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First-principles calculations of point defects in semiconductors: Formation energies, electronic properties, and diffusion

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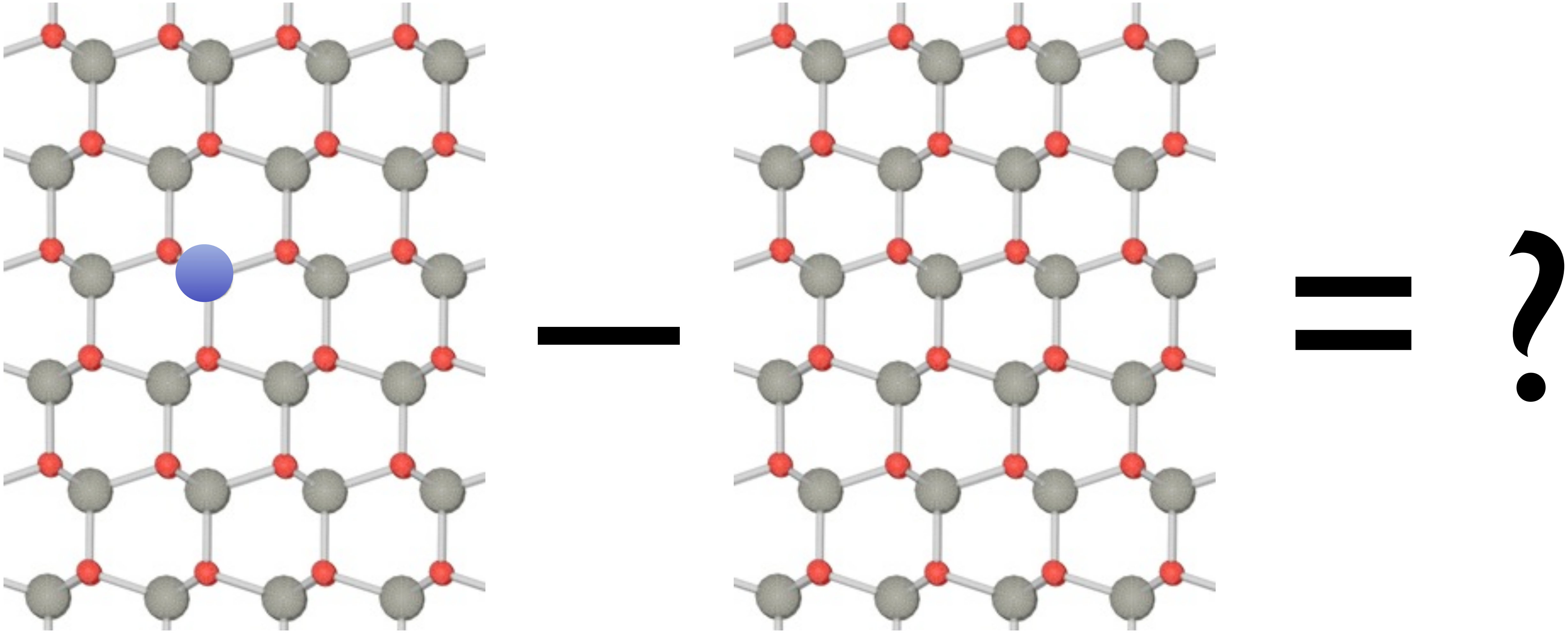
Methodological aspects



Doping of a semiconductor

- What does it mean ?
  - introduce an impurity that may occur in different charge states
  - the charge state should be accessible by putting a small amount of energy into the system (~ thermal energy);
    e.g. for silicon, P may be P^0 or P^+, Al may be Al^0 or Al^-
  - the ionized impurity may act as a donor or acceptor,
    e.g. for P^+, there is a rather extended conduction-band-like electron around P; for Al^-, there is an extended unoccupied, valence-band-like state around Al
- shallow and deep donors (or acceptors)
  - **shallow:** the wavefunction of the ionized impurity state has strong orbital character from the conduction band (the valence band)
  - **deep:** the wavefunction of the ionized impurity state has the orbital character of the impurity

Formation energy

- **thermodynamics:** Formation energy must be calculated with respect to reservoirs
  Example: carbon (C) in ZnO

$$E_{\text{form}}[\text{C}] = E_{\text{tot}}[\text{C/ZnO}] - E_{\text{tot}}[\text{ZnO}] - \sum_{\text{species } i} n_i \mu_i$$

$$\mu_{\text{Zn}} + \mu_{\text{O}} = \mu_{\text{ZnO}}$$

- **in crystal growth:** limiting values for the chemical potentials can be defined in terms of "growth conditions"

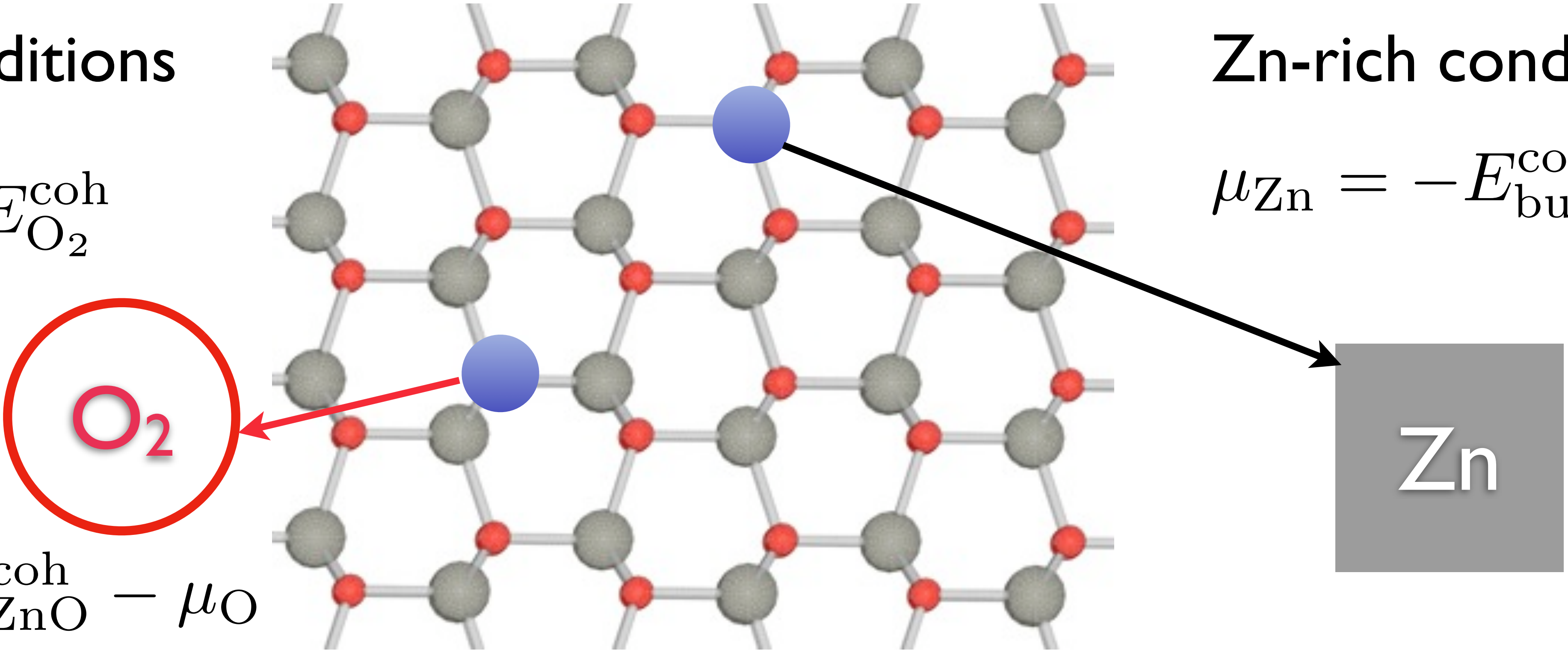
O-rich conditions

$$\mu_{\text{O}} = -\frac{1}{2} E^{\text{coh}}_{\text{O}_2}$$

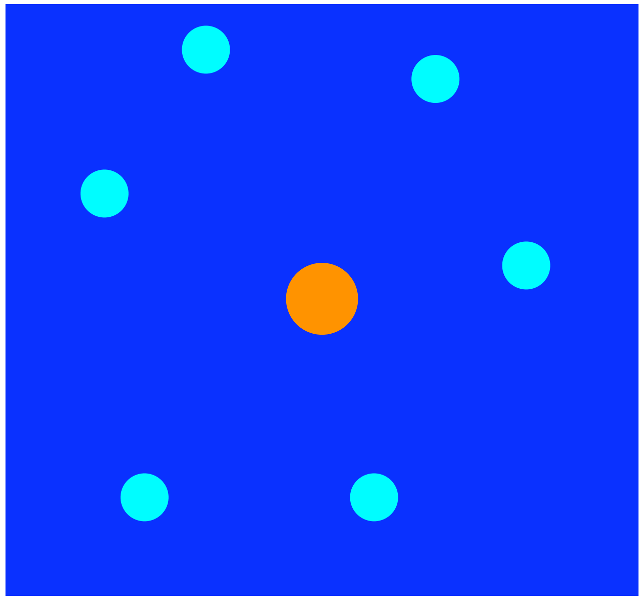
$$\mu_{\text{Zn}} = -E^{\text{coh}}_{\text{ZnO}} - \mu_{\text{O}}$$

Zn-rich conditions

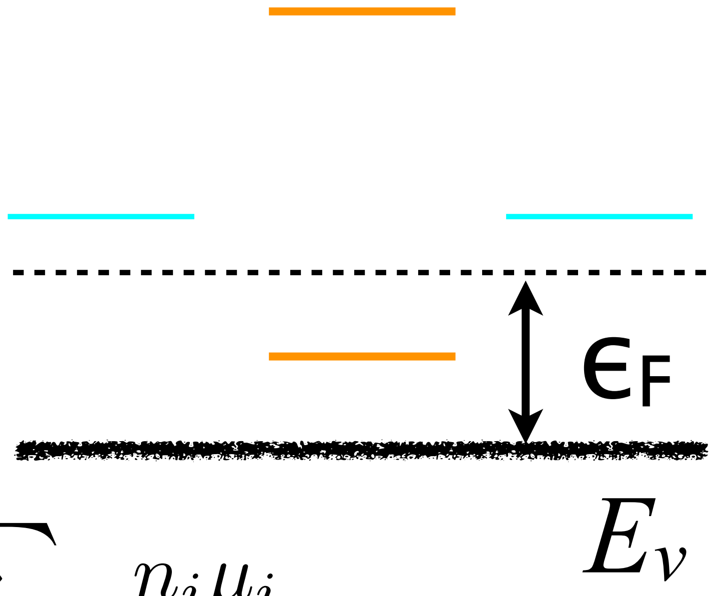
$$\mu_{\text{Zn}} = -E^{\text{coh}}_{\text{bulk-Zn}}$$



Charge transfer level



- Apart from intentional doping, a semiconductor always contains (small concentrations of) intrinsic defects or other, unwanted impurities
- The chemical potential of the electrons (the "Fermi level") is not an intrinsic property, but rather is determined by overall charge neutrality
- We want a descriptor for the behavior of a dopant in the environment of a "real" semiconductor: if the chemical potential hits the **charge transfer level** $\varepsilon(q'|q)$ of the dopant, it will be 50:50 ionized or neutral



$$E_{\mathrm{form}}[\mathrm{C}^{(\mathrm{q})}] = E_{\mathrm{tot}}[\mathrm{C/ZnO}^{(\mathrm{q})}] - E_{\mathrm{tot}}[\mathrm{ZnO}] - \sum_{\mathrm{species}\ i} n_i \mu_i \\ + q(\varepsilon_{\mathrm{F}} + E_v)$$

Basics about DFT

- The total energy is a unique functional of the electronic density (Hohenberg-Kohn theorem)
- consider an **auxiliary system** of non-interacting electrons to estimate the kinetic energy (Kohn-Sham)

$$E_{\mathrm{KS}} = T_0 + \int d\mathbf{r}\, v^{(0)}(\mathbf{r}) n(\mathbf{r}) + E_{\mathrm{Hartree}}[n] + E_{\mathrm{XC}}[n] + V^{ion-ion}$$

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + v[n](\mathbf{r}) \right) \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r})$$

$$v[n](\mathbf{r}) = v^{(0)}(\mathbf{r}) + V_{\mathrm{Hartree}}[n](\mathbf{r}) + V_{\mathrm{XC}}[n](\mathbf{r})$$

- for the “rest” E_{XC}, approximations may be used, e.g. LDA, GGA, ...

Known problems with DFT

- The **Kohn-Sham levels** cannot (and should not, for any "reasonable" approximation to E_{XC}) describe the **band gap** in a semiconductor
- The **self-interaction error** is not fully cancelled by an approximate E_{XC}
- Both deficiencies pose the question if **charge transfer** between an impurity and a host can be described correctly in a KS scheme
- in particular, how to find the charge transfer level in the (too small) KS band gap ?

