First-Principles Studies of Zinc Oxide

Chris G. Van de Walle

Materials Department, UCSB

KITP Spintronics Program
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Acknowledgments

- **Collaborations**

  A. Janotti (UCSB)

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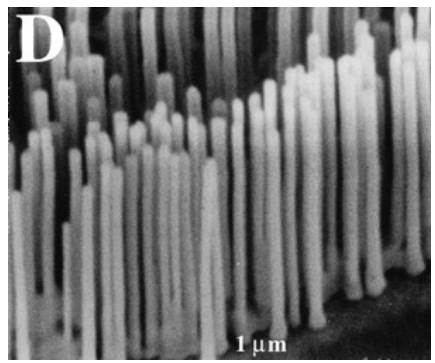
Applications of zinc oxide

Electronics
- Varistors (surge protectors)
- Transducers
- Radiation hardness
- Host for magnetic impurities

Chemistry
- Catalysis
- Sensors



Huang *et al.*, Science 292, 1897 (2001)

ZnO crystals
Bulk substrates

Wet etching

Optoelectronics
- Direct band gap: 3.4 eV!
- Photodetectors
- LEDs, lasers

Nanostructures
- Nanocrystals
- Nanowires

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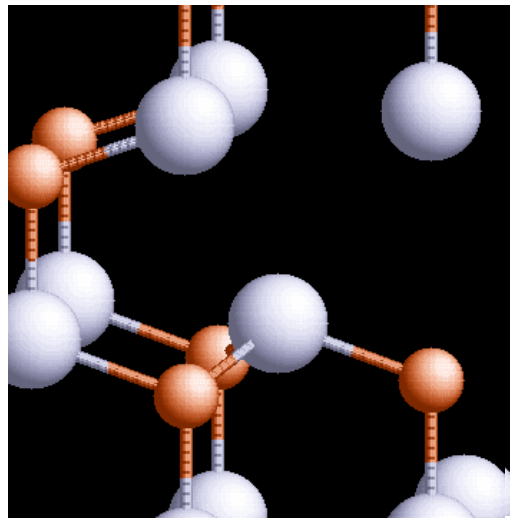
ZnO for optoelectronics

- **Large excitonic binding energy**
  - ZnO: 60 meV; GaN; 25 meV
  - Efficient excitonic emission at RT
- **Optically pumped lasing**
  - Platelets [Reynolds *et al.*, Solid State Commun. 99, 873 (1996)]
  - Thin films [Bagnall *et al.,* Appl. Phys. Lett. 70, 2230 (1997)]
- **Prospects for injection lasers/ LEDs:**
  - Heterojunctions with MgZnO, CdZnO
  - Require controlled doping!

Motivation and Outline

- **Devices: Control of conductivity required!**
- **Zinc oxide: typically *n*-type**
  - Cause: heavily debated
  - Traditionally attributed to oxygen vacancies
- **Investigations:**
  - Cause of *n*-type doping
  - Role of native point defects
  - Prospects for *p*-type doping
- **First-principles calculations**
  - Density functional theory, pseudopotentials
  - Comprehensive theoretical framework



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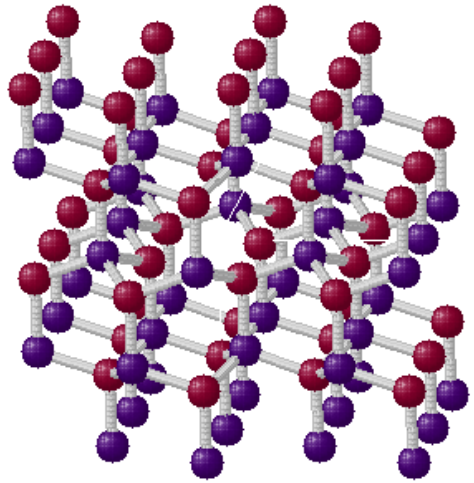
Formalism



- **E_{form}: formation energy**

  Concentration of defects or impurities:

  $C = N_{sites} \exp [- E_{form}/kT]$

- **Example: oxygen vacancy in ZnO**

  $E_{form}(V_O^{2+}) = E_{tot}(V_O^{2+}) - E_{tot}(\text{bulk}) + \mu_O + 2\,E_F$

  μ_O: energy of oxygen in reservoir, i.e., oxygen chemical potential

  E_F: energy of electron in its reservoir, i.e., the Fermi level

- **First-principles calculations:**
  - Density-functional theory (DFT), local density approximation (LDA)
  - Supercell geometry (96 atoms); pseudopotentials; plane waves

    Review: Van de Walle & Neugebauer, J. Appl. Phys. **95**, 3851 (2004).
  - Previous calculations:

Kohan *et al.* PRB **61**, 15019 (2000)
Zhang *et al.* PRB **63**, 75205 (2001)
Oba *et al.* JAP **90**, 824 (2001)
Lee *et al.* PRB **64**, 85120 (2001)

- **Need to correct for DFT-LDA deficiencies**

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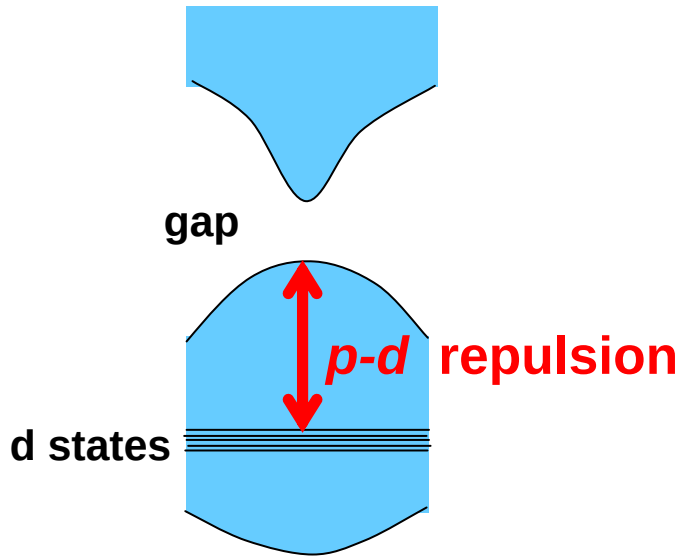
Role of Zn *d* states

- **Semicore *d* states play important role**
  - 3*d* states ~8 eV below the valence-band maximum (VBM)
  - *p-d* interaction
    - » VBM: anion *p* states
    - » *p-d* repulsion pushes the VBM up
  - Affects
    - » band lineups
    - » deformation potentials
    - » defect levels
    - » exchange coupling



- **Problem: DFT-LDA underestimates the binding energy of the semicore *d* states**
  - → **Over**estimates *p-d* couping
  - → Band gap too small / Band offsets wrong
  - → Deformation potential for VBM too small

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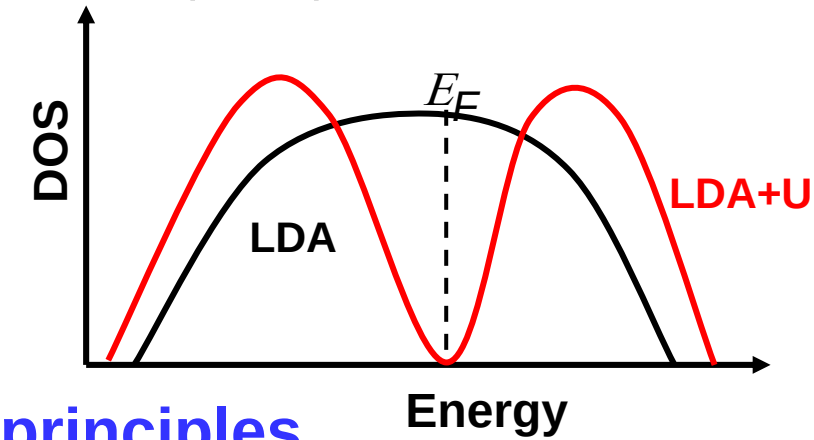
Our approach: LDA+*U*

- **Orbital-dependent correction to LDA potential**
  - Anisimov *et al.,* PRB **48**, 16929 (1993)
  - Liechtenstein *et al.*, PRB **52**, 5667 (1995)
  - Applied to filled *d* shell



- ***U* determined from first principles**
  - Atomic calculations
  - Screening in solid
- **Application to ZnO**
  - LDA → LDA+*U* to correct transition levels
    - » Lany and Zunger (2005)
  - Use to extrapolate to experimental gap

