

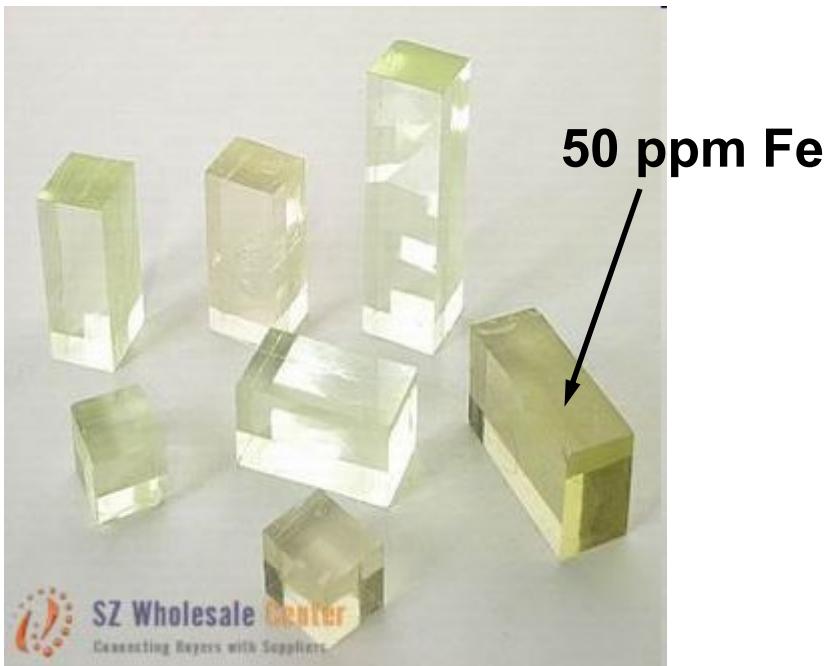
# **Advanced Materials Modeling:**

## **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



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: $\text{Al}_2\text{O}_3$



V: $\text{Al}_2\text{O}_3$



Fe: $\text{Al}_2\text{O}_3$



Fe: $\text{Al}_2\text{O}_3$

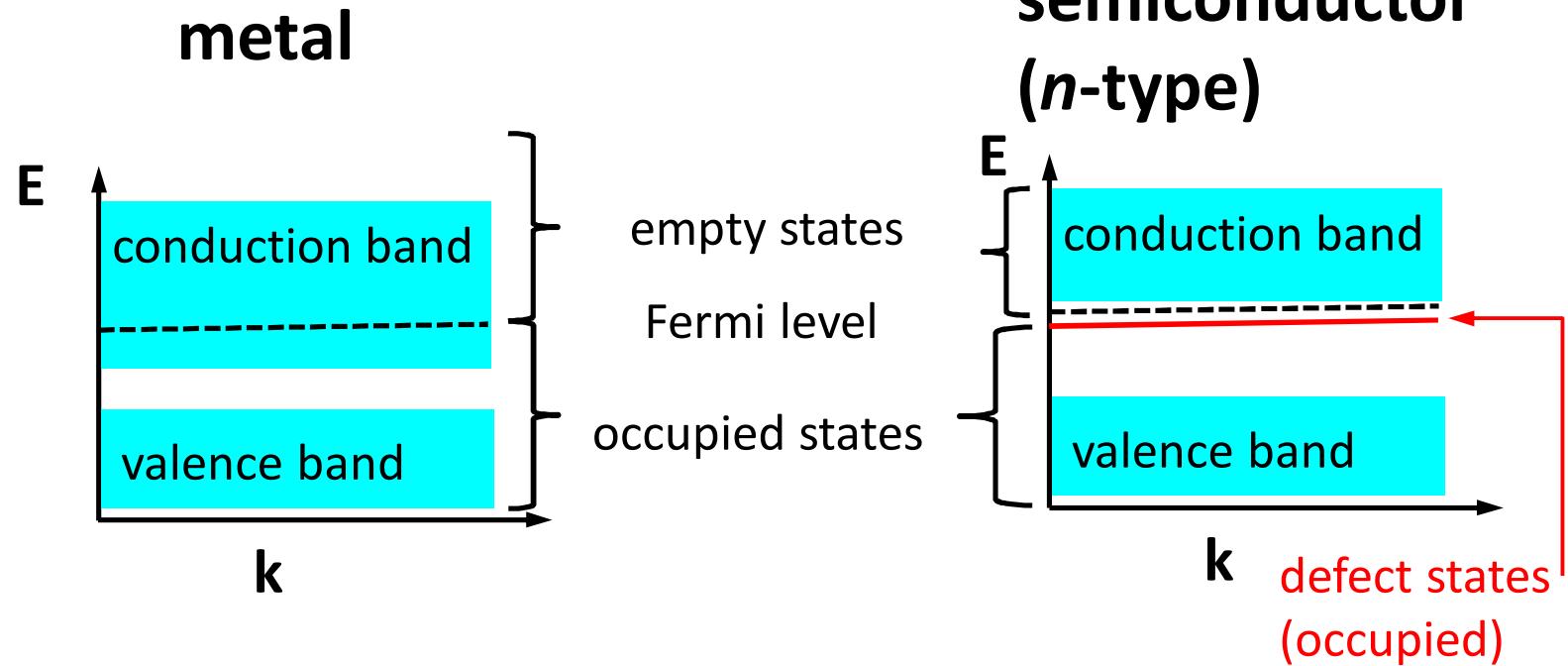
Impurities are responsible for the color of sapphire and many other precious stones

Typical concentrations: 100-10000 ppm



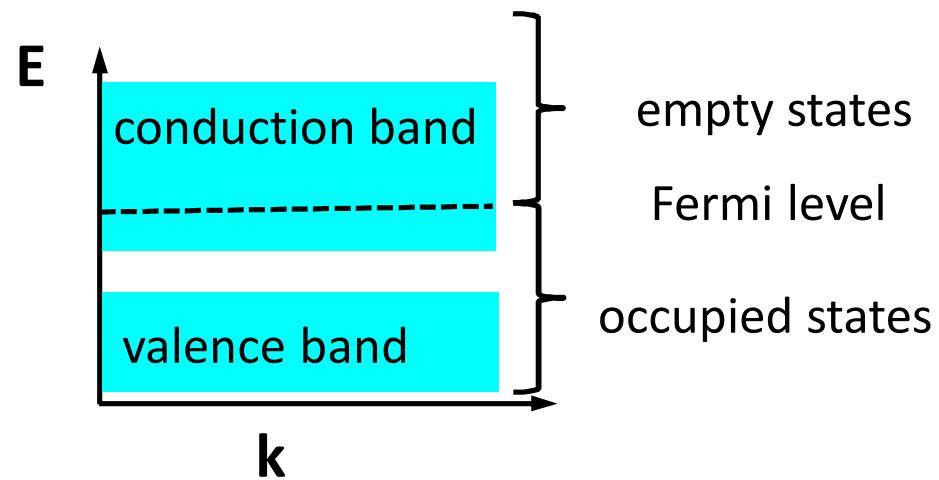
Fe,Ti: $\text{Al}_2\text{O}_3$

# Semiconductors

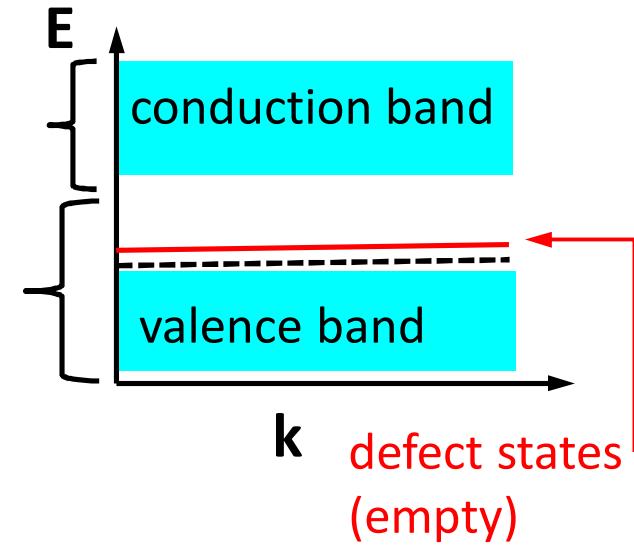


# Semiconductors

metal

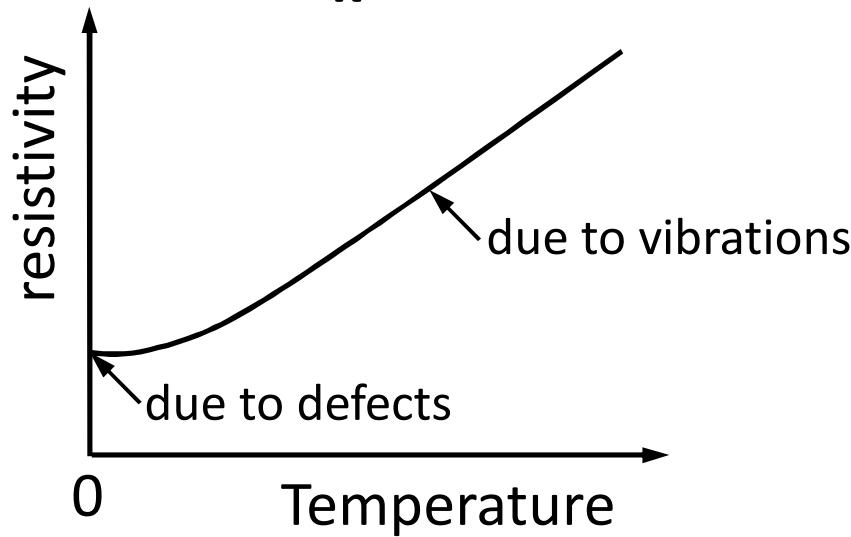
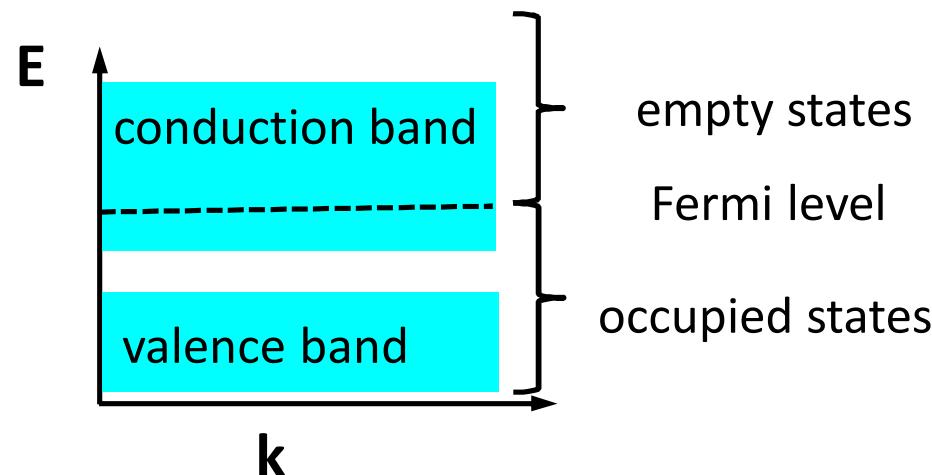


semiconductor  
(*p*-type)

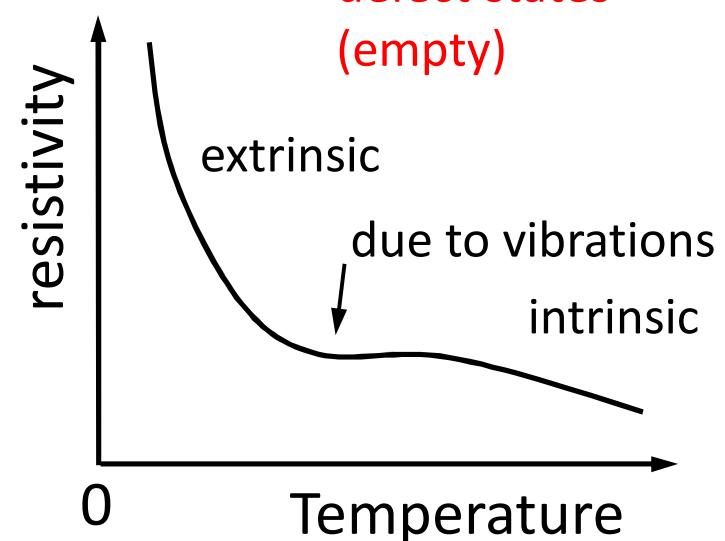
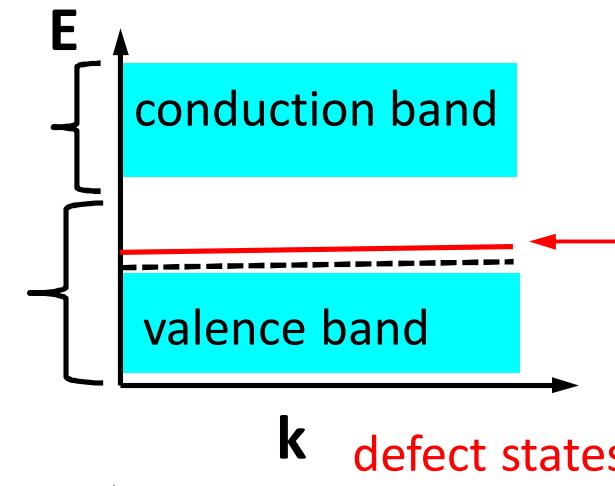


# Semiconductors

metal

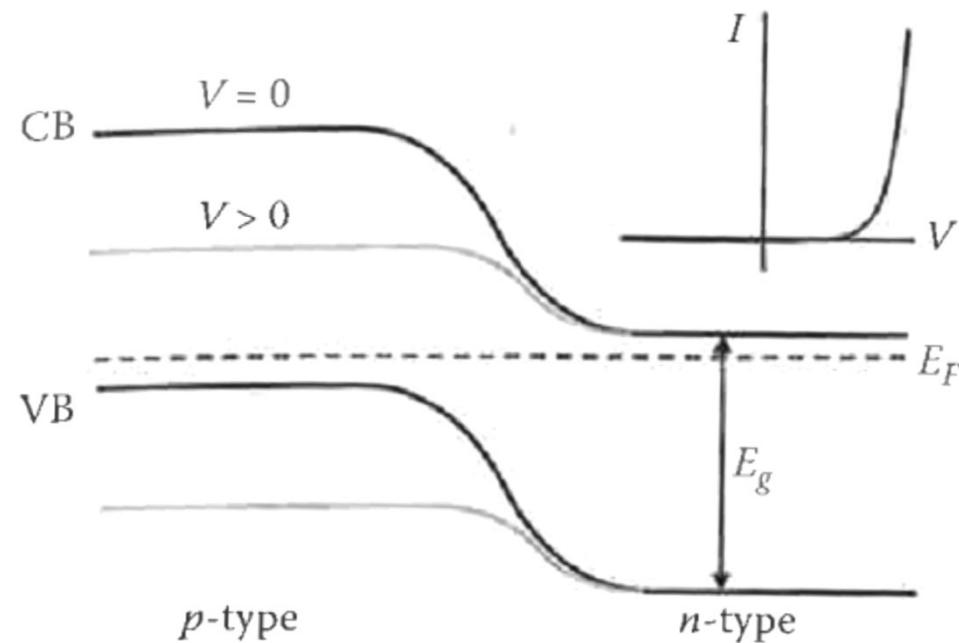


semiconductor  
(*p*-type)



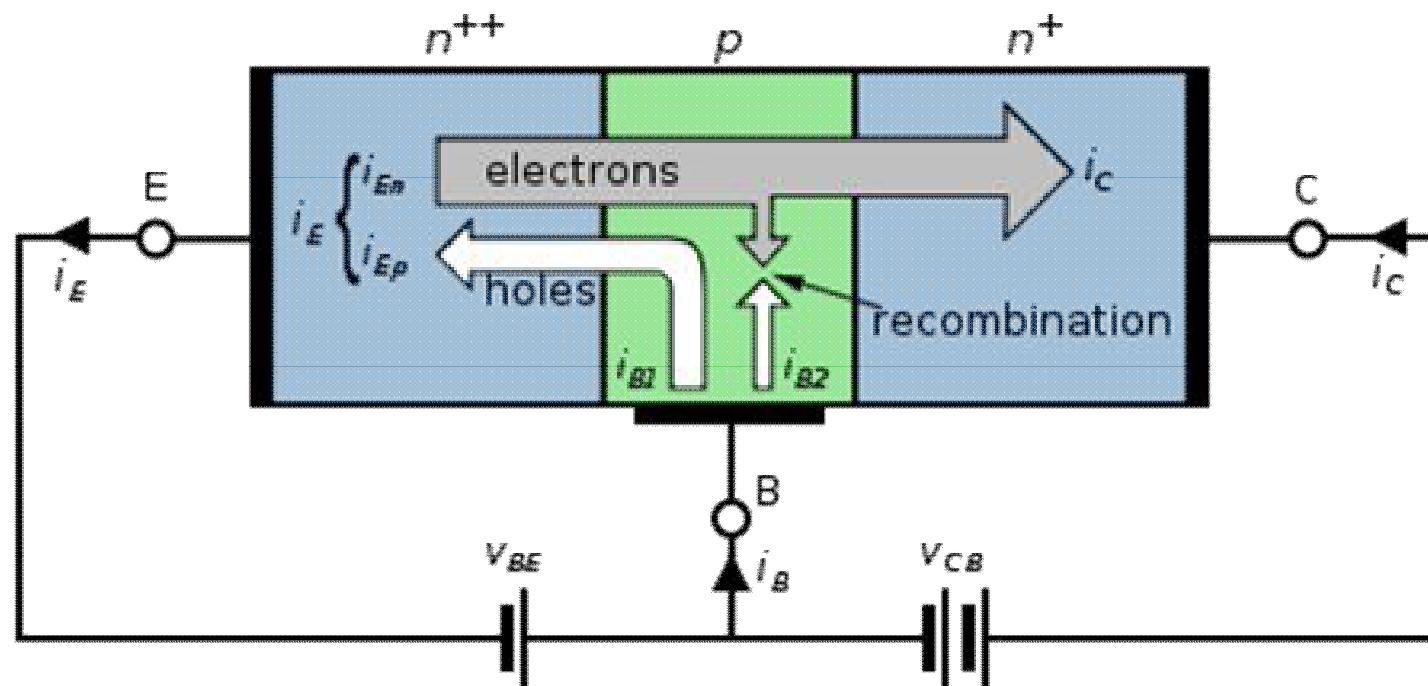
# “Physics of dirt”

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



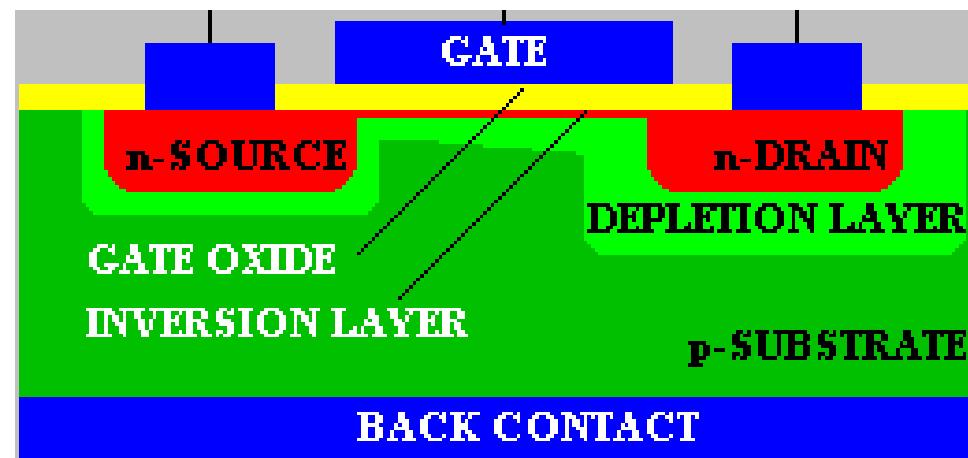
Emitter: heavily P-doped Si, base: B-doped Si,  
collector: lightly *n*-doped Si

# 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<sub>2</sub>-Si) – basis of modern electronics

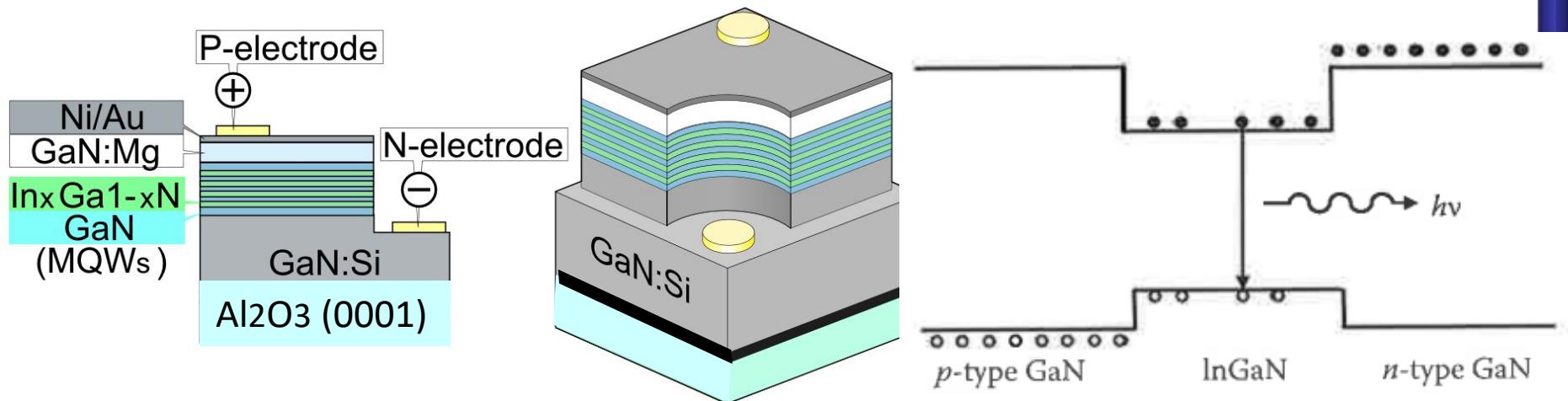


# “Let there be light!”: solid-state lighting

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

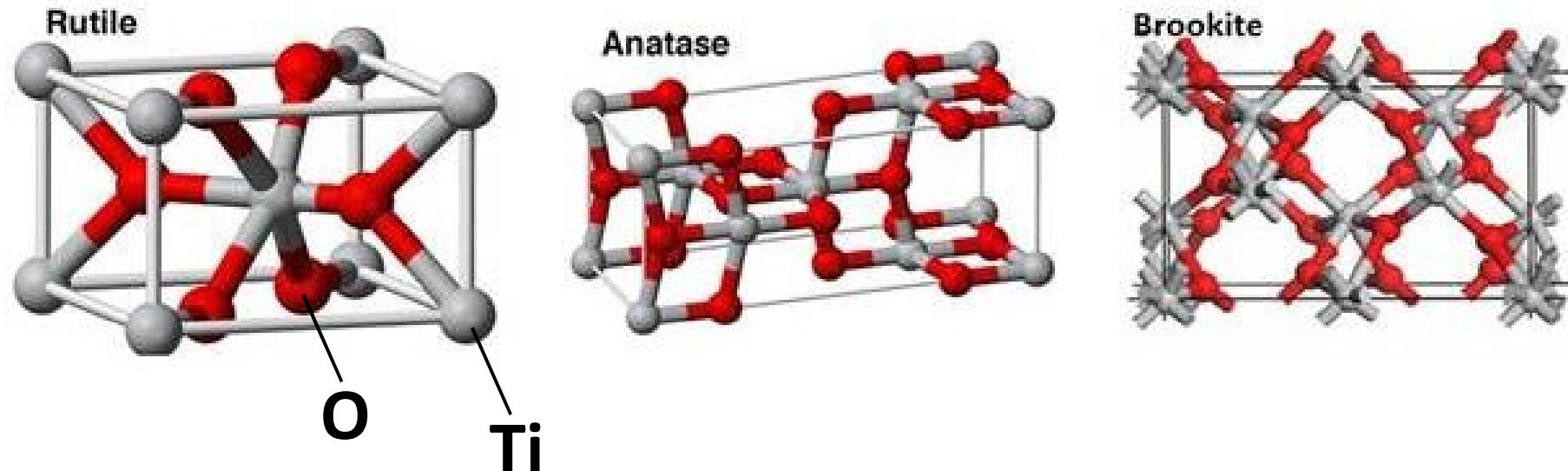
1962: Infrared and red LEDs and lasers (GaAs, AlGaAsP)

~1990: First blue LEDs (GaN)



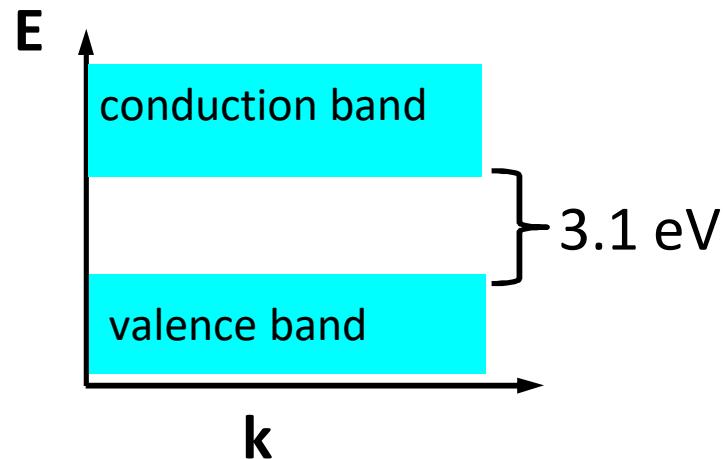
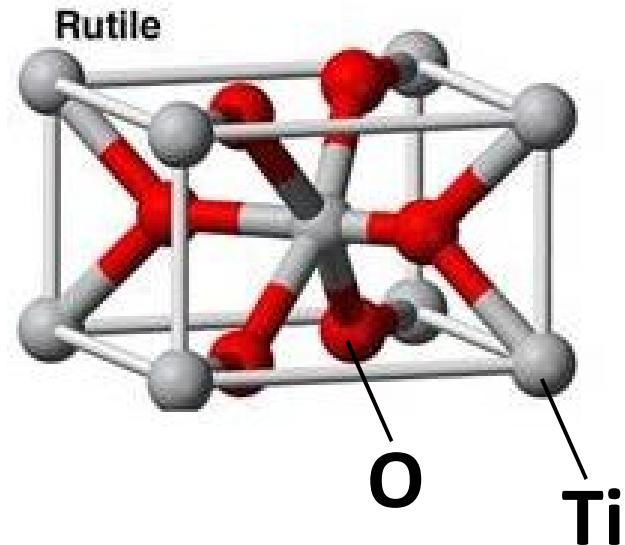
# Why oxides are semiconductors?