How to obtain the charge transfer level

- DON'T use the Kohn-Sham level of the defect
- BETTER: compare the **total energies** of a neutral defect and a charged defect in a compensating background

$$E_{\mathrm{form}}[C^{(q-1)}](\varepsilon_{\mathrm{F}}) = E_{\mathrm{form}}[C^{(q)}](\varepsilon_{\mathrm{F}}) \implies \varepsilon(q-1|q) = \varepsilon_{\mathrm{F}}$$

- alternative (for deep defects): "Slater's transition state" rule applied to levels of the neutral and the charged system

$$\varepsilon(0|1) = \frac{\varepsilon_{H+1}(N) + \varepsilon_{H+1}(N+1)}{2}$$

- BEST: calculate the electronic structure in the GW method and use the result to apply a correction to DFT total energies

Generalized Kohn-Sham schemes

- use explicit self-interaction corrections via "Hubbard U" acting on some (e.g. 3d, 4f) **occupied** orbitals
- use the (orbital-dependent) Fock operator to calculate the exchange contribution

$$\hat{F}\psi_i(\mathbf{r}) = -e^2 \sum_{j,\mathrm{occ}} \psi_j(\mathbf{r}') \int d\mathbf{r} \frac{\psi_j^*(\mathbf{r})\psi_i(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

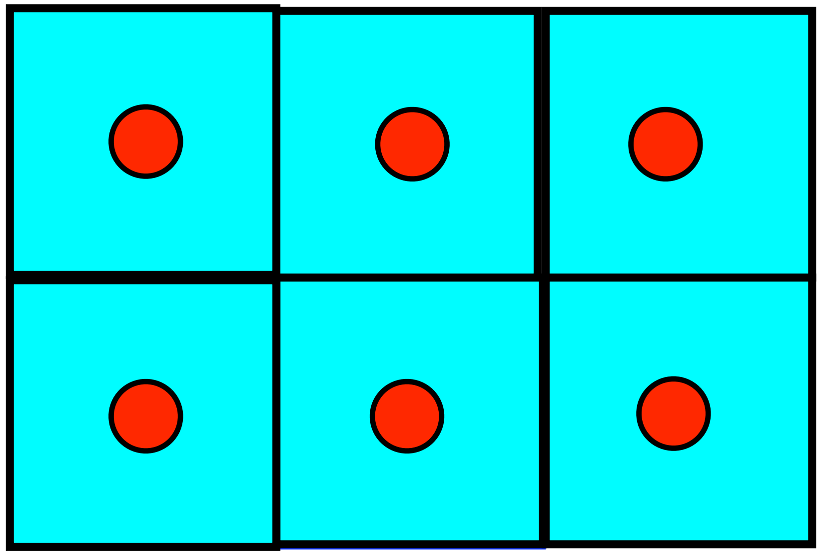
- <u>various realizations:</u>
  hybrid functionals (PBE0, B3LYP, ..):
  mixing factor α of Fock exchange and parameterized E_X

$$v[\{\psi_i[n](\mathbf{r})\}] = v^{(0)}(\mathbf{r}) + V_\mathrm{Hartree}[n](\mathbf{r}) + \alpha\hat{F}[\{\psi_i(\mathbf{r})\}] + (1-\alpha)V_\mathrm{X}[n](\mathbf{r}) + V_\mathrm{C}[n](\mathbf{r})$$

  range separation (screening of Fock kernel):
  HSE functionals

- compromise between good total energies (and lattice constants, ...) and energy levels accessible to a physical interpretation
- mixing parameter α obtainable via Janak's theorem
  [S. Lany & A. Zunger, PRB **81**, 205209 (2010)]

Supercell calculations



- large supercells (several hundred atoms) required to minimize defect-defect interactions
- in plane-wave codes: homogeneous compensating background is easily realized
- Makov-Payne correction for **charged** defects [PRB **51**, 4014 (1995)]

$$E_{\mathrm{form}}[C^{(q)}] \to E_{\mathrm{form}}[C^{(q)}] + \frac{\alpha}{2\epsilon L}q^2 + \frac{2\pi Q}{3\epsilon L^3}q$$

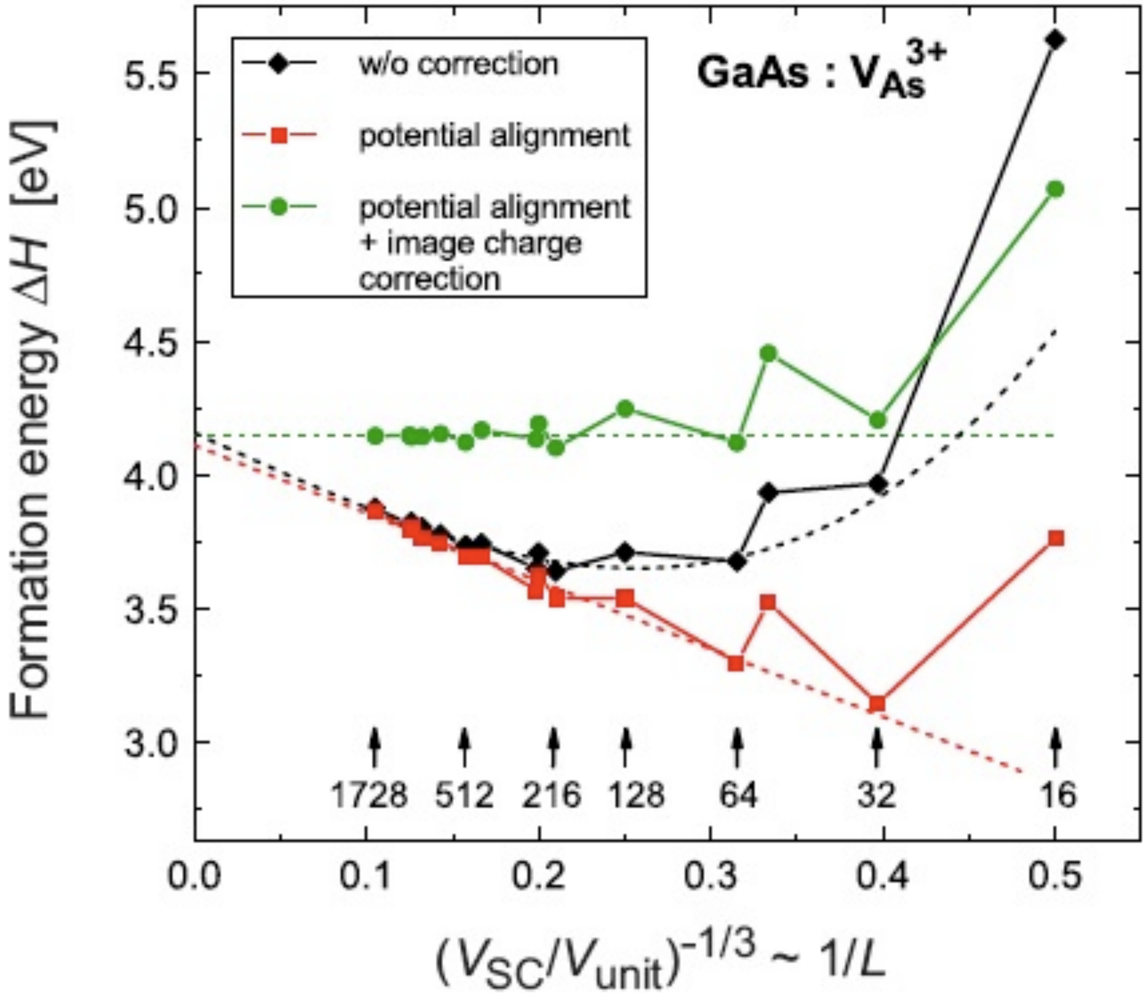
- in practice: linear (in q) term is calculated as a potential-alignment correction ΔV

$$E_{\mathrm{form}}[C^{(q)}] \to E_{\mathrm{form}}[C^{(q)}] + \frac{\alpha}{2\epsilon L}q^2 + \Delta V q$$

Periodic-image correction

- Example: oxygen vacancy in ZnO

S. Lany and A. Zunger,
PRB **78**, 235104 (2008)

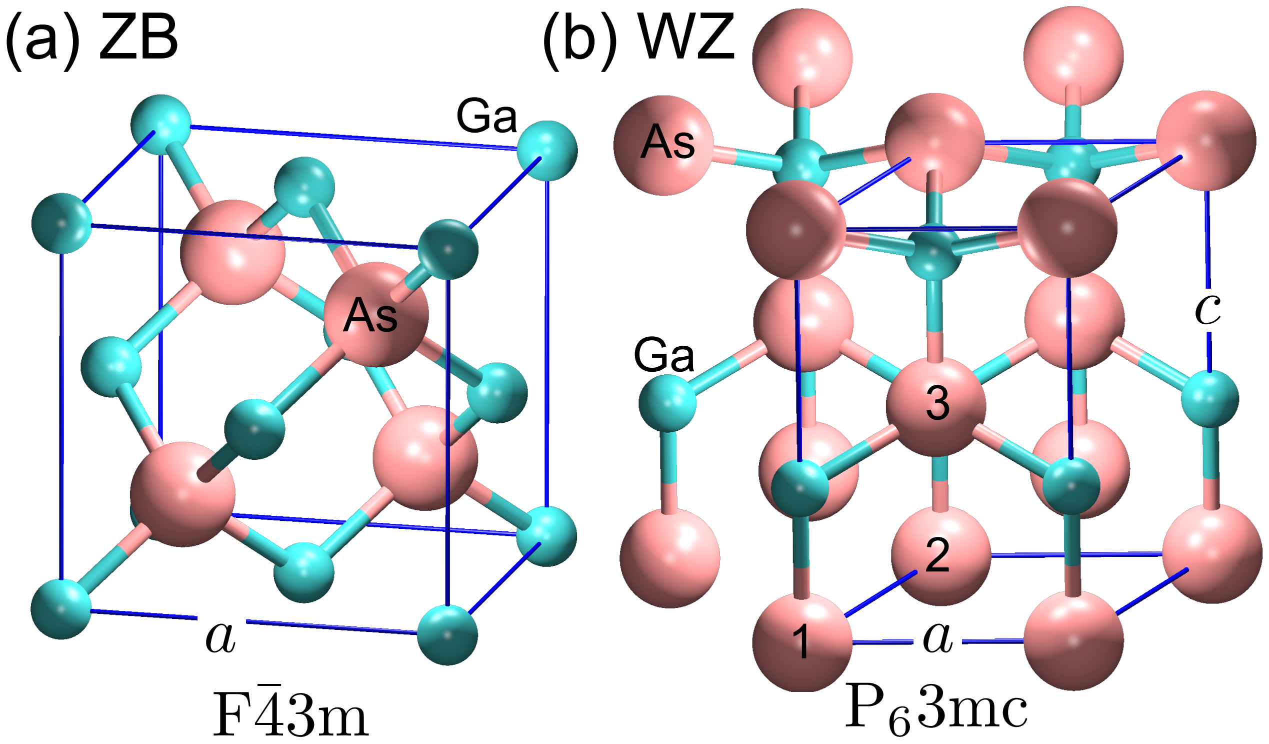


- N.B.: Corrections must be applied with great care, in particular if defect wavefunction is long-ranged,
  see eg. C. Freysoldt, J. Neugebauer & C. van de Walle, PRL **102**, 016402 (2009)

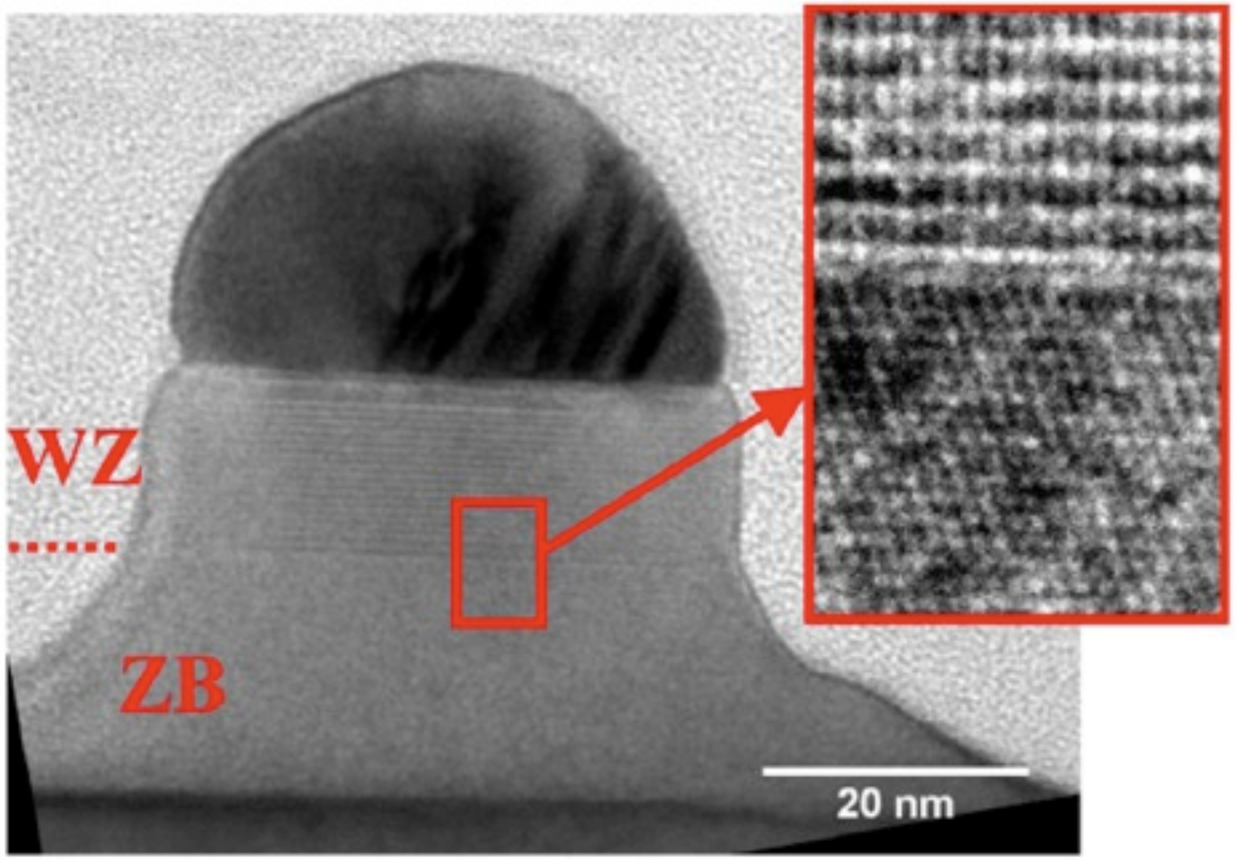
Application I:
Defects in wurtzite GaAs

Polytypism in GaAs nanopillars

- self-assembled growth of GaAs nanopillars possible both with metal catalyst (gold) or "self-catalysed"
- growth zone below the metal particle
- solubility of Ga (As) is high (low) in the metal particle



F. Glas, J.-C. Harmand & G. Patriarche,
PRL **99**, 146101 (2007)



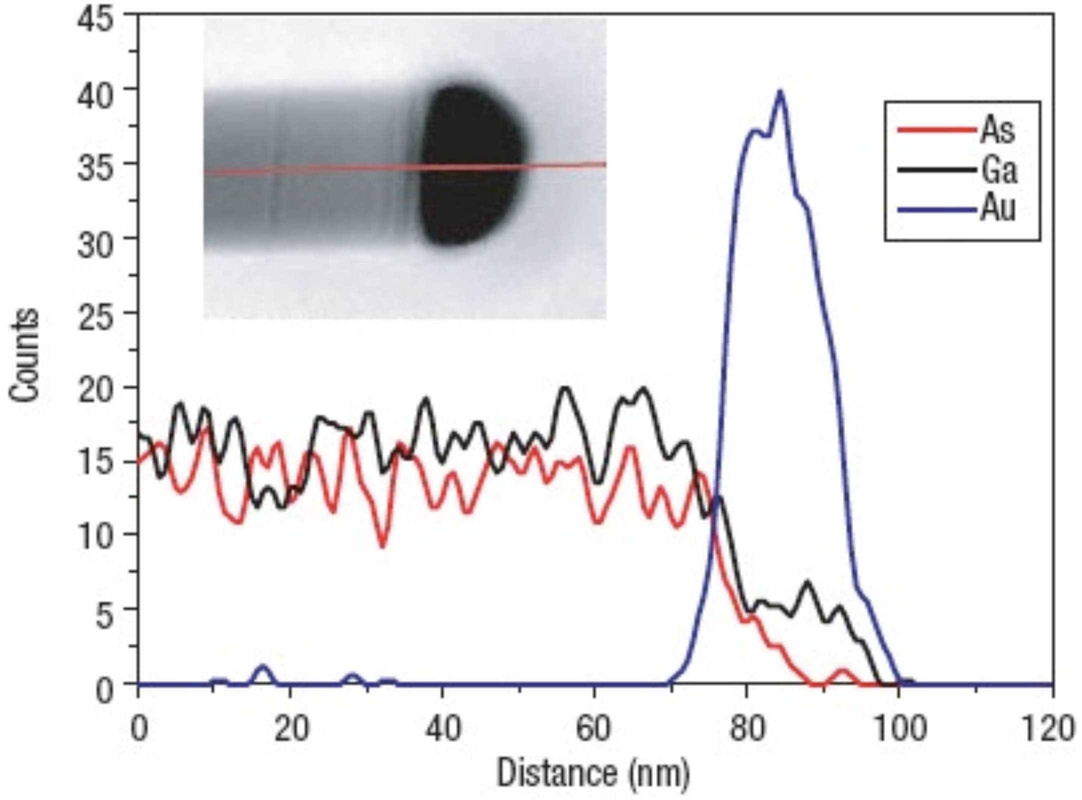
Non-stoichiometric growth zone

- relative deficiency of As (compared to Ga) in as-grown nanopillars
- possible incorporation of Au in Au-catalysed growth
- disappointingly low carrier lifetimes in GaAs nanopillars due to recombination at point defects ?

