Advanced Materials Modeling:

Defects

Center for Energy Science and Technology (CEST)
Skolkovo Institute of Science and Technology
Moscow, Russia

Thermodynamics of Defects

- **Very small concentrations of defects can significantly alter materials properties**

50 ppm Fe

Small concentration of Fe impurities are visible by naked eye in intrinsically transparent MgO

Si semiconductors contain 10^{-9}-10^{-3} intentional impurities per atom

"My precious!": Perfect defected gems

$Cr:Al_2O_3$

$V:Al_2O_3$

$Fe:Al_2O_3$

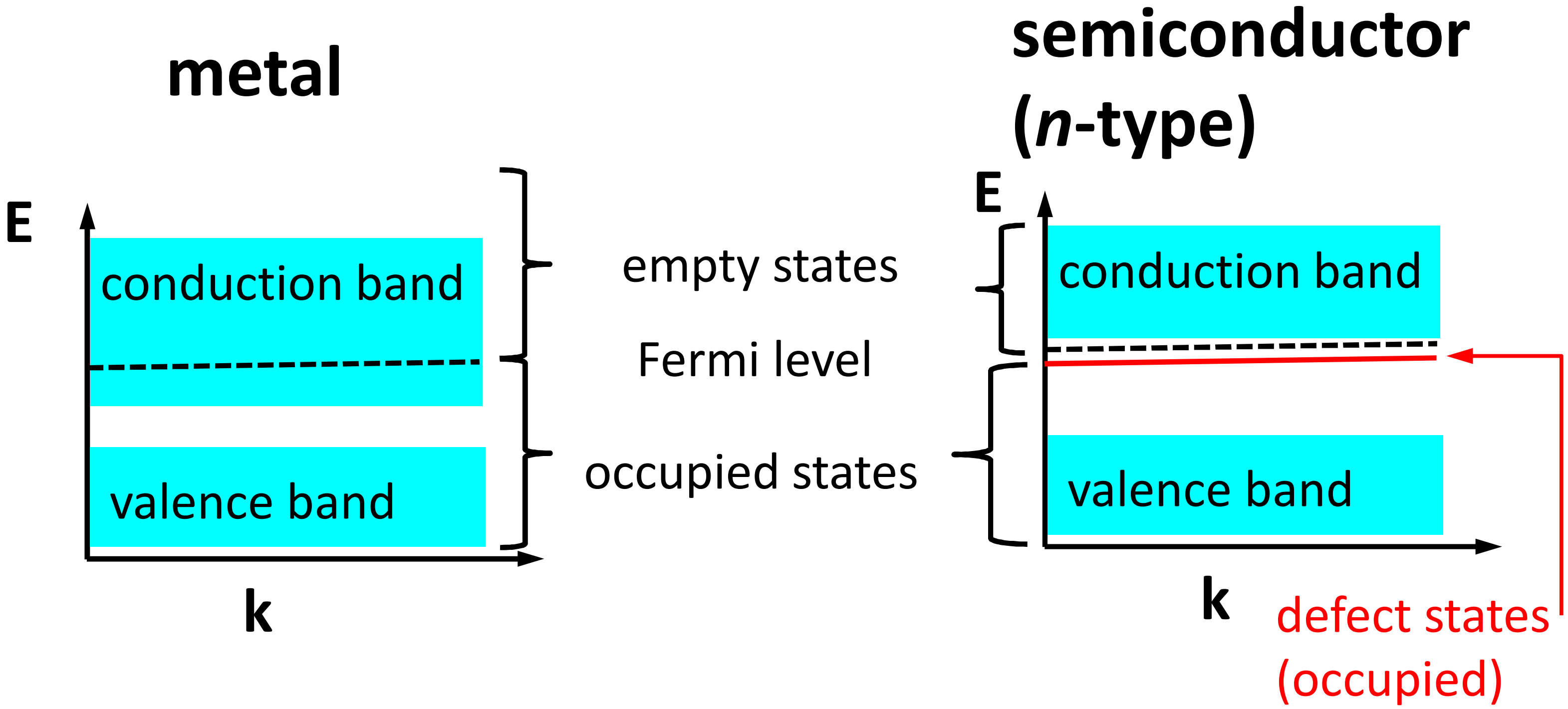
$Fe:Al_2O_3$

Impurities are responsible for the color of sapphire and many other precious stones

Typical concentrations: 100-10000 ppm

$Fe,Ti:Al_2O_3$

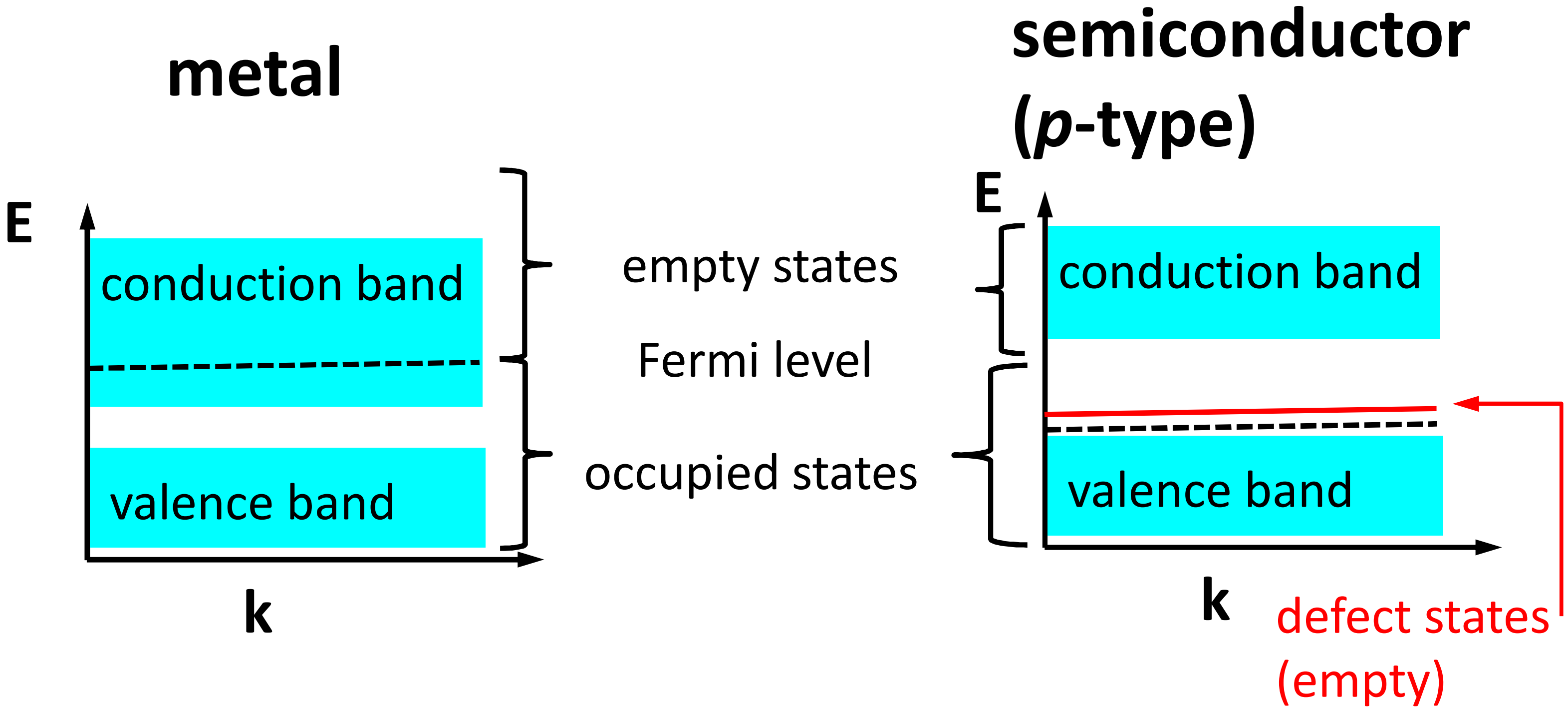
Semiconductors



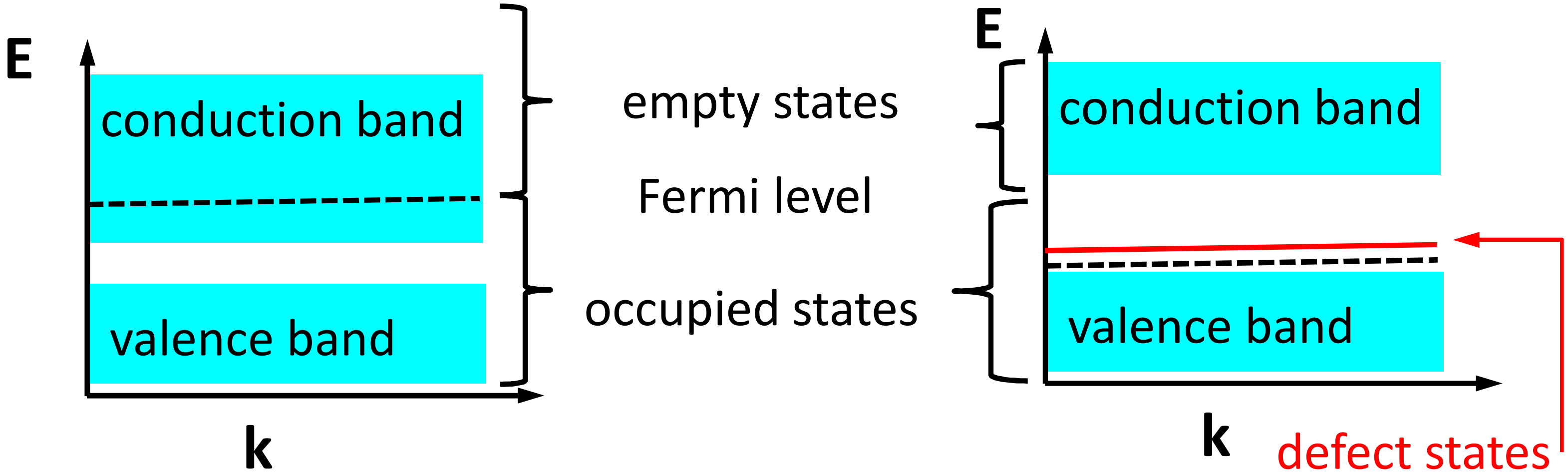
metal

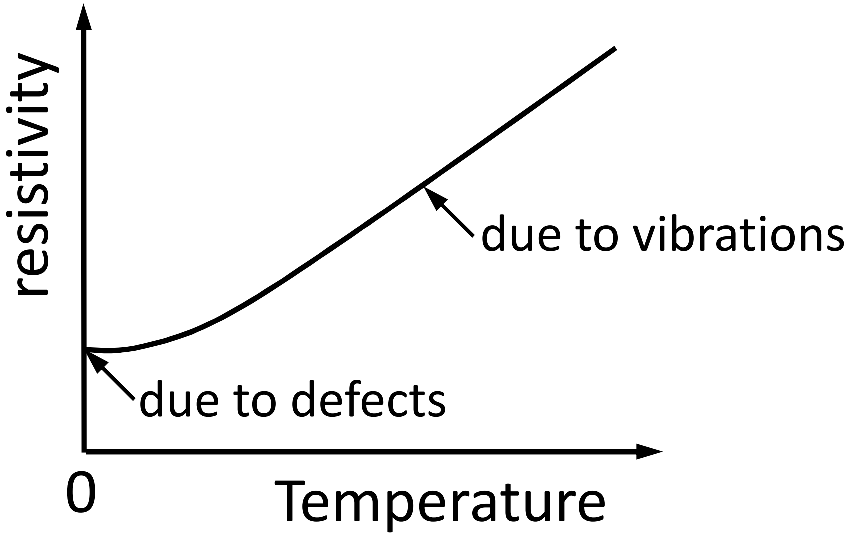
semiconductor (*n*-type)

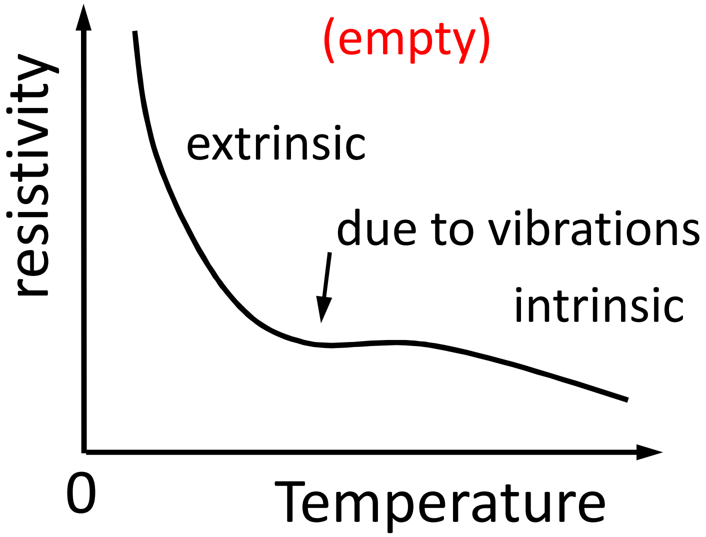
Semiconductors



Semiconductors

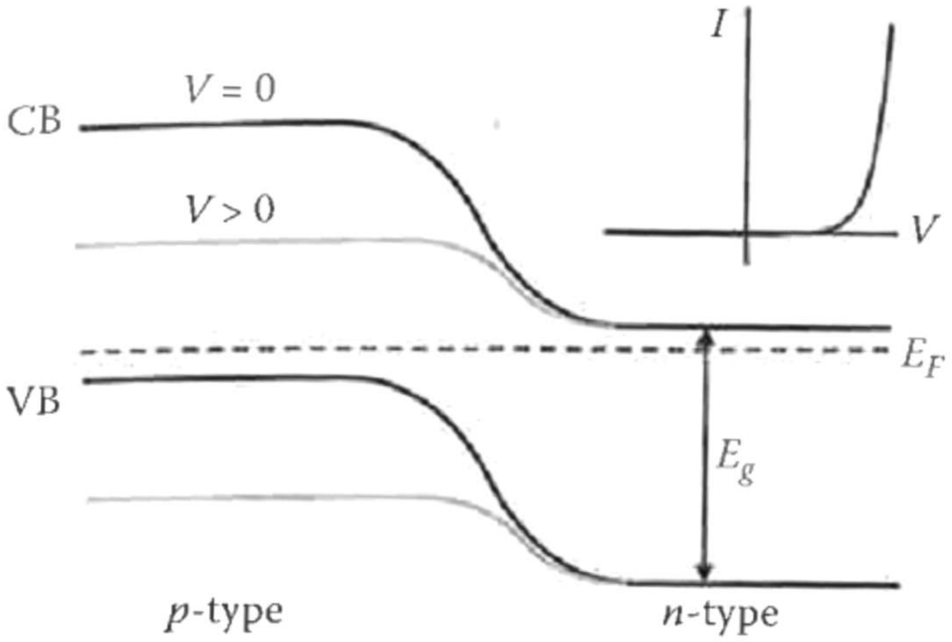






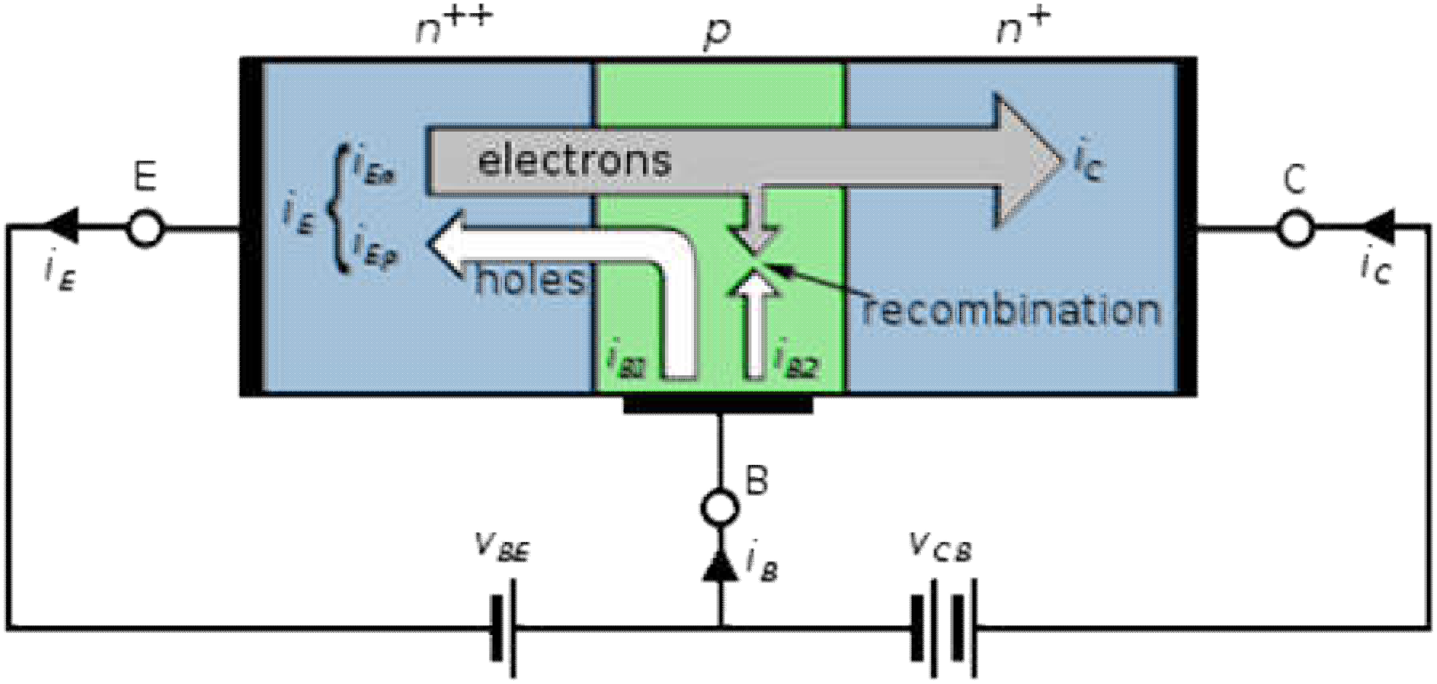
“Physics of dirt”

1939: First *p-n* junction made at Bell Labs (accidental observation of light effect on resistivity of a cracked silicon crystal)



“Physics of dirt”

1948: W. Shockley (Bell Labs) – First bipolar (*n*-*p*-*n*) transistor design (eliminate delicate point contacts)



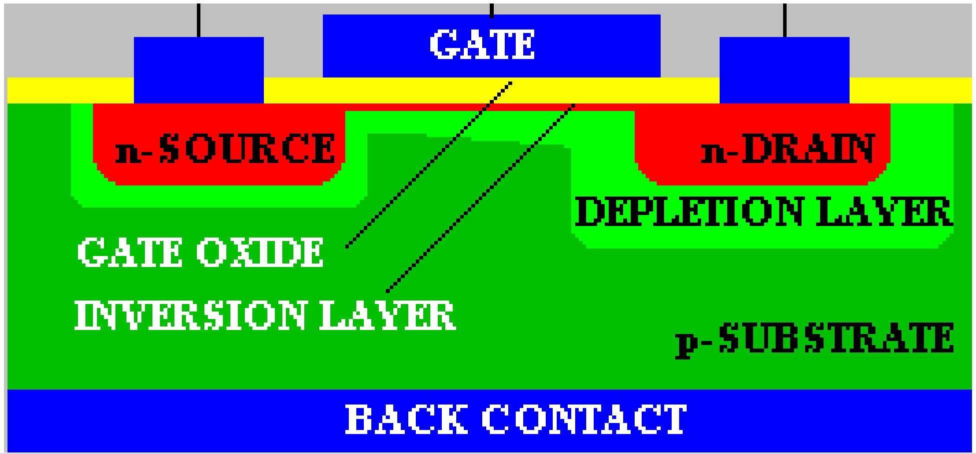
Emitter: heavily P-doped Si, base: B-doped Si, collector: lightly *n*-doped Si

Technology: fine control of “dirt” (doping)

1950-1954: (Bell Labs) – High-precision doping of a purified Ge (but the small band gap of Ge made the device properties temperature-dependent)

1958: J. Kilby (Texas Instruments) – First integrated circuit on Ge; R. Noyce (Fairchild Electronics, CA) – First integrated circuit on Si

1960: J. Atalla (Bell Labs) – First metal-oxide-semiconductor (MOS) field-effect transistor (Al-SiO_2-Si) – basis of modern electronics

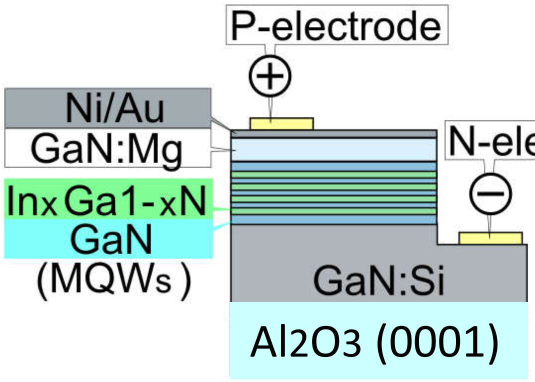


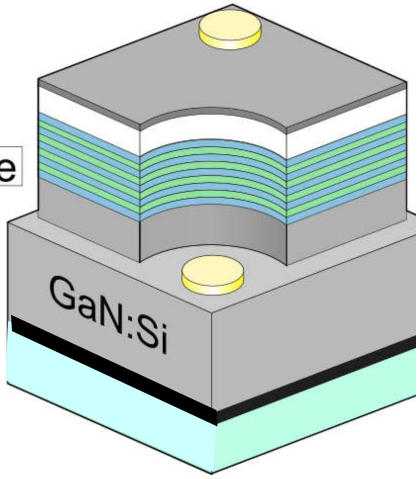
“Let there be light!”: solid-state lighting

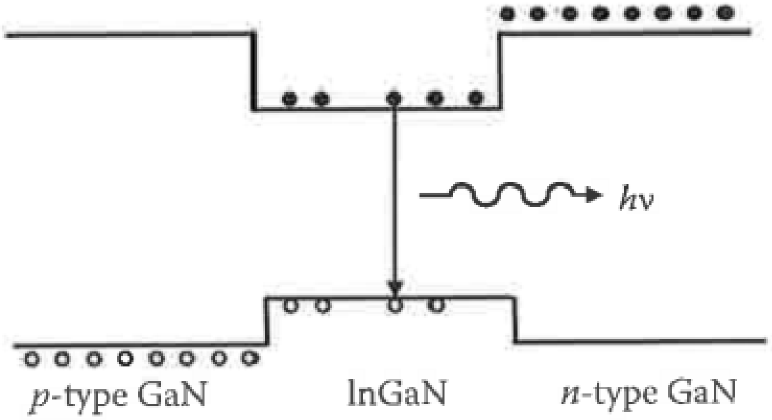
1907: H.J. Round – discovery of light emission from SiC diode under a voltage bias; this was the first light-emitting diode (LED), but very inefficient

1962: Infrared and red LEDs and lasers (GaAs, AlGaAsP)

~1990: First blue LEDs (GaN)

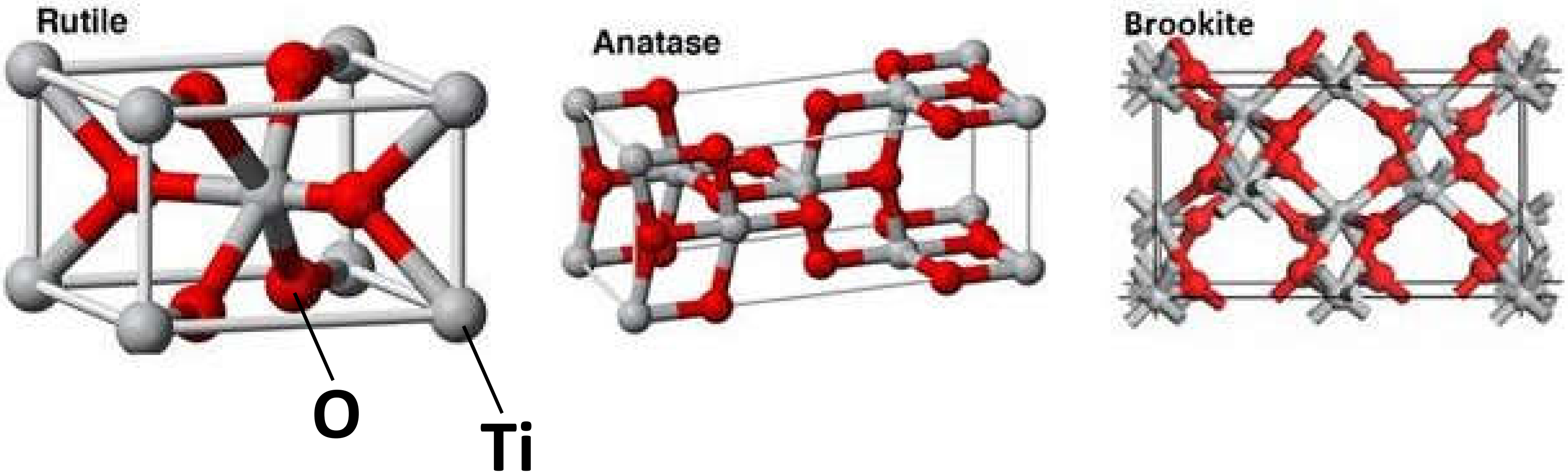






Why oxides are semiconductors?

