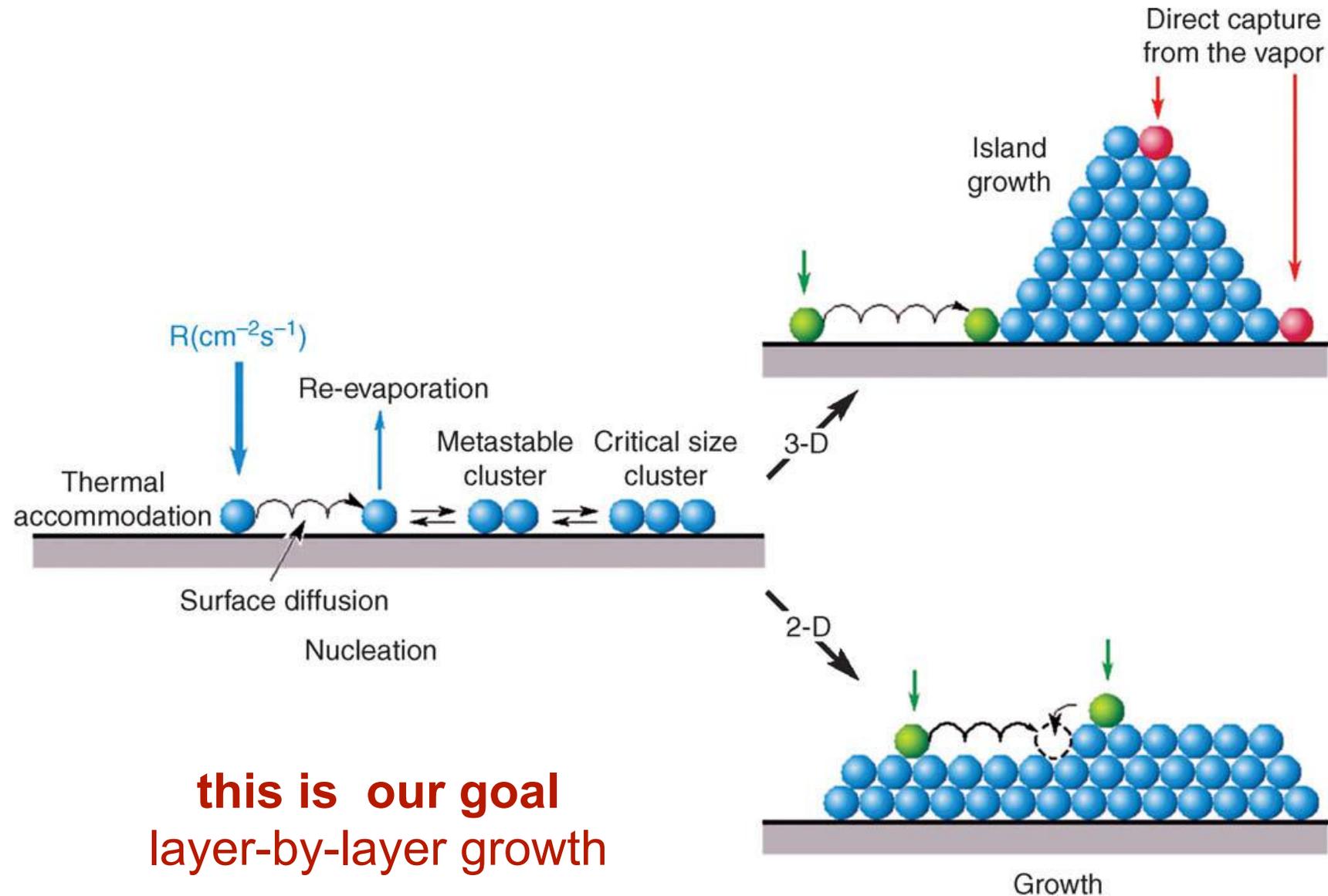
Designer's toolkit
for making
synthetic quantum materials

Epitaxial Stabilization 101

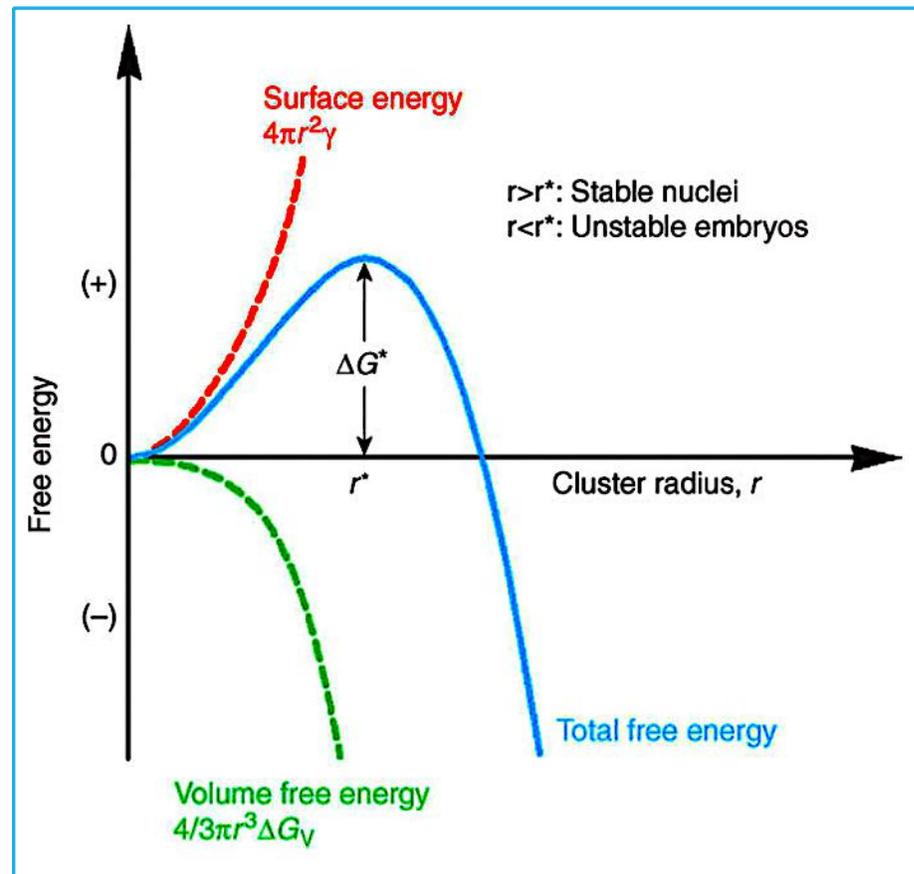
or

Why do films grow **far away**
outside of their thermodynamic
stability range ?

Nucleation and initial growth



How crystals grow and why films are not thin bulk crystals



Formation of a solid spherical crystal inside homogeneous liquid:

Gibbs energy $\longrightarrow \Delta G = 4\pi r^2 \gamma + 4\pi r^3 \Delta G_V / 3$ (1)

surface > 0 free energy per volume < 0

$$d(\Delta G)/dr = 0 \quad \longrightarrow \quad r^* = -2\gamma / \Delta G_V \quad (2)$$

In modern literature the critical size r^* is represented as l^* in units of atoms

For the critical radius, the critical energy barrier to the new phase:

$$\Delta G^* = 16\gamma\pi^3 / 3(\Delta G_V)^2$$

$$r^* \propto \gamma / \Delta G_V \quad \text{and} \quad \Delta G^* \propto \gamma^3 / (\Delta G_V)^2$$

Nucleation of a new crystal phase from physical vapor

For practical purpose we better use the equation from the 1st and 2d laws of thermodynamics :

$$r^* = 2\Omega\gamma/kT_s \ln(\zeta) \quad \text{Here } \zeta = P/P_{vp} \quad \text{or} \quad \zeta = J/J_{vp} \quad \text{and is known as **supersaturation**}$$

$$\text{From the kinetic equation we can get flux: } J(\text{cm}^{-2} \text{ s}^{-1}) = 3.513 \times 10^{22} P/(mT)^{1/2}$$

Example of Au growth on NaCl (100) surface

J is about $1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ ($\sim 0.01 \text{ ML/s}$) and $m_{\text{Au}} = 196.97 \text{ amu}$ $T_s = 300 \text{ K}$
which corresponds to the deposition pressure $P_{\text{Au}} \sim 7 \times 10^{-8} \text{ torr}$.

The extrapolated vapor pressure P_{vp} of Au at 300 K is $\sim 10^{-30} \text{ Torr}$

Thus, ζ in this hypothetical experiment is $\sim 7 \times 10^{22}$

together with $\Omega_{\text{Au}} = 12.51 \text{ \AA}^3$ with $A_{\text{Au}} = 12.51 \text{ \AA}^3$ and the energy cost for surface $\gamma_{\text{NaCl}} = 0.014 \text{ eV/\AA}^2$ with $\gamma_{\text{Au}} = 0.088 \text{ eV/\AA}^2$ into Eq. (2)

yields $r^* = 1.37 \text{ \AA}$ which corresponds approximately to $i^* = 1$

A paradox of thin film growth or why films are not crystals

Consider EuNiO_3 perovskite

Bulk EuNiO_3 synthesis requires

$T > 1400$ °C and $P > 100$ Bar (<50 micron in size)

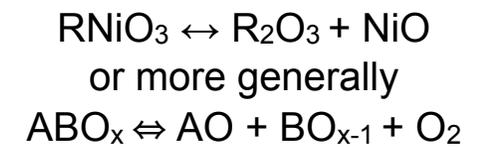
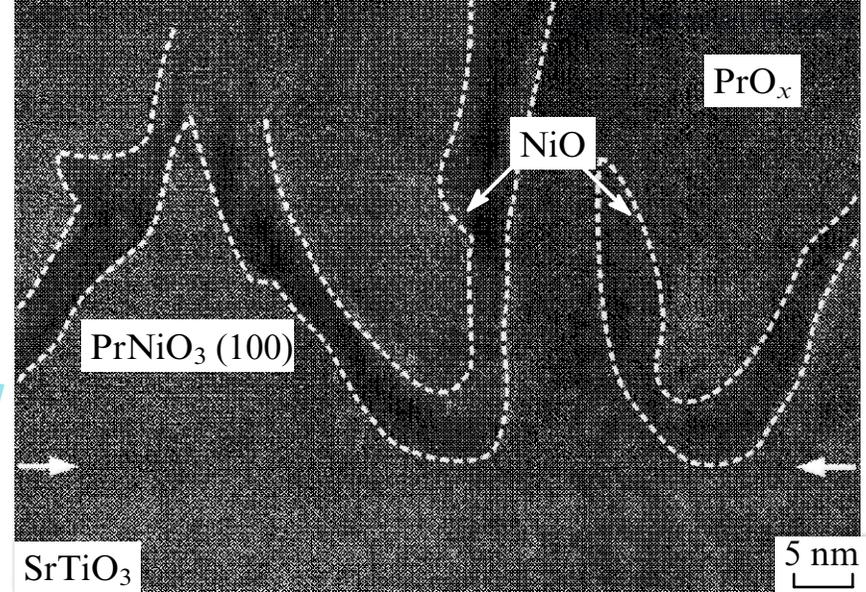
But we grow EuNiO_3 thin films at $T = 600-700$ °C and
 $P = 1.3 \cdot 10^{-4}$ Bar (5 mm x 5 mm in size) !!?

Q: How is it possible at all ?

Why do the films grow ?

Growth of single-phase films can occur under thermodynamic conditions ($P_{O_2} - T$) where a compound as a bulk material is thermodynamically unstable

Phase composition of polycrystalline thin films is the same as predicted by bulk phase diagrams.



If interface is coherent → a dramatic decrease in contribution to the free energy from the film/substrate interface.

$$\Delta E^{ic} - \Delta E^c = h \left[\frac{\Delta g_V^{ic}}{<0} - \frac{\Delta g_V^c}{>0} - \frac{\mu}{1-\nu} \epsilon^2 \right] + \left[\frac{\sigma_s^{ic}}{>0} - \sigma_s^c \right], \quad \Delta g_V^{ic} < \Delta g_V^c, \quad \sigma_s^c \ll \sigma_s^{ic}$$

ES /epitaxial stabilization/ is an extension of the $P - T - x$ space of the thermodynamically stable epitaxial phase with respect to the bulk phase or the phase which is free from the interface

Question: Why do the films grow outside of phase diagram conditions ?

Answer: Because of epitaxial stabilization
meaning

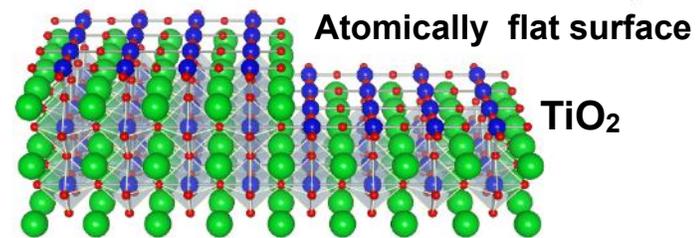
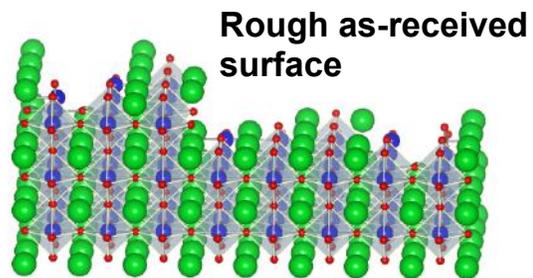
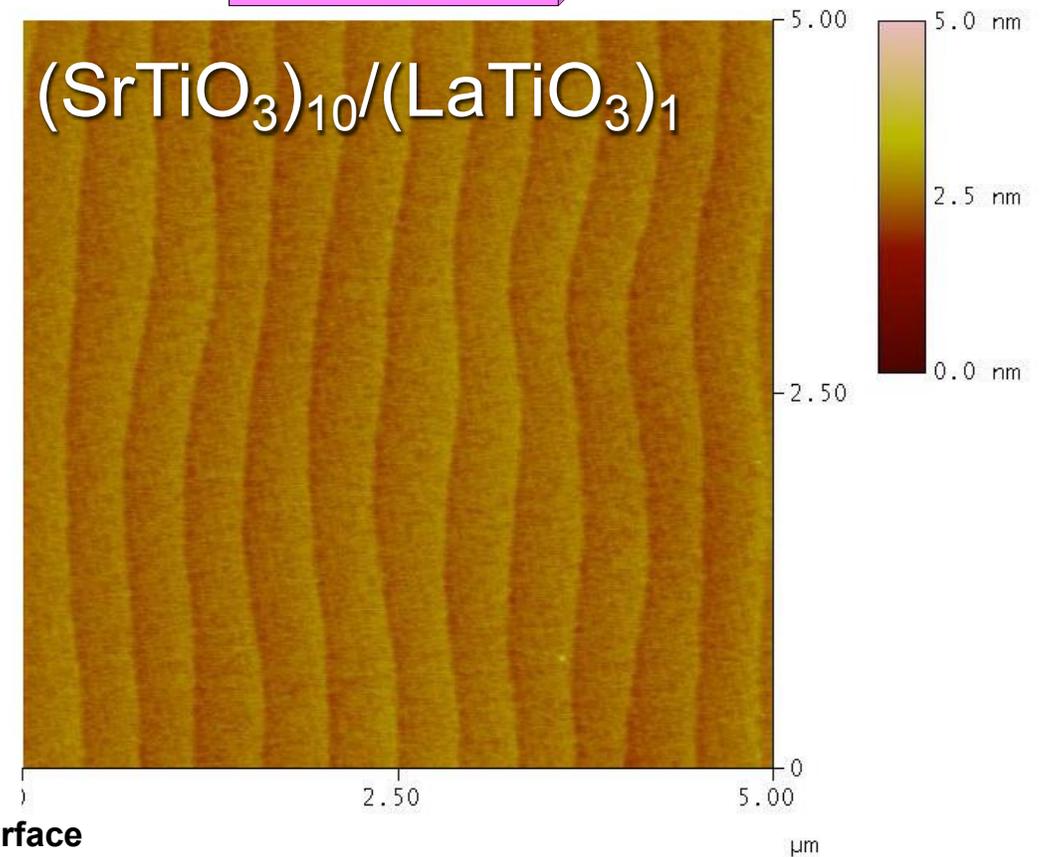
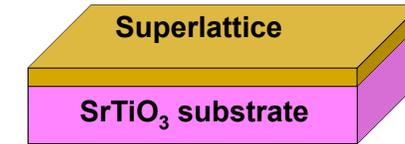
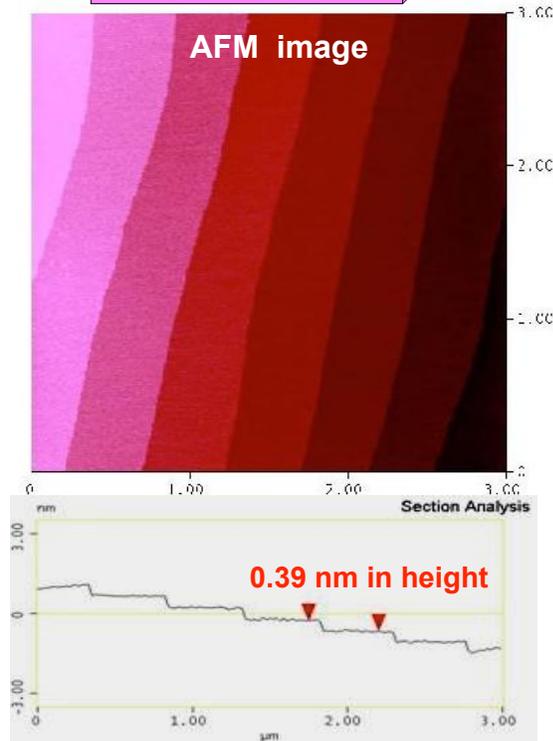
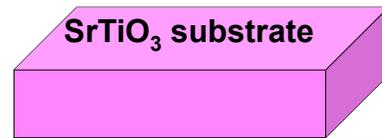
If 2 or more chemical phases compete during the nucleation
the phase with lattice most coherent to substrate wins.