Topics to be studied:

- Formation energy of defects in **both** wurtzite and zincblende GaAs
- deep charge transfer levels due to Au impurities ?
- mobility of As vacancy ?
(important for possibility of healing by anneal cycle)

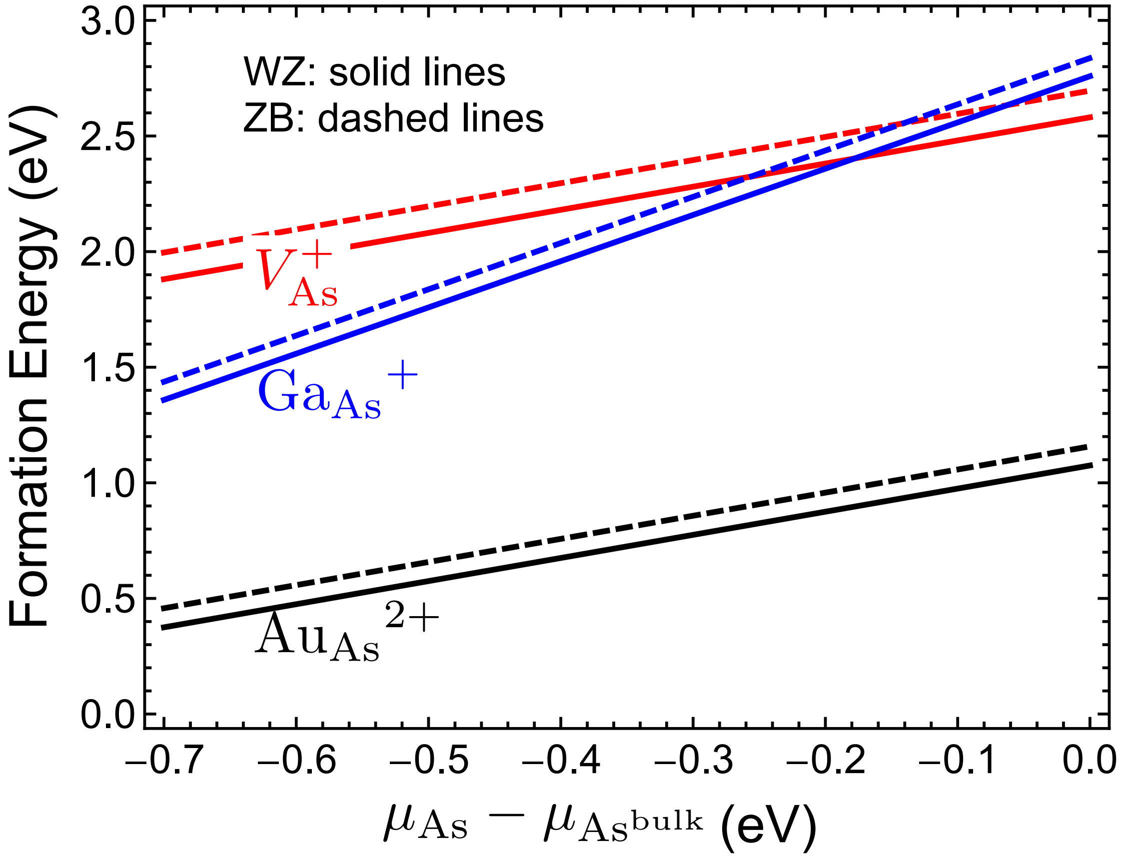
element-specific XEDS analysis
A.I. Persson et al.,
Nature Materials **3**, 667 (2004)



Growth-related point defects

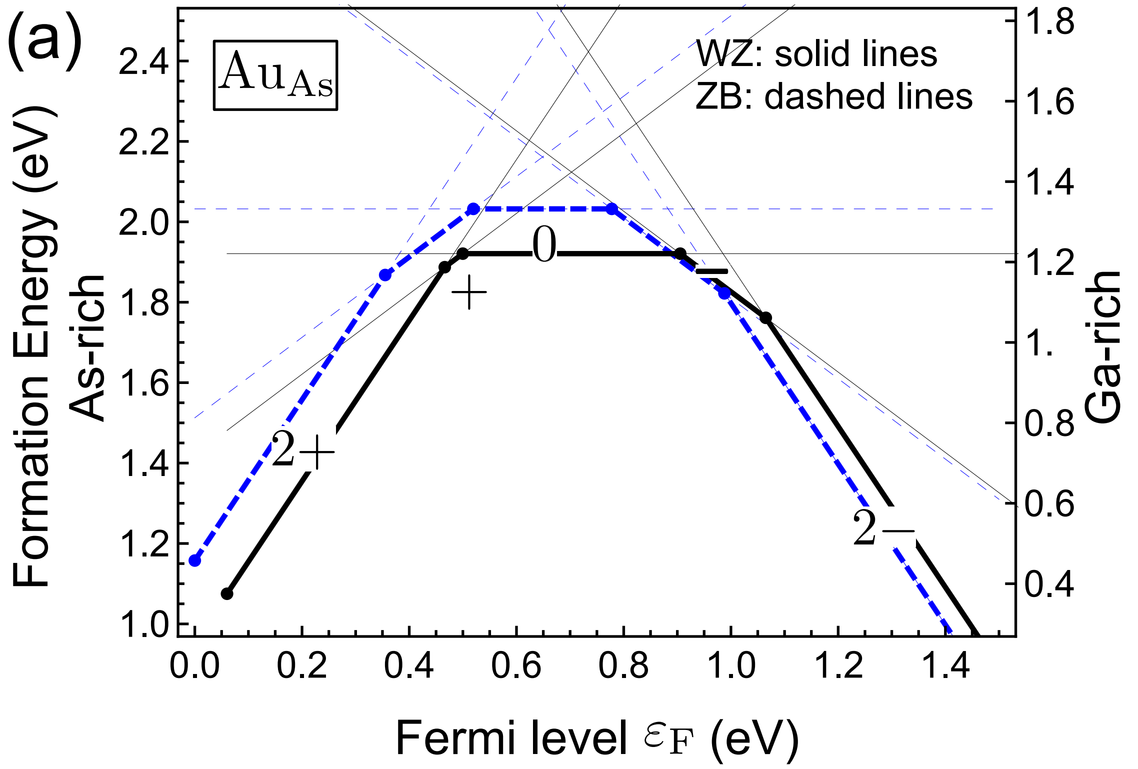
- Calculations performed with PBE functional in 216-atom (ZB) or 96-atom (WZ) supercell
- Growth with Au catalyst particle: substitutional Au defects are lower in energy than intrinsic V_{As} or Ga_{As} defects
- self-catalysed growth (no Au): V_{As} or Ga_{As} may form in low concentrations, depending on growth conditions

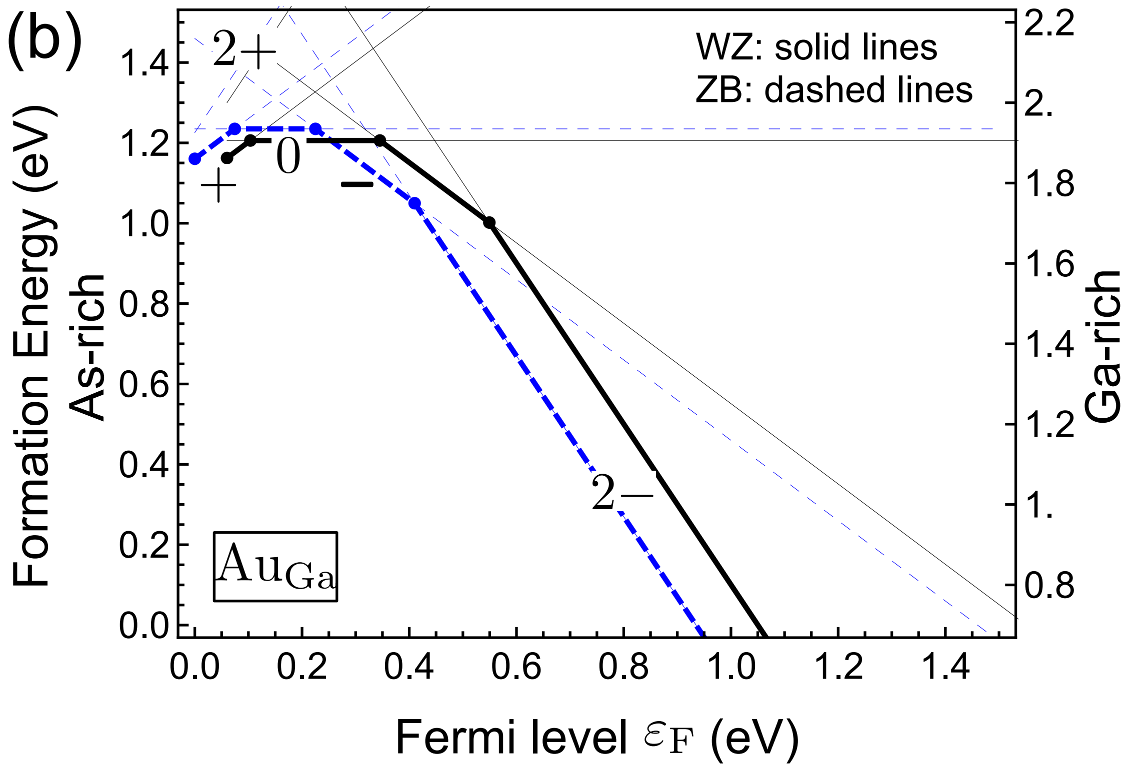
defects related to deficiency of As in *p*-type GaAs



Gold as deep center in GaAs

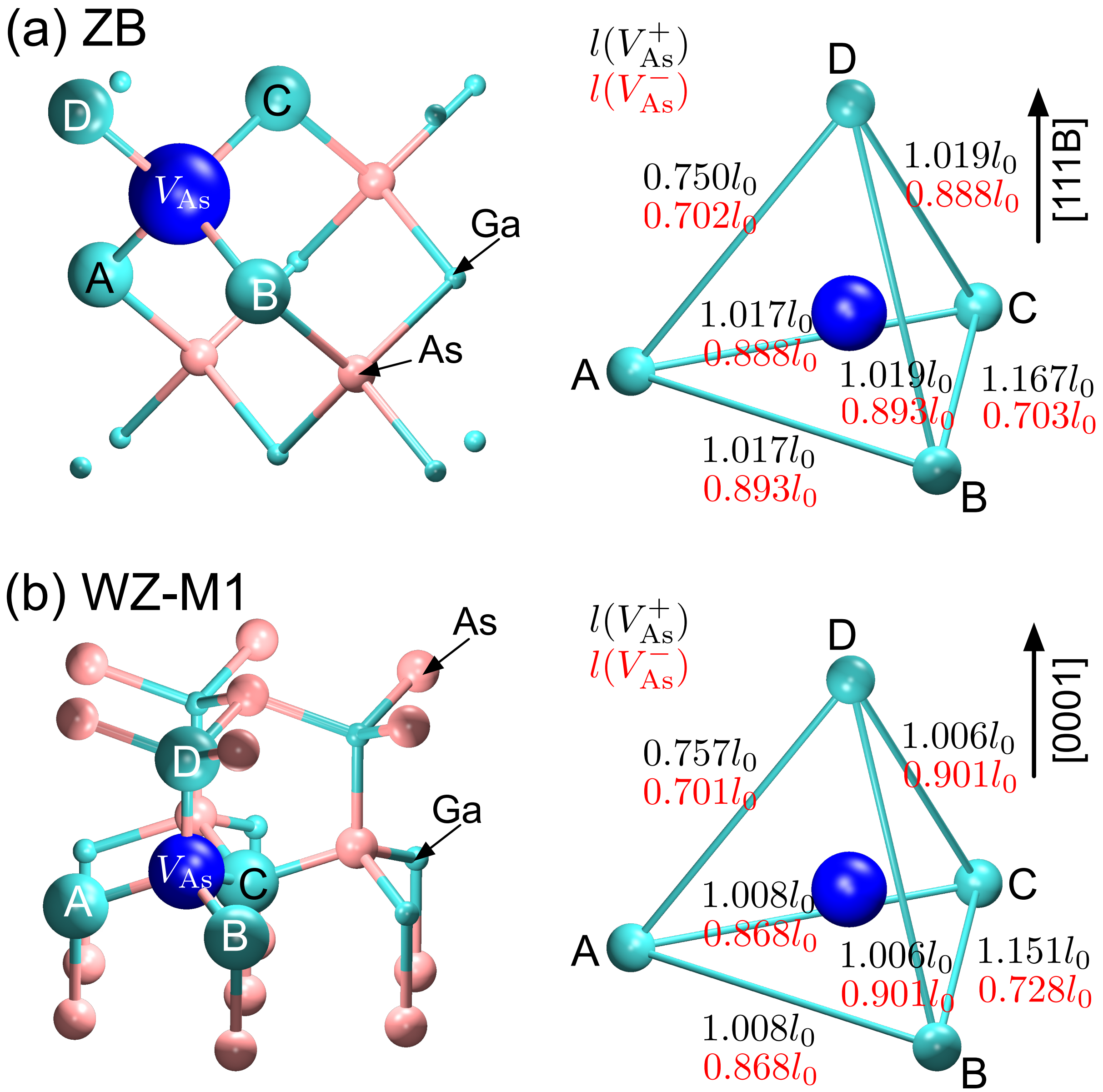
- formation energy for Au_{Ga} generally lower than for Au_{As}
- various charge states from 2+ to 2−
- experiment: charge transfer level $\varepsilon(0|-)$ at ~0.4 eV seen in deep-level transient spectroscopy