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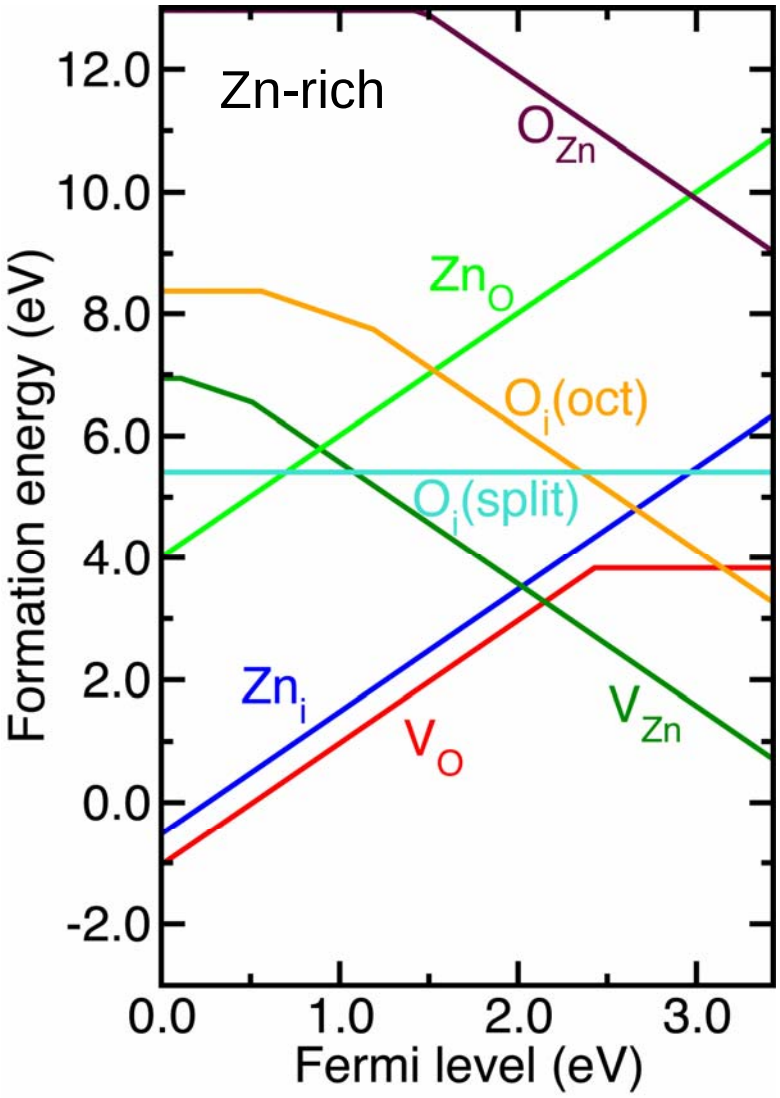
Native point defects in ZnO



- V_O, V_{Zn} dominate
- V_{Zn}: deep acceptor
- V_O: **deep donor**
  - does *not* cause unintentional *n*-type doping

A. Janotti and C. G. Van de Walle, Appl. Phys. Lett. **87**, 122102 (2005).

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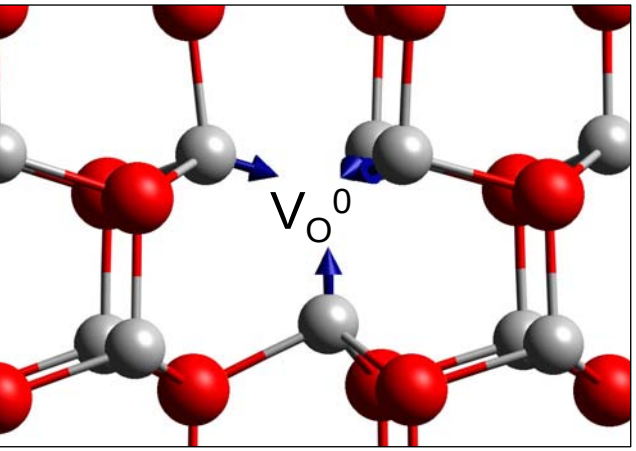
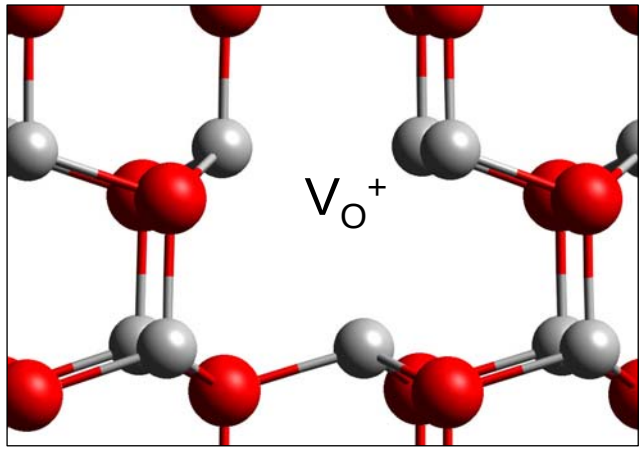
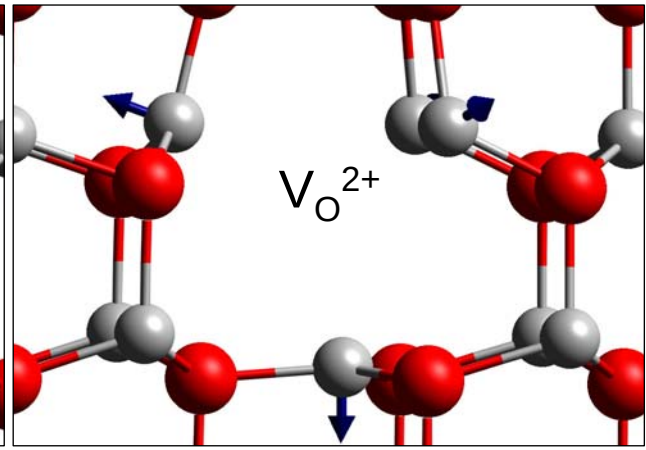
Oxygen vacancies



