Defects in Solids at Realistic Conditions

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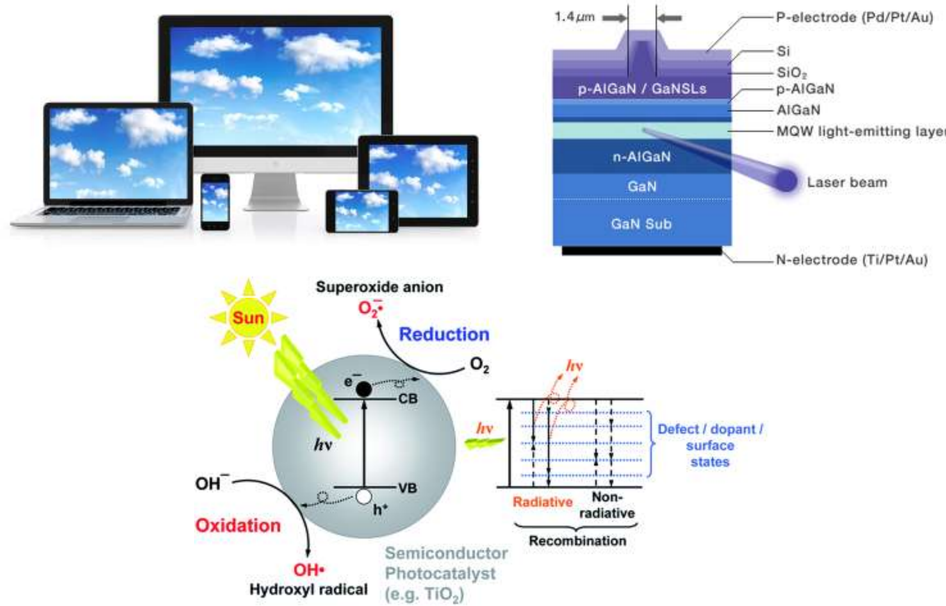
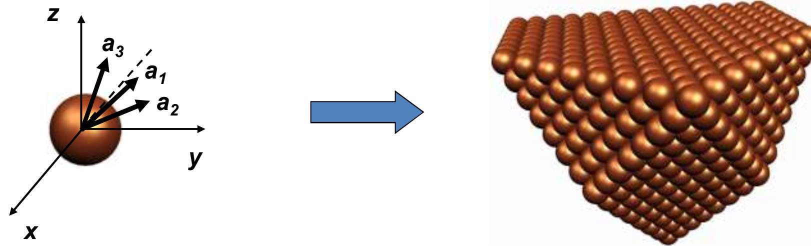
Defects at work: Semiconductors



Materials modeling



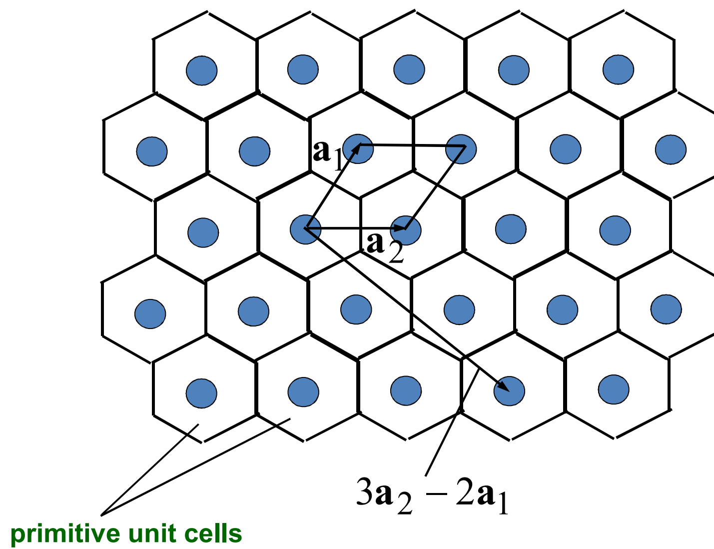
Position of every atom in the crystal (Bravais lattice):

$$\mathbf{r}(n_1,n_2,n_3) = \mathbf{r}(0,0,0) + n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

lattice vector: $$\mathbf{R}(n_1,n_2,n_3) = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

$$n_1,n_2,n_3 = 0,\ \pm 1,\ \pm 2,\ldots$$

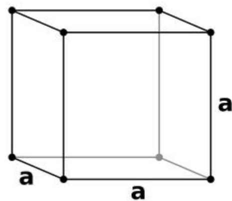
Example: two-dimensional Bravais lattice



The form of the primitive unit cell is not unique

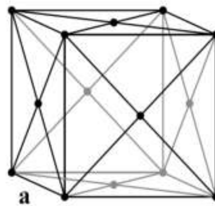
Most common crystal structures

primitive cubic



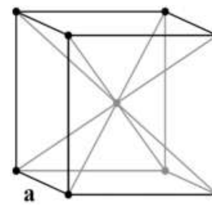
$$\mathbf{a}_1 = a(1,0,0)$$
$$\mathbf{a}_2 = a(0,1,0)$$
$$\mathbf{a}_3 = a(0,0,1)$$

face-centered cubic (fcc)



$$\mathbf{a}_1 = a/2\,(1,1,0)$$
$$\mathbf{a}_2 = a/2\,(1,0,1)$$
$$\mathbf{a}_3 = a/2\,(0,1,1)$$

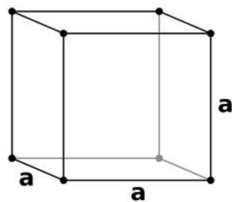
body-centered cubic (bcc)



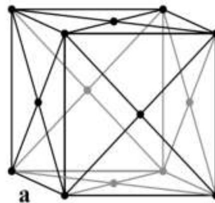
$$\mathbf{a}_1 = a/2\,(1,1,-1)$$
$$\mathbf{a}_2 = a/2\,(-1,1,1)$$
$$\mathbf{a}_3 = a/2\,(1,-1,1)$$

Most common crystal structures

primitive cubic

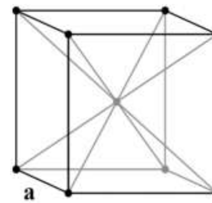


face-centered cubic (fcc)



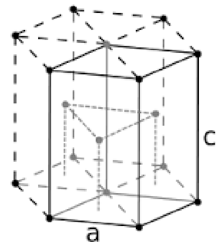
$$\mathbf{a}_1 = a/2\,(1,1,0)$$
$$\mathbf{a}_2 = a/2\,(1,0,1)$$
$$\mathbf{a}_3 = a/2\,(0,1,1)$$

body-centered cubic (bcc)



$$\mathbf{a}_1 = a/2\,(1,1,-1)$$
$$\mathbf{a}_2 = a/2\,(-1,1,1)$$
$$\mathbf{a}_3 = a/2\,(1,-1,1)$$

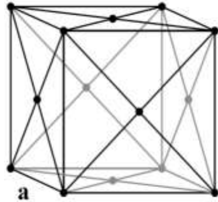
hexagonal



$$\mathbf{a}_1 = a(1,0,0)$$
$$\mathbf{a}_2 = a(-1/2, \sqrt{3}/2, 0)$$
$$\mathbf{a}_3 = c(0,0,1)$$

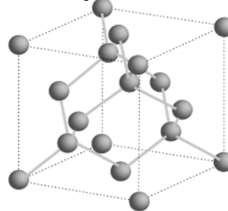
Most common crystal structures

face-centered cubic (fcc)



$\mathbf{a}_1 = a/2\,(1,1,0)$
$\mathbf{a}_2 = a/2\,(1,0,1)$
$\mathbf{a}_3 = a/2\,(0,1,1)$

