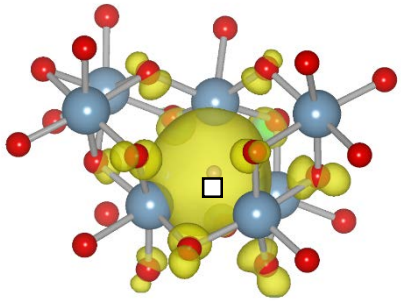
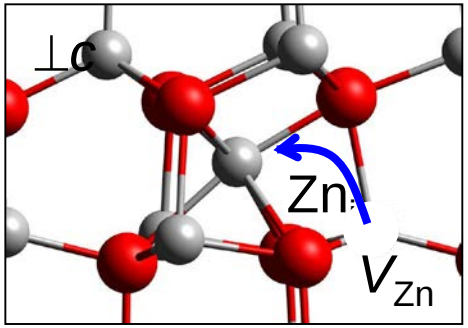
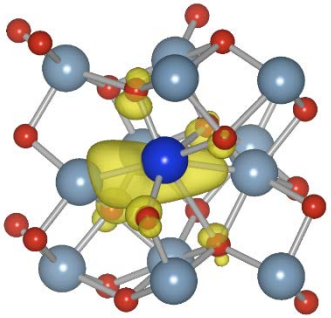






First-principles modeling of defects and hydrogen in oxides

Chris G. Van de Walle

Materials Department, University of California, Santa Barbara, USA

with Minseok Choi (Inha U., South Korea), Justin Weber (Intel),
Anderson Janotti (U. Delaware), John Lyons (NRL)

Supported by ONR and SRC

International Workshop on Models and Data for Plasma-Material Interaction in Fusion Devices (MoD -PMI 2019)
National Institute for Fusion Science, Tajimi, Japan
June 18-20, 2019

Van de Walle Computational Materials Group

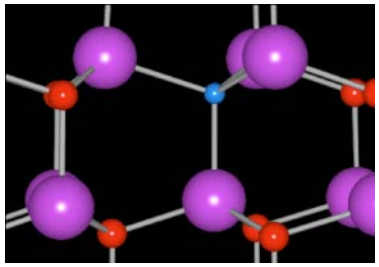
www.mrl.ucsb.edu/~vandewalle

First-principles calculations

Density functional theory, many-body perturbation theory

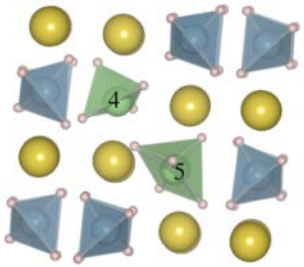
Oxides

- Transparent conductors
- Dielectrics
- Thermal barriers
- Complex oxides



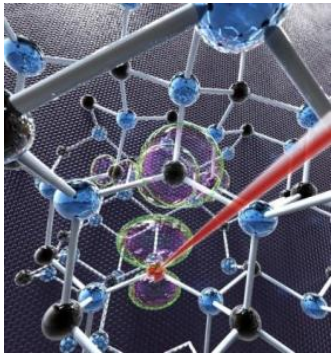
Hydrogen as a fuel

- Kinetics
- Complex hydrides
- Metal hydrides
- Proton conductors



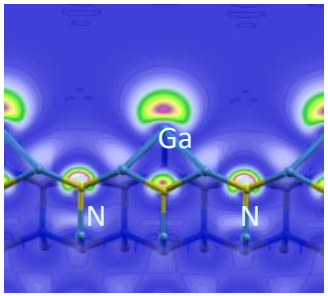
Quantum computing with defects

- Qubits
- Single photon emitters



Nitrides

- Doping
- Surfaces
- Interfaces
- Efficiency, loss



Computational Approach

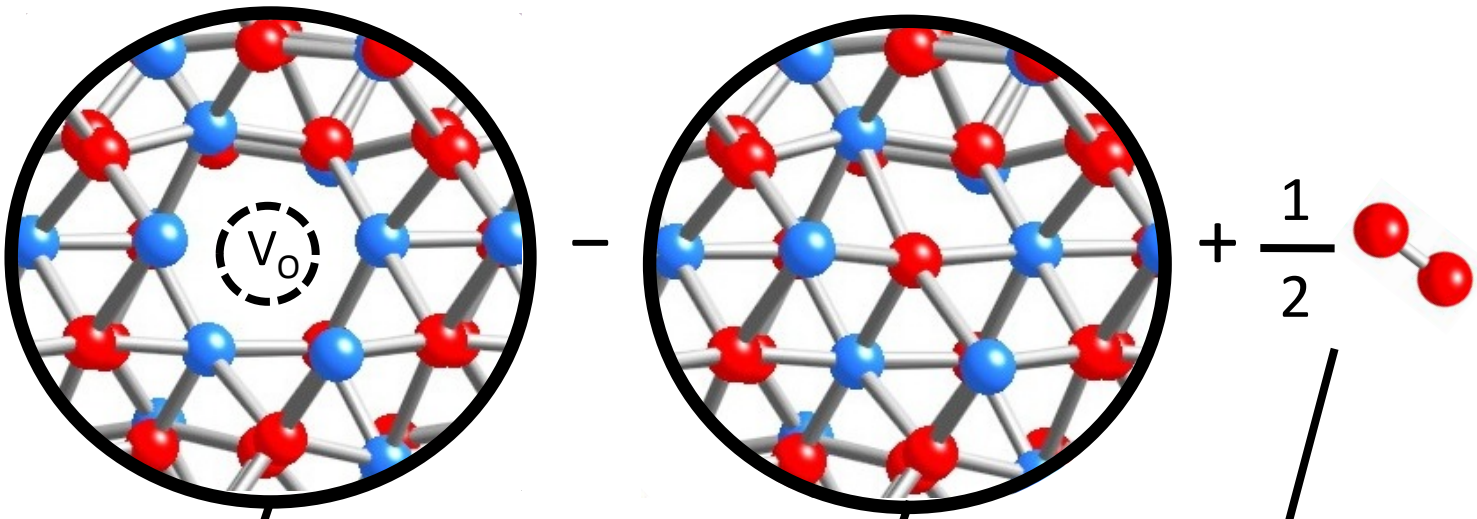
- Traditional density functional theory approach
  - Local or semi-local density approximation
- Hard to interpret due to band-gap problem
- Major problem when addressing defects or surface/interface states
- Our approach: Hybrid functional calculations
  - The HSE hybrid functional
- A fraction of screened Hartree-Fock exchange
- Accurate band gaps and defect levels
- 120-atom supercell, 400 eV cutoff energy, 2x2x1 *k*-point mesh