Films, unlike crystals, are metastable phases.

A recommended review:

Gorbenko et al, Chem. Mat. 2002, 14, 4026

Preparation of atomically flat surfaces



Growth by Pulsed laser deposition (PLD) or Laser MBE

Q: How do we know how atomic layers we grow ?

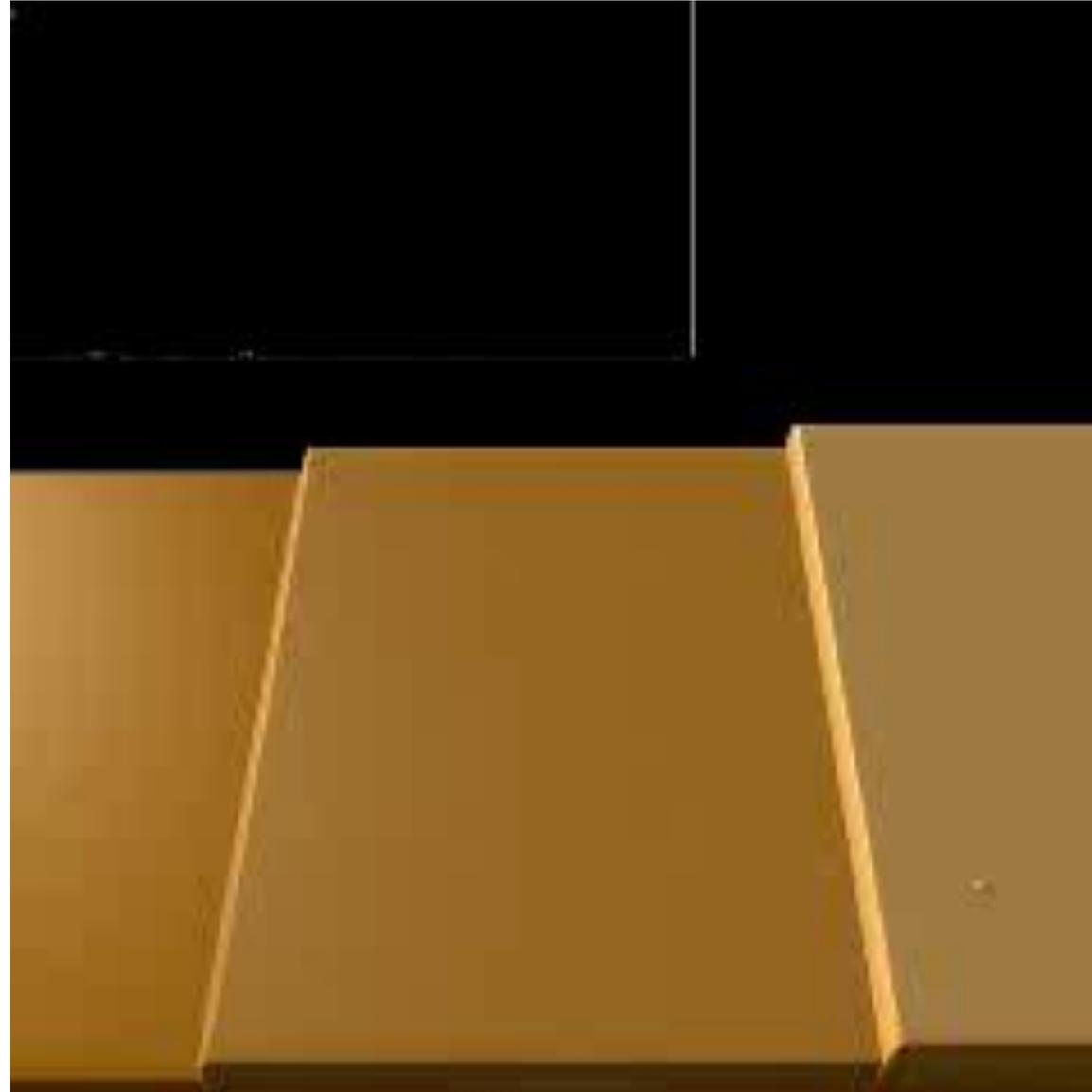
A: In-situ 'eyes' for thickness and symmetry

RHEED = Reflected High

Energy Electron Diffraction

Laser MBE deposition sequence (not a simulation!)

After a series of laser pulses
an AFM scan is performed



Movie courtesy of University of Twente, D. Blank group

What is
strain ?

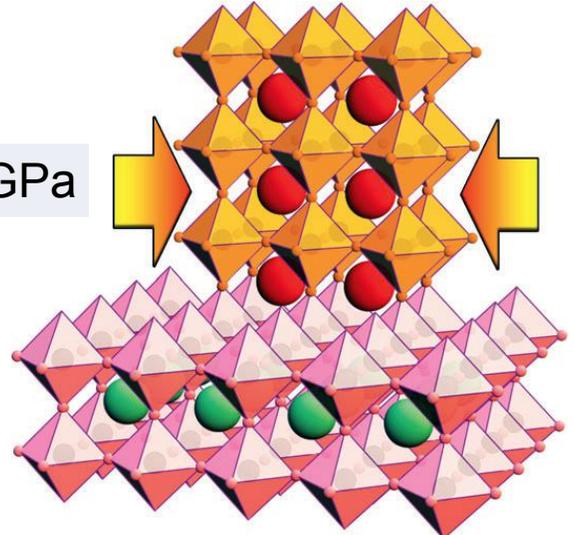
and how to use it

Strain defined

lattice mismatch $\epsilon = (a_{\text{film}} - a_{\text{sub}}) / a_{\text{sub}}$

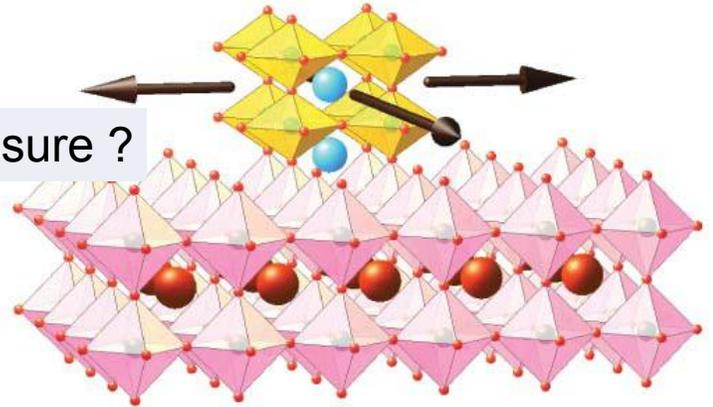
- When two dissimilar materials are clamped across interfaces compressive strain $\epsilon < 0$

1% strain = 2 GPa

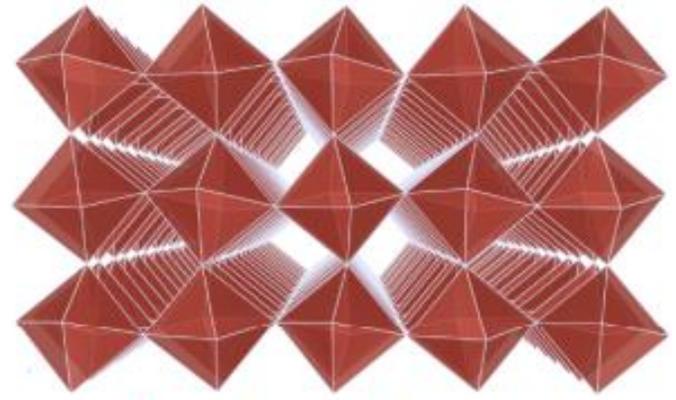


tensile strain $\epsilon > 0$

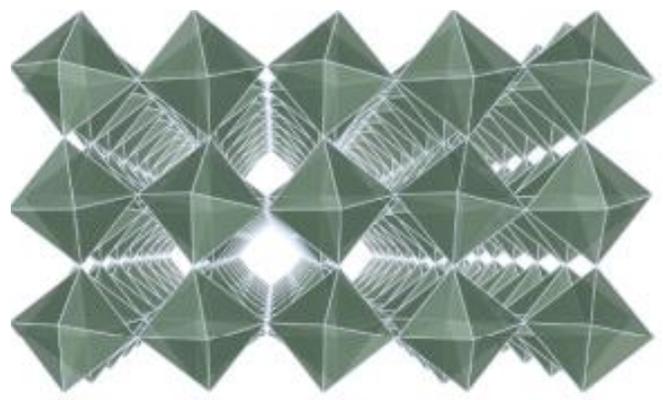
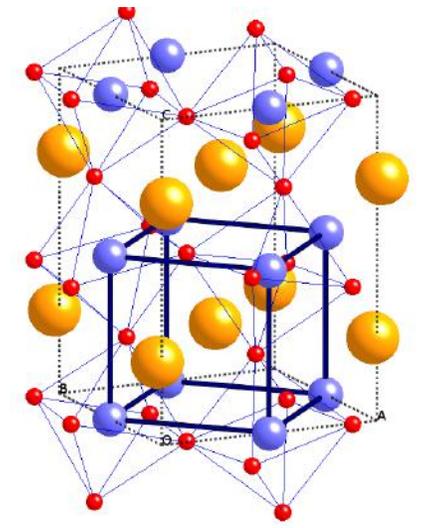
Negative pressure ?



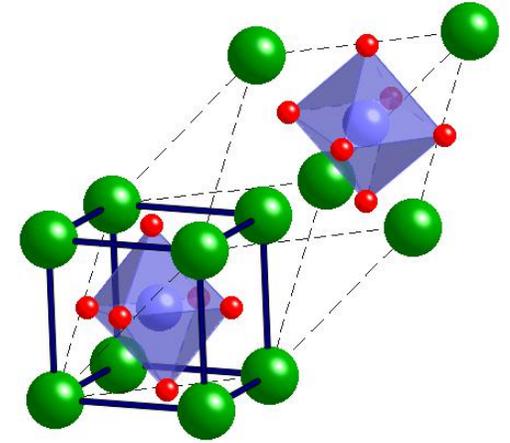
symmetry mismatch



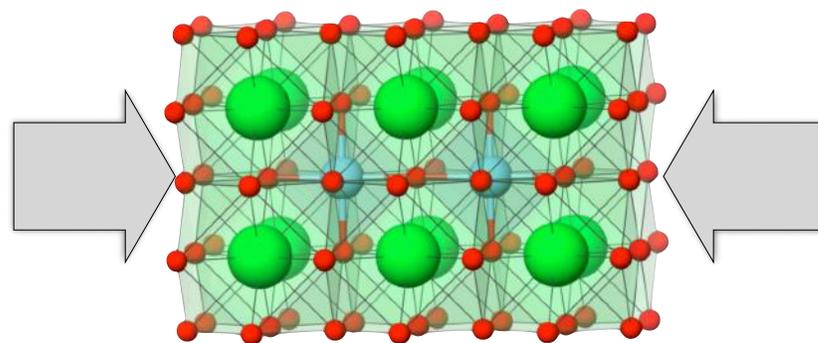
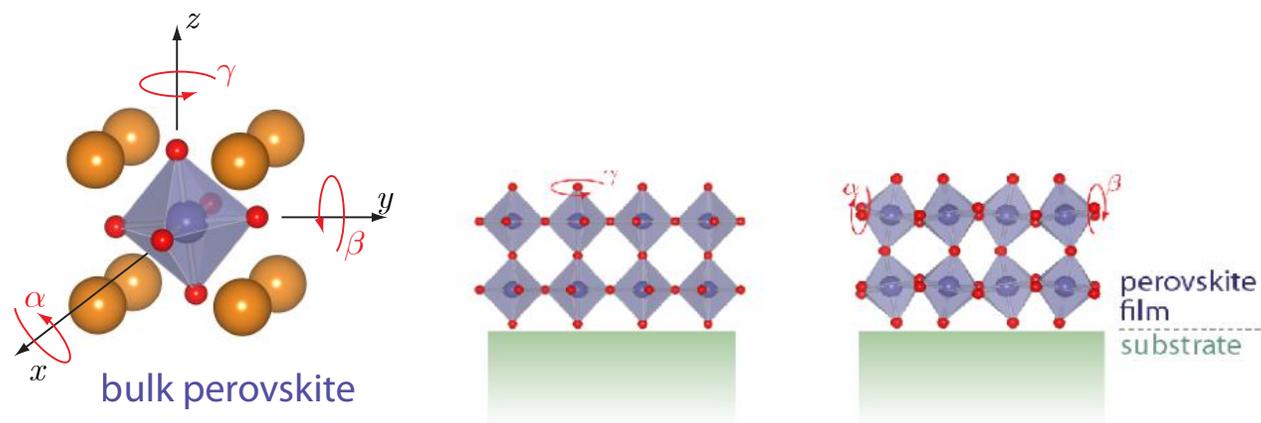
orthorhombic ($Pbmn$)
 $a^- a^- c^+$



rhombohedral ($R\bar{3}c$)
 $a^- a^- a^-$



Strain in complex oxide materials

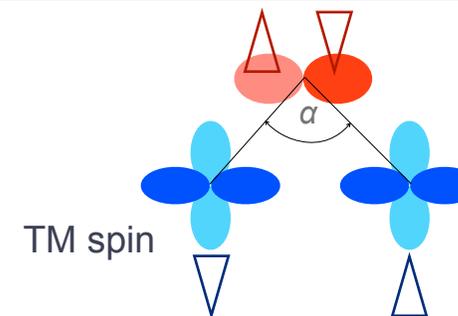


Symmetry between film and substrate is the key element

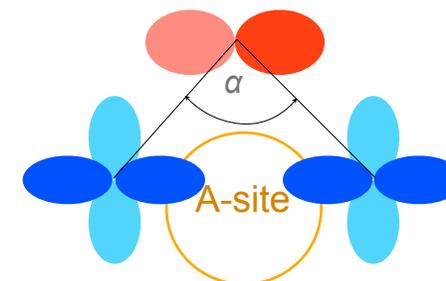
1 altered covalency and hopping



2 altered magnetic ground state



3 altered Madelung energy

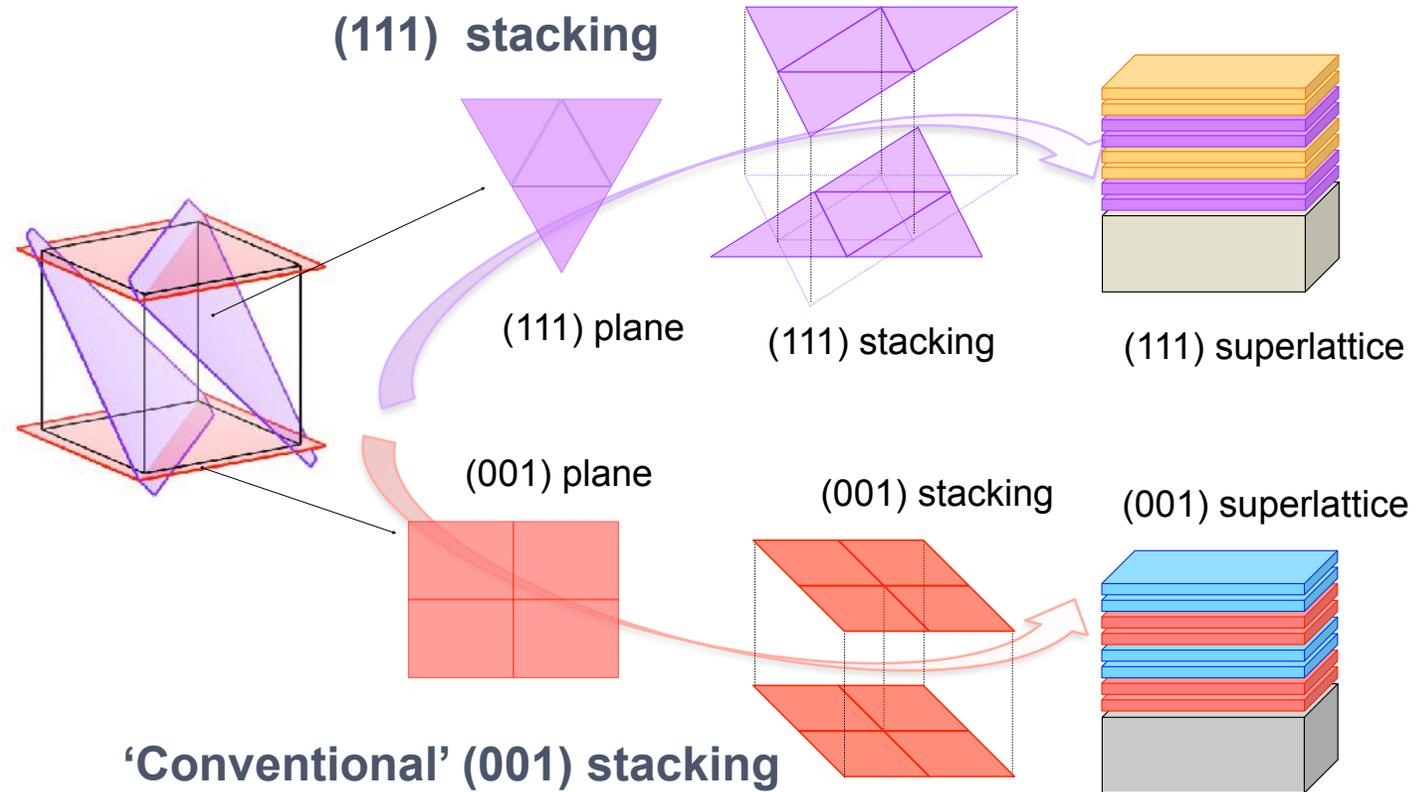


Geometric lattice engineering /GLE/

Geometrical lattice engineering of complex oxide heterostructures: a designer approach to emergent quantum states