Most elemental semiconductors (C, Si, Ge):

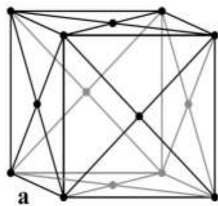


diamond structure

one more atom per cell at $a(1/4, 1/4, 1/4)$

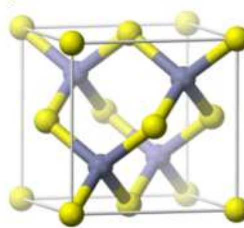
Most common crystal structures

face-centered cubic (fcc)



$\mathbf{a}_1 = a/2\,(1,1,0)$
$\mathbf{a}_2 = a/2\,(1,0,1)$
$\mathbf{a}_3 = a/2\,(0,1,1)$

Most compound semiconductors (GaAs, InP, GaSb, ZnSe, CdTe):

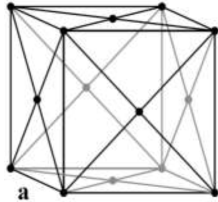


zincblende structure

one more atom per cell at $a(1/4, 1/4, 1/4)$

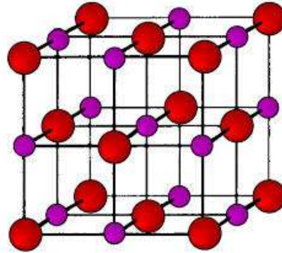
Most common crystal structures

face-centered cubic (fcc)



$\mathbf{a}_1 = a/2\,(1,1,0)$
$\mathbf{a}_2 = a/2\,(1,0,1)$
$\mathbf{a}_3 = a/2\,(0,1,1)$

PbS, MgO, ZnO at high pressure:

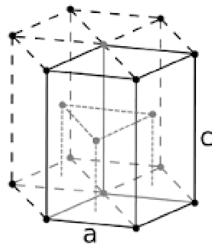


rocksalt structure

one more atom per cell at $a(1/2,1/2,1/2)$

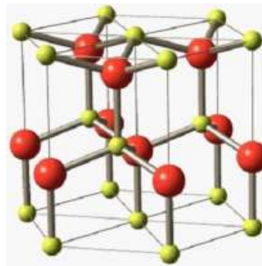
Most common crystal structures

hexagonal



$\mathbf{a}_1 = a(1,0,0)$
$\mathbf{a}_2 = a(-1/2,\sqrt{3}/2,0)$
$\mathbf{a}_3 = c(0,0,1)$

CdS, GaN, ZnO:

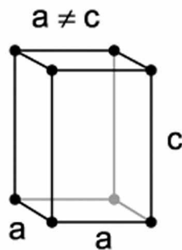


wurtzite structure

four atoms per unit cell

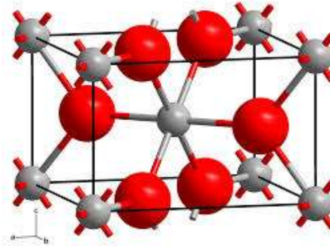
Most common crystal structures

tetragonal



$$\mathbf{a}_1 = a(1,0,0)$$
$$\mathbf{a}_2 = a(0,1,0)$$
$$\mathbf{a}_3 = c(0,0,1)$$

TiO_2, SnO_2:



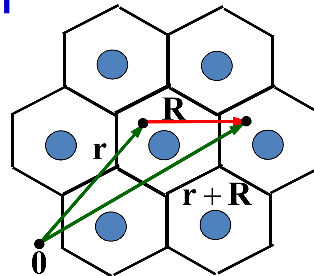
rutile structure

six atoms per unit cell

Bloch's theorem

Periodic potential $U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$
(translational symmetry)

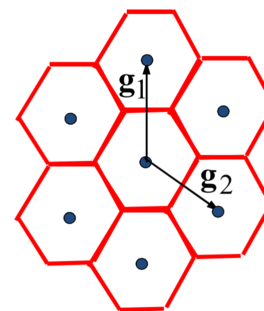
$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$



In an infinite periodic solid, the solutions of the one-particle Schrödinger equations must behave like

$$\psi(\mathbf{r}+\mathbf{R}) = \exp(i\mathbf{k}\mathbf{R})\psi(\mathbf{r})$$

Index **k** is a vector in *reciprocal space*



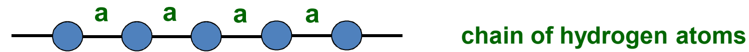
$$\mathbf{k} = x_1\mathbf{g}_1 + x_2\mathbf{g}_2 + x_3\mathbf{g}_3 \qquad \mathbf{g}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$$

$$\mathbf{g}_l = 2\pi\frac{\mathbf{a}_m \times \mathbf{a}_n}{\Omega}$$ *– reciprocal lattice vectors*

Consequently:

$$\psi(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})u(\mathbf{r}), \;\; u(\mathbf{r}+\mathbf{R}) = u(\mathbf{r})$$

The meaning of k

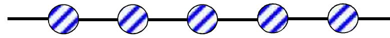


chain of hydrogen atoms

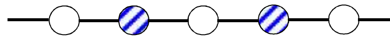
$$\psi_k = \sum_j \exp(ikx_j)\chi_{1s}(j \cdot a)$$

k shows the phase with which the orbitals are combined:

k = 0: $\psi_0 = \sum_j \exp(0)\chi_{1s}(j \cdot a) = \chi_{1s}(a) + \chi_{1s}(2a) + \ldots$



k = $\frac{\pi}{a}$: $\psi_0 = \sum_j \exp(i\pi \cdot j)\chi_{1s}(j \cdot a) = -\chi_{1s}(a) + \chi_{1s}(2a) - \chi_{1s}(3a) + \ldots$



k is a symmetry label and a node counter, and also represents electron momentum

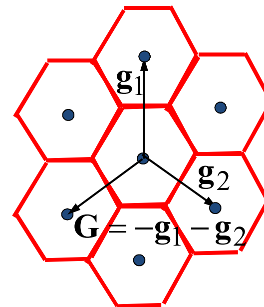
Adapted from: Roald Hoffmann, Angew. Chem. Int. Ed. Engl. **26**, 846 (1987)

Bloch's theorem: consequences

In a periodic system, the solutions of the Schrödinger equations are characterized by an integer number *n* (called *band index*) and a vector **k**:

$$\hat{h}\psi_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}$$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{kr})u_{n\mathbf{k}}(\mathbf{r}),\ \ u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$



For any reciprocal lattice vector

$$\mathbf{G} = n_1\mathbf{g}_1 + n_2\mathbf{g}_2 + n_3\mathbf{g}_3$$

$$\psi_{n\mathbf{k}+\mathbf{G}} = \exp(i\mathbf{kr})[u_{\mathbf{k}+\mathbf{G}}\exp(i\mathbf{Gr})] = \exp(i\mathbf{kr})\tilde{u} = \psi_{n'\mathbf{k}}$$

a Bloch state at k+G with index *n*

a lattice-periodic function $\tilde{u}$

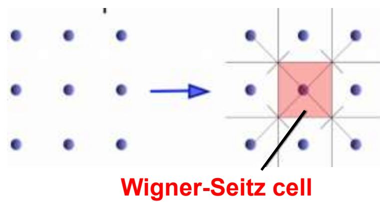
a Bloch state at k with a different index *n'*

Can choose to consider only k within single primitive unit cell in reciprocal space

