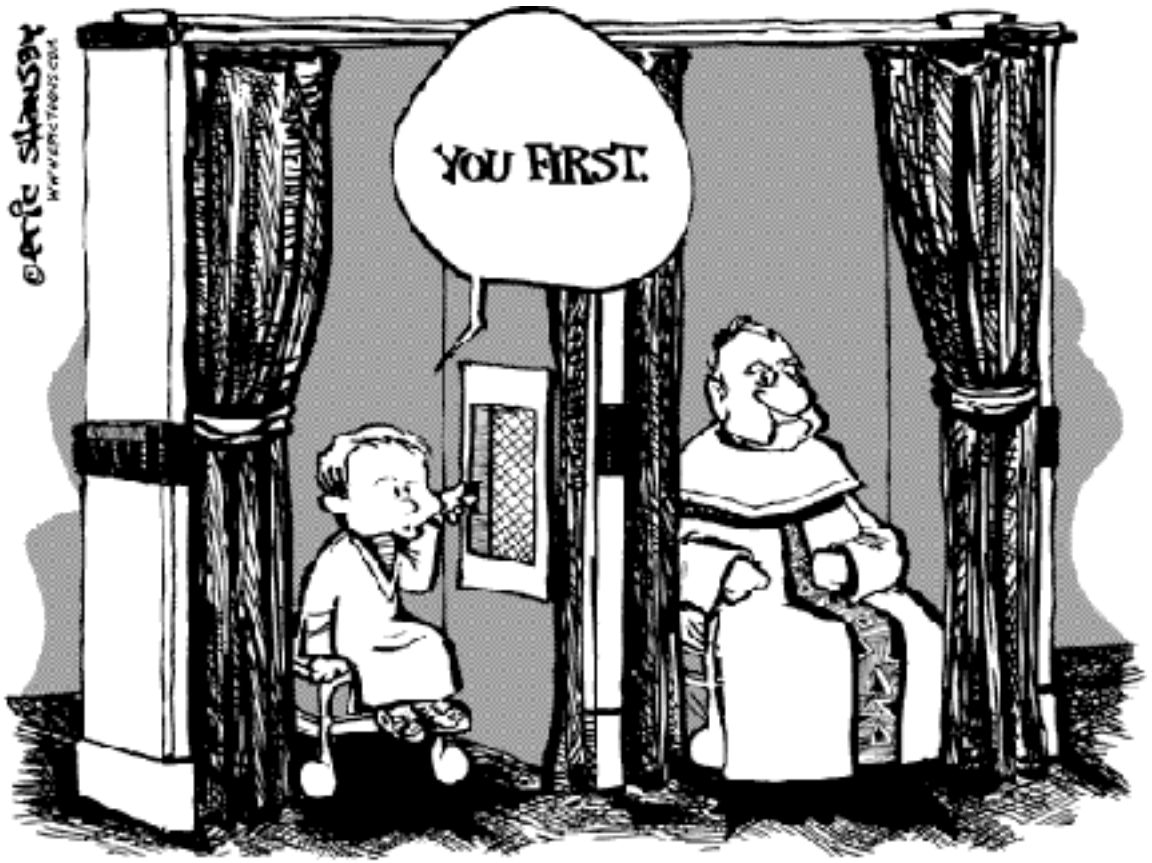
Confessions of a Materials Scientist



Confessions of a Materials Scientist:

Defect Behaviour of Strontium Titanate

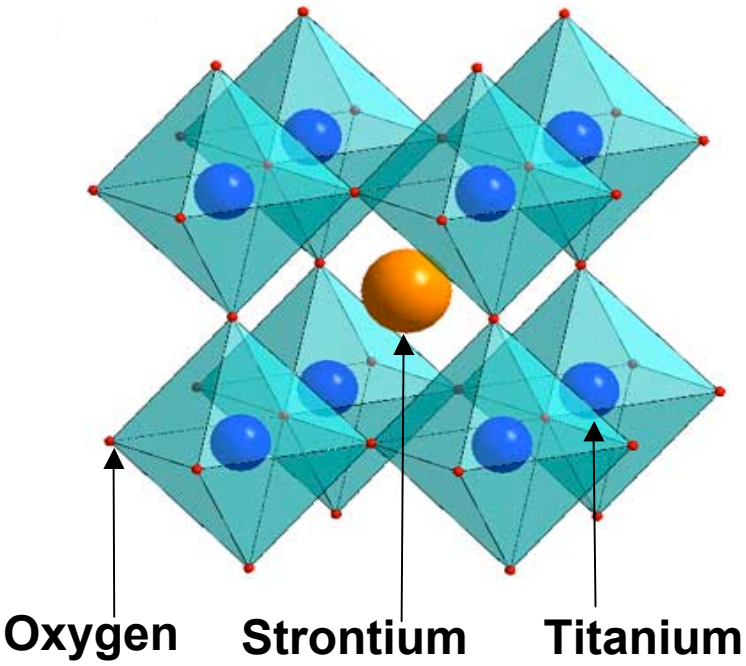
Elif Ertekin

Quantum Monte Carlo in the Apuan Alps VI
Vallico Sotto, Italia
25-30th July 2010

In collaboration with Varadharajan Srinivasan, Jeffrey Grossman, Wolter Siemons, Jayakanth Ravichandran, and R. Ramesh.

Confession #1: I am not a QMC Girl

Strontium Titanate

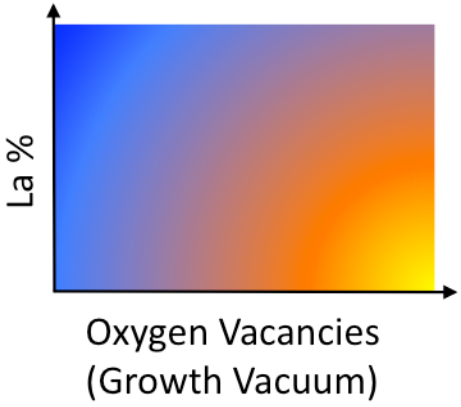


- cubic perovskite,
- large dielectric constant paraelectric down to 0K (in pure form)
- band insulator / wide band gap semiconductor (gap = 3.3 eV, bulk, indirect)

- **INSULATOR-METAL TRANSITION** via:

  - substitutional doping
    - La (III) for Sr (II)
    - one electron per dopant

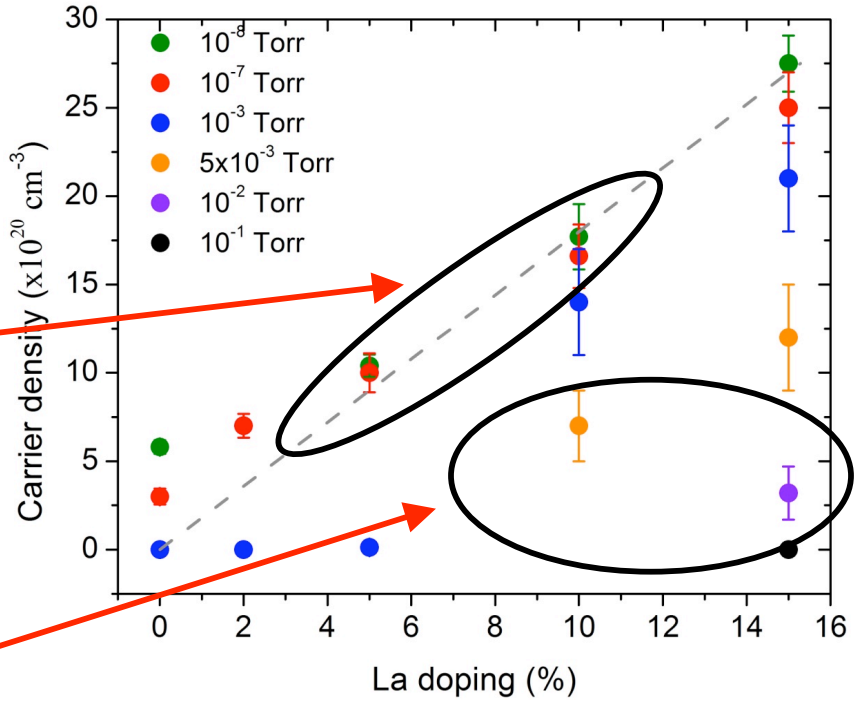
  - doping with Oxygen vacancies
    - "two electrons" per dopant
    - associated with defect band



What would happen to the transport/electronic structure if both La dopants and Oxygen vacancies are introduced simultaneously?

Low O_2 growth pressures, High vacancy concentrations

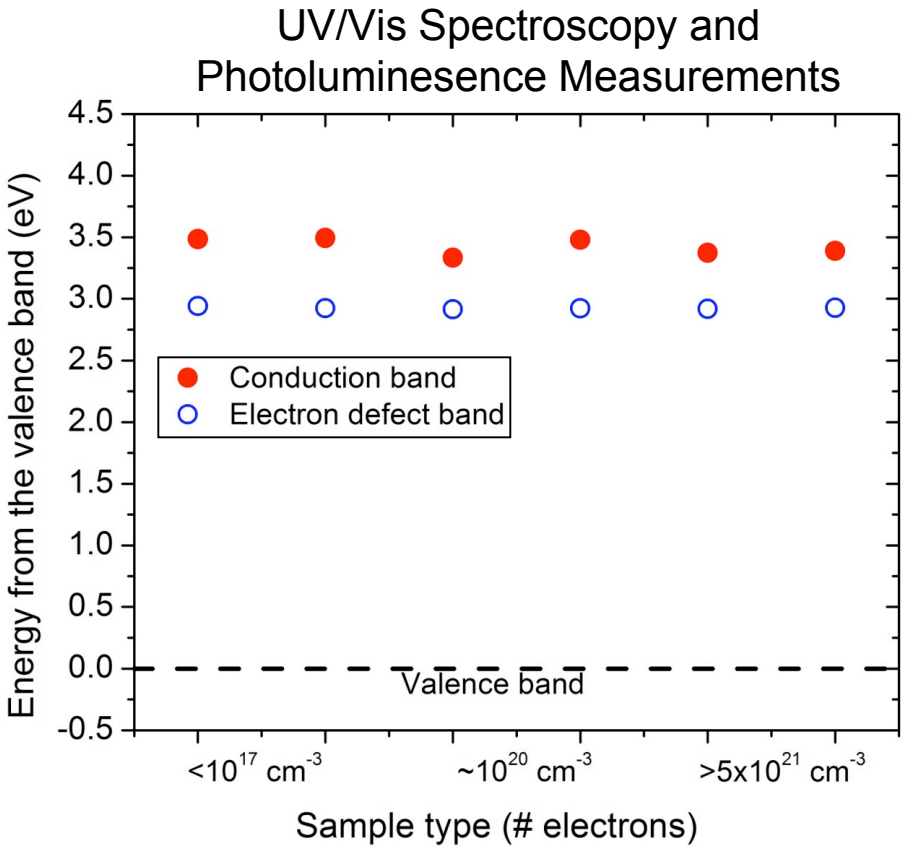
High O_2 growth pressures, Low vacancy concentrations

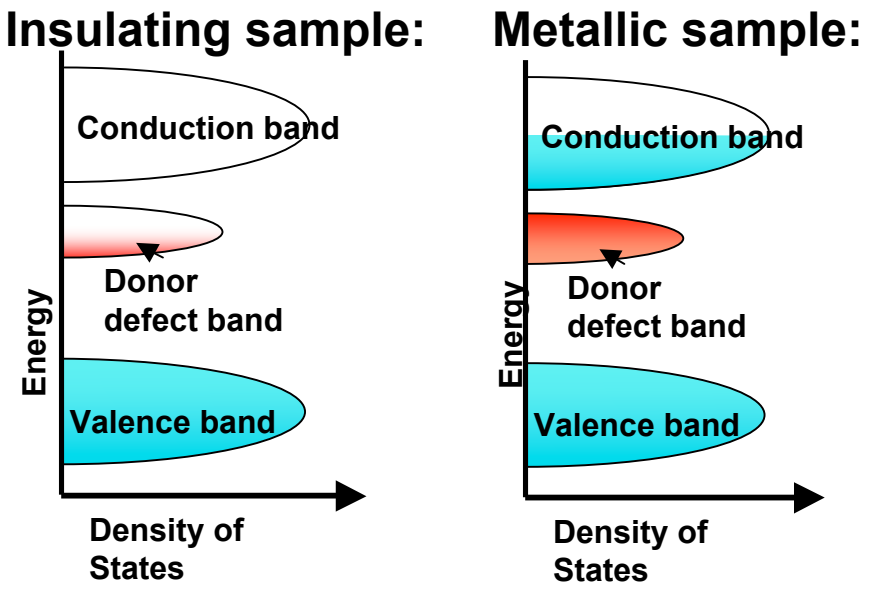


Courtesy: W. Siemons, J. Ravichandran, R. Ramesh

- Expect high $[O_V]$ at low pressures, low $[O_V]$ at high pressures
- La concentration seems to regulate the number of carriers at higher $[O_V]$ (insulator-metal transition observed)
- At low $[O_V]$, insulator-metal transition appears suppressed

Defect Levels in the Gap … A Possible Explanation

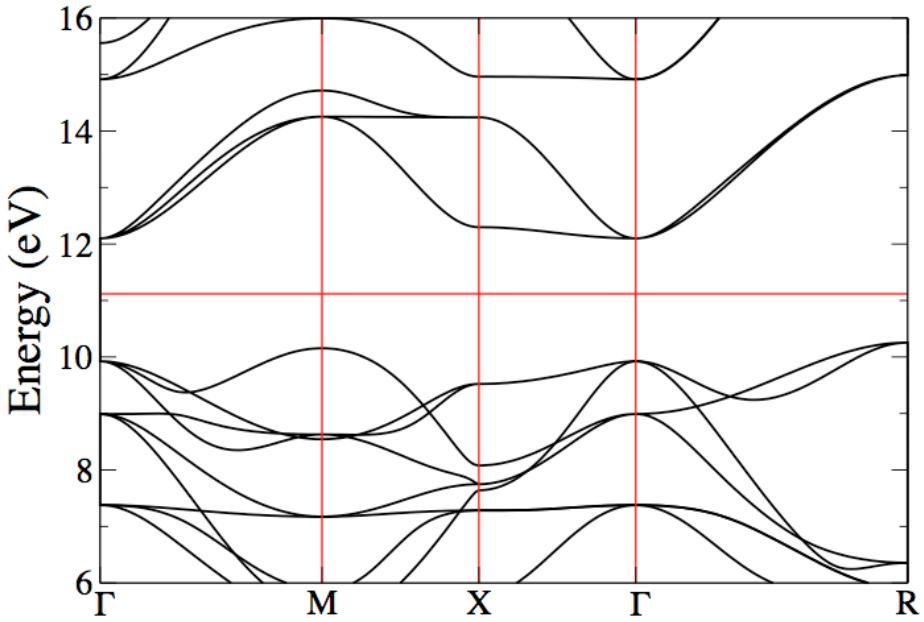


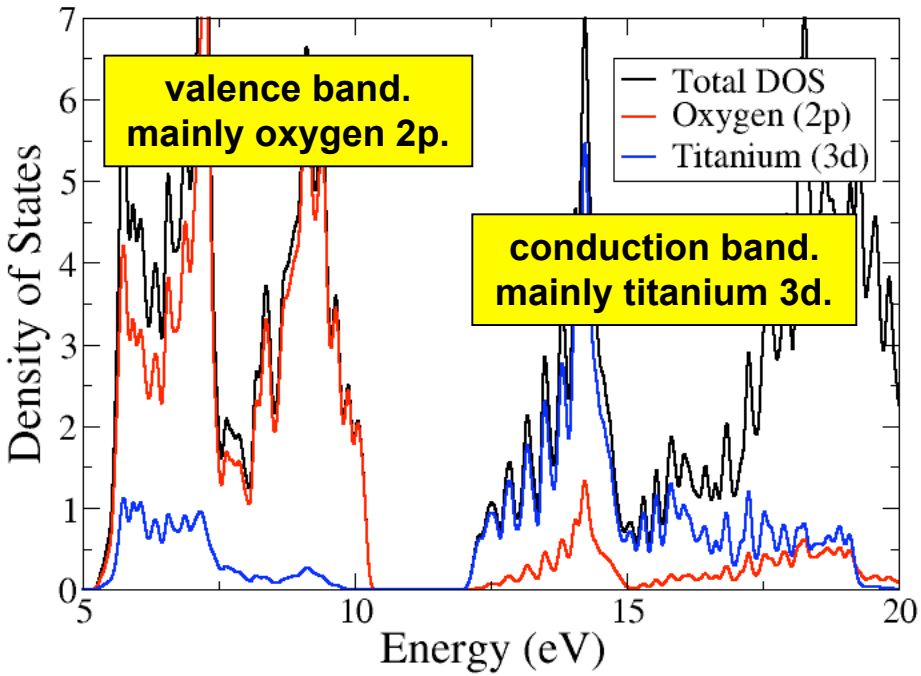


Courtesy: W. Siemons, J. Ravichandran, R. Ramesh

- PL spectra shows evidence for the creation of defect states in the gap.
- At low [O_V], excess electrons are stuck in defect states, hence no metallic behavior is observed.
- At high [O_V], the defect states are completely filled and the conduction band is partially filled, resulting in metallic behavior.