J. Heyd, G. E. Scuseria, M. Ernzerhof, J. Chem. Phys **118**, 8207 (2003).

Defect Formation Energy

Determine defect concentrations: $[D]=N_O \exp(-E^f/kT)$

$$E^f[\mathrm{V_O}] = E^{tot}[\mathrm{V_O}] - E^{tot}[bulk] + \mu_\mathrm{O}$$



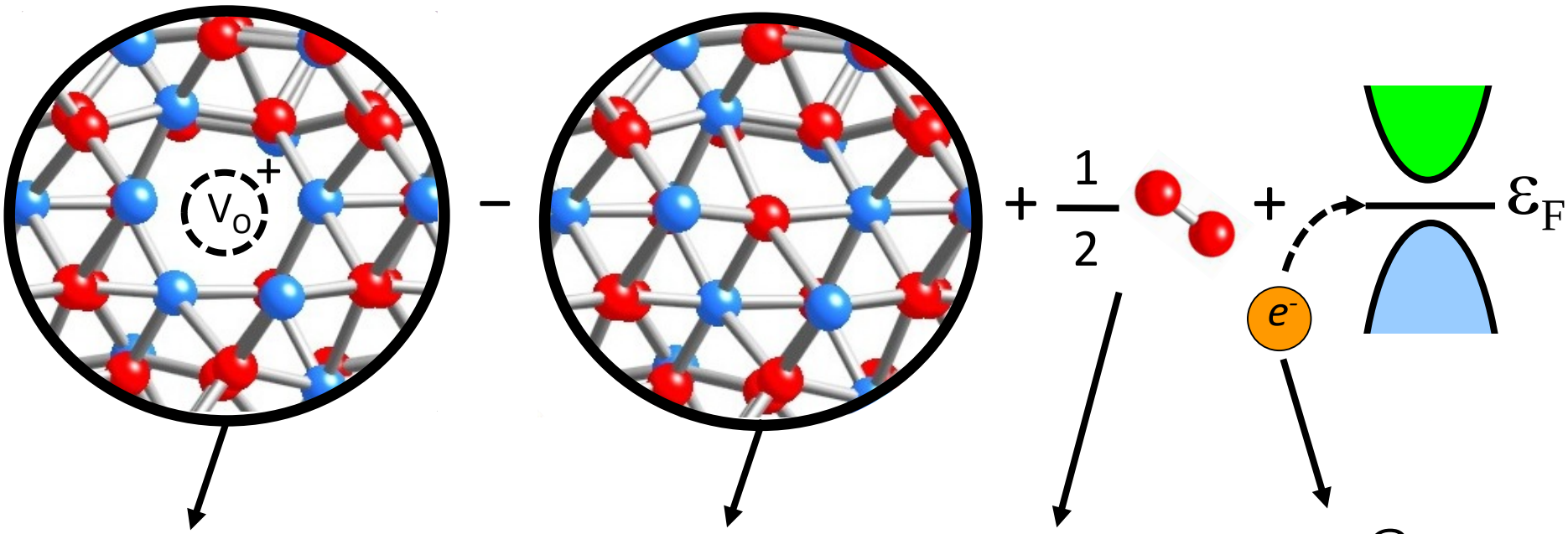
Al_2O_3: V_O Al_2O_3 ½ O_2

O chemical potential

Defect Formation Energy

Determine defect concentrations: $[D]=N_O \exp(-E^f/kT)$

$$E^f[\mathrm{V_O^+}] = E^{tot}[\mathrm{V_O^+}] - E^{tot}[bulk] + \mu_\mathrm{O} + \varepsilon_F$$



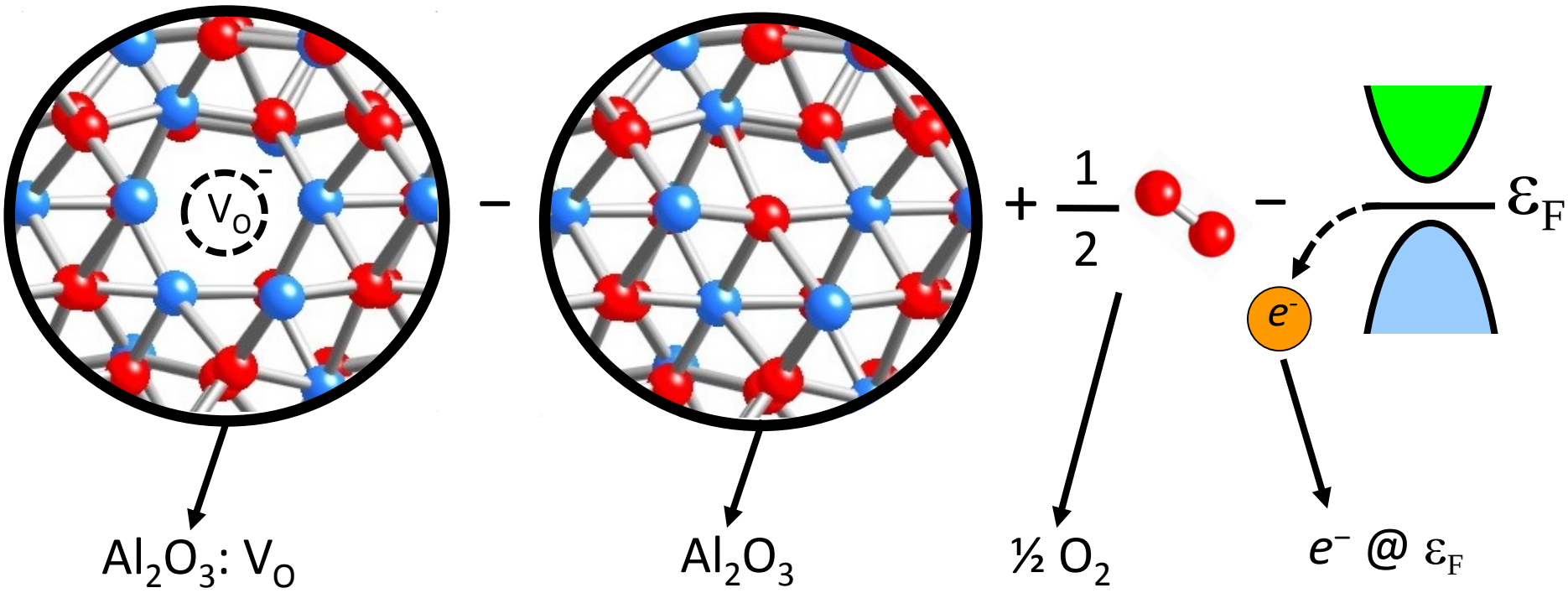
Al_2O_3: V_O $\quad$ Al_2O_3 $\quad$ ½ O_2 $\quad$ e^- @ ε_F

O chemical potential

Defect Formation Energy

Determine defect concentrations: $[D]=N_O \exp(-E^f/kT)$

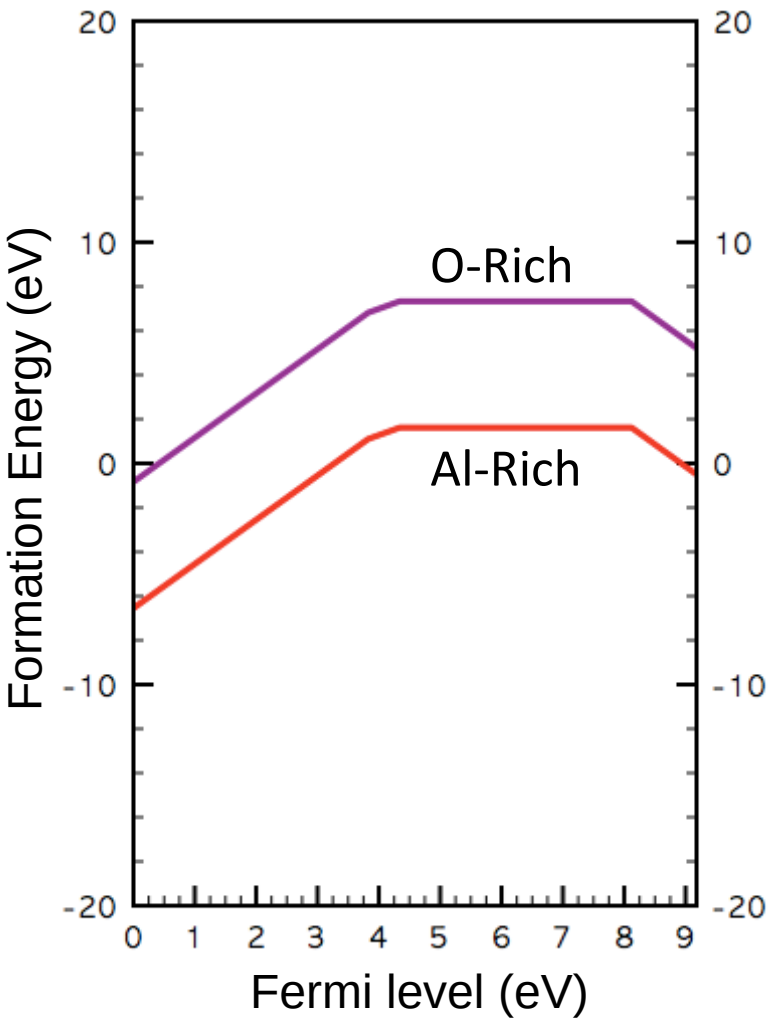
$$E^f[\mathrm{V}_\mathrm{O}^-] = E^{tot}[\mathrm{V}_\mathrm{O}^-] - E^{tot}[bulk] + \mu_\mathrm{O} - \varepsilon_F$$



"First-principles calculations for point defects in solids",
C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse,
A. Janotti, and C. G. Van de Walle, Rev. Mod. Phys. **86**, 253 (2014).

