Doping and defects in oxide semiconductors

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Acknowledgments

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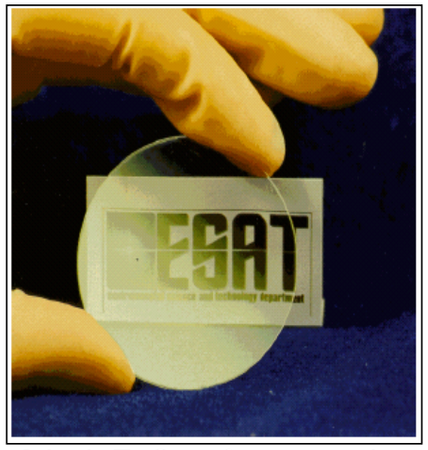
Oxide semiconductors

- **Wide range of crystal structures with interesting properties**
  - Transparent and conductors
  - “invisible” electronics
  - Light emitting diodes and laser diodes



2-inch ZnO wafer grown by Eagle-Picher Technologies

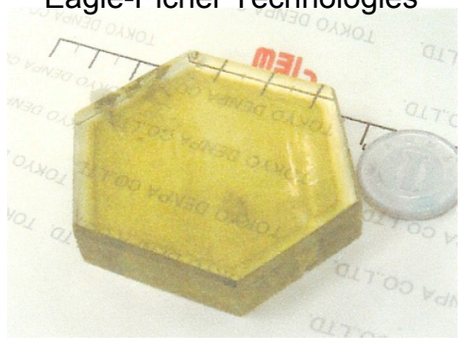
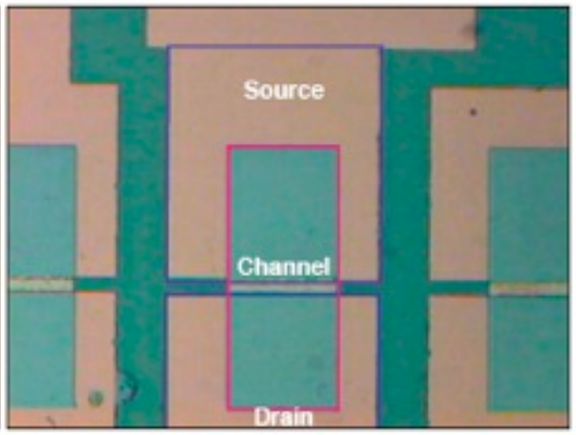
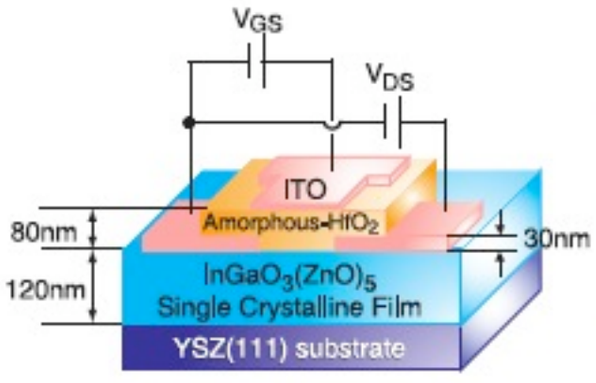


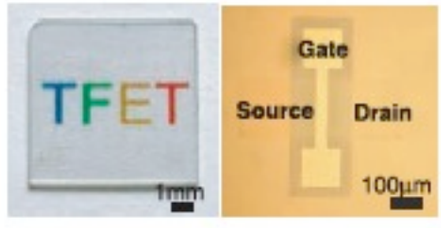
Figure 2. Photograph of a 2 inch ZnO single crystal. Maeda *et. al.*, Semicond. Sci. Technol. **20** (2005) S49-S54

ZnO

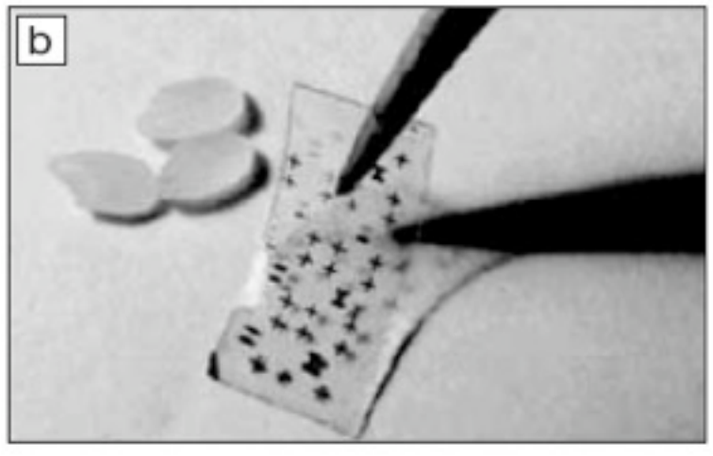


ZnO-based transparent transistors,
J. F. Wager, Science 300, 1245 (2003)





K. Nomura et al, Science 300, 1269 (2003)



“Invisible” ZnO transistor
MRS Bulletin (2003)

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Zinc oxide

"Old" multifunctional material

- most applications use polycrystalline phase

Electronics

- Nonlinear resistance in poly-ZnO
  - varistors: surge protectors
- Large piezoelectric constants
  - transducers

Chemistry

- cosmetics, sun-burn cream (block ultraviolet light)
- tire (improve abrasion resistance, tear strength)
- painting
- catalysis, gas sensors (electrical response to adsorbing molecules)

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Zinc oxide for optoelectronics

- Injection lasers
- Light-emitting diodes
  - need high crystal quality in bulk and thin films
    - low concentration of defects
  - need to control electrical conductivity
    - both *n*-type and *p*-type doping

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ZnO main problem: control of conductivity

- **As-grown ZnO is always *n*-type**
  - bulk substrates ~10^{15} - 10^{16} cm^{-3}
  - epitaxial films ~10^{16}-10^{19} cm^{-3}
- **Cause of *n*-type conductivity has been widely debated**
  - Traditionally attributed to native point defects
    - oxygen vacancies and zinc interstitials
    - conductivity varies with oxygen partial pressure
- **Very difficult to achieve *p*-type doping**

Kroger, *The Chemistry of imperfect crystals*, (North-Holland Publishing Co., Amsterdam, 1964)

Tomlins, Routbort, & Mason. J. Appl. Phys. Rev. **87**, 117 (2000).

Look, Hemsky, and Sizelove, Phys. Rev. Lett. **82**, 2552 (1999)

Look et. al., Phys. Rev. Lett. **95**, 225502 (2005)

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First-principles calculations for defects/impurities

- **Density functional Theory**
  - projector augmented wave potentials
  - local density approx. and LDA+*U*
  - periodic boundary conditions, supercells
- **Properties of interest**
  - formation energies (defect/impurity concentrations)
  - transition levels (shallow/deep donor/acceptor)
  - migration barriers (stability)
  - configuration coordinate diagrams (optical transitions)
  - frequencies of local vibration modes (direct comparison with exp.)

C. G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004)
A. Janotti and C. G. Van de Walle, Phys. Rev. B **76** 165202 (2007)

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Formalism

E_{form}: formation energies

- V_O^q oxygen vacancy in charge state q

  $E_{form}(V_O^q) = E_{tot}(ZnO{:}V_O^q) - E_{tot}(ZnO) + \mu_O + q\,E_F$

- H_i^+ interstitial hydrogen in the positive charge state

$E_{form}(H_i^+) = E_{tot}(ZnO{:}H_i^+) - E_{tot}(ZnO) - \mu_H + E_F$

μ_O: energy of oxygen in reservoir, varies from Zn-rich to O-rich

$\mu_O + \mu_{Zn} = \Delta H_f(ZnO) = -3.6$ eV formation enthalpy of ZnO

μ_H: energy of hydrogen in reservoir, H_2 molecule

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

Review: C. G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004)

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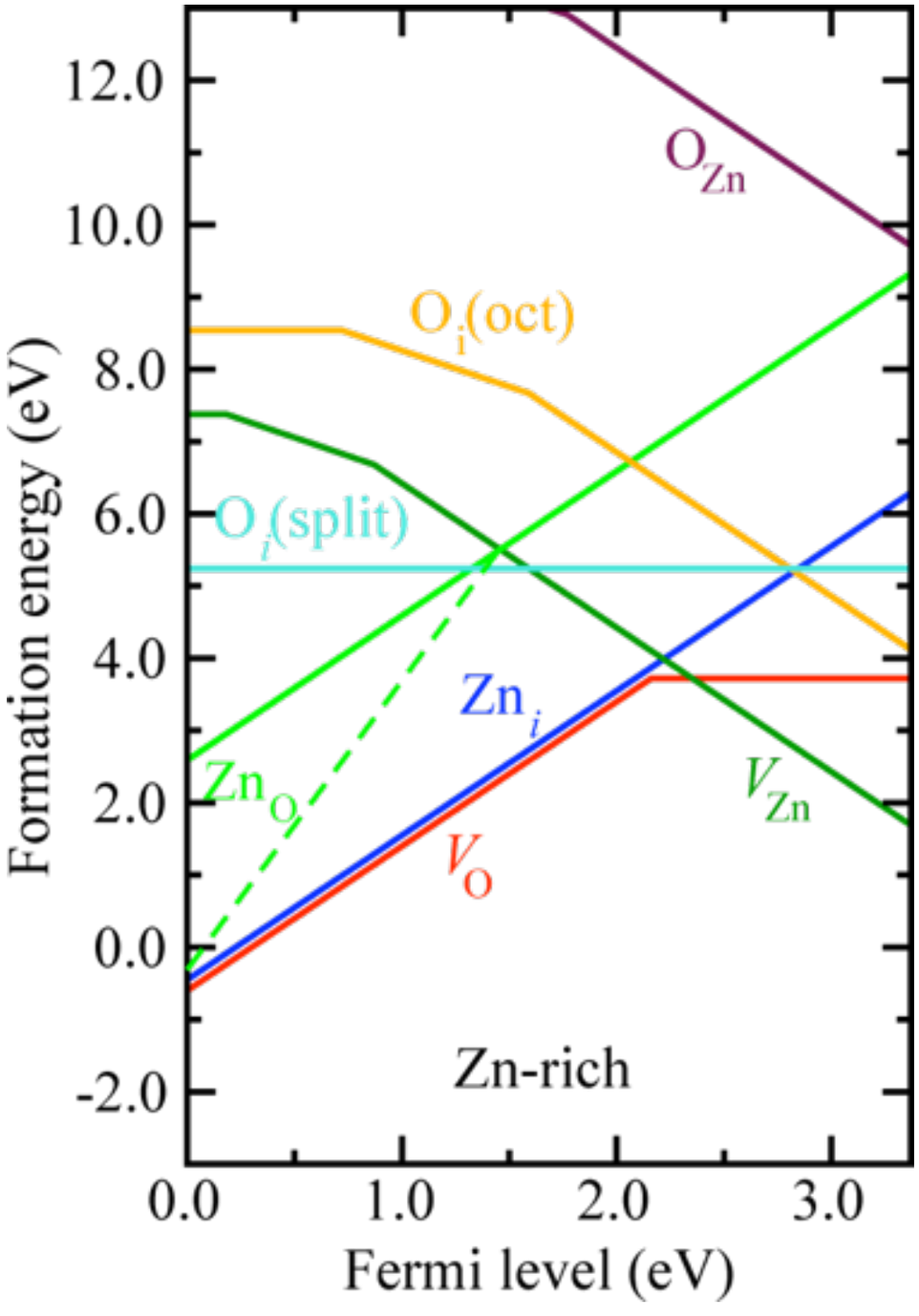
Native point defects in ZnO (Zn-rich)



Most relevant:

- Oxygen vacancies (V_O)
- Zinc interstitials (Zn_i)
- Zinc vacancies (V_{Zn})

A. Janotti and C. G. Van de Walle, Phys. Rev. B **76** 165202 (2007); Appl. Phys. Lett. **87**, 12210 (2005); J. Cryst. Growth **287**, 58 (2006)

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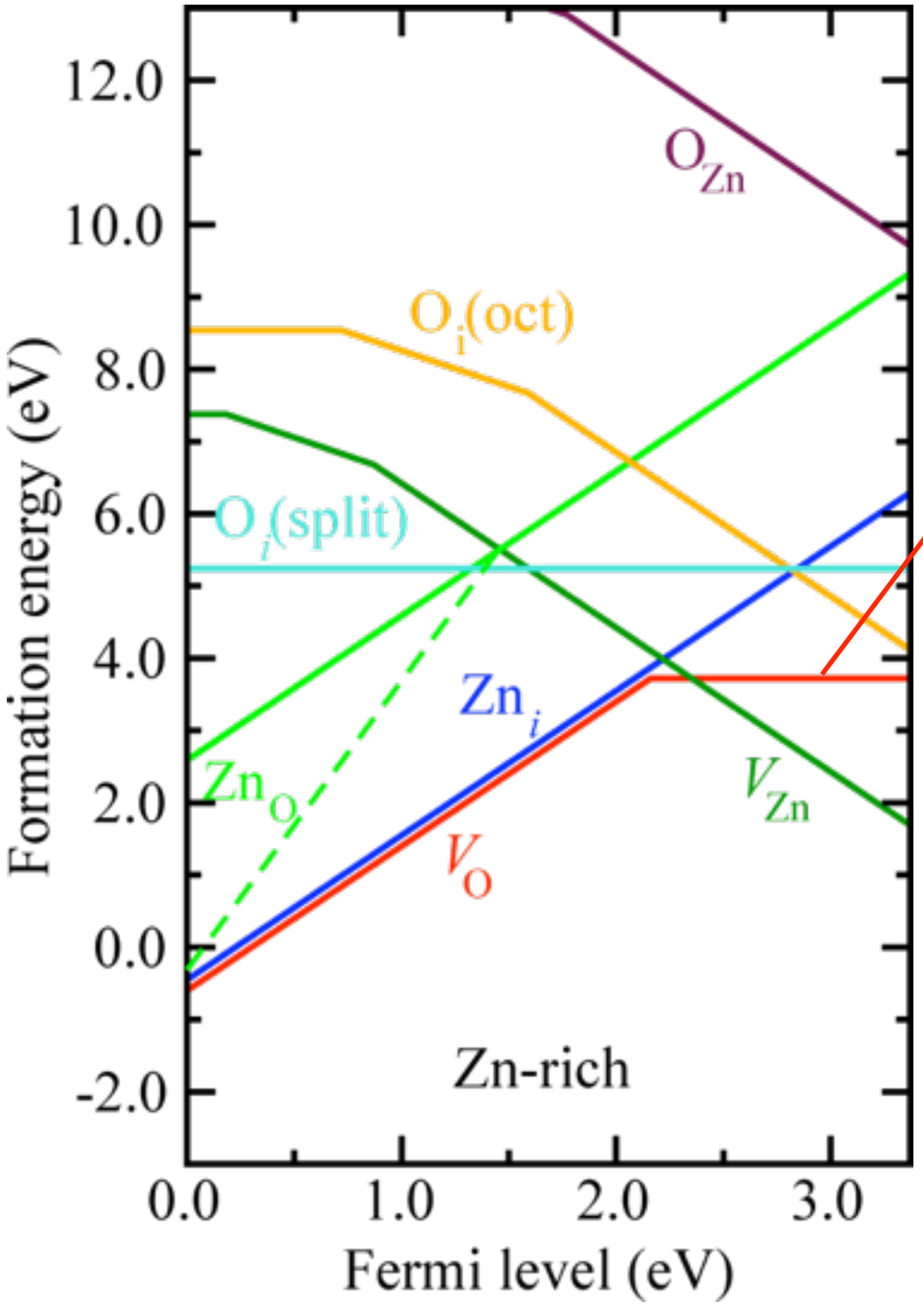
Oxygen vacancy



V_O

- deep donor - (2+/0) at ~1 eV below CBM
  cannot contribute to *n*-type conductivity
- high formation energy in *n*-type samples
  low concentrations
- low formation energy in *p*-type samples
  can compensate acceptors

A. Janotti and C. G. Van de Walle, Phys. Rev. B **76** 165202 (2007);
Appl. Phys. Lett. **87**, 12210 (2005); J. Cryst. Growth **287**, 58 (2006)

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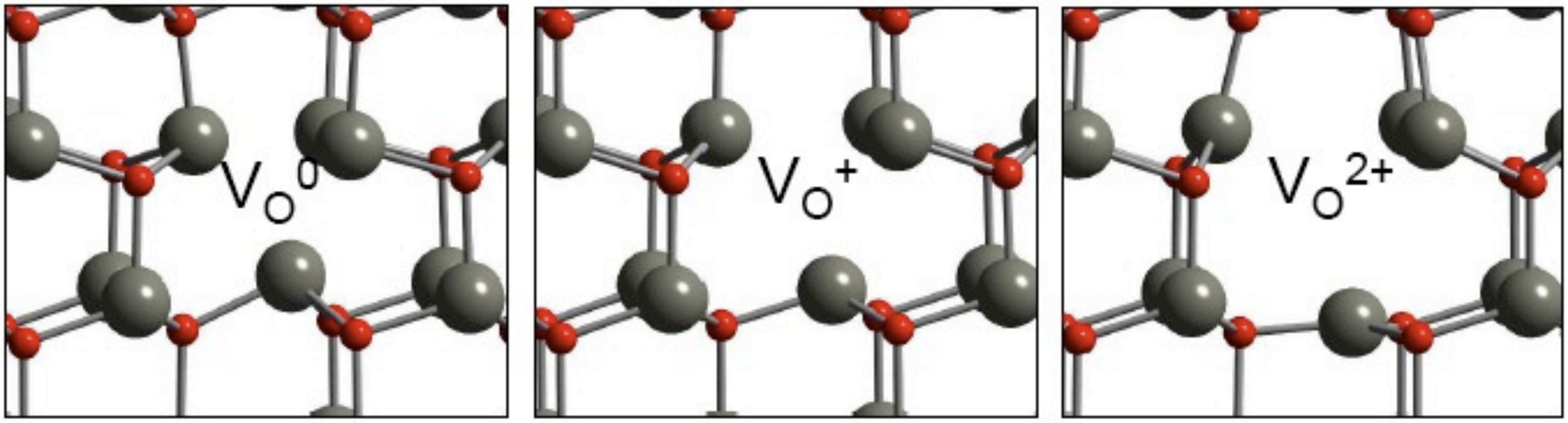
Oxygen vacancy - very large local relaxations



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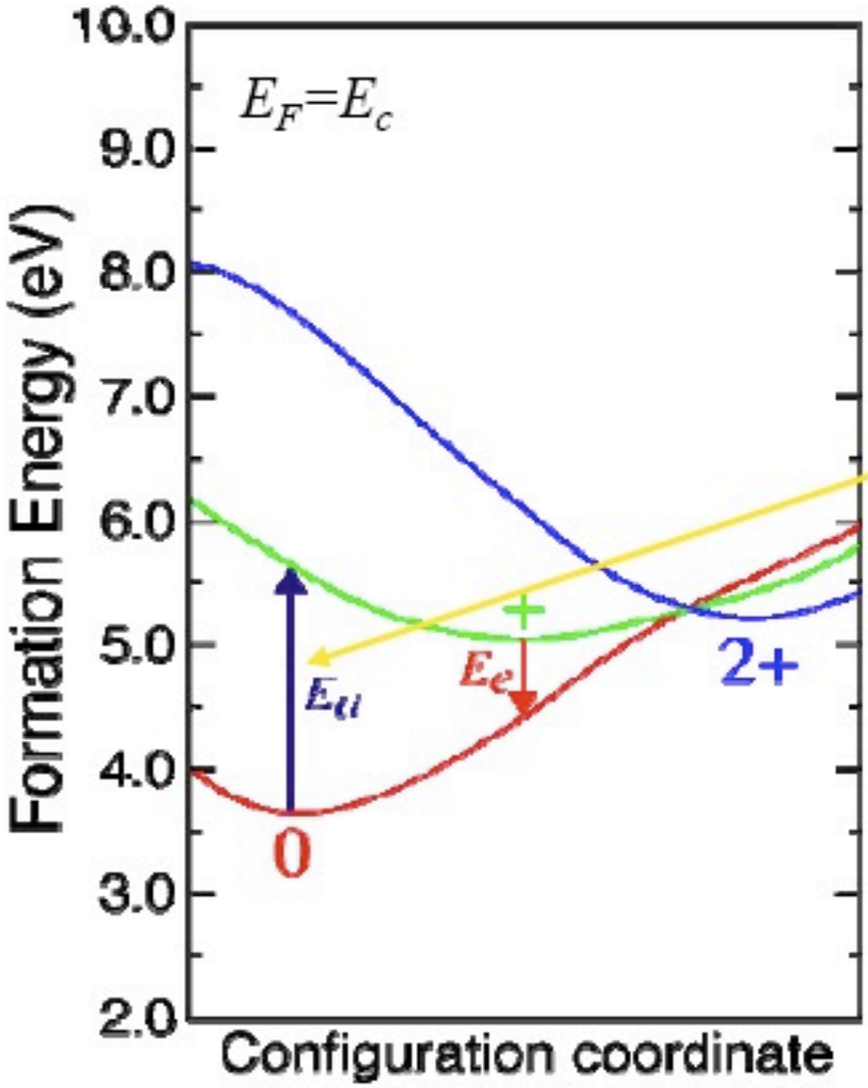
Oxygen vacancy - comparison with experiments

Evans, Giles, Halliburton & Kappers, J. Appl. Phys. **103**, 043710 (2008).

