First-principles study of point defects and doping limits in CaO

Zhenkun Yuan and Geoffroy Hautier

Dartmouth Engineering

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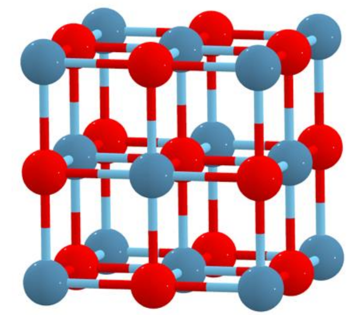
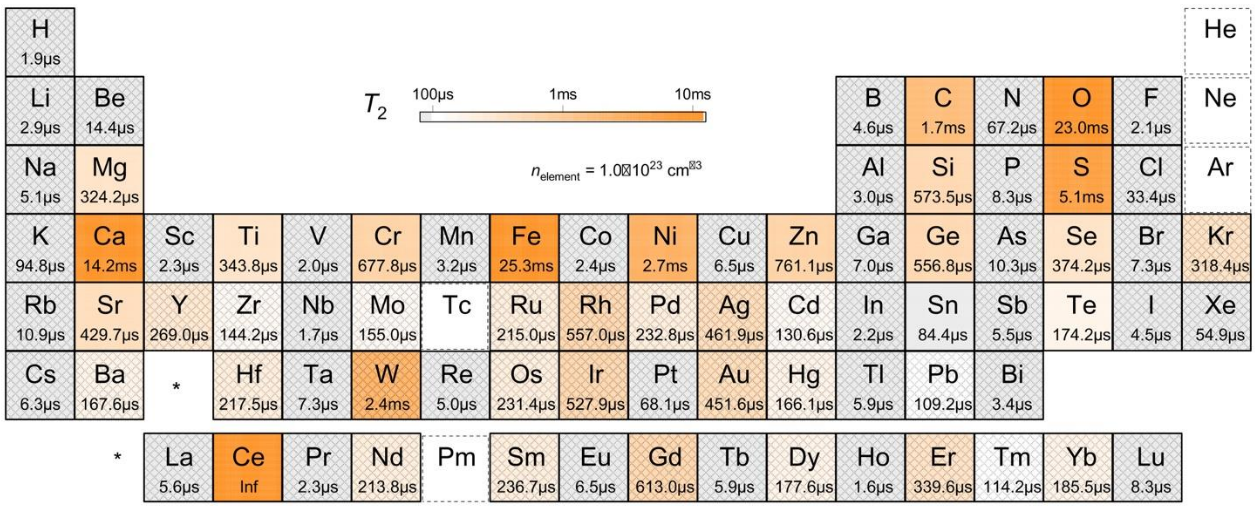
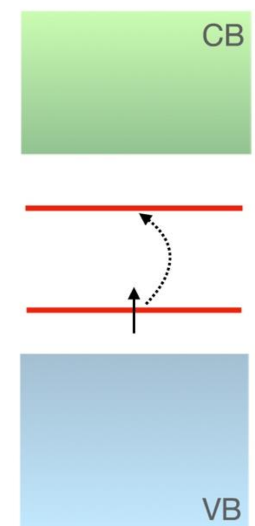
CaO as a new quantum-defect host



- Ultra-wide band gap (7.09 eV)
- Low density of spinful nuclei ⟹ long electron spin coherence times (T_2)
  - beats most known materials



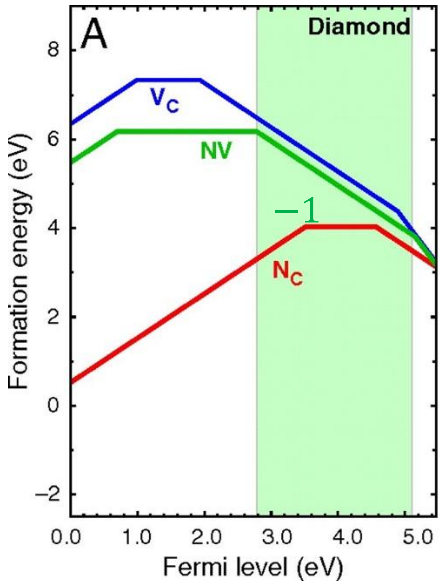


- Computational evidence of NV-like centers
  - $X_{Ca}V_O$ (X = Sb, Bi, and I)