Xiaoran Liu, S. Middey, Yanwei Cao, and M. Kareev, Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA
J. Chakhalian, Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA

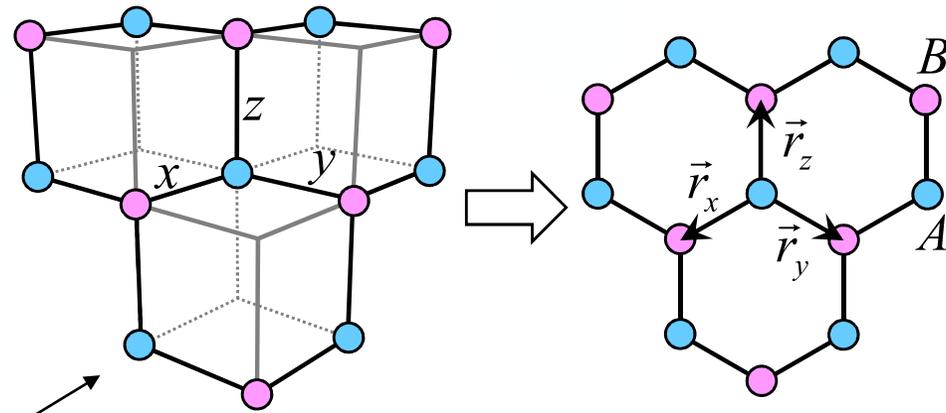
MRS Communications (2016)



New Phases by Geometric Lattice Engineering

2 unit cells of perovskite ABO_3

Monolayer of a Kitaev magnet



$\langle 111 \rangle$

Theory:

S. Okamoto, Phys. Rev. Lett. **110**, 066403

Di Xiao et al, Nat. Comm. 2011

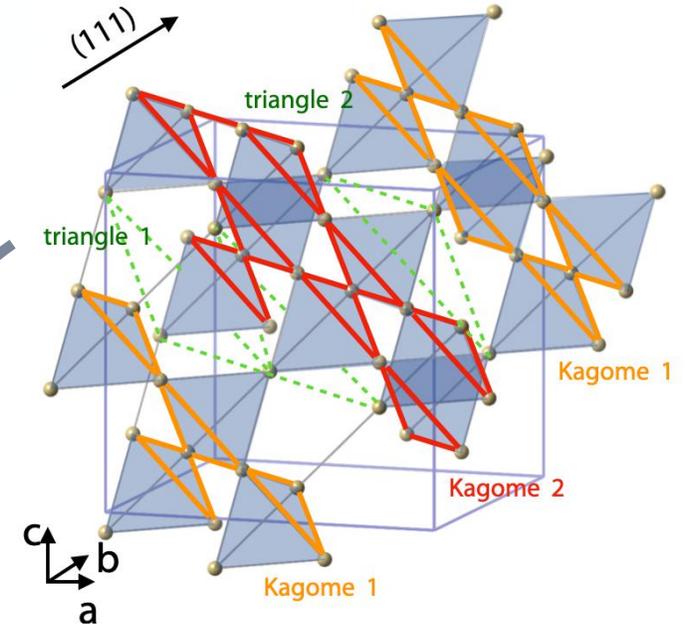
Experiments:

Xiaoran Liu, JC, MRS Communications **6**, 133–144 (2016)

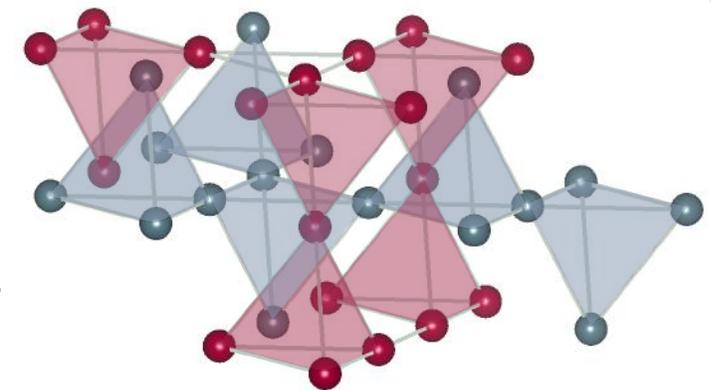
Xiaoran Liu, JC, et al, Nano Lett. 2019, 19, 12, 8381–8387

Xiaoran Liu, JC et al, Nano Lett. 2021, 21, 2010–2017

3D pyrochlore lattice $A_2B_2O_7$



Bilayer of Kagome (B) + Triangular(A)



$\langle 111 \rangle$

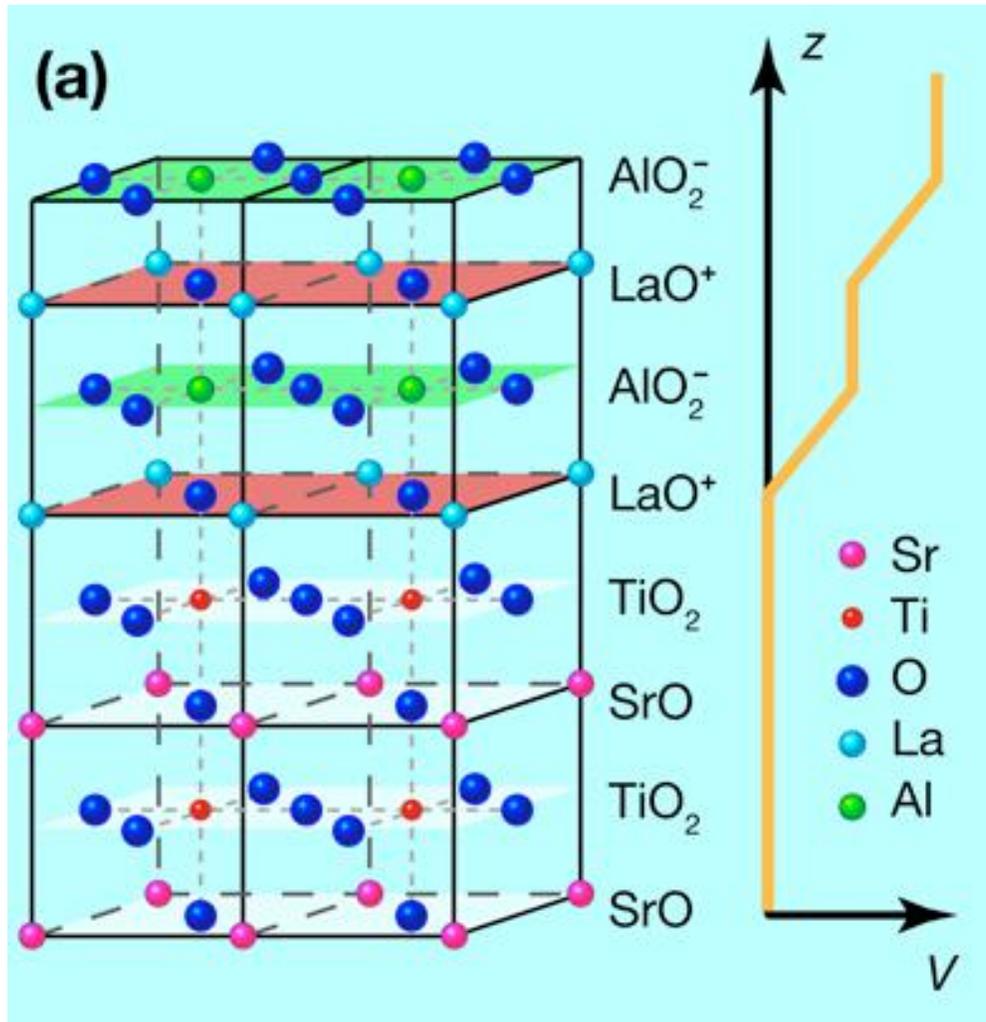
High symmetry directions like $[111]$ are often polar

Polar Mismatch

or

avoided 'polar catastrophe'

Polar mismatch and avoided catastrophe problem from the polar interface



Potential developed across a unit cell of perovskite structure:

ABO_3 which is $../\text{A}^{3+}\text{O}_2^-/\text{B}^{3+}\text{O}_2^-/\text{A}^{3+}\text{O}_2^-/\text{B}^{3+}\text{O}_2^-/..$

the answer is few 10 of eV per u.c.!

Recall gap in insulators is about 1-5 eV.

Theoretically: Conduction band will “run” into valence band resulting in rapid metallization of thin films

Experiment suggests much more complex picture

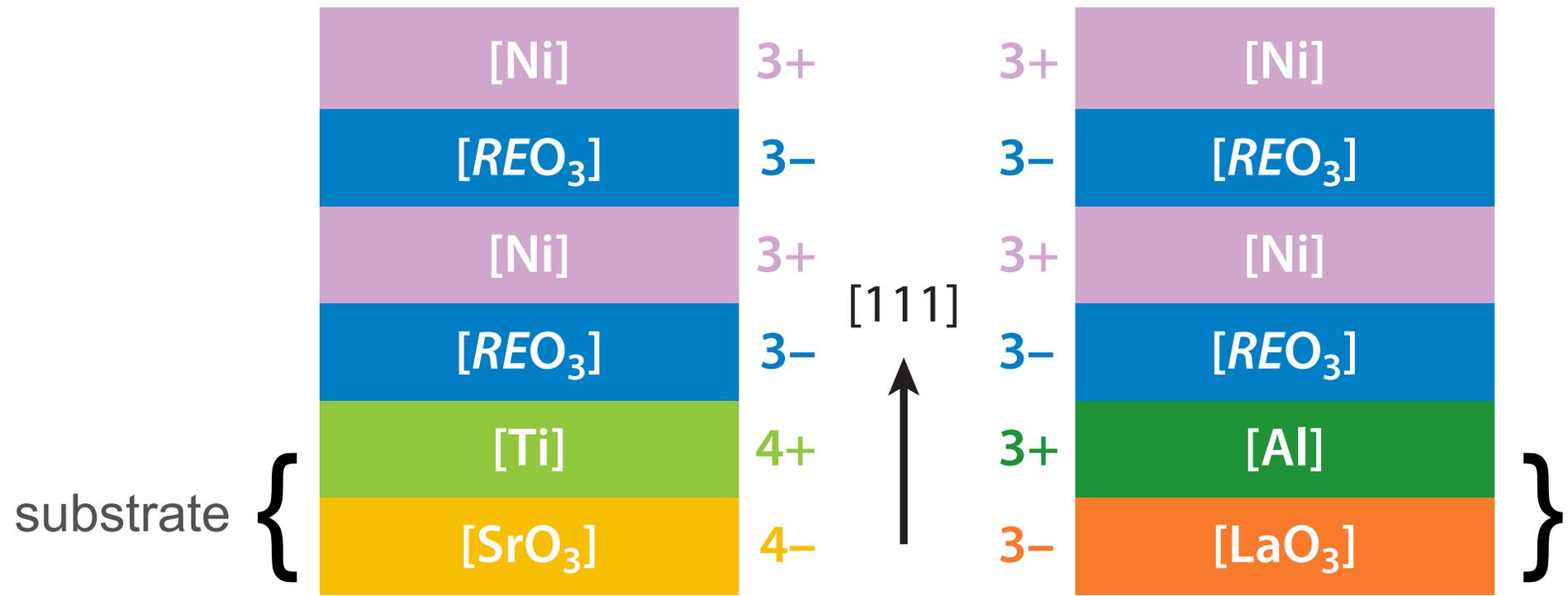
JC et al, Scientific Report, 4:6819 (2015)

