



Doping and defects in oxide semiconductors

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Acknowledgments

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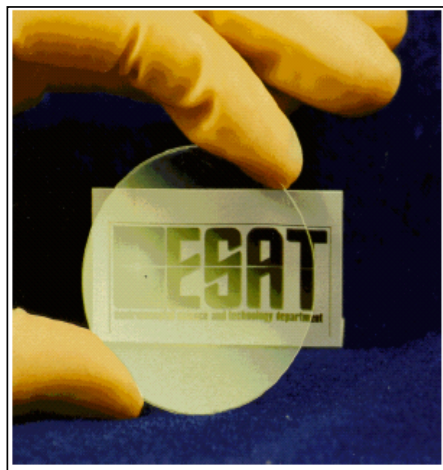
Solid State Lighting and Energy Center at UCSB

CNSI and Teragrid computer facilities

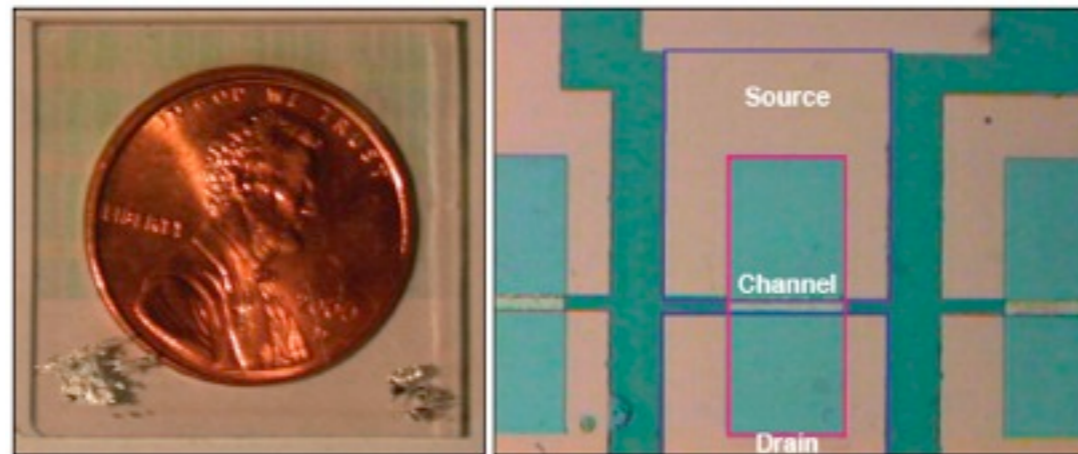
Oxide semiconductors

● Wide range of crystal structures with interesting properties

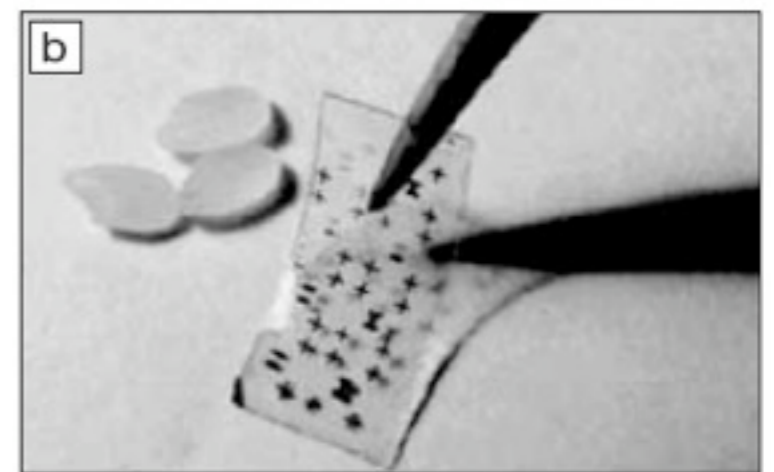
- Transparent and conductors
- “invisible” electronics
- Light emitting diodes and laser diodes



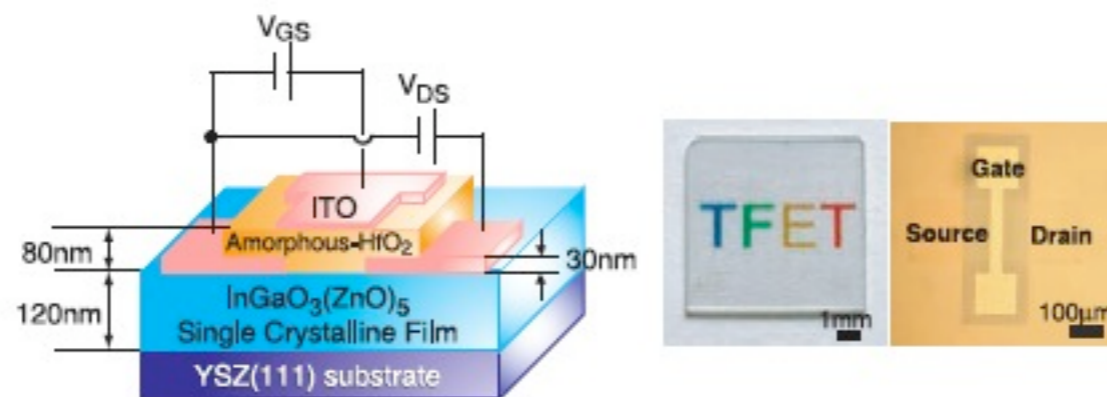
2-inch ZnO wafer grown by Eagle-Picher Technologies



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



“Invisible” ZnO transistor MRS Bulletin (2003)



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



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

ZnO

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)

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

ZnO main problem: control of conductivity

As-grown ZnO is always *n*-type

- bulk substrates $\sim 10^{15} - 10^{16} \text{ cm}^{-3}$

- epitaxial films $\sim 10^{16} - 10^{19} \text{ cm}^{-3}$

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

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

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)

Formalism

E_{form} : formation energies

● V_{O}^q oxygen vacancy in charge state q

$$E_{\text{form}}(V_{\text{O}}^q) = E_{\text{tot}}(\text{ZnO}:V_{\text{O}}^q) - E_{\text{tot}}(\text{ZnO}) + \mu_{\text{O}} + q E_{\text{F}}$$

● H_{i}^+ interstitial hydrogen in the positive charge state

$$E_{\text{form}}(H_{\text{i}}^+) = E_{\text{tot}}(\text{ZnO}:H_{\text{i}}^+) - E_{\text{tot}}(\text{ZnO}) - \mu_{\text{H}} + E_{\text{F}}$$

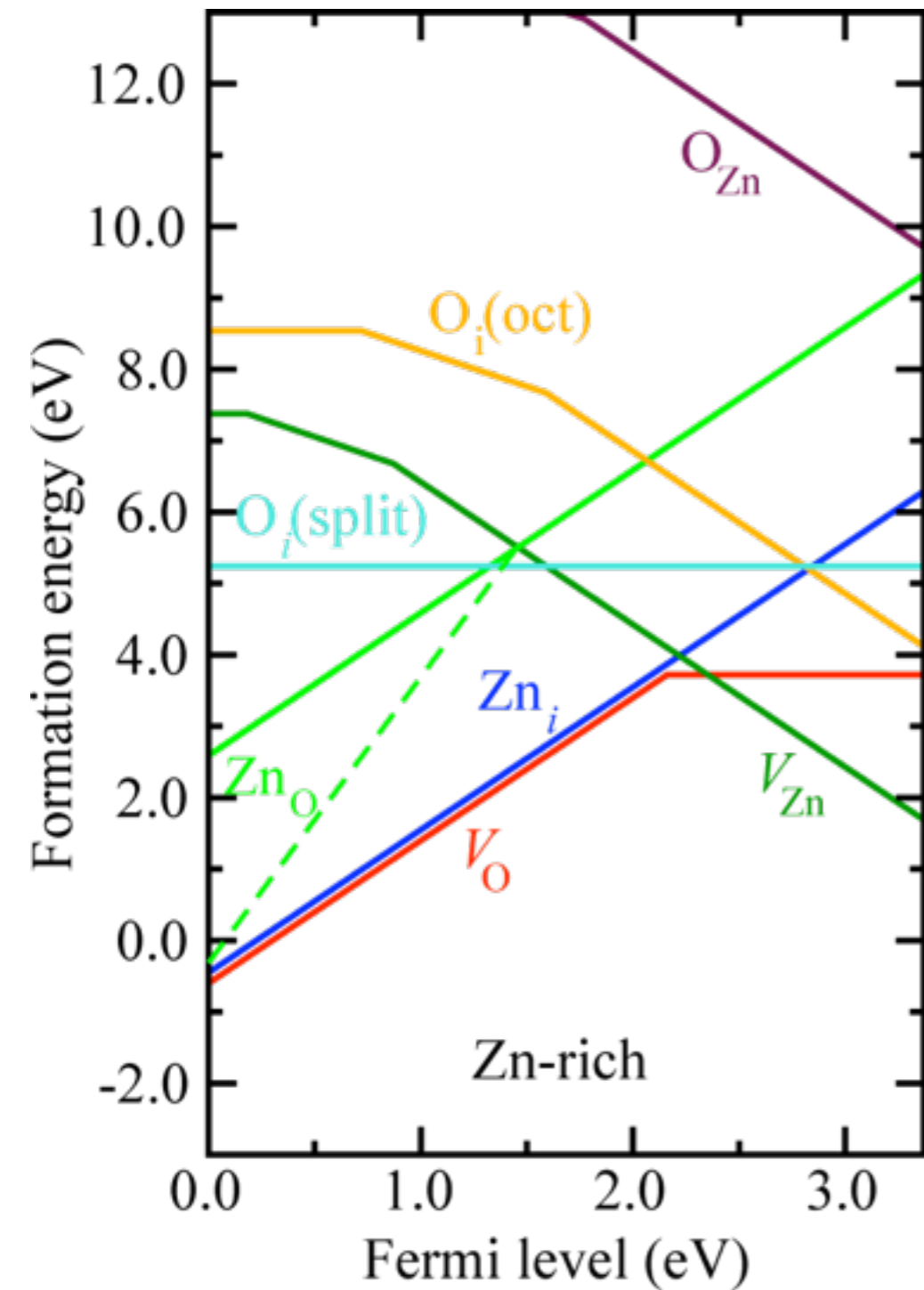
μ_{O} : energy of oxygen in reservoir, varies from Zn-rich to O-rich

$$\mu_{\text{O}} + \mu_{\text{Zn}} = \Delta H_{\text{f}}(\text{ZnO}) = -3.6 \text{ eV} \text{ formation enthalpy of ZnO}$$

μ_{H} : energy of hydrogen in reservoir, H_2 molecule

E_{F} : energy of electron in its reservoir, i.e., the Fermi level

Native point defects in ZnO (Zn-rich)

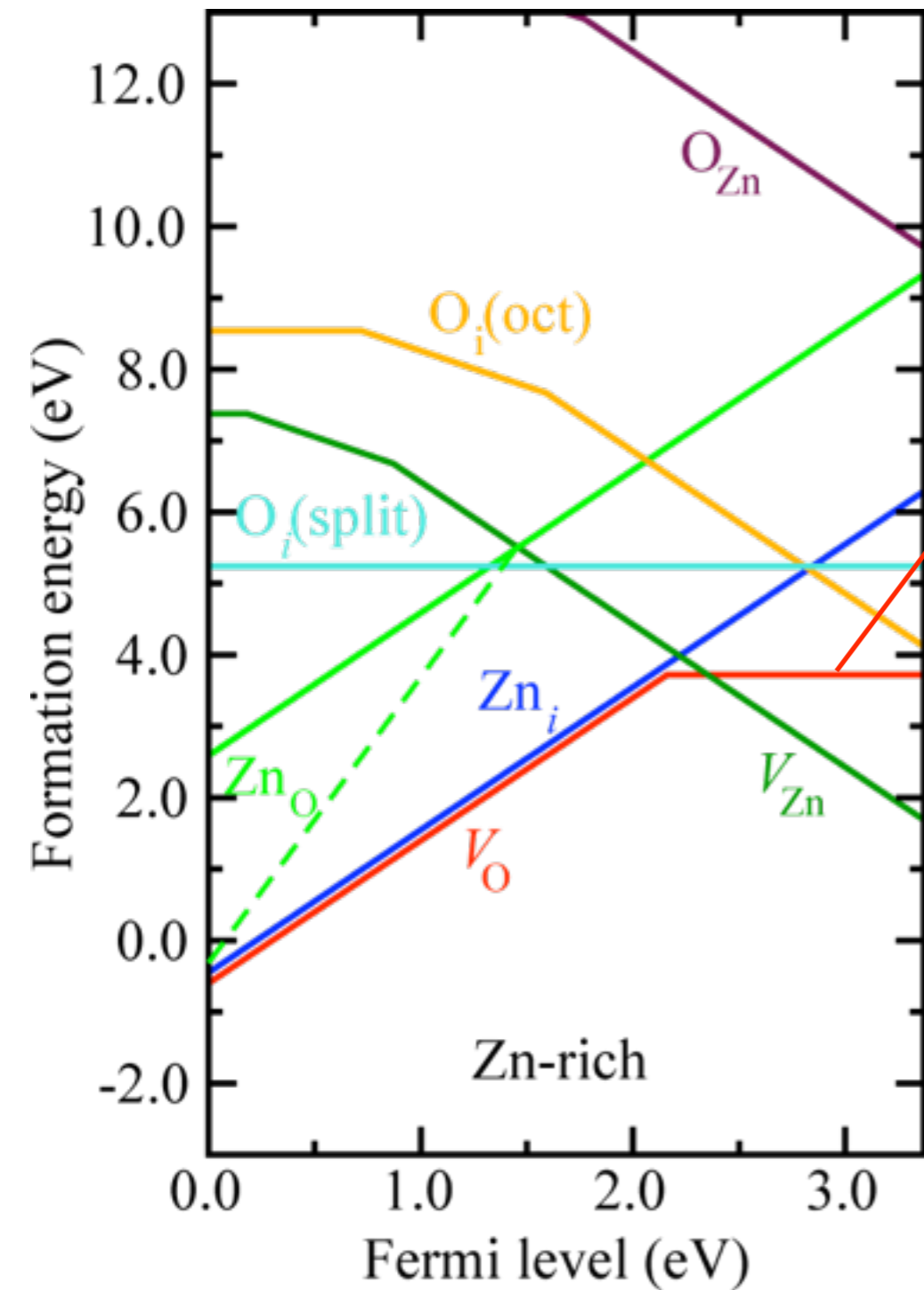


Most relevant:

- ▶ 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)

Oxygen vacancy

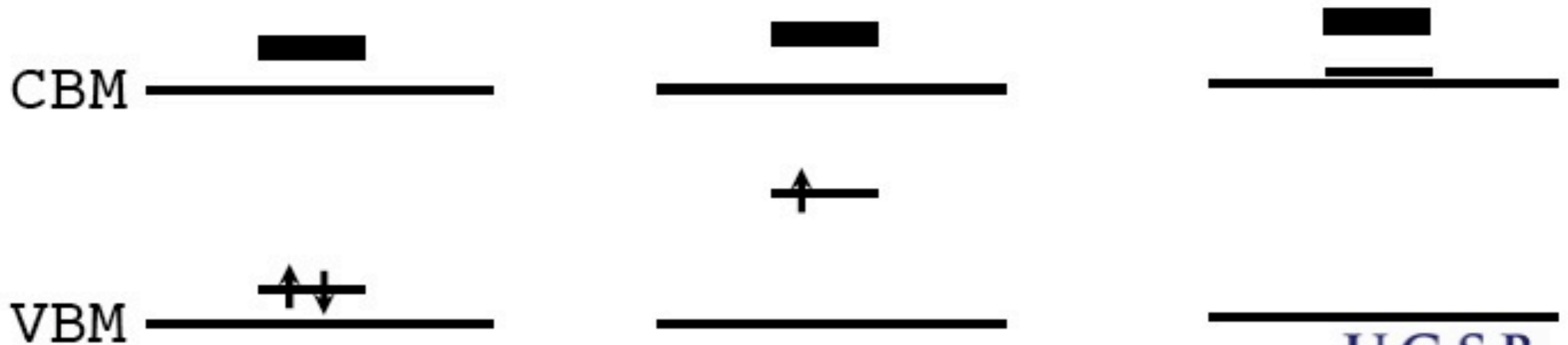
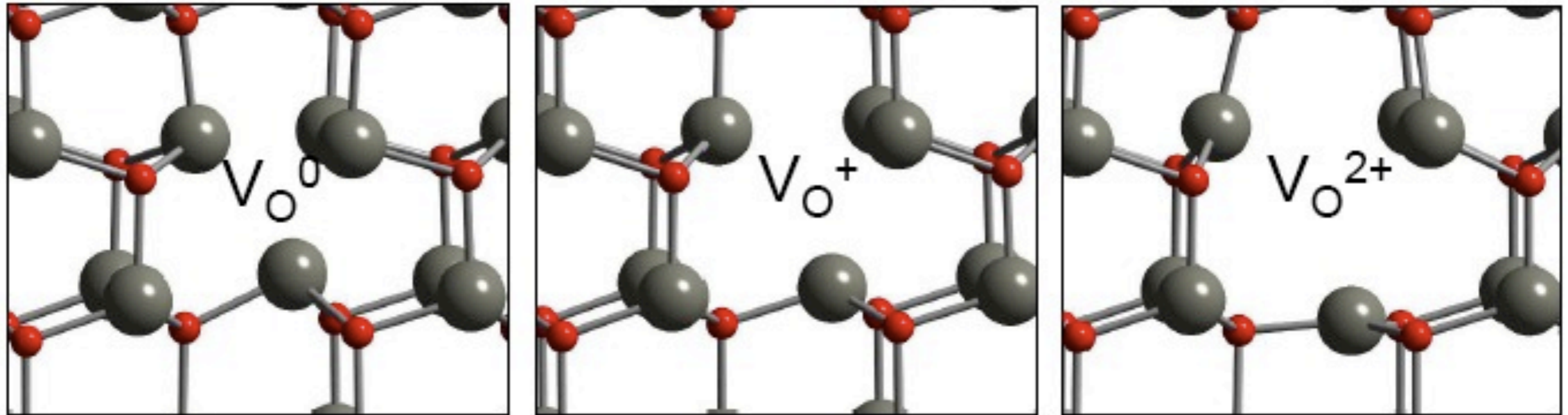


V_O

- ▶ 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)

Oxygen vacancy - very large local relaxations



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 threshold for $V_O^0 \rightarrow V_O^+ + e$