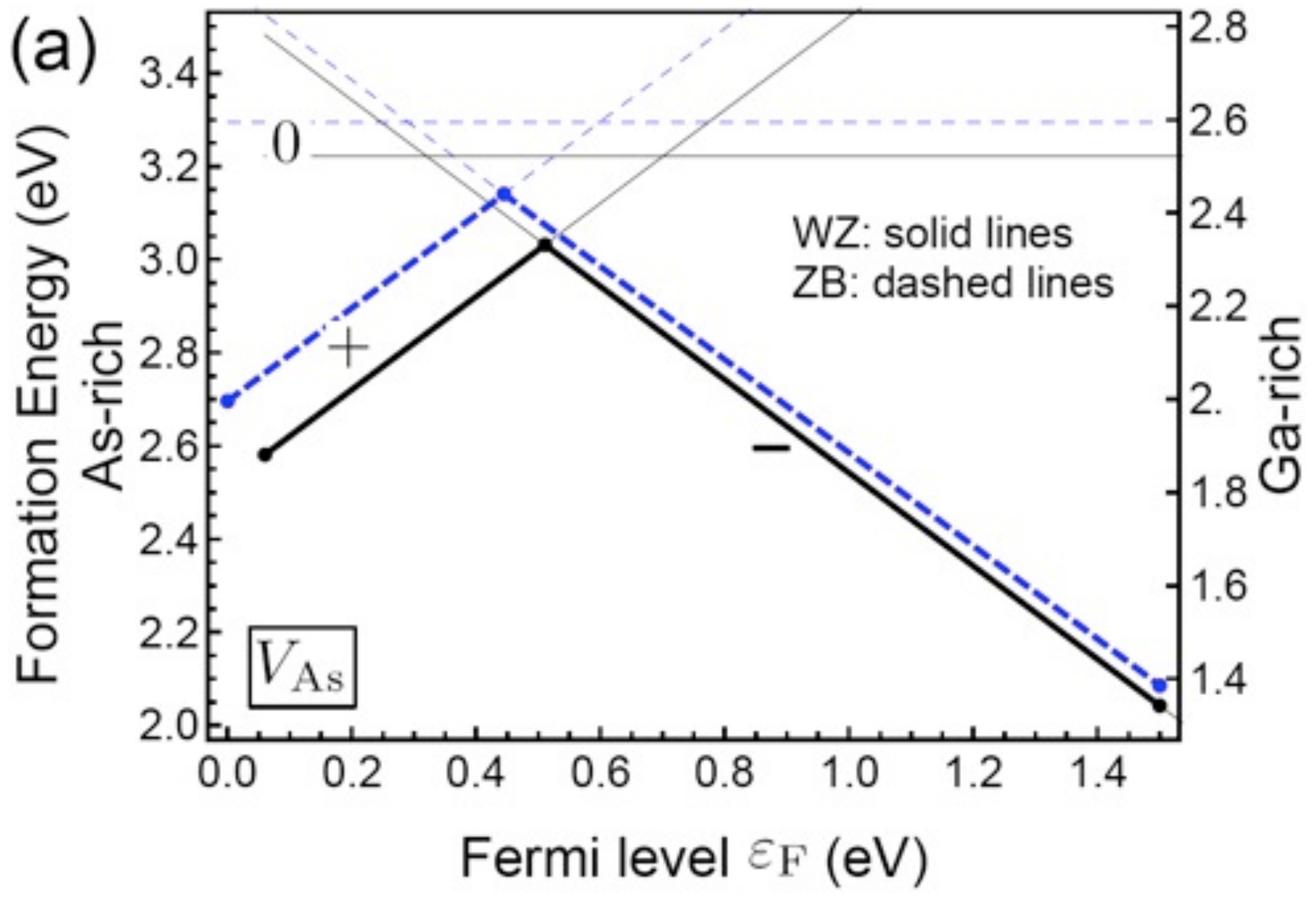




Arsenic vacancies

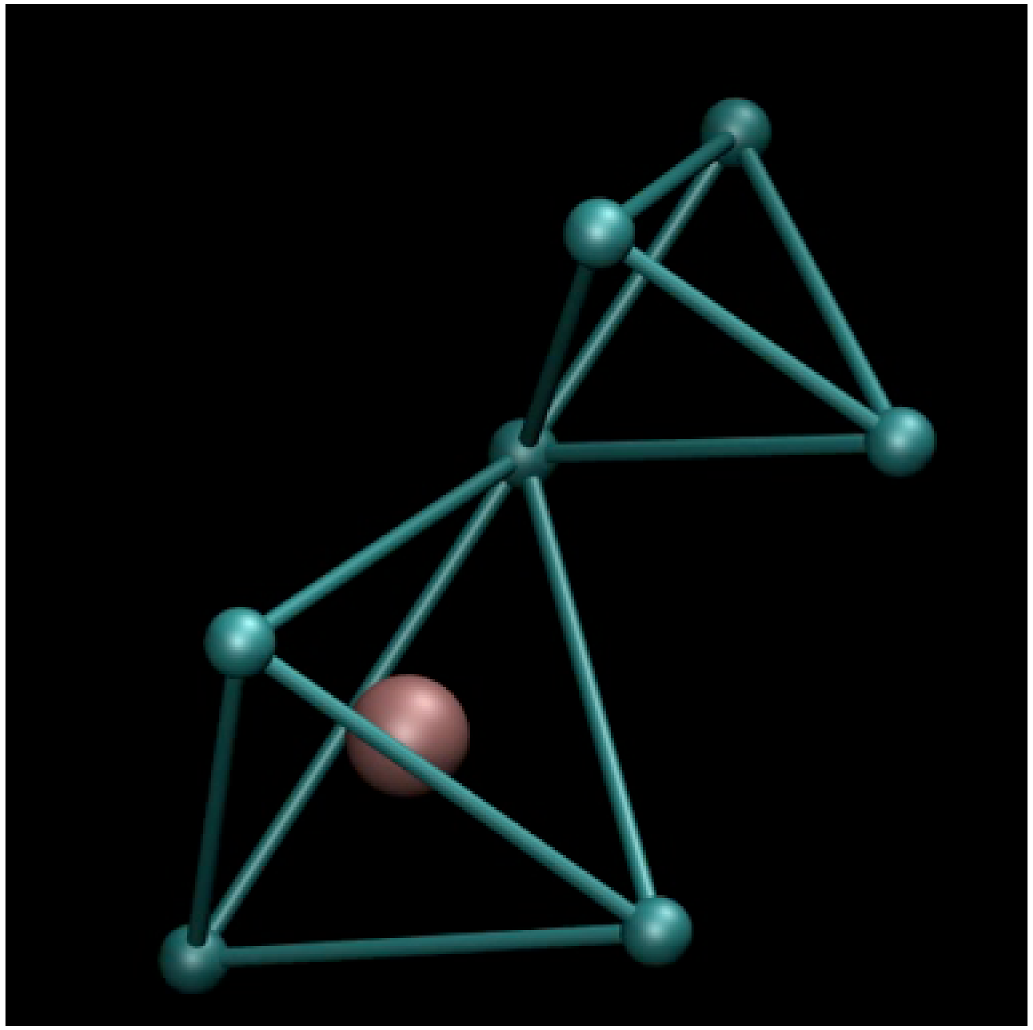
- unstable as neutral vacancy (a so-called "negative-U" system)
- strong contraction of the vacancy tetrahedron for negatively charged vacancy, as bonding linear combination of Ga dangling bonds becomes occupied



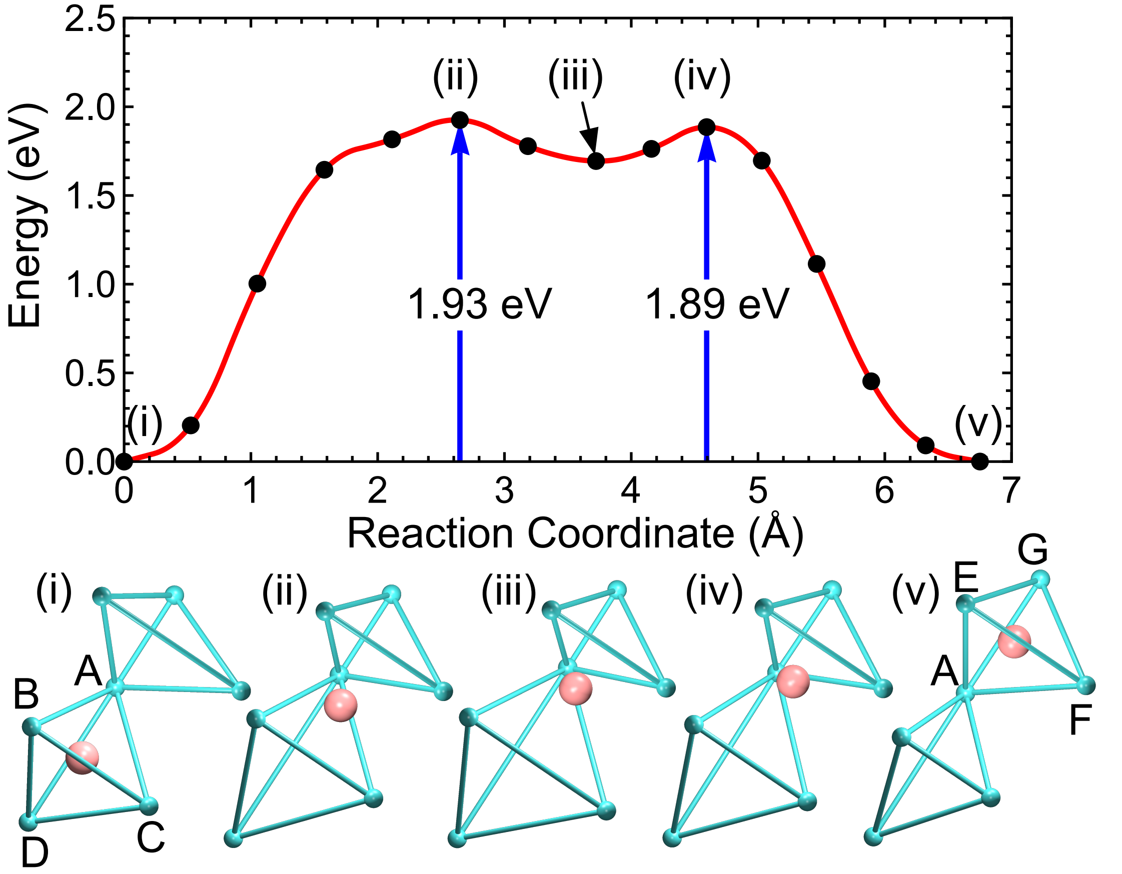


V_{As} diffusion in ZB

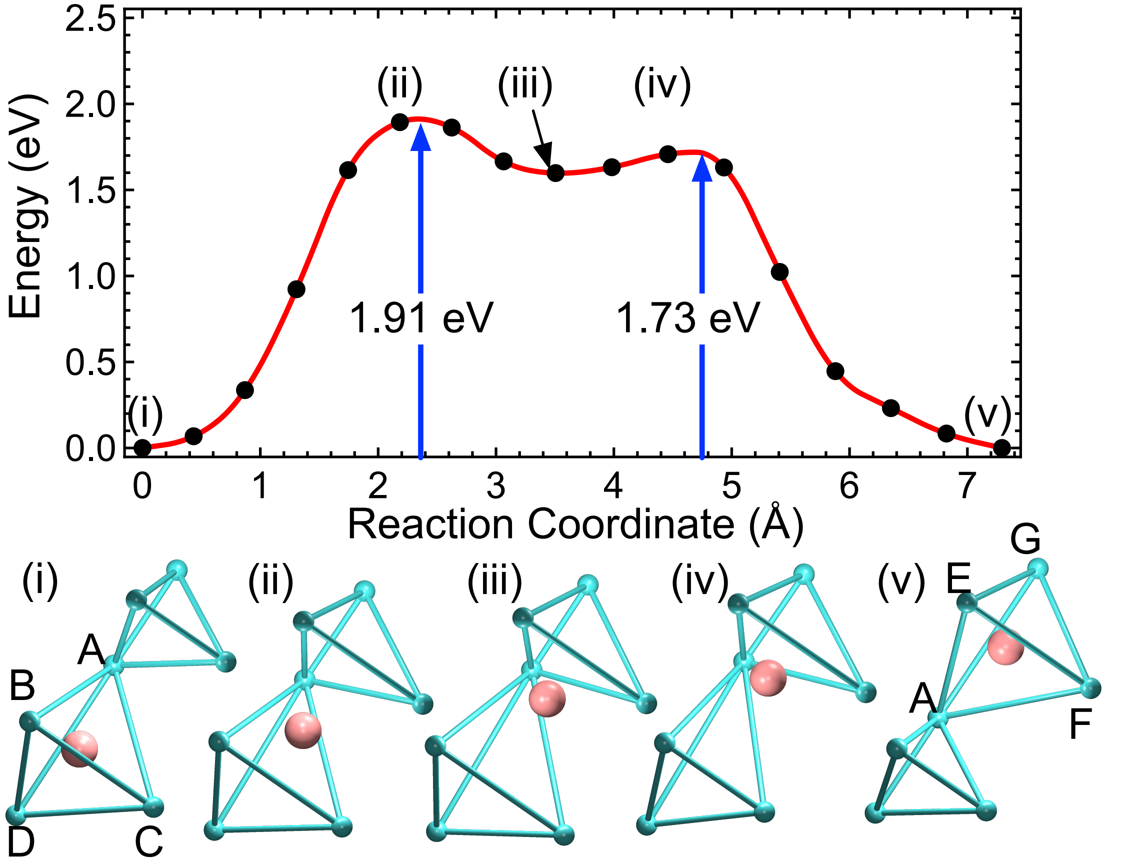
- octahedral interstitial as intermediate minimum
- Asynchronous diffusion of electronic charge and of As atom



