

# 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

# Transition metal oxides

|    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|
| Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| Y  | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| Lu | Hf | Ta | W  | Re | Os | Ir | Pt | Au | Hg |
| Lr | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | Cn |

Highly directional and spatially confined orbitals

————> Electronic correlations and strong sensitivity to the lattice

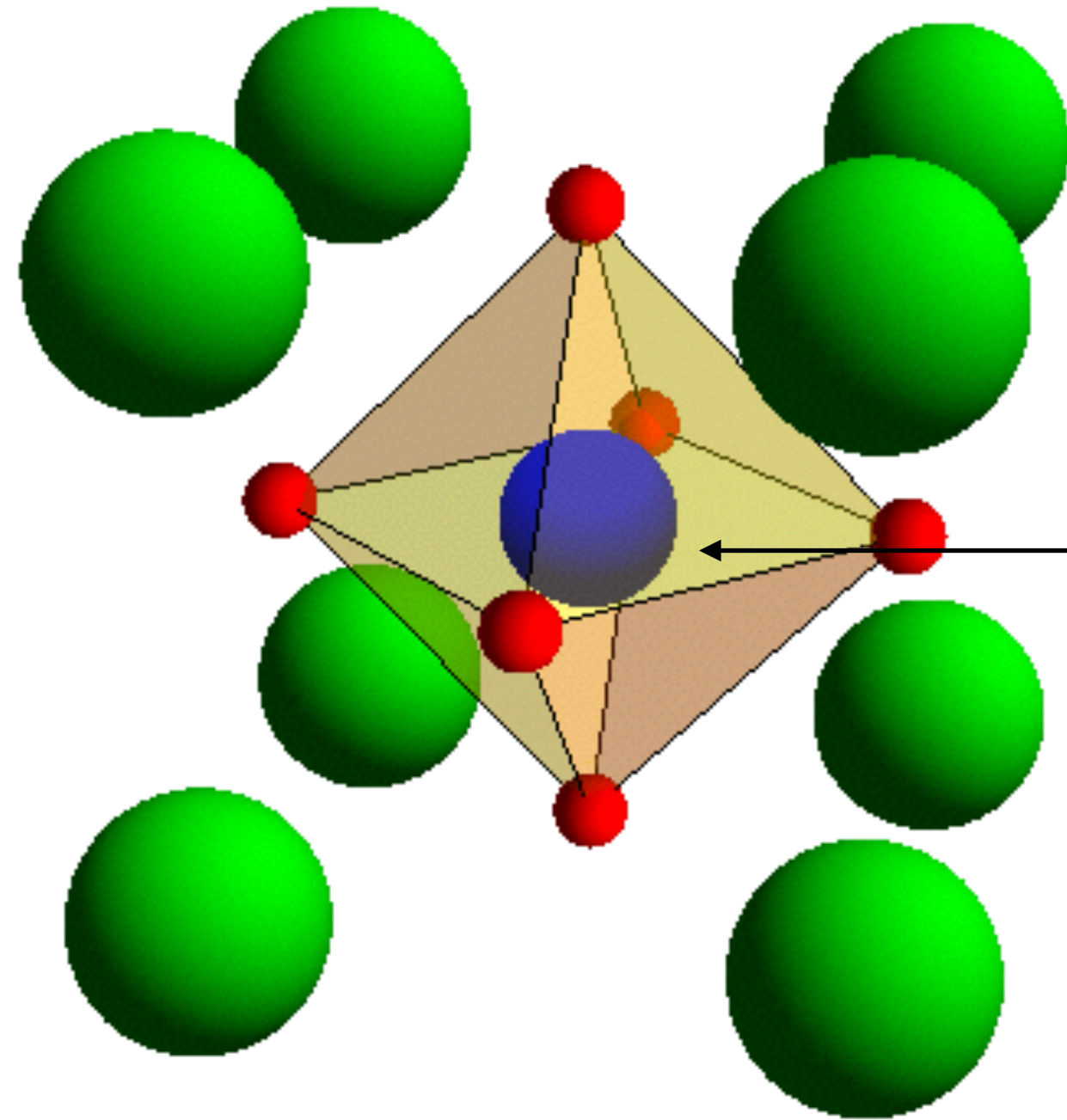
Transition metal d - oxygen p orbitals are compatible

————> Hybridisation physics

Many available valence states

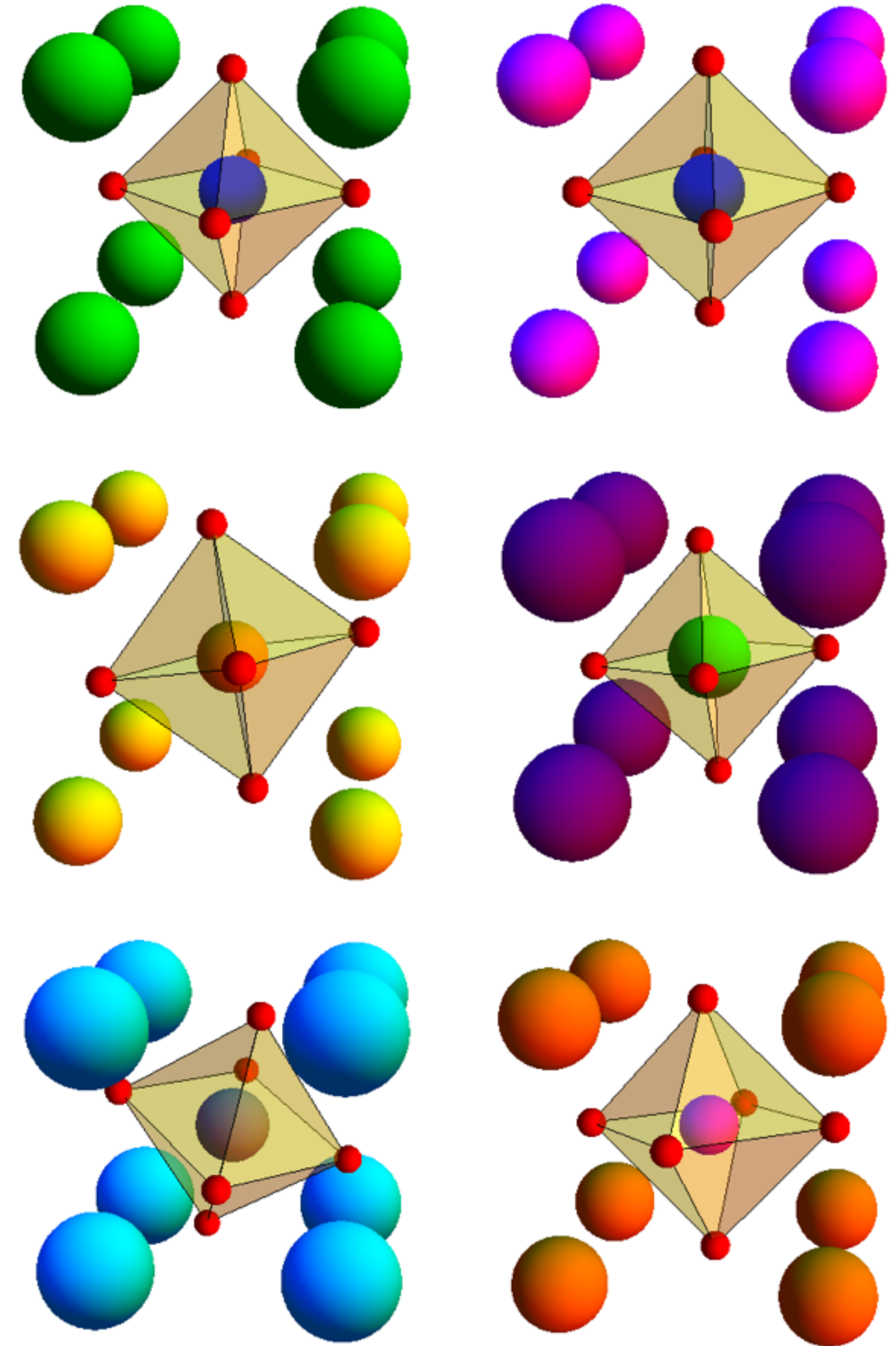
————> Rich chemistry

# Perovskite structure

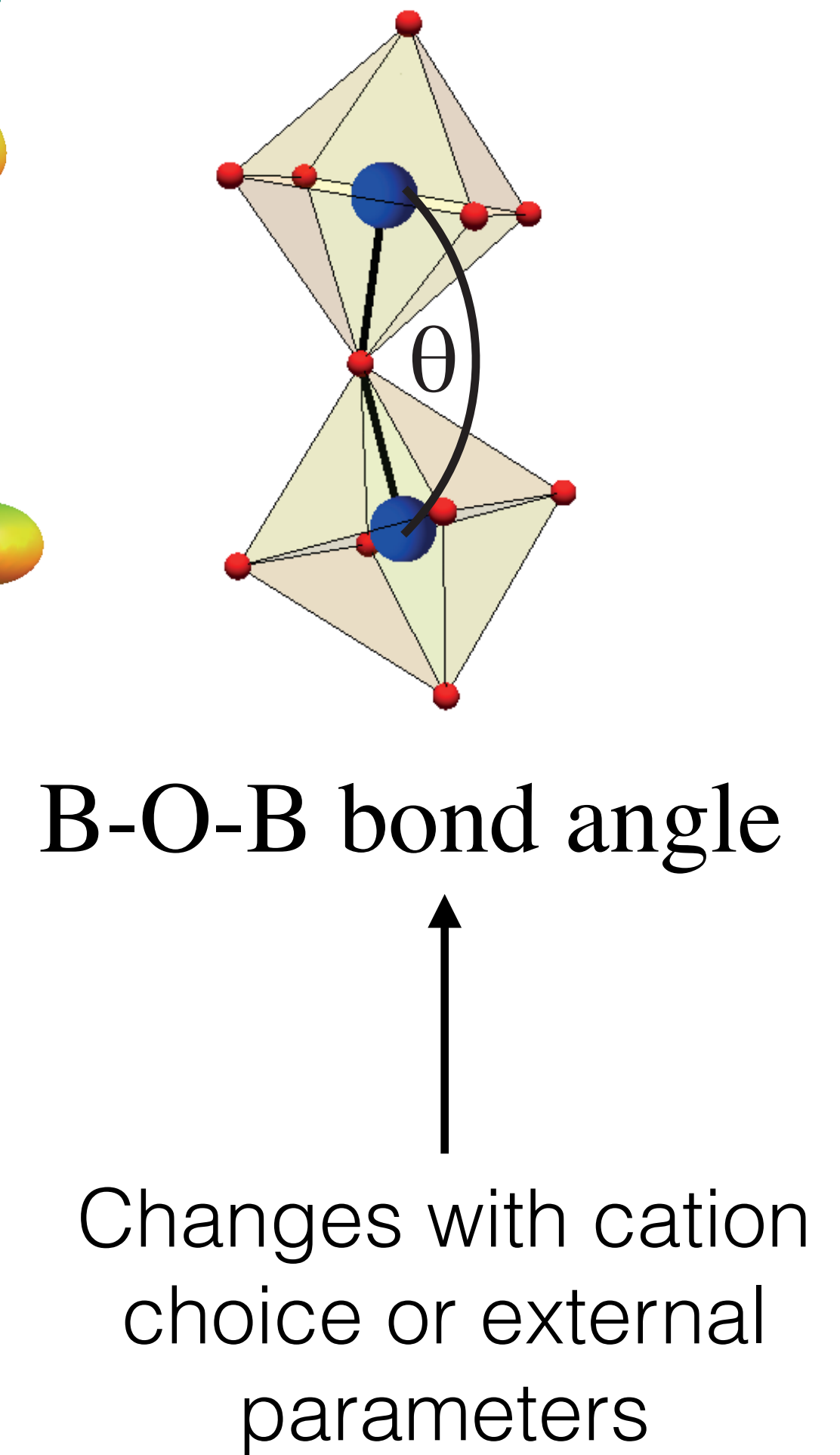
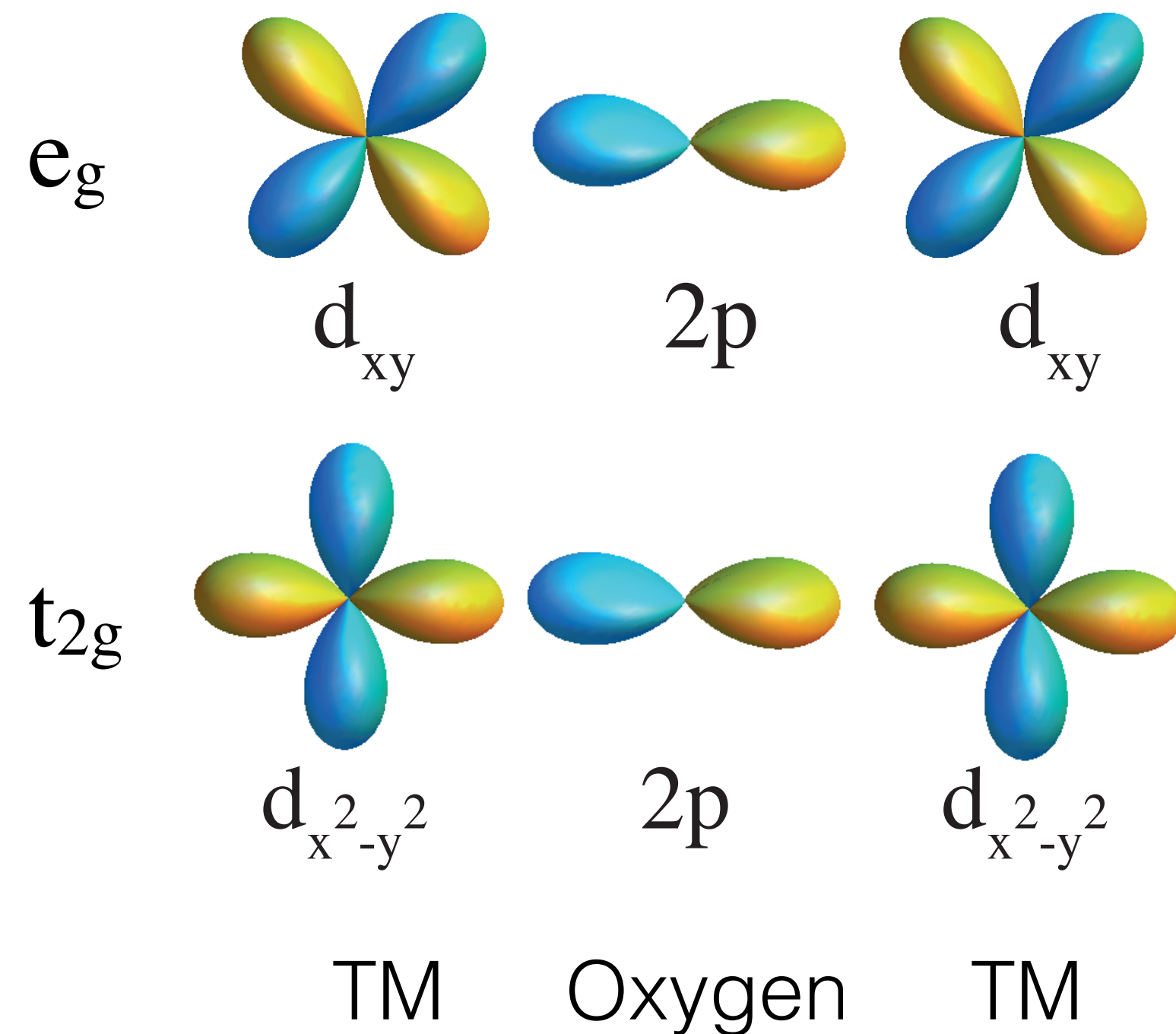
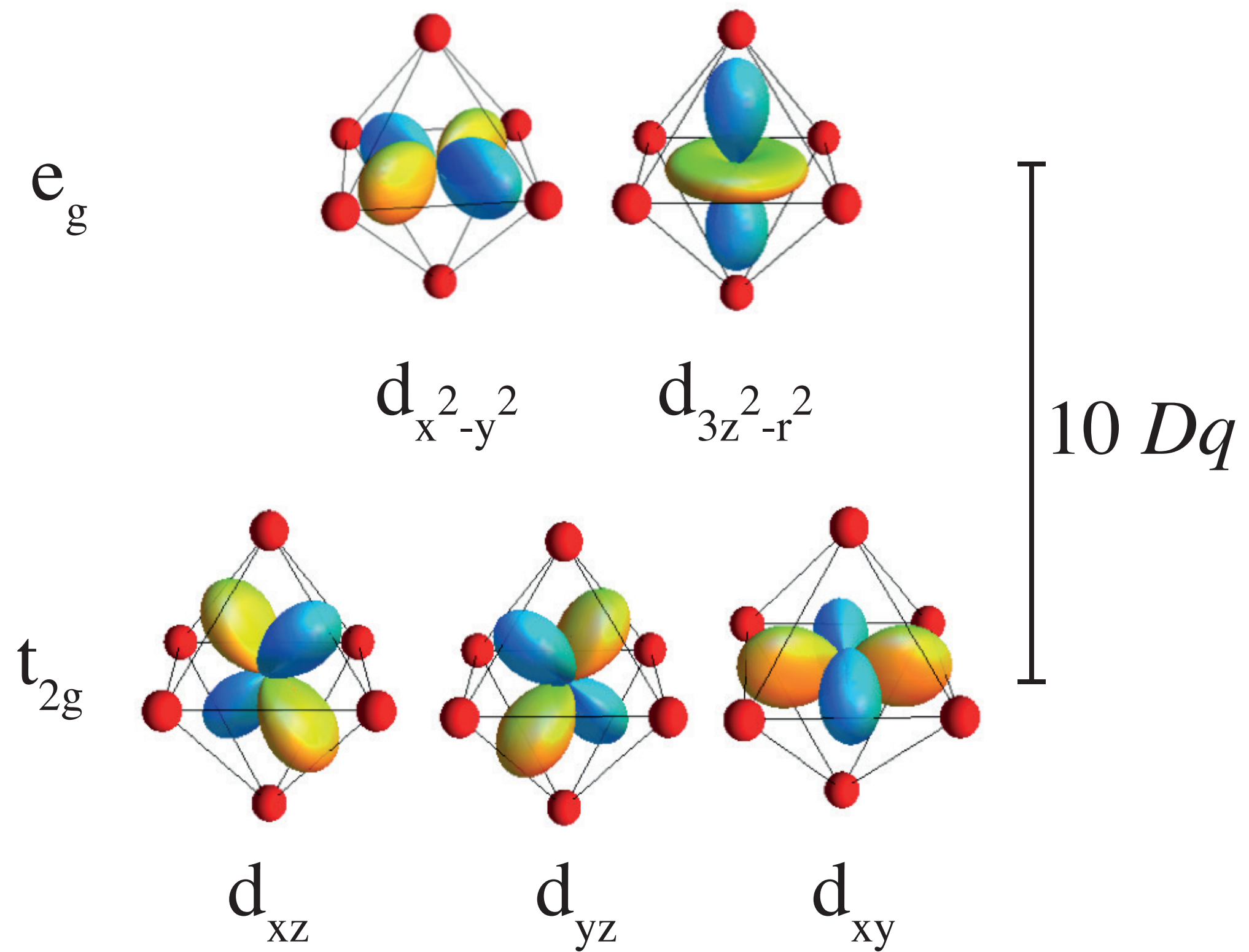


- Alkali metal
- Alkali earth metal
- Rare earth lanthanoid
- Transition metal
- Post-transition metal

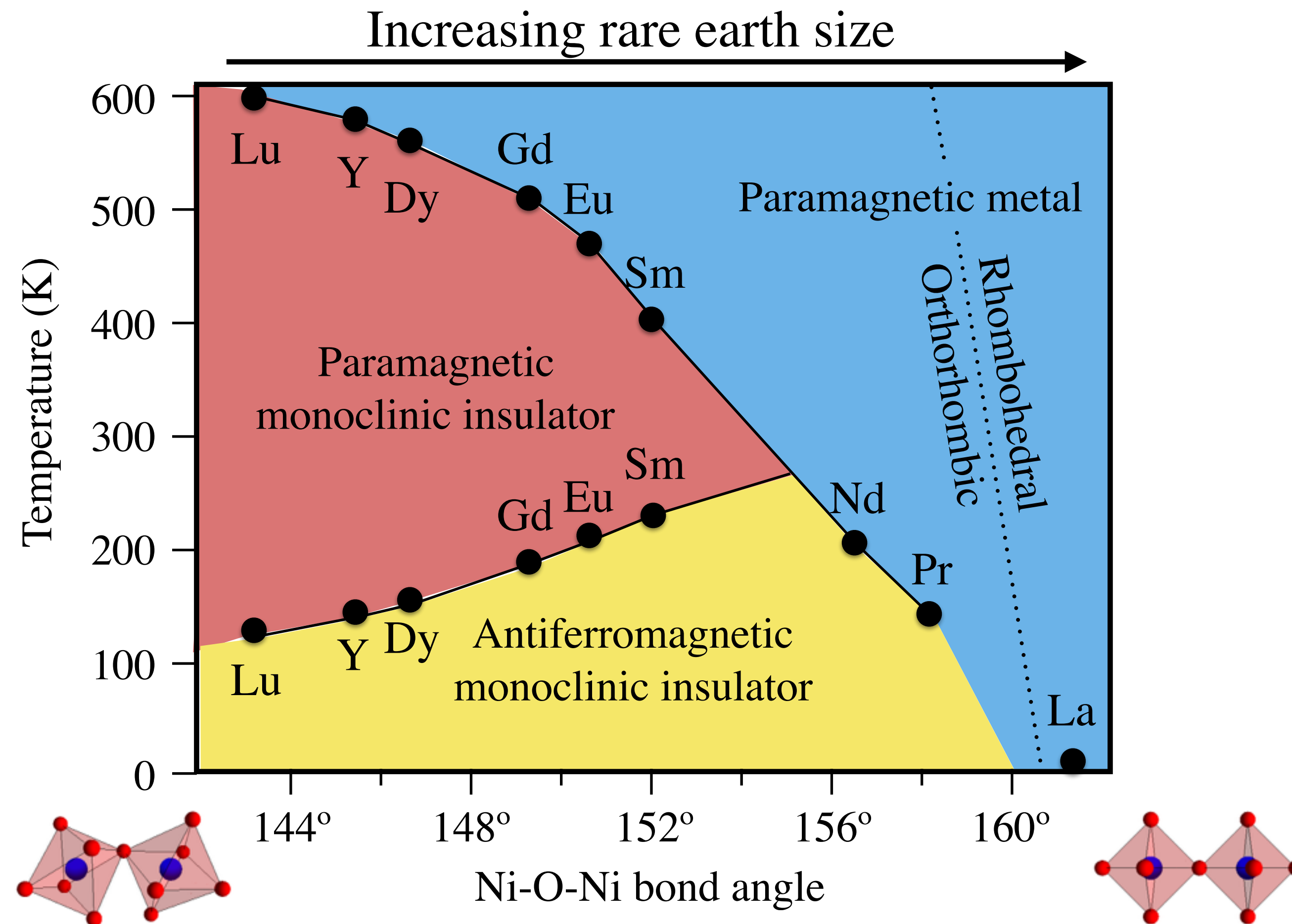
ABO<sub>3</sub> is a flexible formula unit