$\text{TiO}_2$  – a versatile functional material (paint, sunscreen, photocatalyst, optoelectronic material)

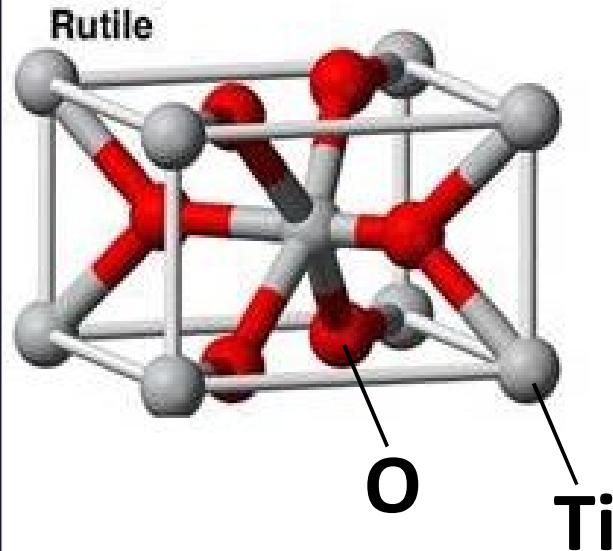


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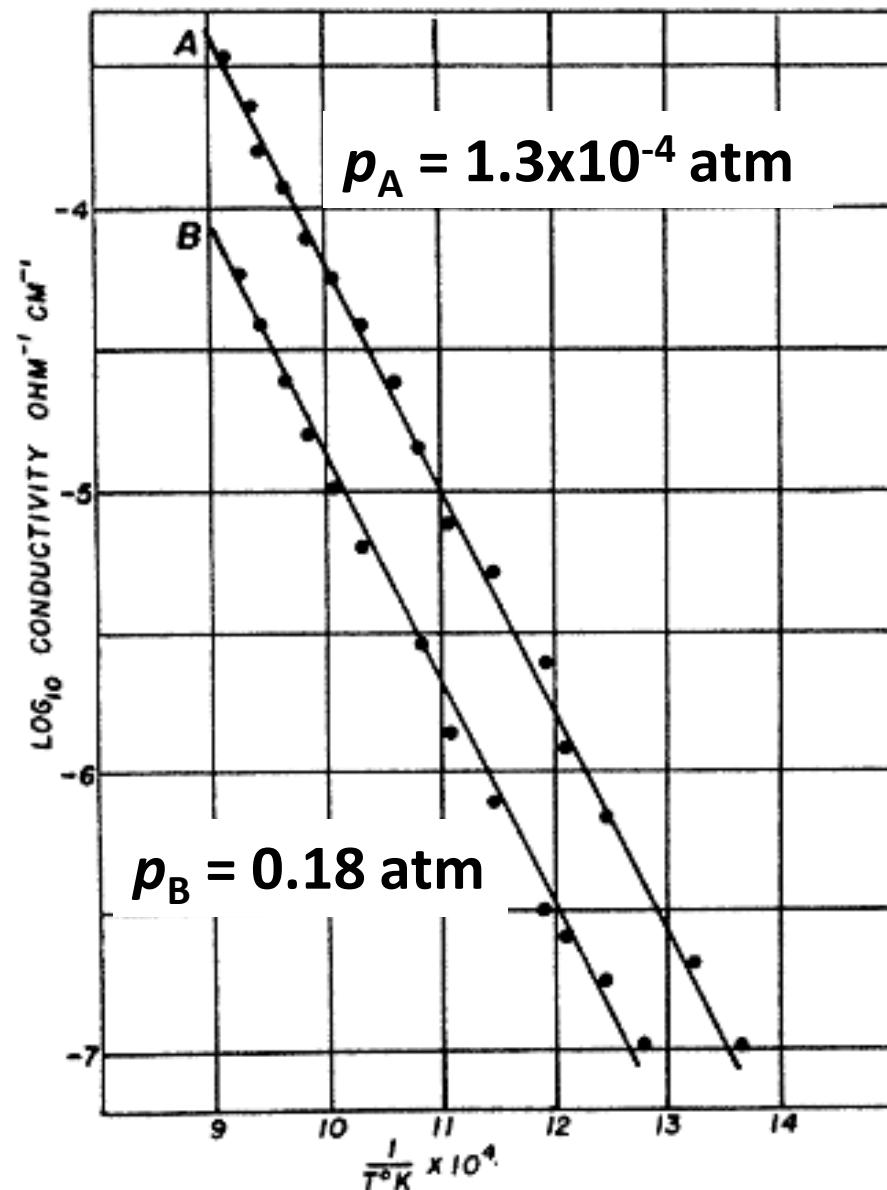


# Why oxides are semiconductors?

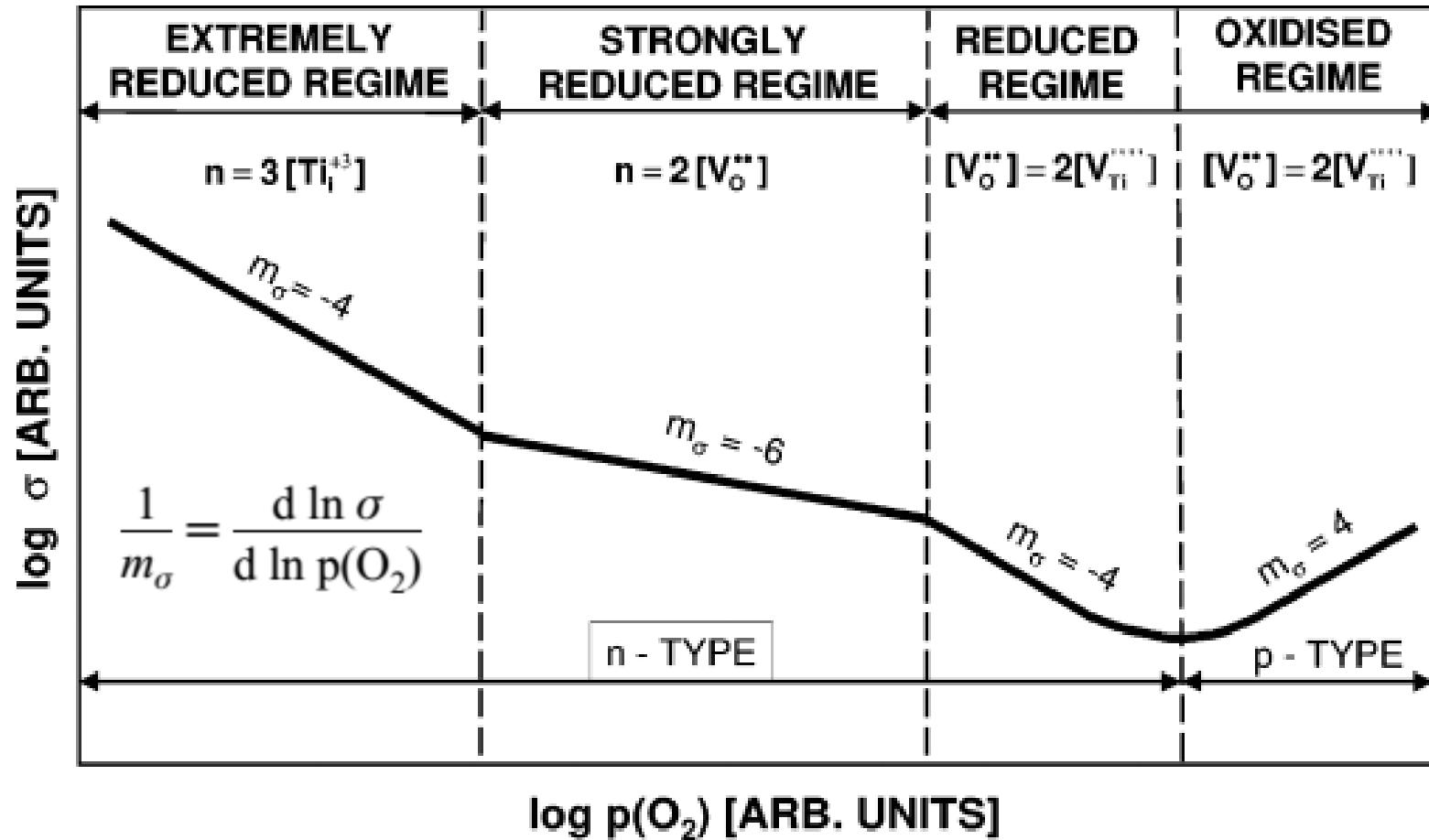


**TiO<sub>2</sub> is an *n*-type semiconductor, whose conductivity depends on O<sub>2</sub> pressure**

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



# Why oxides are semiconductors?

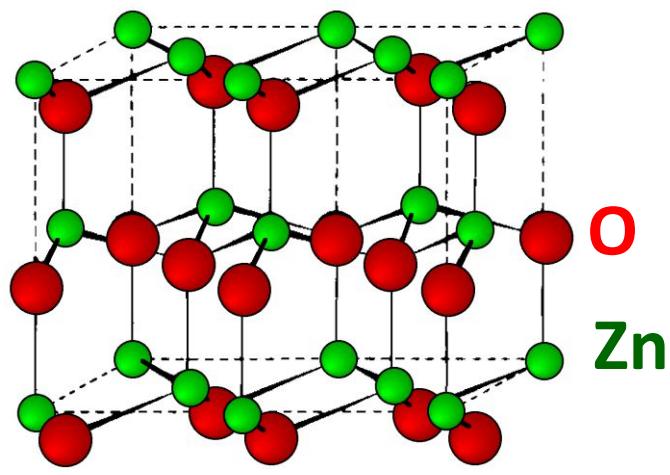


Different regimes correspond to different intrinsic defect distributions in ultrapure  $TiO_2$

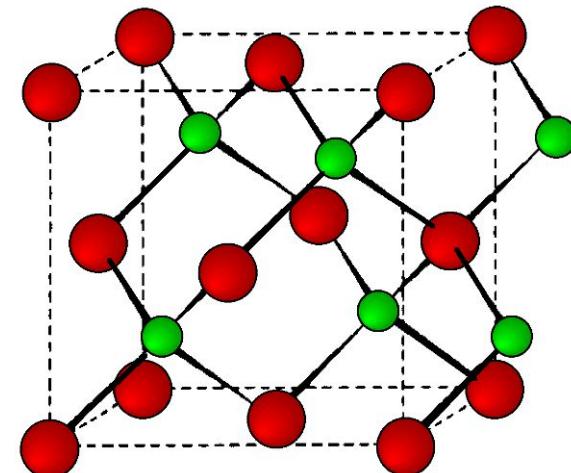
M. K. Nowotny, T. Bak, and J. Nowotny,  
J. Phys. Chem. B **110**, 16270 (2006)

# Why oxides are semiconductors?

ZnO – another example of a very promising functional material, understood less than TiO<sub>2</sub>



wurtzite (stable)

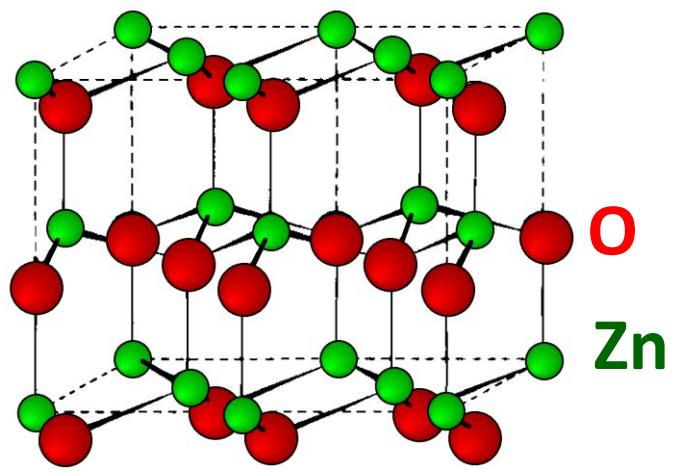


zinkblende (can be obtained by growth on substrates with cubic lattice structure)

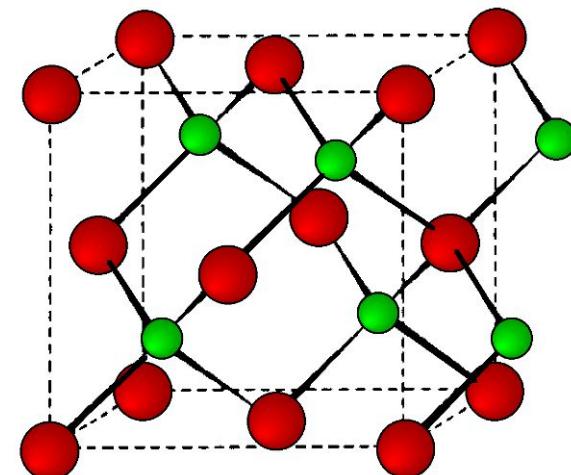
Band gap ~3.3 eV (direct), but (almost?) exclusively *n*-type semiconductor

# Why oxides are semiconductors?

ZnO – another example of a very promising functional material, understood less than TiO<sub>2</sub>



wurtzite (stable)

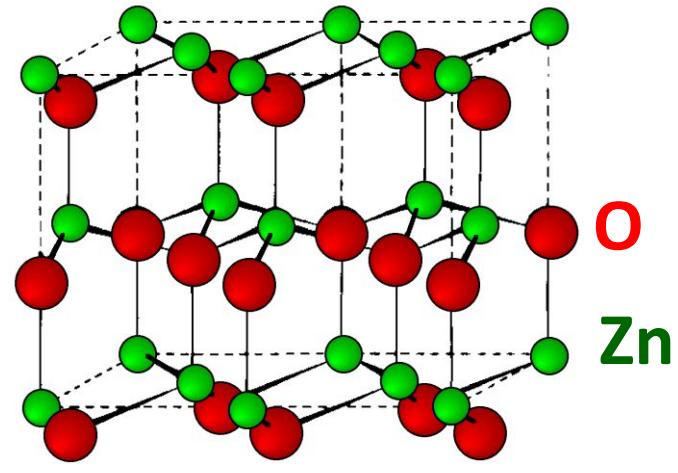


zinkblende (can be obtained by growth on substrates with cubic lattice structure)

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<sub>2</sub>



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.)**



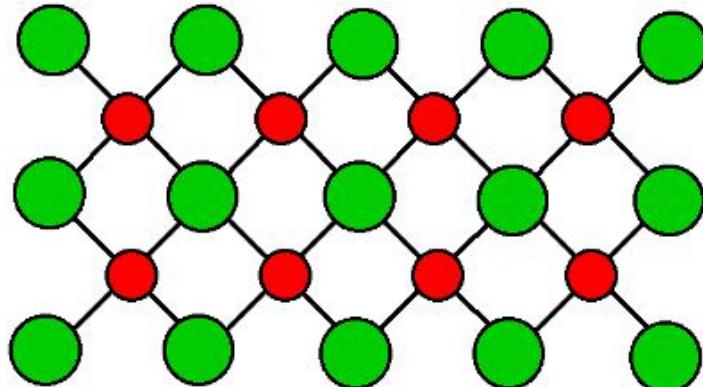
**Understanding the electronic and atomic structure of defects is of great importance**

## The “invisible agent”

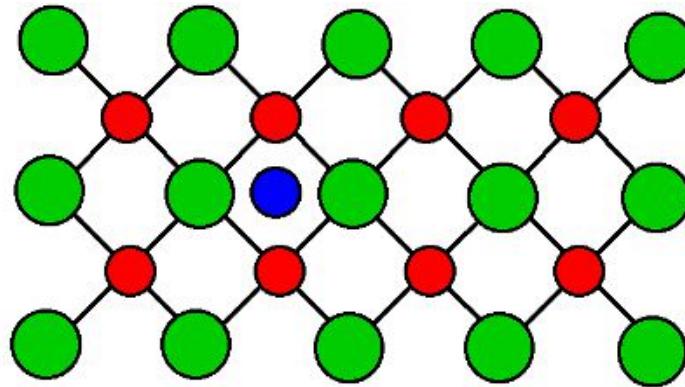
“...The problem is that defects are often elusive species, highly diluted, and therefore difficult to detect. It is as if one wanted to identify all the men with a beard among the population of Europe from a satellite which is a few hundreds of kilometers away from the earth surface: the task is difficult, 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**

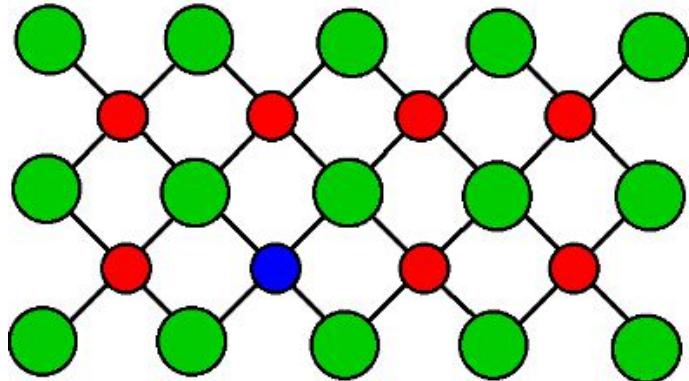
# Common point defect types



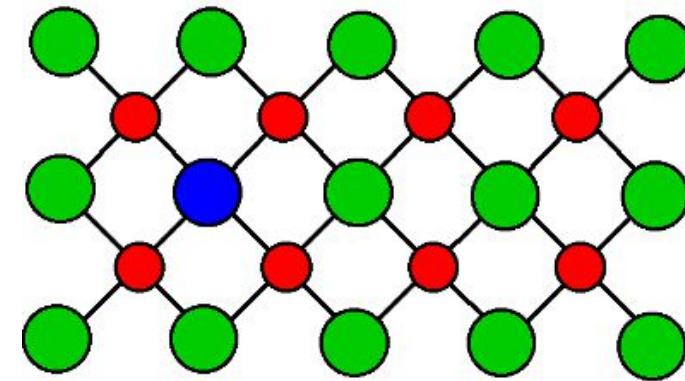
(a) perfect lattice



(b) interstitial impurity

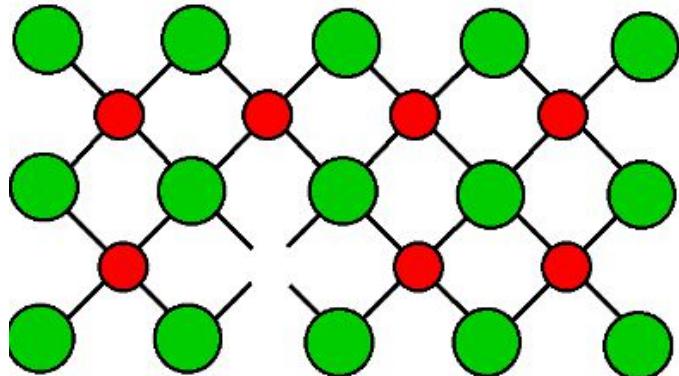


(e) substitution of cation

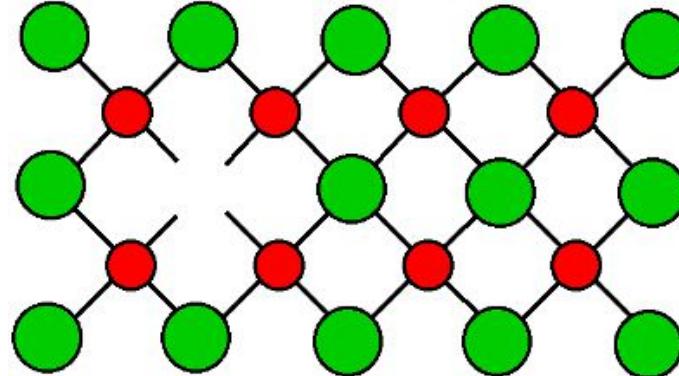


(f) substitution of anion

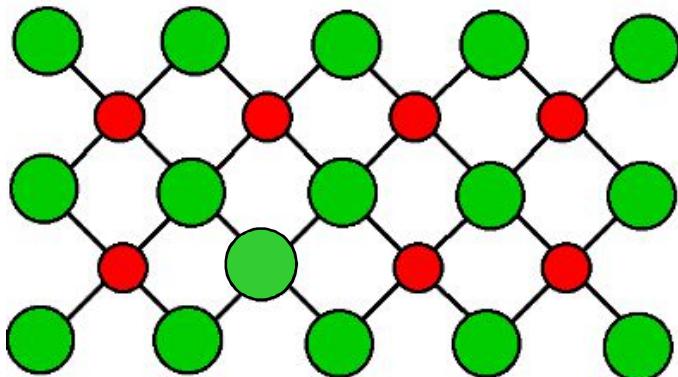
# Common point defect types



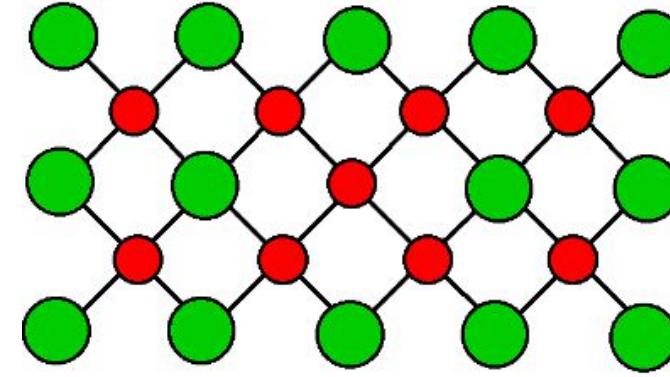
(c) cation vacancy



(d) anion vacancy



(g)  $B_A$  antisite defect

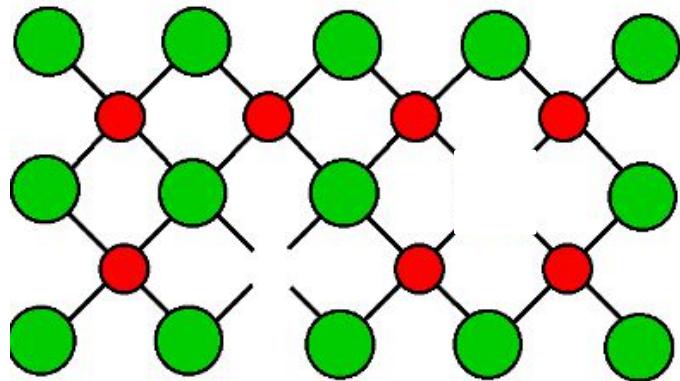


(h)  $A_B$  antisite defect

# Common point defect types

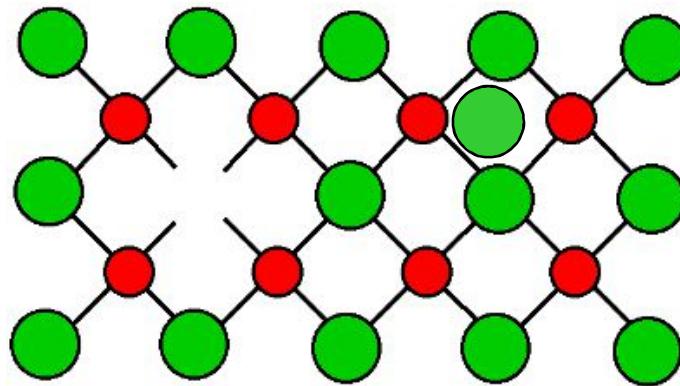
## Defect complexes

### 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

100 nm

precipitates, interfaces, grain  
boundaries, surfaces, etc.