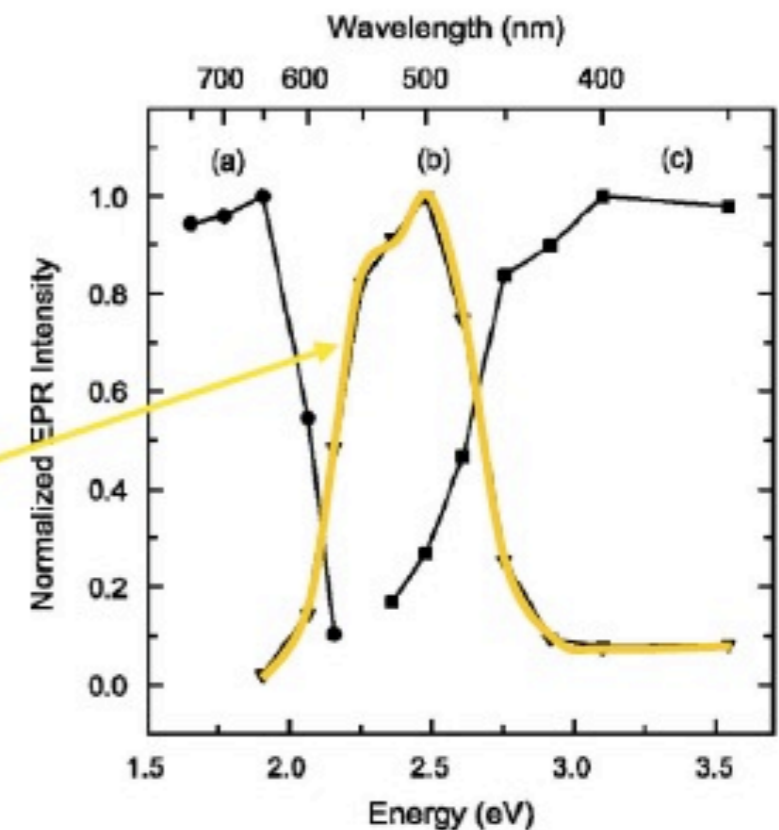
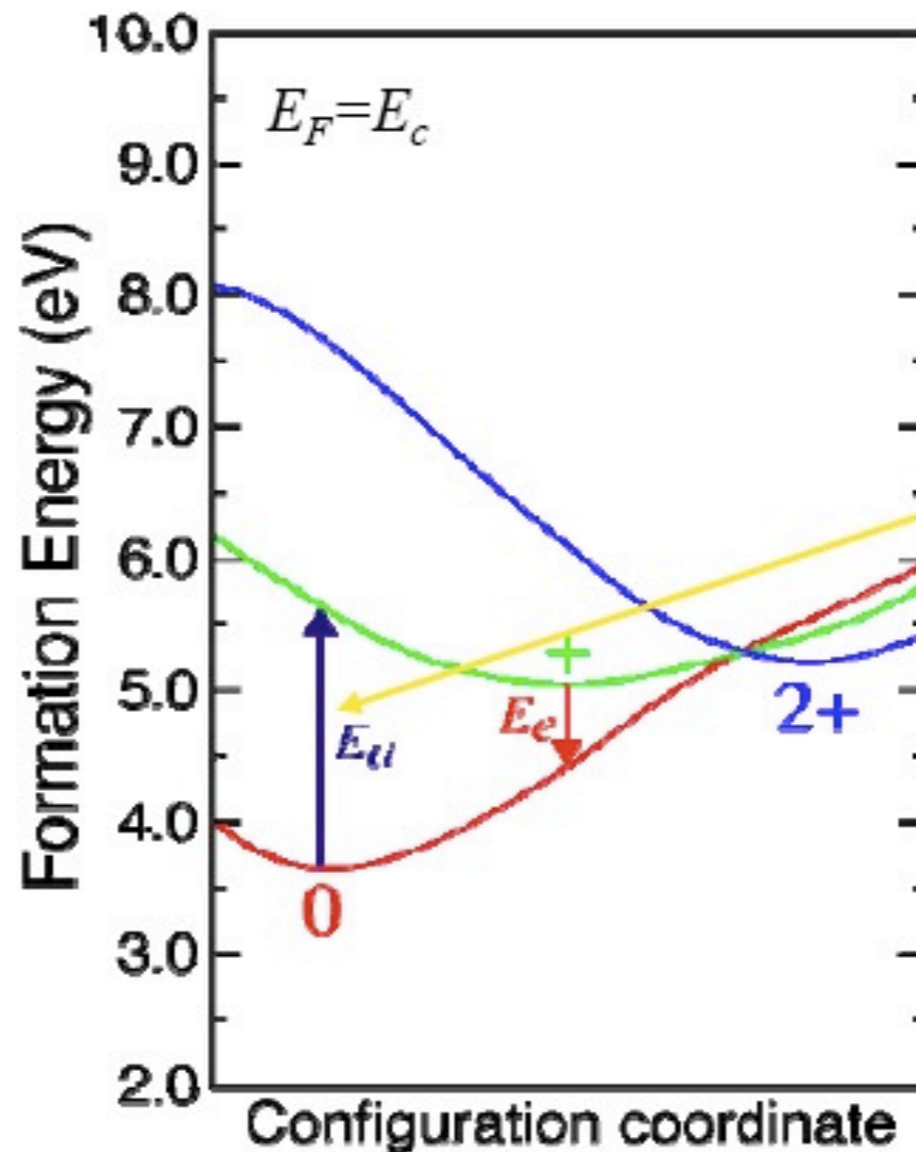
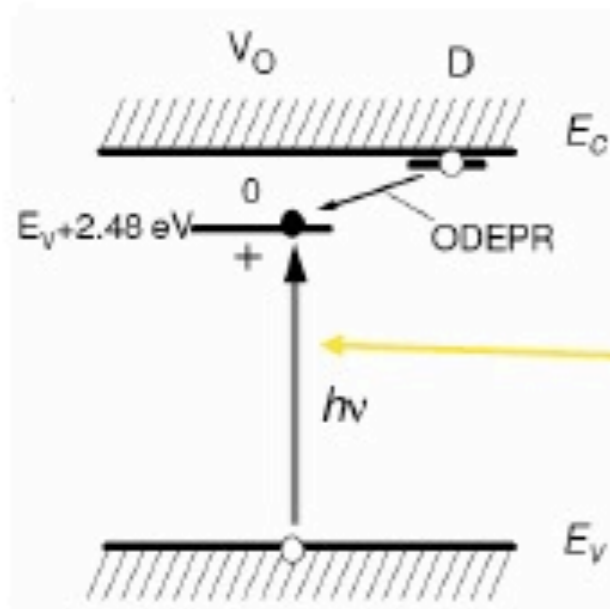


FIG. 4. Wavelength dependence of changes in charge state while illuminating at 30 K. The monitored EPR signals are (a) Fe³⁺ ions, (b) singly ionized oxygen vacancies (V_O^+), and (c) zinc vacancies with a OH⁻ ion at an adjacent oxygen site, i.e., $(V_{Zn}^- - H^+)^0$ centers.

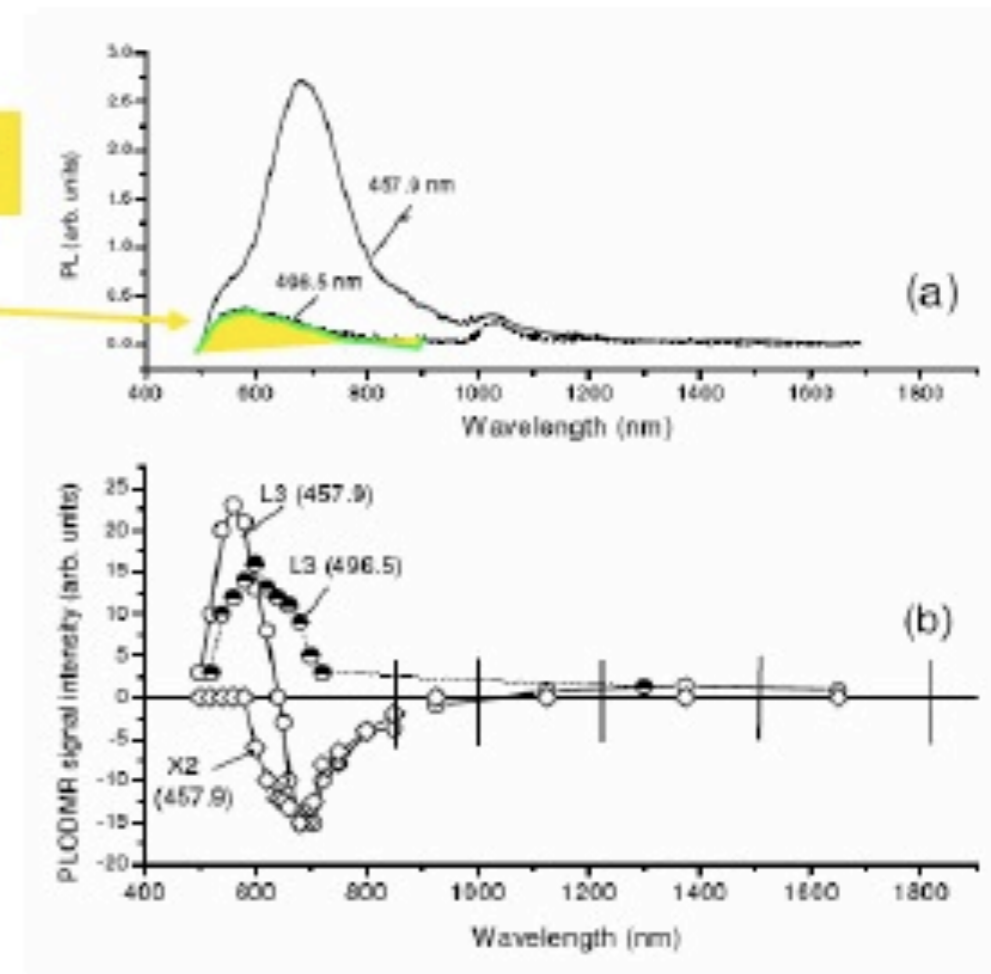
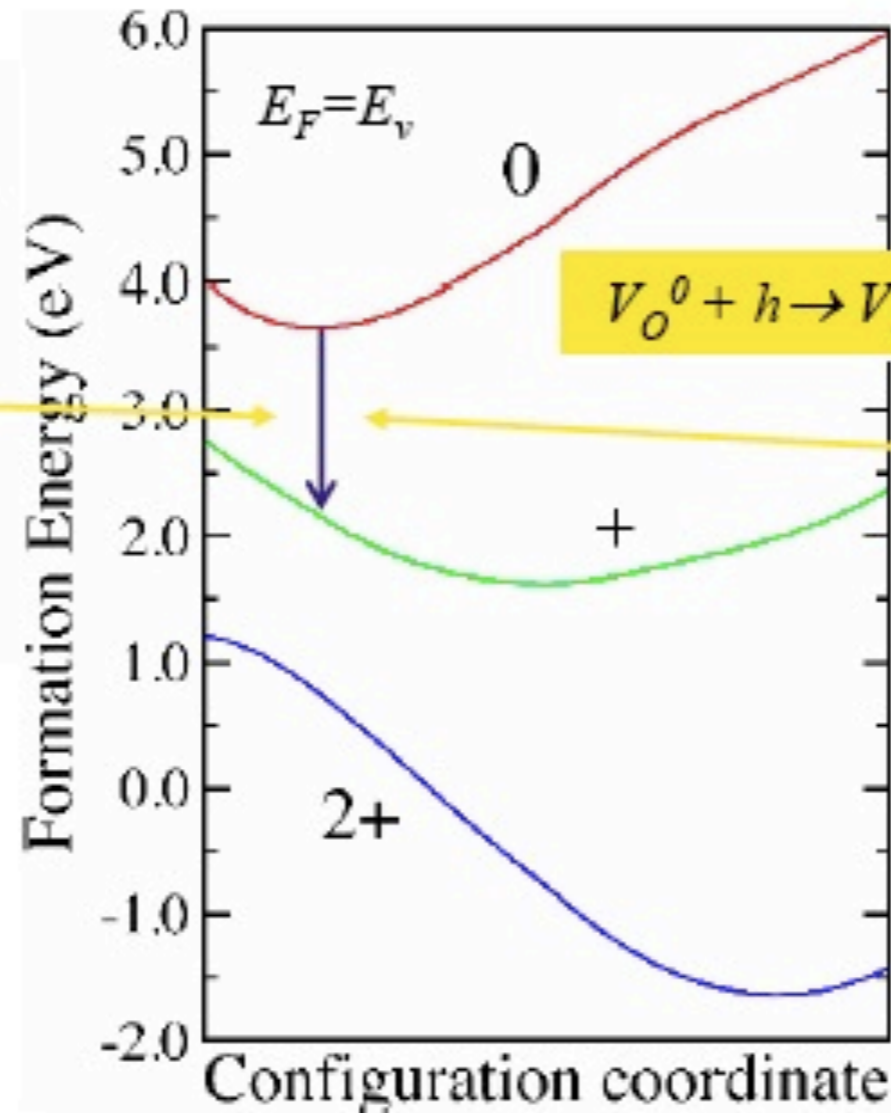
Oxygen vacancy - comparison with experiments

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

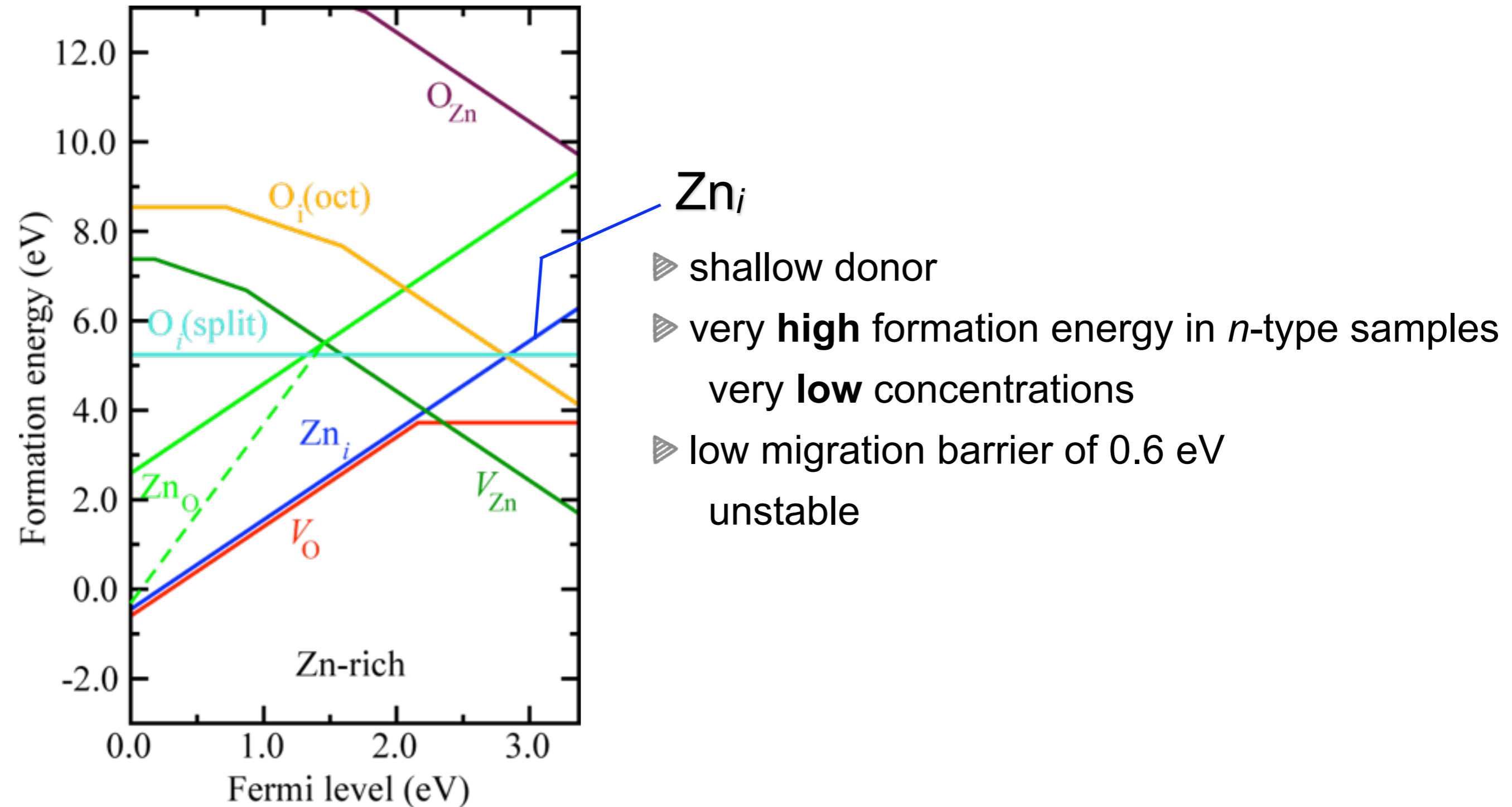
A. Janotti and C. G. Van de Walle, Appl. Phys. Lett. 87, 122102 (2005).



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

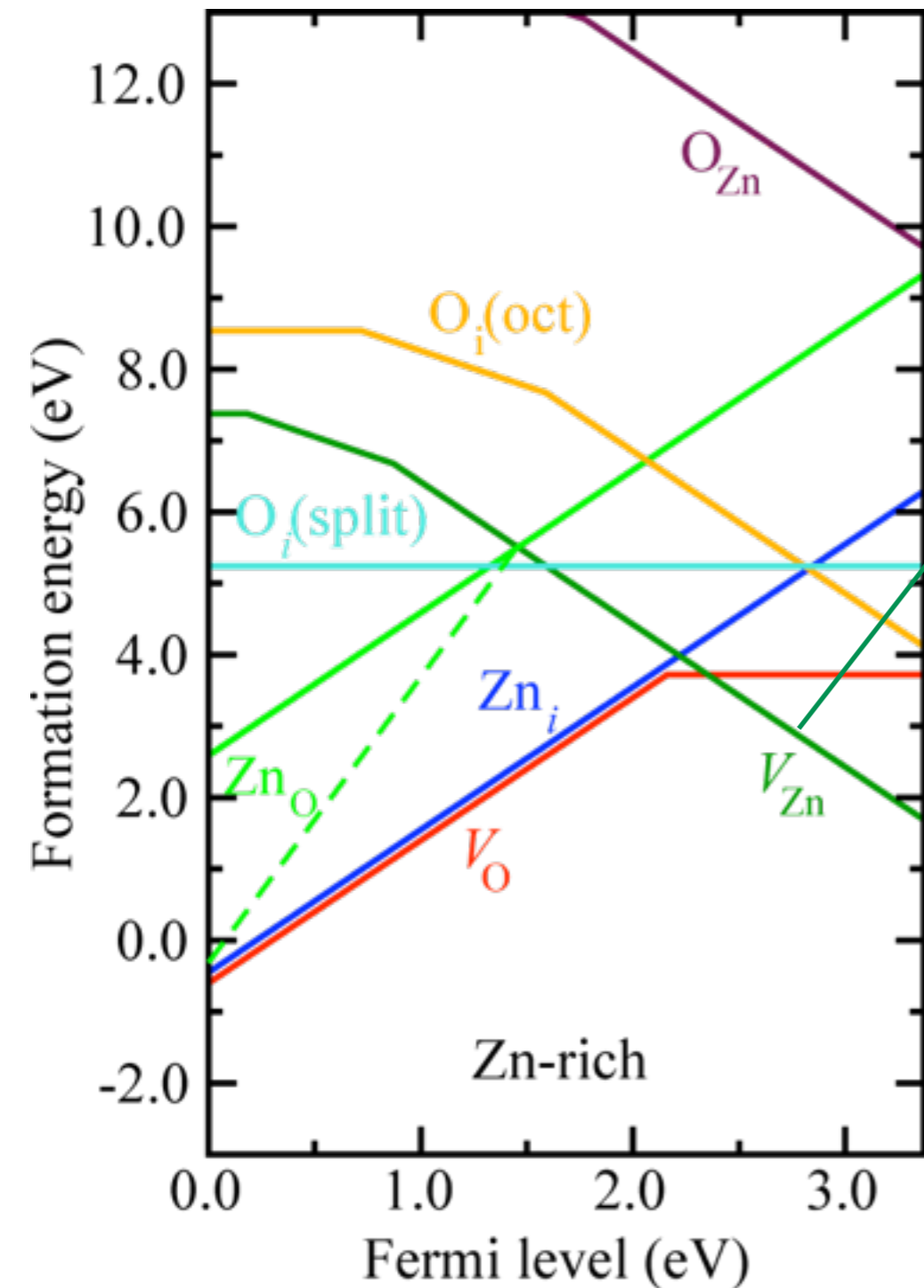


Zinc interstitial



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)