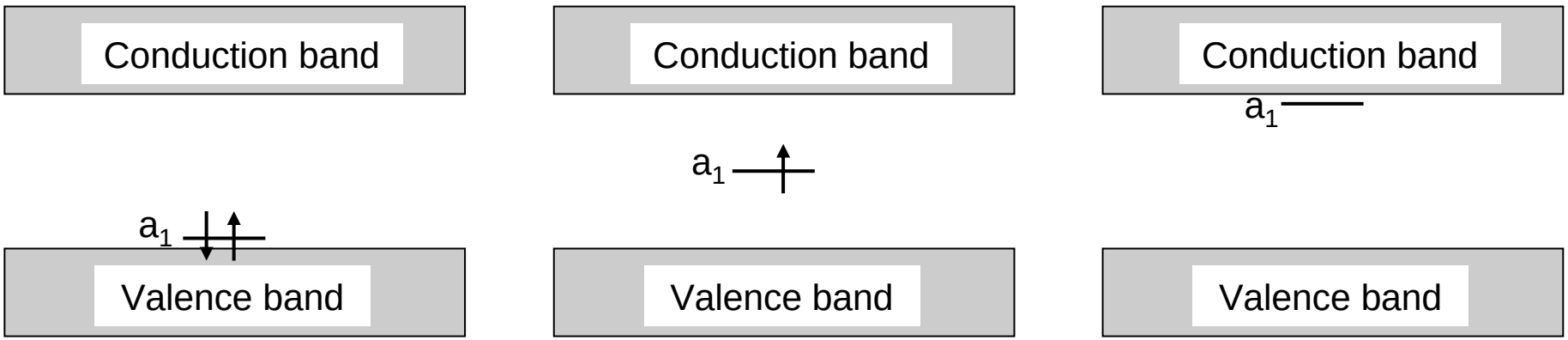




Relaxation: inward 12%

outward 2%

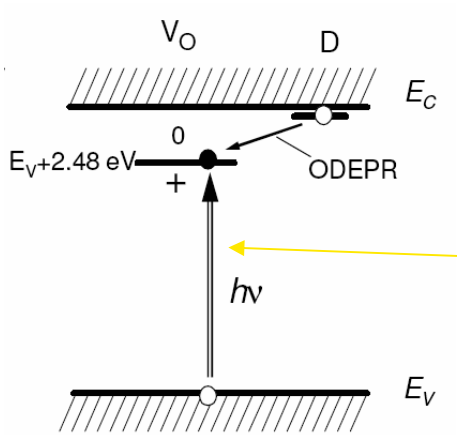
outward 23%

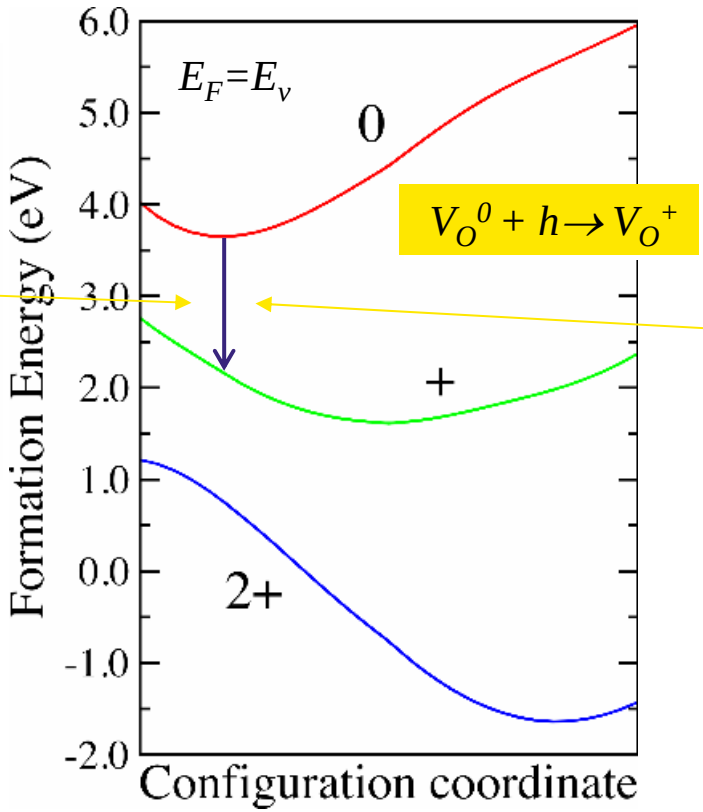


Large relaxations of nearest-neighbors Zn atoms dependent on charge state

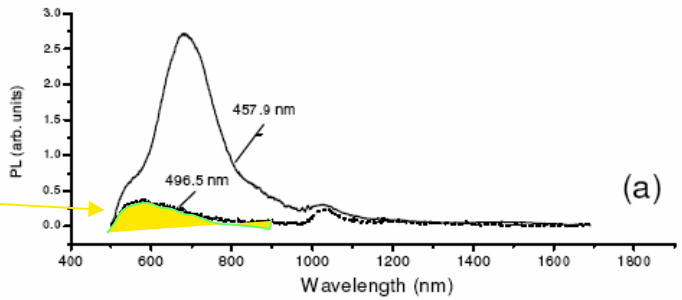