10 nm

clusters (aggregates)

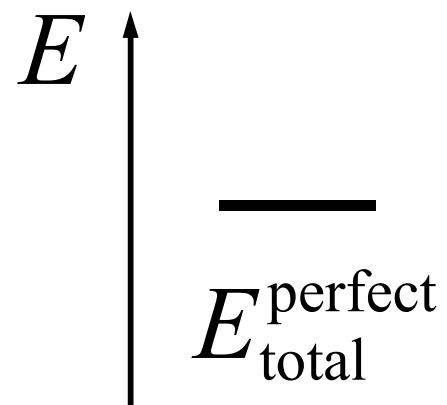
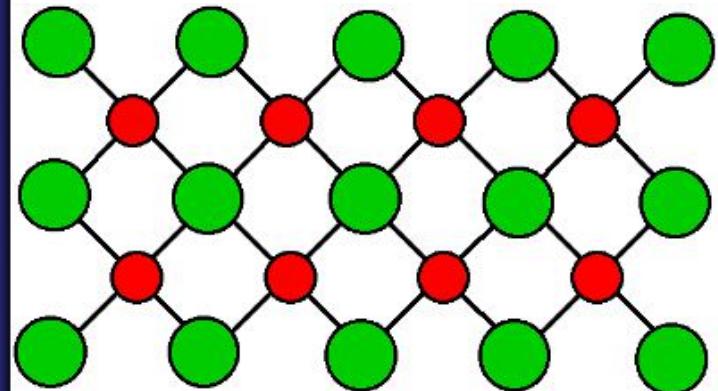
1 nm

point defects and complexes

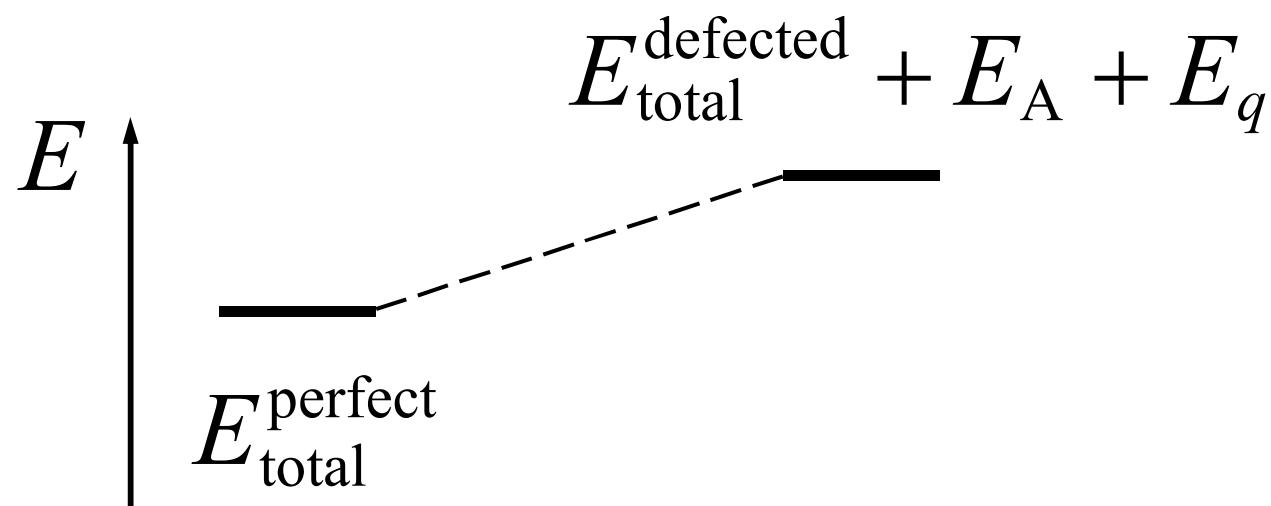
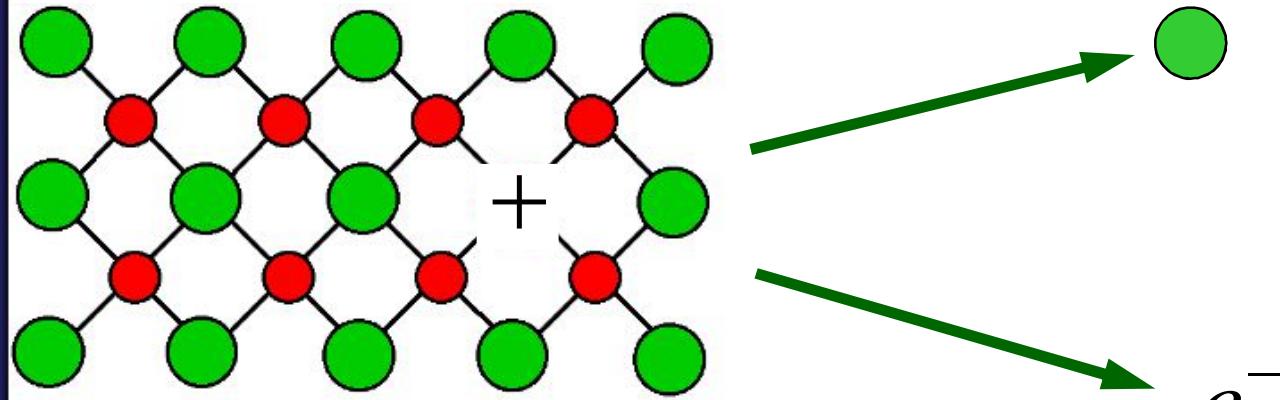
0.1 nm

Nanometer-size defects are building blocks for the larger defects

# Defect formation energy ( $T=0$ )

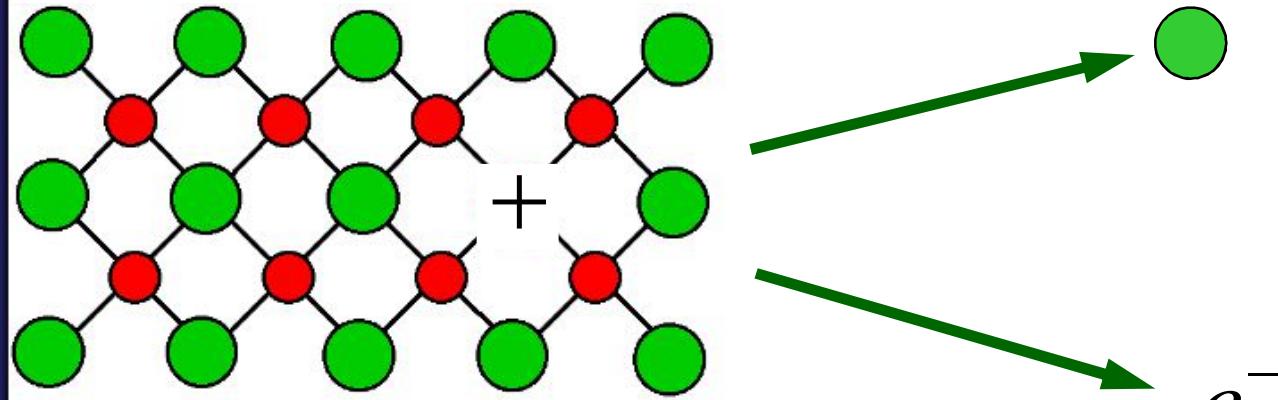


# Defect formation energy ( $T=0$ )



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

# Defect formation energy ( $T=0$ )



$E$

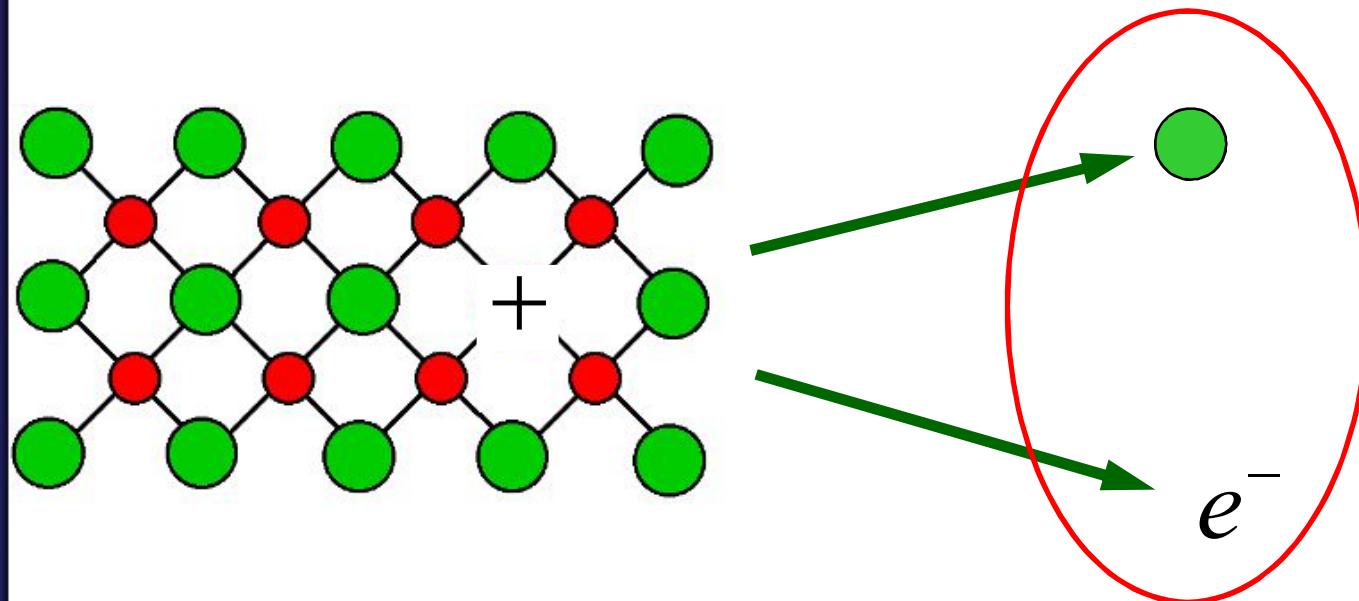
$E_{\text{total}}^{\text{perfect}}$

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

**zero-point energy  
contribution**

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

# Defect formation energy ( $T=0$ )



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

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

# Defect formation energy ( $T=0$ )

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

**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

$T = 0:$

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



$T > 0:$

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

## Electronic chemical potential

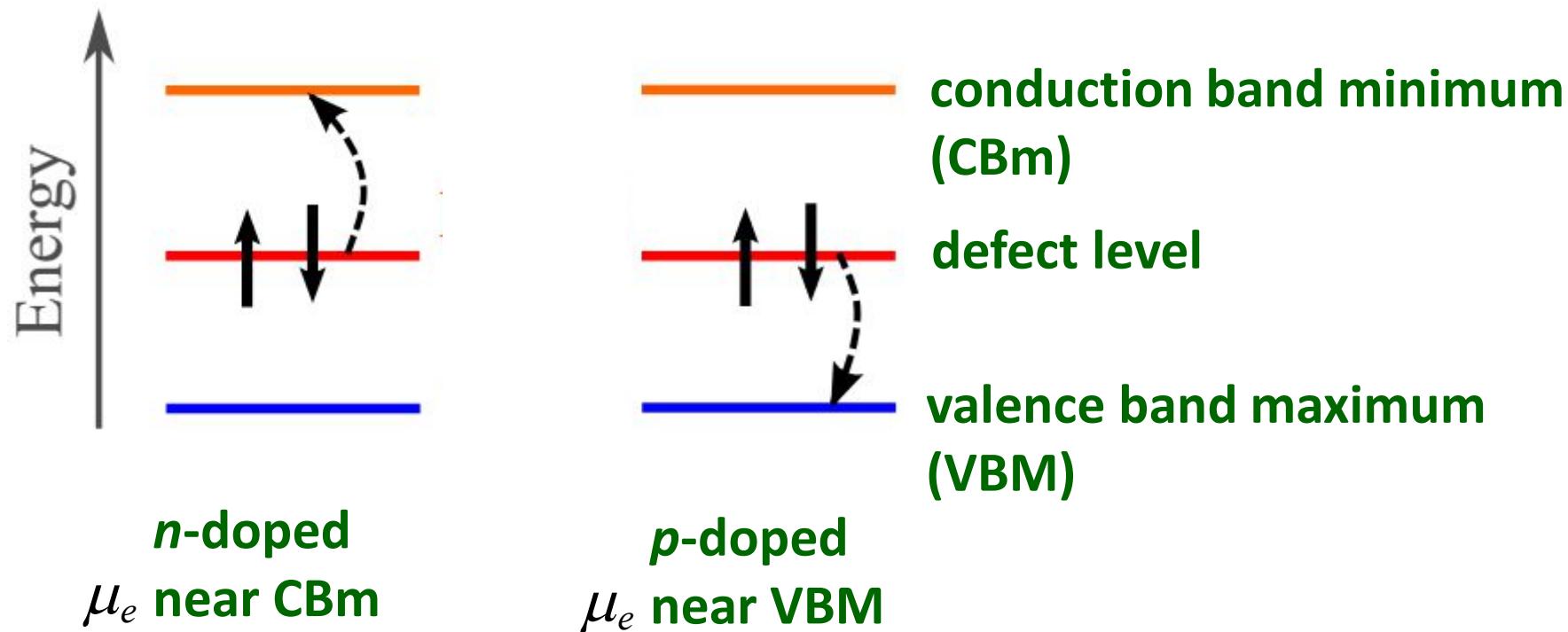
$$\Delta G_f(T, \{p\}) = G^{\text{defected}}(T, \{p\}) - \sum_i \mu_i(T, p_i) \Delta N_i + q\mu_e(T) \\ - G^{\text{perfect}}(T, \{p\})$$

$\mu_e$  is a property of the electronic reservoir

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

# Electronic chemical potential

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

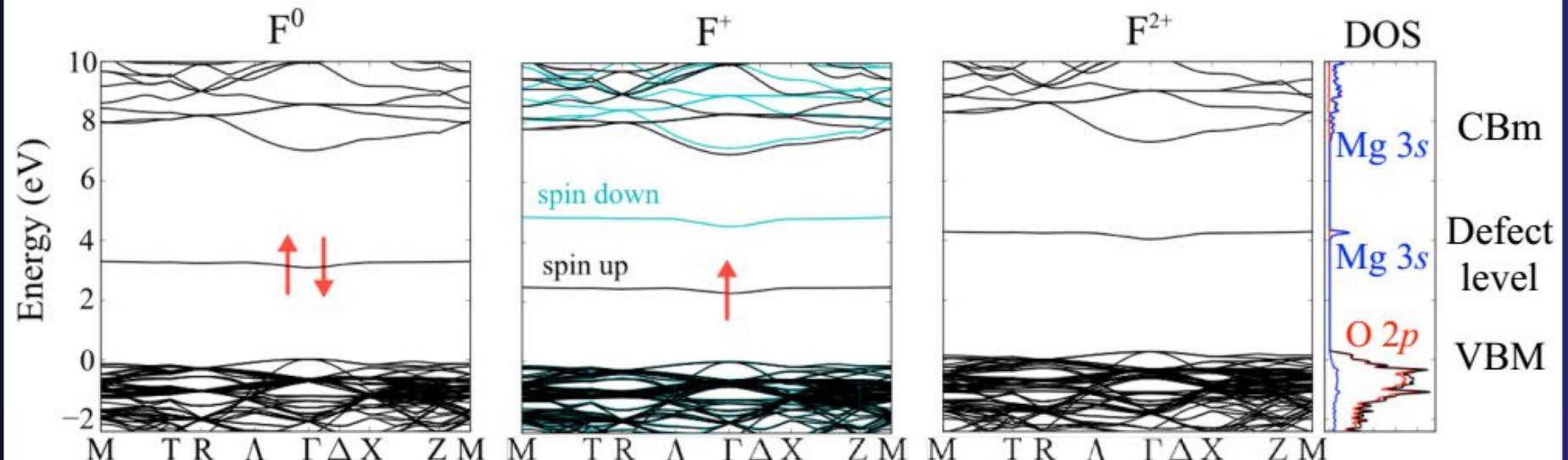


The defects will charge when  $\mu_e$  is below the defect level

# Electronic chemical potential

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

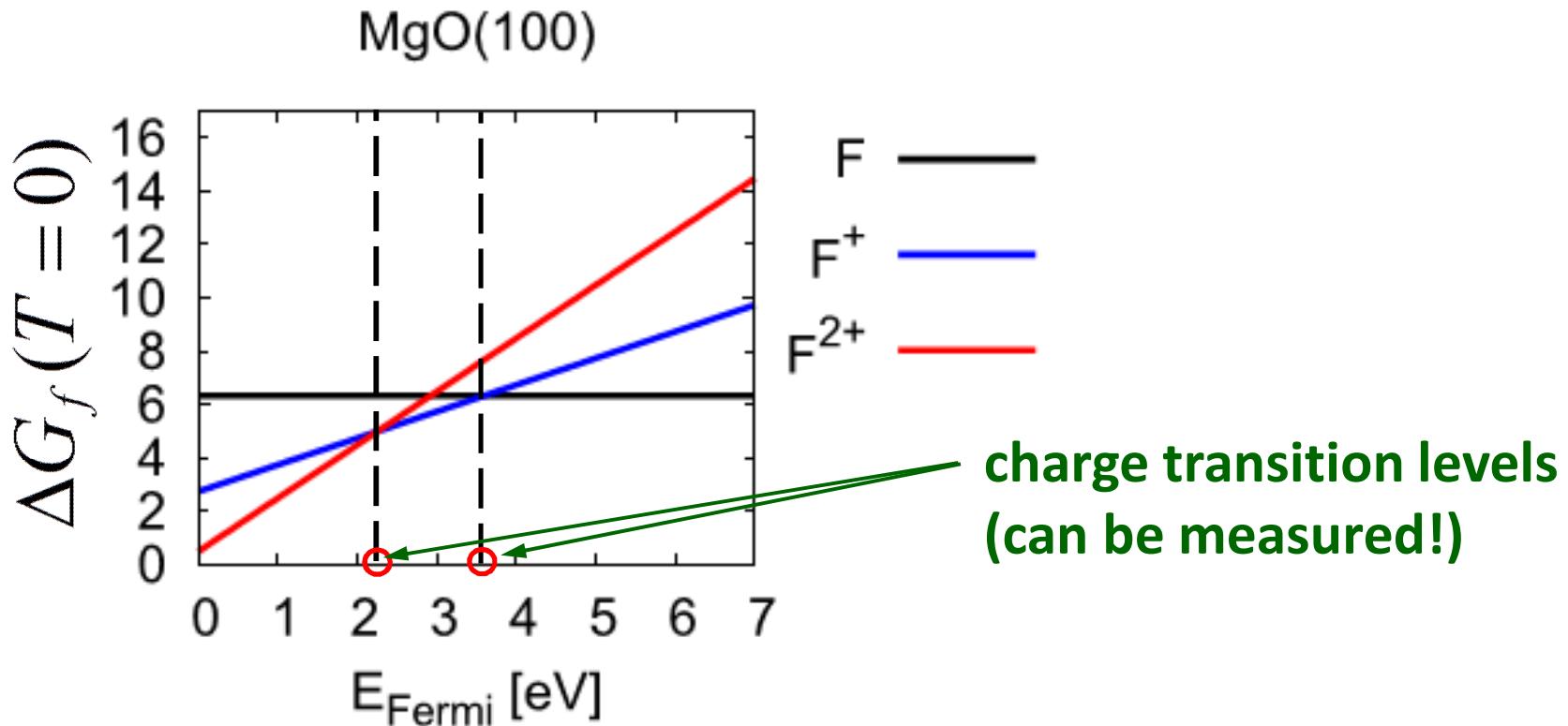
Band structures of O vacancies in MgO bulk (HSE06)



$F^0$  Defect wave function localized in the O vacancy

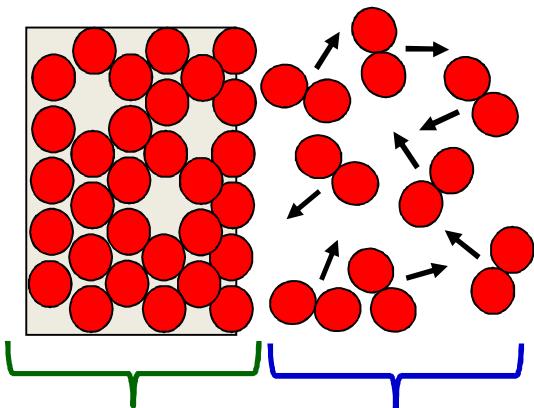
## Electronic chemical potential

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



# Entropy

$$G = U + pV - TS$$



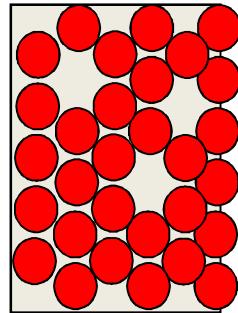
$$S = k \ln \Omega$$

$\Omega$  – number of microstates

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

# Configurational entropy

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



$N$  equivalent defect sites in the sold

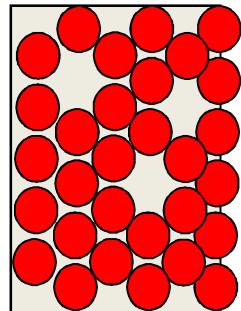
$n$  defects

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

sum over different defect  
distributions

# Configurational entropy

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



$N$  equivalent defect sites in the sold

$n$  defects

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

Stirling's formula:

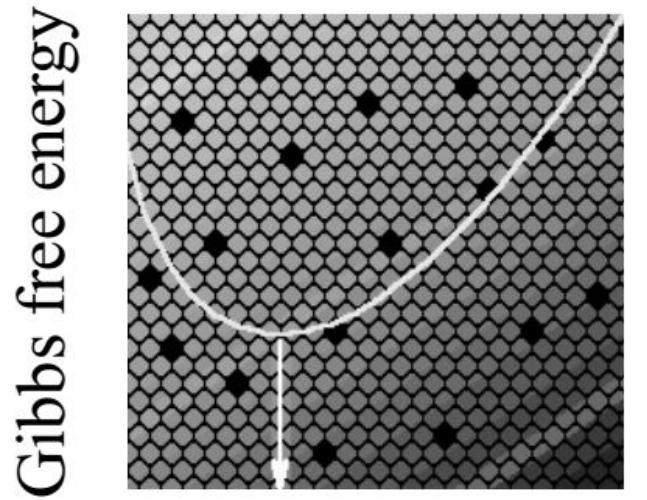
$$\ln(n!) = n(\ln n - 1 + \delta), \quad n \gg 1, \quad \delta \sim \frac{\ln(2\pi n)}{2n}$$

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

Good approximation only on a macroscopic scale

# Defect concentration

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



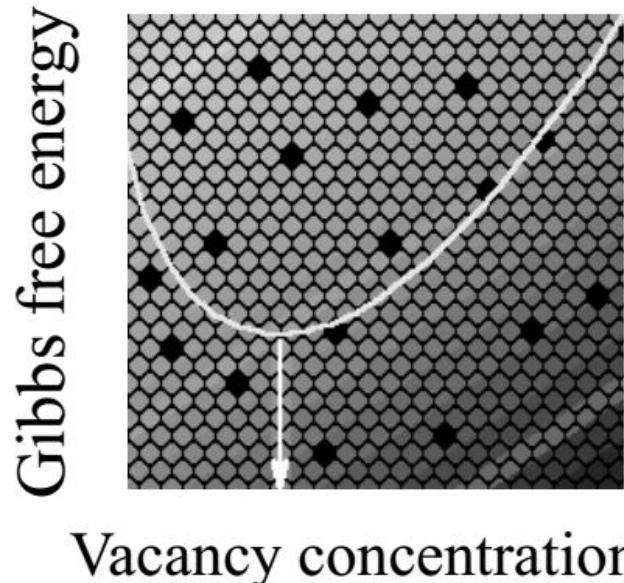
$$G(n) = \tilde{G}_0 + n\Delta G_f - TS_{\text{config}}(n)$$

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

$$\frac{\partial G}{\partial n} = 0$$

# Defect concentration

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



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

If defects do not interact:

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

$$\frac{n}{N} \ll 1 \Leftrightarrow \exp(\Delta G_f/kT) \gg 1$$

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

# Internal defect disorder

.. .. ; ; ..