STO: Band Structure

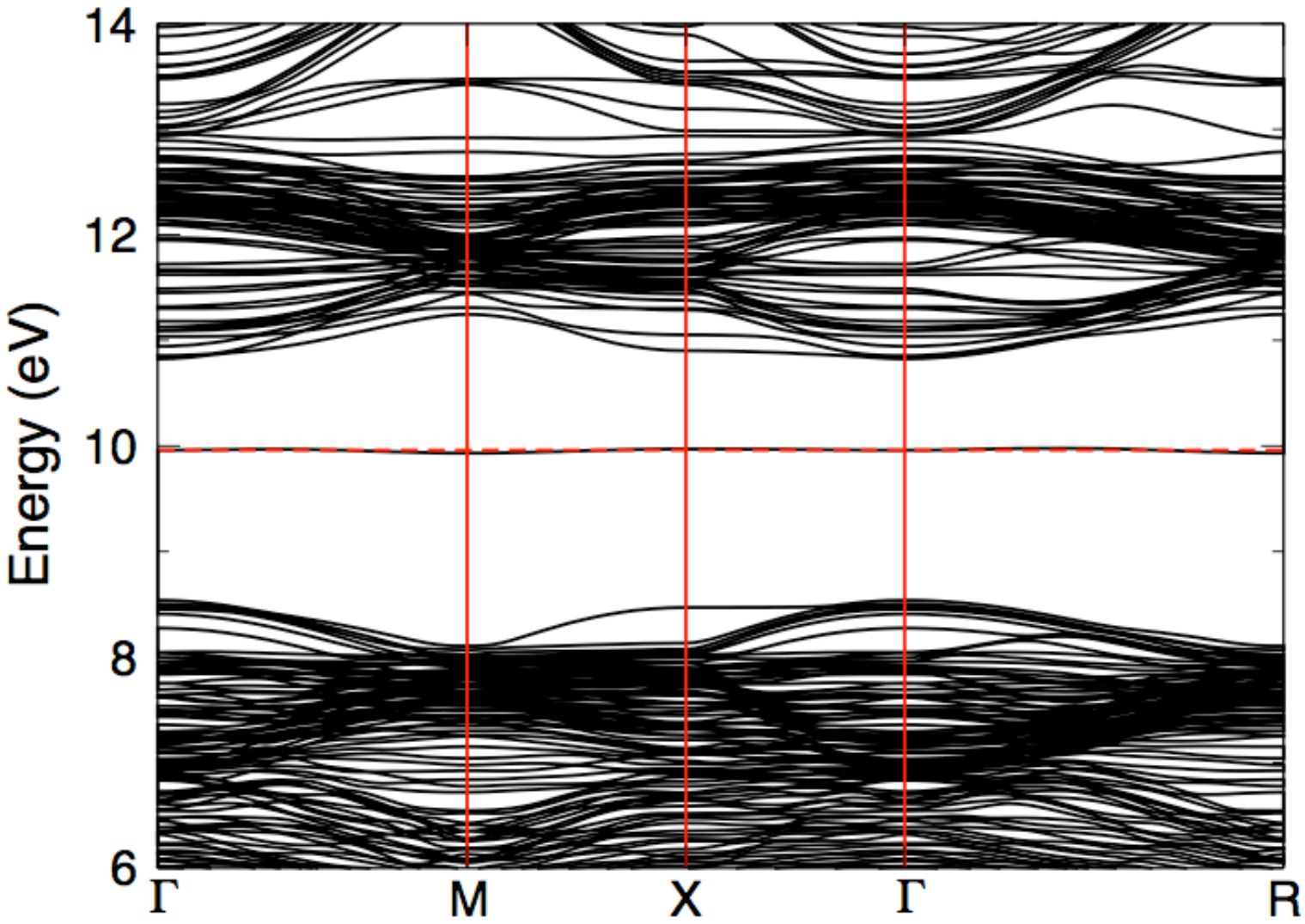




- pure STO band structure: PBE gap 1.82 eV R -> Γ (exp 3.3 eV)
- is it possible to create a defect band in this system using intrinsic and extrinsic defects?

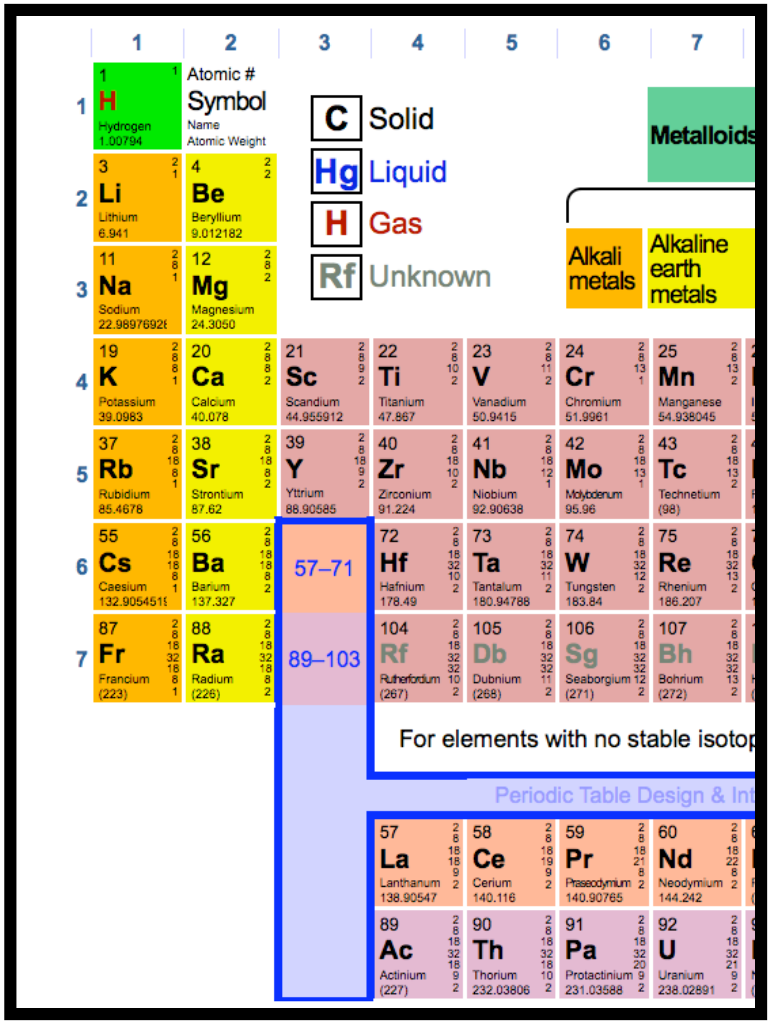
A Smattering of Defects and Voila ...

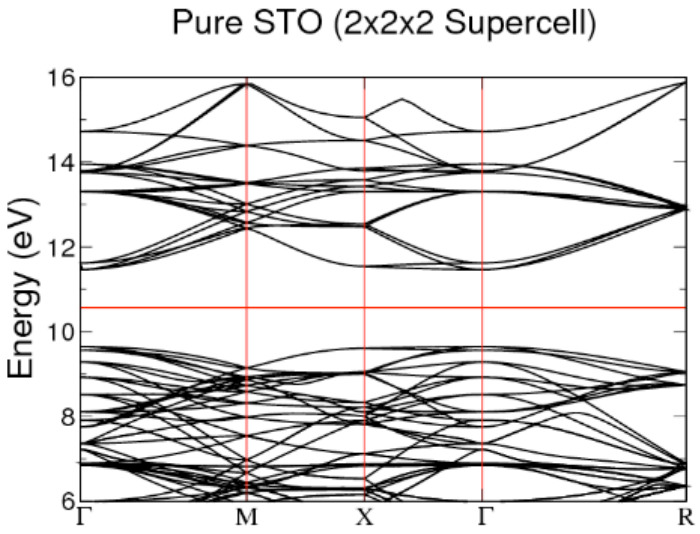
Oxygen Divacancy, 2 Strontium Vacancies, and 1 Substitutional La

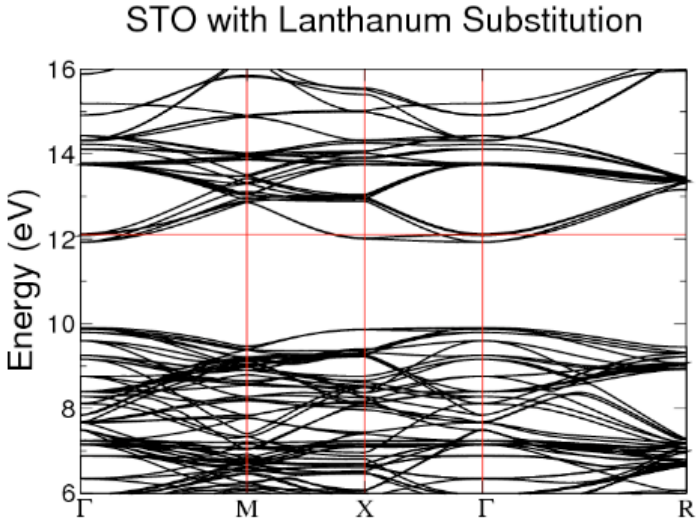


Why This Works: Simple Analysis

- La, a substitutional defect for Sr, is a shallow electron donor







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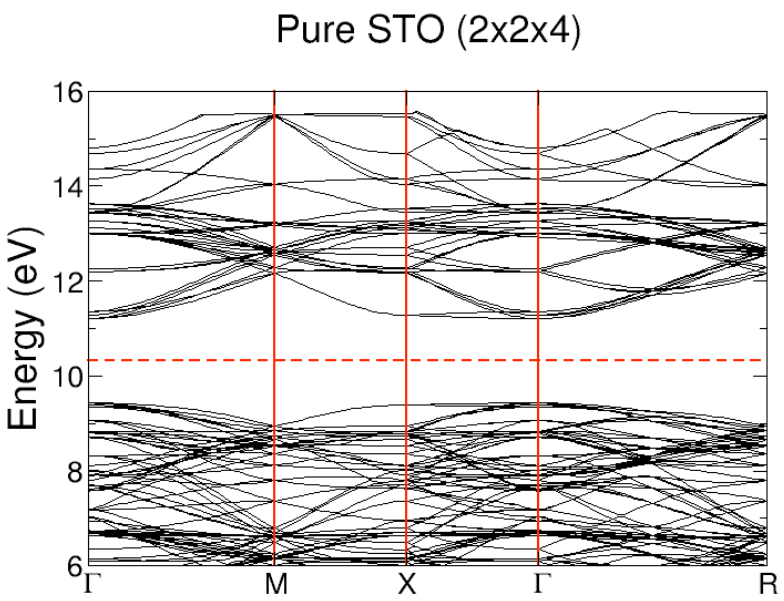
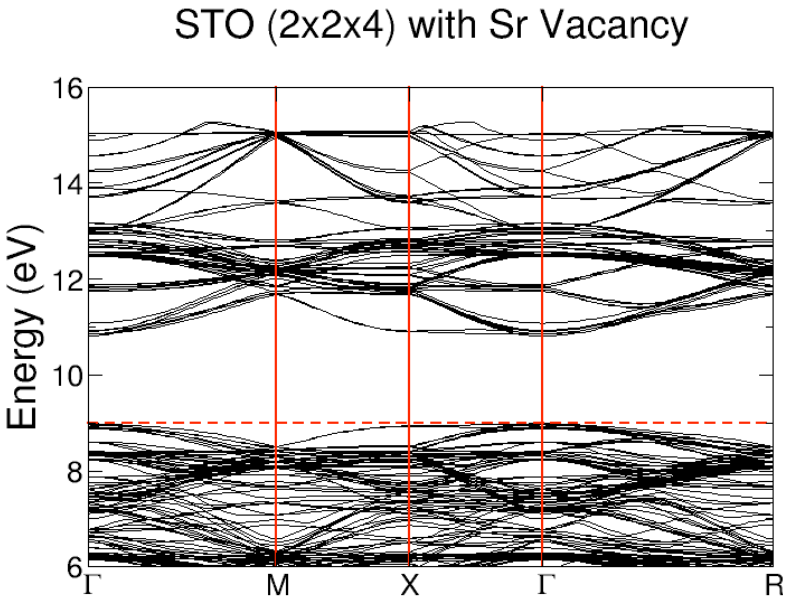
$$(Sr^{+2})(Ti^{+4})(O^{-2})_3$$





