An approach to phonon-engineering motivated by transition metal oxides

“Quantum cavities and excitonic insulators” workshop
CCQ, 9th July 2019

J. Fowlie, J.-M. Triscone
University of Geneva
Y. Laplace
École Polytechnique, Paris

Discussions at CCQ
Outline

• Introduction to perovskite transition metal oxides
• Heteroepitaxy
• Nickelates
• Strontium titanate
• Solid state cavities
• Outlook
Highly directional and spatially confined orbitals

Electronic correlations and strong sensitivity to the lattice

Transition metal d - oxygen p orbitals are compatible

Hybridisation physics

Many available valence states

Rich chemistry
Perovskite structure

- Alkali metal
- Alkali earth metal
- Rare earth lanthanoid
- Transition metal
- Post-transition metal

ABO$_3$ is a flexible formula unit
Perovskite transition metal oxides

$\text{e}_g$

$\text{d}_{x^2-y^2}$  $\text{d}_{3z^2-r^2}$

$\text{t}_{2g}$

$\text{d}_{xz}$  $\text{d}_{yz}$  $\text{d}_{xy}$

$10\, Dq$

$\theta$

B-O-B bond angle

Changes with cation choice or external parameters

Nickelates introduction

- Metal-insulator transition
- Néel transition
- 2 x symmetry lowering structural transitions
Nickelates introduction

- Metal-insulator transition
- Néel transition
- $2 \times$ symmetry lowering structural transitions

Transition metal oxides contain rich physics
Heteroepitaxy: Growing one material on top of another one.

- Compressive: $\varepsilon_{xx} < 0$
- Tensile: $\varepsilon_{xx} > 0$

**Bulk**

- Bond length modifications
- Defect formation
- Octahedral rotations

**Film**

- Bond length modifications
- Defect formation
- Octahedral rotations

Heteroepitaxy: Growing one material on top of another one.
Heteroepitaxy

- Radio frequency off-axis magnetron sputtering
- Pulsed laser deposition
- Molecular beam epitaxy

LaVO$_3$

DyScO$_3$
Heteroepitaxial effects in TMOs

Heterostructure → Chemical discontinuity

- polar discontinuity
- charge transfer
- confinement
- dimensionality

- phase discontinuity
- domain wall cost
- spin transfer
- frustration

- spin discontinuity
- orbital
- lattice
- structural coupling

- biaxial strain
- lattice parameter mismatch

- Coulomb
- crystal field
- bandwidth
- symmetry mismatch
Heteroepitaxial effects in nickelates

Charge transfer at LaNiO$_3$/LaMnO$_3$ interfaces

Orbital polarisation in LaNiO$_3$-based superlattices

Strain dependence of $R$NiO$_3$ metal-insulator transition

...uced antiferromagnetism in a bulk par...
Heteroepitaxial effects in nickelates

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Induced antiferromagnetism in a bulk paramagnet
Strain dependence of RNiO$_3$ metal-insulator transition

S. Catalano et al, APL Mater. 2, 116110 (2014)
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Charge transfer at LaNiO$_3$/LaMnO$_3$ interfaces

M. Gibert et al, Nat. Mater. 11, 3224, (2012)
Heteroepitaxial effects in nickelates

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Induced antiferromagnetism in a bulk paramagnet
Orbital polarisation in LaNiO$_3$-based superlattices

Motivation: Turning the nickelate electronic structure into the high $T_c$ cuprate one

50% orbital polarisation

100% orbital polarisation may never be possible
Heteroepitaxial effects in TMOs

- Heterostructure
- Chemical discontinuity
- Polar discontinuity
- Charge transfer
- Confinement
- Dimensionality
- Induced heterostructure effects
- Physical mechanisms
- Structural coupling
- Symmetry mismatch

- Phase discontinuity
- Domain wall cost
- Frustration
- Biaxial strain
- Lattice parameter mismatch

- Spin discontinuity
- Spin
- Coulomb
- Crystal field
- Hund
- Orbital
- Bandwidth

- Charge
- Crystal field
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Strontium titanate

3d⁰ paramagnetic wide-gap band insulator

The “drosophila” of solid state physics
Quantum paraelectricity

M. Gabay & J.-M. Triscone
Ferroelectric materials

The softening of the phonon to zero frequency is connected with the appearance of the ferroelectric state.

Superconductivity

SrTiO3

Sr1-xLa_xTiO3 → SrNbxTi1-yO3 → SrTiO3-δ

Superconductivity

Enhancing superconductivity

\[ \text{Sr}_{1-x}\text{La}_x\text{Ti}(^{16}\text{O}_{1-z}^{18}\text{O}_z)_3 \]

See also A. Stucky et al, Sci. Rep. 6, 37582 (2016)

\[ \text{Sr}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta} \]

Superconductivity and ferroelectricity

SrTiO$_3$ superconductivity may be controlled by the ferroelectric soft mode phonon

See also S. E. Rowley et al, arXiv 1801.08121 (2018)

Possible “charged phonon” effect in SrTiO$_3$

D. van der Marel et al, arXiv 1903.08394 (2019)
Solid state cavities motivation

The interest in phonon spectra
- Ferroelectric materials
  - Increase Curie temperature
- Quantum paraelectric materials
  - Induce ferroelectricity
- Superconductors
  - Increase critical temperature

Strontium titanate compounds cover all of these properties
Molecular cavities

A. Shalabney et al, Nat. Commun. 6981, 1038 (2014)

Could affect chemical reactivity rates and yields
Motivation (for us)

- Cavity coupling to a vibrational mode may affect chemical reactivity.
- Cavity coupling to a phonon mode may affect...
  - The ferroelectric soft mode, can we increase $T_c$? Or induce $T_c$ in a paraelectric?
  - Enhance superconductivity in doped SrTiO$_3$?
  - Phonon-electron coupling crucial in e.g. superconductors
  - Further coupling mechanisms?
Close to resonance ($\nu_c = \nu_p$) there is avoided crossing.

Cavity combined with dipole phonons

Rabi splitting ($2\Omega$)
Perpendicular electric field

Todorov et al, Optics Express 18, 13886 (2010)
Heterostructure cavities

\[ w = \frac{\lambda}{2} = \frac{c}{2v_p \sqrt{\varepsilon}} \]
Conclusions

Introduction to perovskite transition metal oxides and heteroepitaxy

The interest in phonon spectra
Ferroelectric materials
Quantum paraelectric materials
Superconductors

Solid state cavities

Rich phases