V_O: Comparison with experiment

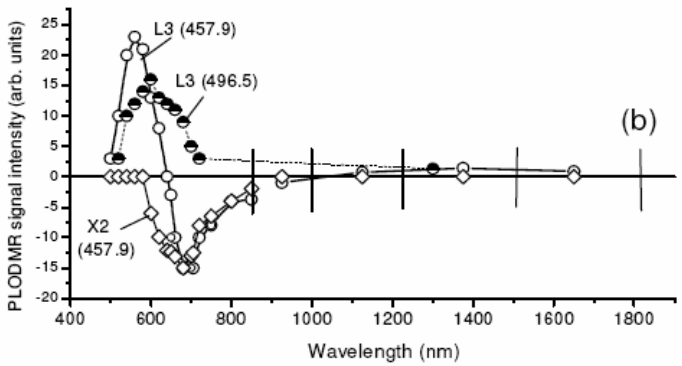
Vlasenko & Watkins, Phys. Rev. B **71**, 125210 (2005).





$V_O^0 + h \rightarrow V_O^+$





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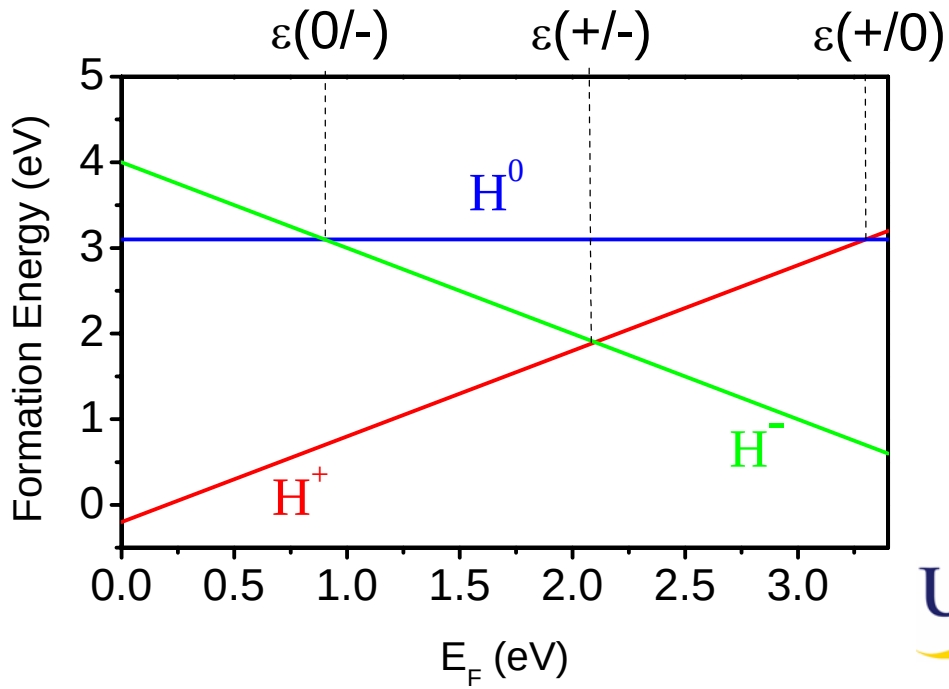
Hydrogen ???