Y. Xiong *et al.*, *Mater. Quantum. Technol.* **4**, 013001 (2024)
S. Kanai *et al.*, PNAS **119**, e2121808119 (2022)
J. Davidsson *et al.*, arXiv preprint, 2023

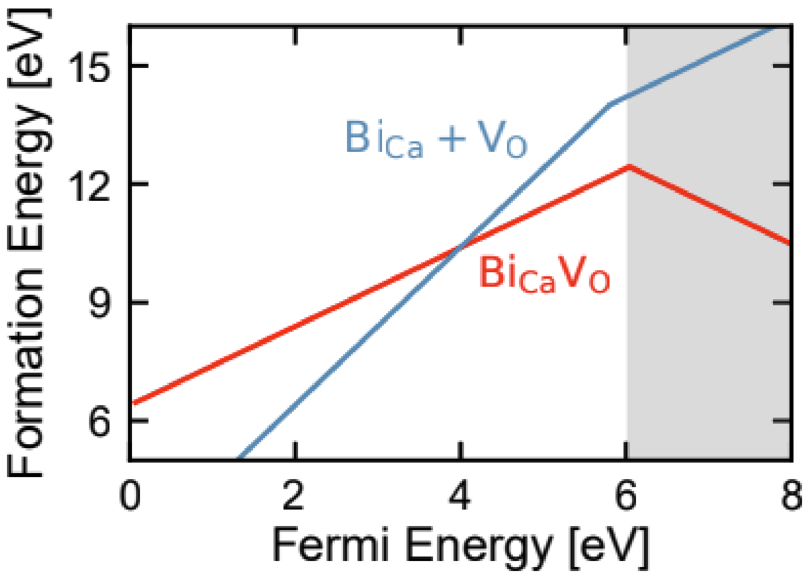
What is range of Fermi levels in CaO?

NV center in Diamond



J. Weber *et al.*, PNAS **107**, 8513 (2010)

NV-like center in CaO



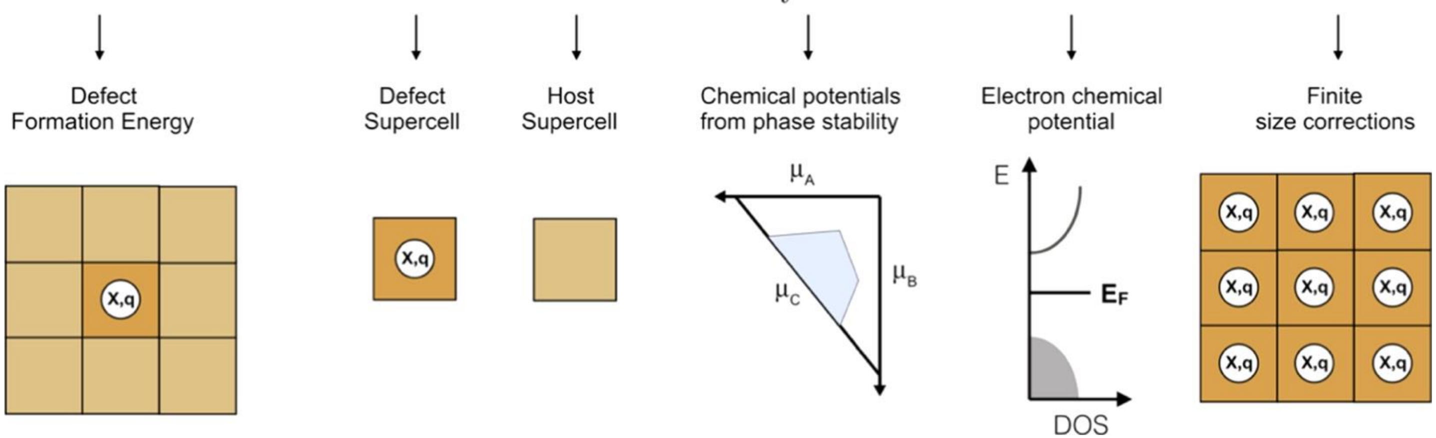
J. Davidsson *et al.*, arXiv preprint, 2023