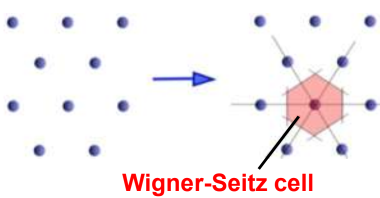
Brillouin zones

A conventional choice for the reciprocal lattice unit cell

For a square lattice

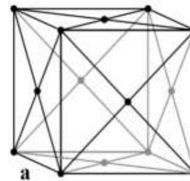


For a hexagonal lattice

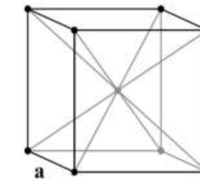


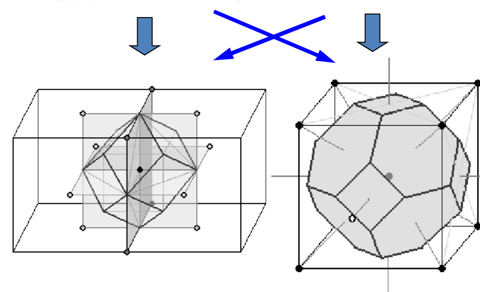
In three dimensions:

Face-centered cubic (fcc) lattice

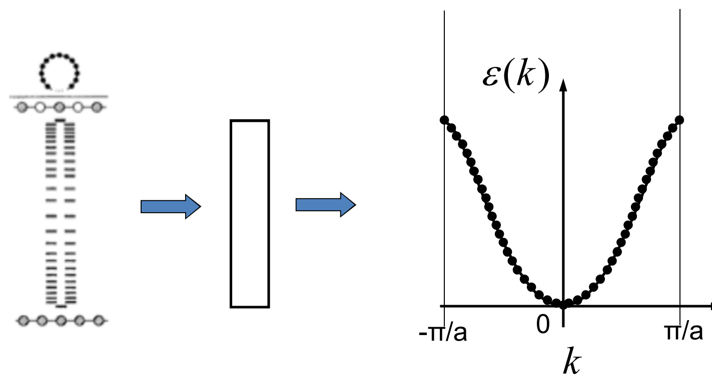


Body-centered cubic (bcc) lattice





Electronic band structure

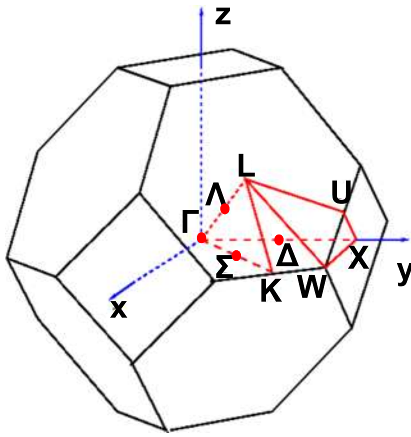


Band structure represents dependence of $\varepsilon_{n\mathbf{k}}$ on k

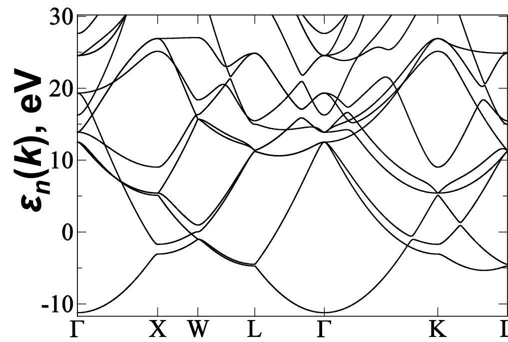
For a periodic (infinite) crystal, there is an infinite number of states for each band index *n*, differing by the value of k

Electronic band structure in three dimensions

Brillouin zone of the fcc lattice

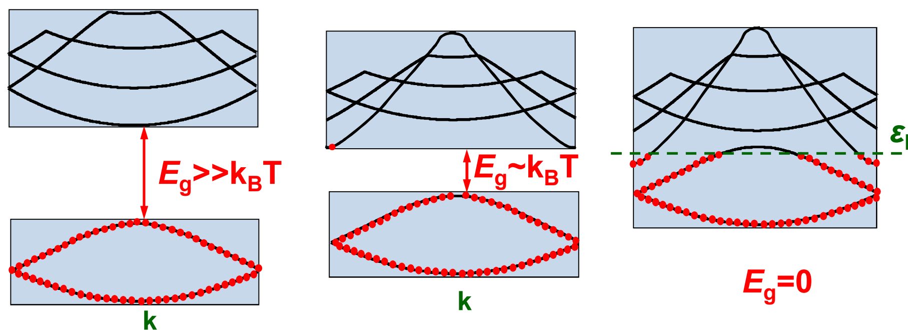


Al band structure (DFT-PBE)



By convention, $\varepsilon_{n\mathbf{k}}$ are measured (angular-resolved photoemission spectroscopy, ARPES) and calculated along lines in k-space connecting points of high symmetry

Insulators, semiconductors, and metals



Insulators (MgO, NaCl, ZnO,…)

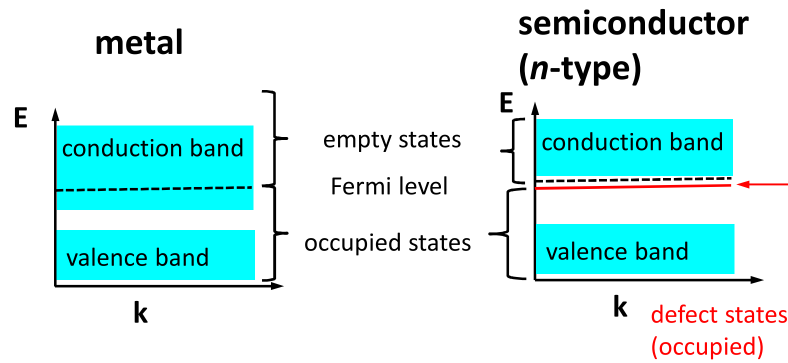
Semiconductors (Si, Ge,…)

Metals (Cu, Al, Fe,…)

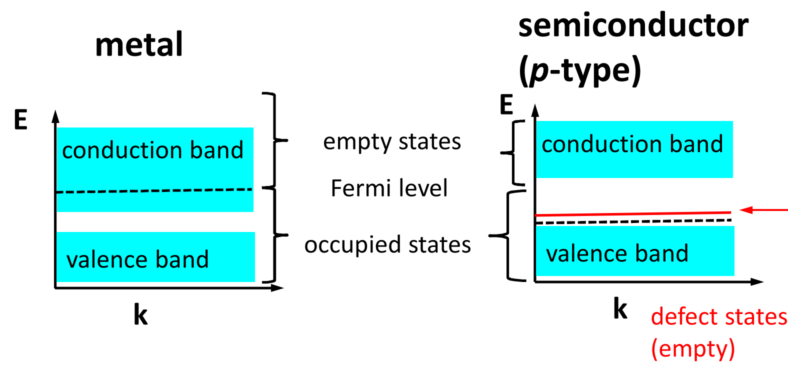
In a metal, some (at least one) energy bands are only partially occupied