Zinc vacancy



V_{Zn}

- ▶ deep acceptor, $(-1/2-)$ ~ 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)

Possible donor impurities in ZnO

hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]					
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]											

* Lanthanide series

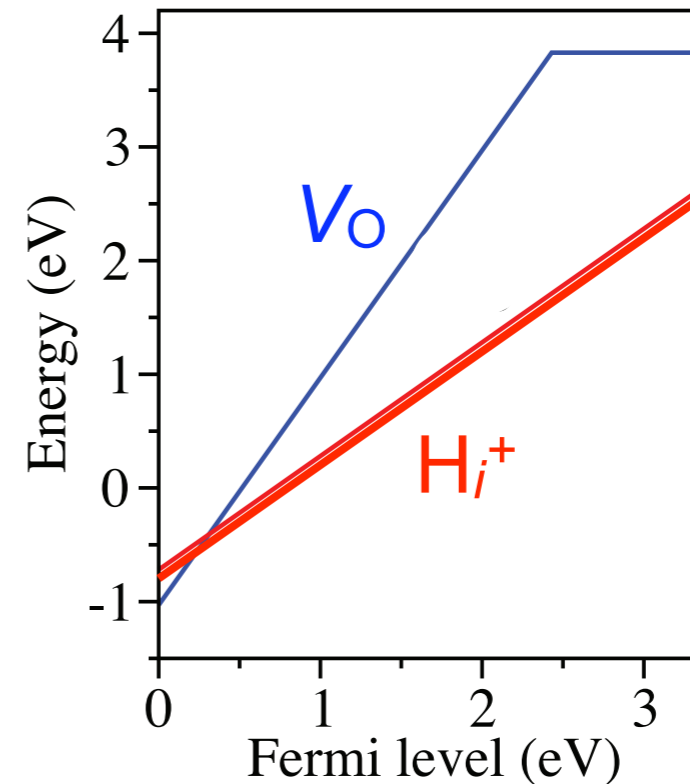
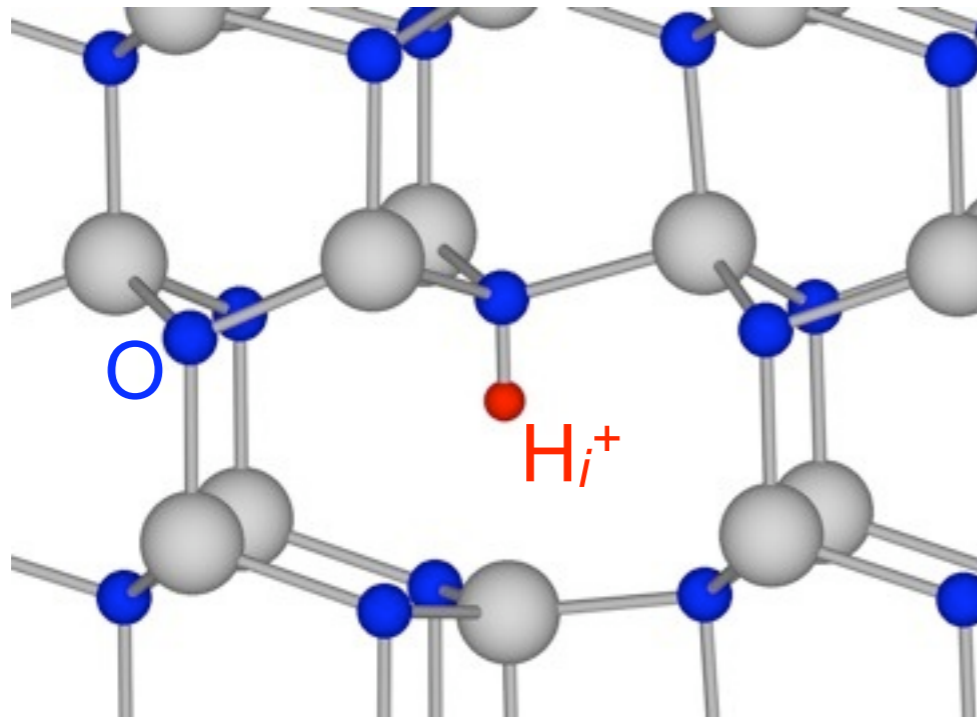
lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

** Actinide series

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

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)

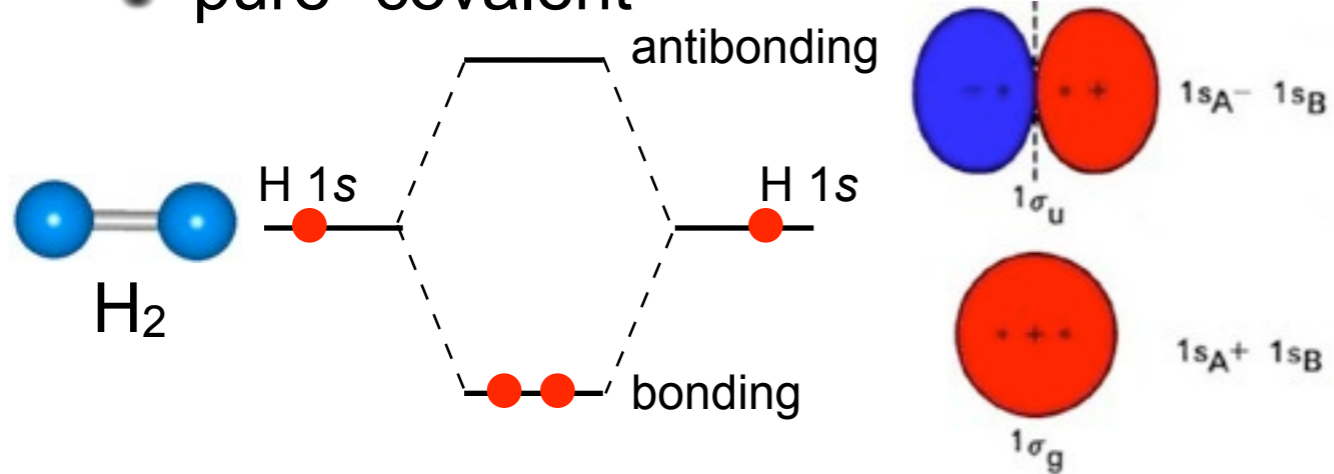
Jokela and McCluskey, Phys. Rev. B **72**, 113201 (2005)

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

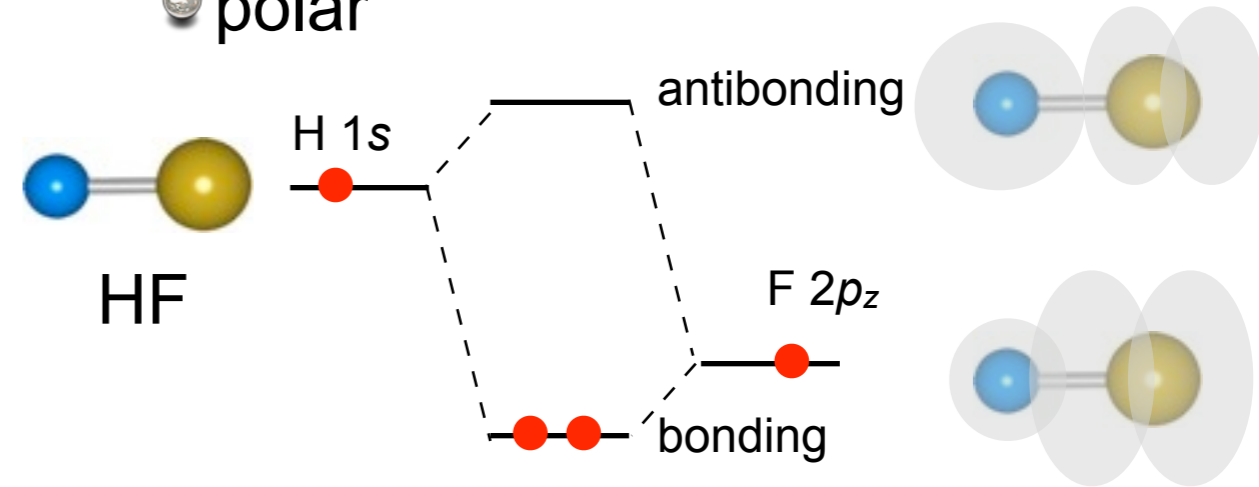
**Have to reconsider
the role of hydrogen...**

Hydrogen in molecules

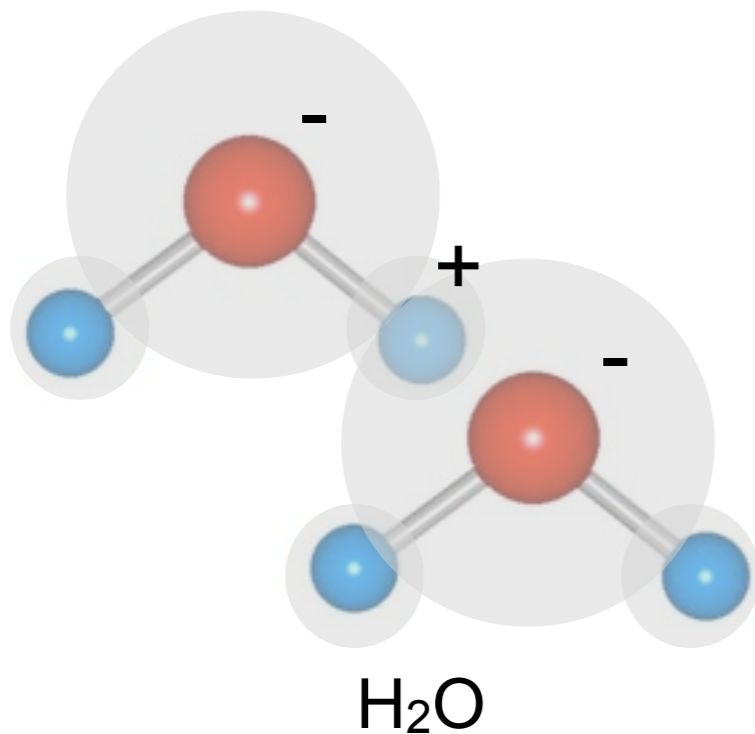
“pure” covalent



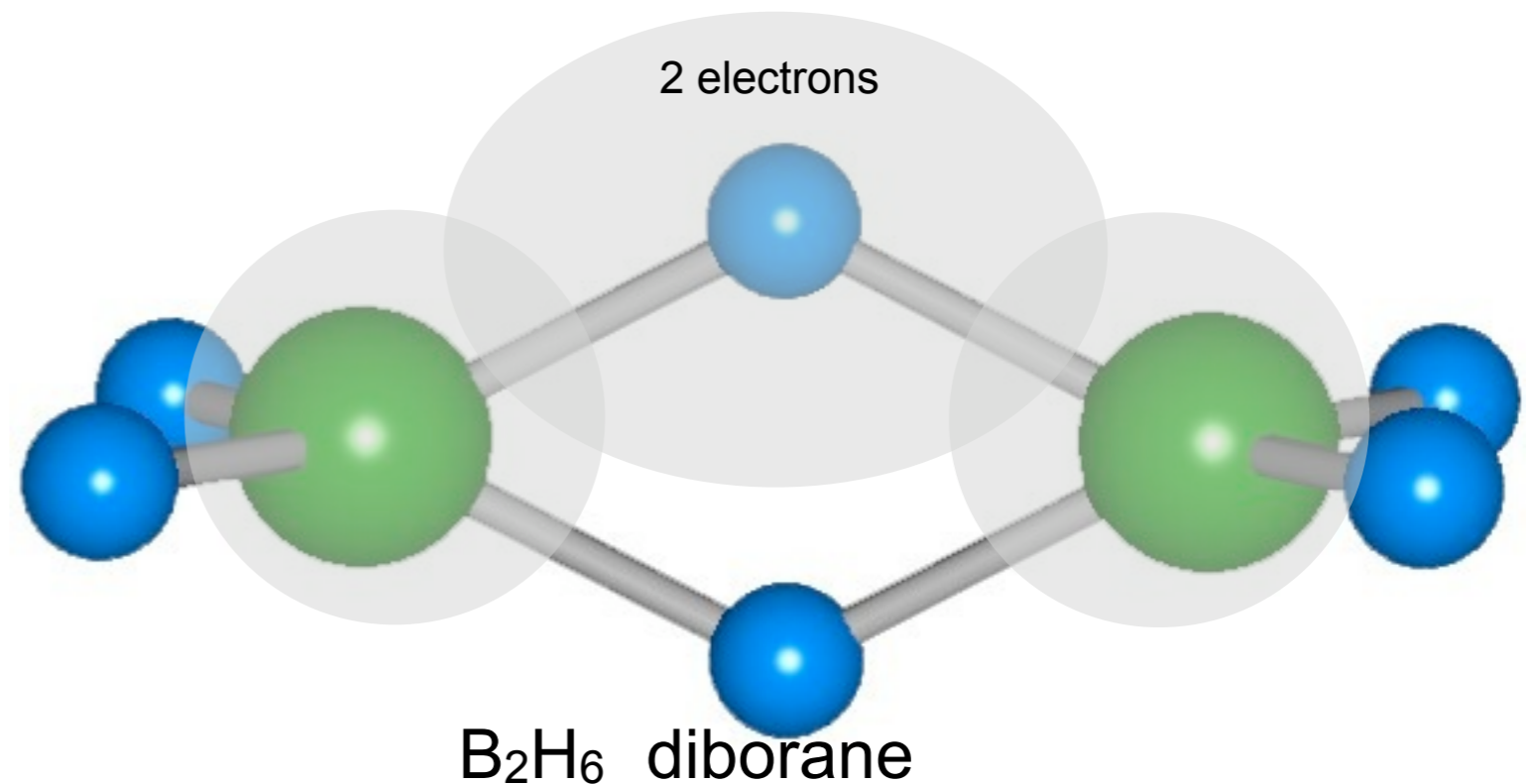
polar



intermolecular
(hydrogen bonding)



3-center 2-electron bonds
(Lipscomb, Nobel Prize in Chemistry 1976)



Hydrogen in solids

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

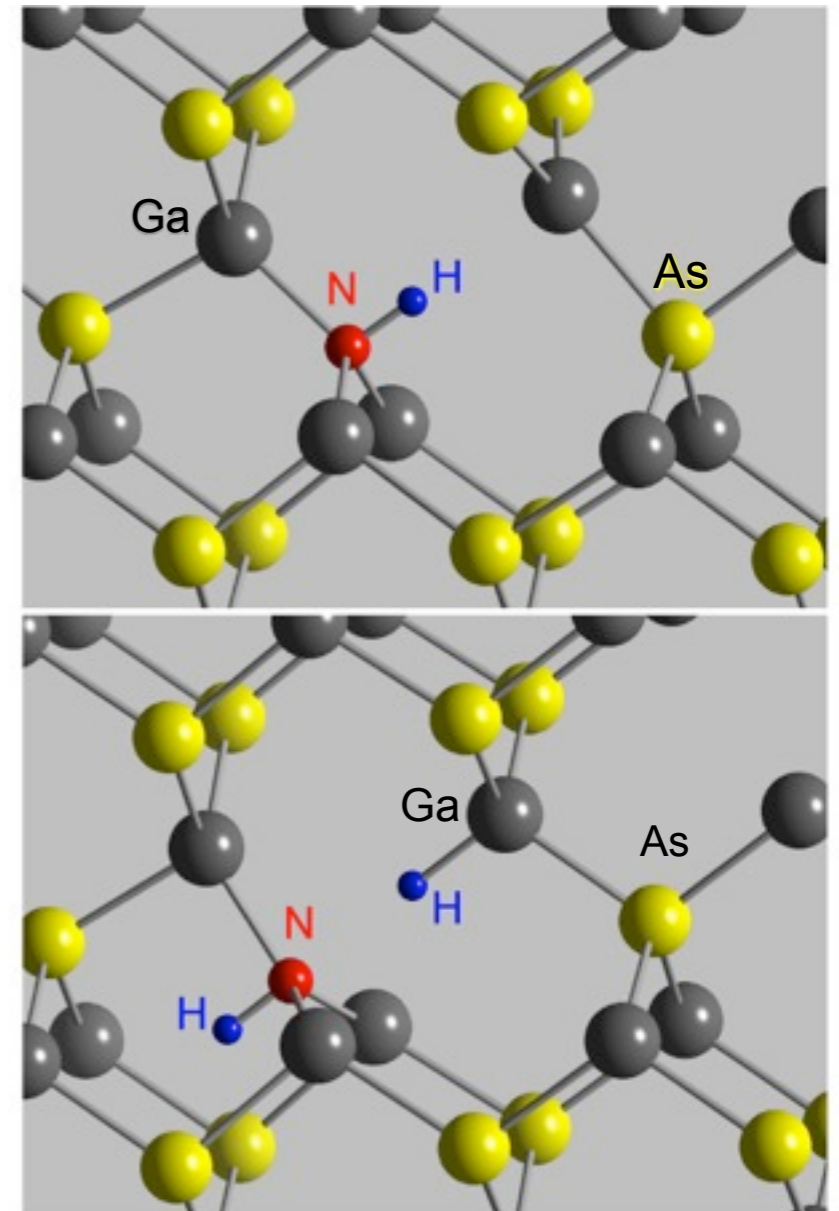
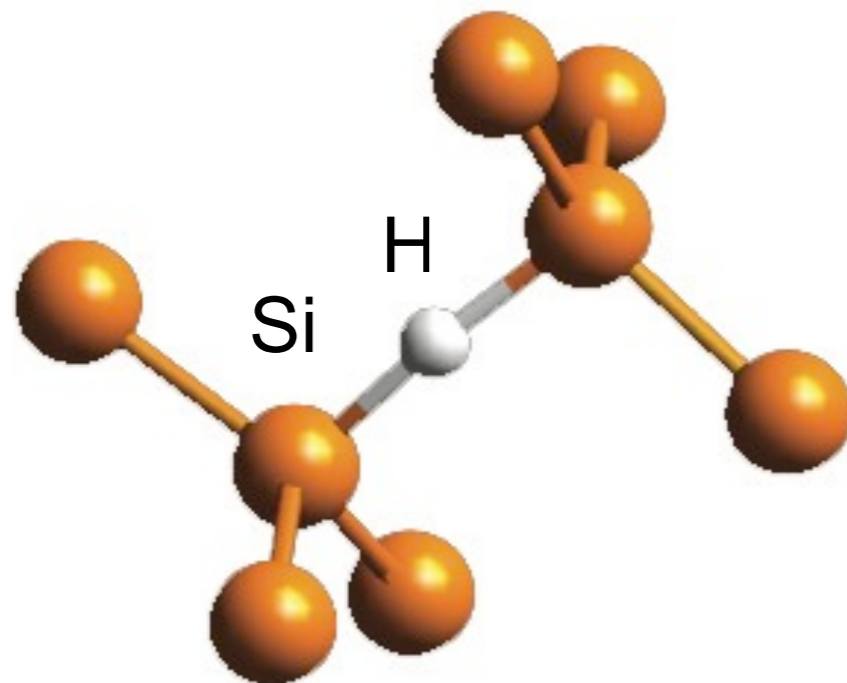