TiO_2 – a versatile functional material (paint, sunscreen, photocatalyst, optoelectronic material)



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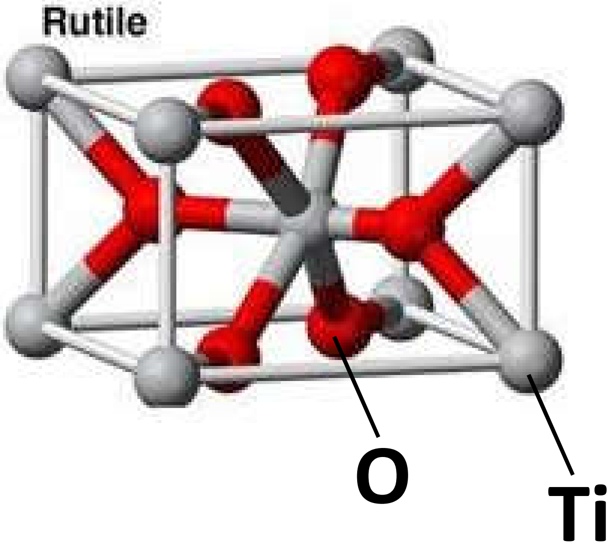
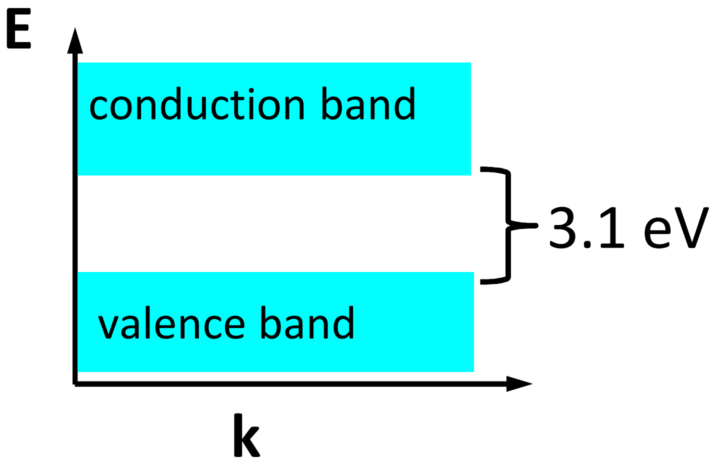
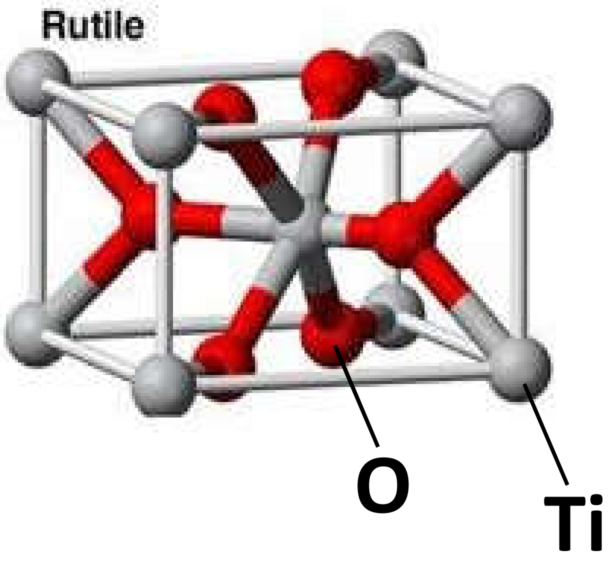
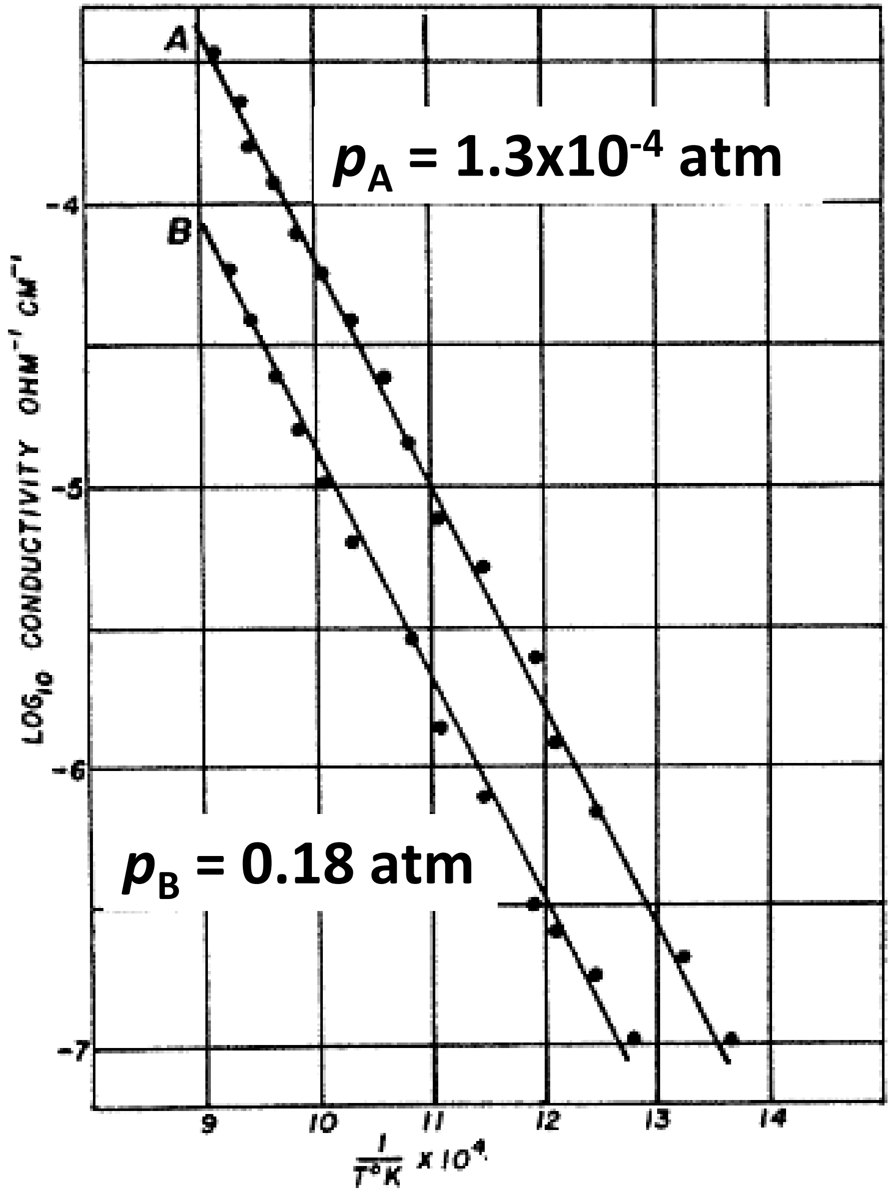




Why oxides are semiconductors?



TiO_2 is an *n*-type semiconductor, whose conductivity depends on O_2 pressure

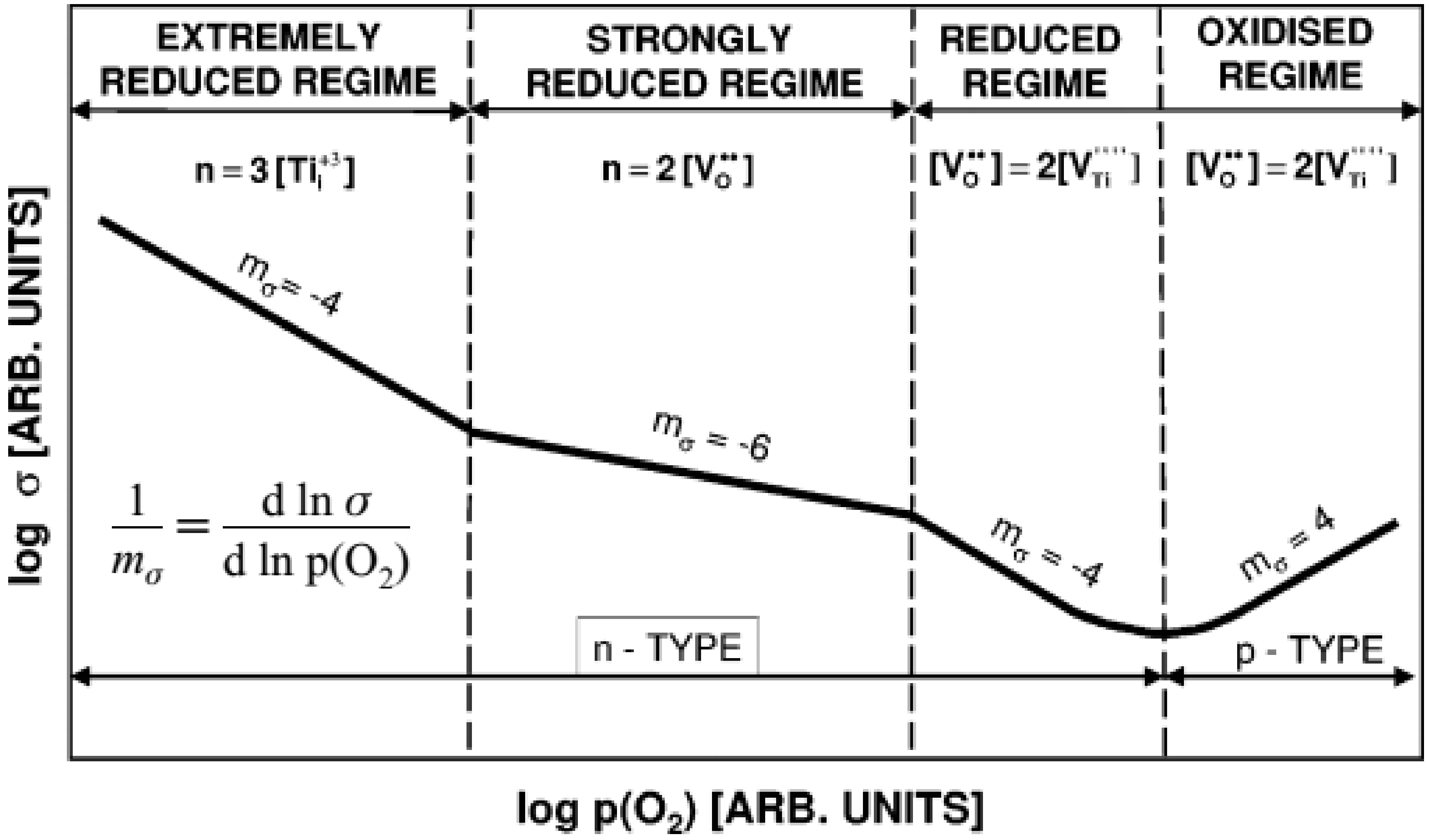


p_A = 1.3x10^{-4} atm

p_B = 0.18 atm

M.D. Earle, Phys. Rev. **61**, 56 (1941)

Why oxides are semiconductors?

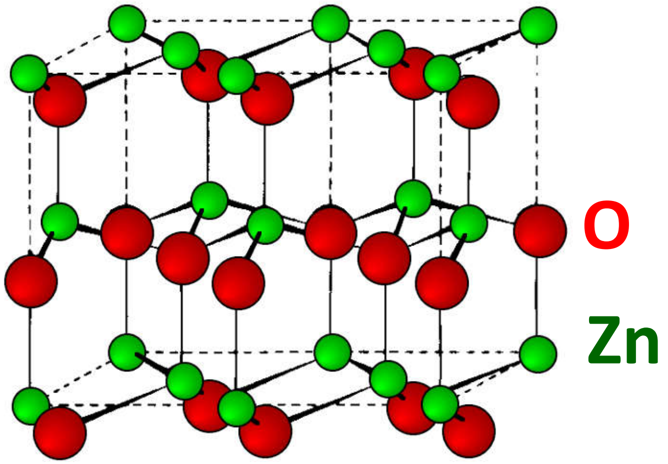


Different regimes correspond to different intrinsic defect distributions in ultrapure TiO_2

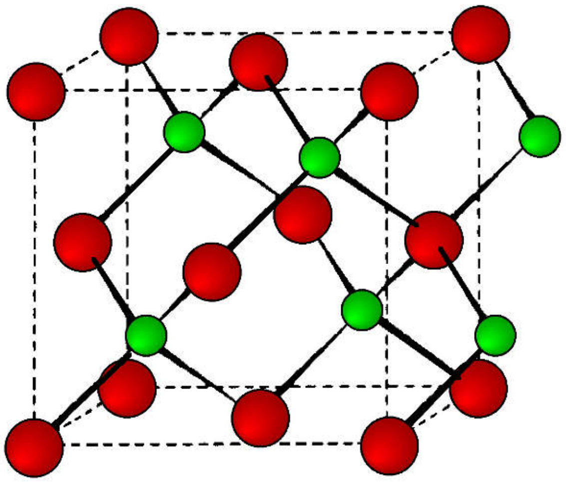
M. K. Nowotny, T. Bak, and J. Nowotny, J. Phys. Chem. B **110**, 16270 (2006)

Why oxides are semiconductors?

ZnO – another example of a very promising functional material, understood less than TiO_2



wurtzite (stable)

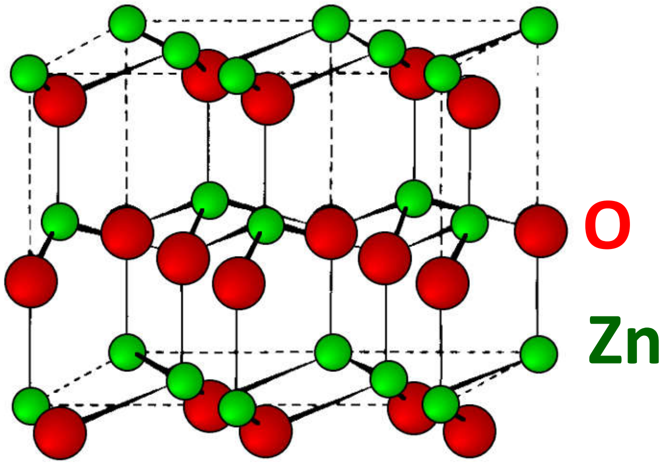


zinkblende (can be obtained by growth on substrates with cubic lattice structure)

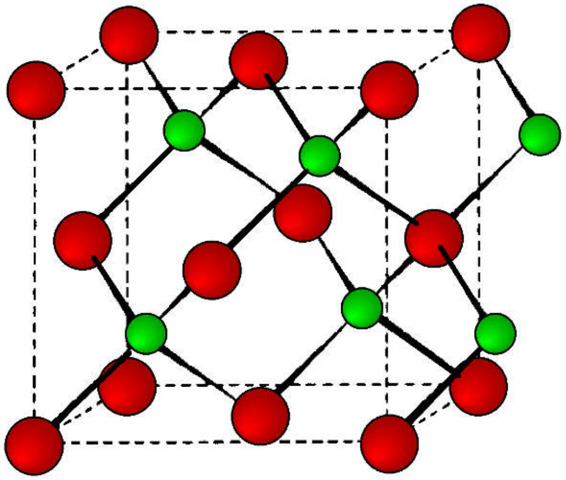
Band gap ~3.3 eV (direct), but (almost?) exclusively *n*-type semiconductor

Why oxides are semiconductors?

ZnO – another example of a very promising functional material, understood less than TiO_2



wurtzite (stable)

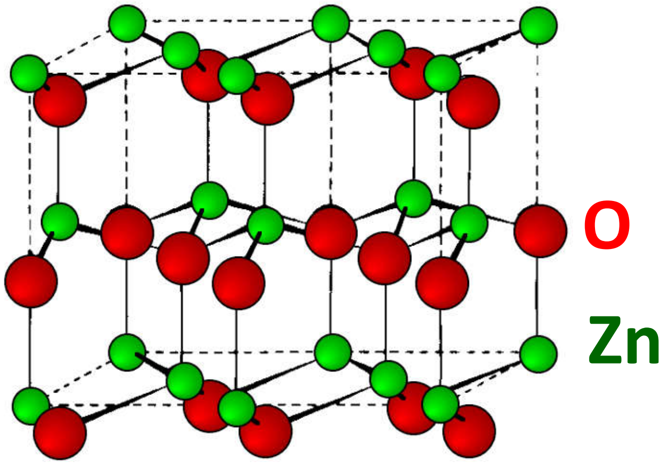


zinkblende (can be obtained by growth on substrates with cubic lattice structure)

Can be used for blue/UV LED/lasers, and, in contrast to GaN, is available as large bulk single crystals

Why oxides are semiconductors?

ZnO – another example of a very promising functional material, understood less than TiO_2



wurtzite (stable)

There is no consensus on the nature of *n*-type conductivity, and whether reliable *p*-type doping is possible. However, there is hope (GaN story repeats itself):

"…native point defects cannot explain the often-observed *n*-type conductivity, but the latter is likely to be caused by the incorporation of impurities during growth or annealing."

A. Janotti and C.G. van de Walle, Rep. Prog. Phys. **72**, 126501 (2009)

When imperfections are useful

Tailoring defect properties has a tremendous potential for designing novel functional materials in many areas of technology (electronics, optics, catalysis, photocatalysis, thermoelectrics, optoelectronics, spintronics, etc.)

↓

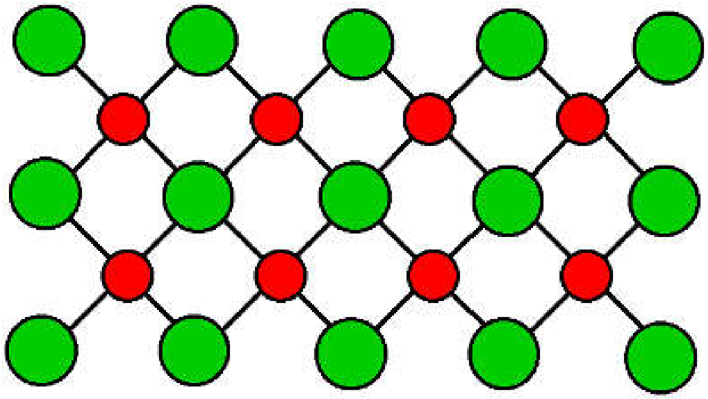
Understanding the electronic and atomic structure of defects is of great importance

The “invisible agent”

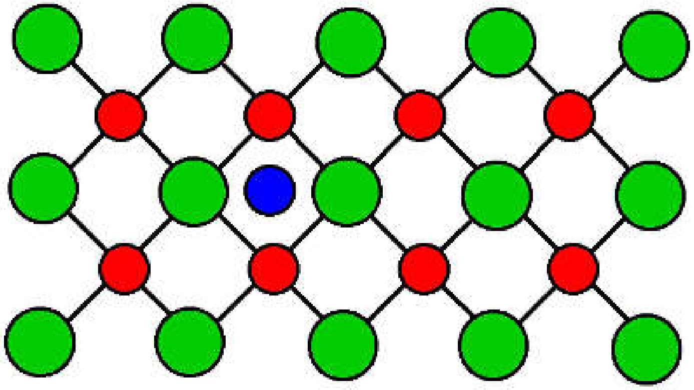
“…The problem is that defects are often elusive species, highly diluted, and therefore difficult to detect. It is as if one wanted to identify all the men with a beard among the population of Europe from a satellite which is a few hundreds of kilometers away from the earth surface: the task is difficult, and it is easy to get confused.” (G. Pacchioni, ChemPhysChem **4**, 1041 (2003))

In fact, the situation is even more complex: The nature and concentration of defects depend on temperature, pressure, and charge-carrier doping

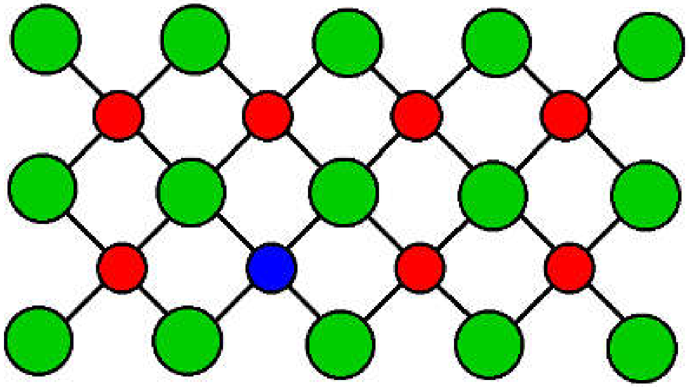
Common point defect types



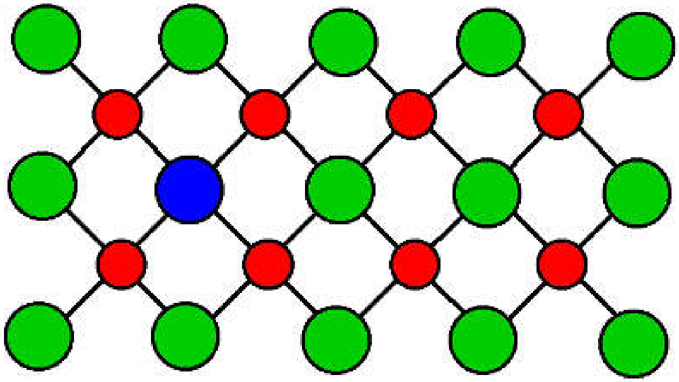
(a) perfect lattice



(b) interstitial impurity

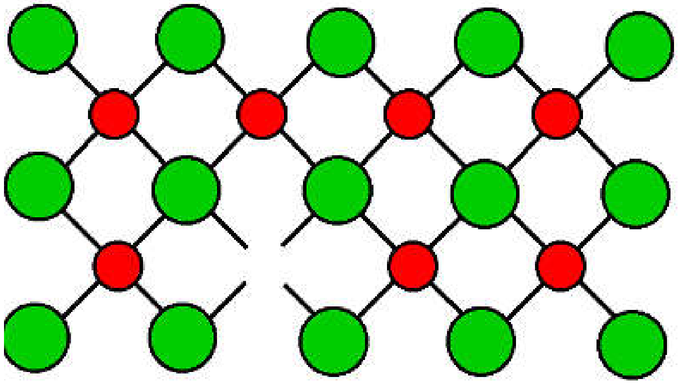


(e) substitution of cation

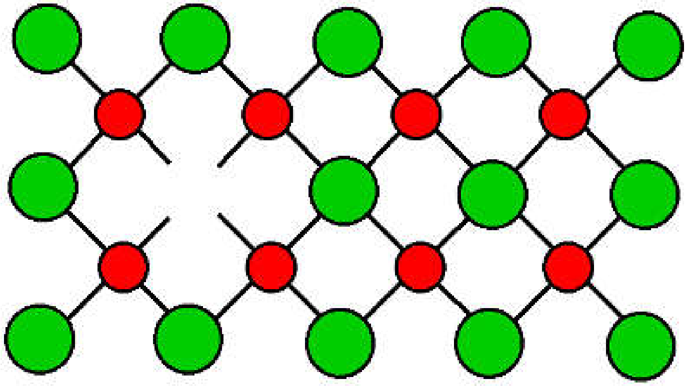


(f) substitution of anion

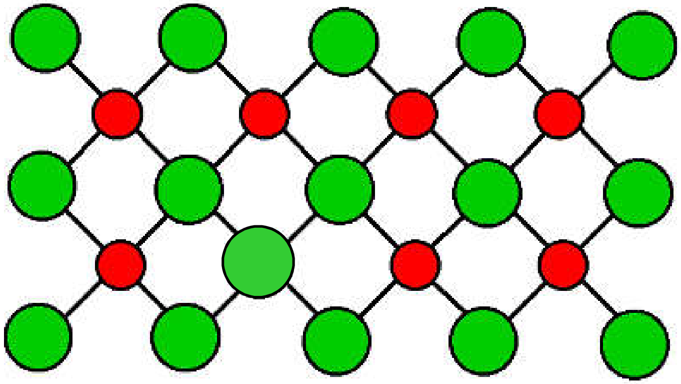
Common point defect types



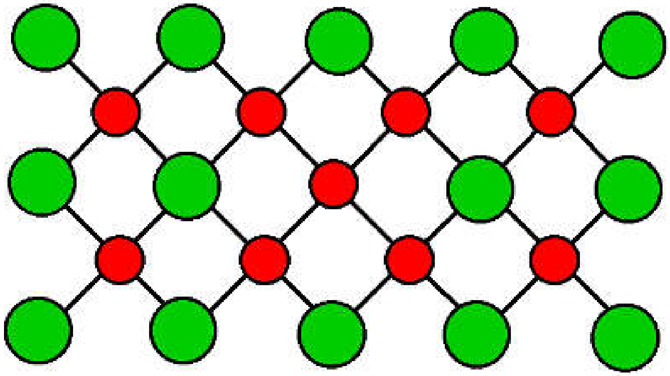
(c) cation vacancy



(d) anion vacancy



(g) B_A antisite defect

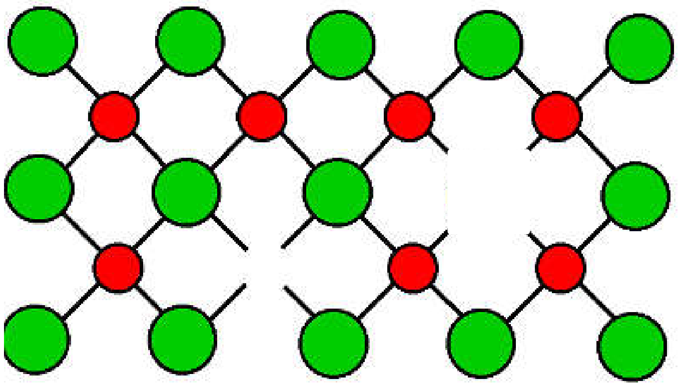


(h) A_B antisite defect

Common point defect types

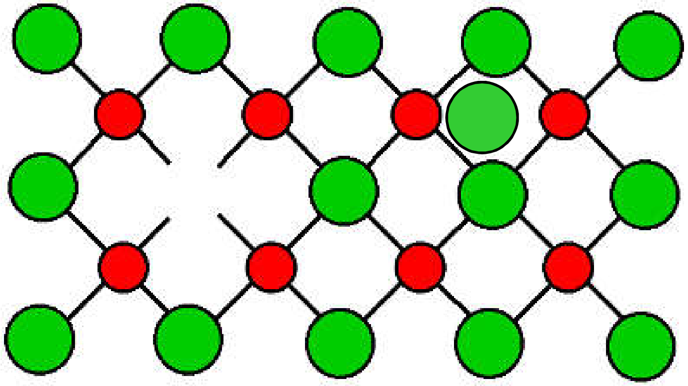
Defect complexes

Schottky defects



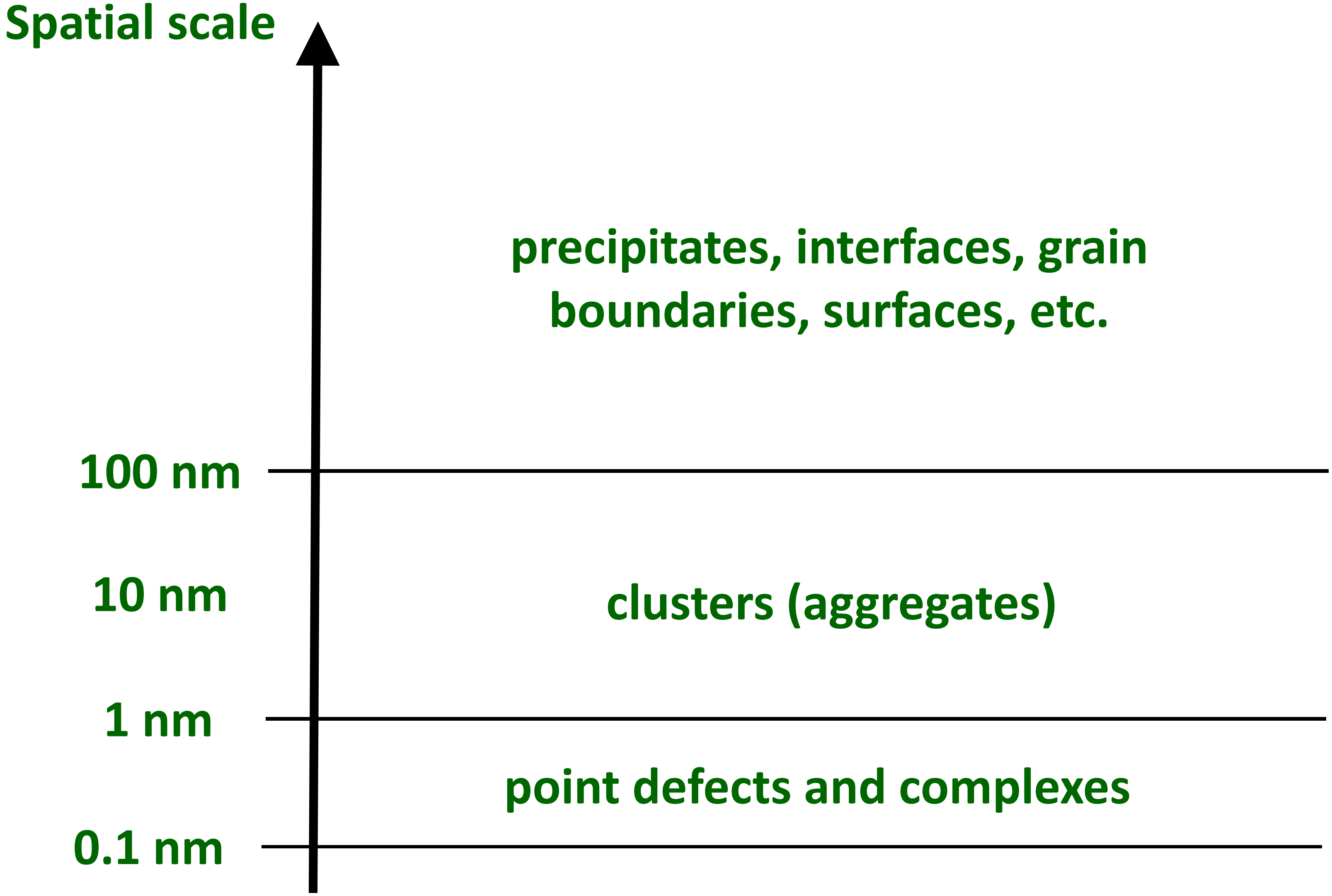
Stoichiometric charge-compensated vacancy combinations (V_{Na}^{-} +V_{Cl}^{+}, V_{Ti}^{4-}+2V_{O}^{2+}, etc.)