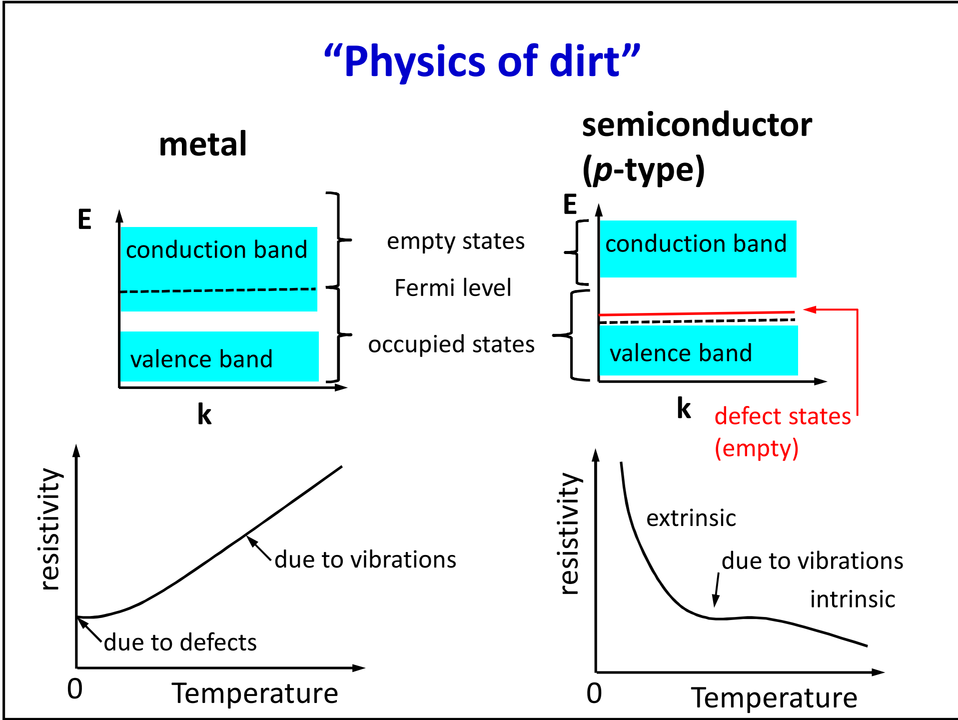
The Fermi energy ε_F separates the highest occupied states from lowest unoccupied

"Physics of dirt"



"Physics of dirt"





"My precious!": Perfect defected gems

$Cr:Al_2O_3$

$V:Al_2O_3$

$Fe:Al_2O_3$

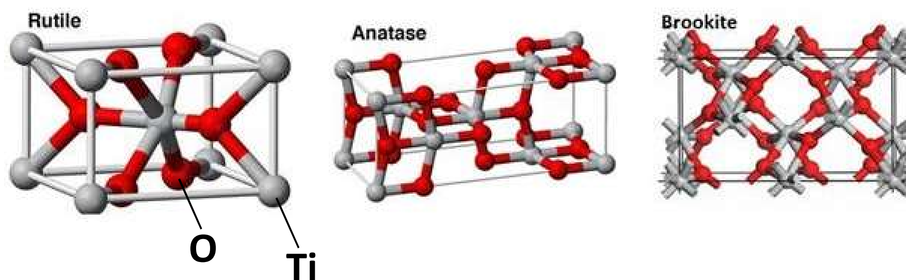
$Fe:Al_2O_3$

$Fe,Ti:Al_2O_3$

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

Why oxides are semiconductors?

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



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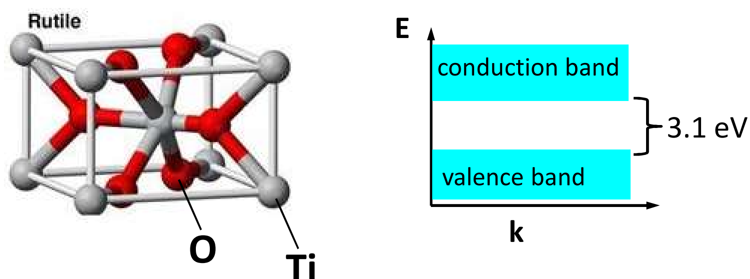

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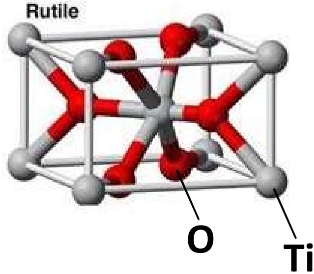
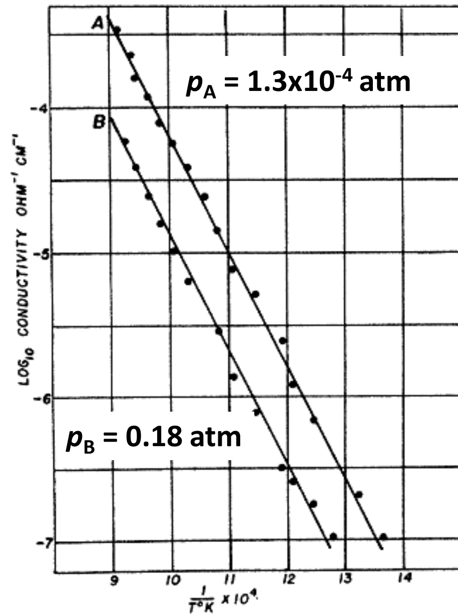
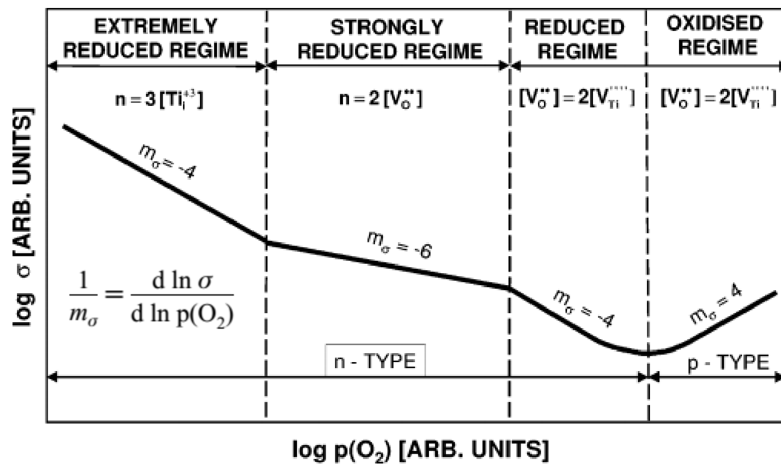




TiO_2 is an *n*-type semiconductor, whose conductivity depends on O_2 pressure

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

Why oxides are semiconductors?

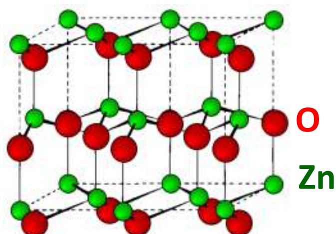


Different regimes correspond to different intrinsic defect distributions in ultrapure TiO_2

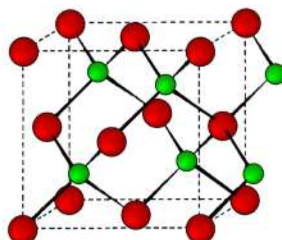
M. K. Nowotny, T. Bak, and J. Nowotny, J. Phys. Chem. B **110**, 16270 (2006)

Why oxides are semiconductors?

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



wurtzite (stable)

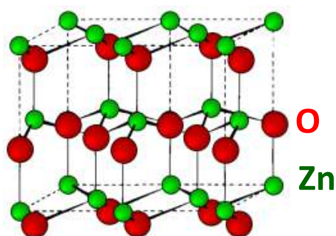


zinkblende (can be obtained by growth on substrates with cubic lattice structure)

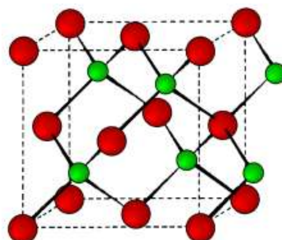
Band gap ~3.3 eV (direct), but (almost?) exclusively *n*-type semiconductor

Why oxides are semiconductors?