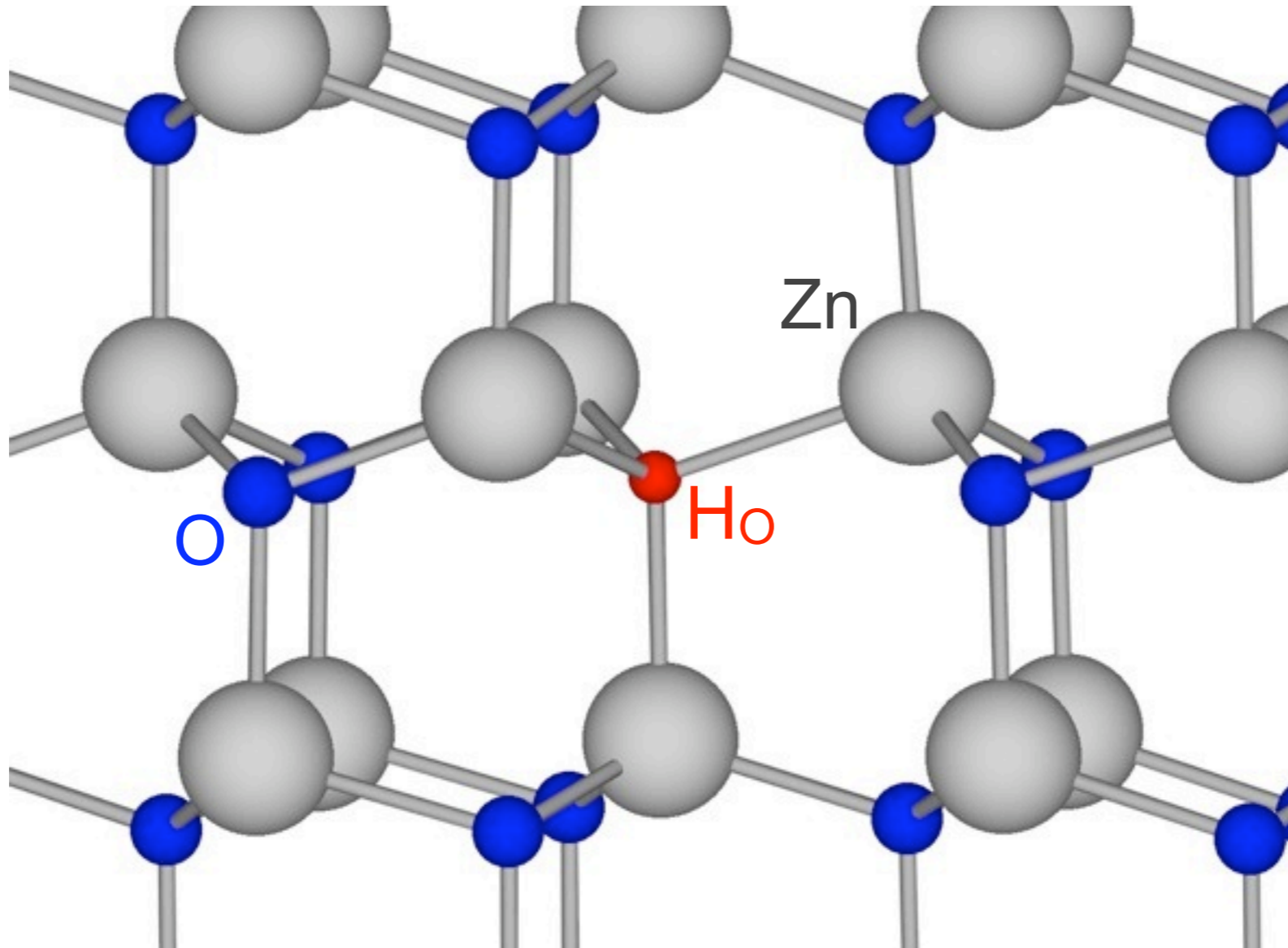
Fig 1. (a) N-H and (b) N-H₂* models in dilute GaAsN alloys

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)

Oxygen vacancy in ZnO

O vacancy

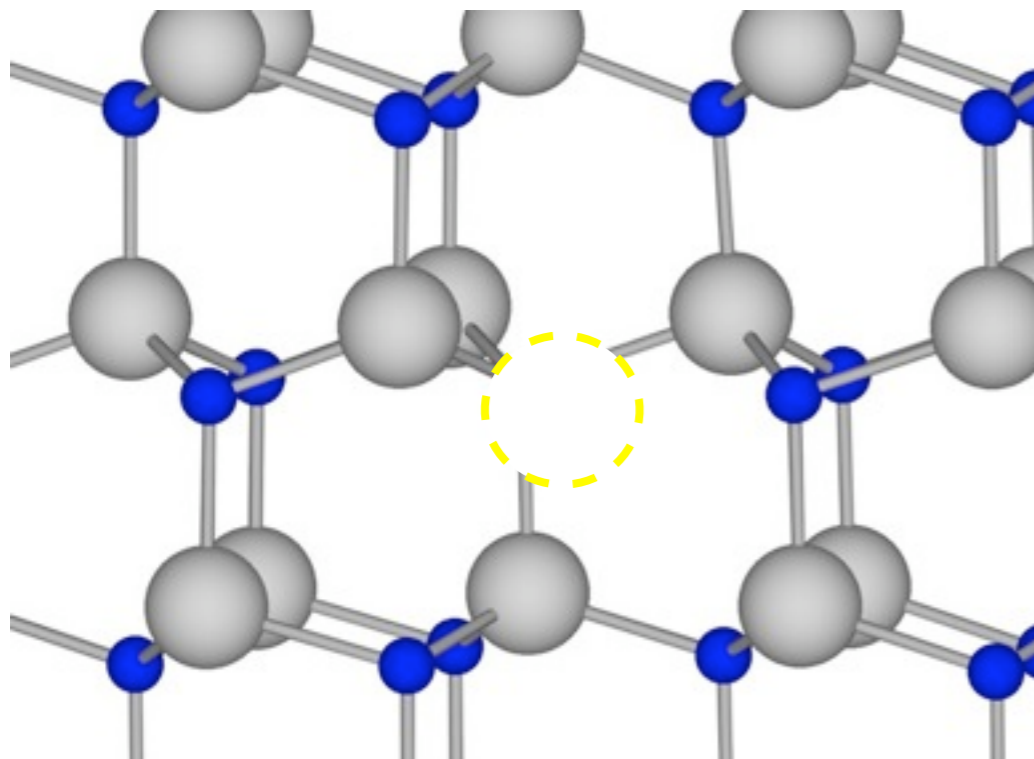
Zn dangling bonds



conduction band

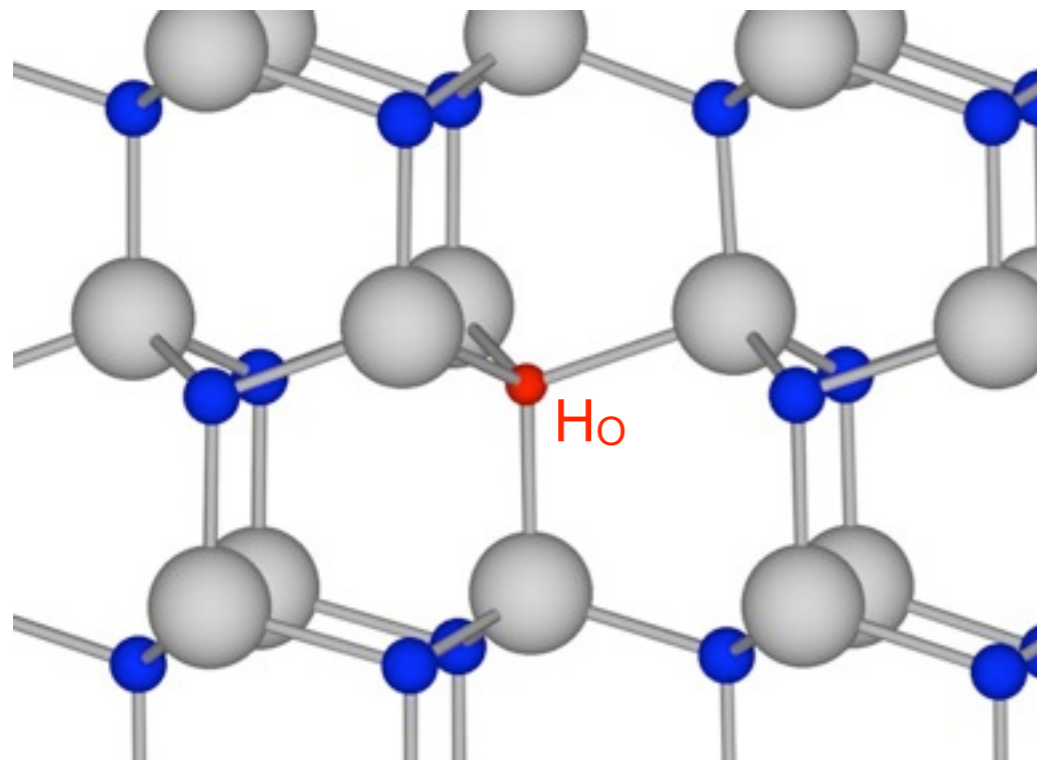
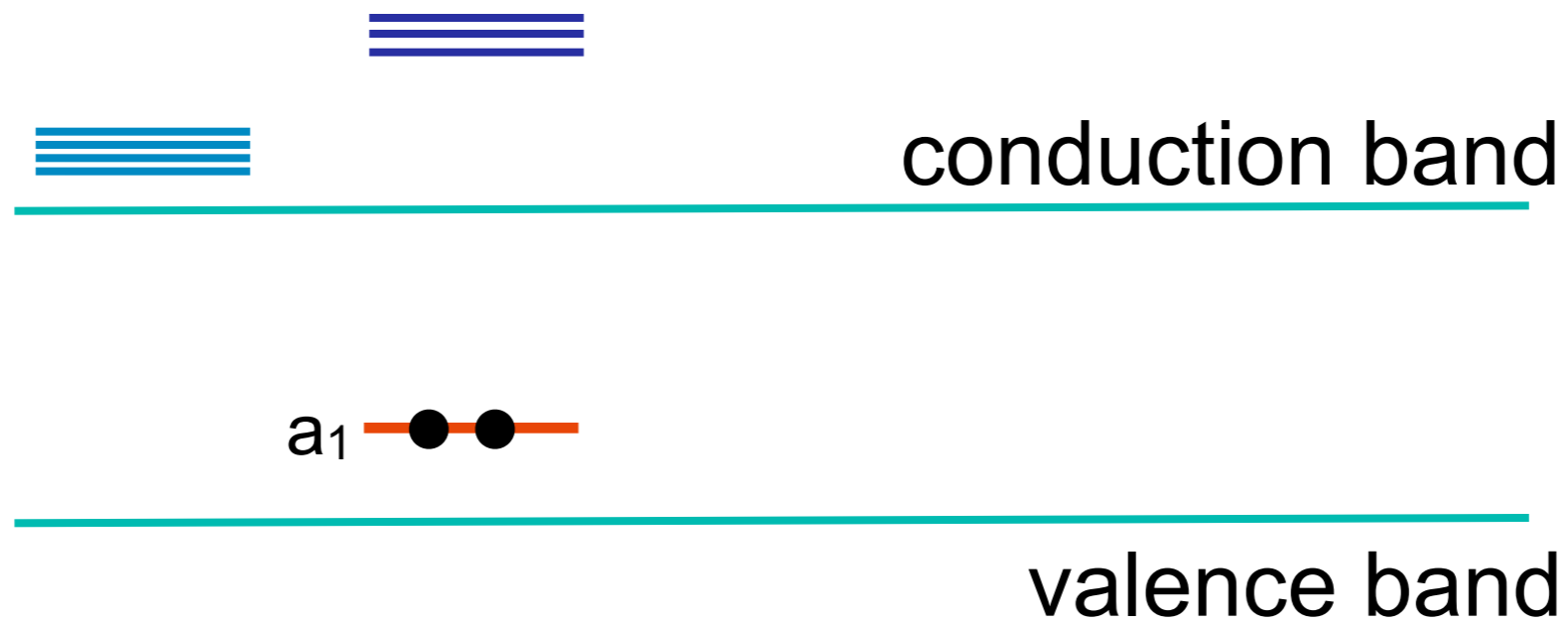
a_1

valence band



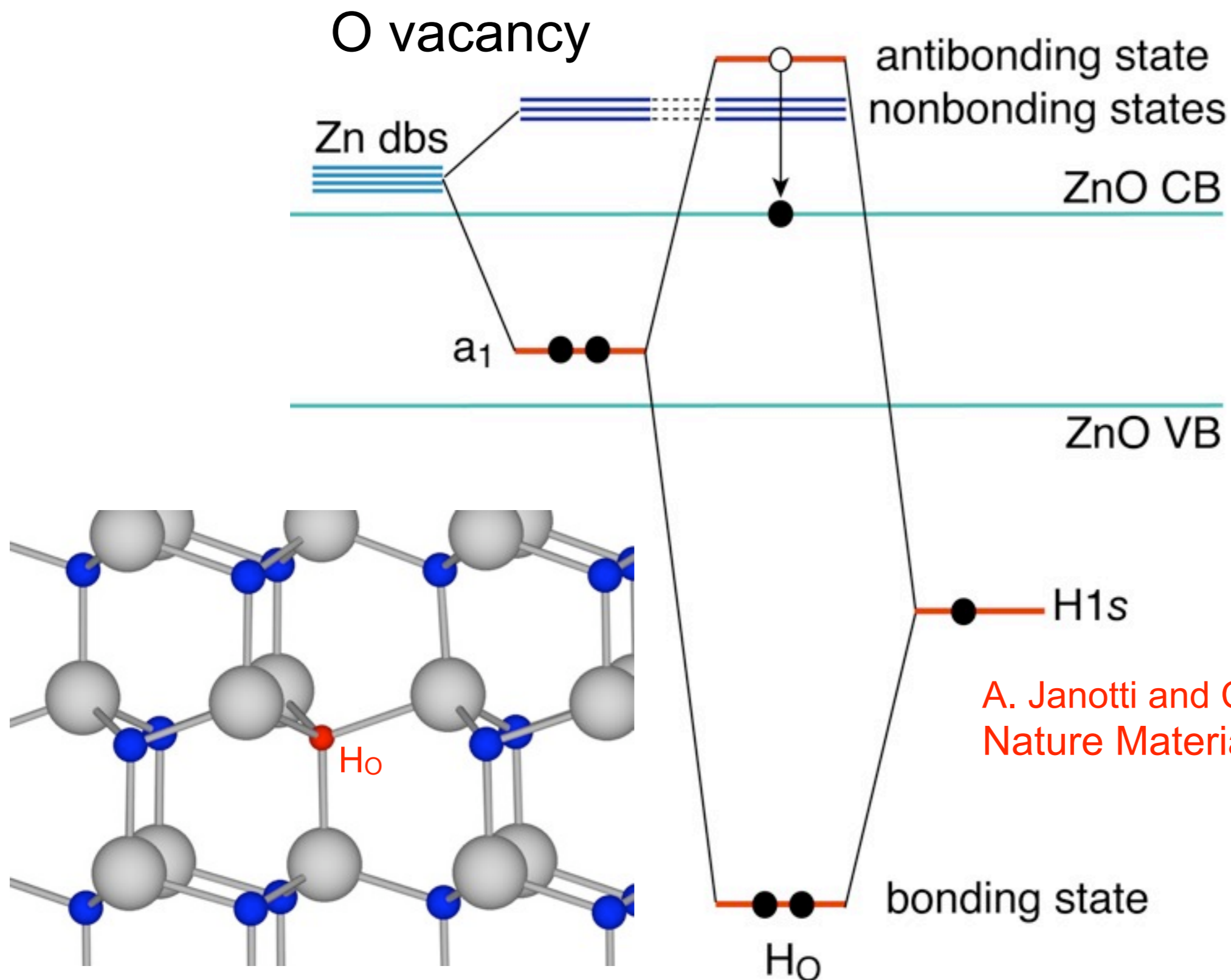
Hydrogen multicenter bond in ZnO

O vacancy



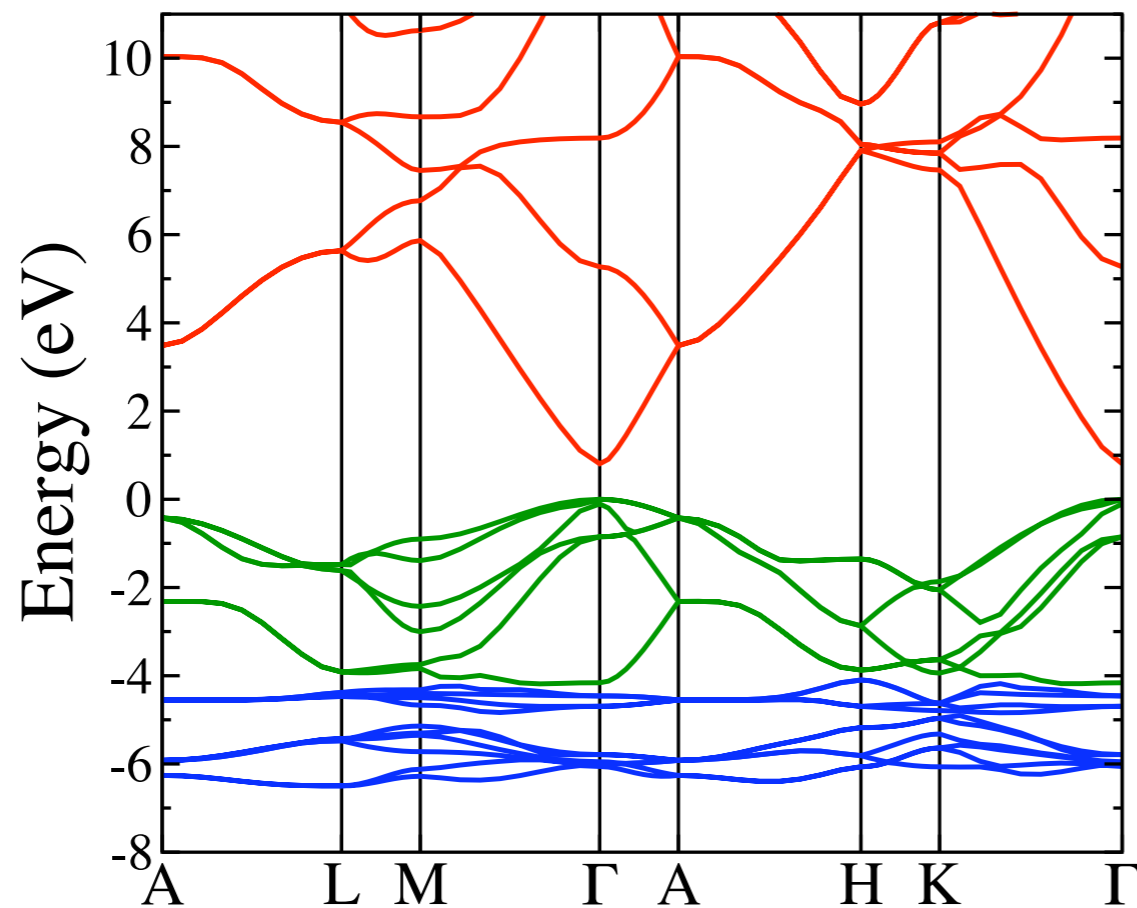
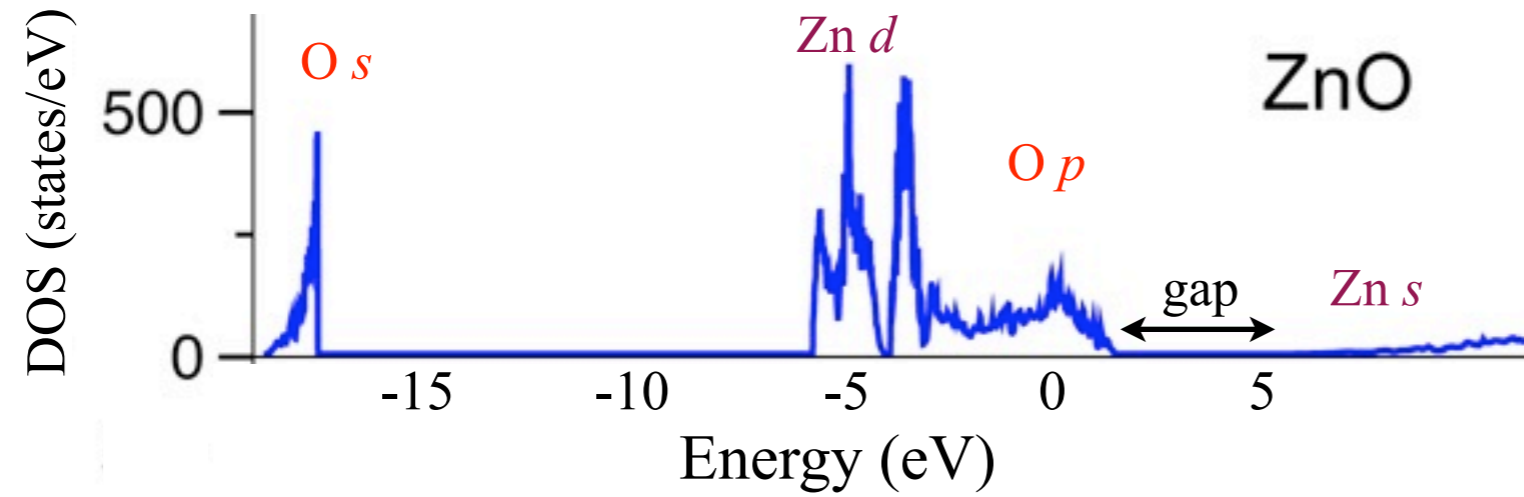
 H 1s