# Perovskite transition metal oxides



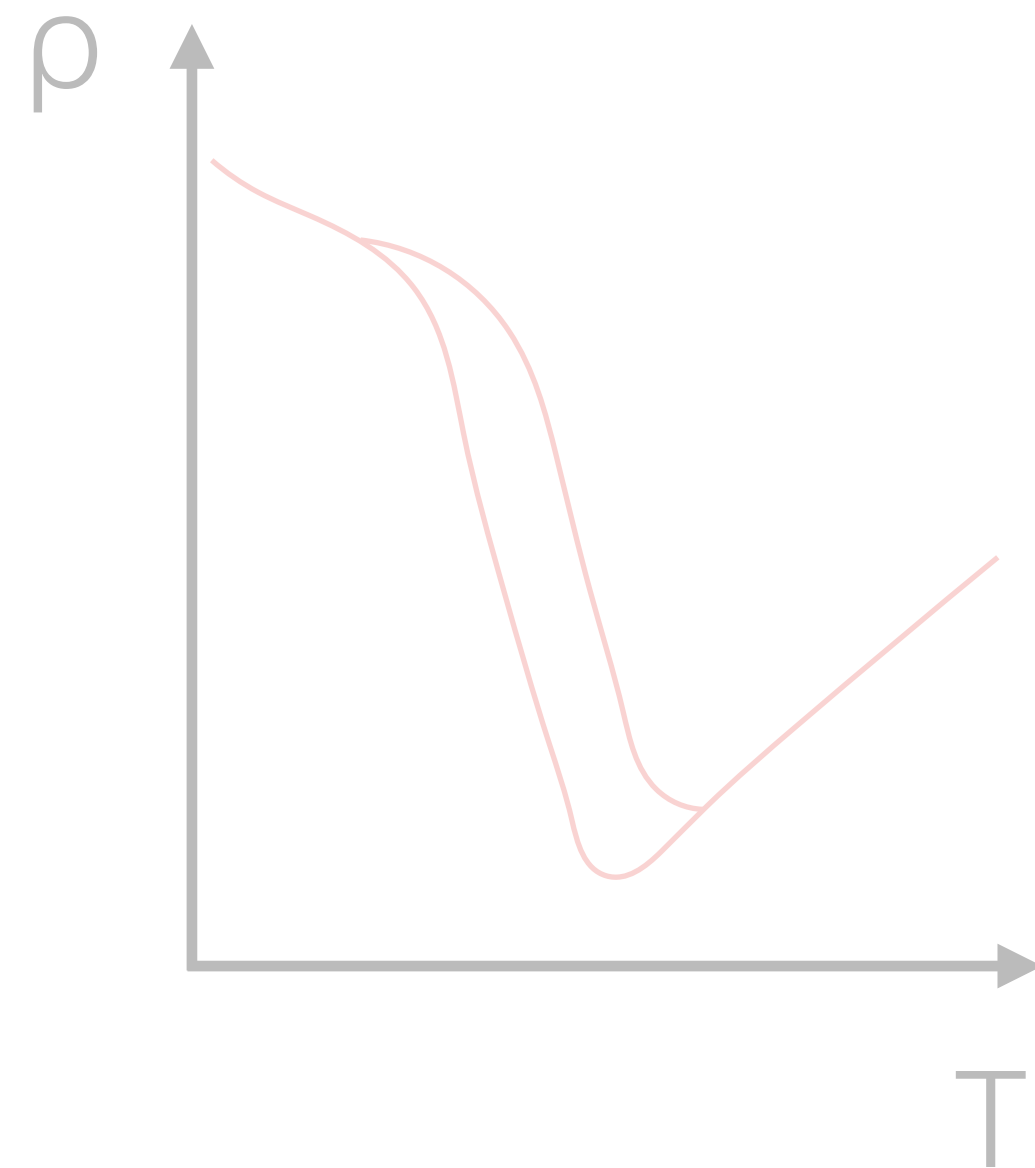
# Nickelates introduction



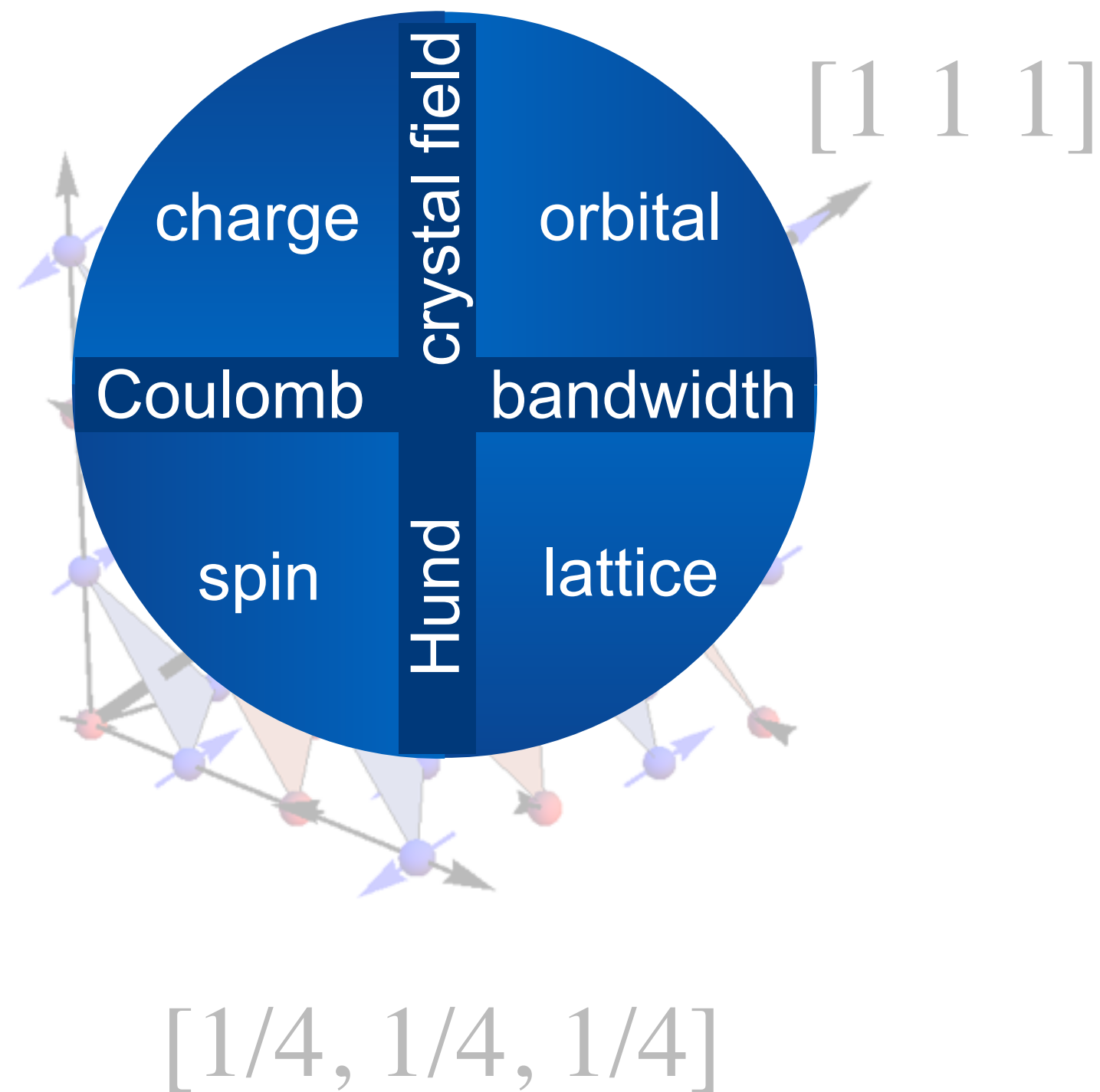
- Metal-insulator transition
- Néel transition
- 2 x symmetry lowering structural transitions

# Nickelates introduction

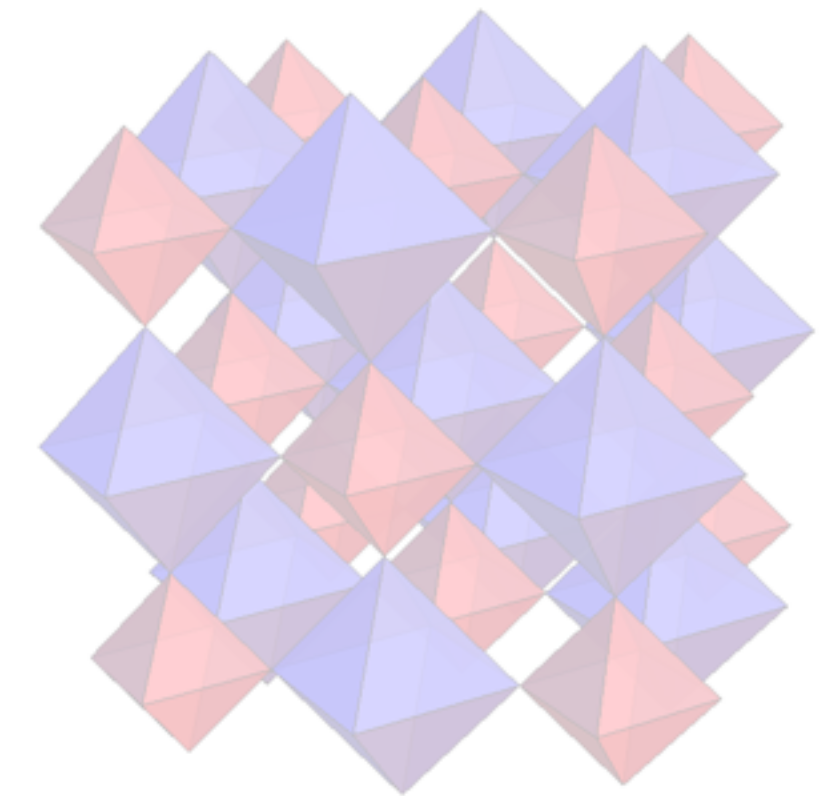
- Metal-insulator transition



- Néel transition



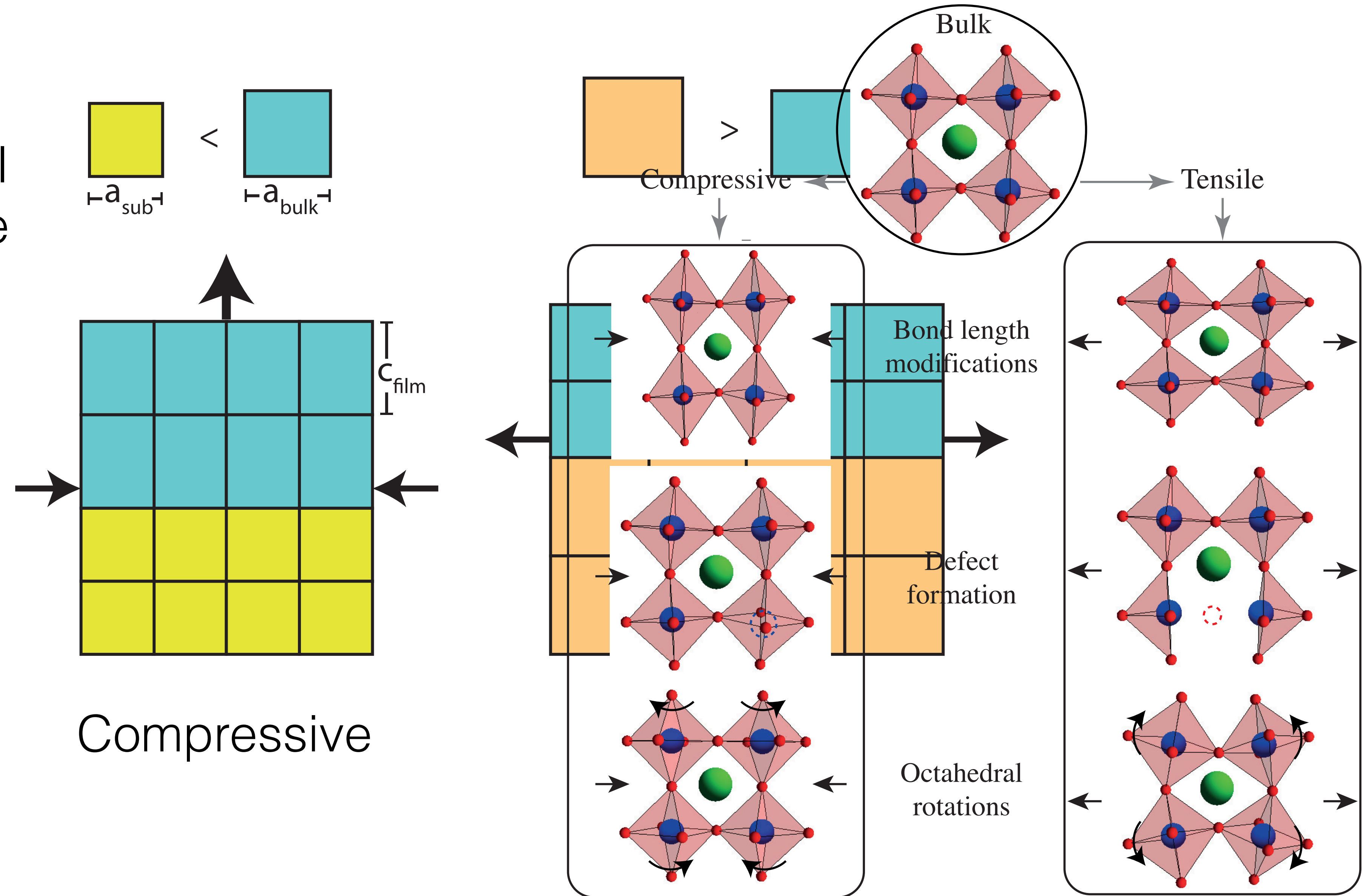
- 2 x symmetry lowering structural transitions



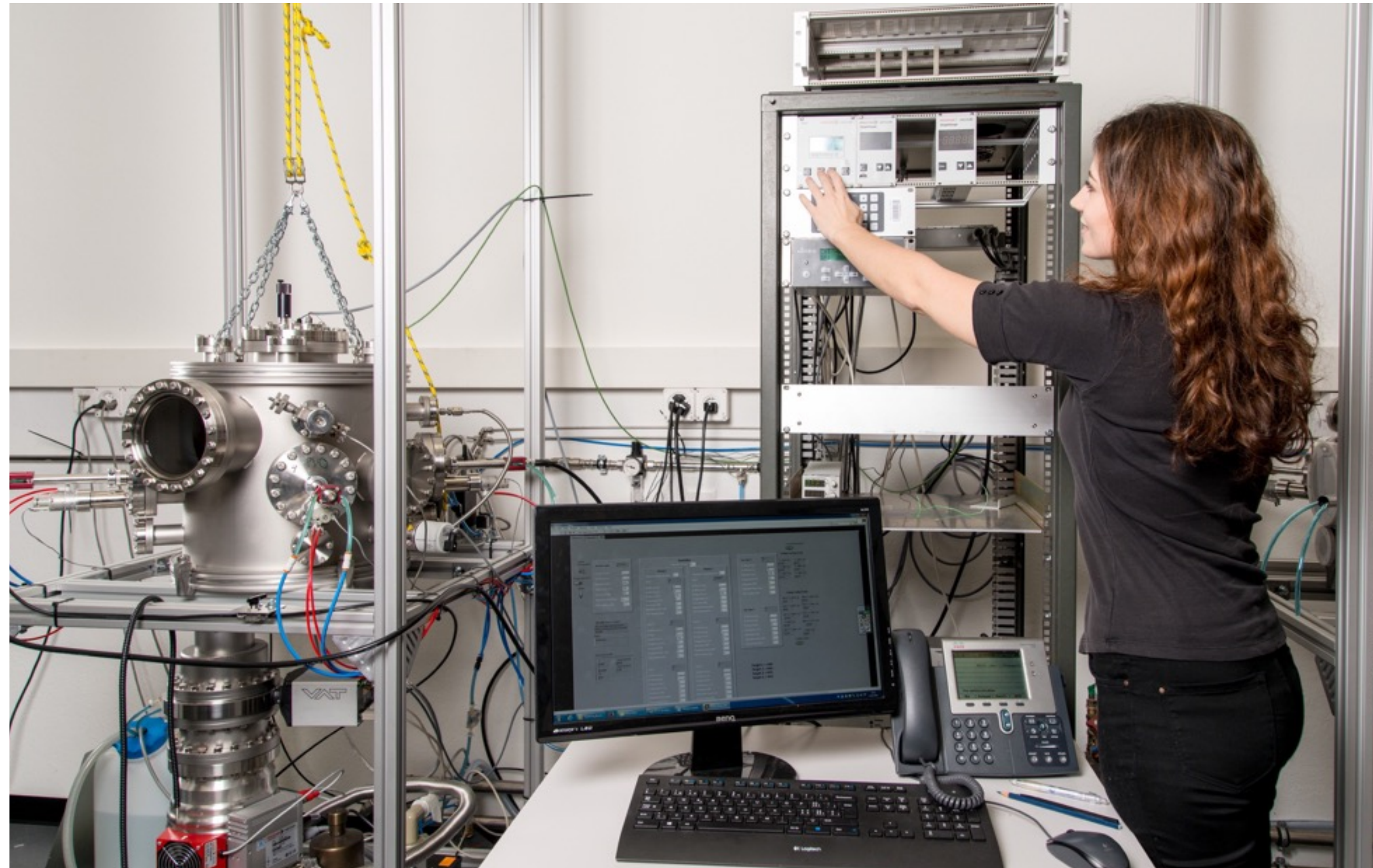
Transition metal oxides contain rich physics

# Heteroepitaxy

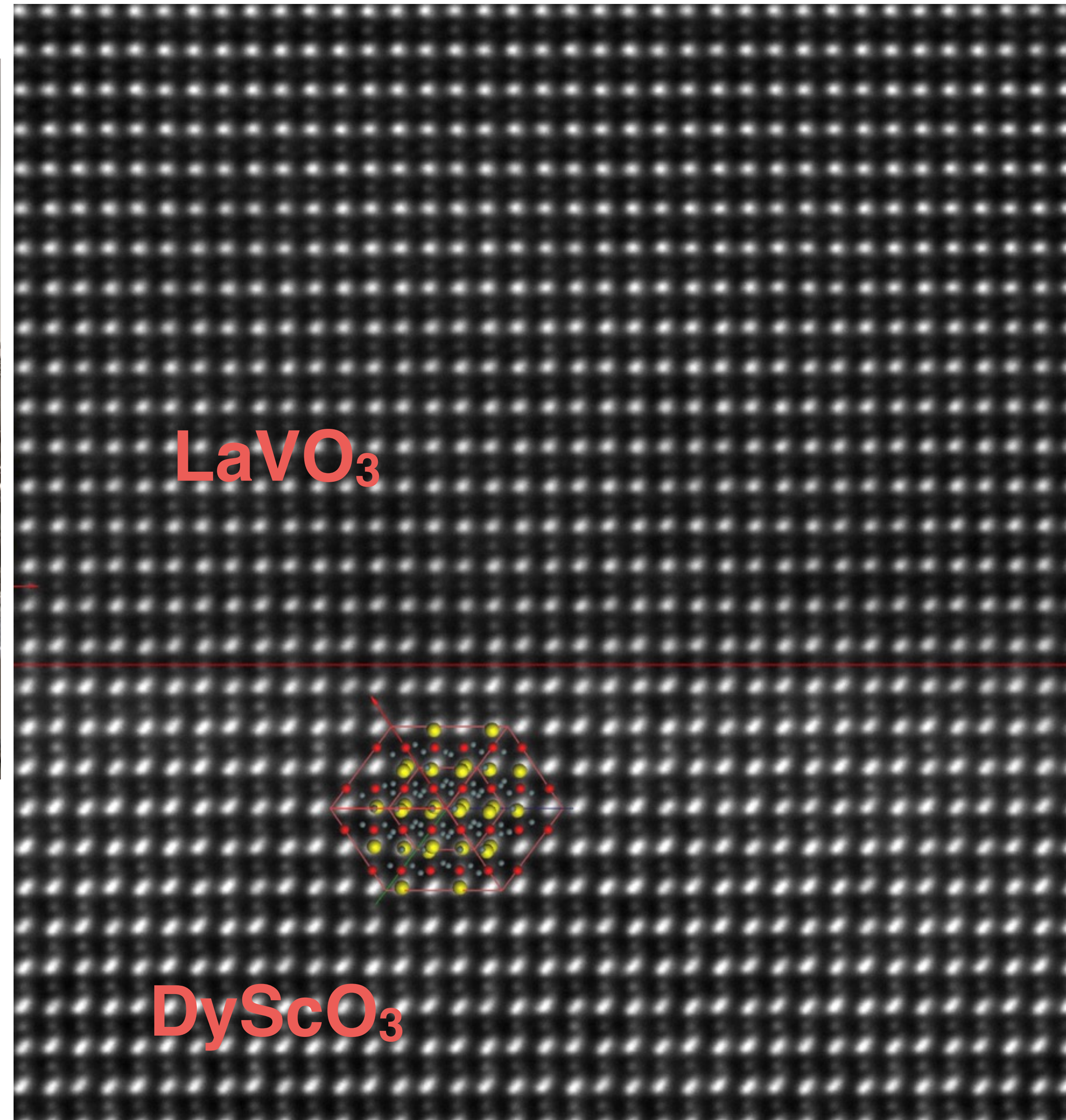
Heteroepitaxy:  
Growing one material  
on top of another one



