



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

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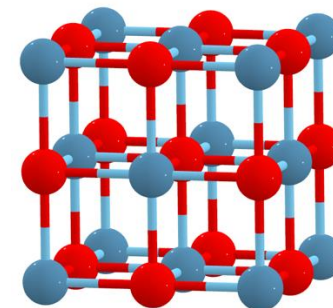
Dartmouth Engineering

APS March Meeting 2024, Minneapolis



CaO as a new quantum-defect host

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

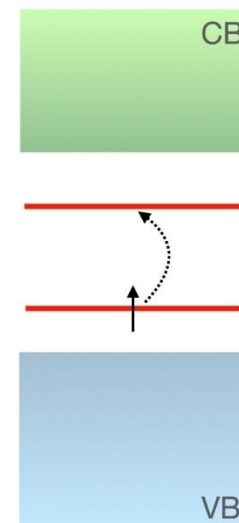
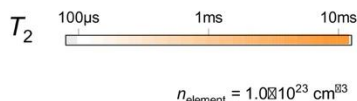


H 1.9μs																	He	
Li 2.9μs	Be 14.4μs																	Ne
Na 5.1μs	Mg 324.2μs																	Ar
K 94.8μs	Ca 14.2ms	Sc 2.3μs	Ti 343.8μs	V 2.0μs	Cr 677.8μs	Mn 3.2μs	Fe 25.3ms	Co 2.4μs	Ni 2.7ms	Cu 6.5μs	Zn 761.1μs	Ga 7.0μs	Ge 556.8μs	As 10.3μs	Se 374.2μs	Br 7.3μs	Kr 318.4μs	
Rb 10.9μs	Sr 429.7μs	Y 269.0μs	Zr 144.2μs	Nb 1.7μs	Mo 155.0μs	Tc	Ru 215.0μs	Rh 557.0μs	Pd 232.8μs	Ag 461.9μs	Cd 130.6μs	In 2.2μs	Sn 84.4μs	Sb 5.5μs	Te 174.2μs	I 4.5μs	Xe 54.9μs	
Cs 6.3μs	Ba 167.6μs	*	Hf 217.5μs	Ta 7.3μs	W 2.4ms	Re 5.0μs	Os 231.4μs	Ir 527.9μs	Pt 68.1μs	Au 451.6μs	Hg 166.1μs	Tl 5.9μs	Pb 109.2μs	Bi 3.4μs				
		*	La 5.6μs	Ce Inf	Pr 2.3μs	Nd 213.8μs	Pm	Sm 236.7μs	Eu 6.5μs	Gd 613.0μs	Tb 5.9μs	Dy 177.6μs	Ho 1.6μs	Er 339.6μs	Tm 114.2μs	Yb 185.5μs	Lu 8.3μs	

T_2

100μs 1ms 10ms

$n_{\text{element}} = 1.0 \times 10^{23} \text{ cm}^{-3}$



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

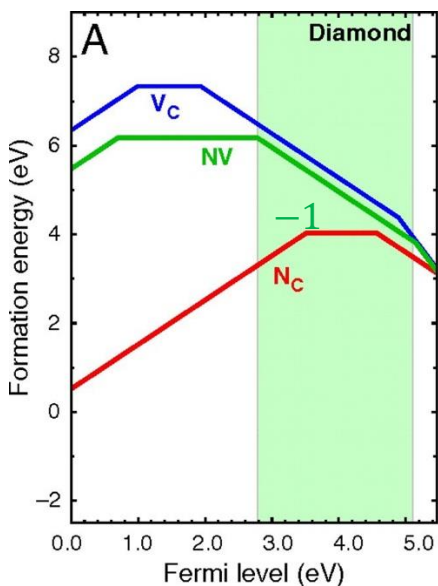
Y. Xiong *et al.*, *Mater. Quantum. Technol.* **4**, 013001 (2024)