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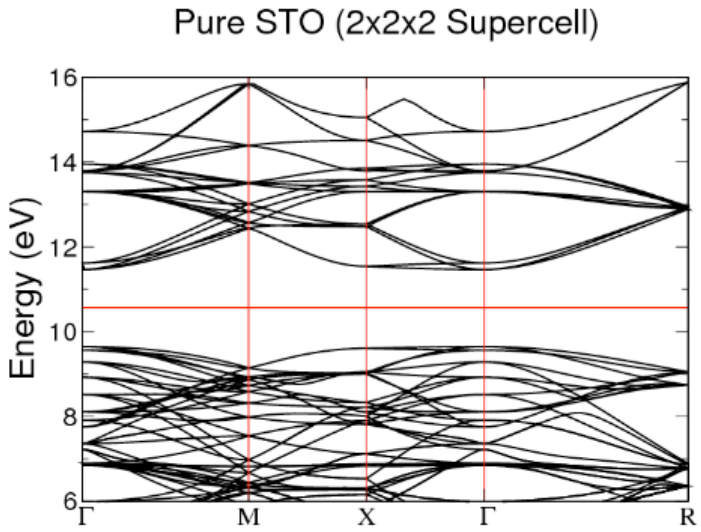
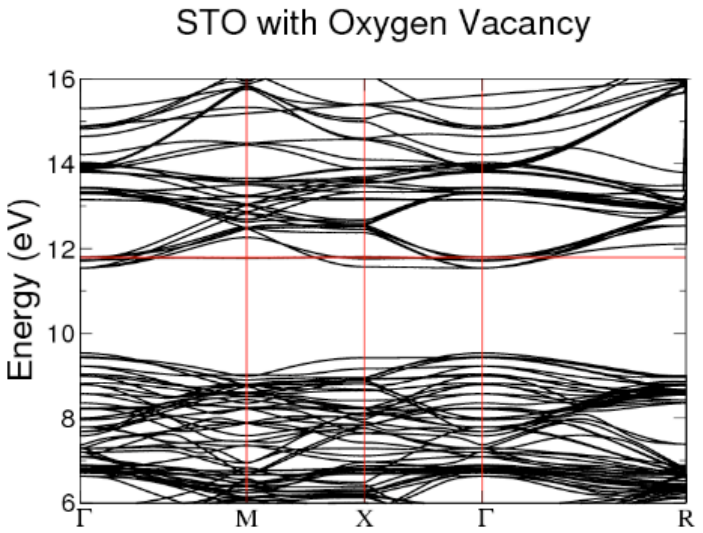
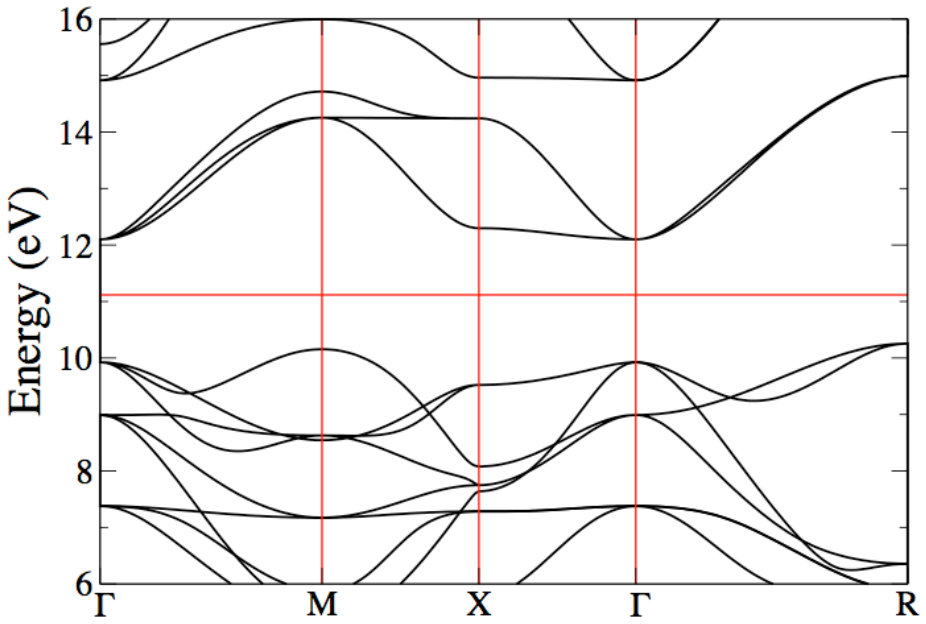


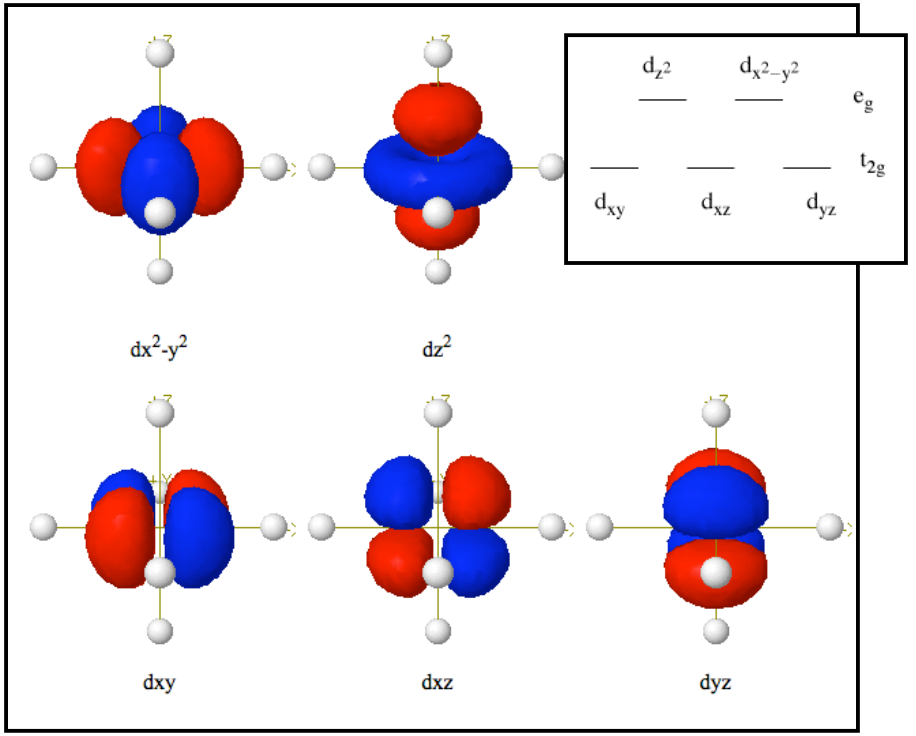


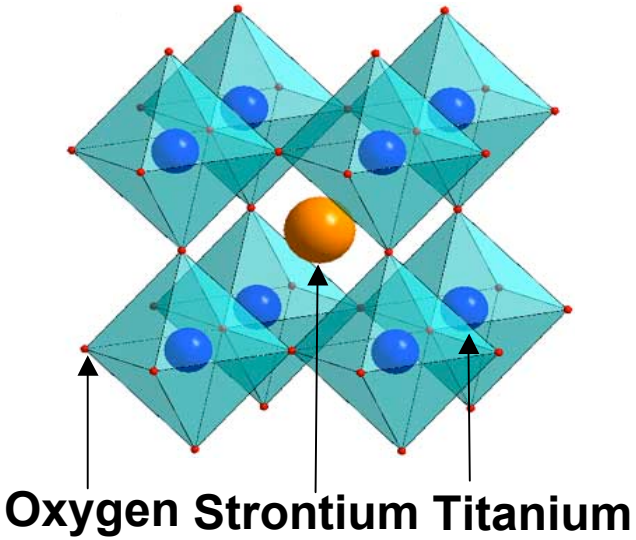
$(Sr^{+2})(Ti^{+4})(O^{-2})_3$

localized defect state around CB minimum … so each O vacancy donates less than 2 electrons

d-orbital splitting in an octahedral field







- lowest conduction band states appear at Γ (3x)
- together with the next two conduction band levels at Γ, these five states are derived from the five Ti d orbitals
- t_{2g} (π bonds), e_g (σ bonds) splitting
- removing an O stabilizes an e_g level

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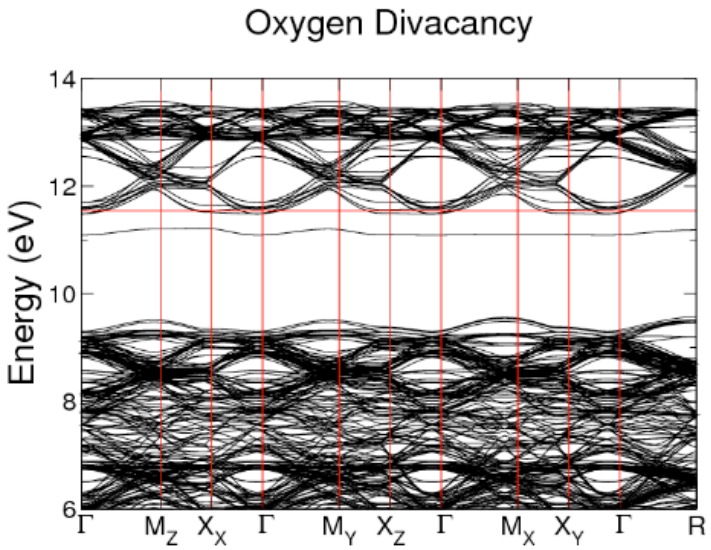
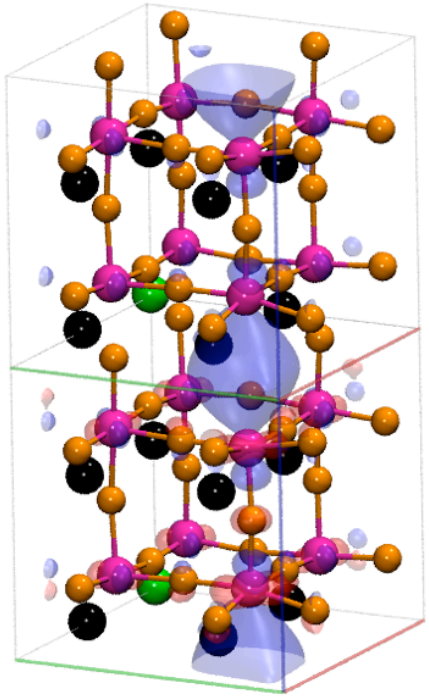
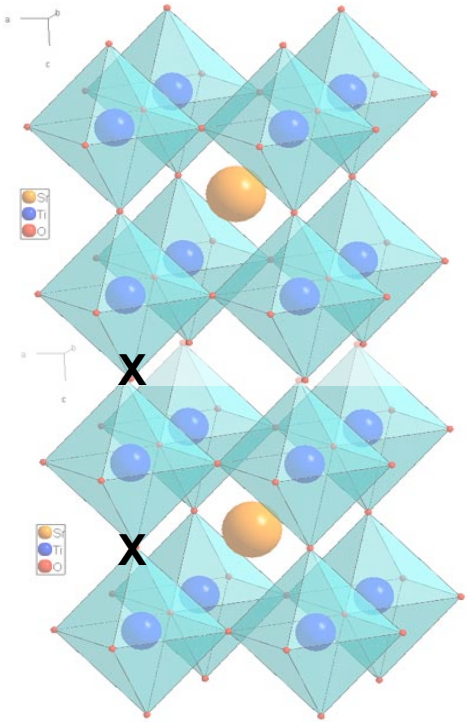
- Oxygen divacancies are electron donors and introduce a localized state offset from the conduction band edge







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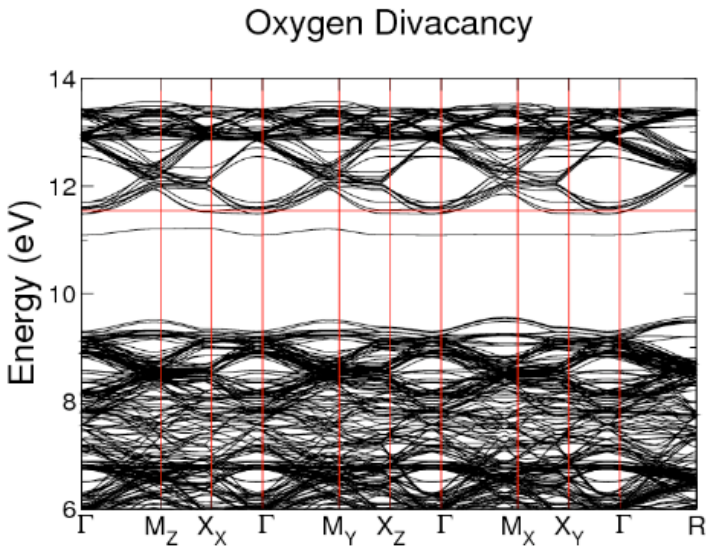

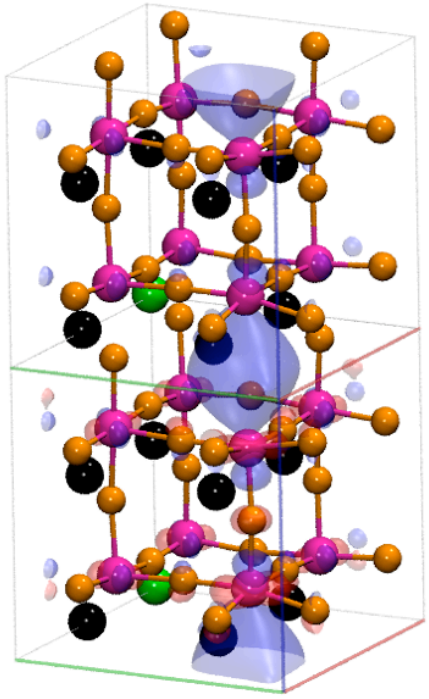

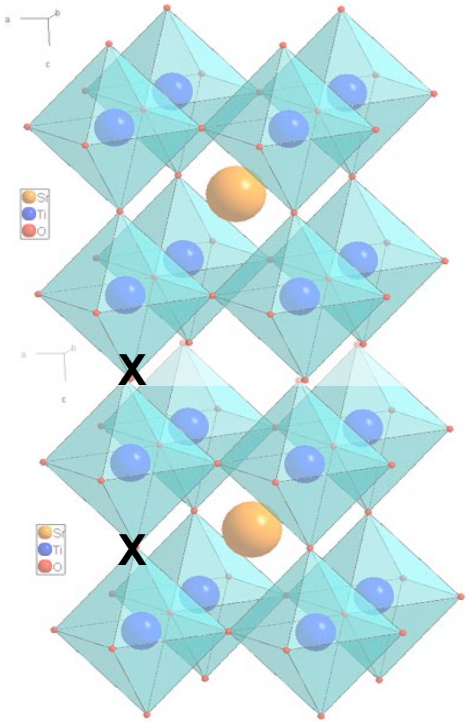

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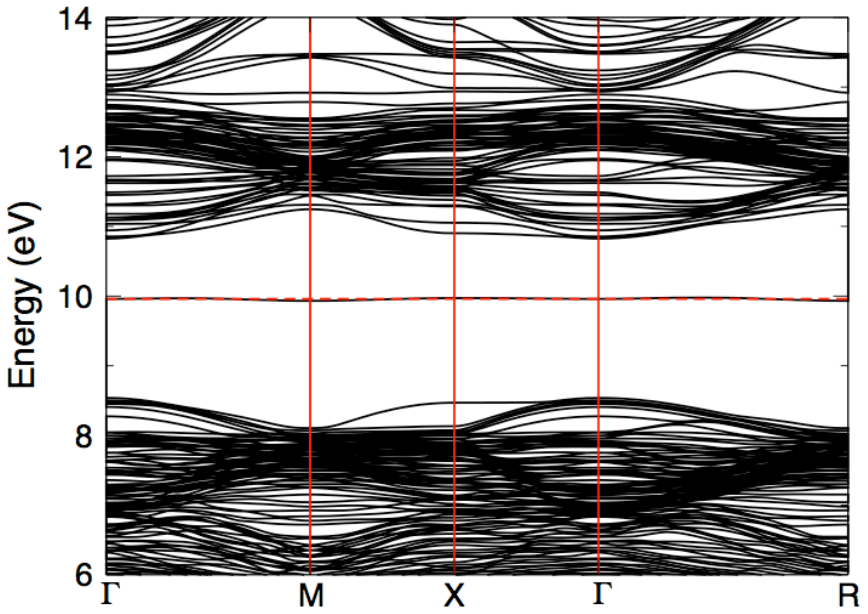


- Oxygen Divacancy creates single filled flat level in the gap and two additional electrons in the CB

-Two Sr vacancies remove electrons from CB and defect state

- La substitution puts a single electron back in the defect state

- But: is this defect interplay reasonable for a given set of growth conditions? Defect energetics …