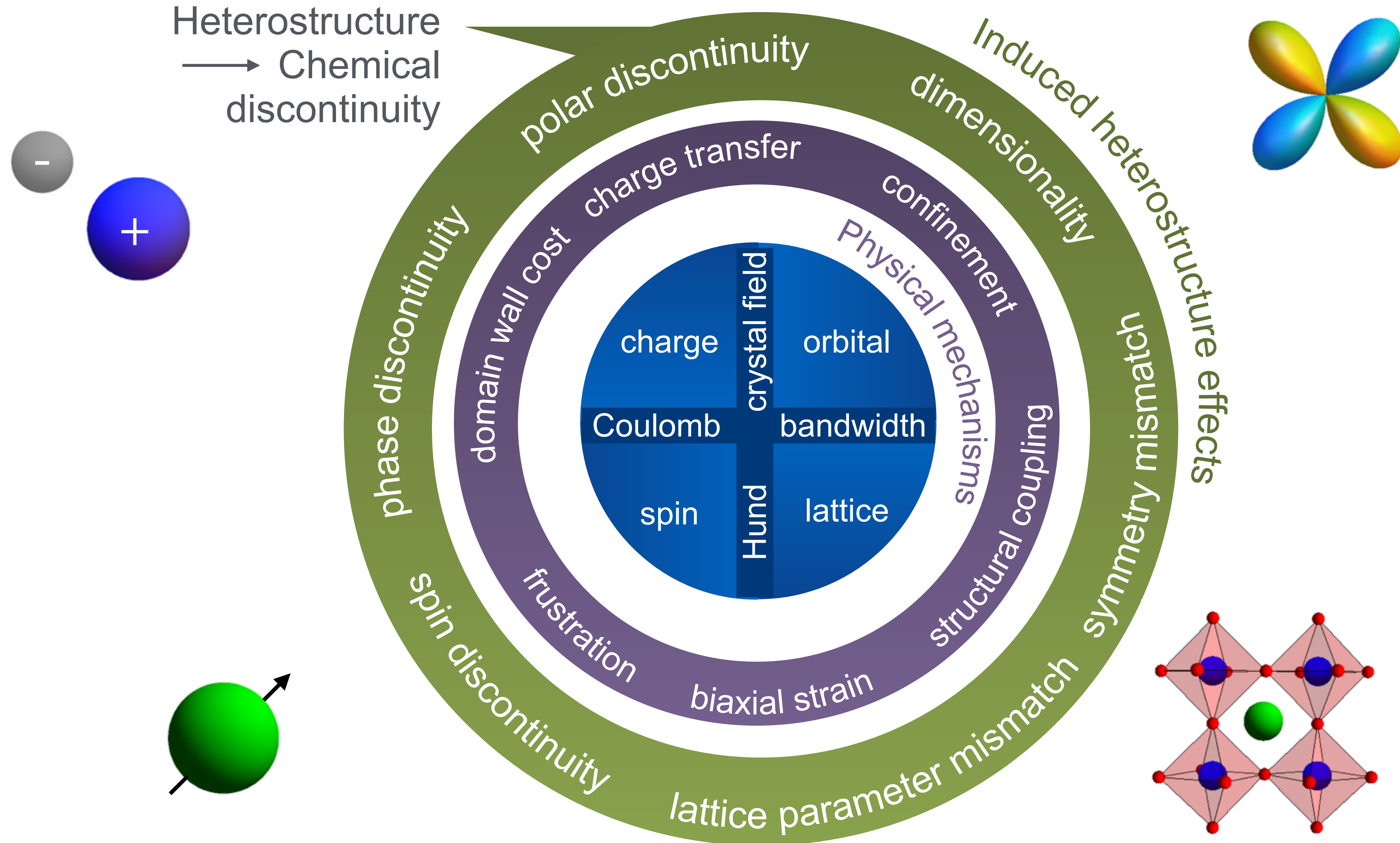
# Heteroepitaxy



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

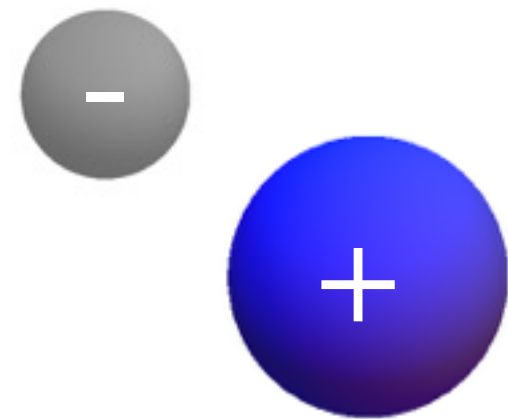
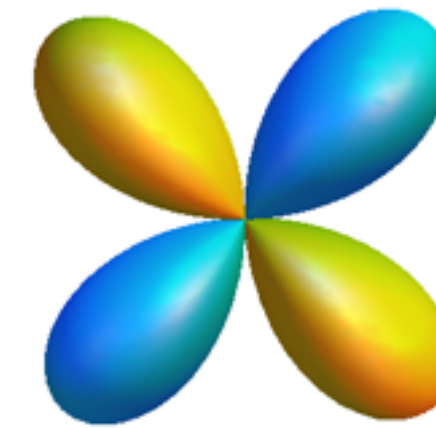


# Heteroepitaxial effects in TMOs



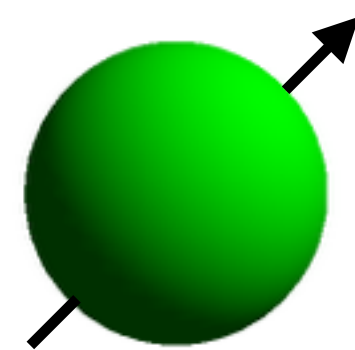
# Heteroepitaxial effects in nickelates

Charge transfer at  $\text{LaNiO}_3/\text{LaMnO}_3$  interfaces

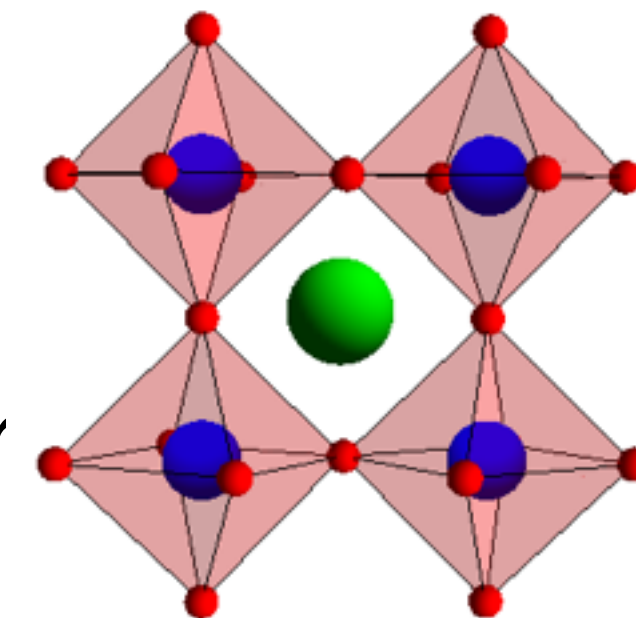


Orbital polarisation in  $\text{LaNiO}_3$ -based superlattices

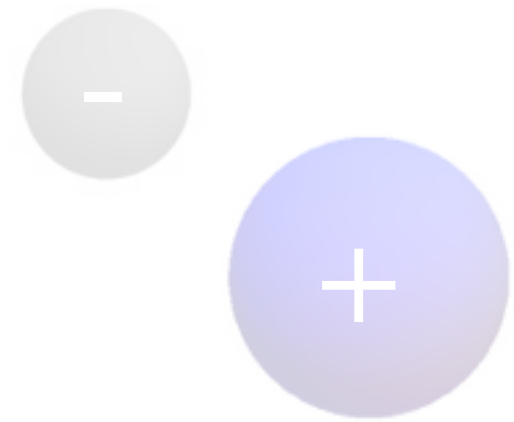
Strain dependence of  $R\text{NiO}_3$  metal-insulator transition



Induced antiferromagnetism in a bulk par



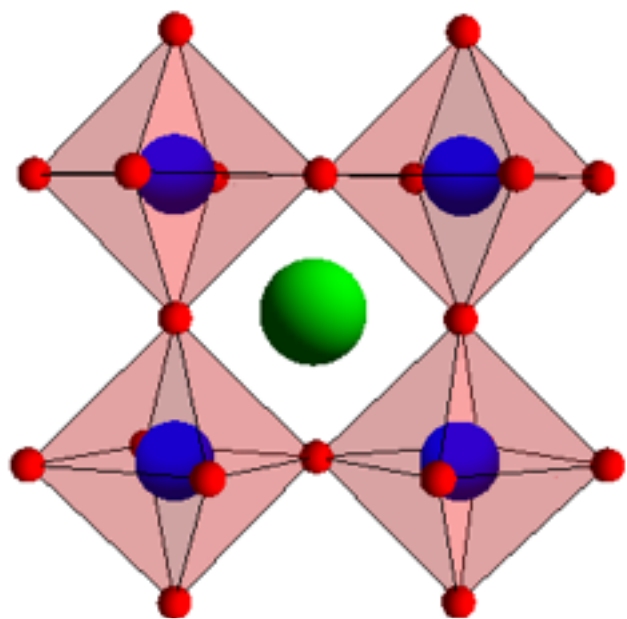
# Heteroepitaxial effects in nickelates



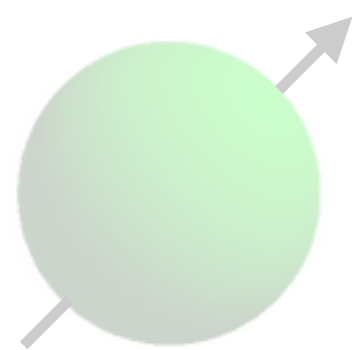
Charge transfer at  $\text{LaNiO}_3/\text{LaMnO}_3$  interfaces



Orbital polarisation in  $\text{LaNiO}_3$ -based superlattices

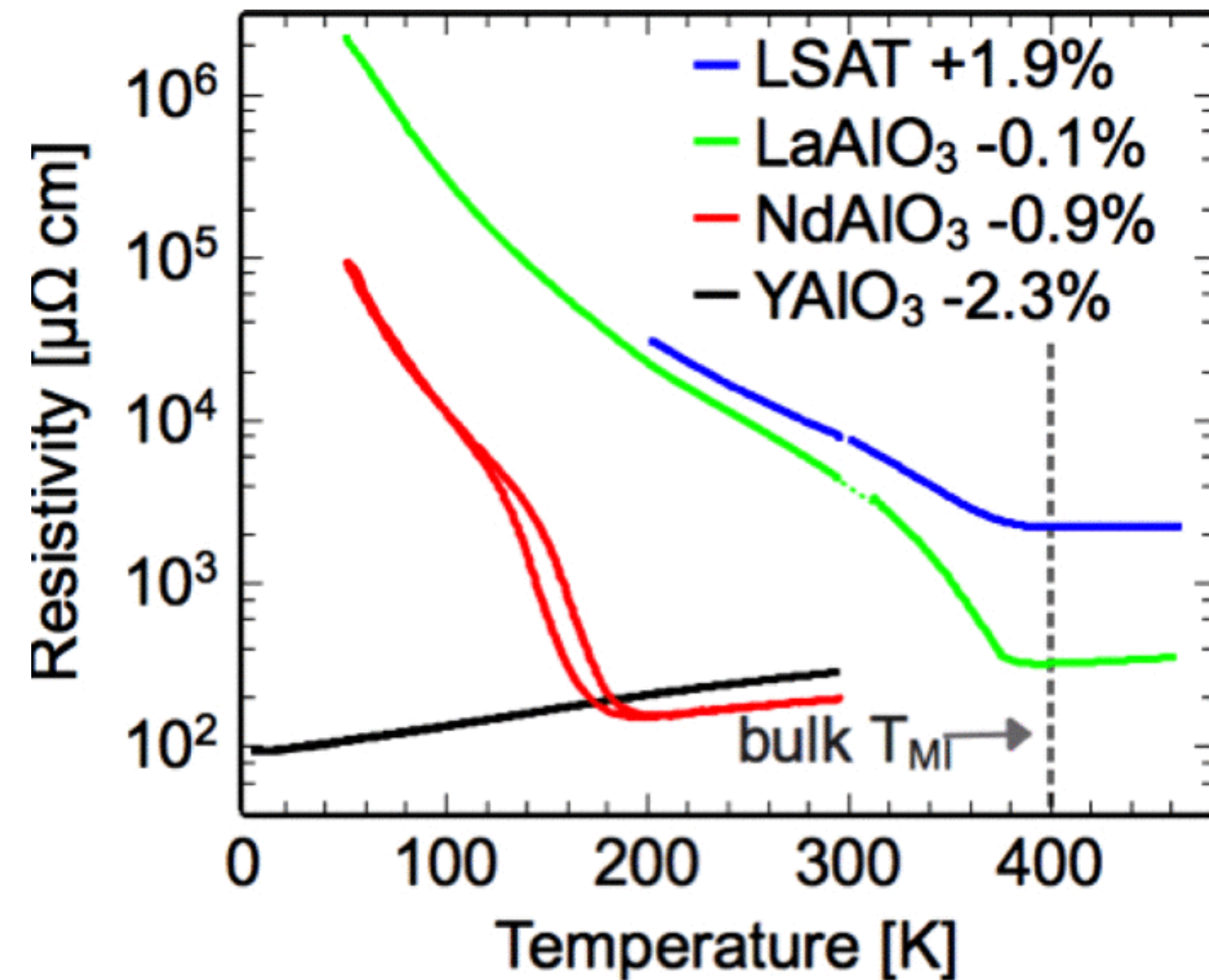


Strain dependence of  $R\text{NiO}_3$  metal-insulator transition

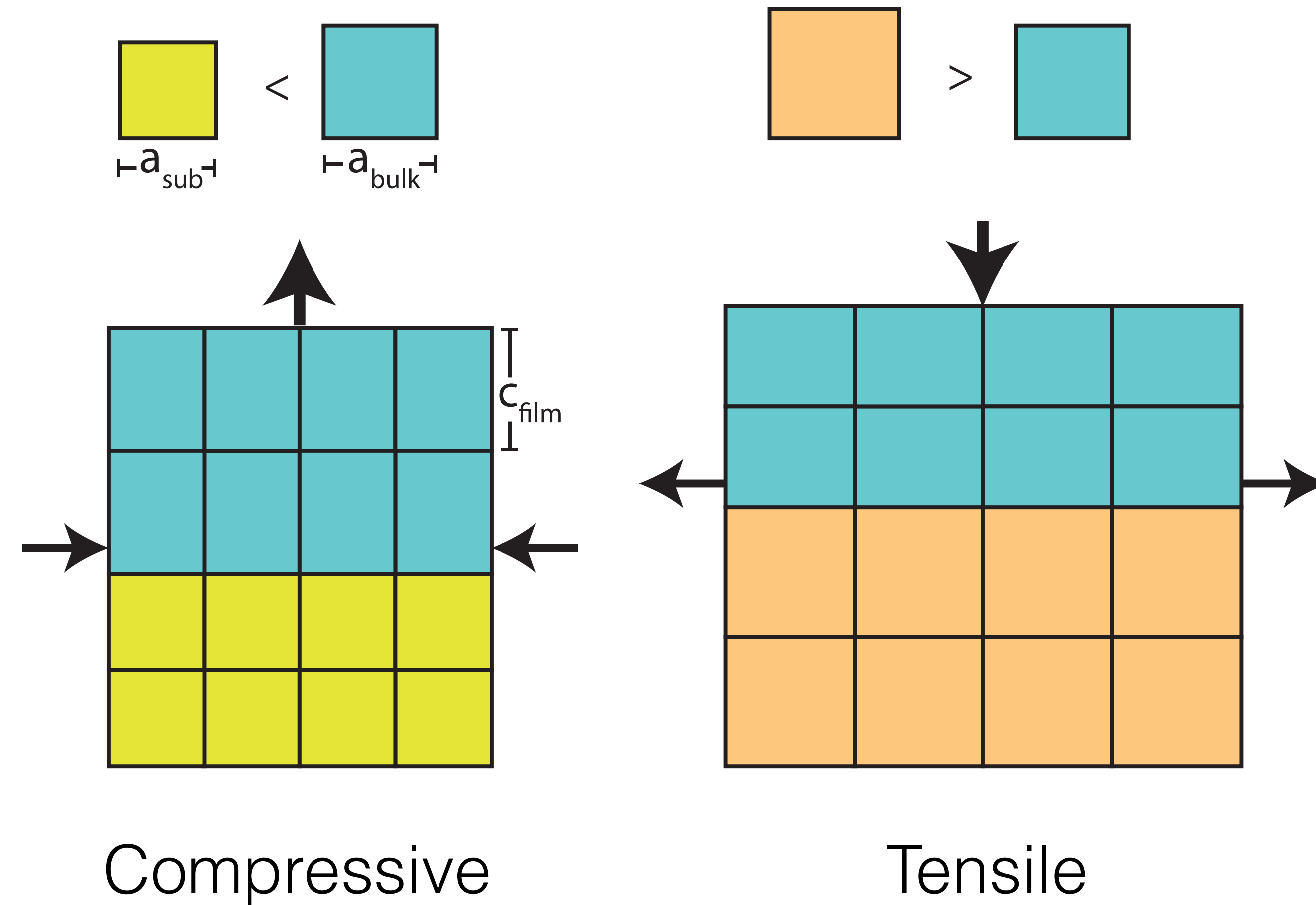


Induced antiferromagnetism in a bulk paramagnet

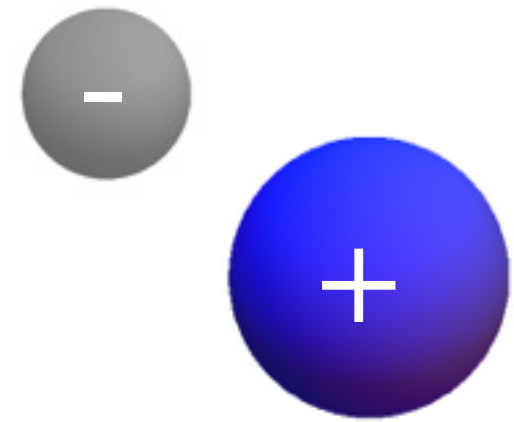
# Strain dependence of $\text{RNiO}_3$ metal-insulator transition



S. Catalano et al, APL Mater. 2, 116110 (2014)



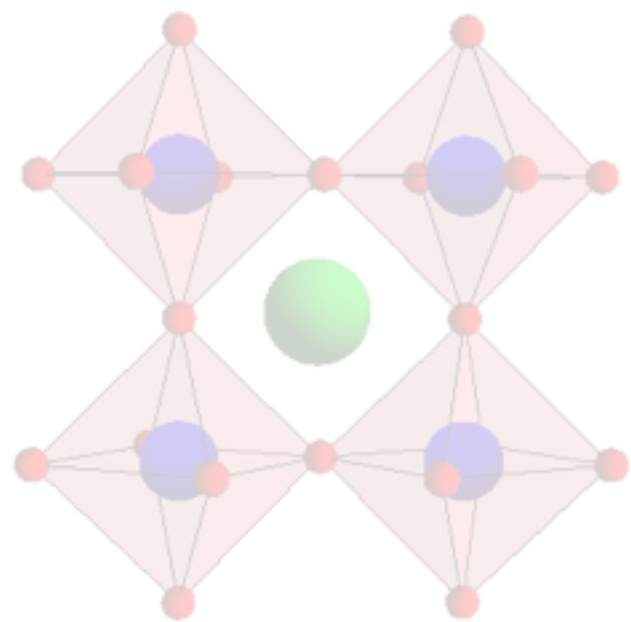
# Heteroepitaxial effects in nickelates



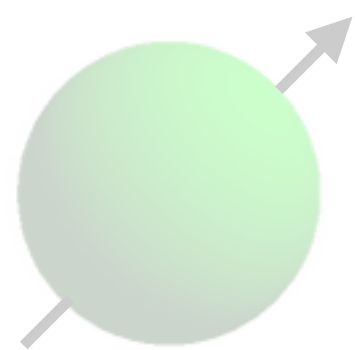
Charge transfer at  $\text{LaNiO}_3/\text{LaMnO}_3$  interfaces