Doping bottlenecks prevail in wide-band-gap materials, often caused by intrinsic defect compensation

Zhang, Wei, and Zunger, Phys. B Condens. Matter **273**, 976 (1999)

First-principles calculations of point defects

$$\Delta H_{\mathrm{X,q}}(E_F,\mu) = [E_{\mathrm{X,q}} - E_{\mathrm{H}}] - \sum_i n_i\mu_i + qE_F + E_{\mathrm{corr}}(q)$$

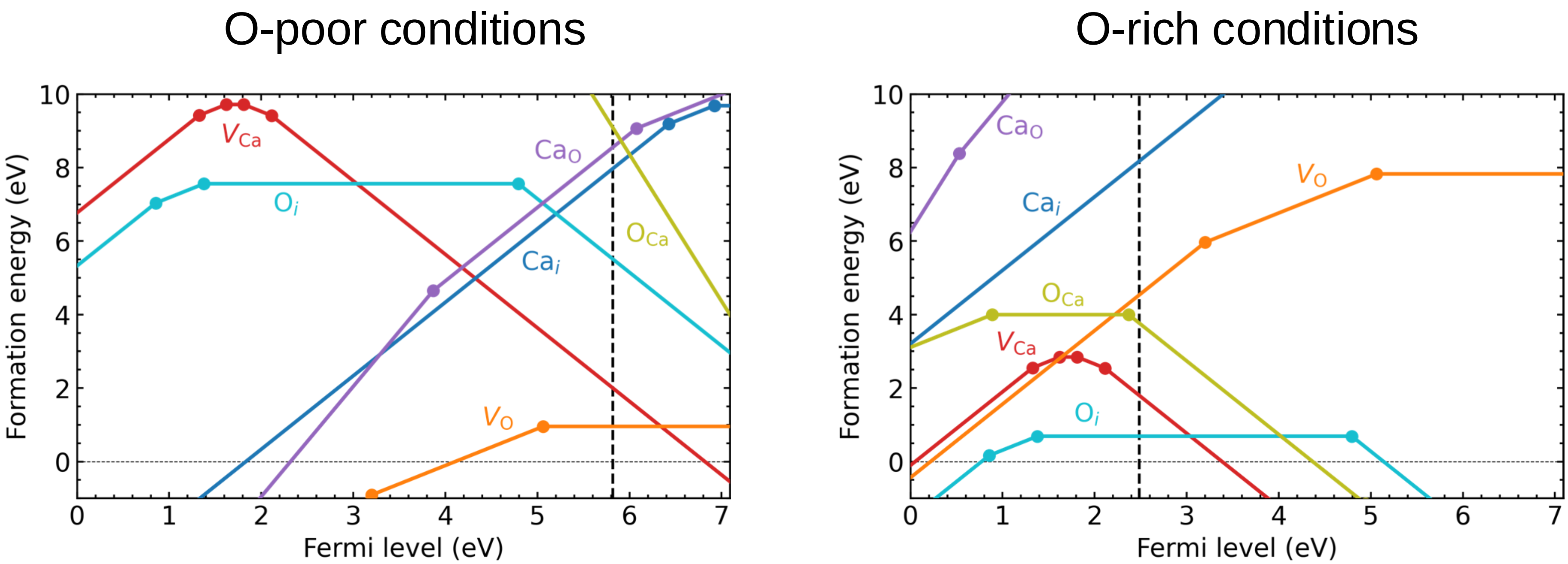


Plot by Seán Kavanagh

- HSE screened hybrid functional with $\alpha = 0.498$
  - reproduce experimental band gap (7.09 eV)
  - lattice constant $a = 4.78$ Å (Expt. 4.78 – 4.808 Å)