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

V_O created by irradiation

2.1 eV treshold for $V_O^0 \rightarrow V_O^+ + e$



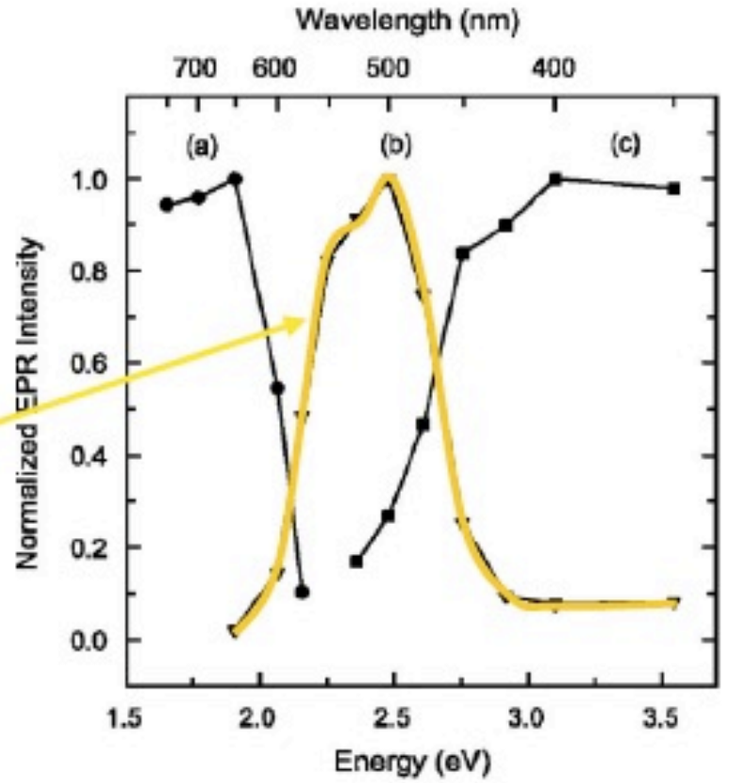


FIG. 4. Wavelength dependence of changes in charge state while illuminating at 30 K. The monitored EPR signals are (a) Fe^{3+} ions, (b) singly ionized oxygen vacancies (V_O^+), and (c) zinc vacancies with a OH^- ion at an adjacent oxygen site, i.e., $(V_{Zn}^-\text{-}H^+)^0$ centers.

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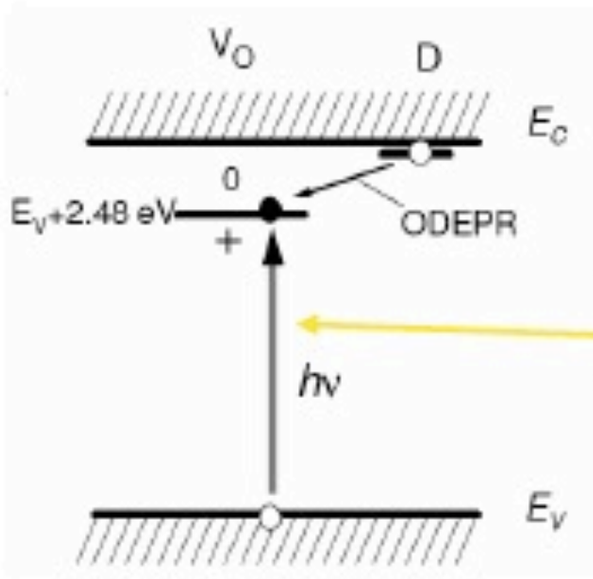
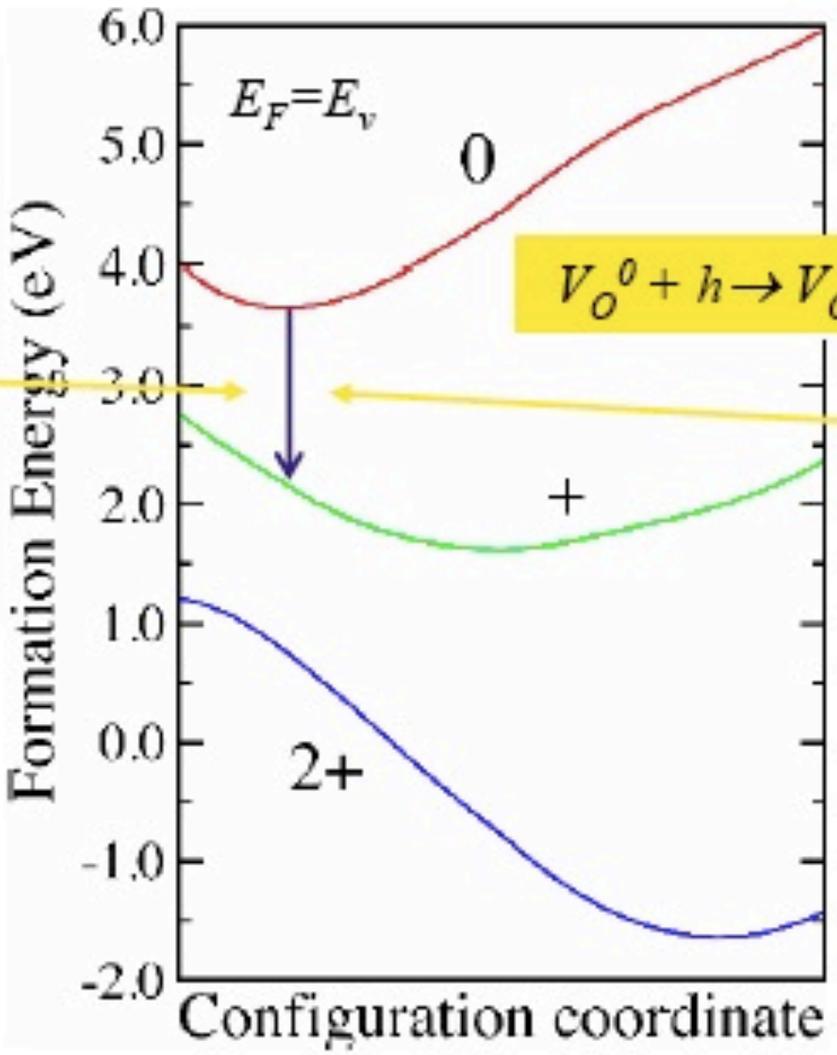
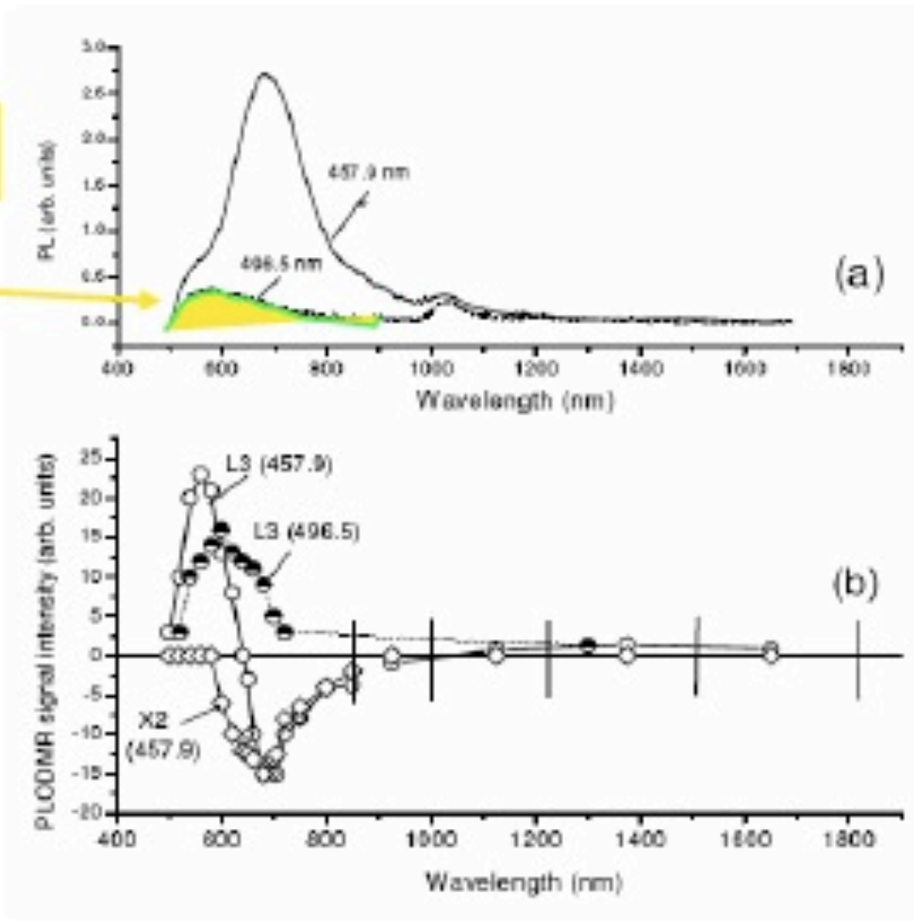
Oxygen vacancy - comparison with experiments

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

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







Need to ***create*** V_O by irradiation!
No V_O observed in as-grown material.
Consistent with high formation energy.

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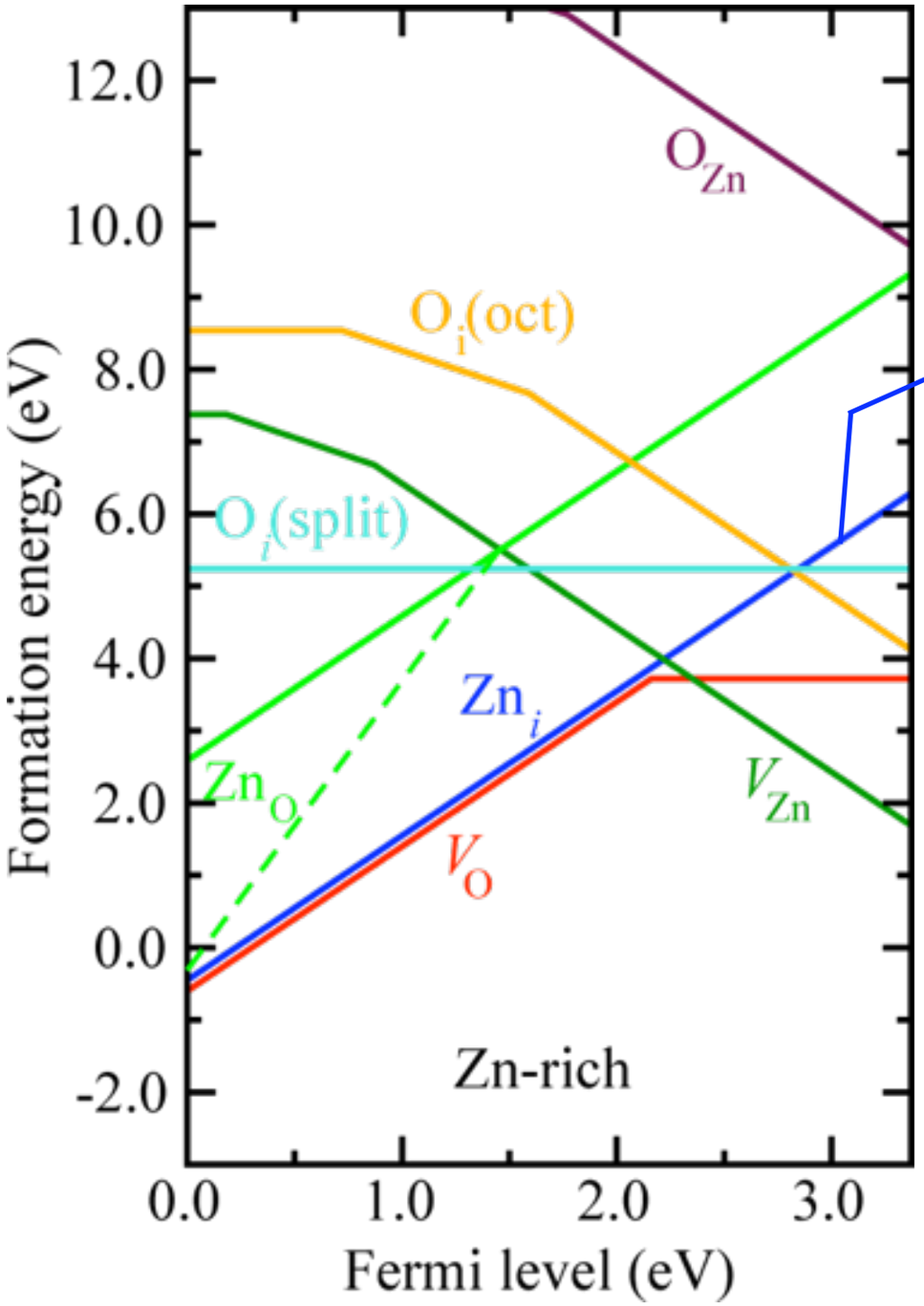
Zinc interstitial



Zn_i

- shallow donor
- very **high** formation energy in *n*-type samples
  very **low** concentrations
- low migration barrier of 0.6 eV
  unstable

A. Janotti and C. G. Van de Walle, Phys. Rev. B **76** 165202 (2007);
Appl. Phys. Lett. **87**, 12210 (2005); J. Cryst. Growth **287**, 58 (2006)

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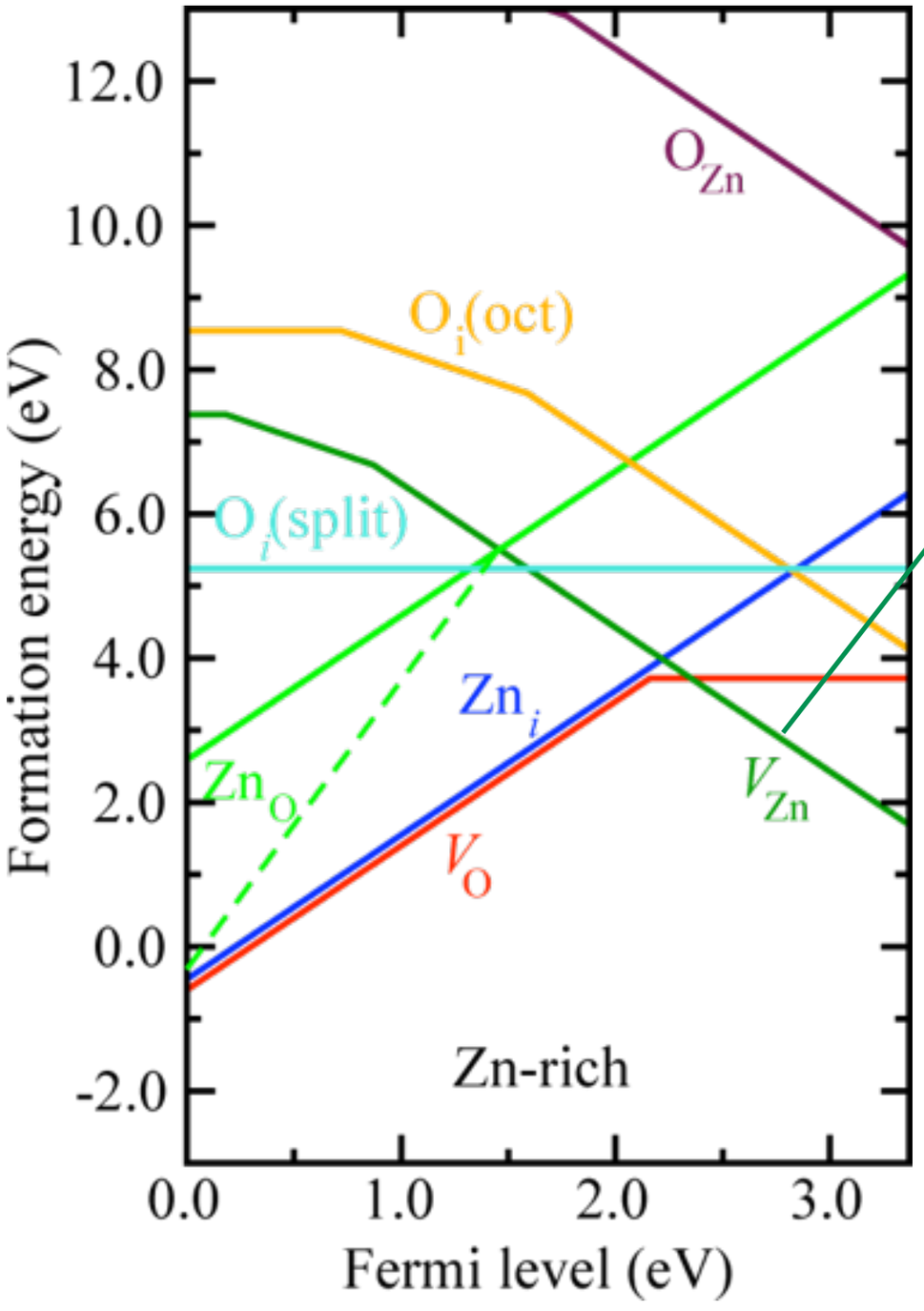
Zinc vacancy



V_{Zn}

- deep acceptor, (-/2-) ~0.9 eV above VBM
- low formation energy in *n*-type samples
  - high concentrations
- likely cause of green luminescence
- not relevant in *p*-type samples

A. Janotti and C. G. Van de Walle, Phys. Rev. B **76** 165202 (2007); Appl. Phys. Lett. **87**, 12210 (2005); J. Cryst. Growth **287**, 58 (2006)