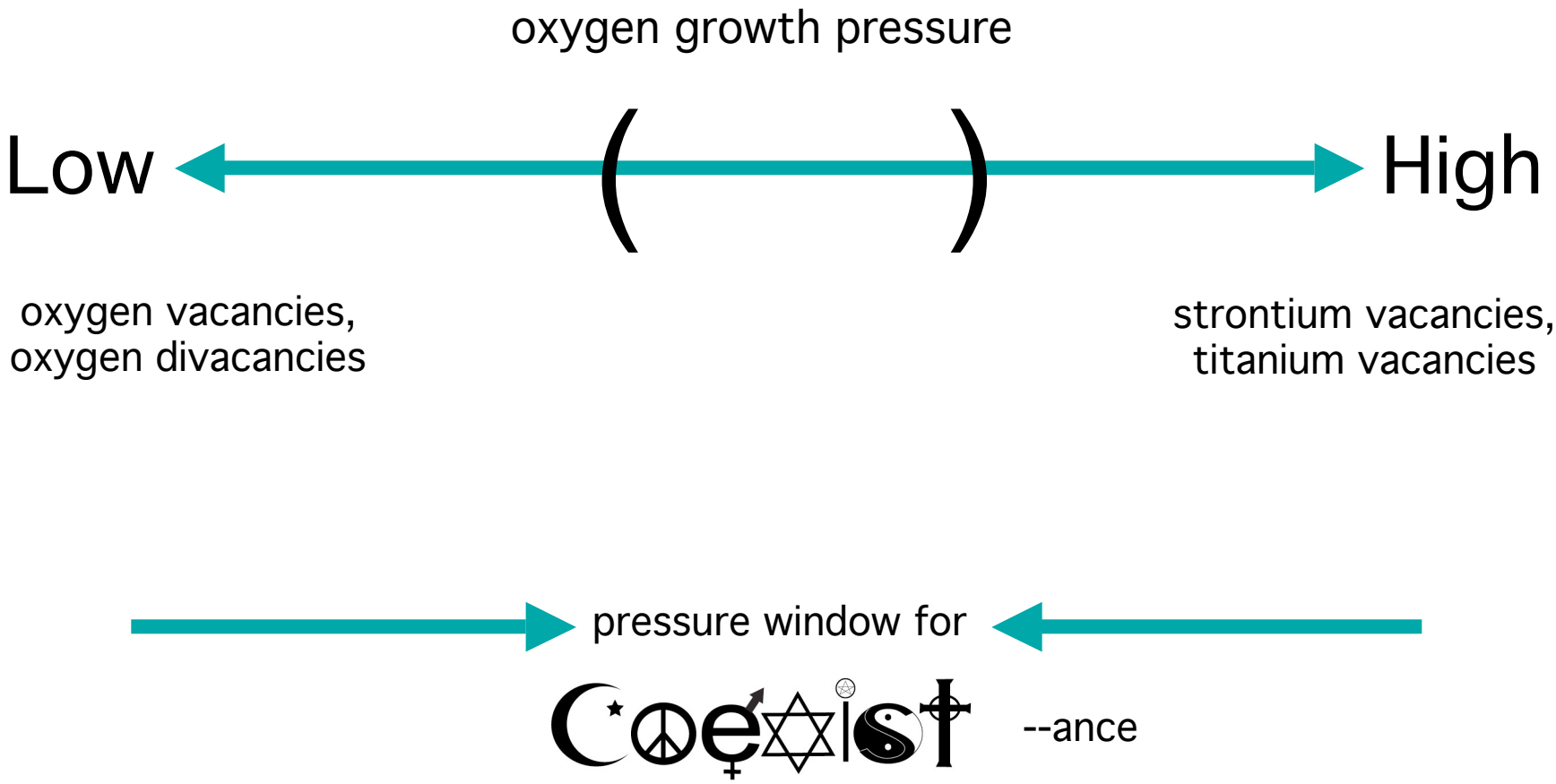
Defect Behavior

oxygen growth pressure

oxygen vacancies,
oxygen divacancies

strontium vacancies,
titanium vacancies

Defect Behavior



Thermodynamics of Defect Formation

Defect Concentration

$$\sim N_{sites} \exp[\ \frac{\#G_f}{kT}]$$

quantity of interest:

$$\Delta G_f = \Delta E_f - T\Delta S_f - P\Delta V_f$$

compute

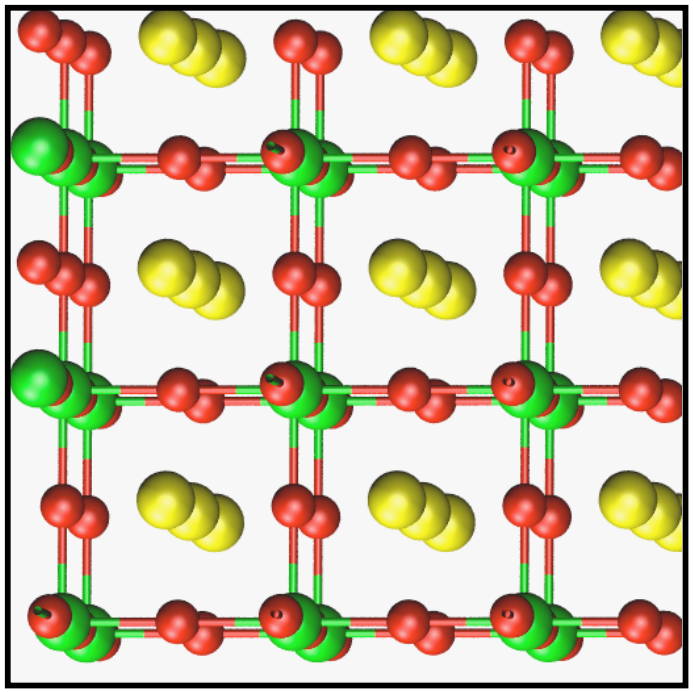
- for a defect forming reaction conserving total number of atomic nuclei and electrons
- using total energy electronic structure methods (DFT) and supercell approach

neglect for solid phases

neglect for solid phases

Thermodynamics of Defect Formation

$$\Delta E_f = \Delta E_{D,q}(E_F, \mu_\alpha)$$
$$= (E_{D,q} - E_{STO}) + n_{Sr}\mu_{Sr} + n_{Ti}\mu_{Ti} + n_{Sr}\mu_{Sr} + qE_F$$



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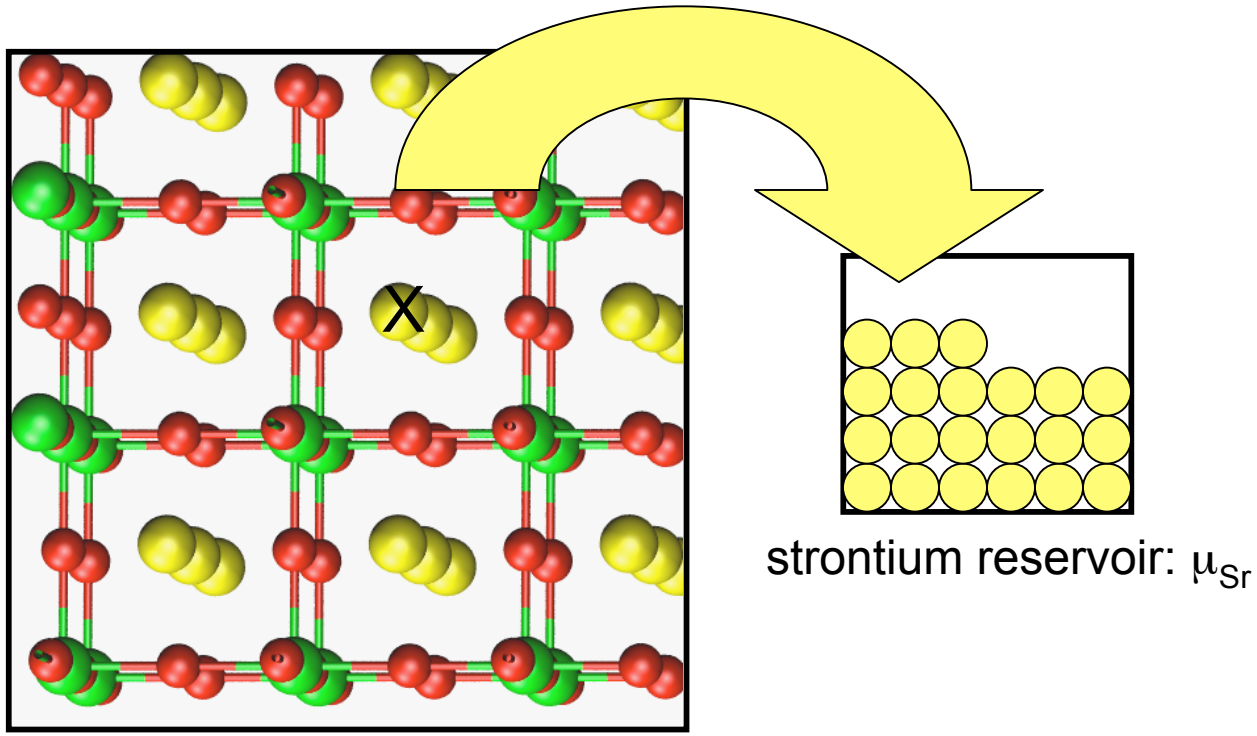

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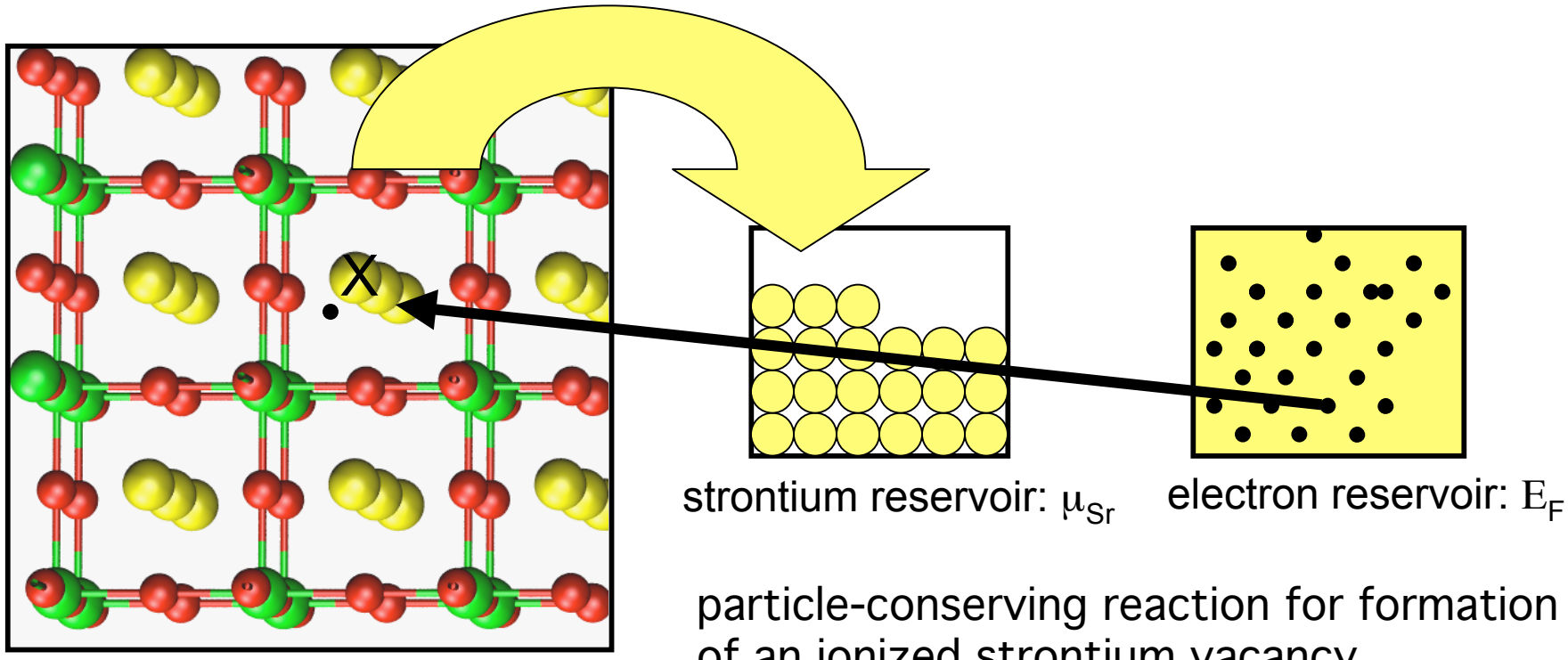

particle-conserving reaction for formation of an ionized strontium vacancy

Defects Considered

explicitly: strontium vacancies, titanium vacancies, oxygen vacancies, oxygen divacancies (in neutral and ionized state)

implicitly: lanthanum doping

$$\Delta E_f = \Delta E_{D,q}(E_F, \mu_\alpha) = (E_{D,q} - E_H) + \sum_\alpha n_\alpha \mu_\alpha + q E_F$$

Thermodynamics of Growth Conditions

$$\mu_{STO} = \mu_{Sr} + \mu_{Ti} + 3\mu_{O}$$

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$$\mu_{STO} = \mu_{Sr} + \mu_{Ti} + 3\mu_O$$

$$\Delta H(STO) = \Delta\mu_{Sr} + \Delta\mu_{Ti} + 3\Delta\mu_O$$

$$\mu_{Sr} = \Delta\mu_{Sr} + \mu_{Sr}^{\,b} \quad ; \quad \Delta\mu_{Sr} \le 0$$

