Ab initio characterization of defect states in materials for next-generation technology

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Motivations & State-of-the-art

- Incoming **limitations** of **Si-technology** & drive for improving **application range** of materials
- **New** complex non-Si-based **materials** (chalcogenides, metal-oxides, ferroelectrics, etc.)
- **Highly defective**, disordered and **amorphous** [1] with complex physical effects (electrical switching, quantum confinement, topology, spin, etc.)
- **Material characteristics** ⟷ interplay ⟷ **Devices performances** (complex **architectures**, device reliability, etc.)
- **Characterization/identification/control** of **defect states**: crucial to characterize properties of emerging **materials**, hence for design/optimization of **next-generation** electronic **devices**

KPMG Global Semiconductor Survey 2017

Crucial also for understanding properties of already known **materials** at the **atomic level** [2] and reveal the connections between **atomic** and **electronic** structures

Engineering such materials through selective introduction of defects and/or dopants in order to **improve** their **application range**

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[1] M.-J. Lee, *et al.*, *Nat. Commun.* **4**, 2629 (2013); F. Tavanti *et al.*, *ACS Appl. Electron. Mater.* **2**, 2961 (2020)

[2] P. Mazzolini, *et al.*, *Adv. Electron. Mater.* **2**, 1500316 (2016); J. Osorio-Guillén *et al.*, *Phys. Rev. Lett.* **100**, 036601 (2008); J. Nowotny, *et al.*, *Chem. Soc. Rev.*, **44**, 8424 (2015); M. Gerosa, *et al.*, *Nat. Mater.* **17**, 1122 (2018)

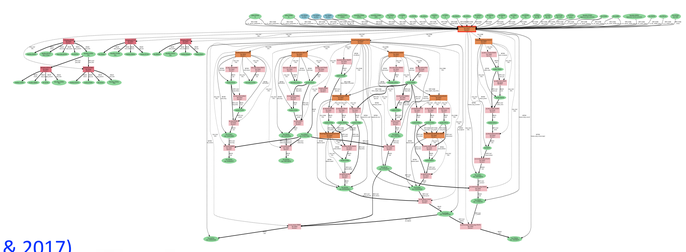
Methods

Defect formation energy: $E^f[X^q] = E_{tot}[X^q] - E_{tot}[bulk] - \sum_i n_i\mu_i + q[E_v + E_F] + q\Delta V_{corr}$

- E_{tot} , E_v ➔ DFT-based (supercell) calculations
- μ_i ➔ DFT calculations + thermodynamic considerations
- $E_{corr} = q\Delta V_{corr}$ contains several contributions:
  - Potential alignment;
  - Image charge interaction;
  - Spurious interactions;
  - …

Electrostatic **Gaussian counter-charge scheme**

Approach developed by Freysoldt, Van de Walle and others, and generalized by Komsa and Pasquarello

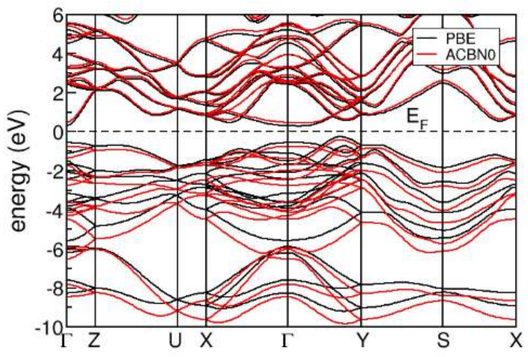


Towards full **automation** of defect calculations

P. Giannozzi *et al.*, *J. Phys.: Condens. Matter* **21**, 395502 (2009 & 2017)
C. Freysoldt, *et al.*, *Phys. Rev. Lett.* **102**, 016402 (2009)
C. Freysoldt, *et al.*, *Rev. Mod. Phys.* **86**, 253 (2014)
J. Buckeridge, *et al.*, *Comput. Phys. Commun.* **185**, 330 (2014)
J. Buckeridge, *Comput. Phys. Commun.* **244**, 329 (2019)
H.-P. Komsa, *et al.*, *Phys. Rev. Lett.* **110**, 095505 (2013)
I. Dabo, *et al.*, *Phys. Rev. B* **77**, 115139 (2008)
G. Pizzi, *et al.*, *Comp. Mat. Sci.* **111**, 218 (2016)
http://www.aiida.net