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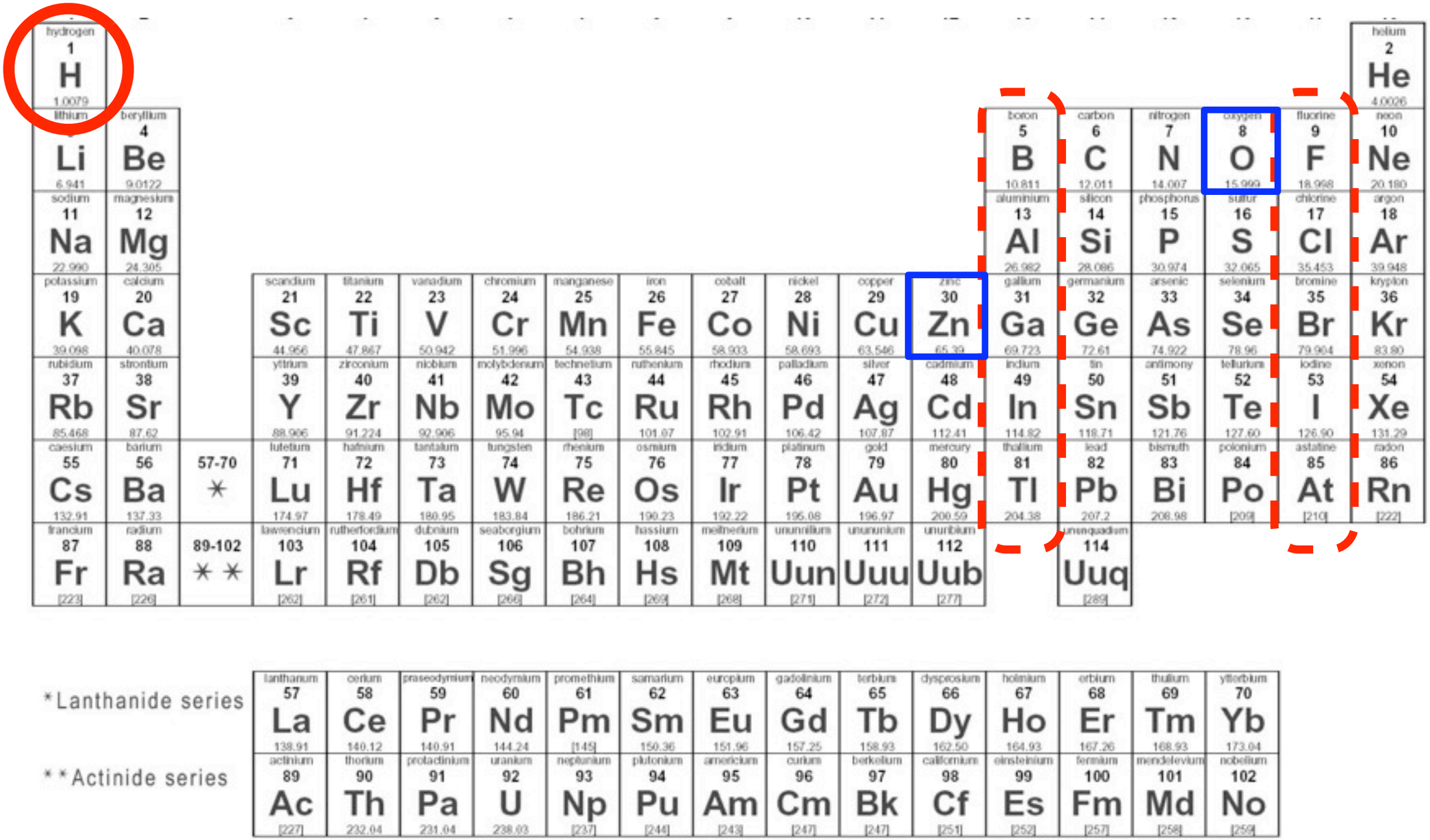
Possible donor impurities in ZnO



- **Hydrogen is present in almost growth and processing environments**
- **difficult to avoid hydrogen incorporation**

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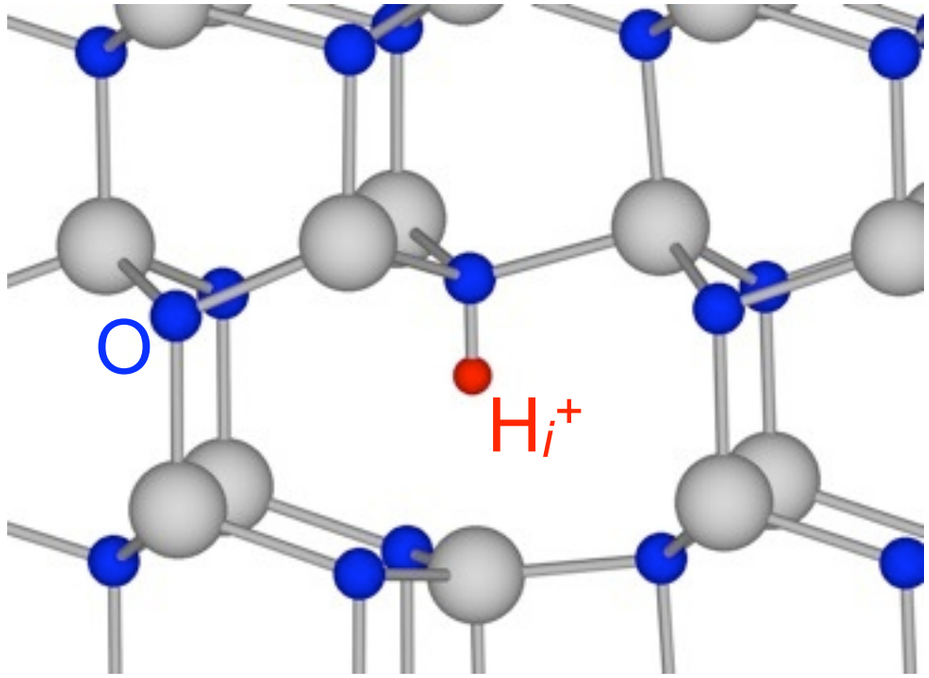
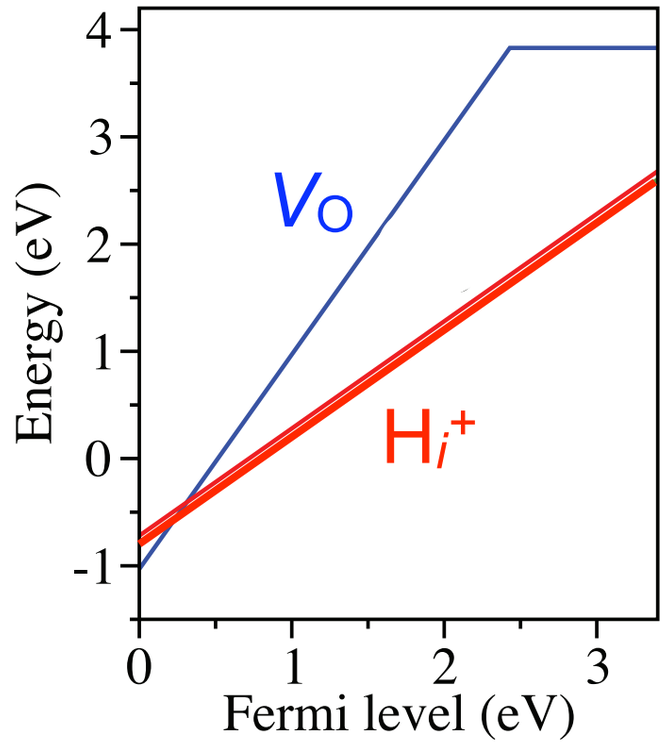
Interstitial hydrogen in ZnO

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





- **Low formation energy** (consistent with observed solubility)
- **Shallow donor** (consistent with observed electron concentrations)
- **Low migration barrier of ~0.9 eV**

  [unstable at temperatures where *n*-type conductivity is known to persist (~500°C)]
- **Cannot explain observed dependence of conductivity on oxygen pressure**

  (main argument in favor of oxygen vacancies)

Hofmann et. al, Phys. Rev. Lett. **88**, 45504 (2002)
Jokela and McCluskey, Phys. Rev. B **72**, 113201 (2005)
Shi, et. al, Phys. Rev. B **72**, 195211 (2005)

Have to reconsider the role of hydrogen...

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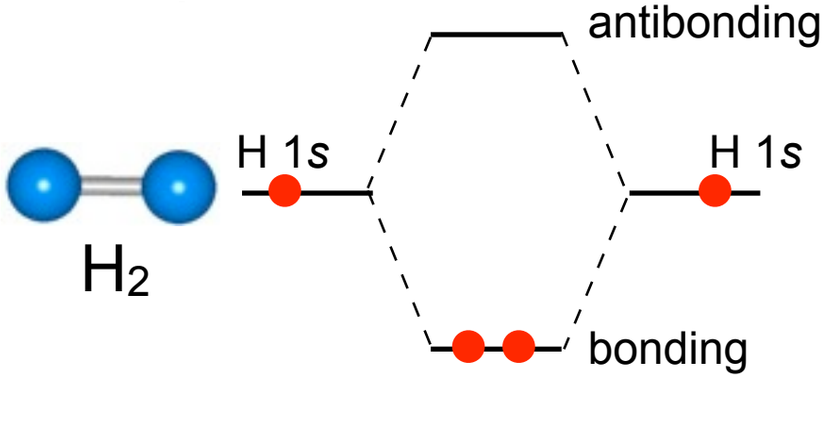
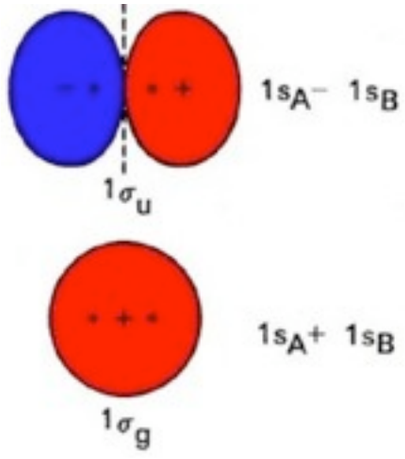
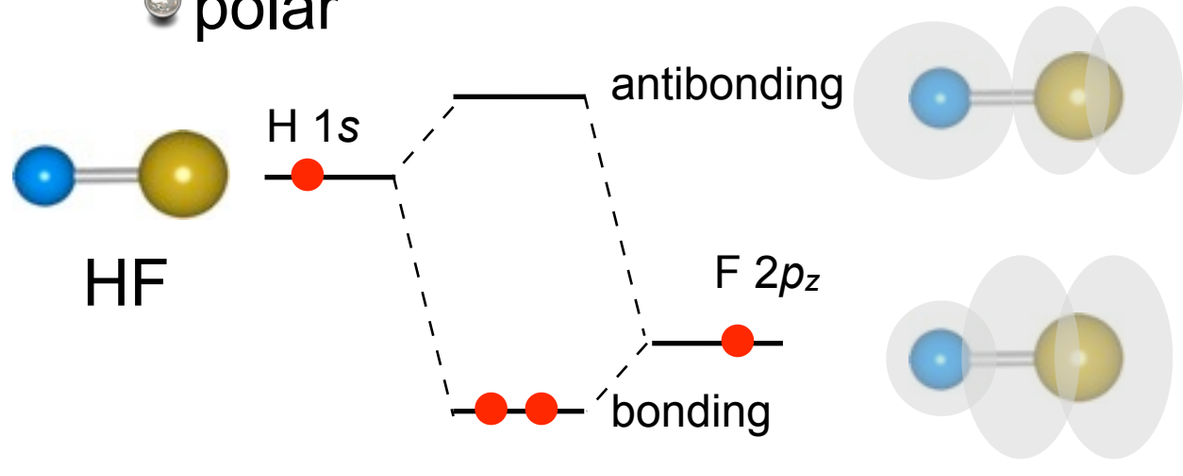
Hydrogen in molecules

- “pure” covalent

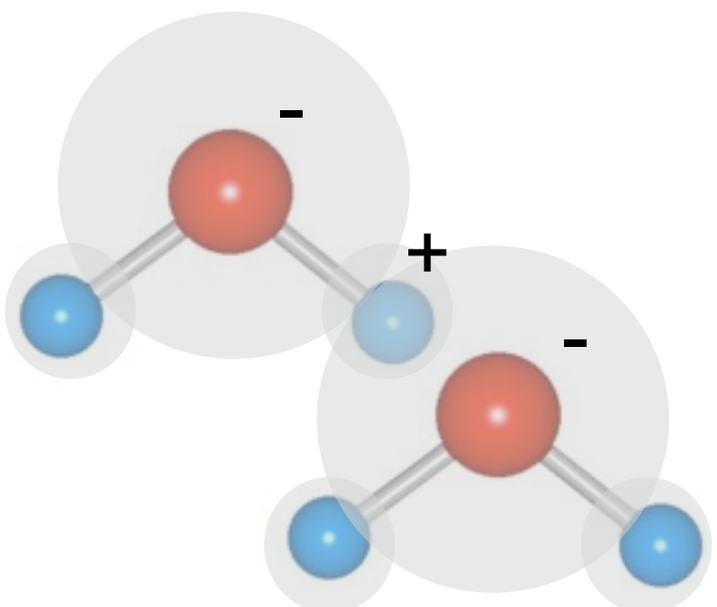




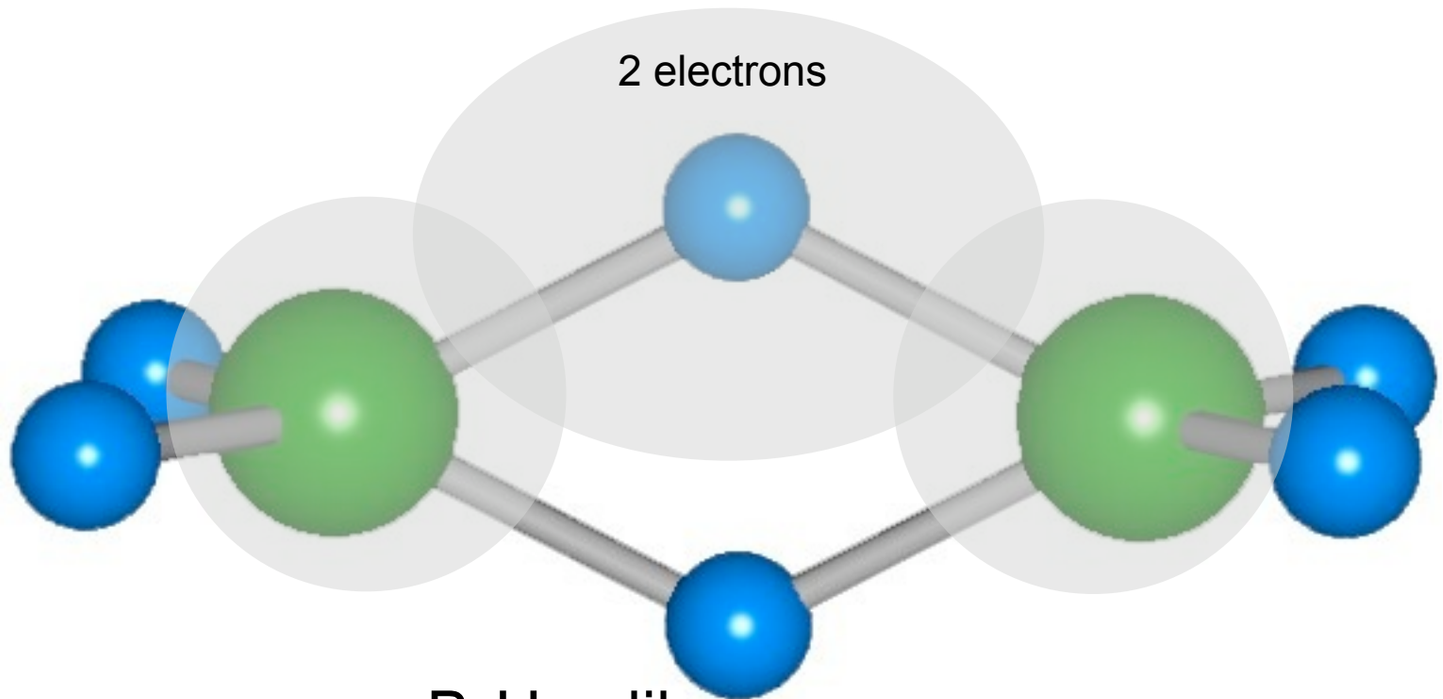
- polar



- intermolecular
(hydrogen bonding)

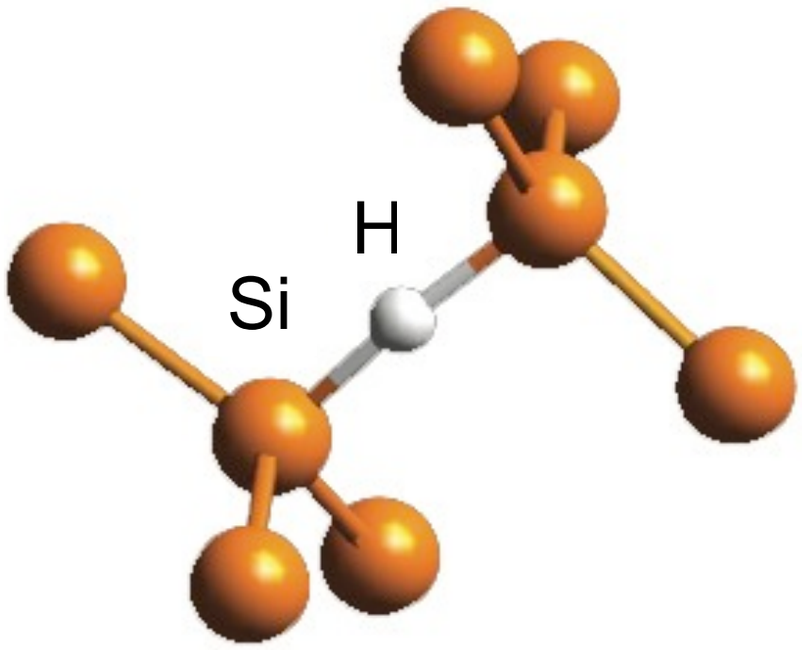


- 3-center 2-electron bonds
(Lipscomb, Nobel Prize in Chemistry1976)



Hydrogen in solids

- can bond to different types of host atoms
  - bonds to the anion
  - bonds to the cation
  - bond-center (Si-H-Si)