Hydrogen multicenter bond in ZnO

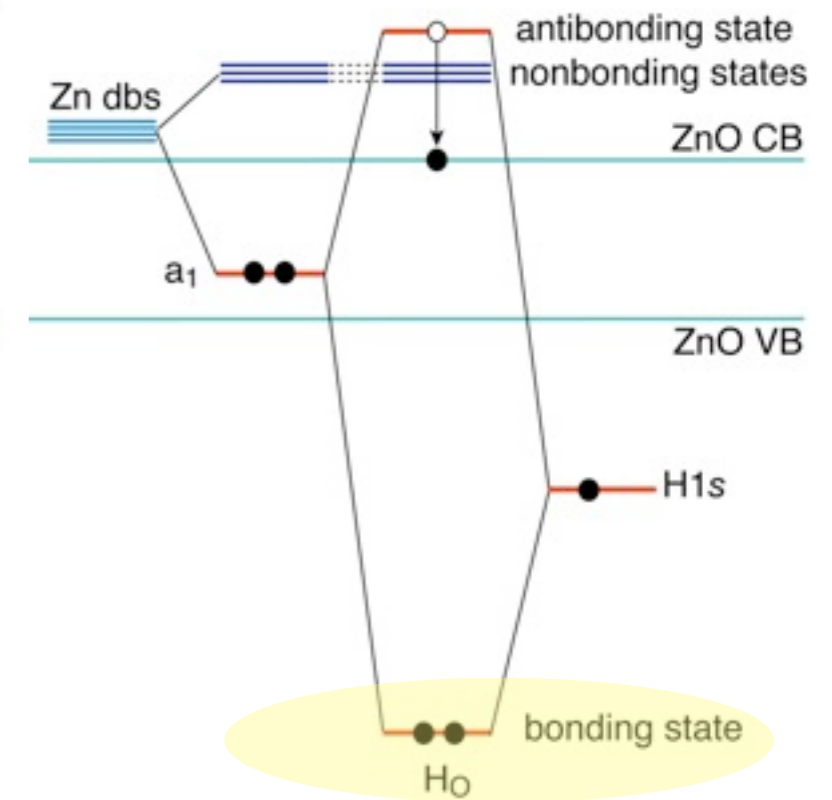
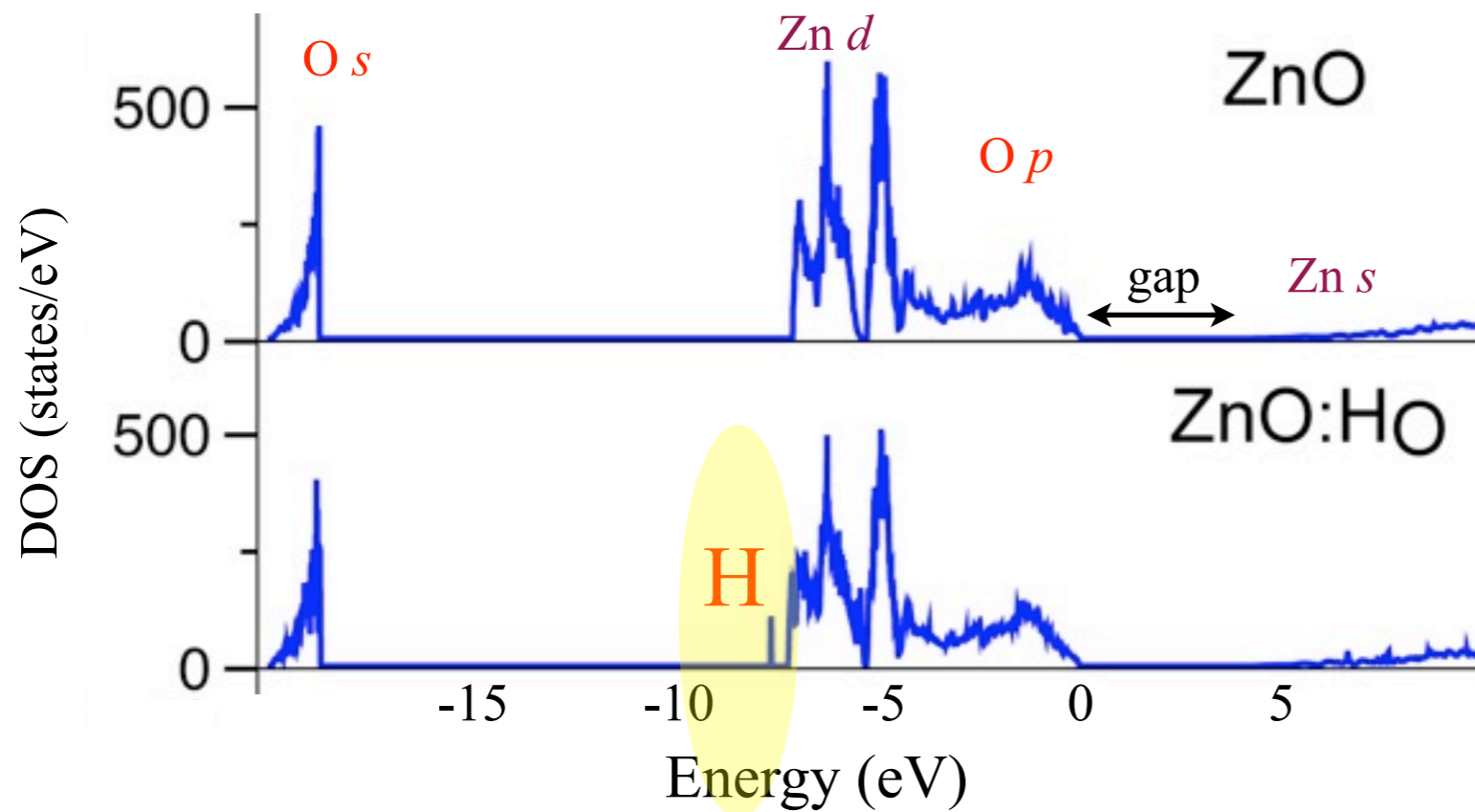


A. Janotti and C. G. Van de Walle,
Nature Materials **6**, 44 (2007)

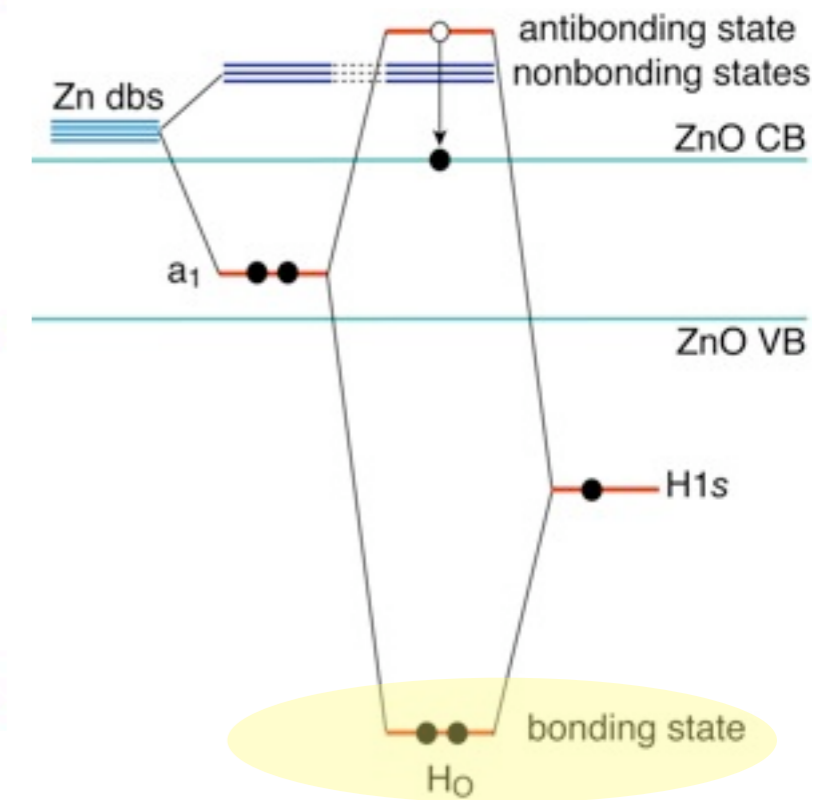
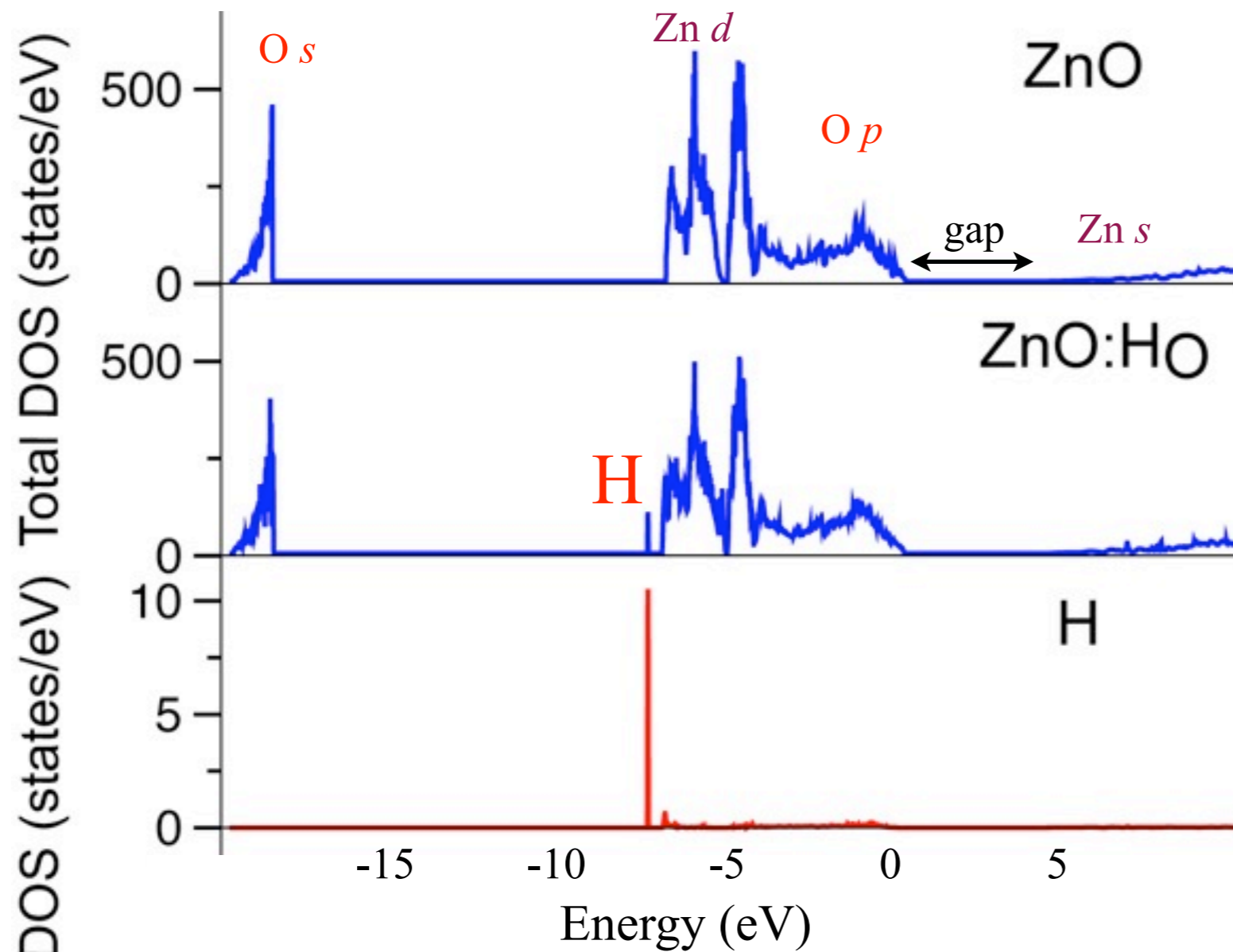
Density of States of ZnO



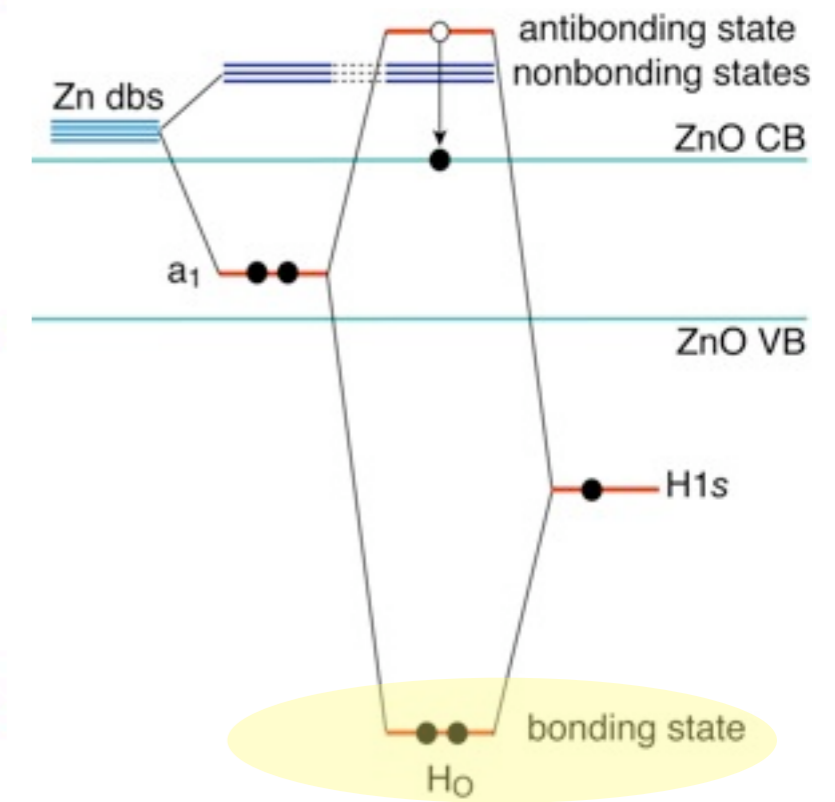
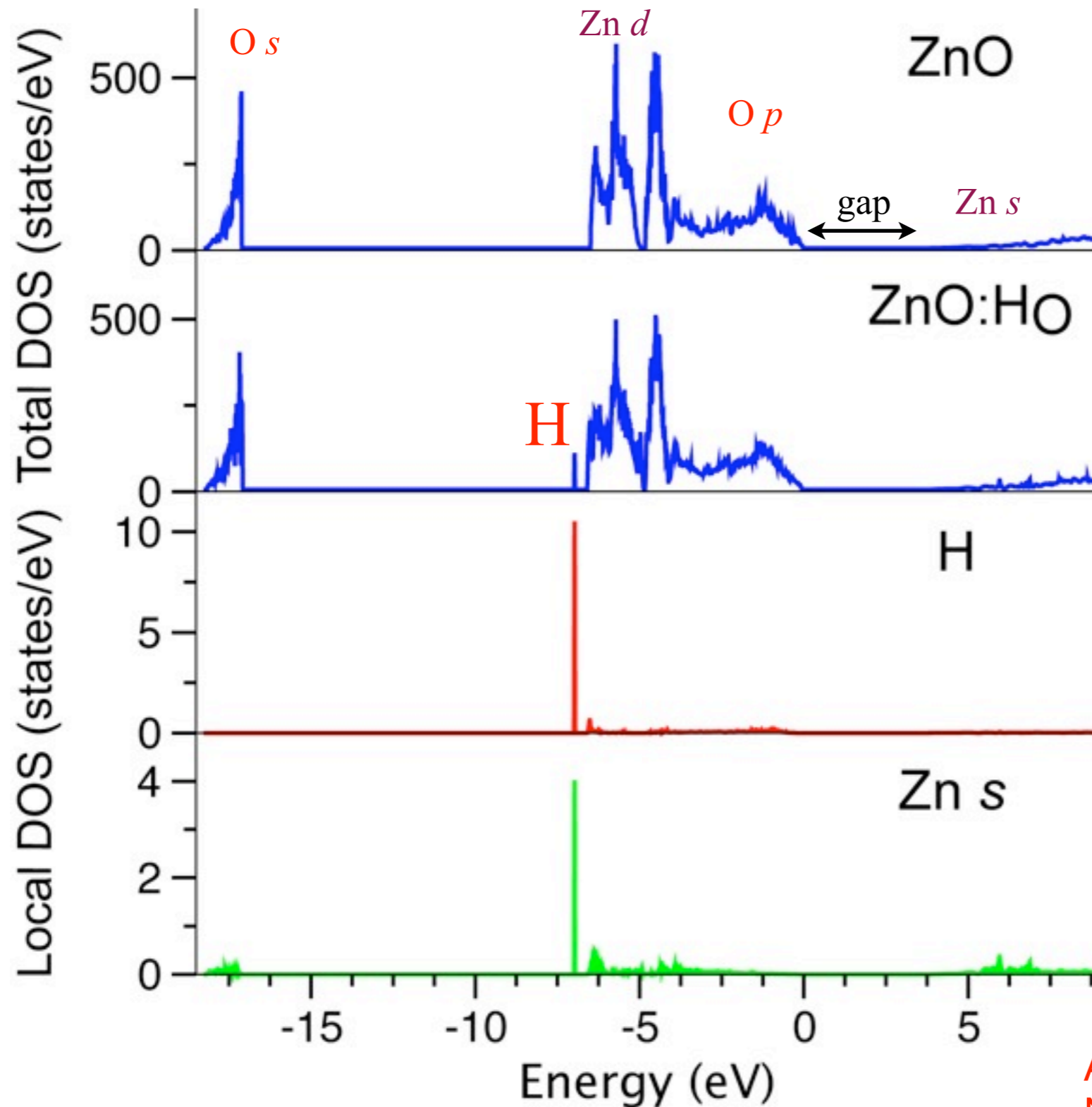
Density of States of Ho in ZnO