S. Kanai *et al.*, *PNAS* **119**, e2121808119 (2022)

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

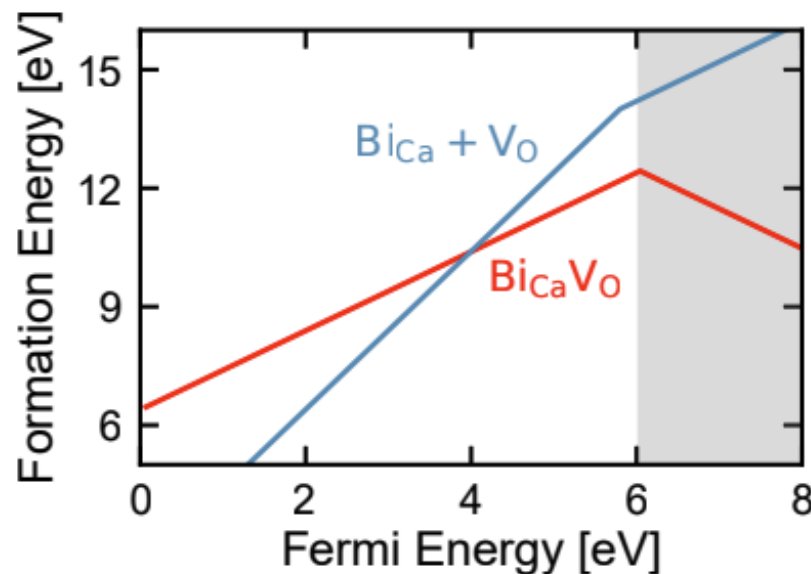
What is range of Fermi levels in CaO?

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

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

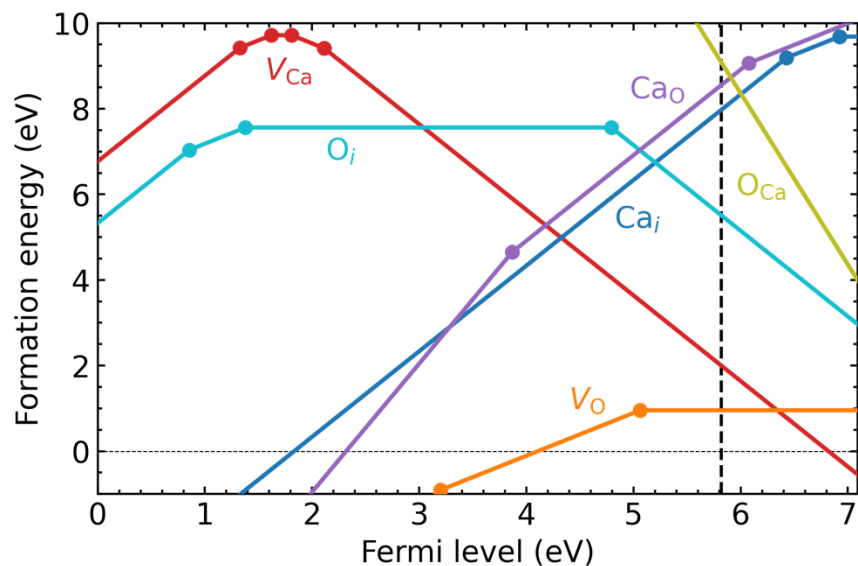
\downarrow Defect Formation Energy
 \downarrow Defect Supercell \downarrow Host Supercell
 \downarrow Chemical potentials from phase stability
 \downarrow Electron chemical potential
 \downarrow Finite size corrections

Plot by Seán Kavanagh

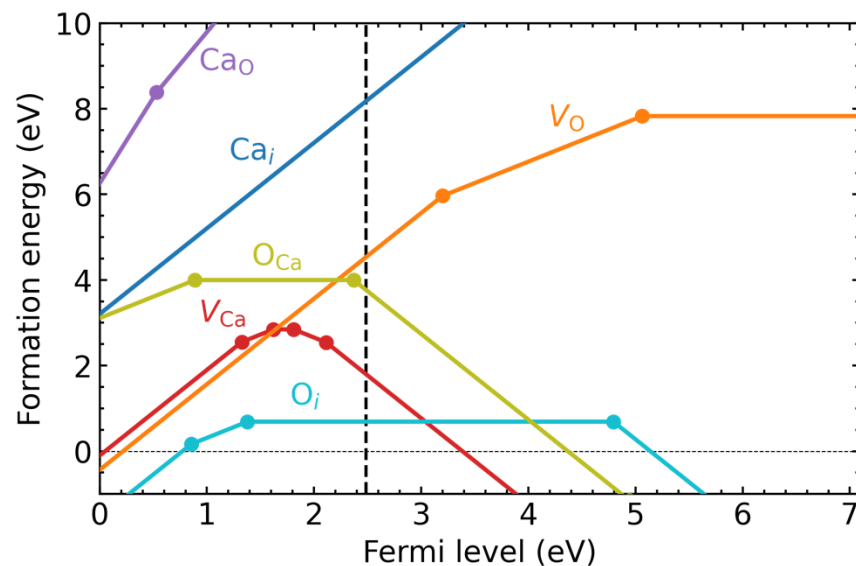
- HSE screened hybrid functional with $\alpha = 0.498$
 - reproduce experimental band gap (7.09 eV)
 - lattice constant $a = 4.78 \text{ \AA}$ (Expt. $4.78 - 4.808 \text{ \AA}$)
- 512-atom supercell, Γ -only **k**-point sampling

