Defects and impurities in semiconductors

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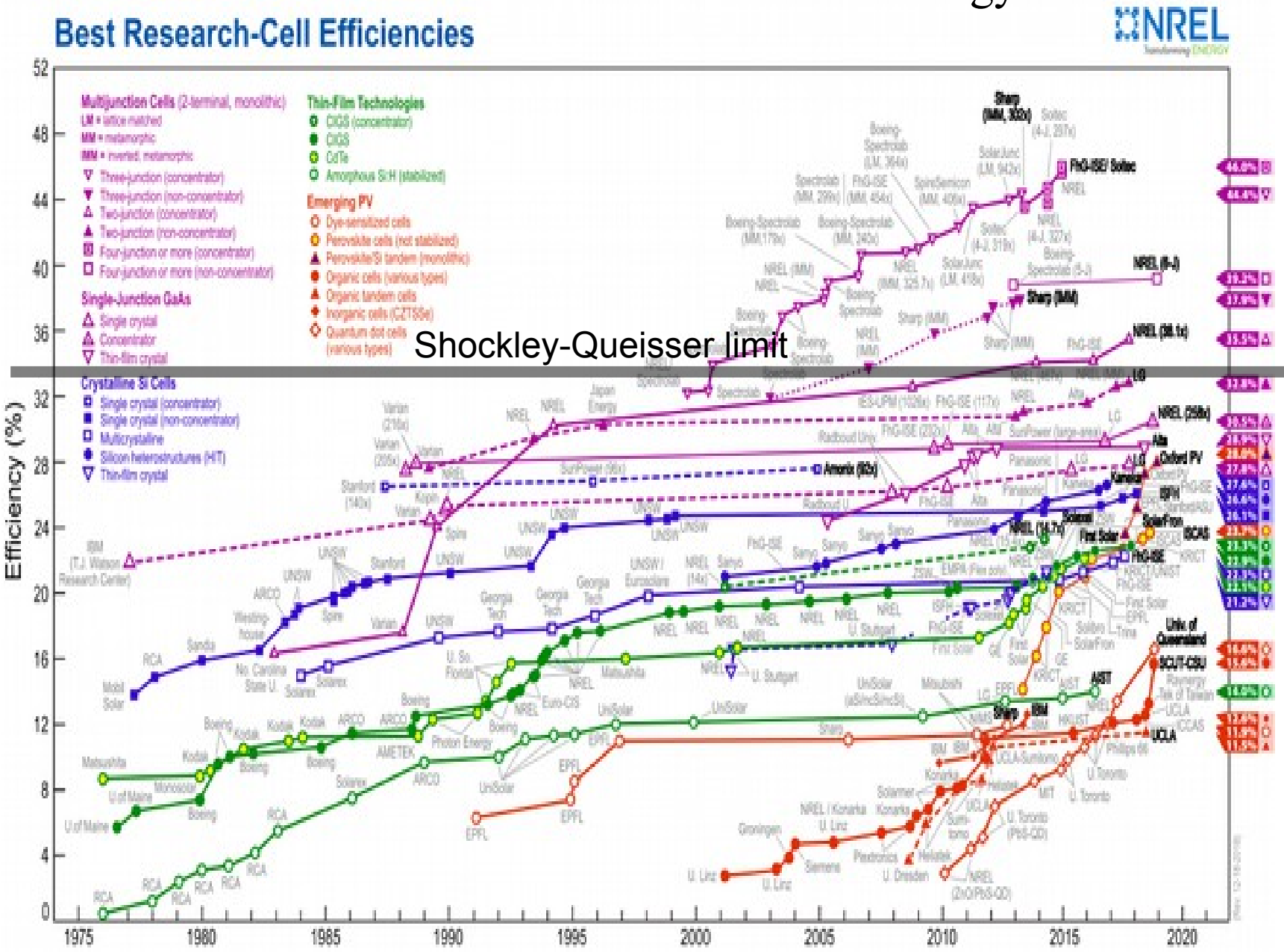
Outline

- Solar cells.
- Semiconductor concepts.
- Defects, formation energy.
- Thermodynamics of defects.
- Calculation details.
- Conclusions.

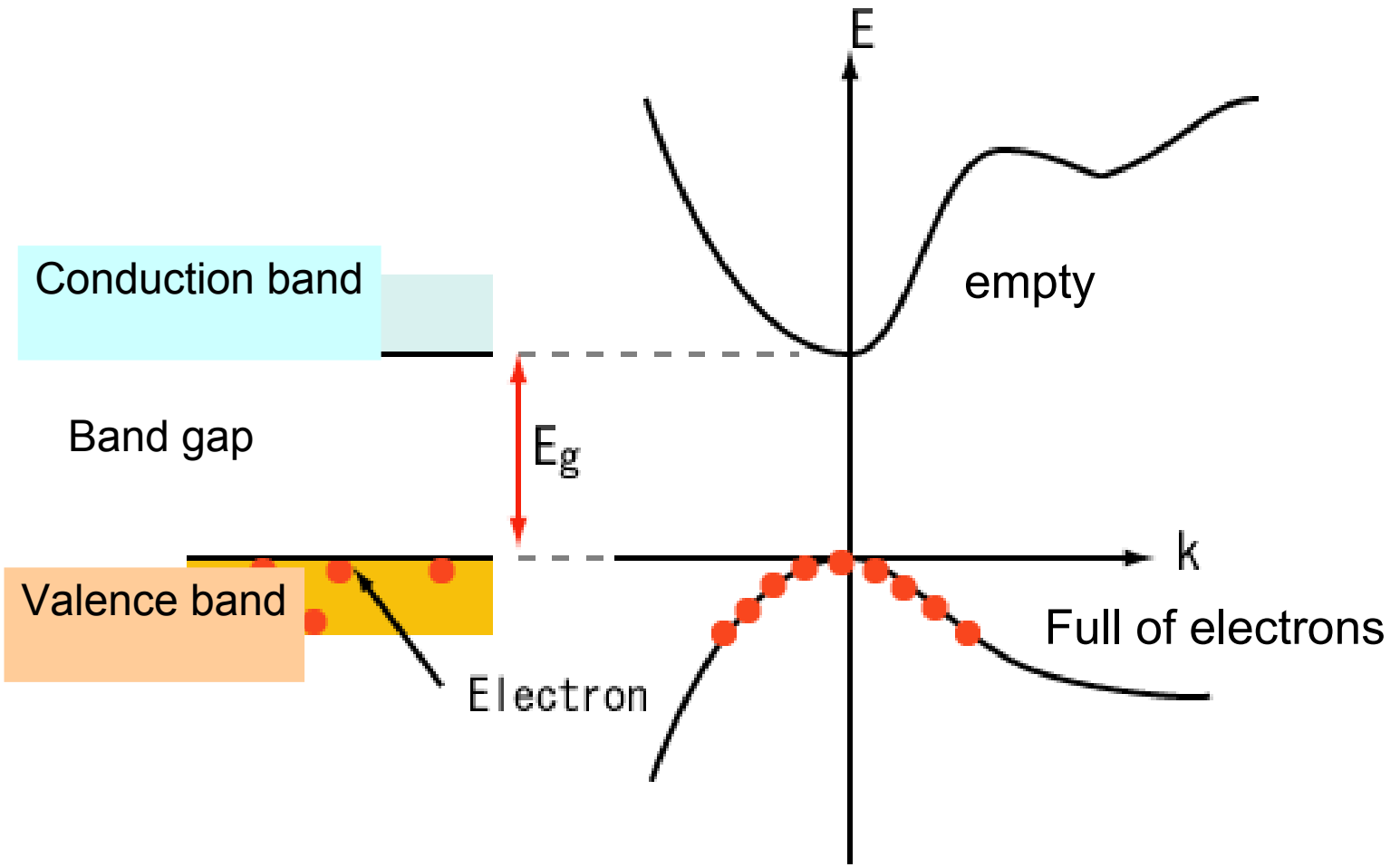
$$\text{Efficiency} = \frac{\text{Output electric energy}}{\text{Incident solar energy}}$$



Best cheap thin films: CdTe/CdS, CIGS, Perovskite?

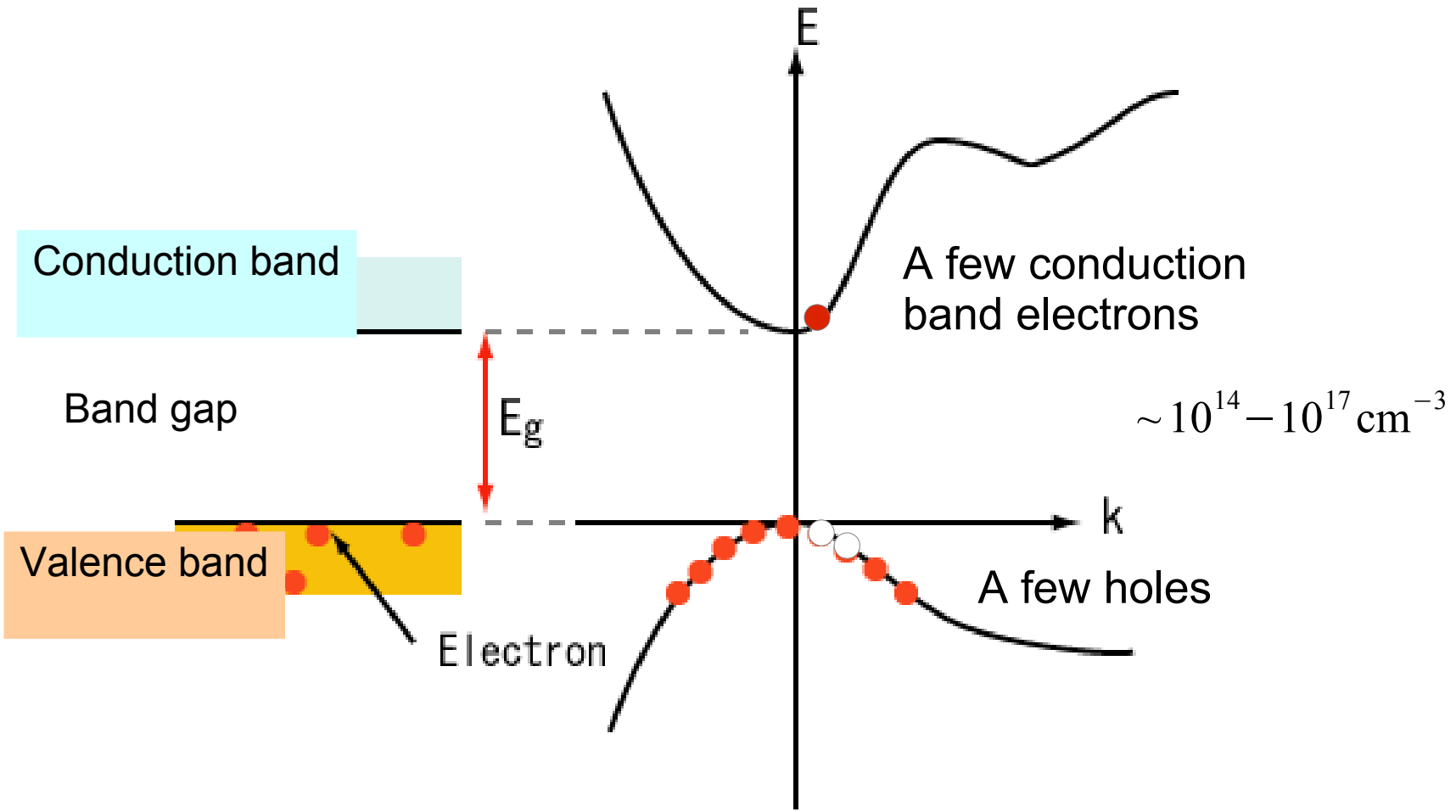
Rather than efficiency, the main problem is cost, including health and environmental costs.

Electronic structure of a perfect semiconductor



In this state it is a perfect insulator. Not very interesting, all perfect insulators are the same.

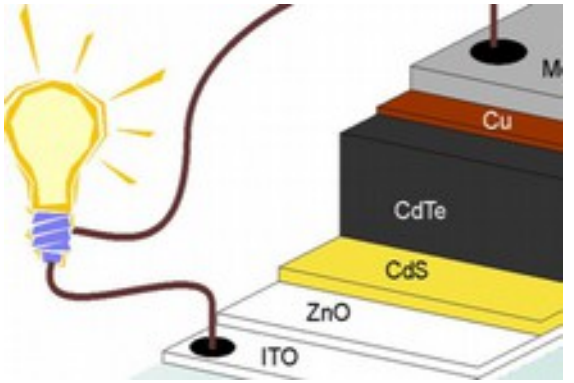
Electronic structure of a not perfect & excited semiconductor



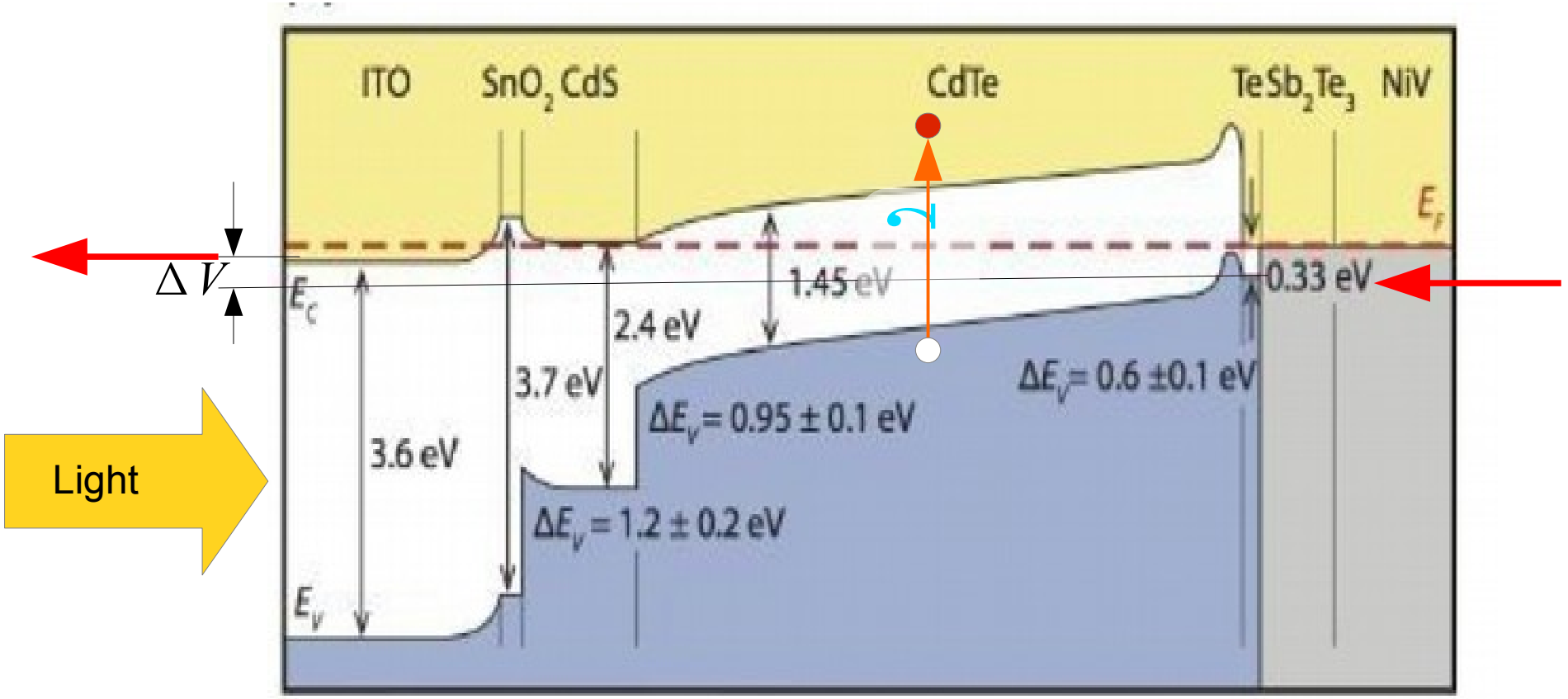
$$\text{conductivity } \sigma = e\,p\,\mu_h + e\,n\,\mu_e$$

High control of conductivity is possible in semiconductors

Energy en CdTe/CdS solar cell (η>22%)



The Fermi level determines how do the bands align across de interfaces.
Conductivity determines the voltage drop along CdTe.
The CNE with input from DFT calculations allows to model the effect of different dopants.



Source: A. Smetz et al, Solar Energy, UIT Cambridge (2018).

Charge carrier concentration

in thermodynamic equilibrium

$$p = N_V \exp\left(\frac{E_V - E_F}{kT}\right), \qquad n = N_C \exp\left(\frac{E_F - E_C}{kT}\right)$$

N_C (N_V) are the DOS of conduction (valence) band.

E_C y E_V are band edge energies.

E_F is the Fermi level.

$$\text{conductivity } \sigma = e\,p\,\mu_h + e\,n\,\mu_e$$

Control of the Fermi level E_F is crucial. This can be done by means of impurities or controlling the defect concentration during growth and annealing.

Band alignment

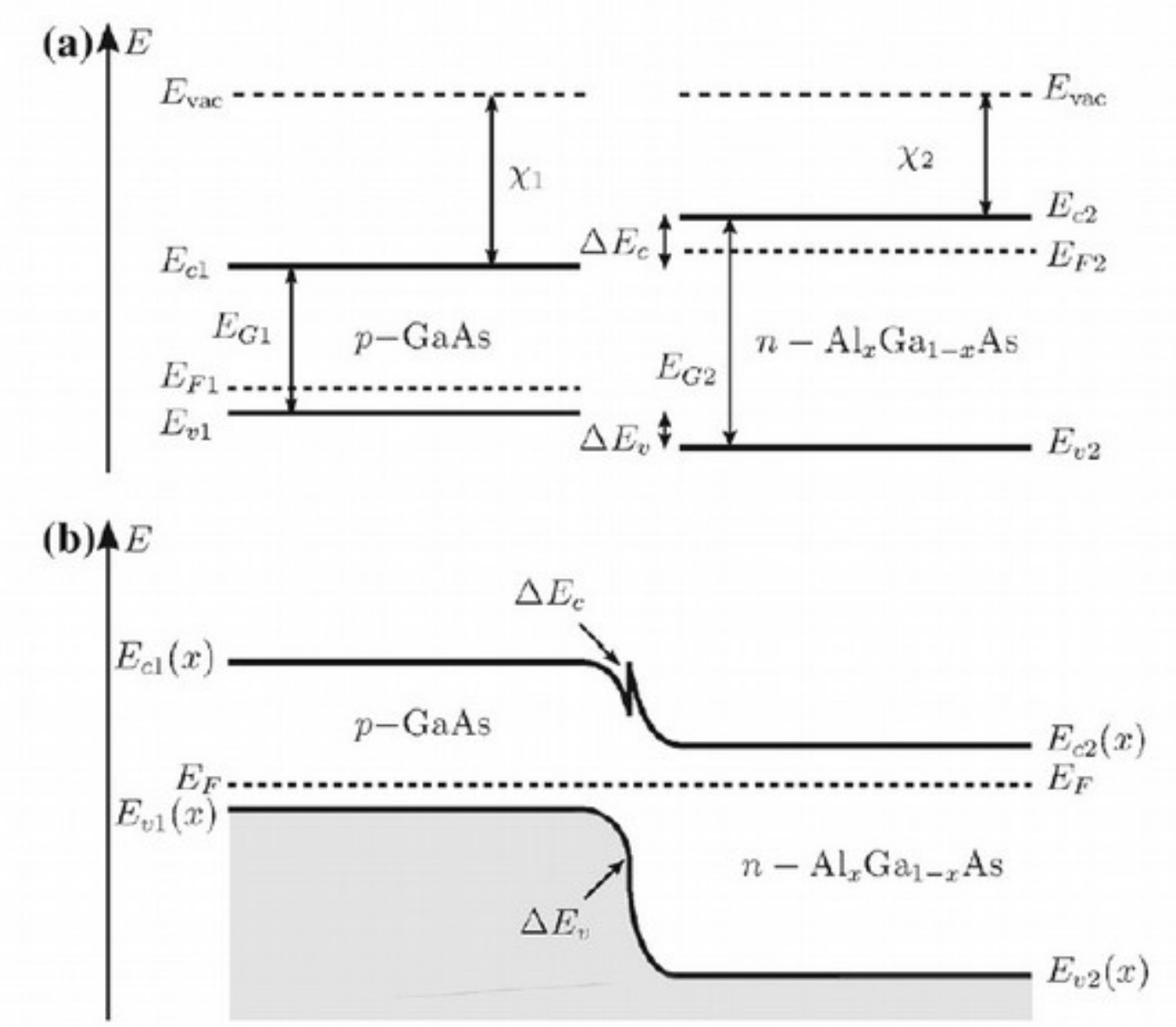
The barrier depends on the difference of the Fermi levels of separated materials.

In the junction, the Fermi level becomes unique.