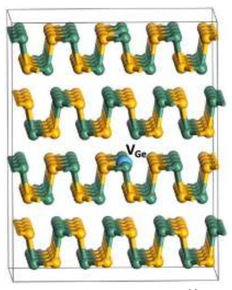
Point defects in crystalline GeSe

Bulk electronic structure of GeSe

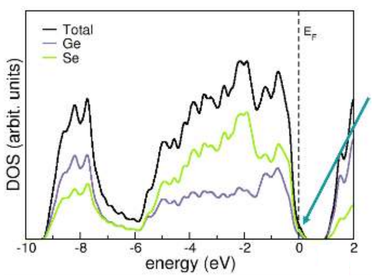


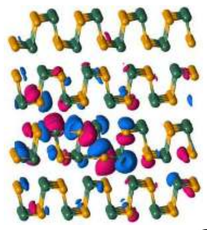
- ✓ Crystalline and amorphous chalcogenides promising for applications spanning from photoelectrocatalysis to memory devices and selectors for next generation electronics [1]
- ✓ **GeSe**: Energy gap, **Eg ≈ 1.1 eV**, Fermi level (E_F) indicated
- ✓ Orthorhombic cell
- ✓ **Supercells** used for defect simulations
  - 3x2x1 (48 atoms)
  - 4x4x2 (256 atoms)
  - 5x4x2 (320 atoms)

Ge vacancy

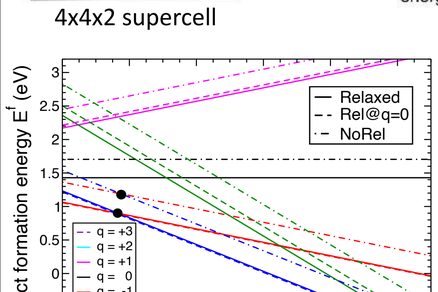


4x4x2 supercell



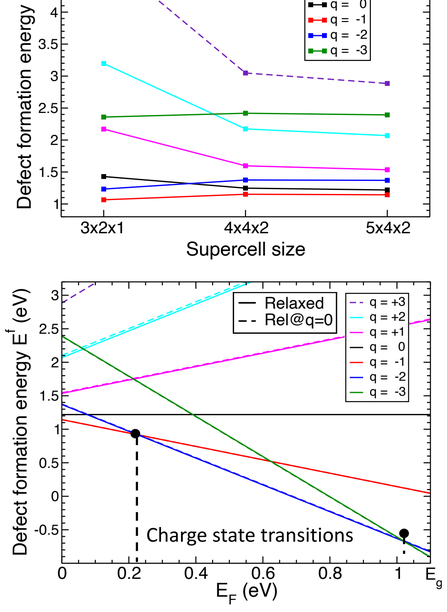


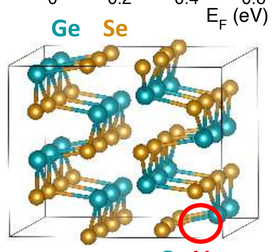
When a **Ge** vacancy is created, the density of states (**DOS**) shows a **partially occupied state** in the energy gap



Defect formation energies as a function of **supercell size**: **convergence** is reached

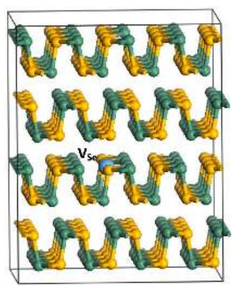
Effect of **structural relaxation** on defect stability: @charge state q vs @q=0 vs no relaxation at all (3x2x1 supercell)

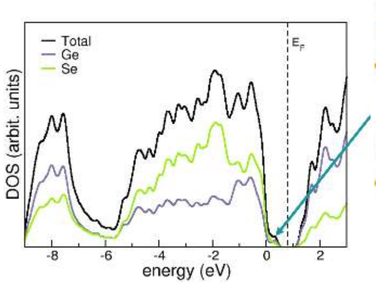


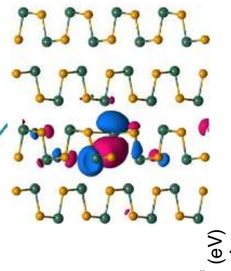


Characterization of **Ge vacancy** in crystalline GeSe: **stable charge states** across the gap & **charge state transitions** – well converged results (5x4x2 supercell)