Orbital polarisation in  $\text{LaNiO}_3$ -based superlattices

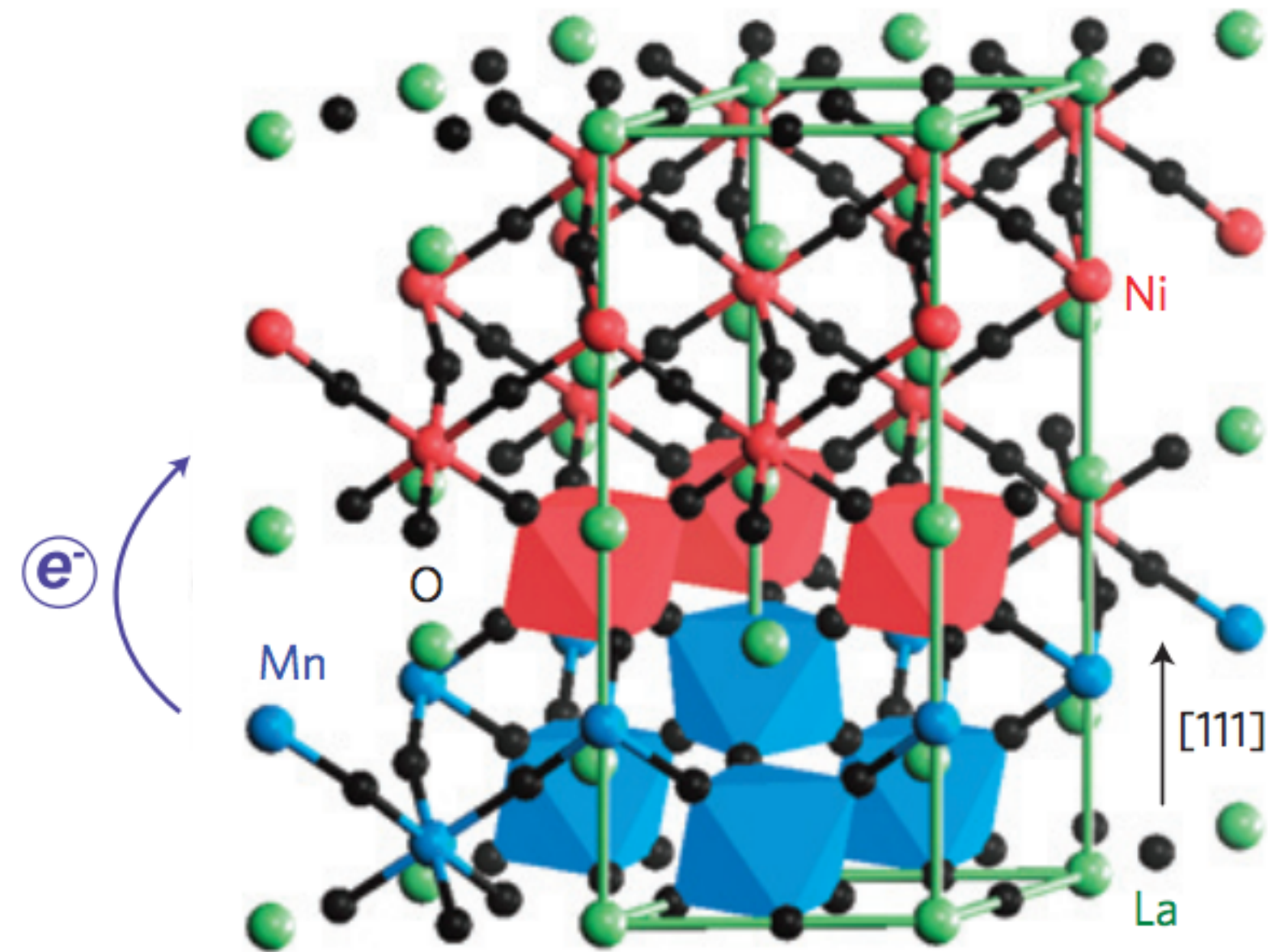


Strain dependence of  $R\text{NiO}_3$  metal-insulator transition



Induced antiferromagnetism in a bulk paramagnet

# Charge transfer at $\text{LaNiO}_3/\text{LaMnO}_3$ interfaces

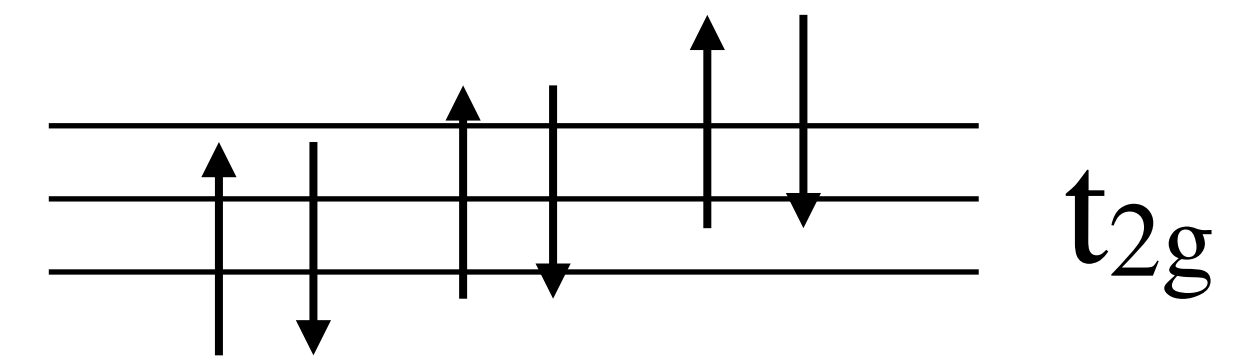
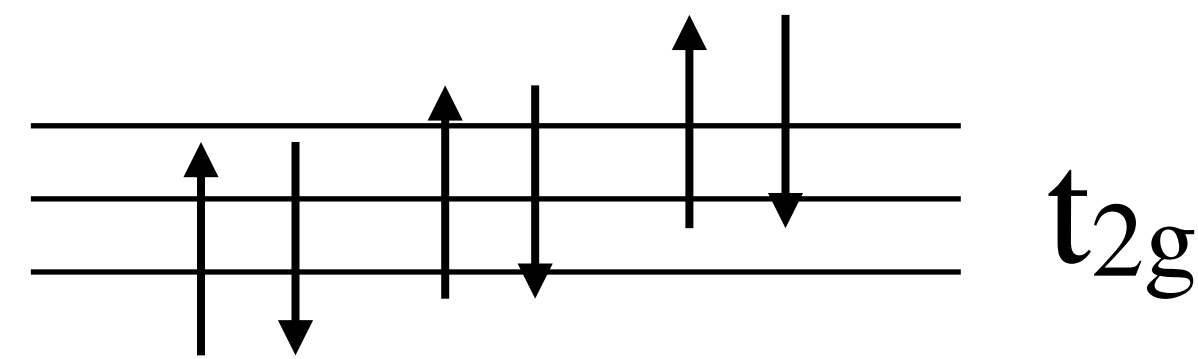
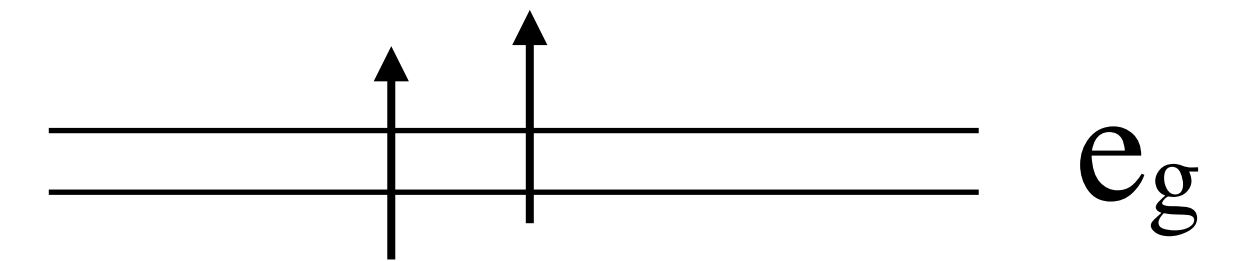
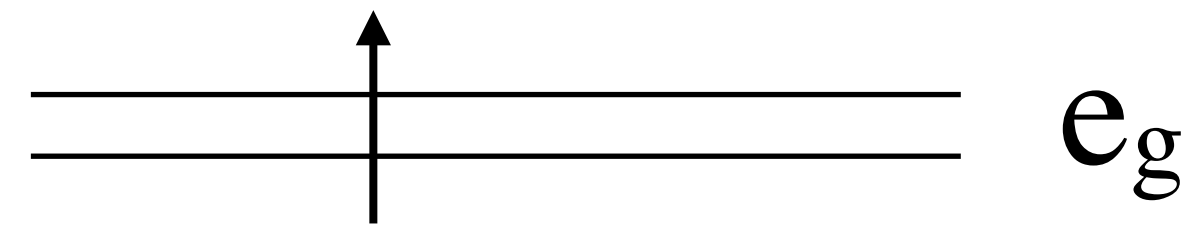


M. Gibert et al, Nat. Mater. 11, 3224, (2012)

$\text{Ni}^{3+}$



$\text{Ni}^{2+}$



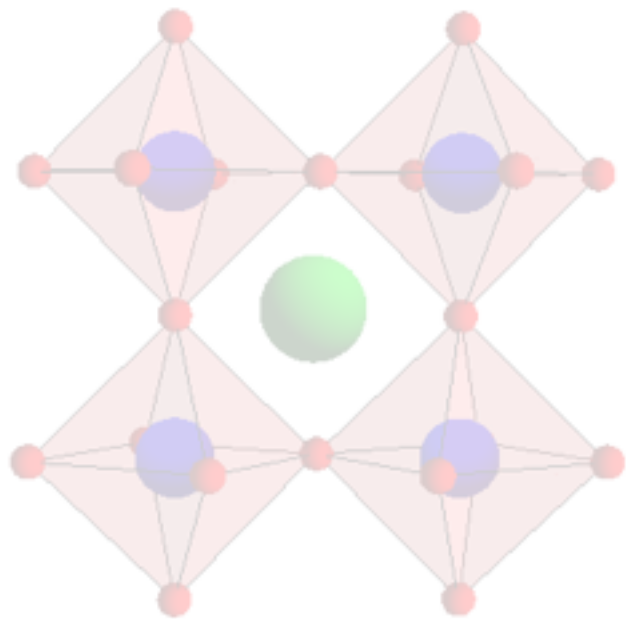
# Heteroepitaxial effects in nickelates



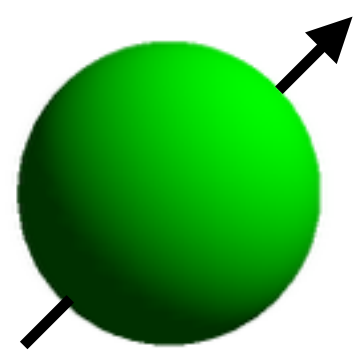
Charge transfer at  $\text{LaNiO}_3/\text{LaMnO}_3$  interfaces



Orbital polarisation in  $\text{LaNiO}_3$ -based superlattices

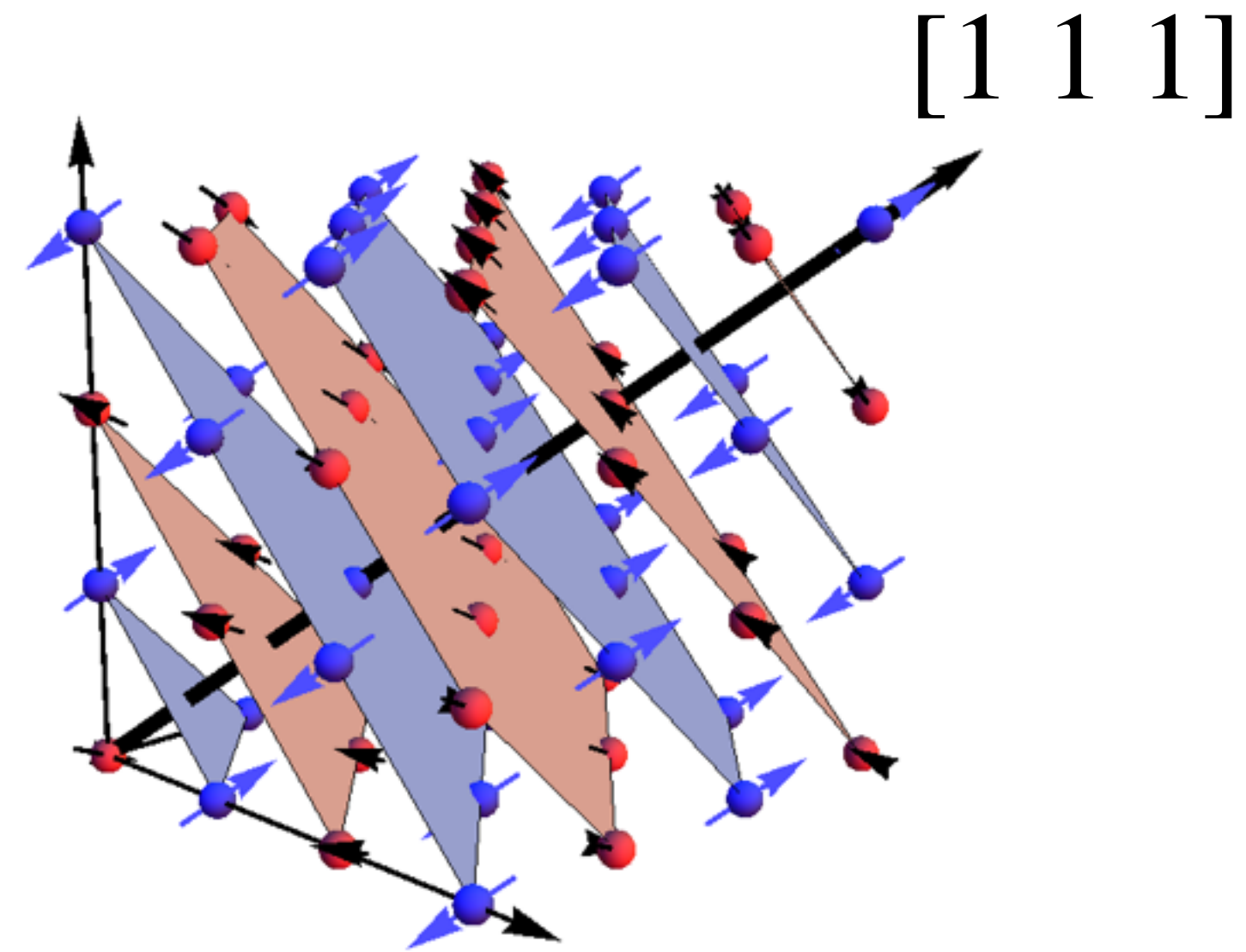


Strain dependence of  $R\text{NiO}_3$  metal-insulator transition

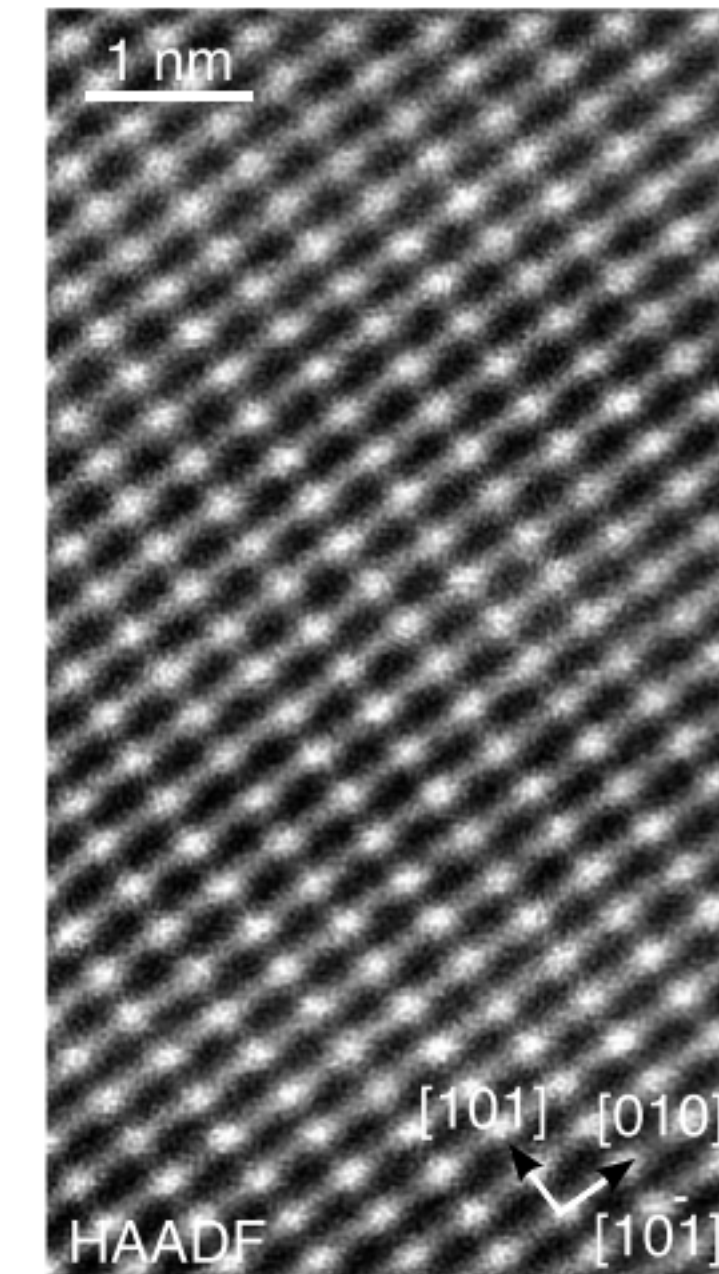
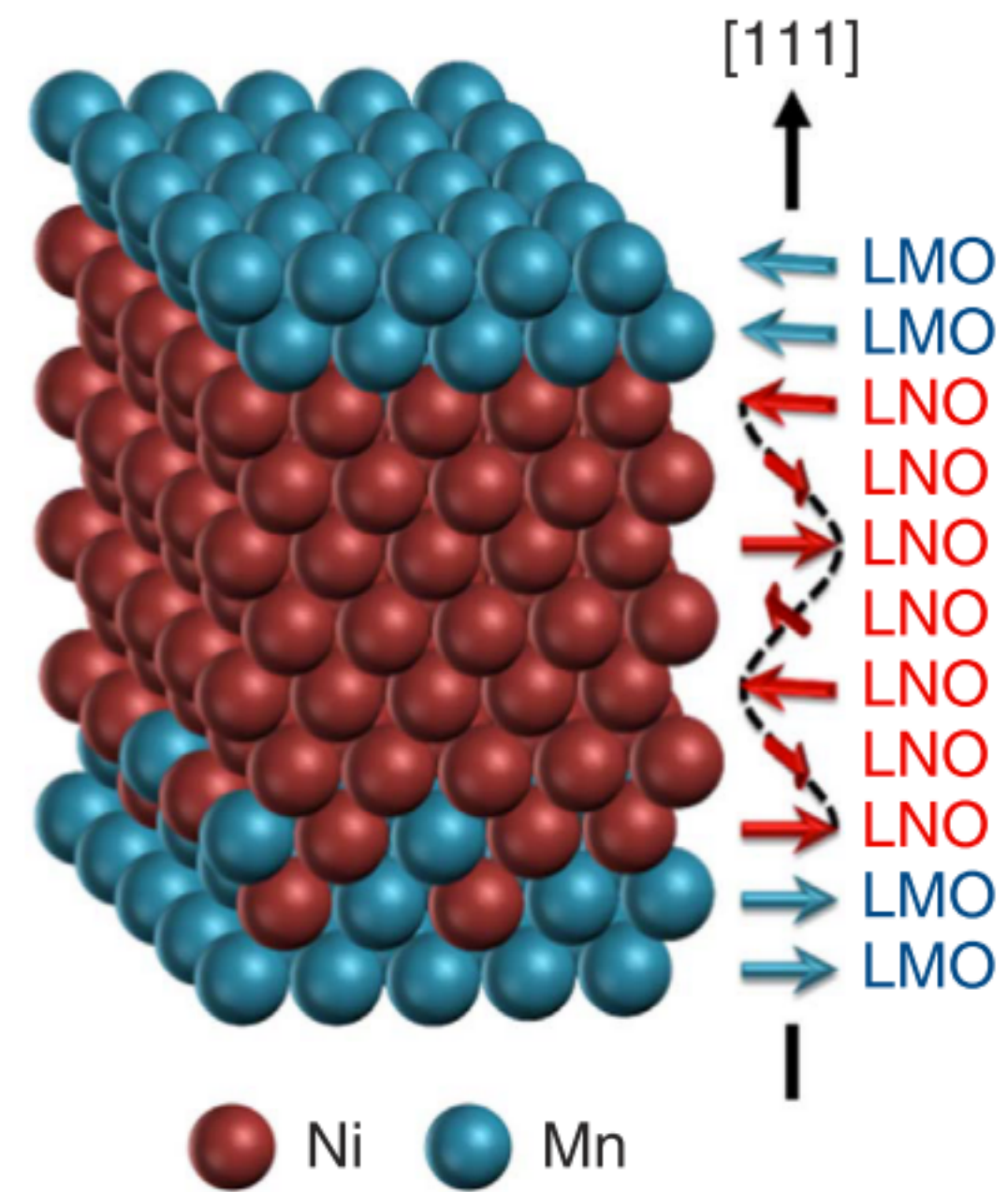


Induced antiferromagnetism in a bulk paramagnet

# Induced antiferromagnetism in a bulk paramagnet



$[1/4, 1/4, 1/4]$



M. Gibert et al, Nat. Commun. 7:11227, (2015)

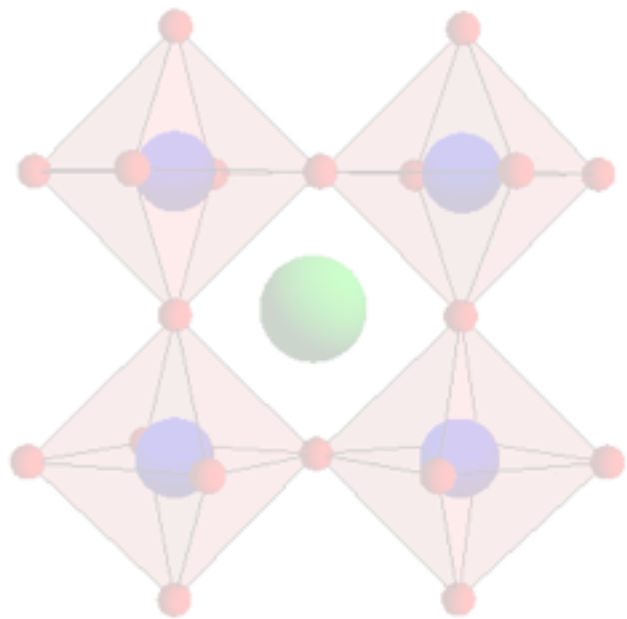
# Heteroepitaxial effects in nickelates



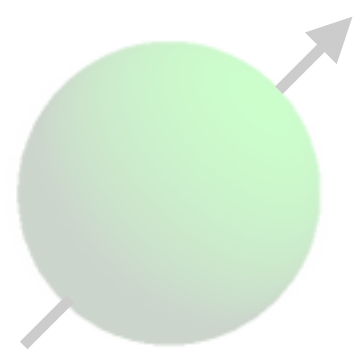
Charge transfer at  $\text{LaNiO}_3/\text{LaMnO}_3$  interfaces



Orbital polarisation in  $\text{LaNiO}_3$ -based superlattices



Strain dependence of  $R\text{NiO}_3$  metal-insulator transition

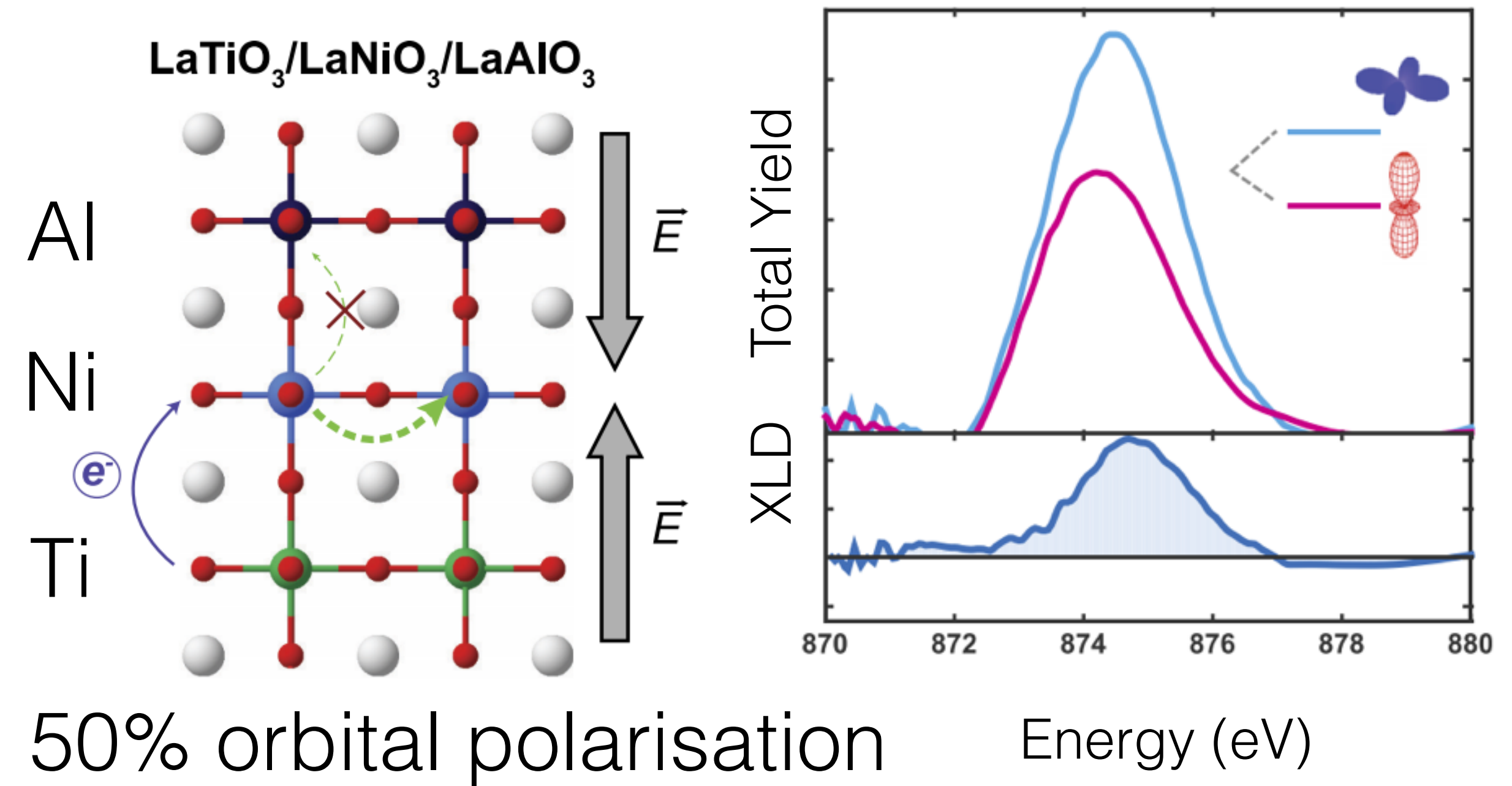


Induced antiferromagnetism in a bulk paramagnet

# Orbital polarisation in $\text{LaNiO}_3$ -based superlattices

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

|  |                                        |                                     |                                      |
|--|----------------------------------------|-------------------------------------|--------------------------------------|
|  | 28<br><b>Ni</b><br>Nickel<br>58.693    | 29<br><b>Cu</b><br>Copper<br>63.546 | 30<br><b>Zn</b><br>Zinc<br>65.38     |
|  | 46<br><b>Pd</b><br>Palladium<br>106.42 | 47<br><b>Ag</b><br>Silver<br>107.87 | 48<br><b>Cd</b><br>Cadmium<br>112.41 |