- 512-atom supercell, Γ-only **k**-point sampling

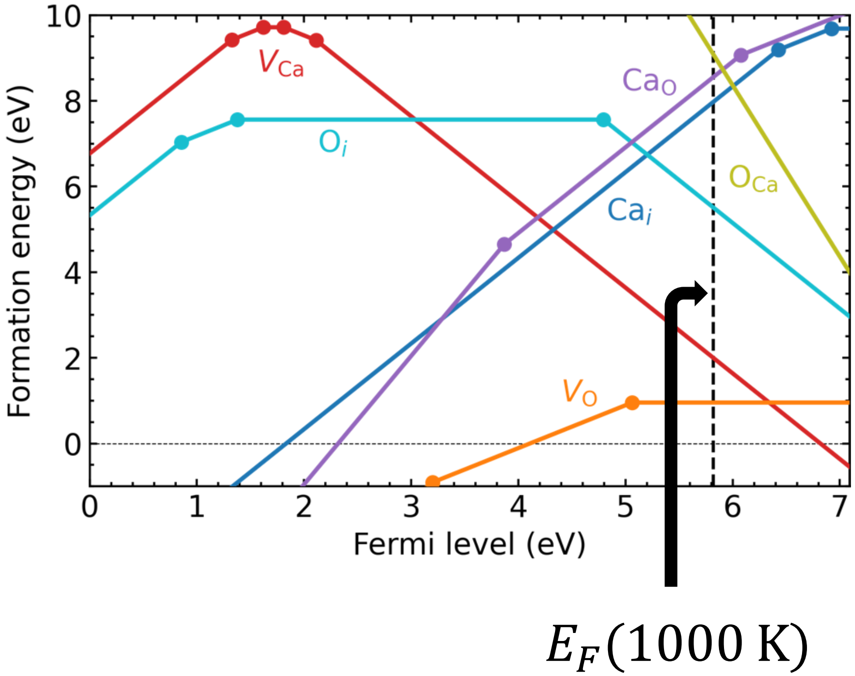
Intrinsic defects and doping in CaO



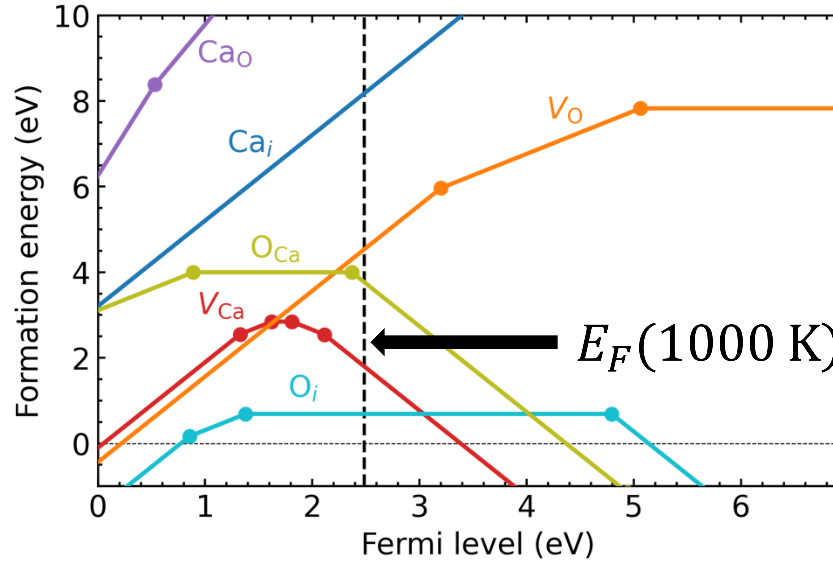
- Formation energies change significantly when Fermi level moves over the band gap
- Dominant defects: V_{Ca}, V_{O}, and O_i