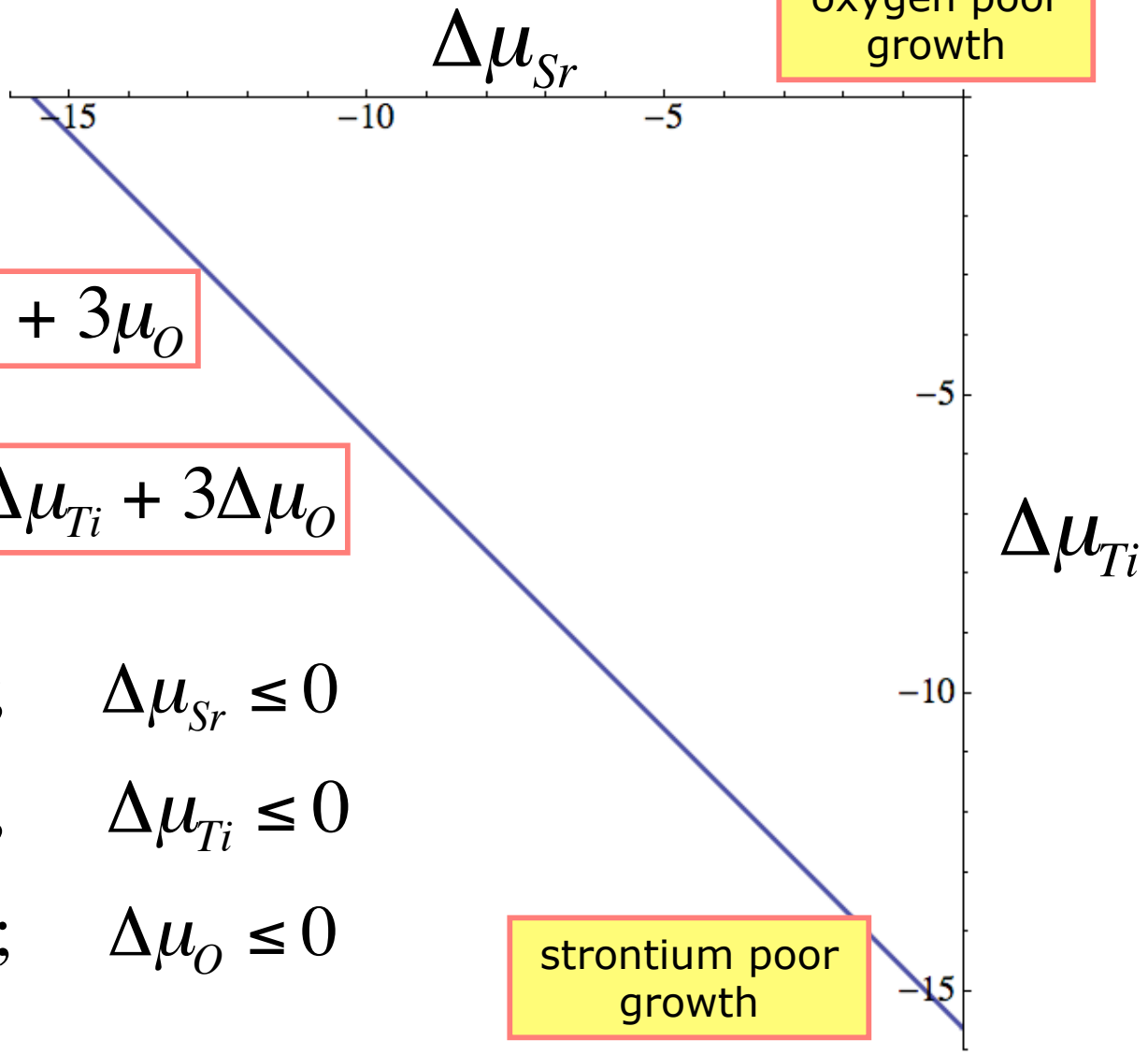
$$\mu_{Ti} = \Delta\mu_{Ti} + \mu_{Ti}^{\,b} \quad ; \quad \Delta\mu_{Ti} \le 0$$

$$\mu_O = \Delta\mu_O + \frac{1}{2}\mu_{O_2} \quad ; \quad \Delta\mu_O \le 0$$

Thermodynamics of Growth Conditions

titanium poor growth

oxygen poor growth



strontium poor growth

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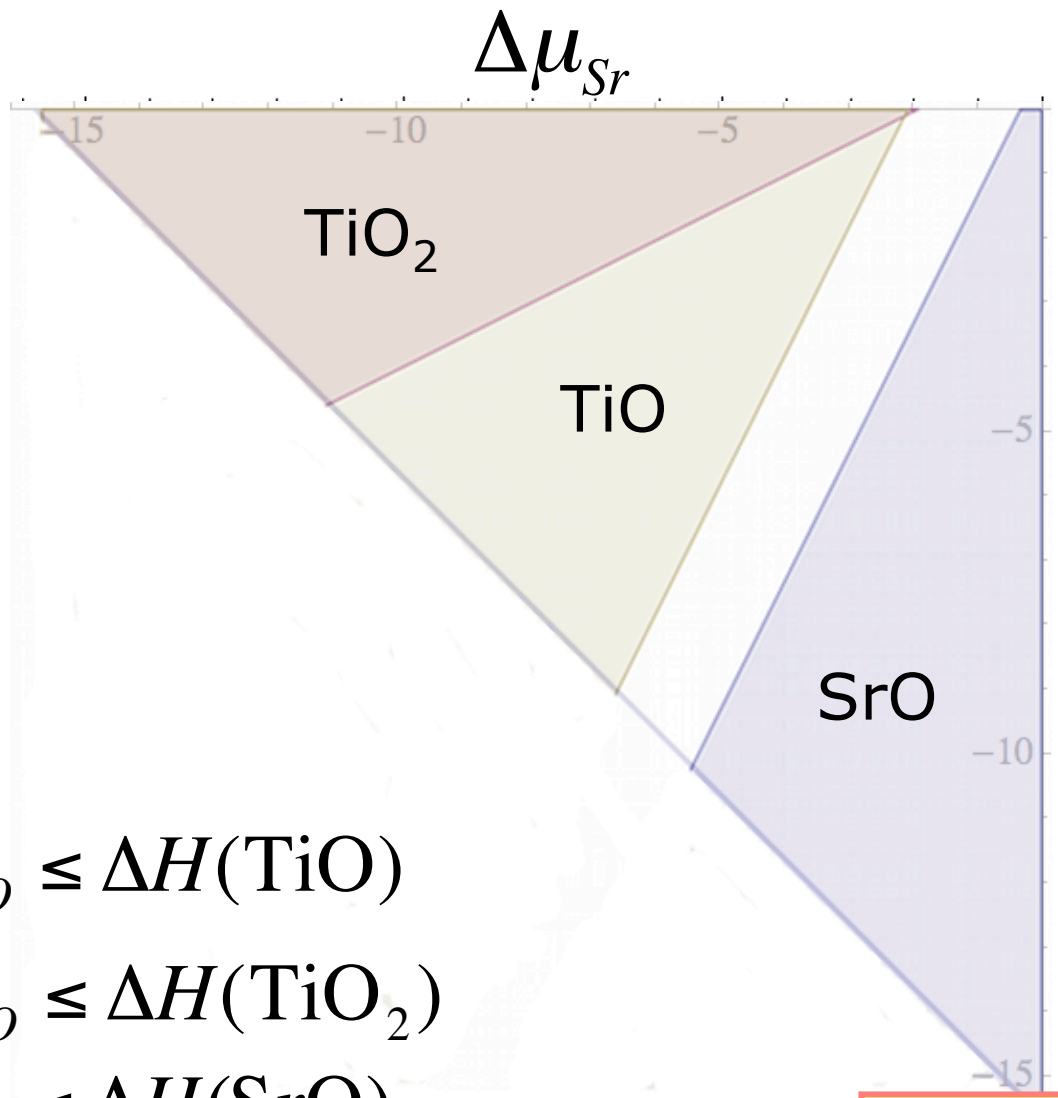


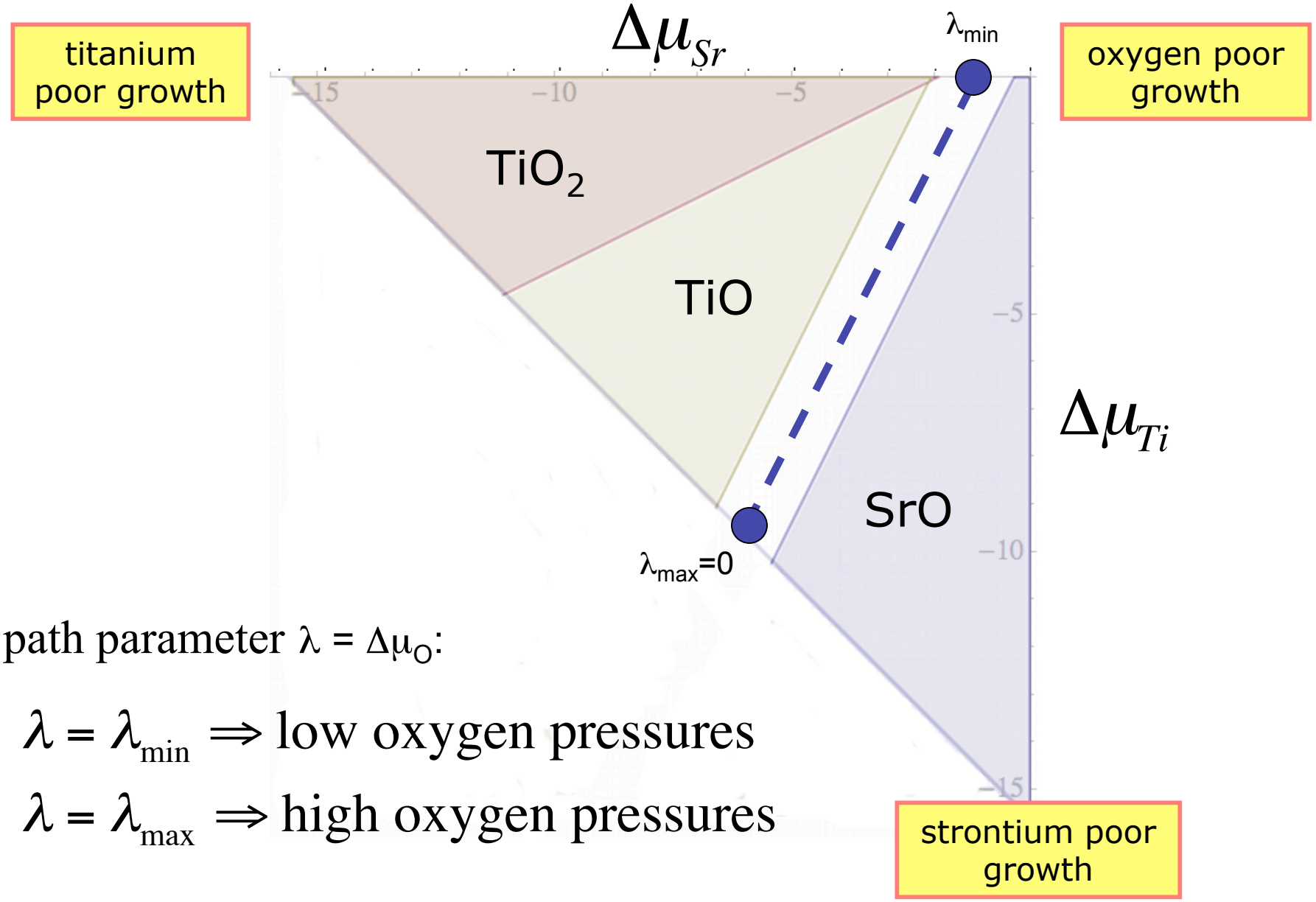
strontium poor growth

$$\Delta\mu_{Ti} + \Delta\mu_O \leq \Delta H(\mathrm{TiO})$$

$$\Delta\mu_{Ti} + 2\Delta\mu_O \leq \Delta H(\mathrm{TiO_2})$$

$$\Delta\mu_{Sr} + \Delta\mu_O \leq \Delta H(\mathrm{SrO})$$

Thermodynamics of Growth Conditions



path parameter $\lambda = \Delta\mu_O$:

$\lambda = \lambda_{min} \Rightarrow$ low oxygen pressures

$\lambda = \lambda_{max} \Rightarrow$ high oxygen pressures

Problems with DFT Supercell Calculations

Sources of Error in DFT-based supercell calculations of total energies

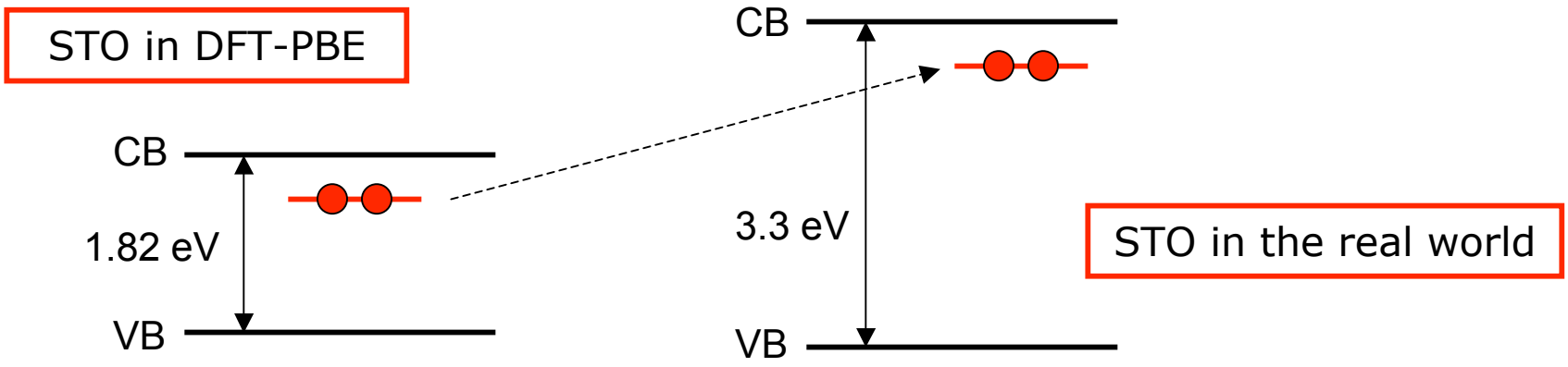
band gap situation

- lousy band gap
- relative location of kohn-sham defect levels

supercell finite size effects

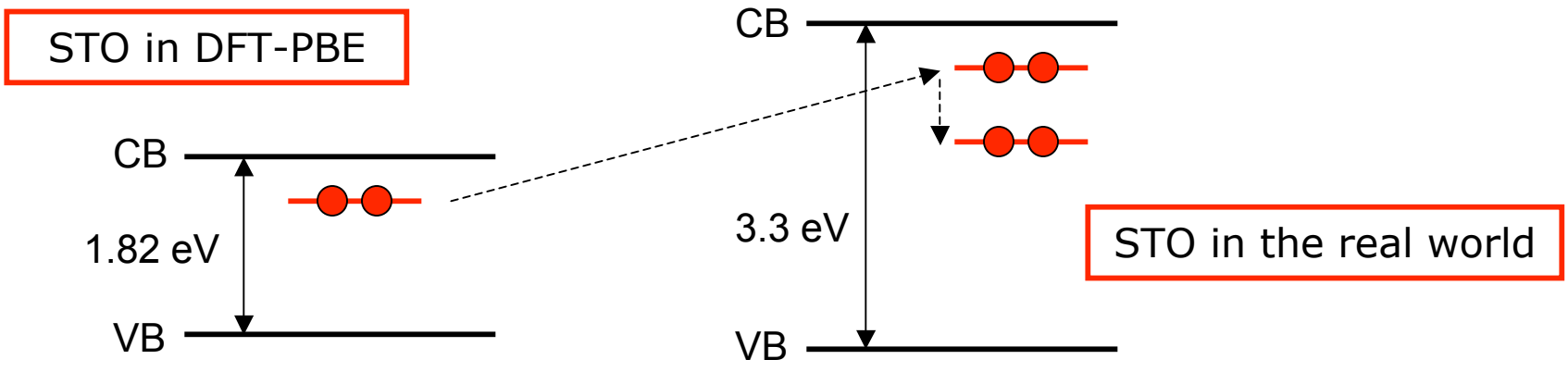
- image effects for charged defects
- elastic image effects
- valence band alignment issues for charged defects
- defect-defect interaction band dispersion effects

Band Gap and Defect Level Errors



- example: PBE gap in STO is 1.82 eV, experimental gap is 3.3 eV.
- example: oxygen divacancy is not bound in LDA calculations, E_B = -0.4 eV. However, LDA+U calculations give E_B = 1.0 eV.