Intrinsic defects and doping in CaO

O-poor conditions



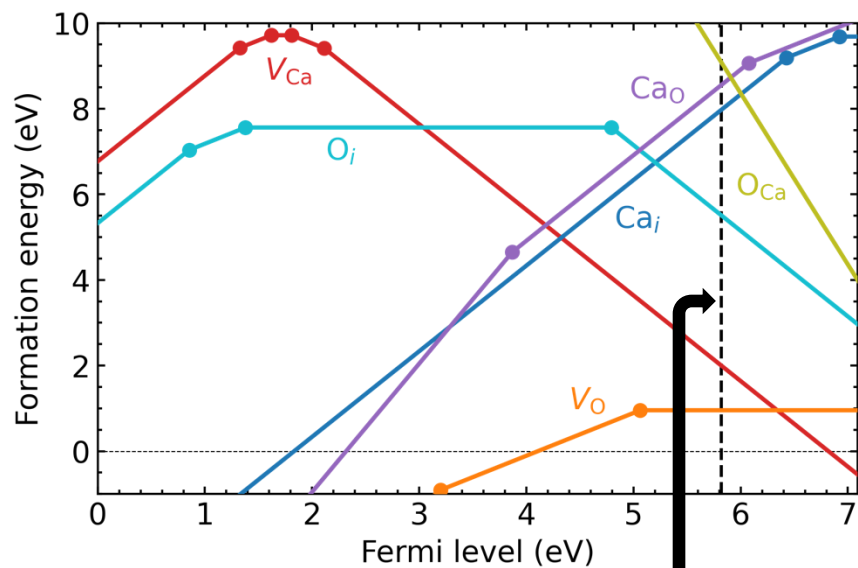
O-rich conditions



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

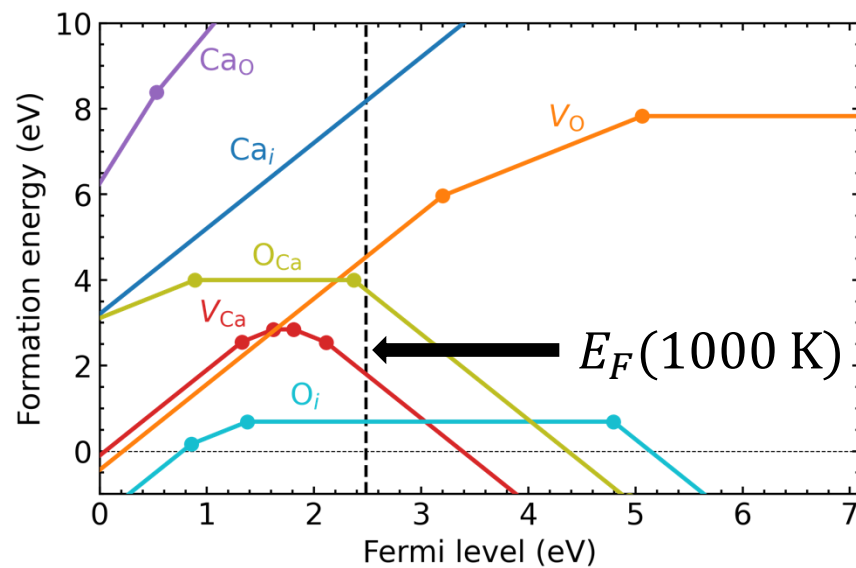
Intrinsic defects and doping in CaO

O-poor conditions



$E_F(1000\text{ K})$