Frenkel defects



Pairs of a vacancy and the corresponding self-interstitial (V_{Na}^{-} + Na_{i}^{+})

Larger-scale symmetry breaking



Spatial scale

precipitates, interfaces, grain boundaries, surfaces, etc.

100 nm

10 nm

clusters (aggregates)

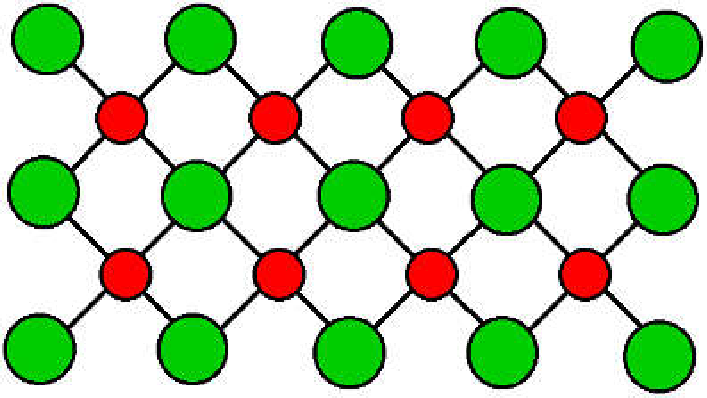
1 nm

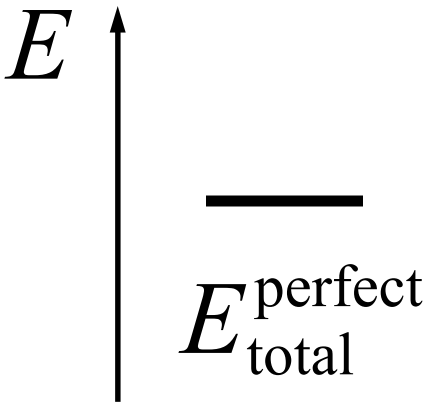
point defects and complexes

0.1 nm

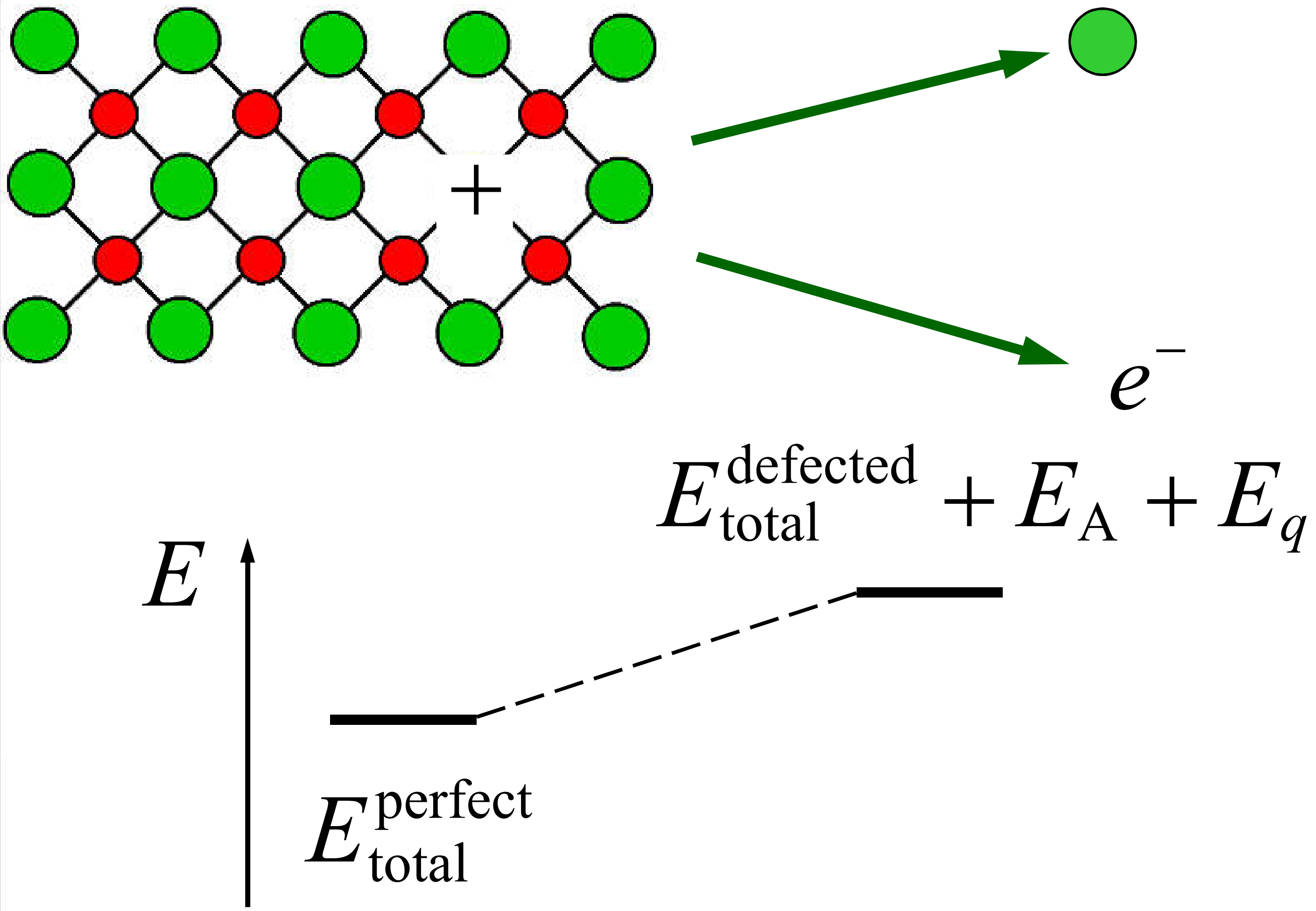
Nanometer-size defects are building blocks for the larger defects

Defect formation energy (*T*=0)





Defect formation energy (*T*=0)



e^-

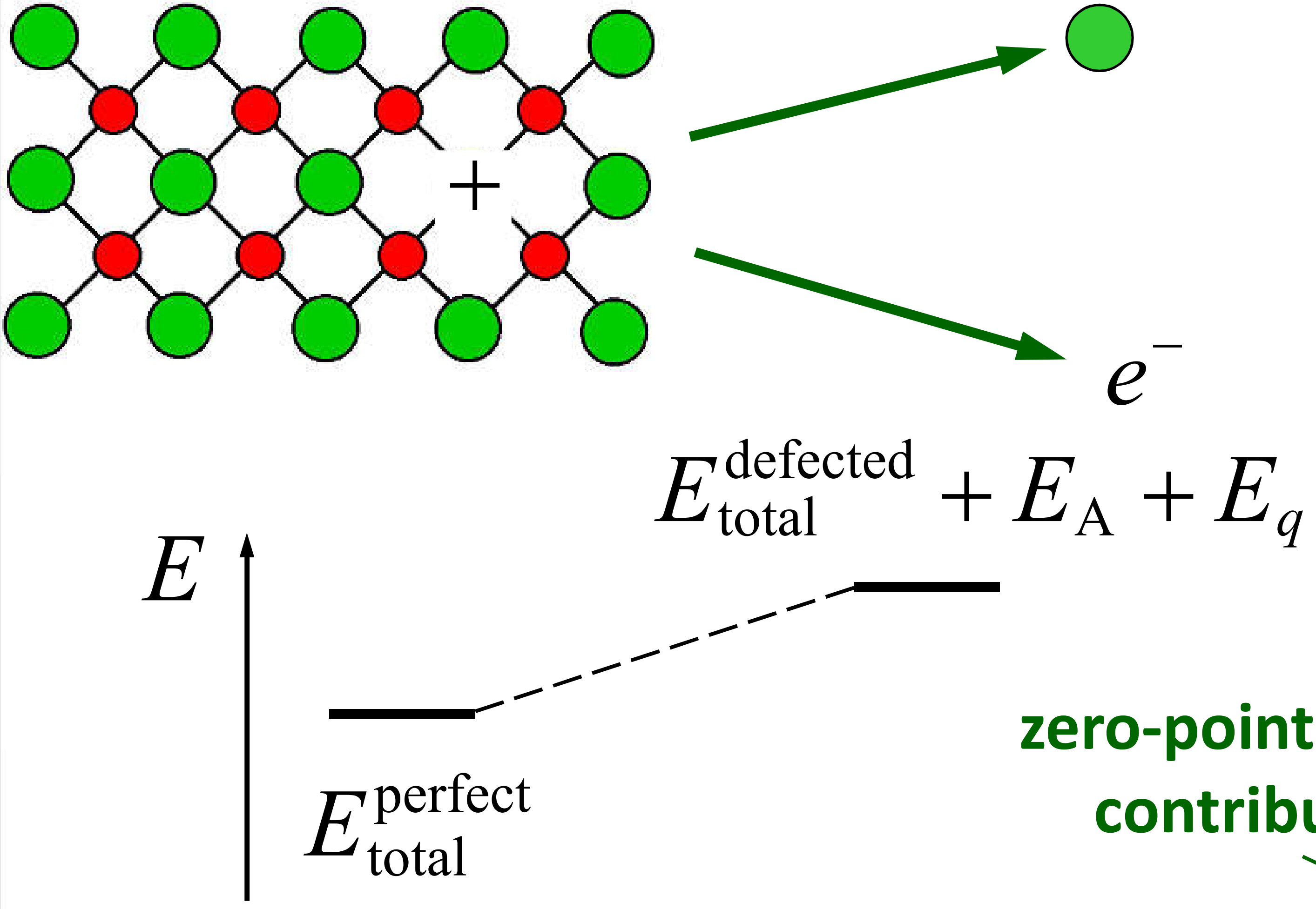
$E_{\text{total}}^{\text{defected}} + E_{\text{A}} + E_q$

E

$E_{\text{total}}^{\text{perfect}}$

$$\Delta E_f = E_{\text{total}}^{\text{defected}} + E_{\text{A}} + E_q - E_{\text{total}}^{\text{perfect}}$$

Defect formation energy (*T*=0)



e^{-}

$E^{\text{defected}}_{\text{total}} + E_{\text{A}} + E_q$

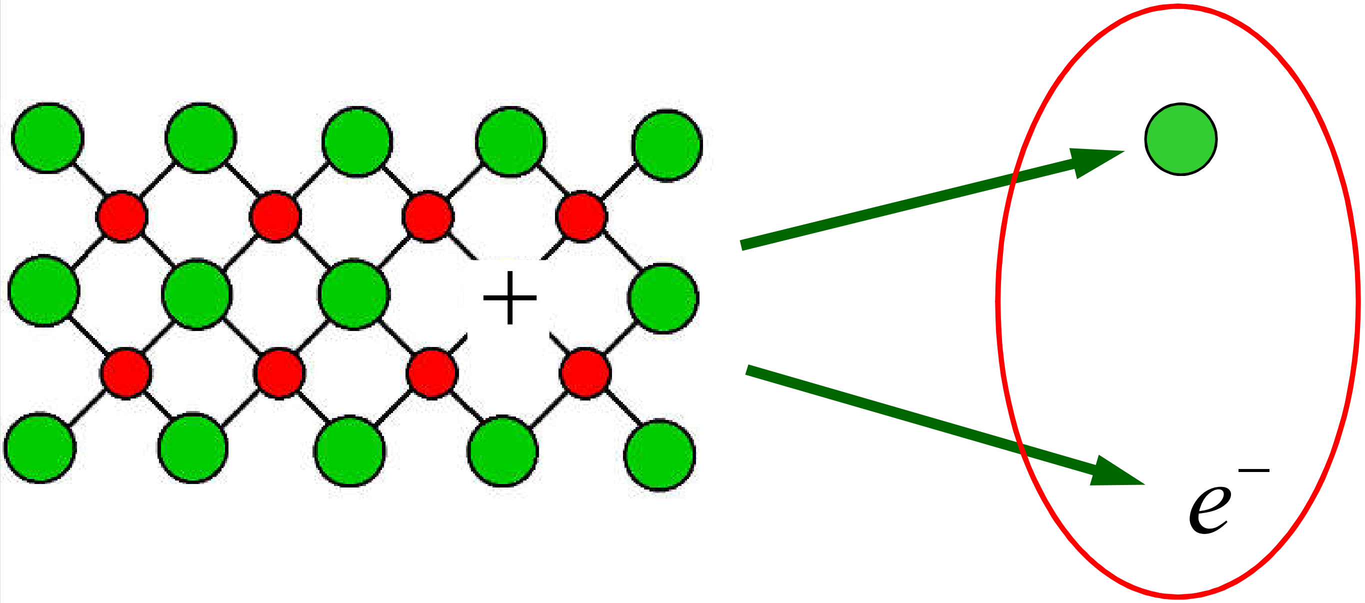
E

$E^{\text{perfect}}_{\text{total}}$

zero-point energy contribution

$$\Delta E_f = E^{\text{defected}}_{\text{total}} + E_{\text{A}} + E_q - E^{\text{perfect}}_{\text{total}} + \Delta E_{\text{ZPE}}$$

Defect formation energy (*T*=0)



$$\Delta E_f = E_{\text{total}}^{\text{defected}} + \boxed{E_{\text{A}} + E_q} - E_{\text{total}}^{\text{perfect}} + \Delta E_{\text{ZPE}}$$

Formation energy depends on the final (initial) state of the removed (added) species

Defect formation energy (*T*=0)

$$\Delta E_f = E_{\text{total}}^{\text{defected}} + E_{\text{A}} + E_q - E_{\text{total}}^{\text{perfect}} + \Delta E_{\text{ZPE}}$$

Contributions to the formation energy:

1) Bond breaking/making
2) Atomic relaxation and polarization (screening)
3) Change in zero-point vibrational energy
4) Final/initial state of removed/added atoms and charges

Gibbs free energy of defect formation

$T = 0$:

$$\Delta E_f = E_{\text{total}}^{\text{defected}} + E_{\text{A}} + E_q - E_{\text{total}}^{\text{perfect}} + \Delta E_{\text{ZPE}}$$

$$\Downarrow$$

$T > 0$:

$$\Delta G_f(T,\{p\}) = G^{\text{defected}}(T,\{p\}) - \sum_i \mu_i(T,p_i)\Delta N_i + q\mu_e(T) - G^{\text{perfect}}(T,\{p\})$$

Electronic chemical potential

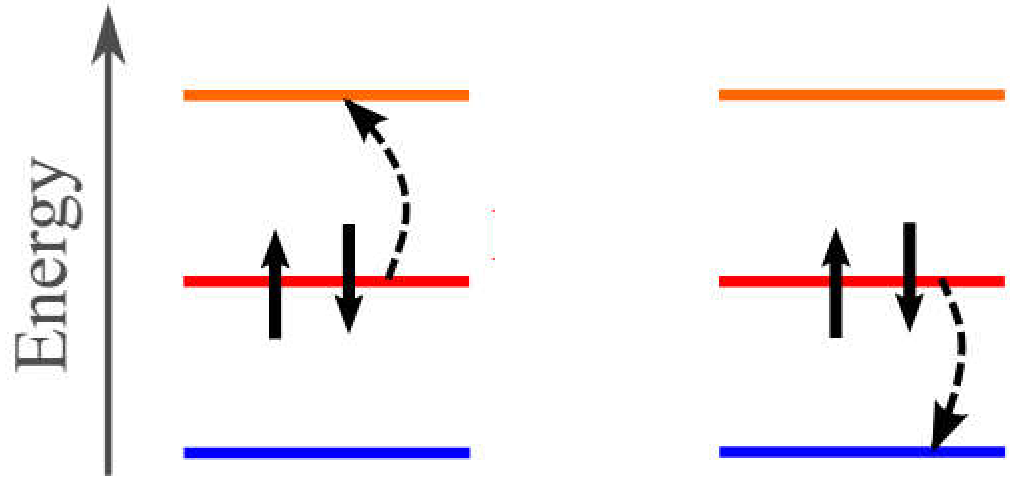
$$\Delta G_f(T,\{p\}) = G^{\text{defected}}(T,\{p\}) - \sum_i \mu_i(T,p_i)\Delta N_i + q\boxed{\mu_e(T)}$$
$$- G^{\text{perfect}}(T,\{p\})$$

μ_e is a property of the electronic reservoir

In a doped system, μ_e is close to the Fermi level (the energy level separating occupied states from the empty states at *T* = 0)

Electronic chemical potential

$$\Delta G_f(T,\{p\}) = G^{\text{defected}}(T,\{p\}) - \sum_i \mu_i(T,p_i)\Delta N_i + q\boxed{\mu_e(T)} - G^{\text{perfect}}(T,\{p\})$$



conduction band minimum (CBm)

defect level

valence band maximum (VBM)

***n*-doped**
μ_e **near CBm**

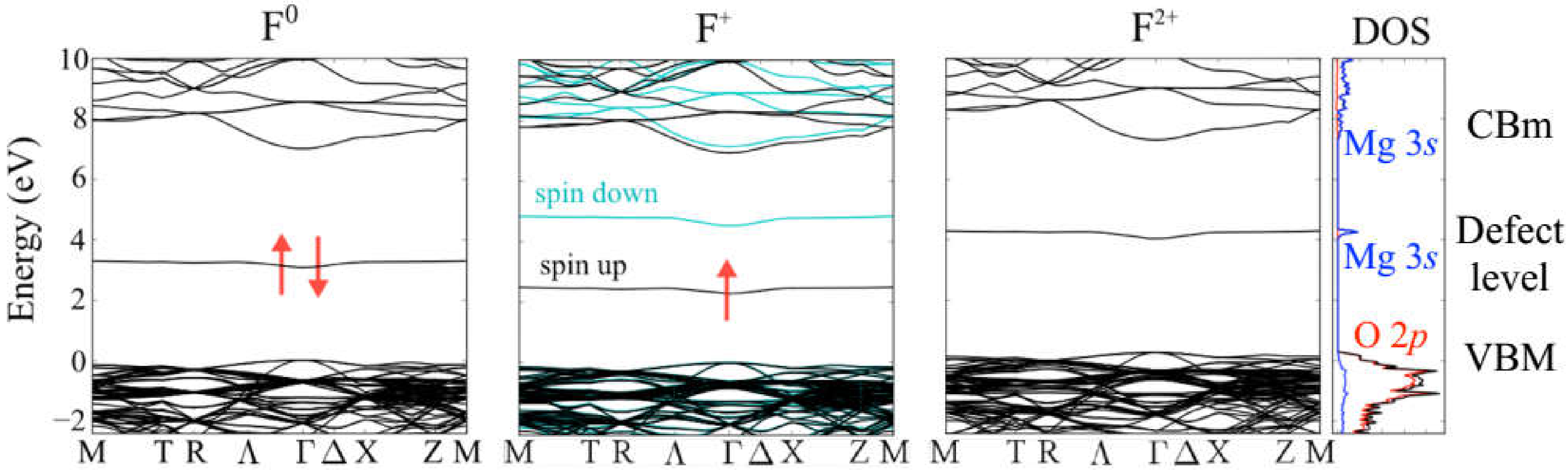
***p*-doped**
μ_e **near VBM**

The defects will charge when μ_e is below the defect level

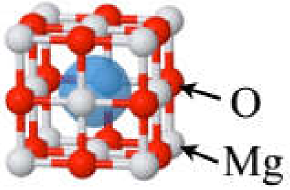
Electronic chemical potential

$$\Delta G_f(T,\{p\}) = G^{\text{defected}}(T,\{p\}) - \sum_i \mu_i(T,p_i)\Delta N_i + q\boxed{\mu_e(T)} - G^{\text{perfect}}(T,\{p\})$$

Band structures of O vacancies in MgO bulk (HSE06)



F^0

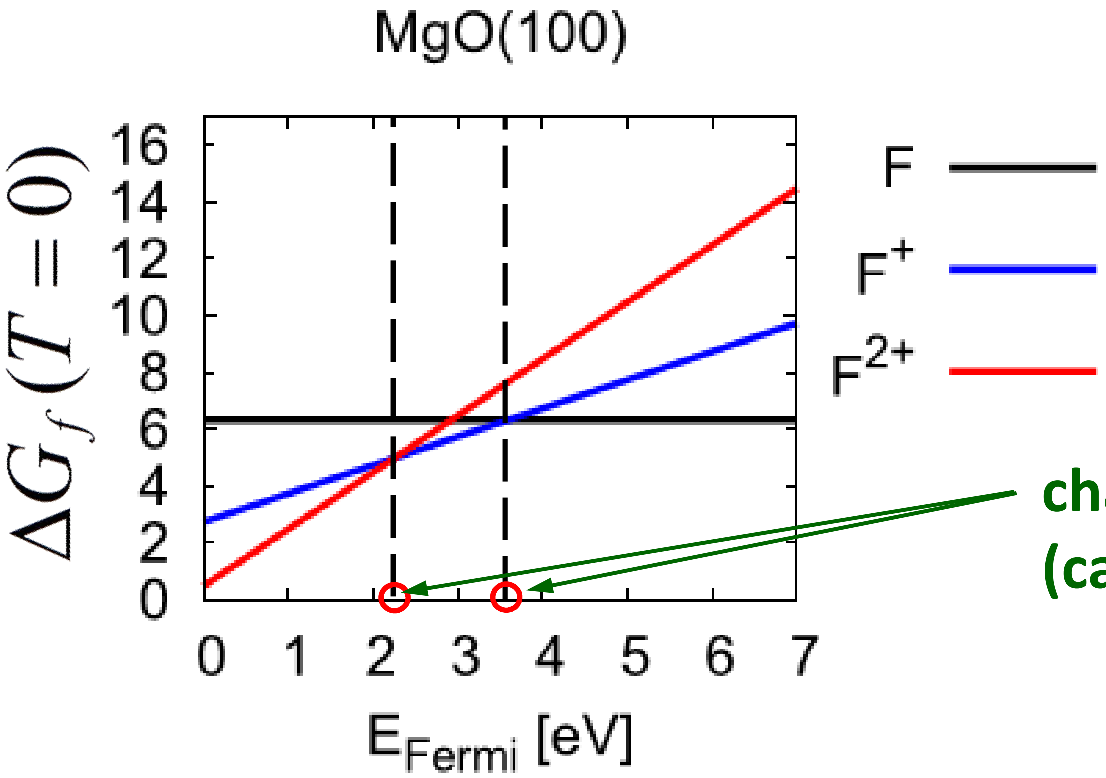


Defect wave function localized in the O vacancy

Electronic chemical potential

$$\Delta G_f(T,\{p\}) = G^{\text{defected}}(T,\{p\}) - \sum_i \mu_i(T,p_i)\Delta N_i + q\boxed{\mu_e(T)}$$

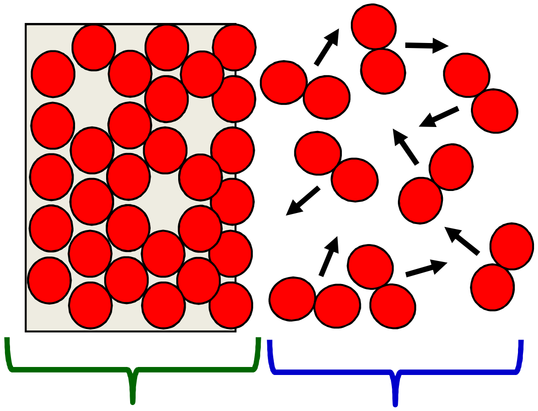
$$-G^{\text{perfect}}(T,\{p\}) + \Delta F^{\text{vib}}(T)$$



charge transition levels
(can be measured!)