(a) $V_{\mathrm{As}}^{+}/\mathrm{ZB}$

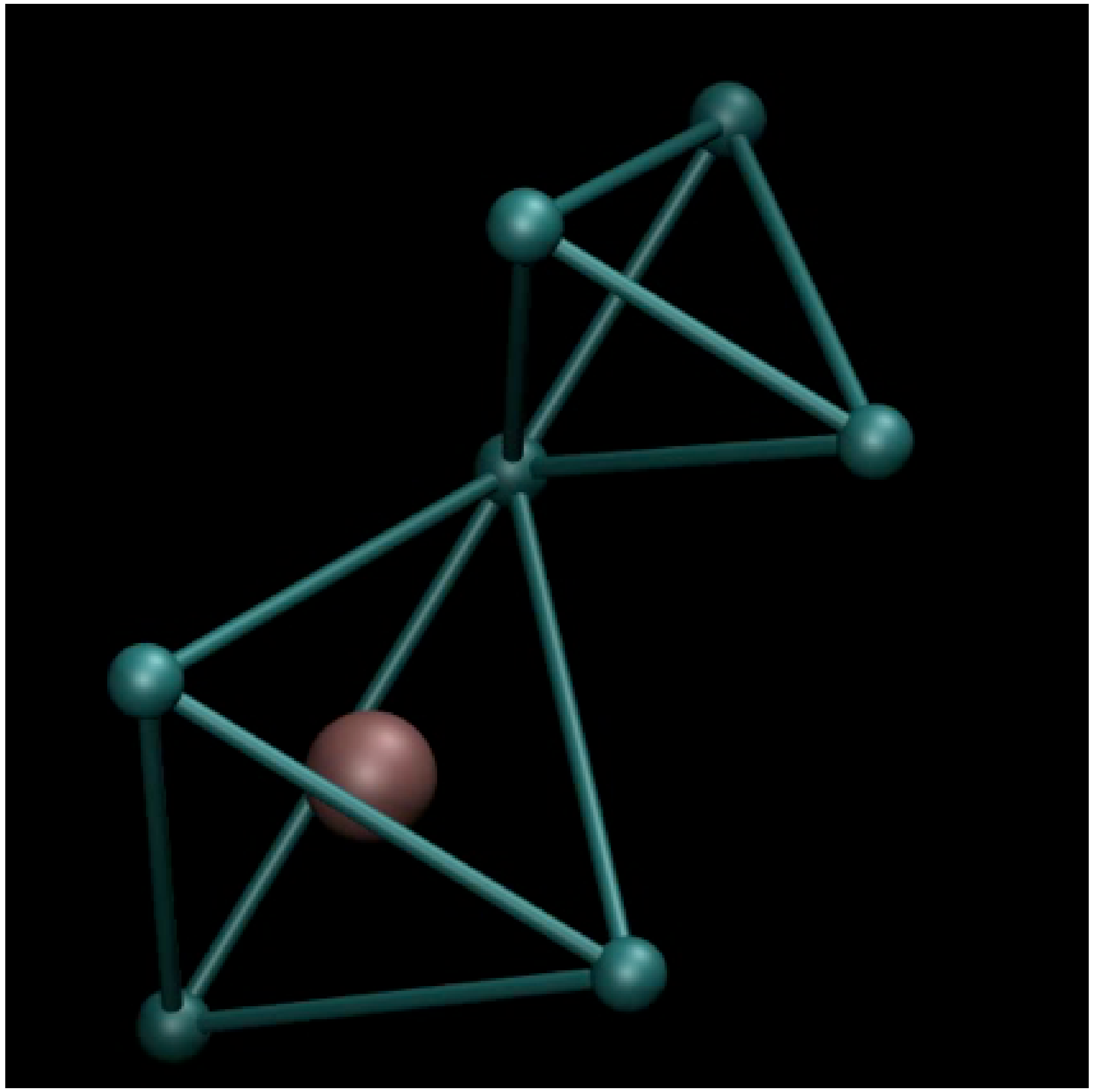


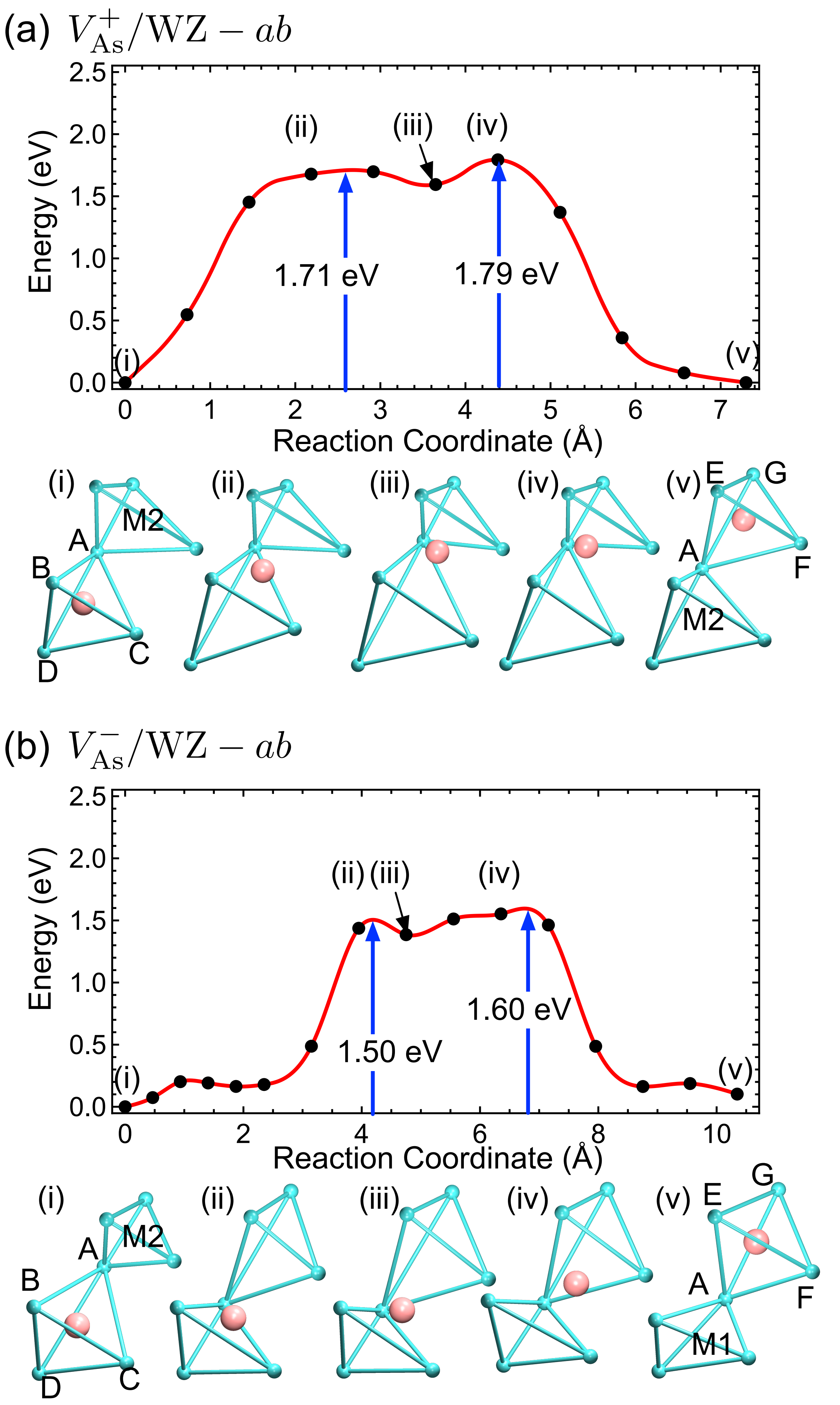
(b) $V_{\mathrm{As}}^{-}/\mathrm{ZB}$



V_{As} diffusion in WZ

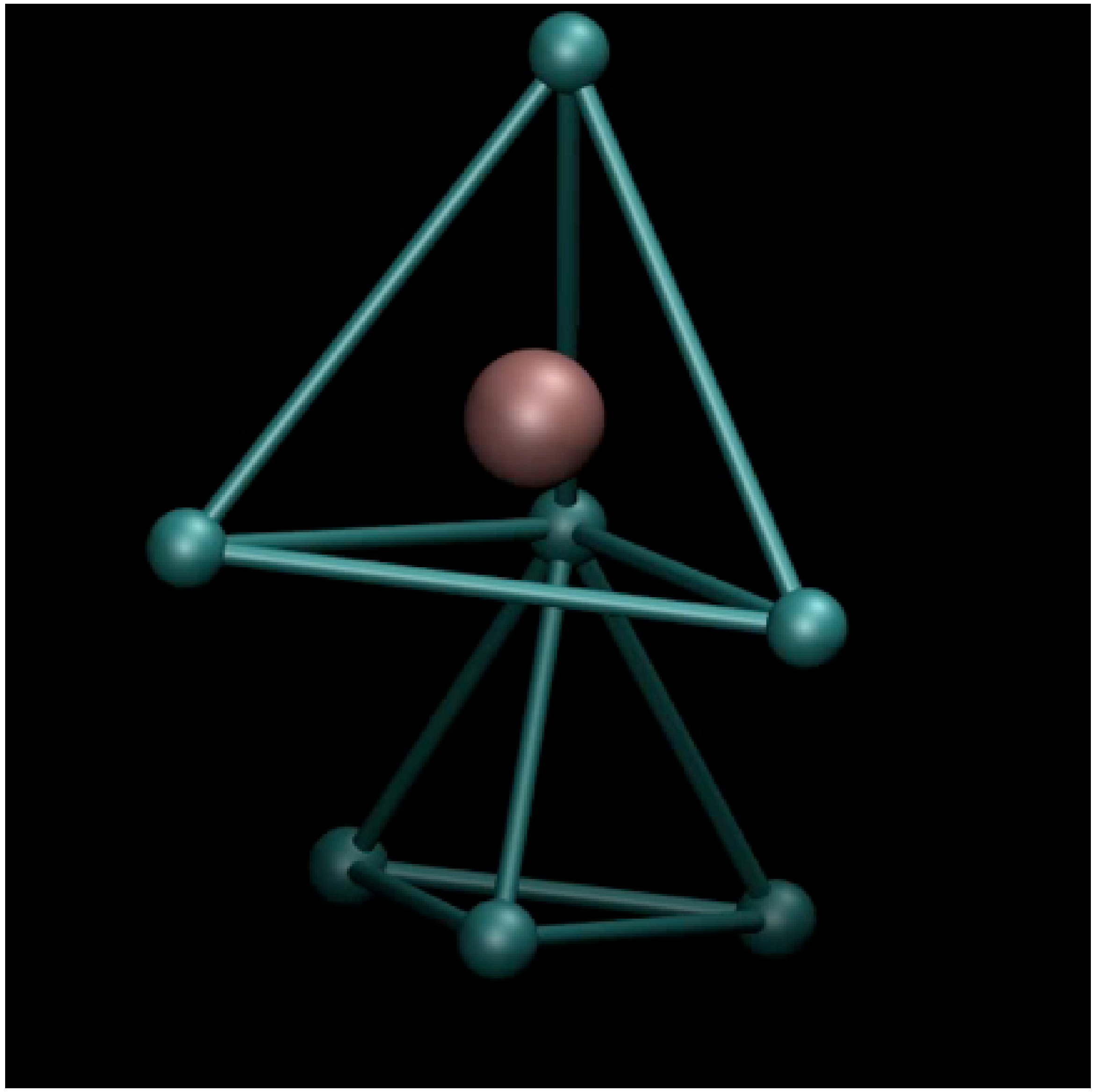
- in wurtzite *ab*-plane, barriers are lower as compared to ZB case



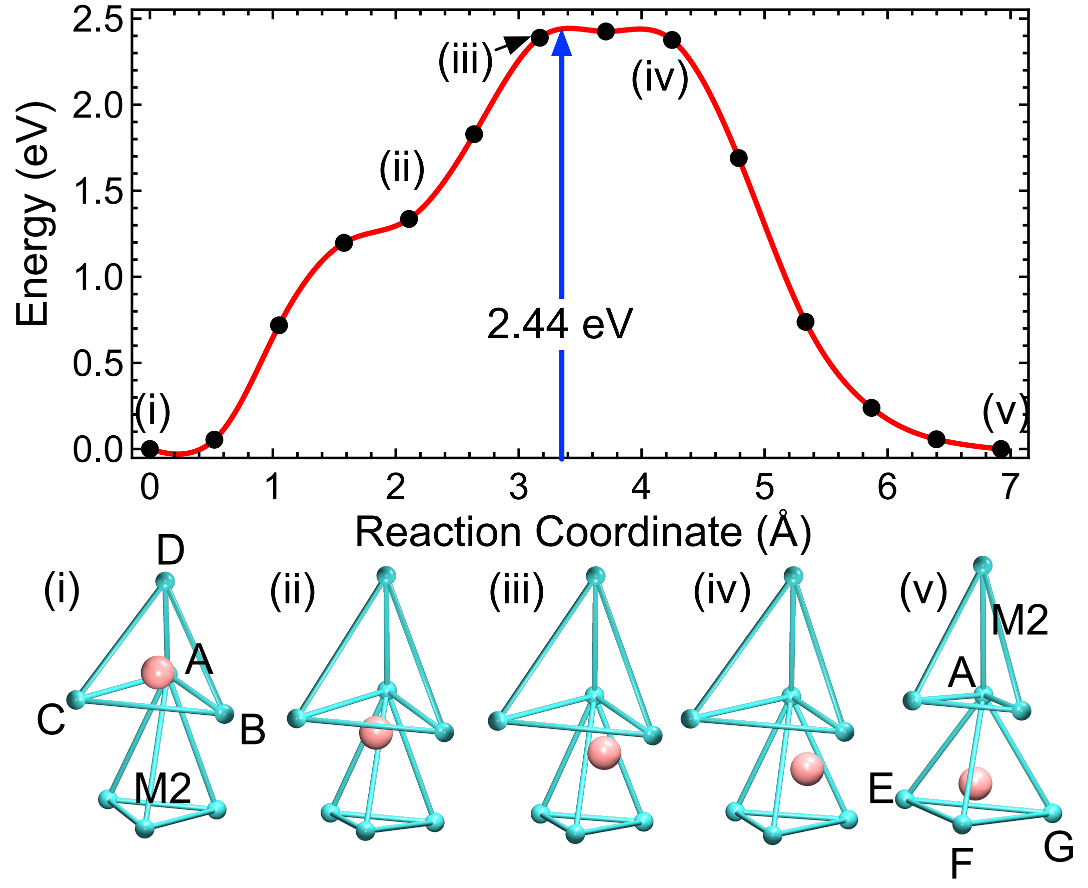


V_{As} diffusion in WZ

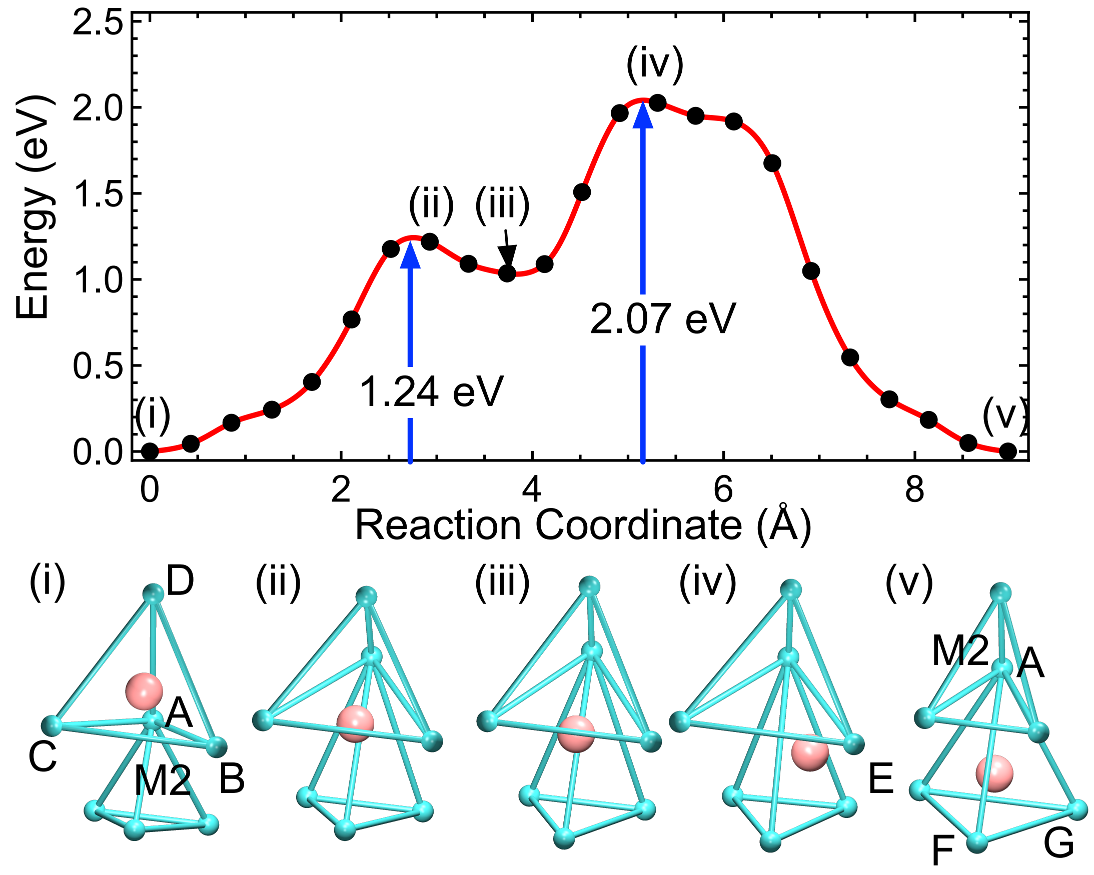
- along the c-axis, V_{As} needs to go a detour to avoid crossing the Ga-Ga coordination line → higher barrier than in ZB