Band Gap and Defect Level Errors

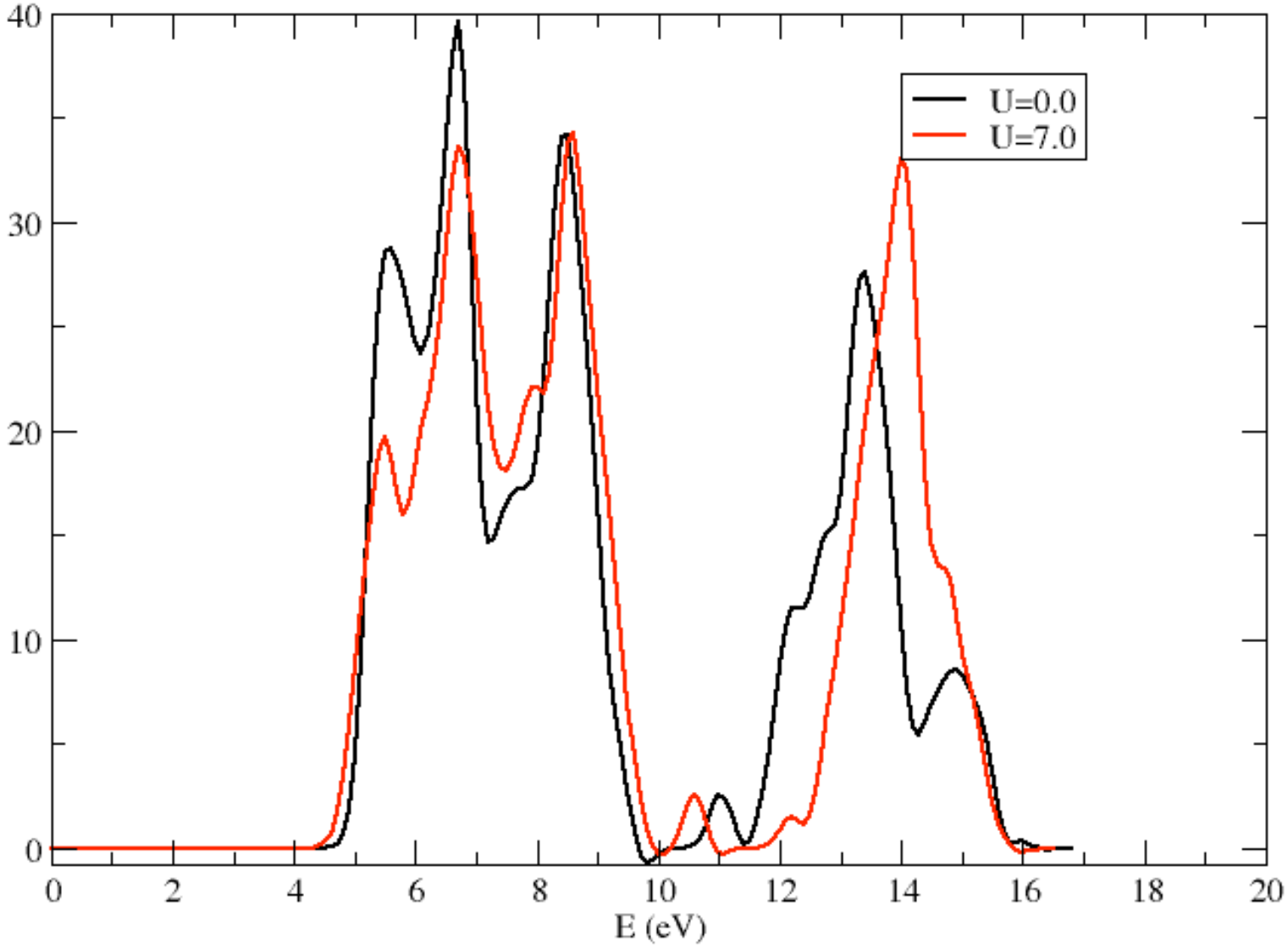


Confession #2: I wish I had a better way to nail down these defect levels.

- **corrections applied**:

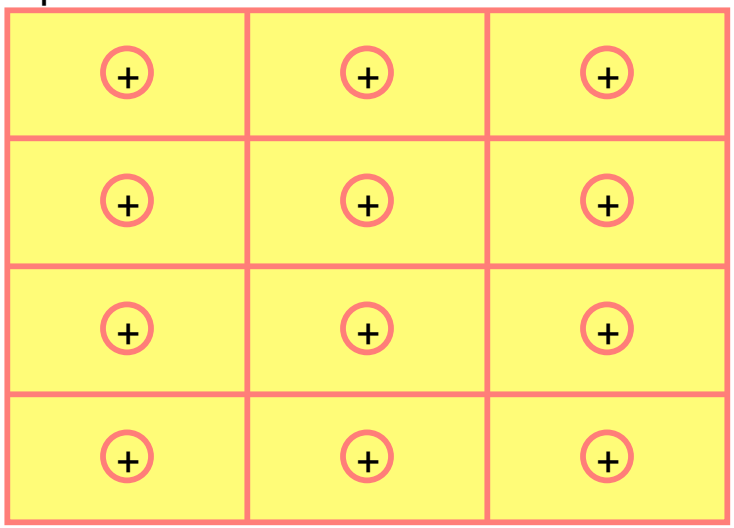
  - open the band gap to the experimental value by an upwards shift of the CB; apply this shift to the Kohn-Sham levels of the oxygen defect states.

  - shift the oxygen vacancy and divacancy levels down by 0.1 and 0.6 eV respectively

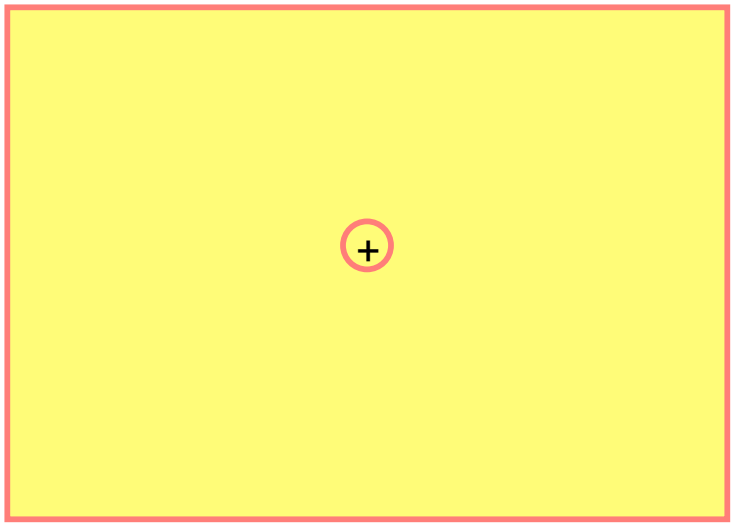

U=0.0
U=7.0
40
30
20
10
0
0
2
4
6
8
10
12
14
16
18
20
E (eV)

Charged Image Interactions (Finite Size Effects)

supercell calculation:



dilute limit:



Makov-Payne correction to total energy applied to localized oxygen divacancy state:

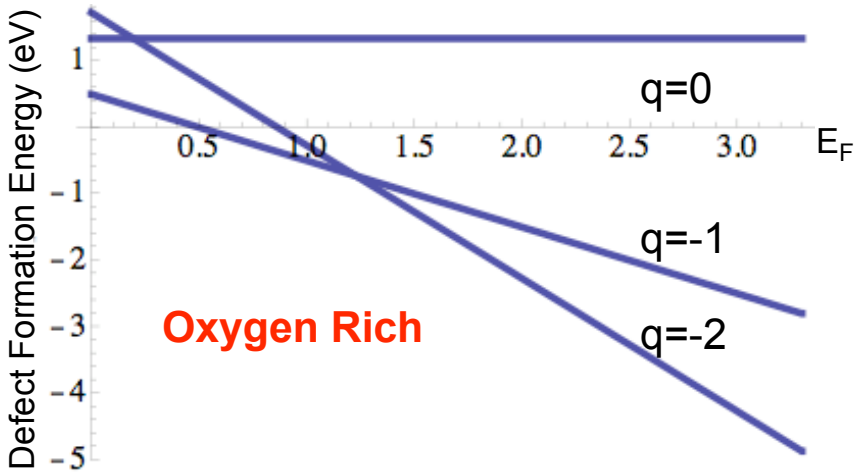
$$\Delta E(D,q) = + \frac{q^2 \alpha_M}{2\varepsilon_o V^{1/3}} + \frac{2\pi q Q}{3\varepsilon_o V} + O\left(V^{-5/3}\right)$$

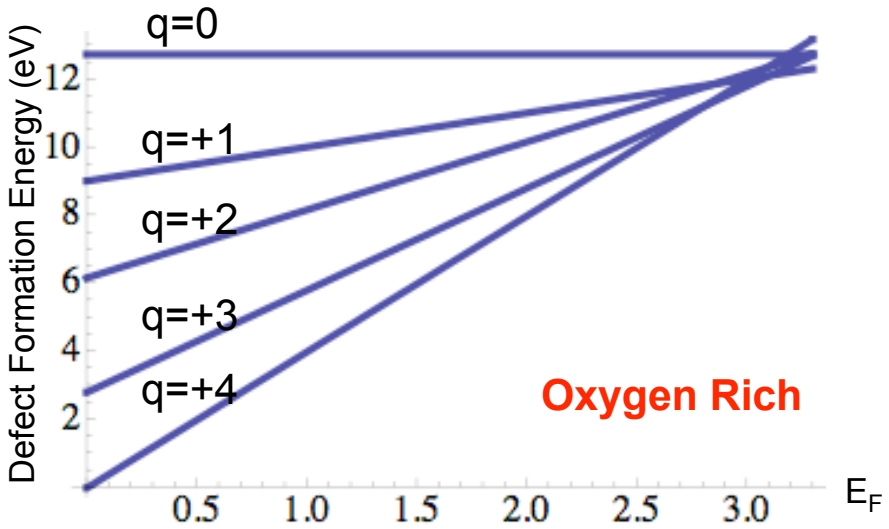
Some Results

Strontium Vacancies

$$\Delta E_f = \Delta E_{D,q}(E_F, \mu_\alpha) = (E_{D,q} - E_H) + \sum_\alpha n_\alpha \mu_\alpha + qE_F$$