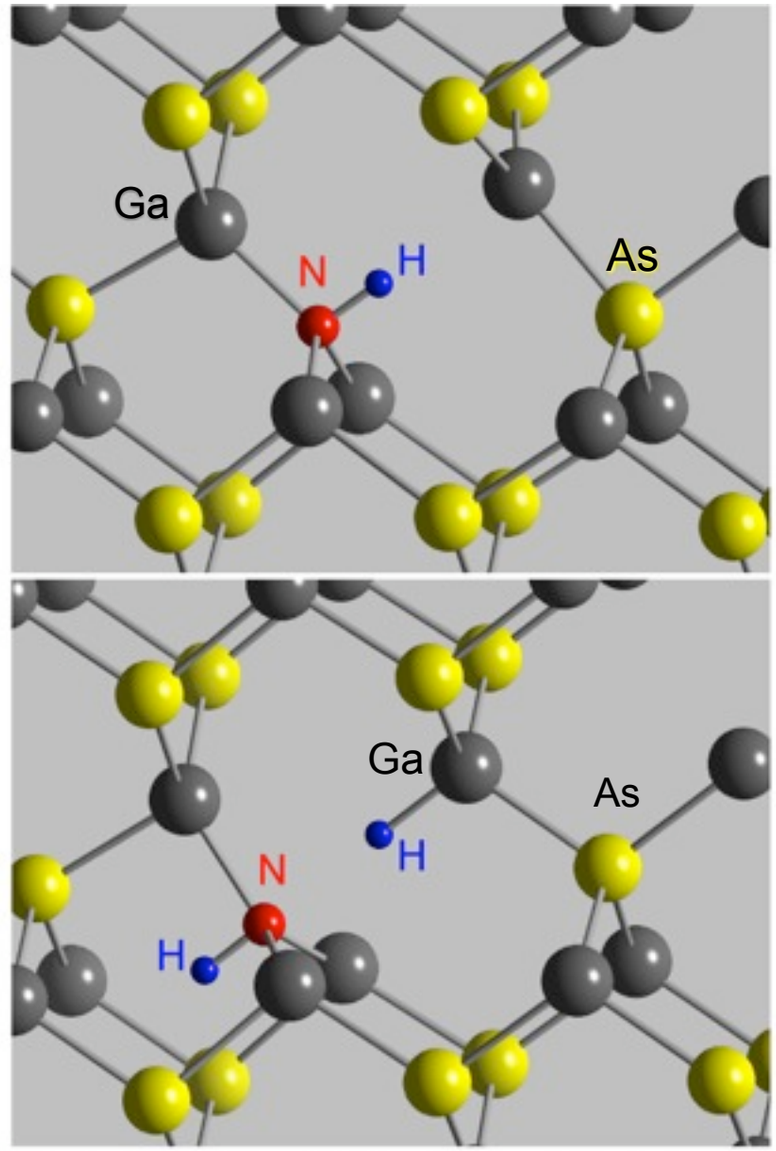


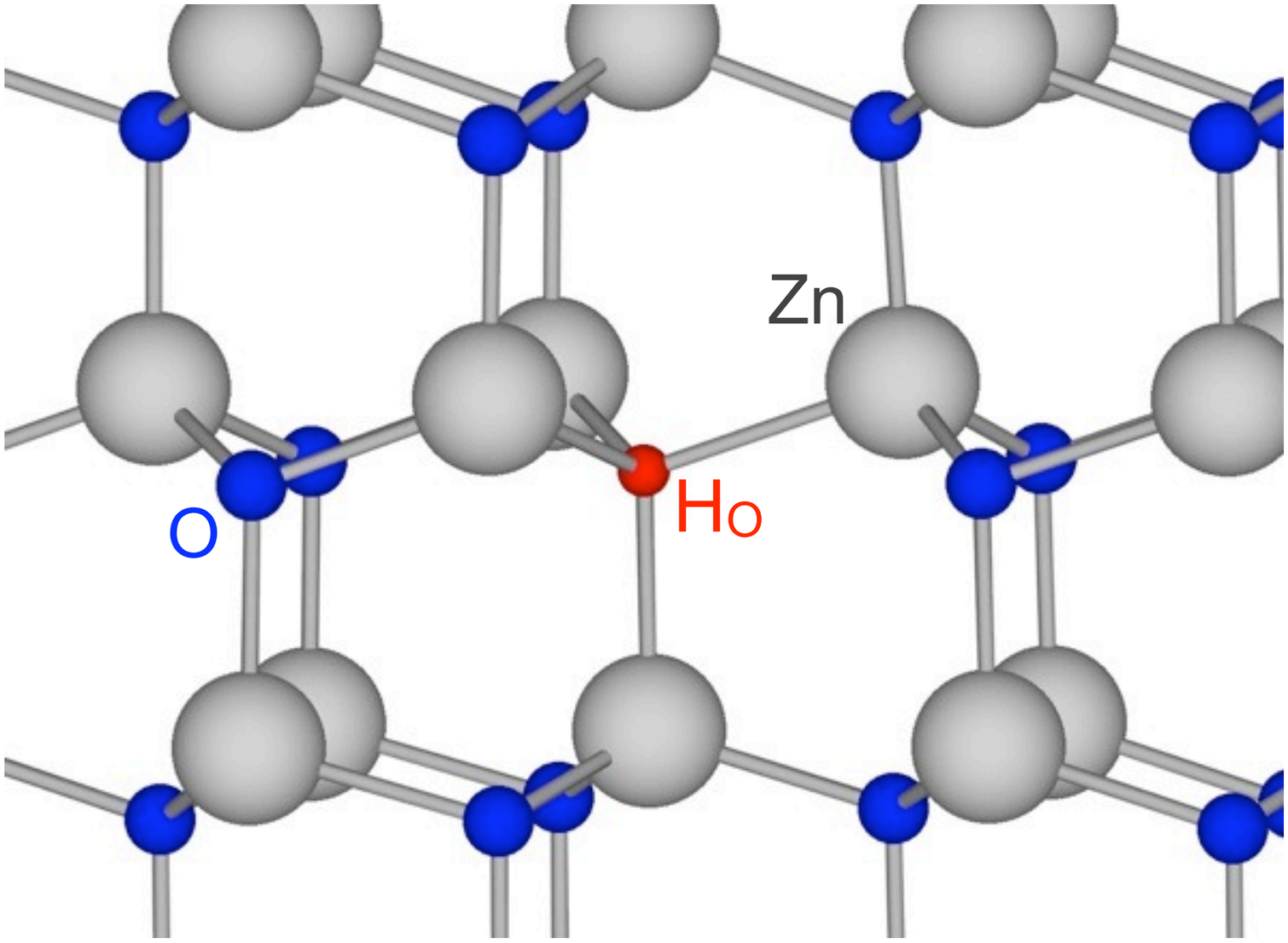
Fig 1. (a) N-H and (b) N-H_2* models in dilute GaAsN alloys

Janotti, Wei, Zhang, Van de Walle, Phys. Rev. Lett. 89, 086403 (2002)

Current understanding

- **hydrogen bonds to only one atom**
- **in exceptional cases, to two other atoms**

Hydrogen can also occupy O sites in oxides



- **H forms a multicenter bond**
- * *equally* bonds to the four Zn neighbors

A. Janotti and C. G. Van de Walle, Nature Materials **6**, 44 (2007)

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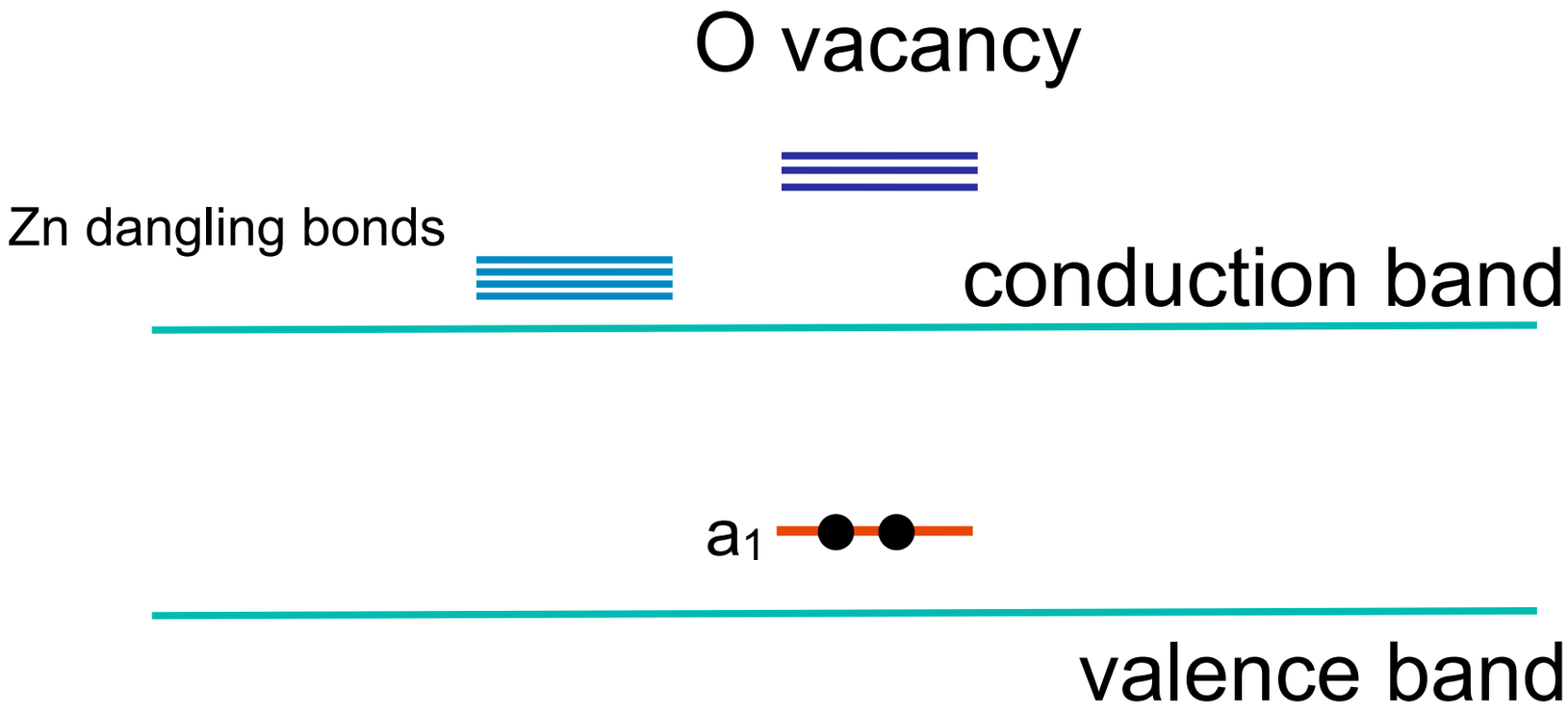
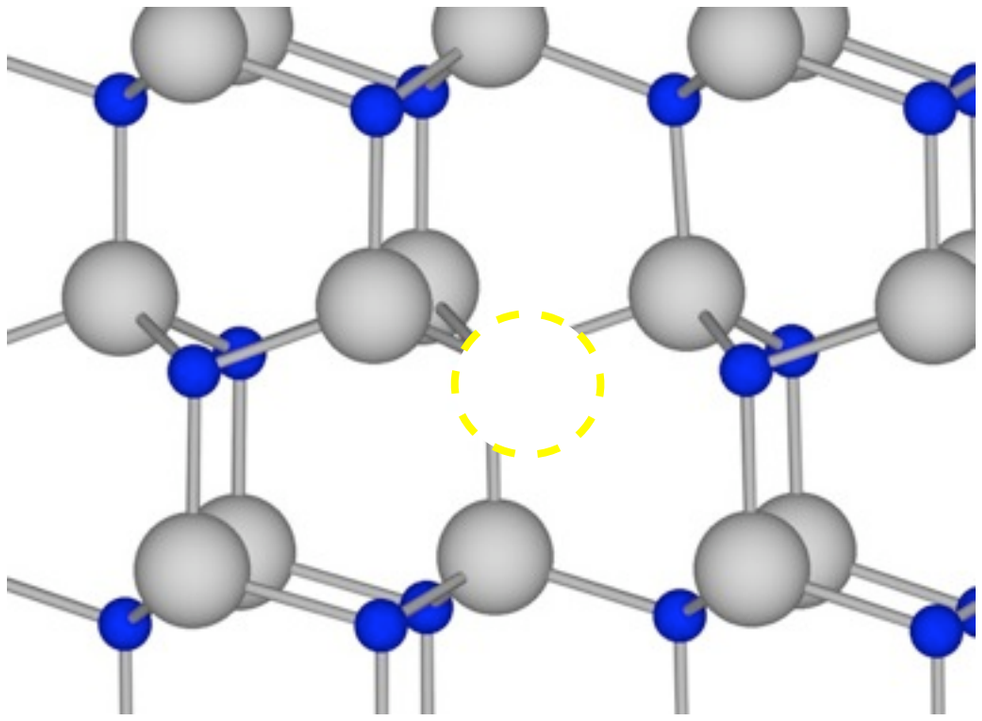
Oxygen vacancy in ZnO





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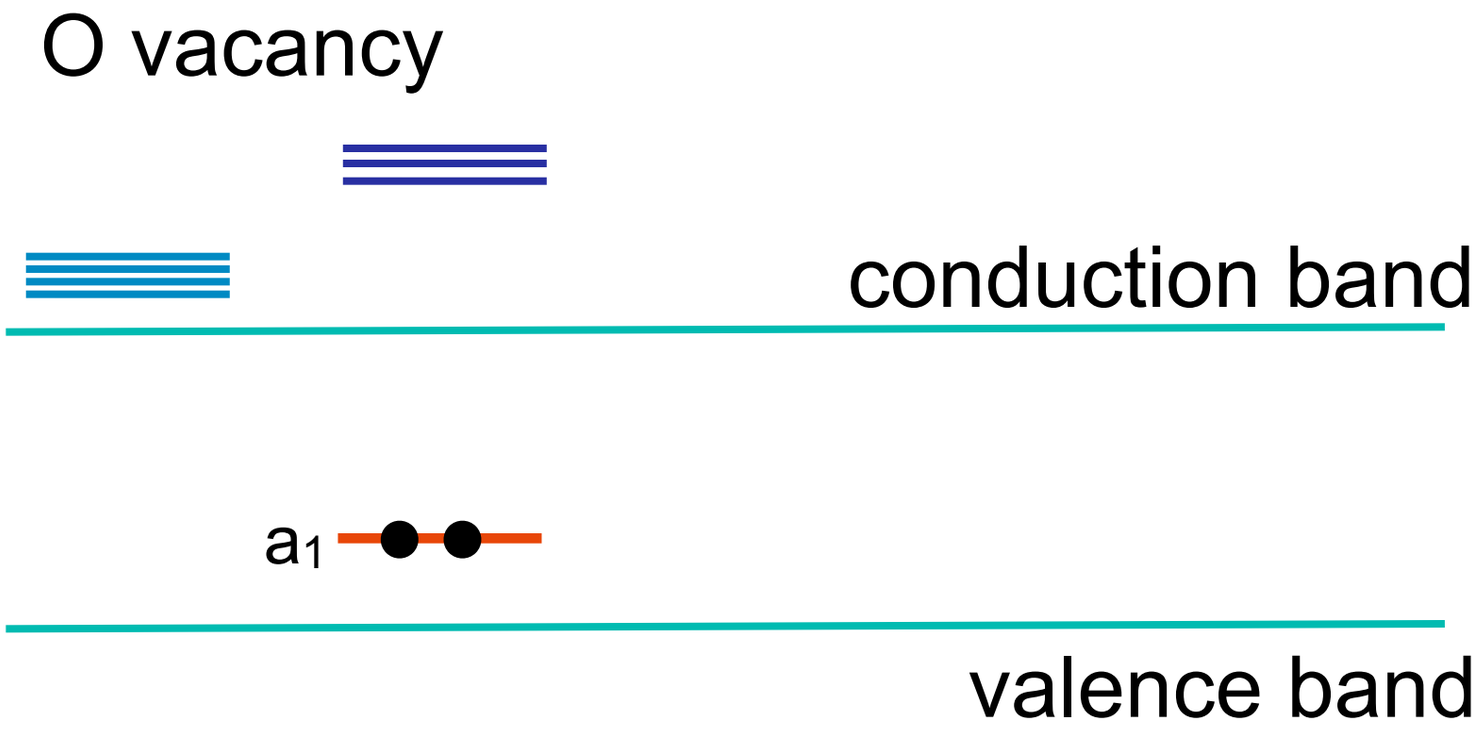
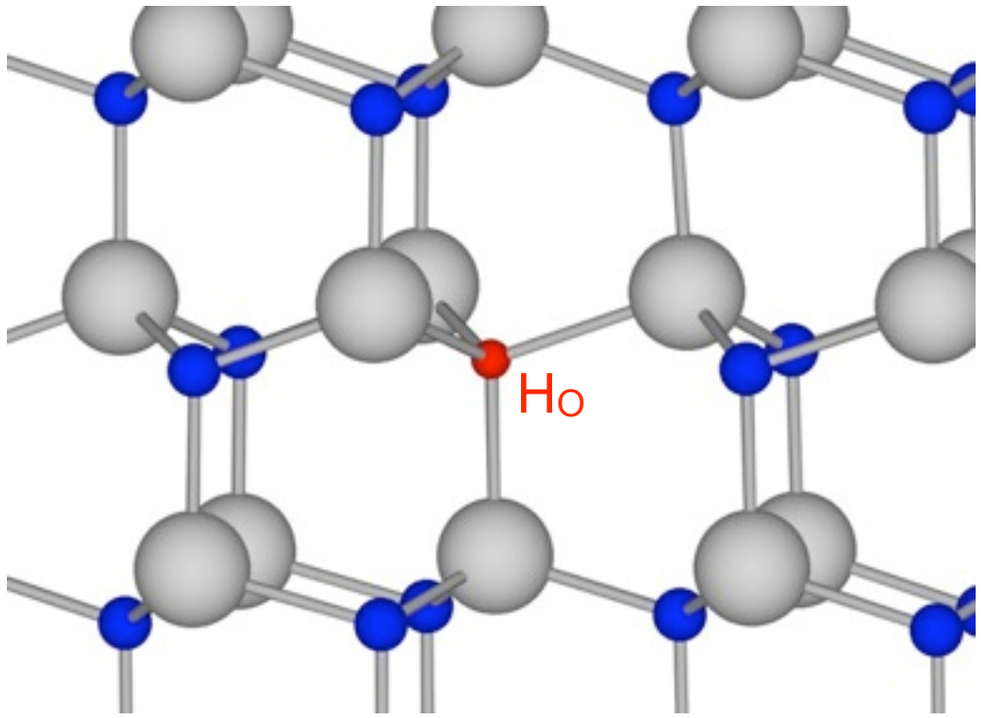
Hydrogen multicenter bond in ZnO





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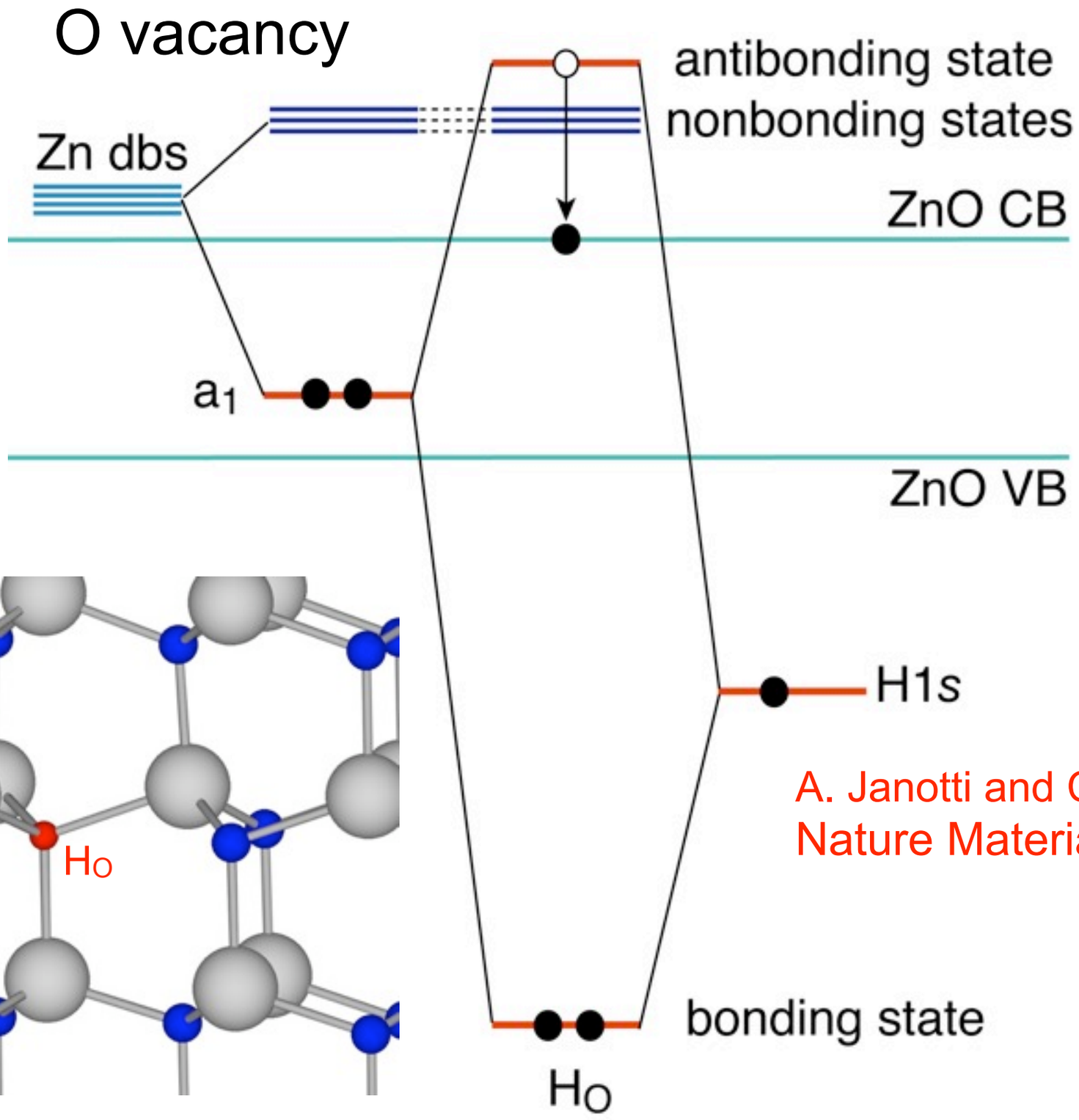
Hydrogen multicenter bond in ZnO