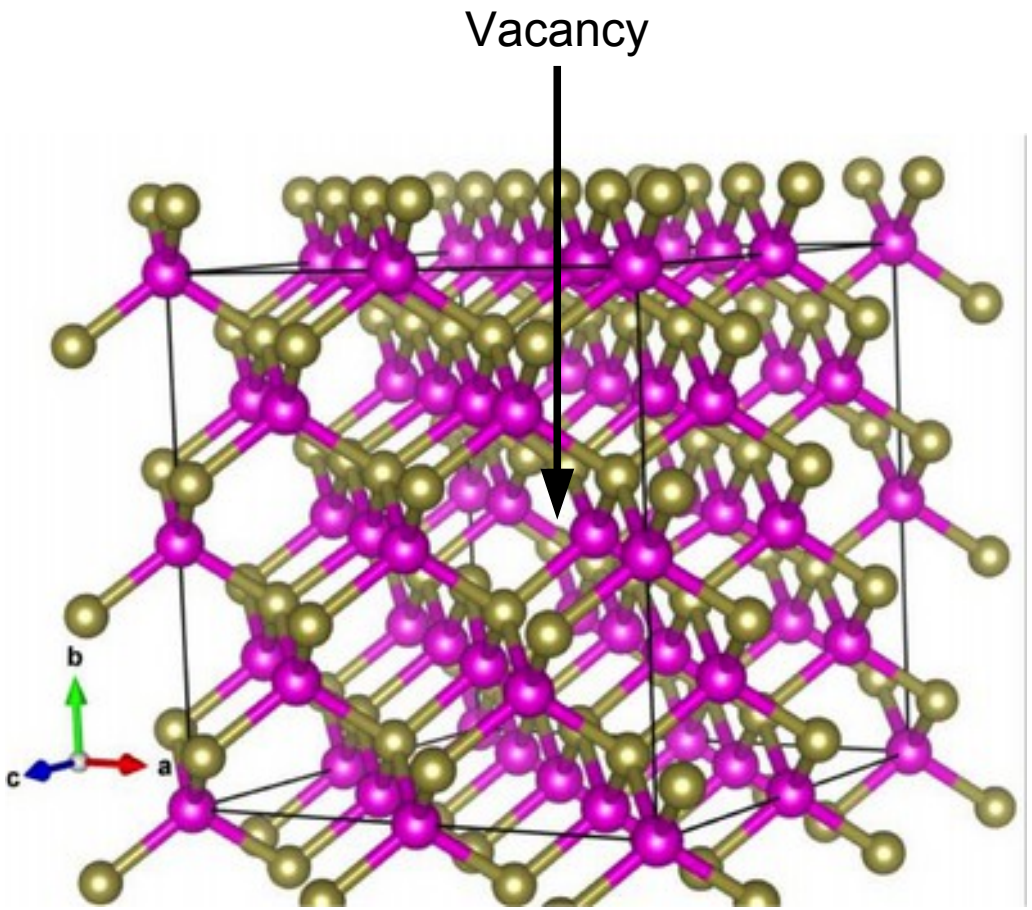
Barrier:

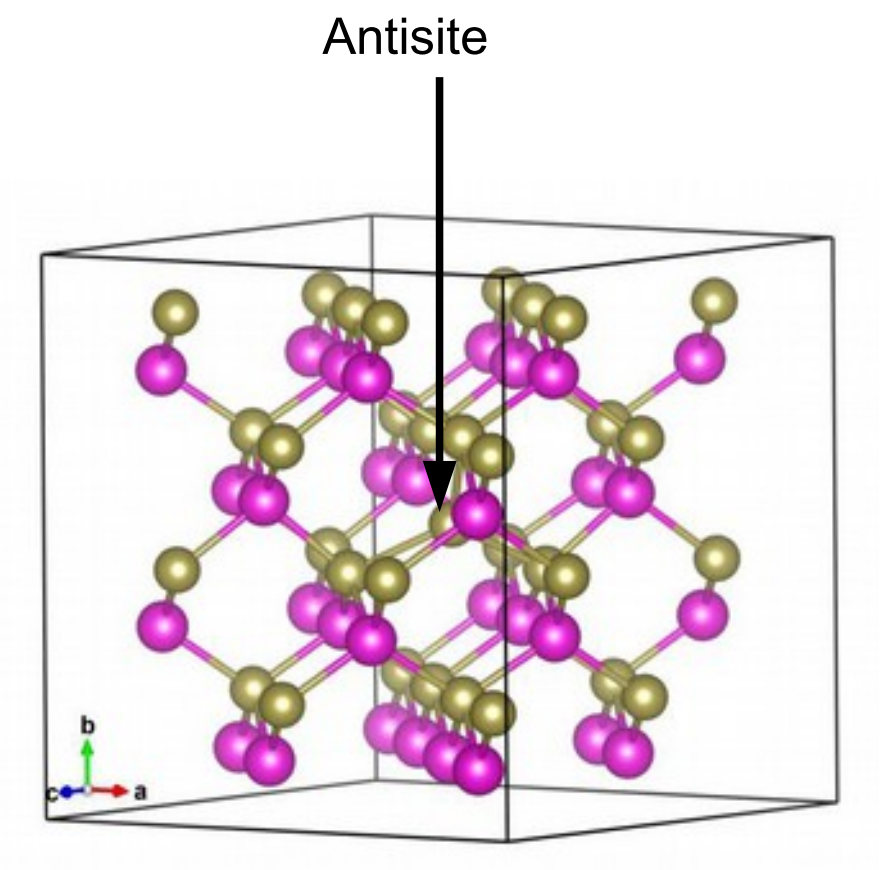
$$e\phi_{bi} = E_{F2} - E_{F1}$$

$$\Delta E_c = \chi_2 - \chi_1$$



Defects





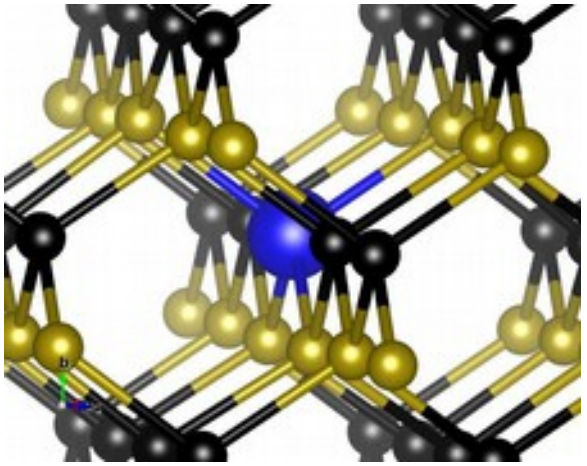
Other defects: self-interstitials, di-vacancies, vacancy-intertstitial, etc

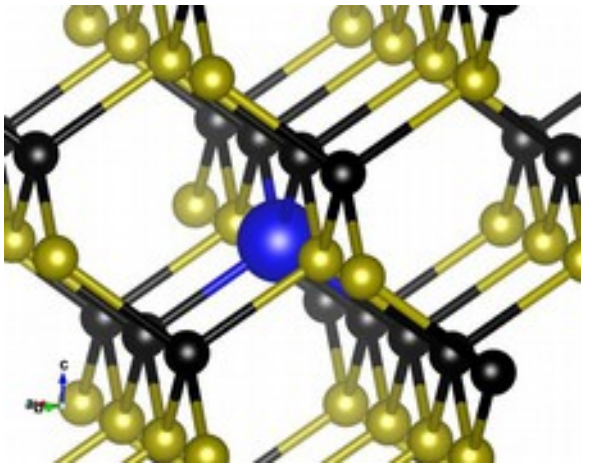
Always present:

Thermodynamic concentration: $N_i = N_{sites} N_{\text{config}} \exp\left(\frac{-\Delta H^f}{k_B T}\right)$ ← Formation energy

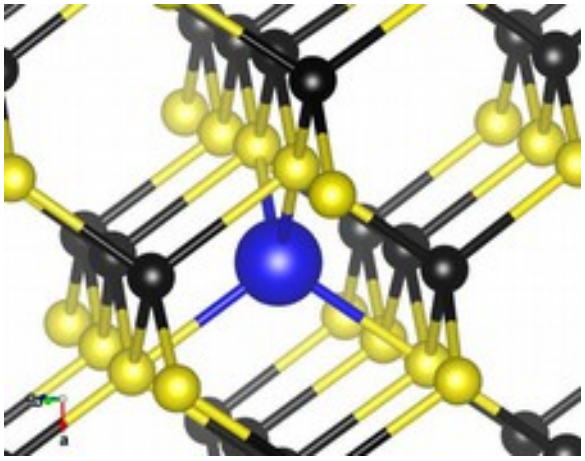
Impurities

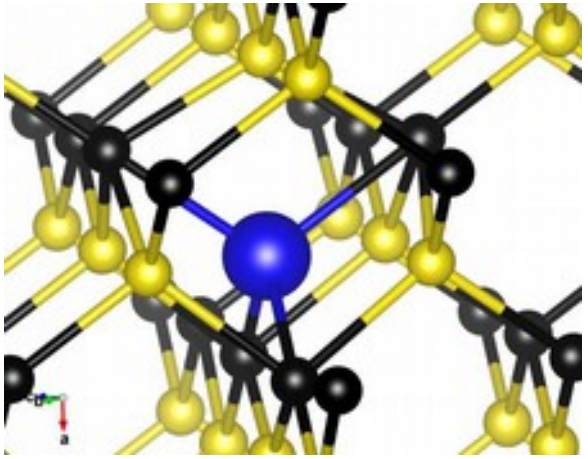
Substitutional

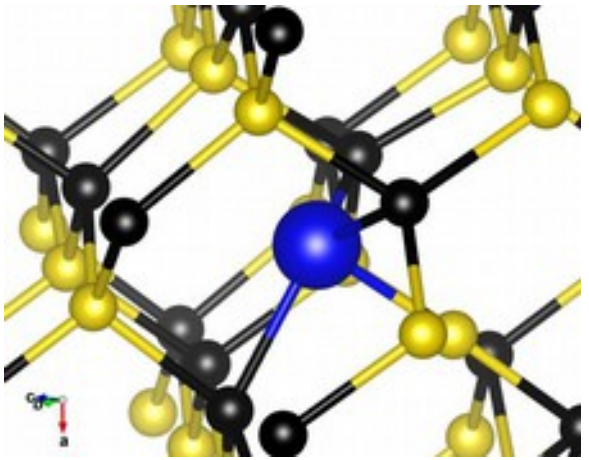




Interstitial

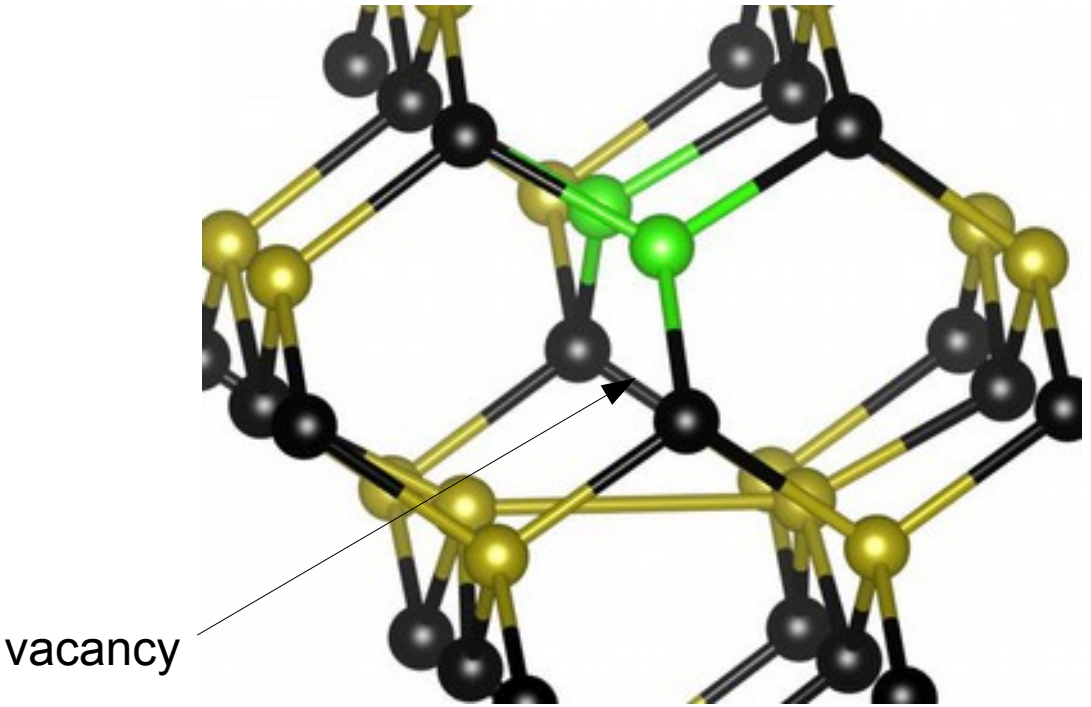






Complexes of defects & impurities

$2Cl_{Te}-V_{Cd}$ in CdTe



Caution:
Defects and impurities can accept or donate electrons.
Understand simple defects before going to the complex ones.

Defects & impurities make interesting the semiconductors

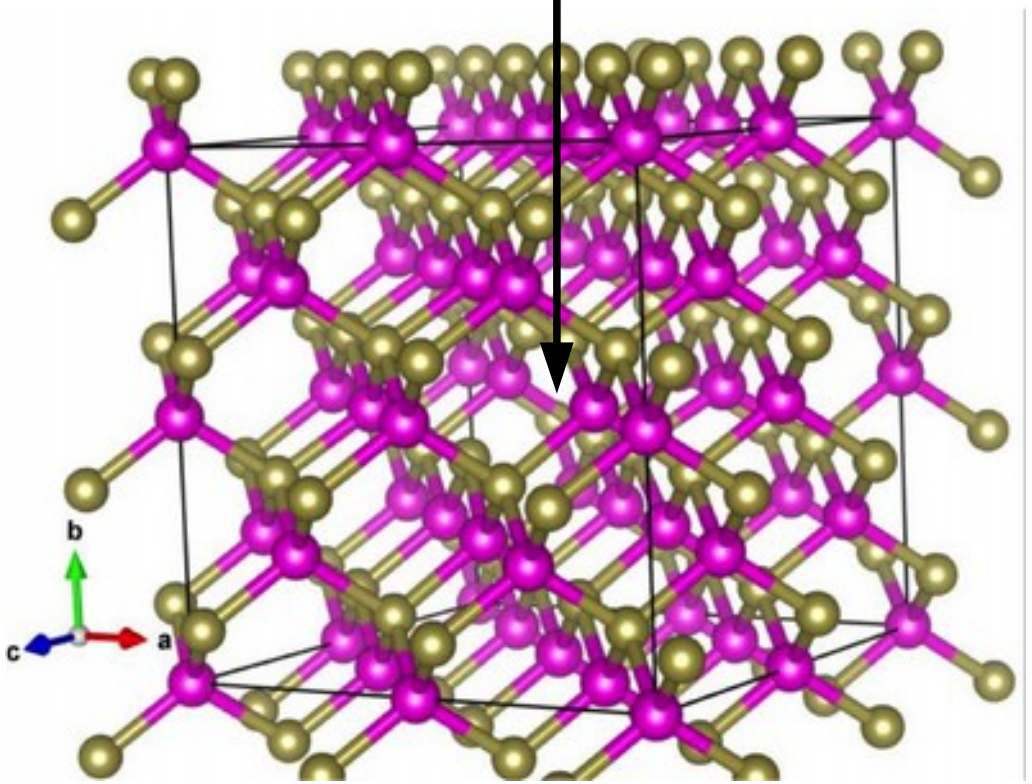
Example: vacancy

Formation energy

$$\Delta H^f(X,q) = E(X;q) - E(0) - \sum_\alpha n_\alpha \mu_\alpha$$

← Chemical potentials

Vacancy



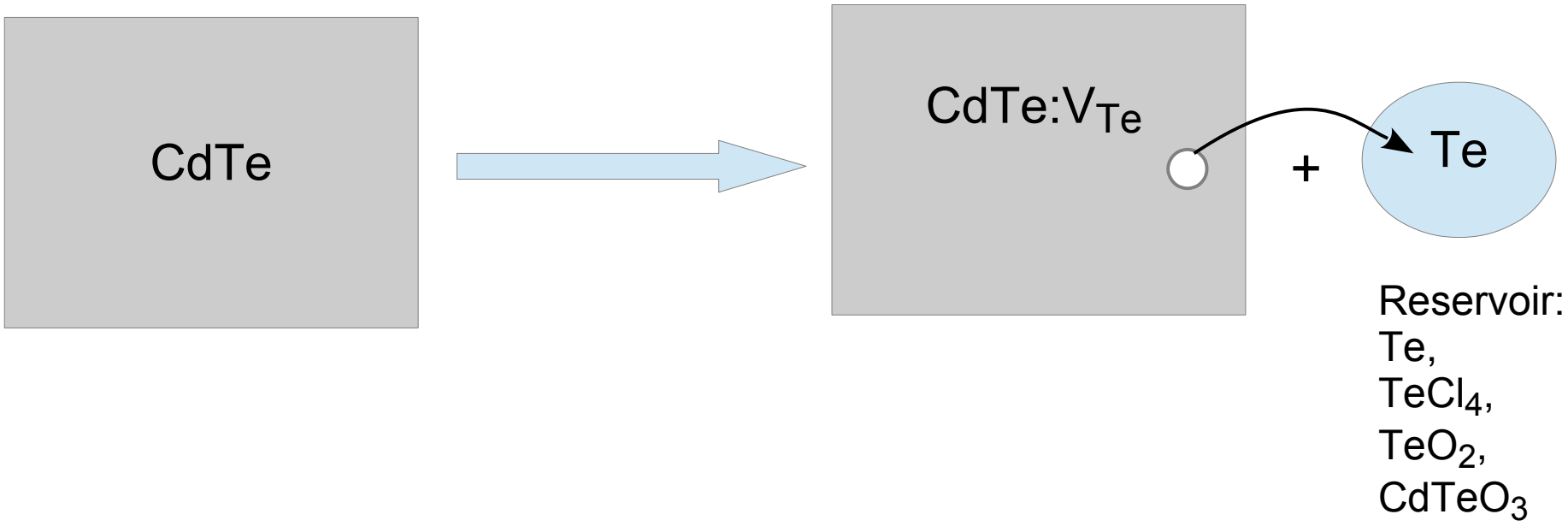
Esentially, μ_α and n_α are the energies and numbers of the added species (atoms and electrons) in the reservoir.

n_α<0 for a vacancy

Te vacancy and Te chemical potential

$$\Delta H^{f}(V_{Te}) = E(Cd_{32}Te_{31}) - E(Cd_{32}Te_{32}) + \mu(Te) + q E_{F} + \Delta E_{\text{size}}$$

One Te atom is exchanged between CdTe and a reservoir



Te vacancy and Te chemical potential

$$\Delta H^f(V_{Te}) = E(Cd_{32}Te_{31}) - E(Cd_{32}Te_{32}) + \mu(Te) + qE_F + \Delta E_{\text{size}}$$

One Te atom is exchanged between CdTe and a reservoir

$\mu(Te) = E(Te)$ Solid Te. Te-rich condition.

$\mu(Te) = E(Te) + \Delta\mu_{Te}, \Delta\mu_{Te} \le 0$ Greater probability to create vacancies if there is less Te available. Excess of Te cause precipitation

$\Delta\mu_{Cd} + \Delta\mu_{Te} = \Delta H(CdTe) < 0$ Equilibrium with the crystal of CdTe

$\Delta\mu_{Cd} \le 0$ Excess of Cd would cause Cd precipitation

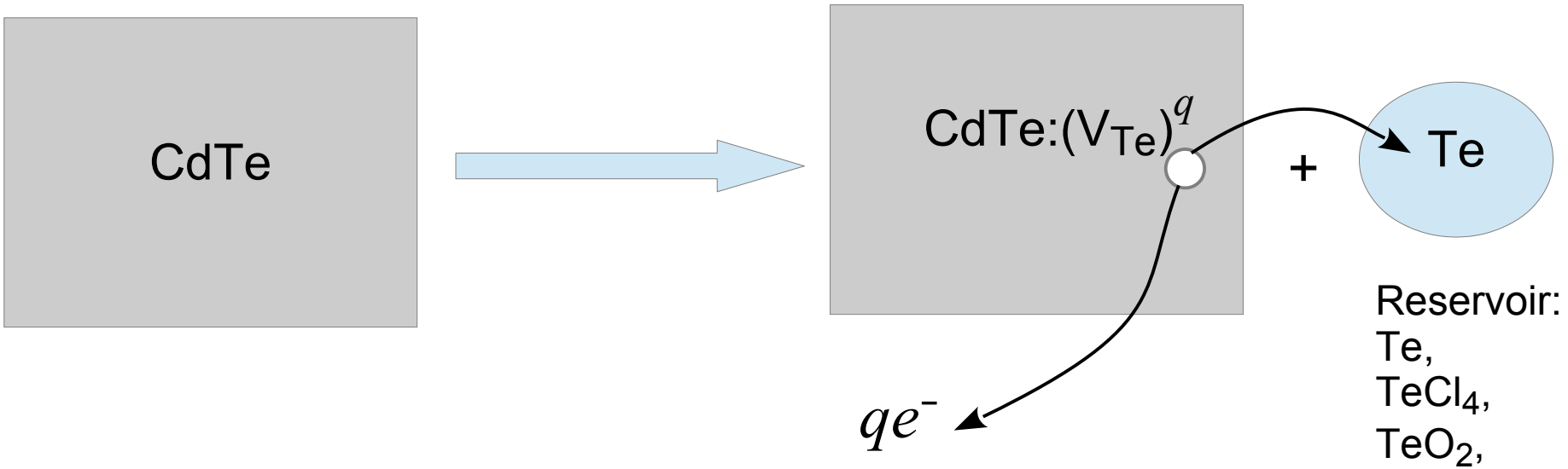
$\Delta H(CdTe) \le \Delta\mu_{Te} \le 0$ ← Te-rich, Cd-poor

↑ Cd-rich, Te-poor.