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

spatial , spin, electronic  
degeneracy

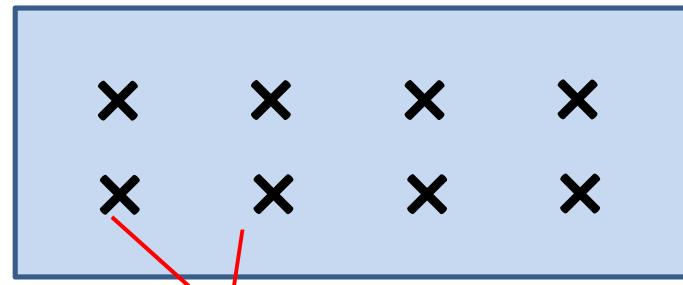
$$\Delta G_f \Rightarrow \Delta G_f - kT \ln(W_{\text{internal}})$$



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

# 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

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

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

# Constrained equilibrium: Competing defects

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

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

$$\begin{aligned} S_{\text{config}} &= k \ln \left( \frac{N_0!}{N_1! (N_0 - N_1)!} \frac{(N_0 - N_1)!}{N_2! (N_0 - N_1 - N_2)!} \times \cdots \times \frac{(N_0 - \sum_{k \neq i} N_k)!}{N_i! (N_0 - \sum_k N_k)!} \right) \\ &= k \ln \left( \frac{N_0!}{N_1! N_2! \dots N_i! (N_0 - \sum_k N_k)!} \right) \end{aligned}$$

## Constrained equilibrium: Competing defects

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

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

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

## Constrained equilibrium: Competing defects

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

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

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

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

# Constrained equilibrium: Competing defects

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

Coupled equations, but easy to solve:

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

All concentrations can be expressed through one:

$$N_k = N_k(N_i)$$

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

# 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:

$$\sum_i n_i \leq 1$$

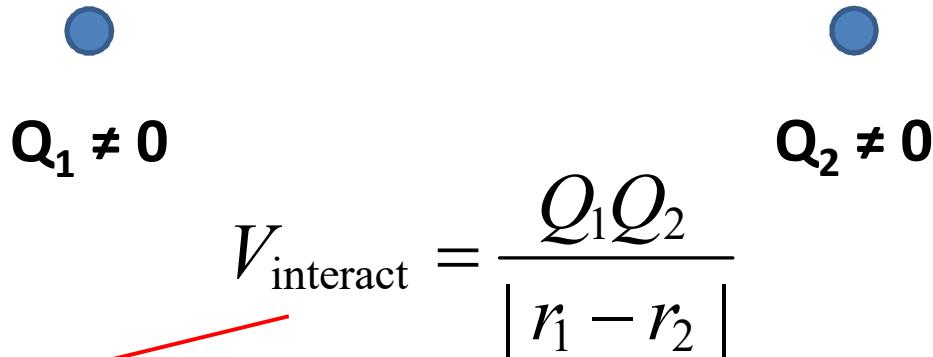
is *automatically fulfilled*, due to the correctly counted microstates

# Charged defects and charge compensation

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

for non-interacting defects

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


$$Q_1 \neq 0 \quad Q_2 \neq 0$$
$$V_{\text{interact}} = \frac{Q_1 Q_2}{|r_1 - r_2|}$$

Coulomb interaction – long-range!

# Charged defects and charge compensation



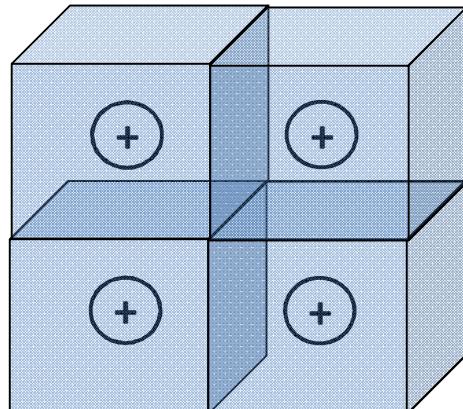
$$Q_1 \neq 0$$



$$Q_2 \neq 0$$

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

For a system of charges:



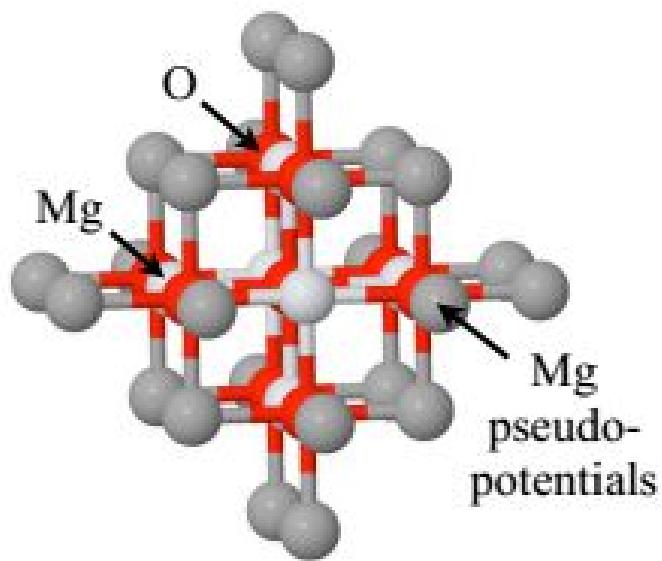
$$V_{\text{interact}} = \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{|r_i - r_j|}$$

In the thermodynamic limit ( $N \rightarrow \infty$ ) 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

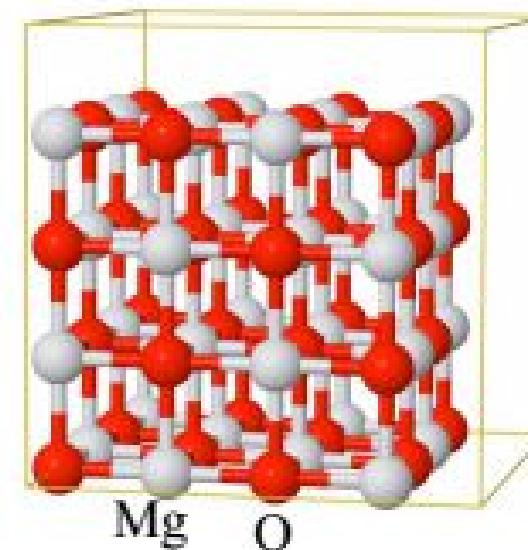


+ Higher-level *ab initio* methods can be applied

+/- Defects in dilute limit

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

## Periodic model



+ Robust boundary conditions

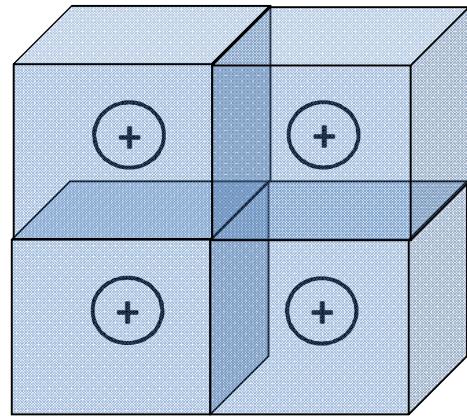
+ Higher defect concentrations

+/- Higher defect concentrations

- Artificial defect-defect interactions

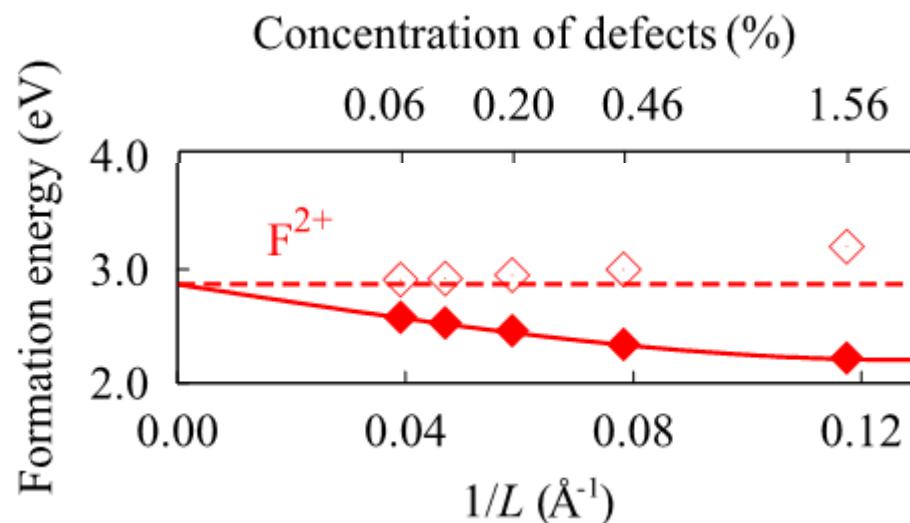
# Charged defects and charge compensation

For a system of charges:



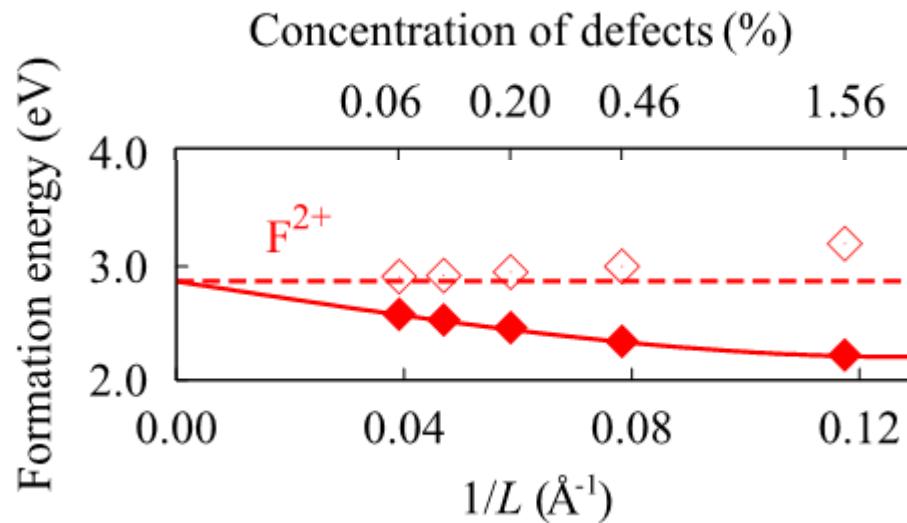
$$V_{\text{interact}} = \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{|r_i - r_j|}$$

In the thermodynamic limit ( $N \rightarrow \infty$ ) 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

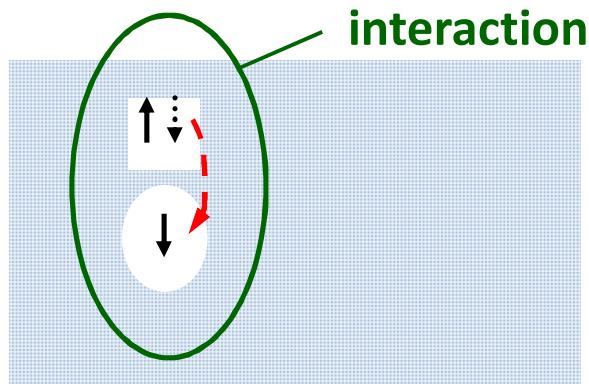
In standard periodic calculations the charge per unit cell is compensated by a uniform background charge (occurs naturally as a regularization of the Ewald summation)

The compensated defects interact much weaker with each other

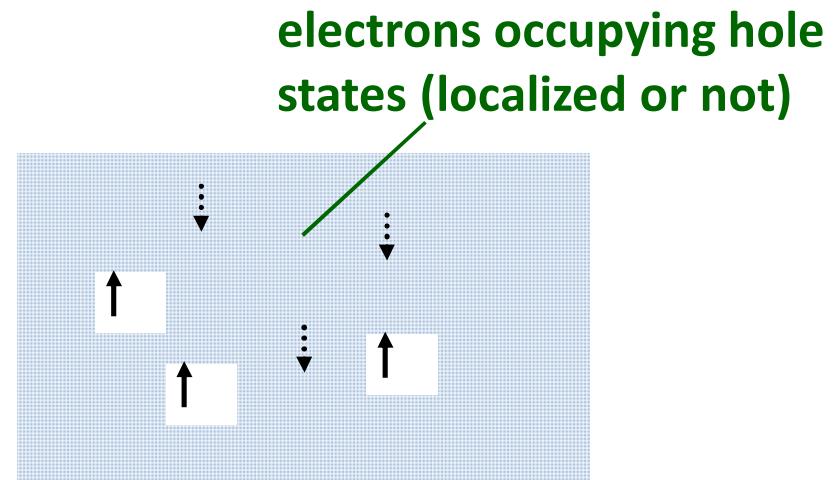
But they do interact strongly with the background ( $\sim 1/L$ )

# Local and global effects of doping

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



Local effect of doping  
(chemical bond formation)



Global effect of doping  
(interaction with the  
compensating charge)

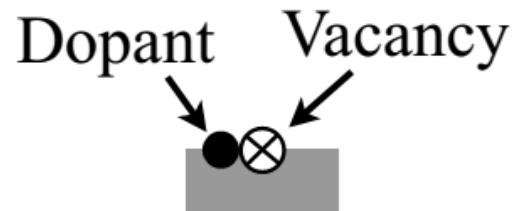
Formation energy and concentration of charged defects depend strongly on the distribution of the defects and the compensating charge

# Defect-defect interactions

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

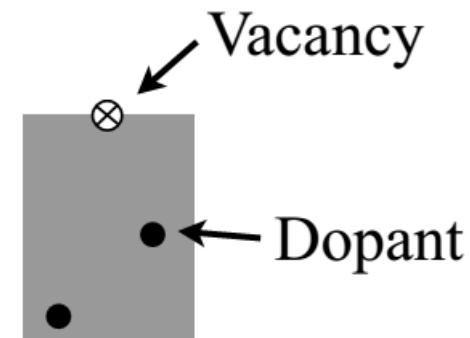
## Local interactions:

- 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

$$\Delta G(n) = n\Delta G_f(n \rightarrow 0) + \frac{1}{2}\epsilon_0 \int \epsilon(\mathbf{r}) |\mathbf{E}|^2 d^3r - TS_{\text{config}}(n)$$


**formation energy  
in the dilute limit**


**electrostatic energy  
at finite  $n$**

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

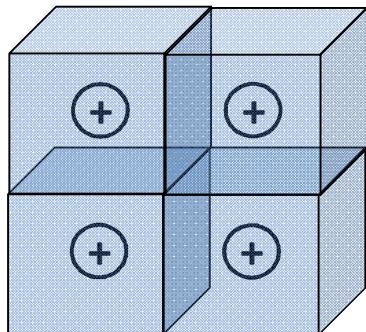
**The charged defects are screened by the compensating charge:**

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

# Charged defects must be compensated

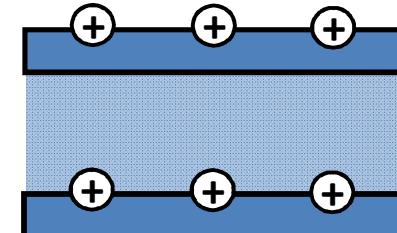
The compensation depends on the spatial distribution of the density of states near the Fermi level

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



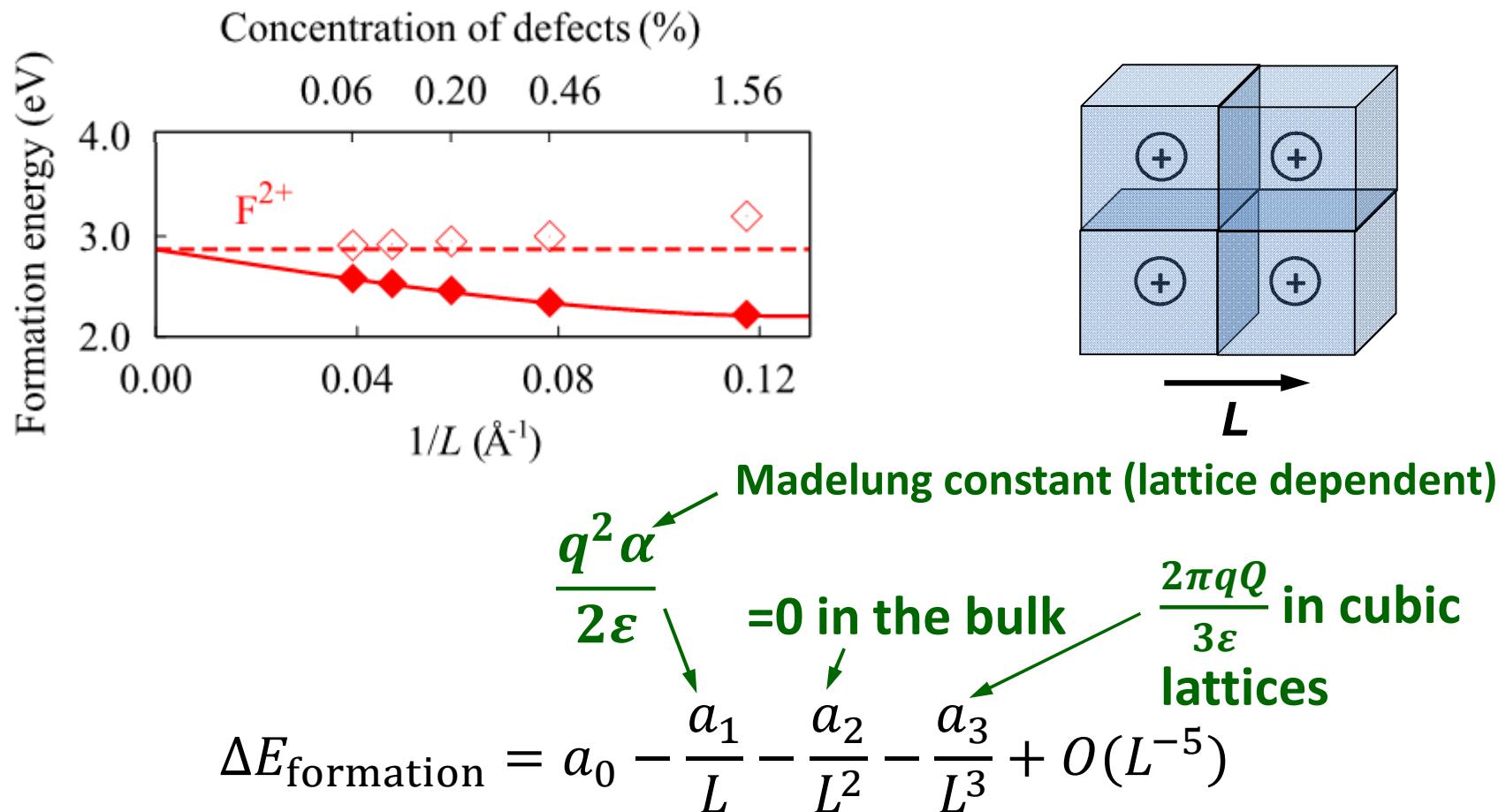
Bulk – OK  
(somewhat  
artificial)

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)

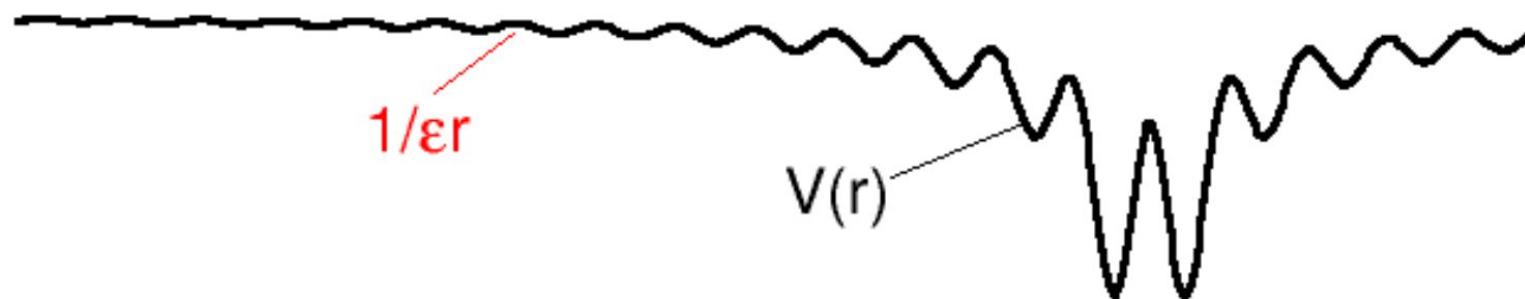


Problems: can be easily calculated only for cubic lattices, only isotropic materials ( $\epsilon$  scalar versus tensor)

G. Makov and M. C. Payne, Phys. Rev. B 51, 4014 (1995)

# Freysoldt-Neugebauer-Van de Walle correction

Isolated charged defect:



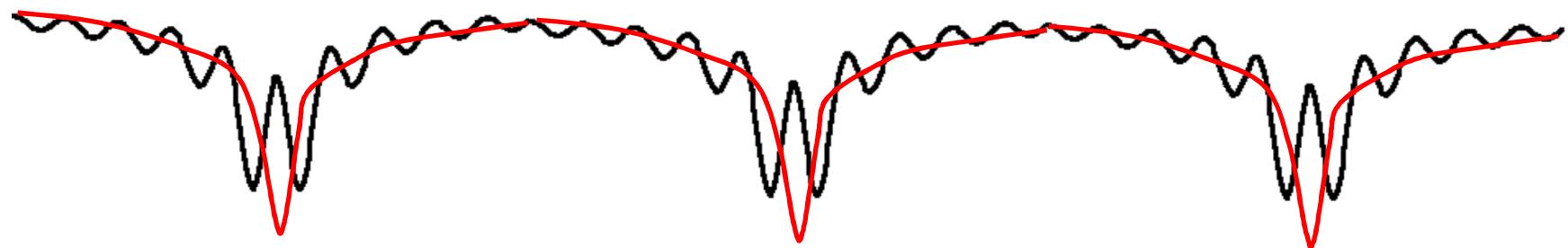
Charged defect in a supercell:



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

# Freysoldt-Neugebauer-Van de Walle correction

Charged defect in a supercell:



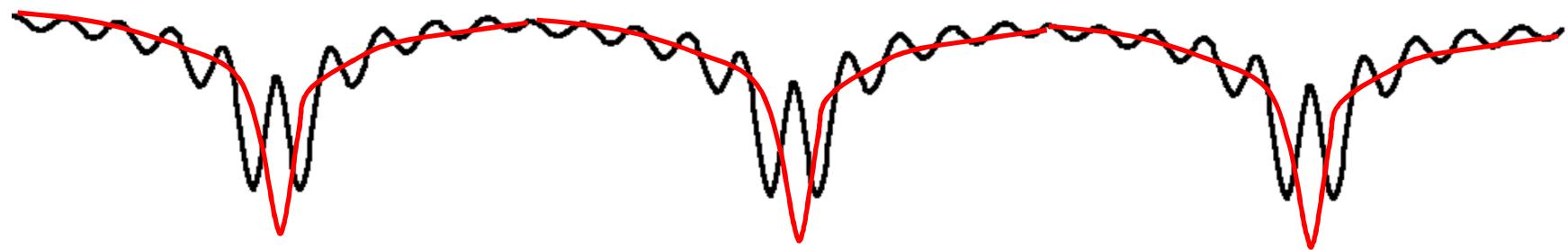
$$V(\mathbf{r}) = V^{\text{short-range}}(\mathbf{r}) + V^{\text{long-range}}(\mathbf{r})$$

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

lattice sum      model charge distribution

# Freysoldt-Neugebauer-Van de Walle correction

Charged defect in a supercell:



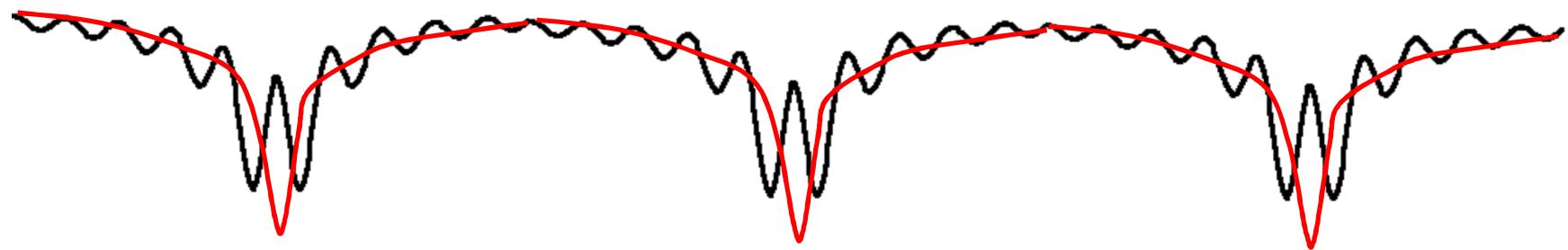
$$V(\mathbf{r}) = V^{\text{short-range}}(\mathbf{r}) + V^{\text{long-range}}(\mathbf{r})$$

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

→ Ewald summation (long-range part)      ↑ remove self-interaction

# Freysoldt-Neugebauer-Van de Walle correction

Charged defect in a supercell:



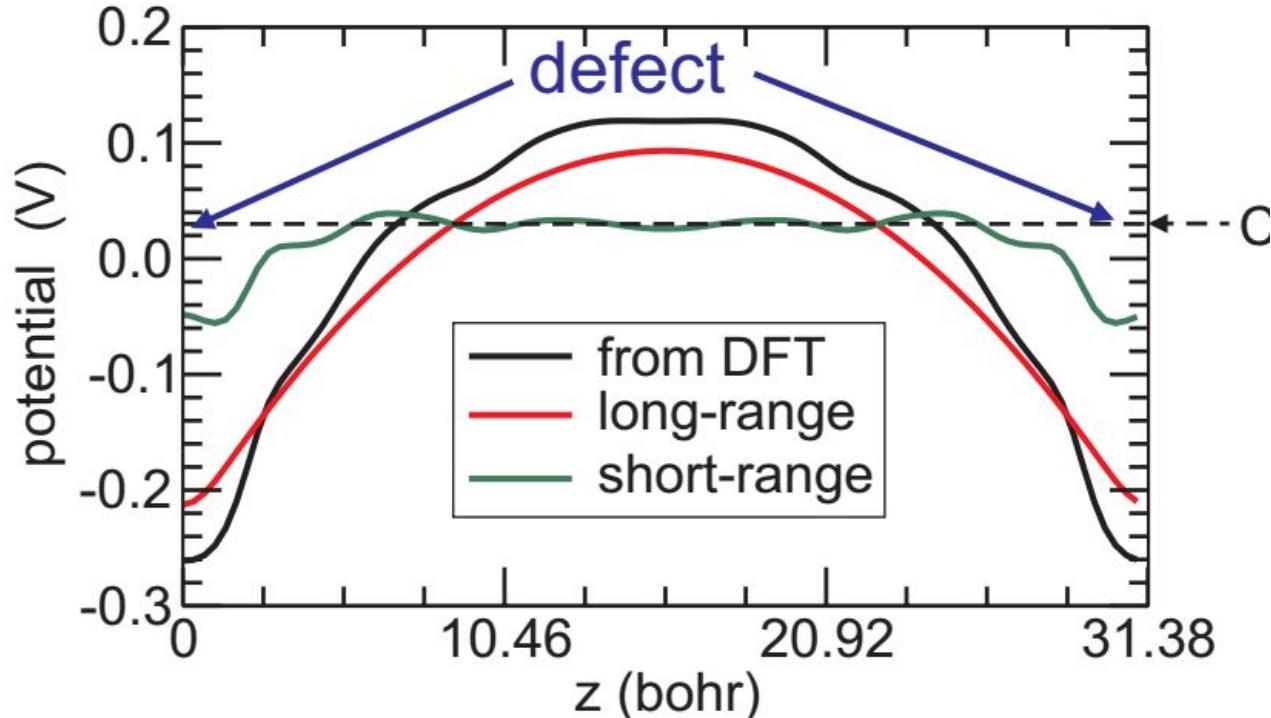
$$E^{\text{long-range}} = \frac{2\pi}{\varepsilon\Omega} \sum_{G \neq 0}^{|G| < G_{\text{cut}}} \frac{\{q^{\text{model}}(|G|)\}^2}{|G|^2} - \frac{1}{\pi\varepsilon} \int dG \{q^{\text{model}}(G)\}^2$$

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

from compensating background (alignment term)

# Freysoldt-Neugebauer-Van de Walle correction

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



$$C = \frac{1}{\Omega} \int d^3r \left\{ V_{\text{model}}^{\text{short-range}}(\mathbf{r}) - V_{\text{defect}}^{\text{short-range}}(\mathbf{r}) \right\}$$

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

# Freysoldt-Neugebauer-Van de Walle correction

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

screened Coulomb interaction:

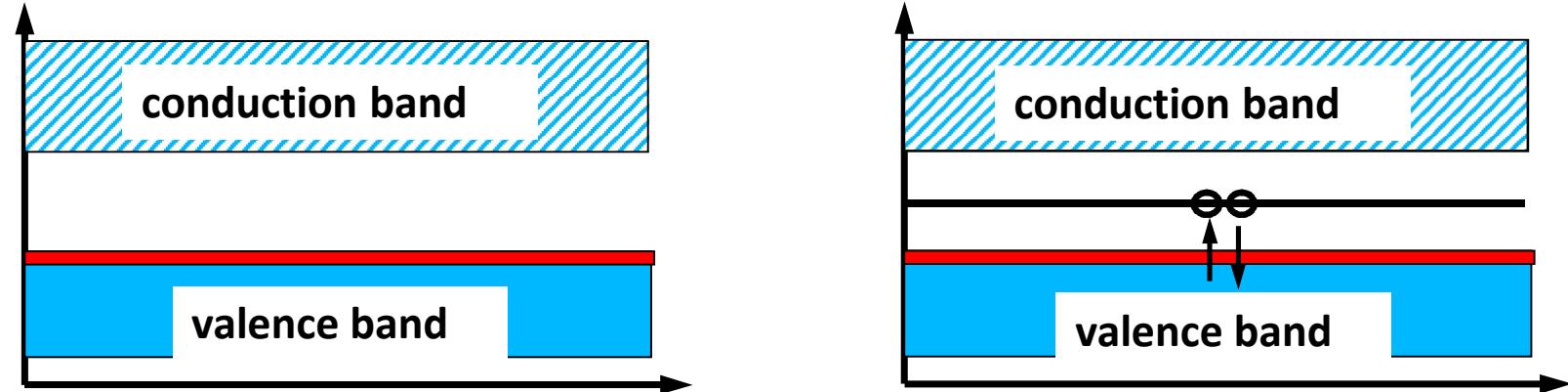
- originally formulated for electronic response only ( $\varepsilon_\infty$ )
- was shown to work when ionic response is included ( $\varepsilon_0$ ), but this is not general (can fail for polarons)
- can be easily generalized to anisotropic materials ( $\varepsilon \rightarrow \varepsilon_{ij}$ )

The method is for calculating formation energy of isolated defect

# 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

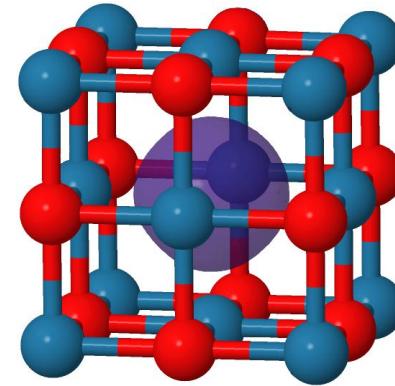
$$q_{\text{Mg}} = 12 - q_{\text{defect}}/N_{\text{Mg}} \rightarrow p\text{-type doping in MgO}$$



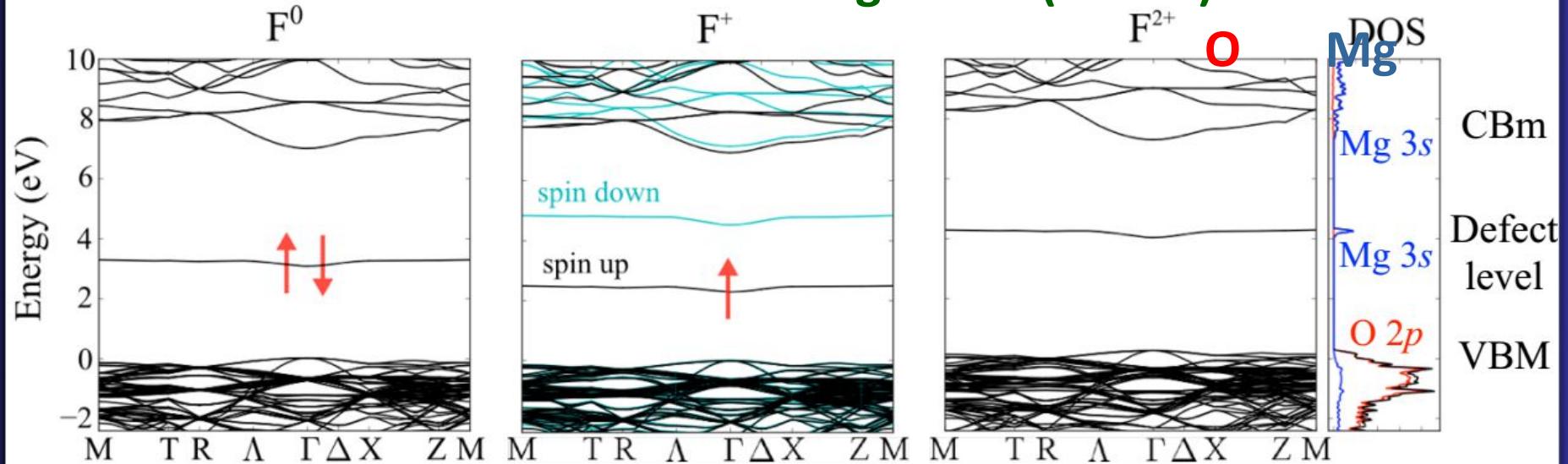
L. Vegard, Z. Phys. **5**, 17 (1921); M. Scheffler, Physica B+C **146**, 176 (1987); O. Sinai and L. Kronik, Phys. Rev. B **87**, 235305 (2013)

# O vacancies (F-centers) in MgO

MgO bulk with  
oxygen vacancy

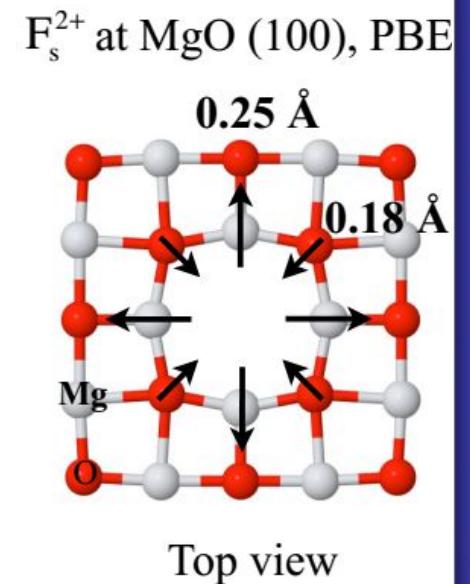
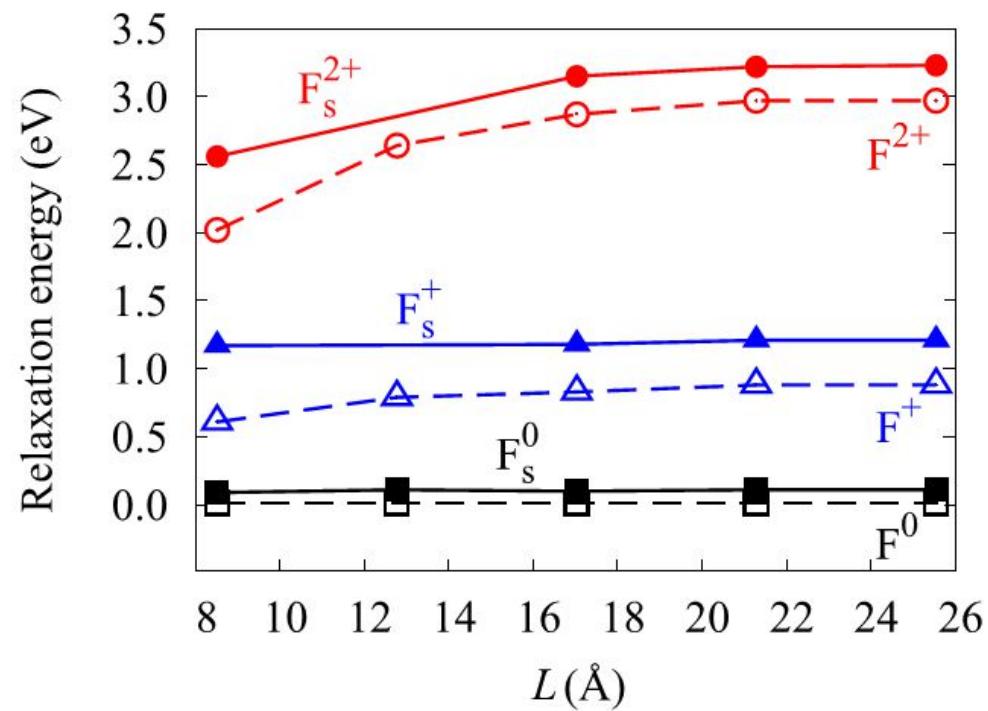
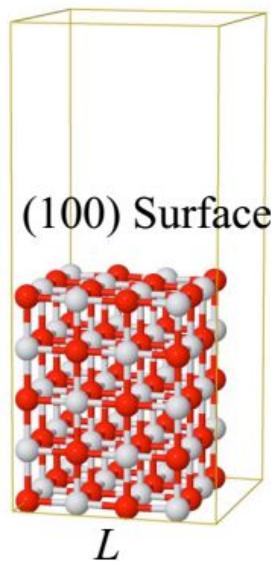


Band structures of O vacancies in MgO bulk (HSE06)



# Atomic relaxation

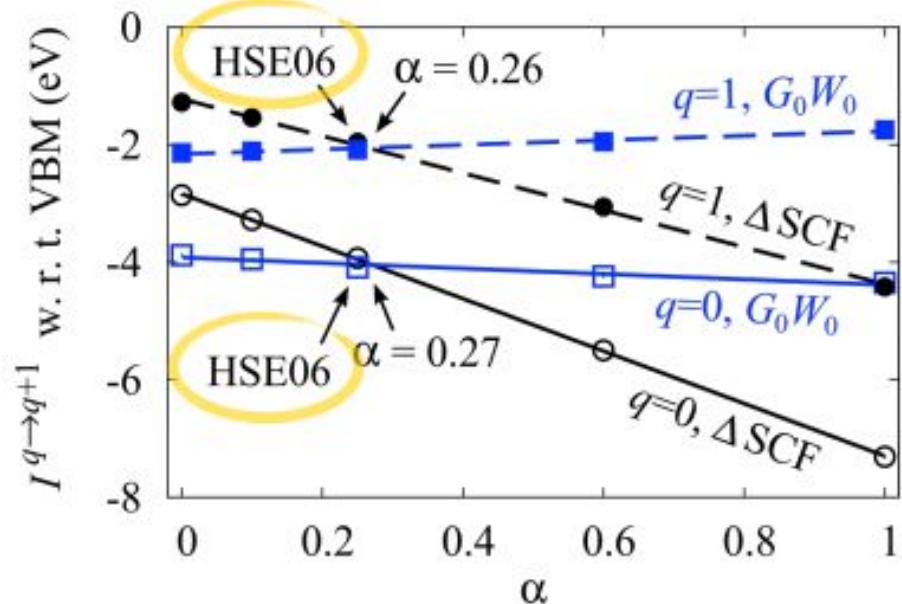
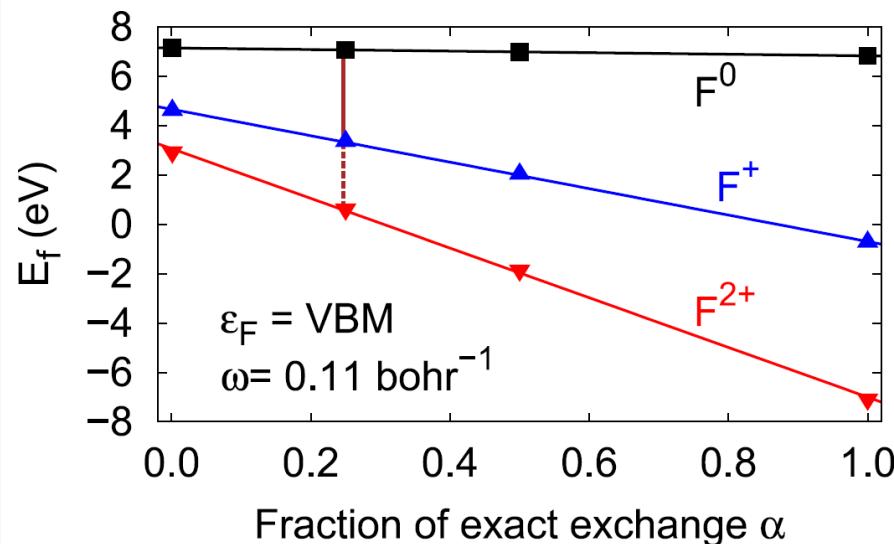
Relaxation energies for F centers in MgO bulk and at MgO (100)



# Sensitivity to approximations in DFT

Energy differences between different charge states<sup>1)</sup>

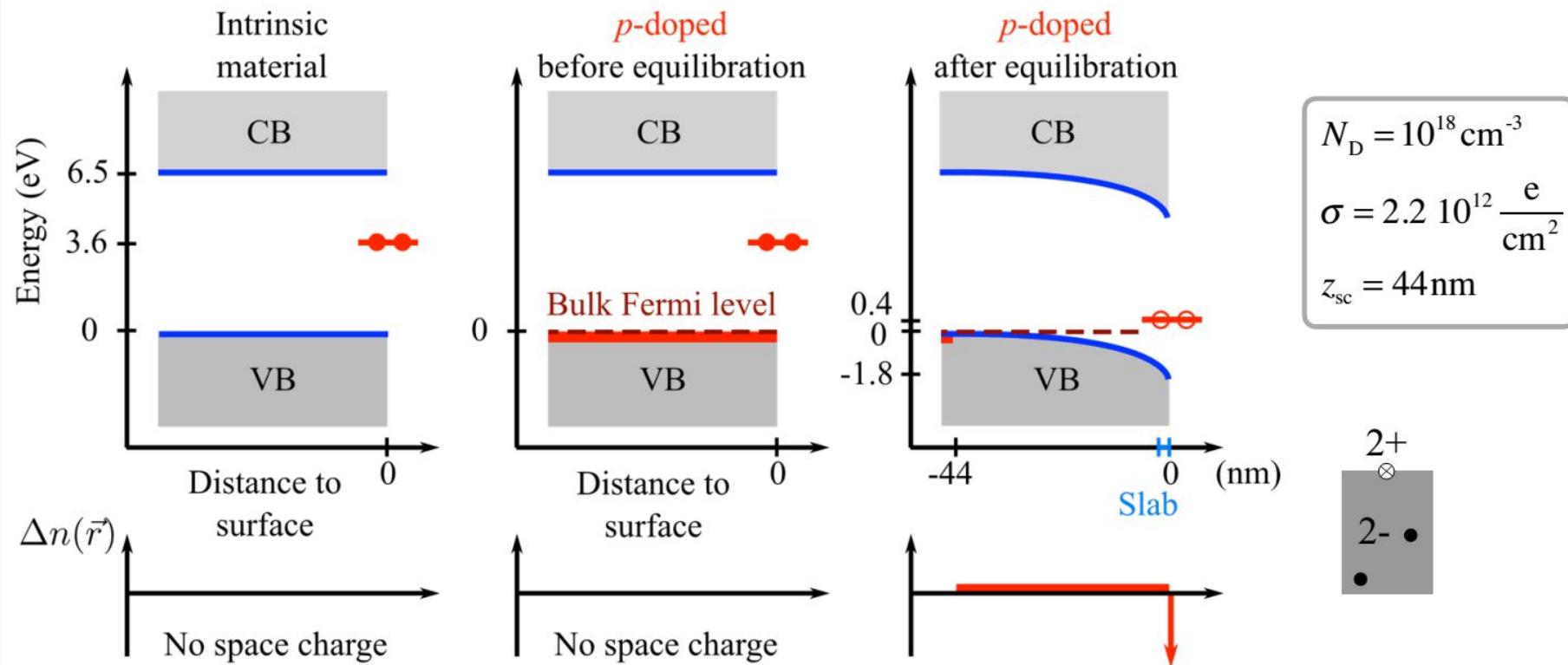
$$\Delta G_f^D(q = +1) = \underbrace{\Delta G_f^D(q = 0) - \Delta_{+1}^0}_{\text{DFT}} + \underbrace{\text{IP}_{\text{defect level}} - \text{IP}_{\text{VBM}}}_{G_0 W_0}$$