Density of States of Ho in ZnO

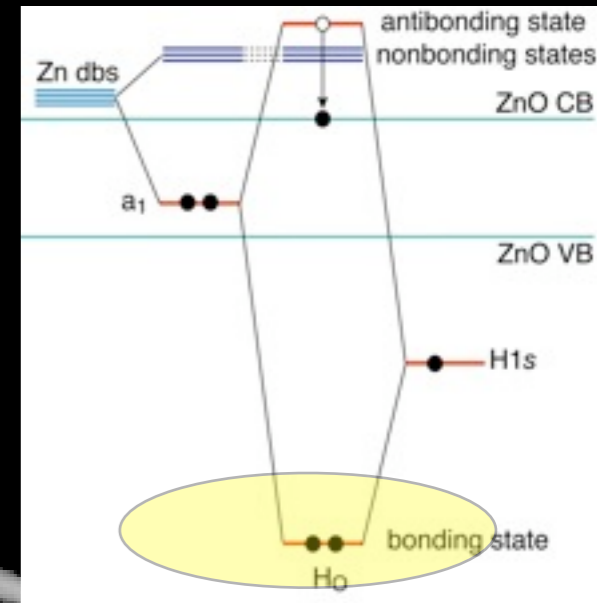
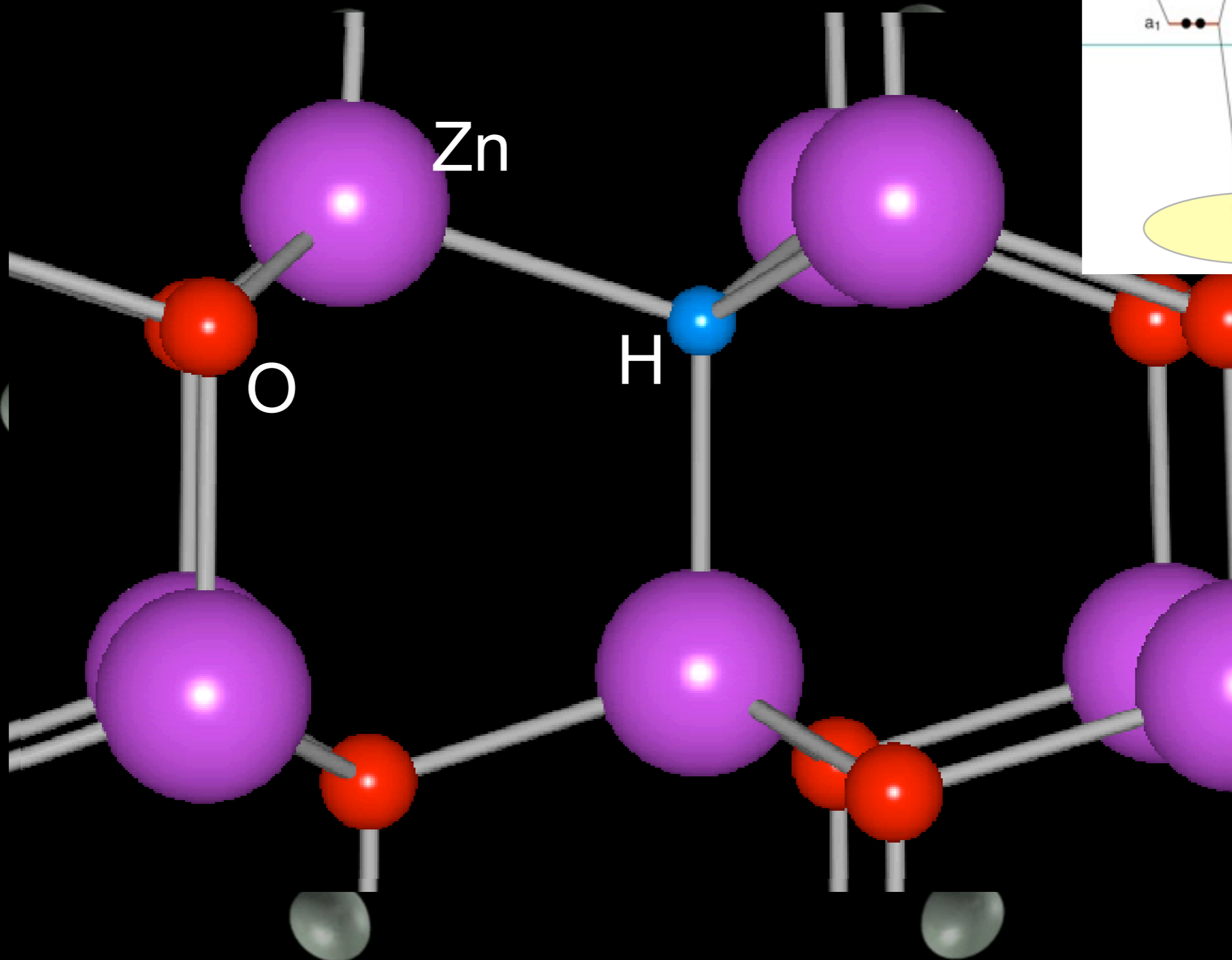


Density of States of Ho in ZnO

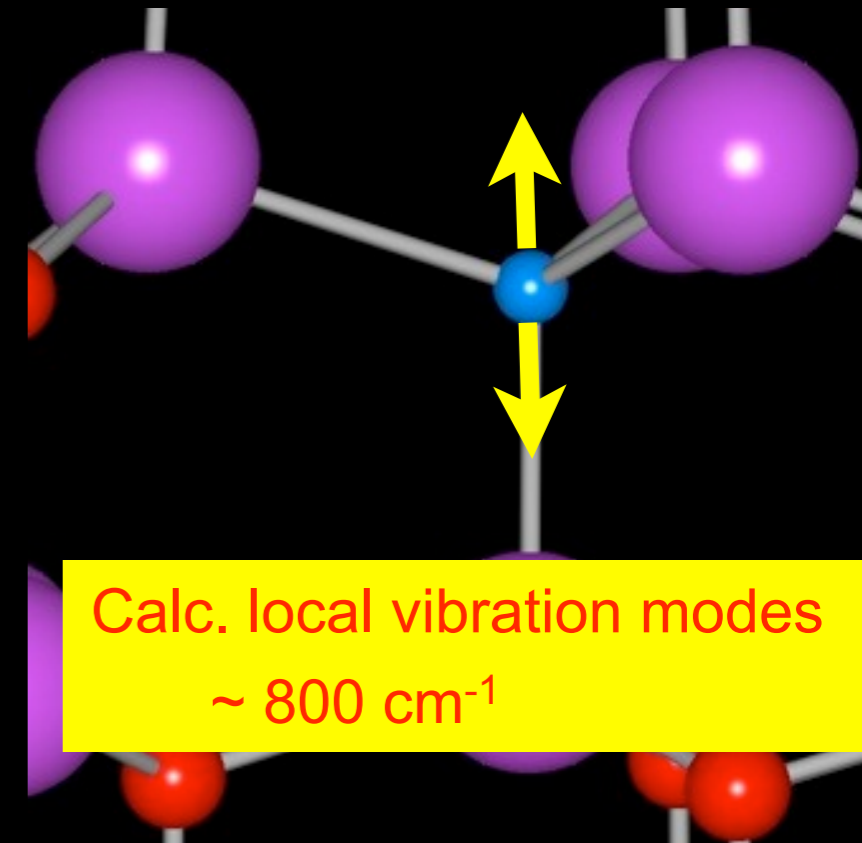
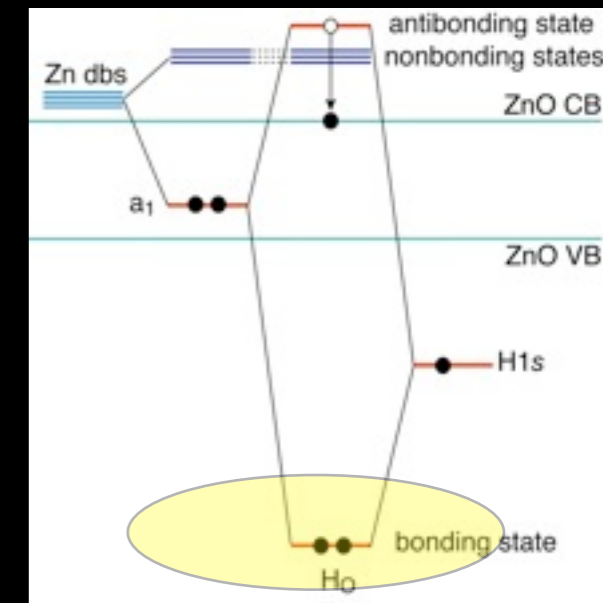
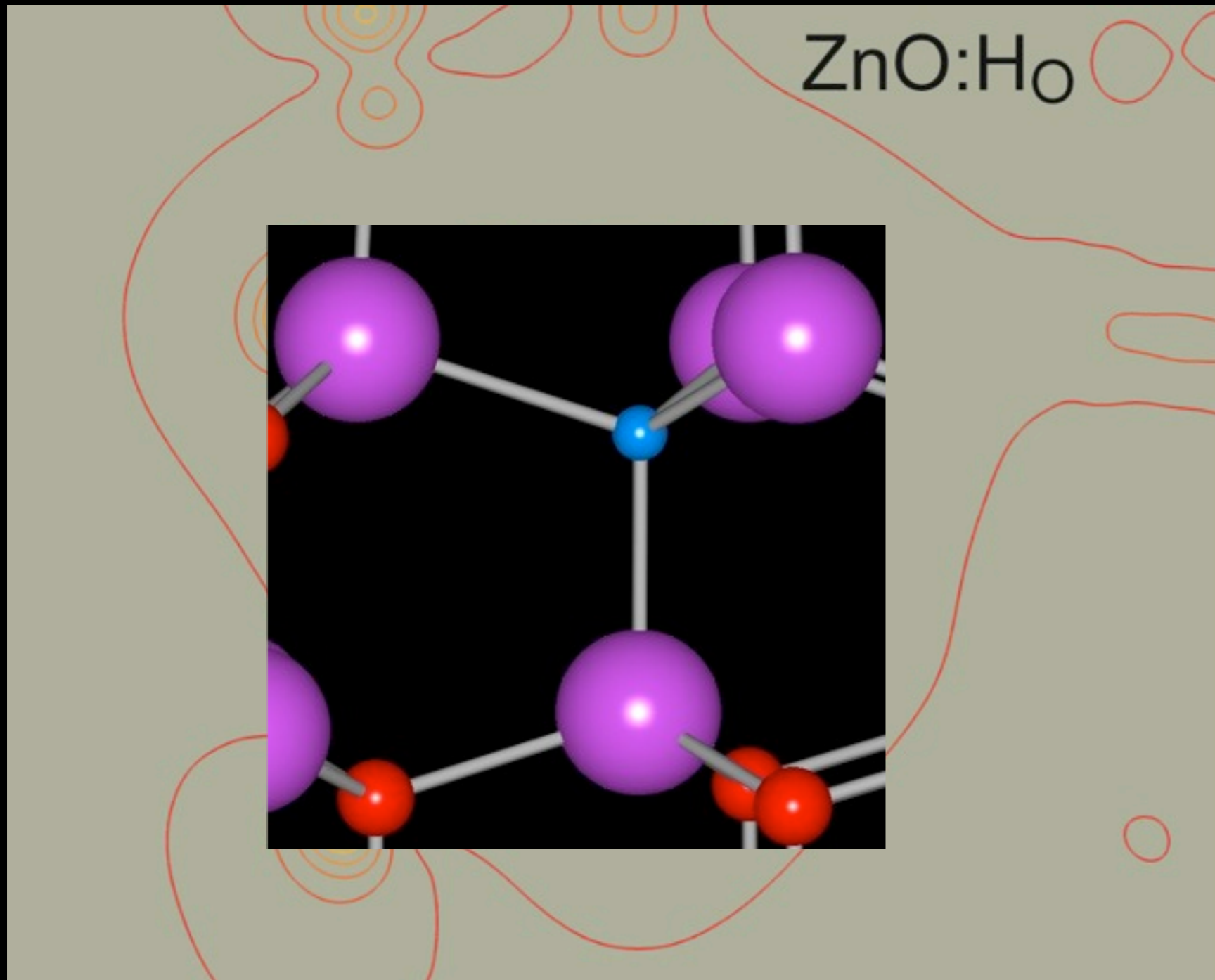


A. Janotti and C. G. Van de Walle,
Nature Materials 6, 44 (2007)

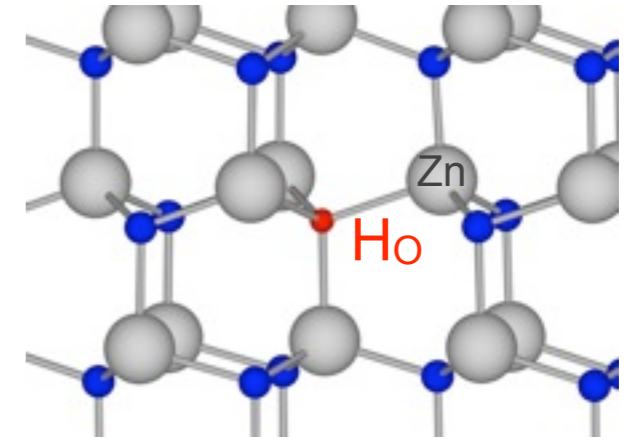
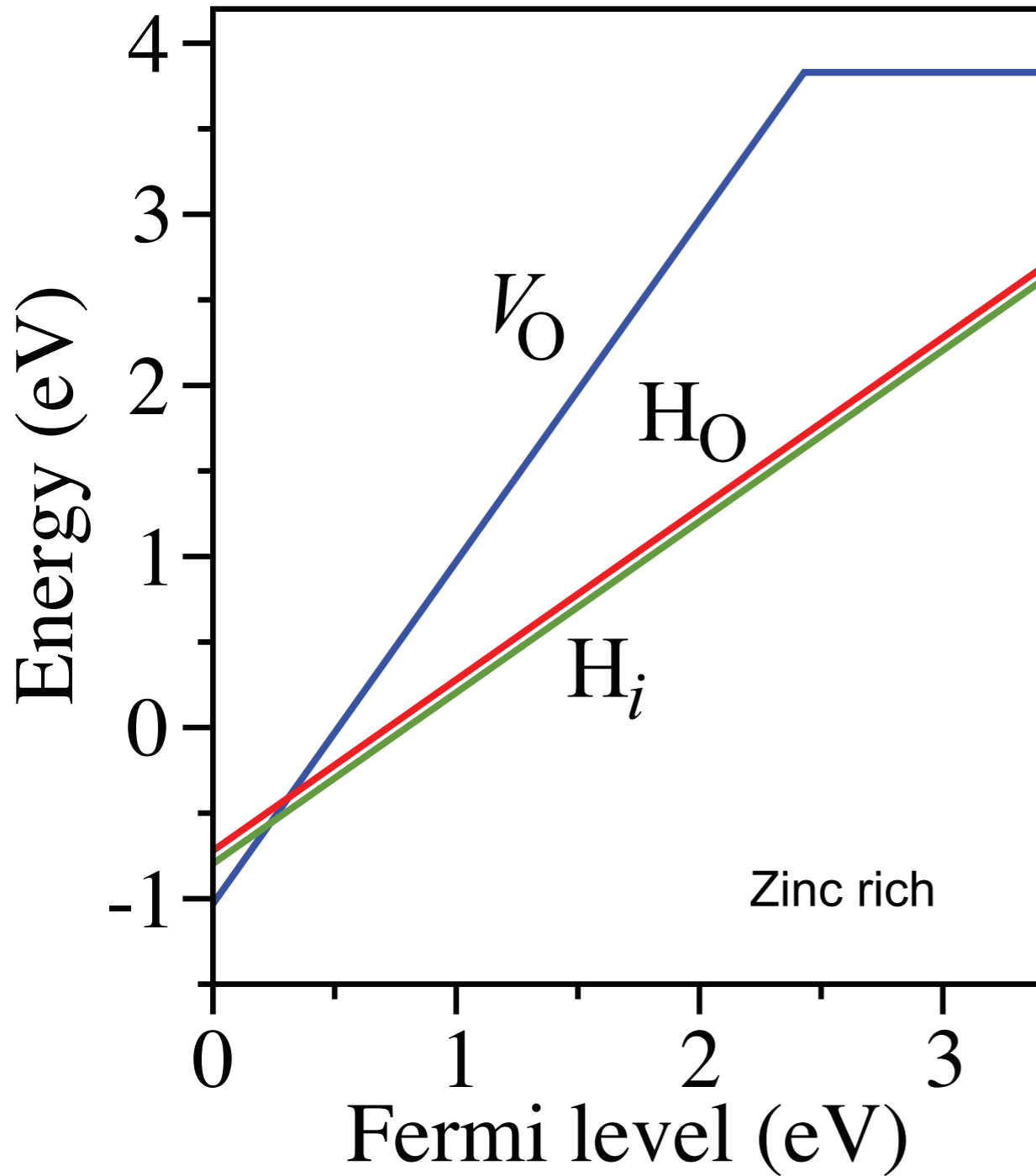
Charge density H multicenter bond in ZnO