Defect Formation Energies

example: V_O

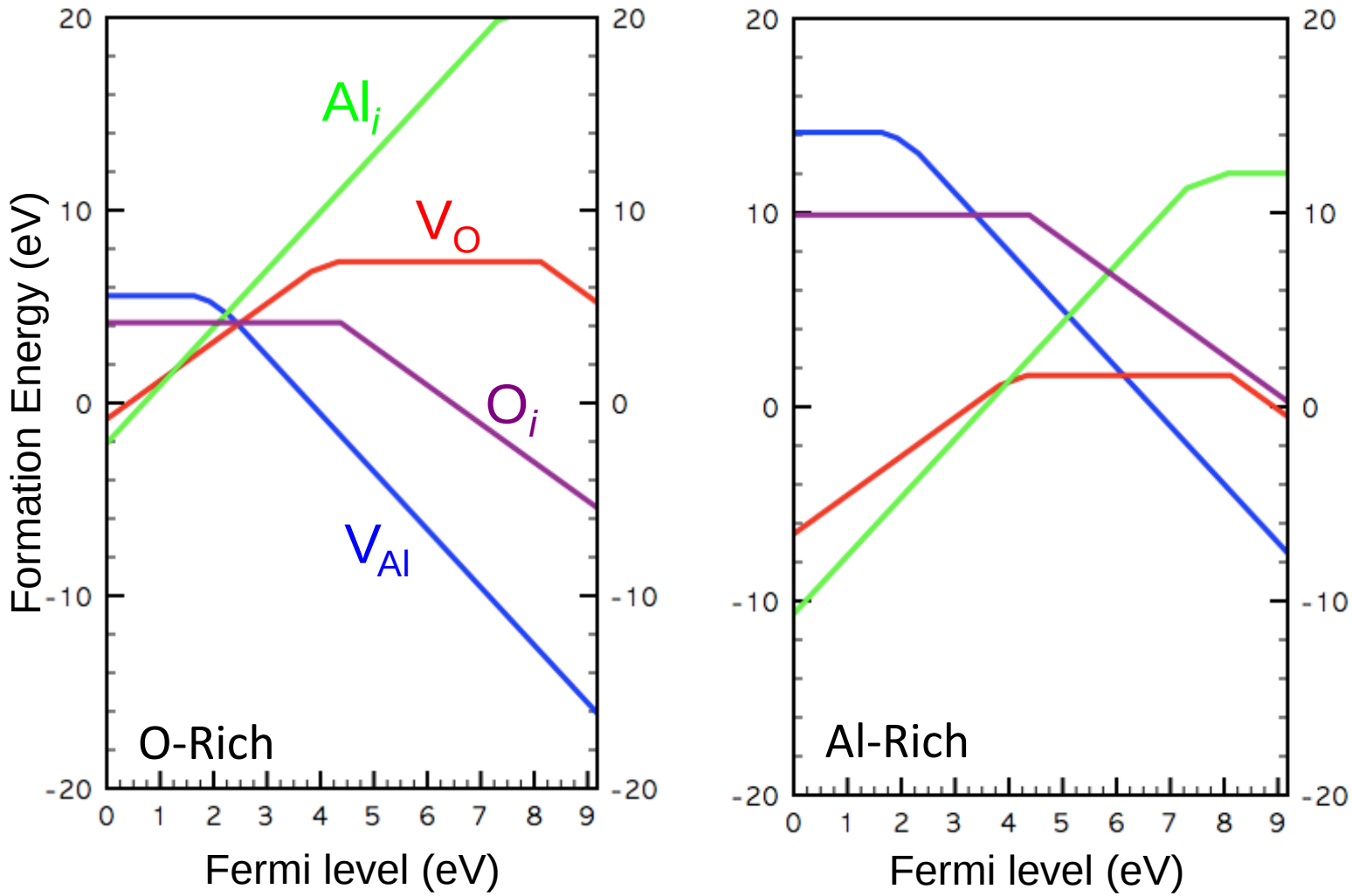


- Plotted for extreme Al-rich and O-rich limits
  - Very wide range given by ΔH_f (Al_2O_3)= -17.36 eV

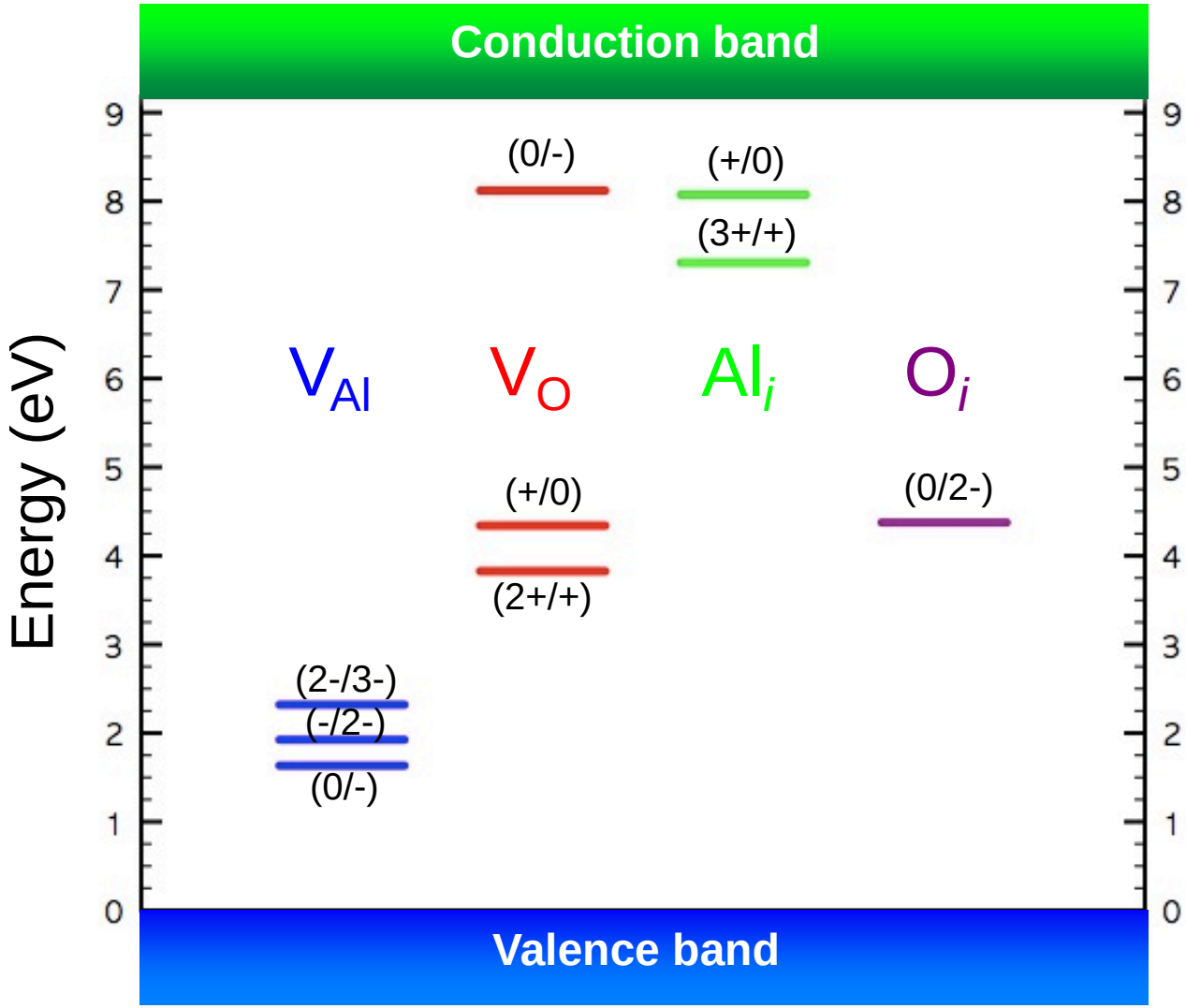
•Actual chemical potential is somewhere in between