Electron chemical potential (Fermi level)

$$\Delta H^f(V_{Te}) = E(Cd_{32}Te_{31}) - E(Cd_{32}Te_{32}) + \mu(Te) + q E_F + \Delta E_{size}$$

One Te atom is exchanged between CdTe and a reservoir

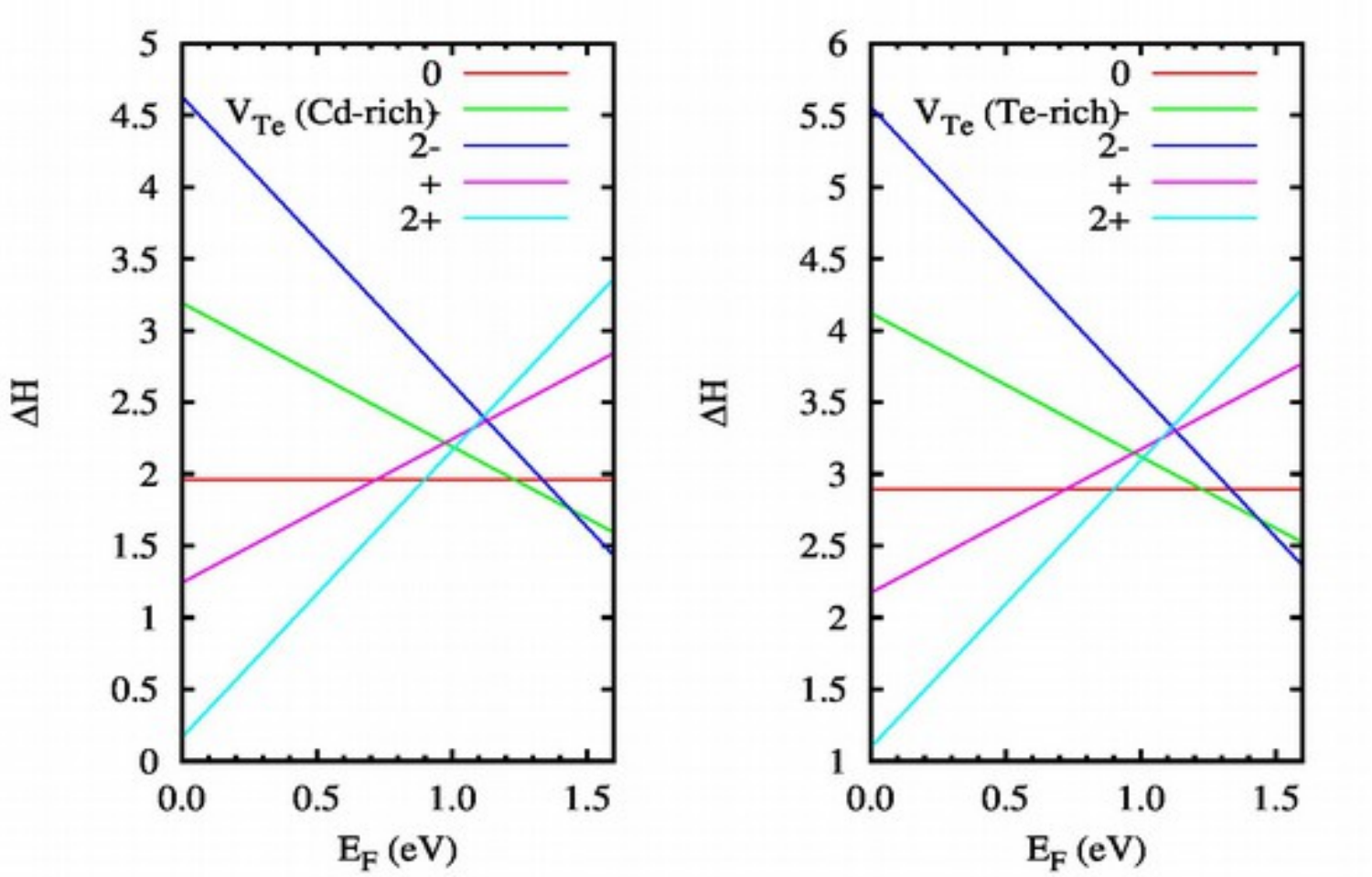


q>0 : donor
q<0: acceptor

Typical report: formation energy

V_{Te} , 63 atoms supercell, without gap correction, and size corrections

$$\Delta H^f\left(V_{Te}^q\right)=E\left(Cd_{32}Te_{31};q\right)-E\left(Cd_{32}Te_{32}\right)+\mu\left(Te\right)+q\left(E_V+E_F\right)+\Delta E_{\text{size}}$$



notation change

$$E_F \rightarrow E_V + E_F$$

Here E_F is relative to the valence band maximum

Impurities

Example: substitutional chlorine

$$\Delta H^f\left(Cl_{Te}^q\right)=E\left(Cd_nTe_{n-1}Cl;q\right)-E\left(Cd_nTe_n\right)+\mu\left(Te\right)-\mu\left(Cl\right)+q\left(E_V+E_F\right)$$

$$\mu\left(X\right)=E\left(X\right)+\Delta\mu\left(X\right),\qquad X=Cd,Te,Cl$$

$$\Delta\mu_{Cd}\le 0,\qquad \Delta\mu_{Te}\le 0,\qquad \Delta\mu_{Cl}\le 0$$

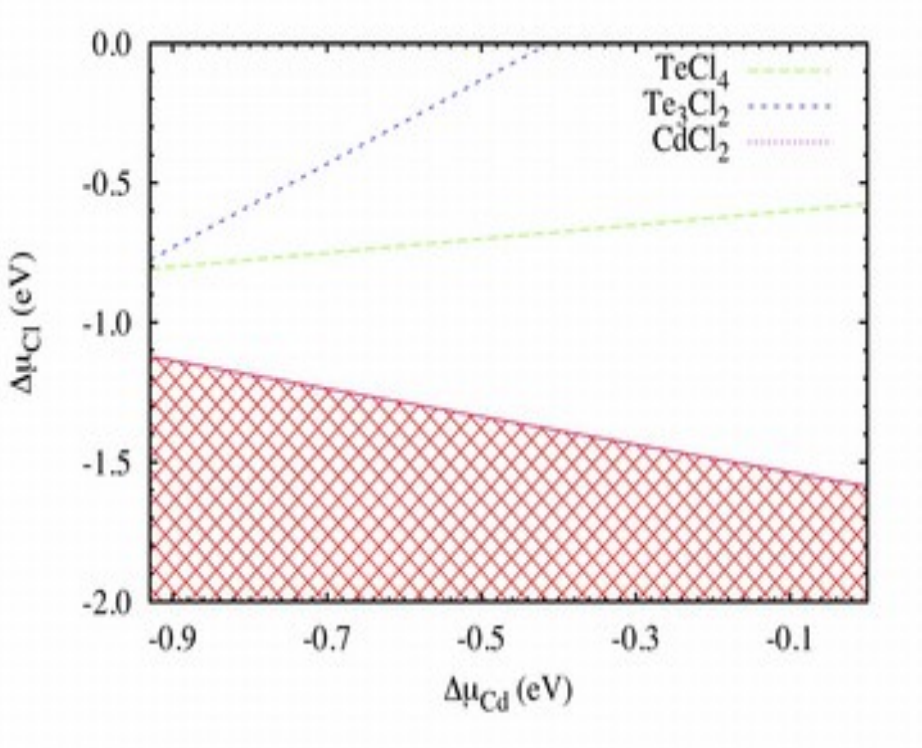
$$\Delta\mu_{Cd}+\Delta\mu_{Te}=\Delta H\left(CdTe\right)=-1.17\ \text{eV}$$

$$\Delta\mu_{Cd}+2\Delta\mu_{Cl}\le\Delta H\left(CdCl_2\right)=-3.59\ \text{eV}$$

All known compounds must be considered

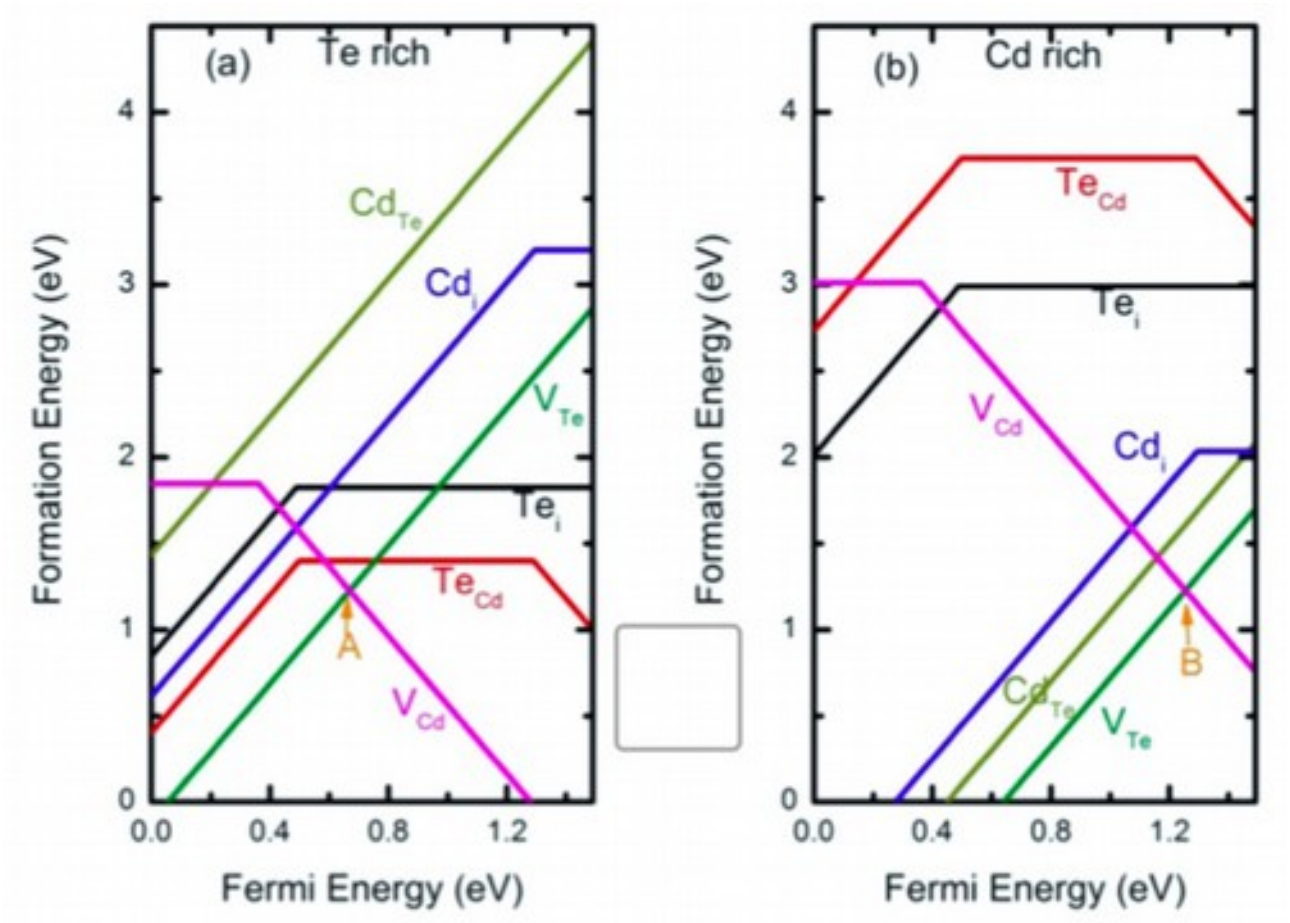
$$\Delta\mu_{Te}+4\Delta\mu_{Cl}\le\Delta H\left(TeCl_4\right)$$

$$3\Delta\mu_{Te}+2\Delta\mu_{Cl}\le\Delta H\left(Te_3Cl_2\right)$$



- What information provide the formation energies?
- How to compute accurate formation energies?

All intrinsic defects in CdTe



Intrinsic defect formation energies versus E_F in CdTe.
Source: Yang et al (S-H Wei), Semicond. Sci. Technol. 31 (2016) 083002.

Thermodynamic conditions

Mobile charge concentration

$$p = N_V \exp\left(\frac{E_V - E_F}{kT}\right), \qquad n = N_C \exp\left(\frac{E_F - E_C}{kT}\right)$$

Fixed charge concentrations: defects and impurities

$$n(\alpha, q) = n_{sites}\, g_q \exp\left(-\frac{\Delta H(\alpha, q, E_F)}{kT}\right)$$

Charge neutrality equation determines the Fermi level E_F

$$p + \sum_i q_i\, n\left(D_i, q_i^+\right) = n + \sum_j q_j\, n\left(A_j, q_j^-\right)$$

Can be solved self-consistently

Defect formation energies, ΔH can be obtained from quantum mechanics calculations (see later).

Thermodynamics calculations

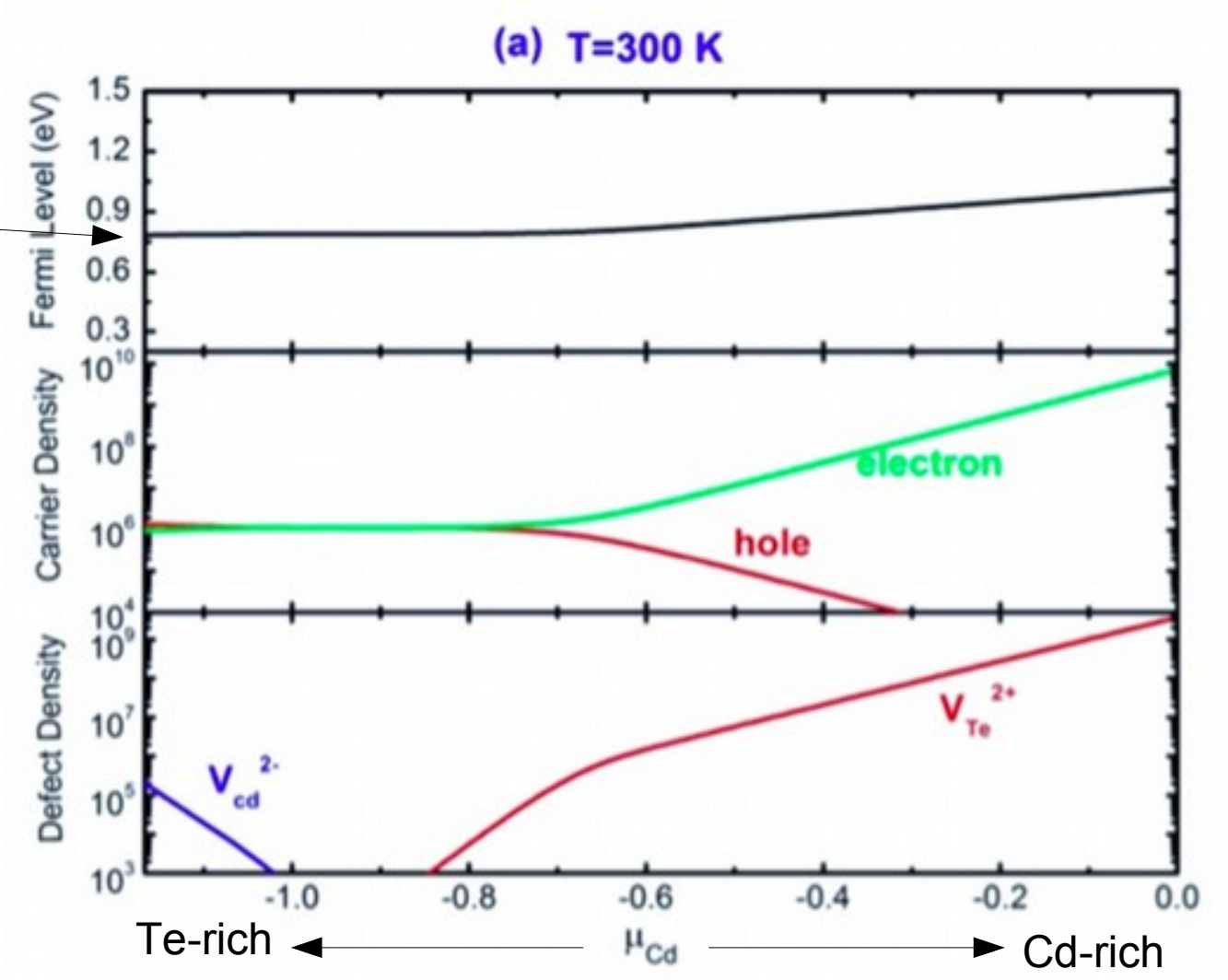
solutions of the charge neutrality equation for CdTe

Too deep in the gap

$$p = N_V \exp\left(\frac{E_V - E_F}{kT}\right),$$

$$n = N_C \exp\left(\frac{E_F - E_C}{kT}\right)$$

Definitely not a p-type Semiconductor.

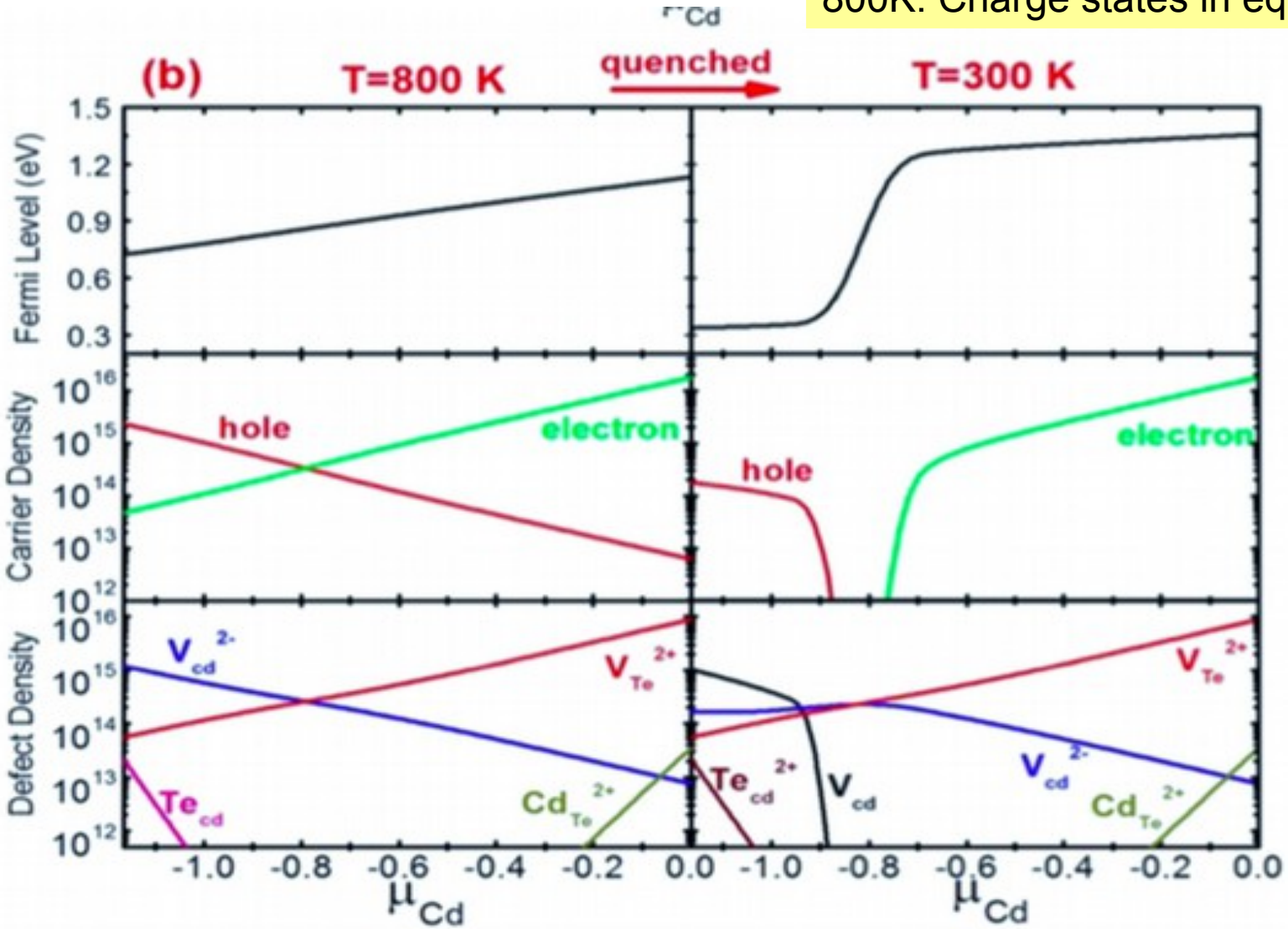


From Yang et al, Semicond. Sci. Technol. 31 (2016) 083002

Thermodynamics calculations

solutions of the charge neutrality equation for CdTe

Impurity & defect concentration fixed at 800K. Charge states in equilibrium at 300K



From Yang et al, Semicond. Sci. Technol. 31 (2016) 083002

This explains how CdTe can be made p-type or n-type, just with intrinsic defects.

Impurities can be included in the CNE, and simulate doping.

Plan:

- What information provide the formation energies?
- How to compute accurate formation energies?

Ab Initio Quantum Mechanics

Most used method: density functional theory (DFT)

- Hohenberg, Pierre; Walter Kohn (1964). "Inhomogeneous electron gas". Physical Review 136 (3B): B864–B871.
- Density Functional Theory. See, e.g. Nobel conference by W. Kohn, Rev. Mod. Phys. Vol. 71, No. 5, October 1999.

Idea: The electronic density, not the wavefunction, is the important magnitude, and it determines the properties of the ground state of a quantum electron system.
DFT guides the search of practical ways to compute energies, forces, etc.

Other methods: Quantum Monte Carlo, GW, RPA, HF, post-HF, ACFDT-RPA.

DFT Kohn-Sham equation (1965)

The ground state energy is given by

$$E_{total}=\sum_{i=1}^{N} f_i\langle\phi_i|-\frac{1}{2}\nabla^2+V(\boldsymbol{r})|\phi_i\rangle+\frac{1}{2}\iint d\boldsymbol{r}\,d\boldsymbol{r}'\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}+E_{xc}[n(\boldsymbol{r})]$$

Initial guess for density: $n(\boldsymbol{r})$

$$V_{eff}(\boldsymbol{r})=V(\boldsymbol{r})+\int d\boldsymbol{r}'\frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}+v_{xc}(\boldsymbol{r}),\quad \text{con } v_{xc}(\boldsymbol{r})=\frac{\delta E_{xc}}{\delta n(\boldsymbol{r})}$$

$$\left(-\frac{1}{2}\nabla^2+V_{eff}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r})=\epsilon_i\phi_i(\boldsymbol{r})\rightarrow\{\epsilon_i,\phi_i(\boldsymbol{r})\}\rightarrow$$

$$\rightarrow n_{nueva}(\boldsymbol{r})=\sum_i f_i|\phi(\boldsymbol{r})|^2,\quad 0\le f_i\le 1 \text{ is the occupation number}$$

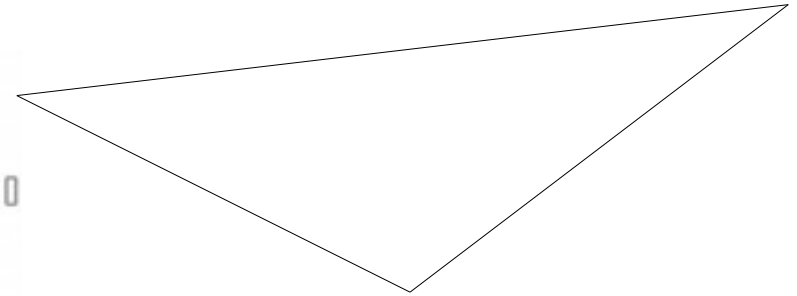
compare $n_{new}(\boldsymbol{r})$ con $n(\boldsymbol{r})$

if not equal, then $n(\boldsymbol{r})=\alpha\, n_{nueva}(\boldsymbol{r})+(1-\alpha)n(\boldsymbol{r})$

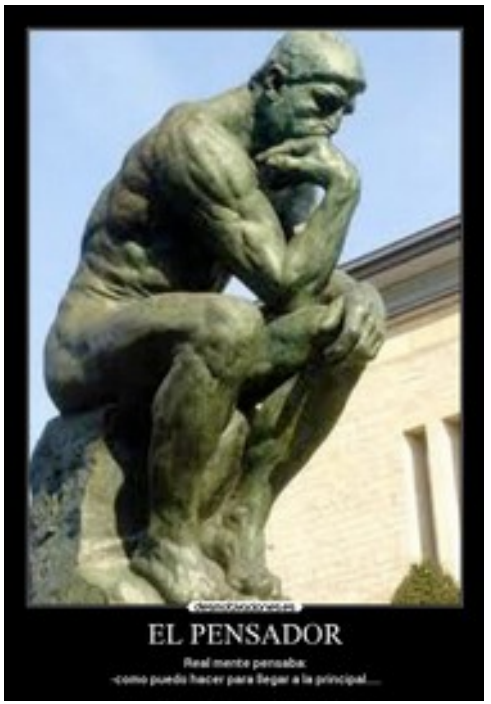
DFT in practice

Software

Devices



Think



Method DFT (Density Functional Theory).