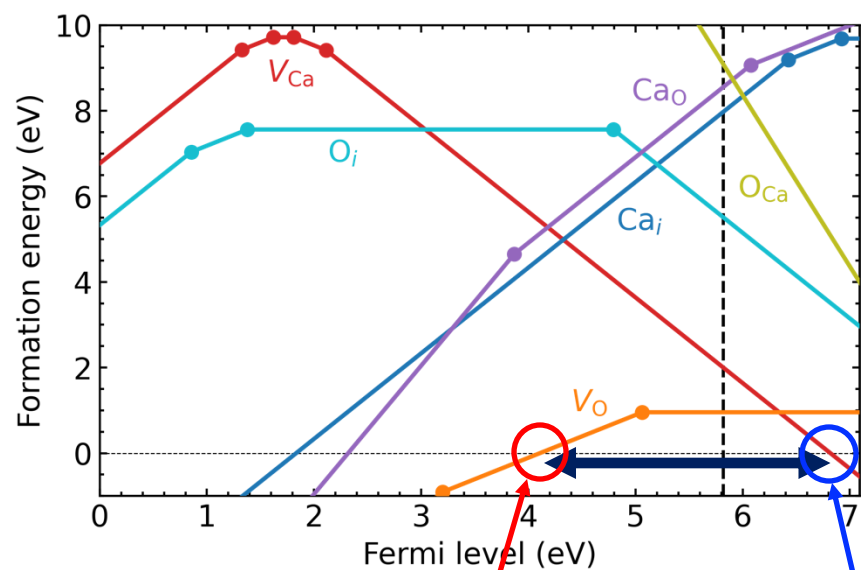
O-rich conditions



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

Compensation and doping limits in CaO

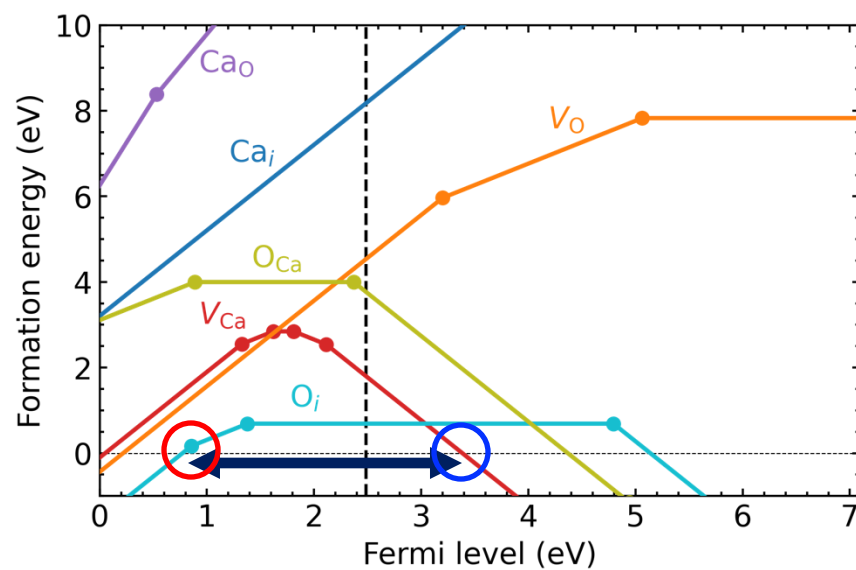
O-poor conditions



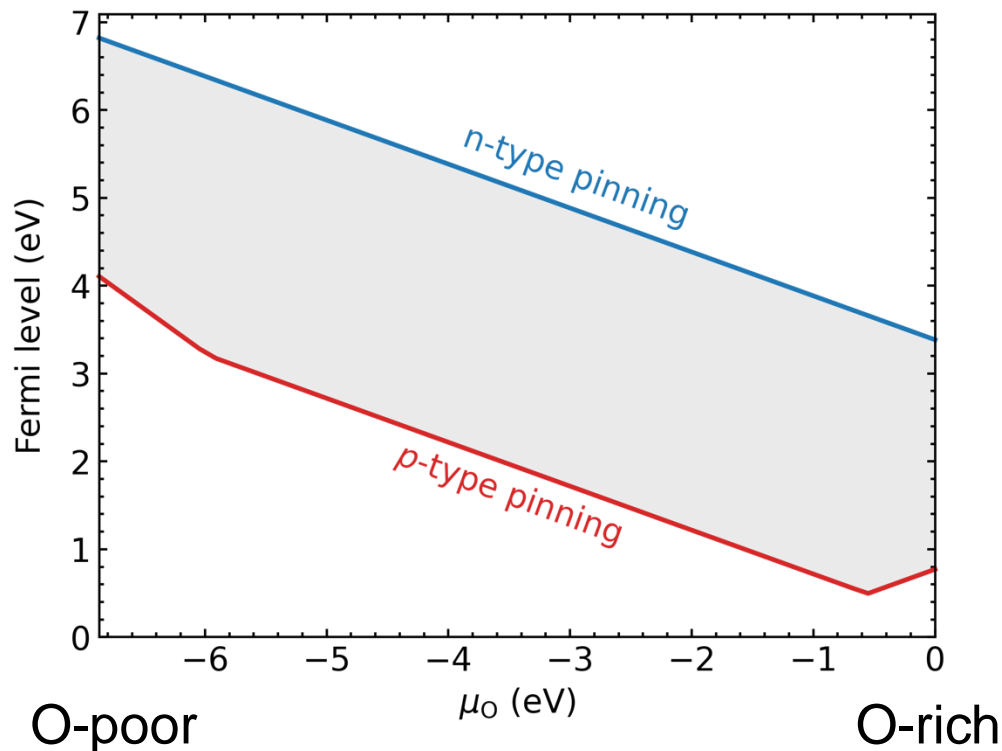
p -type pinning
energy