Entropy

$$G = U + pV - TS$$



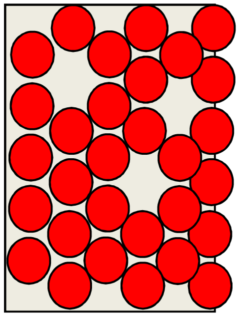
$$S = k \ln \Omega$$

Ω – number of microstates

1) Solid: vibrational entropy (phonons)
2) Solid: electronic entropy
3) Gas: vibrational, rotational, translational, etc. (part of μ_i)
4) Solid: defect disorder

Configurational entropy

$$G = [U + pV - T(S - S_{\text{config}})] - TS_{\text{config}} = \widetilde{G} - TS_{\text{config}}$$



N **equivalent defect sites in the sold**

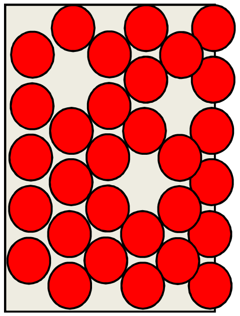
n **defects**

$$S = k\ln Z + kT\frac{\partial \ln Z}{\partial T},\ Z = \sum_i e^{-E_i/kT}$$

sum over different defect distributions

Configurational entropy

$$G = [U + pV - T(S - S_{\text{config}})] - TS_{\text{config}} = \widetilde{G} - TS_{\text{config}}$$



N **equivalent defect sites in the sold**

n **defects**

If defects do not interact: $S_{\text{config}} = k \ln \dfrac{N!}{n!(N-n)!}$

Stirling's formula:

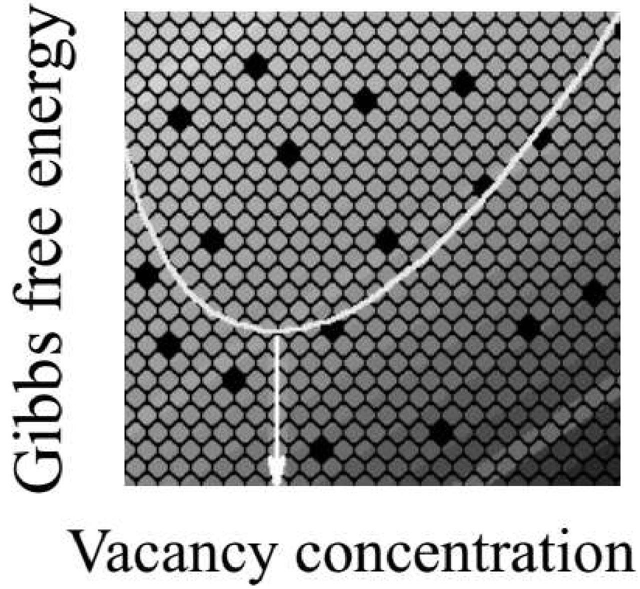
$$\ln(n!) = n(\ln n - 1 + \delta),\ n >> 1,\ \delta \sim \frac{\ln(2\pi n)}{2n}$$

$$S_{\text{config}} \approx k\left[N \ln N - n \ln n - (N-n)\ln(N-n)\right]$$

Good approximation only on a macroscopic scale

Defect concentration

Minimize the free energy of the system with respect to the number of defects



$$G(n) = \widetilde{G}_0 + n\Delta G_f - TS_{\mathrm{config}}(n)$$

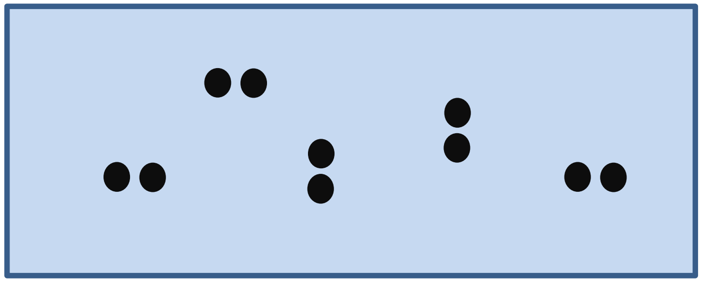
If defects do not interact:

$$\frac{n}{N} = \frac{1}{\exp\left(\Delta G_f / kT\right) + 1}$$

$$\frac{n}{N} << 1 \Leftrightarrow \exp\left(\Delta G_f / kT\right) >> 1$$

$$\frac{n}{N} \approx \exp\left(-\Delta G_f(T,p)/kT\right)$$ **– textbook formula**

Internal defect disorder



spatial , spin, electronic degeneracy

$$S = k\ln\left(W_{\text{internal}}W_{\text{external}}\right) =$$
$$= S_{\text{internal}} + S_{\text{external}}$$

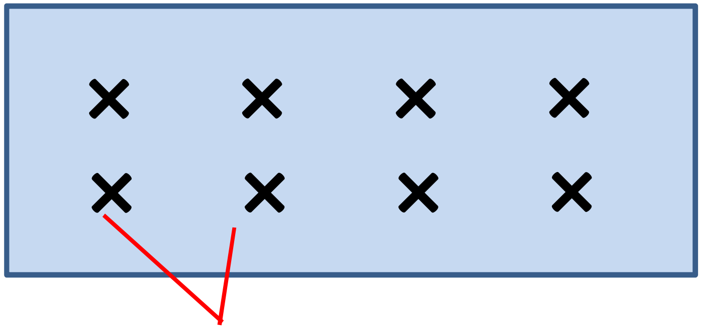
$$\Delta G_f \Rightarrow \Delta G_f - kT\ln\left(W_{\text{internal}}\right)$$

$$\Downarrow$$

$$\frac{n}{N} = \frac{1}{\dfrac{1}{W_{\text{internal}}}\exp\left(\Delta G_f / kT\right) + 1}$$

Constrained equilibrium: Competing defects

A practically relevant constrained defect equilibrium (e.g., at surfaces):



spatially separated sites

Let there be a global equilibrium (gas + surface)

What is the number of *different* defects (without assuming small concentrations)?

Constrained equilibrium: Competing defects

$$G = G_0 + \sum_k N_k (\Delta G_{fk} - kT \ln W_k) - TS_{\mathrm{config}}$$

$$\frac{\partial G}{\partial N_i} = 0, \ \sum_i N_i \le N_0$$

$$S_{\mathrm{config}} = k \ln \left(\frac{N_0!}{N_1!\,(N_0 - N_1)!} \frac{(N_0 - N_1)!}{N_2!\,(N_0 - N_1 - N_2)!} \times \cdots \times \frac{(N_0 - \sum_{k \neq i} N_k)!}{N_i!\,(N_0 - \sum_k N_k)!} \right)$$

Constrained equilibrium: Competing defects

$$G = G_0 + \sum_k N_k (\Delta G_{fk} - kT \ln W_k) - TS_{\text{config}}$$

$$\frac{\partial G}{\partial N_i} = 0, \ \sum_i N_i \leq N_0$$

$$\frac{\partial S_{\text{config}}}{\partial N_i} = -k \ln\left(\frac{N_i}{N_0 - \sum_k N_k} \right)$$

Constrained equilibrium: Competing defects

$$G = G_0 + \sum_k N_k (\Delta G_{fk} - kT \ln W_k) - TS_{\text{config}}$$

$$\frac{\partial G}{\partial N_i} = 0, \ \sum_i N_i \le N_0$$

$$\Downarrow$$

$$\Delta G_{fi} - kT \ln W_i + kT \ln \left(\frac{N_i}{N_0 - \sum_k N_k} \right) = 0$$

$$N_i \frac{1}{W_i} \mathrm{e}^{\frac{\Delta G_{fi}}{kT}} = N_0 - \sum_k N_k$$

Constrained equilibrium: Competing defects

$$N_i \frac{1}{W_i} \mathrm{e}^{\frac{\Delta G_{fi}}{kT}} = N_0 - \sum_k N_k$$

Coupled equations, but easy to solve:

$$N_k \frac{1}{W_k} \mathrm{e}^{\frac{\Delta G_{fk}}{kT}} = N_i \frac{1}{W_i} \mathrm{e}^{\frac{\Delta G_{fi}}{kT}}$$

All concentrations can be expressed through one:

$$N_k = N_k(N_i)$$

$$N_i \frac{1}{W_i} \mathrm{e}^{\frac{\Delta G_{fi}}{kT}} = N_0 - \sum_k N_k(N_i) \Rightarrow N_i$$

Constrained equilibrium: Competing defects

$$n_i = \frac{N_i}{N_0} = \frac{W_i e^{-\Delta G_{fi}/kT}}{1 + \sum_l W_l e^{-\Delta G_{fl}/kT}}$$

The condition:

$$\sum_i n_i \leq 1$$

is *automatically fulfilled*, due to the correctly counted microstates

Charged defects and charge compensation

$$\frac{n}{N} = \frac{1}{\exp\left(\Delta G_f / kT\right) + 1}$$

for non-interacting defects

But can charged defects be considered as non-interacting?!

$Q_1 \neq 0$

$Q_2 \neq 0$

$$V_{\text{interact}} = \frac{Q_1 Q_2}{|r_1 - r_2|}$$

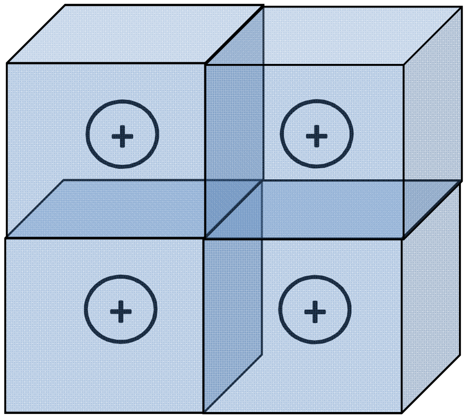
Coulomb interaction – long-range!

Charged defects and charge compensation

$Q_1 \neq 0$ **$Q_2 \neq 0$**

$$V_{\text{interact}} = \frac{Q_1 Q_2}{|r_1 - r_2|}$$

For a system of charges:



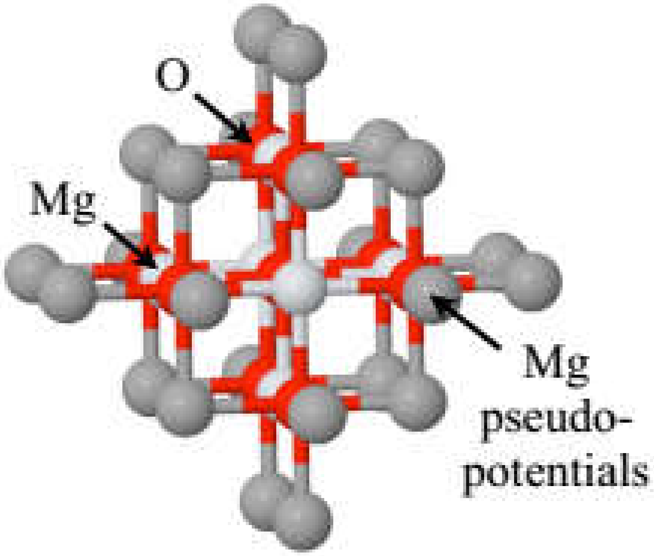
$$V_{\text{interact}} = \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{|r_i - r_j|}$$

In the thermodynamic limit (*N* → ∞) the electrostatic energy of charges with any finite concentration *diverges*

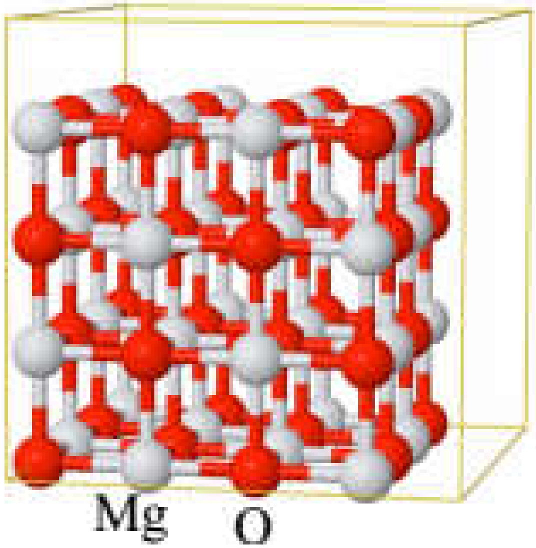
Charged defects *must be compensated* in realistic materials

Periodic and cluster models of defects

Embedded cluster model



Periodic model



+ Higher-level *ab initio* methods can be applied

+/- Defects in dilute limit

- Effect of embedding on the electronic structure and Fermi level – ?

+ Robust boundary conditions

+ Higher defect concentrations

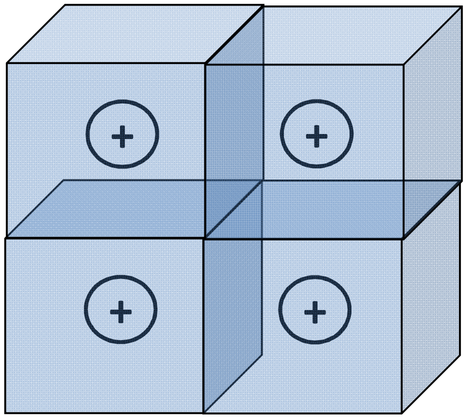
+/- Higher defect concentrations

- Artificial defect-defect interactions

P.V. Sushko, A.L. Shluger, and C.R.A. Catlow, Surf. Sci. 450, 153 (2000)

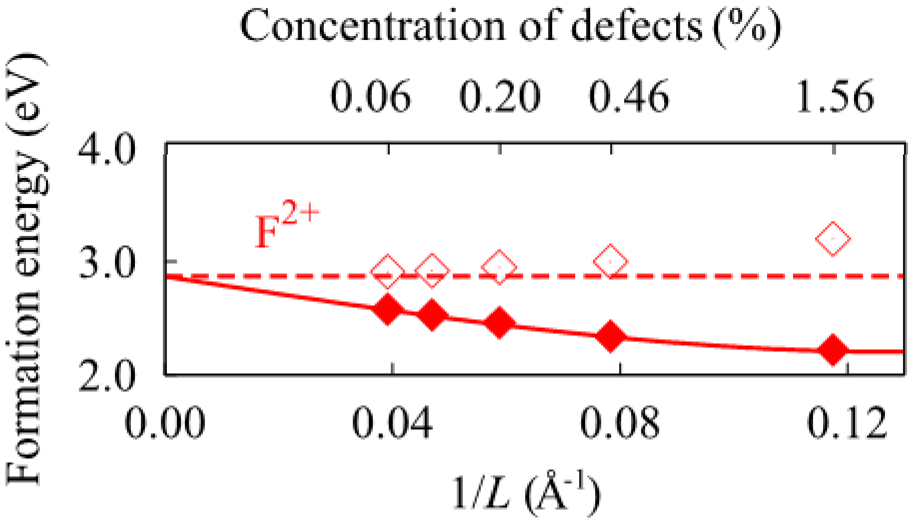
Charged defects and charge compensation

For a system of charges:



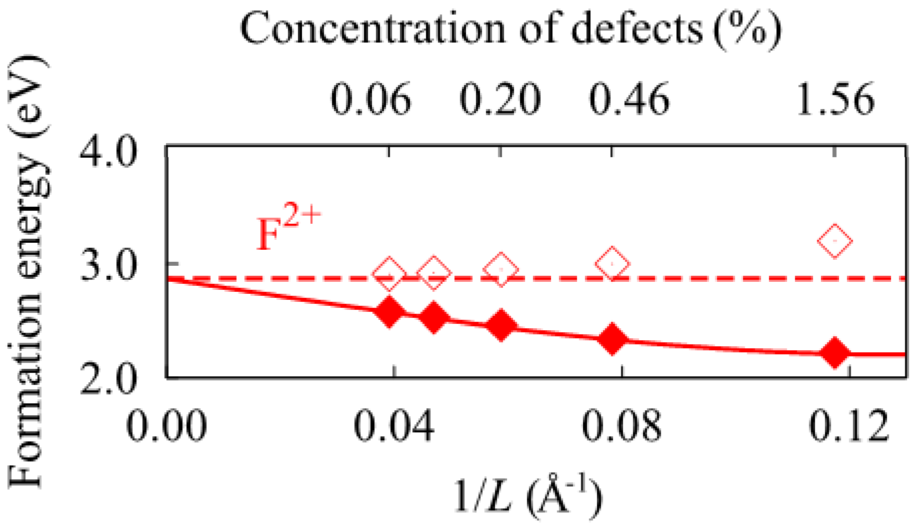
$$V_{\text{interact}} = \frac{1}{2}\sum_{i\neq j}\frac{Q_i Q_j}{|r_i - r_j|}$$

In the thermodynamic limit (*N* → ∞) the electrostatic energy of charges with any finite concentration *diverges*



Typical dependence of the defect formation energy as a function of unit cell size

Charged defects and charge compensation



Typical dependence of the defect formation energy as a function of unit cell size

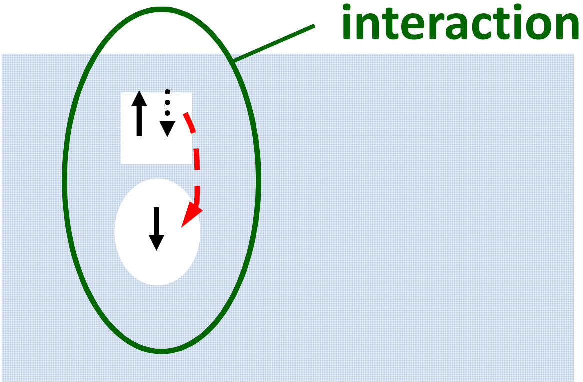
In standard periodic calculations the charge per unit cell is compensated by a uniform background charge (occurs naturally as a regularization of the Ewald summation)

The compensated defects interact much weaker with each other

But they do interact strongly with the background (~1/L)

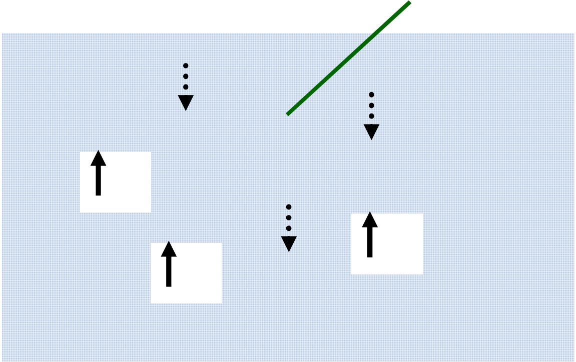
Local and global effects of doping

In realistic semiconductors, charged defects can be compensated by the *depletion* of charge carriers (electrons or holes)



interaction

Local effect of doping
(chemical bond formation)



electrons occupying hole states (localized or not)

Global effect of doping
(interaction with the compensating charge)

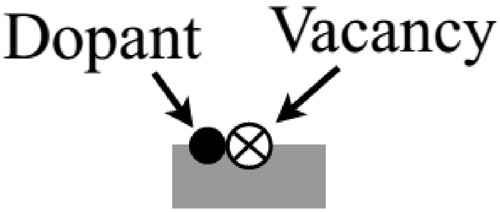
Formation energy and concentration of charged defects depend strongly on the distribution of the defects and the compensating charge

Defect-defect interactions

$$\frac{\partial G(T,\{p\},\mu_e,\{n\})}{\partial n_i} = 0 \cancel{\Rightarrow} n_i \sim n_{\text{sites}} \exp(-\Delta G_f/kT)$$

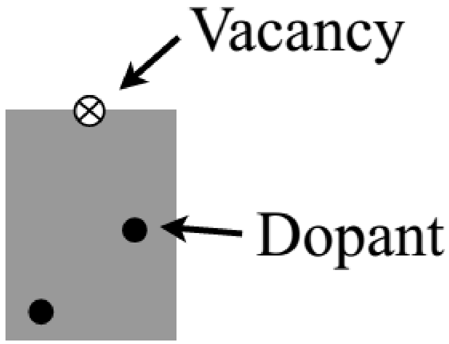
Local interactions:

- **Local relaxation**
- **Chemical bonding**



Long-range (global) interactions:

- **Charging**
- **Fermi level shifting**



Charged defects at any finite concentration cannot be considered non-interacting and must be compensated

Charged defects in a doped material

$$\Delta G(n) = n\Delta G_f(n \to 0) + \frac{1}{2}\varepsilon_0 \int \varepsilon(\mathbf{r})\left|\mathbf{E}\right|^2 d^3 r - TS_{\text{config}}(n)$$

formation energy
in the dilute limit

electrostatic energy
at finite *n*

$$S_{\text{config}} = k\ln Z + kT\frac{\partial \ln Z}{\partial T},\ Z = \sum_i e^{-E_i/kT}$$

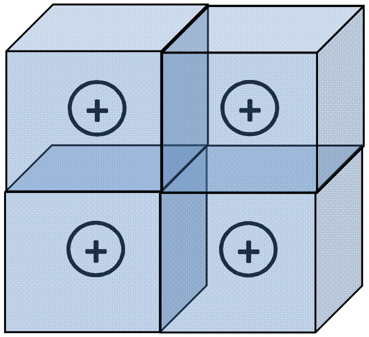
The charged defects are screened by the compensating charge:

$$S_{\text{config}} \approx k\ln\frac{N!}{n!(N-n)!}$$

Charged defects must be compensated

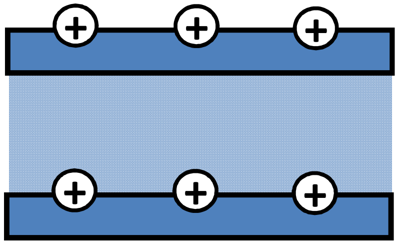
The compensation depends on the spatial distribution of the density of states near the Fermi level

1) A standard model for a uniform distribution: uniform background charge



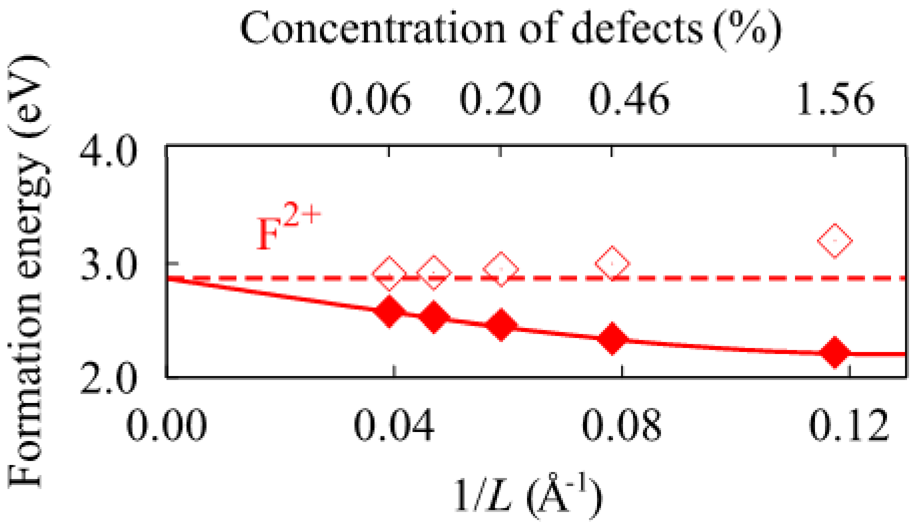
Bulk – OK (somewhat artificial)

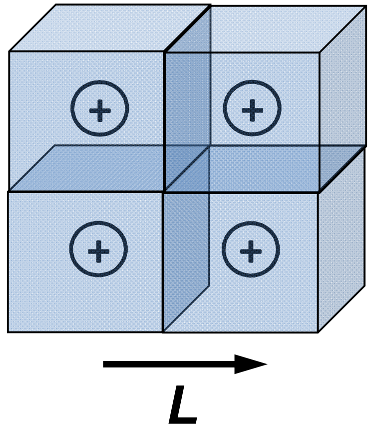
Surface: compensating density largely in the vacuum region (*a posteriori* corrections exist)



H.-P. Komsa and A. Pasquarello, Phys. Rev. Lett. **110**, 095505 (2013);
C. Freysoldt and J. Neugebauer, Phys. Rev. B **97**, 205425 (2018)

Makov-Payne correction (bulk)





Madelung constant (lattice dependent)

$\frac{q^2\alpha}{2\varepsilon}$

=0 in the bulk

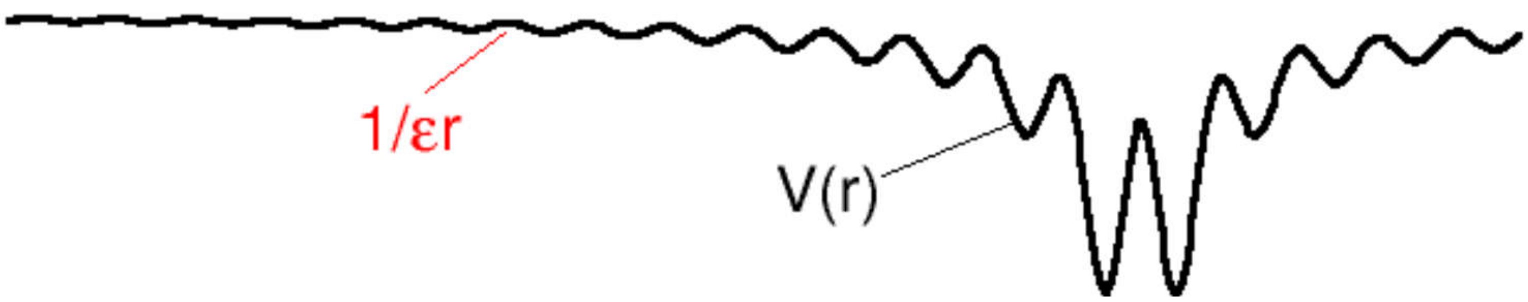
$\frac{2\pi q Q}{3\varepsilon}$ in cubic lattices

$$\Delta E_{\mathrm{formation}} = a_0 - \frac{a_1}{L} - \frac{a_2}{L^2} - \frac{a_3}{L^3} + O(L^{-5})$$

Problems: can be easily calculated only for cubic lattices, only isotropic materials (ε scalar versus tensor)

Freysoldt-Neugebauer-Van de Walle correction

Isolated charged defect:



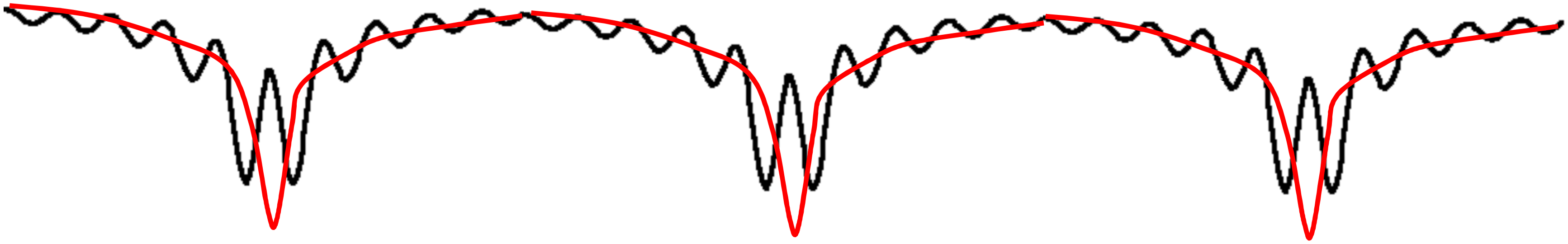
Charged defect in a supercell:

$$V(\boldsymbol{r}) = V^{\text{short−range}}(\boldsymbol{r}) + V^{\text{long−range}}(\boldsymbol{r})$$

C. Freysoldt, J. Neugebauer, and C.G. Van de Walle, Phys. Status Solidi B 248, 1067 (2011)

Freysoldt-Neugebauer-Van de Walle correction

Charged defect in a supercell:



$$V(\boldsymbol{r}) = V^{\text{short-range}}(\boldsymbol{r}) + V^{\text{long-range}}(\boldsymbol{r})$$

$$V^{\text{long-range}}(\boldsymbol{r}) = \sum_{\boldsymbol{R}} \int d^3r' \, \frac{q^{\text{model}}(\boldsymbol{r}')}{|\boldsymbol{r}+\boldsymbol{R}-\boldsymbol{r}'|}$$

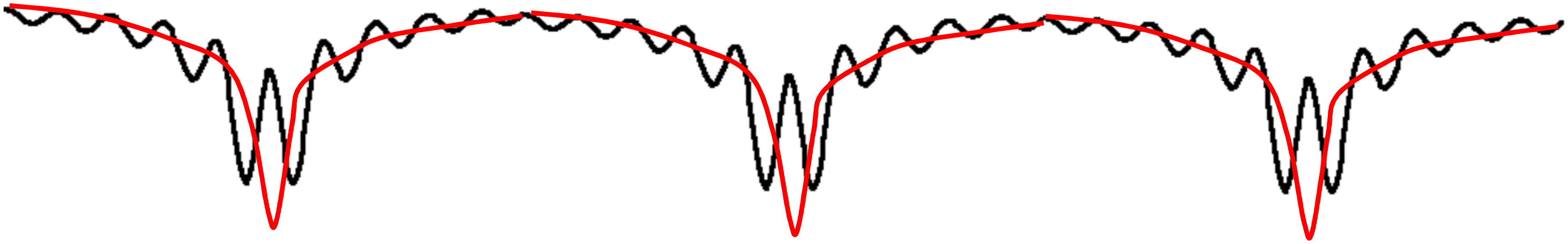
model charge distribution

lattice sum

C. Freysoldt, J. Neugebauer, and C.G. Van de Walle, Phys. Status Solidi B 248, 1067 (2011)

Freysoldt-Neugebauer-Van de Walle correction

Charged defect in a supercell:



$$V(\boldsymbol{r}) = V^{\text{short-range}}(\boldsymbol{r}) + V^{\text{long-range}}(\boldsymbol{r})$$

$$E^{\text{long-range}} = \frac{2\pi}{\varepsilon\Omega} \sum_{\boldsymbol{G}\neq 0}^{|\boldsymbol{G}|<G_{\text{cut}}} \frac{\{q^{\text{model}}(|\boldsymbol{G}|)\}^2}{|\boldsymbol{G}|^2} - \frac{1}{\pi\varepsilon} \int dG \{q^{\text{model}}(G)\}^2$$

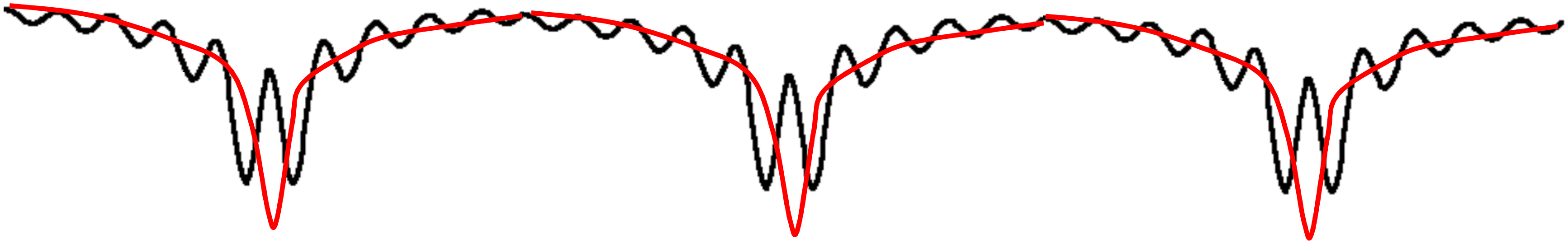
Ewald summation (long-range part)

remove self-interaction

C. Freysoldt, J. Neugebauer, and C.G. Van de Walle, Phys. Status Solidi B 248, 1067 (2011)

Freysoldt-Neugebauer-Van de Walle correction

Charged defect in a supercell:



$$E^{\text{long-range}} = \frac{2\pi}{\varepsilon\Omega} \sum_{\boldsymbol{G}\neq 0}^{|\boldsymbol{G}|<G_{\text{cut}}} \frac{\left\{q^{\text{model}}(|\boldsymbol{G}|)\right\}^2}{|\boldsymbol{G}|^2} - \frac{1}{\pi\varepsilon}\int dG\left\{q^{\text{model}}(G)\right\}^2$$

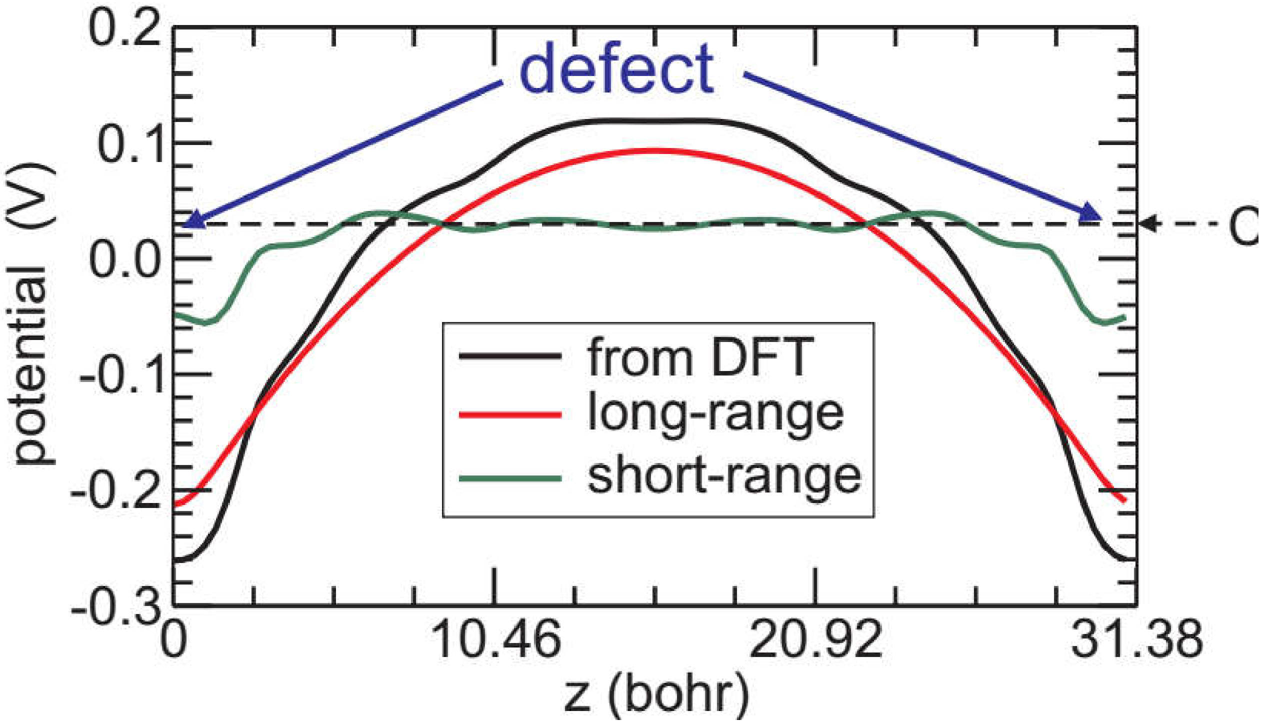
$$G_{\text{formation}}^{\text{isolated}}(q) = G_{\text{formation}}^{\text{suercell}}(q) - E^{\text{long-range}} + qC$$

from compensating background (alignment term)

C. Freysoldt, J. Neugebauer, and C.G. Van de Walle, Phys. Status Solidi B 248, 1067 (2011)

Freysoldt-Neugebauer-Van de Walle correction

$$G^{\mathrm{isolated}}_{\mathrm{formation}}(q) = G^{\mathrm{suercell}}_{\mathrm{formation}}(q) - E^{\mathrm{long-range}} + qC$$



$$C = \frac{1}{\Omega}\int d^3r\left\{V^{\mathrm{short-range}}_{\mathrm{model}}(\boldsymbol{r}) - V^{\mathrm{short-range}}_{\mathrm{defect}}(\boldsymbol{r})\right\}$$

C. Freysoldt, J. Neugebauer, and C.G. Van de Walle, Phys. Status Solidi B 248, 1067 (2011)

Freysoldt-Neugebauer-Van de Walle correction

$$E^{\mathrm{long-range}} = \frac{2\pi}{\varepsilon\Omega} \sum_{\boldsymbol{G}\neq 0}^{|\boldsymbol{G}|<G_{\mathrm{cut}}} \frac{\left\{q^{\mathrm{model}}(|\boldsymbol{G}|)\right\}^2}{|\boldsymbol{G}|^2} - \frac{1}{\pi\varepsilon}\int dG \left\{q^{\mathrm{model}}(G)\right\}^2$$

screened Coulomb interaction:

- **originally formulated for electronic response only (ε_∞)**

- **was shown to work when ionic response is included (ε_0), but this is still under investigation (can fail for polarons)**

- **can be easily generalized to anisotropic materials ($\varepsilon \rightarrow \varepsilon_{ij}$)**

The method is for calculating formation energy of isolated defect

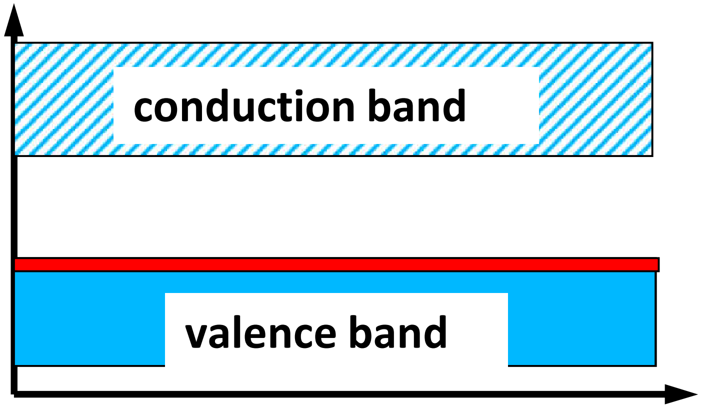
C. Freysoldt, J. Neugebauer, and C.G. Van de Walle, Phys. Status Solidi B 248, 1067 (2011)

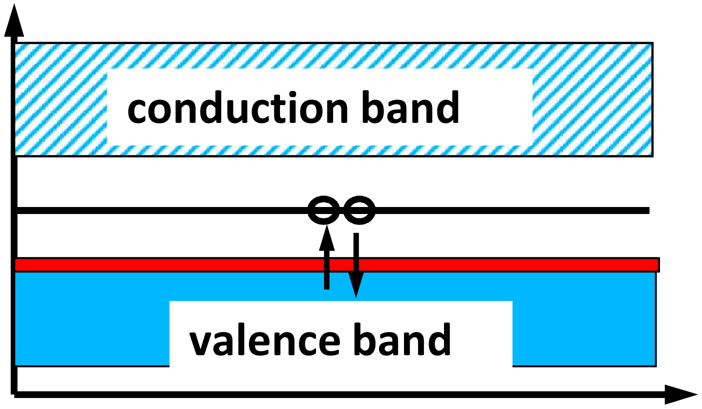
Charged defects must be compensated

2) Impurity donors/acceptors – large concentrations, artificial interactions

3) Simulate distributed doping with virtual crystal approximation – arbitrarily small concentrations with finite unit cells, correction for the dilute limit is needed

$q_{\mathrm{Mg}} = 12 - q_{\mathrm{defect}}/N_{\mathrm{Mg}} \Longrightarrow$ ***p*-type doping in MgO**

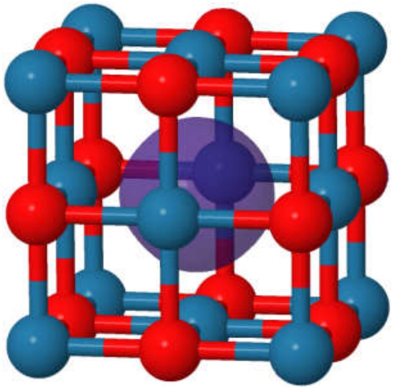




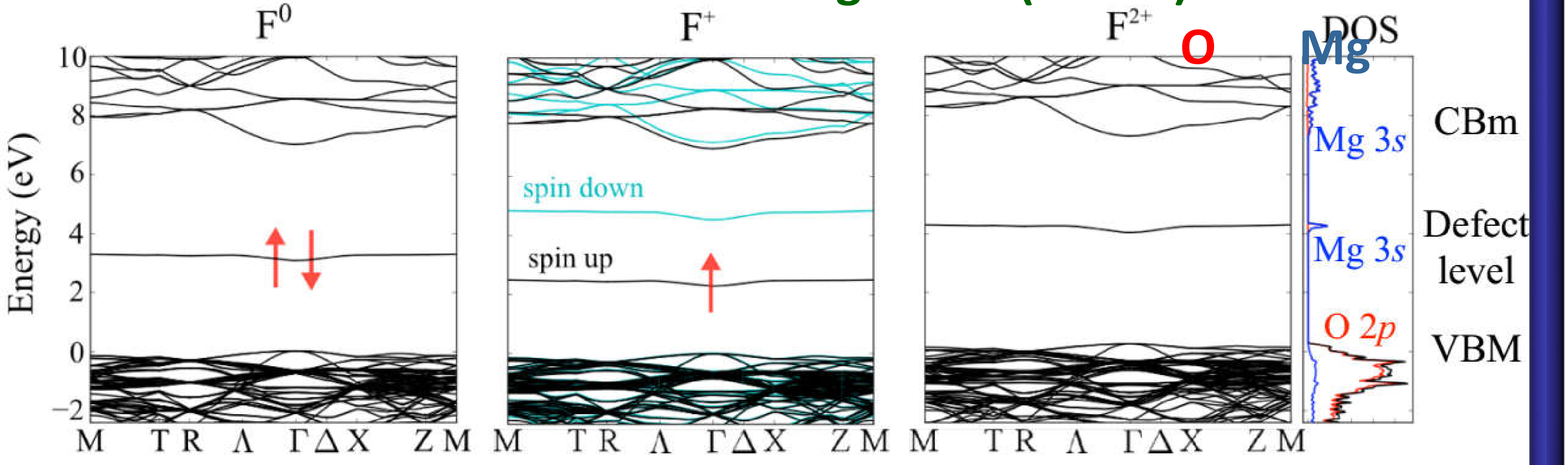
L. Vegard, Z. Phys. **5**, 17 (1921); M. Scheffler, Physica B+C **146**, 176 (1987); O. Sinai and L. Kronik, Phys. Rev. B **87**, 235305 (2013)

O vacancies (F-centers) in MgO

MgO bulk with oxygen vacancy

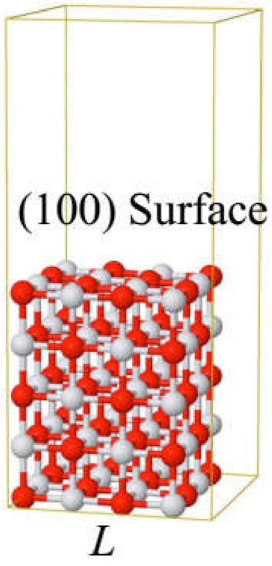


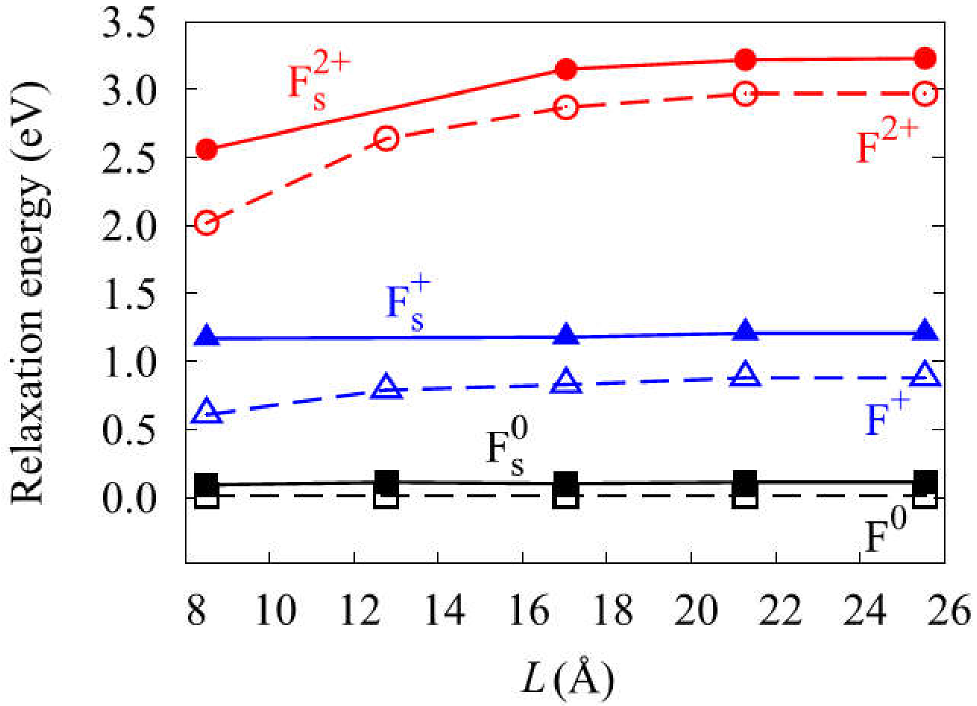
Band structures of O vacancies in MgO bulk (HSE06)

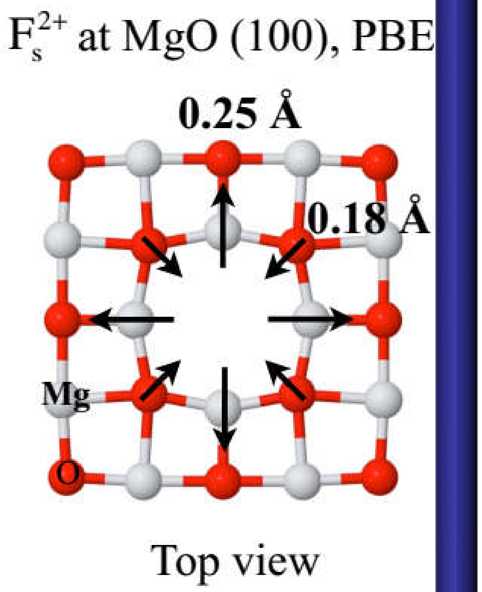


Atomic relaxation

Relaxation energies for F centers in MgO bulk and at MgO (100)



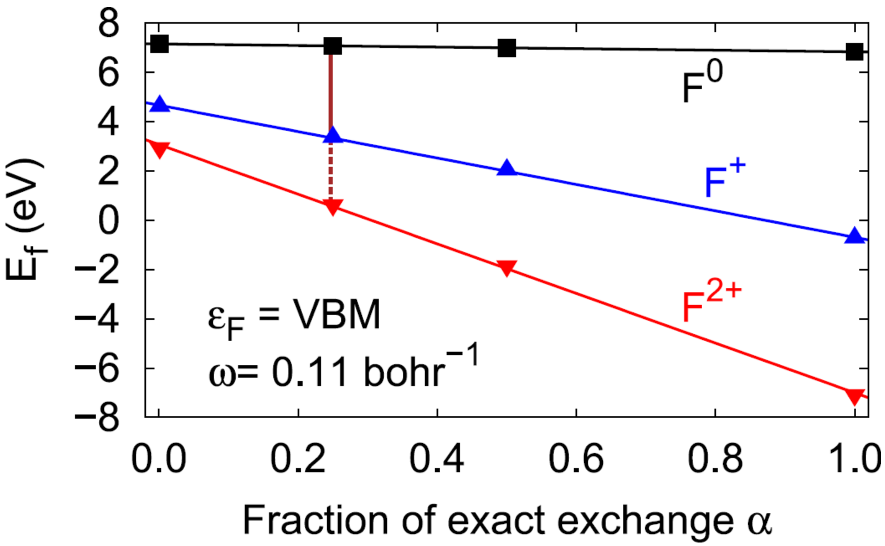


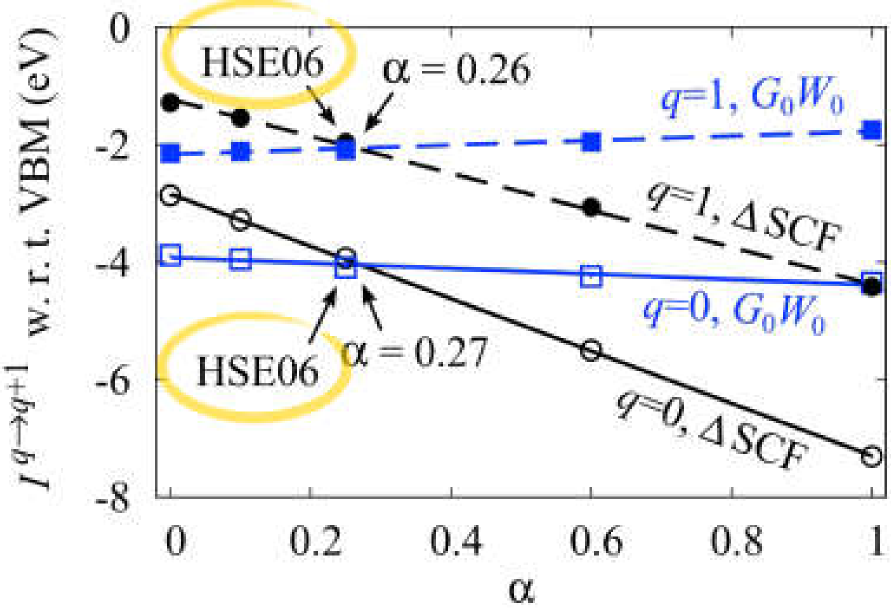


Sensitivity to approximations in DFT

Energy differences between different charge states$^{1)}$

$$\Delta G_{\mathrm{f}}^{\mathrm{D}}(q=+1) = \underbrace{\Delta G_{\mathrm{f}}^{\mathrm{D}}(q=0) - \Delta_{+1}^{0}}_{\textbf{DFT}} + \underbrace{\mathrm{IP}_{\text{defect level}} - \mathrm{IP}_{\text{VBM}}}_{\boldsymbol{G_0W_0}}$$



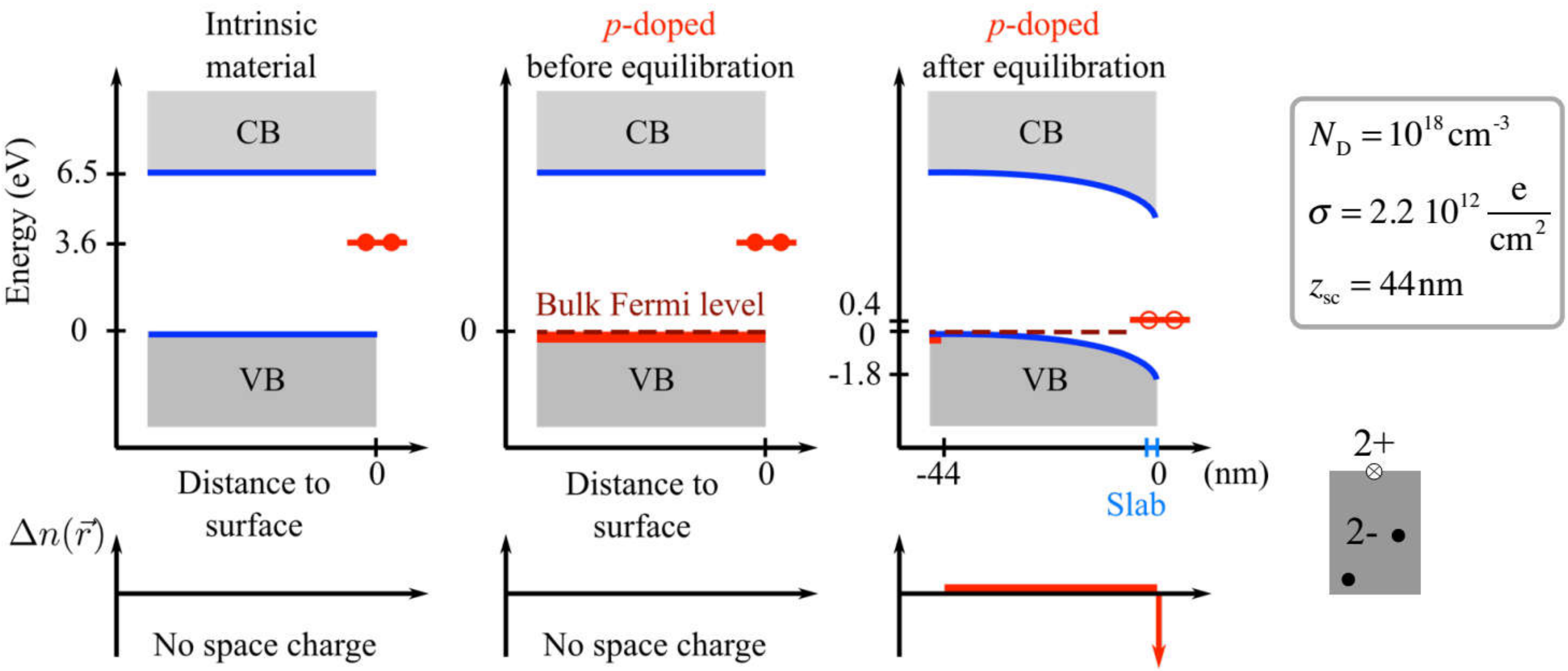


(Mg$_6$O$_9$ embedded cluster model)