Hohenberg, Pierre; Walter Kohn (1964). "Inhomogeneous electron gas". Physical Review 136 (3B): B864–B871.

Crystal with defects

In *Happyland*: we would like to perform an electronic structure calculation for a piece of crystal containing several millions of atoms, containing all possible defects, and obtain directly the Fermi level.

In real world we can calculate ~ 10^2 átomos.

→ Calculate isolated defects, and do thermodynamics of open systems

How to compute defects & impurities

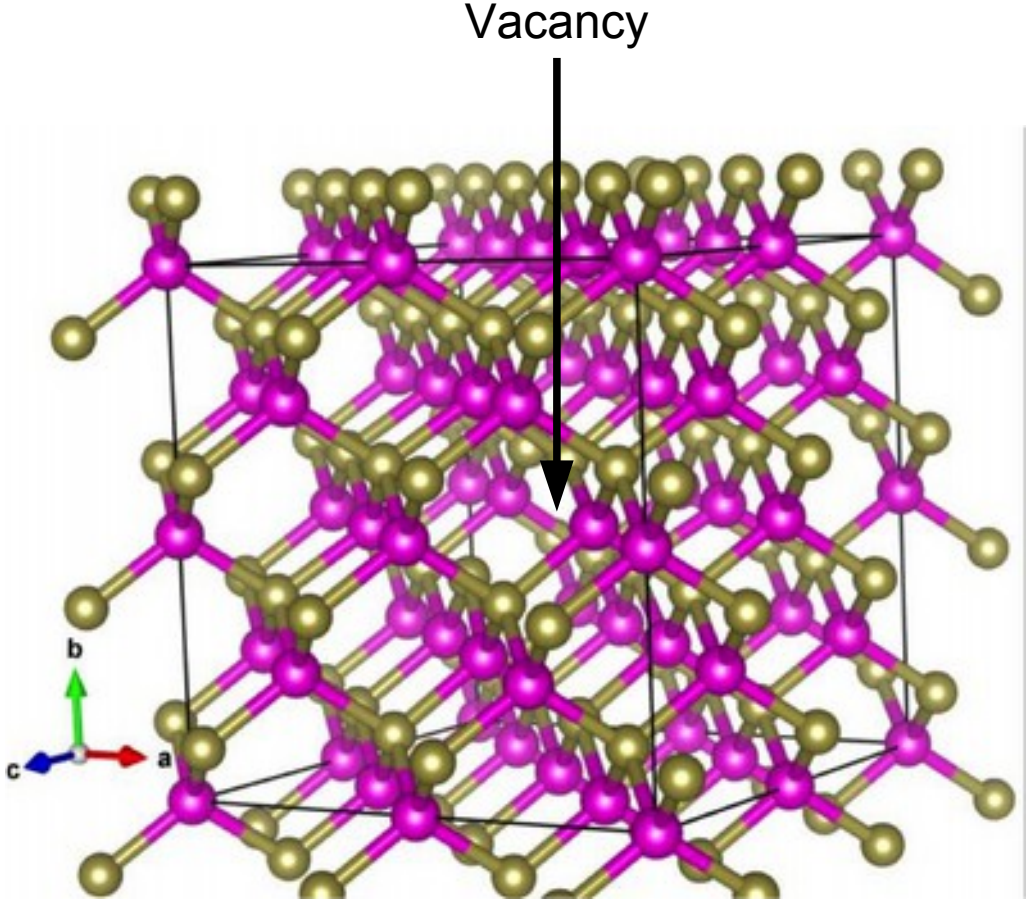
- Choose a supercell for the pure material.
- Choose a functional.
- **Use the Γ point with a large supercell**.
- Find cutoff, lattice constant, relaxed structure.
- Find reference states for the exchanged atoms.
- Design starting configurations for defects or impurities in the supercell, relax.
- Apply size effect corrections or extrapolate.

Simulation supercel

Formation energy

$$\Delta H^f(X,q) = E(X;q) - E(0) - \sum_\alpha n_\alpha \mu_\alpha$$

← Chemical potentials



Esentially, μ_α and n_α are the energies and numbers of the added species (atoms and electrons) in the reservoir.

n_α<0 for a vacancy

Warning:
This is a popular, but small supercell.
Need to use a k-point grid.
Other problems.

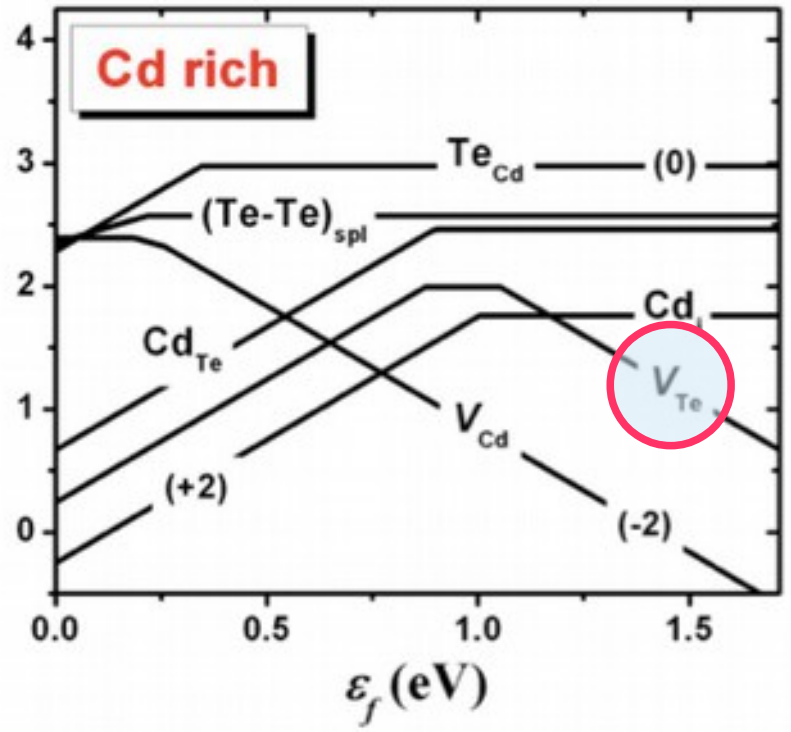
Use a larger supercell, and find the appropriate computer.

Te vacancy in literature

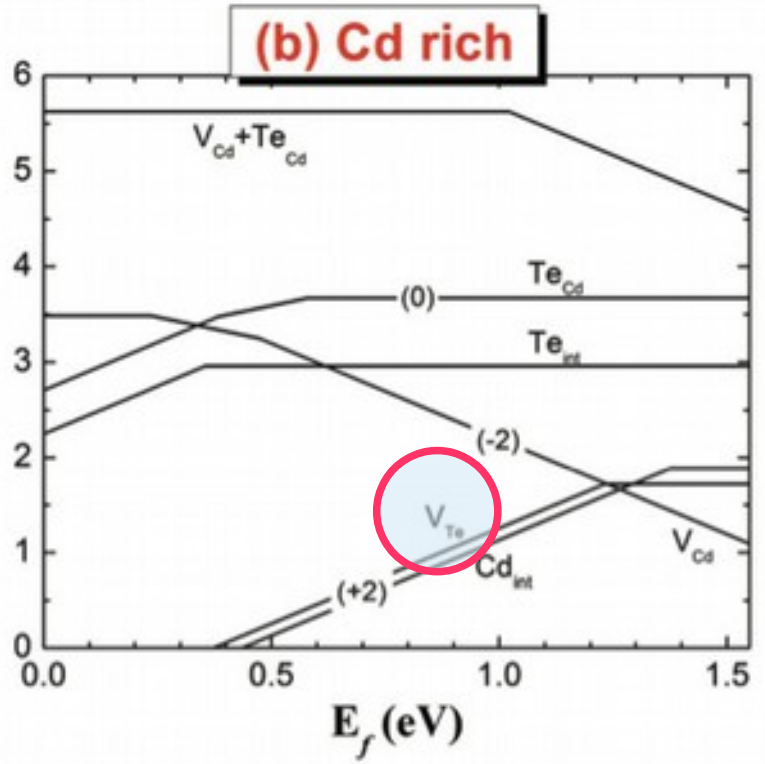
$$\Delta H^f(V_{Te}) = E(Cd_{32}Te_{31}) - E(Cd_{32}Te_{32}) + \mu(Te) + q(E_V + E_F) + \Delta E_{\text{size}}$$

Contradictory results:

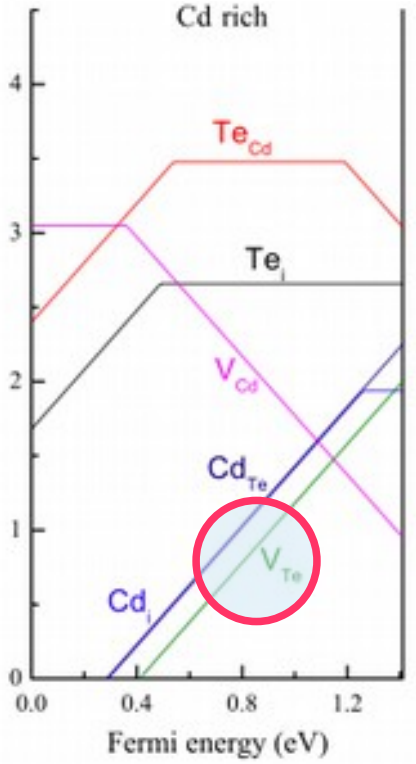
PRB B 77, 094122 (2008)



NJP 4, 063020 (2012)



PRL 111, 067402 (2013)

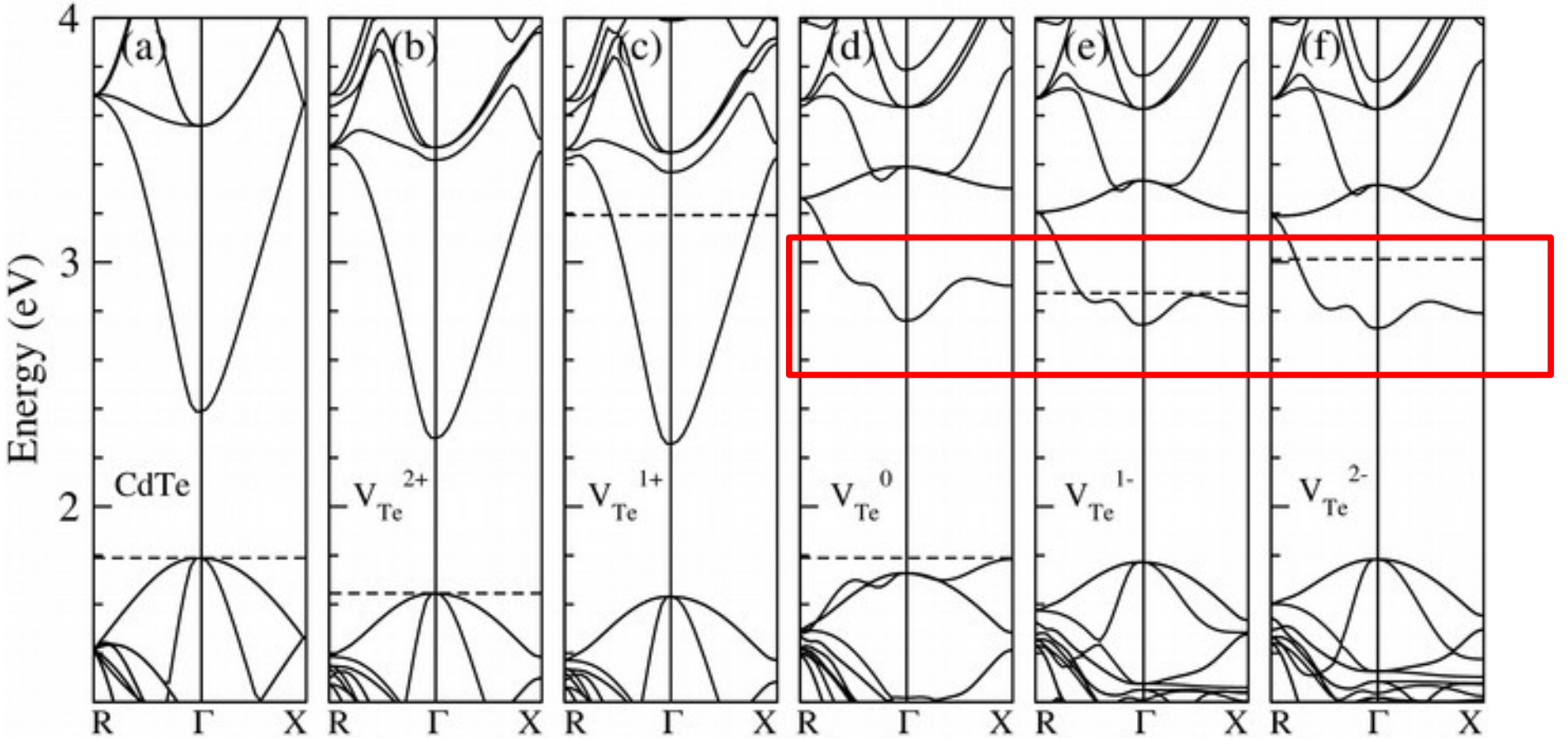


Different charge states

What about formation energies < 0 ?

V_{Te} bands for standard 64/63-atom supercell

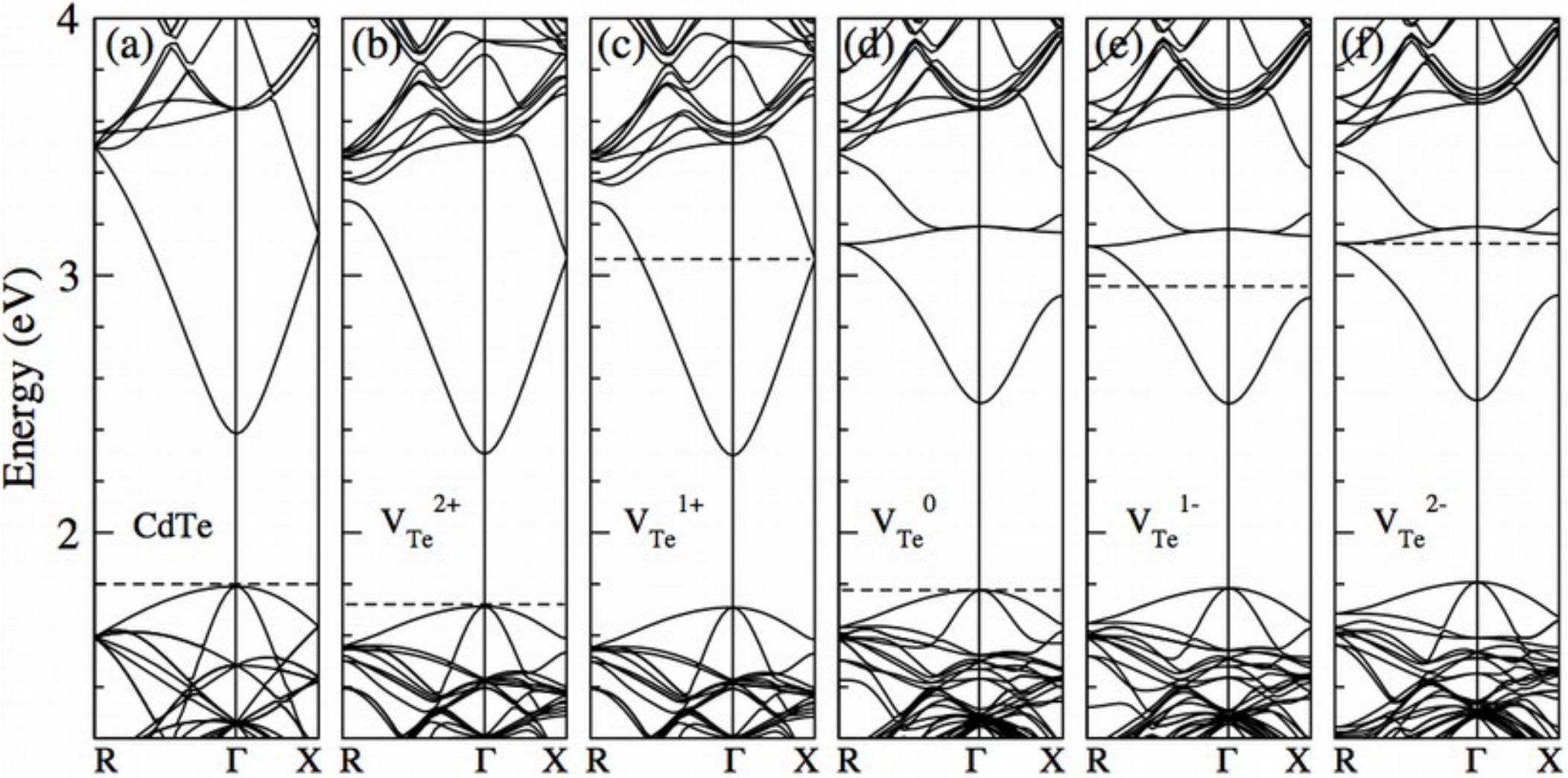
Phys. Status Solidi B 252, 2649-2656 (2015)



A diluted point defect is not expected to destroy the conduction band. A point defect is a perturbation.

The standard 64/63 atom supercell is not appropriate.

V_{Te}: Bands for 216/215-atom supercells



Surprise: Why in state +1 (one missing electron) the conduction band is populated?

Size corrections

$$\Delta H^{f}(V_{Te}) = E(Cd_{32}Te_{31}) - E(Cd_{32}Te_{32}) + \mu(Te) + q(E_V + E_F) + \Delta E_{\text{size}}$$

Defect concentration in the simulation supercell (1-2%) is much larger than in real semiconductor (ppm).

Corrections:

- Image charge effect.
- Electrostatic potential alignement.
- Band dispersion.

Periodic image charges

Makov-Payne

$$\Delta E_{mp} = \frac{\alpha_M q^2}{2 \epsilon V^{1/3}} + \frac{2 \pi q Q}{3 \epsilon V} + O\left(V^{-5/3}\right)$$

Lany-Zunger

$$\Delta E_{mp} = (1+f) \frac{\alpha_M (q e)^2}{2 \epsilon V^{1/3}}, \text{ with } f \simeq -1/3 .$$

And other more ellaborate methods, e.g. sxdefectalign: PRL 102, 016402 (2009).

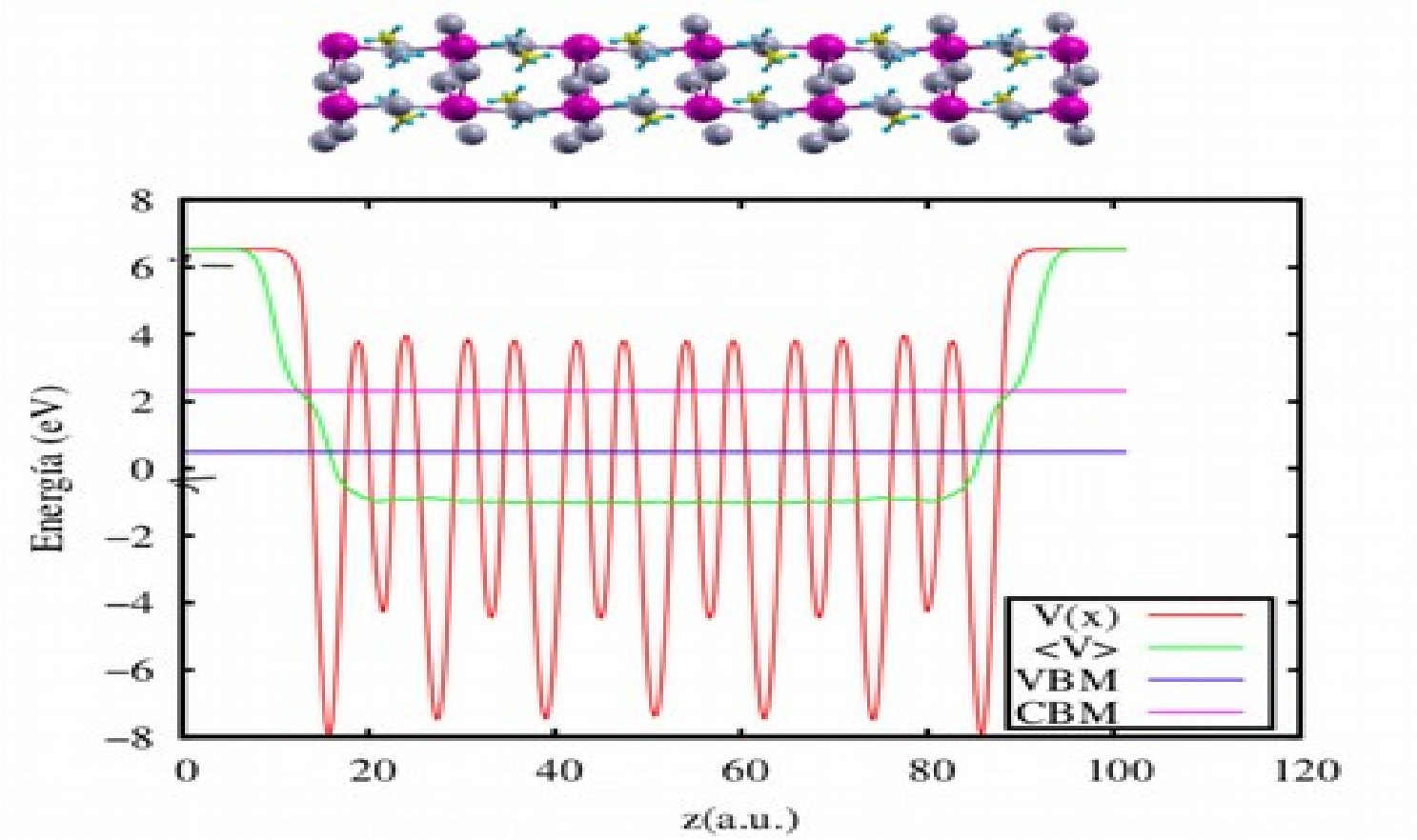
Potential alignement

- In many DFT calculations with periodic boundary condictions the average electrostatic potential is set to zero or other arbitrary value.
- Total energies and eigenvalues are computed with respect to that reference.
- Vacancies, impurities, and extra charges modify the reference.