Oxygen Vacancies



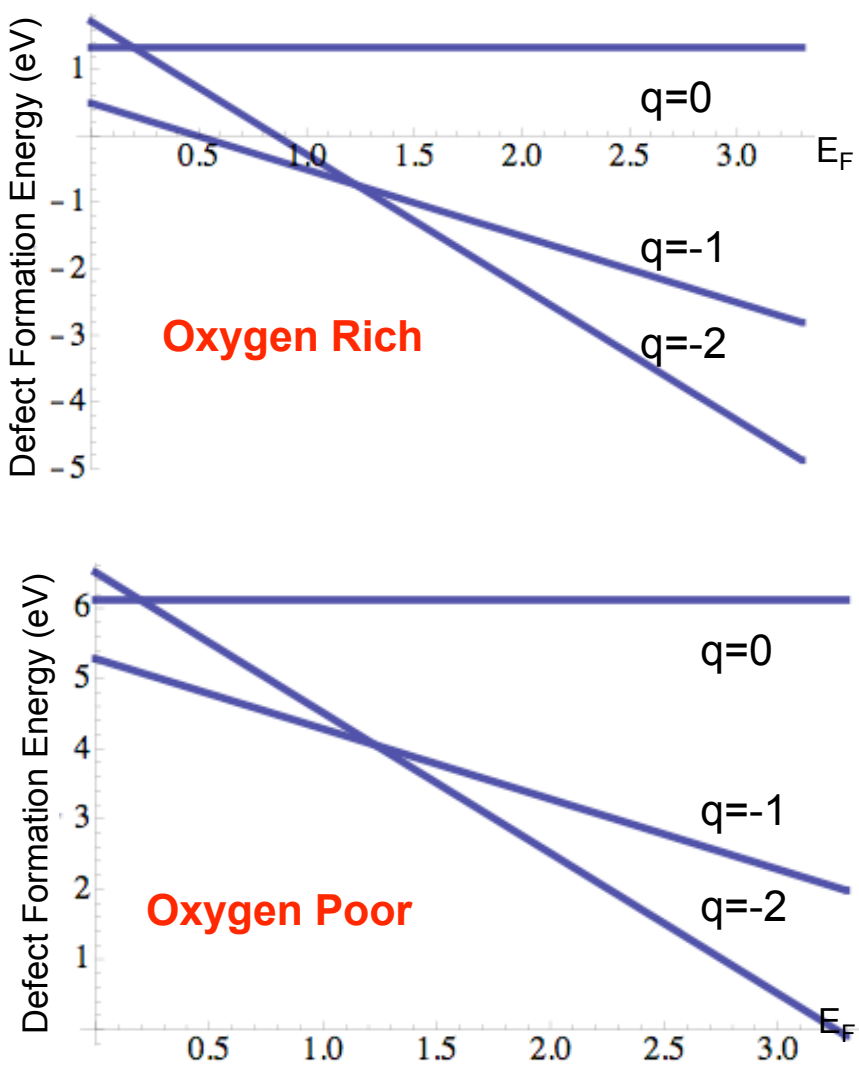


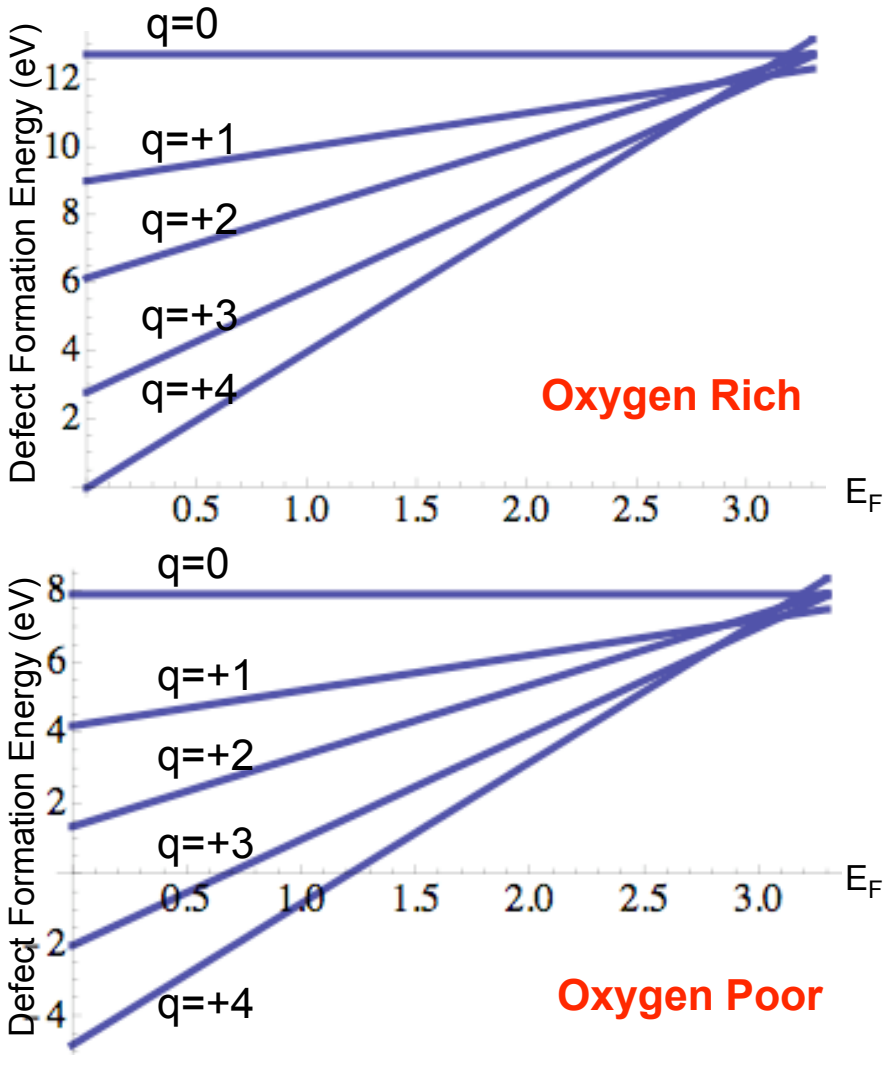
Some Results

Strontium Vacancies

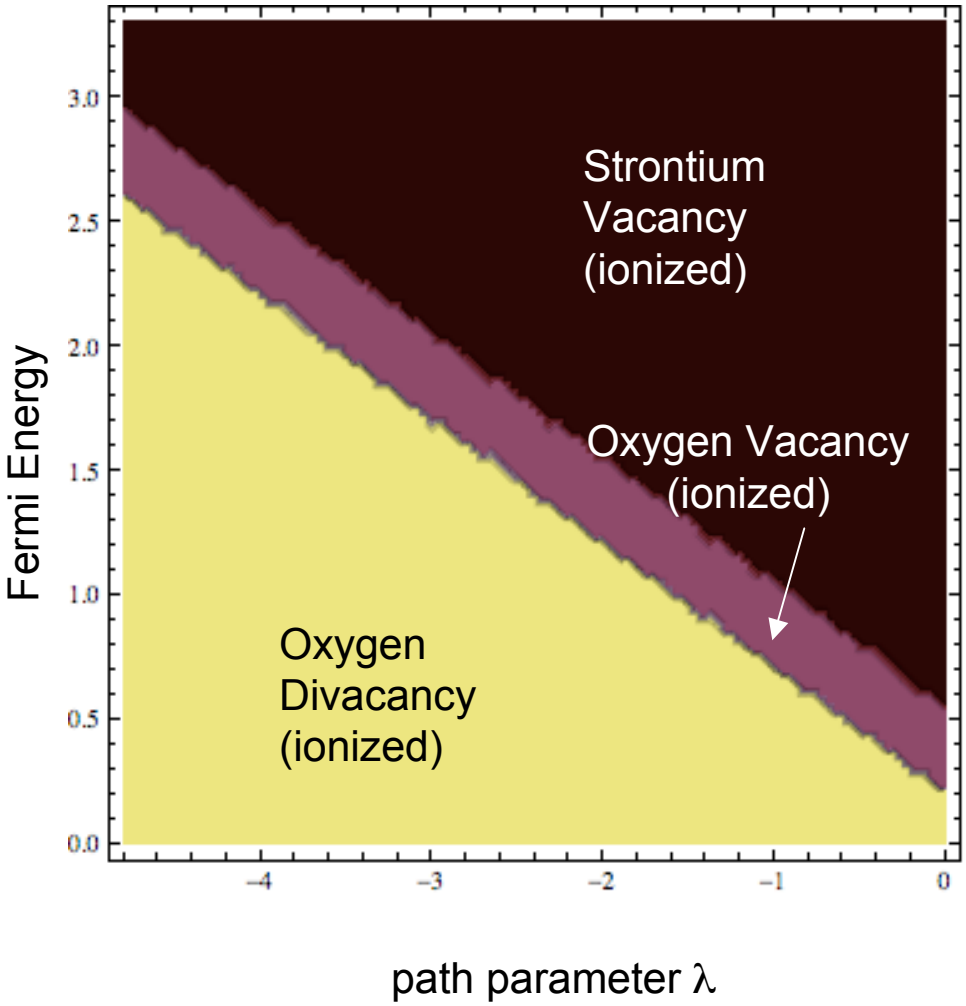
$$\Delta E_f = \Delta E_{D,q}(E_F, \mu_\alpha) = (E_{D,q} - E_H) + \sum_\alpha n_\alpha \mu_\alpha + qE_F$$

Oxygen Vacancies

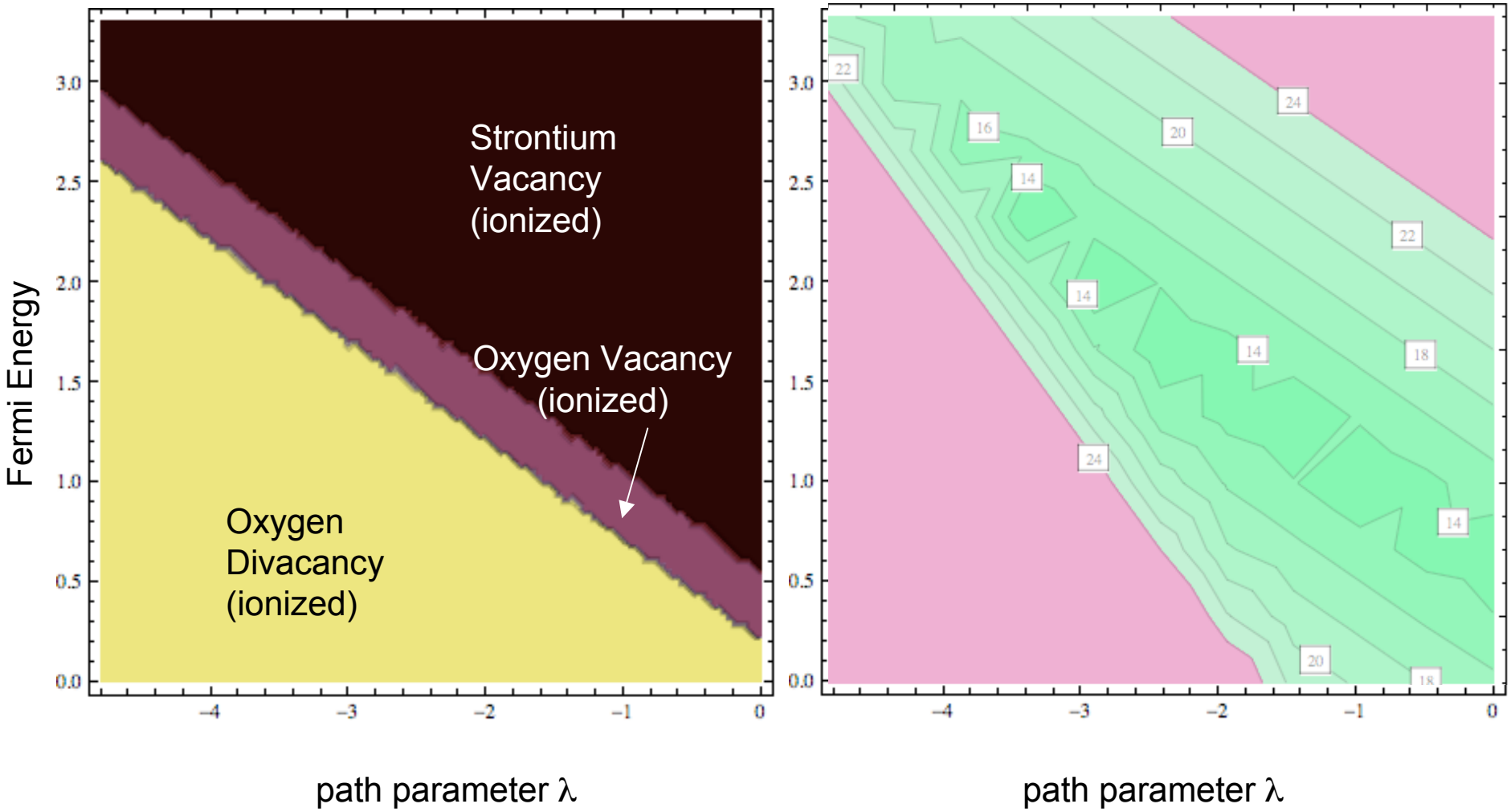




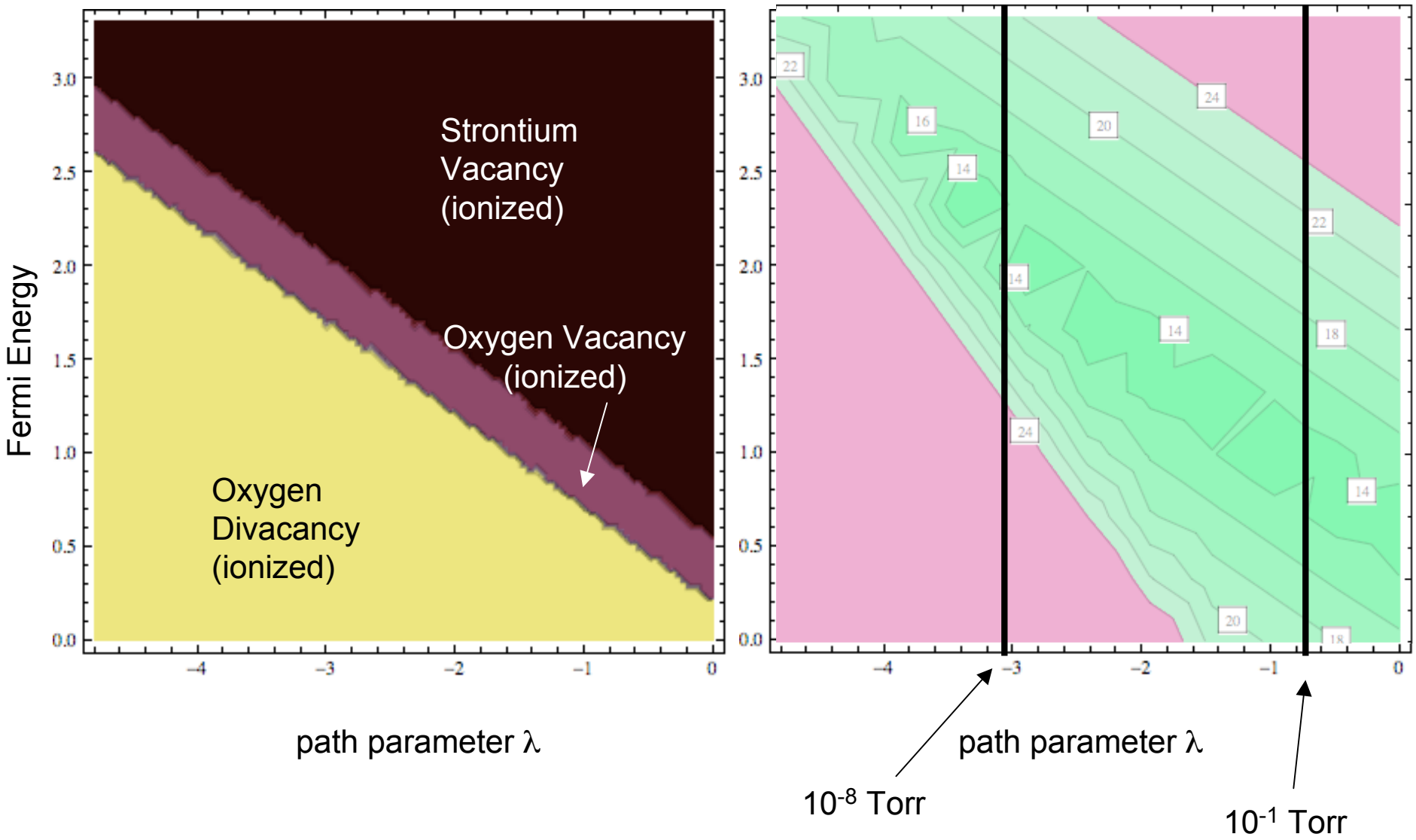
Dominant Defect

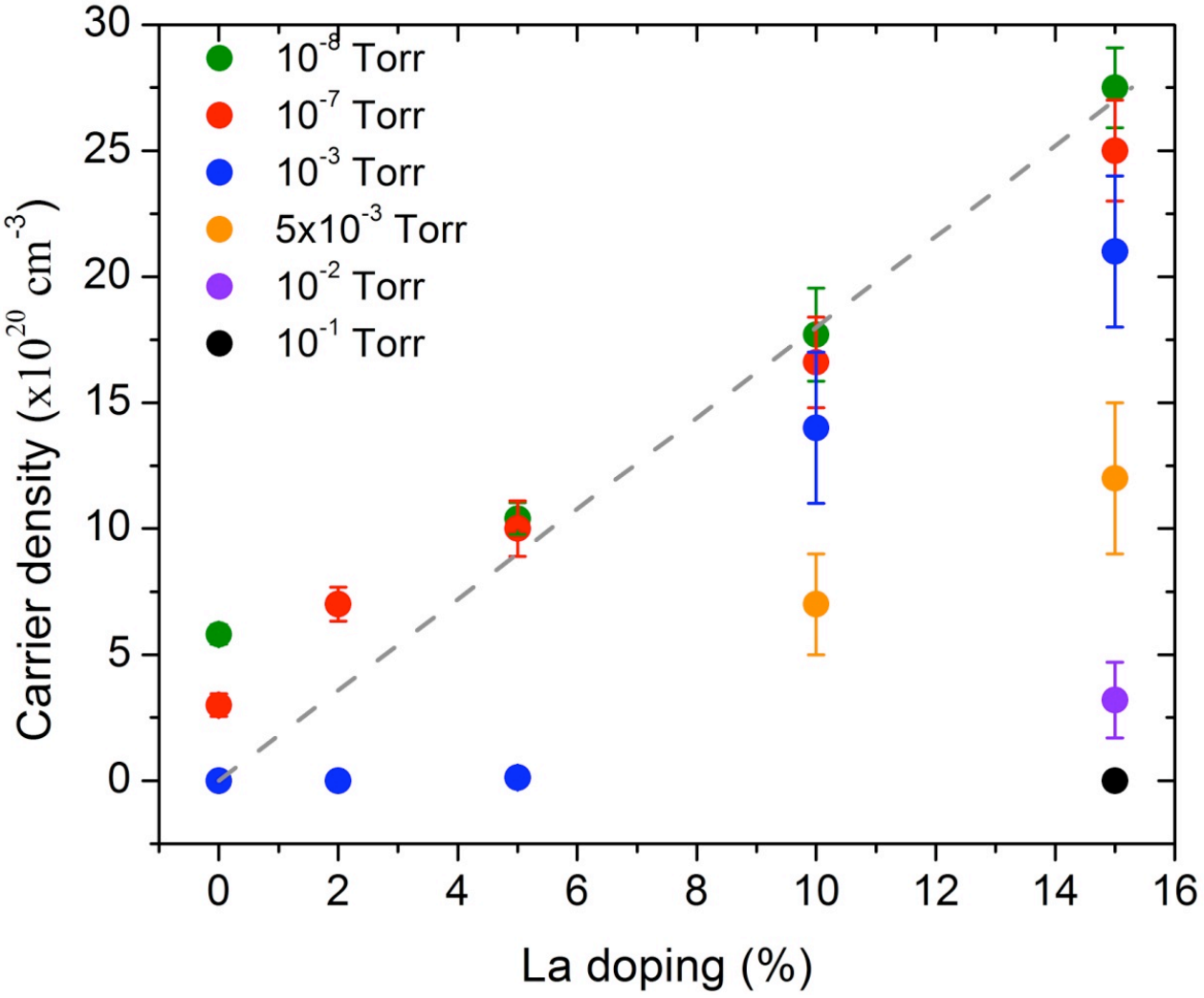


Dominant Defect



Dominant Defect





Courtesy: W. Siemons, J. Ravichandran, R. Ramesh

Conclusions

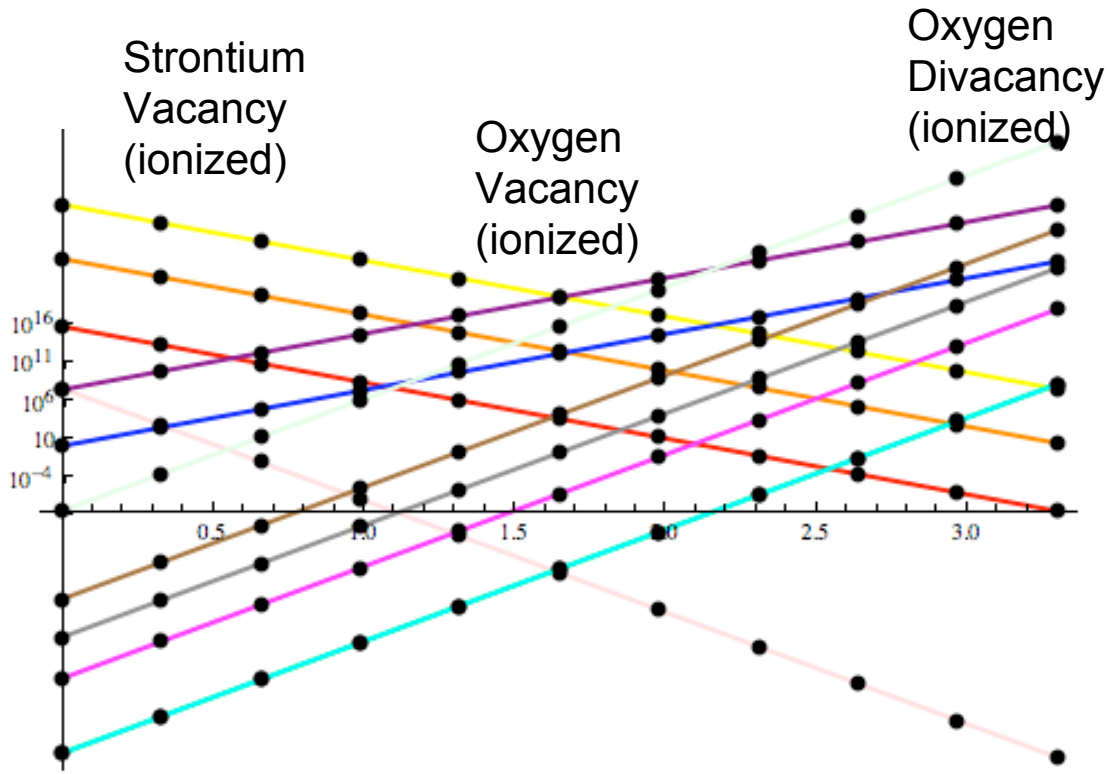
- Defect behavior can be rich and complex, even from only a few numbers
- Sometimes we can even get reasonable agreement with experiments
- But … there are many open avenues for improved modeling

Confession #3: Actually, sometimes I wish I were a physicist.