A. Disa et al, APL Mater. 3, 062303 (2015)

J. Chaloupka and G. Khaliullin, Phys. Rev. Lett. 100, 016404, (2008)

See also

P. Hansmann et al, Phys. Rev. Lett. 103, (2009)

P. Hansmann et al, Phys. Rev. B, 82, (2010)

E. Benckiser et al, Nat. Mater. 10, (2011)

H. Chen et al, Phys. Rev. Lett. 111, (2013)

H. Chen et al, Phys. Rev. Lett. 110, (2013)

M. Wu et al, Phys. Rev. B, 88, (2013)

A. Disa et al, Phys. Rev. Lett. 114, (2015)

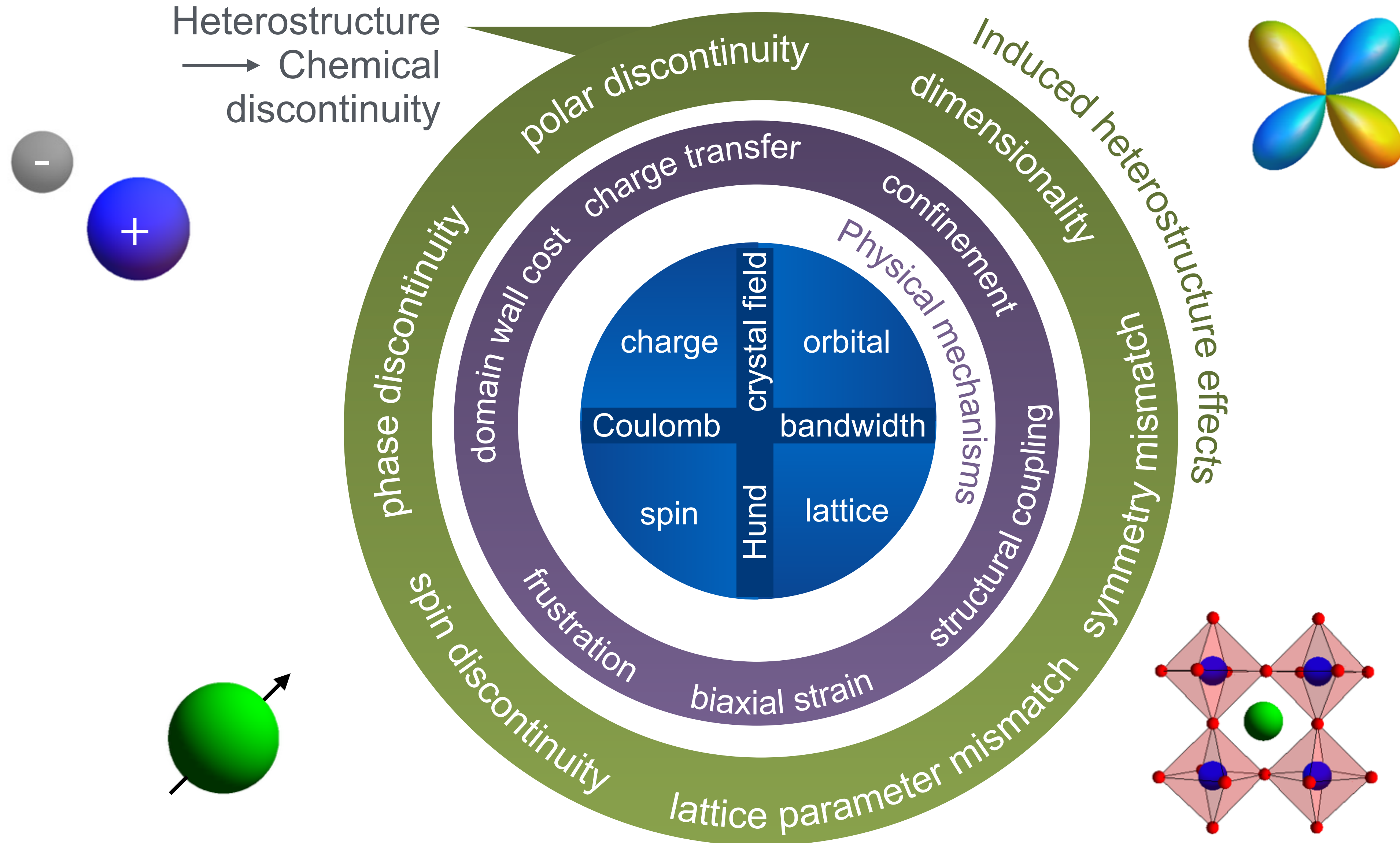
100% orbital polarisation may never be possible

M. J. Han et al, Phys. Rev. Lett. 107, (2011)

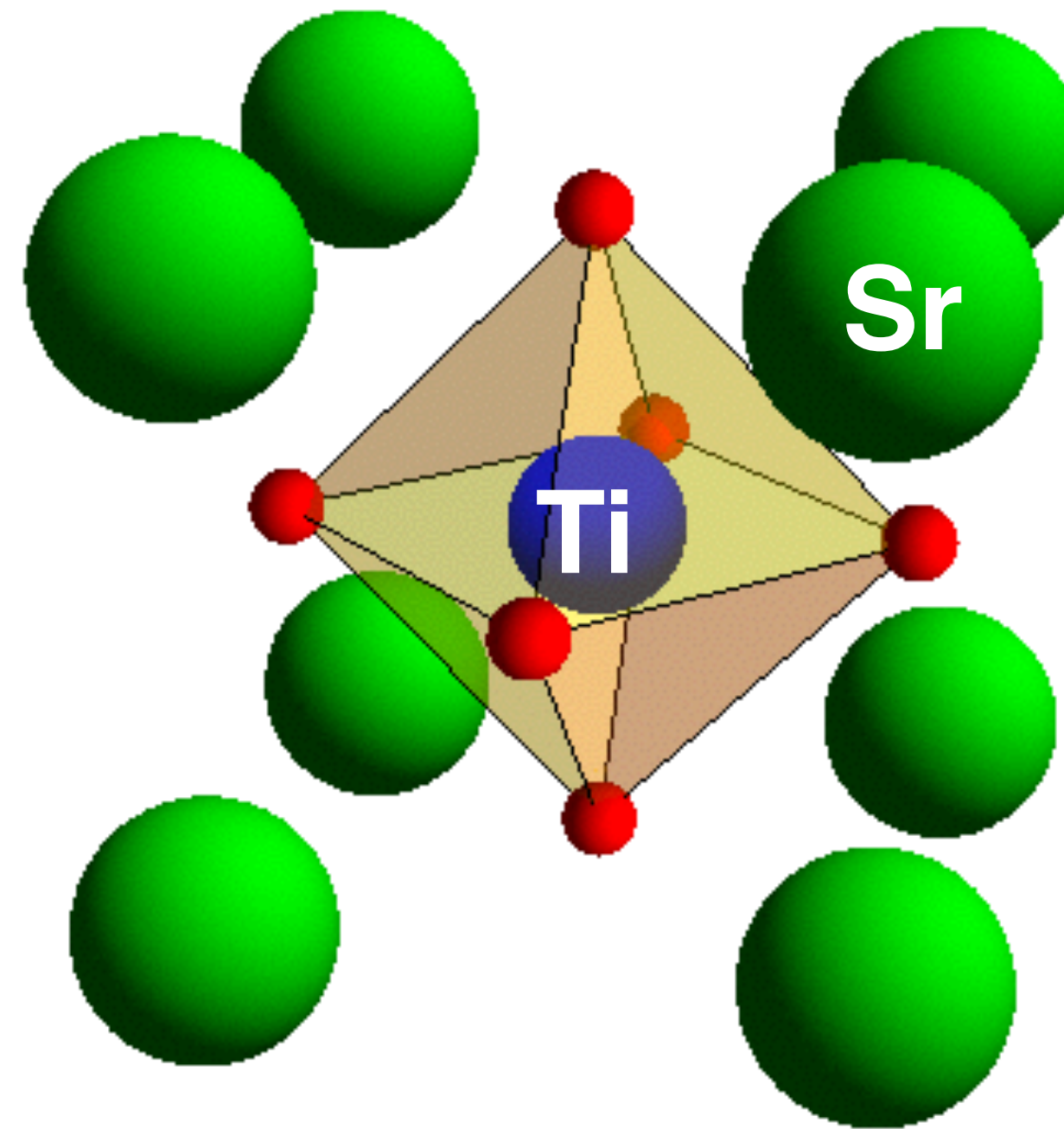
O. E. Peil et al, Phys. Rev. B 90, (2014)

G. Fabbri et al, Phys. Rev. Lett. 117, (2016)

# Heteroepitaxial effects in TMOs



# Strontium titanate

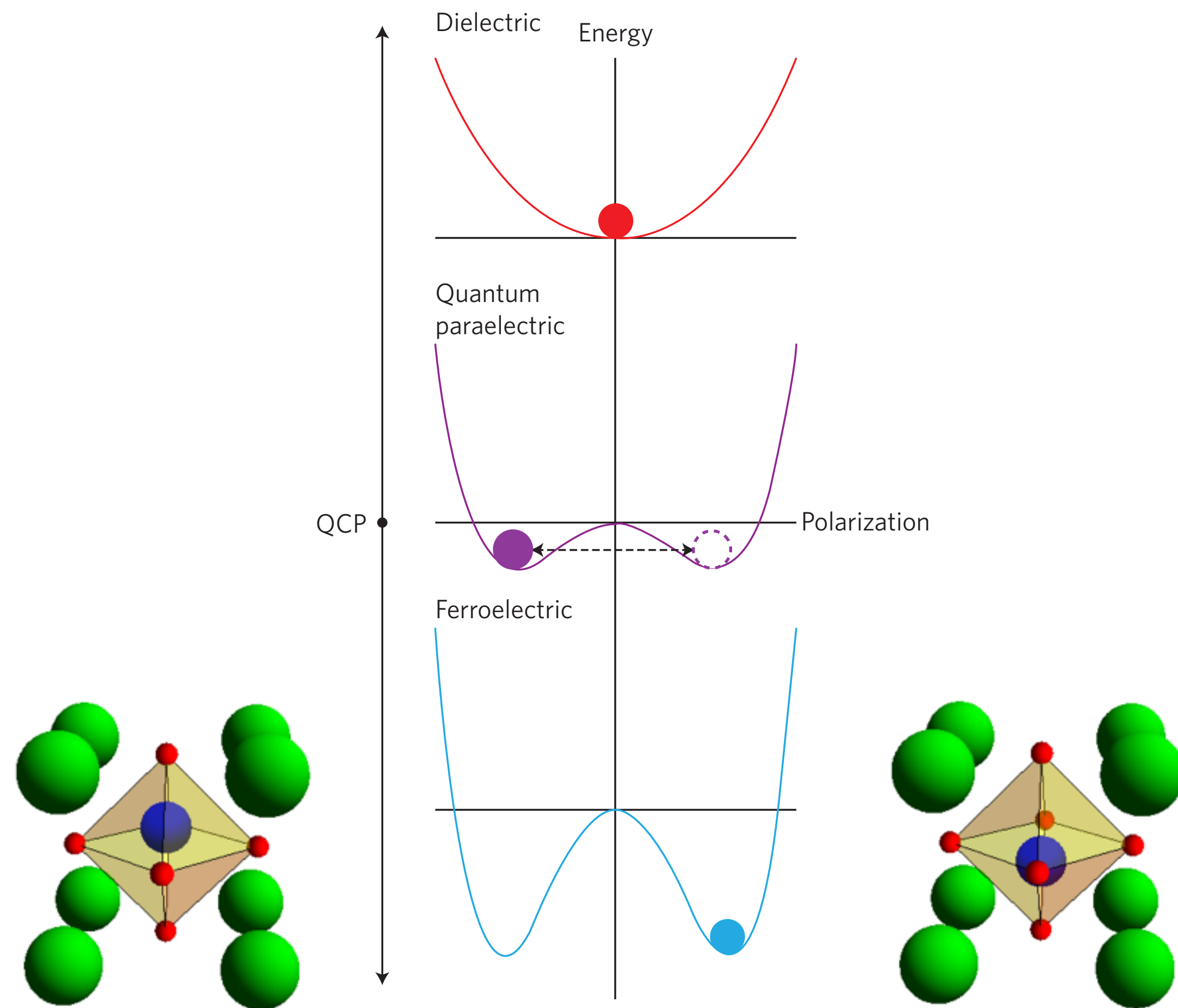


$3d^0$  paramagnetic wide-gap band insulator

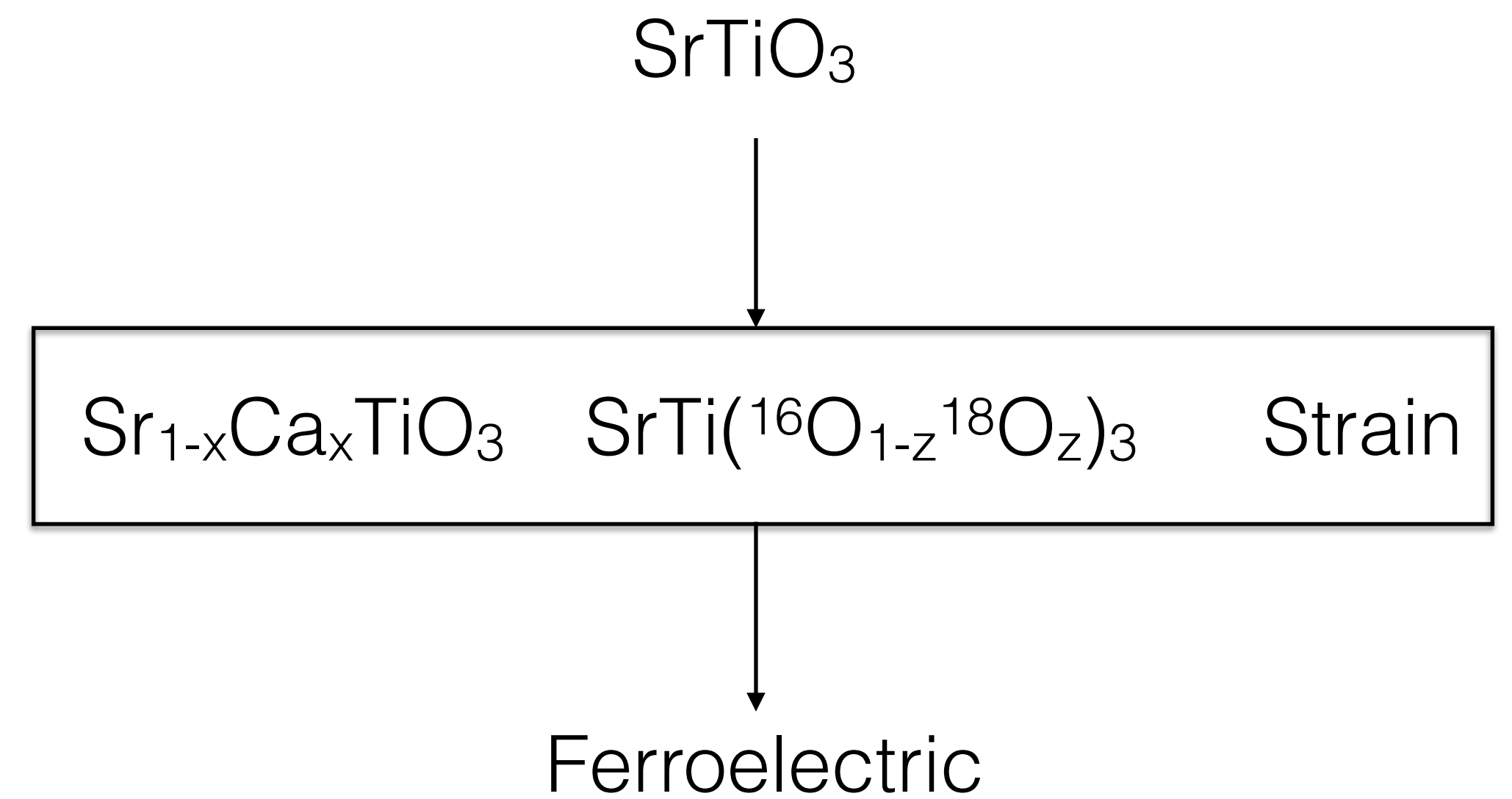
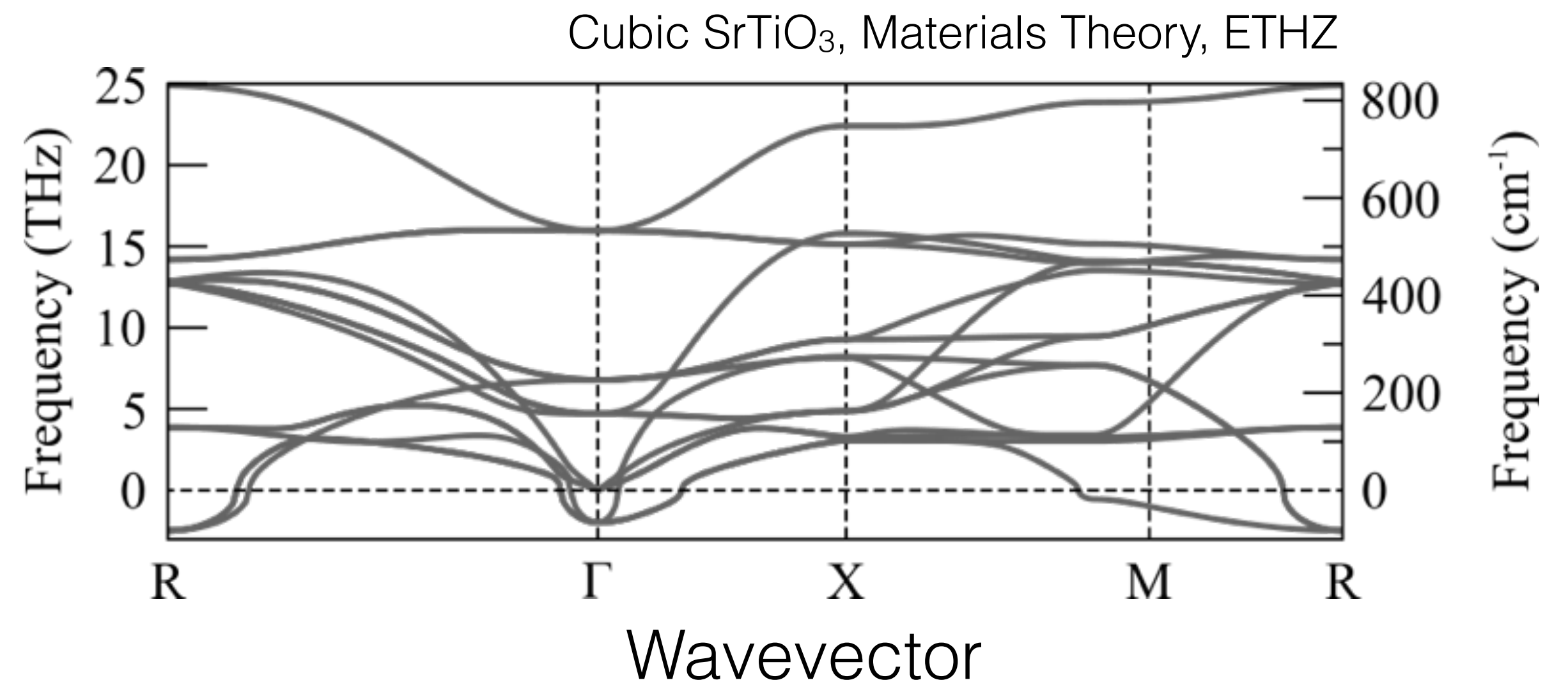