- **In Si, Ge, GaAs, AlAs, AlN, ZnSe, …: Hydrogen amphoteric**
  - H^+ favorable in *p*-type
  - H^- favorable in *n*-type
  - always counteracts prevailing conductivity
- **Example:**
  - H in GaN



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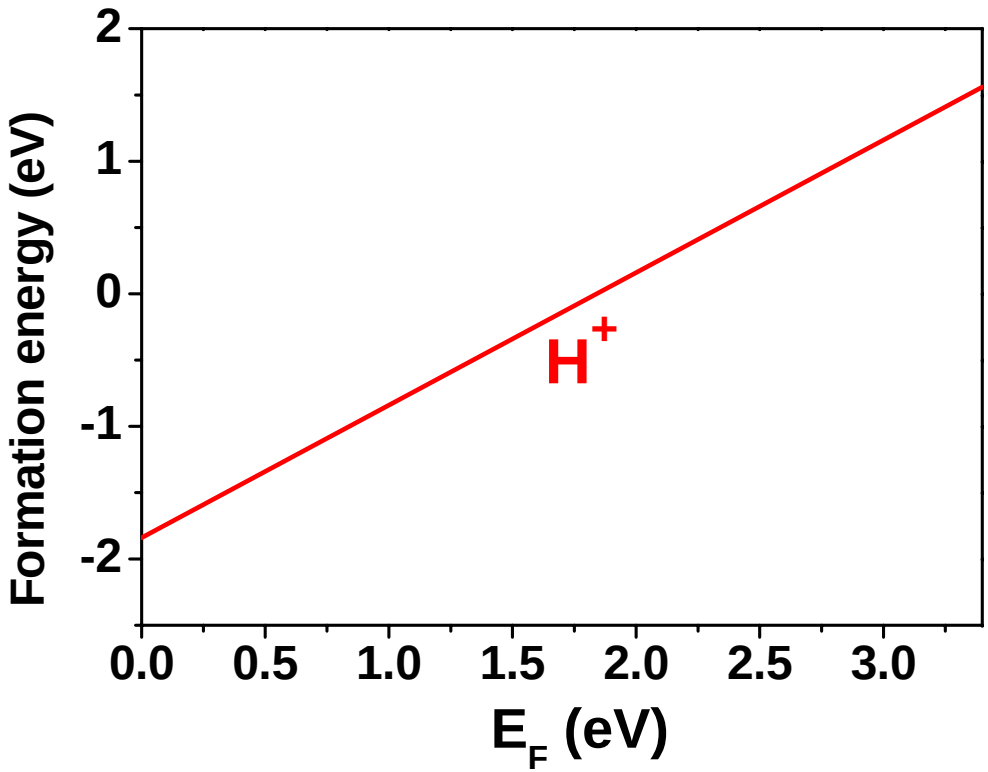
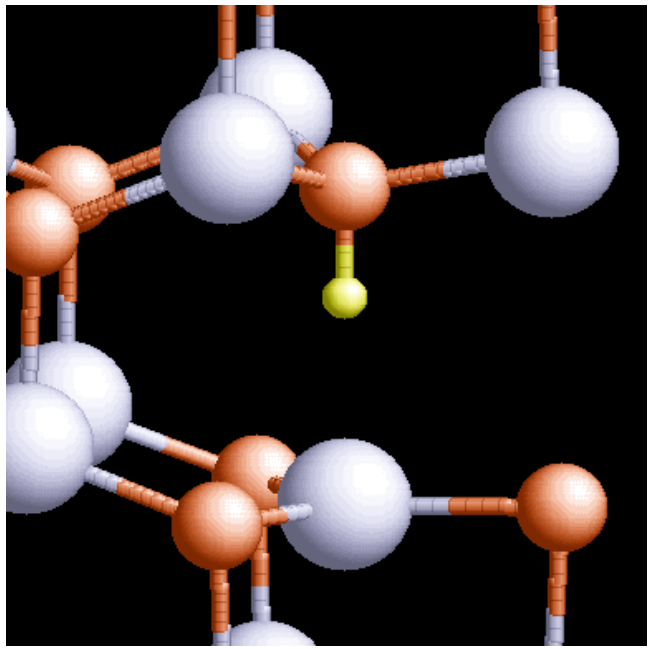
Hydrogen in ZnO





H^+ is the only stable charge state

C. G. Van de Walle, Phys. Rev. Lett. 85, 1012 (2000)

Acknowledgement: J. McCaldin

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Experiment

- **Muon spin rotation**
  - Muonium: pseudo-isotope of hydrogen
    - » Cox *et al*., Phys. Rev. Lett. **86**, 2601 (2001)
- **Electron paramagnetic resonance + ENDOR**
    - » Hofmann *et al.*, Phys. Rev. Lett. **88**, 045504 (2002)
- **Effusion**
  - Pronounced peak in effusion spectra
    - » Nickel and Brendel, PRB **68**, 193303 (2003)
- **Vibrational spectroscopy**
  - Microscopic identification of defects and complexes through calculation of local vibrational modes
- **Hydrogen as an unintentional dopant:**
  - vapor-phase transport, hydrothermal growth
  - MOCVD (sources, carrier gas), MBE (residual gas)
  - laser ablation, sputtering (H_2 atmosphere)
  - forming gas anneal