Correction to the total energy of charged systems

$$\Delta E(q) = q \Delta V$$

Potential alignment

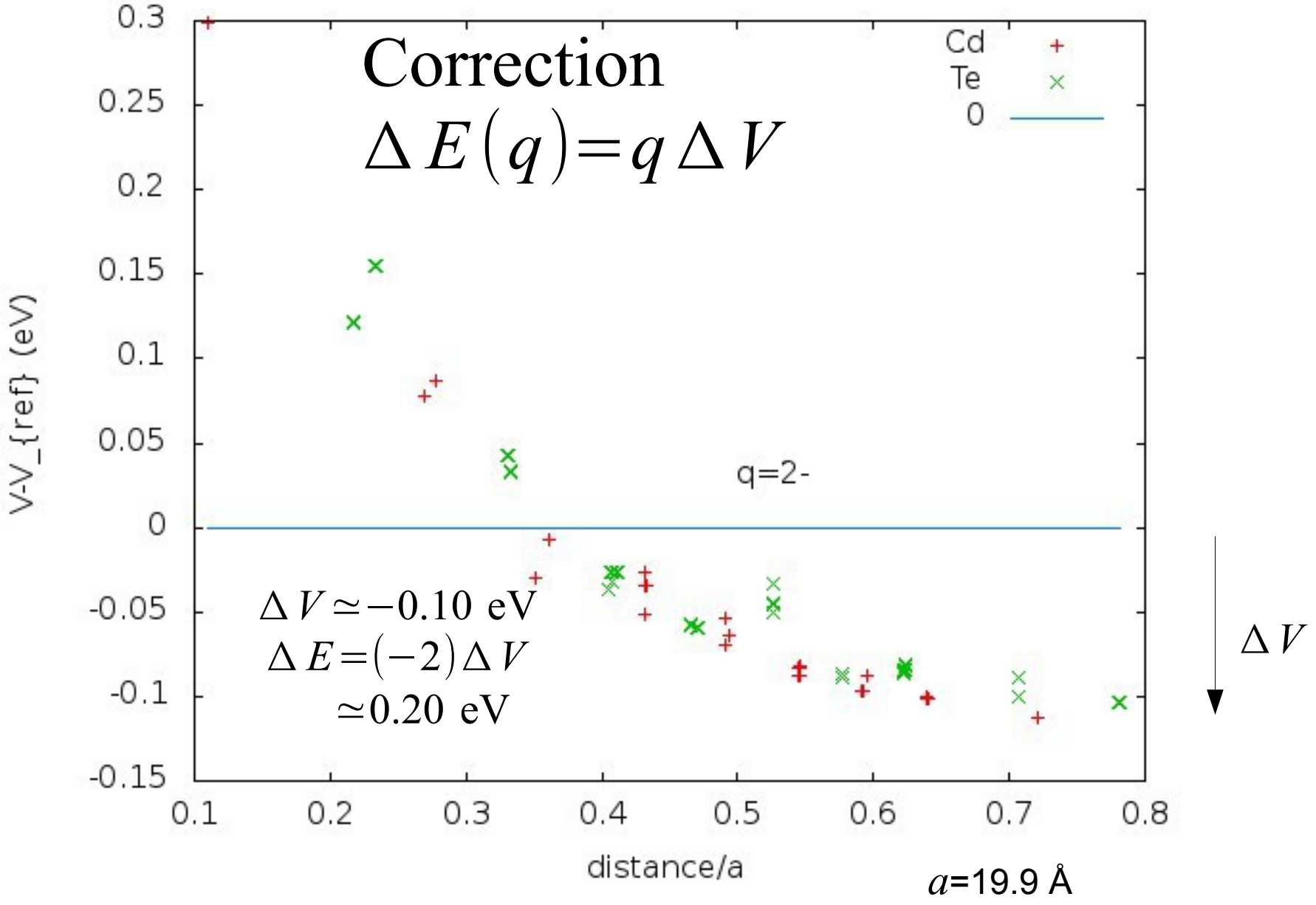


Electrostatic potential energy for a MAPI slab.

The zero of potential energy depends on the supercell size, the atoms present, and the net charge.
To compare eigenvalues and total energies, alignment correction is need.

Potential (energy) alignment

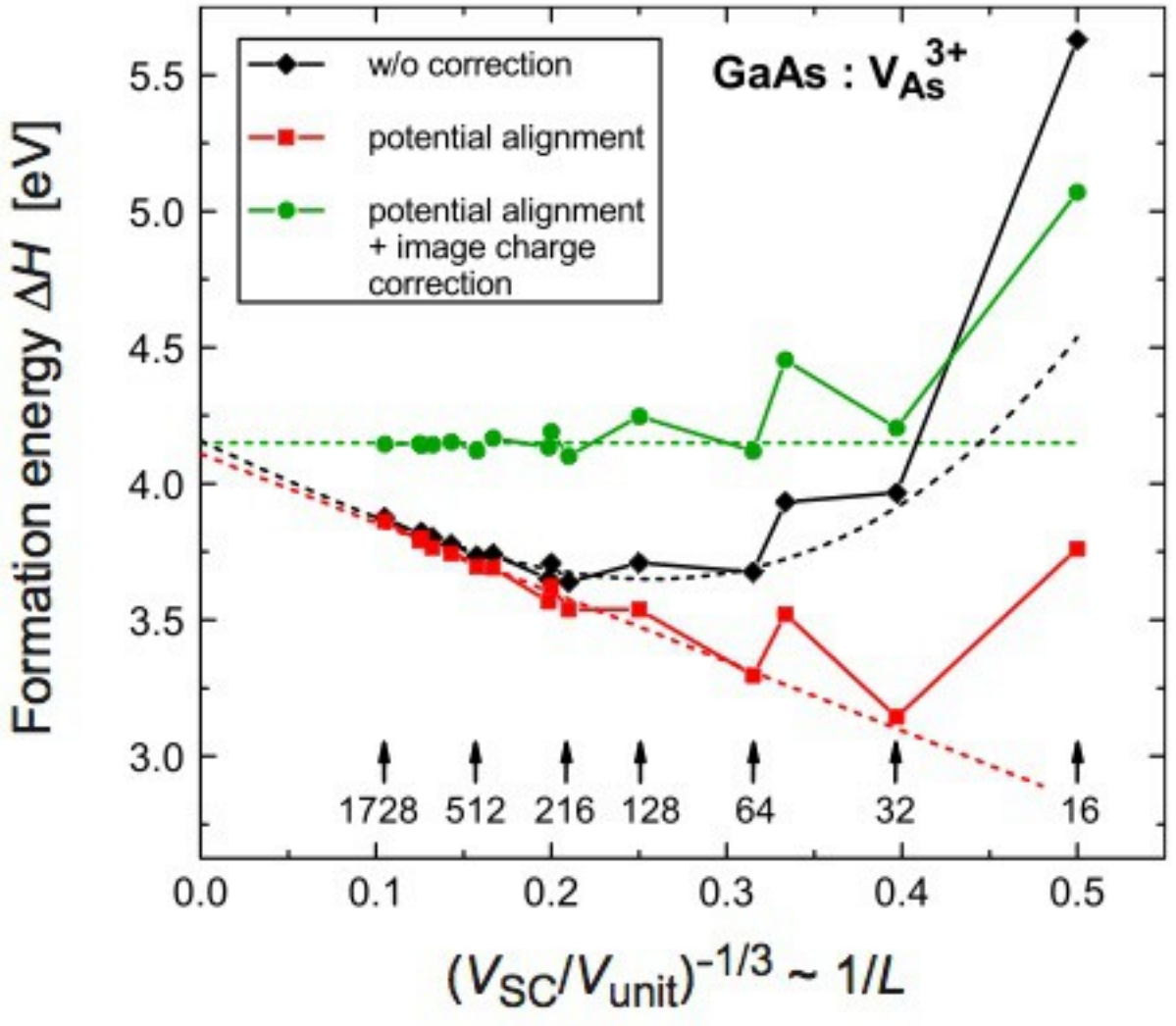
core level shifts vs distance to defect



a=19.9 Å

Total correction:

potential alignment+ image charge

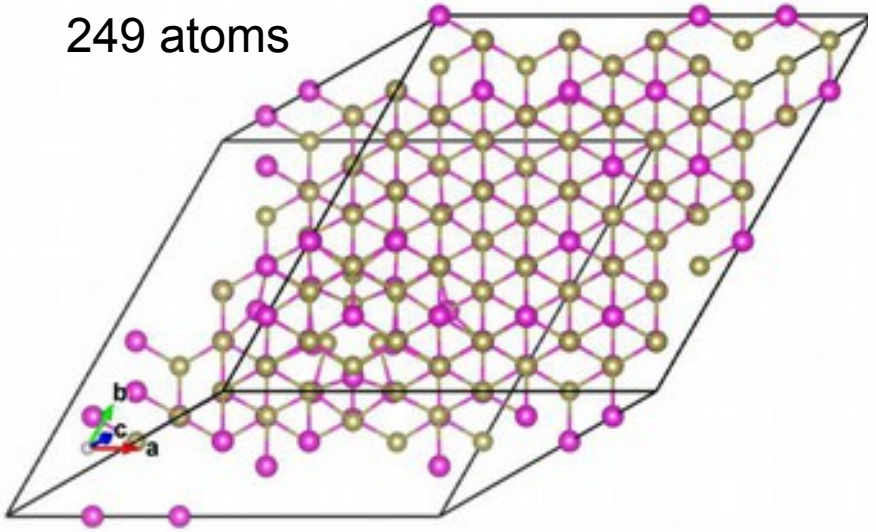


Note: that was a test, without relaxing the system,

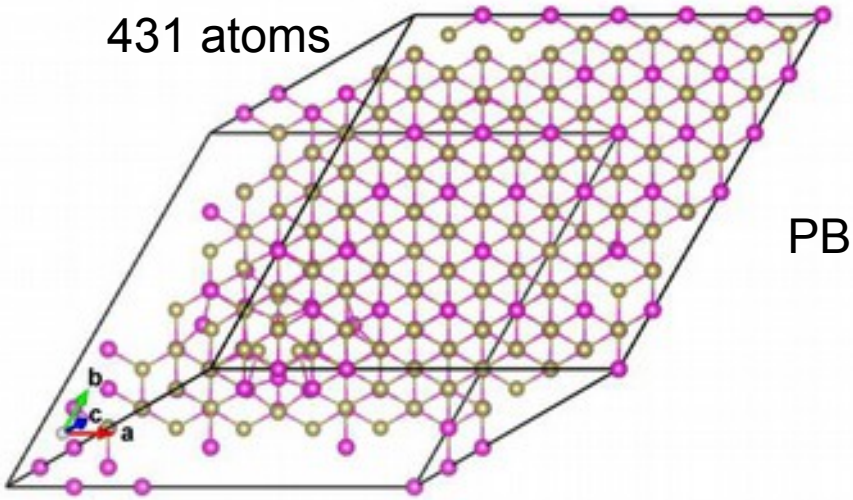
Lany and Zunger, PHYSICAL REVIEW B **78**, 235104 (2008)