The “drosophila” of solid state physics

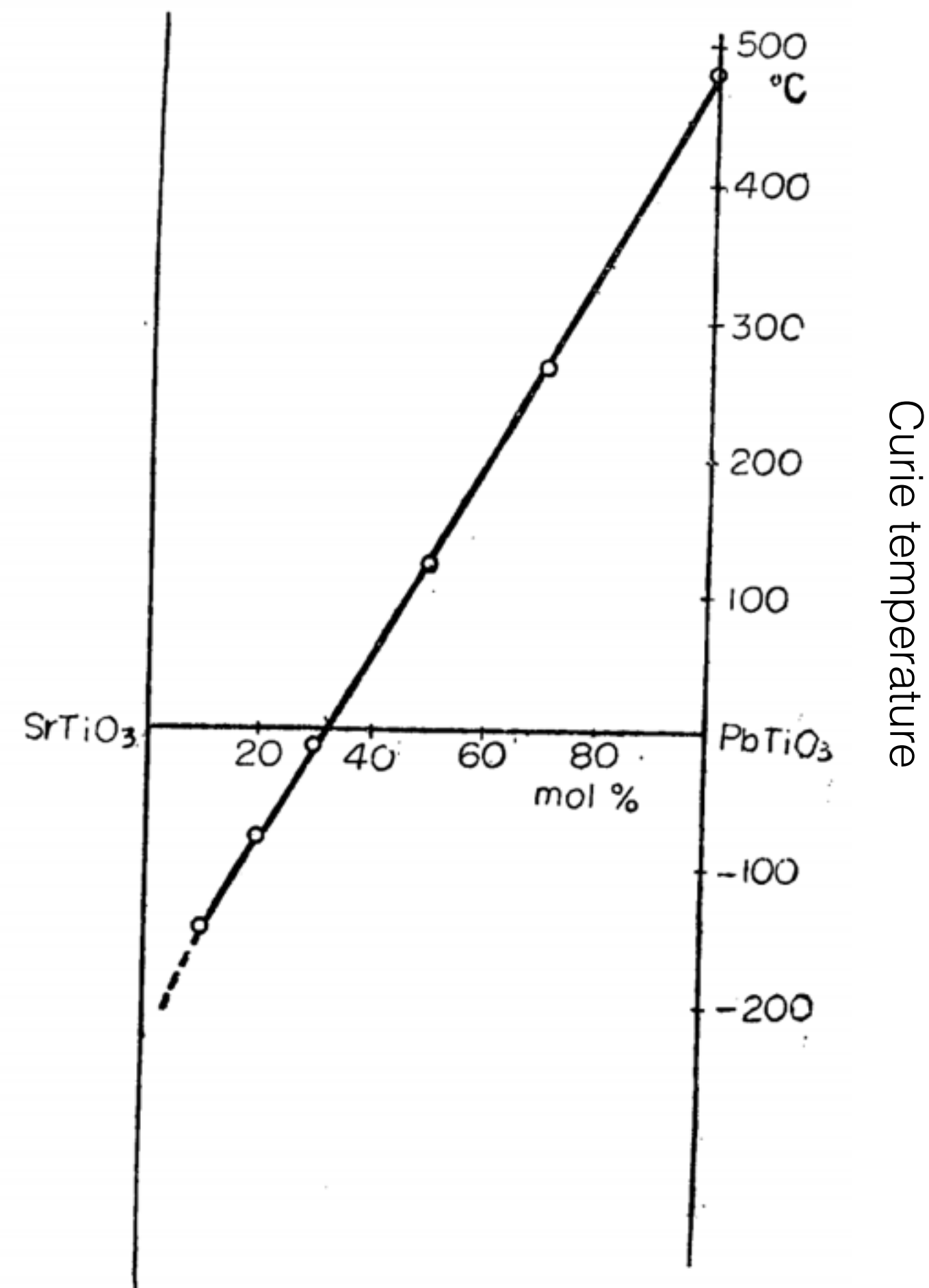
# Quantum paraelectricity



M. Gabay & J.-M. Triscone  
N&V Nat. Phys. (2017)

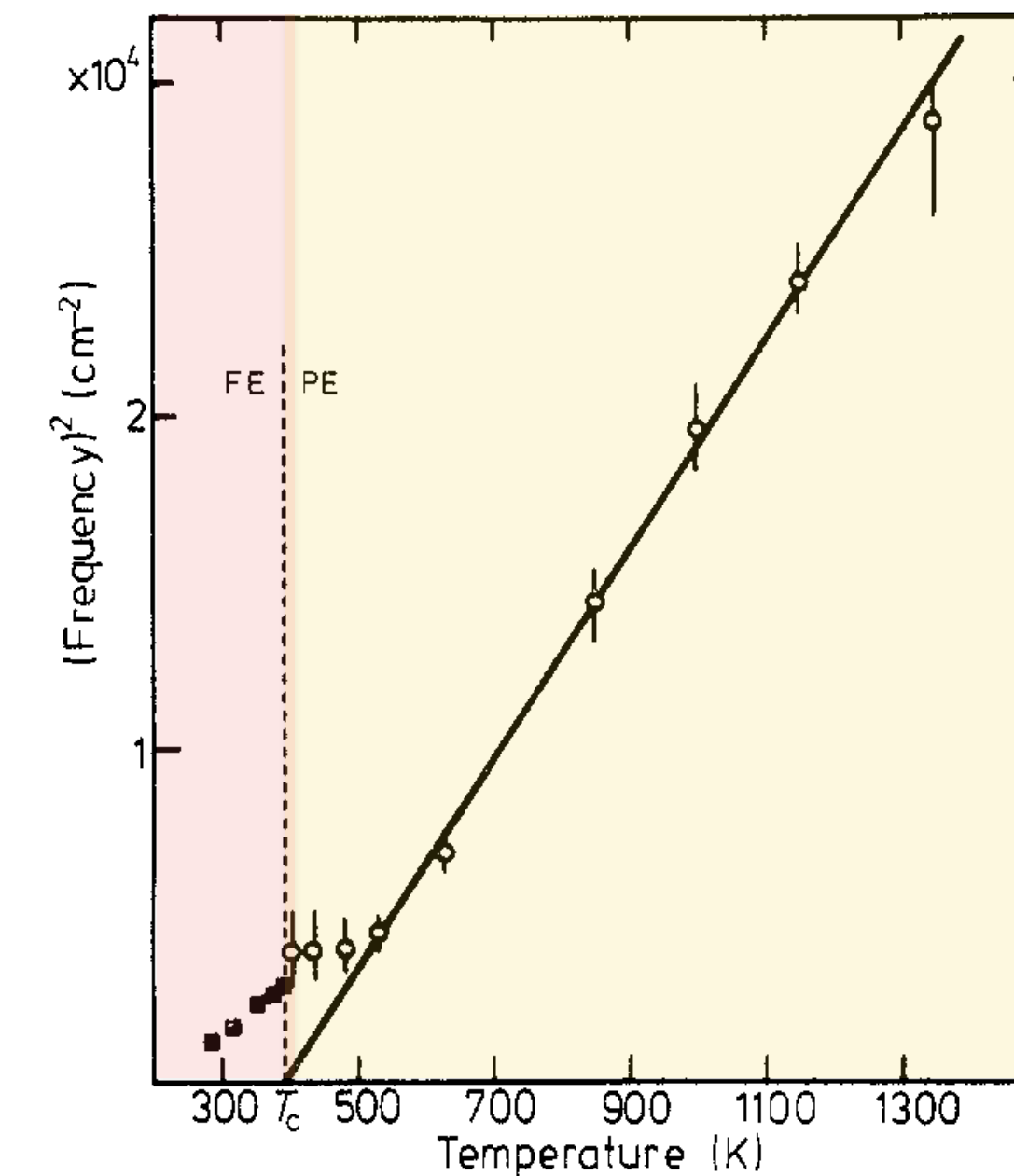


# Ferroelectric materials



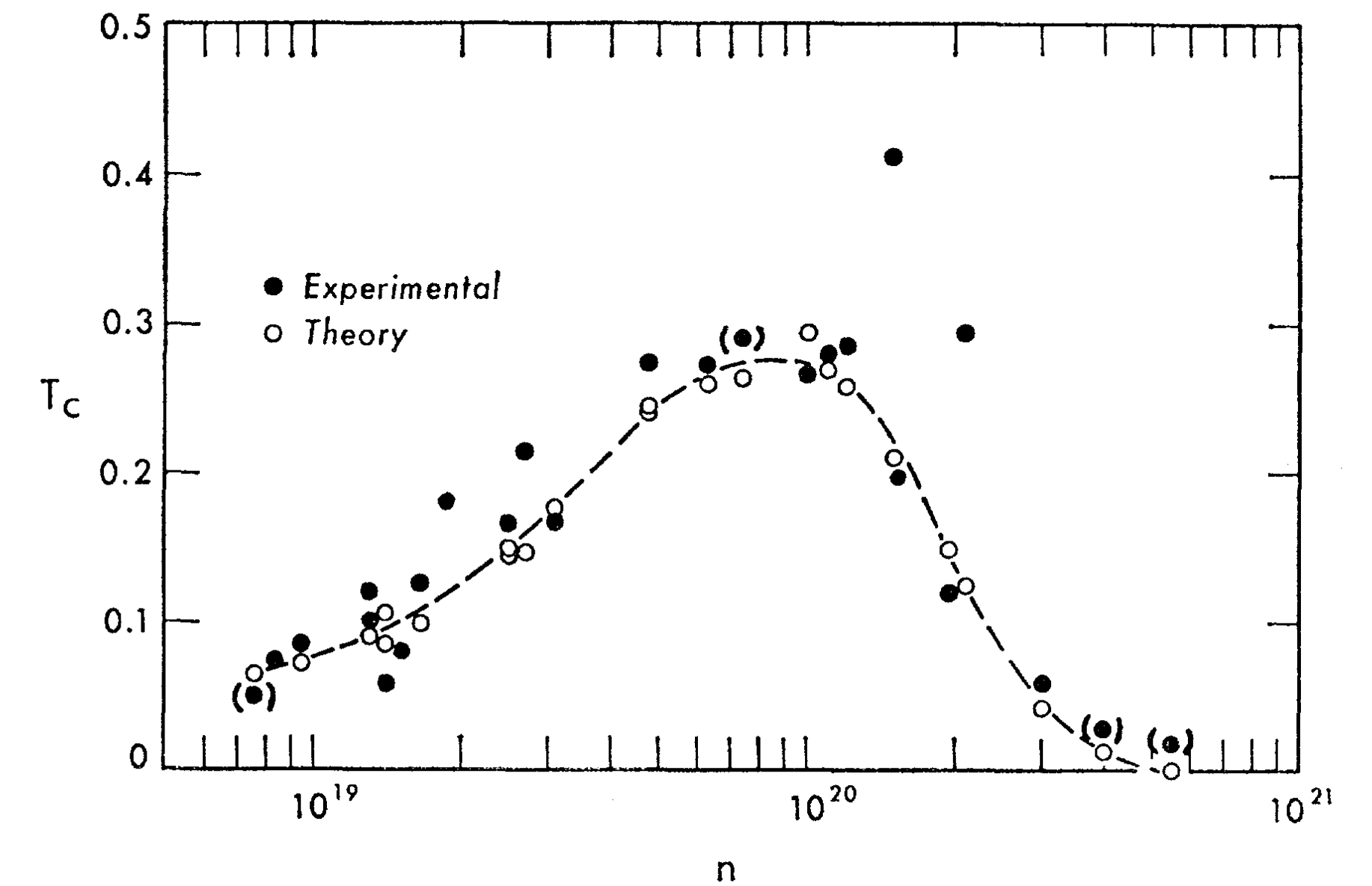
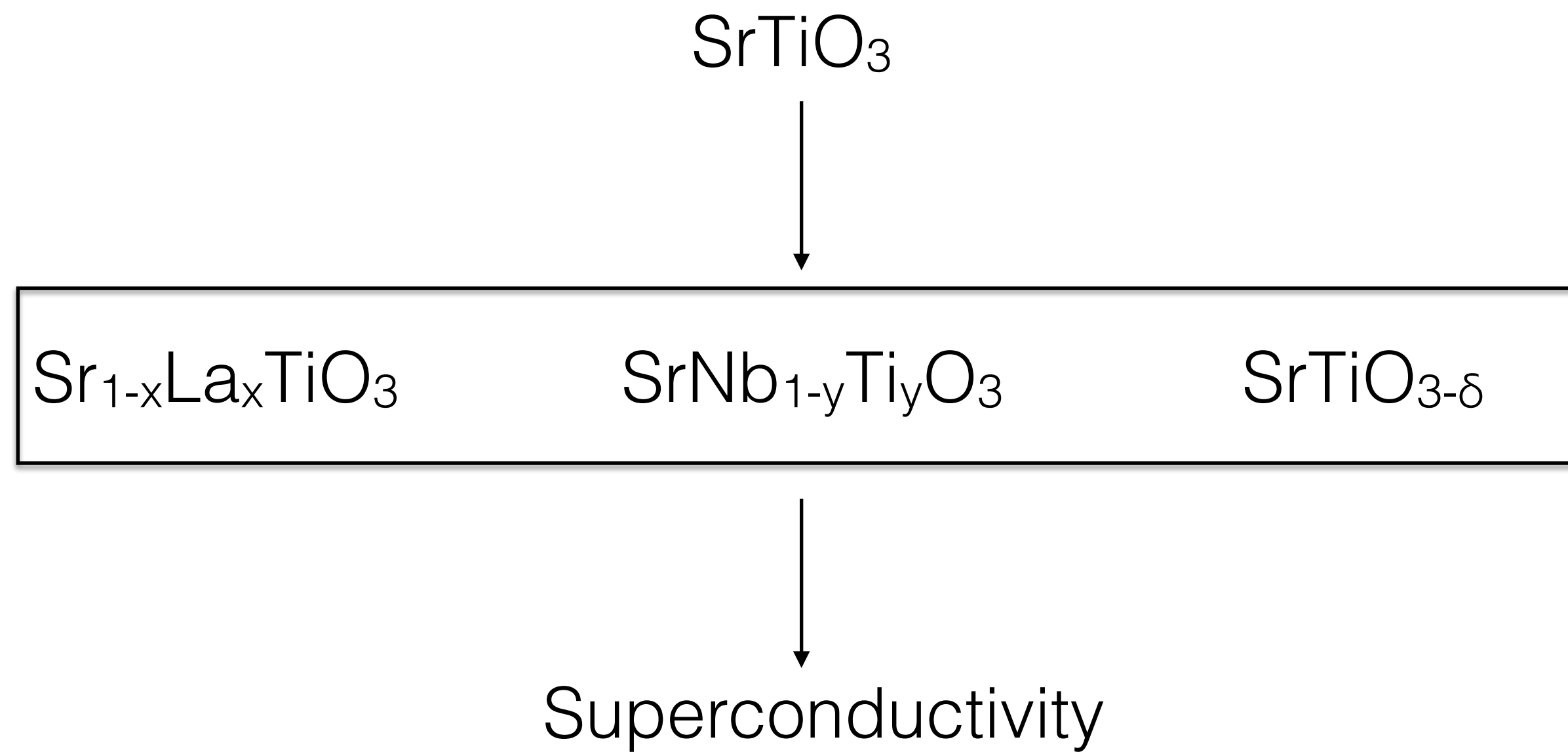
The softening of the phonon to zero frequency is connected with the appearance of the ferroelectric state

Lowest transverse optical mode in BaTiO<sub>3</sub>



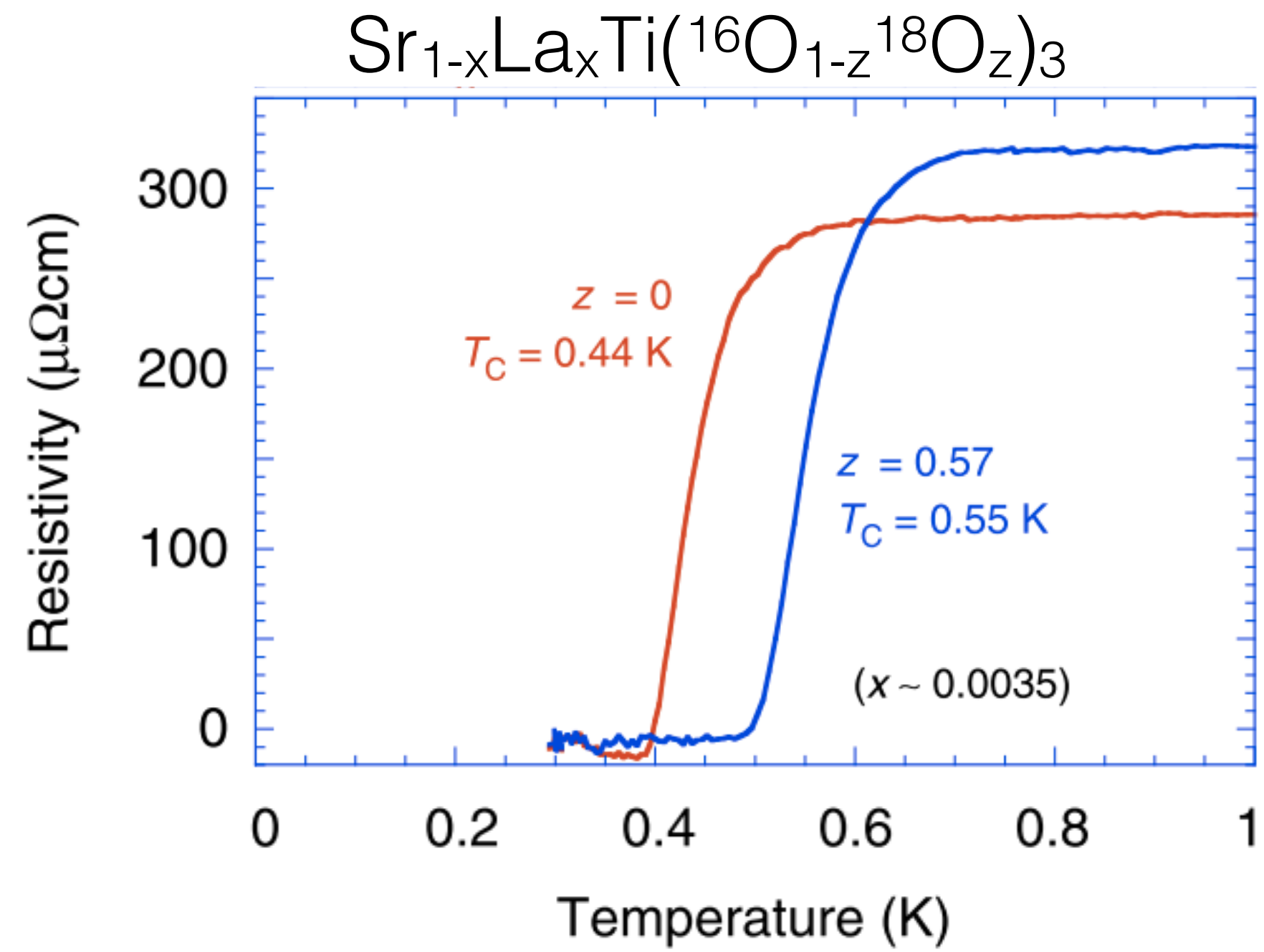
Y. Luspín et al, J. Phys. C: Solid State Phys. 13 3761 (1980)