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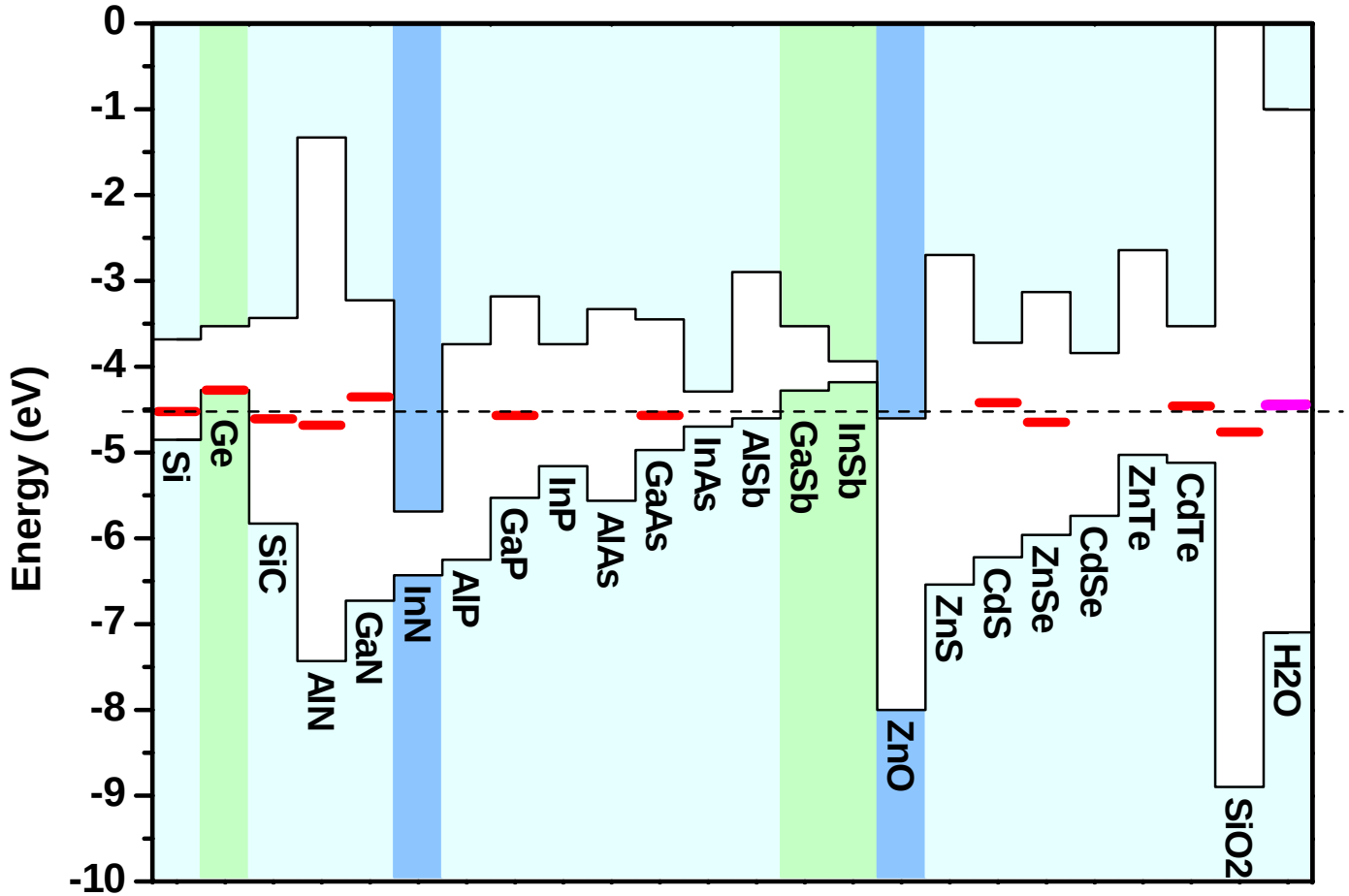
Universal alignment of hydrogen levels