Charge density H multicenter bond in ZnO



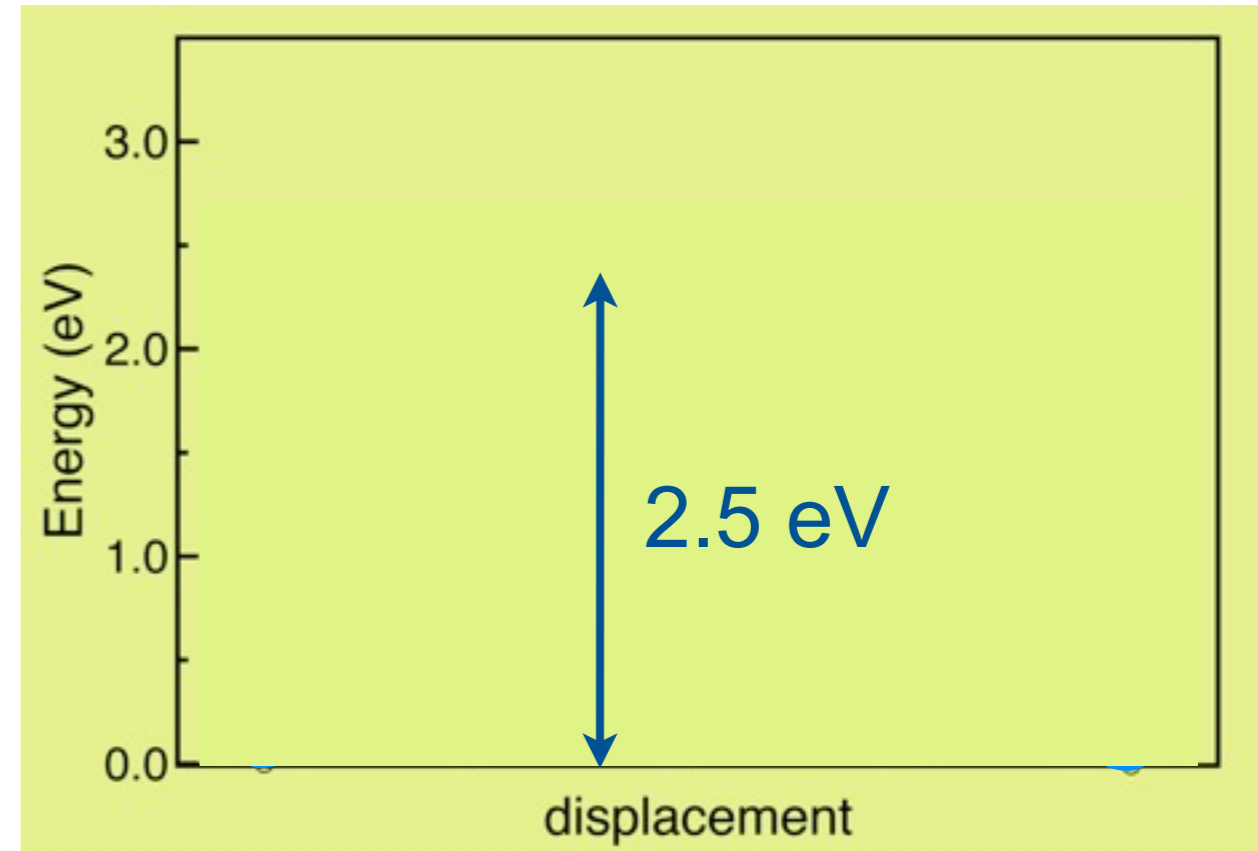
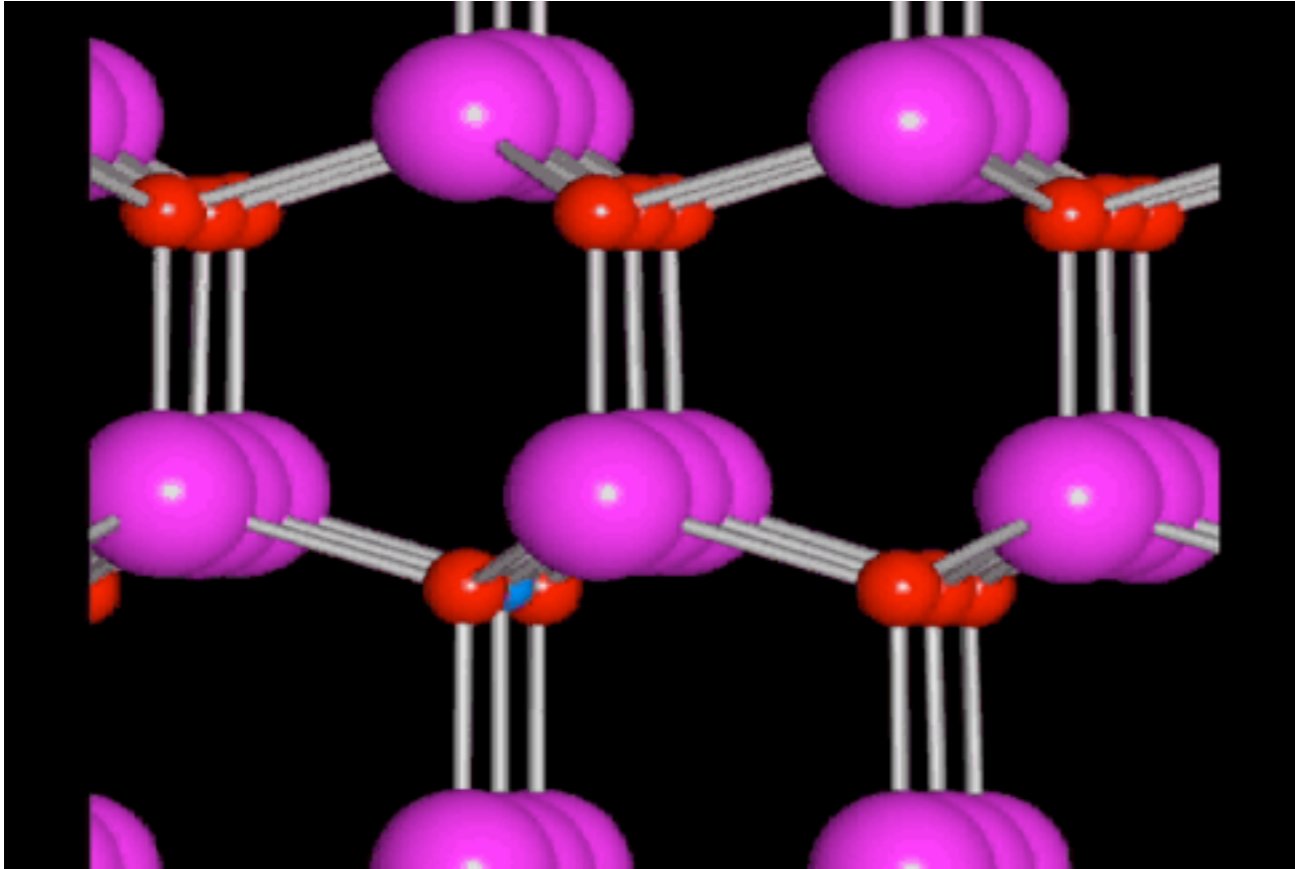
H₀ in ZnO - Formation energy



- ▶ H₀ has low formation energy
- ▶ shallow donor
- ▶ stable against dissociation

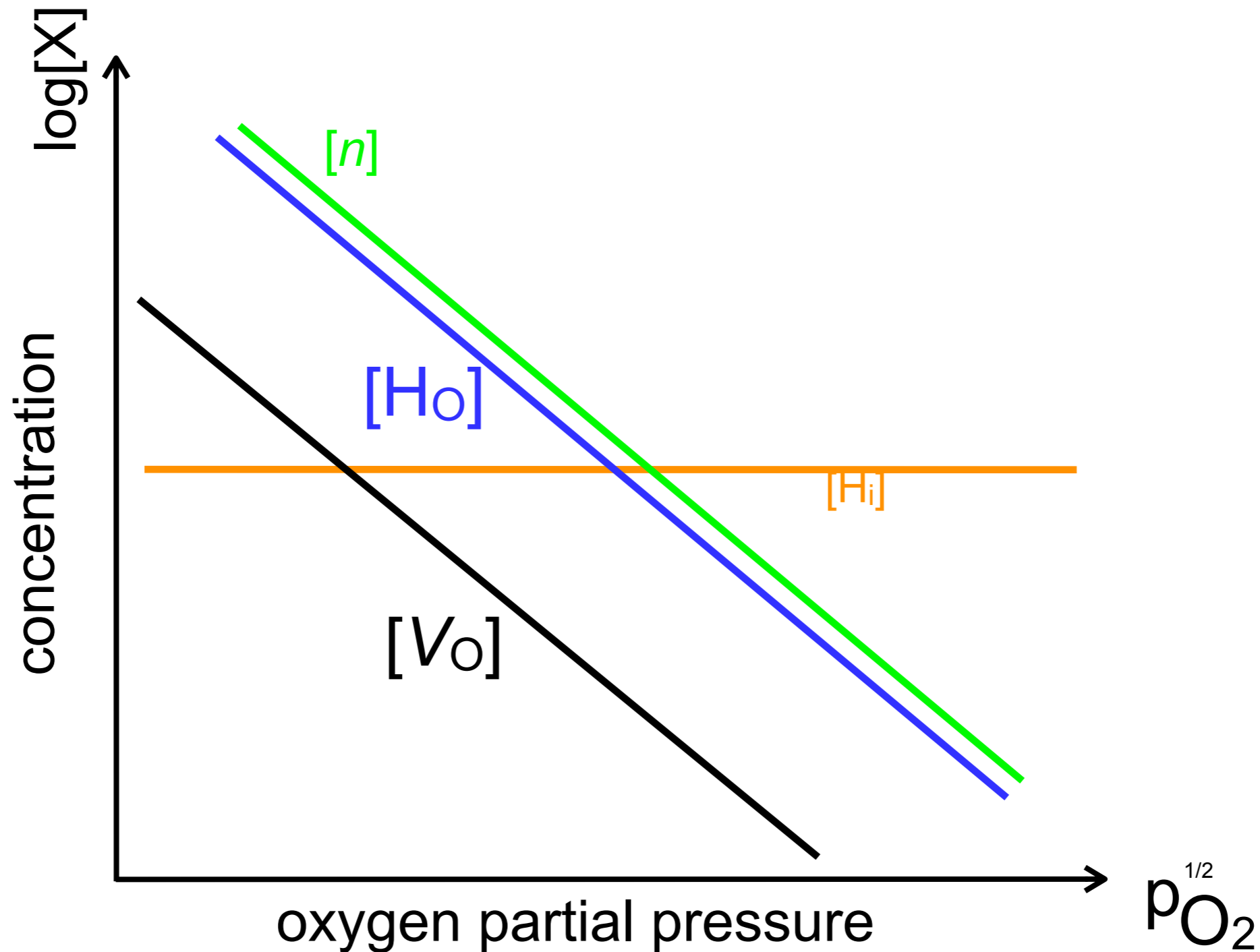


H_o migration in ZnO



- ▶ migration barrier of 2.5 eV
 - ▶ becomes mobile at $\sim 500^\circ\text{C}$
 - ▶ consistent with experimental observations
- Shi, *et al.*, Phys. Rev. B 72, 195211 (2005)

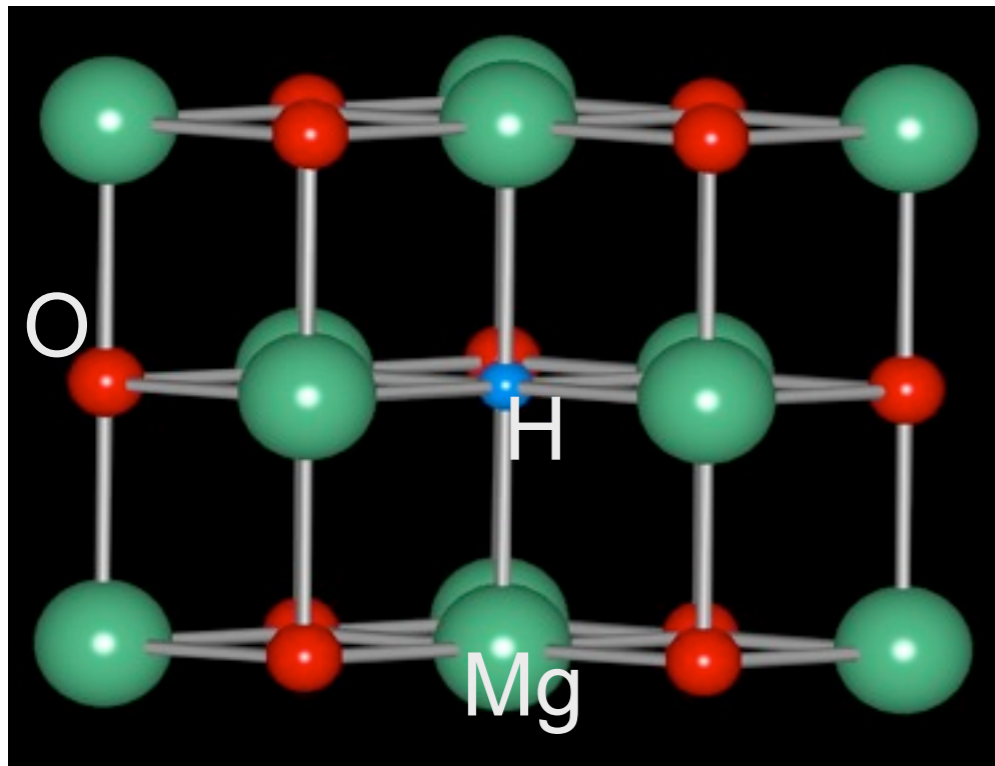
Unintentional *n*-type conductivity in ZnO



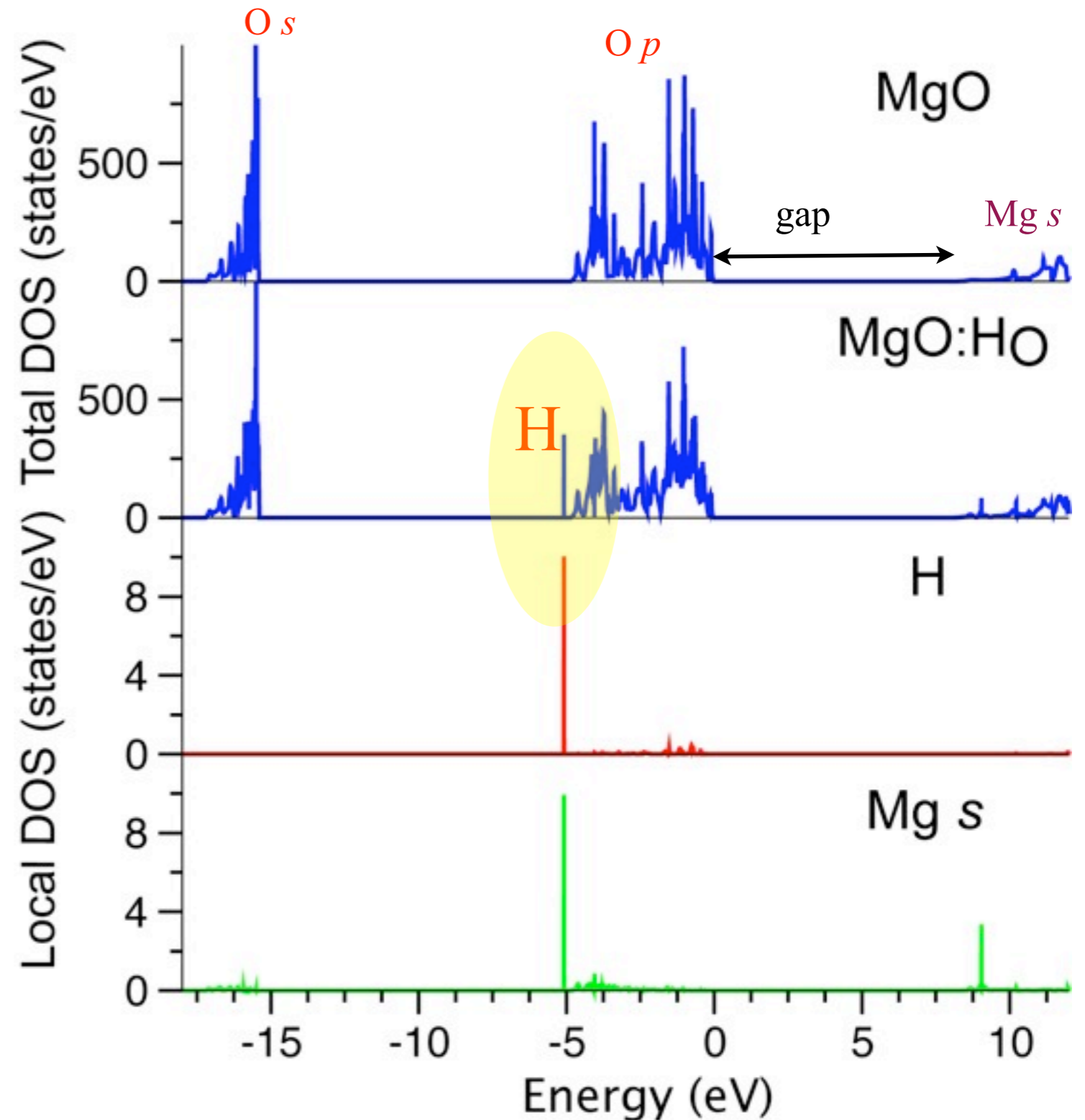
► H_o explains the dependence of *n*-type conductivity on oxygen partial pressure

Hydrogen multicolor bond in MgO

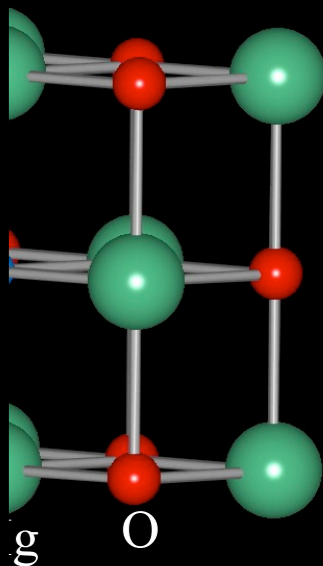
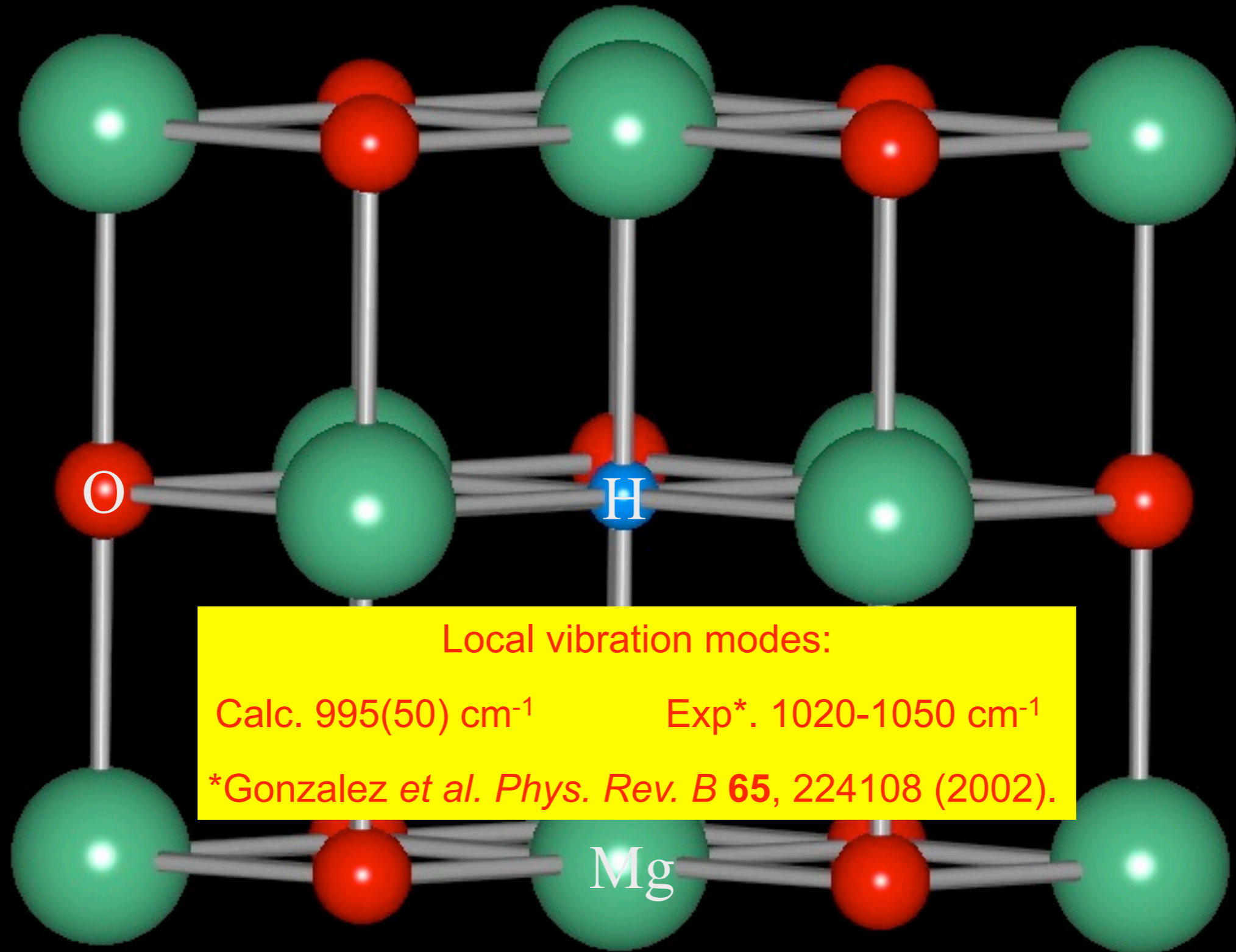
MgO: rocksalt structure



H sixfold coordinated !