# Superconductivity

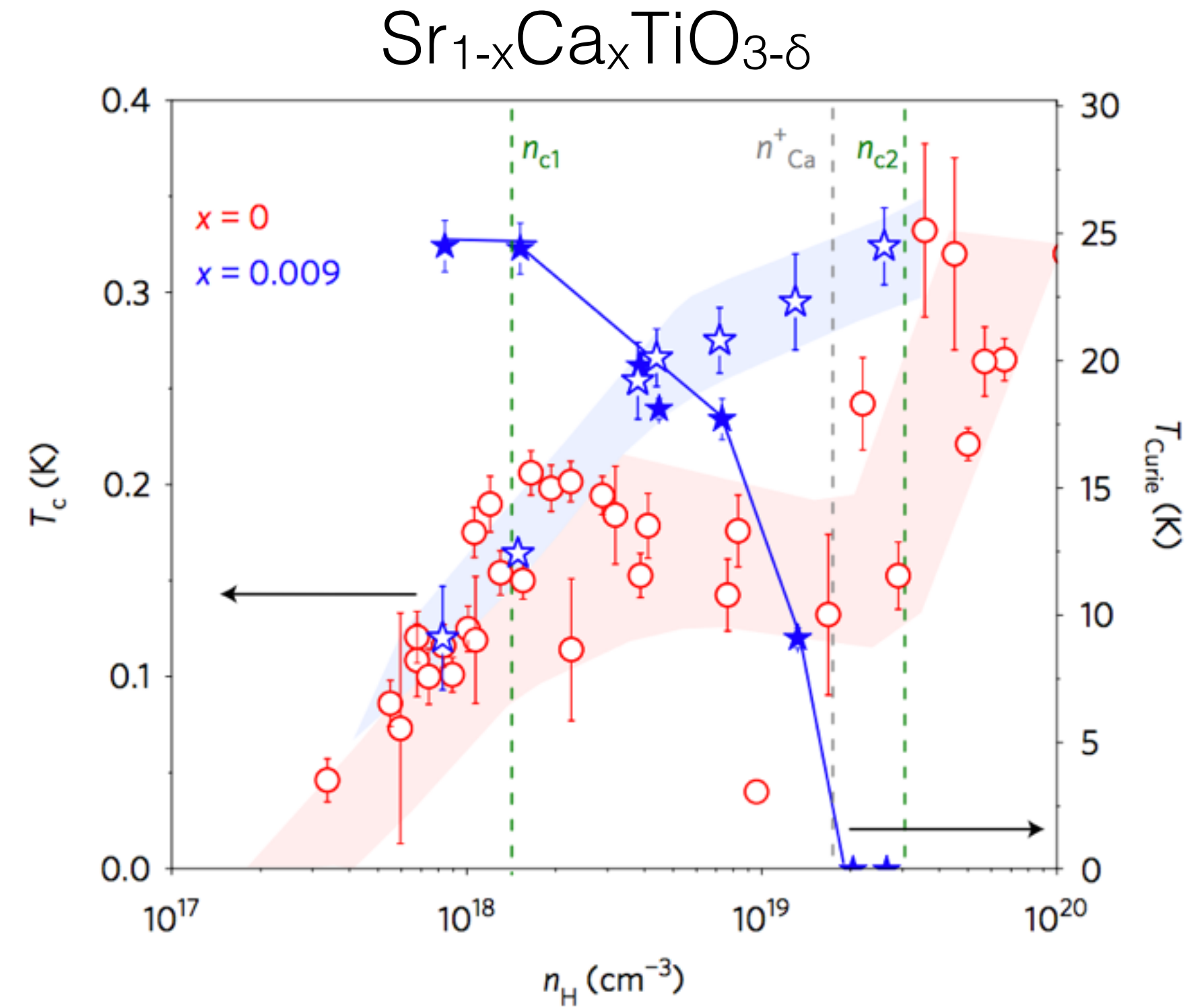


C. S. Koonce et al, Phys. Rev. 163, 2 (1967)  
X. Lin et al. Phys. Rev. Lett. 112, 207002 (2014)

# Enhancing superconductivity

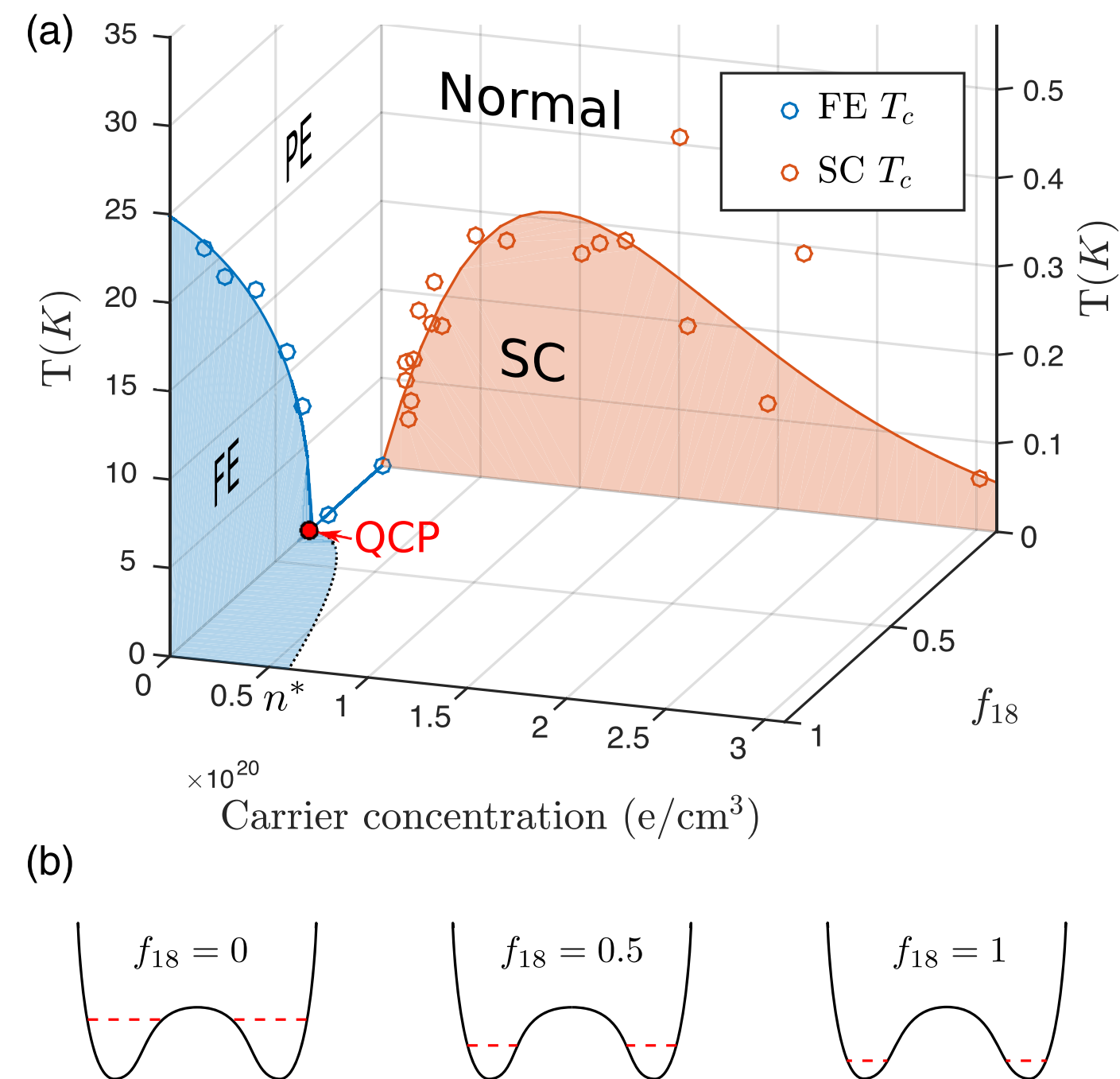


Y. Tomioka et al, Nat. Commun. 10, 738, (2019)  
See also A. Stucky et al, Sci. Rep. 6, 37582 (2016)



C. W. Rischau et al, Nat. Phys. 13, (2017)

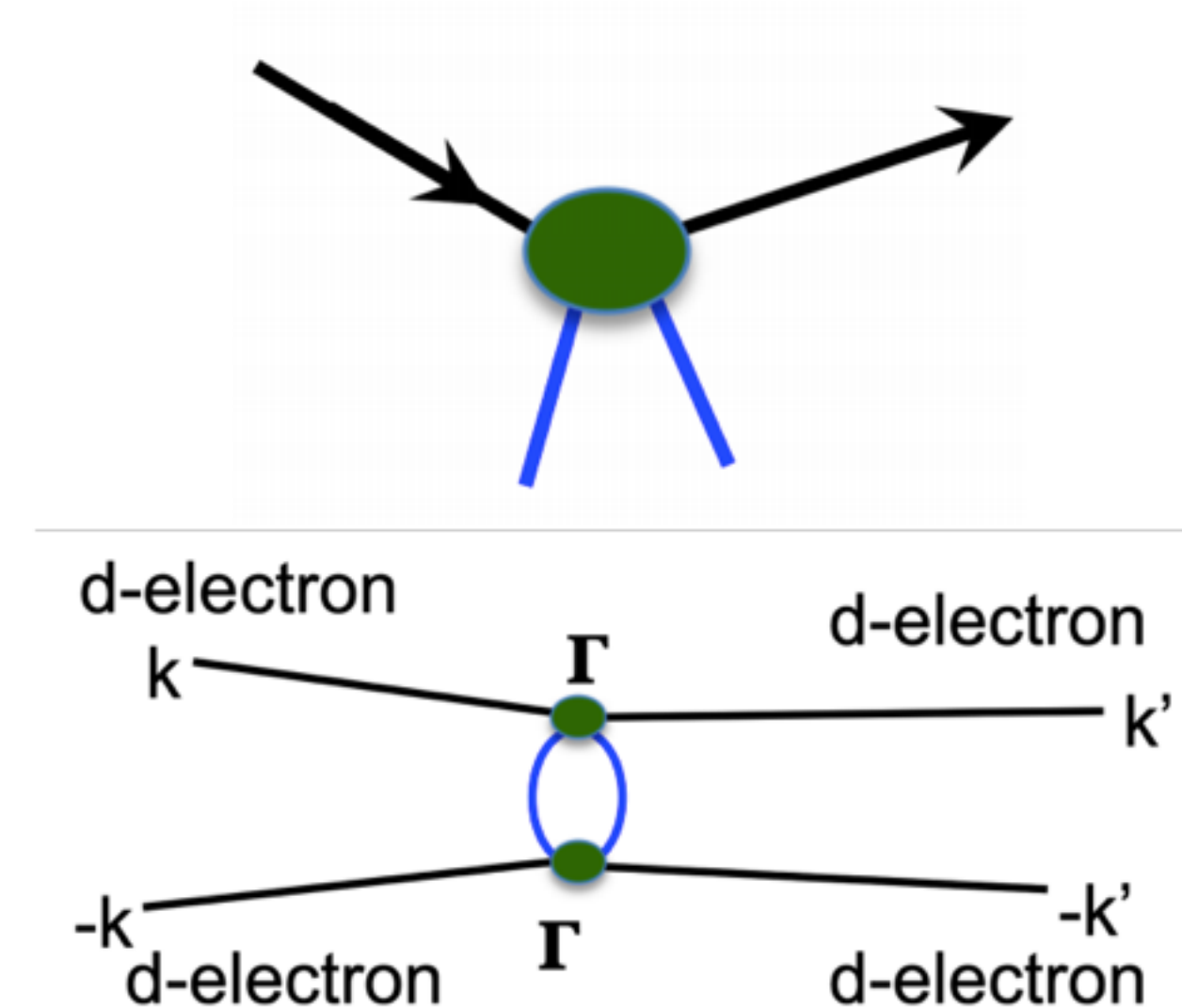
# Superconductivity and ferroelectricity



J. Edge et al, Phys. Rev. Lett. 115 (2015)

SrTiO<sub>3</sub> superconductivity may be controlled by the ferroelectric soft mode phonon

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



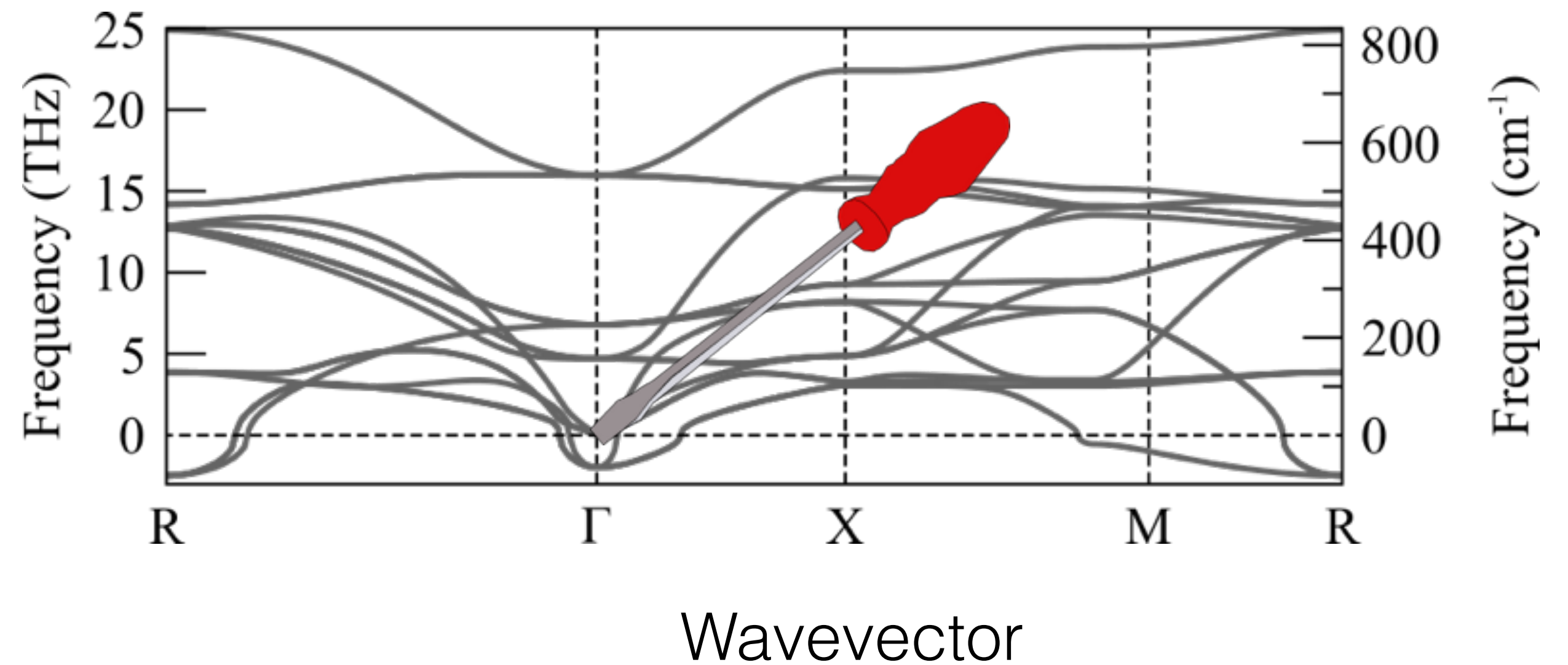
Possible “charged phonon” effect in SrTiO<sub>3</sub>

D. van der Marel et al, arXiv 1903.08394 (2019)

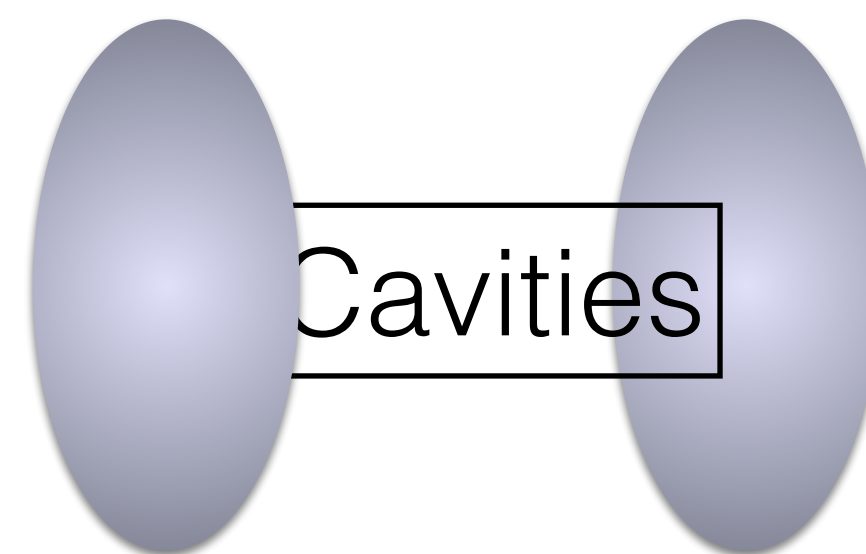
# Solid state cavities motivation

The interest in phonon spectra

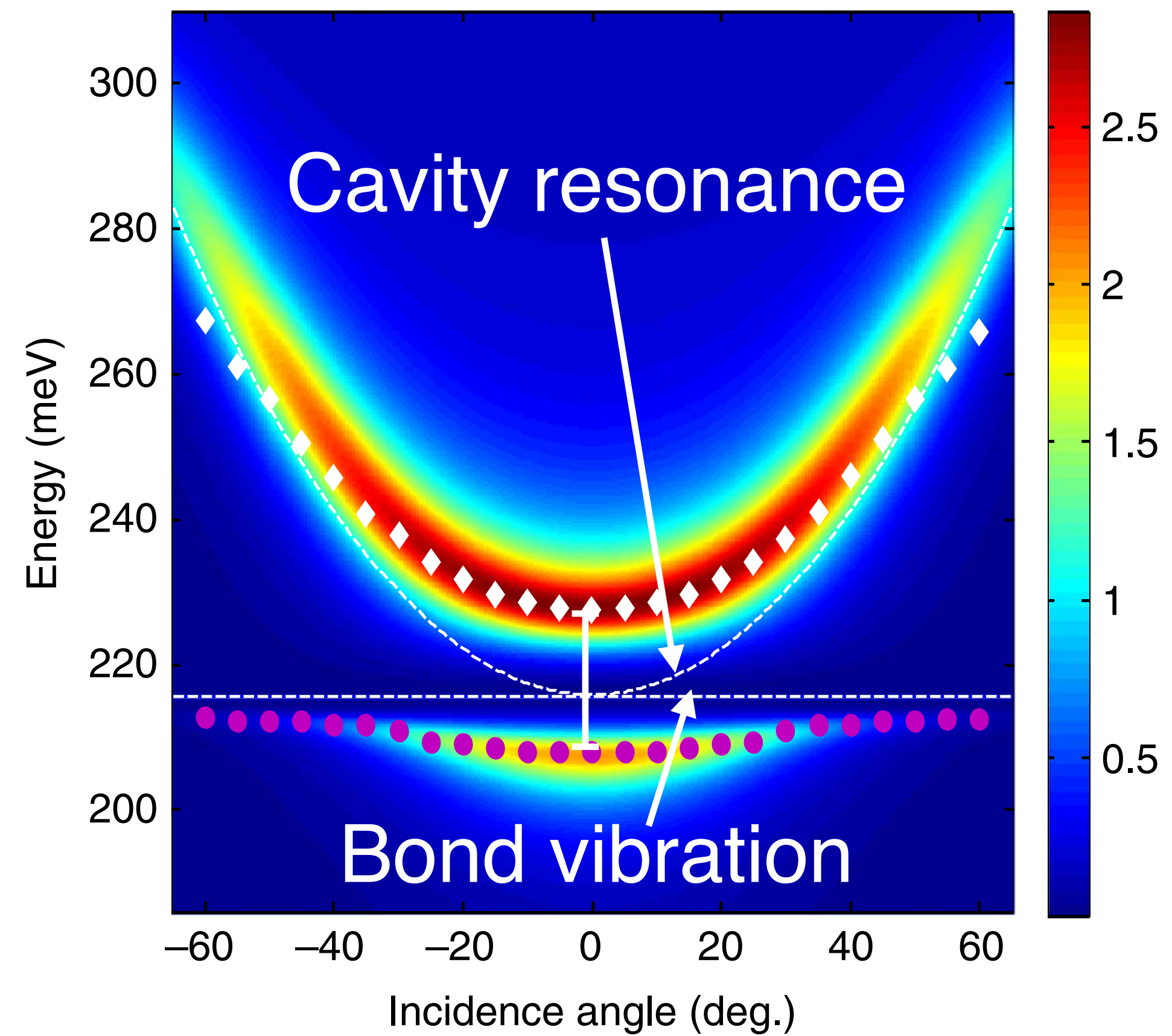
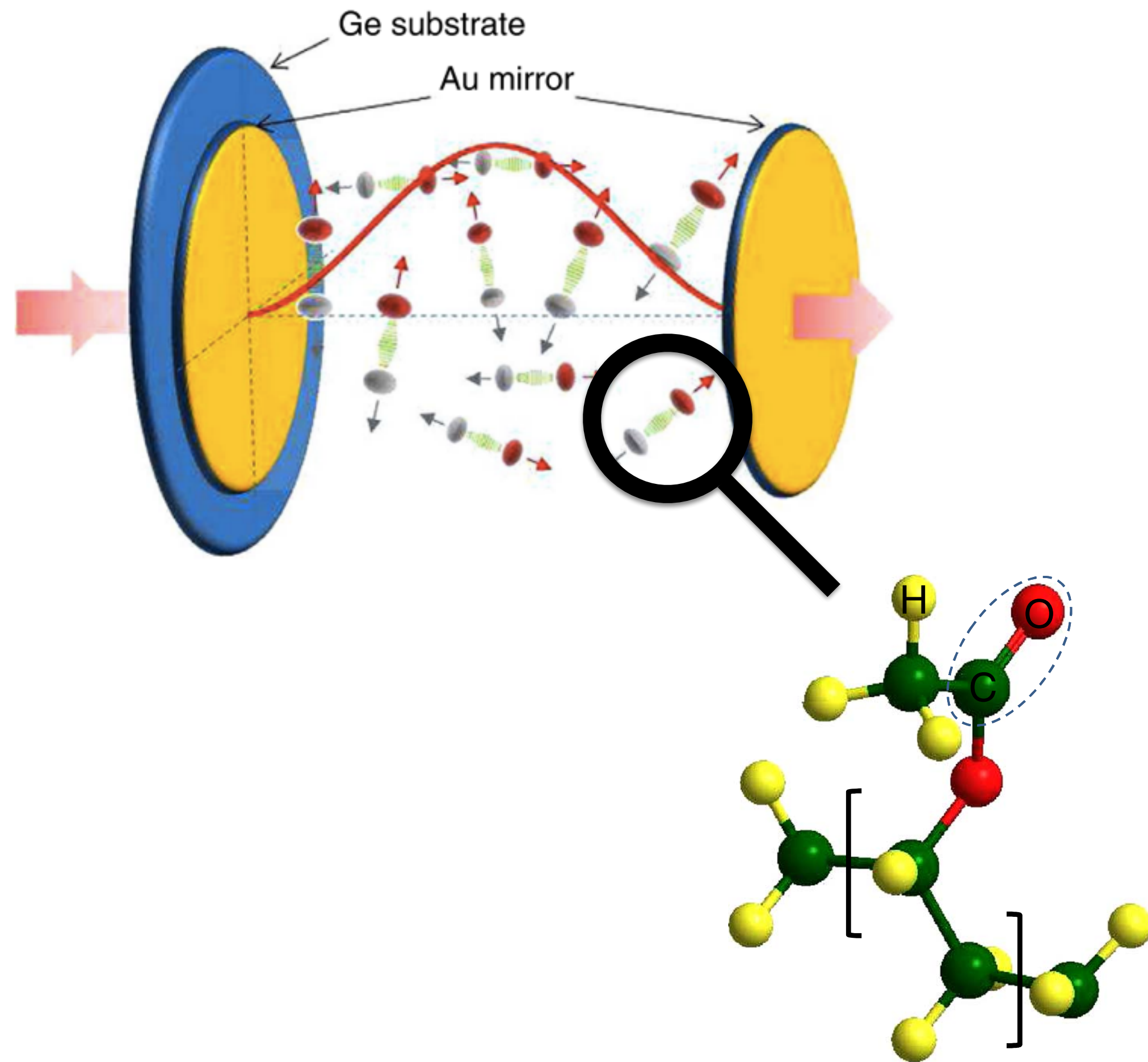
- Ferroelectric materials
  - Increase Curie temperature
- Quantum paraelectric materials
  - Induce ferroelectricity
- Superconductors
  - Increase critical temperature



Strontium titanate compounds cover all of these properties



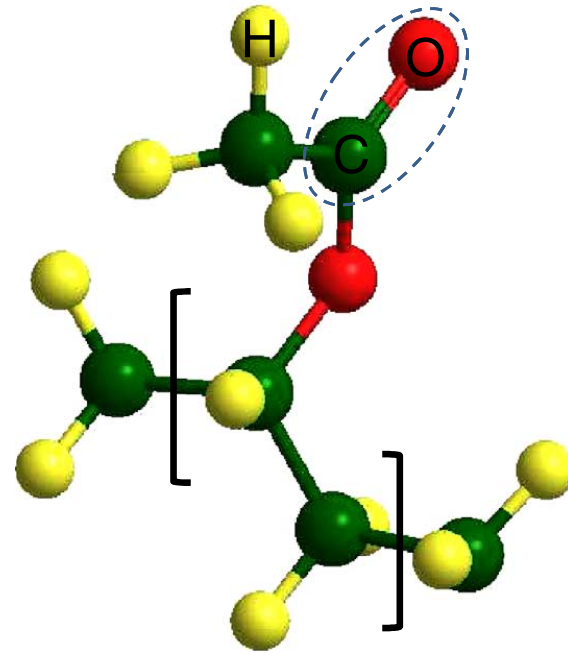
# Molecular cavities



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

Could affect chemical reactivity rates and yields

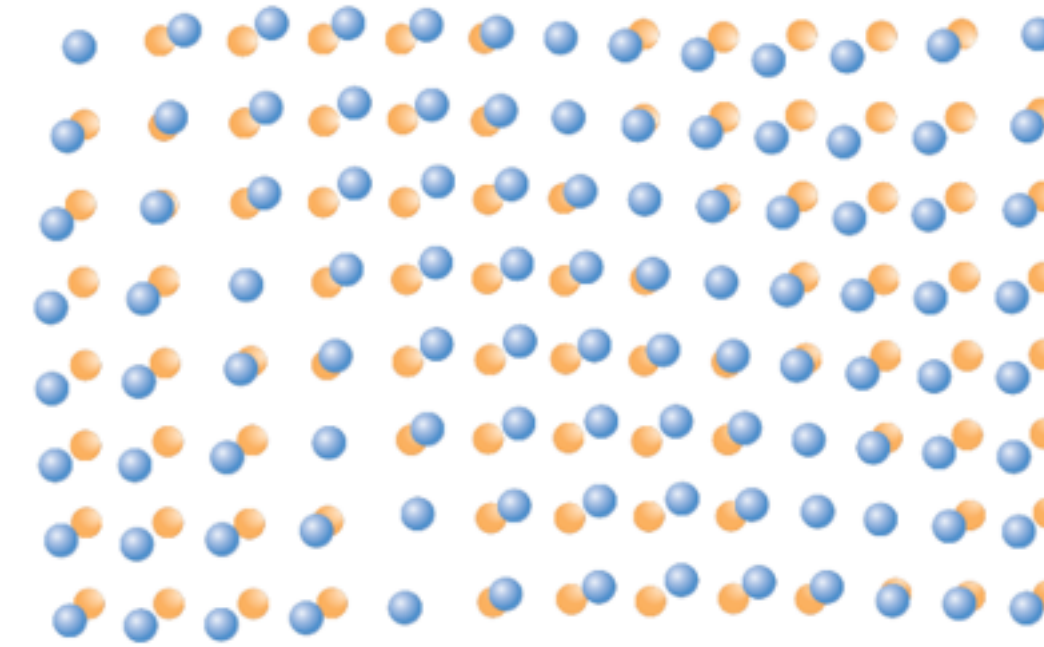
## Motivation (for us)



in a molecule

cavity coupling to a vibrational mode

may affect chemical reactivity



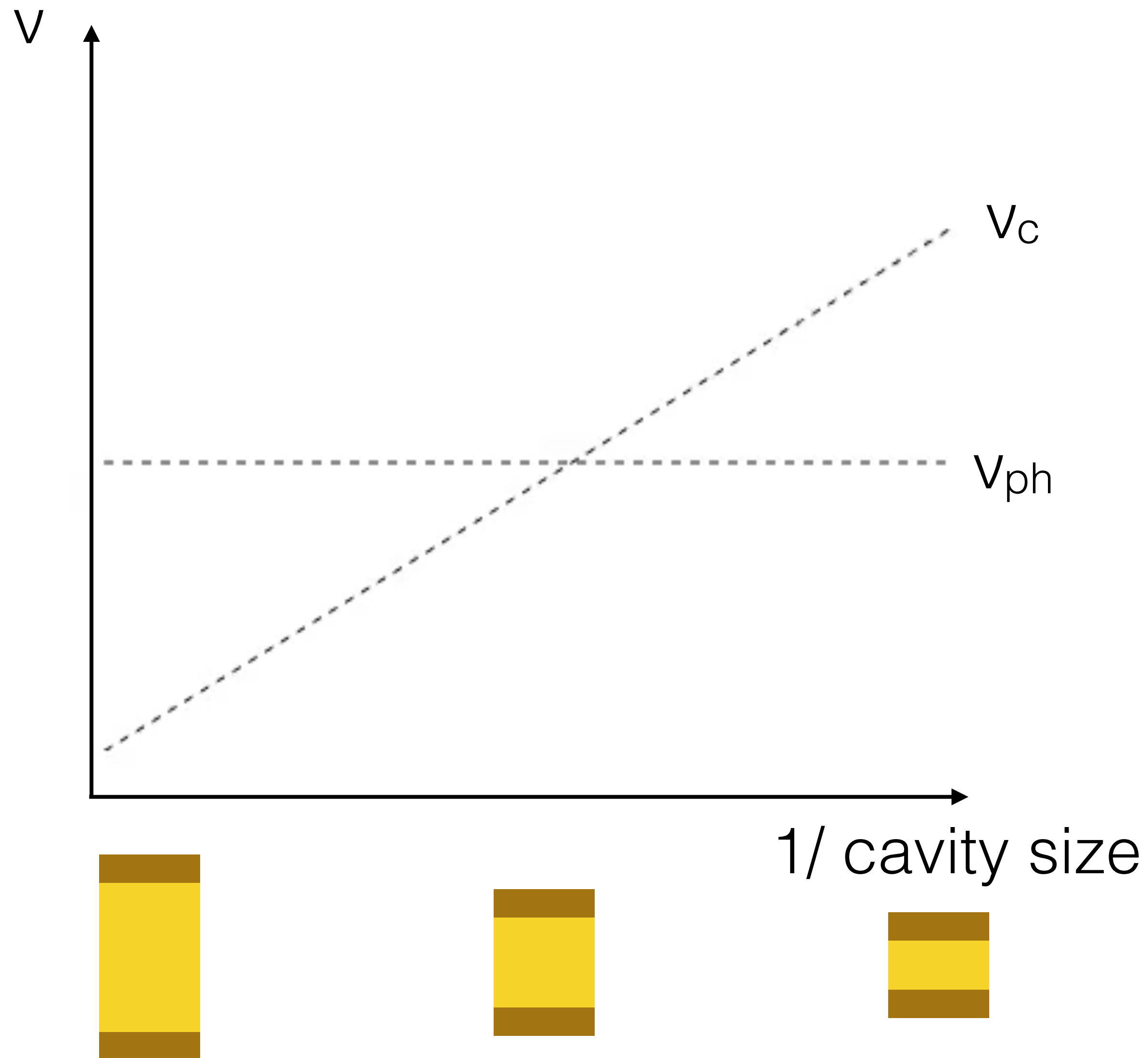
in a crystal

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  $\text{SrTiO}_3$ ?
- Phonon-electron coupling crucial in e.g. superconductors
- Further coupling mechanisms?