Polar mismatch can be avoided by substrate choice

Initial growth of a correlated oxide metal LaNiO_3

on polar (111) surface

on non-polar (111) surface



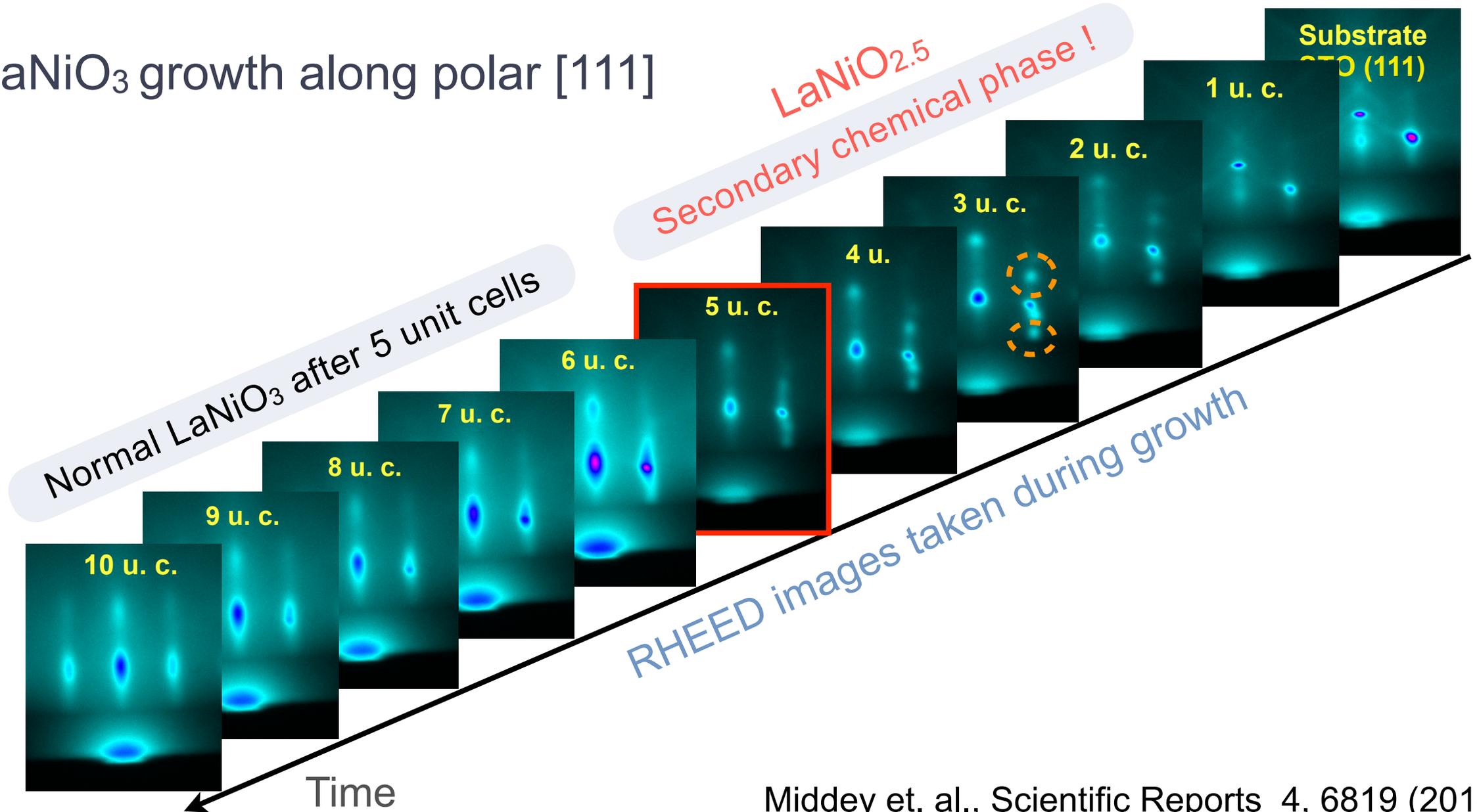
SrTiO_3
polar jump

Polarity issue

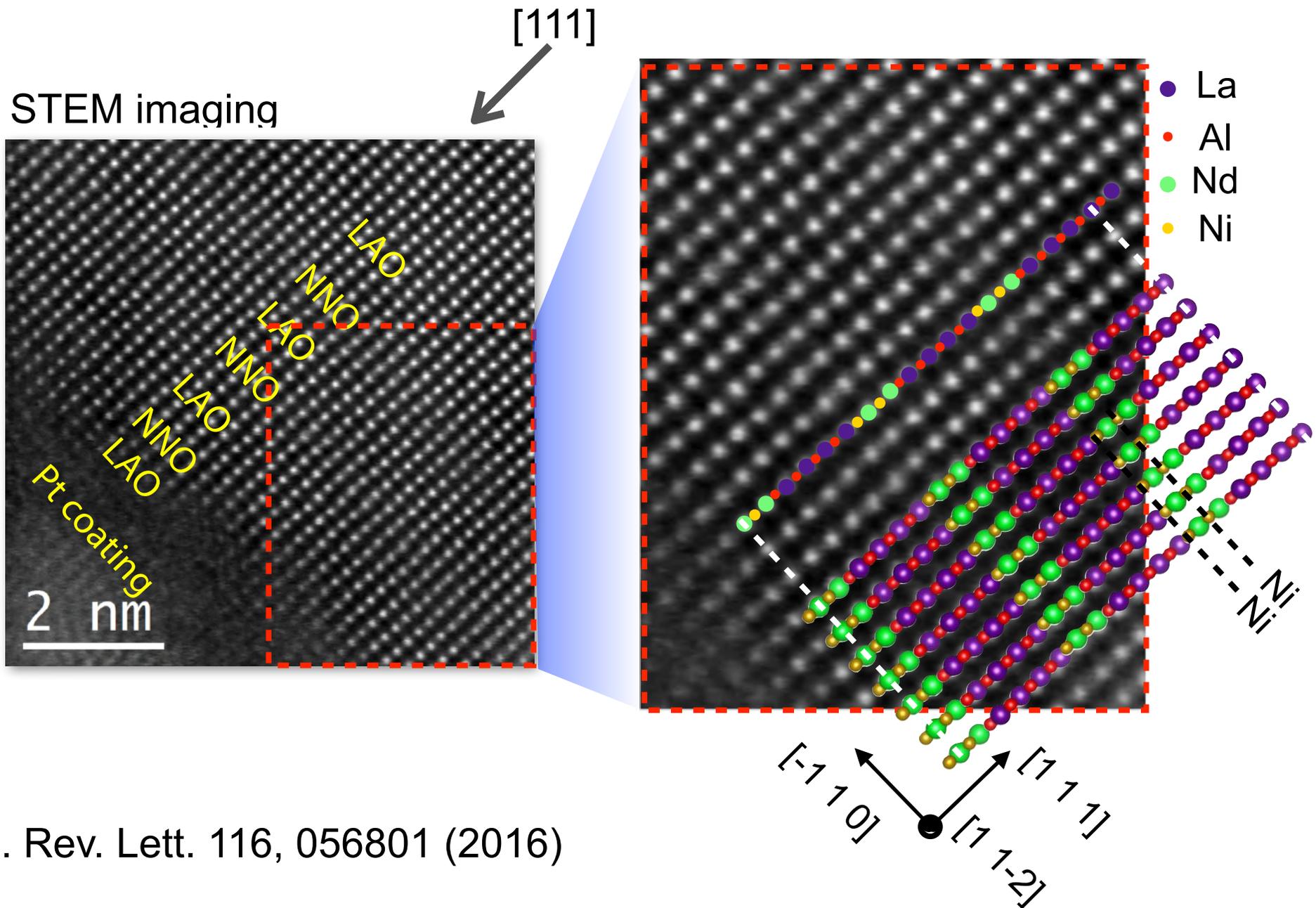
LaAlO_3
no polar jump

Polar compensated during the growth

LaNiO₃ growth along polar [111]



Chemistry and structure of Honeycomb NdNiO₃



Middey et. al., Phys. Rev. Lett. 116, 056801 (2016)

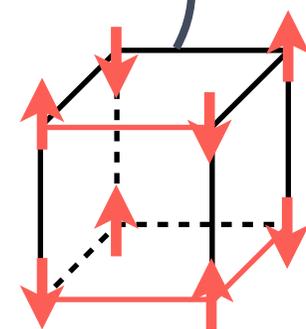
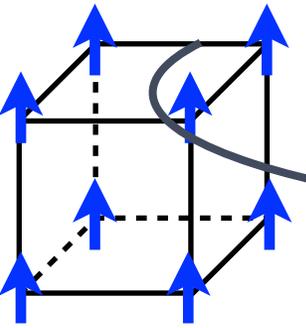
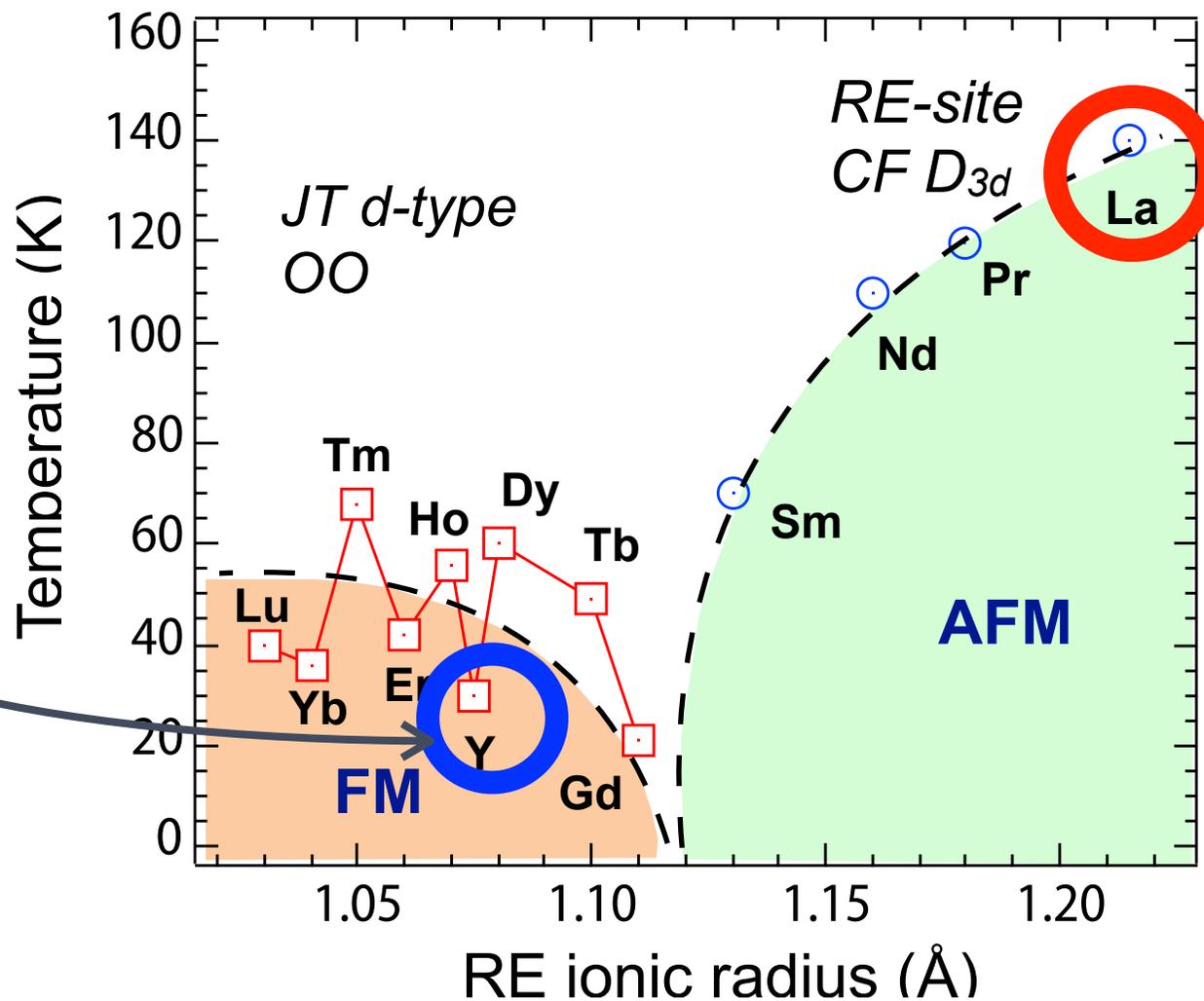
Two Examples

1. Spin and Orbit 2D electron gas
2. Quantum gapless spin liquid

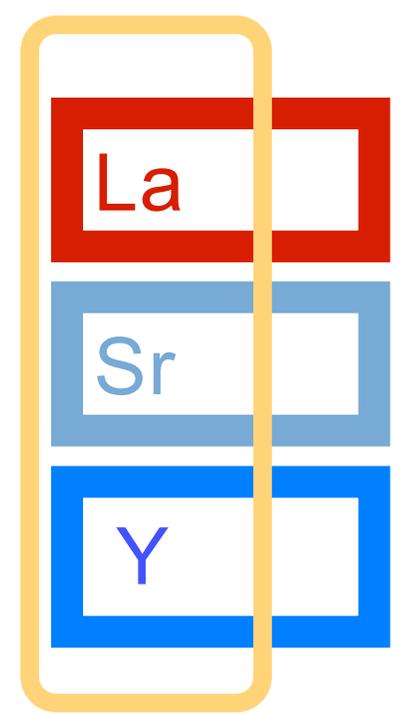
Examples

Orbital and spin polarized
synthetic 2D metal

Constituent layers - bulk $RETiO_3$ phase diagram



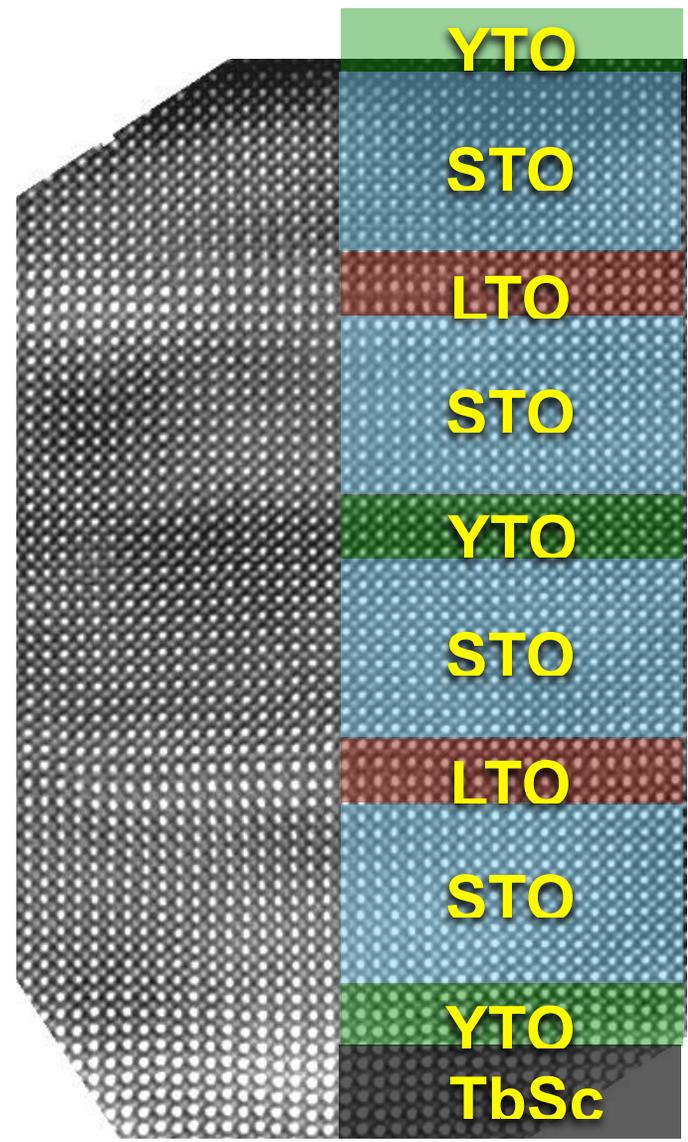
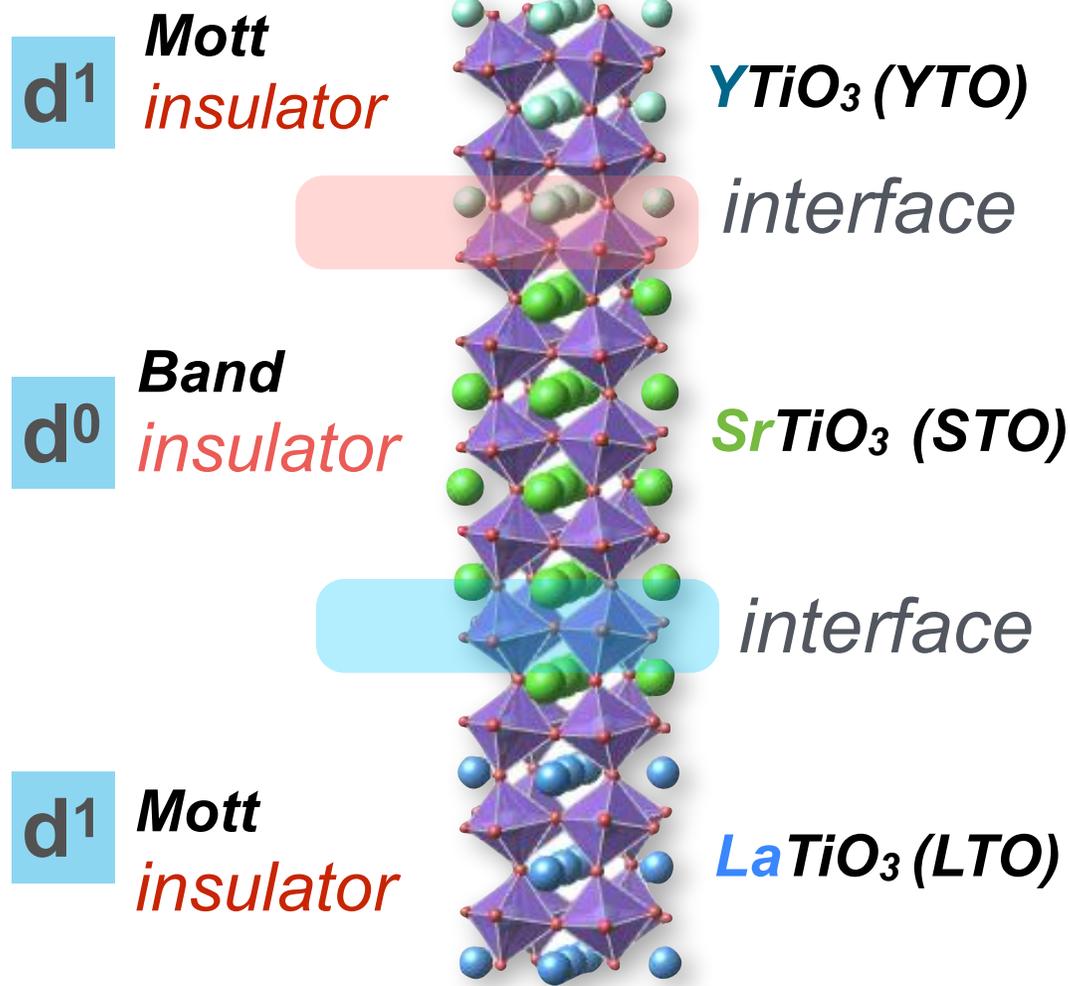
3-color SL



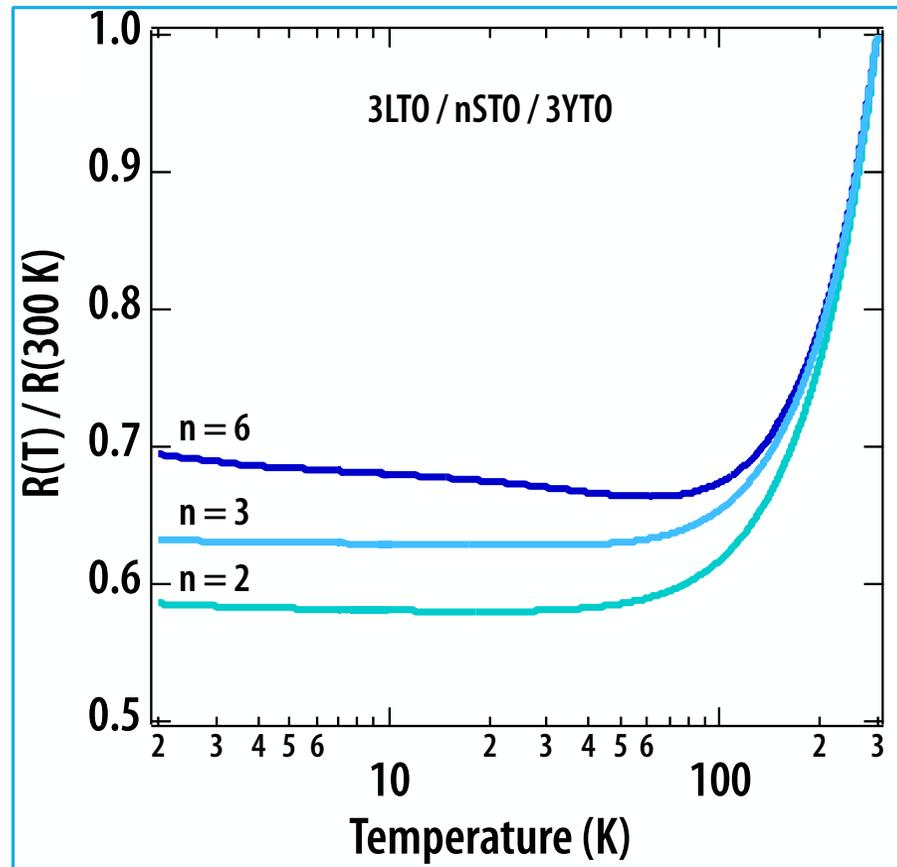
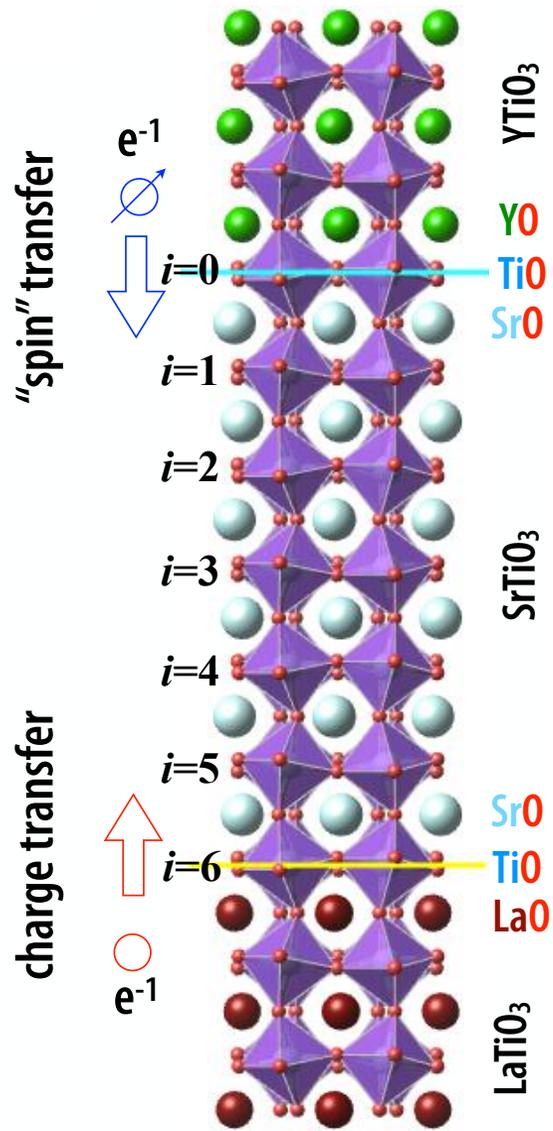
Large distortion ← → Small distortion
 Zhou & Goodenough JPCM 17, 7395 (2005)