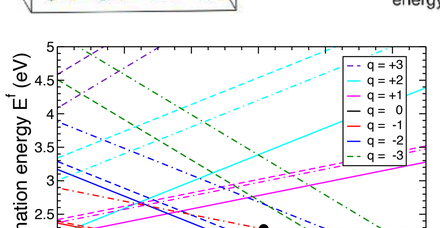
Se vacancy





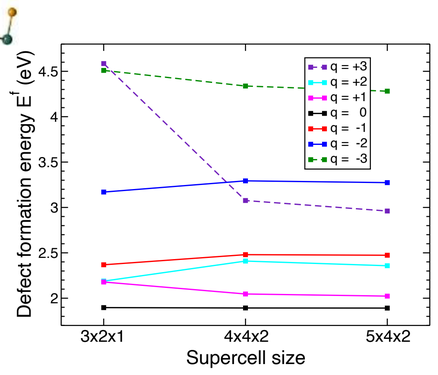


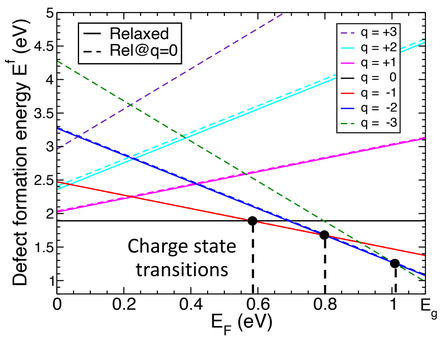
Defect state in the gap

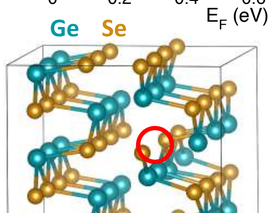


Defect formation energies as a function of **supercell size**: **convergence** is reached

Effect of **structural relaxation** on defect stability: @charge state q vs @q=0 vs no relaxation at all (3x2x1 supercell)







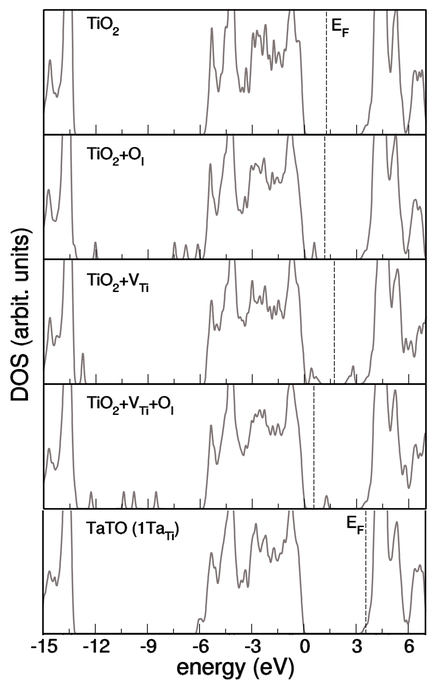
Characterization of **Se vacancy** in crystalline GeSe: **stable charge states** across the gap & **charge state transitions** – well converged results (5x4x2 supercell)

Defects dynamics was addressed through nudged elastic band (**NEB**) simulations, which predict slightly **higher diffusion barriers** for **Se** vacancies (1.1 – 2.1 eV), compared to **Ge** ones (0.8 – 1.7 eV) – depending on the inequivalent diffusion path and charge state selected.

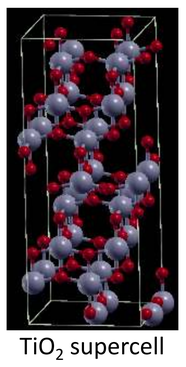
L. Bursi *et al.*, *to be submitted*

Point defects in anatase TiO_2

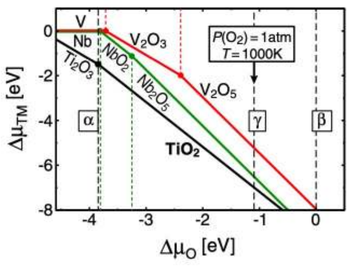
Electronic structure of anatase TiO_2: host and selected defective structures



- ✓ **TiO_2** – well-known material with a wide range of applications spanning form photocatalysis to memory devices and transparent conductivity (TC)
- ✓ Relatively less studied Ta-doped TiO_2 (**TaTO**) – promising mobility and dopant solubility for TC [2]. Here we focus on O-rich condition
- ✓ TiO_2: **Eg ≈ 3.3 eV**, E_F indicated
- ✓ Defects introduce deep **states in the gap**
- ✓ **Supercell** used for defect simulations: 2x2x2 (96 atoms)