A test for V_{Cd} q=+2, and 0

249 atoms

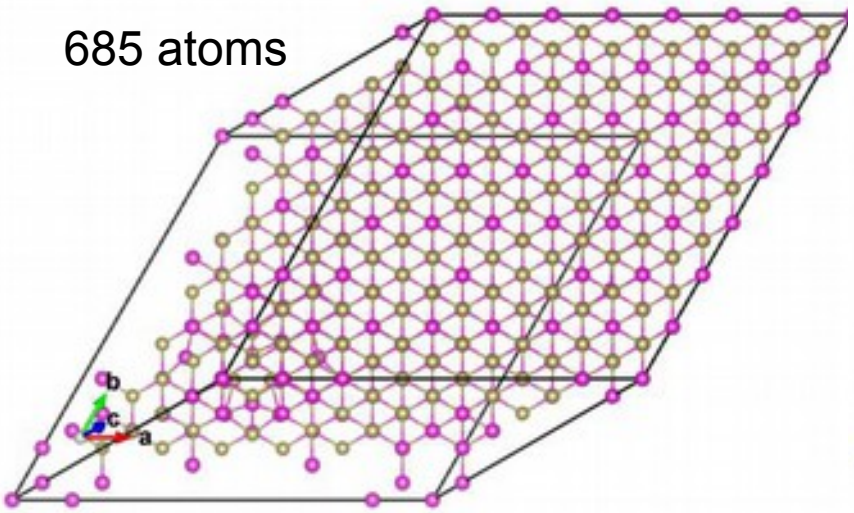


431 atoms

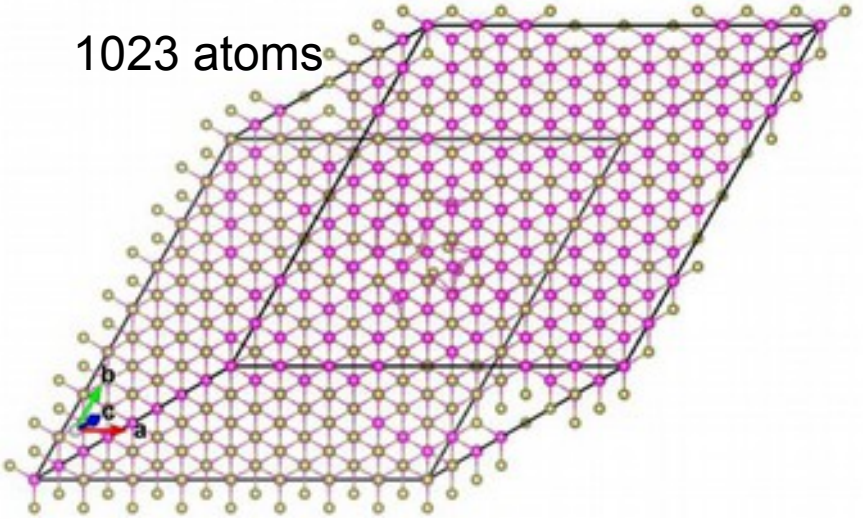


PBE funcional

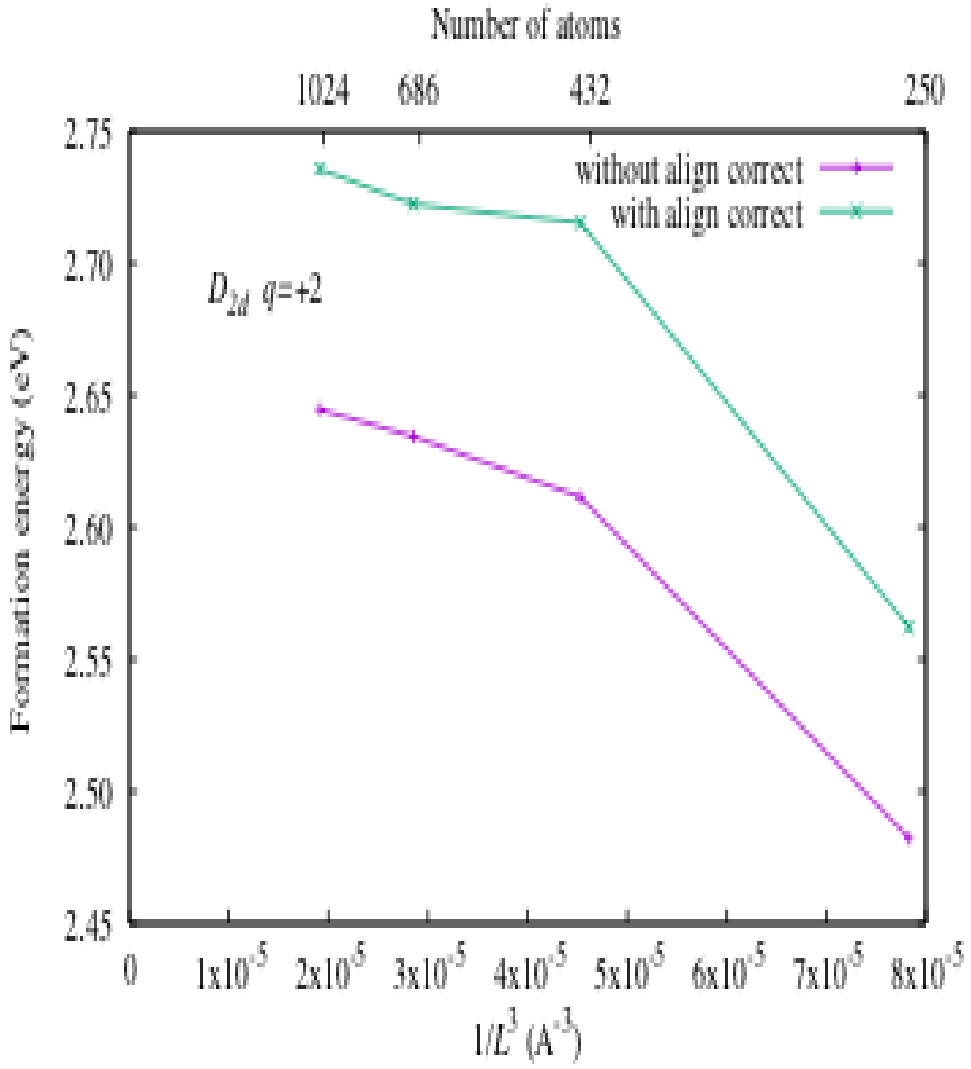
685 atoms

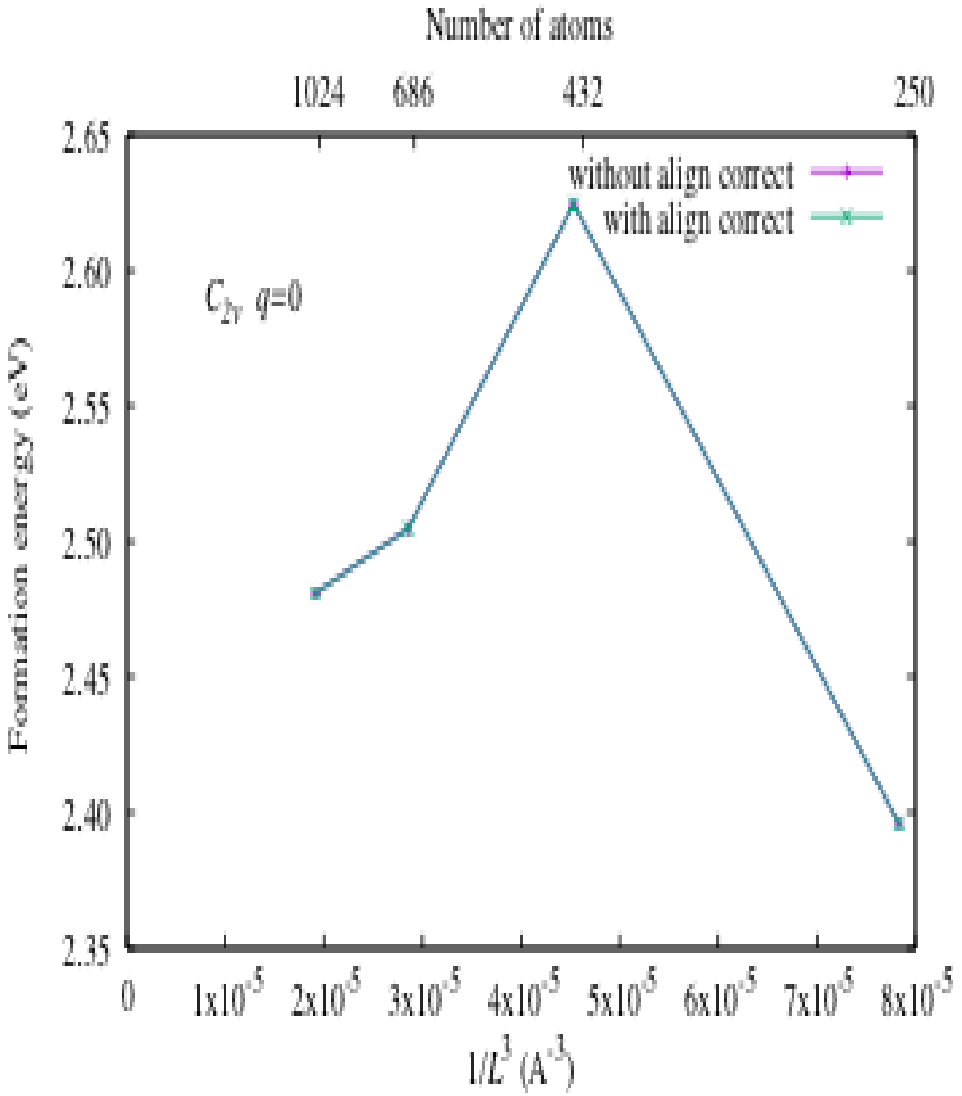


1023 atoms



A test for V_{Cd} q=+2, and 0

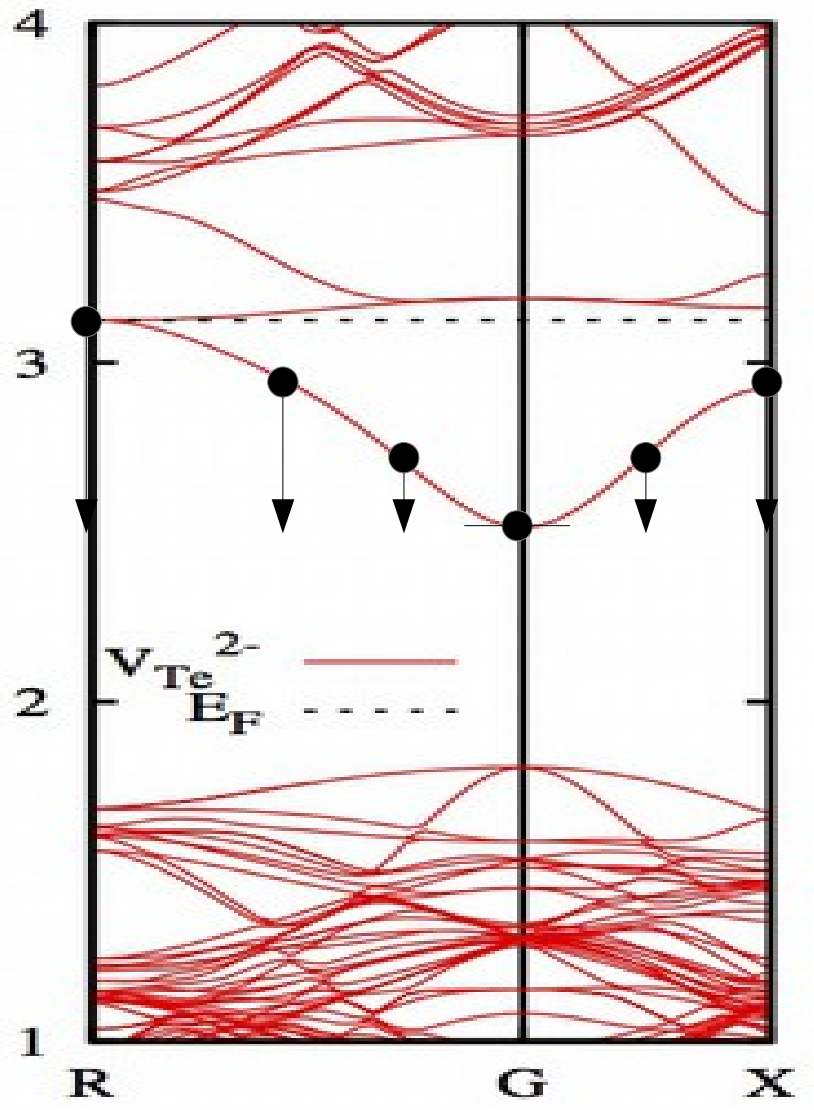




$\Delta E \sim 1/L^3$ not $1/L$

Every defect behaves differently.
Not only electrostatic effects. Elasticity.
Do your own tests.

Band-filling correction



In a large enough supercell one uses only one k-point. Electrons in the conduction band occupy the minimum . In a small supercell, several k-points are needed for convergence, some of them with high energy.

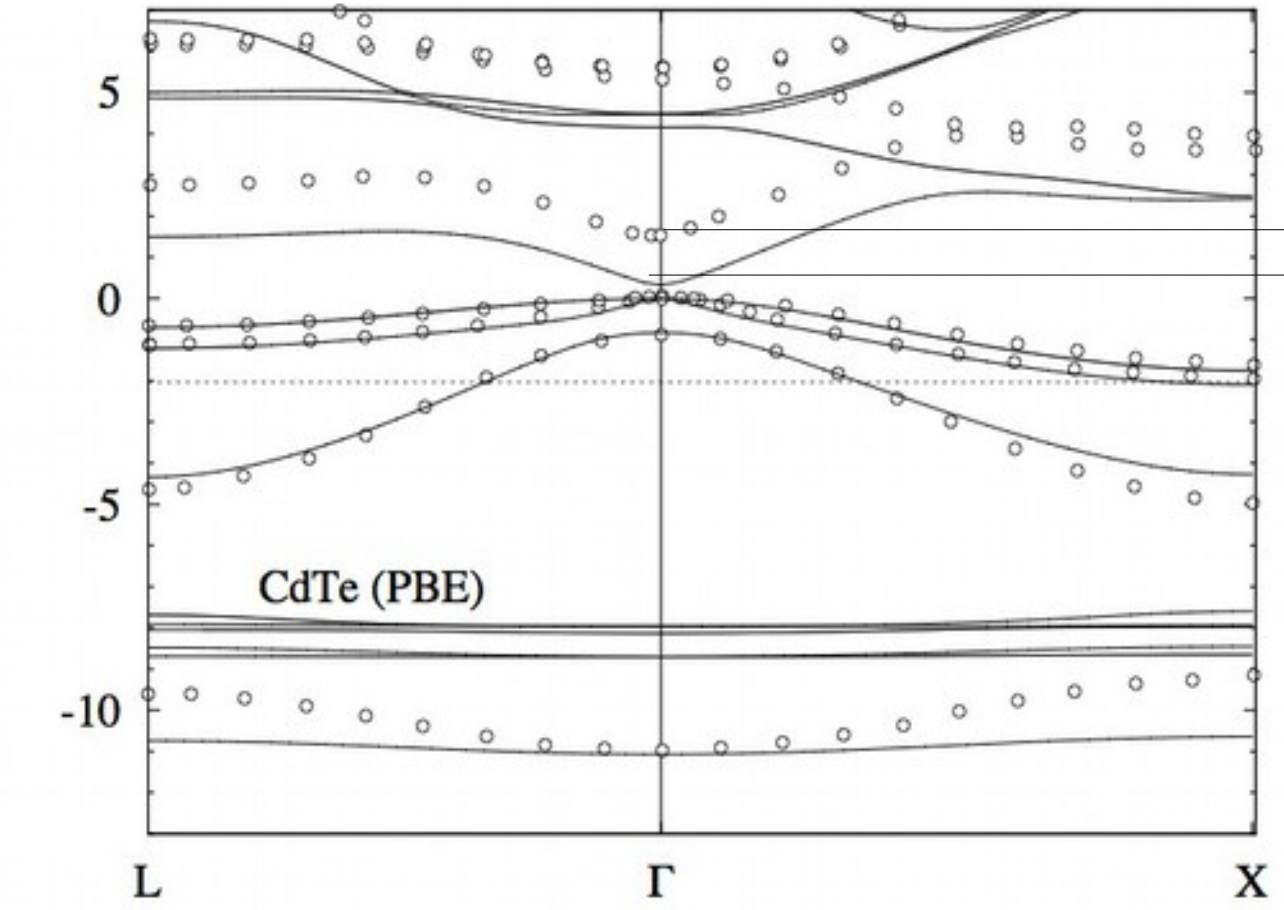
$$\Delta E_{b.f.} = -\sum_{n,k} \Theta\left(e_{n,k} - \tilde{e}_C\right)\left(w_k \eta_{n,k} e_{n,k} - \tilde{e}_C\right).$$

Lany & Zunger, Phys. Rev. B 78, 235104 (2008)

Not recommended. se a large supercell, with only the Γ point.

Gap (quasi-particle) error

(old DFT problem)



Gap error

Modifies the total energy if the defect introduces electrons in the CB or holes in the VB.

DFT errors in ionization energies: the case of perfect material

PRL 112, 096401 (2014) PHYSICAL REVIEW LETTERS week ending 7 MARCH 2014

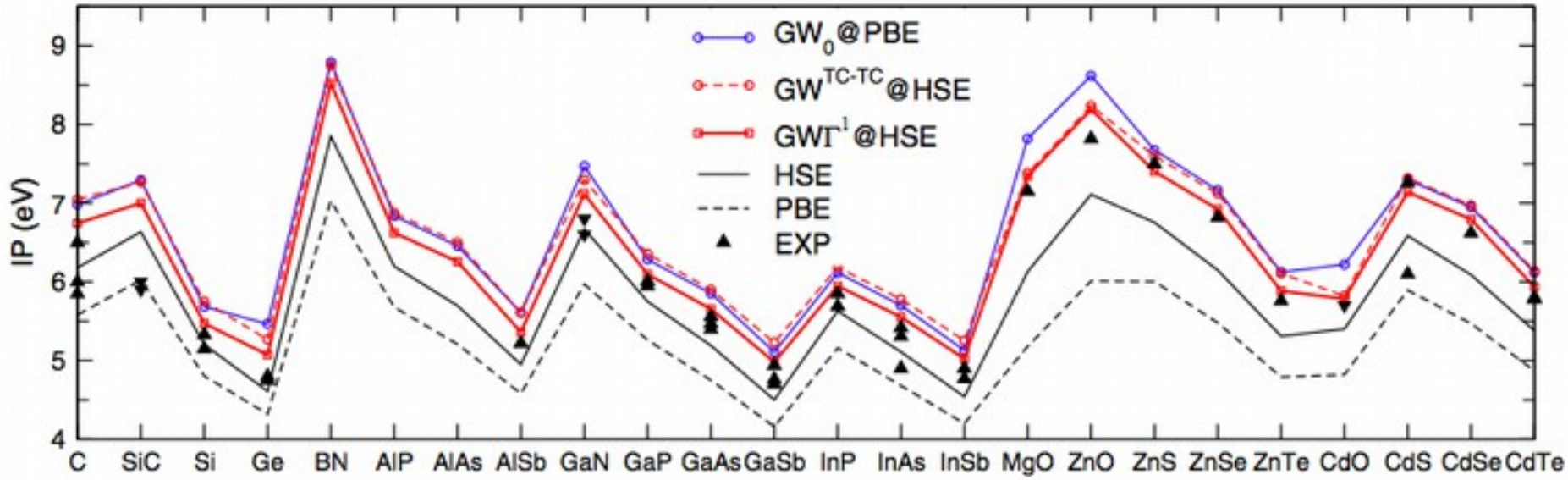
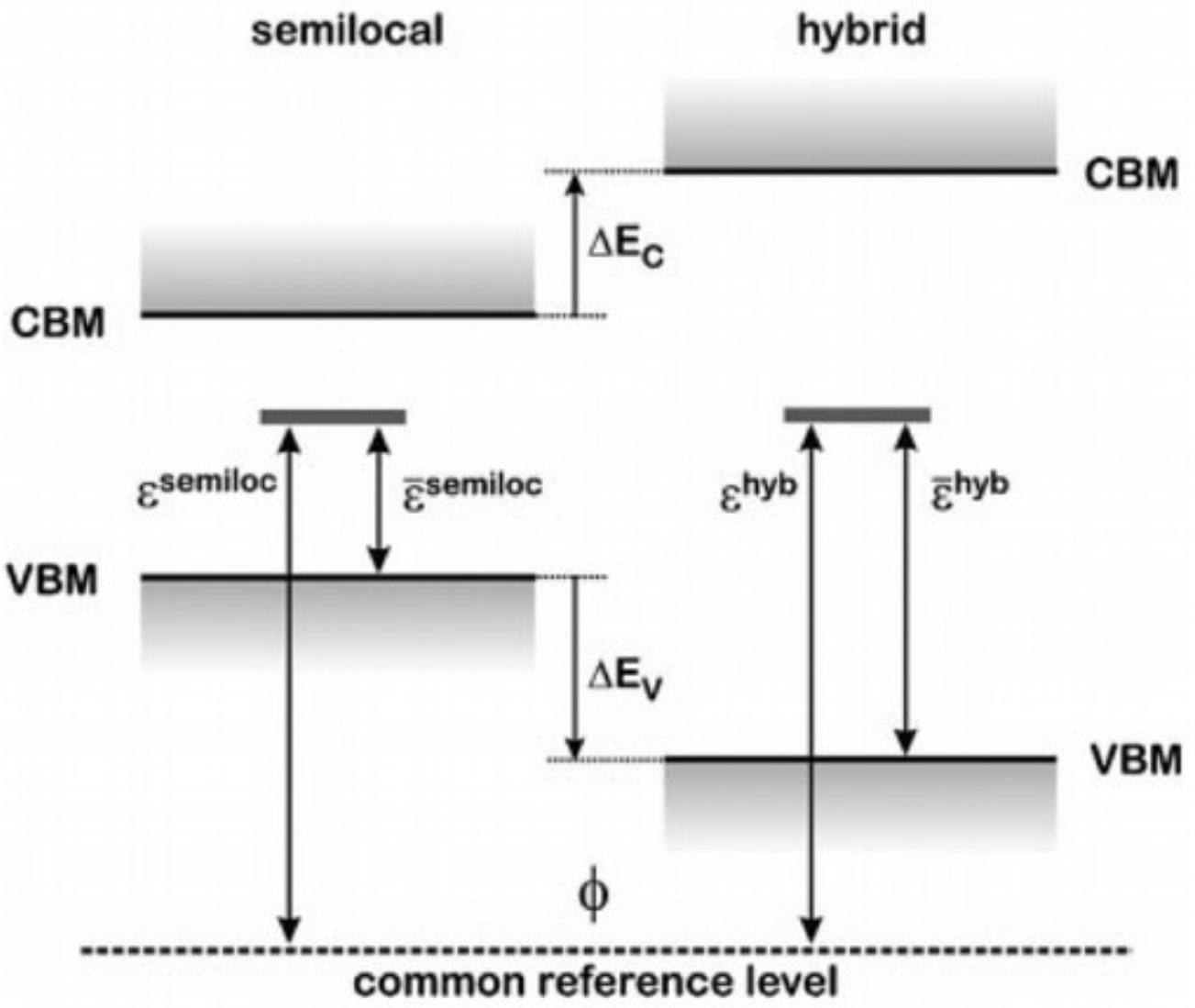


FIG. 2 (color online). Ionization potentials of various semiconductors and insulators obtained for nonpolar surfaces using PBE, HSE, GW_0@PBE, $GW^{TC\text{-}TC}$@HSE, and $GW\Gamma^{1}$@HSE [16]. Experimental (EXP) values for the corresponding nonpolar surfaces are shown

$$IP = E_{vacuum} - E_{VBM}$$

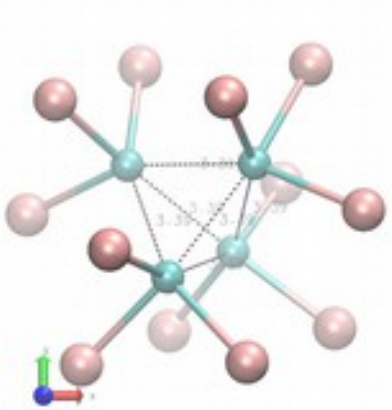
Error in IP means error in the VBM, and viceversa.
Also means error in the energy of q=+1 charge state.

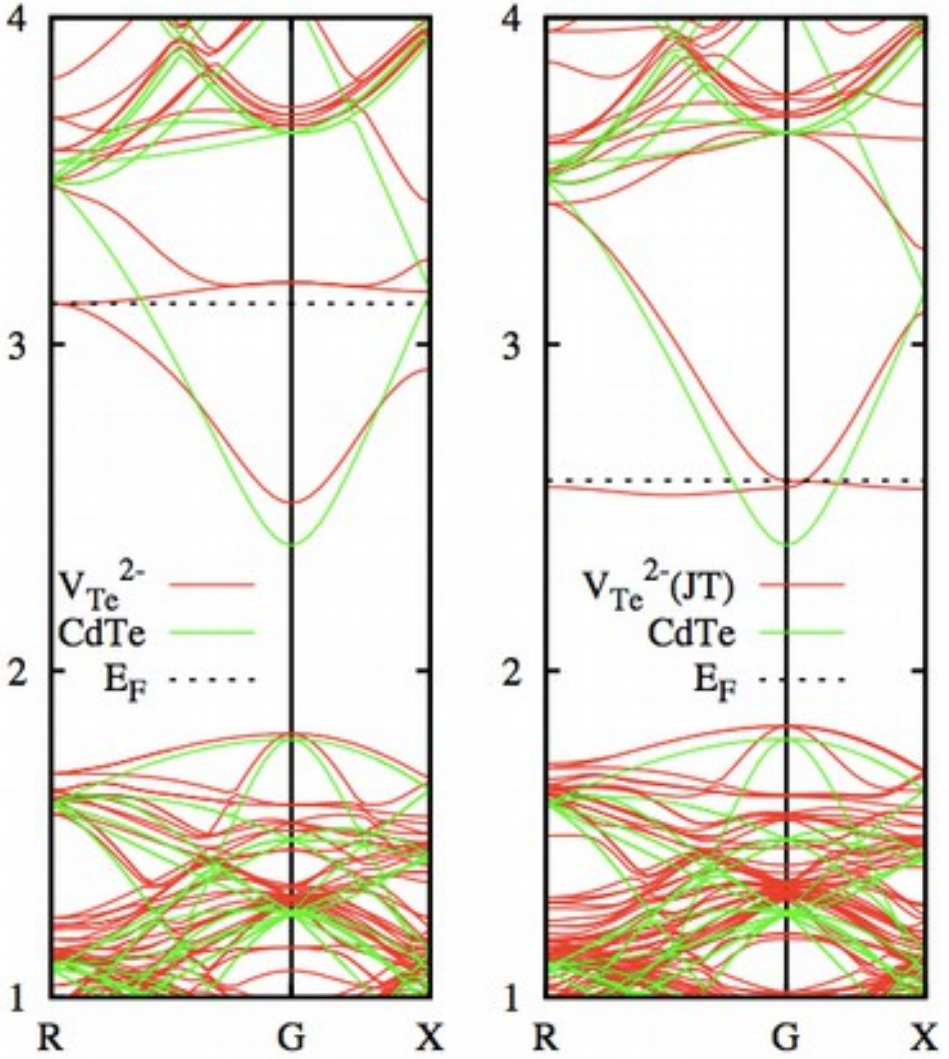
DFT Gap error & band edge alignment

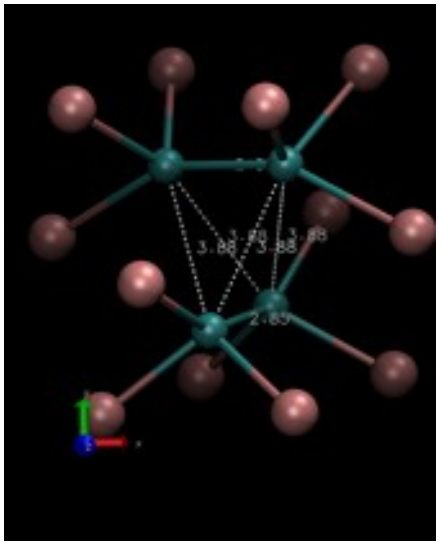


Alkauskas, Broqvist y Pasquarello, in Advanced Calculations for Defects in Materials