Designer tri-color superlattice with controlled interactions

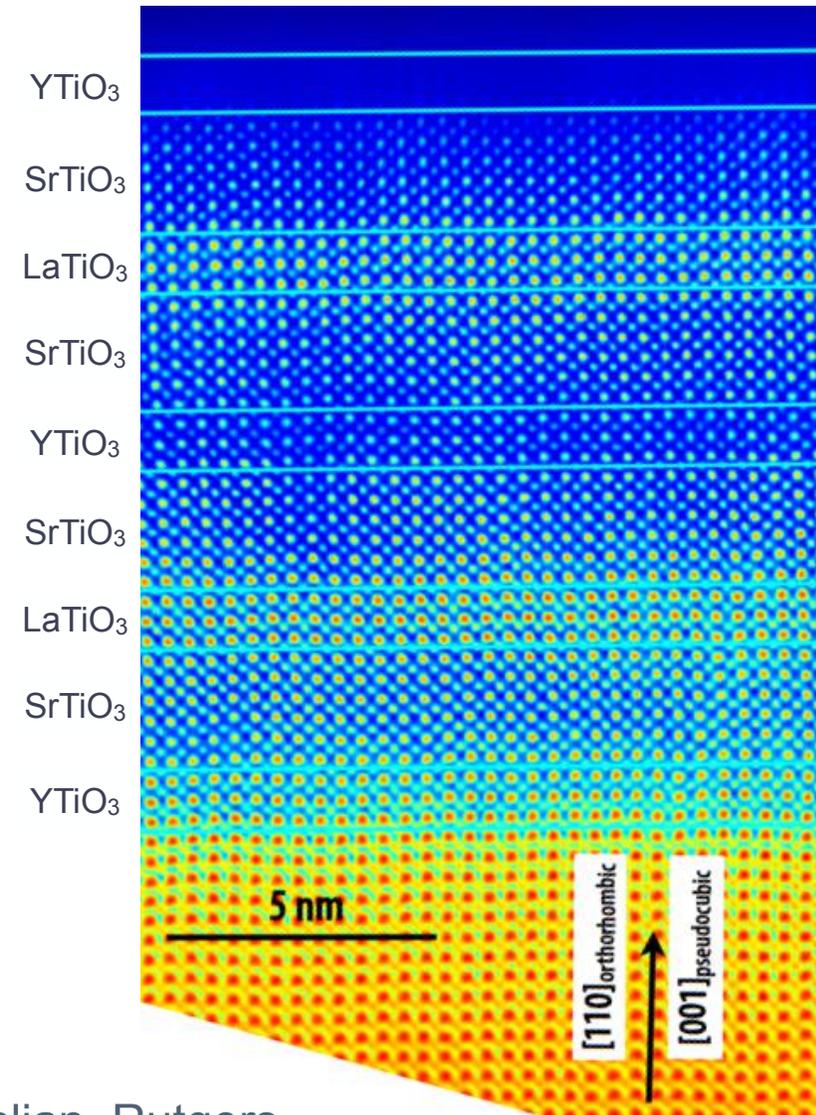
playground



Interfacial charge and "spin" transfer

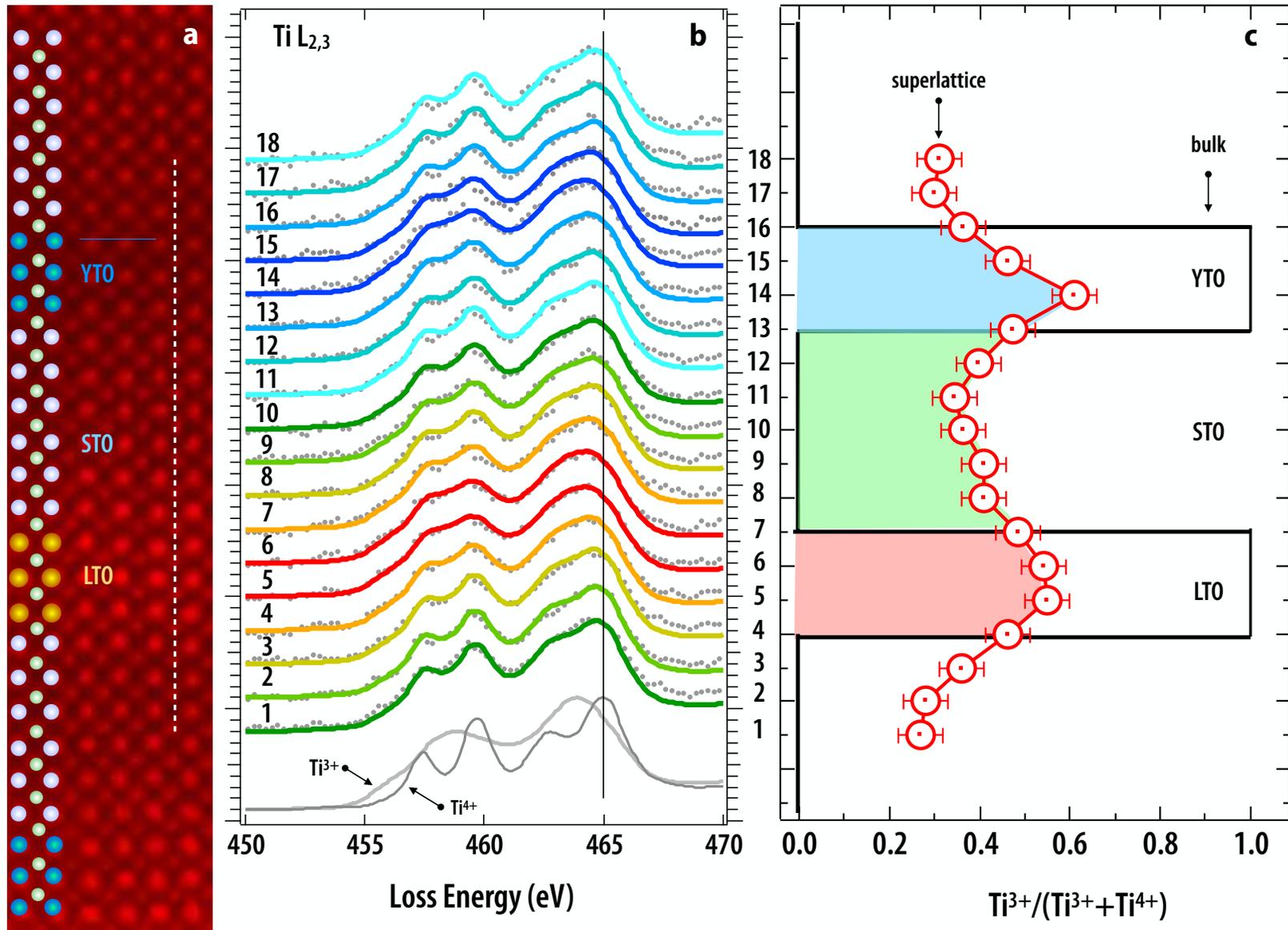


Yanwei Cao et al, PRL 116, 076802 (2016)



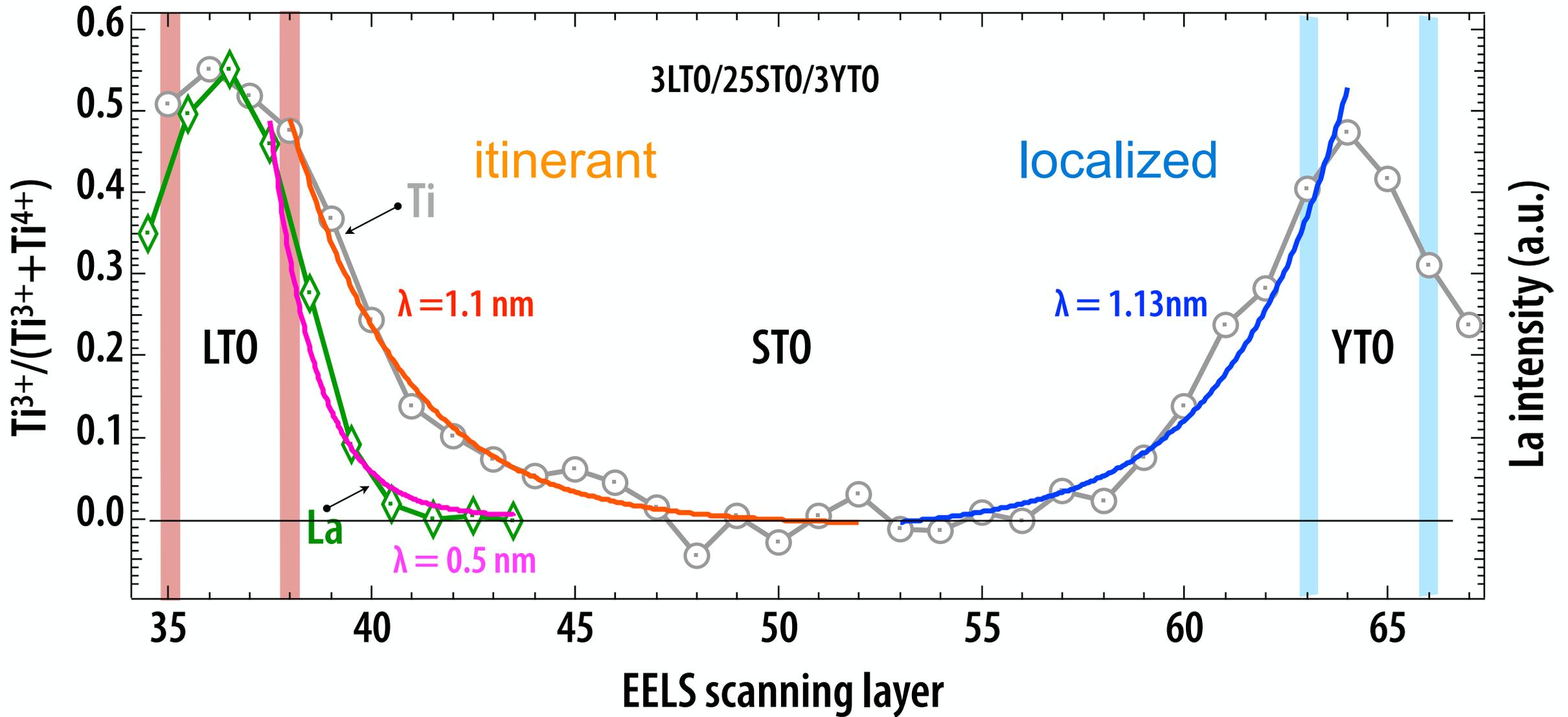
Charges across the interfaces

Collaboration with Lin Gu
and Jiandong Guo, IOP China

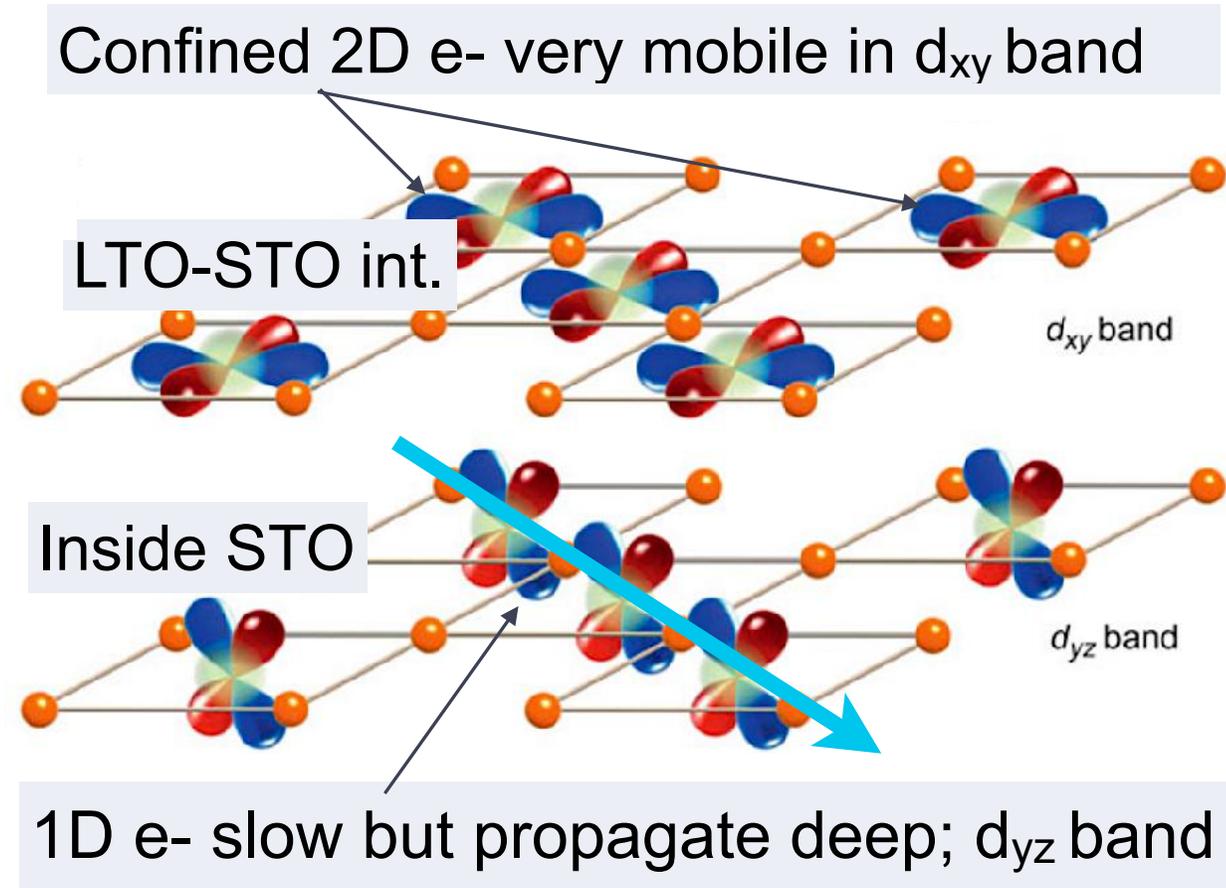
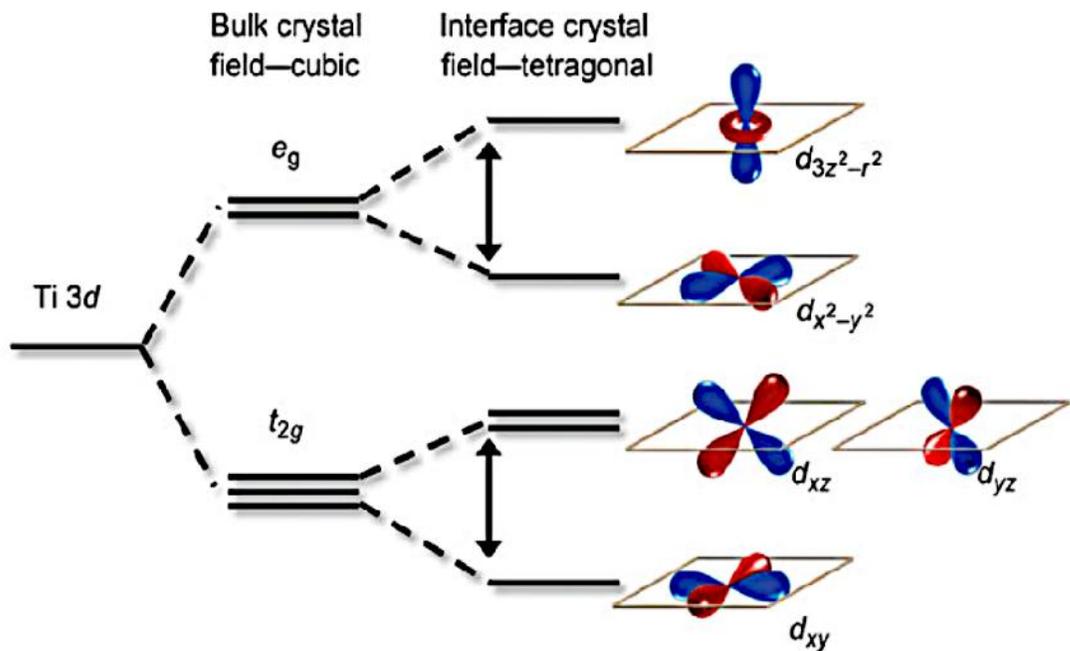