Also important for optical properties

1) Rinke *et al*., Phys. Rev. Lett. **108**, 126404 (2012)
2) Kappers, Kroes, and Hensley, Phys. Rev. B **1**, 4151, (1970)

Interacting defects: Space-charge effects



$$N_D = 10^{18}\,\text{cm}^{-3}$$

$$\sigma = 2.2\ 10^{12}\,\frac{\text{e}}{\text{cm}^2}$$

$$z_{sc} = 44\,\text{nm}$$

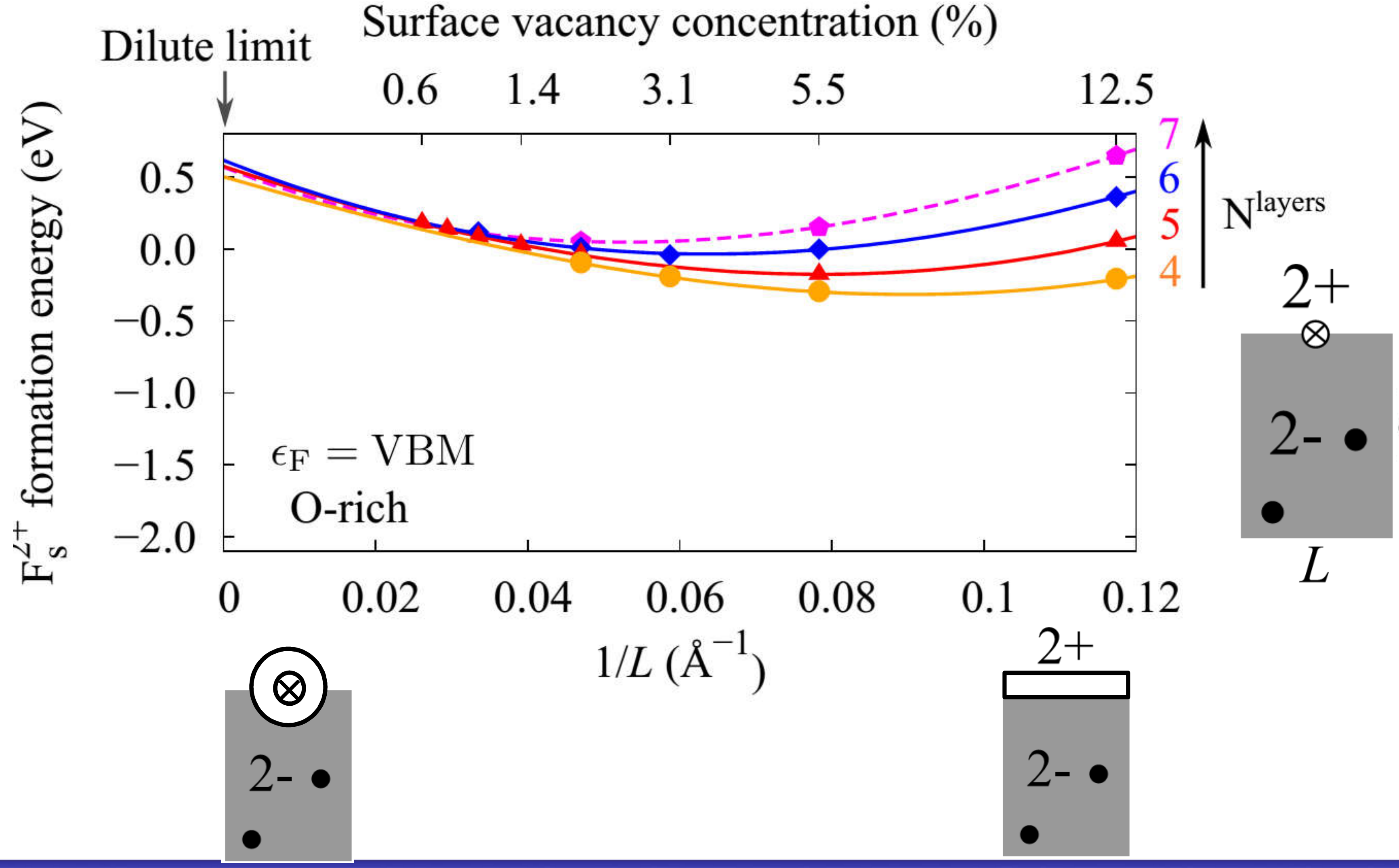
Space charge region $z_{sc} = \dfrac{\sigma}{e\ N_D}$ causes band bending and electric field

N_D : Dopant concentration

σ : Surface charge due to vacancy concentrations $\sigma = (e\eta_1 + 2e\eta_2)$

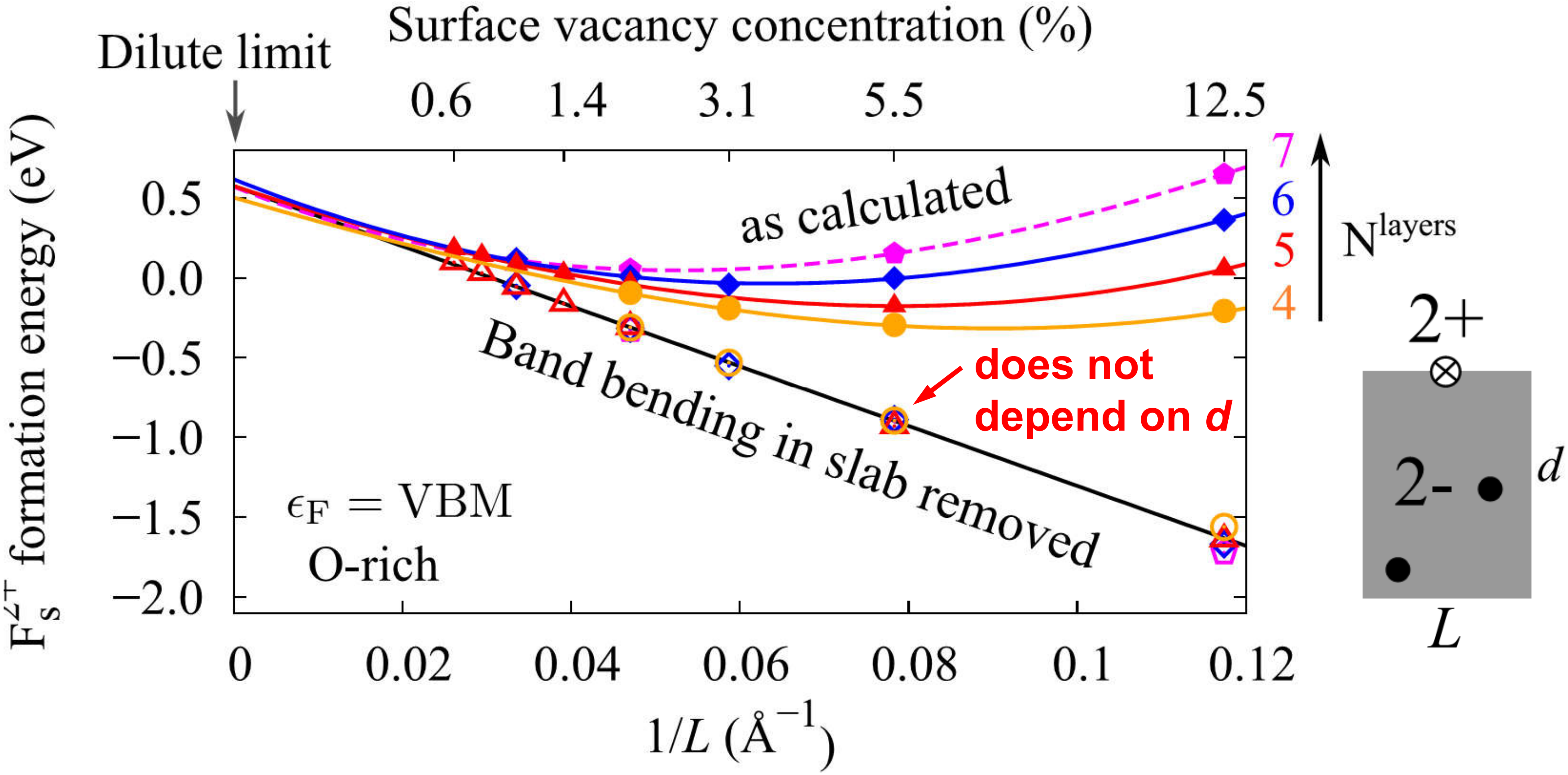
Electrostatics in periodic calculations of charged defects

$$\Delta G_{\mathrm{f}}^{\mathrm{VCA}}(\sigma,d)=E_{\mathrm{vac}}^{q}(\sigma,d)(+q\varepsilon_{\mathrm{VBM}})-E_{\mathrm{host}}(\sigma,d)+\frac{1}{2}E_{\mathrm{O}_2}$$



Electrostatics in periodic calculations of charged defects

$$\Delta G_{\mathrm{f}}^{\mathrm{VCA}}(\sigma,d) = E_{\mathrm{vac}}^{q}(\sigma,d)(+q\varepsilon_{\mathrm{VBM}}) - E_{\mathrm{host}}(\sigma,d) + \frac{1}{2}E_{\mathrm{O}_2}$$



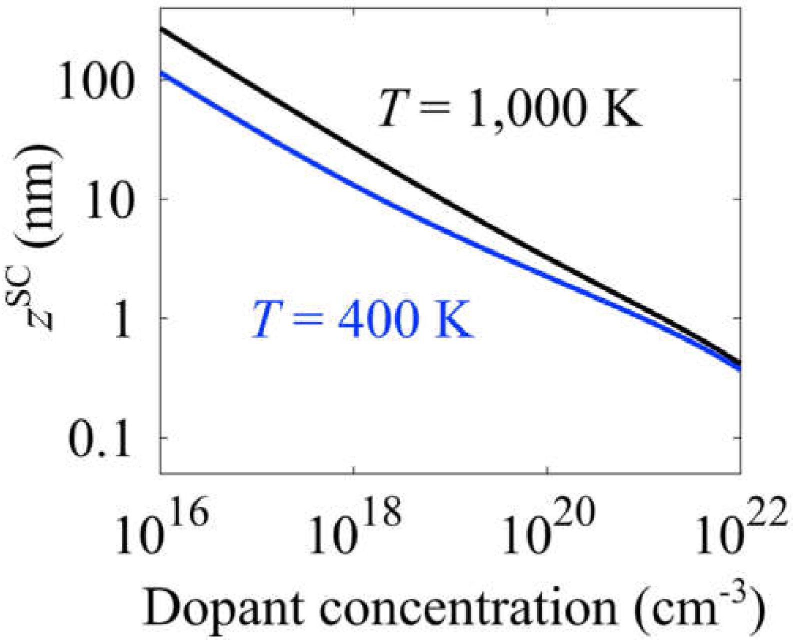
does not depend on *d*

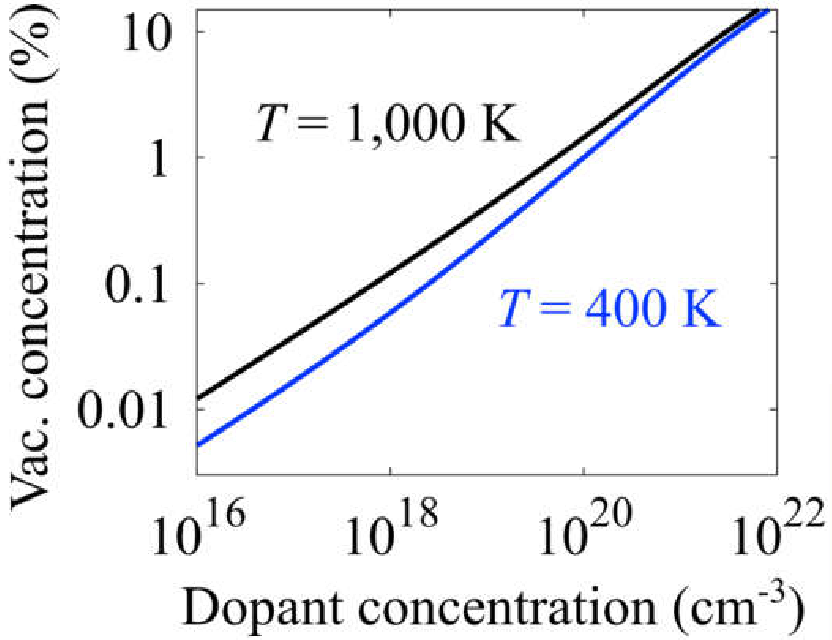
$$\frac{1}{2}\varepsilon\varepsilon_0\int\left|\mathbf{E}\right|^2 d^3r = -C\sqrt{|\sigma|} + qE^{\mathrm{SC}}(d),\ E^{\mathrm{SC}}(d) = \frac{e|\sigma|}{6\varepsilon\varepsilon_0}d$$

F^{2+} concentration at *p*-MgO(001)

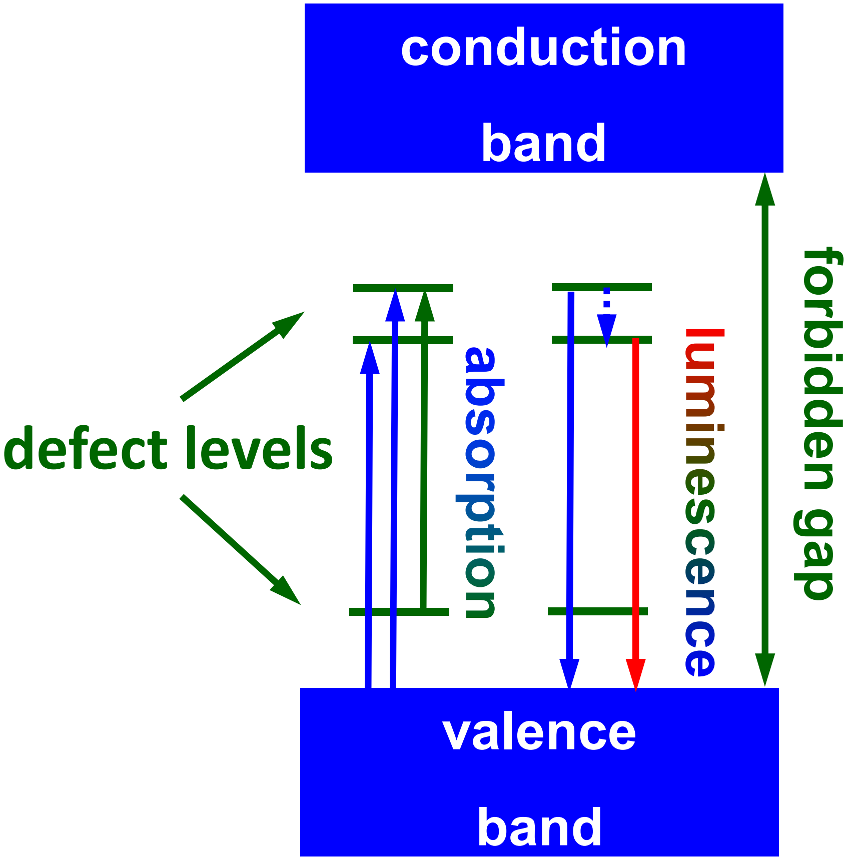
$$\Delta G_f^{\mathrm{semi-infinite}} = \Delta G_f^{\mathrm{slab}} - E_{\mathrm{band\ bending\ in\ slab}} + E_{\mathrm{real\ band\ bending}}$$

$$z^{\mathrm{SC}} = \frac{\sigma}{eN_{\mathrm{D}}}$$



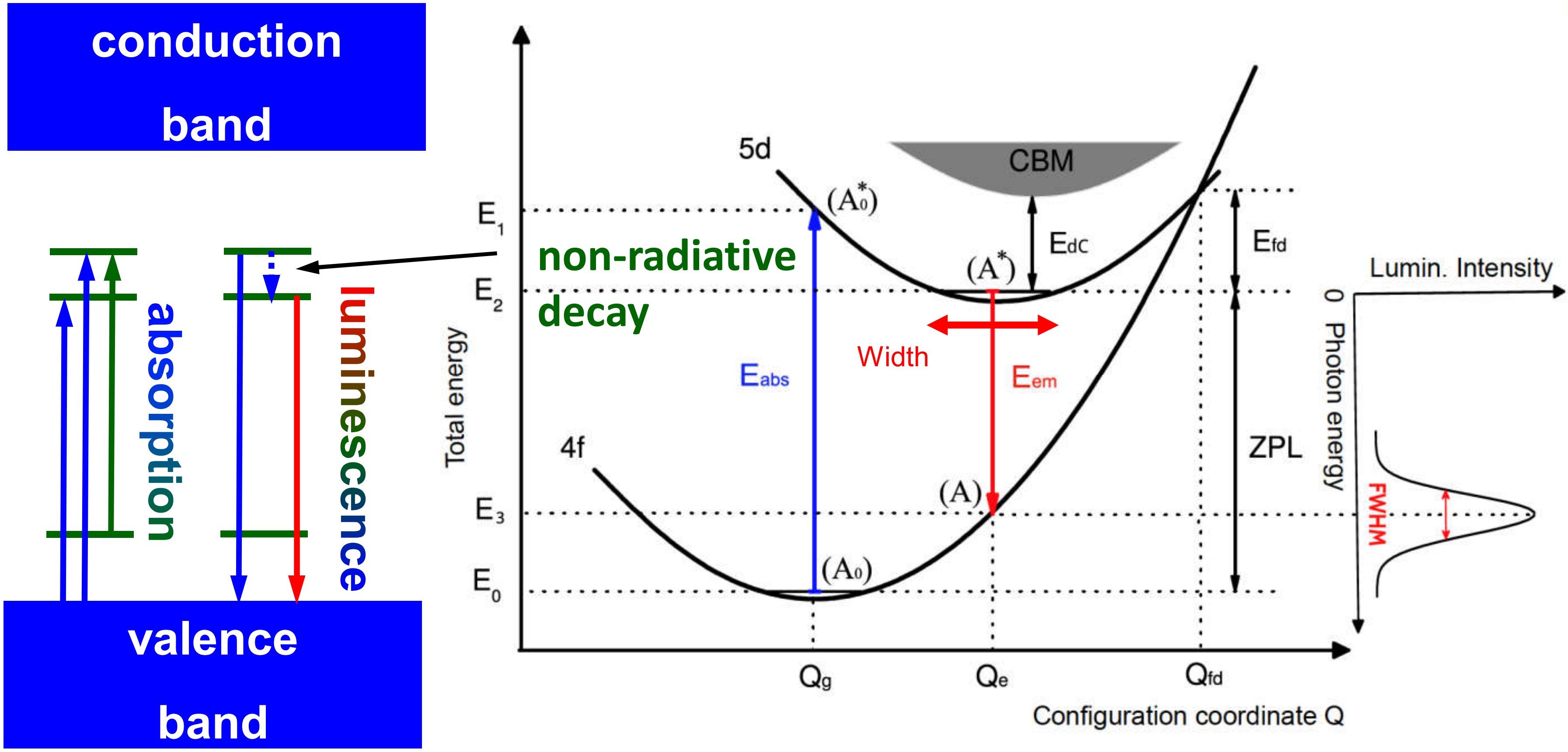


Optical properties of defects



Defects provide energy levels in the gap that influence light absorbtion and emission

Optical properties of defects



conduction band

absorption

luminescence

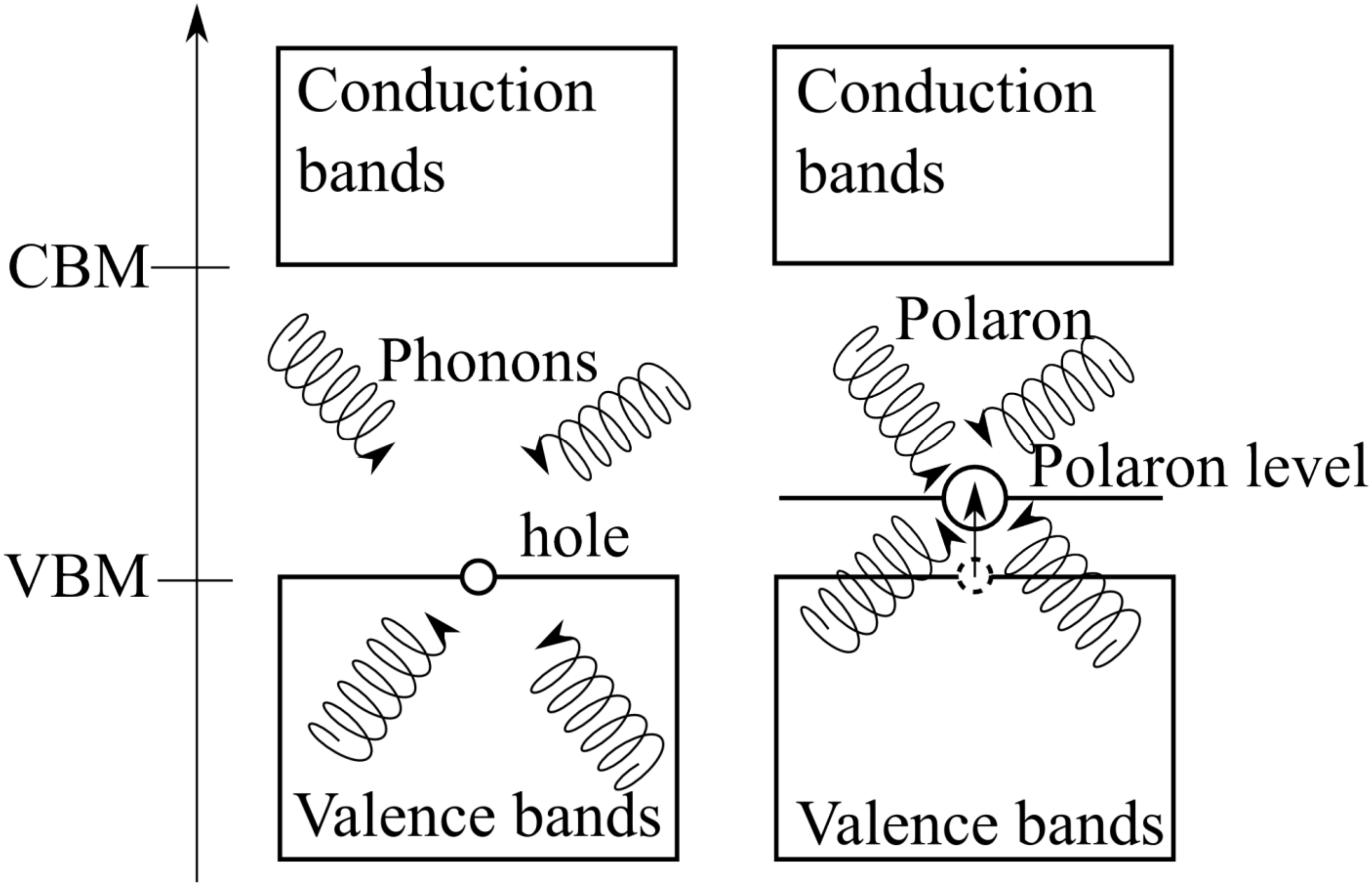
non-radiative decay

valence band

figure courtesy of Xavier

Non-radiative decay: relaxation of excited electron/hole due to release of heat (phonons)

Polarons



Polaron (quasiparticle): An electron or hole dressed in phonons (lattice relaxation)

Polaron properties

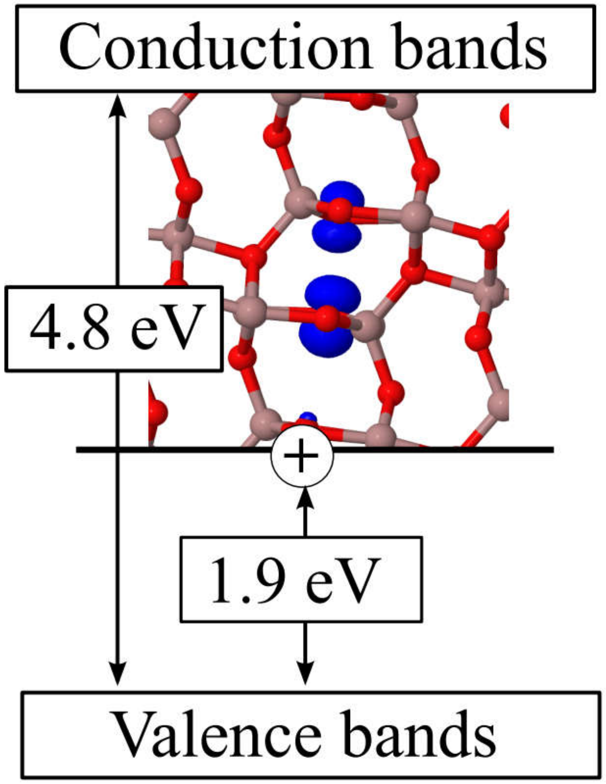
Prediction of polaron properties:

- **Geometry (radius) and orbital character of the polaron**

- **Binding energy (stability, mobility)**

$$E_{\text{bind}} = E_{\text{distort}}(N \mp 1) - E_{\text{perfect}}(N \mp 1)$$

- **Polaron level (luminescence, absorption)**



hole polaron in β-Ga_2O_3

Before modern electronic-structure calculations: Polaron models

Fröhlich model:

$$\begin{aligned}\hat{H}_{\text{polaron}} &= \hat{H}_{\text{kin,eff}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{el-ph}} \\ &= -\frac{\hbar^2}{2m_{\text{b}}}\nabla^2 + \sum_{\boldsymbol{q}} \hbar\omega_{\text{LO}} a^{+}_{\boldsymbol{q}} a_{\boldsymbol{q}} + \sum_{\boldsymbol{q}} \left(V_{\boldsymbol{q}} a_{\boldsymbol{q}} \mathrm{e}^{i\boldsymbol{q}\boldsymbol{r}} + h.c.\right)\end{aligned}$$

frequency of longitudinal optical phonon mode

Fourier components of electron-phonon interaction

$$V_{\boldsymbol{q}} = -i\frac{\hbar\omega_{\text{LO}}}{|\boldsymbol{q}|}\left(\frac{4\pi\alpha_{\text{F}}}{\Omega}\right)^{1/2}\left(\frac{\hbar}{2m_{\text{b}}\omega_{\text{LO}}}\right)^{1/4}$$

With Fröhlich coupling constant:

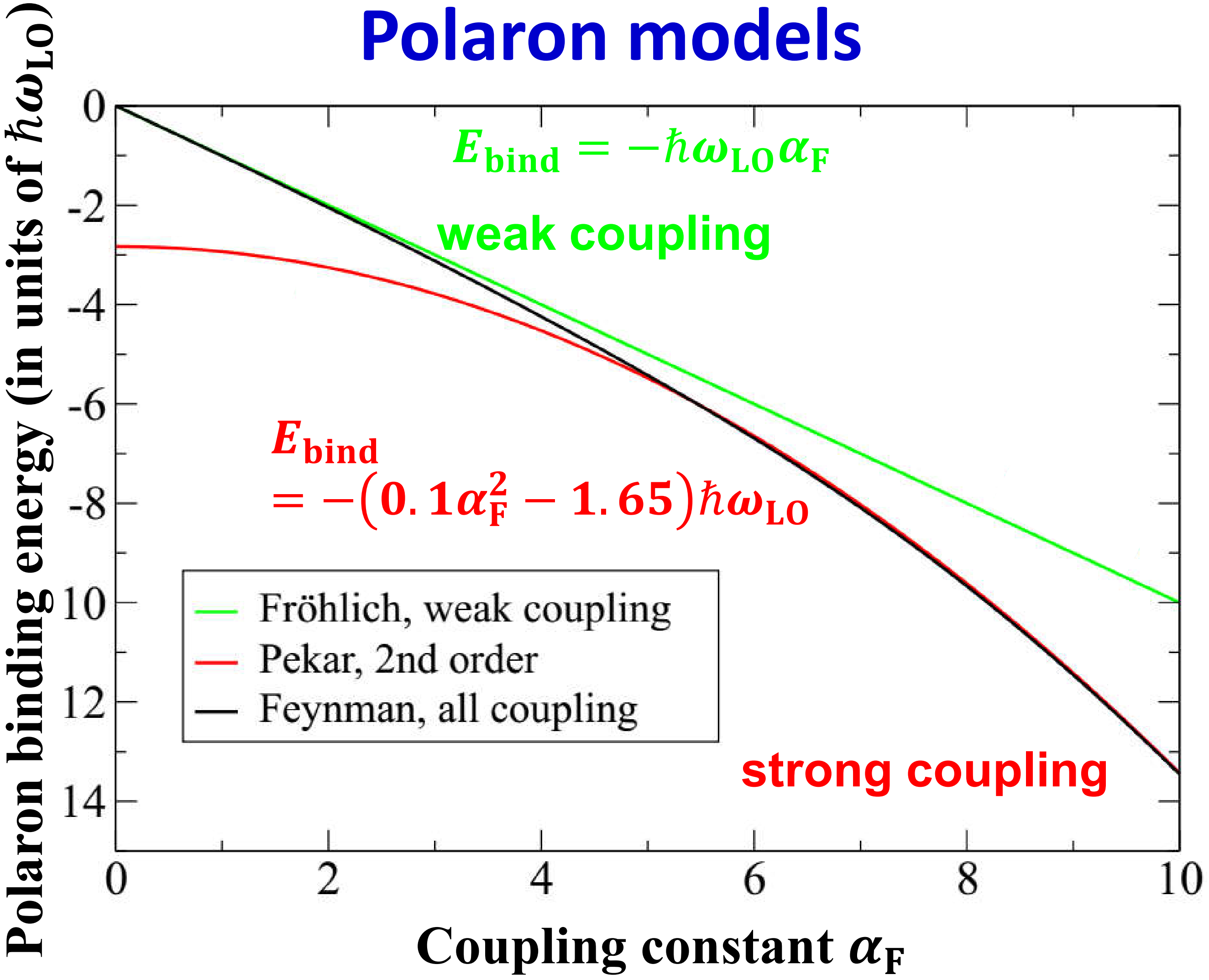
band mass (curvature of band)

$$\alpha_{\text{F}} = e^2\sqrt{\frac{m_{\text{b}}}{2\hbar^3\omega_{\text{LO}}}}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)$$

electronic dielectric response

static dielectric constant

Before modern electronic-structure calculations: Polaron models



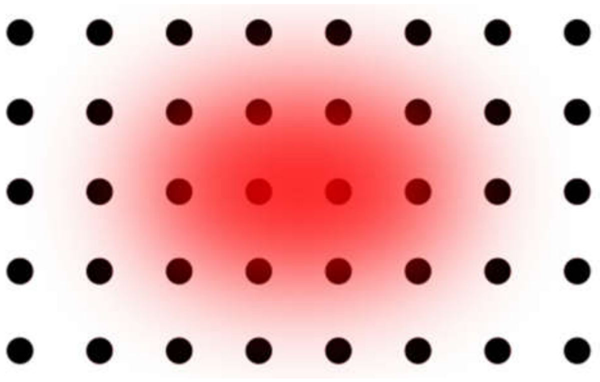
$$E_{\mathrm{bind}} = -\hbar\omega_{\mathrm{LO}}\alpha_{\mathrm{F}}$$

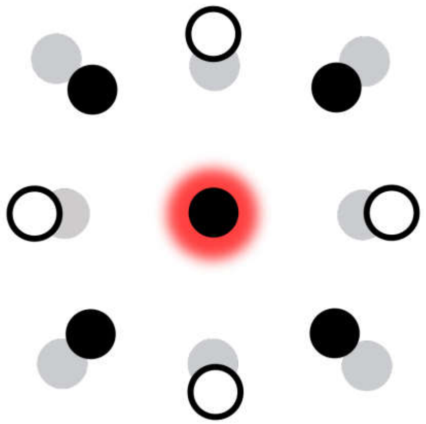
$$E_{\mathrm{bind}} = -\left(0.1\alpha_{\mathrm{F}}^{2} - 1.65\right)\hbar\omega_{\mathrm{LO}}$$

polaron radius: $r_p = 3.2\frac{1}{\alpha_{\mathrm{F}}}\sqrt{\frac{\hbar}{2m_{\mathrm{b}}\omega_{\mathrm{LO}}}}$

Small versus large polarons

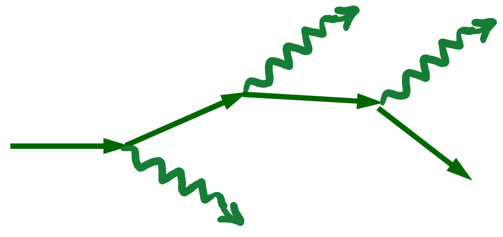
Polaron = Charge + Lattice Distortion

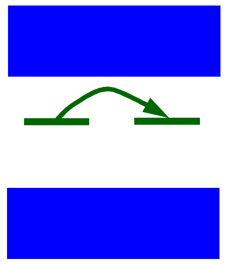




Large (Frölich) polaron (III-V and II-VI materials, alkaline halides)

Small polaron (metal oxides, polymers)





Mobility

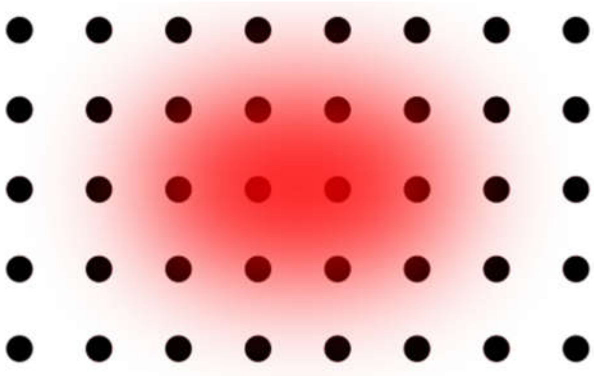
$\sim [\exp(\hbar\omega_{LO}/k_B T) - 1]$

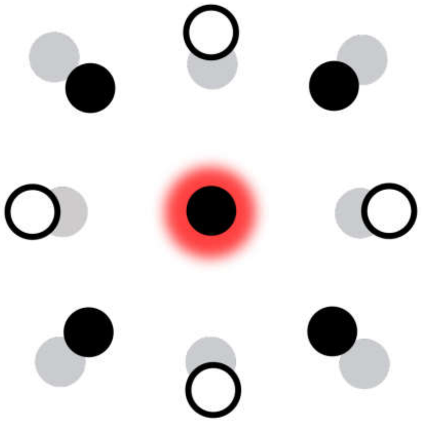
$\sim \exp(-E_a/k_B T)$

Approximations in Fröhlich model

1) Only one LO mode (simple crystals)
2) Polaron radius is large compared to lattice constant
3) LO mode’s dispersion in neglected

Modeling polarons with DFT





Large (Frölich) polaron (III-V and II-VI materials, alkaline halides)

Small polaron (metal oxides, polymers)

Mobility

$$\sim [\exp(\hbar\omega_{LO}/k_B T) - 1]$$

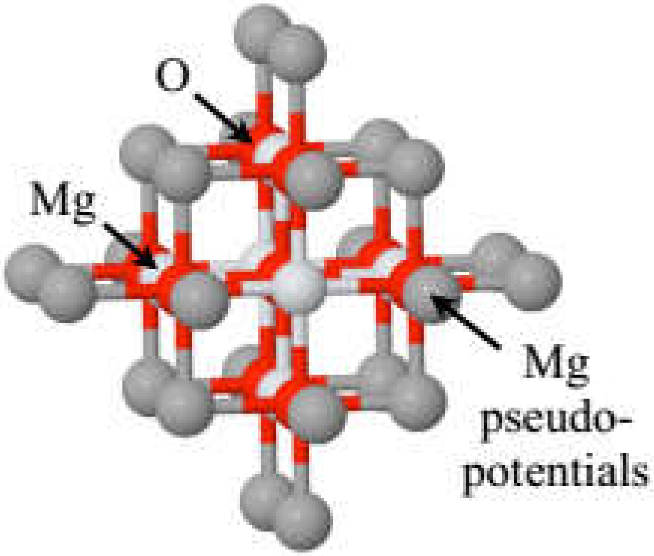
$$\sim \exp(-E_a/k_B T)$$

Perturbation theory

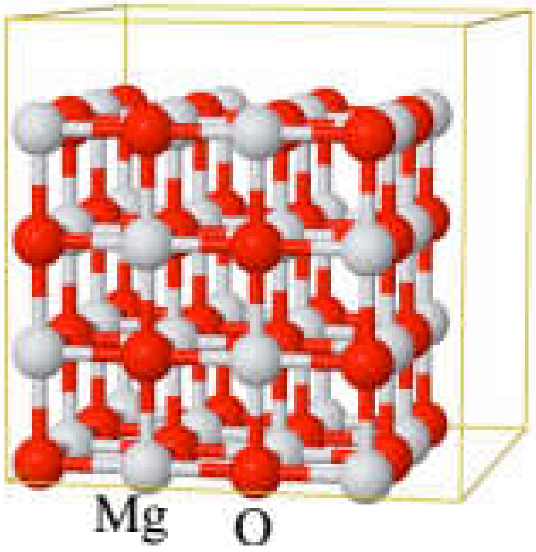
explicit calculation

Modeling polarons with DFT

Embedded cluster model



Periodic model



+ Isolated polaron

+ Higher-level methods can be applied

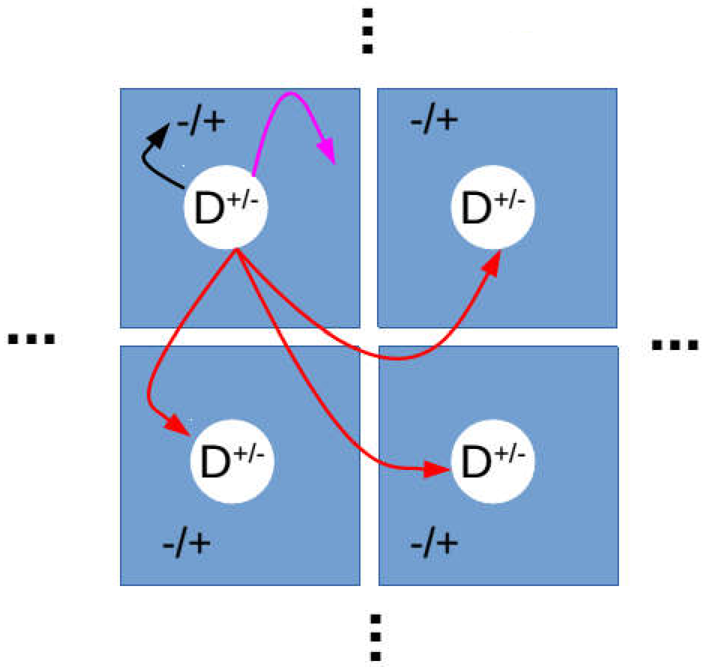
- No long-range phononic response

- Artificial finite-size effects

+ Long-range ionic response

- Artificial periodic repeat (finite-size effects)

Supercell calculations of small polarons



Finite-size errors

Approximation of the exchange correlation functional E_{XC}:
LDA, PBE, EXX, ...

Self-interaction error

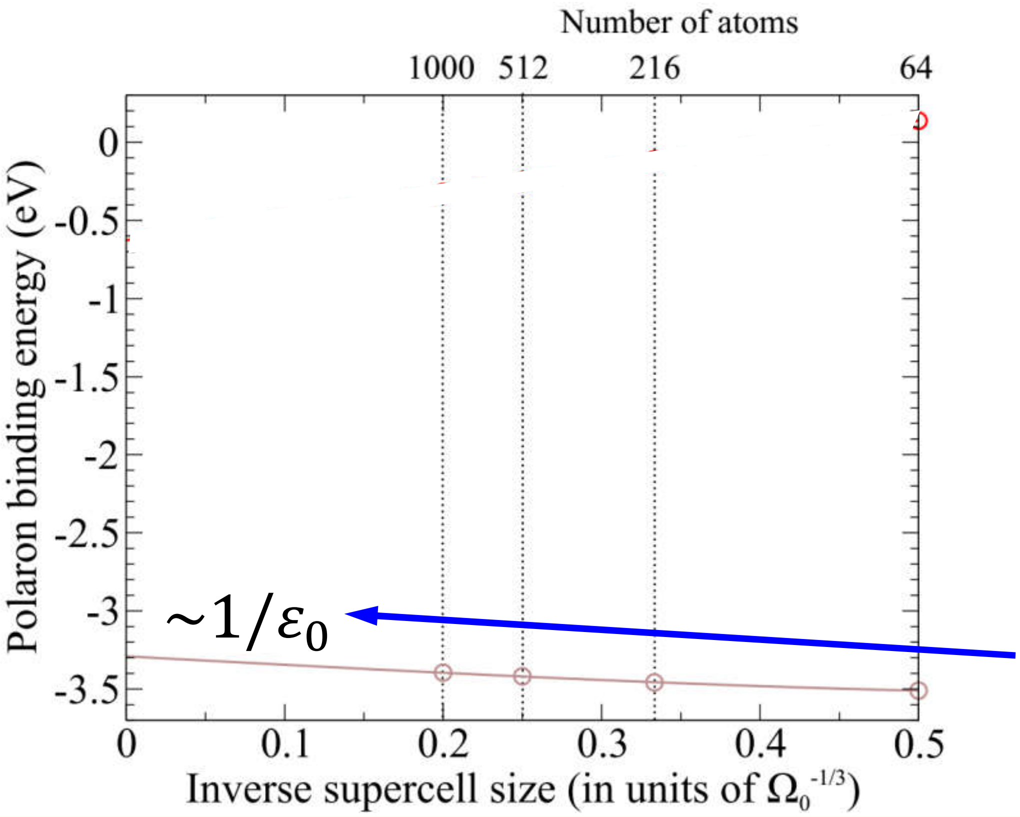
Delocalization - Localization

- Finite-size supercell errors
- Localization/Delocalization errors

The polaron potential energy surface

Conventional approach: Relax charged supercell (add or remove electron):

$$\min_{R_i}\{E(N-1)\}$$

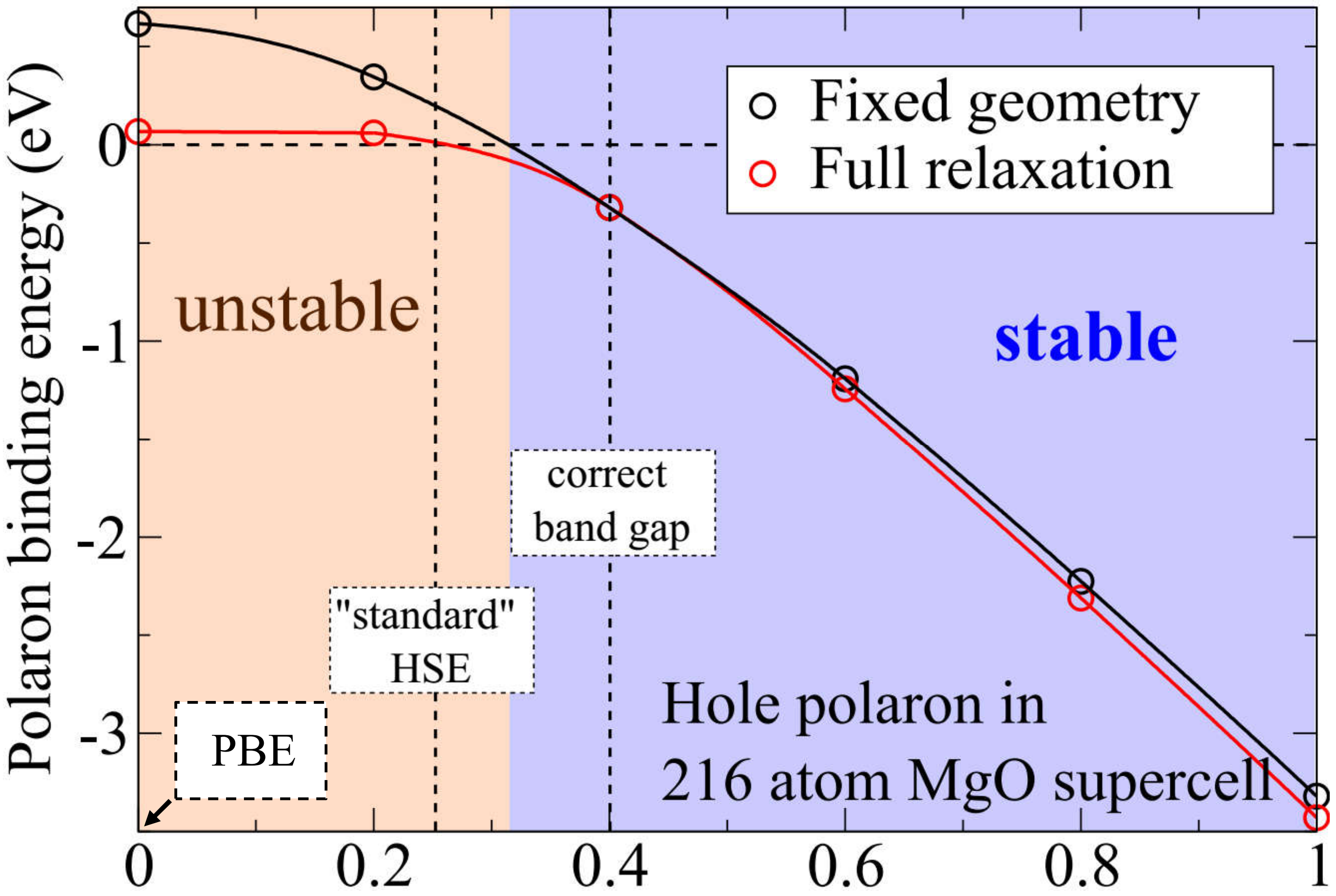


hole polaron in MgO, HSE(α=1)

Finite-size correction ~0.2 eV

Note: for polarons this is not always the case (e.g., TiO_2), depends on coupling strength

Conventional approach: Dependence on functional



Ionized system: *E*(*N*±1)

- Polaron properties show strong dependence on XC functional
- Even qualitative predictions are not possible

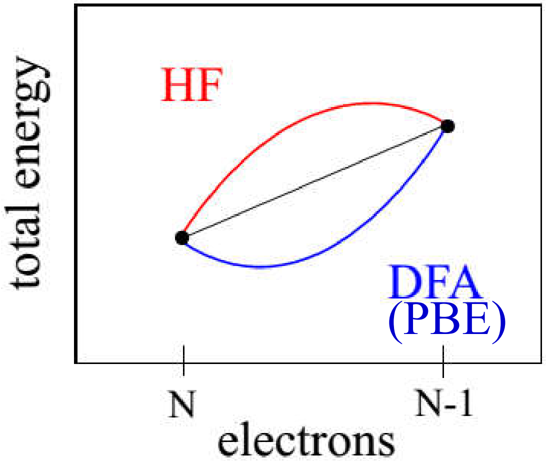
Theoretical challenges

Self-interaction error Σ_i

- Convex curvature
- PBE

Orbital relaxation Π_i

- Concave curvature
- Exact exchange



From (exact) DFT: **IP Theorem**

"Piecewise linearity of total energy with fractional occupation"

$$\boxed{E(N-1)-E(N)=-e_{ho}(N)}+\boxed{\Pi_i}+\boxed{\Sigma_i}+\boxed{\Delta}$$

Finite-size errors

Best hybrid functional [4]:

$$\exists\alpha: \Pi + \Sigma = \Delta_{XC} = 0$$

---

[3] Perdew et al., Phys. Rev. Lett. 49, 1691 (1982)
[4] Lany and Zunger, Phys. Rev. B 80, 085202 (2009)

Polaron binding energy

$$E_{\text{bind}} = E_{\text{distort}}(N-1) - E_{\text{perfect}}(N-1)$$

$$E_{\text{perfect}}(N-1) - E_{\text{perfect}}(N) = -\epsilon_{\text{VBM}}(N)$$
$$+\Pi_{\text{perfect}} + \Sigma_{\text{perfect}} + \Delta_{\text{perfect}}$$

$$E_{\text{bind}} = E_{\text{distort}}(N-1) - \left[E_{\text{perfect}}(N) - \epsilon_{\text{VBM}}(N)\right] + \Pi_{\text{p}} + \Sigma_{\text{p}} + \Delta_{\text{p}}$$

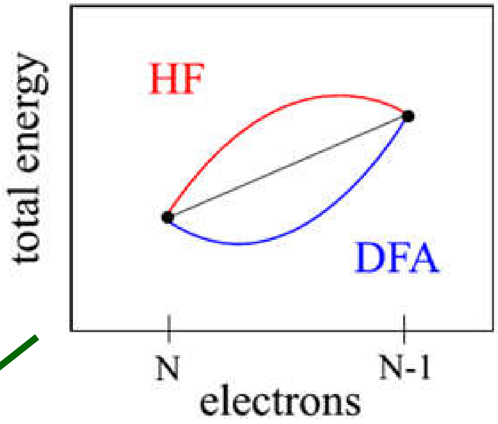
$$E_{\text{distort}}(N-1) - E_{\text{distort}}(N) = -\epsilon_{\text{HO}}(N)$$
$$+\Pi_{\text{distort}} + \Sigma_{\text{distort}} + \Delta_{\text{distort}}$$

$$E_{\text{bind}} = E_{\text{distort}}(N) - E_{\text{perfect}}(N) - [\epsilon_{\text{HO}}(N) - \epsilon_{\text{VBM}}(N)] +$$
$$(\Pi_{\text{d}} - \Pi_{\text{p}}) + (\Sigma_{\text{d}} - \Sigma_{\text{p}}) + (\Delta_{\text{d}} - \Delta_{\text{p}})$$

1) **Only *neutral* system needs to be calculated**
2) **Only *differences* in exchange-correlation corrections are present**

Zawadski et al., Chem. Phys. Lett. 506, 42 (2011)
Sadigh et al., PRB 92 , 075202 (2015)