A. Janotti and C. G. Van de Walle,
Nature Materials **6**, 44 (2007)

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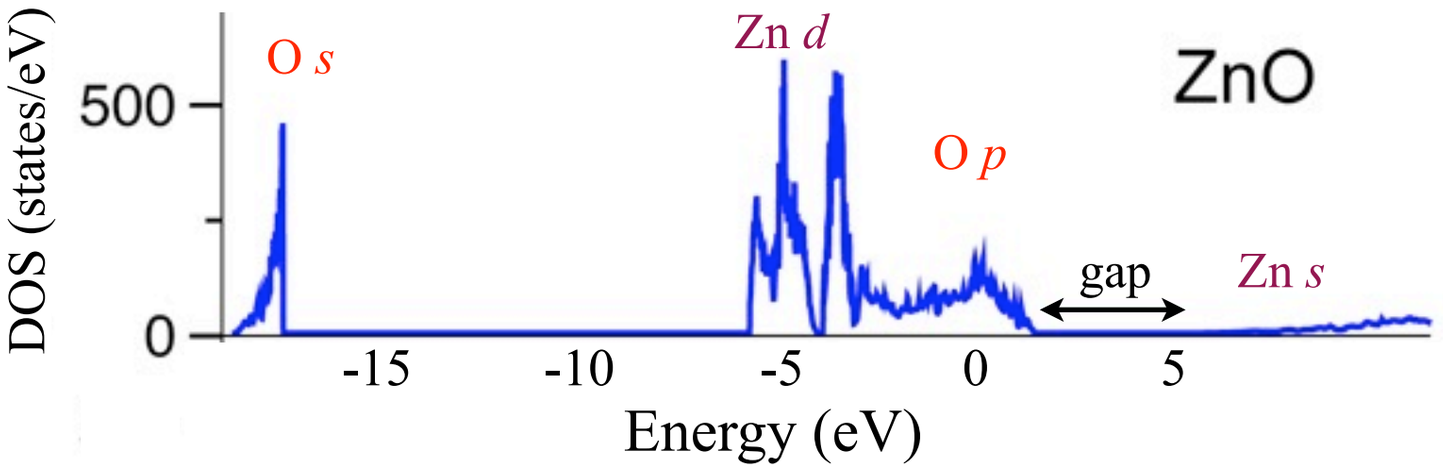
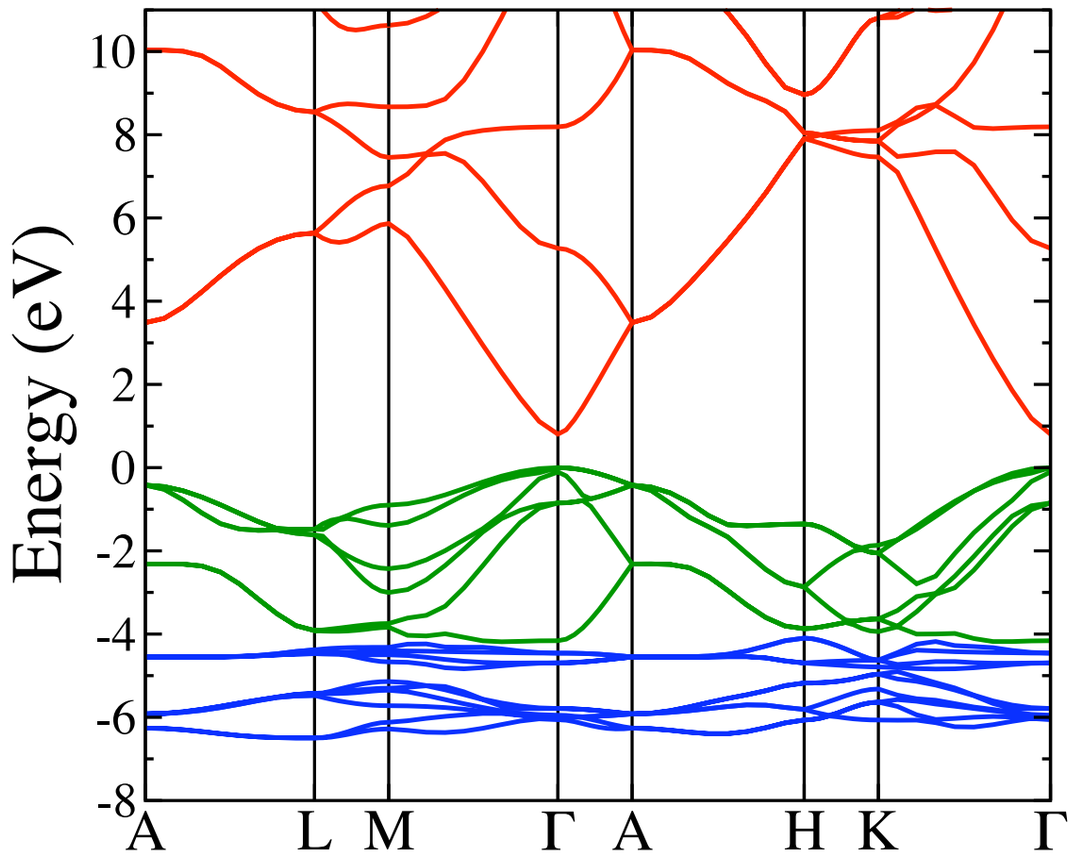
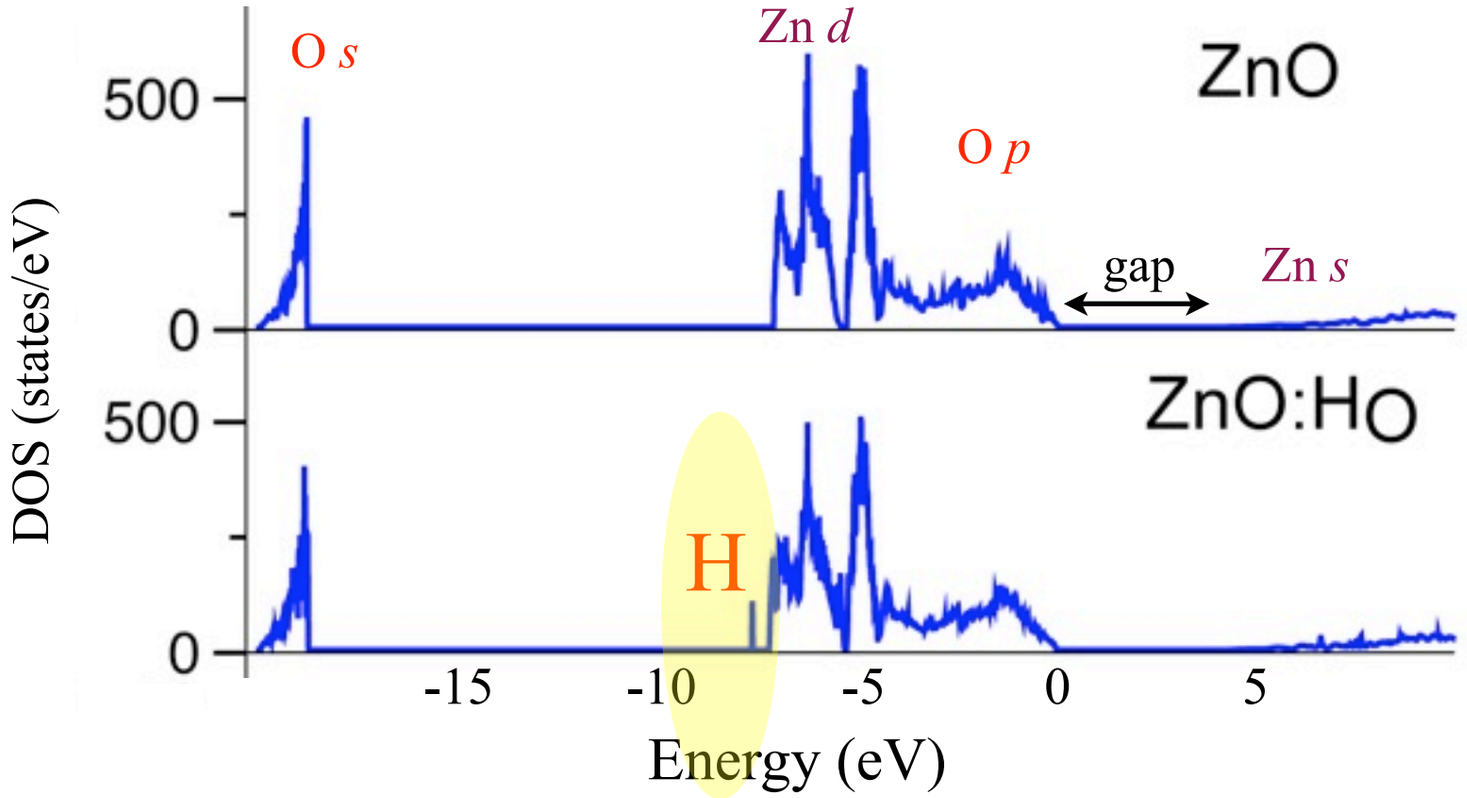
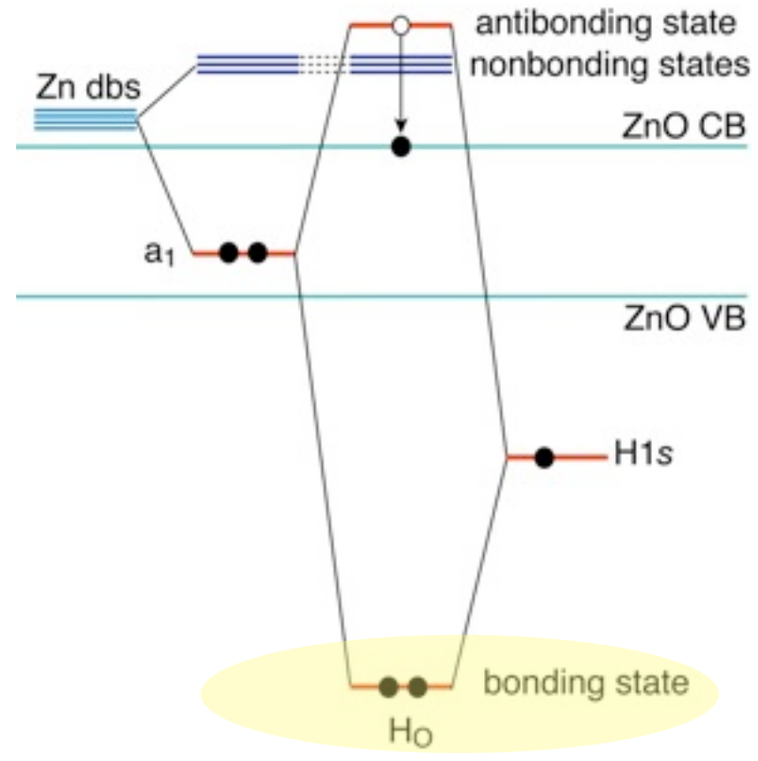
Density of States of ZnO





Density of States of H_O in ZnO





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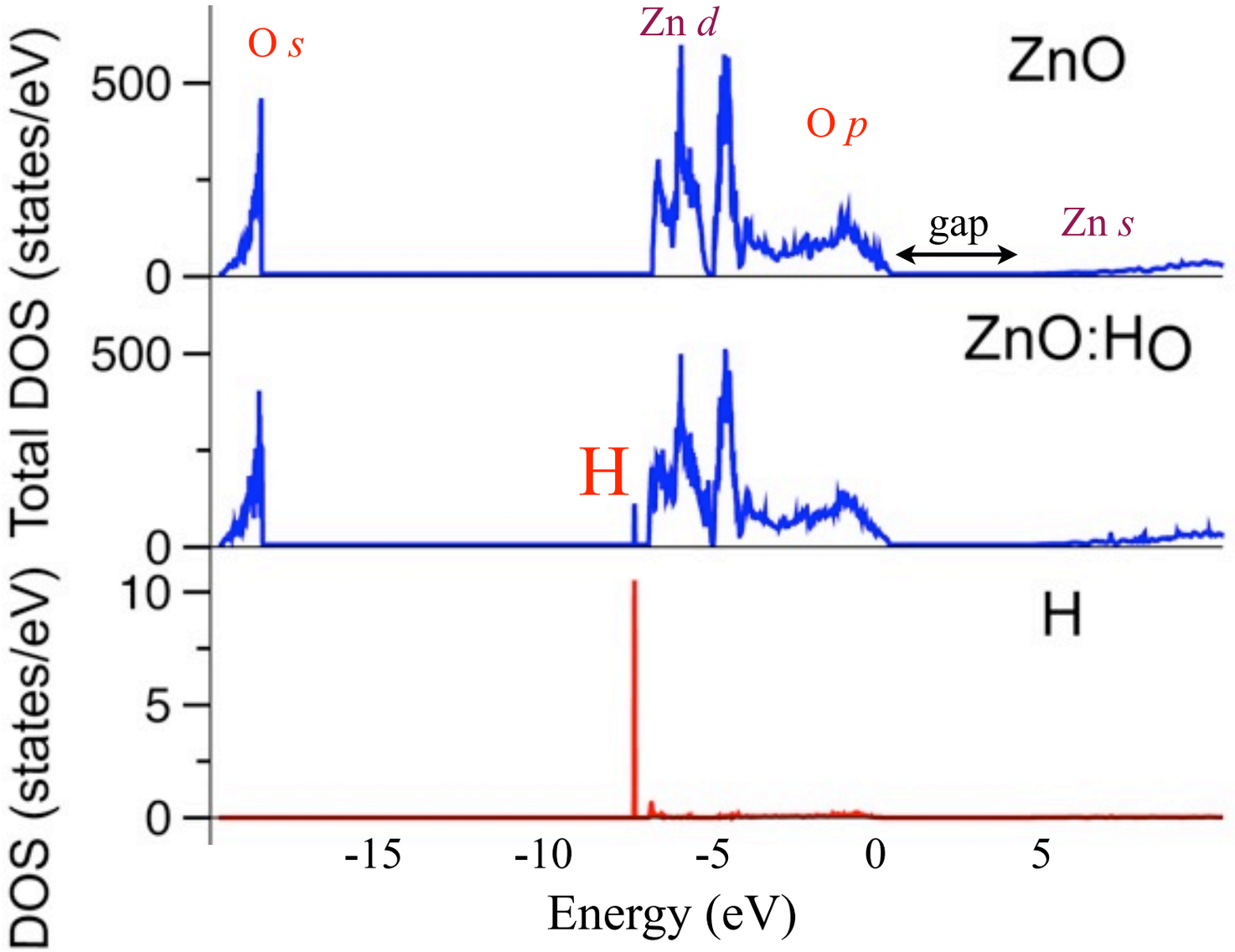
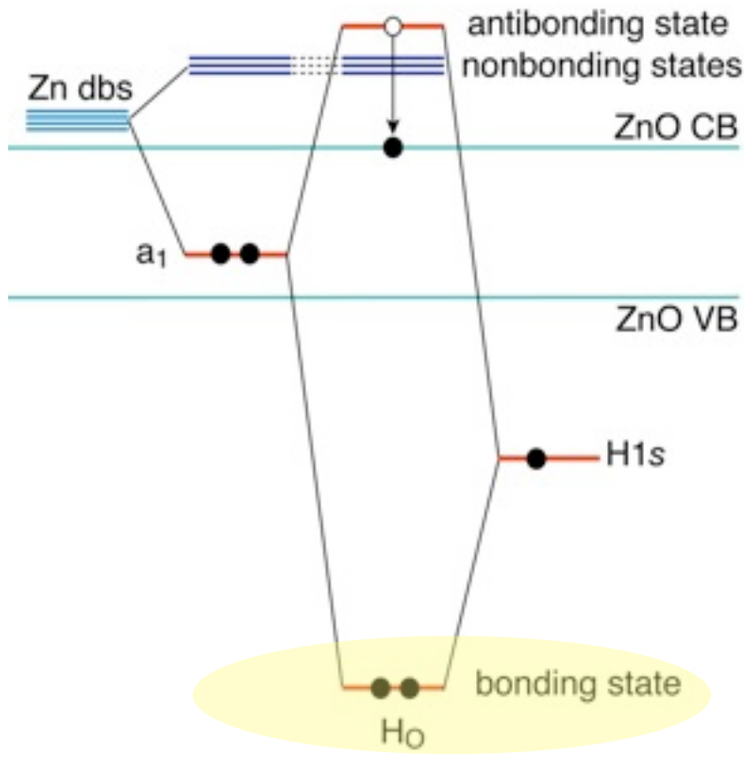
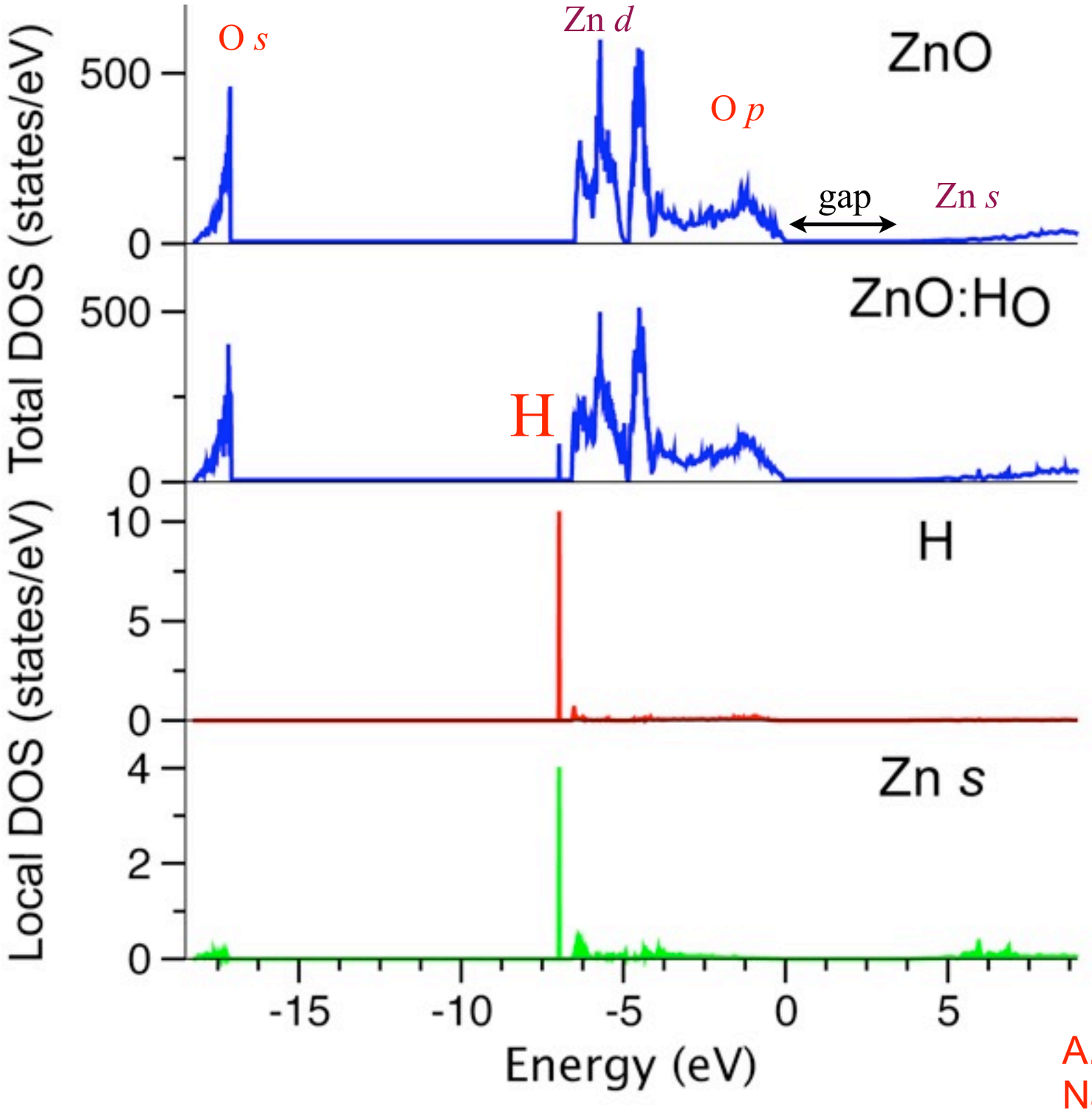
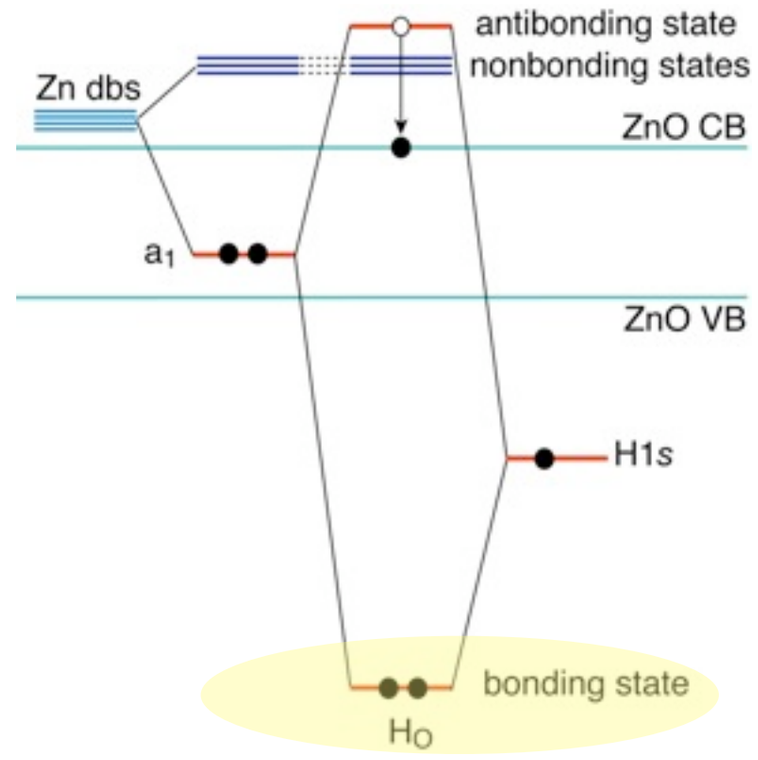




