Space Charge Transfer at Metal-Oxide Surfaces
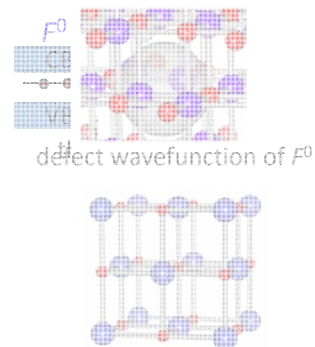
1) Towards validation of DFT calculations for materials
2) Vacancies at MgO (100) and

Anion vacancy in MgO (*F* center)

- "The" classical intrinsic defect in compound insulators.
- Rocksalt structure – simple.
- Many puzzling properties. For example, the positively charged and the neutral vacancy (F^+ and F^0) absorb light at practically identical energies [PRL **108** (2012)].

defect wavefunction of F^0

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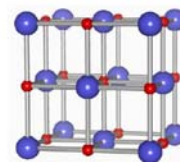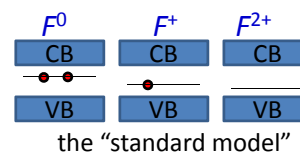
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F^0 F^+ F^{2+}

the "standard model"

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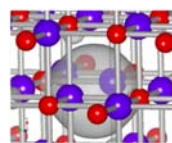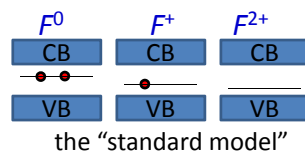Anion vacancy in MgO (*F* center)

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F^0 F^+ F^{2+}

| CB | CB | CB |
| VB | VB | VB |

the "standard model"

defect wavefunction of F^0

Perdew's Dream: Jacob's Ladder in Density-Functional Theory

The exchange-correlation functional

our favorite

5	unoccupied $\psi_i(\mathbf{r})$,	EX + cRPA, as given by ACFD
4	occupied $\psi_i(\mathbf{r})$,	hybrids (B3LYP, PBE0, HSE, …)
3	$\tau(\mathbf{r})$,	meta-GGA (e.g., TPSS)
2	$\nabla n(\mathbf{r})$,	Generalized Gradient Approximation
1	$n(\mathbf{r})$,	Local-Density Approximation

accuracy

$\tau(\mathbf{r})$:   Kohn-Sham kinetic-energy density

EX: exact exchange: $E_x = -\frac{1}{2} \sum^{occ} \iint d\mathbf{r}\, d\mathbf{r}' \frac{\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})\psi_m^*(\mathbf{r}')\psi_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$

cRPA :   random-phase approximation for correlation

ACFD : adiabatic connection fluctuation dissipation theorem

Bohm, Pines (1953); Gell-Mann, Brueckner (1957);
Gunnarsson, Lundqvist (1975, 1976); Langreth, Perdew (1977);
X. Ren, P. Rinke, C. Joas, and M. S., Invited Review, Mater. Sci. 47, 21 (2012)

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$\tau(\mathbf{r})$: Kohn-Sham

EX: exac

cRPA : correlation

ation dissipation theorem

Functionals of level 1 and 2 suffer from severe self-interaction errors.
Functionals of level 1, 2, 3, & 4 are lacking the long-range vdW tails.
With "Level 5 plus" validation (error estimation) is becoming possible.

$$\frac{n(\mathbf{r})\psi_m(\mathbf{r})\psi_m^*(\mathbf{r}')\psi_n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

s (19... ...rueckner (1957);
...ursson, Lun... ..., 1976); Langreth, Perdew (1977);
X. Ren, P. Rinke, C. ...e, and M. S., Invited Review, Mater. Sci. 47, 21 (2012)

O-Vacancy in MgO – The "Best" Density Functional

No empirical fitting

The hybrid functional HSE offers a conveni-ent flexibility. It is defined by two parame-ters: α (mixing) and ω (range separation). PBE, HSE06, PBE0 correspond to (α, ω) = (0, arbitrary), (0.25, 0.11 bohr^{-1}), (0.25, 0).