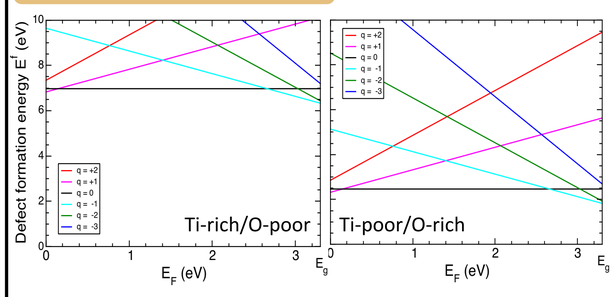


TiO_2 supercell

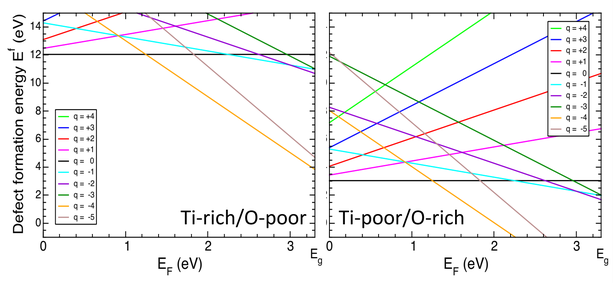


J. Osorio-Guillén *et al.*, *Phys. Rev. Lett.* **100**, 036601 (2008)

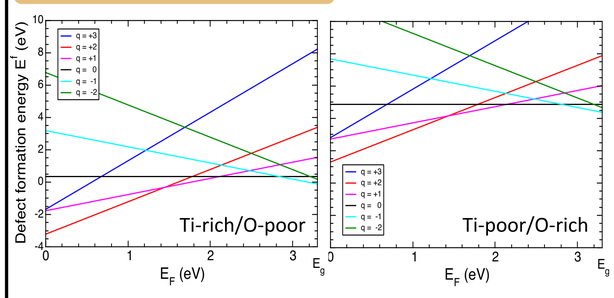
O interstitial, O_i



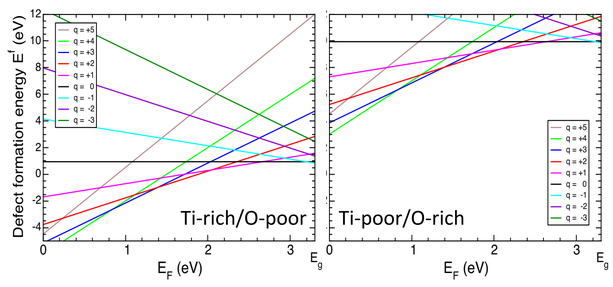
Ti vacancy, V_{Ti}



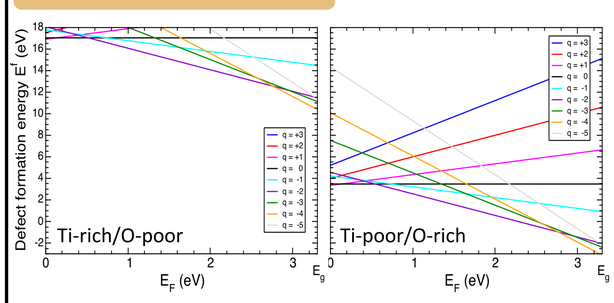
O vacancy, V_O



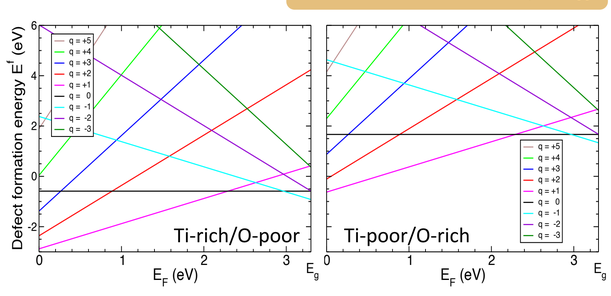
Ti interstitial, Ti_i



Double defect: O_i + V_{Ti}



Ta substitutional, Ta_{Ti}



- ✓ **O_i** and **V_{Ti}** have high formation energies in **O-poor** condition, while **V_O** and **Ti_i** in **O-rich** condition, as expected
- ✓ **Ta_{Ti}** is relatively **easy to form** and has **charge state transitions** within a few meV from the conduction band
- ✓ Similarly, the formation energy of **O_i+V_{Ti}** defect is relatively low in **O-rich** condition
- ✓ Intrinsic acceptors do not form easily under O-poor condition, the situation is more complex in O-rich condition

A. Calzolari, L. Bursi *et al.*, *in preparation*

Conclusion and acknowledgement

Final remarks

- ✓ Search for alternative **materials** and **architectures** for next-generation electronics to overcome incoming **limitations** of **Si**-based technology and **engineering** known materials to improve their **applications**
- ✓ **Automatic** simulations of **point defects thermodynamics** in solids (**GeSe** & **TiO_2**) through the **AiiDA** **workflow**: **Defect formation energies**, stability & **charge state transitions** characterized
- ✓ Defect **dynamics** simulations predict slightly **larger mobility** for **Ge** vacancies compared to **Se** ones

Collaborators: Dr. Conrad Johnston & Dr. Sokseiha Muy from Dr. Marzari's group at EPFL

Funding:

Interoperable Material-to-Device simulation box for disruptive electronics