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



wurtzite (stable)

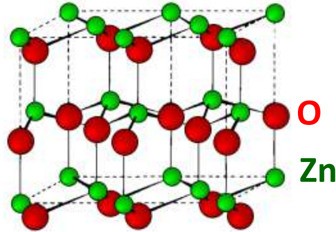


zinkblende (can be obtained by growth on substrates with cubic lattice structure)

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)

Summary: 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))

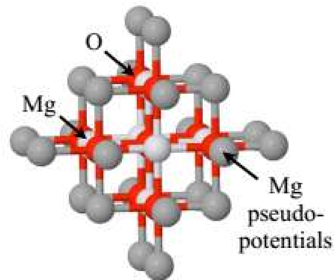
The “invisible agent”

“…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

Periodic and cluster models of defects

Embedded cluster model

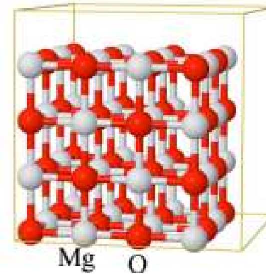


+ Higher-level ab initio methods can be applied

+/- Defects in dilute limit

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

Periodic model



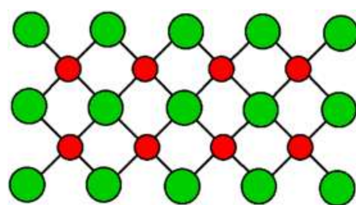
+ Robust boundary conditions

+ Higher defect concentrations

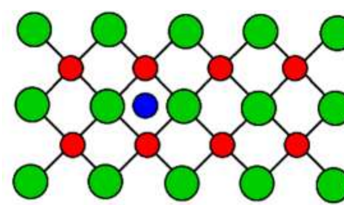
+/- Higher defect concentrations

- Artificial defect-defect interactions

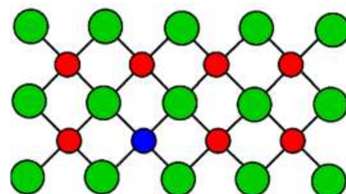
Common point defect types



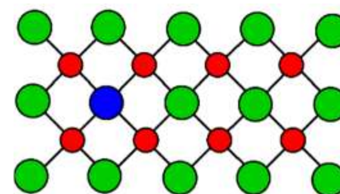
(a) perfect lattice



(b) interstitial impurity

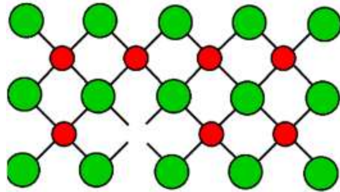


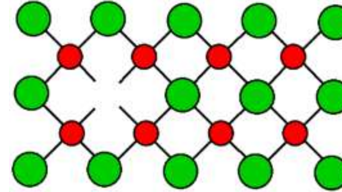
(e) substitution of cation

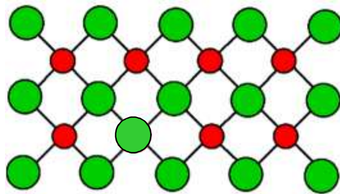


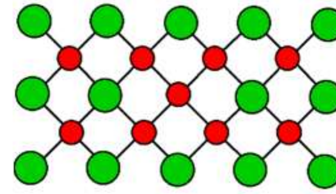
(f) substitution of anion

Common point defect types


(c) cation vacancy


(d) anion vacancy

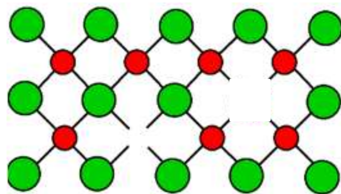

(g) B_A antisite defect


(h) A_B antisite defect

Common point defect types

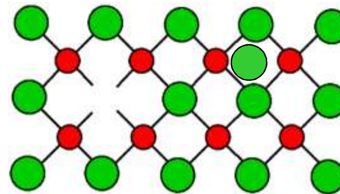
Defect complexes

Schottky defects



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

Frenkel defects



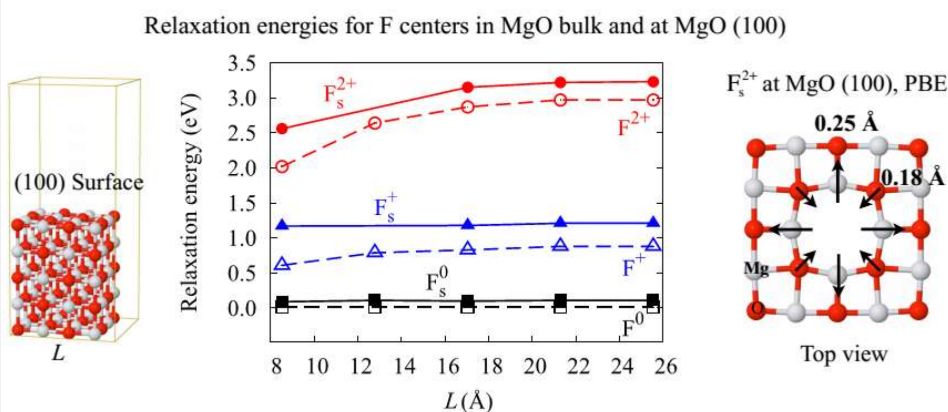
Pairs of a vacancy and the corresponding self-interstitial ($V_{Na}^- + Na_i^+$)

Atomic relaxation

"It was believed that the chemistry of defects in semiconductors is well described in first order by assuming high-symmetry, undistorted, lattice sites. Relaxations and distortions were believed to be a second-order correction. … The critical importance of carefully optimizing the geometry around defects and the magnitudes of the relaxation energies were not fully realized until the 1980s."

D.A. Drabold and S.K. Estreicher (Eds.) *Theory of defects in semiconductors*, Springer 2007

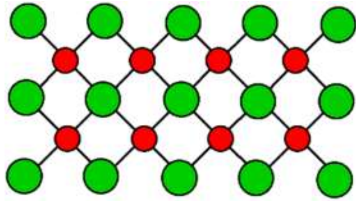
Atomic relaxation



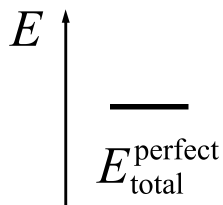
Relaxations are especially important for charged defects

D.A. Drabold and S.K. Estreicher (Eds.) *Theory of defects in semiconductors*, Springer 2007

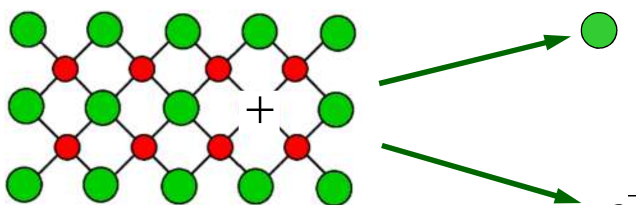
Defect formation energy (T=0)



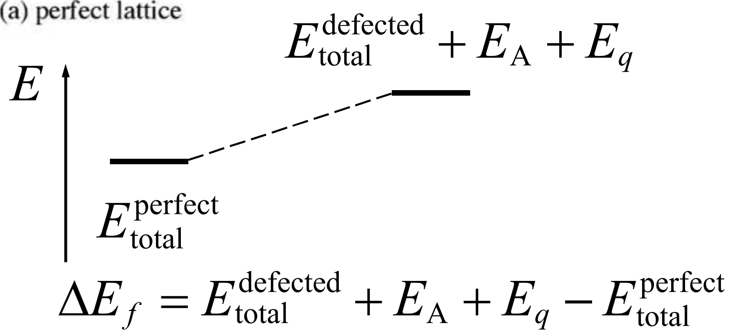
(a) perfect lattice



Defect formation energy (T=0)