C. G. Van de Walle and J. Neugebauer, Nature **423**, 626 (2003)

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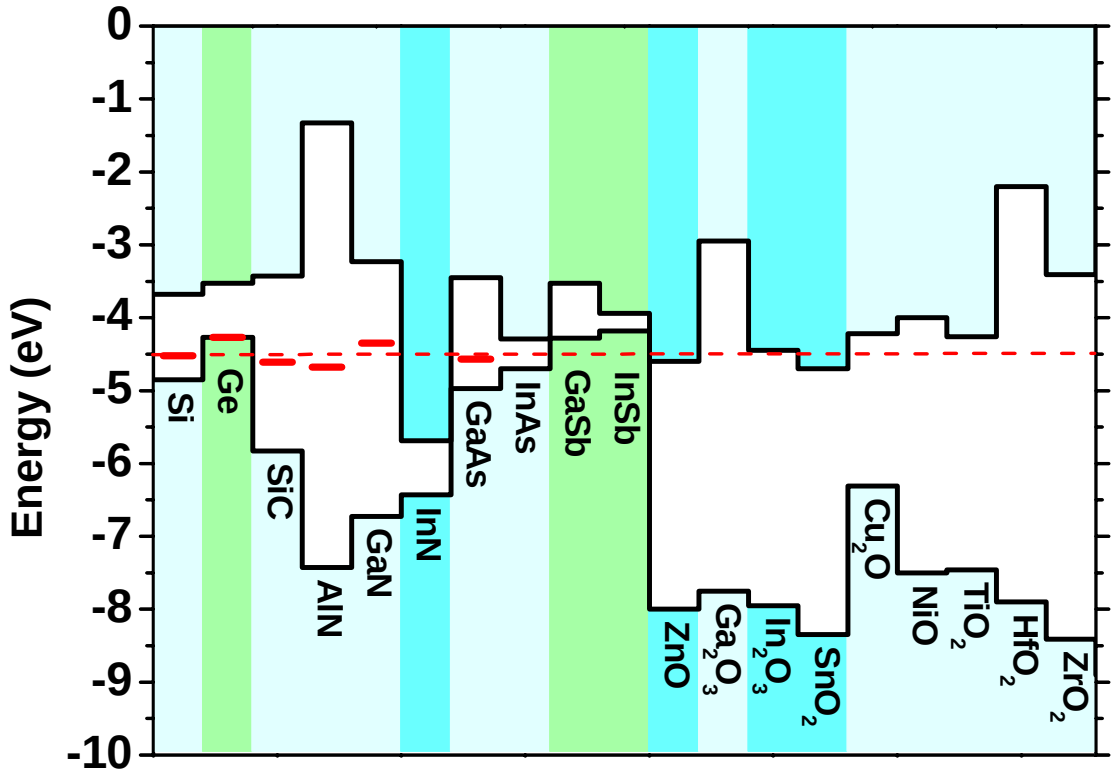
Transparent conductors

- Transparency + (almost) metallic conductivity
- Applications:
  - » Active matrix displays
  - » Solar cells
  - » VCSELS
- Cause of conductivity?

- See also C. Kilic and A. Zunger, Appl. Phys. Lett. **81**, 73 (2002)



C. G. Van de Walle and J. Neugebauer, Nature **423**, 626 (2003)

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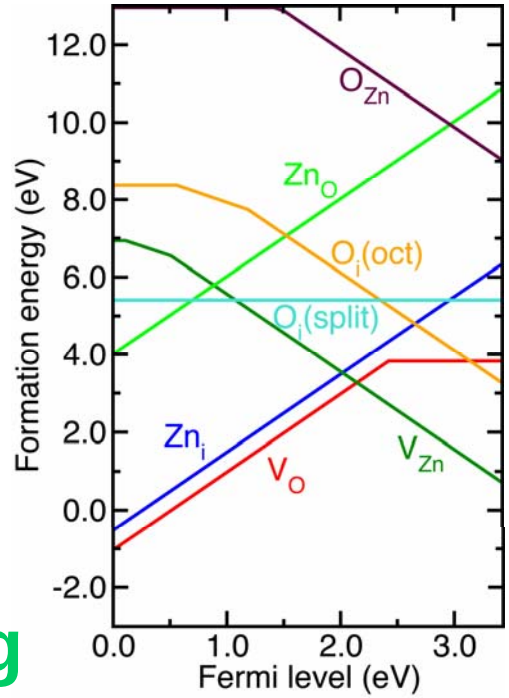
Conclusions



- **Sources of conductivity**
  - role of native defects
    - » Oxygen vacancies
  - hydrogen
- **Defect and impurity engineering**
  - from understanding to control
    - » suppressing native defects
    - » controlling incorporation of hydrogen in ZnO
      - suppressing *n*-type conductivity
      - co-doping with hydrogen to promote *p*-type conductivity
- **Role of anion vacancies in other oxides**
- **Role of hydrogen in other oxides**

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