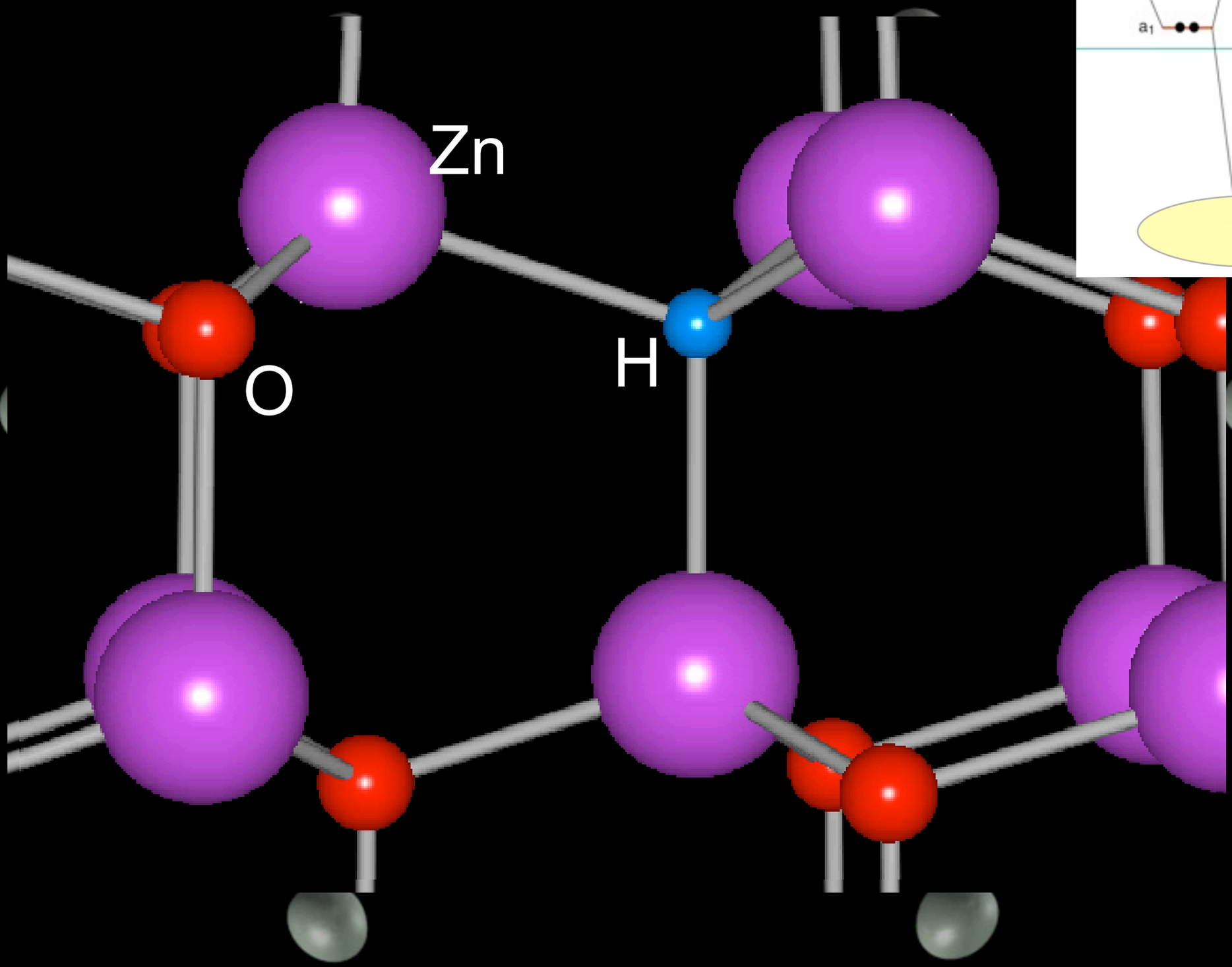
Density of States of H_O in ZnO

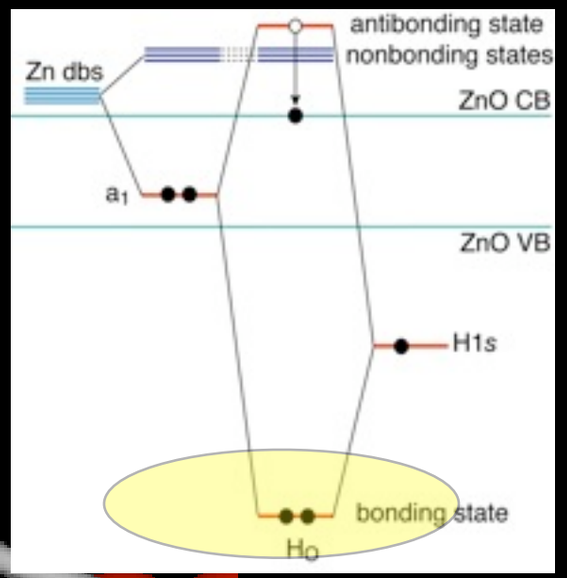




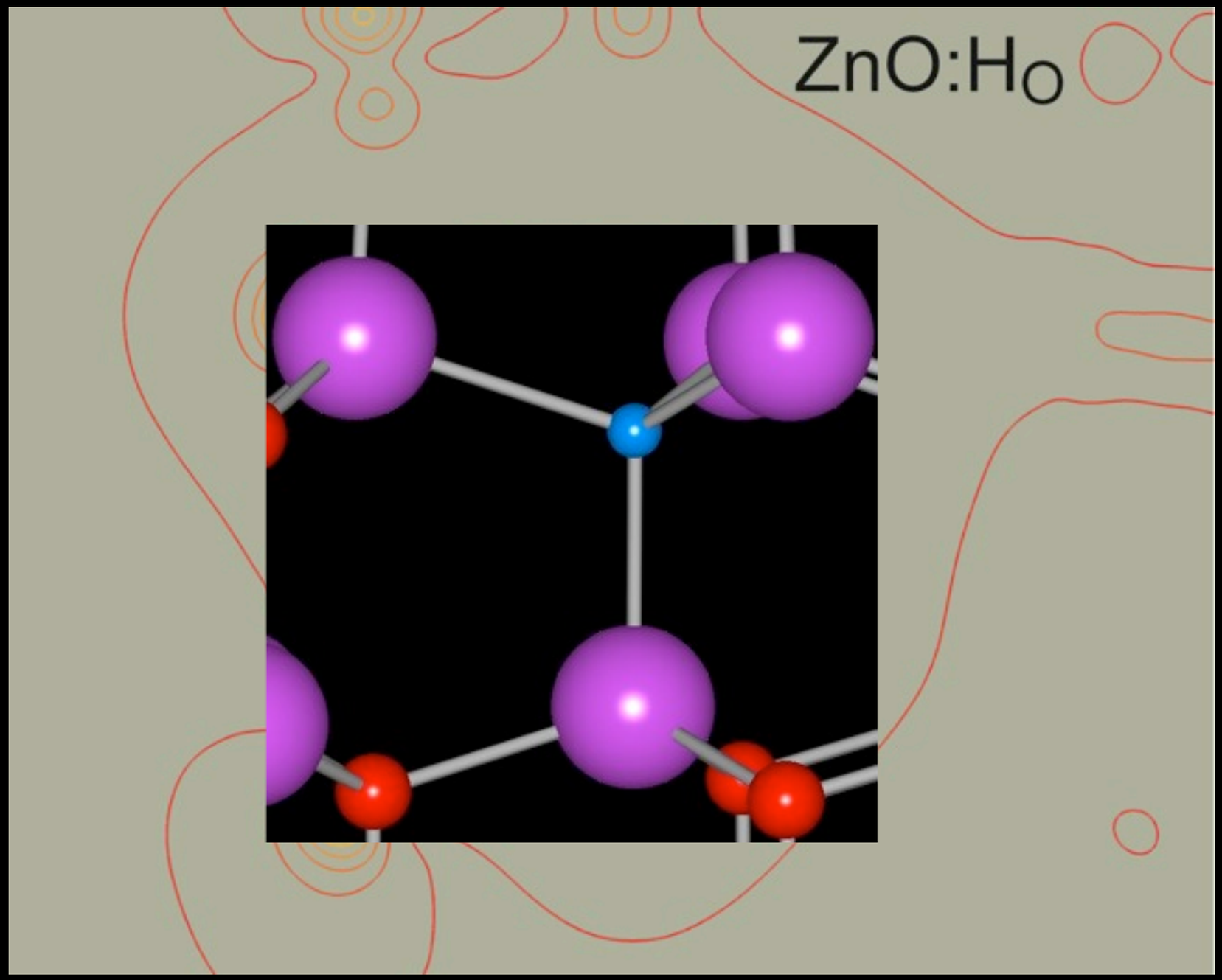
A. Janotti and C. G. Van de Walle,
Nature Materials 6, 44 (2007)

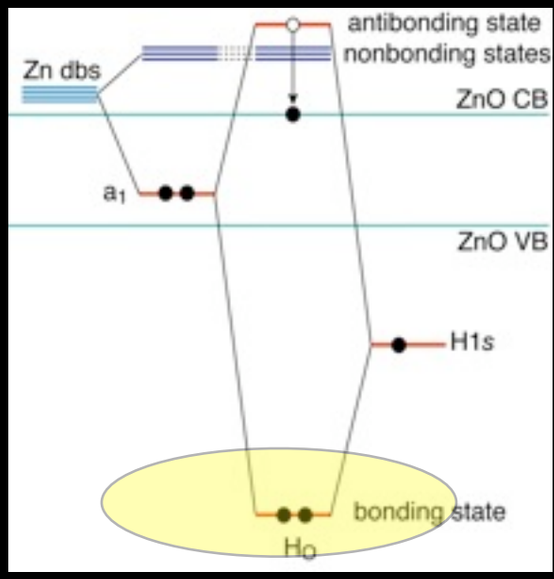
Charge density H multicenter bond in ZnO

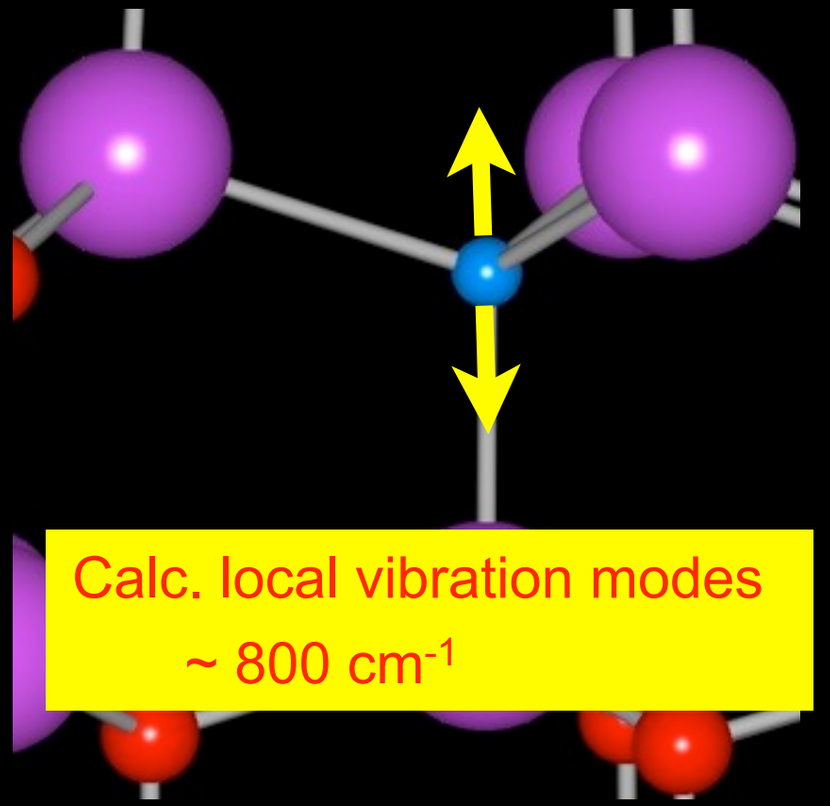




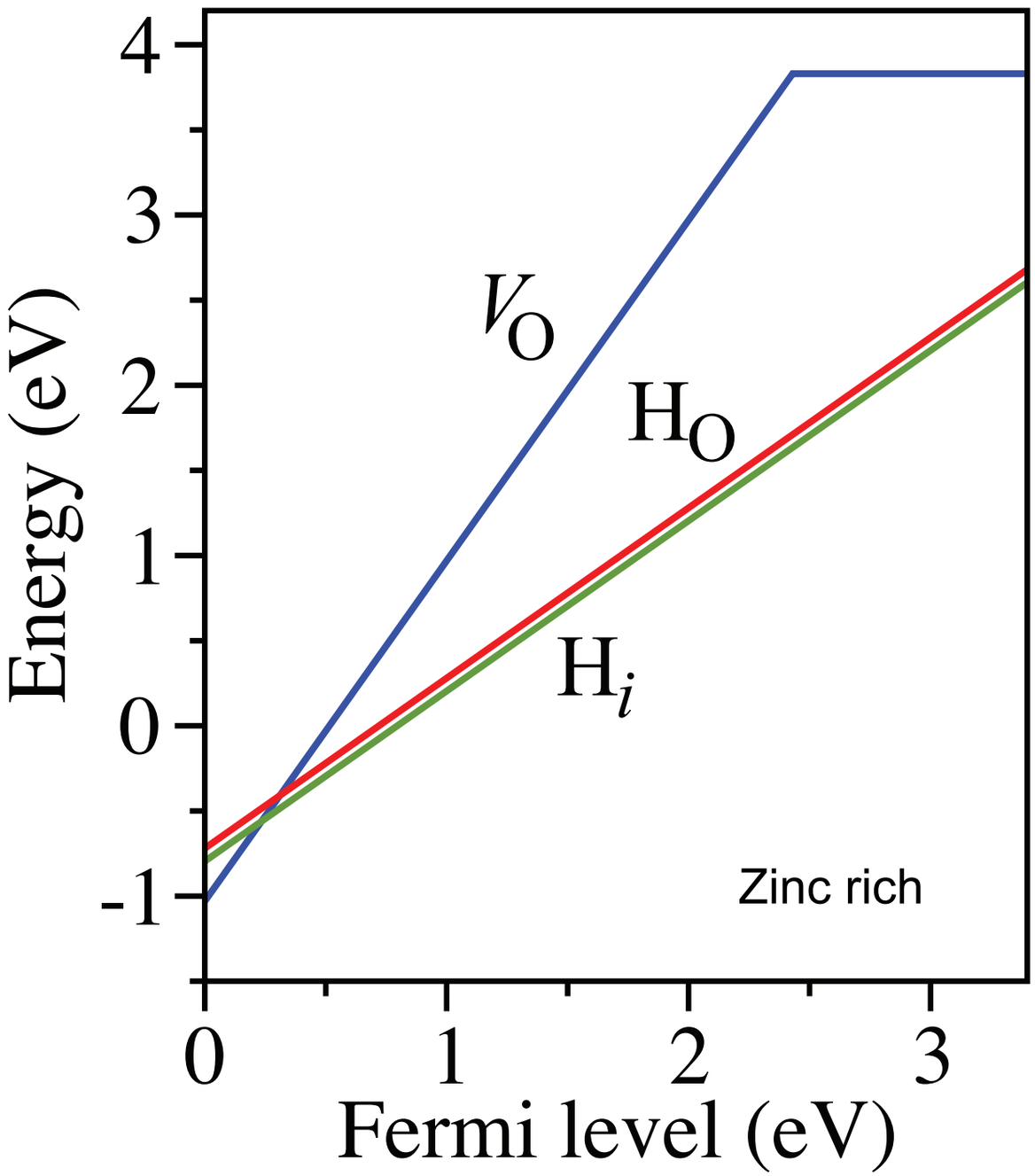
Charge density H multicenter bond in ZnO