- Slope indicates charge
- Kinks: charge transition levels
- Information used to study fixed charge and defect levels

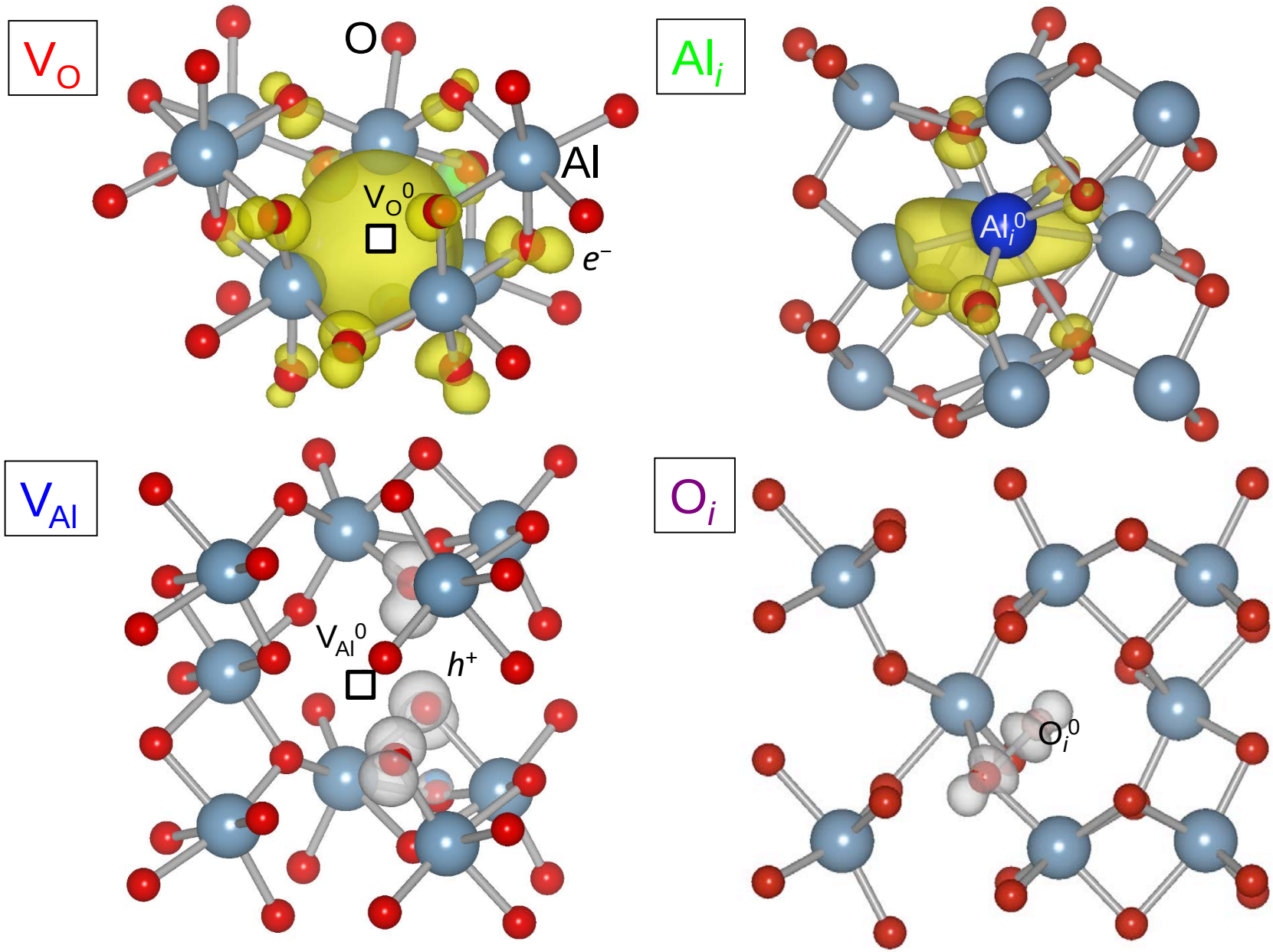
Native point defects in α-Al_2O_3



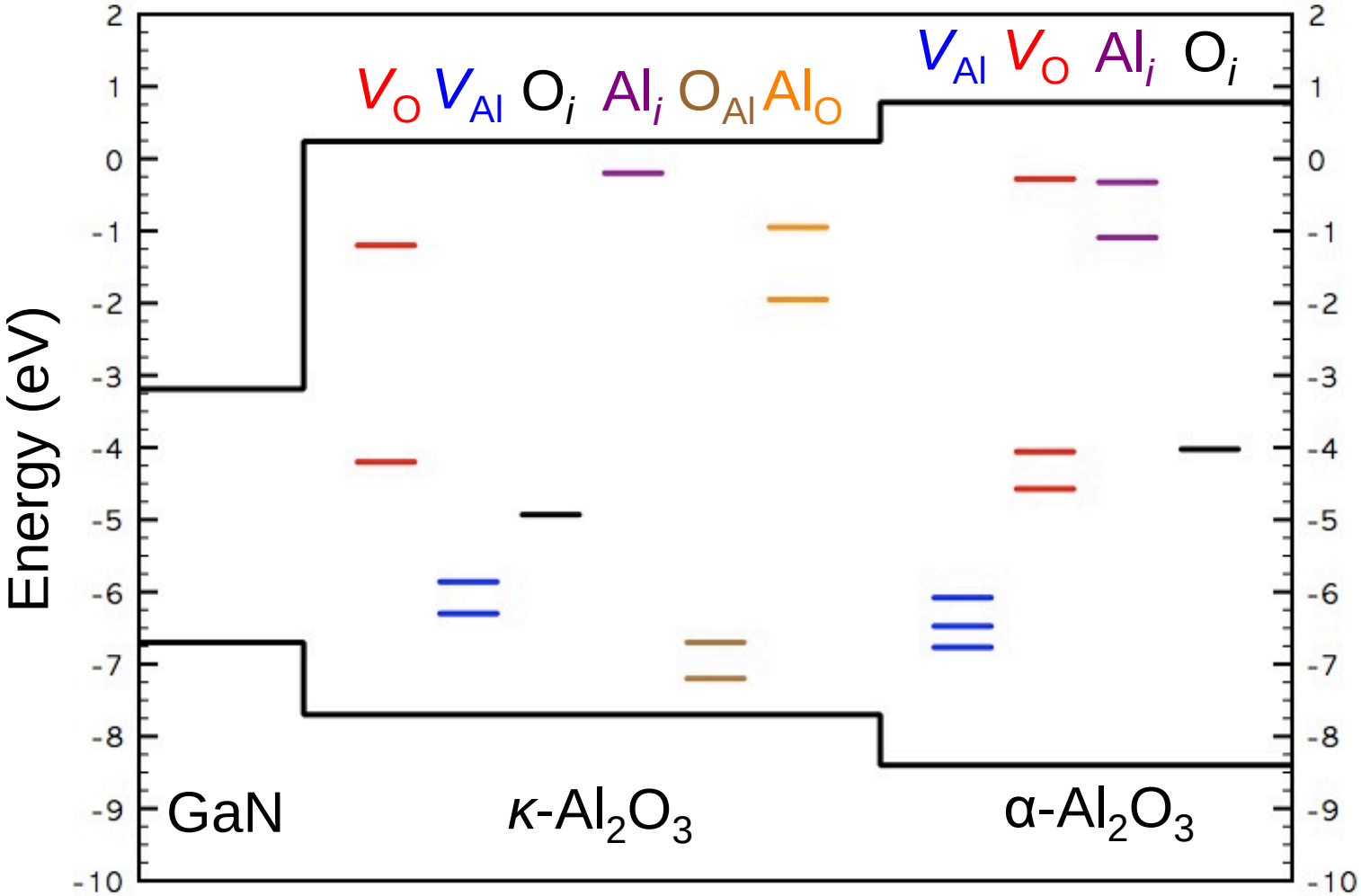
Defect level positions in α-Al_2O_3



Local geometry and charge densities



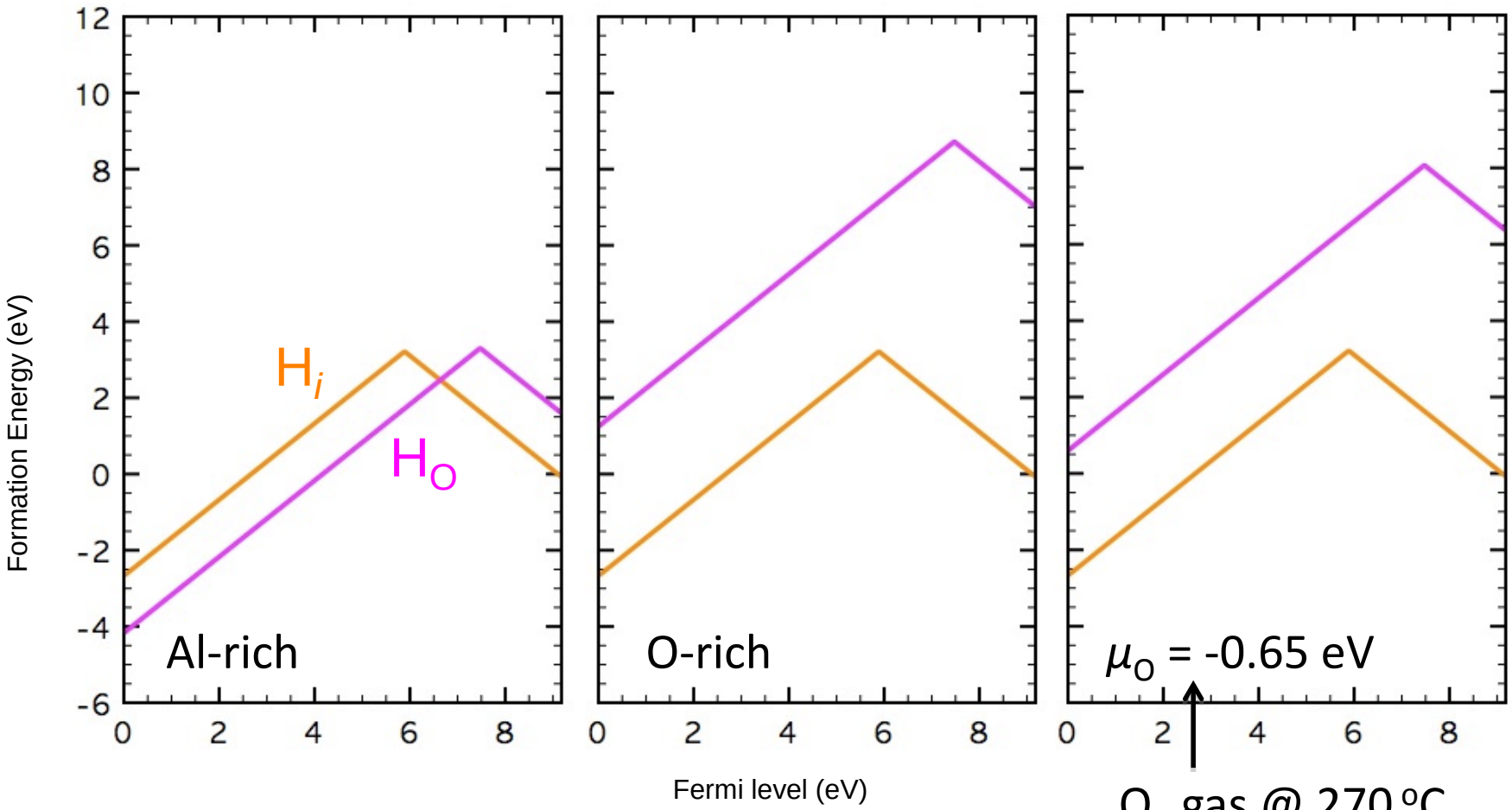
Defect levels in κ- and α-Al_2O_3



κ: J. R. Weber, A. Janotti, and C. G. Van de Walle, J. Appl. Phys. **109**, 033715 (2011).