(a) $V_{\mathrm{As}}^{+}/\mathrm{WZ}-c$



(b) $V_{\mathrm{As}}^{-}/\mathrm{WZ}-c$

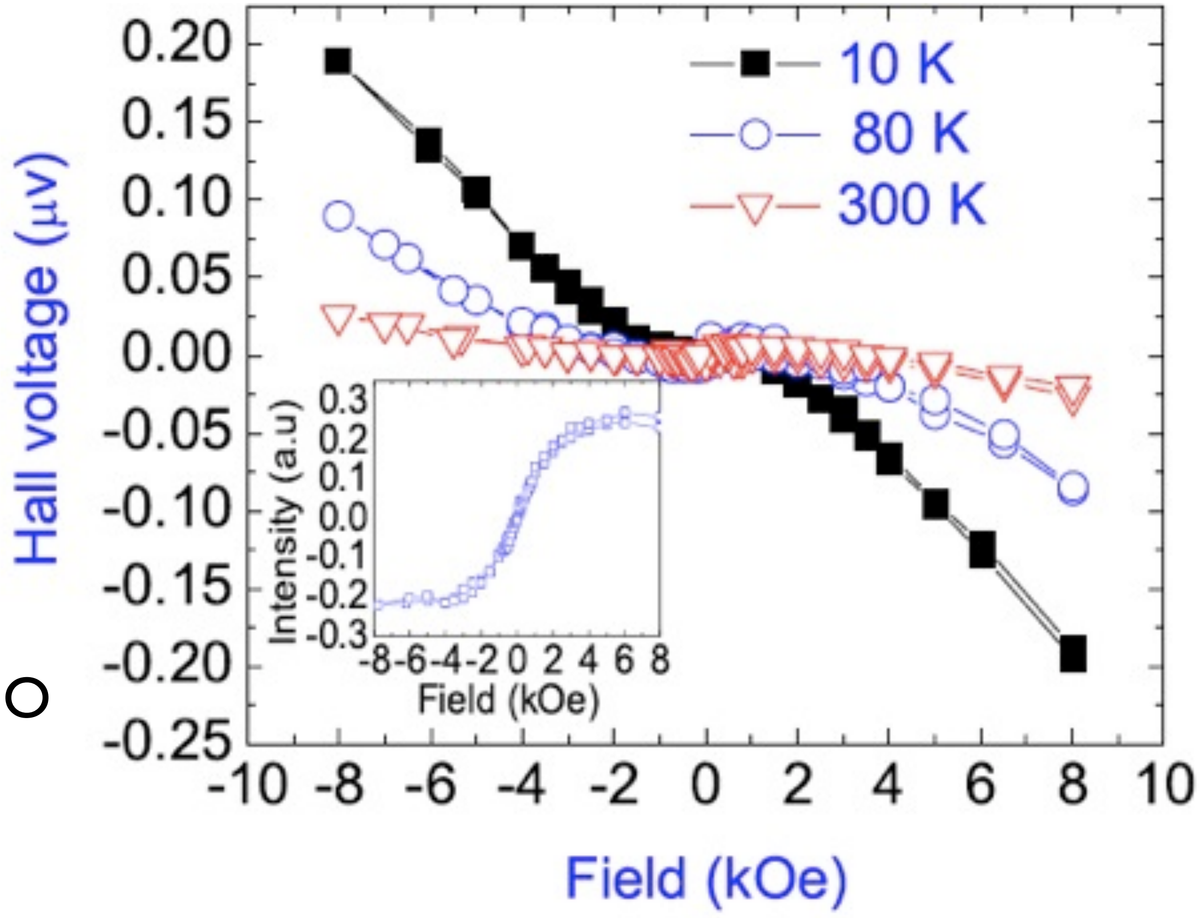


Application II: Impurity pairing for carbon in ZnO

Motivation

- ZnO is a low-cost wide-gap semiconductor that can be synthesised in bulk crystalline form
- **Drawback:** no reproducible strategy for *p*-type doping available. Could C act as acceptor in ZnO ?
- **Ferromagnetism** in ZnO induced by carbon ?

Host-mediated magnetic interaction between C-impurities would require high C concentrations. Pairing of C energetically favorable ?



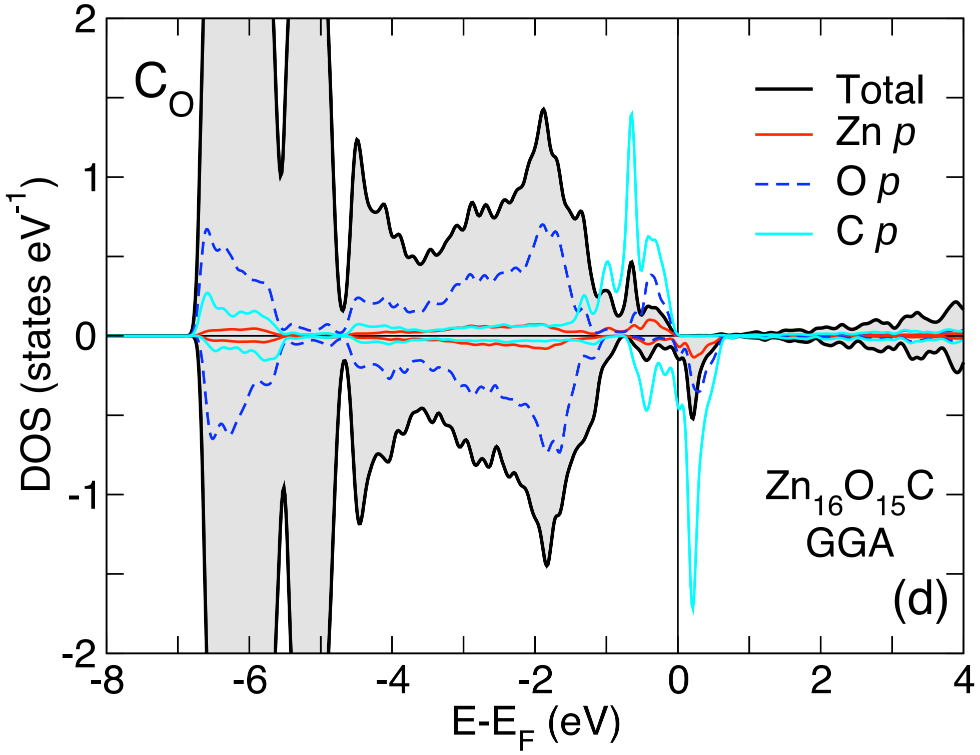
Anomalous Hall effect in n-type C-doped ZnO
H. Pan et al., PRL **99** (2007), 127201

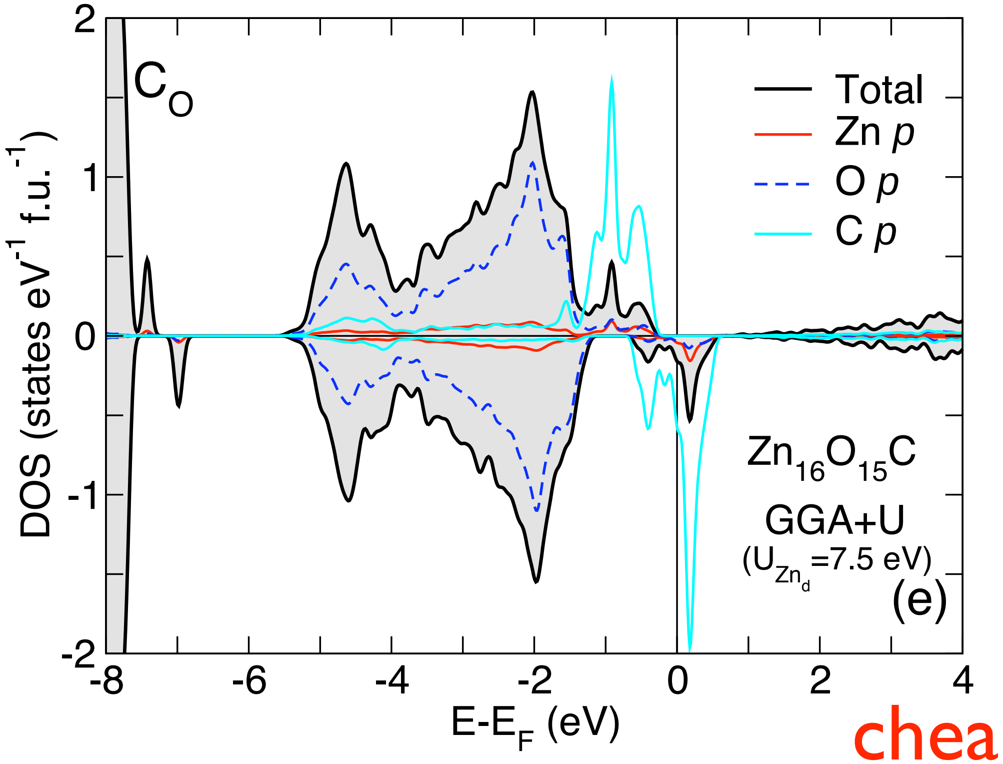
Method comparison

- In LDA and GGA, the oxygen-derived valence band lies too high up in energy
→ spurious hybridization between C and O orbitals

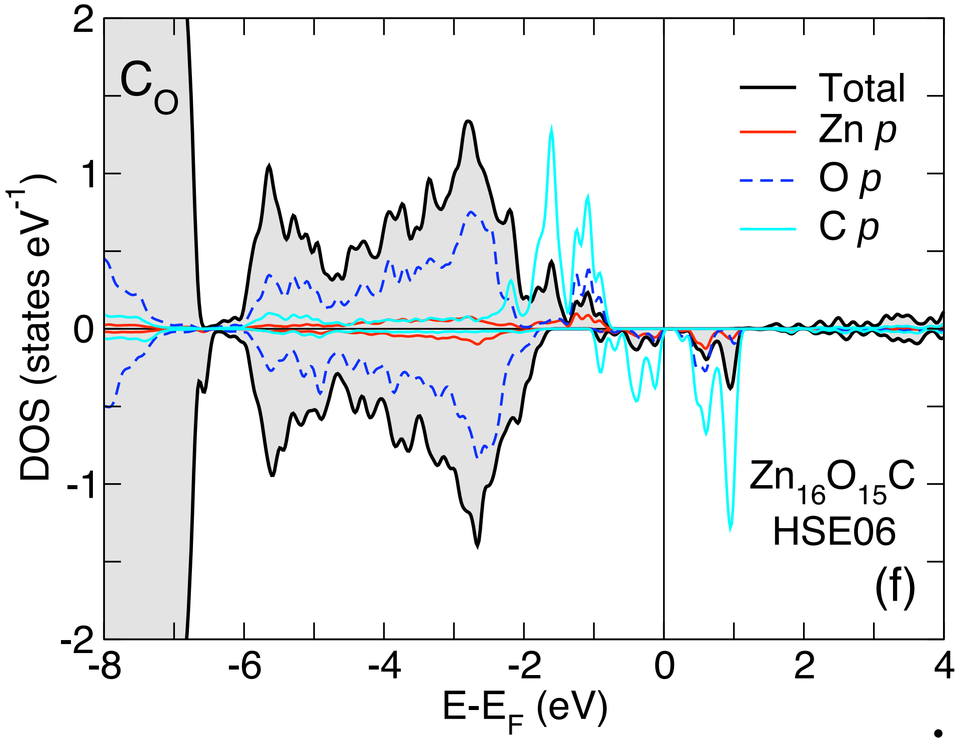
S. Nayak et al. PRB **86**, 054441 (2012)

- correction schemes





cheap !

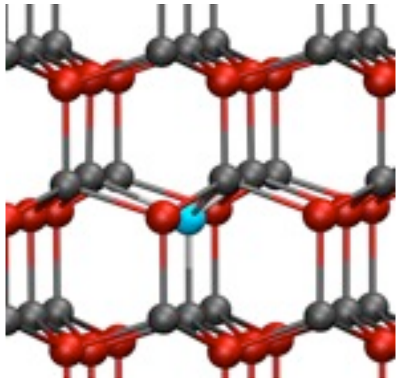


expensive

Single impurities

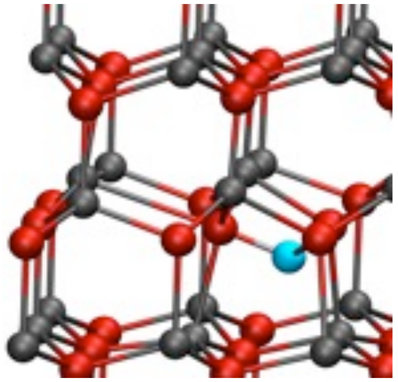
- Reaction of C (stemming from di-ethyl-zinc from the precursor) with O_2 to CO is thermodynamically more favorable than incorporation
- Under O-rich conditions, C_{Zn} is the thermodynamically most stable single impurity