Intrinsic defects and doping in CaO

O-poor conditions



O-rich conditions

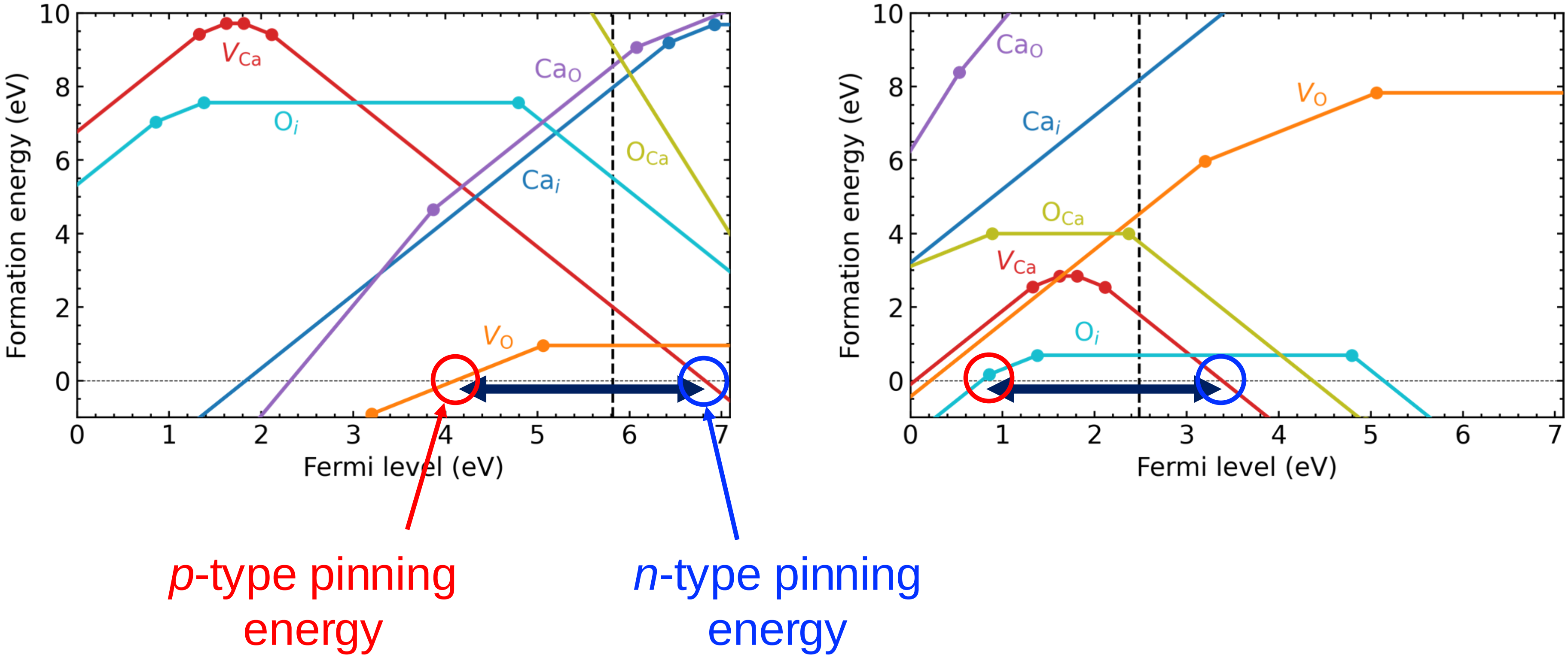


- Under the intrinsic defect doping, the Fermi level is far from the band edges

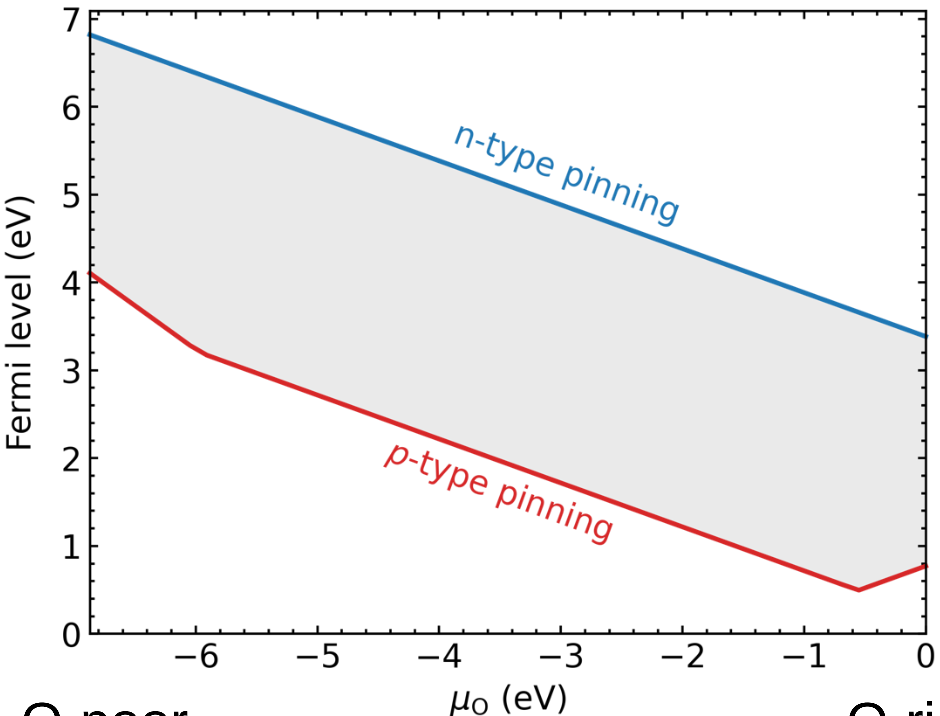