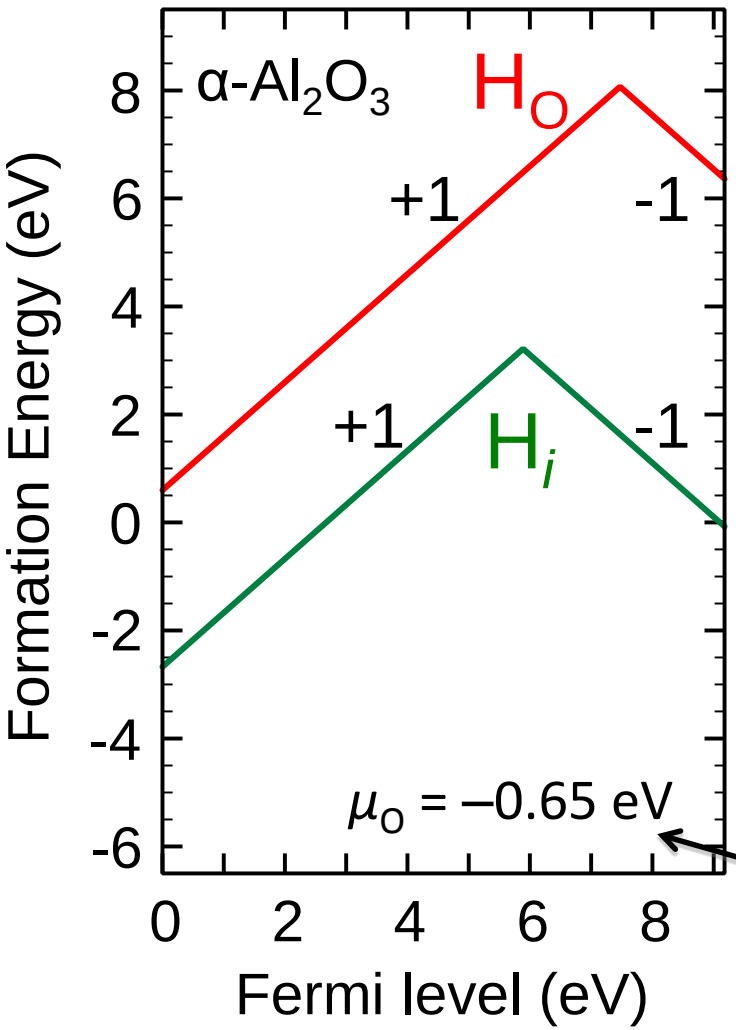
α: M. Choi, A. Janotti, and C. G. Van de Walle, J. Appl. Phys. **113**, 044501 (2013).

Hydrogen in Al_2O_3



O_2 gas @ 270 °C and 1 Torr

Hydrogen in Al_2O_3

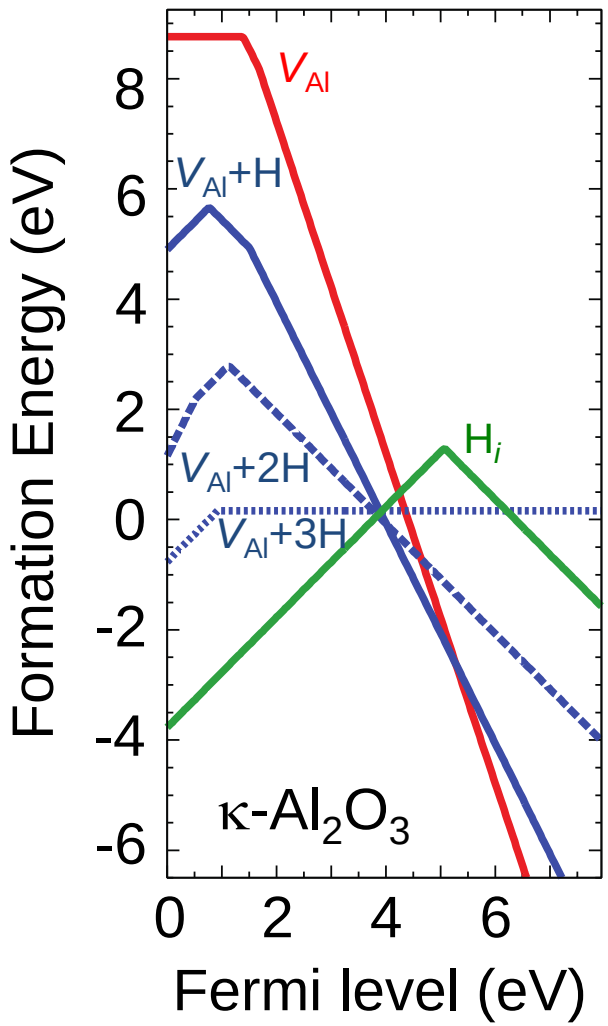


- Hydrogen can easily incorporate into Al_2O_3
- Hydrogen occupies the interstitial site (H_i)
  - (+/-) impurity level near mid-gap
- Low migration energy
- H_i can interact with native defects or impurities in Al_2O_3