Norina Richter   Sergey Levchenko

Request: Ionization energy of DFT with opt-HSE (total-energy difference of *N* and *N-1* particle systems) and of G_0W_0@opt-HSE should agree. → "the best compromise".

N. Richter et al. PRL July (2013)

O vacancy in bulk MgO

HSE06 $\alpha = 0.26$

$q=1$, G_0W_0

$q=1$, ΔSCF

$q=0$, G_0W_0

HSE06 $\alpha = 0.27$

$q=0$, ΔSCF

$I^{q \to q+1}$ w. r. t. VBM (eV)

α

$\omega = 0.11$ bohr^{-1} embedded Mg_6O_8 cluster

Validation of Calculated Formation Energies of Neutral O-Vacancies in MgO Bulk and at The (100) Surface

oxygen-rich conditions

Method	F^0 (eV)	F^0_{surf} (eV)
PBE-pbc	7.09	6.48
HSE06-pbc	7.04	6.34
PBE0-pbc	7.07	6.33
MP2-pbc	8.05	7.60
rPT2@PBE-ec	7.45	6.90
CCSD(T)-ec	7.09	6.52
PBE-ec *correction*	-0.09	-0.26
PBE0-ec *correction*	+0.07	-0.01
B3LYP-ec *correction*	-0.28	-0.28
we conclude:	**6.95 ± 0.1 eV**	**6.28 ± 0.05 eV**

FHI-aims; *periodic boundary conditions (pbc)*: 5 layers, 12.5% "coverage". turbomole; embedded clusters (ec): unrelaxed Mg_6O_9 & Mg_5O_5

exp. estimate: F^0: 9.29 eV [*]

[#] S. Sicolo & J. Sauer   [*] L. A. Kappers, R. L. Kroes, and E. B. Hensley, PRB 1, 4151 (1970)

Get Real!
Consider Temperature, Pressure, and Doping

What controls the equilibrium concentration of vacancies at a surface?

Gibbs free energy of vacancy formation

vacancy concentration

7/24/2013

4
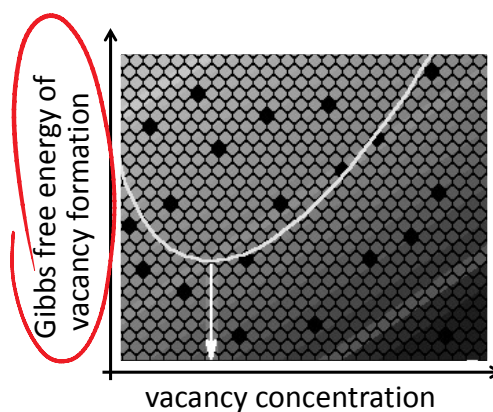
Get Real! Consider Temperature, Pressure, and Doping; *Ab Initio* Atomistic Thermodynamics
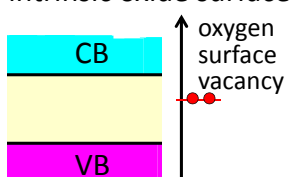
$\mu_{O_2}(T, p)$

C.M. Weinert and M.S., Mat. Sci. Forum 10-12, 25 (1986).
K. Reuter, C. Stampfl, and M.S., in: Handbook of Materials Modeling, Vol. 1. (Ed. Sid Yip), Springer 2005.
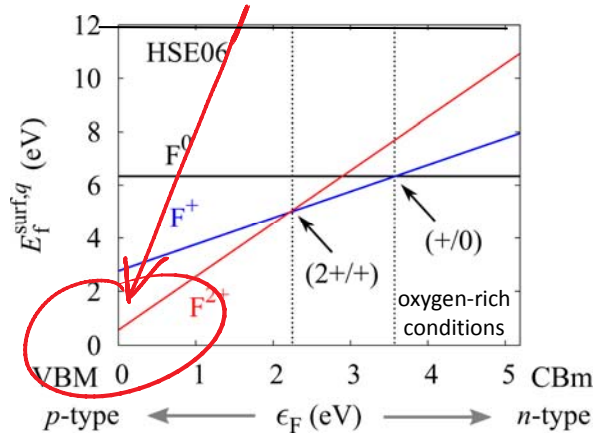
$$G(T, p) = E^{tot} + F^{vib} - TS^{conf} + pV + N\mu_O(T, p) + nE_F$$

DFT

$$\mu_O(T, p) = \tfrac{1}{2}\mu_{O_2}(T, p^0) + \tfrac{1}{2}kT\ln(p/p^0)$$

O Vacancy at MgO (100) Surface:
Electron Chemical Potential and Charge-Transition Levels

intrinsic oxide surface

CB

VB

oxygen surface vacancy

For *p*-type material the formation energy of F^{++} centers is very low. ... too low!