Compensation and doping limits in CaO

O-poor conditions

O-rich conditions



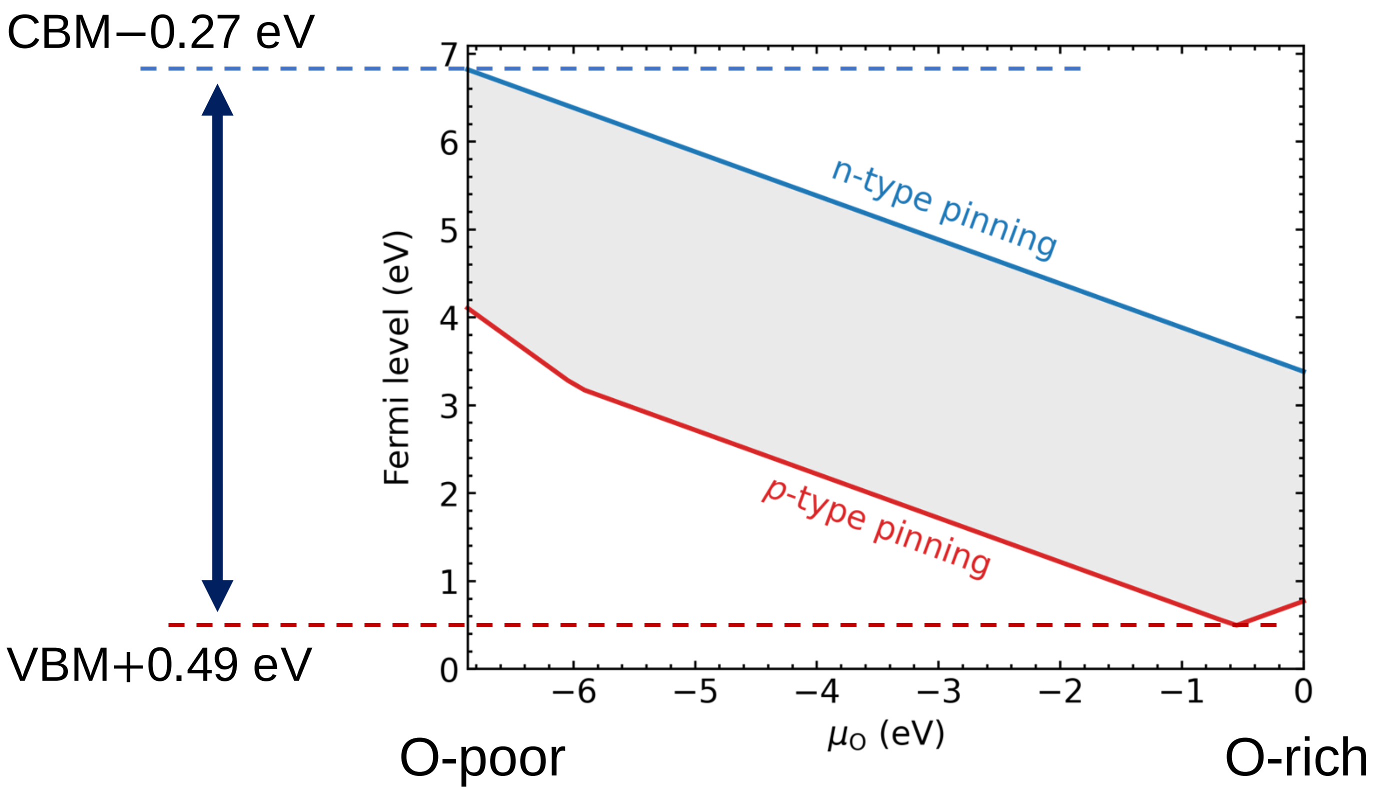
Compensation and doping limits in CaO



O-poor O-rich

- For a given growth condition, the allowed range of Fermi levels is quite limited