O_2 gas @ 270 °C and 1 Torr

MATERIALS
UC Santa Barbara

H complexes with Al vacancy in Al_2O_3

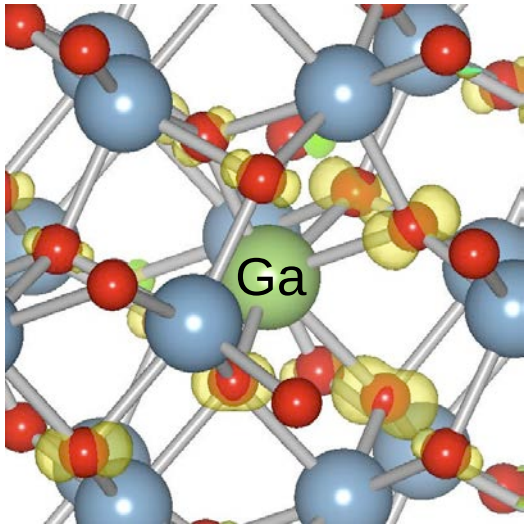


- Al vacancy:
  - –3 charge state over most of Al_2O_3 band gap

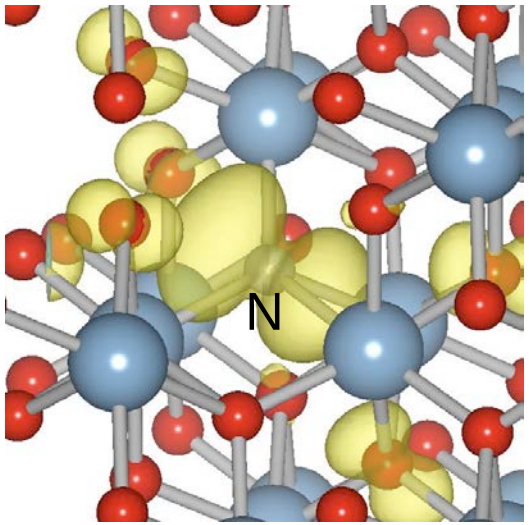
  negative fixed-charge center
- H captured by Al vacancy:
  - V_{Al}+nH (n=1,3) complexes lower the electrical charge of V_{Al}
  - V_{Al}+3H complex is electrically inactive