# Cavity-phonon coupling

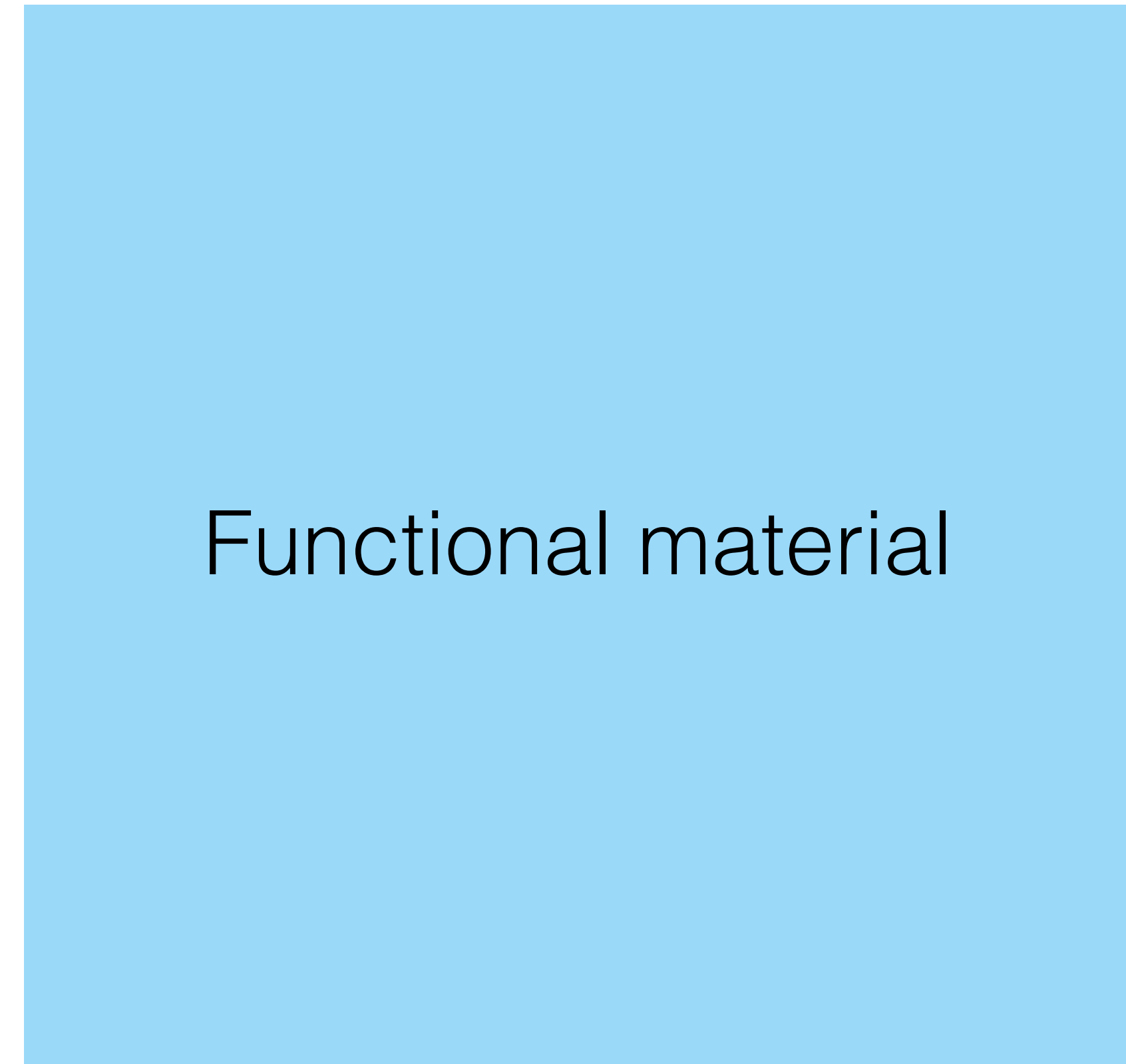
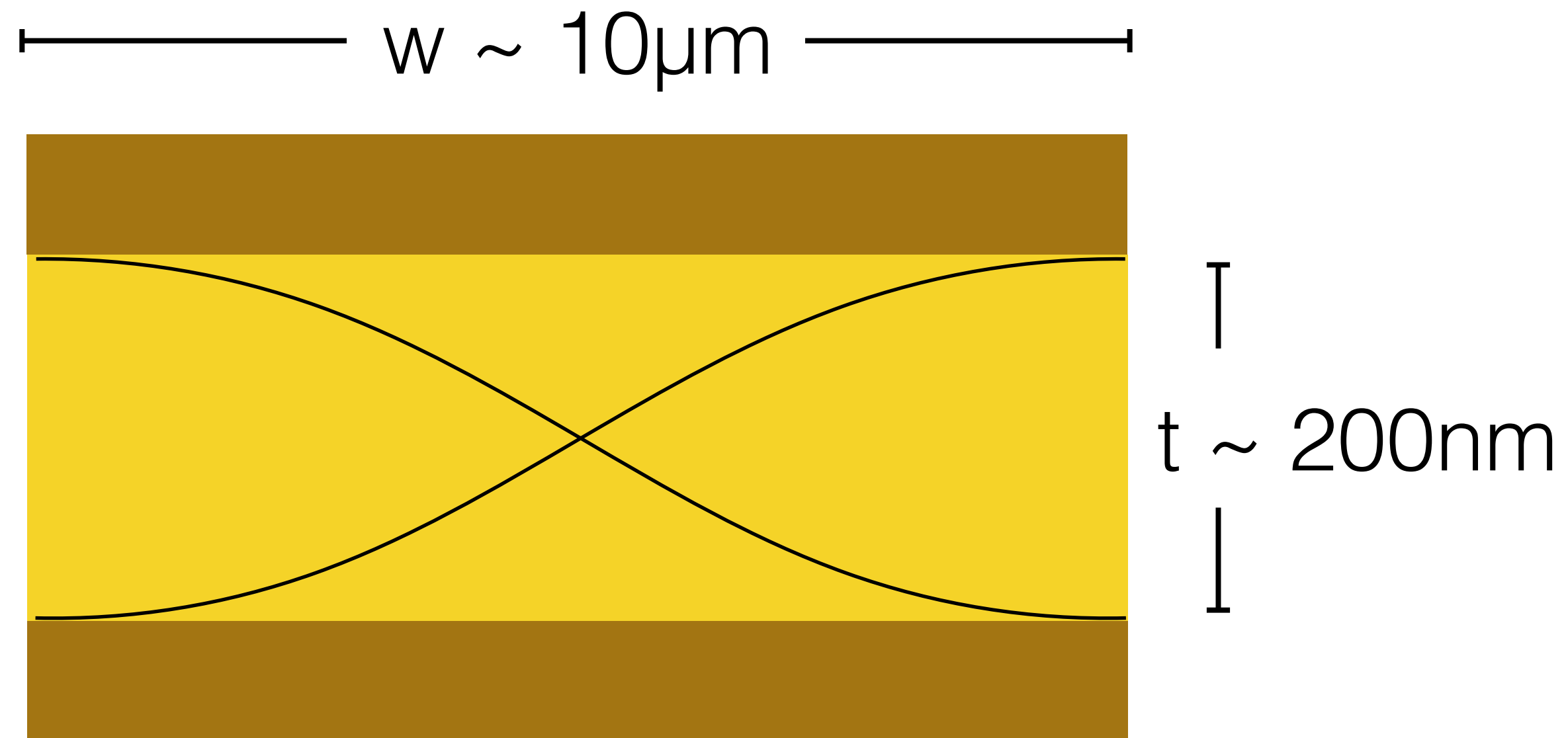


Cavity combined with dipole phonons

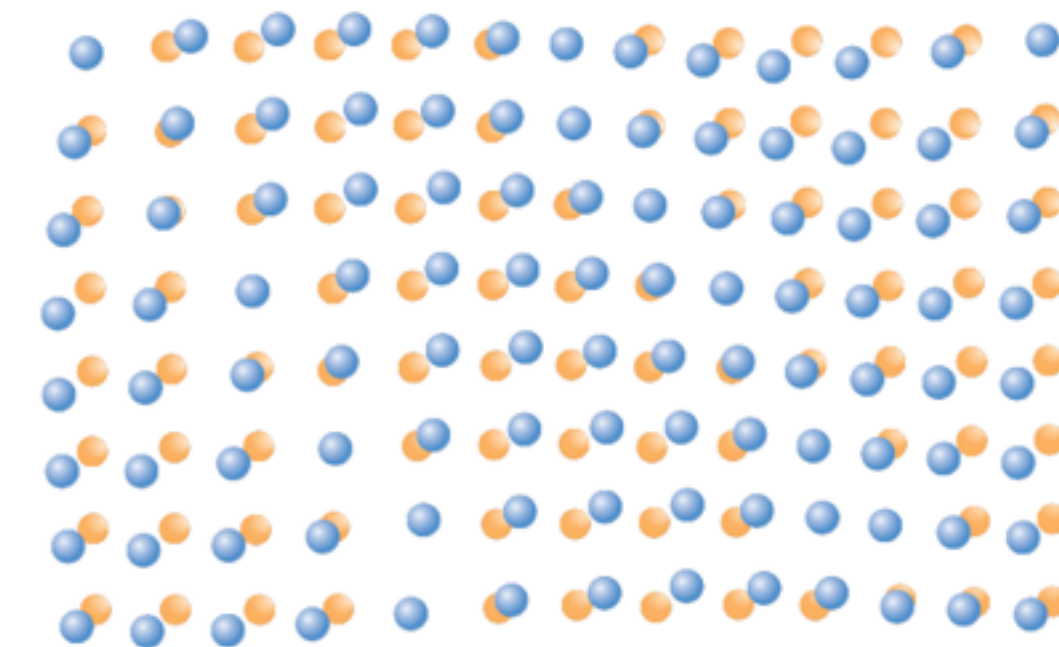
Close to resonance ( $v_c = v_p$ ) there is avoided crossing

Rabi splitting ( $2\Omega$ )

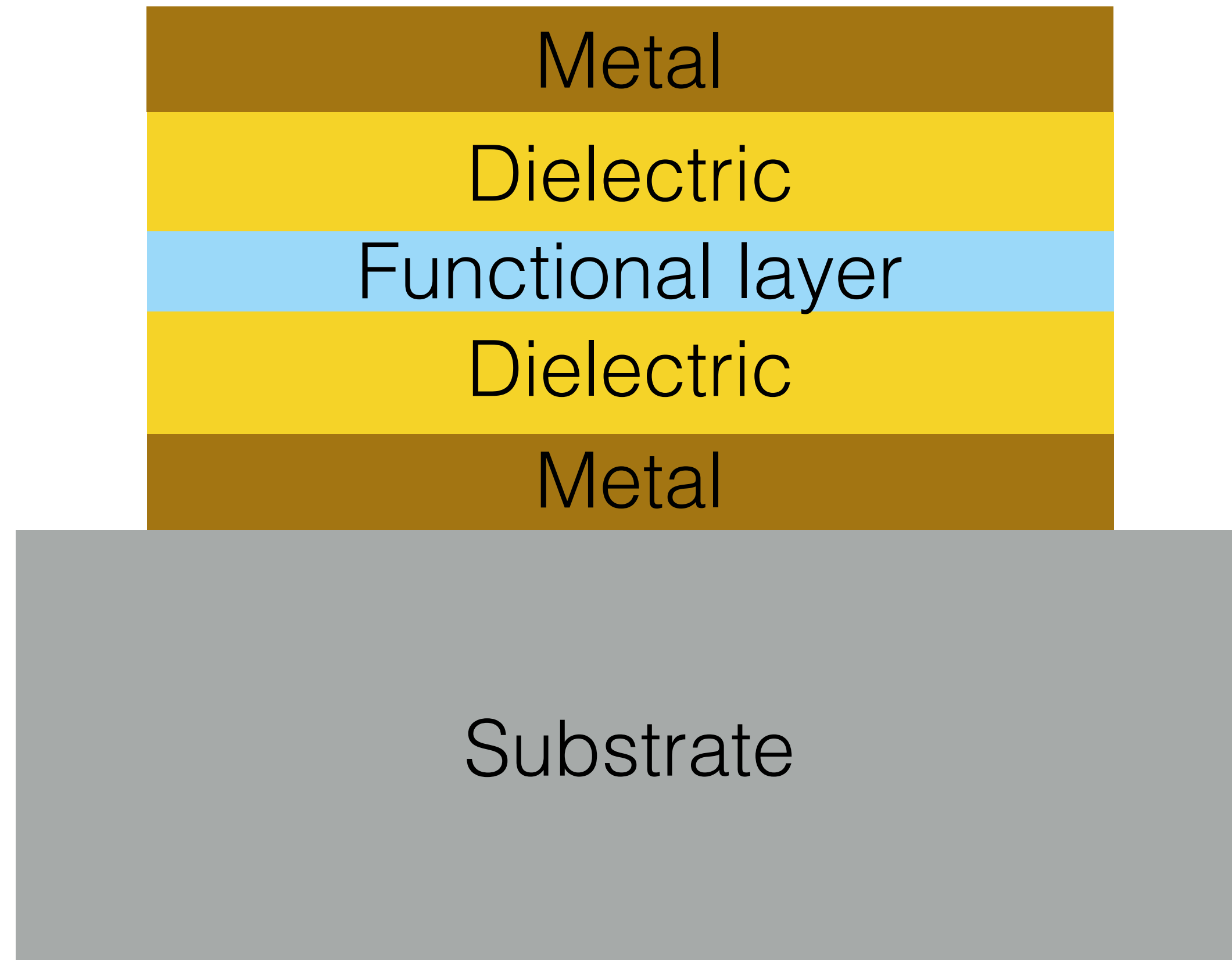
# Perpendicular electric field



Todorov et al, Optics Express 18, 13886 (2010)  
Y. Laplace et al, Phys. Rev. B 93, 075152 (2016)



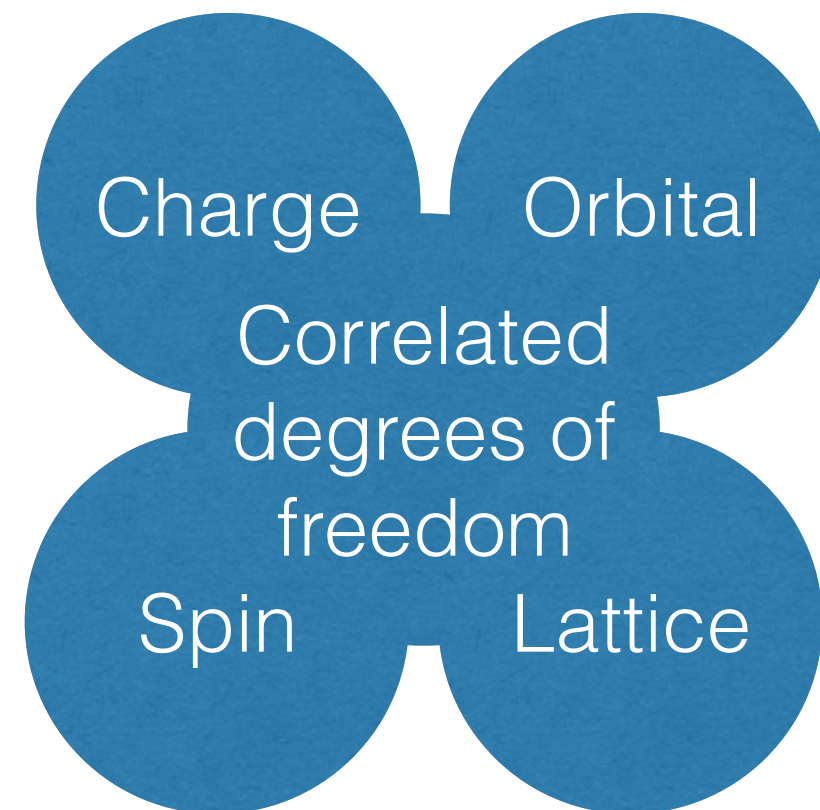
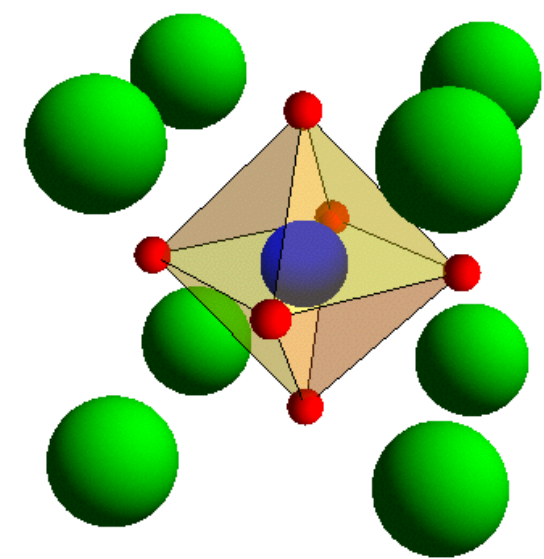
## Heterostructure cavities



$$w = \frac{\lambda}{2} = \frac{c}{2v_p\sqrt{\epsilon}}$$

# Conclusions

Introduction to perovskite transition  
metal oxides and heteroepitaxy



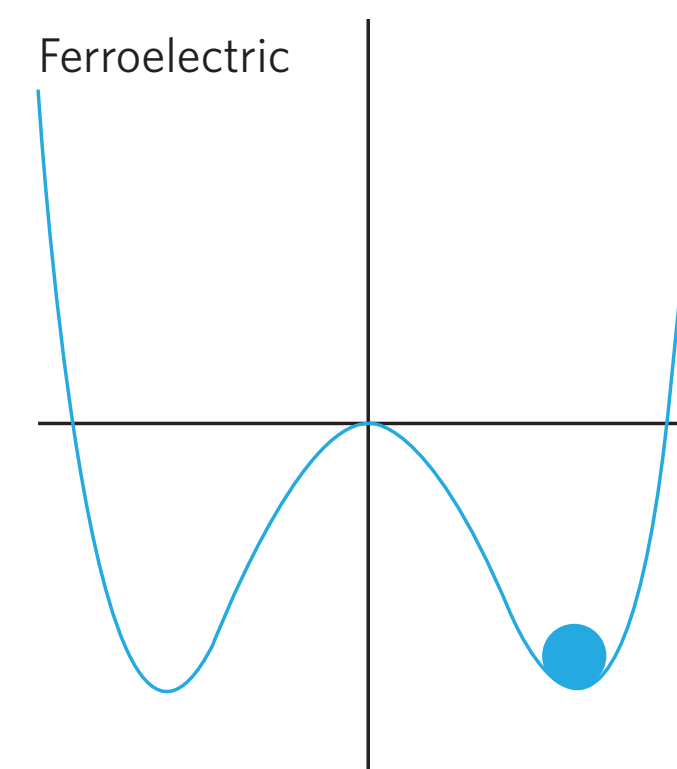
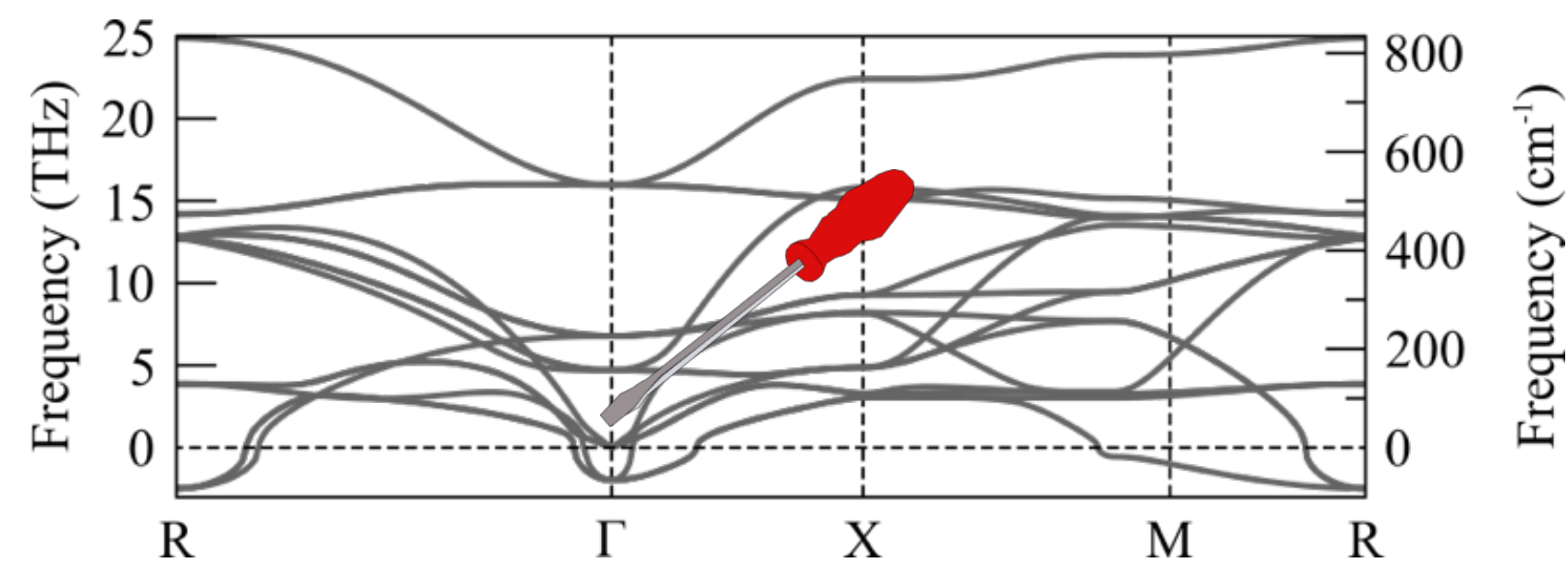
Rich phases

The interest in phonon spectra

Ferroelectric materials

Quantum paraelectric materials

Superconductors



Solid state cavities