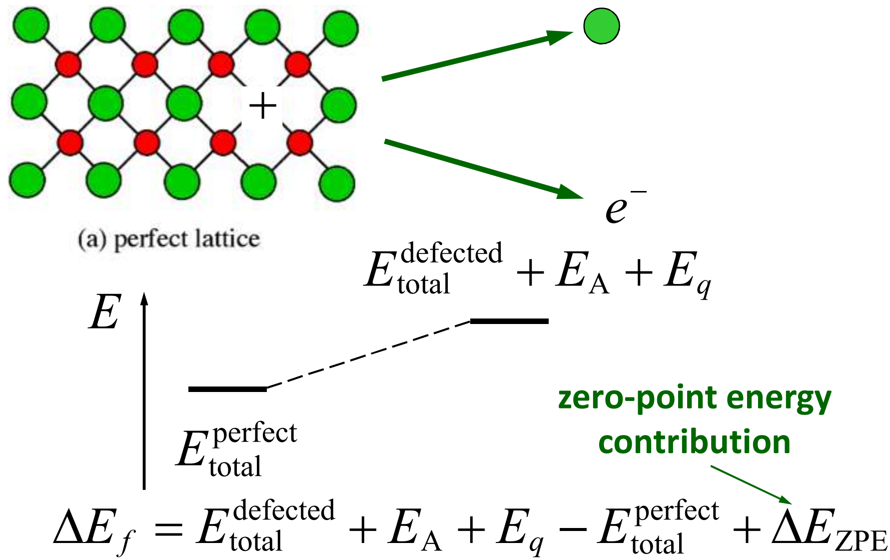


(a) perfect lattice

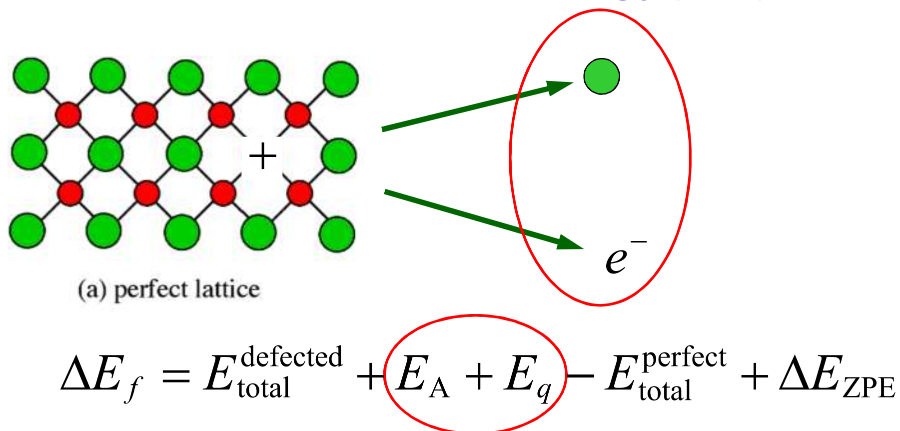


$$\Delta E_f = E_{\text{total}}^{\text{defected}} + E_{\text{A}} + E_q - E_{\text{total}}^{\text{perfect}}$$

Defect formation energy (*T*=0)



Defect formation energy (*T*=0)



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

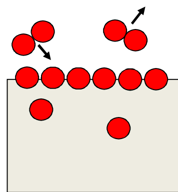
Defect formation energy (*T*=0)

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

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**

T>0



Real materials are *open* systems (in contact with an atmosphere and charge sources)

Two types of disorder at finite *T*:
- **internal (vibrations, defect disorder, electronic disorder)**
- **external (disorder within the environment)**

In thermodynamics, disorder is quantified by *entropy*

Thermodynamics

At finite *T* a material can be characterized by internal energy instead of the total energy

$$E_{\text{total}} \Rightarrow U$$

At constant *T* a system minimizes its *free* energy (-*TS*), not the internal energy U

If also volume *V* is constant, the energy minimized is Helmholtz free energy F :

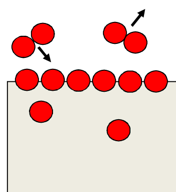
$$F = U - TS$$

Thermodynamics

If (*T*,*p*) are constant, the energy minimized is Gibbs free energy

$$G = U + pV - TS = \sum_i \mu_i N_i$$

Chemical potential μ_i of the *i*-th atom type is the change in free energy as the number of atoms of that type in the system increases by 1



In thermodynamic equilibrium, μ_i is the same in the whole system (surface, bulk, gas)

Gibbs free energy of defect formation

***T* = 0:**

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

***T* > 0:**

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

Gibbs free energy of defect formation

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

$\mu_i(T,p_i)$ **– chemical potential of species *i* with partial pressure p_i**

$\mu_e(T)$ **– electronic chemical potential**

$\Delta N_i,\ q$ **– change in the number of atoms of species *i* and the charge upon defect formation**

$\Delta F^{\text{vib}}(T)$ **– change in the Helmholtz vibrational free energy:**

$$\Delta F^{\text{vib}}(T) = \Delta U^{\text{vib}}(T) - T\Delta S^{\text{vib}}$$

Gibbs free energy of defect formation

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

$\mu_i(T,p_i)$ – **chemical potential of species *i* with partial pressure p_i**

can be easily calculated for an equilibrium with a close-to-ideal gas

Since in thermodynamic equilibrium μ_i is the same in the whole system (surface, bulk, gas), only μ_i in the gas needs to be evaluated

Electronic chemical potential

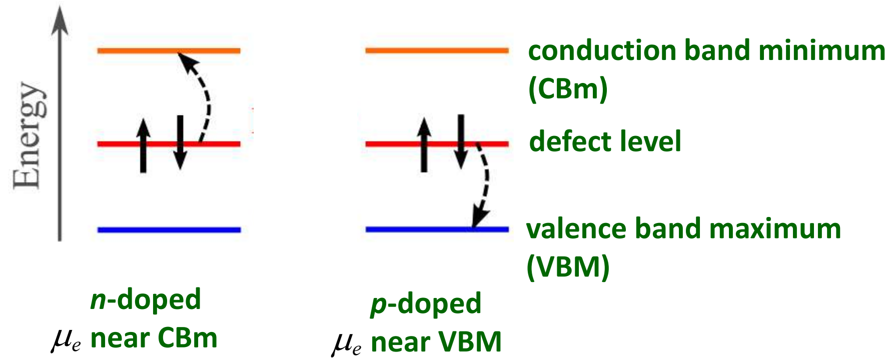
$$\Delta G_f(T,\{p\}) = G^{\text{defected}}(T,\{p\}) - \sum_i \mu_i(T,p_i)\Delta N_i + q\mu_e(T) - G^{\text{perfect}}(T,\{p\}) + \Delta F^{\text{vib}}(T)$$

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

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



***n*-doped**
μ_e near CBm

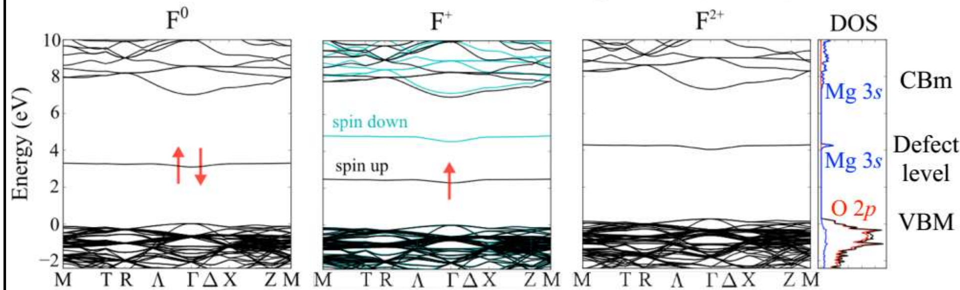
***p*-doped**
μ_e near VBM

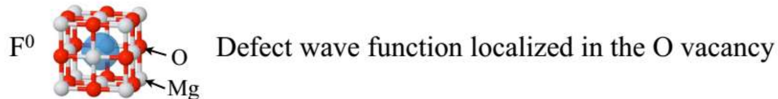
The defects will charge when μ_e is below the defect level