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



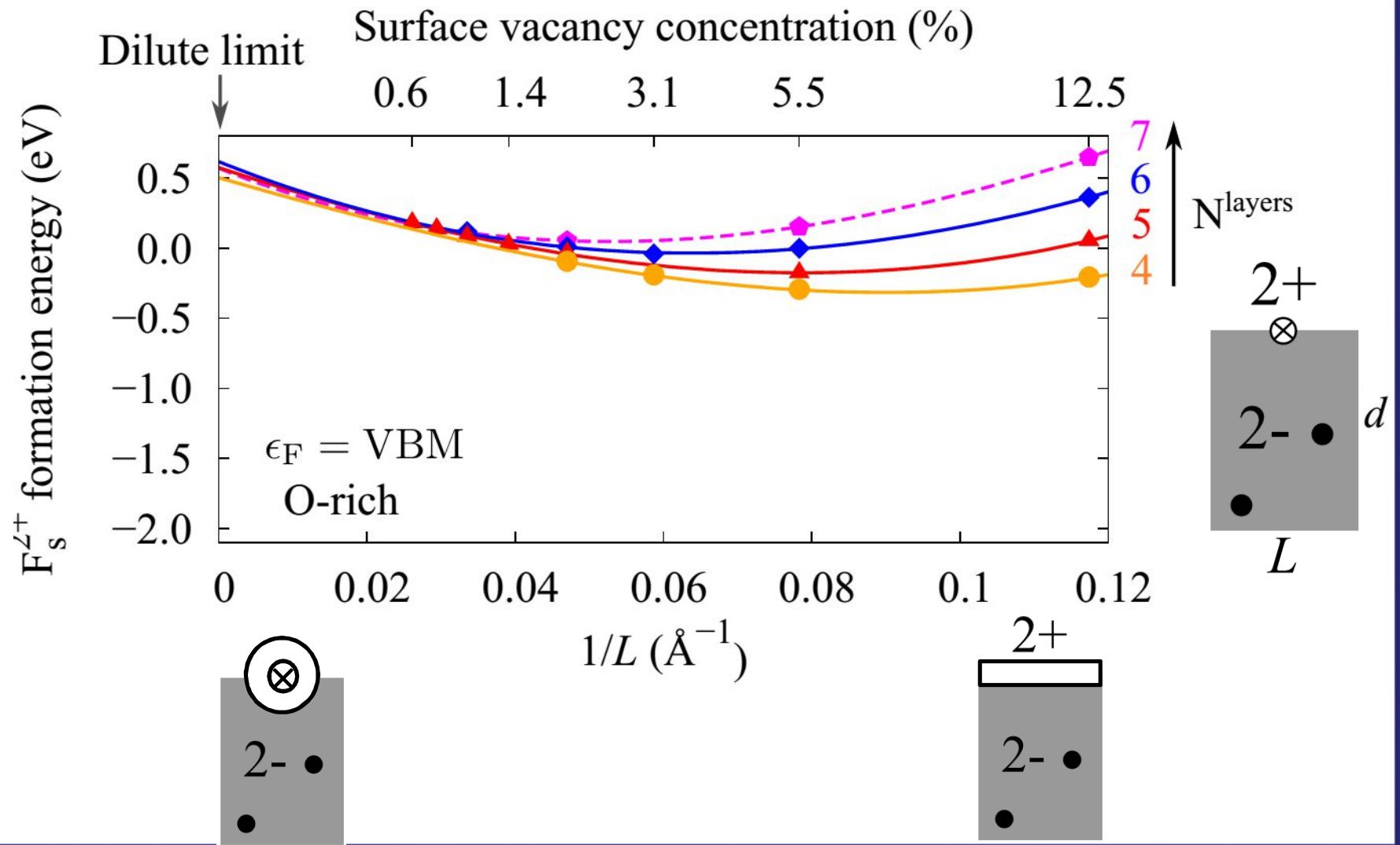
Space charge region  $z_{\text{sc}} = \frac{\sigma}{e N_D}$  causes band bending and electric field

$N_D$  : Dopant concentration

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

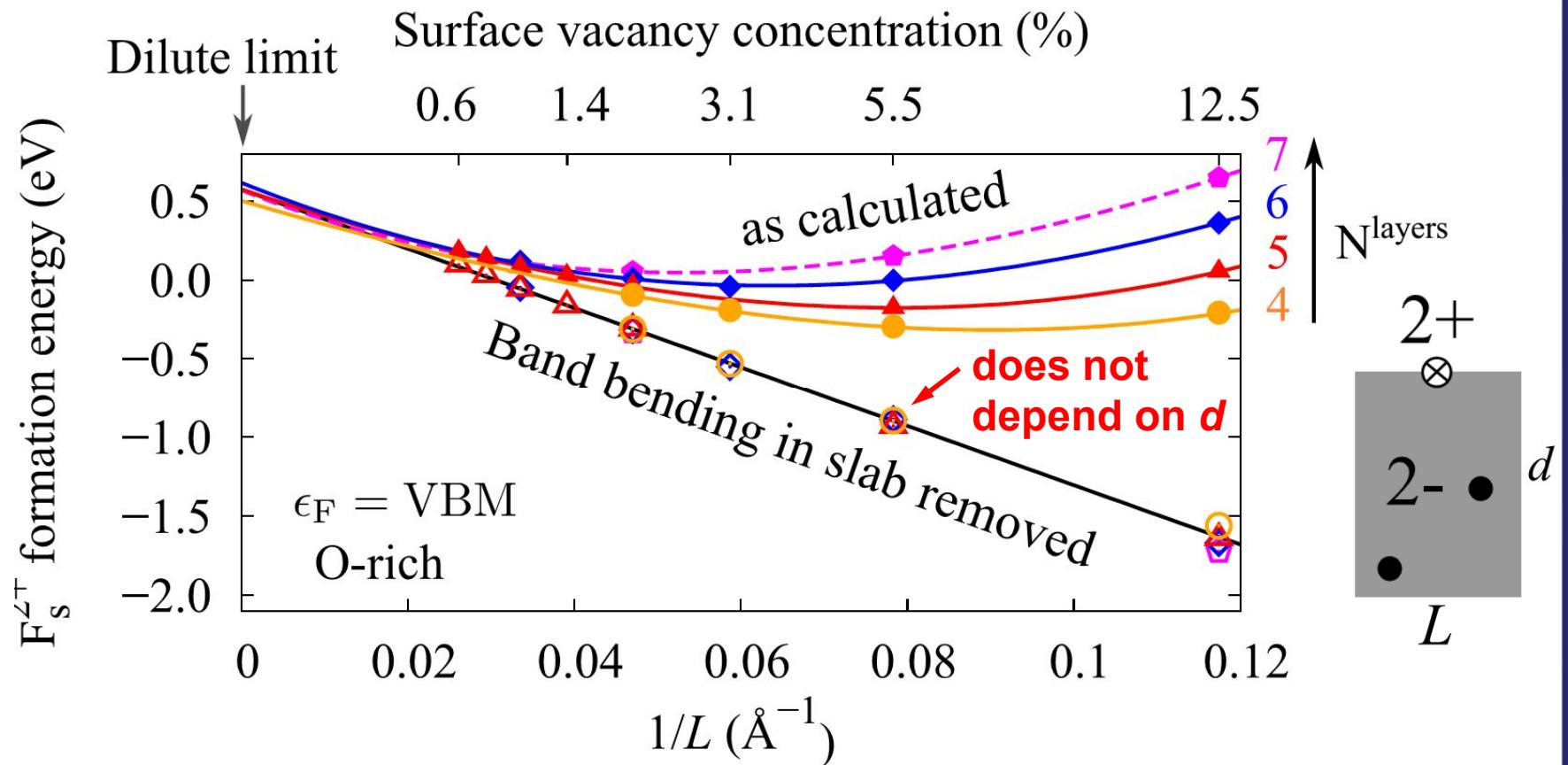
# Electrostatics in periodic calculations of charged defects

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



# Electrostatics in periodic calculations of charged defects

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

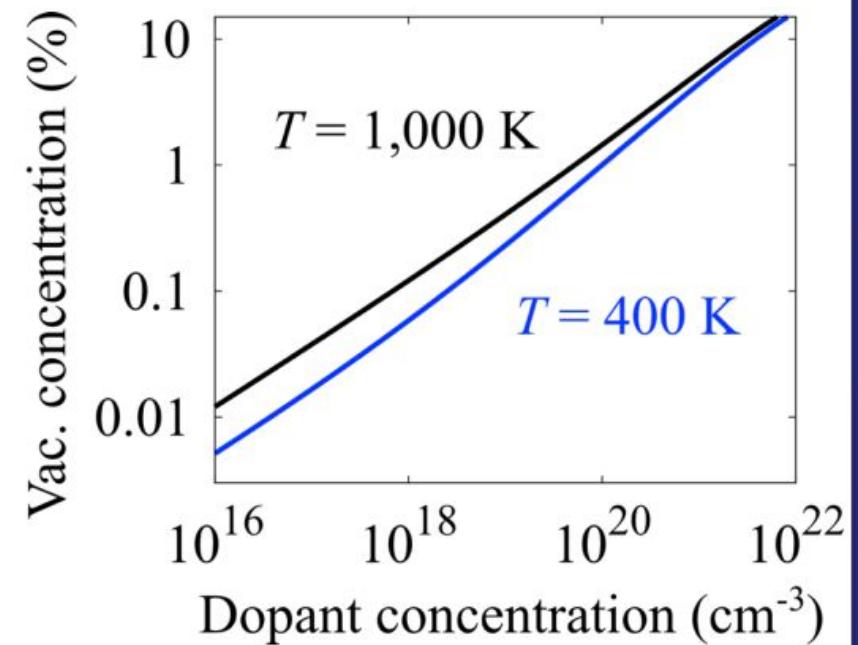
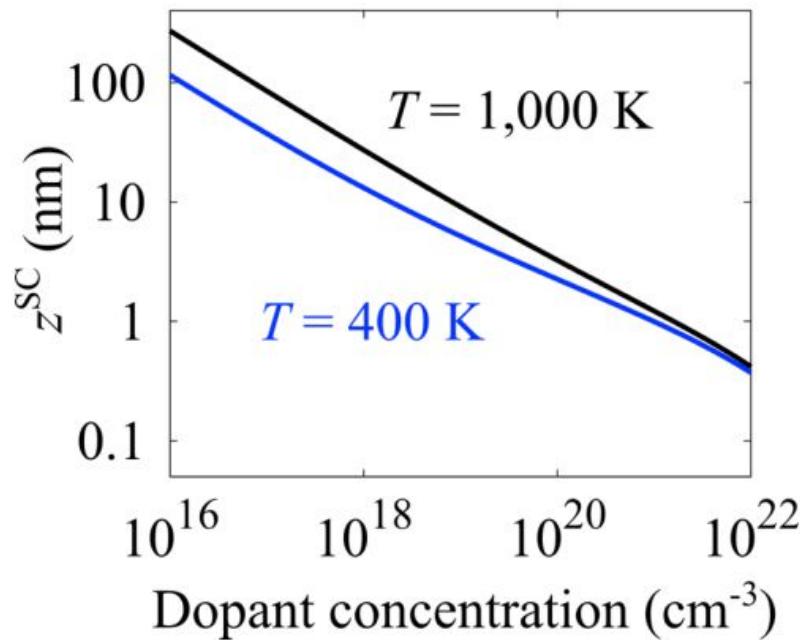


$$\frac{1}{2}\varepsilon\varepsilon_0 \int |\mathbf{E}|^2 d^3r = -C\sqrt{|\sigma|} + qE^{\text{SC}}(d), E^{\text{SC}}(d) = \frac{e|\sigma|}{6\varepsilon\varepsilon_0}d$$

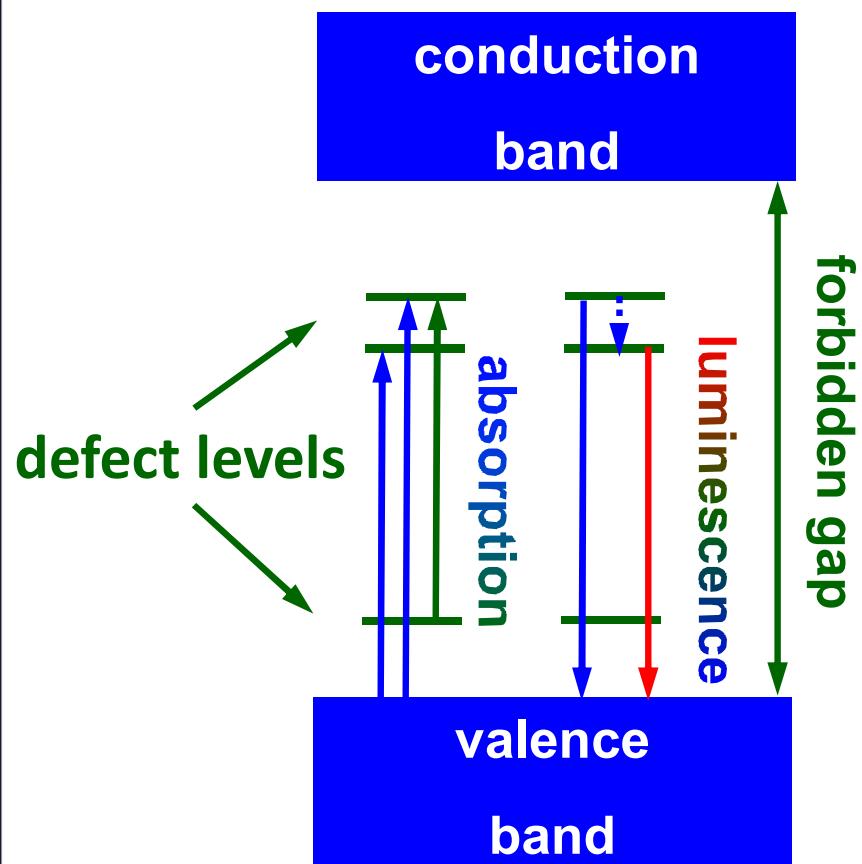
# $\text{F}^{2+}$ concentration at $p\text{-MgO}(001)$

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

$$z^{\text{SC}} = \frac{\sigma}{eN_D}$$



# Optical properties of defects



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

# Optical properties of defects

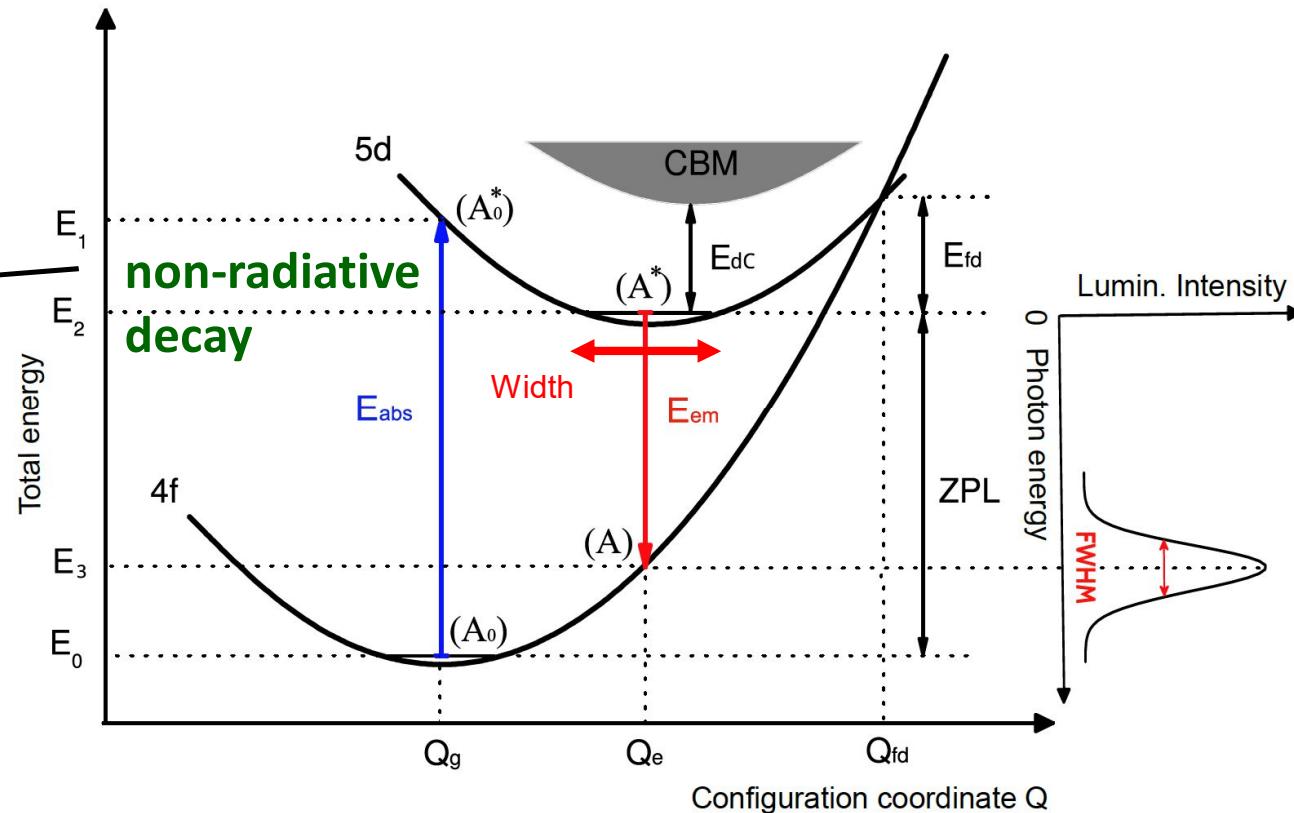
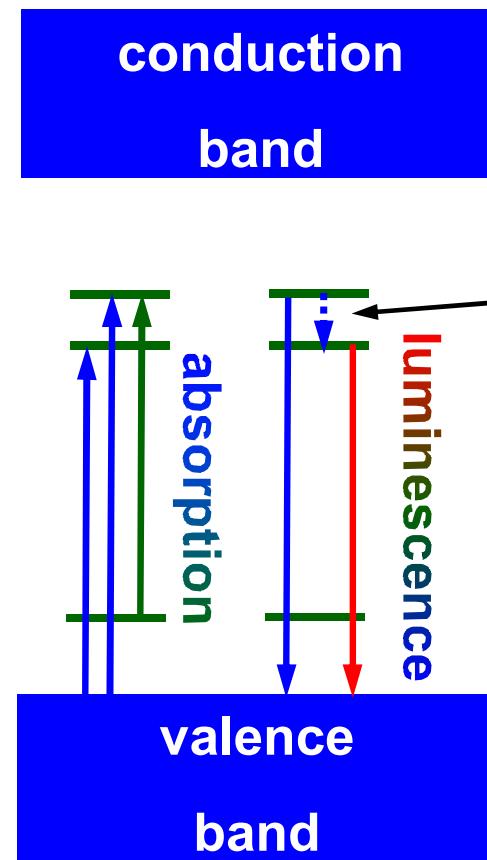
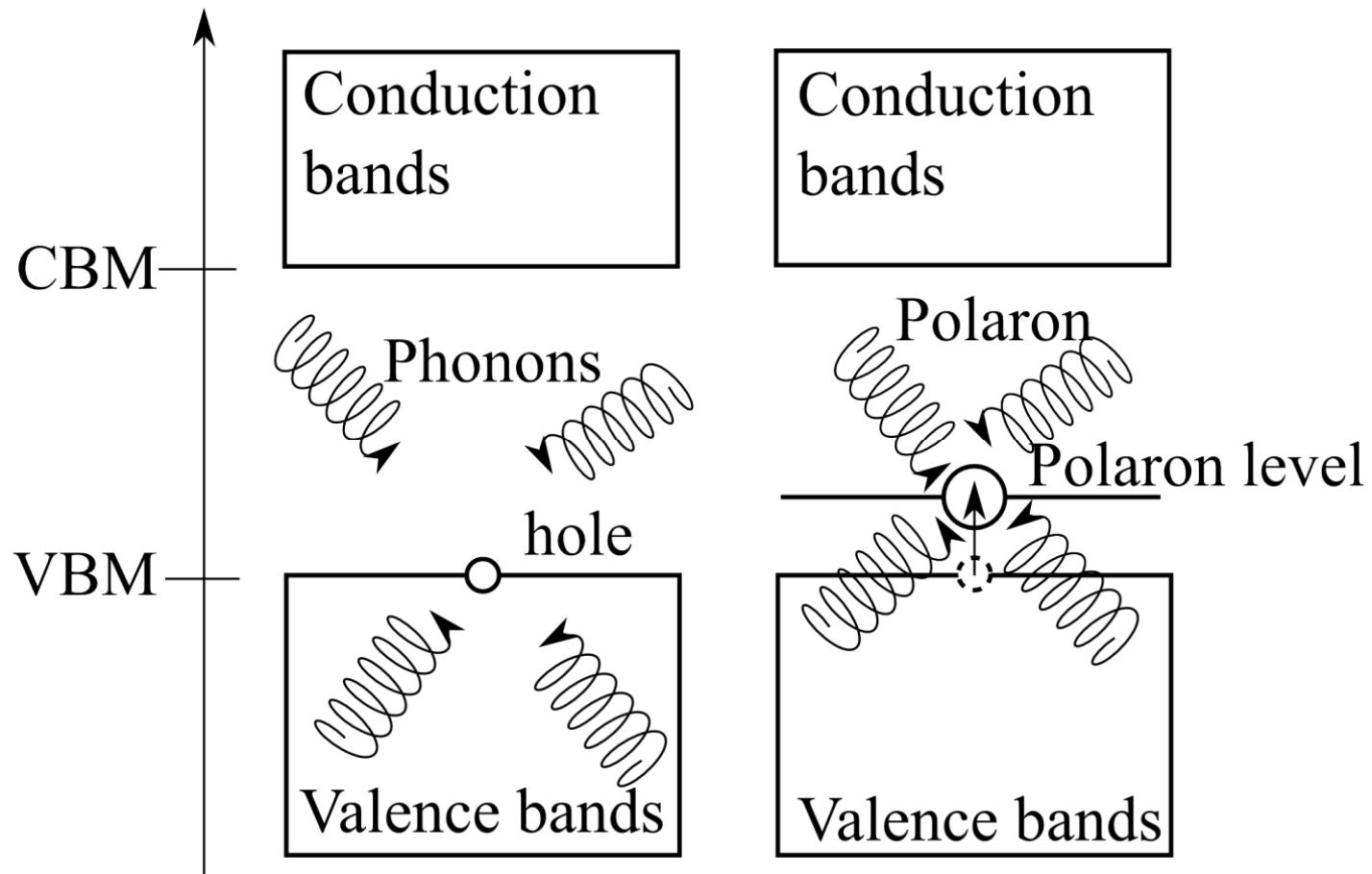


figure courtesy of Xavier

**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)**

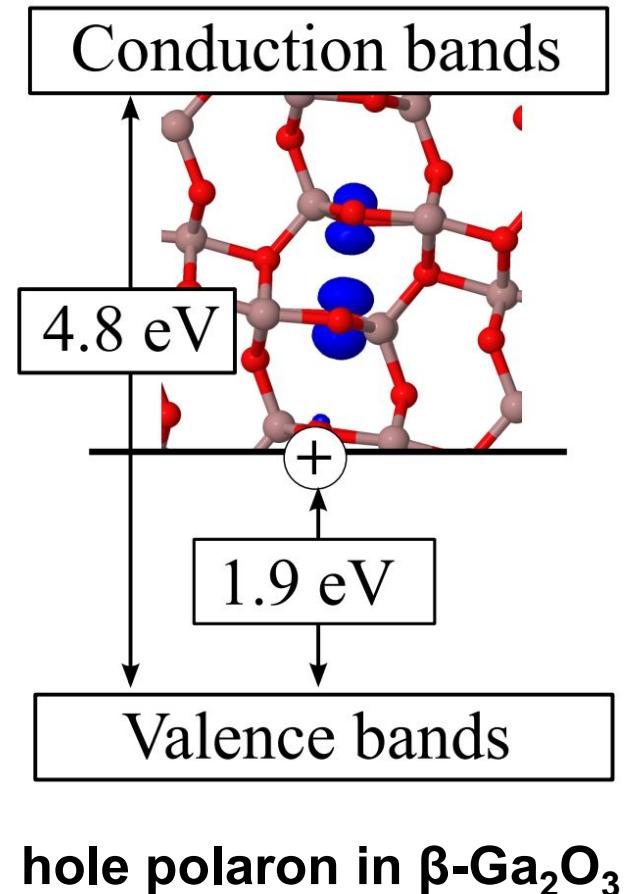
# Polaron properties

## 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)



# Before modern electronic-structure calculations: Polaron models

Fröhlich model:

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

frequency of longitudinal optical phonon mode      Fourier components of electron-phonon interaction

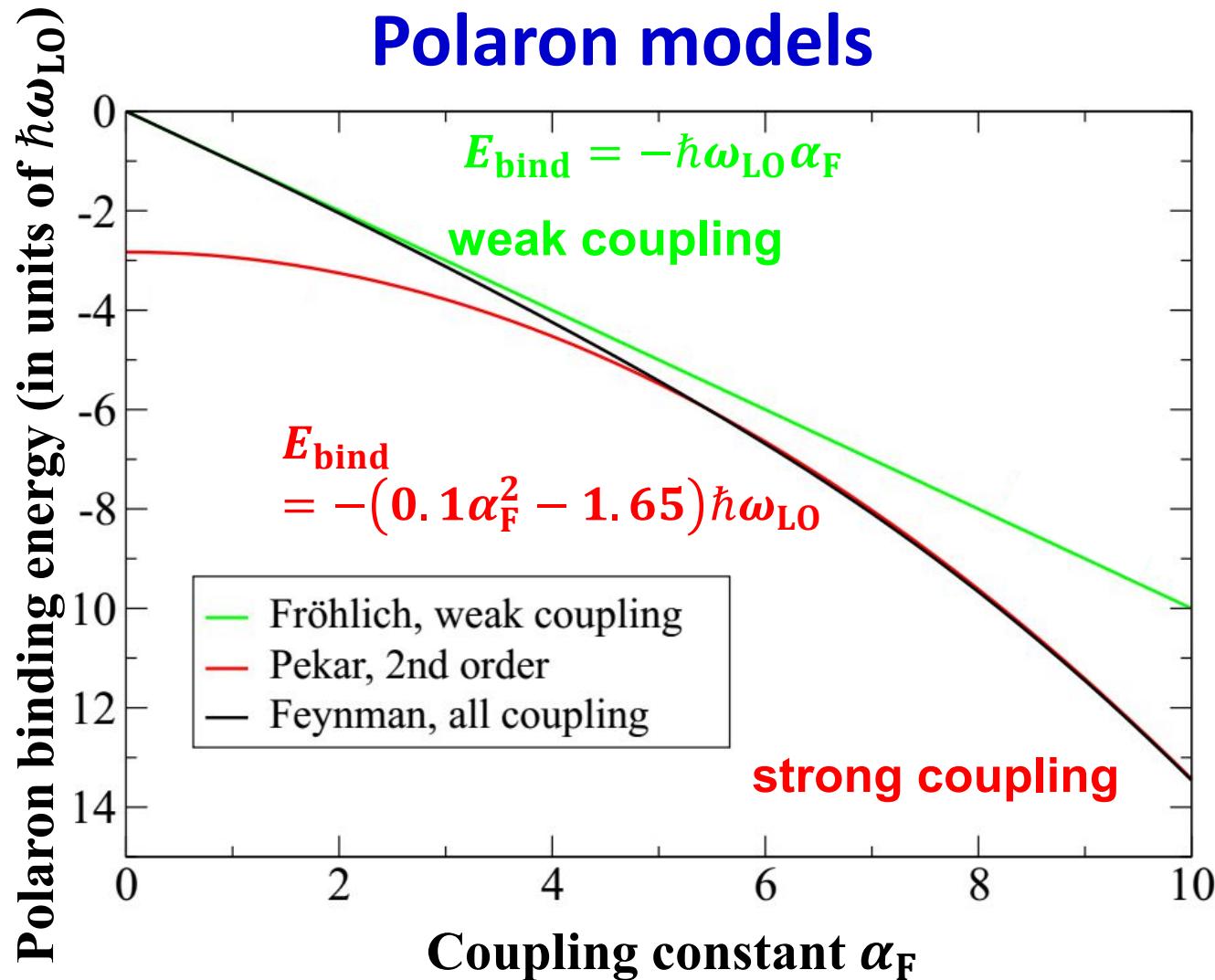
$$V_{\mathbf{q}} = -i \frac{\hbar \omega_{\text{LO}}}{|\mathbf{q}|} \left( \frac{4\pi \alpha_F}{\Omega} \right)^{1/2} \left( \frac{\hbar}{2m_b \omega_{\text{LO}}} \right)^{1/4}$$

With Fröhlich coupling constant:

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

band mass (curvature of band)  
electronic dielectric response      static dielectric constant

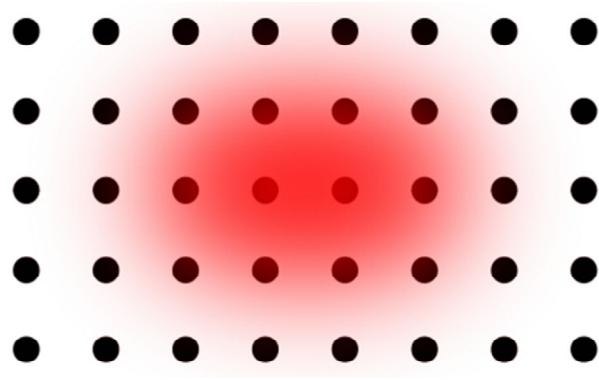
# Before modern electronic-structure calculations: Polaron models



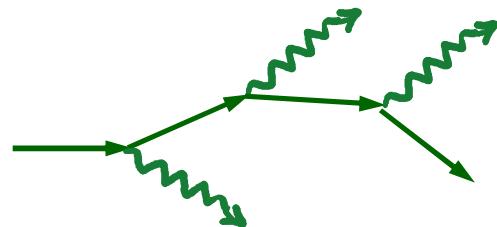
polaron radius:  $r_p = 3.2 \frac{1}{\alpha_F} \sqrt{\frac{\hbar}{2m_b\omega_{\text{LO}}}}$

# Small versus large polarons

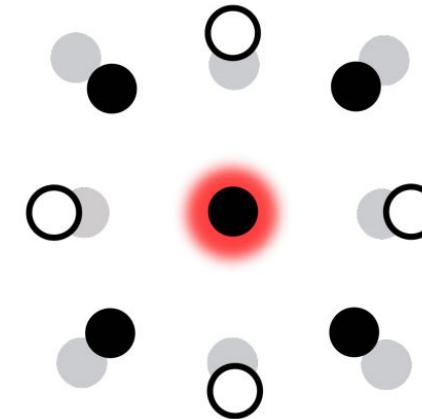
Polaron = Charge + Lattice Distortion



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



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



Small polaron (metal  
oxides, polymers)



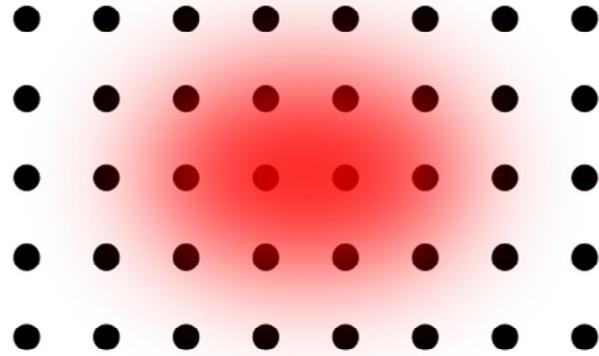
Mobility

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

## **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 is neglected**

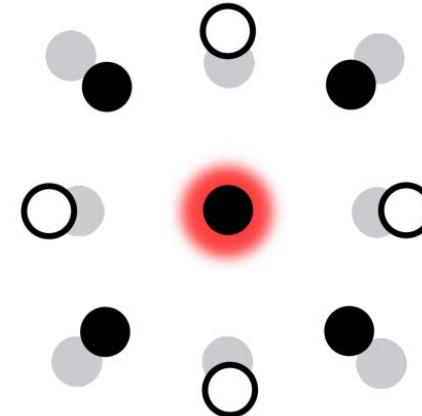
# Modeling polarons with DFT



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

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

**Perturbation theory**



**Small polaron (metal  
oxides, polymers)**

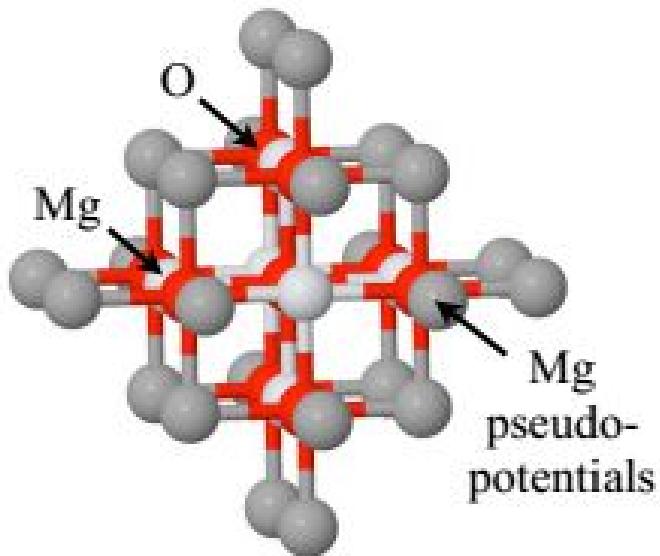
**Mobility**

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

**explicit calculation**

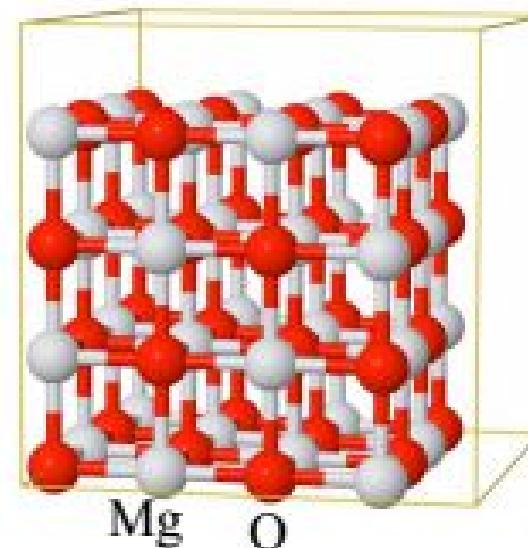
# Modeling polarons with DFT

## Embedded cluster model



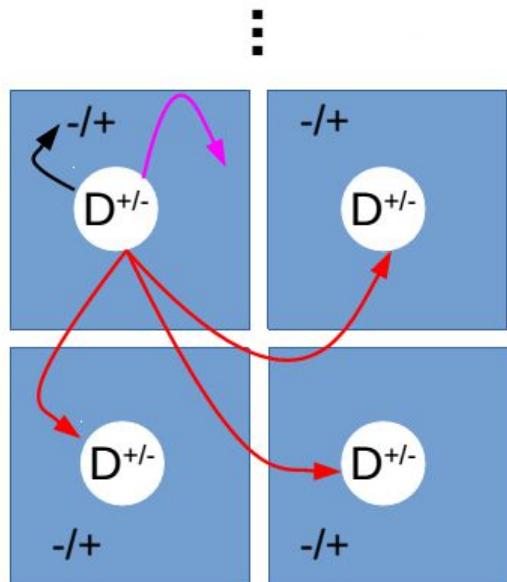
- + Isolated polaron
- + Higher-level methods can be applied
- No long-range phononic response
- Artificial finite-size effects

## Periodic model



- + Long-range ionic response
- Artificial periodic repeat (finite-size effects)

# Supercell calculations of small polarons



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

Finite-size errors

Self-interaction error

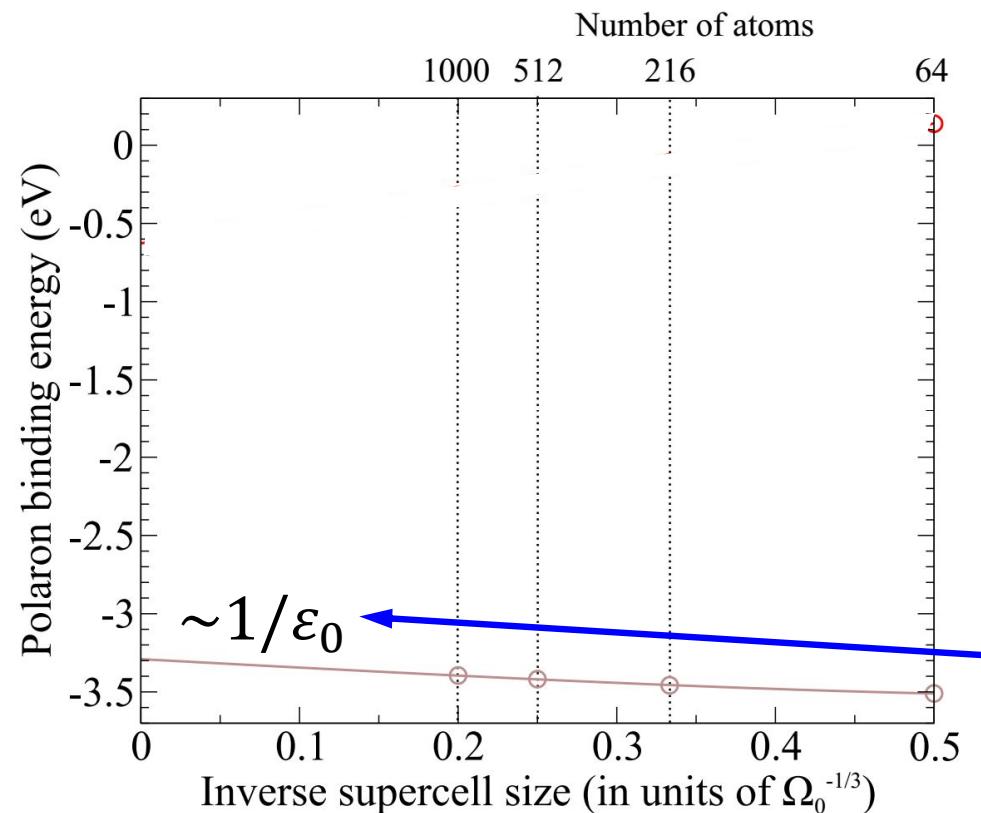
Delocalization - Localization

- Finite-size supercell errors
- Localization/Delocalization errors

# The polaron potential energy surface

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

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

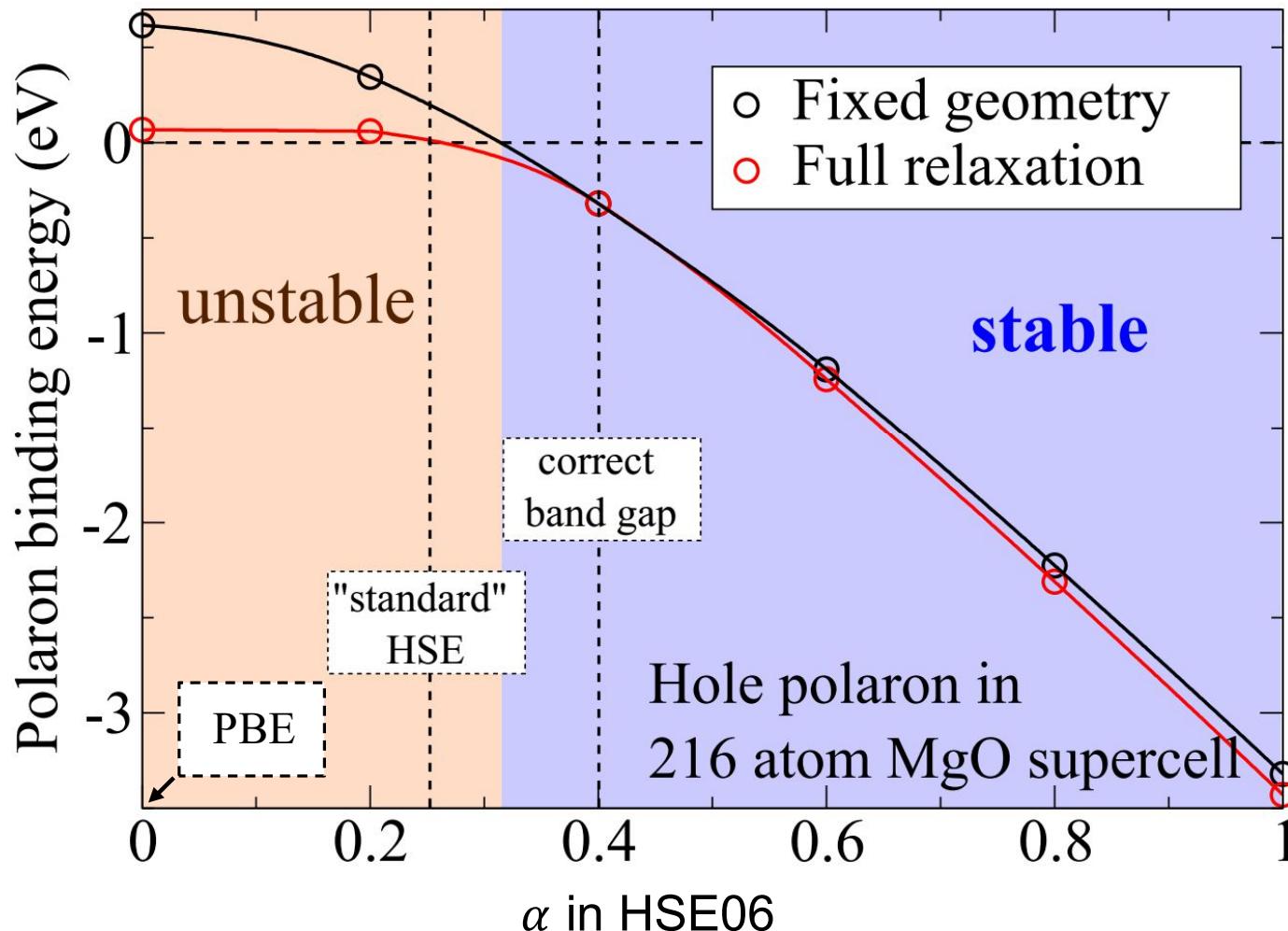


hole polaron in  
MgO, HSE( $\alpha=1$ )

Finite-size  
correction ~0.2 eV

Note: for polarons this  
is not always the case  
(e.g., TiO<sub>2</sub>), depends  
on coupling strength

## Conventional approach: Dependence on functional



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

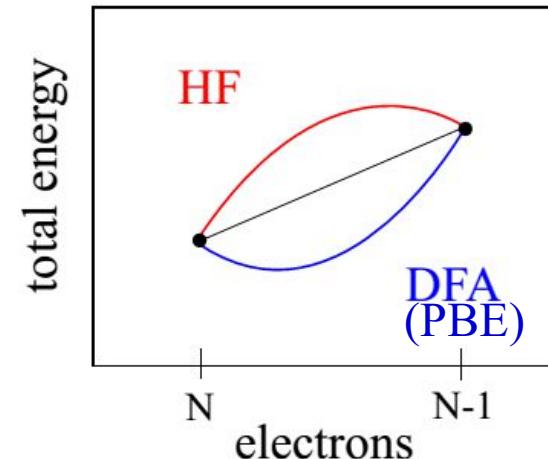
# Theoretical challenges

## Self-interaction error $\Sigma_i$

- Convex curvature
- PBE

## No correlation $\Pi_i$

- Concave curvature
- Exact exchange



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

“Piecewise linearity of total energy with fractional occupation”

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

Best hybrid functional [4]:  
$$\exists \alpha: \Pi + \Sigma = \Delta_{XC} = 0$$

Finite-size errors

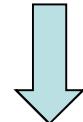
[3] Perdew et al., Phys. Rev. Lett. 49, 1691 (1982)

[4] Lany and Zunger, Phys. Rev. B 80, 085202 (2009)

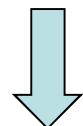
# Polaron binding energy

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

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



$$E_{\text{bind}} = E_{\text{distort}}(N - 1) - [E_{\text{perfect}}(N) - \epsilon_{\text{VBM}}(N)] + \Pi_p + \Sigma_p + \Delta_p$$



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

$$E_{\text{bind}} = E_{\text{distort}}(N) - E_{\text{perfect}}(N) - [\epsilon_{\text{HO}}(N) - \epsilon_{\text{VBM}}(N)] + (\Pi_d - \Pi_p) + (\Sigma_d - \Sigma_p) + (\Delta_d - \Delta_p)$$

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

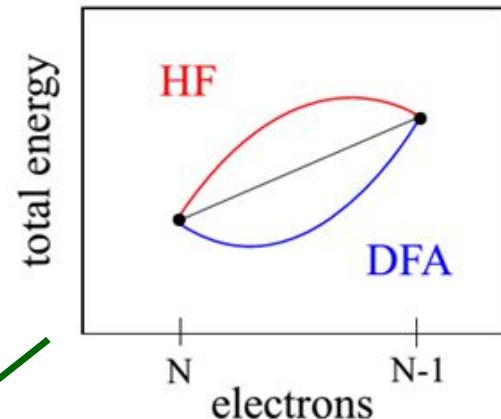
Zawadski *et al.*, Chem. Phys. Lett. 506, 42 (2011)

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

# The polaron potential energy surface

Conventional approach:

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



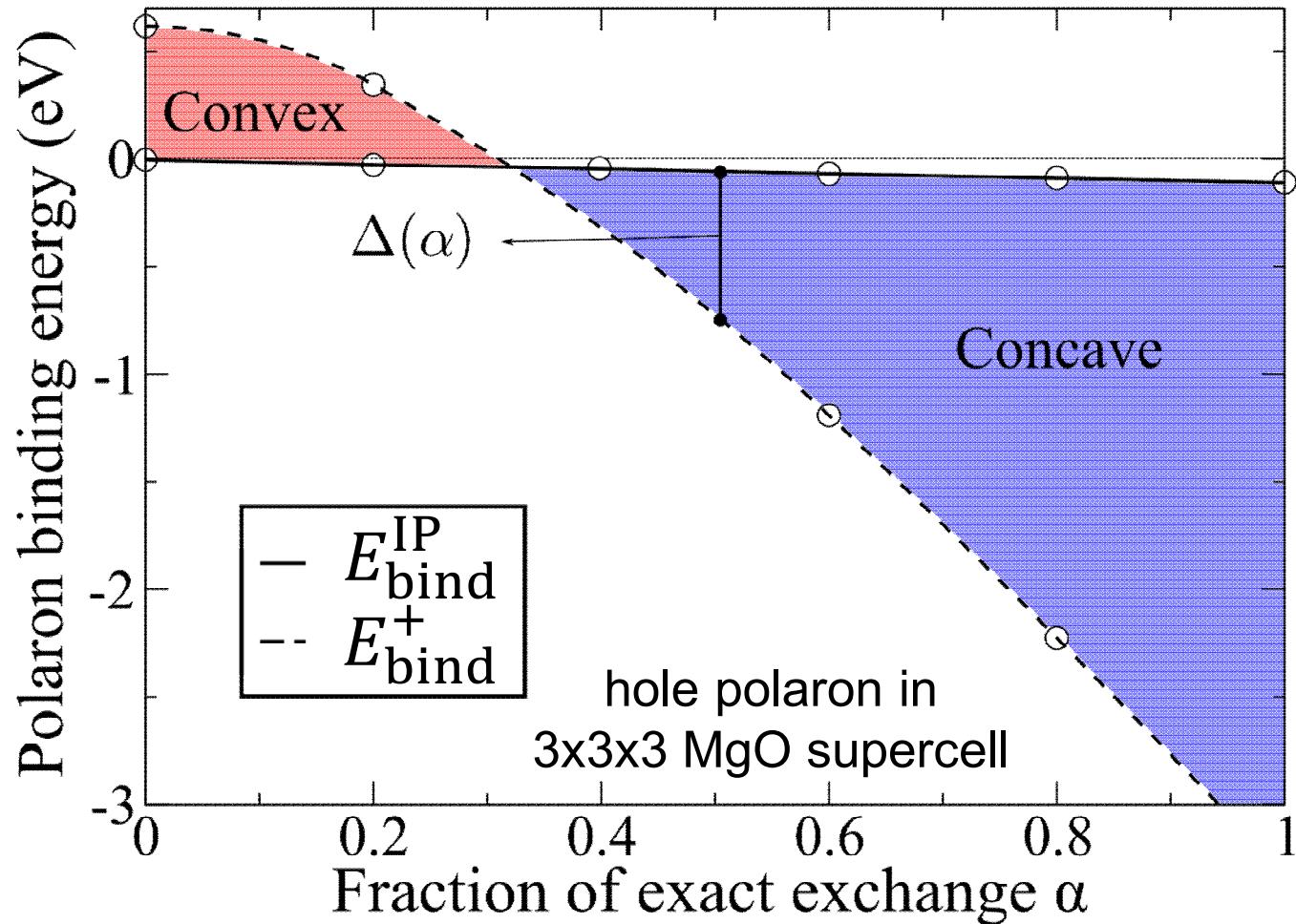
Exact functional:  $E(N - 1) - E(N) = -\epsilon_{HO}(N)$