$C_O{}^0$

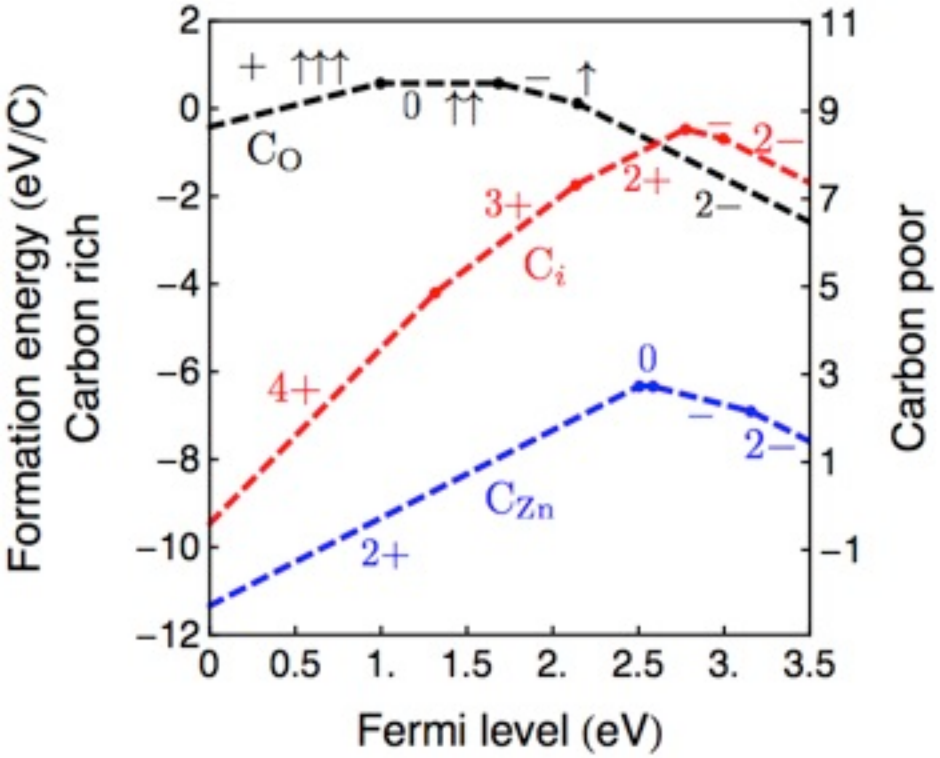


$C_{Zn}{}^0$

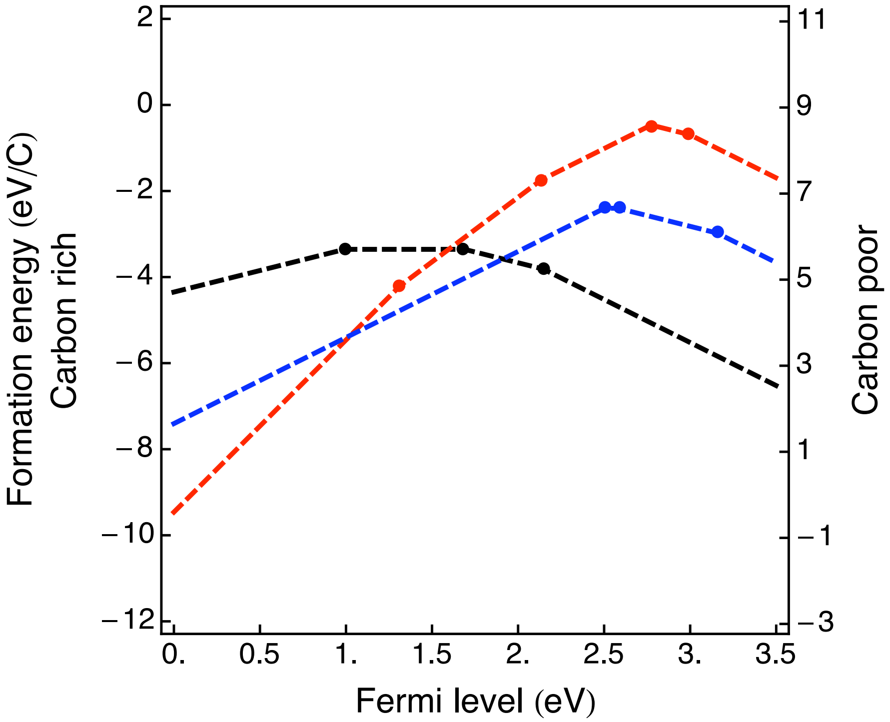
C_i^{2+}



O-rich conditions



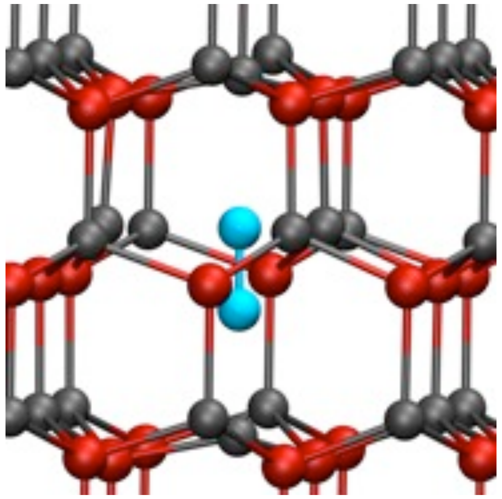
Zn-rich conditions



Defect molecule at oxygen site

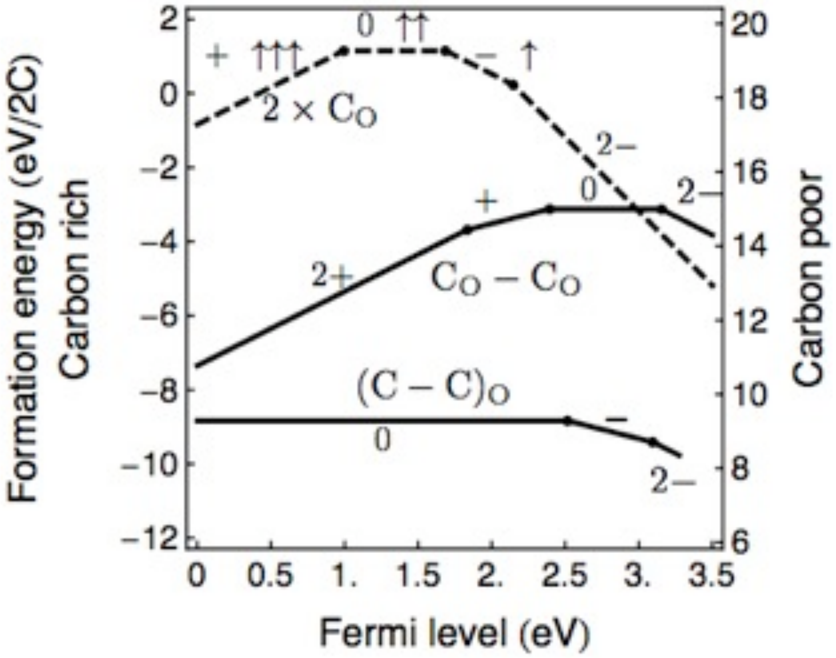
- Formation of C_2 molecule lowers the formation energy compared to the isolated defects

$(C_O - C_O)^0$

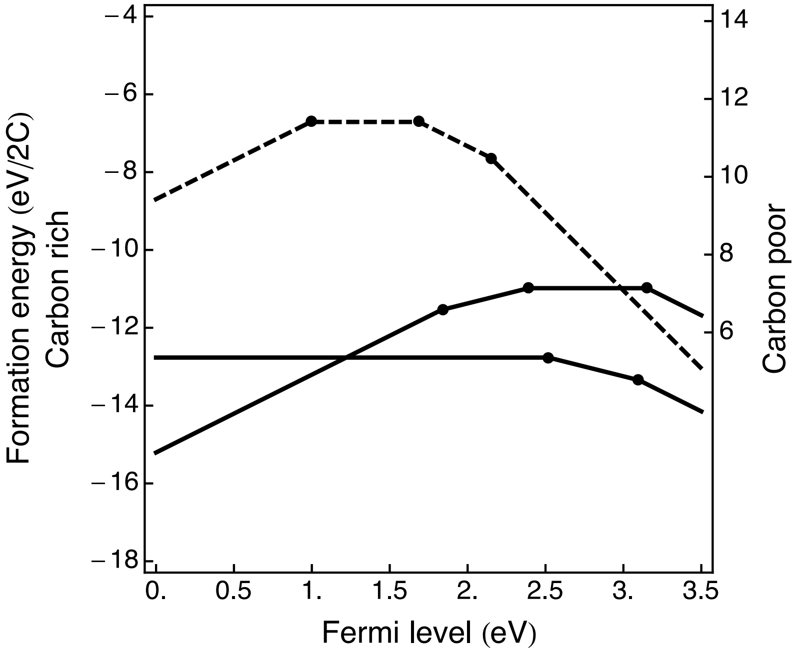


$(C - C)_O{}^0$

O-rich conditions

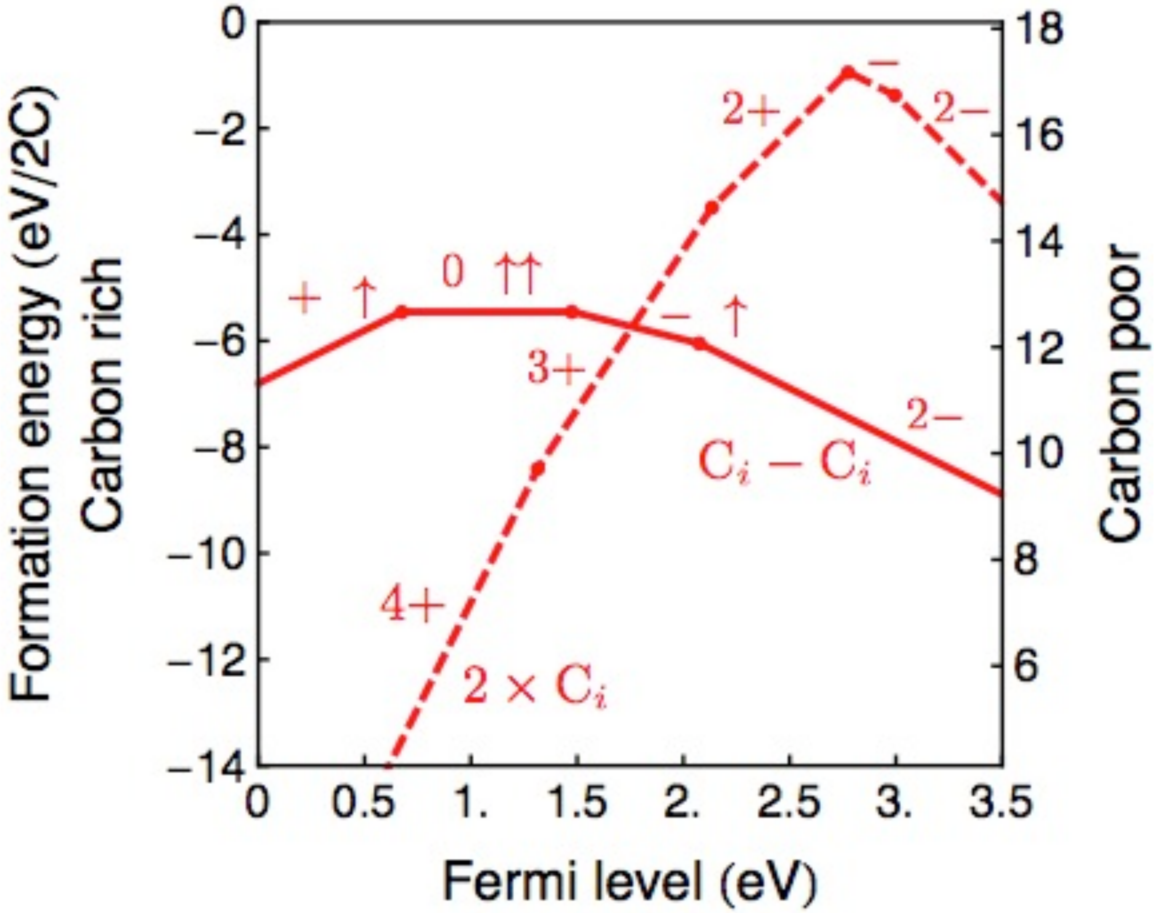


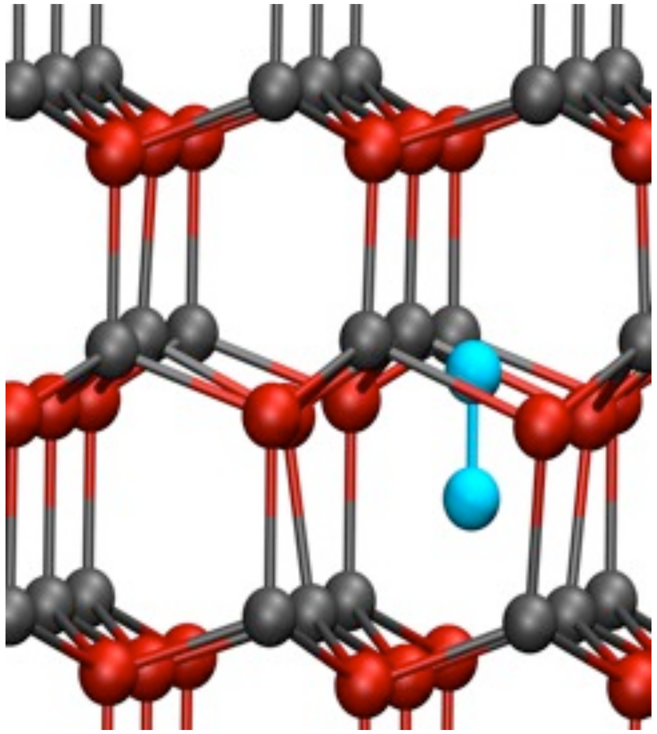
Zn-rich conditions



Defect molecule at interstitial site

- In *p*-type ZnO, pairing is energetically more costly than single interstitials.
- Under *n*-type conditions, undissociated C_2^{2-} molecules or C_2^- radicals (magnetic moment !) may persist.



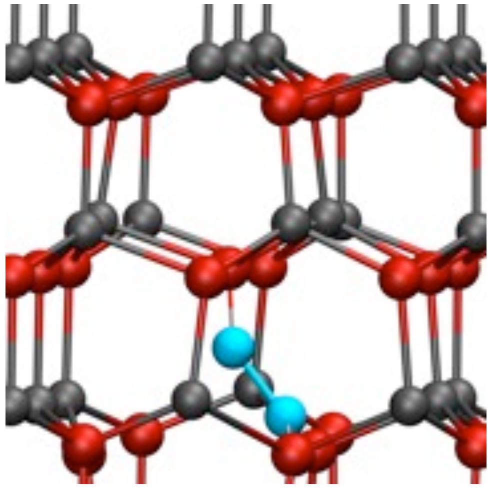


$(C_i - C_i)^0$

Defect molecule at Zn site

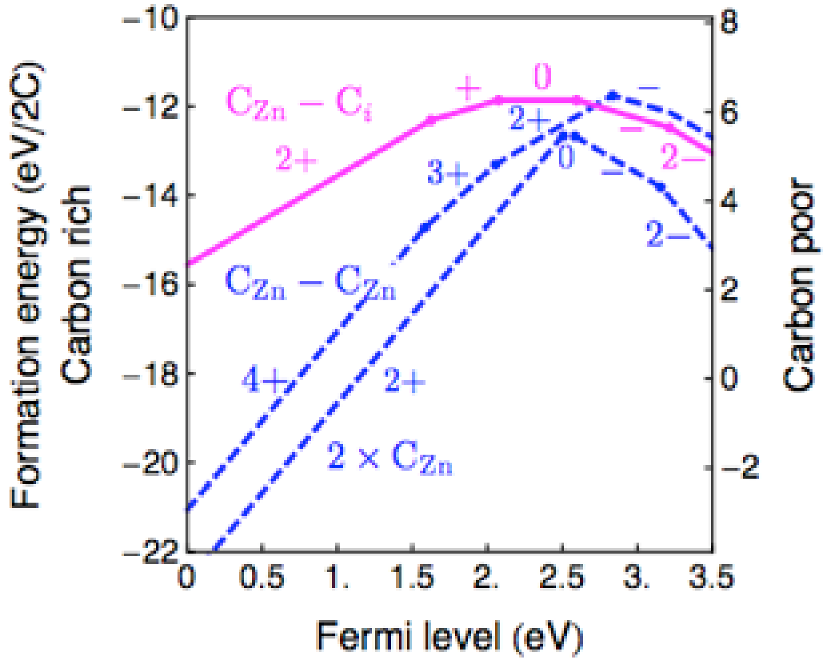
- Overall, C_{Zn} is the most stable species
- Pair of C_{Zn} at neighboring sites is less stable
- C_{Zn} -C_i complex may play a role under Zn-rich conditions