Electronic chemical potential

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

Band structures of O vacancies in MgO bulk (HSE06)

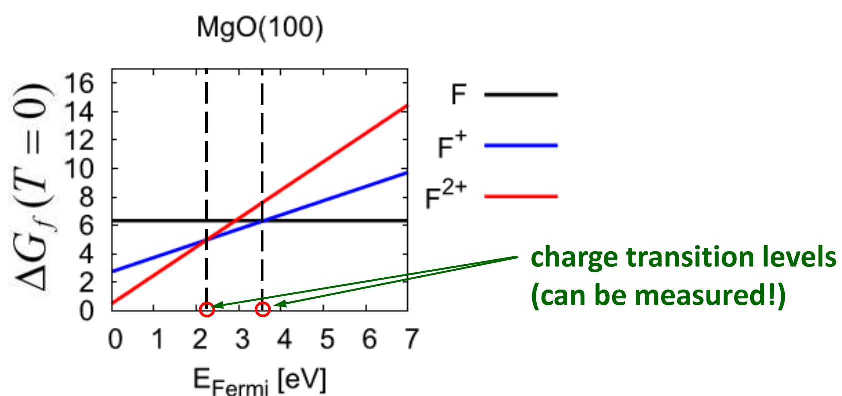




Defect wave function localized in the O vacancy

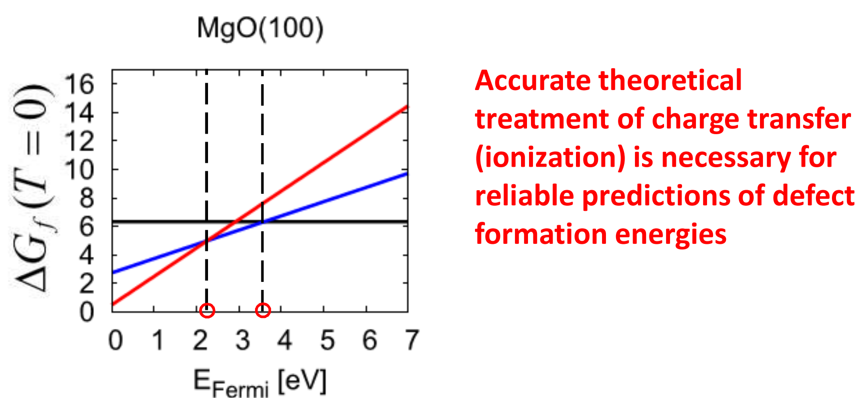
Electronic chemical potential

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



Electronic chemical potential

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

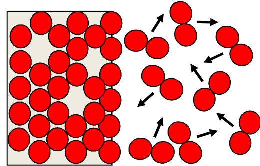


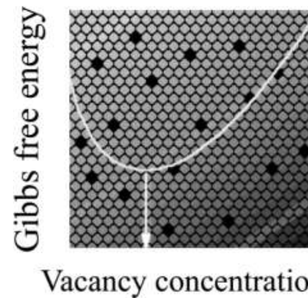
Accurate theoretical treatment of charge transfer (ionization) is necessary for reliable predictions of defect formation energies

Configurational entropy

The system "solid+gas" will tend to the minimum of its free energy :

$$G = U + pV - TS$$



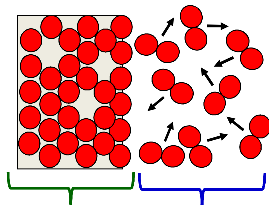


$$S = k \ln \Omega$$

Ω – number of *microstates*

Configurational entropy

$$G = U + pV - TS$$



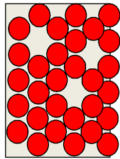
$$S = k \ln \Omega$$

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

$$G = U + pV - TS$$



$$S = k \ln \Omega$$

Ω – number of microstates

N equivalent defect sites in the sold

n defects

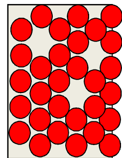
If defects do not interact:

$$\Omega = \frac{N!}{n!(N-n)!}, \quad S_{\text{config}} = k \ln \frac{N!}{n!(N-n)!}$$

Configurational entropy

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:

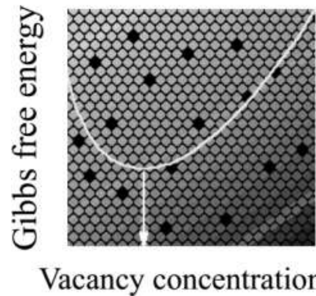
$$\ln(n!) = n(\ln n - 1 + \delta), \; n >> 1, \; \delta \sim \frac{\ln(2\pi n)}{2n}$$

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

Good approximation only on a macroscopic scale

Defect concentration

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



$$G(n) = G_0 + n\Delta G_f - TS_{\text{config}}(n)$$

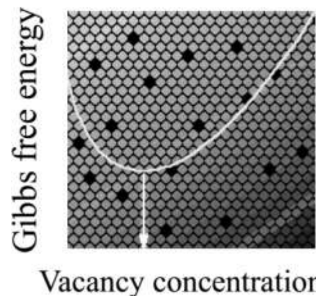
If defects do not interact:

$$\frac{\partial G}{\partial n} = \Delta G_f - T\frac{\partial S_{\text{config}}}{\partial n} = 0$$

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

Defect concentration

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



$$G(n) = G_0 + n\Delta G_f - TS_{\text{config}}(n)$$

If defects do not interact:

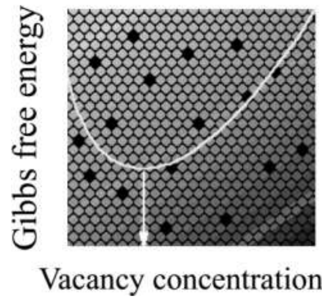
$$\frac{n}{N} = \frac{1}{\frac{1}{\Omega_{\text{internal}}}\exp\left(\Delta G_f / kT\right) + 1}$$

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

$$\frac{n}{N} \approx \Omega_{\text{internal}} \exp\left(-\Delta G_f / kT\right)$$ **– textbook formula**

Defect concentration

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



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

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

exponential dependence → accurate calculations are necessary for reliable predictions

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?!

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

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

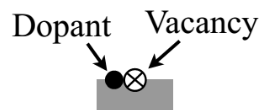
Coulomb interaction – long-range!

Defect-defect interactions

$$\frac{\partial G(T,\{p\},\mu_e,\{n\})}{\partial n_i} = 0 \not\Rightarrow n_i \sim n_{\text{sites}} \exp(-\Delta G_f / kT)$$

Local interactions:

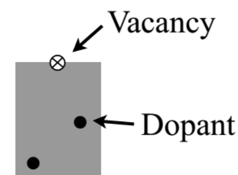
- **Local relaxation**
- **Chemical bonding**



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

Long-range (global) interactions:

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

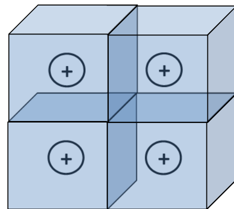


Charged defects and charge compensation

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

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

For a system of charges:



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

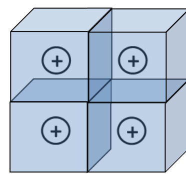
In the thermodynamic limit ($N \rightarrow \infty$) the electrostatic energy of charges with any finite concentration *diverges*

Charged defects *must be compensated* in realistic materials

Charged defects must be compensated

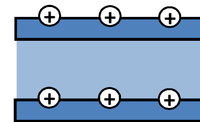
The compensation depends on the spatial distribution of the density of states near the Fermi level