V_{Te} (q=-2)
symmetric vs distorted

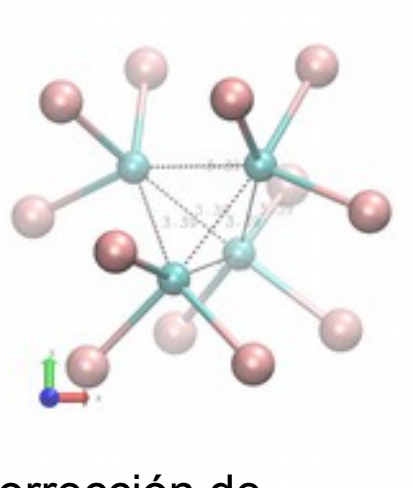






$\Delta E = -0.6$ eV

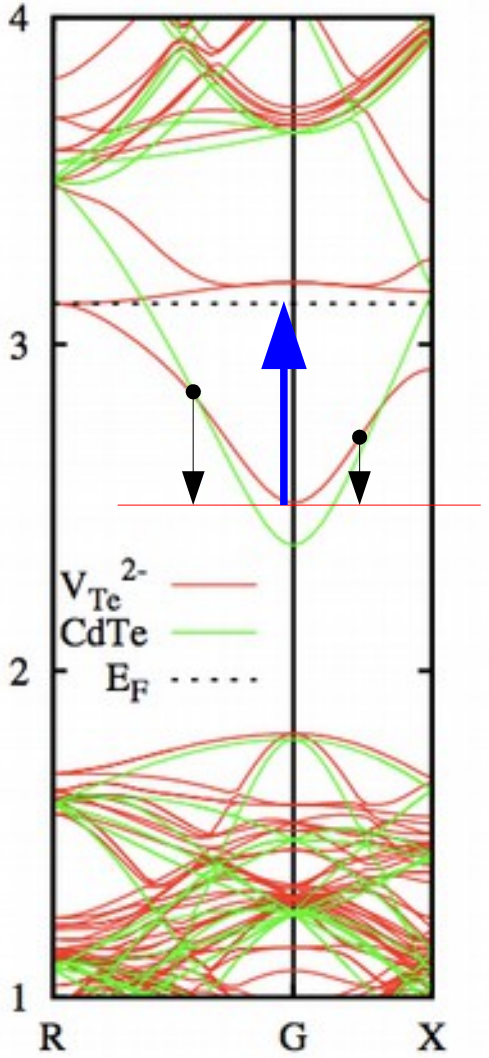
Te vacancy (q=2-): QP correction

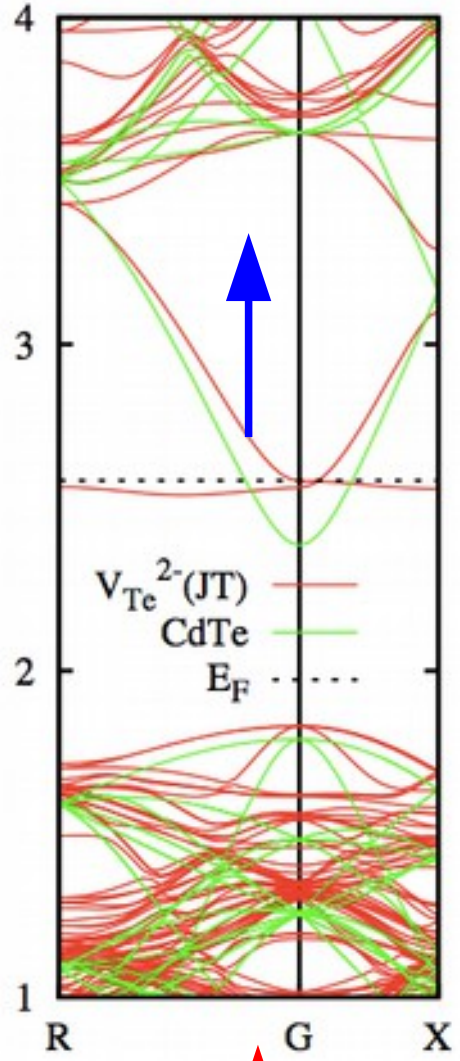


Corrección de llenado de banda

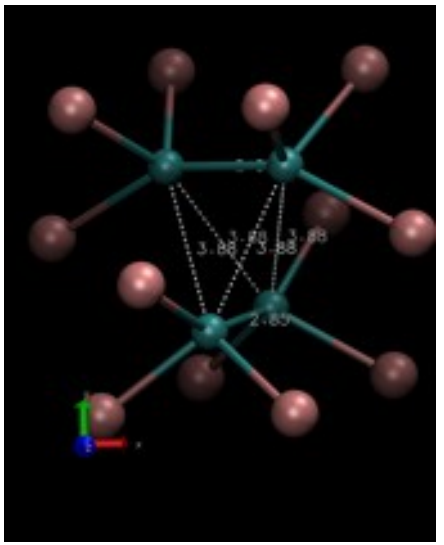
$$\Delta E_{b.f.} = -0.87 \text{ eV}$$

$$\Delta E_{q.p.} = 2 \times 0.48 \text{ eV}$$





Lowest energy



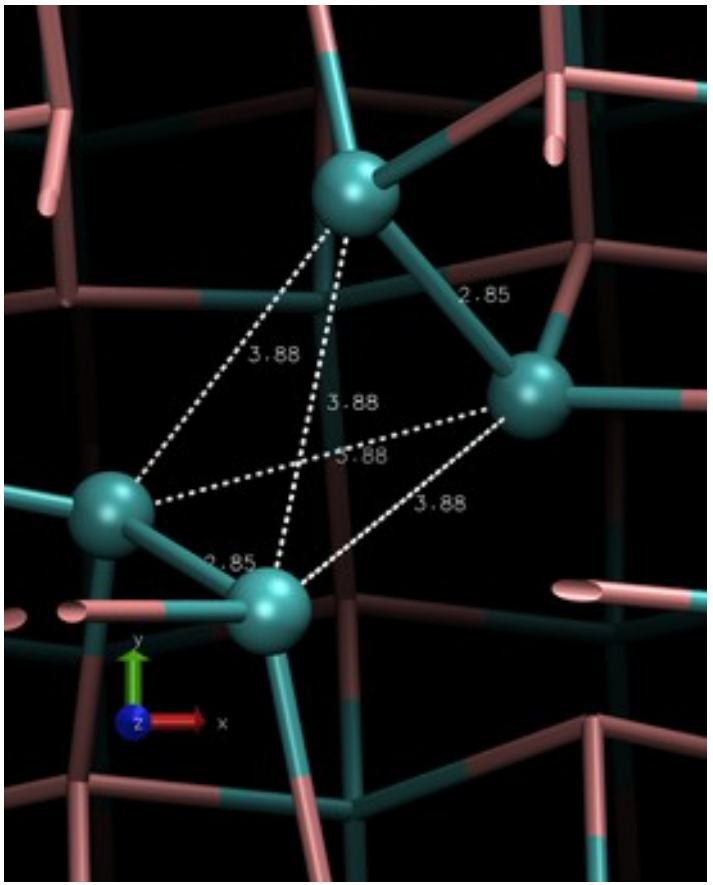
$$\Delta E = -0.6 \text{ eV}$$

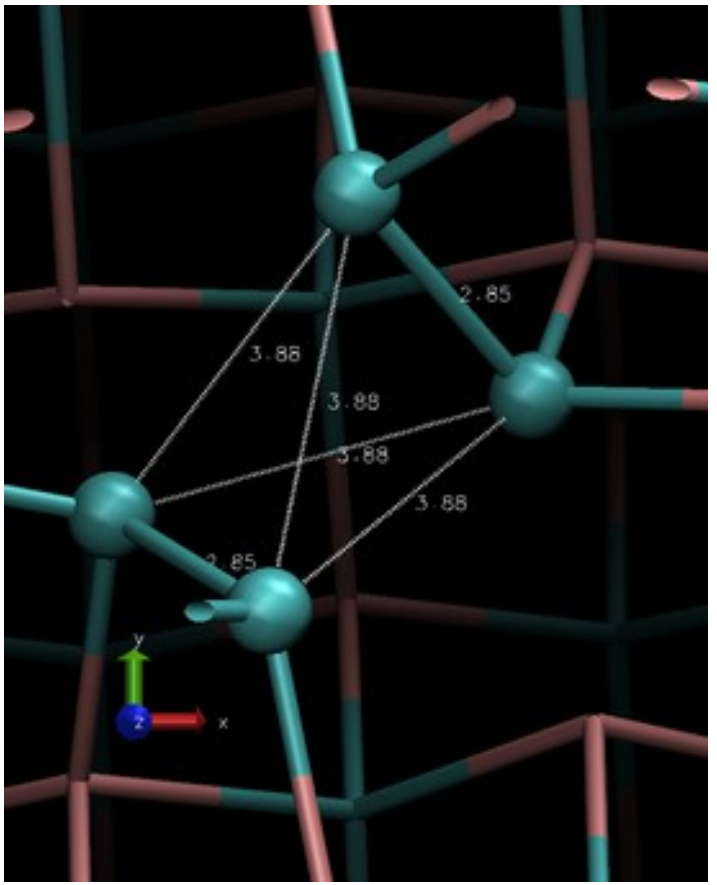
$$\Delta E_{b.f.} = 0 \text{ eV}$$

$$\Delta E_{q.p.} \simeq 0 \text{ eV}$$

Relaxation of Te vacancy (q=2-)
with Γ point, i.e., no band filling error

HSE06 vs PBE





The stability of the two-dimer configuration was predicted before the expensive HSE06 calculation was made. In PBE, it was a local minimum.

In present day, try to obtain CPU time in a supercomputer, and do the big calculation directly.

Starting configurations

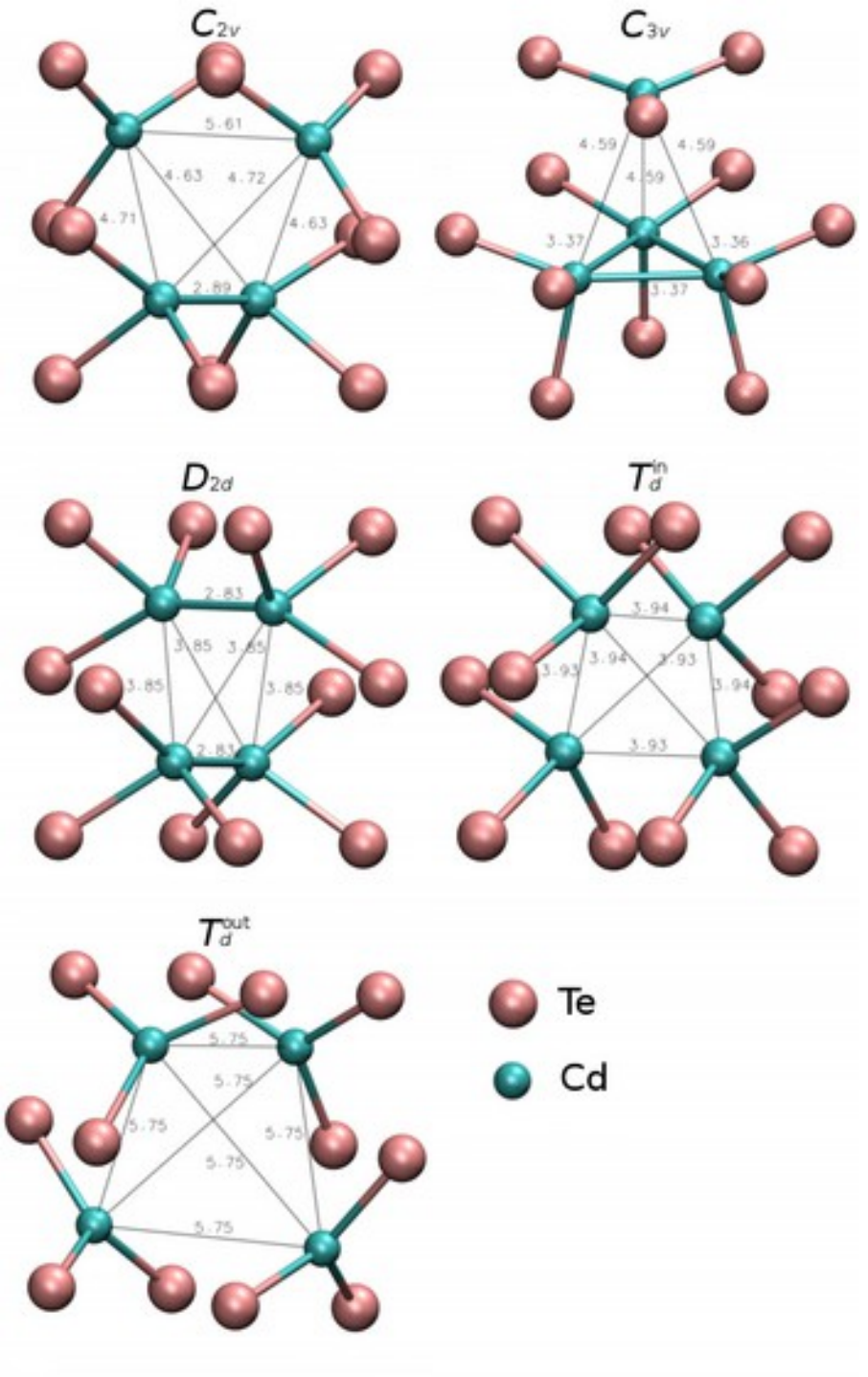
There are many local energy minima. All these configurations of Te vacancy are stable or metastable in some charge state.

Perform a systematic study.
Perform phonon calculations. Imaginary frequencies indicate distortions.

Setup:
215/216-atom supercell.
Γ point.
Hybrid functional HSE06 and modified HSE.
Spin-orbit coupling
GW calculation of the VBM
VASP code.

Calculations with 60-120 cores
Intel E5-2690
2.4 Gb per core.
Infiniband connection.

One year of calculations.



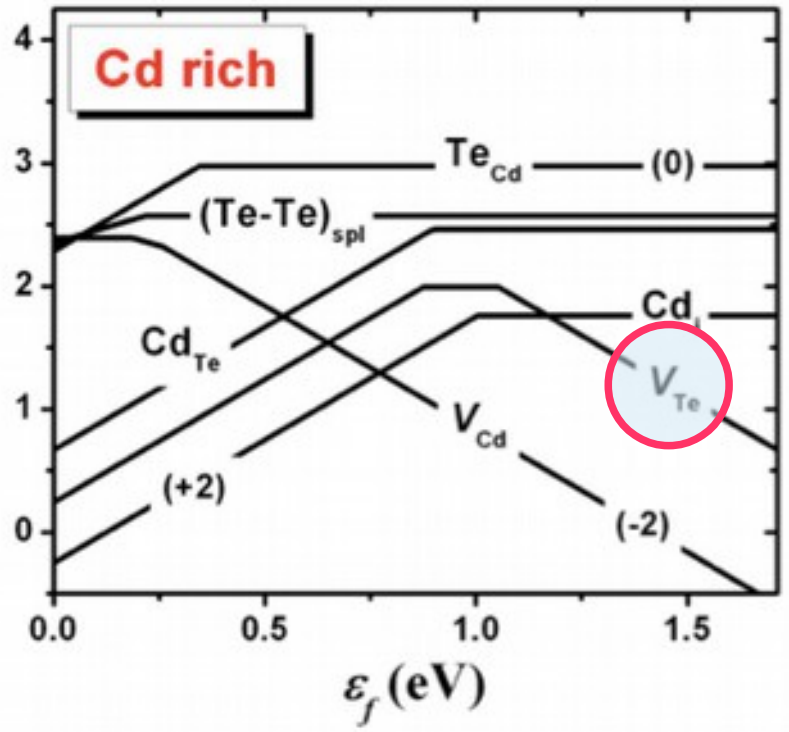
Remind

Te vacancy in literature

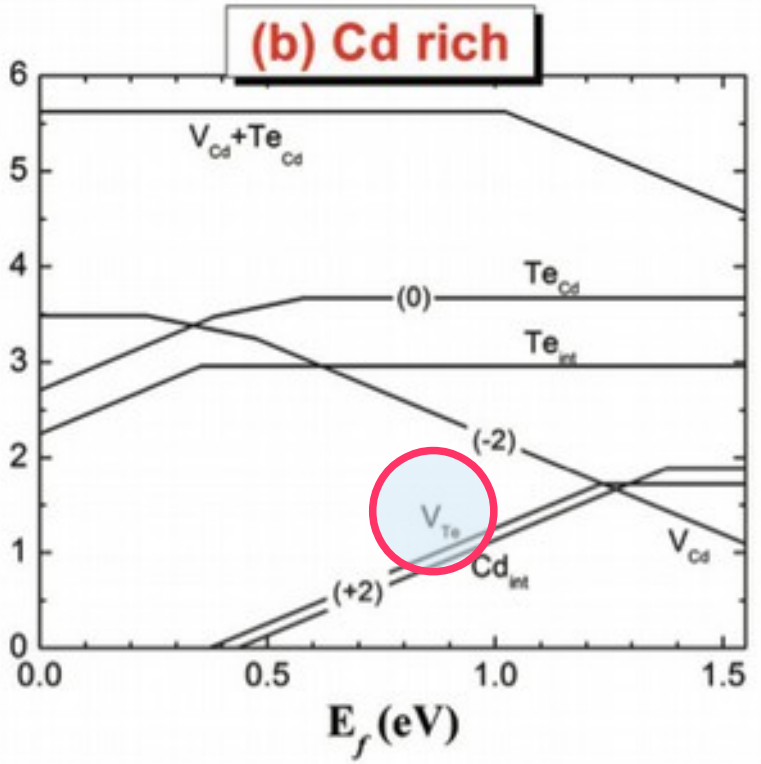
$$E_f = E(Cd_{32}Te_{31}) - E(Cd_{32}Te_{32}) + \mu(Te) + q(E_V + E_F) + \Delta E_{size}$$

Contradictory results:

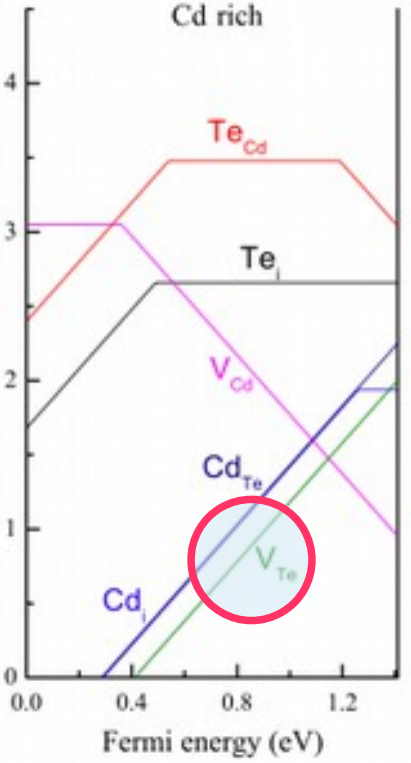
PRB B 77, 094122 (2008)



NJP 4, 063020 (2012)



PRL 111, 067402 (2013)



Different charge states

What about formation energies < 0 ?

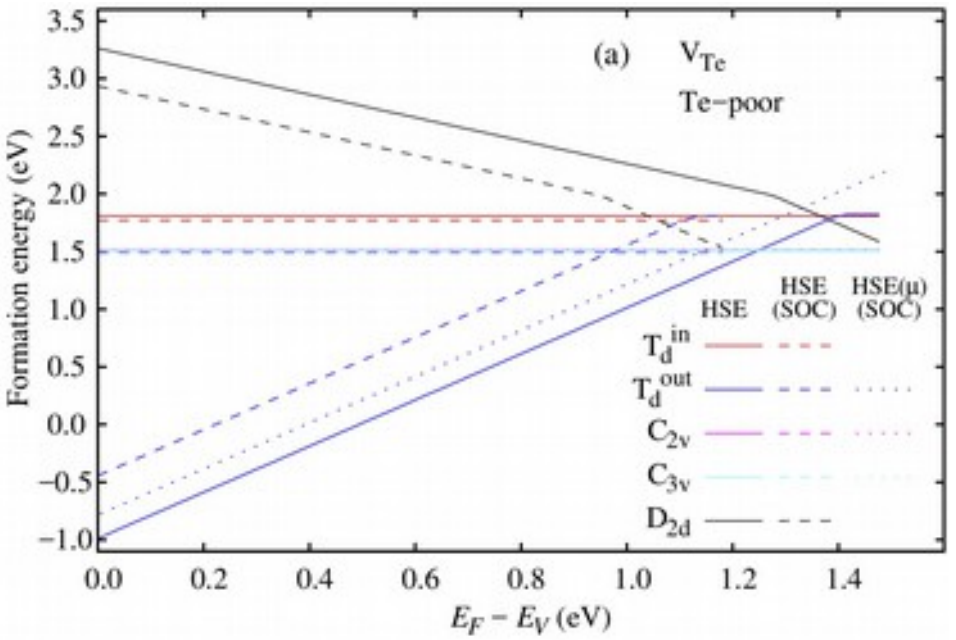
Formation energies of V_{Te}

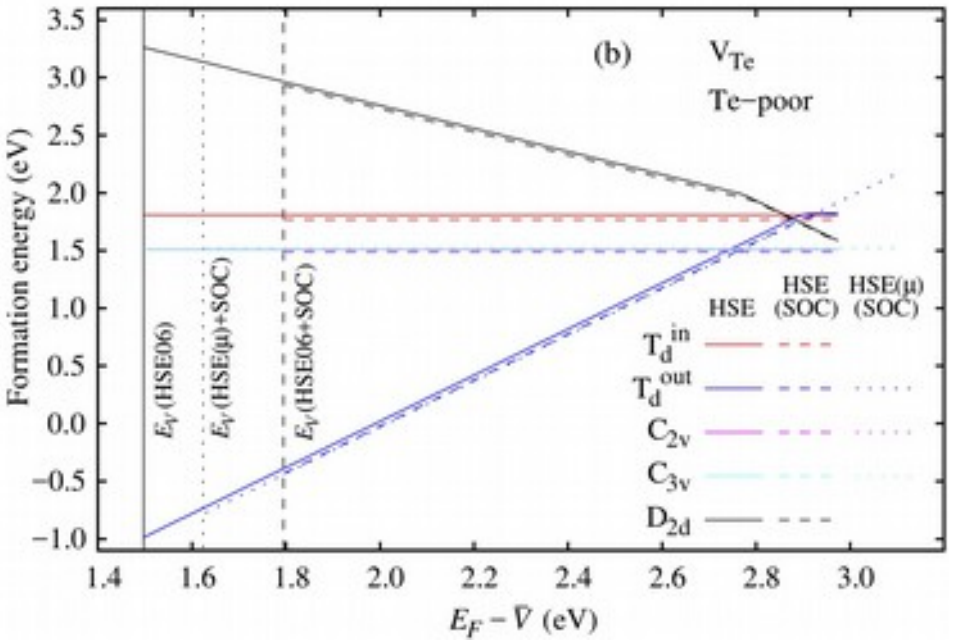
When the Fermi level is relative to the valence band maximum (E_V), the results with different methods look different.

When the Fermi level is relative to the average electrostatic potential, all formation energies coincide. The position of E_V is very sensitive.

Physical conclusion

V_{Te} is stable 0, and 2+ charge states. It is a donor.

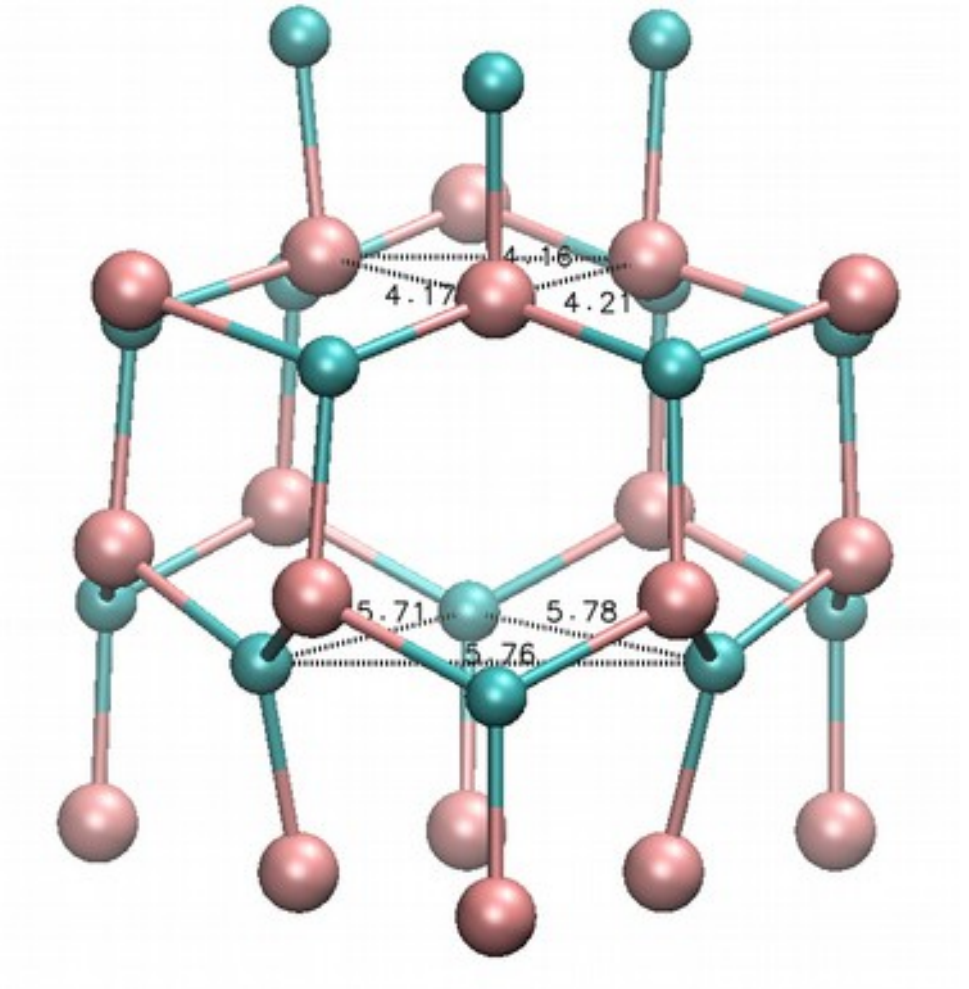




Divacancy

Other studies show that V_{Cd} is an acceptor. In charge state 2-, it may combine with V_{Te} in state 2+, reduce energy due to Coulomb interaction.