$E_f^{surf,q}$ (eV)

HSE06

F^0

F^+

F^{2+}

(2+/+)

(+/0)

oxygen-rich conditions

VBM 0   1   2   3   4   5 CBm

p-type ⟵ ϵ_F (eV) ⟶ *n*-type
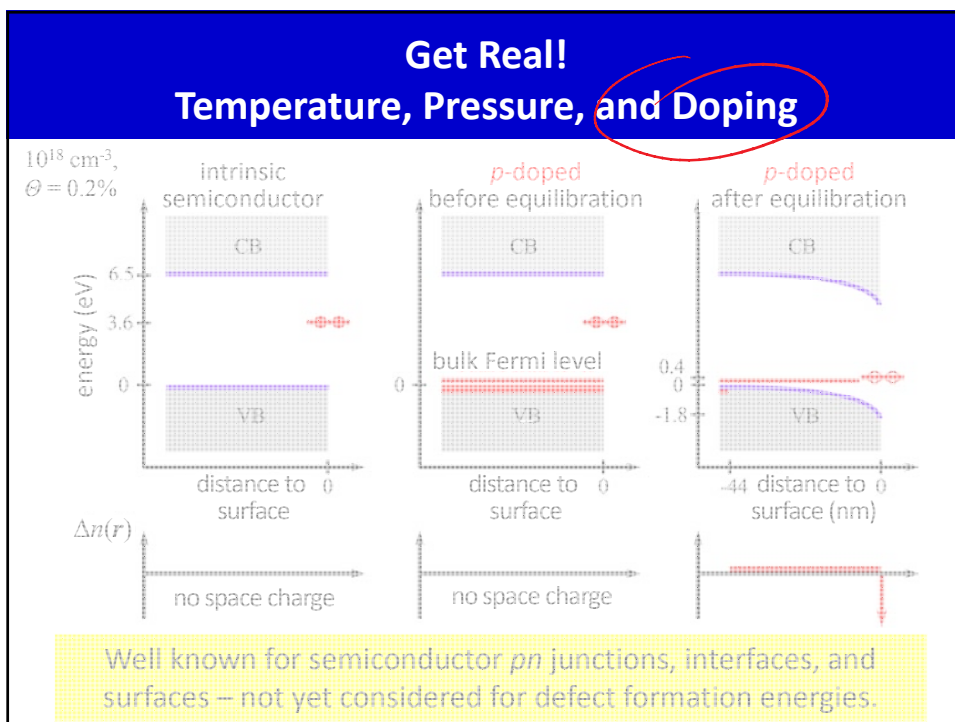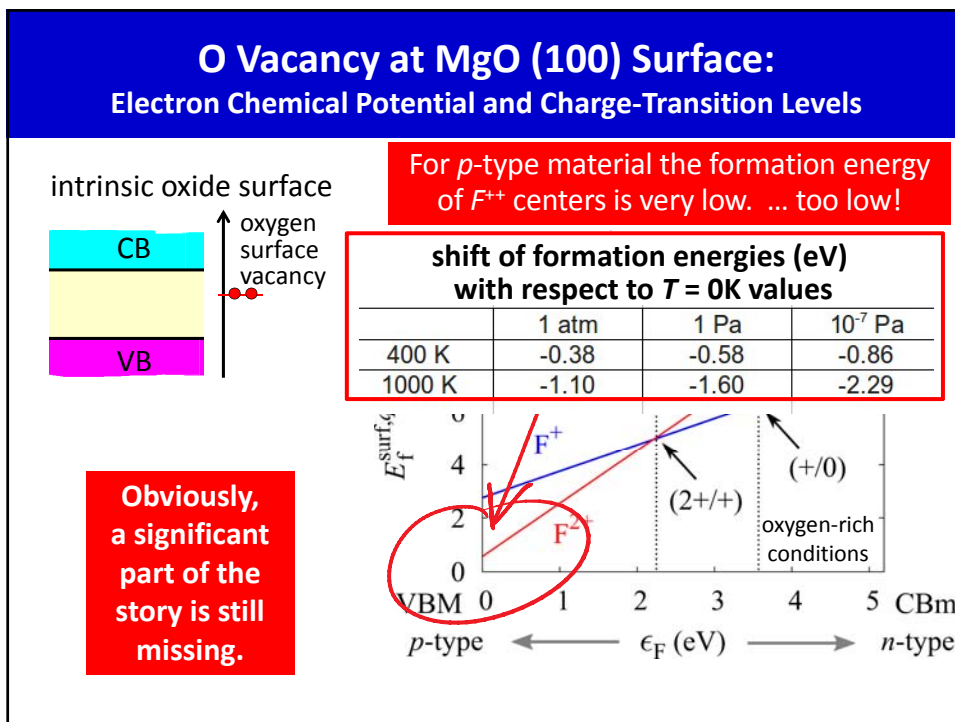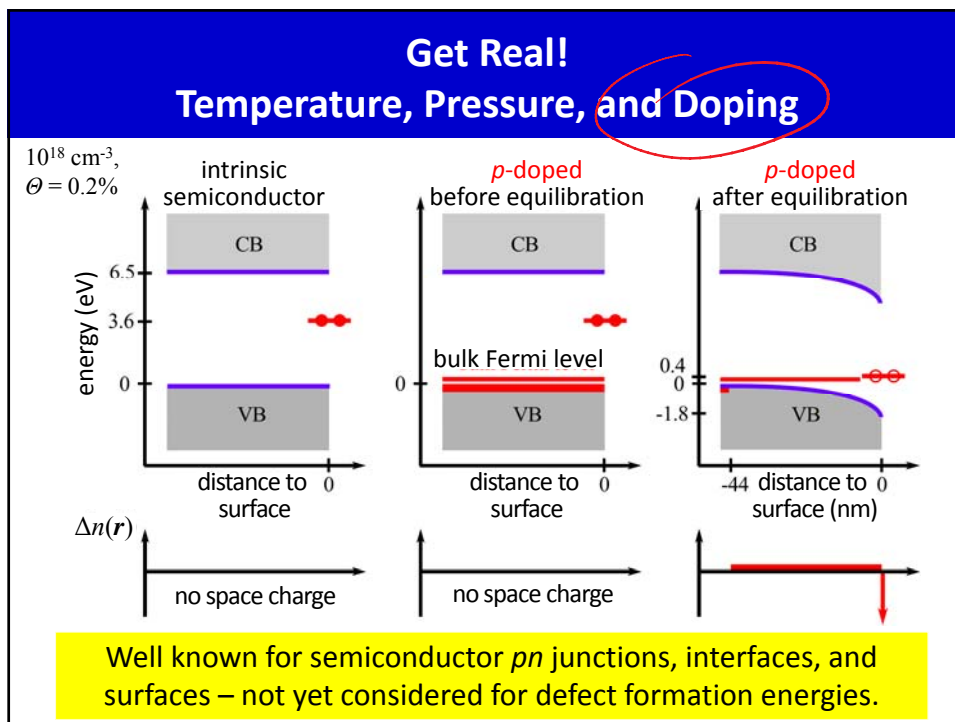
O Vacancy at MgO (100) Surface:
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shift of formation energies (eV) with respect to T = 0K values

	1 atm	1 Pa	10^{-7} Pa
400 K	-0.38	-0.58	-0.86
1000 K	-1.10	-1.60	-2.29

Obviously, a significant part of the story is still missing.

Get Real!
Temperature, Pressure, and Doping

Well known for semiconductor *pn* junctions, interfaces, and surfaces – not yet considered for defect formation energies.