... but I figure we can all

thank you!

Relative Defect Concentrations



Collaborators and Funding

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Strontium Titanate in DFT

density functional theory: a quantum mechanical theory used to investigate the electronic structure (principally the ground state) of many body systems.

our software package: Quantum-ESPRESSO v. 4.1
(P. Giannozzi et al., http://www.quantum-espresso.org).

example: **Strontium Titanate**

- DFT-PBE, TM pseudopotentials
- check for convergence with respect to plane wave cutoff and k-space sampling

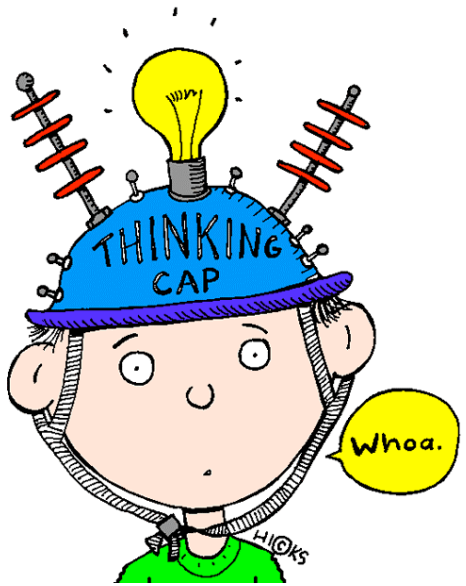
	Experiment	Theory
Lattice Constant	7.38 au	7.45 au
Band Gap	3.25 eV (indirect)	1.82 eV (indirect)

O Vacancies and La in STO

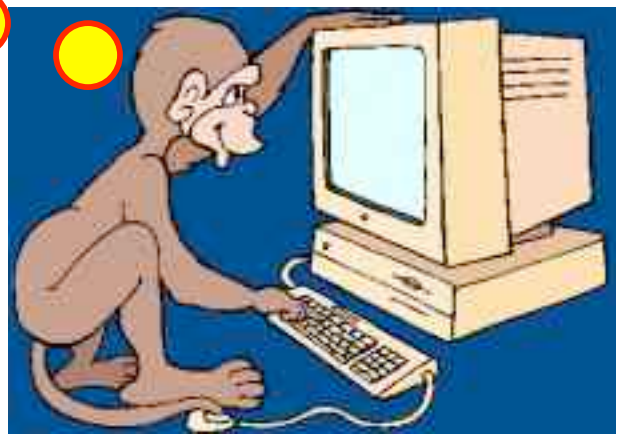
- considered many Oxygen vacancy and Lanthanum defect geometries (isolated, adjacent, etc)
- generally: Oxygen induced defect states become more localized when Lanthanum is introduced
- however, defect states are always filled

How might a half-filled defect band arise?

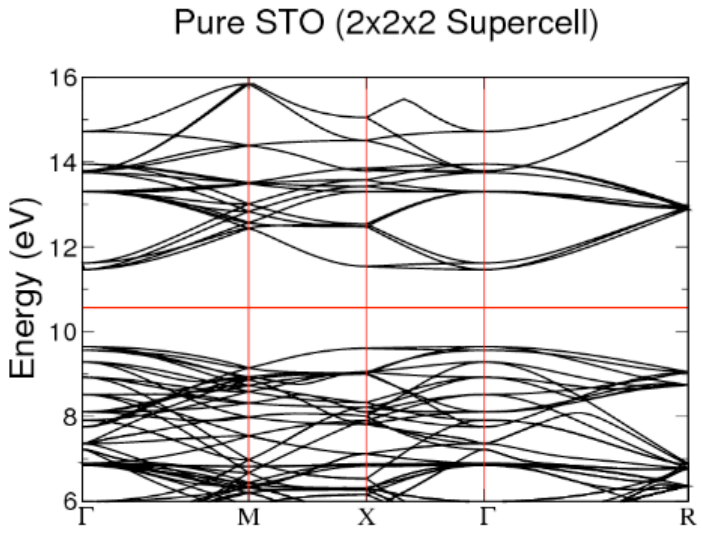
..Oxygen divacancies!



what next?



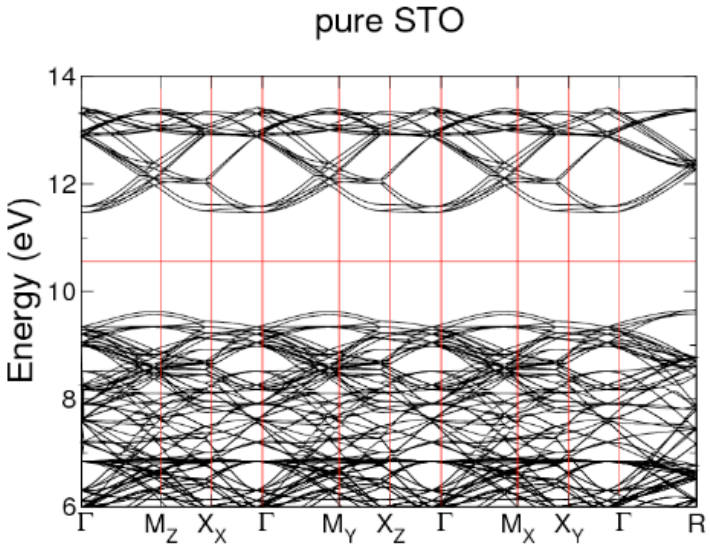
O Vacancies and La in STO

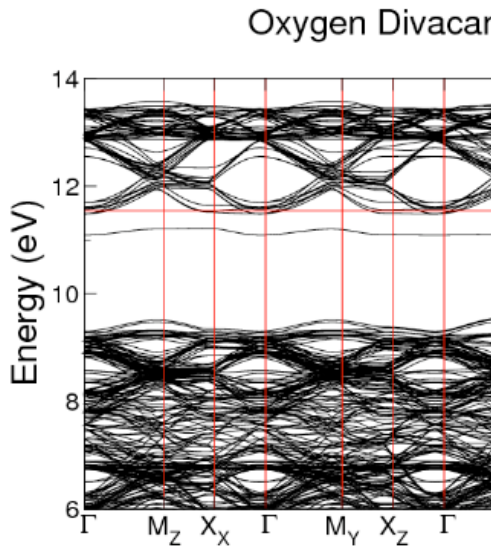


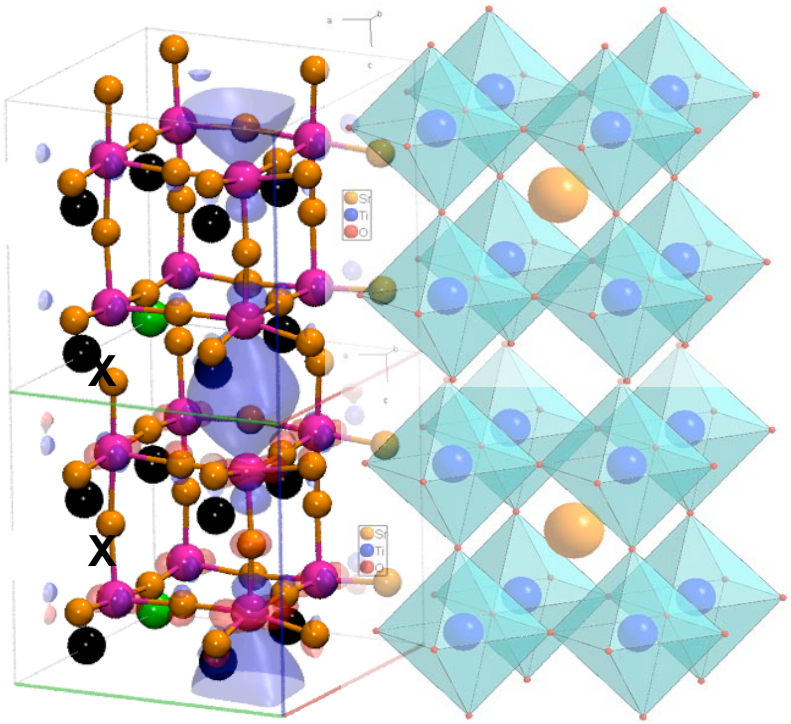
- [illegible]

Luo, Duan, Louie, and Cohen, Phys. Rev. B **70** (2004).

O DiVacancies and La in STO







Cuong, Lee, Choi, Ahn, Han, Lee, Phys. Rev. Lett. **98** (2007).

- [illegible] forbidden region

Sr or Ti Vacancies

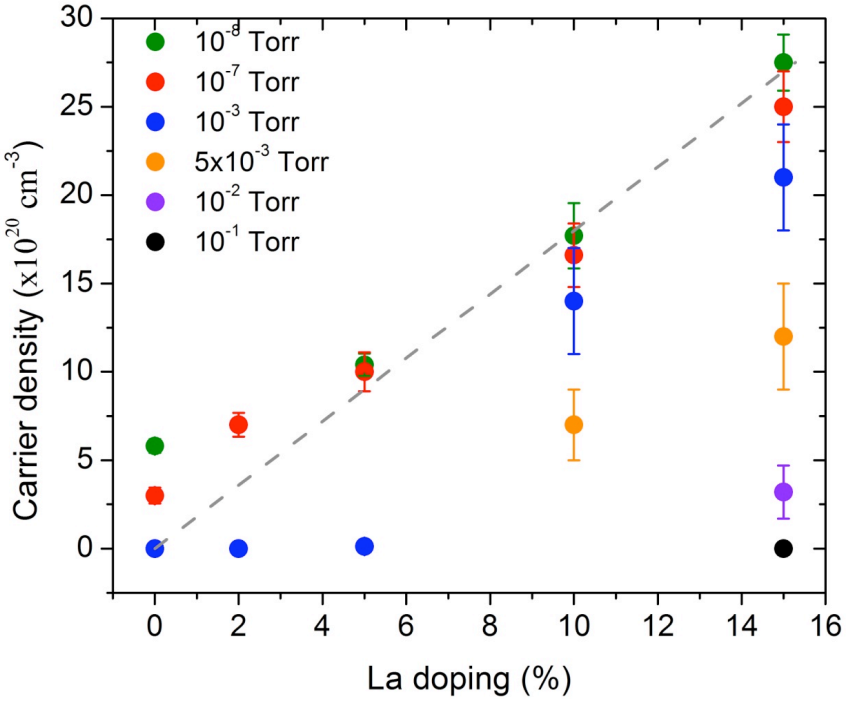
need a new theory to explain experiments …

previous:

- high O growth pressures ⇒ low [O_V]
- low O growth pressures ⇒ high [O_V]

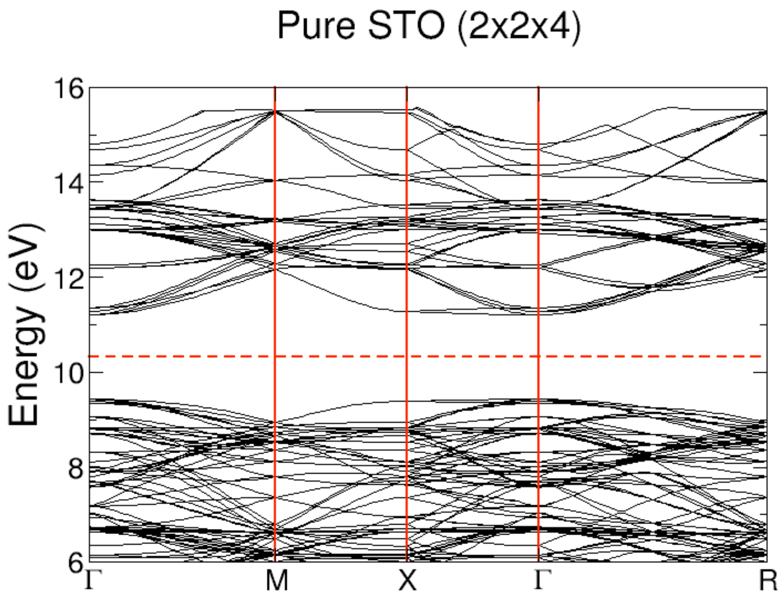
instead:

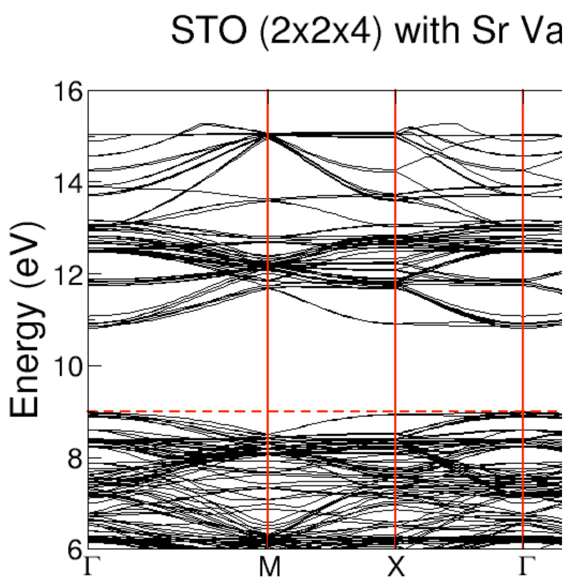
- high O growth pressures ⇒ excess of O
- low growth pressures ⇒ near stoichiometric growth



- Carrier density at low growth pressures should be governed by La content
- At high growth pressures, the excess Oxygen during growth manifests itself by the introduction of Sr or Ti vacancies in the STO
- These vacancies compensate the extra charge introduced by the Lanthanum, supressing the insulator-metal transition

Sr Vacancies and La in STO





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