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* correction exists)



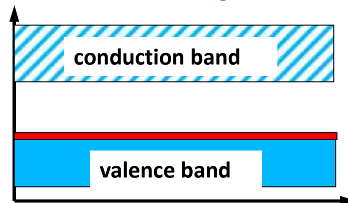
2) Impurity donors/acceptors – large concentrations, artificial interactions

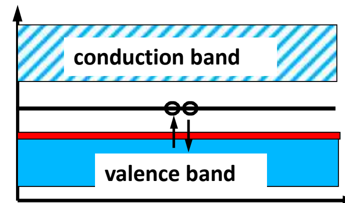
H.-P. Komsa and A. Pasquarello, Phys. Rev. Lett. **110**, 095505 (2013)

Charged defects must be compensated

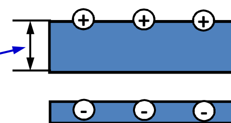
3) Simulate distributed doping with virtual crystal approximation – arbitrarily small concentrations with finite unit cells, correction for the dilute limit is needed

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





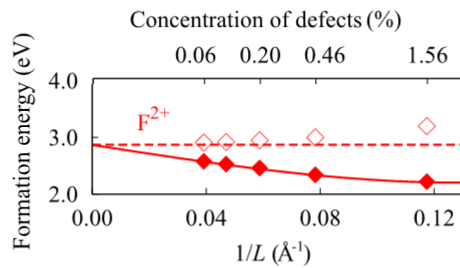
4) Charge plate – strong artificial fields



Δφ > band gap for a 5-layer slab

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)

Charged defects and charge compensation



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

The compensated defects interact much weaker with each other

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

Charged defects in a doped material

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

formation energy in the dilute limit

electrostatic energy at finite *n*

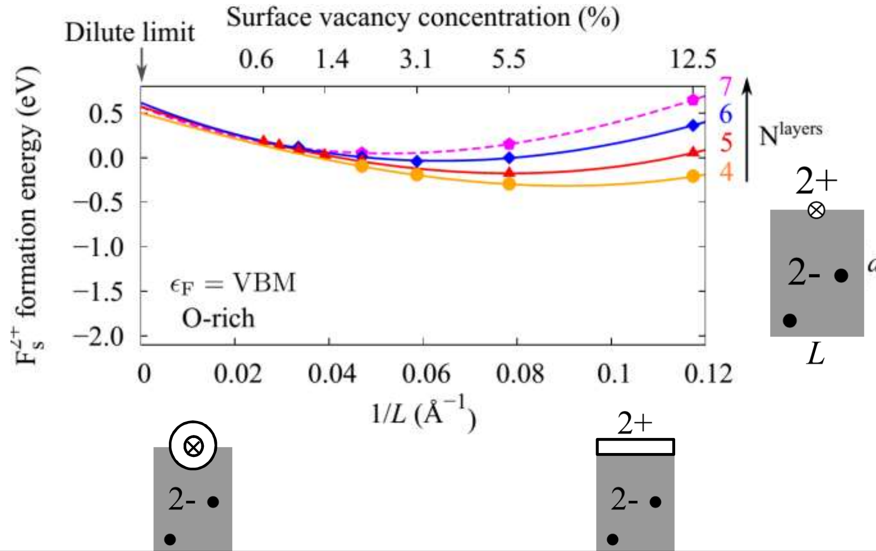
$$S_{\text{config}} = k \ln\left(\sum_m g_m(n)\exp(-E_m(n)/kT)\right)$$

The charged defects are screened by the compensating charge:

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

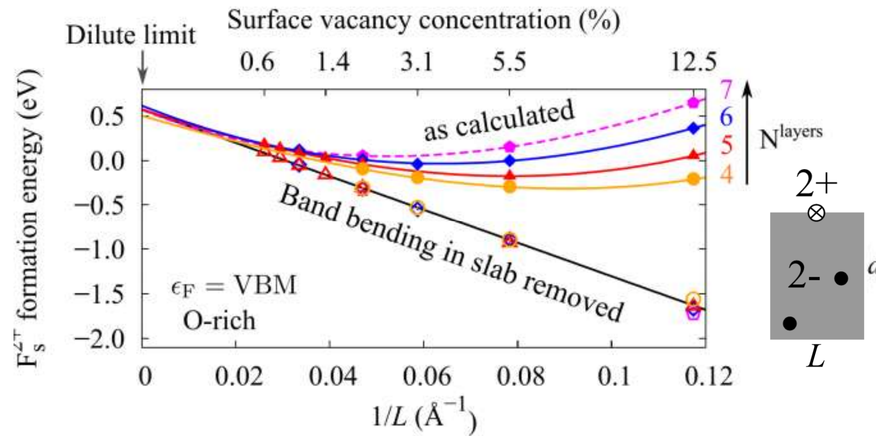
Electrostatics in periodic calculations of charged defects

$$\Delta G_{\mathrm{f}}^{\mathrm{VCA}}(\sigma,d) = E_{\mathrm{vac}}^{q}(\sigma,d)(+q\varepsilon_{\mathrm{VBM}}) - E_{\mathrm{host}}(\sigma,d) + \frac{1}{2}E_{\mathrm{O_2}}$$



Electrostatics in periodic calculations of charged defects

$$\Delta G_{\mathrm{f}}^{\mathrm{VCA}}(\sigma,d) = E_{\mathrm{vac}}^{q}(\sigma,d)(+q\varepsilon_{\mathrm{VBM}}) - E_{\mathrm{host}}(\sigma,d) + \frac{1}{2}E_{\mathrm{O_2}}$$



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

Formation energy of interacting defects

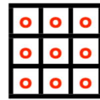
$\sigma = e\sum_q q\eta_q$, η_q surface density of defects with charge q

$$\frac{\partial G}{\partial \eta_q} = \Delta G_f^q - T\frac{\partial}{\partial \eta_q} s_{conf}(\eta_0, \eta_1, \eta_2)$$

$$\Delta G_f^q = \frac{\partial}{\partial \eta_q}\sum_{\tilde{q}} \eta_{\tilde{q}}\left[\Delta G_f^{VCA,\tilde{q}}(\sigma,d) - \tilde{q}E^{SC}(\sigma,d) + \tilde{q}E^{SC}(\sigma,z^{SC})\right]$$

creating defects one-by-one

creating a bunch of defects at once

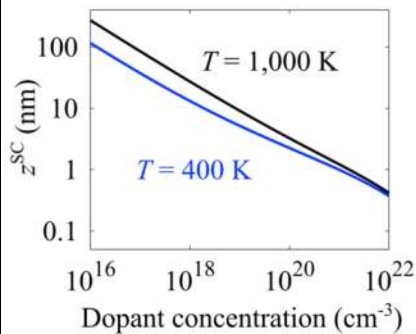


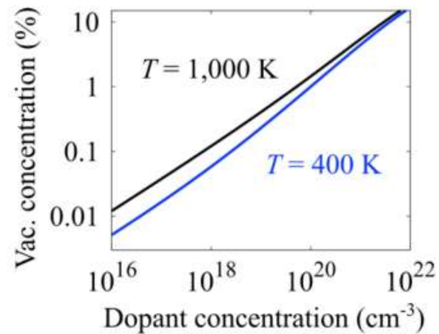
remove band-bending contribution in slab

add realistic band-bending contribution

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

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





Conclusions

• Defect formation energies and charge transition states depend on the spatial distribution of the density of states near the Fermi level

• Use space-charge effects to control interface properties, e.g., surface defect formation, adsorption energies, work function changes

• Model doping with VCA for realistic charge-carrier doping in periodic calculations