Neutral divacancy V_{Cd}-V_{Te} is 1.1 eV more stable than the separated vacancies.



See Menendez-Proupin et al, . Physica B: Phys. Condens. Matter (2019) doi: 10.1016/j.physb.2019.01.013

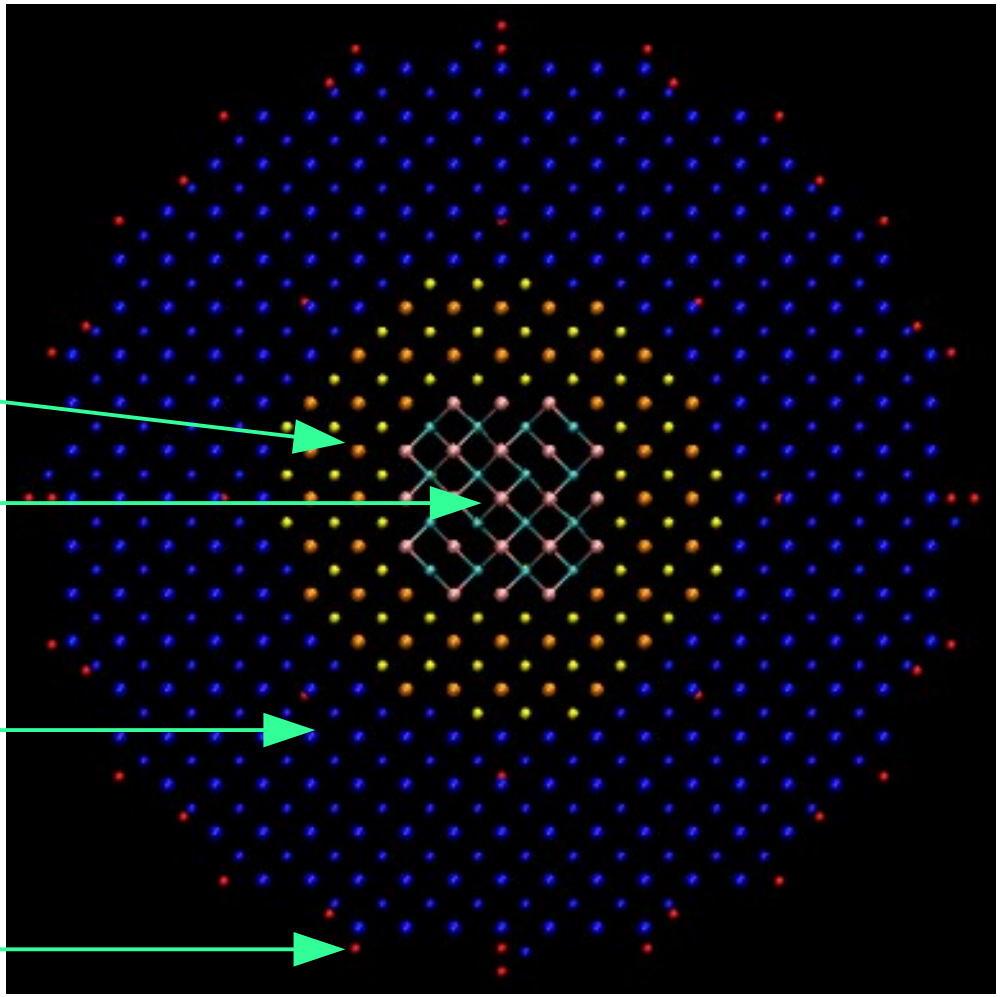
QM/MM method

Active MM MM region:
Pseudopotentials (Cd2+)
and point charges (Te2-)

QM region, DFT.

Fixed MM region: classical atoms with interatomic potentials

Fixed point charges



M. Casanova, M.Sc. Thesis.,
J. Phys.: Conf. Ser. 1043, 012043 (2018)

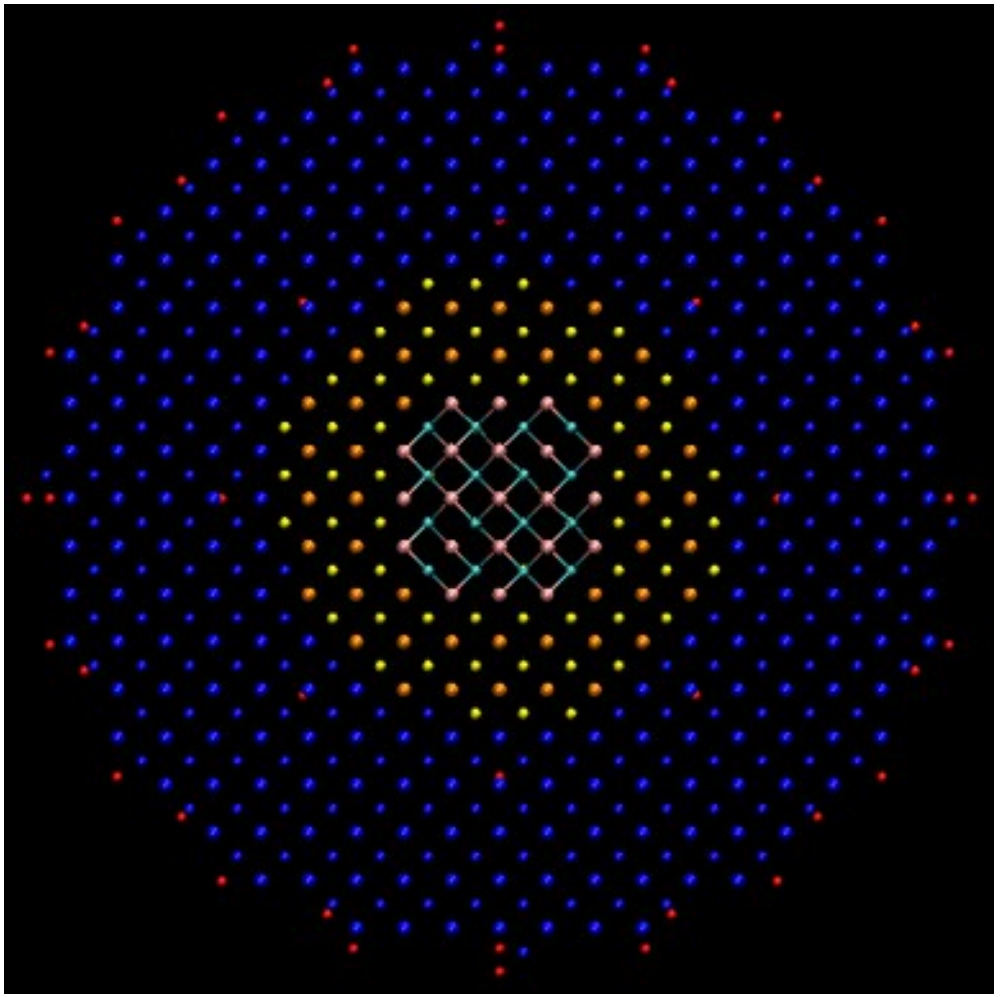
QM/MM method

Advantages:

Avoid the interaction with periodic images.

Allow to compute que QM part with accurate methods not available for periodic systems.

Disadvantage:
Quantum confinement effect.
Tricky.

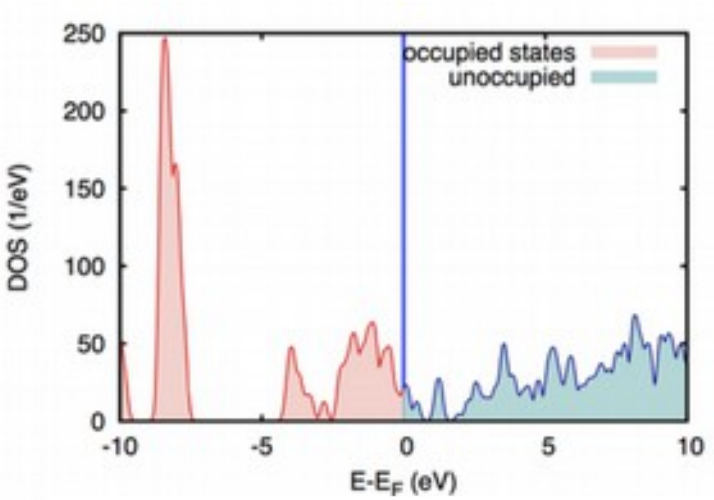


M. Casanova, M.Sc. Thesis.,
J. Phys.: Conf. Ser. 1043, 012043 (2018)

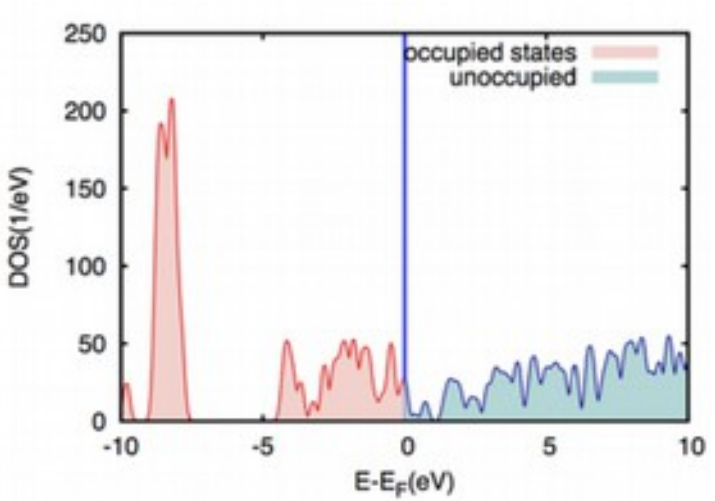
Success story: Berger et al, PRB 92, 075308 (2015)
Casanova & Menendez... not that lucky :-(

QM/MM method

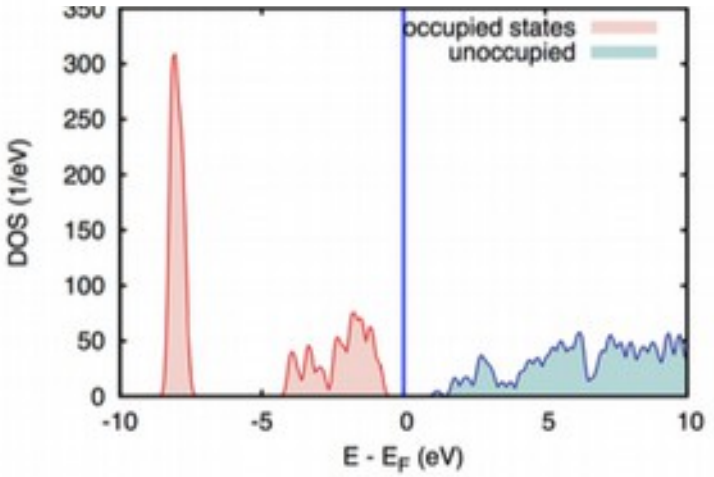
Bare QM-region



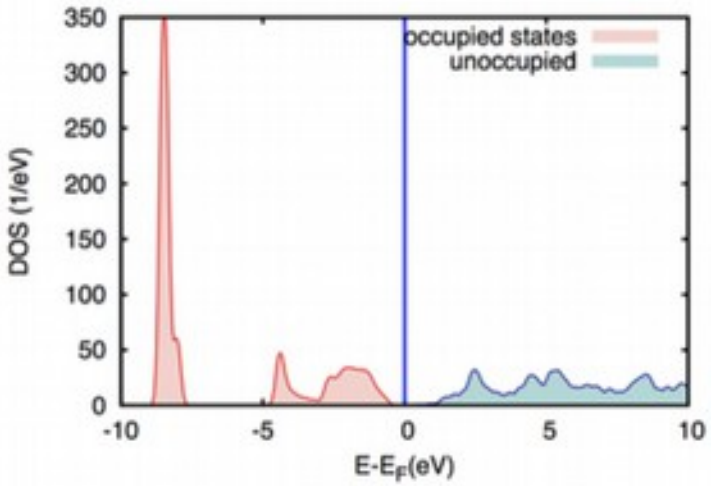
QM-region + point charges



QM+region + point charges
+ pseudopotentials



Periodic DFT approach



However, it was plenty of fine details to match the PBC and QM/MM results for the vacancy. Periodic DFT is simpler to apply.

Typical computer resources

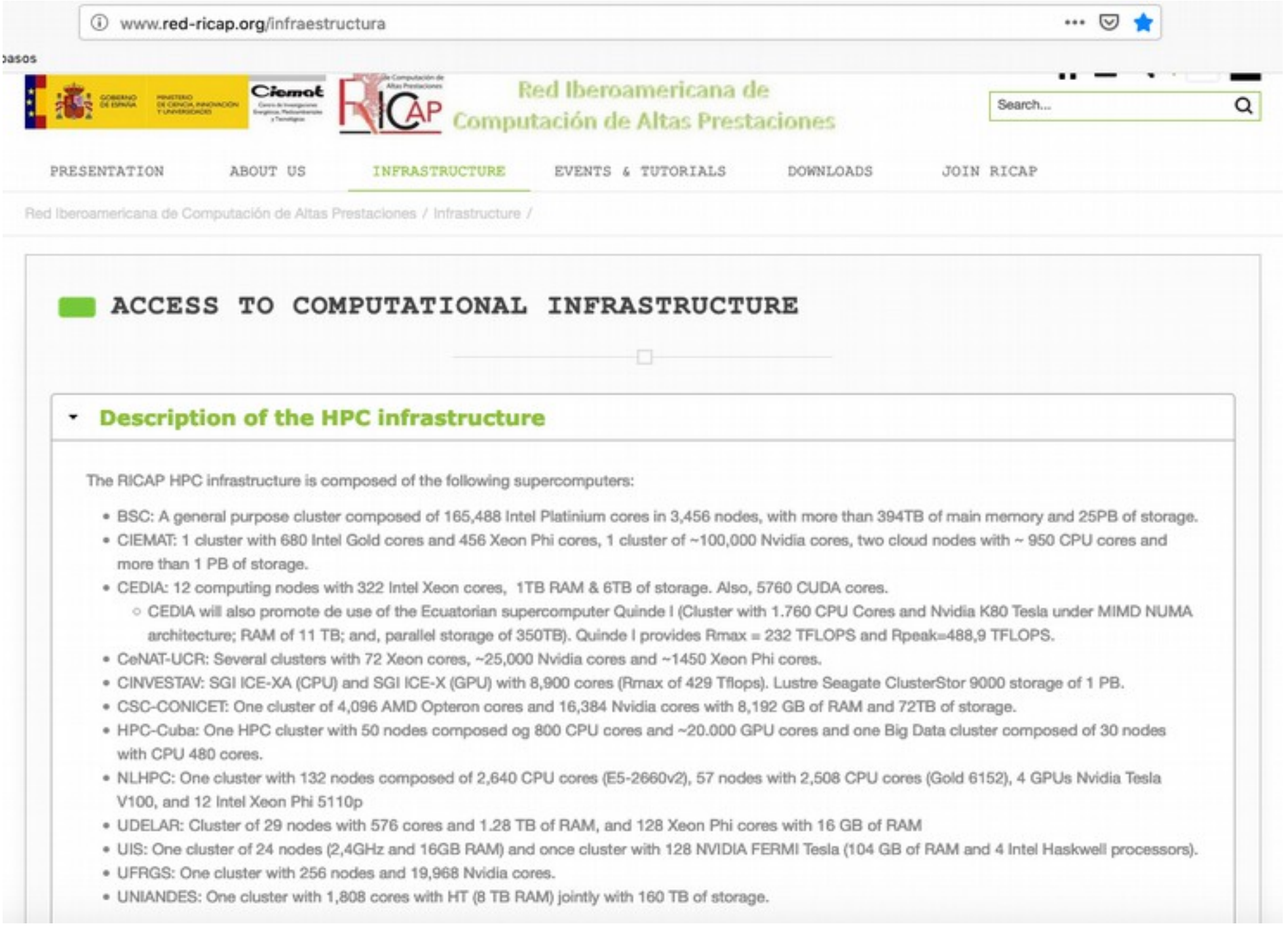
- GGA functional, VASP code.
  - Single machines:
    - 4x AMD Opteron 6272 (16cores) RAM 128 GB
    - 4x Intel Xeon CPU E5-4610 v2 (8cores), RAM 128 GB

    Typical calculation: 1-2 hours SCF.

    Largest calculation: 1024 atoms SCF, 12 hours.
- Hybrid functionals
  - HPC cluster with Intel Xeon CPU E5-2660v2, 20 cores/node

    Typical calculations: 216 atoms, 60-120 cores, 3-4 hours SCF, 9 days for relaxation. 512 atoms, 35 hours SCF.
- GW. WEST code.
  - 127/128 atoms, 264 cores, 4 GB/core. Time: ?

http://www.red-ricap.org

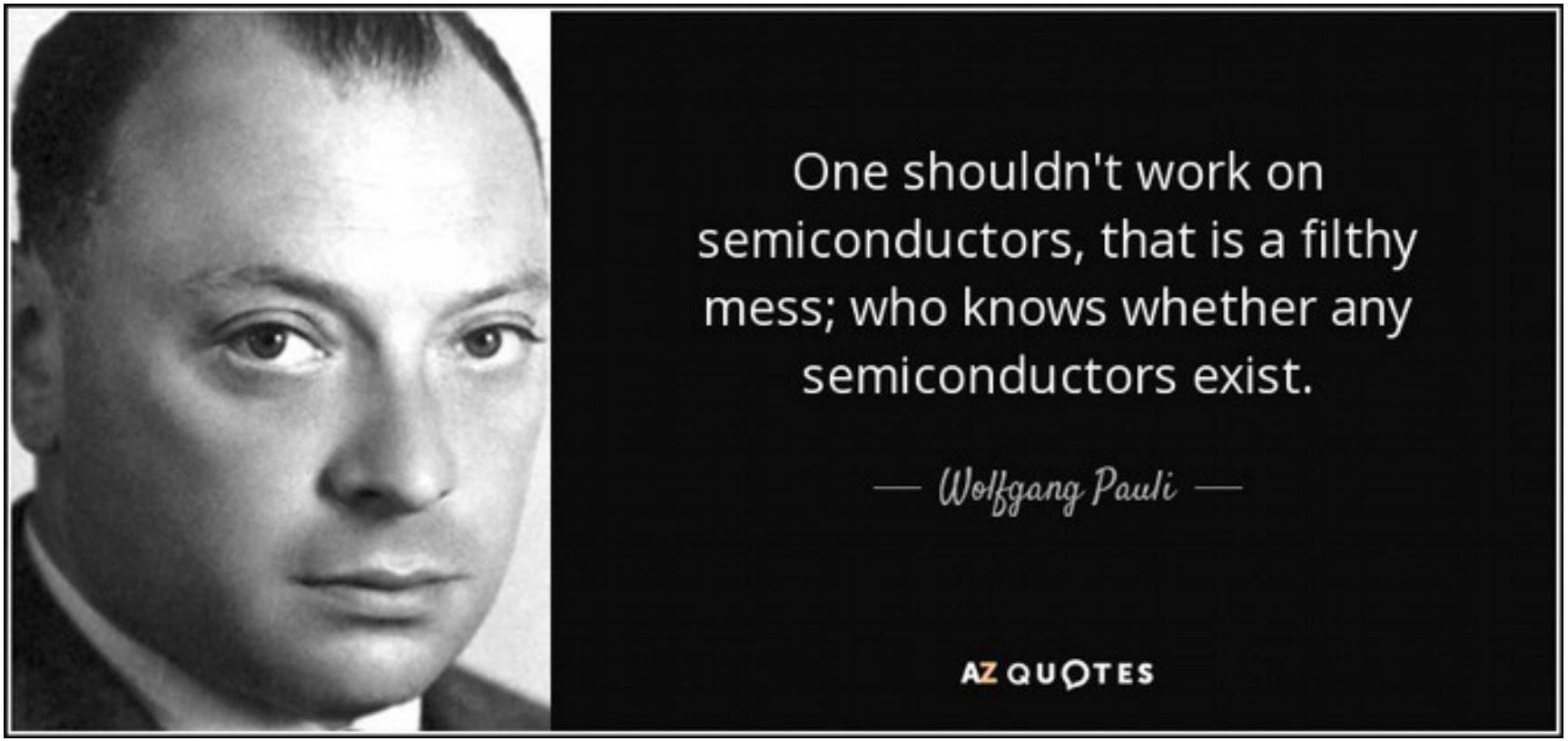


Acknowledgements

- CONICYT/FONDECYT Regular Grants No. 1130437, 1171807.
- National Laboratory of High Performance Computing. URL: www.nlhpc.cl
- W. Orellana, M. Flores, M. Casanova, J.A. Rios, J.L. Peña, P. Wahnón.

Thank you!

Think it!



Letter to Peierls". "Scientific Correspondence with Bohr, Einstein, Heisenberg a.o. Volume II: 1930–1939" by Wolfgang Pauli, September 29, 1931.
https://www.azquotes.com/quote/1100831