Get Real!
Temperature, Pressure, and Doping

10^{18} cm^{-3}, $\Theta = 0.2\%$

intrinsic semiconductor

p-doped before equilibration

p-doped after equilibration

energy (eV)

CB

6.5

3.6

0

VB

distance to surface

CB

bulk Fermi level

0

VB

distance to surface

CB

0.4
0
-1.8

VB

-44 distance to surface (nm)

$\Delta n(\boldsymbol{r})$

no space charge

no space charge

Well known for semiconductor *pn* junctions, interfaces, and surfaces – not yet considered for defect formation energies.

How To Treat Charged Surface Defects and Doping of The Substrate

Supercells must be neutral!

A) neutralizing constant charge density (the standard approach). ... bad idea.

B) Introduce shallow impurities. Too high defect concentration (> 10^{21} cm^{-3}) and direct vacancy-defect interactions.

C) Virtual crystal concept. Slightly modify all Mg nuclei: $Z \rightarrow Z + \Delta Z$. Probably the best approximation of reality.

supercell, approx. 100 atoms

constant background charge density – here and everywhere

Start from C), correct for the supercell effect, and add the space charge contribution to the Gibbs free energy of formation.

Doping Concentration and Space-Charge Layer Control
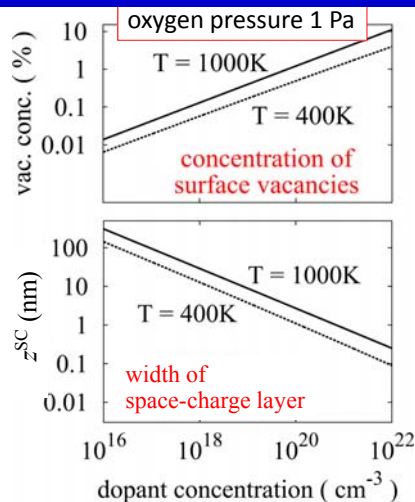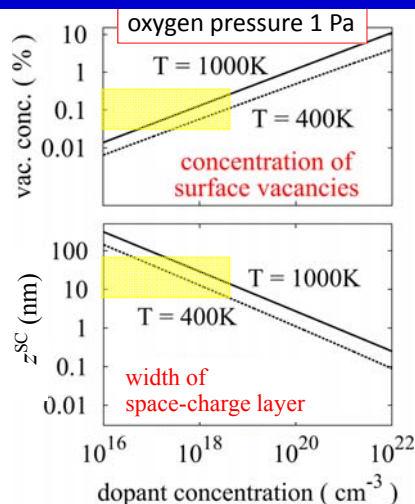## The Defect Charge State and Concentration

Simple electrostatics: Assume that all layers are homogeneous (we are at nm scale, not Å). --> Width of the space charge layer at $T = 0$ K:

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

Building the space-charge layer costs energy. The resulting Gibbs free energy of defect formation is:

$$G_{\mathrm{f}}^{\mathrm{VCA},q}(\sigma) = G_{\mathrm{f}}^{\mathrm{VCA},q}(\sigma, d) - qE^{\mathrm{SC}}(\sigma, d)$$
$$+ qE^{\mathrm{SC}}(\sigma, z^{\mathrm{SC}})$$

$$E^{\mathrm{SC}}(\sigma, z^{\mathrm{SC}}) = \frac{e\sigma}{6\epsilon_{\mathrm{r}}\epsilon_0} z^{\mathrm{SC}}$$

Summary

Accurate defect formation energies of O vacancy in MgO bulk and at the (100) surface with reliable error bars.

p-doping gives rise to charged vacancies and a pronounced space-charge layer.

Space-charge layer and associated band bending limit the concentration of vacancies:

surf. vacancies (%) at $n_d = 10^{18}$ cm^{-3} and 3 O_2 pressures

T (K)	1 atm	1 Pa	10^{-7} Pa
400	0.089	0.168	0.242
1.000	0.319	0.396	0.484

For *n*-type MgO no vacancies are expected. Thus, the catalytic behavior for *n*- and *p*-type MgO should be very different.

<< F4TCNQ @ZnO: Significant effect of space-charge region on adsorption energies, charge transfer, workfunction. >>

Need exp. information about dopant concentration dependence of energies etc. and doping profiles at the interface.