localized non-
mobile magnetic
electrons

mobile electrons
2D electron gas

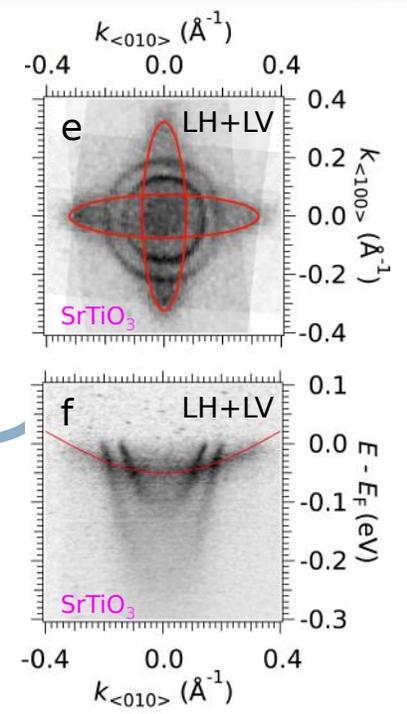
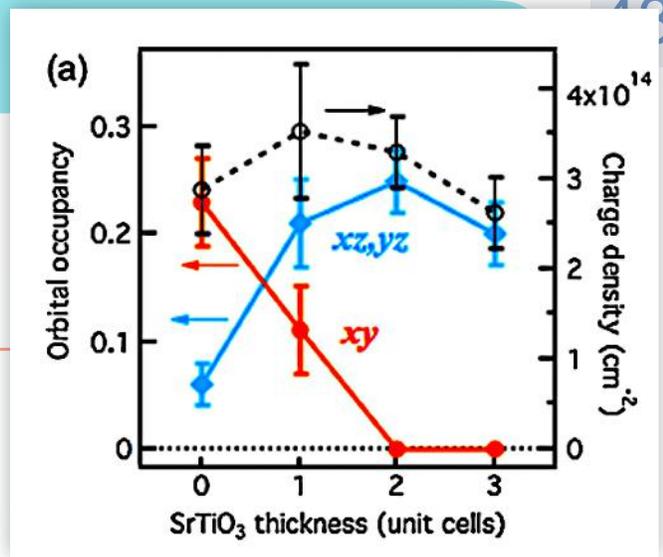
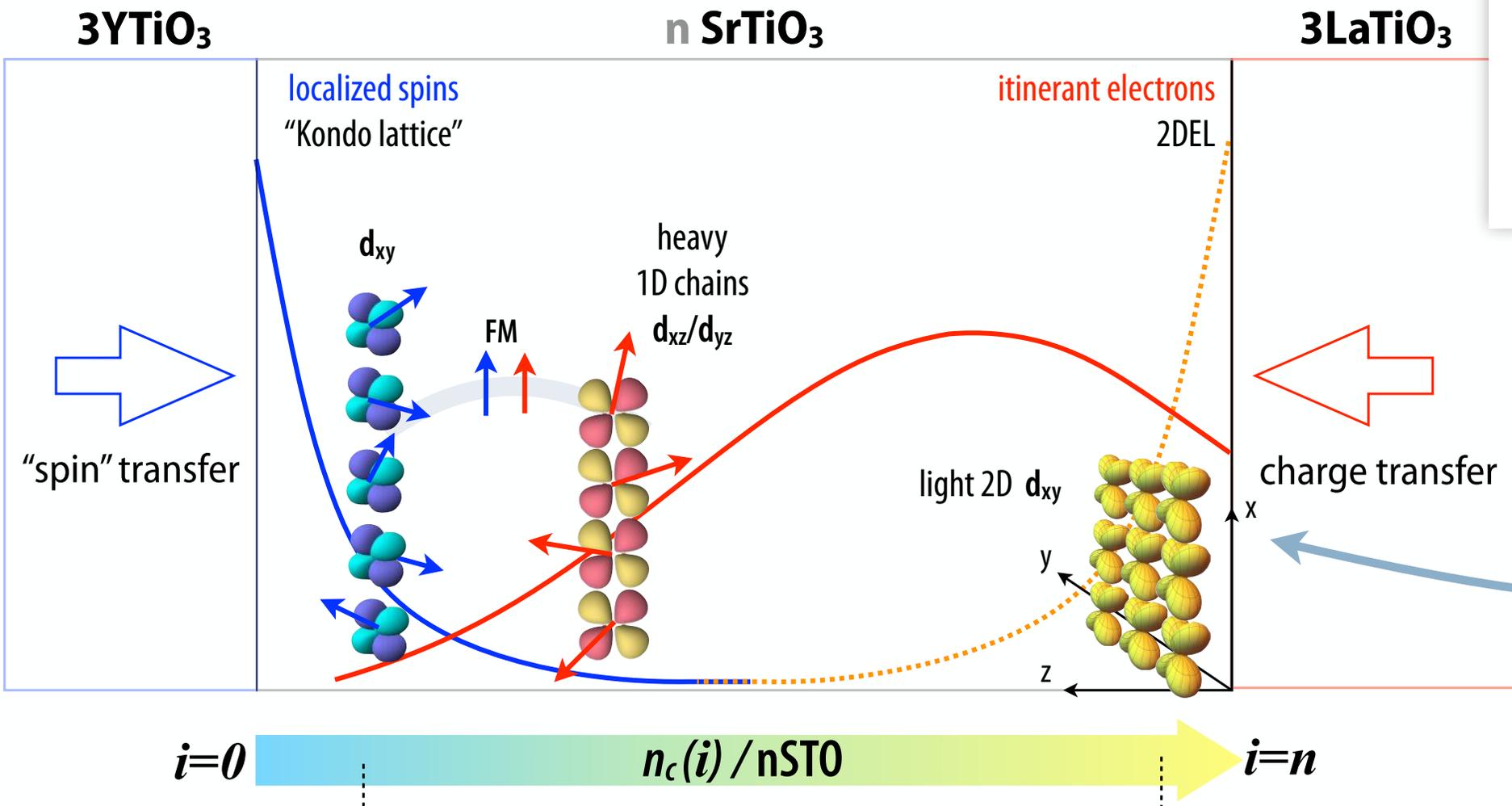


Orbitally selective Kondo effect



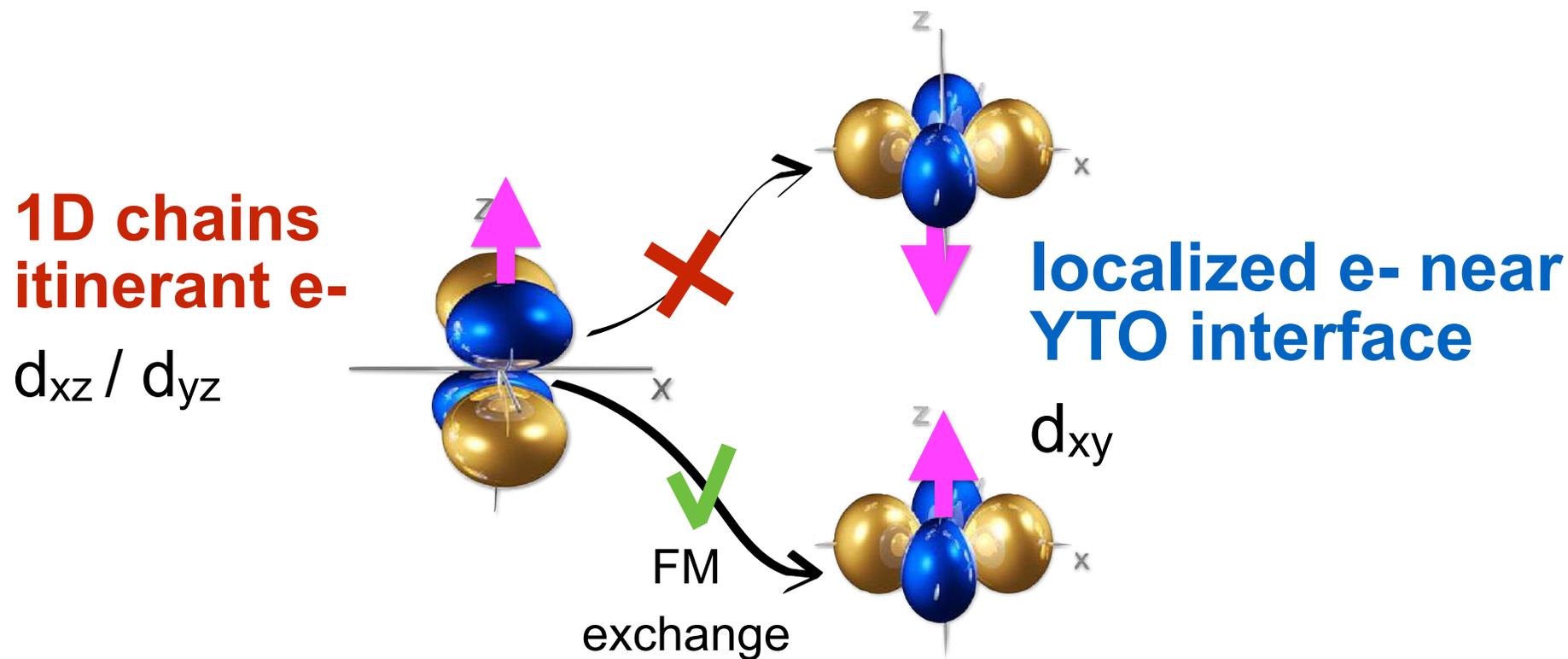
The spatial separation of d_{xy} and d_{xz}/d_{yz} is the combined effect of electrostatic energy and crystal field splitting.

orbitally selective interactions: 2DEG + magnetic e-



FM interaction between localized and itinerant electrons

Electrons from 1D “chains” interact **FM** with YTiO_3 electrons



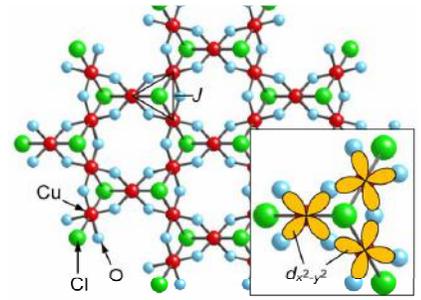
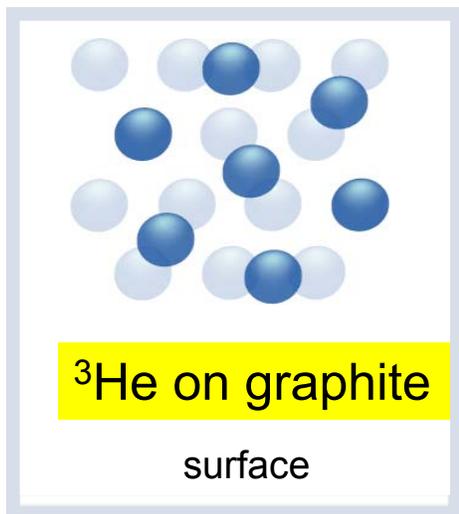


How to liquify spins ?
Fractionalized
fermions, topological
order and all that

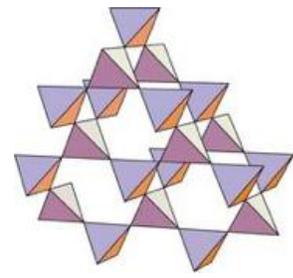
WHY QUANTUM SPIN LIQUIDS (QSL) ARE INTERESTING ?

1. Most QSLs are flat band systems, if doped may result in high (room ?) T_c SC.
2. for $D > 1$ fractional excitations interact with each other through emerging gauge fields, giving rise to *string- and loop-like non-local excitations*.
3. QSLs sustain a new type of non-local order, called *“topological order” without Landau broken symmetry*.

ARE THERE REAL QSL MATERIALS ?

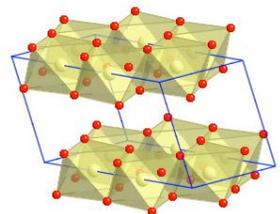


Herbertsmithite



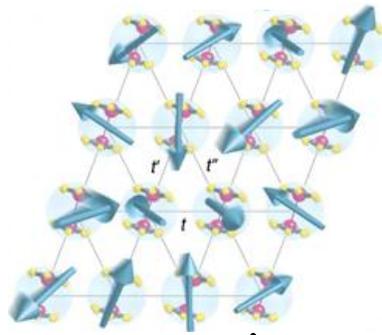
Yb₂Ti₂O₇
...

Quantum spin ice



Na₂IrO₃,
(α , β , γ)-
Li₂IrO₃
 α -RuCl₃

Kitaev materials



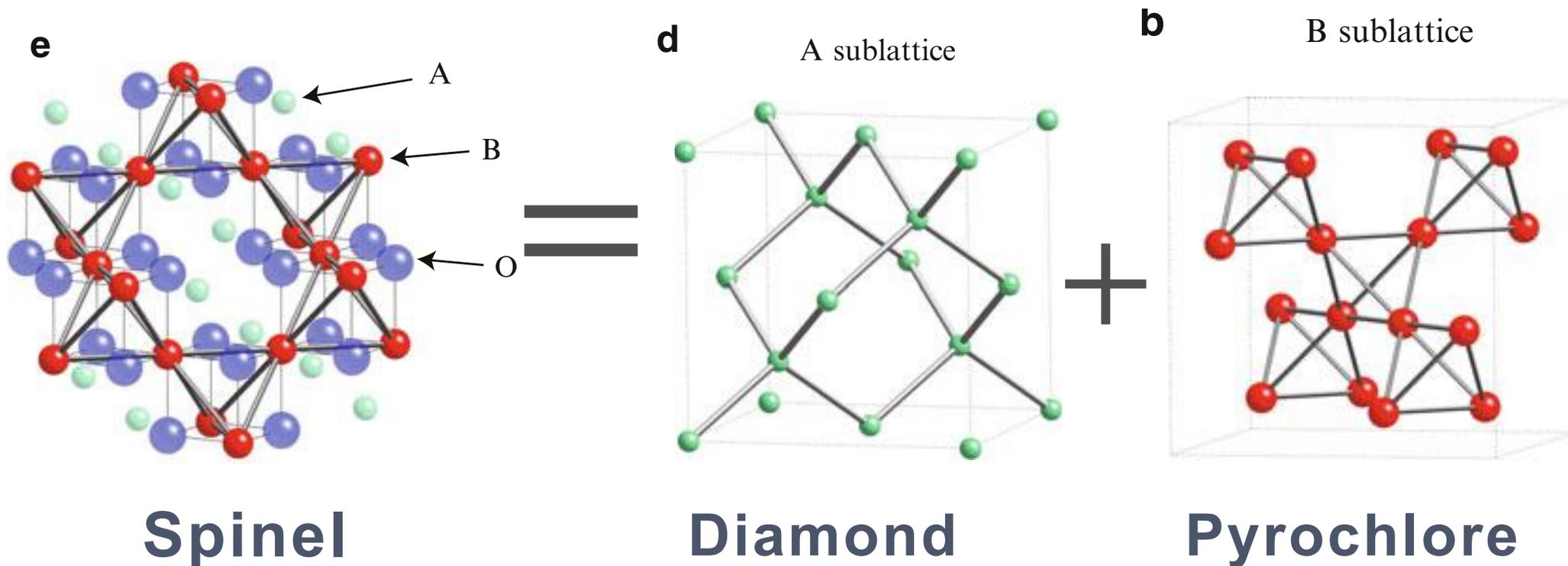
organics

/ Figure from L. Balents presentation /

For D>1 crystals ALL real compounds **order magnetically** ('proximal' QSL) or **defective or not verified** below 1.5K