$(C_{Zn} - C_{Zn})^0$

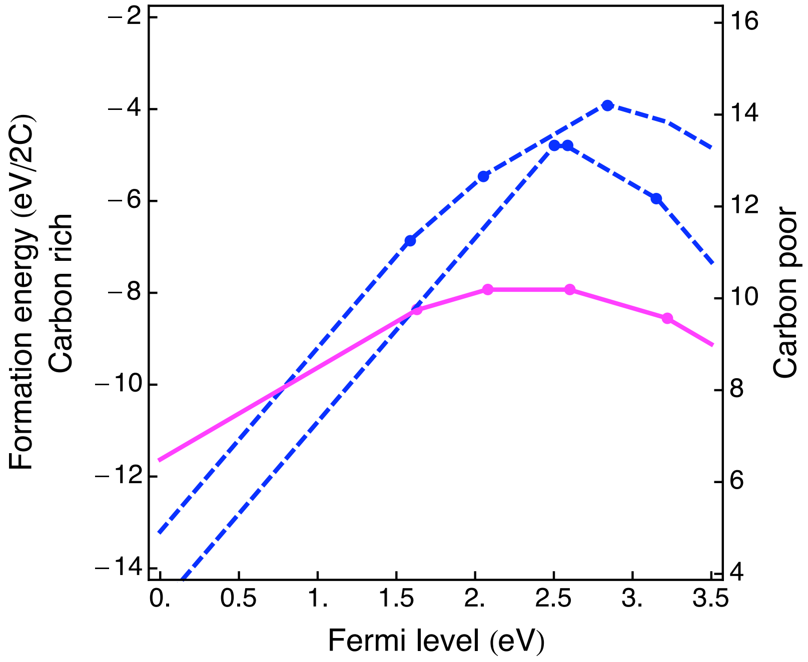


$(C_{Zn} - C_i)^{2+}$

O-rich conditions

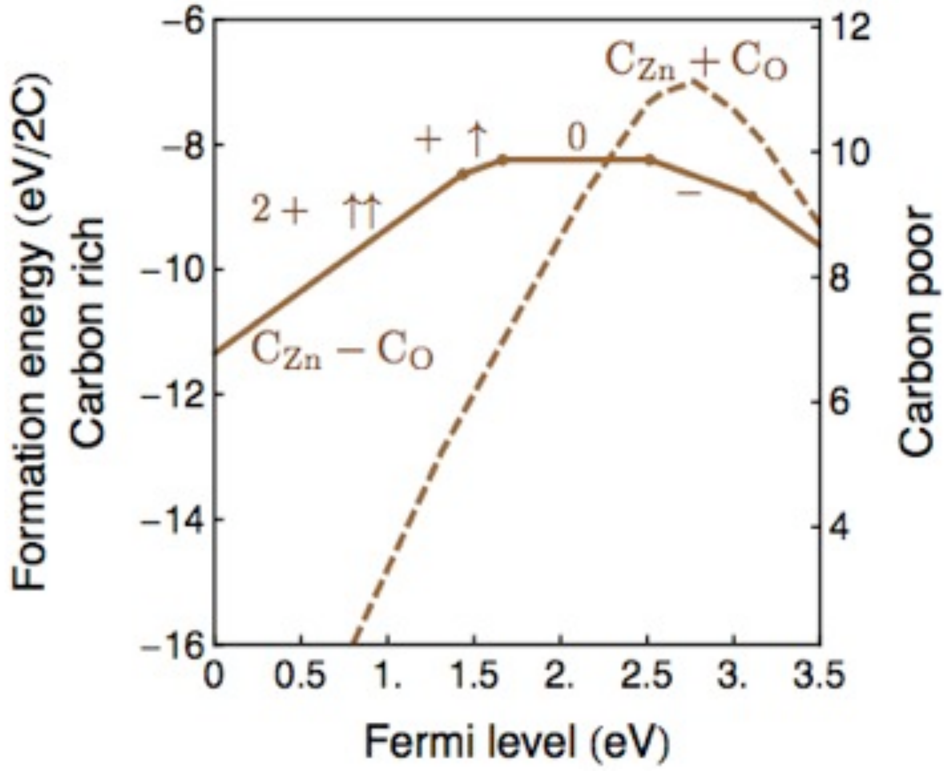


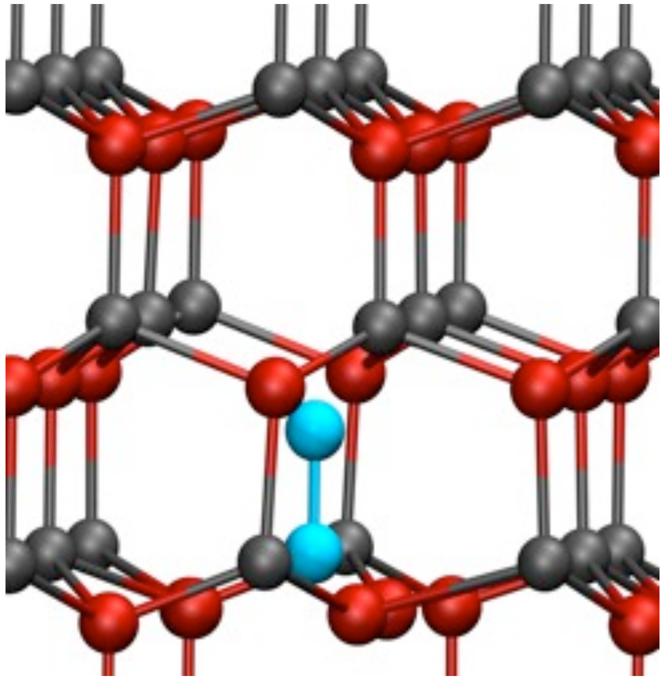
Zn-rich conditions



C_2 substituting a ZnO unit

- Pairs are less stable than $2C_{Zn}$, and less stable than $C_o + C_{Zn}$ under *p*-type conditions.
- Molecular magnetic moment possible, but only in the (metastable) *p*-type conditions





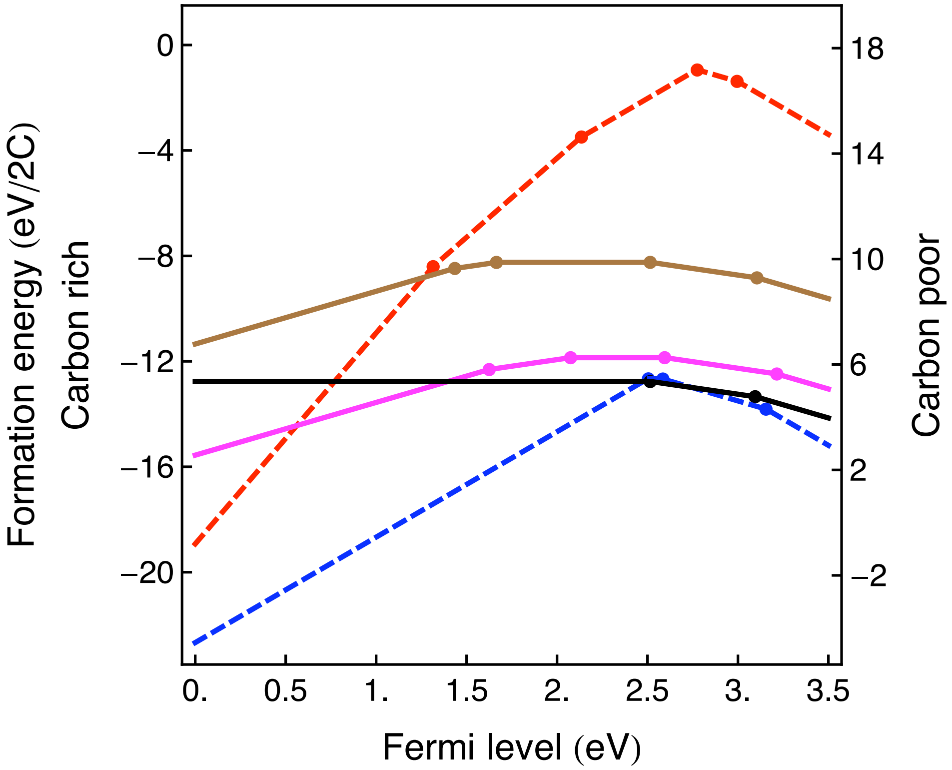
$(C_{Zn} - C_O)^{2+}$

S. Sakong & P. Kratzer,
Semicond. Sci. Technol. **26**, 014038 (2011)

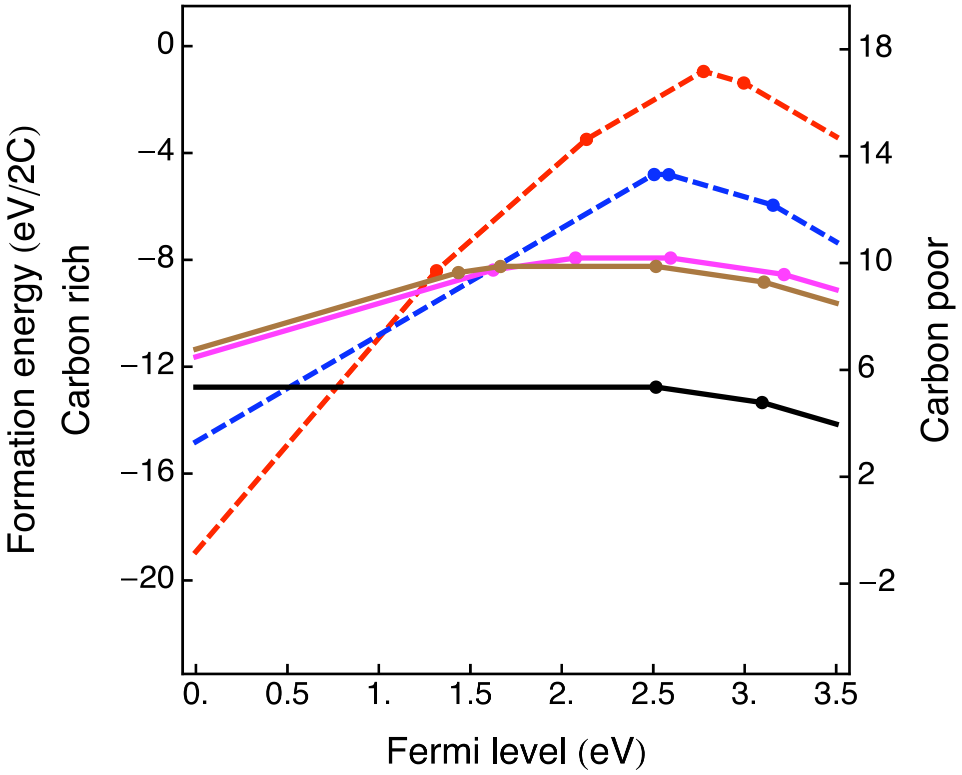
Comparison of stable defect pairs

- **O-rich conditions:** C_{Zn}, no pairing
- **Zn-rich conditions:** C_i^{3+} in *p*-type regime,
  (C-C)$_O$ in *n*-type regime

O-rich conditions



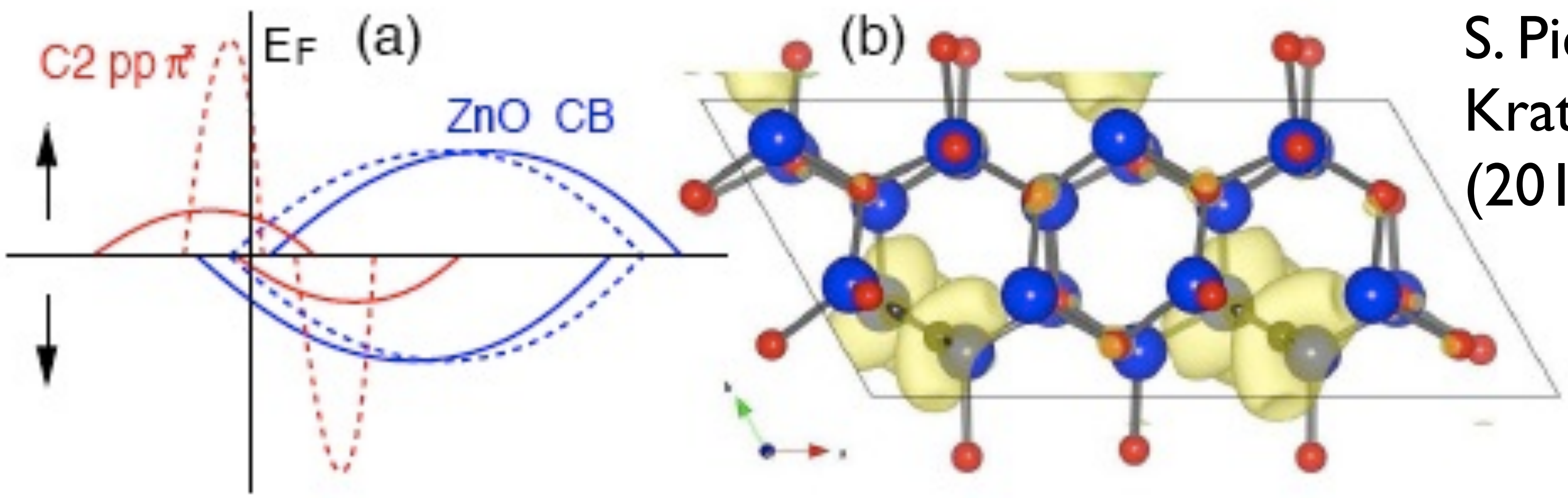
Zn-rich conditions



Magnetism due to molecular triplet

- formation of a $(C\text{-}C)_O$ out of two C_O in *n*-type ZnO
- studied by HSE calculation with $\alpha=0.37$ (band gap 3.3 eV)
- antibonding C_2 triplett becomes resonant with ZnO conduction band
- ferromagnetic interaction favored over antiferromagnetic by 36 meV

H. Wu, A. Stroppa, S. Sakong, S. Picozzi, M. Scheffler & P. Kratzer, PRL **105**, 267203 (2010)



Summary

GaAs nanopillars:

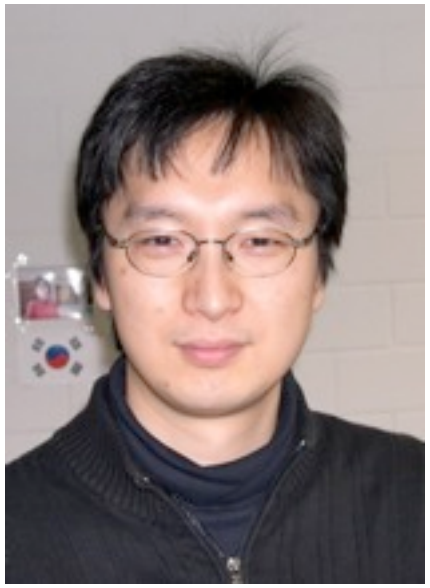
- Au impurities have lower formation energy than intrinsic defects
- In contrast to zincblende, arsenic vacancy diffusion is anisotropic in wurtzite GaAs (slow along *c*-axis)
- for a wurtzite nanopillar of 20 nm in diameter, V_{As} can be annealed in 30 min at T=700K

C-doped ZnO:

- Under O-rich conditions, C_{Zn} strongly favored
- C_O stable under Zn-rich conditions, but not useful as acceptor for *p*-type doping
- C-induced magnetism in n-type ZnO could be explained by V_O+$(C\text{-}C)_O$ triplets resonating with the conduction band

Acknowledgements

- Sung Sakong



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