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

Force evaluation from *neutral system* properties:

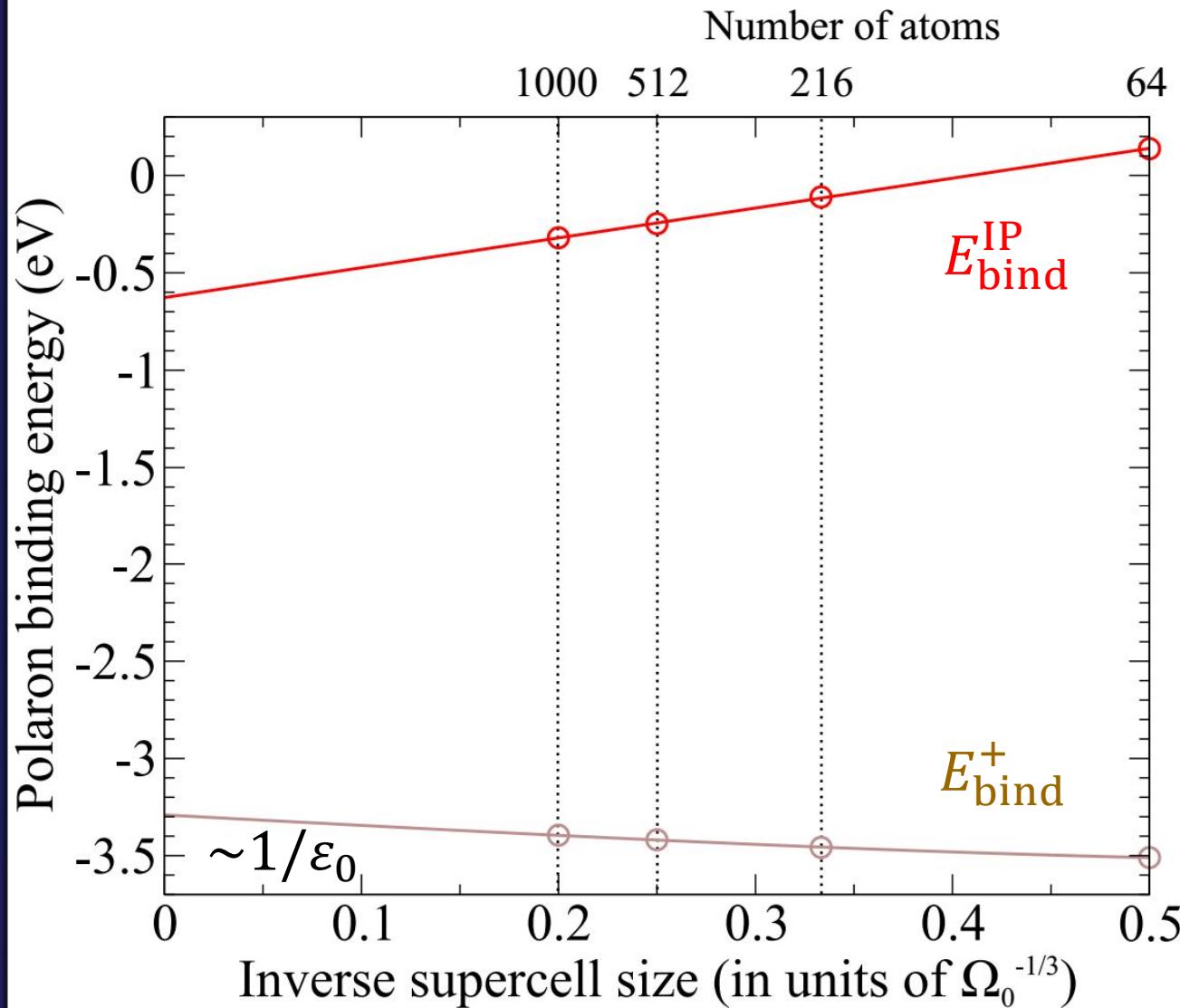
$$F_i = \frac{\partial}{\partial R_i} (E(N) - \epsilon_{HO}(N))$$

# Functional dependence for the new potential energy surface



The functional dependence is greatly reduced!  
Qualitatively correct for the whole range of  $\alpha$

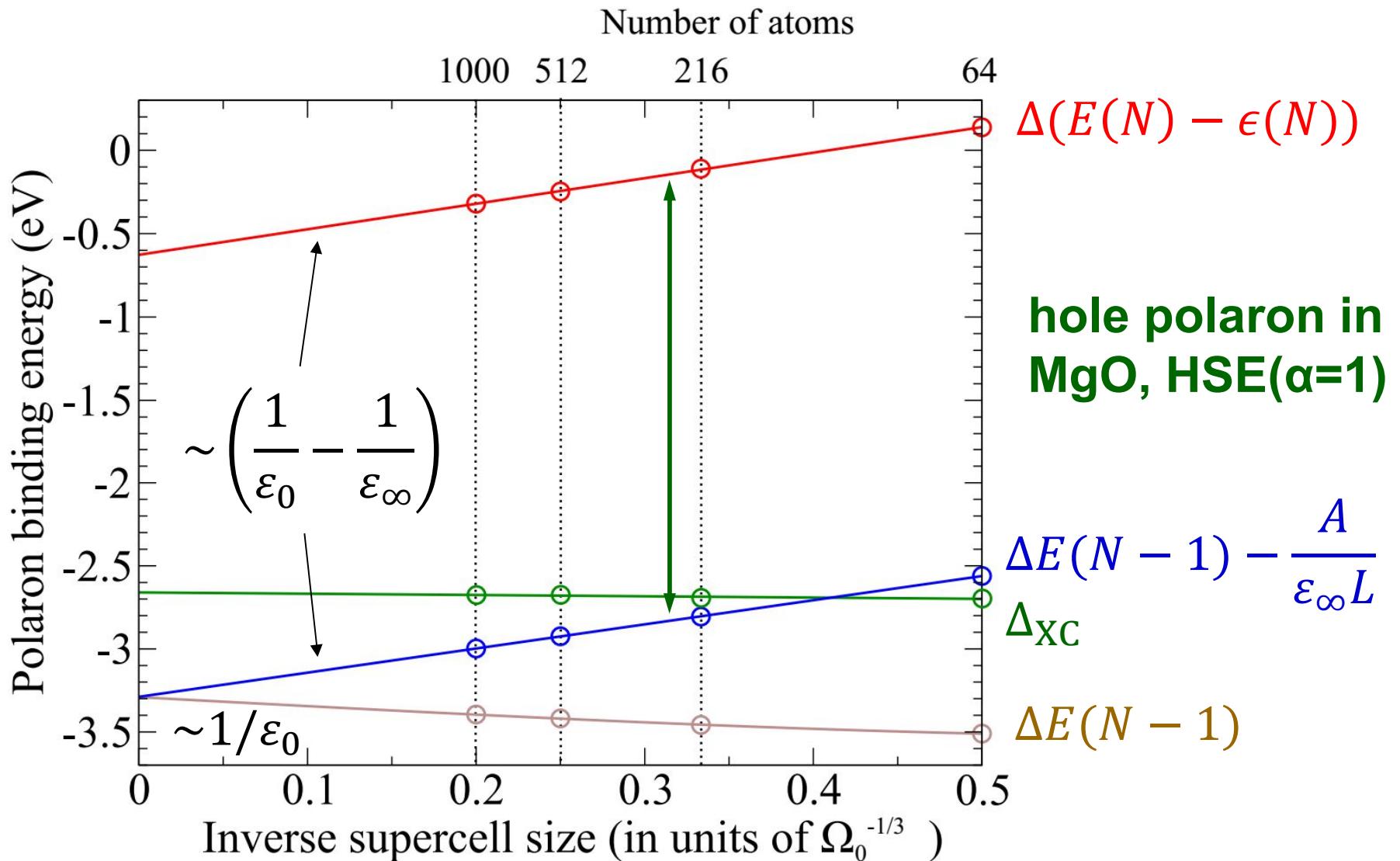
## Finite-size effects



hole polaron in  
MgO, HSE( $\alpha=1$ )

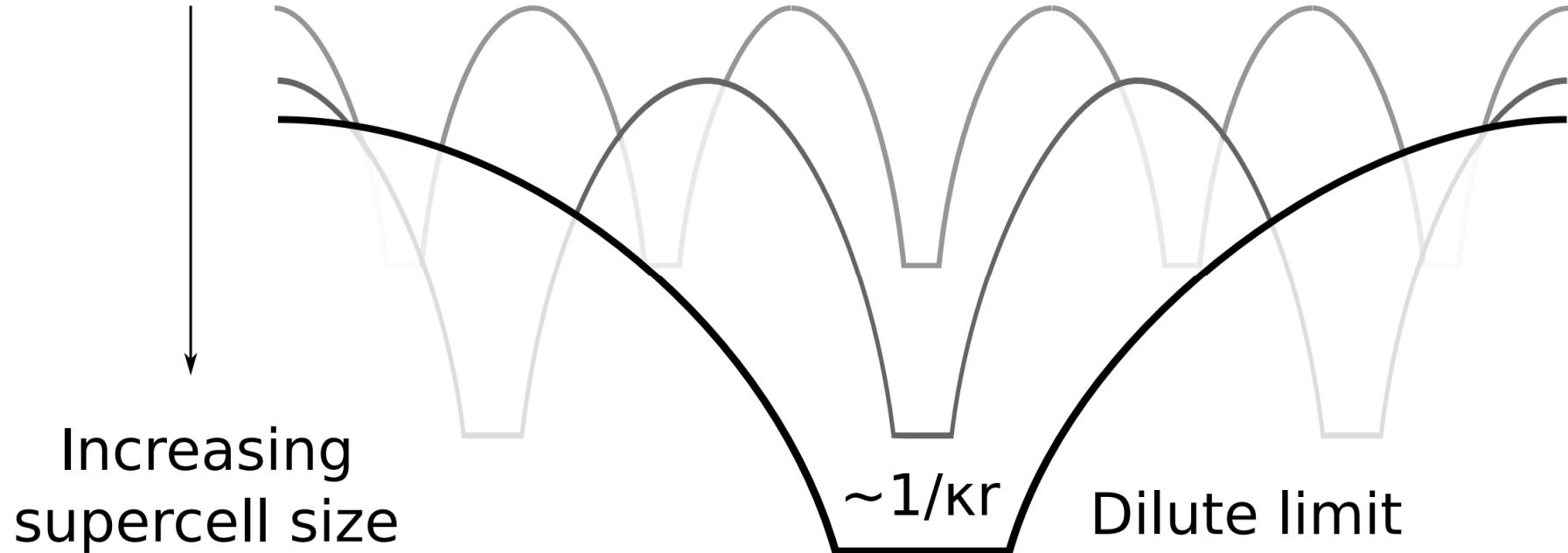
The supercell dependence is stronger for the “neutral” potential energy surface!

# Finite-size effects



**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**  $\rightarrow V_{\text{el-ph}}^{\text{lr}} \sim \left( \frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_\infty} \right) \frac{1}{r}$

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

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

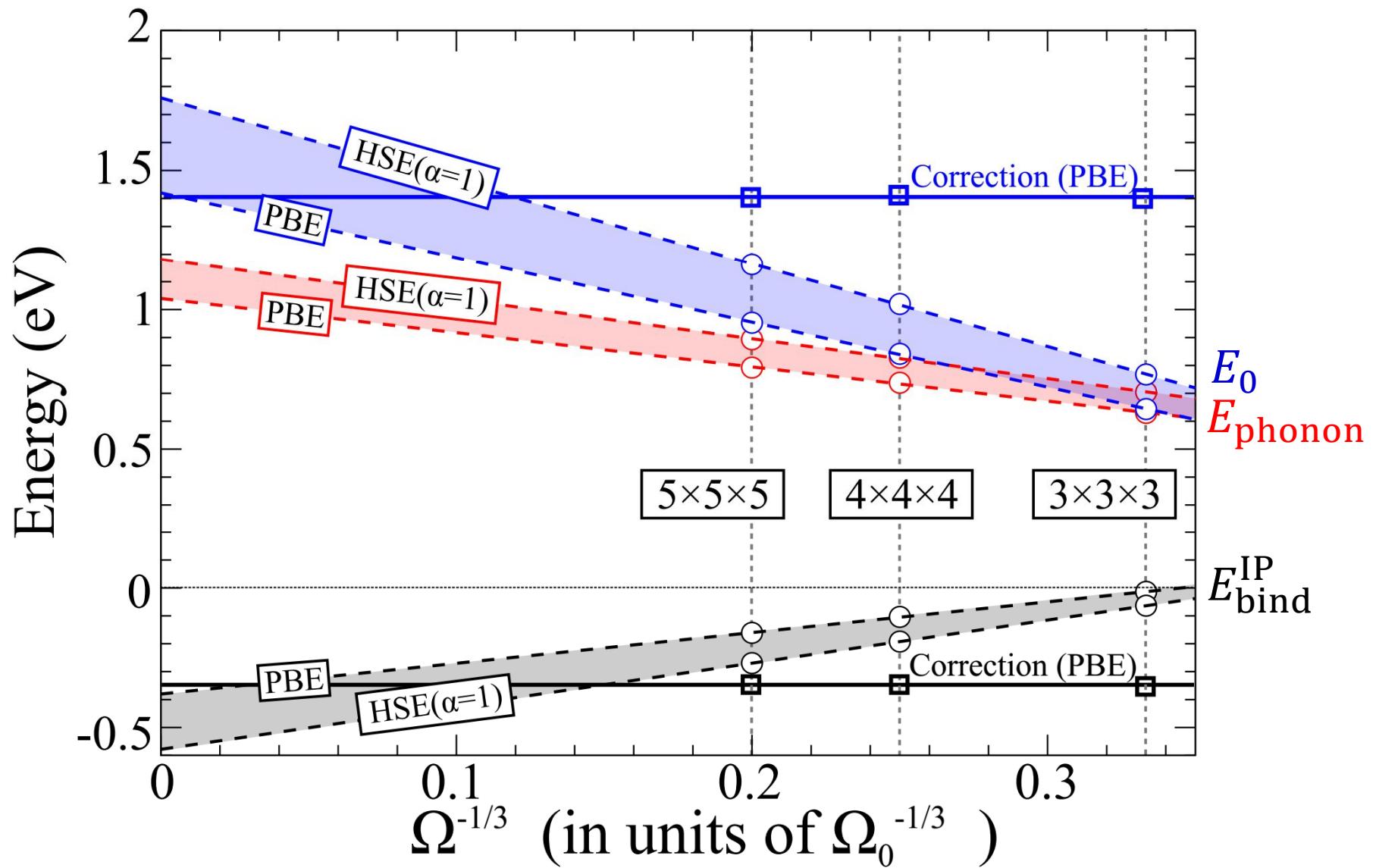
Pekar's 1:2:3:4 theorem (strong coupling):

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

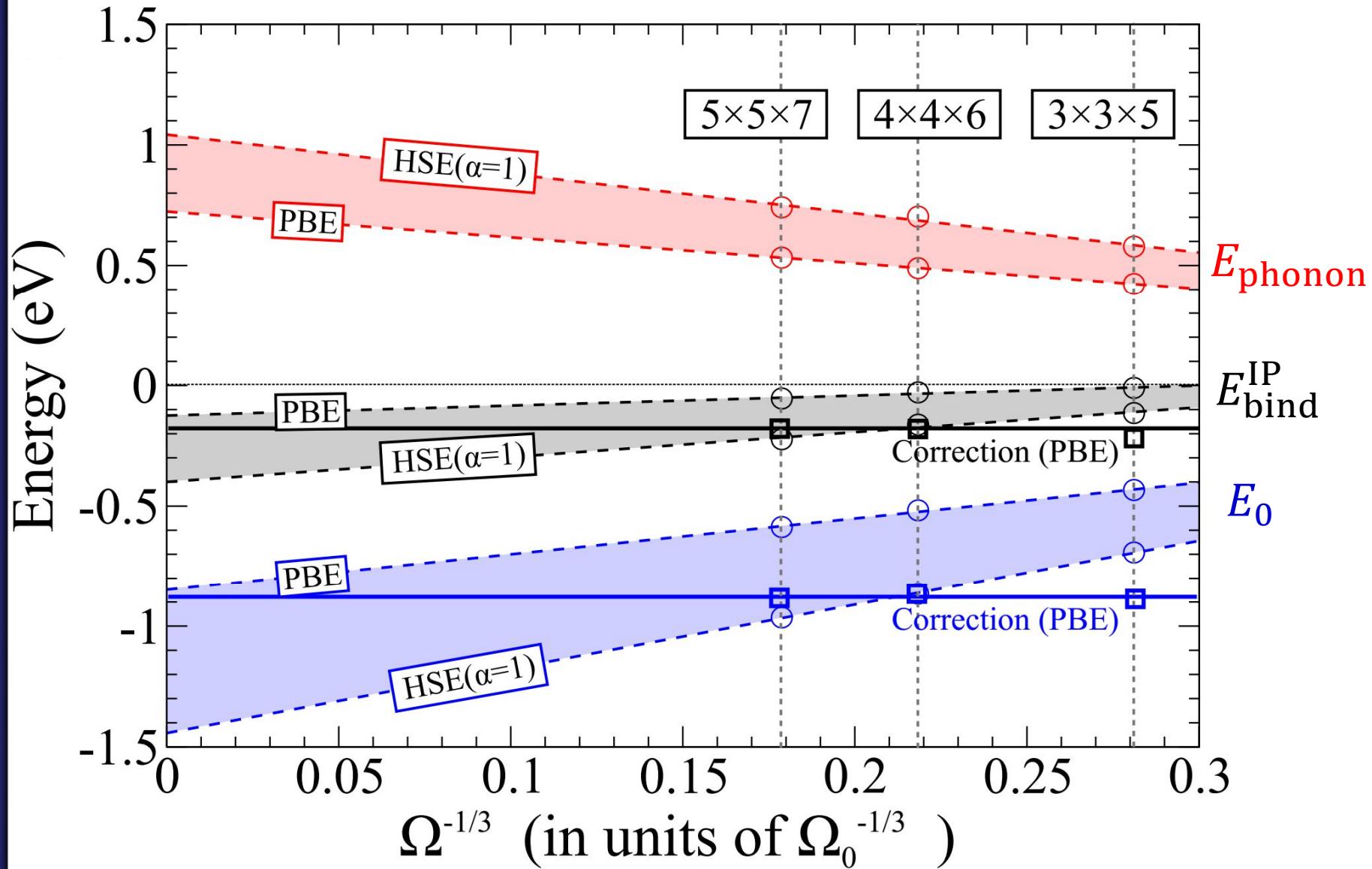
$$E_{\text{kinetic}} : E_{\text{phonon}} : -E_0 : -E_{\text{el-ph}} \approx 1 : 2 : 3 : 4 \rightarrow$$

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

# Hole polarons in rock-salt MgO

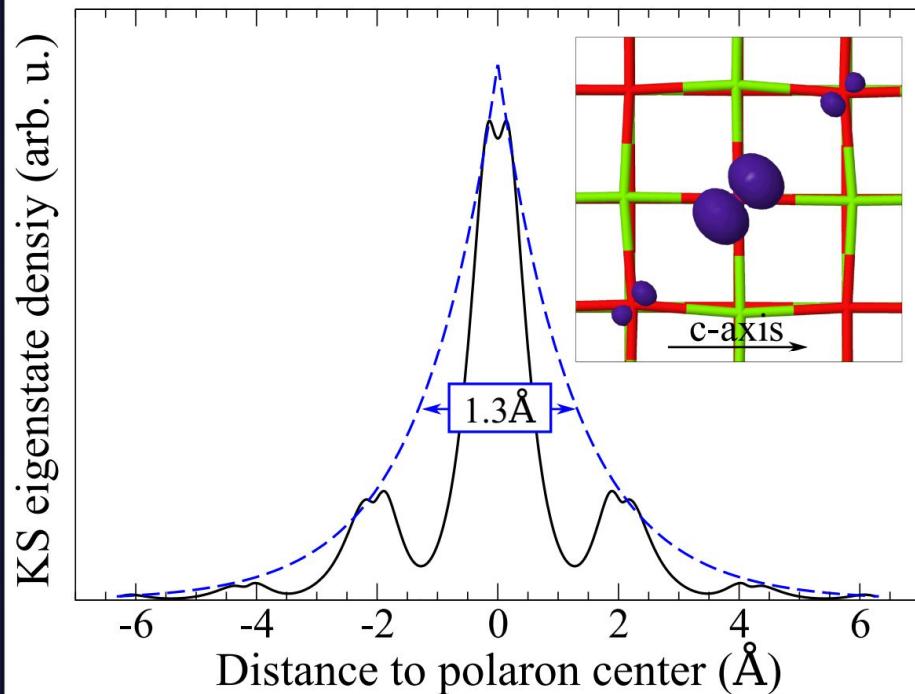


# Electron polarons in rutile $\text{TiO}_2$

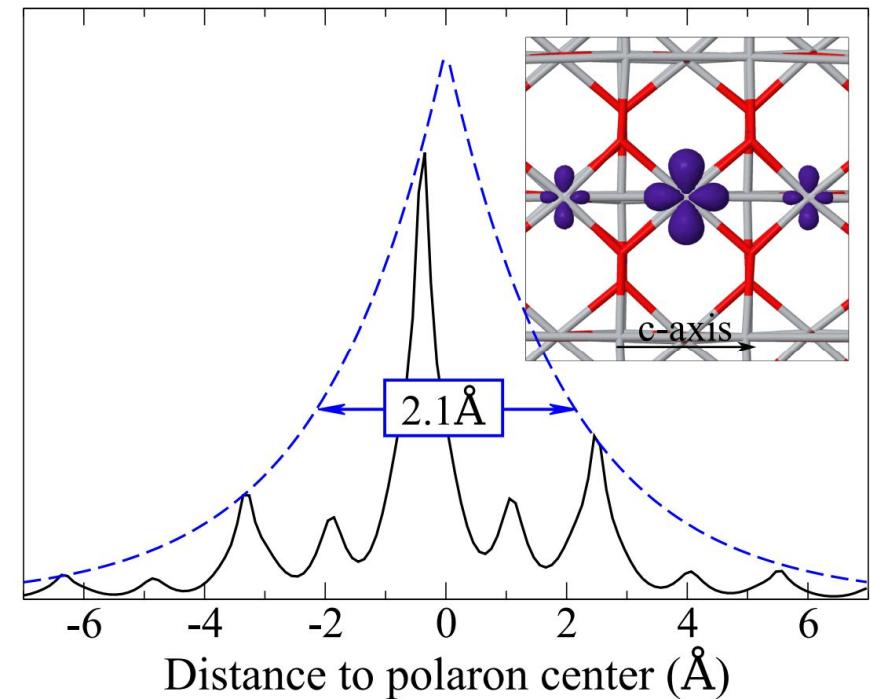


# Polaron eigenstate density and radius

hole polaron in MgO



electron polaron in rutile TiO<sub>2</sub>



**Fröhlich coupling constant**  $\alpha_F = \sqrt{\frac{m_b}{2\omega_{LO}}} \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right)$ :

$$\alpha_F = 4.4$$

$$\alpha_F = 2.6$$