n -type pinning
energy

O-rich conditions

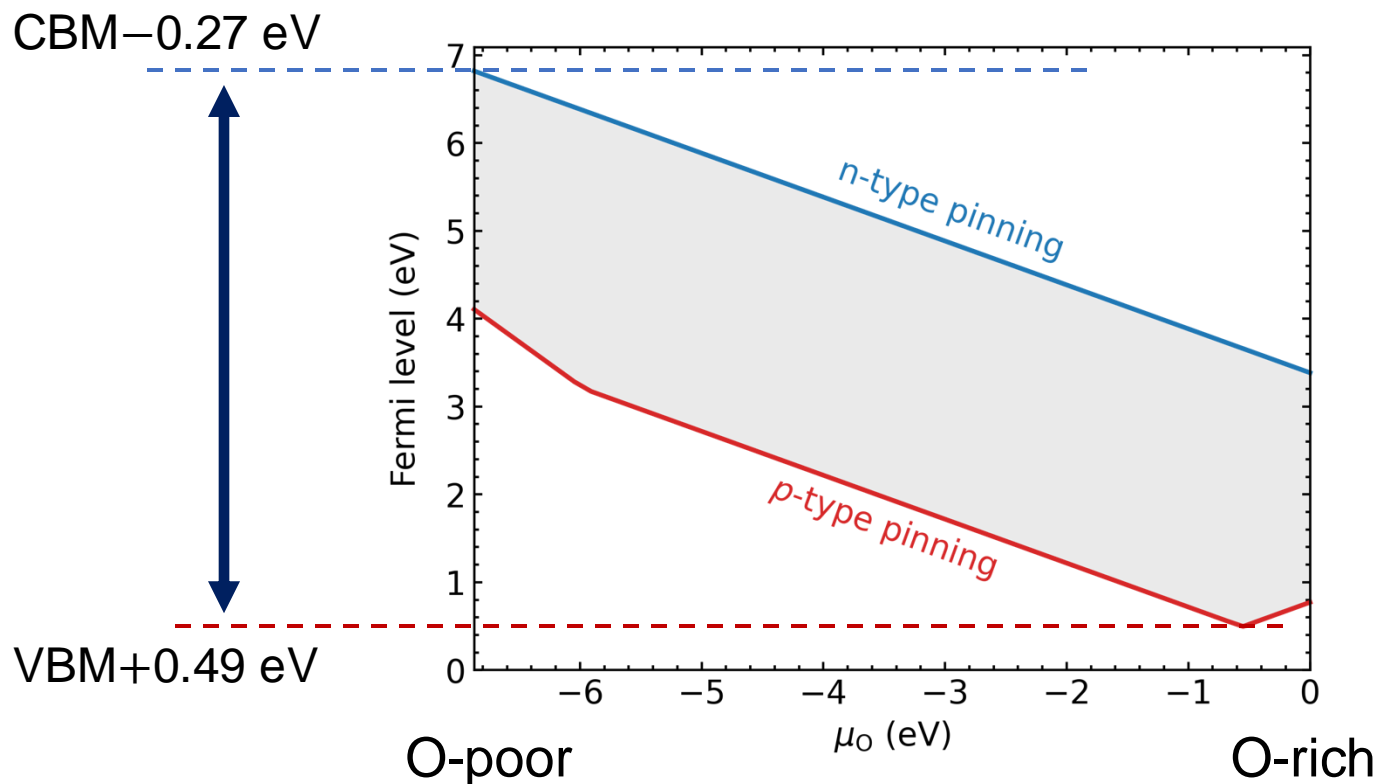


Compensation and doping limits in CaO



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

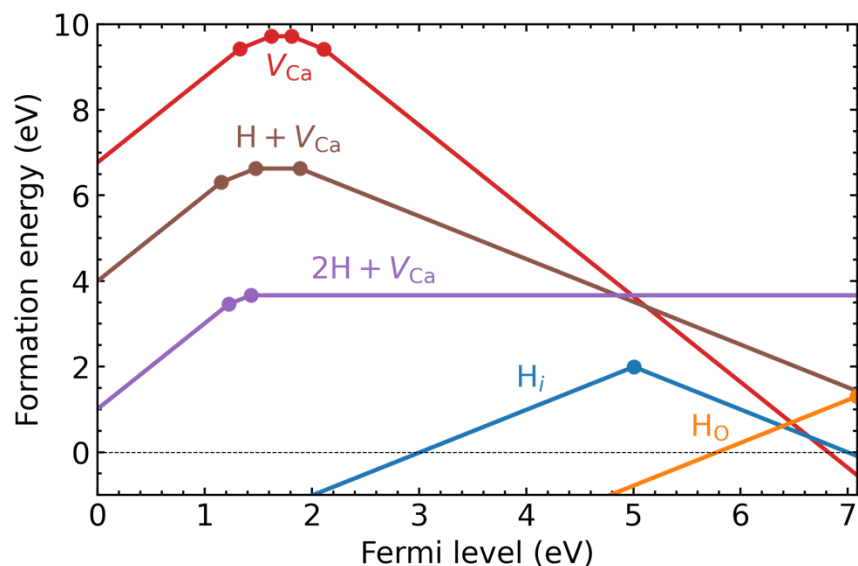
Compensation and doping limits in CaO



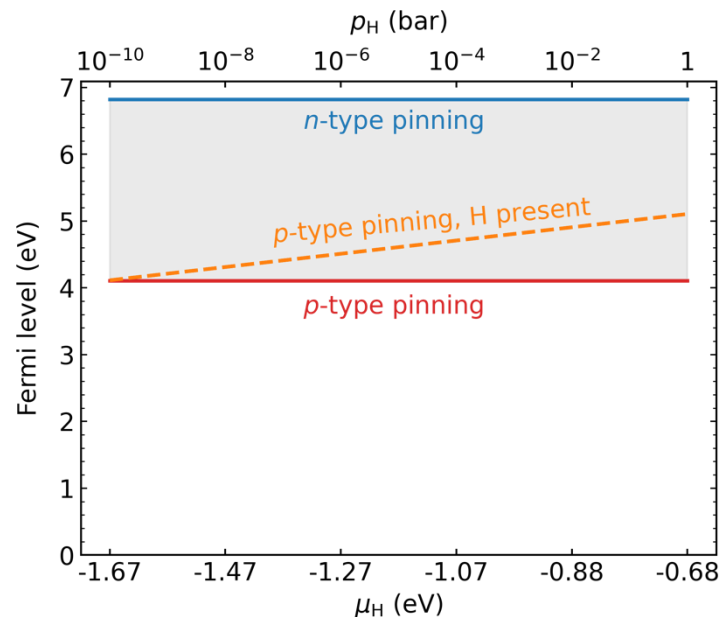
- Overall doping-limit energy range: VBM+0.49 eV to CBM-0.27 eV
- Extrinsic dopants needed to reach the doping limits
- O-poor (O-rich) conditions for *n*-type (*p*-type) doping

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



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