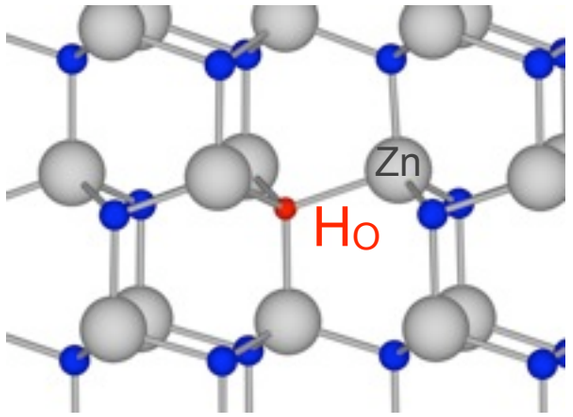






H_O in ZnO - Formation energy

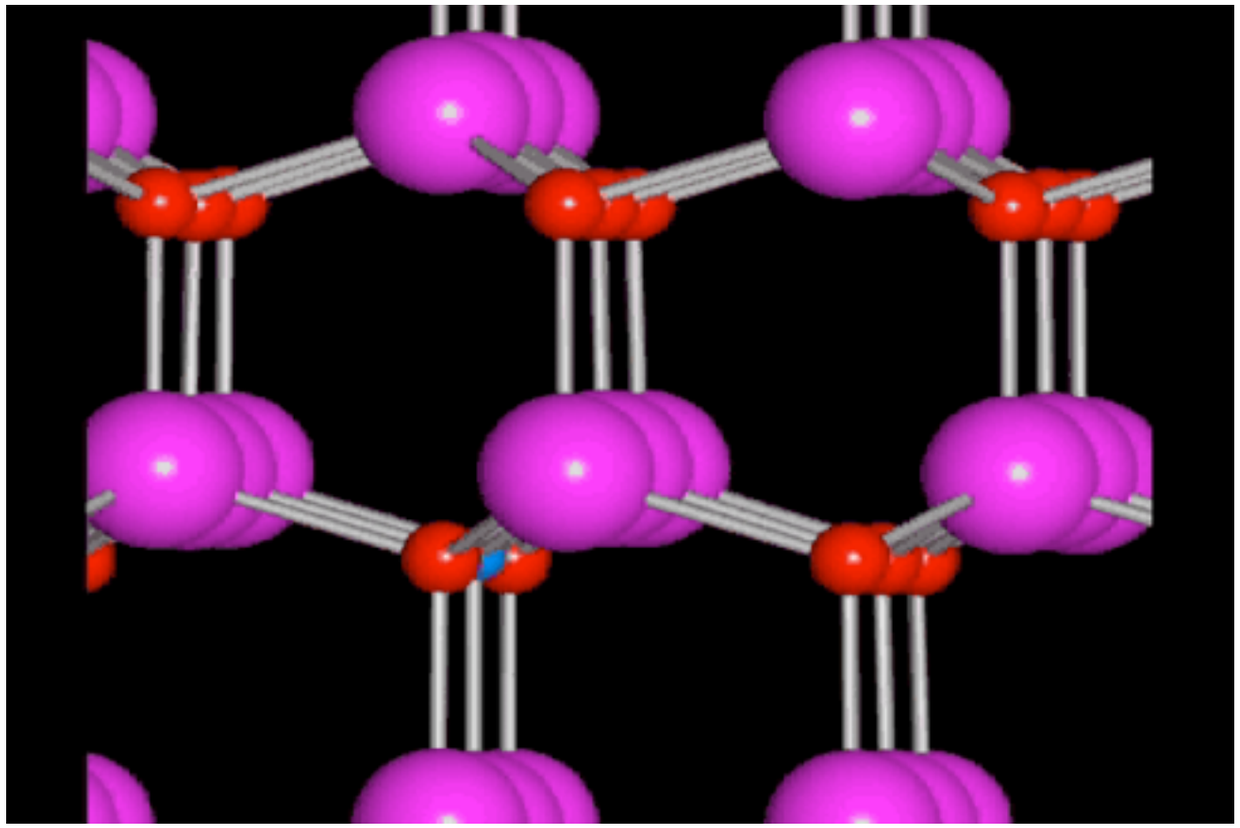


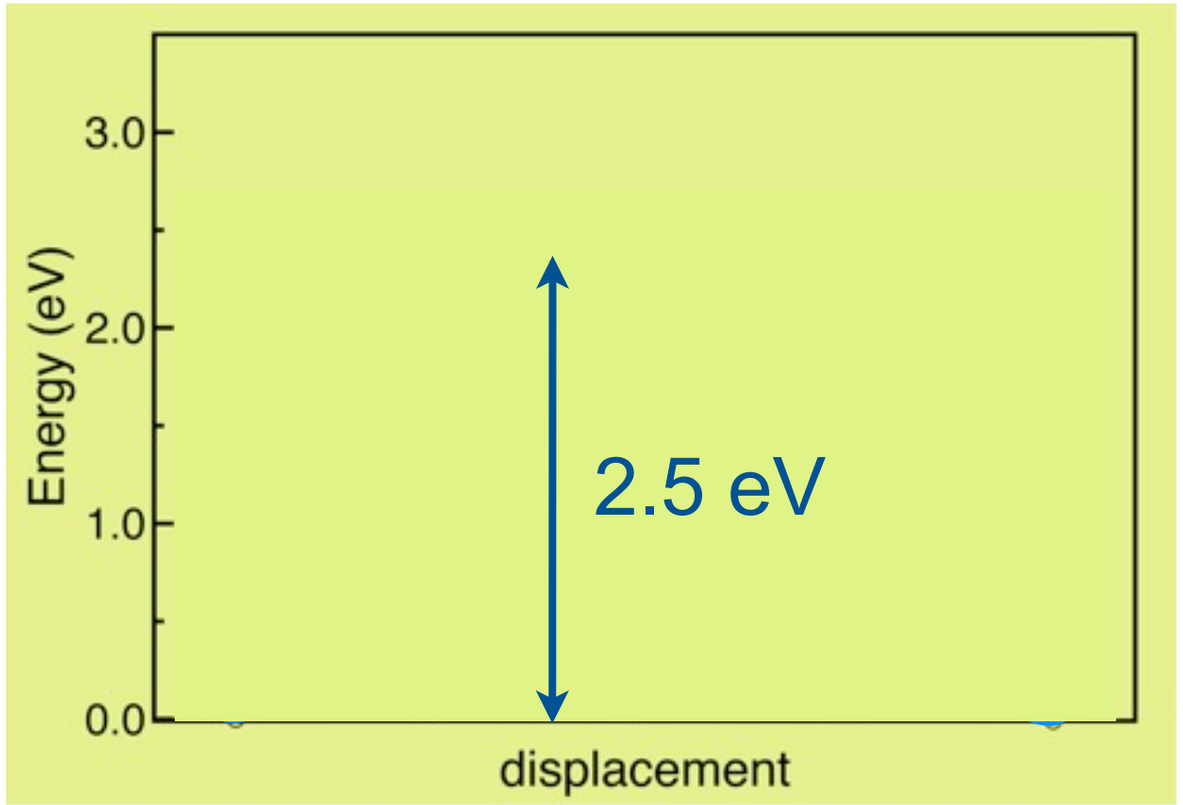


- H_O has low formation energy
- shallow donor
- stable against dissociation

$$H_O^+ \rightarrow H_i^+ + V_O^0$$

H_O migration in ZnO





- migration barrier of 2.5 eV
  - becomes mobile at ~500°C
  - consistent with experimental observations

Shi, *et al.*, Phys. Rev. B 72, 195211 (2005)

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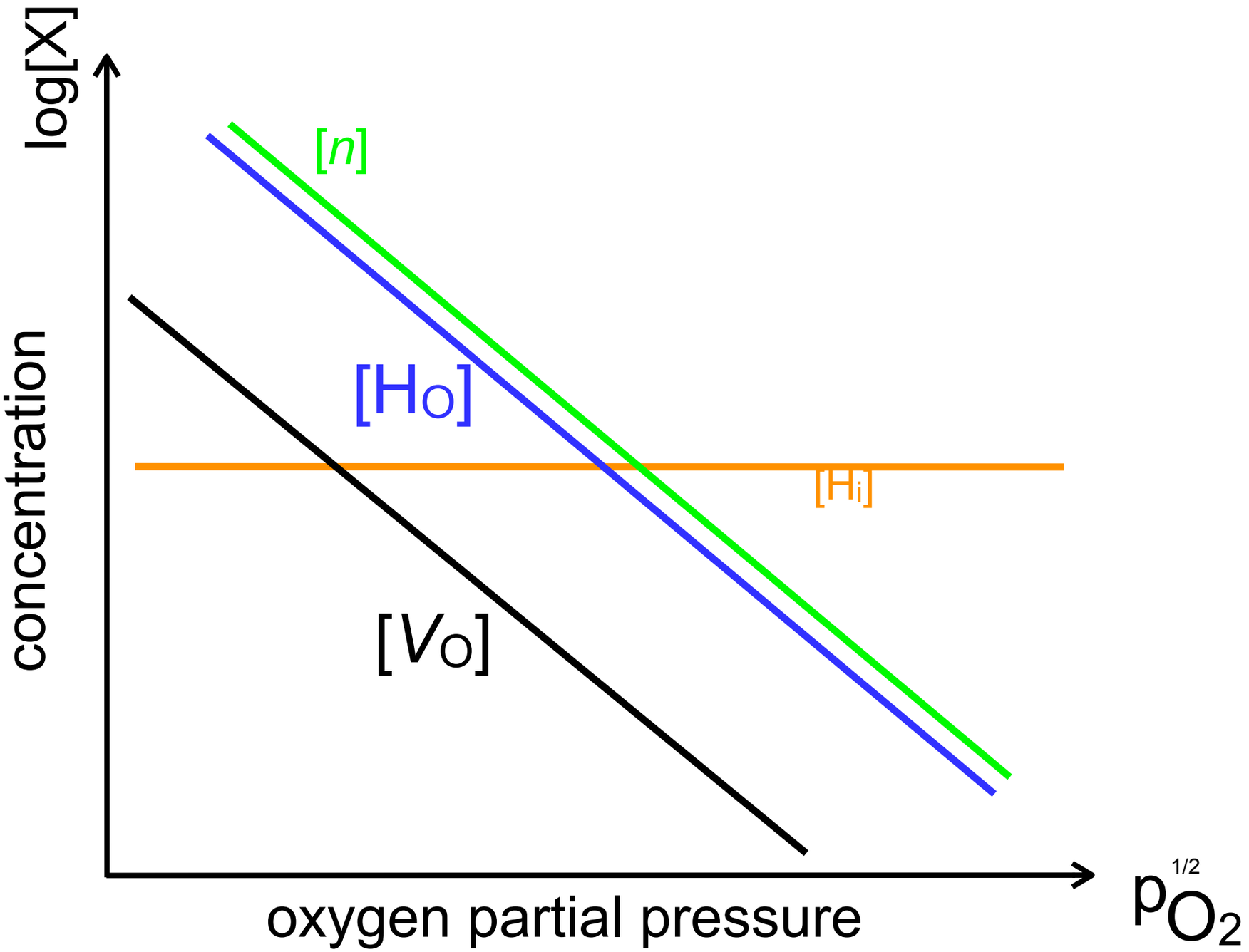
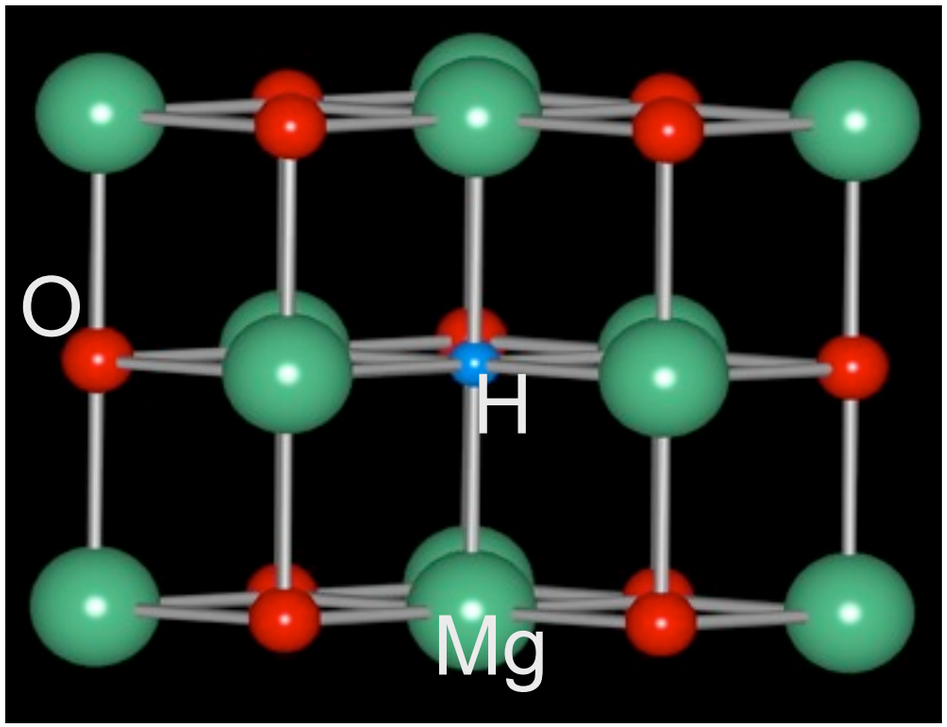
Unintentional *n*-type conductivity in ZnO



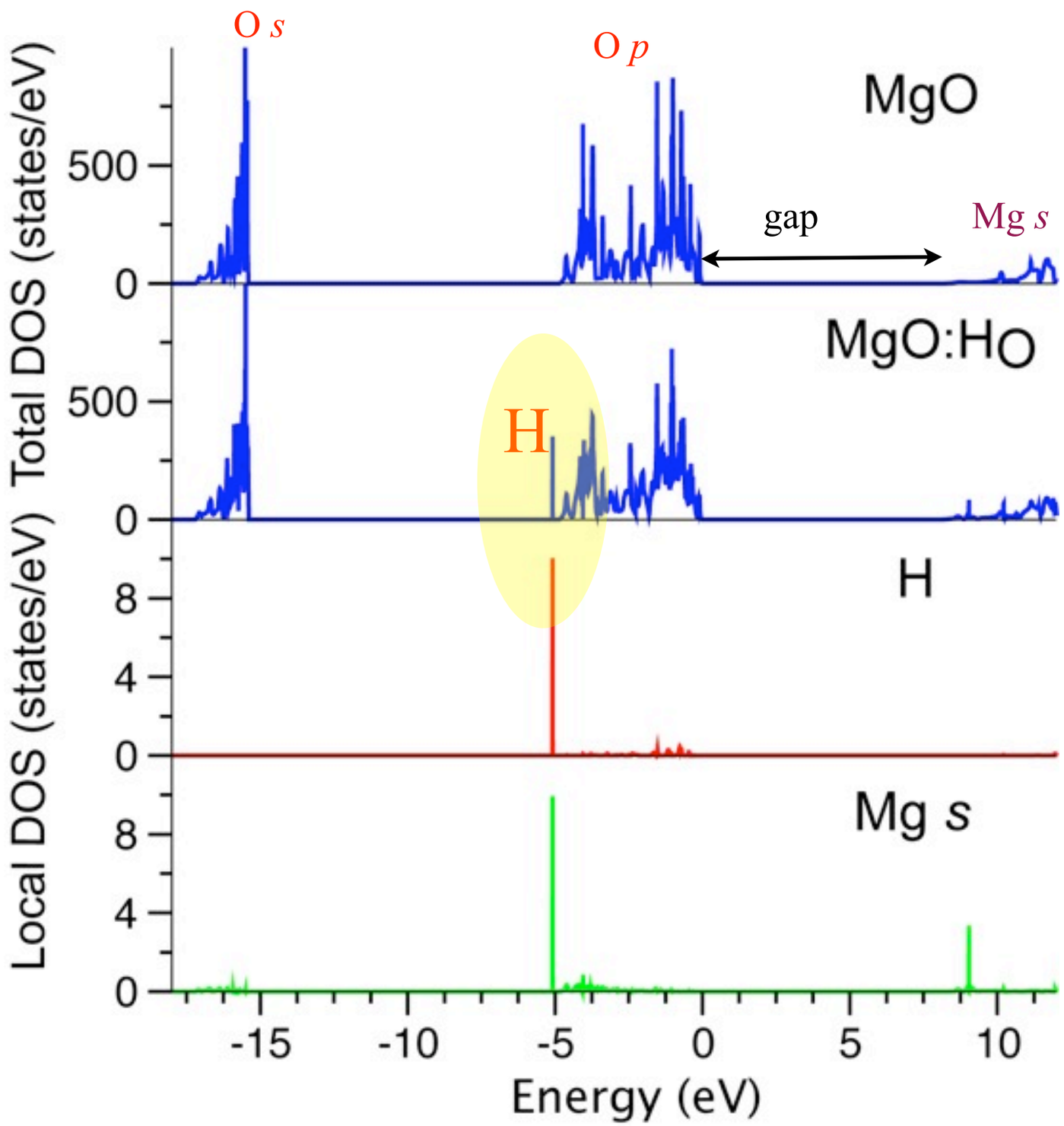
- H_O explains the dependence of *n*-type conductivity on oxygen partial pressure

Hydrogen multicenter bond in MgO

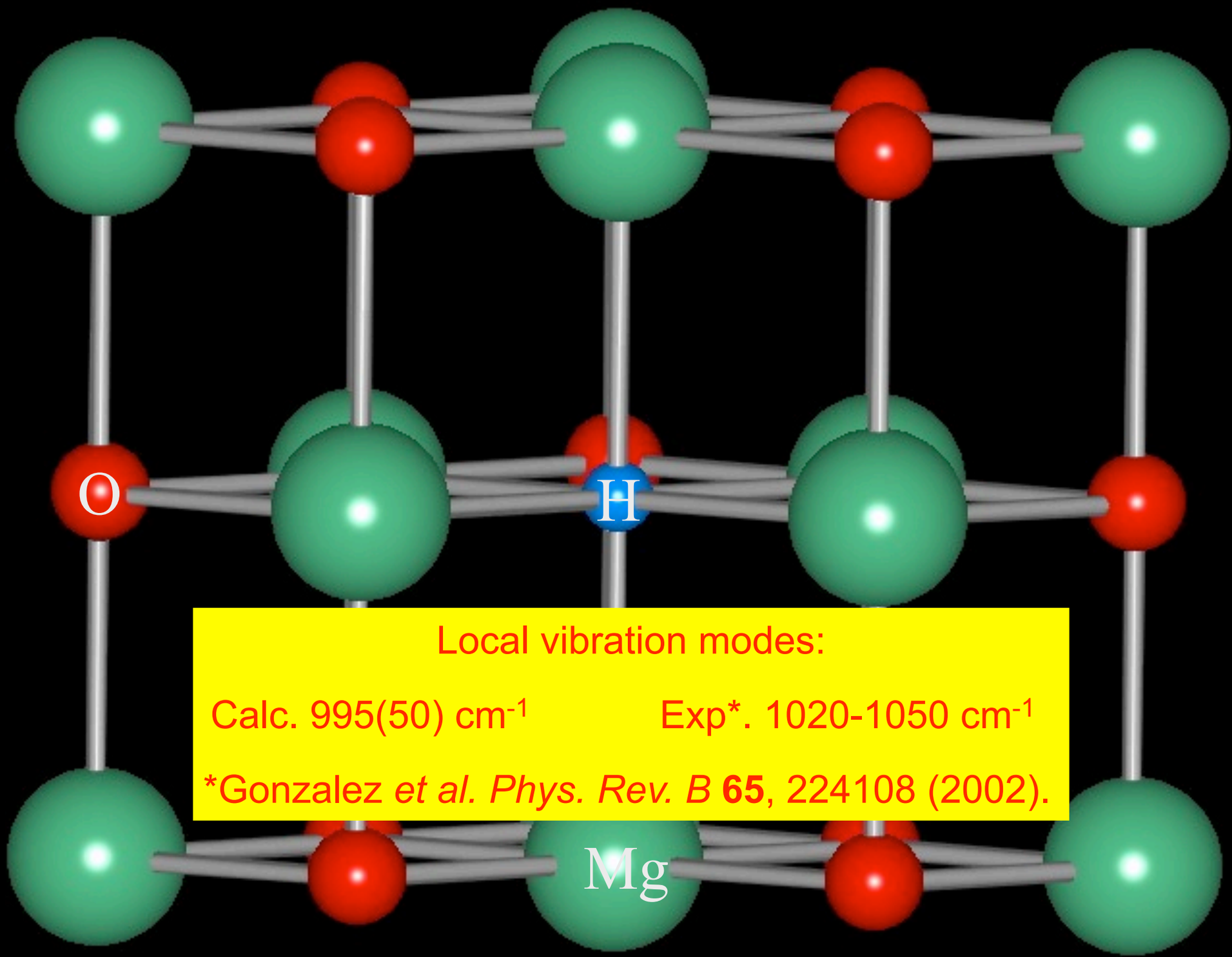
MgO: rocksalt structure



H sixfold coordinated !