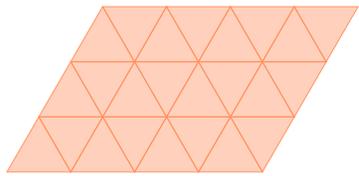
DESIGNER EXTREMELY FRUSTRATED MAGNETS: A WAY TO LIQUIFY ORDERED SPINS

We start from a normal spinel oxide AB_2O_4 , e.g. $CoCr_2O_4$

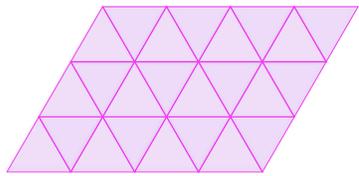


DESIGNER FRUSTRATED MAGNETS

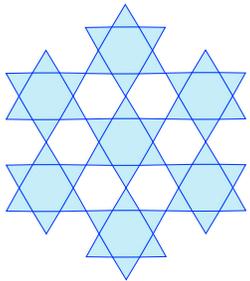
Lattice viewed
along 111



triangular B

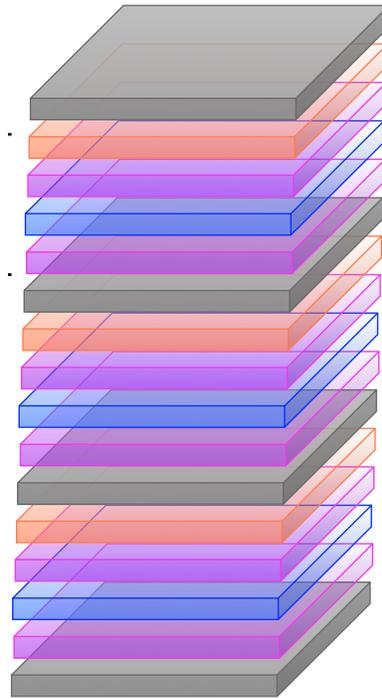


triangular A



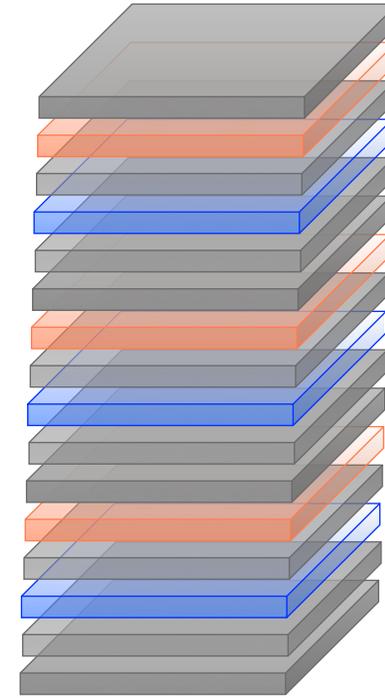
Kagomi B

A and B active



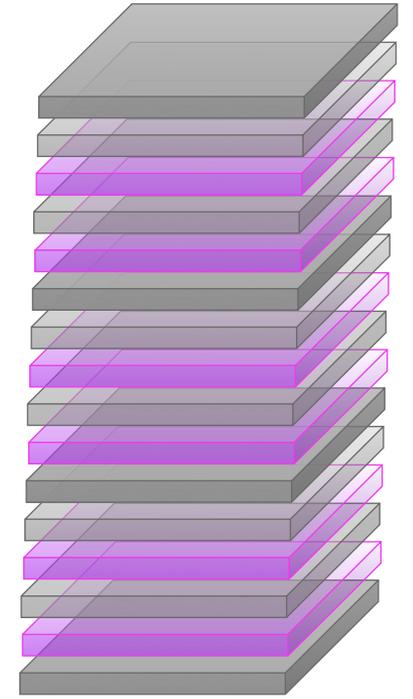
T(A)/K(B)/T(A)/T(B)
or 1 QL

Inactive A-site



planes of
T(B) / K(B)

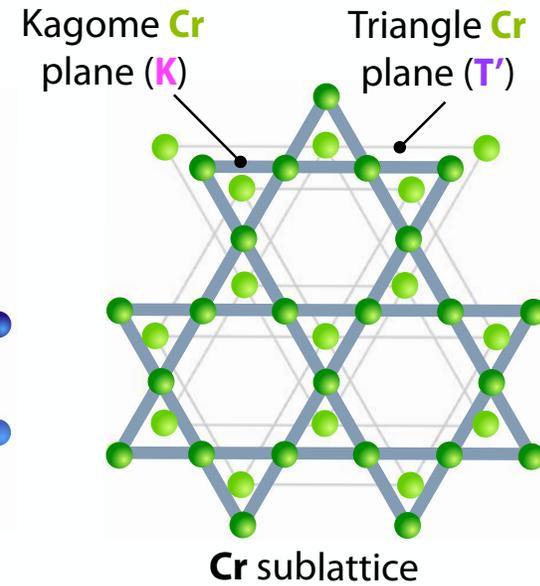
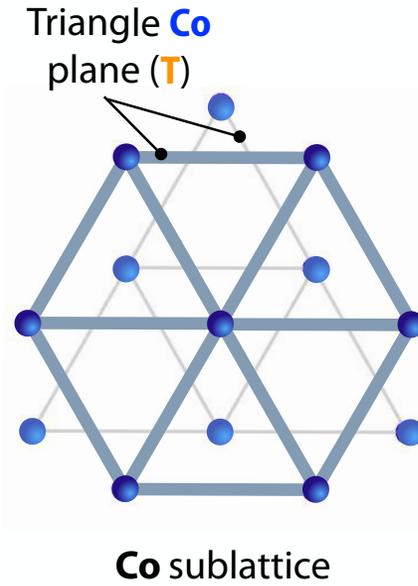
Inactive B-site



atomic
planes of T(A)

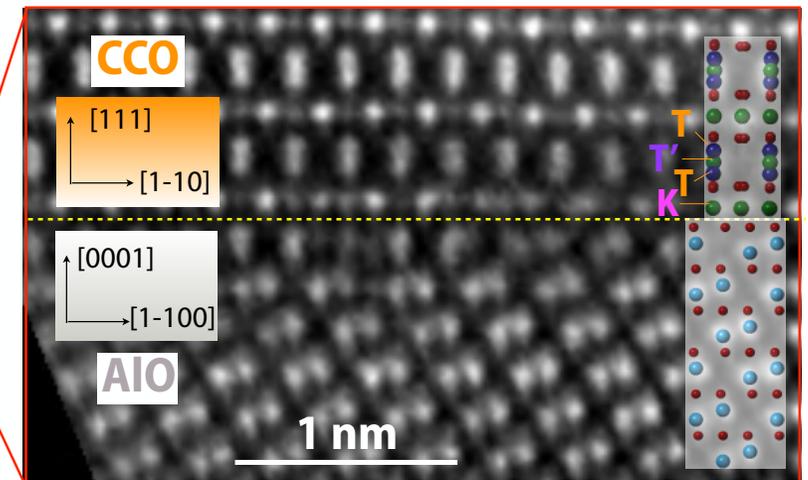
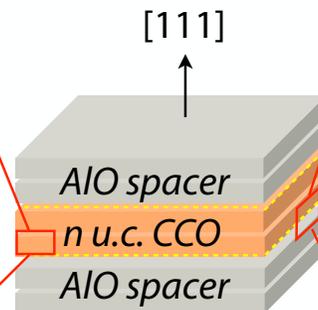
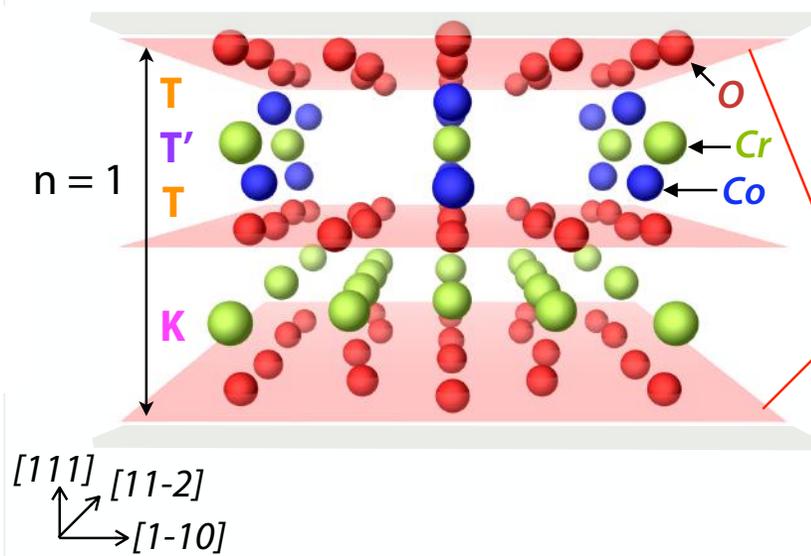
NEW SYNTHETIC QUANTUM STRUCTURE /CCO111/

B



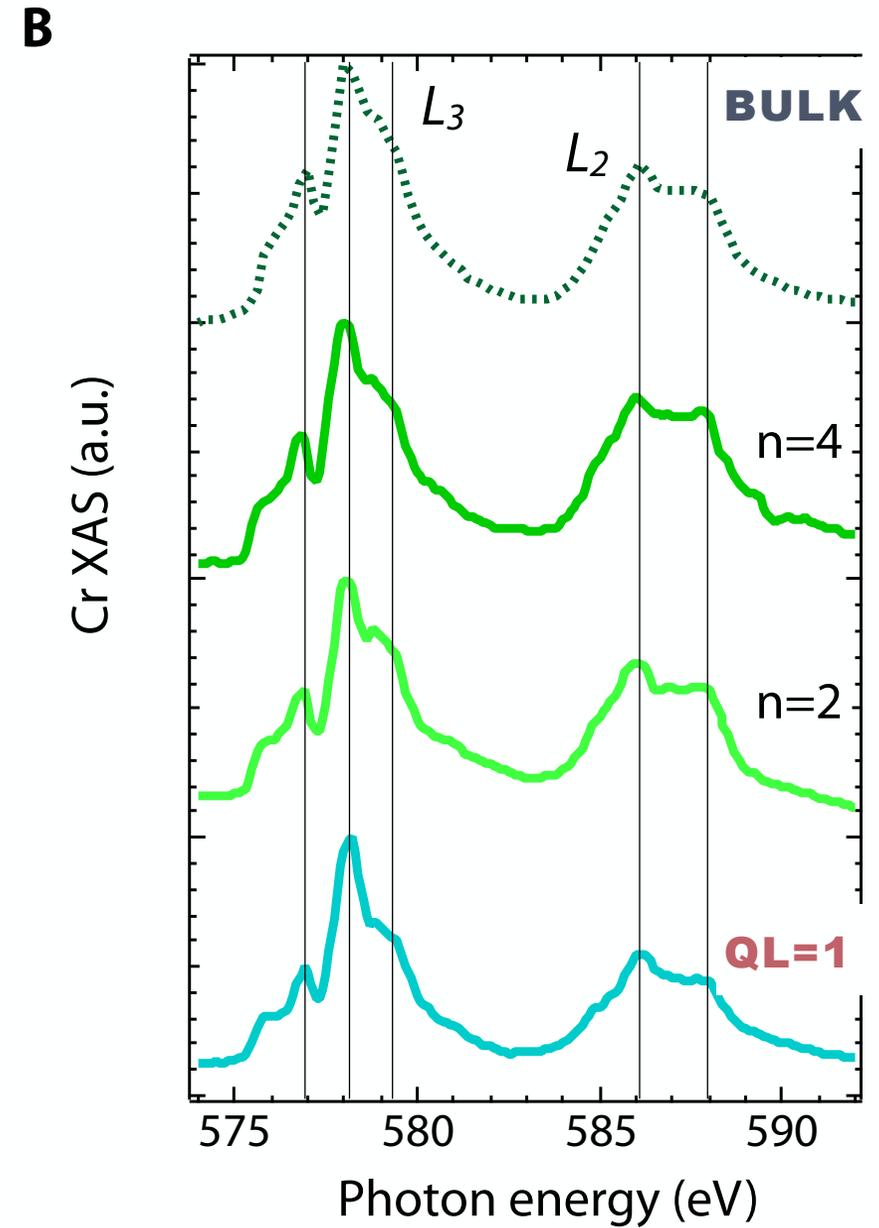
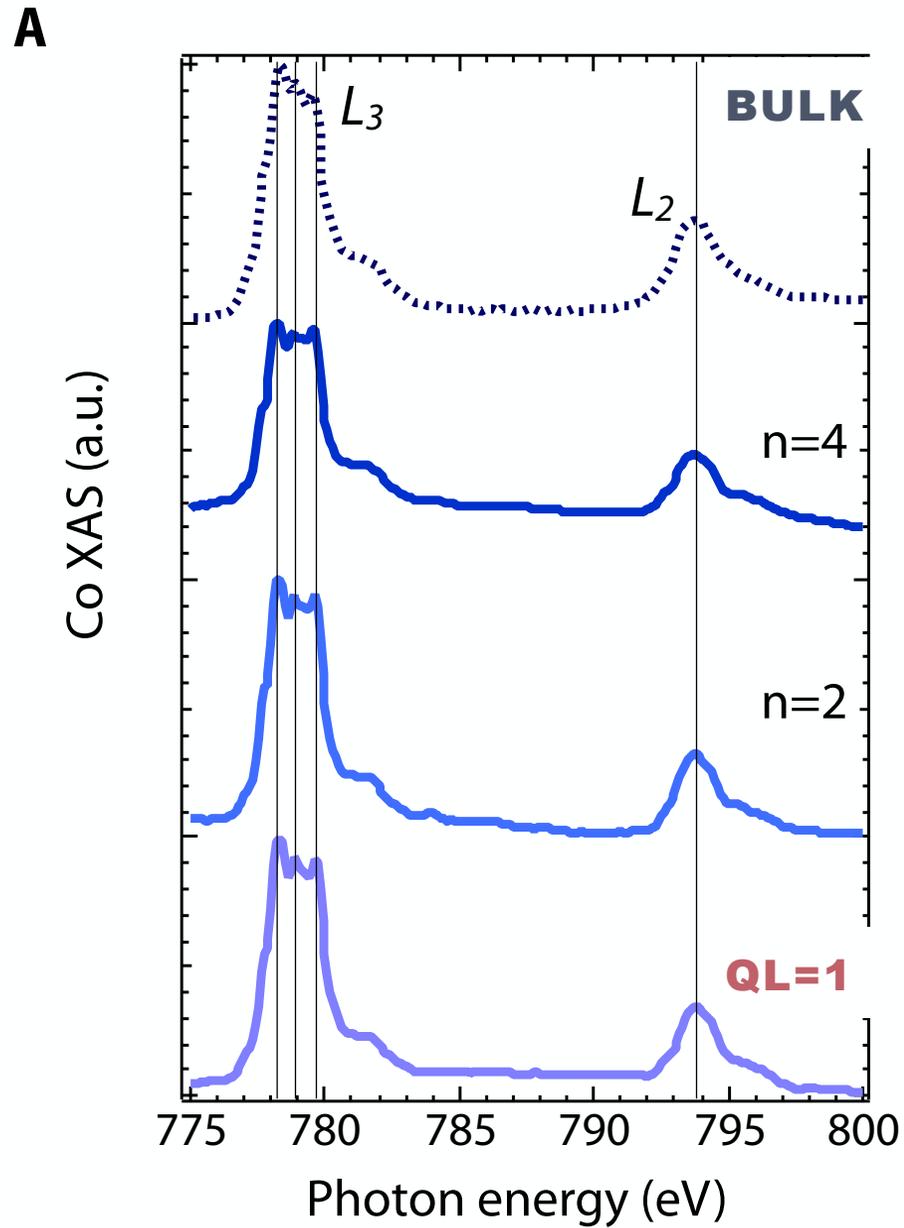
C

unit cell
 $1QL=TT'TK$
 $=4.9\text{\AA}$



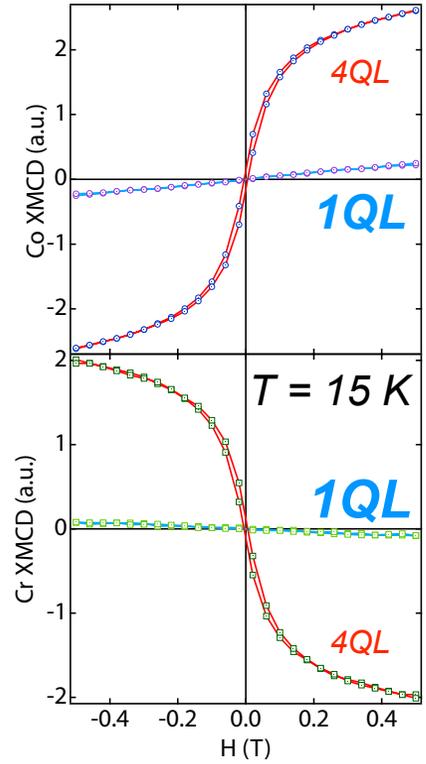
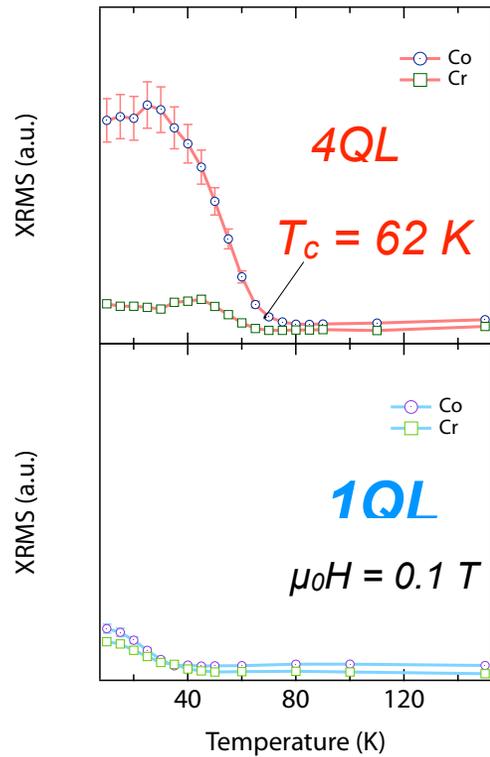
TEM work by Lin Gu (IOP,CAS)