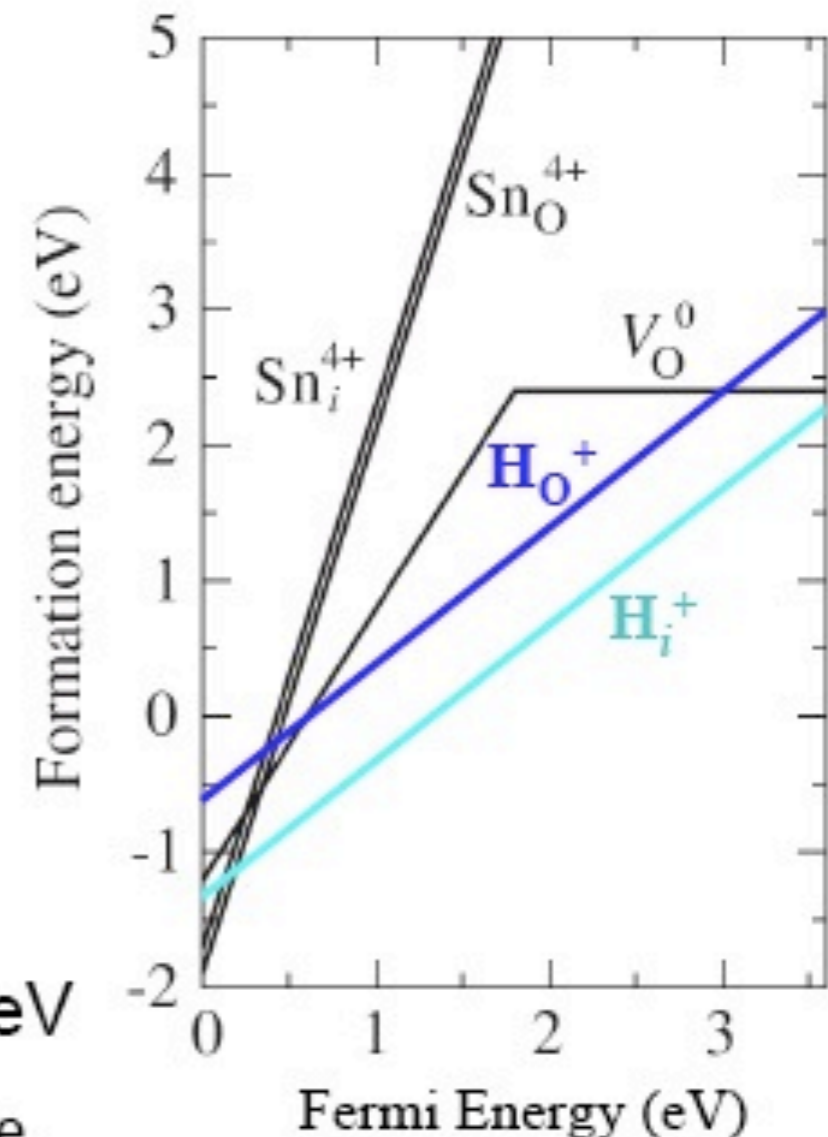
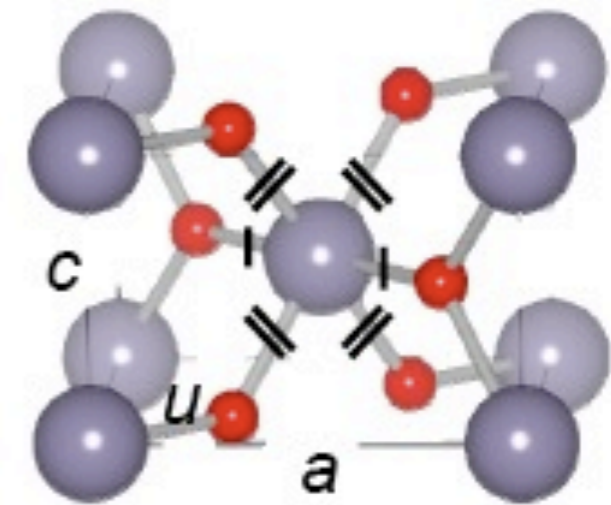


Hydrogen multicenter bond in MgO



Conductivity in SnO₂

- **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



Conductivity in SnO₂

- **p-type doping**

- Difficult in ZnO

- » N: high formation energy

- » Group-I on Zn site:
deep acceptors, or self-compensation

- Potentially more feasible in SnO₂:

- » Group-III on Sn site

- **Acceptors**

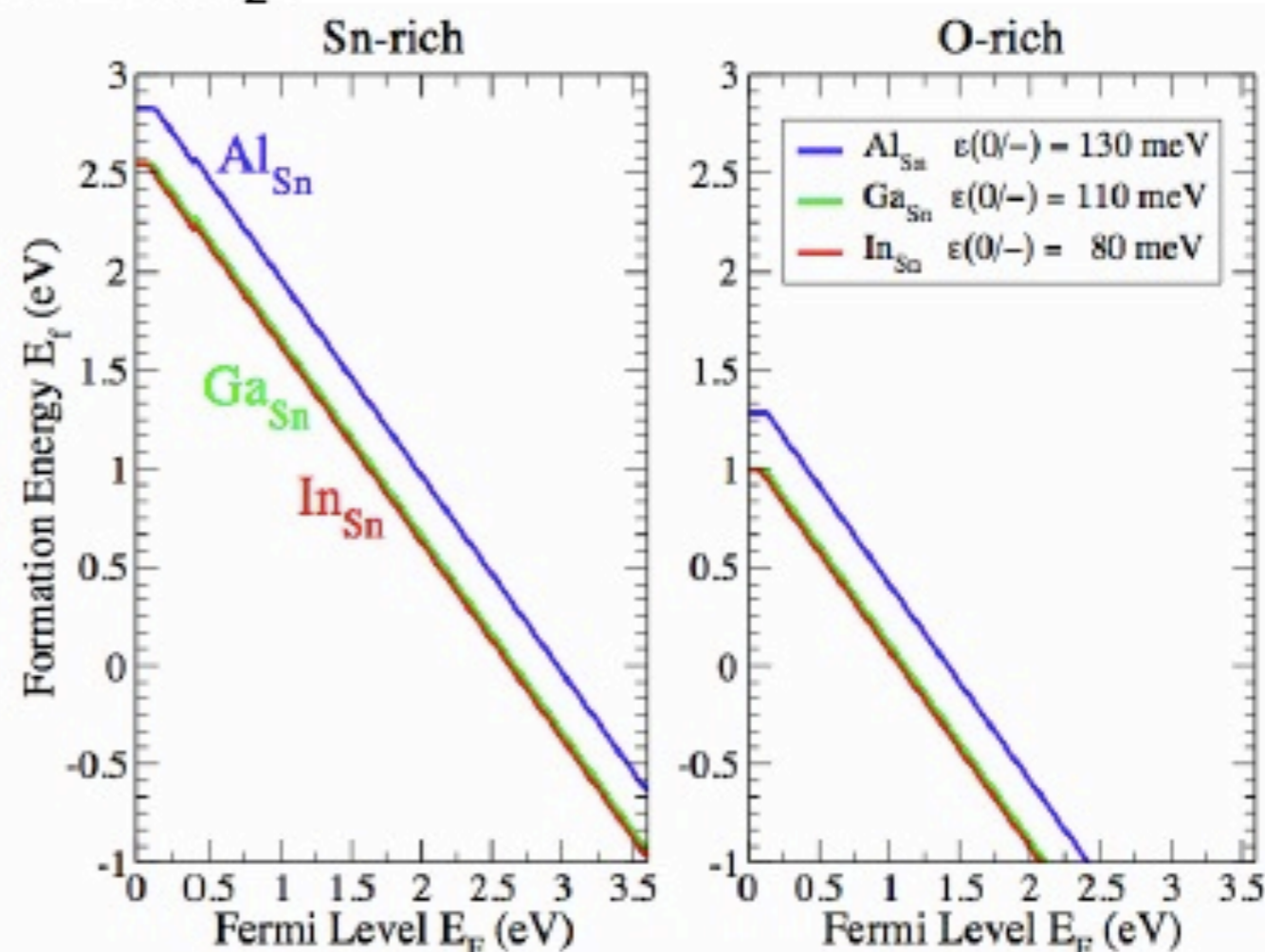
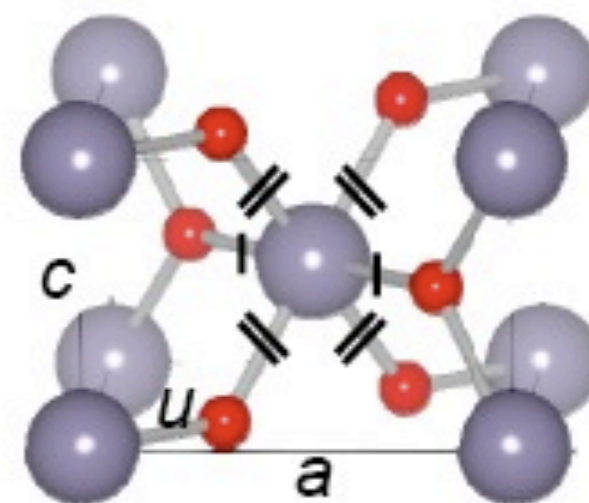
- Al, Ga, In on Sn site

- Low ionization energy

- Modest formation energy

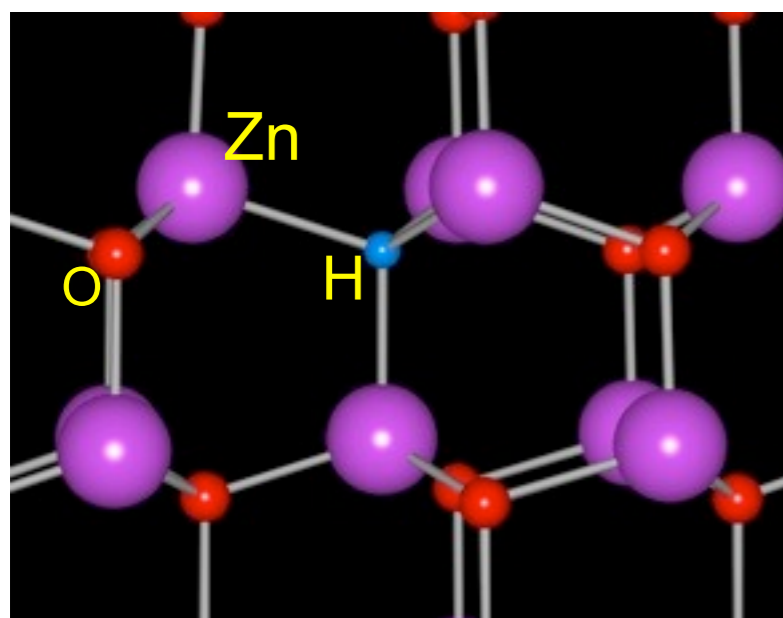
- **Complexes**

- Al-H, Ga-H, In-H

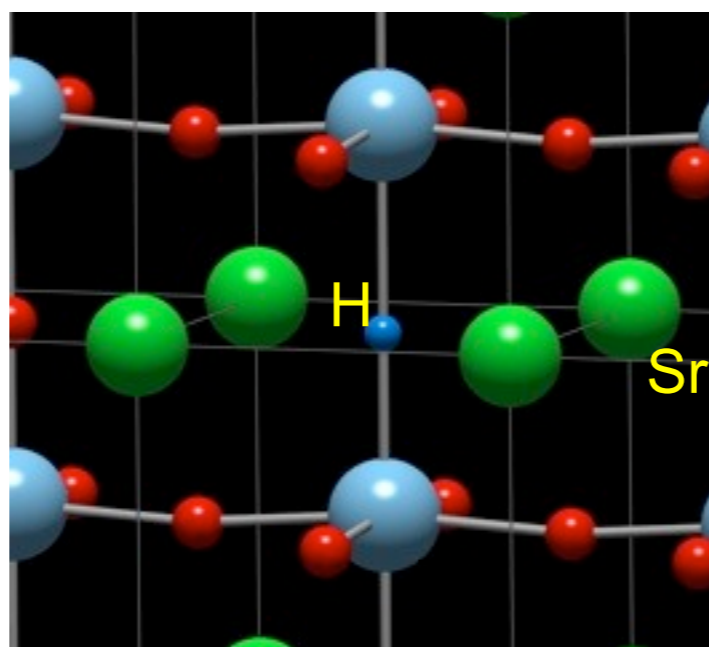


Hydrogen multicenter bonds in oxides

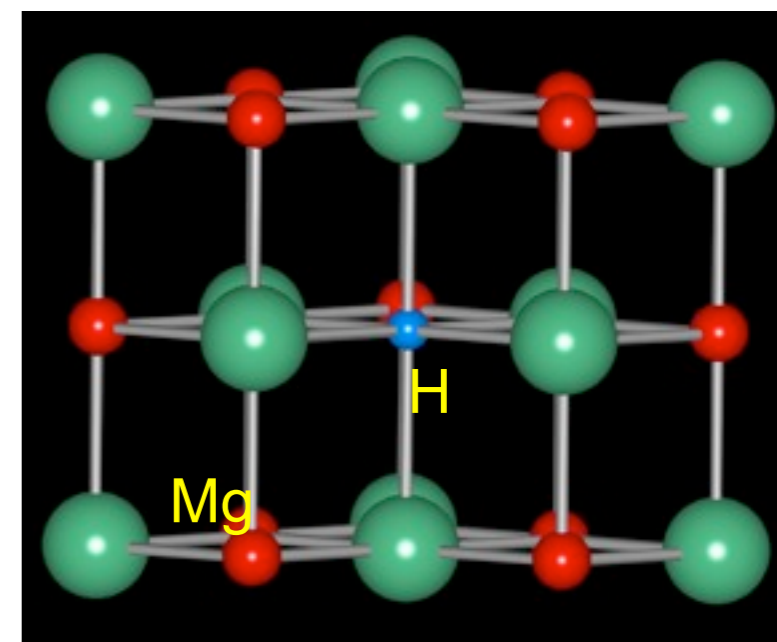
ZnO wurtzite
5-center bond



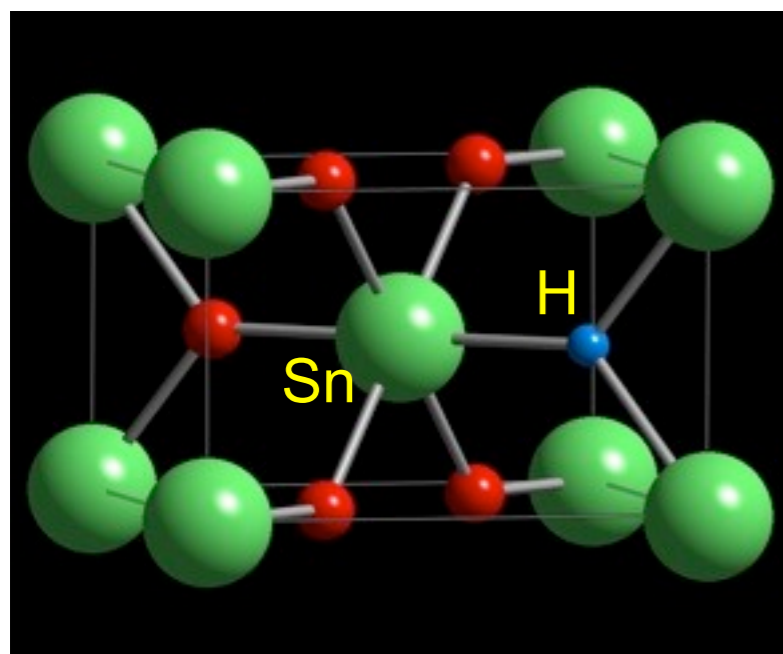
SrTiO₃ perovskite
3-center bond



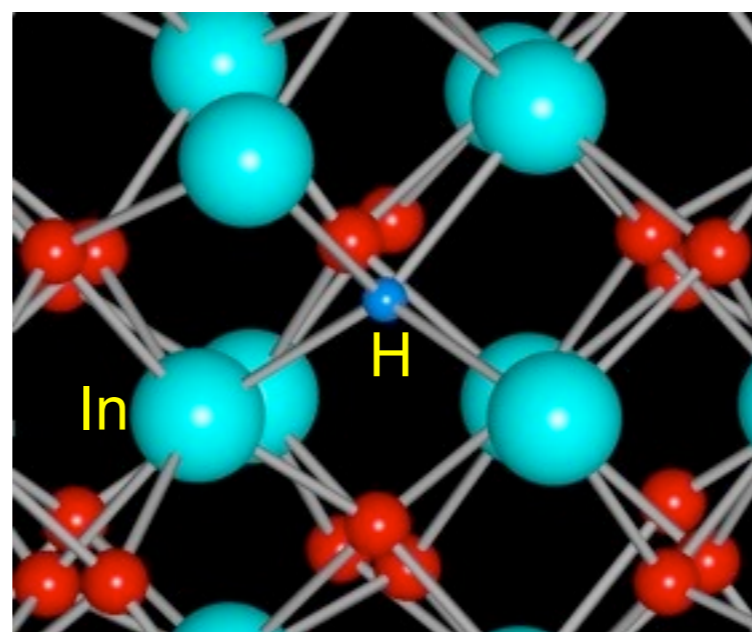
MgO rocksalt
7-center bond



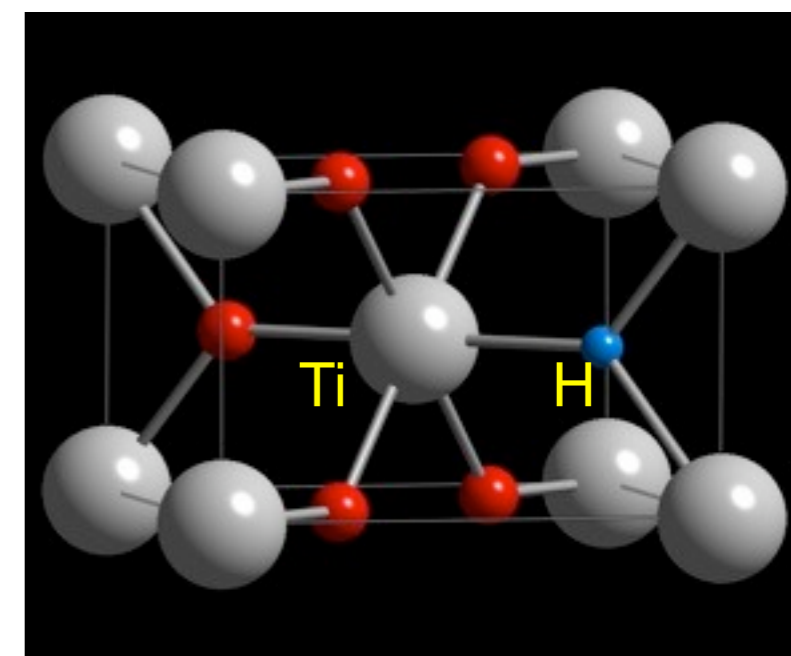
SnO₂ rutile
4-center bond



In₂O₃
5-center bond



TiO₂ 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 SnO₂, In₂O₃, TiO₂

[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)