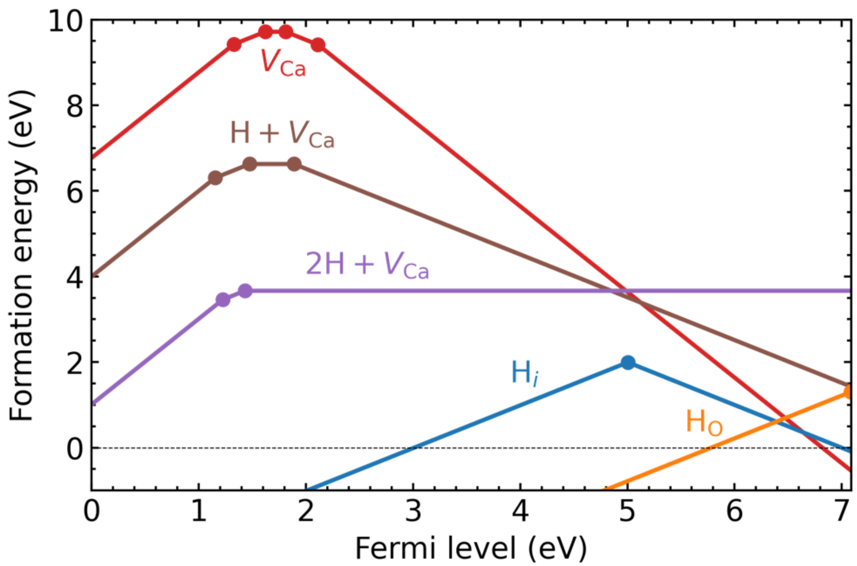
Compensation and doping limits in CaO



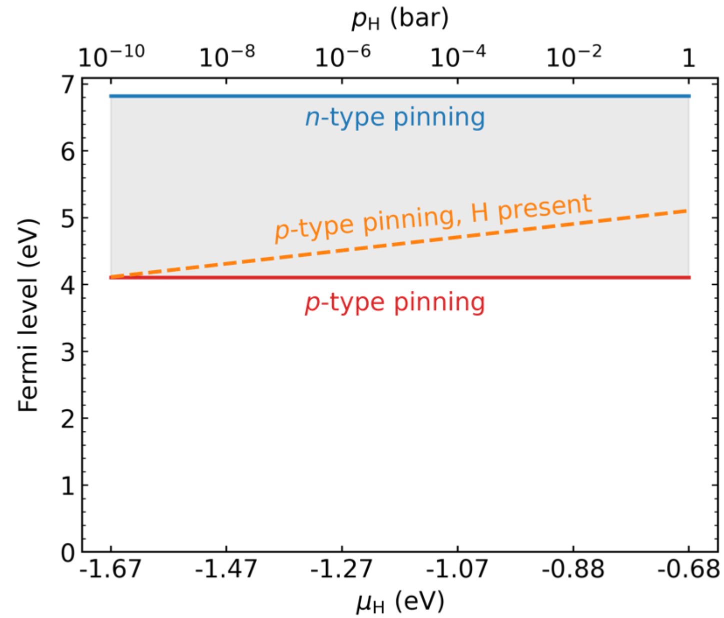
- Overall doping-limit energy range: VBM+0.49 eV to CBM−0.27 eV
- Extrinsic dopants needed to reach the doping limits
- O-poor (O-rich) conditions for *n*-type (*p*-type) doping

Impact of hydrogen impurities

O-poor conditions & H-rich limit ($\mu_H = 0$ eV)



O-poor conditions
H_2 atmosphere at $T = 1000$ K



- H_i always a compensation center
- Under O-poor and H-rich conditions, H_O severely restricts the *p*-type doping limit
- H_O can shift the Fermi level closer to the conduction band

Conclusions

- CaO has a wide doping-limit energy range
- Varying growth condition and extrinsic dopants needed to approach the doping limits
- Hydrogen impurities should be avoided not to cause extra limits to *p*-type doping

Acknowledgments