PERFECT CHEMICAL QUALITY OF CCO111

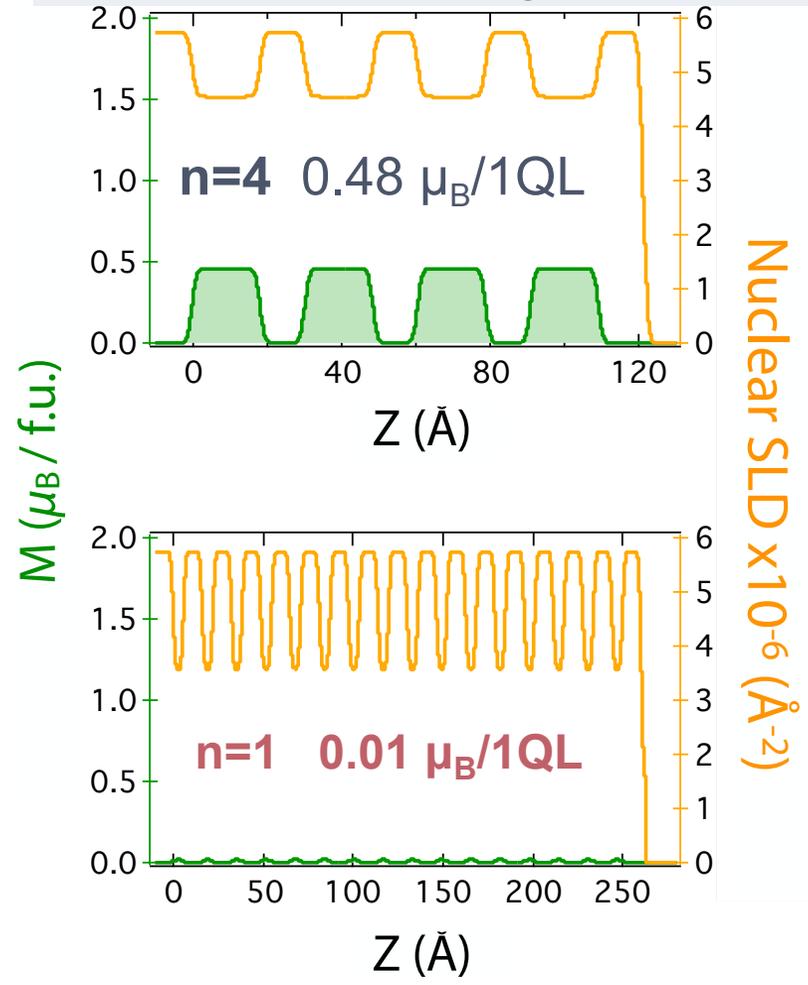


MAGNETIC PROPERTIES OF CCO111

X-ray magnetic dichroism Co and Cr L edge

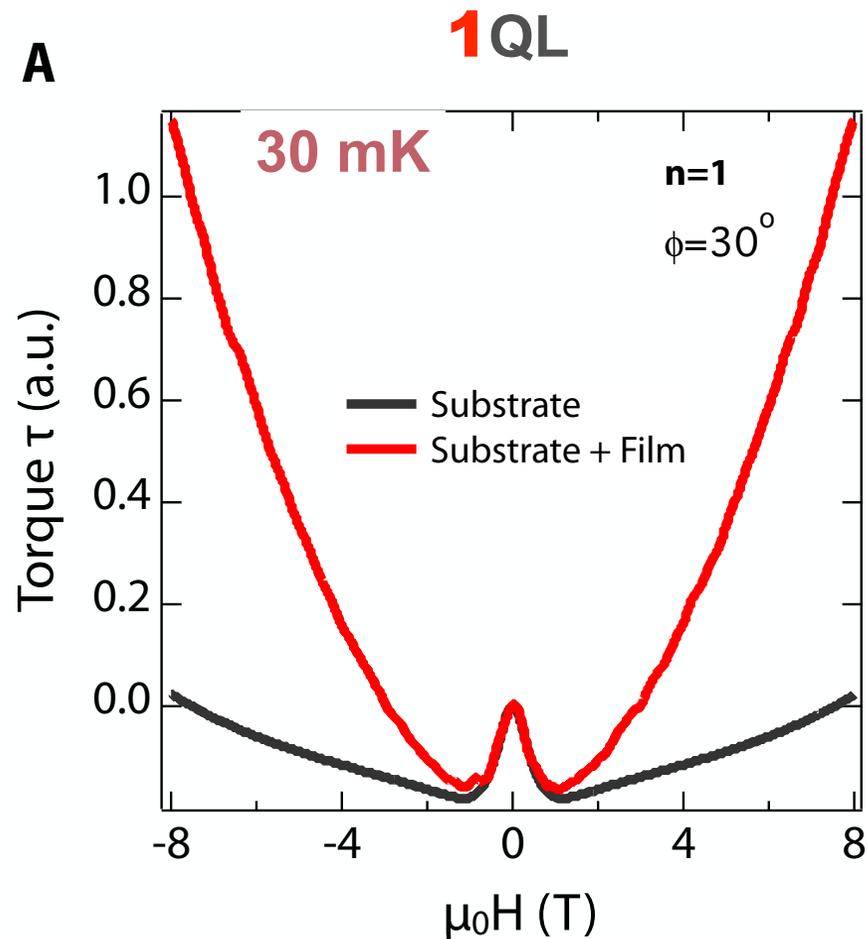
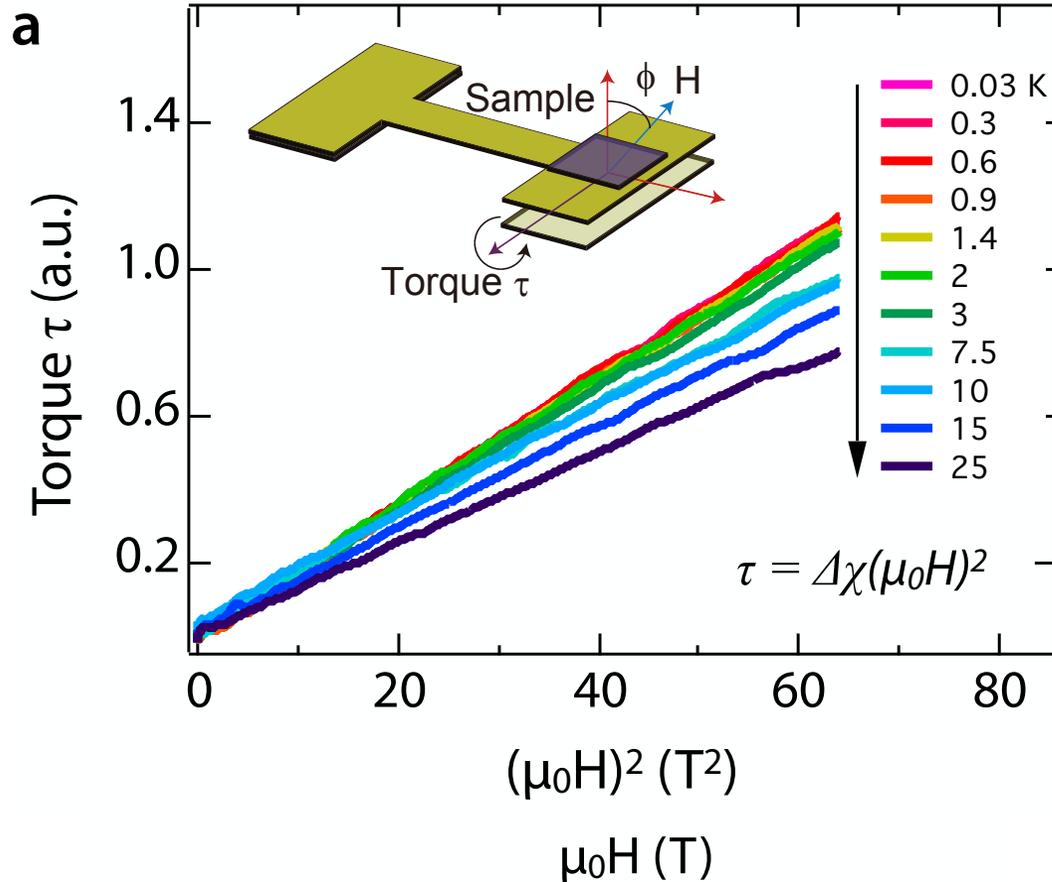


Spin polarized neutron reflectivity



4QL - ferrimagnetic transition at 62 K
 1QL - **No order in CCO111 down to 15 K**

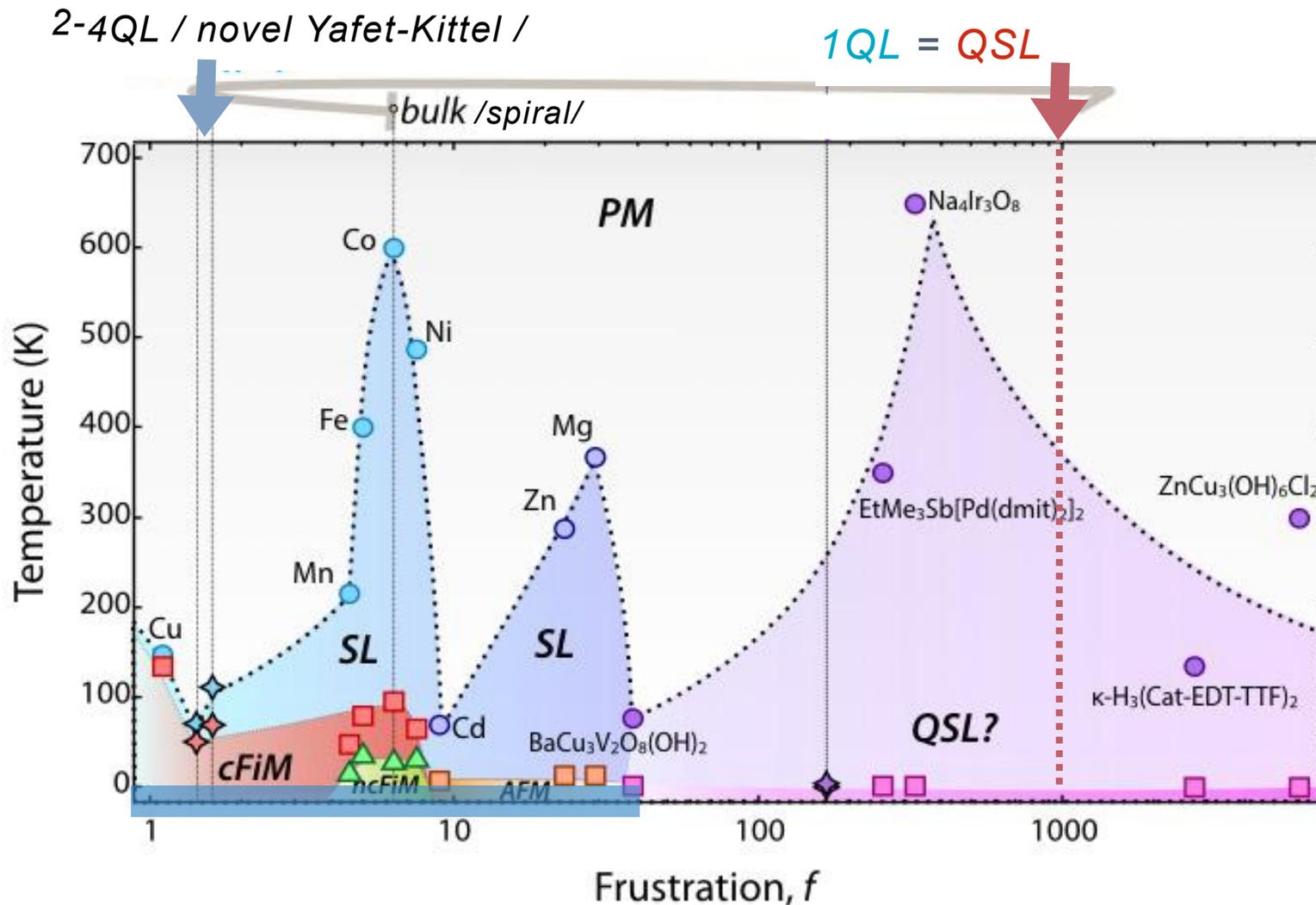
TORQUE MAGNETOMETRY



/Collaboration with Lu Li, Michigan U/

CCO111 - No long-range spin order down to 30 mK and 8T (!)

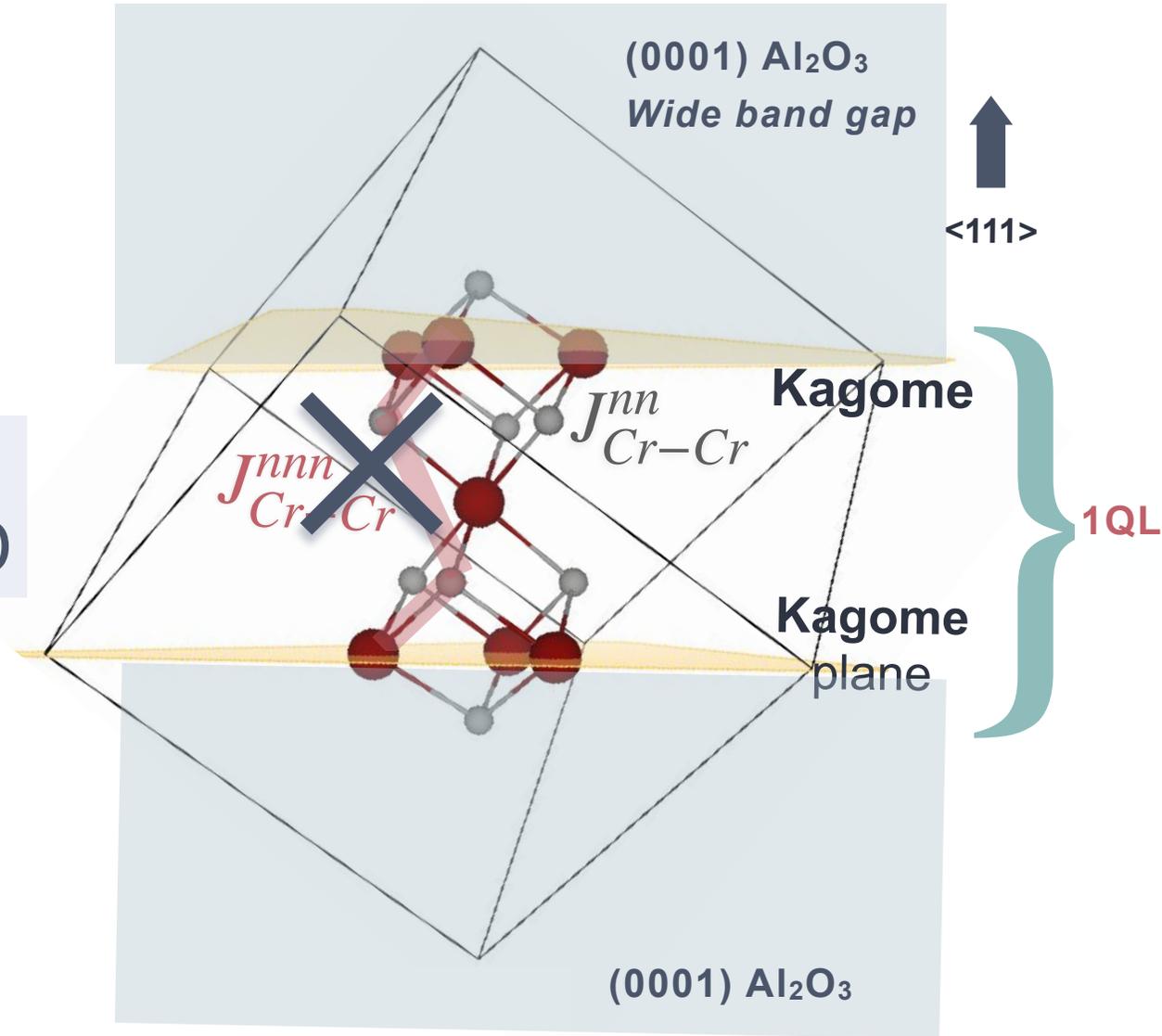
WHAT KIND OF QSL ?



**Frustration factor $f = \Theta_{cw}/T_c$ around - 100-1000
best candidates for QSL**

QSL ARISES FROM INTERACTIONS DUE TO INTERFACE !

Without J_{nnn}
the system is 2D



Interface 'kills' J_{nnn}^{Cr-Cr} term and **amplifies frustration**

IDEAS and CHALLENGES

more in Chapter 9 in the lecture notes

1. If you replace a nano-seconds **UV laser** with a **femtoseconds** one, what **synthesis** regime can we reach? The intrigue here is in the femtosecond regime. There is no time for heat dissipation as phonons are too slow / pico-seconds timescale /.
2. What happens if you **combine different topological classes** and antagonistic orders e.g. Dirac electrons with Cooper pairs or Cooper pairs and magnetic monopoles of a spin-ice?
3. Can you think of a design approach for structures that can **'zoom in' on a specific term of a Hamiltonian?**
4. Can you create **structures** holding **quantum chaos?**
5. What about **structures** that reach **quantum hydrodynamics?**
7. What designer structures can **directly reveal** the **entanglement** of fermions ?

Q: Is there unseen universe hidden in the interface ?

Thank you !
Questions ?



A: “ There is no question there is an **unseen universe**.

The question is: how far is it from midtown, and how late is it open ? ”

Woody Allen