Local geometry and charge density

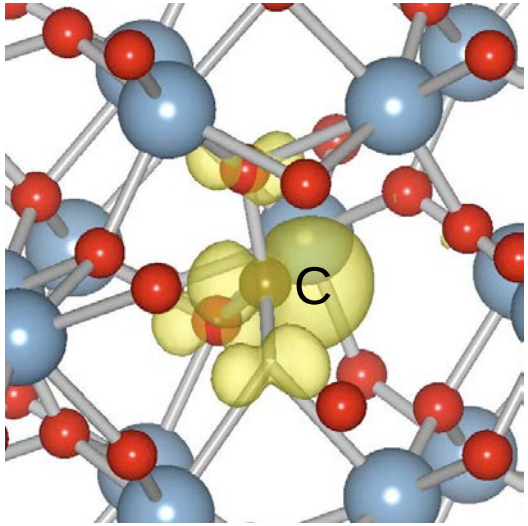
Ga_{Al}^{0}



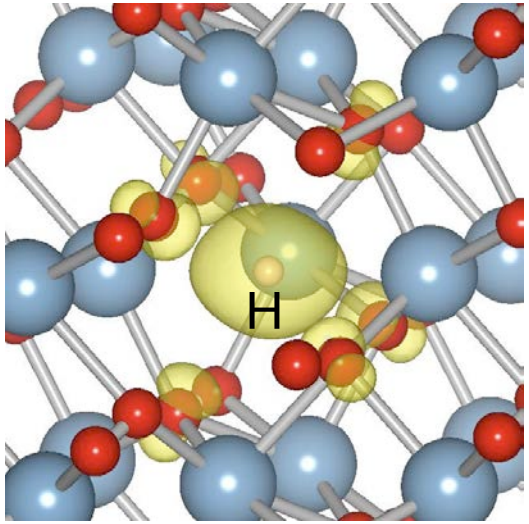
N_{O}^{0}



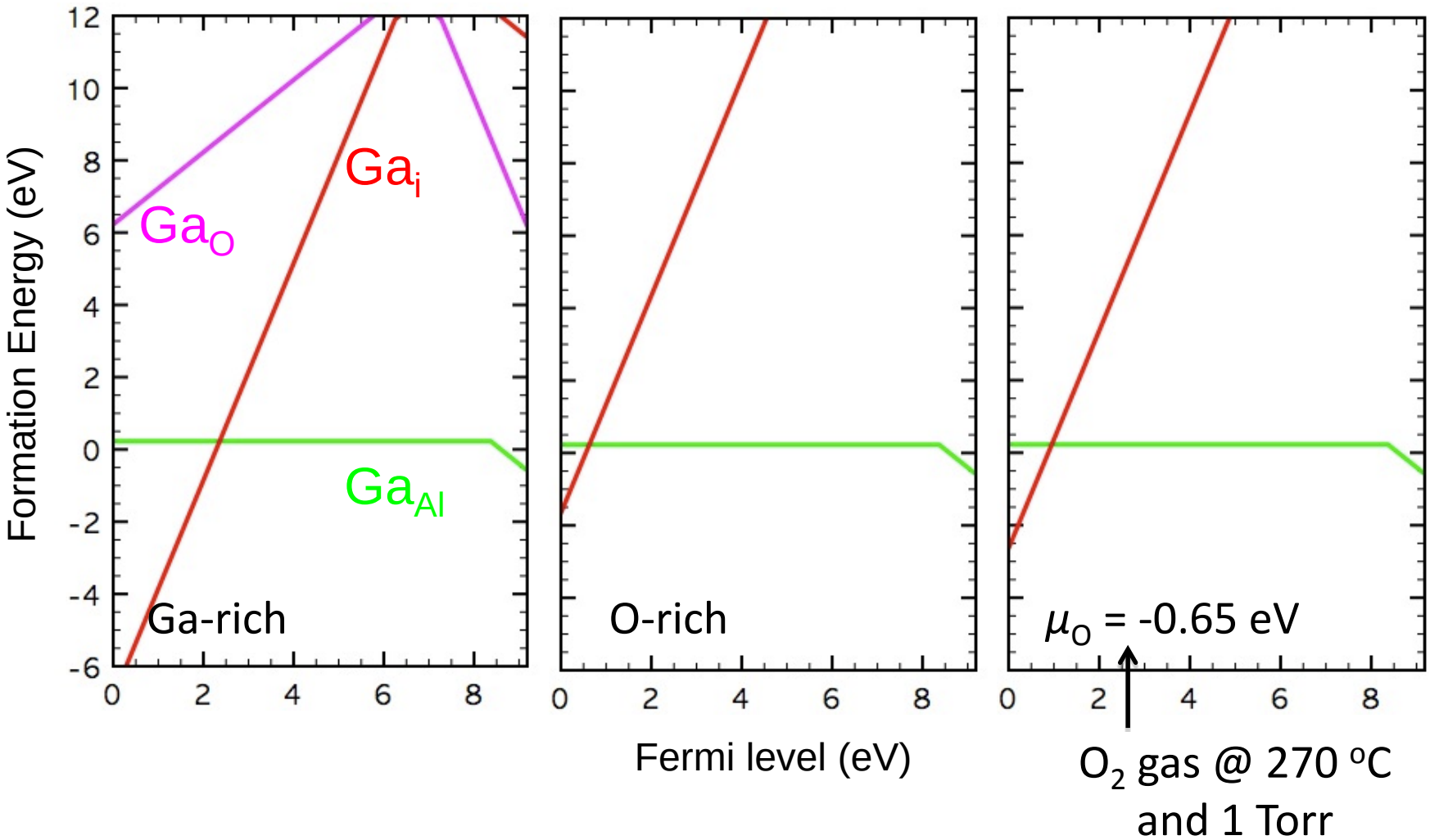
C_{Al}^{0}



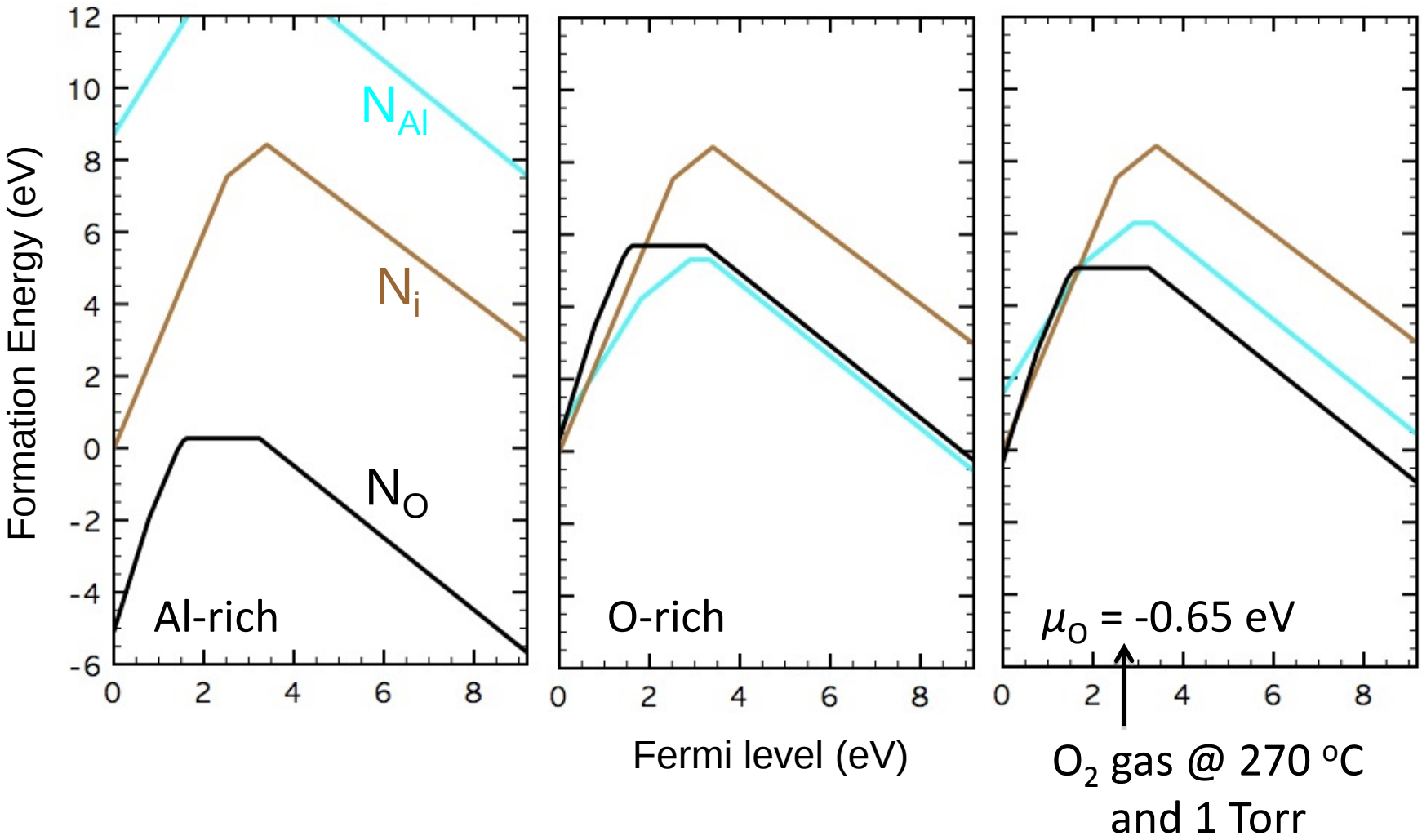
H_{i}^{0}



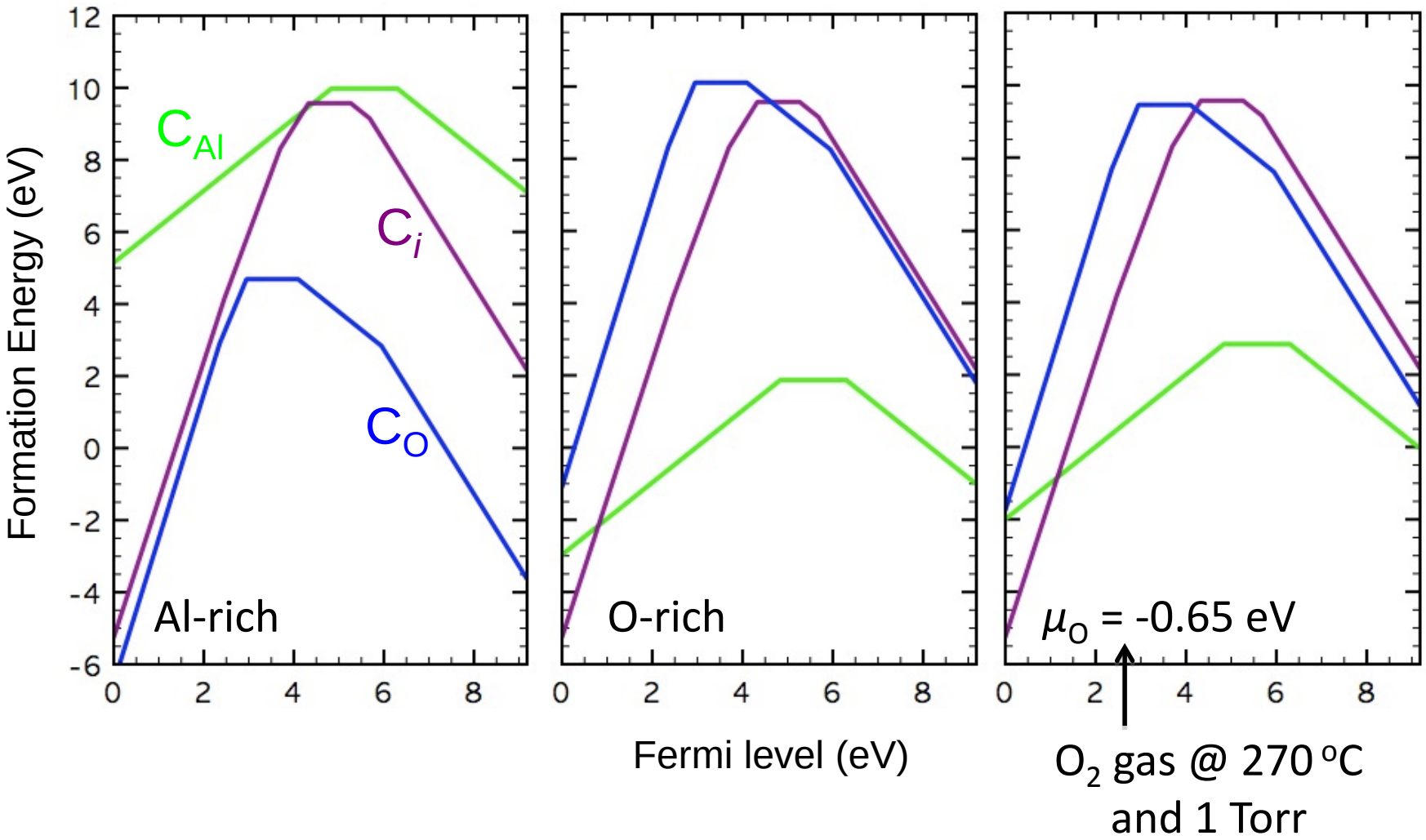
Gallium in Al_2O_3



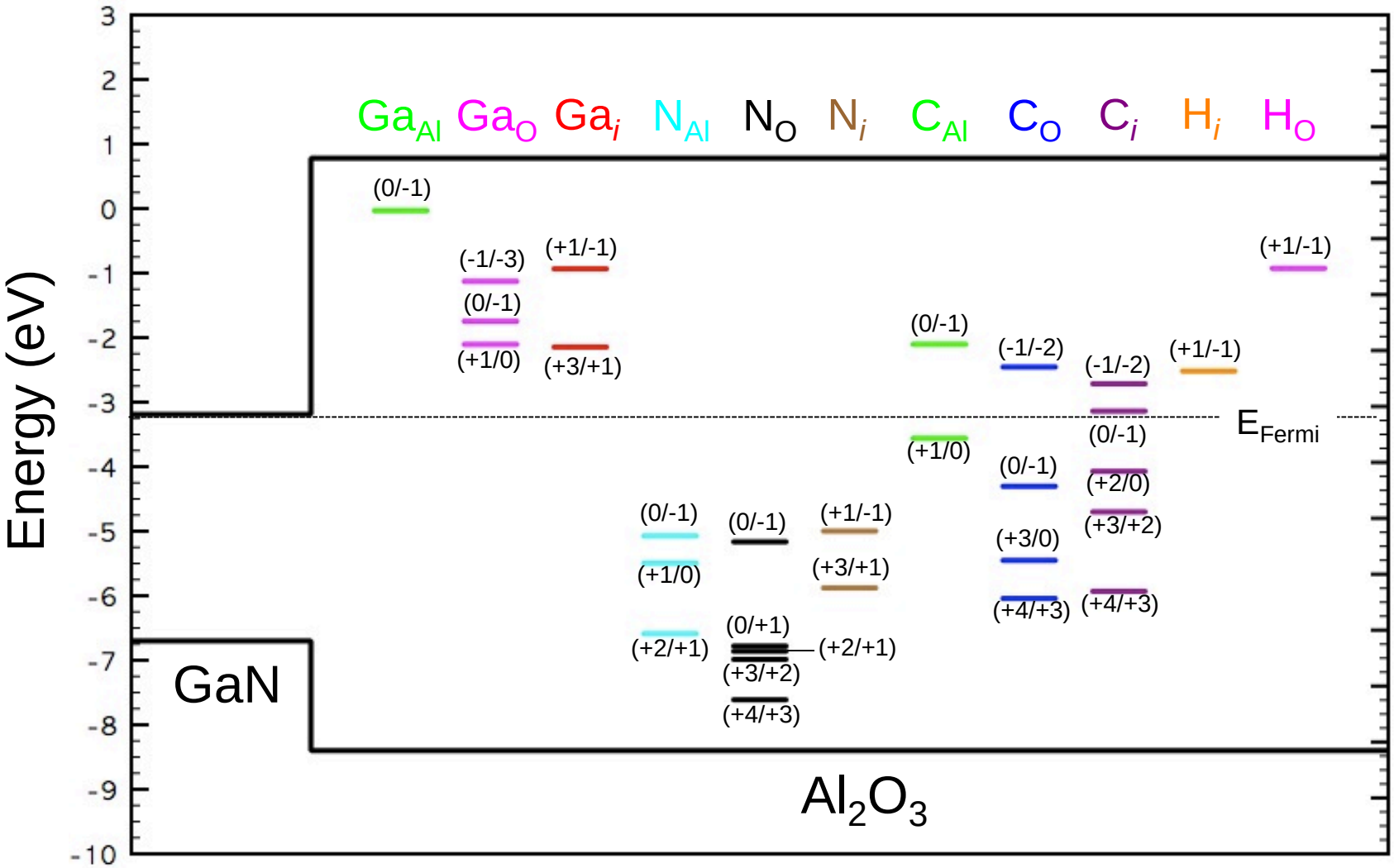
Nitrogen in Al_2O_3



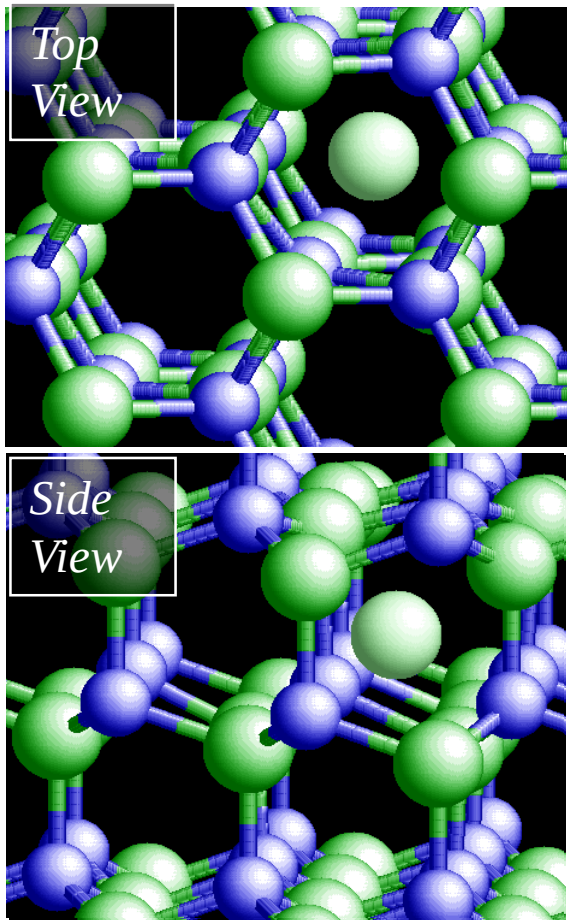
Carbon in Al_2O_3



Impurity Levels in Al_2O_3



Diffusion of point defects



- **Relevant for …**
  - growth
    - » Defects ‘frozen in’ or not
  - Ion implantation
    - » Anneal damage
  - Degradation
  - Irradiation
- **Zinc interstitial:**
  - E_m=0.57 eV

UCSB

Annealing temperature of point defects

$$\Gamma = \Gamma_0 \exp\left(-\frac{E_b}{kT}\right) \qquad \Gamma_0 \approx 10^{13}\,\mathrm{s}^{-1} \qquad \Gamma \approx 1\,\mathrm{s}^{-1}$$

	E_b (eV)	T annealing (K)
Zn_i^{2+}	0.57	219
V_{Zn}^{2-}	1.40	539
V_O^{2+}	1.70	655
V_O^{0}	2.36	909
O_i^{0}(split)	0.87	335
O_i^{2-}(oct)	1.14	439

A. Janotti and C. G. Van de Walle, Phys. Rev. B **76**, 165202 (2007).

Summary

- First-principles calculations provide qualitative insights and quantitative details for point defects
- Native defects and impurities in Al_2O_3
- References
  - **Defects**: C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C. G. Van de Walle, Rev. Mod. Phys. **86**, 253 (2014).
  - **κ-Al_2O_3**: J. R. Weber, A. Janotti, and C. G. Van de Walle, J. Appl. Phys. **109**, 033715 (2011).
  - **α-Al_2O_3**: M. Choi, A. Janotti, and C. G. Van de Walle, J. Appl. Phys. **113**, 044501 (2013).
  - **ZnO**: J. L. Lyons, J. B. Varley, D. Steiauf, A. Janotti and C. G. Van de Walle, J. Appl. Phys. **122**, 035704 (2017).
  - **GaN**: J. L. Lyons and C. G. Van de Walle, NPJ Comput. Mater. **3**, 12 (2017).