The polaron potential energy surface



Conventional approach:

$$\min_{R_i}\{E(N-1)\}$$

Exact functional: $E(N-1) - E(N) = -\epsilon_{\mathrm{HO}}(N)$

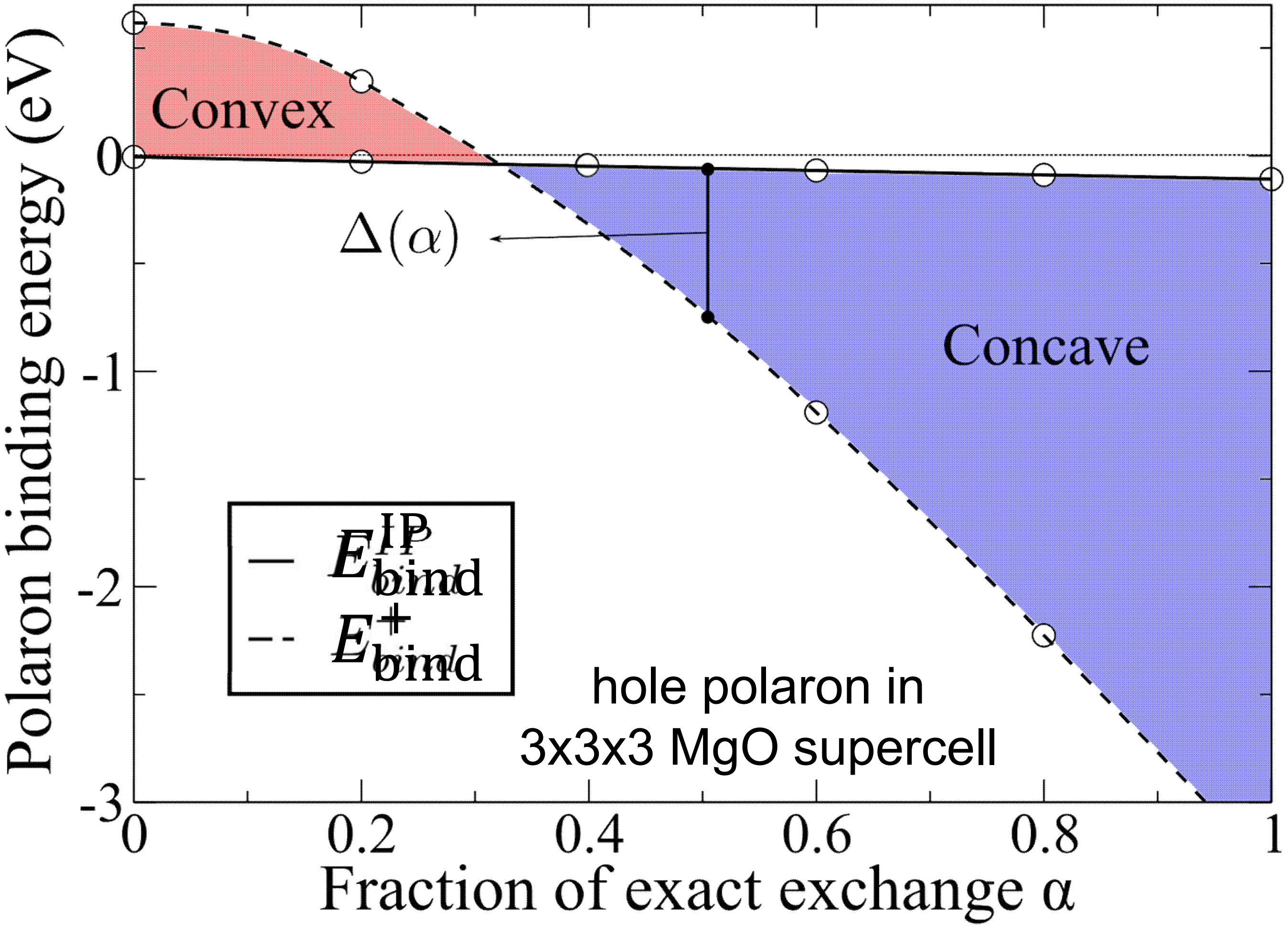
$$\min_{R_i}\{E(N) - \epsilon_{\mathrm{HO}}(N)\}$$ **-- closed-shell calculations!**

Force evaluation from *neutral* system properties:

$$F_i = \frac{\partial}{\partial R_i}\left(E(N) - \epsilon_{\mathrm{HO}}(N)\right)$$

Sadigh et al., PRB 92 , 075202 (2015)

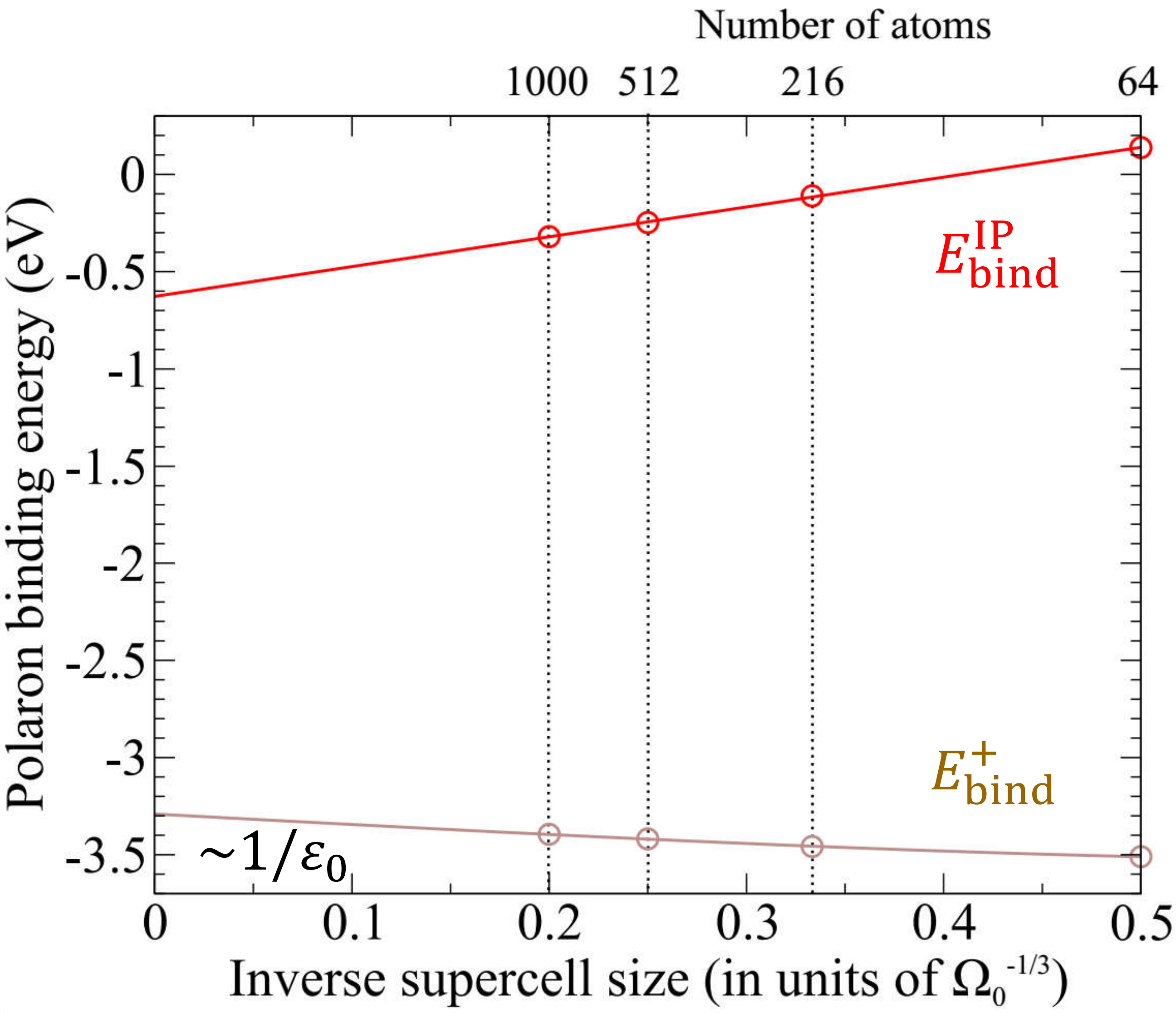
Functional dependence for the new potential energy surface



The functional dependence is greatly reduced!

Qualitatively correct for the whole range of α

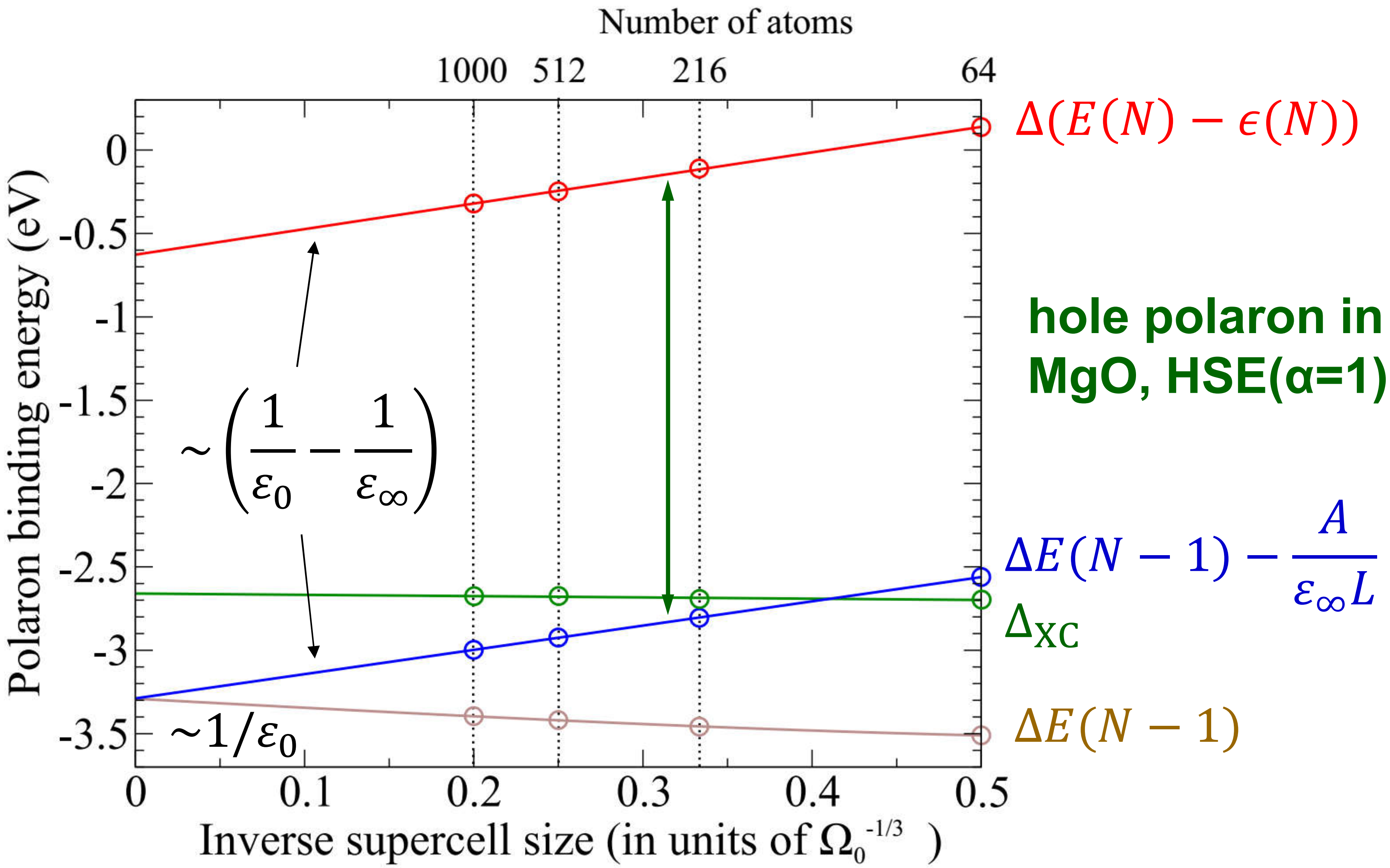
Finite-size effects



hole polaron in MgO, HSE(α=1)

The supercell dependence is stronger for the "neutral" potential energy surface!

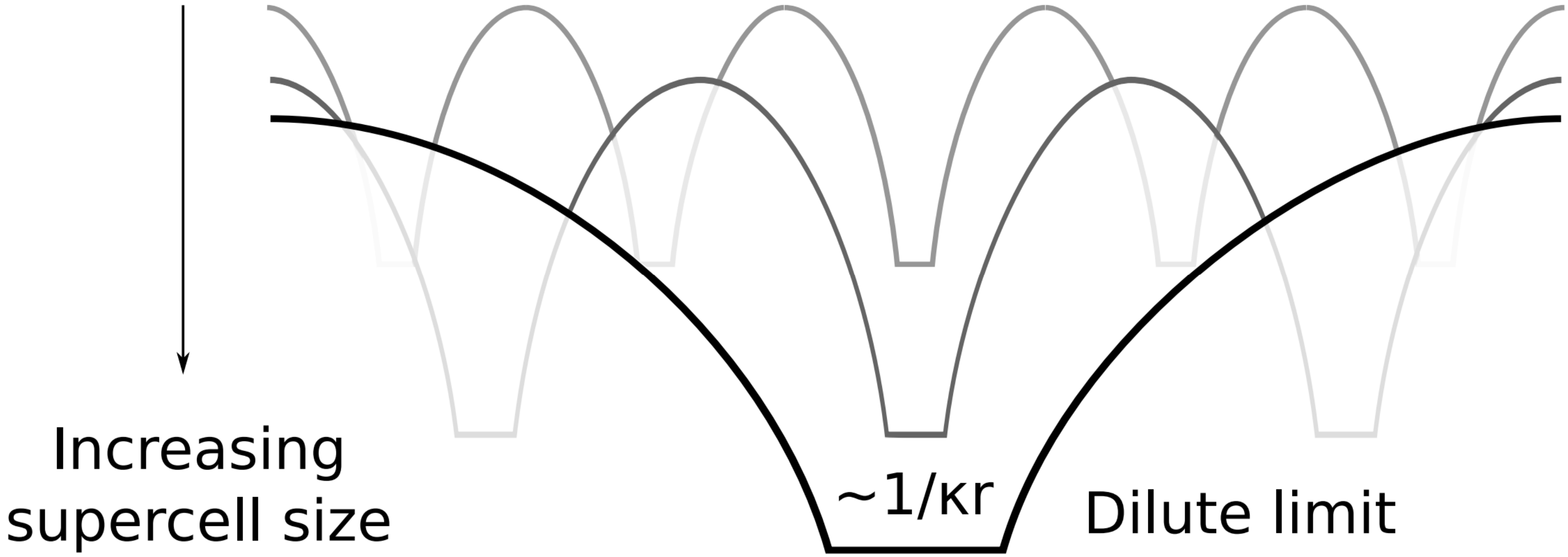
Finite-size effects



hole polaron in MgO, HSE(α=1)

Exchange-correlation correction is converged even in the smallest supercell

Long-range behavior of the polaron



Landau-Pekar: Small polarons in a classical polarizable medium → $V^{\mathrm{lr}}_{\mathrm{el-ph}} \sim \left(\frac{1}{\varepsilon_0}-\frac{1}{\varepsilon_\infty}\right)\frac{1}{r}$

Pekar, Zh. Eksp. Teor. Fiz 16, 335 (1946)

Long-range behavior of the polaron level E_0 with respect to the band edge

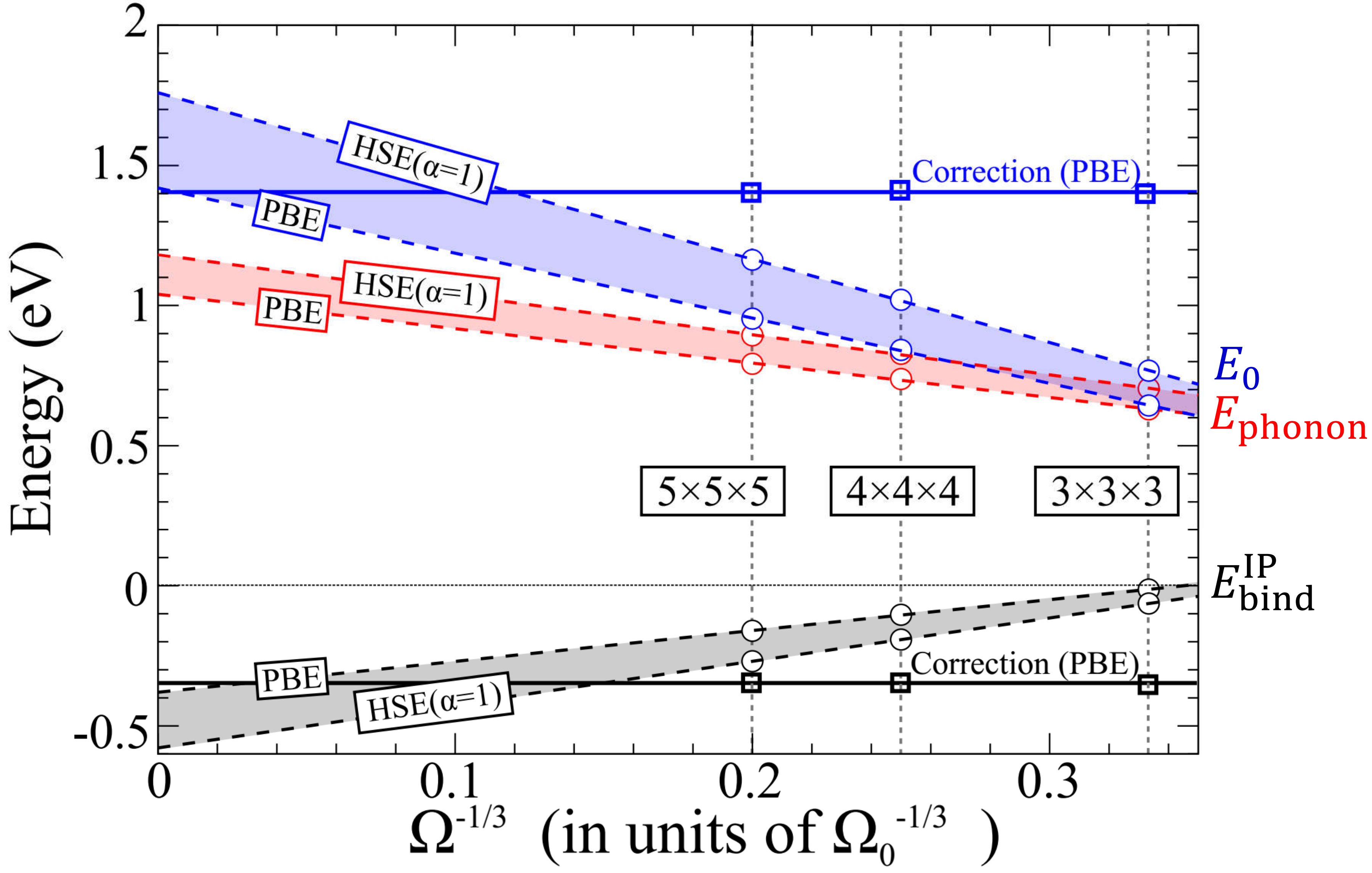
Pekar's 1:2:3:4 theorem (strong coupling):

$$H_{\text{polaron}} = H_{\text{kinetic}} + H_{\text{phonon}} + H_{\text{el}-\text{ph}} \rightarrow$$

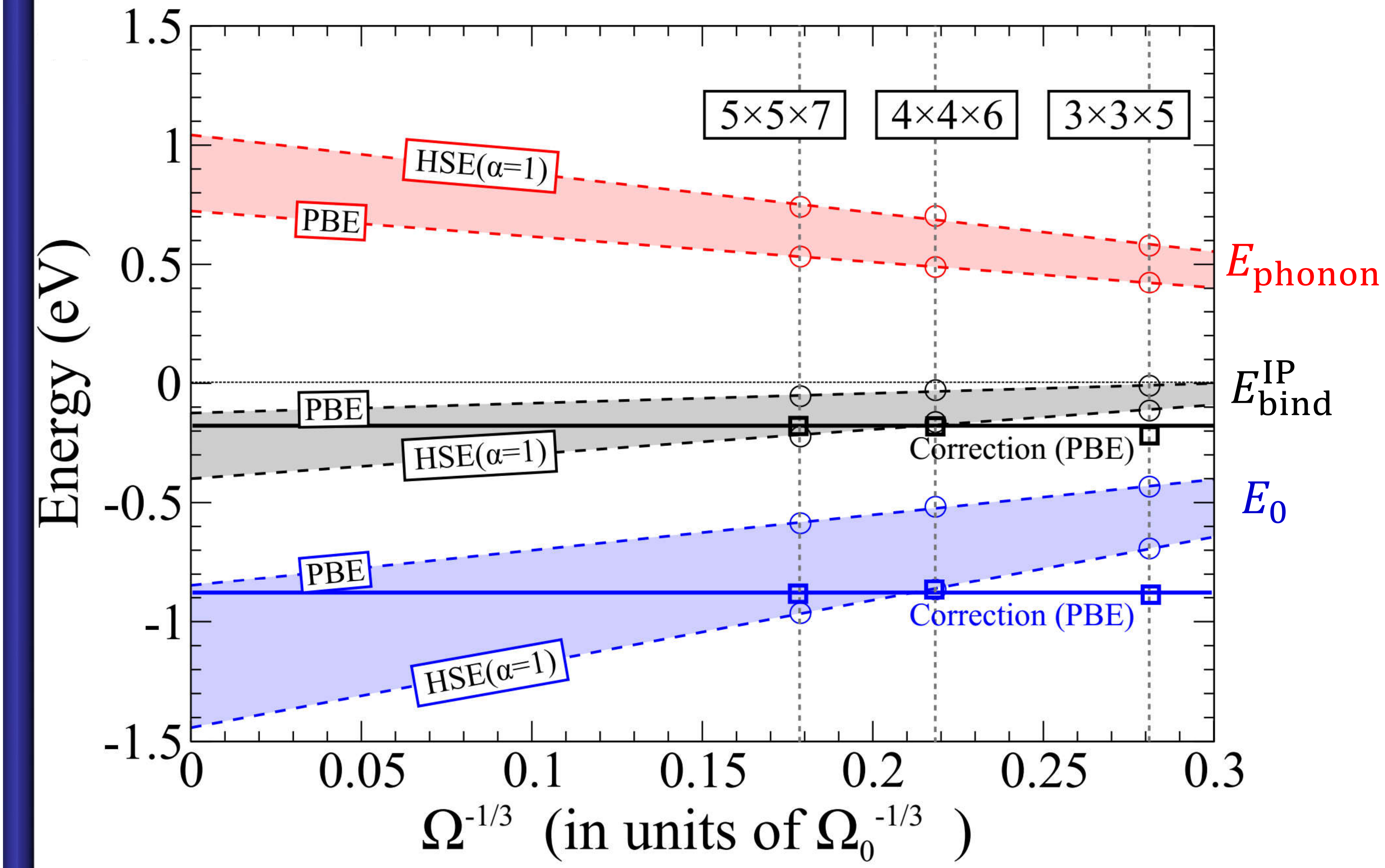
$$E_{\text{kinetic}} : E_{\text{phonon}} : -E_0 : -E_{\text{el}-\text{ph}} \approx 1:2:3:4 \rightarrow$$

$$E_{\text{bind}} = E_{\text{kinetic}} + \boxed{\frac{1}{2}E_{\text{el}-\text{ph}}},\ E_0 = E_{\text{kinetic}} + \boxed{E_{\text{el}-\text{ph}}}$$

Hole polarons in rock-salt MgO

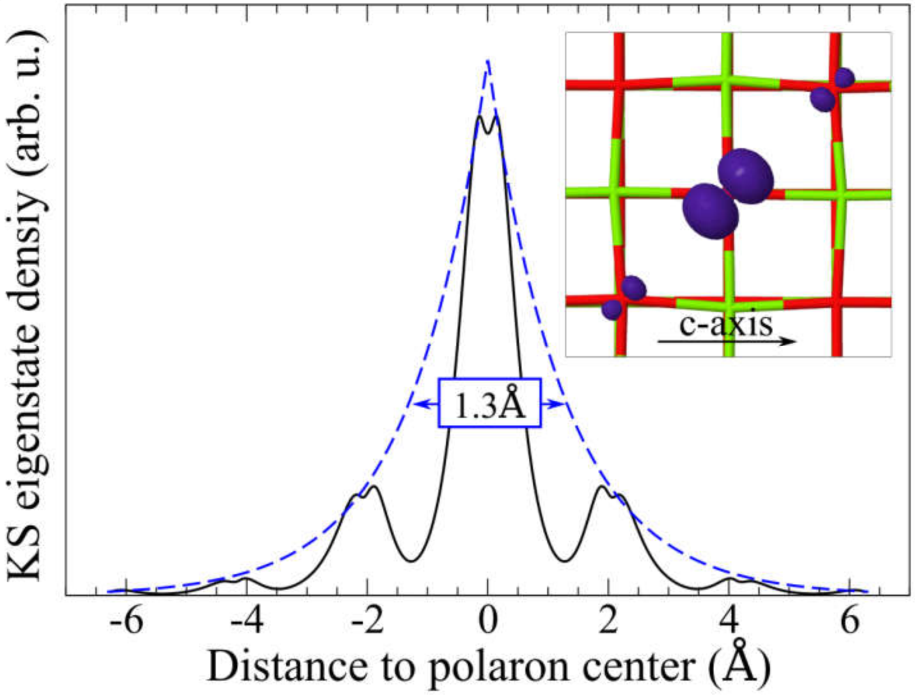


Electron polarons in rutile TiO_2

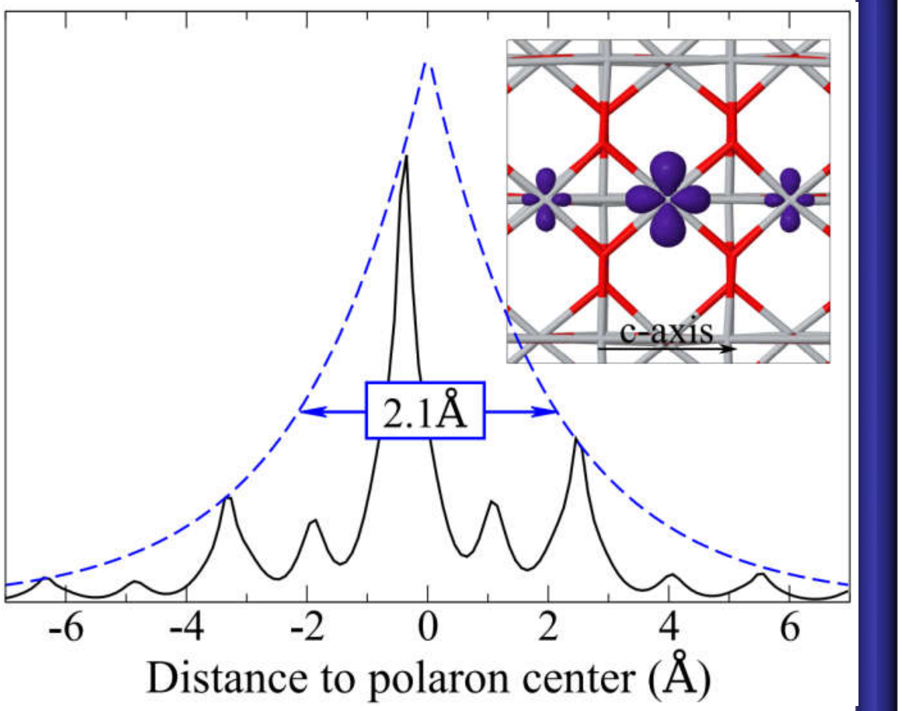


Polaron eigenstate density and radius

hole polaron in MgO



electron polaron in rutile TiO_2



Fröhlich coupling constant $\alpha_{\mathrm{F}} = \sqrt{\frac{m_{\mathrm{b}}}{2\omega_{\mathrm{LO}}}}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)$:

$\alpha_{\mathrm{F}} = 4.4$

$\alpha_{\mathrm{F}} = 2.6$