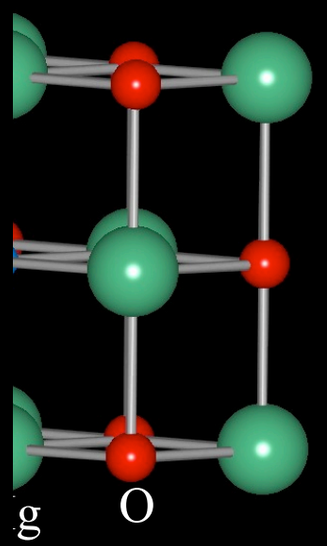
Hydrogen multicenter bond in MgO



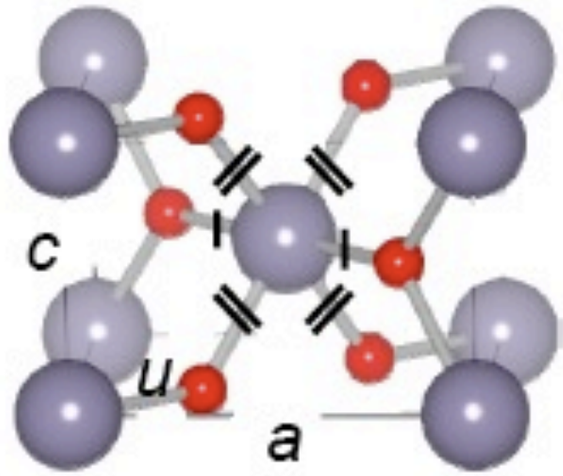
Local vibration modes:

Calc. 995(50) cm^{-1} Exp*. 1020-1050 cm^{-1}

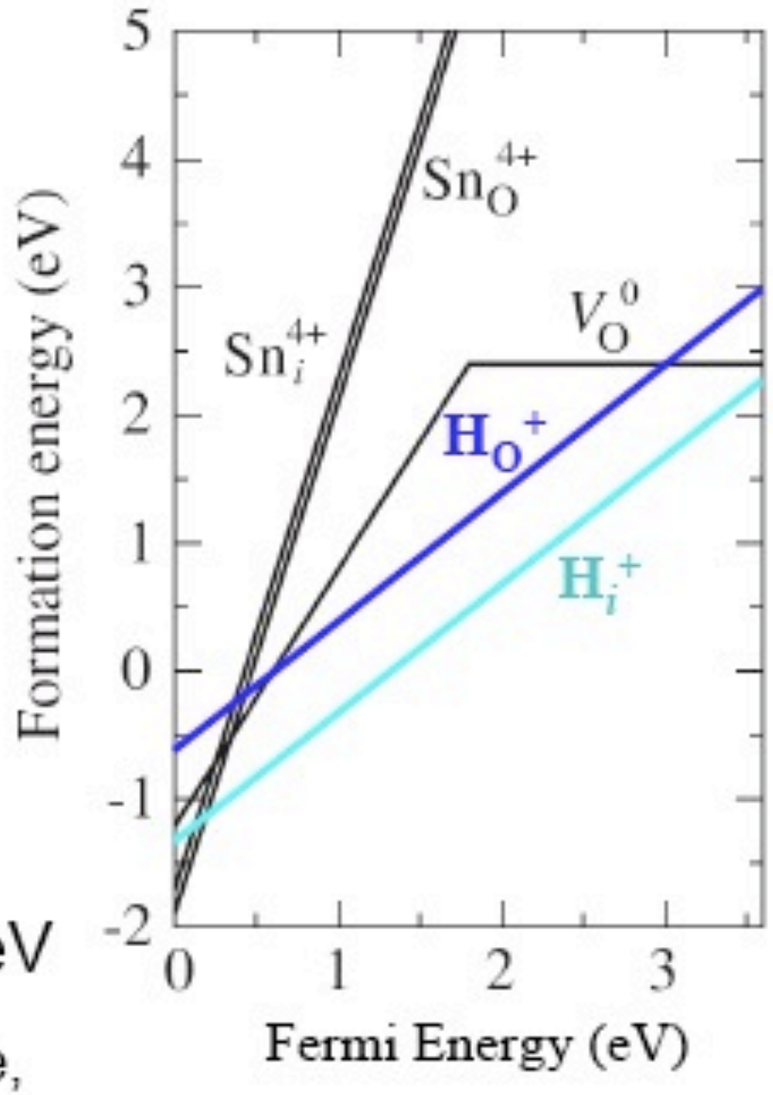
*Gonzalez *et al. Phys. Rev. B* **65**, 224108 (2002).



Conductivity in SnO_2



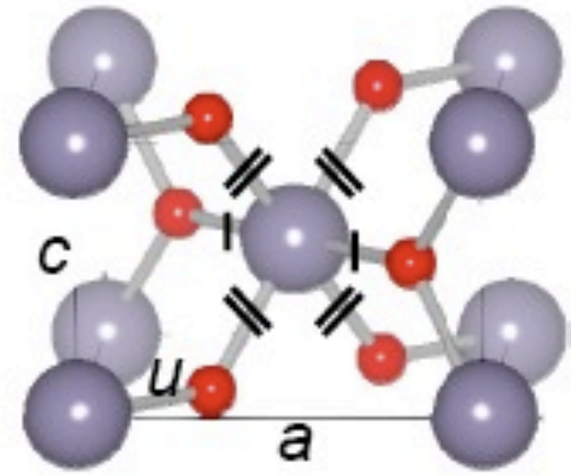
- **Rutile structure; band gap: 3.6 eV**
  - Sensors
  - Transparent conductor
- ***n*-type conductivity:**
  ***not* due to intrinsic point defects**
  - V_O high formation energy, deep donor
  - Sn_i, Sn_O: high formation energy
- **Impurities?**
- **Hydrogen**
  - Interstitial hydrogen:
    Shallow donor, Low diffusion barrier
  - Substitutional hydrogen:
    Shallow donor, Diffusion barrier: 2.2 eV

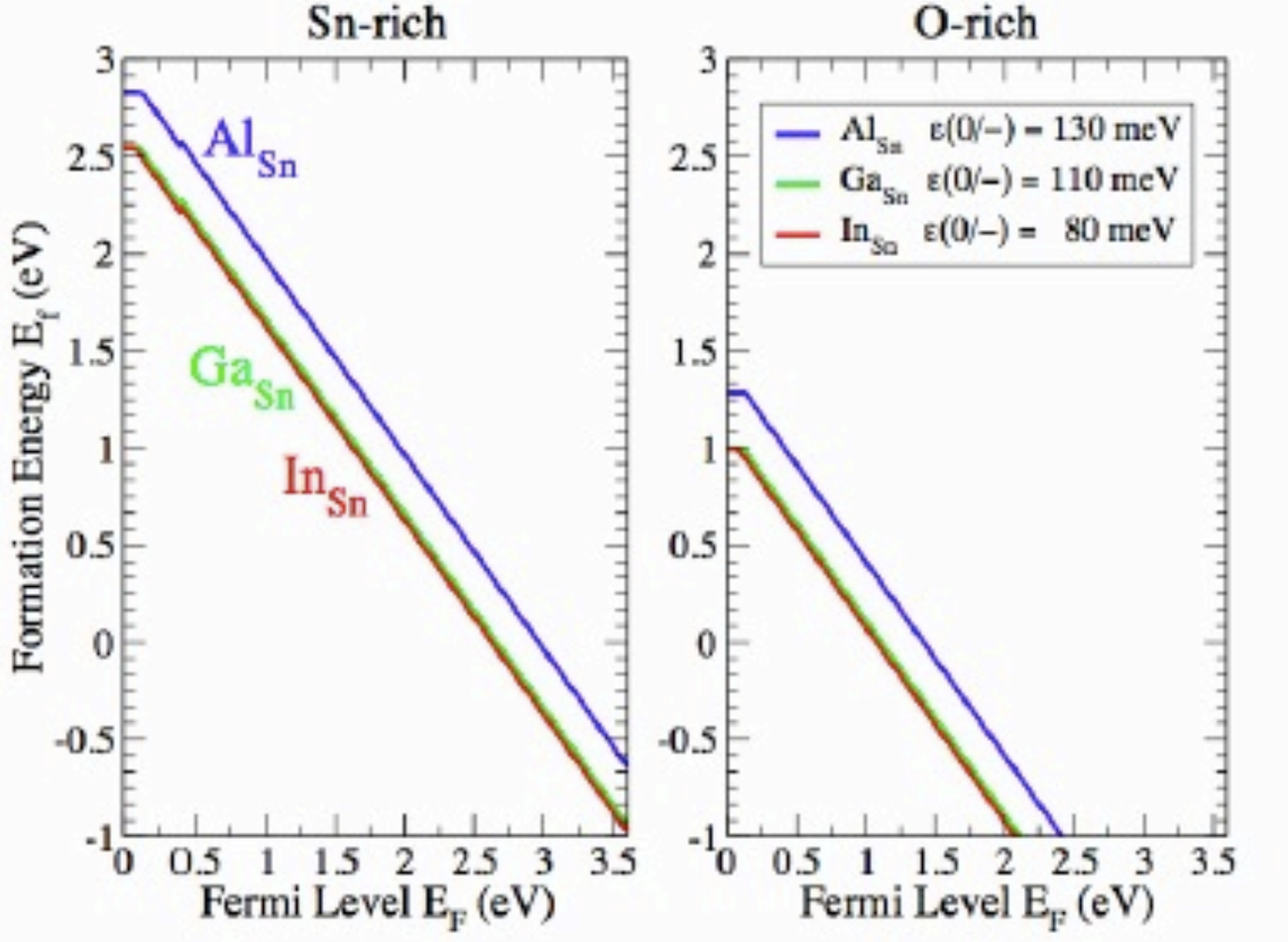


A. K. Singh, A. Janotti, M. Scheffler, and C. G. Van de Walle, Phys. Rev. Lett. **101**, 055502 (2008).

Conductivity in SnO_2

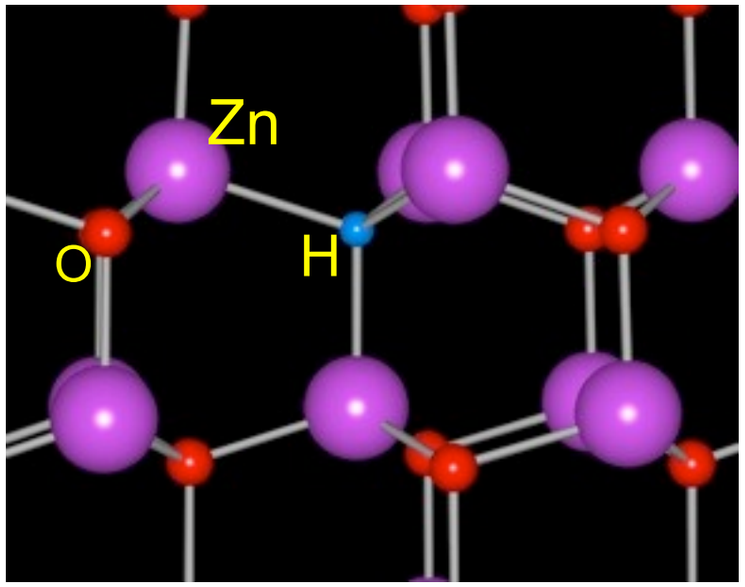
- ***p*-type doping**
  - Difficult in ZnO
    - » N: high formation energy
    - » Group-I on Zn site:
      deep acceptors, or self-compensation
  - Potentially more feasible in SnO_2:
    - » Group-III on Sn site
- **Acceptors**
  - Al, Ga, In on Sn site
  - Low ionization energy
  - Modest formation energy
- **Complexes**
  - Al-H, Ga-H, In-H



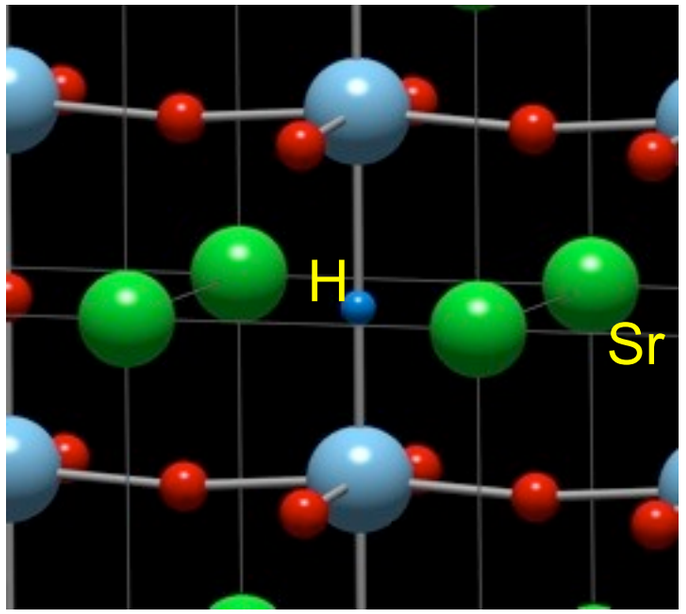


Hydrogen multicenter bonds in oxides

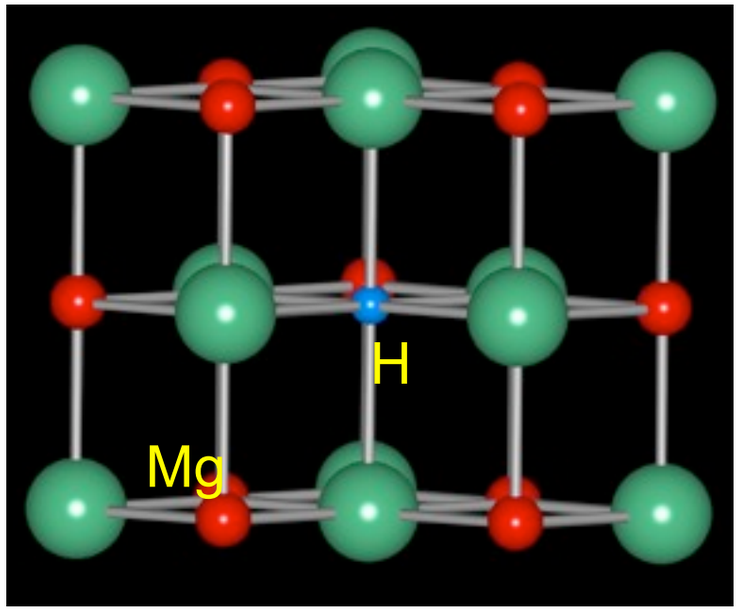
ZnO wurtzite
5-center bond



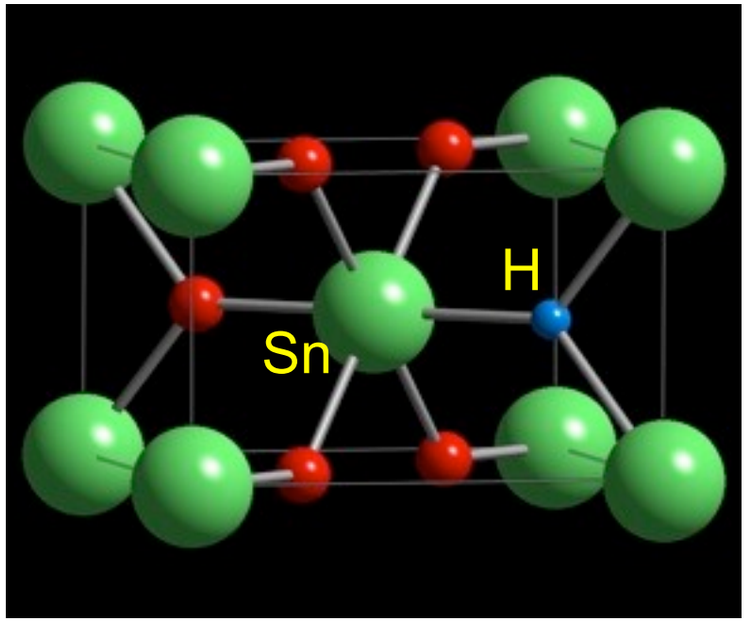
$SrTiO_3$ perovskite
3-center bond



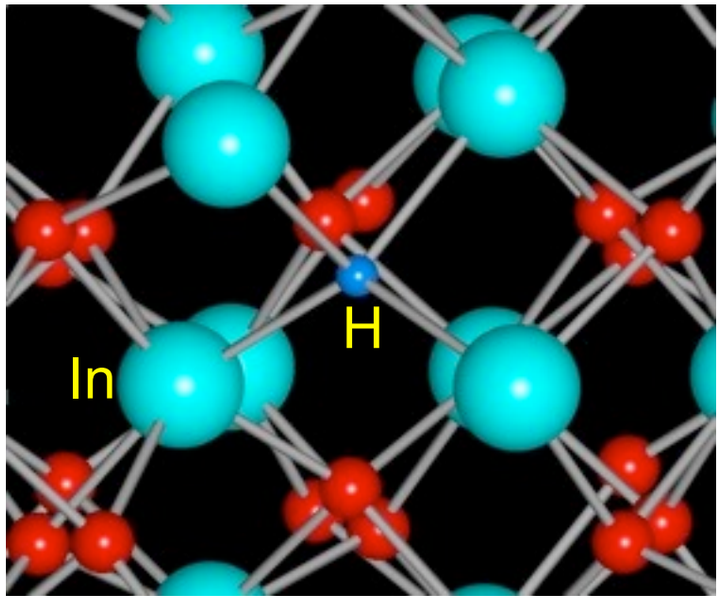
MgO rocksalt
7-center bond



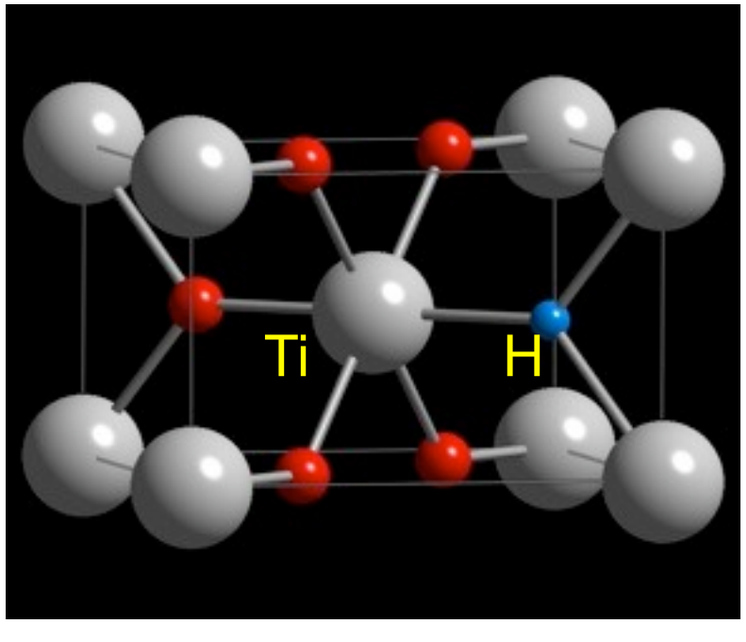
SnO_2 rutile
4-center bond



In_2O_3
5-center bond



TiO_2 rutile
4-center bond



Conclusions

- Unintentional *n*-type conductivity in ZnO cannot be explained by native defects
  - Oxygen vacancy is a deep donor
  - Zinc interstitial is unstable

- Hydrogen is a plausible source of unintentional *n*-type conductivity in ZnO
  - H occupies O sites and form a multicenter bond
    - Shallow donor
    - Low formation energy
    - Stable up to ~500 °C
    - Concentration varies with oxygen partial pressure
  - Similar behavior in SnO_2, In_2O_3, TiO_2

[Singh, Janotti, Scheffler, Van de Walle, Phys. Rev. Lett. **101**, 055502 (2008)]

A. Janotti and C. G. Van de Walle
Nature Materials **6**, 44 (2007)
Phys. Rev. B **76** 165202 (2007)
Appl. Phys. Lett. **87**, 12210 (2005)
J. Cryst. Growth **287**, 58 (2005)

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